FLASH PYROLYSIS OF BIOMASS FOR LIQUID FUELS

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Master of Philosophy

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SUMMARY

Conventional pyrolysis produces char, a crude organic liquid, sometimes referred to as "bio-oil", and gas in approximately equal proportions. However, if flash pyrolysis is used, very high yields of over 60 wt% (dry basis) of bio-oil are produced. This oil can be used as a low grade boiler fuel or can be upgraded to products such as gasoline and diesel. The principle of flash pyrolysis for liquids production is the combination of very high heating rates with moderate temperatures and rapid quenching of liquid intermediate pyrolysis products. Several techniques have been employed including fluid beds, entrained flow reactors, cyclone and vortex reactors; and the principles employed include gas-solid heat transfer as in entrained flow reactors and solid-solid heat transfer as in ablative pyrolysis.

This thesis reviews the reaction mechanisms, pathways and kinetics of pyrolysis by reference to the flash pyrolysis technologies employed to date. A preliminary design of a 5 kg/h "bullet" shaped laboratory ablative pyrolysis unit was developed from specifications laid down for process performance by evaluating known theories of reaction pathways and mechanisms, and by examining the resultant technical requirements.

In addition, simple empirical relationships were derived by fitting the data to a polynomial. Better relationships were obtained using data from Waterloo than using data from the various technologies described in the thesis.

Key Words: Biomass; Ablative Pyrolysis; Modelling; Liquid Fuels; Pyrolysis Technologies

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CHAPTER ONE

INTRODUCTION

Transportation fuels account for approximately 29% of energy usage in the UK [1] and at similar levels in other industrialised countries. The most convenient forms of transportation fuels are liquid fuels and they account for almost all the energy requirements for vehicles. Since the fuel is a liquid, it can be easily stored and transported. Moreover it is a high energy density substance. This liquid fuel is normally obtained from fossil fuels that will be available for several decades but are becoming more expensive and increasingly difficult to exploit. Hence, there is a need to look at alternative sources for liquid fuels. One option is the conversion of coal to oil. Another alternative is renewable energy where renewable refers to any material that can be restored when the initial stock has been exhausted. Biomass is the only renewable energy form that is capable of meeting this specification.

Biomass is any organic matter that may be used as a source of energy and/or chemicals, generally of plant origin [2]. Examples of biomass include wood, straw, bagasse, animal wastes, industrial wastes such as paper and domestic refuse.

There are two main routes for converting biomass into liquid fuels; biologically which is conversion by the enzymatic action of living organisms such as bacteria and yeast (see Figure 1.1), or thermochemically which is conversion by heat and chemical reaction(see Figure 1.2). Biological conversion processes, such as fermentation and digestion, are best suited for sugar based and/or high moisture content materials. Lignin one of the major components of biomass is not sugar based so only a fraction of biomass will be converted into energy. Another requirement for biological conversion is that each component of biomass must be processed separately (see Figure 1.1). Such restrictions do not apply to thermochemical conversion and therefore, it is potentially the most promising route for producing liquids from biomass.

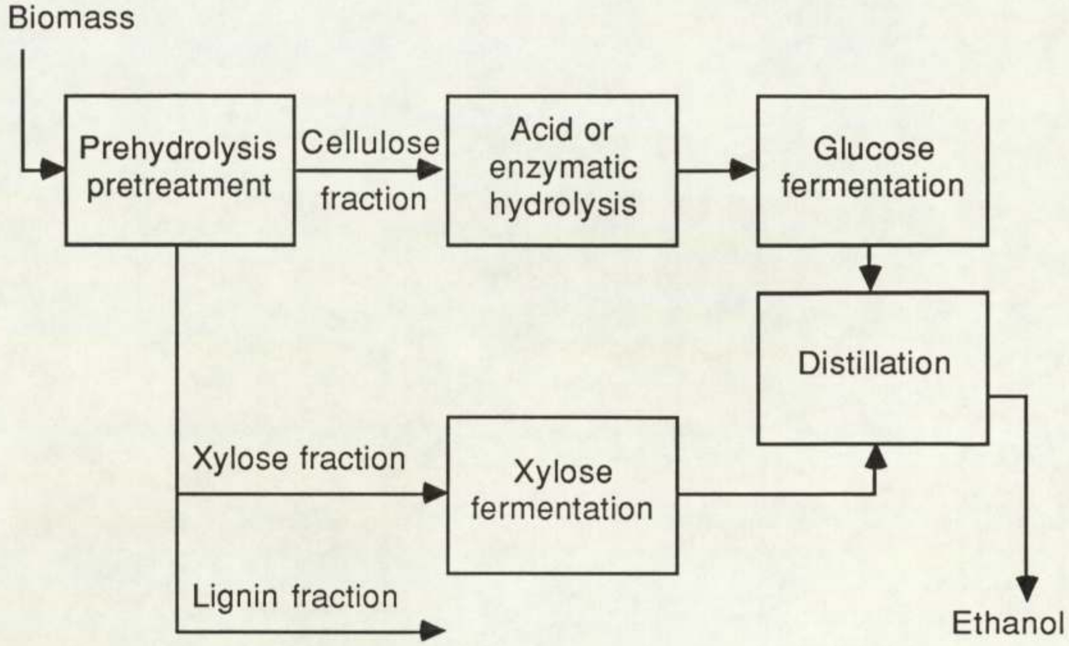


Figure 1.1 Conversion of Biomass via a Biological Route [2].

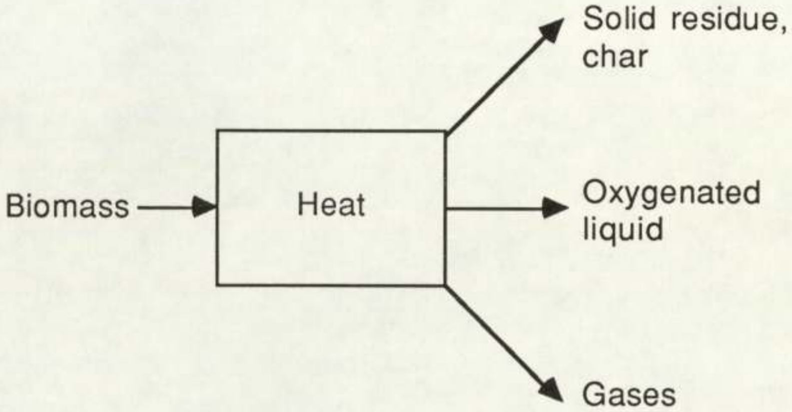


Figure 1.2 Conversion of Biomass via a Thermochemical Process.

Pyrolysis is one of the various thermochemical conversion processes being developed to directly convert biomass into liquid fuels, with liquefaction at high pressure being the alternative, but related route. Indirect liquefaction via gasification has also received considerable attention but is not considered further.

The pyrolysis of biomass, especially of wood, is an ancient process. Pyrolysis has been used for centuries for producing charcoal. Ancient Egyptians used the pyrolysis liquid for embalming purposes while the Greeks and the Romans used it for filling seams and joints in wooden ships [4]. Prior to the development of the petrochemical industry in the 1920's, wood pyrolysis was the major source of chemicals such as acetone, acetic acid and methanol [5]. As large quantities of low cost crude petroleum and natural gas became widely available and their associated industries developed, the use of wood as the source for both fuel and chemicals soon declined. However, as a response to the oil crises in the 1970's, interest was revived in the use of biomass as a renewable energy resource. More recent justification is the neutral effect of biomass with regard to the Greenhouse effect of rising CO_2 levels in the atmosphere.

Pyrolysis is an irreversible, thermal degradation process that occurs either in a non-oxidising environment or with such a limited supply of oxidising agent that partial gasification occurs to provide reaction heat. Three products are usually produced, namely, a solid char residue, a gas and a complex, oxygenated, hydrocarbon liquid product; the relative yields and compositions of these products are dependent on the process variables. The liquid product is very valuable because it can be upgraded to a substitute gasoline-like fuel and/or high octane enhancers by high pressure catalytic hydrotreatment or by the use of zeolite catalysts.

Due to the complex and transient nature of the pyrolysis process a sound understanding of the reactions, pathways and effects of process parameters on product yield and characteristics is essential for design and optimisation. The main objectives of this research were therefore :

(i) to produce a model that incorporated sufficient features to adequately represent the pyrolysis process; was relatively simple to use and solve and gave realistic and useful answers;

(ii) to propose conceptual designs for an experimental pyrolyser based on the ablative pyrolysis concept, to produce high yields of liquids.

The contents of this thesis are set out thus:

Chapter 2 describes the physical structure and the chemical composition of biomass materials in order to evaluate their potential as feedstocks for the conversion to fuels and chemicals.

Chapter 3 describes the various process variables that will affect the rate of pyrolysis and also how they affect product yields.

Chapter 4 is a critical review of the various mathematical models of biomass pyrolysis which have been developed by other workers in this field. Because wood is anisotropic, these pyrolysis models are normally partial differential equations of heat and kinetic equations. Therefore, these models are not very 'user friendly'.

Chapter 5 is an overview of the pyrolysis technologies, concentrating mainly on the production of liquid products. This chapter also describes in detail the more recent and/or well developed pyrolysis activities around the world.

Chapter 6 covers the proposals of conceptual designs of an ablative pyrolyser because ablative pyrolysis seems to be one of the most promising routes that can be employed for the production of high yields of liquid fuels.

Chapter 7 is a discussion of the material covered in this dissertation. The contents of Chapter 8 are the conclusions and recommendations for further work in this area of research.

CHAPTER TWO
PATHWAYS OF BIOMASS PYROLYSIS

2.1 INTRODUCTION

An understanding of the physical structure and the chemical composition of biomass materials is necessary in order to evaluate their potential as feedstocks for conversion to fuels and chemicals. This chapter first describes the main biomass feedstocks and their important characteristics with respect to pyrolysis. Next, a description of the physical structure of biomass and its components is presented since they influence the properties of biomass during pyrolysis. Finally, the thermal degradation reaction pathways and mechanisms for biomass and its major constituents are discussed, as whole biomass appears to behave as the sum of its components.

2.2 FEEDSTOCKS

Wood is the most popular form of lignocellulosic biomass material to be used as a feedstock in thermochemical conversion processes. Other feedstocks that have been tested include agricultural byproducts such as straw and rice hulls, bagasse and refuse. Some advantages of using wood over other biomass materials are that:

- the chemical composition is relatively uniform from different sources of wood; moisture content however, varies considerably;
- it is readily available in the form of processing residue (from sawmills, pulp and paper mills), forest residue, whole trees from thinnings (trees removed so as to improve the remaining crop) and short rotation forestry;
- it has a low ash content (ash affects heat balance and causes slagging and sintering in the reactor);
- it has a low sulphur and nitrogen content;
- it can be harvested at any time while agricultural residues are normally obtained once a year. If storage of wood is required, it can be done in open piles, under cover to protect it from rain or in

silos and live bottomed bins [6]. The type of storage chosen is influenced by scale of operation and climatic factors;

- it is less susceptible to microbiological deterioration than non-woody biomass [5,7,8]. However, whole tree chips pose a problem during storage. Due to their high moisture and foliage content, they decompose rapidly (1-5% per month) during storage and may develop microfungi spores which represents a serious health hazard [6]. Therefore, special care has to be taken during storage;
- on average, the bulk density is greater for wood than for agricultural wastes and Municipal Solid Waste. Bulk density affects handling and transport costs; lower bulk density results in high handling and transport charges [6,7]. Some typical bulk density values are given in Table 2.1.

Table 2.1
Typical Bulk Density of Different Biomass Types
(wet kg/m^3) [6,7]

Biomass Type	Bulk Density
Sawdust	150-200
Wood chips	200-300
Logwood (30-100 cm in length)	200-500
Pellets of sawdust/chips	400-600
Chopped straw	50
Straw bales	100
Straw pellets	300-500
MSW (fluff)	100

Lignocellulosic materials are composed of three types of polymers namely, cellulose, hemicellulose and lignin. These are combined with small amounts of ash and extractives such as waxes, resins and terpenes. These extractives are soluble in either water or solvents such as ether and dichloromethane. Some typical analytical analyses are given in Table 2.2.

Table 2.2
Typical Reported Analyses of Some Biomass Types, wt % [9].

Types	Total ash	Solvent soluble	Water soluble	Lignin	Hemicellulose	Cellulose
Softwood	0.4	2.0	--	27.8	24.0	41.0
Hardwood	0.3	3.1	--	19.5	35.0	39.0
Wheat straw	6.6	3.7	7.4	16.7	28.2	39.9
Rice straw	16.1	4.6	13.3	11.9	24.5	30.2
Bagasse	1.6	0.3	--	20.2	38.5	38.1

Typical delivered fuel costs varies from £28-36/dry t for conventional forestry to £41/dry t for short rotation forestry; agricultural wastes, such as cereal straw, has a delivered fuel cost of £22/dry t [6]. The cost of refuse derived fuel (RDF) products is dependent on the disposal cost/credit (the cost associated with refuse disposal either by landfill or incineration), and the pretreatment processes such as demetalling to remove cans, shredding and screening. Using a disposal credit of £10/t raw refuse, it is estimated that dried RDF pellets may cost £16.90/t dried pellets [6].

2.3 PHYSICAL STRUCTURE OF BIOMASS

A description of the physical structure of wood and its major structural components is presented below in order to explain the effects of pyrolysis on the individual components and on whole biomass. This chapter will be limited to the description of wood since straw and baggase have a chemical make-up similar to wood (see Table 2.2).

2.3.1 Wood

Wood tissues have a fibrous structure which are made up of various types of cells interlinked mainly through pits (openings) in the longitudinal direction and to a lesser extent by rays (cells that extend outward from the centre of the stem to the bark) [10-14]. The main functions of these cells are to store food, transport fluids and impart stiffness and strength to the wood. The cells are bound together by intercellular materials known as the middle lamella, forming a complex porous structure [14]. Each cell has a lumen (or hole) which is surrounded by a cell wall. The cell wall, which consists of several layers, is made up of cellulose microfibrils which is embedded in a matrix of lignin and hemicellulose (middle lamella). The thickness of the cell wall strongly influences the density of the wood [10,13].

Figure 2.1 is a diagrammatic cross section of the ultrastructure of the wood cell wall. This shows the strongly anisotropic structure of wood which has a major effect on the thermal properties such as thermal conductivity and permeability along different axes [15-18]. For example, it has been found that the thermal conductivity along the grain is two times that across the grain [16]. Furthermore, the rate of both heat and mass transfer is influenced by the grain orientation with resistance greater in the direction perpendicular to the wood grain [17].

The elementary chemical analysis shows that apart from minute traces of nitrogen, wood is composed of about 50% carbon, 6% hydrogen and 44% oxygen and can be represented by the empirical formula $CH_{1.44}O_{0.66}$ [4] or by the formula $C_6H_9O_4$ [19]. Because of the high oxygen content, wood has a relatively low heat of combustion between 18-21 MJ/kg on a dry basis.

As well as being physically heterogeneous, wood is chemically heterogeneous. The cell wall components, representing the bulk of wood, can be divided into two fractions, hollocellulose (cellulose and hemicellulose) which forms the fibrous part of the cell wall and lignin which forms the cementing agent for the hollocellulose. These components are described in Section 2.3.2 to 2.3.5.

2.3.2 Cellulose

Cellulose is the main component of wood and is predominantly located in the cell wall. The content varies from 30 to 45% of dry wood (see Table 2.2) [4,9,20]. It is a linear polymer of β-1, 4 D-glucopyranose units linked together by glycosidic (ether-type) bonds, generally represented by the formula $(C_6H_{10}O_5)_n$ (Figure 2.2). Values for the degree of polymerisation vary from 7,000 to 10,000 for wood to as high as 15,000 for cotton [21].

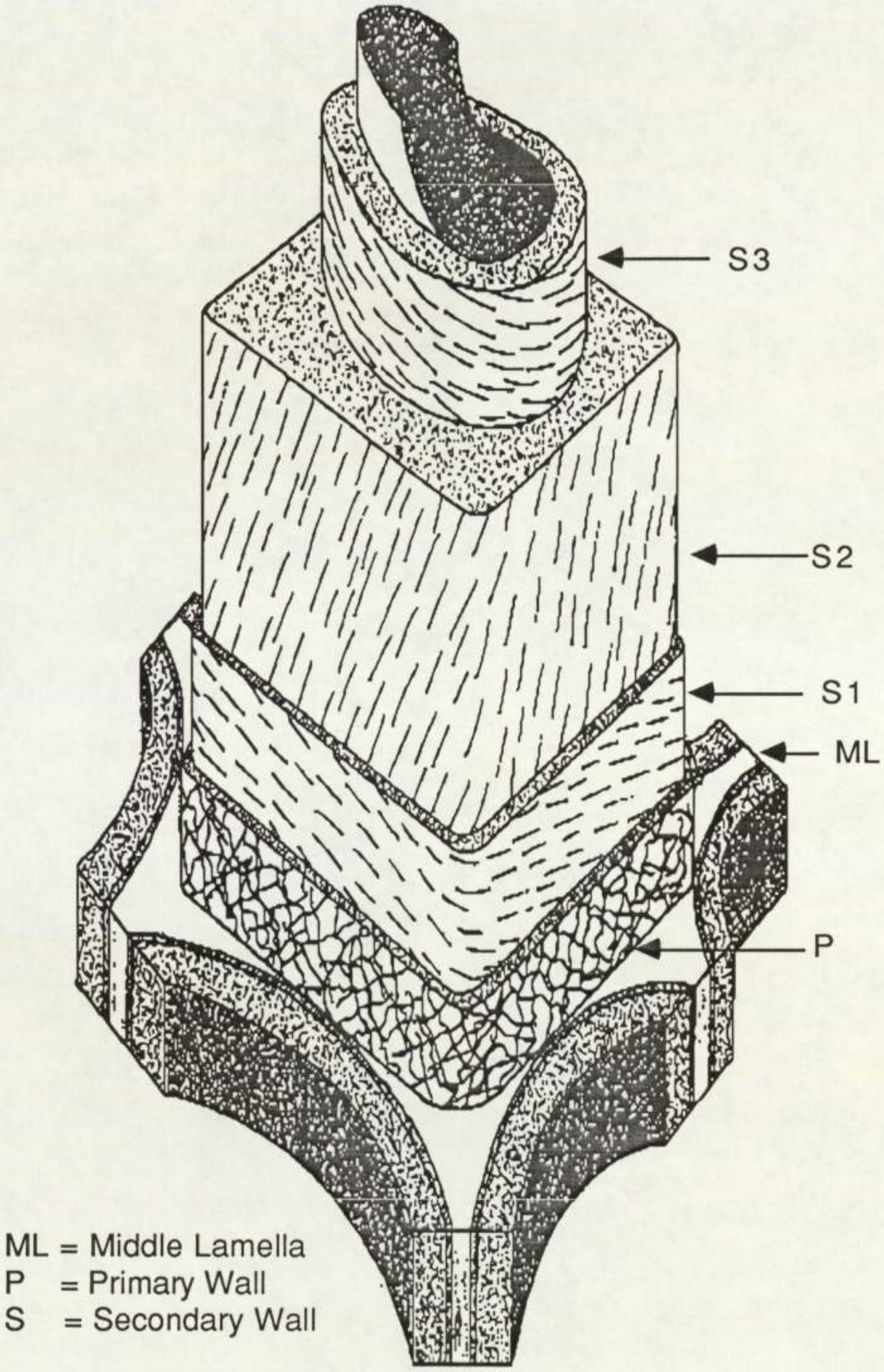


Figure 2.1 The Ultrastructure of Wood Cell Wall

The cellulose chains have a structure which strongly favours the formation of intra- and inter- molecular hydrogen bonds between hydroxyl groups and between ring oxygens and hydroxyl groups. This interlinking of the cellulose units into bundles results in the formation of microfibrils and eventually cellulose fibres. These fibres which are rigid and are characterised by an orderly and largely crystalline structure, give rise to the fibrous structure of wood [13,20].

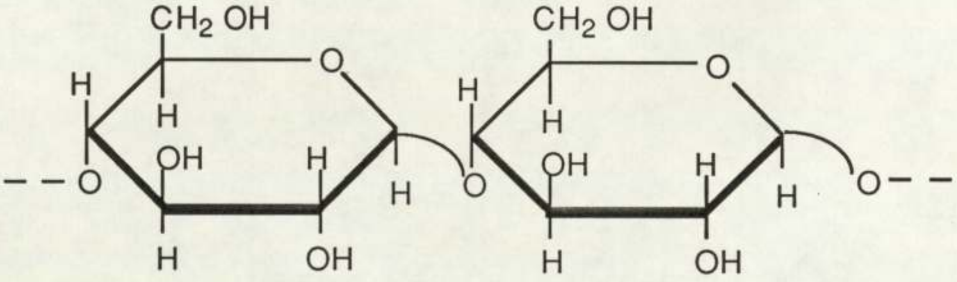


Figure 2.2 **Cellulose structure** [20].

As explained above, this fibrous structure has a major effect on the physical and chemical properties of wood in different axes, and these effects have to be considered in modelling any degradation process.

2.3.3 Hemicellulose

Hemicelluloses are closely associated with cellulose in the cell wall as well as to lignin in the middle lamella (see Figure 2.1) [13,20]. They are amorphous polysaccharides which are usually built up hexoses (C_6 sugars) in softwoods, and pentoses (C_5 sugars) in hardwoods with 1, 4 β- linkages between the sugar monomers. Unlike cellulose, they exhibit a branched rather than a linear structure which decreases the number of inter-molecular hydrogen bonds and hence reduces the degree of polymerisation to typically 100 to 200 units. Because of this low degree of polymerisation, they pyrolyse readily forming volatile matter rather than char [13,20].

Xylan, which is a polymer of d-xylose ($C_5H_{10}O_5$), forms the main hemicellulose of the hardwoods and is illustrated in Figure 2.3 while mannan, which is a polymer of d-mannose ($C_6H_{12}O_6$), forms the principal hemicellulose of softwoods and is depicted in Figure 2.4 [4,13,20].

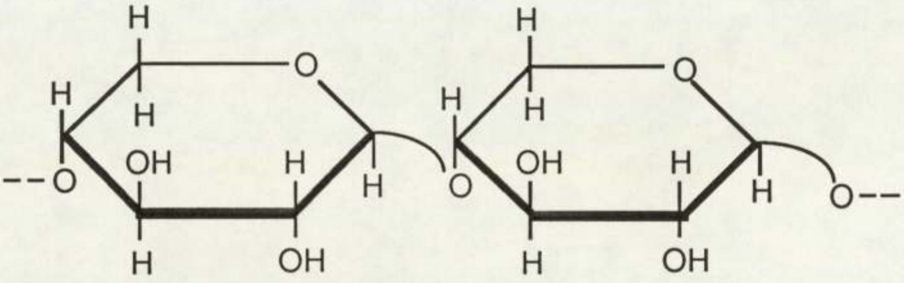


Figure 2.3 Xylan hemicellulose structure [20].

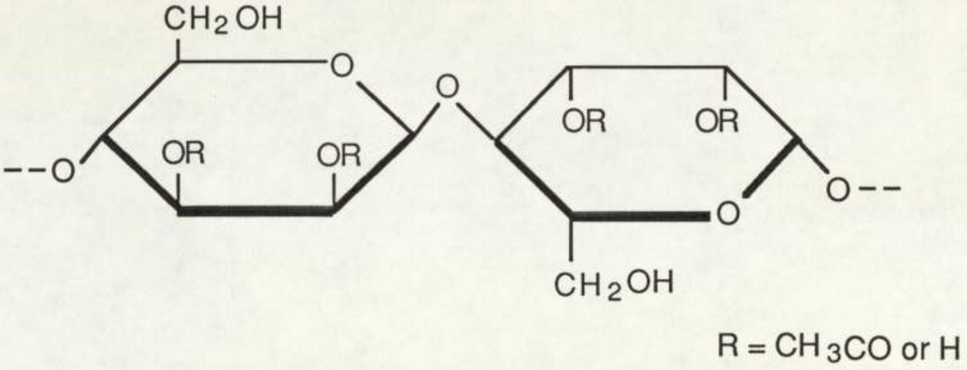
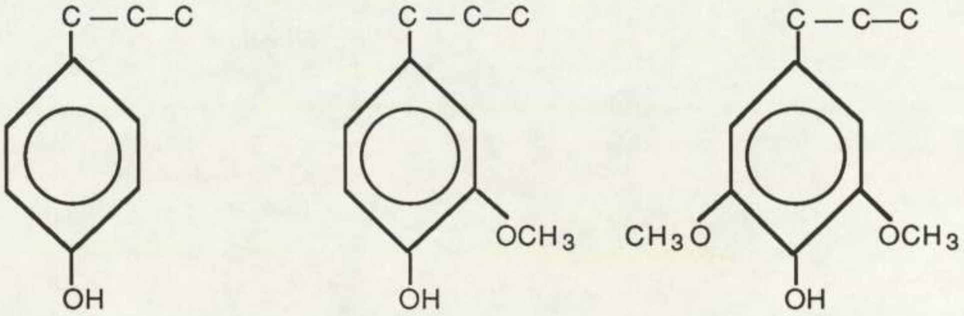


Figure 2.4 Mannan hemicellulose structure [20].

2.3.4 Lignin

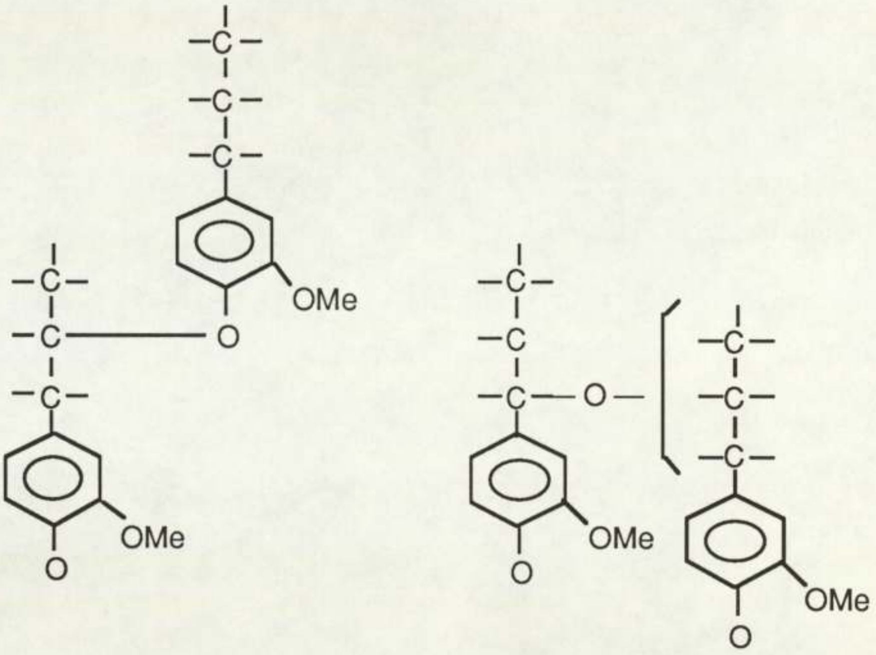
Unlike cellulose and hemicelluloses which are polysaccharides, lignin is composed of phenolic polymers. Lignin is the amorphous material that surrounds cellulose fibres and cements them together; in addition, it serves as a reinforcement agent within the fibres [13,21-23]. Lignin also protects wood against degradation from weathering and biodegradation [21-22].

Lignin is a random, three dimensional polymer made up of phenyl propane units where the unit may either be a guaiacyl or syringyl or hydroxyl. Figure 2.5 shows illustrations of the lignin units. These units are bonded together in several ways, the most common of which are the α- or β-ether linkages which are depicted in Figure 2.6 and the least common is carbon-carbon linkages [3].



p-Hydroxylphenylpropane Guaiacylpropane Syringylpropane

Figure 2.5 Lignin monomers [13].



β - 4' Ether bonding α - Alkylether bonding

Figure 2.6 Ether bonds in lignin [12].

Its exact structure is not known but one proposal is an approximate elemental analysis of ($C_{10}H_{11}O_2$) [24], and another is an empirical formula of ($CH_{1.7}O_{0.7}$) [3], which shows the diversity of opinion over composition. An abbreviated skeletal schematic of the lignin structure found in conifers is shown in Figure 2.7 [22].

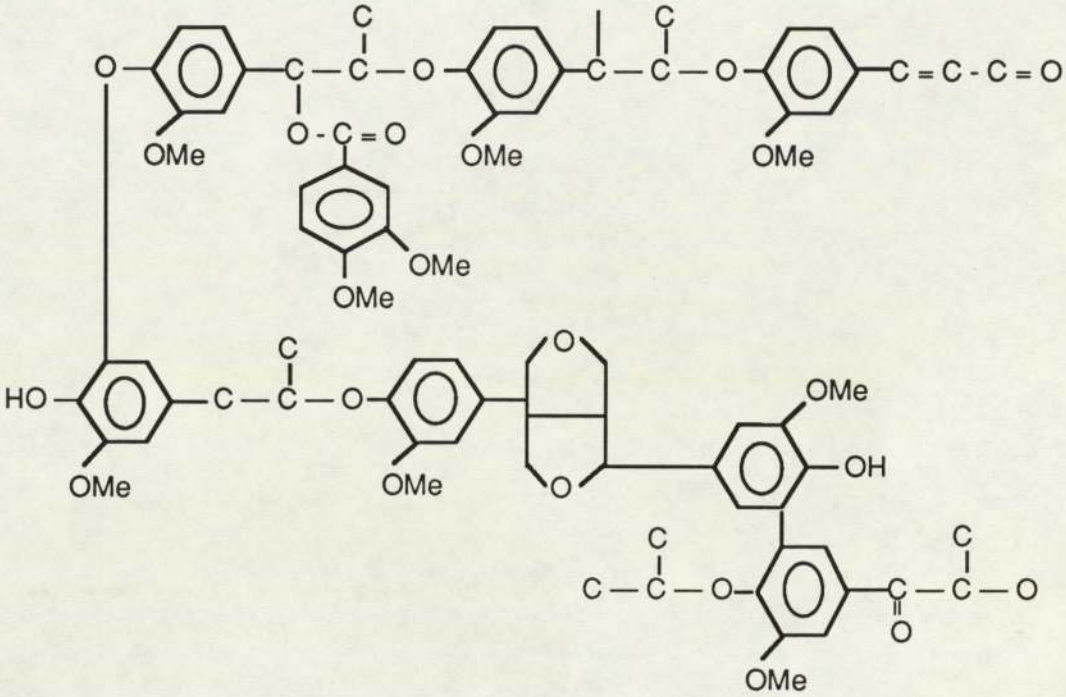


Figure 2.7 An abbreviated depiction of conifer lignin [22].

Lignin has a relatively high energy content 26.7 MJ/kg, compared to 17.5 MJ/kg for cellulose and 15.7 MJ/kg for hemicellulose, due to its low oxygen content and its aromatic nature [23]. Variations in the proportions of the organic components in wood determine its energy content. Whereas hemicellulose and cellulose, on heating, break down readily at the glycosidic linkages to form volatile products, lignin yields a considerable amount of char because of the greater stability of the aromatic rings [24].

Like hemicellulose, softwood and hardwood lignins differ in the balance of their constituent units. The softwood lignin contains guaiacyl propane units (one methoxyl group) while hardwood lignin, in addition to this, contains syringyl propane units (two methoxyl groups) [4,13].

2.3.5 Other Components

Within the lumen and adhering to the walls are minor components which are known collectively as extractives because they can be removed from wood by their solubility in either water or organic solvents such as ether.

They play a minute role in the formation of wood pyrolysis products. As seen in Table 2.2, the amount of extractives typically found in wood varies from 1-5% on a dry wood basis [19]. They include many different types of materials such as resins, starches, waxes, lipids, hydrocarbons and various phenolic compounds such as tannin [13,14,19]. Besides extractives, wood contains about 0.3% to 1.0% ash which is composed of approximately, 50% of CaO, 20% of K_2O, and Na_2O, MgO, SiO_2, Fe_2O_3, P_2O_5. Ash can play a catalytic role in some pyrolytic reactions [4,9,12,13].

2.4 REACTION PATHWAYS AND MECHANISMS

As wood is heated, its components become unstable and break down. A number of studies on the pyrolysis of wood and its components have revealed that they are chemically reactive at temperatures as low as 150°C. Hemicellulose primary pyrolysis has been observed to occur at 150 to 350°C [25]; cellulose from 275 to 350°C [25] and lignin at 250 to 500°C [25]. Wood is claimed to starts to pyrolyse at 250°C [26]. Figure 2.8 shows, as an example, the thermal analysis of cottonwood and its components [24].

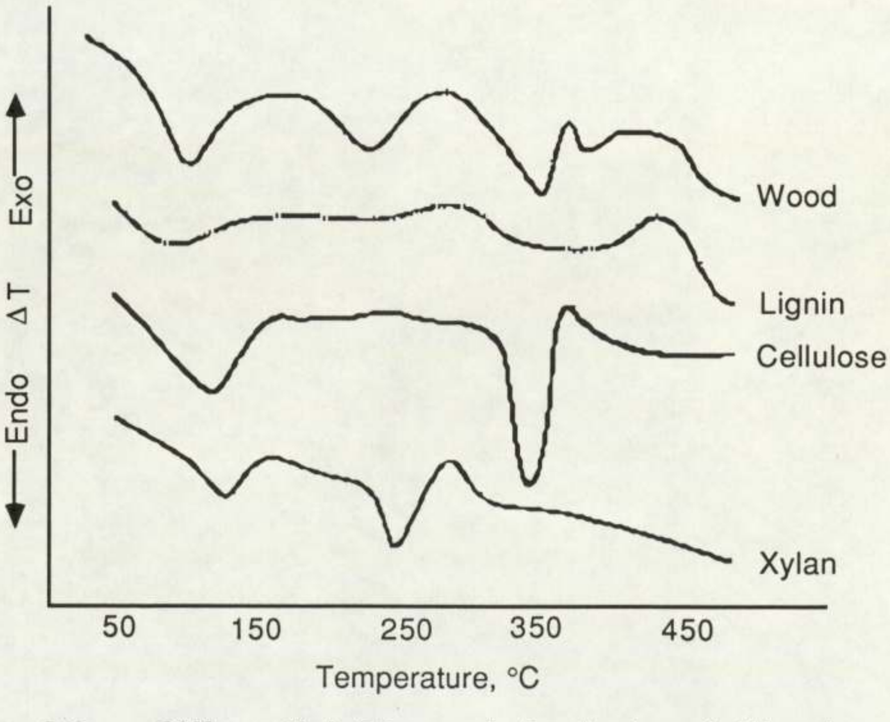


Figure 2.8 **Differential Thermal Analysis of Wood and Its Components** [24].

Table 2.3 shows typical compounds that have been identified within the liquid product obtained by flash pyrolysis (pyrolysis at high heating rates) of wood [27].

Table 2.3
Composition of Oils Obtained by Flash Pyrolysis of Wood [27].

	Waterloo 1	Waterloo 2	SERI
Wood type	Poplar	Maple	Poplar
Moisture content	0	5.9	4.6
Particle size, mm	3.00	0.59	1.00
Temperature, °C	504	508	500
Pressure, bar	1	1	1
Residence time,s	0.48	0.47	0.75
Product yields as analysed (% based on moisture free feed material)			
Oil	77.0	77.2	64.3
Char	11.8	13.7	12.0
Water + water solubles	N/A *	N/A *	N/A *
Gas	11.0	9.8	16.0
Some constituents in liquid (based on % weight of constituent in oil) :			
Glycolic acid	0.55	0.66	0.54
Formic acid	1.48	1.48	0.97
Acetic acid	3.09	2.89	4.08
Propionic acid	0.16	0.13	0.33
Other carboxylic acids	0.38	0.38	0.98
D-xylose	0.06	0.18	--
Levoglucosan	1.02	1.50	1.99
2-butenone	--	0.05	--
Acetel	2.85	1.75	4.08
2-Furaldehyde	0.46	0.37	0.66
phenol	--	--	0.73
5-methyl furfural	--	--	0.06
4-butyrolactone	0.20	0.17	0.26
methyl cyclopentenelone	--	--	0.44
p-cresol + m-cresol	0.06	--	0.13
eugenol + isoeugenol	0.07	0.10	0.13
2,6-dimethoxy phenol	--	0.23	0.66
syringaldehyde	0.38	0.42	0.37

* water is included in oil yield

This liquid product consists of a mixture of phenolic and non-phenolic compounds. The non-phenolic compounds such as the carboxylic acids, lactones, aldehydes, ketones, furans and alcohols are the main products of the carbohydrate fraction of wood, namely cellulose and hemicellulose while lignin contributes to the formation of the aromatic or phenolic compounds such as phenol and cresols at temperature less than 600°C. Therefore, the pyrolytic behaviour of cellulose, hemicellulose and lignin will be described first in order to gain an understanding of the thermal degradation of wood.

The reactions of all lignocellulosic materials can be simplistically divided into primary and secondary pyrolysis reactions. Primary pyrolysis is reactions that directly involves the solid feed material, whereas secondary pyrolysis refers to those reactions involving the decomposition of the intermediate pyrolysis products formed during primary pyrolysis.

2.4.1 Cellulose Pyrolysis

2.4.1.1 Introduction

Of all the components of wood studied, the pyrolysis of cellulose has received the most attention. This is due to its abundance in most biomass materials (around 50% by weight), its well defined structure and the ease of purification and specification [24-40].

It is generally considered that primary pyrolysis of pure cellulose occurs by two competing pathways; one involves dehydration and the formation of char, CO_2 and H_2O and the second involves fragmentation or depolymerisation resulting in the formation of tarry products consisting mainly of levoglucosan as depicted in Figure 2.9 [9,29,31,34,35,40]. These two competing pathways are discussed below.

2.4.1.2 Lower Temperature Pyrolysis

The reactions in the upper half of Figure 2.9, which dominates at lower temperatures, that is temperatures below 300°C, involve a reduction in the molecular weight or degree of polymerisation (DP), formation of free radicals, elimination of water, formation of carbonyl, carboxyl and hydroxyl groups, evolution of CO_2 and CO and finally the production of a charred residue [9,29,31,34-39]. It is not certain however, whether these reactions occur in sequence or in parallel.

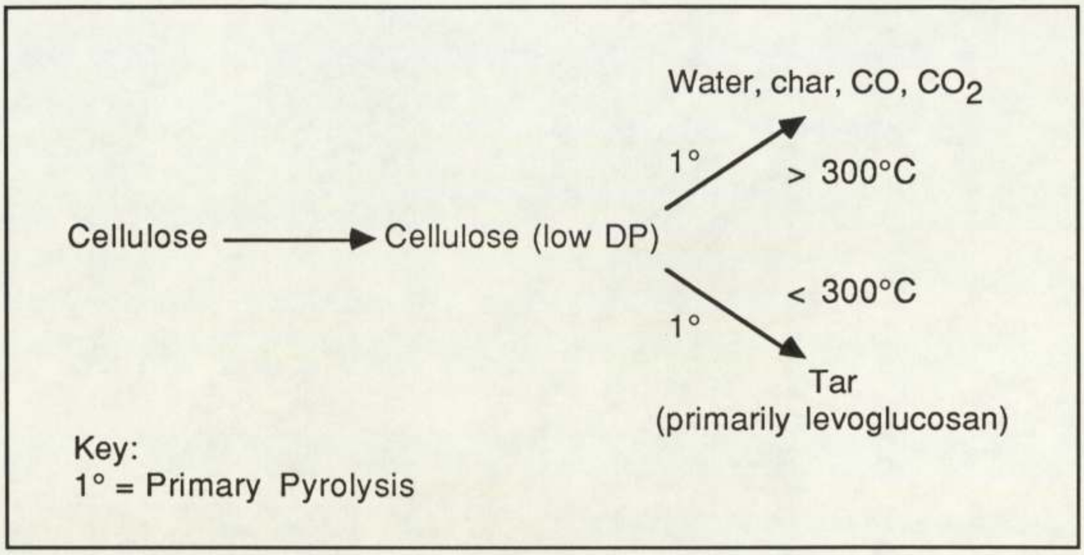


Figure 2.9 Temperature dependency of primary cellulose pyrolysis [9,29,3134].

The decrease of the degree of polymerisation, typically from between 1000 and 2000 to 200, occurs at temperatures between 200°C and 250°C. Shafizadeh argued that this decrease was due to the random bond scission process [9,34-36]. However, Broido et al. inferred from their experiments using amorphous cellulose, that bond cleavage occurred at points of maximum strain along the boundary where the crystalline and the amorphous region met in the polymer [32]. "Active cellulose" or "dehydrocellulose" formed after this reduction in degree of polymerisation, which subsequently decomposes to form char. It has been found that the presence of ash or mineral matter such as sodium or potassium as hydroxide or carbonate enhances char formation (see Section 3.5).

2.4.1.3 Moderate Temperature Pyrolysis

At temperatures greater than 300°C, fragmentation or transglycosylation predominates. This involves the conversion of cellulose into mainly a liquid product. This liquid product (which is normally termed as tar) consists of levoglucosan and related anhydrosugars, with levoglucosan identified as the key intermediate (see lower half of Figure 2.9). Two hypotheses have been proposed to explain transglycosylation - free radical and heterolytic depolymerisation. Both points of view have some experimental support, but the evidence is inconclusive.

The first asserts that the glycosidic bonds are broken homolytically and that depolymerisation proceeds by a free radical mechanism [28,33]. The second assumes the transglycosylation mechanism to be heterolytic with depolymerisation proceeding by a carbonium ion intermediate [29,31,34-37]. Shafizadeh [9,34-36] suggested that changes in structure of cellulose and increased flexibility are required for heterolytic transglycosylation to occur and that this is achieved by the breaking of hydrogen bonds at or near a glass transition point. The complex chemistry involved in both mechanisms has been extensively covered in the literature [29,30] and therefore will not be covered here.

Levoglucosan and other intermediates such as 1,6-anhydro-β-D-glucofuranose, 1,2-anhydride and 1,4-anhydride, then participate in secondary reactions in the vapour state to form the final products. These secondary reactions include repolymerisation or recombination of the intermediates to form char and/or polymeric tars which contain aromatic compounds such as toluene and phenol and cracking and reforming reactions. Cracking reactions result in the formation of permanent gases such as CH_4, H_2, CO and CO_2 and low molecular weight products such as formic and acetic acid, acetaldehyde, glyoxal, acrolein and methanol [29,30,41]. The reaction pathways for pure cellulose pyrolysis is illustrated in Figure 2.10. These reactions are dependent on the vapour residence time, pressure, ash, heating rate, temperature and reactor environment (see Chapter 3).

2.4.1.4 Glycolaldehyde (Hydroxyacetaldehyde) Formation

The identification of levoglucosan as the major product of cellulose pyrolysis was based on fundamental research carried out at low heating rates (up to 100°C/min) and under vacuum (see Antal's review [29,30]). However, pyrolysis of wood or the pyrolysis of cellulose with some ash present, gave low yields of levoglucosan. Furthermore, under conditions that enhance liquid production (moderate temperatures and high heating rates), glycolaldehyde (hydroxyacetaldehyde) has been identified as one of the principal products, as exemplified in Table 2.4 [39,40,42].

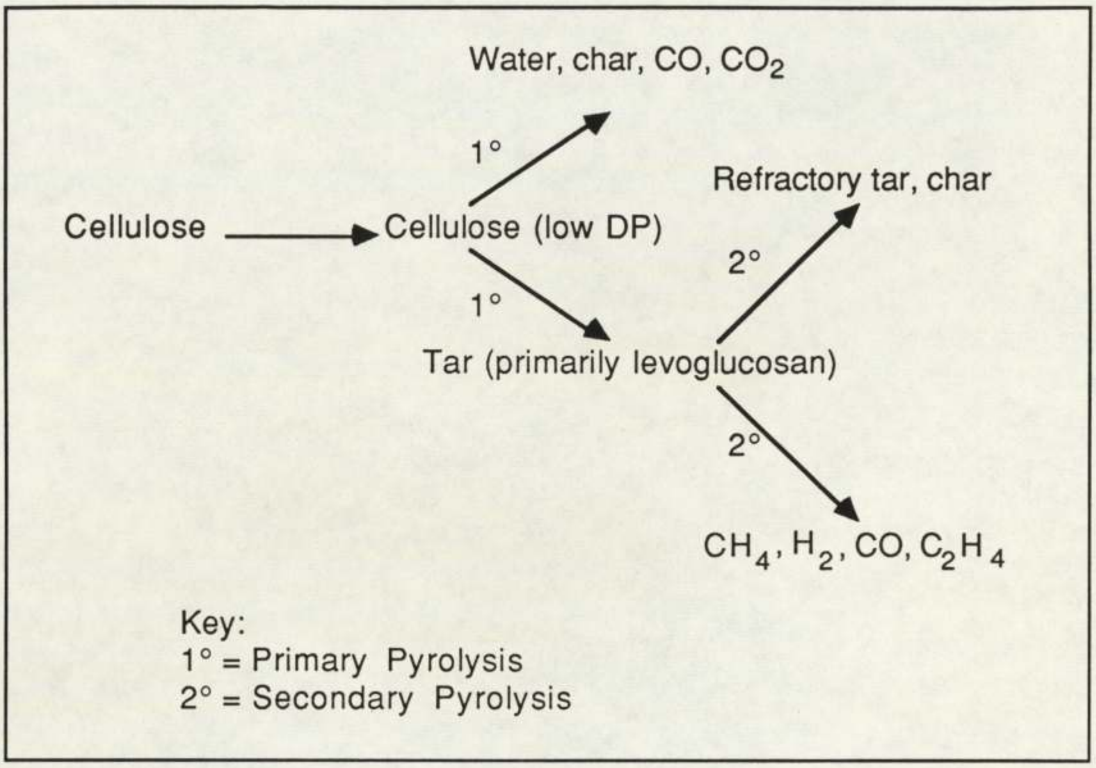


Figure 2.10 Pathways of pure cellulose pyrolysis [9,29,31,34].

This has led to the recent proposal that levoglucosan and glycolaldehyde are formed in parallel competing reactions that are dependent on process conditions. This subsection will describe the formation of glycolaldehyde.

Scott et al. originally suggested that levoglucosan was a precursor of glycolaldehyde. This formation of glycolaldehyde resulted from the successive sequential decomposition of levoglucosan [39,42]. However, they are now, in agreement with the proposal of Richards [43] in which glycolaldehyde is derived from the C_5 and C_6 of the cellulose monomer. The remaining fragments of the glucose unit are thought to rearrange to produce other products such as hydroxyacetone, formic and acetic acids and ethylene glycol.

Table 2.4
Pyrolytic Products from Cellulose at 500°C [39].

Overall yields, % mf of feed as reported: *	
Organic liquid	72.5
Water	10.8
Char	5.4
Gas	7.8
Major constituents in liquid, % mf of feed:	
Glycolaldehyde	15.3
Levoglucosan	7.0
Cellobiosan	4.0
Glucose	1.0
Fructose	2.0
Glyoxal	3.5
Methylglyoxal	0.8
Formic acid	5.5
Acetic acid	4.9
Ethylene glycol	1.7
Formaldehyde	1.2
Acetol	2.2

* Pyrolysis was carried out in a fluidised bed with a gas residence time of ~0.5 s, in a nitrogen atmosphere with a particle size of 90 μm.

This proposal is illustrated in Figure 2.11 [34,43]. He also suggested that glycolaldehyde is predominantly formed from the amorphous rather than from the crystalline regions of cellulose.

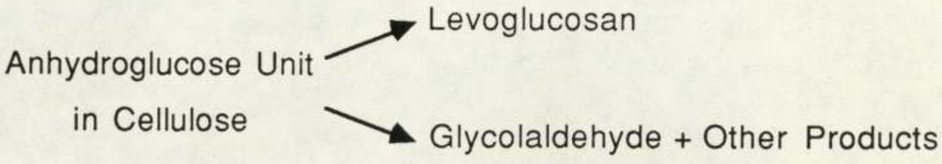


Figure 2.11 Richards model of cellulose pyrolysis [40,43].

Continuing on the theme proposed by Richards, Scott et al. proposed the Waterloo model which takes into account the two major competing pathways for the primary decomposition of cellulose in fast pyrolysis, each of which is capable of minor rearrangement reactions to account for the variety of different products produced; these reaction pathways and products are summarised in Figure 2.12 [39].

