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Biodiesel production from palm oil and mixed dimethyl/diethyl carbonate with controllable cold flow properties

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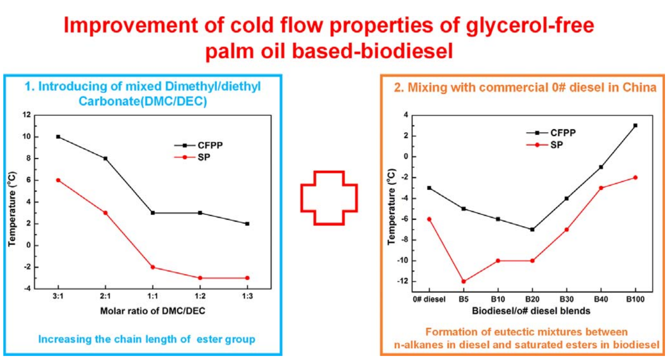
GRAPHICAL ABSTRACT



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ABSTRACT

The transesterification of palm oil and mixed dimethyl/diethyl carbonate (DMC/DEC) was investigated to produce glycerol-free biodiesel with improved cold flow performance. The potassium hydroxide (KOH) was used as the cheap heterogeneous catalyst. The biodiesel yield could reach 90.8% and the molar ratio of FAMEs/FAEEs was fixed as 2:1 over the following optimal reaction conditions: Molar ratio of DMC/DEC was 1:1, molar ratio of mixed DMC/DEC and oil was 14:1, KOH amount was 15 wt% (based on the oil), reaction temperature was 100 °C and reaction time was 20 h. The biodiesel had a cold filter plugging point of 3 °C and a solidifying point of −2 °C, which met the cold flow requirements of commercial 0# diesel in China. Finally, the cold flow properties of biodiesel/diesel blends were carefully characterized. Interestingly, due the formation of eutectic mixtures between *n*-alkanes in diesel and saturated esters in biodiesel, the cold flow performance of diesel could be significantly improved by adding no more than 30 v% of biodiesel.

1. Introduction

Biodiesel is the mixture of long chain fatty acid alkyl esters derived from various kinds of vegetable oils or animal fats [1]. In recent years, due to the shortage of fossil fuels, biodiesel has become an important substitute of the petroleum diesel worldwide [2]. Nowadays, the edible vegetable oils still account for about 95% of the biodiesel feedstocks, e.g., the biodiesel in European Union, United States and tropical countries are mainly produced from rapeseed oil, soybean oil and palm oil, respectively [1,2]. Among all the widely used edible oils, the palm oil shows great advantages in producing biodiesel due to the higher per unit yield and lower cost [3]. Considering the controversy of fighting

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for food with human beings, many non-edible oils, such as Jatropha oil, Karanja oil, micro-algal oil, etc., have been developed as the new generation feedstocks of biodiesel [4,5], and these feedstocks can be planted in barren environment and will be harmless to the conventional food crops. China has a huge population to feed and the selection of feedstock oil is particularly harsh. Generally, the waste cooking oil is reported to be a significant feedstock of biodiesel in China [4]. Fortunately, it is well known that China is one of the biggest importer of palm oil (about 4.9 million tons a year [6]) in the world and a large amount of palm oil are wasted in fried food industry. As a result, it will be potential to utilize the waste palm oil and develop the palm oil-based biodiesel in China.

As an alternative fuel, the biodiesel must have the similar properties to petroleum diesel, like viscosity, density, heating value, cetane index, oxidation stability, cold flow properties and so on [7]. Generally, the biodiesel contained higher percentage of saturated fatty acids exhibits greater oxidation stability but poorer cold flow properties [7–9]. Unfortunately, the palm oil based-biodiesel has more than 40% of saturated fatty acid esters, which will limit its use in low temperature environment. Therefore, a lot of efficient methods have been designed to improve the cold flow properties of biodiesel [10], such as blending [8], winterization [11,12], hydroisomerization [13], adding cold flow improver [9,14], as well as reacting with long chain alcohols [4,15,16]. Among these methods, transesterification of oil with long chain alcohols seems a simple and fascinating way to produce biodiesel with good cold flow performance. Nevertheless, the usage of long chain alcohols may also have some disadvantages like larger costs, lower reaction activity and higher viscosity. Therefore, the mixed ester exchange reagents with different alcohols were investigated to produce biodiesel, e.g., the mixed methanol/ethanol system even showed a good synergistic effect on improving the biodiesel yield [17–21]. Because on the one hand, the ethanol could enhance the solubility of oil in methanol, and on the other hand, the methanol could weaken the steric hindrance and emulsification effect of ethanol.

