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Optimization of ethyl ester production assisted by ultrasonic irradiation

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ABSTRACT

This study presents the optimization of the continuous flow potassium hydroxide-catalyzed synthesis of ethyl ester from palm oil with ultrasonic assistance. The process was optimized by application of factorial design and response surface methodology. The independent variables considered were ethanol to oil molar ratio, catalyst concentration, reaction temperature and ultrasonic amplitude; and the response was ethyl ester yield. The results show that ethanol to oil molar ratio, catalyst concentration, and ultrasonic amplitude have positive effect on ethyl ester yield, whereas reaction temperature has negative influence on ethyl ester yield. Second-order models were developed to predict the responses analyzed as a function of these three variables, and the developed models predicts the results in the experimental ranges studied adequately. This study shows that ultrasonic irradiation improved the ethyl ester production process to achieve ethyl ester yields above 92%.

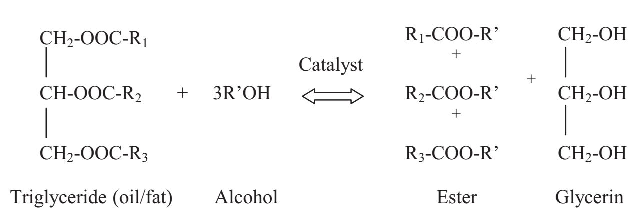
1. Introduction

Biodiesel is an alternative fuel to petroleum products derived from renewable resources. It has lower emissions than petroleum-based diesel, biodegradable and helps reduce both greenhouse gas and sulfur emissions to the atmosphere [1,2]. Biodiesel is synthesized by transesterification of vegetable oils or animal fats with alcohol. Methanol is commonly used in the commercial biodiesel production by the transesterification reaction of triglyceride with methanol, and the most common form of biodiesel is methyl ester [3]. In Thailand, commercial biodiesel is produced from palm oil and methanol, called palm methyl ester (PME). The methanol used in "conventional" biodiesel production is obtained from petrochemical process.

Vegetable oils and animal fats contain different types and various concentrations of fatty acids. These fatty acids contain different carbon atoms in the molecules comprising different numbers of single bond, double bond, and triple bond in the molecular chain. The fatty acids' chemical structures influence the characteristics of vegetable oil/animal fat, and so the biodiesel properties, namely, cetane number, density, viscosity, pour point, heating value and flash point, derived from these various sources, are generally influenced by the choice of feedstock [4] as shown in Table 1 [5–7].

The current biodiesel production is basically carried out in a batch process with mechanical agitation. The oil and alcohol are not completely miscible because of low mixing efficiency of mechanical stirring [4]. At low agitation speed, only a very small volume fraction of alcohol gets dispersed into the oil phase. When the agitation speed is increased, a greater fraction of alcohol is dispersed into the oil because of more vigorous liquid circulation. The drop size of alcohol increases at higher volume of reagent or due to inefficient dispersion action of the agitator [8]. Larger drop size of alcohol decreases the methanol–oil interfacial area that leads to low rate of reaction. If the agitation intensity is inadequate or the reaction temperature is low, transesterification reaction will not occur effectively [9]. In conventional biodiesel production, therefore, the reagents (oil, methanol, and catalyst) need to be stirred for around 1.5–2 h and are kept at about 60 °C to allow the reaction to reach its equilibrium level.

The transesterification reaction of triglyceride and alcohol can be represented by [10]:



(1)

R_1, R_2, R_3: Alkyl group.

Glycerin obtained as a by-product has a number of applications in cosmetics, pharmaceutical, food and plastics industries.

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Table 1
Biodiesel properties from different feedstock.

