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Simultaneous development of biodiesel synthesis and fuel quality via continuous supercritical process with reactive co-solvent

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ABSTRACT

This work addresses the simple and effective technique to simultaneously improve biodiesel synthesis and fuel quality. The co-solvent technology was applied to fulfill this purpose. Experiments were performed through the transesterification of palm oil and ethanol in a microtube reactor under the supercritical conditions. The *iso*-propanol was added in the system and played the roles as a source of reactant to produce isopropyl esters and co-solvent to enhance the homogeneity of the mixture. Upon the application of *iso*-propanol, high yield of biodiesel was attained under the milder conditions than those reported in the literature in terms of reaction temperature, pressure, residence time, and ethanol-to-oil molar ratio. The influence of operating conditions on the %Ester was investigated and optimization of %Ester was carried out via response surface methodology. The improvement of biodiesel quality was achieved particularly the cloud and pour points which were better quality than that of the conventional biodiesel production.

1. Introduction

At present, most commercial biodiesel production is performed via liquid alkali-catalyzed transesterification in a stirred-batch reactor. However, the use of this technique is uneconomical and environmentally harmful due to the high-quality feedstock requirement, un-reusable catalyst, and large wastewater generation [1]. The application of solid catalysts is perceived as one of the possible means to overcome these challenges. Biodiesel production can be both economically viable and environmentally friendly due to the reduced amount of wastewater from purification, reusability of solid catalyst, and simple separation of catalyst from the product [2]. At present, the main barriers for this route to develop the industrial-scale process include the requirements of high-quality feedstock and long residence time as well as the low catalyst activity and stability [3]. These problems are due to the side reaction (saponification) and mass-transfer limitation [4]. One of the promising approaches to overcome these problems is the synthesis of biodiesel through the catalyst-free transesterification reaction at high temperature and high pressure, which is known as a supercritical process.

Although short residence time for the supercritical process is satisfying for the industrial-scale biodiesel production, other requirements remain the major hurdles such as high temperature, high pressure, and high molar ratio of alcohol-to-oil in order to achieve high conversion of oil. The supercritical process has been continuously developed to reduce these limitations. For instance, two-step supercritical process, known as Saka-Dadan process [5], is firstly performed with the hydrolysis of triglyceride in subcritical water followed by esterification of fatty acid in supercritical alcohol. This process greatly reduced the requirements for reaction temperature, pressure, and molar ratio of alcohol to oil. The addition of catalyst in the system such as $Cs_{2.5}PW_{12}O_{40}$ [6], ZnO [7], and CH_3ONa [8] is another effective option to reduce the extreme supercritical operation conditions. However, these methods are complicated and require expensive instruments [9]. Therefore, the use of non-reactive solvent known as co-solvent has been proposed to deal with these problems. Several non-reactive solvents were studied including both gas and liquid phases such as propane [10], hexane [11], and carbon dioxide [12]. All reports suggested that the addition of co-solvent in the system could increase the solubility of triglyceride and alcohol, improving the mass transfer and the overall production rate of biodiesel.

The advance of biodiesel synthesis by applying the co-solvent technology has been extensively reported. *Iso*-propanol is one of the best candidates for co-solvent to enhance the performance of biodiesel

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synthesis under subcritical conditions [13,14]. Chueluecha et al. [14] presented that the addition of *iso*-propanol as a co-solvent could improve the yield of biodiesel as well as improve the energy savings. The simple separation of *iso*-propanol from the biodiesel and alcohol was demonstrated. Besides, due to the mild operating temperature (below 65 °C), *iso*-propanol is a non-reactive co-solvent. However, *iso*-propanol can react with triglycerides to form biodiesel at high temperature (usually higher than *iso*-propanol's boiling point [15]) and sufficiently long residence time. In this case, it is regarded as a reactive co-solvent. Despite the advanced biodiesel production, the development of biodiesel synthesis under supercritical conditions by the application of reactive co-solvent has never been studied.

One major issue of biodiesel derived from vegetable oil is their cold-flow properties (cloud point, pour point, and cold filter plugging point). The cold-flow properties of biodiesel obtained from both subcritical and supercritical short-chain alcohol processes are much poorer than that of diesel fuel [16,17]; thus limiting the use especially in freezing conditions. Therefore, the cold-flow properties of biodiesel should be improved. Instead of the common short-chain alcohol, the application of long-chain alcohol is a rather simple way to overcome this problem. *Iso*-propanol is the long-chain alcohol and can be used as a reactant to convert triglyceride into biodiesel (isopropyl esters). As shown in Table 1, the cold-flow properties of isopropyl esters are better than those of the other esters. Though the improved cold flow properties by using *iso*-propanol can be clearly noticeable, the product becomes more viscous due to the higher molecular weights. Furthermore, the conversion of triglyceride with *iso*-propanol is lower than that of the other ones [18]. Apart from providing high conversion rate, ethyl esters (as fuel) exhibit good kinematic viscosity and mild cold flow properties. Consequently, the addition of *iso*-propanol as a co-reactant may be applied to improve the fuel quality of biodiesel especially the cold flow properties.

