Research Status and Future Development of Biomass Liquid Fuels

Ji Zhang,^{a,b} Junling Yang,^a Huafu Zhang,^a Zhentao Zhang,^{a,*} and Yu Zhang ^a

Due to the combined pressures of energy shortage and environmental degradation, bio-liquid fuels have been widely studied as a green, environmentally friendly, renewable petroleum alternative. This article summarizes the various technologies of three generations of biomass feedstocks (especially the second-generation, biomass lignin, and the third-generation, algae raw materials) used to convert liquid fuels (bioethanol, biodiesel, and bio-jet fuel) and analyzes their advantages and disadvantages. In addition, this article details the latest research progress in biomass liquid fuel production, summarizes the list of raw materials, products and conversion processes, and provides personal opinions on its future development. The aim is to provide a theoretical basis and reference for the optimization of existing technology and future research and development of biomass liquid fuels.

Keywords: Biomass liquid fuel; Bioethanol; Biodiesel; Biomass jet fuel

Contact information: a: Key Laboratory of Energy Saving Technology of Food and Pharmaceutical Storage and Processing and Transportation Equipment in Good Quality (China National Light Industry), The Technical Institute of Physics and Chemistry of the Chinese Academy of Sciences, Beijing 100190, China; b: College of Forestry, Jiangxi Agricultural University, National Forestry and Grassland Bureau Woody Spice (East China) Engineering Technology Research Center, Nanchang 330045, China; Tianjin 300222, China; *Corresponding author: zzt@mail.ipc.ac.cn

INTRODUCTION

The development of modern industry provides prosperity but leads to the wasting of biomass resources. In recent years, the transformation and utilization of these green, inexpensive, and readily available waste biomass resources have become urgent and important issues in the fields of environmental protection and chemical industry. Coupled with the dual pressures of energy shortage and environmental deterioration, countries around the world have begun to compete to develop safe, environmentally friendly, and renewable biomass energy. The development and application of biomass liquid fuels have attracted unique attention and extensive research in many countries. Biomass liquid fuels generally refer to liquid fuels, such as bioethanol, biodiesel, and bio-jet fuel, which are converted from biomass using various technologies. Biomass liquid fuel technology has developed rapidly in the past three decades. Biomass liquid fuel has become the most promising class of alternative fuel, and biodiesel and bioethanol have achieved particularly large-scale development (Dabros *et al.* 2018; Efeovbokhan *et al.* 2019).

As shown in Table 1, current biomass liquid fuels are mainly developed from three generations of raw materials. The first generation of biofuels mainly uses food crops and animal fats as raw materials. Bioethanol and biodiesel are produced *via* fermentation and transesterification reactions. The relevant production technology has a long history of use, but due to food scarcity concerns, it has become a less favorable option. The second-generation biofuels mainly use non-grain crops, such as lignocellulosic biomass as raw

materials, which include straw, hay, bagasse, rice husks, wood chips, and others. The use of second-generation biofuels causes many technical problems, and there are major problems with conversion rates and production costs.

| Biomass Fuel | Feedstock | Method | Product |
|---------------------|-----------------|-----------------|----------------------------|
| First- | Food crops and | Biochemical | Bioethanol and biodiesel |
| generation | animal fats | Diochemical | Bioethanioi and biodiesei |
| Second- | Lignocellulosic | Biochemical and | Bioethanol, biodiesel, and |
| generation | biomass | thermochemical | bio-jet fuel |
| Third- | Algel biomage | Biochemical and | Bioethanol, biodiesel, and |
| generation | Algal biomass | thermochemical | bio-jet fuel |

Table 1. Generations of Biomass Fuel

In the past few decades, in-depth research on second-generation biomass materials had focused on the enhancement of biomass pretreatment, the production of cellulolytic enzymes, and the improvement of strains and processes. Such efforts have eliminated some major technical bottlenecks. However, there is a need to further reduce processing costs to obtain sufficient market competitiveness. In particular, it is important to reduce the energy requirements in the pretreatment process, increasing sugar concentration, improving enzyme activity and strain recycling, and increasing the utilization of by-products (Guerrero *et al.* 2018). The third-generation biofuels mainly use algae as a raw material to extract oil and fat. Algae has wide distribution, high oil content, strong environmental adaptability, a short growth cycle, and high yield. Its growth does not occupy the two major resources of land and fresh water, but the production process is still in the laboratory stage. To achieve commercial large-scale production, many technical problems need to be solved (Kabir *et al.* 2019; Vintila *et al.* 2019)

