



# A more robust model of the biodiesel reaction, allowing identification of process conditions for significantly enhanced rate and water tolerance



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## HIGHLIGHTS

- Development a comprehensive kinetic model of base-catalysed transesterification.
- Determine rate constants for FAME and oil saponification.
- Determine activation energies for FAME and oil saponification.
- Obtained >95% conversion of oil to FAME at less than 2 min.
- Found operating conditions to obtain >95%FAME yield for wet feedstock (1%wt water).

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## ABSTRACT

A more robust kinetic model of base-catalysed transesterification than the conventional reaction scheme has been developed. All the relevant reactions in the base-catalysed transesterification of rapeseed oil (RSO) to fatty acid methyl ester (FAME) were investigated experimentally, and validated numerically in a model implemented using MATLAB. It was found that including the saponification of RSO and FAME side reactions and hydroxide–methoxide equilibrium data explained various effects that are not captured by simpler conventional models. Both the experiment and modelling showed that the “biodiesel reaction” can reach the desired level of conversion (>95%) in less than 2 min. Given the right set of conditions, the transesterification can reach over 95% conversion, before the saponification losses become significant. This means that the reaction must be performed in a reactor exhibiting good mixing and good control of residence time, and the reaction mixture must be quenched rapidly as it leaves the reactor.

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## 1. Introduction

Transesterification of oils/fats with alcohols is the most common process for producing biodiesel, a bioenergy alternative to petro-diesel that can be used in conventional compression-ignition engines without any modifications (Ma and Hanna, 1999). Biodiesel is superior to diesel in various ways: higher flash point, lower sulphur content, higher lubricity, smaller carbon footprint, and reduced particulate emissions (Di Serio et al., 2008; Li et al., 2009; Yan et al., 2010). There has been a great increase in biodiesel consumption/production globally in the last few years due to uncertainty about energy security and environmental concerns. For instance, biodiesel production increased in Europe from 3184 million metric tonnes in 2005 to 21,904 million metric tonnes in 2010 (EBB, 2009).

Transesterification involves three stepwise and reversible reactions and can be carried out in the presence of acid or base

catalysts (Balat and Balat, 2010; Cardoso et al., 2009) or in a supercritical alcohol process that requires no catalyst (Zabeti et al., 2009). Base catalysts such as hydroxides/methoxides of potassium and sodium are the most commonly used catalysts in the commercial production of biodiesel (Balat and Balat, 2010). However, base-catalysed transesterification requires feedstocks containing less than 0.3 wt% moisture and 0.5 wt% free fatty acid (FFA) to prevent soap formation, which makes the separation of biodiesel from by-product glycerol more difficult (Canakci and Van Gerpen, 2003; Freedman et al., 1984; Ma et al., 1998).

Freedman et al. (1986) studied the kinetics of soybean oil transesterification with butan-1-ol and methanol at 6:1 and 30:1 alcohol-to-soybean oil molar ratios using NaOBu catalyst (Freedman et al., 1986). A second-order rate was proposed for the 6:1 M ratio, and a pseudo-first-order scheme was suggested for the 30:1 M ratio. Further studies on the kinetics of base-catalysed homogenous transesterification of soybean oil with methanol at molar ratio of 6:1 and 0.2 wt% NaOH (Noureddini and Zhu, 1997) showed that the reactions followed second-order rate kinetics. The kinetics of palm oil transesterification with methanol using KOH catalyst and a methanol to oil

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molar ratio of 6:1 were also investigated (Darnoko and Cheryan, 2000a). The best kinetic model for the reactions was pseudo-second-order for the initial stages of the reaction, followed by the first-order or zero-order kinetics. The kinetics of palm oil transesterification with ethanol was also studied, assuming a second order kinetic model (Shahla et al., 2012).

The rate constants for base-catalysed homogeneous transesterification reactions have been inconsistently reported. The values of the transesterification rate constants are further obscured by the dependency of the rate of transesterification on: the alkaline medium, the agitation and the extent of triglyceride and biodiesel saponification side reactions. Consequently, the rate constants for base-catalysed homogeneous transesterification reported in literature (Bambase et al., 2007; Darnoko and Cheryan, 2000a; Freedman et al., 1986) tend to be only “apparent” values.

Triglyceride and FAME saponifications occur in alkali-catalysed homogeneous transesterification. These strongly depend on the hydroxide–alkoxide equilibrium, which determines the availability as well as the actual concentrations of the alkoxide catalytic species and the OH<sup>-</sup> required for the glyceride and biodiesel saponification reactions.

The effect of these saponification reactions in this process have not been thoroughly investigated before, indeed, the extents of these reactions are not apparent in any previous kinetic studies. This may explain much of the lack of agreement in the reported orders and rate constants in homogeneous base-catalysed transesterification.

