



Continuous production of biofuel from refined and used palm olein oil with supercritical methanol at a low molar ratio



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ABSTRACT

The high energy consumption and high environmental impact in the supercritical methanol (SCM) process primarily originates from the preheating of reactants and the recovery of excess alcohols. This work demonstrated the synthesis of biofuel using a lowered methanol to oil molar ratio of 12:1, instead of the 40:1–42:1 ratios that are commonly employed in conventional SCM. The apparent density of the reacting mixture was measured and applied to accurately calculate residence times in a continuous reactor. The effects of residence time were considered from 10 to 25 min. The results revealed that excessive residence times reduced the ester content, especially for unsaturated esters, in the resulting biofuel. A residence time of 20 min was recommended to simultaneously achieve a maximum ester content of 90% and a triglyceride conversion of up to 99%. Used palm olein oil with high free fatty acid (4.56 wt.%) can be employed as a feedstock and give a maximum ester content of 80%. In addition, the side reaction between glycerol and methanol at 400 °C and 15 MPa showed a positive effect in increasing fuel yield by 2%–7%.

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1. Introduction

Biofuels are a source of renewable energy derived from living organisms and can be used as a substitute for petroleum fossil fuels. The obvious advantages of biofuels, such as being biodegradable, nontoxic, and environmentally friendly, have attracted many researchers to develop biofuel production methods, especially biodiesel. The supercritical alcohol (SCA) process through the transesterification reaction is a novel technology for producing biodiesel due to its many advantages over the conventional catalyst biodiesel process. For example, the process is catalyst-free, has a short time reaction, offers high yields of biodiesel and high purity of the by-product (glycerol), and involves simple separation and purification steps [1–4]. The main operating parameters that influence the transesterification under supercritical conditions are temperature, pressure, alcohol to oil molar ratio, and reaction time. As shown in Table 1, the supercritical reaction of a variety of refined vegetable oils has been investigated over a wide range of operating temperatures (280–350 °C), pressures (20–35 MPa), and reaction times (4–30 min), depending on the types of feedstock and reactor.

A very high fatty acid alkyl ester (FAAE) content, up to 80–100%, has been reported. Note that the investigated range of alcohol to oil molar ratio was narrow, 40:1–42:1. Furthermore, the supercritical alcohol (SCA) process is able to use waste cooking oil (high FFA and water contents) as feedstock, as also illustrated in Table 1. The high FFA and water content, up to 36 and 30 wt.%, respectively, do not significantly reduce the yields and reaction rates [5,6].

However, the synthesis of biodiesel using the SCA process suffers a drawback from its alcohol to oil molar ratio (40:1–42:1), which is high when compared with the stoichiometric ratio of 3:1. As proposed in a life cycle assessment (LCA) of biodiesel production with supercritical methanol (SCM) [7], a high methanol to oil molar ratio requires a large energy input for preheating and recovering alcohols. Such inputs produce a significant environmental load. In addition, Wang et al. [8] and Anitescu et al. [9] noted that preheating and recovery of alcohols result in high energy consumption and high production costs in biodiesel production using supercritical methanol.

The SCA process conducted at high temperature (400–450 °C) and moderate pressure (10.0–20.0 MPa) has been investigated and shown the ability to markedly reduce the alcohol to oil molar ratio to 9:1–12:1, including in batch and continuous operations [9–11]. In addition, use of a laboratory batch reactor for biofuel production from palm olein oil with SCM and supercritical ethanol (SCE) at 400 °C and 15 MPa was successfully evaluated in our

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Table 1
Summary of literature-reported experimental data using the SCA process.

Oil type	Temperature (°C)	Pressure (MPa)	Methanol to oil molar ratio	Residence time (min)	Process type	FAME/CV (%)	Refs.
Coconut	350	19	42	6.67	Continuous	95% FAME	[14]
Palm oil	350	19	42	6.67	Continuous	96% FAME	[14]
Soybean	300	32	40	25	Continuous	77% FAME	[15]
Palm oil	372	15–25	40	16	Batch	81.5% FAME	[16]
Palm olein oil	400	15	12	10	Batch	80% FAME ~100% CV	[12]
Chicken fat	400	37.6	6	5	Batch	88% FAME	[10]
Rapeseed	350	43	42	4	Batch	95% FAME	[1]
Castor	350	20	40	40	Batch	~100% CV	[17]
Linseed	350	20	40	40	Batch	~100% CV	[17]
Sunflower	400	20	40	40	Batch	96% CV	[18]
Chicken fat	400	30	9	6	Continuous	80% FAME 99% CV	[11]
Soybean	400	20	6	1.75	Continuous	>98% CV	[9]
Canola	450	40	11–45	4	Continuous	~100% CV	[19]
Waste cooking oil	287	N/A	41	30	Batch	99.6% FAME	[20]
Waste canola oil	270	10	50	45	Continuous	~102% FAME	[21]

FAME: % Ester content, CV: % Conversion.