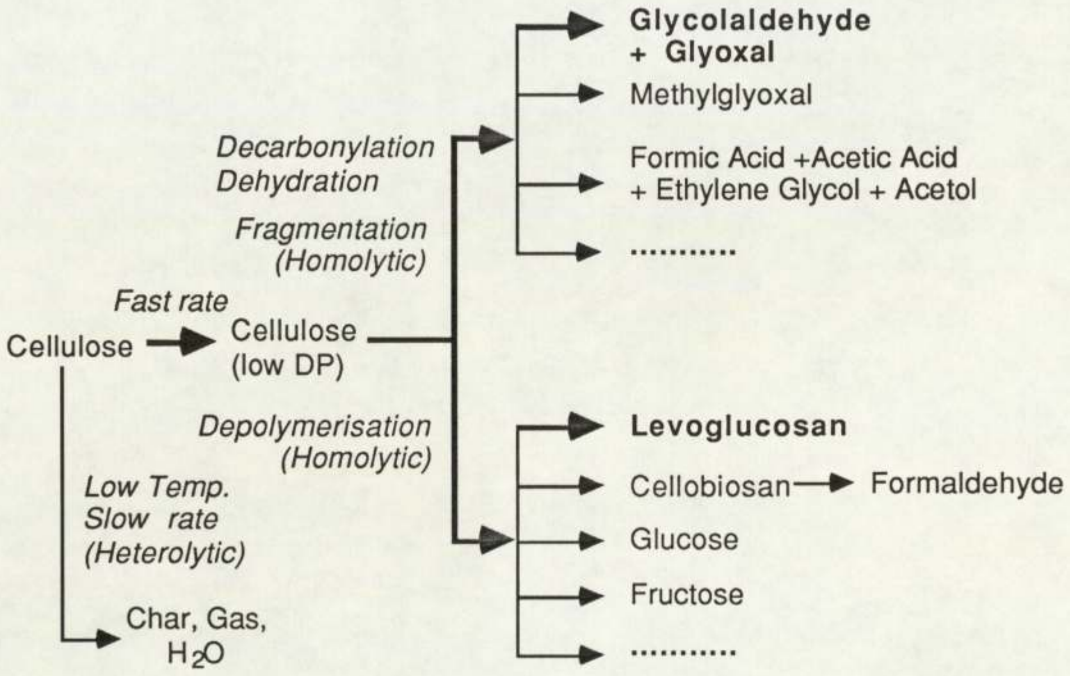


Figure 2.12 Proposed decomposition mechanisms of cellulose in fast pyrolysis - Waterloo model [39].

The pathway taken will be dependent on the morphology of the cellulose, its degree of polymerisation, the presence of alkaline cations and other factors such as temperature and heating rate. Levoglucosan formation is thought to be by cellulose chain depolymerisation while hydroxyacetaldehyde is formed by ring scission (see Section 3.5). The minor pathways, shown in Figure 2.12, account for those compounds which appear to be formed either in the same reaction or in parallel reactions along with each of the two major competing routes. These intermediates can then participate in secondary reactions (see Section 2.4.1.3).

The mechanisms and reactions pathways are important because they show how cellulose pyrolysis contributes to the formation of anhydrosugars, furfural acids and lactones found in the liquid product of wood pyrolysis (see Table 2.3).

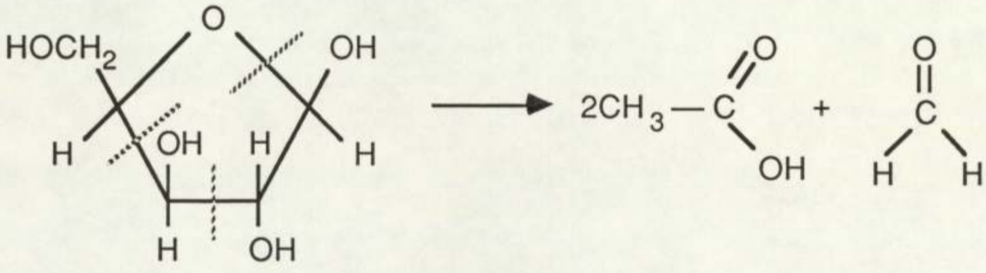
2.4.2 Hemicellulose Pyrolysis

2.4.2.1 Introduction

Hemicellulose has received less attention than cellulose and lignin, partially due to its lesser abundance in wood and partially due to its variety of constituents. It is the most reactive of the three major components of biomass and undergoes thermal degradation very rapidly at temperatures between 150-350°C possibly due to its lack of crystallinity (refer to Section 2.2.3 and see Figure 2.8) [44].

2.4.2.2 Hemicellulose Degradation

Generally, hemicellulose pyrolysis is thought to be analogous to cellulose pyrolysis in its reaction mechanisms, the intermediate levoglucosan being replaced by a furan derivative [37,38]. However, studies have shown that low yields of furfural, a furan derivative, have been obtained. For example, pyrolysis in a high vacuum at 300°C produced only 6% furfural [12]. These low yields may be due to the high reactivity of furfural which can undergo many secondary reactions under pyrolytic conditions [12,45]. Furthermore, there is the probability that the pentosan molecules split into low molecular fragments and thus cannot form furan rings [12,46]. This is exemplified in Figure 2.13.



---- represent bond cleavage

Figure 2.13 Formation of acetic acid and formaldehyde from xylan [46].

Soltes and Elder [47] reported a two-step degradation. The first step is depolymerisation to water soluble fragments which is then followed by decomposition to volatiles. They also stated that, in comparison with cellulose, hemicelluloses produce more gases, less tar and about the same amount of aqueous distillate. No data, however, was given to confirm this assertion. Table 2.5 gives examples of the hemicellulose pyrolysis products; methanol and acetic acid are derived from the methoxy and acetyl groups [48].

Table 2.5
Pyrolysis Products from a Hemicellulose (Xylan) at 500°C Under Vacuum [48].

Overall yields, based on % weight of sample:	
Char	10.0
Liquid	64.0
Water	7.0
Gas	8.0
Some constituents in liquid, based on % weight of sample:	
Methanol	1.3
Acetaldehyde	2.4
Acetic acid	1.5
Furan	Trace
1-Hydroxy-2-propanone	0.4
2-Furaldehyde	4.5
Acetone-propionaldehyde	0.3
2-3-Butanedione	Trace
3-Hydroxy-2-butanone	0.6

Like cellulose, the products obtained from hemicellulose pyrolysis contribute to the acids and lactones, aldehydes, alcohols and ketones found in the liquid product derived from wood pyrolysis (see Table 2.3).

2.4.3 Lignin Pyrolysis

2.4.3.1 Introduction

Lignin is the most complicated, least understood and most thermally stable component of wood. This lack of understanding can be attributed to the complex structure of lignin (see Figure 2.7) which varies significantly according to the source of the lignin and its method of isolation. Minor decomposition appears to begin at a lower temperature than for cellulose (250°C), but most lignin pyrolysis occurs at higher temperatures (see Figure 2.8) [28,30,44]. To date, the most detailed insights into lignin pyrolysis have been obtained from model compound studies.

2.4.3.2 Lower to Moderate Temperature Pyrolysis

Primary pyrolysis of lignin starts with thermal softening at temperatures around 200°C. This occurs due to the cleavage of the hydrogen bonds and aromatic skeletal vibrations [30]. As temperature increases lignin pyrolysis occurs by structurally controlled depolymerisation. Initially, higher molecular weight products such as coniferyl alcohol and sinapyl alcohol, are formed. This is due to the formation of double bonds in the alkyl side chain of the lignin structure. Subsequent products are lower molecular weight and are mainly light aromatics such as guaiacol and syringol. The formation of lower molecular weight products tends to peak towards the end of pyrolysis.

Evans and Milne [37,38], using data obtained from molecular-beam mass spectrometry, suggested that this late evolution was due to lignin becoming more hydrogen deficient during the formation of the alkenyl aromatics such as coniferyl alcohol. They further claimed that condensation reactions can occur due to bonds cleavage in the hydrogen deficient matrix which leads to the formation a more refractory solid as pyrolysis progressed. This solid could then undergo further devolatilisation by hydrogen transfer to form stable aromatic species such as guaiacol. Anvi [49,50] proposed a similar reaction mechanism.

Most of the char obtained in wood pyrolysis is obtained from the lignin fraction. This is because the aromatic rings present within lignin are much harder to break than the glycosidic linkages present in hemicellulose and cellulose which cleave readily. Char yields of over 50% by weight can be obtained at low reaction temperatures ($\leq$ 400°C) and low heating rates ($\leq$ 100°C/min) in lignin pyrolysis [4,30,45,51-53]. Shafizadeh et al., using results obtained from CP/MAS ^{13}C-NMR (cross polarisation/magnetic angle spinning, carbon 13 - nuclear-magnetic-resonance) studies, suggested that these significant yields of char were due to the presence of methoxy phenyl groups that had survived thermal decomposition; they obtained a char yield of 73.3 wt % with a formula of $C_6H_{5.0}O_{1.3}$ from lignin heated for 5 minutes in a preheated furnace at

400°C in nitrogen environment (60 ml/min) [53]. The char was found to be a highly cross-linked, aromatic structure which bears some resemblance to lignite [4,45,53].

As shown in Table 2.3, aromatic compounds, such as phenol, dimethoxy phenol and cresols, are produced during wood pyrolysis. Presumably, these products are formed as a result of fragmentation reactions as opposed to condensation reactions which result in the formation of char during lignin pyrolysis. Experimental results appear to support this hypothesis.

In this temperature range, single ring aromatic compounds have been identified in the liquid product. Jegers and Klein investigated the pyrolysis of Kraft lignin in microtubing bomb reactors, using a temperature range of 300°C to 500°C [56,57]. They identified and quantified 33 products including 12 gases, water, methanol and 19 aromatic compounds such as phenol, cresol and guaiacol. Iatridis and Gavalas [54] studied the pyrolysis of kraft lignin at 400 to 700°C for 10 to 120 s by using a captive sample reactor. They obtained a total volatiles yield of around 60 wt % which included 3-4 wt % light (single ring) phenolic compounds. Nunn et al. [58], using high heating rates with a captive sample reactor, obtained liquid as the main product above 500°C with a maximum of 53 wt% at 625°C which was aromatic in nature. Multi-ring aromatic compounds have also been identified as products of lignin pyrolysis. Formation of these compounds will be described in the following sub-section.

2.4.3.3 Higher Temperature Pyrolysis

At temperatures greater than 600°C, the aforementioned products can undergo further reactions such as cracking, dehydrogenation, condensation, polymerisation and cyclisation. Cracking reactions result in the formation of products such as CO, CH_4, other gaseous hydrocarbons, acetic acids, hydroxyacetaldehyde and methanol. Polyaromatic, refractory condensible materials/compounds such as benzene, phenylphenols, benzofurans and naphthalenes are formed by other secondary reactions such as polymerisation and condensation

[27,29,30,37,38,49,50,59].

The competitive reaction mechanism between the formation of refractory condensible materials and permanent gases and low molecular weight products was confirmed by Antal [54,55] during his investigation of the gas-phase pyrolysis of cellulose- and kraft lignin- derived volatile matter in the temperature range of 500-750°C (see Section 4.4.5 for further details). He found that as temperature increased, gas yields increased while tar yields decreased . Evans and Milne [37,38] obtained similar results.

2.4.3.4 Model Compound Studies and Mathematical Modelling

A method commonly used to obtain reaction mechanisms and reaction kinetics for lignin pyrolysis is model compound studies. Klein and Virk [30,56,57] have proposed a mechanism of alkyl-aryl ether cleavage for lignin pyrolysis based on the pyrolysis of model compounds such as phenethylphenyl ether (PPE). From kinetic studies, they proposed a concerted pericyclic hydrogen transfer mechanism (pericyclic reactions are reactions that involve transition states when bonds are broken or made so as to create a cyclic compound) as opposed to a free radical mechanism.

Because the structure of lignin is so complex and not well known some workers have proposed mathematical models to predict the structure and its thermal degradation. The Monte Carlo technique, a technique that introduces degrees of randomness, has recently been used to simulate the pyrolysis of lignin [61,62]. The overall simulation is comprised of two Monte Carlo simulations: the construction of the lignin structure and then the degradation of the oligomers. The simulation combined model compound reaction pathways and kinetics into a Markov-chain based simulation of the reaction of lignin polymers which, subsequently, predicted yields of hydrocarbons, phenols, guaiacols and catechols in the tar fraction. However, accuracy was dependent on the model compound rate constants and the lignin structural information employed.

A sensitivity analysis of the Monte Carlo simulation of Kraft lignin to the value of the model rate constant of Diphenylethane (DPE) was carried out. They found that the prediction and the experimental data for the formation rate constant of the primary product were quite similar (3.1 versus 2.7 (10^{-4} s^{-1}) respectively), whereas the agreement for the decomposition rate constant of the primary product was poor (2.7 x 10^{-4} versus 0.86 s^{-1}). They concluded that the Monte Carlo prediction required assessment of the influence of each model compound rate constant and the structural distribution functions. Furthermore, the accuracy of the estimate of the standard deviation had to be addressed.

Other mathematical models developed for lignin pyrolysis include the models of Solomon et al. to predict the molecular weight distribution of lignin pyrolysis tars [50,63] and Anvi et al. which simulated the evolution of lignin pyrolysis gases by the removal of functional groups such as carbonyl as CO and hydroxyl as H_2O [49,64].

Compound studies and mathematical descriptions are often used to provide some insight into the complex mechanisms and chemistry of lignin pyrolysis. However, accuracy is dependent on the model compounds, model compound rate constants, the lignin structural information used as well as the statistical values used for solving the models. This adds to the complexity of the mathematics used in solving these models and therefore limits usage.

Consequently, model compound studies and mathematical models of lignin have limited use in the production of liquid from biomass unless they can be used to identify conditions that result in the selective formation of a few high value products such as phenols and BTX (benzene, toluene and xylene).

2.4.4 Wood Pyrolysis

2.4.4.1 Introduction

The pyrolytic behaviour of wood could be expected to reflect the pyrolytic behaviour of its three main components. Because of the presence of three peaks on DTG, DTA and DSC data obtained from wood pyrolysis, some researchers have concluded that the mechanism of wood pyrolysis is a linear combination of the mechanisms of its three main components. Furthermore, Shafizadeh et al., using cottonwood as an example, obtained DTA information which showed that the peaks exhibited by the wood curve corresponded qualitatively to peaks obtained from its components (see Figure 2.14) [24].

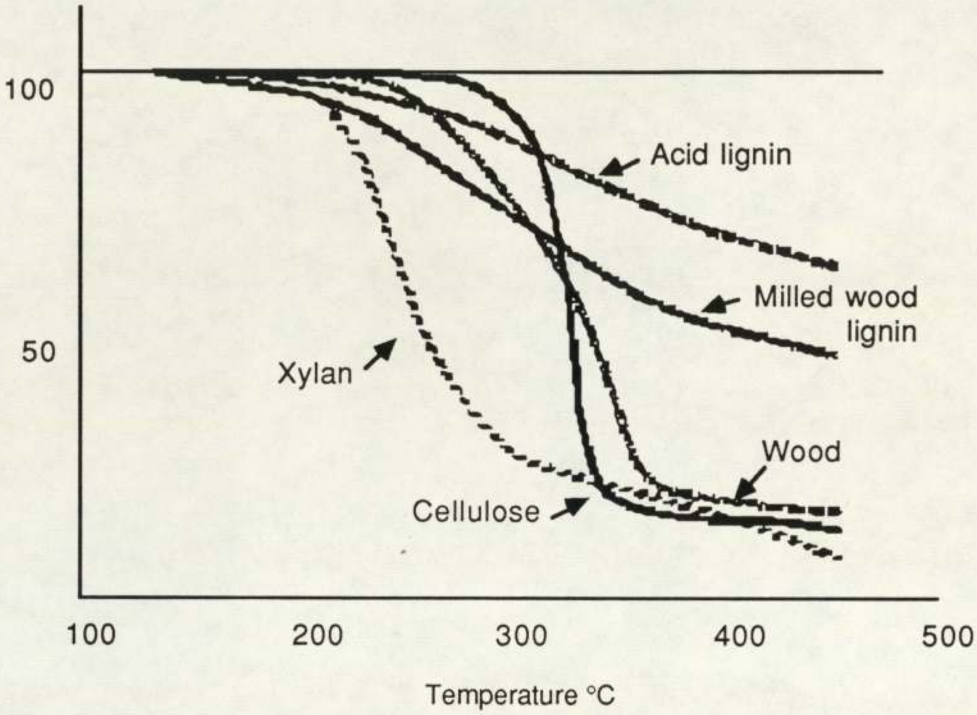


Figure 2.14 Thermogravimetry of Wood and Its Components [24].

Antal and other workers argue that there should be both qualitative and quantitative evidence to infer this linear combination (see Antal's review [30]). Hence, they proposed that there are interactions among the components during wood pyrolysis. In the review, Antal suggested that these interactions are very complex and are manifested in the diverse pyrolysis product slate obtained during wood pyrolysis. In the closing remarks, he proposed that more research was needed in this area in order to identify these interactions. Lately, Evans and Milne using molecular beam, mass spectrometry to study the evolving pyrolysis vapours and gases from pyrolysing biomass, could not identify any interactions among the major components of wood which possibly could have resulted in a new product being formed. Therefore, the author believes that it is possible to infer that the mechanism of wood is a summation of the behaviour of its three major constituents.

2.4.4.2 Flash/Fast Pyrolysis of Wood

As current interest is focussed on liquid fuels produced by fast or flash pyrolysis of biomass, this subject will be covered in this sub-section. Three major theories have been proposed and each of these theories will be described [37,66,67].

2.4.4.2.1 Copper Mountain Theory of Fast Pyrolysis

The earliest hypothesis to explain fast pyrolysis in depth was outlined by J Diebold and is illustrated in Figure 2.15. This reaction scheme was derived from a general consensus of pyrolysis specialists, who attended a Workshop on the Fast Pyrolysis of Biomass, held at the Solar Energy Research Institute in October 1980 [66].

Interest, at that time, was directed to the production of olefins. The pathways leading to olefin formation, are shown as the horizontal sequence of reactions within the rectangular box of Figure 2.15.

The first decomposition reaction is the depolymerisation of wood to form primary tars. Once the liquid primary tars are formed on the biomass surface, high temperatures, high heating rates and low vapour partial pressures promote olefin production. These process conditions encourage vaporisation of the primary tars to occur before the primary tars rearrange and possibly repolymerise to more form stable secondary tar liquids. The vaporised primary tars are then thermally cracked to produce transient oxygenated fragments. These fragments are very active species and rapidly crack to form hydrogen, carbon oxides and olefins and other hydrocarbons.

The primary pyrolysis vapours at high pressure could be converted to either secondary tar at low temperatures or vapour-phase-derived-tar at high temperatures. If the secondary tar liquids are not heated to a higher temperature, they further repolymerise and rearrange to form solid charcoal (having macroscopic cellular features), water and carbon oxides.

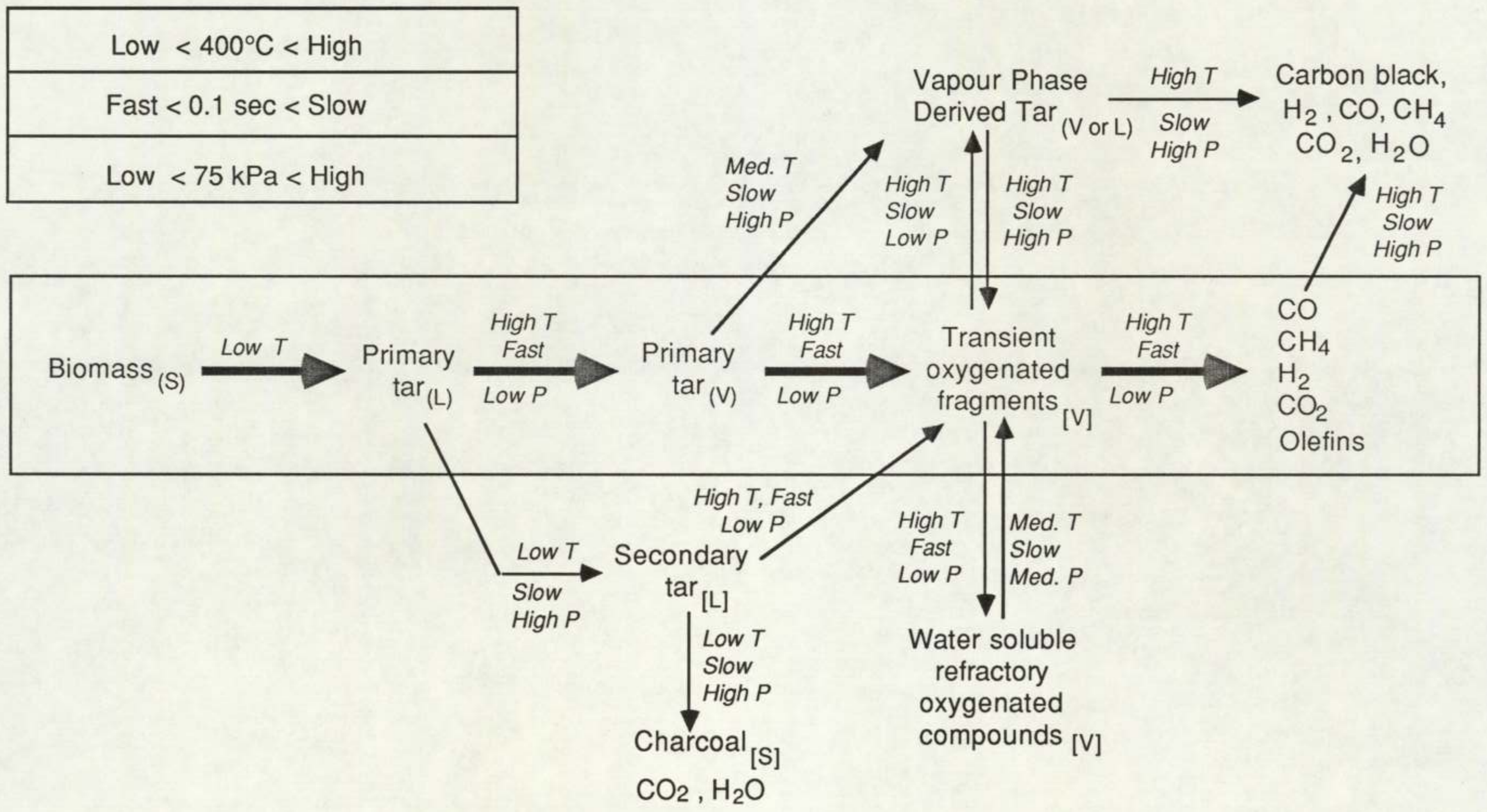


Figure 2.15 Fast Pyrolysis Reactions of Wood as Proposed in 1980 [61].

The vapour-phase-derived-tar could undergo further reactions at high temperatures and long residence times, to form carbon black, aromatic liquids and gases such as H_2, carbon oxides and CH_4. At low pressures and high temperatures, cracking of any of the above mentioned tars or the refractory water soluble oxygenated compounds result in the formation of transient oxygenated fragments. However no details are given about the changes in the composition of pyrolytic liquid.

2.4.4.2.2 Diebold's Simple Proposal

Diebold later proposed a more simple reaction scheme as illustrated in Figure 2.16 [67].

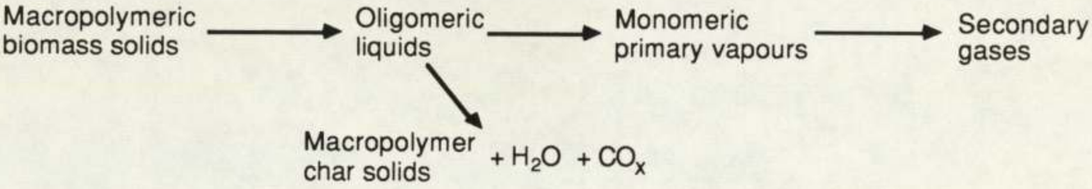


Figure 2.16 Reaction Scheme as Proposed by Diebold in 1985 [67].

Diebold et al. suggested that the first reaction in fast pyrolysis is the depolymerisation of wood macropolymers to form viscous primary oil precursors [67]. These precursors are formed with almost no by-products, and consequently their elemental structure is similar to wood. With low heating rates, much of the primary oil precursors can repolymerise to thermally stable polymers through the elimination of water to eventually form char. They suggested that physical evidence for a liquid state was the physical shrinkage of wood, which occurred during charring in a manner analogous to heat shrinkage of polyethylene tubing.

If wood is heated very rapidly, to temperatures above 450°C, most of the primary oil precursors can crack and vaporise before they form char. In the vapour state, the primary vapours are quite dilute which slows possible second-order polymerisation reactions. This dilution allows any unstable primary vapours to be converted by first order reactions to more stable compounds, which can be collected from a reactor designed to have a short gaseous residence time followed by rapid quenching. Thermal stability is relative, however, and these stabilised primary oil vapours readily crack to gases.

2.4.4.2.3 Evans and Milne Proposal

The most recent hypothesis on reaction pathways of fast pyrolysis has been proposed by Evans and Milne and this is depicted in Figure 2.17 [37]. Pyrolysis severity is defined as the increase in temperature, heating rate and vapour residence time.

They postulated that the initial reaction in fast or flash pyrolysis is the depolymerisation of the wood to form viscous primary oil precursors. These precursors or vapours are formed with almost no by-products under both high pressure (but in the absence of catalysts or reactive environments) and low pressure conditions and as a result, have a composition very similar to wood [37].

Under high pressure conditions, the direct formation of a liquid product mixture is due to the pyrolysis of wood that has become "plastic" at the temperatures and pressures involved. This has been confirmed by Diebold [68] and Lédé et al. [69] who have both shown that under direct-contact fast pyrolysis conditions, wood exhibits many properties of a "molten plastic state".

At atmospheric pressure and below, it is not clear whether a liquid phase exists, after the cleavage of the main polymer bonds and before volatilisation of the major components of wood. Evans and Milne [37] could not confirm this hypothesis as their experimental system does not provide any insight into the condensed phase transitions that occur during char formation. Therefore, they recommended that this suggestion should be further explored. Associated with char formation is the direct formation of permanent gases which consist primarily of CO_2, H_2O and CO. They further suggested that there is a sequential transformation of the primary precursors at low pressure. This transformation occurs in three stages as shown in Figure 2.17 [37].

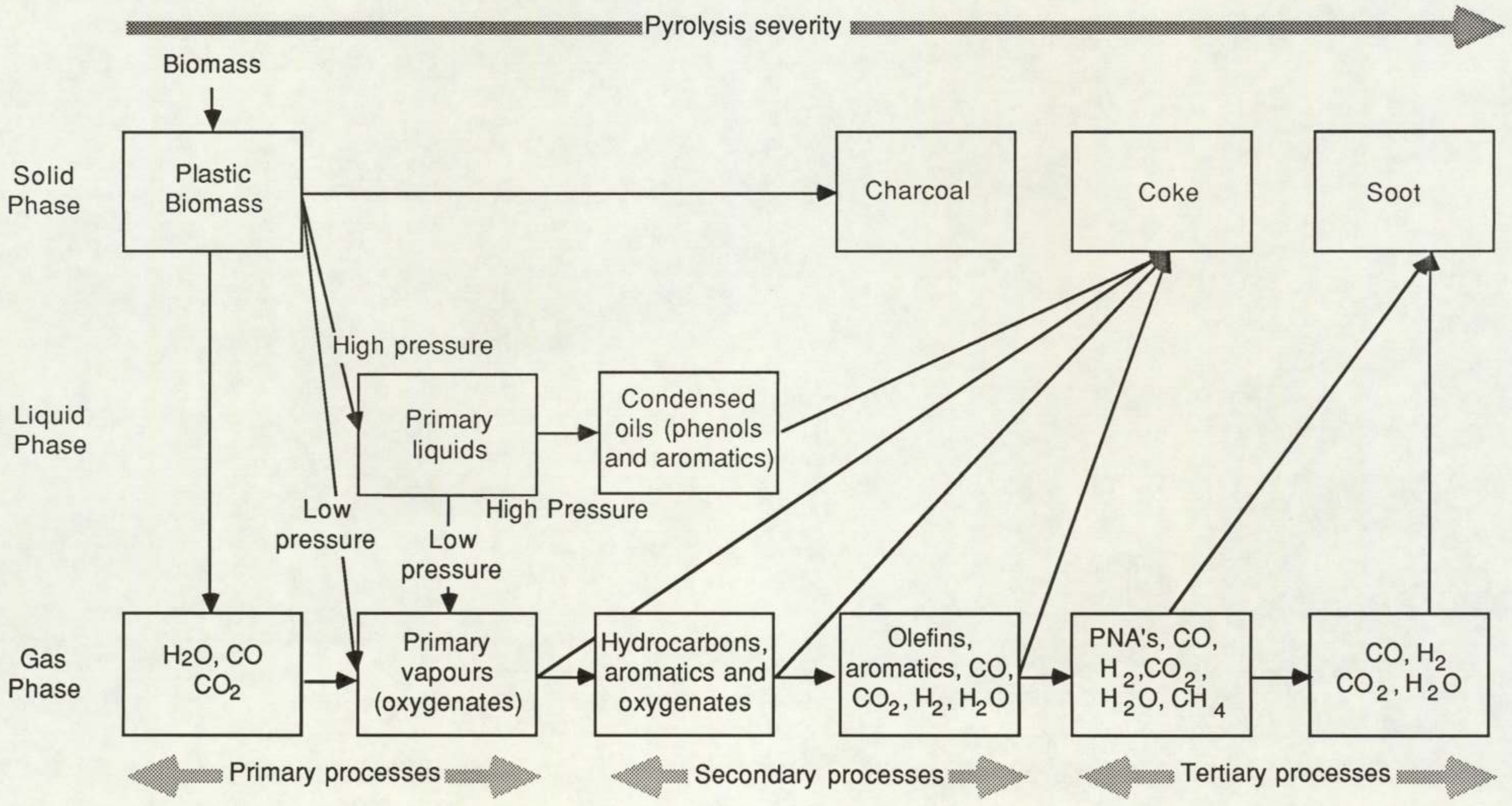


Figure 2.17 Biomass Pyrolysis Global Mechanism as Proposed by Evans and Milne, in 1987 [33].

The first stage involves slight cracking, at temperatures between 500-600°C, such as the cracking of higher molecular weight lignin products to lighter, single-ring aromatics (such as guaiacol and phenols) and oxygenates. The second stage occurs from about 600-700°C with the formation of secondary products characterised by CO, light olefins and more aromatics. Aromatics are also formed from the primary products of carbohydrate degradation at this stage. The third stage, which occurs at temperatures above 700°C, results in tertiary products from thermal degradation such as CO, CO_2, H_2, CH_4, low molecular weight saturated and unsaturated hydrocarbons and some polycyclic aromatics and eventually soot.

2.4.4.2.4 Flash Pyrolysis Transformations

All three proposals suggest that the first stage for pyrolysis involves the depolymerisation of wood. The Copper Mountain proposal suggests that primary tars are produced first. However, the formation of primary vapours seems more likely than liquid formation, due to the rapid heating of the pyrolysing particle and the use a temperature range of 400-550°C. Therefore to obtain a liquid product, rapid removal and quenching of the primary vapours is required. In addition, the probability of secondary and tertiary reactions occurring, is minimised. It is also believed that wood passes through a transient plastic stage and that this stage most likely occurs during char formation.

These primary pyrolysis liquids/vapours have been found to have a similar elemental composition to that of wood and therefore the following reactions can be considered to occur in moderate temperature flash pyrolysis :

$$
\begin{array}{rcl}
2C_6H_9O_4 & \longrightarrow & 2C_6H_7O_3 + 2H_2O \\
4C_6H_9O_4 & \longrightarrow & 16CO + 8CH_4 + 2H_2 \\
2CO + 2H_2O & \longrightarrow & 2CO_2 + 2H_2 \\
\hline
6C_6H_9O_4 & \longrightarrow & 2C_6H_7O_3 + 14CO + 8CH_4 + 4H_2 + 2CO_2
\end{array}
$$

2.4.4.2.5 Higher Temperature Pyrolysis

Evans and Milnes's proposal gives the most details of the transformation of the primary vapour precursors by secondary and tertiary reactions. The Copper Mountain proposal and Diebold's simplified reaction scheme appear to consider only secondary reactions.

Secondary reactions occur at temperatures between 550-700°C. The vapours become more aromatic in nature and olefins, CO, CH_4 are produced. All three components contribute to the formation of high molecular weight refractory aromatic compounds at this stage. The formation of aromatic compounds may occur by the scission of labile bonds around aromatic rings to eliminate side chains containing carbonyl and methoxy groups leading to the formation of catechols (an example is the conversion of guaiacol to catechol). Another is by condensation reactions resulting in the formation of double-ring and polycyclic compounds such as naphthalene and benzofurans [27,60].

Above 700°C, further cracking, deoxygenation and condensation reactions characterise tertiary reactions resulting in the formation of tertiary products such as CO, CO_2, H_2, CH_4, low molecular weight saturated and unsaturated hydrocarbons and some polycyclic aromatics (PAH) and eventually soot.

These sequential transformations correlate well with the chemicals identified by Elliott in low pressure, short residence time liquid products derived from wood (see Table 2.6 and Figure 2.18) [60,70]. Low temperature pyrolysis products in Table 2.6 are similar to the products listed in Table 2.3.

$\xrightarrow{400^\circ C}$ Mixed oxygenates $\xrightarrow{500^\circ C}$ Phenolic ethers $\xrightarrow{600^\circ C}$ Alkyl phenolics $\xrightarrow{700^\circ C}$ Heterolytic ethers $\xrightarrow{800^\circ C}$ PAH $\xrightarrow{900^\circ C}$ Larger PAH

Figure 2.18 General Pathway of Tar Degradation with Temperature [60,70].

Table 2.6
Chemical Components in Wood Tars [70]

Low Temperature Flash Pyrolysis (450-550°C)	*High Temperature Flash Pyrolysis (600 - 650°C)*
Acids	Benzenes
Aldehydes	Phenols
Ketones	Catechols
Furans	Naphthalenes
Alcohols	Biphenyls
Complex oxygenates	Phenanthrenes
Phenols	Benzofurans
Guaiacols	Benzaldehyde
Syringols	
Complex phenolics	

Thus, high yields of liquid products can be obtained by using temperatures around 500°C, combined with rapid quenching of the primary oil precursors so that the vapours are preserved and the occurence of secondary reactions, such as cracking, repolymerisation and condensation are minimised.

2.5 Conclusions

In summary, this chapter described the physical structure, the reaction pathways and mechanisms, and products of wood and its components. The reactions can be divided into primary (these occur at temperatures less than 600°C) and secondary and tertiary (above 600°C) pyrolysis reactions.

A controversy exists in the literature concerning the mechanism of levoglucosan formation from cellulose namely, via a free radical mechanism or by heterolytic depolymerisation. Both proposals have some experimental support but the evidence is inconclusive. Limited information is available on hemicellulose degradation but it is thought to have a mechanism analogous to cellulose, with a furan derivative replacing levoglucosan. Lignin pyrolysis proceeds by structurally controlled degradation resulting in the formation of lignin monomers. Model compound studies and mathematical models have also been proposed to describe lignin pyrolysis but further research is still needed in this area.

Wood pyrolysis appears to reflect the behaviour of its major components as no chemical species has been identified that could be derived from a chemical interaction of the components. Since these components are polymeric, wood degradation results in a wide range of complex organics. In the following chapter, the factors enhancing liquid production will be discussed.

CHAPTER THREE

PARAMETERS INFLUENCING LIQUID PRODUCTION

3.1 INTRODUCTION

As biomass is a heterogeneous material, its thermal degradation proceeds through a series of highly complex, competing reactions occurring between primary and secondary pyrolysis products as described in Chapter 2. The amount and quality of the end products are strongly dependent on the type and characteristics of the feedstock and the process conditions. By manipulating these parameters, the production of a desired product may be enhanced or optimised. This chapter will describe those parameters necessary to optimise liquid production or other desired products, illustrated by examples. The liquid product and the other products of pyrolysis are discussed in more depth in Section 5.4.

The factors will be divided into two categories, those related to the operation of the pyrolysis reactor and those related to the feedstock such as the physical structure, particle size and shape and chemical composition. These parameters are discussed in more depth below.

3.2 PROCESS CONDITIONS

The process variables described below, were selected because they are considered by most researchers to significantly affect both the yields and the composition of pyrolysis products. These parameters include heating rate, reactor temperature, solid and vapour residence time, pressure, gaseous environment.

3.2.1 Heating Rate

Pyrolysis has been used for centuries to produce charcoal, tars, alcohols such as ethanol and methanol and other solvents. This was usually carried out in kilns and retort furnaces where slow or conventional pyrolysis occurred [12,47,71]. Conventional pyrolysis is characterised by slow heating rates ranging from 0.01°C/s to up to 2°C/s, relatively low reactor temperatures (< 500°C) and relatively long solids and volatiles residence times (greater than 5 s for volatiles; solids residence times can be minutes, hours or days) [44,72]. Char, tars and gases are formed in approximately equal proportions due to the slow degradation of the feed and the secondary coking and polymerisation (recombination) reactions which take place in the reactor after primary pyrolysis (see Section 2.4.4.3) [73].

Recent studies have shown that by increasing the heating rate, the pathways of pyrolysis and the rates of of the reactions can be modified (see Section 2.4.4) resulting in a significant change in the proportions of the solid, liquid and gas products of pyrolysis. This process is known as flash or fast pyrolysis.

Flash pyrolysis is a process in which gas or liquid products are maximised at the expense of char formation, according to the temperature employed, and by rapid heating [12,74-81]. This process involves heating rates up to 10^6°C/s (see section 5.4.2). At reactor temperatures greater than 650°C, gases are produced at the expense of condensable vapours. This is due to the cracking and reforming reactions of the primary pyrolysis vapours taking place (see Section 2.4.4.3). Consequently, if the desired product is liquid, the reactor temperature should be kept between 400 and 650°C. In addition, rapid quenching should be employed so that the pyrolysis vapours generated are condensed before further secondary reactions occur (see Section 2.4.4.3). Liquid yields of over 60 wt% on a dry feed basis have been obtained by employing flash pyrolysis [74-76].

The heating rate of any system is influenced by the reactor configuration and the particle size of the feedstock (this will be discussed in Section 3.3.3). The reactor configurations most commonly employed for flash and fast pyrolysis are fluidised bed reactors, entrained flow reactors and cyclone or vortex reactors. These configurations have been shown in the past to be capable of high heating rates; they will be discussed further in Section 5.5.

3.2.2 Reactor Temperature

Reactor temperatures normally quoted in the literature refer to the maximum temperature inside of the reactor.

Because the reactor temperature can affect both the primary and secondary pyrolysis products as shown in Figure 3.1, the chemical components found in the liquid product of wood pyrolysis also vary with temperature (see Section 2.4.4.3 and Table 2.6). Changes in the organic compounds found in the liquid reflect the secondary and tertiary pyrolysis reactions that are taking place as the temperature is increased (see Section 2.4.4.3).

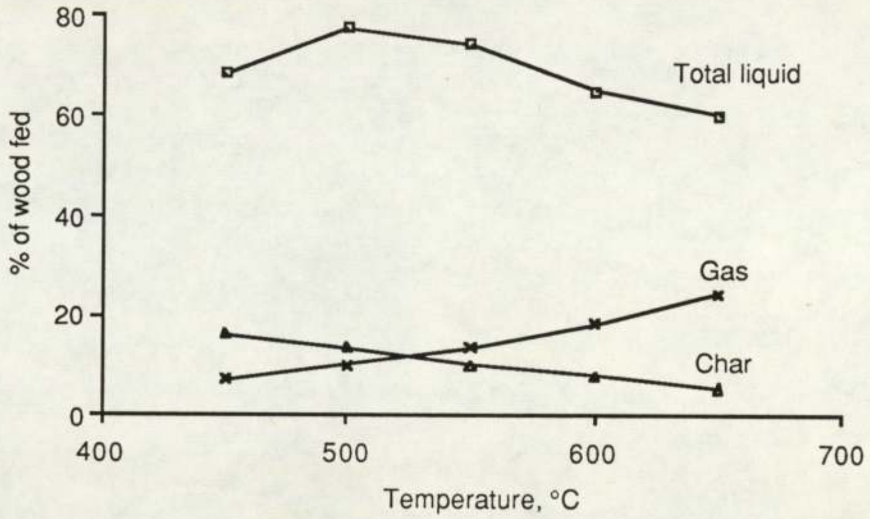


Figure 3.1 Product Yields as a Function of Temperature [81].

Because reactor temperature affects the chemical composition of the liquid product, the H/C ratio and the oxygen content are also affected. The oxygen content of any fuel is one of the criteria used to classify whether it is a high-grade or a low-grade fuel. The lower the oxygen content, the higher the energy content of the fuel. As the primary pyrolysis liquids have a high oxygen content, similar to that of wood, this liquid can be termed a low-grade fuel (see Table 3.1). Consequently, in order to use this liquid as a gasoline-substitute, some upgrading is necessary (see Section 5.4.3.2).

Table 3.1
Chemical Composition of Wood and Derived Pyrolysis Liquids [82].

	Wood	Liquid 1*	Liquid 2**	Liquid 3***	No. 6 oil
C	50.0	54.7	52.2	53.8	87.2
H	6.0	6.4	6.2	6.2	10.7
O	44.0	38.9	41.4	40.0	2.1
H/C ratio	1.44	1.40	1.43	1.38	1.47
O/C ratio	0.66	0.53	0.60	0.56	0.02

* obtained from a fluidised bed reactor at 500°C, University of Waterloo
** obtained from an entrained flow reactor at 500°C, GTRI
*** obtained from an externally heated vortex tube reactor at 625°C, SERI

At temperatures greater than 650°C, the H/C and O/C ratios decrease, as shown in Figure 3.2. These changes represent the conversion of the primary oxygenated vapours to more thermally stable less oxygenated compounds such as benzene and naphthalene, by secondary and tertiary reactions such as condensation and polymerisation which occur at these higher temperatures (see Section 2.4.4.3) [70,82].

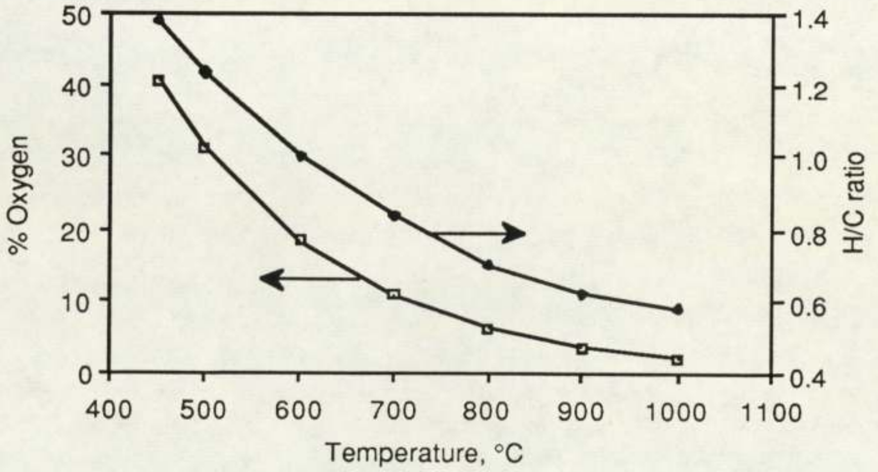
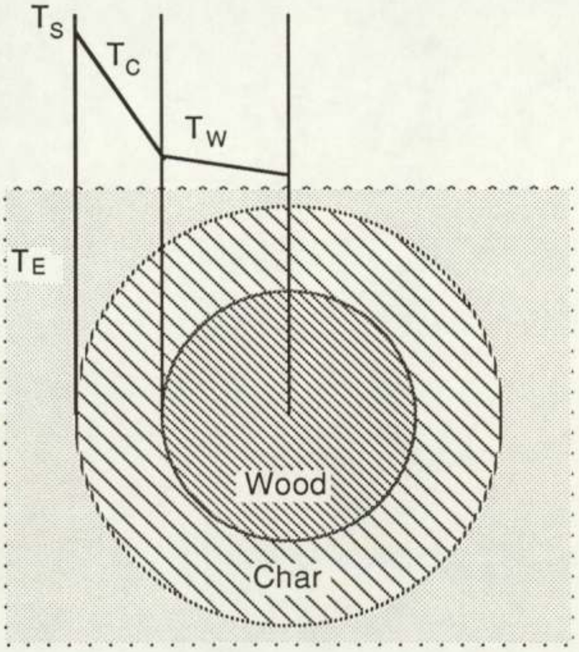


Figure 3.2 The Effect of Temperature on the Oxygen Content and the H/C Ratio of Bio-oil [70]

As temperature influences yield, chemical composition and both the physical and chemical characteristics of the liquid product, this parameter must be carefully controlled.

3.2.2.1 Particle Temperature

According to the reactor conditions employed, the temperature of the feedstock will differ from that of the reactor because of the difference in the rate of heat transfer to the particle's outer surface (convection, conduction and/or radiation) and inner surface (conduction) and the rates of heat loss due to the outflow of the volatiles produced and the heat of reaction. Figure 3.3 illustrates a temperature profile of a particle within a reactor. Therefore, depending on the particle size, temperature and the rate of heating, the rate of reaction may be controlled by either heat transfer or the chemical kinetics of the pyrolytic reactions. This will be discussed in more depth in Chapter 4.



where:

T_E environmental temperature
T_S surface temperature
T_C char temperature
T_W wood temperature

Figure 3.3 Pyrolysis Scheme of a Single Particle Showing the Different Temperature Gradients.

3.2.3 Residence time

As with heating rate, the residence times of both the reactant and the vapour and gases are also influenced by reactor configuration. Residence times normally quoted in the literature apply to the vapour residence time and this should be carefully controlled for liquid production. Long residence times allow the primary pyrolysis vapours to further react to form gaseous products (see Section 2.4.4.3) [76-80]. Therefore, these vapours must be quickly removed from the reactor so that the residence time is shortened and also rapidly quenched so that the liquid intermediate products can be condensed and collected. For fast or flash pyrolysis, short vapour residence times of 1 second or less are normally used [37,72,74,75-80]. Both Table 3.2 and Figure 3.4 shows the effect of residence time on product yields.

The effect of the residence time of the vapour will also affect the oxygen content and the H/C ratio of the liquid product since the short residence time of the vapours within the reactor will minimise the possibility of secondary reactions occurring. Therefore, vapour residence time and temperature interactively affect product yields and composition.

Table 3.2
The Effect of Residence Time on Pyrolysis Products Obtained from a Fluidised Bed Reactor [81].

Operating conditions *:				
Residence time of vapour, (s)	0.38	0.44	0.54	0.68
Average Temperature, (°C)	545	547	548	551
Product yield as reported (% of wood feed):				
Char	11.3	9.9	9.1	9.1
Tar	57.5	57.5	51.7	50.0
Gas	9.6	13.6	11.9	16.9

* Poplar aspen sawdust 105-250 mm, 5% moisture.

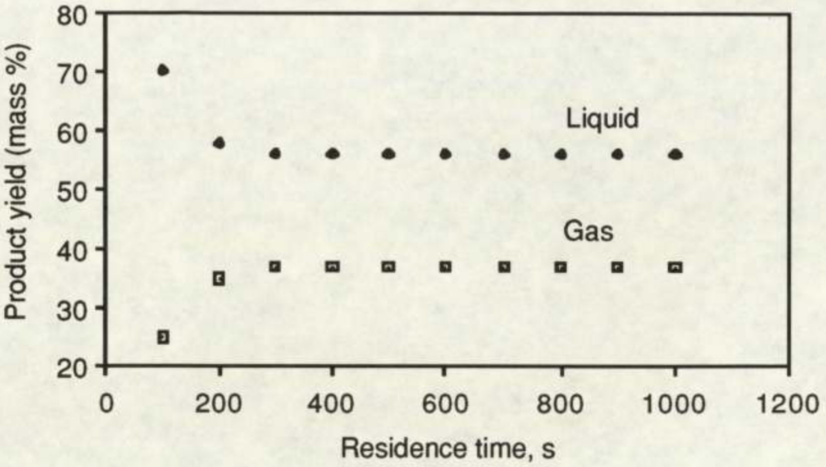


Figure 3.4 Effect of Residence Time on Product Yields at 700°C [83].

3.2.4 Pressure

Pressure also affects biomass pyrolysis especially secondary pyrolysis reactions according to whether pyrolysis is carried out under vacuum or, in a high pressure environment. Contact pressure of the feed with the heated reactor surface/wall is another type of pressure effect.

3.2.4.1 Vacuum or Low Pressure Pyrolysis

High liquid yields should be obtained from low pressure or vacuum pyrolysis because the extent of secondary reactions, such as cracking and repolymerisation, are minimised due to the rapid removal and quenching of the pyrolysis vapours from the reactor zone (see Section 2.4.4). Roy et al. have demonstrated that vacuum pyrolysis can result in relatively high yields of liquid. They obtained liquid yields of 50% by weight of wood with a char yield of 25%, using a multiple hearth furnace operated at a reactor temperature of 450°C and pressures less than 80 mmHg absolute (10 kPa) [84]. A description of their pilot plant is given in Section 5.5.4. Shafizadeh [9] also obtained high liquid yields under vacuum as shown in Table 3.3.

Table 3.3
Analysis of The Pyrolysis Products of Cellulose at 300°C Under Nitrogen [9].

	760 mm Hg (%)	1.5 mm Hg (%)	1.5 mm Hg, 5% $SbCl_3$ (%)
Product yield as reported:			
Char	34.2	17.8	25.8
Tar	19.1	55.8	32.5

3.2.4.2 High Pressure

Mok and Antal [85-87] carried out studies to investigate the effects of pressure on char yields and gas analysis by pyrolysing biomass in a tubular, laminar flow micro-reactor system. The reactor system was pressurized with either steam or argon; steam and argon also served as carrier gases. A gas residence time of about 1-2 seconds was used. Tar collection was not possible with this system but from previous studies, they found that tar formation was minimal under the experimental conditions they employed. The feedstocks used were either 10 mg of Avicel cellulose or Whatman filter paper.

