Review

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Progress in lignocellulosic biomass valorization for biofuels and value-added chemical production in the EU: A focus on thermochemical conversion processes

Fatih Güleç, Low Carbon Energy and Resources Technologies Research Group, Faculty of Engineering, University of Nottingham, Nottingham, UK; Advanced Materials Research Group, Faculty of Engineering, University of Nottingham, Nottingham, UK
Anburajan Parthiban, Department of Environmental Engineering, Seoul National University of Science and Technology, Seoul, South Korea; Institute of Environmental Technology, Seoul National University of Science and Technology, Seoul, South Korea
Great C. Umenweke, University of Kentucky Center for Applied Energy Research, Lexington, Kentucky, USA
Umaru Musa, Low Carbon Energy and Resources Technologies Research Group, Faculty of Engineering, University of Nottingham, Nottingham, UK; Department of Chemical Engineering, School of Infrastructure, Process Engineering Technology, Federal University of Technology, Minna, Nigeria
Orla Williams, Advanced Materials Research Group, Faculty of Engineering, University of Nottingham, Nottingham, UK
Yasna Mortezaei, Earth and Ecosystem Science, Central Michigan University, Mount Pleasant, Michigan, USA
Hyun Suk-Oh, Department of Environmental Engineering, Seoul National University of Science and Technology, Seoul, South Korea; Institute of Environmental Technology, Seoul National University of Science and Technology, Seoul, South Korea
Edward Lester, Advanced Materials Research Group, Faculty of Engineering, University of Nottingham, Nottingham, UK
Chukwuma C. Ogbaga, Independent Researcher, Middlesbrough, North Yorkshire, UK
Burcu Gunes, School of Biotechnology and DCU Water Institute, Dublin City University, Dublin, Ireland
Jude A. Okolie, Gallogly College of Engineering, University of Oklahoma, Norman, Oklahoma, USA

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Correspondence to: Fatih Güleç, Low Carbon Energy and Resources Technologies Research Group, Faculty of Engineering, University of Nottingham, Nottingham, UK.
E-mail: Fatih.Gulec1@nottingham.ac.uk
Jude A. Okolie, Gallogly College of Engineering, University of Oklahoma, Norman, Oklahoma, USA.
E-mail: jude.okolie@usask.ca

Abstract: The demand for sustainable energy sources has increased owing to environmental concerns, such as climate change, rising energy demand and rapid industrialization. Biomass utilization for bioenergy and value-added chemical production has become essential for creating a circular low-carbon bioeconomy and sustainable waste management techniques. This review focuses on thermochemical processes and analyzes the trends of biomass utilization for energy production in the EU over the last decade. It discusses the current state-of-the-art of gasification, pyrolysis, advanced combustion and liquefaction technologies, and presents the individual challenges and prospects of each process. A comprehensive overview of previous studies related to each conversion technology is provided to pave the way for future thermochemical, biochemical and integrated biomass valorization studies. Additionally, the review discusses biomass thermochemical conversion processes, which are combined with carbon capture, such as gasification, liquefaction and pyrolysis. These processes offer the potential to achieve negative net atmospheric carbon emissions, which can contribute to global warming mitigation efforts.

Key words: gasification; pyrolysis; CO_2 capture; liquefaction; thermochemical processes

Introduction

The rapidly increasing global energy demand owing to industrialization and population growth is a major challenge of the modern era. With a projected world population of 9 billion by 2050, energy demand is expected to increase by 50%.[1] Despite this, traditional resources like fossil fuels still provide 80% of the world's energy supply and 66% of electricity generation, yet they emit large amounts of greenhouse gases (GHGs) into the atmosphere.

Atmospheric CO_2 levels have risen consistently over the past three decades, from 1.42 ppm during 1985–1995 to 1.86 and 2.06 ppm from 1995 to 2005 and from 2005 to 2015 respectively.[2] In 2019, the amount of atmospheric CO_2 was recorded at 410.5 ± 0.2 ppm, which is 130 ppm higher than in the preindustrial period.[3] The World Health Organization reports that air pollution causes the deaths of 3 million people annually and only 10% of people live in areas that meet air quality standards. The Intergovernmental Panel on Climate Change predicts that without action to mitigate the problem, GHG emissions will increase dramatically and reach levels of between 750 and 1300 ppm CO_2 equivalents and potentially higher by 2100.[4] This increase in GHG emissions leads to global warming and climate change. In 2015, the UN countries agreed at the Paris Climate Conference to limit the global temperature increase to below 2°C compared with preindustrial levels.[5] The average temperature in 2020 was reported to be 1.2 ± 0.1°C higher than the baseline of 1850–1900.[6]

Owing to the pressing issue of excessive dependence on non-renewable fossil fuels, the substitution of these traditional fuels with sustainable and renewable energy sources can help mitigate the problem.[3] In 2018, the European Union (EU) Renewable Energy Directive declared that 20% of the EU's energy demand should be met by renewable energy sources by 2020.[7] By 2019, 19.7% of the energy consumed in EU countries was generated from renewable sources, leaving only a 0.3% gap to reach the 2020 target.[8] Energy Roadmap 2050 projects that 30% of the EU's total energy consumption could be derived from renewable energy sources by 2030.[9]

Biofuels, which have similar properties to petroleum-based fuels, are widely recognized as a crucial sustainable energy source for various applications, such as transportation, energy generation, and industrial boilers.[10] A life cycle assessment of biofuels shows that the amount of CO_2 released during the entire biofuels production process, from raw material procurement to the final combustion in engines, is lower compared with traditional fuels.[11] The production of biofuels in Europe has significantly increased over the past two decades, rising from 29.2 to 649.8 petajoules in 2019. Germany and France were the leading biofuel producers, generating 143.4 and 113 petajoules, respectively, in 2019.[11] The production of biofuels in various European countries is depicted in Fig. 1.

The efficient development of biofuel production is highly dependent on the type of feedstock used. Biofuels can be categorized into different generations based on the biomass source. First-generation biofuels, derived from food sources, have been linked to numerous environmental and economic challenges, including increased land use, food crises,

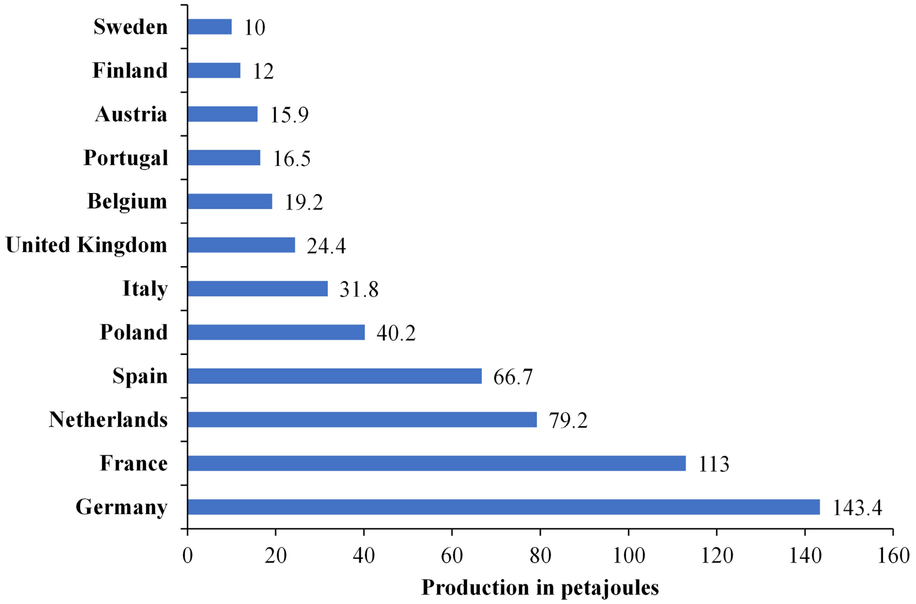

Figure 1. Biofuel production in selected European countries 2019.[8]

elevated food prices, ecological degradation and elevated GHG emissions.[12] As a result, the European Commission Renewable Energy Directive reduced the number of food-based biofuels allowed in the 10% renewable energy target to 5% in 2012.[13] The growing conflict between food supplies and first-generation biofuel production has led to an increased focus on second-generation biofuels, which are made from lignocellulosic biomass and non-edible materials.

Lignocellulosic substrates can be further divided into various groups, including agricultural residues (e.g. rice straw, rice husks, corn stover, sugar cane bagasse and wheat bran), energy crops (e.g. switch grass, cotton stalk, miscanthus and jatropha curcas), industrial residues (e.g. newspaper, pulp, wood residues, black liquor, skins and waste from palm oil mills) and agro-industrial residues (e.g. wood chips, potato and orange peel, paper pulp and spent coffee grounds). The significant advantage of lignocellulosic biomass is that the feedstock source is not in competition with the food supply and does not require arable land for cultivation. Additionally, lignocellulosic biomass is abundant worldwide and relatively inexpensive. In contrast, third-generation biofuels are biofuels made from algae, while fourth-generation biofuels are biofuels made from synthetic biology and metabolic engineering. Third-generation biofuels offer benefits such as higher biofuel yields per unit area, the ability to grow in saltwater, and carbon dioxide removal during growth. However, they also have disadvantages like being an emerging technology with limited commercial viability, high costs of production and difficulties in harvesting and processing. Fourth-generation biofuels are still in the development stage and have ethical, safety and regulatory hurdles to overcome. Both third- and fourth-generation biofuels aim to improve traditional biofuels but face significant challenges before they can be fully commercialized.

Despite the advancement and plethora of studies on biomass valorization for biofuels and value-added chemicals, there are limited reviews on progress and advancement in thermochemical conversion technologies, especially in the EU context. To address the knowledge gaps, the present study provides an overview of advanced thermochemical conversion technologies in the EU context. An overview of biomass utilization in the EU is presented, following the advantages and limitations associated with thermochemical processes such as gasification, pyrolysis and liquefaction. It is expected that the present study will be a useful resource for researchers or practitioners working on biorefining.

Overview of lignocellulosic biomass distribution in the EU

In many developing countries, the main source of energy is still provided by the burning of biomass, which is not a sustainable and environmentally friendly method. With the emergence of new technologies, biomass can be converted into different forms such as solid, liquid and gaseous, and utilized to produce energy more effectively. Lignocellulose biomass is one of the most abundant and sustainable resources for biofuel production and has gained significant attention in recent years. It is estimated that there is a global production of 181.5 billion tons of lignocellulose waste each year.[14] Different groups of lignocellulose substrates are illustrated in Fig. 2. Lignocellulose materials used for producing biofuels are primarily sourced from agricultural and forestry residuals and dedicated energy crops.[15]

The major sources of lignocellulose biomass are wheat, maize, rice and sugarcane, which produce up to 5300 million tons of dry lignocellulosic waste annually, while other agricultural residues constitute a smaller proportion of the total global biomass.[16] Corn stover, with a global yield of 1.0 kg/kg corn grain or 4.0 ton/acre, is a leading source for biofuels production, obtained from the residues of harvested corn kernels such as stalks, leaves, cobs and husks.[17] Wheat straw has a production rate of 1–3 tons/acre annually, while rice straw, with an estimated production rate of 731 million tons/year, is also a promising source of agricultural residues.[18] Bagasse, produced from the processing of sugarcane, has a global yield estimated to be in the range of 317–380 million tons/year.[19] The global yield of plant biomass is around 20 million tons per year, although only about 8–20 million tons of this biomass is available for biofuel production.[18]

In recent years, several studies have focused on the resource availability of lignocellulosic biomass in Europe, considering geographical constraints. Central Europe has potential sources of forestry-derived lignocellulosic biomass such as aspen, alder, birch, willow and poplar.[20] Willow is mainly found in Denmark, the Netherlands, the UK and Ireland, while poplar is predominantly produced in warmer regions like France, Italy and Spain.[21] Among dedicated energy crops, miscanthus is considered a suitable source for biofuel production in Europe, given its wide climate adaptability.[22] However, only a small portion of cropland in the EU countries is dedicated to lignocellulosic crops such as miscanthus, switchgrass, willow and poplar.[23] Wheat straw is recognized as the most abundant lignocellulosic biomass from plant residues.[24] Agricultural crop residues, including stalks and leaves of cereals, sugar and vegetable crops, have an estimated realistic potential of 74.89 Mt per year in the EU, while forestry residues (stumps, branches, treetops, needles and leaves) have lower potential.[25] The estimated production of brewer's spent grain in the EU is around 3.4 million tonnes per annum.[26] Considering environmental constraints, the estimated annual amount of straw and stover in the EU-27 is in the ranges 45–214 Mt in 2017, 115–185 Mt in 2020 and 110 –165 Mt in 2030.[27] In the UK and Europe, miscanthus and short rotation coppice are the primary focus for biofuel production from herbaceous and woody crops.[28] Italy mainly utilizes sorghum and short-rotation forestry as feedstock.[29]

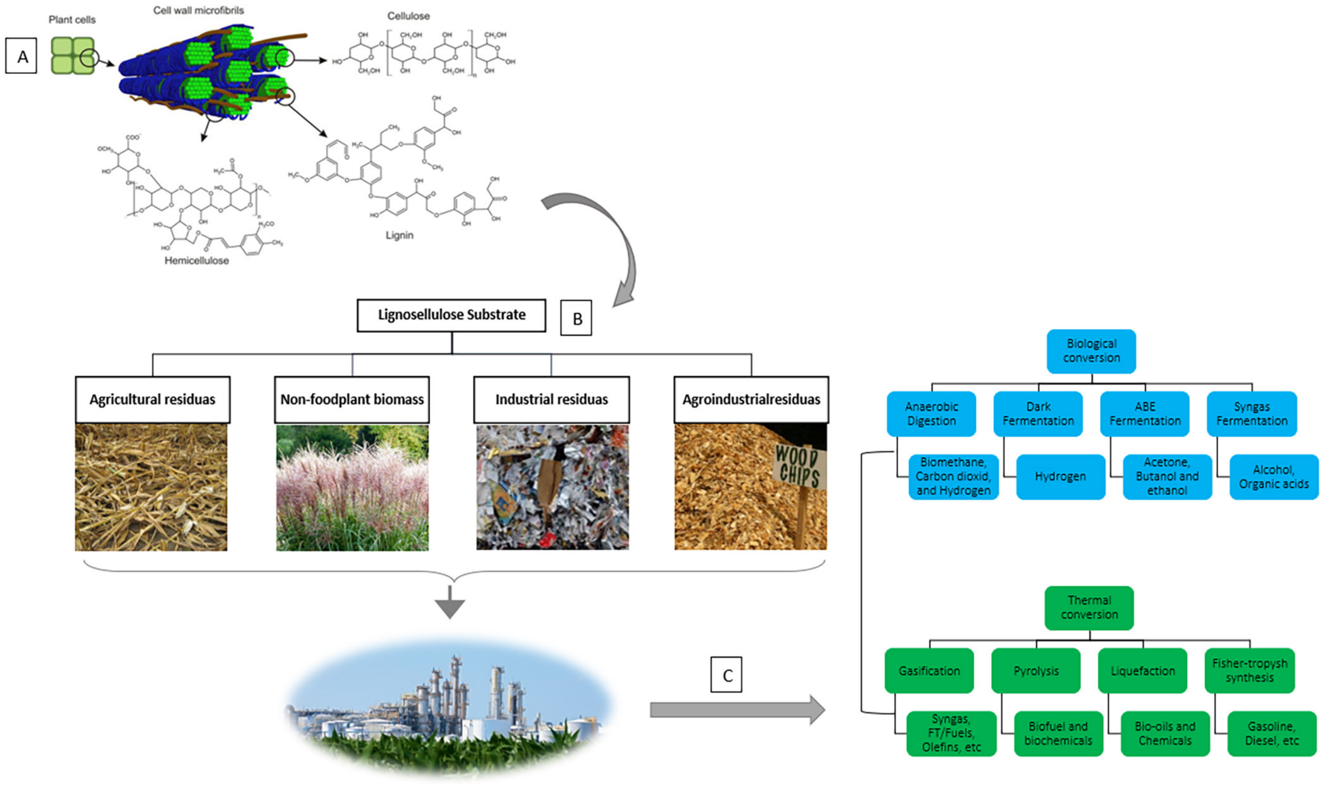

Figure 2. Second-generation biofuels production from lignocellulose materials: (a) schematic of lignocellulose biomass;[36] (b) different groups of lignocellulosic substrates; and (c) different ways of Lignocellulosic biomass conversion to biofuels.