In this study, a more robust kinetic model of base-catalysed transesterification than the conventional reaction scheme was developed and evaluated. It explains various phenomena that previous models cannot by including the main saponification reactions and the hydroxide/methoxide equilibrium. The kinetics of the saponification side reactions were studied by the saponification of rapeseed oil (RSO) and fatty acid methyl esters (FAME) in a 0.5 M KOH–methanol solution at various reaction temperatures (40, 50 and 60 °C) and operating conditions similar to those used in a homogeneous base-catalysed transesterification. The kinetic data for RSO and FAME saponifications combined with the kinetic parameters for the consecutive reversible transesterification reactions, free fatty acids (FFA) neutralisation and hydroxide–methoxide equilibrium were used to build the kinetic model for the homogeneous alkali-catalysed biodiesel processes. The model was simulated using MATLAB (R2011a) and validated using both experimental and literature data.

## 2. Experimental methods

### 2.1. Materials

The materials used in the experiments, including potassium hydroxide (90% purity), anhydrous methanol (99.8% purity), hydrochloric acid (36.5–38.0% purity), potassium hydrogen phthalate (99.5% purity) and other analytical standard chemicals such as methyl heptadecanoate (99.0% purity), methyl oleate (99.0% purity) were purchased from Sigma–Aldrich. The rapeseed oil (RSO) was obtained from Henry Colbeck. The fatty acid methyl esters (97.85 wt% purity) used in the saponification was obtained via a simple conventional transesterification reaction, as described in previous studies (Phan et al., 2012).

### 2.2. Methods

#### 2.2.1. Saponification of rapeseed oil (RSO) in the 0.5 M methanol–KOH solution

RSO saponification in methanol–KOH solution was studied to obtain data for triglyceride saponification in alcoholic hydroxide. Methanol was chosen as the media for the saponification because

it is by far the most commonly used alcohol in alkali-catalysed biodiesel production. The experiment was carried out using a 100 mL three-neck jacketed glass reactor assisted with a magnetic stirrer, which connect with a condenser, a thermocouple for monitoring the reaction temperatures. About 75 mL methanol–KOH solution 0.5 M was heated in the batch reactor to a temperature of 40, 50 °C or 60 °C through the circulation of hot water inside the jacket. As soon as the desired temperature was reached, 6 g of pre-heated RSO was transferred into the reactor and mixed vigorously using a magnetic stirrer at 600 rpm (Noureddini and Zhu, 1997; Vicente et al., 2005). This corresponds to transesterification at an approximately 300:1 methanol to RSO molar ratio and 35 wt% KOH (based on RSO). The ratio of the RSO and methanol–KOH solution (w/v) was similar to a procedure which has been reported for the saponification of fats and oils in ethanol-hydroxide solution (AOCS, 1998). This procedure was also used to monitor the FAME profile at very high KOH catalyst concentrations.

Approximately 10 mL of the reaction mixture was collected at various time intervals for 60 min using a 10 mL pipette and transferred into a 100 mL conical flask containing 10 mL of HCl 0.5 M. The amount of excess HCl was then determined via titration using 0.5 M methanol–KOH. This analysis was done to determine the rate of saponification of RSO in the methanol–KOH solution. Another 0.5 mL of the reaction mixture was taken and transferred into 2 mL pre-weighed vial containing 0.5 mL HCl 0.5 M for FAME analysis. The collected samples were stored in a freezer, and then analysed for FAME content using gas chromatography.

#### 2.2.2. Transesterification of RSO with methanol using KOH catalyst

The same procedure as described in Section 2.2.1 was used for transesterification of RSO at a 300:1 methanol-to-RSO molar ratio, 0.5 wt% KOH over a temperature range of 40–60 °C. The use of large methanol: RSO molar ratio and low catalyst concentration was to minimise the amount of hydroxide ions existing in the methanol–KOH solution in order to eliminate saponification of RSO and FAME. Two set of RSO transesterification were carried out to obtain more data for the model validation, e.g. (i). 3:1 methanol to RSO molar ratio, 60 °C and 0.5 wt% KOH and (ii). 6:1 M ratio, 60 °C and 1 wt% KOH. Lower KOH catalyst concentrations were used at 3:1 M ratio to minimise RSO and FAME saponification. Approximately 0.5 mL samples were taken at various times, (1, 2, 5, 8, 10, 15, 20, 30, 40, 50 and 60 min) and transferred into a 2 mL pre-weighed vial containing 0.05 mL HCl 0.1 M to quench the reaction immediately. These samples were stored in a freezer for further analysis.

#### 2.2.3. Saponification of FAME in 0.5 M methanol–KOH solution

FAME was dried in an oven for 12 h at 105 °C to eliminate water. Approximately 6 g of the dried FAME was saponified in 75 mL of 0.5 M methanol–KOH solution at a temperature of 40, 50 °C or 60 °C using the procedure in Section 2.2.1. Effect of water on the FAME saponification was investigated at water contents in the range of 2.5–12.5 vol%. About 0.5 mL of reacting mixture was collected at the various time intervals for 60 min using a 1 mL micropipette. The sample was quenched immediately in a pre-weighed 2 mL vial containing 0.5 mL of 0.5 M HCl and the stored in the freezer for FAME analysis.

#### 2.2.4. Analysis

The FAME content was determined using a 5890 Hewlett Packard Series II gas chromatograph (GC), equipped with a 30 m length, 0.25 µm film thickness and 0.32 mm internal diameter BPX70 CP wax capillary column. The temperature of the column was set at 210 °C (isothermal), while the injector and FID detector tempera-

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