

Brief Analysis on the Research Progress of Biodiesel Preparation from Microalgae

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Abstract

Energy is the lifeblood of modern development, and fossil energy is still the mainstream. With the growth of the world population, the rapid development of the world's industrial production and so on. Fossil energy is over-used and over-dependent, which leads to increasingly prominent environmental and energy problems. Human beings urgently need to find new, renewable and clean energy as an alternative. Microalgae, as a sustainable bio-energy raw material, has gradually entered people's field of vision. In this paper, three key problems of biodiesel production from microalgae are described :(1) the types of energy microalgae that can produce biodiesel, (2) the preparation process, and (3) the preparation of usable catalysts. The prospect of microalgae biodiesel is also prospected.

Keywords

Energy Micro Algae; Catalyst; Biodiesel.

1. Introduction

With the continuous growth of the world's population, the rapid development of the world's industrial level, the human demand for energy is also increasing, the world energy crisis is increasingly serious. Conventional petroleum fuels are expected to run out by 2050[2]. On the other hand, the use of fossil fuels releases a large amount of greenhouse gases, resulting in a rapid increase of greenhouse gases in the environment. Therefore, it is urgent to seek a renewable and clean energy to solve the energy problem. Among many biomass energy raw materials, microalgae have many advantages such as variety, fast growth rate, strong carbon sequestration ability and low growth environment requirements, and are considered as the most potential biological resources to replace traditional fossil fuels. In this paper, the key issues such as the types of catalysts and the preparation methods of biodiesel from microalgae were summarized, hoping to provide reference for the subsequent research.

2. Progress in Biodiesel Production from Microalgae

2.1 Species of Oil-Producing Microalgae

Table 1. Oil content of some algae

Micro algae	Oil content (dry weight) %
Brown's algae	25~75
Crack pot of algal	50~77
Implicit dinoflagellates	20
Diamond algal	45~47
Dunaliella cells	23
Micro green found	31~68
Trichoderma	20~30

Polyunsaturated fatty acids can be produced by algae in the class chrysophyllata, xanthophyllata, diatoms, chlorophyllata, cryptophycida and dinoflagellata, and the oil composition extracted from microalgae is similar to that of vegetable oil.

At present, the main energy microalgae studied at home and abroad are green algae and diatoms, such as Chlorella, Brown graphyella, Dunaliella salina, Trichochroma, micrococcus, etc.

2.2 Preparation of Biodiesel from Microalgae

The oil content of some algae accounts for 25% ~ 77% of their dry weight, which is significantly higher than that of land crops rich in oil. The fatty acid chain length is C15 ~ C22, and the raw material with lower unsaturated level is most suitable for biodiesel production. The preparation methods of biodiesel include physical method and chemical method, among which physical method includes direct mixing method and microemulsification method, and chemical method includes pyrolysis, esterification and transesterification method. Transesterification is a common method to prepare biodiesel, that is, transesterification reaction between natural oils and alcohols (such as methanol) under the action of catalyst (acid, base, enzyme). At the same time, there are some special methods such as supercritical method and in situ esterification method[1]. The advantages and disadvantages of some preparation processes are shown in Table 2.

Table 2. Shows the advantages and disadvantages of the preparation method

The preparation methods	Advantages	Disadvantages
Mix or use directly	Easy to prepare, renewable	Poor combustion performance, damage the engine
Micro emulsion method	Simple preparation and low viscosity	Easy to accumulate carbon, pollution of lubricating oil
Thermal cracking method	Product variety, high utilization rate of raw materials	High energy consumption and low product purity
Chemical catalytic transesterification	Low operation cost and stable product property	Waste water, catalyst separation difficult to recover
Supercritical transesterification	Fast, high yield, easy to separate	High equipment requirements, high energy consumption
Transesterification catalyzed by biological enzymes	Conditions are mild and green	Slow reaction rate and low yield

2.3 Catalyst for Biodiesel Production from Microalgae

2.3.1 Acidic Catalyst

Acid catalyst The reaction rate is not greatly affected in oils with high acid number. However, due to its acidity, it can cause corrosion of reactive vessels, which is usually costly to care for. And its reaction rate is slow, so it has not been widely used in general commercial. Fang Zheng[5] prepared nano-flake SO₄2-/ZrO₂ solid acid and investigated the reaction yield under different reaction temperatures and molar ratios of alcohol to oil. The results show that the optimal reaction temperature of solid acid is 120°C and the molar ratio of alcohol to oil is 12:1. Li Dianhong[6] used microalgal residue as raw material, on the basis of one-step production of glyceryl carbon-based solid acid catalyst discovered by Prabhavathi Devi and Song Xuili, produced microalgal carbon-based solid acid catalyst to catalyze biodiesel synthesis by phosphoric acid activation method. The influences of raw material type, carbonization temperature, carbonization time, sulfuric acid concentration, volume of 30% phosphoric acid solution and activation on catalyst were studied. The results showed that the catalyst efficiency was prepared when carbonization temperature was 250°C, carbonization time was