RESEARCH STATUS OF BIOETHANOL TECHNOLOGY

Bioethanol refers to the conversion of various biomass into fuel alcohol via the fermentation of microorganisms. In contrast with first-generation biomass ethanol, which uses sugar- and starch-based crops as raw materials, second-generation biomass ethanol is mainly produced from lignocellulosic biomass, which can be divided into agricultural, forestry residues, energy crops (such as bagasse, rice husk, and straw). Second-generation bioethanol is produced through pretreatment, hydrolysis, and fermentation (Ayodele et al. 2019). Table 2 shows current research of bioethanol produced from second-generation biomass using different pretreatment methods, microorganisms, and fermentation conditions. The purpose of biomass pretreatment is to reduce the crystallinity of cellulose, increase the specific surface area of the substrate, break the barrier effect of hemicellulose and lignin, and facilitate the contact and reaction of cellulose with hydrolytic enzymes. The pretreatment of lignocellulose can adopt physical (such as mechanical communication and irradiation), chemistry (such as acid, alkali, ionic liquid, organic solvent, and ozone pretreatment), physical chemistry (such as steam explosion, ammonia fiber, and CO₂ explosion) and biological (such as microorganism) pretreatment methods. Among them, steam explosion is a particularly promising pretreatment method for large-scale production of bioethanol. Guerrero et al. (2018) used steam explosion to pretreat banana waste and found that it has a high hemicellulose recovery rate and cellulose enzymatic hydrolysis efficiency, low energy consumption, and a lack of recycling issues. The hydrolysis process is the degradation of the hemicellulose and cellulose polymeric sugars in the raw materials into fermentable monosaccharides. The fermentation reaction uses the hydrolyzed monosaccharide as a raw material, and it is transformed into bioethanol by the metabolism of yeast or bacteria.

| Feedstock | Pretreatment | Microorganisms | Fermentation Conditions | Conversion Process | Yield (%) | Yield (g/L) | Reference |
|--|---|--|----------------------------|-----------------------|--------------|----------------|--|
| Sugarcane bagasse | Alkaline pretreatment | Cellulase and Saccharomyces cerevisiae | 4.5 pH, 34 °C | 34% WIS/ /SHF | 77.2 | 82.8 | (Ye <i>et al.</i> 2018) |
| Sugarcane leaf | Ammonia fibre explosion pretreatment | Saccharomyces Cerevisiae (424A LNH-ST) | 4.8 pH, 30 °C | 17.7 % WIS/PSSCF | 91.6 | 35.8 | (Krishnan <i>et</i> <i>al</i> . 2010) |
| Banana waste | Acid-catalyzed steam explosion | Saccharomyces cerevisiae and ethanol red | 4.8 pH, 38 °C | 17.6% WIS /PSHF | 87.0 | 42.1 | (Guerrero <i>et</i> <i>al.</i> 2018) |
| Hardwood waste | Hydroperoxide and acetic acid pretreatment | Saccharomyces cerevisiae and Pichia stipites | 5.0 pH, 37 °C | 5.0% WIS/SHF | 80.7 | 14.8 | (Song <i>et al.</i> 2019) |
| Vetiver grass | Alkaline-acid pretreatment | Saccharomyces cerevisiae TISTR 5339 | 5.0 pH, 30 °C | 5.0% WIS/ SHF | 73.8 | 21.1 | (Subsamran <i>et al.</i> 2019) |
| H ₂ SO ₄ | | Saccharomyces cerevisiae | 4.8 pH, 34 °C | 9% WIS/ SSHF | 70.8 | 39.2 | (Olofsson <i>et al.</i> 2008) |
| Brave straw | SO ₂ catalyzed steam explosion pretreatment | Saccharomyces cerevisiae (TMB3006, TMB3400), Pichia stipitis CBS 6054 | 5.5 pH, 30 °C | 8% WIS/ SSHF | 87.0 | 40.2 | (Carrasco et al. 2010) |
| Corn stover explosion pretreatment Saccharomyces | | | 5.5~6.0 pH, 37 ℃ | 18% WIS/ SSHF | 92.7 | 47.2 | (Lau and Dale 2010) |
| WIS: Water insoluble solid SHF: Simultaneous hydrolysis and fermentation PSHE: Pre-bydrolysis and simultaneous bydrolysis and fermentation | | | | | | | |

| Table 2. | Production | of Bioethanol | Usina | Second-gen | eration | Raw Materials |
|----------|------------|---------------|-------|-------------|---------|---------------|
| | 1 TOGUCION | | USing | Occorra gen | cration | |

PSHF: Pre-hydrolysis and simultaneous hydrolysis and fermentation

The common processes after pretreatment mainly include separate consolidated bioprocessing, separate hydrolysis and fermentation, and simultaneous hydrolysis and fermentation (SHF). Among them, the SHF method after steam pretreatment of the second-generation biomass feedstock is widely regarded as one of the most promising methods for producing bioethanol. To maximize ethanol production in bioethanol production, it is necessary to consider the use of xylose in the hemicellulose portion of lignocellulose while minimizing the inhibitory effect on the fermentation process. As *Saccharomyces cerevisiae* cannot effectively ferment xylose, Subsamran *et al.* (2019) studied the engineered strain of *Saccharomyces cerevisiae* and found that it can effectively co-ferment glucose and xylose, thereby greatly improving the ethanol yield. The final yield of bioethanol mainly depends on the pretreatment technology, hydrolysis process, and fermentation efficiency.

