



Intrinsic Transesterification Rate of Coconut, Palm and Sunflower Oils with Methanol

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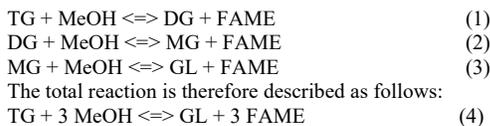
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Abstract: In general, most of the transesterification studies are using pseudo first order kinetics that does not reflect the precise phenomenon of the reaction. It is very likely that the observed reaction rate is affected by physical mass transfer between two immiscible reactants (methanol and oil). Therefore, in the present study, the transesterification of coconut, palm and sunflower oils with methanol were conducted in a single phase by adding methylethylketone in order to eliminate the physical mass controlled region. At 50 °C, the oil conversion of coconut, palm and sunflower oils reached 0.98 within first 10 minutes. The reaction rate constant decreased and the activation energy increased as the order of coconut, palm and sunflower oils. The activation energy of intrinsic transesterification for coconut, palm and sunflower oils were 27.9, 38.0 and 57.1 kJ/mol.

Keywords: Intrinsic transesterification, coconut oil, palm oil, sunflower oil, activation energy.

1. INTRODUCTION

Transesterification is an important reaction for converting lipids and fats (triglycerides) to fatty acid methyl ester, so-called biodiesel oil (Schwab *et al.*, 1987). Ma and Hanna (1999) compared the four representative methods to convert triglycerides to biodiesel fuel: blending, microemulsion, thermal cracking and transesterification, and concluded that transesterification is the most promising method. In this reaction, lipids are transesterified with methanol catalyzed by a catalyst, typically homogeneous alkaline. Transesterification reaction of triglyceride consists of three successive reactions as follows:



Where TG is triglyceride; DG is diglyceride; MG is monoglyceride; GL is glycerol; MeOH is methanol; FAME is fatty acid methyl ester.

Due to its significance, academic reports of lipid transesterification are therefore huge in number. A variety of research studies including catalyst, reaction medium and energy supply method were carried out. Catalysts include non-catalyst (Diasakou *et al.*, 1998), acid or base homogeneous (Jain *et al.*, 2011), enzyme (Tran *et al.*, 2013), solid (Chantrasa *et al.*, 2011). Reaction media include ionic liquid (Sun and Chen, 2015) and supercritical fluid (Varma and Madras, 2010). Energy supply methods include microwave

(Patil *et al.*, 2011) and ultrasonic (Thanh *et al.*, 2014), as well as conventional thermal heat-up.

Nowadays, commercial production of biodiesel by transesterification of oil is catalyzed by homogeneous alkaline catalyst in a batch-wise reactor at around 40-60 °C. Therefore kinetic studies for transesterification catalyzed by homogeneous catalyst have been reported by many researchers from 1990s to now. In earlier years, pseudo-homogeneous kinetics were major (Diasakou *et al.*, 1998; Berrios *et al.*, 2007; Slinn and Kendall, 2009; Issariyakul and Dalai, 2012; Reyero *et al.*, 2015), although the reaction mixture is constituted by liquid (oil) – liquid (methanol and catalyst) two-phase. The pseudo-homogeneous model is using the following kinetics:

$$-r = -\frac{dC_{TG}}{dt} = k_1 C_{TG} C_{MeOH} - k_2 C_{GL} C_{FAME} \quad (5)$$

This can be simplified when the methanol to oil ratio is sufficiently high as follows:

$$-r = -\frac{dC_{TG}}{dt} = k C_{TG} \quad (6)$$

These two equations above are completely relevant if the reaction occurs in one homogeneous phase. However, this model is ignoring that the reaction mixture consists of liquid-liquid two phases. Very recently the kinetic studies in this field have started to incorporate the idea of intraphase and interphase mass transfer into the model (Klofutar *et al.*, 2010).

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(Csernica *et al.* 2012) (Richard *et al.*, 2013). (Likozar *et al.* 2014). However, all these studies are only estimating reaction kinetic parameters from their mass transfer model. Now obviously we need more reliable empirical reaction kinetics parameters measured directly in homogenous system.

