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Eze VC, Phan AN, Harvey AP. [A more robust model of the biodiesel reaction, allowing identification of process conditions for significantly enhanced rate and water tolerance.](#) *Bioresource Technology* 2014, 156, 222-231.

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DOI: 10.1016/j.biortech.2014.01.028

Further information on publisher website: <http://www.elsevier.com/>

Date deposited: 29th October 2014

Version of article: Accepted

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Manuscript Number: BITE-D-13-05312R3

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Article Type: Original research paper

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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.

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:

1. Developed a comprehensive kinetic model of base-catalysed transesterification
2. Determined rate constants for FAME and oil saponification
3. Determined Arrhenius activation energies for FAME and oil saponification
4. Obtained > 95% conversion of oil to FAME (FAME yield) at less than 2min
5. Found operating conditions to obtain >95% FAME yield for wet feedstocks (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, 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 3,184 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, 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 0.3wt% moisture and 0.5wt% 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). ~~Transesterification involves three stepwise and reversible reactions as shown in Eqs (1)–(3).~~

~~Where: TG: triglyceride; DG: diglyceride; MG: monoglyceride; GL: glycerol; MA: methyl alcohol~~

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 molar ratio, and a pseudo-first-order scheme was suggested for the 30:1 molar ratio. Further studies on the kinetics of base-catalysed homogenous transesterification of soybean oil with methanol at molar ratio of 6:1 and 0.2wt% 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 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 as shown in Eqs. (6) and (7). These strongly depend on the hydroxide-alkoxide equilibrium in Eq. (5), which determines the availability as well as the actual concentrations of the alkoxide catalytic species and the OH⁻ required for the glyceride and biodiesel saponification reactions.

NB: Soap is the alkali metal salt of the fatty acids

~~The concentration of the hydroxide is inversely proportional to the alcohol to catalyst molar ratio, and the water concentration in either the oil feedstock or the alcohol.~~ 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 0.5M 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) neutralization 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 (97.85wt% purity) used in the saponification was obtained via a simple conventional transesterification reaction, as described in previous studies (Phan et al., 2012).

2.2. Experimental methods

2.2.1. Saponification of rapeseed oil (RSO) in the 0.5M 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 100mL three-neck jacketed

glass reactor assisted with a magnetic stirrer, which connect with a condenser, a thermocouple for monitoring the reaction temperatures. About 75mL methanol-KOH solution 0.5M was heated in the batch reactor to a temperature of 40°C, 50°C or 60°C through the circulation of hot water inside the jacket. As soon as the desired temperature was reached, 6g 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 35wt% 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 10mL of the reaction mixture was collected at various time intervals for 60min using a 10mL pipette and transferred into a 100mL conical flask containing 10mL of HCl 0.5M. The amount of excess HCl was then determined via titration using 0.5M methanol-KOH. This analysis was done to determine the rate of saponification of RSO in the methanol-KOH solution. Another 0.5mL of the reaction mixture was taken and transferred into 2mL pre-weighed vial containing 0.5mL HCl 0.5M 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 2.2.1 was used for transesterification of RSO at a 300:1 methanol-to-RSO molar ratio, 0.5wt% 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 0.5wt% KOH and (ii). 6:1 molar ratio, 60°C and 1wt% KOH. Lower KOH catalyst concentrations were used at 3:1 molar ratio to minimise RSO and FAME saponification.

Approximately 0.5mL samples were taken at various times, (1, 2, 5, 8, 10, 15, 20, 30, 40, 50 and 60min) and transferred into a 2mL pre-weighed vial containing 0.05mL HCl 0.1M to quench the reaction immediately. These samples were stored in a freezer for further analysis.

2.2.3. Saponification of ~~fatty acid methyl esters~~ (FAME) in 0.5M methanol-KOH solution

FAME was dried in an oven for 12hrs at 105°C to eliminate water. Approximately 6g of the dried FAME was saponified in 75mL of 0.5M methanol-KOH solution at a temperature of 40°C, 50°C or 60°C using the procedure in 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 0.5mL of reacting mixture was collected at the various time intervals for 60 min using a 1mL micropipette. The sample was quenched immediately in a pre-weighed 2mL vial containing 0.5mL of 0.5M 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 30m length, 0.25µm film thickness and 0.32mm internal diameter BPX70 CP wax capillary column. The temperature of the column was set at 210°C (isothermal), while the injector and FID detector temperatures were set at 250 and 260°C, respectively. The amount of FAME in the sample was quantified using a methyl heptadecanoate internal standard according to the British standard (BS EN 14103: 2003). The FAME yield in the transesterification and the conversion of FAME to soap in saponification reactions were calculated as follows (Eqs:1-2):

$$\text{FAME yield (X}_t\text{):} \quad X_t = \frac{\text{conc.of FAME}}{3 * \text{Conc.of RSO}} \quad (1)$$

$$\text{Conversion of FAME (X}_s\text{):} \quad X_s = \frac{W_0 - W_t}{W_0} \quad (2)$$

In the RSO saponification, the RSO conversions to soap (X_r) were calculated from the titration data using the equation (3).

$$X_r = \frac{0.5 (V_t - V_a)}{3 * n_0} \quad (3)$$

Where:

n_o : amount of RSO in the 10 mL sample (mmol); V_t : 0.5M methanol-KOH titre values (mL);
 V_a : 0.5M methanol-KOH blank/FFA titre (mL); w_t : weight fraction of FAME in a sample; w_o :
weight fraction of FAME in methanol-FAME mixture without hydroxide (blank)

2.3. Numerical method for alkali-catalysed homogeneous transesterification

In homogeneous alkali-catalysed biodiesel production, other reactions such as the hydroxide-alkoxide equilibrium reactions, triglyceride saponification, ~~fatty acid methyl esters (FAME)~~-saponification and ~~free fatty acid (FFA)~~ neutralisation occur alongside the desired transesterification of triglycerides.

2.3.1. Hydroxide-alkoxide equilibrium reactions

Metal hydroxides such as potassium and sodium hydroxides, are commonly used as catalysts in homogeneous alkali-catalysed transesterification. They dissolve in alcohols to generate alkoxides, which are the actual catalytic species. These metal hydroxides and their corresponding alkoxides exist in equilibrium when dissolved in alcohols (Caldin and Long, 1954; Glass, 1971).