| Macroalgae | Pretreatment Methods | Preprocessing Steps | Fermentable Reducing Sugar | Reference |
|---|---|---|----------------------------------|--|
| | | Chlorophyta | e agai | |
| Green seaweed (<i>Ulva rigida</i>) | Thermal acid hydrolysis | Green seaweed was dried in an oven at 60 °C for 24 h and ground into powder through a blender. Algal powder of 10% (w/v) was treated with 4% (v/v) H₂SO₄ for 60 min. | 34 g/L | (El Harchi <i>et al.</i> 2018) |
| Green macroalgae (<i>Ulva lactuca</i>) | Liquid hot water pretreatment; Enzymatic hydrolysis | 1. 15 g algal biomass was mixed with 150 mL distilled water for 2 h at 170 °C. 2. The enzymatic hydrolysis experiments were performed at 50 °C and with an enzyme activity equal to 10 U/g of biomass. | 62.9/100 g DM* | (Jmel <i>et al.</i> 2018) |
| <i>Chaetomorpha</i> sp. and <i>Ulva</i> sp. | Alkali pretreatment; Enzymatic hydrolysis | Chaetomorpha sp. and Ulva sp were autoclaved for 20 min at 120 °C (1.5 bars) without a catalyst in the presence of 3% NaOH. An enzyme activity of 25 U/mg of proteins (10.96 U CMCase**) hydrolyzed 5% biomass at 120 rpm and 45 °C for 40 h. | 210 mg/g | (Yahmed <i>et al.</i> 2018) |
| | | Phaeophyta | | |
| Brown (Sargassum latifolium) | 1. Neutral thermal hydrolysis; 2. Fungal hydrolysis | 10 g wet macroalgae biomass was previously subjected to thermal hydrolysis, then was kept in an autoclave at 120 °C for 15 min (1.5 bar, 5.5 pH). 2. Trichoderma asperellum RM was kept under static conditions for 21 d at 30 °C. | 510 mg/g | (Soliman <i>et al.</i> 2018) |
| Brown seaweed (Sargassum crassifolium) | Brown seaweed (Sargassum crassifolium)1. Physical and chemical pretreatment; 2. Enzymatic hydrolysis1. Sulphuric acid (0.2 M) was kept at 121 °C for 15 min with 15 Ps. 2. Cellulase (0.5 g/ mL) was kept at 30 °C for 10 min (1500 rpm, 5.5 pH). | | 68.3 g/L | (Widyaningrum <i>et al.</i> 2016) |
| Brown seaweed (<i>Sargassum</i> sp.) | 1. Mechanical pretreatment; 2. Acid hydrolysis; 3. Enzyme hydrolysis | Rhodophyta 1. The powdered seaweed was desalinated, filtered or centrifuged, and spray dried on steam heated drums. 2. The 4% concentration of H₂SO₄ was held in an autoclave at 121 °C for 30 min and then placed in a | 110.0 mg/g | (Saravanan <i>et</i> <i>al.</i> 2018) |

Table 3. Summary of Pretreatment Processes of Bioethanol from Macroalgae

| | | centrifuge at 150 rpm for 1 h at 30 °C. 3. Cellulase (53 FPU/g) and pectinase (20 U) were held at 50 °C for 4 h (150 rpm, 5.0 pH). Then they were centrifuged at 8000 rpm for 10 min. | | |
|-----------------------------------|--|--|-----------|---|
| <i>Gracilaria</i> spp. | 1. Acid hydrolysis; 2. Enzymatic hydrolysis | Gracilaria spp. was mixed with 0.1 N hydrochloric acid and 2% seaweed slurry, then kept for 15 mins at 121°C. Acid hydrolysis products were mixed with recombinant enzyme (aga 50 D 0.5 U/mg + NABH 0.5 U/mg) in a laboratory incubator at 200 rpm for 48 h. Then, after the sample was boiled for 5 min, it was centrifuged at 30,000 g for 20 min. | 47.4% | (Kim <i>et al.</i> 2018) |
| Gelidium amansii | Dicationic acidic ionic liquids (DAILs) | DAILs were synthesized from oligo (ethylene glycol), methanesulfonyl chloride, N-methylimidazole and H₂SO₄, then vacuum dried for 1 h at 60 °C. 5 wt% <i>Gelidium amansii</i> was mixed with DAILs (0.5 mmol) and kept for 3 min at 120 °C. | 67.5 wt% | (Malihan <i>et al.</i> 2017) |
| | | Macroalgal Residual Biomass | | |
| Brown seaweed spent biomass | Mild acid treatment | 1. 10 % (w/v) substrate concentration and 50 mL of 1% H ₂ SO ₄ were autoclaved at 121 °C for 20 min. | 13.1 mg/g | (Sudhakar <i>et</i> <i>al.</i> 2016) |
| * DM: Dry matte ** CMCase: Ca | | ulase | | |

The second-generation bioethanol mainly uses lignocellulosic materials as raw materials. The main limitation is that it contains a large amount of lignin and requires a large amount of arable land or forest land for cultivation. The use of algae raw materials, such as microalgae and macroalgae, to produce ethanol is called third-generation bioethanol. Macroalgae is a particularly rich source of carbohydrates in bioethanol production. Due to the high carbon and low lignin content of algae raw materials, the third-generation bioethanol, which uses algae as raw materials, has higher octane number, higher heat of vaporization, and less greenhouse gas emissions (Yahmed *et al.* 2018). The production of bioethanol from macroalgae consists of mechanical pre-processing, pretreatment, and microbial fermentation. The most important step is pretreatment, which destroys or changes the cell wall through physical, chemical, and biological means and releases biomolecules, such as cellulose and sugar polymers, thereby improving the