Although the data were very scattered, they found that increasing pressure enhances char formation and reduces the yield of volatiles. Figure 3.5 shows the effect of pressure on char yields. In addition, they observed that an increase in pressure favours CO_2, and H_2 formation while the yields of CO, CH_4, C_2H_4, C_2H_6 and C_3H_6 were reduced. They also carried out an experiment to study the effect of residence time on product yield. The experimental conditions used were a pressure of 5 atm and residence times of 1 and 10 seconds. They observed that a long residence time encouraged the formation of C_2H_6 at the expense of CO and C_3's. It also favoured the formation of char and CO_2.

Although the work of Steinberg et al. [77,88-89] mainly involves the investigation of the flash pyrolysis of wood in an entrained flow reactor with reactive and non-reactive gases, different gas pressures were used which resulted in different pyrolysis products.

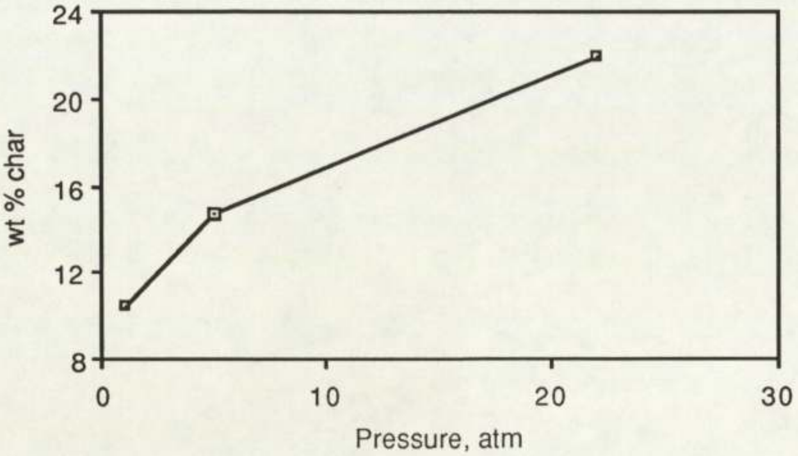


Figure 3.5 The Effect of Pressure on Char Yield [85].

Steinberg et al. [77,88-89] employed a temperature range of 800-1000°C and therefore high yields of gaseous products were obtained (see Section 3.2.2). Using H_2 pressures of 50 psi (0.345 MPa), 200 psi (1.38 MPa) and 500 psi (3.45 MPa), they observed that the yields of hydrocarbons (CH_4, C_2H_6 and C_2H_4) and CO were significantly affected by the pressure employed and also by the residence time. In this study the effect of temperature, pressure and residence time on gas yields were determined simultaneously. Using pressures of 500 psi, they found that the main product accounting for the highest total carbon conversion was CH_4 whereas at 50 and 200 psi, it was CO, when a vapour residence time of 1 second was used. This occurrence they suggested could be explained by the following equation:

$$CO + 3H_2 \longrightarrow CH_4 + H_2O \qquad +201.9\ \text{KJ/mole}$$

Applying Le Chatelier's principle, it could be seen that higher pressure favours the methanation reaction. Furthermore, they observed that the pressure at which methanation occurred, decreased with increasing temperature. Using reaction temperatures of 800, 900 and 1000°C, they observed methanation pressures of 350, 300 and 250 psi, respectively. In addition, they found that at all the pressures studied, the yields of CO_2, C_2H_4 and BTX decreased with increasing temperature due to secondary reactions.

Increasing the methane pressure from 20 psi (0.138 MPa) to 200 psi (1.38 MPa) at 1000°C, Steinberg et al. found that the major product was CO reaching a maximum of about 55% at 100 psi [89]. In addition, the ethylene yield increased with decreasing pressure reaching a maximum of 22% at 50 psi. The BTX yield remained almost constant at about 10 to 12%. At all helium pressures studied, CO was also the major product.

High pressures, promotes secondary and tertiary reactions and depending on the temperatures and residence times used, char formation and or gas production is enhanced. Therefore, for liquid production, low pressure pyrolysis with moderate temperatures (see Section 3.2.2) and short vapour residence times (see Section 3.2.3) should be used.

3.2.4.3 Contact Pressure

It has been found that contact pressure pyrolysis, more commonly known as ablative pyrolysis, can result in the almost exclusive production of liquid and gases. The higher the contact pressure, the quicker the feed will be heated to form vapours which, if rapidly removed and quenched, will result in high liquid yields [69]. Further details about ablative pyrolysis are described in Section 5.4.2 and Section 6.2.

3.2.5 Moisture Content

Fresh wood contains between 66-150% (dry basis) or 40-60% water (wet basis) which is present in wood lumens and/or bound to the cell walls (see Figure 2.1) [7,90,91]. However, this parameter can be controlled by drying the feed prior to pyrolysis. In a commercial plant, the drying fuel would be obtained from the hot pyrolytic gases produced during the process, waste heat streams from the process or by burning some of the feedstock or charcoal. In most laboratory experimentation, drying is carefully controlled and monitored; the feed is normally dried to a uniform moisture content of 7-10% on a wet basis [92].

The main aim of the study carried out by Kelbon [93,94] was to investigate the synergistic influence of moisture content, particle size and heat flux on particle temperature. The levels of moisture content investigated were 10, 60 and 110%, dry basis (9.1, 37.5 and 52.4%, wet basis) with applied heating rate intensities of 2, 4 and 6 cal/cm^{2}s and wood pellets of thicknesses 0.5, 1.0 and 1.5 cm. She found that increasing moisture content affected the thermal history of the pellet by delaying the onset of pyrolysis by as much as 150 s thus lowering the initial rate of temperature rise within the pellet and limiting the fraction of the pellet which reacted during a fixed time period by as much as 20% because heating of the particle is hindered by the heat requirement of moisture evaporation. Consequently, pyrolysis takes place at a lower temperature. Milne and Evans [95] also noticed a similar delay in pyrolysis when investigating the effect of moisture on biomass pyrolysis.

Kelbon also found that liquid yields were greater for intermediate moisture content (60%), particle size (1 cm) and heating rates (4 cal/cm^{2}s); consequently, she concluded that the optimum tar production for moist feed is dependent on heating rate and particle size used within the experimental system.

Maniatis and Buekens [80] studied the effect of moisture by pyrolysing a dry particle and particle with 10 wt% (dry basis) moisture. The pyrolysis of the moist particle resulted in about 10% more water in the product gas. They concluded that the water produced by the dry sample was due to the pyrolysis process.

Three sorts of water may be present in the pyrolysis derived liquids. These are the moisture content of the pyrolysing particle, steam which is sometimes used as a carrier gas and water produced during the pyrolysis process. The presence of water has several effects on the liquid products and these are described in Section 5.4.3. For example, it influences both the chemical and physical stability of the liquid product. This may result in phase separation of the tarry and aqueous fractions during liquid recovery.

This aqueous phase often contains organic matter such as acetic acid, phenols and cresols (see Section 2.4.4) and therefore represents a major problem of disposal and utilisation. Kelbon [93,94] noticed some increase in the production of methanol and acetic acid during her experiments. The liquid product obtained when a feedstock with a moisture content of 7-10% has been pyrolysed, is most often a single-phase, homogeneous fluid which pours readily and is quite stable at room temperature but decomposes when heated above 100°C (see Section 5.5.) [70,74,95].

Therefore, an optimum moisture content, that will enhance liquid production should be used so that proper temperature control of the reactor can be maintained and also to avoid the associated problem of disposing of the aqueous phase. This optimum will be dependent on the particle size and the heating rate of the system.

3.2.6 Gaseous Environment

The gaseous environment is any gas used as a carrier gas in the pyrolysis system. This gas may be N_2, steam, H_2, helium, product gases (mainly CO, H_2O, CO_2 and CH_4) or CH_4. This parameter does not affect primary pyrolysis as much as secondary pyrolysis [77,81,88,89,95]. Thus while, primary pyrolysis can be considered to be a heat driven reaction, secondary pyrolysis is the reaction of the primary pyrolysis vapours. These secondary reactions can include the vapours reacting with the surrounding gaseous environment.

Steinberg et al., reported studies of the effect of flash pyrolysis of biomass in hydrogen, nitrogen, argon, helium and methane atmospheres (see Section 3.2.2) [77,88,89]. Pyrolysis in hydrogen resulted in CH_4 being the major product whereas with methane, nitrogen, helium and argon, the major gaseous product was CO. However, with methane, the yields of C_2H_4 and BTX were found to be greater than those where an inert gas was used. For example, it was found that pine wood pyrolysed at 1000°C and 50 psi yielded eight times as much C_2H_4 with methane than with helium. Yields of C_2H_4 and C_6H_6 greater than 50% based on wood carbon conversion were obtained at methane-to-wood ratios of six or more [89].

Two mechanisms were proposed by Steinberg et al. to explain the increase in yields of benzene and ethylene [89]. The first proposal was that the wood surface acted as a catalyst to thermally decompose methane. The second proposal, which Steinberg et al. thought was more likely to occur, suggested that free radicals were formed during the pyrolysis of wood which subsequently reacted with methane forming methyl radicals. These radicals then combined to form ethane which in turn, cracked to form ethylene as outlined in the equations below :

$$\underset{\text{Wood}}{(CH_{1.4}O_{0.7})} \xrightarrow[\Delta H]{} \underset{\text{Free radicals}}{(CH^\bullet, CH_2^\bullet, CH_3^\bullet, \text{etc.})} + H_2O + CO$$

wood free radicals then react with the methane gas :

$$\begin{aligned} CH_2^\bullet + CH_4 &= CH_3^\bullet + CH_3^\bullet \\ CH_3^\bullet + CH_3^\bullet &= C_2H_6 \\ C_2H_6 &= C_2H_4 + H_2 \end{aligned}$$

In order to establish the exact mechanism, an isotopic tracer experiment based on natural C^{13} content found in C_2H_4 was carried out to determine how much of the carbon present was from methane and the feedstock respectively. However, because of the statistical averaging in the $\delta^{13}C$ ratio analysis, the possibility of a catalytic reaction could not be eliminated.

Evans and Milne [60,95] also carried out experiments in the presence of methane as well as in helium. They found that primary pyrolysis is not significantly influenced by the reactor gaseous environment. However, for secondary and tertiary reactions, they observed that the gaseous environment does affect the products formed. Like Steinberg et al., they observed an increase in olefins when methane was used as the gaseous environment. Furthermore, they also postulated that olefins enhancement in methane was probably due to the chemical interactions of the biomass-derived vapours with methane.

Scott and Piskorz [81] also carried out flash pyrolysis in methane in order to determine its influence on product yields; methane was used to fluidised the bed and to convey the feed to the reactor. There was no significant difference in the products obtained using methane as opposed to the nitrogen. Nitrogen was the normal carrier gas used in their bench scale fluidised bed reactor. These experimental results support Evans and Milne's [60,95] view that primary pyrolysis is not significantly influenced by reactor environment. For example, total liquid yield (including water) at 500°C was about 77 wt% wood fed for methane while in a nitrogen environment it was 75 wt% although they suggested that the light organic yields such as acetic acid, aldehydes and methanol were about 25% higher in the methane atmosphere. Char yields were lesser in methane than in nitrogen but the maximum difference in yield was 3 wt % (at 450°C). Below 550°C, gas yields were higher in methane than in nitrogen with a maximum difference in yield of 5 wt %. There was little difference between gas yields above 550°C.

Steam is sometimes used as a carrier gas because it can be readily separated from the volatiles by condensation. It is relatively cheap and readily available. At temperatures greater than 650°C, there is the possibility of steam reforming reactions taking place resulting in the formation of CO_2 and H_2 or reacting with the char to form H_2 and CO [29,30].

Therefore, at temperatures below 600°C, the gaseous environment does not appear to have much effect on liquid yields. The most common gaseous environment used in pyrolysis systems are nitrogen, steam, helium and combustion products of wood or pyrolysis products. In general, cost, availability and product specification (liquid versus gas) will determine which environment, whether it being reactive or not, will be used in a commercial venture.

3.2.7 Influence of Ash, Catalysts and Acid Washing

3.2.7.1 Influence of Ash and Catalysts

The study of the effects of adding inorganic salts and ash has been extensively investigated, primarily in fire research because they have been known to catalytically enhance char formation at the expense of flammable volatiles formation [29,34,39,96-100]. This occurrence is due salt impregnation hindering the heat transfer rate.

Shafizadeh et al. have carried out numerous studies on the effect of alkaline and acidic compounds on the pyrolysis of cellulosic material [9,34]. They observed that acidic compounds, such as $FeCl_3$ and $CoCl_2$, strongly influenced dehydration and condensation reactions, enhanced the formation of levoglucosenone and a variety of furan derivatives, and char. Alkaline catalysts, such as Na_2CO_3 and NaOH, favour fission and disproportionate reactions, enhancing the yields of glyoxal, acetaldehyde, and lower molecular weight carbonyl compounds as well as char (see Section 2.4.1) [39]. Therefore for the production of liquids, inorganic materials should be kept as low as possible since on a whole they promote char forming reactions. Variations in product yield with inorganic addition are shown in Table 3.4.

Table 3.4
Influence of Catalyst on Wood Pyrolysis [96,100]

	Wood*	$FeCl_3$*	NaOH*	$CoCl_2$#	$CoCl_2$#
Overall products yields as reported *					
Char	27.40	34.70	36.60	28.10	41.30
Liquid (wet)	61.30	54.70	44.30	54.60	46.10
Gas	11.20	9.80	19.70	27.80	24.86
Major compounds in liquid					
Acetic acid	6.33	5.40	5.50	7.40	7.20
2-Furaldehyde	0.63	2.28	0.26	3.30	7.50
Water	13.40	24.90	22.10	23.60	23.20
Minor compounds in liquid					
Methanol	0.85	0.66	1.24	0.50	1.40
Propionic acid	0.14	0.09	0.50	0.13	0.42
1-Hydroxy-2-butanone	0.97	0.07	0.73	--	--

* Yields on dry wood basis; temperature, 350°C; particle size, 0.05 to 125 mm [96].

\# Yields on dry almond shells basis; temperature, 500°C; particle size, 0.297-0.5 mm [100].

3.2.7.2 Acid Washing

Acid washing also influences wood pyrolysis. Wood pyrolysis, whether slow or fast, normally gives low yields of anhydrosugars, particularly levoglucosan. Scott and Piskorz et al. [39,42,101] found that if wood is pretreated with acid, high yields of anhydrosugars are obtained. For example, when wood was treated with 5% sulphuric acid at 100°C and then flash pyrolysed (500°C, 0.46 s gas residence time, N_2, -590 μm particle size), they obtained a product that corresponded to about 80% conversion of cellulose to glucose [39,42,101]; untreated wood pyrolysis resulted in 20% conversion of cellulose to glucose. Other products formed were a pentose solution and aromatic fraction which can be used to provide food aromas and chemicals. Therefore if the liquid product is to be used as a chemical feedstock or for chemicals, acid washing prior to pyrolysis is one route to explore.

3.3 INTRINSIC PROPERTIES OF THE FEEDSTOCK

The intrinsic properties of the feedstock includes the wood type, the physical structure of wood, and particle size and shape.

3.3.1 Type of wood

The yields of pyrolysis products obtained from softwoods and hardwoods are shown in Table 3.7. As explained in Section 2.4.3, char is usually obtained from the lignin fraction of the biomass. As more lignin is present in softwoods, one would expect more char formation for softwoods than for hardwoods (see Table 3.5).However, as can be seen from Table 3.5, yields are similar.

Another difference would be in the chemical compounds found in the liquid product because of the different lignin and hemicellulose structures present in both hardwoods and softwoods (see Section 2.3.3 and 2.3.4).

Elliott [60] carried out studies to determine the characteristics of liquid products obtained from pyrolysis and gasification condensates. He found that although the liquid products obtained from flash pyrolysis of both hardwoods and softwoods exhibited similarity in chemical composition, the product spectra differed slightly.

Table 3.5
Yields of Pyrolysis Products from Different Wood Species * [74].

	Hardwood White Spruce	Softwood Brockville Poplar
Reactor temperature, °C	500	508
Moisture content, wt%	7.0	5.9
Particle top size, µm	1000	590
Apparent vapour residence time, s	0.65	0.47
Yields as reported, wt% of moisture free wood		
Organic liquids	66.5	67.9
Water	11.6	9.8
Char	12.2	13.7
Gas	7.8	9.8
Major components in liquid product, wt% of moisture free wood		
Acetic acid	3.86	5.81
Formic acid	7.15	6.35
Hydroxyacetaldehyde	7.67	7.55
Glyoxal	2.47	1.75
Elemental analysis of liquid, wt% of moisture free wood		
H/C molar ratio	1.51	1.40
O/C molar ratio	0.54	0.53

* Results are obtained from a fluid bed pyrolyser

Using gas chromatography/mass spectrometry (GC/MS), Elliott observed that the single major difference between the two liquids was that the liquid product from softwood contained almost no dimethyoxyphenolics whereas the hardwood liquid contained a considerably amount; no actual figures were quoted. This variation, he suggested, was due to the difference between the lignin structures present in hardwoods and softwoods as outlined in Section 2.3.4.

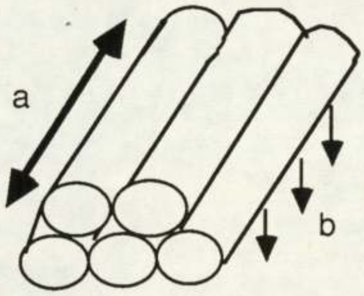
Evans and Milne also observed that more acetic acid was formed during hardwood pyrolysis than in softwood pyrolysis [37]. This increase, they suggested, was due to the xylan present in hardwoods which has more acetyl groups in its structure (see Section 2.2.2).

Therefore the effect of wood type seems to be the difference in the chemical compounds found in the liquid. The differences in hemicellulose and lignin structures present in hardwoods and softwoods account for this observation.

3.3.2 Physical Structure of Wood

All the other variables up to this point can be controlled. This parameter however, cannot be controlled but it influences the products and the process.

As explained in Section 2.3.1, wood has an open porous grain-like structure that is anisotropic in nature. It has been found that the longitudinal permeability may be as high as 10^4 times that across the grain for some species [15,16] and hence escape of the volatile products is expected to occur primarily parallel to the grain as illustrated in Figure 3.6.



a - in direction of grain
b - in direction across grain

Figure 3.6 Direction of Flow of Volatile Matter in Wood.

It also affects properties such as specific heat and thermal conductivity [46,47].

Low permeabilities affect the product distribution by increasing the residence time of the primary products within the particle (which is also dependent on particle size), thereby increasing the probability that they will participate in secondary reactions such as polymerisation and cracking. [13]. This results in the formation of more char and permanent gases.

Lee et al. [102] using a 250 watt CO_2-laser radiation source, studied wood pyrolysis at fire-level heat fluxes (~ 4.2 to 12.6 J/cm^2 s). They measured a maximum pressure gradient of 220 kPa/cm (2.2 atm/cm) with a maximum internal gas pressure of 30 kPa gauge (0.3 atm) across the grain while the pressure gradient measured parallel to the grain was 100 Pa/cm (0.001 atm/cm) with a maximum internal gas pressure of 300 Pa gauge (0.003 atm). This large difference in internal gas pressure, they suggested, was reflective of the low permeability across the grain. They also observed that more cracks were formed during parallel heating. These cracks could be a consequence of the release of volatiles from within the particle to the surface, due to the internal pressure build-up.

Chan et al. [103] also investigated the effects of parallel and perpendicular heating relative to wood grain direction. At lower heat fluxes (2 cal/cm^2s) the effect of the grain direction on volatiles release rate was small.

For heat fluxes of 6 cal/cm^2s, perpendicular heating resulted in an increased resistance to volatiles efflux. Figure 3.7 shows this effect qualitatively.

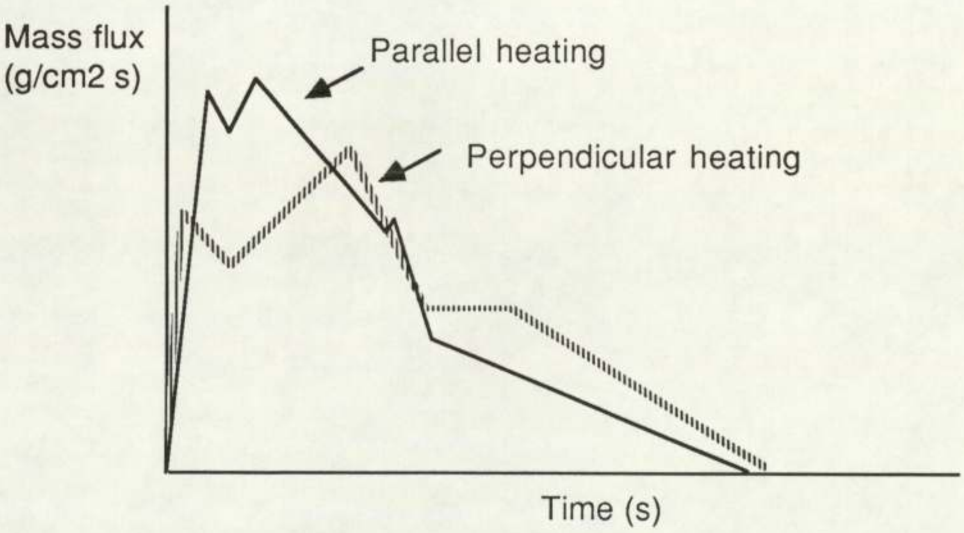


Figure 3.7 **Variation of Mass Flux with Time as a Function of Parallel and Perpendicular Heating** [103].

Initially, volatiles release rate rose faster and the maximum of mass flux was lower, with respect to parallel heating, because of the lower interior temperature resulting from heating perpendicular to the grain. There was also about 20% shrinkage of the char layer. This shrinkage was due to the char becoming more friable, resulting in a more rapid transfer of heat to the interior and therefore the latter volatile surge.

Heating parallel to the grain offered less resistance to volatiles outflow and therefore the volatiles peak appeared earlier relative to the profile for perpendicular heating (see Figure 3.6).

Simple particle 1-dimension reactors were used in this investigation of heating the particle in a particular direction to the grain [30,31,49,50]. Here, it is possible to heat one face of the particle and insulate the other sides. However, in practice, all the sides of the particle are available for heating. Therefore it is not possible to control in which direction heating will take place.

To summarise, because of the anisotropic nature of wood, the physical structure will affect product yields and distribution. Heating in the direction of the grain allows a rapid efflux of the primary products which lessens the possibility of secondary cracking and polymerisation occurring. In contrast, release of the volatiles is delayed when heat is applied in the direction perpendicular to the grain and therefore secondary reactions may occur. In practice, however, both modes of heating will take place.

3.3.3 Particle Size and Shape

3.3.3.1 Particle size

Particle size will affect the heating rate of the feed. It may be inferred that as the particle size increases, the rate of heat transferred within a particle will decrease thus resulting in a lower heating rate which, as discussed in Section 3.2.1, enhances char formation and minimises liquid production. Figure 3.8 shows some yields of liquid product. This postulate has been confirmed by the following works described below.

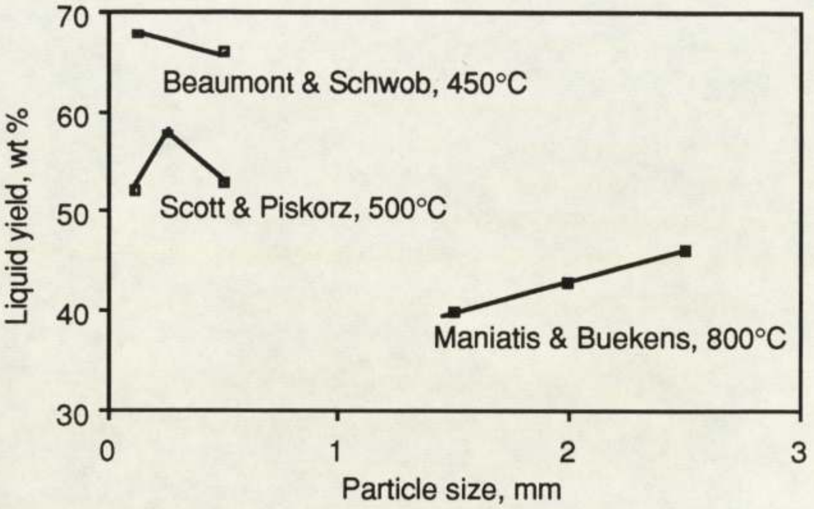


Figure 3.8 **The Effect of Particle Size on Liquid Yields** [80,81,96].

Beaumont and Schwob [96], investigated the effect of particle size on product yields by using beech wood between 0.05 mm and 0.5 mm, a temperature range of 300-500°C and nitrogen as the gaseous environment. Under flash pyrolysis conditions, they found that the coarser/thicker particles yielded more char and gas but less tar. The differences in yield were small (approximately 2 wt% of dry wood). No effect was observed for slow pyrolysis.

Scott and Piskorz [81] flash pyrolysed different size fractions of Aspen poplar sawdust but found the results ambiguous. Their results indicated that char yields increased as particle size decreased, and that gas yields were higher for larger particles. This discrepancy in the char yields for the smallest particles (0.044-0.105 mm), they suggested, was due to the particles being either overheated or blown out of the reactor too quickly.

Gas yields were higher for the largest particles (0.25-0.50 mm) because the char particles remained in the sand bed for a longer time thus decomposing the lignin-fraction to a greater extent, to mainly gases (see Section 2.4.3). The highest liquid yields were obtained for the middle sized fraction (0.105-0.25 mm). Thus they concluded that, for a given reactor, and set of fluidising parameters, there would be an optimum particle size that would produce the highest liquid yield.

Maniatis and Buekens [80] also did work in this area. They found, using a final temperature of 800°C, a holding time of 20 s, and particle diameters between 1.5 to 2.5 mm in a pyroprobe that, there was a slight increase in char yield from 18 to 20 wt%, an increase in the tar yield from 40 to 46 wt% and a decrease in the gas yield from 39 to 32 wt %. They suggested that a temperature gradient was created between the inner core and the surface, due to the increase in the time required to heat up the inner core of the sample to the final temperature as particle size increased. Pyrolysis at the inner core thus occurred at a lower temperature and resulted in increased tar formation (see Section 3.2.2). The slight increase in the char yield was attributed to enhanced thermal cracking of tar on the hot surface of the particle resulting in carbon deposition. It is not expected however, that the liquid yields would be high because the experimental conditions employed here are not suitable for liquid production.

Therefore an optimum particle size must be found since optimum liquid production conditions changes with process variables such as heating rate, temperature and moisture content. If the particle is too small, it may not be retained in the reactor zone long enough to thermally degrade. If it is too large, the heat penetration time increases so, on average, the particle temperature is lower. Furthermore, secondary reactions can occur within the particle that may lead to excessive formation of char and gases. Most of the work carried out for liquid production uses a particle size of less than 5 mm (see Section 5.5).

3.3.3.2 Particle shape

Particle shape also has some effect on pyrolysis because it influences how fast a particle is heated up. Saastamoinen [104], using particles in the form of a plate, cylinder and sphere with the same volume/area ratio, found that mass loss was faster for plates and slowest for the sphere. This is expected because the rate of heat transfer within the plate will be faster than for the sphere.

Maniatis and Buekens [80] also studied the effect of geometry; cylindrical (with a diameter 1.4 mm), rectangular (1.4 x 1.4 mm) and flat (0.5 x 1.4 mm). They found that at temperatures between 600-900°C, that the highest tar yields were obtained with the cylindrical geometry followed by the rectangular and the flat geometries. Presumably, this occurred because the rate of heat transferred to the cylindrical particle was the slowest and therefore pyrolysis occurred at a lower temperature in side the particle which enhanced tar formation.

Roy et al [105] also investigated the effect of particle shape on pyrolysis (see Table 3.6). The highest yield of oils were obtained from flour because here, the resistance to heat and mass transfer is minimal.

Table 3.6
The Effect of Particle Shape on Vacuum Pyrolysis of Aspen Poplar at 450°C [105].

Product *	1 cm chip	1 cm pin	Flour
Oils	50.7	56.7	60.8
Water	16.3	13.9	12.8
Char	20.4	18.1	15.8
Gas	12.6	11.1	10.6

* (%wt, moisture ash free wood)

It must be pointed out that Roy et al. [105] obtained the highest oil yields for oil with flour while for Maniatis and Buekens [80] it was with the cylindrical particle. This difference can be explained by the varying experimental conditions used. Roy et al. considered moderate temperature pyrolysis under vacuum as opposed to higher temperature pyrolysis considered by Maniatis and Buekens.

The geometry and the physical size of the reactor limit what particle shape can be used within the system. For example, 'pins' (ie typical length, depth, breadth ratio 5:1:1 or greater) are found to be unsuitable because they are prone to bridging and do not flow easily in a free flowing system [106]. Also if too many fines are present within the feed, this results in high pressure drops within the reactor.

Therefore particle shape has some effect on product distribution and yield.

3.4 CONCLUSIONS

This chapter described the effects of various process parameters on liquid production. It appears that the main factors affecting liquid yields and composition are heating rate, reactor temperature and vapour residence times while the others have secondary effects because their influences are dependent on the temperature, heating rate and the vapour residence time. Chapter four will discuss the models that have been proposed to describe some of the effects that these parameters have on pyrolysis.

CHAPTER FOUR

MODELLING OF THE PYROLYSIS PROCESS

4.1 INTRODUCTION

Mathematical modelling may be defined as the art of obtaining a solution, given specified input data, that is representative of the response of the process to a corresponding set of inputs [107]. Such models may be used to develop a conceptual design of a process, to modify/retrofit a process or to specify instrumentation and control schemes for a process unit or for the whole process. The development of a mathematical model can be mechanistic (theoretical) using physico-chemical principles, empirical based on experimental data, statistical, judgmental as in an expert system or any combinations.

The goals of this chapter are:

(i) to outline the objectives and the features of a pyrolysis model;
(ii) to critically evaluate the different types of models developed to represent the pyrolysis process;
(iii) to produce a "best" model that incorporates sufficient features to adequately represent the pyrolysis process; is sufficiently simple to be able to use and solve; and gives realistic and useful answers.

4.2 OBJECTIVES OF A PYROLYSIS MODEL

Mathematical modelling is utilised in pyrolysis to account for the effects of the interaction of the parameters on the end products. Therefore, the objectives of a mathematical pyrolysis model should include:-

(i) the development a diagnostic tool in order to evaluate the importance of the various system parameters such as particle size, heat of pyrolysis (reaction) and thermal properties of the feedstock and products;
(ii) the prediction of the effects of process variables (particle size) on the process and product yields and characteristics in order to aid

optimisation of the pyrolysis process;

(iii) the establishment of better reactor design techniques in order to specify reactor type and size.

4.3 MODELLING TYPES AND APPROACHES

4.3.1 Kinetic Models

Most modelling studies reported have investigated and modelled the pyrolytic behaviour of a single biomass particle under conditions usually employed in pyrolysis, gasification and combustion. The results obtained may then be use to provide suitable correlations of feedstock characteristics and process conditions to pyrolysis products, thus determining reactor simulations more accurately.

Different modelling techniques are used for large and small biomass particles. Kinetic studies are usually carried out on small particles (< 1 mm) because physical transport effects will be minimal and therefore, can be neglected. Arrhenius type rate equations are normally derived from these studies which, it is hoped, represent the intrinsic reaction rates of pyrolysis.

4.3.2 Analytical Models

A different approach is applied for large particles (> 1 mm) as the effects of both heat and mass transfer cannot be ignored. These models involve solving dynamic heat and mass balances as well as kinetics, and are referred to as Analytical Models.

4.3.3 Empirical Models

The simplest model that may be proposed is based on the overall mass balance approach, that is:

$$\text{wood} \longrightarrow x\ \text{char} + y\ \text{liquids} + z\ \text{gases} \qquad (4.1)$$

No rate processes, such as kinetics, and heat and mass transfer effects, are included in this approach and therefore it is used to predict yields and provide simplistic stoichiometry.

Functional or empirical relationships between yield of a pyrolysis product and process variables such as temperature, particle size, pressure, and moisture content may be derived but this involves collecting a considerable amount of data. One drawback of this technique is that the data available will be constrained by the reliability of reported data, the process technology employed and the required product. For example, at the University of Waterloo, Canada, flash pyrolysis is carried out in a fluid bed to obtain a liquid product. Therefore, experimental data available is restricted to conditions that enhance liquid production (temperatures around 500°C, volatiles residence times of about 0.5s and particle size of 1 mm or less) and also maintain proper fluidisation of the bed [81].). No work has been found that uses this method.

Both the kinetic and analytical approaches are discussed in full below.

A fourth type of model describes the pathways that pyrolysing biomass can follow as it degrades. This is described in Section 2.4.

4.4 KINETIC MODELLING

As can be deduced from Chapters 2 and 3, there are many homogeneous and heterogeneous reactions occurring either simultaneously and/or consecutively during pyrolysis which are dependent on the reactor conditions. Furthermore, these reactions result in hundreds of products and intermediates being formed. Therefore, the true kinetics of the reactions are very difficult to determine.

Three major steps have been taken to derived kinetics for pyrolysis of small particles. The first considers biomass going to char and volatiles and an overall rate equation in terms of generation of volatiles or weight loss is proposed. The second method tries to grasp the complexity of pyrolysis by proposing stepwise degradation of the biomass to form primary products. The final technique used considers both the primary and secondary pyrolysis reactions of biomass.

4.4.1 Overall Rate Expressions

The kinetics of wood and its components have been and still are obtained by measuring the rate of weight loss of the sample as a function of time and temperature. The most common technique for this investigation is thermogravimetric analysis (TGA). TGA involves continuous weighing and recording of data obtained from a sample, heated at either constant temperature or a fixed heating rate, enclosed in a furnace [9,24,25,28,29,30,36,65,108-113]. These experiments are normally carried out under vacuum or in a nitrogen atmosphere at both low temperatures and heating rates. Some workers have used steam as the gaseous environment in their experimental system [112-114]. As there is no provision for the collection of volatile pyrolysis products, the TGA data are normally used to derive overall kinetic expressions.

The global thermal degradation process can be described by a simplistic reaction scheme as shown in Equation 4.2.

$$\text{Biomass} \longrightarrow \text{Char} + \text{Volatiles} \tag{4.2}$$

and the rate of the above reaction is then described in the form of a first order Arrhenius type rate law as shown in equation 4.3.

$$dW / dt = - A \exp (- E / RT) (W - W_f) \tag{4.3}$$

where
W residual weight fraction
W_f final weight
A pre-exponential (frequency) factor
E activation energy
R Universal gas constant

If the sample is heated at a constant rate M, then

$$dW / dt = - A / M \exp (- E / RT) (W - W_f) \tag{4.4}$$

where $M = dT / dt$

Sometimes the weight term is replaced by a density term. It is assumed here that no shrinkage occurs during char formation.

The Arrhenius kinetic parameters, the activation energy (E) and the pre-exponential (frequency) factor (A) are derived by :

(i) obtaining best fit curves through the experimental data;

(ii) solving the Arrhenius rate law, using a least squares method.

Selected values of activation energy and frequency/pre-exponential factor are listed in Table 4.1.

Table 4.1
Experimental Kinetic Parameters for Overall Reaction Rate Expressions

Data source	Sample	Temperature Range (°C)	Activation Energy (kJ/mol)	Frequency Factor (s-1)
Akita & Kase [115]	a Cellulose	250-330	224.0	1.0×10^{17}
	Modified cellulose	250-330	134.0	1.7×10^{10}
Brown and Tang [116]	Ponderosa	-	149.9	
Chatterjee [117]	Cotton	-	227.3 138.1	
Lewellen et al.[41]	Cellulose	-	139.8	6.8×10^{9}
Maa [118]	Birch wood	400-1200	31.4	0.10 cm/s
	Douglas fir	400-1200	14.7	0.03 cm/s
Stamm [119]	Douglas fir sawdust	110-220	104.7	2.4×10^{5}
	a Cellulose	110-220	108.8	6.0×10^{5}
	Hemicellulose	110-220	111.8	7.1×10^{6}
	Lignin	110-220	96.3	1.1×10^{4}
	Coniferous wood	95-250	123.5	6.2×10^{7}
Tran & Rai [110]	Douglas fir bark	100-850	101.7 + 142.7 X **	2.1×10^{8}
	Catalysed bark *	100-850	102.6 + 86.2 X **	2.3×10^{8}

* bark with 15% K2CO3

** X denotes fractional conversion

With the exception of Maa, all the workers listed in Table 4.1 derived their kinetic pyrolysis parameters based on weight loss data. Maa and Bailie [120] however, derived their kinetic parameters by applying their experimental data obtained from a isothermal TGA to the unreacted shrinking core model such that the rate of pyrolysis is given by the following equation :

$$dr_c / dt = - A \exp (- E / RT_c) \tag{4.5}$$

where dr_c / dt is the reaction rate in terms of the unreacted core
T_c is the reaction core temperature

Although a simple rate equation can be obtained by using Equation 4.3 or Equation 4.4, a value for the final char weight is required and this value is not known beforehand and generally varies according to the operating conditions.

Tran and Rai [110] tried to account for the complexity of the pyrolysis process by assuming that the activation energy was dependent on the extent of pyrolysis. They used Jack pine wood in their experiments. However, Alves et al. [121], found that this assumption was not always true for lignocellulosic materials. Other workers have used two or more consecutive steps of zero or first order reactions to describe pyrolytic behaviour of biomass [28,122-128]. However, these models still require a final char weight value. Table 4.2 shows examples of the steps assumed and kinetic data derived by various workers to describe the pyrolysis of biomass and its components.

As can be seen from Tables 4.1 and 4.2, the kinetic parameters vary widely. These discrepancies may be accounted for by :

(i) the neglect of temperature variation during the heating-up period of the sample, using the steady state temperature as the reaction temperature;
(ii) the use of too simple a kinetic model may lead to different kinetic parameters being valid at different temperatures/heating conditions, as different reactions will be rate controlling under different conditions;
(iii) the presence of ash and impurities which has some influence on the pyrolysis rate.

These models can only be used to predict weight loss and density changes. For the prediction of product distribution, stepwise modelling should be used.

Table 4.2
Approaches Used to Derive Overall Pyrolysis Kinetics Relationships

Data source	Sample	Stages	Reaction order	Activation Energy (KJ/mol)	Frequency Factor (s-1)
Lipska & Parker [122]	Cellulose	Rapid initial decomposition			
		up to T = 288°C	0	175.8	
		T = 288-308°C	1	175.8	
Tang [28]	Wood	T = 280-325 °C	1	96.3	3.2×10^5
		T = 325-350 °C	1	226.0	6.5×10^{16}
	α-Cellulose	T = 240-308 °C	1	146.5	6.4×10^9
		T = 308-360 °C	1	234.4	3.9×10^{17}
	Lignin	T = 280-344 °C	1	87.9	1.6×10^4
		T = 344-435 °C	1	37.7	9.3×10^{-1}
Tinney [123]	Wood	$0.5 < r/ro < 0.67$	1	124.7	7.5×10^8
		$\rho/\rho_O > 0.67$	1	90.0	2.0×10^9
Shivadev & Emmons [124]	Cellulose	< 380 °C	1	108.8	5.9×10^6
		> 380 °C	1	226.0	1.9×1016^6
Barooah & Long [125]	Wood	< 330 °C	1	18	5.0×10^{-2}
		> 300 °C	1	84	2.3×10^4

4.4.2 Stepwise Modelling

Stepwise modelling describes the change of wood to intermediates and final products as shown in Equation 4.6 :

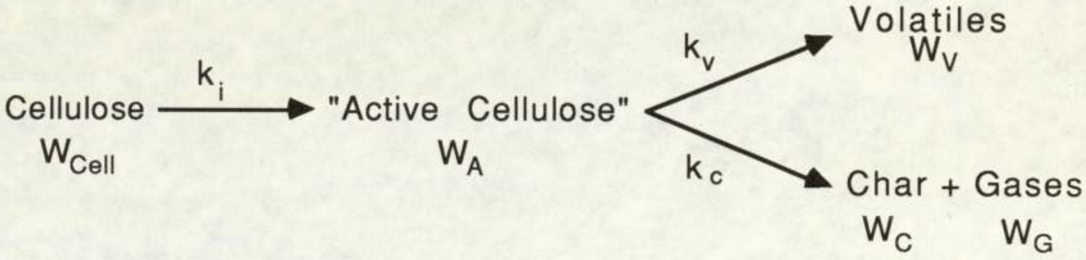
$$\text{Wood} \longrightarrow \text{Product}_i \qquad (4.6)$$

In a single step model, the rate of formation of an individual product $_i$ in yield V_i at time t is given by the expression

$$dV_i / dt = k_{oi} \exp(-E / RT)(V_i^* - V) \qquad (4.7)$$

The quantity V_i^* is the ultimate attainable yield of product $_i$, that is the yield at high temperature and long residence times [128]. The constants k_{oi}, E_i and V_i^* cannot be predicted beforehand and must be estimated from experimental data, a problem that increases as the number of reactions postulated increases. It was suggested that this model should be viewed as a method for correlating data and comparing results from different biomass materials. However it does provide a simple scheme that can be used to predict product yields, This method has been used by Krieger et al. in their analytical model [17].

A different type of stepwise modelling based on a competitive mechanism, has also been proposed to account for the variations in product yields. One example is shown in Figure 4.1.



where

$$\frac{-d\,(W_{Cell})}{dt} = k_i\,[W_{Cell}]$$

$$\frac{d\,(W_A)}{dt} = k_i\,[W_{Cell}\ ] - (k_v + k_c)\,[W_A]$$

$$\frac{d\,(W_C)}{dt} = 0.35\ k_c\,[W_A]$$

and

$$k_i = 1.7 \times 10^{21}\ \exp\left(\frac{-58\,000}{RT}\right)\ \text{min}^{-1}$$

$$k_v = 1.9 \times 10^{16}\ \exp\left(\frac{-47\,000}{RT}\right)\ \text{min}^{-1}$$

$$k_c = 7.9 \times 10^{11}\ \exp\left(\frac{-36\,000}{RT}\right)\ \text{min}^{-1}$$

Figure 4.1 Model Proposed by Bradbury et al. for the Pyrolysis of Pure Cellulose [111].

Bradbury et al. [111] used this approach for their kinetic model shown in Figure 4.1. This model was based on the pyrolysis of pure cellulose (see Section 2.4.1.3).

Theoretical and experimental results for weight loss agreed to within ± 5%. As a consequence this model has been used to account for char yields in the models of large particle pyrolysis [17,129-131].

Koufopanos et al.[108-109] and Nunn et al. [128] proposed that the biomass pyrolysis rate could be related to the individual pyrolysis rate of the biomass components ie.

$$biomass = a\ (cellulose) + b\ (hemicellulose) + c\ (lignin) \tag{4.8}$$

where the terms within the brackets represent the fractions of the biomass components not transformed into gases or volatiles

a, b, c are the weight fractions of the corresponding biomass components in the virgin biomass.

The reaction scheme of the individual components then followed a similar reaction scheme as shown in Figure 4.1. In both cases, theoretical and experimental results for the weight loss agreed to within ± 10%. However, for the model of Koufopanos et al.[108-109], there was no indication that it could be used to predict product yields. Nunn et al. [128] found that, in general, the calculated values fitted laboratory data within ± 7% for temperatures up to about 950-1000°C. However, the tar evolution kinetics were not analysed with this model because they believed that single-reaction, first order kinetics alone could not predict a maximum in yield.

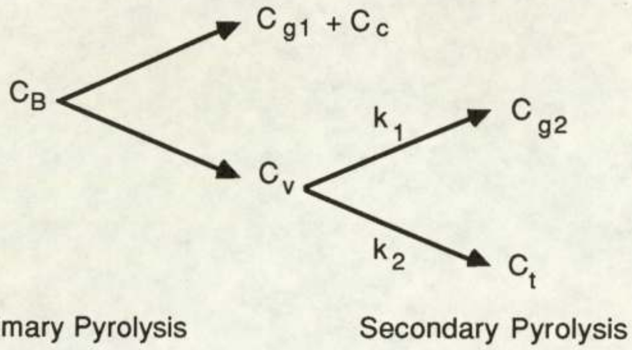
All the models described above have been based on the solid phase or primary pyrolysis. In the section below, kinetics with secondary pyrolysis reactions included will be described.

4.4.3 Secondary Pyrolysis Kinetics

Most modellers have considered only the conversion of the primary vapours/liquid to secondary products as secondary pyrolysis.

Antal [112-113] proposed that the primary vapours could be converted to either gases or refractory tars by a temperature based competitive mechanism as shown in Figure 4.2.

The first reaction produced more permanent gases by cracking the reactive volatile matter to smaller, less reactive species. The second reaction produced refractory condensible materials, which may be tar or some combination of water-soluble organic compounds.



where C_B the mass fraction of carbon in biomass
C_v the mass fraction of carbon composing the reactive volatile matter (carbon in volatile matter/carbon in sample pyrolysate)
C_{g1}, C_{g2} the mass fraction of carbon composing the permanent gases
C_t the mass fraction of carbon composing the refractory condensible materials, including the tars.

Figure 4.2 Antal's Reaction Scheme [112-113].

Antal found that for cellulose, the first reaction had an apparent activation energy E_1 of 49 kcal/mol (205 kJ/mol) while reaction two had an apparent activation energy E_2 of 15 kcal/mol (63 KJ/mol). For lignin, the value E_1-E_2 = 13 kcal/mol (54 kJ/mol) was derived, but further analysis was hindered due to the lack of experimental data. This model has limited use since the experimental data needed must be based on the carbon atom.

Recently kinetic models for the secondary decomposition of primary pyrolysis tars have been proposed by Liden [132], Diebold [114] and Knight et al.[133]. They assumed that the production of oil from wood and the subsequent decomposition of oil are first order reactions. The yield of liquid products is then estimated as a function of the pyrolysis temperature and the residence time of the volatiles in the reaction zone.

Lidén [132] and Diebold [114] using different reactor configurations, proposed similar kinetic models. The reaction scheme used is shown in Figure 4.3.

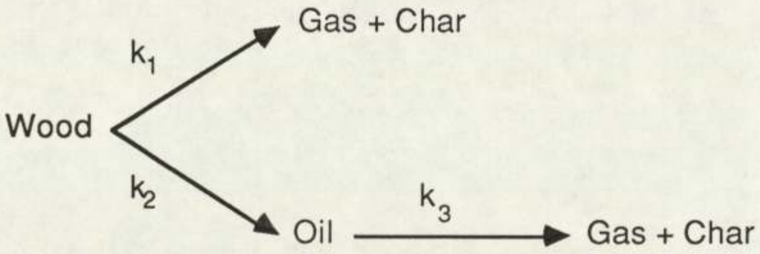


Figure 4.3 Reaction Scheme Used by Liden and Diebold [114,132].

The kinetic expression used for the estimation of the yield of liquid products and the values of the kinetic parameters used for each model are listed below:

$$x = x_o\,[1 - \exp(-k_3)\,] / k_3\,\theta \tag{4.9}$$

where

k_3 = the reaction rate constant for the oil decomposition step [s^{-1}]

θ = the mean residence time for the oil decomposition [s]

x_o = the theoretical 'ultimate' oil yield

with

$$k_3 = 4.28 \times 10^6 \exp(-\frac{107\ 500}{RT})\ \ s^{-1},\ \ x_o = 0.703$$

and

$$k_3 = 1.55 \times 10^5 \exp(-\frac{87\ 634}{RT})\ \ s^{-1}\ \ x_o = 0.78 \text{ or } 0.76$$

for Lidén and Diebold respectively.

The reaction scheme used by Knight et al. [133] is shown below in Figure 4.4:

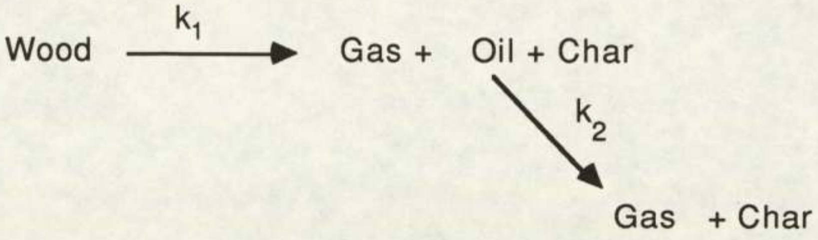


Figure 4.4 The Reaction Scheme of Knight et al. [133].

with the following reaction rate expression :

$$x = (k_1 b_5) / (k_2 - k_1) [\exp (-k_2 t)] \qquad (4.10)$$

with

$$k_1 = 1.483 \times 10^6 \exp \left(- \frac{21\,380}{RT} \right) \; s^{-1}$$

$$k_2 = 23.12 \exp \left(- \frac{7\,060}{RT} \right) \; s^{-1}$$

$$b_5 = 0.811$$

where,

k_1 = the reaction rate constant for the first order production of oil
k_2 = the reaction rate constant for the first order decomposition of oil
b_5 = the maximum fractional conversion of wood to oil

Vasalos et al. [133] and Scott and Piskorz [74] tested the above models using their own experimental data.