This equilibrium also exists to some extent when metal alkoxides are used for transesterification instead of hydroxides. The alkoxide reacts with any traces of water in the transesterification reactants (vegetable oil and/or alcohol) to form hydroxides. The concentration of the hydroxide and alkoxide ions in the equilibrium solution is dependent on the concentration of the catalyst prepared, the nature of alcohol and the moisture content of the alcohol. An average K_{eq} value of 0.73 ($C_{\text{ROH}} \cdot K_{\text{eq}} = 12.5 \text{ mol.L}^{-1}$) was calculated from the NaOH-ethoxide data (Caldin and Long, 1954). As the acidity of methanol is approximately 4.4 times higher than that of ethanol (Reeve et al., 1979), K_{eq} for NaOH-methoxide system

was estimated at 3.21 ($C_{ROH} \cdot K_{eq} = 79.5 \text{ mol.L}^{-1}$). The K_{eq} value calculated for the NaOH – methoxide systems was assumed to be same as for KOH-methoxide.

2.3.2. Transesterification of vegetable oils with alcohols

The stepwise and reversible reactions occurring during transesterification proceed via diglyceride (~~DG~~) and monoglyceride (~~MG~~) intermediates are shown in Eqs (5) – (7).

Where: TG: triglyceride; DG: diglyceride; MG: monoglyceride; GL: glycerol; MA: methyl alcohol

The rate constants ($k_1 - k_6$) for the numerical modelling were obtained from literature (Bambase et al., 2007) as the initial values – these values were adjusted until the model fits the experimental data. The initial rate constants were calculated by dividing the reported “apparent” rate constants by the catalyst concentration.

2.3.3. Saponification of vegetable oil and FAME product.

During transesterification in alkali-catalysed process, the ~~triglyceride molecule (TG)~~ in the vegetable oil is saponified by hydroxide ions. The fatty acid moieties in the TG are sequentially displaced by the hydroxide ions in an irreversible reaction, to form soap and glycerol (Eq.8). In transesterification reactions, ~~diglyceride (DG)~~ and ~~monoglyceride (MG)~~ are transient species with negligible concentrations. The rate kinetics for saponification of DG and MG were not included in the model. The overall rate constant for the TG saponification is, therefore, represented by k_7 .

NB: Soap is the alkali-metal salt of the fatty acids

The FAME also undergoes saponification in the presence of the hydroxide ions. For instance, in methanolysis of vegetable oils using metal hydroxide catalyst, the FAME reacts with the OH^- from the catalyst to form soap and methyl alcohol (MA) as shown in the Eq. (9):

The experimental data for RSO and FAME saponifications were used to model the saponification side reactions in the alkali-catalysed transesterification.

2.3.4. Neutralisation of Free Fatty Acids (FFA) in the vegetable oil

In alkali-catalysed transesterification, FFA react with both hydroxide and alkoxide ions to form soap as shown in Eq. 10. FFA neutralisation data used for the numerical modelling were obtained from previous work (Morgunov et al., 1977). Soap formations in 2.3.3 and 2.3.4 are assumed to irreversible.

The combined rate expressions for all the chemical reactions occurring during the homogeneous alkali-catalysed transesterification are described in Eqs. (11) – (21):

$$r_{\text{CH}_3\text{O}^-} = \frac{d[\text{CH}_3\text{O}^-]}{dt} = k_x[\text{MA}][\text{OH}^-] - k_y[\text{H}_2\text{O}][\text{CH}_3\text{O}^-] - k_9[\text{FFA}][\text{CH}_3\text{O}^-] \quad (11)$$

$$r_{\text{OH}^-} = \frac{d[\text{OH}^-]}{dt} = k_y[\text{H}_2\text{O}][\text{CH}_3\text{O}^-] - k_x[\text{MA}][\text{OH}^-] - k_9[\text{FFA}][\text{OH}^-] - k_7[\text{TG}][\text{OH}^-] - k_8[\text{FAME}][\text{OH}^-] \quad (12)$$

$$r_{\text{TG}} = \frac{d[\text{TG}]}{dt} = [\text{CH}_3\text{O}^-](-k_1[\text{TG}][\text{MA}] + k_2[\text{DG}][\text{FAME}]) - k_7[\text{TG}][\text{OH}^-] \quad (13)$$

$$r_{\text{DG}} = \frac{d[\text{DG}]}{dt} = [\text{CH}_3\text{O}^-](k_1[\text{TG}][\text{MA}] + k_4[\text{MG}][\text{FAME}] - k_2[\text{DG}][\text{FAME}] - k_3[\text{DG}][\text{MA}]) \quad (14)$$

$$r_{\text{MG}} = \frac{d[\text{MG}]}{dt} = [\text{CH}_3\text{O}^-](k_3[\text{DG}][\text{MA}] + k_6[\text{GL}][\text{FAME}] - k_4[\text{MG}][\text{FAME}] - k_5[\text{MG}][\text{MA}]) \quad (15)$$

$$r_{FAME} = \frac{d[FAME]}{dt} = [CH_3O^-](k_1[TG][MA] + k_3[DG][MA] + k_5[MG][MA] - k_2[DG][FAME] - k_4[MG][FAME] - k_6[GL][FAME]) - k_8[FAME][OH^-] \quad (16)$$

$$r_{MA} = \frac{d[MA]}{dt} = [CH_3O^-](k_2[DG][FAME] + k_4[MG][FAME] + k_6[GL][FAME] + k_y[H_2O] - k_1[TG][MA] - k_3[DG][MA] - k_5[MG][MA]) + k_8[FAME][OH^-] - k_x[MA][OH^-] \quad (17)$$

$$r_{GL} = \frac{d[GL]}{dt} = [CH_3O^-](k_5[MG][MA] - k_6[GL][FAME]) + k_7[TG][OH^-] \quad (18)$$

$$r_{Soap} = \frac{d[Soap]}{dt} = [OH^-](k_7[TG] + k_8[FAME] + k_9[FFA]) \quad (19)$$

$$r_{FFA} = \frac{d[FFA]}{dt} = -k_9([FFA][OH^-] + [FFA][CH_3O^-]) \quad (20)$$

$$r_{H_2O} = \frac{d[H_2O]}{dt} = k_x[MA][OH^-] - k_y[H_2O][CH_3O^-] + k_9[FFA][OH^-] \quad (21)$$

Where:

r_A : Rates of formation of species A ($\text{mol.L}^{-1}.\text{time}^{-1}$); k_i : Rate constants of the reactions ($\text{L.mol}^{-1}.\text{time}^{-1}$) as described in sections 2.3.1 – 2.3.4 above

The k values ($\text{L.mol}^{-1}.\text{time}^{-1}$) in Eqs. (11) – (21) are the reaction rate constants as described in the sections 2.3.1 – 2.3.4 above. These equations were numerically modelled in MATLAB 7.12.0 (R2011a) using ODE45 solver (Runge-Kutta method). The MATLAB models were applied to predict the effects of temperature, molar ratio of methanol to oil, water and FFA content on transesterification and were validated using experimental data.

