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Gasification, Catalytic Technologies and Energy Integration for Production of Circular Methanol: New Horizons for Industry Decarbonisation

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Abstract:	The Intergovernmental Panel on Climate Change (IPCC) recognises the pivotal role of renewable energies in the future energy system and the achievement of the zero-emission target. Major opportunities for decarbonisation arrive with the use of renewables. Moreover, decentralised deployment will also provide security of energy supply and boost domestic jobs. Renewable fuels, including synthetic and biofuels, provide long-term solutions for the transport sectors, particularly for applications where fuels with high energy density are required. At the same time, it helps reducing the carbon footprint of these sectors in the long-term. Information on biomass characteristics and properties is an essential factor to consider when scaling-up gasification from the laboratory to industrial-scale. Biomass properties impact the downstream processing steps and the quality of the final products. Therefore, information on biomass feedstock is essential to design biofuel production units correctly. This review analyses an innovative approach to transform biogenic residues into a valuable bioenergy carrier like biomethanol as the liquid sunshine based on the combination of modified mature technologies such as gasification with other solutions such as membranes and microchannel reactors. Tar abatement is a critical process in product gas upgrading since tars compromise downstream processes and equipment, for this, membrane technology for upgrading syngas quality is discussed in this paper. Microchannel reactor technology with the design of state-of-the-art multifunctional catalysts provides a path to develop decentralised biomethanol synthesis from biogenic residues. This bioenergy carrier's distributed production will increase rural communities' wealth through territory-based solutions for agricultural residues or marginal land production. Finally, the development of a process chain for the production of (i) methanol as an intermediate energy carrier, (ii) electricity and (iii) heat for decentralised applications based on biomass feedstock flexible gasification, gas upgrading and methanol synthesis is analyzed.
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Seville, 27th March 2023,

Dear editor,

We are delighted to propose to you our latest study entitled: "**Gasification, Catalytic Technologies and Energy Integration for Production of Circular Methanol: New Horizons for Industry Decarbonisation**" by the authors L.F. Bobadilla, L. Azancot, M. González-Castaño, E. Ruiz-López, L. Pastor-Pérez, F.J. Durán-Olivencia, R. Ye, K.J. Chong, P.H. Blanco-Sánchez, Z. Wu, T.R. Reina and J.A. Odriozola.

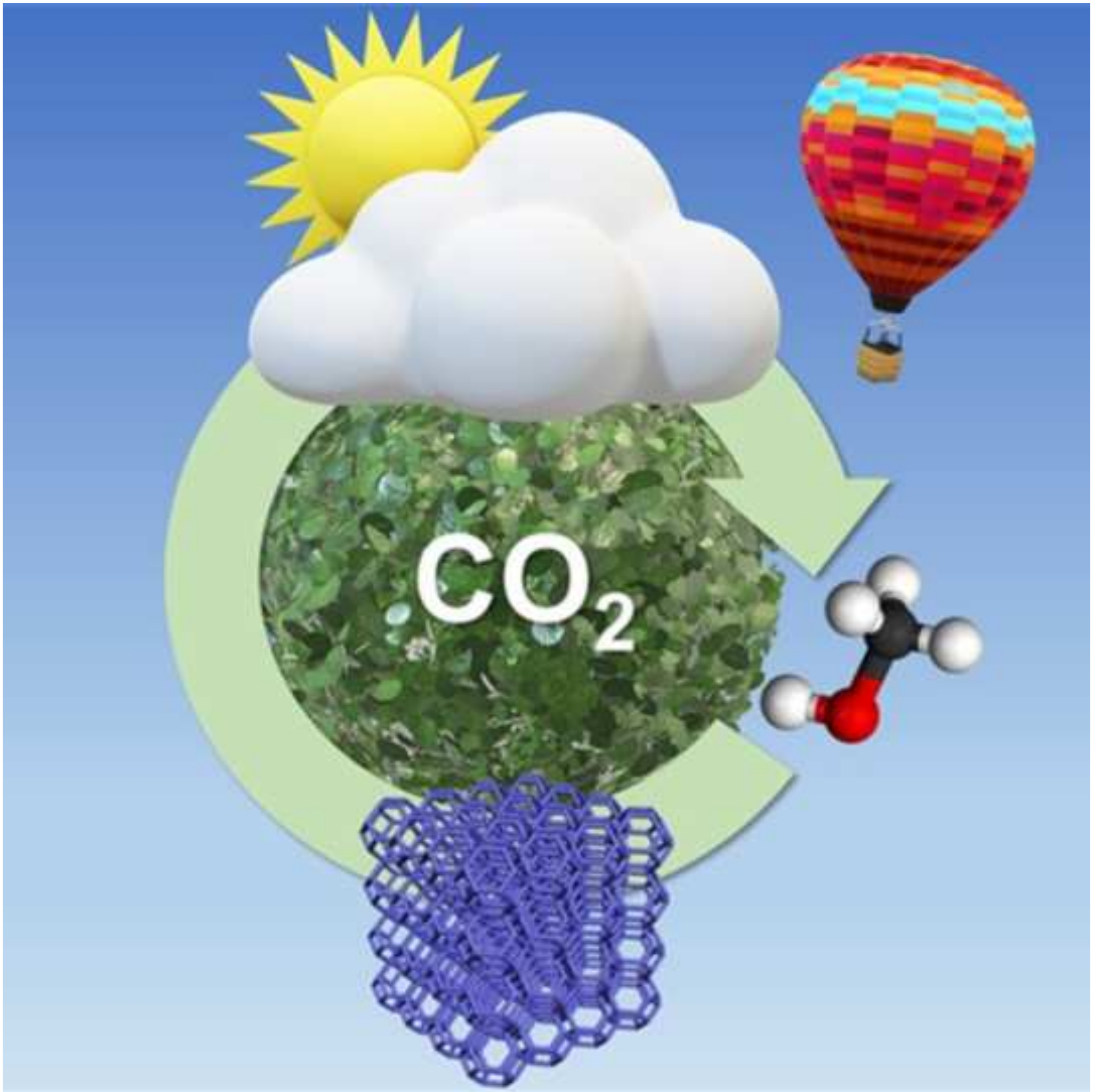
Renewable fuels, including synthetic and biofuels provide long-term solutions for the transport sectors, in particular for applications where fuels with high energy density are required, while at the same time help reducing the carbon footprint of these sectors in the long-term. This review focus in the catalytic system perspectives and innovative approach to transform biogenic residues into a valuable bioenergy carrier such as biomethanol. While there is increasing publication in this field, the reports related to the achievements into the engineering aspects of biomethanol production are still limited. In this work, we offer a new perspective of the developed technologies at multiple scales, using differing gasification techniques to evaluate both their technical performance and their contributions to cost and energy reductions, in comparison with conventional methods.

