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Synthesis of biodiesel in subcritical water and methanol

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HIGHLIGHTS

- Biodiesel was produced by reacting oil with methanol under subcritical condition.
- The method is new and high yield of biodiesel can be achieved.
- The method can be applied to refined oil and oil with high FFA/water content.
- The process is simple and no traditional acid/base catalyst is required.

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ABSTRACT

A novel method for biodiesel production without the need of conventional catalyst such as potassium hydroxide and sulfuric acid was proposed in this study. In the presence of water, biodiesel can be produced by reacting methanol with feedstock oil under subcritical condition. When refined soybean oil was used, high biodiesel conversion (96.4%) can be achieved in a reasonable short time (4 h). The conversion was 92.6% when soybean oil with a water content of 9 wt.% was used. The possibility of using oils with high acid and water contents as feedstock was also investigated. Since no catalyst was employed, the process is simpler and more environmental friendly than traditional methods.

1. Introduction

Because of the gradual depletion of world petroleum reserves and the impact of environmental pollution of increasing exhaust emissions, there is an urgent need for suitable alternative fuel for use in diesel engines. In view of this, biodiesel is a promising alternative because it has several advantages: it is biodegradable, nontoxic, renewable, and environmentally friendly [1]. Biodiesel is a mixture of fatty acid alkyl esters, which are generally produced through transesterification using feedstocks containing triglycerides. More than 300 feedstocks have been identified which could be used to produce biodiesel. These include edible oils, non-edible oils, wild oils, used cooking oils, and animal fats [2].

Currently industrial production of biodiesel uses refined vegetable oil as feedstock which undergone transesterification with methanol in the presence of homogeneous base catalysts such as sodium or potassium hydroxide. However, this conventional process is inefficient when using low-cost feedstock such as waste vegetable oil containing high amounts of free fatty acids (FFAs) and water [3,4]. These impurities are known to consume the alkali catalysts via saponification reaction, thereby decreasing biodiesel yields. Moreover, a mixture of soap, biodiesel and un-reacted compounds cause emulsification during a washing process which makes it difficult to obtain biodiesel of high quality [5]. Due to constantly increasing prices of fresh vegetable oils, the inability to use low-cost feedstocks becomes a major drawback of the conventional method. This can be overcome by using heterogeneous solid catalysts which are able to tolerate high FFAs contents in feedstock oils [6,7]. However, the solid catalysts have low catalytic activity due to mass transfer limitation between liquid reactants and solid catalyst [8].

Recently, production of biodiesel under supercritical condition has been suggested to overcome the drawbacks related to the homogeneous catalytic process. Under supercritical condition, feedstock oil and methanol become one phase thus complete mixing is achieved and such that high conversion (>95%) can be obtained in a few minutes without the need of catalyst. Since no catalyst is required, the formation of soap is avoided even feedstock with high FFA and water contents is used. A supercritical fluid has mass transfer rate and permeating capacity superior to its corresponding liquid state due to its lower viscosity and larger diffusion coefficient [9].

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Several investigators have synthesized biodiesel in supercritical methanol. Although methanol has a critical temperature and critical pressure of 240 °C and 8.09 MPa, respectively; in the so-called supercritical methanol production biodiesel, due to the presence of acylglyerides (AGs) and FFAs, usually much higher temperature and pressure are required. In earlier studies of the transesterification of oils in supercritical alcohols, high temperature (300–350 °C), high pressure (20–35 MPa) and high alcohol to oil molar ratio (40:1–42:1) were employed [10–13]. These operating parameters were moderately reduced to 250–280 °C, 15–20 MPa and an alcohol to oil molar ratio of 24:1–30:1 by techniques such as the addition of co-solvents and using heterogeneous catalysts. The addition of co-solvent in combination with supercritical conditions seems to be an efficient means to reduce the operating temperature. The addition of co-solvents such as hexane, CO_2, toluene, and a small amount of catalyst such as zirconia-based catalysts into the reaction mixture can decrease the operating temperature, pressure and the amount of alcohol required. However, the use of co-solvent has negative effects on environment and the purity of biodiesel produced [14,15].

The operating temperature is the key parameter to determine the conversion and rate of reaction in the supercritical methanol process. Reaction under supercritical condition requires huge amount of energy to carry out the reaction at elevated temperature and pressure and subsequently cool down to room temperature when the reaction is completed. The enormous energy to provide heat to the reactor and cooling effect upon reaction completion leads to claims that supercritical fluid is an energy-intensive process [16]. Therefore, it is still a hot issue to search for better methods of biodiesel preparation which are energy efficient and environmentally friendly.

