DOCTOR OF PHILOSOPHY

Novel biomass conversion routes

ammonia from biomass, and marine macroalgae for energy

Sarah Alexander

2013

Aston University

NOVEL BIOMASS CONVERSION ROUTES: AMMONIA FROM BIOMASS, AND MARINE MACROALGAE FOR ENERGY

SARAH LOUISE ALEXANDER

Doctor of Philosophy

Chemical Engineering

ASTON UNIVERSITY

December 2012

Aston University

Novel biomass conversion routes: ammonia from biomass, and marine macroalgae for energy

Sarah Louise Alexander

Doctor of Philosophy

2012

Summary

This thesis presents a techno-economic investigation of the generation of electricity from marine macroalgae (seaweed) in the UK (Part 1), and the production of anhydrous ammonia from synthesis gas (syngas) generated from biomass gasification (Part 2).

In Part 1, the study covers the costs from macroalgae production to the generation of electricity via a CHP system. Seven scenarios, which varied the scale and production technique, were investigated to determine the most suitable scale of operation for the UK. Anaerobic digestion was established as the most suitable technology for macroalgae conversion to CHP, based on a number of criteria. All performance and cost data have been taken from published literature. None of the scenarios assessed would be economically viable under present conditions, although the use of large-scale electricity generation has more potential than small-scale localised production.

Part 2 covers the costs from the delivery of the wood chip feedstock to the production of ammonia. Four cases, which varied the gasification process used and the scale of production, were investigated to determine the most suitable scale of operation for the UK. Two gasification processes were considered, these were O_2-enriched air entrained flow gasification and Fast Internal Circulating Fluidised Bed. All performance and cost data have been taken from published literature, unless otherwise stated.

Large-scale (1,200 tpd) ammonia production using O_2-enriched air entrained flow gasification was determined as the most suitable system, producing the lowest ammonia-selling price, which was competitive to fossil fuels. Large-scale (1,200 tpd) combined natural gas/biomass syngas ammonia production also generated ammonia at a price competitive to fossil fuels.

Keywords: Macroalgae, anaerobic digestion, ammonia, biomass gasification

Acknowledgement

I would like to thank the following:

- Dr John Brammer for his guidance and support throughout this study
- Professor Tony Bridgwater for the opportunity and advice
- The Engineering and Physical Sciences Research Council (EPSRC) for funding this work
- The SUPERGEN Biomass and Bioenergy consortium for its friendly and supportive environment
- The Aston bioenergy researchers for precious coffee breaks that restored sanity
- Gary Sutton, Venetia Headlam and Rina Ghatoara for listening and laughter
- Stephen, Carolyn and Ian Alexander, for their love and encouragement

Contents

Tables

Tables continued

Tables continued

Tables continued

Figures

Figures continued

Glossary and acronyms

Additional capital: further capital outlays made after the initial capital investment

AGA: American Gas Association

AGR: Acid gas removal

aMDEA: activated methyl diethanolamine

ASU: Air separation unit

BESP: Break-even selling price

BFB: Bubbling fluidised bed gasification

BTL: Biomass-to-liquid

CAPEX: Capital expenditure

CFB: Circulating fluidised bed gasification

Chlorophyceae: Green macroalgae

CHP: Combined heat and power

CPO: Catalytic partial oxidation

CPW: Cost per worker

DAF: Dry ash free

DCFROR: Discounted cash flow rate of return

DECC: Department of Energy and Climate Change

DEFRA: Department for Environment, Food and Rural Affairs

DENA: German Energy Agency (Deutsche Energie-Agentur GmbH)

Digestate: Solid residue by-product of anaerobic digestion

DME: dimethylether

DOE: United States Department of Energy

ECN: Energy research Centre of the Netherlands

EEZ: Exclusive Economic Zone

EISA: Energy Independence and Security Act

EPSRC: UK Engineering and Physical Sciences Research Council

FC: Fixed carbon

FICFB: Fast Internal Circulating Fluidised Bed

GHG: Greenhouse gas

GHSV: Gas hourly space velocity

HAB: Harmful algal blooms

HHV: Higher heating value

HRT: Hydraulic retention time

HS: High solid anaerobic digestion

HTS: High temperature water gas shift

IBERS: Aberystwyth University

IC engine: Internal combustion engine

IFREMER: Institut Français de Recherche pour l'Exploitation de la mer

IGCC: Integrated gasification combined cycle

IRR: Internal rate of return

ISC: Irish Seaweed Centre

LHV: Lower heating value

LS: Low solid anaerobic digestion

LTS: Low temperature water gas shift

Macroalgae: Marine plants commonly also known as seaweed

MC: Moisture content

MEA: monoethanolamine

MESP: Minimum ethanol selling price

MHSP: Minimum hydrogen selling price

MIT: Massachusetts Institute of Technology

MS: Medium solid anaerobic digestion

MSW: Municiple solid waste

NCF: Net cash flow

NEDO: New Energy and Industrial Technology Development Organisation

NPV: Net present value

NREL: National Renewable Energy Laboratory

ODS: Oven dried solid

OPEX: Operating expenditure

PEC: Purchase equipment cost

Phaeophyceae: Brown macroalgae

PSA: Pressure swing adsorption

PUFAs: polyunsaturated fatty acids

RED: Renewable Energy Directive

RES: Renewable Energy Strategy

RHI: Renewable Heat Incentive

Rhodophyceae: Red macroalgae

RME: Rape methylester

ROC: Renewable Obligations Certificates

ROI: Rate of investment

ROR: Rate of return

SAMS: Scottish Association for Marine Science

SCGP: Shell Coal Gasification Process

SCWG: Supercritical water gasification

SMR: Steam methane reforming

SNG: substitute natural gas

SRC: Semi-refined carrageenan

SSD: Superheated steam dryer

Syngas: synthesis gas

TCI: Total capital investment

TEA: Techno-economic assessment

TIC: Total installed costs

TPEC: Total purchase equipment cost

TPC: Total plant costs

TPO: Total partial oxidation

TRR: Target rate of return

TS: Total solid content

USDA: US Department of Agriculture

VS: volatile solid content

WGS: Water gas shift

WUR: Wageningen UR

1 Introduction

Disruption to fossil fuel supply chains, driven by political and social instability has led to unstable energy markets, causing economic anxiety worldwide. Moreover, climate change due to Greenhouse gas (GHG) and CO_2 emissions from these resources has led to international agreements, such as the Kyoto Protocol to reduce GHG emissions through the implementation of renewable energy sources.

The UK is obligated to reduce GHG and CO_2 emissions by 80% by 2050 as part of the Climate Change Act (2008) [1]. Additionally, 15% of the country's energy demand must be obtained from renewable sources by 2020 in order to fulfil the Renewable Energy Directive (RED) [2].The Renewable Energy Strategy (RES) proposes that biomass will make a significant contribution to the country's energy requirement [3].

The term biomass refers to organic materials, such as wood, agricultural and forestry process residues, aquatic plants and human and animal waste. These materials are considered renewable forms of carbon, which, if produced sustainably (economically with limited negative environmental impact), are a carbon-neutral fuel [4]. Biomass is the most readily available resource for large-scale energy production, without incurring large economic and environmental penalties [5]. Currently, biomass usage covers 14-15% of the worldwide energy consumption [6].

However, in order for biomass to achieve these targets, a guaranteed secure supply with maintained quality is required [7]. At present, the primary resource is terrestrial-based materials, whose availability is limited by factors affecting annual growth [8], such as productivity and increased land rivalry with the need to supply food [9].

This has led to the proposal of novel practises in order to increase production and maintain suitability.

1.1 Research questions

The work completed in this study addresses the techno-economic impact of two novel biomass-based practises through the following research questions:

- Can macroalgae (seaweed) be used as a source of marine biomass in the UK?
- Can nitrogen-based fertiliser be produced using biomass in order to reduce GHG and carbon emissions in the UK?

The rise in land rivalry has led to an increased interest in utilising aquatic materials, such as macroalgae, to supplement biomass production. With more than three quarters of the earth's surface covered in water, 80% of all living organisms being aquatic based and the subsequent immense organic biodiversity, there is immense potential for aquatic biomass [9].

The objective is to carry out a techno-economic assessment that evaluates the potential of utilising macroalgae as a marine bioenergy resource in the UK.

N_2-based fertilisers are produced primarily from ammonia and are used worldwide for the cultivation of food and non-food crops. Ammonia is manufactured via conventional technologies such as the Haber-Bosch process, which combines H_2 from natural gas steam reforming and N_2 from air [10]. However, these methods account for approximately 1.2% of the world's energy demand [11] and generate 0.93% of global GHG emissions [12].

Since the demand for fertiliser is predicted to increase due to social changes (population increase etc.) [13], the energy demand and GHG emissions will also increase.

The substitution of H_2 rich, biomass-derived synthesis gas (syngas) for natural gas during ammonia production could help reduce the negative environmental impact of fertiliser manufacture, and reduce the use of fossil fuel resources. At present, the production of ammonia from biomass syngas has yet to be implemented. However, syngas from biomass gasification is considered to be a viable feedstock for the production of chemicals and biofuels [14-16], including H_2, which is the precursor gas to ammonia.

It is the purpose of this study to assess the validity of ammonia from biomass through the implementation of a techno-economic assessment.

All work is completed as part of the SUPERGEN II Biomass and Bioenergy Consortium.

1.2 SUPERGEN II Biomass and Bioenergy consortium

SUPERGEN Biomass and Bioenergy is a consortium of academic, research and industrial organisations created by the UK Engineering and Physical Sciences Research Council (EPSRC). It is one of the 13 consortia that form SUPERGEN, which has been established for the purpose of developing sustainable power generation and supply using a range of technologies.

The purpose of the SUPERGEN Biomass and Bioenergy Consortium is to study the production, conversion and application of biomass and bioenergy products. SUPERGEN Bioenergy Consortium I was concerned with development of energy from biomass via pyrolysis, gasification and combustion for power generation applications including engines, turbines and boilers.

SUPERGEN Bioenergy Consortium II built upon the work completed in Phase I. For Phase 2 the consortium comprised Aston University, University of Leeds, Cranfield University, Imperial College, Manchester University and the University of Sheffield, as well as Rothamsted Research Institute, the Institute of Grassland, Policies Studies Institute and Forest Research. The industrial partners were Alstom, E.ON UK, AMEC, Bical, Johnson Matthey, RWE nPower, Biffa, Rural Generation, Biomass Engineering, Coppice Resources and BP. The associate academic partners were the Irish Seaweed Centre (ISC), Scottish Association for Marine Science (SAMS), Aberystwyth University (IBERS), the University of Oxford and the University of Ulster.

The work was organised into eight work package themes:

- Theme 1 Resources (subtheme: Marine);
- Theme 2 Characterisation (subtheme: Nitrogen);
- Theme 3 Conversion;
- Theme 4 Power & Heat;
- Theme 5 Transport Fuels, Biorefinery (subtheme: Ammonia);
- Theme 6 Systems;
- Theme 7 Innovation;
- Theme 8 Dissemination.

The work presented in this PhD thesis comprises of two tasks from the consortium subthemes: the Marine Biomass plus activity and the Ammonia plus activity.

1.2.1 Marine Biomass plus activity

The Marine Biomass plus activity is a sub-theme of Theme 1 (Resources). It investigates the potential of marine biomass production and utilisation in the UK. The sub-theme was led by University of Leeds and included Aston University, ISC, SAMS, Manchester University and IBERS.

The subtheme comprised of six tasks, which were:

- 1G – Species evaluation and selection
- 1H – Culturing of selected candidates for farming
- 1J – Characterisation and evaluation
- 1K – Techno-economic evaluation

- 1L – Environmental and social assessment
- 1M – Evaluation of potential to the UK

Part 1 of the present study was funded under Task 1K - the techno-economic evaluation, which encompasses the entire marine biomass utilisation process, from feedstock growth to end-product usage.

1.2.2 Ammonia plus activity

The Ammonia plus activity is a subtheme of Theme 5 (Transport Fuels, Biorefinery) and investigates the production and usage of ammonia from biomass. It was led by Aston University and included Manchester University, the University of Sheffield and the Hydrogen Consortium (the University of Oxford).

The subtheme comprised of four tasks, which were:

- 5D – Slow release fertiliser production by nitrogenolysis
- 5E – Production of ammonia in a novel gasifier
- 5F – Evaluation of ammonia and fertiliser production
- H_2 – Ammonia for hydrogen storage & transport (Hydrogen Consortium)

Part 2 of the present study was funded under Task 5F and focuses on the techno-economic evaluation. This work covers the production process from the delivery of the feedstock to the manufacture of anhydrous ammonia, which is the raw material for fertiliser [17].

1.3 Techno-economic assessment

Whilst the novel practises assessed in this study are distinct, the common theme of the work is the techno-economic assessment.

A techno-economic assessment (TEA) is a '*cost-benefit comparison*' [18, p.3], which evaluates the economic viability of a project, often where there are a range of process options which must be compared or optimised. Such assessments are distinguished from pure economic analysis by the requirement to link the technical performance of individual process items or steps to their capital and/or operating costs. It can include an investigation of the cash flow over a project lifetime, as well as the effect of different operating conditions and scales [18].

There are numerous methods for completing a TEA. This work assesses economic viability using the Internal Rate of Return (IRR). The IRR, also known as the Rate of

Return (ROR) or Discounted Cash Flow Rate of Return (DCFROR), is the rate of return that results in the Net Present Value (NPV) of the total cash flows being equal to zero. This is calculated using the following equation:

$$NPV = \frac{NCF}{(1+r)^y}$$

Where NPV: Net present value, NCF: Net cash flow, r: internal rate of return and y: year of analysis

The resultant IRR is then used to judge the economic quality of the potential investment. In order for a project to be attractive, the IRR needs to be higher than the return from other investment options, taking into account the associated degree of risk. Normally, this is determined by evaluating whether a greater return could be achieved by depositing the investment in a bank. If the IRR is less than the banking return, it is considered low. Projects with low IRR are not attractive for investment since there is no guarantee of a profitable return. If the IRR is higher, the project is a potentially profitable investment [11].

Using this method of assessment allows multiple project comparison, regardless of technology and scale. Additionally, the effect of process variables, such as feedstock and technology selection, can be evaluated using sensitivity analyses. A sensitivity analysis calculates the change in the IRR based on alterations to the project investment, allowing multiple process routes to be compared. Each TEA is treated as an independent assessment, however; all work is presented on a 2009 base date and uses the following exchange rates:

- £1 = US$1.5645 [19].
- £1 = €1.1230375 [20].

1.4 Thesis presentation

Due to the distinct objectives of each task, it is the intention of the author to present this thesis as a two-part document.

In Part 1 (Chapters 2 - 9) the potential of macroalgae (seaweed) as marine biomass is investigated in order to complete the TEA (§1.1.1). Chapters 2 and 3 provide background on macroalgae in addition to a summary of previous work regarding marine biomass. Chapter 4 presents the objectives and methodology of this study, whilst Chapters 5 and 6 cover the evaluation, selection and performance of macroalgae conversion and utilisation. In Chapters 7 and 8, the cost of marine biomass is determined and analysed further through sensitivity evaluation. In addition, the potential of macroalgae as marine biomass is discussed. Finally, Chapter 9 summarises the principal findings and presents recommendations for further study.

Part 2 (Chapters 10 - 17) investigates the use of biomass gasification derived syngas as a source of ammonia, which concludes with the completion of the TEA (§1.1.2). The layout of the study is similar to Part 1. Background for ammonia production and biomass gasification and a summary of previous work are presented in Chapters 10 and 11, whilst Chapter 12 discusses the objectives and methodology of the project. Chapters 13 and 14 cover process performance and modelling, whilst in Chapters 15 and 16, the cost of biomass-derived ammonia production is determined and evaluated, finishing with a discussion on the potential of biomass-based ammonia. Part 2 concludes with Chapter 17, which summarises the principal findings and presents recommendations for further study.

Certain methods and parameters are used for both assessments, however; these are clearly presented and discussed in the relevant chapters.

2 Background (marine)

2.1 Macroalgae

Macroalgae, commonly known as seaweeds, are multicellular plants that grow in salt water [9]. Like all plants, terrestrial and aquatic, macroalgae contain chlorophyll, which is required for photosynthesis [21].

As shown in Figure 2.1, the basic physical composition of macroalgae comprises of a holdfast and fronds. The holdfast attaches the plant to a rocky surface, providing anchorage against water motion. The fronds are branches that sprout from the holdfast. Unlike terrestrial plants, macroalgae do not have roots [22] since water and nutrients are absorbed from the surrounding waters through the fronds, which provide a greater surface area for ingestion [23].

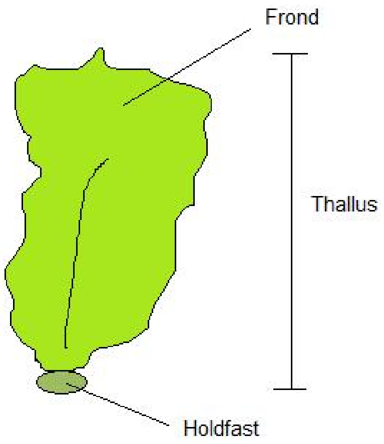

Figure 2.1: Foliose macroalgae (based on [22])

Together the fronds and holdfast make up the thallus (body) of the plant [21], which is often used to classify the species of macroalgae since the shape and structure varies with genera [22].

Two physical types of macroalgae have been identified; these are foliose and leathery. Foliose macroalgae (Figure 2.1) normally comprise of a holdfast and frond only. These species are made up of sheets of tissue that form a fragile structure [22]. Leathery macroalgae (Figure 2.2) are complex structures, which are tough and contain many adaptations to their surroundings in order to survive.

Figure 2.2: Leathery macroalgae [22]

Depending on the species, these adaptations include air bladders, receptacles and the stipe. The air bladders are gas filled spherical pockets, which keep the plant upright or afloat during submergence. The receptacles are the reproductive organs of the plant and comprise of conceptacles and receptacles. The stipe is an extremely strong stem-like structure that joins the fronds to the holdfast, giving the plant durability against strong tidal action [22].

Macroalgae species that have a holdfast are often referred to as attached, since they require a fixed position to grow. Certain species, such as *Gracilaria*, *Ulva* and *Sargassum* do not have holdfasts [22] and are referred to as non-attached or free-floating [24].

2.1.1 Species

There are over 9,000 species of macroalgae worldwide [25] with 3,000 to 4,000 inhabiting the Chinese coast alone [26]. Macroalgae are normally classified by three colours; green *(Chlorophyceae)*, red *(Rhodophyceae)* and brown *(Phaeophyceae)* [9]. These groups are sometimes referred to as *Chlorophyta*, *Rhodophyta* and *Phaeophyta* [7, 27], which is a variation of the taxonomy terminology, a common occurrence in macroalgae literature. The majority of macroalgae are characterised as *Rhodophyceae* (6,000 species), followed by *Phaeophyceae* (2,000 species) and *Chlorophyceae* (1,200 species) [25].

A fourth group called *Cyanophyta* (blue algae) is occasionally included in the taxonomy [7]. However the group is generally considered to be a form of microalgae due to the unicellular rather than a multicellular structure and is normally referred to as *Cyanbacteria* [9, 25, 27], which are often found in algal blooms.

The *Chlorophyceae* group, shown in Figure 2.3 a), contains chlorophyll that is unmasked by pigment, resulting in its green colour. The physical properties range from minute single-cell plants to larger, multicellular frond or thread foliage. An example of this group is *Ulva lactuca* (sea lettuce) which is common in Britain and Europe. *Rhodophyceae*, shown in Figure 2.3 b), contain the red pigment phycoerythin, which masks the chlorophyll. This group comprises exclusively of multicellular structures, which are small to moderate in size. *Gracilaria verrucosa* is a common example of *Rhodophyceae* [21].

Aston University

Illustration removed for copyright restrictions

Figure 2.3: Macroalgae colour groups a) *Chlorophyceae*, b) *Rhodophyceae* and c) *Phaeophyceae* [28, 29]

Phaeophyceae (Figure 2.3 c) are multicellular plants, which are normally attached to a substrate and are frequently large in size. The pigment fucoxanthin masks the chlorophyll, resulting in the brown colouring [21]. Variations in categorisation and taxonomy of the *Phaeophyceae* species in literature are common. Figure 2.4 presents a brief summary of *Phaeophyceae*, noting the more prominent sub-groups.

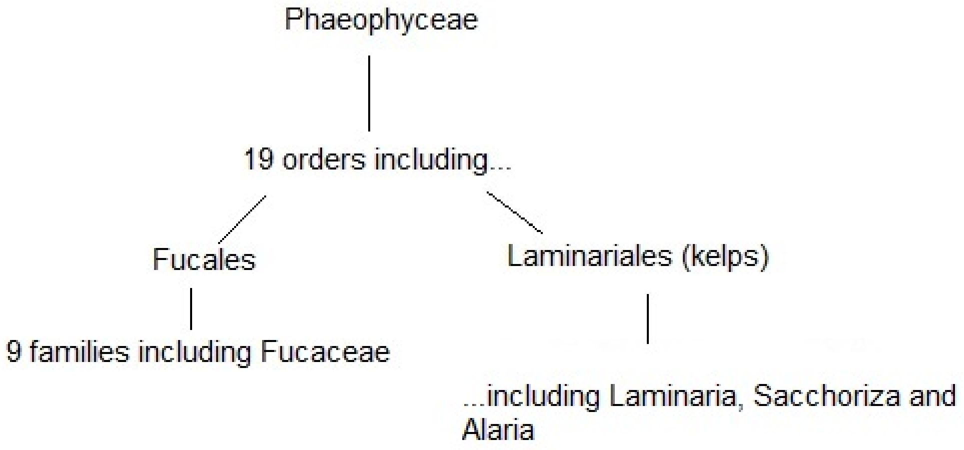

Figure 2.4: *Phaeophyceae* taxonomy

As shown, there are nineteen orders of *Phaeophyceae* including *Fucales* and *Laminariales*. They grow at intertidal and sub-tidal levels, providing a dense canopy due to bed formation [27].

The *Fucales* order comprises of nine families, one of the most prominent being *Fucuceae*. The *Fucuceae* family consists of thirteen genera, including *fucus* (also known as fucoids) but also including *ascophyllum,* which is also present in the UK [24].

Laminariales (kelps) are large upright, macroalgae that thrive in sub-tidal conditions [27], and are some of the largest macroalgae in European waters [24]. Although a similar taxonomy structure to *Fucales* exists [24]*, Laminariales* are normally referred to by their kelp families, which include *Laminaria*, *Sacchorize* and *Alaria* [30, 31]. *Laminaria* grow in abundance in the UK and can reach a length of up to 4 m [31]. The most dominant *laminaria*, particularly Scotland are *Laminaria hyperborea*. Other species are present in lower abundance such as *Laminaria digitata*, found in shallower habitats, *Saccharina latissima* (formerly known as *Laminaria saccharina*) and *Saccorhiza polyschides*, which grow in deeper waters [27]. These genera are smaller than international species, with a maximum length of 3 m [7].

2.1.2 Growth and reproduction

Macroalgae are fast growing and can reach up to 60 m in length [7]. They are responsible for approximately 40% of the planet's photosynthetic productivity [32]. The average photosynthetic efficiency (light energy converted to chemical energy via photosynthesis) for aquatic biomass is 6-8% [4, 33] whilst the terrestrial level is between 1.8-2.2% [33].

For macroalgae, growth behaviour is divided into two categories, perennial and opportunistic. Perennials are slow growing species that can store large quantities of nutrients. Opportunistic species are commonly annuals with rapid growth and nutrient uptake ability, mainly due to their high surface area to volume ratio. However, they have lower nutrient storage capabilities than perennials and little defence against predators [27].

Laminaria sp. have a seasonal growth rhythm, with fast growth rates in winter and spring, which slow in summer. This is believed to be synchronised with the amount of available daylight increasing the production of phytoplankton, which reduce the nutrient concentration of the surrounding waters. The short days of winter mark the period of new growth [27, 34].

Macroalgae can reproduce either asexually (vegetative) or sexually (reproductive). Vegetative reproduction occurs when the plant divides itself to produce new plants. Clonal macroalgae species for instance can reproduce vegetatively from thallus fragments [35]. During reproductive breeding, adult macroalgae produce spores, known as zoospores, which attach themselves to available substrates. These zoospores then grow into miniscule male and female plants, known as gametophytes. The male gametophyte fertilises the female gametophytes eggs, which develop into young macroalgae plants, which are referred to as sporophytes [36]. This method is known to strengthen the species gene pool [35].

The life cycles of many macroalgae species can be complex due to the different reproductive and growth processes. This results in life history forms which are either a repetition of the same life cycle (isomorphic) or different forms at different life cycle stages (heteromorphic). These are normally known as the alternation of generations. Awareness of the diverse life cycles of macroalgae is significant for the control and understanding of reproduction and growth [35].

2.1.3 Environment and distribution

The natural environments attached macroalgae are rocky substrates, where they grow into multi-layered vegetation, capturing almost all available light and nutrient resources [9]. These macroalgae inhabit two areas of water depth, intertidal and sub-tidal. Intertidal areas are under water at high tide, but exposed at low tide. Sub-tidal areas are found below the low tide watermark and are rarely exposed, though they can be uncovered during the Spring tides [21, 27]. However, macroalgae are not found more than 20 m below the water level due to the lack of light [27], which is required for photosynthesis. Free-floating macroalgae drift with the water currents and can be dense enough to block sunlight from the habitat beneath, resulting in the disruption of aquatic sites [37].

There are three levels of macroalgae abundance; these are sporadic occurrence, common occurrence and dominant [38]. Abundance and distribution of intertidal macroalgae, particularly in the northern hemisphere, is reduced by storms, ice action and pollution [39]. Currently, losses in macroalgae populations have also been recorded due to the effects of climate change, particularly the recent onset of cold winters in northern areas [27]. The wider ecological impact however is still unknown.

Rhodophyceae inhabit temperate and warm waters, such as the Mediterranean coastline [40], whilst *Phaeophyceae* do not flourish in these conditions [21]. Instead, they thrive in temperate waters, making them the dominant aquatic flora along Northern European coastlines such as Norway, Iceland, Ireland, the UK and Atlantic France [40].

The presence of surplus *Chlorophyceae* algae in coastal areas causes phenomena called ‘green tides’ and harmful algal blooms (HAB), where shorelines are coated in micro- and macroalgal growths, becoming an expensive environmental problem [41, 42]. These green tides are caused by agricultural run offs, atmospheric and waste nutrients from fish farms and artificial ponds entering shoreline waters [41]. In Florida, USA, the blooms cause the quality of near shore water to deteriorate, affecting tourism, particularly since this is a periodic and seasonal problem [42]. Excess shoreline macroalgae was originally treated as waste, harvested and sent to landfill; now however the EU (Directive 1999/31/EC) forbids this practice [38].

2.1.4 Chemical composition

The chemical composition of macroalgae differs significantly from terrestrial biomass. Macroalgae have high moisture contents (MC) of normally 80-90% [43, 44]. This results in a lower solid content, as well as a larger bulk density than terrestrial sources.

The chemical composition of macroalgae varies with species, season and habitat [45]. Whilst seasonal variance in the quality of macroalgae has been reported [7], macroalgae are less limited by seasonal change than terrestrial plants [25]. Table 2.1 shows the proximate and ultimate analyses, presented to 1 d.p., of several species of macroalgae in comparison to terrestrial biomass sources.

Table 2.1: Proximate and ultimate analyses of macroalgae and terrestrial biomass

Species	Proximate (%) air dried				Ultimate (%) air dried				
	VS^a	FC^b	Ash	MC	C	H	O	N	S
L. hyperborea [7]	53.5	21.5	11.2	12.4	35.0	5.3	35.1	1.1	2.1
L. digitata [7]	53.4	25.3	10.0	13.7	31.6	4.9	34.2	0.9	2.4
Gracilaria cacalia [46]	54.5	19.0	14.8	11.7	31.1	5.6	33.9	0.8	2.1
Enteromorpha clathrata [46]	41.8	7.8	37.1	13.3	22.7	6.3	16.2	3.1	1.3
L. japonica [46]	38.5	15.0	33.0	13.4	20.5	4.6	25.4	2.5	0.5
Miscanthus giganteus [47]	*70.4*	-	*1.3*	*14.2*	*41.5*	*5.4*	*37.1*	*0.3*	*0.1*
Rapeseed residue [47]	*68.7*	-	*3.7*	*5.9*	*40.3*	*5.0*	*44.6*	*0.5*	-
Wood chip (Värnamo, Sweden) [47]	*65.5*	-	*1.6*	*13.3*	*44.6*	*5.2*	*35.1*	*0.3*	*<0.1*

^{a} Volatile solid; ^{b} Fixed carbon

As shown, macroalgae have higher ash contents than several types of terrestrial biomass. This ash contains greater levels of potassium, sodium, calcium, phosphate, silicon and magnesium [25]. *Phaeophyceae* have naturally higher ash contents than other genera [7] with a range of 30.1-39.3 wt%, whilst *Rhodophyceae* have a range of 20.6-21.1 wt% [45].Terrestrial crops are predominantly chlorine based whilst macroalgae contains bromine and iodine, are lower in carbon, hydrogen and oxygen and higher in nitrogen and sulphur [7]. The N_2 content of *Phaeophyceae* is high at 2-4 wt% due to the *'protein component'* [48, p.3]. The rate of nitrogen uptake is influenced by water temperature and motion, the availability of light, the ionic form of the element and the age of the plant itself [23]. In terms of the ionic form of nitrogen, ammonia is the preferred structure to be ingested, though too much can be poisonous [27].

Macroalgae do not contain the same lignocellulosic structure as terrestrial crops. Therefore, it is commonplace for seaweed to be characterised in terms of protein, carbohydrate and lipid content.

2.1.4.1 Protein

The average protein content of macroalgae is approximately 15 wt% dry ash free (DAF) [27]. *Phaeophyceae* contain more uniform protein compositions, normally in the form of amino acids [49] and generally have a low protein content of about 3-15% of dry weight [50]. *L. digitata* has a protein dry mass percentage of 8-15% [51] whilst the *fucus spp*. has a protein percentage of 3-11% [52].

The level of protein found in macroalgae is affected by seasons and location [53, 54]. This is because the protein level correlates with the amount of nitrogen present in the environment, which changes seasonally [27]. During the period of March to June/July, there is increased photosynthesis, which corresponds with low protein levels in *Laminariales*, especially in *L. digitata* and *L. hyperborea* [53].

2.1.4.2 Carbohydrates

Macroalgae carbohydrates store energy for the winter growth [55]. The average carbohydrate content of macroalgae is estimated at 80% of the DAF weight [27]. Structural cellulose, hemicellulous and xylans contents are generally low in marine algae [56], whilst storage polysaccharides, which include laminarian, mannitol, carageenan and alginates, are more specific to macroalgae. These have textural and stabilising properties, which are extracted and utilised by the hydrocolloid industry for food and other applications [57]. *Laminaria* species contain approximately 55 wt% (dry) carbohydrates laminarin and mannitol [24]. The peak time for laminarin and mannitol production is during summer and autumn, decreasing throughout winter [54]. There is no evidence however to suggest that carbohydrates play a significant role in the initiation of growth [58].

2.1.4.3 Lipids

Macroalgae lipid contents can be up to 2% of dry weight. Species found in temperate climates mainly consist of polyunsaturated fatty acids (PUFAs) with Omegas 3 and 6, making them useful for human food and supplements [27].

2.1.4.4 Phenol

Normally plants contain two types of phenol; these are hydrolysable tannins and phenylpropanoids (lignin). The hydrolysable tannins are acid esters of sugars and glucose [27]. Lignin provide a defence against predators (microbial and herbivores) and UV light. However macroalgae, particularly sub-tidal species do not contain lignin since they requires less protection from UV light underwater [27, 56]. *Phaeophyceae* contain phlorotannins, a type of phenol, which is exclusively found in these genera, constituting 1-20% of the dry weight [27]. Their main task is to precipitate proteins from solutions [59].

Polyphenols are also present, particularly in the outer tissues of *Phaeophyceae,* where they are in greater abundance than in the remainder of the plant [27]. These compounds provide a low-level immune system or bacterial defence [60] by intercepting, binding and releasing toxic heavy metals [61-63]. Macroalgae species with low polyphenol levels have high growth rates whilst those with high levels demonstrate slow growth [59]. *Laminariales* are often but not always less rich in polyphenols than other brown macroalgae families [27].

2.1.4.5 Metals and minerals

Macroalgae have higher levels of cadmium, iron and copper than terrestrial plants. *Phaeophyceae* are a good source of copper, magnesium, iron, zinc and iodine for the human diet [27].

Macroalgae have the ability to biosorb, therefore their metal contents reflect the background levels of the surrounding environment. These metals come from two sources, which are natural reserves from soil leaching, rock weathering and volcanic activity and human activity such as mining, fossil fuels, waste disposal and other industrial applications. The latter type makes the concentrated metal levels far higher than normal, mainly because the ultimate destination for waste is the sea, via inland waterways [27]. Wild macroalgae can contain trace amounts of mercury, though contamination risks are negligible since the levels are normally below regulatory limits [38]. Heavy metals are also present [45].

Fish farming is another source of marine metal, releasing zinc, copper and cadmium [64]. This has led to the proposed integration of macroalgae and fish farming facilities, where the macroalgae are fed the excess nutrients from fish excrement [27].

As well as metals and minerals, arsenic may also be present in trace amounts, which is not seen as a health risk [57], though concentrations can be as high as 100 mg/kg [7].

The most common form of arsenic present in *Phaeophyceae* is the salt arsenate (pentavalent arsenic) [65]. It is acknowledged that the kelp drying industry during the 19th century may have contributed to arsenic contamination of the surroundings [7, 65].

2.2 The Macroalgae Industry

Approximately 200 species of macroalgae are used worldwide, 10 of which are intensively cultivated; these are *Laminaria, Undaria*, *Porphyra, Eucheuma*, *Kappaphycus, Gracilaria*, *Monostroma* and *Enteromorpha* [66]. Current uses for macroalgae include food, feed, chemicals, cosmetics and pharmaceutical products [9]. *Phaeophyceae* and *Rhodophyceae* are industrially exploited whilst *Chlorophyceae* are mainly consumed as food [9, 67].

China, The Philippines, North and South Korea, Japan and Indonesia have large macroalgae industries, mainly for food production. In Europe, macroalgae are predominantly used for the production of hydrocolloids and other chemicals [7]. Throughout the 18th and 19th century macroalgae were dried and burnt to produce a product known as *kelp* [68], which was used for glass and soap manufacture, as well as bleaching linen [65]. It was also used as a feedstock in the potash industry, which turned macroalgae into an economically attractive commodity during the early 20th Century. However, the industry declined in the 1930s, leading to a loss of interest [69].

In terms of market value, macroalgae are seen as a high volume, low value crop in comparison to other aquaculture species, such as shellfish [27]. In terms of the worldwide aquaculture production, aquatic plants represent only 9.7% of the total economic value, despite producing the second highest output by volume [70]. The total global production of all aquaculture products in 2004 was 59.4M t with a total value of £38.4B (US$70.3B). However aquatic plants, represented almost a quarter by weight, but only a tenth by value (£3.7B (US$6.8B)) [71]. This also signifies a reduction in value from 2003, where approximately 7.5-8M t of wet macroalgae had a market value of approximately £3.67B (US$6B) [72].

The food industry dominates the macroalgae market and was worth £3B (US$5B) in 2003 alone. Hydrocolloids were valued at approximately £358M (US$585M), with agar, alginate and carrageenan being worth £81M (US$132M), £119M-130M (US$195M-US$213M) and £147M (US$240M) respectively [72]. The cosmetics industry represents a smaller area of the market, yet produces higher value end-products compared to food and chemicals.

2.2.1 Uses

2.2.1.1 Food

Food grade macroalgae are known as sea vegetables [31] with Japanese Nori and Kombu being the most common dishes [72, 73 & 74].

In Japan macroalgae are now being used as a raw material for noodles, tea, wine, jam and cheese [75]. Macroalgae as a food source has begun to spread to the West, particularly as a supplement for those wishing to eat a healthy diet [72].

2.2.1.2 Chemicals

In Europe macroalgae are used primarily for the production of hydrocolloids [7], which are non–crystalline, water-soluble substances that act as thickening agents. They are used in a number of industries including food, where they thicken solutions into gels or jellies and stabilise ice cream. Hydrocolloid production requires approximately 1M t/y of macroalgae to produce 55,000 t of hydrocolloid. Three types of hydrocolloid are produced and exploited. These are agar, alginate and carrageenan, which are water-soluble carbohydrates [72, 76, 77 and 78].

2.2.1.2.1 Agar

This substance is extracted from two species of *Rhodophyceae*, *Gracilaria* and *Gelidium*, known as agarophytes. The agar is obtained via hot water extraction, though an alkaline prewash can improve the quality of the final product. The hot water extraction is performed at 95-110°C for 2-4 hours, depending on the macroalgae species. The mixture is then processed into a gel and often bleached to remove any colour before being washed again. The final product is a food grade agar (1% agar, 99% water) that can be sold in strips or as a powder [72].

2.2.1.2.2 Alginate

Alginates are extracted from *Phaeophyceae* species *Ascophyllum, Durvillaea* and *Laminaria*. In terms of extraction, the aim is to produce sodium alginate in a dry powdered form. Alginate is separated from water by adding a chemical to create a non-water-soluble material. There are currently two methods in use, the first using acid to make alginic acid, the second using a calcium salt which makes calcium alginate. An advantage of using alginate gels is that no heat is required in the process, unlike agar gels [72].

In France, *Laminaria hyperborea* is harvested for alginate production. However, the industry is believed to be in decline after predicted increases in alginate industry demand and production did not materialise [79].

2.2.1.2.3 Carrageenan

This hydrocolloid is extracted from a small *Rhodophyceae* group including *Chondrus crispus* (Irish Moss). There are three types of carrageenan; these are Iota, Kappa and Lambda. Iota is an elastic gel, whilst Kappa is a strong, rigid gel. Lambda is used to form high viscosity liquids or solutions.

Carrageenans are extracted using two methods. The first uses filtration, which has been used since the 1970s but is difficult and expensive. The second method dissolves macroalgae in alkali and water, which is relatively cheaper. The product is dried and sold as semi-refined carrageenan (SRC), which is used as flour for canned pet food due to its good gel properties [72].

2.2.1.3 Cosmetics

Macroalgae are also used in cosmetics, not only as thickening gels but extracts have been proven to improve skin moisture retention [72], making it an attractive ingredient in anti-aging products [80]. Macroalgae are also used for treating blemish prone or oily skin [81, 82], as shown in Figure 2.7, and are now an active ingredient in combating cellulite in the form of seaweed soap [83].

2.2.1.4 Farming

Its high fibre and mineral content make macroalgae a good fertiliser source, with tests producing promising results. It is used as a soil supplement in either solid form or liquid extract, where 10,000 t (wet) macroalgae produce 1,000 t fertiliser extract [38, 72]. The industry was originally disbanded after the introduction of synthetic fertilisers; however, the resurgence of organic farming has led to a revival, though it has yet to reach large-scale potential [72].

The costs of drying and transportation have limited its use to coastal areas [72]. In Brittany, France macroalgae are used to fertilise spring produce [41], whilst in Ireland it is a popular fertiliser for coastal golf courses [31]. The use of excess shoreline macroalgae as a fertiliser is seen as the most suitable use for a feedstock whose quality and abundance is hard to predict and therefore unattractive to the larger macroalgae-based industries [38].

In Norway *Phaeophyceae* have been used as a source of animal feed since the 1960s using 50,000 t/y wet macroalgae to produce 10,000 t/y of meal at a market value of £30.6M (2003) (US$5M) [72]. In France *Ascophyllum Nodosum* is used for cattle feed and other animal products; however this is a declining industry [79].

2.2.1.5 Environmental

Microalgae GHG abatement has been recognised for many years [9]; however macroalgae also absorb large amounts of CO_2 and release O_2, reducing the effect of eutrophication, particularly in ocean areas [25]. They can also transform, remove or sequester other pollutants like xenobiotics (chemical compounds which are foreign to an organism [84]), and excess nutrients using a process known as phycoremediation [9]. The resulting macroalgae can be used as a source of algal biomass for the production of biofuels, biogas and chemicals [85].

Macroalgae are also an inexpensive and readily available material for removing toxic heavy metals [9, 86]. *Phaeophyceae* have been proven to be superior to most other types of terrestrial biomass, especially for removing cadmium, lead and copper [86].

Proposals have also been made to use macroalgae for reducing sand losses in coastal areas in the form of weed screens. These are closed caged macroalgae systems, which break up the rip current and stabilise sand losses. This is seen as more economically attractive than power generation [87].

2.2.1.6 Medical

The antiviral properties of algae attract the interest of the medical world [31]. Carrageenan sourced from macroalgae is also used to produce Carraguard™, a drug that is being developed to prevent women contracting sexually transmitted diseases and HIV/AIDS [88]. *Corallina officinalis* is collected for medical purposes and after processing, is used as bone forming material [89]. Macroalgae can also be used in a range of hydrotherapy treatments to relieve osteoporosis and rheumatism [72]. Alginate may also become an important supplement for weight loss, after being proven to absorb larger quantities of fat than current over-the-counter diet aids [90].

Macroalgae can also benefit the health of domestic animals. It is used to remove tartar from the teeth of cats and dogs, improving the health of teeth and gums and reducing the need for extractions. It is sold as a powder, which is added as a supplement to meals [91]. It can also be used to improve the health of human teeth [92].

The broad scale of uses for macroalgae highlights a greater need to divide the resources between more industries, resulting in competition. However, integrated utilisation systems could produce a large range of products including energy, food, cosmetics, fertiliser and other chemicals. This would also reduce production costs due to the range of prices of the outputs [9].

2.2.2 Production

Currently macroalgae are grown in purpose built cultivation farms or harvested from natural standing stock, depending on geographic location. Approximately 97% of Asian *Phaeophyceae* species are grown as monocultures [93, 94] to avoid high variability in quality and composition. In Europe, macroalgae are traditionally harvested from natural standing stock, which produces high variability in quality and composition [95].

Macroalgae cultivation farms worldwide are estimated to produce 13.9M t/y (wet), whilst 1.8M t/y (wet) is harvested from natural stock. The latter is mainly harvested for production of marine colloids [35]. In 2001 1.68M t (wet) (based on 90 wt% MC) of macroalgae were harvested for carrageenan extraction worldwide [72].

Cultivation takes place in either inshore (land-based), nearshore (coastal) or offshore facilities. Inshore cultivation takes place in ponds or lochs situated near a saltwater supply. The salinity is usually controlled by a series of locks and gates that allow measured amounts of sea and freshwater in and out. The ponds are positioned in sheltered areas since exposure to strong winds can affect the macroalgae, particularly free-floating species [72]. Harvesting is carried out in nearshore or offshore areas where macroalgae is found naturally.

2.2.2.1 Cultivation

Over 90% of utilised macroalgae worldwide are grown in cultivated systems [70]. *Gracilaria* and *Gelidium,* used for agar production, have been successfully cultivated since the 1960-70s and expanded in the 1990s to cope with the growing industry. *Chondrus crispus,* which was considered a limited wild resource, is now cultivated in warm water areas with low labour costs [72].

The level of establishment varies with geography. In Asia cultivation is a well-established process, which produces most of the world’s macroalgae [27]. European cultivation is limited, with Brittany, France, being one of Europe’s largest cultivators of macroalgae, producing 25 t/y [27, 70]. The potential of marine aquaculture in Europe can often be overlooked. In Germany alone, there is very little political support for the utilisation of marine culture, meaning that it does not attract investors [96].

In addition to the factors that affect the natural resource, such as nitrogen and light availability, cultivation productivity is based on the photosynthetic efficiency of the macroalgae and assumptions of scale up [9]. An understanding of the chosen species life cycle is also beneficial to macroalgae cultivation, since this knowledge improves cultivation practices and species selection, which in turn enhances economic performance. Life cycle based discoveries have revolutionised the culture of specific genus in Japan, China, and Korea [35].

Obtaining reliable yield data is difficult since statistics based on published estimates are commonly used. Differentiation between actual and optimised yields can also be an issue due to the variation in production outputs. For instance, *Laminaria japonica* cultivated in China yields 150 t/ha/y (dry) on average, though yields of up to 600 t/ha/y (dry) have been recorded [27]. In terms of typical productivity nearshore *Laminaria* has a maximum yield of 84-192 t/ha/y [adapted from 7-16 DAF t/ha/y at 20 wt% ash and 90 wt% water] [97, 98 p.39].

Optimised productivities have been achieved using very dense planting and highly controlled environments. However, the productivity costs are high and the quality of the macroalgae produced low, reducing the potential for future scale up and commercialisation [98, 99].

2.2.2.1.1 Epiphytes

Outdoor cultivation exposes macroalgae to predators and weed-like plants called epiphytes. Epiphytes or epiphytic algae are a form of *Ulva* whose growth is promoted by a good availability of underwater light and space [66]. They do not directly damage macroalgae via parasitic behaviour, but epiphytes are known to monopolise light and space resources. Systems used for free-floating cultivation are frequently affected because of the difficulty accessing macroalgae below the water line. This results in the systems not being as regularly inspected and maintained as fixed systems [72]. Nevertheless, ephitytic growth can be successfully controlled by growing macroalgae in high densities since it reduces the availability of light and space. This process does affect the growth rate of the macroalgae but the overall yield is still high due to the dense amount present [66].

2.2.2.1.2 Cultivation practises

Since macroalgae breed through either vegetative or reproductive methods, the cultivation processes vary. Vegetative cultivation involves placing small macroalgae cuttings into a suitable environment, such as a salt-water tank, loch or artificial pond, allowing them to germinate and grow. Free-floating *Gracilaria* undergo vegetative cultivation in ponds, where small pieces of macroalgae are sprinkled throughout. The enclosed space reduces the dispersion and dilution of the macroalgae [72].

Reproductive cultivation involves collecting zoospores from adult macroalgae in order to produce gametophytes and subsequent sporophytes. They are cultivated into young plants through a variety of systems, normally based outdoors [100]. This is the most common type of cultivation because *Phaeophyceae* can only be bred reproductively [72].

The microscopic nature of the reproductive cycle means that the initial stages of cultivation are carried out in land based cultivation tanks, known as cultivators [72]. Adult thallus samples are collected during winter and often partially dried before being submerged in containers of seawater, releasing zoospores [101]. The liberated zoospores are transferred to large seawater basins containing plastic frames wrapped in propylene culture line [95]. The zoospores readily attach themselves to the culture line, which acts as an artificial surface (substratum). The reproductive cycle then begins, producing sporophytes, which are cultivated in water of 8-10°C [101].The frames are normally rotated every other day. Lamps provide artificial light for a specific duration each day in order to replicate natural growth conditions. Investigations have proven that subjecting *Laminaria digitata* to 8 hours of sunlight produces a continuous high growth rate that can be maintained throughout the summer, a season hampered by slow growth [102]. *Laminaria saccharina* on the other hand requires 10 hours of sunlight [95].

The seawater is regularly filtered and can be enhanced if required. A supplement called Provasoli Solution is specifically designed for the *'enrichment of media'* [103, p.445] during macroalgae cultivation, promoting growth. Germanium (IV) oxide can also be added to prevent non-intentional algae (diatom) growth [95]. Additional air agitation results in each layer of the macroalgae being cultivated separately [66].

The process takes approximately 2 to 3 months, when the first sporophytes reach an average length of 1-3 cm [95, 101]. The cultivation lines and sporophytes are then transplanted to the outdoor cultivation system to complete the growth process.

The following sections describe various methods of attached cultivation based inshore, nearshore and offshore.

2.2.2.1.2.1 Tank

Whilst the majority of sporophytes grown in tanks are transported to outdoor cultivation systems, some species are grown exclusively in the cultivator. This allows macroalgae to be grown continuously all year by replicating the short days of early winter in indoor facilities. The artificial conditions override the period of slow growth in the summer and may reduce epiphytic growth. The success of cultivators is credited to the continuous nutrient supply, the absence of predators and grazers as well as a reduction in parasitic activity [66].

2.2.2.1.2.2 Raft

Floating raft cultivation is used extensively in China. A floating carrier line is suspended at the water surface by floats and anchored to the sea bed. From these carrier ropes kelp ropes are attached. The juvenile sporophytes are normally removed from their culture lines and are inserted into the twists of kelp ropes, which can accommodate about 30 juvenile plants for every 2 m [101].

There are two methods of raft cultivation in practise; these are the single-raft (hanging-kelp) and double raft (horizontal kelp) methods. For the single-raft method, shown in Figure 2.5, the kelp ropes hang vertically down from floating line and are normally anchored by a small piece of stone. Whilst this method has better water movement, it is prone to uneven macroalgae growth.

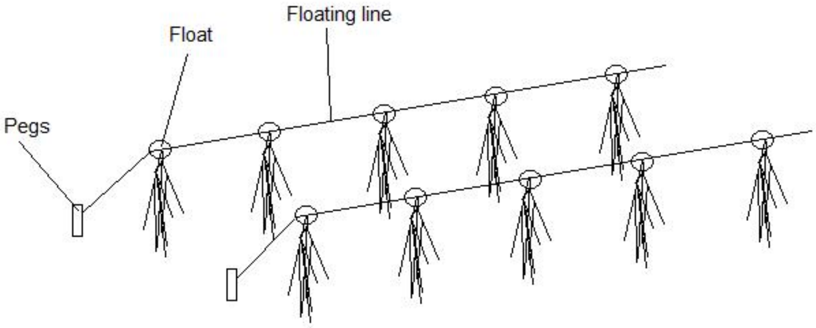

Figure 2.5: Single raft (hanging kelp) method (based on [104])

A variation on the single-raft is the bottom method (stake and nylon-line method). Stakes are pegged a specified distance apart and the pre-seeded culture line, normally monofilament nylon, is suspended between them [105].

The double-raft method (Figure 2.6) consists of tying two kelp ropes together at one end and attaching other ends to floating lines. This method produces an even growth of macroalgae, though the system is more resistant to water motion [101].

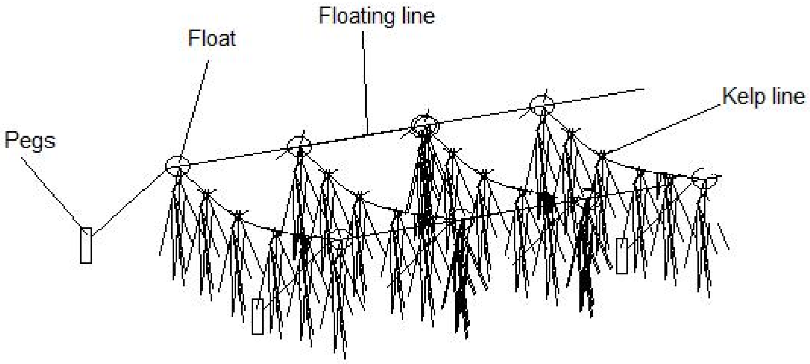

Figure 2.6: Double raft (horizontal kelp) method (based on [104, 106])

2.2.2.1.2.3 Longline/ladder/grid

The longline method, shown in Figure 2.7 is used for mussel farming as well as macroalgae and is very similar to single-raft cultivation.

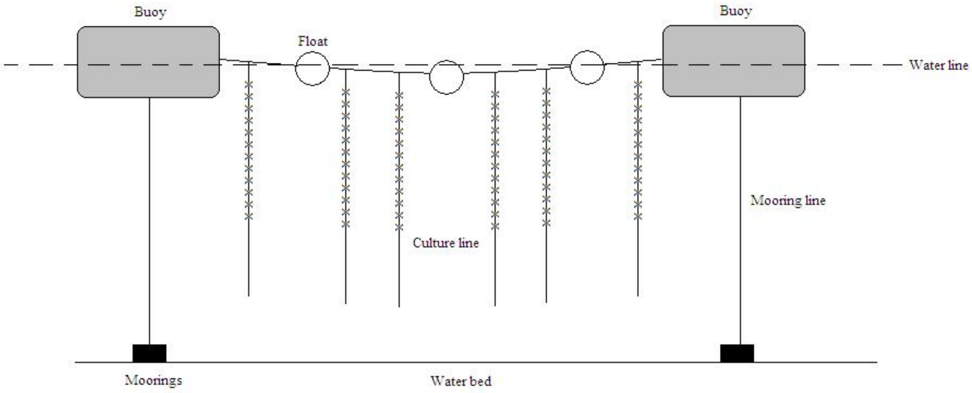

Figure 2.7: Longline cultivation (adapted from [107])

The carrier ropes are suspended horizontally across the cultivation pool, and are submerged at a specified depth depending on light availability. From the carrier ropes culture lines are fastened at regular intervals, hanging vertically into the water. This method is considered the most suitable for inshore cultivation systems in irregular shaped water areas [107].

The offshore system (Figure 2.8 a)) is modified to survive turbulent conditions and has been tested and employed successfully [40, 108].

Figure 2.8: a) Longline, b) ladder and c) grid cultivation [95]

The carrier ropes are secured using a heavy anchorage system whilst the culture lines are fastened perpendicular to the water surface and loaded using concrete weights. Sporophytes are knotted onto the carrier line at regular intervals. Adjacent culture lines are also added to create a v-shape layout [95]. The ladder and grid systems are variations of the longline (Figure 2.11 b and 2.11 c respectively).

The ladder, or tandem longline, design is similar to the double raft method and has been tested for offshore cultivation. Carrier ropes are secured into a structure, resembling a ladder and anchored securely to the seabed. In between the ladder steps, culture lines are knotted [95]. The grid is an improved ladder design, which has been used off the Isle of Man [40] and the Brittany coast [108]. The design consists of framework of carrier ropes, anchored to the seabed. From the framework, culture lines are secured in a grid-like pattern. This design has proven more stable than the ladder system [95].

2.2.2.1.2.4 Net

Like the longline method, net-based cultivation has been adapted from mussel farming. The system (Figure 2.9) was proposed by Energy research Centre of the Netherlands (ECN) [109].

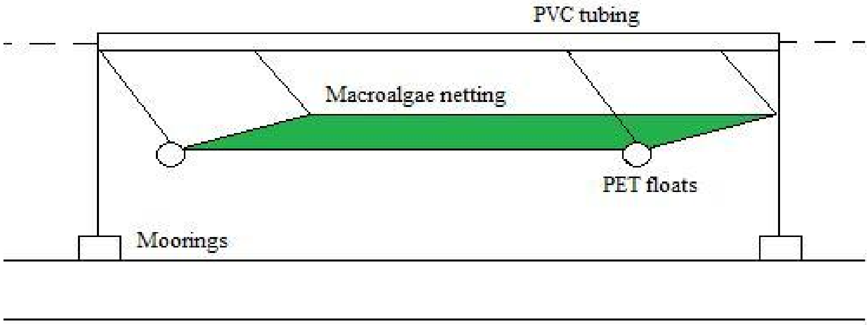

Figure 2.9: Net cultivation (adapted from [109])

The nets act as the macroalgae substrate and are anchored for stability. PE tubes provide buoyancy, whilst PVC tubes stretch the nets in order to increase the cultivation surface area [109]. Pilot-scale tests are in progress, which use steel cables, suspended 2 m below the water surface, as anchorage for the nets [110].

2.2.2.1.2.5 Ring

Another design is the ring, shown in Figure 2.10, which has been tested successfully for offshore cultivation. This design consists of a circular polyethylene ring of a specific diameter. For the North Sea demonstration a ring diameter of 5 m was used, though the American offshore trials found that a circular ring structure of 15 m diameter was more favourable [95, 98].

Figure 2.10: The ring design [95]

The rings are anchored by steel cables and buoyed. Carrier ropes are suspended radially and culture line is fastened around to resemble a cobweb.

The design has a major advantage; it can be seeded onshore before being towed offshore and fixed into position using a ship-based crane. The rings can also be lifted easily for sampling and towed back to shore for harvesting. If conditions dictate that the macroalgae cannot be examined at the site, the ring is towed to a more suitable location [95].

2.2.2.1.3 Offshore cultivation

Reliance on nearshore and inshore sites for cultivation is not recommended since environmental law protects many of these areas [95]. An alternative option for macroalgae production is offshore cultivation. This is an attractive prospect since approximately 66% of the Earth’s surface is covered in ocean [111].

Whilst yield data is unavailable, growth rates in offshore conditions are believed to be limited by nutrient availability. However, there is the possibility of upwelling nutrients in open ocean areas [9], though the process is not economically attractive. The survival rate of cultivation lines in offshore facilities varies with sea conditions. The loss of anchors and entanglement of lines are seen as common problems. Often ropes are stripped of macroalgae by a strong current, a consequence of incompatible dynamics between the lines and the tide, though this can be prevented by adjusting line tensions and the systems geometry.

In 1968, Howard Wilcox conceived the idea of large open ocean macroalgae culture farms to provide alternative sources of food, chemicals, fertiliser and energy. Fuelled by the oil crisis of the 1970s, the US Navy embarked on an ambitious cultivation project for *Macrocystis pyrifera*. This was later taken over by the several large energy-governing bodies, such as the American Gas Association (AGA) and the U.S. Department of Energy (DOE) and remodelled into the U.S. Marine Biomass Energy Program. The original offshore cultivation farms were based on the Wilcox method (1975), a longline system submerged 10-30 m below the water surface. The systems were towed and positioned by ships before being anchored to the seabed or a system of buoys. Tests have shown that the survival rate of cultivation lines varies with sea conditions, though the loss of anchors and entanglement of lines are seen as common problems. Often ropes are stripped of macroalgae by a strong current, a consequence of incompatible dynamics between the lines and the tide, though this can be prevented by adjusting line tensions and the systems geometry [98].

Along with the USA, countries such Canada, France, Germany and the Netherlands are currently trying to establish large-scale offshore cultivation [9]. However, experience gained from offshore farming, particularly kelps, has shown that there are difficulties in the collection process [112].

2.2.2.1.3.1 The North Sea

The North Sea is the focal area for offshore cultivation in Northern Europe. Though it is seen as a *‘high energy environment’* [96, p. 96] with wind speeds of up to 150-180 km/h, and wave heights commonly reaching 5-8 m [95], macroalgae cultivation has potential in the more sheltered southern region, which requires less protection from the elements [87].

Buck & Buchholz [95] completed an extensive study on the offshore cultivation potential of *Laminaria saccharina*, testing four types of cultivation rig (longline, ladder, grid and ring) in the North Sea. The longline test had a relatively poor outcome, with only 46% of the cultivation lines retrieved. Loss of lines was caused by a series of storms, which also resulted in the lines being maintained and replenished infrequently throughout the trials. In addition, the anchorage weights were not heavy enough to stabilise the structure and the current frequently used them to damage and tangle the cultivation lines. Mechanical abrasion due to turbulence was also a factor, tearing off weaker culture lines. The ladder suffered from durability problems, and was particularly sensitive around the points where the weights were connected, which were considered to be potential braking points. The buoys situated on the corners were also found to be very unstable and had to be replaced on numerous occasions, increasing the amount of maintenance required. These problems led to the longline and ladder systems being considered unsuitable for the North Sea; particularly due to the amount of damage suffered [95].

The grid proved to be more stable; however, unnecessary damage was caused by a domestic yacht entering the clearly marked test zone, causing losses. Whilst this is an unfortunate accident, it does emphasise the need to provide offshore farms with protection from their surroundings. The grid system proved to be the most underproductive and was susceptible to fouling [95].

The ring showed superior performance in the North Sea, remaining stable and in position during rough weather, provided the moorings were regularly checked. In terms of production approximately 0.4 t/ring (wet) macroalgae is estimated. However, the ring is not suitable for nearshore production. During the trials, a negative growth period was recorded for one of the nearshore rings situated within a harbour. This was due to fouling by epiphytes and resulted in substantial blade deterioration [95].

2.2.2.1.4 Production costs

There is a significant difference between terrestrial and aquatic biomass production costs. Data for macroalgae is often out of date, however the equivalent 2009 £ has been calculated. Typical terrestrial biomass production costs vary between £20-30 /t (US$0.04-0.06 /kg) [9], whilst macroalgae from offshore cultivation costs between £60-437 /t (wet) (US$0.045-0.31 /kg, 1981) [98, 113, 114]. However, the production of microalgae is more expensive than macroalgae [9].

Reasons for the high cost have been agreed to be due to non-renewable and renewable inputs during the growth stage [33, 115]. The North Sea offshore ring trials require capital of £690 (€1,000 (2004)) per ring, as well as an additional £69 /y (€100 /y (2004)). Labour requirements for offshore, line-based systems are very high since the seeded culture lines have to be attached by hand from a rowing boat. This can only be done during the slack tide period in calm conditions, resulting in the need to increase the size of the workforce to complete the task. In addition, the availability of qualified divers and ships can cause delays in construction and maintenance [95].

It is still considered economically unattractive to cultivate macroalgae required for the alginate industry. In 2001 126.5 kt (dry) of macroalgae was harvested worldwide for alginates. Tank cultivation is a very expensive process due to the need to replicate ideal conditions, often resulting in the costs not being recovered when the macroalgae is sold [72].

For offshore cultivation, the utilisation of wind farms in conjunction with open ocean aquaculture systems (Figure 2.11) has been suggested, in order to provide both protection and capitalise on the limited available space [96].

Figure 2.11: The offshore wind farm aquaculture system [96]

An integrated system provides the opportunity to launch new technology that would not necessarily be economically attractive as a standalone system. Costs associated with maintenance are spread across several budgets as opposed to one [96].

Investigations have been made into the use of various cultivation structures within the infrastructure of an offshore wind farm [116]. At present, trials are underway in the Netherlands, where small-scale (20 m^2) net-based cultivation modules have been constructed within wind farms. These trials will determine whether offshore wind farms provide suitable protection for macroalgae cultivation, particularly in harsh North Sea conditions, without affecting survival and growth rates. The ecological impact can also be measured [110].

Multipurpose aquaculture systems look promising, though the harvesting process has proven to be labour intensive and the economic potential has yet to be fully researched [9]. In addition to this, conflicts are expected between respective stakeholders, especially since there is limited legislation concerning ownership and responsibility of coastal areas [96].

2.2.2.2 Harvesting

Wild macroalgae are normally harvested from natural water basins where they are seasonally available [43]. The harvestable amount of natural macroalgae is approximately a fifth of the standing stock, due to constraints with equipment, location and sustainability [27]. European coastlines have a considerable natural abundance of macroalgae [117], which has allowed for harvesting. Fifteen genera are exploited including *Laminaria*, *Ascophyllum* and *Fucus*. *Laminaria hyperborea* is one of the most exploited genera in Europe [79].

2.2.2.2.1 Manual harvesting techniques

Gathering storm cast macroalgae from beaches and shorelines is a popular method in several countries, like Spain, Portugal and Argentina, where two people drag a net across shallow water bays [72]. *Laminaria hyperborea* is commonly collected as drift, at some sites in large concentrations [79]. This is due to the plants stiff stipe, which increases the effect of wave action on the holdfast, making it more sensitive [118]. In Ireland *Laminaria hyperborea* drift is collected after spring storms. This process has an annual production of 7,000 t stipe and 2,500 t blades. The drift is also harvested by hand in Orkney and the Hebrides, Scotland. The process is labour intensive and employs 30-150 people, where the most skilled collectors can harvest 200 t/y. The drift harvesting season is between October and March [79].

Along the French Atlantic shoreline, *Ascophyllum Nodosum* is found in easy to reach coastal areas, resulting in the macroalgae being cut by hand and loaded directly onto tractors. Until recently, *Laminaria digitata* beds on the French Atlantic coast were harvested manually using the *'guillotine'*, a long shafted sickle that cuts the stipes from the plant and lifts the blades onto the boat. This instrument is limited to nearshore use due to the need to see where the blade is cutting. The guillotine was succeeded by the *scoubidou*, which has a hook and crank instead of a blade [79].

In Scotland intertidal species such as *Fucus vesiculosus* are cut from rocks midway between the high and low water lines whilst sub-tidal *Laminaria digitata* is gathered from rock pools and areas around the watermark [65]. When harvesting *Ascophyllum Nodosum*, due to topography, small boats are used for access. This particular species have air bladders, which allows it to float to the water surface after cutting. The macroalgae is then collected in nets and towed to shore. Each net typically holds 1 t of macroalgae, giving a daily output of 7-8 t/person [79].Alternatively, divers are employed to pick macroalgae off underwater rocks. However, this is not considered good practise since it is likely to remove the entire plant, eliminating re-growth [72].

2.2.2.2.2 Mechanical harvesting techniques

Mechanical harvesting is implemented using specially designed boats, which allow the collection and storage of macroalgae. Whilst there are several variations, the boat normally consists of a cutter and suction system. The cutter literally mows the macroalgae, leaving about 25 cm for re-growth. The cuttings are then sucked into the boat by the suction tube, which is often positioned by a diver [72]. There are limitations however, since some mechanical harvesting processes cannot operate at wave heights of over 70 cm [79].

For harvesting *Ascophyllum Nodosum* in Iceland a low draught barge propelled by two paddle wheels is used. A sawtooth blade moves back and forth to cut the macroalgae, which falls onto a steel conveyor belt and is transported to a storage container, as shown in Figure 2.12.

Figure 2.12: The paddle wheel barge [119]

On average, the height of the cut is 13 cm and is controlled by the relative height of the blade, which is lifted and lowered accordingly. This method leaves a macroalgae reserve 10-20%. Once the cutting barge is full (1.4 t) the macroalgae is transferred to a collecting barge. Due to the low efficiency propulsion, this process is limited to sheltered areas [79].

The mechanical harvesting of Scottish *Laminaria hyperborea* began in the 1940s. A reciprocating cutter enclosed in an iron grating cage, connected to the boat by a rubber tube, was towed across the water bed, mincing macroalgae before it was sucked up to the boat. However, this method removed the entire plant. Alternative designs included a hooked conveyor, which harvested 12 t/h macroalgae at a water depth of 6 m, and a hydraulic based cutting and suction system. The latter is no longer practised due to hydraulic problems [79].

In France, the first mechanised system for harvesting *Laminaria digitata* was a trawler with an open grating in the hold, from which a suction pipe was fed. The macroalgae are cut by a scuba diver with a sickle and pumped through the pipe and into the hold, which has a 7 t capacity and grating for water drainage. This design was hampered by pumping issues, the age of the macroalgae collectors (over forty) and the high price of professional scuba divers. The unloading process also took 6 hours. An alternative design is the mechanised Scoubidou (Figure 2.13), where the large hook acts as a gimlet and pulls macroalgae out.

Figure 2.13: The mechanised Scoubidou [120]

When the Scoubidou is hoisted aboard the gimlet is reversed, releasing the macroalgae. This process has a collection rate of approximately 1.2 t/h. The boats are normally 8-12 m long and produce daily harvests of 10-30 t, with the larger boats equipped with two Scoubidous. In terms of investment a 10 m boat costs approximately £123,500 (2009) (600,000 FrF, 1984), whilst the 12 m version costs £257,300 (2009) (1.25M FrF, 1984). The harvesting season is between May and September [79].

Laminaria hyperborea however is harvested after spring storms. A dredge system has been developed to only harvest mature stipes [121], which has been confirmed to work successfully. In addition, a sorting device has been developed to separate blade and stipe during collection. The stipes are chopped to reduce their size and storage requirements on-board. This process has been met with strong opposition from fishermen, who believe the dredge is collecting more than macroalgae [79].

Norway has a well-established mechanical harvesting scheme with a substantial turnover. It has an estimated standing stock of 10M t, and an annual *Laminaria hyperborea* harvest of 130,000-180,000 t [122]. *Laminaria hyperborea* harvesting has been mechanised since 1964 [123] and comprises of a cutting dredge and trawl net. The dredge is towed by crane and cuts the macroalgae 5-20 cm above the holdfast. The dredge bottom is made of metal sheeting, whilst the sides and top is iron grating, allowing macroalgae collection and suitable water drainage. The dredging depth varies between 1 m and 20 m. A low quantity of macroalgae is lost during operation, though debris is also collected, particularly in rocky areas. The dredges are available in a range of sizes from 7 m to 21 m, though

14-17 m is the most common size. A 7-8 m dredge collects 0.3 t whilst 12-21 m versions can 1 t. Daily harvests depend on boat size, with small boats collecting 6 t and large boats 20-25 t. The boats require a two-man crew in order to both locate suitable beds and operate the dredge.

Ascophyllum Nodosum is collected using the suction cutter system. Macroalgae is cut using a wing blade at the end of a steel suction pipe. It is then drawn through the pipe and deposited in a net on the quarter-deck. Once the net is full, it is ejected and replaced. The nets are either towed to shore or collected by a cargo boat (capacity 300 t) at a later time. Leaving the nets in the sea is a good storage method for keeping it fresh, especially if there is a large distance between the source and processing plant [79].

2.2.2.2.3 Recovery and regulations

Many countries operate a strict licensing system for controlling kelp harvesting. This is because the process may lead to the ecosystem being irreversibly damaged [7]. In order to protect areas of heavy exploitation, macroalgae beds are often divided into sites and subjected to a rotation plan, in order to allow bed recovery.

Ireland harvest macroalgae all year round, and employ site rotation in 3-4 year cycles, whereas Scotland performs the same over 2-3 year period [79]. Norway has a highly regulated harvesting policy [122]. The macroalgae are sourced from four regions, which are in turn divided into five areas and harvested on a five-year cycle [124]. It is estimated that it takes five years for a kelp forest to re-establish its original level, though it has been seen that it does not recover so fast [125]. It has also been found that the location does affect the populations, particularly in terms of growth and mortality [27].

In Nova Scotia, where mechanically harvested areas are exploited at a rate 40-60%, a 2-3 year fallow period is required for recovery [126]. There has been an emerging trend away from mechanised to manual harvesting in the past 10 years to the point where no mechanical methods are used [127]. The move towards manual harvesting is a result of restrictions in allowable yield, which has rendered the boats useless [72].

French regulations 2606 P4 and 34 forbid the hand collection of macroalgae and the disruption of their habitat by stone turning. Two cuts are permitted per year at times specified by the Head of Maritime Affairs and the Institut Français de Recherche pour l’Exploitation de la mer (IFREMER). *Laminaria digitata* harvesting fleets are also limited to 70 boats by law in exploited areas [79].

2.2.2.3 Logistics and processing

2.2.2.3.1 Transport

The transportation of macroalgae is restricted by the *'prohibitive cost...of this slippery, bulky and wet material'* [31, p.11]. This results in the costs potentially cancelling out other economic gains [8]. For this reason, macroalgae users such as agar producers are often situated locally to the source [72], where the feedstock is normally delivered fresh in modest volumes for further processing [128].

Ireland and Scotland operate a similar system for transporting *Ascophyllum Nodosum.* The macroalgae is towed to the coast before being transported by road. Alternatively, the macroalgae is directly transported via cargo boat to the processing plant. Norwegian *Laminaria hyperborea* is shipped to shore where it is unloaded by cranes into hoppers at coastal processing centres. In France *Laminaria digitata* harvested using the mechanised scoubidou is unloaded by replacing the hook for a fork, which results in 20 t unloaded in 2.5 h. For larger harbours the unloading and transportation of macroalgae is controlled by the alginate industry using trucks and grabs. With an unloading rate of 0.5-0.6 t/grab it takes less than 40 minutes to unload 35 t of *Laminaria* [79].

2.2.2.3.2 Storage and processing

Due to transportation problems, processing and storage facilities are normally situated on coasts. There are six processing centres along the Norwegian coast [79]. At present macroalgae are normally dried and chopped or ground for use in industries such as food, phycocolloids and cosmetics.

For drying, suggestions have been made for utilising solar energy or recovered heat in order to keep the process environmentally benign [33]. Icelandic *Ascophyllum Nodosum* is dried using geothermal energy [79], which is an abundant native heat source. However, the potential of solar energy is only feasible in countries subjected to a considerable and frequent amount of sun. For areas such as the UK, this method will not be feasible. Areas like Norway rely on oil-fired furnaces to dry macroalgae, which are affected by the price of fossil fuels [72]. This is an important factor to consider, particularly in terms of the economic influence on potential production processes. Drying would not be necessary for some conversion processes such as anaerobic digestion and liquefaction, which makes these processes more attractive [33].

If possible, the macroalgae undergoes preliminary drying outdoors, which reduces the moisture content to 30 wt% (wet). This process is called dehydration and lasts 2-3 weeks (weather permitting) between May and September. In Ireland *Laminaria digitata* is partially dried in open air before being oven dried at the processing plant [79].

In France *Ascophyllum Nodosum* is dried using a rotary drum and ground for use. Alternatively, it is placed in ventilated drying cupboards, which are normally used in the tobacco industry. Scottish *Laminaria hyperborea* is dried on iron gratings allow air circulation, whilst *Ascophyllum Nodosum* is dehydrated on a drying belt and ground to make powder. Irish *Laminaria hyperborea* stipes are oven dried and then powdered [79]. Norway relies on oil-fired furnaces to dry macroalgae, which are affected by the price of fossil fuels [72].

Ensiling macroalgae was suggested during the 1950 and 1960s [129, 130] though it has yet to be fully tested. In Norway *Laminaria hyperborea* is dried, finely ground and ensiled using formaldehyde. Freeze-dried macroalgae products are made for dietetic and cosmetic use. *Ascophyllum Nodosum* is used to make 'seaweed creams' for expensive products, presumable cosmetics by freezing and then grinding the macroalgae [79]. Freezing macroalgae has distinct advantages by keeping the plant in a fresh state. This allows for the analytic comparison of varying species found worldwide in the same place and time. It also means that macroalgae can be stockpiled, resulting in harvesting being less reliant on pinpointing favourable tides and weather [31]. However, the economic potential of freezing macroalgae for bulk or low cost products has yet to be completed. Alternatively mixing in a minimal amount of ligneouscellulosic substrate is effective in stabilising macroalgae for storage. The mixture cake can be used for organic enhancing and as a fertilising agent [131].

2.3 Macroalgae for Biomass and Bioenergy

At present, large-scale marine biomass utilisation does not exist since macroalgae are classed as a residual biomass, which are harvested in order to reduce problems related to eutrophication [115]. In terms of biomass production macroalgae needs to be highly productive, easily harvested by mechanical techniques, withstand open ocean water conditions and be produced at a cost equal to or less than that of other available biomass [9]. Currently the latter criteria cannot be met; since macroalgae have high technical and economic uncertainties in relation to large scale, open ocean production [98].

The following sections summarise the potential macroalgae conversion methods and their current status.