This is an original piece of research that has not been published, and it is not under consideration to be published in any journal. Given the fundamental insights provided in our work and its applicability in multidisciplinary areas such as chemistry/applied sciences/catalysis/low-carbon energy, we believe that this paper fits well with the scope of the **Science of the Total Environment** and we will be glad if you could consider it for publication.

Yours sincerely,

Luis F. Bobadilla on behalf of the all the co-authors.

Graphical Abstract



Highlights

- Biomethanol production from biomass gasification represents a circular economy approach for chemicals production
- Advanced configurations based on membranes for obtaining cleaning syngas from biomass are discussed
- The implementation of microchannels reaction technology is proposed to enhance the chemical engineering aspects of biomethanol production
- The production of biomethanol has an important socio-ecomnomic impact

Gasification, Catalytic Technologies and Energy Integration for Production of Circular Methanol: New Horizons for Industry Decarbonisation

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Abstract: The Intergovernmental Panel on Climate Change (IPCC) recognises the pivotal role of renewable energies in the future energy system and the achievement of the zero-emission target. Major opportunities for decarbonisation arrive with the use of renewables. Moreover, decentralised deployment will also provide security of energy supply and boost domestic jobs. Renewable fuels, including synthetic and biofuels, provide long-term solutions for the transport sectors, particularly for applications where fuels with high energy density are required. At the same time, it helps reducing the carbon footprint of these sectors in the long-term. Information on biomass characteristics and properties is an essential factor to consider when scaling-up gasification from the laboratory to industrial-scale. Biomass properties impact the downstream processing steps and the quality of the final products. Therefore, information on biomass feedstock is essential to design biofuel production units correctly. This review analyses an innovative approach to transform biogenic residues into a valuable bioenergy carrier like biomethanol as the liquid sunshine based on the combination of modified mature technologies such as gasification with other solutions such as membranes and microchannel reactors. Tar abatement is a critical process in product gas upgrading since tars compromise downstream processes and equipment, for this, membrane technology for upgrading syngas quality is discussed in this paper. Microchannel reactor technology with the design of state-of-the-art multifunctional catalysts provides a path to develop decentralised biomethanol synthesis from biogenic residues. This bioenergy carrier's distributed production will increase rural communities' wealth through territory-based solutions for agricultural residues or marginal land production. Finally, the development of a process chain for the production of (i) methanol as an intermediate energy carrier, (ii) electricity and (iii) heat for decentralised applications based on biomass feedstock flexible gasification, gas upgrading and methanol synthesis is analyzed.

Keywords: *Biogenic residues; Gasification; Biomethanol; Circular Economy; Microreactors*

1. Introduction

Over the years, many efforts have been made to shift from the use of fossil fuels to renewable energy due to the polluting nature of fossil fuels, their decreasing reserves, and their volatile prices. The current scenario indicates that, although increasingly utilised, renewable energy is still far from becoming a primary energy resource for a simple reason: it is not yet economically profitable compared to fossil fuels. Thus, global energy demands still rely heavily on fossil fuels, comprising more than 68% of the world's primary energy supply in 2018 and contributing up to 35% of global greenhouse gas (GHG) emissions. Moreover, the demand for all fuels has continued to rise, with fossil fuels meeting nearly 79 % of demand in 2021, with only 19% obtained from renewable sources (Moodley and Trois, 2021).

In the future envisaged by the long-term climate strategy, research and innovation activities must be organised to work on solutions across sectors such as energy, transport, infrastructure, and buildings. Therefore, developing a wide range of advanced low and zero-carbon technologies is needed, optimising research and innovation activities from a value chain perspective, supporting the circular economy, and reducing environmental footprint and pollution arising from different stages (Figure 1).

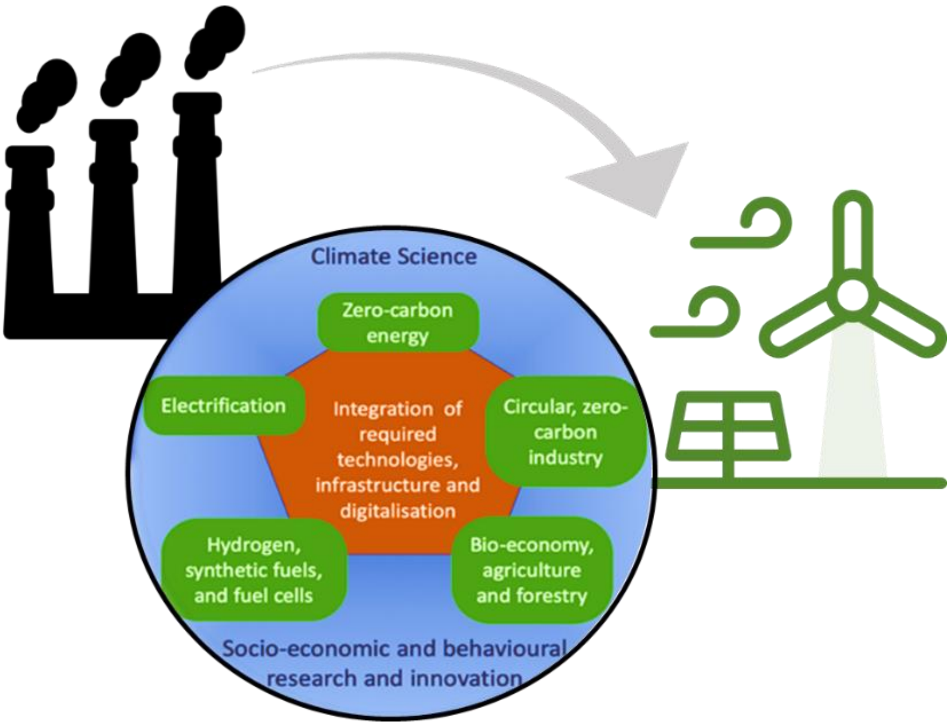

Figure 1. Chain perspective to achieve the transition from fossil fuels to renewable energies

In this sense, placing renewable energy in a competitive position with respect to fossil fuels necessarily involves minimisation of the production cost and a reduced environmental impact. Based on this premise, biomass, particularly biomass residues, represent a promising substitute for fossil fuels. During its short life cycle, all carbon in biomass comes from the atmosphere and soil, which is liberated into the environment when burned (Singh et al., 2016). Therefore, biomass is ideally considered a carbon-neutral feedstock if it is sustainably sourced. Consequently, bioenergy development is an effective countermeasure to extend fossil fuel reserves, reduce greenhouse gas (GHG) emissions, and mitigate global warming and climate change. In line with these concerns, during the 27th EUBCE European Biomass

Conference and Exhibition in 2019, the European Commission reached the following conclusions:

1) For bioenergy and biofuels, certain value chains are established, but the production costs and volumes of materials readily available represent a limitation.