2h, 30% phosphoric acid dosage was 60ml, sulfonation temperature was 90°C, sulfonation time was 12h, and the transesterification reaction of trioleate glyceride and methanol was performed in the reaction kettle at 120°C for 5h. The yield of biodiesel reached 99.8%. The catalytic efficiency did not decrease significantly after repeated use for 6 times. Yin Chunhua and Xu Pei[7] used ionic liquid acid [C4MIm]HSO₄ as catalyst to explore the effects of different temperatures, different molar ratios of alcohol to oil, catalyst dosage and reaction time on the yield. The results showed that the yield of biodiesel was 64% when the molar ratio of alcohol to oil was 9:1, the amount of catalyst was 8% of algal fat, the reaction time was 6 h, and the reaction temperature was 150°C.

2.3.2 Alkaline Catalyst

Alkaline catalysts such as NaOH, KOH, etc., have a faster reaction rate and lower cost. However, the catalytic efficiency will be greatly reduced due to saponification reaction of oils that are easily delized and face high acid value. Chen Ying[8] prepared calcium, magnesium and aluminum composite metal oxide catalysts by co-precipitation method and high temperature calcination, and investigated the effects of calcination temperature, alkalinity, alkali earth metal content, alcohol-oil ratio and reaction temperature on biodiesel conversion. When the calcination temperature of the catalyst is 400°C, the molar ratio of calcium, magnesium and aluminum is 1.5:4.5:2, the molar ratio of alcohol and oil is 14:1, the mass fraction of the catalyst is 4.5%, the reaction temperature is 65°C, and the reaction time is 5h, the conversion rate reaches 93%. Ma Guixia[9] KOH/Al₂O₃ as catalyst explored the effects of KOH loading, catalyst roasting temperature, reaction temperature, reaction time, catalyst dosage and methanol concentration on biodiesel yield. The results showed that when the load was 35wt.

When the calcination temperature was 700°C, the catalytic capacity of KOH/Al₂O₃ reached the maximum of $89.53 \pm 1.58\%$ when the catalyst content was 10wt % and methanol concentration was 8mL/g for 5h at 60°C. The formation of K₂O on the surface of solid catalyst was the main reason for the strong activity of the catalyst. Zhang Jing[10] prepared solid base catalyst KOH/CeO₂, and explored the effects of KOH loading, calcination temperature, calcination time, catalyst dosage, methanol dosage, reaction temperature and reaction time on biodiesel yield. The results showed that when the KOH load was 50%, the calcination temperature was 350°C, the calcination time was 3h, the amount of catalyst was 14wt%, the amount of methanol was 6mL /g, the reaction temperature was 60°C, the reaction time was 8h, the conversion rate of chlola biodiesel could reach 92.9%.

2.3.3 Enzyme Catalyst

Compared with the process catalyzed by acid and base, esterification reaction catalyzed by enzyme catalyst has high efficiency. However, due to the complexity of enzyme structure, its high cost and easy inactivation limit the use of enzyme in biodiesel production. Wang yao[11] used lipase to explore the effects of alcohol/oil molar ratio, enzyme dosage, reaction time and reaction temperature on biodiesel yield. The results showed that when the reaction conditions were: oil/tert-butanol ratio 1:1; Oil/methanol molar ratio 1:12; Enzyme dosage 10%; The maximum conversion rate was 99.1% after 4 hours of reaction at 25 °C and 250 RPM. The enzyme showed high stability in the system, and the enzyme activity remained more than 90% after 165 hours of pretreatment. Ku Liupeng[12] studied the conversion technology of Novozym435 lipase catalyzed microalgae oil and ethanol. The effects of lipase dosage, molar ratio of alcohol to oil, temperature and reaction time on biodiesel yield were investigated. The results showed that when the lipase dosage was 6.0%, the molar ratio of alcohol to oil was 4.0:1, the temperature was 44.7°C, and the reaction time was 17.6h. Meslinsek uses lipase to catalyze chlrella oil. The effects of lipase content, molar ratio of alcohol to oil, temperature, reaction time, PH value and rotational speed on biodiesel yield were investigated. The results showed that the yield of biodiesel was 80.1% when the lipase content was 8%, the molar ratio of alcohol to oil was 4:1, the temperature was 35°C, the PH was 6.0, the rotational speed was 180rpm, and the reaction time was 10h.

3. Looking Forward To

The research and development of microalgae bio-energy, especially biodiesel and bio-oil, will have a very bright prospect in transportation. The economy of microalgae biodiesel is affected by both the existing technology level and the price of traditional fossil fuels. The development of large-scale industrial application is limited, and the cost of microalgae biodiesel needs to be reduced. In conclusion, there are various types of energy microalgae, and the selection and cultivation of a high oil producing microalgae is a key issue at present. At the same time, the current preparation method of microalgae biodiesel is mainly transesterification, and the transesterification method is closely related to the catalyst. An efficient and recyclable catalyst can greatly reduce the cost of industrial production. Therefore, the catalyst for microalgae biodiesel has become one of the current research hotspots.

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