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Biodiesel production using unrefined methanol as transesterification agent and the research of individual effect of impurities

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ABSTRACT

In this study, we produced biodiesel by utilising waste cooking oil as a raw material, unrefined methanol produced by a chemical plant as a transesterification agent and sodium hydroxide as a catalyst. The yield and heating value of the biodiesel produced with unrefined methanol were respectively 1.09% and 0.23 MJ/kg higher than those of the biodiesel prepared with pure methanol. The biodiesel characteristics met the standard of the ASTM (American Society for Testing and Materials). We investigated the effects of four impurity types in the unrefined methanol on biodiesel preparation. Alcohol impurities acting as co-solvents and transesterification agents can increase the yield and heating value. Organic solvent impurities can only act as co-solvents; thus, they can only improve the yield. Ester impurities (methyl formate) exhibited no effects on the yield and heating value because they evaporated in the ester exchange reaction. Water impurities significantly reduced the yield by affecting the miscibility of waste cooking oil and pure methanol. However, the negative effects of these impurities were alleviated when water was mixed with the organic solvent impurities. This study has a great significance for the resource and energy of unrefined methanol.

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1. Introduction

The heavy use of non-renewable fossil resources has become a global environmental concern in recent decades [1,2]. Scientists have discovered biodiesel as an environmental-friendly alternative to diesel produced by fossil fuel [3]. Biodiesel is mostly produced by the esterification of free fatty acids or the transesterification of animal fats, vegetable oils or waste frying oils with short-chain alcohols (methanol or ethanol) in the presence of suitable catalysts [4–6]. Researchers have successfully produced biodiesel using various short-chain alcohols, including methanol [7] and ethanol [8]. Methanol is a reactant used to synthesise biodiesel on a commercial scale, because of its wide availability and low cost [9]. However, methanol occupies a large proportion in the cost of biodiesel preparation; in addition, this transesterification agent can

only be derived from fossil fuel sources, such as petroleum and natural gas, making biodiesel not a completely renewable fuel [10]. Therefore, finding a suitable transesterification agent aside from methanol (e.g. unrefined methanol or ethanol) is the key to reduce biodiesel cost.

The quantity of unrefined alcohol produced by the chemical industry annually increases in China [11]. The impurity composition of unrefined alcohol is complex. The use of methanol and acetylene as raw materials in poly (vinyl alcohol) preparation produces waste methanol. Synthesising 1t of poly (vinyl alcohol) can produce 1.4t of waste methanol. Unrefined methanol obtained after distilling waste methanol contains methanol (91%), ethanol (4%), long-chain alcohol (1.7%), methyl formate and acetone (1.3%) and water (2%). Waste methanol is also produced after ammonia synthesis under a high pressure. Synthesising 1t of ammonia can produce 1.2t of waste methanol. Unrefined methanol obtained after distilling waste methanol contains methanol (85%), normal alkane (6%), formic acid and long-chain alcohol (2%) and water (7%).

Currently, unrefined methanol obtained after distilling waste methanol is sold to chemical manufacturers as raw materials to

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produce formaldehyde, acetic acid, methyl chloride, methyl amine, dimethyl formaldehyde and other products. However, impurities affect chemical plants and introduce potential pollution and risk [11–13]. In formaldehyde production, alkane impurities in the raw material methanol generate carbon on the surface of the silver catalyst, thereby affecting catalysis [11]. Long-chain alcohol impurities (e.g. propanol and butanol) increase the acidity of methanol products. Unrefined methanol is used to produce plastics, coatings, paints, perfumes, pesticides, pharmaceuticals and man-made fibres because of the small amounts of impurities which affect the purity and performance of products [14].

Methanol rectification is crucial to guarantee the quality of products, but the rectification costs are relatively high, particularly during distillation, when alcohol and water form an azeotrope. Hence, completely evaporating alcohol is difficult and may lead to explosion; the explosion limit of an explosive mixture with methanol vapour and air ranges from 6.0% to 6.5% [15,16].

In recent years, the research of vegetable oil feedstock for biodiesel production is more and more widely. Xue et al. [17] reported that a maximum biodiesel yield of 85.4% was achieved under the best conditions (373 K, 30 min, methanol/oil molar ratio of 15/1 and catalyst of 4 wt%) using soybean oil as raw material and Heterogeneous CaFe_2O_4 – $\text{Ca}_2\text{Fe}_2\text{O}_5$ -based as catalyst. Nasreen et al. [18] found that the triglyceride conversion of soybean oil to biodiesel reached above 99% using the catalyst with La: Mn molar ratio of 2:1 calcined at 600 °C for 90 min under such transesterification reaction conditions as methanol:oil molar ratio of 12:1, 3% catalyst amount, reaction temperature and time of 180 °C and 90 min. The catalyst can resist free fatty acid to some extent. However, it is sensitive to water. At present, Influence of impurities on biodiesel production is focus on the raw material, Lim et al. [19] investigated the effects of water and FFA content on the yield of biodiesel, it found that supercritical reactive extraction, which employed a lower operating temperature and had a higher tolerance to impurities for biodiesel production. Niza et al. [20] reported that both non-catalytic supercritical methyl acetate and supercritical methanol processes show a high tolerance toward the presence of impurities in the reaction medium with consistent high biodiesel yield. But the replaced transesterification agent and influence of impurities on the transesterification agent for biodiesel production has not been reported.