saccharification and bioethanol production efficiency. The efficiency of the pretreatment process is mainly determined by cellulose crystallinity, hemicellulose fraction, and the accessible surface area for enzymatic hydrolysis. In addition, an effective pretreatment method should retain some portion (such as pentose) of hemicellulose and reduce the formation of fermentation inhibitors (Dave et al. 2019). Table 3 summarizes recent examples of the production of bioethanol using macroalgae as a raw material and using different pretreatment methods, such as mechanical, chemical, and enzymatic pretreatment. In most cases, enzymatic hydrolysis after dilute acid treatment or alkali treatment is an economically viable pretreatment method for the production of bioethanol. Saravanan et al. (2018) found that, prior to saccharification, mechanical pretreatment of the macroalgal biomass, such as washing, drying, and grinding, coupled with acid and enzymatic hydrolysis, could improve saccharification efficiency. Chemical methods using weak base treatment or dilute acid treatment have also been widely used. The disadvantage of alkaline pretreatment is that it requires a large amount of water for desalination, which increases production costs. In acid pretreatment, dilute sulfuric acid can be used for almost every kind of macroalgae. The factors that ultimately affect the pretreatment process include pH, temperature, processing time, substrate concentration, and the reagents used for pretreatment.

RESEARCH STATUS OF BIODIESEL TECHNOLOGY

| Production | Advantages | Disadvantages | Reference |
|-------------------------|---|--|---|
| Technologies | Advantages | Disadvantages | |
| Catalytic distillation | Easily separable products | Equipment is easily corroded, and production consumes large amounts of energy | (Singh <i>et al.</i> 2019a; Wong et al. 2019) |
| Dilution | Easy process | Poor quality of prepared biodiesel | (Mahlia <i>et al</i> . 2020) |
| Micro-emulsion | Easy process | Poor stability, short storage time, and high cost of emulsifiers | (Fazal <i>et al</i> . 2019) |
| Microwave technology | Mild reaction conditions, simple process, fast reaction, and high conversion rate | Greatly affected by catalyst activity | (Gude <i>et al.</i> 2013) |
| Pyrolysis | Strong adaptability to raw materials, simple operation, and lack of by-product glycerin | Large energy consumption and immaturity of the technology | (Koh <i>et al.</i> 2011) |
| Reactive distillation | Reduced methanol consumption, enhanced heat and mass transfer efficiency, and fast reaction speed | High energy consumption and strong influence of catalyst efficiency | (Joda and Ahmadi <i>et al.</i> 2019) |
| Super fluid method | No added catalyst required, fast reaction rate, and high conversion efficiency | High price of production equipment and high energy consumption | (Chua <i>et al.</i> 2020) |
| Transesterification | Ability to produce high quality biodiesel and suitability for large scale industrial production | Lower conversion efficiency and inability to reuse catalyst | (Quah <i>et al.</i> 2019; Yesilyurt <i>et</i> <i>al.</i> 2019) |

Table 4. Advantages and Disadvantages of Various Biodiesel Production Technologies

Biodiesel mainly refers to long chain fatty acid alkyl esters, which are formed by transesterification and esterification of alkyl alcohol with lipid biomass raw materials, such as animal oils, vegetable oils, and marine microalgae. The common biodiesel production technologies and their advantages and disadvantages are shown in Table 4. The production of biodiesel through the catalytic distillation method is a green process that could reduce costs and improve economy. Because of the high cost of traditional precious metal catalysts, low-cost new catalysts that could be recycled and high-activity and highselectivity enzymatic catalysis had been extensively studied (Singh et al. 2019a). The reaction conditions of bio-enzyme-catalyzed synthesis of biodiesel are relatively mild, and the reaction process is more environmentally friendly, but the activity and stability of lipase need to be further improved (Wong et al. 2019). Dilution was a method of reducing the amount of solute in a solution by increasing the amount of solvent. Bioethanol and biodiesel could be used as solvents for diluting oil, but the result of this process was that the density and viscosity of the oil were reduced (Mahlia et al. 2020). Fazal et al. (2019) found that the use of micro-emulsification technology could increase the viscosity of biodiesel. As the temperature increased, the viscosity of the micro-emulsified oil gradually decreased. The processing of microemulsions was easier. But, less volatility, less stability, and high viscosity were still some issues with micro-emulsification. Gude et al. (2013) used microwave technology to produce biodiesel and found that it had the following advantages: low energy consumption, greatly reduced reaction time and solvent requirements, improved selectivity, improved conversion rate, and less by-product formation. However, this method had higher requirements for catalyst, solvent and temperature control. Pyrolysis is a method of preparing biodiesel at high temperature in isolation of air or in an inert atmosphere.

Koh and Ghazi (2011) used *Jatropha curcas* seed as a raw material to successfully produce biodiesel through pyrolysis and passed the ASTM 7554-10 test, but the production cost was relatively high. Joda *et al.* (2019) found that biodiesel that was produced by reactive distillation technology had higher reaction conversion efficiency and yield. Compared with the traditional method, its production cost decreased by 15.54%, and the power consumption increased by 2.28%. The supercritical catalytic method for preparing biodiesel has a short reaction time and simple pre-reaction and post-reaction treatments, but extreme process conditions and high equipment costs restrict its further development (Chua *et al.* 2020).

