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Continuous transesterification of coconut oil with pressurized methanol in the presence of a heterogeneous catalyst

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ABSTRACT

In this study the effect of a heterogeneous catalyst on the transesterification of coconut oil with pressurized methanol was examined in a continuous operation system. The obtained experimental results indicated that the supercritical methanol transesterification was catalyzed by the surface of the stainless-steel 316 (SS316) reactor, but this catalyst became inactive after 10 h. To maintain a high and stable transesterification rate, MnO_2 was found to be the most effective catalyst among various metal oxides tested in this study. The presence of MnO_2 was essential for the complete conversion of coconut oil to biodiesel under mild conditions; the conversion was less than 10% during catalyst-free operation. The effect of temperature on biodiesel yield was more pronounced than that of pressure; the latter was apparent only at pressures far below the critical pressure of methanol and before the formation of a homogeneous liquid phase from the methanol/coconut oil mixture. The significant effect of higher temperature resulted from increases in both the reaction rate and the miscibility of coconut oil and methanol. At 200 °C and 4.14 MPa, the methanol/coconut oil mixture formed a homogeneous liquid phase; the apparent activation energy decreased from 107.7 kJ/mol at temperatures below 180 °C to 35.3 kJ/mol at temperatures above 220 °C – that is, the conditions were more favorable for transesterification. When the molar ratio of methanol to coconut oil increased from 12:1 to 60:1 (*i.e.* fivefold), the apparent rate constant (k) also increased (4.45-fold) from 0.00476 to 0.02118 s^{-1}.

1. Introduction

Because of increased crude oil prices, environmental concerns for pollution from the exhaust of cars, and demands to decrease greenhouse gas emissions, nontoxic, biodegradable, and renewable biodiesel – produced through transesterification of biological materials (*e.g.* edible and inedible oils and animal fats) with alcohol [1–3] – has received much attention in recent years as an alternative fuel for diesel engines [4–6].

In the transesterification of oils with alcohol, the short-chain alcohol replaces the glycerol units of the triglycerides of the oils. This process can be catalyzed by alkalis, acids, or enzymes. For an alkali-catalyzed transesterification, the reactants – glyceride and alcohol – must be anhydrous to avoid saponification; soap lowers the yield of the resulting esters and complicates their separation and purification. In addition, oils having low free fatty acids (FFAs) contents are required for alkali-catalyzed transesterification processes. Water and FFAs are, however, permissible in the feeds of acid-catalyzed processes, but long reaction times, corrosion, and separation of the catalyst after transesterification are all drawbacks. To overcome these problems, the transesterification of oils with supercritical alcohols or acetates has been proposed [7–15]. With this approach, no catalyst is added and the reaction time is decreased significantly relative to that obtained under conventional atmospheric conditions. In addition, purification of the products is simpler and easier, and the requirements for water and the FFAs content in the oil are not stringent. Nevertheless, the temperatures and pressures used in supercritical transesterification processes are high, generally within the temperature range 350–400 °C and the pressure range 20–45 MPa. Although biodiesel can be produced successfully through transesterification with supercritical methanol, the need to perform this process at a high temperature, high pressure, and high methanol-to-oil molar ratio hinders its industrial practicality, due to high capital and operational costs and high energy consumption.

The introduction of a catalyst can result in milder operating conditions for supercritical transesterification [16–26]. Both liquid-phase alkaline [16–18] and acidic [19] catalysts have been used in supercritical/subcritical methanol transesterifications, providing results superior to those obtained under catalyst-free conditions. Although these liquid catalysts result in faster reaction rates, problems persist regarding product purification and waste

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management. Heterogeneous solid catalysts, on the other hand, not only possess the conventional advantages of homogeneous catalysts but also can be readily separated and recycled for subsequent use, rendering them practicable for transesterification. Many reports have indicated that the addition of a heterogeneous catalyst during the transesterification of vegetable oils with supercritical methanol can indeed decrease the temperature, pressure, methanol-to-oil ratio, and reaction time while maintaining a fast reaction rate [20–28]. As a result, supercritical methanol transesterification can become more economically feasible.

Metal oxides comprise positive metal ions (cations, Lewis acid) and negative oxygen ions (anions, Bronsted base) in structure, and provide sufficient adsorptive sites for methanol, in which the O-H bonds readily break into methoxide anions and hydrogen cations, and then methoxide anions react with triglycerides to form corresponding fatty acid methyl esters [28]. The reaction rates of metal oxides depend on the basicity of the oxide, especially of the strong basic sites. Magnesium oxide (MgO) has the weakest basic strength and solubility in methanol among group II oxides; however, under supercritical methanol conditions, nano MgO showed high catalytic activity for the transesterification of soybean oil [22]. Calcium oxide (CaO) received more attention for biodiesel synthesis [20,21,24], due to its cheap price, minor toxicity and relatively high availability. Singh and Fernando [20] studied the reaction kinetics of soybean oil transesterification with different metal oxides, and found that the rate constant of Cao was fourfold the value of MgO. Yoo *et al.* [24] compared the base strength and surface area of several metal oxide catalysts used in supercritical methanol transesterification of rapeseed oil. Although zinc oxide (ZnO) has weaker basic strength than SrO and CaO, it produced a similar yield of FAMEs with them over the temperature of 250 °C.