2) Biofuels and biomass combined heat and power (CHP) must play an important role in decarbonising the European economy due to their versatility, dispatchability, absence of infrastructure requirements, and large emissions reduction potential.

3) An integrated approach of strong policy measures, research, innovation and improved financing solutions by international cooperation with non-European and European countries is necessary.

Therefore, to achieve economically sustainable advanced biofuels and bring them closer to the market, we must seek revolutionary technologies that represent a step ahead in biomass conversion, unlocking the potential for this resource through the generation of added-value products and liquid fuels like methane, methanol, etc. The current global methanol (CH_3OH) production is about 45 million tons per year, and it takes place via catalytic conversion of fossil fuels, mainly natural gas . Biomethanol is chemically identical to conventional methanol, but it can be produced from a wide range of biomass feedstocks, including under-utilised resources such as biogenic residues or energy crops from marginal lands. Biomass gasification, combined with other downstream processes, can yield high-quality biomethanol with diverse applications ranging from transport fuels to electricity . This pathway to yield biomethanol can bring the reduction of fossil fuel usage and greenhouse gas emissions as an additional benefit.

For methanol synthesis, some reviews dealing with the lattest advances on heterogeneous catalysis (Ali et al., 2015; Guil-López et al., 2019) and strategies for optimizing from the reactor design perspective (Bozzano and Manenti, 2016) have been recently published. Instead, this review focuses on approaches to maximise the conversion of biogenic residues and wastes into valuable bioenergy carriers like biomethanol. As illustrated in Figure 2, different approaches suitable for decentralised deployment will be analysed, making systems available to address local feedstock supply chains, capacity ranges and production strategies. This work aims at underlining the major action lines using gasification as the primary conversion route capable of processing a range of biomass feedstock to yield biomethanol. For that purpose, the importance of biomethanol and the biomass to biomethanol process using a fixed-bed gasification reactor is exposed. Afterward, novel combinations of improved biomass gasification concepts, gas cleaning, upgrading and new reactor concepts for methanol synthesis will be discussed to define novel product gas routes that increase the efficiency of biomass conversion to biomethanol and thus create sustainable bioenergy products.

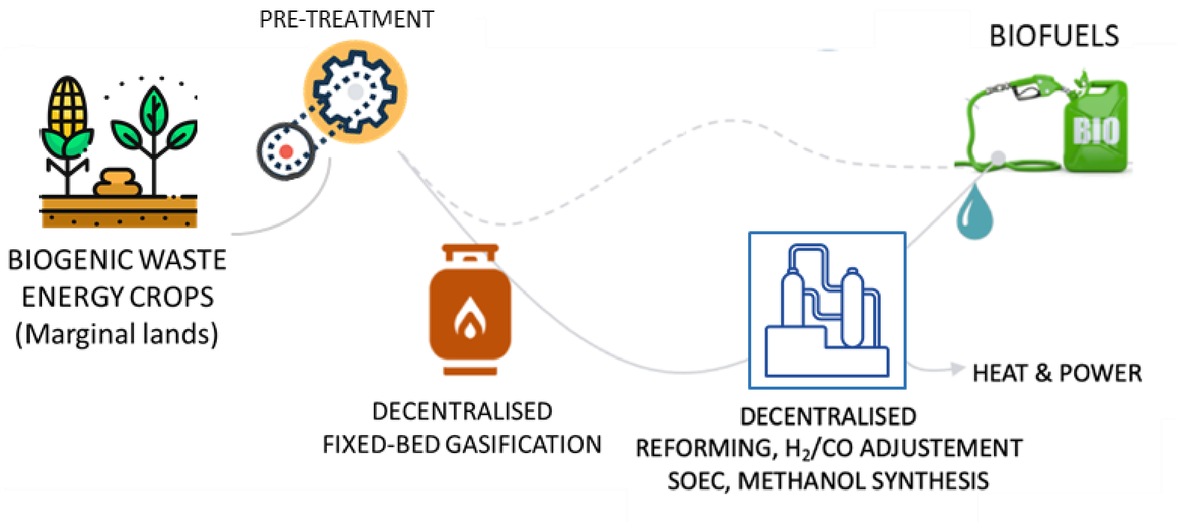

Figure 2. Biogenic waste-to-chemicals/fuels overall concept

2. Importance of biomethanol

Methanol is one of the top chemicals produced in the world with a high octane number of 110 that allows it to be blended up to 10-20 wt.% with other fuels such as gasoline (Huber et al., 2006). In addition, methanol contributes to other sectors: for instance, it can be combusted directly in modified engines and used as platform chemical to obtain a wide range of added-value products, including formaldehyde, methyl tert-butyl ether (MTBE), dimethyl ether (DME), polymers and synthetic chemicals, including pharmaceutical products . Furthermore, methanol is also used in the methanol-to-olefins process to manufacture other liquid fuels (Tian et al., 2015).

Compared to widely used methanol production from natural gas, biomethanol production is a relatively new process and still under development. The main drawback of using biomass as raw material for biomethanol production is the higher production cost (1.5 to 4 times higher) due to the differences in feedstock, pretreatment and processing conditions (Eichler et al., 2015; Farsi, 2021). However, the increased financial penalties on CO_2 emissions from fossil sources will drastically reduce this difference. Besides, the techno-economic aspects associated with the Objectives for Sustainable Development shift the focus from the economy of scale to distributed process that will contribute to the feasibility of the biomethanol process (Carvalho et al., 2017; Resasco et al., 2018).

3. Biomass-to-biomethanol process based on fixed-bed downdraft gasification

Methanol production from biomass typically consists of feedstock pretreatment, gasification, gas cleaning, water-gas shift to obtain the appropriate H_2:CO ratio, methanol synthesis and purification, as shown in Figure 3 (Hamelinck and Faaij, 2002). Furthermore, one of the main challenges for gasification technologies is the presence of unwanted components in the product gas, including tars, H_2S, HCl, etc. Therefore, to enable the downstream upgrading and conversion of product gas into methanol, the product gas should ideally contain low concentrations of contaminants (Quinn et al., 2004).