Among these conversion technologies, transesterification is the most economical and common method for preparing biodiesel, and the biodiesel produced has properties comparable to diesel. The key to the preparation of biodiesel by transesterification is the catalyst. According to the different catalytic methods, transesterification can be divided into homogeneous acid-base catalysis, heterogeneous acid-base catalysis, biological enzyme catalysis, and supercritical catalysis (Quah *et al.* 2019). Heterogeneous alkali catalysts have the advantages of easy recovery, low corrosion, and environmental friendliness, but the active center of the catalyst is easily lost, the stability is poor, and the preparation steps are complicated. Heterogeneous acid catalysts have high stability and low corrosivity, and they are easily recovered, regenerated, and separated from products. However, the catalytic activity is not high, and the reaction needs to be performed under high pressure and high temperature over a long duration (Yesilyurt *et al.* 2019).

| Feedstock | Alcohol | Molar Ratio (Alcohol : Oil) | Catalyst | Catalyst Size (nm) | Reaction Conditions | Yield (%) | Reference |
|-----------------------------|---------|--------------------------------------|--|--------------------------|------------------------------|--------------|---------------------------------------|
| Sunflower oil | CH₃OH | 12:1 | 3 wt% MgO/MgAl₂O₄ | 2.4 to 21.3 | 110 °C, 180 min | 95.00 | (Vahid and Haghighi 2017) |
| Sunflower oil | CH₃OH | 18:1 | 3 wt% MgO- La ₂ O ₃ | 15.0- 17.8 | 65 °C, 300 min | 97.70 | (Feyzi <i>et al.</i> 2017) |
| Edible oil | CH₃OH | 15:1 | 4 wt% ZnO/ BiFeO₃ | | 65 °C, 300 min | 95.40 | (Salimi and Hosseini 2019) |
| Castor oil | CH₃OH | 8:1 | 11 wt% Ni-ZnO | 31.5 | 55 °C, 60 min | 95.20 | (Baskar <i>et al.</i> 2018) |
| Cotton seed oil | CH₃OH | 24:1 | 12 wt% 5- Na/ZnO | 16 | 65 °C, 240 min | 98.00 | (Malhotra and Ali 2019) |
| Refined vegetable oil | CH₃OH | 12:1 | Cs-Ca/TiO ₂ - SiO ₂ | 40 to 50 | 60 °C, 500 rpm,120 min | 98.00 | (Feyzi and Shahbazi 2015) |
| Recycled cooking oil | CH₃OH | 7:1 | 3 wt% CaO- MgO | 61 to 69 | 65 °C, 360 min | 98.95 | (Tahvildari <i>et al.</i> 2015) |
| Waste cooking oil | CH₃OH | 8:1 | 12 wt% CZO nanocomposite | 80 | 55 °C, 50 min | 97.71 | (Gurunathan and Ravi 2015) |
| Palm oil | CH₃OH | 6:1 | TiO ₂ -ZnO | 85 to 87 | 60 °C, 300 min | 92.20 | (Madhuvilakku and Piraman 2013) |

In the production of biodiesel, nano-catalyst technology has been widely studied as a new method with high catalytic efficiency. Nano-catalyst technology has high opposition to saponification, high specific surface area, high stability, high activity, and good reusability (Cao *et al.* 2019; Singh *et al.* 2019b). As shown in Table 5, various nanocatalysts have been used in transesterification reactions and have achieved extremely high conversion efficiency. Feyzi and Shahbazi (2015) mixed refined vegetable oil and Cs-Ca/TiO₂-SiO₂ nano-catalyst to produce biodiesel with a yield of 98% through the transesterification reaction. The research found that the factors that affect the catalytic activity were the specific surface area, pore size, pore volume, and surface-active site concentration of the catalyst. At the same time, the viscosity, density, and refractive index of biodiesel decreased as the yield increased.

DEVELOPMENT STATUS AND TECHNICAL ANALYSIS OF BIOMASS JET FUEL

Development Status of Biomass Jet Fuel

Jet fuel has stricter standards, which require that it be mainly composed of a certain structure and proportion of carbon-based liquid alkanes. The composition of conventional jet fuel is 20% straight-chain alkanes, 40% branched alkanes, 20% cycloalkanes, and 20% aromatic hydrocarbon. Good low temperature performance, high stability, good lubricity, non-corrosiveness, and low static electricity are required (Mawhood *et al.* 2016).

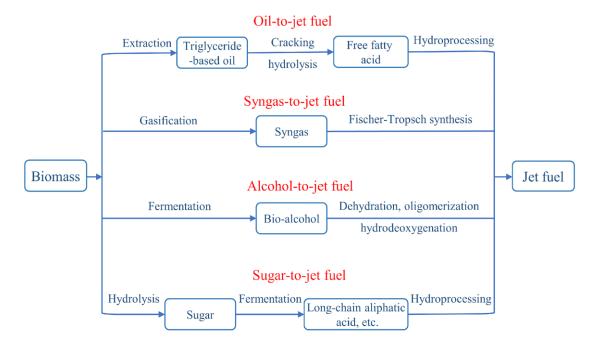


Fig. 1. The main ways to produce jet fuel from biomass

| Table 6 | . The Main | Ways to | Produce | Bio-jet Fuel |
|---------|------------|---------|---------|--------------|
|---------|------------|---------|---------|--------------|