2.3.1 Anaerobic digestion

Anaerobic digestion is a naturally occurring process, which takes place in environments where little or no O_2 is present. Microorganisms degrade organic material to produce a biogas product of 50-80 vol% CH_4, 20-50 vol% CO_2 as well as trace levels of H_2, CO, N_2, O_2 and H_2S, depending on the feed used, and a solid residue (digestate) [132, 133]. The process is also referred to as biological gasification or methanisation and utilises wet feedstocks economically at low temperatures. The anaerobic digestion of organic matter for the generation of biogas is an important process, which is currently used for the treatment and management of organic waste, including sewage [56, 132].Aquatic plants, such as macroalgae and water hyacinth have been linked with research into biogas production via anaerobic digestion [134].

The time taken for the digestion process to be completed is commonly known as the retention time, which varies with the feedrate, type of feed and process temperature. Anaerobic digestion operates using feeds of various solid contents. In general, systems containing ≥30 wt% total solids (TS) are classed as dry digestion, whilst ≤15 wt% TS systems are considered wet [1]. However to be more specific Low Solid Digestion (LS) operates at less than 10 wt% TS, Medium Solid Digestion (MS) between 15 wt% and 20 wt% TS and High Solid Digestion from 22 wt% to 40 wt% TS [135].

Macroalgae contain 5-10 wt% solid material [134], resulting in the use of LS digestion unless de-watering technologies are implemented. Single species and algae blends (multiple species of macroalgae combined into a single feedstock) have been investigated, with single species feeds producing more biogas [56, 136].

The feedstock is harvested, coarsely chopped and fed into a reactor in the presence of the corresponding micro-organisms, normally provided by an innoculum [136]. Due to the solubility of the feedstock, the retention time is referred to as the hydraulic retention time (HRT), which is the average length of time that the soluble material remains in a reactor. This period can last up to 60 days [41] though a HRT of 20-30 days is more common [136].

Data compiled by Carlsson et al. [9] (Table 2.2) shows the methane yields per kg volatile solid (VS) of several macroalgae species compared to other feedstocks.

Table 2.2: Methane yield data

Feedstock	Methane yield (m^3/kg VS)
Laminaria sp. [137]	0.26-0.28
Sargassum sp. [138]	0.12-0.19
Macrocystis pyrifera [137]	0.39-0.41
Food waste [137]	0.54
Water hyacinth [137]	0.13-0.21

As shown, macroalgae produce less methane than food waste, but more than water hyacinth. This is due to several limiting factors linked to the physical and chemical properties of the feedstock.

In previous work the solid conversion process is normally only 60% complete [136]. In most cases small-scale batch digestion (single stage, non-continuous feeding) is used, which is less efficient than multiple stage, continuous processes [132].Higher methane yields from macroalgae have however been recorded using continuous, multiple stage digestion [44, 56].

Concerning chemical properties, salt, polyphenols and sulphated polysaccharides present in macroalgae are believed to inhibit fermentation-based processes [128]; although feedstock pre-treatment (washing) reduces the negative impact. Furthermore, the remaining polysaccharides (alginate, mannitol and laminarin) are easier to convert than the lignin and cellulose present in terrestrial feedstocks [56].

The low solid content (5-10 wt%) is the most significant limiting factor since a substantial mass of macroalgae is required in order to generate reasonable biogas yields (comparable to terrestrial systems), regardless of the VS-to-methane conversion rate. In terms of economics, it is believed that the macroalgae-based facilities must operate continuously all year in order to be profitable, possibly with the addition of other feed sources [38]. However, in Japan a continuous macroalgae-fed digestion system is already in operation as part of a gas fuelled power generator facility, which has encouraged the consideration of wider macroalgae utilisation in the future [44].

2.3.2 Fermentation

Fermentation is defined as the biological conversion of sugars into ethanol and CO_2 with the aid of yeasts [31]. The purpose of fermenting biomass is to produce bio-ethanol, which is easy to store and transport [136].

Generally, macroalgae do not contain lipids, however their natural sugars and carbohydrates are under consideration for fermentation into alcohol-based fuels [128]. Since terrestrial biomass is the principal feedstock for bio-ethanol production, little work has been done with macroalgae [30]. The studies that have been completed however produced less than satisfactory results [139, 140].

Sub-optimal conversion rates and yields are mainly caused by the microbes used to degrade the macroalgae. Until recently, the microbes have been of terrestrial origin, which have been incompatible due to the high concentrations of salts present acting as a limiting factor. At present enzymes found on the macroalgae skin are believed to have significant potential as fermentation microbes because of their tolerance to high salt levels. Utilising these microbes may prove more effective than using terrestrial based enzymes [31].

Very few species have been tested for bio-ethanol production, resulting in requests for more research into different species of macroalgae and marine microbes that have potential, as well as pre-treatment for yield optimisation [31].

The economic potential of macroalgae fermentation has been the subject of some discussion in literature. For general biomass, Chynoweth et al. [136] stated that the requirement of extensive feed pre-treatment as well as the need to maintain a pure bacterial culture, coupled with the low overall energy efficiency due to processing and separation requirements. Morand et al. [140] also declared that the bioconversion of Brittany macroalgae to ethanol in Brittany would require very long-term investments with specific conditions.

It is believed that the economic potential of macroalgae fermentation could be enhanced by using alginate extraction waste by-products as raw feedstock, thereby eradicating the costs associated with marine cultivation. This is because the alginate waste is mainly contains laminarin and mannitol, which are the best substrates for bioethanol production. In terms of the process itself it was noted that the cost of enzymes has decreased considerably, making ethanol production more affordable. There have also been recent improvements in technology and methods, which means that it will take years rather than decades to reach optimum yields and conversion rates [27].

2.3.3 Combustion

Combustion is defined as the thermal conversion of a feedstock in the presence of air, which produces heat. The process is implemented in power stations for heat and power production using either fossil fuels or biomass via co-firing. Large power stations, fossil fuel or biomass, have efficiencies of approximately 33% [33]; however, the costs relating to biomass plants are higher due to the moisture content of the fuel [4].

Combustion and co-firing of macroalgae have yet to be evaluated to a wide extent [7], though there are claims of a large number of studies being completed [46]. The process is considered to be a conventional way of producing energy from macroalgae, either boiler or steam turbine based [33], however the high moisture content and ash properties of the feedstock are not attractive for this process [7].

In terms of thermal characteristics, algal biomass ignites easily but is hard to burn and has a low thermal heating value. It is recommended that macroalgae should be used for combustion in fluidised bed boilers [46] or as a component of a blended fuel source in order to keep the quantity of ash at an acceptable level [7].

2.3.4 Gasification

Gasification is defined as the thermochemical conversion of a solid, carbon-based feedstock in the presence of an oxidising agent, which is normally a gas. This produces a synthesis gas (syngas) product predominantly composed of H_2 and CO [141]. Conventional gasification technology requires a low moisture content feedstock (<50 wt%), since high moisture content feeds produce a less clean gas and lead to lower process efficiencies and condensate problems [142].

To gasify macroalgae it is believed that process temperatures in the range of 2000°C would be required [43] and that operational problems may occur due to the feedstock's high ash content [7]. Little research has been published on macroalgae gasification. Ross et al. [7] refer to a large-scale macroalgae gasification project operating in Japan, however, information is difficult to obtain.

The gasification of wet biomass has been performed successfully [48] and operates in either hydrothermal or supercritical conditions. Currently, these processes utilise raw sewage sludge and animal manures, which are high-energy feeds [143].

Hydrothermal gasification is a low temperature, high-pressure process, which operates at the sub- or near critical water point with the aid of a catalyst. Depending on the catalyst used, operating temperatures and pressures range from 200-350°C and 210-220 bar respectively [144]. The process has a residence time of approximately 15 minutes. There are no residual organics or fugitive emissions to air and, because the process uses the water present in the feed as the gasification medium, no air or O_2 is required [143]. The end-product is a biogas of mainly methane and CO_2 [144].

Supercritical water gasification (SCWG) operates at 600-700°C and 300 bar to convert biomass into a syngas of H_2 and CO. Although the process does not use catalyst for biomass conversion, an activated carbon catalyst is present to stop the formation of a solid by-product. SCWG systems can suffer from severe corrosion, regardless of the level of pre-treatment, due to the high operating pressure and requires an efficient heat exchange system to make the process attractive [145].

There are however, issues that can arise from the utilisation of biomass, terrestrial or marine. According to Ro et al. [143], trace components in the biomass feed can cause some processing difficulties, especially in the reactor system of fixed catalyst beds. In fact, the authors suggest that, like combustion, gasification should only be attempted if the macroalgae is used as part of a blended fuel.

2.3.5 Pyrolysis

Pyrolysis is defined as the high temperature conversion of dry biomass in the absence of air. The resultant products are bio-oil or bio-crude, charcoal residue (char) and a hydrocarbon rich gas mixture. Altering the operating conditions varies the amount of each product created. Fast (flash) pyrolysis operates at low temperatures, high heating rates and short gas residence times, which maximises the yield of liquid products. Slow pyrolysis however operates at low temperatures and heating rates, which increases the char yield. The fuel gas is maximised by running the system at high temperatures, a low heating rate and a long gas residence time [5, 146].

Whilst the process requires a low moisture fuel [146], both macroalgae and microalgae have been utilised as feedstocks [69, 147]. In fact, the pyrolysis of macroalgae is not a recent development, having been recorded by Stanford in 1862. Research into pyrolysis products continued until the 1930s, ending when the potash industry stopped utilising macroalgae as a feedstock [69].

Small-scale studies have however been carried out in more recent years. Work involving the pyrolysis of brown macroalgae *Fucus serratus,* discovered that drying to a 15 wt% moisture content prior to use was a sufficient enough water reduction to produce acceptable results. However, the overall potential of the process was not regarded as favourable and the majority of the discussion referred to the need to improve the process in order to make it successful [69].

In general, the suitability of macroalgae as a feedstock has caused a division of opinion. Numerous sources [9, 69 & 146] state that pyrolysis prefers dried or low moisture content feeds (up to 15 wt%) and will therefore not favour macroalgae. It is also unlikely that flash pyrolysis alone would be an economic potential in the future since most of the organics require further processing [69].It is also believed that the pyrolysis of macroalgae would require operating temperatures of 500°C to be successful, thereby increasing the energy input of the system. However, the correct forms of pre-treatment may provide the necessary improvements [43].

However, the difference in composition and ignition temperature [148, 149], the lower thermal stability of macroalgae [150] and the possibility that the volatile fraction of may make macroalgae easier to pyrolyse than woody biomass [46]. It is also believed that the alkali and heavy metals present in macroalgae catalyse the pyrolysis process and potentially influence combustion habits [48]. This area however still requires further investigation.

2.3.6 Liquefaction

Liquefaction is described as a low temperature, high-pressure thermochemical process that uses catalyst to produce a liquid product [5]. The process is more tolerant to moisture than gasification and pyrolysis, recovering liquid products from wet biomass sources [151].

Demirbaş [152] estimated that macroalgae liquefaction needed to operate at approximately 300°C and 10 bar in order to produce a significant quantity of oil. In a series of small-scale experiments using *Chlorophyceae*, Aresta et al. [43] produced bio-oil at 250-395°C and 30 bar (N_2). The oil produced is also a higher quality than terrestrial biomass oil, which often contains gums that cause clogging.

3 Previous work (marine)

Very little analysis has been completed regarding the utilisation of macroalgae as marine biomass [35], resulting in a limited number of techno-economic studies. In most cases, the economic assessment relies heavily on work completed by the Marine Biomass Program (1968-1990) (§3.1.3), which to date is the most significant investigation attempted. The majority of reports are preliminary assessments that are mainly descriptive. These are presented in conjunction with other analyses such as chemical and physical breakdowns, environmental impact evaluations and most commonly an in-depth history of macroalgae production as well as a considerable list of recommendations.

Nevertheless, these studies form the background for the subject and define the limitations of past and current investigations. The papers and reports selected for this review discuss a range of activities proposed for macroalgae utilisation. Several papers present the evolution of proposed production and conversion practises from a particular institution. This relationship means that some results have not been achieved independently.

Utilising papers from various sources presents data quoted in a range of units, currencies, base dates and assumptions. This means that direct comparison is not possible without a common base. However, in this review, a range of data are comparable, these are:

- Scale of macroalgae production
- Cultivation techniques
- Feedstock yields
- Products and conversion rates
- Cost of production considerations
- Labour
- Concluding remarks

In some cases a base date is not given, therefore economic data are presented as published. To ensure relevance, only information relating to macroalgae is included.

There are several techno-economic papers that assess the cultivation of macroalgae, which are not included in this review. This is because these studies refer to small-scale farming in Asia and do not utilise the feedstock as biomass. In addition to this, papers documenting the technical performance of macroalgae as marine biomass are not included, however these reports are utilised in subsequent chapters.

3.1 Comments on individual papers

3.1.1 A Beavis, RH Charlier, C De Meyer, 1986

Laminaria ssp. as energy source [87]

Although this is not a recent publication, this paper provides one of the more detailed economic analyses for the growth and utilisation of macroalgae. It evaluates the potential of macroalgae marine biomass in Belgium, covering the cultivation and anaerobic digestion of *laminaria sp.*

The study asks two questions:

- What (if any) are the possible economic advantages of macroalgae cultivation in Belgium?
- Can the anaerobic digestion of cultivated macroalgae lead to the extraction of methane gas?

The work is based on results obtained from a test scale, cage cultivation farm, which is considered too small for commercial success, but satisfactory for research. Additional information is sourced from literature. The investment data are presented in 1986 US$.

This paper is one of the few studies that highlight the problems surrounding the accuracy of published cultivation yield data, especially the difference between projected and measured data.

3.1.2 DP Chynoweth, JO Owens, R Legrand, 2001

Renewable methane from anaerobic digestion of biomass [136]

This journal paper, written by the University of Florida, provides a summary of biomass-based anaerobic digestion, including several genera of macroalgae, and the relative projected costs. The authors propose a generic digestion system, operating at 35°C, with a HRT of 20-30 days. This produces a biogas of approximately 60 vol% methane and 40 vol% CO_2.

The cultivation of macroalgae is not included and, like Beavis et al. (§3.1.1), the cited data are relatively out of date (1987), though this has been converted to 1990 US$, based on the gas price of that year.

3.1.3 DP Chynoweth, 2002

Review of biomethane from marine biomass (DRAFT) [98].

This report reviews the history, results, and conclusions of the Marine Biomass Program. The scope of the program was to determine the technical and economic feasibility of the production of substitute natural gas (SNG) from marine biomass anaerobic digestion. The work was completed under the sponsorship of the U.S. Navy, the gas industry (AGA and Gas Research Institute), and the DOE. A range of near- and offshore cultivation practises are included in the assessment for use in the United States waters, concentrating mainly on the production of native kelp *Macrocystis pyrifera*.

The program ended due to low fossil fuel energy prices and reduced emphasis in renewable energy in the U.S.; however, some alternative ideas for macroalgae cultivation and end-product (methanol) are included from more recent discussions. Economic data are presented for a range of years in US$ and are cited by several of the studies included in this review.

3.1.4 JH Reith, EP Deurwaarder, K Hemmes, AP Curvers, P Kamermans, W Brandenburg, G Zeeman, 2005

Grootschalige teelt van zeewieren in combinatie met offshore windparken in de Noordzee [116].

This study, completed by ECN and Wageningen UR (WUR), assesses the feasibility of macroalgae cultivation in the North Sea, and its utilisation as marine biomass. It forms the basis for several reports included in this review.

Three species of macroalgae native to the North Sea are under evaluation; however only work regarding *Laminaria sp.* is included in this review. Various published cultivation processes are assessed, including the use of wind farms as anchoring structures. However, pilot scale wind farm experiments are recommended, since this proposal has yet to be fully tested. The anaerobic digestion of macroalgae for biogas production and ethanol fermentation are the two bioenergy processes considered alongside a variety of non-bioenergy based chemical synthesis systems, in order to acquire the maximum amount of product from the feedstock. Production costs are presented for several bioenergy case studies in €, though a base date is not given.

3.1.5 MS Kelly, S Dworjanyn, 2008

The potential of marine biomass for anaerobic biogas production: a feasibility study with recommendations for further research [132].

Also referred to as the Crown Report or the Marine Estate Report, this study draws on a range of literature in order to assess the feasibility of macroalgae growth and conversion in the UK (Scotland). Whilst Scotland has the capacity to meet its electrical energy needs through other renewable energy schemes, the production of alternative transport fuels is proving difficult since natural conditions do not support the growth of terrestrial biomass. However, the extensive coastline provides a platform for marine biomass. In this report inshore, nearshore and offshore cultivation are under consideration.

As the title suggests, the primary conversion method is anaerobic digestion for biogas (CH_4) for the generation of power or fuel. This report includes a number of case studies for current state-of-the-art anaerobic digestion systems, which are used to forecast the feedstock requirement and production capacity of marine biomass. A preliminary analysis for *Lamina sp.* is included, which is assumed to be in 2007-2008 £.

3.1.6 G Roesijadi, A Copping, M Huesemann, J Forster, J Benemann, 2008

Techno-Economic Feasibility Analysis of Offshore Seaweed Farming for Bioenergy and Biobased Products [35]

This study, completed by the Pacific Northwest National Laboratory (Battelle), Forster Consulting Inc. and Benemann Associates, is a preliminary techno-economic assessment of offshore macroalgae cultivation to produce biofuel. According to the authors, macroalgae have unrealised potential as biomass.

The report presents a review of past and current attempts of offshore cultivation for biofuel and the relevant problems encountered. Whilst a substantial amount of information is taken from the Marine Biomass Program, recent work from Europe and the Far East is also included. The economic assessment is based on a 100 ha offshore cultivation farm, which feeds a Marine Biorefinery. Cost data are presented in US$ for a range of base dates, though the year of the assessment is not specified. The paper advises that the production of higher value products in conjunction with biofuel will improve revenue.

3.1.7 T Bruton, H Lyons, Y Lerat, M Stanley, MB Rasmussen, 2009

A Review of the Potential of Marine Algae as a Source of Biofuel in Ireland [128]

Commissioned by Sustainable Energy Ireland, this report assesses the potential of macroalgae and/or microalgae utilisation for the production of biofuel for the transport sector. The proposed biofuels obligation scheme sets a biofuel usage target of 10% (energy basis) by 2020. This study reports that by 2020, macroalgae can potentially supply around 0.2%, based on current fuel demand.

The work focuses on the native kelps of Ireland, which are *Laminaria digitata, L. hyperborea, Saccharina latissima, Sacchorhiza polyschides* and *Alaria esculenta.* Macroalgae undergo conversion using either anaerobic digestion or ethanol fermentation, which are both under investigation as part of a potential bio-refinery scheme.

This report also presents a supply-chain analysis, which identifies the technologies and research required to evaluate commercial potential of macroalgae for energy. From this, the assessment outlines three scenarios, high, medium and low, which represent the various levels of implementation the project may achieve. Cost data are presented from various literature sources, including Reith, Deurwaarder et al. (§3.1.4), in a range of base dates and currencies.

3.1.8 H Reith, W Huijgen, J van Hal, J Lenstra, 2009

Seaweed potential in the Netherlands [29]

This document provides a summary of several topics covered by Reith, Deurwaarder et al., and was presented at the Macroalgae Bioenergy Research Forum, held in Plymouth, UK in June 2009. In this case, the work focuses on the offshore cultivation of macroalgae as part of a wind farm-based aquaculture system. The presented costs are derived from Reith, Deurwaarder et al., and have not been adjusted. Projections for 2015 and 2030 are included, which expect an improved energy revenue as knowledge develops.

3.1.9 J Lenstra, H Reith, J van Hal, 2010

Economic perspectives of seaweed [109]

This document was presented at the Fourth International Algae Congress, held in Amsterdam, The Netherlands in December 2010, and discusses the economic potential of offshore macroalgae cultivation in the North Sea. Like Reith, Huijgen et al., (§3.1.8), the preliminary information is derived from Reith, Deurwaarder et al., however, the case studies presented for the economic assessment are for different farm scales. The cultivation system suggested is based on mussel catching facilities, using nets as the macroalgae substrate. Whilst the report is brief, the economic breakdown is one of the most detailed to date, with the cost data expressed in €, though no base date is given.

3.1.10 G Roesijadi, SB Jones, LJ Snowden-Swan, Y Zhu, 2010

Macroalgae as a Biomass Feedstock: A Preliminary Analysis [153].

This report is written by Pacific Northwest National Laboratory (Battelle) for the DOE, as part of the Energy Independence and Security Act (EISA), building on information published in Roesijadi, Copping et al. (§3.1.4). In this study, macroalgae are cultivated offshore for biofuel production via anaerobic digestion, fermentation and hydrothermal liquefaction.

The authors present a preliminary assessment, which is adapted from literature, including costs derived from Reith, Deurwaarder et al., based on the production and conversion of 500k t (dry) macroalgae. The cost data are expressed in 2008 US$.

3.1.11 J Lenstra, J van Hal, H Reith, 2011

Economic aspects of open ocean seaweed cultivation [154]

This document is a continuation of Reith, Deurwaarder et al., and was presented at the Alg’n Chem in Montpellier, France in November 2011. It discusses the offshore cultivation of floating macroalgae for marine biomass. The macroalgae grow in large netted areas, known as colonies or biological deserts. The macroalgae is utilised for bio-ethanol production, economic data are presented in €, no base date specified.

3.2 Data comparison

3.2.1 Scale of macroalgae production

The potential scale of macroalgae cultivation varies with experience and optimism. Older studies present highly ambitious, large-scale farming situations, for instance, Chynoweth (2002), citing Bird [113], state that a systems analysis for a 2,670 ha *Macrocystis pyrifera* farm has been completed, though results are not included. Bruton et al. also refer to past projects for large-scale cultivation of up to 4,100 ha.

Recent publications tend to be more modest, specifying a cultivation farm size of 100-500 ha. Lenstra, Reith et al. (§3.1.9) and Roesijadi, Copping et al. (§3.1.6) both specify an offshore cultivation of 100 ha. Bruton et al. (§3.1.7) state that, optimistically, near-shore and offshore farms of 500 ha and 200 ha respectively, are possible in the near future. According to Bruton et al., projections should remain modest until preliminary production targets become achievable. However Reith, Deurwaarder et al. consider large-scale production, assessing the potential of 2,100 ha and 10,000 ha offshore cultivation farms, producing 100,000 t/y and 500,000 t/y macroalgae (wet) respectively.

3.2.2 Cultivation techniques

Reviews or discussions of cultivation techniques, based on literature, are commonplace in the majority of reports. However, in cases such as Bruton and Kelly & Dworjanyn, the economic assessment does not specify a particular practice. It is possible that the author’s intention is to calculate whether the overall project is economically attractive before finalising the sub-system details.

Other sources however, assess a specific practise. Beavis et al. investigate the use of cages, which are based on mussel farming techniques. Lenstra, Reith et al. discuss line and net cultivation, favouring net due to the potential of fully mechanised harvesting, which is under investigation. Lenstra, van Hal et al. (§3.1.11) also consider net cultivation, although this is for non-attached species.

3.2.3 Feedstock yields

In the papers under review, a range of feedstock yield data are presented, which cover various *Phaeophyceae* genera, farm constructions and feedstock forms (wet, dry and DAF). This makes the comparison of raw data difficult without firstly converting to a common base. Beavis et al., for example, presents a range of annual offshore cultivation yield data from several literature sources, which are quoted in various forms (Table 3.1).

Table 3.1: Macroalgae yields presented by Beavis et al. [87]

As shown, presenting data in various feedstock forms can cause confusion. There are also significant differences between projected and measured yields, resulting in misleading performance, an issue this paper emphasises. In their report, the authors state that Jackson [159] and Morley & Jones [160] are the most reliable results, though no reason is given.

A large number of reports in this review use yield data that precedes 1990, either directly or indirectly. For instance, several papers quote Chynoweth, who in turn cites Bird [113].

Some studies suggest modest yield estimates. Reith, Deurwaarder et al. estimates an annual offshore yield of 20 t/ha (dry) macroalgae, without the use of nutrient upwelling. Bruton et al. also specify a production rate of 20 t/ha for *Laminaria sp.*, 35 t/ha optimised, based on a literature review. They also estimate that an annual productivity rate of 25 t/ha (dry) is a modest, realistic research goal. Though the use of different species is taken into account, these figures differ significantly from the projected figures in Table 3.1, and are more in line with Jackson [159] and Morley & Jones [160].

Several studies specify higher production rates. Reith, Deurwaarder et al., and later Reith, Huijgen et al. and Lenstra, Reith et al., estimate that an annual offshore yield of 50 t/ha (dry) macroalgae is achievable using nutrient upwelling and plant layering techniques.

In addition to cultivation, Bruton et al. also consider the collection of driftwood as a supplementary macroalgae source, approximately 50,000 t (assumed annually). This raises the question of whether macroalgae production would be more attractive as a multiple sourced system.

3.2.4 Products and conversion rates

All studies under review consider anaerobic digestion and/or fermentation. This is due to the high water content of the feed, which limits feedstock utilisation without extensive drying. Reith, Deurwaarder et al. do consider thermochemical conversion processes such as combustion and gasification. They are not discussed in detail; though their operation using macroalgae is still considered to be realistic.

A significant amount of work has been completed for macroalgae anaerobic digestion in past projects, such as the Marine Biomass Program, making it a well-established research process.

Conversion rates range between 0.26-0.42 m^3/kg VS; however, most of the studies cite data from the 1980s. Bruton and Roesijadi, Jones et al. (§3.1.10) both cite Matsui et al. [44], who give a conversion rate of 22 m^3/t macroalgae, based on their 1 tpd test scale macroalgae digestion plant.

Several papers consider the production of ethanol from fermentation, though data are less available than anaerobic digestion. In terms of conversion, Roesijadi, Jones et al. cite Aizawa et al. [161], who provide a conversion rate of 0.27 kg/kg macroalgae (dry).

The choice of conversion process is also dependent on the economic output. Chynoweth et al. and Chynoweth conclude that although macroalgae have the potential to produce comparable CH_4 yields to many terrestrial feedstocks, the cost of production is significantly greater. According to Chynoweth, bio-ethanol production is favoured in the United States, due to the growing need to provide renewable transportation fuel. Reith, Deurwaarder et al. believe that macroalgae fermentation has considerable potential in the longer term, whilst anaerobic digestion is feasible in the short term.

Several projections regarding energy production from macroalgae are presented, though it is acknowledged that these are mainly optimistic, due to the uncertainties of offshore farming. In Ireland, Bruton estimates that macroalgae could potentially generate up to 447 TJ of energy by 2020, which in terms of biofuel, is approximately 0.2% of current national fuel demand. Based on Chynoweth & Isaacson [162] and Legrand & Warren [163], Chynoweth et al. estimate an annual marine energy potential of >100 EJ in the U.S., however this requires 243M ha of ocean for feedstock cultivation, an area roughly the same size as Argentina.

Reith, Huijgen et al. cite Ecofys [164], who estimate that the global energy potential from macroalgae ranges between 35 EJ and 6,000 EJ, depending on cultivation process. Near-shore sites will produce the lowest, whilst offshore colonies the greatest, mainly due to the vast surface area of ocean available.

3.2.5 Cost of production considerations

In the studies under review, the capital and non-capital costs of macroalgae utilisation are often expressed as the cost of production. This is normally presented as a break-even selling price (BESP) either the feedstock or the end-product. The vast majority of papers cite economic data by Bird [113], directly or indirectly via Reith and Deurwaarder et al. or Chynoweth. Kelly and Dworjanyn calculate a preliminary cost of feedstock production; however, this is based on unsupported assumptions, including a feedstock cost of £1,000 /t/ha, which is the equivalent to the most expensive terrestrial crop.

In some cases, studies provide cost breakdowns. Beavis et al. present the actual construction cost for a pilot scale farm, separating the costs into materials (69%), installation (17%), indirect (insurance, maintenance) (4%) and contingency (10%).Whilst no figures are presented, Roesijadi, Copping et al. assume that the production cost comprises mainly of the operating costs (40%), the annualised capital (20%) and depreciation and maintenance (15%). The authors also specify a modest ROR of 5%.

Recent studies cite cost analyses completed by ECN, particularly Reith, Deurwaarder et al., shown in part in Table 3.2. Although the authors acknowledge that the technical information is from the Marine biomass Program, the economic data are based on their own calculations.

Table 3.2: Cost data by Reith, Deurwaarder et al.

Operating costs are estimated at 10% of the investment capital, which is lower than the Roesijadi, Copping et al. estimate. As shown, the increase in scale produces a comparatively small increase in the break-even cost. This effect of scale is an important, yet infrequently discussed factor for macroalgae production. In the studies under review Beavis et al., Reith, Deurwaarder et al. and Lenstra, Reith et al. provide cost analyses for multiple scales, which provide some idea of the effect. From Table 3.2, a 500% increase in productivity reduces the costs per t macroalgae by ~34%. Lenstra, Reith et al., also present data, shown in Table 3.3, provides similar relationships.

Table 3.3: Cost data by Lenstra, Reith et al.

From above, increasing the farm scale by a factor of 10 reduces the material cost by 30% and the installation cost by 22%. Here, the operating costs are assumed the same, regardless of scale, whilst harvesting costs reduce and plateau.

The work presented by Beavis et al. applies two cost discounts, which are from the farm manufacturers. The first is based on the farm layout allowing the multiple use of specific equipment (-40%), the second is for mass fabrication (-20%).

3.2.6 Labour

Limited data are available regarding the labour requirements for marine biomass utilisation, however some papers state that labour contribute significantly to the production costs.

Bruton et al. believe that the main obstacle in European cultivation will be labour cost since, for microalgae, 45% of the production cost is labour. Whilst it is a common belief that the low cost of macroalgae in Asia is due to low labour costs, the authors state that this is in fact due to advanced cultivation techniques. Chynoweth also state that cultivation costs are primarily labour based. According to the author, the costs are mainly associated with the use of seamen, who adhere to union wages and restrictions. Bruton et al. suggest that growing macroalgae as part of an aquaculture system means that labour costs are shared amongst the parties.

3.2.7 Concluding remarks

From the studies under review, it is possible to draw several conclusions.

Firstly, more research is required in order to fill in the knowledge gaps. Roesijadi, Copping et al. and Kelly & Dworjanyn both provide an extensive list of recommendations, which emphasise the need for more research into marine biomass, particularly offshore cultivation, in order to improve the accuracy of techno-economic assessments. Additional, updated economic data are also requested.

Secondly, additional revenue is required in order to make macroalgae an attractive source of marine biomass. Beavis et al., Bruton et al., Reith et al. all favour a marine biorefinery system, with the additional manufacture of non-biomass, high-end products.

Nevertheless, Lenstra, Reith et al. conclude that North Sea cultivation has economic potential providing robust systems can be built and a range of products, in addition to energy, can be produced. Roesijadi, Jones et al. believe that, due to the vast amount of available coastline and the subsequent surface area, the United States has a high marine biomass resource potential.

4 Objectives and methodology (marine)

4.1 Scope of study

The purpose of this study is to carry out a techno-economic assessment that evaluates the potential of utilising macroalgae as a marine bioenergy resource in the UK. To provide a basis for comparison, it will be specified that the final energy product will be the delivery of electrical power and heat in a Combined Heat and Power (CHP) scheme. Whilst the production of biofuels from macroalgae has potential, a broader range of conversion technologies may be evaluated for CHP generation, which do not require extensive product upgrading processes. It is the intention of this assessment to define the most technically feasible and economically attractive exploitation route. The study covers the entire process, from the production of the macroalgae to the supply of the energy product, and comprises of the following objectives:

- To propose a range of growth scenarios, in order to identify the most suitable scale of production for the UK.
- To evaluate current biomass conversion routes to energy products, and select the most suitable for macroalgae based on a range of criteria.
- To calculate mass, energy and power balances for each of the scenarios.
- To compile a full economic evaluation for each scenario in order to produce a cost of production, which will identify the most promising systems.
- To assess the economic suitability and determine the most favourable and unfavourable conditions using sensitivity analyses.
- To identify the current boundaries of macroalgae utilisation in the UK.

Techno-economic studies for bioenergy from macroalgae are limited in number and often incomplete. Available reports normally provide preliminary assessments, since accessible data are either non-existent or difficult to obtain. However, the majority of studies reviewed in Chapter 3 have similar scopes, which can be summarised as follows:

- The cultivation of *Phaeophyceae* species is favoured over harvesting from natural stock, with the scale of farming being at least 100 ha.
- Anaerobic digestion and fermentation are the primary conversion processes, due to their high moisture tolerance, however thermochemical processes, such as combustion and gasification, have potential.
- Additional revenue from the sale of conversion co-products can increase the processes ROR. In addition to this, the proposal of a macroalgae biorefinery is economically attractive.

It is the intention of this techno-economic assessment to go beyond these boundaries, in order to evaluate the potential of UK based macroalgae utilisation.

4.2 Scale of production

The availability of feedstock is an important consideration. As discussed in Chapter 3, scale dictates the production techniques and the resultant costs. This work investigates a range of macroalgae production scales, based on information supplied by project partners and current developments in literature.

Since harvesting of the UK's macroalgae natural resource is already performed by numerous industries [165] and will be subject to strict regulations for environmental protection in the future [31], the majority of production systems concentrate on macroalgae cultivation.

The following sections discuss the potential scale of production that could be developed in the UK.

4.2.1 Cultivation

4.2.1.1 Inshore

In the UK, inshore aquaculture farms operate at relatively small-scale, dictated by the availability area of water. At present, there is no definite strategy for macroalgae cultivation site expansion. In this study, individual inshore cultivation sites have been limited to 3 ha, based on current planning applications. However, connecting sites by waterways will create larger farm networks, which may be operated as a single system. The maximum size of the cultivation network has been limited to 12 sites, though 5 to 6 sites are more realistic for a small geographic area [107].

4.2.1.2 Offshore

The scale of offshore cultivation is difficult to estimate due the vast ocean surface area. ECN propose that by 2040 approximately 9% (8.77%) of the Dutch Exclusive Economic Zone (EEZ) will be used for macroalgae cultivation, which is the equivalent of 0.5M ha [based on Dutch EEZ of 5.7M ha] [116]. Applying the same principle to the UK, which has a larger EEZ, assigns an area of 6.8M ha of water solely for the production of macroalgae [based on 8.77% of 77M ha [166]]. Since the UK has yet to implement offshore cultivation, this is a highly ambitious scale of production to achieve, even by 2040. In addition, the negative implications of offshore installations require consideration. These range from disruptions to marine navigation, shipping and commercial fishing to damage and destruction of natural habitats [35], all of which will be applicable to UK waters. For this work, the size of stand-alone offshore cultivation sites is restricted to 1,000 ha (0.001% of EEZ), which should comply with the above limitations but still produce a satisfactory macroalgae yield.

To increase offshore productivity, farms will be installed within offshore wind farms as part of an open ocean aquaculture system (§2.2.2.1.4). The structural layout of a wind farm has the potential to provide protection to cultivation systems, which would not be available for stand-alone open ocean macroalgae farms. In addition, using a multipurpose aquaculture system requires less ocean area than individual structures, reducing the negative impact on the environment (protection of natural areas), trade and other ocean activities. Furthermore, there is also the potential to cultivate a cooperative management system, where all parties involved share the responsibilities of operating an aquaculture system [96].

Current UK wind farms range from approximately 500 ha to 11,200 ha, with 1,000 ha being the most common [based on sites that are either in operation or under construction] [160]. There are also larger sites, ranging from approximately 12,400 ha to 24,500 ha in the planning stages, which are also considered. All wind farm sites are situated within the 22.2 km (12 Nautical miles) of the Crown Estate coastal zone.

4.2.2 Harvesting

Macroalgae is readily available on the coastlines of Ireland and Scotland, though the actual quantity is difficult to determine. Ireland has an estimated 3M t kelp standing stock; however, this estimation is based on a regional survey with a ±40% margin of error [128]. In Scotland, Walker [167, 168] completed the only large-scale macroalgae survey, which is the most comprehensive record to date. The data presented in Table 4.1 have been extrapolated from the original survey [132].

Table 4.1: Scottish macroalgae resources (based on [132, 167 & 168])

Location	Standing crop of kelp (1947) (Mt)	Area (ha)	Coast length (km)	Density (t/ha)
Orkney	10.88	22,663	805	48
W. Kintyre & Gigha	0.18	4,452	80	41
Outer Hebrides	0.63	16,593	137	38
Crail	0.02	526	11	38
Skye	0.27	7,285	354	37
E. Kintyre	0.04	1,052	35	34
Loch Eriboll	0.02	526	21	34
Tiree & Coll	0.27	8,094	93	34
Dunbar	0.05	1,376	18	33
Islay	0.05	1,619	18	28
Luce Bay	0.02	648	6	28
Shetland	0.55	22,663	1,127	24
Girvan	0.04	1,700	34	23
Colonsay	0.02	809	10	22
Mull	0.02	931	24	19
Arran	0.05	2,752	77	18
Helmsdale	0.02	1,174	16	17
Tarbat Ness	0.01	648	13	14
Enard Bay – Lochlash	0.11	9,713	257	11
Fraserburgh	0.05	7,285	97	7

As shown, areas such as Orkney and the Outer Hebrides provide a large standing stock and high macroalgae density, which would be attractive for harvesting. However, exploitation needs to be controlled to avoid degradation of natural resources. In Norway and Northern Ireland, harvesting is limited to a maximum annual rate of 5% standing stock [based on 6-17% over 5 years] [27,132]. This figure has been adopted for this study, therefore a maximum annual production of 0.5M t (wet), could be achieved in Scotland.

It will be demonstrated in a later chapter that these scales of production are well suited to CHP schemes as currently deployed.

4.3 Methodology

4.3.1 Process selection and modelling

The selection of the most suitable conversion process is discussed in Chapter 5. The selection process is based on a criterion, which considers the technical feasibility of utilising macroalgae.

All modelling is completed using Microsoft Excel®, in order to produce mass, energy and power balances. Process parameters are taken from relevant literature, or are based on assumptions, which are noted. The systems are divided into sub-systems, which are discussed in Chapter 6.

4.3.2 Assessment criteria

The cost of marine biomass production and utilisation is calculated by estimating the total capital and operating costs over the system lifetime and then dividing by the annual production rate of either the feedstock or the product. In this study, the production cost is presented in both ways, depending on the context.

For this study, the following costs are included in the assessment:

- Investment costs of the macroalgae production system
- Total plant costs (TPC) of the conversion process
- Fixed and variable operation and maintenance costs, including labour, overheads and supplementary fuel costs
- Costs related to the transportation of feedstock
- The revenue from conversion by-products

The following costs are excluded:

- Costs related to the initial growing of feedstock (laboratory)
- Costs related to the decommissioning and demolition of the plant at the end of its lifespan
- Government subsidies

TPC data are corrected for scale using the following equation (4.1):

$$C_{scaled} = \frac{C_{original}}{\left(\frac{P_{original}}{P_{scaled}}\right)^{n}} \tag{4.1}$$

Where C_{scaled}: Capital cost of the scaled plant, $C_{original}$: Capital cost of the original plant, $P_{original}$: Original production capacity, P_{scaled}: Scaled production capacity.

For moderate to large-scale biomass plants, the scaling factor is normally between 0.6-0.7 [169]. In this study, a scaling factor of 0.65 is used. Plant data are adjusted to 2009 (January) UK £ prices using either plant cost index US CECPI (1957-1959 = 100) or a relevant rate of inflation.

However, standard scaling practises used for chemical plant equipment are not suitable for cultivation farms since they are not representative. As shown in Chapter 3, the effect of scale on costs is dependent on the discounts applied to the material and investment costs.

In this study, the discounts applied to materials and investment costs are based on Lenstra et al. [109] (Table 3.3). The use of this data and its validity is discussed in §7.1.2.

4.3.3 Target rate of return

In Chapter 3, most studies refer to the BESP, which is the minimum price the system must obtain in order to cover the investment and operating costs only. Again, the BESP is expressed in terms of either the feedstock, normally dry, or the product.

However, as discussed in §1.2, in order for a project to be economically attractive for investment the IRR must be higher than the return from alternative investments. Setting a product price and a target rate of return (TRR) assesses the potential profit and associated risk of each system. This provides a benchmark for comparison for the calculated ROR of the systems presented in this work. If the TRR is met or exceeded, the system is economically attractive.

Previous aquaculture studies present rates of return of up to 19% [87,170]. However, according to Lisac & Muir [171], a rate of return between 20% and 25% may be more suitable for assessing the investment risk. For this work, a TRR of 20% is assumed, which complies with the literature but also reflects the financial risk involved.

5 Process configurations (marine)

5.1 Process evaluation & selection

In §2.3 six technologies are proposed for the conversion of macroalgae, based on previous studies and recommendations. These are anaerobic digestion, fermentation, combustion, gasification, liquefaction and pyrolysis. Gasification and pyrolysis each comprise two sub-technologies, dry and wet gasification (hydrothermal and SCWG) and fast and intermediate pyrolysis.

Several studies reviewed in Chapter 3 suggest the use of a biorefinery concept, in order to improve revenue by producing non-biomass high-end products. However, this work will focus on utilising macroalgae in a single conversion process, since macroalgae biomass is a novel concept in the UK and several potential technologies have yet to be investigated. Additionally, the composition of the feedstock at the intermediate processing stages has yet to be determined; therefore, the product yields and quality are subject to conjecture.

5.1.1 Process summary

Figure 5.1 shows the process routes and primary end-product of the eight technologies, based on information obtained during the review presented in Chapters 2 and 3. At this stage in the assessment, all steps are presented as “black boxes”.

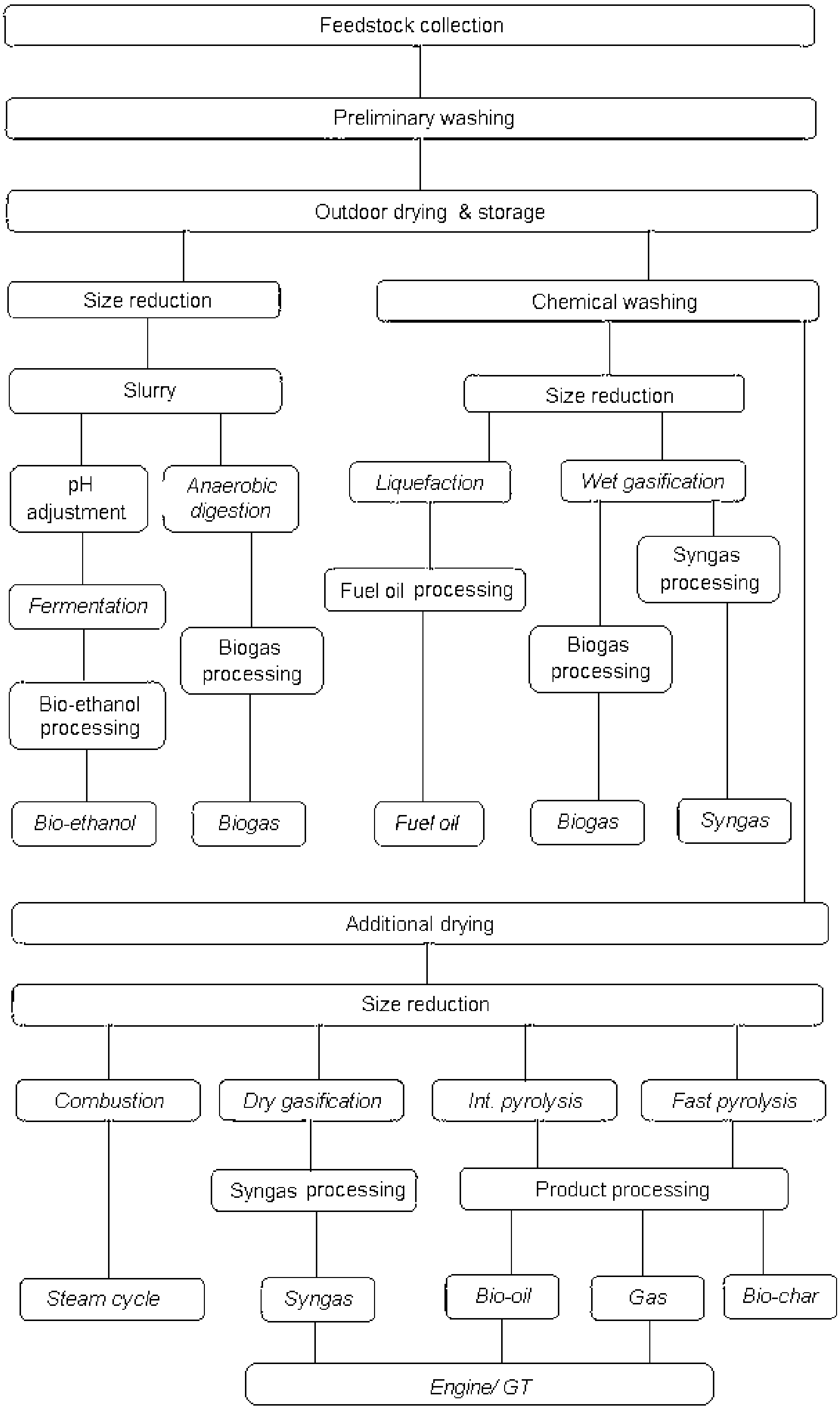

Figure 5.1: Process route summary

As shown, there are common processing stages that are performed before the feedstock arrives at the conversion plant. Preliminary washing is important, since it removes debris and excess salt, which can inhibit processes such as digestion. In all cases, the feedstock undergoes size reduction prior to conversion, though the size requirement varies, particularly for dry gasification. For anaerobic digestion, the feedstock requires shredding, since whole plant digestion has proven difficult [132].

Additionally, the feedstock will water loss during transportation and storage, prior to pre-treatment and conversion.

Fermentation and anaerobic digestion both operate using feedstock slurry, requiring addition water [30, 44 & 132]. Anaerobic digestion operates at a 30-day HRT (assumed) and a temperature range of 20-70°C, which achieves up to 60 wt% solid conversion. This produces a biogas of approximately 60 vol% CH_4 and 40 vol% CO_2, and a solid digestate by-product [136]. Biogas production varies with macroalgae species and digester conditions, as shown in (Table 2.2). The biogas is processed to remove H_2S (<1 vol%) and excess water (humidity) [172, 173]. For fermentation, the slurry undergoes pH balancing to pH6 before it is fed into the fermentation unit with the correct enzymes (e.g. *Ethanol red* yeast) [30]. The primary end-product is bio-ethanol, which undergoes processing before use.

In both cases a solid residue by-product is also produced, which is a potential source of fertiliser as it is normally rich with nutrients. However, the level of potentially toxic compounds (heavy metals, arsenic etc.) becomes concentrated in the solid, particularly after dewatering. Therefore, the solid may require pre-treatment before it is can be used, especially in food production [132].

Due to the high ash content of macroalgae, thermochemical conversion routes require the feedstock to undergo additional washing. Washes using water or acid solutions reduce ash and metal levels considerably. Washing in water reduces around 30-40% of the Mg, K and Na, whilst washing in acid removes over 90% of the Mg, K, Na and Ca and a large proportion of trace mineral matter. However, results from macroalgae acid pre-treatment have indicated the removal of mannitol and fucoidan as well as the partial removal of the laminarin [48].

Liquefaction operates at 300-350°C [174] and 100 bar [152] to produce fuel oil, which requires processing before use. Wet gasification, either hydrothermal or SCWG, operates between 200°C and 700°C in a pressure range of 210-300 bar, with hydrothermal gasification requiring a metal catalyst [143-145]. Hydrothermal gasification produces a biogas, whilst SCWG generates syngas, both of which will require processing before use.

In combustion, the macroalgae enters the boiler or furnace and is combusted to produce steam for CHP production. Ash is produced as a by-product, which will require removal from the equipment. Combustion can tolerate a moisture content of <50 wt% [175]; however, the high moisture content reduces the process thermal efficiency. Therefore, some feedstock drying would be necessary.

Gasification takes place at 850-1000°C to produce syngas, which is cooled and cleaned to remove components such as sulphur and tar before use. This process also produces ash as a by-product, which requires removal from the gasifier and gas cleaning equipment [142]. The operating temperature is normally dictated by the properties of the feedstock ash. Biomass ash has a lower melting point in comparison to other solids, such as coal, and becomes very aggressive in its molten state [176]. This leads to problems such as agglomeration, deposition, sintering, erosion and corrosion, which have a negative impact on process equipment [177]. Dry gasification requires the feedstock to be dried to a moisture content of ≤15 wt% (wet) [149].

Fast pyrolysis process operates at ~525°C [178] and solids residence times of 1-2 seconds to produce bio-oil, char and a hydrocarbon gas mixture. The product mixture undergoes separation to remove the bio-oil, which requires processing before use. Intermediate pyrolysis is performed in an auger-screw pyrolyser at a temperature range of 300°C to 550°C and solid residence times of a few minutes [179] to produce a mixture of char (30-40%), liquid (35-45%) and gas (20-30%). The prepared feedstock is fed into the reactor, and again the products undergo separation and processing before use. Fast and intermediate pyrolysis can tolerate moisture contents of ≤25 wt% (wet) [146] and ≤20 wt% (wet) [180] respectively.

A preliminary energy balance is presented in Table 5.1, which for purposes of comparison is based on final conversion to electrical power in the range 1-10 MW_e in an IC engine based CHP scheme (except for the combustion case which assumes a Rankine cycle). The process stage efficiencies are adapted from relevant literature and are discussed below.

Table 5.1: Preliminary energy balances

Process	Feed preparation (%)	Drying (%)	Conversion (%)	Product to electricity (%)	Overall efficiency (%)
Anaerobic digestion	100	-	56	32	18
Fermentation	100	-	45	32	14
Combustion	100	100	25	-	25
Dry gasification	100	100	70	32	22
Wet gasification	100	-	65	32	21
Fast pyrolysis	100	100	60 (energy yield)	32	19
Intermediate pyrolysis	100	100	53	32	17
Liquefaction	100	-	80	32	26

The feedstock preparation and drying are assumed to be 100% efficient, based on negligible VS losses. It is assumed that heat required for drying will be supplied by the processes via heat recovery; however, it is important to recognize that this is not reflected in Table 5.1. In practice, drying would utilize the heat in the exhaust gases of the engine, which would reduce the heat available for export. It may be the case that the heat available is not sufficient, in which case supplementary fuel may be necessary. In the case of combustion, drying duty may require a reduction in conversion efficiency to allow sufficient residual heat in the boiler exhaust.

For anaerobic digestion, the parasitic demand of the digester(s) for maintaining process temperature and compensating surface heat loss dictates the energy efficiency. The digestion process efficiency is based on Puchajda & Oleszkiewicz [181] [average energy efficiency of three published systems]. The combustion efficiency of 25% is based on work completed by Bridgwater et al. [182], as is the dry gasification efficiency, which ranges between 60% and 79%, depending on operation conditions and assumptions. Wet gasification is based on data from Luterbacher et al. [183] (interpreted by Stucki et al. [184]) (hydrothermal) and Matsumara et al. [185] (SCWG). The efficiency of intermediate pyrolysis is derived from Hornung [180], whilst values for liquefaction and fast pyrolysis are adapted from work completed by Changing World Technologies [186] and Rogers & Brammer [187] respectively. The efficiency for fermentation is adapted from Hamelinck et al [188].

The efficiency from product to electricity in all cases except combustion is that of a modern stationary IC engine, taken to be 32% from the Crown Estate Report into anaerobic digestion [132]. This agrees with a range given elsewhere of 25-40% [189], and is assumed to be independent of the fuel.

5.1.2 Process evaluation

Constraints with time and resources mean that it is not possible include all of these technologies in the TEA; therefore, it is necessary to determine which have the most realistic potential at present. In order to determine the most suitable process route(s), the systems are evaluated in terms of:

- End-product
- Feedstock tolerance
- Energy efficiency
- Technology status

Due to the poor availability of economic data for these systems, economic performance has been cautiously inferred from terrestrial biomass systems. Table 5.2 summarises the processes under consideration.

Table 5.2: Process summary

Process	End-product (secondary product)	Estimated energy efficiency to electricity (%)	Technology status
Anaerobic digestion	“biogas” (solid residue)	18	Ready
Fermentation	“bio-ethanol” (solid residue)	14	Under investigation
Combustion	Power	25	Yet to be investigated
Dry Gasification	“syngas”	22	Under investigation
Wet gasification	“biogas”or “syngas”	21	Yet to be investigated
Fast pyrolysis	“bio-oil”, char, gas	19	Under investigation
Intermediate pyrolysis	“bio-oil”, char, gas	17	Yet to be investigated
Liquefaction	fuel oil	26	Under investigation

5.1.2.1 End-product

As shown, macroalgae have the potential to produce a range of products.

5.1.2.1.1 Biogas

Generally, biogas (the term used for the product gas from anaerobic digestion of biomass) is used for heat and power production via a CHP engineas a standalone fuel or as part of a blend, increasing its heating value [132]. In terms of revenue, biogas is a low value product, which as discussed in Chapter 3, is still more expensive to produce from marine biomass than from fossil fuels or terrestrial biomass like grass or wood [136]. However, in geographically remote areas where the feedstock is available it is a valuable source of untapped energy.

5.1.2.1.2 Bio-ethanol

Investigations into macroalgae fermentation have found that yields of bio-ethanol (the term given to the liquid product of biomass fermentation) are generally not as high in comparison to established fermentation processes [190]. Roesijadi et al. [153] summarises several macroalgae fermentation studies [191-193], concluding that a bio-ethanol production rate of ~80-120 kg/t dry macroalgae is expected. Aizawa et al. [161]

however, quote a potential bio-ethanol production rate as 29.6 kg/ton (short) (~27 kg/t). Table 5.3 shows the bio-ethanol production comparison with other biomass sources.

Table 5.3: Bio-ethanol production data [153, 161]

Feedstock	Bio-ethanol production (kg/t)
Corn	327
Barley	353
Wheat	349
Rice	342
Sweet potato	146
Sugarcane	70
Macroalgae *(Sargassum horneri)*	27

As shown, macroalgae perform poorly in comparison to terrestrial biomass.

5.1.2.1.3 Bio-oil (and fuel oil from liquefaction)

Bio-oil (the term given to the liquid product from pyrolysis of biomass) is a potential feedstock for the production of heat and power, transport fuel (biodiesel) and chemicals [146]. Bio-oil derived from macroalgae contains a selection of useful products such as phenols, carboxylic acids, CO, ammonia and organic bases, though the large organic fractions are considered complex mixtures that are potentially less valuable [69].

Fuel oil (the term given to the liquid product from liquefaction of biomass) is used as a source of biodiesel [43] for transportation or heat and power production via a combustion engine. Macroalgae derived biodiesel has yet to be utilised, though several studies highlight the potential [5, 35,128, 153].

5.1.2.1.4 Syngas

Syngas (the term given to the gaseous product of gasification) is a flexible product, which is suitable for power production, H_2 production, and chemical synthesis. It can be produced directly via gasification or indirectly from upgrading biogas.

5.1.2.1.5 Secondary products

In most cases, secondary products are normally manufactured in the form of solid residue for fertiliser and steam from heat recovery. Wang et al. [25] believe that the residue ash has a potential as a fertiliser.

5.1.2.2 Feedstock tolerance

The presence of salt, polyphenols and sulphated polysaccharides may inhibit fermentation-based processes, which will require careful management. In most cases water washing the feedstock seems to satisfy this. Macroalgae sugars are not in the form of starch, glucose and sucrose, therefore, standard fermentation processes are not technically feasible [128]. This means that macroalgae will require specialist pre-treatment, though very little has been published other than Horn [193-195] and Adams et al. [30].

The organic components of macroalgae differ from terrestrial crops, influencing their thermal behaviour [7]. This will affect the performance of thermochemical processes, influencing product quality. The comparatively high ash content is a potential problem, reducing the utilisation efficiency and lifespan of process equipment [25]. Preliminary investigations regarding chemical washes have produced promising results, reducing ash and alkali metal contents significantly [48]; however, these processes are yet to operate at commercial scale.

5.1.2.3 Energy efficiency

The preliminary energy efficiencies to electricity range between 14% and 26%, with liquefaction and combustion having the highest. The preliminary energy efficiencies to electricity range between 14% and 26%, with liquefaction and combustion having the highest. The values for anaerobic digestion, dry and wet gasification, fast pyrolysis and intermediate pyrolysis are all ≥17%. The overall efficiency to electricity of these technologies is lower than liquefaction and combustion due to losses during conversion, although the impact of drying has not been considered yet. However, the effect of drying could be negligible. Sewage sludge has a similar solid content to macroalgae, and proposals have been made to achieve 98% heat recovery during drying under certain conditions (small-scale plant, use of pebble heaters) [196]. If successful this technology could be adapted for marine biomass. For fermentation, the energy efficiency is normally low due to processing and separation requirements, as described by Chynoweth et al. [136].

In literature, energy efficiency is also indicated by energy consumption, where the high water content of the feedstock is a dominant factor, since evaporation has a considerable energy demand [136]. Macroalgae have a negative lower heating value (LHV) [128], resulting in biological conversion being widely favoured over thermochemical. In general, anaerobic digestion is the most suitable option for marine sources due to its high moisture tolerance [43, 197]. Liquefaction has a higher tolerance to moisture than gasification and fast pyrolysis and is therefore believed to have more potential [5, 43 & 48], since feedstock drying is not required [152].

Data compiled by Aresta et al. [5], shown in Table 5.4, summarises the expected energy consumption of specific conversion processes. These figures do not include the energy demand for feedstock production.

Table 5.4: Process energy consumption [5]

The majority of sources relate to either microalgae or non-marine biomass, which increases the uncertainty in the data. Microalgae can require more dewatering/drying than macroalgae [153], therefore the energy consumption may be lower than anticipated for macroalgae. However, anaerobic digestion has the lowest energy demand per kg of feedstock. The energy consumption of liquefaction and pyrolysis vary with product output, resulting in high yield processes requiring large energy inputs.

5.1.2.4 Technology status

Anaerobic digestion is a well-established technology and previous trials using macroalgae indicate that the process is technically viable [128]. Japan Ocean Industries currently operate a 1 tpd macroalgae digester, converting *Laminaria sp.* to biogas at a CH_4 production rate of 22 m^3/t [44]. Fermentation, fast pyrolysis and liquefaction have all been investigated only at small-scale [30, 43, 48, 174, 203 & 204].

Several thermochemical conversion processes have yet to be thoroughly tested with a marine feedstock [5]. Macroalgae combustion has been studied from a compositional perspective [25, 46], but not for power production. The New Energy and Industrial Technology Development Organisation (NEDO) in Japan are reviewing the use of macroalgae for energy production, including gasification [7, 46]. However, at present only results regarding anaerobic digestion has been published [44].

5.1.3 Process selection

Ultimately, anaerobic digestion fulfils the most criteria. It is currently easily the most technically established route for marine biomass and operates at a range of scales [205, 206]. The process and feedstock pre-treatment are relatively simple, which is technically attractive for the use of a novel feedstock. The absence of a heavy drying duty will enhance overall efficiency to CHP. On these grounds, the TEA will be limited to anaerobic digestion for CHP production only.

The remaining technologies (particularly liquefaction) have potential and may form part of a wider assessment at a future date, when resources allow.

5.1.4 Proposed production scales

For this study, the following scales of production are under investigation, based on information in §4.2.1 and §4.2.2:

- Scenario 1: 15 ha inshore cultivation network comprising of 5 3 ha farms
- Scenario 2: 36 ha inshore cultivation network comprising of 12 3 ha farms
- Scenario 3:1,000 ha offshore cultivation farm as part of a wind farm aquaculture system
- Scenario 4: 3,000 ha offshore cultivation farm as part of a wind farm aquaculture system
- Scenario 5: 24,500 ha offshore cultivation farm as part of a wind farm aquaculture system
- Scenario 6: Harvesting from standing stock with an output equivalent to scenario 2
- Scenario 7: 1,000 ha standalone offshore wind farm, comparable to scenario 3

Scenarios 1 and 2 are based on information provided by SAMS, which reflects current planning applications and potential future proposals. The scales adopted for Scenarios 3, 4 and 5 are based on the common sizes of offshore wind farms currently under operation or construction within UK water territory [207]. Scenario 6 provides a comparison between macroalgae cultivation and harvesting, whilst the purpose of Scenario 7 is to provide a comparison for different offshore cultivation techniques (the use of wind farm vs. standalone structures).

Project partners SAMS and ISC provide the production rates used in this work.

Yield data for inshore cultivation is provided by SAMS [107], based on results from their inshore test farms, which specify an annual productivity of 120 t/ha (wet) macroalgae. Assuming a water content of 85-90 wt%, this is equivalent to 12-18 t/ha (dry) annually, which is roughly comparable to the figures presented §3.2.2 which do not account for losses due to shedding, disease, marine predators (fish, urchins etc.) and epiphytic activity.

Unfortunately, offshore cultivation is not under investigation; therefore, macroalgae productivity is based on relevant literature. In this study, a yield of 120 t/ha/y (wet) is assumed since offshore production rates vary between 80-200 t/ha/y (wet), as described in §2.2.2.1. Whilst proposed yields of 200-500 t/ha/y (wet) [90% water content assumed] are presented in §3.2.2, utilising a lower yield figure will account for losses. For offshore cultivation, losses due to equipment failure and weather damage are the most significant because overall productivity normally exceeds the grazing demand, resulting in negligible damage from marine predators and epiphytic activity [35].

The wind farm based systems are limited to macroalgae and mussel cultivation at present, based on Buck et al. [96]. The effect of collective production is assumed to already be considered, since the expected yield rate is relatively low in comparison to the forecasted data.

For the harvesting potential, an annual yield of 30 t/ha (wet) macroalgae is assumed [208]. This means that a larger source area will be required in order to meet the production rate of Scenario 2. Table 5.5 shows the annual macroalgae output (wet) expected for each scenario.

Table 5.5: Scenario feedstock estimations

Scenario	Ha	Macroalgae yield (wet) t/y
1	15	1,800
2	36	4,320
3	1,000	120,000
4	3,000	360,000
5	24,500	3,048,000
6	-	4,320
7	1,000	120,000

5.1.5 Preliminary output estimates

Preliminary estimates regarding the biogas production and the resultant CHP outputs have been made for each scenario in order to define the process parameters and most suitable use of the CHP system. These estimates are later refined as part of the scenario mass, energy and power balances.

The preliminary estimates are based on work completed by the Kelly & Dworjanyn [132], who estimate that a 1 ha macroalgae farm yielding 150 t/ha/y macroalgae (wet) produces approximately 1.1 kW_e/ha (~1.8 kW_{th}), based on the following assumptions:

- Macroalgae oven dried solid (ODS) content of 7.5 wt%, which is assumed to be convertible solid only.
- A CH_4 heating value of 55 MJ/kg (HHV)
- A digestion conversion rate of 0.27 m^3 CH_4/kg ODS, producing a biogas of 60 vol% CH_4.
- 365 d/y CH_4 production and CHP utilisation.

- A CHP engine with an overall efficiency of 85%, which is divided into an electrical efficiency of 32% and thermal efficiency of 53%.

Using the same method for a 1 ha farm producing 120 t/ha/y, the expected electrical output is:

→ 1 ha @ 120 t/ha/y = 120 t/y wet = 9 t/y ODS = 9,000 kg/y.

→ 9,000 kg/y * 0.27 m^3 CH_4/kg ODS * 0.6556 m^3/kg (CH_4 density) = ~87,621 MJ/y CH_4

→~87621 MJ/y * 55 MJ/kg = 2.78 kJ/s = 2.78 kW.

→kW_e = 2.85 * 0.32 = 0.89 kW_e/ha.

→kW_{th} = 2.85 * 0.53 = 1.47 kW_{th}/ha.

Therefore, a 120 t/ha/y farm produces approximately 0.9 kW_e/ha and 1.5 kW_{th}/ha. Table 5.6 shows the estimated scenario outputs, which will also be used to assess the validity of the process modelling. Note that all of the calculated electrical power scales fall within the recognised range of applicability for IC engine based CHP schemes [189, 209].

Table 5.6: Scenario preliminary calculations (estimated)

Scenario	Ha	Macroalgae yield (wet)	Macroalgae yield (dry) (7.5 wt%)	Biogas	Electricity	Heat
		kt/y	t/y	km^3/y	kW_e	kW_{th}
1	15	2	135	61	14	23
2	36	4	324	146	33	55
3	1,000	120	9,000	4,050	913	1,513
4	3,000	360	27,000	12,150	2,740	4,538
5	24,500	3,048	228,600	102,870	22,374	37,058
6	-	4	324	146	33	55
7	1,000	120	9,000	4,050	913	1,513

Initially, all power outputs are for domestic use. Assuming that the annual average household electricity consumption is 4000 kWh [210, 211], at an annual rate of 8,760 h, and approximately four people per household, the estimated size of the area supplied is calculated, as shown in Table 5.7.

Table 5.7: Electricity utilisation area

Scenarios	Electricity (kW_e)	Houses	Population
1	14	30	120
2	33	72	288
3	913	2,000	8,000
4	2,740	6,000	24,000
5	22,374	49,000	196,000
6	33	72	288
7	913	2,000	8,000

From these results, it is clear that Scenarios 1, 2 and 6 are more suitable for small-scale, local production, providing an additional source of power during winter (November to March), when the demand is greatest [212].

The scale of Scenarios 3, 4, 5 and 7 provides the potential to operate continuously throughout the year. Scenarios 3, 4 and 7 may be suitable for supplying heat and power to municipal buildings such as schools, leisure facilities and local government buildings, which are in use for the majority of the year. The expected output of Scenario 5 could potentially be for industrial usage, providing either plants or industrial estates with power, particularly in coastal areas.

6 Process modelling (marine)

The scale of macroalgae production, the selection of the conversion technology, the end-product and the expected outputs are defined in Chapters 4 and 5. In this chapter, the scenario sub-systems, configurations, process modelling and subsequent mass, energy and power balances are presented and discussed.

6.1 Scenario sub-systems

As described in §4.3.1, the marine biomass scenarios are divided into sub-systems in order to fully assess their performance. These are:

- Feedstock procurement
- Feedstock preparation
- Anaerobic digestion
- Biogas processing and use

The following sections describe the sub-systems.

6.1.1 Feedstock procurement

This sub-system covers the installation, collection and delivery of the macroalgae to the conversion plant. In this study, macroalgae cultivation and harvesting from natural stock are under investigation. The following sections discuss the various systems.

6.1.1.1 Inshore cultivation

A potential aquaculture site must satisfy certain logistical and environmental constraints, such as site access and nutrient availability [128]. In this study, it is assumed that the correct sites have been located and nutrients are naturally available to produce 120 t/ha/y macroalgae.

Macroalgae seedlings are purchased from commercial growers, ready to be installed. This practise is common for macroalgae cultivation in Asia [213-215], and in general aquaculture production worldwide [171, 216]. It is assumed that the seedlings are supplied attached to culture line.

Inshore cultivation (Scenarios 1 and 2) is carried out using the longline method, described in §2.2.2.1.2.3. The carrier ropes are distributed across the water surface (Figure 6.1).

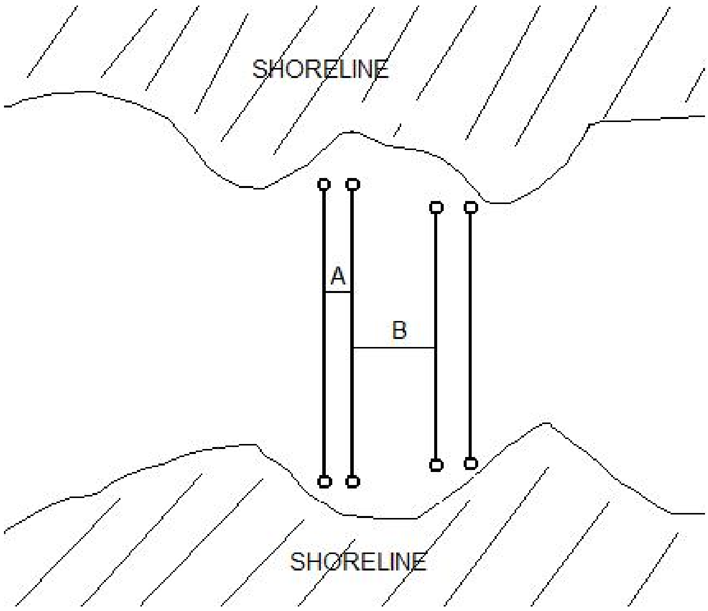

Figure 6.1: Inshore carrier rope distribution

As shown, the distance between the ropes varies. Distance A is approximately 1-1.5 m, to provide growing space for the seedlings. Distance B is approximately 10-15 m to provide a large enough channel for a boat, which is used for seeding, maintenance and harvesting. The macroalgae lines are attached to the carrier ropes at 1 m intervals by twisting the carrier rope open, attaching the line and then re-twisting the carrier rope closed.

This practise is reversed when the macroalgae is harvested, when the lines are removed, taken into the boat and stripped. The macroalgae is placed into nets for storage, which can be towed behind the boat and deposited at the shoreline. The entire plant is removed during harvesting, which means that the farms are re-seeded on an annual basis.

6.1.1.2 Offshore cultivation

Two offshore cultivation production methods are under investigation, these are the longline system (§2.2.2.1.2.3) and the net system (§2.2.2.1.2.4). Technically, the ring design (§2.2.2.1.2.5) is the most attractive system, which has been successfully tested in numerous locations worldwide [9, 95] and is considered to be the best system with regards to lifespan and stability. However, the cultivation and collection processes are labour intensive, resulting in high production costs. At present, there is no potential for mechanical harvesting, and the design of the equipment means that an economy of scale cannot be realised [116].Furthermore, mechanical harvesting a single system within an aquaculture scheme without disturbing other systems may prove to be extremely difficult.

6.1.1.2.1 Longline

The longline method is used within the wind farm structures selected for Scenarios 3, 4 and 5. The positioning of the carrier ropes will depend on the level of accessibility required, primarily for the wind turbines, but also for additional aquaculture systems. In this study, the longlines (Figure 6.2) are situated within the wind farm complex, but are not attached to the turbines in order to provide accessibility.

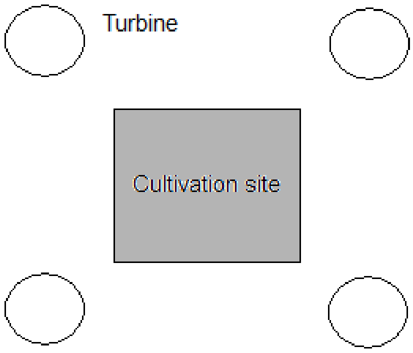

Figure 6.2: Longline positioning within wind farms

The carrier ropes are anchored to the seabed and buoys attached where necessary, based on the structural arrangements tested by [88]. The seeding and collection process is the same as for inshore, since there may be restrictions regarding the use of mechanical harvesting techniques to avoid damaging the turbines and other aquaculture facilities.

As shown, the offshore farms are a network of smaller cultivation farms. Each farm is approximately 50 ha in size (based on a 1000 ha wind farm comprising of 30 turbines) [207]. This means that Scenarios 3, 4 and 5 comprise of 20, 60 and 490 sites respectively.

6.1.1.2.2 Net

The net cultivation system, described in §2.2.2.1.2.4, is utilised for Scenario 7. The nets are seeded before anchorage, where the sporophytes are attached manually by untwisting the net fibres, positioning the seedlings and then re-twisting the net. The seeded nets are then suspended 2 m below the surface using steel cables, which will require anchoring to the seabed [110].

The process has great potential for mechanised harvesting [109]. ECN have proposed a number of mechanised systems, including the continuous harvester, shown in Figure 6.3, which is used in this study.

Figure 6.3: Continuous harvester [109]

This system is based on current harvesting technology used in Norway. The harvester operates in the same way as a lawnmower, travelling across the macroalgae, cutting off a specific length of the plants with rotating blades. A suction tube placed behind the rotating blades gathers the macroalgae, which is deposited in a collection barge travelling adjacent to the harvester [109].

6.1.1.3 Harvesting from natural stock

Large-scale mechanised harvesting has yet to be practised in the UK, though a significant amount of manual collection occurs. According to the Crown Report [132], Norway has similar macroalgae densities to the UK (Scotland); therefore, it is believed that the Norwegian harvesting methods will be suitable for Scottish macroalgae. These practises have been adopted for Scenario 6. Macroalgae is sourced from four separate sites, which are split in to five sub-sections and harvested at 5-year intervals at an average annual rate of 5% standing stock [27, 132]. The harvesting is completed using the cutting dredge and trawl net, described in §2.2.2.2.2.

6.1.1.4 Macroalgae composition

In order to improve feedstock yield only sub-tidal *Phaeophyceae* species native to UK waters are under investigation. At present intertidal species are not suitable for bioenergy production due to their high polyphenol content, which can inhibit fermentation-based processes such as anaerobic digestion [27, 30 & 128]. However, as discussed in §2.1.4, the macroalgae will contain a significant amount of ash.

The cultivation of *Laminaria digitata, Laminaria hyperborea, Laminaria saccharina* and *Saccorhiza polyschides* are undergoing investigation, as part of the Supergen II Marine Biomass plus activity. In this study, these species combine to make a macroalgae litter feedstock. The litter will vary in chemical and physical composition, depending on individual productivities. A generic composition (Table 6.1) is assumed using relevant literature [24, 48, 174, 217 & 218].

Table 6.1: Cultivated macroalgae composition

Species	*L. digitata, L. hyperborea, L. saccharina* and *Saccorhiza polyschides*
Moisture content (wt%)	90
Ash content (wt%)	2.36 (dry), 23.6 (wet)
Chemical Composition (%wt dry)	
C	40.1
H	5.2
O	33.4
N	1.3
S	2.2
HHV (MJ/kg)	18.2

From these figures the VS accounts for about 7.6 wt% of the wet feedstock, which is comparable to Kelly & Dworjanyn [132] (7.5 wt%).

The harvesting of macroalgae from natural standing stock is under investigation by ISC, as part of the Supergen II Marine Biomass plus activity. The work concentrates primarily on harvesting *Laminaria hyperborea*, which is the dominant genera found in UK waters. Again a generic composition has been compiled (Table 6.2) using the relevant literature [7, 48& 219].

Table 6.2: Harvested macroalgae composition

Species	*L. hyperborea*
Moisture content (wt%)	90
Ash content (wt%)	2.24 (dry), 22.4 (wet)
Chemical Composition (dry)	
C	35.4
H	5.4
O	34.7
N	1.1
S	2.0
HHV (MJ/kg)	18.5

Here, the VS content is 7.8 wt% of the wet feedstock, which again is comparable to Kelly & Dworjanyn [132].