Except for the cold flow properties, the surplus byproduct glycerol can also be a great burden of the traditional biodiesel industry. In our previous works, the dimethyl carbonate (DMC) was used as a new acyl acceptor to produce the glycerol-free biodiesel [22–24]. The heterogeneous base and lipase catalyzed transesterification of palm oil and DMC were carefully investigated and the possible reaction mechanisms were proposed. Nevertheless, the cold flow properties of DMC based-palm oil biodiesel still need further improvements. Diethyl carbonate (DEC), the long chain homologue of DMC, is another potential acyl acceptor to produce the fatty acid ethyl esters (FAEEs). According to the hitherto researches, the transesterification of DEC and oil is hard to proceed and only several special and expensive ways, such as the lipase [25] and supercritical methods [26], were reported to be used in the reaction between DEC and oil. Meanwhile, in order to obtain the similar biodiesel yield, the unreported data in our group showed that the reaction time of DEC system was four times higher than the DMC system at the catalysis of potassium hydroxide (KOH). Hence, the mixed DMC/DEC system will be investigated and it can not only enhance the cold flow performance of biodiesel, but also avoid the formation of cheap byproduct glycerol.

In this paper, the transesterification of palm oil and mixed DMC/DEC was studied at the catalysis of heterogeneous KOH. Firstly, the effect of the reaction parameters were optimized to obtain the optimal yield of biodiesel and the suitable molar ratio of FAMEs/FAEEs. Then the cold flow properties of the palm oil based-biodiesel, as well as the blends of biodiesel and commercial 0# diesel, were also characterized to determine their application prospects in cold regions.

2. Materials and methods

2.1. Materials

Refined palm oil was provided by Shanghai Shinewe Bio-tech Co., Ltd, and its main fatty acid compositions are: Myristic acid 1.77%, palmitic acid 42.88%, stearic acid 3.78%, oleic acid 40.15%, and linoleic acid 11.42%. The standard substances, which include methyl myristic, methyl palmitate, methyl heptadecanoate, methyl stearate, methyl oleate, methyl linoleate, ethyl myristic, ethyl palmitate, ethyl stearate, ethyl oleate and ethyl linoleate, were all purchased from Sigma-Aldrich. The other reagents, such as KOH, DMC and DEC were of analytical pure and obtained from Sinopharm Chemical Reagent Co. Ltd.

2.2. Biodiesel preparation

The biodiesel was prepared in a 250 ml three-necked flask, which contained 42.35 g palm oil (0.05 mol), 31.53 g DMC (0.35 mol), 41.35 g DEC (0.35 mol) and 6.35 g KOH (15 wt% of oil). The mixture was reacted at 100 °C for 20 h with rapid mechanical agitation (150 rpm). Then the KOH catalyst was filtered to stop the reaction and the DMC/DEC was distilled to obtain the biodiesel.

2.3. Analysis of mixed FAMEs/FAEEs

The mixed FAMEs/FAEEs samples were analyzed by an Agilent 7890A gas chromatography. The internal standard method was used to calculate the yield of FAMEs/FAEEs and a detailed description was shown in our previous articles [24]. The retention time of the fatty acid alkyl esters were shown in Fig. 1: (1) methyl myristate: 8.632 min, (2) ethyl myristate: 9.203 min, (3) methyl palmitate: 10.207 min, (4) ethyl palmitate: 10.763 min, (5) methyl heptadecanoate: 10.999 min, (6) methyl linoleate and methyl oleate: 11.633 min, (7) methyl stearate: 11.839 min, (8) ethyl linoleate and ethyl oleate: 12.218 min, and (9) ethyl stearate: 12.491 min.

2.4. Fuel properties of biodiesel

The main fuel properties, containing density, heating value, kinematic viscosity, acid value, cold filter plugging point (CFPP) and solidifying point (SP), were tested by Chinese standard method GB/T 20828-2007. The phase transformation behavior of biodiesel was investigated by the differential scanning calorimetry (DSC, type: Diamond, PerkinElmer Inc, USA), with a temperature range of −30 °C

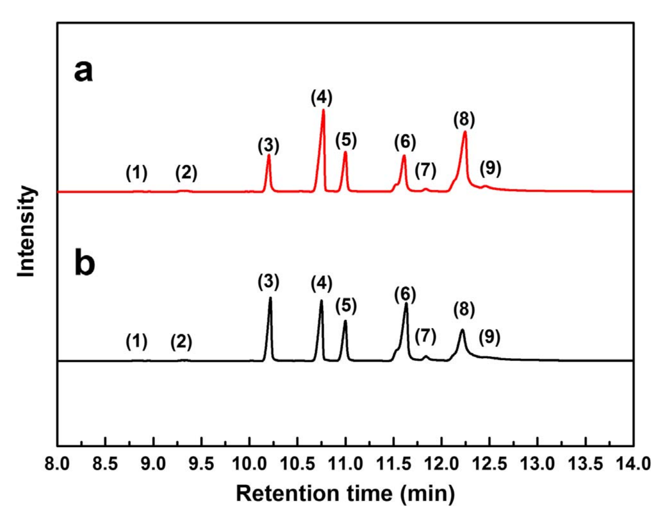

Fig. 1. Chromatogram of FAMEs/FAEEs standards (a) and Actual FAMEs/FAEEs in biodiesel samples (b).