Vasalos et al.[133] found that using Lidén's parameters, they obtained a better fit of the liquid yields of -20% for the particle size range 300-425 mm, while Diebold's parameters gave a better fit of ± 10% for the particle size range 500-600 mm. Knight's et al. model did not predict satisfactorily liquid yields for either particle size range. They concluded that the variations between the predicted values and the experimental results could be attributed to the exclusion of the water yield in the reaction mechanism, the residence times used, and the type and size of biomass tested.

Scott and Piskorz [74] found when testing the models of Lidén and Diebold, that the predicted liquid yields agreed with achieved yields within ± 10% for the temperature range 500-700°C with residence times of up to 1 second. Low predictions of liquid yields at the highest temperature were attributed to to the assumed water yield, the constant x_o parameter or the total yield being normalised to 100%.

4.4.4 Summary

As pyrolysis is a very complex process and the different intermediates formed are difficult to collect and identify, various approaches have been used to develop kinetic models. Most predict weight loss rather than product yield and distribution. The kinetic parameters vary from one model to another because they are very sensitive to experimental conditions. One research group found that even a decrease of 1 kcal/mol (from 31.8 to 30.8) in the activation energy of tars caused the predicted value of the liquid yield to increase by approximately 16 % [135]. Hence research in this area of pyrolysis requires further investigation.

4.5 ANALYTICAL MODELS FOR LARGE PARTICLES

For small particles the kinetics are sufficient to predict the reaction rate. However, for large particles, both the physical and the chemical changes are essential for obtaining a global pyrolysis rate.

4.5.1 Formulation of An Analytical Pyrolysis Model

A comprehensive list of all known parameters that can influence the pyrolysis process is given in Table 4.3. These affect the energy and mass flows into and out of a pyrolysing particle as shown in the following steps which have been deduced from the extensive studies of mechanisms and reactions reviewed in Chapters 2 and 3 as being:

- heat transfer from the reactor environment to the particle surface by convection, and/or radiation and and/or conduction;
- heat transfer from the outer surface of the particle into the interior of the particle by conduction and possibly to a lesser degree by convection;
- heat transfer between the volatile reaction products leaving the reaction zone and the solid matrix - convection;
- primary pyrolysis: substrate —> gas + char + primary liquid

product;

- secondary and tertiary pyrolysis: primary product —> gas + char + secondary liquid product; primary products + secondary products;
- changes in enthalpy and heats of reaction of the biomass;
- diffusion of volatiles out of the solid;
- diffusion of volatiles away from the particle surface.

Table 4.3
Process Parameters that Influence Pyrolysis and Their Effects

- Anisotropic nature
  heat capacity, permeability, rate of heat transfer, diffusion

- Moisture content
  temperature profile, weight/density change, product yields and distribution, amount of water released initially during the drying stage, rate of heat transfer

- Reactor temperature
  temperature profile, weight/density change, product yields and distribution, competing reactions, properties such as thermal conductivity and heat capacity, heat of reaction

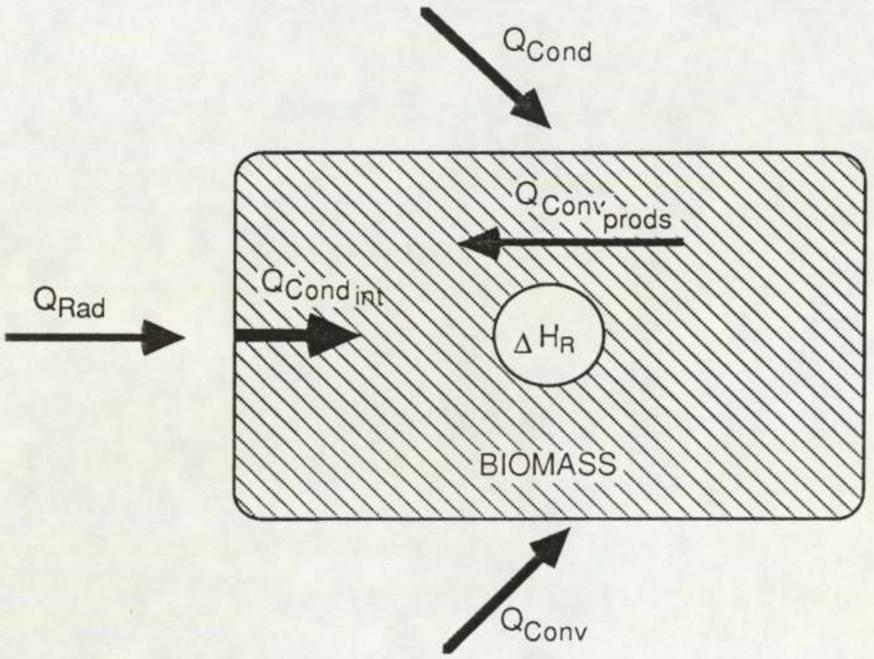
- Particle size
  temperature profile, weight/density change, product yields and distribution, release rate of products, rate of heat transfer, reaction time

- Heat flux
  rate of heat transfer, temperature profile, reaction profile

- Vapour residence time
  product yield and distribution

effects are in italics

These processes are all temperature dependent and, since temperature changes with time and space, they will also be time and spatially dependent. Furthermore, they will also be dependent on the physical structure of the particle along with its properties such as density, thermal properties, size and the orientation of the particle with respect to grain. The energy flows are summarised in Figure 4.5.



where :

Q_{Conv}	Heat flux convected to particle surface (between gaseous environment and particle)
Q_{Rad}	Heat flux radiated to particle surface (between reactor wall - particles or particles - particles)
Q_{Cond}	Heat flux conducted to particle surface (between reactor walls and particles)
$Q_{Cond_{int}}$	Net heat flux conducted to particle interior
$Q_{Conv_{prods}}$	Outflowing volatiles convecting heat from the interior of particle
ΔH_R	Heat of reaction/pyrolysis and the latent heat of water

Figure 4.5 Schematic of Heat Transfer Processes Occurring During Pyrolysis

When a large particle is used, the pyrolysis process will be at different stages at different parts of the particle. Also biomass is anisotropic. Therefore, it is very difficult to formulate.

A complete pyrolysis model containing all the complex reactions as well as heat and mass transfer occurring simultaneously and/or in parallel is extremely difficult to formulate and/or solve. Hence, a number of models incorporating some of the above processes have been proposed.

4.5.2 Pyrolysis Models Derived

A table that summarises analytical models found is given in Table 4.4. An expanded version that includes the formulation and assumptions is given in Appendix II.

4.5.2.1 Pyrolysis Models With No Convection Term

The first two models in Table 4.4 are examples of early models proposed to account for the generation of gas which then passed to the surface of the particle and ignited. The main aim for these models was to predict burning times. As a starting point, the physical properties were considered constant, as at that time there was not enough data available to account for the changes that occur as pyrolysis proceeds. In addition, there were not many numerical techniques that could be used to solve partial differential equations and therefore it was easier to solve numerically the transient heat and kinetic equations assuming constant properties. Bamford et al. [135] devised their own numerical method to solve their problem while Panton et al. [136] used the methods of integral relations. The heat balance equation considered conduction and the heat of reaction as necessary for predicting the local temperature.

The model of Bamford et al. was the first theoretical model proposed for pyrolysis [135]. He concluded that there was a satisfactory agreement between experimental and simulated results. However, this was obtained by using the activation energy and the pre-exponential factor as adjustable parameters to fit the calculated central temperature curve to the experimental plot.

Panton and Rittmann were the first to consider a complex reaction scheme. They considered that the density and the effective thermal conductivity decreased as the porosity increased. The model showed that the competing reactions were sensitive to the heat flux but broke down at a higher heating flux.

Table 4.4
Summary of Single Particle Pyrolysis Models

Authors	Predictions	Shortcomings
Bamford et al. [135]	• Predicts temperature and weight loss profiles • Predicts rate of evolution of volatiles	• Cannot be used to predict product yields or composition • No sensitivity analyses were carried out • No convection term • Assumed constant physical properties
Panton and Rittmann [136]	• Predicts temperature and reaction rate profiles • Predicts gas generation rate • Suggests that heat of reaction and activation energy are important parameters for gas generation • Suggests that competing reactions are sensitive to the heat flux	• Cannot be used to predict product yields or composition • No convection term • Breaks down at higher heating flux when investigating the effect of heating rate on the competing reactions
Kanuary et al. [137]	• Shows that the convection term is needed in the heat balance equation • Suggests that the burning rate depends on particle size	• Can only be used to investigate the importance of convective heat transfer
Kung [138-139]	• Predicts temperature and density profiles • Predicts volatiles release rate • Suggests that both the thermal conductivity and specific heat of char, the heat of reaction and particle size are important parameters in wood pyrolysis	• Cannot be used to predict product yields or composition
Maa and Bailie [118,120]	• Predicts under what conditions heat transfer or chemical reaction is rate controlling • Predicts reaction rate and temperature profiles • Predicts reaction times • Derived simple expressions to estimate reaction time by using either effective thermal conductivity (large particles) or	• Cannot be used to predict product yields or composition • Does not predict volatiles evolution rate

	effective activation energy (small particle)	
Fan et al. [140-142]	• Introduces a new parameter called the Lewis No. which is the ratio of thermal diffusivity to mass diffusivity • Predicts concentration and temperature profiles • Suggests that the higher the Lewis No., the greater the conversion of the solid and the smaller the temperature gradient within particle • Suggests that heat of reaction affects pyrolysis rate	• Cannot be used to predict product yields or composition • Does not predict volatiles evolution rate
Kansa et al. [143]	• Predicts mass loss, pressure and temperature profiles • Suggests that heat of reaction, both the thermal conductivity and specific heat of char, and the permeability constant are important parameters in wood pyrolysis	• Cannot be used to predict product yields or composition • Does not predict volatiles release rate
van Ginneken et al. [144]	• Predicts product distribution • Temperature and particle size influences product distribution	• Does not predict temperature profiles • Assumed constant physical properties
Desrosiers et al.[145]	• Predicts temperature profile Predicts reaction time • Suggests that the values of pyrolysis temperature, char thermal conductivity and heat of reaction significantly affect wood pyrolysis	• Cannot be used to predict product yields or composition • Does not predict volatiles release rate • Assumed constant physical properties
Capart et al. [127-146]	• Predicts reaction rate and time • Predicts both internal and surface temperature and mass loss	• Cannot be used to predict product yields or composition • Does not predict volatiles evolution rate
Phillips et al. [147]	• Predicts mass loss profiles • Predicts surface and internal temperature profiles • Predicts char yields	• Does not predict volatiles yields • Does not predict volatiles release rate • Assumed constant physical properties • For large particles, kinetics

		and heat transfer are not coupled
Saastamoinen [104]	• Predicts temperature, mass loss and density histories • Predicts moisture distribution • Predicts moisture and volatiles release rate Predicts generation of steam and volatiles	• Neglect of mass transfer resistance which may play a role in pyrolysis
Léde et al. [148-149]	• Predicts under what conditions heat transfer or chemical reaction is rate controlling • Introduces a thermal Thiele Modulus (ratio of heat penetration time to reaction time) • Predicts temperature profile • Predicts reaction time	• Cannot be used to predict product yields or composition • Does not predict volatiles evolution rate • Thermal properties are assumed to remain constant
Pyle and Zaror [150-151]	• Introduced two pyrolysis numbers, Py (ratio of reaction time to heat penetration time) and Py' (product of Biot No. and Py) • Evaluated the importance of external and internal heat transfer • Derived four simple models • Predicts conversion and temperature profiles • Predicts conversion times • Particle size affects conversion • Carried out sensitivity study	• Cannot be used to predict product yields or • Does not predicts volatiles release rate composition • No convection term
Stiles [152]	• Predicts char yields • Predicts cracking activation energies	• Cannot be used to predict volatiles yields or composition • Does not predicts volatiles evolution rate • No convection term • Predicts that smaller particles produce more char than larger ones
Kothari and Antal [129-130]	• Predicts temperature histories • Predicts weight loss • Calculates reaction times • Derived simple expressions to calculate heat up time and devolatilisation time • Pyrolysis is complete at 500°C	• Cannot be used to predict product yields or composition • Does not predict volatiles release rate

Chan et al [17,103,153]	• Predicts product yields and composition • Predicts volatiles release rate • Predicts temperature profile • Predicts effects of moisture • Carried out sensitivity studies	• Neglect of mass transfer resistance which may play a role in pyrolysis
Krieger-Brockett et al. [134]	• Predicts product yields and composition • Predicts volatiles release rate • Predicts temperature profile • Predicts effects of moisture • Carried out sensitivity studies	• Neglect of mass transfer resistance which may play a role in pyrolysis

4.5.2.2 Models with Convection Term

Kanuary and Blackshear proposed their model to investigate the influence of internal convection on transient pyrolysis [137]. They appear to be the first workers to introduce this concept.

They proposed that the pyrolysing particle could be divided into two parts: a solid matrix which remained inert and an entrained active part which gasified. They also assumed that there was local thermal equilibrium between gas and the solid. They found, by order of magnitude analysis, that the convection term should be included in the heat balance. They suggested that it was needed to predict, accurately, the internal temperatures and the temperature history of the particle.

As wood is a porous material, Pyle and Zaror [14,150-151], using Roberts hypothesis [16], suggested that the volatiles would leave along approximately isothermal planes parallel to the wood grain and then through the cracks. Therefore, they argued that, convective heat transfer between volatiles and solid was unlikely to play a major role under those circumstances. However, the above situation is mostly likely to occur towards the end of pyrolysis and hence a convection term should be included to account for lowering of the inward conduction heat transfer rate.

As previous workers were mainly concerned with predicting combustion rates, heat of reaction was normally assumed to be exothermic. Kung is believed to be the first worker to consider an endothermic heat of reaction [138]. He too, like Kanuary and Blackshear [137], divided the pyrolysing wood into a reactive part and a non-reactive part by assuming that these parts have different thermal properties. He also considered the thermal properties such as thermal conductivity, specific heat and density, to vary and that these changes could be modelled as a function of the extent of reaction. The effects of slab thickness, char conductivity and decomposition endothermicity on the pyrolysis rate were evaluated.

He found that char conductivity had a pronounced effect on the pyrolysis rate of a thermally thick slab. He later compared his theoretical results with experimental data from Roberts and Clough's work; the comparison was claimed to be a good one.

Variation in the properties of wood should be included in the model as they decrease as the material pyrolyses and in turn, cause an increase in the reaction rate [138-139]. This is due to the anisotropic nature of biomass (see Section 2.3). Most workers modelled the changes as linear relationships of the initial and final (char) values of either porosity or density [138-144]. Chan et al. found that the best relationship to account for the changes in the thermal conductivity, was to include a conduction term which was density-dependent and a radiation term which was temperature dependent [17,103, 153]. This model was later used by Krieger-Brockett and Glaister (see Section 4.5.2.6 [134]).

4.5.2.3 Shrinking Core Model

Maa and Bailie [118, 120] appear to be the first workers to use the shrinking core technique with the addition of an unsteady convective heat transfer. This application was based on the assumption that the low thermal conductivity and high reactivity of wood results in a narrow, advancing zone of pyrolysis when exposed to a high temperature zone and pyrolysis occurs at the interface of the char and the unreacted wood. However, this formulation had to be simplified to obtain a numerical solution. They assumed that a steady state temperature profile could be used and that the rate of the process could be calculated by an Arrhenius expression evaluated at the temperature of the unreacted core. They indicated that pyrolysis was controlled by two competing mechanisms:

kinetics or the heat transfer considerations. From a sensitivity study they found that wall temperature, Arrhenius parameters, effective conductivity, heat of reaction and wood density influence pyrolysis. This model appears to be useful for estimating temperature profiles in the char layer formed during pyrolysis.

4.5.2.4 Moving Boundary Models

Taking Maa and Bailie's model one step further, Desrosiers and Lin further developed a "moving boundary" model by considering that the controlling rate step was the heat transfer step and that the progress of pyrolysis was determined by the rate of advance of a sharp boundary [145]. This boundary was defined as the locus of points at a fixed pyrolysis temperature. This model accounts for the temperature gradient that exists in the unreacted wood core and its magnitude is determined by the heat of reaction and the thermal properties of the two solids. Because of this, the process was considered as a phase change one (from wood to char). No kinetic equation was used. Consequently, it cannot be used to predict product yields and distributions.

Saastamoinen also used a moving boundary approach [104]. He considered pyrolysis consisting of three boundaries :

(i) a moving core where there was no vaporization or pyrolysis taking place at $T < 373$ K (initial step of pyrolysis);
(ii) a moving core where the vaporization of liquid water takes place at $T = 373$ K and steam is generated;
(iii) a moving core where the generation of the pyrolysis products takes place at $T > 373$ K.

By using these approximations, the locations of cores as opposed to temperature distribution, were calculated as a function of time. For example, the transient location of the drying front can be obtained directly from this model. Instead of using the customary Arrhenius rate (see Equation 4.2) to determine the local generation of volatiles or the disappearance of the solid matter, they developed a new relationship to account for the temperature dependent asymptotic yield of volatiles. The local density was expressed as :

$$\rho_f = \rho_o \quad e(T) \tag{4.12}$$

where ρ_o is the initial density
e(T) is the transient mass/initial dry mass ratio of the particle obtained experimentally.

Although the yield can be predicted by using this model, the prediction of the composition of the volatiles is not possible and therefore the use of a multi-step, competitive, multi-component kinetic mechanisms seems a more feasible approach for obtaining qualitative results (see Section 4.5.2.6).

4.5.2.5 Models Including Mass Transfer Effects

Fan et al.[140-142] considered both unsteady heat and mass transfer. However, they found in their study that the progress of the pyrolysis reaction was fairly insensitive to mass transfer and suggested that the overall rate could be determined by considering heat transfer and chemical reaction only. Kansa et al., Antal and Kothari and Stiles also considered mass transfer resistances.

Kansa et al. considered hydrodynamic flow to account for the outflow of the volatiles generated by introducing a momentum balance term in their model. In addition, they considered convective heat transfer between the solid matrix and the gaseous pyrolysis products within the particle, in contrast to the local equilibrium normally assumed between the two phases by other investigators [103,135,137-142].

Once again, simplifications had to be made in order to solve the model and this effect was later dropped. The predicted temperature distribution within a 5 cm wood slab almost coincided with the experimental data. The model also predicted the trend and magnitude of the pressure history within the particle; however, the predicted pressure peak had a lead of about 2 minutes compared to the experimental observations. They inferred that both the structural effects and the inclusion of secondary pyrolysis reactions are required to account more fully for the experimental observations.

Kothari and Antal [129-130] accounted for hydrodynamic flow, by introducing a permeability term, in their model for pyrolysis of cellulose particles with diameters up to 0.5 mm. They predicted that there was no accumulation of volatiles within the particle and pressure gradients did not exist. For that reason, no attempt was made to solve that part of the model which included mass transfer resistances. They also concluded that there existed strong analogies between cellulose pyrolysis at high heating rates and phase change phenomena and that the pyrolysis temperature,T_p, could be considered as a "phase change" temperature. T_p was found to be about 500°C.

Lédé et al. [148-149] like Antal and Kothari found that they could obtain a simple expression for calculating the total pyrolysis time. They also obtained a thermal Thiele modulus which is the reciprocal of the Pyrolysis number defined by Pyle and Zaror [14,150-151]. Both models can be used to investigate whether internal or external heat transfer plays a major role.

Stiles assumed that a proportion of the volatiles participated in secondary charring reactions and that the rest left the particle either by hydrodynamic flow for flash pyrolysis or by diffusion if slow pyrolysis occurred [152]. He further suggested the use of distribution activation energies, in the Gaussian form, was more suitable to account for the different reactions occurring during thermal degradation; he used identical frequency factors. The integral limits of $E \pm 3s$ was chosen so that 99.7% of the total reactions could be covered. He obtained poor results for both pyrolysis processes. He concluded that this was probably due to the poor choice of the primary reaction scheme and also the exclusion of parameters, such as temperature, which contributed to the observed particle size effects.

4.5.2.6 Uncoupled Heat and Kinetic Approach

Phillips et al. considered that the chemical reaction as independent of the heat transfer for large particles. This proposal seems unfeasible since for large particles, the heat transfer rate will influence the chemical reactions of the system.

4.5.2.7 Models Which Predict Product Yield and Distribution

Capart et al. [127,146] found from their experimental results using rods of wood, with diameters up to 22 mm, and the profile of the enthalpy-analysis curves, as well as internal temperature measurements that there exist a threshold temperature at 380-390°C above which the wood is converted into char. From the temperature histories, the average density could be calculated. The predicted weight loss was comparable to the measured values.

van Ginneken used his model to predict product distribution. Initially he predicted values of char and tar plus water yields increased and decreased respectively as temperature increased. To overcome this problem, he included a secondary reaction of the primary tar forming more char and gases. He solved this extended reaction model by considering only the kinetic effects although when he compared the predicted values to experimental results, he claimed that a good agreement was obtained.

The models of Chan et al. and Krieger-Brockett are the most comprehensive models proposed to date [17,103,134,153]. In addition to the normally heat balance equation, a reaction scheme for the conversion of biomass into both primary secondary products was included. The model predicted the temperature profile within the particle and the relative amounts of gas, tar and char for the pyrolysis of a wood slab fairly well. Krieger-Brockett's model is an extended version of Chan et al which considered 2-dimensional effects.

4.5.3 Conclusions

Several single particle models have been proposed to account for the interactive effects of the process parameters on pyrolysis. As pyrolysis is initially a heat driven process [150-151], all these models assumed that the heat is transferred to the inner parts of the pyrolysing particle mainly by conduction. Furthermore, the presence of moisture will delay this heat transfer as heat is now used to vaporise water.

Several assumptions have been used in order to simplify the model so that a reasonable numerical solution can be obtained. What is still required of these models are more complex reaction schemes to predict product yield and distribution. The most complex used to date is that of Chan et al. and Krieger et al [17,103,135,152,153]. They considered that the conversion of biomass to gas, char and liquid as three separate reactions as opposed to competing reactions. In this case they are making use of data provided by kinetic stepwise modelling (see Section 4.4.2).

Kinetic data obtained from real time studies of the formation of pyrolysis products, such as those carried out by Evans and Milne [36-37], could be one method for obtaining this type of information. Furthermore, more robust models can be derived by using numerical mathematics routines which can handle stiff systems as encountered in pyrolysis modelling. This information can then be used to specify what reactors to employ and under what conditions they should be operating at. Chapter five looks at the pyrolysis technologies currently available for the conversion of biomass into valuable fuels and chemicals.

CHAPTER FIVE

A REVIEW OF BIOMASS PYROLYSIS AND PYROLYSIS TECHNOLOGIES

5.1 INTRODUCTION

The potential offered by biomass and solid wastes for solving some of the world's energy problems is widely recognised. The energy in biomass may be realised either by direct use as in combustion, or by upgrading into a more valuable and usable fuel such as fuel gas or fuel oil or higher value products for the chemical industry. This upgrading may be by physical, biological, chemical or thermal methods to give a solid, liquid or gaseous fuel.

This chapter presents an overview of the technologies of thermochemical conversion as pyrolysis and liquefaction, and in particular considers the production and properties of liquid fuels. All the aspects outlined are described in more depth in the rest of this thesis, and this introductory chapter serves to explain the opportunities and constraints in which liquid fuel production by biomass pyrolysis has to operate, and the complex interactions that affect implementation.

The range of thermochemical technologies is first characterised in terms of process parameters and products in order to provide a comparison between the various thermochemical conversion technologies. Pyrolysis processes are then described in more detail, concentrating on process principles, state of development, unresolved problems, and opportunities and potential from which an R&D strategy is proposed. The most advanced examples of each mode of pyrolysis are described in detail.

All aspects of pyrolysis liquids upgrading and utilisation are covered in the succeeding chapter of this thesis, and reference will be made to these further details when relevant.

5.2 THERMOCHEMICAL TECHNOLOGIES

There are four main thermochemical methods of converting biomass:

pyrolysis, liquefaction, gasification and combustion. Each gives a different range of products and employs different equipment configurations operating in different modes. These are summarised below in Table 5.1, and depicted in Figure 5.1.

Table 5.1
Thermochemical Conversion Technologies and Products

Technology	Primary Product	Example of application
Pyrolysis	gas	fuel gas
	liquid	liquid fuel substitution
	solid char	solid fuel or slurry fuel
Liquefaction	liquid	liquid fuel substitution
Gasification	gas	fuel gas
Combustion	heat	heating

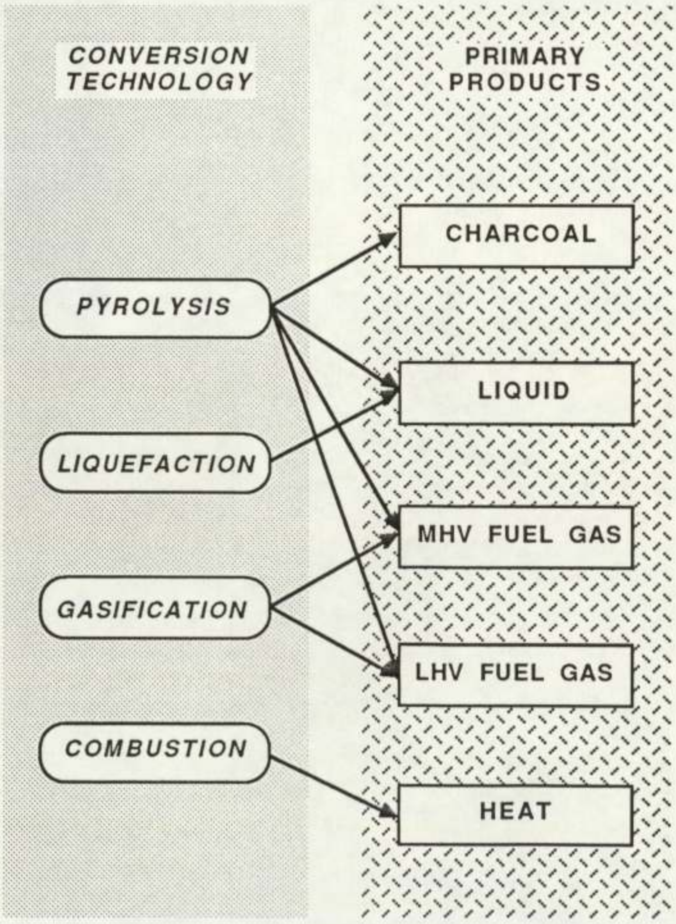


Figure 5.1 Primary Products from Biomass Conversion

The main characteristics of these processes are summarised in Table 5.2 to give some indication of the processing constraints and limitations of each technology. While combustion is a thermochemical process, it is not considered further as it is well established and has limited development opportunities for satisfying longer term energy requirements. It is worth noting in Table 5.2 the different feed requirements for the various technologies, the scale to which each has been developed, and the variation in types and proportions of products that are produced by the different processes.

Table 5.2
Characteristics of Thermochemical Conversion Technologies

Figures quoted are typical, and can vary considerably according to technology and operating conditions

		Pyrolysis		Liquefaction	Gasification
		Slow	Flash		
FEEDSTOCK					
Feed size		any	small	very small	mixed, large
Moisture content		low	very low	very low	50% max
PARAMETERS					
Temperature, °C		400-600	450-900	250-400	700-1500
Pressure, bar		0.1-1	1	100-200	up to 20
Maximum throughput, dry t/h, achieved to date		5	0.05	0.1	40
PRODUCTS (dry basis on dry feed)					
Gas	yield, % wt	up to 40	up to 70	20	100-250
	HHV, MJ/Nm^3	5-10	10-20	2-6	5-15
Liquid	yield, % wt	up to 30	up to 70	up to 50	up to 3
	HHV, MJ/kg	23	23	30	23
Solid	yield, % wt	30	up to 15	up to 25	nil (ash)
	HHV, MJ/kg	30	30	30	-

5.3 PRODUCTS

Some materials directly produced from a thermochemical conversion process can be used more readily than raw biomass and may be considerably more valuable. These primary products can be used as such, or further converted into even more useful and/or valuable secondary fuel or chemical products. The main products are outlined below and characterised later in this chapter, and in more detail in individual chapters of this thesis.

5.3.1 Primary products

The primary products from thermochemical conversion can be gas, liquid, and/or solid char depending on the conversion technology employed. These primary products can be used directly, or they may be subjected to further chemical processing to give a higher quality and value fuel or chemical products which is described below. The possible primary products and their processing origins are summarised in Table 5.3. The technologies for upgrading and likely viable size ranges are summarised in the relevant sections below.

Table 5.3
Thermochemical Conversion Primary Products and Technologies

Product	Form	Components	Source
Fuel gas	LHV	CO, H_2, CO_2, CH_4, N_2	Pyrolysis, Air gasification
	MHV	CO, H_2, CO_2, CH_4, and higher hydrocarbons	Pyrolysis, O_2 gasification
Liquid	Oil	Water insoluble oxygenates	Pyrolysis, Liquefaction
	Char-oil slurry	Charcoal, oil	Pyrolysis
	Char-water slurry	Charcoal, water, stabiliser	Pyrolysis
Aqueous	Waste water	Water soluble oxygenates e.g. acetic acid }	Pyrolysis Liquefaction Gasification
Solid	Charcoal		Pyrolysis
Heat	Hot gas		Combustion

Much of the present interest in thermochemical conversion centres on liquid products due to their high energy density which reduces the cost of storage and transport as shown in Table 5.4, and potential for premium liquid fuel substitution which is discussed later. Oil and slurry mixtures have a clear advantage over woodchips and straw in energy density, and for longer distances this difference may be a decisive factor.

Table 5.4
Some Characteristics of Biomass and Fuel Derivatives

	Bulk density kg/m3	Heating value dry basis, GJ/t	Energy density, GJ/m3
Straw	~ 100	20	2
Woodchips	~ 400	20	8
Pyrolysis liquid	~ 1200	23	27
Char	~ 300	30	9
Char-water slurry (50/50)	~ 1000	15	15
Char-oil slurry (20/80)	~ 1150	24	28

The gas is a low to medium heating value fuel gas that may be used as such for process heat (e.g. for feed drying) or power generation either on the plant or for export. While it could be physically and chemically upgraded to higher value products such as methanol or gasoline, conversion by gasification is more efficient.

The liquid approximates to biomass in elemental composition, and is composed of a very complex mixture of oxygenated hydrocarbons. The complexity arises from the degradation of lignin, and the broad spectrum of phenolic compounds that result from uncontrolled degradation. The liquid is often referred to as "oil" or "bio-oil", but more resembles tar. This liquid can also be upgraded to liquid hydrocarbon fuels. Utilisation of this material is discussed later. The crude pyrolysis liquid is a thick black tarry fluid with up to 20% wt water and with viscosity ranging from gas oil to heavy fuel oil. More details of characteristics and uses are included later in this chapter.

The solid product from pyrolysis processes is char, which has limited current applications in developed countries for metallurgical and leisure industries. An alternative approach to a liquid product lies in grinding the char and slurrying it with water with a stabiliser as in coal-water mixtures. Stable and mobile char and water slurries with concentrations of up to 60% wt charcoal have been reported. Slurries can also be made from the oil and char with reported maximum charcoal concentrations of 25%. Slurries from oil, char and water pose still unresolved problems of stability.

Water is also produced from any moisture in the biomass feed and as a reaction product from pyrolysis. This often contains very high levels of organic matter which makes disposal an important consideration in process design.

5.3.2 Secondary Products

A wide range of secondary products can be produced from the primary products summarised above, including hydrocarbon transport fuels, oxygenate transport fuels, power, bulk chemicals including hydrogen and ammonia, and chemical specialties. Examples of the more significant possibilities are shown in Figure 5.2 and summarised in Table 5.5. Some of the processes for effecting these transformations are commercially available and proven, while others are still at the exploratory research and development stage, and the status of these upgrading and refining technologies is summarised in Table 5.6, with an indication of what development work is still required and a possible timescale before they could become commercially availability. This latter point does, however, significantly depend on how fossil fuel prices change, and represents a situation where there is considerable market pull.

5.3.3 Utilisation

Relatively unconventional fuels such as bio-oil and fuel alcohol will require their own marketing infrastructure to be developed, whereas synthesised conventional fuels such as gasoline and diesel can, in principle, be readily accommodated in the established fossil fuel infrastructure. There are some overlaps such as bio-oil might be incorporated into a refinery feed stream for example, but the distribution, storage and handling aspects of product utilisation must not be ignored.

Of the primary pyrolysis products, char is very stable and will not deteriorate, and liquids are relatively stable if stored correctly. Liquids, however, have significant advantages over solids in handling and transport, but potential disadvantages could arise from the chemical and physical instability of pyrolytic liquids, slurries and mixtures, although there are mixed reports on such problems. These are discussed later, but unless the properties of these liquids can be completely controlled, their advantages cannot be fully realised.

Generally liquid or gaseous products are easier to handle in the combustion process and this is important in retrofitting existing equipment. Existing oil fired burners cannot be fuelled directly with solid biomass without major reconstruction or replacement of the unit, which may not be attractive in uncertain fuel markets. However pyrolytic oils, char/oil slurries and char/water slurries are likely to require only relatively minor modifications of the equipment or even none in some cases. Powdered coal fired furnaces can relatively easily accept charcoal as a partial fuel replacement, as long as the volatile content is compatible with the furnace design.

It may be possible to fire turbines and modified diesel engines with pyrolytic oils or upgraded pyrolytic oils, and perhaps even char/water slurries, but there is little recent practical experience.

5.4 THE PROCESS OF PYROLYSIS

5.4.1 Principles

Pyrolysis is thermal degradation either in the complete absence of oxidising agent, or with such a limited supply that gasification does not occur to an appreciable extent which may be described as partial gasification. Relatively low temperatures are employed of 500-800°C, compared to 800 to 1100°C in gasification. Three products are usually produced: gas, liquid and char, the relative proportions of which depend very much on the pyrolysis method and reaction parameters.

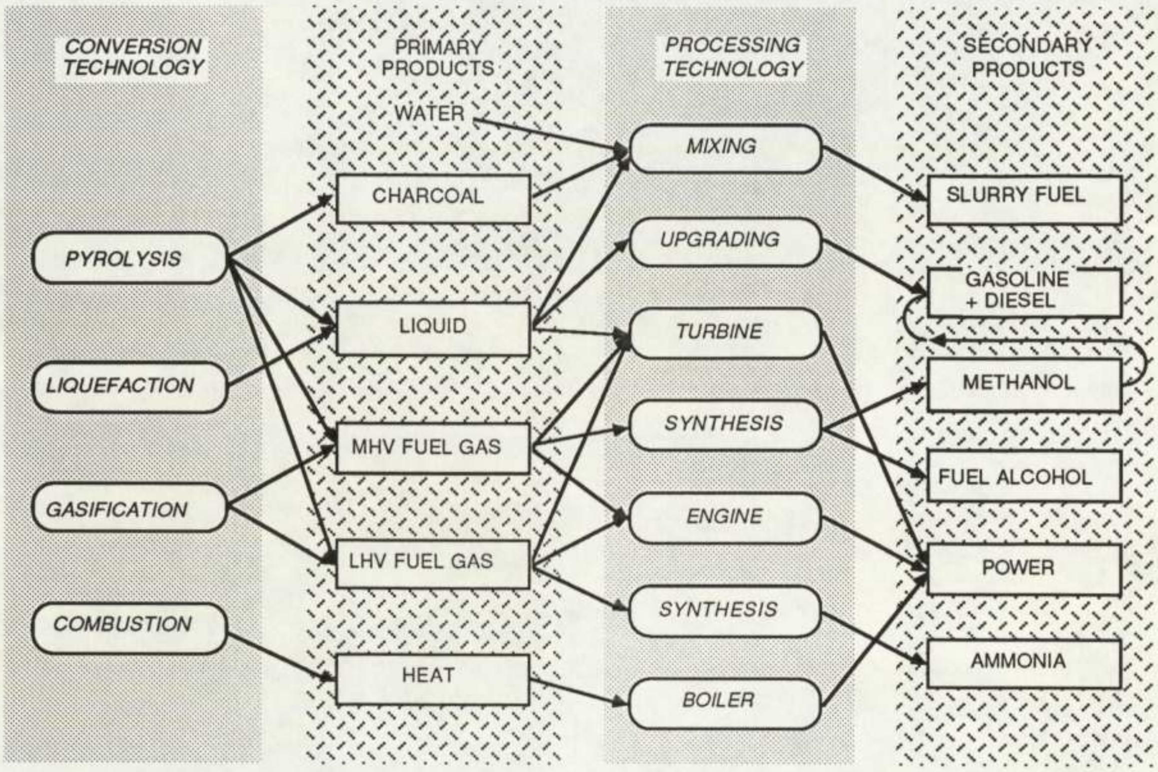


Figure 5.2 Primary and Secondary Products from Thermochemical Conversion

Table 5.5
Secondary Products and Sources

Secondary product	Source	Process
Hydrocarbon Fuels		
Gasoline	pyrolysis	hydrotreating + refining
	pyrolysis	zeolites + refining
	liquefaction	hydrotreating + refining
	gasification via methanol	MTG
Diesel	pyrolysis	hydrotreating + refining
	pyrolysis	zeolite + MOGD
	liquefaction	hydrotreating + refining
	gasification via methanol	MOGD
Fuel oil	pyrolysis	stabilisation
	liquefaction	stabilisation
Oxygenate Fuels		
Methanol	gasification	synthesis
Fuel alcohol	gasification	synthesis
Power		
Power	pyrolysis	turbine
	gasification	engine, turbine or rankine cycle
	combustion	rankine cycle
Chemicals		
Hydrogen	gasification	conversion
Ammonia	gasification	synthesis
Specialty chemicals	pyrolysis	extraction and/or conversion
	liquefaction	extraction and/or conversion

Notes
MTG Mobil's methanol to gasoline process
MOGD Mobil olefins to gasoline and distillate

Table 5.6
Transformation Technologies and Timescales

Technology	Product	Current status	Time *	Time ¶
Combustion & steam turbine	power & heat	commercial	0	0
Engines, spark ignition & diesel	power	commercial	0	0
Ammonia synthesis	ammonia etc	commercial	0	15
Methanol synthesis	methanol	commercial	0	15
Methanol to gasoline	gasoline	commercial	0	15
Refining hydrocarbons	gasoline etc	commercial	0	15
Hydrogen production	hydrogen	commercial	0	25
Gas turbines	power & heat	demonstration	5	10
Fuel alcohol synthesis	fuel alcohol	pilot	5	15
Methanol to gasoline & diesel	gasoline etc	demonstration	5	15
Hydrotreating	hydrocarbons	laboratory	10	20
Zeolite upgrading	gasoline & BTX	laboratory	15	25

* approximate time in years before being commercially available
¶ approximate time in years before commercially implemented

As stated earlier (see Section 3.2.1), Fast or flash pyrolysis, for example, is used to maximise either gas or liquid products according to the temperature employed; while slow pyrolysis is known as carbonisation and is used to maximise solid charcoal production. The range of primary products that are derived from pyrolysis were described above and are summarised with typical applications in Figure 5.3. The variations in processing technologies and their effect on the product mix are summarised in Section 5.4.2 below.

Pyrolysis is attractive because solid biomass and wastes which are difficult and costly to manage, can be readily converted to liquid products. These liquids, as liquid or slurry, have advantages in transport, storage, combustion, retrofitting, and flexibility in production and marketing. The energy density advantages were summarised above in Table 5.4.

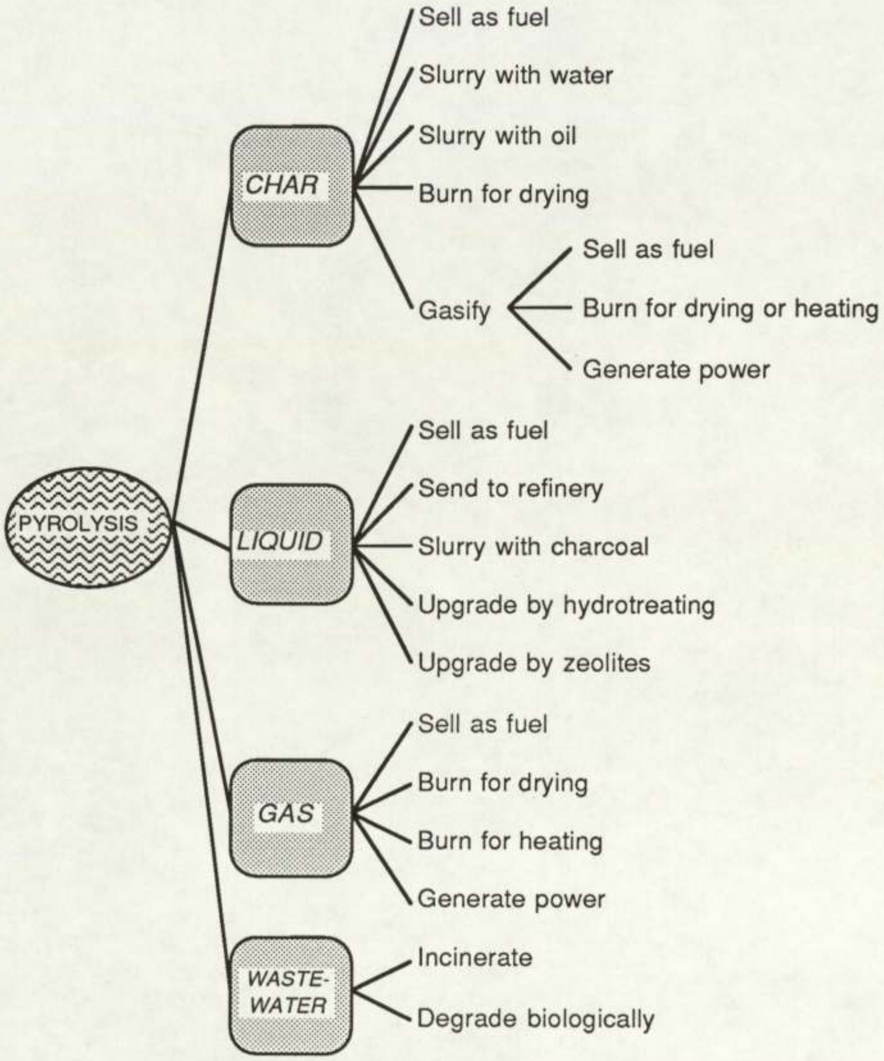


Figure 5.3 Primary Products from Pyrolysis and Applications

5.4.2 Pyrolysis Technologies

Pyrolysis has been practised for centuries for production of charcoal. This requires relatively slow reaction at low temperatures to maximise solid char yield. More recently, studies into the mechanisms of pyrolysis have suggested ways of substantially changing the proportions of the gas, liquid and solid products (see Section 2.4.4). This is achieved by changing the rate of heating, and the reaction temperature.

Flash or fast pyrolysis can give high yields of liquids or "bio-oil" of up to 70 wt% on a dry feed basis on a laboratory scale. This process involves very high heating rates combined with moderate temperatures of less than 650°C, short residence times and rapid quenching of liquid pyrolysis products. These high heating rates, of up to a claimed 1000°C/s or even 10 000°C/s, at temperatures below about 650°C and with rapid quenching, causes the liquid intermediate products of pyrolysis to condense before further reaction breaks down higher molecular weight species into gaseous products (see Section 3.2.2). The high reaction rates also minimise char formation, and under some conditions no char is apparently formed. At higher maximum temperatures the major product is gas. Pyrolysis at these high heating rates is known as fast, flash, or ultra pyrolysis according to the heating rate and residence time, although the distinctions are blurred. Other work has attempted to exploit the complex degradation mechanisms by carrying out pyrolysis in unusual environments. The characteristics of the main modes of pyrolysis are summarised in Table 5.7, and variants are summarised in Tables 5.8 and 5.10 and described later in Section 5 of this chapter.

Table 5.7
Pyrolysis Technology Variants

	Residence time	Heating rate	Temp. °C max	Major product
Carbonisation	hrs-days	very low	400	charcoal
Conventional	5-30 m	low	600	bio-oil, charcoal & gas
Fast	0.5-5 s	fairly high	650	bio-oil
Flash - liquid	<1 s	high	<650	bio-oil
Flash - gas	<1 s	high	>650	chemicals & fuel gas
Ultra	<0.5 s	very high	1000	chemicals & fuel gas
Vacuum	2-30s	medium	400	bio-oil
Hydro-pyrolysis	<10s	high	<500	bio-oil & chemicals
Methano-pyrolysis	<10 s	high	>700	chemicals

Table 5.8
Characteristics of Pyrolysis Processes

Figures quoted are typical, and can vary considerably according to process, feedstock, and operating conditions

		Carbonisation	Slow	Flash Low temp.	Flash High temp.
PARAMETERS					
Temperature, °C		300-500	400-600	450-600	700-900
Pressure, bar		1	0.1-1	1	1
Maximum throughput, achieved to date, dry t/h		5	1	0.05	0.10
PRODUCTS (dry basis on dry feed)					
Gas	yield, % wt	up to 150	up to 60	up to 30	up to 80
	HHV, MJ/Nm^3	3-6	5-10	10-20	15-20
Liquid	yield, % wt	up to 25	up to 30	up to 70	up to 20
	HHV, MJ/kg	20	20	24	22
Solid	yield, % wt	up to 40	up to 30	up to 15	up to 15
	HHV, MJ/kg	30	30	30	30

Most flash pyrolysis processes are based on indirect heating of biomass by gas phase heat transfer from a hot surface such as the reactor wall in the case of a rotary kiln, or hot solids such as sand in a twin fluid bed system. Heat transfer in such processes is mainly by convection, although radiative heat transfer can also be significant. The relatively low heat transfer rates between gas and solid that result from this method of heating can necessitate longer contact times as well as larger reactor volumes for the heat transfer gas.

A more recent approach is ablative pyrolysis which relies on heat transfer from a hot surface through a liquid film to the pyrolysing particle of biomass. This approach is claimed to be capable of producing similar high liquid product yields, as well as offering potential advantages of higher reactor specific capacities and smaller equipment sizes (see Section 6.2).

The heat required for pyrolysis can be added indirectly in a variety of ways such as indirect firing, hot gas, or hot liquid such as metal or molten salt, or directly by partial gasification with limited addition of oxidising agent such as air to give direct heating.

5.4.3 Liquid product

The process of pyrolysis is complex, but the most accepted theory is that primary vapours are first produced, the characteristics of which are most influenced by heating rate. These primary vapours then further degrade to secondary tars and gases if held at a high temperature long enough for secondary reactions to occur. The proportions and characteristics of these secondary materials are a function of temperature and time. Yields of liquids from pyrolysis can thus be influenced by the rate of reaction, with fast or flash pyrolysis at lower temperatures of typically 450-650°C giving the highest liquid yields, and progressively high temperatures giving progressively higher gas yields and lower liquid yields. Examples are described and illustrated later.

The liquid product, known as bio-oil, may be readily burned and has been employed for this purpose. Some problems have, however, been reported in use, particularly in storage where phase separation, polymerisation, and corrosion of containers can occur. In addition the high oxygen and water content make it incompatible with conventional fuels although it may be utilised in a similar way. Some conversion or upgrading for oxygen and water removal and stabilisation is necessary to give a product that is fully compatible with conventional fuels. Upgrading technology is not well developed with most attention being paid to hydrotreating and more recently some attention has been afforded to zeolite synthesis to give synthetic gasoline, other hydrocarbons and olefins. The main characteristics are outlined below to demonstrate the complexity of pyrolysis technology and product utilisation.

5.4.3.1 Characteristics and Utilisation

The liquid product is a highly oxygenated hydrocarbon with an appreciable proportion of water from both the original feed moisture and reaction product. Solid char may also be present. These properties make it relatively unstable in both chemical and physical terms and may cause problems in utilisation and upgrading. It is readily combustible, but care has to be taken in storage, handling and atomisation. Some of the characteristics are discussed below.

The water content is important as it has several effects: it lowers heating value, affects pH (acidity), reduces viscosity, influences both chemical and physical stability, reduces potential pollution problems from waste water disposal and could affect subsequent upgrading processes. The interactions are poorly understood. The water is difficult to measure and remove, since evaporation or distillation at normal temperatures of around 100°C or higher can cause significant and potentially deleterious physical and chemical changes in the liquid. Lower temperature drying is not successful due to the nature of the relationship between water and the organic component in which the water seems to be chemically combined, such as water of hydration. This phenomenon also makes early claims of water content and consequently oxygen content of liquids on a dry basis subject to uncertainty, although recent analytical advances have overcome such problems. Utilisation and consideration of oil on a "wet" or "as-produced" basis therefore seems to be more sensible.

Particulate levels may be high from char and ash carry-over. Separation of solids from liquids is poorly researched, and reliance is usually placed on primary separation in the vapour phase downstream of the reactor before condensation of liquids. Char levels of up to 15% by weight in the liquid have been reported (see Section 5.5.1).

The oxygen content of the pyrolysis liquid is very high, at up to 40% wt. (see Table 5.9). When produced from dry or low moisture content feeds it typically has a heating value a little above that of the biomass feed, in the range 20 - 25 MJ/kg.

A low pH arises from the organic acid content (e.g. acetic and formic acids), and is therefore corrosive. Mild steel is not suitable for handling or storage. Polypropylene piping, for example, has been used to overcome this problem.