3. Results and Discussion

It was found that the reaction rates at various molar ratios of methanol to oil over tested range of temperatures were mixing independent at mixing speeds $\geq 540\text{rpm}$. Therefore, all the experiments were carried out at a mixing speed of 600rpm.

3.1. Saponification of ~~fatty acid methyl esters (FAME)~~ and ~~rapeseed oil (RSO)~~

The rates of saponification of RSO and FAME increased with temperature (40 to 60°C) as shown in Fig.1(a)&(b), indicating that they are both endothermic reactions. The

1 conversions of FAME to soap (Fig.1(b)) were 1.1 – 1.4 times higher than that of RSO
2 (Fig.1(a)) at the reaction temperatures of 40-60°C. ~~For instance, the conversions were 18%,~~
3 ~~35% and 53% at 40°C, 50°C and 60°C for RSO (Fig.(1a)), and 25%, 41% and 59% for FAME~~
4 ~~(Fig.(1e)) after 60min reaction time.~~ The analysis of the reaction mixtures collected during
5 the RSO transesterification in 0.5M methanol-KOH at 60°C (Fig.1(e)) indicates that the
6 reaction proceeds via FAME formation. There was an extremely rapid conversion of RSO to
7 FAME, which was then gradually saponified. The decrease in the total alkali concentration in
8 the RSO saponification experiment may be due to FAME saponification. At the methanol-to-
9 RSO molar ratio of 300:1, the initial rate of RSO transesterification was 110 times faster than
10 that of RSO saponification because 99.1mol % of the KOH existed as methoxide in the
11 methanol-KOH solution. This greatly reduced the rates of RSO saponification.

12 FAME saponification in methanol-KOH led to a reduction in the FAME yield in Fig
13 1. (b) and (e), which is consistent with previous work (Phan et al., 2012), in that there existed
14 a maximum in the FAME yield versus reaction time for alkali-catalysed transesterification.
15 For transesterification of RSO, the maximum FAME yield was obtained at a much shorter
16 reaction time, about 2min, at higher catalyst concentrations (here: 35wt% KOH based on
17 RSO). This provides more insight into the competitive reactions occurring in alkali-catalysed
18 transesterification processes, and explains why there is a decrease in the concentration of
19 biodiesel after the maximum yield was achieved (Darnoko and Cheryan, 2000b; Keera et al.,
20 2011; Phan et al., 2012). To prevent the unwanted competitive saponification reactions, the
21 reaction mixture would have to be neutralised with dilute acid as soon as the maximum
22 FAME yield is achieved.

3.2. Kinetics of the RSO and FAME saponification in methanol-KOH solutions

23 Saponification of the RSO and FAME in the 0.5M methanol-KOH solution was
24 investigated in detail to provide a better understanding of the effect of these reactions on
25 homogenous base-catalysed transesterification. The rates of saponification reactions were
26 analysed assuming a second-order reaction mechanism in which RSO and FAME were the

limiting reactants as described in Eq. (22). The apparent rate constants at various temperatures for the saponification reactions (k') and therefore actual rate constants (k) were obtained from experimental data using Eq. (23) and listed in Table 1.

$$-\frac{d[RA]}{dt} = k\beta[RA]_0^2 (1 - X)(\theta_B - nX) \quad (22)$$

$$\frac{1}{(\theta_B - n)[RA]_0} \cdot \ln \left[\frac{(\theta_B - nX)}{\theta_B(1 - X)} \right] = k\beta t = k' t \quad (23)$$

Where:

k' : Apparent saponification rate constant ($\text{L.mol}^{-1}.\text{min}^{-1}$); k : Actual saponification rate constant ($\text{L.mol}^{-1}.\text{min}^{-1}$); $[RA]$: Concentrations of the RSO or FAME (mol/L); $[RA]_0$: Initial concentrations of the RSO or FAME (mol/L); X : Conversion of the RSO or FAME to soap. θ_B : Ratio of the original concentrations of methanol-KOH solution to RSO or FAME; n : Moles of KOH required for saponification of 1 mole of RSO or FAME; β : Mole fraction of unreacted KOH in the KOH-methanol solution

As shown in Table 1, saponification rate constants for the RSO and FAME increased with temperature. The rate constants increased from $1.15 \text{ L.mol}^{-1}.\text{min}^{-1}$ to $5.62 \text{ L.mol}^{-1}.\text{min}^{-1}$ for RSO and from $1.44 \text{ L.mol}^{-1}.\text{min}^{-1}$ to $5.93 \text{ L.mol}^{-1}.\text{min}^{-1}$ for FAME when the reaction temperatures increased from 40°C to 60°C . There was 5-20% difference in the saponification rate constant between the RSO and FAME in the methanol-KOH solution, probably due to larger size of the RSO molecule. The activation energy for FAME saponification in this study was 61.2 kJ.mol^{-1} , similar to that for saponification of short chain carboxylic acid ethyl esters (Levenson and Smith, 1940; Smith and Levenson, 1939) as shown in Table 2.

The estimated actual rate constants for FAME saponification 40°C and 50°C were similar to those for the ethyl laurate saponification at 45°C and 55°C . The similarity in the activation energies suggests that saponification occurs by the same mechanism regardless of the chain length of ester, as would be expected. The activation energy for the RSO saponification (69.1 kJ.mol^{-1}) was close to that for the fatty acid alkyl esters, indicating that the RSO was saponified by the same mechanism as fatty acid alkyl esters.