Sub-critical water (SCW) treatment is an environmentally friendly technique with a wide range of applications such as extraction, hydrolysis and wet oxidation of organic compounds. SCW is defined as hot water at temperatures ranging between 100 and 374 °C under high pressure to maintain water in the liquid state. Dielectric constant, which can be changed by temperature, is the most important factor when using water as an extraction solvent. It decreases from 80 at room temperature to 27 at 250 °C which is almost equal to that of ethanol at ambient temperature. Recently growing attention has led to extensive research activities using SCW for hydrolysis and conversion of biomass and carbohydrates to useful compounds [17–19]. Moreover, SCW can also act as an effective catalyst for a hydrolysis or biodegradation reactions and to increase the extractable neutral lipids from activated sludge [20,21]. Base-catalyzed biodiesel productions under subcritical methanol condition were investigated by Yin et al. [22,23]. However, there is no report on the production of biodiesel under subcritical conditions of water and methanol without the use of catalyst.

In this study the feasibility of producing biodiesel under subcritical conditions of water and methanol was investigated. Refined soybean oil was used as the model substrate. The possibility of using other feedstock oil with high FFA content was also discussed.

2. Material and methods

2.1. Material

Refined edible soy bean oil was obtained from commercial source (Taiwan Sugar Corp, Tainan, Taiwan). Standard of fatty acid methyl esters (FAMEs) mixture (47885-U, 37 components FAME Mix) was purchased from Supelco (Bellefonte, PA, USA). All solvents and reagents were either high performance liquid chromatography (HPLC) or analytical reagent grade, obtained from commercial sources. Thin-layer chromatography (TLC) aluminum plates (20 cm × 20 cm × 250 μm) were provided by Merck KGaA (Darmstadt, Germany). Qualitative filter paper (Grade No. 2, 0.26 mm thickness, 80% collection efficiency) was acquired from Advantec MFS, Inc. (Dublin, CA.).

2.2. Biodiesel production by subcritical methanol–water transesterification

Refined soy bean oil (1 g) was mixed with deionized water and methanol (24 g) in a high pressure reactor (HC Scientific and Instrument Co., Taipei, Taiwan) equipped with an external electrical furnace and magnetic stirrer. The reactor was made of stainless steel and can withstand an estimated maximum pressure of 30 MPa. Eight M8 screws which can afford 12.8 tons of tensile force were used for tightening the reactor with its cap. Fig. 1 is the schematic diagram of the reactor set up.

Temperature in the reactor was measured by a thermocouple and controlled at 175 ± 1 °C. Pressure (3.5 MPa) which is higher than the saturated vapor pressure of water (0.89 MPa) and methanol (2.38 MPa) was applied to the reaction mixture by using nitrogen to ensure all experiments were carried out under subcritical condition of water and methanol. Phase behavior of the reactant mixture at different experiment conditions was presented via the critical properties of the mixtures (Table 1). The calculation was based on Berthelot-type mixing rules [24].

After a pre-determined time, pressure inside the reactor was rapidly reduced by releasing the gas phase in the reactor. Reaction in the reactor stopped as soon as the pressure dropped below the vapor pressure of methanol. The released vapor was collected and condensed in an ice water bath. Liquid in the reactor was collected and combined with liquid from the condensed vapor. Hexane (50 mL) and sodium chloride solution (5 wt.%, 20 mL) were added and the mixture was shaken vigorously. The mixture was then centrifuged (Avanti J-25, Beckman Coulter, California, USA) at 20 °C and 15000*g*. The upper hexane phase which contained FAME was withdrawn. The extraction procedure was repeated

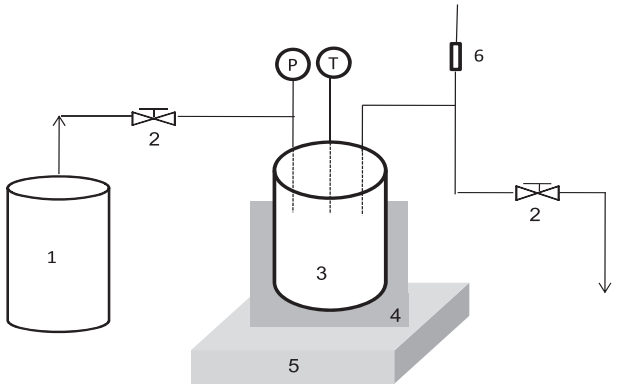

Fig. 1. Schematic diagram of reaction set-up (1) nitrogen cylinder, (2) needle valve, (3) reactor, (4) electric heater, (5) magnetic stirrer plate, (6) rupture disc, (P) pressure gauge, (T) thermocouple.

Table 1
Critical properties of reaction mixture at various water contents. Reaction temperature and pressure was controlle d at175 °C and 3.5 MPa, respectively.

Properties	Mass ratio of soybean to water (water content wt.%)			
	1:5 (83%)	1:1 (50%)	1: 0.1 (9%)	1: 0.05 (5%)
T/Tc	0.83	0.86	0.87	0.87
P/Pc	0.35	0.41	0.43	0.43