Since the annual exploitation limit for harvesting is 5%, the potential sites will require a standing stock of at least 432,000 t [4,320 t equal to 5%, requiring 5 86,400 t sites]. From the data shown in Table 4.1, there are three possible harvesting sites in Scotland; these are Orkney, the Outer Hebrides and Shetland. From these sites, the Outer Hebrides is the most suitable because the macroalgae population inhabits less coastline (137 km), resulting in a wider harvesting area (137 km by 1.2 km). Orkney has a greater macroalgae density, however the long coastline (805 km) results in a thin harvesting area

(805 km by <1 km), which may prove difficult to manoeuvre mechanical harvesting equipment, especially as the coastline is particularly rocky.

6.1.1.5 Logistics

All macroalgae are harvested during the summer period (June-September), which should provide suitable weather conditions. This period also coincides with the peak carbohydrate (laminarin and mannitol) levels (§2.1.4.2).

In this study, the logistics of transporting the macroalgae from the scenario sites to the processing plants are considered, however, movement within these sites is not included. In all scenarios, the feedstock is transported to shore by boat. For Scenarios 1 and 2 some road travel to the plant will be required, though this is limited to no more than 16 km (10 miles) from the boat landing stage.

For the remaining scenarios the conversion plant is located in a coastal position, therefore road transportation is limited to the plant's internal logistics system, which is not investigated.

For each of the offshore scenarios (3-7), the distance from shore will vary. Generally, UK offshore wind farms are situated approximately 20 km to 200 km from the shoreline, with large-scale farms being further from shore. For protection, Scenario 7 is assumed to be based within the 12 km Crown Estate coastal zone, which will provide suitable protection [207]. The distance travelled for Scenario 6 is based on the Outer Hebrides coastal length data, presented in Table 4.1, which has a roundtrip of approximately 270 km (274 km).

During transportation, nominal water loss is expected, however this is assumed to be ≤10 wt%. Realistically, this may be greater, however assuming 10 wt% accounts for wet weather conditions.

It is assumed that the logistics associated with feedstock procurement is managed by an external company, therefore; the energy consumed during this stage (fuel oil) is not included in the energy balances, but is considered in the TPC.

6.1.2 Pre-treatment and storage

Since feedstock is collected throughout the summer, short to medium term storage is required for all scenarios. Terrestrial biomass, such as wood chip, is stored outdoors, which is cheap and allows for passive drying [220]. Storing macroalgae outdoors can reduce the moisture content of macroalgae to 30 wt% (wet), in dry atmospheric conditions. However, this process only lasts up to 3 weeks before degradation and associated emissions becomes a significant factor [79]. Several studies have calculated the potential emission rate of degrading macroalgae. According to Briand & Morand [201], 11,000 t of beach harvested *Ulva* left to decompose emits 20 t N_2 and 2 t P. On an annual basis of three harvests the emissions discharged are equivalent to those generated from the waste of a city with a minimum population of 12,000 [42].

The most significant emission however is H_2S, which is extremely harmful to health. Macroalgae derived emissions are responsible for a large number of animal fatalities in Northern France, resulting in the media referring to it as 'killer seaweed'. Human casualties have yet to be officially recorded, though there are investigations underway for suspected cases [221, 222].

As a result, outdoor storage must be rejected in order to conform to relevant health and safety regulations, particularly regarding the welfare of the plant employees. Instead, macroalgae is fed into a shredder to reduce particle size before being sent to a receiver tank via a conveyor, which operates at atmospheric temperature. Additional water is added to create a slurry containing 10 wt% solid [205]. The receiver tank is used as storage based on the assumption that digestion does not occur.

6.1.3 Anaerobic digestion

In this study, all anaerobic digestion processes operate as low solid digestion (LS) systems, which have a maximum solid content of 10 wt% [135, 136].

There are two conventional operating temperature conditions; these are mesophilic and thermophilic. Mesophilic digestion occurs at approximately 20°- 45°C (ambient temperatures) or optimally at 37°- 41°C [132]. Thermophilic digestion processes operate at ~55°C [181]. Thermophilic conditions induce more rapid decomposition and biogas production resulting in a shorter HRT; though operating in the mesophilic range is cheaper and less sensitive to changes in feedstock quality [132]. Alternatively, macroalgae digestion may operate using a combination of these conditions [44, 181].

Anaerobic digestion operates as either a batch or continuous process [134]. Batch digestion is the simplest method, since a single feedstock batch is fed into the digester to produce biogas, however, odour issues can occur during operation. The process is the cheaper option, though the performance is less efficient as the conversion process can often be unfinished. Continuous digestion is more commonly used since the constant supply of organic matter results in more consistent biogas production. Unconverted material can also be recycled after settling [132].

In this study, both processes are considered.

6.1.3.1 Batch digestion

Batch digestion operates as a single unit system [132]. In this study, the process is adapted from Yokoyama et al. [173], who state that single unit digestion of *Phaeophyceae* (*L. japonica*) at 35°C produces a methane yield of 0.25 Nm^3/kg VS (0.49 Nm^3/kg VS biogas).

As shown in Figure 6.4, the feedstock slurry is pumped from the receiver tank to the fermentation tank (35°C) where it digests for 30 days [223] to produce biogas. The biogas production begins within 24 h and continues at a generally linear rate throughout the HRT [224].

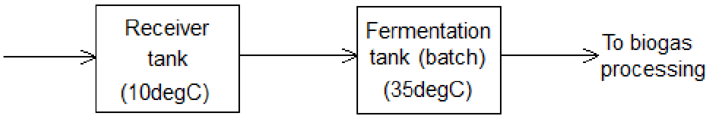

Figure 6.4: Batch digestion

The digestate, which comprises of unconverted volatile material and ash, is removed from the fermentation tank, dewatered using a screw press and sold as fertiliser. A fraction of the residual water (leachate) is recycled for slurry production.

6.1.3.2 Continuous digestion

Continuous digestion normally operates as a multiple digester system, which physically separates the process in order to increase biogas production [132]. Currently, two-stage digestion is commonly used, though investigations into three-stage anaerobic digestion have been recorded [225]. For two-stage digestion, the process is separated into acid production (hydrolytic/acetogenic stage) and biogas production (methanogenic stage), though biogas production can occur during the hydrolytic/acetogenic stage [56]. These stages are also referred to as pre-fermentation and fermentation [44], which is used in this study.

In this study, the continuous digestion system is adapted from work completed by Matsui et al. [44], which reports a CH_4 yield of 0.35 Nm^3 [CH_4]/kg VS. As shown in Figure 6.5, the slurry is pumped from storage to the pre-fermentation tank, which operates at 30°C for 3 days.

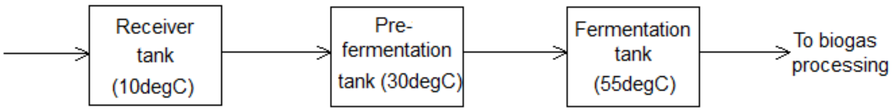

Figure 6.5: Continuous digestion

The slurry and gas mixture is then pumped into the fermentation digester, which operates at 55°C and produces the remaining biogas and digestate over a 20-day HRT [44]. The digestate is pressed using a screw press and the dry digestate is used as fertiliser, whilst a fraction of the leachate is recycled for slurry production.

6.1.3.3 Process start-up and availability

The anaerobic digestion processes must be in operation prior to the CHP start-up date in order to ensure that the CHP system is ready to begin electricity production. In this study, the digestion start-up period is assumed to be equivalent to the HRT of the specific processes so that the maximum amount of biogas is available. Therefore, the batch digestion systems begin operation 30 days prior to the CHP system and the continuous systems 23 days before. After the initial start-up period, biogas is fed into storage continuously, though for batch production the throughput is smaller.

The availability of the digestion and CHP systems depends on the scenario. As discussed in §5.2.3, Scenarios 1, 2 and 6 operate for local electricity production throughout the winter period. In this study, the "winter" timeframe is defined November to March, which is about 151 days (3,624 h). However, the systems operate for 181 days (4,344 h) due to the start-up period for the digester, although the CHP system will only operate for about 83% of this time. The availability of the anaerobic digestion and CHP systems is assumed to be 100% since maintenance is performed during the remaining 7 months of the year.

Scenarios 3, 4, 5 and 7 operate continuously throughout the year. The annual availability of the overall production system is assumed to be ~90% (7920 h), based on Zamalloa et al. [170].

6.1.3.4 Biogas composition

Table 6.3 shows the expected dry biogas composition for batch and continuous anaerobic digestion, based on Matsui et al. [44] and Yokoyama et al. [173].

Table 6.3: Expected biogas compositions (dry)

	Batch	Continuous
	vol%	vol%
CH_4	54.0	60.0
CO_2	45.0	39.4
H_2S	0.6	0.6
HHV (MJ/kg)	30.0	33.0

The higher heating value (HHV) is calculated using a CH_4 HHV of 55.5 MJ/kg. As shown, the batch process produces less CH_4 than continuous, due to incomplete digestion [136].

Due to the high moisture atmosphere of the digester(s), the biogas will also contain water in the form of humidity. This water is not treated as part of the biogas, but as an additional output. Based on data by Biogas Products Ltd [226], a 60:40 (volumetric) CH_4/CO_2 biogas contains 0.08 kg [H_2O]/kg [biogas] (0.098 kg [H_2O]/ m^3 [biogas]).

6.1.4 Biogas processing and use

6.1.4.1 Biogas processing

After leaving the digester(s), the biogas contains a considerable amount of water (humidity) and H_2S, which require removal.

Firstly, the biogas is sent to a H_2S removal unit, which operates at 38°C and atmospheric pressure. The unit is a packed biological scrubber, which uses sulphur oxidation bacteria from the *Thiobacillus* genus. The bacteria thrive in moist conditions provided there is a supply of air and the temperature of the process remains in the range of 25-60°C [226]. It is assumed that all H_2S is removed in a single stage process.

After desulphurisation, the biogas enters the dehumidification unit, which operates at approximately 20°C. The water content of the gas is reduced to approximately 53 wt% [assumed mass basis], which, based on data published by Biogas Products Ltd [226], is equivalent to 0.04 kg [H_2O]/kg [biogas] (0.052 kg [H_2O]/ m^3 [biogas]).

The processed biogas is sent to storage before being used in the CHP system. All scenarios include biogas storage facilities, which will be required in case of CHP system failure. The biogas is stored in membrane gasholders, shown in Figure 6.6, which are inflating/deflating half sphere shaped chambers.

Figure 6.6: Membrane biogas holders (Ankara, Turkey) [226]

The chambers are stored on concrete bases, which results in a comparatively lower capital cost than using concrete and steel domed structures and the membrane is easy to repair and maintain. At present, the largest gasholders have a capacity of 16,000 m^3, which were installed in Ankara, Turkey by Ecomembrane SrL (Italy) [226].

6.1.4.2 CHP system

The biogas is combusted with air in the engine, which operates using 20 vol% excess air. In this study, the CHP system uses an internal combustion engine, which is more robust and has a higher tolerance to contaminants than a gas turbine [227].

The engine is assumed to have an overall efficiency of 85% (32% electrical and 53% thermal), based on the Greenfinch digester plant [132].

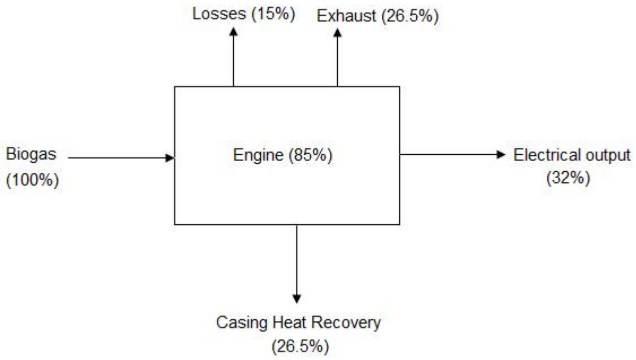

Figure 6.7: CHP efficiency diagram

As shown in Figure 6.7, the thermal efficiency is divided equally between the exhaust and heat recovered from the engine casing.

6.2 Scenario configurations

With the sub-systems outlined, it is possible to compile the scenario process configurations. Table 6.4 presents the final configurations for each scenario.

Table 6.4: Scenario configurations

Scenario	Feedstock source	Harvesting technique	Logistics	Digestion process	CHP duration	Availability (h/y)
1	Inshore cultivation	Manual	Boat/road	Batch	Winter	4,344
2	Inshore cultivation	Manual	Boat/road	Batch	Winter	4,344
3	Offshore cultivation (wind farm)	Manual	Boat	Continuous	Continuous	7,920
4	Offshore cultivation – wind farm	Manual	Boat	Continuous	Continuous	7,920
5	Offshore cultivation – wind farm	Manual	Boat	Continuous	Continuous	7,920
6	Harvesting from natural stock	Mechanical	Boat	Batch	Winter	4,344
7	offshore cultivation	Mechanical	Boat	Continuous	Continuous	7,920

As shown the majority of scenarios utilise manual harvesting techniques, which will have a significant impact on the labour requirement and subsequent costs.

6.3 Process modelling

As discussed in §4.3.1, process modelling is carried out using Microsoft Excel®.

6.3.1 Feedstock procurement

For Scenarios 1, 2, 3, 4, 5, and 7 the inputs/outputs are shown in Figure 6.8.

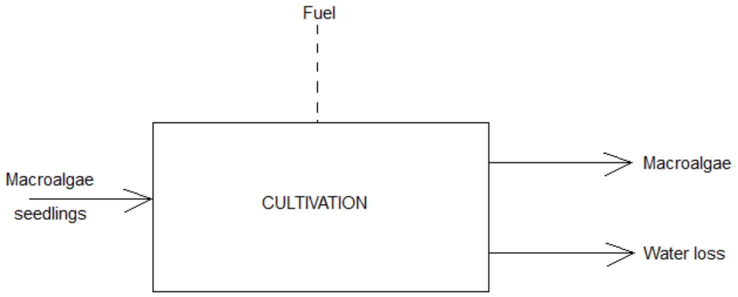

Figure 6.8: Macroalgae cultivation balance

During this stage, the macroalgae seedlings are the only input, whilst the outputs are the adult macroalgae plants and the water loss associated with the logistics. As discussed in

§5.2.2, plant losses are assumed to be covered in the proposed production rates, which are lower than published predicted rates.

As discussed in §6.1.1.5, the harvested macroalgae undergoes a 10 wt% water loss during shipping, which reduces the overall mass, though no solid is lost.

In terms of energy, data compiled by Aresta et al. [5] determines that the production and harvesting of offshore-cultivated macroalgae requires approximately 12.2 MJ/kg algae [assumed dry], as shown in Table 6.5. In this study, it is assumed that this energy is in the form of diesel fuel.

Table 6.5: Energy demand of offshore macroalgae cultivation [151, 198, 228-230]

Process	Energy demand (MJ/kg algae)
Cultivation	2.15
Nutrient supply	4.55
Harvesting	5.5
Drying	0.0 (solar)
Total	*12.2*

As discussed in §6.1.1.1, nutrients are readily available, therefore upwelling is not required reducing the energy consumption is 7.65 MJ/kg algae. This figure is also used for inshore cultivation, which should be representative since the consumption is based on kg algae produced.

6.3.2 Feedstock preparation

In this stage, the macroalgae is shredded and turned into slurry for storage, as shown in Figure 6.9.

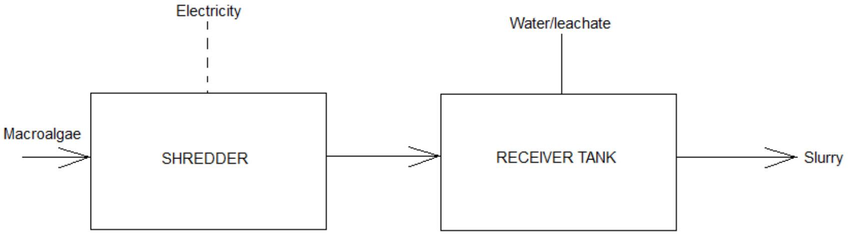

Figure 6.9: Feedstock preparation

In the shredder, mass losses are assumed negligible. Water is added in the receiver tank in order to make a 10 wt% (solid) slurry. The flowrate is determined by the Excel Goal Seek solver to an accuracy of ±0.01 wt%. No energy is required during this stage since the receiver tank operates under atmospheric conditions. The recycled leachate produces slurry with a temperature of ~12°C and ~14°C for batch and continuous digestion respectively. The temperature of the slurry is calculated using the Excel Goal Seek solver.

Electrical power is required to operate the shredder, which is included in the processes overall power demand, discussed in §6.4.3.

In Scenario 6, the macroalgae is readily available; therefore, the primary input is equivalent to 5 wt% (wet) of the sites population. The model for Scenario 6 is shown in Figure 6.10.

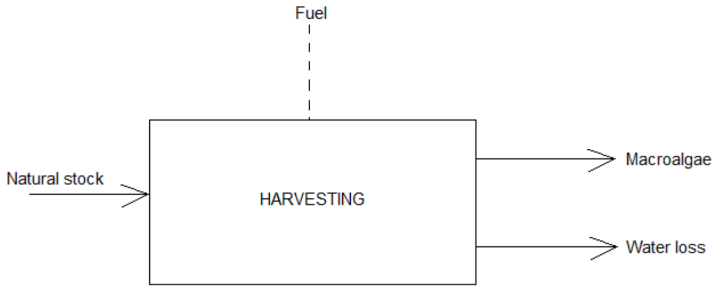

Figure 6.10: Macroalgae harvesting model

Again, the outputs are the adult macroalgae and the water loss. Energy demands are considered lower than cultivation (5.5 MJ/kg algae), since there are no requirements for installations or artificial enhancement.

For all scenarios, it is assumed that no power is consumed at this stage.

6.3.3 Anaerobic digestion

There are two anaerobic digestion models, batch and continuous.

Batch digestion, shown in Figure 6.11, is modelled as a single unit, as dictated by the process configurations.

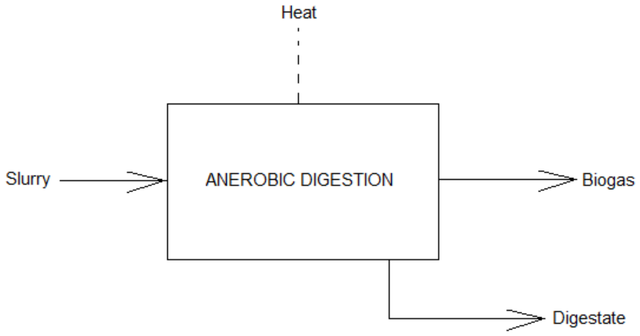

Figure 6.11: Batch digestion model

In mass terms, the slurry enters the digester and is converted into biogas (25 Nm^3/kg VS) and digestate. The conversion process is about 59% complete, which corresponds with [136], who state that the conversion process is normally only 60% complete.

Continuous digestion, shown in Figure 6.12, is more complex because biogas is produced in both digesters at a rate of 35.1 Nm^3/kg VS overall.

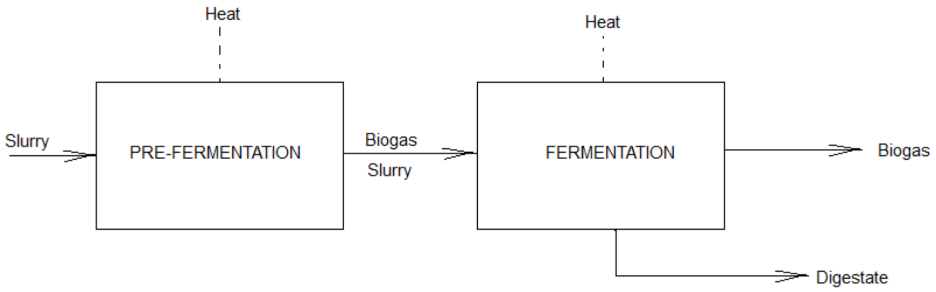

Figure 6.12: Continuous digestion model

Investigations by Vergara-Ferńandez et al. [56] found that 30 vol% of the total biogas output is produced in this stage over a 9-day period, which means that approximately 9.5 vol% is produced in 3 days [assuming linear biogas production [224]]. As expected, the rate of solid conversion is higher at approximately 71% because of the use of multiple digesters.

Anaerobic digestion is endothermic, due to the parasitic heat demand of the digester(s) [231] and the thermal losses [181]. In this study, the heat losses are included and are adapted from Puchajda & Oleszkiewicz [181]; which for batch and continuous digestion is equivalent to 10% and 15% of the biogas energy content respectively. For continuous digestion the 15% loss is for the whole process, which in this study is divided into 5% loss during pre-fermentation and 10% loss during fermentation.

For batch digestion, using recycled leachate, which has a temperature of 35°C, reduces the energy demand by about 55%. For continuous digestion, the leachate has a temperature of 55°C and reduces the energy demand of the pre-fermentation stage by 85% and the overall demand by 32%. However, additional heat is still required, which for all scenarios is provided by recovered process heat, normally using the CHP engine exhaust.

The percentage of electricity consumed by the process depends on how the digester(s) are heated. Maintaining the operating temperature of a single digester using electrical heaters can consume approximately a third of the electrical output of the CHP system [232]. This would mean that the continuous digestion processes would consume at least two thirds of the electrical output. However, the process heat demand is met by heat recovery, therefore the power requirements for the system are:

- The macroalgae shredder
- The conveyor from the shredder to the receiver tank
- The slurry pumps
- The screw press for the digestate

The electrical consumption of thermally heated systems ranges between 3-10% [172, 233] depending on the scale of the system. Since the scale of electricity consumption is non-linear an assumed percentage is used for all systems in order to provide a rough estimate for the consumption. Based on the above percentages the electricity consumed by each system is assumed as 7% of the electricity produced. The electricity required for biogas processing is also included in this figure.

6.3.4 Biogas processing and use

As described in §6.2.1, biogas processing comprises of H_2S removal and dehumidification, shown in Figure 6.13.

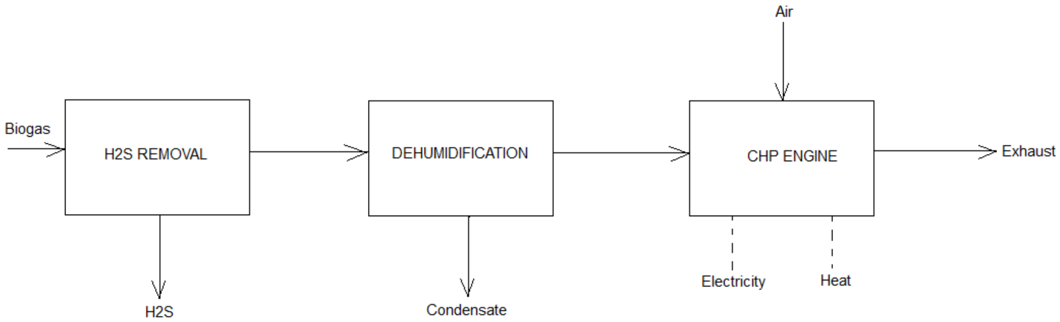

Figure 6.13: Biogas processing model

In mass terms, the main inputs are biogas and air, whilst the outputs are the engine exhaust (Table 6.6), H_2S and condensate.

Table 6.6: Exhaust composition

	vol%
CO_2	21.0
H_2O	9.9
O_2	3.3
N_2	65.8

As shown, the exhaust is predominantly N_2 and CO_2 because of the 20 vol% additional air used during biogas combustion.

Biogas processing is exothermic, based on Biogas Products Ltd. [226] and allows for the recovery of heat, though this is at relatively low temperatures (20-38°C). The CHP system is also exothermic, with the exhaust leaving the engine at between 440°C and 460°C. This stream is then to meet the heat demand of the anaerobic digestion processes. In this study, additional heat recovery is performed on the engine casing to produce district heat, which in this study is defined as water at 90°C. This is carried out using water in a heat exchanger with an 82% efficiency, based on Biogas Products Ltd. [226].

For all scenarios, the thermal output of both the exhaust and the engine casing is large enough to supply the process; therefore, no external sources of heat are required.

In terms of power consumption, the dehumidification unit requires 0.084 MJ/m^3 biogas.

6.4 Mass, energy and power balance results

After completing the process modelling, the mass, energy and power balances of the seven scenarios are determined. The following sections present and discuss the results.

6.4.1 Mass

Table 6.7 presents the mass balance results for each scenario. Since feedrate is dependent on the operating period of each scenario, the outputs are expressed based on the annual production (t) of macroalgae (wet).

Table 6.7: Scenario mass balance results

Scenario	1	2	3	4	5	6	7
FEEDSTOCK PROCUREMENT							
Inputs (t)							
Macroalgae seedlings (90 wt% wet)	1,800	4,320	120,000	360,000	3,048,000	4,320 (natural)	120,000
Total	*1,800*	*4,320*	*120,000*	*360,000*	*3,048,000*	*4,320*	*120,000*
Outputs (t)							
Macroalgae (as received)	1,638	3,931	109,200	327,600	2,773,680	3,931	109,200
Water loss	162	389	10,800	32,400	274,320	389	10,800
Total	*1,800*	*4,320*	*120,000*	*360,000*	*3,048,000*	*4,320*	*120,000*
FEEDSTOCK PREPARATION							
Inputs (t)							
Water/recycled leachate	162	389	10,800	32,400	274,320	389	10,800
Macroalgae (as received)	1,638	3,931	109,200	327,600	2,773,680	3,931	109,200
Total	*1,800*	*4,320*	*120,000*	*360,000*	*3,048,000*	*4,320*	*120,000*
Outputs (t)							
Slurry	1,800	4,320	120,000	360,000	3,048,000	4,320	120,000
Total	*1,800*	*4,320*	*120,000*	*360,000*	*3,048,000*	*4,320*	*120,000*
ANAEROBIC DIGESTION							
Inputs (t)							
Slurry	1,800	4,320	120,000	360,000	3,048,000	4,320	120,000
Total	*1,800*	*4,320*	*120,000*	*360,000*	*3,048,000*	*4,320*	*120,000*
Outputs (t)							
Biogas (dry)	81	194	6,458	19,375	164,039	199	6,458
Humidity	6	13	523	1,568	13,276	14	523
Digestate (dry)	99	238	5,546	16,639	140,880	233	5,546
Leachate	1,614	3,875	107,473	322,418	2,729,805	3,874	107,473
Total	*1,800*	*4,320*	*120,000*	*360,000*	*3,048,000*	*4,320*	*120,000*
BIOGAS PROCESSING AND USE							
Inputs (t)							
Air	503	1,207	47,059	141,177	1,195,298	1,239	47,059
Biogas (dry)	81	194	6,458	19,375	164,039	199	6,458
Humidity	6	13	523	1,568	13,276	14	523
Total	*590*	*1,414*	*54,040*	*162,120*	*1,372,613*	*1,452*	*54,040*
Outputs (t)							
H_2S	1	1	49	146	1,233	1	49
Exhaust	586	1,407	53,746	161,238	1,365,149	1,445	53,746
Condensate	3	6	245	736	6,231	6	245
Total	*590*	*1,414*	*54,040*	*162,120*	*1,372,613*	*1,452*	*54,040*
Water circ.	860	2,065	81,688	245,065	2,074,881	2,119	81,688

As expected, the results for similar scale scenarios are the same, with the exception of Scenarios 2 and 6. The difference in biogas production is due to the composition of the macroalgae, because the harvested macroalgae has a higher VS content, proving that the selection of potential species is important to production.

During feedstock preparation, all scenarios require a recycled leachate/macroalgae ratio of ~10:1 to produce the slurry. This compensates for the water loss during transportation. Furthermore, the largest mass throughput is water in all cases, which is to be expected considering macroalgae contains only 10 wt% solid. This means that there is enough leachate produced to recycle for slurry. The residual liquid, along with the condensate from dehumidification is treated as wastewater.

The biogas produced accounts for roughly 4-6 wt% of the digester(s) output due of the amount of water present, Table 6.8 shows the mass balance data, which is presented per t biogas (dry).

Table 6.8: Mass balance data per t biogas (dry)

Scenario	1	2	3	4	5	6	7
Inputs (t/t_{biogas} (dry))							
Macroalgae (90 wt% wet)	22.22	22.27	18.58	18.58	18.58	21.71	18.58
Water/ recycled leachate	2.00	2.01	1.67	1.67	1.67	1.95	1.67
Air	6.21	6.22	7.29	7.29	7.29	6.23	7.29
Outputs (t/t_{biogas} (dry))							
Water loss (natural)	2.00	2.01	1.67	1.67	1.67	1.95	1.67
Digestate (dry)	1.22	1.23	0.86	0.86	0.86	1.17	0.86
Wastewater	17.96	18.00	15.01	15.01	15.01	17.54	15.01
Exhaust	7.23	7.25	8.32	8.32	8.32	7.26	8.32
H_2S	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

As shown, the continuous digester scenarios produce more biogas per t macroalgae (wet). This is due to the use of multiple digesters, which based on the conversion rates cited in this study; increase the VS conversion rate by ~20%.

This results in a lower dry digestate and wastewater outputs. More air is required for these scenarios because the biogas has a marginally higher CH_4, which increases the O_2 demand for combustion.

With regards to the batch scenarios (1, 2 and 6), the effect of the feedstock composition is significant. Since the harvested macroalgae used in Scenario 6 has a fractionally higher VS content, more biogas is produced, which results in a reduction in the input/output data. The air demand is the same since the increase in biogas production offsets the increased demand.

6.4.2 Energy

Table 6.9 presents the net energy balances of the seven scenarios, which are expressed in GJ and represent the energy demand of the overall process operation. For the biogas processing and use figures, the exhaust accounts for about 56% of the overall output, whilst the remaining 44% is in the form of district heat produced by the engine casing.

Table 6.9: Scenario net energy balance results (GJ)

Scenario	1	2	3	4	5	6	7
Feedstock procurement	+1.4 (fuel)	+3.3 (fuel)	+91.8 (fuel)	+275.4 (fuel)	+2,332 (fuel)	+2.4 (fuel)	+91.8 (fuel)
Feedstock preparation	-	-	-	-	-	-	-
Anaerobic digestion	+183	+439	+37,132	+111,395	+943,142	+370	+37,132
Biogas processing & use	-735	-1,763	-68,659	-205,976	-1,743,926	-1,809	-68,659
Net total (GJ)	*-551*	*-1,323*	*-56,554*	*-169,661*	*-1,436,463*	*-1,439*	*-56,554*
Net GJ/t biogas	*-6.8*	*-6.8*	*-8.8*	*-8.8*	*-8.8*	*-7.2*	*-8.8*
Net GJ/t macroalgae (dry)	*-3.1*	*-3.1*	*-4.7*	*-4.7*	*-4.7*	*-3.3*	*-4.7*

As shown, all scenarios are exothermic and the heat produced during biogas processing is suitable for use during anaerobic digestion. In addition, the production of 1 t biogas produces at least 3.1 GJ of usable heat.

In literature, the energy demand for macroalgae anaerobic digestion is cited as 2.7 GJ/t macroalgae (2.66 MJ/kg assumed dry), which is used for heating and pre-processing [201, 202], though the operating conditions are not stated. In this study, the average energy demand is ~2.1 GJ/t macroalgae, which is not unreasonable in comparison since the receiver tank does not require heat and the feedstock does not undergo artificial drying.

6.4.3 Power

Table 6.10 presents the power balances for the scenarios.

Table 6.10: Scenario power balances (GJ)

Scenario	1	2	3	4	5	6	7
Demand (GJ)	+36	+87	+3,340	+10,020	+84,835	+89	+3,340
Available (GJ)	-434	-1,041	-40,571	-121,714	-1,030,510	-1,068	-40,571
Net (GJ)	*-397*	*-954*	*-37,231*	*-111,694*	*-945,674*	*-979*	*-37,231*
Net GJ/t biogas	*-4.9*	*-4.9*	*-5.8*	*-5.8*	*-5.8*	*-4.9*	*-5.8*

As shown, at least 4.9 GJ of electricity is produced per t of biogas. If the digester(s) were heated using electrical heaters this would not be the case, since the heaters could consume up to two thirds of the CHP electrical output. For Scenario 6, the additional power demand is compensated by the increased electrical output of the engine.

6.5 Comparison of CHP outputs with predicted data

In Chapter 5 (§5.2.3) the CHP outputs of each scenario were predicted using assumptions made by Kelly & Dworjanyn [132]. Table 6.11 presents the predicted data and the modelling results. This figures quoted are based on the annual (365 d/y) clean biogas output.

Table 6.11: Comparison of biogas predicted and actual yield

Scenario	1	2	3	4	5	6	7
Predicted biogas output (km^3/y)	*61*	*146*	*4,050*	*12,150*	*102,870*	*146*	*4,050*
Actual biogas output (km^3/y)	63	150	5,301	15,904	134,654	154	5,301

In all scenarios, the biogas output is higher than predicted. The main reason for this is that both feedstocks have a fractionally higher VS content than used by Kelly & Dworjanyn [132]. This means that the biogas production is increased by the solid throughput, even though the conversion rate used for the batch scenarios is lower than quoted by Kelly & Dworjanyn [132]. In addition, the significant increase in biogas production for Scenarios 3, 4, 5 and 7 is also due to the large VS conversion rate, which is ~30% higher than Kelly & Dworjanyn [132].

Table 6.12 presents the predicted and actual CHP system outputs.

Table 6.12: Predicted and actual CHP outputs

Scenario	*Predicted electricity output*	Actual electricity output	*Predicted heat output*	Actual heat output
	kW$_e$	kW$_e$	*kW$_{th}$*	kW$_{th}$
1	*14*	13	*23*	17
2	*33*	30	*55*	42
3	*913*	1,181	*1,513*	1,793
4	*2,740*	3,542	*4,538*	5380
5	*22,374*	29,987	*37,058*	45,550
6	*33*	31	*55*	46
7	*913*	1,181	*1,513*	1,793

Scenarios 1, 2 and 6 produce ~8% less electricity than predicted. The reason for this is that the biogas contains 6 vol% less CH_4, resulting in a lower energy content fuel for the CHP engine. Scenarios 3, 4, 5 and 7 however produce biogas containing 60 vol%, which generates ~30% more electricity than predicted due to the increased volume of biogas available. However, the predicted figures do not include the power consumption of the processes, which is equivalent to 7-8% of the output. Therefore, they do not represent the net output.

The outcome is the same for the thermal output, since the predicted figures do not represent the net output. Based on the data in Table 6.9, the thermal demand of the digestion processes is on average 50% of the output.

Therefore, it can be assumed that the scenarios operate at or above the predicted scale.

7 Process economics (marine)

This chapter investigates the capital and operating costs for marine biomass utilisation. With these costs established, the cost of heat and power production from macroalgae can be determined, resulting in the selection of the most promising systems. The economic data used is adapted from relevant literature sources, which are referenced where applicable.

7.1 Project assumptions

The following sections discuss the assumptions made in order to determine the capital and operating costs.

7.1.1 Economic life

The anaerobic digestion, biogas processing and CHP plants are assumed to have a plant life of 20 years [205]. The operational life of the cultivation farms are more complicated to determine, since this is dependent on the lifespan of the equipment and the macroalgae, which is up to 10 years [98, 215 & 234]. However, the economic life expectancy varies in literature from 10 to 20 years [87, 98 & 214].

In this study, an overall operational life of 20 years is assumed, though the individual equipment lives are considered. This will result in multiple capital investments, referred to in this study as “Additional capital” throughout the economic life of the project.

7.1.2 Discounts for scale

As discussed in §4.3.2, standard practises for scaling chemical plant equipment are not suitable for cultivation farms since they are not representative. Instead, the effect of scale on costs is dependent on the discounts applied to the material and investment costs as scale increases, normally calculated by the manufacturer. In this study, these discounts have been estimated using data published by Lenstra et al. [109], which assesses the cost of a 100 ha, 1,000 ha and 10,000 ha offshore cultivation farm, based on a 10% rate of investment (ROI). The discounts are presented in Table 7.1 on either a 3 ha or 50 ha basis.

Table 7.1: Material and installation discounts for cultivation farms

	Inshore			Offshore			
Scenario	3 ha	1	2	50 ha	3	4	5
Materials	0%	15%	36%	0%	60%	64%	89%
Installation	0%	11%	26%	0%	44%	49%	74%

For inshore cultivation, the discounts are calculated on a per 3 ha basis, since the scenarios comprise of networks of 3 ha farms. The discount is applied to the materials and installation cost for a 3 ha farm, which is then multiplied by the number of farms.

For offshore cultivation, the 50 ha base case represents the assumed area available between the wind turbines (§6.1.1.2.1), which is used to calculate the discounts applied to Scenario 3, 4 and 5.

Discounts are not applicable for Scenario 7 since cost data for the correct method and scale of production is available. The materials discount is also not applied to certain equipment, such as boats and trucks. This is because the number of items required is not a linear function of the scale of production; therefore, the discounts are not representative.

7.2 Capital cost

The capital cost is the sum of the capital investment required for feedstock procurement and the TPC of the anaerobic digestion and CHP plant.

7.2.1 Feedstock procurement

7.2.1.1 Cultivation

In literature, the capital investment for macroalgae cultivation is divided between materials and installation [109].

7.2.1.1.1 Inshore cultivation

The majority of materials and cost data for inshore cultivation, is adapted from data for a 1 ha inshore *Palmaria palmate* attached cultivation farm in the UK [234]. The farm comprises of 40x100 m longlines, each requiring anchorage and fastenings. This data was scaled to represent a 3 ha farm (no discounts applied) before use. Instead of increasing the length of the longlines from 100 m, more lines are installed. Table 7.2 shows the materials requirements and cost for Scenarios 1 and 2. Additional information regarding transport and equipment lifespans is taken from [216].

Table 7.2: Initial materials data for inshore macroalgae cultivation

			3 ha	Scenario 1	Scenario 2
Equipment	Cost/ item (2009 £)	Lifespan	No. of items		
Longline (100m)	2,569	5	120	600	1,440
Floats	70	5	2,400	12,000	28,800
Anchor rope	348	5	120 bundles	600 bundles	1,440 bundles
Assorted fixtures	6 - 11	5	960	4,800	11,520
Mooring blocks	216	10	240	1,200	2,880
Cost per 3 ha (2009 £)			*616,890*	*524,357*	*394,810*
Materials cost (2009 £)			*616,890*	*2,621,783*	*4,737,715*
Boats	21,574	20	2	2	3
Trucks	37,264	20	2	2	2
Additional cost (2009 £)			*117,676*	*117,676*	*203,970*
Total cost (2009 £)			*734,566*	*2,738,459*	*4,941,685*

The boats used in these scenarios are specified as non-motorised. The number of boats and trucks required includes a standby to ensure transport is available continuously. As shown, a lifespan of 5-10 years is assumed for the majority of equipment. This results in additional capital investments in Years 6, 11, 12 and 18 of the project.

The cost of installation for inshore cultivation (Table 7.3) is adapted from Hurtado et al. [215]. Since the original data is for a cultivation farm in South East Asia, a location factor of 0.9 (Malaysia, 2004) is applied.

Table 7.3: Installation costs for Scenarios 1 and 2

Scenario	Installation cost/ 3ha (2009 £)	*Installation cost (2009 £)*
3 ha	74,492	*74,492*
1	66,298	*331,488*
2	54,826	*657,911*

This cost is applied in the first year only, after this installation is covered in the maintenance cost (§7.3.3).

7.2.1.1.2 Offshore cultivation

7.2.1.1.2.1 Longline

Materials and cost data for the offshore longline cultivation farms is adapted from Buck et al. [235] based on the longline cultivation of mussels within a wind farm. In this study, a 50 ha farm comprises of approximately 70 longlines at 700 m each (670 m after anchorage) and ~10 m apart to allow for access. The v-shape culture lines are situated at 2 m intervals along the 670 m of usable longline, whilst the floats (71 per longline) are placed at 10 m intervals along the whole line. Each longline also has eight anchorage points, to withstand the turbulent conditions. Table 7.4 presents the materials and cost data for a 50 ha longline farm.

Table 7.4: 50 ha longline farm materials data

Equipment	No. of items (50 ha)	Lifespan	*Cost/ item (2009 £)*
Longline (670 m)	70	5	*1,249*
V-shape culture lines (2.5 m)	23,450	5	*4*
Floats	4,970	5	*26*
Anchorage	560	10	*179*
Other (assumed fixtures etc.)	49,000	5	*1*
Materials cost per 50 ha (2009 £)			*467,308*

In terms of lifespan, Buck et al. [235] assume a usable life of 4 to 6 years for the majority of equipment, whilst anchorage can last up to 10 years. As with Scenarios 1 and 2, there will be additional capital investments in Years 6, 11, 12 and 18 of the project. Since the logistics associated with feedstock procurement are assumed to be operated by an external company, the purchase of boats is not necessary. In addition, the logistics regarding the movement of the macroalgae within the conversion plant is not considered in this study; therefore, trucks are not included in the capital cost.

As discussed, the costs for Scenarios 4 and 5 are calculated on a 1,000 ha basis, using Scenario 3 as the base case. Table 7.5 presents the initial material cost data for Scenarios 3, 4, and 5.

Table 7.5: Scenarios 3, 4 and 5 material cost data

	Cost (2009 £M)		
Materials	Scenario 3	Scenario 4	Scenario 5
Cost per 1,000 ha (2009 £)	*5,273,313*	*3,401,999*	*990,692*
Materials cost (2009 £)	*5,273,313*	*10,205,997*	*24,271,955*

The cost of installation is also adapted from Buck et al. [235], which is £137k per 50 ha. Table 7.6 presents the installation cost for Scenarios 3, 4, and 5.

Table 7.6: Installation costs for Scenarios 3, 4 and 5

	Cost (2009 £M)		
Installation	Scenario 3	Scenario 4	Scenario 5
Cost per 1,000 ha (2009 £)	*1,534,853*	*1,433,553*	*707,567*
Installation cost (2009 £)	*1,534,853*	*4,300,658*	*17,335,396*

As with Scenarios 1 and 2, additional installation costs are covered in the maintenance budget.

7.2.1.1.2.2 Net

The economic data for net cultivation is taken from Lenstra et al. [109] for a 1,000 ha farm. The data, presented in Table 3.3, is based on a productivity rate of 500 t/ha/y; however, no adjustments have been made since the costs are associated with the physical size of the farm and not its output. The total investment cost (materials and installation) of £160.4M. In addition to the cultivation farm, it is assumed that this includes the harvesting equipment as well as the additional capital required for replacing equipment and the subsequent indirect costs.

7.2.1.2 Harvesting from natural stock

Like Scenarios 3, 4, 5 and 7, an external company manages the macroalgae harvesting, hiring the necessary equipment (Scoubidou). Therefore, the capital cost is for feedstock procurement is nil.

7.2.2 Anaerobic digestion and CHP plant

In literature, the anaerobic digestion, biogas processing and CHP system costs are either presented individually or as a single TPC, depending on the scale of the plant.

For Scenarios 1, 2 and 6 the conversion plant is based on the 5,000 tpd Greenfinch digester and CHP plant, which had an investment cost of £2.7M (£2.5M 2006). This includes all auxiliary stages and is assumed to include the cost of installation [236].

For Scenarios 3, 4, 5 and 7, the conversion plant TPC is based on the Valorga two-stage mesophilic digestion plant in Tilburg, Netherlands. The plant has a feedrate of ~47,000 t annually and a TPC of £24.5M ($17.5M 2006), which is assumed to include installation [205]. The CHP TPC is calculated using an average of data compiled by Juniper [236], which is equivalent to £2,995 per kW_e installed.

7.2.3 Land

This refers to the land required for the macroalgae conversion plant, which is assumed to be 4.2% of the TPC [220, 237]. In this study, this is calculated using the TPC of the conversion plant only.

7.2.4 Indirect costs

In this study, the indirect costs include engineering, design, supervision and management costs for the installation of the entire project. Based on Zamalloa et al [170], this is equivalent to 15% of the materials and equipment cost, including installation (not including land).

7.3 Operating costs

In literature, the operating costs for marine biomass are normally presented as a lump sum and not in the individual categories. In this study, the costs are divided between materials, labour, maintenance, leasing and permits and other fixed costs.

For Scenario 7, the operating and maintenance costs for feedstock procurement are presented as a single cost of £66.8k /ha/y (2009) [109]. It is assumed that this includes materials, maintenance and the associated fixed costs. However, in this study, labour, logistics and leasing are treated separately.

7.3.1 Materials

In this study, “materials” covers the cost of the feedstock and logistics, general process materials and waste disposal.

7.3.1.1 Feedstock

As discussed in §6.1.1.1, the macroalgae seedlings are purchased from commercial growers on pre-seeded cultivation line. This is because the production of juvenile sporophytes is labour and cost-intensive [72].

Cost data for purchasing seedlings is normally obtained from Asian aquaculture literature. In this study, the cost of the macroalgae seedlings is £205 /ha (5350 Ps/ha 1996) [213], which is for a 1 ha *Kappaphycus alvarezii* farm based in the Philippines. A location factor of 0.9 (Malaysia, 2004) is used to convert the costs to the UK. For Scenarios 1 and 2, the seedlings are supplied attached to the culture line, which has an additional cost of £1.08k /ha (£1k /ha 2006) [234]. In order to cover the costs of production, which are high, no discount is applied.

7.3.1.2 Logistics costs

Estimating the cost of transporting marine biomass is comparatively more difficult to calculate than for terrestrial. This is due to data availability and the effect of unknowns, such as weather and water conditions at specific times and locations, which dictate the availability of labour, equipment and working hours. In addition, macroalgae has a low bulk density; therefore estimating loading and unloading rates can be an issue.

The following sections discuss the logistics costs for the different scenarios.

7.3.1.2.1 Inshore

For Scenarios 1 and 2, the boats and trucks are purchased as part of the initial capital cost and it is assumed that the staff will load/unload the macroalgae as part of their duties. This means that the logistics cost is limited to the fuel required. However, the boats are non-motorised, therefore the only cost is diesel required for the trucks.

This is calculated assuming a truck capacity of 32 t (assumed to be operating at 10 t due to rate of harvesting and the bulk density of the feedstock), which has a fuel consumption rate of 8.4 mpg [238]. The price of diesel is assumed as £1.05 /litre, based on the 2009 UK price average [239].

7.3.1.2.2 Offshore

For offshore macroalgae production, the following costs must be considered:

- Vessel chartering/hiring
- Unloading
- Fuel consumed

Labour is treated as a separate cost (§7.3.2), since the workforce will be employed all year round for scheduled and emergency maintenance and other activities. For Scenario 7, the cost of chartering is not considered since the harvesting equipment is included in the capital cost.

The cost of vessel chartering varies with route, time, and market; therefore, generic prices are not available [240]. According to Hamelinck et al. [240], a 4,000 t ship costs £7,911/day (€9,700 (2002)), which is split between the charter costs (vessel, crew etc.) and any additional fees, such as port charges (~66 p/t cargo (~€0.6 /t cargo)). This is equal to ~£2 /t/day [assuming charter fees are calculated on a linear basis]. The charter cost for larger vessels reduces with capacity, with a 63,000 t ship and a110,000 t ship costing £1.30 /t/day and £1.26 /t/day respectively. The authors do not specify specifically whether fuel costs are included, therefore, it is assumed they are not. Furthermore, a crew is not required since several are already employed by the project, although the costs have not been adjusted. The vessel capacity has not been specified since this will vary with scale and will be dictated by availability of hire.

Table 7.7 shows the estimated annual vessel chartering fee for the offshore scenarios, based on 122 days harvesting (maximum).

Table 7.7: Macroalgae collection annual chartering fees

Scenario	Macroalgae yield t/y (wet)	*Annual chartering fee (2009 £)*
3	120,000	*240,000*
4	360,000	*720,000*
5	3,048,000	*6,096,000*
6	4,320	*8,640*
7	120,000	*240,000*

It is acknowledged that the actual fee may vary with scale and availability. As stated, the macroalgae collection period is specified as 122 days, which results in a daily harvest requirement of 35 - 25,000 t (wet).

The cost of unloading is taken as £5.6 /t (2009) [241], based on data for a small ship. The fuel cost is taken from Lisac & Muir [171], who assume a fuel cost of £64 /t mariculture (US$ 0.08 /kg mariculture (2002)).

7.3.1.3 Water

Water is required for heat recovery and in the initial start-up of the anaerobic digestion plant (for slurry). In this study, all required water is treated as cooling water, which costs 1.7 p/t [242].

7.3.1.4 Waste disposal

In this study, waste disposal is considered part of the materials costs. The production of biogas produces solid waste and wastewater, which requires treatment and disposal. The solid waste is in the form of captured H_2S collected from the biogas processing system, which costs ~£17 /t (US$18 /ton (1994)) for disposal [15]. The wastewater treatment costs £0.53 /t (~US$0.02 /100 ft^3 (2004)) [15].

7.3.2 Labour

In this study, labour is divided into feedstock procurement requirements and conversion requirements. This is because the feedstock procurement processes require specialist skills, such as diving, which increase the salary. According to The Independent [165], macroalgae harvesters in the UK are currently earning up to £250 /day, due to the specialist nature of their work.

Data regarding the labour requirement and subsequent cost is limited in literature. In this study, the labour and costs are adapted from various European aquaculture studies. The labour cost is primarily dependant on the type of feedstock procurement process used.

7.3.2.1 Inshore cultivation

Since inshore mechanical harvesting has yet to be developed, the seeding, maintenance and collection procedures operate manually. Sanderson [234] assumes a workforce of two is required for a 1 ha, longline-based macroalgae cultivation farm. Since the sites under investigation are limited to an individual size of 3 ha, a workforce of 6 is assumed to satisfy the labour requirement. Given that harvesting is performed over a four-month period and assuming the same period for seeding, a single workforce team should be able to service a large area within this period. Additionally, each site within the scenario network will be inspected at different intervals; therefore, a single workforce could maintain a network of 5 sites (Scenario 1). However, a workforce of 10 is assumed to be reasonable for Scenario 2, which has a total of 12 sites to manage. In both cases, it is assumed that each member also participates in general activities, such as management, accounting and logistics.

7.3.2.2 Offshore cultivation

7.3.2.2.1 Longline

As expected, labour requirements are greater for offshore cultivation, though the use of an integrated aquaculture system means that the associated costs are shared between all parties. Kaiser et al. [243] estimate a workforce range of eight to thirty-two for offshore oil or gas structure-based aquaculture, whilst Kam et al. [216] assume fifteen employees for a cage-based aquaculture system covering up to 4.5 ha. This figure comprises of seven full-time divers, one part-time diver, two captains (also divers), two harvesters and three general staff (truck driving, management and accounting).

In this study, divers are required for installation and maintenance of the anchorage system, but not for seeding and collection. Additionally, the labour intensive seeding and collection practise will require more support. Therefore, this study will consider a workforce of thirteen, consisting of six harvesters and four divers (two captains) for Scenarios 3 and 4, operating as two teams overseen by a single manager. Scenario 5 operates using a workforce of nineteen, which comprises of nine harvesters and nine divers (three captains), operating as three teams with a single manager.

7.3.2.2.2 Net

Since mechanised harvesting is used, the labour requirement is less than the longline method. However, divers (four) will be required for installation and maintenance, though the harvesting will only require a four-man team (two to pilot harvester, two pilot collection barge) who also complete general activities.

7.3.2.3 Harvesting

Due to the mechanised harvesting process, the labour requirement comprises of a two-man workforce for harvesting, overseen by a manager.

7.3.2.4 Anaerobic digestion and biogas usage

For Scenarios 1, 2 and 6 the labour requirement is considerably low. In this study, it is assumed that a team of six may operate the plants (two shifts including a manager each).

For the larger scale digestion plants, the labour requirement is based on Verma [205], who assume an administrative and operating workforce of twenty for a 52,000 ton (short)/y anaerobic digestion facility (Tillburg, Netherlands). It is assumed that the workforce will not increase significantly with feedstock throughput since the plants will be controlled electronically from a control room. Therefore, based on a four-shift system, Scenarios 3 and 7 require thirty-two people, Scenario 4 requires forty, and Scenario 5 requires forty-eight.

7.3.2.5 Workforce summary and costs

Table 7.8 presents the summary of the labour requirement for each scenario.

Table 7.8: Scenario labour requirements

Scenario	Feedstock procurement	Anaerobic digestion and biogas usage	Total
1	6	6	12
2	10	6	16
3	13	32	45
4	13	40	53
5	19	48	67
6	3	6	9
7	8	32	40

For inshore the salary is £37.75k (£35k 2006) based on Sanderson [234]. Labour costs are slightly more complex for offshore, since divers can demand a higher salary due to their specialist skill. In this study, the salary for offshore staff is £45k.

Data for the digestion plant labour requirement are adapted from terrestrial biomass plants. For the conversion plant staff, a standard salary of £30.49k (US$40k (2002)) is assumed, which includes all benefits, based on Verma [205].

7.3.3 Maintenance

Maintenance is taken as 5% of the capital cost, based on Zamalloa et al. [170]. This figure is higher than the general rate of 2.5% applied to a biomass conversion system [182] because additional costs such as installation of replacement materials are included. This figure is used for all scenarios, regardless of feedstock procurement practise, however for Scenarios 6 and 7 it is applied to the conversion plant TPC only.

7.3.4 Water leasing and harvesting permits

Areas of water, such as ponds and ocean sectors are leased from the Crown Estate at an annual fee; therefore, these costs are treated as an operating cost. No discounts are applied since water leasing is operated by a governing body and is therefore not a competitive market. However, based on Kam et al. [216], only half of the annual cost is paid in the first year since no product is produced.

7.3.4.1 Inshore

For their work on open pond microalgae cultivation, Zamalloa et al. [170] assume the economic value of an inshore pond is equivalent to low value agricultural land. Using data published by Eurostat [244] this equates to an annual cost of £89 /ha/y (€100 ha/y).

7.3.4.2 Offshore

Offshore sites may be leased as part of a long-term contract over a period of years [245]. This approach is used in this study, with the selected sites being leased for 20 years. An annual lease is assumed to be approximately £1k /ha/y, based on Kam et al. [216].

7.3.4.3 Harvesting permits

Harvesting macroalgae from natural beds is also subject to leasing and permission. An annual licensing fee is applied. In Ireland, the fee for commercial-scale harvesting is £126.9 /y (€150 /y (2005)) [246], which is used in this study.

7.3.5 Other fixed costs

Insurance, taxes and other legal fees are covered in this section, which is equivalent to 2% of the capital cost of each scenario [15].

7.4 Additional revenue

In this study, the revenue from the sale of the digestate and district heat is included. The price of the digestate is taken from the Brecht digestion plant, North Belgium, which uses a price of £10.92 /t (dry) (US$13 /ton compost (2002)) [205]. The price of district heat for the UK is 7 p/kWh, which is taken from [247].

7.5 Cost of marine biomass utilisation

7.5.1 Capital cost summary

Table 7.9 presents the capital costs for the scenarios.

Table 7.9: Scenario capital costs (2009 £M)

Scenario	1	2	3	4	5	6	7
Feedstock procurement	3.11	5.60	10.88	29.81	78.02	-	160.40
Materials	2.78	4.94	9.35	25.51	60.68	-	89.11
Installation	0.33	0.66	1.53	4.30	17.34	-	71.29
Additional Capital	7.43	13.42	9.15	25.00	59.42	-	-
Anaerobic digestion & CHP system	1.29	2.27	28.01	60.59	290.19	2.27	28.01
Anaerobic digestion	1.29	2.27	24.47	49.98	200.38	2.27	24.47
CHP	-	-	3.54	10.61	89.81	-	3.54
Land	0.05	0.10	1.18	2.54	12.19	0.10	1.18
Indirect	0.66	1.18	5.83	13.56	55.23	0.34	4.20
TOTAL	*12.54*	*22.57*	*55.05*	*131.50*	*495.05*	*2.71*	*193.79*

As expected, the capital increases with scale, resulting in Scenario 5 having the largest capital investment. Scenario 6 has the smallest capital cost since investments related to cultivation are not required. The higher investment required for Scenario 7 in comparison to Scenario 3 determines that stand-alone cultivation farms will require larger investments than protected sites. Figure 7.1 presents the capital breakdown for the seven scenarios on a percentage basis.

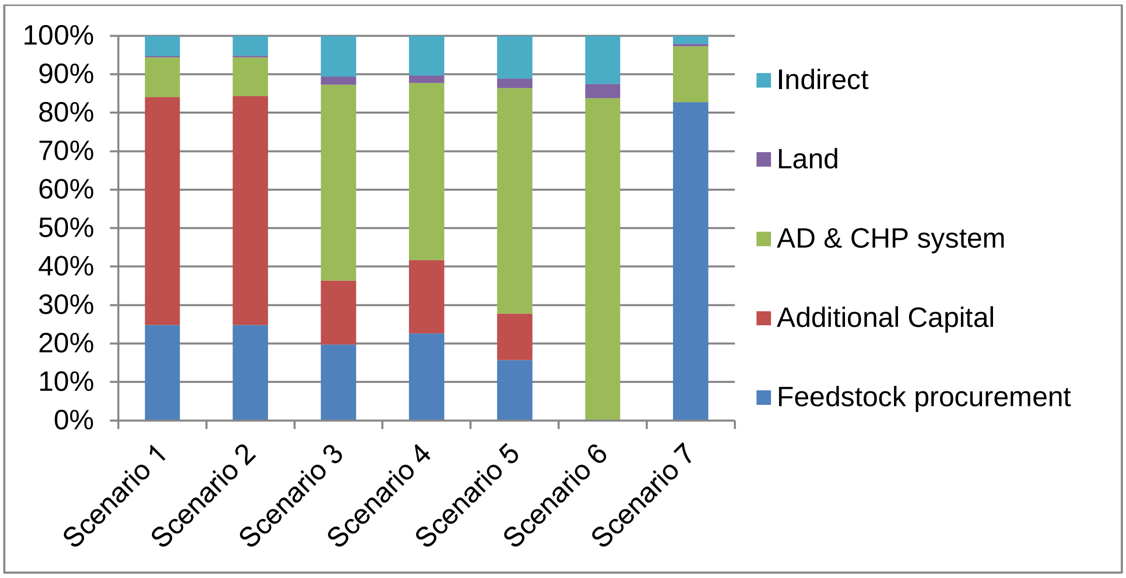

Figure 7.1: Scenario capital breakdown

As shown, feedstock procurement (including additional capital) accounts for 84% of the total project capital for Scenarios 1 and 2.

For Scenarios 3, 4 and 5, the cost of the anaerobic digestion and CHP plant are the largest investment, due to the scale of operation. The capital cost of Scenario 6 is also predominantly the anaerobic digestion and CHP system, however this is because the cost of feedstock procurement is nil. For Scenario 7, the cost of feedstock procurement accounts for 83% of the capital, which includes harvesting equipment as well as additional anchorage required for a standalone farm.

7.5.2 Operating cost summary

Table 7.10 presents the operating costs for the seven scenarios.

Table 7.10: Scenario operating costs (2009 £k)

Scenario	1	2	3	4	5	6	7
General O&M	-	-	-	-	-	-	66.8
Materials	164.4	394.6	8,851	26,552	224,655	311.2	8,406
Feedstock	19.3	46.2	204.9	614.6	5,019	-	-
Feedstock logistics	144.3	346.4	8,592	25,776	218,237	309.3	8,352
Water	<0.1	<0.1	1.6	4.8	74.3	<0.1	1.6
Waste disposal	0.8	1.9	52.2	156.5	1,325	1.9	52.2
Labour	371.7	560.5	1,561	1,805	2,319	296.2	1,336
Maintenance	627.0	1,128	2,753	6,575	24,753	135.5	1,669
Leasing & permits	1.3	3.2	1,000	3,000	24,500	0.1	1,000
Other fixed costs	250.8	451.3	1,101	2,630	9,901	54.2	3,876
TOTAL	*1,415*	*2,538*	*15,266*	*40,562*	*286,128*	*797.2*	*16,354*

As shown, Scenario 6 has the smallest annual operating cost, primarily due to comparatively low labour and leasing costs in addition to the feedstock costs being nil. Scenario 5 has the greatest operating cost, which is expected due to the scale of production. Whilst the use of mechanised harvesting reduces the labour, Scenario 7 is less economically attractive than Scenario 3, primarily due to the fixed costs, which are a function of the capital. Figure 7.2 presents the operating cost breakdown for the seven scenarios on a percentage basis. In this case, the feedstock and logistics costs are treated as a single cost.

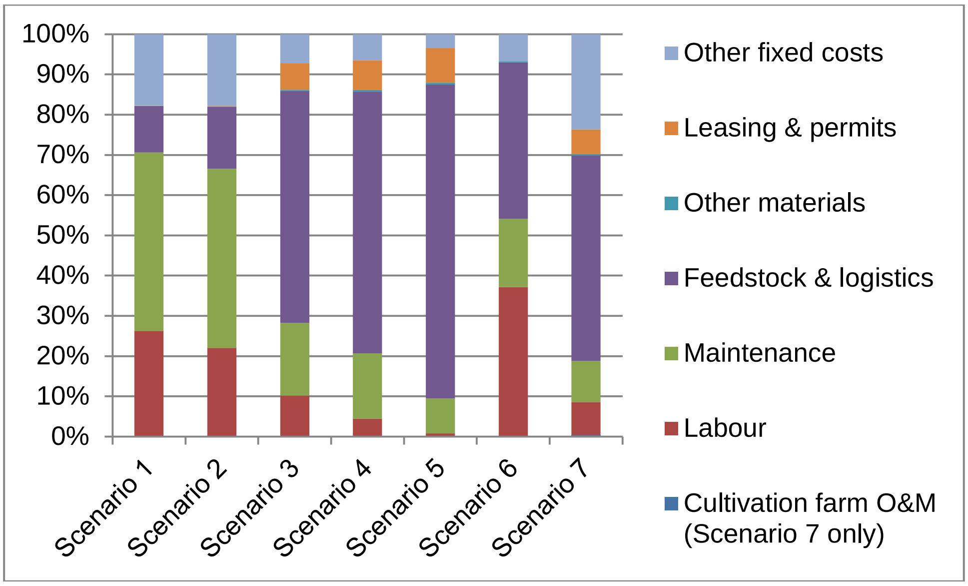

Figure 7.2: Operating cost breakdown

For Scenarios 1 and 2, the largest operating cost is maintenance, which accounts for about 44% of the total cost. The cost of the feedstock and logistics is the largest fraction for Scenarios 3, 4, 5 and 7, which is approximately 51-78% of the total cost. This is due to the logistics costs, in particular fuel. The operating cost of Scenario 6 is dominated by the logistic and labour costs, which is reasonable since the maintenance cost is a function of conversion plant only.

For all scenarios, the cost of leasing/permission and materials (non-feedstock) are comparatively low, accounting for up to 8% of the total cost. Other fixed costs are also low, ranging from 3% to 24%. Labour varies between 1% and 30%, depending on the scenario, with Scenario 5 being the lowest and Scenario 6 the highest.

7.5.3 Additional revenue

Table 7.11 presents the additional revenue raised by the seven scenarios.

Table 7.11: Additional revenue (2009 £k)

Scenario	1	2	3	4	5	6	7
District heat	9.5	25.7	1,100	3,299	27,931	19.0	1,100
Digestate	1.1	2.6	60.6	181.8	1,539	2.5	60.6
Total	*10.6*	*28.3*	*1,161*	*3,481*	*29,470*	*21.5*	*1,161*

The revenue from district heat accounts for ~93% of the revenue on average. The difference in revenue between Scenarios 2 and 6 is due to differences in the feedstock affecting the conversion process.

7.5.4 Cost of electricity production

The cost of marine biomass utilisation for electricity production is calculated using the assessment criteria outlined in §4.3.2, based on a TRR of 20% (§4.3.3). In addition to the data and assumptions presented in the previous sections, the cost of production is based on the following assumptions:

1. Construction is carried out in the first two years of the project, with an initial capital outlay of 50% in Year 0 and 50% in Year 1.
2. The working capital is assumed as 10% of the initial capital, which is paid in Year 1 and returned in Year 21.
3. Operation begins in Year 2, assuming full production, and ends in Year 21.
4. Additional capital investments are included in Years 6, 11, 12 and 18.
5. The scrap value of process equipment is assumed as 5% of the project capital.

Table 7.12 presents the calculated price of electricity (kWh) to achieve a TRR of 20%.

Table 7.12: Calculated price of electricity (£/kWh)

Scenario	1	2	3	4	5	6	7
Electricity price (£/kWh)	26.77	19.96	2.49	2.07	1.39	5.30	6.07

As shown, increasing the scale of production reduces the cost of electricity. Therefore, small-scale cultivation is less attractive than large-scale. The significant difference between Scenarios 2 and 6 shows that small-scale electricity production is also more favourable using harvested macroalgae as opposed to cultivated. At 1,000 ha (Scenarios 3 and 7), net cultivation is less attractive than longline, mainly due to the higher capital investment, which are not compensated by the operating costs.

The following figures present the electricity price breakdown of each scenario. The categories are categorised using the following abbreviations:

- Capital costs: Feedstock procurement (FP), Anaerobic digestion and CHP (AD & CHP), Additional capital (AC), Land (LAND), Indirect costs (IND)
- Operating costs: Labour (LAB), Maintenance (M), Leasing and permits (L & P), Other fixed costs (OFC), Other materials (OM)

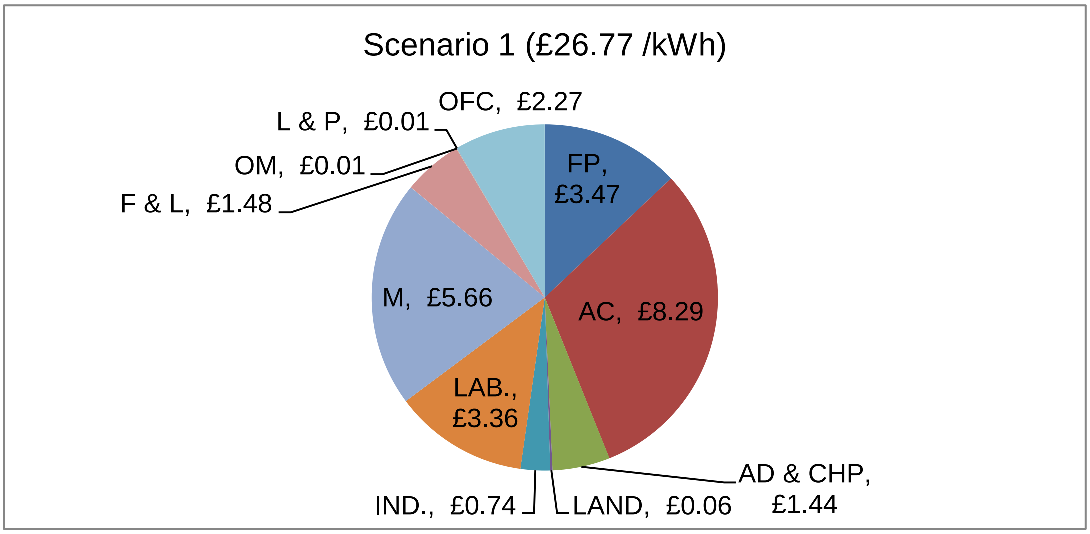

Figure 7.3: Scenario 1 electricity price breakdown

For Scenario 1 (Figure 7.3), the largest cost is additional capital, followed by maintenance. The additional capital accounts for about 59% of the total capital, therefore it is not surprising that it has the greatest effect on the electricity price. The maintenance is expressed as a function of the total capital, which includes the additional capital; hence, the effect on the electricity price is to be expected.

Labour and feedstock procurement also make a significant contribution to the electricity price, whilst the cost of land, other materials leasing and permission all have little effect.

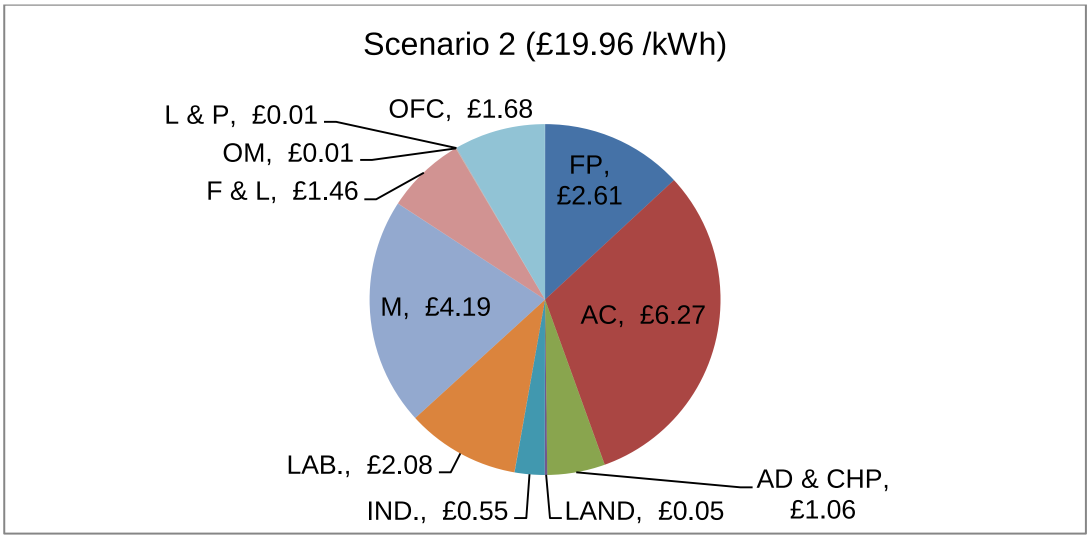

Figure 7.4: Scenario 2 electricity price breakdown

Like Scenario 1, the electricity price for Scenario 2 (Figure 7.4) is predominantly driven by the additional capital and maintenance costs. Therefore, in order to reduce the generated prices for inshore cultivation, improvements to the durability (lifespan) of the feedstock procurement equipment is required. This will reduce the additional capital and in turn any capital-derived costs, such as maintenance.

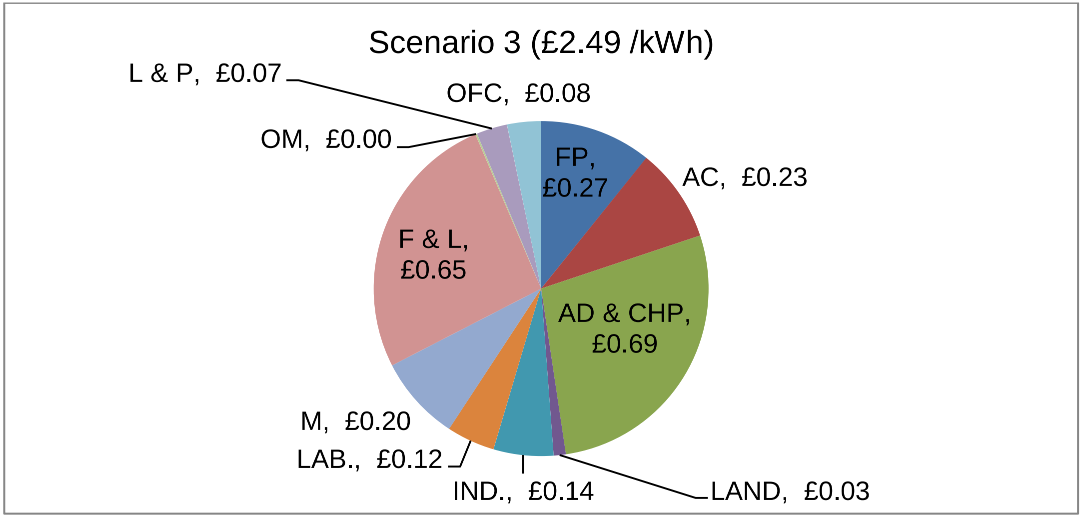

Figure 7.5: Scenario 3 electricity price breakdown

For Scenario 3 (Figure 7.5) the electricity price is primarily generated by the anaerobic digestion plant capital in addition to high feedstock and logistics costs. This is to be expected due the scale of operation, which requires the transportation and conversion of a large quantity of feedstock material. This is also the case for Scenario 4 (Figure 7.6), again due to the scale of feedstock production and conversion required.

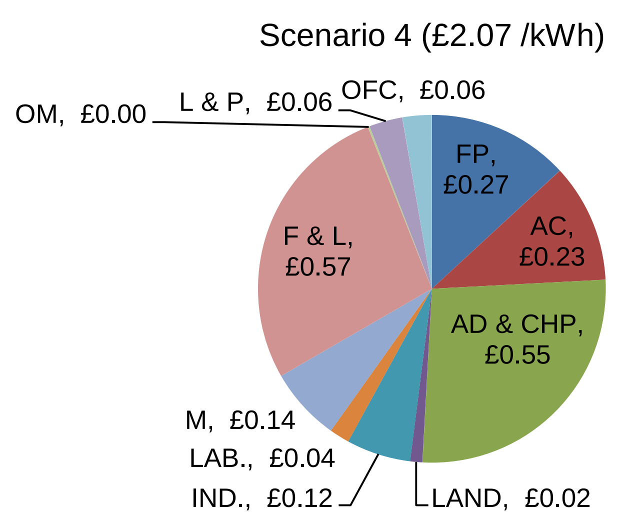

Figure 7.6: Scenario 4 electricity price breakdown

The electricity price for Scenario 5 (Figure 7.7) is primarily driven by high feedstock and logistics costs due to the sheer volume of feedstock being transported.

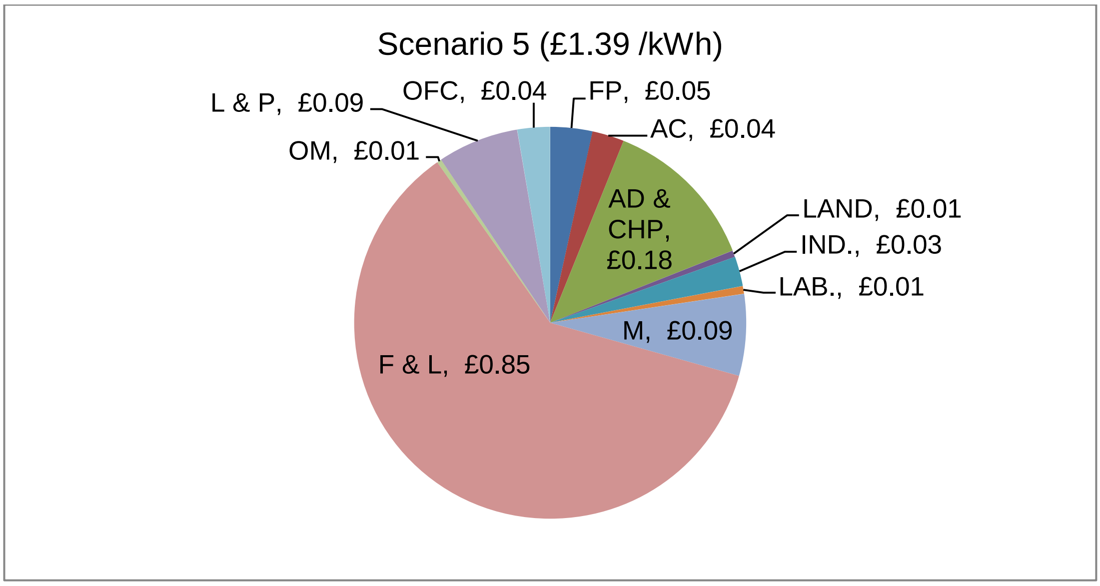

Figure 7.7: Scenario 5 electricity price breakdown

The remaining costs have a minor impact on the electricity price; therefore, the cost of production may be reduced by making improvements to the feedstock collection process.