3.3. Effect of water on FAME saponification

The effect of water on saponification of FAME is shown in Table 3 at 60°C using 0.5M methanol-KOH solution containing 0 – 12.5 vol% water. The FAME concentration decreased over time due to saponification. The rate of decrease in FAME concentration in Table.3 was a function of the water content. For instance, at 10 min reaction time, FAME concentrations decreased by 20, 43, 56 and 70% of the initial values for 0 vol%, 2.5 vol%, 5 vol% and 12.5vol% water, respectively. The increase in FAME saponification rate due to the presence of water was because the hydroxide – methoxide equilibrium reaction (~~shown below~~) moves to the reactant side, producing more hydroxide ions, which cause saponification. As shown in Table 4, the apparent rate constants (k') increased significantly with increasing water content. The mole fractions of the KOH (β) increased with water content. This confirms that the presence of water leads to backward shift in the hydroxide-methoxide equilibrium, producing more hydroxide ions.

3.4. Modelling

The kinetic parameters used in the numerical model for the alkali-catalysed homogeneous transesterification are shown in Table 5. The initial rate constants ($k_1 - k_6$) in modelling were derived from literature (Bambase et al., 2007), and from experimental data (k_7 - k_8) (Table 1).

Rate constants in (~~Bambase et al., 2007~~) were chosen because the trend in the FAME concentration predicted using them were consistent with experimental values obtained in this study. These initial values were adjusted to obtain the line of best fit (<5% error) through the experimental data. It was found that the modelled rate constants for the transesterification reactions (k_1 - k_6) were 1.75 times higher than those in literature, probably due to higher mixing intensity in the experiments. The FAME saponification rate constants for KOH-catalysed transesterification of RSO with methanol were 15% lower than those calculated for FAME saponification in 0.5M methanol-KOH. The lower apparent rate constants for the

FAME saponification were attributed to the removal of the hydroxide ions by the glycerol produced during transesterification as mentioned in section 3.2, thereby reducing the mole fraction of OH^- and slowing down the rates of FAME saponification. Therefore, modification of the kinetic model will be required to take into account the glycerol-hydroxide interactions.

3.4.1. Comparison modelling and experimental results

As shown in Fig.2, the modelling results using the data in Table 5 agreed well with the experimental data for all cases. The results show that for KOH-catalysed transesterification of RSO at operating conditions: 0.5wt% KOH (based on RSO), 3:1 methanol to RSO molar ratio and 60°C reaction temperature, the model predicted 72.2% FAME yield at 60min reaction time, which was very close to experimental data of 74%. It increased from 72.2% to 91.0% at 60min reaction time when a molar ratio of methanol to oil increased from 3:1 to 6:1. When high catalyst concentration (35wt%) and methanol molar ratio (300:1) were used, 98% FAME yield could be achieved in 2min, which then decreased significantly due to the saponification of FAME.

3.4.2. Effect of reaction temperature on alkali-catalysed transesterification

Fig.3 shows modelling and experimental results for RSO transesterification with methanol at reaction temperatures of 30-70°C, 0.5wt% KOH and methanol to oil molar ratios of (a) 300:1 and (b) 6:1.

The FAME yield increased with temperature for both methanol molar ratios due to the endothermicity of the reactions (Vicente et al., 2004). At a 300:1 molar ratio in Fig.3(a), the predicted FAME yields at 30, 40, 50, 60 and 70°C were 8.5%, 20.4%, 39.6%, 69.8% and 94.3% after 5min reaction time, which were similar to those obtained experimentally (23%, 41% and 67% at 40, 50 and 60°C). At these conditions, the mole fractions of the available hydroxide ions are too small to cause saponification; hence the reaction simply reaches its equilibrium. At a 6:1 molar ratio (Fig.3(b)), the predicted FAME yield at 30, 40, 50, 60 and 70 °C were 21.4%, 44.2%, 69.6%, 85.7% and 91.6% after 5min reaction time. The transesterification reaction was much faster at 6:1 than 300:1 methanol to RSO molar ratio

1 due to the dilution of the catalytic species. A large excess of methanol (300:1) pushes the
2 hydroxide-methoxide equilibrium further towards methoxide formation, which reduces the
3 mole fraction of hydroxide ions and prevents RSO and FAME saponification. Although
4 transesterification is much faster at the 6:1 than at 300:1 methanol to RSO molar ratio, the
5 saponification of RSO and FAME was also further accelerated at the 6:1 molar ratio due to
6 increased hydroxide ion concentration. The maximum FAME yields were approximately 93%
7 at 40°C, 50°C and 60°C and 92% at 70°C for RSO transesterification at 6:1 methanol to RSO
8 molar ratio after 60min reaction time.
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10 As shown in Fig.3(a), at a 300:1 methanol to RSO molar ratio, the FAME yield was
11 99.9% in all tested temperatures after 60min reaction time. The lower maximum FAME yield
12 at the 6:1 molar ratio was due to the increased RSO and FAME saponification. Higher molar
13 ratio of methanol will be required to shift the KOH-methoxide equilibrium in equation (11),
14 towards methoxide. This will greatly reduce the rates of RSO and FAME saponification. The
15 modelling maximum FAME yields at 30°C were 90.6% at a 6:1 molar ratio and 87.1% at a
16 300:1 molar ratio at 60min reaction time. These results suggest that more than 60min reaction
17 time is required for transesterification reactions at both 300:1 and 6:1 molar ratio to reach
18 maximum FAME yield at 30°C reaction temperature, which is in agreement with findings in
19 literature (Nakpong and Wootthikanokkhan, 2010). Transesterification reaction was faster at
20 300:1 molar ratio because of the dilution of methoxide catalytic species in larger excess of
21 methanol. A slight decrease (1%) in the maximum FAME yield after 60min reaction time at
22 the 6:1 methanol to RSO molar ratio when the temperature increased from 60°C to 70°C. This
23 could be due to the increased rate of RSO and FAME saponification with temperature. The
24 **highest** rates of transesterification and saponification were at 70°C, leading to the shortest
25 time to achieve the equilibrium (93% FAME yield at 7min reaction time and 6:1 molar ratio)
26 and the highest rates of FAME saponification unless the reaction is quenched. This prediction
27 is in accordance with other findings (Dorado et al., 2004), in which the FAME yield
28 decreased when temperature increased from 60 to 70°C in alkali-catalysed methanolysis of
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1 used olive oil. However, the authors explained the results due to the acceleration of glyceride
2 saponification at 70°C. The findings in this study suggest that both glyceride and FAME
3 saponifications are accelerated when the temperature increased from 60 to 70°C.
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6 **3.4.3. Effect of methanol to oil molar ratios and hydroxide catalyst concentration on** 7 **alkali-catalysed transesterification.** 8 9