Polymerisation or deterioration of the liquid can be caused by temperatures above around 100°C and/or exposure to air (through oxidation) which adversely affect physical properties such as viscosity, and phase separation with deposition of a bitumen-like substance. Heating the liquid to reduce viscosity for pumping or atomisation needs to be considered carefully and thoroughly tested. Exposure to air alone also causes deterioration, but at a slower rate than temperature increase. Maintenance in a sealed enclosure has been claimed to cause substantial pressure increases, so some minimal venting is necessary to avoid pressure build-up, but minimise exposure to oxygen. Pyrolysis liquid has been reported as having been stored in this way in a useable form for up to two years without problems.

Health hazards associated with pyrolysis liquids are also poorly understood. Some toxicity and health tests on primary bio-oils have been reported as comparatively less hazardous than equivalent fossil fuel liquids.

Compatibility with conventional fuels is variously reported as immiscible but compatible. Pyrolysis liquids cannot be expected to be assimilated into a conventional fuel marketing infrastructure without some conversion or upgrading to give a product that is wholly compatible with conventional fuels. The alternative is to create a discrete pyrolysis liquids storage, distribution and utilisation system, that is managed by experts who understand the special problems of this fuel. It is likely that in the short term, dedicated applications will be developed, possibly in multi-fuel applications.

Some properties that have been reported are summarised in Table 5.9.

Table 5.9
Bio-oil Properties

	Alten	GTRI	Laval	SERI	Tubingen	Waterloo	BASA
Elemental Analysis (wet basis)							
C (% wt)	61.90	39.5	49.9	48.6	72.62	54.70	58.12
H (% wt)	6.00	7.5	7.0	7.2	10.75	6.90	6.55
O (% wt)	31.02 (a)	52.6	43.0	44.2	15.06 (a)	38.4 (a)	34.81
N (% wt)	1.05	< 0.1	-	< 0.1	1.27	-	0.52
S (% wt)	0.03	-	-	-	0.24	-	-
Cl (% wt)	-	-	-	-	0.06	-	-
H/C ratio	1.16	2.28	1.68	1.78		1.51	1.35
O/C ratio	0.18	1.00	0.65	0.68		0.53	0.45
Moisture (% wt)	14.60	29.0	18.4	-	-	18.70	4.5
pH	2.0	-	-	-	-	2.40	2.7
Ash (% wt)	1.50	0.2	-	-	-	-	< 0.05
Char content (% wt)	9.20	9.2	-	-	-	-	-
Viscosity, cp	55.	10.	-	1300.	-	40	250.
	@70°C	@60°C		@30°C		@40°C	@60°C
HHV, MJ/kg (wet)	26.3	24.3	21.1	22.3		23.2	22.2
Specific gravity (15/4 °C)	1.195	1.23	-	-	-	-	-
Density, g/cm^3 @ 55°C	-	-	1.23	1.23	-	1.20	1.216
Pour point, °C	27	-23	-	-	-	-	-

a by difference

5.4.3.2 Upgrading

Upgrading technology is based either on orthodox hydrotreating technology to produce successively lower oxygen content hydrocarbons, or the evolving zeolite technology to produce hydrocarbon fuels directly. The chemical principles are summarised in Figure 5.4.

Hydrotreating (Laboratory scale)

C_2H_3O	+	1.5 H_2	—>	2 $(CH_2)_n$	+	H_2O
bio-oil		hydrogen		gasoline, etc		water

Zeolites (Fundamental research)

2 C_2H_3O	—>	3 $(CH_2)_n$	+	CO_2
bio-oil		gasoline, etc		carbon dioxide

Figure 5.4 Conceptual Chemistry of Bio-oil Upgrading Processes

Hydrotreating is based on technology that is established in the petroleum industry and is in principle readily adaptable. Preliminary results indicate that conventional hydrotreating processes may be readily adapted to pyrolysis liquids. The product is a low grade gasoline that would require orthodox refining and blending to give a marketable product. There are two approaches to hydrotreating:

1 A dedicated purpose designed and built hydrotreating operation.
2 Assimilation of bio-oil into a conventional oil refinery to utilise the existing hydrotreating operation.

Zeolite based synthesis has been extensively demonstrated for alcohol feeds, and a commercial plant is currently operating in New Zealand. A little experience has been gained on upgrading products of biomass pyrolysis, but there is insufficient data to draw any robust conclusions. A significant feature is the high yield of aromatics which gives a premium value gasoline product, and from which benzene, xylene and/or toluene could be recovered. There are three basic approaches to synthesising hydrocarbons from pyrolysis liquids. In all cases the crude hydrocarbons would need to be subjected to orthodox refining.

1 Convert primary pyrolysis vapours to hydrocarbons in a close-

coupled operation. The primary product is aromatic-rich gasoline with a significant olefin by-product that could be alkylated to yield more hydrocarbons.

2 Condense the liquids, then process them with zeolites in the liquid phase, which could be a remote operation to take advantage of the economies of scale.

3 Condense the liquids then revaporise them for zeolite upgrading in the gas phase, which again could be a remote operation to take advantage of the economies of scale.

Neither of these upgrading technologies is yet available commercially, nor have robust mass balance and performance data been produced. Hydrotreating is, however, more developed and could use conventional hydrotreating practice for earlier implementation.

An alternative approach is to reduce the oxygen content to a sufficiently low level that it may be satisfactorily blended with conventional fuels. This might be achieved by less complete hydrogenation. Simple distillation over activated clay such as bentonite has been claimed to give a stable and storable product in one low cost step. No work on blending requirements of partially upgraded products is known to have been carried out.

5.4.3.3 Blending

It has been suggested that limited quantities of crude bio-oil could be assimilated into a conventional refinery operation to use existing standard refinery operations for upgrading and refining. This has not yet been explored. Bio-oil has a relatively high oxygen content and oxygen is not easy to remove, being placed in this respect between nitrogen and sulphur contaminants in oil.

5.4.4 Solid product

5.4.54.1 Charcoal

When pyrolysis is optimised for charcoal production, yields of up to 30% wt on dry feed (volatile free basis) are obtained. This occurs in slow pyrolysis with reaction times of hours or days. Partial carbonisation gives higher yields, when the product contains a high level of volatiles, and this is also referred to as torrified wood. At the very high heating rates encountered in fast and flash pyrolysis, very low char yields result, and have been reported as approaching zero under some process conditions. Char yields can be optimised for production of material for char-water slurries, although an integrated approach is necessary for maximum energy recovery.

5.4.4.2 Slurries

A possible outlet for the char is slurrying with the bio-oil, or with water, or with both oil and water. Only a limited amount of char can be introduced into oil as unacceptably high viscosities result from a char concentration higher than about 25% wt. The maximum concentration of char in water that can be handled is about 60% to retain mobility. The costs of the additives are significant at up to 1/3 of the slurry preparation cost. A recent development is the production of a ternary mixture of char, water, and mineral oil which is claimed to have several advantages.

Coal/water slurries are increasingly used in large boilers and these slurries can be simply and/or partially replaced by char/water slurries. The char/water slurry cannot, however, be an outlet for pyrolytic waste water as unstable sludge formation results. The ash content of the char is an important consideration in developing liquid fuels, and de-ashing is necessary. Although in principle it seems to be attractive to remix all products of pyrolysis processing into one single liquid biomass derived fuel, this does not currently seem possible.

5.4.5 Chemicals

Many hundreds of chemical constituents have been identified to date in pyrolysis liquids, and increasing attention is being paid to the possibility of recovering individual compounds or families of chemicals. The potentially much higher value of specialty chemicals compared to fuels could make recovery of even small concentrations viable. An integrated approach to chemicals and fuels production offers interesting possibilities.

5.4.6 Water

A key feature of the pyrolysis process is that water is produced in significant quantities of typically between 20 and 40% wt on the feed, depending on feed moisture content. The water phase is highly contaminated with dissolved and suspended organics, with a COD of typically 150 000 ppm. This therefore represents a major problem of disposal or utilisation. This waste water must be considered in the specification, evaluation and selection of pyrolysis technologies. If biological treatment is not appropriate or too expensive, part of the heat of combustion of the products will be required for incineration of this heavily contaminated water fraction. The pyrolysis gas could be used for this purpose but this may not be enough in cases where the primary feedstock has a high water content and the gas is required for feed drying.

Design specifications of future liquid fuel production processes are likely to require oil condensation above 100°C to avoid production of a discrete water phase. The water and lower boiling point organics would thus remain in the gas stream to be burnt i.e. incinerated.

The water content can be considered an advantage because it reduces the viscosity of the liquid (see Section 3.2.5). In this respect, therefore, the raw oil can be considered an outlet or disposal route for some of the pyrolysis water. Phase separation is likely to occur at water concentrations greater than 20% which could only be counteracted by costly emulsifiers. Moreover the water could render the oil more unstable and more corrosive. Methanol has been suggested as a possible additive but not evaluated.

5.4.7 Gas product

The gaseous product from pyrolysis is usually a MHV fuel gas around 15-22 MJ/Nm^3, or a LHV fuel gas of around 4-8 MJ/Nm^3 from partial gasification depending on feed and processing parameters. It has a high level of hydrocarbons, particularly methane, and saturated and unsaturated hydrocarbons from the complex thermal degradation processes. The heating value is enhanced if the gas is used hot, from the sensible heat, and the relatively high tar content. The gas may be used for feed drying, process heating, power generation, or export for sale.

5.4.8 Pyrolysis Status

A demonstration plant of 500 kg/h is currently operating in Italy for liquid production with plans for a series of small commercial units there, and in Spain and in Greece. A number of demonstration plants for flash pyrolysis are operating in North America at a scale of up to 25 kg/h with plans for several commercial developments ranging up to 20 t/h, including a commercial installation planned for California based on the SERI ablative pyrolyser. Examples of current activities are described below in Section 5.5.

5.5 PYROLYSIS TECHNOLOGIES

Pyrolysis produces a solid char, liquid products (tar and pyroligneous acid) and a fuel gas, the proportions of which are dependent on the process conditions and the nature of the feedstock. It has been found that heating rate and temperature play an important role in the distribution of the pyrolysis products. At low heating rates between 0.01°C/s and 2°C/s and at relatively low temperatures of less than 500°C, char, gas and liquid products are produced in approximately equal amounts. Flash and fast pyrolysis are claimed to involve extremely high heating rates from 1000°C/s up to 1×10^6°C/s. This high heating rate and the very low residence times maximise the production of liquid products (at temperatures up to 600°C) or gaseous products (at temperatures above 700°C) while minimising char formation.

Examples of recent and/or well developed pyrolysis activities are summarised below to show how different groups of researchers have tackled the problems of high heating rate, low temperature and rapid quenching of products to maximise yields of preferred products. The examples are listed in Table 5.10 with cross reference to the section where they are described, and the key features of each process are summarised in Table 5.11. The rest of this chapter is devoted to a description of each of the processes referred to in Tables 5.10 and 5.11.

Table 5.10
Examples of Pyrolysis Technologies

Pyrolysis technology	Organisation	Section
Liquids		
Conventional for liquids	Alten (KTI + Italenergie)	5.1
Transport for liquids and gases	Ensyn Engineering	5.2
Fast entrained flow for liquids	Georgia Tech Research Inst.	5.3
Vacuum for liquids and chemicals	Laval University	5.4
Ablative for liquids and chemicals	Solar Energy Research Inst.	5.5
Low temperature for liquids and charcoal	Tübingen University	5.6
Flash fluid bed for liquids and chemicals	Waterloo University	5.7
Solids		
Conventional for charcoal and liquids	Bio-Alternative SA	5.8
Gases		
Molten salt pyrolysis for gases	Aston University	5.9
Methanopyrolysis for gases & chemicals	Brookhaven National Lab.	5.10
Hydropyrolysis for gases and hydrocarbons	Toronto University	5.11
Twin fluid bed fast pyrolysis for gases	TNEE	5.12
Free fall radiation for gases	University of Zaragoza	5.13
Chemicals		
Transport for liquids and gases	Ensyn Engineering	5.2
Vacuum for liquids and chemicals	Laval University	5.4
Ablative for liquids and chemicals	Solar Energy Research Inst.	5.5
Flash fluid bed for liquids, chemicals, sugars; also hydropyrolysis for hydrocarbons	Waterloo University	5.7
Molten salt for gases and chemicals	Aston University	5.9
Methanopyrolysis for gases & chemicals	Brookhaven National Lab.	5.10
Hydropyrolysis for gases and hydrocarbons	Toronto University	5.11

Table 5.11
Comparison of Process Technology

Institution	Reactor type	Capacity, kg/h	Reaction temp. °C	Additives	Reaction time, s	Main product(s)	Yield on dry feed, % wt	Special features	Section number
Alten	Stirred bed with air	500	500	Air	1-20	Char, bio-oil	25, 20	Pyrolysis by partial gasification.	5.1
Ensyn	Jet with heat carrier	10	600-1000	Hot sand	0.05-0.9	Gas	80	Reactor is more compact as heat is provided by hot sand.	5.2
		30	450-800	Hot sand	0.3-1.5	Bio-oil	76		
		100	450-600	Hot sand	0.6-1.5	Bio-oil, chemicals	74		
GTRI	Entrained flow	57	400-550	Hot gas	1	Bio-oil	60		5.3
Laval University	Multiple hearth (x6)	30	250 at top 450 at base	None	10-40	Bio-oil, char	50, 25	Vacuum process, <0.1 bar Fractionation of products.	5.4
SERI	Vortex/cyclone	30	475-625	Steam or N_2	1	Bio-oil	55	Ablative pyrolysis gives high reactor heat transfer rates	5.5
Tubingen University	Rotary furnace	80	280-350	None	15-30 min			Very low oxygen product.	5.6
Waterloo University	Shallow fluid bed	3	425-625	Hot gas	0.5	Bio-oil	68	Catalyst can be used in place of sand to yield new products.	5.7
Bio-Alternative	Fixed bed	2000	500-800	Air	15-30 min	Char, oil	30, 15	Oil recovery at >100°C gives	5.8

								dry product and no water.	
Aston University	Molten salt	3	250-500	Salts	15-30	Gas	up to 100	Gas is relatively pure as impurities are left in the melt.	5.9
Brookhaven	Entrained flow	1	600-1000	CH_4 etc	1	Gas	88	Methanolysis produces C_2H_4 and C_6H_6 @ 275 bars pressure.	5.10
Toronto University	Autoclave	0.1	300-350	H_2	180	Liquid	50	Uses wood chips instead of slurries @ 240 bars pressure.	5.11
TNEE	Twin fluid bed	500	650-1000	None	1	Gas	80		5.12
Zaragoza University	Free fall radiation	110	1000-2200	Hot N_2	<1	Gas	78-98	Heated by radiation. Tubular reactor with biomass in free fall.	5.13

5.5.1 Conventional pyrolysis for liquids

Example: Alten - Alternative Energy Technologies (A consortium of KTI and Italenergie, but no longer in partnership)

The aim of this activity is to develop a small scale pyrolysis process to convert wood and agricultural wastes into marketable fuel products such as fuel oil, charcoal and char-water slurries. The application envisaged was a network of small scale pyrolysis plants to produce bio-oil to fire a 27MW power station in the context of the Avezzano LEBEN project [155-158].

5.5.1.1 Introduction

The pyrolysis plant, developed by Alten (KTI and Italenergie), has been in operation since 1985, and is the largest biomass pyrolysis unit dedicated to bio-oil production in Europe. The design capacity of the plant was 1 t/h dry biomass, but only 300 to 500 kg/h has been achieved on a continuous basis.

5.5.1.2 Description and operation

Figure 5.5 shows the arrangement of equipment. The feed is screened, rechipped and dried in a rotary drier before entering the fluid bed reactor. Drying fuel is currently propane, but the product fuel gas would be used in a commercial venture. Air is added to the reactor to give a partial gasification reaction to provide reaction heat. This results in a poor quality, low heating value fuel gas. The reaction temperature and pressure are about 500°C and 1 atm respectively. The char formed is separated from the vapour stream in a hot gas cyclone. The char is cooled in a sequence of water cooled screw conveyors and stored in a silo.

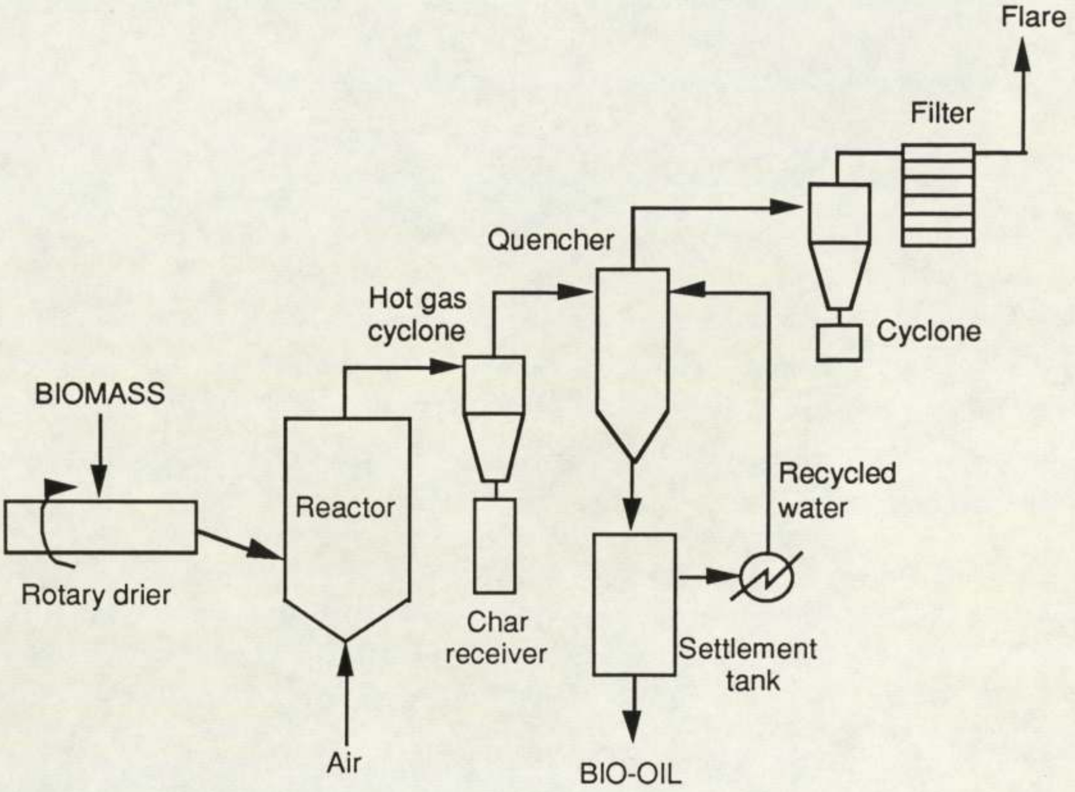


Figure 5.5 ALTEN (KTI + Italenergie) Pyrolysis System

The vapour and gas streams pass through a quench vessel where they are cooled and condensed by direct contact with recycled product water. The mixture of oil and water is separated in a settlement tank before sending the oil to storage and recycling the water through an air cooler. Excess water is removed to maintain a constant height interface. The resulting water condensate has a very high COD at around 150000 ppm and requires treatment prior to disposal. Further liquid is removed from the product gas in a cyclone and filter, before burning the gas in a flare.

The gas from the drier is also sent to the flare to eliminate pollutants. If the gas is required for electric power generation, the gas would have to be first cooled and dried to about 30°C before used in a gas engine. The gas may also be used internally as a fuel source for drying the feed or other process heat applications.

Feedstocks tested include wood chips, olive husks, straw and vine trimmings.

5.5.1.3 Results

A typical mass balance and energy output are shown in Table 5.12.

Table 5.12
Typical Mass Balance

Basis: 100 kg d.a.f. biomass feed

INPUTS	kg	OUTPUTS	kg	% Energy
Dry biomass	100.0	Charcoal	20.5	30
Moisture	2.0	Bio-oil	20.5	23
Pyrolysis air	33.0	Fuel gas	68.0	37
		Steam + organic vapours	26.0	5
		Losses	-	5
TOTAL	135.0	TOTAL	135.0	100

5.5.1.4 Properties of Products

The bio-oil is black and fairly viscous and contains a significant proportion of charcoal of up to 15% by weight of the oil. This caused a "lumpy" texture in early samples. A typical bio-oil analysis is shown in Table 5.13, and a gas analysis in Table 5.14.

The char is a coarse powder with particle sizes ranging from 40-50 microns to several mm, which are mainly needle shaped and similar to the size and shape characteristics of the feed. It has a high porosity and a large surface area, about 15-20% volatiles, a very low sulphur content and a low oxygen content. The char has an empirical formula $CH_{0.25}O_{0.07}$ and a higher heating value of 29.5 MJ/kg. Experiments are being carried out to obtain a pumpable charcoal-water slurry that can be burnt in industrial installations. Up to 60% weight solid slurries have been successfully produced. Char-bio-oil slurries have also been produced, but the maximum solids content is 30%.

Table 5.13
Typical Bio-oil Analysis

Elemental Analysis (wet basis)	
C (% wt)	61.90
H (% wt)	6.00
N (% wt)	1.05
S (% wt)	0.03
O (by difference)	31.02
H/C ratio	1.16
O/C ratio	0.18
Moisture (% wt)	14.60
Ash (% wt)	1.50
Char content (% wt)	9.20
Viscosity, cp @ 70°C	55
HHV, MJ/kg	26.3
Specific gravity (15/4 °C)	1.195

Table 5.14
Gas Analysis-Dry basis

CO	27.6	% vol
CO_2	21.8	% vol
H_2	4.7	% vol
O_2	0.7	% vol
N_2	38.2	% vol
CH_4	4.7	% vol
C_2H_4	0.4	% vol
C_2H_6	0.3	% vol
Others (by difference)	1.6	% vol
Higher Heating Value	5 MJ/Nm^3	

5.5.1.5 Special features and problems

It was the first substantial plant for bio-oil production to be designed and built in Europe, and remains the only large scale plant. Its performance has not yet been optimised.

Particular problems reported include:

- reactor control of temperature and solids flowrate
- char separation from the pyrolysis vapours
- char in the bio-oil product

- waste water disposal
- gas cleaning prior to flaring
- drying energy requirement
- scale-up

5.5.2 Fast entrained flow pyrolysis for gases and chemicals

Example: Ensyn Engineering Associates Inc, Canada

This project was initiated around 1986 with the main objective of employing fast pyrolysis to produce non-equilibrium chemicals such as ethylene and propylene on a continuous commercial scale. The process can also be used to produce pyrolytic liquids for fuel oil and chemicals production [72,76,159-162].

5.5.2.1 Introduction

Around 1981, a fast pyrolysis experimental programme (Ultrapyrolysis) was started at the University of Western Ontario in collaboration with the Forintek Canada Corporation with support from the ENFOR programme of the Canadian Forestry Service (Environment Canada and Energy Mines and Resources, Canada). The aim was to develop a new reactor design in order to exploit and optimise fast pyrolysis product yields. An Ultra-Rapid Fluidised reactor (URF), with a maximum feed rate of 1 kg/h, was designed and constructed.

The URF system utilises either a solid heat carrier such as sand or a gas heat carrier like nitrogen, to carry heat, into a turbulent vertical contactor , (a cyclonic mixer termed a "thermovortactor") where rapid mixing between the feed particles and heat carrier occurs within 30 ms. This rapid heating causes fast pyrolysis which leads to the production of non-equilibrium chemical intermediates such as ethylene. This reaction continues in the plug-flow entrained reactor. The reactor is a 1 m length of Inconel pipe heated by an electric oven. The products are initially quenched in the "cryovortactor" (also a cyclonic mixer with cryogenic nitrogen as the coolant) while additional cooling is carried out in a water cooled coil heat exchanger. This cooling helps to freeze the intermediates before subsequent decomposition and/or repolymerisation occurs.

Feed rates of up to 0.3 kg/h have been achieved along with reactor temperatures in the range 650-1000°C and gas residence times of 50-900 ms. Over 500 runs have been carried out using the above system with feedstocks such as Avicel cellulose (100 mm powder), IEA poplar, red maple and lignin. For cellulose, it was found that the asymptotic total gas yield increased from 28% (by mass) to 88% as the temperature was increased from 650 to 900°C. Kinetic data have also been obtained from this system.

The success of this process led to the design, construction and testing of a Rapid Thermal Processing (RTP) reactor system, rated nominally at 10 kg/h which is about 20 times the capacity of the URF system. Two additional upflow (transport) reactors have been designed and tested at wood feed rates of 30 and 100 kg/h. Results were consistent with the 10 kg/h downflow unit. Three more RTP units are scheduled

5.5.2.2 Description and operation

Figure 5.6 shows the arrangement of equipment of the RTP downflow process. Upflow reactor patents have been filed and are not disclosed at present.

Hot sand flows from two heat carrier feeders to the jet reactor system where they are injected towards the centre of the RTP reactor. The feedstock is delivered from a feeder to the top of the reactor and then injected into the cloud of turbulent hot solids. Heat is transferred to the feedstock as the feed and hot sand are mixed together. After mixing, the feed and sand pass through a tubular reactor, the length of which can be adjusted to control the residence time. Furnaces are used to heat the sand feeders, mixer and the reactor lengths, and these are activated about 8 hours before an experiment. The sand feeder ovens are set at a temperature about 150°C higher than the desired reaction temperature to make up for the heat losses due to the transport/reactor system and also to provide the heat required to raise the feedstock from ambient to reaction temperature.

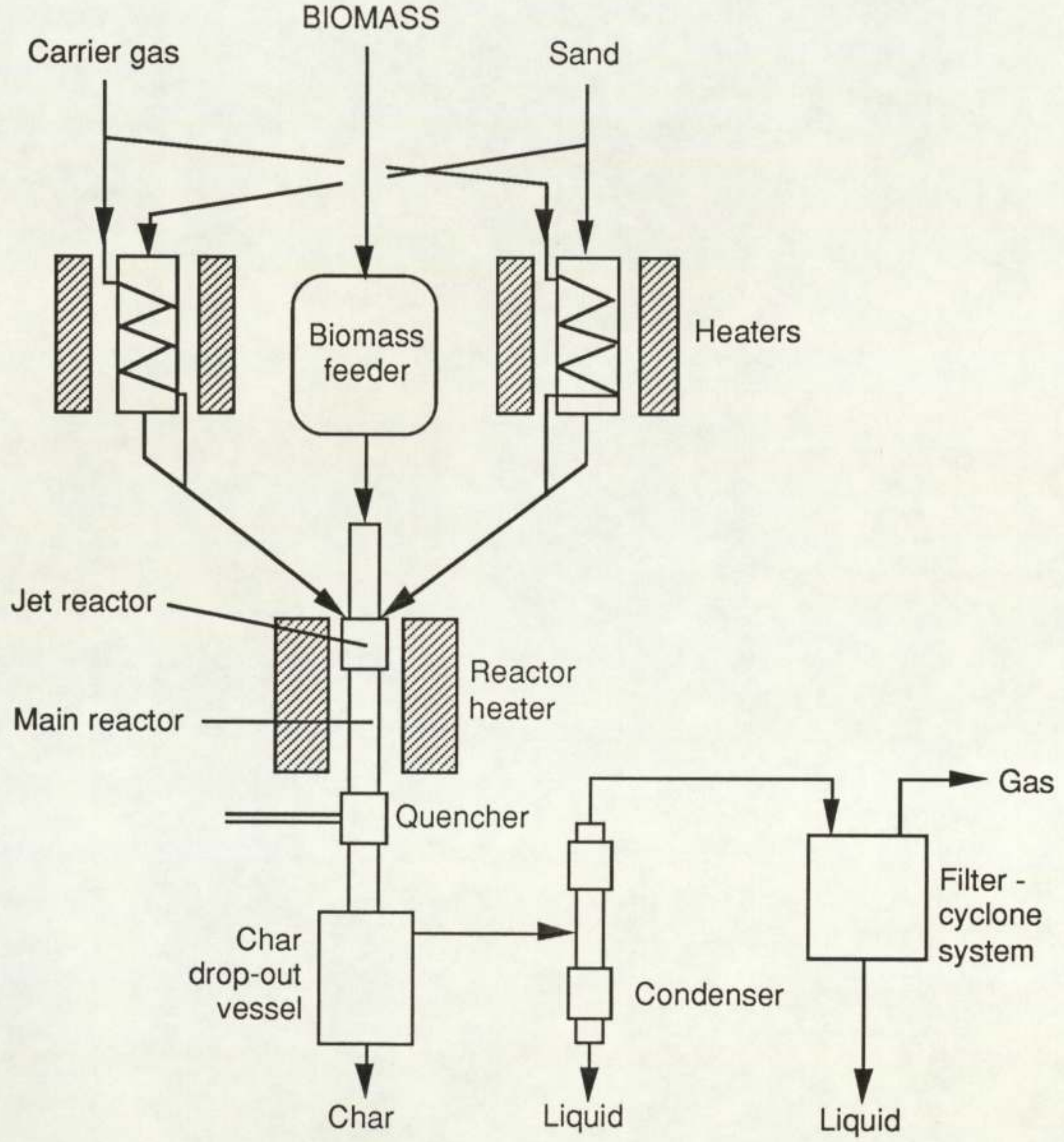


Figure 5.6 Ensyn Entrained Flow Pyrolysis System

The sand flow rates are adjusted to maintain the desired reactor temperature and to ensure isothermal conditions. The products are rapidly quenched in a quench vessel and the solids are removed in a drop-out vessel. A condenser and filter/cyclone system are then used to separate the liquids from the gaseous products. The fluid products are sampled and identified by standard analytical procedures. An electrostatic precipitator is used when aerosol yields are high.

Gas samples are collected in sampling bags and are analysed for hydrogen, carbon dioxide, carbon monoxide and C1 to C6 hydrocarbons.

5.5.2.3 Results

Table 5.15 shows typical results that were obtained using the RTP and the URF unit. The results obtained are similar. The maximum total liquid yield obtained from poplar to date is 80% at 500°C and 250 ms. The maximum total liquid yield from cellulose is 90% at 650°C and 100 ms residence time, and for hardwood, maximum total liquid yield is 77% at 550°C and 250 ms residence time. Char yields ranged from 15% at 500°C to approximately 3% at 800°C. An analysis of the liquid product has been carried out but results are not available. Over 900 experiments have been carried out with mass balance closures from 91-110%.

Table 5.15
Poplar Pyrolysis - Gas Yields

(dry wood basis, % by mass)

	RTP (20 kg/h)					URF (1kg/h)
Temperature, °C	650			800		800
Residence time, ms	800	210	570	190	527	195
Gas composition						
CO	16.5	13.5	43.3	38.0	41.9	40.0
CO_2	9.9	6.9	6.8	8.4	10.8	10.0
H_2	0.1	0.1	0.5	0.5	0.9	0.8
CH_4	3.3	1.1	6.7	4.3	5.6	5.0
C_2H_4	1.6	1.4	4.0	3.3	4.3	3.9
Others	1.5	1.9	2.3	2.2	5.6	5.4
Total gas yield	32.9	24.9	63.6	56.7	69.1	65.1

5.5.2.4 Special features and problems

Because sand is used to heat the feedstock instead of gas, the design is more compact since the heat capacity of solids is higher per unit volume than for gas.

Solids are more easily separated from the product gas allowing less dilution and a corresponding higher energy density.

The size of a scaled-up reactor will depend to a large extent on the heat flux

Problems include:

- Materials of construction at high temperature with abrasive solids, which is overcome with the upflow design,
- Residence time control in a scaled-up process.

5.5.3 Fast entrained flow pyrolysis for liquids

Example: Georgia Tech Research Institute, USA

This project was initiated in 1980 with support from the US Department of Energy (USDoE). The aim of this project is to determine the conditions required to optimise oil yields from wood using an entrained flow pyrolyser [163-169].

5.5.3.1 Introduction

Earlier research in the 1970's showed that higher oil yields could be obtained by using a rotating tube furnace (typically 28 wt%) rather than a stationary one (typically 17 wt%). This increase was attributed to the "showering" of the wood particles through the gases in the rotating tube furnace as opposed to the "packed-bed" mode of the stationary type. Based on the above observation plus literature reports on the pyrolysis of sawdust in fluidised beds, an entrained flow bed reactor was designed for the production of oil.

A process research unit was built and completed in 1983. In 1985, modifications were made so that optimisation of the oil yield could be further investigated, based on experience gained in the operation of the pilot plant and the results of the commissioning runs. The major changes were the replacement of the 8 in. diameter (20.32 cm) reactor tube with a 6 in. (15.24 cm) tube, the addition of a quench vessel and a second demister. The nominal operating feed rate is 56.8 kg/h of dry biomass.

5.5.3.2 Description and Operation

Figure 5.7 shows the arrangement of the equipment of the process.

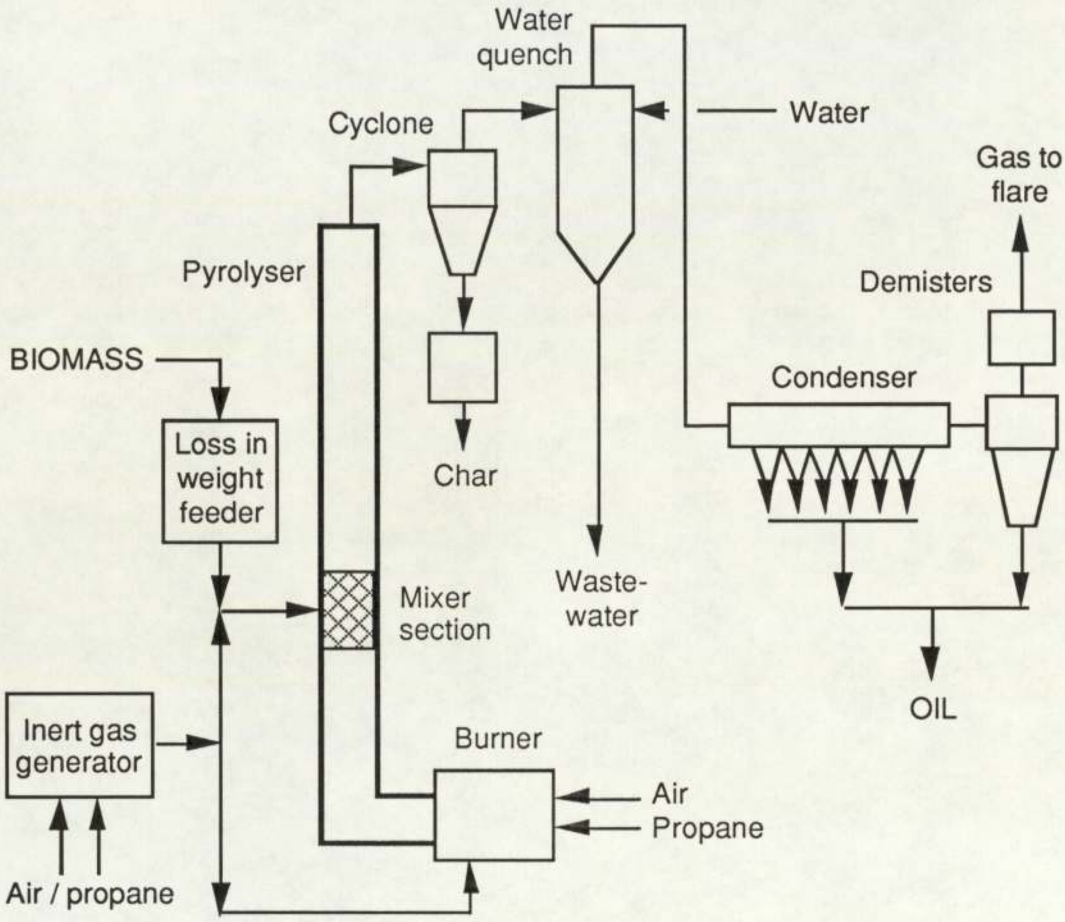


Figure 5.7 GTRI Entrained Flow Pyrolysis System

The feed is dried, hammer-milled to about 1.5 mm and fed from a loss-in-weight feeder into the reactor via a rotary valve. The reactor used is a 6 in. inner diameter vertical tube made of stainless steel. The initial feed point was the refractory lined mixing section, located below the reactor tube. However, by introducing the feed into feed ports higher up the reactor, the effective length of the reactor could be reduced which in turn reduced the residence time.

The wood particles are entrained in a stream of hot combustion gas (1700°F, 927°C) obtained by burning propane gas and air stoichiometrically. Gas and wood flow cocurrently upwards through the reactor tube in which pyrolysis takes place; the resulting mixture consists of non-condensible gases, water vapour (moisture plus pyrolytic reaction water), pyrolysis oil vapours and char.

A cyclone separator is used to remove most of the char particles. The exiting gas stream consists of non-condensible gases, water vapour, pyrolysis oil vapours and some char fines. The hot effluent enters a water-sprayed quench vessel where it is rapidly cooled. Following the quench vessel, the mixture enters an air-cooled condenser in which the pyrolysis vapours are condensed with some water vapour. The condensed phases are removed via sumps and receivers and the gaseous product is passed through two demisters connected in series. Most of the aerosols present in the gaseous product are removed in the demisters. The remaining effluent, consisting of non-condensible gases, water vapour and remaining aerosols, enters a flare where it is burnt and the combustion products are exhausted to the atmosphere.

5.5.3.3 Results

Table 5.16 shows some of the most recent results with liquid yields approaching 60% wt on feed. Recent modelling and optimisation studies have produced predictive models which indicate that yields of 70 wt% are achievable with a well designed reactor and system.

Table 5.16
GTRI Product Yields (Modified Reactor)

Run No.	2-11/0	2-12/0	3-17	3-18	3-19
Temperature, °C	501	524	499	504	500
Yields (% wt dry ash free feed)					
Oil	48.1	53.8	52.1	60.0	54.9
Char	7.6	8.4	10.0	12.1	21.2
Total gas*	44.3	37.8	37.9	27.9	23.9

* by difference

5.5.3.4 Properties of Products

The oils are highly oxygenated with no phase separation. They have an initial boiling point range from 70°C to 90°C. They are heat sensitive and will decompose when heated to temperatures greater than 185°C-195°C. The oils are acidic, have an acrid odour and also exhibit corrosive properties with some metals. A typical bio-oil analysis is shown in Table 5.17.

Table 5.17
Typical Bio-oil Analysis from GTRI

Elemental Analysis (wet basis)	
C (% wt)	39.5
H (% wt)	7.5
N` (% wt)	< 0.1
S (% wt)	-
O (% wt)	52.6
H/C ratio	2.28
O/C ratio	1.00
Moisture (% wt)	29.0
Ash (% wt)	0.2
Char content (% wt)	27-31
Viscosity, cp @ 60°C	10
HHV, MJ/kg	24.3
Density, g/cm^3	1.23

5.5.3.5 Special features and problems

A reactor model has been devised and tested that predicts that yields of over 70% are achievable.

Recent design studies show that with current wood and biomass prices in the USA, and current energy costs, a 2 t/h module can be economically viable and give an acceptable payback time on the investment.

In the scaled up process waste water production will be minimised or eliminated by controlled cooling and condensation of oil.

Problems include:

- accumulation of tarry material in the first stages of the air-cooled condenser,
- design of high temperature bio-oil cooler/condenser to avoid water condensation,
- lack of operational experience on recycled product gas for reactor heating.

5.5.4 Vacuum pyrolysis for fuels and chemicals

Example: University of Laval, Canada

The objective of this project is to investigate the potential of low pressure pyrolysis to produce high yields of condensible vapours and selectively condense fractions from different sections of the reactor to examine the potential for fractionation and recovery of chemicals [84,105,170-173].

5.5.4.1 Introduction

Early studies carried out by the University of Sherbrooke indicated that pyrolysis under reduced pressure can be employed to convert biomass into chemical and fuel products. This method is characterised by low pressure and short residence time of the vapour products within the reactor. A series of experiments were conducted batchwise by using a retort operated at temperatures between 207-534°C. The optimum temperature range was found to be between 350-400°C and a yield of 60 wt % (on a dry ash free wood basis) of pyrolytic oil was obtained at an average heating rate of 10°C/min and at a total system pressure between 0.3 and 2.3 mmHg (40-307 Pa). The feedstock used was aspen poplar. In view of the high yields of pyrolytic oil obtained using low pressure pyrolysis, a 30 kg/h vacuum pilot plant, based on this technique, was designed, constructed and tested.

5.5.4.2 Description and Operation

Figure 5.8 shows the arrangement of equipment of the process.

The feed is wood chips with a particle size from 1/4" to 1/2" Tyler mesh (6 mm to 12.7 mm). They are fed via a hopper on the top of the reactor, which is hermetically sealed. This is equipped with a variable rate feeding device that feeds the chips into the preheated reactor at a constant feed rate of between 0.8 to 4 kg/h.

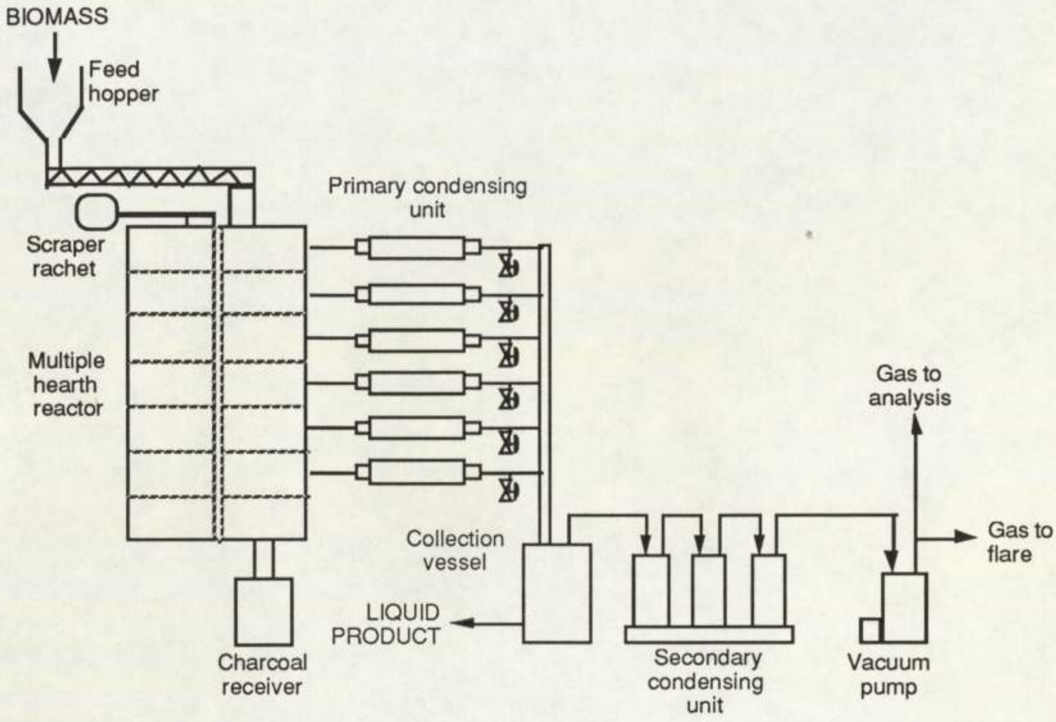


Figure 5.8 University of Laval System

The reactor is a multiple hearth furnace 2 m high and 0.7 m diameter, with six hearths. Electric heating elements are used to heat the reactor. The temperatures of the heating plates increase from top to bottom of the reactor. A typical temperature profile is 200°C to 400°C. At steady state conditions, the absolute system pressure of the system is less than 80 mmHg (10.7 kPa). The organic vapours and gaseous products are removed from the reactor by a mechanical vacuum pump via six outlet manifolds which correspond to the six heating plates. The char falls to the bottom of the reactor where it is collected in a metallic jar on a load cell. The process unit is connected to a central microprocessor which simultaneously gathers data and controls about 75 operating parameters.

The clean-up system is a series of shell and tube heat exchangers (primary condensing unit) and a train of receivers (secondary condensing unit). Each outlet manifold is connected to a heat exchanger where the vapours are condensed and recovered as organic liquid in individual receivers. Cool to warm tap water is used as the cooling medium on the shell side. The vapours from the heat exchangers are then collected in the secondary condensing unit where the aqueous phase is primarily recovered. The first receiver is immersed in a bath of water-ethylene glycol mixture. The next two are immersed in baths of dry ice-acetone while the final receiver is filled with glass wool at room temperature. The non-condensible gases are pumped into a 500 litre vacuum vessel.

5.5.4.3 Results

Some results obtained using the multiple hearth reactor are shown in Table 5.18. The highest yields of "bio-oil" are obtained at the lowest pressure and the higher temperature conditions. The optimum temperature range for maximum oil yield from wood was found to be between 425-450°C at the bottom of the reactor.

Table 5.18
Product Yields for Low Pressure Pyrolysis at Laval University

Temperature, °C	425	363	465	450
Pressure, mm Hg	12	18	80	12
Feedstock, kg	5.98	5.99	3.39	15.43
Yields (% wt wood organic basis)				
Oil	46.4	41.6	39.7	50.9
Water	18.2	14.9	21.6	16.5
Char	24.2	33.0	24.7	21.3
Total Gas	11.2	10.5	14.0	11.3
Gas composition (vol%, dry basis)				
CO	59.2	60.4	60.0	60.7
CO_2	33.6	34.9	31.4	31.6
CH_4	2.4	0.9	3.3	2.7
H_2	0.9	0.1	0.7	-
Others	3.9	3.7	4.6	5.0

One potential advantage of using a multiple-hearth reactor configuration is the capacity to fractionate the pyrolysis products by use of multiple outlets at different levels (see Table 5.19). The separation of the aqueous and the oil phases is important at the industrial level because the recovery of chemicals during distillation of a large amount of water is less economical.

Table 5.19
Separation of Water and Pyrolytic Oil During Condensation

Run no	Reactor Pressure (mm Hg)	Temperature, °C		Primary Condensing Unit		Secondary Condensing Unit	
		Hearth VI	Cooling Water	Oil (%)	Water (%)	Oil (%)	Water (%)
C019	80	465	11-28	52.2	19.2	7.4	21.2
C023	12	450	50-55	32.2	1.5	36.7	29.6
C024	30	450	30-35	39.8	1.6	27.2	31.4
C025	10	450	15-20	47.8	3.4	27.2	21.6

Percentages are based on total condensates

5.5.4.4 Properties of Products

A typical analysis of the oil is shown in Table 5.20. This oil is highly oxygenated and consists of phenols, sugars and both aliphatic and aromatic hydrocarbons. The gases are mainly CO and CO_2.

Table 5.20
Elemental Analysis of Bio-oil from Laval University

Elemental Composition, wt%	
Carbon	49.9
Hydrogen	7.0
Oxygen	43.0
Nitrogen	-
H/C ratio	1.68
O/C ratio	0.65
Ash	-
Moisture	18.4
Density, g/cm^3@ 55°C	1.23
Viscosity, cp	-
Heating Value, MJ/kg	21.1

5.5.4.5 Special Features and Problems

Low pressure removes the primary products quickly and avoids secondary reactions.

Fractionation provides some separation of liquids evolved at different temperatures in a continuously operating system.

Recent testing of this unit at throughputs of 30 kg/h showed that the primary condensing unit composed of six shell and tube heat exchangers were inefficient due to clogging problems. The six individual exchangers were substituted by a single spray type condensing unit, similar to the secondary condensing unit. The new system proved to work very satisfactorily.

Other problems include:

- Heat transfer to the hearths in a scaled-up operation,
- High volume of reactor and other equipment from vacuum operation,
- Development of very large capacity vacuum pumps,
- Uncertain scale-up potential for wood feedstocks.

5.5.5 Ablative pyrolysis for liquids and chemicals

Example: Solar Energy Research Institute, USA

The original aim was to convert biomass into non-equilibrium gases in a low pressure process without the addition of a catalyst. This aim was modified in 1984 to produce liquid fuels in high yield, and more recently it has been modified again to consider production of hydrocarbon fuels such as gasoline, aromatics such as benzene, xylene and toluene, and chemical fractions such as polyphenols [67,68,114,174-176].

5.5.5.1 Introduction

In 1980 it was demonstrated that when biomass was moved relative to a red-hot Nichrome wire, rates of pyrolysis of up to 3 cm/s were measured as a localised surface phenomenon. Extremely high heat fluxes were attained by this technique and it was found to be two orders of magnitude greater than black body radiation at similar wall temperatures.

Initially a smooth walled vortex reactor without a recycle loop, made from Inconel 800H in order to withstand temperatures of 1000°C, was used.

However, early experimentation demonstrated that severe coke deposits were formed at wall temperatures much above 625°C. Since a lower reactor temperature of 625°C was needed, a vortex reactor made from stainless steel was designed, constructed and tested. Very high organic vapour yields resulted from this lower wall temperature operation. The design capacity of the vortex reactor is 50 kg/h biomass but the maximum throughput achieved to date is 32 kg/h.

5.5.5.2 Description and Operation

Figure 5.9 shows the current configuration of the reactor system.

