



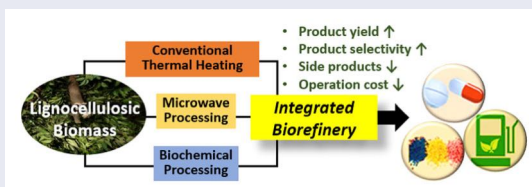
Chemicals from lignocellulosic biomass: A critical comparison between biochemical, microwave and thermochemical conversion methods

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ABSTRACT

The past decades have seen an increasing interest in developing pathways to produce bio-based chemicals from lignocellulosic biomass and organic waste as renewable resources. Using biomass as a source of chemical building blocks is critical to a future sustainable chemical industry. The successful development of bio-chemicals will also have a profound impact in terms of the innovations of new polymers and materials, new solvents, and new bio-active compounds. This article provides a broad review of conventional thermal heating, microwave processing, and biochemical processing for the production of value-added bio-based chemicals. The potentially important but currently little exploited microwave-assisted processes are given particular attention and the microwave-specific, non-thermal effects are explored. The comparative merits of different approaches are evaluated from the techno-economic and environmental perspectives. The opportunities of integrated biorefineries are articulated, with the aim to actualize carbon-efficient valorization of lignocellulosic biomass and organic waste for synthesizing an array of products.



Abbreviation: ABE: Acetone-butanol-ethanol; AC: Activated carbon; BTX: Benzene, toluene, and xylene; CAP: Combined Algal Processing; CSHL: Crude waste softwood hydrolysis lignin; FAME: Fatty acid methyl ester; GGE: Gallon gasoline equivalent; GHG: Greenhouse gas; GMO: Genetically modified organism; GVL: γ -Valerolactone; HHV: higher heating value; HMF: Hydroxymethylfurfural; HTC: Hydrothermal carbonization; HTG: Hydrothermal gasification; HTL: Hydrothermal liquefaction; HTP: Hydrothermal process; LA: Levulinic acid; LCA: Life-cycle assessment; LG: Levoglucosan; LGO:

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Levogluconone; MIBK: Methyl isobutyl ketone; ROI: Return of investment; SCG: Spent coffee ground; SSF: Simultaneous saccharification and fermentation; TEA: Techno-economic analysis

KEYWORDS Bio-based chemicals; lignocellulosic biomass; sustainable biorefinery

1. Introduction

The term “biomass”, according to EU Directive 2003/30/EC, refers to the biodegradable fraction of products, wastes, and residues from agriculture, forestry as well as the biodegradable fraction of industrial and municipal waste. The motivation for seeking renewable biomass for the production of chemical building blocks (platform chemicals) is derived from the expected transition from a fossil fuel-based economy to one based on renewable resources (Tuck et al., 2012). Bio-based platform chemicals, as reported by the US DOE (Werpy et al., 2004) (top bio-based chemicals) and Bozell and Petersen (Bozell & Petersen, 2010) (additional chemicals listed), can be subsequently used to produce a wide range of valuable chemicals, pharmaceuticals, food additives, and biofuels.

Biomass can be converted into platform chemicals through different processes, depending on the type, property, and quantity of feedstock and the chemical products required (Cao, Yu, Liu, et al., 2018; Xiong et al., 2019). Three categories of the technologies have been separately reviewed: biochemical methods that convert carbohydrates of biomass into sugars and then into products such as ethanol, butanol, and other chemicals via fermentation (Straathof, 2014); conventional thermochemical methods that include pyrolysis (mainly fast pyrolysis), hydrothermal treatment, and gasification producing bio-oils and synthesis gas (CO, H₂) (Gollakota et al., 2018; Igalavithana et al., 2020); and microwave processing, an emerging technology potentially superior to conventional heating in terms of higher efficiency and non-thermal effects (Beneroso et al., 2017; Gaudino et al., 2019).

However, limitations exist for each type of the technologies. For instance, biological methods can only use the carbohydrate fractions of biomass. Although thermochemical processes can exploit biomass more, the outputs are often a complex mixture of compounds each at low concentration, and vary with the composition of lignocellulosic biomass, i.e. cellulose, hemicellulose, and lignin (Zheng et al., 2017). These components can undergo reactions simultaneously under thermal conditions, which makes it challenging to achieve selective production. Thus, the economic feasibility of obtaining value-added chemicals from biomass is often questioned at present (Meng et al., 2016).

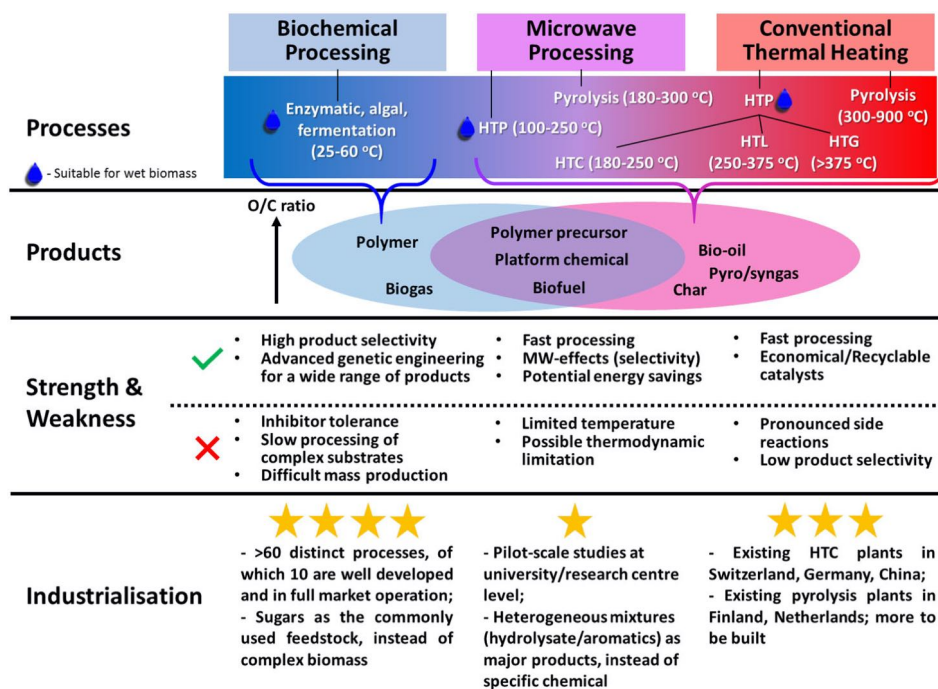


Figure 1. Summary of biomass conversion technologies.

A biorefinery, where several primary conversion processes are combined and integrated with separations and downstream upgrading operations, is attractive because it would maximize the feed utilization and the value of the products. It is recommended that a biorefinery is the best solution to maximize economic and environmental benefits, while minimizing waste and pollution. Previous reviews addressed a specific category of conversion technologies (Gaudino et al., 2019; Gollakota et al., 2018) or certain types of feedstocks (Cao, Yu, Liu, et al., 2018; Igalavithana et al., 2020). However, comparison is often missing from the literature among the biological, conventional thermochemical, and microwave processes.

This review includes a comprehensive summary of the biological and thermochemical (conventional and microwave) technologies for biomass conversion to chemicals. The biochemical technologies have dominated early commercial biorefinery-related processes (Straathof, 2014), whereas the thermochemical routes have received increasing attention recently to pursue cost-effectiveness (Figure 1). In particular, microwave heating has been adopted in novel biorefinery processes, of which the recent research outcomes and mechanistic insights are addressed in this review, fostering further technological advancements. We discuss the possible integrations of technologies for complementary biorefinery, which are often overlooked in the existing reviews, by comparing the merits of different approaches and

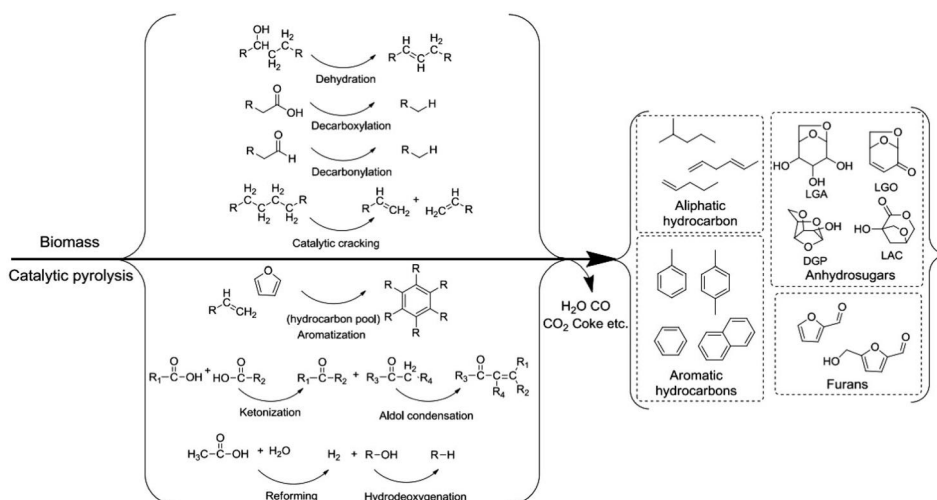


Figure 2. Schematic of the chemical reactions for biomass catalytic pyrolysis (Wang, Dai, et al., 2017).

recent achievements in research. Techno-economic and environmental considerations are also discussed to aid decision making in designing sustainable biorefinery.

2. Technologies for the production of chemicals from lignocellulosic biomass

2.1. Conventional thermal heating

2.1.1. Conventional pyrolysis

Pyrolysis and hydrothermal processes are two promising thermochemical technologies that can convert biomass into chemicals, which are often separated or undergo secondary conversion (Bu et al., 2011; Lyu et al., 2015). Pyrolysis, which takes place in the absence of oxygen, converts organic materials into solid, liquid, and gaseous products (Mohan et al., 2006). Due to the complexity of the biomass structure and various pyrolysis reaction pathways, hundreds of organic compounds exist in the complex liquid outputs which are collectively called pyrolysis oil (or bio-oil), and include a low content of value-added chemicals (Wang, Dai, et al., 2017). Adding specific catalysts or other additives under optimal conditions can increase the yields of specific chemicals during selective pyrolysis (Casoni et al., 2016; Kan et al., 2016; Leng et al., 2014).

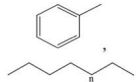
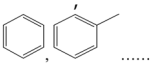
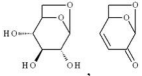




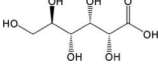
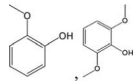

To obtain value-added platform chemicals, selective pyrolysis of biomass to control the pathways has been attractive in recent years, by using catalysts such as zeolites, aluminas, silica-aluminas, and metal oxides (Lu et al., 2013). Figure 2 summarizes the major chemical reaction pathways involved

in the biomass catalytic pyrolysis, including deoxygenation, cracking, aromatization, ketonization, aldol condensation, hydrotreating, and reforming. These reactions may occur selectively depending on the catalysts and reaction conditions to significantly promote the formation of target products, while inhibiting other pyrolytic routes. Typical platform chemicals such as levoglucosan and levoglucosone (Dobele et al., 2005; Meng et al., 2016), aromatic hydrocarbons (Oh et al., 2013), acetic acid (Leng et al., 2014; Lu, Dong, et al., 2011; Qi et al., 2006), furfural (Branca, Blasi, et al., 2010; Oh et al., 2013; Seungjin et al., 2015), phenols (Lu et al., 2013), crotonic acid (Mullen et al., 2014), methanol (Kamarudin et al., 2013), etc. obtained from pyrolysis processes are listed in Table 1.