The significant digits are the same as in the original sources.

previous work [12]. At optimal alcohol to oil molar ratios of 12:1 and 18:1 for the SCM and SCE processes, respectively, the biofuel samples were largely in accord with the diesel and biodiesel standard specifications and have offers the prominent advantage of an increase in fuel yield of approximately 5% and 10% for SCM and SCE, respectively [12]. Furthermore, the use of less alcohol is reflected in a lower energy requirement for alcohol preheating and recovering over that of the conventional SCA processes with a 42:1 alcohol to oil molar ratio. For instance, in the computer simulation SCM process base on 1.10×10^5 tons of biodiesel per year, usage of high pressure steam was reduced from 9.44×10^6 kJ/h to 5.07×10^6 kJ/h. Furthermore, total steam consumption significantly decrease from 100.46×10^6 kJ/h to 24.57×10^6 kJ/h [13].

The first objective of the present work was to synthesize biofuel by using a lowered methanol to oil molar ratio, the reaction temperature of 400 °C and 15 MPa was chosen. According to the optimal operating condition (Table 1), it is clearly seen that temperature more than 400 °C and pressure in the rage of 10–40 MPa are suitable to apply with low methanol to oil molar ratio. Methanol to oil molar ratios of 6:1–15:1 were selected for preliminary study of biofuel production in a continuous flow process at 400 °C and 15 MPa. Second, the effects of residence time on ester content and triglyceride conversion were investigated from 10 to 25 min by regulating the reactant flow rate. For accurate calculation of residence time, the density of reacting mixtures at the molar ratio of 6:1–15:1 was measured by an isochoric method. Third, the effects of refined palm olein oil (RPO) and used palm olein oil (UPO) on ester content and triglyceride conversion were compared. It has been reported that the cost of feedstock is a crucial economic factor in the viability of biodiesel production [4]. Therefore, the effects of oil type in the resultant biofuel samples were also investigated. Fourth, the relationship between increased fuel yield and the miscibility of products from the etherification of glycerol and methanol in the fuel phase was investigated. These reaction products were quantitatively and qualitatively analyzed by high-performance liquid chromatography (HPLC) and gas chromatography–mass spectrometry (GC–MS), respectively.

2. Materials and methods

2.1. Materials

In this study, RPO was provided by Morakot Industries Co., Ltd., and UPO was collected from a local restaurant near Chulalongkorn University, Bangkok, Thailand. The physical and chemical properties of the RPO and UPO are summarized in Table 2. Methanol

(99.9%) was purchased from Fisher Scientific. Glycerol (>99.9%) was purchased from Sigma–Aldrich. For the gas chromatography (GC) analysis of product samples, analytical grade methyl heptadecanoate (99.5%) (Fluka) was used as an internal standard, and n-heptane (99.5%) (Fisher) was used as an analytical solvent. For the HPLC analysis of samples, HPLC-grade acetonitrile (Burdick and Jackson) was used as the mobile phase.

2.2. Apparatus and experimental procedure

2.2.1. Continuous transesterification

The experimental setup is shown in Fig. 1. It consisted of two high-pressure liquid pumps (Jasco, model PU-1580 and PU-2080) for delivery of oil and methanol, respectively. The weighing and timing method was used to check the mass flow rate of the methanol and oil mixture in real-time. The reactants were separately pumped into coiled pre-heaters (stainless steel (SUS316) tubing of 3.17 mm o.d., 0.71 mm thickness, and 150 cm length) and passed through a coiled tubular reactor (stainless steel (SUS316) tubing of 6.35 mm o.d., 0.89 mm thickness, and 600 cm length). Both the coiled pre-heaters and the tubular reactor were immersed in a fluidized sand bath (OMEGA Model FSB-3, USA). K-type thermocouples (VSC advance Co., Ltd, Thailand) and a PID controller (Sigma Model SF48, USA) were employed to monitor and control temperature, respectively. After the outlet flow rate was steady, the back-pressure regulator (Swagelok, UK) was closed to increase the system pressure. External cooling water was flowed through a shell-side of a double-pipe heat exchanger to cool the obtained product. At the reactor outlet, the liquid product was collected in a glass flask and placed into a rotary evaporator at 50 °C and 15 mbars (1.5 kPa) for 30 min to remove excess methanol. The biofuel samples were then quantitatively analyzed by gas chromatography (GC).

2.2.2. Density measurements

The density of the reacting mixtures at supercritical condition was measured in a constant-volume cell using an isochoric method. The reactor was made from stainless steel tubing (closed at both ends) of 9.52 mm o.d., 1.24 mm thickness, and 58 cm length, with a volume at room temperature of 22.58-mL. The pressure was measured with a Wika Pressure Gauge (63.50 mm, Lower Mount, 6.35 mm NPT fitting, and 0–5000 psi working pressure). The temperature was monitored by a K-type thermocouple which was fitted directly into the cell. The mixture of methanol and oil at a constant molar ratio of 6:1–15:1 was added into the cell while global density values (mass/reactor volume) were varied between

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