(Boocock. *et al.*,1998) carried out transesterification of a few types of lipid with methanol in homogenous phase by using tetrahydrofuran (THF) as a co-solvent. Since then there have not been much effort to accumulate intrinsic reaction kinetic data of transesterification in this research field.

In the present study, reaction rates of transesterification of three types of lipid, coconut, palm and sunflower oils, with methanol were measured directly in homogenous phase catalyzed by potassium hydroxide at 20-60 °C. In order to make reaction mixture homogeneous, methylethylketone (MEK) was used as a co-solvent.

2. MATERIALS AND METHODS

2.1 Materials

Refined, food-grade cooking oils: Country Farm brand coconut oil, Seri Murni brand palm olein and Krytsal brand sunflower oil were purchased from local stores. Analytical grade chemicals: 2-propanol, acetic acid (glacial), methanol, n-hexane and potassium hydroxide pellets were purchased from Merck Sdn Bhd whereas methylethylketone (MEK) was supplied by R&M Chemicals and methyl heptadecanoate was bought from Sigma-Aldrich.

2.2 Methods

2.2.1 Batch Transesterification

Reactions were performed in a 500 mL three necked round bottom flask equipped with a reflux condenser, a thermometer and a sampling port. The reactor was immersed in a constant temperature water bath equipped with a temperature controller at atmospheric pressure. Agitation was maintained at 400 rpm throughout the experiment with a magnetic stirrer to ensure uniform heating and mass distribution. Experimental conditions were fixed as follows: molar ratio of methanol: oil, 6:1; and molar ratio of alkaline catalyst: oil, 0.175:1. Initially, the reactor was filled with vegetable oil, followed by MEK and heated up to a desired temperature. Next, addition of methoxide solution (dissolved potassium hydroxide pellet in the methanol solution) to the reactor was recorded as time at zero. The concentration of reactants, catalyst and co-solvent for the present experimental work is shown in (Table-1).

Table-1: Concentration (mol/L) of reactants, catalyst and co-solvent for the present experimental work

Component	Transesterification of coconut oil	Transesterification of palm oil	Transesterification of sunflower oil
Vegetable oil	0.596 mol/L	0.596 mol/L	0.569 mol/L
Methanol	3.576 mol/L	3.576 mol/L	3.415 mol/L
Potassium hydroxide	0.104 mol/L	0.104 mol/L	0.099 mol/L
Methylethylketone	4.778 mol/L	3.215 mol/L	3.511 mol/L

2.2.2 Reaction Sampling and HPLC Analysis

A set of 7 mL-vials were filled with 15 µL pure acetic acid and 3 mL of HPLC mobile phase (n-hexane:2-propanol (97:3, v/v)). Then, mass of each vial prepared was measured and recorded. Samples of 200 µL were withdrawn at a pre-specified time interval using a micropipette and placed into the prepared 7 mL-vial immediately, and then the mass of sample was weighted. This neutralization of catalyst by acetic acid and dilution of sample were capable to stop the reaction instantly. Next, the samples were analyzed for the oil concentration by high performance liquid chromatography with refractive index detector (HPLC-RID), Shimadzu brand, and model: RID-10A. The analysis was carried out using a mixture of n-hexane and 2-propanol (97:3, v/v) as mobile phase. The separation column used was a Shim Pack CLC-SIL (M) – (150 x 4.6 mm, 5 µm). The column temperature was maintained at 40 °C.

2.2.3 Determination of Oil Concentration

The oil concentration of the sample reaction mixture, C_R (mol/L) after HPLC analysis was calculated according to Equation 7 (Kupiec, 2004).

$$C_R = \left(\frac{A_R/M_R}{A_S/M_S} \right) C_S \quad (7)$$

Where A_R is the oil peak of the sample reaction mixture; M_R is the mass of sample reaction mixture (mg); A_S is the oil peak area of the oil standard (triglyceride); M_S is the mass of oil standard (triglyceride) (mg); C_S is the oil concentration of the standard (mol/L).