10 The effect of molar ratio of methanol to RSO and hydroxide catalyst concentration on
11 FAME yield in homogeneous KOH-catalysed transesterification of RSO at 60°C is shown in
12 Fig.4.
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15 The results in Fig.4(a) above show that FAME yield increases with methanol molar ratio.
16 Excess methanol in the reaction not only drives the transesterification equilibrium towards the
17 product side and increases the rate of the reaction, but it also shifts the hydroxide-methoxide
18 equilibrium towards the formation of more methoxide ions, reducing FAME saponification.
19 At low methanol molar ratios (e.g. 6:1), FAME saponification is evident after the maximum
20 e.g. the decrease in the FAME yield from 91% at 5min to 89% at 60min reaction time, 6:1
21 methanol to RSO molar ratio, 60°C and 1.5wt% KOH from the modelling results. A higher
22 equilibrium FAME yield was obtained in continuous transesterification using the meso-OBR
23 (96.2%) than in a batch reactor (92.3 %) perhaps due to enhanced mixing in the baffled
24 reactor. There was a more rapid decrease in the FAME yield in the meso-OBR after the
25 equilibrium FAME yield was reached, indicating that both transesterification and
26 saponification reactions were intensified in the OBR.
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47 At the lowest catalyst concentration (0.5wt% KOH), there was a reduction in
48 hydroxide ion concentration in the solution which slows down the rates of RSO and FAME
49 saponifications. This accounts for the increase in the predicted equilibrium FAME yields.
50 However, the rate of the RSO transesterification also decreases with the catalyst
51 concentration.
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59 The effect of varying catalyst concentration on the rates of FAME production in a
60 homogenous alkali-catalysed transesterification was numerically investigated as shown in
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Fig.4(b). The FAME yield increased with catalyst concentration. As a result, the time to achieve the maximum FAME yield decreased with increasing catalyst concentration, e.g. it decreased from 22min at 0.5wt% KOH to 3.5min at 2.0wt% KOH. The maximum FAME yield also reduced from 93% at 0.5wt% KOH to 90% at 2.0wt% KOH. At 60min, the predicted FAME yields decreased from 93% to 86.6% as the KOH catalyst concentration increased from 0.5wt% to 2.0wt% at 6:1 methanol to RSO and 60°C.

Fig.4 (b) indicates that the greater the catalyst concentration, the greater the rate of RSO and FAME saponification. However, this can be minimised by using higher methanol molar ratios, for example 12:1. For instance, the predicted FAME yield was 97.1% at a 12:1 methanol to RSO molar ratio compared to 89.0% at a 6:1 methanol to RSO molar ratio at 60°C, 2.0wt% KOH and 2min reaction time. The FAME yield of 97.1% at 2min decreased to 90.1% after 1h reaction time due to FAME saponification. Therefore, the reaction must be quenched as soon as the maximum FAME yield was reached to prevent any loss of the FAME product. This requires a reactor with tight control of residence time and a high degree of uniform mixing. Generally, achieving high FAME yield in a short reaction time and minimising saponifications by either operating at high alcohol to oil ratios or high catalyst loads will reduce the capital cost. However, the disadvantages of these strategies are increasing the separation costs and costs of the catalyst and costs associated to neutralisation of which the separation costs are more significant than the latter.

3.4.4. Effects of moisture and FFA in the alkali-catalysed transesterification

Fig.5 shows the effects of moisture and ~~free fatty acids (FFA)~~ on the alkali-catalysed transesterification at 60 °C, 1.0 wt% KOH catalyst and 6:1 methanol to RSO molar ratio. The water content was 0 – 1.0 wt% in the reaction mixture and FFA content was 0 – 1.0 wt% in RSO. Clearly, FAME yield decreased when water was added. This was due to the backward shift in the hydroxide-methoxide equilibrium reaction, producing hydroxide ions, which accelerate the rates of both triglyceride and FAME saponification. More methanol may be required to push the hydroxide-methoxide equilibrium forward to reduce the amount of

hydroxide ions and to minimise saponification reactions. The numerical results for RSO transesterification at 60°C, 1.0wt% KOH catalyst, 1.0wt% water and 12:1 methanol to oil molar ratio shown in Fig.5 support this theory. For example, at 60min reaction time, 93.6% FAME yield was obtained at 12:1 methanol to RSO molar ratio but only 83.8% FAME yield at a 6:1 molar ratio of methanol to RSO.

The findings in this study indicate that water had a more significant effect on FAME yield than FFA for alkali-catalysed transesterification. When the amount of FFA in RSO increased from 0wt% to 1.0wt%, FAME yield remained almost constant at 91% as shown in Fig.5. Due to the high concentration of methoxide ions in the alkali-catalysed transesterification, reaction mixtures compared to the hydroxide ions, FFA neutralisation by methoxide ions is favoured ~~as presented below~~. This is a non-equilibrium reaction that removes catalytic species from the alkali-catalysed transesterification process.

The main problem of FFA in the alkali-catalysed transesterification is the soap produced during FFA neutralisation, which leads to emulsification and gel formation, thereby inhibiting the separation of glycerol and FAME (Canakci and Van Gerpen, 2003). This removes the catalytic species from the reacting mixture and slows down the reaction. FFA and moisture contents must not exceed 0.5wt% and 0.3wt% respectively (Freedman et al., 1984; Ma et al., 1998) in alkali-catalysed biodiesel process to avoid excessive soap formation. However, the findings in this study suggest that higher moisture content ($\approx 1.0\text{wt} \%$) can be tolerated at methanol molar ratios above 12:1. Furthermore, at these conditions the reaction time required is only $\sim 5\text{min}$, significantly shorter than the reaction times usually used in industry (over 60min).