| Conversion Pathway | Conversion Methods | Features |
|-------------------------|---|--|
| Oil-to-jet fuel | Hydroprocessing | 1. The preparation process requires strict control of reaction conditions. 2. Industrial applications have been achieved, but raw material sources are limited and prices are higher, which has resulted in high preparation costs (Jamil <i>et al.</i> 2017). |
| Syngas-to- jet fuel | Gasification, Fischer-Tropsch, and hydroprocessing | 1. The Fischer-Tropsch method has a sufficient supply of biomass raw materials and mature technology, and the by- products in the production process are close to petrochemical products. The products have a lower sulfur content, aromatic content and carbon dioxide emission. 2. Problems include the long follow-up processing route of synthesis gas, poor product selectivity, complicated processing procedure, harsh operating conditions, high investment cost, and choking danger (Wang <i>et al.</i> 2018; Klayborworn and Pakdee 2019) |
| Alcohol-to- jet fuel | Dehydration, oligomerization, and hydrogenation | 1. This method is highly dependent on raw materials and obtaining higher yields of low-carbon alcohols from non-edible lignocellulose is difficult. 2. There are many challenges in the highly selective dehydrogenation and polymerization of alcohols during the preparation process (He <i>et al.</i> 2018; Nie <i>et al.</i> 2018) |
| Sugar-to-jet fuel | Hydrolysis, fermentation, and hydroprocessing | This method has the advantages of a mild process and simple product after-treatment, but the efficiency is low, the yield of the obtained product is low, and it is difficult to use it industrially. The direct conversion of biomass into aviation-grade alkane through fermentation has been a hotspot in biomass bioconversion in recent years. By cultivating engineered bacteria and regulating metabolic pathways, this method is expected to make breakthrough progress (Wei <i>et al.</i> 2019). |

At present, jet fuel is mainly obtained from petrochemical raw materials through cracking, distillation, and isomerization reforming. The use of biomass to produce directly usable jet fuel is a challenging goal. Figure 1 is an adaptation of Wang *et al.* 2019 (Fig 1). Figure 1 and Table 6 show that researchers have developed several methods for preparing jet fuel from biomass, but most of them can only prepare a certain component of jet fuel (Du and Yan 2016). Jamil *et al.* (2017) used *Phoenix dactylifera* kernel oil as the raw material for hydrodeoxygenation. It was found that large fraction of paraffinic hydrocarbons accounted for 91.1% of the oil. Using Pd/C catalyst to produce jet fuel fraction, the product had the density of 0.88 kg/m³, the viscosity of 3.49mm²/s, and the calorific value of 44.11 MJ/kg.

Table 7 is an adaptation of Wang *et al.* 2019 (Table 1). As shown in Table 7 some bio-jet fuels have been successfully developed on a commercial scale and met the requirements of the American Society for Testing and Materials (ASTM) D7566-17 (2017) standard. These biomass jet fuels can be mixed with petroleum-derived jet fuels with a mixing ratio of up to 50%. Their production costs are mainly affected by raw material prices, catalyst prices, energy consumption, the efficiency of the conversion process, and related value-added products (Wang *et al.* 2019). Current commercial airlines reduced carbon emissions by blending bio-jet fuel derived from vegetable oil with fossil jet fuel. Klein *et al.* (2018) studied the production technology of bio-jet fuel produced by Brazil's sugarcane biorefinery and found that the carbon emissions of bio-jet fuel produced were reduced by 70% compared to fossil jet fuel. Among them, hydroprocessed esters and fatty acids technology had the highest production capacity. The Fischer-Tropsch synthesis method had the best economic benefits, but the yield was relatively low.

| Conversion Pathway | Feedstocks | Certification Level* | Yield** | Price (\$US/gal) | References |
|--|--|-------------------------|--------------|---------------------|---|
| Oil-to-jet fuel | Plant oils, waste oils, algal oils, and pyrolysis oils | D7566-17 annex A2* | 19 to 120 | 2.6 to 34.7 | (Gutiérrez-Antonio <i>et al.</i> 2017; Klein <i>et al.</i> 2018; McGarvey and Tyner 2018) |
| Syngas-to- jet fuel | Wood raw materials and biomass waste | D7566-17 annex A1* | 9 to 89 | 4.8 to 16.2 | (Okeke and Mani 2017; Sikarwar <i>et al.</i> 2017; Neuling and Kaltschmitt 2018) |
| Alcohol-to- jet fuel | Carbohydrates and lignocellulose | D7566-17 annex A5* | 11 to 81 | 4.1 to 14.4 | (Yao <i>et al.</i> 2017; Jang and Choi 2018; Michailos 2018) |
| Sugar-to-jet fuel | Carbohydrate, sugars in lignocellulose | D7566-17 annex A3* | 24 to 45 | 4.3 to 25.4 | (Li <i>et al.</i> 2018; Olcay <i>et al.</i> 2018; Shen <i>et</i> <i>al.</i> 2019) |
| * ASTM D7566-17 (2017): "Standard specification for aviation turbine fuel containing synthesized hydrocarbons" was formulated by American Society for Testing and Materials; | | | | | |