2.1.1.1. Levoglucosan and levoglucosone. Levoglucosan (LG) and levoglucosone (LGO), mainly derived from cellulose fast pyrolysis, are versatile precursors to pharmaceuticals and other value-added chemicals including solvents such as the new commercial product Cyrene (Sherwood et al., 2014). In the direct fast pyrolysis of cellulose or biomass, LG is one of the main products and almost no LGO is formed. The production of LG is favorable at fast heating rate (Zheng et al., 2017). Direct products contain more than 400 compounds and LG is hard to separate (Meng et al., 2016). Selecting the proper catalysts for biomass pyrolysis can facilitate LG and LGO formation. Dobele et al. studied the catalytic effect of Fe^{3+} ions and obtained high yields of LG (27%) and LGO (26%) from wood (Dobele et al., 2005). Weak acids such as formic acid and acetic acid could enhance LG (by 88%) yield, whereas sulfuric acid and phosphoric acid promoted the yield and selectivity (62%) of LGO (by 61.8%) by inhibiting LG production (Meng et al., 2016). Branca et al. also investigated acid-catalyzed pyrolysis of corncobs using a packed-bed, and the production of LGO was significantly enhanced from trace amounts to 4.5% (Branca, Galgano, et al., 2010). Additionally, magnetic $\text{SO}_4^{2-}/\text{TiO}_2\text{-Fe}_3\text{O}_4$ and solid phosphoric acid catalysts have been proposed to produce LGO from the fast pyrolysis of cellulose and biomass (Lu et al., 2014; Zhang, Lu, et al., 2015).

2.1.1.2. Hydrocarbons. Recently, research has focused on the production of hydrocarbons from biomass by adding catalysts (Oh et al., 2013). Zeolites are capable to remove oxygen from lignocellulosic biomass, giving rise to unparalleled selectivity to hydrocarbon platform products (Ma et al., 2012; Puértolas et al., 2017) (Figure 3). HZSM-5 displayed high thermal stability, strong acidity, and unique pore structure (Ding et al., 2017). The high acidity HZSM-5 catalysts with low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios ($\text{Si}/\text{Al} = 23$) could maximize the conversion of *Spirulina* to aromatic hydrocarbons, but lower acidity catalysts increased the production of aliphatic hydrocarbons,

Table 1. Typical chemicals formed through catalytic pyrolysis processes.

Chemicals	Structure	Catalysts or other processing methods	Precursors	Applications
Hydrocarbons		Zeolites and HZSM-5 (Carlson et al., 2009; Ma et al., 2012; Puértolas et al., 2017)	Carbohydrates, cellulose, and hemicellulose	Gasoline, solvents or synthesis of various products
Benzene, toluene and xylenes		HZSM-5 treated 0.3 M NaOH (Ding et al., 2017); Dope of Mg on Al-MCM-41 (Karnjanakom et al., 2017)	Cellulose or lignin	Gasoline, solvents or synthesis of various products
Levoglucosan and levoglucosone		Silica catalyst (Behrensa et al., 2017), Fe ³⁺ ions (Dobele et al., 2005), acid-catalyst (Branca, Galgano, et al., 2010; Meng et al., 2016)	Cellulose or sugars	Medicines, biodegradable surfactants or polymers
Furfural		ZnCl ₂ (Branca, Blasi, et al., 2010; Oh et al., 2013; Seungjin et al., 2015)	Hemicellulose or xylose	Platform for synthesis and oxygenates
Acetic acid		Injection methanol additive (Leng et al., 2014); Zeolite NaY (Qi et al., 2006); Impregnated with ZnCl ₂ (Lu et al., 2011b);	Carbohydrates, cellulose and hemicellulose	Reagents and intermediates
Methanol		Adding ethyl acetate (Leng et al., 2014)	Carbonaceous materials	Building block
Alkyl phenols		KH ₂ PO ₄ /AA (Wang, Dang, et al., 2017)	Lignin	Detergent, lubricating oil and additive
Gluconic acid		Fast pyrolysis and hydrolyzed and partially oxidized (Santhanaraj et al., 2014)	Glucose or cellulose	Chemicals synthesis
Phenolic compounds		Impregnated with K ₃ PO ₄ (Lu et al., 2013)	Lignin	Pharmaceuticals and pesticides, dyes and food additives
Xylan		H ₂ SO ₄ (Jiang et al., 2017)	Hemicellulose	Health care food and medical use

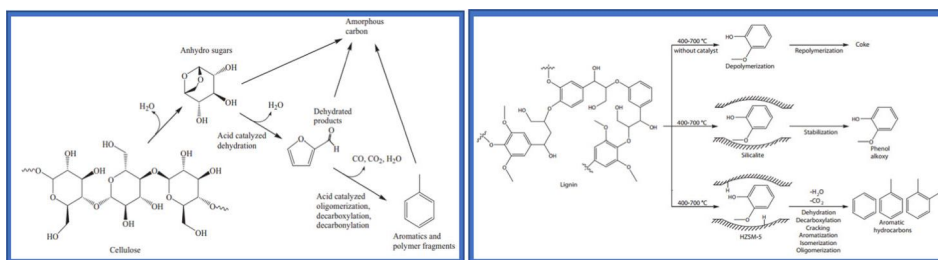


Figure 3. Reaction mechanism of cellulose and lignin pyrolysis (Carlson et al., 2009; Ma et al., 2012).

phenols, and certain nitrogenates (Chagas et al., 2016). HZSM-5 treated by 0.3 M NaOH solution increased the carbon yield of aromatic hydrocarbons by 44% and that of benzene, toluene, and xylenes (BTXs) by 82%, compared to the parent HZSM-5 (Ding et al., 2017). The doping of Mg in Al-MCM-41 (Si/Al = 30) catalyst was also reported to enhance yields of hydrocarbon and especially BTXs (Karnjanakom et al., 2017).

2.1.1.3. Furfural. Furfural has emerged as an important platform molecule for the manufacture of pharmaceuticals, fine chemicals, agrochemicals polymers, and fuels (Puértolas et al., 2017). A promising alternative to acid-promoted dehydration for furfural production is the pyrolysis of lignocellulosic biomass. In particular, corncob is a common feedstock for furfural production due to its rich contents of pentosans and cellulose (Branca, Blasi, et al., 2010). During the pyrolysis of ZnCl₂-impregnated corncobs, ZnCl₂ catalyzed the primary paths of furfural formation via dehydration of pentosyl and glucosyl residues (Branca, Blasi, et al., 2010). The furfural yield was 8 wt% when using ZnCl₂-impregnated corncob in fast pyrolysis (Oh et al., 2013). The furfural yield increased from 0.6 wt% to 11.5 wt% using a similar feedstock (corn stover) when it was pretreated before pyrolysis, and toluene extraction was effective in recovering furfural from the complex product mixtures (Seungjin et al., 2015).

2.1.1.4. Phenolic compounds. Various phenolic compounds can be derived from lignin and used as phenol replacements in the production of phenolic resins (Cao, Chen, et al., 2019; Lu et al., 2013). Lignin, which constitutes 10–25 wt% of biomass, decomposes at 280–500 °C to phenolic compounds (Mamaeva et al., 2015). Adding appropriate catalysts into the pyrolysis process can upgrade the products *in situ* for higher selectivity of phenolic compounds. KH₂PO₄/AA was found to selectively promote the formation of alkyl phenols and inhibit alkoxy phenols in the pyrolysis of corn straw fermentation residue (Wang, Dang, et al., 2017). K₃PO₄ inhibits the decomposition of cellulose and promotes the decomposition of lignin to mainly

phenol and 2,6-dimethoxy phenolic compounds from poplar wood (Lu et al., 2013). The addition of activated carbon (AC) to peanut shell can improve the phenolic yield in liquid product (Mamaeva et al., 2015).

2.1.1.5. Syngas. As a versatile building block in the chemical industry and fuel synthesis, synthesis gas (syngas) plays an important role in industry (Lu et al., 2017). Biomass has been considered as a promising raw material to partially replace fossil resources in syngas production in the future. Increasing the gasification temperature from 700 to 850 °C improved the gas yield from biomass and reduced the formation of char (Hamad et al., 2016). High temperature tends to accelerate reactions and promote secondary cracking and reforming reactions (Yang et al., 2017). However, large-scale syngas production through pyrolysis faces the challenges of low hydrogen content and tar formation. The catalyst Fe/CaO with uniform morphology and particle size showed superior H₂ reducibility and CO₂ adsorption capacity during the biomass pyrolysis (Yang et al., 2017). A maximum syngas yield of 63 wt% containing H₂ of 172 mL/g was reported for the catalytic pyrolysis of sawdust biomass. Syngas (H₂ + CO) of 90% was obtained using Ni/CaAlO_x (3:1) catalyst for sawdust pyrolysis (Chen et al., 2016). Supported noble metal catalysts such as Rh, Ru, and Pt have also been reported to increase syngas yield (Maroño et al., 2008).

2.1.1.6. Other chemical products. Other target chemicals including cyclopentanones, acetic acid, gluconic acid, xylan, methanol, and acetone have also been studied. The use of ZrO₂ and TiO₂ increased the amount of cyclopentanones and aromatics during pyrolysis (Behrensa et al., 2017). In the pyrolysis of bamboo over zeolite NaY, acetic acid was the major product and its content was more than two times higher than that from a non-catalytic process (Qi et al., 2006). Acetic acid yields of ~4 wt% were obtained from biomass materials impregnated with ZnCl₂ (Lu, Wang, et al., 2011) while acetic acid selectivity was reported as high as 98.3% by injecting methanol additive to mushroom scrap pyrolysis (Leng et al., 2014).

Multi-step processing can also increase the selectivity of target chemicals. A solution rich in LG representing over 30% of the carbon produced from red oak was filtered, followed by hydrolysis and partial oxidation to yield gluconic acid with high purity and selectivity (Santhanaraj et al., 2014). Almost all of the hemicellulose (99.7%) was hydrolyzed to xylan (86%) during acid hydrolysis of corncobs hemicellulose, increasing the LG yield by 450% from the residue after fast pyrolysis (Jiang et al., 2017). Using additives can also enhance product selectivity. The selectivity of methanol from sugarcane bagasse and acetone from corncob was 66% and 73%, respectively, when adding ethyl acetate during HZSM-5-catalyzed pyrolysis (Leng et al., 2014).

2.1.2. Conventional hydrothermal process

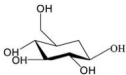



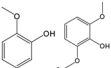

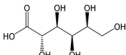
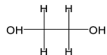
Hydrothermal process (HTP) utilizes water as the solvent and reaction medium, enabling the use of wet biomass without the prior energy-intensive dewatering step. By avoiding the vaporization of water or the use of expensive or hazardous chemicals, HTP is simple, cost-effective, and potentially environmentally benign (Garrote et al., 1999), complying with the principles of Green Chemistry (Anastas & Warner, 1998).

The HTP starts with hydrolysis, where water reacts with extractives, hemicellulose, or cellulose, breaking ester and ether bonds to yield a wide range of products, such as soluble (oligo-) saccharides and monomers. The derivatives can undergo dehydration and condensation reactions to form hydrochar at 180–250 °C, of which the process is defined as hydrothermal carbonization (HTC) (Biller & Ross, 2016). At a higher temperature of 250–375 °C, hydrothermal liquefaction (HTL) takes place, in which bio-oils are produced via further hydrolysis of macromolecules, dehydration/decarboxylation, and rearrangement reactions. Bio-oils may contain glucose (Chambon et al., 2011; Onda, 2012; Onda et al., 2008; Takagaki et al., 2008), furanic compounds (Bond et al., 2014; Jeong, 2015; Antal et al., 1990; Lee & Jeong, 2015; Seri et al., 2002), monomeric phenols (Li et al., 2012; Zhang et al., 2013; Zhou et al., 2016), lactic acid (Sánchez et al., 2012; Younas et al., 2016), levulinic acid (Chang et al., 2007; Jeong, 2015; Licursi et al., 2015; Tukacs et al., 2017; Wang, Xie, et al., 2015), formic acid (Yun et al., 2007; Yun et al., 2016), etc., of which the composition can be tuned by using different catalysts (Table 2). When the temperature further increases to > 375 °C, over the critical point of water, then hydrothermal gasification (HTG) becomes significant, generating syngas comprising H₂, CO, CH₄, and light hydrocarbons via steam-reforming, water-gas shift, and methanation reactions.

2.1.2.1. Glucose. On an industrial scale, glucose is produced from starch by enzymatic hydrolysis, with corn as a common feedstock. Cellulose and hemicellulose in lignocellulosic biomass could dissolve to form oligomers and other water soluble products, such as glucose and xylose (Hashaikeh et al., 2007). Sulfuric acid-catalyzed hydrolysis of cellulose to glucose is a well-established process and sulfonated carbon catalysts (C-SO₃H) with abundant acid sites and large surface specific area are particularly efficient for cellulose hydrolysis in HTP (Chambon et al., 2011). The use of a hydrothermally stable sulfonated AC catalyst resulted in high glucose yields of ~44 C% from cellulose (Onda, 2012).

