Review

Thermochemical Conversion of Lignocellulosic Biomass into Mass-Producible Fuels: Emerging Technology Progress and Environmental Sustainability Evaluation

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ABSTRACT: Lignocellulosic biomass is increasingly recognized as a carbon-neutral resource rather than an organic solid waste nowadays. It can be used for the production of various value-added chemicals and biofuels like bio-oil. However, the undesirable properties of bio-oil such as chemical instability, low heating value, high corrosivity, and high viscosity are greatly restricting the utilization of bio-oil as a drop-in fuel. As a consequence, bio-oil should be upgraded. Recently, several emerging methods, such as electrocatalytic hydrogenation, atmospheric distillation, and plasma-assisted catalysis, have been developed for improving the bio-oil quality under mild conditions. Here, we overview the new knowledge on the molecular structure of lignocellulosic biomass gained over the past years and discuss the future challenges and opportunities for further advances of the bio-oil production and upgrading from lignocellulosic biomass. The development of sustainable biomass resource recycle systems with improved efficiency and minimized environmental impacts is analyzed in details. Also, their environmental impacts and sustainability are evaluated. Lastly, the remaining knowledge gaps are identified, and the future research needs that may lead to massive production of biofuels from lignocellulosic biomass are highlighted.

KEYWORDS: Lignocellulosic biomass, Biofuels, Bio-oil upgrading, Thermochemical conversion, Sustainability evaluation
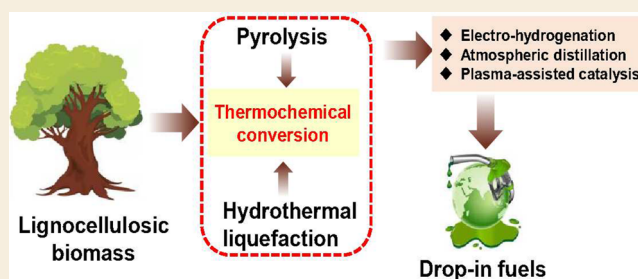
INTRODUCTION

The shortage of fossil energy and increasingly severe environmental pollution and global climate change are pushing countries all over the world to actively develop clean and renewable energy. In this regard, developing clean and renewable energy to replace fossil energy is greatly needed. Lignocellulosic biomass is the fourth major energy source behind coal, petroleum, and natural gas in Earth. Biomass is recognized as a carbon neutral resource as it is produced from green plant photosynthesis using carbon dioxide in the atmosphere as a raw precursor.[1] Large-scale recycling of the biomass can help achieve the goal of "carbon neutrality".

The world produces more than 20 billion tons of lignocellulosic biomass waste ever year.[2] This waste mainly includes agricultural and forest waste like corn stalks, wheat straws, and sawdust. Due to the strict laws and regulations as well as low economic benefits, most of the waste is not treated in the right way. Much of it is just burned outside or during home cooking in many rural areas.[3] Nevertheless, the combustion of biomass outside will inevitably result in severe environmental pollution problems.[4,5] First, burning of biomass produces heavy smog, thus reducing the visibility, affecting the air quality, and causing road traffic accidents.[6,7] Second, the incomplete combustion of biomass will produce large amounts of persistent organic pollutants (POPs), including oxygenated polycyclic aromatic hydrocarbons (OPAHs) and dioxins.[8] Third, burning of biomass is also an important contributor to the formation of fine particulate matter like $PM_{2.5}$ and PM_{10}.[9] Apart from its solid waste nature, biomass is also a renewable and abundant resource and could be used as a promising alternative to fossil fuels for the production of chemicals and fuels.[10] Moreover, conversion of biomass into fuels and chemicals is recognized as a carbon-neutral circular framework, which is particularly appealing for our sustainable society.[11]

Microbe-mediated transformation and thermochemical conversion are the two most widely used methods for converting biomass waste into value-added resources.[12] Anaerobic and aerobic digestion are two different pathways involved in the microbially mediated biomass transformation processes. Both of them involve various metabolic reactions
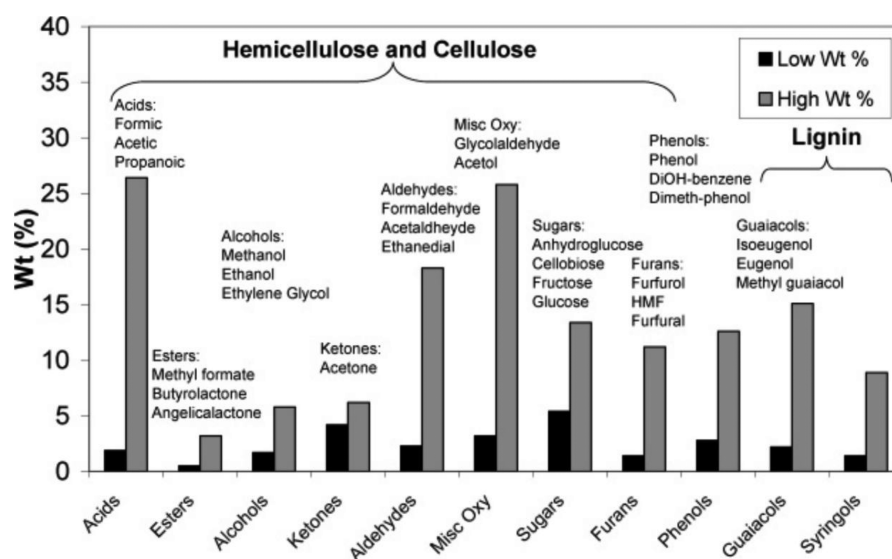
Figure 1. Typical organic compounds in bio-oil and their contents. (Reproduced from ref 11. Copyright 2006 American Chemical Society.)

like acidogenesis, methanogenesis, hydrolysis, and oxidation. These reactions usually proceed very slowly and are hard to control.[13] In these reactions, besides the desired products, large amounts of greenhouse gas (GHG), such as carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O),[14] are also produced and released to the atmosphere, greatly accelerating global climate warming.

Unlike the microbially mediated transformation, the thermochemical approach can efficiently convert the biomass into fuels or chemicals in a sustainable and very rapid way.[15] Many thermochemical methods such as pyrolysis,[16] gasification,[17] and hydrothermal liquefaction,[18] have been widely used for biomass conversion. Among all these methods, hydrothermal liquefaction and pyrolysis have been reported to be two of the most economically feasible and environmentally friendly routes for biomass conversion.[19]

The most important product formed in the hydrothermal liquefaction and pyrolysis of biomass waste is bio-oil, which is a free-flowing, dark brown oily liquid with a distinctive smoky odor.[20] From the viewpoint of chemistry, bio-oil can be regarded as a mixture of various organic compounds and water.[21] As shown in Figure 1, the organic compounds in bio-oil usually include phenols, aldehydes, ketones, and carboxylic acids as well as some oligosaccharides and pyrolytic lignin produced primarily from the partial decomposition of cellulose, hemicellulose, and lignin.[22] Some of these compounds are the main contributors to the undesirable features of bio-oil, such as chemical instability, low heating value, and strong corrosiveness.[23] An efficient upgrading process is therefore greatly needed to improve the bio-oil quality before it can be used as a drop-in fuel. Conventional bio-oil upgrading methods include hydrogenation,[24] catalytic cracking,[25,26] and steam reforming.[27,28] After upgrading, the unstable compounds (e.g., phenols, aldehydes, and ketones) in bio-oil can be converted into light hydrocarbons and aromatics as well as syngas (CO and H_2). Hydrodeoxygenation, ketonization/aldol condensation, aromatization, as well as cracking are the main chemical reactions occurring in the bio-oil upgrading processes. For example, in the catalytic cracking of bio-oil, C–C bond cleavage, isomerization, aromatic side-chain scission, H_2 transfer, and deoxygenation reactions (e.g., dehydration,

decarbonylation, and decarboxylation) are the main chemical reactions, producing light hydrocarbons and aromatics. The bio-oil, after coprocessing with petroleum feedstock or renewable feedstock like rapeseed oil, can be directly used as a drop-in fuel.[29,30] The coprocessing technology is therefore regarded as one of the most promising options for upgrading bio-oil. For more detailed information on the conventional bio-oil upgrading technologies, readers can refer to many previous excellent review articles and book chapters by Zhou et al.,[31] Xiao and Beach,[32] Graça et al.,[33] Wang et al.,[34] Liu et al.,[35] and Ardiyanti et al.[36] and references therein.

