Review on Preparation of Biodiesel by Transesterification of Inedible Oil

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Abstract:

Biodiesel attracts widespread attention as an excellent alternative energy for diesel. By consulting databases such as CNKI, Scopus, the relevant literature on biodiesel preparation was summarized, and the latest research progress in biodiesel preparation by catalytic transesterification was overviewed to help researchers in this field. This paper raises the following viewpoints: The current research tends to prepare biodiesel from nonedible oil as raw material by heterogeneous catalysis transesterification. Catalysts are evolving towards multi-functionality and magnetic responsiveness. Supported catalysts prepared with stable catalyst carriers and catalytically active materials have aroused concern, and environmentally friendly catalysts prepared from waste biomass have received particular attention. Hydrodynamic cavitation, microwave and electrolysis have also been used to assist transesterification. In addition, this paper reviews quantitative evaluation of biodiesel from multiple aspects of conversion rate, methyl ester purity and mass yield to improve the accuracy in evaluation.

Keywords: *biodiesel; inedible oil; high acid value; waste biomass; heterogeneous catalytic transesterification*

I. INTRODUCTION

With the development of human society, people gradually raise higher requirements for environmental protection. Traditional fossil fuels can no longer meet people's growing consumption needs. Biomass energy will become the future primary energy. Biodiesel has similar properties to diesel, boasting advantages of easy degradation, low toxicity, low exhaust emission, renewability. With rich varieties of raw materials it is considered as the best substitute for diesel[1][2]. It is estimated that there is a total growth rate of about 5.48% in the global biofuel market during the period 2018-2026 [3]. China has successfully commercialized biodiesel technology, but still faces some problems in promoting biodiesel. In recent years, the high cost of biodiesel relative to low international oil price has hindered its commercialization [4], which is an issue studied in a lot of researches. This paper reviews the latest research progress in the preparation of biodiesel by transesterification, summarizes the effective methods

for evaluating the biodiesel yield, and suggests the future research directions.

II. FEEDSTOCKS OF BIODIESEL

2.1 Non-edible Oil

70%-90% cost of biodiesel derives from its raw materials[5]. Traditional biodiesel feedstock oils are generally sourced from oil crops, including edible oils (rapeseed oil, soybean oil, palm oil, corn oil) and non-edible oils (jatropha oil, castor oil, cottonseed oil)[6,7]. In order to control the biodiesel cost and avoid competition between fuel oil and edible oil for resources, researchers tend to use non-edible oils as raw materials, such as jatropha oil, castor oil, rice bran oil, algae oil, and kitchen waste oil.

Jatropha has a short growth cycle and strong survivability to adapt to various types of soil. With low water and fertilizer requirements, it barely requires management after planting. Jatropha seeds have an oil content of 30%-60%, ranking second among oil crops[8]. Jatropha seeds are highly toxic to humans and animals, whose residue after oil extraction is difficult to utilize. Regarding this problem, some people proposed to use the remaining biomass for composting, or convert it into heat resources and electric energy[9]. Guadalupe et al.[10] found a non-toxic jatropha species from Mexico, whose residue after oil extraction can be used for food processing and feeding.

Castor bean has rich oil content of up to 42%~48%. Castor bean oil is a light yellow, highly viscous bio-oil, which boasts the advantages of high oxygen content, high cetane number and low sulfur content. Castor oil plant has a shorter growth cycle than crops such as palm, jatropha. Moreover, castor oil can replace edible oil in the production of biodiesel[11].

Rice is one primary food for mankind. According to the International Grains Council (IGC), the global rice production is expected to reach 508.6 million tons in 2020-2021, the by-product rice bran production can reach 5 wt%-14.8 wt% of the total weight, and the oil content of rice bran is about 16 wt%-32 wt%. Due to the presence of active lipase, most rice bran oil has high free fatty acid content, making it inappropriate for direct consumption. However, it can be used to produce biodiesel. At the same time, rice bran has a protein content up to 14%~16%, and the remaining residue after oil extraction can be used for feed processing[12].

Algal oil is a high-quality raw material for biodiesel production. As early as more than 3 decades ago, the Aquatic Species Program (ASP) of the U.S. Department of Energy (DOE) clarified the potential of algae in providing biomass energy. Microalgae is a kind of photosynthetic microorganism with a growth rate 10-50 times that of terrestrial plants. With a large amount of esters (20-50%) in its cells, it has an oil production 15-300 times that of traditional oil crops. Meanwhile, algae has low growing environment requirements, does not compete with crops for resources, and can rely on wastewater and waste gas in growth [13,14].