However, the use of biomass feedstocks for monosaccharide production faces two critical challenges, which are the difference in reactivities of biomass components and the re-polymerization of the dissolved oligomers

Table 2. Chemicals through catalytic hydrothermal process.

Chemicals	Structure	Catalysts or other processing methods	Constituent derived from	Applications
Glucose		C-SO ₃ H (Chambon et al., 2011; Onda, 2012; Onda et al., 2008), HNbMoO ₆ (Takagaki et al., 2008), silicotungstic acid (Kumar et al., 2015)	Cellulose	Various chemicals, fuels, foods, and medicines
Lactic acid		NaOH (Yan et al., 2010), Ca(OH) ₂ (Sánchez et al., 2012; Yan et al., 2010), CaO (Jeon et al., 2016), Zn(II) catalyst (Raina & Bolia, 2005; Xiong et al., 2017) and Lewis solid acids (Chambon et al., 2011)	Cellulose and hemicellulose	Biodegradable plastics, ethyl lactate generation
Furfural		H ₂ SO ₄ (Antal et al., 1990; Lee & Jeong, 2015), HCl (Bond et al., 2014), Lewis acid (Seri et al., 2002) and Brønsted acid (Jeong, 2015)	Cellulose, hemicellulose and sugars	Synthesis of plastics, pharmaceuticals, fine chemicals
Levulinic acid		HCl and H ₂ SO ₄ (Chang et al., 2007; Licursi et al., 2015; Tukacs et al., 2017), Brønsted acid (Jeong, 2015) and Nb/Al oxide (Wang, Xie, et al., 2015)	Cellulose or sugars	Synthesis of liquid fuels, chemicals and diesel fuel additives
Monomeric phenols		CuZnAl catalyst (Zhou et al., 2016), alkaline catalyst (Zhang et al., 2013) and Ni-W2C (Li et al., 2012)	Lignin	Pharmaceuticals and pesticides, dyes and food additives
Formic acid		NaOH (Yun et al., 2016) and KOH (Yun et al., 2007)	Cellulose and hemicellulose	Organic chemical, H ₂ carrier
Gluconic acid		Pt/AC-SO ₃ H catalyst (Onda, 2012)	Cellulose or sugars	Coagulants and food preservatives
Ethylene glycol		Ni-W2C (Li et al., 2012)	Cellulose and hemicellulose	Surfactant, synthetic fiber, cosmetics and explosives
Syngas	H ₂ , CH ₄ , CO, CO ₂ , C ₂ -C ₄ compounds.	Ca(OH) ₂ and Na ₂ CO ₃ as catalysts led to selective production of H ₂ (Deniz et al., 2015; Kumabe et al., 2017)	Carbonaceous material	Chemicals synthesis and generate electricity

(Hashaikeh et al., 2007). Cellulose is organized into microfibrils surrounded by hemicellulose and encased inside a lignin matrix (Gomez et al., 2008). Despite the similar chemical compositions, hemicellulose is much more reactive than cellulose due to the amorphous nature. In the case of willow hydrolysis, lignin and hemicellulose start dissolving much earlier than cellulose (Hashaikeh et al., 2007) and the initial products undergo isomerization, dehydration, fragmentation, and condensation reactions (Antal et al., 2000), resulting in precipitation on the surface of cellulose. These precipitates inhibit access of water to the cellulose, and as a result, the cellulose material is blocked and tends to dehydrate and form char-like solids inside the HTP reactor. To solve the problem, sequential reactions or fractionation treatments have been reported. For example, glucose (>80%) and xylose (>70%) recoveries were achieved from the a two-stage hydrothermal treatment of lignocellulose, with diluted H_2SO_4 -catalyzed hemicellulose hydrolysis in the first stage (150 °C, 6 min) and lime-mediated lignin removal in the second (202 °C, 30 min) (Guo et al., 2013).

2.1.2.2. Furfural and 5-hydroxymethylfurfural. Furfural and hydroxymethylfurfural (HMF) are dehydration products of C5 and C6 monosaccharides, respectively, after HTC or HTL (Figure 3) (Jeong, 2015), in which mineral acids are commonly used as catalysts (e.g. 53% HMF from fructose over H_2SO_4 (Antal et al., 1990)). Using cellulose as a substrate, a HMF yield of 19% can be achieved over LaCl_3 as a Lewis acid catalyst in water at 250 °C and over 150 s (Seri et al., 2002). The maximum HMF yield of 7.57 g/L (12.1 wt% yield) can be obtained from chitosan over sulfuric acid catalyst (174 °C, 37 min) (Lee & Jeong, 2015) while the yield was increased to 25.2% in the 1-butyl-3-methylimidazolium hydrogen sulfate aqueous solution over AlCl_3 as the catalyst (180 °C, 5 h) (Feng et al., 2015). As for biomass feedstocks, red maple had 85% of the hemicellulose sugars recovered as xylo-oligomers. The oligomers were subsequently introduced to a biphasic reactor along with HCl and tetrahydrofuran to form furfural of 90% carbon yield, which was recovered in the tetrahydrofuran phase along with acetic acid (Bond et al., 2014).

HMF is recognized as an important versatile platform chemical for the synthesis of plastics, pharmaceuticals, and fine chemicals (Yu & Tsang, 2017). The first commercial plant of renewable HMF synthesis was commissioned by AVA Biochem in 2014 and sugarcane sirups are used as the feedstock (Kläusli, 2014). It remains challenging to selectively convert lignocellulosic biomass to HMF because of the relatively low reactivity of cellulose and the unstable nature of HMF, which easily transforms to levulinic acid and humins as the secondary products under hydrothermal conditions. Catalytic systems are often modified to improve HMF yields. For

example, by adding dimethyl sulfoxide and AlCl_3 to the ionic liquid media containing a modified AC catalyst, the highest HMF yield of 88% (w.r.t. to polysaccharide content) can be obtained from Catalpa wood, as a result of improved solubility of polysaccharide and suppressed side reactions (Tyagi et al., 2019).

2.1.2.3. Monomeric phenols. A mixture of monomeric phenols can be produced from the lignin fraction of biomass via HTL, such as 4-ethyl-phenol, 2-methoxy-phenol, 2-methoxy-4-ethyl-phenol, and 2,6-dimethoxy-phenol, often in the presence of catalysts. The maximum yield of total monomeric phenols from the HTL of rice straw reached 27% (based on lignin mass) over the reductive CuZnAl catalyst (Zhou et al., 2016). Target monomeric compounds, i.e. phenol, 2-methoxy-phenol, and 2,6-dimethoxyphenol were obtained from corn stalk lignin in yields of 7.2%, 7.9%, and 8.2%, respectively, by using alkali (disodium tetraborate decahydrate) (Zhang et al., 2013). Using a carbon-supported Ni- W_2C catalyst, the cellulose and hemicellulose in raw wood were selectively converted to ethylene glycol and other diols with a total yield of up to 76% (based on the amount of cellulose and hemicellulose), while the lignin was converted to monophenols with a yield of 47% (based on lignin) (Li et al., 2012). However, the repolymerisation or cross linking of the degraded lignin intermediates and catalyst deactivation were the main technical bottlenecks to high product yield and selectivity. Hurdles also exist in quantifying and separating individual phenolic compounds, due to the high heterogeneity of the product mixture (Zhang et al., 2013).

2.1.2.4. Lactic acid. Lactic acid, an organic acid bearing a hydroxyl group and acid function, has gained particular interest for use in producing biodegradable polymers, solvents, metal pickling, and food additives (Datta et al., 1995). Lactic acid yields of 20–27% were achieved from hydrothermal conversion of carbohydrate biomass using NaOH and $\text{Ca}(\text{OH})_2$ as alkaline catalysts (Yan et al., 2010). Lactic acid of 44% (based on the total content of cellulose and hemicellulose) was obtained from corn cobs using the $\text{Ca}(\text{OH})_2$ catalyst (Sánchez et al., 2012). A higher yield of 59% was reported by using NaOH at high temperatures and with NiO nanoplates reckoned to assist the degradation of cellulosic rice straw (Younas et al., 2016). The use of the basic CaO can result in lactic acid yields of 14.7% (Jeon et al., 2016). Zn(II) catalysts were also found effective in the conversion of glucose, e.g. 42% lactic acid over ZnSO_4 as the catalyst at 300 °C and 25 MPa (Raina & Bolia, 2005). The highest lactic acid yield with Zn/Ni/AC catalysts reached 55% (Xiong et al., 2017) and Zn can improve lactic acid yield more markedly than Ni or AC.

2.1.2.5. Levulinic acid. Levulinic acid (LA) can be used as a diesel fuel additive, polymer building block, and herbicide (Mascal & Nikitin, 2010). Mineral acids such as HCl and H₂SO₄ are the most common catalysts for converting lignocellulosic biomass to LA. Tukacs et al. obtained a maximum LA yield of 8.6 wt% from hazelnut shells under conventional heating at 170 °C for 8 h, using dilute H₂SO₄ as a catalyst. The LA yield achieved 12 wt% by using microwave heating for only 0.5 h (Tukacs et al., 2017). Licursi et al. used HCl in the conversion of giant reed, yielding LA of 24 wt% after 1 h of reaction at 190 °C (Licursi et al., 2015). Wheat straw is another promising and popular feedstock, which yielded 20 wt% LA in the presence of H₂SO₄ under the best experimental conditions (209 °C, 38 min) (Chang et al., 2007). Similarly in the presence of H₂SO₄, *Helianthus tuberosus* L. substrate gave optimal amounts of 323 g LA/kg at 185 °C for 34 min (Jeong, 2015).

As for heterogeneous catalysis, kiwifruit waste residues can yield 15 wt% LA over the Nb/Al oxide catalyst in water at 190 °C for 15 min (Wang Xie, et al., 2015). However, the major problem during the hydrothermal acid catalysis is the formation of humins (Figure 4), which represent the main solid by-products of the reaction (Antonetti et al., 2016). The deposition of humins and/or lignin-derived residues can deactivate heterogeneous catalysts (Chen, Maneerung, et al., 2017). Besides, the complexity and heterogeneity of lignocellulosic biomass make pretreatment a mandatory step to improve the reaction rates (Antonetti et al., 2016).

2.1.2.6. Formic acid. Formic acid can be produced from alkaline oxidation of carbohydrates or acid rehydration of HMF. As for hydrothermal oxidation, formic acid yield was the highest when glucose was used as the substrate, followed by starch and then cellulose (Yun et al., 2010), and ca. 27% formic acid was obtained from cellulose (Yun et al., 2013). The addition of alkali enabled a high selectivity of formic acid. A remarkably high yield of 80–85% was obtained from monosaccharides and disaccharides at a lower temperature (423 K) after only 15–20 min in the presence of NaOH (Yun et al., 2016) while as much as 74% was achieved from glucose (24% without alkali) at 250 °C for 60 s in the presence of oxygen (Yun et al., 2007). Only 4.9% of formic acid could be obtained from alkali lignin (Zeng et al., 2010).

2.1.2.7. Syngas. The syngas platform can be used for synthesis of various fine chemicals in combination with Fischer–Tropsch synthesis. HTG could improve syngas production (mainly composed of H₂, CH₄, CO, and CO₂) as water promotes hydrolysis and water–gas-shift reactions, increasing the gas yield and reducing the char/tar formation (Jayaraman & Gökalp, 2015).

