



Full Length Article

Intensified one-step biodiesel production from high water and free fatty acid waste cooking oils

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ABSTRACT

Homogenous alkali-catalysed biodiesel production from waste cooking oil (WCO) requires acid-catalysed pre-treatment steps due to high free fatty acid (FFA) contents. This study investigated strategies to obtain high yields of fatty acid methyl esters (FAME) from one-step base-catalysed transesterification of WCO containing high levels of free fatty acids (up to 5.5 wt%) and 3 wt% of water by altering operating conditions. About 98% FAME yield in homogeneous NaOCH₃-catalysed transesterification was obtained within 5 min reaction time at methanol to WCO molar ratios of 12:1–18:1 and 3 wt% catalyst loading for WCO containing 1.53% FFA and 0.12 wt% water. It was found that high molar ratios of methanol to oil (> 6:1) could prevent saponification. At 5.5 wt% FFA and 3 wt% water contents, ≥ 96.5% FAME yield was achieved at 18:1 M ratio of methanol to WCO within 5 min compared to only 62.8 ± 1.2% for a molar ratio of 6:1. Mathematical modelling (MATLAB) was used to predict FAME yields at various conditions and validated using experimental data. Sets of conditions identified in this study can be used to rapidly produce biodiesel from low quality triglyceride sources in a single step base-catalysed process.

1. Introduction

Biodiesel is a mixture of fatty acid alkyl esters (≥ 96.5% according EN14214) which is used as a renewable alternative to petro-diesel. This accounts for about 82% of the biofuels production in the EU [1]. Biodiesel is usually produced via transesterification of triglyceride-containing feedstock (vegetable oils, animal fat etc.) with short chain alcohols, such as methanol, ethanol, propanol or butanol [2]. The most commonly used alcohol is methanol due to its low prices and availability, producing a mixture of fatty acid methyl esters as shown in Fig. 1.

Generally, biodiesel production reactions are catalysed using base catalysts [3–6], acid catalysts [7–9], and biocatalysts or enzymes [10–12]. Non-catalytic processes such as supercritical fluid processing can also be used for biodiesel production [13–15]. The biocatalysts and supercritical fluid processes are not commonly used because of their high operating costs. Supercritical methanolysis of oils is not cost-effective due to the high pressure (~ 8 MPa) and temperature (~ 350 °C) required for the reaction [13], whereas the enzyme-catalysed biodiesel process remains too expensive to be used for any meaningful industrial application because of the high cost of enzymes, slow reaction rates, and deactivation of the enzymes [12]. Consequently, developments in catalysis of biodiesel production reactions have mainly focused on acid

and base catalysts.

Base-catalysed homogeneous transesterification is the most commonly used process in conventional biodiesel production. This process uses base catalysts such as alkali metal hydroxides and methoxides (NaOH, KOH, NaOCH₃, KOCH₃), particularly sodium methoxide which accounts for than 60% of the commercial biodiesel plants [6]. The use of alkaline catalysts is preferred because of the higher reaction rate of these catalysts, typically about 4000 times faster than acid catalysts at moderate temperatures [16]. A major disadvantage of base catalysts for biodiesel production is that pre-treatment steps are required if low quality feedstock, such as WCO which may contain high FFAs ≥ 0.5 wt% and water ≥ 0.3 wt%, is used [9,17]. This is due to the saponification of triglycerides and FAME [18], leading to emulsification and difficulties in the products separation [19]. Therefore, either an acid-catalysed transesterification, or a two-step process requiring acid-catalysed pre-treatment becomes necessary for biodiesel production from feedstocks with high FFA and water. In both cases, esterification of the FFA (Fig. 2) occurs in the presence of the acid catalyst.

A number of acid catalysts such as sulphuric acid, phosphoric acid, hydrochloric acid and organic sulphonc acids have been investigated for catalysis of biodiesel production reactions [4,20,21]. Among these acid catalysts, the sulphuric and organic sulphonc acids are the most widely used, especially H₂SO₄ because of its higher activity, low price

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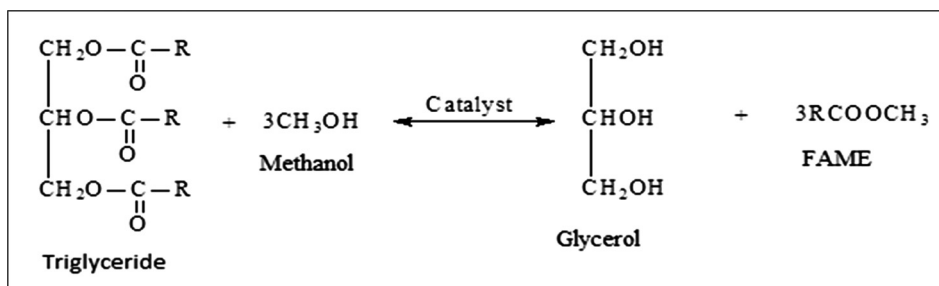


Fig. 1. Triglyceride transesterification reaction.



Fig. 2. Free fatty acid esterification.

and availability [22,23]. One of the challenges of acid catalysts is that long reaction times and high temperatures are required for the acid-catalysed transesterification. It has been reported that approximately 20 h are required to achieve high FAME yield (99%) in a homogeneous acid-catalysed transesterification of soybean oil with methanol at 120 °C using H₂SO₄ catalyst [24]. Another disadvantage of the acid-catalysed homogeneous biodiesel process is that all the equipment has to withstand the corrosive effect of the acids. The cost of corrosion resistant vessels significantly increases the capital cost of acid-catalysed process.