For Scenario 6 (Figure 7.8) the capital cost of the anaerobic digestion and CHP plant makes the largest contribution to the electricity price. This is primarily because the capital for feedstock procurement is nil.

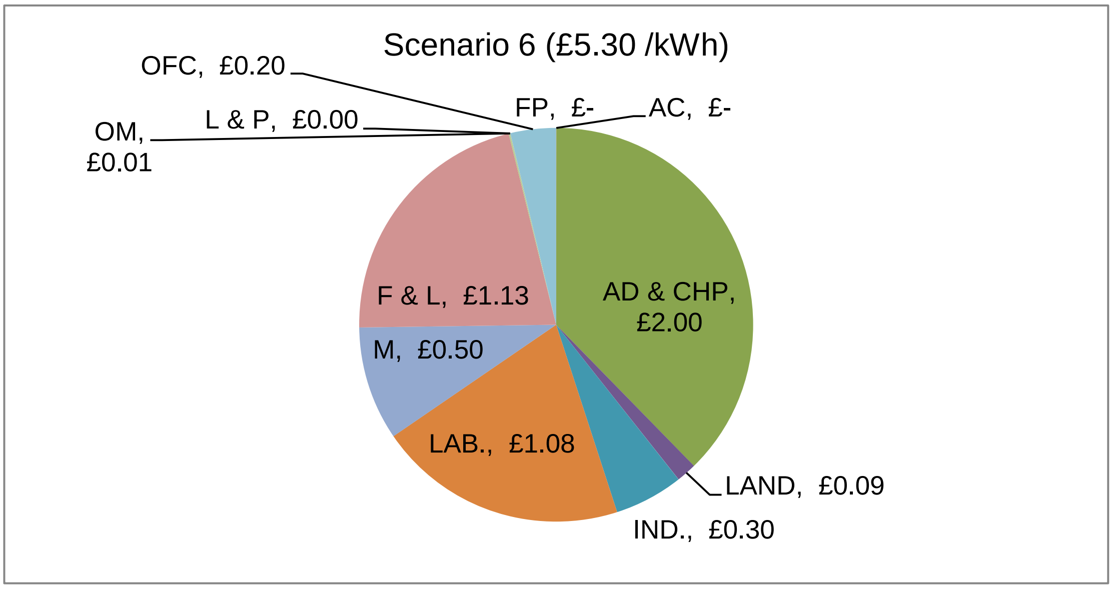

Figure 7.8: Scenario 6 electricity price breakdown

Like Scenarios 3, 4 and 5, the feedstock and logistics has a substantial impact, albeit not as significant as Scenario 5. Labour also has a greater effect; however, this is linked more with the conversion plant requirement than feedstock collection.

The use of net cultivation for Scenario 7 (Figure 7.9) has the largest impact on the electricity price. This is due to the use of a standalone cultivation system, which requires more structural reinforcement than Scenarios 3, 4 and 5.

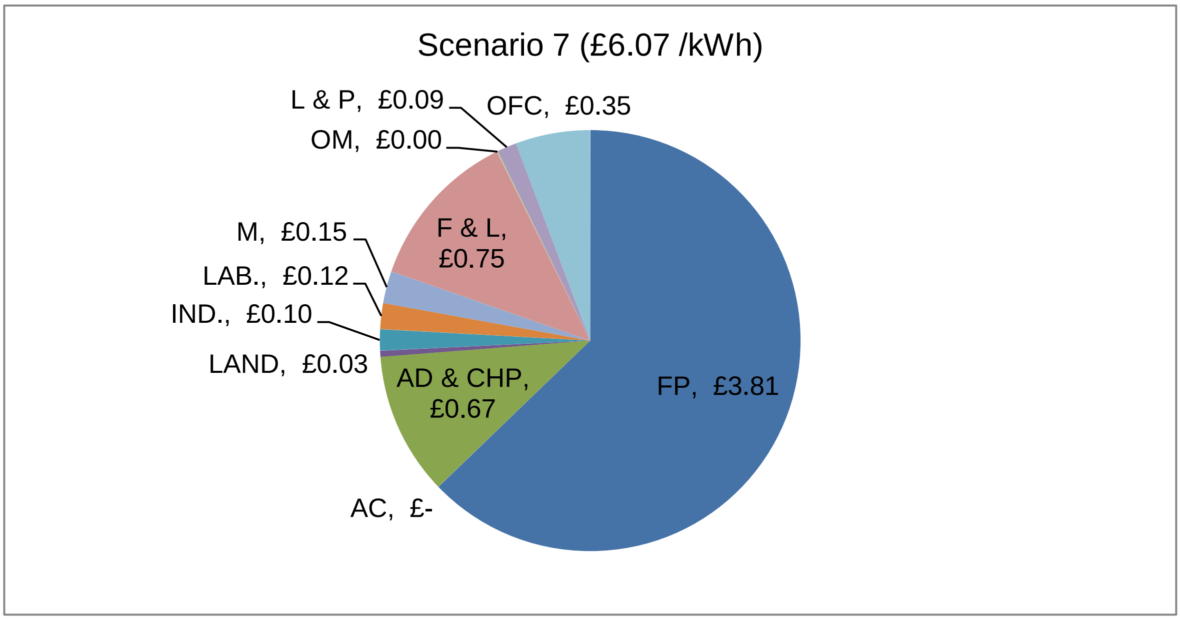

Figure 7.9: Scenario 7 electricity price breakdown

However, the use of mechanised harvesting techniques does not increase the electricity price substantially in comparison to Scenarios 3 and 4, which increases the appeal.

The effect of the additional revenue varies between 8-12 p/kWh, with the smallest effect measured for Scenario 6 and the greatest for Scenario 4.

Comparison with published data is difficult to determine, since the information is either unavailable or presented under different conditions. Burton [128], based on data by Reith et al. [116] calculate an electricity price of 1.4 p/kWh as the break-even price for a 100 kt/y (dry) system, however, this does not include raw material costs, which, as shown in §7.5.2 accounts for a considerable part of the operating costs. Zavalla et al. [170] calculate the profitability of microalgae derived electricity production using an electricity price of 14 p/kWh, using a variable IRR, whilst Cheshire and Ferry [248] specify an electricity price of roughly 10 p/kWh for a terrestrial feedstock based digestion and CHP system.

With the above data as an approximate guide, it is clear that the cost of macroalgae-derived electricity is excessively high, particularly for small-scale production.

7.5.5 Preliminary sensitivity analyses

Two preliminary sensitivity analyses are completed in order to measure the effect of fluctuations in the capital and operating costs. They also provide additional information in order to determine the most promising systems.

7.5.5.1 Capital cost variation

In this sensitivity, the initial capital cost (not including additional capital) is varied by ±10% in order to account for discrepancies in the cost data. The effect of this on the price of electricity is presented in Table 7.13.

Table 7.13: Capital sensitivity results

Scenario	Calculated electricity price (baseline) (£/kWh)	Electricity price (£/kWh) (-10% capital)	Electricity price (£/kWh) (+10% capital)
1	26.77	25.31	30.89
2	19.96	17.87	22.06
3	2.49	2.36	2.62
4	2.07	1.97	2.18
5	1.39	1.35	1.44
6	5.30	5.06	5.55
7	6.07	5.61	6.53

The effect of a ±10% variation in capital varies with each scenario. A -10% capital variation reduces the electricity price by -5% to -10%, with Scenario 2 achieving the highest. However, a +10% capital variation increases the electricity price by 5% to 16%, with Scenario 7 achieving the highest. These are substantial impacts, highlighting the risk associated with large capital investments for novel processes, particularly when the cost of the product is higher than that of similar conventional feedstocks and technologies.

For Scenarios 1 and 2, the additional capital had a significant impact on the electricity prices, therefore a ±10% additional capital variation is implemented, and presented in Table 7.14.

Table 7.14: Additional capital sensitivity results

Scenario	Calculated electricity price (baseline) (£/kWh)	Electricity price (£/kWh) (-10% AC)	Electricity price (£/kWh) (+10% AC)
1	26.77	26.30	27.24
2	19.96	19.61	20.32

A -10% additional capital variation reduces the electricity price by -2%, whilst a +10% additional capital variation increases the electricity price by 2%. Whilst the electricity prices are affected, the impact is not as significant as a ±10% variation in initial capital.

7.5.5.2 Feedstock logistics variation

In this sensitivity, the feedstock logistics cost is varied by ±50%. This is assumed to replicate fluctuations in logistics and fuel costs caused by external factors, both positive and negative. The effect of this on the price of electricity is presented in Table 7.15.

Table 7.15: Feedstock logistics sensitivity results

Scenario	Calculated electricity price (baseline) (£/kWh)	Electricity price (£/kWh) (-50% logistics cost)	Electricity price (£/kWh) (+50% logistics cost)
1	26.77	26.12	27.43
2	19.96	19.31	20.62
3	2.49	2.08	2.93
4	2.07	1.66	2.51
5	1.39	0.99	1.83
6	5.30	4.74	5.90
7	6.07	5.66	6.47

Like the capital costs, the effect of varying the logistics costs varies with each scenario. A -50% logistics variation reduces the electricity price by -2% to -30%, with Scenario 5 achieving the highest. As shown, the most significant variations are recorded for the offshore scenarios, in particular Scenarios 3, 4 and 5. This is expected since the logistics costs are calculated on a feedstock mass basis. A +50% logistics cost variation increases the electricity price by 2% to 29%, with Scenario 5 again achieving the highest, due to the high rate of production.

The effect of a variation in the logistics costs is more significant than a change in the capital costs, highlighting the need for long term, low cost macroalgae collection techniques.

7.6 Selection of most promising systems

The scenarios are separated into small- and large-scale production and the most promising system is selected from each group, based on the cost of electricity and the sensitivity results.

For small-scale (Scenarios 1, 2 and 6), Scenario 6 is by far the most promising, producing electricity at ~23% of the price of Scenarios 1 and 2. Whilst the effect of the logistics cost is more significant, the effect of capital is not and since the capital regarding feedstock procurement is nil, it is far more attractive. Although the price of electricity is higher than several offshore scenarios, the potential for increasing production is significant and should be considered. For large-scale (Scenarios 3, 4, 5 and 7), Scenario 5 is the most promising, producing the cheapest electricity, even during the preliminary sensitivities.

However, this does not mean that other scenarios, such as 3 and 4 which produce electricity at the second and third lowest price, do not have potential.

8 Process improvements

In Chapter 7, the cost of electricity production from macroalgae for the seven scenarios was calculated based on the capital and operating costs of the relevant sub-systems. During the preliminary analysis it was determined that Scenarios 5 and 6 had the most potential, although the electricity selling prices were still higher than anticipated in comparison to published data. In this chapter, these scenarios undergo a series of additional sensitivity analyses, which evaluate the use of alternative practises in an attempt to reduce the electricity selling price further. In this study, an approximate electricity selling price range of up to 14 p/kWh is considered as acceptable, based on the published data presented in §7.5.4, although a selling price of up to 20 p/kWh would not be considered excessive.

The sensitivity analyses presented in this chapter concentrate reducing the costs associated with the feedstock supply chain, which has a significant impact on the electricity price of the selected scenarios. The chosen practises are derived from the work carried out in the previous chapters or are based on recommendations from relevant literature. In all cases, it is assumed that the composition and subsequent biogas yield from the macroalgae are the same as the original assessment presented in Chapter 6.

In addition to the four sensitivity analyses, there is a written evaluation of the use of alternative technology, based on the outcomes of this study in addition to recommendations for further work.

8.1 Alternative collection processes

In the original assessment, harvesting was completed over a maximum of 122 days. This resulted in a daily macroalgae collection yield of ~25,000 t (wet) for Scenario 5 and 35 t (wet) for Scenario 6.

In §2.2.2.2.2 *Ascophyllum Nodosum* is harvested into nets, which are ejected from the harvesting craft and collected later by a larger craft [79]. This means that the harvesting vessel has to make fewer trips to shore. Alternatively, a larger vessel may be used, which includes a smaller harvesting craft that can disembark for use. Since the cost of chartering is calculated on per tonne per day basis, increasing the capacity of the vessel and reducing the number of days for harvesting should reduce costs.

Due to the difference in scale between the two scenarios, it would be impractical to implement the same system for both.

For Scenario 5, a 75 000 t capacity vessel is used, which has a maximum speed of 27.8 km/h and a fuel oil consumption rate of 44 tpd. Scenario 6 uses a 4,000 t capacity vessel, with a maximum speed of 28.7 km/h and a fuel oil consumption rate of 19 tpd [240, 249]. Assuming a maximum 400 km roundtrip, based on §6.1.1.5, a single vessel makes 1 trip/day. The price of fuel oil is assumed as £160 /t [250]. Data regarding chartering and unloading is adapted from [240, 241].

In the original assessment, the collection fleet used for Scenarios 5 and 6 makes 122 trips/y. However, using larger vessels reduces the numbers to 41 and ~2 respectively. Table 8.1 presents the sensitivity results for both scenarios.

Table 8.1: Alternative collection processes sensitivity results

Scenario	5	6
Baseline electricity price (£/kWh)	1.39	5.30
Alternative collection electricity price (£/kWh)	0.63	4.29

As shown, changing the macroalgae collection process has a clearly positive impact on both scenarios. For Scenario 5, the electricity selling price is reduced by about 55%, which is a significant difference. In addition, the price does not exceed 70 p/kWh at any point in the analysis, and is also more comparable to results published by Zamalloa [170] and Chesshire and Ferry [248] (§7.5.4), than the original price of £1.41 /kWh. For Scenario 6 the electricity selling price is reduced by around 20%, which again is an improvement. However, the price does not drop below £4 /kWh, which is still excessive, particularly in comparison to Scenario 5.

8.2 Imported macroalgae

The costs associated with feedstock procurement have a significant impact on the overall cost of the systems. One way of reducing this impact is by importing macroalgae from Asia, where production is far more cost effective than in Europe, due to the level of establishment and different working ethic.

In this sensitivity, macroalgae is imported from The Philippines to shoreline conversion plants, assuming a macroalgae cost of ~£1.70 /t (wet) (£150 /t (dry)), based on data compiled by Reith et al. [116]. No discounts are applied for bulk purchases since macroalgae is a sought-after commodity in Asia for larger industries such as food.

Maintenance costs are also still assumed as 5% of the capital. The macroalgae is shipped from Manila, The Philippines to Felixstowe, UK, and the logistics data and costs (Table 8.2) are adapted from Croatian Shipbuilding Corporation [248], Hamelinck et al.

[240] and Searates [251]. The distance travelled is one-way, since it is assumed that the vessel would be used for transporting other materials on its return journey.

Table 8.2: Logistics data and costs [240, 248 & 251]

Capacity of vessel	75,000 t
Distance travelled	17694 km
Journey duration (speed)	28 days, 10 hours (27.8 km/h)
Fuel oil consumption	44 tpd
Number of journeys	41 (Scenario 5); 1 (Scenario 6)
Fuel cost	£160 /t fuel oil
Charter costs	£9,000 /trip
Loading/unloading cost	£2/t

Table 8.3 presents the results of the sensitivity analysis for both scenarios.

Table 8.3: Imported macroalgae sensitivity results

Scenario	5	6
Baseline electricity price (£/kWh)	1.39	5.30
Imported feedstock electricity price (£/kWh)	1.17	3.84

As shown, there is some benefit in considering imported macroalgae instead of cultivation. For Scenario 5, the use of imported macroalgae reduces the electricity selling price by 17% to £1.17, which is due to a ~30% reduction in the capital costs. The capital costs of Scenario 6 are unchanged as expected; however, the decrease in the operating costs results in a 28% reduction in the electricity selling price to £3.84 /kWh.

8.3 Utilising macroalgae waste

This sensitivity is adapted from work published by Charlier et al. [41], and suggests the use of imported waste macroalgae, which is a combination of alginate residue and macroalgae litter collected from beaches. Due to their status as waste, it may not incur a cost, only a fee for logistics.

Utilising alginate residue is already recognised as being economically and technically attractive since it removes the initial costs related to feedstock production. It also reduces the amount of competition for resources with the established macroalgae industries, such as food, that dominate the macroalgae market [72, 132]. In addition, if the residue is supplied as slurry the amount of pre-treatment can be reduced for biological conversion processes. Although alginate residue is highly enriched in the sugars mannitol and laminaran [132], details regarding the exact composition and available quantity of alginate residue are difficult to obtain since the majority of data is currently unpublished. It is for this reason that alginate residue was not treated as a primary feedstock in the earlier stages of this study.

The decline of the European alginate industry means that a supply of locally sourced feed is not as consistent as once thought. To provide a suitable supply the residue would need to be imported from countries with large alginate industries, such as China [132] at additional cost. In this sensitivity, alginate residue is imported from Asia (The Philippines).Table 8.4 presents the data and costs for alginate residue from The Philippines, which uses Manila as the reference point.

Table 8.4: Logistics data and costs for The Philippines to Felixstowe [240, 248 & 251]

Capacity of vessel	70,490 t
Distance travelled	17694 km
Journey duration (speed)	28 days, 10 hours (27.8 km/h)
Fuel oil consumption	44 tpd
Number of journeys	41 (Scenario 5)
Fuel cost	£160 /t fuel oil
Charter costs	£9,000 /trip
Loading/unloading cost	£2/t

As discussed in §2.1.3, excessive macroalgae production due to environmental factors has become a regular occurrence. Utilising this as a feedstock will not only reduce costs but also have a positive environmental impact, which may qualify for governmental aid. In this sensitivity, the waste macroalgae is transported from France (Brittany), assuming that approximately 11,000 t of macroalgae are available from Brittany [41]. The alginate residue provides the remaining tonnage required. Table 8.5 presents the data and costs for waste macroalgae from Brittany, which uses Brest as the reference point.

Table 8.5: Logistics data and costs for Brittany to Felixstowe [240, 248 & 251]

Capacity of vessel	70,490 t
Distance travelled	756 km
Journey duration (speed)	1 day, 3 hours (27.8 km/h)
Fuel oil consumption	44 tpd
Number of journeys	1 (both scenarios)
Fuel cost	£160 /t fuel oil
Charter costs	£9,000 /trip
Loading/unloading cost	£2/t

The results of the sensitivity analysis are shown in Table 8.6.

Table 8.6: Waste macroalgae sensitivity results

Scenario	5	6
Baseline electricity price (£/kWh)	1.39	5.30
Waste macroalgae electricity price (£/kWh)	1.15	3.81

Like importing macroalgae, there is some benefit in considering waste macroalgae and residues instead of cultivation. For Scenario 5, the electricity selling price is reduced by 23% to £1.15, whilst the electricity selling price for Scenario 6 undergoes 29% reduction in to £3.81.

8.4 10% target rate of return

In this study, the electricity selling price has been calculated using a 20% IRR to reflect the investment risk (§4.3.3). However, as shown in Chapter 7, this leads to uncompetitive prices.

Several large-scale biomass projects assume a 10% TRR [15, 220 & 252] as part of their economic strategy. For Dutta et al. [252], this rate of return represents the repayment of a low interest (8%) loan, which provides ~60% of the project capital. For the production of algal-based biofuel, an IRR of 10% is common [253, 254].

In this sensitivity, a 10% TRR is assumed on the basis that the capital is funded by a loan with a 5% to 10% interest rate, which is supplied by a governmental body as part of a renewable energy scheme. It is acknowledged that this level of return will not compensate for the level of risk involved and that the cost and conditions of the loan will vary with the economic climate.

Table 8.7 presents the electricity selling prices calculated under the above conditions.

Table 8.7: 10% TRR results

Scenario	5	6
Baseline electricity price (£/kWh)	1.39	5.30
10% TRR (£/kWh)	1.22	4.19

As shown, the effect of setting a 10% TRR is a reduction in the price for both scenarios. For Scenario 5 there is a 13% reduction in the electricity selling price. The impact is greater for Scenario 6, with a 21% reduction in the electricity price.

8.5 Discussion and project barriers

8.5.1 Selling price comparison

All of the sensitivity analyses reduce the electricity selling price, however the impact varies with each analysis. Figure 8.1 presents the sensitivity selling price summary for Scenario 5.

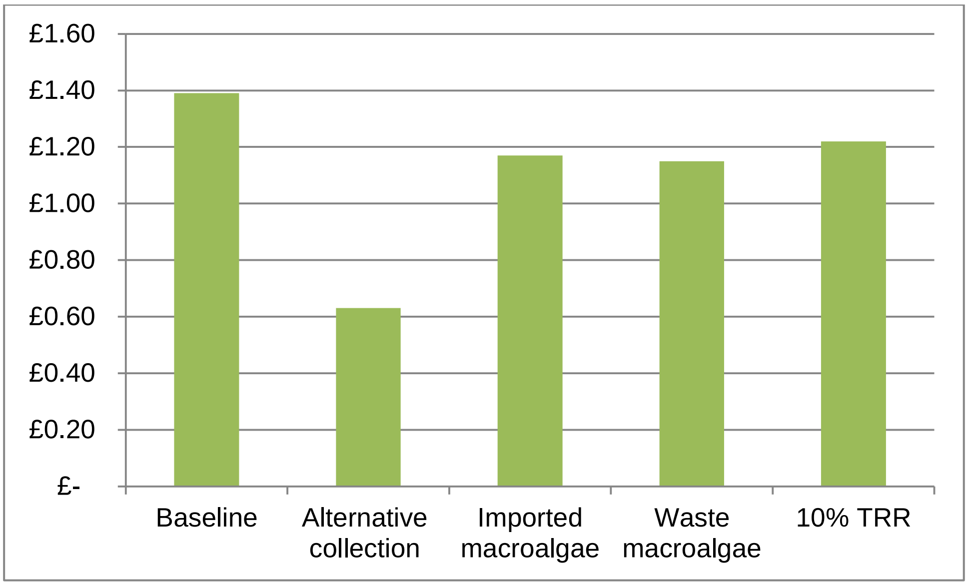

Figure 8.1: Scenario 5 sensitivity results summary

It is clear that utilising an alternative collection process is beneficial; generating the lowest electricity selling price, whilst setting a 10% TRR produces electricity at the highest price. There is also little difference in price between using imported or waste macroalgae.

Figure 8.2 presents the sensitivity selling price summaries for Scenario 6.

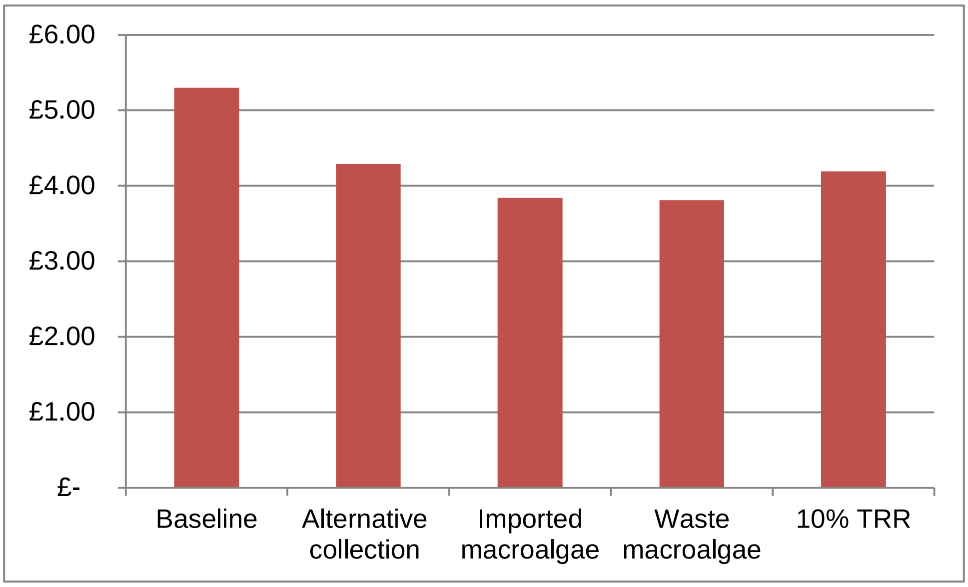

Figure 8.2: Scenario 6 sensitivity results summary

As shown, the utilisation of waste macroalgae is the most economically attractive option in terms of electricity selling price, followed by using imported macroalgae and setting a 10% TRR. Unlike Scenario 5, using an alternative collection process generates the highest price. In addition, the variation between the selling prices is not as great as Scenario 5. Again, this is due to the scale of production considered, which generates comparatively lower logistics costs since less mass is involved.

8.5.2 Evaluation of analysis

Implementing an alternative macroalgae collection process is the simplest physical improvement to make to the scenarios. This sensitivity has a greater influence on large-scale production, as shown with Scenario 5, generating the lowest electricity selling price (63 p/kWh).

Using imported or waste macroalgae also reduces the cost, though not as significantly as expected. For Scenario 5, the sensitivity is inhibited by the high logistical costs associated with transporting the feedstock, which accounts for ~88% of the operating costs due to the number of trips required to meet the system requirement. This is not the case for Scenario 6, since a single trip fulfils the requirement, resulting in the logistic costs accounting for less than 3% of the operating costs.

For both scenarios, using imported macroalgae is only 2 p/kWh more expensive than using waste macroalgae. In Asia, *Phaeophyceae* species are generally grown as monocultures to avoid high variability in quality and composition [93-95]. Since macroalgae is under investigation in order to guarantee a secure supply of biomass with maintained quality and suitability in the future, producing large quantities of macroalgae with minimal variation in quality and composition is extremely attractive.

The composition of alginate residue will vary with macroalgae species and age [132]. The composition of the residue will also vary with the type of alginate extraction process used. In addition, the composition of the waste macroalgae will vary as well as the supply; however, importing the waste from countries such as France, where the problem is great may provide a suitable feedstock. However, the species normally associated with green tides are *Chlorophyceae*, typically *Ulva*, which will affect the composition and production rate of the biogas, thereby affecting the electricity selling price. Considering this, it would be more appropriate to import a purpose grown feedstock, particularly for large-scale CHP production, although waste macroalgae may prove to be a suitable feedstock for small-scale, batch CHP production.

Setting a 10% TRR does reduce the electricity selling price and has a greater impact than utilising an imported feedstock. In general, Scenario 6 undergoes the largest reduction. However, operating under these conditions is not as economically attractive for the electricity producer, particularly at large-scale (Scenario 5) since the financial risk of undertaking this novel process is not compensated by a profitable IRR (20%). For Scenario 6, where a small-scale macroalgae system is used to produce supplementary electricity during winter, operating under such conditions may be more acceptable, especially if the system is treated as a back-up supply. In addition, the scale of operation under use may qualify for financial aid, such as the Renewable Heat Incentive (RHI) (non-domestic heat production) [255] or Renewable Obligations Certificates (ROCs) (dedicated biomass CHP) [189].

8.5.3 Financial viability

In this chapter, four sensitivity analyses are presented, all of which reduce the electricity selling price for both scenarios. Each sensitivity was treated as an individual assessment; however combining the adjusted operating conditions will generate the lowest achievable electricity selling price.

Table 8.8 presents the combined sensitivities and the generated electricity selling prices.

Table 8.8: Combined sensitivities and electricity selling prices

Scenario	5	6
Baseline electricity price (£/kWh)	1.39	5.30
Alternative collection process at 10% TRR (£/kWh)	0.44	3.13
Imported macroalgae at 10% TRR (£/kWh)	1.02	2.68
Waste macroalgae at 10% TRR (£kWh)	1.00	2.66

As shown, a minimum electricity selling price of 44 p/kWh is achievable, under reasonable conditions. Whilst this is considerably lower than the baseline price, it is still excessive in comparison to the acceptable price range.

In Chapter 7, two preliminary sensitivity analyses (±10% capital, ±50% logistics costs) were presented in order to determine the economic impact of operating under optimistic and pessimistic conditions. Table 8.9 presents the results of the combined sensitivities operating under optimistic conditions (-10% capital and -50% logistics costs).

Table 8.9: Combined sensitivities electricity prices (optimistic conditions)

Scenario	5	6
Baseline electricity price (£/kWh)	1.39	5.30
Alternative collection process at 10% TRR (optimistic) (£/kWh)	0.38	2.95
Imported macroalgae at 10% TRR (optimistic) (£/kWh)	0.72	2.53
Waste macroalgae at 10% TRR (optimistic) (£kWh)	0.57	2.51

As shown, a minimum electricity selling price of 38 p/kWh is achieved under optimistic conditions. This is a further reduction of ~14% in comparison to the minimum selling price under reasonable conditions, however the price is still higher than the acceptable price range.

Since Scenario 5 is clearly more economically attractive than Scenario 6, macroalgae marine biomass utilisation is more suitable as a large-scale offshore operation, particularly in conjunction with wind farm aquaculture, although the financial risk and expected variation in the selling price is greater.

Nevertheless, it is believed that the benefits of using harvested macroalgae are not realised at such a small-scale production, especially since Scenario 6 produces electricity at ~23% of the price the equivalent cultivation farm (Scenario 2). In order to fully evaluate the potential, a range of scales should be investigated.

In general, the calculated electricity selling prices are still higher than anticipated, even under optimistic conditions. Whilst the electricity selling price of both scenarios can be reduced by implementing the sensitivities described in this chapter, their overall impact does not improve the economic competitiveness of macroalgae CHP production.

8.5.4 Scenario performance

In Chapter 5, the area supplied by each scenario was estimated (Table 5.7) in order to determine the scale of operation.

Scenarios 1, 2 and 6 were treated as small-scale, local production systems (up to 72 houses) providing an additional source of power during winter to rural or isolated areas. Whilst electricity is sometimes imported from the urban areas or the mainland for islands, remote areas which are both "off-grid" and off the gas pipeline are heavily dependent on fuel oil and diesel for heating and local power generation [256, 257]. According to the Department for Environment, Food and Rural Affairs (DEFRA) [258], the cost of heavy fuel oil per household is ~£24 /week, which is equivalent to ~953 kWh/week at about 3 p/kWh [assuming a heavy oil average price of £25.19 /MWh [248]]. Since the average household consumes approximately 2,000 kWh electricity during winter [212] in addition to the 953 kWh/week, based on a heavy oil cost of 3 p/kWh, the winter energy consumption is ~£617 per household.

For Scenarios 1 and 2, which generated an electricity selling price of £26.77 /kWh and £19.96 /kWh, the winter electricity consumption alone will cost £53.54k and £39.9k respectively. These figures are clearly excessive in comparison to utilising fuel oil and it is doubtful that the use of ROCs or the RHI scheme will make a significant reduction should the scenarios qualify. Since rural areas are more vulnerable to "fuel poverty" than urban [258] Scenarios 1 and 2 would be met with strict opposition from the key stakeholders, particularly since CHP systems are normally used to reduce energy costs [189]. Scenario 6, which generates a minimum electricity selling price of £2.66 /kWh, is a comparative improvement to Scenarios 1 and 2 although the winter electricity consumption is still £5.3k. However, the use of either ROCs or the RHI scheme may have a positive impact on the system, particularly since the electricity selling price is ~90% lower than Scenario 1, though this cannot guarantee that the scenario would be financially attractive.

Scenarios 3, 4 and 7 were developed for continuous operation throughout the year, supplying heat and power to either municipal buildings or 2,000 to 6,000 homes. It is assumed that a district of this size would be connected to the National Grid; therefore, the scenarios would need to generate electricity at a competitive price in order to attract customers.

Assuming an annual consumption of 4,000 kWh, fossil fuel generated electricity costs about 14p/kWh (inc. VAT), whilst a standard green tariff starts at about 22 p/kWh, reducing to around 13 p/kWh after a specified number of kW_e have been consumed (in this case 720 kW_e) [259]. This results in an annual cost of £560/y on the fossil fuel tariff and ~£655/y using green energy. The three scenarios generate electricity at a selling price of £2.49 (Scenario 3), £2.07 (Scenario 4), £6.07 (Scenario 7), which will cost each household between £8.3k and £24.3k a year. Considering this, the consumer will undoubtedly decide to use another tariff.

Alternatively, rather than supplying the customer directly the scenarios may operate as a “feed-in” source to the Grid, as part of the RES. At present, certain government schemes, such as RHI, do not offer financial support for biomass CHP systems generating >1,000 kW_{th}, although the three scenarios may be eligible for ROCs.

Scenario 5 has the potential for industrial usage, providing either plants or industrial estates with power, particularly in coastal areas. According to the Department of Energy and Climate Change (DECC) [247], the manufacturing industry pay an average electricity price of 7.27 p/kWh (2009), though the actual price varies with scale. The lowest electricity price generated by Scenario 5 is 44 p/kWh (38 p/kWh optimistic), which is six times greater than the current tariff. However, with industry under legislative pressure to reduce carbon outputs and the potential to recoup losses via ROCs, there is some serious scope for utilising this scenario. In addition, since the electricity price is in pence as opposed to pounds, financial aid might be more forthcoming.

8.5.5 Project barriers and limitations

Several barriers have been identified during this study, which pertain to the macroalgae utilisation process.

8.5.5.1 Yield performance

The electricity prices calculated in this TEA are based on a specified macroalgae yield of 120 t/ha/y (wet), which corresponds with current cultivation capabilities (80-200 t/ha/y (wet) as described in §2.2.2.1). Since proposed yields range between 200 and 500 t/ha/y (wet) the use of 120 t/ha/y (wet) may be considered pessimistic.

8.5.5.2 Variation in feedstock composition

In this study, any variation in the feedstock composition is assumed to be negligible; however, in reality this is would not the case. Seasonal variation, in addition to the effect of the external factors described in Chapter 2, will have a significant impact on the quality and quantity of biogas produced. Although seasonal variation is believed to be less significant than experienced with terrestrial biomass [3], fluctuations in the electricity selling price should be expected.

This is also the case in the sensitivity analyses, where the composition of the macroalgae and the resultant biogas are assumed the same. This would definitely not be the case, particularly when utilising waste macroalgae, which normally consists of *Ulva sp*. In this case, a separate assessment on the utilisation of these species would be recommended.

8.5.5.3 Feedstock solid to water ratio

The high electricity selling prices are primarily due to the physical composition of the feedstock, which contains very little solid (~10 wt%), regardless of the species or growing conditions. In conjunction with the moderate anaerobic digestion solid conversion rate (59 wt% to 71 wt%), this produces a very low product-to-feedstock ratio, which in this study was calculated to be between 1:18.6 kg [biogas]/kg [macroalgae] and 1:22.3 kg [biogas]/kg [macroalgae]. The study has shown that large-scale production has the potential to compensate for this to some extent; although the electricity selling price is still excessive.

Though the high water content is attractive for anaerobic digestion, it presents additional problems in terms of the logistics. As shown Chapter 7, the cost of transporting the macroalgae from its source to the conversion plant has a significant impact on the operating costs and the resultant electricity selling price. In this chapter, the effect has been investigated further and although additional reductions have been made, the cost and effect of any fluctuations is still significant. Furthermore, there will be additional issues that will require consideration, such as providing suitable drainage facilities during transportation, especially to protect other cargo.

Finally, the solid/water ratio also affects the use of feedstock storage. In this study, macroalgae is stored as a slurry until required. This method of storage has yet to be fully investigated, however it was felt to be more suitable than drying, which increases the process energy demand considerably. In addition, due to the comparatively faster rate of degradation, and the subsequent problems with emitted gases, macroalgae cannot be stored in similar ways to terrestrial biomass.

8.5.5.4 Assumptions regarding macroalgae collection

A harvesting period of four months (June to September) has been assumed for all scenarios. This period is then used to calculate the logistics costs, assuming no loss of time due to external factors. However, whilst this period may guarantee suitable weather conditions for offshore activity, this period will be affected by storms as well as turbulent tidal conditions. Another factor will be the availability of crew, particularly in the wind farm aquaculture systems where certain activities may take priority over macroalgae harvesting.

The labour requirement for cultivation was adapted from various publications, which were scaled to represent the scale of production using an assumed workforce/ha rate. The actual labour used may differ from the figures used in this study since the requirement does not scale linearly.

8.5.5.5 Aquaculture synergy

Scenarios 3, 4 and 5 operate as part of a wind farm aquaculture system. In cost terms however, this is only represented by the cultivation site capital, which was from a wind farm specific reference. Aquaculture synergy (shared responsibility) may have a significant impact on operating costs such as maintenance and site leasing. Since data regarding the impact of this synergy is not yet available, the potential has not been fully realised.

8.5.5.6 Consistency of cost data

Whilst every effort has been made to use cost data specifically for macroalgae, in several cases, the costs presented represent a “best fit”, using data from equivalent biomass or aquaculture systems.

For instance, the cost data used for offshore longline macroalgae cultivation is adapted from offshore longline mussel cultivation [235]. Since the macroalgae process was derived from this type of mussel farming, the use of cost data is considered reasonable. The conversion plant TPC is adapted from various terrestrial biomass and municipal solid waste (MSW) fed systems, which, except for some minor variations in the pre-treatment processes, are reasonably representative of the proposed macroalgae systems. However, data for the transportation of macroalgae was not obtainable; therefore, the logistics costs were calculated using data from other aquaculture and terrestrial biomass systems. Since macroalgae have a high water content and a low bulk density, the costs, although calculated on a wet feed basis, may not be completely representative.

Where possible, data has been taken from either European or North American studies, which are more comparable with conditions in the UK, both physically and economically. However, in some cases data has been adapted from studies based in either Asia or South America, which are not as comparable. Although a location factor has been used to adjust the costs, like the process scaling equation presented in §4.3.2 this method of adjustment is primarily for chemical plants and may not be representative of a cultivation farm, especially since it has not been calculated to consider the effect of the level of process establishment and environmental conditions.

8.5.5.7 Availability of comparable data

As shown in Chapters 3 and 5 there is a lack of comparable data in which to determine whether the outcomes of this study are economically attractive. Whilst several of the papers reviewed in Chapter 3 estimate a product selling price based on previous work and published data, these figures are either not explained fully or include omissions, as shown in §7.5.4, which have a significant impact on the validity of the price.

In addition, many of the investigations into the conversion of macroalgae have yet to move beyond pilot scale. At present a 1 tpd macroalgae anaerobic digestion system is in operation in Japan [44], however the biogas supplements a city gas (natural gas based) CHP system, therefore any negative economic impact is compensated by the use of co-firing.

A significant barrier encountered in this study was the availability of data for the secondary macroalgae utilisation processes, such as transportation and storage. Previous work has concentrated on growth and/or conversion, presenting the intermediate stages as black box systems. This has led to the inclusion of several unsupported assumptions and the use of alternative cost data, as discussed in §8.5.3.4.

8.5.5.8 Alternative conversion technology

Although the operating costs are dominated by the production and collection of the feedstock, the TPC of the conversion plant accounts for 59% (Scenario 5) and 84% (Scenario 6) of the capital costs.

As discussed in Chapter 6, the systems presented in this study operate under Low Solid Digestion conditions (solid content of ≤10 wt% TS [135]), which is appropriate for the low solid content of the feedstock. Operating under Medium Solid Digestion (15-20 wt% TS) or High Solid Digestion (22-40 wt% TS) conditions [135] will reduce the start-up water requirement, however since the total water demand of the system only accounts for <0.1% of the operating costs, the impact on the electricity selling price would be negligible. In addition, to operate under dryer conditions may require the implementation of drying technology, which will increase both the energy demand and the TPC of the systems, both of which will have a negative impact on the electricity selling price, particularly since the biogas production rate will remain unchanged.

For Scenario 6, the biogas production rate may be improved by replacing the single stage digestion system with a multiple stage system, which can increase production by ~20%. However, the biogas will still only represent ~6 wt% of the digester(s) output, as determined in Chapter 6, which would not compensate for the larger TPC associated with the multiple stage systems, resulting in a potential negative impact on the electricity selling price.

In Chapter 5, a selection of conversion technologies were discussed and evaluated. Although anaerobic digestion was considered the most suitable technology at present (availability of real data, level of current establishment), the remaining technologies still have potential in the near future. Combustion, dry and wet gasification, fast pyrolysis and liquefaction all performed better in the preliminary energy balance than anaerobic digestion for CHP production. From these technologies wet gasification and liquefaction both tolerate “wet” feedstocks (>50 wt% wet). However, it is very unlikely that the electricity selling price would be more cost competitive than anaerobic digestion due to the increase in energy demand [5] and the potentially higher TPC, particularly since both technologies operate at elevated pressure.

Therefore, it can be assumed that a standalone macroalgae-based CHP system is not as economically attractive as the terrestrial biomass or fossil fuel equivalent. This leaves two alternative routes to take for macroalgae utilisation; CHP production as part of a biorefinery concept or the production of a different end-product.

As shown in Chapter 6, anaerobic digestion can leave up to 41 wt% VS as unconverted digestate. In this study, the digestate is sold to provide additional revenue, however it could be used for the production of additional bioenergy products as part of a biorefinery concept, which uses multiple technologies to maximise the value of the feedstock through the production of multiple end-products. Alternatively, the use of a biorefinery concept to manufacture both bioenergy and non-bioenergy products, as suggested by Beavis et al. [88]; Bruton et al. [128] and Reith et al. [116], has great potential, especially if bioenergy is produced in conjunction with high-value goods such as cosmetics.

A range of end-products can be manufactured by the conversion technologies discussed in Chapter 5. In particular, fermentation (ethanol), liquefaction and wet gasification all tolerate “wet” feedstocks, which may be more suitable for macroalgae utilisation than dry gasification and pyrolysis. The selection of the most suitable product however, will be based on the cost of production, the product selling price and the market demand. The results generated from this study suggest that the manufacture of specialist products would be more suitable for macroalgae utilisation than the production of commodities.

9 Conclusions and recommendations (marine)

9.1 Review of the study

9.1.1 Objectives of the study

The primary objective of this study was to investigate the potential of utilising macroalgae as a source of marine bioenergy in the UK. This was achieved by completing the following tasks:

- The evaluation of a range of potential scenarios to identify the most suitable scale of production for the UK
- The selection of the most suitable biomass conversion technology for macroalgae, which in this study was anaerobic digestion CHP production by evaluating current biomass to energy (CHP) routes
- The identification of the most promising scenario systems based on the calculation of the lowest achievable electricity selling price
- Assessment of the economic suitability and identification of the most favourable conditions
- The identification of current boundaries for macroalgae utilisation in the UK

9.1.2 Structure

A review of relevant literature sources was carried out to provide a background document on macroalgae, describing its chemical and physical composition, as well as other characteristics such as species, environment and growth habits. In addition, the current market environment was also established in order to put the results of this study into context.

In Chapter 3, a detailed literature review of previous techno-economic assessments regarding macroalgae for bioenergy was completed. This identified the scale of production and range of technologies under consideration, the assessment methods used, the limitations of previous work and the subjects where a general agreement had been reached. These findings were then used in Chapter 4 to refine the scope of this study and select an appropriate methodology.

An evaluation of potential conversion technology was completed in Chapter 5, which concentrated on the production of CHP using a combustion engine. The expected biogas and CHP outputs of each scenario were then estimated. A detailed assessment of the macroalgae production and conversion systems technical performance was carried out and reported in Chapter 6. Estimations of the thermal energy and electrical power requirements of the sub-systems were also made in this chapter.

The capital and operating costs of the sub-systems were investigated in Chapter 7. The capital costs of feedstock procurement were calculated using data for various inshore and offshore cultivation farms. Discounts were applied to the relevant materials and installation costs for scaling purposes. The conversion plant capital was adapted from equivalent terrestrial biomass systems. Land and indirect costs were also included.

The operating costs were divided into materials, labour, maintenance, water leasing and permission and other fixed costs, which were derived from marine and non-marine biomass systems. Additional revenue from the sale of digestate and district heat was also calculated. Finally, the electricity selling price at the TRR (20%) was also calculated for the seven scenarios.

In Chapter 8, a series of process improvements were investigated for Scenarios 5 and 6 in order to reduce the electricity selling price. These improvements were:

- Implementing an alternative feedstock collection process
- The use of imported macroalgae
- The use of waste macroalgae and macroalgae residues
- Setting a lower TRR of 10%

9.2 Conclusions

9.2.1 Macroalgae scenarios

Seven scenarios were compiled to assess the potential of utilising macroalgae as a source of marine biomass in the UK. These were:

- Scenario 1: 15 ha inshore cultivation network (5 3 ha farms)
- Scenario 2: 36 ha inshore cultivation network (12 3 ha farms)
- Scenario 3:1,000 ha offshore cultivation farm (wind farm aquaculture system)
- Scenario 4: 3,000 ha offshore cultivation farm (wind farm aquaculture system)
- Scenario 5: 24,500 ha offshore cultivation farm (wind farm aquaculture system)
- Scenario 6: Harvesting from standing stock (output equivalent to Scenario 2)
- Scenario 7: 1,000 ha standalone offshore farm

Scenarios 1 and 2 were based on information from project partners concerning the realistic potential of inshore cultivation within the UK. Scenarios 3, 4 and 5 were derived from data regarding current and near-future UK wind farm systems. Scenario 6 was created to compare the use of cultivation and natural stock harvesting, whilst Scenario 7 investigated the effect of unsheltered offshore farming. Table 9.1 presents the estimated macroalgae outputs.

Table 9.1: Estimated scenario macroalgae outputs

Scenario	Farm size	Macroalgae yield (wet)
	Ha	kt/y
1	15	2
2	36	4
3	1,000	120
4	3,000	360
5	24,500	3,048
6	-	4
7	1,000	120

The following sections summarise the principle findings for the seven scenarios.

9.2.2 Lowest cost of electricity generation

The electricity selling prices calculated for the seven scenarios are presented in Table 9.2 and include the results from the capital and feedstock logistics sensitivities.

Table 9.2: Scenario electricity selling prices

Scenario	1	2	3	4	5	6	7
Calculated electricity price (£/kWh)	26.77	19.96	2.49	2.07	1.39	5.30	6.07
Electricity price (£/kWh) (-10% capital)	25.31	17.87	2.37	1.98	1.36	5.08	5.61
Electricity price (£/kWh) (+10% capital)	30.89	22.06	2.64	2.19	1.46	5.57	6.53
Electricity price (£/kWh) (-50% logistics cost)	26.12	19.31	2.08	1.66	0.99	4.74	5.66
Electricity price (£/kWh) (+50% logistics cost)	27.43	20.62	2.93	2.51	1.83	5.90	6.47

The lowest electricity selling price was generated by Scenario 5, which was a 24,500 ha offshore cultivation farm producing 29,987 kW$_e$ electricity at a selling price of £1.39 /kWh (99 p/kWh optimistic).

Further reductions in price were made to Scenarios 5 and 6 by implementing the process improvements listed in §9.1.2, as shown in Table 9.3.

Table 9.3: Process improvement electricity prices

Scenario	5	6
Baseline electricity price (£/kWh)	1.39	5.30
Alternative collection process (£/kWh)	0.63	4.29
Imported macroalgae (£/kWh)	1.17	3.84
Waste macroalgae (£/kWh)	1.15	3.81
10% TRR (£/kWh)	1.22	4.19
Alternative collection process at 10% TRR (optimistic) (£/kWh)	0.44 (0.38)	3.13 (2.95)
Imported macroalgae at 10% TRR (optimistic) (£/kWh)	1.02 (0.72)	2.68 (2.53)
Waste macroalgae at 10% TRR (optimistic) (£kWh)	1.00 (0.57)	2.66 (2.51)

As shown, the lowest electricity selling price in this study was generated by Scenario 5, which produced electricity at 44 p/kWh (10% TRR, alternative collection) under reasonable conditions (38 p/kWh under optimistic conditions).

9.2.3 Financial viability

None of the scenarios generated electricity within the acceptable price range (up to 14 p/kWh). In addition, the cost of electricity from macroalgae was excessive in comparison to published data, although the price varied with scale and operating conditions. For all scenarios, it was determined that the costs associated with feedstock procurement, had the greatest impact on the electricity selling price.

In Chapter 5 (§5.2.3), the scenarios were categorised in terms of the level of distribution (number of households) expected based on the scale of electricity production. In Chapter 8, the scenarios were then compared to the current electricity production processes used.

Scenarios 1, 2 and 6 were treated as small-scale, local production systems (up to 72 houses) providing additional power during winter to rural, non-grid areas. In comparison to fuel oil, the primary source of heat and power, all three scenarios generated excessive winter electricity costs per household, which ranged from 5.3k (Scenario 6) to 53k (Scenario 1) (39.9k Scenario 2), in comparison to the estimated equivalent fossil fuel cost of ~£617 per household.

For Scenarios 1 and 2 it is doubtful that the use of ROCs or the RHI scheme will make a significant reduction should the scenarios qualify. Scenario 6 is a comparative improvement to Scenarios 1 and 2 although the winter electricity cost is still high. The use of either ROCs or the RHI scheme may reduce the production cost, although this cannot guarantee that the scenario would be financially attractive.

Scenarios 3, 4 and 7 were developed for continuous operation throughout the year, supplying heat and power either to municipal buildings or up to 6,000 homes. Since a district of this size would normally be connected to the National Grid, the scenarios need to generate electricity at a competitive price.

Using available tariff data, the annual electricity cost per household was estimated at £560/y for fossil fuels and ~£655/y using green energy. The equivalent electricity cost for the three scenarios was calculated as between £8.3k and £24.3k a year. Considering this, the consumer would undoubtedly decide to use a cheaper fossil fuel or green tariff. Alternatively, the scenarios may operate as a “feed-in” source to the Grid, as part of the RES, especially since the three scenarios may be eligible for ROCs.

Scenario 5 has the potential for industrial usage, providing either plants or industrial estates with power, particularly in coastal areas. The lowest electricity price generated by Scenario 5 is 44 p/kWh (38 p/kWh optimistic), is six times greater than the current tariff (~7-8 p/kWh). However, with industry under legislative pressure to reduce carbon outputs and the potential to recoup losses via ROCs, there is some serious scope for utilising this scenario.

Although the electricity selling price still requires further reduction, Scenarios 5 and 6 were identified as the most promising systems, producing the lowest cost electricity at large- and small-scale respectively. However, Scenarios 3 and 4 also have potential, generating the second and third lowest electricity prices overall. It is clear that large-scale offshore cultivation, particularly as part of an aquaculture system is the most economically attractive route for the UK, provided the systems achieve their projected production rates. Further investigation into co-operative aquaculture systems, in particular the use of offshore transportation may also be beneficial.

At present, CHP from macroalgae in the UK is not an economically attractive source of bioenergy. Implementing large-scale macroalgae production will have a positive impact on the generated electricity prices, provided the proposed production rates are achieved. However, the CHP products need to be relatively competitive without government help [255], which is not possible under current operating conditions.

9.2.4 Additional revenue

In Chapter 3, the literature under review suggests that additional revenue is required in order to make macroalgae an attractive source of marine biomass. For the seven scenarios, the additional revenue generated from the sale of digestate and district heat has a positive effect; however, it does not have a significant impact on the overall electricity selling price.

9.2.5 Sensitivities of the electricity selling price

Implementing an alternative macroalgae collection process was determined as the simplest physical improvement, which had greater influence on large-scale production. The use of imported or waste macroalgae also reduces the cost, though not as significantly as expected, primarily due to the high logistical costs involved (Scenario 5). For both scenarios, the use of imported macroalgae was considered more attractive due to the higher quality of feedstock produced, which generated electricity at only 2 p/kWh more than the waste equivalent.

Setting a 10% TRR also reduces the electricity selling price, having a greater impact on Scenario 6. Since this scenario operates either to supplement an existing electricity system or to provide “off-grid” areas, operating under such conditions is more acceptable, particularly if it qualifies for financial aid.

Combining the above sensitivities generated a minimum electricity selling price of 44 p/kWh under reasonable conditions and 38 p/kWh under optimistic conditions; however the prices were still higher than the acceptable price range (up to 14 p/kWh).

9.2.6 Distribution of costs

For Scenarios 1, 2 and 7, feedstock procurement (including additional capital) accounts for 83-84% of the total project capital. For Scenarios 3, 4, 5 and 6 the cost of the anaerobic digestion and CHP plant is the largest investment, due to the scale of operation.

In terms of operating costs, Scenarios 3, 4, 5, 6 and 7 are dominated by the logistics costs associated with the macroalgae feedstock. For Scenarios 1 and 2, the largest operating cost is maintenance (44% of the total cost).

9.2.7 Impact of scale

Although different methods of calculation have been used, as the scale of production increases, the electricity selling price of the scenarios decreases.

9.2.8 Process selection and modelling

In Chapter 5, eight technologies were identified for the conversion of macroalgae to power via a CHP engine, these were:

- Anaerobic digestion
- Fermentation (ethanol)
- Combustion
- Dry gasification
- Wet gasification (hydrothermal or SCWG)
- Liquefaction
- Fast pyrolysis
- Intermediate pyrolysis

Each technology was assessed based on a criterion in order to determine the most suitable technology. In this study, anaerobic digestion was determined to be the most suitable technology. It is easily the most technically established route for marine biomass and operates at a range of scales. The pre-treatment and conversion processes are relatively simple, which is technically attractive for the use of a novel feedstock and the absence of heavy drying duty enhance the overall efficiency to CHP.

The scenarios were modelled using two types of anaerobic digestion process, depending on the scale of macroalgae production. It was determined that all scenarios produced enough thermal energy and electricity to sustain the conversion plant. The biogas and electrical outputs calculated were compared to the predicted data in Chapter 5, which determined that the scenario systems were operating at or above the expected level.

9.3 Barriers and limitations

As discussed in Chapter 8, several project barriers and limitations have been identified regarding the utilisation of macroalgae as marine biomass.

9.3.1 Yield performance

The TEA uses a specified macroalgae yield of 120 t/ha/y (wet). Since proposed yields range between 200 and 500 t/ha/y (wet) the use of 120 t/ha/y (wet) may be considered pessimistic.

9.3.2 Variation in feedstock composition

In this study, any variation in the feedstock composition was ignored. However, compositional variation, seasonal or environmental will have a significant impact on the quality and quantity of biogas produced. This means that fluctuations in the electricity selling price should be expected.

9.3.3 Feedstock solid to water ratio

Macroalgae contain very little solids (~10 wt%), regardless of the species or growing conditions, which in conjunction with the moderate anaerobic digestion solid conversion rate (59 wt% to 71 wt%) produces a very low product-to-feedstock ratio, resulting in excessive electricity prices. Large-scale production only compensates for this to some extent. The high water presents additional problems in terms of the logistics costs, which have a significant impact on the operating costs and the resultant electricity selling price. Whilst further investigations and additional reductions have been made, the cost and effect of any variations in the capital and operating costs are still significant.

In addition, the solid/water ratio also affects the choice of feedstock storage. Standard drying practises are not suitable for macroalgae since they increase the process energy demand considerably. Outdoor storage is also considered unsuitable due to the comparatively faster rate of degradation, and the subsequent problems with emitted gases. In this study, macroalgae is stored as a slurry, however, this method of storage has yet to be fully investigated.

9.3.4 Assumptions regarding macroalgae collection

A harvesting period of four months is assumed for all scenarios, which is then used to calculate the logistics costs, assuming no loss of time due to external factors. However, this period will be subject to external factors, such as storms and the availability of crew.

The labour requirement for cultivation was estimated from various publications, which were scaled using an assumed workforce/ha rate. Since the requirement does not scale linearly, the actual labour demand may differ.

9.3.5 Aquaculture synergy

Scenarios 3, 4 and 5 operate as part of a wind farm aquaculture system, although the costs are not directly representative. Since data regarding the aquaculture synergy is not yet available, the potential has not been fully realised.

9.3.6 Consistency of cost data

Whilst every effort has been made to use cost data specifically for macroalgae, in several cases, the costs presented represent a “best fit”, using data from equivalent biomass or aquaculture systems.

This is the case for offshore longline macroalgae cultivation, which is adapted from offshore longline mussel cultivation. However, the macroalgae process was derived from this type of mussel farming, therefore the cost data is considered reasonable. The conversion plant TPC is adapted from various terrestrial biomass and MSW fed systems, which are believed to be reasonably representative of the proposed macroalgae systems.

Data for the transportation of macroalgae was not obtainable; resulting in the logistics costs being estimated using data from other aquaculture and terrestrial biomass systems. Although the costs are calculated on a wet feed basis, they may not be completely representative of macroalgae.

Where possible, European or North American studies have been used since these are more comparable with conditions in the UK, both physically and economically. However, in some cases data has been adapted from studies based in either Asia or South America, which are not as comparable. Although a location factor has been for adjustment this method is for chemical plants, and does not consider the factors pertaining to a cultivation farm and may therefore not be representative.

9.3.7 Consistency of cost data

Whilst every effort has been made to use cost data specifically for macroalgae, in several cases, the costs presented represent a “best fit”, using data from equivalent biomass or aquaculture systems.

This is the case for offshore longline macroalgae cultivation, which is adapted from offshore longline mussel cultivation. However, the macroalgae process was derived from this type of mussel farming, therefore the cost data is considered reasonable. The conversion plant TPC is adapted from various terrestrial biomass and MSW fed systems, which are believed to be reasonably representative of the proposed macroalgae systems.

Data for the transportation of macroalgae was not obtainable; resulting in the logistics costs being estimated using data from other aquaculture and terrestrial biomass systems. Although the costs are calculated on a wet feed basis, they may not be completely representative of macroalgae.

Where possible, European or North American studies have been used since these are more comparable with conditions in the UK, both physically and economically. However, in some cases data has been adapted from studies based in either Asia or South America, which are not as comparable. Although a location factor has been for adjustment this method is for chemical plants, and does not consider the factors pertaining to a cultivation farm and may therefore not be representative.

9.3.8 Selection of conversion technology

There is sufficient information available in literature to model the anaerobic digestion of various macroalgae species with reasonable accuracy. However, this is not the case for the remaining seven technologies, where data from equivalent terrestrial biomass systems is required for conversion rates, which affects the accuracy of the study.

9.3.9 Availability of comparable data

There is a general lack of good quality data from other studies against which to assess and validate the results presented here. What data exist is either not explained fully or include omissions, which have a significant impact on the validity of the price. Many of the published investigations have also yet to move beyond pilot scale.

This study determined that a significant barrier is the availability of data for the secondary macroalgae utilisation processes, such as transportation and storage. This has led to the inclusion of several unsupported assumptions and the use of alternative cost data.

9.4 Recommendations for future work

9.4.1 Yield sensitivity work

The electricity prices are based on a macroalgae yield of 120 t/ha/y (wet). Since there is a range of proposed yield data, an assessment measuring the effect of increased production is required to evaluate the impact on the electricity selling price, in addition to any variations in the quality of the feedstock and biogas product.

9.4.2 Feedstock trials for macroalgae litter

The cultivated macroalgae considered in this study is a combination of various *Phaeophyceae* species, used as a “litter”. Utilising multiple species of macroalgae will result in variations in the composition of the litter, which will have a significant impact on the performance conversion plant and the electricity selling price. Therefore, investigations into the level of variation expected and its effect are needed to confirm that the feedstock is suitable.

9.4.3 Harvesting and storage possibilities

In this study, macroalgae are harvested annually and stored as slurry until required. However, this method of storage has yet to be investigated fully; therefore, its effect on the chemical composition of the slurry is not known. Alternatively, macroalgae may be harvested at multiple intervals throughout the year and placed into short-term storage. In order to assess which method is most suitable, trials are required to investigate the impact of harvesting and storage on the feedstock, in particular considering changes in the feedstock composition and its impact on electricity production and selling price.

9.4.4 Offshore cultivation trials

Whilst several small-scale trials have been performed, offshore cultivation, especially wind farm based has yet to be fully tested. Trials are needed in order to demonstrate large-scale offshore macroalgae cultivation and to determine realistic production rates based on actual performance.

9.4.5 Economies of scale

In this study, discounts representing the effect of scale were derived from data published by Lenstra et al. [109] for materials and installation costs of macroalgae cultivation. Whilst every effort was made to represent the effect of scale reasonably, more information is required in order to measure the effect of variable such as different cultivation technologies, and the use of inshore or offshore cultivation.

9.4.6 Large-scale harvesting in the UK

Harvesting from natural stock was only investigated at small-scale (<5,000 t/y (wet)) during this project. Whilst the generated electricity selling price was considerably higher in comparison to large-scale offshore cultivation, harvesting performed far better than the equivalent scale of cultivation. Therefore, trials into larger scale harvesting are needed as it is felt that the process has yet to be fully realised.

9.4.7 Economics of aquaculture systems

Whilst the offshore wind farm scenarios were assumed part of an aquaculture system, the full extent of this was not fully realised in terms of economics. Investigations into the level of co-operation and the expected economic benefits are required in order to increase the economic potential of offshore aquaculture processes.

9.4.8 Alternative conversion technology and biorefinery potential

In this study, anaerobic digestion to CHP production was considered the most suitable technology for macroalgae marine biomass. However, the electricity selling prices generated by the seven scenarios were not competitive. Therefore, further research is required regarding the remaining seven conversion technologies outlined in Chapter 5 to determine whether macroalgae are more suitable for the manufacture of alternative products. In addition, the concept of a marine biorefinery needs investigation to establish its realistic potential.

9.4.9 Alginate residue

The potential of alginate residue as a biomass feedstock is generally well received; however, data regarding the available mass and subsequent composition has to be published. Investigations into the properties and availability of this residue are needed to determine its suitability as a biomass feedstock.

9.4.10 Biomethane injection

Since the electricity selling prices generated in this study are excessive, the potential of biomethane injection into the grid should be considered, particularly since this process qualifies for Governmental aid under the RHI scheme [255].

10 Background (ammonia)

10.1 Ammonia

Ammonia (NH_3) is a colourless, pungent gas, which is the most stable combination of H_2 and N_2 and is often used as a building block for chemical synthesis [260]. It is used as nitrogenous fertiliser in forms such as anhydrous ammonia, ammonium nitrate and urea, which accounts for 80% of ammonia usage. In addition to this ammonia is also a raw material for the production of explosives, nitric acid, polymeric resins and plastics, fibres and is also used as a refrigerant [261, 262].

10.1.1 Production processes

Currently, over 90% of ammonia worldwide is produced from steam reforming of natural gas, or naphtha (India) [176]. Steam methane reforming (SMR) of hydrocarbons has been in operation since 1930 [263]. Gasification of coal or heavy oil accounts for residual production [176]. The scale of ammonia production is typically between 1,000-2,000 tpd. Larger plants are expected in the future, with new builds now designed for up to 2,200 tpd [176, 262].

10.1.1.1 Natural gas production

The production of ammonia from natural gas is completed in six process stages; desulphurisation, SMR, water gas shift (WGS), CO_2 removal, methanation and ammonia synthesis (Haber Bosch). The initial five stages condition the gas, converting or removing CO, CO_2 and H_2S, which are poisonous to the synthesis catalysts [10]. The conditioning stages operate at pressures of 25-35 bar [264, 265], whilst the synthesis stage normally operates in the region of 100-250 bar [176, 264].

Elevated pressures are used for several reasons, these are:

- The volume of feed gas increases by 100% during SMR. It is therefore more economically attractive to work at pressure, reducing equipment size requirements [265].
- The natural gas feed does not need to undergo decompression before use. In the UK natural gas pipelines operate at up to 85 bar though higher pressure systems are in development [266].
- Carbon oxide removal stages operate more efficiently under higher pressure [265].
- The loading on the final compression stage, prior to ammonia synthesis is reduced [267].

- High-pressure steam can be produced, which is a valuable commodity [265].
- Smaller volumes of catalyst are required as well as less refrigeration [176, 265-267].

The following sections discuss the process stages.

10.1.1.1.1 Desulphurisation

Natural gas contains sulphur or sulphur compounds, which are known to poison process catalysts, specifically those containing nickel. Catalyst poisoning allows carbon to deposit on the bed, causing irreversible damage, reducing the life of the catalyst [265].

The gas is heated to 350-400°C and fed into a desulphurisation vessel, which dehydrogenates the sulphur compounds into H_2S with the use of a cobalt molybdenum catalyst. The H_2S is then adsorbed by a pelletised zinc oxide bed.The overall process is expressed as:

$$R\text{-}SH + H_2 \rightarrow H_2S + RH \tag{10.1}$$

$$H_2S + ZnO \rightarrow ZnS + H_2O \tag{10.2}$$

The *R-SH* are mercaptans, which are used as an odorant in natural gas. This method of desulphurisation can reduce the sulphur content of the syngas to less than 0.1 ppm [264].

If the sulphur compounds are already in the form of H_2S dehydrogenation is not required. Instead, the gas is heated to 400°C and reacted with zinc oxide [10], resulting in the following reaction:

$$ZnO + H_2S \rightarrow ZnS + H_2O \tag{10.3}$$

This method is known as high temperature zinc oxide absorption. The level of sulphur absorbed is up to 18-20 wt%, which limits the process to low sulphur feeds. The zinc oxide bed is replaced once a year.

An alternative method is adsorption on activated carbon at ambient temperatures. Like zinc oxide this method is only suitable for low sulphur levels. However, problems such as the release of chlorine and reduction in sulphur capacity due to the sorption of higher hydrocarbons have been noted [265]. Other methods of sulphur removal are based on acid gas treatment, which involves the use of a solvent and scrubber. This process is normally completed during the CO_2 removal stage [176, 265 & 267].

Desulphurisation can be performed at a number of stages throughout the ammonia production process, depending on the choice of process catalysts. Originally, the process was implemented after WGS and prior to ammonia synthesis since the presence of H_2S did not harm the catalysts [267]. However, the introduction of nickel-based catalysts for both steam reforming and water gas shift provided limitations to this flexibility.

10.1.1.1.2 Steam methane reforming (SMR)

Natural gas is predominantly composed of methane, which is a valuable source of H_2. The purpose of SMR is to convert the methane into H_2 and CO. This is performed in two stages known as primary and secondary reforming [264, 265].

The sulphur-free feed gas is mixed with steam to increase the stream temperature to 500-600°C. This stream is then fed into the primary reformer, which contains a nickel-based catalyst [264]. The process is highly endothermic; therefore, natural gas is combusted to provide the heat required to raise the gas temperature to 780-830°C.

This process reforms approximately 30-40% of the feed and is controlled by the following reversible reactions:

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO \qquad (10.4)$$

$$CH_4 + H_2O \leftrightarrow H_2 + CO \qquad (10.5)$$

Reaction (10.4) is the most desirable for the process [264]. The temperature of the system ensures that the reactions are not allowed to reverse [10]. Nickel based catalysts, typically nickel-chromium [264, 265], are preferable for this process; however the process can be performed without the use of catalyst, though the operating temperature increases to 1300°C [267].

The secondary reformer completed the conversion process by raising the temperature of the gas. This is done by combusting part of the feed gas with air, causing the following reaction:

$$2O_2 + CH_4 \leftrightarrow 2H_2O + CO_2 \qquad (10.6)$$

This also provides the correct ratio of H_2 and N_2 for the final synthesis stage [10]. The air is compressed to the process pressure and heated to approximately 600°C prior to use. The secondary reformer also requires a nickel based catalyst, normally $Ni\text{-}CaO\text{-}Al_2O_3$ [265].

The outlet temperature of the gas is approximately 1000°C and contains 0.2-0.3 vol% (dry gas base) CH_4 [264]. Process economics dictate that several percent of CH_4 should be left in the gas after the reforming process to enable the methanation stage to be successful [265]. The gas leaving the secondary reformer is known as the synthesis gas [10] and is cooled to 350-400°C, allowing heat to be recouped for producing superheated steam [264].

10.1.1.1.3 Water gas shift (WGS)

CO retains H_2 and poisons the ammonia synthesis catalyst [265]; consequently, it must be removed. The water gas shift process converts CO into H_2 and CO_2 in the presence of H_2O using the following reaction [264]:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (10.7)$$

This is the Bosch reaction, which is exothermic and uses catalysts to promote the reaction at lower temperatures [267].

This reaction does not however remove all CO present, resulting in the need to implement methanation downstream. Residual levels of CO must be kept as small as possible for two reasons. Firstly, it is important for the process efficiency [264], but most importantly, it reduces the amount of H_2 used during the methanation process. CO levels of 0.7 vol% (dry gas) and more are considered to be too high [265]. Presently the shift reactions are able to reduce CO levels to 0.2-0.4 vol% (dry gas) [264].

Presently water gas shift is completed using the high and low temperature shift reactors in conjunction [263]. The high temperature shift reactor (HTS) operates at 400°C over a bed of iron oxide (Fe_2O_3) catalyst with a chromium oxide promoter and reduces the CO level to about 3 vol% (dry gas) [264]. The catalyst mix contains approximately 55 wt% Fe and 6 wt% Cr [265]. Copper catalysts can also be used to increase conversion [264], though iron oxide is more commonly used due to its high resistance, which tolerates up to 200ppm of H_2S without significant loss of catalyst activity [265].

The gas is cooled and waste heat recovered before the gas enters the low temperature shift (LTS) reactor [264]. The LTS operates at 200-220°C over a copper oxide/zinc oxide bed ($\geq$ 37 wt% ZnO, $\geq$ 37 wt% CuO) though Al_2O3 is often added (to balance wt%) [264, 268]. The low temperature reaction is more sensitive to poisoning from sulphur and chlorine than the high temperature reaction. It is also less reliable in terms of operation, though catalyst behaviour is improved at elevated pressures [265]. This process reduces the CO level 0.2-0.4 vol%. The syngas now mainly comprises of H_2, N_2, CO_2 and excess process steam. The gas is cooled, condensing most of the steam [264].

10.1.1.1.4 CO_2 removal

In general natural gas SMR systems produce approximately 1.22 t[CO_2]/t[NH_3] [265]. The CO_2 is removed via chemical or physical adsorption methods such as scrubbing [264] and is commonly used to manufacture urea in on-site facilities [176].

Chemical adsorption is often performed using solutions such as monoethanolamine (MEA), activated methyl diethanolamine (aMDEA) or hot potassium carbonate. Physical adsorption uses solvents such as propylene carbonate and glycol dimethylethers (Selexol). MEA scrubbing is typically the standard CO_2 removal process, though alternative technology is being investigated due to the high energy demand of MEA regeneration [264].

Pressure Swing Adsorption (PSA) and molecular sieves can also be used. PSA systems adsorb at high pressure (15-30 bar) and desorb at low pressure. This process is not limited to CO_2 removal and can be used to purify or separate substances such as H_2. Molecular sieves operate in the same way as conventional sieves, only on a far smaller scale. They are mainly used to remove CO_2 and water [176].

10.1.1.1.5 Methanation

The residual amounts of CO and CO_2 present in the gas poison the synthesis catalysts; therefore, they are converted to CH_4 and H_2O via methanation at 300°C. CH_4 is considered an inert in the synthesis process and is not removed. The water is normally condensed and removed before the gas enters the synthesis system [264].

The conditioned gas is then compressed from 25-35 bar to 100-250 bar [176, 264]. The choice of operating pressure has little effect on the energy demand of the process in the region of 130-180 bar [176].

10.1.1.1.6 Ammonia synthesis (Haber Bosch)

The Haber Bosch process operates at high pressure (100-250 bar [176, 264]) over a catalyst. N_2 and H_2 are converted to ammonia through the following reaction:

$$N_2 + 3H_2 \leftrightarrow 2NH_3 \qquad (10.8)$$

This reaction is reversible, though the reversal occurs only under increased temperature conditions [267].

The catalysts used are predominantly iron oxides, though some processes are now utilising other materials such as ruthenium and magnetite [176, 263]. Magnetite catalysts operate between 130-150 bar whilst ruthenium based catalysts operate at 90 bar [176]. The system has a minimum working temperature of 350-400°C since the catalyst will not function below this range. The initial process heat is supplied by external sources, however once the synthesis reaction begins heat is recovered from the gases leaving the catalyst and utilised [267].

The gas leaves the reactor via a purge stream at 100-200°C and has an initial ammonia content of 10-20% [267]. The ammonia is removed from the purge by scrubbing with water whilst the remaining gas is returned to the synthesis reactor via a recycle loop [264]. The overall conversion efficiency of the synthesis loop system is up to 98% [269]. The ammonia product, known as anhydrous ammonia, is then vaporised, compressed and liquefied for refrigerated storage [264].

10.1.1.2 Heavy oil partial oxidation

This process is used as an alternative to SMR and allows the use of feedstocks such as heavy fuel oils and coal, which choke reformer catalysts [264, 267]. This method does require air separation technology, which means that N_2 must be added further downstream in the process, often as a liquid wash to remove syngas impurities [264].

Partial oxidation combusts part of the syngas in a sub-stoichiometric amount of oxygen [267] to produce a syngas of CO and H_2, CO_2, CH_4 and soot. Any sulphur present in the feedstock is converted to H_2S. After waste heat recovery, the gas is water scrubbed to removes any solids [264]. The gas is then conditioned to produce ammonia.

There are two types of partial oxidation in use, Catalytic Partial Oxidation (CPO) and Thermal Partial Oxidation (TPO). CPO operates at up to 800°C [270] using supported platinum-metal or nickel-based catalysts [271]. The catalysts are prone to poisoning from sulphur compounds; therefore, desulphurisation has to be performed prior to this process if the feedstock contains considerable amounts of sulphur. TPO does not use a catalyst and operates between 1300°C and 1500°C. Desulphurisation is not required prior to operation. The process is seen to be simpler, more rugged and flexible than steam reforming [265] allowing the use of more economically attractive, less clean feedstocks.

However, synthesis gas produced from partial oxidation contains more CO than H_2. In addition to this, partial oxidation systems have higher tonnes CO_2/tonnes ammonia ratios than natural gas reforming. The process was used in ammonia production up to the 1960s; however, the need for air separation technology made it economically unattractive [265].

10.1.1.3 Coal gasification

Coal is pulverised and either dry or slurry fed into the gasification unit, depending on the type of process used. It is then gasified at 1000-1500°C in the presence of air, O_2 or steam to give a syngas of predominantly H_2 and CO [272]. This syngas can then be processed to produce ammonia. There are a number of coal gasification systems in operation such as the Texaco, Shell and Sasol processes. The technologies differ in terms of feed preparation, ash removal, operation parameters and the type of coal used [176, 272].

In Europe and USA, coal gasification is no longer in use for ammonia production. This is because the process was considered neither economically nor environmentally attractive. However, uncertainties regarding the cost and availability of natural gas may make coal gasification more attractive in the future [264, 273].