With the increase in population, the consumption of edible oil grows at an unprecedented pace. According to the United States Department of Agriculture (USDA), the global consumption of vegetable oil reaches 209.85 million tons in 2020, with 2% increase annually[15] . According to reports, the production of kitchen waste oil can reach 20% of the total consumption of animal and vegetable oils [16]. These waste oils undergo biochemical reactions such as oxidation and hydrolysis to produce foul-smelling aldehydes, acids and other products that deteriorate the ecological environment. At the same time, it may contain heavy metals and carcinogens, which may enter the food chain and endanger human health [17,18]. In addition, most kitchen waste oil is dumped into the drainage system, garbage bins or directly discharged into the natural environment, increasing the burden on the wastewater treatment system [15], affecting soil permeability and dissolved oxygen content in water, leading to eutrophication of water bodies, and destroying the ecological balance. According to reports, the price of kitchen waste oil is 2-3 times cheaper than that of virgin vegetable oil [9,19]. The use of kitchen waste oil to produce biodiesel can effectively lower the raw material cost of biodiesel and reduce the harm of kitchen waste oil emissions to the ecological environment and human health, thus achieving recycling of kitchen waste oil.

In addition, some researchers developed new raw materials for biodiesel preparation by using waste biomass as a microbial culture medium. Bioconversion of durian peel was used as raw material to produce biodiesel. After extracting the oleaginous yeast KKUSY14 from the soil of a cattle farm, they converted the durian peel hydrolysate into microbial lipids, and then let wet cells undergo base-catalyzed transesterification reaction under microwave-assisted heating[20]. It was found that 1000 g durian peel could be converted into 15.86 g biodiesel. Su et al. [21] used volatile fatty acid, an intermediate product of anaerobic digestion process, to cultivate oil-producing microorganisms for biodiesel production. Under the optimum conditions, the biomass yield was 125.17 mg/(L·d), with 29.54% oil content. This method also removes nitrogen and phosphorus pollutants from wastewater.

2.2 Pretreatment of low grade biomass oil

It is still challenging to use low-grade biomass oil for large-scale biodiesel production. After storage of biomass oil for a long time, the oil in it will be hydrolyzed to generate free fatty acid, resulting in increased acid value, so it is generally unsuitable for direct transesterification. Kitchen waste oil has complicated components, and the acid value of glycerides may reach 57.49 mg KOH/g after high-temperature hydrolysis[22–24]. Therefore, biomass oil deacidification attracts widespread attention. At present, deacidification methods include alkali refining deacidification, distillation deacidification[25], solvent extraction deacidification[26], enzymatic deacidification[24], adsorption deacidification[27], chemical esterification deacidification[28], etc.

Alkali refining deacidification is to let alkali solution react with acid oil to produce soap and water, which are then removed by centrifugation, washing processes. The soap produced by alkali refining deacidification will absorb and encapsulate neutral oil, resulting in a great loss. Inappropriate for high acid value oil, it also produces much wastewater. Distillation deacidification is a method to achieve liquid-liquid separation based on the difference in the liquid boiling point or the difference in the mean free path

of molecular motion. Jin et al. [25] refined and decolorized rice bran oil through multi-stage molecular distillation to remove free fatty acids. The supercritical carbon dioxide extraction deacidification method reported by Qin et al. [26] can reduce the free fatty acid from 34% to 10%, and this treatment method reduces the acetone insoluble matter in the oil. The limitations of distillation deacidification and supercritical extraction lie in demand for higher reaction conditions, consumption of excessive energy, and high cost. Enzymatic deacidification is to convert free fatty acids into glycerides or other[24] derivatives under the catalysis of lipase. Li filtered the lipase SMG1 and transformed it into lipase SMG1-F278N. After enzymatic deacidification of high acid value rice bran oil, squid oil and kitchen waste oil (with free fatty acid content of 25.14%, 13.84%, 28.69% respectively), the free fatty acid content decreased to less than 0.06% within 8 h, but the high cost of enzymes limits the application of enzymatic deacidification. The magnesium silicate adsorbents was prepared with silica from rice husk ash and different proportions of magnesium oxide[27]. Under optimal conditions, per gram of adsorbent has an adsorption capacity of 185 mg against free fatty acid from crude palm oil. Chemical esterification deacidification enjoys wide applications. Generally, chemical catalysts (mainly acids, metal hydrate salts, etc.) are used to catalyze the reaction between free fatty acids and glycerol to convert it into glycerides, or it can react with alcohols to produce methyl esters. Studies have shown that metal hydrates can form acidic alcohol-water complexes in alcohols, which can effectively catalyze the esterification of free fatty acids. It was found that catalytic activity is ranked in descending order as that of $Al^{3+} > Fe^{3+} \approx Sn^{2+} > Cu^{2+} > Mn^{2+} > Ni^{2+} > Cd^{2+} > Mg^{2+} > Co2+ \approx Zn^{2+} \approx Ca^{2+} \approx Cu^{+}$, and the acid value of the oil phase can be reduced to 0.75 mg KOH/g[28]. In addition Marcos et al.[23] used activated carbon-supported calcium hydroxide nanoparticles to deacidify soybean oil through efficient reactive adsorption, finding that the deacidification agent had an oleic acid removal capacity of up to 2750-7000 mg/g, demonstrating good separation effect after deacidification.