3.4.5. Proposed overall reaction scheme for alkali-catalysed homogeneous transesterification

Although KOH-methoxide system was used to study, the hydroxide-methoxide equilibrium can be also used for the NaOH –methoxide system. It was found that at the same

concentrations and reaction conditions, NaOH and KOH in methanol behave similarly in triglyceride transesterification and FAME saponification.

The reaction scheme in Fig.6 has been proposed for the alkali-catalysed homogeneous transesterification of vegetable oils with methanol, based on findings and understandings of the process. This is a particularly complex process. The reaction starts by equilibrium reactions of alkali-metal hydroxide (OH^-) with methanol (CH_3OH) to form methoxide (CH_3O^-) catalytic species and water. The hydroxide-methoxide equilibrium favours formation of methoxide due to higher acidity of methanol compared to water (Reeve et al., 1979).

The OH^- and CH_3O^- in the solution participate in various reactions. CH_3O^- reacts with triglyceride to form fatty acid methyl esters (FAME) and glycerol. Apart from glycerol, glycerides (diglyceride and monoglyceride) are also produced during the transesterification. The CH_3O^- consumed in the transesterification is regenerated by the reactions of the glyceride ions with methanol. CH_3O^- also participates in neutralisation of FFA to form soap and methanol. Any CH_3O^- involved in the irreversible reaction with FFA is lost in soap formation and cannot be regenerated. This accounts for the decreased rate of FAME yield at higher FFA shown in the Fig.5.

On the other hand, the OH^- species ~~is~~ participates in several soap formation reactions such as triglyceride and FAME saponifications, and FFA neutralisation. These reactions impact negatively on the rates of triglyceride transesterification and FAME yield. Concentration of OH^- must, therefore, be minimised to achieve high FAME yield. Addition of water into the alkali-catalysed transesterification process shifts the hydroxide-methoxide equilibrium in Fig.6 towards the formation of the metal hydroxide. Water also reacts with glyceride ions to form more OH^- in the system. These reactions lead to increased OH^- concentration and consequently accelerations in saponification of triglyceride and FAME. This agrees well with the findings in the experimental (Fig.1 and Table 4) and the numerical modelling (Fig.5) results which indicate that water has negative effect on the alkali-catalysed homogeneous transesterification. It is important to note that even when metal alkoxide

($\text{CH}_3\text{O}^-\text{M}^+$) is used as catalyst, any water in the system would react with the $\text{CH}_3\text{O}^-\text{M}^+$ to form methanol and metal hydroxide, in accordance with the hydroxide-methoxide equilibrium.

To achieve high FAME yield, triglyceride and FAME saponifications must be minimised. Saponification of TG and FAME can be slowed down by using low catalyst loading and anhydrous reagents to reduce OH^- regeneration. However, reduction in the catalyst loading also slows down the rates of the triglyceride transesterification. Fig. 6 indicates that a more feasible condition that allows for rapid biodiesel production would be to use large excess methanol. This moves the hydroxide-methoxide equilibrium far towards CH_3O^- formation, minimising OH^- concentration. Large excess of methanol also reduces the chances of OH^- regeneration even at 0-1wt% water (Fig.5), as the collision of glyceride ions with methanol becomes more probable than with water.

4. Conclusions

Rapid biodiesel production (reaction times <2 min) at economically viable conversions can be achieved by increasing base catalyst and methanol concentrations without significant problems due to excess soap formation, even in the presence of water and FFAs. The experiments and model suggested that methanol: oil molar ratios of above 9:1 are required to obtain high FAME (96.3% maximum) yield at higher catalyst concentrations (> 1.5wt% KOH). An increased methanol to oil molar ratio above 12:1 could be used for feedstocks containing 0 – 1.0wt % water. Free fatty acids had little effect on saponification of triglyceride or FAME up to 1%.

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Fig. 1: (a) RSO saponification (300:1 methanol to RSO molar ratio and 35wt% KOH) and (b) FAME saponification (100:1 methanol to FAME molar ratio and 35wt% KOH) and (c) RSO transesterification (300:1 methanol to RSO molar ratio and 35wt% KOH) at mixing intensity of 600rpm over a temperature range of 40 – 60°C

Fig.2: Homogeneous alkali-catalysed transesterification of RSO at 60°C and mixing intensity of 600rpm: (i) 3:1 methanol to RSO molar ratio and 0.5wt% KOH; (ii) 6:1 methanol to RSO molar ratio and 1wt% KOH and (iii) 300:1 methanol to RSO molar ratio and 35wt% KOH (dots: experimental data; lines: modelling results)

Fig.3: Homogeneous alkali-catalysed transesterification at 0.5wt% KOH, mixing at 600rpm, 30 – 70°C temperatures and a molar ratio of methanol to RSO of (a) 300:1 and (b) 6:1 (dots: experimental data; lines: modelling results)

Fig. 4: Homogeneous KOH-catalysed transesterification of RSO with methanol at 60°C: (a) 0.5wt% and 1.5wt% KOH catalyst, 600rpm and 3:1 to 24:1 methanol to RSO molar ratios; (b) numerical results at 6:1 methanol to oil molar ratio (* molar ratio of methanol to oil of 12:1) over a range of KOH catalyst concentrations of 0.5 – 2.0wt% (dots: experimental data; lines: modelling results)

Fig. 5: Numerical results for RSO transesterification at 60°C, 1.0wt% KOH catalyst, 6:1 (*12:1) methanol to oil molar ratio over water content of 0 – 1.0%wt and FFA content of 0-1.0%wt

Fig.6: Proposed reaction scheme for alkali-catalysed homogeneous transesterification

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Table 5: Rate constants used in modelling

Fig. 1: (a) RSO saponification (300:1 methanol to RSO molar ratio and 35wt% KOH) and (b) FAME saponification (100:1 methanol to FAME molar ratio and 35wt% KOH) and (c) RSO transesterification (300:1 methanol to RSO molar ratio and 35wt% KOH) at mixing intensity of 600rpm over a temperature range of 40 – 60°C

Fig.2: Homogeneous alkali-catalysed transesterification of RSO at 60°C and mixing intensity of 600rpm: (i) 3:1 methanol to RSO molar ratio and 0.5wt% KOH; (ii) 6:1 methanol to RSO molar ratio and 1wt% KOH and (iii) 300:1 methanol to RSO molar ratio and 35wt% KOH (dots: experimental data; lines: modelling results)