In Germany, maize is the primary source of lignocellulosic biomass for energy production.[30]

In Europe, switchgrass, reed canary grass, miscanthus and giant reed are identified as the most promising perennial grasses for biofuel production.[31] The yield of different lignocellulosic biomass used for biofuel production is variable, probably owing to environmental conditions and the potential of various species to produce biomass. For instance, the yields of switchgrass, reed canary grass, miscanthus and giant reed across Europe are in the ranges 9–25, 3–14, 10–30 and 7–61 Mg/ha, respectively.[32] The yield level of some agricultural crop residues in EU-27 is represented in Tables 1 and 2.[25] The substantial variation in these biomass yields is attributed to their adaptability to regional climate conditions. Reed canary grass is reported to be more adapted to northern European climates, while switchgrass and miscanthus have higher adaptability in northern and central Europe. On the other hand, the giant reed seems to be better suited for the Mediterranean region.[33]

Overview of biofuel production technologies

Lignocellulosic biomass can be converted into biofuels through two approaches: biological processes and thermochemical conversion processes. Biological processes involve the use of different microorganisms to produce biofuels and green chemicals through the anaerobic digestion of organic substrates or fermentation of sugars. On the other hand, thermochemical conversion encompasses a range of processes such as gasification, pyrolysis, liquefaction and carbonization, which require more energy input.[34] Figure 2(c) presents the various technologies of second-generation biofuels generated from lignocellulose materials. It should be mentioned that the focus of this study is on thermochemical conversion processes. The thermochemical processes have some advantages over biological processes in converting lignocellulosic biomass into biofuels. Some of these advantages are listed below:

- High conversion efficiency – Thermochemical processes typically have higher conversion efficiencies compared with biological processes, meaning that a larger portion of the biomass is converted into biofuels.
- Flexibility – Thermochemical processes are more flexible in terms of feedstock selection and can process a wider range of lignocellulosic biomass, including waste materials, compared with biological processes, which may have limitations in terms of feedstock type and quality.
- Lower processing time – Thermochemical processes tend to have a shorter processing time compared with biological processes, which may take several days to weeks to complete.
- Low maintenance costs – Thermal conversion processes have relatively low maintenance costs compared with biological processes, which require the maintenance of microorganisms and an optimal environment for their growth.
- Lower operating costs – In general, thermochemical processes have lower operating costs compared with biological processes, owing to their lower energy requirements, lower maintenance costs, and higher conversion efficiencies.

It is important to note that both thermochemical and biological conversion processes have their advantages and limitations, and the best approach will depend on the specific requirements of the application, such as feedstock availability, end-product specifications and cost considerations. As a result, Okolie *et al.*[35] study detailed a comprehensive analysis of the advantages and limitations of each technology. The authors also provided a discussion on the integration of both processes to attain a circular economy, minimize material wastage and promote effective energy optimization.

Thermochemical conversion technologies

Biomass is a crucial component of the global carbon cycle and can serve as a cost-effective, environmentally friendly and clean source for energy production and the creation of value-added chemicals.[37] Its potential to replace fossil fuels in energy processes, such as the production of heat, electricity and transportation fuels, makes biomass a promising and attractive energy resource.[38] As a result, the utilization of biomass is playing a crucial role in meeting the EU's Green Deal targets for net-zero energy. In 2019, bioenergy applications accounted for roughly half of the renewable energy sources in the EU, and a significant increase in biomass use and demand for bioenergy is projected owing to energy and climate change strategies.[38] The European bioeconomy is now valued at over €621 billion and contributes 4.2% to the EU GDP, employing 18 million people.[39] Biomass feedstocks can be transformed into clean energy and value-added chemicals through a variety of thermal conversion technologies, including pyrolysis, hydrothermal conversions, gasification, combustion, advanced combustion and torrefaction. These technologies will be discussed in the next section.

There are still several challenges that hinder the commercialization of bioenergy and bioproducts through these technologies. These challenges include sourcing biomass, differences in physical, chemical and biological structures, lack of cost-competitive bioproducts, insufficient

Table 1. The yield level of some agricultural crop residues in EU-27.[25]

	Yield range (t/ha)				
Crop	Low	Medium	High	Lowest	Highest
Wheat	Bulgaria, Cyprus, Czech Republic, Estonia, Greece, Portugal, Romania, Spain	Austria, Finland, Hungary, Italy, Latvia, Lithuania, Luxembourg, Malta, Poland, Slovakia, Slovenia, Sweden	Belgium, Denmark, Germany, Ireland, Netherlands, UK, France	Portugal (1.6)	Ireland (8.8)
Barley	Cyprus, Estonia, Greece, Latvia, Lithuania, Portugal, Romania, Spain	Austria, Bulgaria, Czech Republic, Denmark, Finland, Hungary, Italy, Luxembourg, Poland, Slovakia, Slovenia, Sweden, UK, Malta	Belgium, France, Germany, Ireland, Netherlands	Cyprus (1.6)	Belgium (8.0)
Rye	Bulgaria, Lithuania, Romania, Spain, Hungary, Portugal, Greece	Austria, Finland, Czech Republic, Italy, Latvia, Poland, Slovakia, Slovenia, Estonia, Netherlands, Ireland	Denmark, France, Germany, Luxembourg, UK, Belgium, Sweden	Portugal (0.9)	UK (9.6)
Oat	Bulgaria, Lithuania, Romania, Cyprus, Estonia, Latvia, Spain, Greece, Portugal, Slovakia	Austria, Czech Republic, Hungary, Italy, Luxembourg, Poland, Slovenia, Finland, Sweden	Denmark, Belgium, Germany, Netherlands, Ireland, UK, France	Cyprus (1.0)	Ireland (7.4)
Maize	Bulgaria, Lithuania, Romania, Poland	Czech Republic, Denmark, Hungary, Italy, Luxembourg, Slovakia, Slovenia, Portugal	Austria, Belgium, France, Germany, Netherlands, Spain, Greece	Romania (3.6)	Netherlands (11.8)
Rapeseed	Bulgaria, Estonia, Finland, Italy, Lithuania, Romania, Spain	Austria, Belgium, Czech Republic, Greece, Hungary, Latvia, Poland, Slovenia, Slovakia, Sweden	Denmark, France, Germany, Ireland, Luxembourg, Netherlands, UK	Estonia (1.4)	Belgium (4.0)
Sunflower	Portugal, Romania, Slovenia, Spain	Bulgaria, Germany, Greece, Poland, UK	Austria, Czech Republic, France, Hungary, Italy, Slovakia	Portugal (0.56)	Austria (2.6)
Sugar beet	Bulgaria, Finland, Latvia, Lithuania, Romania, Slovenia	Czech Republic, Denmark, Germany, Hungary, Ireland, Poland, Portugal, Slovakia, Sweden, UK, Italy	Austria, Belgium, France, Greece, Netherlands, Spain	Bulgaria (18.7)	France (85.3)
Wine	Bulgaria, Cyprus, Malta, UK	Austria, Czech Republic, France, Hungary, Portugal, Romania, Slovakia, Slovenia, Spain	Germany, Italy, Greece, Luxembourg	Bulgaria (3.3)	Luxembourg (14.5)

biomass refinery technologies, scalability limitations and limited or unstable supply of biofuels and bioproducts.[40] The variations in the chemical and biological composition of different biomass feedstocks can lead to significant differences in their handling, biochemical composition and resulting biochar structures.[40,41]

The selection of the most appropriate biomass valorization routes involves several factors, including the type and characteristics of biomass, its location, quantity, environmental regulations, economics and the desired end products (solid, liquid or gas). Gas products can be utilized to synthesize value-added chemicals through methods such as Fisher-Tropsch (alkanes), oxosynthesis (alcohols/aldehydes), fermentation (ethanol), isosynthesis (isobutane) and water-gas-shift (hydrogen/methanol).[42-44] Similarly, liquid products can be transformed into valuable chemicals and transportation fuels through cracking (thermal or catalytic cracking)[41,45] or anaerobic digestion.[46] Biochars (or hydrochars) offer versatility and have a broad range of applications, such as energy production,[47] water purification,[48] soil amendment,[49] CO_2 capture[50] and nanoparticles (for making composites) owing to their physicochemical properties.[51] The choice of processing route has a direct impact on the potential applications of the

Table 2. The yield level of some agricultural crop residues in the EU-27.[25]

Crop	Yield level	Country	Crop yield (t/ha)	Residue yield (t/ha)
Wheat	Lowest	Portugal	1.64	0.79
	Medium	Poland	4.03	2.90
	Highest	Ireland	8.78	8.43
Barley	Lowest	Cyprus	1.6	0.77
	Medium	Denmark	5.27	3.32
	Highest	Belgium	7.96	6.21
Rye	Lowest	Portugal	0.94	0.51
	Medium	Luxembourg	6.25	4.69
	Highest	UK	9.6	9.17
Oat	Lowest	Cyprus	0.96	0.52
	Medium	Denmark	4.7	3.25
	Highest	Ireland	7.4	6.17
Maize	Lowest	Romania	3.6	3.24
	Medium	Luxembourg	7.86	8.26
	Highest	Netherland	11.75	14.10
Rapeseed	Lowest	Russia	1.9	1.21
	Medium	Poland	2.72	3.37
	Highest	Belgium	4	5.79
Sunflower	Lowest	Portugal	0.56	0.90
	Medium	Poland	1.7	3.27
	Highest	Austria	2.6	6.02
Sugar beet	Lowest	Bulgaria	18.7	1.49
	Medium	Lithuania	37.4	6.13
	Highest	France	85.3	12.79
Wine	Lowest	Bulgaria	3.3	9.78
	Medium	Greece	8.7	31.28
	Highest	Luxembourg	14.5	60.83

primary gas, liquid and solid products. An illustration of thermal conversion technology routes is provided in Fig. 3.

Gasification

Gasification is a thermochemical conversion technique used for the production of synthesis gas (syngas) from different organic or carbonaceous materials using gasifying agents under high temperatures and an inert atmosphere.[52] There has been significant work on biomass gasification, with ~18 329 publications using the keywords 'Biomass Gasification' published according to the Web of Science between 2010 and 2023. Among these publications, ~6899 papers were published from countries in Europe. Most of the biomass gasification studies (~2182 publications) were specifically detected using the keyword 'Biomass Steam Gasification'; ~430 publications were detected using the keyword 'Biomass Supercritical Water Gasification'. In addition to these two common gasification technologies, there are ~170 publications on 'Biomass Partial Oxidation Gasification' and ~117 publications on 'Biomass Autothermal Gasification'. The process of biomass gasification is complex and involves several endothermic and exothermic reactions that complement each other.[53] Gasification can typically be divided into two categories: (i) conventional gasification and (ii) supercritical water gasification (SCWG) also known as hydrothermal gasification. The difference between both types of gasification has been meticulously described elsewhere.[35] Furthermore, a detailed review of the role of gasification in a carbon-negative economy has been recently published.[53] The reactions involved include pyrolysis, oxidation, partial oxidation, reduction, steam reforming and water-gas shift reactions.[54,55] Pyrolysis is an endothermic decomposition process at high temperatures in an inert atmosphere (absence of air or steam) that produces gaseous, liquid tar and residual solid char products.[56] During oxidation or partial oxidation

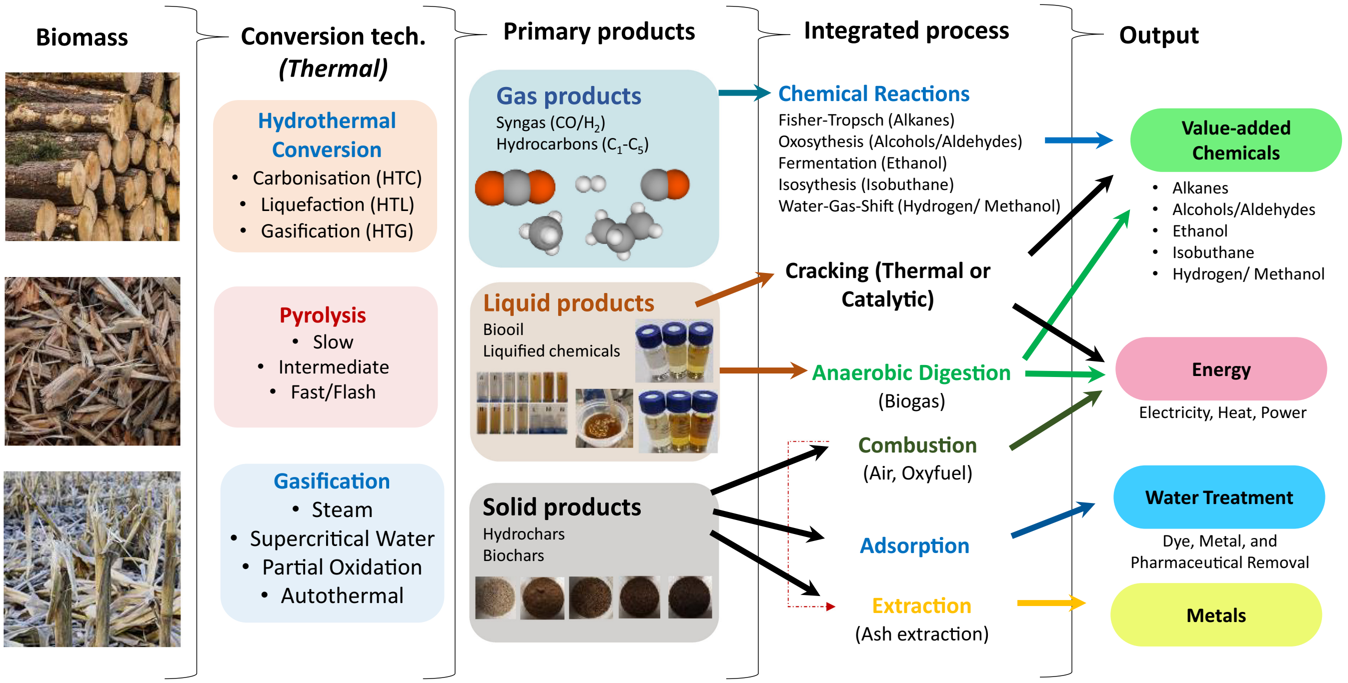

Figure 3. Thermal conversion technologies that can convert biomass into products.

reactions, the products from the pyrolysis reaction react with oxygen to produce more gas and release heat. The final step in gasification involves upgrading the gases produced *via* steam reforming, in which low molecular weight hydrocarbons, such as methane (CH_4), are converted into carbon monoxide (CO) and hydrogen (H_2). The carbon monoxide further reacts with water vapour through a water-gas shift reaction to generate H_2 and CO_2. Other side reactions, such as methanation, also occur in gasification, but to a lesser extent.[57] Table 3 lists the main reactions that occur during gasification to produce gaseous products.

Syngas, which is the primary product of biomass gasification, contains mainly non-hydrocarbon (CO, H_2, CO_2) and hydrocarbon (CH_4).[52] The gas may also contain some traces of hydrocarbons such as C_2H_2, and C_2H_6, the amount of which is dependent upon the gasifier configuration and biomass type.[61] The syngas H_2:CO ratio flexibility enables its wide range of applications, including power generation, heating, alternative transportation fuel and the production of synthetic value-added chemicals such as ammonia, acetic acid, dimethyl ether and methanol.[58] In addition, high-purity H_2 derived from syngas is also used in fuel cell applications. Syngas is produced at a low cost and has reduced emissions of harmful gases to the environment. In addition to the syngas, tar-like liquid products and solid carbon residue known as char are also formed during gasification.[59,60] Theoretically, nearly all types of biomass materials containing moisture content in the range of 5–30 wt% can be used as feedstock for gasification. Nevertheless, it is known that biomass characteristics, such as particle size, specific surface area, particle shape, carbon content, moisture content, volatile matter, carbon content, gasifier configuration, mode of operations, gasification process conditions and agents are variables that significantly influence the extent of gasification.