* ASTM D7566-17 (2017): "Standard specification for aviation turbine fuel containing synthesized hydrocarbons" was formulated by American Society for Testing and Materials; Annex A1: Fischer-Tropsch hydroprocessed synthesized paraffinic kerosene; Annex A2: Synthesized paraffinic kerosine from hydroprocessed esters and fatty acids; Annex A3: Synthesized iso-paraffins from hydroprocessed fermented sugars;

Annex A5: Alcohol-to-jet synthetic paraffinic kerosene (ATJ-SPK);

** Yield: Gallon of gasoline equivalent/biomass dry ton

Han *et al.* (2017) used sugar-to-jet to prepare bio-jet fuel from corn stover *via* both biological and catalytic conversion. Compared with petroleum jet fuel, the product could

reduce greenhouse gas emissions by 59%. The degree of environmental protection and emission reduction were largely depended on the hydrogen source. Alcohol-to-jet produced bio-jet fuel from sugary, starchy, and lignocellulosic biomass *via* fermentation of sugars to ethanol or other alcohols. Among them, using sugarcane as a raw material had lower costs and fewer risks. Technical uncertainty was the most important factor that affected the economics of the production route. Changes in by-product revenue would greatly affect profitability (Yao *et al.* 2017).

Technical Analysis of Biomass Jet Fuel

Figure 2 shows that the production of biomass jet fuel can be accomplished by onestep, two-step, and three-step methods. Wu *et al.* (2017) used vegetable oils as raw materials to convert into jet fuel through a three-step process. The zeolite catalyst was first used to catalytic crack the vegetable oil into light aromatics, then the ionic liquid was used to aromatically alkylate the light aromatics, and finally the aromatics were hydrogenated. In terms of heat of combustion, H/C molar ratio, and average molecular composition, the production of cycloparaffinic and aromatic biofuels could meet the requirements of bio-jet fuels. The three-step process of bio-jet fuel production can also be simplified into a twostep process. Xu *et al.* (2018) used algae as a raw material to produce biodiesel through a two-step process (hydrothermal liquefaction followed by catalytic upgrading). The final product had similar characteristics to jet fuel. The one-step process is generally simpler than the three-step process, but it has a lower yield. Yield can be improved by further improving the production materials and production processes in a one-step process (Perkins *et al.* 2019; Yang *et al.* 2018).

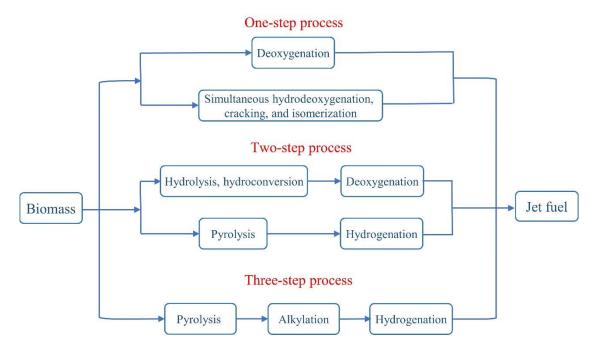


Fig. 2. Summary of current biomass jet fuel preparation technology

| Table 8. Summar | y of Current Biomass Jet Fuel Preparation Technology |
|-----------------|--|
| | |

| Feedstocks | Production Steps | Yield (%) | Major Findings | Reference |
|---|---|--------------|---|-------------------------------|
| Commercial vegetable oil | 1. Pyrolysis; 2. Alkylation; 3. Hydrogenation | 84.3 | step Process 1. C₆-C₉ aromatic hydrocarbons can be obtained by catalytic pyrolysis from plant oil with a catalyst such as HZSM-5. 2. When the carbon number is between 8 and 15, the carbon number distribution of the aromatic hydrocarbons can be adjusted by changing the reaction temperature and time in the catalytic cracking reaction. | (Wu <i>et al.</i> 2017) |
| Straw stalk | Pyrolysis; Alkylation; Hydrogenation | 88.4 | Synthesis of aromatics with 8 to 15 carbon atoms can be achieved via alkylation reaction. Synthesis of cycloalkanes with 8 to 15 carbon atoms can be achieved via hydrogenation reaction of aromatic hydrocarbons. | (Wang <i>et al.</i> 2015) |
| Saw dust | 1. Pyrolysis; 2. Alkylation; 3. Hydrogenation | 80.4 | Hydrocarbons produced from sawdust can be used for aviation and diesel fuels after subjection to suitable conversion methods. Hydrocarbons with 8 to 15 carbon atoms can be prepared <i>via</i> alkylation of ionic liquids. | (Zhang <i>et al.</i> 2015) |
| | | Two- | step Process | |
| Eucalyptus sawdust and discarded soybean frying oil | 1. Pyrolysis; 2. Hydrogenation | 60.0 | Adding discarded soybean frying oil to eucalyptus sawdust could increase the yield of oil produced by pyrolysis of biomass lignin 40% to 50%. The hydrogenation reaction can greatly improve the stability and quality of biomass liquid fuels. | (Shah <i>et al.</i> 2019) |
| Algae lipid | 1. Hydroconversion; 2. Gas-liquid; separation | 38.0 | Neutral lipids extracted from wet algae biomass can be directly converted into aviation fuel range paraffin through a one-step catalytic hydrocracking reaction of composite catalysts, such as Pt / Meso-ZSM-5. Compared to the mixed solvent extraction method, the metal content of the neutral lipid-rich fractions prepared from wet algae is lower by solvent step-by-step extraction. | (Ju <i>et al.</i> 2018) |
| Microalgae | Hydrothermal liquefaction; Hydro upgrading | 54.4 | Microalgae that contains a large amount of lipids has a higher yield than macroalgae when producing biomass oil. Crude bio-oils made from Schizochytrium limacinum have a | (Xu <i>et al.</i> 2018) |

