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Catalyst free esterification of fatty acids with methanol under subcritical condition

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ABSTRACT

This study provides an alternative way to produce biodiesel from low quality feedstock oil. Feedstock oil with high water and free fatty acid contents can be hydrolyzed into fatty acids using conventional methods or subcritical water processes. Fatty acids produced can be reacted with methanol to produce fatty acid methyl esters under conditions developed in this work, which is much milder than the supercritical methanol condition and without the use of catalyst. Using palmitic acid and oleic acid as the model free fatty acid, at 175–205 °C, 2.0–2.8 MPa and with a fatty acid:methanol:water ratio of 1:2:0.05 (w/w/w), a conversion of 96.5% can be achieved in 3–4 h. The method can be applied to feedstock with water content up to 15%.

1. Introduction

Biodiesel is a biodegradable and non-toxic alternative for petro-diesel, derived from animal fats, plant oils or lipids from various microorganisms. It has received much attention in recent years due to reasons such as, it is capable of replacing petro-diesel in boilers and internal combustion engines without the need of major modification [1], it provides a near-zero sulfur and aromatic content fuel, and it produces lower exhaust emissions in terms of unburnt hydrocarbon, carbon monoxide and particulate matter hereby reducing harmful emissions [2,3]. Blending of biodiesel from different oil sources helps improve its physical and chemical properties and resolves cold flow properties and oxidative stability [4,5]. Recent research also shows that biodiesel blended in low-sulfur diesel fuel greatly improved its lubrication properties without negative effects to the diesel fuel properties [6].

Despite of several advantages of biodiesel over petro-diesel, economical considerations have posed certain limitations to its industrialization. Many studies have suggested that oil feedstock covers the biggest portion of biodiesel production cost. Globally there are more than 350 oil-bearing crops identified as potential sources for biodiesel production and selecting the cheapest, industrial scale feedstock is vital to lower down the cost of biodiesel production [1,4]. The use of non-edible oils may significantly reduce the cost of biodiesel production [4]. Cheap feedstock such as waste cooking oil, activated sludge and low quality rice bran oil may lower down the cost of biodiesel feedstock but poses additional problems during biodiesel production due to its high moisture and high free fatty acid contents as well as content of impurities, which later requires more purification steps, thus still resulting in high production cost.

Many attempts to overcome such problems have been explored. Enzyme-catalyzed reaction has been employed to overcome problems associated with feedstock impurities and provides easy product recovery and separation, but the cost of enzyme is still too expensive to justify its commercialization [7]. Heterogenous catalysis including ion exchange technologies and catalyst immobilization have also been investigated to simplify post-reaction separation but still fail to lower down production cost, mainly due to requirement of feedstock purification. Biodiesel production under supercritical methanol condition has been explored, which can tolerate high content of free fatty acid and moisture in feedstock oil and has no need of conventional acid/base catalyst [8,9]. However, operating at severe temperature and pressure conditions

Abbreviations: AOCS, American Oil Chemists' Society; FA, fatty acids; FFA, free fatty acids; FAME, fatty acid methyl esters.

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requires a well-engineered process that can efficiently recover the spent energy [10], which probably needs very high capital cost and for the moment is not feasible to commercialize. An alternative route to produce biodiesel is the esterification of fatty acids. Through hydrolysis, low quality feedstock oil such as waste cooking oil, beef tallow and palm distillate waste can be turned into mixtures of free fatty acids, from which biodiesel can then be produced following the solid acid-catalyzed esterification route, thus avoiding the use of a neutralization step in biodiesel production [11]. Kusdiana and Saka [9] on the other hand employed this procedure by firstly turning the feedstock oil into fatty acids (FAs) and then turned the FAs into fatty acid methyl esters under supercritical conditions in the hope of lowering down the process cost and avoiding the use of catalyst. The drawback of this approach was the need to use supercritical conditions during the esterification step, which could probably lead to degradation of the products.

Many efforts have been put into finding alternative ways to efficiently produce biodiesel. Each alternative offers a different set of advantages and disadvantages. A recent development by Ju et al. [12] opens the possibility of producing biodiesel under subcritical condition without the need of conventional acid/base catalyst. Their initial study used soybean oil as the model feedstock oil. The method was later employed for the in *in-situ* production of biodiesel from wet activated sludge [13] and wet microalgae *Chlorella vulgaris* [14] where in both cases the feedstock lipid had high free fatty acid content. A challenge still needed to be addressed in the previous works is to lower down the amount of methanol used under subcritical conditions.