10.1.2 Production costs

Natural gas based ammonia production systems are more economically attractive in terms of capital cost, however the operating costs tend to be higher. For instance a 1,800 tpd (short) has a capital cost of \$339M (2007) (£224.2M (2009)), with an operating cost of \$497.55/t (short) (2007) (£329.07/t (2009)). A corresponding coal gasification system has a capital cost of \$678M (2007) (£448.4M (2009)), but an operating cost of \$366.96/t (short) (2007) (£242.69 (2009)) [274].

The main reason for this is that the production costs are dictated by the current price of natural gas. This can equate to up to 79% of the materials costs [275], which in turn represents 52-68% of overall cost [276].

10.1.3 Worldwide production

Ammonia is the world's most manufactured bulk chemical [176] with 129.3M t produced annually worldwide (2010) [277]. Table 10.1 shows the worldwide ammonia production figures for 1999-2010.

Table 10.1: Worldwide ammonia production figures 1999-2010 [277]

As shown, ammonia production has steadily increased, except for 2001, 2008-2009 due to the social and economic climate. These production levels reflect the increasing demand for crops, both for food and fuel, resulting in larger fertiliser requirements [278]. Approximately 90% of ammonia produced worldwide is processed or used in its country of origin [279]. The European Union produces approximately 11M t ammonia annually (2001), from about fifty plants [262]. Table 10.2 shows worldwide production and consumption per region (2010).

Table 10.2: Worldwide ammonia production and consumption (2010) (based on [277])

Region	Production (%)	Consumption (Apparent) (%)	Balance (%)
West Europe	7.0	8.5	-1.5
Central Europe	3.3	3.4	-0.1
Eastern Europe & Central Asia	13.3	10.8	2.5
North America	9.3	12.9	-3.6
Latin America	6.3	3.3	3
Africa	4.0	3.7	0.3
West Asia/Middle East	8.1	6.9	1.2
South Asia	10.9	12.1	-1.2
East Asia	36.5	37.4	-0.9
Oceania	1.2	0.9	0.3

Regions such as West Europe and North America require imports to satisfy the ammonia demand. These areas have no or comparatively little fossil feedstock sources (natural gas) for producing enough ammonia to meet the demand. North America was the largest importer (34.7%) in 2010, followed by Western Europe (18.4%) and East Asia (15.8%) [277].

Regions such as Latin America, the Middle East and Eastern Europe have larger reserves of fossil fuels, producing enough ammonia to meet their own demands and supply other regions through exports. In 2010, Latin America was the largest exporter of ammonia, supplying 29.6% of the worldwide market. Eastern Europe and the Middle East also had significant exports of 22.1% and 15.5% respectively [277].

10.1.4 Ammonia production in the UK

There are a number of companies producing various types of fertiliser for the UK market, ranging from independent organic specialists to large joint ventures. There are three natural gas based ammonia production sites currently in operation, which are owned by either Yara or their joint venture (with CF Industries) GrowHow UK [280]. The plants are situated in Hull, Ince and Billingham [262].

The Hull, Yorkshire plant is owned by Yara and is located on the BP Acetyl production site. It is used solely for the production of ammonia and has an annual capacity of 270,000 t. The Ince and Billingham plants are operated under the GrowHow UK venture and have annual capacities of 400,000 t and 550,000 t respectively. These two plants have been subjected to numerous shutdowns in recent years due to the economic downturn making ammonia production unprofitable in the UK, in comparison to exports. However, both sites are fully operational at present [281, 282].

An additional GrowHow plant at Severnside, near Bristol had an annual capacity of 265,000 t of ammonia and 500,000 t of ammonium nitrate. However due to the economic downturn the plant was due to cease production in January 2008 [283]. It has since been dismantled and transported overseas [284].

10.2 Biomass gasification

10.2.1 Gasification

Gasification is defined as the thermochemical conversion of a carbon based feed at elevated temperatures to produce a synthesis gas (syngas) as well as char, tar (condensable organic compounds) and ash as by-products [141, 142 & 285]. The process is endothermic; with heat being provided either by the process itself via partial oxidation or an external source. These categories are known as direct and indirect respectively [142].

10.2.1.1 Direct

For direct gasification, an oxidising agent is used to partially oxidise the feedstock. This can be air, O_2 or a combination of both (enriched air). These reactions supply the process heat, maintaining the high temperature of the system [142]. Higher levels of tar and hydrocarbons are present in the syngas, giving it a high heating value [142]; though these compounds are normally removed via gas cleaning in order to reduce their impact on downstream equipment. Gasification with air produces a syngas with a H_2 content of approximately 8-14 vol% [286, 287]. The syngas contains a large volume of inert gas (N_2), which can be up to 45-55% of the product gas composition [288]. The large volume of N_2 can cause economic challenges, by increasing the size of plant equipment in order to compensate the syngas dilution [142].

The advantage of gasification with air is that the process does not entail the costs and hazards that are associated with O_2 and steam [142]. It also provides the potential to use different biomass feeds in one gasifier without huge process alterations, thus making the process more flexible [289]. These factors have resulted in air gasification being the most economically attractive method [290] and the most widely used [142].

Using O_2 as the oxidising agent produces a syngas with a low N_2 content [142, 288], which improves volumetric efficiency [291, 292].O_2 is either imported in or produced onsite using air separation units (ASU) for an additional investment cost [288]. ASU are commonly cryogenic distillation systems [293], which compress, dry, cool and distil air into O_2 and N_2 [176]. O_2 enriched air also requires air separation but is less expensive to use than O_2.

10.2.1.2 Indirect

Indirect gasification requires heat from an external source as no oxidising agent is present for partial oxidation [141].Instead steam is added, which produces a gas with a lower tar and nitrogen content than direct gasification [288]. Adding steam improves the tar conversion efficiency, thereby encouraging high H_2 formation in the syngas [294].

Since the process is endothermic, high temperature steam (over 700°C) is used to provide heat, increasing the overall cost of the system [295]. The overall energy efficiency of the process can be improved with the implementation of a suitable heat recovery system. Alternatively, the system can sustain a level of self-sufficiency by combusting the char by-product in order to raise steam. This has been successfully demonstrated by processes such as the Fast Internal Circulating Bed (FICFB) and the SilvaGas system [141, 290 & 296].Steam flowrates require constant monitoring since the presence of an excess amount will cause a shift reaction, increasing CO_2 levels [297].

10.2.2 Product description

The end-product gas from gasification can be referred to as product gas or synthesis gas (syngas), depending on its use.

Product gas is used directly for power generation, in either CHP or co-firing plants. It is also used for the production of SNG [298].

Syngas is a widely used feedstock in the chemical industry. Fossil fuel syngas is used mainly for the synthesis of ammonia for fertiliser production (53% market), whilst the remaining supply is consumed by oil refining, which requires H_2 (23% market), methanol production (11% market), gas-to-liquids (8% market) and other processes, such as electricity production (~5% market in total) [298].

10.2.3 Biomass gasification

Gasification requires a carbon based feedstock that is suitably homogeneous [141]. This means the process can utilise purpose grown biomass, such as energy crops and wood, as well as by-products such as forestry residue and agricultural wastes.

In terms of its properties, biomass is a young coal, which allows comparisons to be drawn with coal gasification due to the broadly similar temperatures required for complete thermal gasification [176]. In addition, biomass sulphur levels are not considered a major concern since they are comparatively lower than coal [141].

However, problems arise from utilising biomass feeds that are not experienced with coal. These include the behaviour of the feedstock ash and the resultant tar content of the syngas.

Compared to coal, biomass ash has a lower melting point and is very aggressive in its molten state [176], though the K_2O content can have a positive catalytic effect on gasification performance [299]. Biomass ash often reduces the utilisation efficiency of equipment and shortens service life [25]. This is caused by the presence of alkali metals and chlorides, which can cause agglomeration, deposition and corrosion in thermochemical conversion equipment [7, 300]. Ash removal is required from the gasifier, cyclones, hot gases and washing waters. Normally 1-2 wt% of dry weight is collected from the gasifier alone [141].

The production of syngas from biomass feed can be problematic due to the formation of tar and char, regardless of process temperature. This is because biomass has a higher reactivity than coal and produces more tar [301]. The lower the operating temperature, the more tar and char are produced [302]. Gases produced from processes with counter current flow tend to contain higher levels of tars. Co-current processes operate better but there are issues with blast distribution, which affect the scaling potential [176].

Wood is the preferable feedstock material for gasification since residues such as sawdust can produce a H_2-rich gas [289]. Several large-scale biomass gasification systems operate, or have operated successfully using wood [287, 303].

10.2.4 Gasification processes

There are several types of gasification process in operation or under development. The following sections summarise the most common systems.

10.2.4.1 Fixed-bed gasification

Fixed-bed gasifiers, also known as moving bed, contain a packed bed, which remains in a fixed position. The process utilises gravity by introducing the feedstock at the top of the unit resulting in the solid to gas conversion occurring during the feedstock's downward path [142, 304]. As the feed moves down the bed it undergoes several distinct stages, these are drying, pyrolysis, reduction and combustion [142, 176, 294, 304 & 305]. The maximum operating temperature for fixed-bed gasification is approximately 1000°C [141]. The oxidising agent is introduced to the gasifier in various places depending on the type of fixed-bed used.

Two types of fixed-bed gasifier are in operation, these are updraft and downdraft.

10.2.4.1.1 Updraft

The process flow in an updraft gasifier is counter-current with the oxidising agent being fed in from the bottom, as shown in Figure 10.1.

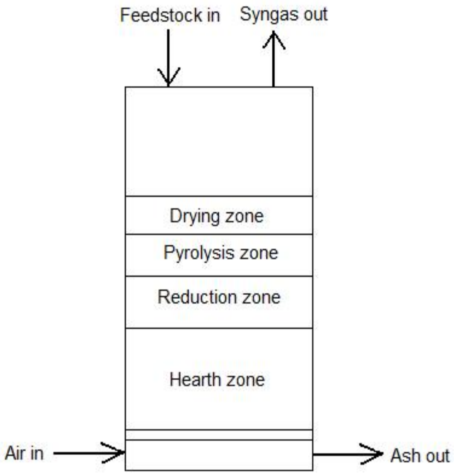

Figure 10.1: Updraft gasifier (based on [141, 304])

As the feedstock travels down the gasifier the product gas rises and leaves out of the top of the unit [141]. The counter-current flow of the gasifier produces a high methane content gas [176]. However, the syngas contains high concentrations of tar, which have been carried from the pyrolysis zone by the hot gas and not subjected to the gasification reactions [141].

10.2.4.1.2 Downdraft

The downdraft gasifier operates with co-current flow with the oxidising agent entering through the sides of the unit and the product gas leaving from the bottom [141, 304], as illustrated in Figure 10.2.

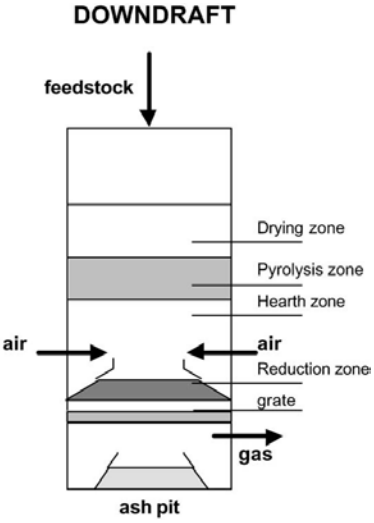

Figure 10.2: Downdraft gasifier [141, 304]

Unlike the updraft system, a constricted throat within the gasifier supports the downdraft packed bed. The environment surrounding the throat is turbulent with high temperatures, which assist the cracking of pyrolysis tars. The gasification process is completed below the throat on the residual char bed [142].

10.2.4.2 Fluidised bed gasification

Fluidised bed gasification was developed in order to overcome the operational problems associated with the fixed bed process [304].

Fluidised bed gasifiers operate isothermally [142], using an inert material such as silica sand [176, 305]. This results in the gasification bed transforming into a liquid-like state as it comes into contact with the upward flowing gas [305]. The behaviour of the bed means that there are no distinct gasification zones [176]. This promotes high rates of reaction, heat and mass transfer, due to good mixing between the oxidant and feed [142, 176]. The char mixes with the bed material and takes part in the combustion reaction [306], whilst tar is converted into gas during the fluidisation.

The operating temperature range is approximately 700-900°C [141], with most of the conversion taking place within the bed. In terms of carbon conversion, fluidised bed gasifiers generally have an efficiency of approximately 97% due to the unreacted matter often being removed with the reacted [176].

At present, the technology is widely considered to be well suited for biomass gasification [142]. Fluidised beds can operate below the ash softening point (800-950°C) of several biomass sources, making the process attractive for biomass utilisation. However, the lower operating temperatures result in increased levels of tar in the syngas caused by limited thermal cracking. Nevertheless fluidised bed gasification coupled with downstream gas cleaning technology are considered to be the most feasible method for biomass at present, even though there are problems striking the correct balance between the temperature limits [176].

There are two types of fluidised beds currently in operation, the bubbling (BFB), the circulating (CFB).

10.2.4.2.1 Bubbling fluidised bed (BFB)

In the bubbling fluidised reactor, oxidising agent has a low upward velocity of 1-3 ms^{-1}. This results in the bed material and char only occupying part of the gasifier, as shown in Figure 10.3 [304, 307 & 308].

Figure 10.3: Bubbling fluidised bed [141]

The level of the tar in the product gas is generally in the range produced by downdraft and updraft gasifiers [142] resulting in the need for product gas cleaning prior to use. Bubbling fluidised beds require more monitoring than other fluidised processes due to the possibility of de-fluidisation and the removal of too many fine particles from the bed [176].

10.2.4.2.2 Circulating fluidised bed

The circulating fluidised bed has a velocity of 5-10 ms^{-1} [307, 308]. This increased velocity means that the bed expands to fill entire reactor, as shown in Figure 10.4.

Figure 10.4: Circulating fluidised bed [141]

The extension of the fluidisation zone results in bed material and char being carried out with the syngas. These particulates however are captured and recycled by a cyclone intercepting the gas stream [309].

10.2.4.3 Entrained flow gasification

Entrained flow gasifiers operate between 1200°C and 1500°C, depending on whether O_2 or air is used [142], with the feedstock and agent flowing co-currently [176]. The high temperatures are required to ensure good conversion of the feedstock during the very short residence time of the process. The high temperatures and low residence time produce a syngas with low tar and condensable gas concentrations [142] since the tars and oils are destroyed in the high temperature environment [176]. This process produces a higher quality syngas than fixed or fluidised beds, resulting in considerably less gas cleaning [176]. The process is very attractive; however, it is hampered by feed particle size and O_2 demand. In terms of particle size entrained flow gasifiers require a finely reduced feedstock [142, 176], which results in a high level of feed pre-treatment. The high temperatures used in this system create a high O_2 demand that can require the use of enriched air or O_2, which in turn introduces the need for air separation technology and its additional cost [176].

10.2.4.4 Twin bed gasification (char indirect gasification)

Twin bed gasification, also known as char indirect gasification is an extension of the CFB technology. The process physically separates the gasification process into two zones, the gasification and combustion zones [176], as shown in Figure 10.5.

Figure 10.5: Twin bed gasification [310]

In the gasification zone biomass is added, heated, dried and devolatised before being converted into CO, CO_2, CH_4, H_2, H_2O and char in the presence of steam [310]. Simultaneous to this the water vapour reactions occur, which are strongly endothermic.

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (10.9)$$

$$C + H_2O \rightarrow CO + H_2 \qquad (10.10)$$

In the presence of a steam oxidising agent this process produces a syngas that is largely free of N_2 with a high heating value of 12-14 MJ/Nm^3 [310]. The char is carried with the bed material to the combustion zone where it is oxidised in the presence of air to produce heat and ash [311]. The hot bed material is then recirculated to the gasification zone to provide the process heat. Additional fuels, such as waste streams from gas cleaning, can be added to the combustion zone if necessary [288].

The process utilises either two fluidised beds, like the SilvaGas (BCL/FERCO) process [312, 313] or an internally circulating fluidised bed, such as the FICFB process [314]. Unlike other gasification processes, the twin bed produces a flue gas stream, which is an additional source of useful heat [303].

10.2.4.5 Gas indirect gasification

Gas indirect gasifiers, shown in Figure 10.6, comprise of a steam fluidised bed unit with bed heat exchange tubes [294, 309]. In order to provide process heat, a portion of the combustible gas is burned with air in a pulse combustor [294, 309 & 315].

Figure 10.6: Gas indirect gasifier [141]

Not only are gas indirect gasifiers tolerant to a wide range of feeds [294], they also produce high quality combustible gas. The process is more expensive than other gasification processes; requiring highly efficient energy recovery in order to reduce process losses [141].

10.2.4.6 Molten metal gasification

Molten metal gasification is based on the Klöckner molten iron process [176]. AlChemix originally developed the process by adapting the technology of bath smelting from 20 plants, thus resulting in the process being granted 206 claims of invention in the US [316].Process development has been on-going for some time under different companies, with Diversified Energy's HydroMax® being the most recent incarnation [176].

This process produces two separate product streams, one of H_2 and one of CO, as shown in Figure 10.7. The advantage of this method is that large volumes of H_2 gas are produced in a separate stream.

Aston University

Illustration removed for copyright restrictions

Figure 10.7: Molten metal gasification [317]

The process comprises of two stages oxidation and reduction. In the oxidation reaction steam is injected into a molten metal bed of Fe to produce hydrogen and a metal oxide. Steam injection also adjusts and maintains the temperature of the reaction. The metal oxide is in a fluidised particulate form to allow the metal formation to be rapid. The hydrogen is sent to a condenser to remove excess water vapour. The H_2 content in the product gas is approximately 99%, preferably >99.9% after water removal.

The metal oxide is then subjected to the second stage, the reduction reaction, which has a maintained temperature of 800-1300°C. The purpose of the reduction process is to convert the metal oxide back into metal. The carbon source (either coal or biomass) is reacted with O_2 or air to produce a CO reduction gas.

$$\tfrac{1}{2}O_2 + C \rightarrow CO \qquad (10.11)$$

$$CO_2 + C \rightarrow 2CO \qquad (10.12)$$

The reducing gas contains approximately 90 wt% CO, though 95 wt% is preferable. The reduction gas then converts the metal oxide into CO_2 and metal, in this case FeO into Fe.

$$FeO + CO \rightarrow Fe + CO_2 \qquad (10.13)$$

The CO_2 is recycled and the excess CO is removed from the process in order to eliminate the amount of O_2 which corresponds to the amount of H_2 being separated. This excess CO is used as process heat thereby maximising its utilisation. The temperatures of the oxidation and reduction reactors are maintained at no greater than 1000°C, preferably 700-900°C [318].

In terms of bed metal, iron or tin are the most suitable, with several hundred tonnes of iron being required, though minimal supplementation is needed [318].

10.2.5 Gas cleaning

Prior to use syngas requires additional processing to remove materials such as tars, particulates and compounds such as chlorine and sulphur, in order to prevent corrosion and erosion in downstream equipment. The level of gas contamination and subsequent cleaning varies with feed and chosen process [141].

A certain amount of gas cleaning could be implemented during gasification by self-modification, where parameters within the gasification process are altered to reduce the amount of tar within the gasifier, improving the quality of the syngas. The most influential parameters are temperature, pressure, oxidising agent, equivalence ratio (the stoichiometric ratio of fuel to oxidising agent) and residence time. The process however is not yet fully understood or used commercially [285, 319]. Normally secondary gas cleaning technologies, which treat the hot product syngas downstream of the gasifier, are implemented. These systems are very effective but can be economically unattractive [319].

Initially the syngas is cooled to prevent thermal damage to the equipment. The level of cooling implemented depends on the syngas temperature and the required temperature boundary of the cleaning system. This process is a good area to recover heat [141].

There are three common methods of gas cleaning; adsorption, absorption and membrane filtration. The following sections outline some of the available gas cleaning technology.

10.2.5.1 Adsorption

During this process, impurities in the syngas are adsorbed onto a solid carrier bed. This is performed using systems such as molecular sieve adsorption and PSA. Molecular sieves are mainly used to remove CO_2, NO_x, water and unsaturated hydrocarbons.

In terms of syngas cleaning, PSA is used to purify the H_2 content. Currently the H_2 yield is between 80-92%, though this is affected by changes in the operating pressure and the quality of the feed gas. Some H_2 is removed with the particulates found in the gas, therefore an increased concentration of particulates means that more H_2 is lost [176].

10.2.5.2 Absorption

Syngas impurities are removed by washing or scrubbing the syngas with a liquid solvent. This is implemented water as well as chemical and physical solutions. Chemical washes are mainly used for the removal of acid gas and CO_2. Physical washes are utilised to remove CO_2, H_2S and COS [176].

Scrubbing is used to remove particulates and tars [285]. Venturi scrubbers remove between 51-91% of the tar present in the gas. Water scrubbers can reduce tar levels to 20-40 mg/Nm^3 and particulates to 10-20 mg/m^3 [320]. The systems can be fairly expensive and generate a lot of contaminated water [285].

10.2.5.3 Membrane filtration

This process utilises permeable gas separation membranes to remove certain materials from the product gas. There are three ranges of permeability, which are quick, intermediate and slow. Quick permeability removes H_2 and H_2S, whilst intermediate and slow remove CO_2 and CO, CH_4 and N_2 respectively [321].

10.2.5.4 Tar removal

The presence of tars in the syngas is caused by incomplete conversion of pyrolysis products [141]. Therefore, by converting the tars into permanent gases, the gasification process is completed. Two methods of conversion are thermal cracking and catalytic cracking [141, 322].

For thermal cracking the syngas is heated to 800-1300°C [142, 304 & 323], cracking the tars into lighter hydrocarbon gases [324, 325].

For catalytic cracking, the gasifier bed is either replaced or impregnated with catalyst. Alternatively, a second reactor containing the catalyst can be added as demonstrated in the TPS gasifier in Sweden [142]. Using a secondary reactor is preferred as a single combined reactor is less effective [326].

There are three groups of catalyst: nickel, alkali metal and dolomite. Nickel based catalysts are used extensively in petrochemicals for naphtha and methane reforming, resulting in wide range of commercially available types [285]. Metal catalysts are more susceptible to deactivation than others, which is thought to be caused by either low H_2 levels in the gas or sulphur stripping [142]. Dolomite ($CaMg(CO_3)_2$) is a calcium magnesium ore for magnesium manufacturing. The presence of Dolomite has been proven to effectively reduce tar levels [327-329]; though it is difficult to reach or exceed 90-95% tar conversion [330]. It does not however affect the gaseous hydrocarbon concentrations and can have difficulty converting heavy tars [285].

10.2.6 Operation and economics

Gasification systems operate at either atmospheric or elevated pressures, depending on the system requirements. For biomass, there is little thermodynamic or reaction-kinetic advantage for using either pressurised or atmospheric gasification. Pressurised systems however require a lower volume capacity than atmospheric [142].

The difference is in capital costs, with pressurised processes requiring higher equipment and construction costs, though the equipment is smaller [142, 331]. The feeding systems for pressurised systems are more complex and costly and also have a high inert gas requirement for purging. In many cases, the feeding system can cost more than the gasifier due to the need to reduce the risk of blockages [142].

However, pressurised gasification systems can keep tars above their condensation temperature. The pressurised hot gas is then cleaned by mechanical filters, meaning thermal and pressure energy losses are reduced, making this method simpler and less costly [142]. Atmospheric systems have fewer constraints but may require additional compression of the syngas, resulting in additional cooling being required (Bridgwater, 1995). It is believed that biomass gasification under pressure will be more economically attractive once industrially mature [332].

Biomass gasification units are currently smaller than coal fed systems, which can operate at feed rates of 2,000 tpd (Nuon IGCC, Buggenum) [333]. The Sydkraft CFB operated at a flowrate of 96 tpd (~20 wt% wet), whilst the Güssing FICFB operates at just over 43 tpd (~30 wt% wet) [287, 303]. Large-scale biomass gasification has been proposed, with feed rates of 2000 tpd (dry) [15, 220].

Investment costs for biomass gasification can be difficult to obtain and it is often necessary to use data for coal gasification and factor in additional costs. In terms of capital costs a 53 tpd FICFB gasification system costs approximately £15.1M (2009) (€9M 2004) [334]. Large-scale system costs are subject to assumptions made during scale up, both technical and economic. This results in large variations in the cost of different gasification technology. For instance a 2,000 tpd (dry) system is estimated to cost £44.9M (2009) ($67.8M 2007) for entrained flow [220] and £90.6M (2009) ($12.9M 2005) for a char indirect gasifier [15].

10.3 Biomass gasification for ammonia production

The steam reforming of natural gas for ammonia production is still more economically and commercially attractive than gasification. However, the availability and volatile price of natural gas has led to renewed interest in gasification, for the production of chemicals such as H_2 for industrial applications [14, 16, 272], which is the precursor to ammonia.

In order to create a more environmentally acceptable fertiliser it has been suggested that the ammonia source should be produced from a biomass gasification derived syngas. Biomass gasification has been in operation for over 100 years but has had little commercial impact due to the availability of fossil fuels. In the past 20 years, there has been renewed interest in the technology, which has continued to intensify [142]. The process is also seen as a more attractive alternative treatment to combustion for solid waste energy recovery. This is due to the higher overall efficiencies and flexibility associated with gasification, as well as the potential to utilise small-scale installations close to the feedstock source, thus eliminating storage and transport costs [141, 289 & 310].

The slow uptake of biomass gasification is due to the feedstock itself, which comes at a relatively high cost and lacks established supply chains. This has meant that very few gasification processes have proven to be economically viable. However, with the increase in expertise and knowledge modern gasification processes are more capable of dealing with biomass feedstock [142].

11 Previous work (ammonia)

The production of ammonia from biomass gasification is not a recent development, though the availability of published work is limited. A technical study by Rutherford and Ruschin [330] reports the production of ammonia synthesis gas from wood fuels, whilst Spath and Dayton (§11.1.3) cite a publication by Dietz et al. [335], which relates to the production of ammonia from Brava Cane. However, these sources are out of date and provide very limited useful information.

With this in mind, it has been necessary to include techno-economic studies that cover the production of other chemicals through similar methods. In this case, the production of hydrogen from biomass gasification is the most relevant, particularly as ammonia is a precursor and carrier. In some cases, techno-economic studies relating to biofuel and ethanol production have been included. Whilst the production systems are not as comparable as those for hydrogen are, they provide valuable information that is transferrable to ammonia production.

The papers and reports selected for this review cover a range of activities required for biomass derived ammonia that are not covered in reports for ammonia production from fossil fuels. They have been selected because they are current, present clear methodology and are from a range of sources. A number of the papers chosen present the evolution of numerous ideas from a particular institution, drawing on earlier work. The relationship of these papers, shown in Figure 11.1, produces data, which has not been achieved independently, but adjusted to suit the needs of specific projects.

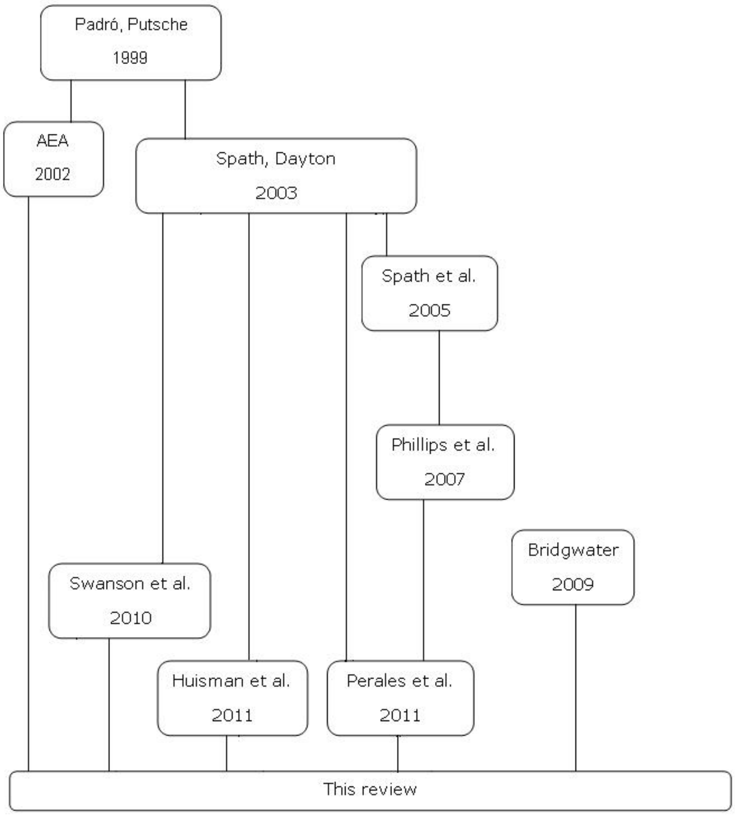

Figure 11.1: Relationship of reviewed literature

As expected, utilising papers from various sources and for different products results in data quoted in a range of units, assumptions, currencies and base dates. This means that direct comparison of the papers is not possible without a common base. In addition to this, it is not feasible to compare typical areas, such as product yield and overall production cost.

Instead, this review covers the following sections:

- Feed preparation capital costs
- Gasification capital costs
- Labour requirements
- Land costs
- Working capital
- Additional revenue

All economic data has been converted to 2009 £, with non-capital costs quoted on an annual basis. To ensure relevance, only information relating to ammonia production is included in this review. Where studies have covered multiple process routes, only those suitable for ammonia production are included. These studies provide an indirect background to this work and identify the limits of current investigations.

There are several key techno-economic papers relating to the production of ammonia from fossil fuels, which are not included in this review. In addition, techno-economic reports based on power production from biomass gasification are not included. This is on the basis that although these provide important data, they do not address the potential of competitive biomass-based production. For the case of power production, the quality of syngas required differs significantly from that of chemical production, providing a misleading assessment.

11.1 Comments on individual papers

11.1.1 CEG Padró, V Putsche, 1999.

Survey of the Economics of Hydrogen Technologies [336].

Although this is not a recent publication, it provides cost data and information that form the basis of several reports. The paper is published by the National Renewal Energy Laboratory (NREL), as part of the DOE, providing a survey of the economics of hydrogen, from production to end use, based on available literature. It briefly summarises and assesses technologies that are in operation or are no more than twenty years from commercialisation, including gasification.

The gasification process under consideration is the BCL/FERCO indirect system (SilvaGas), based on data derived from detailed studies by Mann [337] and Larson & Katofsky [338]. The economic data presented has been standardised to mid-1998 US$. Capital costs are shown as the Total Capital Investment (TCI), which is expressed in $\$/GJ_{LHV}$ hydrogen produced annually.

11.1.2 AEA Technology, 2002.

The feasibility, costs and markets for hydrogen [339].

AEA Technology compiled this paper for British Energy, in order to provide a techno-economic summary of current and potential hydrogen production technologies, including gasification. This paper is based largely on data published by Padró and Putsche (§11.1.1), however additional information is presented and the costs have been adjusted to 2000 £. Like Padró and Putsche, this paper focuses on the BCL/FERCO indirect gasification process only, citing the same sources of data.

11.1.3 PL Spath, DC Dayton, 2003.

Preliminary Screening - Technical and Economic Assessment of Synthesis Gas to Fuels and Chemicals with Emphasis on the Potential for Biomass-Derived Syngas [340].

This paper is the forerunner of several NREL publications under review (Spath, Phillips, and Swanson). Like Padró and Putsche, this paper is a desktop study, which summarises the technologies and considerations of producing hydrogen, but also ammonia and other chemicals. As the title suggests there is an emphasis on biomass derived production processes. In addition to this, the paper presents economic data for ammonia production, though unfortunately it is brief and considerably out of date [335].

11.1.4 P Spath, A Aden, T Eggeman, M Ringer, B Wallace, J Jechura, 2005.

Biomass to Hydrogen Production Detailed Design and Economics Utilizing the Battelle Columbus Laboratory Indirectly-Heated Gasifier [14].

This NREL paper builds on ideas suggested by Spath & Dayton and forms part of the DOE Biomass Programme. It is a desktop techno-economic assessment, which utilises ASPEN Plus® simulation software for process modelling. Due to the quality of the work, the information presented is also utilised by other papers presented in this review (Phillips, Swanson).

The gasification processes under assessment is the BCL/FERCO indirect gasifier, which is considered the 'nth' plant design. Two design scenarios are presented; these are the current plant and goal plant, which produce 57M kg/y and 61M kg/y hydrogen respectively. The differences in the scenarios are due to expectations concerning the technology, though both systems operate at 100% capacity. All scenarios use a woody biomass feedstock, which is poplar wood chip.

The economic assessment is based on the calculated minimum hydrogen selling price (MHSP) and expresses all costs in 2002 US$. Equipment costs are from Questimate, which is equipment cost estimating software, provided by ASPEN Plus®. Cost factors by Peters et al. [341] are then applied, with an expected accuracy of ±30%. According to the authors, this method of calculation compensates for the fact that the figures are not from vendors. Capital costs are expressed as percentages of the total plant equipment costs (TPEC). The fixed operating costs are derived from Aden et al. [342], whilst variable operating costs are taken from relevant literature.

11.1.5 S Phillips, A Aden, J Jechura, D Dayton, T Eggeman, 2007.

Thermochemical Ethanol via Indirect Gasification and Mixed Alcohol Synthesis of Lignocellulosic Biomass [15].

Neoterics International Inc. and NREL published this report in order to address the policy initiative to broaden the United States' domestic production of economic, flexible, and secure energy fuels and reduce the countries oil demand, through the application of DOE research. According to the authors the specific goal for biomass is *"to foster the breakthrough technologies needed to make cellulosic ethanol cost competitive with corn-based ethanol by 2012"* [15, p i].

This paper presents a desktop assessment for the production of ethanol derived from the gasification of corn stover, based on the technological expectations and projections for 2012. This paper focuses on the Battelle (BCL/FERCO) indirect gasification process, operating at 890°C and 1.6 bar and a feedrate of 2,000 tpd (oven dry). The feedstock is specified as wood chip. The methodology uses Spath (§11.1.4) as the basis, adjusting where necessary. All costs are expressed in 2005 US$.

11.1.6 AV Bridgwater, 2009.

Technical and Economic Assessment of Thermal Processes for Biofuels [343].

Bridgwater provides a comprehensive techno-economic assessment of the current and future prospects of biomass-to-liquid processes (BTL). This report considers alternative thermochemical process routes, covering a range of pre-treatment and preparation technologies, and the primary conversion route is gasification. The technology considered are entrained flow and fluidised bed gasification technology, preferably oxygen blown and pressurised.

All costs are based on case studies made by the German Energy Agency (DENA) [344], which have been converted to 2008 £. The costs are divided into 4 sectors, these are capital cost, capital related costs, feedstock (delivered) and other variable costs.

11.1.7 RM Swanson, JA Satrio, RC Brown, A Platon, DD Hsu, 2010.

Techno-Economic Analysis of Biofuels Production Based on Gasification [220].

This report, completed by NREL, Iowa State University and ConocoPhillips Company, investigates the economic feasibility of biomass gasification to renewable transportation fuels (BTL). Its objective is to compare capital investment costs and production costs of the ‘nth’ plant, using either high-temperature entrained flow (slagging) gasification or low-temperature fluidised bed (dry-ash) gasification.

Entrained flow is under consideration due to its commercial application with coal (GE, Siemens, Shell, and ConocoPhillips) and its potential for use with biomass. Fluidised bed gasification is under investigation because of the collective experience of the author’s institutes and the availability of data. The feedstock is agricultural residue (corn stover).

The majority of the process modelling is completed using ASPEN Plus® software, with equipment sizing and costs using ASPEN Icarus®. The fluidised bed gasifier model however, is a mass balance calculation, which assumes that all the char is utilised in combustion. The methodology is based on the work completed by both Spath and Phillips (§11.1.5), with costs adjusted to 2007 US$.

11.1.8 GH Huisman, GLMA Van Rens, H De Lathouder, RL Cornelissen, 2011.

Cost estimation of biomass-to-fuel plants producing methanol, dimethylether or hydrogen [16].

This paper is a desktop study, which estimates the cost of biomass-to-fuel plants producing methanol, dimethylether (DME) or hydrogen, considering two process designs based on current and near-future technology, both based on the CHRISGAS gasification project. The paper considers high-pressure steam and oxygen blown fluidised bed gasification, which operates between 850°C and 900°C with a federate of ~980 tpd (dry). The biomass feedstock is specified as wood chip with a 50 wt% moisture content at the plant gate.

Due to the range of products included in this study, the economic assessment is based on the sale of district heating as the primary source of revenue. The capital expenditure (CAPEX) is based on estimated figures, which are adjusted to reflect the technology and plant scale under investigation. The operation expenditure (OPEX) is handled in the same manner. Equipment costs are taken from investment costs for equipment or entire packaged units in literature. Cost data is presented in 2009€.

11.1.9 AL Villanueva Perales, C Reyes Valle, P Ollero, A Gómez-Barea. 2011.

Techno-economic assessment of ethanol production via thermochemical conversion of biomass by entrained flow gasification [237].

Like Huisman (§11.1.8), this paper is a desktop study, assessing current and future scenarios, though the product focus is on ethanol. The gasification technology under investigation is a 2,140 tpd (dry) entrained flow gasifier (1300°C). The processes are modelled using ASPEN Plus® 2006.5 Simulation Software, which is used to solve mass and energy balances.

The economic assessment is based on the minimum ethanol selling price (MESP) and costs have been adjusted to 2010 US$, using the Consumer Price Index. The fixed capital and operating costs are taken from a range of sources, including vendor quotes, scientific publications and engineering handbooks. The direct capital costs are based on Phillips (percentage of the purchased equipment costs (PEC)), whilst the indirect are expressed as a percentage of the TIC. Fixed operating costs are also presented as percentages of the TIC, whilst the variable costs are sourced from literature.

11.2 Data comparison

As discussed at the beginning of this chapter, the nature of the available literature means that there are difficulties with comparing specific areas of cost, such as production. However, there are areas that may be evaluated, which are now presented.

11.2.1 Gasification capital costs

Several gasification systems are under investigation. For Padró and Putsche, AEA (§11.1.2), Spath and Phillips the gasification process under consideration is the BCL/FERCO indirect system (SilvaGas), based on data derived from detailed studies by Mann [333] and Larson & Katofsky [338].

Padró and Putsche do not consider a specific gasifier size, but a scale range of 0.02 to 0.7 M Nm^3/d syngas, based on Mann [337], which in turn is used by AEA. Cost data is presented in \$/GJ H_2 and £/GJ H_2 respectively.

Spath and Phillips assume that the gasifier is the ‘nth’ plant design, with a capacity of 2,000 tpd (dry), operating at 870-890°C and 1.6 bar. Spath derives the capital costs from literature, calculating an average. Phillips adjusts the costs presented by Spath.

Several studies investigate the use of entrained flow gasification. Based on work completed by DENA [344], Bridgwater (§11.1.6) considers oxygen blown entrained flow, which operates at approximately 2,400 tpd (dry). Swanson (§11.1.7) also investigates high-temperature entrained flow (slagging) gasification, with a feedrate of 2,000 tpd (dry). The capital costs are calculated using ASPEN Icarus® and refer to the installed costs. However, the author’s state that since the simulation installation scaling-factor is considerably lower than literature figures, an overall factor of 2.35 is used based on work by Reed et al. [345].

Several studies also consider fluidised bed technology. Based on DENA [344] Bridgwater assesses oxygen blown, pressurised fluidised bed gasification technology operating at approximately 2,400 tpd (dry), whilst Swanson investigates a 2,000 tpd (dry) oxygen blown fluidised bed (dry-ash) gasifier. Huisman considers high-pressure steam and oxygen blown fluidised bed gasification, which operates between 850°C and 900°C with a federate of ~980 tpd (dry). The ASU is based on a Linde turn-key plant.

Table 11.1 summarises the capital costs of the various gasification units under review. All costs include syngas cleaning and air separation, if required, and refer to the installed cost. In the case of Huisman, the installation cost is included in the capital overhead, however a substantial mark-up factor has been added (1.18), which for the purpose of this review, is assumed to cover installation. For comparison, the data below has been scaled to a biomass feedrate of 2,000 tpd (dry).

Table 11.1: Gasification capital costs

Author	Gasification	Cost 2009£k
Swanson	O_2 blown slagging entrained flow	79,747
	O_2/steam blown fluidised bed	48,889
Spath	Indirect BCL/FERCO	13,821
	Direct GTI	54,182
Phillips	Indirect BCL/FERCO	36,551
Bridgwater	O_2 blown entrained flow (slagging)	42,554
	O_2 blown entrained flow (pyrolysis oil)	37,352
	O_2 blown fluidised bed	45,864
Huisman	O_2/steam blown fluidised bed (current)	62,289
	O_2/steam fluidised bed (future)	48,578

It is clear that the entrained flow gasification presented by Swanson is the least economically attractive process, even in comparison to the figures quoted by Bridgwater. The use of indirect gasification has a significant economic advantage; this is mainly due to the inclusion of air separation technology in the direct gasification processes. The difference in the figures quoted by Huisman is based on the expectation that the ASU will be 25% smaller and cost around 20% less for the near-future design. On average, O_2 blown fluidised bed gasification is only slightly more economically attractive than entrained flow.

Concerning indirect gasification, Spath is considerably lower than Phillips, which has included an additional source of data [346]. Reasons for this are not given.

Figure 11.2 shows the breakdown of the above costs. Spath and Bridgwater are not included since data on the individual processes are not provided.

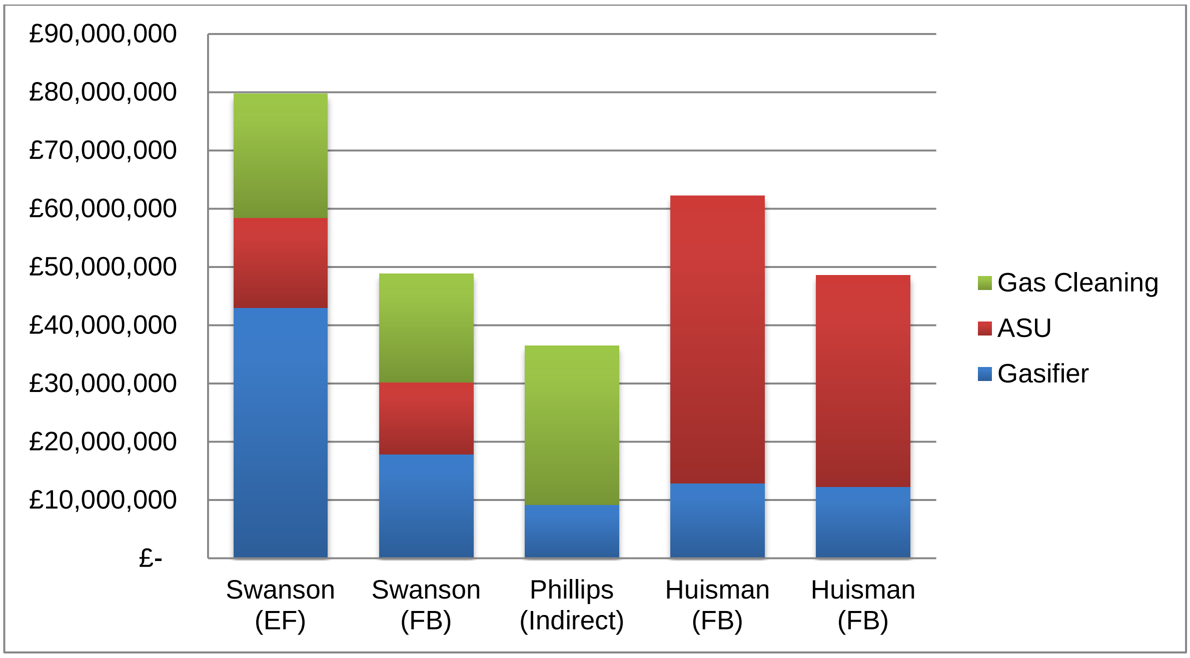

Figure 11.2: Gasification capital cost breakdown

In most cases, air separation and gas cleaning equate to at least half of the overall capital. In terms of gas cleaning technology, indirect gasification is the least economically attractive, which is to be expected due to the scale of cleaning required. Theoretically entrained flow gasification should require the least amount of gas cleaning, resulting in the smallest capital cost. This is not the case; however, comparison with additional literature is required. The cost of ASU technology varies significantly, which is dictated by the oxygen demand of the process.

11.2.2 Feed preparation plant costs

Most of the studies under review assess the use of a specific feedstock.

Spath, Phillips, Huisman and Perales use wood chip with a moisture content of 30-50 wt% at the plant gate. For these reports the feed preparation comprises of particle screening (Spath, Phillips) size reduction and drying. All sources specify a rotary drum dryer, which operates using waste heat streams (mainly flue gas) from the production plant. Due to the type of gasifier under investigation, Perales (§11.1.9) also includes pyrolysis, which is performed after drying. For Spath and Phillips feed delivery and storage is presented in detail, with outdoor storage being carried out on a cement slab. Neither Huisman nor Perales include this information, though Huisman state that this has been purposely done.

In terms of plant costs, Spath and Phillips use the same methods described in §11.2.1. Huisman provide an estimated preparation cost, which cites Scandinavian Energy Projects [347] as the dryer reference. Perales only presents the capital cost of the pyrolysis plant, though it is assumed that feed preparation costs are included in this figure. All of these figures either refer to installed costs or are assumed to do so, due to the use of mark ups, which have been factored in.

Swanson uses agricultural residue (corn stover) with a moisture content of 25 wt% at the plant gate. The feedstock is delivered in bales, which again are stored outdoors before being shredded, dried and ground before use. This system is used for both high and low temperature scenarios. Due to the physical properties of the feedstock, a handling and transportation system prior to preparation has been included. As stated in §11.2.1, the installed costs are derived from ASPEN Icarus®, however in this case the data is adjusted with a scaling factor of 3.02, based on work by Peters et al. [341].

Not all of the papers present a specific feedstock. Padró and Putsche, Spath and Dayton and AEA all refer to the feedstock as generic biomass. These sources also do not give a method of preparation. In the case of Bridgwater, a range of biomass types are under investigation, resulting in the use of an unspecified feedstock (assuming a 30 wt% moisture content) for the assessment. Based on DENA, the biomass undergoes shredding or milling, depending on the gasifier, and drying. Like Perales, pyrolysis is included; however the costs are presented separately. Torrefaction is also considered as a suitable form of pre-treatment; however, cost data is not presented, though Bridgwater estimates the capital as approximately 75% of the capital for an equivalent size pyrolysis unit. As described in §11.2.1, the cost data presented is from the DENA case studies and are assumed to be the installed costs. Table 11.2 shows the cost of the wood chip preparation plants only. The figures have been scaled to a gasification feedrate of 2,000 tpd (dry).

Table 11.2: Feed preparation plant costs

Reference	Biomass feedstock	Cost 2009 £k	Difference from average
Spath	Wood chip	24,855	-18.6%
Huisman	Wood chip	40,914	34.0%
Phillips	Wood chip	25,861	-15.3%
(Average)		30,543	

According to Rogers [348], based on Garret [349] preliminary stage plant cost estimates are likely to be -35% and +20 % of the final plant cost. Whilst Spath and Phillips comply with these boundaries, Huisman does not. This is possibly due to the generalised cost estimate.

11.2.3 Labour

Estimating labour can be difficult since a range of factors dictate workforce requirement, based on the needs of each specific process. The studies under review are desktop-based and therefore draw information from relevant literature and not from real-time operation situations. However, steps are taken to ensure that the data presented is reasonable.

Not all of the papers under review present details on labour, however several reports do provide detailed information. Note the cost data is presented its original form, though the totals have been converted to 2009 £.

According to Bridgwater, labour data has limited availability. Health and safety regulations suggest a minimum workforce of 2 per shift for pre-treatment; however, this does not provide enough information to populate a whole plant. With this in mind, Bridgwater and Perales set the labour costs as a percentage of the plant capital charges (12%), and the capital cost (1.56%) respectively.

For Spath, Phillips and Swanson, labour and salary data is adapted from Aden et al. [342], who provide a list of individual positions and their respective salary. Table 11.3 shows the cost comparison data between the sources in conjunction with changes made by Spath, which are used by both Phillips and Swanson. The figures quoted are basic salaries and do not include tax, insurance and pension contributions. Instead, a general overhead, which is approximately 95% of the basic salary, covers these areas as well as security and other staffing. All connected sources specify a four-shift system.

Table 11.3: Labour cost based on Aden et al. [342]

Aston University

Illustration removed for copyright restrictions

In comparison to Aden et al. [342], Spath reduce the workforce by approximately 30%, in order to reflect differences in the process technology, particularly the feed preparation. In addition to this, management and administration undergo streamlining. Phillips and Swanson adjust these figures to the required base year. The adjustments are made using data from the Bureau of Labor Statistics [350]. Swanson does not include the labour figure for some unknown reason. Converting the total labour cost from 2005 US$ to 2009 £, gives an annual labour cost of approximately £1.59M for a workforce of 54 people. Applying the general overhead (95%) increases the labour cost to £3.11M.

Huisman et al. use a slightly different approach by assuming a five-shift operation. In terms of the labour requirements, there are managerial staff as well as an additional 15 people included as “staff”, which covers departments like security. 41 operators and 3 process engineers are employed as well as a plant manager. The salaries, shown in Table 11.4 include taxes, pension, shift compensation and overtime.

Table 11.4: Labour requirements and salaries [16]

Converting the total to 2009 £ gives an annual labour cost of £4.36M, which is a considerable increase on the data used by Spath, Phillips and Swanson. Although Huisman specifies a larger workforce, the cost per worker (CPW) (£69,164) is still significantly higher than Spath, Phillips and Swanson (£57,556). The primary factor affecting the CPW is the use of a ‘standard’ £53,465 (€60,000) salary, which is applied across a wide range of job titles. In some cases, this is not a suitable approximation, particularly for administration.

11.2.4 Land Costs

The cost of land can be difficult to calculate accurately since the layouts of chemical plants can vary significantly. According to Huisman, the area required is almost entirely dominated by the space required for the biomass storage. The authors estimate that for a hydrogen production plant, based around a 980 tpd (dry) gasifier, requires 2.19 ha for fuel storage, handling and drying, 0.48 ha for the syngas production plant and 0.08 ha for the hydrogen production plant. The cost ranges between £1.2M and £1.3M, based on an assumed ground price of £0.45M per ha (50€m^{-2}) for an industrial location is used. The authors acknowledge that the exact price will strongly depend on the location and infrastructure required. This method is however only suitable for this particular scale of production plant and would require significant adjustments to account for the different equipment layouts.

A simplified method is presented by Spath, which is used by Phillips, Swanson and Perales. The cost of land is presented as a percentage (6%) of the TPEC, which is taken in the first year of construction.

11.2.5 Working capital

Working capital is calculated in several ways. Spath and Phillips specify it is 5% of the TCI, whilst Swanson assumes a working capital of 15% of fixed capital investment. Together the working capital and fixed capital make up the TCI. Perales however, express the working capital as equivalent to one month's operating costs. No reason is given for this assumption.

11.2.6 Additional revenue

Several papers under review discuss the potential of additional revenue from the sale of secondary products, such as district heat, in order to increase the project rate of return. In the case of Huisman, the sale of district heat is used as the basis for calculating the price of the various final products. A district heat price of £58 /MWh (€65 /MWh) is used, based on Veab [351]. Phillips and Perales include the sale of other alcohols, which are produced during ethanol production. In some cases the sale price of these alcohols are more economically attractive than ethanol, though Phillips states that the production rates are small. Swanson however generates electricity as a co-product. In most cases, the additional revenue is presented as co-product credits.

11.2.7 Concluding remarks

Generally, it is agreed that biomass gasification can potentially produce a range of cost-competitive chemical outputs, however, there are limitations. Bridgwater states that '*gasification technology needs to be demonstrated at a sufficient scale to be technically* *and financially acceptable'* [343, p. 29]. According to AEA, large-scale biomass gasification may encounter limits to the supply of feedstock due to land constraints.

Overall, the TPC and feedstock costs are the two main drivers in the cost of the end-product. In terms of gasification technology, Swanson concludes that the use of entrained flow gasification results in higher TPC than fluidised bed, though the technical performance is superior. Perales believe that pressurised O_2 production and pressurised gasification feeding both require further development to make entrained gasification more competitive.

Several recommendations have been made in order to reduce the feedstock cost. Huisman suggests the use of a cheaper feedstock, preferably wood or agricultural waste. Swanson agrees, stating that utilising a feedstock with a lower ash content will result in a more attractive product price. Spath suggests that altering the steam to feedstock ratio has a significant effect on the product selling price. Alternatively, Huisman believes the use of a larger scale of production reduces the overall production cost, though Bridgwater states that this has its limitations, since multiple equipment items will be required after a certain scale.

12 Objectives and methodology (ammonia)

The purpose of this study is to produce a techno-economic assessment, evaluating the production of anhydrous ammonia from biomass-derived syngas. It is the intention of this assessment to define the most technically feasible and economically attractive production route, in order to manufacture biomass-based fertiliser in and for the UK.

The study assesses the overall production process, from the delivery of the feedstock to the processing of the ammonia product, and comprises of the following objectives:

- To propose a range of scale case studies, in order to identify the most suitable scale of production for the UK.
- To evaluate and select the most technically feasible biomass gasification processes, which produce a syngas that is suitable for ammonia production.
- To develop and model an ammonia production process based on the biomass syngas specification and current production practises.
- To calculate mass, energy and power balances for each of the case studies.
- To compile a full economic evaluation for each case study in order to produce an ammonia production cost, which will identify the most promising systems.
- To assess the economic suitability and determine the most favourable and unfavourable conditions using sensitivity analyses.
- To identify the current boundaries of ammonia production in the UK.

Techno-economic studies of biomass-derived ammonia production are either out of date or non-existent. Most of the studies reviewed in Chapter 11 have similar scopes, which can be summarised as follows:

- The conversion of biomass-derived syngas into a range of chemical products is achievable.
- A single gasifier supplies syngas to a product production plant.
- The operating scale of the gasifier is between 980 tpd (dry) and 2,400 tpd.
- The feedstock is commonly wood chip.
- Additional revenue from the sale of co-products can potentially increase the rate of return of the process.

It is the intention of this techno-economic assessment to go beyond these boundaries, in order to evaluate the potential of UK based ammonia production from biomass-derived syngas.

12.1 Biomass-based ammonia production

As described in Chapter 11, biomass gasification has the potential to produce a range of chemicals and fuels at commercial-scale. In most cases, the systems are developed through process modelling, which uses fossil fuel-based processes as the foundation, adapting the system to suit the specification of the biomass syngas.

Currently, commercial-scale ammonia production operates using fossil fuels as the feedstock. As discussed in §10.1.1, the feedstock undergoes a six stage process to produce ammonia. These stages are:

- Sulphur removal
- CH_4 conversion (normally SMR)
- Water gas shift
- CO_2 and H_2O removal
- Methanation
- Ammonia synthesis (Haber Bosch)

Biomass-derived syngas will require a similar level of processing in order to convert or remove the quantities of CH_4, CO, CO_2, H_2O and H_2S that are normally produced during gasification.

Commercial scale biomass gasification processes are designed to produce and utilise syngas as part of a closely coupled system. Therefore, theoretically, ammonia may be produced by replacing the natural gas pipeline with the biomass preparation and gasification processes, which in turn feed syngas into the conditioning and synthesis stages.

There are two distinct approaches that may be adopted to create the necessary syngas composition for ammonia synthesis (an H_2-N_2 mixture in a 3:1 volumetric ratio). In the first, the gasification and gas conditioning stages aim to produce the necessary composition directly, within the primary product gas stream. This may be achieved in a number of ways depending on the gasification technology used, and may involve the use of enriched-O_2 air. In the second, the gasification and gas conditioning stages aim to produce pure H_2, which is then subsequently mixed with pure N_2 to achieve the necessary composition. This route usually requires pure O_2, and therefore full air separation.

12.2 Biomass gasification

In the studies described in Chapter 11 entrained flow, fluidised bed and indirect gasification processes were under investigation. For this work, the selection is based on scale potential and syngas composition.

12.2.1 Selected systems

12.2.1.1 Entrained flow gasification

Entrained flow gasification has been selected due to its commercial availability using coal and its potential for biomass utilisation. The process uses O_2 as the oxidising agent and operates at high temperatures, which are above the ash melting point. This results in the production of a comparatively clean syngas since the ash is removed as slag. The syngas is also CH_4-free; therefore, CH_4 reforming will not be required, reducing the number of process stages.

The process does have a relatively low cold gas efficiency (the chemical energy of the syngas if reduced back to cold conditions), and will require air separation technology. One option is to operate with full air separation so that the gasification and gas conditioning product is H_2, which is then mixed with N_2 from the air separation stage to achieve the correct composition. Nevertheless, it may also be possible to operate with O_2-enriched air instead, so that the gasification and gas conditioning product is the correct H_2:N_2 mixture. This may however increase the size of the process equipment due to N_2 dilution. This has the advantage that the scale and cost of air separation is significantly reduced, but it would be necessary to ensure that the gasification temperature remains above slagging level.

12.2.1.2 Indirect gasification

Indirect gasification is the process most often reviewed in Chapter 11. This is because the process itself does not require air separation technology while producing a nearly N_2-free syngas. The FICFB gasification process (§10.2.4.4.) operates successfully using biomass, though at relatively small-scale (43 tpd). However, increasing the scale of operation is seen as quite practicable within limits [352]. The syngas in this case does include CH_4; therefore a CH_4 reforming stage will be necessary.

12.2.2 Rejected systems

Although direct fluidised bed gasification has proven a successful technology at large-scale, the syngas composition is not as suitable for ammonia production as entrained flow or indirect. In order to allow the bed to fluidise, the process must operate at temperatures below the ash melting point, which normally requires using air as the oxidising agent. However, using air produces a syngas with an excessive N_2 content, so that the syngas would need to undergo an N_2 separation, requiring air separation technology.

Regardless of oxidising agent, the low operating temperature of the fluidised bed results in the production of a more complex gas, which contains a significant amount of tar [301] as well as some CH_4. Therefore, further reforming and/or partial oxidation would be necessary.

12.3 Scale of production

Ammonia production plants normally operate between 1,000 tpd and 2,000 tpd [256]. In this study, ammonia production is initially limited to a maximum capacity of 1,200 tpd, in order to account for current limitations of biomass usage, primarily the availability of feedstock [136].

Four operating cases will undergo investigation in order to assess the suitability of various gasification configurations and production rates. The cases are:

- Case 1: Large-scale entrained flow gasifier feeds a large-scale (1,200 tpd) ammonia plant.
- Case 2: Multiple small-to-medium scale FICFB gasifiers feed a large-scale (1,200 tpd) ammonia plant.
- Case 3: Small-to-medium scale FICFB gasifier feeds a small-scale (<100 tpd) ammonia plant.
- Case 4: 1,200 tpd ammonia plant fed with a mixed feed of natural gas and FICFB derived syngas, based on a feed ratio of 90:10 natural gas/biomass syngas.

It is unlikely that an ammonia production plant could operate commercially at the current FICFB gasifier unit scale (<50 tpd biomass), even when utilising multiple units. Therefore, for this work, the scale is increased by a factor of 5 to approximately 620 tpd, which is considered realistic [352]. The scaling is applied linearly and reductions in heat losses have not been included.

12.4 Methodology

12.4.1 Process modelling

In order to establish the feasibility of and obtain mass, energy and power balances for the case studies, process models of the gasification and ammonia production processes are required. These will be developed using the ASPEN Plus® flowsheeting package.

ASPEN Plus® is a FORTRAN-based steady-state chemical process simulator, developed by the Massachusetts Institute of Technology (MIT) [353]. The software features a large number of unit operations and process equipment, which are referred to as “blocks” [354, 355]. It also has an extensive physical property database, based on data compilations by the American Institute of Chemical Engineers [355, 356], in addition to convergence algorithms for closed loop system calculations. This means that specifying the operating conditions and the flow of material, heat, and work streams makes it possible to represent a process plant in ASPEN Plus® [355].

This software is widely used, especially in energy and chemical production [357]. It has also been used to simulate coal fed gasification as part of an Integrated Gasification Combined Cycle (IGCC) system [355, 358-361], as well as individual processes such as CO_2 removal, partial oxidation and water gas shift [356, 358, 362-364].

ASPEN Plus® will be used to model the full ammonia production process downstream of the gasification stage. It will also be used to model the entrained flow gasification process, since the conversion process corresponds closely to equilibrium conditions. This allows the use of the available equilibrium models with reasonable confidence [365]. However, the FICFB gasification process is not modelled using ASPEN Plus®, since the reacting environment is far from equilibrium [220]. Instead, T U Wien have generously provided a full operational account for the gasification process, which is used to produce mass, energy and power balances in Microsoft Office Excel 2007®.

12.4.2 Assessment criteria

There are a number of criteria to compare chemical production systems, which combine both capital and operating costs. In Chapter 11, several studies refer to a product minimum selling price, which is the minimum price the plant must get for its product in order to cover only construction and operating costs. This is calculated by estimating the total fixed and variable costs over the plant lifetime and then dividing by the annual production rate of the product.

However, the biomass-derived ammonia will be competing primarily with imported fossil fuel based ammonia, therefore it is necessary to assess whether the system will be economically attractive when providing ammonia at a competitive price. This is achieved by setting a price and a TRR, which is then compared with the calculated ROR of the cases presented in this work.

For this study, the following costs will be included in the assessment:

- Total plant costs (TPC).
- Fixed and variable operation and maintenance costs, including labour, overheads and supplementary fuel costs.
- Costs related to the transportation of feedstock.

The following costs will be excluded:

- Additional revenue from the sale of CO_2, steam and district heat.
- Costs related to the growing of feedstock.
- Costs related to the decommissioning and demolition of the plant after its 20-year lifespan.
- Government subsidies.

TPC data is corrected for scale using the equation 4.1 (§4.3.2).

Again, a scaling factor of 0.65 is used. In terms of biomass applications, Boerrigter [169] state that a scaling factor between 0.6 and 0.7 are suitable for moderate to large conversion plants. In the studies under review in Chapter 11 values for n range from 0.574 to 0.75. All data are adjusted to 2009 (January) UK £ prices using either plant cost index US CECPI (1957-1959 = 100) or a relevant rate of inflation.

12.4.3 Target rate of return (TRR)

For a novel biomass-based process, a TRR of 20% (real basis) is assumed in order to assess the financial viability of such a project. Given that typical values for established processes range from 6% to 15% [366, 367], this is a reasonable target.

13 Process configurations (ammonia)

The case studies presented in §12.4 do not exist as real biomass-fed plants; therefore the process performance needs to be assessed before the process configurations can be implemented. To do this the overall process is divided into a series of sub-systems, these are:

- Feedstock handling – reception, storage, drying, size reduction and feeding
- Syngas production – biomass gasification, air separation, syngas cleaning and compression
- Gas conditioning and ammonia synthesis – gas conditioning, ammonia synthesis and ammonia storage

Each sub-system has been investigated prior to this study, therefore published literature and data are available. Once the sub-system configurations are determined, the process plant may be modelled to produce mass, energy and power balances.

13.1 Feedstock handling

All cases operate using standard wood chip of typical size 30-40 mm (maximum dimension), which is the preferred feedstock for the FICFB and demonstration scale entrained flow gasifiers [303, 368]. It is also the most commonly utilised feedstock in Chapter 11. The composition, shown in Table 13.1, is adapted from data provided by TU Wien [352] and is presented on a dry basis. Additional information is taken from references relevant to Pröll [352] [44, 288].

Table 13.1: Wood chip composition

Proximate analysis	wt% (dry)
Ash	1.0
Moisture	0.0
VS	83.2
FC	15.9
Ultimate analysis	wt% (daf)
C	50.4
H	6.2
O	43.1
N	0.3
S	<0.1
HHV (MJ/kg)	19.9

Since the availability of forestry biomass and waste wood within the UK is limited [369, 370], the use of imported wood chip is assumed.

Wood chip is procured from the Northern State forests of Poland, which has high biomass production potential and convenient export routes [371, 372]. The logistics information is shown in Table 13.2.

Table 13.2: Feedstock logistics

Stage	Transport	Distance travelled (km)
Forest roadside to wood chipper	Truck/road	40 (roundtrip)
Wood chipper to storage	Truck/road	40 (roundtrip)
Storage to port (Gdansk)	Rail	170
Gdansk (port) to Felixstowe (port) [244]	Ship	1,350
Port to plant	Truck/road	32 (roundtrip)
Total (km)	-	1,632

In all cases, the ammonia production plant is situated no more than 16km (10 miles) from a port. The feedstock arrives at the plant in chip form, with a moisture content of 35 wt% (wet) [373].

The feedstock handling systems are relatively simple and are adapted from previous biomass gasification studies.

13.1.1 Reception and storage

The feedstock is delivered by truck 230 days annually during standard business hours. The trucks pass through reception, and are weighed upon entering and exiting the plant. The wood chip is then deposited on concrete slab, which acts as the storage bay until the feedstock is reclaimed for processing [343]. The slab provides sufficient elevation for excess water drainage. The wood chip stockpile also includes an additional five days wood chip in order to reduce process disruption if deliveries cannot be met. The structure of the plant's wood chip transportation system is not specified.

13.1.2 Drying

Since the as-received moisture content of the wood chip is 35 wt% (wet), feedstock drying is required. In this study, the entrained flow and FICFB gasification processes operate using wood chip with a moisture content of 12 wt% (wet) and 20 wt% (wet) respectively.

Standard drying methods are often used which are limited in efficiency but relatively well established. Rotary kilns, fluid bed and steam dryers have all been used successfully with biomass, using waste heat [142]. In order to improve the overall process efficiency, the dryers operate wherever possible using recovered process heat, which is either in the form of steam or flue gas.

In this study, two dryer types will be considered, a superheated steam dryer (SSD), and a rotary drum dryer. The SSD operates using high-pressure steam (250°C, 30 bar), using enough steam to dry the material and maintain the steam conditions [374]. Approximately 90% of the steam is re-circulated, whilst the remaining 10% is removed and condensed, which represents the water separated from the biomass [375, 376]. Rotary drum dryers on the other hand use process flue gas, which is contacted with the feedstock in a rotating drum, which improves the heat and mass transfer [374]. Any possible feedstock contamination from the flue gas is assumed to be negligible.

13.1.3 Size reduction and feeding

The feedstock particle size is an important consideration, since a reduction in size can under certain circumstances increase the syngas yield and improve the carbon conversion efficiency of the process [290].

The FICFB gasifier operates satisfactorily without further reduction in the wood chip particle size; therefore, the feedstock is fed directly to the gasifier after drying. The gasifier feeding system operates at atmospheric pressure and consists of a hopper, conveyors (screw and bucket) and a metering bin [303].

Entrained flow gasification requires a small particle size, therefore a hammer mill is used to reduce the particle size to <2 mm [377]. The feedstock is then transported to the gasifier, where it is fed under pressure (30 bar). This process will require specialist feeding equipment, which will entail an additional cost.

13.2 Syngas production

As discussed in Chapter 12, two gasification processes are under investigation, entrained flow and indirect (FICFB). The following sections describe these processes.

13.2.1 Entrained flow gasification

In this study, pressurised entrained flow gasification is under investigation. Operating at high temperatures and pressures produces a tar-free syngas in which the fuel gases are CO and H_2 only, which simplifies downstream gas cleaning and conditioning and removes the intermediate compression stage before synthesis [378].

The technology is based on the Shell Coal Gasification Process (SCGP), which is a dry-fed pressurised process operating at 1200-1600°C and 30-40 bar [379]. Conventional operation is with pulverised coal and 95 vol% purity O_2 from a dedicated ASU, with heat removal to maintain the required temperature.

In the case of ammonia production, the syngas requires a specific N_2 content so it would be advantageous to save on separation costs and supply O_2-enriched air of the correct composition to the gasifier rather than high purity O_2. It will be necessary to determine what this correct composition needs to be, and to ensure that it is sufficiently O_2-rich to maintain the required gasification temperature of 1200°C assumed here (note that in practice the temperature may need to be slightly higher depending on the biomass ash slagging characteristics). In terms of pressure, the system operates at 30 bar, which reduces compressor loading prior to ammonia synthesis.

After gasification, the syngas passes through a cyclone to remove solid particulates. No further gas cleaning is required before gas conditioning. The syngas is then cooled to 400°C, producing high-pressure process steam (250°C, 30 bar), which is fed into a process steam loop. The ash is collected from the bottom of the gasifier as slag, which is treated as solid waste.

13.2.1.1 Air separation

The major factor impeding the use of O_2 gasification is the cost of the gas itself, which is either imported or produced in onsite facilities, resulting in additional investment costs [288]. Onsite air separation facilities are widely used in medium- and large-scale gasification plants (non-biomass) due to the considerable O_2 demand and the high risk of disruption to operation should problems occur within the supply chain [176].

The most common method of air separation is cryogenic distillation, which separates air via compression, drying, cooling and distillation, producing O_2 and N_2 [176]. Cryogenic air separation is the most mature separation technology, producing O_2 at +99 vol% purity. It is economically feasible for large-scale operation and has excellent by-product capability, producing high purity N_2 and Argon streams without additional processing [380].

In this study an ASU is used to produce O_2 at 30 bar, which is then mixed with a pressurised (30 bar) air stream to obtain the correct level of enrichment. This method is more economically attractive than producing the enriched gas within the ASU because a smaller separation unit is required, reducing the TPC.

13.2.2 Indirect gasification

In this study, indirect gasification is based on the FICFB process (§10.2.4.4). This twin bed indirect gasification system, developed by TU Wien, operates using internally connected gasification and combustion zones. The bed material is circulated between the two zones, acting as the heat carrier [381]. The FICFB forms part of the 8 MW CHP plant

(Figure 13.1) in Güssing, Austria, where it has the capacity to meet the total electrical demand of the area [314].

Figure 13.1: FICFB CHP process [303]

The gasification unit is a compact construction, which reduces heat losses [314]. The system uses some of the heat recovered from the gas streams internally for steam production and stream pre-heating [303, 382], whilst the remaining heat is used for district heating [383]. Any combustible waste from the system is recycled to the gasifier combustion zone as an additional source of fuel [303, 384]. A small portion of the clean syngas is also fed into the combustion zone as part of a recycle loop [303]. Utilising syngas and waste in the combustion zone provides enough heat to sustain the process satisfactorily. The only waste streams leaving the plant are the clean flue gas and the feedstock ash.

Wood chip is fed into the system at a moisture content of 20 wt%, and is gasified in the presence of steam (250°C) [352] at 850-900°C and atmospheric pressure [303]. The char is circulated to the combustion zone by the bed material to provide process heat, which is then fed back into the gasification zone. The bed material used is olivine, which is made of silicon, iron and magnesium oxides (39.2 wt% SiO_2, 18.8 wt% FeO, and 42.1 wt% MgO) [385]. Additional bed material is fed into the gasifier to compensate for losses [352].

Two gas streams leave the gasification unit, the raw syngas and the combustion flue gas [383]. The raw syngas is cooled to 150°C prior to cleaning, condensing both H_2O and tar and recovering process heat [303, 383]. The heat is recovered using a pressurised water (11 bar) heat exchanger [352]. The condensed H_2O is used to produce steam for the gasification process [383].

The cooled gas stream is passed through a fabric filter to remove dust. The filter has a particle separation efficiency of +99% and a tar separation efficiency of 20-30% [311].The filtered solid is fed into the combustion zone as additional fuel [383].

After filtration, the syngas stream enters a scrubber that utilises an oil wash, in this case rape methylester (RME) [311]; to reduce tar, ammonia and acid gas impurity levels [383].The syngas temperature is also reduced to approximately 40°C [382].The spent scrubber liquid is vaporised to regenerate the RME and the tar and condensate liquor is fed into the combustion zone as additional fuel. A make-up stream of fresh RME is supplied continuously to the scrubber to compensate for losses during regeneration [303]. The syngas then passes through a blower, leaving the gas cleaning process at 62°C and ~1 bar [352]. The gas, shown in Table 13.3, comprises mainly of H_2, CO and CO_2.

Table 13.3: Indirect syngas composition

	vol%
H_2	35.5
CO	21.3
CO_2	20.6
CH_4	10.0
N_2	1.7
H_2O	7.9
C_3H_8	0.8
C_2H_4	2.2
H_2S	<0.1

The flue gas leaves the combustion zone and passes through a cyclone before leaving the gasifier [303]. The gas is then cooled from 997°C to 158°C and heat is recovered for a range of uses, such as biomass drying and steam production. The cooled gas is then filtered and sent to stack [303]. The composition of the flue gas at the stack, shown in Table 13.4, is comparatively similar to conventional combustion flue gas [383].

Table 13.4: Indirect flue gas composition [352]

The feedstock ash is collected from the flue gas filter and the bottom of the gasifier. Since the carbon content of the ash is relatively low (<0.5 wt%), it is similar to biomass combustion ash and can therefore be treated as such, which is advantageous in comparison to other gasification processes [303, 384].

13.3 Gas conditioning and ammonia synthesis

In §12.2 two distinct approaches for ammonia production are outlined, these are:

- Producing the necessary composition directly within the primary gasification and gas conditioning stages
- Producing a H_2 gas stream during the gas conditioning stages, that is then mixed with pure N_2 to obtain the correct H_2:N_2 ratio

For Case 1, the entrained flow gasification process operates using O_2-enriched air as the oxidising agent, which allows the required H_2:N_2 level to be achieved, provided enrichment is properly controlled. Therefore, the syngas conditioning process may be adapted from the conventional ammonia production system for natural gas. However, the syngas does not contain CH_4 or higher hydrocarbons, therefore the reforming stages are not required.

For Cases 2 and 3, the presence of CH_4, higher hydrocarbons and tars in the syngas results in either steam methane reforming (SMR) or partial oxidation being required, both of which require air or O_2 as the oxidising agent. Using O_2 would require air separation technology; however, the residual N_2 could be added to the syngas downstream, producing the required H_2:N_2 composition. Alternatively, air may be used as the oxidising agent. If the flow of air is properly controlled, the required H_2:N_2 gas composition may be achieved without the need for air separation technology. The syngas conditioning process can then be adapted from the conventional ammonia production system.

Case 4 comprises of two separate gas conditioning streams, which are merged prior to ammonia synthesis. The natural gas stream will undergo conventional ammonia production technology, described in §10.1.1.1, which includes SMR in order to convert the large volume of CH_4 into CO and H_2. The biomass syngas stream is produced using the indirect gasification technology used in Cases 2 & 3; therefore, the gas conditioning process used in these cases may be used for Case 4.

13.3.1 Gas conditioning

The purpose of the gas conditioning process is to convert or remove gas components that are either harmful to the Haber Bosch process or are an unconverted source of H_2. Differences in the syngas composition from the two gasification processes will result in differences in the gas conditioning process; however, certain processes such as water gas shift, H_2S removal, CO_2/H_2O removal, methanation and compression will be required for all cases. In all cases, gas conditioning operates at 30 bar, which reduces the compression loading prior to the Haber Bosch process.