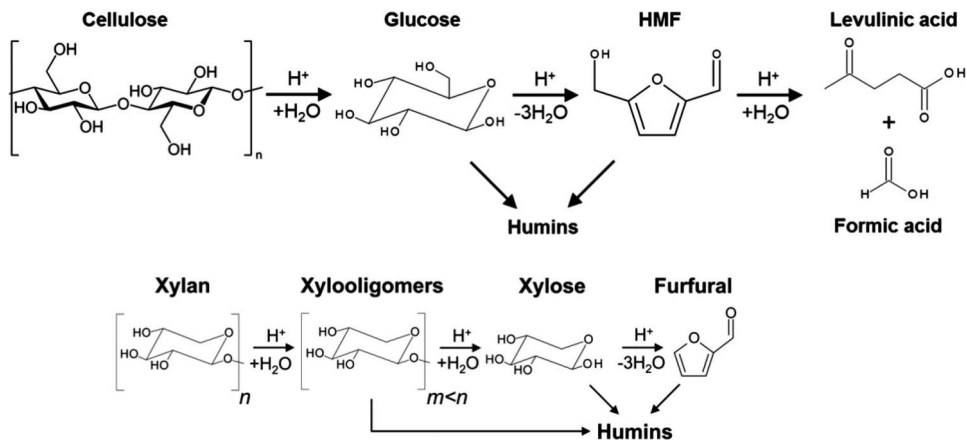


Figure 4. The hydrolysis reactions of cellulose and hemicellulose leading to the formation of furfural, 5-hydroxymethylfurfural, levulinic acids, and formic acids.

The HTG of biomass was net energy positive when the solid content of the feedstock is above 2% (Ro et al., 2007). The reaction temperature significantly affected gasification, but pressure had little effect (Kumabe et al., 2017). Two approaches of HTG were low-temperature catalytic gasification (350–600 °C) and high-temperature supercritical water gasification (500–750 °C) without catalyst or with nonmetallic catalysts (Matsumura et al., 2005). The best yields of hydrogen (10.4 mol/kg) and methane (6.3 mol/kg) were attained at 600 °C in the HTG of *Posidonia oceanica* (Deniz et al., 2015). H_2 can be selectively produced over $\text{Ca}(\text{OH})_2$ and Na_2CO_3 catalysts (Kumabe et al., 2017). However, challenges lie in reactor corrosion by the homogeneous catalysts and their recovery.

2.2. Microwave processing

Despite the common and easy application, conventional heating via conduction and convection has disadvantages such as uneven heat distribution, high cost of heating, and often long process time. In comparison, microwave irradiation allows more effective internal heating because energy is directly transferred to the molecules to raise temperature via dipole rotation and ionic conduction (Sweygers, Alewaters, et al., 2018). It significantly shortens the reaction time from hours to minutes, improves the quality of value-added products, and reduces the processing costs (Hesas et al., 2013; Motasemi & Afzal, 2013). In addition, synergy between biomass components and microwave has been proposed to enhance the efficiency of biomass conversion. Thus, microwave processing potentially plays a role in the reaction mechanisms, beyond generating thermal energy.

2.2.1. Microwave pyrolysis

The different heat sources in microwave-assisted and conventional pyrolysis lead to differences in their system features, such as feedstock requirements, operation conditions, and potentially, the reaction mechanisms. In comparison to conventional pyrolysis where dried feedstock is demanded, as-received feedstock that usually contains moisture is favorable in microwave pyrolysis, because water is polar and absorbs microwave for generating thermal energy. The latter can be also facilitated by using microwave-absorbing additives (e.g. biochar) (Nhuchhen et al., 2018; Yang et al., 2018). While conventional pyrolysis is performed at higher temperatures of 300–900 °C, microwave pyrolysis is considered as the low-temperature pyrolysis, i.e. 180–300 °C (Al Shra'ah & Helleur, 2014; Bouxin et al., 2019; De Bruyn et al., 2016). For the latter, heating starts from the center of biomass with the heating zone expanding outwards (Gadkari et al., 2017), and a reverse direction of conductive heat transfer in conventional heating.

Similar to conventional pyrolysis, three major categories of products arise from microwave pyrolysis of biomass: (1) bio-oil as a mixture of molecules, such as LGO, HMF, and phenolics, in the liquid phase; (2) biochar as the insoluble and carbonaceous solid fraction; and (3) syngases comprising CO, CO₂, H₂, and CH₄. In general, biomass decomposes to small molecules in bio-oil and syngas, and the decomposition products undergo condensation and rearrangement reactions to give biochar. While conventional pyrolysis relies on solely thermal energy, microwave exerts also the non-thermal effect, e.g. triggering the rotation of polar groups (Budarin et al., 2010). The difference may even lie in their pyrolysis pathways in view of the distinctive product species in bio-oils from the conventional (e.g. phenol) and microwave pyrolysis (e.g. furanic compounds) of amorphous cellulose (Al Shra'ah & Helleur, 2014). In the presence of water, hydrolytic reactions producing sugars, furans, and LA are expected in microwave pyrolysis (Bouxin et al., 2019). As for lignin, microwaves can promote the production of bio-oils rich in phenols, hydrocarbons, and esters, whereas guaiacols are the dominant products in conventional pyrolysis (Bu et al., 2014).

2.2.1.1. Levoglucosan and levoglucosenone. LG and LGO are anhydrosugars mainly derived from sugars and cellulose (Table 1). Residual saccharides in crude waste softwood hydrolysis lignin (CSHL) can be efficiently activated with microwaves at a moderate temperature of 180 °C to give an improved LGO yield (8 wt%) compared to conventional pyrolysis at 310 °C (6% LGO) (De Bruyn et al., 2016). Microwave pyrolysis (180 °C) coupled with self-induced steam distillation has recently been developed to give yields of 8.6% of LGO, 2.1% of LG, and 2.6% of furfural from wet barley straw (Bouxin et al., 2019). Addition of a small amount of H₂SO₄ (0.4%)

significantly improved ramping under a fixed power supply, possibly due to the improved microwave absorption. Upon formation, LGO was isolated by steam distillation as water evaporated from the feedstock creating a microwave-transparent gaseous environment to suppress LGO degradation. This demonstrates the opportunity of controllable reactions as microwave activation can be easily tuned by varying the system conditions. A decreasing acid concentration shifted the selectivity toward the pyrolytic reactions producing LG and LGO, over the hydrolytic reactions that yielded furfural and LA (Bouxin et al., 2019). At low acid loading, the decomposition temperature remained high, at which water was vastly evaporated, creating a pseudo-dry condition that favored LGO formation. Amorphous cellulose gave a higher LG yield than microcrystalline cellulose due to the weaker hydrogen bonding, suggesting the significance of the cellulose properties (Al Shra'ah & Helleur, 2014).

2.2.1.2. Hydrocarbons. While the microwave pyrolysis of fossil-based feedstocks, e.g. oil sands and coal, can give oils containing light hydrocarbons (Abdelsayed et al., 2018; Li et al., 2019), they are hardly produced from lignocellulosic biomass due to the high oxygen content (38–53%) (Huang et al., 2018). Catalysts are generally needed to increase the selectivity of hydrocarbons in bio-oils, which also applies in conventional pyrolysis (Section 2.1). The use of SiO₂-modified HZSM-5 as an acid catalyst was found to be conducive to the formation of aliphatic and aromatic hydrocarbons in the microwave pyrolysis of corn stover (Zhang, Zhong, et al., 2015). The SiO₂ deposit suppressed coke formation and the associated pore blockage, allowing for deoxygenation reactions to take place in the internal structure of HZSM-5. No hydrocarbons were observed in the absence of HZSM-5, underscoring that microwave by itself hardly promoted the reactions. However, we may not exclude the possible complementary role of microwaves in terms of reactant activation.

2.2.1.3. Furfural and 5-hydroxymethyl furfural. HMF and furfural are products from the dehydration of monosaccharides (Table 1). A recent pilot-scale study demonstrated successful microwave pyrolysis of 1.5–3.5 kg wood pellets producing 36–46% bio-oils, in which the furfural concentration decreased from 5552 $\mu\text{g g}^{-1}$ at 2000 W to 4203 $\mu\text{g g}^{-1}$ at 3000 W (Nhuchhen et al., 2018). This possibly implies the promotion of secondary reaction of furfural at increasing microwave power. Bouxin et al. obtained furfural and HMF of up to 4.1% and 0.7%, respectively, from wet barley straw in an open microwave system (Bouxin et al., 2019). Addition of acid can lower the operating temperature, mitigating water evaporation in an open system to enable hydrolytic reactions for furfural production.

2.2.1.4. Phenolic compounds. Microwave-assisted pyrolysis of Douglas fir sawdust pellets at 500 °C resulted in 24.7 C% aromatics (C₈–C₁₆), using AC powder as a microwave absorber and zeolite ZSM-5 as a catalyst (Zhang, Lei, et al., 2015). Upon irradiation, hot spots or even micro-plasmas were created on the AC surface, at which the temperature was higher than that in the bulk material, facilitating secondary cracking of the pyrolysis volatiles (e.g. deoxygenation and dehydration) (Yang et al., 2018). AC derived from the carbonization of H₃PO₄-impregnated corn stover was recently used in producing bio-oils rich in phenols (yield 2.46 mg mL⁻¹, selectivity 75%) (Yang et al., 2018). The phosphoric groups on AC may provide Brønsted acid sites for promoting the deoxygenation of guaiacols (lignin depolymerization products) to phenols, and even further deoxygenation of the latter to aromatic hydrocarbons. These findings highlight the important role of additives in controlling the product distribution in microwave pyrolysis. In addition, an increasing microwave power was reported to increase the yield of phenol and 3-methylphenol, as a result of improved thermal degradation of lignin (Nhuchhen et al., 2018). The selective decomposition of phenols is possible under intensive microwave heating as these are more polar than alkanes do (Abdelsayed et al., 2018). In addition, aromatic formation may be inhibited by a high polysaccharide content in biomass, which transformed to char-like materials via carbonization, blocking lignin from microwave activation (Bouxin et al., 2019).

The resultant aromatics could undergo hydrogenation, e.g. over RANEY® nickel catalysts giving cycloalkanes as jet fuel additives with a high selectivity (84.6%) (Zhang, Lei, et al., 2015). Nevertheless, attention should be paid to the high water content of 32–69%, which originated from the wet feedstock and dehydration reactions during pyrolysis (Nhuchhen et al., 2018; Undri et al., 2015). With moisture > 30%, the organic phase with higher energy content is miscible with the aqueous phase, limiting the application of the bio-oils (Nhuchhen et al., 2018). This could be less significant in conventional pyrolysis where dried feedstocks are usually used, while moisture is commonly present in microwave pyrolysis for wave energy absorption. Quenching rate and efficiency of vapor condensation may also determine the water content in bio-oils, by controlling the secondary reactions (Undri et al., 2015).

2.2.1.5. Syngas and biochar. The distribution among bio-oil, syngas, and biochar depends on the pyrolysis conditions. Increasing power was found to reduce the solid and gas yields and improve oil production, while the opposite occurred for increasing biomass loading (Nhuchhen et al., 2018). In particular, the biochar surface area substantially increased from 37 m² g⁻¹ at 2000 W to 132 m² g⁻¹ at 3000 W, due to the intensified interaction between carbon and microwave. Biochar with high surface area is favorable

for its application in environmental remediation (Jeon et al., 2018; Rajapaksha et al., 2018; Sun et al., 2019; Vikrant et al., 2018; Yoo et al., 2018) and catalysis (Xiong et al., 2017). In the presence of a microwave absorber, e.g. AC, the ZSM-5-catalyzed microwave pyrolysis of sawdust pellets resulted in 37.4% char, 34.6% syngas, 24.7% aromatics, and 3.4% coke (Zhang, Lei, et al., 2015). Changing the absorber from carbon to Fe was suggested so as to increase the char yield by promoting condensation via radical coupling (Undri et al., 2015). Without any absorbers, pyrolysis reactions may take place in a less homogeneous and less controllable manner, leading to unpredictable variation in the product distribution (Undri et al., 2015). Biomass composition can alter the heating efficiency under a fixed power supply (Huang et al., 2018). The density of the feedstocks affected the heating rate, the diffusion rate (of volatiles), and the product distribution, as demonstrated in the microwave pyrolysis of cellulose pellets (Fan et al., 2013).

Chemical pretreatments can be adopted to change the product profile. A recent study reported 54% H₂ in the syngas from KOH-activated corn grain waste, which was higher than that from non-activated corn waste (19%) (Grycová et al., 2018). Moreover, biochar in the former showed an improved specific surface area ($420 > 138 \text{ m}^2 \text{ g}^{-1}$), making it a potentially more useful sorbent. Reduction in the biochar content was observed when biomass was subjected to alkali-microwave pretreatment producing monosaccharides from polysaccharides (Gautam & Verma, 2018), yet the microwave-specific effects were not discussed. Doroshenko et al. reported that the presence of Ni in hyperaccumulator plant biomass stabilized hemicellulose during microwave pyrolysis (Doroshenko et al., 2019). This consequently led to a lower gas yield due to the limited decomposition of glucuronic and galactonic acid in hemicellulose. Similar effects may occur in pyrolysis of other phytoremediation plants (Rizwan et al., 2018), which deserve future investigations.