Relative to batch operation, continuous operation modes have the advantages of simpler and superior control of temperature, pressure, and reaction (residence) time, as well as having greater potential for scale-up [14]. Nevertheless, continuous operation of transesterifications with supercritical methanol has rarely been reported in the open literature. Bunyakiat *et al.* [9] were the first to study the transesterification of coconut oil in supercritical methanol ($T_C = 239.6\ ^\circ\mathrm{C}$; $P_C = 8.09$ MPa) in a continuous mode. They observed that the optimal conditions were a temperature of 350 °C, a pressure of 19.0 MPa, and a methanol-to-coconut oil molar ratio of 42. Therefore, for this study coconut oil was chosen as the feedstock so that our results could be compared with those of previously reported catalyst-free reactions.

The objective of this study was to examine the effects of heterogeneous catalysts and to select the most appropriate one among various metal oxide catalysts that have been reported in the literature [20,22–24,27–29] for the transesterification of coconut oil with pressurized methanol under continuous operation conditions. Herein, the yields of biodiesel from these operations performed in the presence of catalyst were compared with those in the absence of catalyst. After selecting the most-appropriate catalyst, the effects of the operating variables, namely the temperature, pressure, methanol-to-coconut oil molar ratio, and residence time, on the yield of biodiesel were systematically examined.

2. Experimental

2.1. Materials

Coconut oil was purchased from First Cosmetics Works (Taiwan); its fatty acid composition was measured through gas chromatography (GC) analysis using the AOCS Ce 2-66 method (Table 1). The acid and saponification values of the coconut oil were determined through the IUPAC 2.201 and ISO 3657 methods to be 0.061 mg KOH/g and 259.32 mg KOH/g, respectively; the average molecular weight calculated from these values was 650 g/mol. The properties of biodiesel produced from coconut oil meet the B100 biodiesel standards, as specified in ASTM D6751-02, allowing it to replace low-speed diesel fuel [9].

Table 1
Fatty acid composition of coconut oil.

Fatty acid	Composition (wt%)
Caprylic acid (C8:0)	7.7
Capric acid (C10:0)	6.4
Lauric acid (C12:0)	48.6
Myristic acid (C14:0)	17.8
Palmitic acid (C16:0)	8.9
Stearic acid (C18:0)	2.2
Oleic acid (C18:1)	6.8
Linoleic acid (C18:2)	1.6

Methanol and *n*-hexane (purity: 99.5%) were purchased from Echo Chemical (Taiwan) and used as received. The methyl ester standards for analysis – methyl caprylate (Sigma), methyl caprate (Aldrich), methyl laurate (Fluka), methyl myristate (Fluka), methyl palmitate (Riedel-de Haen), methyl stearate (Alfa Aesar), methyl oleate (Aldrich), and methyl linoleate (Sigma), with methyl undecanoate (Sigma) as the internal standard – were all used as received.

SS316 packing was purchased from Pope Scientific (USA). The metal oxide catalysts aluminum oxide (Al_2O_3), copper oxide (CuO), magnesium oxide (MgO), manganese dioxide (MnO_2), and zinc oxide (ZnO) were purchased from Sigma (USA). Quartz sand and oxalic acid were obtained from Yakuri Pure Chemicals (Japan). All metal oxides and quartz sand were sieved to 80–100 mesh prior to use.

2.2. Transesterification

Transesterification was performed in the continuous reaction system displayed schematically in Fig. 1. Stainless-steel 316 (SS316) seamless tubing (OD: 1.27 cm; length: 20 cm; capacity: 18 mL) with 2-μm SS frits at both end caps was used as the reactor. The reaction temperature was maintained at a desired value (deviation: ±2 °C) in a high-temperature oven (Yih-Der, Taiwan); the pressure (variation: <0.2 MPa) was controlled using a back-pressure regulator (Tescom, USA).

Coconut oil and methanol were fed at constant flow rates using two syringe pumps (ISCO, Model 260D). These two streams were preheated first and then mixed together prior to entering the reactor. Both methanol-to-coconut oil molar ratio and the (apparent) residence time were controlled by changing flow rates

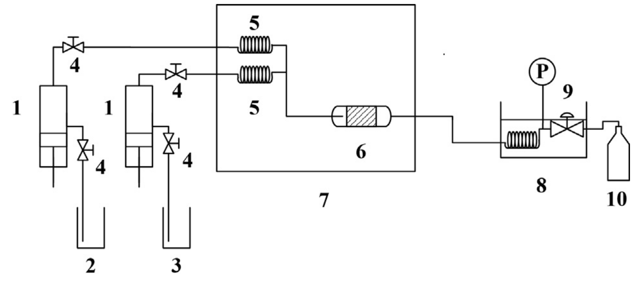

Fig. 1. Schematic representation of the continuous reaction system. (1) Syringe pump; (2) oil tank; (3) methanol tank; (4) needle valve; (5) pre-heating coil; (6) tubular reactor; (7) high-temperature oven; (8) water bath; (9) back-pressure regulator; (10) sample tank.