This work dealt with the use of a simple and effective means to enhance both biodiesel synthesis and biodiesel fuel quality simultaneously by using a continuous process under supercritical co-reactant conditions. One one hand, *iso*-propanol was used as a solvent to reduce the mass-transfer resistance across the boundary layer of reactants (oil and ethanol). At the same time, *iso*-propanol was also used as a reactant to produce biodiesel. The effects of reaction temperature, molar ratio of ethanol-to-oil, weight ratio of *iso*-propanol-to-oil, and residence time on the purity of biodiesel were investigated in this work. Moreover, the optimization of the operating conditions was performed via response surface methodology (RSM). The efficiency of biodiesel synthesis and biodiesel fuel properties were determined and compared to the literature data.

Table 1
Physico-chemical properties of biodiesel and diesel fuels from the literature.

Properties	No. 2 diesel fuel[a]	Methyl esters[a,c]	Ethyl esters[b,c]	Isopropyl esters[a,c]
Cetane number	42.2	50.4	48.2	51.5
Net heat combustion (Btu/lb)	18,235	16,072	17,200	16,155
Density (60 °C)	0.85	0.87	0.88[d]	0.87
Viscosity (40 °C, mm^2/s)	2.89	4.59	4.41	5.26
Cloud point (°C)	−18	−2	1	−9
Pour point (°C)	−30	−6	−4	−12

[a] Wang et al. [19].
[b] Encinar et al. [20].
[c] Soybean oil.
[d] at 25 °C.

2. Materials and methods

2.1. Materials

Refined palm oil, as a source of triglycerides, was purchased from the local market. (Morakot palm oil, manufactured by Morakot Industries PCL., Thailand). Ethanol (AR grade, ≥99.9%) was purchased from Merck company. *Iso*-propanol (HPLC grade, ≥99.9%) as a co-reactant was supplied by RCI Labscan company. HPLC grade of acetone (≥99.8%) and acetonitrile (≥99.9%) for high performance liquid chromatography analysis were obtained from RCI Labscan and Honeywell company, respectively. The physico-chemical properties of raw materials are shown in Table 2.

Table 2
Physico-chemical properties of raw materials.

Properties	Unit	Refined palm oil	Ethanol	*Iso*-propanol
Molecular weight	kg/kmol	848.2	46.7	60.1
Density[a]	kg/m^3	0.885	0.785	0.785
Viscosity[b]	Mm^2/s	41.5	1.1	2.1
Critical Temperature	°C	912[c]	241	236
Critical pressure	MPa	0.74[c]	6.3	4.9
Acentric factor	–	–	0.644	0.655

[a] at 25 °C.
[b] at 25 °C.
[c] Cunico et al. [21].

2.2. Transesterification

The continuous transesterification reaction of palm oil and co-reactant was carried out in a stainless steel microtube reactor (1/16″ OD × 0.012″ W/T) under supercritical alcohols (ethanol and *iso*-propanol). First, *iso*-propanol was mixed with palm oil to obtain a homogeneous solution at the desired weight ratio (based on oil weight). Then, the mixture (palm oil and *iso*-propanol) and ethanol were separately fed into a T-way micromixer (0.02″ thru hole) via two HPLC pumps (2150 HPLC pump, LKB Bromma) at different volumetric flow rates based on the ethanol-to-oil molar ratio and residence time. Prior to entering the micromixer, the feedstocks were preheated to the desired reaction temperature. After that, the mixture was introduced into the reaction zone (reactor volume; 1.85 mL) where the reaction took place. The microtube reactor was placed inside a convection oven to maintain the reaction temperature. A back-pressure regulator, installed at the outlet of the microtube reactor located outside of the convection oven, was used to control the pressure of this system. The product stream exiting the microtube was rapidly cooled down in order to stop the reaction. The outlet product was collected for purification and analysis. The sample product was purified by rinsing with deionized water and was centrifuged to obtain the purified product. To ensure the steady state condition, the product sample was collected after six folds of residence time was elapsed. The experimental setup for transesterification supercritical process is shown in Fig. 1.