These review articles on bio-oil upgrading focus on the hydrogenation, catalytic cracking, steam reforming, and some other conventional thermochemical methods. However, as there are large amounts of unstable carbonyl compounds in bio-oil, it tends to polymerize and produce carbon deposition under high temperature and pressure conditions, resulting in reactor blockage and catalyst deactivation. Thus, several emerging methods, such as electrocatalytic hydrogenation, atmospheric distillation, and plasma assisted catalysis, have been developed for improving the quality of bio-oil under mild conditions (e.g., ambient temperature and/or atmospheric pressure). Since the significance of resource recovery and sustainable development has been widely recognized and is increasingly practiced today, it is not only important but also very timely to systematically review the progress of bio-oil upgrading with emerging technologies under mild conditions. Therefore, in this Review, we provide critical information on the research advances in this field and look to future development trends and research directions. For this purpose, the existing technologies for converting biomass wastes, mainly lignocellulosic biomass, to bio-oil, then to mass-producible biofuels under mild conditions will be discussed. Also, the potential science and engineering research pathways, process and product challenges, as well as future directions addressing these challenges will be highlighted.

STRUCTURE AND COMPOSITION OF LIGNOCELLULOSIC BIOMASS

Before discussing the thermochemical conversion of lignocellulosic biomass into fuels, a primary illustration of the structure
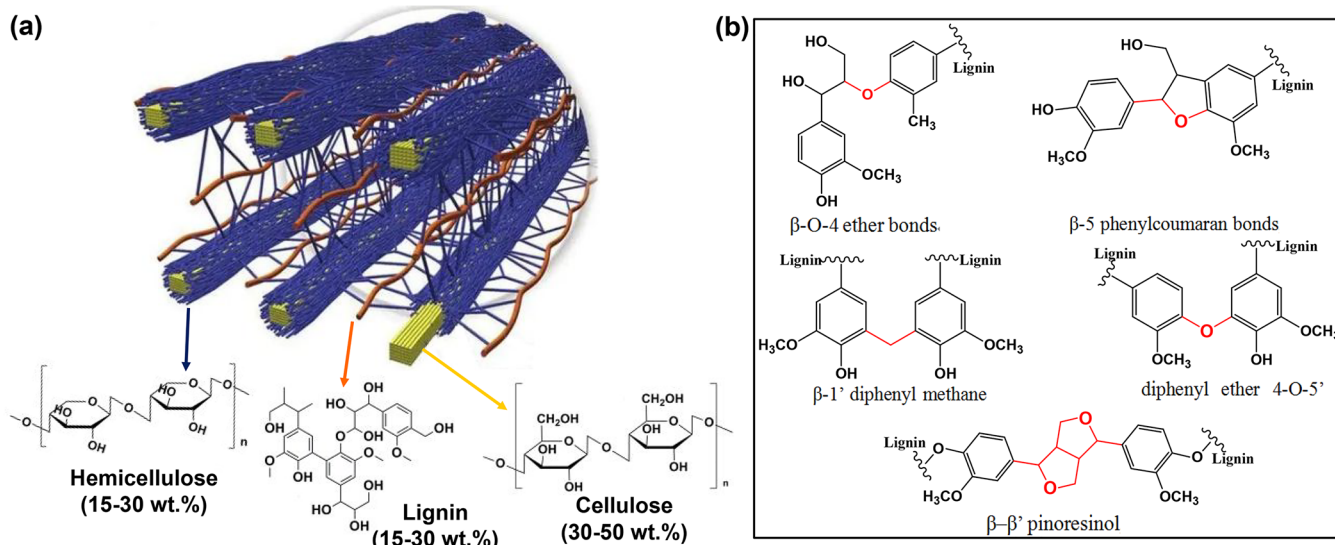
Figure 2. (a) Schematic analysis of the location and structure of hemicellulose, cellulose, and lignin in lignocellulosic biomass; (b) five typical bonding patterns in a lignin matrix structure.

and composition of lignocellulosic biomass is essential to provide a scientific base for understanding the behaviors and mechanisms of the thermochemical conversion processes. As shown in Figure 2a, cellulose, hemicellulose, and lignin are the three key building blocks of lignocellulosic biomass.[37] Among them, cellulose is the most abundant component in lignocellulosic biomass, which often composes 40−50% of its total weight. Cellulose is a homopolysaccharide consisting of more than 3000 β-glycosidic bond linked β-D-glucopyranose units, acting as one of the basic structural components of plant cell walls.[38] Unlike cellulose with a homopolymer nature, hemicellulose is an amorphous branched polysaccharide composing 15−30% of the total biomass weight. Xyloglucan, xylans, mannans and glucomannans, and β-(1 → 3, 1 → 4)-glucans are identified as the main structure units of the hemicellulose.[39,40]

Differing from cellulose and hemicellulose with polysaccharide structures, lignin is a recalcitrant polymer consisting of phenyl-propane units, filling the spaces of hemicellulose and cellulose, and holding together the matrix of the whole plant cell.[41] Lignin composes 15−30% of the total biomass weight, with three primary monomers as the structure unites, i.e., p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol.[42] Five linkage patterns are identified in the matrix of lignin (Figure 2b), including β-O-4 ether, diphenyl 4-O-5′ ether, β-β’ pinoresinol, β-5 phenylcoumaran, and β-1’ diphenylmethane. Among them, β-O-4 ether is the primary linkage of lignin, and effectively breaking the β-O-4 ether bond is regarded as the key point for the lignin valorization.[43] Unlike cellulose and hemicellulose, lignin is usually more hydrophobic as it contains more aromatic structures.[44] Meanwhile, the chemical valencies of the carbon atoms in lignin molecules are lower than those in cellulose and hemicellulose, which have an average redox number of about −0.4, as compared to the redox number of 0 in cellulose and hemicellulose.[45] This suggests that lignin may have a higher energy content than cellulose and hemicellulose.

In addition to the main elements C, H, and O in cellulose, hemicellulose, and lignin, other heteroatoms, such as N, S, P, Cl, and metals (alkali and alkaline earth metals), are also found in lignocellulosic biomass.[46,47] These heteroatoms, despite being a very small percentage of the total biomass weight, may have much influence on the thermochemical conversion process. For example, alkali and alkaline earth metals, on the one hand, may act as catalysts in biomass thermochemical conversion process; on the other hand, they could be actively involved in the erosion, corrosion, and even breakdown of reactors for thermochemical conversion.[48,49] Therefore, illustrating the detailed structure and composition of lignocellulosic biomass is essential to find effective approaches to selectively convert biomass into the desired products (e.g., gas and liquid fuels) with high quality and suppress the formation of undesired products (e.g., pollutants and tar).

■ PRODUCTION OF BIO-OIL FROM LIGNOCELLULOSIC BIOMASS

Bio-oil is the liquid product obtained from thermochemical conversion, which has been recognized as an environmentally friendly resource because of its carbon-neutral nature. Bio-oil contains a large number of organic compounds like aldehydes (e.g., benzaldehydes and furfurals), acids (e.g., acetic and propanoic acids), ketones (e.g., cyclopentanones), phenols (e.g., guaiacols, cresols, and dimethyl phenol), and levoglucosan. Thus, bio-oil is regarded as a promising feedstock to produce high quality biofuels and value-added chemicals.[50,51] Two basic thermochemical processes are available for converting lignocellulosic biomass into bio-oil, i.e., pyrolysis and hydrothermal liquefaction. Both of them have been widely used to convert dry and wet lignocellulosic biomass.