III. RESEARCH ADVANCES OF BIODIESEL PREPARATION BY TRANSESTERIFICATION

The preparation of biodiesel is mainly to process biomass feedstock oil through physical and chemical methods to result in properties similar to that of diesel. The current preparation methods mainly include dilution method[9,29], micro-emulsion method[30,31], pyrolysis[32,33] and transesterification.

Transesterification gradually converts triglycerides and short-chain alcohols into methyl esters, diglycerides, monoglycerides, and glycerol in multiple consecutive reversible reactions, which represents the most promising method for the preparation of biodiesel[2]. Where, by-product glycerol can be used in industries like cosmetics. Transesterification reactions can be categorized into non-catalytic transesterification and catalytic transesterification[29,34]. Non-catalytic transesterification is mainly a supercritical method, which uses supercritical conditions to make bio-oil and alcohol mutually soluble to facilitate the transesterification reaction without the addition of an external catalyst. According to research, metal reactors play a catalytic role in the reaction[35]. Catalytic transesterification can be classified into homogeneous catalysis and heterogeneous catalysis. Catalysts include base catalysts, acid catalysts, as well as enzyme catalysts and some new catalysts.

3.1 Improvement of catalyst

So far, research on biodiesel mostly adopts heterogeneous catalysts. Compared with homogeneous catalysts, heterogeneous catalysts are recyclable and reusable, the prepared biodiesel has simple subsequent purification process, and the post-treatment process produces little wastewater[36]. Where, alkaline earth metal oxides, hydroxides (calcium oxide, strontium oxide, magnesium oxide, calcium hydroxide, etc.) and transition metal oxides have received the most attention. Nonetheless, heterogeneous catalysis has lower mass transfer efficiency than homogeneous catalysis, which generally requires higher methanol-oil ratio and longer reaction time[37].

The preparation of heterogeneous catalysts using waste biomass materials (such as carapace, bone, feces, and plant leaves and peels, etc.) has become a research hotspot (Table I). It contributes to resource utilization of waste biomass and further reduces the cost of biodiesel.

Multifunctional solid catalyst (acid-base bifunctional catalyst, magnetically responsive catalyst, etc.) is another research hotspot of heterogeneous catalysts.

The acid-base bifunctional catalyst can simultaneously catalyze the esterification of free fatty acids and the transesterification of glycerides. Rose et al.[38] prepared the bifunctional catalyst PKSHAC-$K_2CO_{3(20\%)}CuO_{(5\%)}$ with palm shell, they prepared porous palm shell biochar by hydrothermal assisted carbonization, then increase its biochar acidity (1.05-1.48 mmol/g) and basicity of (1.73-5.73 mmol/g) by sodium hydroxide, potassium carbonate and oxidized copper. Experiments show that this catalyst can catalyze the conversion of kitchen waste oil within 2 h and attain biodiesel yield of 95.36 $\pm$ 1.4%.The yield decreased to 82.5 $\pm$ 2.5% after 5 cycles of recycling. Ali et al.[39] designed a SrO-ZnO/Al$_2$O$_3$ bifunctional catalyst to catalyze the reaction of kitchen waste oil with 18% free fatty acid content and ethanol at 75 °C for 5 h, and the biodiesel yield was 95.7%, but the high leaching rate of strontium made this catalyst unsuitable for repeated use. Nasar et al. [40] prepared bimetallic tungsten-zirconium oxide and supported calcium oxide (WO$_3$-Zr$_2$O$_3$/CaO) to catalyze the preparation of biodiesel from crude palm oil containing 5.5% free fatty acids. Under the optimum reaction conditions (reaction at 80 ℃ for 1 h, methanol-oil ratio at 15:1), the yield of fatty acid methyl ester was 94%, and the catalyst can maintain the yield of 79.3% after 5 consecutive uses. Shahabaldin et al.[41] prepare a compressible bifunctional foam catalyst by LaPO4 supported nickel foam, which has a porous structure, large specific surface area and good stability, and is easier to separate than powder catalysts. The yield of fatty acid methyl ester reached 91% after transesterification of kitchen waste oil and methanol at 90 °C for 2 h.