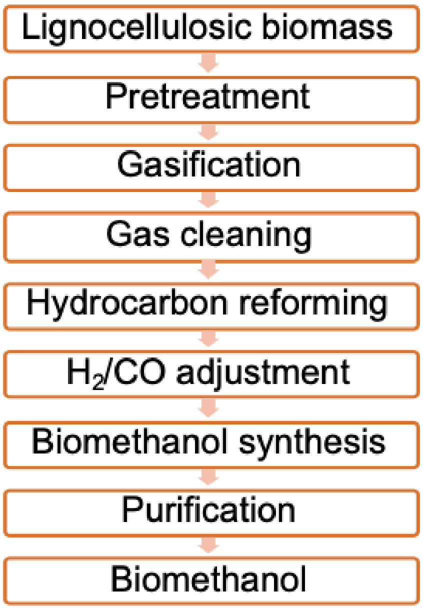

Figure 3. Simplified scheme of biomass gasification for biomethanol production

3.1. Identification and selection of feedstock

A key issue regarding the viability of bioenergy lies in developing reliable, integrated biomass supply chains from cultivation, harvesting, transport and storage through to conversion and by-product use. A secure, long-term supply of sustainable feedstock is essential to the economics of bioenergy plants (Junginger et al., 2011). In the last decades, several biomass availability studies have been performed. However, due to their approaches, their results are difficult to compare and interpret directly. Many have studied, for example, forest biomass (Avitabile and Camia, 2018; Gallaun et al., 2010), animal manure, straw and grass potentials (Kaltschmitt and Weber, 2006; Meyer et al., 2018), but only one-third of the available potential of solid biofuels in EU-15 countries were used. A summary of biomass resources reported in the literature for the case of Spain can be found in Table 1.

Table 1. Biomass availability, price and properties for biomass existing in Spain

Feedstock	Availability [10^3 tons of dry matter / yr]	Price [€-PJ]	M: moisture (% wet basis) A: ash-content (% dry basis)
Agricultural	25 000	2.5-5	M: 12.5-92.1 A: 0.3-35.4
Forestry	63 000	5-10	M: 5-52 A: 0.4-5
Fishery waste and marine biomass	2 600	2-3	M: 4-40 A: 3-26
Sewage sludge	12 000	2-4	M: 5-60 A: 18-45
Waste biomass included biodegradable, food and green waste	12 000	2.5-5	M: 5-45 A: 2-17

Waste and non-food biomass, is presently combusted in power plants to generate electricity at low efficiency (Pędziwiatr et al., 2021). For example, biogenic residues from the olive oil industry are normally combusted in the Mediterranean Basin. An alternative to combustion is gasification to create higher-quality products such as methanol from processing these feedstock's.

As the output from the energy conversion systems is highly dependent on the quality of the biomass put into the system, there are problems associated with using different biomass sources, which include variations in properties between biomass types or even within individual species (Nunes et al., 2016). Crop and harvesting conditions involve varied key biomass composition, impacting the final product's quality (Barr et al., 2020). In the face of increasing competition for access to biomass feedstock, there is a need to better understand the availability and physicochemical properties of different types of biomass, mainly waste biomass, both now and in the future.

Currently available biomass databases provide information on the physicochemical properties of organic materials, waste plastics and the products obtained from thermal conversion. However, they tend to lack key detailed information on the conditions of thermal conversion and products. Indeed, the Phyllis database, which contains information on the composition of biomass, macro- and micro-algae, feedstock for biogas production, biochar and torrefied biomass, does not provide any information about the availability of biomass in the EU or other countries of the world and whilst one algorithm in this database calculates the heat of combustion, there are no methods to predict other physicochemical properties, *e.g.* solid products obtained after thermal conversion . Similar databases are also provided by scientific research units researching solid biofuel analysis (Sajdak et al., 2013). Moreover, the spectrum of analytical data depends on the capabilities of a particular institution's apparatus, which also translates into a lack of standardisation.

3.2. Pretreatment

Pretreatment methods aim to prepare the biomass feedstock to aid the gasification process and increase the yield and quality of gaseous products. Pretreatment methods typically focus on reducing moisture content, achieving specific particle size or densification, and reducing the amount of contaminants that can be detrimental to gasification.

Downdraft gasifiers require feedstock with a moisture content <15 wt.%, therefore requiring some feedstock drying. The most common method for drying uses heat. Particle size reduction is typically achieved by chipping, grinding or milling, and pelletisation is achieved using specific high-pressure equipment.

For reducing specific feedstock components, leaching biomass with water or/and acid solutions represents an alternative option to optimise fuel properties. These methods help remove ash, potassium (K), sodium (Na), calcium (Ca) and chlorine (Cl), which is beneficial, particularly considering biomass with high ash content, which can significantly reduce the efficiency of the gasification process. Leaching can remove between 15% to 40% of the original ash content and around 60% of K, Na, Ca, and Cl, depending on the type of biomass (Deng et al., 2013). Although various leaching methods exist, water extraction is preferred as the most environmentally friendly method, depending on the structure of the biomass, since significant fractions of alkali metals, chlorine, sulphur and phosphorous can be removed within a short time. The disadvantage is that further drying is required after the pretreatment takes place.

An additional pretreatment method commonly used is torrefaction. This pretreatment is a relatively mild thermochemical process in which biomass is heated at 200 – 300 ºC under an inert atmosphere (Li et al., 2022). Torrefaction can aid the grindability of difficult-to-pulverize biomass, make a more homogeneous feedstock that improves pelletisation, avoid feedstock absorbing moisture, avoid fuel degradation, low O/C ratios, and enhance the gasification process by achieving a coal-like feedstock as shown in Figure 4 .

Whilst numerous benefits have been demonstrated for using torrefaction in the pretreatment of biomass, there is a need to better understand the process variables and the influence of feedstock variables. Many industrial projects have encountered difficulties in producing torrefied biomass (Nunes, 2020a; Nunes, 2020b). These difficulties are due to the fact that not all the variables associated with thermochemical conversion are well understood and considered. Moreover, the intrinsic characteristics of the raw material, namely their chemical and structural composition, and the behaviour of each of these compounds during the torrefaction process are often neglected. Although most of the challenges related to the technical operation of a torrefaction unit have been largely corrected, there is still a need to better understand the different forms of biomass and how they react in the torrefaction process.

Figure 4. Raw (left side) and torrefied (right side) energy willow

3.3. Gasification and producer gas conditioning

Gasification is a thermochemical process which converts the pretreated biomass feedstock mostly into gaseous products that can be used in diverse applications. Gasification can exploit energy from biomass via the conversion of the solid fuel into a producer gas, mainly composed of carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2), steam (H_2O), methane (CH_4), tars as well as chlorinated, sulphur compounds, and impurities (Asadullah, 2014; Deshmukh et al., 2013; Kumar et al., 2009). This process takes place at 400-600°C either below stoichiometric oxidation conditions with air as a gasification agent ("autothermal gasification") (Gulyurtlu et al., 2013) or in a steam atmosphere ("allothermal gasification") (Kaur et al., 2019). The working medium (*gasifying agent, temperature, catalyst*) modifies the product gas composition and its heating value, and it might have an effect on the final tar concentration too. Optimal H_2O: biomass ratios result in gaseous products with elevated H_2 concentrations (60% H_2, 30% de CO_2 and 10% CO) (Narváez et al., 1996). Table 2 summarises the gas composition for a selection of allothermal processes.