On the basis of these findings, one may conclude that additional parameters (e.g. properties of microwave absorber and feedstock) should be considered in microwave pyrolysis experiments for better control of the product yield and selectivity, in addition to those that are important in conventional pyrolysis (e.g. heating rate and feedstock loading). Mechanical/chemical modification of absorber and feedstock are potential approaches to tune the product profile for achieving efficient and selective microwave pyrolysis. Novel microwave absorbers are exemplified by hierarchically porous magnetic biochar (Zhao et al., 2019) and SiC whisker-biochar composites (Dong et al., 2019).

2.2.2. Microwave hydrolysis

Microwave hydrolysis is undertaken in an aqueous medium at a lower temperature (100–250 °C) compared to pyrolysis (limited moisture in feedstock,

180–300 °C). The dominant hydrolytic products are water-soluble monomers such as glucose, organic acids, and furans. They may undergo polymerization/condensation to form humins or hydrochar as an insoluble product, in case of intensive heating (e.g. high temperature and/or long retention time).

While conventional hydrolysis of biomass relies on conductive heat transfer, a polar medium is needed in microwave hydrolysis to absorb and convert wave energy to thermal energy. It is advantageous to have water in a hydrolytic system because it is a good microwave absorber reducing energy consumption. In addition to the thermal effect, microwave was reported to activate specific CH₂OH groups in cellulose and glucose for accelerating their reactions (Fan et al., 2013; Sweygers, Alewaters, et al., 2018). Nevertheless, there is little discussion of the direct involvement of microwaves in the decomposition mechanisms for hemicellulose and lignin. Generally, the orientation, rotation, and collision of polar species in an electromagnetic field are believed to reduce the activation energy for reactions (Qi et al., 2008).

2.2.2.1. Glucose. Glucose is mainly produced from glucans such as cellulose and starch in biomass (Table 2). While the catalyst-free microwave-assisted hydrothermal treatment of lignocellulosic biomass is usually performed as a pretreatment (Li et al., 2015; Onumaegbu et al., 2019; Santomauro et al., 2018) or extraction process (Luo et al., 2017), its use for monosaccharide production is not thoroughly evaluated.

Microwave photons can reach the CH₂OH groups in cellulose at > 180 °C (i.e. the cellulose softening temperature) and trigger their rotation for improved reactivity (Fan et al., 2013). The on-set temperature for such activation may vary among different biomass feedstocks, according to the finding that cellulose in *pubescens* remained intact at 200 °C, at which selective dissolution of hemicellulose was achieved (Luo et al., 2017). It is noted that the rotation of polar groups was particularly active in the amorphous phase of cellulose (Budarin et al., 2010), underscoring the importance of feedstock crystallinity. The microwave activation also depends on power density, e.g. 800 W L⁻¹ resulted in 11% glucose from cellulose, which was significantly higher than that at 35 W L⁻¹, in spite of the same temperature (220 °C) (Fan et al., 2013). In general, the reactivity of model compounds toward microwave hydrothermal degradation follows the ascending order: cellulose < hemicellulose < alginic acid (Remón et al., 2018). Microwave-assisted HTP offers an energy-efficient route to hydrolyze cellulosic biomass with less secondary breakdown products. Fan et al. achieved a high glucose yield and selectivity of 21% and 75%, respectively, in the cellulose conversion (Fan et al., 2013).

Jiang et al. recently proposed the use of salt (NaCl) to assist the hydrolysis of cellulose and xylo-oligomers under microwave heating, via increasing the proton adsorption on substrate and disrupting the hydrogen bond network (Jiang, Budarin, et al., 2018; Jiang, Fan, et al., 2018). Salt addition can also improve microwave absorption, lowering the power needed to attain the target temperature.

By using catalysts, microwave-assisted monosaccharide production from cellulose in lignocellulose biomass is feasible at 120–170 °C (Abu-Saied et al., 2018; Chen, Wang, et al., 2018; Teh et al., 2017). Hydrolysis of fiber waste by microwave coupled with H₂SO₄ or HNO₃ gave significantly higher glucose yields (48–80 mg dL⁻¹) than that by ultrasound and autoclaving with the same acid present (12–25 mg dL⁻¹) (Abu-Saied et al., 2018). However, when using HCl, the performance of microwaves (97 mg dL⁻¹) was comparable to that of autoclaving (108 mg dL⁻¹) (Abu-Saied et al., 2018), suggesting that the promotional effects by microwave may vary with the type of catalyst used, which should be further investigated in future studies. Another recent study reported a glucose yield of 87% from rice waste over H₃PO₄-activated wood biochar catalyst under microwave heating (Cao, Yu, Tsang, et al., 2018).

2.2.2.2. Furfural and 5-hydroxymethyl furfural. Furfural and HMF are the dehydration products of C5 and C6 monomers, respectively, which can be obtained from hemicellulose, cellulose, and starch in biomass (Table 2). Recent studies evaluated the one-pot catalytic transformation of starch-rich food waste under mild microwave heating (120–160 °C for 10–40 min), giving rise to 20–30% HMF over metal chlorides that provided both Lewis and Brønsted acid sites in aqueous media (Yu, Tsang, Chen, et al., 2017; Yu, Tsang, Su, et al., 2018; Yu, Tsang, Yip, et al., 2017; Yu et al., 2018c). As for the use of Brønsted acid catalyst alone, e.g. H₃PO₄-activated or sulfonated biochar, 30% HMF was obtained from bread waste, yet at a higher temperature of 180 °C (Cao, Yu, Chen, et al., 2018; Cao, Yu, Tsang, et al., 2018), due to the higher activation barrier for the direct glucose dehydration than that for the Lewis acid-involved pathway (Yu & Tsang, 2017). Using lignocellulose biomass as feedstocks is more challenging. A microwave-assisted biphasic system (methyl isobutyl ketone and acidified aqueous phase) was reported to produce 42 mol% HMF and 49 mol% furfural (w.r.t. cellulose and hemicellulose content, respectively) from bamboo (Sweygers, Harrer, et al., 2018). In the absence of catalysts, Luo et al. reported a furfural yield of 5 wt% from bamboo after two-stage microwave heating, along with 11.1 wt% acetic acid (Luo et al., 2017).

A recent study reported the need for 1.7 times more energy for conductive heating of cellulose, compared to microwave heating to attain the same

temperature (Sweygers, Alewaters, et al., 2018). In addition, with the same temperature profile, the hydrolysis of cellulose to glucose and isomerization of glucose to fructose were 2.3–2.5 times faster than that under conventional heating (Sweygers, Alewaters, et al., 2018). Chen et al. reported a significantly higher HMF yield (23%) from cellulose under microwave irradiation (vs. <0.1% in conventional heating), suggesting that microwave may also accelerate the dehydration of C6 sugars (Chen et al., 2019). Microwaves can activate the CH₂OH groups as microwave irradiators, generating microscopic and localized hot spots to accelerate the reactions (Fan et al., 2013; Sweygers, Alewaters, et al., 2018). Such speculation was reinforced as the dehydration of xylose showed the same kinetics under conventional and microwave heating (Weingarten et al., 2010). However, contrasting arguments have been raised that CH₂OH in glucose was not selectively activated due to the significant energy loss to the surrounding water molecules (Fan et al., 2013). Starch also interacts with microwaves, which promoted molecular rearrangements and changed the polarization characteristics (Fan et al., 2017). The significance of such behavior in a biomass conversion system should be further investigated.

The microwave absorptivity of the solvent media should be considered. Systems with green solvents such as propylene carbonate and γ -valerolactone (CO₂- and biomass-derived, respectively) enabled a faster bread waste-to-HMF conversion than acetone-containing medium did (Yu et al., 2018c). The solvents have a higher dielectric constant, which possibly favor microwave absorption compared to tetrahydrofuran with a low polarity (Yu, Tsang, Chen, et al., 2017). Nevertheless, there is little discussion on the significance of the interplay between media and microwaves in determining conversion efficiency. More studies are needed to bridge the knowledge gaps between solvent chemistry and solvent application in the context of biorefineries.

2.2.2.3. Monomeric phenols. Lignin is usually isolated from hemicellulose and cellulose prior to phenol production. A recent study suggested that microwaves efficiently isolated lignin of high purity from softwood, with the performance superior to that of the traditional Klason method (Zhou, Budarin, et al., 2017). Palm empty fruit bunch lignin was subjected to oxidative depolymerization in the presence of Cu(OH)₂ and Fe₂O₃ catalysts, NaOH, and H₂O₂ under microwave heating (Panyadee et al., 2018). The process generated 92% phenolic compounds, including syringol, vanillin, acetovanillone, syringaldehyde, and acetosyringone. Rapid decomposition of lignin (7 min) was reported over CuSO₄ and H₂O₂ under microwave heating at 110 °C (Dai et al., 2018). The corresponding yield of low-molecular-weight molecules was 2.6 times higher than that in autoclaving, given the

same temperature and reaction time. It was suggested that microwaves promoted the CuSO_4 -catalyzed hydroxyl radical formation from H_2O_2 , which attacked the lignin leading to its degradation. Alternatively, polyphenols can be easily extracted from phenolics-rich algae under simple microwave hydrothermal conditions without the need for a catalyst (Yuan et al., 2018).

2.2.2.4. Lactic acid. Lactic acid is derived from cellulose and hemicellulose in biomass (Table 2). Post-harvest tomato plants were subjected to microwave heating at 220°C to give a lactic acid yield of 34% as well as 21% glycolic, using $\text{Pb}(\text{NO}_3)_3$ as the catalyst in a pressurized system (3 MPa) (Carnaroglio et al., 2015). The reaction time was significantly shortened to 2 min (vs. 4 h in conventional heating). The authors successfully demonstrated continuous conversion of milled cellulose in a flow-through microwave reactor, and highlighted the differences in the optimal conditions when compared to batch reactors. Microwave-assisted polycondensation of lactic and glycolic acid was also performed, producing oligomers for potential medical applications. The authors remarked a decreasing polarity as polymerization proceeded, which required a higher microwave power to maintain the target temperature. Lactic acid is commonly produced via fermentation, for which microwaves can also serve as a pretreatment (Gavilà et al., 2015; Liu et al., 2012).

2.2.2.5. Levulinic acid and formic acid. LA and formic acid are the products of HMF rehydration (Table 2). Microwave heating was employed for producing LA (17 mol%) from vegetable waste as a cellulose-rich substrate over a Brønsted acid catalyst (Amberlyst 36), after only 5 min of heating at 150°C (Chen, Yu, et al., 2017). The conversion rate greatly depends on the fiber length, according to a study comparing paper towels made of virgin and recycled pulp as the substrates, which obtained up to 46% LA with 10% formic acid (Chen, Wang, et al., 2018). The use of potato peel and fungus resulted in LA of 49% and 62%, respectively, over H_2SO_4 and CrCl_3 as the catalysts (Lappalainen et al., 2018). Microwave irradiation consumed significantly lower energy to maintain the reaction temperature ($\leq 90\text{ W}$) compared to an oil bath (600 W) because of less heat loss in the former (Lappalainen et al., 2018). The HCl-catalyzed conversion of agro-industrial wastes, including brewery wastes, apple pomace wastes, and starch industry waste, resulted in LA yields of 160–204, 49–66, and 12 g kg^{-1} , respectively (Maiti et al., 2018). The yield further increased to 341–409 g kg^{-1} after optimization. Li et al. synthesized bifunctional zirconia-zeolite catalysts for facilitating the one-pot conversion of cellulose to methyl levulinate as a potential biofuel (up to 27%) under microwave heating at 180°C (Li et al., 2017).