Pyrolysis of Biomass

Pyrolysis is a thermochemical process for the decomposition of lignocellulosic biomass in the absence of oxygen or with a very limited oxygen supply at 300−800 °C. The main product of biomass pyrolysis, bio-oil, can be upgraded into drop-in fuels like gasoline and diesel.[52,53] More than 50 large-scale pyrolysis facilities have been built over the world. For example, the Empyro plant in The Netherlands could treat about 40 000 tons of dry lignocellulosic biomass to produce 25 000 tons of bio-oil every year.[54]

Pyrolysis, based on its heating rates, could be roughly classified into fast pyrolysis and slow pyrolysis, and the former
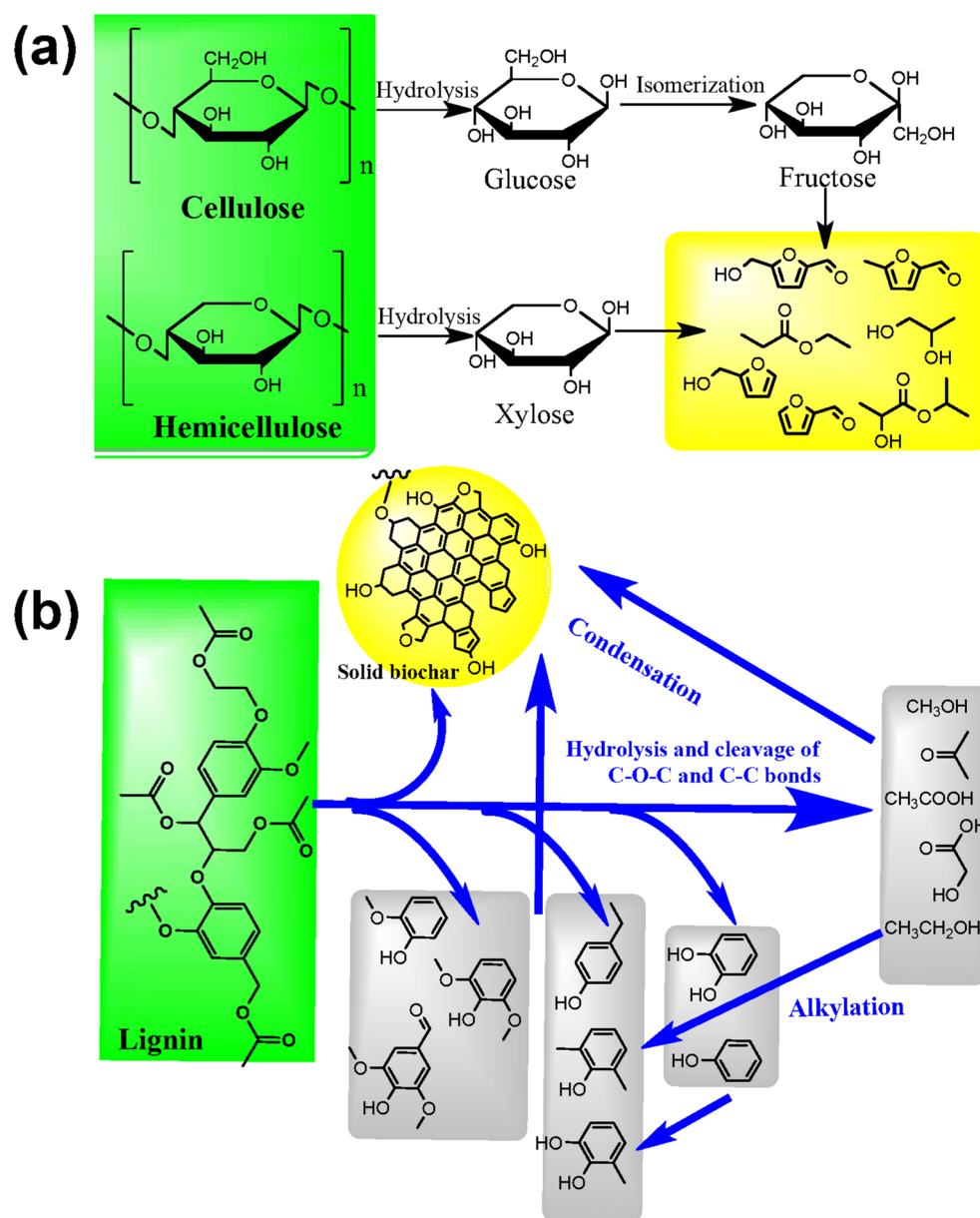
Figure 3. Possible mechanism for the hydrothermal conversion of lignocellulosic biomass. (a) Cellulose and hemicellulose and (b) lignin.

is regarded as a better process than the latter in the production of liquid fuels. The heating rates of fast pyrolysis are greater than 500 °C/s, which can yield more liquid products rather than biochar and gas products.[55,56] Due to the high heating rates and heat transfer rates at the particle interface and the low thermal conductivity nature, a finely ground biomass feedstock with an average particle size of 3 mm or less is required to facilitate the heat transfer process for fast pyrolysis. Meanwhile, to maximize the yield of liquid fuels, the temperature of fast pyrolysis usually needs to be carefully controlled at 500–600 °C, with the vapor residence time being lower than 2 s, in which case the secondary cracking of the vapor species produced in biomass pyrolysis could be greatly suppressed. Unlike the conventional fast pyrolysis of biomass, which needs small particles of biomass as feedstock, the ablative pyrolysis could employ large pieces of biomass rather than only small particles as feedstock, saving grinding costs. In a typical ablative pyrolysis process, the biomass with large pieces usually goes through a series of melting and/or sublimation reactions.

A steep temperature gradient is formed on the biomass surface, leading to the generation of a thin superficial reacting solid layer.[57] Although ablative pyrolysis is not the best process in the view of energetic efficiency, it is definitely the only process with great potential for a mobile application that is crucial to decrease the price of bio-oil.[58]

Although fast pyrolysis could be used for large scale conversion of lignocellulosic biomass into liquid fuels, its practical application is greatly limited by the uncontrollable quality of bio-oil originating from the complex and versatile chemical compositions of lignocellulosic biomass. In particular, the heteroatoms, including N, P, S, Cl, and alkali and alkaline earth metals, in the biomass may critically affect the quality of the bio-oil produced from the pyrolysis process. Moreover, some pollutants like NO_x, SO_x, and polycyclic aromatic hydrocarbons (PAHs), may be formed in the transformation of these heteroatoms in the pyrolysis process, resulting in some environmental pollution problems. To maximize the production of high quality bio-oil and suppress the possible

Table 1. Main Undesirable Properties of Bio-oil and Their Possible Impacts on Further Applications

undesirable properties	main causes	possible impacts
strong acidity	carboxylic acids formed in the pyrolysis of cellulose, hemicellulose, and lignin	strong corrosiveness
chemical instability	presence of compounds with carbonyl (C=O) and/or other unsaturated bonds (e.g., C=C), presence of large amount of oxygenated compounds.	increasing the viscosity of bio-oil; leading to a phase separation; lowering the chemical stability of the bio-oil
presence of small solid particles	incomplete solid−liquid separation	leading to catalyst poisoning during further upgrading of the bio-oil; leading to solid deposition during bio-oil combustion
presence of N, S, and P elements	biomass feedstock contains N, S, and P elements	leading to catalyst poisoning during further upgrading of the bio-oil; increasing the corrosiveness of the bio-oil; bringing some unpleasant odor
poor distillable property	presence of large amount of heat-labile compounds	reducing the separability of bio-oil; increasing the costs of value-added chemical separation from the bio-oil
high viscosity	presence of some oligomers of lignin, cellulose, and hemicellulose	reducing the mobility of the bio-oil
high moisture	high moisture contents in the biomass feedstock	reducing the heating value of the bio-oil

environmental impacts, several improved pyrolysis processes have been proposed, such as catalytic fast pyrolysis and copyrolysis of lignocellulosic biomass with other organic solid wastes like plastics and sludge.

Hydrothermal Liquefaction of Biomass

Hydrothermal liquefaction can be defined as a physical and chemical conversion of biomass with aqueous medium at high temperatures (250−374 °C) and pressures (4−22 MPa) under pressure-tight conditions.[59] Treating lignocellulosic biomass under hydrothermal conditions can increase its solubility, accelerate the physical and chemical interactions between the biomass and aqueous medium, and finally lead to the efficient decomposition of cellulose, hemicellulose, and lignin in the biomass to form liquid products. For cellulose and hemicellulose, their hydrothermal conversion starts with the hydrolysis of glucosidic bonds to form glucose and xylose, respectively.[60,61] Glucose and xylose can be further dehydrated and decomposed to form a series of furans and other C2−C5 compounds (Figure 3a).

For lignin, cleavage and hydrolysis of C−C and C−O−C bonds, alkylation, demethoxylation, and condensation are the main reactions, which are in competition with each other in the hydrothermal conversion process.[62,63] Among all the reactions, the cleavage of β-O-4 and $^{\alpha}$C−$^{\beta}$C bonds in the side chain has precedence,[64] while the bonds of aromatic rings are hardly affected under the hydrothermal conditions.[65] Lower temperature and shorter reaction time are in favor of the formation of phenolic monomers and dimers via preliminary cleavage of aliphatic C−C bonds and hydrolysis of C−O−C bonds.[66] As temperature and reaction time are increased, demethoxylation and alkylation of phenolic compounds may occur, producing more alkyl phenols (Figure 3b).[63]

One main advantage of hydrothermal liquefaction over fast pyrolysis may be that the former is able to deal with the high-moisture biomass feedstock directly without an energy-intensive drying operation.[66] However, unlike fast pyrolysis process, which has been an industrialized application for decades,[67] although hydrothermal liquefaction has been developed at a pilot scale,[68] there is still a long way to achieve its industrialized applications. The requirements of special reactor and separator designs, and high capital investments should be the main obstacles for the industrialized applications of hydrothermal liquefaction. Moreover, continuous operation of hydrothermal liquefaction is difficult because feeding biomass feedstock into the reactor under high pressures

remains a big challenge, which should be a major problem for operating a full-scale plant.[66] Though several disadvantages still remain before its commercialized utilization, hydrothermal liquefaction technology has immense potential to convert lignocellulose biomass into valuable chemicals and fuels once the above-mentioned problems are solved.