The following sections discuss the conditioning processes, which are required for each case.

13.3.1.1 Methane conversion

The syngas in Cases 2, 3 and 4 will contain CH_4, which will require conversion via SMR or partial oxidation (described in §10.1.1.1.2 and §10.1.1.2 respectively).

The choice of methane conversion technology depends on the syngas composition. For instance, the two-stage SMR process is more suitable for converting a large volume of CH_4, such as in natural gas (Case 4). The biomass syngas produced by the indirect gasifier contains significantly less CH_4 (~85% less) than natural gas, therefore a single stage partial oxidation conversion process is sufficient for Cases 2 and 3. In this study, TPO operating between 1300°C and 1500°C is under investigation for CH_4 conversion since the process is tolerant to H_2S and does not require a catalyst. The CH_4 is converted in the presence of air, which if properly controlled will provide the correct amount of N_2 for the N_2:H_2 ratio. However, the temperature reached may not be sufficient and may require supplementary indirect heating from natural gas combustion. In addition, the gas will contain more CO than H_2 as well as a higher CO_2 content than the gas produced from SMR [265].

13.3.1.2 Water gas shift

All case studies require water gas shift, which converts the CO into H_2 and CO_2 in the presence of H_2O. In this study, the two-stage shift process, described in §10.1.1.1.3, is used since the syngas contains a significant amount of CO. The high and low temperature water gas shift stages operate at 400°C and 200°C respectively. The HTS stage occurs in the presence of high pressure steam (250°C, 30 bar) and can be performed before H_2S removal since the catalyst is tolerant. However, the LTS stage uses a nickel-based catalyst that can be poisoned by H_2S, requiring prior removal.

13.3.1.3 H_2S removal

In this study, the sulphur is normally in the form of H_2S, which may be removed as part of an acid gas removal (AGR) system which removes H_2S and CO_2 from the gas stream, or as a standalone process, as described in §10.1.1.1.1.

This study assumes the standalone method, which operates at 400°C using a zinc oxide bed. This technology provides flexibility in terms of its location within the gas conditioning process.

13.3.1.4 CO_2/H_2O removal

The CO_2 is removed by chemical adsorption using MEA. The solvent composition is assumed to be 30 wt% MEA, 70 wt% H_2O, which is seen as the maximum safe concentration to use since higher concentrations lead to equipment corrosion [363]. The process operates at approximately 60°C [362], with an adsorption rate of 0.4 mole CO_2 absorbed per mole of MEA is used [362, 386 & 387], and a CO_2 removal efficiency of 98 wt% is assumed [388]. The solvent undergoes regeneration at 120°C using steam before being recycled, and a make-up stream compensates for losses. The condensate, which comprises mainly water, is removed either before or after scrubbing.

13.3.1.5 Methanation

Methanation is carried out at 300°C [264] and converts residual CO and CO_2 into CH_4, which is inert within the Haber Bosch process.

13.3.1.6 Compression

After methanation, the gas is compressed to from 30 bar to 130 bar, ready for ammonia synthesis. In this study, the compression is completed in four stages in order to reduce the loading.

13.3.1.7 Heat recovery

Heat recovery is performed within the gas conditioning process where possible. In this study, the recovered heat is used to produce process steam. The cases use both high and low pressure steam either as a process stream or for heating. The steam is generated and sent to a steam loop, from where it is sent to the required locations. Since two types of steam are in use two steam loops are in operation, the high-pressure loop and the low pressure loop.

13.3.2 Ammonia synthesis and storage

Ammonia synthesis is performed using the Haber Bosch process, which operates at 130 bar and has an ammonia conversion efficiency of 98% overall [269]. In this study, the product removal and storage are presented as black box processes, though the relevant costs are included. In general, the ammonia is removed from the gas stream using a water scrub and is sent to refrigerated storage [264].

13.4 Case Configurations

The following sections outline the process configurations for each case. At this stage, Cases 2 and 3 are presented as one section since the configurations are the same.

13.4.1 Case 1

Figure 13.2 presents the process configuration for Case 1. Firstly, the biomass is dried, milled and fed into the entrained flow gasification unit. After gasification, the syngas undergoes heat recovery, reducing the temperature from 1200°C to 400°C. The cooled gas then enters the HTS reactor, followed by H_2S removal, which prepares the gas for the LTS stage. Additional heat recovery is also performed at this stage reducing the gas temperature from 400°C to 200°C. The syngas then enters the LTS reactor to complete the shift process.

After further heat recovery (200°C to 60°C), the syngas undergoes CO_2 and H_2O removal. In this study, CO_2 removal is performed first, followed by H_2O removal. This is because CO_2 removal is better performed at a higher temperature due to equipment loading [387]. It is acknowledged that this process will increase the scale of the CO_2 removal unit; however, the overall impact is considered negligible. At this stage, the syngas is predominantly H_2, N_2 and H_2O.

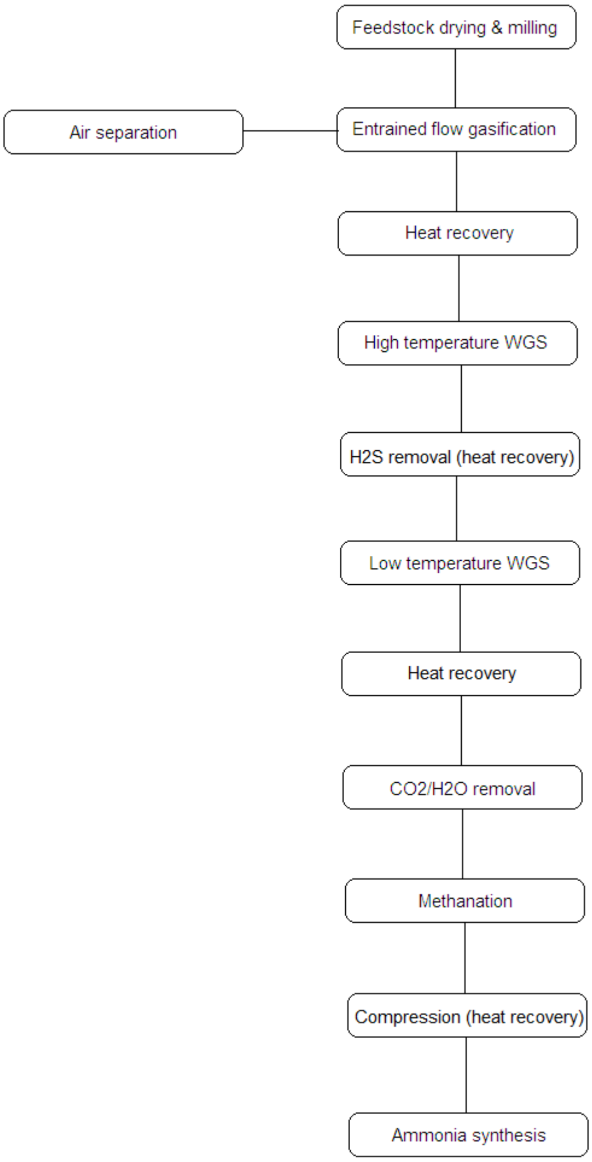

Figure 13.2: Case 1 process configuration

Methanation is then performed in order to convert residual CO and CO_2 into CH_4 followed by compression. The conditioned gas then enters the ammonia synthesis reactor to produce ammonia. The ammonia is separated from the recycle loop and sent to storage.

13.4.2 Cases 2 and 3

Figure 13.3 presents the process configurations for Cases 2 and 3. The biomass is dried and fed into the indirect gasification and gas cleaning system. The syngas is then compressed to 30 bar. Heat recovery is not performed afterwards since the increase in stream temperature is beneficial for TPO, which operates at >1300°C.

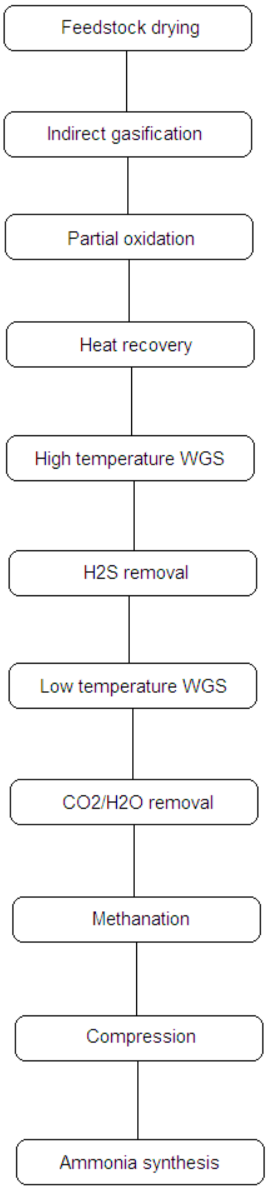

Figure 13.3: Cases 2 and 3 process configurations

After TPO, the process configurations continue the same as Case 1.

13.4.3 Case 4

Case 4 has the most complex process configuration because two ammonia production processes are used. As described in §12.4, the plant operates using natural gas and biomass syngas as the feedstock. The feedstock split is based on the ammonia output, which results in the ammonia produced being 90 wt% natural gas and 10 wt% biomass syngas derived. As discussed, the two feed streams are conditioned separately and merged before ammonia synthesis, meaning that the natural gas stream could continue to run if the biomass stream went down. Theoretically, biomass syngas could be added at various stages in the gas conditioning process. In this study, two options are considered, these are:

1. Fully condition the biomass syngas, as presented in Cases 1, 2 and 3 and add just before ammonia synthesis (after compression) – using this option will mean that there will be two streams of gas conditioning operations, which will have a significant impact on the TPC. However, since the natural gas route does not require modification an existing plant may be refitted, reducing costs.
2. Partially condition the biomass syngas and add at the HTS stage – this option reduces the number of process units required, though some conditioning (compression, partial oxidation, and H2S removal) is needed. H_2S removal is required since the natural gas undergoes desulphurisation prior to SMR. As with Option 1, an existing plant may be refitted, however the process will be more complex and may increase the TPC.

The process configurations are presented in Figure 13.4 and 13.5.

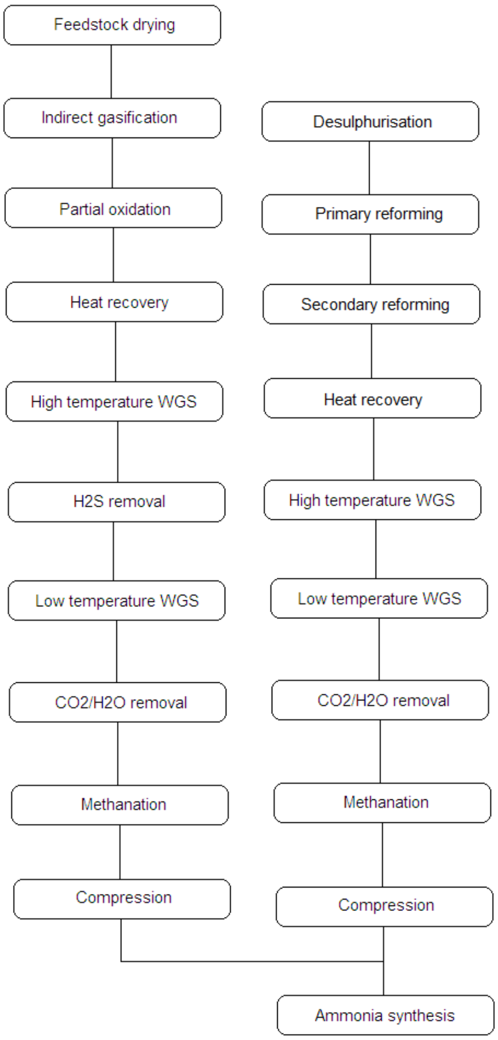

Figure 13.4: Case 4 process configurations (separate route)

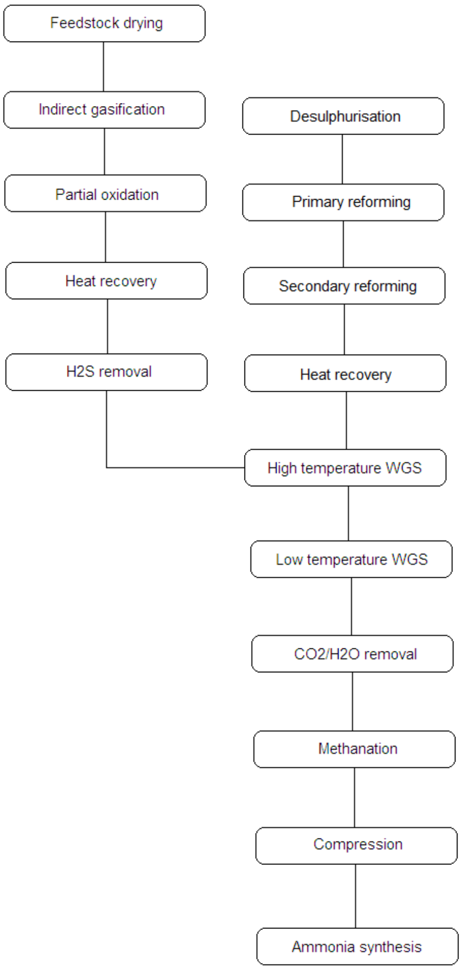

Figure 13.5: Case 4 process configuration (HTS route)

The natural gas input arrives by pipeline at 15°C and 30 bar [389]. It is assumed that the natural gas undergoes processing prior to arrival. The natural gas undergoes desulphurisation (400°C) before entering the primary (600°C) and secondary (1000°C) reformers. After this, the gas is cooled to 400°C it fed into the HTS reactor where it is mixed with the biomass syngas.

For biomass syngas production, the biomass is dried and fed into the indirect gasification and gas cleaning system. The syngas then enters the partial oxidation unit (1300°C) followed by heat recovery (1300-400°C). Finally, the gas undergoes H_2S removal before being fed into the HTS reactor.

After the streams are combined in the HTS reactor, the gas conditioning process continues with LTS, CO_2/H_2O removal, methanation, compression and ammonia synthesis.

14 Process modelling (ammonia)

Process modelling is used to determine the mass, energy and power balances. The following sections discuss the modelling of the process technology, leading to the presentation of the mass, energy and power balances for each case.

As discussed in §12.5.1, process modelling is carried using ASPEN Plus® (2006.5) and Microsoft Excel©. Table 14.1 presents the template and setting details used for ASPEN Plus® modelling.

Table 14.1: ASPEN Plus® model template and settings

Template	Engineering with metric units (SICBAR)
Base method	Ideal
Flowrate units	kg/h &kmol/h
Component units	Mole-frac (kmol) & Mass-frac (kg)

In all cases, the ASPEN Plus® models operate using a nominal specified feedrate. The numerical outputs obtained are used in the Excel model, which also scales the data to represent the required ammonia production rate of each case (98 tpd and 1,200 tpd). All models are subjected to direct linear scale up, with any improvements in heat recovery/loss ignored. A list of unit modelling parameters for the cases is presented in Appendix A.

The following sections discuss the modelling of the four cases.

14.1 Case 1 (Single EF gasifier to large ammonia plant)

14.1.1 Feedstock handling

In all cases, the feedstock preparation is represented in the Excel model based on the assumptions made in Chapter 13.

The mass inputs for the SSD are the wood chip (35 wt% wet) and the high-pressure steam (250°C and 30 bar). The steam is supplied by the high-pressure steam loop and acts as an indirect heating medium to dry the wood chip. The energy demand of the process is based on the thermal energy required to evaporate the feedstock moisture. The residual steam, which is the evaporated wood chip water, is treated as wastewater.

For the hammer mill, losses in mass are assumed negligible. The electrical demand is 0.003 kW/kg [biomass] based on data by Bio Green Tech Ltd. [390].

14.1.2 Syngas production

14.1.2.1 Entrained flow gasification

Pressurised entrained flow biomass gasification has yet to be implemented at commercial scale; therefore, a suitable model must be developed in order to determine the mass, energy and power requirements. Entrained flow gasification has been modelled successfully and validated using coal feedstocks and systems [391, 392].

In this study, entrained flow gasification is modelled using ASPEN Plus®, which has been used to simulate coal-fed systems effectively [355, 359-361], using a simple equilibrium assumption based on Gibbs free energy minimisation [364, 393].

Since biomass is not included in the physical properties database for this version of ASPEN Plus®, the feedstock is treated as a non-conventional solid. The stream type is specified as mixed non-conventional (MIXNC), since particle size unknown. The gasification process is separated into two stages, shown in Figure 14.1, in order to represent the conversion of a non-conventional solid.

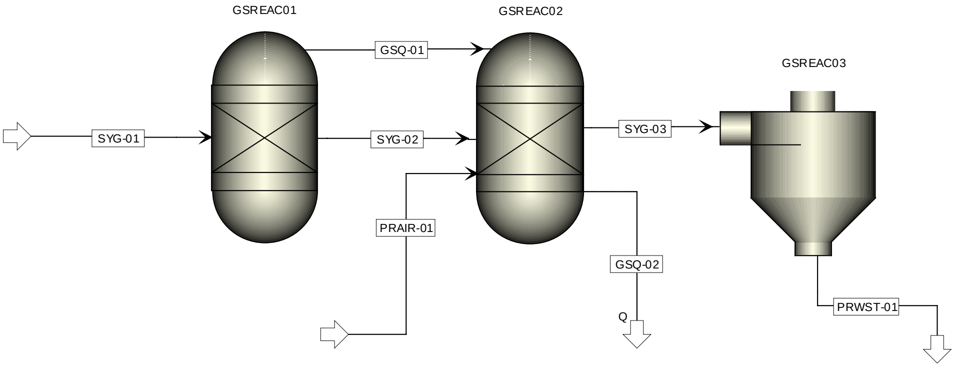

Figure 14.1: Entrained flow gasification ASPEN Plus® model

The feedstock firstly passes through a RYield reactor (GSREAC01), which decomposes the feedstock into conventional elemental components (C, H_2, O_2 etc.). After this, the components enter the RGibb reactor (GSREAC02) for gasification. In addition, a stream of pressurised oxidising agent is fed into the gasifier.

The two reactors are connected by heat stream GSQ-01 to account for the heat associated with the decomposition. Since the operation temperature is specified, an additional heat stream is required (GSQ-02) to prevent the model from assuming adiabatic operation. From this reactor the gas is fed into a cyclone to separate the ash, which is modelled as a SSPLIT block (GSREAC03). Cyclone efficiency is normally +95% [394, 395], however in this study the cyclone operates at 100% efficiency, since the level residual ash in the syngas after the cyclone is assumed to be negligible.

Validation of the model is carried out using data for the Buggenum (Demkolec) SCGP IGCC plant (now owned by NUON). The gasifier operates at 1400-1700°C (normally ~1600°C) [333, 379] and 26 bar [333], using ~1,900 tpd Drayton coal as the feedstock [379]. The coal is gasified in the presence of O_2 (95 vol%) and steam at O_2/feed and steam/feed ratios of 0.88 and 0.08 respectively [379].

A specific Drayton coal composition is not provided, though the ash and moisture contents are given to be 12.2% ash (dry), 2% moisture [379]. Instead, a composition published by [396] is used, shown in Table 14.2, which has similar ash and moisture contents.

Table 14.2: Drayton coal composition [396]

In the model, the coal is treated as a nonconventional solid (MIXNC since particle size is not known).The RYield and RGibbs blocks operate at 25°C and 1600°C respectively. The oxidising agent composition is assumed to be 95 vol% O_2, 4 vol% N_2 and 1 vol% Ar. Steam is also added at the specified steam/feed ratio. The resultant syngas composition is presented (dry basis) in Table 14.3 and compared to data published by Eurlings & Ploeg [379].

Table 14.3: Syngas composition results

	Validation model (vol%)	Demkolec (vol%)	Difference
H_2	31.3	28.4	-2.9
CO	63.4	63.4	-
CO_2	1.2	1.5	0.3
N_2	3.6	6.2	2.6
Other	0.4	0.5	0.1

The differences in the syngas composition are believed to be due to two factors.

Firstly, the chemical composition of the coal feedstock will have a significant effect on the syngas composition. Since the exact composition of the coal used for the production of the Buggenum data is unknown, replication of the results is difficult without an extensive trial and error exercise, especially since the N_2 content of the coal can vary significantly (0.3-1.8 wt%) [396-399].

Secondly, the composition of the O_2 oxidising agent will have some effect on the accuracy of the model. Whilst flowrate ratios and the purity of the O_2 (95 vol%) are known [379], the composition of the remaining 5% of the gas is unknown and subsequently assumed. This in turn will affect the amount of N_2 passing through the system, resulting in variations in the syngas product.

According to Ni & Williams [391], the O_2-to-coal ratio is the most important control variable for an entrained flow gasification model. However, this ratio is known, therefore the assumptions made regarding the feedstock composition are believed to be the cause of the variations in the syngas composition.

Nevertheless, the model simulates coal-fed entrained flow gasification satisfactorily and is suitable for use with the wood chip feedstock.

In this study, wood chip and wood chip ash are treated as two separate materials. This does not affect the operation of the model, since the overall composition of the feed stream represents the feedstock. The density and enthalpy of these materials is calculated using the ASPEN Plus® coal models DCOALIGT and HCOALGEN, which require proximate and ultimate analysis to be specified. The heat of combustion (HHV) for wood chip is specified as 19.9 MJ/kg, based on literature [47, 352].

In GSREAC01, the wood chip is separated into the elemental components shown in Table 14.4.

Table 14.4: Biomass elemental composition

Component	wt%
H_2	5.5
C	44.3
H_2O	12.1
N_2	0.3
O_2	37.9
S	303 ppm

The components then enter GSREAC02 for gasification, which is carried out in the presence of pressurised O_2-enriched air. For the model, the gasifier temperature was set as 1200°C. Upon leaving the gasifier, the syngas stream enters the cyclone GSREAC03, which removes the ash. The composition of the clean syngas is presented in Table 14.5.

Table 14.5: Entrained flow syngas composition

	vol%
H_2	22.7
CO	33.2
CO_2	9.9
H_2O	16.7
N_2	17.5
H_2S	<0.1

As shown, the syngas is predominantly CO and H_2. The stream temperature is approximately 1200°C. The cold gas efficiency is 85% on a DAF basis.

14.1.2.2 Air separation

Air separation is modelled in order to determine the flowrate and required level of enrichment of the gasifying agent. In this study, the ASU is modelled using both ASPEN Plus® and Excel.

The level of enrichment was determined using ASPEN Plus® as part of the entrained flow gasifier model. The most suitable level of enrichment would produce the correct final H_2:N_2 ratio (after methanation) at the lowest gasifier heat duty and O_2 concentration. A series of manually controlled sensitivity analyses were performed, which varied the flowrate of the oxidising agent (15-500 kmol/h at 10 kmol intervals) and the concentration of O_2 (95 vol% to 5 vol% at 5 vol% intervals). At each interval the net heat duty of the gasifier and syngas composition were recorded. It was determined that an O_2 concentration of 50-55 vol% produced the correct H_2:N_2 at the lowest gasifier heat duty and O_2 concentration. A further sensitivity analysis, which varied the O_2 concentration in 1 vol% intervals was implemented, determining an enrichment level of 53 vol% as the most suitable for this study, with the gasifier operating under slightly exothermic conditions.

This value was added to the Excel model in order to determine the required mass of air, as well as the energy and power inputs. Atmospheric air is assumed to be ~20 vol% O_2, 79 vol% N_2 and ~1 vol% “other”. No thermal energy is required during separation, although the power demand is 175 kWh/t [O_2], which is from data published by Beysel [400].

14.1.3 Gas conditioning and ammonia production

Since the CH_4-free syngas leaves the gasifier at 1200°C and 30 bar, compression and stream pre-heating are not required. Therefore, after heat recovery (§14.1.5) the syngas undergoes water gas shift.

14.1.3.1 Water gas shift

This reaction approaches equilibrium, and in literature there are examples of water gas shift reactors modelled using both RGibbs and REquil blocks [358, 401]. However, since the reaction scheme is relatively simple the REquil model is the more commonly used [220, 358, 364 & 402], sometimes using a 10°C (50°F) temperature approach [402]. Figure 14.2 presents the water gas shift system, including the integrated H_2S removal and heat recovery stages.

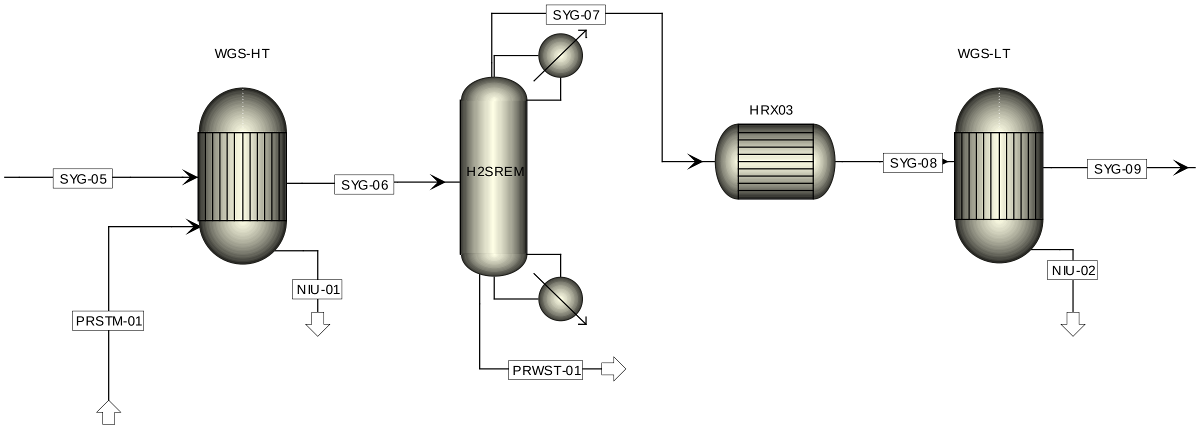

Figure 14.2: Water gas shift system

As shown, there are two additional exit streams (NIU-01, NIU-02), which are required by the model but are not used. The HTS (WGS-HT) and LTS (WGS-LT) blocks operate at 400°C and 200°C respectively. Additional steam (250°C) is fed into WGS-HT, controlled by a design specification, which ensures a CO content of approximately 0.3 vol% (dry) after WGS-LT [264]. The heat duty of both blocks is significantly exothermic, corresponding with Harding [267], producing additional process heat via heat recovery.

14.1.3.2 H_2S removal

The H_2S removal unit H2SREM (Figure 14.2) is modelled as a separator (Sep2), which represents the zinc oxide bed. The syngas stream enters at 400°C, the correct operating temperature for the zinc oxide bed and it is assumed that all H_2S is removed and treated as solid waste. No additional energy or power is required to complete the process.

14.1.3.3 CO_2/H_2O removal

Chemical adsorption of CO_2 using MEA has been modelled successfully using ASPEN Plus$^{®}$ [362, 363 & 403]; however, the process is often presented as a complex model, which involves multiple-stage splitters requiring a significant amount of chemical data. Here, the ASPEN Plus$^{®}$ model (Figure 14.3) is simplified to a separator (CO2R01), which splits the CO_2 from the gas in the presence of the solvent, feeding the loaded solvent into the regeneration process. Energy consumption data is adapted from literature and used in the energy balances, therefore the process is represented with reasonable accuracy.

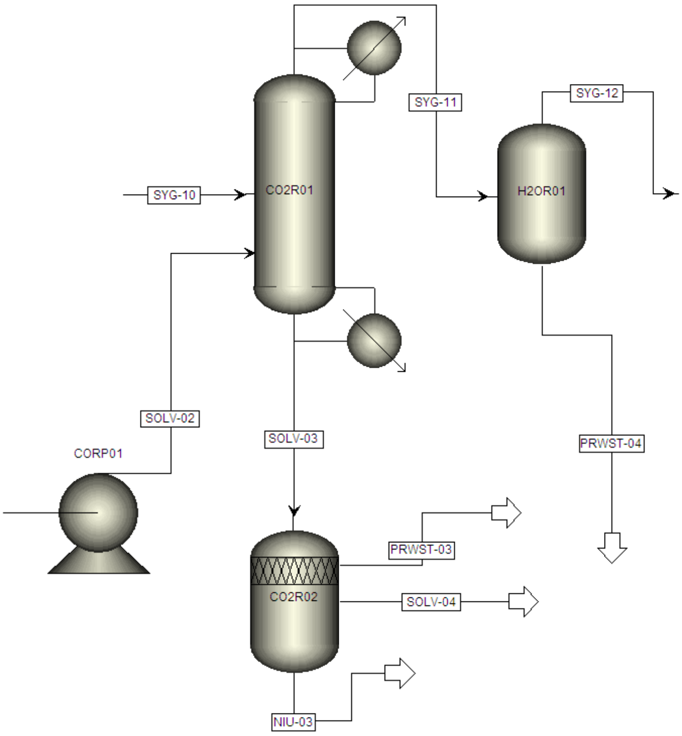

Figure 14.3: CO_2 and H_2O removal system

There are two exit streams from the CO_2 separator; the CO_2-free syngas (SYG-11) and the loaded solvent (SOLV-03).Some water loss is recorded in the syngas stream, though this is comparatively small.

The loaded solvent stream is sent to a flash drum (CO2R02), which decompresses the stream to 1.2 bar, subsequently separating the gas and liquid phases. The gas stream is 92 wt% CO_2, with the remaining balance comprising of solvent vapour. In literature, stream purities of >99% can be achieved [388]; therefore some additional cleaning will be required before use. The lean solvent undergoes regeneration at 120°C [362, 386] using process steam from the low-pressure steam loop (~126°C).

The regeneration energy is calculated in the Excel model, based on work completed by Chakma [385], who state that the energy required for regeneration is represented as:

Total energy = Heat of reaction + Sensible heat + Latent heat of vaporisation of H_2O *+*
Latent heat of vaporisation of solvent (MEA)

where the enthalpy and heat of vaporisation of a 30 wt% MEA solution are 72 kJ/mol of CO_2 and 826 kJ/kg respectively [387]. The regenerated solvent is then compressed to 30 bar, ready for use. Losses are assumed to be ~0.5 wt%, which are compensated for by an equivalent solvent makeup stream.

The H_2O removal stage (H2OR01) is modelled as a flash drum (Flash3), which operates at 40°C. The wastewater stream also contains small amounts of CO, CO_2, H_2 and N_2; however, the losses do not significant impact on the production of ammonia. Power is required for the solvent pump.

14.1.3.4 Methanation

In this study, methanation is modelled as an RGibbs reactor (METH01), which produces selected products only in order to prevent premature ammonia production. The selected products are H_2, CO, CO_2, H_2O, N_2 and CH_4. The reaction is endothermic; however, heat is supplied by process heat recovery.

This process is endothermic; however, the demand is met using recovered process heat. The methanised syngas stream at this stage comprises of H_2 (17 wt%), CH_4 (2 wt%), H_2O (4 wt%) and N_2 (77 wt%).

14.1.3.5 Compression

Compression prior to ammonia synthesis is completed in four stages in order to reduce the overall loading. The stages are completed in 25 bar increments (55 bar, 80 bar, 105 bar, 130 bar) and heat recovery is performed between each stage (Figure 14.4).

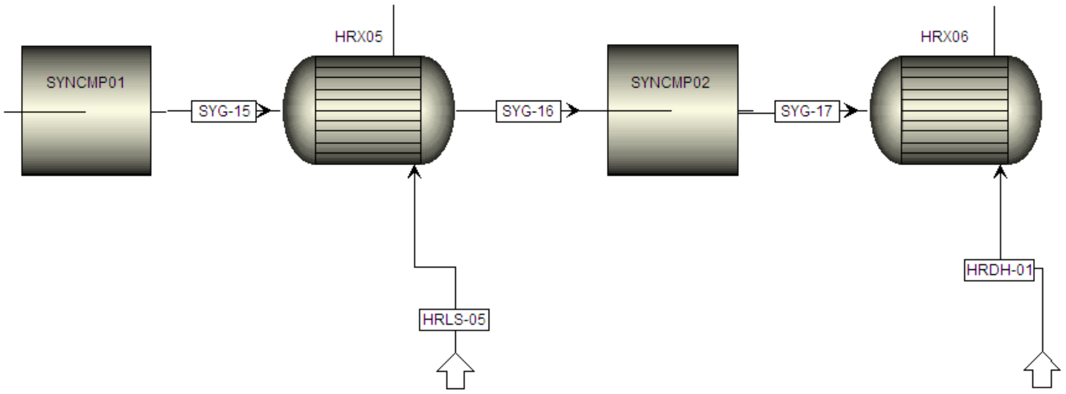

Figure 14.4: Compression with heat recovery stages (partial section)

The compressors are modelled as isentropic, with an isentropic efficiency of 80%.

14.1.3.6 Ammonia synthesis

As discussed in §10.1.1.1.6, N_2 and H_2 are converted to ammonia using the Haber Bosch reaction:

$$N_2 + 3H_2 \leftrightarrow 2NH_3 \qquad (10.8)$$

The ammonia conversion efficiency is assumed as 98% [269]. Since the process equation and the conversion efficiency are known, the ammonia synthesis reactor is modelled using an RStoic block, as shown in Figure 14.5.

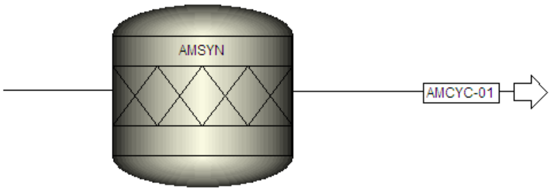

Figure 14.5: Ammonia synthesis reactor

The outlet stream AMCYC-01 is 94 wt% ammonia and 6 wt% unreacted products, which is predominantly H_2O and CH_4.

14.1.4 Heat recovery

In Case 1, heat recovery is performed using water to produce high and low pressure steam and district heat, which is defined in §6.4.4 as water heated to 90°C. All heat exchangers are modelled as counter-current.

The high-pressure steam loop (Figure 14.6), which produces superheated steam at 250°C and 30 bar, comprises of HRX1 (heat recovery after gasification) and HRX2 (heat recovery after H_2S removal).

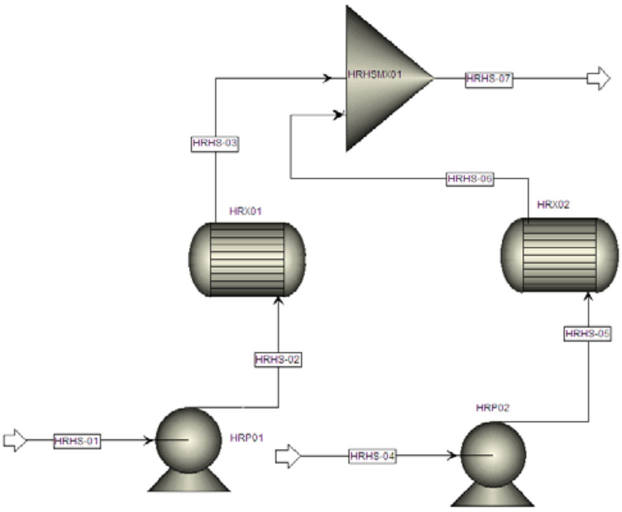

Figure 14.6: High-pressure steam loop

Pumps HRHSP01 and HRHSP02 supply the pressurised water, whilst the steam streams are mixed using a mixer block (HRHSMIX01) representing the steam loop. The pump power demand is calculated by ASPEN Plus® based on an isentropic efficiency of 80%.

The low-pressure steam loop produces saturated steam at approximately 125°C and 1.2 bar, which is used to provide heat to endothermic process units. The steam is raised using heat recovered from several process units in addition to specific heat exchangers. Table 14.6 presents data for the sources of low-pressure steam.

Table 14.6: Low-pressure steam cycle sources

Source	Location	Temperature of steam (°C)	Percentage of overall production (%)
HRX3	After LTS	104.8	22.7
HRX4	After methanation	108.9	7.7
HRX5	During compression	104.8	23.2
HRSR	During solvent regeneration	105	35.4
Ammonia synthesis (AMSYN)	-	300	7.7
LTS (WGS-LT)	-	175	1.3
HTS after methanation heating (WGS-HT)	-	310	2.0
Average (°C) / Total (%)	-	*125.2*	100.0

These data are a combination of results from the ASPEN Plus® model (heat recovery heat exchangers) and the Excel model (process unit heat recovery).

District heat is produced during the final compression stage from heat exchangers HRX6, HRX7 and HRX8.

14.2 Cases 2 & 3 (Multiple FICFB to large ammonia plant & Single FICFB to small ammonia plant)

14.2.1 Feedstock handling

As described in §13.1.2, Cases 2 and 3 utilise a rotary drum dryer, which operates using process flue gas. The mass inputs for the Excel model are the wood chip (35 wt% water) and the flue gas (1166°C, 1.2 bar), which is derived from the numerous pre-heating systems implemented.

The flue gas/wood chip ratio is approximately 0.93 kg/kg wood chip, which increases to 1.15 kg/kg wood chip at the dryer exit due to the additional condensate. The wood chip condensate is treated as wastewater. The energy demand of the process is calculated based on the temperature required to convert the moisture into steam.

14.2.2 Syngas production

14.2.2.1 Indirect gasification

As discussed in §13.5.1, the indirect gasification process is represented in the Excel model, based on data provided by T U Wien.

During gasification, the mass inputs are wood chip and steam (492°C), in addition to the air (510°C) and recycled combustible materials that are fed into the combustion zone. Olivine is also added to compensate for losses in the bed, which is assumed to have a composition of ~39 wt% SiO_2, ~19 wt% FeO and 42 wt% MgO. In this study, the gasifier operates at 850°C at atmospheric pressure and it is assumed that all char is used for combustion. The outputs are the syngas (850°C), the flue gas (997°C) and the biomass ash, which is calculated by difference.

During gas cleaning, the mass inputs are the syngas, pre-coating material (filtration) and fresh RME (scrubbing). The outputs are the filtrate and spent RME scrub products, both of which are fed into the gasifier (combustion). The syngas (Table 13.3) leaves the process at approximately 62°C. Approximately 13 wt% of the syngas is recycled to the gasifier as part of the combustible materials. For the flue gas cleaning system, the only output is the flue gas filtrate, which is treated as solid waste.

The overall system is exothermic, with the heat recovered from the raw syngas and flue gas generating the necessary steam and hot air required for the process stages. The gasifier is supplied with char and combustible materials for combustion, therefore no external heat sources (natural gas etc.) are required. The cold gas efficiency is 76%. The overall power requirement of the system is approximately 12.5 MW.

14.2.3 Gas conditioning and ammonia synthesis

14.2.3.1 Stream compression and preheating

After gas cleaning, the syngas is compressed to 30 bar using an isentropic compressor block (SYNCMP01), increasing the syngas temperature to 537°C. Heat recovery is not performed since the increase in stream temperature reduces the thermal demand of the partial oxidiser. A stream pre-heating system (Figure 14.7) is also implemented to increase the stream temperature in order to achieve the correct H_2:N_2 ratio during TPO.

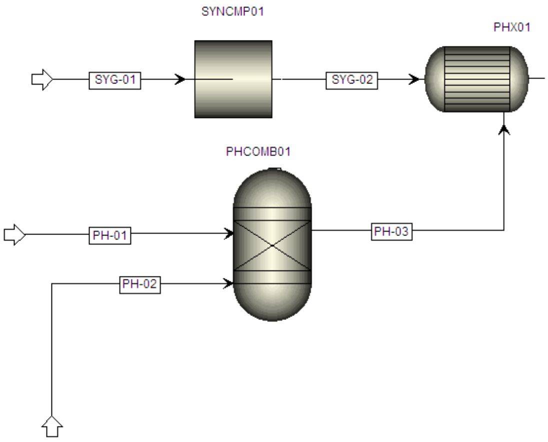

Figure 14.7: Compression and pre-heating model

As shown, the preheating system is modelled as a simple combustor, where natural gas is combusted with air using an RGibbs reactor (PHCOMB01), allowing all products. Since the composition of natural gas can vary significantly, a generic composition based on published literature [404, 405], shown in Table 14.7, is used.

Table 14.7: Natural gas composition

	vol%
CH_4	95.0
C_2H_6	4.9
C_3H_8	2.5
n-butane	2.5
H_2S	0.1

The natural gas/O_2 ratio is 0.4:1 (kmol). The temperature of the combustor is controlled by a design specification, which specifies a temperature difference of 55°C between the flue gas and the heated gas. This is done by varying the flow of natural gas to the combustor. The syngas leaves the preheating system at 1115°C and the flue gas at 1170°C, which is used for heat recovery.

Like the syngas, the air required for partial oxidation is preheated via the combustion (PHCOMB02) of natural gas under the same conditions. In this case the air is heated to 1097°C, producing a flue gas of 1152°C, which again is used as a source of heat.

14.2.3.2 Partial oxidation (TPO)

In this study, TPO (Figure 14.8) is modelled using an RGibbs (PARTOX01), which has been used to successfully model the process with natural gas [356]. The model operates at 1200°C and 30 bar, with the possible products specified since premature production was noted in earlier tests.

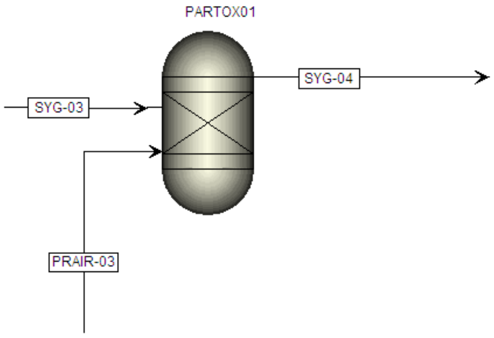

Figure 14.8: Partial oxidation model

A design specification controls the flow of pre-heated air in order to produce the correct N_2:H_2 ratio, whilst still completing the oxidation process. The net-duty of the partial oxidiser is significantly endothermic, as dictated in literature, though the heat demand is lower in comparison to SMR (§14.3.3.2).

14.2.3.3 Gas conditioning and ammonia synthesis

The remaining process stages (WGS, $H_2S/CO_2/H_2O$ removal, methanation, compression and ammonia synthesis) are modelled under the same conditions as Case 1.

14.2.4 Heat recovery

Like Case 1, high and low-pressure steam and district heat are produced from heat recovery throughout the process.

The high-pressure steam loop, (250°C, 30 bar) comprises of HRX2 (heat recovery after TPO) and HRX3 (heat recovery after H_2S removal). Pressurised water is supplied by pumps HRP01 and HRP02 and the steam streams are mixed by HRHSMIX01, which represents the steam loop.

The low-pressure steam loop produces saturated steam at 134°C and 1.2 bar to provide heat to endothermic process units. The steam is raised using heat recovered from several process units in addition to specific heat exchangers, shown in Table 14.8.

Table 14.8: Low-pressure steam cycle sources

Source	Location	Steam temperature (°C)	Percentage of overall production (%)
HRX4	Heat recovery after LTS	104.8	34.6
HRSR	During solvent regeneration	105	40.4
Pre-heating flue gas	-	130	10.4
Ammonia synthesis (AMSYN)	-	300	11.9
LTS (WGS-LT)	-	160	1.5
HTS after methanation heating (WGS-HT)	-	320	1.1
Average (°C) / Total (%)	*-*	*134*	*100.0*

Again, the data presented above is a combination of results from the ASPEN Plus® model and (heat recovery heat exchangers) and the Excel model (process unit heat recovery).

District heat is produced during the final compression stage from heat exchangers HRX5 to HRX9. In addition pressurised hot water (115°C, 11 bar) is produced during gasification and gas cleaning (HRX1) as part of the system setup [352].

14.3 Case 4 (Scaled FICFB and Natural gas to large ammonia plant)

14.3.1 Feedstock handling

The feedstock handling system for both configurations is modelled as for Cases 2 and 3 (§14.2.1).

14.3.2 Syngas production and preparation

The gasification and gas-cleaning systems for both configurations are modelled as for Cases 2 and 3 (§14.2.2).

For configuration 1, the syngas then undergoes compression, pre-heating, TPO, water gas shift, CO_2/H_2O removal, methanation and finally compression, all of which have been discussed in the previous sections. The syngas that joins the natural gas stream is ready to enter the ammonia synthesis reactor.

For configuration 2, the syngas is again compressed, pre-heated and sent to the TPO; however, after this the syngas undergoes H_2S removal and is then fed into the HTS reactor of the natural gas route. Since the catalysts required for SMR contain nickel, the natural gas stream undergoes desulphurisation first. Since the sulphur is in the form of H_2S a zinc oxide bed is used, as discussed in §14.1.3.2.

14.3.3 Gas conditioning and ammonia synthesis

In both configurations, the primary production route is the natural gas route. This is modelled as a conventional SMR system based on data collected from several working ammonia plants.

14.3.3.1 Steam methane reforming (SMR)

The SMR (Figure 14.9) reactors are modelled as RGibbs reactors (SR01 and SR02), operating at 800°C and 1200°C respectively.

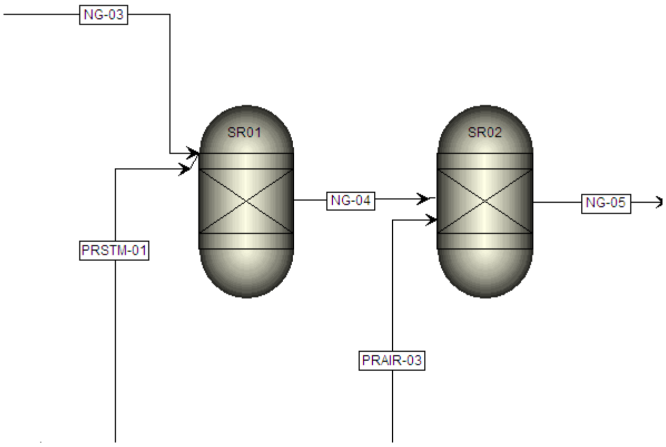

Figure 14.9: The SMR reactors

The mass inputs are the natural gas and the pre-heated air stream (600°C), which is fed in to the secondary reformer. Since the process is endothermic, heat energy is required for both units, which is supplied by the combustion of additional natural gas. Heat is recovered from the subsequent flue gases.

14.3.3.2 Ammonia production

The remaining process stages (WGS, $H_2S/CO_2/H_2O$ removal, methanation, compression and ammonia synthesis); including the addition of biomass syngas, are modelled as for Cases 1, 2 and 3.

14.3.3.3 Pre-heating systems

In total, there are six pre-heating systems for Case 4, which are required for SMR, TPO and air preheating. These systems produce five pre-heating streams since two smaller streams are combined.

14.3.4 Configuration selection

The selection of the most suitable configuration is based on the comparison of the mass, energy and power balances.

In terms of mass, most of the mass inputs/outputs, including the wood chip requirement, are the same. However, there are some variations in the inputs, which are shown in Table 14.9 in kg/kg [NH_3].

Table 14.9: Differences in configuration mass inputs in kg/kg [NH_3]

	Configuration 1	Configuration 2
Natural gas	0.53	0.52
Water for steam	1.14	1.13
MEA solvent circulation	1.73	1.56
Air	3.67	3.70

Apart from the increased air requirement, configuration 2 demands less natural gas, water and solvent than configuration 1. The large demand for MEA solvent for configuration 1 is due to the process operating two separate removal systems, which, as shown, is not as attractive as using a single unit. A reduction in natural gas demand is economically attractive since the price can fluctuate significantly.

The energy balance is roughly the same, each requires 4 kW/kg [NH_3] and produces 5 kW/kg [NH_3] therefore, there is no gain or loss with choosing the processes. The power balance however is different. Configuration 1 requires ~0.4 kWh/kg [NH_3], whilst configuration 2 requires ~0.3 kWh/kg [NH_3]. The increased demand for configuration 1 is due to the separate compression stages both gas streams undergo before ammonia synthesis.

Since there is a general reduction in process requirements, configuration 2 is selected as the most suitable and will therefore be considered as Case 4 from this point.

14.3.5 Heat recovery

Heat is recovered in the form of high and low-pressure steam and district heat for both Case 4 configurations. High-pressure steam is produced from heat exchangers HRX1 (after SMR), HRX2 (after HTS natural gas route), HRX9 (after TPO biomass route) and HRX10 (after H_2S removal biomass route).

Low-pressure steam is produced from various heat sources, as shown in Table 14.10.

Table 14.10: Low-pressure steam cycle sources

Source	Location	Steam temperature (°C)	Percentage of overall production (%)
Gasification flue gas	-	130	13.7
HRSR	During solvent regeneration	105	40.3
Ammonia synthesis (AMSYN)	-	300	20.6
LTS (WGS-LT)	-	120	2.3
HTS (WGS-HT)	-	250	6.1
Pre-heating flue gas (1)	-	200	3.6
Pre-heating flue gas (2)	-	200	1.8
Pre-heating flue gas (3)	-	200	0.2
Pre-heating flue gas (4) (after methanation)	-	200	7.7
Pre-heating flue gas (5)	-	200	3.6
Average (°C) / Total (%)	*-*	*164*	*100.0*

As before, the data presented above is a combination of results from the ASPEN Plus® model and (heat recovery heat exchangers) and the Excel model (process unit heat recovery).

District heat is produced from the remaining heat exchangers, although pressurised hot water (11 bar) is produced after gasification for both configurations.

14.4 Catalyst

Catalyst data for ammonia production are difficult to obtain, particularly since the operating pressure range can vary. In this study, the catalyst data are required for costs and do not affect the overall performance of the process since the catalysts only accelerate the conversions.

Some data was available from Crawford et al., [275]; however, this is for an atmospheric pressure system. According to Harding [267], operating at elevated pressures reduces the amount of catalyst required, though by how much is uncertain.

Comparing literature provides an approximation, for instance work by Swanson et al. [220] can be adapted to determine that a 26 bar WGS process would use ~3 vol% (per tonne) of the catalyst volume of an atmospheric reactor [275] based on the volumetric flowrate and an assumed gas hourly space velocity (GHSV). However, this may not be the case for the remaining processes.

In this study, data published by EFMA [264] for a 1,500 tpd plant is adapted to provide an approximate estimation of the catalyst requirements (Table 14.11). Additional information regarding bulk density is taken from BASF Catalysts [268] and Engelhard Catalysts [406].

Table 14.11: Catalyst data

Catalyst	Requirement (t)
Primary reforming	10,350
Secondary reforming	19,672
Sulphur removal	12,000
HTS	24,000
LTS	48,000
Methanation	4,800
Ammonia synthesis	8,000

The catalyst beds are replaced every 3 years [16].

14.5 Mass, energy and power balances

14.5.1 Mass

Table 14.12 presents the mass balance data in kg/kg [NH_3] for Case 1.

Table 14.12: Case 1 mass balance per kg ammonia product

DRYING (SSD)			
Input (kg/kg[NH_3])		Output (kg/kg[NH_3])	
Wood chip (35 wt% wet)	2.71	Wood chip (12 wt% wet)	2.00
Steam	0.65	Residual steam/ water vapour	1.36
GASIFICATION (ENTRAINED FLOW)			
Wood chip (12 wt% wet)	2.00	Syngas	3.74
Enriched air (53% O_2)	1.76	Ash	0.02
AIR SEPARATION (53 wt% O_2)			
Air	4.22	Enriched air	1.76
-	-	Other products	2.46
AMMONIA PRODUCTION			
Syngas	3.74	*Ammonia*	*1.00*
Steam	1.19	H_2S	<0.01
Solvent make-up	0.02	Waste water	0.70
-	-	Synthesis recycle	0.07
-	-	CO_2	3.16
-	-	Solvent losses	0.02
CIRCULATED MATERIAL (kg/kg[NH_3])			
MEA solvent			4.15
Catalyst			2.93
Process water			7.66
HP steam cycle (residue)			0.44
LP steam cycle (residue)			2.04

As shown, 2.71 kg wood chip (35 wt% wet) produces 3.74 kg syngas, which in turn produces 1 kg ammonia. Regarding the overall system, the largest input is the air required for air separation, whilst the largest output is the CO_2 removed during MEA adsorption. In terms of the circulated material, a considerable amount of process water is required to feed the three heat recovery systems, discussed in §14.1.4, followed by the solvent circulation.

Table 14.13 presents the mass balance data in kg/kg [NH_3] for Cases 2 and 3.

Table 14.13: Cases 2 and 3 mass balance per kg ammonia product

DRYING (ROTARY DRUM)			
Input (kg/kg[NH_3])		Output (kg/kg[NH_3])	
Wood chip (35 wt% wet)	3.18	Wood chip (20 wt% wet)	2.58
Flue gas	2.96	Flue gas & residual liquid	3.56
GASIFICATION (INDIRECT)			
Wood chip (20 wt% wet)	2.58	Syngas	1.87
Steam	0.62	Ash	0.08
Air	4.56	Flue gas	5.51
Additional fuel	1.44	Flue gas filtrate	0.45
Fresh bed and coating material	0.21	Tar	<0.01
Fresh solvent (RME)	0.02	Bed material losses	0.01
-	-	Waste for additional fuel	1.44
AMMONIA PRODUCTION			
Syngas	1.87	*Ammonia*	*1.00*
Steam	1.19	H_2S	<0.01
Solvent make-up	0.02	Wastewater	0.68
Natural gas	0.15	Synthesis recycle	0.07
Air	3.86	CO_2	2.34
-	-	Pre-heating flue gas	2.96
-	-	Solvent losses	0.02
CIRCULATED MATERIAL (kg/kg[NH_3])			
MEA solvent			3.07
Catalyst			2.93
Bed material			72.51
RME			37.95
Process water			39.10
HP steam cycle (residue)			0.73
LP steam cycle (residue)			1.65

In these cases, 3.18 kg wood chip (35 wt% wet) produces 1.87 kg syngas, which in turn produces 1 kg ammonia. Like Case 1, the largest input is the air for gasification, whilst the largest output is the gasification flue gas, which is a valuable source of heat energy. The circulated material requirement is far greater for these cases, since additional materials, such as RME and the olivine gasification bed, need consideration. Again, a considerable amount of process water is required to feed the three heat recovery systems.

Table 14.14 presents the mass balance data in kg/kg [NH_3] for Case 4.

Table 14.14: Case 4 mass balance per kg ammonia product

DRYING (ROTARY DRUM)			
Input (kg/kg[NH_3])		Output (kg/kg[NH_3])	
Wood chip (35 wt% wet)	0.32	Wood chip (20 wt% wet)	0.26
Flue gas	0.94	Flue gas & residual liquid	1.00
GASIFICATION (INDIRECT)			
Wood chip (20 wt% wet)	0.26	Syngas	0.19
Steam	0.06	Ash	0.01
Air	0.46	Flue gas	0.55
Additional fuel	0.14	Flue gas filtrate	0.04
Fresh bed and coating material	0.02	Bed losses	0.01
Fresh solvent (RME)	<0.01	Waste for additional fuel	0.14
-	-	Tar	<0.01
AMMONIA PRODUCTION			
Syngas	0.19	*Ammonia*	*1.00*
Steam	1.08	H_2S	<0.01
Solvent make-up	<0.01	Wastewater	0.44
Natural gas	0.52	Synthesis recycle	0.06
Air	3.24	CO_2	1.32
-	-	Pre-heating flue gas	2.27
-	-	Solvent losses	<0.01
CIRCULATED MATERIAL (kg/kg[NH_3])			
MEA solvent			1.56
Catalyst			2.54
Bed material			7.25
RME			3.80
Process water			5.39
HP steam cycle (residue)			0.44
LP steam cycle (residue)			2.03

For Case 4, 0.4 kg natural and 0.32 kg wood chip (35 wt% wet) are required to produce 1 kg ammonia. Once again, the largest input for the system is air, whilst the largest output is the pre-heating flue gas, which is a valuable source of heat energy. The circulated material requirement is more comparable with Case 1, since the mass requirement for gasification is far smaller than Cases 2 and 3.

14.5.2 Energy

Table 14.15 presents the energy balance data in kW/kg [NH_3] for Case 1.

Table 14.15: Case 1 energy balance kW/kg [NH_3]

HEAT DEMAND			
	Temperature (°C)	kW/kg NH_3	Source
Steam for SSD	250	0.51	HP steam cycle
Steam to HTS	250	0.91	HP steam cycle
Heat for solvent regeneration (CO_2 removal)	120	2.47	LP steam cycle
Heat for solvent make-up preheating (CO_2 removal)	65	<0.01	LP steam cycle
Heat for solvent decompression (CO_2 removal)	65	0.18	LP steam cycle
Heat for methanation	300	0.20	LP steam generated by HTS
Total demand	-	*4.27*	-
AVAILABLE HEAT			
	Temperature (°C)	kW/kg NH_3	Use
HP steam cycle	251	-1.52	Process steam
LP steam cycle	125	-4.39	Process steam
HTS	400	-0.40	Heat to methanation & LP steam
CO_2 removal	65	-2.47	Exportable product
District heat	~90	-0.26	Exportable product
Total available	-	*-9.04*	-
Net available	-	*-4.77*	-

The process is exothermic and is able to meet the SSD demand and still export a surplus of steam and hot water.

Table 14.16 presents the energy balance data in kW/kg [NH_3] for Cases 2 and 3.

Table 14.16: Cases 2 and 3 energy balance kW/kg [NH_3]

HEAT DEMAND			
	Temperature (°C)	kW/kg NH_3	Source
Heat to rotary drum dryer	104	0.43	Pre-heating flue gas
Steam to FICFB	492	0.58	Flue gas heat recovery
Air pre-heating (FICFB)	47-510	0.55	Flue gas heat recovery
Steam to HTS	250	0.90	HP steam cycle
Heat for solvent regeneration (CO_2 removal)	120	1.83	LP steam cycle
Heat for solvent make-up preheating (CO_2 removal)	65	<0.01	LP steam cycle
Heat for solvent decompression (CO_2 removal)	65	0.13	LP steam cycle
Heat for methanation	300	0.21	LP steam generated by HTS
Heat to TPO	*1200*	*Natural gas combustion*	
Total demand	-	*4.63*	-
AVAILABLE HEAT			
	Temperature (°C)	kW/kg NH_3	Use
Gasification flue gas	997	-1.69	Stream pre-heating
Pre-heating flue gas	1166	-1.01	Rotary drying & LP steam cycle
HP steam cycle	274	-1.57	Process steam
LP steam cycle	134	-1.32	Process steam
HTS	400	-0.32	Heat to methanation & LP steam cycle
CO_2 removal	65	-0.04	Exportable product
District heat	~90	-0.39	Exportable product
Total available	-	*-6.34*	-
Net available	-	*-1.71*	-

The heat demand of TPO is not included in the total energy demand since it is an external heat source. As shown, the overall system is exothermic, although natural gas combustion is required for TPO, which is an endothermic process that cannot be met by recovered heat.

Table 14.17 presents the energy balance data in kW/kg [NH_3] for Case 4.

Table 14.17: Case 4 energy balance kW/kg [NH_3]

HEAT DEMAND			
	Temperature (°C)	kW/kg NH_3	Source
Heat to rotary drum dryer	104	0.04	Pre-heating flue gas (2)
Steam to FICFB	492	0.06	Flue gas heat recovery
Air pre-heating (FICFB)	47-510	0.05	Flue gas heat recovery
Steam to primary reformer	300	0.27	HP steam cycle
Steam to HTS	250	0.57	HP steam cycle
Heat for solvent regeneration (CO_2 removal)	120	1.03	LP steam cycle
Heat for solvent make-up preheating (CO_2 removal)	65	<0.01	LP steam cycle
Heat for solvent decompression (CO_2 removal)	65	0.08	LP steam cycle
Heat for methanation	300	0.22	Pre-heating flue gas (4)
Heat to TPO	*1200*	*Natural gas combustion*	
Heat to primary reformer	*800*	*Natural gas combustion*	
Heat to secondary reformer	*1200*	*Natural gas combustion*	
Total demand	-	*2.32*	-
AVAILABLE HEAT			
	Temperature (°C)	kW/kg NH_3	Use
Gasification flue gas	997	-0.82	Stream pre-heating
Pre-heating flue gas (2)	1166	-0.21	Rotary drying & LP steam cycle
Pre-heating flue gas (4)	1255	-0.42	Methanator & LP steam cycle
HP steam cycle	331	-1.18	Process steam
LP steam cycle	~164	-2.00	Process steam
CO_2 removal	65	-0.02	Exportable product
District heat	~90	-0.38	Exportable product
Total available	-	*-5.03*	-
Net available	-	*2.71*	-

As shown, the overall system is exothermic; however, a considerable amount of natural gas combustion is required.

14.5.3 Power

14.5.3.1 Case 1

Imported electrical power is required for the hammer mill, air separation, and compression of the syngas prior to ammonia synthesis and for pumping water for specific heat recovery stages. The total electricity requirement for the system is 0.36 kWh/kg [NH_3].

14.5.3.2 Cases 2 and 3

For Cases 2 and 3, imported electrical power is required for the FICFB gasification system, compression of the syngas prior to the TPO and ammonia synthesis stages in addition to pumping water for specific heat recovery stages. The total electricity requirement for the system is 0.93 kWh/kg [NH_3].

14.5.3.3 Case 4

Imported electrical power is required for the FICFB gasification system, compression of the syngas prior to the TPO and compression of the combined gas stream prior to ammonia synthesis. In addition, electricity for pumping water for specific heat recovery stages. The total electricity requirement for the system is 0.34 kWh/kg [NH_3].

14.6 Comparison of ammonia production cases

Table 14.18 presents a summary of mass inputs and outputs for comparison. Materials, such as ash and H_2S have not been included since the same feedstock composition was assumed for all cases; therefore, the figures are the same.

The difference in CO_2 outputs highlights the variation in the composition of the feed gases. For instance, it is clear from Case 4 that the natural gas route produces far less CO_2 than biomass syngas-derived ammonia production. This is due to the use of SMR, which has a lower tonnes CO_2/tonnes ammonia ratio than partial oxidation [265]. The larger output produced by Case 1 is due to the increased production of CO during gasification caused by the higher operating temperatures, which results in a higher CO_2 conversion rate during the water gas shift reaction. However, since CO_2 can be either used to produce urea or sold for additional revenue, the increased production does not have an altogether negative impact.

Table 14.18: Mass balance summary

Case	1	2	3	4
Inputs (kg/kg[NH_3])				
Wood chip (35 wt% wet)	2.71	3.18	3.18	0.32
Steam	1.84	1.81	1.81	1.14
Air	4.22	8.42	8.42	3.70
Natural gas	-	0.15	0.15	0.52
MEA solvent make-up	0.02	0.02	0.02	<0.01
Outputs (kg/kg[NH_3]				
Flue gas	-	8.47	8.47	2.82
Waste water	0.70	0.68	0.68	0.44
CO_2	3.16	2.34	2.34	1.32

From the results above, Cases 2 and 3 have the greatest wood chip requirement per kg [NH_3]. As expected Case 4 has the lowest wood chip demand, since the feed stream is predominantly natural gas. Case 1 has the highest steam requirement, mainly due to the use of a SSD for biomass drying. As shown, this results in Case 1 having the largest output of wastewater. Case 4 has the lowest air demand since the gasification system is the smallest. Cases 2 and 3 have the greatest since the FICFB process requires a considerable amount of air. In terms of natural gas usage, Case 4 understandably has the greatest requirement. Case 1 however does not require any natural gas, since the syngas does not need to undergo TPO. This is also the case for flue gas production, particularly since entrained flow gasification only produces syngas.

Table 14.19 presents the net energy results for the four cases.

Table 14.19: Energy balance summary

Case	1	2	3	4
Net energy (kW/kg [NH_3])	-4.77	-1.71	-1.71	-2.71

As shown, all processes produce excess heat energy, however for Cases 2, 3 and 4 additional heat is provided through the combustion of natural gas. Therefore, Case 1 is the most attractive process in terms of energy.

The power requirement for each case is presented in Table 14.20.

Table 14.20: Power requirement summary

Case	1	2	3	4
Power output (kW/kg [NH_3])	0.36	0.93	0.93	0.34

It is clear that Cases 2 and 3 have the highest electricity demand, mainly due to the production of syngas at atmospheric pressure resulting in the need of an additional compression system. This is also true for Case 4; however the demand is compensated by the scale of the biomass system.

In general, Case 1 is the most attractive process from a technical perspective since it requires the least amount of feedstock in comparison to Case 2. It also has the second lowest electricity demand and, more importantly does not require natural gas for process heat.

15 Process economics (ammonia)

This chapter investigates the capital and operating costs for biomass syngas derived ammonia, in order to determine the cost of production for the four cases. The economic data used are adapted from relevant literature sources, with cost averages calculated where multiple sources are available.

15.1 Project assumptions

The following sections discuss the assumptions made in order to determine the capital and operating costs.

15.1.1 Availability

The operating costs depend on the operational hours of the plant [16], which are calculated based on availability. In literature, gasifier availability varies between 85%-96% [15, 16, 220, 244 & 407], depending on gasifier type and the syngas conversion process. Ammonia synthesis availability is currently high, with 96% availability measured between 2002 and 2005 based on number of days for forced plant shutdown [408].

This study assumes an overall plant availability of 95% or 8,280 operating h/y, in order to remain competitive with fossil fuel based ammonia production. Although this is at the top end of the range of gasifier availability specified above, it can be defended on the grounds of plant scale and the associated high standard of engineering. This value will be applied to all cases, though for Case 4, gasifier unavailability will not cause production to cease as the gasifier provides only a small percentage of the feed gas.

The effect of varying the availability of the gasifier is measured as part of the sensitivity analysis (Chapter 16).

15.1.2 Plant life

According to Bartels and Pate [274], a natural gas fed ammonia synthesis plant has an expected plant life of 30 years, whilst a coal-fed entrained flow gasifier has a 25-year lifespan. However, the studies under review in Chapter 11 concur that a plant life of 20 years is suitable for biomass-derived syngas chemical production.

In this study, a plant operating life of 20 years is assumed. However, it is acknowledged that as biomass technology advances a plant life of 30 years may be achieved in the future.

15.2 Capital costs

In this study, the capital costs are separated into five sections: feedstock preparation, gasification (including air separation), gas conditioning and ammonia synthesis, land and indirect (legal, engineering, construction and contingency costs). The data presented represents the TPC, and includes equipment, materials, installation and any contingencies.

15.2.1 Feed preparation

As discussed in §13.1.1, the feed handling system is the same for all cases. The data used in this study is adapted from Swanson et al. [220], which cover the wood chip storage space and internal transportation system.

The SSD capital costs are calculated using data from Wardrop Engineering Inc. [409] and Thek & Obernberger [410], whilst the rotary dryer costs are adapted from data by Frea [411]. The cost of the hammer mill is adapted from Thek & Obernberger [410] and Hamelinck et al. [241].

15.2.2 Syngas production

Entrained flow gasification costs are derived from Swanson et al. [220] and Williamson & McCurdy [412] and include the preceding compression and feeding stages required for gasification, in addition to the subsequent ash removal stage. The costs are for a slurry-fed entrained flow biomass gasifier and a slagging entrained flow biomass gasifier with a mass feed rates of 2,000 tpd (dry), which have been scaled accordingly. The ASU cost is also adapted from Swanson et al. [220], which is based on a 735 tpd, 28 bar stand-alone unit producing 95 vol% pure O_2.

The cost of the FICFB gasification system, including gas cleaning, is adapted from Aichernig et al. [383], Bolhar-Nordenkampf et al. [384] and O'Connor [413], based on the 8 MW_{th} plant currently in operation, which is assumed to include the costs of the olivine bed material and the circulated RME. For Case 2, the costs are scaled from 8 MW_{th} to 40 MW_{th} and then multiplied by the number of units required. In addition, each gasifier requires its own gas cleaning system since a significant amount of material is recycled within the process.

15.2.3 Gas conditioning and ammonia synthesis

Gas conditioning and ammonia synthesis costs are calculated using data for a 1,361 tpd (1,500 short tpd) natural gas ammonia production plant [275], and represent the purchase cost of the individual process units and the heat recovery system. Since the operating pressure is not stated the costs are assumed to be the same for a pressurised 1,200 tpd plant. For Cases 2, 3 and 4, the cost of the TPO is assumed the same as a secondary SMR, since it operates under relatively similar conditions. The cost of installation is calculated using an installation factor of 3.02, based on Peters et al [341] cited by Swanson et al. [220]. Units requiring catalyst are supplied with a pre-installed bed, which entails an additional cost. This information is taken from Andersson et al. [414] and Crawford et al. [275].

The MEA CO_2 removal unit costs are taken from Phillips et al. [15] and Singh et al. [415] and include the cost of the circulated solvent. The subsequent water removal stage is treated as a water separator, based on Swanson et al. [220]. The purchase cost of the compressors is adapted from Swanson et al. [220], using an installation factor of 1.2.The piping, separation, electrical and control costs are all adapted from Crawford et al. [275], which represent the installed cost.

15.2.4 Indirect

The indirect costs, which include legal, construction, engineering and contingency costs are adapted from Crawford et al. [275], Spath et al. [14] and Perales et al. [237], who assume a cost range of 20-40% of the installed cost.

15.2.5 Land

The land cost is based on Swanson et al. [220] and Perales et al. [237] and is equivalent to 6% of the TPEC. This is equal to approximately 2.4% of the TIC [14].

15.3 Operating costs

15.3.1 Feedstock and logistics

It is unlikely that biomass conversion systems will operate using high cost feeds [182]; therefore, a price of £40 /t (dry) is used for the base analysis [343].

As discussed in §13.1, wood chip is imported from the Northern State forests of Poland by road, rail and sea. In this study, an external company controls the logistics; therefore, the logistics costs comprise of the charter, fuel and loading/unloading costs. Losses of feedstock during transportation are also accounted for [372].

For road travel, the charter cost is adapted from Hamelinck et al. [233], whilst the fuel cost and consumption are based on data published by the AA [231] and Coyle [230]. The cost of loading/unloading is also adapted from Hamelinck et al. [240], assuming a wood chip density of 500 kg/m^3. The number of delivery days per year is assumed as 230, based on Rogers [348].

Table 15.1 presents the logistic data for road travel.

Table 15.1: Logistics data and costs for road travel

Truck capacity	32 t
Distance travelled	112 km
Fuel consumption	8.4 mpg
Delivery days	230 d/y
Fuel cost	£1.05 /litre diesel
Charter costs	£28 /trip
Loading/unloading cost	41p /m^3

For rail travel (Table 15.2), the charter cost is adapted from Hamelinck et al. [240], whilst the fuel cost and consumption are based on data published by the AA [239] and Fact Check [416]. The cost of loading/unloading is also adapted from Hamelinck et al. [240], again assuming a wood chip density of 500 kg/m^3. The costs are assumed to be for one-way travel only, assuming that the freight train would be used to transport other materials on its return journey.

Table 15.2: Logistics data and costs for rail travel

Freight capacity	1,000 t
Distance travelled	170 km
Fuel consumption	474.9 tonne-mile/gallon
Fuel cost	£1.05 /litre diesel
Charter costs	£37 /km
Loading/unloading cost	41p /m^3

Table 15.3 presents the logistic data for sea travel.

Table 15.3: Logistics data and costs for sea travel

Cargo capacity	~42,400 t
Distance travelled	1350 km
Trip duration	2.1 days
Fuel oil consumption	44 tpd
Fuel cost	£160/ t fuel oil
Charter costs	£9,000 /trip
Loading/unloading cost	2 /t

The charter cost is adapted from Hamelinck et al. [210], whilst the fuel cost and consumption are based on data published by Top kWh [417] and Croatian Ship Building Corporation [249]. The cost of loading/unloading is also adapted from Hamelinck et al. [240]. Like freight travel, the costs are assumed to be for one-way travel only.

15.3.2 Labour

Labour requirements and costs are based on Phillips et al. [15] and operate on a four-shift system. Table 15.4 presents the labour costs for Cases 1, 2 and 4.

Table 15.4: Labour requirement and costs (Cases 1, 2 and 4)

Position	Number of workers	Annual labour cost (ex. benefits) (2009 £)
Plant Manager	1	83,848
Plant Engineer	1	49,547
Maintenance Supervisor	1	45,735
Lab Manager	1	38,113
Shift Supervisor	5	171,508
Lab Technician	2	53,358
Maintenance Technician	8	243,922
Shift Operators	20	609,805
Contractors	12	228,677
Administration	3	57,169
Total	*54*	*1,581,682*

Since Case 3 operates on a smaller scale, the workforce is considerably less, as shown in Table 15.5.

Table 15.5: Case 3 labour requirement and costs

Position	Number of workers	Annual labour cost (ex. benefits) (2009 £)
Plant Manager	1	83,848
Plant Engineer	1	49,547
Maintenance Supervisor	1	45,735
Lab Manager	1	38,113
Shift Supervisor	5	171,508
Lab Technician	1	26,679
Maintenance Technician	1	30,490
Shift Operators	5	152,451
Contractors	3	57,169
Administration	1	19,056
Total	*20*	*674,596*

The figures above refer to the basic salaries only. Benefits and non-primary staffing (security etc.) are covered under a general overhead, which is equivalent to 95% of the total basic labour cost.

15.3.3 Materials and utilities

As before, cost information for catalysts is based on Andersson et al. [414] and Crawford et al. [275]. The solvent make up cost is also taken from Singh et al. [415], which is approximately 70 p/kg pure MEA. For Cases 2, 3 and 4, the cost of natural gas is specified as 1.9 p/kWh, based on the manufacturing industry average purchase price (2009) [247].

The FICFB gasification system used in Cases 2, 3 and 4 requires additional materials as make up streams. The olivine bed material costs ~£120 /t [15], whilst the RME costs 40 p/litre [418] (assuming a density of 0.89 kg/m^3 [419]). The pre-coat material is treated as course $CaCO_3$, with a cost of £120 /t [242].

Two types of water are used in this study; mains/process water and cooling water, which cost 60 p/t and 1.5 p/t respectively. Process electricity is assumed to cost 8.31 p/kWh for large-scale industrial usage [420]. An additional cost equivalent to 10% of the overall electricity cost is included to cover overheads.

In this study, waste disposal of solid materials and wastewater is required. The solid waste comprises of biomass ash, flue gas filtrate and captured H_2S, whilst the wastewater is generated during the water removal stage. Solid disposal costs ~£17/t and wastewater treatment costs 53 p/t [15].

15.3.4 Maintenance

The maintenance cost is taken as 2.3% of the project capital, based on Bridgwater et al. [182], Peters et al. [341] (cited by [15]), Perales et al. [237 and Huisman et al. [16].

15.3.5 Other fixed costs

This covers insurance, taxes and other legal fees and is equivalent to 2% of the TPC [15].

15.4 Product revenue

Annual price figures for anhydrous ammonia are difficult to obtain. In this study, price data is adapted from US Department of Agriculture (USDA) [421], based on US anhydrous ammonia import prices over a 15 year period (1995 – 2009).