TABLE I. Catalyst prepared from waste biomass and their properties

Material	Processing Method	Catalyst	Reaction Conditions (methanol-oil ratio; time; temperature)	Biodiesel Yield (%)	Literature
Egg shell	Calcination	Calcium oxide	6:1; 11 h; room temperature	97	[6]
Crab shell	Calcination	Calcium oxide	8:1; 2 h; 65 ℃	94	[42]
Oyster shell	Calcination	Calcium oxide	9:1; 3 h; 65 ℃ (microwave)	87.3	[43]
Chicken bones, coconut residue	Calcination, acid hydrolysis	Calcium oxide/ nano-crystal cellulos /polyvinyl alcohol	6:1; 4h; 65℃	98.4	[44]
Moringa leaf	Calcination	inorganic carbonate minerals	6:1; 2 h; 65 ℃	86.7	[45]
Rice husk	Calcination and impregnation	Rice husk char/ $K_2O_{20\%}$/ $Fe5_\%$ magnetic heterogeneous catalyst	12:1; 4 h; 75 ℃	98.6	[46]
Citrus sinensis peel	Burning and extracted deionized water	Citrus sinensis peel ash@Fe_3O_4 nanoparticles (calcium oxide, potassium oxide, silicon dioxide)	6:1; 3 h; 65 ℃	98	[47]
Palm kernel shell	Hydrothermal assisted carbonization	$K_2CO_{3(20\%)}CuO_{(5\%)}$- activated carbon bifunctional catalyst	12:1; 2 h; 70 ℃	95.4	[38]
Pineapple leaves	Calcination	Magnesium oxide, phosphatase, potassium sulfate, etc.	40:1; 0.5 h; 60 ℃	98	[48]

Magnetically responsive catalysts are usually magnetized by doping iron and nickel, which can be separated from the system by an external magnetic field to facilitate the purification of biodiesel and the recycling of catalysts. Muhammad et al.[49] prepared a solid base catalyst CES-Ni by doping metal nickel in egg shells and burned at high temperature, which catalyzed the reaction of kitchen waste oil at 65 °C for 2 h, and the resulting biodiesel yield approached 100% (methanol-oil ratio 16:1). However, in this study, kitchen waste oil must be dehydrated at 110 °C for 24 h, and pre-esterified at 65 °C for 2 h by adding methanol and sulfuric acid. Balkis et al.[46] reported a potassium oxide and iron-supported supermagnetic biochar catalyst prepared by impregnation. When the molar ratio of methanol to kitchen waste oil was 12:1, the maximum yield of biodiesel was 98.6% after catalysis of transesterification reaction at 75 °C for 4 h.

Bishwajit et al.[47] prepared magnetic nanoparticle solid base catalyst CSPA@Fe$_3$O$_4$ by coating magnetic nano-iron oxide with citrus peel ash extract, and used this catalyst to catalyze the reaction of kitchen waste oil with 1.1% free fatty acid content at 65 ℃ for 2 h. The measured biodiesel conversion yield was 98%, the methanol-oil ratio required for the reaction was 6:1, and the catalyst could be recycled 9 times.

Heterogeneous catalysts generally require materials with stable properties as carriers. In addition to traditional activated carbon, materials like metal-organic frameworks (MOFs), zeolites, chitosan are often used as catalyst carriers.