■ EMERGING TECHNOLOGIES FOR UPGRADING BIO-OIL INTO RENEWABLE BIOFUELS

Bio-oil and char (biochar or hydrochar) are two main products obtained from the pyrolysis or hydrothermal conversion of lignocellulosic biomass. Char is defined as a carbon-rich solid produced by the thermal decomposition (pyrolysis or hydrothermal conversion) of biomass at moderate temperatures (150−300 °C for hydrothermal conversion and 400−700 °C for pyrolysis) with little air. The raw char usually has a relatively low surface area and porosity, while it contains abundant surface functional groups (e.g., C=O, C−OH, and C−O−C) and minerals like N, P, S, Ca, Mg, and K.[69] These characteristics allow it to be used as an adsorbent, catalyst, or catalyst support after activation or functionalization.[70] Moreover, the easily tuned porosity and surface functionality of the char make it a promising platform for the preparation of various functional carbon materials, which can be applied in many interesting fields. A number of functional carbon materials have been prepared via the functionalization of char, and their applications can be found in the fields of catalysis,[71] energy storage,[72] pollutant removal,[73] and CO_2 capture.[74]

Bio-oil produced from either pyrolysis or hydrothermal conversion of lignocellulosic biomass has been regarded as a sustainable energy fuel because its combustion generates much lower amounts of GHG than those of conventional fossil fuels.[75] It has been reported that the combustion of bio-oil from woody biomass in an industrial boiler produces a NO_x emission of only 88 mg/MJ, much lower than that from the combustion of heavy fuel oil under similar conditions (193 mg/MJ).[76] However, some undesirable properties, such as chemical instability, strong corrosiveness, low heating value, and the presence of some solid particles, make bio-oil unsuitable for drop-in fuels.[77−79] Table 1 lists the main undesirable properties of bio-oil and their possible impacts on further applications. Among all the disadvantages of bio-oils, the most important ones affecting the fuel characteristics of bio-oil and its compatibility with other liquid fossil fuels

Table 2. Summary for the Advantages and Disadvantages of the Conventional Bio-oil Upgrading Technologies

upgrading methods	description	advantages	disadvantages
emulsification	blending the biodiesel or diesel into bio-oil with a surfactant to form a emulsion, aiming to improve the stability and heating value of the bio-oil	simple and easy-operation	high fossil fuel input; corrosion problems; high cost of surfactant
solvent addition	adding polar organic solvents (e.g., methanol, ethyl acetate, glycerol, ethanol, and n-butanol) into the bio-oil to decrease the viscosity and increase the stability of the bio-oil	simple and easy operation	cannot remove undesirable compounds from the bio-oil; organic solvent input; increasing overall cost for bio-oil upgrading
hydrotreatment	treating the bio-oil with H_2 in the presence of catalysts at high temperature and pressure	increasing the heating value and chemical stability of the bio-oil; effective to remove heteroatoms like N and S; well-established technology	high H_2 consumption; high temperature and pressure needs extra precautionary steps; catalyst deactivation and coke formation
steam reforming	upgrading the bio-oil through gasification to produce syngas at 700–1000 °C over Ni-based catalysts	producing H_2 as a clean energy resource	coke formation; catalyst deactivation; high reaction temperature associated with a high operating cost
catalytic cracking	removing oxygen from the bio-oil via the formation of H_2O, CO_2, CO in a fixed-bed or fluidized-bed reactor at temperatures more than 350 °C with a pressure up to 14 MPa	high yields of light hydrocarbon products	coke formation; Catalyst deactivation; High reaction temperature associated with a high operating cost
supercritical fluid reforming	upgrading the bio-oil in supercritical H_2O, methanol, or ethanol to enhance the energy content, reduce the acid number, heteroatoms content, and viscosity of the bio-oil	higher yields of light hydrocarbon products; better fuel quality with lower oxygen content and viscosity	high-cost of solvent; high-pressure resistant reactor required

Table 3. General Comparison between the Conventional Bio-oil Upgrading Processes and the Emerging Technologies

	carbon yield (based on the bio-oil)[a,c]	energy efficiency (based on the bio-oil)[b,c]	product quality			product application
			heating value[c]	stability[c]	deoxygenation degree[c]	
emulsification	~100%	~100%	36−45 MJ/kg	stable for 30−40 days	~0	drop-in fuels
solvent addition	~100%	~100%	24−36 MJ/kg	high resistance to aging	~0	drop-in fuels
hydrotreatment	65−95%	65−95%	38−48 MJ/kg	high resistance to aging	60−95%	drop-in fuels/bulk chemicals
steam reforming	<20%	35−50%	40−70 MJ/kg	stable in the absence of air	30−75%	syn-gas/H_2
catalytic cracking	60−75%	70−85%	35−42 MJ/kg	stable in the absence of air	40−80%	drop-in fuels/bulk chemicals
supercritical fluid reforming	35−85%	35−85%	28−36 MJ/kg	stable in the absence of air	25−60%	drop-in fuels/bulk chemicals
direct distillation	60−75%	50−75%	22−25 MJ/kg	stable in air	35−50%	biocoals
electrochemical hydrogenation	~100%	~100%	20−25 MJ/kg	high resistance to aging	<10%	bulk chemicals
plasma-assisted catalysis	60−75%	70−85%	35−42 MJ/kg	stable in the absence of air	70−80%	biofuels/bulk chemicals

[a]Carbon yield = 100% − (carbon released out of the products/carbon in the initial bio-oil) × 100%. [b]Energy efficiency = 100% − (energy released out of the products/energy in the initial bio-oil) × 100%. [c]These values were summarized based on the data reported in the references.

include the high moisture and oxygen contents, presence of solids (biochar particles), high viscosity, and chemical instability.[80,81] Therefore, upgrading processes are essential to reduce the impacts of the above-mentioned properties and improve the quality of the bio-oil before it can be used as a drop-in fuel.

The conventional bio-oil upgrading methods usually include physical and chemical approaches, such as emulsification, solvent addition, hydrotreatments, steam reforming, catalytic cracking, and supercritical fluid reforming.[82,83] The main advantages and disadvantages of these approaches are summarized in Table 2.

There are many review papers on conventional bio-oil upgrading methods from the past few years. To name a few, Zhang and co-workers[84] summarized the advances, challenges, and prospects of bio-oil upgrading via catalytic hydrotreatments, addressing future directions and important knowledge gaps. Hansen et al.[79] comprehensively reviewed the state-of-technology for upgrading the bio-oil into liquid hydrocarbon fuels. They highlighted the critical challenges of current bio-oil upgrading methods and pointed out the potential research directions for bio-oil upgrading to meet the market requirements. Mortensen et al.[85] reviewed the conventional chemical bio-oil upgrading methods from the aspects of catalyst development, carbon forming mechanisms elucidation, reaction kinetics and catalyst deactivation analysis, and sustainability evaluation. More detailed information on the conventional bio-oil upgrading processes could be found in the excellent reviews by Zhou et al.,[31] Xiao et al.,[32] Graça et al.,[33] and Wang et al.[34] and the references therein. Since the conventional bio-oil upgrading technologies have been extensively reviewed previously, in the present paper, only the emerging technologies, such as direct distillation and physicochemical bio-oil upgrading technologies like electrochemical and plasma, for upgrading bio-oil into renewable fuels are summarized. A general comparison between the conventional bio-oil upgrading processes and these emerging technologies is presented in Table 3.

