CHEMICAL ENGINEERING TRANSACTIONS

VOL. 37, 2014

A publication of
AIDIC
The Italian Association
of Chemical Engineering
www.aidic.it/cet

Guest Editors: Eliseo Ranzi, Katharina Kohse- Höinghaus
Copyright © 2014, AIDIC Servizi S.r.l.,
ISBN 978-88-95608-28-0; **ISSN** 2283-9216

DOI: 10.3303/CET1437096

Blending Study of Palm Oil Methyl Esters with Rubber Seed Oil Methyl Esters to Improve Biodiesel Blending Properties

Awais Bokhari[a], Suzana Yusup*[a], Ruzaimah Nik M. Kamil[b], Junaid Ahmad [a]

[a]Biomass Processing Laboratory, Green Technology, Department of Chemical Engineering, Universiti Teknologi PETRONAS,31750, Tronoh, Perak Malaysia.
[b]Department of Fundamental and Applied Science, Universiti Teknologi PETRONAS, 31750, Tronoh, Perak, Malaysia.
drsuzana_yusuf@petronas.com.my

Palm oil methyl esters (POME's) significantly contributed towards biodiesel production commercially. Rubber seed oil methyl esters (RSOME's) with non-edible properties and significant amount of unsaturated fatty acid content contributed to enhancement of low temperature properties along with remedy on food scarcity dilemma. Post blending of POME's and RSOME's at different volumetric ratios improved the low temperature properties of fuel. POME's resulted in excellent oxidation stability with induction period (IP) of 25.52 h compared to RSOME's which only exhibited IP of 3 h. Contrarily, RSOME's showed positive behavior towards low temperature properties. GC analysis determined the significant improvement in low temperature properties as the saturated methyl esters composition is reduced in post blended mixture. The optimized blend value where both low temperature properties and oxidation stability were determined at acceptable limits was found at blend ratio of POME's to RSOME's at 20:80. All the blends satisfied the international biodiesel criteria of EN and ASTM. Transesterification kinetics of POME and RSOME were investigated and followed pseudo-first order kinetics. Activation energy for POME was found to be 33.2 kJ/mole and for RSOME was found to be 43.4 kJ/mole. Frequency factor for POME and RSOME was found to be 2.4 x 10^3 min^{-1} and 1.3 x 10^3 min^{-1} respectively.

1. Introduction

Being a clean bio-fuel, Fatty Acid Methyl Esters (FAME) or biodiesel is an alternative to petro diesel which is converted from vegetable oils in the presence of methanol and homogenous catalyst followed by base transesterification process (Martins et al., 2013). International biodiesel market aims to achieve approximately 30% annual growth rate till year 2016 with production of 140BL of biodiesel yearly (Ng.et al.,2012). Malaysia has a huge capacity of crude palm oil (CPO) for the production of biodiesel. Being edible oil, CPO has some socio limitations is it utilized as a biodiesel feedstock at commercial level. CPO high prices will negatively affect the economic growth of country which directly has influenced on people by disturbing the human food chain. Rubber seed oil (RSO) has proved to be affirmative alternative to CPO because of its non-edible characteristics (Ahmad et al., 2013). Although, Malaysia has large number of rubber seeds plantations across the country but rubber seeds are still un-utilized. These seeds potentially contribute in avoiding food utilizing as a fuel thus promotes an economic stabilize society (MRB, 2012). Pre-blend of CPO and RSO was successfully investigated by researchers to conform with international biodiesel standards (Yusup and Khan, 2010).

The main problems associated with produced methyl esters were its appropriate low temperature properties and stability towards oxidation. These problems directly linked with fatty acid composition chemical structure of the feedstock which was converted to methyl esters. Palm oil methyl esters (POME) has major constituents of saturated methyl esters (SME) which exhibits poor low temperature properties and it nucleates in the low temperature climate zones which restricted smooth fuel flow for ignition (Atabani et al., 2013). Reversely, rubber seed oil methyl esters (RSOME) have lesser amount of SME and have huge content of poly-unsaturated methyl esters which contains double bonds. Unsaturated methyl esters are more sensitive to autoxidation because it depends upon the number of double bonds and its sites.

Please cite this article as: Bokhari A., Yusup S., Faridi J.A., Kamil R.N.M., 2014, Blending study of palm oil methyl esters with rubber seed oil methyl esters to improve biodiesel blending properties, Chemical Engineering Transactions, 37, 571-576 DOI: 10.3303/CET1437096

Poor oxidation stability of biodiesel deteriorates its fuel properties such as viscosity, acid value and peroxide value which leads towards engine malfunctioning (Kim et al., 2012). Blending of different methyl esters shows significant improvement in these properties of biodiesel. Park et al., (2008) investigated methyl esters blends of different feedstocks and improved its fuel properties.

Current study focused on the post blending of POME with RSOME at variable ratios to improve its low temperature properties and oxidation stability by obtaining most suitable optimized ratio. Similarly, all the post blends products were tested according to international biodiesel standards of EN 14214 and ASTM D671 (Ahmad et al., 2013). Kinetic parameters were calculated for base transesterification reaction of POME and RSOME.