2.2.4 Determination of Oil Conversion

The conversion of oil during batch transesterification at specific time was computed based on Equation 8 (Fogler, 2005).

$$\text{Oil conversion} = \frac{C_o - C_t}{C_o} \quad (8)$$

Where C_o is the initial oil concentration (mol/L); C_t is the oil concentration at time t (mol/L).

2.2.5 Determination of Rate Constant

Integral method was used to determine the reaction order and rate constant, k by plotting the concentration-time data by the equation summarized in (Table-2) where C_e (mol/L) is the oil concentration at equilibrium stage.

Table-2: Summary of rate law and integrated rate law for first-, second- and third-order reaction (Fogler, 2005)

Reaction order	First-order	Second-order	Third-order
Rate law	$\frac{dC_t}{dt} = k_1(C_t - C_e)$	$-\frac{dC_t}{dt} = k_2(C_t - C_e)^2$	$-\frac{dC_t}{dt} = k_3(C_t - C_e)^3$
Integrated rate law	$k_1 t = \ln \frac{C_o - C_e}{C_t - C_e}$	$k_2 t = \frac{1}{C_t - C_e} - \frac{1}{C_o - C_e}$	$2k_2 t = \frac{1}{(C_t - C_e)^2} - \frac{1}{(C_o - C_e)^2}$

2.2.6 Determination of Activation Energy

The k values from the best reaction model were used to determine the activation energy by using the Arrhenius plot (Fogler, 2005).

$$\ln(k) = -\frac{E_a}{R} \frac{1}{T} + A \quad (9)$$

Where E_a is the activation energy (kJ/mol); R is the gas constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$); T is the absolute temperature (K); A is the preexponential factor.

2.2.7 Determination of Fatty Acid Composition by GC-FID

The remaining reaction mixture after 24 hrs was quenched with acetic acid solution. The oil phase was washed and centrifuged three times with distilled water. Then, the mixture was dried at $105 \text{ }^\circ\text{C}$ for 30 minutes, in order to evaporate the co-solvent completely. $50 \text{ } \mu\text{L}$ fatty acid methyl ester (FAME) was collected and mass was measured, and then mixed with 1 mL solution of 5.5 mg/mL methyl heptadecanoate in heptane. The sample was then analyzed by gas chromatography with flame ionization detector (GC-FID), Shimadzu brand, model: GC-2010 plus. Helium was used as the carrier gas with BPX-BD20 ($32 \text{ m} \times 0.32 \text{ mm}$) column. Initial column temperature was set at $150 \text{ }^\circ\text{C}$, which was gradually increased to $240 \text{ }^\circ\text{C}$, at $15 \text{ }^\circ\text{C/min}$, whereas the injector and FID were $250 \text{ }^\circ\text{C}$. The injection volume was $1 \text{ } \mu\text{L}$ with a split ratio of 10:1. Methyl heptadecanoate was used as the internal standard for quantitative analysis of individual FAMES content, C_X which computed by Equation 10 (Uta *et al.*).

$$C_X = -\frac{A_X}{A_{ISTD}} \times \frac{C_{ISTD} \times V_{ISTD}}{m} \times 100\% \quad (10)$$

Where A_X is the signal area of methyl ester from fatty acid X ; A_{ISTD} is the signal area of the internal standard heptadecanoic acid methyl ester C17:0; C_{ISTD} is the concentration of heptadecanoic acid methyl ester in internal standard solution; V_{ISTD} is the volume of internal standard solution added (ml); m is the mass of lipid sample (mg).

Table-3: Fatty acid composition (wt%), average carbon number, double bond, molecular weight, and empirical formula for different vegetable oils (coconut, palm and sunflower oils)