Direct Distillation of Bio-oil for Biocoal Production

Distillation is a cost-effective and easily operated technique for the separation of individual components from liquid mixtures. It is a unit operation in modern chemical engineering and has been widely applied over one century. However, due to the thermal instability of bio-oil, conventional distillation is not efficient for bio-oil upgrading. Although molecular distillation has been successfully used for separating bio-oil, the total carbon recovery efficiency in light distillates is very low (less than 17%).[86] The main problem of bio-oil distillation is the thermal polymerization of phenol, aldehyde, and lignin oligomers.[87,88]

Rather than alleviating the thermal polymerization process, we proposed a novel approach by accelerating thermal polymerization in the distillation process, thus converting bio-oil into a solid fuel, which is named as biocoal.[89] Generally, there are several advantages of producing biocoal from bio-oil: (1) biocoal is a renewable and mass-produced fuel, which can be quickly produced at a large scale from bio-oil; (2) besides the production of biocoal, some liquid chemicals can also be harvested in the bio-oil distillation process; (3) compared to bio-oil, biocoal is more stable, which means it can be conveniently transported and stored for a long time; and (4) biocoal is a carbon sink and can achieve "carbon-neutral" utilization of biomass.

The biocoal production process is illustrated in Figure 4a. The lignocellulose biomass (e.g., rice husk, corn stalk, and saw dust) is pyrolyzed at 500 °C in a N_2 flow to obtain biochar (about 40−50% yield) and bio-oil (about 35−45% yield). The bio-oil is then distilled from room temperature to about 240 °C, during which the stable light hydrocarbons is vapored out. Phenols and aldehydes tend to polymerize to form solid resin analogues via a pathway similar to the phenolic resin production (Scheme 1), and pyrolytic lignin oligomers tend to polymerize again. The phenolic resin analogues and polymerized lignin oligomers are the two main components of the biocoal.

As shown in Figure 4b, biocoal is a blocky solid with a glossy black surface, showing a similar appearance to conventional
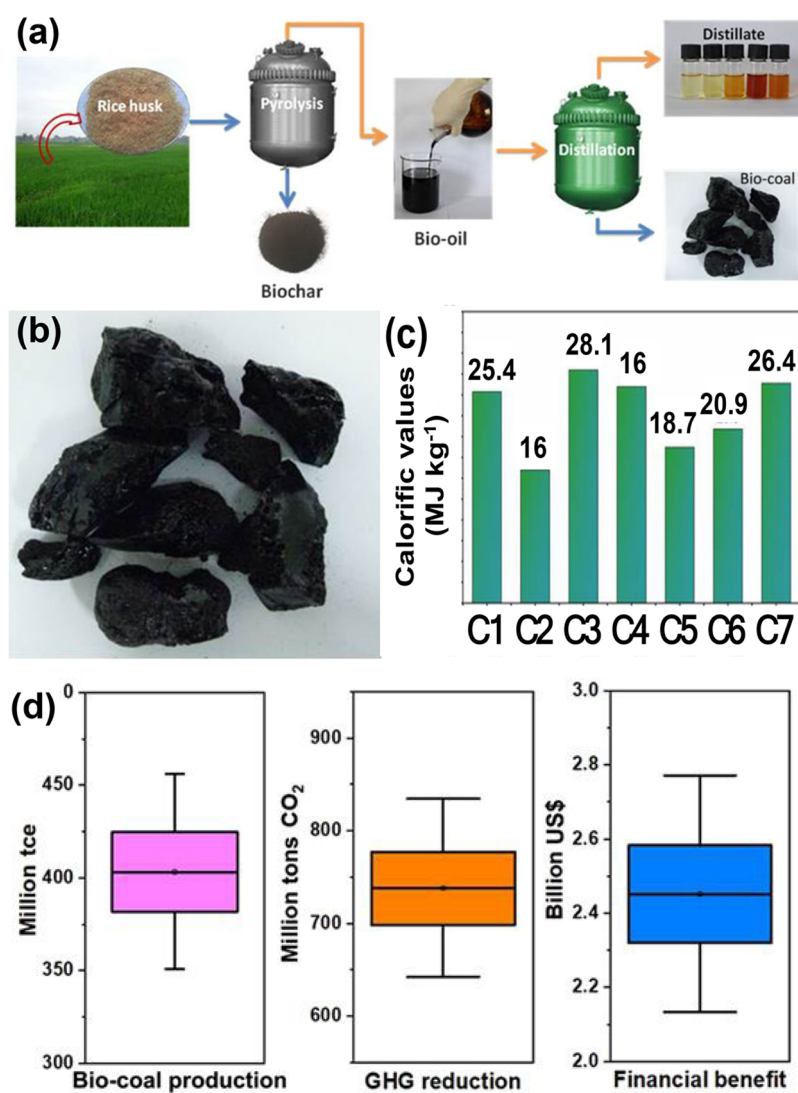
Figure 4. (a) Schematic illustration for the production of the biocoal from lignocellulosic biomass. (b) Photograph of the biocoal. (c) Energy densities of the biocoal and other conventional coals (C1, biocoal; C2, rice husk; C3, Indonesian Tinto coal; C4, Australian collie coal; C5, Yangquan Anthractite; C6, Alberta sub-bituminous coal; C7, Pingdingshan bituminous coal). (d) Prediction of the biocoal production, greenhouse gas reduction, and financial benefit via a Monte Carlo simulation (center lines represent median values, boxes refer to 25−75th percentiles, and bars represent 5−95th percentiles). (Reprinted with permission from ref 89. Copyright 2020 from the authors.)

Scheme 1. Possible Mechanism for the Formation of Biocoal in the Distillation of Bio-oil
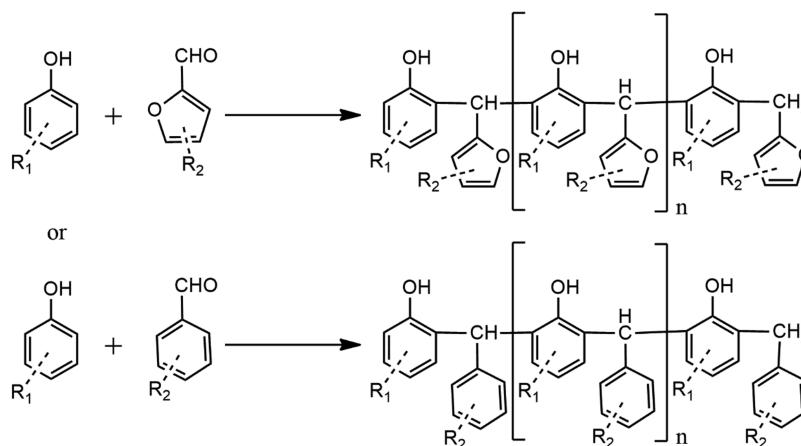
coal. Meanwhile, biocoal also has a comparable energy density (~25 MJ/kg) to the coals produced from different mines (Figure 4c). Table 4 further compares the other main characteristics between biocoal and conventional coal samples.

Table 4. Comparison of the Main Characteristics between Biocoal and Conventional Coal[89−91]

items	biocoal	conventional coal
elemental composition (wt %)		
C	30−50	45−60
H	7−10	4−6
O	40−60	20−25
N	0.2−1	0.4−2
S	0−0.005	0.3−1.5
total heavy metals (Cd, Pb, Cr, Zn, Mn, Ni, Cu)	<0.00005	<0.05
proximate analysis		
moisture content (wt %)	1−5	6−32
volatiles (% dry base)	10−12	15−30
fix carbon (% dry base)	40−50	35−55
ash	5−10	5−45
density (kg/m^3)	750−850	640−920
energy density (MJ/kg)	24−26	23−27

Compared to conventional coal, which usually has a considerable amount of heteroelements like N, S, and heavy metals,[90] biocoal has very low N (minimum 0.16 wt %, produced from sawdust biomass derived bio-oil) and S (minimum 0.37 wt %, produced from bagasse biomass derived bio-oil) contents. As for the heavy metals, the contents of Cd, Pb, Cr, Zn, and Mn in biocoal are extremely low and Cu and Ni cannot be detected. These results suggest that the pollution of NO_x, SO_2, and heavy metals can be greatly suppressed in the combustion of biocoal.