2. Experimental

2.1 Materials

The CPO was procured from Felcura Chemicals Sdn. Bhd. Perak, Malaysia. RSO was purchased from Vietnam via Kinetic Chemicals, Malaysia. All the chemicals were of analytical grade and supplied by Merck Chemical Company, Germany. The FAME standards were delivered by Sigma Chemical Company, MO, USA.

2.2 Feedstock Properties and Acid Pre-treatment

The feedstock was characterized for properties such as kinematic viscosity, acid value and moisture content. Prior to base transesterification acid value of feedstock was reduce to an acceptable limits by acid esterification process using sulphuric acid as catalyst. Alcohol to oil molar ratio of 10:1 was used at reaction temperature of 65^oC and reaction time of 3 h. Catalyst amount for CPO was used as 1.5 wt % and for RSO 10 wt%.

2.3 Base Transesterification

Transesterification reaction in the presence of potassium hydroxide (KOH) as catalyst was carried out in 3 neck round bottom flask equipped with thermometer and reflux condenser to avoid methanol losses. The reaction was carried out at alcohol to oil molar ratio of 6:1, catalyst amount of 1.5wt%, reaction temperature of 65 ^oC and reaction time of 3 h. After completion, the product was poured into a separating funnel to separate it from glycerol. After separation, the upper layer was collected as methyl esters and washed several times with warm deionised water to remove impurities. The FAME conversion was identified with the help of gas chromatographer (GC, SHIMADZU,Japan) equipped with flame ionization detector (FID) with column specification at 30mX0.25 mm i.d, film thickness 0.20 µm. Nitrogen was used as the carrier gas with maximum column temperature of 240 ^oC. FAME percentage was calculated and was compared with retention time of reference standards.

2.4 Blending of Samples and Fuel Properties

POME and RSOME was post blended (POME and RSOME separately produced and then blended) at different volumetric ratios of 20-80 vol% in a beaker with constant stirring to ensure uniform blending. The cloud point (ASTM D2500), pour point (ASTM D97) and cold filter plugging point (ASTM D6371) were analyzed by using cloud –pour point (CPP) 5G’s with digital sensors. Biodiesel Rancimat (873, Rancimat Metrohm AG, Switzerland) was used to determine the oxidation stability of the blends by referring to standard method of EN 14112. 3 g of sample was heated at constant temperature of 110 ^oC under constant air flow of 10 L/h. Other fuel properties were analyzed in accordance with EN 14214 and ASTM D671 international biodiesel standards. Total and free glycerine determined using GC-FID (GC, 2010, Shimadzu) followed ASTM D6584 method.

3. Results and Discussion

3.1 Feedstock Characteristics

The CPO exhibits the following properties; acid value of 12.42 mg KOH/g, water content of 0.033 % and kinematic viscosity of 33.5 mm^2/s at 40 ^oC. Similarly acid value for RSO was found to be 45.5 mg KOH/g, water content of 0.026 % and kinematic viscosity of 36.8 mm^2/s at 40 ^oC .

3.2 POME, RSOME and Their Blends Quality

Fatty acid profile of methyl esters was determined by using GC to examine its quality. It was found that POME has significant amount of palmitic (42.88 %) and oleic acid (41.40 %) contents which are highly saturated. The RSOME mainly contains linoleic (40.2 %), linolenic (17.1 %) and oleic acid (25.8 %) content which is considerably unsaturated. Their equivolume blends are distributed in both saturated and unsaturated fatty acid contents and will enhance the fuel properties.

3.3 Blending Effect on Low Temperature Properties and Oxidation Stability of Biodiesel

As seen in Figure 1, POME (Palm oil methyl esters) has CP, PP and CFPP values of 11.25 °C, 10.2 °C and 10.9 °C respectively. Similar values were measured for RSOME (Rubber seed oil methyl esters) and the values are 3.4 °C (CP), -1.3 °C (PP) and 0 °C (CFPP) respectively. Park et al. (2008) results for POME in previous report are comparable with current reported values. For comparison with previous study the low temperature properties of RSOME, are CP of 4 °C and PP of 2 °C which closely conformed with the values observed in recent study (Ahmad et al., 2013). The blends of biodiesels were examined to study the effect of both edible and non-edible methyl esters on low temperature properties. As per results shown in Figure1 , blending of 20 % rubber seed oil (non-edible oil) methyl esters with POME has significantly reduced the cloud point to 6 °C, pour point to 0.5 °C and cold filter plugging point to -1 °C. The increasing fraction of non-edible methyl esters (RSOME) in the blends has gradually improved the overall low temperature properties. From the results, it is proven that RSOME exhibit better low temperature properties as compared to POME. The enhanced low temperature properties of POME versus RSOME attributed because RSO has lower content of saturated fatty acids as compared to POME. Based on previous studies, it has been determined that small level of saturated FAME influenced the low temperature properties of biodiesel which result in higher melting points. In addition, higher content of polyunsaturated fatty acids also contributed considerably to the increasing number of double bond content. It should be noted that melting point decreases significantly in the presence of double bond such as melting point of methyl esters of stearic is C18:0 is 37.7 °C, oleic is C18:1 is -20.2 °C, linoleic is C18:2 is -43.1 °C and linolenic is C18:3; is -57 °C quoted by (Atabani et al., 2013). RSOME contains higher amount of polysaturated fatty acid as compared to POME.