It is still a challenge to develop an efficient process that is able to use low quality feedstock such as activated sludge, waste cooking oil, low quality rice bran oil, yeast cells (*Yarrowia lipolytica*) and microalgae for biodiesel production. Most of these feedstocks have high free fatty acid and water contents. Currently, most published works on non-catalytic esterification of fatty acids were carried out under supercritical methanol condition [8–10]. Since the presence of water and free fatty acids in low quality feedstock is inevitable, it is preferable to hydrolyze acylglycerides in feedstock oil fatty acids, which then can be esterified into FAME. The objective of this study was to investigate the effects of amount of water and methanol on the esterification of free fatty acids with methanol under subcritical condition, with goals to effectively utilize the presence of water in the reaction mixture and lower down the amount of methanol required. The successful development of such a process greatly increases the likelihood of using low quality feedstock for economical biodiesel production.

2. Materials and methods

2.1. Materials

Palmitic acid (98%) and oleic acid (98%) was purchased from Acros Organics (NJ, USA) and Showa Chemical Corporation Ltd. (Tokyo, Japan), respectively. Standards of fatty acid (FA) and fatty acid methyl esters (FAMEs) were obtained from Supelco (Bellefonte, PA, USA) and used as received. All solvents and reagents used were either high performance liquid chromatography (HPLC) or analytical reagent grade, obtained from commercial sources.

2.2. Subcritical water–methanol esterification of fatty acids

Fatty acid (4 g, palmitic or oleic) was mixed with predetermined amounts of deionized water and methanol in a glass chamber (190 ml capacity) and placed in a high-pressure reactor (290 ml) provided by HC Scientific and Instrument Co. (Taipei, Taiwan)

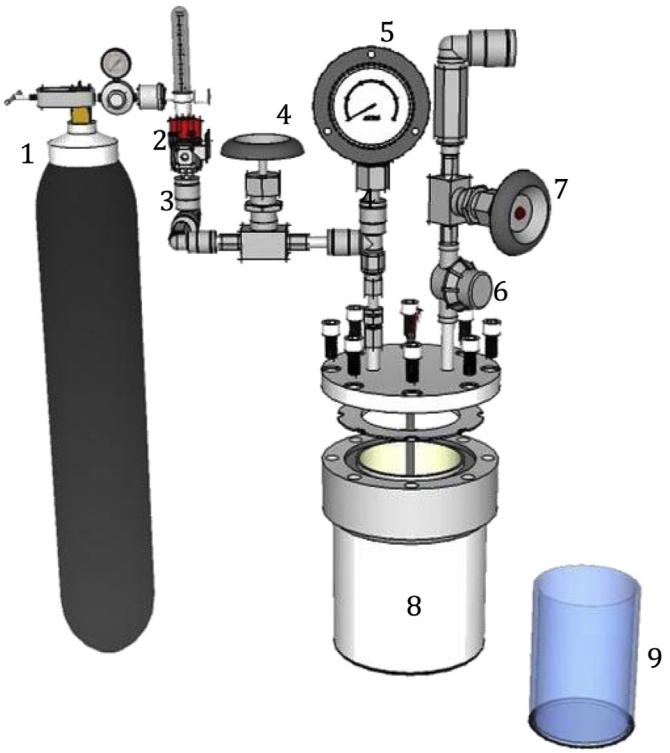

Fig. 1. Subcritical Water Reactor (1. Nitrogen gas cylinder, 2. Safety valve, 3. Check valve, 4. Inlet valve 5. Pressure gauge, 6. Filter, 7. Outlet valve, 8. Reactor, 9. Glass chamber).

(Fig. 1). The reactor is capable of withstanding a pressure up to 30 MPa. The reactor is equipped with an external electric heater.

Temperature in the reactor was measured using a thermocouple and controlled using a PID (proportional-integral-differential) controller to within ±2 °C. A pressure of at least 2.0 MPa, which is higher than the saturated vapor pressure of water (0.89 MPa) at 175 °C, can be applied to the reaction mixture using high purity nitrogen gas (4N5). This was to ensure all experiments were carried out under subcritical condition of water and methanol and to avoid any oxidation reactions.

After a predetermined time, pressure inside the reactor was released to rapidly stop the reaction in the reactor. The released vapor was collected and condensed in an ice-water bath. Products in the reactor were collected as soon as the reactor is cooled down to room temperature. Hexane (50 ml) and sodium chloride solution (5 wt.%, 20 ml) were added and the mixture was shaken vigorously inside a separation funnel and allowed to settle and separate into two phases. The upper hexane phase, which contained fatty acid methyl ester (FAME), was withdrawn and the remaining liquid phase was re-extracted with hexane to recover the products. Hexane from the combined extracts was evaporated under vacuum using a rotary evaporator. The recovered product was weighed and analyzed for its FAME and FA contents. Experiments were carried out in triplicates.

2.3. Conventional acid catalyzed esterification (H_2SO_4)

Acid catalyzed esterification at various water and methanol loadings were also investigated with sulfuric acid as the catalyst. Fatty acids (4 g), methanol and water at different ratios were premixed at room temperature. A specified amount of catalyst was then added to the mixture. The mixture was placed in a Teflon lined screw cap bottle and the bottle was then immersed in a 70 °C water

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