The environmental footprints of biocoal production were assessed via a life cycle assessment (LCA), demonstrating that the biocoal production process can achieve a negative carbon emission as well as considerable environmental and financial benefits. It is estimated that 402 million tons of biocoal can be produced with all the agricultural and forest waste produced in China. If this amount of biocoal is used as an alternative for conventional coal, 14% of the total coal consumption in China can be reduced. As a consequence, 738 million tons of CO_2 emission can be reduced, bringing about a total financial benefit of US$2.4 billion (Figure 4d).[92]

Electrochemical Upgradation of Bio-oil for Liquid Fuel Production

Electrochemical upgrading, i.e., electrocatalytic hydrogenation, is a well-known approach for converting unstable compounds with unsaturated bonds (e.g., C═C and C═O bonds) into stable hydrocarbons and C−OH compounds. Electrochemical upgrading can effectively improve the chemical stability and heating value of bio-oil.[93,94] It has been recently regarded as a sustainable alternative to the conventional hydrogenation process, which is generally performed at high temperatures (150−300 °C) and H_2 pressures (0.5−20 MPa). Electrochemical bio-oil upgrading is usually conducted in a membrane electrochemical cell. Figure 5a displays a typical electrochemical cell used for the upgrading of bio-oil. The cell is made up of anode and cathode compartments, which are separated by a cation or anion exchange membrane. In the anode side, water is oxidized into O_2 with electricity, producing free protons and electrons (eq 1). The protons and electrons are then transferred to the cathode side via a cation exchange membrane and the circuit, respectively. The electrochemical hydrogenation of bio-oil proceeds in the cathode side (eqs 2 and 3, based on average elemental composition).[95] The hydrogen evolution reaction (HER) is the main complete reaction of electrochemical bio-oil hydrogenation. Thus, an efficient catalyst is required to reduce the overpotential of HER
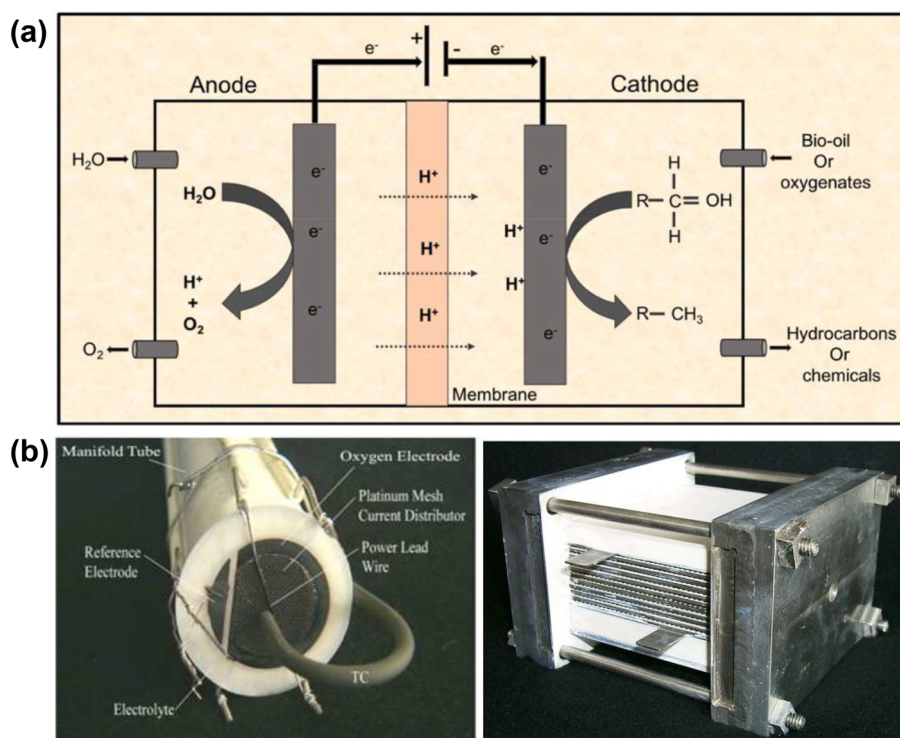

Figure 5. (a) Schematic diagram of the electrochemical cell for bio-oil upgrading. (b) Photograph image of the electrochemical button cell (left) and a stack (right) for real bio-oil upgrading. (Reprinted rom ref 94. Copyright 2018 American Chemical Society.)
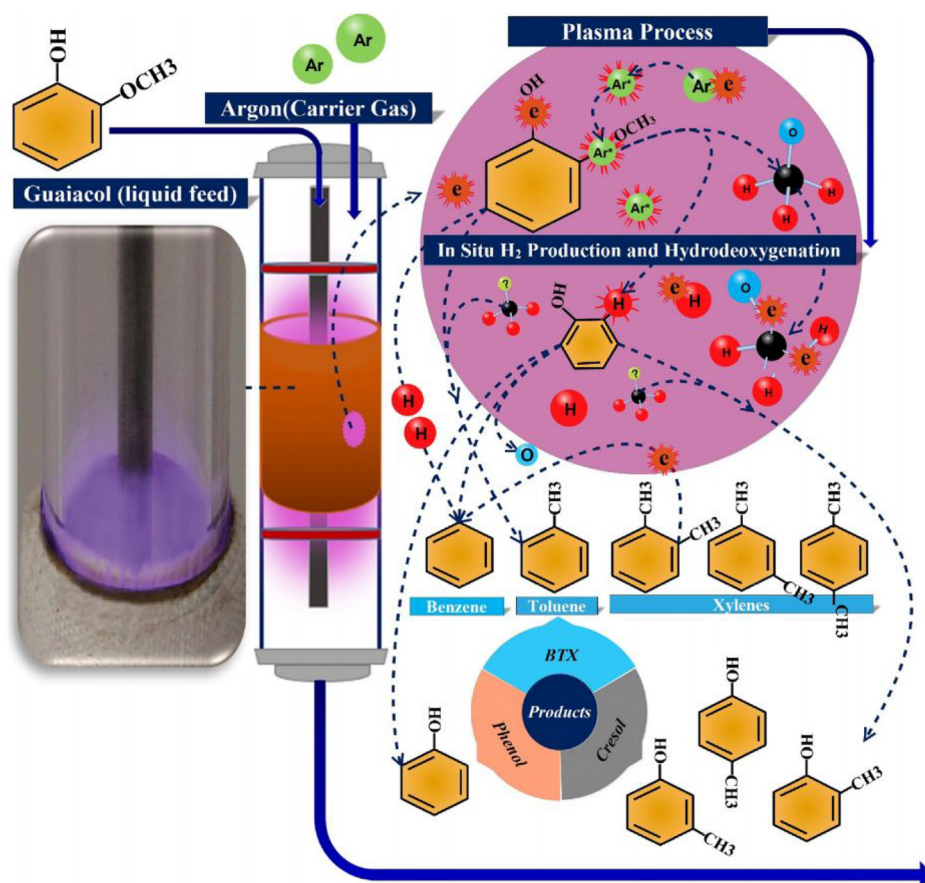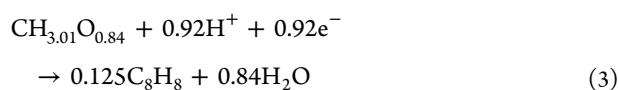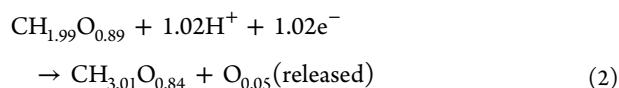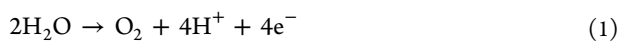
Figure 6. Schematic analysis of the dielectric barrier discharge plasma reactor and the mechanism for the upgradation of a bio-oil model compound. (Reprinted with permission from ref 101. Copyright 2019 Elsevier B.V.)

and suppress HER, thus increasing the efficiency of bio-oil upgrading to the desired products.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{1}$$

$$CH_{1.99}O_{0.89} + 1.02H^+ + 1.02e^-$$
$$\rightarrow CH_{3.01}O_{0.84} + O_{0.05}(\text{released}) \tag{2}$$

$$CH_{3.01}O_{0.84} + 0.92H^+ + 0.92e^-$$
$$\rightarrow 0.125C_8H_8 + 0.84H_2O \tag{3}$$

Since bio-oil is a very complex liquid mixture, before the real bio-oil upgrading, the electrocatalytic hydrogenation of bio-oil model compounds to valuable compounds has been explored. For example, Zhao and co-workers investigated the electrocatalytic hydrogenation of furfural, a typical bio-oil model compound, into furfuryl alcohol over a H-type electrochemical cell with different metal or metal–carbon electrodes.[96] Although the Pt cathode presented a better selectivity of about 99% toward furfuryl alcohol as compared to Cu, Pb, and Ni cathodes, its conversion efficiency was very low (less than 8%) due to the low surface area of the Pt electrode. To enhance the furfural conversion efficiency, the Pt cathode was modified with high-surface-area activated carbon fiber catalysts, and the furfural conversion efficiency was increased from 8% to 82%. Similarly, Li and co-workers studied the electrocatalytic hydrogenation of a phenolic compound (guaiacol, another typical model compound of bio-oil) over a two-chamber H-type electrochemical cell with a Ru/activated carbon

cathode.[97] Cyclohexanol was the main product of electrocatalytic guaiacol hydrogenation, and phenol was an intermediate product. Unlike conventional high temperature and pressure hydrogenation, in which demethylation is the dominant deoxygenation pathway, in electrochemical guaiacol hydrogenation, demethoxygenation is the major deoxygenation reaction. The electrochemical process can retain more carbon in the upgrading products than in the conventional hydrogenation process and thus is more advantageous for bio-oil upgrading.