MOFs are crystalline porous materials with periodic network structures formed by interconnecting inorganic metals and organic ligands. In order to optimize the separation and reuse performance of the catalyst, Xie et al.[50] coat Fe$_3$O$_4$ nanoparticles by MOFs porous material as the shell and form a magnetic material with a core-shell structure, and then fixed the basic ionic liquid on the magnetic carrier through coordination bonds to form a solid base catalyst. The catalyst could catalyze the reaction system with a methanol-oil ratio of 30:1 to attain a conversion rate of 92.3% within 3 h. The catalyst has very complicated preparation process, but can be recycled and reused. Imidazole molecular zeolite frameworks (ZIFs) are a kind of MOFs materials with a zeolite-like structure. Abdelmigeed et al. [51] magnetize ZIF-8 by ferric chloride solution co-precipitation and supported it with sodium hydroxide to prepare magnetic catalysts, but the conversion rate was merely 70% under optimal conditions. Chen et al. [52] modified ZIF-67 by phosphotungstic acid (HPW) as an acid-base bifunctional catalyst to catalyze the preparation of biodiesel from microalgae oil, and the catalytic conversion rate was as high as 98.5%. A stable W-O-N coordination bond can be formed between HPW and ZIF-67 to optimize the recyclability of the catalyst. After 6 times of recycling, the conversion rate dropped to 91.3%.

Zeolite catalyst has large number of pores and a large specific surface area. In order to increase mass transfer efficiency, Majid et al.[37] designed a KOH/zeolite solid catalyst. During the catalytic reaction, the zeolite forms a microchannel reactor, so that the two phases of methanol and oil are fully mixed in the microchannel, thereby effectively shortening the reaction time. The study showed that under methanol-oil ratio of 10.5:1, it only took 13.4 min to produce biodiesel with a fatty acid methyl ester content of 97.45%. In this study, kitchen waste oil needs to undergo catalytic esterification by sulfuric acid at 65 °C for 2 h to reduce the free fatty acid content. Fly ash, a harmful by-product of the coal-burning industry, can be used to synthesize zeolite-like porous materials. Faisal et al.[53] used kaolinite as a precursor to prepare a sulfated zeolite catalyst and catalyzed the production of biodiesel from shea butter. After reaction at 200 °C for 6 h in a stainless steel reactor, the highest biodiesel yield was 90.76%. Li et al.[54] prepared Li$_2$CO$_3$/NaY zeolite catalyst with fly ash as raw material to catalyze the transesterification reaction of ethanol and castor oil. The yield of fatty acid ethyl ester was 98.6% after 2 h reaction under methanol-oil ratio of 18:1.

Chitosan is a natural high molecular polymer containing a large number of amino and hydroxyl functional groups. It exhibits catalytic activity in the process of alkali catalysis and has good chelating ability against metal ions, which is an excellent catalyst carrier. It has been reported[55] that immobilized

enzyme catalysts can be prepared by using chitosan to improve the stability of enzyme catalysts. When used as catalyst carrier with Fe_4O_3 at the same time, it can be made into magnetic immobilized enzyme catalysts supporting easy recovery, but the reaction time is long, usually taking 12-72 h. The metal ion modified catalyst prepared by chitosan and solid base catalyst also have high biodiesel yield (>90%) in transesterification.

Botti et al. [56] applied a "direct ink writing" additive manufacturing technology to the preparation of transesterification catalysts. This technology can be used to fabricate various three-dimensional objects with complex void structures and then control the mechanical strength, wettability and other properties of the catalyst carrier by changing the structure. In this study, a solid base catalyst was prepared using an aluminum silicate-based ceramic polymer containing potassium and sodium as an "ink", which catalyzed the transesterification reaction with the highest yield of 85.3%.

Despite some progress made in the research of new catalysts, there are still common problems that the heterogeneous catalysis method requires higher methanol-oil ratio and longer reaction time.

3.2 Improvement of transesterification and its auxiliary process

Homogeneous catalysts have low cost and high mass transfer efficiency in the reaction, but are difficult to recover and cannot be reused, making it difficult to purify biodiesel and producing a large amount of waste water. At the same time, homogeneous base catalysts are sensitive to water and free fatty acids, which are difficult to apply to transesterification of non-edible oils[22]. Some researchers have modified the traditional homogeneous base-catalyzed transesterification process. Wu Lian et al.[4] used bentonite as a water absorbing agent to inhibit the hydrolysis of oil, and used diethyl ether as a co-solvent to increase the mutual solubility between oil and alcohol and therefore the mass transfer efficiency. Nevertheless, this process still faces difficulty in separation and purification of biodiesel.

In recent years, researches have reported methods of using electrolysis, cavitation, microwaves, and special reactors to assist biodiesel production.