Fatty acid	Fatty acid composition (wt%)								
	Coconut oil (0.60 M)			Palm oil (0.60 M)			Sunflower oil (0.57 M)		
	27.0 °C	35.5 °C	50.0 °C	23.0 °C	35.0 °C	50.0 °C	20.0 °C	35.0 °C	50.0 °C
C6:0	7.8 ± 0.1	7.6 ± 0.1	7.4 ± 0.1	0	0	0	0	0	0
C8:0	6.0 ± 0.1	5.8 ± 0.1	5.7 ± 0.1	0	0	0	0	0	0
C12:0	48.8 ± 0.4	47.3 ± 0.3	46.5 ± 0.2	0	0	0	0	0	0
C14:0	17.7 ± 0.2	17.2 ± 0.2	17.2 ± 0.2	0.6 ± 0.1	0.7 ± 0.1	0.8 ± 0.0	0	0	0
C16:0	7.1 ± 0.1	6.9 ± 0.1	7.0 ± 0.1	31.9 ± 0.5	34.5 ± 0.4	34.1 ± 0.2	5.6 ± 0.1	6.1 ± 0.2	5.5 ± 0.1
C18:0	2.4 ± 0.1	2.4 ± 0.1	2.5 ± 0.1	3.1 ± 0.1	3.4 ± 0.1	3.3 ± 0.1	3.3 ± 0.1	3.5 ± 0.1	3.0 ± 0.1
C18:1	3.9 ± 0.1	3.8 ± 0.1	3.9 ± 0.1	57.2 ± 0.9	57.4 ± 0.7	55.9 ± 0.9	24.0 ± 0.6	25.6 ± 0.8	22.2 ± 0.5
C18:2	0	0	0	0.6 ± 0.1	0.7 ± 0.1	0.5 ± 0.0	62.2 ± 0.9	66.6 ± 1.4	58.4 ± 0.9
Average carbon number	12.3			17.3			17.9		
Average double bond	0			0.6			1.6		
Empirical formula	C12.3:0.0			C17.3:0.6			C17.9:1.6		
Average molecular weight (g/mol)	653			856			877		

3. RESULTS AND DISCUSSION

3.1 Fatty acid composition for coconut, palm and sunflower oils

The sample of 24hr-reaction for different vegetable oils at different temperatures were analyzed by GC-FID, and the result is shown in (Table-3). In the presented experimental data, coconut oil (CO) had the shortest carbon chains and saturated fatty acids which consisted of 47.6 wt% of C12:0, 17.3 wt% of C14:0, and 7.6 wt% of C6:0. Then, palm oil (PO) had shorter carbon chain than sunflower oil which consisted of 57.1 wt% of C18:1, 33.4 wt% of C16:0, and 3.3 wt% of C18:0. Whereas, sunflower oil (SO) had the longest and the most unsaturated carbon chain which consisted of

61.4 wt% of C18:2, 23.7 wt% of C18:1, and 5.7 wt% of C16:0. The average carbon number for coconut oil (12.3 carbons) was longer than palm oil (17.3 carbons) and sunflower oil (17.9 carbons). The average double bond in fatty acid increased as the order of coconut (saturated), palm (0.6 double bonds) and sunflower (1.6 double bonds) oils. The empirical formula for coconut, palm and sunflower oil were C12.3:0.0, C17.3:0.6, and C17.9:1.6, respectively. The average molecular weight for coconut, palm and sunflower were 653, 856, 877 g/mol, respectively.

3.2 Coconut, palm and sunflower oils conversion

Fig. 1 shows the progress of intrinsic transesterification in the first 180 min for different vegetable oils (coconut, palm and sunflower oils) and at different temperatures (room temperature, 35.0, and 50.0 °C). Generally, in the initial stage of the reaction, oil conversion increased rigorously, then approached constant asymptotically.