Fig.3: Homogeneous alkali-catalysed transesterification at 0.5wt% KOH, mixing at 600rpm, 30 – 70°C temperatures and a molar ratio of methanol to RSO of (a) 300:1 and (b) 6:1 (dots: experimental data; lines: modelling results)

Fig. 4: Homogeneous KOH-catalysed transesterification of RSO with methanol at 60°C: (a) 0.5wt% and 1.5wt% KOH catalyst, 600rpm and 3:1 to 24:1 methanol to RSO molar ratios; (b) numerical results at 6:1 methanol to oil molar ratio (* molar ratio of methanol to oil of 12:1) over a range of KOH catalyst concentrations of 0.5 – 2.0wt% (dots: experimental data; lines: modelling results)

Fig. 5: Numerical results for RSO transesterification at 60°C, 1.0wt% KOH catalyst, 6:1 (*12:1) methanol to oil molar ratio over water content of 0 – 1.0%wt and FFA content of 0-1.0%wt

Fig.6: Proposed reaction scheme for alkali-catalysed homogeneous transesterification

Table 1: Rate constants for the RSO and FAME saponification ($\text{L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$)

Reaction temperature ($^{\circ}\text{C}$)	Apparent rate constants ($k' * 10^{-3}$)		Actual rate constants (k)	
	RSO	FAME	RSO	FAME
40	7.9	9.9	1.15	1.44
50	18.9	19.5	2.74	2.92
60	29.7	31.6	5.62	5.93
Activation energy ($\text{kJ} \cdot \text{mol}^{-1}$)	-	-	69.1	61.2

Table 2: Kinetic parameters for the RSO, FAME and some other alkyl esters saponification

Substance and the saponification media	k (L.mol ⁻¹ .min ⁻¹)		Ea (kJ.mol ⁻¹)	References
	40°C	50°C		
Ethyl acetate and 0.05M NaOH in aqueous ethanol	3.88	8.07	61.5	(Smith and Levenson, 1939) [#]
Ethyl propanoate and 0.05M NaOH in aqueous ethanol	1.98	4.10	61.5	(Smith and Levenson, 1939) [#]
Ethyl laurate and 0.05M NaOH in aqueous ethanol	1.57 @ 45°C	3.17 @ 55°C	63.2	(Levenson and Smith, 1940) [#]
RSO and 0.5M methanol-KOH	1.27	2.74	69.1	This study
FAME and 0.5M methanol-KOH	1.44	2.92	61.2	This study

[#]Rate constants were calculated from the data reported by the authors

Table 3: FAME saponification at 60°C and 0 – 12.5 vol% water in methanol

Time (min)	FAME contents at the various water levels in methanol			
	0 vol%	2.5 vol%	5 vol%	12.5 vol%
0	9.20	8.97	8.77	8.23

1	8.95	8.15	7.63	6.41
2	8.34	7.40	6.94	5.79
5	7.90	6.35	5.50	4.27
10	7.32	5.15	3.86	2.48
20	6.30	3.86	2.20	0.93
30	5.59	2.78	1.42	0.62
40	4.79	2.07	1.01	0.31
50	4.12	1.56	0.61	0.21
60	3.87	1.22	0.41	0.21

Table 4: Apparent rate constants (k') for FAME saponification at various water contents in methanol

Water in methanol (vol %)	k' (L.mol ⁻¹ .min ⁻¹)	Mole fraction (β) of KOH (%) mole fraction)	R ²
0	0.032 ^a	0.69 ^a	-

2.5	0.104	3.25	0.999
5.0	0.175	5.47	0.998
12.5	0.344	10.75	0.985

^aMole fraction and k' values for the reaction at zero water content were estimated using the equilibrium constant for KOH-methoxide reaction from equation (4).

Table 5: Rate constants used in modelling

Rate constant (L. mol ⁻¹ .min ⁻¹)	Reactions	References
$k_1 = 4.260 \times 10^9 e^{-\frac{58,740}{RT}}$	TG $\longrightarrow$ DG	**

$k_2 = 4.304 \times 10^6 e^{-\frac{44,930}{RT}}$	DG $\longrightarrow$ TG	**
$k_3 = 2.176 \times 10^{11} e^{-\frac{67,146}{RT}}$	DG $\longrightarrow$ MG	**
$k_4 = 6.559 \times 10^9 e^{-\frac{58,184}{RT}}$	MG $\longrightarrow$ DG	**
$k_5 = 8.679 \times 10^5 e^{-\frac{30,010}{RT}}$	MG $\longrightarrow$ GL	**
$k_6 = 1.975 \times 10^7 e^{-\frac{46,009}{RT}}$	GL $\longrightarrow$ MG	**
$k_7 = 1.269 \times 10^{11} e^{-\frac{69104}{RT}}$	RSO $\longrightarrow$ Soap	This study
$k_8 = 1.962 \times 10^{10} e^{-\frac{61,160}{RT}}$	FAME $\longrightarrow$ Soap	This study
$k_9 = 6.136 \times 10^5 e^{-\frac{31,394}{RT}}$	FFA $\longrightarrow$ Soap	(Morgunov et al., 1977)
$K_{eq} = \frac{k_x}{k_y} = 3.2 (79.5 \text{ (mol.L}^{-1}\text{)})$	$\text{OH}^- \rightleftharpoons \text{CH}_3\text{O}^-$	(Caldin and Long, 1954; Reeve et al., 1979)

** $k_1 - k_6$ are the modified rate constants from (Bambase et al., 2007)

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Table 1: Rate constants for the RSO and FAME saponification ($\text{L.mol}^{-1}.\text{min}^{-1}$)

Reaction temperature ($^{\circ}\text{C}$)	Apparent rate constants ($k' * 10^{-3}$)		Actual rate constants (k)	
	RSO	FAME	RSO	FAME
40	7.9	9.9	1.15	1.44
50	18.9	19.5	2.74	2.92
60	29.7	31.6	5.62	5.93
Activation energy (kJ.mol^{-1})	-	-	69.1	61.2

Table 2: Kinetic parameters for the RSO, FAME and some other alkyl esters saponification

