Research Progress on Preparation of Biodiesel by Transesterification

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Abstract. The preparation of biodiesel by transesterification was systematically described. According to the different types of catalysts, four transesterification methods, such as acid catalysis, alkali catalysis, enzymatic catalysis and supercritical method, were introduced in detail. The advantages and disadvantages of these four methods are analyzed, aiming at providing reference for the research and development and application of biodiesel in transesterification.

1. Introduction
With the rapid development of the economy, the economy based on fossil energy is increasingly constrained by the shortage of petroleum resources and environmental pollution. Biodiesel is a sustainable, non-toxic, biodegradable alternative to diesel fuel. Compared to traditional fossil fuels, biodiesel has lower sulfur and aromatic content, higher flash point, higher cetane number, better lubricity and lower pollution. It can be partially added to ordinary diesel and can be used without modification to existing diesel engines[1]. In recent years, biodiesel as a substitute for petroleum fuel has attracted widespread attention from scholars at home and abroad. The preparation of biodiesel has gradually become the focus of research and development of new energy. Therefore, the biodiesel market has great potential and has great development prospects.

Biodiesel is fatty acid methyl ester, it refers to the fatty acid methyl ester obtained by replacing the glycerol group in the animal and vegetable oil with a short-chain alcohol such as methanol or ethanol by esterification reaction [2]. Biodiesel is a typical “green energy”. Compared with traditional fossil energy, biodiesel has a wide range of raw materials. It can be made from vegetable oil, animal oil and catering waste oil. It is a renewable diesel fuel that can replace ordinary diesel. At the same time, biodiesel is very friendly to the environment. Compared with ordinary diesel, it can greatly reduce the emission of hydrocarbons, particulate matter, CO and polycyclic aromatic hydrocarbons. It can be biodegraded under natural conditions and greatly reduce environmental pollution [3]. In addition to the environmental performance unmatched by traditional fossil fuels, biodiesel also has good fuel performance, biodiesel has higher flash point, safer combustion, more oxygen content and better lubricity. Moreover, biodiesel can be used as fuel in an arbitrary mixing ratio with ordinary diesel, and it can be directly used in ordinary diesel engines without revamping the engine and other equipment. The popularization cost of biodiesel is low [4].
2. Preparation of Biodiesel

At present, the main preparation methods of biodiesel include direct mixing, microemulsification, pyrolysis and transesterification [5]. Microemulsification and pyrolysis have problems of coking and lubricating oil failure. The pyrolysis process needs to be carried out at high temperature, the equipment is expensive and the reaction is difficult to control. The product is a mixture of bio-gasoline and biodiesel, and the calorific value of the product is low. The transesterification process consumes less energy, and the viscosities of biodiesel produced by transesterification process are also lower [6]. Therefore, transesterification is a common method for industrial production of biodiesel. According to the different kinds of catalysts used in the reaction process, transesterification can be divided into the following four methods: acid catalysis, alkali catalysis, enzyme catalysis and supercritical extraction [7].

2.1 Acid Catalysis

The traditional acid catalysis method usually uses liquid acid (such as hydrochloric acid or sulfuric acid) as catalyst, but when using liquid strong acid as catalyst to prepare biodiesel, there are some problems, such as difficult separation of products, serious corrosion to equipment and easy to produce waste liquid. Therefore, most of the current studies use new solid superacid as catalyst to prepare biodiesel.

Duan et al. [8] used magnetic nanoparticles as carriers to synthesize novel core-shell heteropoly acid solid acid catalysts by one-step method. The conversion rate of palm oil reached 90.4% under the conditions of reaction temperature 65℃, molar ratio of methanol to palm oil 6:1, catalyst dosage 8.2 wt% and reaction time 2h. Moreover, the new solid acid catalyst has high stability and reusability. After five cycles of use in the experiment, the catalytic activity still has no obvious loss. Moreno et al. [9] prepared $\text{SO}_4^{2-}/\text{SnO}_2$ solid superacid catalyst by precipitation and impregnation method. When the molar ratio of alcohol to oil is 10:1, the amount of catalyst is 3 wt%, the reaction temperature is 80℃and the reaction time is 4h. The conversion rate of the reaction reaches 50%, and the catalyst can be reused. Chen Weihong et al. [10] used $\text{SO}_4^{2-}/\gamma\text{Al}_2\text{O}_3$ solid superacid catalyst to catalyze the preparation of biodiesel from waste oil. Under the conditions of catalyst dosage 0.5%, alcohol-oil ratio 1:6, reaction time 4 h and reaction temperature 60℃, the yield of biodiesel reached 80%. The condensation point, density, acidity value, kinematic viscosity, flash point and pour point of biodiesel are in accordance with the national standards. Wang Zhehan et al. [11] used phosphotungstic acid to catalyze castor oil to produce biodiesel. At 65℃for 3 hours, the amount of catalyst was 8%. The relative content of methyl palmitate, methyl stearate and biodiesel was 2.93%, 4.85% and 78.17% respectively. Zhang Baohua et al. [12] used carbon-based solid acid catalyst to prepare biodiesel. The reaction temperature was 60℃and the reaction time was 7 h. The amount of catalyst and methanol was 4% and 30% of the waste cooking oil input. The acid value of kitchen waste oil can be reduced from 64.0 mg KOH/g to 1.2mg KOH/g. The mass fraction of fatty acid methyl ester obtained by esterification is more than 95%.