2.2.2.6. Lipids/fatty acids and biodiesel. Microwave effectively assisted the lipid extraction (98% recovery) from spent hen waste in a dichloroform-methanol mixture at 80 °C, mainly recovering oleic, linoleic, and palmitic acids (Safder et al., 2019). Hao et al. compared microwave to a high-temperature ethanol process, freeze-thawing, and thermal-alkaline treatment for algal oil extraction, under their respective optimal conditions (Hao et al., 2019). In terms of cell disruption, the performance of microwave was the lowest, while it ranked the third after alkaline and ethanol treatments in terms of extraction efficiency. Nevertheless, it should be noted that a very low microwave power of 8 W was adopted in the study. The authors pointed out that intermittent application of microwaves showed higher performance than continuous irradiation did, because the temperature difference between the cell wall and internal created tensile and compressive stresses that ruptured the algal cell.

A two-stage microwave pretreatment-solvent extraction was evaluated for extracting lipids from microalgae, achieving 42% recovery (Onumaegbu et al., 2019). Another study reported a four-fold increase in the yield of microalgal oil with microwave pretreatment, which was favored by increasing the irradiation time (Cancela et al., 2019). The resultant fatty acids could undergo steam reforming for H₂ generation (Hao et al., 2019) and esterification/transesterification for biodiesel production. Apart from fatty acids (long-chain carboxylic acids), biomass-derived short-chain carboxylic acids are also potential biofuel precursors. For instance, 98% esterification of LA was achieved over a zeolite-based acid under microwave heating, producing methyl levulinate with 99% selectivity (Umrigar et al., 2018). The required reaction time of 1 h was substantially shorter than 24 h in a conventional process. However, the mechanistic effects of electromagnetic waves are yet to be discussed in detail. A one-step microwave-assisted production of fatty acid methyl ester (FAME; up to 40% yield) from algal biomass has been reported (Patil et al., 2012). The reduced polarity of methanol (transesterification agent) at elevated temperature favored lipid solubility, leading to a higher yield of algal biodiesel. It was remarked that higher microwave energy efficiency can be achieved at a higher substrate loading and shorter reaction time, which require better mechanistic understanding in the future.

2.2.2.7. Hydrochar. Previous studies investigated the synthesis of hydrochar from algae (Cao, Yu, et al., 2019; Teh et al., 2017), plant shell (Elaigwu & Greenway, 2016), and dairy manure (Gao et al., 2018) via microwave-assisted hydrothermal treatment at 180–240 °C. The hold time could be significantly shortened from 240 min for autoclaving to 20 min for microwave, to produce plant shell-derived hydrochars with similar physicochemical

properties in terms of ultimate composition and energy content (Elaigwu & Greenway, 2016). Gao et al. remarked that the formation of carbon microspheres during hydrothermal treatment could enhance microwave absorption, further accelerating the production of dairy manure hydrochar (Gao et al., 2018). The authors also suggested that retention time exerted a greater impact on the chemical features of microwave-synthesized hydrochar compared to that in the conventional hydrothermal process. The microwave hydrochar has a higher heating value (HHV) of 15–23 MJ kg⁻¹ (Cao, Yu, et al., 2019; Elaigwu & Greenway, 2016; Gao et al., 2018; Teh et al., 2017), while the HHV range is wider for conventional hydrochar (17–30 MJ kg⁻¹) (Gao et al., 2016; Guo et al., 2017; Volpe et al., 2018), possibly because of the higher operating temperatures (up to 300 °C) used in the latter case.

2.2.2.8. Fractionation and pretreatment. Fractionation maximizes the use of different components in biomass, producing a wide spectrum of value-added chemicals. In microwave acidolysis of woody biomass, liquefaction of cellulose and hemicellulose can be efficiently and selectively achieved with the lignin fraction well preserved in the residue, which usually takes a longer residence time in conventional practices (Zhou, Budarin, et al., 2017). In another microwave-HTC study, hemicellulose can be selectively separated from cellulose and lignin in bamboo at ≤ 200 °C without any addition of acids (Luo et al., 2017). The separated hemicellulose can be hydrolyzed to monomeric molecules, or serve as a raw material for film synthesis, whereas the cellulose and lignin can be used for production of glucose and aromatics. It is noteworthy that the activation temperature of hemicellulose varied from 180 to 200 °C for different biomass feedstocks (softwood, wheat straw, and bamboo) (Luo et al., 2017). The ability of microwave to partially hydrolyze feedstock makes it a viable pretreatment method for anaerobic digestion of sewage sludge (Akgul et al., 2017; Gil et al., 2018) and microalgae (Passos et al., 2015). The microwave pretreatment potentially enables operation at higher loading rates in digesters with smaller volume without compromising the biogas generation (Kor-Bicakci et al., 2019).

Microwave-assisted biorefinery is an emerging research area and pilot-scale studies are in progress. It has been suggested that inadequate energy efficiency could be a challenge to field-scale applications (Akgul et al., 2017; Kor-Bicakci et al., 2019). Currently, there are commercial scale microwave magnetrons (e.g. 100 kw) available, as well as commercial scale microwave reactors for drying applications (e.g. used in the food/ceramic/wood industries). However, there are only pilot scale microwave-assisted biorefineries produced in research centers, for example: The Green

Chemistry Center of Excellence and the Biorenewables Development Center, which are based at the University of York, UK. They have established two pilot scale microwave systems; the first one is a semi-continuous 30 L hydrothermal microwave system for the pretreatment of biomass; and a second microwave pyrolysis unit, which has been established to test continuous flow reactor principles for biomass pellets up to 30 kg h⁻¹. More scale-up studies are anticipated for future industrial applications. To date, bioprocesses dominate the market of bio-based products, yet they have limitations such as the use of expensive enzymes and restrictions on feedstock quality. It is advantageous to integrate thermochemical and biological technologies, which have complementary edges, to achieve carbon-efficient conversion of biomass. The following [Section 2.3](#) will introduce the pilot-scale and commercial bioprocesses, providing insights into the potential of combining them with the advanced thermochemical routes.

2.3. Biochemical processing

Biochemical processes include enzymatic hydrolysis of biomass, both whole cell and with defined enzymes, phototrophic and heterotrophic algal processes as well as aerobic and anaerobic fermentation processes, which convert sugars and other substrates to useful products (Brennan & Owende, 2010; Tekin et al., 2014). The majority of commercial production from biomass is currently biochemical in nature. There are over 60 distinct processes for production of bulk chemicals, nutraceuticals, pharmaceutical precursors, enzymes, and fuels, of which 10 processes are well developed and in full market operation (Tables 3 and 4) (Saxena et al., 2009).

2.3.1. Enzymatic conversion

To ferment lignocellulosic biomass effectively, the biomass structure must be disrupted for enzymatic hydrolysis of polysaccharides to mono- and disaccharides. Industrial processing has been well established for decades (Kirk et al., 2002), and has been well discussed in recent review articles and over 5000 research papers in the last decade (Bilal et al., 2018; Guo et al., 2018).

The release of sugars enzymatically remains one of the largest challenges in biological processing due to its high cost, e.g. up to 30% of the operating costs for lignocellulosic ethanol production. The on-site production of enzymes is also a major contributor to the capital costs of biorefinery plant (Klein-Marcuschamer et al., 2012). Recent studies have aimed to reduce the costs through more efficient pretreatments (Ibrahim et al., 2017), increasing tolerance and yields of enzymes (Li & Zheng, 2017), efficient simultaneous saccharification and fermentation systems (SSF) (Mesa et al., 2017) and

Table 3. Bulk chemicals and fuels produced on the commercial scale, or close to, through genetically modified organism (GMO) whole cell catalysis; data adapted primarily from (SynBio project).

Compounds	Company	Microbe	Feedstock	Production start	Plant location	Capacity (kt/yr)	Application
Butanol	Green Biologics	<i>Clostridium</i> spp.			USA		Solvent, chemical building block, liquid fuel
Diesel type hydrocarbons	Gevo	<i>Saccharomyces cerevisiae</i>			USA		Fuel
Farnesene	Renewable Energy Group (REG)	<i>Escherichia coli</i>					
	DSM (purchased from Amyris)	<i>Saccharomyces cerevisiae</i>	Sugarcane	2012	Brazil	24	Cosmetics (e.g. squalane), fragrances, polymers, lubricants, detergents, and jet and diesel fuel
Lactic acid	GC Innovation America (Myriant)	<i>Escherichia coli</i>	Conventional sugars	2008	USA		Polylactic acid
Nootkatone	Evolve (including Allylix acquired)						Flavour, fragrance
	Isobionics/DSM						
1,3-Propanediol	DuPont Tate & Lyle Bio Products	<i>Escherichia coli</i>	Corn glucose	2006	USA		Polymers, cosmetics, liquid detergents
Resveratrol	Evolve (purchased from Fluxome)	<i>Saccharomyces cerevisiae</i>		2014			Food supplement, pharmaceutical, cosmetics
Stevia	Evolve (including Allylix acquired) /Cargill	<i>Saccharomyces cerevisiae</i>		2018	USA		Sweetener
Succinic acid	GC Innovation America (Myriant)	<i>Escherichia coli</i>	Corn glucose	2013	USA, Germany	14	Adhesives, coatings, food preservatives, plasticizers, polymers, sealants, urethanes
	Succinity (BASF, Corbion)	<i>Basfia succiniproducens</i>	Variable, e.g. glycerol, sugars	2014	Spain	10	
	Bioamber, Mitsui	<i>Candida krusei</i>	Corn glucose	2015	Canada	30	
	Reverdia (DSM, Roquette)	<i>Saccharomyces cerevisiae</i>	Corn starch hydrolysate	2012	Italy	10	
Valencene	Evolve (including Allylix acquired)			2011			Fragrance
	Isobionics/DSM						

Table 4. Bulk chemicals and fuels produced biologically that have been recently commercialized or are close to commercialization; data adapted primarily from (SynBio project).

Compound	Company	Application
Acrylic acid	Myriant, OPX biotechnologies, Metabolix, Novozymes, Cargill	Coatings, adhesives, paints
Adipic acid	Verdezyne, Bioamber, Rennovia	Platform chemical, polymers
Amino acids	Metabolic Explorer	Food
Artemisinic acid	Amyris	Pharmaceutical precursor
Bioisoprene	Dupont, Goodyear, Amyris, Michelin, Lanzatech	Synthetic rubber, biofuel precursor
Fatty acids and adducts	OPX biotechnologies, REG, Verdezyne	Fuels and polymer precursors
Fumaric acid	Myriant	Paints and coatings, platform chemicals
Hexamethylenediamine	Rennovia	Polymers
3-Hydroxy propionic acid	Novozyme, Cargill	Platform chemical, polymers
Isobutanol	Gevo	Fuel, platform chemical
Isobutene	Global Bioenergies	Synthetic rubber, biofuel precursor
Mandelic acid	MONAD	Healthcare, polymer precursor
Muconic acid	Myriant	Polymer precursor
Polyhydroxylalkanoates	Metabolix	Polymers
Pomecin	Evolve	Antimicrobial
Sabacic acid	Verdezyne	Polymer precursor
Triglycerides	Corbion	Biofuels, nutraceutical
Vanillin	Evolve	Food

combining enzymatic depolymerization with other unit operations such as extrusion (Gatt et al., 2018). Despite these promising developments, the use of enzymes is likely to remain a major cost in the processing of biomass.

2.3.2. Major industrial processes

The majority of industrial processing is based around the use of first generation feedstocks. Fermentation of starch and sugar-based raw materials into bioethanol is by far the largest bioprocess in the world, with over 85 million tonnes of fuel ethanol sold globally in 2018. The pilot-scale lignocellulose-to-ethanol processing has been well demonstrated with production capacities of a few hundred thousand liters of EtOH per year. In the last five years, a number of commercial enterprises have been developed including the joint venture between Raizen Energia and Iogen (30,000 tonnes ethanol yr⁻¹) and GranBio (65,000 tonnes ethanol yr⁻¹) both in Brazil, as well as Abengoa and Du Pont in the US. However, most enterprises in the USA had halted production by 2017, due to the strict blending ceiling for ethanol and being uncompetitive with first generation bioethanol plants on both price and volume. Another promising development is through the C1 fermentation of syngas, which can be generated through the gasification of biomass. Lanzatech currently produces bioethanol from off-gas with a plant capacity of 46,000 tonnes yr⁻¹, using the strain *Clostridium autoethanogenum* (Karlson et al., 2018).