Table 2. Typical gasification product composition for several allothermal processes (Virginie et al., 2012)

Gasifying agents	Composition (vol. %)					Heating value (MJ m^{-3})
	H_2	CO	CO_2	CH_4	N_2	
Air	9-10	12-15	14-17	2-4	56-59	3-6
O_2	30-34	30-37	25-29	4-6		10-15

H_2O/CO_2	24-50	30-45	10-19	5-12	12-20

Several gasification technologies, including fixed-bed, fluidised bed and entrained flow, have been studied for biomass gasification at different process conditions (Alauddin et al., 2010; Hernández et al., 2010; Higman and van der Burgt, 2008; Karl and Pröll, 2018). However, fixed-bed gasification systems are usually applied in decentralised systems due to plant complexity and cost-related reasons (Bozzano and Manenti, 2016).

One of the major barriers to developing biomass gasification is the presence of impurities in the produced gas, including organic contaminants or tars and other pollutants such as particulate matter, NH_3, H_2S, HCl, NO_x and SO_x (Nunes, 2020a). The impurities in the producer gas represent a real challenge for its utilisation (Font Palma, 2013) as they create severe operational problems in downstream applications (Corton et al.; Milne et al., 1998; Shen and Yoshikawa, 2013). Acids such as hydrochloric acid (HCl) are formed during gasification due to the conversion of halides found in biomass and can create corrosion and attrition issues. Other species, such as KCl, have been associated with dioxin and furan formation in syngas downstream applications. Furthermore, sulphated and chlorinated compounds can have detrimental effects on catalysts when the gas is upgraded via catalytic approaches (Zhao-Tie et al., 1994). Sulphur contained in biomass feedstocks can be converted into hydrogen sulphide and sulphur dioxide during gasification, which have a high adsorption affinity on the active sites of catalysts, thus promoting premature deactivation (i.e. poisoning).

It has been reported that operational parameters, including temperature, gasifying agent, residence time, and gasifier design can affect the formation of tars (Surisetty et al., 2012). The minimum allowable limit for tar is highly dependent on the subsequent process or gas end-user application. For the downstream conversion of product gas into fuels, the producer gas must contain very low concentrations of tars and other impurities. Generally, tar starts condensing at temperatures below 350 °C, causing blockages and clogging of equipment as the temperature is reduced, and as it can polymerise into more complex structures (Basu, 2010; Devi et al., 2003). Average tar concentrations of 1 g Nm^{-3}, 10 g Nm^{-3}, and 50 g Nm^{-3} can be found in gases from downdraft, bubbling fluidised-bed gasifiers, and updraft biomass gasifiers, respectively (Basu, 2010).

3.4. Gas cleaning

To achieve a reduction or removal of tars, H_2S, HCl and NH_3 catalytic processes can be used. This allows the gas to meet the purity requirements of the downstream methanol synthesis process. Several methods for tar abatement have been reported in the literature, although the two main approaches are primary (*in-situ*) and secondary (*ex-situ*) methods (2009). Primary methods involve modification of parameters that can prevent tar from forming by modifying operating conditions, bed additives or catalyst beds (Blanco et al., 2013), and reactor design modification. Several catalytic approaches have been evaluated as primary methods. These include nickel-based catalysts, dolomites, magnesites, zeolites, olivine and iron catalysts (Z. Abu El-Rub et al., 2004). Dolomite and olivine are quite efficient for tar removal, whilst Ni- or Fe- supported olivine catalysts boost their tar cracking performance (Michel et al., 2013; Virginie et al., 2010). In addition, using olivine in support of Ni catalysts improves their resistance to carbon deposition, improving catalyst lifetime (Świerczyński et al., 2007). Whilst active zeolite catalysts quickly deactivate due to coke deposition (Liu et al., 2016) biochars- or activated char-supported Fe or Ni catalysts can reach a tar removal efficiency of ~95% (Bhandari et al., 2014).

Secondary methods include the treatment of the gas from the gasifier (normally downstream) to reduce impurities. This has been studied using dry or wet downstream cleaning approaches, with systems such as venturi scrubbers, wash towers, wet/dry electrostatic precipitators, adsorbing beds or cyclones. However, some of these systems have reported significant heat and energy efficiency losses and waste stream generation (Abdoulmoumine et al., 2015). Wet, dry, and adsorptive filtering could be alternatives, but they require intensive research, development and piloting (Basu, 2010).

As an advanced and efficient process for separation and selective catalytic reactions, membrane technology has been widely investigated and adopted for purification in water, environmental and energy-related applications (Abdoulmoumine et al., 2015; Armor, 1998; Kim and Van der Bruggen, 2010; Koros and Fleming, 1993; Lu et al., 2007). Membrane separation mainly relies on the selective transport of species through membranes via mechanisms of size exclusion and/or solution diffusion. It is also widely used as a means of process intensification by combining membranes with other separation technologies, such as absorption and distillation, saving energy and reducing waste (Gabelman and Hwang, 1999; Lawson and Lloyd, 1997). Despite the widespread adoption of membranes in various applications, especially water and wastewater treatment, where the modular nature of the technology facilitated simple scale-up from laboratory research, the potential of membrane technology in the bioenergy industry has rarely been explored. In an interdisciplinary effort, recent works have focused on harnessing the latest innovations in ceramic membrane technology for abating tar and other contaminant gases from producer gas (Koonaphapdeelert et al., 2009; Mahyon et al., 2019; Wu et al., 2010), as shown in Figure 5.