Because of its corrosive nature, acid catalysis usually requires excessive methanol in the reactor. Biodiesel has a slow reaction speed and high requirement for reaction equipment, so biodiesel is not prepared directly by acid catalysis in industry. However, waste oils usually contain a large amount of free fatty acids, which can not be converted into biodiesel by alkaline catalysts. Therefore, the raw materials of high free fatty acids are usually pretreated with acid catalysts to convert free fatty acids into esters, and then triglycerides are transesterified by alkaline catalysts.

2.2 Alkali Catalysis

Alkali catalysis usually uses NaOH and KOH as catalysts to produce biodiesel. Compared with acid catalysis, alkali catalysis has higher transesterification reaction rate. At present, alkali catalysis is the main method of biodiesel production in China.

Chen Xuemei et al. [13] prepared KF/MgFeLa solid base catalyst with 10% KF loading, 20:1 molar ratio of alcohol to oil, 5% catalyst amount, 85℃ reaction temperature and 4h reaction time. The yield of biodiesel could reach 98.5%. Sun et al. [14] prepared Ca/SBA-15 solid base catalyst, which catalyzed the transesterification of sunflower oil and methanol to produce biodiesel in a high-pressure reactor at 200℃. The yield of biodiesel reached 95.9% when the ratio of alcohol to oil was 27:1 and the amount
of catalyst was 5% for 8 hours. Mohammed used KOH/ZrO2 solid base as catalyst, and the yield of biodiesel reached 90.8% after optimizing the catalyst. The solid base catalyst has good reusability, and its catalytic activity has not decreased significantly after five reuses. Zhou Song et al. prepared Biodiesel Catalyzed by supported calcium oxide solid base and potassium fluoride doped solid base respectively. The catalyst had high catalytic activity for the first time, and the conversion of castor oil could reach about 90%. However, the solid base catalyst used in the experiment had poor reusability. Huang Zhenxu et al. prepared MgO@SBA-15 solid base catalyst by impregnation method. The solid base catalyst has good catalytic activity for transesterification of soybean oil with methanol. The yield of biodiesel reached 91.83% when the molar ratio of alcohol to oil was 9:1, the amount of catalyst was 3% of the mass of soybean oil and the reaction time was 3h.

2.3 Enzymatic Catalysis

The enzyme catalysis is a method for preparing a biodiesel by using a biological enzyme as a catalyst, and the commonly used enzyme catalyst is a lipase. Gao et al. used macroporous resin to immobilize Candida sp.99-125 lipase to catalyze the preparation of biodiesel. The transesterification efficiency reached 97.3%. After 19 reuses, the conversion efficiency still reached 70.2%. Reem Shomal et al. used microalgae as raw material and immobilized lipase as catalyst to prepare biodiesel. The biodiesel yield of 19.3% was obtained under the conditions of 6 hours reaction time, 35°C temperature and 8:1 molar ratio. Although the yield is lower than that obtained by separate extraction and reaction processes, the whole biodiesel production process can be simplified and made more economical by synchronous production process. Zhu Guangqi et al. used lipase to catalyze palmitic acid to produce biodiesel in microemulsion system. The amount of lipase was 14% of the mass of palmitic acid, the reaction temperature was 34°C, and the reaction time was 3h. The yield of ethyl palmitate was 97.5%. Liu Weiwei et al. biodiesel was prepared from kitchen waste oil catalyzed by lipases from different sources. Biodiesel prepared by porcine pancreatic lipase and candida rugosa lipase was hydrolyzed more than 90% under the corresponding optimal hydrolysis conditions.

Compared with acid and alkali catalysis, enzyme catalysis is more efficient and the products are pollution-free, and easy to be separated. However, because of the complexity of enzyme structure, it has higher cost and is easy to inactivate, which limits the use of enzyme in biodiesel production.

2.4 supercritical extraction

Supercritical extraction is the conversion of methanol to supercritical methanol, which has the advantages of high gas diffusion and high liquid solubility under supercritical condition. Supercritical methanol not only acts as a solvent to dissolve oil, but also participates in esterification as a reactant in catalytic reaction. Supercritical extraction has strong adaptability to raw materials and can be directly processed without pre-esterification for high acid value raw materials. It is very suitable for the situation of high acid value difference in oil products in China.