At present, lignocellulosic ethanol is unable to compete with fossil gasoline or first generation ethanol, which gives little market incentive for further development in this area. The major challenge in the bioethanol

industry lies in the high processing cost of which 33% is accounted by biomass pretreatment (Kang et al., 2014), as well as the high cost of enzymes. Incentive policies would be necessary to promote its development with proposed minimum direct subsidy of \$1.20/gal EtOH (Zhao et al., 2015). It is economically attractive to use bioethanol as a feedstock for a biorefinery producing higher value products than just biofuels. One example is the commercialized dehydration of ethanol to ethylene and subsequent polymerization to polyethylene (Morschbacker, 2009).

Butanol is also produced industrially from biomass and is generally sold in the commodity chemical market rather than as a biofuel. Renewable n-butanol is globally produced through acetone-butanol-ethanol (ABE) fermentation originally using *Clostridium acetobutylicum*, which has been operated on industrial scale for over 100 years (Sauer, 2016). After being outcompeted by its synthetic equivalent in the 1950s, nowadays, most efforts toward commercial ABE fermentation take place in China (Green, 2011). To produce high-quality n-butanol with *Clostridium* strains, Green Biologics purchased an ethanol plant (Little Falls, USA) in 2014 and retrofitted it. In addition to *Clostridium* spp., *Saccharomyces cerevisiae* is frequently modified to produce n- and iso-butanol. For example, both Gevo (Luverne, USA, 5,000 tonnes capacity, 2016) and Butamax (Scandia, USA), a joint venture of BP and DuPont, produce isobutanol at the industrial scale. Both companies retrofitted existing ethanol plants, in response to market saturation in the ethanol market. Producing butanol from lignocellulosic hydrolysates is more challenging due to the lack of substrate flexibility and low inhibitor tolerance of strains (Amiri & Karimi, 2018). Consolidated bioprocessing, where the enzymes for substrate hydrolysis and the fermentation are completed in one reactor, is being developed and small titers of butanol have been produced on cellulose and xylans with recombinant bacteria and mixed cultures. Despite promising results, this work has yet to be commercialized, and titers would need to be improved substantially for an economic process (Jiang et al., 2019).

Other successful bulk chemicals include lactic acid. There has been a rapid and steady increase in global lactic acid production since 2008, mainly driven by the demand in the bakery industry and the development of lactic acid esters and poly(lactic acid). The lactic acid market is approximately 1 million tonnes, in which PLA amounts to approximately 200,000 tonnes. Currently all lactic acid produced biologically is from first generation feedstocks, and the cost of raw materials is one of the key impacts on the lactic acid economy. Research is ongoing to process lignocellulosic biomass. For example, *Lactobacillus brevis* and *Lactobacillus pentosus* have been used in a mixed culture to produce lactic acid using wheat straw hemicelluloses (Eş et al., 2018). Significant work in process intensification and

SSF for lactic acid production has been published recently, producing second generation lactic acid, which is potentially cost comparable to lactic acid from first generation sources (Marques et al., 2017).

A range of diols are also produced industrially, or are close to commercialization, the most successful being 1,3-propanediol that has been produced on a large scale by Du Pont and Tate & Lyle since 2006. Production is still underway effectively, and a large increase of a further 15,000 tonnes was announced in 2018. While still produced from first generation feedstocks currently, a large research effort is underway to produce a lignocellulosic route, however, costs remain prohibitive on the large scale.

The biological production of succinic acid has also been developed recently. Succinic acid can be used in manufacture of 1,4 butanediol, polymer and esters, polybutylene succinate, solvents and coatings, polyester polyols and plasticizers, with 1,4 butanediol having the largest market (Nghiem et al., 2017). It can also replace butane-based maleic anhydride which has since played a crucial role in bio-refining process. Roquette produces Biosuccinium® using an acidophilic yeast platform and corn starch hydrolysate as growth medium while Myriant has already developed a lignocellulosic process using sorghum grains as feedstock. In 2014, Corbion, in collaboration with BASF- Spain (Succinity GmbH), fully commercialized the process using *Basfia succiniciproducens*, with an initial capacity of 10,000 tonnes. The market for bio-based succinic acid is expected to face significant growth over the next five years (Nghiem et al., 2017). This growth is significantly driven by increase in the number of emerging applications, such as (non-phthalate) plasticizers, resins, and polyester polyols for polyurethanes. Key market players include BASF SE and Corbion N.V. (Succinity GmbH), Myriant Corporation, Koninklijke DSM N.V and Roquette Frères S.A (Reverdia) and BioAmber Inc. Overall, substantial capital requirement and high processing cost remain bottlenecks to the market growth, despite the relatively high price of succinic acid. Recent studies have shown the superior economics of the bio-based process when compared with the nonrenewable route (Nghiem et al., 2017).

Terpenes are also commercialized products, which contain no heteroatoms and so have a wide range of applications in advanced biofuels and biopolymers. The first system to be commercialized was farnesene, a branched sesquiterpene (α - and β -isomers), which naturally occurs in plants and animals, and is microbially produced as a pure enantiomer on industrial scale by engineered *Saccharomyces cerevisiae*. Through chemical modifications it constitutes a precursor for a large variety of products including cosmetics (e.g. squalane), fragrances, polymers, lubricants, detergents, and jet and diesel fuel. The strain has been developed by Amyris utilizing heterologous expression of β -farnesene synthase and strain

improvements through synthetic biology (Kirby et al., 2016; Meadows et al., 2016; Sandoval et al., 2014; Westfall et al., 2012). Commenced in 2012 and running on sugarcane, the 1200 m³ production plant is located in Brotas, near São Paulo, Brazil, producing up to 24,000 tonnes/yr farnesene (Benjamin et al., 2016). The company announced the production cost of β -farnesene as \$1.75 in 2015, but there were challenges concerning production rates and consistent yields at scale. In 2016, an alliance to investigate utilization of lignocellulosic feedstock was formed, but shortly after, at the end of 2017, the Amyris Brasil Ltda, which owned and operated the production facility, was sold to DSM. This deal included the intellectual property on farnesene production and was designed to fund Amyris' specialty plants – away from high-volume and toward sweetener production.

2.3.3. Promising novel bioproducts under development

While the compounds discussed above are the most developed to date, a range of alternative platforms for chemical manufacture are recently at, or very close to, commercialization. These include muconic acid, fumaric acid, isobutanol, artemisinic acid, acrylic acid, fatty acids, triglycerides and fatty alcohols, vanillin, resveratrol, saffron, stevia, valencene, nootkatone, cephalixin, adipic acid, sabacic acid, hexamethylenediamine, amino acids, alternative diols, mandelic acid, isoprene, butenes as well as a range of biopolymers such as polyhydroxylalkanoates (Tables 3 and 4).

2.4. Comparisons

The opportunities and limitations of biological, conventional thermal, and microwave processes from the technical perspective are summarized in Figure 1. The biological methods are versatile as demonstrated by a wide range of compounds synthesized on the laboratory scale, including fermentation alcohols, aldehydes, ketones, aromatics, hydrocarbons etc. With advances in genetic engineering and directed evolution, any desired small precursor could potentially be produced by a microorganism effectively. Bioprocessing is capable to assimilate complex feedstocks and produce one well-defined molecule, which is extremely attractive for bulk chemical production. However, only a handful of organisms are currently used for industrial biotechnology in view of some critical hurdles in large-scale production. These hurdles include the lack of sterility at high production volumes, microbial culturing in extreme conditions and at the required cell density, the need for a wide sugar and oligosaccharide catabolism, and the inhibitor tolerance for processing lignocellulosic hydrolysates. From a processing perspective, aerobic routes are limited by the oxygen requirement and difficult mass and gas transfer issues in large scale fermenters. All

lignocellulosic processes are associated with extremely high capital expenditures and the high cost of enzymes and separations, especially of complex fermentation broths, can add substantially to the production cost. As for social concern, the lack of acceptance of genetically modified organism (GMO) products in some sectors also poses challenge to commercial bioprocessing.

In comparison, thermochemical processes employ economical catalysts in place of expensive enzymes in bioprocessing, which enable faster reactions in general to reduce operating time. The use of solid catalysts allows for recycling and reuse of the spent catalysts, which may further lower the production cost. However, thermal processes often suffer from the formation of side products, particularly when the feed is a complex mixture and extreme conditions are adopted. While conventional thermal processes remain popular at both research and industrial levels, microwave draws increasing attention in view of its potential in selective activation of substrate and lower energy demand. However, microwave may not entirely replace conventional heating in view of the temperature limit, in which thermodynamic hurdle could take place. Considering the opportunities and limitations of these technologies, novel combination of thermochemical routes with biological processes shows a potential economic advantage over traditional bioprocesses in preliminary studies (Leow et al., 2018), which are further discussed in Section 4.

3. Techno-economic and environmental considerations

3.1. Biochemical routes

A key driver for the implementation of biofuels and biochemicals is the potential to reduce greenhouse gas (GHG) emissions compared with crude oil derivatives. The ethanol production via biochemical conversion of lignocellulosic biomass has been evaluated via life-cycle assessment (LCA) (Borrion et al., 2012; Morales et al., 2015; Singh et al., 2010). In the UK, GHG emissions from the 2nd generation energy crops range from -7 g CO₂ eq/MJ to 310 g CO₂ eq/MJ, which is highly dependent on the land-use change (Azapagic, 2014). Considerable variations in the emissions are also seen for the biorefinery of wood (-90 to 40 g CO₂ eq/MJ), switchgrass (-70 to 6 g CO₂ eq/MJ), and other agricultural waste (13–72 g CO₂ eq/MJ) (Morales et al., 2015). In biochemical industry, emissions from succinic acid production range from 0.87 kg CO₂ eq kg⁻¹ (industrial scale based on Myriant Corporation data) (Moussa et al., 2016) to 2.4 kg CO₂ eq/kg⁻¹ using corn stover (Adom et al., 2014). Meta-analysis of different LCA results suggested that the production of most bio-based chemicals reduced GHG emissions compared to their fossil-derived counterparts, except for p-

xylene, acetic acid, and adipic acid, while emission information for several lignin-based priority chemicals are missing (Montazeri et al., 2016). In addition to global warming potential, studies have often shown relatively high human toxicity, ecotoxicity, acidification and eutrophication impacts relating to agricultural practices. From an economic perspective, feasibility is often highly dependent on feedstock cost and initial capital investment. ABE fermentation using corn stover is estimated to yield butanol priced at \$0.6–1.8/L (Baral & Shah, 2016), whilst a break-even price for succinic acid has been estimated at \$660 (AU\$990) (Ghayur et al., 2019), \$2,260 (Efe et al., 2013), and \$9,000 (Lam et al., 2014) per metric tonne, depending on feedstock cost, fermentation productivity, and system performance.

3.2. Thermochemical routes

Previous work reviewing the production costs associated with methanol production from gasification (including upgrading) estimated this to be \$0.29–0.45/kg, with the hydrogen production cost lower for forest residues (\$1.17–1.3/kg) than that for agricultural residues (\$1.29–\$1.33/kg) (Patel et al., 2016). For pyrolysis of energy crops, the price of bio-oil is estimated at \$12–26/GJ (Patel et al., 2016; Rogers & Brammer, 2012), where selling the biochar by-product can reduce the production cost by up to 18%, rendering the process economically feasible (Patel et al., 2016). Production cost is highly dependent on what the end products are and which thermochemical conversion technology is employed. Microwave-assisted pyrolysis has been demonstrated to yield a return of investment (ROI) of 45.34%/year or a pay-back for the investment in only 2.2 years (Wang, Lei, et al., 2015). Here, ROI is the most sensitive to the yield and selling price of bio-oil. As for environmental significance, a reduction in GHG emissions is generally demonstrated in LCA studies, compared to conventional petroleum-derived products, while feedstock is a major determinant of the emissions similar to the case of bioprocesses. Global warming potential from fast pyrolysis ranges from –0.6 to 2.9 kg CO₂ eq/L and that for slow pyrolysis (biochar production) amounts to –1500 to 160 kg CO₂ eq/dry ton relative to fossil fuel systems (Roy & Dias, 2017). For unconventional heating, microwave-assisted extraction of pectin from waste orange peel was shown to be environmentally preferable to acid-assisted conventional heating across all impact categories assessed (Garcia-Garcia et al., 2019).