The present study investigated the feasibility of using unrefined methanol produced by polyvinyl alcohol synthesis to replace pure methanol as a transesterification agent for biodiesel production. It also analysed the effects of impurities (ethanol, propanol, butanol, hexane, acetone, methyl formate and water) in unrefined methanol on the biodiesel yield and heating value. The allowable concentration ranges of organic and water impurities were set. This study provides a scientific basis for using unrefined methanol as a transesterification agent to produce biodiesel, thereby reducing costs and promoting waste recycling.

2. Material and methods

2.1. Materials

Waste cooking oil was obtained from the restaurant of the University of Science and Technology Beijing. The waste methanol is taken from a chemical plant which produced polyvinyl alcohol in southern China. Methanol (purity 99.8%), sodium methoxide and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co., Ltd. Pure methyl esters, ethyl esters, propyl ester, butyl ester such as methyl palmitate, methyl stearate, methyl oleate, ethyl linoleate etc and other pure esters with purity of more than

99% were purchased from Beijing Century Aoke Biological Technology Co., Ltd.

2.2. Equipment

Transesterification reaction was conducted in a 250 mL conical flask reactor and a water bath pot equipped with a thermocouple and magnetic stirrer. The reactor temperature was controlled by a heater with a programmable temperature controller. The flux unit caused the methanol and ethanol to remain in the liquid phase for the entire duration of the reaction.

2.3. Ester preparation

Before biodiesel synthesis, the waste cooking oil was pretreated by the following procedure. First, wipe off the bone, paper, plastic, vegetables and other debris of waste cooking oil manually, then added the activated clay (20 g/100 g oil), centrifugation (4000 r/min), filtration, at last, deacidification by utilizing the method of extraction (acid value below 2 mg KOH/g) and remove water (moisture below 0.5%). Biodiesel was synthesised in a reactor by using sodium hydroxide as a catalyst following the method described by Lang et al. [21]. The reaction was conducted by using 99.5% excess alcohol; the molar ratio of alcohol to oil was 8:1, and the mass of catalyst was 1% of the oil. The reaction was performed in a reactor. Oil (100 g) was placed in a dry Erlenmeyer flask equipped with a magnetic stirrer and a thermometer. In another dry Erlenmeyer flask, 1.0 g of sodium hydroxide was mixed with pure methanol or unrefined methanol. This mixture was then added to the oil and then vigorously stirred for 1 h at 80 °C. After the reaction, crude glycerol was separated by gravity. The ester layer was washed three to four times with water to remove the catalyst. Traces of moisture and unreacted alcohol were removed by vacuum distillation. The distillation was continued until the loss in weight of ester was constant, confirming the complete removal of moisture and unreacted methanol. Furthermore, impurities (ethanol, propanol, butanol, hexane, acetone, methyl formate and water) were added to the system. Then, the experiments were conducted under the same experimental conditions. All experiments were performed in three repetitions.

2.4. Ester characterisation

Qualitative analysis of fatty acids and quantitative analysis of fatty acid esters were performed as previously described [22]. Waste cooking oil was subjected to rapid methyl esterification and then qualitatively analysed through GC–MS to determine the main components. The identity and relative composition of fatty acid methyl esters were analysed by a DSQ type of gas chromatograph and mass spectrum equipped with a DB-5 medium polar capillary column (30 m × 0.25 mm × 0.25 μm). Helium was used as a carrier gas. The flow rate was 1.0 mL/min, the sample split ratio was 20:1 and the inlet temperature was 280 °C. The temperature program was as follows: initial column temperature of 50 °C for 2 min, holding temperature of 280 °C for 5 min, heating rate of 10 °C/min and ion source temperature of 250 °C from an EI source with an electron energy of 70 eV. The scanning quality number ranged from 50 AUM to 650 AUM during NIST98 library searching. The percentage of each component was calculated through normalisation. The components of waste cooking oil (fatty acid) were detected by GC–MS. As shown in Fig. 1, palmitic, oleic, linoleic and stearic acids were the principal components of waste cooking oil. The physical properties and fatty acid components of waste cooking oil are summarised in Table 1.

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