Apart from the upgrading bio-oil model compounds, the electrochemical method has been further applied in upgrading real bio-oil. The effectiveness of electrochemical bio-oil upgrading depends on the exact composition of the bio-oil and the surrounding chemical environment, such as acidity and conductivity.[97] Elangovan and co-workers[98] upgraded the real bio-oil over oxygen ion conducting ceramic membrane-based electrochemical cells using Ni doped ZrO_2 cermet as a fuel electrode and Sr doped $LaMnO_3$ as an air electrode (Figure 5b). After electrochemical upgrading, about 24.5% of the oxygen content in the bio-oil could be reduced, accompanied by a 16% increase in the carbon content. These changes in oxygen and carbon contents could be attributed to the hydrogenation of the oxygenated compounds into hydrocarbons. More recently, Lister and co-workers[94] upgraded the bio-oil obtained via pine wood pyrolysis over a dual membrane electrochemical cell. After upgrading, the bio-oil showed significant improvements in many properties. For example, the total acid number of the bio-oil was decreased from 193 to

149 mg of KOH/g-bio-oil, accompanied by a significant pH value increase from 2.6 to 4.5.

Although the electrochemical upgrading has been demonstrated to be effective in converting bio-oil into biofuels or chemicals, this process has not been widely applied for upgrading real bio-oil because of the following challenges: (1) the low conductivity and high viscosity of bio-oil require the use of costly membrane electrode assemblies; (2) the electrochemical bio-oil upgrading is an energy-intensive process as it requires a lot of electricity input; and (3) bio-oil is a very complex mixture with many different organic compounds, and many side reactions will occur in the electrochemical process, thus decreasing the yield of desired products. Overall, further investigations are needed to make the electrochemical technique more efficient and advanced for real bio-oil upgrading at the pilot scale and future full scales.

Plasma-Assisted Catalytic Bio-oil Upgrading

Nonthermal plasma (NTP)-assisted catalysis is an emerging bio-oil upgrading technology with the combination of free radicals initiated by NTP and catalytic reactions induced by catalysts. The NTP-assisted catalysis has several advantages, e.g., increasing the catalytic reaction rate, decreasing the activated temperature, and alleviating catalyst poisoning. Because of these advantages, NTP-assisted catalysis shows great potential to overcome the problems existing in conventional catalytic bio-oil upgrading.[99,100] For example, Taghvaei and Rahimpour[101] investigated the catalytic hydrogenation of a bio-oil model compound with the active hydrogen species produced via a combination of a dielectric barrier discharge plasma and catalyst (Figure 6). The active hydrogen species came from the cracking of the methyl groups of the bio-oil. The operating parameters, such as discharge voltage, bio-oil, and argon flow rate, were optimized to achieve the maximum guaiacol (the bio-oil model compound) upgrading efficiency. The combination of plasma discharge and Pt−Cl/Al$_2$O$_3$ achieved a highest conversion rate of 92%, as compared to a conversion rate of 57% with either catalyst or plasma alone.

Furthermore, Hosseinzadeh and co-workers[102] investigated the upgrading of the real bio-oil sample over a dielectric barrier discharge plasma reactor. They studied the effects of carrier gas type, discharge voltage, and pulse repetition frequency of the plasma on the upgrading efficiency. The reaction temperature, electron energy, and density were found to be the main factors governing the efficiency of the NTP-assisted catalytic bio-oil upgrading process. Hydrogenolysis, demethylation, and trans-alkylation were the key reactions occurring in the upgrading process, in which p-xylene, 4-methylphenol, and 2,4-dimethylphenol were the main upgrading products. The highest conversion efficiency reached 29% when argon was used as a carrier gas with a discharge power of 77 W.

Apart from the NTP-assisted catalysis, other plasma technologies have also been used for bio-oil upgrading. For example, Lee and Park[103] evaluated the potential for H$_2$ production from the lignin derived bio-oil with a solution plasma process. The main variables, including discharge voltage and time, current, and electrode distances, were tuned to achieve a high production of H$_2$ from bio-oil. Guénadou and co-workers[104] converted bio-oil into syngas (H$_2$ and CO) over a self-designed thermal plasma apparatus. A maximum yield of syngas (95 mol % of CO + H$_2$) was achieved in the plasma treatment at a high temperature of 2500

K, while the formation of tars and solid particles can be greatly suppressed.

Similar to the electrochemical upgrading technologies, plasma-assisted catalysis also has several disadvantages, which limit its wide application for upgrading real bio-oil: (1) the plasma reactor is usually complex, and a large amount of electricity input is needed to generate a stable plasma flow, making plasma-assisted catalysis an energy-intensive process; and (2) bio-oil is very complex and inhomogeneous, and the plasma treatment will induce partial overheating in the bio-oil, resulting in many side reactions, thus decreasing the yield of desired products. Overall, more efforts should be made to make the plasma-assisted catalysis process more efficient and cost-effective to deal with real bio-oil upgrading.

■ ENVIRONMENTAL IMPACTS AND SUSTAINABILITY ASSESSMENT

Converting lignocellulosic biomass into drop-in fuels, however, also encounters challenges for environmental sustainability. The biomass collection and pretreatment, thermochemical conversion, bio-oil upgrading, biochar functionization, and end-of-life treatment of the final products may all introduce sustainability trade-offs. In order to minimize such trade-offs, it is crucial to identify and efficiently reduce the related environmental impacts. Thus, a systematic assessment of the environmental sustainability performance of the thermochemical biomass conversion systems is highly desired.

LCA is a powerful tool to evaluate the environmental impacts and sustainability of a production process. In LCA, the environmental impacts of whole life stages of a product are evaluated, from raw materials and pretreatments, through production process, finally to the end-of-life. The environmental sustainability of the first-generation biofuels produced from corn sugar (bioethanol) and vegetable oils (biodiesel) has been evaluated via LCA. The LCA results suggest that these food-based biofuels are not environmentally sustainable and socially acceptable as they pose significant risks to our food security.[105] Meanwhile, they also bring about water and carbon footprints due to the direct and indirect land-use.[106,107] The second-generation biofuels produced from nonfood lingocellulosic biomass are a promising alternative to the food-based biofuels in terms of sustainability and social acceptability.

The prospect of the second-generation biofuels produced from thermochemical conversion of lignocellulosic biomass and subsequent bio-oil product upgrading has prompted extensive LCA studies toward evaluating the associated environmental impacts.[108−110] For instance, Dang et al.[111] and Zhang et al.[112] evaluated the net global warming potential of the biofuels produced from hydroprocessing of the bio-oil obtained from corn stover pyrolysis via a cradle-to-grave LCA. They reported the global warming potential ranging from 69.1% to 147.5% for an array of process scenarios within a cradle-to-grave system boundary. Han and co-workers[113] reported 60−112% reduction in the cradle-to-grave GHG emissions by using the biofuels produced from the thermochemical conversion of lignocellulosic biomass as an alternative to the fossil fuels under various scenarios. More recently, Peters and co-workers[109] carried out a cradle-to-gate LCA on a biofuel process chain on the basis of hybrid poplar pyrolysis and subsequent bio-oil upgrading. The produced biofuel was compared with the equivalent fossil fuel to quantify its potential environmental benefits and identify the processes with the highest environmental impact. The LCA results

indicate that GHG emission savings of 54.5% can be achieved for the biofuel as compared to the equivalent fossil fuels. Electricity consumption was found to be the highest contributor to the overall environmental impacts. These studies indicate that the bio-oil upgrading should be an environmentally viable route for the second-generation biofuel production.