Steam gasification of biomass

Steam gasification of biomass is an environmentally friendly process for the production of biofuels and sustainable materials.[62] This process yields syngas with a higher hydrogen (H_2) content and a higher heating value of 12–14 MJ m^{-3}.[63,64] Additionally, the residence time is shorter, and the formation of tar and char is reduced.[65] Biomass steam gasification is mostly driven by carbon gasification reactions such as primary steam reforming (Eqn 2), secondary steam reforming (Eqn 3) and methane steam reforming (Eqn 3), respectively.[66]

Generally, municipal solid waste and agricultural waste produced a higher amount of CO and CO_2 than other waste feedstocks during gasification.[67] Theoretically, nearly all types of biomass containing moisture content in the range of 5–30 wt% can be used as feedstock for gasification.[67] Biomass feedstock containing a higher amount of moisture, however, needs to be oven-dried or dewatered to a satisfactory limit before conventional gasification using either steam or nitrogen.[68] In addition to the above drawback, the gasification

Table 3. Main reactions during gasification.[58-60]

Reaction type	Reaction	ΔH_{298K}(kJ/mol)	Equation no.
Carbon (Boudouard) reaction	$C + CO_2 \leftrightarrow 2CO$	+172	1
Primary (1°) water gas shift	$C + H_2O \leftrightarrow CO + H_2$	+131	2
Secondary (2°) water gas shift	$C + H_2O \leftrightarrow CO_2 + H_2$	+90	3
Hydrogasification	$C + 2H_2 \leftrightarrow CH_4$	−74.8	4
Oxidation	$C + 0.5O_2 \rightarrow CO$	−111	5
	$C + O_2 \rightarrow CO_2$	−394	6
	$CO + 0.5O_2 \rightarrow CO_2$	−284	7
	$CH_4 + 2O_2 \leftrightarrow CO_2 + H_2O$	−803	8
	$H_2 + 0.5O_2 \rightarrow H_2O$	−242	9
Water gas shift	$CO + H_2O \leftrightarrow CO_2 + H_2$	−41.2	10
CH_4 formation	$2CO + 2H_2 \rightarrow CH_4 + CO_2$	−247	11
	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	−206	12
	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	−165	13
CH_4 reforming	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	+206	14
	$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$	−36	15

process emits sulfur in the form of H_2S which could lead to complexity in gas separation and treatment. This necessitates an efficient gas treatment unit for high-sulfur-containing biomass.[67] A major challenge with this process is the amount and number of contaminants in the produced gas that need to be removed before utilizing the gas. These gas contaminants are key to the design and operation of downstream gas conditioning equipment, where it is crucial to limit fouling.[69] In particular, gas cooling is a challenging step, during which the equipment can become clogged with ash, particles or tar, or a mixture of all three.[70]

Supercritical water gasification of biomass

Supercritical water gasification is a promising conversion technology that appears to provide a feasible solution to the challenges of conventional gasification. Supercritical water gasification is mostly carried out within the temperature range of 375–700°C and pressures of >22.1 MPa with or without a homogenous/heterogeneous catalyst.[71] Supercritical water gasification is capable of transforming waste biomass to H_2-rich syngas with low CO and CH_4 content at high temperatures and elevated pressures in single-step gasification, thereby eliminating downstream shift or reforming. The production of H_2 at high pressure eliminates the need for downstream compression of the gas. The process permits easy product purification and collection of H_2. Another advantage of the SCWG is that inorganic impurities become insoluble, and heteroatoms like S, N and halogens become soluble in supercritical water, which eases their removal.[72] The process does not require biomass drying and can handle biomass with up to 80 wt% moisture, thus eliminating additional drying costs.[73] Compared with conventional gasification processes, SCWG requires a lower temperature to produce H_2. The gaseous product from SCWG can be burnt directly in engines or turbines to produce electricity.[74] Supercritical water gasification has the favourable advantage of avoiding water evaporation and thereby enabling the water to serve as an effective solvent media for organics and some gas synthesis, thus making the process more energy-efficient compared with thermal gasification.[75] The process is characterized by less tar and char formation. It produces a significant amount of additional H_2 from the water used as a reaction medium. One of the drawbacks of the process is that supercritical water exhibits high acidity, and thus, the reactor wall is susceptible to corrosion. The process is also disadvantaged because of its high capital investment costs. The presence of supercritical water facilitates the degradation of hydrolysis, pyrolysis, hydrogenation, dehydration, Boudouard reaction, condensation, decarbonylation, decarboxylation and dehydrogenation to produce H_2, CO, CO_2, CH_4 and other gases. The main reaction governing this process includes a steam reforming reaction (Eqn 2), water-gas shift (Eqn 3) and methanation of CO (Eqn 12) and CO_2 (Eqn 13), hydrogenation (Eqn 17) and Boudouard reaction (Eqn 1).[76,77] Equation (16) represents the overall SCWG reaction

$$CH_n\,O_m + (2-m)\,H_2O \rightarrow (2-m+0.5x)\,H_2 + CO \quad (16)$$

The biomass elemental molar ratios n and m defined by H/C and O/C respectively are prime determinants of syngas composition. A summary of selected biomass feedstocks in the SCWG is presented in Table 4.

Review of non-catalytic gasification

According to a study,[75] high temperatures and long residence time are known to enhance char formation through polymerization. The Inconel material that makes up the reactor has a catalytic impact for suppressing repolymerization and provides higher yields at high temperatures with long residence times. Thus, a higher temperature (750°C) and a long residence time (300 s) promote gasification reactions of black liquor resulting in cold gas efficiency (87.8%) and H_2 yield (24.92 mol/kg dry-ash-free) respectively. Another study[75] found that H_2 yields increased with temperature until an efficiency level of about 100% was attained at a temperature of 560°C and a residence time of 6 s, while the feed concentration rates had the contrary effect; thus, H_2 yields decreased with an increase in biomass concentration.[74] Kumar and Reddy[78] demonstrated that the presence of a high amount of lignin in biomass feedstock inhibits H_2 yield when they reported H_2 yields of 9.5 and 13.8 mol H_2 kg^{-2} biomass from mosambi peels and sugarcane bagasse containing 23 and 20 wt% respectively. In the study of the SCWG of the wheat straw, optimum conditions of 550°C with 20 wt% feed concentration for 60 min resulted in higher yields of H_2 (2.98 mmol g^{-1}) and total gases (10.6 mmol g^{-1}) respectively.[79] An optimum H_2 yield of 112.5 ± 6.2 mol H_2/kg waste dry condition was obtained from the SCWG of olive mill oil waste. In another study, it was found that the maximum H_2 yields were obtained at higher temperatures, longer residence times and lower feed concentration and flow rates. The author stated that the optimum yield was obtained at 700°C, 230 bar, a flow rate of 3 g min^{-1}, a 40.8 s residence time and 7.8 ± 0.1 g O_2 l^{-1} initial COD from olive mill wastewater.[80] Batch SCWG of different types of 1 wt% concentration of biomass samples at 440°C and 25 MPa and a residence time of 15 min reaction time revealed that the lignin content was inversely proportional to total gas yields while the cellulose content showed a directly proportional relationship with the total gas yields. The total gas yields were in order of walnut shell < almond shell < barley straw < rice straw < wheat straw < canola stalk.[81] In another related study, it was found that the SCWG of different types of biomass at 440°C and 25 MPa produced the highest H_2 yields of 4.1, 4.6 and 7.3 mol kg^{-1}, obtained after a reaction time of 15, 20 and 10 min from the almond shell, walnut shell and wheat straw, respectively. The study demonstrates that wheat straw containing higher cellulose and the least amount of lignin produced the highest H_2 yield within the shortest reaction time.[82] Sivasangar

Table 4. Summary of studies related to the non-catalytic supercritical water gasification (SCWG) of biomass.

Biomass	Reactor configuration	Operating Conditions	Optimum conditions	Primary products yield	References
Black liquor	Stainless steel (SS) and Inconel reactors	600–750°C and short (133–162 s) vs. long (300 s) residence times temperatures	750°C at 300 s	24.92 mol kg^{-1} dry-ash-free hydrogen yield	Özdenkçi *et al.*[75]
Cellulose	Laboratory-scale Stainless steel continuous-flow system	450–560°C, organic matter (0.25–2 wt%), 6, 8 and 10s	560°C in 6 s, 0.3 g cellulose L^{-1} concentration rate	Hydrogen gasification efficiency (HGE) ~112.74%	García-Jarana *et al.*[74]
Wheat straw	Tubular stainless steel SS316 batch reactor	450–550°C 20–35 wt%, 40–70 min	550°C 20 wt% feed concentration, 60 min	Hydrogen and total gases (2.98 and 10.6 mmol g^{-1})	Nanda *et al.*[79]
Almond shell Walnut shell Barley straw Canola stalk Wheat straw	23 mL batch stainless steel (SS) microreactor	440°C, 25 MPa, 1 wt% feed mixture (0.05 g biomass + 5 g water), 15 min		13, 12.5, 17, 20.5, 17.5 and 13.5% HGE for rice straw, canola straw, almond shell, barley straw, wheat straw and walnut shell	Salimi *et al.*[81]
Empty fruit bunches from oil palm	13 mL Batch SS tubing reactor	380°C, 24 MPa, 0.05–0.5 g biomass, 8 mL H_2O, heating rate 10°C min^{-1}, 8–32 min	0.3 g biomass, 32 min	74 mol H_2 L^{-1} of feedstock	Sivasangar *et al.*[83]
Wheat straw pulping black liquor	Hastelloy C-276 tube	400–600°C, 25 MPa, 4.94–13.71 s	600°C, 13.71 s	Hydrogen yield of 40.2–61.02%.	Cao *et al.*[85]

et al.[83] showed that an increase in SCWG reaction time of 0–8 min results in a significant increase in H_2 yields from 0 to 50 mmol mL^{-1}. However, a further increase to 32 min only increased the H_2 yield to 73 mmol mL^{-1} with no appreciable increase beyond 32 min during the SCWG of empty palm fruit bunches at 380°C, 24 MPa using 0.3 g of biomass and 8 mL of water. During the SCWG of alkaline black liquor in a continuous flow system, the increase in temperature and residence time and the decreasing feeding concentration favour the gas yield during SCWG. Supercritical water gasification of beech sawdust, municipal solid waste, hydrothermal char and malt spent grains in a different reactor (stainless steel, autoclaves and Inconel 625, ceramic with internal alumina inlay) for 16 h batch tests at 400°C with real biomasses and model compounds showed that the three devices have similar performance patterns in terms of gas yield. The ceramic reactor produced higher yields of C^{2+} hydrocarbons owing to the ability of Al_2O_3 to promote the cracking reaction of intermediate compounds at the expense of observed intergranular corrosion from scanning electron microscope observation.[84]

Review of catalytic gasification

The major drawback of steam gasification compared with SCWG is the high probability of condensable heavy hydrocarbon (tar) formation during the process.[86] Tar is a complex mixture of aldehydes, alcohols, aromatic and phenolic compounds.[87] The formation and accumulation of tar in the biomass gasifier might cause serious operational challenges such as pipeline clogging, corrosion and thereby lowering the gasification efficiency,[57] and increasing operational and maintenance costs.[87] Table 5 shows different catalysts and their effect on the product yields from the gasification of biomass. The use of catalysts during steam gasification is known to be a viable approach that promotes tar cracking and reforming of the heavy condensable hydrocarbon fractions.[85] In contrast, SCWG is highly energy intensive, which leads to high processing costs. Catalysts are therefore used in the SCWG process to maximize the gas yield and increase carbon gasification while enhancing the selectivity of H_2 and minimizing heat requirements through operating temperature reduction. Catalysts commonly used in both gasification routes include alkaline earth metallic catalysts [KOH, NaOH, K_2CO_3, $KHCO_3$, Na_2CO_3, Na_3PO_4, MgO and $Ca(OH)_2$], metal-based catalysts (e.g. Ni, Ce, La, Fe, Ce) and natural mineral catalysts such as carbonates ($MgCO_3{\cdot}CaCO_3$) and olivine ($2MgO{\cdot}SiO_2$). These catalysts can be added by direct mixing with the raw precursor or placed in another secondary reactor to crack newly formed tar during gasification.[88] Practicable catalysts speed up the cleavage of the C—C, C—O, C—H, and O—H bonds to yield an H_2-rich gas mixture.

Borges *et al.*[89] reported that the catalytic activity of $NiFe_2O_4$ favours water gas shift reaction and steam reforming reactions. The authors found that the H_2 yield was enhanced by 45% when 2 g of $NiFe_2O_4$ catalyst was used during SCWG of eucalyptus wood chips compared with the non-catalytic test. After the third reaction cycle, the results of XRD demonstrated the formation of coke which caused the deactivation of the $NiFe_2O_4$ and consequently, a 13.6% reduction in H_2 mol% and a 5.6% reduction in biomass conversion. The combination of K_2CO_3 with CaO showed excellent performance for high-yield H_2 production with 71.9% H_2 selectivity during the optimization of SCWG of sorghum and lignite coal blends.

It has been observed that total gas volume and H_2 volume were directly affected by the water volume in the reactor and the coal ratio of the coal–biomass mixtures. The highest total gas and H_2 volumes can be achieved under the conditions where the higher levels of the water volume of the reactor and lower levels of coal percentage of the coal/biomass mixture were combined.[90] In the study of the catalytic SCWG of eucalyptus wood chips using $NiFe_2O_4$ optimum conditions of 450°C, 2 g of $NiFe_2O_4$ catalyst and 60 min gave the highest H_2 mol%. The increase in the $NiFe_2O_4$ concentration promoted degradation of the eucalyptus wood chips (eucalyptus wood milled or ground into smaller particles) compounds water gas shift reaction, leading to higher H_2 and CH_4 yield and lower CO_2 production. Char also diminished in the presence of $NiFe_2O_4$. Nearly 66% of the carbon compounds in wood chips were converted to gaseous products in the presence of 2 g of $NiFe_2O_4$ catalyst at 500°C and 60 min, with CH_4 becoming the most abundant gas at this condition.[96]

Comparative evaluation of the different metal-doped (Ru/Al_2O_3 and Ni/Si- Al_2O_3) catalyst on SCWG of wheat straw shows that H_2 and total gas yields were optimal with maximum values up to 4.18 and 5.1 mmol g^{-1} for H_2 yield, along with a corresponding total gas yields of 15 and 18.2 mmol g^{-1}. This value is relatively high compared with the H_2 yield of 2.98 mmol g^{-1} and the yield of total gases of 10.6 mmol g^{-1} obtained for the non-catalytic gasification under similar conditions.[79] In another study by Peng *et al.*[94] a commercial 5% Ru/C catalyst exhibited good catalytic performance during the continuous catalytic SCWG of *Chlorella vulgaris* throughout 55 h. Characterization of the spent 5% Ru/C catalyst revealed that the deactivation of the catalyst was primarily caused by sulfur poisoning and sintering. The further application of zinc oxide adsorbent upstream of the catalyst bed, together with a

Table 5. Summary of SCGW of biomass – heterogeneous catalysis.