In order to offset fluctuations within the data, 5 year price averages have been calculated (Table 15.6), based on the corresponding UK £ and metric tonne capacity.

Table 15.6: Periodic anhydrous ammonia prices

Period	Price (£/t)
1995 – 1999	134.94
1995 – 2009	200.32
2000 – 2004	146.62
2000 – 2009	233.01
2005 – 2009	319.38

In addition, a 10 year (2000 - 2009) and a 15 year (1995 - 2009) average have been included to assess the economic potential over a longer period of time.

15.5 Cost of ammonia production

15.5.1 Capital cost summary

Table 15.7 presents the capital costs for Case 1.

Table 15.7: Case 1 capital costs

AREA	COST 2009 (£)	%
FEED PREPARATION	9,892,583	5.7
Storage & Handling	1,194,355	0.7
Drying	8,038,667	4.6
Milling	659,561	0.4
SYNGAS PRODUCTION	69,588,468	40.1
Air separation	21,552,278	12.4
Gasification	48,036,190	27.7
GAS CONDITIONING & AMMONIA SYNTHESIS	48,357,276	27.9
Water gas shift	1,351,711	0.8
H_2S removal	399,607	0.2
CO_2 removal	11,792,245	6.8
H_2O removal	107,463	0.1
Methanation	276,214	0.2
Ammonia synthesis	429,371	0.2
Additional facilities	34,000,666	19.6
INDIRECT COSTS	38,077,379	21.9
LAND	7,670,300	4.4
TOTAL	*173,586,007*	*100.0*

As shown, syngas production is the largest cost, particularly the entrained flow gasifier, which operates at pressure, increasing the capital [142]. For entrained flow gasification, the capital also includes a specialist feeding system to supply the feedstock at pressure. The ASU is normally worth 10-15% of the TPC [176]; therefore, the results correspond with published data.

Table 15.8 presents the capital costs for Case 2.

Table 15.8: Case 2 capital costs

AREA	COST 2009 (£)	%
FEED PREPARATION	4,141,796	0.9
Storage & Handling	1,325,222	0.3
Drying	2,816,574	0.6
SYNGAS PRODUCTION	316,024,800	67.8
GAS CONDITIONING & AMMONIA SYNTHESIS	45,282,340	9.7
Thermal partial oxidation	230,099	0.0
Water gas shift	459,976	0.1
H_2S removal	399,607	0.1
CO_2 removal	8,211,963	1.8
H_2O removal	74,444	0.0
Methanation	276,214	0.1
Ammonia synthesis	429,371	0.1
Additional facilities	35,200,666	7.6
INDIRECT COSTS	91,935,784	19.7
LAND	8,770,774	1.9
TOTAL	*466,155,493*	*100.0*

Syngas production is by far the largest cost since thirteen individual gasification and gas-cleaning systems are installed. This also increases the indirect costs, which are a function of the plant capital. Feedstock preparation has the lowest capital since only storage, handling and drying is required.

Table 15.9 presents the capital costs for Case 3.

Table 15.9: Case 3 capital costs

AREA	COST 2009 (£)	%
FEED PREPARATION	868,366	1.7
Storage & Handling	256,573	0.5
Drying	611,792	1.2
SYNGAS PRODUCTION	24,307,448	48.5
GAS CONDITIONING & AMMONIA SYNTHESIS	13,469,943	26.9
Thermal partial oxidation	44,558	0.1
Water gas shift	68,396	0.1
H_2S removal	75,552	0.2
CO_2 removal	1,499,326	3.0
H_2O removal	14,416	0.0
Methanation	46,068	0.1
Ammonia synthesis	67,037	0.1
Additional facilities	11,654,592	23.3
INDIRECT COSTS	10,522,017	21.0
LAND	927,498	1.9
TOTAL	*50,095,272*	*100.0*

Like Case 2, syngas production is the largest cost, although the impact on the TPC is smaller. Feed preparation has the lowest capital requirement, although the impact on the TPC is slightly higher, due to the effect of scale on the dryer.

Table 15.10 presents the capital costs for Case 4. The capital for the natural gas ammonia production route is based on the construction of a 1,200 tpd; therefore, the production rate may be sustained should the biomass gasifier be offline.

Table 15.10: Case 4 capital costs

AREA	COST 2009 (£)	%
FEED PREPARATION	1,004,720	0.9
Storage & Handling	296,890	0.3
Drying	707,830	0.6
SYNGAS PRODUCTION	28,260,347	25.2
Gasification	28,118,818	25.1
Thermal partial oxidation	51,513	0.0
H_2S Removal	90,016	0.1
GAS-CONDITONING & AMMONIA SYNTHESIS	52,668,627	47.0
Steam methane reforming	950,146	0.8
Water gas shift	459,976	0.4
H_2S removal	399,607	0.4
CO_2 removal	8,211,963	7.3
H_2O removal	74,444	0.1
Methanation	276,214	0.2
Ammonia synthesis	429,371	0.4
Additional facilities	41,866,906	37.3
INDIRECT COSTS	28,253,962	25.2
LAND	1,966,409	1.8
TOTAL	*112,154,064*	*100.0*

As shown, the gas conditioning and ammonia synthesis system has the largest cost, which is expected since the plant operates primarily using natural gas.

15.5.2 Operating cost summary

Table 15.11 presents the operating costs for Case 1.

Table 15.11: Case 1 operating costs

AREA	COST 2009 (£/y)	%
BASIC LABOUR	1,581,682	2.1
GENERAL OVERHEAD	1,502,598	2.0
MAINTENANCE	3,393,032	5.2
FEEDSTOCK & LOGISTICS	44,679,911	60.4
Feedstock	29,129,678	39.2
Logistics	15,734,871	21.2
MATERIALS & UTILITIES	17,246,172	25.5
OTHER FIXED COSTS	3,016,029	4.6
TOTAL	*74,238,374*	*100*

As shown, the cost of purchasing and transporting the feedstock is the largest annual cost, followed by materials and utilities.

Table 15.12 presents the operating costs for Case 2.

Table 15.12: Case 2 operating costs

AREA	COST 2009 (£/y)	%
BASIC LABOUR	1,581,682	1.0
GENERAL OVERHEAD	1,502,598	1.0
MAINTENANCE	10,488,499	6.9
FEEDSTOCK & LOGISTICS	53,384,727	35.2
Feedstock	34,183,225	22.4
Logistics	19,440,137	12.8
MATERIALS & UTILITIES	75,826,099	49.8
OTHER FIXED COSTS	9,323,110	6.1
TOTAL	*152,345,350*	*100.0*

The cost of materials and utilities is the largest, mainly due to the large electricity requirement to operate thirteen gasification units. This is followed by feedstock and its logistics, which are higher than Case 1 due to the larger biomass demand.

Table 15.13 presents the operating costs for Case 3.

Table 15.13: Case 3 operating costs

AREA	COST 2009 (£/y)	%
BASIC LABOUR	674,597	4.2
GENERAL OVERHEAD	640,867	3.9
MAINTENANCE	1,127,144	6.9
FEEDSTOCK & LOGISTICS	7,069,192	43.6
Feedstock	2,734,316	16.8
Logistics	4,353,966	26.8
MATERIALS & UTILITIES	5,712,255	35.2
OTHER FIXED COSTS	1,001,905	6.2
TOTAL	*16,245,050*	*100.0*

Like Case 1, the feedstock and logistics costs are the highest annual cost.Table 15.14 presents the operating costs for Case 4.

Table 15.14: Case 4 operating costs

AREA	COST 2009 (£/y)	%
BASIC LABOUR	1,581,682	1.7
GENERAL OVERHEAD	1,502,598	1.6
MAINTENANCE	2,523,466	2.7
FEEDSTOCK & LOGISTICS	8,273,300	8.8
Feedstock	3,421,982	3.6
Logistics	4,879,005	5.2
MATERIALS & UTILITIES	78,168,232	82.9
OTHER FIXED COSTS	2,243,081	2.4
TOTAL	*94,292,359*	*100.0*

The materials and utilities cost is the largest operating cost, with the natural gas demand accounting for 79% of this. The feedstock and logistics costs for the wood chip are relatively small, which is to be expected considering the small-scale gasification system in operation.

15.5.3 Case comparison

Figure 15.1 compares the capital costs for the four cases.

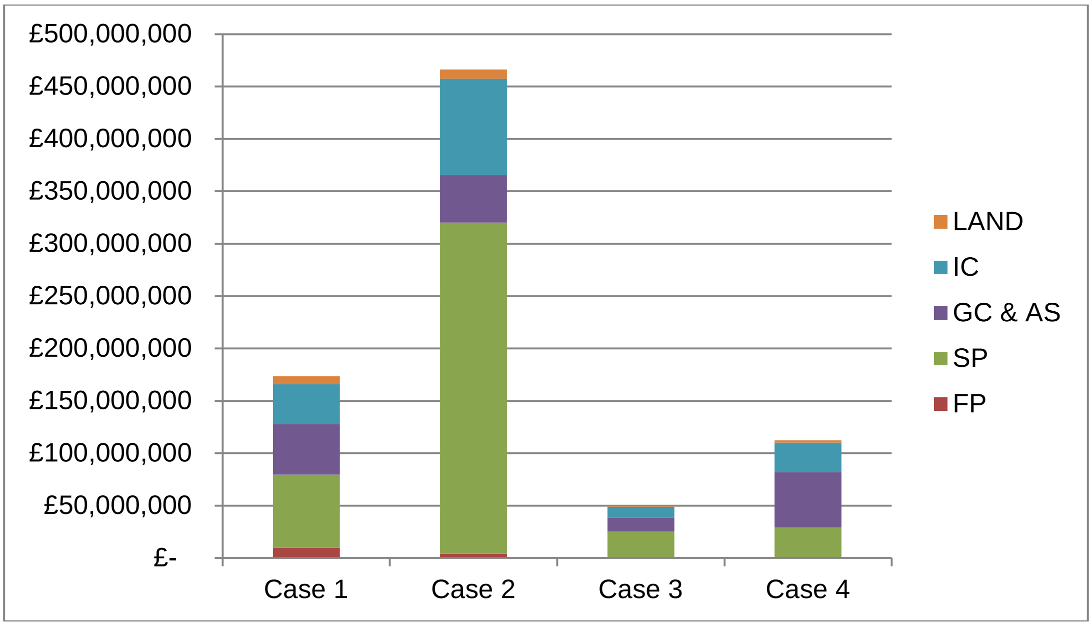

Figure 15.1: Capital cost comparison

As shown, in all cases syngas production (SP) is the largest capital outlay. For Cases 1, 3 and 4, this is followed by gas conditioning and ammonia synthesis (GC & AS), and the indirect costs (IC) for Case 2. The cost of feed preparation (FP) and land is comparatively small for all cases, regardless of scale.

Figure 15.2 compares the operating costs for the four cases.

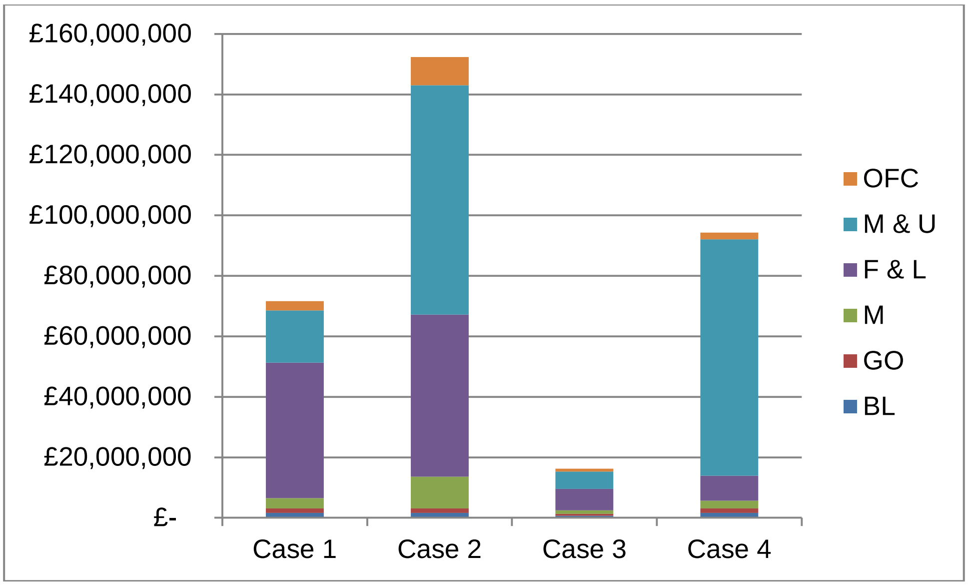

Figure 15.2: Operating cost comparison

The operating costs are dominated by the materials and utilities costs (M & U) and feedstock and logistics costs (F & L), regardless of scale. Since maintenance (M) and other fixed costs (OFC) are a function of the TPC, the impact varies with each case. In all cases, the labour (L) and the general overhead (GO) costs are comparatively small.

15.5.4 Cost of ammonia production

The cost of ammonia production from biomass syngas is calculated using the assessment criteria outlined in §13.5.2, based on a specified TRR of 20% (§13.5.3).

The cost of production is based on the following assumptions, in addition to the data and assumptions presented in the previous sections:

6. Construction is completed in the first two years of the project, with an initial capital outlay of 50% in Year 0 and 50% in Year 1.
7. The working capital is assumed as 10% of the initial capital, which is paid in Year 1 and returned in Year 21.
8. Operation begins in Year 2, assuming full production, and ends in Year 21.
9. Additional capital investments are included in Years 6, 11, 12 and 18.
10. The scrap value of process equipment is assumed as 5% of the project capital.

Table 15.15 presents the calculated anhydrous ammonia prices (2009 £/t) at the 20% TRR.

Table 15.15: Calculated anhydrous ammonia prices (2009 £/t)

Case	1	2	3	4
Ammonia price (£/t)	278.30	644.60	862.18	294.38

As shown, the effect of scale and gasification process has a significant impact on the price of ammonia. Large-scale entrained flow gasification is the most economically attractive system, although using small-scale FICFB to supplement natural gas ammonia production is more attractive than the equivalent standalone systems.

In literature, Bartels and Pate [274] give an ammonia price of £184 /t (US$367 /t (2007)) for a 1,800 tpd coal based plant and ~£250 /t (US$498 /t (2007)) for a 1,800 tpd natural gas based plant. Allowing for scale difference, the four cases are not competitive at a 20% IRR, although Cases 1 and 4 have potential since the generated prices are nearly inside the range.

In §15.4, a range of ammonia prices for specific time periods are presented, highlighting the fluctuations experienced by the ammonia market. To assess the long-term cost competitiveness of the four cases, the prices generated in this chapter are compared to the published data in Table 15.6 in order to calculate the expected rate of return. Table 15.16 presents the results. A dash indicates that the IRR is negative, so the project is not viable under any circumstances.

Table 15.16: Calculated IRR (1995 - 2009)

Period	Price (£/t)	Case 1	Case 2	Case 3	Case 4
1995 – 1999	134.94	-	-	-	-
1995 – 2009	200.32	1.7%	-	-	-
2000 – 2004	146.62	-	-	-	-
2000 – 2009	233.01	10.5%	-	-	-
2005 – 2009	319.38	27.6%	-	-	27.2%

As shown, the fluctuation in the ammonia price has considerable impact on the profitability of the four cases. Case 1 is the most economically attractive system, although a TRR of 20% is only achieved with the price applied in 2005 - 2009. For Case 4, the ammonia price cannot fall below £300 /t, whilst Cases 2 and 3 are not economically attractive at any of the specified intervals.

15.5.5 Preliminary sensitivity analyses

Three preliminary sensitivity analyses are completed in order to measure the effect of fluctuations in the capital and operating costs, in addition to providing additional information to determine the most promising cases. In this study, the effect of these sensitivities is measured on the calculated IRR (Table 15.16) as well as TRR (20%) price.

15.5.5.1 Capital cost variation

In this sensitivity, the capital cost is varied by ±10% to account for discrepancies in the cost data. The results are presented in Table 15.17 and 15.18.

Table 15.17: -10% capital cost sensitivity results

Case	1	2	3	4
Baseline ammonia price (£/t)	278.30	644.60	862.18	294.38
IRR (baseline price)	23.0%	22.2%	22.2%	22.2%
IRR (1995 – 1999 price)	-	-	-	-
IRR (1995 – 2009 price)	3.0%	-	-	-
IRR (2000 – 2004 price)	-	-	-	-
IRR (2000 – 2009 price)	12.2%	-	-	-
IRR (2005 – 2009 price)	30.6%	-	-	29.9%

Table 15.18: +10% capital cost sensitivity results

Case	1	2	3	4
Baseline ammonia price (£/t)	278.30	644.60	862.18	294.38
IRR (baseline price)	18.1%	18.3%	18.3%	18.3%
IRR (1995 – 1999 price)	-	-	-	-
IRR (1995 – 2009 price)	-	-	-	-
IRR (2000 – 2004 price)	-	-	-	-
IRR (2000 – 2009 price)	8.5%	-	-	-
IRR (2005 – 2009 price)	24.6%	-	-	25.1%

Reducing the capital cost results in an increase in IRR and vice versa. The sensitivity varies depending on the ammonia price. At the baseline ammonia price, a +10% change in capital cost reduces the IRR by a factor of 0.01 (Case 1) and 0.09 (Cases 2, 3 and 4), whilst a -10% change in capital cost gives an increase of 0.15 (Case 1) and 0.11 (Cases 2, 3 and 4). These are substantial impacts, illustrating the risk associated with large capital investments in novel processes, where the risk of cost over-runs would generally be considered higher than for a conventional plant. However, for Cases 2 and 3 the overall economic performance is unchanged.

15.5.5.2 Feedstock sensitivity (Cases 1, 2 and 3)

The selling price of European sourced woody biomass varies by location from about £9 to £142 (€10 to €160) [182]. Therefore, the possible variations in the large price range should be examined, which in this study, is varied by ±50% based on Huisman et al. [16]. The results are presented in Tables 15.19 and 15.20.

Table 15.19: -50% feedstock cost sensitivity results

Case	1	2	3
Baseline ammonia price (£/t)	278.30	644.60	862.18
IRR (baseline price)	28.1%	22.9%	22.2%
IRR (1995 – 1999 price)	-	-	-
IRR (1995 – 2009 price)	11.6%	-	-
IRR (2000 – 2004 price)	-	-	-
IRR (2000 – 2009 price)	18.8%	-	-
IRR (2005 – 2009 price)	34.8%	-	-

Table 15.20: +50% feedstock cost sensitivity results

Case	1	2	3
Baseline ammonia price (£/t)	278.30	644.60	862.18
IRR (baseline price)	14.1%	17.0%	17.8%
IRR (1995 – 1999 price)	-	-	-
IRR (1995 – 2009 price)	-	-	-
IRR (2000 – 2004 price)	-	-	-
IRR (2000 – 2009 price)	1.2%	-	-
IRR (2005 – 2009 price)	22.0%	-	-

Again, the sensitivity varies depending on the ammonia price. At the baseline ammonia price, a +50% variation in feedstock price reduces the IRR by a factor of 0.18 (Cases 2 and 3) and 0.42 (Case 1), and a -50% variation in feedstock price gives a 0.12 (Cases 2 and 3) and 0.41 (Case 1) increase. Therefore, feedstock price has the potential to greatly influence the economic viability of a project. This highlights the need to guarantee long-term feedstock contracts at a fixed price where possible.

15.5.5.3 Natural gas sensitivity (Case 4)

For Case 4, varying the biomass feedstock costs will have little impact on the economic viability due to the scale of biomass-derived production envisioned. Instead, the cost of natural gas is varied by ±50%, as shown in Table 15.21, to represent the potential market fluctuation.

Table 15.21: ±50% natural gas cost sensitivity results (Case 4)

	-50% natural gas cost	+50% natural gas cost
Baseline ammonia price (£/t)	294.38	294.38
IRR (baseline price)	40.0%	-
IRR (1995 – 1999 price)	-	-
IRR (1995 – 2009 price)	13.9%	-
IRR (2000 – 2004 price)	-	-
IRR (2000 – 2009 price)	-	-
IRR (2005 – 2009 price)	17.7%	-

As shown, the price of natural gas has considerable impact on the economic viability of the system. At the TRR ammonia price, a +50% variation in natural gas price results in the IRR not being met, whilst a -50% variation in feedstock price gives a 0.5 increase.

15.6 Selection of most promising systems

It is clear that Case 1 is the most economically attractive system, producing ammonia at the lowest selling prices, although a fluctuation in the biomass feedstock price has a significant impact. Case 4 also has potential; however, the impact of a fluctuation in natural gas price is considerable. Cases 2 and 3 are not economically attractive in the current economic climate, even when operating under optimistic conditions. Therefore, Cases 1 and 4 are considered the most promising, although Cases 2 and 3 may have potential in the future.

16 Results analysis

In Chapter 15, the cost of biomass derived ammonia production for the four cases was calculated based on the capital and operating costs of the relevant sub-systems. During the preliminary analysis it was determined that Cases 1 and 4 had the most potential, although the expected ammonia prices were not cost-competitive with fossil fuel based production. In this chapter, the two cases undergo a series of additional sensitivity analyses, which evaluate the use of alternative practises in an attempt to reduce the ammonia price further to become competitive with fossil fuels. To measure the cost competitiveness a maximum ammonia price of £250 /t is specified, based on Bartels and Pate [274].

In addition to process improvements, the sensitivity analyses presented in the chapter also evaluate variations in the expected performance of Case 1 based on the availability of the gasifier. The chosen practises are derived from the work carried out in previous chapters or are based on recommendations from relevant literature. In all cases, the wood chip and syngas composition and subsequent ammonia yield are the same as presented in Chapter 14.

16.1 Feedstock source & logistics (Case 1)

The slow uptake of biomass gasification is due to the feedstock, which comes at a relatively high cost and lacks established supply chains. This has meant that very few gasification processes have proven to be economically viable [142].

In Chapter 15, the preliminary feedstock sensitivity analyses determined that the cost of the feedstock and the subsequent logistics has a significant impact on the cost competitiveness of Case 1. For Case 4, the biomass consumption and subsequent costs are significantly smaller in comparison to natural gas therefore the effect is minimal.

At Güssing, biomass supply is secured by long-term contract, which have a fixed price for up to ten years. This is particularly attractive during the early stages of operation. However, as operation continues cheaper contracts are sourced in order to secure more suitable wood biomass at reduced costs [384]. Since the cost of securing and delivering feedstock accounts for ~63% of the operating costs, sourcing wood chip from other countries is a practical way of reducing costs.

Table 16.1 presents five potential alternative sources. The prices displayed are in 2009 £/odt and refer to the biomass price at source.

Table 16.1: Potential feedstock sources

Wood chip source	Price £/odt (2009)
Sweden [422]	£43.41
Canada [423]	£22.68
Croatia [424]	£25.28
Russia [425]	£36.29

In all cases, wood is assumed to be chipped at the source. In addition, the 32 km roundtrip from the port to the plant is included.

16.1.1 Logistic routes

As before, the feedstock is shipped to Felixstowe port. Road distances are approximate and unless otherwise stated are adapted from Google Earth [426]. Shipping distances are from Searates [251], assuming 15 knots average speed.

16.1.1.1 Sweden

The wood chip is Värnamo wood chip, sourced from Växjo. It is transported 131 km (262 km roundtrip) by road to Tranemo, where it is shipped by train to Gothenburg (110 km). The feedstock then travels from Gothenburg port to Felixstowe (967 km [966.7 km], taking 1 day 11 hours).

16.1.1.2 Canada

The wood chip is sourced from the Armstrong, Ontario area [423]. The wood chip is transported 530 km by train to Toronto port, which is more cost effective over longer distances [241]. It is then shipped from Toronto Port to Felixstowe. This journey is approximately 5,745 km (5,744.9 km) and takes 8 days 15 hours.

16.1.1.3 Croatia

The wood chip is sourced from Gospić, Croatia. It is transported by rail (1,685 km) to Zeebgrugge, where it is shipped to Felixstowe (144 km [144.5 km], 5 hours).

16.1.1.4 Russia

Wood chip is sourced from the Leningrad region (Tikhvin). It is transported by road to St. Petersburg (~193 km) [427]. It is then shipped from St. Petersburg to Felixstowe (2,141 km [2140.9 km], 3 days 5 hours).

The results of the sensitivity are presented in Table 16.2.

Table 16.2: Feedstock sources and logistics sensitivity results

Feedstock source	Feedstock cost (2009 £)	Feedstock & logistics cost (2009 £)	Ammonia price (20% IRR) (£/t)
Poland (Baseline)	29,129,678	44,679,911	278.30
Sweden	31,612,983	47,514,679	284.70
Canada	16,516,527	39,244,824	264.73
Croatia	18,380,827	29,747,716	241.79
Russia	26,427,900	35,342,685	255.30

IRR (%)

Period	Price (£/t)	Poland (baseline)	Sweden	Canada	Croatia	Russia
1995 – 1999	134.94	-	-	-	-	-
1995 – 2009	200.32	1.7%	-	5.7%	11.4%	8.2%
2000 – 2004	146.62	-	-	-	-	-
2000 – 2009	233.01	10.5%	9.0%	13.5%	18.3%	15.5%
2005 – 2009	319.38	27.6%	26.4%	29.9%	33.8%	31.6%

As shown, using imported wood chip from Croatia produces ammonia at the lowest price, reducing the cost by 13% in comparison to the baseline price. Whilst a change in the feedstock source affects the IRR values, the overall picture for Case 1 is unchanged, with the 1995-1999 and 2000-2004 periods giving negative IRR. As expected, using Swedish wood chip is less attractive than the baseline since the feedstock costs are greater. Again, operating using Croatian wood chip is the most economically attractive, generating the highest IRR for all periods.

Figure 16.1 presents the feedstock and logistic cost breakdown.

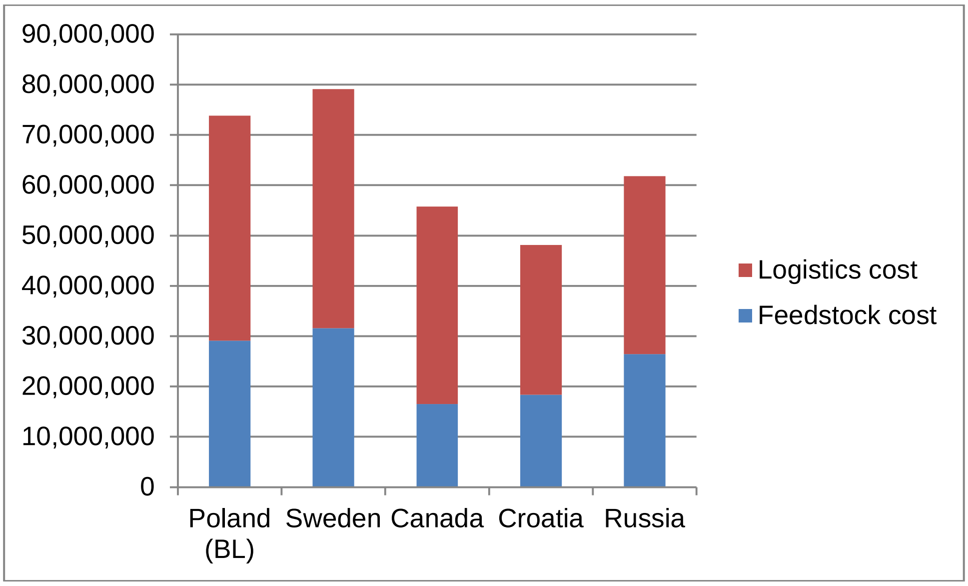

Figure 16.1: Feedstock and logistic cost breakdown

As shown, logistics are the primary cost for all potential feedstock sources, although the impact varies with each source. Canada has the largest logistics to feedstock cost variation, which is to be expected due to the distance travelled. This cost also negates the comparatively low price of the wood chip.

16.2 Production capacity (both cases)

In this study, ammonia production is limited to a maximum of 1,200 tpd. At present, plants operate between 1,500-2,000 tpd [176, 274]. For this sensitivity, the effect of production capacity on production costs is measured at 1,500 tpd, 1,800 tpd and 2,000 tpd.

Huisman et al. [16] determined that when producing biomass gasification derived chemicals an increase in scale generally reduces the production costs. However, the relationship is discontinuous because the gasifier has a maximum capacity and additional units become necessary. At the point at which an extra unit becomes necessary, production costs can rise. For Case 1 at 1,800 tpd and 2,000 tpd, two gasifiers (of feed rate ~1,600 tpd and 1,750 tpd respectively) are required, whereas at 1,500 tpd only one gasifier is needed. For Case 4, where the feedstock is predominantly natural gas, a single gasifier is used.

In this sensitivity, the capital and materials costs are adjusted with scale, which in turn affect the maintenance, land and fixed costs. Labour costs however, remain unchanged.

Table 16.3 presents the results of the sensitivity for Case 1.

Table 16.3: Production scale sensitivity results (Case 1)

Production rate (tpd)	1,200 (baseline)	1,500	1,800	2,000
Ammonia price (baseline IRR) (£/t)	278.30	265.08	320.16	251.41
IRR (%)				
1995-1999 price	-	-	-	-
1995-2009 price	1.7%	3.9%	-	6.6%
2000-2004 price	-	-	-	-
2000-2009 price	10.5%	12.8%	5.6%	15.6%
2005-2009 price	27.6%	30.8%	19.8%	34.4%

As shown, the impact of scale of production varies. For 1,800 tpd, the increase in production does not negate the increase in the capital and operating costs, in particular the increase in capital from the use of two gasifiers. Operating at 1,500 tpd reduces the ammonia price by 4.9%; however, operating at 2,000 tpd reduces the baseline price by 9.7%, achieving a selling price comparable to Bartels and Pate [274], albeit at a larger scale. Like the previous sensitivity, a change in the production rate affects the IRR, although the overall performance of Case 1 is unchanged. In terms of feedstock availability, supplying the 1,800 tpd and 2,000 tpd plants with enough feedstock may be difficult.

Table 16.4 presents the results of the sensitivity for Case 4.

Table 16.4: Production scale sensitivity results (Case 4)

Production rate (tpd)	1,200 (baseline)	1,500	1,800	2,000
Ammonia price (baseline IRR) (£/t)	294.38	281.44	277.23	273.53
IRR (%)				
1995-1999 price	-	-	-	-
1995-2009 price	-	-	-	-
2000-2004 price	-	-	-	-
2000-2009 price	-	-	0.7%	1.9%
2005-2009 price	27.2%	32.1%	33.8%	36.5%

An increase in the scale of production is economically attractive for Case 4, mainly because the capital costs are not subject to limitations in gasification scale. Increasing the scale of production by 40% reduces the ammonia price by 7%; however, the selling price is still higher than the prices quoted by Bartels and Pates [274]. Like Case 1, the TRR improves with an increase in scale; however, the overall performance of Case 4 is unchanged.

16.3 Existing plant refurbishment (Case 4)

According to the European Commission [262], rising feedstock prices and hard market competition has resulted in numerous ammonia producers considering the potential of refurbishing and/or modernising older, less efficient plants to stay competitive. In most cases, these projects result in a moderate increase in capacity, as the process equipment and operation is improved. This process is more economically attractive and involves less risk than building a new plant.

In this study, whilst both cases have potential, Case 4 may be the most suitable since the system operates primarily using the conventional natural gas route. The only major alteration required is the switching of the CO_2 and H_2O units. The gasification and feed handling systems are built as standalone units, which feed biomass syngas to the HTS by pipeline. For Case 1, the following alterations are required:

- Removal of SMR units
- Installing the gasification, air separation and feedstock handling processes
- Switching of the CO_2 and H_2O units, possibly replacing the CO_2 unit altogether
- Addition of the relevant steam loops

In addition, the composition of the biomass syngas is significantly different to natural gas; therefore, certain units may need to be replaced with larger vessels. Whilst the conversion of a natural gas based plant would not be impossible to achieve, plant refurbishment is not as attractive as it is for Case 4.

In this sensitivity, the production scale is specified as 1,200 tpd. Land costs are not included in the capital, since this is already be owned by the plant. The capital for CO_2 and H_2O removal are included in order to cover un-installation and reinstallation costs. The costs associated with piping and instrumentation and indirect are all scaled accordingly, whilst the operating costs are unchanged.

Table 16.5 presents the results of the sensitivity.

Table 16.5: Refurbishment sensitivity results (Case 4)

Case	4 (baseline)	4 (refurbishment)
Ammonia price (baseline IRR) (£/t)	294.38	265.05
IRR (%)		
1995-1999 price	-	-
1995-2009 price	-	-
2000-2004 price	-	-
2000-2009 price	-	1.3%
2005-2009 price	27.2%	43.1%

As shown, opting for plant refurbishment reduces the ammonia price by 11%. Table 16.6 presents the results for the three additional production scales considered in the previous sensitivity.

Table 16.6: Additional refurbishment sensitivity results (Case 4)

Case	4 (baseline)	4 (1,500 tpd)	4 (1,800 tpd)	4 (2,000 tpd)
Ammonia price (baseline IRR) (£/t)	294.38	255.59	252.89	250.30
TRR analysis				
1995-1999 price	-	-	-	-
1995-2009 price	-	-	-	-
2000-2004 price	-	-	-	-
2000-2009 price	-	5.7%	7.5%	8.9%
2005-2009 price	27.2%	50.4%	52.0%	54.3%

As shown, implementing plant refurbishment at larger scale reduces the ammonia price; however, the impact is not as significant, mainly due to the high costs of gasification and feed handling in addition to the operating costs.

16.4 10% target rate of return

The baseline ammonia selling price has been calculated using a 20% TRR (§13.5.3). However, as shown in Chapter 15, the prices generated are not cost competitive.

Several large-scale biomass projects assume a 10% TRR [15, 220 & 252] as part of their economic strategy, which agrees with the target range of 6-15% outlined in §13.5.3. In this sensitivity, a 10% TRR is assumed.

Table 16.7 presents the electricity selling prices calculated under the above conditions.

Table 16.7: 10% TRR results

Case	1	4
Baseline ammonia price (£/t)	278.30	294.38
10% TRR ammonia price (£/t)	230.87	263.73

As shown, the effect of setting a 10% TRR is a reduction in the price for both cases. For Case 1 there is a 17% reduction in the ammonia price, whilst for Case 4 there is 10% reduction in the ammonia price. For Case 1, operating at a 10% TRR produces ammonia at a lower price than with natural gas [274].

16.5 Gasifier availability (Case 1)

In §13.1.2 an overall plant efficiency of 95% is assumed in order to remain competitive with fossil fuel based ammonia production. However, gasifier availability varies between 85%-96%, depending on gasification process. The purpose of this sensitivity is to measure the economic effect of a lower percentage of gasifier availability.

Since the effect of gasifier availability will negligible for Case 4, this sensitivity is only applied to Case 1. The effect of gasifier availability on the cost of ammonia is measured at 2 intervals, 85% (7,446 h) 90% (7,884 h) and compared to the results determined at 95% (8,280 h), which is the baseline ammonia price.

Certain costs, such as the capital costs will not be affected by a change in gasifier availability because the plant is built to achieve a specific capacity. In addition, the labour requirement and costs will also remain the same since the workforce will be involved in repairing the gasifier and restarting the process. The overhead electricity consumption is assumed to be unchanged since non-process buildings and systems will still require power, whether the process is on or offline. The number of catalyst bed changes will remain the same since the additional time is assumed to be negligible.

However, a variation in the overall operating costs is expected, since the gasifier availability will determine the amount of feedstock and other process materials required. For the feedstock logistics, the shipping logistics are not altered, though the rail and road are to avoid over-stockpiling at the plant.

Table 16.8 presents the results of the sensitivity analysis.

Table 16.8: Gasifier availability sensitivity results

Availability (%)	85	90	95 (baseline)
Operating h/y	7446	7884	8280
Ammonia production (kt/y)	372.3	394.2	414.0
Ammonia price (baseline IRR) (£/t)	297.75	288.08	278.30
IRR (%)			
1995 – 1999 price	-	-	-
1995 – 2009 price	-	-	1.7%
2000 – 2004 price	-	-	-
2000 – 2009 price	7.4%	8.8%	10.5%
2005 – 2009 price	23.7%	25.6%	27.6%

As expected, the ammonia price is highest at 85% availability, when the rate of production is at its lowest. However, the price remains under £300 /t, which is not unreasonable.

16.6 Discussion and project barriers

16.6.1 Ammonia price comparison

With exception to gasifier availability, all of the sensitivity analyses reduce the ammonia price; however, the impact varies with each analysis. Figure 16.2 presents the lowest prices obtained for Case 1.

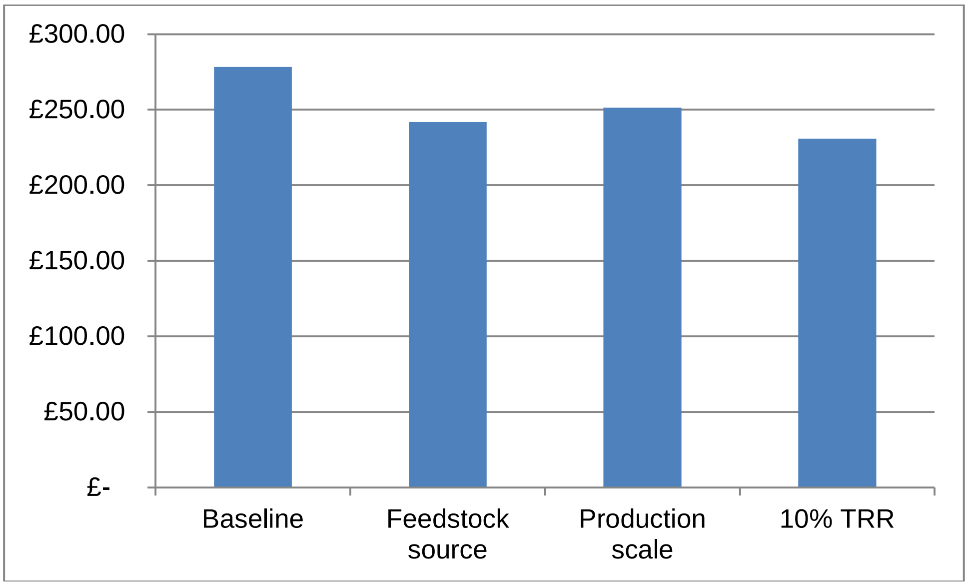

Figure 16.2: Case 1 sensitivity results summary

It is clear that setting a 10% TRR is beneficial; producing the lowest ammonia price, whilst increasing the scale of production generates the highest price. However, all sensitivities produce ammonia at lower price than the baseline and are comparable to Bartels and Pate [274].

Figure 16.3 presents the sensitivity ammonia price summaries for Case 4.

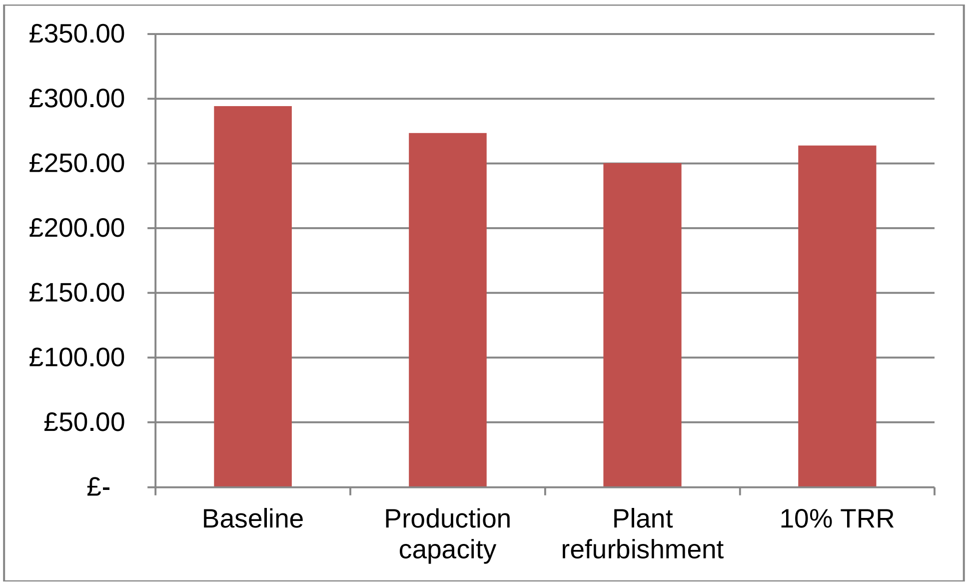

Figure 16.3: Case 4 sensitivity results summary

As shown, implementing a plant refurbishment, in this case at 2,000 tpd, is the most economically attractive option in terms of ammonia price, followed by setting a 10% TRR. Like Case 1, increasing the production scale generates the highest price, although all sensitivities produce ammonia at a lower price than the baseline.

16.6.2 Evaluation of analysis

For Case 1, changing the source of wood chip is the simplest physical improvement, reducing the ammonia price by 13%, although the overall performance of the project remains unchanged.

Increasing the scale of ammonia production also reduces the cost, though not as significantly as expected. For Case 1, the sensitivity is mainly inhibited by the implementation of multiple gasifiers, which increases the capital. This is seen at 1,800 tpd, where the inclusion of an additional gasifier generates an ammonia price 13.2% higher than the baseline figure. For Case 4, the gasifier is not an issue; however, the increased rate of production has a significant impact on the operating costs, mainly due to the natural gas requirement. Nevertheless, for both cases operating at 2,000 tpd has a positive impact on the ammonia price.

For Case 4, existing plant refurbishment reduces the ammonia price by 11%. When combined with the increased scale of production (2,000 tpd) an ammonia price of ~£250 /t is achievable, which is comparable to natural gas production [269] and therefore competitive.

Setting a 10% TRR also reduces the ammonia price for both cases, although the impact is greater for Case 1. Since this case generated the lowest ammonia price, this is to be expected.

In addition, the effect of gasifier availability was examined for Case 1. The results of this sensitivity suggested that a reduction in the availability (85%) would increase the ammonia price by 6%.

16.6.3 Financial viability

The sensitivity analyses are presented in this chapter all reduce the ammonia price for both cases. With one exception, each sensitivity was treated in isolation; however, it is possible to combine the sensitivity cases to achieve a lower price still.

For Case 1, operating at 2,000 tpd using Croatian wood chip and setting a 10% TRR is investigated, whilst for Case 4 operating at 2,000 tpd using a refurbished plant and setting a 10% TRR is considered. Table 16.9 presents the combined sensitivities and the generated ammonia prices.

Table 16.9: Combined sensitivities and ammonia prices

Case	1	4
Baseline ammonia price (£/t)	278.30	294.38
2,000 tpd & Croatian wood chip (£/t)	215.99	-
2,000 tpd, Croatian wood chip & 10% TRR (£/t)	176.24	-
2,000 tpd & plant refurbishment (£/t)	-	250.23
2,000 tpd, plant refurbishment & 10% TRR (£/t)	-	234.56

As shown, the lowest achievable ammonia price for both cases is under £250 /t and therefore cost competitive. In fact, both cases achieve a competitive price at the baseline IRR (20%), although setting a 10% TRR is far more competitive, especially for Case 1.

In Chapter 16, two preliminary sensitivity analyses (±10% capital, ±50% logistics costs) were presented in order to determine the economic impact of operating under optimistic and pessimistic conditions. Table 16.10 presents the results of the combined sensitivities operating under optimistic conditions (-10% capital and -50% logistics costs).

Table 16.10: Combined sensitivities electricity prices (optimistic conditions)

Case	1	4
Baseline ammonia price (£/t)	278.30	294.38
2,000 tpd, Croatian wood chip & 10% TRR (£/t) (optimistic)	149.39	-
2,000 tpd, plant refurbishment & 10% TRR (£/t) (optimistic)	-	228.60

As shown, a minimum ammonia price of £149.39 /t is achieved under optimistic conditions for Case 1. This is a further reduction of 15% in comparison to the price achieved under reasonable conditions. For Case 4, a minimum ammonia price of £228.60 /t is achieved, which is 2.5% lower than the price achieved under reasonable conditions.

16.6.4 Alternative CO_2 removal technology

Whilst the sensitivities in this chapter have successfully reduced the ammonia price, further, albeit minor reductions may be possible. The four cases used to evaluate biomass-derived ammonia production are modelled using established conventional conditioning technologies. However, these technologies may not be the most suitable. The following sections discuss various alternative technologies that have potential.

As shown in Chapters 14 and 15, the CO_2 removal stage makes a significant contribution to the energy demand and TPC. The following sections discuss other available technology.

16.6.4.1 MDEA scrubbing

Using an alternative chemical solvent to MEA is an attractive option, particularly if considering a more cost effective retrofit. MDEA is a potential alternative, which consumes 18.8 kJ/mol [CO_2] less energy and has a significantly lower heat of vaporisation (550 kJ/kg) than MEA [387].

A solvent of 50 wt% MDEA has a CO_2 removal rate of 0.5 kmol/kmol MDEA [387], which is 0.1 kmol/kmol solvent higher than using MEA. Although the cost of MDEA is considerably higher than a conventional MEA solvent, Bantrel [428] state that the cost of using MDEA is 25% lower than MEA.

16.6.4.2 Physical adsorption

Due to the significant heat demand associated with chemical adsorption processes, modern ammonia plants consider the use of physical adsorption technology as an alternative [275]. According to EFMA [264], PSA is the “Best available technology” (BAT) for the removal of CO_2 since the process is designed for *‘zero heat consumption’* [264, p. 13], though the mechanical energy demand will need to be considered.

As discussed in §10.1.1.1.4, multiple materials may be removed from the product stream in one operation [176, 264].

According to Crawford et al. [275], a PSA unit for a 1,361 tpd ammonia plant costs £111,110 (2009) (US$168,000 2007). This converts to a capital cost of £102,380 (2009) for a 1,200 tpd ammonia plant. In terms of the operating costs, Swanson et al. [220]

assume a catalyst/packing cost of £328,701 (2009) ($497,000 2007) for a system based on a 2,000 tpd (dry) entrained flow gasifier, which is replaced every three years.

16.7 Project barriers and limitations

Several barriers have been identified during this study, which pertain to the conversion of biomass syngas to ammonia.

16.7.1 Variation in feedstock composition

In this study, a generic wood chip composition was used, based on the assumption that any variations were negligible; however, this would not be the case in reality. Compositional variations, caused by seasonal and environmental factors will occur, influencing the quality of the wood chip and the subsequent products.

In addition, the generic composition used in this study is "best fit" between data provided by project partners and estimations based on published literature. Therefore, minor variations in the performance of the four cases should be expected.

16.7.2 Availability of feedstock

For the four cases and the subsequent sensitivity analyses, it is assumed that the feedstock requirement can be met by a single source. However, this may not the case in reality due to environmental and economic factors such as mishandled forestry management and natural disasters. If the feedstock has to be sourced from multiple countries, this will have a significant impact on the operating costs, thus affecting the ammonia price.

16.7.3 1.7.3 Syngas composition

Whilst every effort has been made to ensure the models represent the process performance realistically, some inaccuracies are inevitable. In particular, the models are based on a specific biomass syngas composition; although in reality the composition will vary with feedstock composition and the operating conditions at a given time. Therefore, the effect of variations in the syngas composition must be taken into account.

16.7.4 Status of technology

In this study large-scale biomass gasification (>2,000 tpd (dry)) is under consideration, assuming negligible differences in performance from small-scale technology. As discussed in §10.2.6, current biomass gasification technology operates at under 100 tpd

(20% wet). Whilst large-scale systems (2,000 tpd (dry)) have been proposed by numerous sources, the technology has yet to be tested. Although the general consensus is that large-scale biomass gasification has potential, the effects of scale on the performance of the gasifier(s) is not altogether known. Therefore, inaccuracies in the performance of the four cases presented should be expected.

16.7.5 Availability of technology

In §16.4, it is assumed that a suitable natural gas based ammonia production process is available for refurbishment. However, this may not be the case, particularly since ammonia production in the UK is in rapid decline.

16.7.6 Combining data from multiple sources

Often in this analysis, multiple sources of data (particularly economic) have been combined to provide an average figure. Whilst this is a sound practice for reducing error margin, it can remove the specificity to particular scales and types of operation.

17 Conclusions and recommendations (ammonia)

17.1 Review of the study

17.1.1 Objectives of the study

The primary objective of this study was to investigate the production of ammonia from biomass derived syngas in the UK.

This was achieved by completing the following tasks:

- The proposal of a range of scale case studies, identifying the most suitable scale of production for the UK
- The evaluation and selection of the most technically feasible biomass gasification processes, in this case O_2-enriched entrained flow gasification and FICFB indirect gasification, which produce a syngas that is suitable for ammonia production.
- The development and modelling of biomass syngas derived ammonia production using ASPEN Plus® simulation software and Microsoft Excel®, which also led to the calculation of the mass, energy and power balances for each of the cases.
- Assessment of the economic suitability and identification of the most favourable conditions for the production of ammonia
- The identification of the current boundaries and limitations of ammonia production in the UK

17.1.2 Structure

A review of relevant literature sources was completed to provide a background document on conventional ammonia production, in addition to current gasification and biomass gasification technologies. The current ammonia market environment was also established in order to put the results of this study into context.

In Chapter 11, a detailed literature review of previous techno-economic assessments regarding biomass-to-chemical production was completed. This identified the scale of production anticipated and range of gasification technologies under consideration, the method of assessment used, the limitations of previous work and the subjects where a general agreement had been reached. These findings were then used in Chapter 12 to refine the scope of this study and select an appropriate methodology. In addition, the types of gasification under consideration were also selected and the four cases under investigation outlined.

A detailed assessment of the technical performance of biomass syngas ammonia production was carried out and reported in Chapters 13 and 14. The systems were divided into three sub-systems: feedstock handling, syngas production and gas conditioning and ammonia synthesis, which were assessed individually. Estimations of the thermal energy and electrical power requirements of the sub-systems were also made in this chapter.

The capital and operating costs of the sub-systems were investigated in Chapter 15. The expected revenue from the sale of ammonia was also calculated. Finally, the ammonia selling price (20% IRR) was calculated for the four cases. In Chapter 16, a series of process improvements were completed for Cases 1 and 4 in order to reduce the ammonia price to ≤£250 /t. These improvements were:

- Implementing an alternative feedstock source (Case 1)
- Increasing the scale of ammonia production
- Considering the refurbishment of an existing ammonia plant (Case 4)
- Setting a lower TRR of 10%

In addition, the effect of gasifier availability was investigated for Case 1.

17.2 Conclusions

In Chapter 12, four ammonia production case studies were proposed in order to investigate various gasification technology and production scales, these were:

- Case 1: Large-scale entrained flow gasifier feeds a large-scale (1,200 tpd) ammonia plant.
- Case 2: Multiple small-to-medium scale FICFB gasifiers feed a large-scale (1,200 tpd) ammonia plant.
- Case 3: Small-to-medium scale FICFB gasifier feeds a small-scale (<100 tpd) ammonia plant.
- Case 4: 1,200 tpd ammonia plant fed with a mixed feed of natural gas and FICFB derived syngas, based on a feed ratio of 90:10 natural gas/biomass syngas.

The following sections summarise the principal findings for these four cases.

17.2.1 Lowest ammonia price

Table 17.1 presents the ammonia prices generated by the four cases.

Table 17.1: Calculated anhydrous ammonia prices (2009 £/t)

Case	1	2	3	4
Ammonia price (£/t)	278.30	644.60	862.18	294.38

As shown, the lowest ammonia price generated in this study was generated by Case 1, which was a large-scale entrained flow gasifier system, producing 1,200 tpd anhydrous ammonia. The highest price was generated by Case 3, which was a small-scale (96 tpd) FICFB gasifier system.

These prices were then compared to the ammonia prices for 1995 - 2009 (Table 15.6), and the IRR for each interval (optimistic and pessimistic) calculated, shown in Table 17.2. Only the year ranges that gave non-negative IRRs in at least one case are shown.

Table 17.2: Calculated rates of return (1995-2009)

Period	Case 1	Case 2	Case 3	Case 4
IRR (1995 – 2009 price)	1.7%	-	-	-
IRR (2000 – 2009 price)	10.5%	-	-	-
IRR (2005 – 2009 price)	27.6%	-	-	27.2%
IRR (%) -10% Capital cost sensitivity results				
IRR (1995 – 2009 price)	3.0%	-	-	-
IRR (2000 – 2009 price)	12.2%	-	-	-
IRR (2005 – 2009 price)	30.6%	-	-	29.9%
IRR (%) +10% Capital cost sensitivity results				
IRR (1995 – 2009 price)	-	-	-	-
IRR (2000 – 2009 price)	8.5%	-	-	-
IRR (2005 – 2009 price)	24.6%	-	-	25.1%
IRR (%) -50% feedstock cost sensitivity results				
IRR (1995 – 2009 price)	11.6%	-	-	n/a
IRR (2000 – 2009 price)	18.8%	-	-	n/a
IRR (2005 – 2009 price)	34.8%	-	-	n/a
IRR (%) +50% feedstock cost sensitivity results				
IRR (2000 – 2009 price)	1.2%	-	-	n/a
IRR (2005 – 2009 price)	22.0%	-	-	n/a
IRR (%) -50% natural gas cost				
IRR (2005 – 2009 price)	n/a	n/a	n/a	17.7%

As shown, the fluctuation in the ammonia price has considerable impact on the profitability, illustrating the risk associated with novel processes, where the risk of cost over-runs would generally be considered higher than for a conventional plant.

Case 1 was the most economically attractive system, although a TRR of 20% is only achieved with the price applied in 2005-2009, albeit under both optimistic and pessimistic conditions. This is also true for Case 4 (except at +50% natural gas cost), whilst Cases 2 and 3 are not economically attractive at any of the specified intervals.

The above results determined that Cases 1 and 4 had the most potential for competitive ammonia production, although the prices were still in excessive in comparison to fossil fuel based production. Further analysis (Table 17.3) in Chapter 16, aimed to reduce these prices to ≤£250 /t in order to compete with fossil fuels [274].

Table 17.3: Sensitivity analysis results (2009 £)

Case	1	4
Baseline ammonia price (£/t)	278.30	294.38
Alternative feedstock source (Croatia) (£/t)	241.79	-
Production scale increase (2,000 tpd) (£/t)	251.41	273.53
Plant refurbishment (£/t)	-	265.05
10% TRR ammonia price (£/t)	230.87	263.73
2,000 tpd & Croatian wood chip (£/t)	215.99	-
2,000 tpd, Croatian wood chip & 10% TRR (optimistic) (£/t)	176.24 (149.39)	-
2,000 tpd & plant refurbishment (£/t)	-	250.23
2,000 tpd, plant refurbishment & 10% TRR (optimistic) (£/t)	-	234.56 (228.60)

For Case 1, setting a 10% TRR had the greatest impact, whilst increasing the scale of production generated the highest price. This is mainly inhibited by the implementation of multiple gasifiers, which increases the capital. In addition, the effect of gasifier availability suggested that a reduction in the availability (85%) would increase the ammonia price by 6%. Since the sensitivity analyses reduce the ammonia price by at least 13% this is not unreasonable.

For Case 4, the increased rate of production has a significant impact on the operating costs, mainly due to the natural gas requirement. Implementing a plant refurbishment at 2,000 tpd, was the most economically attractive option in terms of ammonia price. Like Case 1, increasing the scale of production generated the highest price, although all sensitivities produced ammonia at a lower price than the baseline.

Combining the sensitivities generated a minimum ammonia price of £176.24 /t for Case 1 (£149.39 /t under optimistic conditions) and £234.56 /t for Case 4 (£228.60 /t under optimistic conditions), both of which are under the £250 /t limit.

17.2.2 Financial viability

At present, the majority of fertiliser consumed in the UK is imported. This is because UK-based production cannot compete with overseas suppliers, especially since the recent economic downturn has made production unprofitable [281, 282].

However, anhydrous ammonia can be manufactured from biomass syngas at a price competitive to fossil fuels (≤£250 /t) using the gasification system described in Case 1, which produces ammonia at the lowest price without the use of fossil fuels, directly or indirectly. Case 4 also produces ammonia at a competitive price; however, the system is still reliant on natural gas.

Cases 2 and 3 were not viable at the study's base date, producing ammonia at a price in excess of £500 /t. These cases were therefore not considered to have potential under current economic conditions.

17.2.3 Impact of scale

As expected, increasing the scale of production decreases the ammonia price. This is most apparent between Cases 2 and 3.

17.2.4 Distribution of costs

For Cases 1, 2 and 3, syngas production is the largest capital cost, whilst for Case 4 the capital is predominantly gas conditioning and ammonia synthesis. In terms of operating costs, all cases are dominated by the materials and utilities costs, followed by feedstock and logistics costs.

17.2.5 Process modelling

The four cases were modelled using ASPEN Plus® simulation software and Microsoft Excel®. The amount of biomass required to produce 1 kg ammonia ranged between 0.32 and 3.81 kg [wood chip]/kg [ammonia]. Case 4 required the least (0.32 kg [wood chip]/kg [ammonia]), since the feedstock was predominantly natural gas and Cases 2 and 3 the most (3.81 kg [wood chip]/kg [ammonia]). Case 1 required 2.71kg [wood chip]/kg [ammonia].

For Cases 2, 3 and 4, natural gas was required for the production of thermal energy, which was equivalent to 0.12 kg [natural gas]/kg [ammonia] for Case 4 and 0.15 kg [natural gas]/kg [ammonia] for Cases 2 and 3. The thermal demand for Case 1 could be met using recovered process heat. All cases required imported electrical power for pumps, compressor and instrumentation.

17.3 Barriers and limitations

In Chapter 16, several project barriers and limitations were identified regarding biomass derived ammonia production.

17.3.1 Variation in feedstock composition

In this study, a generic wood chip composition was used, based on the assumption that any variations were negligible. However, compositional variations will occur, influencing the quality of the wood chip and the subsequent products. In addition, the generic composition used is a “best fit”, therefore; minor variations in the performance of the four cases should be expected.

17.3.2 Availability of feedstock

For the four cases, it is assumed that the feedstock is sourced from a single source, although this may not the case in reality due to environmental and economic factors. Should the feedstock be sourced from multiple countries, the impact on the operating costs and ammonia price would be significant. In addition, operating at a larger scale than the original assessment increases the feedstock demand significantly.

17.3.3 Use of modelling

Some variations in the outputs of the presented models are expected, primarily because the models are based on a specific biomass syngas composition. In reality, the syngas composition will vary with the feedstock composition and operating conditions at a given time.

17.3.4 Status of technology

In this study, large-scale biomass gasification is under consideration. Whilst large-scale systems have been proposed by numerous sources, the technology has yet to be tested. Therefore, variations in the performance of the four cases presented should be expected.

17.3.5 Availability of technology

It is assumed that a suitable natural gas based ammonia production process is available for refurbishment. Should the technology not be available for use, Case 4 may not be as economically attractive as once thought.

17.3.6 Combining data from multiple sources

In some cases, multiple sources of data have been combined to provide an average figure. Whilst this method reduces the effect fluctuations in price, it is not fully representative of specific scale and operating conditions.

17.4 Recommendations for future work

17.4.1 Pilot trials

Whilst the modelling carried out in this study has demonstrated that biomass syngas is a potential feedstock for ammonia production, pilot scale trials are required to support this and to also verify the operating conditions and expected production rates.

17.4.2 Torrefaction trials

Investigations into the use of torrefaction in place of the SSD for Case 1 should be considered, in order to determine what impact the feedstock physical properties has on the production of ammonia.

17.4.3 Biomass/natural gas variation trials

For Case 4, a biomass/natural gas feed ratio of 1:9 was assumed, however the effect of varying this ratio was not investigated. Therefore, trials examining the effect of increasing the biomass input are recommended to determine the ideal feed stream composition, which reduces the natural gas requirement without compromising the quality and quantity of ammonia produced.

17.4.4 By-product revenue

In this study, the ammonia price was calculated based on the production costs and the expected revenue from the product. For future study, it is recommended that the sale of by-products (CO_2, steam and district heat) is considered and their impact on the ammonia price assessed.

17.4.5 Alternative technology

The use of alternative technology, particularly for CO_2 removal should be investigated to reduce the energy demand of the systems and assess the impact the different technology would have on the ammonia output and price.

18 References

1. Crown (2008) Climate Change Act 2008, Chapter 27.Retrieved 26/06/2013, from http://www.legislation.gov.uk/ukpga/2008/27/pdfs/ukpga_20080027_en.pdf
2. The European Parliament and the Council of the European Union (2009). EC DIRECTIVE 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC. *Cited by: McDowall, W., G. Anandarajah, et al. (2010). Optimal use of biomass to address Climate Change: The UK perspective. Bioten conference on biomass, bioenergy and biofuels. Birmingham, UK, CPL Press: 105-116.*
3. DECC (2009). The UK Renewable Energy Strategy. London, Department of Energy and Climate Change. *Cited by: McDowall, W., G. Anandarajah, et al. (2010). Optimal use of biomass to address Climate Change: The UK perspective. Bioten conference on biomass, bioenergy and biofuels. Birmingham, UK, CPL Press: 105-116.*
4. Demirbaş, A. (2001). "Biomass resource facilities and biomass conversion processing for fuels and chemicals." Energy Conversion and Management **42**: 1357 - 1378.
5. Aresta, M., Dibenedetto, A. & Barberio, G. (2005a). "Utilization of macro-algae for enhanced CO2 fixation and biofuels production: Development of a computing software for an LCA study." Fuel Processing Technology **86**: 1679-1693.
6. Yu, Q.-Z., C. Brage, et al. (2007). "The fate of fuel-nitrogen during gasification of biomass in a pressurised fluidised bed gasifier." Fuel **86**: 611 - 618.
7. Ross, A. B., Jones, J. M., Kubacki, M. L. & Bridgeman, T. (2008). "Classification of macroalgae as fuel and its thermochemical behaviour." Bioresource Technology **99**: 6494-6504.
8. Raiko, M., T. Gronfors, et al. (2003). "Development and optimization of power plant concepts for local wet fuels." Biomass & Bioenergy **24**: 27 - 37.
9. Carlsson, A. S., van Beilen, J. B., Möller, R. & Clayton, D. (2007). Micro- and Macro-algae: Utility for Industrial Applications. Outputs from the EPOBIO project. D. Bowles. York, CNAP, University of York.
10. Copplestone, J. C., C. M. Kirk, et al. (2002). Ammonia and Urea Production. H. Wansbrough, Petrochem.
11. Kongshaug, G. (1998). Energy consumption and greenhouse gas emissions in fertilizer production. IFA Technical Conference. Marrakech, Morocco.
12. IFA (2009). Fertilizers, climate change and enhancing agricultural productivity sustainably, International Fertilizers Association.

13. Tenkorang, F. and J. Lowenberg-DeBoer (2008). Forecasting Long-term Global Fertilizer Demand, Food and Agriculture Organization of the United Nations. *Cited by Gilbert et al.[372].*
14. Spath, P. L., A. Aden, et al. (2005). Biomass to Hydrogen Production Detailed Design and Economics Utilizing the Battelle Columbus Laboratory Indirectly-Heated Gasifier.
15. Phillips, S., A. Aden, et al. (2007). Thermochemical Ethanol via Indirect Gasification and Mixed Alcohol Synthesis of Lignocellulosic Biomass. Golden, Colorado, USA, NREL.
16. Huisman, G. H., G. L. Van Rens, et al. (2011). "Cost estimation of biomass-to-fuel plants producing methanol, dimethylether or hydrogen." Biomass &Bioenergy**35**(1): S155–S166.
17. SUPERGEN-bioenergy. (2011). "SUPERGEN-bioenergy" Retrieved 15/08/2012, from www.supergen-bioenergy.net
18. Lauer, M. (2008). Methodology guideline on technoeconomic assessment (TEA), ThermalNet.
19. Antweiler, W. (2009). Pacific Exchange Rate Service: Foreign Currency Units per 1 U.S. Dollar, 1948-2009, University of British Columbia.
20. x-rates. (2012). "Monthly average: GBP per 1.00 euro monthly average." Retrieved 15/08/2012, from http://www.x-rates.com/d/EUR/GBP/hist2009.html
21. Campbell, A. (2004). Seashores and Shallow Seas of Britain and Europe. London, Bounty Books.
22. Davies, A. (2008). "Shapes of Seaweeds." Freakin Fucus - Guide to Intertidal Ecology and Seaweeds Retrieved 06/04/2009, 2009, from http://freakinfucus.co.uk/primers/shapes-of-seaweed/
23. Atkinson, M. J. and S. V. Smith (1983). "C:N:P ratios of benthic marine plants." Limnology and Oceanography**28**(3): 568-574.
24. Guiry, M. D. and G. M. Guiry. (2013). "AlgaeBase." Retrieved 01/07/2013, from http://www.algaebase.org
25. Wang, S., X. M. Jiang, et al. (2008). "Fusion Characteristic Study on Seaweed Biomass Ash." Energy & Fuels**22**: 2229-2235.
26. Xia, B. M. (2000). Flora algarum marinarum sinicarum, Tomus 2 Rhodophyta, No 3 Gelidiales Cryptonemiales Hildenbrandiales (in Chinese). Beijing, China. *Cited by Wang et al. [25].*
27. Kelly, M., J. Ratcliffe, et al. (2008). Potential of Marine Biomass to UK Energy: Fuels and Chemicals, Scottish Association for Marine Science (SAMS) & Irish Seaweed Centre.

28. Alfred Wegner Institute (AWI). From http://www.awi-bremerhaven.de/Biomeer/ .*Cited by Reith et al. [29].*
29. Reith, H., W. Huijgen, et al. (2009). Seaweed potential in the Netherlands. Macroalgae - Bioenergy Research Forum. Plymouth, UK.
30. Adams, J. M., J. A. Gallagher, et al. (2008). "Fermentation study on Saccharina latissima for bioethanol production considering variable pre-treatments." Journal of Applied Phycology.
31. McLaughlin, E., J. Kelly, et al. (2006). Assessment of the Effects of Commercial Seaweed Harvesting on Intertidal and Subtidal Ecology in Northern Ireland.
32. Ado, Y., Y. Asada, et al. (1997). Renewable biological systems for alternative sustainable energy production. Agricultural Services Bulletin – 128, Food and Agriculture Organization of the United Nations (FAO). *Cited by Ross et al. [7].*
33. Lüning, K. (1990). Seaweeds. Their Environment, Biogeography, and Ecophysiology. New York, Wiley. *Cited by Lüning &Pang[66].*
34. Lüning, K. (1993). "Environmental and internal control of seasonal growth in seaweeds." Hydrobiologia**260/261**: 1-14.
35. Roesijadi, G., A. E. Copping, et al. (2008). Techno-Economic Feasibility Analysis of Offshore Seaweed Farming for Bioenergy and Biobased Products, Battelle Pacific Northwest Laboratory.
36. Bord Iascaigh Mhara (BIM) (1999). Seaweed Cultivation. Dun Laoghaire, Co. Dublin, Irish Sea Fisheries Board.
37. Wilson, K. A., K. W. Able, et al. (1990). Predation Rates on Juvenile Blue Crabs in Estuarine Nursery Habitats: Evidence for the Importance of Macroalgae (Ulva lactuca). Marine Ecology Progress Series **January 1990**.
38. Filipkowska, A., L. Lubecki, et al. (2008). "Utilisation of macroalgae from the Sopot beach (Baltic Sea)." Oceanologia**50**(2): 255-273.
39. Sharp, G. J. (1986). Ascophyllum nodosum and its harvesting in Eastern Canada. Case studies of seven commercial seaweed resources, FAO **FAO Technical Report, 281:** 3-46. *Cited by Ugarte & Sharp [119].*
40. Kain, J. M. (1991). Cultivation of attached Seaweeds. Seaweed Resources in Europe: Uses and Potential. M. D. Guiry and G. Blunden. Chichester, UK, Wiley**:** 309-377.
41. Charlier, R. H., P. Morand, et al. (2008). "How Brittany and Florida coasts cope with green tides." International Journal of Environmental Studies**65**(2): 191-208.
42. Charlier, R. H., P. Morand, et al. (2007). "Green Tides on the Brittany Coasts." Environmental Research, Engineering and Management**3**(41): 52-59.

43. Aresta, M., A. Dibenedetto, et al. (2005b). "Production of biodiesel from macroalgae by supercritical CO_2 extraction and thermochemical liquefaction." Environmental Chemistry Letters**3**: 136-139.
44. Matsui, T., T. Amano, et al. (2006). Methane Fermentation of Seaweed Biomass. AIChE 2006 Annual Meeting. San Francisco, USA.
45. Rupérez, P. (2002). "Mineral content in edible seaweeds." Food Chemistry**79**(1): 23-26.
46. Yu, L. J., S. Wang, et al. (2008). "Thermal analysis studies on combustion characteristics of seaweed" Journal of Thermal Analysis and Calorimetry**2**: 611-617.
47. Energy research Centre of the Netherlands (ECN) Phyllis, database for biomass and waste.
48. Ross, A. B., K. Anastasakis, et al. (2009). "Investigation of the pyrolysis behaviour of brown algae before and after pre-treatment using PY-GC/MS and TGA." Journal of Analytical Applied Pyrolysis**85**: 3 - 10.
49. Rossel, K. G. and L. M. Strivastava (1985). "Seasonal variations in total nitrogen, carbon and amino acids in Macrocystis intergrifola and Nereocystis luetkeana (Phaeophyta)." Journal of Phycology**21**: 304-309. *Cited by Kelly et al. [27].*
50. Arasaki, A. and T. Arasaki (1983). Low calories, High Nutrition. Vegetables from the Sea to Help you Look and Feel Better, Japan Publications Inc**:** 39-42. *Cited by Fleurence [67].*
51. Indegaard, M. and J. Minsaas (1991). Seaweed Resources in Europe Uses and Potential. In Animal and Human Nutrition. . M. D. Guiry and G. Blunden, John Wiley & Sons**:** 21-64. *Cited by Fleurence [67].*
52. Munda, I. M. (1977). "Differences in amino acid composition of estuarine and marine fucoids." Aquatic Botany**3**: 273-280. *Cited by Fleurence [67].*
53. Black, W. A. P. and E. T. Dewar (1949). "Correlation of some of the Physical and Chemical Properties of the sea with the chemical constitution of the algae." Journal of Marine Biology Association of the UK**28**: 673-699. *Cited by Kelly et al. [27].*
54. Black, W. A. P. (1950). "The Seasonal variation in weight and chemical composition of the common British Laminariaceae." Journal of Marine Biology Association of the UK**29**(1): 45-72. *Cited by Kelly et al. [27].*
55. Rosenberg, G. and R. J. (1982). "Ecological growth strategies in the seaweeds Gracilia foliifera (Rhodophyceae) and Ulva Sp. (Chlorophyceae): Soluble Nitrogen and reserve carbohydrates." Marine Biology**66**: 251-259.
56. Vergara-Ferńandez, A., G. Vargas, et al. (2008). "Evaluation of marine algae as a source of biogas in a two-stage anaerobic reactor system." Biomass & Bioenergy**32**: 338-344.

57. MacArtain, P., C. Gill, et al. (2007). "Nutritional Values of Edible Seaweeds." Nutrition reviews**65**(12): 535-543.
58. Chapman, A. R. and J. S. Craigie (1978). "Seasonal Growth in Laminaria longicruris: Relations with reserve carbohydrate Storage and Production." Marine Biology**46**(209-213).
59. Ragan, M. A. and K. W. Glombitza (1986). Phlorotannins, brown algal Polyphenols. Progress in Phycological Research. F. E. Round and D. J. Chapman. **4:** 131-241. *Cited by Kelly et al. [27].*
60. Seshadri, R. and J. Sieburth (1971). "Cultural estimation of of yeasts of seaweeds." Applied Microbiology**22**: 507-512. *Cited by Kelly et al. [27].*
61. Bryan, G. W. (1969). "The absorption of zinc and other metals by the brown seaweed Laminaria digitata." Journal of Marine Biology Association of the UK**49**: 225-243. *Cited by Kelly et al. [27].*
62. Ragan, M. A., O. Smidsrod, et al. (1979). "Chelation of divalent metal ions by brown algal polyphenols." Marine Chemistry**7**: 265-271. *Cited by Kelly et al. [27].*
63. Davis, T. A., B. Volevsky, et al. (2003). "A review of the biochemistry of heavy metal biosorption by brown algae." Water Research**37** 4311-4330. *Cited by Kelly et al. [27].*
64. Dean, R. J., T. M. Shimmield, et al. (2007). "Copper, zinc and cadmium in marine cage fish farm sediments: An extensive survey." Environmental Pollution**145**: 84-95.
65. Riekie, G. J., P. N. Williams, et al. (2006). "The potential for kelp manufacture to lead to arsenic pollution of remote Scottish islands." Chemosphere**65**: 332-342.
66. Lüning, K. and S. J. Pang (2003). "Mass cultivation of seaweeds: current aspects and approaches." Journal of Applied Phycology **15**: 115-119.
67. Fleurence, J. (1999). "Seaweed proteins: biochemical, nutritional aspects and potential uses." Trends in Food Science & Technology **10**: 25-28.
68. Kenicer, G., S. Bridgewater, et al. (2000). "The ebb and flow of Scottish seaweed use." Botanical Journal of Scotland**52**: 119 - 148. *Cited by Riekie et al. [65].*
69. Morgan, P. J. and K. Smith (1978). "Potentiality of Seaweed as a Resource: Analysis of the Pyrolysis Products of Fucus serratus." Analyst**103**: 1053-1060.
70. Food and Agriculture Organisation (2006). State of world aquaculture 2006. FAO Fisheries Technical Paper No. 500. Rome, Italy. *Cited by Kelly & Dworjanyn [132].*
71. Chen, J. (2006). China’s Mariculture after strategic transfer of fisheries mode. World Aquaculture Society Meeting 2006. Florence, Italy. *Cited by Roesijadi et al. [35].*
72. McHugh, D. J. (2003). A guide to the seaweed industry. FAO Fisheries Technical Paper No. 441, FAO.
73. Pure. (2011). "Discovering Seaweed - Nori." Retrieved 5/12/2011, from http://thepurebar.com/blog/2011/03/25/discovering-seaweed/nori/

74. Easy and Delicious Recipes with Picture. (2011). "Kombu konbu Laminaria japonica - Japanese seaweed." Retrieved 5/12/2011, from http://www.avrupasu.com/kombu-konbu-laminaria-japonica-japanese-seaweed.html
75. Nisizawa, K., H. Noda, et al. (1987). "The main seaweed foods in Japan." Hydrobiologia**151/152**(5-29).
76. Fankhauser, D. B. (2001). "Agar Overlay Technique " Retrieved 5/12/2011, from http://biology.clc.uc.edu/fankhauser/Labs/Microbiology/Bacterial_Inhibition/Agar_Overlay.htm
77. Lersch, M. (2007). "First experiments with sodium alginate." Retrieved 5/12/2011, from http://blog.khymos.org/2007/03/30/first-experiments-with-sodium-alginate/
78. Made-in-China.com. (2011). "Carrageenan." Retrieved 5/12/2011, from http://www.made-in-china.com/showroom/tianyuanxindafood/product-detailEeFJKqhMfSkU/China-Carrageenan.html
79. Briand, X. (1991). Seaweed Harvesting in Europe. Seaweed Resources in Europe: Uses and Potential M. D. Guiry and G. Blunden. Chichester, UK, John Wiley and Sons**:** 259-308.
80. CosmeticsDesign-Europe.com. (2008). "Seaweed taps into the anti-ageing trend." Retrieved 6/10/2011, from http://www.cosmeticsdesign-europe.com/Market-Trends/Seaweed-taps-into-the-anti-ageing-trend
81. Bohemia Style UK. (2011). "No more Acne: Seaweed Facial creams and Treatments for Clear Complexions." Retrieved 6/10/2011, from http://www.bohemia-style.co.uk/No-more-Acne-Seaweed-Facial-creams-and-Treatments-for-Clear-Com-orderby0-p-1-c-84.html
82. The Body Shop International PLC. (2011). Retrieved 6/10/2011, from http://www.thebodyshop.co.uk
83. Timetospa.co.uk. (2011). "Bliss Serious Seaweed Cellulite Soap." Retrieved 6/10/2011, from http://www.timetospa.co.uk/bath-and-body/bath-and-shower/Bliss-Serious-Seaweed-Cellulite-Soap/
84. Merriam-Webster (2013). Retrieved 5/7/2013, from http://www.merriam-webster.com/dictionary/xenobiotic
85. Munoz, R. and B. Guieysse (2006). "Algal-bacterial processes for the treatment of hazardous contaminants: A review." Water Research**40**: 2799 - 2815. *Cited by Carlsson et al. [9].*
86. Yu, Q., Jose T. Matheickal, et al. (1999). "Heavy metal uptake capacities of common marine macro algal biomass." Water Research**33**(6): 1534-1537.
87. Beavis, A., R. H. Charlier, et al. (1986). "Laminaria SSP, as energy source." Oceans**18**: 621-626.