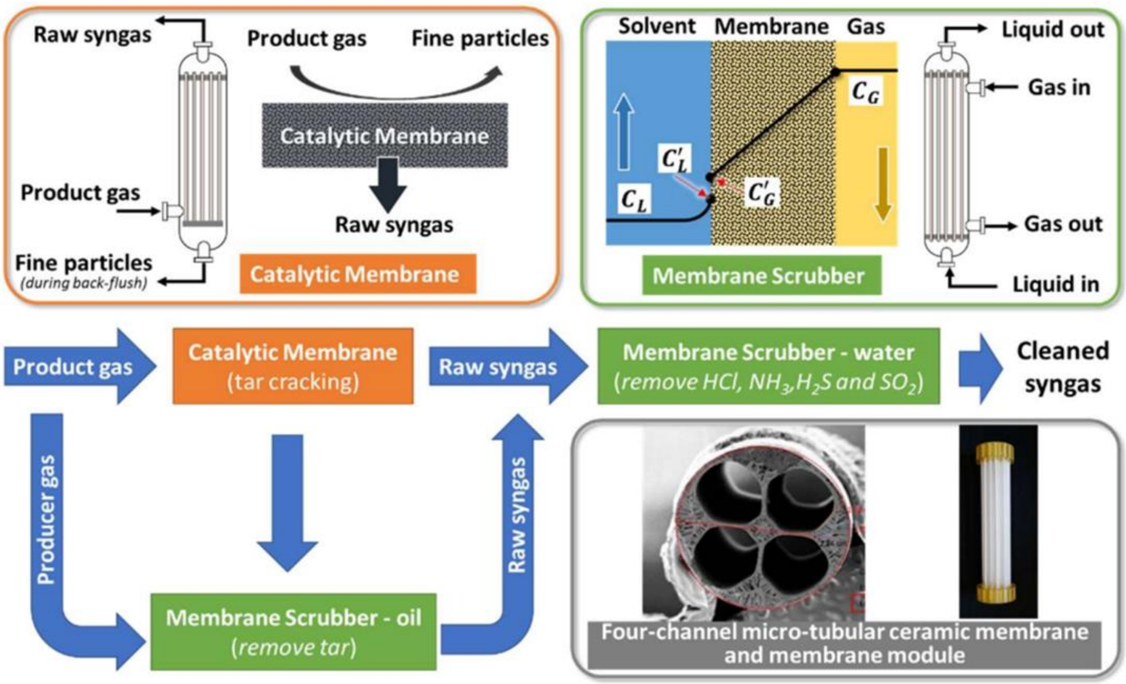

Figure 5. Illustration of different configurations based on membranes for obtaining cleaning syngas

Ceramic membranes are well known for outstanding thermal and chemical robustness, which enables their application for various processes and under a wide range of temperatures, pressures, and pH values. One of the latest innovations in ceramic membrane technology is a phase-inversion assisted extrusion process developed for fabricating micro-tubular ceramic membranes with an advanced bi-modal pore structure (2007) (Figure 5). Micro-tubular ceramic membranes typically have a small diameter (2-5 mm), which is ideal for process intensification by providing a large membrane area within a highly compact unit. Typically, such membranes' area/volume ratio is 500–9000 m^2/m^3, higher than other ceramic membrane geometries such as planar and tubular membranes (Tan and Li, 2011). This eases upscaling of membrane modules and enables deployment flexibility, which is necessary for decentralisation of the bioenergy industry.

The unique bimodal membrane pore structure significantly promotes the transfer of materials inside the membrane, enhancing catalyst utilisation and efficiency of catalytic reactions (Garcilaso et al., 2019; Romero-Sarria et al., 2020), as well as gas-liquid interactions (Okoye-Chine et al., 2019). These provide a solid scientific and technical basis for efficient product gas tar abatement via (1) a catalytic membrane in which less tar cracking catalyst is incorporated for the effective breakdown of tar molecules and (2) a membrane scrubber for effective absorption of tar molecules without the issues of conventional scrubber/contactor such as emulsions, flooding at high flow rates, unloading at low flow rates and density difference between fluids. Moreover, membrane contactors typically offer 30 times more area than is achievable in gas absorbers and 500 times the obtainable levels in liquid/liquid extraction columns, leading to remarkably high separation effectiveness (Barrientos et al., 2017). Therefore, to achieve the extremely low concentration of tar and contaminant gases required for methanol synthesis, catalytic membranes and membrane scrubbers can be combined at a small increase in cost that will provide more thorough conditioning of syngas for methanol synthesis due to the outstanding separation effectiveness of the membrane technologies discussed.

3.5. Syngas conversion into biomethanol

Further to gas conditioning, the methanol synthesis is typically performed in a two-step integrated system comprising a reverse water-gas shift (r-WGS) reactor and methanol synthesis unit. The initial shift step fine-adjusts the H_2/CO ratio to feed the methanol plant. Methanol is typically manufactured using syngas with an H_2/CO ratio of 2:1 according to the overall reaction $CO + 2H_2 \rightarrow CH_3OH$. Fixed-bed reactors with recycling loops are commonly employed to maximise the overall methanol yield. The optimum conditions are selected considering the best temperature/pressure matching between both reactors to facilitate their integration in a single unit. As a result, methanol synthesis is a highly exothermic reaction operated at high pressures (50 – 80 bares) and relatively low temperatures of 200 –300 °C (Poto et al., 2022). Meanwhile, r-WGS is an endothermic reaction that operates favourably at temperatures above 600 °C, and the thermodynamic equilibrium is independent of pressure (Vázquez et al., 2018).

Patented materials based on highly dispersed Cu active phase prepared using Cu-Zn-Al hydrotalcite have been probed as efficient systems for both reactions (Odriozola et al., 2014). Unfortunately, the state of the Cu in the methanol synthesis catalyst is unique and highly defective (Behrens et al., 2012). Nevertheless, after the shift reactor, the formulation leads to a suitable H_2/CO ratio and maximises methanol yields. Nevertheless, the synthesis of methanol has two clear limitations in temperature. On the one hand, the catalyst using Cu as an active phase is very sensitive to deactivation by sintering. Above all, it is a reaction limited by thermodynamic equilibrium due to its reversible exothermic character. Therefore, low temperatures favour the stability of the catalyst and increase the maximum conversion obtainable but penalise the process kinetics (Azizi et al., 2014).

4. New approaches for methanol synthesis: microchannel reactors

Standard technologies for r-WGS and methanol production are based on fixed-bed reactors, resulting in several drawbacks, such as poor thermal control and pressure drops. The structured catalytic systems, structured catalysts and microchannel reactors offer excellent opportunities for overcoming those limitations because they efficiently minimise both the transport limitations and pressure drop simultaneously while improving the radial fluxes of mass and heat and allowing very short contact times (Figure 6) (Almeida et al., 2011; Arzamendi et al., 2011; Laguna et al., 2012). Furthermore, the monoliths with parallel channels, open cell foams and stacked wire meshes can be made of various metallic alloys and cells or pore densities. They can also be coated with any suitable catalyst, thus becoming appropriate for the process of interest. On the other hand, the microchannel reactors can provide an incomparable intensification of the process with excellent temperature control and improved product quality and process safety (Yue, 2022). In addition, the scalability is simplified since it is achieved simply by increasing the number of units. Therefore, they permit the design of compact and, in terms of weight, lighter devices, which are ideal for decentralised applications.