Casas et al. used supercritical fluid extraction technology and oil filter cake as raw material to carry out supercritical CO2 extraction experiments in 2L extractor. The optimum extraction conditions were 40 MPa and 55°C. Under the optimum extraction conditions, acid-catalyzed transesterification was intensified. The conversion of 8:1 molar ratio of alcohol to oil was 90% and that of 12:1 molar ratio of alcohol to oil was close to 100%. Cao et al. added CO2 as co-solvent to the supercritical methanol reaction to improve the reaction conditions. The conversion of methyl ester could reach 98% in 10 minutes under the conditions of reaction temperature 280°C, molar ratio of alcohol to oil 24:1, molar ratio of CO2 to methanol 1:10 and reaction pressure 14.3 MPa, and the reaction pressure was effectively reduced. Gao Yixia et al. prepared palm oil-based non-glycerol by-product biodiesel by Micro-alkali super/near-critical process, and found that the low-temperature fluidity of 0# diesel could be
significantly improved by adding a small amount of biodiesel to 0# diesel. Qiao Baoquan\textsuperscript{[25]} prepared microalgae biodiesel by supercritical extraction. The yield of microalgae biodiesel reached 76\% under the optimum conditions of alcohol-algae ratio 9.91:1, reaction temperature 267.49\,°C and reaction time 50.72\,min.

Compared with acid-base catalysis and enzymatic catalysis, supercritical extraction does not require catalysts, and there is no problem of catalyst separation and simple post-processing. However, the process conditions of supercritical extraction are very harsh, and it is difficult to carry out large-scale industrial applications at present.

3. Development Trend of Biodiesel Production by Transesterification
At present, the methods of preparing biodiesel by transesterification can be basically divided into acid catalysis, alkali catalysis, enzymatic catalysis and supercritical extraction. Although these methods have been proved to be practical, there are still some problems in the traditional methods of preparing biodiesel. For example, although acid catalysis and alkali catalysis, which are widely used in practical production, have the advantages of high catalytic efficiency and high yield, there are some problems in the production process, such as the discharge of acid and alkali waste liquor and the difficulty in the follow-up treatment of waste liquor. The development trend of acid catalysis and alkali catalysis in the future is to develop high performance and easy separation catalysis. Optimization of production process in the production process to reduce the production of acid and alkaline waste liquor. Although alcohols used in enzymatic catalysis can be discharged without pollution, the conversion rate of methanol and ethanol is low, only 40\%-60\%. The by-product glycerol and water are difficult to recover, and short-chain alcohols are toxic to enzymes, resulting in poor reusability of catalysts with short service life. In the future, the development trend of enzymatic catalysis is to improve the conversion efficiency of alcohols and the reusability of catalytic enzymes by optimizing the catalytic enzymes. Supercritical extraction does not need catalyst and avoids the process of dissolution and separation of catalyst, but the process conditions are harsh, the operation cost is high and the energy consumption is high. The development trend of supercritical catalysis in the future is to improve the reaction equipment and reduce the operation cost, but it is difficult to realize the low-cost operation of supercritical reaction equipment in a short time. Therefore, the research of biodiesel preparation process should not only improve the existing technology, but also focus on the exploration of new technology. The preparation process of biodiesel should be continuously explored by searching for new efficient catalysts and improving new equipment.

4. Conclusion
With the continuous development of the national economy and the continuous improvement of people's consumption level, China's energy consumption is also increasing. Biodiesel, as a source of raw materials with wide range, low pollution and renewable energy, has incomparable advantages over traditional fossil energy and has been considered as the best alternative to traditional petrochemical diesel in recent years. Vigorously developing biodiesel is of great significance to the sustainable development of economy and the reduction of environmental pollution. Solving the problem of traditional biodiesel preparation method is the key to the industrialization of biodiesel. Although there are still some problems in the preparation process of biodiesel, the biodiesel market still has great potential and great development prospects. It is of great significance to research the preparation technology of biodiesel, and vigorously develop the biodiesel industry plays a very important role in solving the energy crisis and environmental protection problems.

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References

[1] Talebian-Kiakalaieh A, Amin N A S, Mazaheri H. (2013) A review on novel processes of biodiesel production from waste cooking oil [J]. Applied Energy, 104:683-710.

[2] Zuo T M , Li W M, Zhao Q, Xu Q R, Chen C, Chen L. (2014) Synthesis of biodiesel through catalyzed by a novel transesterification alkaline ionic liquid [J]. Journal of Fuel Chemistry and Technology, 42(2):200-206.

[3] Sheng M, Guo D F, Zhang D H. (2002) Study on the preparation of biodiesel from soybean oil [J]. China Oils and Fats, 27(1):70-72.