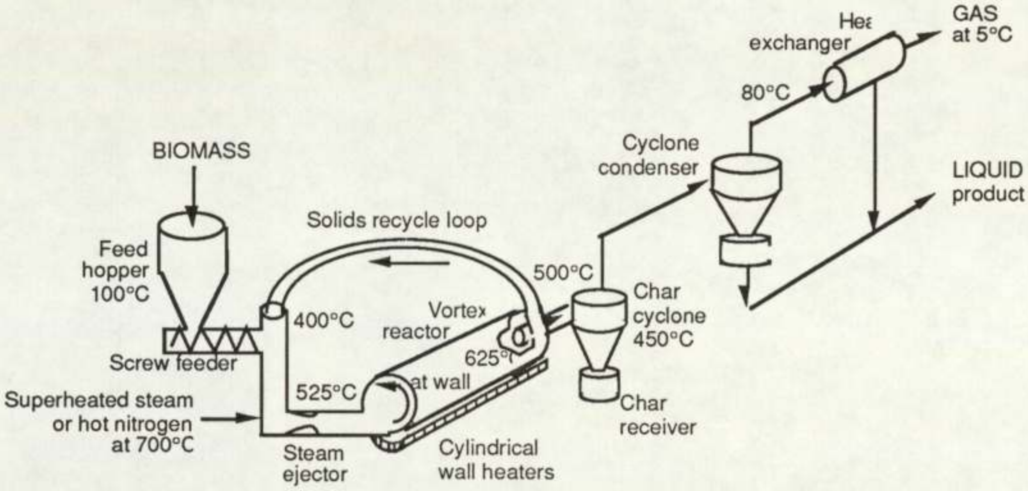


Figure 5.9 SERI Vortex Pyrolysis System

Biomass, with a particle size of about 5 mm, is metered into the system, where it is entrained and mixed with the recycle stream. The biomass particles, entrained in the carrier gas, enter the vortex reactor tangentially at speeds of over 400 m/s so that the particles are forced to the reactor wall by high centrifugal forces.

The reactor is made from 316 stainless steel with a diameter of 13.4 cm and a length 70 cm. The reactor is heated externally by three electric cylindrical furnaces. To force the particles into tighter helical paths than would naturally occur, a helical rib having a pitch of 25 mm and width and height of 3 mm was machined from the wall of the reactor. An insulated recycle loop is also added tangentially at the exit of the reactor to recycle partially pyrolysed feedstock and any large char particles. The fine char, gases and vapours in the reactor leave through the axial exit which extends part way into the reactor.

The wall temperature has to be limited to a maximum of about 625°C to ensure production of a liquid film between the wall of the reactor and the particle which then vaporises and leaves the reactor. Higher wall temperatures result in solid coke formation on the wall which prevents rapid particle movement and quickly fouls the heat transfer surfaces of the reactor.

The product stream then passes through a char cyclone where the char is removed. The diameter is 4 in. (10 cm) and operates at 475-500°C. The vapours pass to the first heat exchanger which is a 38 cm diameter cyclone. The condensed liquids and water are retained in the receiver. The cooled gas stream at about 80°C is then passed to a series of heat exchanger before passing through an orifice meter, and then to flare.

5.5.5.3 Results

Using this experimental layout, oil yields of 67% wt (including moisture on a wet feed basis) or 55 % (dry oil/ on dry feed basis) have been obtained with about 10% wt (on a dry feed basis) char.

5.5.5.4 Properties of Products

The liquid obtained is highly oxygenated, dark brown in colour and acidic with a pH between 2 and 3. Because of this acidity, the oil has been stored in glass or stainless steel tanks. The aqueous and the organic condensates are dissolved in each other. If nitrogen is used rather than steam as the carrier gas, an organic phase and an aqueous phase are both present at water contents above about 25%. Small samples of the oil have appeared to be stable at room temperatures for a prolonged time but exothermal reactions will occur if the temperature of the oil is raised to 100°C or more. The fresh oil vapours have been found to irritate the eyes and the nose; however, when tested to investigate whether they were carcinogenic with cancer-prone mice, they were found not to promote formation of cancer cells. Analytical data is given in Table 5.21.

Table 5.21
Elemental Analysis of Bio-oil from the SERI Process

Elemental Composition, wt% on feed	Result A	Result B
Carbon	48.6	54.4
Hydrogen	7.2	5.7
Oxygen	44.2	39.8
Nitrogen	< 0.1	
H/C ratio (atomic)	1.78	
O/C ratio (atomic)	0.68	
Ash	-	0.05
Moisture	-	15
Density, g/cm3@ 55°C	1.23	
Viscosity, cp	90 @ 30°C	
Heating value, MJ/kg	22.3 *	20.3

* calculated

The phenol fraction has been successfully extracted and polymerised with formaldehyde to form a plywood resin. This process is being commercially exploited.

While MSW has been successfully pyrolysed, problems arose from early deposition of an asphalt like condensate (having a melting point of around 80°C) in the first heat exchanger, which required modification of the condenser train.

The char from wood has a volatile content of 15-45 %, a bulk density between 0.18 to 0.24 g/ml and a higher heating value of 33 MJ/kg. The empirical formula is $CH_{0.53}O_{0.12}$.

5.5.5.5 Special features and problems

a) Very high heat transfer rates are achieved between the hot wall and biomass particles centifuging against the hot reactor wall,

b) unpyrolysed material is easily recycled through the solids recycle loop,

c) the reactor has a very high specific capacity and can in principle be easily scaled up. Although the heat transfer is novel, it has been modelled based on first principles.

d) zeolite synthesis of gasoline and aromatics has been demonstrated on a slipstream,

e) recovery of phenolics for resin production is being commercialised,

f) the concept is planned to be scaled-up for liquid fuel production by Interchem-Pyrotech Inc in Northern California.

Problems include:

- recovery of the oils has been proved to be difficult because of their volatility (due to aldehydes) and their tendency to form stable aerosols,
- many of the condensibles are water soluble.
- MSW pyrolysis gives a heavier and more viscous product with a high melting point that requires different handling and recovery.

5.6 Low temperature pyrolysis for liquids and charcoal

Example: Tübingen University, West Germany

The objective of this research is to convert biomass such as sewage sludge, agricultural wastes and refuse/MSW into fuels or raw materials for the organic chemicals industry [177-182].

5.5.6.1 Introduction

This process was developed as an alternative solution to landfill and incineration of sewage sludge. Several batch and continuous laboratory scale plants up to 5 kg/h have been built and tested. The principle is to use low temperatures of less than 350°C and long reaction times of up to an hour to achieve low oxygen content oils and high yield of fine chemicals. The principle has been licensed to several organisations in Europe, North America and Australia and several plants of up to 2 t/h are operating or under construction based on sewage sludge or MSW.

5.5.6.2 Description and Operation

Figure 5.10 shows one configuration of the reactor system based on dried sewage sludge.

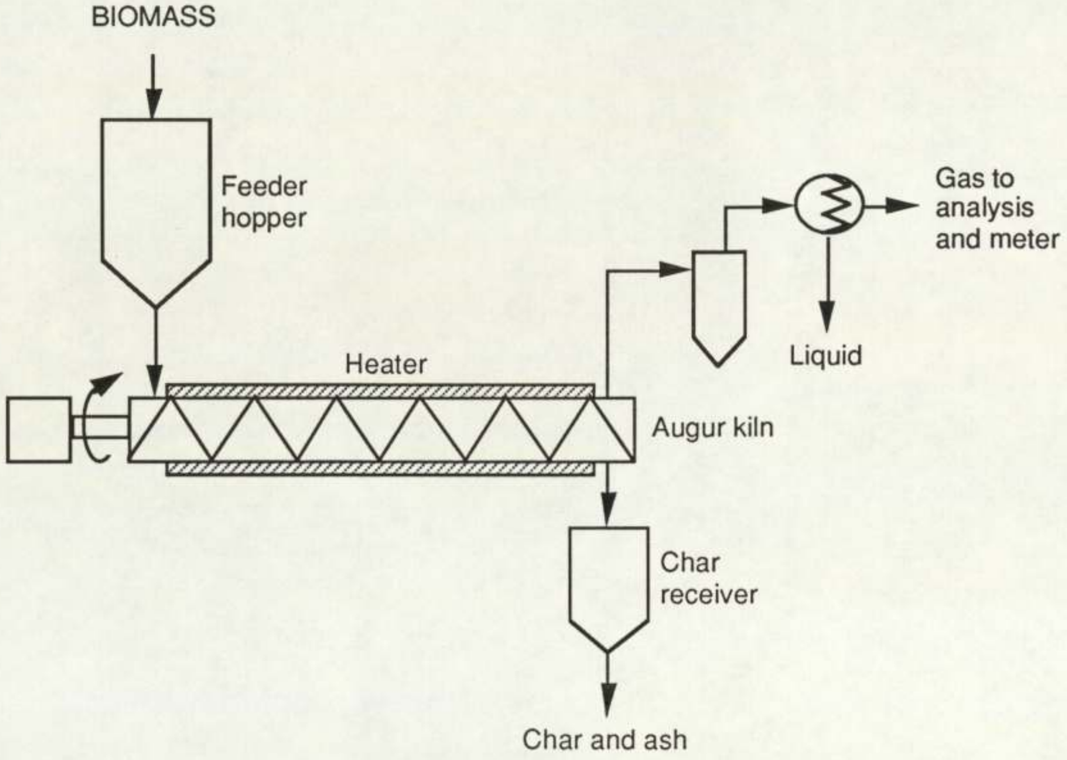


Figure 5.10 University of Tubingen Pyrolysis System

At a laboratory scale, both batch and continuous screw reactors have been used. Sludge dewatered to about 20% wt solids, or other biomass, is heated slowly to 300-350°C in an oxygen free environment for about 20 minutes, and the liquid product collected in an ice-cooled bath. The continuous screw reaction system is shown in Figure 5.10. No additives are needed as the silica, silicates and heavy metals present in the sludge are claimed to act as catalysts. The vapour is condensed and collected. Feedstocks tested include sewage sludge, rape, lupine and Euphorbia.

Four types of equipment have been used on a larger scale for low temperature conversion. There are: a rotary furnace (up to 80 kg/h), a fluidised bed, (up to 400 kg/h), a reactor with a transport belt for MSW conversion (up to 200 kg/h) and a cone screw converter for the conversion of agricultural wastes.

5.5.6 3 Results

Oil yields ranging from 18-27 wt% (feed basis) and char yields from 50-60 wt % (feed basis) have been achieved.

5.5.6.4 Properties of products

Table 5.22 shows the elemental analysis of the products.

Table 5.22
Elemental Analysis of Products

	Oil	Char	Water vapour	Product water
C	72.62	35.05	0.59	4.33
H	10.75	2.92	11.54	10.53
N	1.27	1.24	0.09	0.35
Cl	0.06	1.08	-	0.06
S	0.24	-	0.15	0.14
O (by difference)	15.06	8.59	87.63	84.59
Others	-	51.12	-	-

5.5.6.5 Special Features and Problems

Liquids with very low oxygen content (less than 5% wt oxygen) have been reported from a sewage sludge feed. The low oxygen level and chemical intermediates are claimed to be due to low reaction temperature, natural catalysts in the feed and slow reaction times. The oils contain aliphatic hydrocarbons and fatty acids as the main components.

The sewage sludge derived oil has been reported as being used as fuel for a diesel engine.

Problems include:

- Lack of definitive reaction mechanisms and pathways to account for low oxygen content liquids.

5.7 Flash pyrolysis in a shallow fluid bed for liquids

Example: University of Waterloo, Canada

This program was initiated in the early 1980's with the main objective of establishing conditions for maximising liquid yields from biomass, particularly from forest materials [38,41,81,98,101].

5.5.7.1 Introduction

Initially, a bench scale continuous flash pyrolysis unit using a fluidised bed at atmospheric pressure was employed. The reactor conditions used were feed rates of up to 50 g/h with a particle size range between 140 and 60 mesh (between 105 μm and 250 μm) in a nitrogen atmosphere over a temperature range of 400-650°C. Results indicated that at an apparent vapour residence time of 0.5 second, organic liquid yields of 60-70% (moisture free) could be obtained from hardwoods such as aspen poplar and maple while yields of 40-60% could be obtained from agricultural wastes such as wheat, straw, corn stover and bagasse. Using the results obtained from the bench scale unit, a larger process unit of 3 kg/h was designed, constructed and tested. This has been extensively studied and a 200 kg/h pilot plant based on results from this unit is being constructed in Spain.

5.5.7.2 Description and Operation

A flow diagram of the 3 kg/h process unit at Waterloo is shown in Figure 5.11. The wood is air dried (to 7% moisture), hammer milled and screened to a particle size of -595 μm (-30 mesh). The wood is then conveyed from a hopper by a variable speed twin screw feeder into a cavity where it is conveyed into the reactor by recycled product gas. The feed injection point is within the bed itself. The reactor bed material is sand and the fluidising agent is recycled product gas (a $CO-CO_2-CH_4$ mixture) which is preheated in the inlet line by controlled electric heaters. In addition, the reactor is wrapped with heating coils allowing extra heat to be added either to the bed of sand or to the freeboard space. The feed hopper and feeder are mounted on a hinged platform resting on a load cell, and hopper weight loss is continuously recorded.

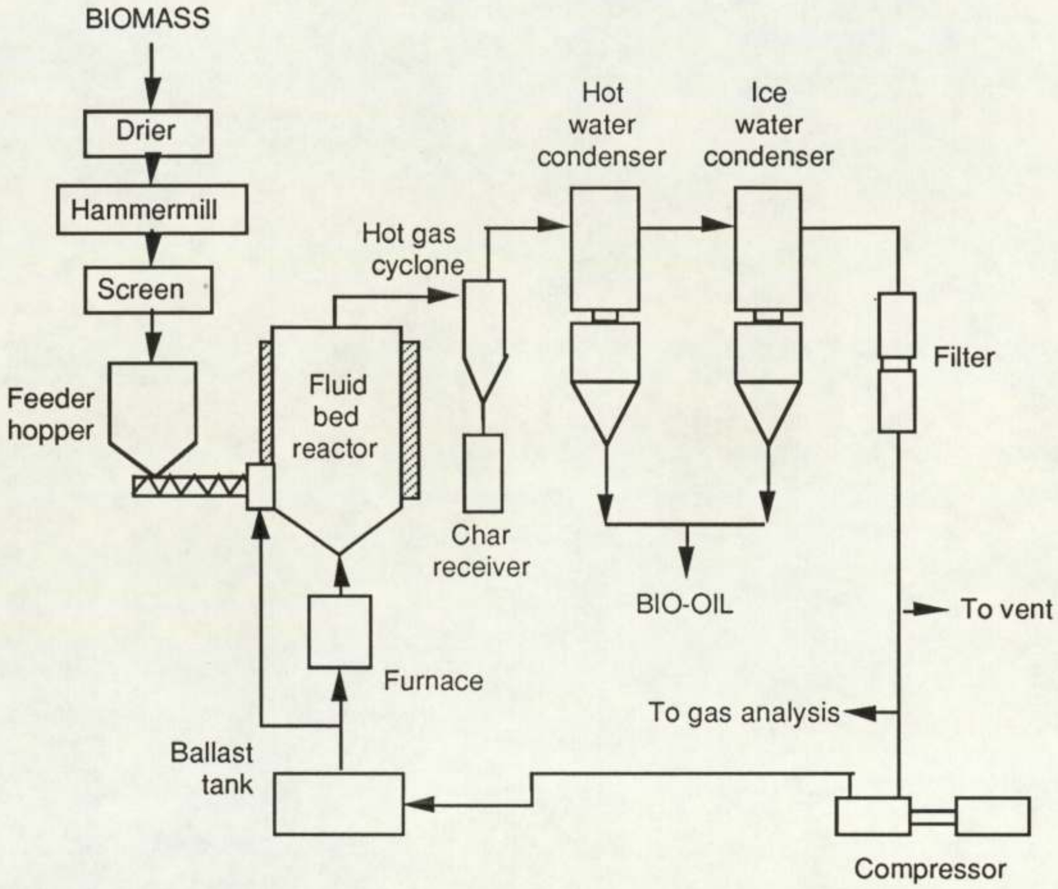


Figure 5.11 University of Waterloo Fast Fluid Bed Pyrolysis System

The fluid bed was designed to entrain the char and blow it from the bed while retaining the sand. This is done by careful selection of sand size, biomass particle size, bed velocity and reactor configuration. This is called the "blow-through" mode of operation since there is a negligible amount of char present in the sand and hence there is no need for sand circulation or replacement.

The reaction temperature (from 425°C to 625°C) is controlled by a thermocouple within the fluid bed which regulates the inlet gas heating coils. The reactor pressure of about 1.25 bars (125 kPa) absolute is monitored by differential and absolute bellows type gauges. Throughputs from 1.5 kg/h to 3 kg/h have been used.

The reaction products pass through a cyclone where char is removed. The vapours and the gaseous product pass through two condensers in series. These condensers are vertical and have pyrolysis gas inside the tubes; each condenser has a clean-out plug at the top and a condensate collection pot at the bottom. The first condenser is held at about 60°C while the second one uses chilled water at around 0°C as the cooling medium. Tarry products are collected in the condensers. The effluent gases then pass through a filter to remove tar mist and then to a recycle compressor. A proportion of this gas stream is taken from the compressor discharge and used to fluidise the reactor bed and convey feed into the reactor, while the excess is vented through a gas analyser and gas meter as product gas. The product gas is analysed for CO and CO_2 in an on-line infra-red gas analyser-recorder. Samples of the product gas are also taken periodically and analysed by gas chromatography.

5.5.7.3 Results

High yields of liquid product were obtained at temperatures around 500 °C which is believed to be due to minimum secondary decomposition reactions occurring at such low temperatures (see Table 5.23).

5.5.7.4 Properties of Products

The liquid product is highly oxygenated with no phase separation. It has a low viscosity and contains 10 to 20 wt% water depending on the moisture content of the feedstock and the reaction temperature employed. It is dark in colour with an acrid smell. The liquid is quite stable at room temperature over a twelve month period. Some properties of the liquid product are outlined in Table 5.24.

The gas produced has a higher heating value of about 14.4 MJ/Nm^3. This value increases at higher reaction temperatures as the CH_4 content increases and the CO_2 content decreases.

Table 5.23
Reported Pyrolysis Yields from Different Woods at Optimal Conditions

	Brockville Poplar	White Spruce	Red Maple
Temperature, °C	504	500	508
Moisture content, wt %	5.20	7.00	5.90
Particle top size, µm	1000	1000	590
Apparent residence time, sec	0.47	0.65	0.47
Feed rate, kg/h	2.10	1.91	1.98
Yields, wt % (dry wood basis)			
Water (reaction product)	9.70	11.60	9.80
Char	16.50	12.20	13.75
Organic liquids (dry)	62.90	66.50	67.90
Gas composition (wt % dry wood basis):			
CO	4.71	3.82	4.12
CO_2	5.89	3.37	4.89
H_2	0.02	0.02	0.01
CH_4	0.44	0.38	0.36
C2H4	0.19	0.17	0.16
Others	0.25	0.04	0.26
Total Gas	11.50	7.80	9.80

Table 5.24
Properties of Pyrolytic Liquids

	Brockville Poplar	White Spruce	Red Maple
Elemental analysis:			
C	54.70	54.00	54.70
H	6.90	6.80	6.40
O (by difference)	38.40	39.20	38.90
H/C ratio	1.51	1.55	1.40
O/C ratio	0.53	0.54	0.53
Water content (wet)	18.70	22.40	18.00
pH	2.40	2.10	2.40
Density, g/cm^3	1.20	1.22	1.19
Higher Heating Value, MJ/kg	23.20	22.70	22.40

5.5.7.5 Special features and problems

a) Char and sand separation is avoided by entraining the char,

b) It is a shallow bed reactor which may have scaling problems from bed instability at high throughputs / large diameters,

c) recycle gas is used for fluidisation and blanketing, thus avoiding dilution

Problems include:

- Stable tar aerosols are formed which pass readily through the condensers and require special handling. Electrostatic precipitators work well.

5.8 Conventional fixed bed pyrolysis for charcoal and bio-oil

Example: Bio-Alternative S.A., Switzerland

The objective is the production of solid fuels and liquid fuel byproducts which can be stored and transported easily from the pyrolysis of wood and solid wastes [183-185].

5.5.8.1 Introduction

The company was started in 1983 as Bio-Carbon Neuchatel SA, and later changed its name to Bio-Alternative SA (B.A.S.A.). A continuous, integrated carbonisation demonstration plant process is situated at the company's headquarters and several commercial sales have been made up to 2 t/h capacity. The charcoal can be used as fuel or converted to char slurries, and the liquid product - bio-oil - has been successfully used as a boiler fuel.

5.5.8.2 Description and Operation

A flow diagram of the 50 kg/h pilot plant in Switzerland is shown in Figure 5.12. Biomass with particle sizes ranging from 5 to 500 mm, is first crushed and dried (optimal moisture content 10 to 15 %) before being transported to the top of the reactor from a feed hopper. The temperature at the top of the reactor is about 120°C. Feed rates of 40 to 100 kg/h have been used in the pilot plant.

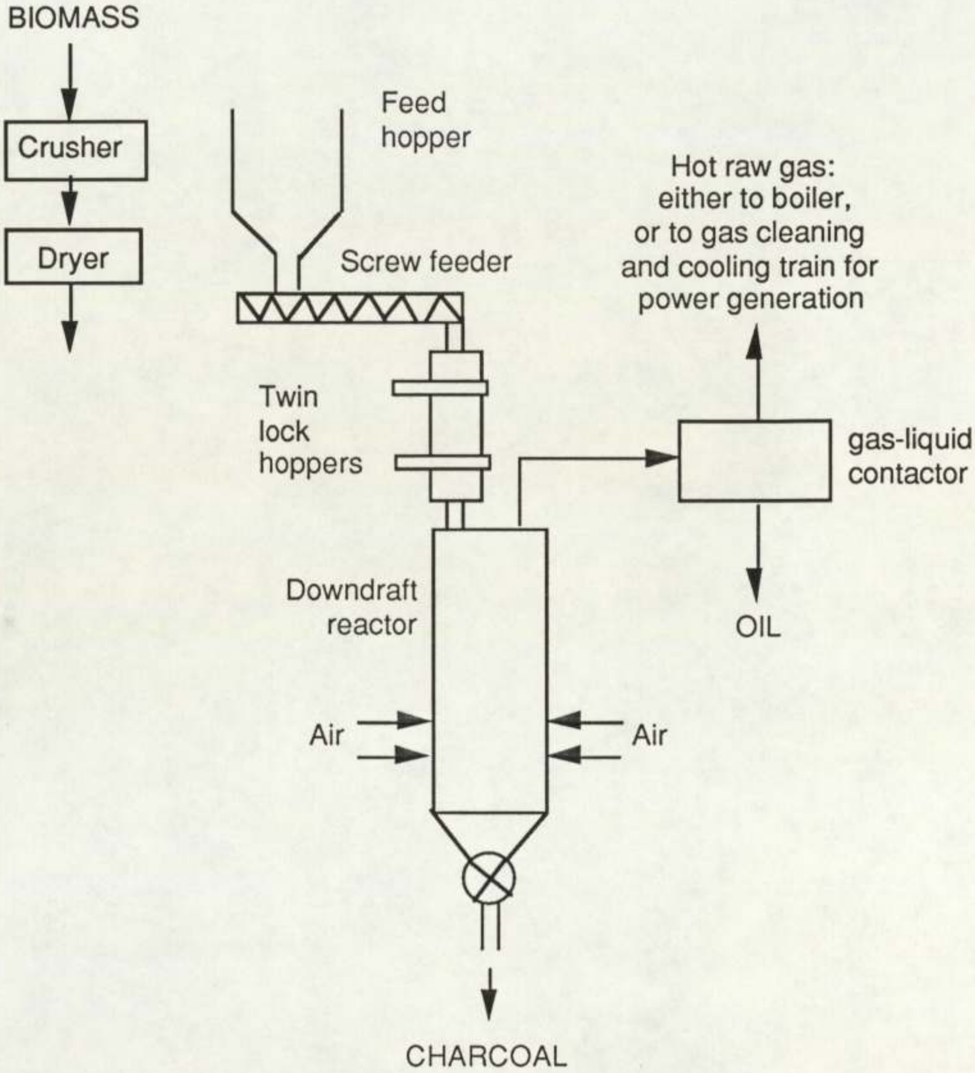


Figure 5.12 **Bio-Alternative S.A. Continuous Carbonisation System**

The pyrolysis pilot unit is a vertical cylinder about 3 m high and 1 m in diameter. It is fitted with a interlocked twin feed hopper fed by screw feeder. A horizontal stirrer and a vibrator are used to prevent bridging of the feed in the reactor. The heat necessary for the reaction is obtained through internal combustion, regulated by a system of air injection into the reactor through tuyeres. Temperature probes are used to measure the temperatures in the reactor. At the edge of the reactor, temperatures of about 1000°C have been measured. However, the temperatures in the interior of the reactor are lower and this results in a radial temperature gradient. The pressure of the system is between 2-5 mbars

(200-500 Pa) below atmospheric.

Char is removed through a rotary valve at the base of the reactor and through a water cooled system (an endless screw) which is at 40-50°C. The char product is stored in plastic bags or steel containers. Product gas leaves the top of the reactor at 120°C containing tar vapours and moisture. This is contacted with hot pyrolysis oil at 110-120°C which condenses the tar but leaves the water vapour in the gas phase. A sight glass is used to control the liquid level in the contactor and the excess liquid is periodically removed by manual discharge. The gas with about 10-20% water is then blown to a boiler for co-firing with fuel oil. Alternatively, the gas may be used for power generation. This requires further cooling by a heat exchanger to remove the water and tars present followed by filtration through a paper cartridge filter to remove tar traces. It is burnt in a 1.6 litre modified Ford engine coupled to a generator.

Feedstocks tested include wood, MSW, bark, sawdust, grape wastes, olive oil wastes and coconut shells.

5.5.8.3 Results

Two sets of data are presented in Table 5.25. The duration of each run was 3.5 hours.

Table 5.25
Results from Test Runs Over 3.5 hours [2]

	Run 1 Fir wood	Run 2 Beech wood
Input		
Wood, kg	255	165.3
Water in wood, kg	-	24.70
Air, kg -	65.90	
Output		
Charcoal, kg	74.25	50.28
Oil, kg	38.40	25.87
Gases and vapours below 100 °C, kg	n.a.	112.94
Yields (% wt of wood)		
Charcoal	29	30.4
Oil (as recovered, reported at 20% water)	15	15.7
Gases and vapours below 100 °C, kg	n.a.	n.a.

5.5.8.4 Properties of Products

The liquid product is viscous with no phase separation. It has been successfully fired in a boiler without any problems. Properties of the oil are summarised in Table 5.26.

Table 5.26
Elemental Analysis Of Bio-oil [2]

	Run 1 - Fir wood	Run 2 - Beech wood
Elemental Composition		
Carbon, wt%	58.12	55.10
Hydrogen, wt%	6.55	7.20
Oxygen, wt%	34.81	35.10
Nitrogen,wt%	0.52	2.00
Sulphur, wt%	-	0.6
H/C ratio	1.35	1.56
O/C ratio	0.45	0.47
Water content, wt%	4.5	14.0
Viscosity, cp	250 @60 °C	10 @70 °C
Net Heating Value, MJ/kg	22.2	20.9
Ash, % wt	< 0.05	-
pH	-	2.7
Density at 15°C, g/cm^3	-	1.216

The char formed is partially crushed, ranging in size from fine dust (extracted from a hood) to lumps up to 30x10x10 mm. At present, this material is briquetted for marketing in the leisure industry for barbecues. The empirical formula for the char is $CH_{0.02}O_{0.01}$, with a volatile content between 12-18 % and it has a net heating value of 29.3-30.0 MJ/kg.

The fuel gas is usually burnt and a typical gas analysis is shown in Table 5.26. It has a heating value on a dry tar free basis of 3.8 - 5.5 MJ/Nm^3.

Table 5.27
Gas Analysis of BASA Process

CO	16.3	% vol
CO_2	13.2	% vol
H_2	7.9	% vol
N_2	48.4	% vol
Oxygen and Hydrocarbons	14.2	% vol

5.5.8.5 Special Features and Problems

a) The oil is condensed at around 110°C, leaving most of the water in the vapour phase for combustion with the fuel gas. This solves the waste-water disposal problem associated with pyrolysis processes.
b) It can accept a wide variety of biomass such as forestry and agro-industrial wastes (wheat, maize or rice straw).
c) Some bridging of the feedstock occurs even with the use of a stirrer and a vibrator.

Problems include:

- As a carbonisation process, the upper limit on liquids production is around 15 - 20%wt on feed, and cannot be improved.

5.5.9 Molten salt pyrolysis for gases, liquids and chemicals

Example: Aston University, UK.

The aim of this project is to develop a molten salt pyrolyser to produce liquid and gaseous fuels from biomass. This work is a continuation of research into thermal processing of biomass and industrial wastes in molten salts which started in 1980 [186-194].

5.5.9.1 Introduction

Over twenty different molten salts systems have been investigated on a laboratory scale in order to determine their ability to dissolve and react biomass. It was observed that ammonia enhanced the solubility of wood in molten salts and that wood dissolved completely in sodium/potassium hydroxide and sodium/potassium ethanoate mixtures. It was found that wastes such as tyres and plastics were soluble in melts of alkali metal carbonates, particularly the eutectic mixture of lithium/sodium/potassium carbonates. Although the lithium/sodium/potassium carbonate mixture has a high melting point, 393°C, which makes it unsuitable for biomass solubility testing because pyrolysis starts below this temperature, it has a high stability and low corrosion rate.

The effect of molten salts is to provide higher heat transfer rates, to dissolve the biomass to give a homogeneous reaction mixture, and to enhance and/or catalyse preferred reactions.

In 1987, A two litre capacity continuous molten salt system was designed, constructed and tested.

5.5.9.2 Description and operation

A flow diagram of the 3 kg/h pilot plant is shown in Figure 5.13.

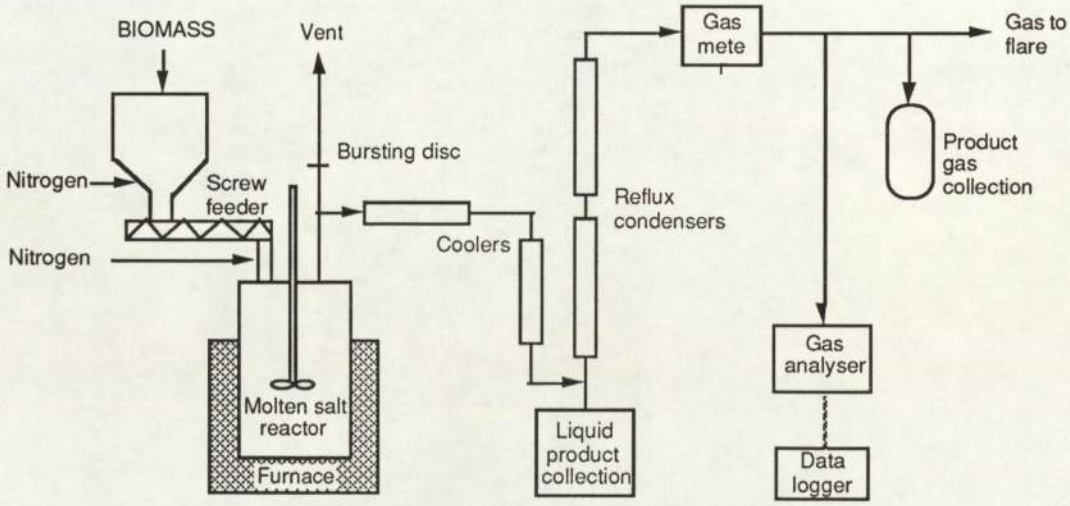


Figure 5.13 Aston University Molten Salt Pyrolysis System

The reactor is a cylindrical, type 304 stainless steel vessel with an inner liner of the same steel for the salt bath. It is fitted with an agitator with a sealed carbon bearing assembly, a pocket for the furnace temperature control thermocouple, a bursting disc assembly to cope with possible violent gas evolution, an inert gas feed line and a vapour offtake, all mounted on the removable lid. The feeder consists of a sealed hopper with agitated sides to prevent bridging, with a variable speed open helical spring screw feeding raw material into a wide mouthed reactor inlet. The reactor is heated by a purpose built 3 kW electric resistance furnace with a three-term electronic temperature controller. Feed rates of up to 3 kg/h are used in the experiments.

Vapours leaving the reactor first pass through horizontal then vertical copper concentric-tube coolers to reduce the vapour temperature. Next two triple helix water-cooled glass reflux condensers are used to condense the liquid product oils which fall into a sealed vessel from which samples are taken for analysis. Gaseous products are metered with a standard dry gas meter and samples are taken for both on-line analysis and collected in plastic bags for gas chromatography or mass spectrometry before passing through a flame trap to an outside flare. The product gas composition is continuously monitored for H_2, CO, CO_2 and CH_4 using dedicated gas analysers and recorded at 10 s intervals by a microcomputer based data-logger. Reactor pressure is measured by a water manometer, the product gas flowrate by a rotameter and the total volume of gas produced by a gas meter. These variables, along with the temperature of the salt bath, are recorded manually.

To prevent air entering the system and to provide a carrier gas for the gas analysis system, the equipment is operated with a nitrogen purge. This purge is introduced at three points, the stirrer, the feeder and the reactor, each of which is metered separately.

Two eutectic mixtures have been tested, the Li:Na:K carbonate eutectic (43.5 mole % Li_2CO_3: 31.5 mole % Na_2CO_3: 25.0 mole % K_2CO_3, melting point 397°C) and Na:K hydroxide eutectic (49 mole % NaOH: 51 mole % KOH, melting point 193°C). The feedstock is in-house manufactured pine 'chips' (no bark) sieved to the size range 0-4.75 mm. For the triple alkaline carbonate eutectic, a salt temperature of 500°C was chosen while 300°C was picked for the Na:K hydroxide eutectic. These temperatures were chosen as they were the midpoints of the solubility range for wood in these salts.

5.5.9.3 Results

Three main areas of experimental work have been carried out to date. It was found that the heating rate in the molten salt is more rapid than in a gaseous environment. The heating rates measured in molten salt were from four to ten times faster than those measured in air. It was also observed that in the alkaline melt, the cellulose core of the wood was dissolved leaving a honeycomb-like structure of lignin.

All runs using the Li:Na:K carbonate eutectic at 500°C were terminated after approximately 20 minutes of feeding. This was due to feed backing up the feed tube. It was found that the wood was not assimilated into the molten salt.

The runs using the Na:K hydroxide eutectic lasted up to 1 hour. In this case the wood dissolved in the melt to produce gaseous, liquid and solid products.

5.5.9.4 Properties of the Products

For runs with carbonate melt, a thick smoke of fine tar particles was formed along with low yields of gas which consisted of primarily CO and CO_2 (up to 95%), the balance being CH_4 and H_2. For hydroxide melts, the liquid product consists of 97-98 % water, the balance being an organic product, which has yet to be analysed. This liquid is alkaline possibly due to entrained particles of hydroxide in the product gas dissolving in the condensate. The gaseous product consists of about 98 % H_2, the balance being mainly methane. The solid product remains within the melt. This consists of an organic residue of mainly formate and ethanoate ions, and carbonates; the carbonates are produced by the reaction of the hydroxide with the carbon from the biomass. The fouled melt may be partially regenerated by heating. Fouled melt was heated to a temperature of 400°C and yielded a gas containing H_2 and CH_4.

5.5.9.5 Special features and problems

a) By dissolving biomass in molten salt, a homogeneous reaction mixture is obtained,

b) Molten salts provide much higher rates of heat transfer,

c) Molten salts also offer opportunities for catalysis or participation in the reactions,

d) High yields of high purity hydrogen (up to 98%) can be obtained.

Problems include:

- If carbonate is formed, the melt has to be regenerated, and processes for this have not yet been evaluated,
- Carbonate and organic residue in the melt lowers its effectiveness, also therefore necessitating melt regeneration,
- The reaction mechanisms and pathways have not been evaluated, and the catalytic effect remains to be identified and quantified.

5.5.10 Methanopyrolysis

Example: Brookhaven National Laboratory, USA

The project was initiated in October 1980 for the purpose of creating a database of the process chemistry for the rapid pyrolysis of biomass (which includes wood and agricultural products) with both reactive and non-reactive gases for the production of liquid and gaseous hydrocarbon fuels and feedstocks [77,88,89195-197].

5.5.10.1 Introduction

This research arose out of work carried out on the flash pyrolysis of coal in a bench-scale, entrained-flow tubular reactor of a 25 mm diameter. It was found that the yields of liquid and gaseous hydrocarbons were up to 50% higher than those obtained by using slow pyrolysis. This bench scale reactor was later modified so that wood could be used as the feedstock. Preliminary experiments with wood indicated similar results and because there was no data available at that time, a database was created.

5.5.10.2 Description and Operation

A flow diagram of the experimental equipment is shown in Figure 5.14. The oven dried wood particles, in the size range of 300 to 1000 mm, drop through the reactor from a wood feeder enclosed in a high pressure vessel. To prevent agglomeration and to provide a good free-fall in the reactor, approximately 15 to 30% of a fine silica flour (Cab-O-Sil) is mixed with the wood feed [3-6]. The gaseous feed is preheated in an electrical resistance tube and entrains the wood particles which then flows cocurrently down the reactor. Feed rates of up to 2 lb/h (1 kg/h) are used.

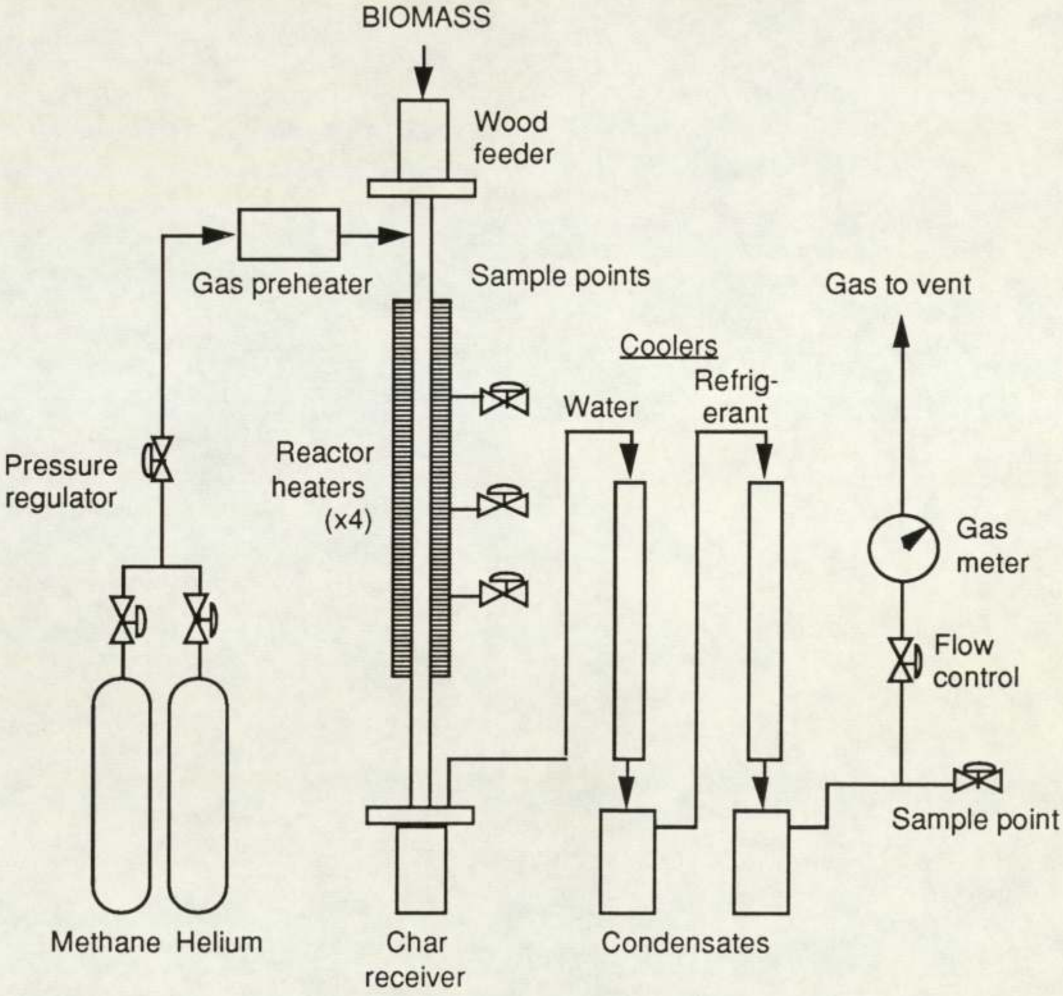


Figure 5.14 Brookhaven National Laboratory Methano-Pyrolysis System

The pyrolyser is a tubular reactor 20.3 cm long and made of Inconel 617. This reactor can operated at pressures of up to 4000 psi (27.6 MPa) and gas temperatures of up to 1000°C. Below the reactor is a 7.6 cm forced air cooling section in which the product gases are cooled to approximately 250 to 300°C. The char is removed from the effluent gas in a pressure vessel which is also maintained at 250-300°C to prevent liquid product condensation. The heavier liquids are collected in a water cooled condenser (~15°C) and the lighter liquids in a Freon cooled condenser (~ - 40°C). The remaining gases are reduced to atmospheric pressure, measured by a positive displacement meter, and vented to the atmosphere.

On-line product analysis was accomplished by a programmable gas chromatograph which determines CO, CO_2, CH_4, C_2H_6 and BTX (benzene, toluene, xylene) concentrations on a 8 minute cycle. Sample ports are provided every 5 cm along the length of the reactor. Products heavier than BTX ($>C_9$) are not measured on-line due to condensation in the sample lines and the temperature limit (230°C) of the gas chromatograph. These products are collected in the condensers and measured at the end of each experiment. Typically, a steady reactor temperature is achieved within 3 to 4 minutes after feeding wood particles into the reactor and a run lasts approximately 60 to 75 minutes.

Feedstocks tested included pine, Douglas Fir and lignin. The gaseous feeds included helium, argon, nitrogen and methane.

5.5.10.3 Results

The product gas consist of ethylene, ethane, BTX (mainly benzene) and carbon monoxide (see Table 5.28). For pine wood at 1000°C and 50 psi (340 kPa), the yields of ethylene was found to be about 8 times higher with methane than with helium. As the methane to wood mass flowrate ratio increases, the ethylene and benzene yield also increases and reaches a saturation point. Ethylene and benzene yields over 50 % based on wood carbon conversion are attained and the CO yields reached over 40 % at high methane-to-wood ratios. The enhancement of hydrocarbons is attributed to the formation of free radicals from the biomass decomposition which subsequently react with methane. Methane balances were performed by mass flow rate into and out of the reactor. Within experimental error, no appreciable net consumption or production of methane was observed.

Table 5.28
Flash Pyrolysis of Pine Wood at 50 psi (340 kPa)

Gaseous feed	Methane		Helium	
Temperature,	900°C	1000°C	900°C	1000°C
Wood feed rate, lb/hr[a]	0.55	0.55	0.49	0.49
Gas feed rate, lb/hr	3.84	3.84	0.95	0.95
Particle residence time, s	1.10	1.30	1.20	1.50
Gaseous feed/wood ratio, lb/lb	6.98	6.98	1.94	1.94
% Carbon conversion to product				
CH_4	-	-	12.10	11.90
C_2H_4	15.70	27.40	14.70	3.70
BTX	11.90	24.60	8.20	8.00
CO	35.60	38.70	44.60	53.00
CO_2	2.40	2.70	3.20	3.50
Total conversion	65.60	93.40	82.80	80.10
C_2H_4 concentration (vol.%)	0.75	1.31	0.65	0.18

[a] Fed with 30 % Cab-O-Sil

5.5.10.4 Special Features and Problems

a) Significant yields of valuable fuels and chemicals feedstocks such as benzene and ethylene are produced,

b) Valuable data on pyrolysis fundamentals was derived.

Problems include:

- A process design optimisation and scale-up for chemicals or fuels production is required using the experimental bench scale data obtained,
- Yields of non-equilibrium chemicals may not be high enough to justify further interest based on the established design,
- An economic assessment of the process based on the data is required to justify further interest for development.

5.5.11 Hydropyrolysis - gases and hydrocarbons

Example: University of Toronto, Canada

The overall objective of this project is the production of a liquid product from wood chips which can be handled in typical chemical engineering processes [198-203].

5.5.11.1 Introduction

This project was one of those initiated as a response to the oil crises in the 1970's. The initial studies on liquefaction of powdered wood/water slurry were carried out in 1 and 2 l batch autoclaves using nickel metal as catalyst with hydrogen as the reducing gas. Water to wood mass ratios of 5:1, wood to nickel ratios around 10:1 and cold hydrogen pressures from atmospheric up to 10.7 MPa were used. At 350°C, oil yields were in the range of 30-40% and contained 10% water. The oxygen content of the oils was between 10 to 15%. The oils had a viscosity from 1 Pa.s up to 10 Pa.s, and had an aromatic carbon content of approximately 33%. Carbon dioxide yields as high as 25% were obtained. In subsequent experiments, wood slurries were processed in a semi-continuous 2 l reactor using nickel carbonate as catalyst with hydrogen. Oil yields of up to 25% were obtained.

Studies investigating the conversion of single chip particles were then carried out using single wood rods of about 1 g with water at a water to wood mass ratio of 3. This was pyrolysed between 330-350°C inside a 10 ml reactor at about 2400 psi (16.6 MPa) resulting in products such as acetone-soluble oil, aqueous-soluble organics and gases. Oil yields of up to 50% were obtained. It was inferred that steam was primarily responsible for liquefaction (swelling and physical disintegration of the wood particle) but liquid water was required for stabilisation of the oil.

On the basis of these results, a laboratory scale, high-pressure, 2 l autoclave, cascade system was designed, constructed and tested. In the single-chip studies, steam was generated from the water within the reactor but with the cascade system, steam was used as the primary liquefaction agent.

The process is different from orthodox liquefaction in a liquid medium in that initially there is no liquid phase carrier to provide heat transfer or transport the reagents and products, although the processing conditions are not dissimilar.

It has been shown that the steam causes an initial high mass conversion rate which is proportional to the initial surface area of the wood. As the wood collapses, a second slower mass conversion occurs which is controlled by heat transfer through the reactor walls and the condensed aqueous phase. For wood chips the former rate dominates in the liquefaction.

5.5.11.2 Description and Operation

A flow diagram of the experimental equipment is shown in Figure 5.15. Wood chips with a moisture content of 5-8 % are loaded into a stainless steel baskets (~100 g) which is then placed into the nitrogen purged, preheated reactor. The reactor was machined from a single ingot of TP316 stainless steel, with an inner diameter of 3.8 cm, an internal volume of 600 ml and 45.72 cm long. It has three steam inlet ports located at 7.6, 22.9, and 38.1 cm from the base. Steam is obtained from a 2 l autoclave usually maintained at 350°C by upper and lower temperature control; it is passed through a two-way valve to the steam injection lines. Three thermocouples and a pressure gauge are used to control the internal conditions of the reactor. Two 1.83 m electrical heaters joined in parallel are wrapped helically around the outside of the reactor. The temperature at the top and middle of the reactor is typically 400-420°C. However, because of conduction, the base temperature falls as low as 300°C. Although a brass block heater partially overcomes this problem, temperature limitations on the outlet valve preclude further heating. A new valve should solve the problem. The reactor is insulated with light weight ceramic brick and layers of glass wool. The design pressure is 3500 psi (24.13 MPa) at 350°C.