Biomass	Reactor	Studied process conditions	Catalyst	Optimal reaction conditions	Maximum H_2 yield	Reference
Eucalyptus wood chips	75 cm^3 non-stirred Hastelloy batch reactor	450–500°C, 1.0 g and 2.0 of catalyst and 2.0 g of biomass for 60 min	$NiFe_2O_4$	450°C, using 2 g of $NiFe_2O_4$ catalyst. The H_2 mol%	H_2 yield was 25 mol%	Borges *et al.*[89]
Sorghum and lignite blends	Batch-type reactor	25.6–100% coal–sorghum blends	3%, K_2CO_3– CaO	5.0 g of 25.6% coal/biomass, 68.5 mL of water, 3%, K_2CO_3–CaO catalysts	The hydrogen selectivity was 70.8%	Secer *et al.*[90]
Wheat straw	Tubular stainless steel SS316 batch reactor	450–550°C, 20–35 wt%, 40–70 min	Ru/Al_2O_3 $Ni–Si/Al_2O_3$	550°C, 20 wt% feed concentration, 60 min	Hydrogen yields of 2.98 mmol g^{-1} and total gases of 10.6 mmol g^{-1}	Nanda *et al.*[79]
Paper industry Black liquor residue	5 mL Pressure resistant batch reactor	350–450°C, 25 MPa, 15–60 min	Cerium oxide nanocatalyst (cubic CeO_2)	450°C, 15 min	–	Boucard *et al.*[91]
Municipal solid waste	75 mL stainless steel Parr reactor	500°C, 29 MPa (0, 30, 60 min), (5–20 wt.% $RuO2/\gamma\text{-}Al_2O_3$	5 wt% $RuO_2/\gamma\text{-}Al_2O_3$	20 wt% $RuO_2/\gamma\text{-}Al_2O_3$ catalyst, 60 min	92% carbon gasification efficiency	Yildirir *et al.*[92]
Fruit pulp	200 mL Inconel 625 batch reactor	400–600 °C, 0–60 min, 2.5–10 wt% feed, 0–40 wt%	Ru on activated charcoal	600°C, biomass ratio of 2.5%, 5 wt% Ru on activated charcoal	Hydrogen yield of 54.8 mol H_2 kg^{-1} fruit pulp	Elif *et al.*[93]
Microalgal (*Chlorella vulgaris*)	1–2 kgh Continuous reactor	400 °C, 28 MPa, 0–100 min	5% Ru/C	400°C, 28 MPa, 55 min	–	Peng *et al.*[94]
Wet biomass	Continuous reactor	400°C, pressures of 26–28 MPa. 10 wt% glycerol in water feed	Ru/C catalyst with sulfur zinc oxide	400°C, pressures of 26–28 MPa, 10 wt% glycerol in water feed	Carbon conversion of 106 ± 15%	Reimer *et al.*[95]

higher ruthenium loading, significantly improved the performance of the continuous catalytic supercritical water gasification process since the zinc oxide adsorbent showed high mechanical stability and satisfactory sulfur adsorption performance under supercritical conditions except for a drop in specific surface area. The co-feeding of H_2 with biomass during catalytic SCWG has been proven to be an efficient way of stimulating CH_4 formation during the catalytic hydrothermal gasification of wet biomass in a continuous test rig using a feed of 10 wt% glycerol in water and a fixed bed of a carbon-supported ruthenium catalyst. The gas produced is composed of about 86 vol% CH_4.[95] The investigation of the catalytic effect of cerium oxide nanocatalyst towards the hydrothermal conversion of black liquor revealed that the catalyst is efficient for the conversion of black liquor owing to the increase in H_2 production and inhibition of coke formation.[97] The investigation of the effect of process parameters on SCWG of fruit pulp using 5 wt% Ru on activated charcoal as a catalyst revealed that the amount of H_2 produced increased nearly five times as temperature increased from 400 to 600°C. The optimum H_2 yield (54.8 mol H_2 kg^{-1} fruit pulp) was obtained at a biomass ratio of 2.5% with a corresponding higher gasification efficiency (150.8%), carbon gasification efficiency (88.1%) and H_2 gasification efficiency (213.5%) respectively.[93]

Hydrothermal conversion technologies (carbonisation and liquefaction)

Hydrothermal processing facilitates the physio-chemical transformation of carbonaceous material under high temperature and -pressure liquid (sub-critical and supercritical) water to produce varieties of green fuel and chemical products.[98] The products of the hydrothermal process include different forms of biofuels (bio-char, bio-oil or biocrude, gaseous hydrogen and methane) and other value-added products (ethanol, acetone and acetic acid). The dominant products obtained are purely dependent upon the choice of operating conditions.[99] The hydrothermal operation takes place in the following states: supercritical (hydrothermal gasification) and subcritical for hydrothermal liquefaction (HTL) temperatures and hydrothermal carbonisation (HTC),[99,100] following the phase diagram of water and its different regions above vapour pressure and critical temperature, as depicted in Fig. 4.

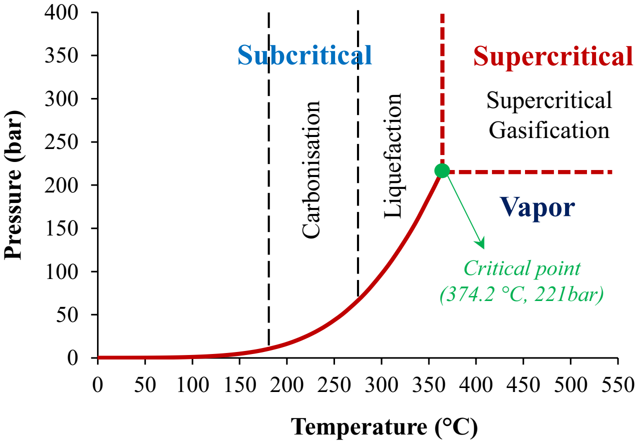

Figure 4. Hydrothermal processing conditions in a water phase diagram.[40]

Hydrothermal processing is one of the most promising technologies, as it can use the high inherent moisture of biomass to its advantage.[101] For other processing techniques, such as pyrolysis and combustion, the high moisture content needs to be removed, which requires a significant amount of energy for drying processes. In contrast, hydrothermal conversion of biomass in hot-compressed water is a viable, scalable and energy-efficient thermochemical route for converting biomass into synthetic solid, liquid or gaseous fuels and chemicals.[102] In hydrothermal treatments, water can be a solvent, a reactant and/or a catalyst in the hydrolysis reactions. The process also leads to by-products that can be used for power generation and the recovery of useful nutrients. In this process, biomass conversion is carried out by several complex reactions depending on the physical properties of the water, which are usually manipulated by changing the temperature, pressure and contact time of the water–biomass in order to obtain the desired products. The hydrothermal conversion is therefore classified into three processes namely carbonisation (HTC), liquefaction (HTL) and gasification depending on the severity of the operating conditions.[103-106] There has been significant work on hydrothermal conversion technologies, with ~5500 publications using the keywords 'Hydrothermal carbonisation' or 'Hydrothermal carbonisation', ~2880 publications using the keywords 'Hydrothermal liquefaction', and ~1478 publications using the keywords 'Hydrothermal gasification' published according to the Web of Science between 2010 and 2021. Among these publications, 1572 (for HTC), 785 (for HTL), and 535 (from Hydrothermal gasification) are from countries in the EU and European Economic Area.

Hydrothermal carbonisation

Hydrothermal carbonisation (180–250°C, 15–40 bar) is a thermochemical process for the pre-treatment of high moisture content biomass to make it viable for energy production. It uses relatively low temperatures and is suitable for any kind of biomass feedstock. Hydrothermal carbonization can convert lignocellulosic materials into solid hydrochar, which have better physicochemical characteristics than raw biomass feedstocks[107] and also produce liquid products that contain organic and inorganic value-added chemicals. The HTC hydrochars exhibit lower O/C and H/C ratios compared with dry torrefaction and turn into more lignin or coal-type materials.[108] HTC hydrochars can be used in a wide range of processes such as soil amendment,[49] CO_2 capture,[50] nanoparticles (for making composites), energy production[47] and water purification[48] thanks to their physicochemical properties.[51] Although the lab-scale research on HTC of various biomass feedstocks has recently progressed and provided significantly promising results, the HTC process needs further investigations in terms of process and reactor types, biomass feedstocks and conditions owing to the complex reaction mechanisms and operational barriers to make this technology a commercial technology. For example, a continuous HTC process would be one of the key components for a potential industrial application of HTC, as most HTC research have been carried out in batch.

Hydrothermal liquefaction

Hydrothermal liquefaction (250–370°C, 50–240 bar) is the wet processing route for high-moisture biomasses to produce liquid fuel (bio-crude or bio-oil),[103] which is similar to petroleum crude and can be upgraded to a range of petroleum-derived fuel products. Since HTL involves the direct conversion of biomass into bio-crude in the presence of a solvent, it eliminates the high drying costs. The HTL process could be operated under subcritical or supercritical conditions for producing bio-oil, water-soluble organics, gaseous products and char.[109] Hydrothermal liquefaction is usually conducted at a moderately higher temperature (280–370°C) and pressure (4–25 MPa) in the presence of a solvent medium.[98,100] This process can be done using either a batch or a continuous reactor. Catalyst addition has been reported to show significant effects on liquid yield and quality. Figure 5 shows a diagrammatic overview of the reaction pathway.

During HTL large biomass undergoes depolymerization to produce smaller monomeric fractions which are subsequently repolymerized into varieties of compounds that form the biocrude. The high operating conditions of the process facilitate the conversion of all lipids, proteins and carbohydrates present in the biomass into the desired bio-oil with a higher yield.[110] The products of HTL constitute biocrude or bio-oil, an aqueous phase containing hydrophilic organics, a gas and solid char (Tables 6 and 7). The bio-oil derived from HTL contains a lower amount of oxygen and has miscibility with water in comparison with bio-oil from other thermochemical processes and therefore can easily be subjected to hydrotreatment. Typically, the oxygen content reduces to a value of 10–15% from 40% contained in the biomaterial.[111] The bio-oils can be substantially purified and used as fuels in burners, boilers and turbines. Bio-oils can also be further upgraded into transportation fuels like automotive gas oil (diesel), premium motor spirit (gasoline) and other important end products such as polymers, asphalt and lubricants. The bio-oil which is the main product of HTL is known to contain several value-added compounds as summarized in Table 6.

The main advantage of HTL is that the energy-consuming drying stage is eliminated. Another cutting-edge benefit of this HTL process is it consumes only 10–15% of the energy in the feedstock biomass, yielding an energy efficiency of 85–90%. Hydrothermal liquefaction can recover more than 70% of the feedstock carbon content that can be utilized for carbon capture procedures. The other technical edge of this process is that the bio-oil that is obtained from this process does not require sophisticated treatment/upgrading procedures for commercial utilization.[113] The details on hydrothermal gasification are presented under Section 3.1.1. Table 7 presents literature studies on the hydrothermal conversion of biomass to value-added products and biofuels.

Pyrolysis

The limitation to biomass valorization in Europe largely depends on factors ranging from utilization to the market (demand and supply), and eventually government policies. The enormous availability of geographically distributed biomass in the EU makes the drive for valorization ready to be ignited. There has been significant work on biomass pyrolysis, with ~31 982 publications using the keywords 'Biomass Pyrolysis' published according to the Web of Science between 2010 and 2023. Among these publications, ~9201 papers were published from countries in Europe, ~1816 publications were specifically detected using the keyword 'Biomass Fast Pyrolysis', ~795 publications were detected using the keyword 'Biomass Slow Pyrolysis' and only ~310 were detected using the keyword 'Biomass Flash Pyrolysis'. The waste-to-energy legislation in the EU proposed a 35% reduction of landfilled wastes by the year 2020 when compared with the levels in previous years.[125] Just like municipal solid waste, other biomass including forest residues, can be valorized into valuable products, hence the term biomass-to-energy. In previous times, incineration was the adopted process required to convert wastes to carbon-based products. However, the process involves the complete oxidation of 'combustible materials' operating at extremely high temperatures above 850°C. The drawback associated with incineration is mainly the high temperature and

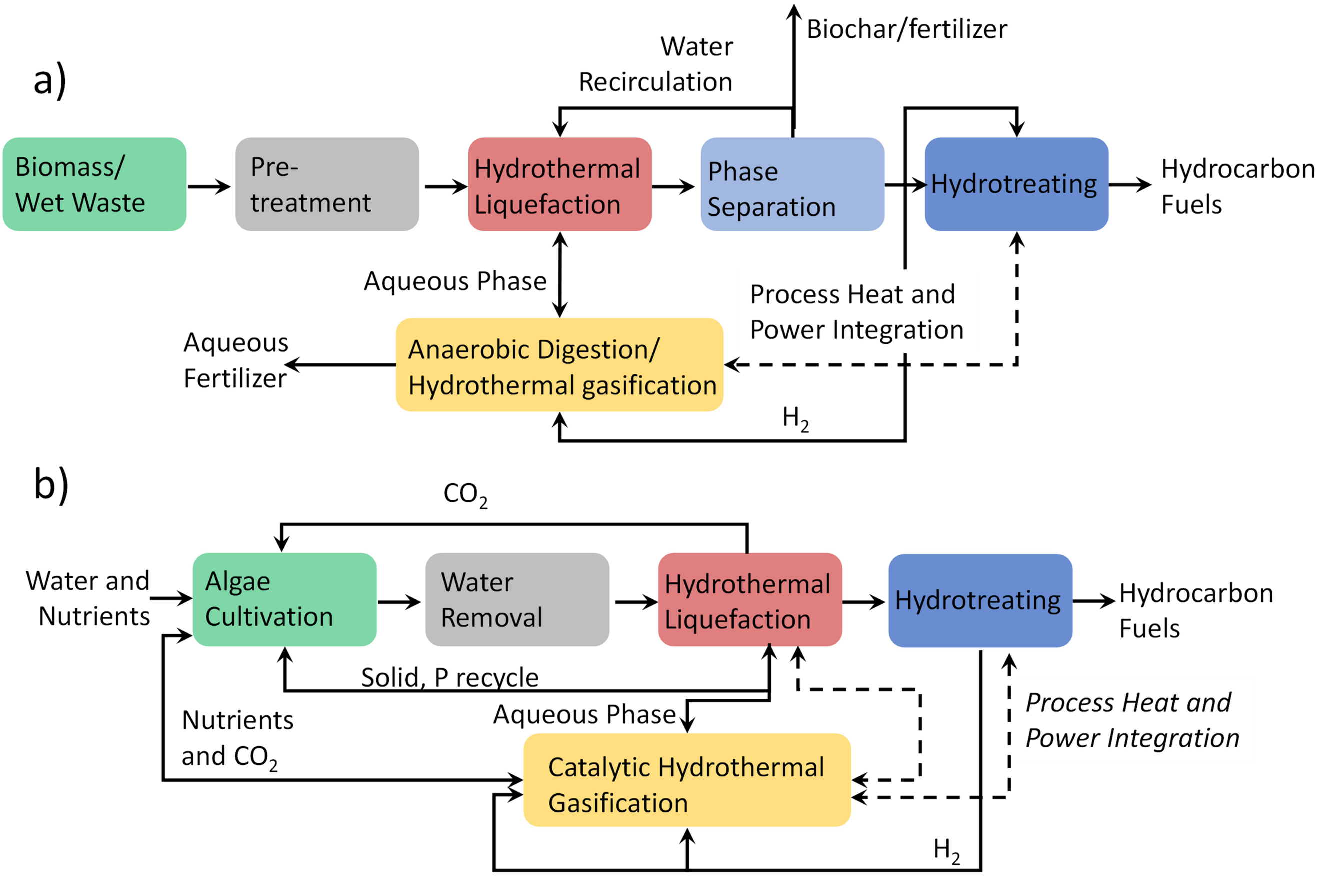

Figure 5. (a) Process flow diagram of the hydrothermal liquefaction (HTL) process of lignocellulose biomass adopted from and (b) process flow diagram of HTL process of algal biomass/wet biomass. These figures were adopted from Biller and Ross[112] and Gollakota *et al*.[113]

oxidative environment, as well as the combustible material required for burning. Gasification can surmount these challenges, as partial oxidation is required, with little (or no) access to air, but this operates at high temperatures (around 500–1800°C). Pyrolysis (just like gasification) allows for the use of various feedstocks and moderately lower temperatures, in the absence of air. The pyrolysis of biomass is capable of generating products in gaseous, liquid and/or solid form, generally known as pyrolysis gas (or pygas), pyrolysis oil (bio-oil) and biochar (or just char), respectively.