Maryam et al.[57] prepared a phosphomolybdic acid/graphene oxide catalyst, and implemented electrolysis to catalyze the conversion of kitchen waste oil into biodiesel. Molybdenum is a transition metal, and phosphomolybdic acid is less corrosive than traditional sulfuric acid and hydrochloric acid catalysts, thus solving the problem of catalyst corrosion to equipment. The transesterification by electrolysis can be carried out at room temperature, and the water in the waste oil facilitates the electrolysis reaction. Under the methanol-oil ratio of 6:1, the yield of biodiesel reached 91%, and the catalyst can be reused four times. However, the reaction required 15 h.

The use of cavitation effect to assist the production of biodiesel has been reported. Due to the cavitation effect, a large number of bubbles are generated in the system. When the bubbles burst, there is instantaneous high temperature and high pressure, which promotes the mixing of the two phases of alcohol

and oil and increases the mass transfer rate. Niraj et al.[58] catalyze the conversion of waste soybean oil into biodiesel by ultrasonic cavitation-assisted, and resulting in a 98% biodiesel yield after reaction at 70 °C for 1 h. Valentina et al.[19] used hydrodynamic cavitation technology to increase the mass transfer efficiency of alcohol-oil phases. SuperPro Designer software was used to analyze the process and compare it with the traditional process based on life cycle cost analysis. Software was used to simulate the use of sodium methoxide to catalyze the transesterification of waste edible oil at 60 ℃. The simulation reveals that 97% biodiesel yield is possible only after 15 min with the assistance of hydrodynamic cavitation technology, which can reduce 40% energy consumption compared with the traditional process.

Microwave is also an effective method to assist the transesterification reaction. Through microwave irradiation, molecules and ions collide and rub each other rapidly, generating heat to hasten the reaction. Lin et al.[43] used CaO prepared from waste oyster shells to catalyze the 180 min reaction of kitchen waste oil under 800 W microwave power and reaction temperature 66 °C, and the yield of biodiesel was 87.3%. Adrian[59] et al. developed a silicon carbide/sodium hydroxide-graphene oxide bifunctional catalyst to assist in catalyzing the esterification and transesterification of chlorella oil with 26% free fatty acid content under microwave (1000 W). It was found that, under optimal reaction conditions, the yield of fatty acid methyl ester was 81%. This method takes only 5 min reaction time, but demands a high methanol-oil ratio (48:1). Sanphawat et al.[60] studied the catalysis effect of green ionic liquid choline hydroxide (ChOH) on the transesterification of palm oil in a microwave-heated continuous reactor. The highest methyl ester yield was 89.72% at a flow rate of 20 mL/min (reaction time about 5 min), and the experimental conditions were that the molar ratio of alcohol to oil was 13.24:1, and the microwave power was 800 W.

The supercritical method can also be used in combination with the catalytic transesterification method. Syazwani et al.[61] used sulfuric acid to react with calcium oxide prepared by calcination of clam shells to prepare catalyst (CAWS), which catalyzed the palm oil fatty acid fraction (with 97%free fatty acid content) under supercritical conditions (290 °C). A biodiesel yield of 98% was achieved in just 15 min under a conventional methanol-oil ratio of 6:1.

Erick et al.[62] used CaO to catalyze the transesterification of kitchen waste oil in a Robinson-Mahoney reactor, achieving a biodiesel yield of 98.7% after 2 h reaction at 60 °C. In this kind of "basket"-shaped device with a fixed catalyst in the middle of the reactor, the impeller continuously drives the liquid to pass the annular "basket", so that the two phases fully contact, thus facilitating the reaction. Matheus et al.[63] designed a molybdenum oxide-strontium ferrite ($MoO_3/SrFe_2O_4$) magnetic catalyst, and carried out transesterification in a PARR 5000 reactor under a methanol-oil ratio of 40:1. After 4 h reaction at 164 °C, the yield was 95.4%.

Moyo et al.[64] used activated carbon-supported KOH heterogeneous catalyst to catalyze the conversion of kitchen waste oil in a TiO_2/Al_2O_3 membrane reactor, and the feedstock oil was pretreated with sulfated zirconia to remove water and free fatty acids. In this study, most of the glycerol and catalyst were separated from biodiesel by TiO_2/Al_2O_3 membrane, which facilitated the subsequent purification of biodiesel and reduced the discharge of washing wastewater. Meanwhile, membrane separation promoted

transesterification reaction to some extent. The yield of biodiesel was 94.03% under optimal conditions. Amberlyst-15 (A-15), a cation exchange resin with sulfonic acid groups as active groups, has been used in biodiesel production, but the water generated in the reaction will inhibit the catalytic performance of A-15[55]. Zhang et al.[65] prepared A-15/Poly (vinyl alcohol) membrane with water absorbency by phase inversion method. The conversion of high acid value kitchen waste oil was catalyzed under methanol-oil ratio 29:1, reaction temperature 65 °C, and flow rate 1.2 mL/min. The reactor ran continuously for 120 min, with the conversion rate maintained above 98.0%.