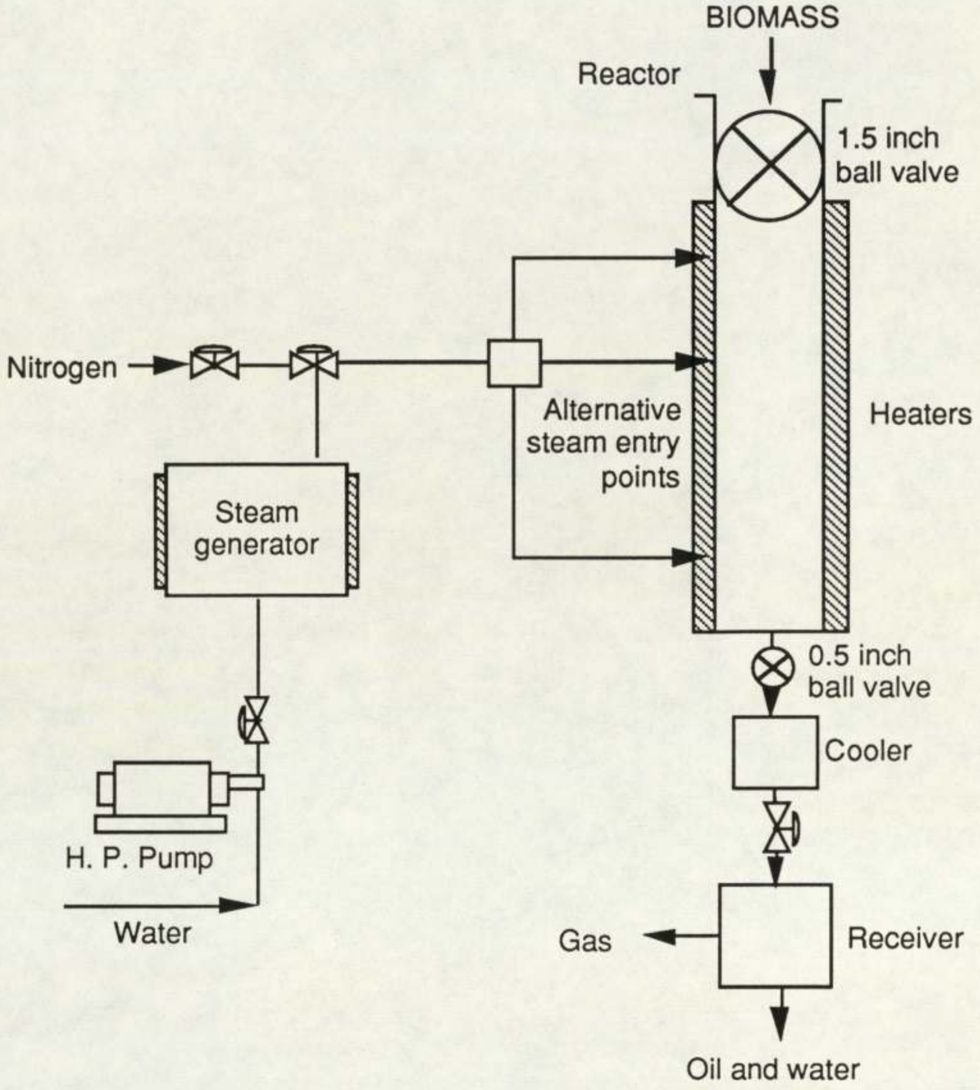


Figure 5.15 University of Toronto Hyro-Pyrolysis System

After the inlet valve is closed, steam is admitted for about 7 s and the temperature is maintained at the desired level for 15-180 s after which the products are discharged into the cooling lock and then passed to the product receiver. The volume of the gas is determined by using a water displacement system.

Feedstocks tested include IEA poplar wood chips with particle sizes ranging from 0.5-1.5 cm, and wood dowels of diameters 1.75, 2.5 and 3.1 cm.

5.5.11.3 Results

Results obtained so far are preliminary since the reactor unit was commissioned only in early 1987. The chips disintegrate fairly rapidly, initially yielding considerable amounts of aqueous phase solids as an oil precursor. Product oil yields of up to 50 % with no solids contamination has been obtained and the oil is easily separated from the aqueous phase. There is a continuous production and reaction of the aqueous phase solids for poplar dowels 1.3 cm diameter and greater. It was found that dowels of 3.1 cm diameter reacted faster than 2.5 cm dowels and in addition, oil yields were higher (50% versus 43%). This observation is attributed to the smaller annular void space in the reactor which forces initially condensed water to the upper hotter walls. Table 5.29 shows results for the 3.1 cm dowels.

5.5.11.4 Properties of Products

The oil typically softens just over 100°C and has an oxygen content between 20 and 25 %wt. The oil is thermally stable up to approximately 200°C. A full characterisation of the oil is, however, not available. Molecular weight determinations were performed by a HPSEC (High Performance Size Exclusion Chromatography). The typical number-average molecular weight of the oil is between 500-550.

The aqueous phase solids are finely divided material which remains suspended in the aqueous phase. It is believed that this material, represents the final precursor of the oil. The product gas contains mainly CO_2 (93%), CO (7%), and traces of methane.

Table 5.29
Detailed Results for 3.1 cm Diameter Dowels

Input and reaction conditions	Run 1	Run 2
Wood dowel (7.65 moisture), g	161.8	167.7
Steam temperature, °C	355	355
Steam injection time, s	5	5
Reaction time, s	120	150
Output		
Acetone-soluble (dry), g	70.9	79.0
Acetone-insoluble (dry), g	13.7	6.1
Gas volume, l	9.0	10.0
Aqueous phase, ml	340.0	290.0
Unconverted wood, g	10.0	0.0
Wood to aqueous ratio	1:2.1	1:1.7
Weight % yield (dry) *	47.4	51.0
% total carbon in acetone-soluble oil **	68.8	73.9

* as acetone-soluble oil
** estimated from runs made under similar conditions

5.5.11.5 Special features and problems

a) Wood chips are used instead of the usual wood slurries used for liquefaction.
b) Catalysts are not needed for this conversion process.

Problems include:

- Solids handling in scale-up.

5.5.12 Twin fluid bed fast pyrolysis for gases

Example: TNEE, France

The objective of this research is to produce medium heating value gas which can be used in an industrial application such as direct firing of a lime kiln in the pulp and paper industry [78,204-206].

5.5.12.1 Introduction

This project arose out of work carried out at TNEE in collaboration with the University of Nancy. The University of Nancy carried out fundamental research on fast pyrolysis using a vertical quartz tube heated by an electric furnace from 500 up to 1000°C. Heating rates of 1000°C/s and residence times less than 1 second were estimated. Feed weights of 100-300 mg with a particle size ranging from 25-400 µm were used with moisture contents from 0 to 100 %. Results indicated that gas yields increased with temperature and moisture content. For dry softwoods, the increase was from 13.9% at 500°C to 61.3% at 1000°C and for hardwoods, the increase was from 16.7% (500°C) to 67.6% (1000°C). The main components were CO, CO_2 and CH_4. The heating value of the pyrolytic gas was a maximum of 20 MJ/Nm^3 at 750°C but this decreased to 18 MJ/Nm^3 at 1000°C.

A 20 kg/h pilot unit was then constructed to pyrolyse pine bark on a continuous basis using a fluid bed, a combustor, and raining packed bed heat exchangers (RPBE). The RPBE is a novel, high efficiency, high temperature, heat transfer system. Two such units are used to recover heat from the combustion of char and transfer it to the incoming combustion air. The results obtained confirmed data collected using the bench scale equipment, particularly, that the pyrolysis gas composition and the heating value could be higher than 17 MJ/m^3 depending on the conditions used. A unit with a nominal throughput of 500 kg/h of dry fir bark was next constructed.

5.5.12.2 Description and Operation

The 500 kg/h process is depicted schematically in Figure 5.16. The feed is milled, sieved to less than 5 mm and dried (optimum moisture content 40%, dry basis) before entering a fluid bed reactor of hot sand. The sand has a mean particle size of 200 µm. The bed is fluidised by recycled product gas, and as fast pyrolysis occurs, a medium heating value fuel gas containing hydrocarbons is produced. The resultant gas leaves the reactor through a special packed contacting zone (RPBE) where it encounters sand raining down at a temperature of 980°C. This contacting zone acted as an efficient countercurrent heat exchanger and the heated tars entrained by the gas were gasified.

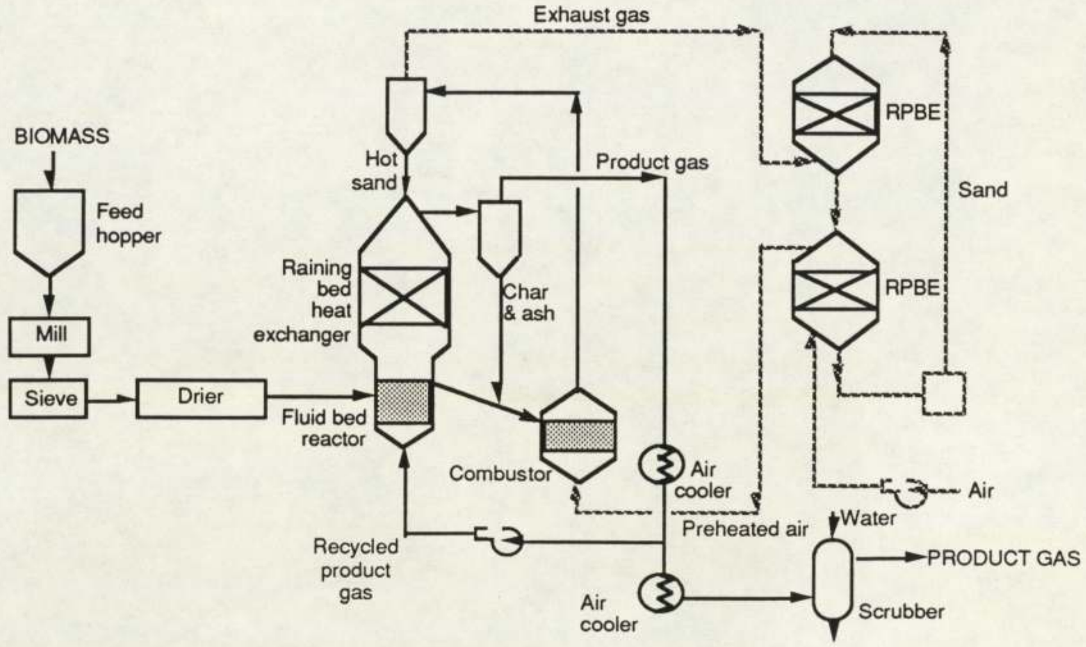


Figure 5.16 TNEE Pyrolysis System

The gas is passed through a cyclone to remove the carrier fines, ash and char which are combined with the overflow stream from the reactor. The gas is cooled by two air cooled exchangers and then passed through a cold water scrubber to condense the moisture. A side stream of the gas is recycled to fluidise the reactor. Steam is sometimes used instead of recycled product gas for fluidisation.

The overflow of sand carried char and ash out of the fluid bed. These are fed into the combustion chamber where the combustion of the char heats up the sand; preheating of the air allows the sand to be raised to about 980°C. The combustion takes place in a circulating bed so that the sand is carried to the top of the pyrolyser by the exhaust gas; the sand is separated from the exhaust gas in a cyclone, and drops into a distributor mounted over the RPBE which in turn surmounts the fluidised bed.

By using a double RPBE, heat is recovered from the combustion exhaust gas and used to preheat the combustion air. The exhaust gas is cooled counter-currently by sand in the first RPBE. The heated sand then enters the second RPBE where it flows countercurrent to the combustion air, which is heated to about 650°C in the process. The preheated combustion air then passes directly to the combustor.

5.5.12.3 Results

Table 5.30 shows typical yields.

Table 5.30
Product Yields from the TNEE Fast Pyrolysis Process

Feed	bark
Moisture content, wt% dry basis	38
Fluid bed temperature, °C	760
Sand temperature at the RPBE entry, °C	980
Sand/bark flow rate ratio	20
Char, kg/kg dry bark	0.210
Tar, kg/kg dry bark	0.038
Gas water content, kg/kg dry bark	0.345
Gas, kg/kg dry bark	0.800
Composition (vol%, dry basis)	
CO	43.00
CO_2	15.70
H_2	22.70
CH_4	17.00
C_2H_4	1.20
C_2H_2	0.40
C_2H_6	Traces
Lower heating value, MJ/Nm^3	14.86
Energy efficiency (based on LHV dry gas)	67 %

5.5.12.4 Properties of Products

There was no mention of what happened to the tar and waste water products. The lower heating value of the gas can be as high as 17 MJ/Nm^3 and its density is about 0.95 kg/m^3. This gaseous product can be used to fire a lime kiln in the paper industry or provide heat for an industrial process.

5.5.12.5 Special features and problems

a) The RPBE permits the pyrolysis process to be energetically self-sufficient through the combustion of char, thereby maximising the gas yield.

b) The process is self-stabilising. For example, when the pyrolysis temperature is too low, more char is produced, the combustion of which increases the temperature of the sand and therefore that of the pyrolysis bed. Conversely, if the temperature increases, the quantity of char decreases which causes a reduction in temperature thereby restoring steady state conditions.

Problems include:

- Process complexity which results in the capital cost being too high for current energy costs,
- Control of solids between the pyrolysis bed and the combustion chamber.

5.5.13 High Temperature Free Fall Radiation Pyrolysis for Gases

Example: University of Zaragoza and Hunosa, Spain

The aim is to use a very high-temperature, tubular reactor, with biomass free fall (formerly named high temperature fluid-wall - HTFW) to flash pyrolyse biomass in order to maximise gas yields [79,207,208].

5.5.13.1 Introduction

Based on a design patented by Matovich in 1976, the (HTFW) reactor was designed and constructed to withstand temperatures of up to 2200°C by Hunosa under the technical direction of the University of Zaragoza. The maximum feed rate used to date is 110 kg/h. The main component of the tubular reactor is a core of a porous refractory material (for example, graphite) capable of emitting sufficient radiant energy to activate the reactants fed into the tubular space. It is this predominant radiative heat transfer mechanism which distinguishes the HTFW reactor from the more conventional pyrolysers that employ convective or conductive heat transfer techniques to transfer heat to the reactants.

5.5.13.2 Description and Operation

A schematic of the experimental equipment is shown in Figure 5.17.

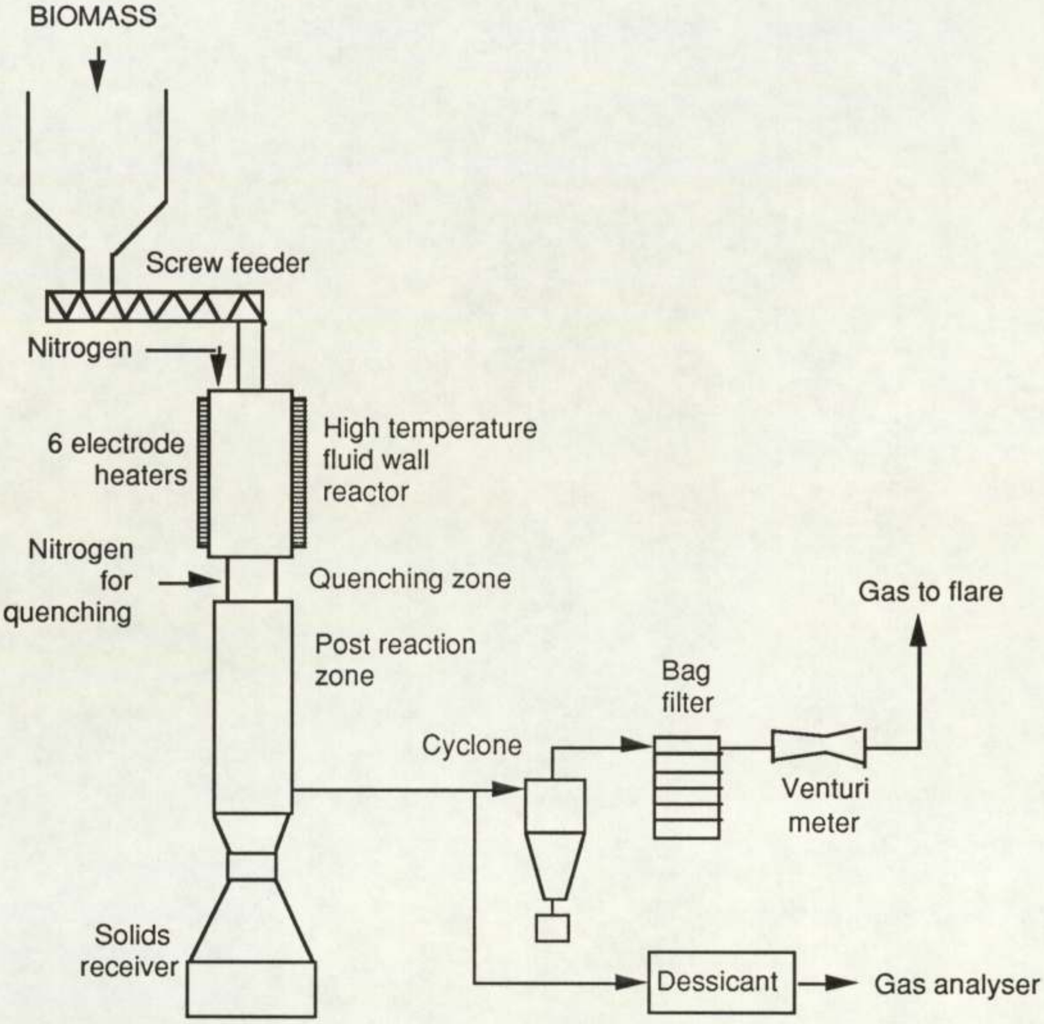


Figure 5.17 University of Zaragoza High Temperature Pyrolysis System

Biomass is fed to the top of the reactor at a rate of 60-110 kg/h from a screw feeder. The feed is entrained by nitrogen into the reactor. The residence time of the particles in the reaction zone is estimated to be between 0.4 and 1.2 seconds, depending on operating conditions. As the feed falls, it is rapidly heated by radiation to the reaction temperature. The heating rate is estimated to be 10^6°C/s.

The reactor has an internal diameter of 30 cm, and an effective length of 1.8 m. The total plant height is 12 m. The reactor core is made from uniformly, porous graphite that allows the permeation of a radiation transparent gas, namely nitrogen, through the reactor wall into the reactor. This nitrogen input creates a protective envelope of gas or a "fluid wall" which blankets the inner side of the reactor wall thus reducing the contact of reactants and products with the radiating surface. The reactor core is heated by a set of 6 electrodes located symmetrically around it.

At the reactor exit, the product stream can be quenched by a supplementary nitrogen stream. Further cooling is achieved by heat exchange with a water-ethylene glycol solution.

The solids (mainly char, ash plus unconverted biomass) are collected in a vessel at the bottom of the reactor, in a cyclone downstream and also in a bag-filter system. It is claimed that absolutely no liquid product is formed during the experiments. The flow rate of the exit gas is measured by a venturi meter.

A gas chromatograph is used to determine the composition of the exiting gas stream from the reactor. In addition, the evolution of CO, CO_2 and H_2 is continuously monitored by on-line analysers. The water content of the gas is determined by measuring the weight increase in a dessicant.

The feedstock tested is pine sawdust (20% moisture and 400 μm average particle diameter).

5.5.13.3 Results

Table 5.31 shows GC analysis results for two different reactor wall temperatures, 1600°C and 1800°C respectively. High gas yields are obtained at these high temperatures with 80% of the biomass gasified at 1800°C. At 2000°C and 250 mm particle size, gas yields of 98% (as kg N_2 free gas / kg biomass d.a.f.) have been achieved.

It was found that as the feed rate is increased the gasification efficiency decreases, that is, although the overall gas production increases when increasing the biomass throughput, the mass of gas produced per unit mass of feed decreases. For example, at a temperature of 1600°C and nitrogen flow rate of 4.2 Nm^3/min, increasing the feed rate beyond 1.4 kg/min caused a decrease in the gas yield. If the nitrogen flow is increased, both the residence time and the conversion rate of the feedstock decreases, the LHV of the exit gas decreases and the cost increases. Then the nitrogen flow must be minimised, or preferably changed to offgas.

Table 5.31
Gas Analysis

	Temperature, °C	
	1600	1800
Biomass feed rate, kg/h	108.0	108.0
Nitrogen flow rate, Nm^3/h	258.0	258.0
Particle diameter, µm	400	400
Gas analysis on a vol% dry basis		
CO	11.30	13.20
CO_2	1.80	1.10
H_2	14.20	16.90
CH_4	1.00	0.30
N_2 (by difference)	71.70	68.50
Gas yield, kg product gas/kg biomass (nitrogen-free basis)	0.75	0.78
Lower Heating Value, MJ/Nm^3	3.24	3.52

5.5.13.4 Properties of the Products

The gas has a lower heating value of between 2.5-4.5 MJ/Nm^3. This low heating value is due to the dilution effect of nitrogen in the product gas. Contaminants such as tars have not been detected in the product gas.

5.5.13.5 Special features and problems

a) By employing this type of reactor, very high temperatures and high heating rates can be achieved to pyrolyse biomass,
b) Radiative heat transfer is uniquely the main mode of heat transfer,
c) No tars or liquids are formed,
d) Very high gas yields of up to 98% have been achieved.

Problems include:

- Nitrogen used for creating the envelope causes dilution of the gas product. Ways of overcoming this problem are currently under study,

- High pyrolysis temperatures increase heat losses and can reduce energy efficiency,
- Costs are too high to make this reactor viable.

CHAPTER SIX
REACTOR DESIGN

6.1 INTRODUCTION

The aim of this chapter is to carry out a critical review of the work done in ablative pyrolysis, from which a specification for a pyrolysis process for liquid production will be deduced. Biomass at feed rates up to 5 kg/h will be used in this unit for high yields of liquids. There must also be potential for simple scale up. It is intended that this specification and design be used to construct a laboratory unit to obtain experimental data and samples of bio-oil. It will also be used to evaluate the influence of process parameters on process performance and product characteristics.

6.2 ABLATIVE PYROLYSIS THEORY

A recently discovered alternative method of pyrolysis relies on direct contact of biomass with a hot reactor surface with heat transfer through a thin film of liquid oil formed by pyrolysis. This gives much higher heat transfer coefficients resulting in potentially higher reactor specific capacities, as well as avoiding the need for a heat transfer gas as used in most flash pyrolysis units. This process is known as ablative pyrolysis. Ablative pyrolysis occurs when the biomass particles make intimate contact with a hot surface under high relative motion conditions, and is typically characterised by a steep temperature gradient at the biomass surface and a thin superficial layer of reacting liquid biomass. The very high rates of heat transfer that occur during this contact are directly proportional to pressure and are also a function of the relative velocity of hot surface and pyrolysing biomass. Gases and liquids are almost exclusively formed with minimum char which also makes this process attractive for conversion to liquid fuels.

All ablative pyrolysis processes are claimed to be capable of producing similar high liquid product yields, as well as offering potential advantages of high reactor specific capacity and hence smaller equipment sizes. The primary organic oxygenated vapours formed in ablative pyrolysis need to be removed and rapidly quenched to prevent polymerisation which leads to char formation and, in order to minimise gas production, moderate temperatures of about 400-600°C are employed.

6.3 EXAMPLES OF ABLATIVE PYROLYSIS SYSTEMS

Most research in this area of ablative pyrolysis has been carried out by Lédé et al. [69,209], Reed [210,211] and Diebold et al. [67,68,114,174-176].

6.3.1 Lédé's work

Lédé et al's. experimental system, as shown in Figure 6.1, was used to study the fundamentals of ablative pyrolysis including the measurement of heat transfer [69,209].

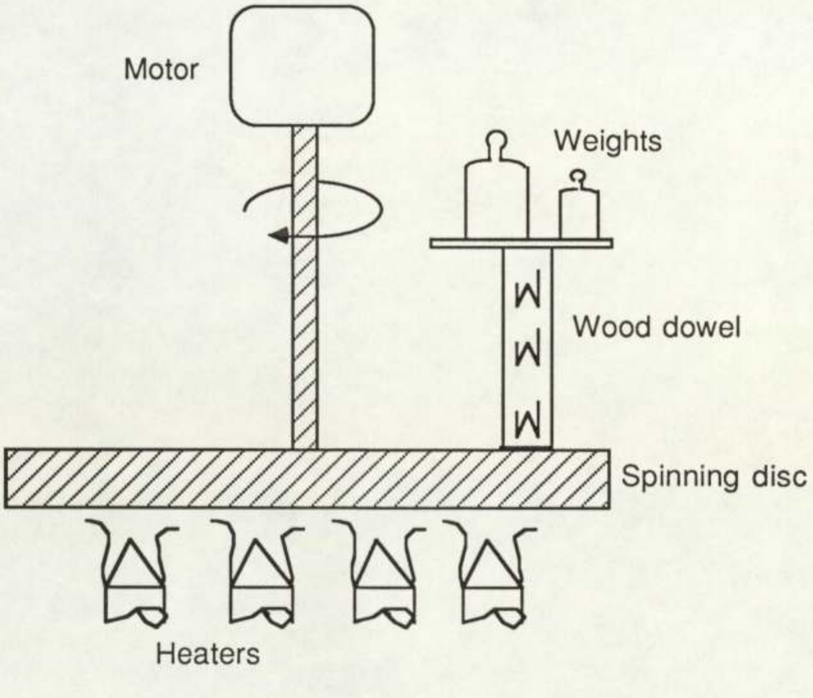


Figure 6.1 Diagram of Lédé's Spinning Disc Pyrolysis Apparatus [69,209].

A stainless steel disc of 7.5 cm diameter, spinning at a constant and controlled speed, was heated to different temperatures by four gas burners underneath. Wood dowels were pressed vertically onto the hot surface by weights on the upper part of the rod. Rods of diameters between 2 mm and 10 mm, applied pressures between 0.1 and 3.5 MPa, and disc temperatures (T_W) between 773 and 1173 K have been used in their work. A jet of argon was directed towards the contact surface to prevent spontaneous inflammation of the pyrolysis products.

Lédé et al. proposed that ablative pyrolysis could be represented by two main parameters: the ablation rate V, the rate at which the reacting layer moved towards the cold unreacted core of the piece of wood and e, the thickness of this reacting layer. The ablation rate, V, was obtained by direct measurement of the time required for a known length of wood to be consumed. The thickness of the ablation layer, e, was estimated by microscopic measurement of the extent of the uniformly darkened zone near the surface; this parameter was sometimes difficult to measure because of the lack of a sharp boundary between fresh and partly reacted wood.

From this work, at steady state conditions, they inferred the following:

- the ablation thickness decreased when the ablation rate increased;
- ablation rates as high as 3 cm/s have been measured;
- the product Ve was roughly constant and equal to the thermal diffusivity of wood (approximately 10^{-7} m^2s^{-1});
- for high disc velocities, the ablation rate was independent of particle size;
- V increased as the relative velocity of the disc increased and then became a constant, V_r^∞ (at speed > 1.2 m/s);
- V increased with disc temperatures T_W and is proportional to the pressure;
- the reaction took place as if wood decomposition occurred at a constant temperature, 466°C independent of reaction conditions.

In addition the following relationships were derived:

(i) $V = a.p$ (6.1)

where V is ablation rate, m/s (speed of consumption of wood dowel)
p is pressure, Pa
a is constant, m $s^{-1} Pa^{-1}$

Later Lédé et al., carried out further experiments with the spinning disc apparatus using materials such as ice, paraffin, lead and Rilsan [209]. A relationship similar to Equation 6.1, was derived. Thus, this confirmed that the flash or ablative pyrolysis of wood can be treated as a simple fusion process with a temperature of fusion of 466°C.

(ii) $h = 0.017 \quad p$ (6.2)

where h is the external heat transfer coefficient, W m^2K^{-4}
p is pressure, Pa

The heat transfer coefficient of equation 6.2, was found to be one to three orders of magnitude higher than radiative heat transfer carried out at similar temperatures. Hence, high rates of heat transfer can occur during ablative pyrolysis.

They also observed that ablative pyrolysis produced almost exclusively gases and liquids. As a collection system for the tars and gases was not attached to the experimental apparatus, yield data were unavailable.

They also carried out experiments using a fixed heated wall surface and a cyclone reactor heated by a solar furnace [69,209].

6.3.2 Reed's work

Reed constructed a 'heat flux concentrator' initially to investigate contact or ablative pyrolysis [210,211]. Wood dowel, fed at a rate of 0.2-0.25 cm/s, was rotated in a drill press and forced into a 1.2 cm diameter tapered hole in a heated copper block. The vapours produced emerged through 12 holes in the bottom of the block and were then condensed and collected in traps and a gas burette. The temperature range used was 500-700°C and yields of over 0.5 g liquid/g wood were obtained. Although the high heat flux caused rapid conversion to vapours, the forced contact of the wood with the concentrator caused it to be plugged with carbon after about 10 g of wood was fed. A 'pyrolysis mill' was next constructed and used to investigate ablative pyrolysis.

The contact pyrolysis reactor was designed using the principles of a conventional mill for grain as depicted in Figure 6.2 [211].

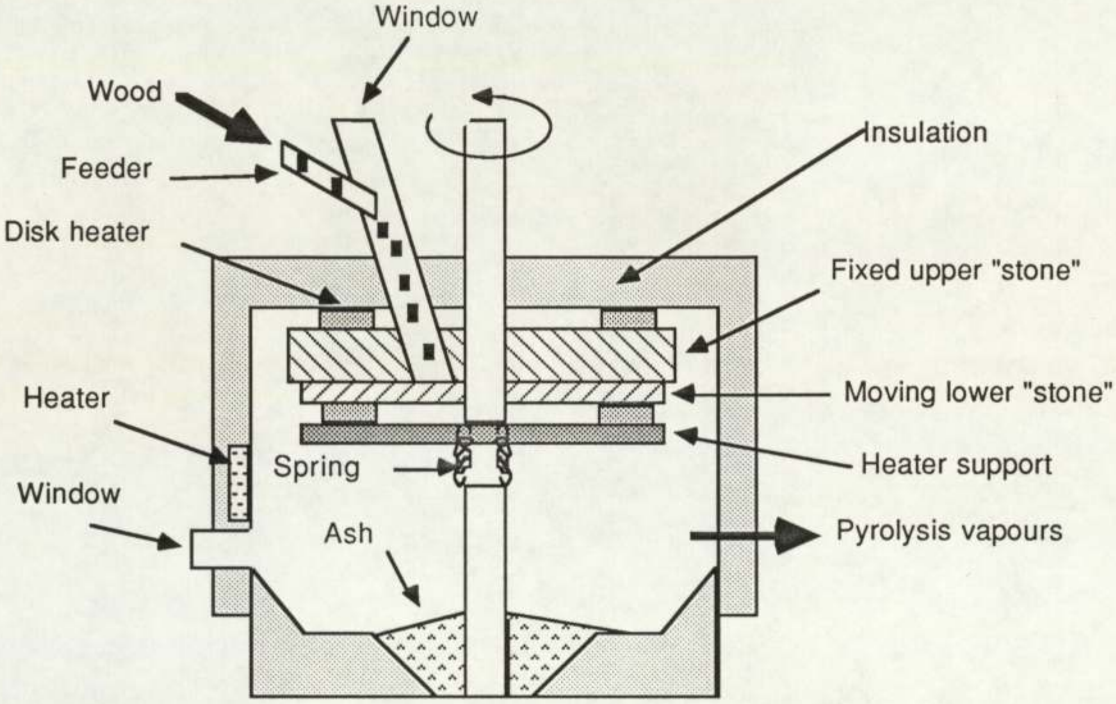


Figure 6.2 Reed's Pyrolysis Mill [211].

The pyrolysis mill consists of two copper, grooved discs, 6.4 cm in diameter, heated by Chromolox heaters. The upper disc is stationary while the lower one rotates at speeds up to 80 revs/min. Contact pressure is regulated by a spring between the two plates. The wood particles are fed centrally between the heated discs where they follow a spiral pathway to the outer rim of the discs and are allowed to fall to the bottom of the furnace. The vapours and gases emerge through the discs to the open space of the furnace and then to a series of four traps where they are collected and weighed. The furnace is heated to temperatures of 300-400°C to prevent condensation of the pyrolysis vapours. Preliminary results have indicated that a maximum liquid yield of 54% (including moisture) has been obtained at disc temperatures of 600°C, a flow of nitrogen purge gas of 0.5 g N_2, and a feeding rate of 13 g/h.

Further work is being carried out to optimise liquid yield and quality and to determine the upper limit of throughput. Potential problems are blockage of the feeder, sealing of the mill, condensation of the vapours in the feed tube (nitrogen is used at present to prevent this occurrence) and secondary cracking of the vapours. However, it is believed that if developmental challenges can be met then this reactor offers a greater decoupling of the purge or carrier gas flow rates than is possible with other fast pyrolysis reactors such as entrained flow or fluidised bed reactors [213].

Using a simple model to describe the operation of the pyrolysis mill, Reed predicted that the rate of pyrolysis and the particle residence time between the two discs, were dependent on contact pressure and rotational speed of the disc. This is in direct contrast to the observation of Lédé who found that the ablation rate was independent of disc speed (see Section 6.3.1).

6.3.3 Diebold and Scahill's work

The work of Lédé and Reed provides examples of simple laboratory pyrolysis systems. The reactor system developed by Diebold et al. is an example of a pilot plant study of ablative pyrolysis.

A full description of the reactor system used by Diebold and Scahill, along with the problems and advantages, are presented in Section 5.5.5.

They have shown that the vortex reactor is one reactor configuration that may be used to produce liquids based on the principles of ablative pyrolysis. Calculations, based on mass balances have shown that 70% of primary pyrolysis vapours can be recovered. However, the best recovery of dry oil to date, has been 55 wt % of the dry feed with a 94% mass closure. This is due to the formation of aerosols which are difficult to recover by methods such as high-pressure sprays, cyclonic separators and impingement or inertia collection techniques.

They too, like Reed, agreed that relationships derived by Lédé et al. are valid for ablative pyrolysis. They then used those relationships to derive the following expressions for their vortex reactor [175]:

(i) $V = t_p\ (u \cos b)^2\ (T_w - T_d)\ /\ (59000\ C_p\ r\ (T_d - T_o))$ (6.4)

where V is the velocity of the ablative pyrolysis front into the particle, m/s

t_p is the thickness of the particle, m

u is the linear particle velocity, m/s

angle b is the inverse tangent of the axial distance advanced per revolution divided by the circumference,

r is the vortex tube radius, 0.07 m

C_p is the heat capacity of wood, 2.8 kJ/kg°C

T_w is the temperature of the wall, 625°C

T_d is the decomposition temperature of wood, 466°C

T_o is the initial feed temperature, 100°C

For a particle thickness of 2 mm, the ablation rate V is 0.012 (1.2 cm/s) when cos b is unity and u is 400 m/s.

(ii) $t_p = t_o \exp [- (u \cos b)^2\ (T_w - T_d)\ (\theta - \theta_o)\ /\ (59000\ C_p\ r\ (T_d - T_o))\ ]$

where θ is the time, s (6.5)

t_o is the thickness in m at the time θ_o

(iii) $u = [\ (u_o^2\ K_f\ r\ 59000)\ /\ (K_f\ r\ 59000 + 2\ u_o^2\ \mu\ (\theta - \theta_o))\ ]^{0.5}$

where u_o is the velocity of the particle at time θ_o, m/s (6.6)

K_f is the thermal conductivity of the film, kJ/sm^2°C.

Equations 6.5 and 6.6 can be used to predict the progress of the pyrolysis of a particle in the vortex reactor. For example, using Equation 6.5, the following exponential decay of a 2 mm thick particle, as shown in Figure 6.3, was obtained; u was 400 m/s (assumed constant), cos b =1, r was 0.07 m, C_p was 2.8 kJ/kg°C, T_w was 625°C, T_d was 466°C and T_o was 100°C.

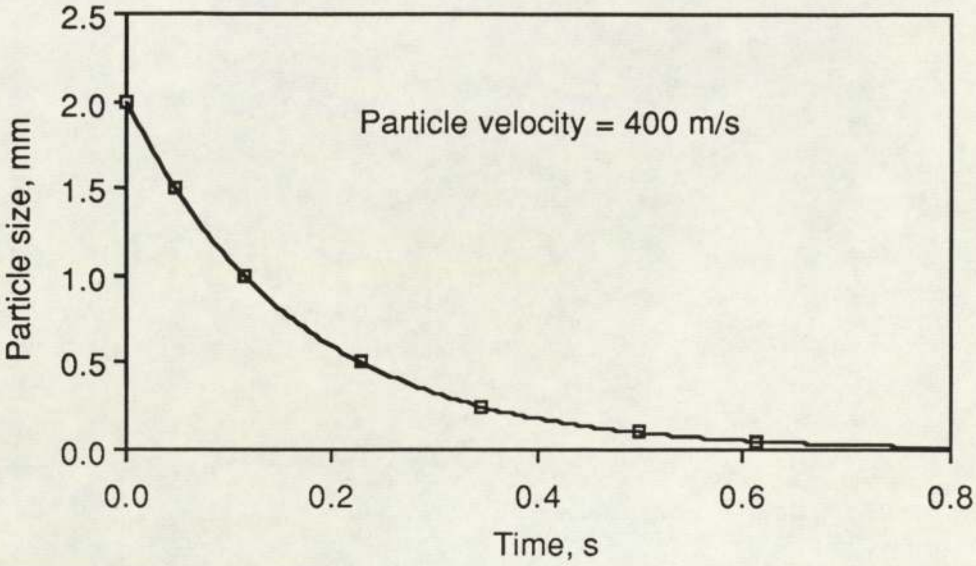


Figure 6.3 **Predicted Pyrolysing Particle History in SERI Vortex Reactor at Constant Velocity** [175].

The results derived from equations 6.4 to 6.6, confirmed as Lédé proved earlier (see Section 6.3.1), that the biomass particles decompose rapidly during ablative pyrolysis. This is due to the pyrolysis front moving very quickly during decomposition.

Relationships for film thickness, deceleration rate of the particle, and frictional forces were also derived [175]. Like Lédé, Diebold noticed that an oil film was needed to ensure that the particle slid along the reactor surface. This oil prevented particles from sticking to the wall which occurred if the film was vaporised too quickly.

6.3.4 Summary

The three works described above all relied on the transfer of heat by intimate contact of the pyrolysing particles with a hot surface. This contact allowed more heat to be transferred to the particle surface. In addition, these particles are in continuous motion. To achieve this, each used a different method. Lédé used the application of weights on the top of the wood dowel on a spinning disc to provide contact and continuous motion. Reed used two specially grooved discs which were stacked one on top of the other. Diebold's apparatus relied on the centrifugal force to keep the particles sliding and bouncing on the inside surface of the heated vortex reactor. Diebold estimated heating rates of 0.5 x 10^6°C/s while the estimates of Lédé were as high as 4 x 10^6°C/s [69,174].

Diebold and Lédé also showed that the ablative front moved very quickly within the particle. For a particle of 2 mm, Diebold calculated that the rate of ablation was 1.2 cm/s while Lédé obtained values as high as 3 cm/s. This rapid decomposition is due to the high rate of heat transfer to the surface of the particle. Lédé suggested that the ablation rate became constant after a certain rotational velocity was reached. This was about 1.2 m/s for his spinning disc system. In contrast, Reed argued that as speed increased, the ablation rate increased. Diebold inferred that high gas velocities permitted very short vapour residence times but did not indicate whether it affected the pyrolysis rate.

All inferred that there should be rapid removal of the primary pyrolysis products formed. For the system used by Lédé et al., rapid removal was achieved by the spinning disc; for Reed it was by the vapours passing out between the stones to the open space in the furnace. Diebold used steam as a carrier gas to remove the vapours from the vortex reactor.

Although this method results in the production of mainly vapours, oil yields have been relatively low. Diebold has to date, recovered only 55wt % oil while Reed has recovered 54 %. There was no product yield data available for Lédé's work. Collection difficulties are due to the formation of stable aerosols. Therefore an effective oil collection system needs to be implemented if ablative pyrolysis is to be used for liquid production.

6.4 SPECIFICATION FOR AN IDEAL PYROLYSIS PROCESS FOR PRODUCING LIQUIDS

The specifications of an "ideal" pyrolysis process are set out in Table 6.1

based on the information available on flash/fast and ablative pyrolysis (see Sections 5.3, 5.4, 6.2 and 6.3).

Table 6.1
Ideal Pyrolysis Process and Product Specification

PROCESS
Minimum feedstock pretreatment and preparation
Maximum feedstock versatility and insensitivity to feedstock characteristics
Minimum heat input to reactor
Minimum heat losses
Minimum reaction temperature
Good separation of oil and water phases
Minimum number of product separation steps
Minimum product stabilisation and/or upgrading
Scaleability

PRODUCTS

Oil	Char	Gas	Water
Maximum oil yield	Minimum char yield	Minimum gas yield	Minimum yield
Maximum oil HHV	Minimum volatiles	As clean as possible	Minimum COD
Minimum char content			Neutral pH
Minimum oxygen content			
Minimum water content			
Neutral pH			
Easy upgradability			
Low viscosity			
Single phase			
High stability			

While clearly these are not all possible and some are contradictory, this does identify the main features that a successful and competitive process has to address. After consideration of the principles of pyrolysis, these are re-examined to form the basis of a potentially successful plant.

6.4.1 Specification Of An Ablative Pyrolyser For Liquid Production

In order to design and construct a reactor system to incorporate the ablative pyrolysis technique for liquid production, the following specifications were deduced from previous reported work as discussed in Section 6.3:

- Provide a hot surface at not more than 600°C to minimise carbonisation and char deposition;
- Maintain a high relative motion of the particle and the hot surface

to increase reaction rates and at the same time remove the char and ash layers which can minimise internal heat transfer;

- Provide sufficient time for the biomass particle to remain in the reactor to ensure complete pyrolysis;
- Keep the residence time of the vapours as low as possible so that rapid removal of the vapours can occur;
- Provide rapid quenching of the pyrolysis vapours to avoid secondary cracking.

The reactor design must be such that the specifications for ablative pyrolysis are met as well as incorporate as many of the ideal specifications outlined in Table 6.1. If the first two conditions are met then the system will require minimum heat input and a minimum reaction temperature. The last three points can be associated with good separation of oil and water phases, minimum number of product separation steps and minimum product stabilisation since the likelihood of viscous liquids and char being formed are reduced. The presence of these materials affect phase separation and product stability.

6.4.2 Preliminary Design Specification

From the specifications outlined in Table 6.1 and information available on ablative pyrolysis, there is the potential for higher reactor specific capabilities and smaller reactor volumes as there is no need for a heat transfer gas. In addition, there should be better temperature control. There is also a potential of high liquid yields.

Based on the relationships derived from Lédé's work, the following results, listed in Table 6.2, were obtained for a 5 kg/h laboratory size ablative pyrolyser.

Table 6.2
Specification of an Ablative Pyrolyser for Liquids Production

	Derived from	Experimental
Biomass throughput, d.a.f. kg/h	Specified	5
Temperature, °C	Literature	600
Pressure (particle on reactor)	Lédé	As high as possible
Heat input, kJ/kg	Reed	2000
Effective area for ablation, m^2	Lédé	3×10^{-3}
Estimated actual area, m^2	Estimated	9×10^{-3}
Minimum relative velocity, m/s	Lédé	1.2

6.4.2.1 Contact Area

Based on a 1 m^2 contact area and a bulk density of wood of 155 kg/m^3 [214] then the throughput (kg/h m^2) is

$$3 \times 10^{-3}\ m^3/s\ m^2 * 155\ kg/m^3 * 3600\ s/h = 1674\ kg/m^2h$$

If the capacity of the reactor is 5 kg/h (dry ash free basis), then the contact area is

$$5/1674 = 3 \times 10^{-3}\ m^2$$

To account for the masking and overlapping of the particles and voidage within the reactor, the actual area was assumed to be 9×10^{-3} m^2, three times the calculated contact area.

6.4.2.2 Energy input

Reed proposed that the enthalpy of flash pyrolysis could be estimated by dividing the reactions into three steps: heating of the wood to 500°C, melting at 500°C to give tar and the vaporisation of tar [212]. He further proposed that the melting and the vaporisation steps may occur as a single-step (sublimation). Based on this approach, he suggested that

$$\Delta H_p = C_p\ T + \Delta H_v \tag{6.7}$$

where ΔH_p is the heat of pyrolysis, kJ/kg
C_p is specific heat, kJ/kg °C
T is the temperature, °C
ΔH_v is heat of vaporisation, kJ/kg

He estimated the heat of pyrolysis to be 2000 kJ/kg.

6.4.2.3 Contact Pressure

The pressure between the particle and the reactor wall needs to be as high as possible for optimum results, but there will be mechanical considerations in meeting this objective. Other aspects that require resolution in the experimental development is the masking effect of multiple particles on the interaction of particle and wall and volatilisation of liquid products. The vaporised liquids require rapid removal and quenching to avoid secondary reactions. A carrier gas under slight pressure could be used to remove the pyrolysis vapours. However, partial vacuum operation would avoid the need for flushing gas.

6.4.3 Reactor Design Configuration

Figure 6.4 shows one example of a reactor configuration that may be used for ablative pyrolysis. A rotating heated "bullet" with threads along its surface is used to provide the continuous contact movement of the wood particles with a heated surface. This bullet is electrically heated via either rod heaters or by heating tapes. Additional heat can be provided by wrapping heating tapes along the outer surface. In this example, the pyrolysis vapours formed are removed via a carrier gas under slight pressure. The bullet is kept stable by using both radial and opposed thrust bearings. The opposed thrust bearings prevent upward and downward movement of the bullet. To prevent air entering the system, the feeder added to the top should be close fitted. The reactor must be sealed tightly to prevent combustion occurring within the reactor. The spindle is spun clockwise so that the wood chips move downwards. In addition, a variable speed drive motor is used so that the effects of different rotation rates may be investigated.

In order to fully design such a reactor the following areas should be considered:

- The feeding system that will be used;

Some popular choices are screw feeder system or a vibratory feeder through a central shaft (see Section 5.5).

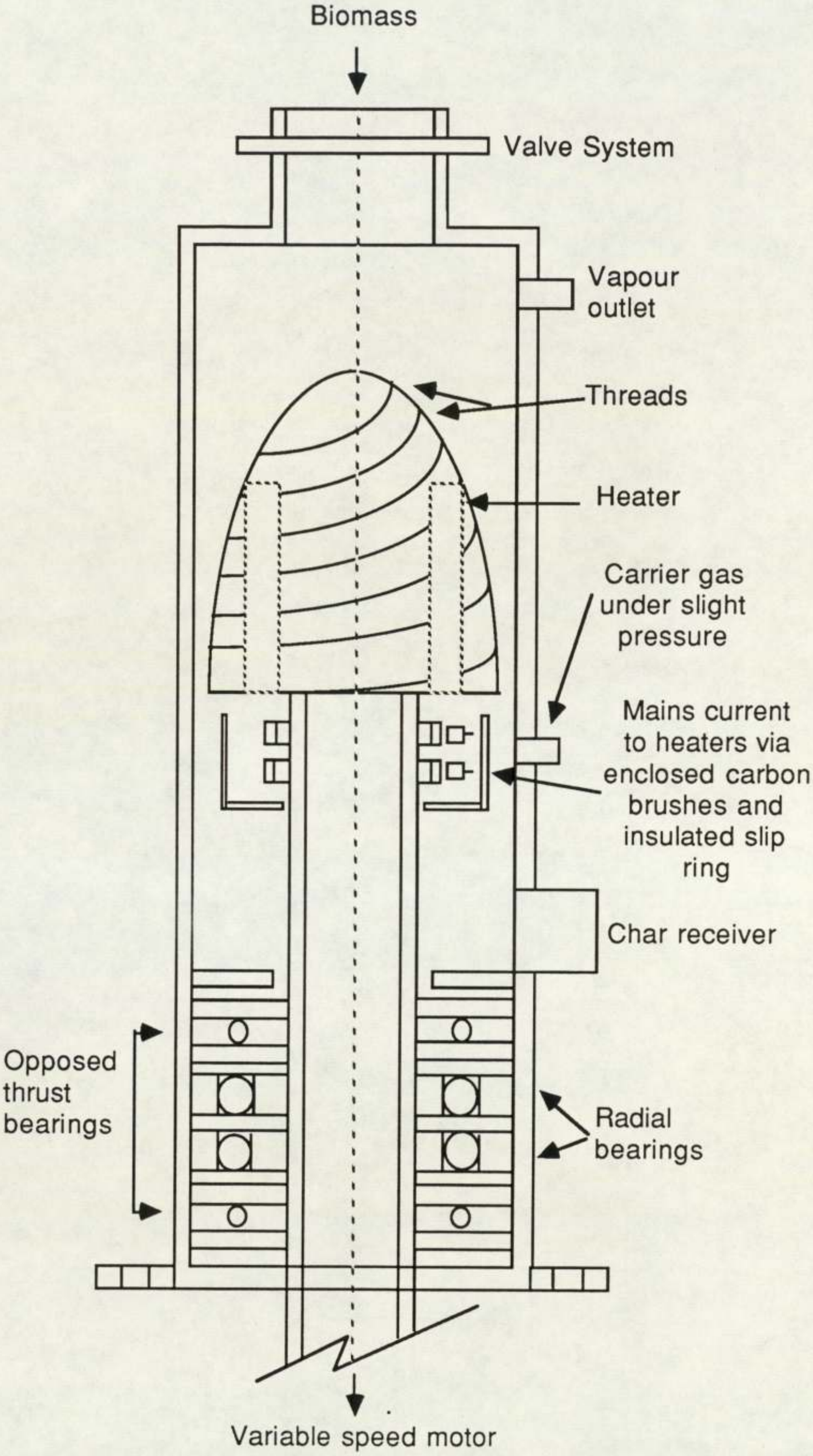


Figure 6.4 A Reactor Configuration for an Ablative Pyrolyser

- An analysis of the energy balance of the system;

This is an important parameter because one needs to consider what type of heat transfer may occur within the reactor such as conduction, point contact of pyrolysing particle to heated surface, heat transfer through the liquid/vapour film formed between the hot surface and pyrolysing particles, radiation, vapour condensation, friction, convection and particle to particle contact. All these methods have to be evaluated for this system to determine how the reactor will be heated whether by heating rods, heating tapes or by a conical heat pipe using Freon or a NaK eutectic as the heating medium.

- Continuous motion between the pyrolysing particle and the heated surface;

This permits frequent, intermittent contact of the particle with the heated surface but at the same time the temperature requirements are met and the char formed is quickly removed from the surface (see Section 6.3). This will be controlled by the rotational speed.

- Problems associated with solid-solid heat distribution such as overlapping and masking, flow of particles, the particle size to be used;

Overlapping of the particles and restriction of the movement of the particles along the heated surface will result in a limited amount of heat being transferred to the pyrolysing particles. In addition, secondary reactions such as cracking and depolymerisation will occur thus resulting in a mixture of primary, secondary and tertiary products (see Section 2.4.4) with some unreacted feed.