Although several reports have shown that numerous biomasses can be valorized via pyrolysis, limited use and interests have been geared toward organic wastes. In the UK (no longer a Member State of the European Union) but a previous member of EU, the drive to improve electricity generation motivated companies to seek to utilize organic wastes for electricity generation. In energy generation, biomass offers an excellent choice for valorization, as it is a natural source of carbon. Several companies and institutions in the UK such as Future Blends Ltd, Anergy Ltd and Torftech Energy Ltd have adopted pyrolysis for the generation of electricity, with plant/forest biomass being the key candidate required for processing. In 2016, the total electricity generated (from bioenergy) *via* pyrolysis in the UK amounted to 30 042 GWh, where about 63% of the raw materials required for processing were sourced from plant biomass.[125]

Biomass pyrolysis is made possible either by slow pyrolysis or by fast pyrolysis, which can be either catalytic or non-catalytic. Fast pyrolysis is mostly adopted, because of the enormous advantages compared with slow pyrolysis. Slow pyrolysis requires moderate temperatures of around 400–500°C, a longer residence time typically within minutes and a heating rate of 0.1–1°C s^{-1}, while fast pyrolysis requires higher temperature, a shorter residence time and a heating rate of 10–200°C s^{-1}, and generates a higher yield of bio-oil, which is suitable for a further upgrade to hydrocarbon-like fuels.[126] Reports on the pyrolysis of food waste have revealed the yield of individual products at different variations as shown in Fig. 6. Biochar is a carbon-rich product that holds significant potential for carbon sequestration, acting as a

Table 6. Major product compounds of bio-oil obtained by the hydrothermal liquefaction (HTL) process.[113,114]

Products	Compounds
Monoaromatics	Benzene, cholesterol, cholestene, phenol, toluene, styrene
Vitamin	Vitamin E
Fatty acids	Arachidic acid, hexadecanoic acid, steric acid/oleic acid, myristic acid, tetradecanoic and octanoic acid, eicosapentaenoic acid, 2-hydroxypropanoic acid, propanoic acid, 2-hydroxy-2-methyl-tetradecanoic acid, octadecanoic acid, azelaic acid, 12,15-octadecatrienoic acid
Alkane/alkene	Docosane and cholestane, hexadecane/hexadecane, heptadecane/heptadecene, phytane/phytene, eicosane, coprostane, triconate, hentriaconate, dotriaconate, cycloalkane
Polyaromatic compounds	Anthracene and phenanthrene, fluorene, naphthalene, indene pyrene and carbazole, quinoline
Nitrogenous compounds	Amides, amines and nitriles, indoles, pyrazines, pyridines, pyrrols/pyrrolidines, piperidines, pyrrolidinones, indoles
Other oxygenated compounds	Acetic acid, alcohols, aldehydes, esters, furans, ketones

stable and long-term sink for atmospheric CO_2. Its porous structure and high surface area enable the trapping of CO_2, and when incorporated into soil, it not only sequesters carbon but also enhances soil fertility, increasing water retention and improving microbial activity. This makes it a multifaceted solution that contributes to both climate change mitigation and sustainable agriculture.

Biochar can also serve as industrial fuel. Moreover, it is characterized by high heating values. In contrast, bio-oil is mostly utilized for bioenergy purposes since it can be upgraded via hydrodeoxygenation or decarboxylation, to generate on-road vehicles or even jet fuels. The percentage yield of pyrolysis products can be optimized to selectively improve the yield of the desired product. Important processing parameters such as temperature, biomass-mixing ratios, feed rate, residence time and atmospheric conditions, and so forth, are factors that influence the yields of the products from pyrolysis. Generating liquids from fast pyrolysis typically requires higher heating and heat transfer rates using finely ground biomass, properly controlled reaction temperatures around 500°C shorter vapour residence times, usually within seconds, and rapid cooling. Other by-products that can be generated include organics, ash and water. Although fast pyrolysis is fast gaining attention, more research is needed to address important issues such as scale-up, cost reduction, yield improvement and drop-in or infrastructural compatibility of the bio-products.

The type of biomass and the process parameters determine the properties of the biochar, which is produced in large quantities by slow pyrolysis. However, as stated earlier, more bio-oil is produced with fast pyrolysis, with a lower heating value, which is because of the presence of moisture content existing as H_2O, O_2 and other carboxylic acids. The pyrolysis gas is a mix of H_2, C_1–C_4 hydrocarbon gases, CO_2, CO and H_2S. An optimum yield is obtained when the biomass has a low moisture content, since the presence of water may result in the formation of tar and an increase in the energy cost of drying the biomass. Additionally, the use of wet biomass can result in a 40% increase in H_2 content in the pyrolysis gas product.[126] In recent times, most companies based in Europe have developed and adopted reactor designs suitable for pyrolysis. The different reactors used in pyrolysis are fixed-bed reactors, rotary kilns, fluidized bed reactors, microwave-assisted reactors and batch and semi-batch reactors.[126]

The bubbling fluid beds have attractive features such as simple construction and operation, moderate temperature control, easy to scale and high liquid yields. As a result, several companies in both Spain (Union Fenosa) and the UK (Wellman), who have built and operated 200 kg h^{-1} and 250 kg h^{-1} units, respectively, have recently selected bubbling fluid beds for development. Ensyn in both Finland (VTT) and Spain (ENEL) has developed other reactor designs for pyrolysis, such as circulating fluid beds and transported beds for commercial use, at 20 and 650 kg h^{-1}, respectively.[127]

The main components of biomass are cellulose, hemicellulose and lignin. The most prevalent biomass class is lignocellulosic biomass, which is a plant-derived biomass that can be classified into hardwood, softwood, farm wastes, and grasses. Among the main components of biomass, lignin has been shown to be the most recalcitrant constituent of the plant cell wall, acting as a protection against chemical and enzymatic degradation of plant cells. Unlike hemicellulose and cellulose, lignin is not a carbohydrate. The thermal processing of biomass (via pyrolysis) helps in degrading these structural blocks that makeup plants. Pre-treatment through acidic or alkaline media can help improve the hydrocarbon and energy contents, thereby decreasing the high moisture generally associated with the process of pyrolysis – which can be a bane to the pyrolysis process.

Shown in Table 8 is the biomass available, and the processing modes required for pyrolysis upgrade in several European countries. According to the European Biomass Industry Association, most biomass ranging from waste wood, fresh wood chips, and industrial sawdust contain

Table 7. Biomass to value-added products *via* hydrothermal processing.

Biomass type	Hydrothermal conditions	Main product	Findings (yields, value-added chemicals, general outputs)	References
Thymbra spicata	Flow rate: 1–3 mL min^{-1} Temperature: 100–175°C Pressure: 20–90 bar Extraction time: 30 min	Essential oils	Global yield: 3.4%. ~90% of carvacrol and thymol contents were observed. *E*-3-Caren-2-ol and enantiomers of *α*-pinene were also identified in the extract. Essential oils (*p*-cymene, *E*-3-caren-2-ol, carvacrol)	Ozel *et al.*[115]
Laminaria digitata, Laminaria hyperborea, Laminaria saccharina, Alaria esculenta	Reactor: batch Temperature: 350°C Heating rate: 25°C min^{-1} Residence Time: 15 min	Bio-crudes	Bio-crudes show similar heating values, but bio-chars had a variation in their higher heating values. High nitrogen content is observed from the bio-oil obtained, which requires an upgrade	Anastasakis *et al.*[116]
Wheat straw	Temperature: 185–205°C Residence time: 30 min	Ethanol	70% of the hemicellulose, 93–94% of the cellulose and 89% of the cellulose in the fibers were recovered and converted into ethanol. Biomass pre-treatment with xylanase increased the cellulose conversion to ethanol	Petersen *et al.*[117]
Carbohydrates (model compounds)	Pressure: 25 MPa Residence time: 3–180 s Temperature: 200–360°C Catalyst: $ZnSO_4$	Lactic acid	A relatively small quantity of carbohydrates was converted to lactic acid under sub- and supercritical water process conditions. Lactic acid yields were significantly increased by adding a small quantity of metal ions [Co(II), Ni(II), Cu(II) and Zn(II)]. The yield of lactic acid was 42–86% at 300°C and 25 MPa	Bicker *et al.*[118]
Glucose (model compound)	Pressure: 23, 27 MPa Temperature: 300–400°C Residence Time: 20s Catalyst: NaOH	Lactic acid	80% of glycolaldehyde yield was observed at 400°C but no lactic acid was found in those conditions. However, using NaOH as a catalyst provides a relatively high lactic acid yield (57% at 400°C, 27 MPa). Both pH and medium play significant roles in product selectivity	Cantero *et al.*[119]
Grape seeds	Pressure: 50–155 bar Reaction Time: 60 min Temperature 250–340°C Water flow rate: 5 mL min^{-1}	Bio-oil	25–35 wt% of solid residue yield. Up to 15.7 wt% of light bio-oil and 16.2 wt% of heavy bio-oil yield were achieved at 340°C	Yedro *et al.*[120]
Brewer's spent grains	Residence time: 20–35 min Temperature: 135–235°C	Bio-butanol	64% of hemicellulosic sugar recovery, 70% of glucose recovery in enzymatic hydrolysate and 2.4 g L^{-1} total inhibitors were observed at 192.7°C and 5.4 min, Enzymatic hydrolysis of brewer's spent grains yielded a sugar solution. This sugar solution was fermented in a butanol concentration of 8.3 g L^{-1} and an overall yield of 46 kg t^{-1} feed	López-Linares *et al.*[121]
Laminaria saccharina	Temperature: 350°C Pressure: 16.5 bar Reactor: muffle furnace	Bio-oil	Up to 79% of bio-oil yield (higher heating value: 35.97 MJ kg^{-1}) was observed at 350°C, with 15 min of residence time. Rapid heating accelerates biomass degradation, reduces unwanted side products, accelerates biomass cell breaking and minimizes char formation and re-polymerization	Bach *et al.*[122]
Nannochloropsis gaditana, Scenedesmus almeriensis	Temperature: 350°C Pressure: 2 MPa Reactor: microautoclave	Bio-oil	Adding dichloromethane in the aqueous phase as an organic solvent increases the biocrude oil yields but also provides higher oxygen and nitrogen contents in biocrude oil	López Barreiro *et al.*[123]
Beechwood	Temperature: 300°C Pressure: 1 MPa Reactor: batch	Bio-oil (iodine)	The bio-oils produced from hydrothermal, and pyrolysis show high acidity, which requires extra modifications in storage and transfer facilities. The bio-oils need to be upgraded to reduce 'acidity' (oxygen content) and saturated double bonds to deal with 'indine', and depolymerize the larger molecules to deal with 'viscosity'	Haarlemmer *et al.*[124]

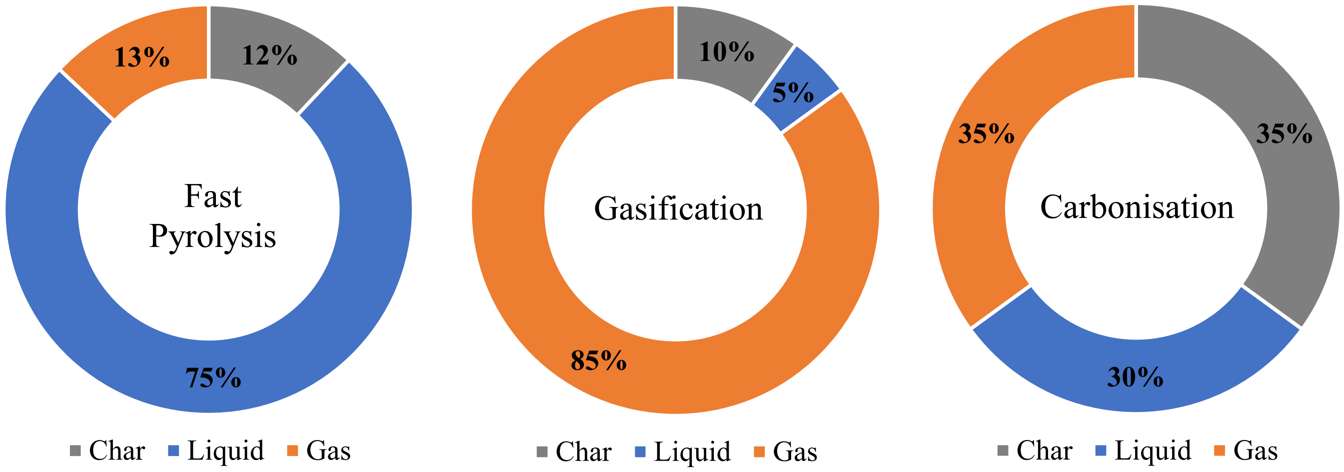

Figure 6. Typical product yields generated from the pyrolysis, gasification and carbonisation of wood.

moisture contents of 10–30, 40–60 and 40–60%.[128] These high amounts of moisture content propose the initial cost challenge associated with most wood biomass in Europe for the initial drying of the biomass before processing.

Integrating thermochemical processes with CO_2 capture

Biomass energy technologies combined with carbon capture and storage (CCS) offer the potential for achieving negative net atmospheric carbon emissions, which can contribute to the mitigation of global warming.[129] Bioenergy with CCS (BECCS) includes several thermochemical conversion pathways (e.g. gasification, pyrolysis and liquefaction), which are discussed further in the next section.

Gasification with CO_2 capture

Among different thermochemical pathways, gasification has the potential to decarbonize fuels and support a circular economy. The potential for BECCS using gasification with CO_2 removal and capture has been evaluated in many studies. Based on previous studies, an integrated gasification and carbon capture with a combined cycle gas turbine was developed with a cost of electric power of 0.082 \$ $(\text{kW h})^{-1}$, mitigation of 140 gC $(\text{kW h})^{-1}$, a CO_2 capture efficiency of 44% and a thermal efficiency of 28%.[130] According to Uddin and Baretto,[131] a 200 MW combined heat and power plant could mitigate 200 kgC with an 85% capture efficiency. Another scenario presented by Kraxner *et al.*[132] could potentially achieve a 90% capture efficiency with 2.5 tons of carbon per year per ha. Converting biomass into hydrogen through gasification, intended for transportation and power production, holds appeal owing to its potential for significant carbon capture.[53] However, this process encounters various obstacles including the challenge of procuring a sufficient amount of biomass on a scale that ensures cost-effective plant operation, as well as the complexities of cost-efficiently and dependably storing CO_2 in either ocean reserves or geological structures.[53]

There are several carbon capture separation methods, including absorption, adsorption, membrane separation and chemical looping. A simulation study was conducted by Shahbaz *et al.* using Aspen Plus for steam gasification of palm kernel shells with CO_2 capture through a sorbent (CaO).[133] The maximum hydrogen content is predicted to be 79.32 vol% and the minimum CO_2 content to be 5.42 vol% under operating conditions which include a temperature of 700°C, a steam/biomass ratio of 1.5 and a CaO/biomass ratio of 1.42.[133] Cormos *et al.* evaluated membrane technology both independently and in combination with gas–liquid absorption. Overall, the results of this study indicated that the CO_2 capture costs for membrane technology are about 50% lower than for chemical or physical absorption.[134]

Chemical looping gasification, a novel gasification technology, is capable of achieving 100% capture efficiency and a low energy penalty. Similar to oxy-fuel combustion, chemical looping involves the replacement of oxygen introduced with the fuel with a metal oxide (e.g. Fe_2O_3, NiO, Mn_2O_3), which acts as an oxygen carrier. Metal oxide and fuel undergo redox reactions, resulting in two different streams of gases, one rich in hydrogen and one rich in CO_2.[129] Acharya *et al.* found that 71% hydrogen and nearly 0% CO_2 were present in the product gas produced in a batch-type fluidized-bed steam gasifier with CaO as the sorbent.[135] According to He *et al.*,[136] biomass-chemical looping gasification coupled with water/CO_2-splitting and $NiFe_2O_4$ oxygen carrier can achieve 93.84% carbon conversion at an optimal CO_2/H_2O mole ratio of 0.15. It is currently possible to successfully

Table 8. Some selected EU countries and their industrial biomass wastes available for pyrolysis.