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| | | | high energy density after hydrogenation treatment, and their N, O, and S contents and viscosity were noticeably reduced and have similar characteristics to aviation fuels. | |
|---|--|-------|---|---|
| Palm olein | Hydrolysis; Simultaneous deoxygenation, cracking, and isomerization | 61.0 | 1. Using palm olein as the raw material and H-beta zeolite catalyst without noble metal as the catalyst for deoxygenation, cracking, and isomerization under low hydrogen pressure (10 bar), biomass hydrocarbons with a freezing temperature of -30 °C could be prepared | (Sousa <i>et al.</i> 2018) |
| Algal oil | 1. Hydrogenation; 2. Hydrogenolysis | 70.0 | 1. The use of load-type Ru catalysts in hydrolysis reactions increases the yield of C ₅ -C ₁₂ alkanes. | (Nakaji <i>et al.</i> 2017) |
| | | One-s | step Process | |
| Waste cooking oil | 1. Simultaneous hydrodeoxygenation, cracking, and isomerization | 39.7 | SBUY-MCM-41 zeolite has a special layered structure, high acidity, and hydrothermal stability. Loading NiMo catalyst on SBUY- MCM-41 could noticeably enhance the selective cracking of hydrocarbons in the jet fuel range by waste cooking oil. | (Zhang <i>et al.</i> 2019) |
| Cotton seed oil dregs | 1. Micro pyrolysis | 32.0 | 1. The presence of water in the biomass feedstock is conducive to cracking reactions, thereby increasing the yield of biomass oil. | (Dos Santos Souza <i>et al.</i> 2018) |
| Bamboo waste and <i>Spirulina</i> <i>platensis</i> | 1. Deoxygenation co-pyrolysis | 36.8 | 1. The co-pyrolysis of bamboo waste and microalgae with biochar catalyst could effectively remove oxygen and maintain oil fraction yield. | (Chen <i>et al.</i> 2018) |
| Camelina, carinata, and used cooking oil | 1. Hydrodeoxygenation | 54.0 | 1. Relatively unsaturated feedstocks consumed more hydrogen and energy than more saturated feed stocks when cracking to produce alkanes. | (Chu <i>et al.</i> 2017) |

The current research and main findings on biomass jet fuel are shown in Table 8. Table 8 shows that the yield of biomass jet fuel from the three-step process is generally high, as it has a minimum yield of 72.5%. The three-step production process can be further simplified to the two-step process. Nakaji *et al.* (2017) used algal oil as a feedstock to perform two steps of hydrogenation and hydrogenolysis, which could produce jet fuel with a yield of up to 64%. One-step production of biomass jet fuel has become the latest research trend. However, there are still many challenges and limitations in the selection of raw materials, catalysts, and reaction parameters. It is necessary to explore more potential raw materials and develop new catalysts suitable for the one-step process (Why *et al.* 2019). The yield of biomass jet fuel from the one-step process is low at generally less than 40%. Chu *et al.* (2017) used nitrogen instead of hydrogen to achieve the deoxidation of bio-oil, thereby increasing the yield of biomass jet fuel by the one-step process to 54%. This

indicates that the use of nitrogen will improve the dependence of the deoxygenation process on hydrogen.

CONCLUDING REMARKS

Biomass liquid fuel can be regarded as the most important form of renewable, green, clean, and recyclable biomass energy. Its development and research will be one of the major hot topics in the world for a long time to come.

Biomass liquid fuel conversion technology can be strengthened by reducing the energy consumption in the process of bio-converting ethanol, developing suitable and economically feasible hydrolysis process steps, and improving the conversion and yield of cellulose and hemicellulose. Genetic engineering should be used to genetically modify cellulase and fermentation microorganisms to improve fermentation efficiency. In addition, the breeding of high-efficiency fermentation strains suitable for complex fermentation environments should also be pursued to increase ethanol production.

The development of cheap catalysts with high activity, high stability, high utilization rate, and environmentally friendly and cost-effective production processes is the key to promoting the large-scale, stable development of biodiesel.

Exploring new reaction paths and simplifying tedious reaction steps using favorable strategies, such as the one-step method, are the future trends of biomass-to-jet fuel. Existing hydrodeoxygenation reactions often rely on precious metal catalysts, and the development of cheap, stable, and efficient catalysts is critical for the industrial application of biomass jet fuels. Research and development of co-production technologies for high-quality biomass fuels and high value-added chemicals can reduce conversion costs and greatly improve resource utilization.

In summary, how to improve the conversion of raw materials and product yields, reduce the side reaction process, and develop clean and efficient new production processes will be hot research topics for the preparation of biomass liquid fuels in the future. In the future development of the energy industry, as a new type of energy strategic industry, further research and development and application of bio-liquid fuels are required to fully elucidate the economic and ecological benefits of bio-liquid fuels.

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