Substance and the saponification media	k (L.mol ⁻¹ .min ⁻¹)		Ea (kJ.mol ⁻¹)	References
	40°C	50°C		
Ethyl acetate and 0.05M NaOH in aqueous ethanol	3.88	8.07	61.5	(Smith and Levenson, 1939) [#]
Ethyl propanoate and 0.05M NaOH in aqueous ethanol	1.98	4.10	61.5	(Smith and Levenson, 1939) [#]
Ethyl laurate and 0.05M NaOH in aqueous ethanol	1.57 @ 45°C	3.17 @ 55°C	63.2	(Levenson and Smith, 1940) [#]
RSO and 0.5M methanol-KOH	1.27	2.74	69.1	This study
FAME and 0.5M methanol-KOH	1.44	2.92	61.2	This study

[#]Rate constants were calculated from the data reported by the authors

Table 3: FAME saponification at 60°C and 0 – 12.5 vol% water in methanol

Time (min)	FAME contents at the various water levels in methanol
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	0 vol%	2.5 vol%	5 vol%	12.5 vol%
0	9.20	8.97	8.77	8.23
1	8.95	8.15	7.63	6.41
2	8.34	7.40	6.94	5.79
5	7.90	6.35	5.50	4.27
10	7.32	5.15	3.86	2.48
20	6.30	3.86	2.20	0.93
30	5.59	2.78	1.42	0.62
40	4.79	2.07	1.01	0.31
50	4.12	1.56	0.61	0.21
60	3.87	1.22	0.41	0.21

Table 4: Apparent rate constants (k') for FAME saponification at various water contents in methanol

Water in methanol (vol %)	k' (L.mol ⁻¹ .min ⁻¹)	Mole fraction (β) of KOH (% mole fraction)	R ²
0	0.032 ^a	0.69 ^a	-
2.5	0.104	3.25	0.999
5.0	0.175	5.47	0.998
12.5	0.344	10.75	0.985

^aMole fraction and k' values for the reaction at zero water content were estimated using the equilibrium constant for KOH-methoxide reaction from equation (4).

Table 5: Rate constants used in modelling

Rate constant (L. mol ⁻¹ .min ⁻¹)	Reactions	References

$k_1 = 4.260 \times 10^9 e^{-\frac{58,740}{RT}}$	TG $\longrightarrow$ DG	**
$k_2 = 4.304 \times 10^6 e^{-\frac{44,930}{RT}}$	DG $\longrightarrow$ TG	**
$k_3 = 2.176 \times 10^{11} e^{-\frac{67,146}{RT}}$	DG $\longrightarrow$ MG	**
$k_4 = 6.559 \times 10^9 e^{-\frac{58,184}{RT}}$	MG $\longrightarrow$ DG	**
$k_5 = 8.679 \times 10^5 e^{-\frac{30,010}{RT}}$	MG $\longrightarrow$ GL	**
$k_6 = 1.975 \times 10^7 e^{-\frac{46,009}{RT}}$	GL $\longrightarrow$ MG	**
$k_7 = 1.269 \times 10^{11} e^{-\frac{69104}{RT}}$	RSO $\longrightarrow$ Soap	This study
$k_8 = 1.962 \times 10^{10} e^{-\frac{61,160}{RT}}$	FAME $\longrightarrow$ Soap	This study
$k_9 = 6.136 \times 10^5 e^{-\frac{31,394}{RT}}$	FFA $\longrightarrow$ Soap	(Morgunov et al., 1977)
$K_{eq} = \frac{k_x}{k_y} = 3.2 (79.5 \text{ (mol.L}^{-1}\text{)})$	$\text{OH}^- \rightleftharpoons \text{CH}_3\text{O}^-$	(Caldin and Long, 1954; Reeve et al., 1979)

** $k_1 - k_6$ are the modified rate constants from (Bambase et al., 2007)

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Fig. 1: (a) (a) RSO saponification (300:1 methanol to RSO molar ratio and 35wt% KOH) and (b) FAME saponification (100:1 methanol to FAME molar ratio and 35wt% KOH) at mixing intensity of 600rpm over a temperature range of 40 – 60°C

Fig.2: Homogeneous alkali-catalysed transesterification of RSO at 60°C and mixing intensity of 600rpm: (i) 3:1 methanol to RSO molar ratio and 0.5wt% KOH; (ii) 6:1 methanol to RSO molar ratio and 1wt% KOH and (iii) 300:1 methanol to RSO molar ratio and 35wt% KOH (dots: experimental data; lines: modelling results)

Fig.3: Homogeneous alkali-catalysed transesterification at 0.5wt% KOH, mixing at 600rpm, 30 – 70°C temperatures and a molar ratio of methanol to RSO of (a) 300:1 and (b) 6:1 (dots: experimental data; lines: modelling results)

Fig. 4: Homogeneous KOH-catalysed transesterification of RSO with methanol at 60°C: (a) 0.5wt% and 1.5wt% KOH catalyst,, 600rpm and 3:1 to 24:1 methanol to RSO molar ratios; (b) numerical results at 6:1 methanol to oil molar ratio (* molar ratio of methanol to oil of 12:1) over a range of KOH catalyst concentrations of 0.5 – 2.0wt% (dots: experimental data; lines: modelling results)

Fig. 5: Numerical results for RSO transesterification at 60°C, 1.0wt% KOH catalyst, 6:1 (*12:1) methanol to oil molar ratio over water content of 0 – 1.0%wt and FFA content of 0-1.0%wt

Fig.6: Proposed reaction scheme for alkali-catalysed homogeneous transesterification

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Fig. 4: Homogeneous KOH-catalysed transesterification of RSO with methanol at 60°C: (a) 0.5wt% and 1.5wt% KOH catalyst, 600rpm and 3:1 to 24:1 methanol to RSO molar ratios; (b) numerical results at 6:1 methanol to oil molar ratio (* molar ratio of methanol to oil of 12:1) over a range of KOH catalyst concentrations of 0.5 – 2.0wt% (dots: experimental data; lines: modelling results)

Fig. 5: Numerical results for RSO transesterification at 60°C, 1.0wt% KOH catalyst, 6:1 (*12:1) methanol to oil molar ratio over water content of 0 – 1.0%wt and FFA content of 0- 1.0%wt

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