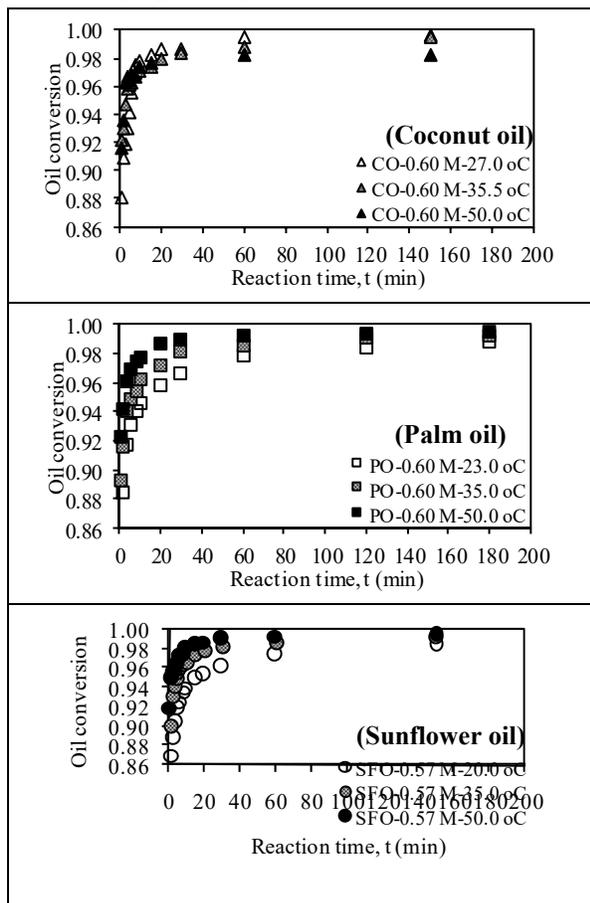


Fig. 1. Oil conversion for different vegetable oils (coconut, palm and sunflower oils) at different reaction temperatures (room temperature, 35.0 °C, and 50.0 °C).

Fig. 1 shows that higher temperature conditions had higher oil conversion. The effect of temperature on oil conversion in the first 60 min is more prominent in

palm and sunflower oils than coconut oil. At 50 °C, the reaction took only 10 min to reach 0.98 of the oil conversion. At 10 min, the oil conversion were 0.983, 0.978, and 0.980 for coconut, palm and sunflower oils, respectively. However, with lower temperature, the reaction took 60 min to reach 0.98 of oil conversion, except sunflower oil at 20 °C

This observation could be due to the smaller hydrocarbon groups in oil molecule resulted in an easier approaching of methanol to the center of oil molecule in order to convert to methyl ester.

3.3 Reaction kinetics

Fig. 2 shows the plot of $1/(C_t - C_e)$ vs. reaction time (t) for the intrinsic transesterification which followed by the second-order reaction model of intrinsic transesterification for different vegetable oils (coconut, palm and sunflower oils) at different temperatures (room temperature, 35.0 °C, and 50.0 °C).

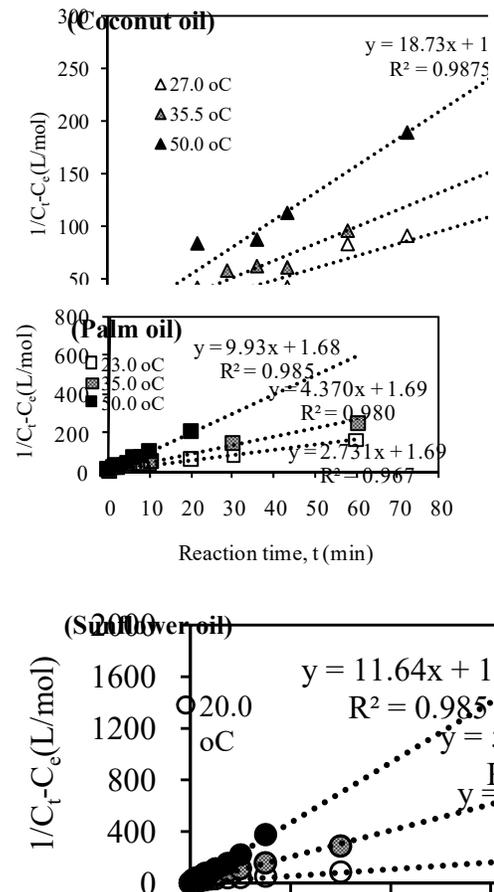


Fig. 2. The plots of $1/(C_t - C_e)$ vs. reaction time (t) of intrinsic transesterification for different vegetable oils (coconut, palm and sunflower oils) at different temperatures (room temperature, 35.0 °C, and 50.0 °C).

The plots of $1/(C_t - C_e)$ vs. reaction time (t) which followed by the second-order reaction model in Figure

2 were straight line with R² value larger than 0.9. Therefore, the best kinetic model for the data in the present study is second-order model, followed by first-order and third-order kinetics. The slope is the reaction constant k with the unit of L mol⁻¹ min⁻¹.