3.3. Comparisons

The sustainability of biomass conversion routes should take into account all technical, environmental, and economic factors - as well as social

Table 5. Conversion of different biomasses in integrated biorefineries.

Biomass	Process	Product	Reference
Spent coffee grounds (SCGs)	Organosolv process Enzymatic hydrolysis Enzymatic isomerization Acid dehydration	35 g HMF/kg SCG	(Pereira et al., 2019)
Green alga (<i>Scenedesmus acutus</i>)	Acid pretreatment Charged polyamide induced flocculation Fermentation Catalytic deoxygenation and/or hydroisomerisation (algal oil upgrading)	60% Succinic acid (purity 98.4%) 47.6% Renewable diesel blendstock	(Knoshaug et al., 2018)
Rapeseed meal	Microwave-assisted depolymerization Fermentation (30 L pilot scale)	12 g/L yeast biomass (22% w/w lipid)	(Santomauro et al., 2018)
Dried distillers grains with solubles	Microwave-assisted depolymerization Fermentation	8.38 g/L yeast biomass (20% w/w lipid)	(Fan et al., 2018)
Food and beverage waste	Enzymatic hydrolysis Enzymatic isomerization Separation in a Simulated Moving Bed Acid dehydration	30 g HMF/kg waste	(Yu, Ong, et al., 2018)

implication which have not been covered in this review. Due to a lack of industrially relevant data, similar challenges exist when assessing both biochemical and thermochemical routes. The considerable variations in environmental and economic impacts are associated with the breadth of system performance assumptions, level and allocation of environmental burdens from agriculture, and feedstock cost. Lack of standardization in terms of methodology and approach (including intrinsic assumptions and boundary conditions) makes direct comparison between biochemical and thermochemical processes highly challenging at present.

4. Integrated Biorefineries

4.1. Recent developments

A few recent reports on integrated biorefineries are shown in Table 5. An effective pretreatment step can fractionate biomass into multiple streams that can then be processed separately, producing an array of products far more efficiently than if the entire biomass is transformed by one processing method. There are multiple routes to achieve this including additive-free microwave processing, mechanochemical routes, thermochemical hydrolysis, and organosolv process. In the organosolv process for example, an organic solvent such as methyl isobutyl ketone (MIBK) is used with water, other co-solvents and an acid catalyst, to fractionate biomass into a lignin enriched bio-oil, a solid cellulose fraction, and a solubilized hemicellulose sugar fraction (Bozell et al., 2011; Katahira et al., 2014). This approach has been demonstrated successfully on multiple feedstocks including corn stover (Katahira et al., 2014). Recently, Pereira et al. demonstrated the suitability of the Organosolv process in the valorization of spent coffee

grounds, effectively converting the cellulose fraction to 5-HMF and fermenting the sugars with an oleaginous yeast (Pereira et al., 2019). However, the authors noted that the use of co-solvents, which are vital to produce more specific fractions, substantially affect the ability to biochemically process the sugar fraction.

An alternative integrated biorefinery process was demonstrated for microalgal fuel production. The Combined Algal Processing (CAP) approach uses a dilute acid pretreatment to hydrolyze the microalgal carbohydrates for fermentation, while making the lipid fraction more available. The entire process is run prior to extractions, and therefore can be used to produce 'green' diesel and ethanol from the same process. The techno-economic analysis (TEA) indicated that the CAP reduced the cost of microalgal biofuel by up to \$0.95 per gallon gasoline equivalent (GGE), over any other configuration (Dong et al., 2016). The authors also demonstrated this process to produce bulk chemicals such as succinic acid alongside the fuel product effectively (Knoshaug et al., 2018).

Similarly, microwave heating can be used in the initial fractionation stage. For example, a microwave-assisted additive-free pretreatment was used to solubilize the majority of the hemicellulose fraction and some of the cellulose. The hydrolysates produced were rich in oligosaccharides, protein, and sugars. These were then converted successfully by the yeast *Metschnikowia pulcherrima* which could produce lipids, 2-phenylethanol, and polyols by catabolising a large proportion of the mono- and oligosaccharides in the hydrolysate (Remón et al., 2018; Zhou, Santomauro, et al., 2017). This process has been demonstrated on multiple feedstocks, including wood residues, rapeseed meal, macroalgae, agricultural residues, and brewing wastes (Fan et al., 2018; Santomauro et al., 2018).

Further examples of integration biological-microwave thermochemical technology have been evaluated for producing HMF from food and beverage waste (Yu, Ong, et al., 2018). Enzymatic hydrolysis and isomerization gave rise to a mixture of glucose and fructose, which were subsequently separated using a Simulated Moving Bed system. The resultant high-fructose sirup (89.0 g/L) appeared as an attractive substrate for HMF formation (yield 71%, selectivity 77%) over a commercially available solid catalyst (i.e. Amberlyst 36) under microwave heating.

These microwave processes tend to leave lignin and cellulose enriched residues. Valorization of the residues via pyrolysis is one of the possible options. However, the application of the pyrolytic products should depend on the chemical composition of the residues. For example, the Sn-containing humins resulted from the SnCl₄-mediated conversion of food waste to HMF could be a potential precursor for the synthesis of Sn-containing catalysts (Yu, Tsang, Yip, et al., 2017). Biochar-supported Al (Yu, Xiong, Tsang,

Wang, et al., 2019), Sn (Yang et al., 2019), N (Chen, Yu, Cho, et al., 2018), phosphate (Cao, Yu, Tsang, et al., 2018), and sulfonate (Cao, Yu, Chen, et al., 2018; Xiong et al., 2018) catalysts have been fabricated for hydrolysis, isomerization, and dehydration of carbohydrates and saccharides. This highlights the potential of humins as a renewable precursor of carbon-based solid catalysts for biomass conversion to achieve a circular bioeconomy.

4.2. Limitations, research gaps, and opportunities

Collection, transportation, land allocation for storage and processing, political incentives, and market analysis and positioning should be figured out before deploying integrated biorefineries in the industry (Maity, 2015). In addition, there are critical technical aspects that deserve more research efforts.

4.2.1. Complex biomass structure

The wide variety of biomass feedstocks has been a concern to commercializing biorefinery technologies yet not the most critical in view of the recent developments of pyrolysis (e.g. Biomass Technology Group, The Netherlands) and hydrothermal processes (e.g. TerraNova Energy GmbH, Germany; AVA Biochem, Switzerland) at the commercial scale. The major challenge rather lies in the complex structure of biomass. Although the above processes are suitable for breaking down sewage sludge and woods, the product streams are often restricted to a heterogeneous mixture, such as biochar and bio-oil, instead of a specific platform chemical with potentially high market value. This reflects the lack of cost-effective organosolv-catalytic techniques for highly selective product control in thermal processes. In comparison, bioprocesses are more mature and capable of producing bulk chemicals, but the feedstocks are often limited to sugar-rich homogeneous matrix and the recalcitrant biomass is not favorable. Therefore, thermal and biological processes own different niches, which should be clearly identified for strategic development of integrated biorefinery, in order to maximize the economic return and carbon efficiency. As thermochemical processes can be selective in a macro-sense (lignin, hemicellulose, cellulose), they may contribute to the first step to rapidly loosen the biomass structure, after which the solubilized fractions can be upgraded by bioprocesses that are molecular-selective. Thermal treatment in advance also achieves sterilization, a prerequisite to maintain microbial activity.

4.2.2. Technological advances

While some conventional thermal processes and bioprocesses have been commercialized, microwave processing of lignocellulosic biomass is in the

embryonic stage as pilot-scale operations start recently at university or research center level. In view of the intriguing experimental observations in the literature, more in-depth studies are needed to capitalize and maximize the potential of microwave and address any technical uncertainties. For organic synthesis (e.g. Pd/C-catalyzed synthesis of benzimidazoles), it was recently reported that a biomass-derived solvent, namely γ -valerolactone (GVL), has a good microwave absorptivity, high stability, and high boiling point (208 °C), which can suppress the formation of destructive hot spots resulted from arcing (Petricci et al., 2018). Hot spots were often reported to lower the efficiency of metal- and carbon-based catalysts in organic synthesis, particularly, under dry conditions and/or high microwave power (Chen et al., 2012; Petricci et al., 2018). Nevertheless, proper control of hot spot generation could be beneficial. Ji et al. devised a solid acid catalyst with a carbon nanotube core, which served to absorb microwave for energy-efficient conversion of saccharide to HMF (Ji et al., 2017). Other carbonaceous materials such as graphene (oxide) (Meng et al., 2018; Yu, Xiong, Tsang, Ng, et al., 2019) may also have the potential of being the catalyst support/core, of which their hotspot effects deserve further examination.

4.2.3. Compatibility

Attentions should be paid to the compatibility between thermochemical and biochemical processes when designing an integrated biorefinery, which requires close and synergetic collaboration between researchers from cross-disciplinary fields. The requirements of the intermediate products that enter the next process must be understood by both chemists and biologists. For instance, HMF, furfural, and organic acids are often present in hydrolysate, which may exert inhibitory effects on microbial growth (Remón et al., 2018). The formation of inhibitors should be suppressed via chemical engineering. Alternatively, detoxification of hydrolysates or protective barriers for yeasts can be considered (Liu et al., 2016). Solvents and catalysts used in a thermochemical process should be carefully chosen or well separated after reaction to avoid potential impacts on the subsequent biological process.

4.2.4. Sustainability assessment

LCA and TEA are common tools to evaluate the sustainability of new technologies. Apart from the lack of industrially relevant data and standardized methodology (Section 3.3), the lack of comprehensive inventory database in the context of biorefinery poses a challenge to researchers. The biomass-derived products are relatively new compared to the conventional

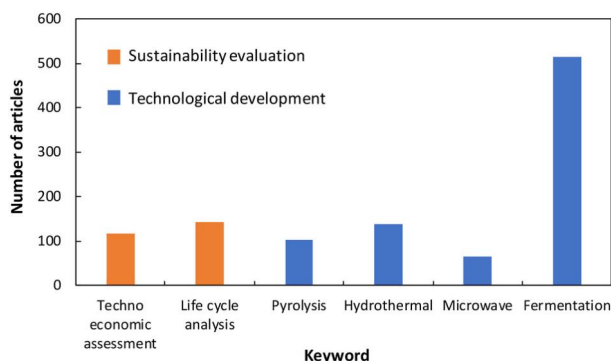


Figure 5. Estimated numbers of articles in regard to sustainability evaluation and technological development according to Scopus (search: keyword and “biorefinery” in *Article title, Abstract, Keywords*; year: 2014-present; document type: *Article*). The numbers for technological articles were obtained by subtracting the numbers of articles additionally containing “life cycle analysis” and “techno economic assessment” from the total number of articles containing the specific keyword and “biorefinery”.

petroleum derivatives so their information could be missing from the database. The same difficulty exists when evaluating the use of emerging materials, such as advanced solid catalysts and green solvents. Understanding of the sustainability of biorefineries is lagging behind their technical advances (e.g. improved product yield and selectivity, decreased energy demand), as reflected by the estimated numbers of research articles in the respective categories in the last five years (Figure 5). More research efforts on validating and quantifying the sustainability of novel biorefinery technologies using standardized performance metrics are encouraged.

5. Conclusions

Lignocellulosic biomass is a renewable resource for the production of value-added chemicals, which are substitutes for their petroleum-derived counterparts for the goal of sustainable development. While biochemical technologies have dominated the early commercial processes, there is a growing number of research studies on thermochemical and microwave-based processes, of which the technological advances are introduced in this critical review. Future investigations should focus on efficient fractionation of lignocellulosic biomass and design of durable and green catalysts, to enhance product selectivity and suppress side reactions, which are one of the major challenges in the thermochemical processes. Microwave-assisted processes have been proven promising, yet the mechanistic roles and untapped potential of electromagnetic waves require more in-depth understanding. Research efforts on integrated thermochemical-biological are encouraged to synergistically promote product yields and diversify the product streams. Examples include microwave pretreatment prior to

anaerobic digestion and microwave hydrolysis followed by fermentation. Sustainable biorefineries can be actualized via cost-effective integrated treatments of lignocellulosic biomass for promoting a circular bioeconomy.

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