EU countries	Biomass available	Pyrolysis mode/design	Findings	References
France	Waste edible oils – around 100,000 tons are produced per year in France	Operating temperature range of 700–800°C. Feeds were pre-treated in the preheating chamber, before processing in the electric oven	An optimal temperature of 800°C was ascertained and CO and CO_2 are also produced but with low molar fractions	Billaud *et al.*[137]
Finland	Woody biomass – wood and peat	High-pressure conversion flash pyrolysis operated on a laboratory scale in batch or continuous units	Peat grades containing low ash content are prime candidates as raw materials for pyrolytic upgrades. The presence of phosphorus and certain metals may limit the use of peat coke in certain applications	Solantausta and SipilÄ[138]
The Netherlands	Fine-sized woody biomass with high moisture content	Drying – enhanced fast pyrolysis of woody biomass. Fluidized bed pyrolysis reactor	The plant operates at a capacity where 5 t h^{-1} of clean wood will be converted into about 3.2 t h^{-1} of pyrolysis oil. Initially designed as a polygeneration plant to simultaneously produce oil and generate electricity	Van de Beld and Muggen[139]
Spain	Olive stones	The pyrolysis was carried out in a vertical tube furnace, within temperature ranges 400–600°C, with heating ramps of 5, 10 and 20°C min^{-1}	Olive stones impregnated with acid gave higher yields of bio-oil. The most suitable temperature for obtaining biochar was 400°C for both non-treated and pre-treated raw materials	Sánchez-Borrego *et al.*[140]
Germany	Lignocellulosic biomass – softwood, hardwood, straw, sugar cane bagasse, lignins and cellulose	High-pressure fast pyrolysis, in batch, semi-continuous fluidized bed reactors	Processing over Pd/C catalysts generated very small amounts of solid residue with lignocellulosic biomass. The oil yields of the lignocelluloses were in the range of 41%. Cellulose and hemicelluloses gave rise to around 30% and lignins to 62% of oil	Meier *et al.*[141]
Sweden	Biomass – wood, solid waste and peat	Experiments were conducted in small batch reactors with heating rates from 10 to 100°C min^{-1}, through an electrically heated reactor tube operating at 500–1000°C	The char fraction after a long residence time (final carbonization of flash char) is almost independent of the temperature between 650 and 1000°C. High heating rates provide a shorter time for the dehydration to take place than low heating rates, which results in more unstable material left for depolymerization to primary volatiles and therefore lower final char yields	Ekstrom and Rensfelt[142]
Italy	Unspecified biomass	Slow pyrolysis 120–150 kg h^{-1} rotary kiln pyrolyzer.	A self-energizing plant, where the pyrolysis process by-product, char, is used to provide the thermal energy required for pyrolysis	Adamiano *et al.*[143]

apply gasification technology to BECCS and combine heat and power. However, further research and technological development are needed to make the process more economically viable.

Liquefaction with CO_2 capture

In BECCS systems, liquefaction is an important process since it does not necessarily capture CO_2 owing to its nature. Liquefaction can mitigate carbon dioxide by addressing the following issues: (i) by converting biomass into a valuable liquid fuel without removing moisture, biomass can be used as a replacement for fossil fuel-based oils; and (2) Pre-treatment is not required, thereby reducing the CO_2 emissions associated with it. Furthermore, owing to the elimination of the drying process, this process produces no CO_2 emissions.[129]

Using HTL of forestry residues and Selexol™ as a physical adsorbent, 95% purity CO_2 was obtained at a capture cost of US\$75 t^{-1}.[144] Furthermore, The HTL process with CCS is shown to be capable of reducing greenhouse gas emissions by 102–113% compared with fossil fuels.[144] Simulations using HTL, based on lignocellulosic biomass waste and urban biomass using Selexol™, indicate that CO_2 purity between 90 and 98 mol% can be obtained for 40–53 EUR t^{-1} and 98–99 mol% purity is achievable for 57–77 EUR t^{-1}.[145] Although the liquefaction process is still being studied at the lab scale, further research and development are required to make it feasible for commercial use, as it can be an invaluable component of the BECCS process that produces liquid fuel and reduces CO_2 emissions.

Pyrolysis with CO_2 capture

In bioenergy systems, pyrolysis has been widely adopted, although it has not been as prevalent in BECCS systems.[129] Notably, the pyrolysis process directly mitigates CO_2, as biochar, the by-product of pyrolysis, offers a potential BECCS option since very little CO_2 is released per unit of char, and carbon can be sequestered when the biochar is buried on land.[146] Biochar derived from pyrolysis presents an appealing option for carbon sequestration owing to its enduring presence in soils and the potential benefits it offers to ecosystems.[53] The gradual pyrolysis method generates substantial quantities of biochar, akin to the carbon capture potential of biofuels produced through gasification.[53] In contrast, rapid pyrolysis yields a smaller amount of biochar, but it boasts more favourable economics since the resulting bio-oil can be transformed into high-energy, carbon-negative liquid fuels or alternative products.[53] A study was conducted to examine the potential of biochar soil application in BECCS, and the results indicated that biochar soil application has a significant potential to reduce greenhouse gas emissions (0.7 Gt CO_2 eq per year worldwide).[147] It is estimated that integrating CCS with pyrolysis would result in a reduction of 2 Mt of CO_2 by 2030.[148] The impact of different CO_2 absorbents (such as CaO) on biomass pyrolysis has been studied in some studies.[149-151] Owing to the relatively high cost of organic calcium compounds, calcined carbide slag can be used in negative-carbon pyrolysis as an alternative to commercially available CaO.[152] Chen *et al.* found that biomass pyrolysis with calcined carbide slag at a mass ratio of 1:1 was the most effective method for minimizing CO_2 production and upgrading products.[146]

The integration of CCS and biomass pyrolysis has been studied from a techno-economic perspective. The study by Cheng *et al.* examined four thermochemical conversion technologies (hydrothermal treatment, pyrolysis, gasification and conventional combustion) in combination with CO_2 capture under a variety of processing conditions.[146] Their results demonstrated that slow pyrolysis of crop residues and woody wastes has the potential to be a negative emissions-producing technology that would lead to global warming potential values ranging from −470 to −200 kg CO_2 eq t^{-1} (without substitution) and from −1050 to −770 kg CO_2 eq t^{-1} (with two substitution benefits: exporting heat generated and using biochar as a fertilizer.[146] In another study, various conversion technologies were compared by Cheng *et al.*,[153] and gasification and combustion with CCS were found to have the highest net negative carbon emissions (1400 kg CO_2 eq t^{-1} biomass on dry weight). It was found that slow pyrolysis of woody wastes and crop residues has the potential to be an economically viable negative emission technology, even without carbon incentives, whereas other technologies require carbon incentives to be successful.[153] Sun *et al.* compared the technical and economic feasibility of different capture technologies appropriate for pyrolysis (monoethanolamine-based chemical absorption, temperature swing adsorption, calcium looping (CaL), and chemical looping combustion (CLC).[154] In comparison with other methods, CLC is found to capture more CO_2 with the lowest energy and exergy penalty, whereas CaL has the highest energy and exergy penalty. It was found that CO_2 capture potential can be directly impacted by the reaction time of the pyrolysis reaction. Furthermore, the levelized costs of CO_2 (LCOC) for CLC and CaL are about 56\$/tCO_2, while monoethanolamine based chemical absorption shows the highest, at 83\$/tCO_2.[154]

Conclusion

This review is centred around the exploration of thermochemical methods, specifically examining the patterns of biomass usage for energy production within the EU during the past 10 years. It goes into detail about the modern and cutting-edge technologies in the field, including gasification, pyrolysis, advanced combustion techniques and liquefaction, all of which are integral to the process of converting biomass into usable energy. Within the discussion of these technologies, the review highlights the unique challenges and opportunities associated with each method, thus offering a nuanced understanding of their individual characteristics.

Furthermore, the review provides an extensive overview of previous research related to each conversion technology, synthesizing the existing knowledge to create a foundation for future studies. This encompasses not only thermochemical but also integrated approaches to biomass valorization, emphasizing the importance of diverse and multifaceted research in this area.

An additional significant aspect of the review is its exploration of biomass thermochemical conversion processes that incorporate carbon capture strategies, like gasification, liquefaction and pyrolysis combined with CO_2 capture. By integrating carbon capture into these processes, the potential for achieving negative net atmospheric carbon emissions is introduced. This offers an exciting possibility for not only producing energy but also actively contributing to the reduction of global carbon levels. In the broader context of climate change and global warming, these processes symbolize promising paths forward, aligning with worldwide efforts to mitigate the adverse impacts of increasing atmospheric carbon concentrations.

Thermochemical processes, such as gasification, pyrolysis, advanced combustion and liquefaction, have been pivotal in advancing technological developments in the biomass sector. These processes enable the efficient conversion of various biomass materials into biofuels and valuable chemicals, laying the groundwork for continued innovation and improvements in this technology. Thermochemical conversion technologies offer flexible and efficient pathways for the utilization of diverse biomass feedstocks, including algae and agricultural waste, thereby supporting feedstock diversity. This advancement is also aligned with economic feasibility, as these technologies are continually being refined to reduce costs and optimize large-scale production. Furthermore, the integration of carbon capture with these processes contributes to sustainability by offering potential solutions for global warming mitigation.

The progress in thermochemical processes also supports the broader framework of market dynamics and regulatory compliance within the EU. By enhancing efficiency and reducing the costs of biofuel and value-added chemical production, these technologies cater to the current and future market demand, shaping the potential for market growth. Concurrently, understanding and aligning with existing policies and regulations within the EU is crucial. Thermochemical processes, through their innovation and adaptability, are poised to navigate the complex regulatory landscape, ensuring that biomass valorization not only meets the technical and economic needs but also adheres to evolving policies, thus contributing to the overall robust and responsible growth of the industry.

In summary, this review serves as a comprehensive guide and resource for those interested in the intricate interplay between thermochemical processes, biomass utilisation and carbon management, setting the stage for continued innovation and progress in these critical fields.

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References

1. Jiménez-Llanos J, Ramírez-Carmona M, Rendón-Castrillón L and Ocampo-López C, Sustainable biohydrogen production by Chlorella sp. microalgae: A review. *Int J Hydrogen Energy* **45**:8310–8328 (2020).
2. World Health Organization, Ambient air pollution: a global assessment of exposure and burden of disease https://apps.who.int/iris/handle/10665/250141.
3. World Meteorological Organization, State of the Global Climate 2021.
4. Pachauri RK, Allen MR, Barros VR, Broome J, Cramer W, Christ R *et al*., *EPIC3Geneva*. IPCC, Switzerland, p. 151 (2014). ISBN: 978-92-9169-143-2.
5. Schleussner CF, Lissner TK, Fischer EM, Wohland J, Perrette M, Golly A *et al*., Differential climate impacts for policy-relevant limits to global warming: The case of 1.5 C and 2 C. *Earth Syst Dynam* **7**:327–351 (2016).
6. Kappelle M, WMO Statement on the State of the Global Climate in 2019 (2019). https://www.researchgate.net/publication/340135130_WMO_Statement_on_the_State_of_the_Global_Climate_in_2019?channel=doi&linkId=5e7ae226299bf1f3873fca46&showFulltext=true.
7. RED, DIRECTIVES (EU).
8. Eurostat, Share of renewable energy in the EU up to 19.7% in 2019-Products Eurostat News-Eurostat https://ec.europa.eu/eurostat/web/products-eurostat-news/-/ddn-20201218-1.
9. Energy roadmap https://doi.org/10.2833/10759.
10. Saladini F, Patrizi N, Pulselli FM, Marchettini N and Bastianoni S, Guidelines for energy evaluation of first, second and third generation biofuels. *Renew Sustain Energy Rev* **66**:221–227 (2016).
11. Statista, Biofuel production worldwide by country 2019 https://www.statista.com/statistics/1136592/global-biofuel-production-volume-by-country/ accessed 17 January 2023.
12. Zabaniotou A, Redesigning a bioenergy sector in EU in the transition to circular wastebased bioeconomy-A multidisciplinary review. *J Clean Prod* **177**:197–206 (2018).
13. European commission, EU: Fuels: Biofuel Policy | Transport Policy https://www.transportpolicy.net/standard/eu-fuels-biofuel-policy/.
14. Paul S and Dutta A, Challenges and opportunities of lignocellulosic biomass for anaerobic digestion. *Resour Conserv Recycl* **130**:164–174 (2018).
15. Ghosh S, Chowdhury R and Bhattacharya P, Sustainability of cereal straws for the fermentative production of second generation biofuels: A review of the efficiency and economics of biochemical pretreatment processes. *Appl Energy* **198**:284–298 (2017).
16. Zaldivar J, Nielsen J and Olsson L, Fuel ethanol production from lignocellulose: A challenge for metabolic engineering and process integration. *Appl Microbiol Biotechnol* **56**:17–34 (2001).
17. Kim S and Dale BE, Global potential bioethanol production from wasted crops and crop residues. *Biomass Bioenergy* **26**:361–375 (2004).
18. Saini JK, Saini R and Tewari L, Lignocellulosic agriculture wastes as biomass feedstocks for second-generation bioethanol production: Concepts and recent developments. *3 Biotech* **5**:337–353 (2015).
19. Sánchez C, Lignocellulosic residues: Biodegradation and bioconversion by fungi. *Biotechnol Adv* **27**:185–194 (2009).
20. Procentese A, Raganati F, Olivieri G, Russo ME, de la Feld M and Marzocchella A, Renewable feedstocks for

biobutanol production by fermentation. *N Biotechnol* **39**:135–140 (2017).