Notwithstanding these problems, acid catalysts are widely used for catalysis of triglyceride transesterification with methanol [25–29], even at moderate FFA (< 4 wt%) and water (≤ 0.2 wt%) contents [26,29]. Acid-catalysed processes were used to achieve 99% FAME yield after 4 h reaction time, in a transesterification of waste frying oil containing 6 wt% FFA, at 70 °C, 169–190 kPa pressure and 1:245:3.8 M ratio of oil:methanol:H₂SO₄ catalyst [27]. In another study, about 95.1% FAME conversion was obtained after 150 min reaction time, using an acid-catalysed (cucurbituril-protected Cs_{2.5}H_{0.5}PW₁₂O₄₀) transesterification of WCO that contained 2.5 wt% FFA, at reported optimum conditions of 2 wt% catalyst, 70 °C and 11:1 methanol to WCO molar ratio [26]. The long reaction time and higher operating temperature required by the acid catalysts adds to the costs of biodiesel production even when using cheaply available WCO feedstock.

Due to the low rates of acid-catalysed processing of biodiesel, a two-step process involving acid-catalysed esterification of the FFA, followed by base-catalysed transesterification has been proposed [29,30]. This method was used to process Chinese oil (3.06 wt% FFA) and trap grease (57.02 wt% FFA), via esterification at 75 °C and 45 min for the oil, 75 °C and 13 h for the grease, and followed by transesterification of the pre-treated oil and grease at 6:1 methanol to oil (grease) molar ratio, 1.2 wt% KOH and 65 °C, to achieve approximately 91.7% FAME yield after 19 min reaction time [29]. A two-step process, involving esterification of a waste fryer grease containing 5.6 wt% FFA and 0.2 wt% water at 3:1 M ratio, 2 wt% H₂SO₄ catalyst and 50 °C for about 5 h, and followed by transesterification at 6:1 M ratio, 50 °C and 60 min reaction time, was used to achieve > 90% FAME yield [30]. The use of an acid-catalysed FFA esterification step and base catalyst for the transesterification step reduces the overall reaction time compared to one-step acid catalysis. However, the overall reaction time remains longer than the base-catalysed process. This leads to a substantial additional energy cost which negates the savings on WCO feedstock when producing biodiesel using two-step process.

Although biodiesel production using WCO could reduce the overall product cost, as the feedstock can contribute up to 60–70% total cost [31,32], the complex treatment steps and long reaction times could

reduce its benefits. There is an urgent need to develop a simple biodiesel process that would allow for utilisation of vast amounts of low quality WCO feedstocks for biodiesel production. For instance, over 250 million litres of used cooking oil was collected in the UK in 2011 [33]. A study on the characteristics of restaurant waste oil has shown that the FFA contents vary from 0.17 wt% to 6.52 wt%, whereas the water contents were less than 0.2 wt% [34]. The FFA contents of WCO in most other studies were less than 6 wt% [28,30,32,35]. Therefore, substantial amount of the available WCO contain low FFA and water contents, and could be processed at reaction conditions similar to the conventional biodiesel process without any modification. This has been demonstrated in an existing study where an alkali-catalysed transesterification was used to achieve 98% biodiesel yield after 20–40 min using waste fryer oil containing 0.5 wt% FFA and 0.08 wt% water, at reaction conditions of 5:1 methanol to oil molar ratio, 0.83 wt% KOH and 50 °C temperature [35].

However, the base-catalysed system is decreasingly effective as the FFA content of the WCO increases. It has been reported that a maximum FAME yield of 89.8% was obtained for transesterification of WCO that contained 3.63 wt% FFA at reaction conditions of 6:1 methanol to oil molar ratio, 1 wt% NaOH, 50 °C and 90 min [30]. Another study also showed that only about 50% FAME yield could be achieved in a transesterification of waste fryer grease containing 5.6 wt% FFA and 0.2 wt% water at reaction conditions of 6:1 methanol to grease molar ratio, 1 wt% KOH catalyst and 30 min reaction time [28]. These studies at higher FFA contents (> 3 wt%) demonstrated that the base-catalysed transesterification at the conventional reaction conditions would not be adequate in achieving an acceptable levels of FAME conversions from WCO. At these FFA and water contents of WCO, it becomes difficult to apply transesterification conditions commonly used for virgin vegetable oils, i.e. methanol to oil molar ratio of 6:1–9:1 and 1–1.5%wt base catalysts [3,18,34,36–39]. The alkali catalysts used in the conventional process become ineffective due to soap formation and deactivation, leading to low FAME yields [17,18,38,40–42]. To ensure that biodiesel is produced from WCO at a competitive market price, a suitable alkali-catalysed processing strategy must be developed to allow for high FAME conversions at these conditions, considering that most of the available WCO have ≤ 6 wt% FFA and ≤ 0.2 wt% water contents. A robust alkali-catalysed process could be developed based on numerical modelling of the kinetics of the transesterification and other side reactions that occur during biodiesel production [18].

1.1. Reactions in base-catalysed transesterification of WCO

There is a general agreement among researchers that the triglyceride transesterification shown in Fig. 1 occurs via three consecutive step-wise reversible reactions [36,43,44]. These reactions are presented in Eqs. (1)–(3).



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