IV. EVALUATION METHOD OF YIELD BIODIESEL

The yield of biodiesel is generally evaluated from three aspects: transesterification conversion rate, methyl ester content of the sample, and mass yield. Quantitative methods include nuclear magnetic resonance (^{1}H NMR), gas chromatography (GC), liquid chromatography (HPLC), thermogravimetric analysis (TGA) et al. Table II summarizes commonly used quantitative methods.

TABLE II. Quantitative evaluation of biodiesel

Evaluation method	Evaluation content	Feature	Literature
^{1}H-NMR	Conversion rate of glyceride	Distinguish methyl esters and glycerides easily, but cannot identify different fatty acid methyl esters, but deuterated reagents are required	[6][39][47][66]
GC, HPLC	Conversion rate of glyceride and content of fatty acid methyl ester	Can identify different methyl esters, glycerides and glycerol, the identification of components depends on standard solutions	[54][63]
TGA	Conversion rate of glyceride	Can distinguish fatty acid methyl esters and bio-oils without additional reagents, but cannot identify different fatty acid methyl esters	[67][68]
Gravimetric method	Conversion rate of glyceride, and mass yield of biodiesel	Judge the conversion rate according to the glycerol yield, calculate the mass yield based on the biodiesel recovery without reagents and complex instruments. However, sample components cannot be identified.	[53][68]

(1) Conversion rate

The conversion rate of the feedstock oil is generally calculated by nuclear magnetic resonance, thermogravimetric analysis, or gravimetric method, while gas or liquid chromatography can be used for

evaluation.

^{1}H-NMR detects the signal intensity of the methoxy group of methyl ester and that of methylene group attached to the carbonyl group in triglyceride and its derivatives, and calculates the percentage of methyl ester in triglyceride of the sample (Eq. 1).

$$C_{NMR}(\%) = \frac{2A_{ME}}{3A_{CH_2}} \times 100 \tag{1}$$

Where C_{NMR} is the conversion measured by ^{1}H NMR, A_{ME} is the peak area corresponding to the methoxy signal of methyl ester, and A_{CH2} is the peak area corresponding to the signal of methylene.

Thermogravimetric analysis (TGA) measures how the sample mass changes with temperature. Fatty acid methyl esters and feedstock oil were evaporated successively at different temperatures (about 150 °C and 350 °C, respectively). The proportion of methyl esters in the samples can be judged according to the mass changes of the samples under different temperature ranges, so that the transesterification conversion rate can be calculated[67,69]. Studies have shown that the errors of conversion rate calculated by thermogravimetric and nuclear magnetic resonance methods are within ± 1.5%[53,68].

Theoretically, the amount of triglycerides per unit substance can be converted into equal amount of glycerol, so the conversion of feedstock oil in the transesterification reaction can also be evaluated according to the glycerol yield (Equation 2)[51].

$$Y_G(\text{wt}\%) = \frac{W_{GT}}{W_G} \times 100 \tag{2}$$

Where: Y_G is the transesterification conversion rate, $W_{biodiesel}$ is the mass of glycerol, and $W_{feedstock}$ is the theoretical yield of glycerol.

(2) Methyl ester content
Generally, GC is used to determine the content of fatty acid methyl esters in samples, though some researchers also use HPLC method. Compared with ^{1}H-NMR and TGA, this method can identify the content of each fatty acid methyl ester and then assess the mixture component. However, it does not pay attention to the conversion of feedstock oil, nor can it accurately measure the overall yield of biodiesel. Equations 3 and 4 are the gas chromatography calculation formulas given by the Chinese national standard NB/SHIT 0831 and the European Union EN 14103 standard, respectively.

$$C(\%) = \frac{(\sum A_i) - A_{EI}}{A_{EI}} \times \frac{c \times V}{m} \times 100 \tag{3}$$

$$C(\%) = \frac{(\sum A_i \times R_i) - A_{EI}}{A_{EI}} \times \frac{c \times V}{m} \times P \times 100 \tag{4}$$

Where: C(%) is the FAME content, $\sum A_i$ is the total area of the chromatographic peaks of different fatty

acid methyl esters from C_{14} to $C_{24:1}$, R_i is the correction factor of fatty acid methyl esters, A is the peak area of the internal standard substance, c is the concentration of the internal standard substance, V is the volume of the internal standard substance solution, m is the product mass, and P is the standard substance purity.