21. Uslu A, NC Gomez and MS Belda, *Demand for lignocellulosic biomass in Europe: Policies, supply and demand for lignocellulosic biomass*. Energy research Centre of the Netherlands, Petten, Netherlands (2010).
22. Lewandowski I, Clifton-Brown J, Trindade LM, Van Der Linden GC, Schwarz KU, Müller-Sämann K *et al*., Progress on optimizing miscanthus biomass production for the European bioeconomy: Results of the EU FP7 project OPTIMISC. *Front Plant Sci* **7**:1620 (2016).
23. Cintas O, Berndes G, Englund O and Johnsson F, Geospatial supply-demand modeling of lignocellulosic biomass for electricity and biofuels in the European Union. *Biomass Bioenergy* **144**:105870 (2021).
24. Limayem A and Ricke SC, Lignocellulosic biomass for bioethanol production: Current perspectives, potential issues and future prospects. *Prog Energy Combust Sci* **38**:449–467 (2012).
25. Y. Iqbal, I. Lewandowski, A. Weinr, B. Wippel, B. Pforte, O. Hadai, O. Tryboi, M. Spöttle and D. Peters, Maximising the yield of biomass from residues of agricultural crops and biomass from forestry, https://scholar.google.de/scholar?hl=en&as_sdt=0,23&cluster=5029390213432946810, (accessed 17 January 2023).
26. Buffington J and Buffington J, The economic potential of brewer's spent grain (BSG) as a biomass feedstock. Advances in Chemical Engineering and Science. **4**:308–318 (2014).
27. Kluts I, Wicke B, Leemans R and Faaij A, Sustainability constraints in determining European bioenergy potential: A review of existing studies and steps forward. *Renew Sustain Energy Rev* **69**:719–734 (2017).
28. Bauen AW, Dunnett AJ, Richter GM, Dailey AG, Aylott M, Casella E *et al*., Modelling supply and demand of bioenergy from short rotation coppice and Miscanthus in the UK. *Bioresour Technol* **101**:8132–8143 (2010).
29. Fiorese G and Guariso G, A GIS-based approach to evaluate biomass potential from energy crops at regional scale. *Environ Model Software* **25**:702–711 (2010).
30. Delzeit R, Britz W and Holm-Müller K, Modelling regional input markets with numerous processing plants. *Environ Model Software* **32**:74–84 (2012).
31. Islam SFU, van Groenigen JW, Jensen LS, Sander BO and de Neergaard A, The effective mitigation of greenhouse gas emissions from rice paddies without compromising yield by early-season drainage. *Sci Total Environ* **612**:1329–1339 (2018).
32. Zegada-Lizarazu W, Parrish D, Berti M and Monti A, Dedicated crops for advanced biofuels: Consistent and diverging agronomic poits of view between the USA and the EU-27. *Biofuels Bioprod Biorefin* **7**:715–731 (2013).
33. Zegada-Lizarazu W, Elbersen HW, Cosentino SL, Zatta A, Alexopoulou E and Monti A, Agronomic aspects of future energy crops in Europe. *Biofuels Bioprod Biorefin* **4**:674–691 (2010).
34. Kainthola J, Kalamdhad AS and Goud VV, A review on enhanced biogas production from anaerobic digestion of lignocellulosic biomass by different enhancement techniques. *Process Biochem* **84**:81–90 (2019).
35. Okolie JA, Epelle EI, Tabat ME, Orivri U, Amenaghawon AN, Okoye PU *et al*., Waste biomass valorization for the production of biofuels and value-added products: A comprehensive review of thermochemical, biological and integrated processes. Process Safety and Environmental Protection. **159**:323–344 (2022).
36. Raud M, Kikas T, Sippula O and Shurpali NJ, Potential and challenges in lignocellulosic biofuel production technology. *Renew Sustain Energy Rev* **111**:44–56 (2019).
37. Kumar M, Olajire Oyedun A and Kumar A, A review on the current status of various hydrothermal technologies on biomass feedstock. *Renew Sustain Energy Rev* **81**:1742–1770 (2018).
38. Andersen SP, Allen B and Domingo GC, Biomass in the EU Green Deal: Towards consensus on sustainable use of biomass for EU bioenergy? https://ieep.eu/publications/biomass-in-the-eu-green-deal-towards-consensus-on-sustainable-use-of-biomass-for-eu-bioenergy.
39. European Commission, 2018, 1–26.
40. Güleç F, Riesco LMG, Williams O, Kostas ET, Samson A and Lester E, Hydrothermal conversion of different lignocellulosic biomass feedstocks-Effect of the process conditions hydrochar structures. *Fuel* **302**:121166 (2021).
41. Güleç F, Meredith W, Sun CG and Snape CE, Demonstrating the applicability of chemical looping combustion for regeneration for fluid catalytic cracking catalysts. *Chem Eng J* **389**:124492 (2020).
42. Street J and Yu F, Production of high-value products including gasoline hydrocarbons from the thermochemical conversion of syngas. *Biofuels* **2**:677–691 (2014). https://doi.org/10.4155/Biofuels.11.141
43. Hurme M and Melin K, Evaluation of lignocellulosic biomass upgrading routes to fuels and chemicals. *Cellulose Chemistry and Technology* **44** (2010).
44. Nkulikiyinka P, Yan Y, Güleç F, Manovic V and Clough PT, Prediction of sorption enhanced steam methane reforming products from machine learning based soft-sensor models. *Energy and AI* **2**:100037 (2020).
45. Güleç F, Meredith W, Sun CG and Snape CE, A novel approach to CO2 capture in fluid catalytic cracking-Chemical looping combustion. *Fuel* **244**:140–150 (2019).
46. Zamri MFMA, Hasmady S, Akhiar A, Ideris F, Shamsuddin AH, Mofijur M *et al*., A comprehensive review on anaerobic digestion of organic fraction of municipal solid waste. *Renew Sustain Energy Rev* **137**:110637 (2021). https://doi.org/10.1016/j.rser.2020.110637.
47. Fan F, Xing X, Shi S, Zhang X, Zhang X, Li Y *et al*., Combustion characteristic and kinetics analysis of hydrochars. *J Environ Chem Eng*. **32**:219–224 (2016).
48. Hao W, Björkman E, Lilliestråle M and Hedin N, Activated carbons for water treatment prepared by phosphoric acid activation of hydrothermally treated beer waste. *Ind Eng Chem Res* **53**:15389–15397 (2014).
49. Subedi R, Kammann C, Pelisseti S, Sacco D, Grignani C and Monaco S, Recycling of organic residues for agriculture: from waste management to ecosystem services https://scholar.google.com/scholar_lookup?title=Recycling%20of%20organic%20residues%20for%20agriculture%3A%20from%20waste%20management%20to%20ecosystem%20services&author=R.%20Subedi&publication_year=2013.
50. Guangzhi Y, Jinyu Y, Yuhua Y, Zhihong T, DengGuang Y and Junhe Y, Preparation and CO2 adsorption properties of porous carbon from camphor leaves by hydrothermal carbonization and sequential potassium hydroxide activation. *RSC Adv* **7**:4152–4160 (2017).
51. Titirici MM, Antonietti M and Baccile N, Hydrothermal carbon from biomass: a comparison of the local structure from poly-to monosaccharides and pentoses/hexoses. *Green Chem* **10**:1204–1212 (2008).

52. Dhyani V and Bhaskar T, A comprehensive review on the pyrolysis of lignocellulosic biomass. *Renew Energy* **129**:695–716 (2018).
53. Brown RC, The Role of Pyrolysis and Gasification in a Carbon Negative Economy. *Processes* **9**:882 (2021).
54. Sutton D, Kelleher B and Ross JRH, Review of literature on catalysts for biomass gasification. *Fuel Process Technol* **73**:155–173 (2001).
55. Guan G, Kaewpanha M, Hao X and Abudula A, Review of literature on catalysts for biomass gasification. *Renew Sustain Energy Rev* **58**:450–461 (2016).
56. Garba MU, Inalegwu A, Musa U, Aboje AA, Kovo AS and Adeniyi DO, Thermogravimetric characteristic and kinetic of catalytic co-pyrolysis of biomass with low- and high-density polyethylenes. *Biomass Convers Biorefin* **8**:143–150 (2018).
57. Chan FL and Tanksale A, Review of developments in Ni-based catalysts for biomass gasification. *Renew Sustain Energy Rev* **38**:428–438 (2014).
58. Prins MJ, Ptasinski KJ and Janssen FJJG, Thermodynamics of gas-char reactions: first and second law analysis. *Chem Eng Sci* **58**:1003–1011 (2003).
59. Basu P, Biomass gasification, pyrolysis and torrefaction: Practical design and theory (2018).
60. Basu P and Mettanant V, Biomass gasification in supercritical water--A review. International Journal of Chemical Reactor Engineering https://doi.org/10.2202/1542-6580.1919.
61. Singh Siwal S, Zhang Q, Sun C, Thakur S, Kumar Gupta V and Kumar Thakur V, Energy production from steam gasification processes and parameters that contemplate in biomass gasifier–A review. *Bioresour Technol* **297**:122481 (2020).
62. Thunman H, Seemann M, Berdugo Vilches T, Maric J, Pallares D, Ström H *et al.*, Advanced biofuel production via gasification – lessons learned from 200 man-years of research activity with Chalmers' research gasifier and the GoBiGas demonstration plant. *Energy Sci Eng* **6**:6–34 (2018).
63. Xu C(C), Liao B, Pang S, Nazari L, Mahmood N, Tushar MS *et al.*, 1.19 Biomass Energy. *Comprehensive Energy Systems* https://www.sci-hub.se/10.1016/B978-0-12-809597-3.00121-8.
64. Larsson A, Kuba M, Berdugo Vilches T, Seemann M, Hofbauer H and Thunman H, Steam gasification of biomass – Typical gas quality and operational strategies derived from industrial-scale plants. *Fuel Process Technol* **212** (2021). https://doi.org/10.1016/J.FUPROC.2020.106609.
65. Loha C, Chatterjee PK and Chattopadhyay H, Performance of fluidized bed steam gasification of biomass–modeling and experiment. *Energ Conver Manage* **52**:1583–1588 (2011).
66. Schweitzer D, Gredinger A, Schmid M, Waizmann G, Beirow M, Spörl R *et al.*, Steam gasification of wood pellets, sewage sludge and manure: Gasification performance and concentration of impurities. *Biomass Bioenergy* **111**:308–319 (2018).
67. Watson J, Zhang Y, Si B, Chen WT and de Souza R, Gasification of biowaste: A critical review and outlooks. *Renew Sustain Energy Rev* **83**:1–17 (2018).
68. Yoshida Y, Dowaki K, Matsumura Y, Matsuhashi R, Li D, Ishitani H *et al.*, Comprehensive comparison of efficiency and CO2 emissions between biomass energy conversion technologies—position of supercritical water gasification in biomass technologies. *Biomass Bioenergy* **25**:257–272 (2003).
69. Ren J, Liu YL, Zhao XY and Cao JP, Biomass thermochemical conversion: A review on tar elimination from biomass catalytic gasification. *Journal of the Energy Institute* **93**:1083–1098 (2020).
70. Larsson A, Gunnasrsson I and Tengberg, F, The GoBiGas Project." Demonstration of the Production of Biomethane from Biomass via Gasification, Goteborg Energi AB (2018).
71. Reddy SN, Nanda S, Dalai AK and Kozinski JA, Supercritical water gasification of biomass for hydrogen production. *Int J Hydrogen Energy* **39**:6912–6926 (2014).
72. Okolie JA, Nanda S, Dalai AK and Kozinski JA, Hydrothermal gasification of soybean straw and flax straw for hydrogen-rich syngas production: Experimental and thermodynamic modeling. *Energ Conver Manage* **208**:112545 (2020).
73. Kıpçak E and Akgün M, Hydrogen production by supercritical water gasification of biomass, 179–220 (2015).
74. García-Jarana MB, Portela JR, Sánchez-Oneto J, de la Ossa EJM and Al-Duri B, A review of the design and performance of catalysts for hydrothermal gasification of biomass to produce hydrogen-rich gas fuel. *Applied Sciences* **10**:5185 (2020).
75. Özdenkçi K, Prestipino M, Björklund-Sänkiaho M, Galvagno A and De Blasio C, Alternative energy valorization routes of black liquor by stepwise supercritical water gasification: Effect of process parameters on hydrogen yield and energy efficiency, *Renew Sustain Energy Rev.* https://doi.org/10.1016/j.rser.2020.110146.
76. Sharma R, Jasrotia K, Singh N, Ghosh P, srivastava S, Sharma NR *et al.*, A comprehensive review on hydrothermal carbonization of biomass and its applications. *Chemistry Africa* **3**:1–19 (2020). https://doi.org/10.1007/S42250-019-00098-3.
77. Okolie JA, Rana R, Nanda S, Dalai AK and Kozinski JA, Supercritical water gasification of biomass: a state-of-the-art review of process parameters, reaction mechanisms and catalysis. *Sustain Energy Fuels* **3**:578–598 (2019).
78. Kumar A and Reddy SN, Hydrothermal treatment of metal impregnated biomass for the generation of H2 and nanometal carbon hydrids. *Environ Res* **205**:112536 (2022).
79. Nanda S, Reddy SN, Vo DVN, Sahoo BN and Kozinski JA, Catalytic gasification of wheat straw in hot compressed (subcritical and supercritical) water for hydrogen production. *Energy Sci Eng* **6**:448–459 (2018).
80. Casademont P, Sánchez-Oneto J, Scandelai APJ, Cardozo-Filho L and Portela JR, Hydrogen production of supercritical water gasification of black liquor: Use of high temperatures and short redidence times in a continuous reactor. *J Supercrit Fluids* **159**:104772 (2020).
81. Salimi M, Safari F, Tavasoli A and Shakeri A, Hydrothermal gasification of different agricultural wastes in supercritical water media for hydrogen production: a comparative study. *International Journal of Industrial Chemistry* **7**:277–285 (2016).
82. Safari F, Salimi M, Tavasoli A and Ataei A, Non-catalytic conversion of wheat straw, walnut shell and almond shell into hydrogen rich gas in supercritical water media. *Chin J Chem Eng* **24**:1097–1103 (2016).
83. Sivasangar S, Zainal Z, Salmiaton A and Taufiq-Yap YH, Supercritical water gasification of empty fruit bunches from oil palm for hydrogen production. *Fuel* **143**:563–569 (2015).
84. Castello D, Rolli B, Kruse A and Fiori L, Supercritical water gasification of biomass in ceramic reactor: long-time batch experiments. *Energies* **10**:1734 (2017).
85. Cao L, Yu IKM, Xiong X, Tsang DCW, Zhang S, Clark JH *et al.*, Biorenewable hydrogen production through biomass gasification: A review and future prospects. *Environ Res* **186**:109547 (2020).
86. Ebadi AG, Hisoriev H, Zarnegar M and Ahmadi H, Hydrogen and syngas production by catalytic gasification of algal biomass (Cladophora glomerata L.) using alkali and alkaline-

earth metal compounds. *Environ Technol* **40**:1178–1184 (2019).

87. Qiu P, Du C, Liu L and Chen L, Hydrogen and syngas production from catalytic steam gasification of char derived from ion-exchangeable Na- and Ca-loaded coal. *Int J Hydrogen Energy* **43**:12034–12048 (2018).
88. Grams J and Ruppert AM, Development of heterogeneous catalysts for thermo-chemical conversion of lignocellulosic biomass. *Energies* **10**:545 (2017).
89. Borges ACP, Onwudili JA, Andrade H, Alves C, Ingram A, de Melo SV*et al*., Catalytic properties and recycling of NiFe2O4 catalyst for hydrogen production by supercritical water gasification of eucalyptus wood chips. *Energies* **13**:4553 (2020).
90. Seçer A, Fakı E, Türker Üzden Ş and Hasanoğlu A, Hydrothermal co-gasification of sorghum biomass and can lignite in mild conditions; An optimization study for high yield hydrogen production. *Int J Hydrogen Energy* **45**:2668–2680 (2020).
91. Boucard H, Watanabe M, Takami S, Weiss-Hortala E, Barna R and Adschiri T, Beneficial use of CeO2 nanocatalyst for black liquor conversion under sub and super critical conditions. *J Supercrit Fluids* **105**:66–76 (2015).
92. Yildirir E, Onwudili JA and Williams PT, Catalytic supercritical water gasification of refuse derived fuel for high energy conten. *Waste Biomass Valorization* **8**:359–367 (2017).
93. Elif D and Nezihe A, Hydrogen production by supercritical water gasification of fruit pulp in the presence of Ru/C. *Int J Hydrogen Energy* **41**:8073–8083 (2016).
94. Peng G, Ludwig C and Vogel F, Catalytic supercritical water gasification: Interaction of sulfur with ZnO and the ruthenium catalyst. *Appl Catal B* **202**:262–268 (2017).
95. Reimer J, Müller S, De Boni E and Vogel F, Hydrogen-enhanced catalytic hydrothermal gasification of biomass. *Biomass Convers Biorefin* **7**:511–519 (2017).
96. Borges ACP, Onwudili JA, Andrade HMC, Alves CT, Ingram A, Vieira de Melo SAB *et al*., Catalytic supercritical water gasification of eucalyptus wood chips in a batch reactor. *Fuel* **255**:115804 (2019).
97. Boucard H, Watanabe M, Takami S, Weiss-Hortala E, Barna R, Adschiri T *et al*., Beneficial use of CeO2 nanocatalyst for black liquor conversion under sub and supercritical conditions. *Journal of Supercritical Fluids*:105 (2015).
98. Kang K, Azargohar R, Dalai AK and Wang H, Hydrogen generation via supercritical water gasification of lignin using Ni-Co/Mg-Al catalysts. *Int J Energy Res* **41**:1835–1846 (2017).
99. Yokoyama S and Matsumura Y, The Asian biomass handbook: a guide for biomass production and utilization. *The Japan Institute of Energy* **1**:61–62 (2008).
100. Tekin K, Karagöz S and Bektaş S, A review of hydrothermal biomass processing. *Renew Sustain Energy Rev* **40**:673–687 (2014).
101. Ruiz HA, Rodríguez-Jasso RM, Fernandes BD, Vicente AA and Teixeira JA, Hydrothermal processing, as an alternative for upgrading agricultural residues and marine biomass according to the biorefinery concept: A review. *Renew Sustain Energy Rev* **21**:35–51 (2013).
102. Pedersen TH, Grigoras IF, Hoffmann J, Toor SS, Daraban IM, Jensen CU *et al*., Continuous hydrothermal co-liquefaction of aspen wood and glycerl with water phase recirculation. *Appl Energy* **162**:1034–1041 (2016).
103. Cherad R, Onwudili JA, Biller P, Williams PT and Ross AB, Hydrogen production from the catalytic supercritical water gasification of process water generated from hydrothermal liquefaction of microalgae. *Fuel* **166**:24–28 (2016).
104. Abdoulmoumine N, Adhikari S, Kulkarni A and Chattanathan S, A review on biomass gasification syngas cleanup. *Appl Energy* **155**:294–307 (2015).
105. Elliott DC, Biller P, Ross AB, Schmidt AJ and Jones SB, Hydrothermal liquefaction of biomass: Developments from batch to continuous process. *Bioresour Technol* **178**:147–156 (2015).
106. Dimitriadis A and Bezergianni S, Hydrothermal liquefaction of various biomass and waste feedstocks for biocrude production: A state of the art review. *Renew Sustain Energy Rev* **68**:113–125 (2017).
107. Álvarez-Murillo A, Sabio E, Ledesma B, Román S and González-García CM, Generation of biofuel from hydrothermal carbonization of cellulose. Kinetics modelling. *Energy* **94**:600–608 (2016).
108. Kambo HS and Dutta A, Strength, storage, and combustion characteristics of densified lignocellulosic biomass produced via torrefaction and hydrothermal carbonization. *Appl Energy* **135**:182–191 (2014).
109. Lappalainen J, Baudouin D, Hornung U, Schuler J, Melin K, Bjelić S *et al*., Sub- and supercritical water liquefaction of kraft lignin and black liquor derived lignin. *Energies* **13**:3309 (2020).
110. Couto EA, Pinto F, Varela F, Reis A, Costa P and Calijuri ML, Hydrothermal liquefaction of biomass produced from domestic sewage treatment in high-rate ponds. *Renew Energy* **118**:644–653 (2018).
111. He W, Li G, Kong L, Wang H, Huang J and Xu J, Application of hydrothermal reaction in resource recovery of organic wastes. *Resour Conserv Recycl* **52**:691–699 (2008).
112. Biller P and Ross AB, Production of biofuels via hydrothermal conversion, *Handbook of Biofuels Production: Processes and Technologies: Second Edition*. Woodhead Publishing, Amsterdam, pp. 509–547 (2016).
113. Gollakota ARK, Kishore N and Gu S, A review on hydrothermal liquefaction of biomass, *Renew Sustain Energy Rev* **81**:1378–1392 (2018).
114. Zhu Z, Rosendahl L, Toor SS and Chen G, Optimizing the conditions for hydrothermal liquefaction of barely straw for bio-crude oil production using response surface methodology. *Sci Total Environ* **630**:560–569 (2018).
115. Ozel MZ, Gogus F and Lewis AC, Subcritical water extraction of essential oils from Thymbra spicata. *Food Chem* **82**:381–386 (2003).
116. Anastasakis K and Ross AB, Hydrothermal liquefaction of four brown macro-algae commonly found on the UK coasts: An energetic analysis of the process and comparison with bio-chemical conversion methods. *Fuel* **139**:546–553 (2015).
117. Petersen MØ, Larsen J and Thomsen MH, Optimization of hydrothermal pretreatment of wheat straw for production of bioethanol at low water consumption without addition of chemicals. *Biomass Bioenergy* **33**:834–840 (2009).
118. Bicker M, Endres S, Ott L and Vogel H, Catalytic conversion of carbohydrates in subcritical water: A new chemical process for lactic acid production. *J Mol Catal A Chem* **239**:151–157 (2005).
119. Cantero DA, Álvarez A, Bermejo MD and Cocero MJ, Transformation of glucose into added value compounds in a hydrothermal reaction media. *J Supercrit Fluids* **98**:204–210 (2015).
120. Yedro FM, García-Serna J, Cantero DA, Sobrón F and Cocero MJ, Hydrothermal hydrolysis of grape seeds to produce bio-oil. *RSC Adv* **4**:30332–30339 (2014).