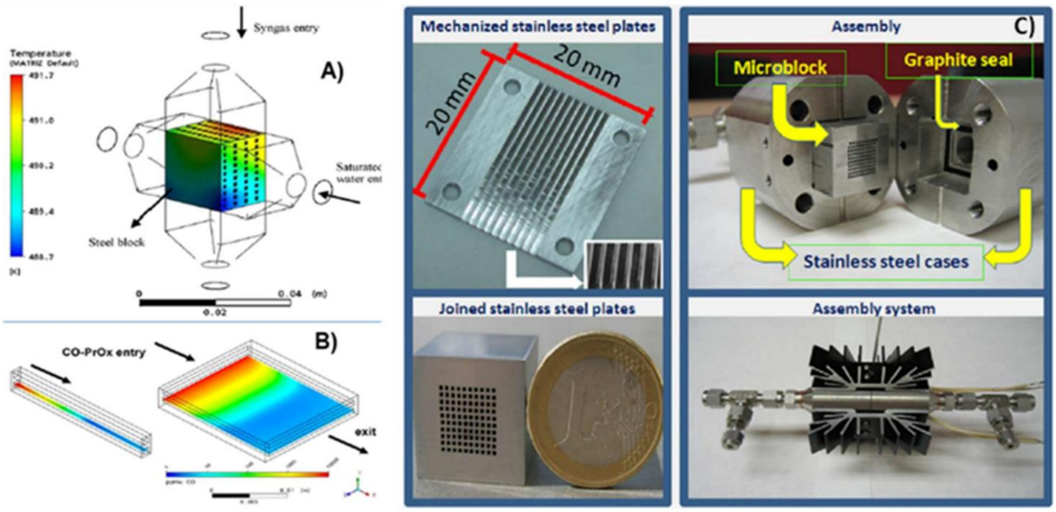

Figure 6. Evidence of thermal (**A**) and composition (**B**) profiles in micro-structured reactors used for a preferential oxidation reaction (PrOx), suggesting heterogeneous heat and mass

transport along the channels (**C**) overview of the microchannel reactor configuration. Adapted from (Arzamendi et al., 2011) and (Laguna et al., 2012).

Implementing microchannel reactors for r-WGS and methanol synthesis could be an interesting strategy for advanced catalytic technologies and reaction engineering. However, up to now, microchannel reactors have only been implemented at a commercial level by Velocys for Fischer-Tropsch synthesis (Loewert et al., 2019). To the best of our knowledge, there are no commercial or pilot processes using this kind of structured reactor for methanol synthesis. Nevertheless, the works of Venvik and Holmen's group are the only ones dealing with methanol synthesis in the structured system and are restricted to the use of conventional Pd/CeO_2 and $CuO/ZnO/Al_2O_3$ catalysts (Bakhtiary-Davijany et al., 2011; Hayer et al., 2011; Phan et al., 2010; Phan et al., 2016; Venvik and Yang, 2017; Visconti et al., 2018). These miniaturised devices allow the improvement of thermal control of the reaction and thus making it more energy-efficient. Moreover, they make the operation at high pressures safer while minimizing pressure drops. In addition, the advanced engineering properties and the microchannel reactor's utilisation significantly reduce the downstream unit's total volume, making the design of portable bio-methanol processors feasible for decentralised applications.

Beyond the technical advantages of microchannel reactors, their simplified scalability makes them ideal for distributed productions and essential for delocalised and seasonal applications, for example, residues in farming and rural scenarios where biomass availability fluctuates. Furthermore, a recent pioneering study demonstrates the feasibility of decentralised Biomass-to-Liquids processes. It has shown that changes from lab scale to pilot scale produce negligible changes in product quality or reaction performances due to the efficiency of structured microreactors (Loewert et al., 2019).

5. Integrated multi-scale process for methanol synthesis and energy production

The validation of the integrated technologies is fundamental for their development. Upscaling or demonstration of ultra-compact liquid biofuels production with the potential to be engineered into a mobile system deployable locally to the most suitable and available feedstocks constitutes key steps for the emergence of new business and supply chain models in the growing biofuel sector. Hence, the exothermic nature of the reactions occurring during the methanol synthesis can allow heat and power to be reintegrated to the process or to be externally valorised (feeding in electricity to the grid and providing process/district heat), thus bringing another added value as well as improving the energy efficiency of the process and thus leading to a better GHG performance and further potential for grid-balancing.

A proven fixed-bed downdraft gasifier concept have been successfully tested (Dabai et al., 2010; Pinilla et al., 2013). This model two-stage Fixed-Bed Reactor Simulating Downdraft Gasifier allows to decouple pyrolysis and reforming stages allowing the study of tar generation and cracking whose content heavily compromises downstream processes. Preliminary mass and energy balances reveal that with such a plant concept 4 tons of biomass per hour can be converted into 2.7 tons per h methanol, 7.2 MW electricity and 11.3 MW heat from the heat recovery downstream the gas turbine.

In Figure 7, a schematic drawing of the biomass to methanol process for decentralised applications is presented. The off-gas from the methanol production can be utilised efficiently in a downstream CHP unit based on a gas turbine process. By this measure, the production of green electricity, as well as process and district heat, increase the overall efficiency of biomass conversion in this process chain. Process optimisation must consider the optimal utilisation of off-gas streams. Operation with oxygen-enriched air supplied from the anode off-gas stream of a Solid Oxide Electrolyser Cell (SOEC) system should be used to provide the additional H_2 needed for methanol synthesis. This aspect is of paramount importance for the economy of the process. In a subsequent step, H_2S, HCl and NH_3 removal, as well as final catalytic tar reforming, shall be realised in order to meet the gas purity requirements of the downstream methanol synthesis process. It is our understanding that the development of gasification-membranes represents a potential integration issues to assess the technology performance when working in a continuous mode for a more extended period of time. Therefore, appropriate reactor concepts and principally suitable sorbents are required.

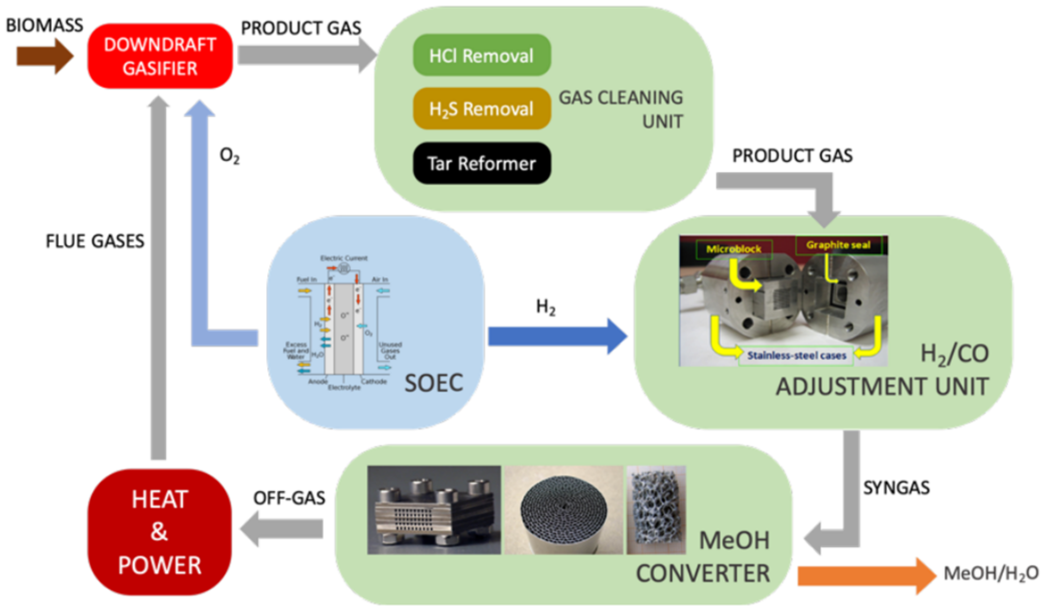

Figure 7. Scheme of the biomass to methanol conversion chain for decentralised applications. Adapted from [83]