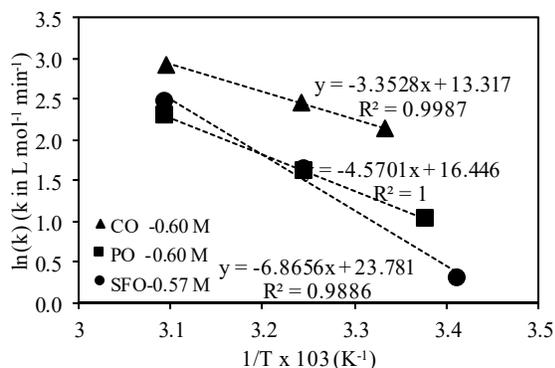


Fig. 3. Arrhenius plot of reaction rate vs. temperature for intrinsic transesterification of different vegetable oils (coconut, palm, and sunflower oils)

The Arrhenius plot is shown in Figure 3, and the activation energy is displayed in Table 4. The activation energy of coconut, palm and sunflower oil in intrinsic transesterification were 27.9, 38.0, and 57.1 kJ/mol, respectively. The reaction constant k and the corresponding correlation coefficient are shown in Table 4. The data shows higher k at higher reaction temperature for all of vegetable oils. At the same reaction temperature, the k of coconut oil was higher than palm and sunflower oil. However, the k of palm oil and sunflower oil was similar at same operating condition.

Vegetable oil	Temperature (°C)	Reaction rate constant, k (L mol ⁻¹ min ⁻¹)	R ²	Activation energy, E (kJ/mol)
Coconut oil	27.0	8.42	0.9576	27.9
	35.5	11.77	0.9351	
	50.0	18.73	0.9875	
Palm oil	23.0	2.73	0.9679	38.0
	35.0	5.02	0.9803	
	50.0	9.93	0.9859	
Sunflower oil	20.0	1.33	0.9164	57.1
	35.0	5.08	0.9554	
	50.0	11.65	0.9858	

Table-4 Reaction rate constant k (L mol⁻¹ min⁻¹) for different vegetable oils (coconut, palm and sunflower oils) at different reaction temperatures (room temperature, 35.0 °C, and 50.0 °C) and the activation energy for different vegetable oils.

Reaction rate constant k (L mol⁻¹ min⁻¹) at different reaction temperatures (room temperature, 35 °C, and 50 °C) and the activation energy for different vegetable oils (coconut, palm and sunflower oils) was showed in

Figure 4. Wherein, the reaction rate constant decreased and the activation energy increased as the order of coconut, palm and sunflower oil. This may be distributed to a steric hindrance effect, by which the larger hydrocarbon groups of palm and sunflower oils prohibited methanol to approach the reaction site, the three ester bonds.

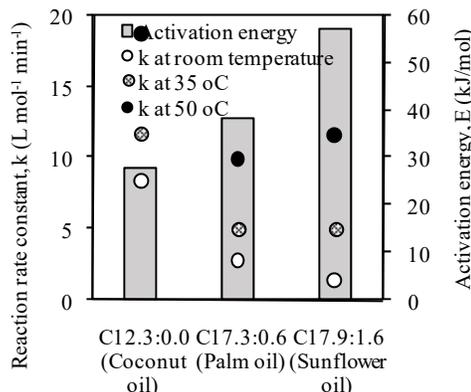


Fig. 4. Reaction rate constant k (L mol⁻¹ min⁻¹) at different reaction temperatures (room temperature, 35 °C, and 50 °C) and the activation energy for different vegetable oils (coconut, palm and sunflower oils).

4.

CONCLUSION

In the present study, the transesterification of coconut, palm and sunflower oils with methanol were conducted in a single phase by adding MEK in order to eliminate the physical mass controlled region. At 50 °C, the oil conversion of coconut, palm and sunflower oils reached 0.98 within first 10 minutes. The reaction rate constant decreased and the activation energy increased as the order of coconut, palm and sunflower oils. The activation energy of intrinsic transesterification for coconut, palm and sunflower oils were 27.9, 38.0 and 57.1 kJ/mol.

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