88. Clacherty, G., B. Friedland, et al. (2004). Testing Carraguard (TM): What you need to know. Johannesburg, Population Council.
89. Tyler-Walters, H. (2003). Alaria esculenta. Dabberlocks. Marine Life Information Network: Biology and Sensitivity Key Information Sub-programme [on-line]. Plymouth, Marine Biological Association of the United Kingdom. *Cited by McLaughlin et al. [31].*
90. Congdon, J. (2010). "Seaweed to help with weight loss." Retrieved 6/10/2011, from http://www.weightworld.co.uk/health-and-diet-news/seaweed-to-help-with-weight-loss-1464.html
91. Yourpetshealth.co.uk. (2011). "Dental Problems." Retrieved 5/12/2011, from http://www.yourpetshealth.co.uk/page44.htm
92. The Healthier Life. (2007). "ProDen PlaqueOff - Norwegian Seaweed Could Help Prevent Gum Disease." Retrieved 5/12/2011, from http://www.thehealthierlife.co.uk/natural-health-articles/oral-health/proden-plaqueoff-prevent-gum-disease-00272.html
93. Fei, X.-G., Y. Bao, et al. (1999). "Seaweed cultivation: traditional way and its reform." Chinese Journal of Oceanology and Limnology**17**(3).
94. Food and Agriculture Organisation (2004). FAO-Fisheries Department, Fishery Information, Data and Statistics Unit. FISHSTAT Plus.(Universal Software for fishery statistical time series) Version 2.3. Rome, Italy. *Cited by Buck & Buchholz [95].*
95. Buck, B. H. and C. M. Buchholz (2004). "The offshore ring: a new system design for the open ocean aquaculture of macroalgae." Journal of Applied Phycology**16**: 355-369.
96. Buck, B. H., G. Krause, et al. (2004). "Extensive open ocean aquaculture development within wind farms in Germany: the prospect of offshore co-management and legal constraints." Ocean & Coastal Management**47**: 95-122.
97. Mann, K. H. (1973). "Seaweeds: their productivity and strategy for growth." Science**182**: 975 - 981. *Cited by Carlsson et al. [9].*
98. Chynoweth, D. P. (2002). Review of Biomethane from Marine Biomass. Gainesville, Florida, Department of Agricultural and Biological Engineering, University of Florida.
99. Tseng, C. K. (1987). Some remarks on the kelp cultivation industry of China. Seaweed cultivation for renewable resources. Developments in aquaculture and fisheries science. K. T. Bird and P. H. Benson. Amsterdam, Elsevier. **16:** 147 - 156. *Cited by Kelly & Dworjanyn [132].*
100. Juanich, G. L. (1998). Manual on seaweed farming: 1. Eucheuma spp., Food and Agriculture Organisation (FAO).

101. Feijiu, W. (1988). Marine Phycoculture in China. Seminar report on the status of seaweed culture in China, India, Indonesia, Korea R., Malaysia, Philippines and Thailand, Fisheries and Aquaculture Department (FAO).

102. Gomez, I. and K. Lüning (2001). "Constant short-day treatment of outdoor-cultivated Laminaria digitata prevents summer drop in growth rate." European Journal of Phycology **36**: 391-395. *Cited by Lüning & Peng [66].*

103. Mansilla, A., M. Palacios, et al. (2007). Growth and survival performance of the gametophyte of Gigartina skottsbergii (Rhodophyta, Gigartinales) under defined nutrient conditions in laboratory culture. Proceedings of the 19th International Seaweed Symposium, Kobe, Japan.

104. Tseng, C. K. (1987). Some remarks on the kelp cultivation industry of China. Seaweed cultivation for renewable resources. Developments in aquaculture and fisheries science. K. T. Bird and P. H. Benson. Amsterdam, Elsevier. **16:** 147 - 156. *Cited by McHugh [72].*

105. Dalli, A. (1988). Seaweed farming in East Malaysia. Seminar report on the status of seaweed culture in China, India, Indonesia, Korea R., Malaysia, Philippines and Thailand, Food and Agriculture Organization (FAO)**:** 129 - 130.

106. Yanti. *Cited by McHugh [72].*

107. Brunner, L. (2010). Marine Feedstock. S. Alexander.

108. Perez, P., R. Kaas, et al. (1992). La culture des algues marines dans le monde. IFREMER. Nantes, France. *Cited by Buck & Buchholz [95].*

109. Lenstra, J., H. Reith, et al. (2010). Economic perspectives of seaweed. 4th International Algae Congress,. Amsterdam, The Netherlands.

110. Ecofys. (2012). "PRESS RELEASE: Ecofys launches test module for seaweed cultivation in offshore wind farms." Retrieved 17/09/2012, from http://www.ecofys.com/en/press/ecofys-launches-trial-module-for-seaweed-cultivation-in-offshore-wind-farm

111. Pidwirny, M. (2010). "Ocean." The Encyclopedia of Earth Retrieved 10/10/2011, from http://www.eoearth.org/article/Ocean

112. Wise, D. L. (1981). "Probing the feasibility of large scale aquatic biomass energy farms." Solar Energy **26**(5): 455-457. *Cited by Ross et al. [7]; Beavis et al. [87].*

113. Bird, K. T. (1987). Cost analyses of energy from marine biomass. Seaweed cultivation for renewable resources. K. T. Bird and P. H. Benson. Amsterdam, Elsevier**:** 327-350. *Cited by Carlsson et al. [9]; Chynoweth [98].*

114. Gao, K. and K. R. McKinley (1994). "Use of macroalgae for marine biomass production and CO2 remediation: a review." Journal of Applied Phycology **6**: 45-60.

115. Bastianoni, S., F. Coppola, et al. (2008). "Biofuel potential production from the Orbetello lagoon macroalgae: A comparison with sunflower feedstock." Biomass &Bioenergy**32**: 619-628.

116. Reith, J. H., E. P. Deurwaarder, et al. (2005). Grootschalige teelt van zeewieren in combinatie met offshore windparken in de Noordzee, ECN.

117. Levring, K. (1977). Potential yields of marine algae – with emphasis on European species. The Marine plant biomass of the Pacific Northwest coast. R. W. Kraus. Corvallis, Oregon State University Press.**:**251 - 270. *Cited by Kain [40].*

118. Kain, J. M. (1971). "Synopsis of biological data on Laminaria hyperborea." Fish Synopsis **87**: 1-68. *Cited by Briand [79].*

119. Ugarte, R. A. and G. J. Sharp (2001). "A new approach to seaweed management in Eastern Canada: the case of Ascophyllum nodosum." CBM - Cahiers de Biologie Marine **42**: 63-70.

120. CEVA. *Cited by Bruton et al. [128].*

121. Braud, J. P. (1984). Essai de dragage de Laminaria hyperborea. Symposium sur les Algues Marines. J. Y. –Floc'h. Brest, Université de Bretagne Occidentale et Chambre de Commerce et d'Industrie de Breas**:** 1 - 19. *Cited by Briand [79].*

122. Jensen, A. (1998). The seaweed resources of Norway. Seaweed Resources of the World. A. T. Critchley and M. Ohno. Yokosuka, Japan, JICA. *Cited by Kelly et al. [27].*

123. Svensen, P. (1972). "Some observations on commercial harvesting and regrowth of Laminaria hyperborea." Soestsykk Av. Fiskets gang.**22**: 448 - 460. *Cited by Briand [79].*

124. Briand (1998). *Cited by Kelly et al. [27].*

125. Christie, H., S. Fredriksen, et al. (1998). "Regrowth of kelp and colonization of epiphyte and fauna community after kelp trawling at the coast of Norway." Hydrobiologia**375/376**: 49-58.

126. Sharp, G. J., P. O. Ang, et al. (1995). Rockweed harvesting in Nova Scotia, Canada: Its socio-economic and biological implications for coastal zone management. Proceedings of the Coastal Zone Conference.

127. Sharp, G. J. and R. E. Semple (1997). Rockweed (Ascophyllum nodosum). CAFSAC Research Document. **97/31:** 10*. Cited by Ugarte & Sharp [119].*

128. Bruton, T., H. Lyons, et al. (2009). A Review of the Potential of Marine Algae as a Source of Biofuel in Ireland.

129. Black, W. A. (1955). "The preservation of seaweed by ensiling and bactericides." Journal of the Science of Food and Agriculture**6**(1): 14 - 23.

130. Hallsson, S. V. (1961). The uses of seaweed in Iceland. Fourth International Seaweed Symposium. France.

131. Morand, P., A. Cruzado, et al. (1992). Macroalgae: pollution or help to the pollution abatement? Depollution planning of the Mediterranean Sea. Recommendations for a sound policy. I. Bertini, G. Scorrano, R. Cipollini and R. Monnanni, Roma: Società Chimica Italiana**:** 57-72. *Cited by Charlier et al. [42].*

132. Kelly, M. and S. Dworjanyn (2008). The potential of marine biomass for anaerobic biogas production. The Crown Estate.

133. Energy Efficiency & Renewable Energy. (2011). "How Anaerobic Digestion (Methane Recovery) Works." U.S. Department of Energy Retrieved 1/9/2011, from http://www.energysavers.gov/your_workplace/farms_ranches/index.cfm/mytopic=30003*. Cited by Kelly & Dworjanyn [132].*

134. Gunaseelan, V. N. (1997). "Anaerobic Digestion of Biomass for Methane Production: A Review." Biomass & Bioenergy **13(1/2)**: 83-114.

135. Tchobanoglous, G., H. Theisen, et al. (1993). Intergrated Solid Waste Management. New York, McGraw-Hill. *Cited by Verma [205].*

136. Chynoweth, D. P., Owens, J. M. & Legrand, R. (2001). "Renewable methane from anaerobic digestion of biomass." Renewable Energy**22**: 1-8.

137. Chynoweth, D. P., C. E. Turick, et al. (1993). "Biochemical methane potential of biomass and waste feedstocks." Biomass & Bioenergy**5**: 95-111. *Cited by Carlsson et al. [9].*

138. Bird, K. T., D. P. Chynoweth, et al. (1990). "Effects of marine algal proximate composition on methane yields." Journal of Applied Phycology**2**: 207 - 213. *Cited by Carlsson et al. [9].*

139. Bird, K. T. and J. H. Ryther (1985). Aquatic plant aquaculture: a multiproduct/multiuse approach. The third technical review meeting on energy from biomass: building on a generic technology base, Argonne, IL, USA, Argonne National Laboratory. *Cited by Vergara-Ferńandez et al. [56].*

140. Morand, P., B. Carpentier, et al. (1991). Bioconversion of seaweeds. Seaweed Resources in Europe: Uses and Potential. M. D. Guiry and G. Blunden. Chichester, UK, John Wiley & Sons**:** 95 - 148.

141. Belgiorno, V., G. De Feo, et al. (2003). "Energy from gasification of solid wastes." Waste Management**23**: 1-15.

142. Bridgwater, A. V. (1995). "The technical and economic feasibility of biomass gasification for power generation." Fuel **74**(5): 631-653.

143. Ro, K. S., K. Cantrell, et al. (2007). "Catalytic Wet Gasification of Municipal and Animal Wastes." Industrial & Engineering Chemistry Research**46**(26): 8839-8845.

144. Kruse, A. (2009). "Hydrothermal biomass gasification." Journal of Supercritical Fluids**47**: 391-399.

145. Kruse, A. (2008). "Supercritical water gasification." Biofuels, Bioproducts & Biorefining**2**: 415–437.

146. Bridgwater, A. V., D. Meier, et al. (1999). "An overview of fast pyrolysis of biomass." Organic Geochemistry**30**: 1479 - 1493.

147. Onay, O. and O. M. Kockar (2003). "Slow, fast and flash pyrolysis of rapeseed." Renewable Energy**28**: 2417-2433. *Cited by Aresta et al. [5].*

148. Ginsburg, B. Z. (1993). "Liquid fuel (oil) from halophilic algae: a renewable source of non-polluting energy." Renewable Energy**3**(2-3): 249-252. *Cited by Yu et al. [46].*

149. Wu, Q. Y., J. B. Dai, et al. (1999). "A renewable energy source - hydrocarbon gases resulting from pyrolysis of the marine nanoplanktonic alga Emiliania huxleyi." Journal of Applied Phycology**11**: 137-142. *Cited by Yu et al. [46].*

150. Wang, J., G. Wang, et al. (2006). "A comparative study of thermolysis characteristics and kinetics of seaweeds and fir wood." Process Biochemistry**41**: 1883-1886.

151. Sawayama, S., T. Minowa, et al. (1999). "Possibility of renewable energy production and CO_2 mitigation by thermochemical liquefaction of microalgae." Biomass & Bioenergy**17**: 33-39.

152. Demirbaş, A. (2000). "Mechanisms of liquefaction and pyrolysis reactions of biomass." Energy Conversion and Management**41**: 633-646.

153. Roesijadi, G., S. B. Jones, et al. (2010). Macroalgae as a Biomass Feedstock: A Preliminary Analysis, Pacific Northwest National Laboratory (Batelle).

154. Lenstra, J., J. van Hal, et al. (2011). Economic aspects of open ocean seaweed cultivation. Alg'n Chem 2011. Montpellier, France.

155. Jackson, G. A. (1977). Biological constraints on seaweed culture. Biological Solar Energy Conversion. A. Mitsui. New York, Academic Press. **4:** 437-447. *Cited by Beavis et al. [87].*

156. Wise, D. L., R. L. Wenhnrorth, et al. (1977). Fuel gas production from selected biomass via anaerobic digestion. Biological Solar Energy Conversion. A. Mitsui. New York, Academic Press**:** 411 - 426. *Cited by Beavis et al. [87].*

157. EUROCEAN (1980). Seaweeds and microalgae pre-study report. Monaco.

158. North, W.J. (1980). Biomass from marine macroscopic plants. Solar Energy Journal**25:** 387-397. *Cited by Beavis et al. [87].*

159. Jackson (1980). *Cited by Beavis et al. [87].*

160. Morley, J. G. and J. M. Jones (1980). Growth of marine biomass on artificial substrates as a renewable source of energy. . 1st EC Energy from Biomass conference, Brighton, UK.

161. Aizawa, M., K. Asaoka, et al. (2007). Seaweed Bioethanol Production in Japan - The Ocean Sunrise Project. Tokyo, Japan, Tokyo Fisheries Promotion Foundation.

162. Chynoweth, D. P. and H. R. Isaacson, (Eds) (1987). Anaerobic digestion of biomass. New York, Elsevier Applied Science Publishers Ltd.

163. Legrand, R. and C. S. Warren (1987). Biogas generation from community-derived wastes and biomass in the US. Tenth Annual Energy-Sources Technology Conference and Exhibition. Dallas, TX. *Cited by Chynoweth et al. [136].*

164. Ecofys. http://www.ecofys.com/. *Cited by Reith et al. [29].*

165. The Independent. (2007). "The wonder of seaweed." from www.independent.co.uk

166. Sea Around Us Project. (1999). "Exclusive Economic Zones." Retrieved 2/9/2011, from http://www.seaaroundus.org/eez/

167. Walker, F. T. (1947a). A seaweed survey of Scotland: Fucaceae. The Linean Society London, UK. *Cited by Kelly & Dworjanyn [132].*

168. Walker, F. T. (1947b). "Sublittoral Seaweed Survey: Part I, Development of the View Box--Spring Grab Technique for Sublittoral Weed Survey. Part II, Survey of Orkney, Scapa Flow. Part III, Survey of Orkney, Bay of Firth." Journal of Ecology**35**(1/2): 166-185.

169. Boerrigter, H. (2006). Economy of Biomass-to-Liquids (BTL) plants. Petten, The Netherlands, ECN.

170. Zamalloa, C., E. Vulsteke, et al. (2011). "The techno-economic potential of renewable energy through the anaerobic digestion of microalgae." Bioresource Technology**102**: 1149 - 1158.

171. Lisac, D. and J. Muir (2000). Comparative economics of offshore and onshore mariculture facilities. Mediterranean Offshore Mariculture. Options Méditerranéennes (Serie B: Études et recherches). . J. Muir and B. Basurco, Publication Based on the Contents of the Advanced Course of the CIHEAM Network on Technology of Aquaculture in the Mediterranean (TECAM), Zaragoza, Spain, October 20–24, 1997. **30:** 203 - 211.

172. Andigestion Ltd. (2008). "Holsworthy Biogas Plant, Devon." from http://www.andigestion.co.uk/content/holsworthy

173. Yokoyama, S., K. Jonouchi, et al. (2007). Energy Production from Marine Biomass: Fuel Cell Power Generation Driven by Methane Produced from Seaweed. World Academy of Science, Engineering & Technology, Prague, Czech Republic.

174. Anastasakis, K. and A. B. Ross (2011). "Hydrothermal liquefaction of the brown macro-alga Laminaria Saccharina: Effect of reaction conditions on product distribution and composition." Bioresource Technology**102**: 4876-4883.

175. McKendry, P. (2002a). "Energy production from biomass (part 2): conversion technologies." Bioresource Technology **83**: 47-54.

176. Higman, C. and M. van der Burgt (2003). Gasification. Amsterdam ; Boston, Gulf Professional Pub./Elsevier Science.

177. Baxter, L. (1993). “Ash deposition during biomass and coal combustion: a mechanistic approach.”Biomass & Bioenergy **4**: 85 - 105. *Cited by Wang, L., C. Weller et al. (2008). "Contemporary issues in thermal gasification of biomass and its application to electricity and fuel production." Biomass & Bioenergy* ***32****: 573 - 581.*

178. Nowakowski, D. (2009). Macroalgae pyrolysis. S. Alexander. Birmingham, UK.

179. Sagi, S. (2010). Intermediate Pyrolysis: A Sustainable Biomass-to-Energy Concept. Birmingham, UK, Aston University

180. Hornung, A. (2009). Intermediate pyrolysis of macroalgae. S. Alexander and J. G. Brammer. Birmingham, UK.

181. Puchajda, B. and J. Oleszkiewicz (2008). "Impact of sludge thickening on energy recovery from anaerobic digestion." Water Science and Technology **57**(3): 395-401.

182. Bridgwater, A. V., A. J. Toft, et al. (2002). "A techno-economic comparison of power production by biomass fast pyrolysis with gasification and combustion." Renewable and Sustainable Reviews **6**: 181-248.

183. Luterbacher, S., M. Froling, et al. (2009). "Hydrothermal Gasification of Waste Biomass: Process Design and Life Cycle Asessment." Environmental Science &Technology **43**(5): 1578 - 1583. *Interpreted by Stucki et al. [184].*

184. Stucki, S., F. Vogel, et al. (2009). "Catalytic gasification of algae in supercritical water for biofuel production and carbon capture." Energy & Environmental Science **2**: 535 - 541.

185. Matsumura, Y. (2002). "Evaluation of supercritical water gasification and biomethanation for wet biomass utilization in Japan." Energy Conversion and Management **43**: 1301 - 1310. *Cited by Kruse [144].*

186. Lemley, B. (2003). Anything into Oil. Discover Magazine, Kalmbach Publishing Co. **May 2003**.

187. Rogers, J. G. and J. G. Brammer (2012). "Estimation of the production cost of fast pyrolysis bio-oil." Biomass & Bioenergy **36**: 208 - 217.

188. Hamelinck, C. N., G. van Hooijdonk, et al. (2005). "Ethanol from lignocellulosic biomass: techno-economic performance in short-, middle- and long-term." Biomass & Bioenergy **28**: 384 - 410.

189. Carbon Trust (2010). Introducing combined heat and power. www.carbontrust.co.uk

190. Hennenberg, K., U. Fritsche, et al. (2009). Aquatic Biomass: Sustainable Bioenergy from Algae? *Cited by Roesijadi et al. [153].*

191. Goh, C. S. and K. T. Lee (2010). "A visionary and conceptual macroalgae-based third-generation bioethanol (TGB) biorefinery in Sabah, Malaysia as an underlay for renewable and sustainable development." Renewable and Sustainable Energy Reviews**14**: 842 - 848. *Cited by Roesijadi et al. [153].*

192. Morchio, R. and C. Cáceres (2009). Macroalgae Current State in Latin America. International Workshop on Sustainable Bioenergy from Algae. Berlin, Germany. *Cited by Roesijadi et al. [153].*

193. Horn, S. J. (2000c). Bioenergy from brown seaweeds. Department of Biotechnology. Trondheim, Norway, Norwegian University of Science and Technology (NTNU). **Doktor ingeniør**.

194. Horn, S. J., I. M. Aasen, et al. (2000a). "Production of ethanol from mannitol by Zymobacter palmae." Journal of Industrial Microbiology & Biotechnology**24**: 51-57.

195. Horn, S. J., I. M. Aasen, et al. (2000b). "Ethanol production from seaweed extract." Journal of Applied Microbiology & Biotechnology**25**: 249-254.

196. Mocker, M., P. Quicker et al. (2007). sludge2energy - Decentralised sewage sludge utilisation. Retrieved 10/7/2013, from http://ec.europa.eu/environment/life/project/Projects/index.cfm?fuseaction=home.showFile&rep=file&fil=SLUDGE2ENERGY_decentralised_EN.pdf

197. Laws, E. A. (1991). "Photosynthetic efficiency optimization studies with the macroalga Gracilaria tikvihae: implications for CO_2 emission control from power plants." Bioresource Technology**37**: 25-33. *Cited by Aresta et al. [5].*

198. Minowa, T. and S. Sawayama (1999). "A novel microalgal system for energy production with nitrogen cycling." Fuel**78**: 1213-1215. *Cited by Aresta et al. [5].*

199. Morris, K. W. (2001). "Fast pyrolysis of bagasse to produce biooil fuel for power generation." International Sugar Journal**103**(1230): 259-263. *Cited by Aresta et al. [5].*

200. Wu, Q., J. Dai, et al. (1999). "A renewable energy source - hydrocarbon gases resulting from pyrolysis of the marine nanoplanktonic alga Emiliana huxleyi." Journal of Applied Phycology**11**(2): 137-142. *Cited by Aresta et al. [5].*

201. Briand, X. and P. Morand (1997). "Anaerobic digestion of Ulva sp. 1. Relationship between Ulva composition and methanisation." Journal of Applied Phycology**9**: 511-524. *Cited by Aresta et al. [5]; Charlier et al. [42]*.

202. Østgaard, K. and M. Inderggard (1993). "Carbohydrate degradation and methane production during fermentation of Laminaria saccharina (Laminariales, Phaeophyceae)." Journal of Applied Phycology**5**: 333-342. *Cited by Aresta et al. [5].*

203. Anastasakis, K., A. B. Ross, et al. (2011). "Pyrolysis behaviour of the main carbohydrates of brown macro-algae." Fuel**90**: 598-607.

204. Wang, S., X. M. Jiang, et al. (2007). "Research on Pyrolysis Characteristics of Seaweed." Energy & Fuels**21**: 3723-3729.

205. Verma, S. (2002). Anaerobic digestion of biodegradable organics in municiple solid wastes. Department of Earth & Environmental Engineering, Columbia University. **Masters of Science**.

206. Fischer, T., A. Krieg, et al. (2002). "Farm-Scale Biogas Plants." Journal of the Korea Organic Waste Recycling Council.**9**: 136−144.

207. Crown Estate. (2012). from http://www.thecrownestate.co.uk/

208. SUPERGEN (2009). Unpublished data.

209. IEA (2008). Clean Coal Centre: "Coal to liquids", Couch. *Cited by IEA (2010). Syngas Production from Coal.*

210. English Heritage. (2011). "Small scale solar electric energy." Climate Change & Your Home Retrieved 24/08/2011, from http://www.climatechangeandyourhome.org.uk/live/small_scale_electric_energy.aspx

211. Saini, A. (2011). "Our Carbon Footprints." Guardian.co.uk Retrieved 24/08/2011, from http://observer.guardian.co.uk/carbontrust/story/0,,1512910,00.html

212. OVO Energy. (2010). "How do we work out your winter consumption?" Retrieved 28/11/2011, from http://www.ovoenergy.com/winterconsumption_calculation_example.pdf

213. Hurtado-Ponce, A. Q., R. F. Agbayani, et al. (1996). "Economics of cultivating Kappaphycus alvarezii using the fixed-bottom line and hanging-long line methods in Panagatan Cays, Caluya, Antique, Philippines." Journal of Applied Phycology**105**: 105-109.

214. Firdausy, C. and C. Tisdell (1991). "Economic returns from seaweed (Eucheuma cottonii) farming in Bali, Indonesia." Asian Fisheries Science**4**: 61-73.

215. Hurtado, A. Q., R. F. Agbayani, et al. (2001). "The seasonality and economic feasibility of cultivating Kappaphycus alvarezii in Panagatan Cays, Caluya, Antique, Philippines." Aquaculture**199**: 295-310.

216. Kam, L. E., P. Leung, et al. (2003). "Economics of offshore aquaculture of Pacific threadfin (Polydactylus sexfilis) in Hawaii." Aquaculture**223**: 63–87.

217. Chynoweth, D. P., K. F. Fannin, et al. (1987b). Biological Gasification of Marine Algae. Seaweed Cultivation for Renewable Resources. K. T. Bird and P. H. Benson. New York, Elsevier**:** 285-303.

218. Sanchez-Machado, D. I., J. Lopez-Cervantes, et al. (2004). "Fatty acids, total lipid, protein and ash contents of processed edible seaweeds." Food Chemistry**85**: 439–444.

219. Moen, E., S. Horn, et al. (1997a). "Alginate degradation during anaerobic digestion of Laminaria hyperborea stipes." Journal of Applied Phycology**9**: 157–166.

220. Swanson, R. M., J. A. Satrio, et al. (2010). Techno-Economic Analysis of Biofuels Production Based on Gasification, NREL.

221. Coastal Care. (2012). "Wild boar deaths linked to green algae: confirmed." from http://coastalcare.org/2011/08/wild-boar-deaths-linked-to-green-algae-confirmed/

222. Lichfield, J. (2011). "Fears rise over French 'killer seaweed' that left 15 wild boar dead." The Independent Retrieved 17/9/2012, from http://www.independent.co.uk/environment/nature/fears-rise-over-french-killer-seaweed-that-left-15-wild-boar-dead-2326492.html

223. Stanley, M. (2009). Fuels from seaweed, BioMara.

224. Migliore, G., C. Alisi, et al. (2012). "Anaerobic digestion of macroalgal biomass and sediments sourced from the Orbetello lagoon, Italy." Biomass & Bioenergy**42**: 69-77.

225. Kübler, H. and C. Schertler (1994). "Three-phase anaerobic digestion of organic wastes." Water Science and Technology**30** (12): 367–374.

226. Biogas Products Ltd. (2012). Retrieved 2011/2012, from http://biogasproducts.co.uk/

227. Bridgwater, A. V. (1994). "Catalysis in thermal biomass conversion." Applied Catalysis A: General **116**: 5–47. *Cited by Belgiorno et al. [141].*

228. Chennubhotla, V. S. (1988). a) Status of seaweed culture in India. b) Manual on seaweed culture: pond culture of Caulerpa and Gracilaria, c) The artificial cultivation of Gracilaria, FAO. **6:** 2–46. *Cited by Aresta et al. [5].*

229. Sawayama, S., S. Inoue, et al. (1995). "CO2 fixation and oil production through microalga." Energy Conversion and Management **36**: 729-731. *Cited by Aresta et al. [5].*

230. Lenzi, M. ICRAM. Rome, Italy. *Cited by Aresta et al. [5].*

231. Smyth, B. M., J. D. Murphy, et al. (2009). "What is the energy balance of grass biomethane in Ireland and other temperate northern European climates?" Renewable and Sustainable Energy Reviews**13**: 2349–2360.

232. Mehta, A. (2002). The Economics and Feasibility of Electricity Generation using Manure Digesters on Small and Mid-size Dairy Farms. Energy Analysis and Policy Program. Madison, Wisconsin, USA, Department of Agricultural and Applied Economics - University of Wisconsin.

233. Herringshaw, B. (2009). A Study of Biogas Utilization Efficiency Highlighting Internal Combustion Electrical Generator Units. College of Food, Agricultural, and Biological Engineering. Columbus, Ohio, USA, The Ohio State University. **Engineering**.

234. Sanderson, J. C. (2006). Reducing the environmental impact of seacage fish farming through cultivation of seaweed. Scottish Association for Marine Science (SAMS). **PhD:** 356.

235. Buck, B. H., M. W. Ebeling, et al. (2010). "Mussel cultivation as a co-use in offshore wind farms: potential and economic feasibility." Aquaculture Economics & Management**14**(4): 255-281.

236. Juniper Consultancy Services Ltd. (2007). Anaerobic digestion technology for biomass projects, Renewables East.

237. Perales, A. L., C. R. Valle, et al. (2011). "Technoeconomic assessment of ethanol production via thermochemical conversion of biomass by entrained flow gasification." Energy**36**(7): 4097–4108.

238. Coyle, M. (2007). Effects of payload on the fuel consumption of trucks, Imise Limited.

239. AA (2011). Fuel Price Report: Petrol and diesel price archive 2000-2010.

240. Hamelinck, C. N., R. A. Suurs, et al. (2003). International bioenergy transport costs and energy balance, Universiteit Utrecht Copernicus Institute Science Technology Society.

241. Hamelinck, C. N., R. A. Suurs, et al. (2005). "International bioenergy transport costs and energy balance." Biomass & Bioenergy**29**: 114–134.

242. Sinnott, R. K. (2005). Coulson and Richardson's Chemical Engineering Volume 6 - Chemical Engineering Design, Elsevier.

243. Kaiser, M. J., Y. Yu, et al. (2010). "Economic feasibility of using offshore oil and gas structures in the Gulf of Mexico for platform-based aquaculture." Marine Policy**34**: 699–707.

244. Eurostat (2009). Agricultural Statistics. 2007–2008, Eurostat, Luxembourg**:** 131.

245. Lum, C. (2002). Moi farm signs 20-year lease. Honolulu Advertiser**:** 1-2. *Cited by Kam [216].*

246. Hillmann, L. G. (2005). Summary of regulations for seaweed harvesting along the west coast of North America, Oregon Parks and Recreation Department.

247. DECC (2011a). "Table 3.1.3 Prices of fuels purchased by manufacturing industry." Retrieved 1/4/2011, from www.decc.gov.uk/assets/decc/statistics/source/prices/qep313.xls

248. Chesshire, M and J. Ferry (2006). Farm scale biogas and composting to improve bathing water quality. Greenfinch Ltd. & Enviros Consulting Ltd. The Scottish Executive, Water Division.

249. Croatian Shipbuilding Corporation (2008). Croatian Shipbuilding - Bulk and multipurpose.

250. March 2009 fuel oil price. Retrieved 13/12/2010, from http://topkwh.50webs.com/

251. Searates. (2012). from http://www.searates.com/

252. Dutta, A., M. Talmadge et al. (2011). Process Design and Economics for Conversion of Lignocellulosic Biomass to Ethanol. Golden, Colorado, USA, NREL.

253. Davis, R. & Aden, A. (2012). Algal Biofuel Pathway Baseline Costs. . Golden, Colorado, USA, NREL.

254. Sun, A., R. Davis et al. (2011). "Comparative cost analysis of algal oil production for Biofuels". Energy **36**: 5169-5179.

255. DECC (2011b). Renewable Heat Incentive Scheme Q&A Index. Retrieved 12/12/2012, from http://www.decc.gov.uk/assets/decc/what%20we%20do/uk%20energy%20supply/energy%20mix/renewable%20energy/policy/renewableheat/1393-rhi-faqs.pdf

256. Halcrow Group Limited (2009). Scottish Government: Economic and Community Benefit Study (Final Report).

257. U-switch.com (2012). Retrieved 13/1/2012, from http://u-switch.com

258. Department for Environment, Food and Rural Affairs (DEFRA) (2012). The Cost of Fuel in Rural Areas.

259. UK Power (2013). Home energy price comparison 16/1/2013. Retrieved from: http://www.ukpower.co.uk/home_energy/compare/electricity/XCDV3855/green 16/1/13

260. Encyclopaedia Britannica (2012). "ammonia (NH_3)" http://www.britannica.com/

261. EPA (1995). Chapter 8: Inorganic Chemistry. Emissions Factors & AP 42, Compilation of Air Pollutant Emission Factors. North Carolina. **Volume 1: Stationary Point and Area Sources**.

262. European Commission (2007). Reference Document on Best Available Techniques for the Manufacture of Large Volume Inorganic Chemicals - Ammonia, Acids and Fertilisers.

263. Agarwal, P. (2009). "Ammonia: The Next Step." The Chemical Engineers Resource Page Retrieved 21/5/2009, 2009, from http://www.cheresources.com/ammonia.shtml

264. EFMA (2000). Production of Ammonia. Best Available Techniques for Pollution Prevention and Control in the European Fertilizer Industry. Brussels.

265. Slack, A. V. (1973). Ammonia: Part I. Ammonia. A. V. Slack and G. R. James. New

York, Marcel Dekker. **2:** 414.

266. HSE (2008). "Pipelines and gas supply industry: Frequently asked questions - FAQs." Retrieved 06/04/2011, from http://www.hse.gov.uk/pipelines/faqs.htm#mhotherpipelines

267. Harding, A. J. (1959). Ammonia Manufacture and Use. London, Oxford University Press.

268. BASF Catalysts. (2007). "Catalyst datasheets." from www.basf.co.uk

269. Johnson Matthey Catalysts (2011). "Industrial Catalysts - Ammonia Synthesis." Retrieved 06/04/2011, from http://resources.schoolscience.co.uk/johnsonmatthey/page7.htm

270. Ahmed, S., M. Krumpelt, et al. (1998). Catalytic Partial Oxidation Reforming of Hydrocarbon Fuels. 1998 Fuel Cell Seminar. Palm Springs, CA.

271. Larminie, J. and A. Dicks (2003). Fueling Fuel Cells. Fuel Cell Systems Explained, John Wiley & Sons.

272. Shoko, E., B. McLellan, et al. (2006). "Hydrogen from coal: Production and utilisation technologies." International Journal of Coal Geology **65**: 213– 222.

273. Rafiqul, I., C. Weber, et al. (2005). "Energy efficiency improvements in ammonia production—perspectives and uncertainties." Energy **30**: 2487–2504.

274. Bartels, J. R. and M. B. Pate (2008). A feasibility study of implementing an Ammonia Economy, Iowa State University.

275. Crawford, J., B. Ellifritz, et al. (2007). Process Design of an Anhydrous Ammonia Production Facility for Dyno Nobel, University of Wyoming.

276. Hassania, J. (2007). "Diversified Energy Corporation Selected to Support Incitec Pivot Ltd Gasification Study." Retrieved 18/11/2008, from http://www.diversified-energy.com/auxfiles/pressReleases/Incitec_Services.pdf

277. International Fertiliser Industry Association (IFA) (2011). Production and trade statistics - Ammonia.

278. Roeder, M., P. Thornley, et al. (2011). Adaptation strategies for sustainable global wheat production. Reframing Sustainability? Climate Change and North-South Dynamics. Helsinki, Finland.*Cited by Gilbert et al. [372].*

279. Maxwell, G. R. (2007). Kent and Riegel's Handbook of Industrial Chemistry and Biotechnology - Chapter 22: Synthetic Nitrogen Products, Springer - Verlag.

280. Yara. (2011). "United Kingdom." Retrieved 13/01/2012, from http://www.yara.com/about/where_we_operate/united_kingdom.aspx

281. ICIS News. (2006). "Kemira GrowHow to restart Ince, UK ammonia unit." Retrieved 13/01/2012, from http://www.icis.com/Articles/2006/02/09/1040882/kemira-growhow-to-restart-ince-uk-ammonia-unit.html

282. Nogger. (2008). "GrowHow halts ammonia production." Retrieved 18/11/2010, from http://nogger-noggersblog.blogspot.com/2008/12/growhow-halts-ammonia-production-at.html

283. ICIS News. (2007). "GrowHow UK to close Severnside plants." Retrieved 12/01/2012, from http://www.icis.com/Articles/2007/10/09/9068710/growhow-uk-to-close-severnside-plants.html

284. The Engineer. (2010). "4,500 tonne UK ammonia plant dismantled for reassembly overseas." Retrieved 13/01/2012, from http://www.theengineer.co.uk/channels/process-engineering/4500-tonne-uk-ammonia-plant-dismantled-for-reassembly-overseas/1003009.article#ixzz1jLGTUGEf

285. Han, J. and H. Kim (2008). "The reduction and control technology of tar during biomass gasification/pyrolysis: An overview." Renewable and Sustainable Energy Reviews**12**: 397–416.

286. Aznar, M. P. and J. Delgado (1992). Biomass for energy and industry. Amsterdam, Elsevier. *Cited by Han & Kim [275].*

287. Ståhl, K. and M. Neergaard (1998). "IGCC power plant for biomass utilisation, Värnamo, Sweden." Biomass & Bioenergy**15**: 205-211.

288. Hofbauer, H., T. Fleck, et al. (1997). The FICFB-gasification process. Developments in thermochemical biomass conversion. A. V. Bridgwater and D. G. B. Boocock. London, Blackie**:** 1016-1025.

289. Lapuerta, M., J. J. Hernández, et al. (2008). "Gasification and co-gasification of biomass wastes: Effect of the biomass origin and the gasifier operating conditions." Fuel Processing Technology**89**: 828-837.

290. Lv, P. M., Z. H. Xiong, et al. (2004). "An experimental study on biomass air-steam gasification in a fluidised bed." Bioresource Technology**95**: 95-101.

291. De Feo, G., V. Belgiorno, et al. (2000). Solid Wastes Gasification. SIDISA International Symposium on Sanitary and Environmental Engineering. *Cited by Belgiorno et al. [141].*

292. Paisley, M. A. (1998). Battelle future energy resources corp. gasification process. Energy Performance Workshop for the Chemical and Pulp and Paper Industries, US Department of Energy**:** 2000–2020. *Cited by Belgiorno et al. [141].*

293. Richardson, J. F., J. H. Harker, et al. (2002). Coulson & Richardson's Chemical Engineering Volume 2: Particle Technology & Separation Processes. Oxford, Butterworth Heinemann.

294. Hauserman, W. B., N. Giordano, et al. (1997). "Biomass gasifiers for fuel cells systems." La Chimica & L' Industria**2**: 199–206. *Cited by Belgiorno et al. [141].*

295. Wu, C. Z., B. Y. Xu, et al. (1995). "Analysis of biomass gasification for MHV fuel gas." Gas Heat (in Chinese)**2**: 8-14. *Cited by Lv et al. [290].*

296. Paisley, M. A. and R. P. Overend (2002). Verification of the performance of future energy resources' SilvaGas(R) Biomass Gasifier—operating experience in the Vermont gasifier. Pittsburgh coal conference Pittsburgh, PA University of Pittsburgh.

297. Dietenberger, M. and M. Anderson (2007). "Vision of the U.S. Biofuel Future: A Case for Hydrogen-Enriched Biomass Gasification." Industrial & Engineering Chemistry Research**46**: 8863-8874.

298. Boerrigter, H. and R. Rauch (2005). Review of applications of gases from biomass gasification (also published as "Syngas production and utilisation"). Handbook: Biomass Gasification. H. A. M. Knoef. The Netherlands, Biomass Technology Group (BTG).

299. Kindig, J. K., R. R. Odle, et al. (2007). Method for the treatment of coal. U. S. P. Office. USA, AlChemix Corporation. **US 7,232,472 B2**.

300. Tortosa Masia, A., B. Buhre, et al. (2007). "Characterising ash of biomass and waste." Fuel Processing Technology **88** (11-12): 1071–1081. *Cited by Wang et al. [25].*

301. Milne, T. A., R. J. Evans, et al. (1998). Biomass Gasification 'Tars': Their nature, Formation and Conversion. *Cited by Higman & van der Burgt [176].*

302. García, L., R. French, et al. (2000). "Catalytic steam reforming of bio-oils for the production of hydrogen: effects of catalyst composition." Applied Catalysis A: General **201**: 225–239.

303. Pröll, T., R. Rauch, et al. (2007). "Fluidized Bed Steam Gasification of Solid Biomass - Performance Characteristics of an 8 MWth Combined Heat and Power Plant." International Journal of Chemical Reactor Engineering**5**: 1-19.

304. Quaak, P., H. Knoef, et al. (1999). Energy from biomass. World Bank technical paper no. 422.

305. Juniper Consultancy Services Ltd. (2000). Pyrolysis & Gasification of Waste. Worldwide Technology & Business Review. *Cited by Belgiorno et al. [141].*

306. Asadullah, M., S.-I. Ito, et al. (2002). "Biomass Gasification to Hydrogen and Syngas at Low Temperature: Novel Catalytic System Using Fluidized -Bed Reactor." Journal of Catalysis**208**: 255-259.

307. CITEC (2000). Le linee guida per la progettazione, la realizzazione e la gestione degli impianti a tecnologia complessa per lo smaltimento dei rifiuti urbani. SEP pollution 18 Salone internazionale servizi pubblici e antinquinamento. *Cited by Belgiorno et al. [141].*

308. Ghezzi, U. (2000). Tecnologie correnti e avanzate per la termodistruzione dei rifiuti. La termodistruzione del rifiuto urbano: recupero energetico ed emissioni. Ed. HYPER s.r.l.*Cited by Belgiorno et al. [141].*

309. Niessen, W. R., C. H. Markes, et al. (1996). Evaluation of Gasification and Novel Thermal Processes for the Treatment of Municipal Solid Waste, NREL. cited by Belgiorno et al. (2003). *Cited by Belgiorno et al. [141].*

310. Bolhàr-Nordenkampf , M., K. Bosch, et al. (2002a). Scale-up of a 100kWth pilot FICFB-gasifier to a 8 MWth FICFB-gasifier demonstration plant in Güssing (Austria). 1st International Ukrainian Conference on BIOMASS FOR ENERGY, Kiev.

311. Hofbauer, H., R. Rauch, et al. (2002). Six years experience with the FICFB-Gasification Process. 12th European Conference and Technology Exhibition on Biomass for Energy, Industry and Climate Protection Amsterdam, The Netherlands.

312. Schiefelbein, G. F. (1989). "Biomass Thermal Gasification Research: Recent Results from the United States DOE´s Research Program." Biomass **19**: 145-159. *Cited by Hofbauer et al. [288].*

313. Paisley (1993). *Cited by Hofbauer et al. [288].*

314. Fercher, E., H. Hofbauer, et al. (1998). Two Years Experience with the FICFB Gasification Process. Biomass for Energy and Industry: Proceedings of the International Conference Würzburg, Würzburg, Germany, C.A.R.M.E.N.

315. Staniewski, E. (1995). "Gasification—The Benefits of Thermochemical Conversion over Combustion." Hazardous Materials Management**October/November**. *Cited by Belgiorno et al. [141].*

316. Horton, R. (2003). HydroMax® - A bridge to the Hydrogen Economy.

317. Diversified Energy. (2008). "HydroMax® - Advanced Gasification Technology." Retrieved 18/11/2008, from http://www.diversified-energy.com/index.cfm?s_webAction=hydromax

318. Kindig, J. K. and R. R. Odle, et al., (2004). Method for the production of Hydrogen gas. U. S. P. Office. USA, AlChemix Corporation. **US 6,682,714 B2**.

319. Devi, L., K. J. Ptasinski, et al. (2003). "A review of the primary measures for tar elimination in biomass gasification." Biomass & Bioenergy**24**: 125-140.

320. Jansen, J. C. and K. Jonsson, Hagman La, M. (2002). "Biological detoxification of tar-water." Water Science and Technology **46**: 59–65. *Cited by Han & Kim [285].*

321. Kubek, D., E. Polla, et al. (1997). Purification and recovery options for gasification. IChemE Conference "Gasification Technology in Practice". Milan, Italy. *Cited by Higman & van der Burgt [176].*

322. Toft, A. J. and A. V. Bridgwater (1994). Interim Report from the IEA Bioenergy Agreement Interfacing Group. *Cited by Bridgwater [142].*

323. Depner, H. and A. Jess (1999). "Kinetics of nickel-catalyzed purification of tarry fuel gases from gasification and pyrolysis of solid fuel." Fuel78: 1369–1377. *Cited by Belgiorno et al. [141]*

324. Bentzen, J. D. (2000). Optimized two-stage gasifier. Proceedings of first world conference on biomass for energy and industry. *Cited by Han & Kim [285].*

325. Colomba, D. B. (2002). "Modeling intra- and extra-particle processes of wood fast pyrolysis." AIChE Journal**48**: 2386–97. *Cited by Han & Kim [285].*

326. Corella, J., J. Herguido, et al. (1988). Pyrolysis and steam gasification of biomass in fluidized beds. Influence of the type and location of the biomass feeding point on the product distribution. Research and Thermochemical Biomass Conversion. A. V. Bridgwater and J. L. Kuester. London, Elsevier Applied Science. *Cited by Bridgwater [142].*

327. Andre, R. N., F. Pinto, et al. (2005). "Fluidised bed co-gasification of coal and olive oil industry wastes." Fuel**84**: 1635–44. *Cited by Han & Kim [285].*

328. Rapagna (1998). *Cited by Han & Kim [285].*

329. Gil, J. and M. A. Caballero (1999). "Biomass gasification with air in fluidized bed: effect of in-bed use of dolomite under different operation conditions." Industrial & Engineering Chemistry Research**138**: 4226–4235. *Cited by Han & Kim [285].*

330. Zhang, X. (2003). The mechanism of tar cracking by catalyst and the gasification of biomass, Zhejiang University (China). **Dissertation**. *Cited by Han & Kim [285].*

331. Bridgwater, A. V. and G. D. Evans (1993). An Assessment of Thermochemical Conversion Systems for Processing Biomass and Refuse, UK Department of Trade & Industry. *Cited by Bridgwater [142].*

332. Ståhl, K., L. Waldheim, et al. (2008). CHRISGAS Project - Clean Hydrogen-rich Gas through Biomass Gasification and Hot Gas Upgrading, DUCENTE AB, TPS – Termiska Processer AB, VVBGC – Växjö Värnamo Gasification Centre AB.

333. de Graaf, J. D. (2008). Shell Coal Gasification Technology. Energy from Biomass.

334. Bolhàr-Nordenkampf , M. and H. Hofbauer (2004). Gasification Demonstration Plants in Austria IV. International Slovak Biomass Forum, Bratislava.

335. Dietz et al. (1978). *Cited by Spath and Dayton [340].*

336. Padró, C. E. G. and V. Putsche (1999). Survey of the Economics of Hydrogen Technologies. Golden, Colorado, USA, NREL.

337. Mann, M. K. (1995a). Technical and economic assessment of producing hydrogen by reforming syngas from the Battelle indirectly heated biomass gasifier, National Renewable Energy Lab. *Cited by Padró & Putsche [332].*

338. Larson, E. D. and R. E. Katofsky (1992). Production of Methanol and Hydrogen from Biomass," The Center for Energy and Environmental Studies, Princeton University.

339. AEA Technology (2002). The Feasibility, Costs and Markets for Hydrogen Production.

340. Spath, P. L. and D. Dayton (2003). Preliminary Screening — Technical and Economic Assessment of Synthesis Gas to Fuels and Chemicals with Emphasis on the Potential for Biomass-Derived Syngas. Golden, Colorado, USA, NREL.

341. Peters, M. S. and K. D. Timmerhaus (2003). Plant Design and Economics for Chemical Engineers. New York, McGraw-Hill, Inc.

342. Aden, A., M. Ruth, et al. (2002). Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover, NREL.

343. Bridgwater, A. V. (2009). Technical and Economic Assessment of Thermal Processes for Biofuels. Life Cycle and Techno-economic Assessment of the Northwest Biomass to Liquids Project, NNFCC.

344. The German Energy Agency (DENA) (2006). Biomass to Liquid – BtL Implementation Report, Summary. Berlin, Germany, Deutsche Energie-Agentur GmbH (DENA). *Cited by Bridgwater [343].*

345. Reed, M. E., L. van Bibber, et al. (2007). Baseline Technical and Economic Assessment of a Commercial Scale Fischer-Tropsch Liquids Facility. Pittsburgh, National Energy Technology Laboratory.

346. Hamelinck, C. N. and A. Faaij (2001). Future Prospects for Production of Methanol and Hydrogen from Biomass. Utrecht, the Netherlands, Utrecht University.

347. Scandinavian Energy Projects AB. Personal communication with Olle Wennberg, Process engineer at Scandinavian Energy Projects; 2009. *Cited by Huisman et al. [16].*

348. Rogers, J. G. (2009). A techno-economic assessment of the use of fast pyrolysis bio-oil from UK energy crops in the production of electricity and combined heat and power. Chemical Engineering & applied Chemistry. Birmingham, Aston University. **PhD:** 376.

349. Garret, D. (1988). Chemical Engineering Economics, Van Nostrand Reinhold

350. U. S. Bureau of Labour Statistics. Fromhttp://www.bls.gov/. *Cited by Phillips et al. [15] and Swanson et al. [220].*

351. Veab (2009) Personal communication with A.C. Tranvik, Head of Chemistry. Växjö Energi AB. *Cited by Huisman et al. [16].*

352. Pröll, T. (2010). Gussing Data. S. Alexander.

353. MIT (1987); ASPEN User Manual; Morgantown Energy Center: Morgantown, West Virginia. *Cited by Akunuri & Frey [355].*

354. JANAF (1979), Thermochemical Tables,Dow Chemical Company. *Cited by Koshnoodi & Lim [356].*

355. Akunari, N. V. and H. C. Frey (1999). Modeling the Performance, Emissions, and Cost of an Entrained-Flow Gasification Combined Cycle System Using ASPEN, Department of Civil Engineering, North Carolina State University.

356. Khoshnoodi, M. and Y. S. Lim (1997). "Simulation of partial oxidation of natural gas to synthesis gas using ASPEN PLUS." Fuel Processing Technology **50**: 275-289.

357. Aspentech (2012). “Aspen Plus®: Process modeling environment for conceptual design, optimization, and performance monitoring of chemical processes”. Retrieved 21/12/2012, from www.**aspen**tech.com/uploadedFiles/Products/.../**Aspen_Plus**.pdf

358. Aspentech (2008). Aspen Plus IGCC Model. Burlington, USA, Aspen Technology, Inc. **7.0**.

359. Biagini, E., A. Bardi, et al. (2009). "Development of an Entrained Flow Gasifier Model for Process Optimization Study." Industrial & Engineering Chemistry Research**48**: 9028–9033.

360. Kunze, C. and H. Spliethoff (2011). "Modelling, comparison and operation experiences of entrained flow gasifier." Energy Conversion and Management**52**: 2135–2141.

361. Zheng, L. and E. Furinsky (2005). "Comparison of Shell, Texaco, BGL and KRW gasifiers as part of IGCC plant computer simulations." Energy Conversion and Management**46**: 1767–1779.

362. Alie, C., L. Backham, et al. (2005). "Simulation of CO2 capture using MEA scrubbing: a flowsheet decomposition method." Energy Conversion and Management**46**: 475–487.

363. Desideri, U. and A. Paolucci (1999). "Performance modelling of a carbon dioxide removal system for power plants." Energy Conversion and Management**40**: 1899-1915.

364. Robinson, P. J. and W. L. Luyben (2008). "Simple Dynamic Gasifier Model That Runs in Aspen Dynamics." Industrial & Engineering Chemistry Research**47** 7784–7792.

365. Frey, H. C. and N. V. Akunari (2001). Probabilistic Modeling and Evaluation of the Performance, Emissions, and Cost of Texaco Gasifier-based Integrated Gasification Combined Cycle Systems using ASPEN [software]. Raleigh, North Carolina State University. *Cited by Swanson et al. [220].*

366. Meier, I. and V. Tarhan (2006). Corporate investment decision practices and the hurdle rate premium puzzle, Mimeo.

367. Tucker, J. (2009). How to set the hurdle rate for capital investments. Qfinance: The Ultimate Resource. D. Stauffer, A & C Black**:** 322-324.

368. E4Tech (2009). Review of Technologies for Gasification of Biomass and Wastes.

369. Royal Commission on Environmental Pollution (2004). Biomass as a Renewable Energy Source, Crown Copyright. *Cited by Rogers [348].*

370. Paul Arwas Associates (2005). Biomass sector review for the Carbon Trust. *Cited by Rogers [348].*

371. Fischer, G., S. Prieler, et al. (2010). "Biofuel production potentials in Europe: Sustainable use of cultivated land and pastures, Part II: Land use scenarios." Biomass & Bioenergy**34**(2): 173-187. *Cited by Gilbert et al. [372].*

372. Gilbert, P., S. Alexander, et al., (2011). Decarbonising the fertiliser industry using biomass gasification. Unpublished paper.

373. Gigler, J. K., G. Meerdink, et al. (1999). "Willow supply strategies to energy plants." Biomass and Bioenergy**17**(3): 185-198. *Cited by Gilbert et al. [372].*

374. Amos, W. A. (1998). Report on Biomass Drying Technology. Golden, Colorado, USA, NREL.

375. Hulkkonen, S., O. Heinonen, et al. (1994). "Drying wood biomass at high pressure steam atmosphere experimental; Research and application." Drying Technology**12**(4): 869-887. *Cited by Amos [374].*

376. Hulkkonen, S., M. Raiko, et al. (1991). "High efficiency power plant processes for moist fuels." IGTI**6***. Cited by Amos [374].*

377. van Swaaij, W., F. van den Aarsen, et al. (1994). A Review of Biomass Gasification. A Report to the European Community DGXII JOULE Programme.

378. Henrich, E. and F. Weirich (2002). Pressurised Entrained Flow Gasifiers for Biomass. IT3´02 Conference. New Orleans, Louisiana.

379. Eurlings, J. and J. Ploeg (1999). Process Performance of the SCGP at Buggenum IGCC. Gasification Technologies Conference. San Francisco, California.

380. Smith, A. R. and J. Klosek (2001). "A review of air separation technologies and their integration with energy conversion processes." Fuel Processing Technology**70**: 115–134.

381. Hofbauer, H. (1982). "Untersuchungen an einer zirkulierenden Wirbelschicht mit Zentralrohr." Chem. Ing.-Tech.**54**(5): 528-529. *Cited by Fercher et al. [314].*

382. Rauch, R., H. Hofbauer, et al. (2004). Steam Gasification at CHP Plant Güssing - Status of the Demonstration Plant. 2nd World Conference and Technology Exhibition on Biomass for Energy, Industry and Climate Protection. Rome, Italy.

383. Aichernig, C., H. Hofbauer, et al. (2004). Biomass CHP Plant Güssing: Successful Demonstration of the Steam Gasification Process. ENEF 2004. Sheffield.

384. Bolhàr-Nordenkampf , M., R. Rauch, et al. (2002b). Biomass CHP Plant Güssing - Using Gasification for Power Generation. Biomass Utilisation. Thailand.

385. Olivine mineral data (2011) http://webmineral.com/data/Olivine.shtml

386. Fennell, P. S. (2008). Current UK Research in CCS. London, Imperial College London.

387. Chakma, A. (1997). “CO_2 capture processes – opportunities for improved energy efficiencies.” Energy Conversion Management.**38**: S51-S56.

388. Wilson, M.A., R. M. Wrubleski, et al. (1992) "Recovery of CO_2 from Power Plant Flue Gases Using Amines," First International Conference on Carbon Dioxide Removal, Amsterdam, The Netherlands, March, Pergamon Press, p. 325-332. *Cited by Gupta, M., I. Coyle, et al. (2003). “CO_2 capture technologies and opportunities in Canada”. 1st Canadian CC&S Technology Roadmap Workshop, Calgary, Alberta, Canada*

389. Zhang, N. and N. Lior (2006). “A novel near-zero CO_2 emission thermal cycle with LNG cryogenic exergy utilization”. Energy**31**: 1666–1679.

390. Bio Green Tech Ltd. (2010). "Biomass Technology: KOTCF Rang Hammer Mills." Retrieved 15/11/2010, from http://www.biogreentech.com/KOTCF158_Hammer_Mill.html

391. Ni, Q. and A. Williams (1995). "A simulation study on the performance of an entrained-flow coal gasifier." Fuel**74**(1): 102-110.

392. Chen, C., M. Horio, et al. (2000). "Numerical simulation of entrained flow coal gasifiers. Part I: modeling of coal gasification in an entrained flow gasifier." Chemical Engineering Science**55**: 3861-3874.

393. Doherty, W., A. Reynolds, et al. (2009). "The effect of air preheating in a biomass CFB gasifier using ASPEN Plus simulation." Biomass and Bioenergy**33**: 1158-1167.

394. Corti, A. and L. Lombardi (2004). "Biomass integrated gasification combined cycle with reduced CO_2 emissions: Performance analysis and life cycle assessment (LCA)." Energy**29**: 2109-2124.

395. Babu, S. (2004). Biomass gasification for hydrogen production - process description and research needs. Des Plaines, IL, Gas Technology Institute.

396. Yun, Y. and Y. D. Yoo (2005). "Comparison of syngas and slag from three different scale gasifiers using Australian Drayton coal." Journal of Industrial and Engineering Chemistry**11**(2): 228-234.

397. Tian, F.-J., J. Yu, et al. (2007). "Conversion of Fuel-N into HCN and NH_3During the Pyrolysis and Gasification in Steam: A Comparative Study of Coal and Biomass."

Energy & Fuels**21**: 517-521.

398. Hahn, W., C. S. Park, et al. (2003). "Characteristics of NOx Reduction in Pulverized Coals Combustion using Drop Tube Furnace." Industrial & Engineering Chemistry Research**9**(3): 275-280.

399. Strezov, V., J. A. Lucas, et al. (2004). "Experimental and modelling of the thermal regions of activity during pyrolysis of bituminous coals." Journal of Analytical and Applied Pyrolysis**71**: 375–392.

400. Beysel, G. (2009). Enhanced Cryogenic Air Separation: A Proven process Applied to Oxyfuel. 1st Oxyfuel Combustion Conference, Cottbus, Germany.

401. Esquivel, R. J. (2008). Coal to Methanol Design Report. American Institute of Chemical Engineers 2008 National Competition. Retrieved 25/09/2010, from http://maecourses.ucsd.edu/ceng124/rpts/gp1_final.pdf

402. Bechtel (1998). Aspen Process Flowsheet Simulation Model of a Battelle Biomass-Based Gasification, Fischer-Tropsch Liquefaction and Combined-Cycle Power Plant. Retrieved 25/09/2010, from http://www.osti.gov/bridge/servlets/purl/7157-NEaa6U/webviewable/7157.pdf

403. Øi, L. E. (2007). Aspen HYSYS Simulation of CO2 Removal by Amine Absorption from a Gas Based Power Plant. SIMS 2007 Conference, October 30-31st. Gøteborg, Sweden.

404. National Physical Laboratory (NPL) (2010). Traceable primary standards for natural gas.

405. NaturalGas.org (2011). “Background”. Retrieved 27/01/2013, from: http://www.naturalgas.org/overview/background.asp

406. Engelhard (2005). Sulphur Removal Technology, Engelhard.

407. Brammer, J. G. (2001). Study of biomass gasifier-engine systems with feed drying for power and CHP. Chemical Engineering & Applied Chemistry. Birmingham, Aston University. **PhD:** 314.

408. Nand, S. and M. Goswami (2006). “Analysis of Downtime in Ammonia and Urea Plants”. The Fertiliser Association of India, New Delhi. Retrieved 02/05/2012, from: http://www.faidelhi.org/Analysis%20of%20Downtime%20in%20Ammonia%20and%20Urea%20Plants.pdf

409. Waldrop Engineering Inc. (1990). Development of Direct Contact Superheated Steam Drying Process for Biomass. Ottawa, Canada. *Cited by Amos [374].*

410. Thek, G. and I. Obernberger (2004). "Wood pellet production costs under Austrian and in comparison to Swedish framework conditions." Biomass & Bioenergy**27**: 671–693.

411. Frea, W. J. (1984). “Forest residue fuel pre-drying, economic analysis”. Biomass Fuel Drying Conference Proceedings, 8th August, Superior, Wisconsin, USA, p. 56-88. *Cited by Amos [374].*

412. Williamson, G. and M. McCurdy (2009). Biomass to Liquids. Lower Hutt, New Zealand, CRL Energy Ltd. Retrieved 25/07/2011, from: http://www.pce.parliament.nz/assets/Uploads/Appendix-B.pdf

413. O’Connor, D., T. Johnson (2005). EPRI biomass interest group European technology mission. Retrieved 23/03/2011, from: http://www.gabioenergy.org/ppt/gabioenergy%20%20OCONNOR.pdf

414. Andersson, M. P., T. Bligaard, et al. (2006). “Toward computational screening in heterogeneous catalysis: Pareto-optimal methanation catalysts”. Journal of Catalysis**239**: 501–506

415. Singh, D., E. Croiset, et al. (2003). “Techno-economic study of CO_2 capture from an existing coal-fired power plant: MEA scrubbing vs. O_2/CO_2 recycle combustion”. Energy Conversion and Management**44**: 3073–3091

416. Fact Check (2010). Retrieved 13/12/2010, from: http://www.factcheck.org/askfactcheck/can_a_freight_train_really_move_a.html

417. March 2009 250 US $/t. Retrieved 13/12/2010, from: http://topkwh.50webs.com/

418. Demirbaş, A. (2008). Biodiesel: A Realistic Fuel Alternative for Diesel Engines. Springer-Verlag London Limited. ISBN 978-1-84628-994-1, eISBN 978-1-84628-995-8

419. Veny, H., S. Baroutian, et al. (2009). “Density of *Jatropha curcas* seed oil and its methyl esters: measurement and estimations”. International Journal of Thermophysics, **30**: 529–541

420. DECC (2011c). Industrial Electricity Prices in the EU. Retrieved 1/4/2011, from www.decc.gov.uk/assets/decc/statistics/source/prices/qep313.xls

421. United States Department of Agriculture (USDA) Economic Research Service (ERS) (2011). Retrieved 27/01/2013, from U.S. Imports (1995-2011) and exports (1990-2011) of selected fertilizers, by country.xls

422. Rosenqvist, H. and M. Dawson (2005). “Economics of willow growing in Northern Ireland”. Biomass & Bioenergy**28**: 7–14.

423. Flann Consulting Services (1994). Woodchip combustion in Eastern Canada. REAP-Canada. http://www.reap-canada.com/online_library/agri_fibres_forestry/29%20Woodchip%20Combustion.pdf

424. Glavonjic, B. (2010). South east Europe wood energy markets. Regional Wood Products Marketing Workshop, 7-9 December. Mavrovo National Park, Macedonia.

425. Gerasimov, Y., V. Goltsev, et al. (2006). Assessment of Energy Wood Resources in the Leningrad Region. Working Papers of the Finnish Forest Research Institute 108.

426. Google Earth (2012).http://www.google.co.uk/intl/en_uk/earth/index.html

427. Wikipedia (2012).www.wikipedia.org

428. Bantrel (2002). CO_2 Capture Technology. Western Canada 2002 GHG Technology Conference & Tradeshow. Calgary, Alberta.

Appendix A: ASPEN Plus® unit modelling parameters

The following tables present the parameters used to model the individual process units using ASPEN Plus®.

Table A-1: Case 1 ASPEN Plus® unit parameters

Unit name	GSREAC01/02/03	WGS-HT	H2SREM	WGS-LT
Process	Entrained flow gasification	High temperature water gas shift	H_2S removal	Low temperature water gas shift
Block type	RYield/ RGibbs/ SSPLIT	REquil	Sep2	REquil
Temperature (°C)	1200	400	400	200
Pressure (bar)	30	30	30	30
Inlet stream	SYG-01/PRAIR-01	SYG-05/ PRSTM-01	SYG-06	SYG-08
Mass in (kg/h)	12000.0 / 10544.6	22442.6 / 7114.5	29557.1	29553.3
Outlet stream	SYG-04/PRWST-01	SYG-06	SYG-07/PRWST-02	SYG-09
Mass out (kg/h)	22442.6 / 102.0	29557.1176	29553.3 / 3.8	29553.3
Heat duty (MW)	$-3.1*10^{-9}$	-2.43	$-7.5*10^{-15}$	-0.54
Unit name	CO2R01/02	H2OR01	METHAN	AMSYN
Process	CO_2 removal	Water removal	Methanation	Ammonia synthesis
Block type	Sep2/Flash	Flash3	RGibbs	Rstoic
Temperature (°C)	65	40	300	350
Pressure (bar)	30 / 1.2	30	30	130
Inlet stream	SYG-10 / SOLV-02	SYG-11	SYG-12	SYG-22
Mass in (kg/h)	29553.3 / 503.0	10597.3	6420.3	6420.3
Outlet stream	SYG-11/SOLV-04/PRWST-03	SYG-12/PRWST-04	SYG-13	AMCYC-01
Mass out (kg/h)	10597.3 / 503.0 / 18956.1	6420.3 / 4177.0	6420.3	6420.3
Heat duty (MW)	1.09	-0.33	1.18	-3.72

Table A-2: Case 1 ASPEN Plus® heat recovery parameters

Exchanger	Location	Q (MW)	T (°C)	m (kg/h)	Composition
HRX1	After gasification	-8.21	250.3	10189.44	HP steam
HRX2	After H_2S removal	-2.79	253.3	3451.73	HP steam
HRX3	After WGS-LT	-4.40	104.8	10448.86	LP steam (sat)
HRX4	Compression stage 1	-1.09	108.9	1495.27	LP steam
HRX5	Compression stage 2	-0.55	104.8	900.76	LP steam (sat)
HRX6	Compression stage 3	-0.33	90.0	3909.32	Hot water
HRX7	Compression stage 4	-0.24	89.9	2800.00	Hot water
HRX8	Before ammonia synthesis	-0.12	90.3	1459.24	Hot water

Table A-3: Case 1 ASPEN Plus® compression unit parameters

Compressor	Location	Inlet pressure (bar)	Outlet pressure (bar)
SYNCMP01	Syngas compression before ammonia synthesis	30	55
SYNCMP02	Syngas compression before ammonia synthesis	55	80
SYNCMP03	Syngas compression before ammonia synthesis	80	105
SYNCMP04	Syngas compression before ammonia synthesis	105	130
HRP01	HRX1 water pump	1.2	30
HRP02	HRX2 water pump	1.2	30
CORP01	Solvent pump	1.2	30

Table A-4: Case 2/3 ASPEN Plus® unit parameters

Unit name	PARTOX01	WGS-HT	H2SREM	WGS-LT
Process	Thermal partial oxidation	High temperature water gas shift	H_2S removal	Low temperature water gas shift
Block type	RGibbs	REquil	Sep2	REquil
Temperature (°C)	1200	400	400	200
Pressure (bar)	30	30	30	30
Inlet stream	SYG-03/ PRAIR-03	SYG-05/ PRSTM-01	SYG-06	SYG-08
Mass in (kg/h)	1493.0 / 838.0	2331.0 / 945.3	3276.3	3276.0
Outlet stream	SYG-04	SYG-06	SYG-07/PRWST-01	SYG-09
Mass out (kg/h)	2331.0	3276.3	3276.0 / 0.3	3276.0
Heat duty (MW)	$-6.0*10^{-12}$	-0.26	$-8.9*10^{-14}$	-0.06
Unit name	CO2R01/02	H2OR01	METHAN	AMSYN
Process	CO_2 removal	Water removal	Methanation	Ammonia synthesis
Block type	Sep2/Flash	Flash3	RGibbs	Rstoic
Temperature (°C)	65	40	300	350
Pressure (bar)	30 / 1.2	30	30	130
Inlet stream	SYG-10 / SOLV-02	SYG-11	SYG-12	SYG-22
Mass in (kg/h)	3276.0 / 12.0	1400.8	854.2	854.2
Outlet stream	SYG-11/SOLV-04/PRWST-02	SYG-12/PRWST-03	SYG-13	AMCYC-01
Mass out (kg/h)	1400.8 / 12.0 / 1875.0	854.2 / 546.6	854.2	854.2
Heat duty (MW)	0.10	-0.05	0.17	-0.50

Table A-5: Case 2/3 ASPEN Plus® heat recovery parameters

Exchanger	Location	Q (MW)	T (°C)	m (kg/h)	Composition
HRX2	After partial oxidation	-0.92	286.6	1116.95	HP steam
HRX3	After H_2S removal	-0.33	240.4	414.35	HP steam
HRX4	After WGS-LT	-0.56	104.8	1351.15	LP steam
HRX5	Compression stage 1	-0.14	89.6	1531.30	District heating
HRX6	Compression stage 2	-0.05	90.0	585.50	District heating
HRX7	Compression stage 3	-0.07	90.3	747.63	District heating
HRX8	Compression stage 4	-0.01	90.7	77.47	District heating
HRX9	Before ammonia synthesis	-0.04	89.5	448.58	District heating

Table A-6: Case 2/3 ASPEN Plus® pre-heating unit parameters

Pre-heater	Location	Outlet temperature (°C)	Exhaust / flue gas temperature (°C)
PHX01	Syngas pre-heater	1115	1170
PHX02	Air pre-heater	1109	1152

Table A-7: Case 2/3 ASPEN Plus® compression unit parameters

Compressor	Location	Inlet pressure (bar)	Outlet pressure (bar)
PRCOMP01	Syngas compression after gasification and gas cleaning	1.061	30
SYNCMP01	Syngas compression before ammonia synthesis	30	55
SYNCMP02	Syngas compression before ammonia synthesis	55	80
SYNCMP03	Syngas compression before ammonia synthesis	80	105
SYNCMP04	Syngas compression before ammonia synthesis	105	130
HRP01	HRX2 water pump	1.2	30
HRP02	HRX3 water pump	1.2	30
CORP01	Solvent pump	1.2	30

Table A-8: Case 4 ASPEN Plus® unit parameters

Unit name	PARTOX01	WGS-HT	H2SREM01/02	WGS-LT
Process	Thermal partial oxidation	High temperature water gas shift	H_2S removal	Low temperature water gas shift
Block type	RGibbs	REquil	Sep2	REquil
Temperature (°C)	1200	400	400	200
Pressure (bar)	30	30	30	30
Heat duty (MW)	-0.0019898	-9.0692932	$5.6*10^{-15}$	-9.0692932
Unit name	CO2R01/02	H2OR01	METHAN	AMSYN
Process	CO_2 removal	Water removal	Methanation	Ammonia synthesis
Block type	Sep2/Flash	Flash3	RGibbs	Rstoic
Temperature (°C)	65	40	300	350
Pressure (bar)	30 / 1.2	30	30	130
Heat duty (MW)	3.82	-2.24	11.04	-30.57
Unit name	SR01	SR02		
Process	Primary steam methane reformer	Secondary steam methane steam		
Block type	RGibbs	RGibbs		
Temperature (°C)	800	1200		
Pressure (bar)	30	30		
Heat duty (MW)	36.0	29.30		

Table A-9: Case 4 ASPEN Plus® heat recovery unit parameters

Exchanger	Location	Q (MW)	T (°C)	m (kg/h)	Composition
HRX1	After SMR	-42.97	334.2	50443	HP steam
HRX2	After WGS-HT	-15.99	322.6	18916	HP steam
HRX3	After WGS-LT	-22.16	104.8	90076.40	District heat
HRX4	Compression stage 1	-7.53	99.2	78366.47	District heat
HRX5	Compression stage 2	-6.43	98.5	67557.30	District heat
HRX6	Compression stage 3	-2.74	98.4	28824.45	District heat
HRX7	Compression stage 4	-1.96	99.3	20357.27	District heat
HRX8	Before ammonia synthesis	-1.53	99.4	53005.61	District heat
HRX10	After partial oxidation	-5.76	316.5	6755.73	HP steam

Table A-10: Case 4 ASPEN Plus® pre-heating unit parameters

Pre-heater	Location	Outlet temperature (°C)	Exhaust / flue gas temperature (°C)
PHX01	Natural gas pre-heater	400	455.1
PHX02	Air pre-heater (SMR)	600	657.4
PHX03	Syngas pre-heater	1115	1167
PHX04	Air pre-heater (TPO)	1103.8	

Table A-11: Case 4 ASPEN Plus® compression unit parameters

Compressor	Location	Inlet pressure (bar)	Outlet pressure (bar)
PRCOMP01	Air compression for SMR	1.2	30
PRCOMP02	Air compression for TPO	1.2	30
SYGCMP02	Syngas compression before ammonia synthesis	30	55
SYGCMP03	Syngas compression before ammonia synthesis	55	80
SYGCMP04	Syngas compression before ammonia synthesis	80	105
SYGCMP05	Syngas compression before ammonia synthesis	105	130
SYGCMP06	Biomass syngas compression before TPO	1.061	30