121. López-Linares JC, García-Cubero MT, Lucas S, González-Benito G and Coca M, Microwave assisted hydrothermal liquefaction as greener pretreatment of brewer's spent grains for biobutanol production. *Chem Eng J* **368**:1045–1055 (2019).
122. Bach QV, Sillero M, Tran K and Skjermo J, Fast hydrothermal liquefaction of a Norwegian macro-alga: Screening tests. *Algal Res* **6**:271–276 (2014).
123. López Barreiro D, Riede S, Hornung U, Kruse A and Prins W, Hydrothermal liquefaction of microalgae: Effect on the product yields of the addition of an organic solvent to separate the aqueous phase and the biocrude oil. *Algal Res* **12**:206–212 (2015).
124. Haarlemmer G, Guizani C, Anouti S, Déniel M, Roubaud A and Valin S, Analysis and comparison of bio-oils obtain by hydrothermal liquefaction and fast pyrolysis of beech wood. *Fuel* **174**:180–188 (2016).
125. Foster W, Azimov U, Gauthier-Maradei P, Molano LC, Combrinck M, Munoz J *et al*., Waste-to-energy conversion technologies in the U.K: Processes and barriers - A review. *Renew Sustain Energy Rev* **135**:110226 (2021).
126. Yogalakshmi KN, Poornima Devi T, Sivashanmugam P, Kavitha S, Yukesh Kannah R, Varjani S *et al*., Lignocellulosic biomass-based pyrolysis: A comprehensive review. *Chemosphere* **286**:131824 (2022).
127. Bridgwater A, Czernik S, Diebold J, Meier D and Oasmaa A, Peacocke C, Piskorz J and Radlein D *Fast pyrolysis of biomass: A handbook*. CPL Press, Newbury (1999).
128. EUBIA, Biomass characteristics, European Biomass Industry Association https://www.eubia.org/cms/wiki-biomass/biomass-characteristics-2/.
129. Shahbaz M, AlNouss A, Ghiat I, Mckay G, Mackey H, Elkhalifa S *et al*., A comprehensive review of biomass based thermochemical conversion technologies integrated with CO2 capture and utilization. *Resour Conserv Recycl* **173**:105734 (2021).
130. Rhodes JS and Keith DW, Engineering economic analysis of biomass IGCC with carbon capture and storage. *Biomass Bioenergy* **29**:440–450 (2005).
131. Uddin SN and Barreto L, Biomass-fired cogeneration systems with CO2 capture and storage. *Renew Energy* **32**:1006–1019 (2007).
132. Kraxner F, Nilsson S and Obersteiner M, Negative emissions from Bioenergy use, carbon capture and sequestration (BECS) - the case of biomass production by sustainable forest management from semi-natural temperate forests. *Biomass Bioenergy* **24**:285–296 (2003).
133. Shahbaz M, Yusup S, Inayat A, Ammar M, Patrick DO, Pratama A *et al*., Syngas production from steam gasification of palm kernel shell with subsequent CO2 capture using CaO sorbent: An Aspen plus modeling. *Energy and Fuels* **31**:12350–12357 (2017).
134. Cormos AM, Dragan S and Cormos CC, Integration of membrane technology for decarbonization of gasification power plants; A techno-economic and environmental investigation. *Appl Therm Eng* **205**:118078 (2022).
135. Acharya B, Dutta A and Basu P, Chemical-looping gasification of biomass for hydrogen-enriched gas. *Energy and Fuels* **23**:5077–5083 (2009).
136. He F, Huang Z, Wei G, Zhao K, Wang G, Kong X *et al*., Biomass chemical-looping gasification coupled with water / CO2 splitting using NiFe2O4 as an oxygen carrie. *Energ Conver Manage* **201**:112157 (2019).
137. Billaud F, Gornay J and Coniglio L, Pyrolysis of secondary raw material from used frying oils. *Récents Progrès en Génie des Procédés*. https://doi.org/10.48550/arxiv.0709.4340.
138. Solantausta Y and SipilÄ K, *Pyrolysis in Finland. Biomass Pyrolysis Liquids Upgrading and Utilization*. Elsevier Science Publisher LTD, London, pp. 327–340 (1991).
139. Van de Beld B and Muggen G, EMPYRO: Implementation of a commercial scale fast-pyrolysis plant in the Netherlands, *artfuelsforum.eu*. (2015).
140. Sánchez-Borrego FJ, Barea de Hoyos-Limón TJ, García-Martín JF and Álvarez-Mateos P, Production of bio-oils and biochars from olive stones: application of biochars to the esterification of oleic acid. *Plan Theory 2022* **11**:70 (2021).
141. Meier D and Berns J, Pyrolysis and hydropyrolysis of biomass and lignins-activities at the Institute of Wood Chemistry in Hamburg, Germany, *researchgate.net*.
142. Ekstrom C and Rensfelt E, Flash pyrolysis of biomass in Sweden, Specialists' Workshop on Fast Pyrolysis of biomass.
143. Adamiano A, Fabbri D, Falini G and Giovanna Belcastro M, A complementary approach using analytical pyrolysis to evaluate collagen degradation and mineral fossilisation in archeological bones: The case study of Vicenne-Campochiaro necropolis (Italy). *J Anal Appl Pyrolysis* **100**:173–180 (2013).
144. Lozano EM, Pedersen TH and Rosendahl LA, Integration of hydrothermal liquefaction and carbon capture and storage for the production of advanced liquid fuels with negative CO2 emissions. *Appl Energy* **279**:115753 (2020).
145. Lozano EM, Petersen SB, Paulsen MM, Rosendahl LA and Pedersen TH, Techno-economic evaluation of carbon via physical absorption from HTL gas phase derived from woody biomass and sewage sludge. *Energy Conversion and Management: X* **11**:100089 (2021).
146. Cheng F, Luo H and Colosi LM, Slow pyrolysis as a platform for negative emissions technology: An integration of machine learning models, life cycle assessments, and economic analysis. *Energ Conver Manage* **223**:113258 (2020).
147. Smith P, Soil carbon sequestration and biochar as negative emission technologies. *Glob Chang Biol* **22**:1315–1324 (2016).
148. Krull L, Meet Pyrolysis-the eco-friendly way to capture and store CO_2: BioChar, Technical University of Denmark. (2021) https://www.reddit.com/r/BioChar/comments/q0kwb0/meet_pyrolysis_the_ecofriendly_way_to_capture_and/.
149. Ding W, Zhang X, Zhao B, Zhou W, Xu A, Chen L *et al*., TG-FTIR and thermodynamic analysis of the herb residue pyrolysis with in-situ CO2 capture using CaO catalyst. *J Anal Appl Pyrolysis* **134**:389–394 (2018).
150. Zhao B, Zhang X, Chen L, Sun L, Si H and Chen G, High quality fuel gas from m biomass pyrolysis with calcium oxide. *Bioresour Technol* **156**:78–83 (2014).
151. Xu A, Zhou W, Zhang X, Zhao B, Chen L, Sun L *et al*., Gas production by catalytic pyrolysis of herb residue using Ni/CaO catalysts. *J Anal Appl Pyrolysis* **130**:216–223 (2018).
152. Cai J, Wang S and Xiao Z, A study on the CO2 capture and attrition performance of construction and demolition waste. *Fuel* **222**:232–242 (2018).
153. Cheng F, Small AA and Colosi LM, The levelized cost of negative CO2 emissions from thermochemical conversion of biomass coupled with carbon capture and storage. *Energ Conver Manage* **237**:114115 (2021).
154. Sun Y, Dong B, Wang L, Li H and Thorin E, Technology selection for capturing CO2 from wood pyrolysis. *Energ Conver Manage* **266**:115835 (2022).

Fatih Güleç

Dr Fatih Güleç is an Assistant Professor in the Department of Chemical and Environmental Engineering at the University of Nottingham. Dr Güleç's research encompasses energy and industrial decarbonization, covering (i) the synthesis and characterization of advanced nanocomposites and their applications in chemical/calcium looping technologies, CO_2 capture, negative emissions, energy storage and catalytic reactions and (ii) process integration/intensification based on waste/biomass-to-energy via thermal conversions.

Umaru Musa

Umaru Musa is an Academic Staff at the Department of Chemical Engineering, Federal University of Technology Minna, Nigeria. His research covers sustainable low-carbon technology and the circular bioeconomy, primarily covering biomass conversion through biochemical and thermochemical processing and techno-economic assessments. He holds a Master's degree from Federal University of Technology Minna, Nigeria in chemical engineering and is currently on the verge of completing his PhD at the Faculty of Engineering at the University of Nottingham, UK.

Parthiban Anburajan

Dr Parthiban Anburajan currently working as a Postdoctoral Research Professor at the Department of Environmental Engineering, Seoul National University of Science and Technology, Seoul. He gained a PhD at the Department of Civil Engineering at Daegu University, South Korea and followed this by postdoctoral research at Yonsei University, South Korea and received the Yonsei Frontiers research fellowship. His research interest is mainly focus on bacterial signaling, biofuel production and biopolymer production. During his period of research he published articles in 30 peer-reviewed journals and one book chapter. He actively participated as reviewer for various reputed journals.

Orla Williams

Dr Orla Williams is an Anne McLaren Research Fellow in the Advanced Materials Research Group at the University of Nottingham. Dr Williams is an expert in biomass processing and is also a Chartered Mechanical Engineer with over 8 years of industrial experience in the rail, defence aerospace, construction and power sectors in the UK and USA. During her engineering doctorate at the University of Nottingham, she focused on the milling of biomass for power generation. Her current fellowship is investigating sustainable biomass-based processing techniques to produce critical raw materials for the circular economy.

Great C. Umenweke

Great C. Umenweke is a graduate research assistant and PhD candidate at the University of Kentucky Center for Applied Energy Research and the Department of Chemistry, respectively. His research interest is in the application of heterogeneous catalysis for the conversion of oleaginous and lignocellulosic biomass into valuable chemicals and drop-in transportation fuels. Great obtained his undergraduate degree in Chemical Engineering from the Federal University of Technology, Owerri (Nigeria). Additionally, Great performed short summer research on *in-situ* X-ray photoelectron spectroscopy analysis of metal oxides and zeolite-supported nickel catalysts at the Laboratory Interdisciplinaire Carnot de Bourgogne, Dijon, France in 2022.

Yasna Mortezaei

Yasna Mortezaei is a PhD student in the Earth and Ecosystem Science program, School of Engineering and Technology, Central Michigan University. Her research focuses on the fate of antibiotic resistance genes in the anaerobic digestion of sludge. Holding a Bachelor's degree in Chemical Engineering from Razi University, Iran, she obtained a Master's degree in Chemical Engineering at the University of Kurdistan, specializing in wastewater treatment and the improvement of biogas production. Her research interests are anaerobic environmental biotechnology, bioenergy and biobased products from waste, reactor design, antimicrobial resistance tracking, communication of microbial communities and identification of the host of antibiotic resistance genes.

Hyun-Suk Oh

Dr Hyun-Suk Oh, an Associate Professor in the Department of Environmental Engineering at Seoul National University of Science and Technology, has focused on studying energy-efficient water treatment and sustainable energy production. During his PhD at Seoul National University, South Korea, he published a pioneering paper on a quorum quenching (QQ) membrane bioreactor (MBR), which has been cited over 470 times and has led to the publication of more than 250 related papers worldwide. He also pioneered the application of QQ bacteria for biofouling control in MBR systems. Drawing from his extensive experience and expertise in leading QQ–MBR studies for several years, he authored a comprehensive review article in the *Journal of Membrane Science*. In his career, he has authored 35 SCIE journal papers and contributed two chapters to books on subjects such as biofilm control, membrane-based water treatment and biogas production.

Edward Lester

Professor Edward Lester is Lady Trent Professor of Chemical Engineering at the University of Nottingham with interests in fuel characterization, combustion science, nanotechnology and nanomaterials.

Chukwuma C. Ogbaga

Chukwuma C. Ogbaga is an enthusiastic researcher/professor who is majorly interested in plant physiology, abiotic stress, biotechnology, biochemistry and machine learning. He is also interested in collaborating with researchers working in any field related to his interests. He holds a Bachelor's degree in Biochemistry, a Master's in Biotechnology from the University of Glasgow, Scotland and a PhD in Plant Sciences from the prestigious University of Manchester, UK. He has visited and worked with top research institutions such as the University of Illinois, USA and Rothamsted Research, Harpenden, UK.

Burcu Gunes

Dr Burcu Gunes holds a degree in Chemical Engineering from Ankara University and an industrial PhD in Environment Technologies Group from Dublin City University School of Biotechnology and Alltech Ltd. Dr Gunes's research focuses on development of environmental technologies for biomass to bioenergy conversion as well as wastewater treatment processes. She also has expertise in mathematical modelling of bioprocesses including the application of Design Expert Software. Her research interests are diverse, ranging from anaerobic digestion of lignocellulosic biomass for industrial 'waste to energy' applications to high-pressure fermentation of synthesis gas for bioethanol production, the development of graphene and biomass-based nanostructure composites for adsorption and the removal of emerging pollutants such as pharmaceuticals and industrial dye from water.

Jude A. Okolie

Dr Jude A. Okolie is currently an Assistant Professor at the College of Engineering, University of Oklahoma. Dr Okolie's research focuses on the thermochemical conversion of waste materials to green fuels and the subsequent utilization of hydrochar/biochars for environmental remediation. In addition, his research includes the application of process simulation and artificial intelligence/machine learning to address climate change, environmental pollution and sustainable agriculture challenges.