Properties	Alkyl esters of palm oil			Alkyl esters of canola oil		Alkyl esters of linseed oil		Alkyl esters of rapeseed oil		Alkyl esters of sunflower oil	
Fatty acid composition (%)	Methyl ester of palm oil	Methyl ester of used palm oil	Ethyl ester of palm oil	Methyl ester of canola oil	Ethyl ester of canola oil	Methyl ester of linseed oil	Ethyl ester of linseed oil	Methyl ester of rapeseed oil	Ethyl ester of rapeseed oil	Methyl ester of sunflower oil	Ethyl ester of sunflower oil
C12		0.3									
C14		0.8									
C16:0		44.3			4.4		5.1		3.1		6.5
C16:1		0.2									
C18:0		5			2.3		3.1				4.9
C18:1		39.1			67.3		14.2		13.9		20.5
C18:2		10.1			18.9		15.2		13.3		68
C18:3		0.1			6.5		62.5		9.4		6.5
C20:1									6.8		
C22:1									53.5		
Density (kg/L)	0.855 (@ 40 °C)	0.8737 (@15/15 °C)	0.857 (@ 40 °C)	0.875 (@ 25 °C)	0.869 (@ 25 °C)	0.887 (@ 25 °C)	0.884 (@ 25 °C)	0.877 (@ 25 °C)	0.873 (@ 25 °C)	0.882 (@ 25 °C)	0.876 (@ 25 °C)
Viscosity (cSt)	@20 °C	14.94		3.79	3.91	3.32	3.64	5.18	5.76	4.24	4.4
Cloud point (°C)	16	0	16	1	−1	0	−2	0	−2	1	−1
Pour point (°C)	15	0	12	−9	−6	−9	−6	−15	−15	−8	−5

The alkali-catalyzed biodiesel production using ethanol is more difficult to produce than that of methanol. This is due to the formation of stable emulsion during ethanolysis. In case of methanolysis, the emulsions formed would break down easily to form a lower layer of glycerin and upper layer of methyl ester. For ethanolysis, because of the presence of larger non-polar group in ethanol, the emulsions formed are more stable. This makes the separation and purification of biodiesel more difficult [11].

Ultrasonic irradiation is widely used in industry for emulsification of immiscible liquids. It helps improve the liquid–liquid interfacial area through emulsification and reaction [10]. The studies of cavitational activity have been conducted for explaining the dependency of the cavitational activity on the design of sonochemical reactors and operating parameters [12,13]. With ultrasonic assistance, the mixing problems could be overcome because during the collapse of cavitational bubbles of methanol, nano-sized drops that are extremely and efficiently mixed could be generated leading to abundantly enhanced reaction surface [4]. Thus, for the continuous transesterification of vegetable oils under ultrasonic irradiation, it has been observed that ultrasounds could successfully replace the mechanical mixing-heating conditions [14]. Nonetheless, an optimum frequency of ultrasound and intensity of irradiation for an operation should be selected. In case of liquid medium, it is expected that the cavitational activity will be reduced at higher operating temperature [12]. However, where chemical reactions occur, an optimum operating temperature might also exist.

A number of studies have been recently conducted on biodiesel production and its characterization [5,15–20], and on optimization by factorial design methodology for biodiesel production [21,22]. A study on methyl ester production from sun flower oil showed that temperature and catalyst concentration had a positive influence on ester yield [23]. For low temperatures, methyl ester conversion increases with increasing catalyst concentration, whereas, at low catalyst concentrations there is a moderate increase in conversion with temperature. Optimum conditions for the production of methyl esters were found to be at mild temperatures (20–50 °C) and at higher catalyst concentration (1.3%).

Waste cooking oil can also produce biodiesel, and catalyst concentration is the most important factor, which however has a negative influence on biodiesel yield due to triglyceride saponification and methyl ester dissolution in glycerin [24]. For obtaining maximum methyl ester yield with a free fatty acid content of 1.88%, the operating conditions were 30 °C and a minimum of 1.3 wt.% catalyst concentration.

In case of ethyl ester production, optimization for biodiesel production from sunflower oil by factorial design has been carried out that included the effects of reaction variables on ester yield. Catalyst concentration was found to have the most significant influence. Ester yield increases with increasing catalyst concentration. The optimal condition for laboratory-scale ethyl ester production by batch process was obtained at 32 °C reaction temperature, 5:1 ethanol/oil molar ratio and 1.5 wt.% catalyst concentration [25].

The effect of ethanol–palm kernel oil ratio on biodiesel yield has also been studied [26]. Experiments were conducted for ethanol–palm kernel oil ratios of 0.1, 0.125, 0.15, 0.175, 0.2, 0.225 and 0.25 by weight under transesterification conditions at 60 °C for 120 min reaction time and 1.0% catalyst concentration. The reaction mixture was allowed to separate by gravity settling. The biodiesel at the top was carefully decanted into a PET bottle. The results gave 29.5%, 54%, 75%, 89%, 96%, 93.5% and 87.2% biodiesel yield for the respective feedstock ratios. This shows increase in biodiesel yield with ethanol–palm kernel oil ratio up to 0.2. Studies on biodiesel production (batch process) assisted by ultrasonic irradiation have also been conducted using coconut oil, corn oil, canola oil, and palm oil with methanol and reaction time was found to