[4] Hu Z T, Wang Y G, Li J X. (2006) Development Situation and Research Progress of Biodiesel [J]. Cereals & Oils, 10:11-14.

[5] Wang Y P, Zhai Y, Zhang J L, Li W, Han Z T. (2003) Research progress in preparation methods of biodiesel [J]. Chemical Industry and Engineering Progress, 22 (1): 8-12.

[6] Dai Y, Shao R, Wu J. (2008) Review on Transesterification Catalysts for production Of Biodiesel [J]. Tractor & Farm Transporter, 35 (6): 6-8.

[7] Chen Y, Lin J Q, Chen Y, et al. (2010) Review on Research Progress in Preparation of Biodiesel Catalysts by Transesterification [J]. Chemical Engineering & Equipment, 8: 156-158.

[8] Duan X, Liu Y, Zhao Q, et al. (2013) Water-tolerant heteropolyacid on magnetic nanoparticles as efficient catalysts for esterification of free fatty acid [J]. RSC Advances, 3(33):13748.

[9] Moreno J J, James R, Gomez R, et al. (2011) Evaluation of sulfated tin oxides in the esterification reaction of free fatty acids [J]. Catalysis Today, 172(1):34-40.

[10] Chen W H, Xie X, Li Y. (2018) Preparation of Biodiesel from Gutter Oil Catalyzed by Solid Superacid SO4^2-/γ-Al2O3 [J]. Shandong Chemical Industry, 47(10): 3-4.

[11] Wang Y H, An H, Liu C, et al.(2018)Study on preparation of biodiesel from castor oil catalyzed by phosphorotungstic acid [J]. Coal and Chemical Industry, 41(12): 116-119.

[12] Zhang B H, Xu L Y, Qi , et al.(2019)Application of carbon-based solid acid catalysts in preparing biodiesels [J]. Journal of Shanghai University (Natural Science Edition), 25(01): 84-94.

[13] Chen X M, Liu L, et al. (2018) Preparation of the Solid Base KF/MgFeLa and Its Application in the Production of Biodiesel [J]. Journal of Xiangtan University (Natural Science Edition), 40(3): 51-57.

[14] Sun H, Han J, Ding Y, et al. (2010) One-pot synthesized mesoporous Ca/SBA-15 solid base for transesterification of sunflower oil with methanol [J]. Applied Catalysis A: General, 390(1): 26-34.

[15] Takase M, Zhang M, Feng W, et al. (2014) Application of zirconia modified with KOH as heterogeneous solid base catalyst to new non-edible oil for biodiesel [J]. Energy Conversion and Management, 80: 117-125.

[16] Zhou S, Zhan G Y T, He YX, et al. (2017) Repetitive performance comparison of supported solid base ascatalyst for biodiesel synthesis [J]. China Oils and Fats, 42(09): 121-125.

[17] Huang Z X , Sun H J , Chen L X, et al. (2019) Preparation of biodiesel by soybean oil catalyzed by MgO@SBA-15 solid base [J]. New Chemical Materials, 47(04): 180-184.

[18] Gao Y , Tan T W , Nie K L , et al. (2006) Immobilization of Lipase on Macroporous Resin and Its Application in Synthesis of Biodiesel in Low Aqueous Media[J]. Chinese Journal of Biotechnology, 22(1):114-118.

[19] Shomal R, Hisham H, Mlhem A , et al. (2019) Simultaneous extraction–reaction process for biodiesel production from microalgae[J]. Energy Reports, 5:37-40.

[20] Zhu G Q , Li F H ,Liu Y, et al. (2018)Lipase-catalyzed preparation of biodiesel from palmitic acid in microemulsion system and its process optimization [J]. Journal of the Chinese Cereals and Oils Association, 33(5):30-36.

[21] LIU W P, PENG Y, MA H, ZHANG Xin, et al.(2017) Hydrolysis of waste cooking oil catalyzed by lipase from different sources [J]. China Oils and Fats, 42(11):56-59.

[22] Casas L, Hernández Y, Mantell C, et al. (2015)Filter Cake Oil-Wax as Raw Material for the Production of Biodiesel: Analysis of the Extraction Process and the Transesterification
Reaction[J]. Journal of Chemistry, 2015:1-9.

[23] Cao W, Han H, Zhang J. (2005) Preparation of biodiesel from soybean oil using supercritical methanol and co-solvent [J]. Process Biochemistry, 84(4):347-351.

[24] Gao Y X , Yan L B, GU J H, et al. (2018) Kinetics of trace KOH catalyzed glycerol — free biodiesel production under super/subcritical and its properties [J]. China Oils and Fats, 43(06): 66-70+107.

[25] Qiao B Q. (2016) Microalgae Biodiesel Production by Supercritical Extraction Coupling Transesterification Reaction [D]. Dalian University of Technology.