In addition to the environmental impacts, one may also wonder about the costs involved in the bio-oil upgrading and the final price of the produced biofuels. In this regard, a number of techno-economic analysis (TEA) studies have been conducted for bio-oil production and various upgrading processes (e.g., steam reforming, hydrotreatment, fluid catalytic cracking).[114−118] Wright and co-workers[119] conducted a TEA on the biomass pyrolysis and bio-oil upgrading to naphtha and diesel range biofuels. Two scenarios for converting 2000 tons of dry corn stover per day were developed: one was the production of H_2 on site via steam reforming a fraction of the bio-oil for the remaining bio-oil fuel upgrading (H_2 production scenario), while another was using commercial available H_2 for the bio-oil upgrading (H_2 purchase scenario). The values of the final biofuels were estimated as $0.82 and $0.56 per liter of equivalent gasoline in the H_2 production and purchase scenarios, respectively. These values are competitive with those of fossil fuels. Sensitivity analysis indicates that the electricity supply and biomass costs in both scenarios contributed mainly to the costs of the final biofuels. Similarly, a TEA of biomass hydrothermal liquefaction to bio-oil and further bio-oil upgrading via hydrotreatment was implemented by Zhu and co-workers.[120] Two scenarios, i.e., a state-of-technology case with the results from the experimental testing and a goal case with future improvements of a commercial biofuel production plant, were proposed to estimate the costs of bio-oil production and upgrading. The annual biofuel production rates for the state-of-technology and goal case scenarios were calculated as $42.9 million and $69.9 million per gallon gasoline equivalent (GGE), respectively. The minimum selling price of the biofuels was estimated as $4.44/GGE and $2.52/GGE for the state-of-technology and goal case scenarios, respectively.

TEA could be applied as a rational way to make effective economic comparison among different pathways for biofuel production and thus, is employed to evaluate the economic feasibility of the upgrading processes. However, it is difficult to compare the TEA results from different studies due to the wide disparities of the scope covered by each TEA study. These disparities mainly include operating conditions, process configuration, plant design and capacity, biomass feedstock type and costs, product yields and selectivity, as well as economic assumptions.[121,122] Therefore, a comparative TEA analysis of different bio-oil upgrading pathways to drop-in biofuels on the same basis is suggested. This will provide an easy comparison among different upgrading pathways in terms of both environmental and economic aspects.

■ CHALLENGES, FUTURE DIRECTIONS, AND CONCLUSIONS

To achieve peak carbon emission and carbon neutrality, a huge amount of fossil fuel should be replaced by carbon-neutral biofuels. Pyrolysis and hydrothermal liquefaction technologies have shown promising potential to convert lignocellulosic biomass into liquid bio-oils, which could be further upgraded into biofuels. The replacement of fossil fuels with carbon-

neutral biofuels is considered as an important approach to achieve the goals. However, some undesirable physicochemical properties like poor chemical stability, low heating value, and high acid content are still great challenges to make bio-oil a commercial drop-in fuel. The production costs, including the costs for bio-oil production and upgrading, are the main factor influencing the commercialization of bio-oil-based drop-in fuels. Previous TEA studies have demonstrated that biomass feedstock sourcing and pretreatments, operating and capital expenses, lower selectivity, and yields are the main contributors to the costs of bio-oil-based drop-in fuels. Also, the sensitivity degree of the above-mentioned parameters varies with different bio-oil upgrading methods. Establishment of bio-oil production plants near biomass feedstock should be a feasible option to reduce the biomass feedstock sourcing and pretreatment expenses. Meanwhile, since the bio-oil upgrading process is similar to that of petroleum refining in some ways, e.g., hydrotreatment and catalytic cracking, integrating bio-oil upgrading units with ready-made petroleum refining infrastructures can minimize the upgrading capital costs. The bio-oil-based drop-in fuels may become market competitive when bio-oil upgrading is directed to a single valuable fuel blendstock such as biojet fuel.[123]

Apart from the economy and policy level challenges and directions for bio-oil-based drop-in fuel production, the challenges at the technology level and possible coping directions should be paid more attention. To date, there are no efficient and cost-effective upgrading pathways for producing drop-in fuels from bio-oil yet. Integrating various energy systems should be a promising strategy to reduce upgrading costs and increase efficiency for producing biomass-derived drop-in fuels and other byproducts. In this regard, electrochemical hydrogenation and ultrasonic cavitation might find applications in the bio-oil upgrading process.[124] Such an integrated system can simplify the upgrading process as a whole to increase the conversion efficiency and reduce the operational/capital costs.[125]

Although electrocatalytic hydrogenation has been demonstrated to be efficient in upgrading bio-oil model compounds like phenols and carbonyl compounds, it is still at an early stage for upgrading real bio-oil. One main challenge for this method is the complex nature of bio-oil, which may impose many undesired side reactions and severe fouling to the electrode and ion exchange membrane. Another main challenge is the use of high-priced membranes. Developing highly efficient and fouling-resistant electrode catalysts as well as high-performance and cost-effective ion exchange membranes is therefore essential to make the electrocatalytic hydrogenation technique effective and economically feasible for bio-oil upgrading. High electricity consumption is also a big challenge in the application of the electrochemical hydrogenation process. Integrating electrochemical hydrogenation with a renewable electricity supply, such as fuel cells or photovoltaic technologies, should be a promising direction to address this challenge. Moreover, detailed LCA and TEA should be performed to optimize the operating and capital costs as well as GHG emission in the electrochemical hydrogenation process.

Ultrasonic cavitation can separate oil and water fractions of bio-oil through phase separation via hydrolysis and cotreatment with transesterification. It could also act as a blending tool to combine the bio-oil with diesel fuel for combustion engines uses. Compared to the conventional physical

separation and transesterification processes, ultrasonic cavitation is advantageous because of its mild operating conditions and avoidance of toxic and flammable chemicals. This process reduces the viscosity and water content of the bio-oil independently. It has been demonstrated to be an efficient supplementary treatment in addition to other bio-oil upgrading methods. In these processes, ultrasonic cavitation can help improve the process efficiency and shorten the reaction time of some catalyst-intensive upgrading approaches. Industrial scale ultrasonic cavitation facilities should be established to elucidate the reaction mechanisms and reduce high capital costs.

In summary, this Review provides an overview of the existing technologies for the conversion of lignocellulosic biomass to bio-oil then to mass-producible biofuels. This Review also highlights the science and engineering research pathways, process and product challenges, as well as future directions addressing these challenges. Since many review articles have been published on the conventional bio-oil upgrading process like hydrotreatments, catalytic cracking, and steam reforming, this paper focuses on the emerging technologies for bio-oil upgrading in terms of system complexity, convention efficiency, GHG emission, and profitability only. The thermochemical treatments such as hydrotreatments, catalytic cracking, and steam reforming are effective for bio-oil upgrading but are less cost-efficient because of their intensive process requirements like high temperature or pressure, flammable and combustible H_2 uses, as well as expensive catalysts. Physicochemical treatments like electrochemical and plasma-assisted catalytic processes may not be as effective as the thermochemical upgrading approaches yet, but they can be operated under mild conditions or incorporated as an integrated unit in conjunction with other treatments. The electrochemical approach has great potential for bio-oil upgrading because of its retention of H_2 from bio-oil compounds or water via a demethylation or deoxygenation reaction, respectively, avoiding supplementary H_2. Plasma can improve the process efficiency and reaction time of catalyst-intensive bio-oil upgrading. Biocoal could be produced with the atmospheric distillation of bio-oil obtained from the fast pyrolysis of various lignocellulosic biomass waste. The obtained biocoals have heating values comparable to those of the commercial coals. The LCA investigation further indicates that net positive energy and considerable financial and environmental benefits can be achieved in the biocoal production process.

The above reviews show that developing more efficient and cost-effective processes to convert lignocellulosic biomass into drop-in fuels is still greatly needed. This would provide a possible feasible solution to various global priorities, including energy security, environmental impacts and GHG emission derived from fossil fuel uses, advanced rural economy and bioindustry, as well as natural resources recovery. To this end, more research should be conducted to promote the development of current bio-oil upgrading technologies toward a highly efficient and economically sustainable future. Further research practices for overcoming the drawbacks of the conventional bio-oil upgrading to drop-in biofuels should be conducted in the future:

(1) to explore emerging spectral or physicochemical technologies for online or in situ analysis of the bio-oil production and upgrading reactions to optimize the conversion processes;

(2) to couple the mild methods, such as electrochemical hydrogenation and ultrasonic cavitation, to the commercialized thermochemical conventional technologies;

(3) to apply theoretical modeling or simulation approaches to analyze the total resources input (mass and energy) and fuel output of various processes;

(4) to develop integrated energy systems such as low pressure catalytic pyrolysis and high-temperature steam electrolysis to produce drop-in biofuels from lignocellulosic biomass and low-emission energy resources like solar and wind;

(5) to produce blended fuels with renewable bio-oil and petroleum-based fuels via quenching and emulsification, bringing the biofuel industry closer to the economical production.

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Notes

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