(3) Mass yield

The unit mass of triglycerides can theoretically be converted into equal mass of fatty acid methyl esters. Hence, the mass yield of biodiesel can be calculated by comparing the mass of recovered biodiesel with that of feedstock oil (Equation 5). However, the methyl ester purity of biodiesel is neglected in mass ratio quantification.

$$Y(wt\%) = \frac{W_{biodiesel}}{W_{feedstock}} \times 100 \qquad (5)$$

Where: Y is the mass yield of biodiesel, $W_{biodiesel}$ is the mass of recovered biodiesel, and $W_{feedstock}$ is the mass of feedstock oil.

To make a more comprehensive and accurate evaluation of biodiesel yield, the researchers combined the fatty acid methyl ester content with the biodiesel mass yield to calculate the mass yield of fatty acid methyl ester[62] (Equation 6).

$$FAME(\%) = \frac{W_{FAME}}{W_{fee\quad ock}} = C \times Y \times 100 \qquad (6)$$

Where: FAME (%) is the fatty acid methyl ester yield, W_{FAME} is the fatty acid methyl ester mass, $W_{feedstock}$ is the feedstock oil mass, C (%) is the fatty acid methyl ester content, and Y is the biodiesel mass yield.

Hazmi[70] prepared rice husk charcoal/ $K_2O_{(20\%)}$/$Ni_{(5\%)}$ magnetic bifunctional catalyst to catalyze the conversion of kitchen waste oil. The yield measured by gravimetric method was multiplied with the fatty acid methyl ester content measured by GC-FID to obtain a final fatty acid methyl ester yield of 98.2%. Using the same method, Bishwajit[47] measured the yield of fatty acid methyl esters at 98%, while the conversion rate measured by nuclear magnetic resonance was 98.7%. Li et al.[71] used GC-MS to evaluate the biodiesel yield, and the conversion rate of triglycerides and the yield of fatty acid methyl esters were measured to be 98% and 95%, respectively. By quantitative evaluation of biodiesel from multiple perspectives, results are more accurate and more reliable.

V. CONCLUSION

With the increasingly prominent contradiction between energy supply and demand, environmental protection policies are increasingly strict, with biomass fuel becoming one of the major energy sources in the future. This paper discusses some research progress in the current biodiesel preparation technology. The main viewpoints and findings are summarized as follows:

(1) For the sake of environmental protection and cost reduction, current research tends to use non-edible oil and waste biomass as raw materials to prepare biodiesel by heterogeneous catalysis.

(2) Waste biomass can also be used as heterogeneous catalyst precursor. Heterogeneous catalysts generally consist of catalytically active substances and carriers. Crustaceans, poultry manure, and bones are mainly calcined into catalytically active calcium oxide and hydroxyapatite. Plant peels, husks and waste wood can be calcined into catalytically active oxides and salts, which can also be made into biochar as a catalyst carrier. In addition to traditional activated carbon materials, heterogeneous catalyst carriers also include MOFs materials, zeolite molecular sieves, chitosan, ceramic polymers, etc. At the same time, bifunctional catalysts suitable for high acid value bio-oil and catalysts recoverable by magnetic force are favored by researchers. Application of these catalysts solves the problem of difficult biodiesel recycling to a certain extent, enhances the reusability of catalysts, thus allowing resource utilization of biomass waste.

(3) In addition to catalyst modification, existing researches introduce auxiliary methods such as electrolysis, microwave, and cavitation in the reaction to achieve a lower methanol-oil ratio without greatly increasing energy consumption and equipment requirements, which attains high yields in a short period of time.

(4) The yield of biodiesel should be comprehensively evaluated from multiple perspectives of conversion rate, methyl ester purity, and mass yield to make the results more accurate and reliable, which will facilitate subsequent related research.

(5) The research on biodiesel preparation mainly focuses on laboratory scale, further attention should be paid to the continuous and large-scale production of biodiesel. In addition, by giving attention to the utilization of the by-product glycerol in the preparation of biodiesel, it is possible to increase the added value of the product and reduce the cost of biodiesel. Updating and formulating relevant policies in a timely manner is also an important means to facilitate the promotion and application of biodiesel.

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