It may be possible to apply the information available on the operation of solid particle contact systems such as solid mixers, rotary driers, grinding systems (ball mill, this has been looked at by Reed), the centrifuge, the cyclone (Diebold has used their principle in the design of his vortex reactor), and the screw conveyor. In addition information available on the removal of surface of solids, such as the motions of a saw, sand paper, a knife or an axe, a plane and a grinder, could be beneficial.

Special attention should be given to an optimum particle size for the process to proceed without encountering problems such as slagging, bridging and bunker flow.

- The speed of rotation, the clearance within the reactor, the feed rate, the system to be used to remove the pyrolysis vapours, the system to be used to collect these pyrolysis vapours;

Speed of rotation is very important because the spinning bullet will force the particle to make contact with the hot surface. If this speed is too low, it is possible that the wood particles may not make contact with the heated surface. If the clearance is too small and/or the feeding rate too large, this may lead to bridging. Therefore special care should be taken when choosing these values. This equally applies to the size of the threads on the bullet.

There are two ways to remove the vapours either by partial vacuum or by carrier gas under slight pressure (see Section 6.4.2). Different collection systems will have to be tested as previous work has shown that collection of vapours is very difficult due to the formation of aerosols (see section 6.3). One possible method that can be used by maintaining the tar aerosols above 100°C and using a high speed blower to knock them out [176].

6.4.4 Empirical Relationships

Once the pyrolyser is constructed and commissioned, laboratory tests can then be carried out to study the effect of particle size, moisture content, reactor temperature, particle pressure, speed of the bullet and residence time of the vapour on performance and product quality. Subsequently, this data can be incorporated into an ablative pyrolysis model.

A plot of the effect of temperature on liquid yields, obtained from the data presented in Section 5.5, is shown in Figure 6.5.

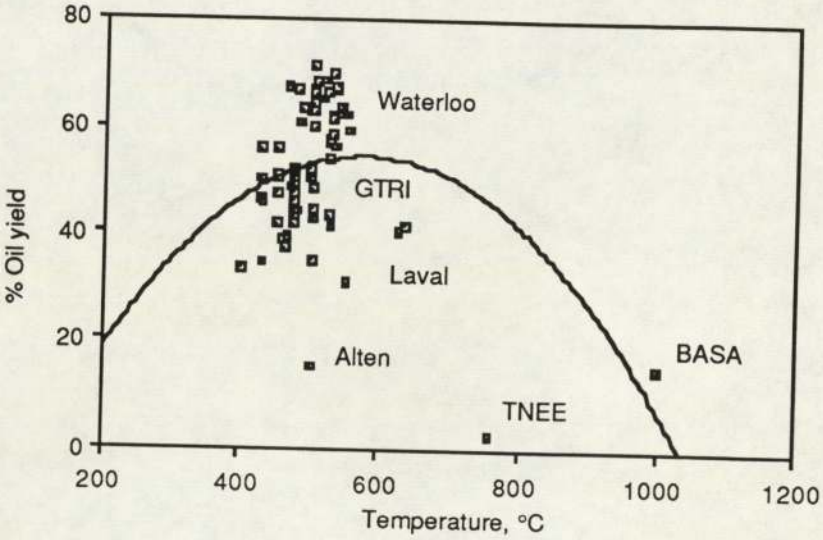


Figure 6.5 **The Variation of Oil Yield with Temperature**

Using the Cricket Graph software package for Apple Macintosh, the following relationship was derived:

Oil yield = $-30.1 + 0.25\ T - 2.56\ \exp(-4\ T^2)$ with $R = 0.55$

where R is the variance in the predicted value; the higher R is the better the fit.

This relationship was obtained from a polynomial fit where n was two; Figure 6.5 is a graphical representation of the above relationship.

If n is three, then the relationship derived is:

Oil yield = $-747.03 + 3.84\ T - 0.006\ T^2$ with $R = 0.68$

Although the relationship derived, when n=3, gives a higher value of R, the shape of the graph obtained does not follow the expected path (see Appendix III). It is expected that the rate of production of oil will increase and then decrease as illustrated in Figure 6.5, (see Section 2.4.4). However, the plot with n=3 resulted in an increase, then a decrease followed by a rapid increase in oil yield as temperature increased.

Although the value of the R is above 0.5, the fit is still relatively poor. This is due the contrasting conditions used to obtained the experimental data.

Thus this confirms that general pyrolysis models are difficult to formulate as these relationships are dependent on the conditions employed (see Section 4.4).

A similar study was carried out on the data obtained from the fluidised bed at Waterloo (see Section 5.5.7). Figure 6.6 shows the plot obtained for liquid yields against increasing temperature.

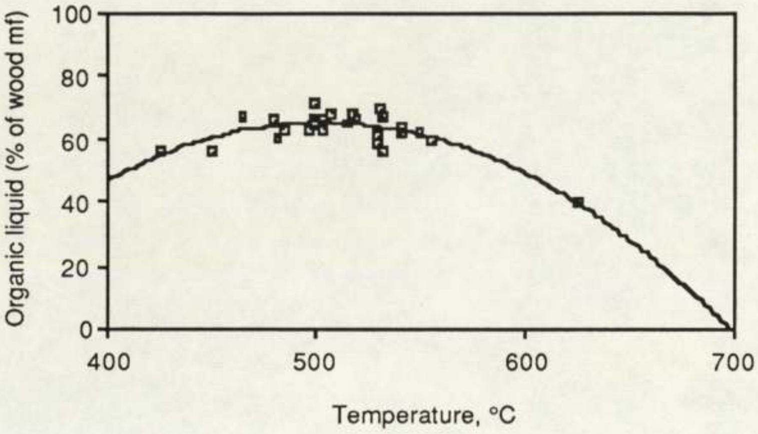


Figure 6.6 Plot of Liquid Yield versus Temperature

The following relationship was obtained for n = 2,

$$\text{oil yield} = 369.1 + 1.7\,T - 1.7E\text{-}3\,T^2 \qquad \text{with } R = 0.84$$

Similar relationships were obtained for char, gas and water (see Appendix III).

$$\text{char yield} = 443.9 * 10\text{^}(0.003\,T) \qquad \text{with } R = 0.78$$

$$\text{water yield} = -140.6 + 0.57\,T - 5.44\,E\text{-}4\,T^2 \qquad \text{with } R = 0.63$$

$$\text{gas yield} = 0.206 * 10\text{^}(0.0034\,T) \qquad \text{with } R = 0.75$$

These relationships gave better fits because the data was obtained at conditions for fluidisation.

6.5 Conclusions

Ablative pyrolysis offers the advantages of high heat transfer rates, low reactor volume, better temperature control and potentially high liquid yields. Based on specifications outlined in Table 6.1 and the theories proposed for ablative pyrolysis, a conceptual design was listed in Table 6.2. A possible reactor configuration has also been proposed, which is a heated moving "bullet" reactor. With the experimental data obtained from this reactor, empirical relationships can be derived, similar to those obtained with the data currently available.

CHAPTER SEVEN

DISCUSSION

To recapitulate, the main aims of this study, as stated in Chapter 1, are:

(i) to propose a simple model that incorporates sufficient features to adequately represent the pyrolysis process;

(ii) to propose conceptual designs for an experimental pyrolyser based on the ablative pyrolysis concept, to produce high yields of liquids.

The pyrolysis of biomass typically results in the formation of char, liquid and gaseous products. Depending on the process conditions selected, it is possible to enhance the yields of any of the three products. The mechanisms for the formation of these products are very complex and are still unfolding. A knowledge of these mechanisms is needed in order to identify chemical pathways which selectively lead to the formation of the desired product whether it be used for fuel, chemicals or both.

Chapter two considered the thermal degradation of biomass with emphasis on the pathways and mechanisms of the pyrolysis of wood and its major constituents, cellulose, hemicellulose and lignin. Different theories have been proposed to account for the hundreds of concurrent and consecutive reactions occurring which result in a variety of products, usually in small amounts (see Section 2.4). However, pyrolysis can be divided into two global competing reactions - dehydration and charring which occurs at temperatures below 300 °C and depolymerisation which occurs at temperatures above 300 °C. At temperatures above 300°C, primary pyrolysis vapours are formed which can then be condensed to form a liquid product. Therefore, the high production of primary pyrolysis vapours by ablative pyrolysis is a consequence of the decomposition of biomass by depolymerisation.

Fundamental and laboratory studies have shown that maximum liquid yields are obtained at moderate temperatures (450-650°C), rapid heating rates of up to 1 x 10^6 °C/s, short vapour residence times (less than 1 s) and low pressures of 1 bar and below. These process conditions not only affect yields but also chemical composition of the products. The primary oxygenated vapours generated are very unstable and will crack to produce gases and repolymerise to form a more stable viscous aromatic liquid (see Section 3.2). Hence, this accounts for the need for rapid removal and quenching of the vapours. Because high heat transfer rates can be achieved during ablative pyrolysis, moderate temperatures in the range 450-500°C should be employed. Particle size also influences the rate of pyrolysis. However for ablative pyrolysis, the ablation rate is roughly independent of particle size (see Section 6.3) Ideally, ablative pyrolysis can be carried with large pieces of biomass and not only with small particles as is often stated for fast/flash pyrolysis.

A number of models have been proposed to account for the interactive effects of the process variables on product yields. These models all account for the transfer of heat within the particle by conduction. Others tried to model the changing properties of pyrolysing wood. Exact relationships are hard to derive as these changes are influenced by the process conditions employed. Most of these properties such as thermal heat capacity and thermal conductivity are related to conversion rate, that is weight or density changes with time.

The most comprehensive model has been developed at Washington University [17,103,153]. They have tried to account for all the possible changes that can occur during wood pyrolysis. Still however, product yield and distribution predictions are lacking because of the complex competing reaction scheme that has to be introduced to account for the various products formed during wood pyrolysis.

Empirical modelling would provide one possible answer. No work has been found that has derived a general pyrolysis model from the data available. Two simple models have been derived (see Section 6.4.4). These were derived by fitting a polynomial relationship to the given data. Relatively poor fits were obtained. As stated in Section 6.4.4, this was due to the different experimental conditions used to obtain the data. This method was also very limiting because it could not be used to study the combined effect of several process parameters on product yield.

One method that can be used to overcome this problem is using software packages with a parameter estimation facility. The data can then be reconciled by giving different weightings to the experimental data. These relationships could then be used within analytical models to give a clearer picture.

Hence, a general empirical model should be able to predict the percentage yield of char, liquid and gas along with both the chemical and physical properties of liquid and gases. For example, the prediction of the liquid characteristics such as ratio of carbon-hydrogen-oxygen (CHO), heating value, water content, viscosity and density would be very useful. For gases, gas composition and its heating value would be sufficient.

Chapter five concentrated on presenting an overall review of biomass pyrolysis and pyrolysis technology. Thirteen examples of recent and/or well developed pyrolysis systems were described. Most of the well developed pyrolysis systems for liquid production can be found in North America. Only the system at Alten, Italy, is at present capable of producing bio-oils in Europe; however, yields to date have been only 15 wt % (see Section 5.5.1).

The most advanced research using the concept of ablative pyrolysis, is that developed by Diebold and Scahill (see Sections 5.5.5 and 6.3.3). The scale-up potential of this design is dependent on the angular momentum of the carrier gases to keep the entrained feed moving on the wall. A feasibility study has also been carried out [175].

Several specifications were derived from information available on pyrolysis in general and on ablative pyrolysis. In addition, a preliminary design was carried out for a 5 kg/h laboratory ablative pyrolysis unit. The reactor configuration chosen was "bullet" shaped. A description of this reactor and its limitations was described in Section 6.4.3.

If an ablative pyrolyser can be built, tested and provides high yields of liquid, then this would be one method that Europe can implement to supply liquid fuel. At present, the Biomass R & D Programme of the Commission of the European Community, is looking at developing mobile conversion units (drying unit and a pyrolyser). As an ablative pyrolyser would be more compact due to the transfer of heat by the hot surface as opposed to a heated carrier gas, then this concept could be used as the basis for such a mobile pyrolysis unit.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

The following conclusions were made :

- Wood is one of the most popular forms of biomass used in pyrolysis systems.
- Wood is a very complex structure and is composed of mainly three polymeric components: cellulose, hemicellulose and lignin. Hence the pyrolysis of wood and its constituents are very complex and consist of both concurrent and consecutive reactions which result in a variety of products, usually in small amounts (see Section 2.4). Many theories have been proposed to explain the phenomenon and are still unfolding.
- The overall mechanism for fast or flash pyrolysis is dehydration, depolymerisation, followed by melting and vaporisation to form vapours and gases with minimum char formation.
- Three hypotheses regarding wood pyrolysis have been described (see Section 2.4.4); the most recent being presented by Evans and Milne. Their series of reactions consist of biomass being converted to primary oil which is further converted sequentially to oxygenates, aromatics and eventually polynuclear aromatics and soot. The results obtained by Elliott, from his study of biomass pyrolysis oil composition, correlates well with their proposal (see Section 2.4.4).
- Many parameters affect the pyrolysis process but the parameters most frequently varied are the reactor temperature, the vapour residence time, the pressure, the heating rate and particle size and shape since they can be controlled much easier than the others.
- For liquid production, moderate temperatures of up to 600°C may be used with vapour residence times of less than 1 second and high heating rates with rapid removal and quenching to preserve the intermediates formed during pyrolysis.

- More research is need to develop an effective oil collection system.
- Most of the kinetic data available is for the prediction of weight or density changes as opposed to product yield and distribution.
- Most analytical models proposed for pyrolysis focus on the effect of heat transfer on the pyrolysis process rather than on the prediction product yield and distribution. In addition, secondary reaction effects are ignored.
- Because these models involve solving partial differential equations, different mathematics techniques, mainly finite differences and method of lines, were used. Therefore these models are not that easy to use or run.
- The most comprehensive model has been proposed by the University of Washington. Both a competing reaction scheme for product yield and distribution and secondary reactions are included in their formulation. Predictions of the temperature profile within the particle and product yields were fairly accurate.
- Models can be more robust with the introduction of competing reaction schemes as opposed to using three separate reaction steps for the conversion of the pyrolysing biomass into the three products - char, gas and liquid.
- Empirical modelling is also another method to use to develop relationships between product yields and quality with process conditions. This could be a good technique if more comprehensive methods of deriving these relationships are used.
- Ablative pyrolysis is one promising route that can be used to produce liquids.
- Ablative pyrolysis offers considerable scale and cost advantage potential if the concept can be applied on a larger scale.

8.2 Major Recommendations

Based on the aims of this study, the following recommendations are proposed:

- To develop more comprehensive empirical models to simulate the relationship between product yield and quality with process conditions. The models derived in this study are too simple to be used for predictions. This can be achieved by using software packages which include a parameter estimation facility. This facility normally uses the least squares mathematical routines. Different relationships can then be derived by combining various process parameters together. In addition, the various experimental data can be reconciled by using different weightings.

- To develop, design, build and test different reactor configurations that employ the concepts of ablative pyrolysis.
- To conduct laboratory tests to determine heat and mass balances of the ablative pyrolyser and also to obtain samples of liquid under different conditions so as to analyse how characteristics are affected by changes in process parameters. Data obtained using this approach can then be compared with the model predictions.

APPENDIX I

PUBLISHED WORK

FLASH PYROLYSIS OF BIOMASS FOR LIQUID FUELS

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ABSTRACT

Fast or flash pyrolysis has been shown to give very high yields of liquid "bio-oil" on laboratory scale processes of up to 70%. The principle of flash pyrolysis for liquids production is that very high heating rates are combined with relatively low temperatures and with rapid quenching of liquid intermediate pyrolysis products. Several techniques have been employed including fluid beds, entrained flow reactors, cyclone and vortex reactors; and the principles employed include gas-solid heat transfer as in entrained flow reactors and solid-solid heat transfer as in ablative pyrolysis. This paper reviews the reaction mechanisms, pathways and kinetics of pyrolysis by reference to the flash pyrolysis technologies employed to date. Conceptual designs for liquid producing pyrolysis processes are developed from specifications laid down for process performance by evaluating known theories of reaction pathways and mechanisms, and by examining the resultant technical requirements.

INTRODUCTION

Pyrolysis produces a solid char, liquid products (tar and pyroligneous acid) and a fuel gas, the proportions of which are dependent on the process conditions and the nature of the feedstock. Current interest is focussed on liquid fuels which include the crude pyrolysis liquid or "bio-oil", upgraded products such as gasoline and diesel, char-water slurries and char-oil slurries. The first of these, bio-oil, is of particular interest as it is a liquid that can readily substitute for conventional hydrocarbon fuel oils, and it has been produced on laboratory scale processes at yields of up to 70% using fast or flash pyrolysis technology.

This paper prescribes a specification for an ideal pyrolysis process. By analysis of reaction mechanisms, reaction pathways, models of pyrolysis processes, and evaluation of technical requirements, a conceptual process is outlined and compared to the initial specification.

SPECIFICATION

The specifications of an ideal pyrolysis process are set out in Table 1. While clearly these are not all possible and some are contradictory, this does identify the main features that a successful and competitive process has to address. After consideration of the principles of pyrolysis, these are re-examined to form the basis of a potentially successful plant.

Pyrolysis liquids approximate to the original biomass in elemental composition by the following idealised relationship:

$$C_6H_9O_4 \longrightarrow C_6H_9O_4$$

In practice the following reactions can be considered to occur in flash pyrolysis:

$$\begin{array}{rcl}
2C_6H_9O_4 & \longrightarrow & 2C_6H_7O_3 + 2H_2O \\
4C_6H_9O_4 & \longrightarrow & 16CO + 8CH_4 + 2H_2 \\
2CO + 2H_2O & \longrightarrow & 2CO_2 + 2H_2 \\
\hline
6C_6H_9O_4 & \longrightarrow & 2C_6H_7O_3 + 14CO + 8CH_4 + 4H_2 + 2CO_2
\end{array}$$

Table 1
Ideal Pyrolysis Process Specification for Liquids Production

PROCESS
Minimum feedstock pretreatment and preparation
Maximum feedstock versatility and insensitivity to feedstock characteristics
Minimum heat input to reactor
Minimum heat losses
Minimum reaction temperature
Good separation of oil and water phases
Minimum number of product separation steps
Minimum product stabilisation and/or upgrading
Scaleability

PRODUCTS

Oil	Char	Gas	Water
Maximum oil yield	Minimum char yield	Minimum gas energy	Minimum yield
Maximum oil HHV	Minimum volatiles	As clean as possible	Minimum COD
Minimum char content			Neutral pH
Minimum oxygen content			
Minimum water content			
Neutral pH			
Easy upgradability			
Low viscosity			
Single phase			
High stability			

REACTION PATHWAYS AND MECHANISMS

Pyrolytic reactions are very complex and consist of both concurrent and consecutive reactions which results in a variety of products. The general overall mechanism for fast pyrolysis is dehydration, depolymerisation followed by melting and vaporisation to form vapours and gases with minimum char formation. However different pathways may be taken depending on the process conditions.

The most recent hypothesis on reaction pathways of fast pyrolysis has been proposed by Evans and Milne (1) based on molecular-beam, mass-spectrometric sampling (MBMS). They postulated that the primary vapours formed in the rapid pyrolysis of biomass under high pressure (but in the absence of catalysts or reactive environments) appear to have the same composition as the vapours obtained directly from low-pressure pyrolysis. Under high pressure conditions, the direct formation of a liquid product mixture is due to the pyrolysis of wood that has become "plastic" at the temperatures and pressures involved. This has been confirmed by Diebold (2) and Ledé et al. (3) who have shown that under direct-contact fast pyrolysis conditions, wood exhibits many properties of a "molten plastic state". At low pressures they found that the charcoal formed, though retaining structural features of the wood, shrinks, which could indicate a plastic state where pyrolysis products pass directly into a liquid state before devolatilisation. The direct formation of gaseous species from primary pyrolysis reactions, known as prompt gases, are primarily CO_2, H_2O and CO. These are largely associated with the char forming reactions.

The sequential transformation of the primary products in the vapour phase is shown in Figure 1 as passing through three stages. In the first stage at temperatures between 500-600°C, slight cracking reactions occur before substantial conversion occurs to permanent gases. The higher molecular weight lignin products are cracked to lighter aromatics and oxygenates. The second stage occurs from about 600-700°C with the formation of secondary products characterised by CO, light olefins and aromatics. Aromatics are also formed from the primary products of carbohydrate degradation at this stage. The third stage above 700°C, gives tertiary products from thermal degradation which include CO, CO_2, H_2, CH_4, low molecular weight saturated and unsaturated hydrocarbons and some polynuclear aromatics. These are generally formed only in high temperature conversion processes such as gasification and combustion, and in low yield.

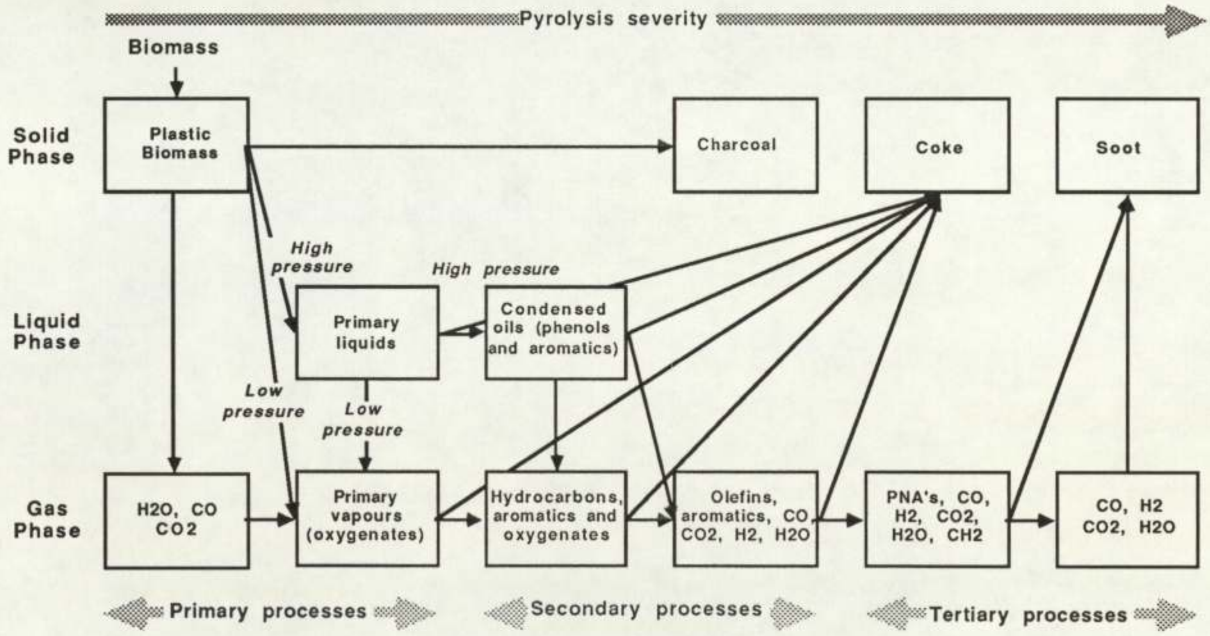

Figure 1
Reaction Pathways in Biomass Flash Pyrolysis [1]

KINETIC MODELLING

The pyrolysis process has been shown to be very complex and is a dynamic process in which reaction quenching is a critical part of the process for obtaining liquid products. The pathway generally quoted for the overall pyrolysis process is

biomass —> char + volatiles

and the rate of the above reaction is described in the form of a first order Arrhenius type rate law:

$$d\rho / dt = - k \exp -E/RT (\rho - \rho_f)$$

where ρ represents the local density, ρ_f the final density, k the pre-exponential (frequency) factor, E, the activation energy and R, the universal gas constant.

If the sample is heated at a constant rate M, then:

$$d\rho / dt = - k / M \exp -E/RT (\rho - \rho_f)$$

The kinetic parameters, E and k, are usually derived from weight loss data obtained by either dynamic or static thermogravimetric analysis (TGA). Owing to the different experimental conditions used to carry out these studies, considerable variations exist in the published values of kinetic constants. This makes it very difficult to generate general pyrolysis models due to the specificity of essential data to specific experimental conditions and feedstocks. These models cannot be used to predict product yields. Other methods used for predicting weight loss have modelled the activation energy as a function of the extent of reaction (4), used constant kinetic parameters but different orders of reaction (5), and used different kinetic parameters for different parts of the reaction (6).

The modelling of biomass pyrolysis in terms of individual products has also been proposed (7). However kinetic parameters cannot be predicted a priori and must be estimated from experimental data, a problem that increases as the number of reactions postulated increases. It has been suggested that this model should be viewed as a method for correlating data and comparing results from different biomass materials.

Rate laws based on a competitive mechanism have also been proposed to account for the variations in product yields with temperature and heating rate. Bradbury, Shafizadeh et al. (8) and Diebold (9) have used this technique to investigate the kinetics of cellulose pyrolysis.

Recently kinetic models for the secondary decomposition of primary pyrolysis tars have been proposed (10,11,12). Testing of these models showed that predicted liquid yields agreed with achieved yields within ± 10% for the temperature range 500-700°C with residence times of up to 1 second (13,14).

Different approaches have been used to develop kinetic models. However, most have been developed for predicting the weight loss of biomass rather than the product yield and distribution. One research group found that even a change of 1 kcal/mol in the activation energy of a competitive, multi-step reaction scheme caused changes in the product yield and distribution (15). Hence research in this area of pyrolysis requires further investigation.

For a complete model of pyrolysis the kinetic equation must be coupled with equations describing transport phenomena.

HEAT TRANSFER

Several reactor configurations have been employed for flash pyrolysis such as fluid beds, entrained flow reactors and cyclone reactors, and each configuration heats the feed in a different way. In fluid beds the feed is heated indirectly by convective and radiative heat transfer from hot solids such as sand, in entrained flow reactors heat transfer is mainly by convection from hot gases, and in cyclones heat transfer is by intimate contact of the particles with the hot wall surfaces. In the latter case, solid-liquid-solid heat transfer occurs which is significantly different from the gas phase heat transfer processes in fluid bed and entrained flow reactors, and this is known as ablative pyrolysis. Higher heat transfer coefficients are achieved using this technique resulting in potentially higher reactor specific capacities and smaller reactor volumes as there is no need for a heat transfer gas. Also this very high rate of heat transfer in ablative pyrolysis results in the almost exclusive production of liquids and gases which makes this process attractive for the conversion of biomass to liquid fuels.

Heating rate

Heating rate and final temperature both play important roles in the product distribution and yields from pyrolysis. At low heating rates of less than 1°C/s and at relatively low temperatures of less than 500°C, char, gas and liquid products are produced in approximately equal amounts. Flash and fast pyrolysis, including ablative pyrolysis, are claimed to involve extremely high heating rates of up to 1×10^{6}°C/s and very short residence times of less than 1 second in order to maximise either liquid or gas production while minimising char formation. If the desired product is liquids, moderate temperatures of between 400°C to not more than 650°C and rapid quenching have to be employed so that pyrolysis vapours are condensed before secondary reactions occur. Higher yields of gases are obtained at temperatures greater than 650°C. The main focus of pyrolysis research in Europe currently, is the production of liquids either for direct use or for upgrading to give high quality hydrocarbon fuels such as gasoline.

CONCEPTUAL DESIGN OF PYROLYSER FOR LIQUID FUELS

Theory

From the specifications outlined in Table 1 and the comparisons of the flash pyrolysis technologies mentioned above, ablative pyrolysis appears to be the most attractive route to employ for the production of liquid fuels. This is due to the high heat transfer rates, low reactor volume, better temperature control, and potentially higher liquid yields resulting from these advantages.

Fundamental research on ablative pyrolysis has been carried out by Ledé et al. (3). A stainless steel disc of 7.5 cm diameter, spinning at a constant and controlled speed, was heated to different temperatures by four gas burners underneath. Wood dowels were pressed vertically onto the hot surface by weights on the upper part of the rod. From their experiments, the following relationships were obtained:

(i) $V = a.p$
where V is ablation rate, m/s (speed of consumption of wood dowel)
p is pressure, Pa
a is constant, $m\ s^{-1}Pa^{-1}$

(ii) $h = 0.017\ p$
where h is heat transfer coefficient, $W\ m^{2}K^{-4}$
p is pressure, Pa

(iii) $T_d = 739$ K (466°C)
where T_d is temperature of decomposition

Ledé believed that decomposition occurs and is completed when the temperature of wood reaches 466°C independent of the reaction conditions. This behaviour of wood was likened to the phase change phenomenon of fusion.

Practice

Based on this work, a conceptual design study produced the specification outlined in Table 2. The pressure between the particle and the reactor wall needs to be as high as possible for optimum results, but there will be mechanical considerations in meeting this objective. Other aspects that require resolution in the experimental development is the masking effect of multiple particles on the interaction of particle and wall and volatilisation of liquid products. The vaporised liquids require rapid removal and quenching to avoid secondary reactions. Partial vacuum operation would avoid the need for flushing gas.

Table 2
Specification of an Ablative Pyrolyser for Liquids Production

	Derived from	Experimental	Commercial
Biomass throughput, d.a.f. kg/h	Specified	5	1 700
Temperature, °C	Literature	600	600
Pressure (particle on reactor)	Ledé	As high as possible	As high as possible
Heat input, kJ/kg	Estimated	2000	2000
Effective area for ablation, m^2	Ledé	3×10^{-3}	1
Estimated actual area, m^2	Estimated	9×10^{-3}	3
Minimum relative velocity, m/s	Ledé	1.2	1.2

CONCLUSIONS

As a result of the above work, the main conclusions are :

- Ablative pyrolysis is a very promising route to employ for the production of liquid fuels based on the ideal pyrolysis process specifications and characteristics outlined.
- Further research is required in the area of the of pyrolysis kinetics.

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APPENDIX II

DETAILED TABLE OF SINGLE PARTICLE PYROLYSIS MODELS

Table II.1

Single Particle Pyrolysis Models

Authors	Formulation and Assumptions	Achievements	Shortcomings
Bamford et al. [135]	• Heat balance equation containing a transient heat accumulation term, a conduction term and a heat of reaction term • First order, exothermic reaction • Thermal constants such as thermal conductivity and specific heat remain constant • Instantaneous release of volatiles	• Predicts temperature and weight loss profiles • Predicts rate of evolution of volatiles	• Cannot be used to predict product yields or composition • No sensitivity analyses were carried out • No convection term • Physical properties were assumed to remain constant
Panton and Rittmann [136]	• Heat balance equation containing a transient heat accumulation term, a conduction term and a heat of reaction term • Pyrolysis is described by three reactions, two competing and one was consecutive • Can be either an exothermic or endothermic reaction • Change in porosity affects both density and thermal conductivity • Efflux of gaseous products does not affect heat transfer	• Predicts temperature and reaction rate profiles • Predicts gas generation rate • Suggests that heat of reaction and activation energy are important parameters for gas generation • Suggests that competing reactions are reactions are sensitive to the heat flux employed	• Cannot be used to predict product yields or composition • No convection term • Breaks down at higher heating flux when investigating the effect of heating rate on the competing reactions
Kanuary et al. [137]	• Heat balance equation containing	• Shows that the convection term is	• Can only be used to

	a transient heat accumulation term, a conduction term, a convection term and a heat of reaction term • Equation of continuity (mass) • First order reaction • Solid matrix is inert while the active part is pyrolysed • Thermal equilibrium exists locally between the gas and the solid	needed in the heat balance equation • Suggests that the burning rate depends on particle size	investigate the importance of convective heat transfer
Kung [138-139]	• Heat balance equation containing a transient heat accumulation term, a conduction term, a convection term and a heat of reaction term • First order endothermic reaction • Variable density, specific heat thermal conductivity • No secondary reactions occurs • Instantaneous release of volatiles • No inward moisture migration • Thermal equilibrium between the volatiles and char • No shrinkage	• Predicts temperature and density profiles • Predicts volatiles release rate • Suggests that both the thermal conductivity and specific heat of char, the heat of reaction and particle size are important parameters in wood pyrolysis	• Cannot be used to predict product yields or composition
Maa and Bailie [118,120]	• Applied shrinking core concepts • Heat balance equation containing a transient heat accumulation term, a conduction term and a convection term • First order reaction • Can be either an exothermic or an endothermic reaction • Specific heat capacities are	• Predicts under what conditions heat transfer or chemical reaction is rate controlling • Predicts reaction rate and temperature profiles • Predicts reaction times • Derived simple expressions to estimate reaction time by using either effective thermal conductivity (large particles) or	• Cannot be used to predict product yields or composition • Does not predict volatiles evolution rate

	constant • Pseudosteady state approximation can be applied • Temperature in the unreacted core is constant • Rate of diffusion of pyrolysis gas is negligible	effective activation energy (small particle)	
Fan et al. [140-142]	• Heat balance equation containing a transient heat accumulation term, a conduction term, a convection term and a heat of reaction term • Mass balance equation for both solid and volatiles • n th order reaction • No shrinkage • Variable material properties • Can be either an exothermic or endothermic reaction	• Introduces a new parameter called the Lewis No. which is the ratio of thermal diffusivity to mass diffusivity • Predicts concentration and temperature profiles • Suggests that the higher the Lewis No., the greater the conversion of the solid and the smaller the temperature gradient within it • Suggests that heat of reaction affects pyrolysis rate	• Cannot be used to predict product yields or composition • Does not predict volatiles evolution rate
Kansa et al. [143]	• Heat balance equation containing a transient heat accumulation term a conduction term, a convection term and a heat of reaction term • Time dependent radiant heat flux • Endothermic, first order reaction • Variable physical properties • Darcy flow of volatiles • Local equilibrium exists between solid and volatiles • No shrinkage	• Predicts mass loss, pressure and temperature profiles • Suggests that heat of reaction, both the thermal conductivity and specific heat of char and the permeability constant are important parameters in wood pyrolysis	• Cannot be used to predict product yields or composition • Does not predict volatiles release rate

van Ginneken et al. [144]	• Heat balance equation containing a transient heat accumulation term, a conduction term, a convection term • Used the Kilzer and Broido reaction scheme [x] and later extended it • No liquid phase present • Thermal equilibrium between gas and solid • No accumulation of vapours • No shrinkage • Constant physical properties • No secondary reactions	• Predicts product distribution • Temperature and particle size influences product distribution	• Does not predict temperature profiles • Assumed that physical properties remained constant
Desrosiers et al.[145]	• Applied a phase change concept (wood to char) • Heat balance equation containing a transient heat accumulation term, a conduction term and a convection term • Reaction occurs instantaneously when wood reaches a fixed pyrolysis temperature, T_p • The temperature of escaping volatiles is always equal to the local char temperature, T_c • Effective values of thermal properties and density are constant	• Predicts temperature profile • Predicts reaction time • Suggests that the values of pyrolysis temperature, char thermal conductivity and heat of reaction significantly affect wood pyrolysis	• Cannot be used to predict product yields or composition • Does not predict volatiles release rate • Assumed that physical properties remain constant
Capart et al. [127,146]	• Heat balance equation containing a transient heat accumulation term, a conduction term, a convection	• Predicts reaction rate and time • Predicts both internal and surface temperature and mass loss	• Cannot be used to predict product yields or composition • Does not predict volatiles

	term and a heat of reaction term • No shrinkage • Thermal diffusivity changes when $T \geq 390^{\circ}C$ • Pyrolysis is a first order reaction occurring in two stages		evolution rate
Phillips et al. [147]	• Chemical reaction and energy transport are uncoupled • Heat balance equation containing a transient heat accumulation term and a conduction term • Thermal conductivity and thermal diffusivity are constants • Thermochemically weak reaction	• Predicts mass loss profiles • Predicts surface and internal temperature profiles • Predicts char yields	• Does not predict volatiles yields • Does not predict volatiles release rate • Assumed that physical properties remained constant • For large particles kinetics and heat transfer are not coupled
Saastamoinen [104]	• Considered phase change phenomenon • Heat balance equation containing a transient heat accumulation term, a conduction term and a convection term, which includes a flow of moisture, and a heat of reaction term which includes the heat of vaporisation of water • The rate equation for the generation of volatiles is based on the temperature dependent asymptotic yield of volatiles • Equation of continuity (mass) • Instantaneous release of volatiles and steam • No secondary char reactions	• Predicts temperature, mass loss and density histories • Predicts moisture distribution • Predicts moisture and volatiles release rate • Predicts generation of steam and volatiles	• Neglect of mass transfer resistance which may play a role in pyrolysis

	• No shrinkage • Variable physical properties • Heat transfer coefficient varies with Stanton No.		
Lédé et al. [145]	• Heat balance equation containing a transient heat accumulation term, a conduction term, a convection term and a heat of reaction term • First order, endothermic reaction • Particle shrinks so as to conserve constant density • No accumulation of vapours • Constant thermal properties	• Predicts under what conditions heat transfer or chemical reaction is rate controlling • Introduces a thermal Thiele Modulus (ratio of heat penetration time to reaction time) • Predicts temperature profile • Predicts reaction time	• Cannot be used to predict product yields or composition • Does not predict volatiles evolution rate • Assumed physical properties remained constant
Pyle and Zaror [14,150,151]	• Heat balance equation containing a transient heat accumulation term, a conduction term and a heat of reaction term • First order reaction • Variable physical properties	• Introduced two pyrolysis numbers, Py (ratio of reaction time to heat penetration time) and Py' (product Biot No. and Py) • Evaluated the importance of external and internal heat transfer effects • Derived four simple models • Predicts conversion and temperature profiles • Predicts conversion times • Particle size affects conversion • Carried out sensitivity study	• Cannot be used to predict product yields or composition • Does not predicts volatiles release rate • No convection term
Stiles [152]	• Heat balance equation containing a transient heat accumulation term and a conduction term • Net enthalpy is zero	• Predicts char yields • Predicts cracking activation energies	• Cannot be used to predict volatiles yields or composition • Does not predicts volatiles evolution rate

	• Substrate is consumed by a first order reaction which yields both a char and a volatile fraction • Volatiles participates in secondary charring reaction • Variable physical properties • Convective heat transfer is negligible • Volatiles escape from solid by either diffusion or hydrodynamic flow • Activation energy is represented by a continuous distribution of energies of Gaussian form		• No convection term • Predicts that smaller particles produce more char than larger ones
Kothari and Antal [129-130]	• Heat balance equation containing a transient heat accumulation term, a conduction term, a convection term, a heat of reaction term and inertia term for the gases • Equation of continuity (mass) • Solid have a constant volume • Good thermal contact between gases and solid • Applied dusty gas model	• Predicts temperature histories • Predicts weight loss • Calculates reaction times • Derived simple expressions to calculate heat up time and devolatilisation time • Pyrolysis is complete at 500°C	• Cannot be used to predict product yields or composition • Does not predict volatiles release rate
Chan et al. [17,103,153]	• Heat balance equation containing a transient heat accumulation term, a conduction term, a convection term and a heat of reaction term which includes the heat of vaporisation of water • Variable physical properties	• Predicts product yields and composition • Predicts volatiles release rate • Predicts temperature profile • Predicts effects of moisture • Carried out sensitivity studies	• Neglect of mass transfer resistance which may play a role in pyrolysis

	• Employs a multi-component reaction scheme • Instantaneous release of volatiles		
Krieger-Brockett et al [134]	• 2-dimensional model • Heat balance equation containing a transient heat accumulation term, a conduction term, a convection term and a heat of reaction term which includes the heat of vaporisation of water • Variable physical properties • Employs a multi-component reaction scheme Instantaneous release of volatiles	• Predicts product yields and composition • Predicts volatiles release rate • Predicts temperature profile • Predicts effects of moisture • Carried out sensitivity studies	• Neglect of mass transfer resistance which may play a role in pyrolysis

APPENDIX III

EXPERIMENTAL DATA AND PLOTS USED TO DERIVE EMPIRICAL RELATIONSHIPS

LIQUID YIELD DATA

Temperature	**Yield** *	**Institute**
500	35.0	GTRI
450	41.8	GTRI
550	31.0	GTRI
400	33.7	GTRI
430	34.6	GTRI
475	49.4	GTRI
475	46.0	GTRI
475	51.3	GTRI
475	47.6	GTRI
475	46.0	GTRI
475	41.9	GTRI
470	48.6	GTRI
473	44.0	GTRI
477	51.0	GTRI
479	44.2	GTRI
502	44.6	GTRI
527	41.4	GTRI
475	43.2	GTRI
474	43.8	GTRI
474	45.0	GTRI
474	44.5	GTRI
461	37.5	GTRI
458	38.7	GTRI
477	50.3	GTRI
500	42.5	GTRI
475	51.8	GTRI
501	48.1	GTRI
524	53.8	GTRI
525	43.4	GTRI
475	51.2	GTRI
498	50.1	GTRI
525	56.8	GTRI
523	57.1	GTRI
499	52.1	GTRI
504	60.0	GTRI
425	46.40	Laval
636	41.60	Laval
430	45.80	Laval
425	50.10	Laval
465	39.70	Laval
450	50.90	Laval
450	47.40	Laval
450	50.00	Laval
518	68.24	Waterloo
532	66.89	Waterloo
530	58.39	Waterloo

530	61.83	Waterloo
482	60.63	Waterloo
480	66.54	Waterloo
500	64.68	Waterloo
500	64.16	Waterloo
532	56.25	Waterloo
531	69.54	Waterloo
530	61.21	Waterloo
425	55.88	Waterloo
465	67.17	Waterloo
500	65.76	Waterloo
500	71.15	Waterloo
541	63.65	Waterloo
625	40.27	Waterloo
541	62.05	Waterloo
450	55.82	Waterloo
500	65.78	Waterloo
550	61.96	Waterloo
497	62.90	Waterloo
504	62.90	Waterloo
555	59.00	Waterloo
485	63.10	Waterloo
500	66.50	Waterloo
520	66.10	Waterloo
532	67.30	Waterloo
508	67.90	Waterloo
515	65.00	Waterloo
500	65.80	Waterloo
504	66.20	Waterloo
760	2.73	TNEE
500	15.18	Alten
1000	15.00	BASA
1000	15.18	BASA

* refer to Section 5.5

DATA FROM FLUID BED - WATERLOO *

Temperature	Liquid Yield	Water Yield	Char Yield	Gas Yield
518	68.24	10.60	13.25	9.98
532	66.89	9.70	9.37	10.02
530	58.39	8.60	17.85	7.27
530	61.83	9.80	14.73	7.96
482	60.63	6.30	20.90	8.42
480	66.54	6.90	12.41	10.51
500	64.68	8.20	12.61	10.27
500	64.16	8.90	9.24	12.31
532	56.25	7.40	9.02	12.05
531	69.54	7.80	9.37	10.35
530	61.21	8.20	10.32	16.51
425	55.88	3.80	30.51	5.95
465	67.17	5.50	18.88	8.53
500	65.76	9.30	12.15	12.45
500	71.15	6.60	11.20	12.07
541	63.65	7.40	8.99	21.22
625	40.27	4.10	7.81	36.65
541	62.05	7.70	9.72	19.11
450	55.82	5.30	25.46	8.57
500	65.78	4.30	13.21	11.85
550	61.96	5.30	10.64	18.56
497	62.90	10.30	14.40	12.00
504	62.90	9.70	16.50	11.50
555	59.00	10.20	10.60	17.40
485	63.10	10.70	16.30	8.10
500	66.50	11.60	12.20	7.80
520	66.10	11.10	12.30	7.40
532	67.30	7.40	9.00	12.10
508	67.90	9.80	13.70	9.80
515	65.00	10.00	12.10	11.60
500	65.80	9.30	12.10	12.40
504	66.20	10.70	11.80	11.00

* refer to Section 5.5.7

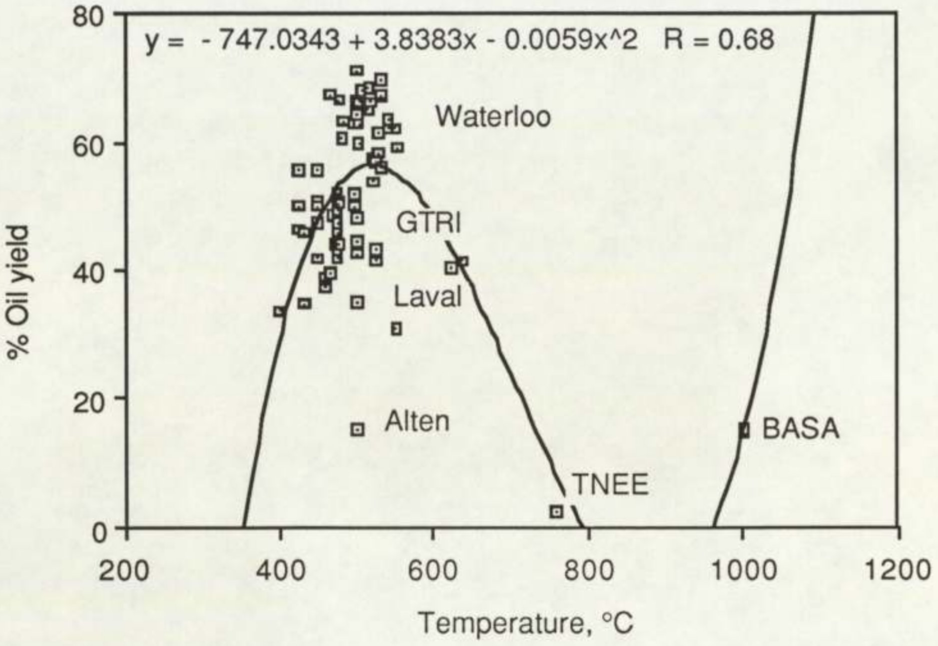
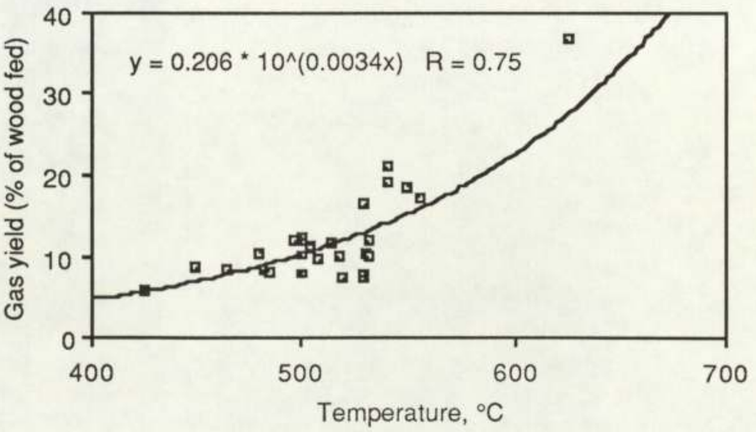
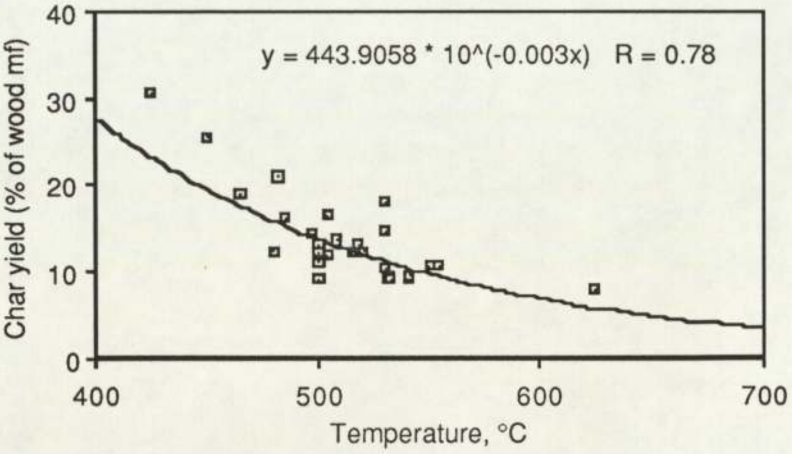


Figure III.1 Oil Yield Plot for n = 3



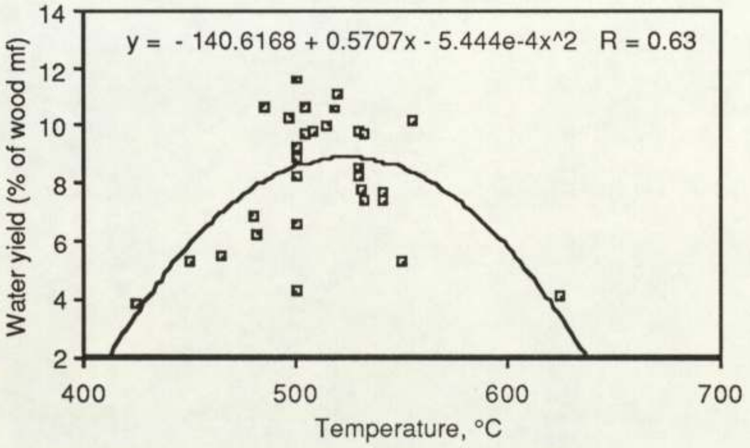
Data from "Data Waterloo"

Figure III.2 Gas Yield Plot



Data from "Data Waterloo"

Figure III.3 Char Yield Plot



Data from "Data Waterloo"

Figure III.4 Water Yield Plot

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