6. Role in the framework of the circular economy: socio-economic impact

The overarching driver of biomethanol production is the ambition of creating clean and efficient catalytic processes in energy related applications that help in fulfilling the Objectives for Sustainable Development. Probably the most challenging problem the world is facing nowadays is the global climate change. There is no doubt that the average surface temperature of our planet has the risk of 6 °C increase by 2050 if the ongoing trend on CO_2 emissions is maintained (Towards Sustainable Urban Energy Systems. OECD/IEA). Therefore, to reduce emissions is mandatory. The ambitious but imperative objective of keeping the global temperature increase below 2 °C must necessarily imply negative CO_2 emissions for the second half of the 21st century (Schellnhuber et al., 2016).

In order to keep climate change below 2°C, the European Council reconfirmed in February 2011 the EU objective of reducing greenhouse gas emissions by 80-95% by 2050 compared to 1990, in the context of necessary reductions according to the Intergovernmental Panel on Climate Change by developed countries . Furthermore, in 2014, a new EU framework on climate and energy for 2030 was proposed, calling for reductions in greenhouse gas emissions of 40% in 2030 (against 1990 levels) and a binding EU target for renewable energies of at least 27% (revised to 32% in 2018), and at least 32.5% improvement in energy efficiency . A shift from centralised to distributed energy generation is required to facilitate this commitment, as well as the utilisation of renewable energy resources through Distributed Energy Systems (DES). This has been recently highlighted "*As a combination of the bioeconomy, which is aimed at manufacturing products from biomass resources, and the Circular Economy, which is aimed at recycling of final products, small-scale and distributed business development in Europe is expected to be promoted in the future by the utilisation of biomass resources and recycled resources*" .

To meet EU 2030 renewable energy targets bioenergy is an essential resource. Residual biomass and organic wastes may contribute to GHG emission reduction, security of energy supply and economic growth by stimulating local economies and employment (de Wit and Faaij, 2010). Sustainable biomass resources are carbon neutral, renewable and are widely available. Biomass conversion has the flexibility to yield a number of bioenergy carriers in the form of gaseous or liquid streams. Gaseous streams such as methane and hydrogen can have direct energy applications, but their drawback is the difficulty for storage and transportation, which can substantially increase costs and limit their application. In this context, liquid bioenergy carriers such as biomethanol have a higher energy density, can be easily stored and transported and can be used for heat and power applications as per demand.

7. Outlook and future perspectives

The dependence of our current energy system on fossil fuels and their harmful effects on the environment are strengthen the development of renewable energy sources. Biomass gasification is a well-known thermal process that converts solid biomass into a gaseous stream or syngas. When combined with other downstream processes such as catalytic cracking and Fischer-Tropsch synthesis, the syngas produced by gasification can be converted into renewable hydrocarbons, enabling the production of a wide range of high-value biofuels and chemicals. The bioenergy carriers that can be delivered from biomass thermal conversion are not intermittent (as wind and solar energy are), they can be stored and are also dispatchable into different energy markets, *e.g.* transport, heat, electricity.

Biomethanol can be used for energy applications with a potential to be combined with energy storage applications to work on-demand, thus improving current infrastructure characteristics. Moreover, biomethanol possesses an increased energy density when compared against their gaseous counterparts (H_2, CH_4), it can be easily and safely stored or transported, bringing advantages for further conversion and dispatchable service, including energy applications. As biomethanol is chemically identical to methanol produced, for example, from the synthesis of natural gas, existing and well-developed infrastructure and processes can be used for its application, thus reducing additional adaptation and modification costs for infrastructure.

However, despite many efforts to scale up these technologies for commercial production of biomethanol by gasification several challenges have slowed their deployment and widespread use, particularly issues with gas quality and composition, the high cost of the reduction or removal of tar content and inefficiencies in the biomethanol conversion process. The production of fuels and chemicals from lignocellulosic biomass and wastes very often involve catalytic processes that are characterised by strong heat exchange requirements due to the high thermal effect of the chemical reactions involved, as well as by the difficulty for simultaneously minimizing transport limitations and pressure drop in conventional fixed-bed reactors. Sometimes, extremely short contact times are also required. As a result, the conventional catalytic technologies operate under non-optimal conditions. In this context, this work reviews analyzes novel biomass conversion technologies to overcome the specific problems of gas quality and composition and conversion efficiency which currently limit the widespread commercial implementation of such systems. Improvements in syngas quality are discussed by harnessing the latest innovations in ceramic membrane technology to abate tar and other contaminants from product gas. The incorporation of catalytic membranes for tar cracking catalytic and a membrane scrubber for effective breakdown of tar molecules and absorption of tar molecules without the issues of conventional scrubbers/contactors are evaluated. Hence, new more compact gas cleaning and tar removal membrane scrubbing and catalytic cracking systems can be developed into products for bio-fuel industries, natural gas and petrochemical industries where gas quality is critical to downstream processes. On the other hand, improvements in conversion efficiency are driven by the design and implementation of micro-channels reactors containing microstructures that enhance control of exothermic reactions and improve mass transfer, heat transfer and reaction throughput. The r-WGS and methanol synthesis microchannels reactor can be integrated into its technology, hence combining both processes into one ‘plug and play’ modular unit with straightforward scale-up potential. In addition, the integration of reactor design with the development of robust catalysts is significant for future synthesis of biomethanol. In particularly, the design of the high-performance catalysts with efficient active sites and long-term stability is challenging. The exothermic nature of the reactions occurring during the methanol synthesis can allow heat and power to be reintegrated to the global process or even to be externally harnessed for the production of green electricity increasing the overall efficiency of biomass conversion in this process chain, and thus leading to a better GHG performance and further potential for grid-balancing.

In summary, we can conclude that biomethanol obtained from the gasification of biogenic residues and wastes can potentially provide a sustainable and cost-effective production route that will contribute to the collective efforts in reducing GHG emissions and work towards achieving the targets set in the Paris Agreement. In particular, designing and implementation of circular methanol production processes represents a step ahead on biomass processing technologies opening a completely new horizon for economically competitive biocarrier production. This pathway aligns with the circular economy strategy, in which materials at the end of their lifecycle and wastes generated in the production of goods are fully recovered and recycled, reducing the environmental impact.

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Declaration of interests

☒The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Authors Contribution Statement

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