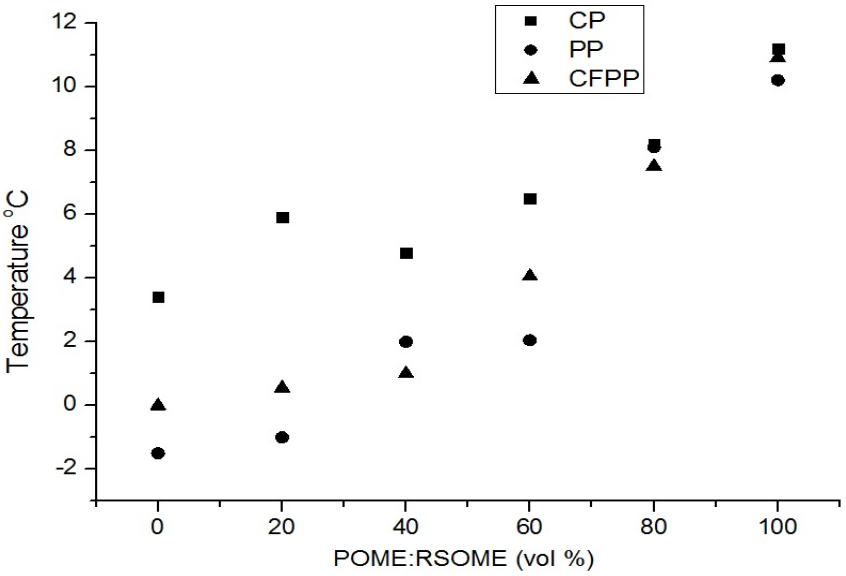


Figure 1: Low temperature properties of pure and post blended methyl esters

It was observed from Figure 2, that as the proportion of POME increases in blended ratio, oxidative stability also increases. For neat biodiesel, POME and RSOME recorded an IP of 4.55 h and 7.63 h respectively. Unsaturated and polysaturated fatty esters are significantly more reactive to oxidation than saturated esters. The reason is that saturated fatty acid chains contain the most reactive sites which are particularly vulnerable to free radical attack (Atabani et al., 2013). The rate of auto-oxidation of FAME is influenced by presence of double bonds that are separated by allylic methylene positions (AMP) with bis-allylic methylene positions (BAMP) being even more prone to oxidation. The reason polyunsaturated fatty acids are particularly vulnerable to auto-oxidation is due to the presence of BAMP. To meet the more stringent specification of ASTM D6751 and to achieve goal of least utilizing of edible methyl esters, blend of 80 % of RSOME and 20 % of POME conforms to the standards requirement. Table 1 shows the characterization of post blends products according to EN 14214 and ASTM D6751 international standards (Ahmad et al., 2013).

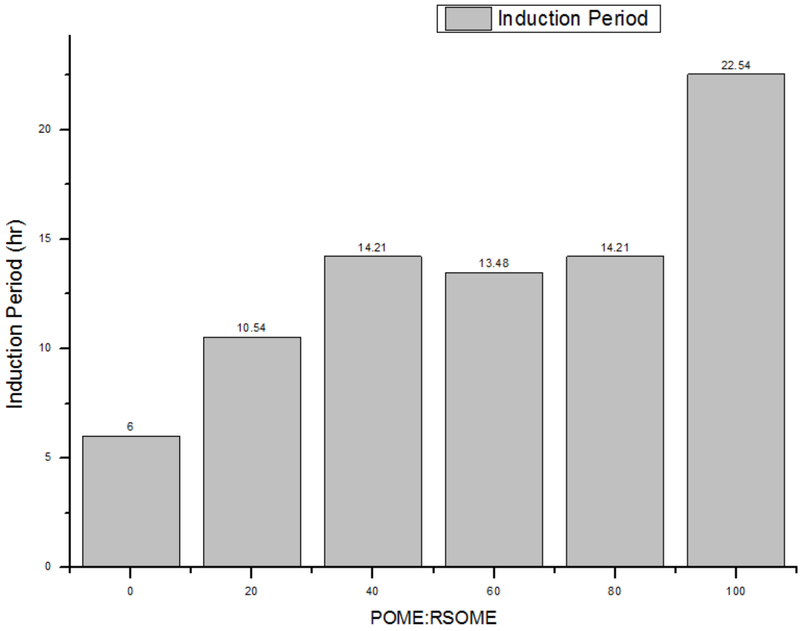


Figure 2: Oxidation stability of pure and post blended methyl esters

Table:1 Post blended biodiesel fuel properties

Fuel properties	Units	EN 14214 Criteria	ASTM D671 Criteria	POME: RSOME (vol %)			
				80:20	60:40	40:60	20:80
Esters	% mass	96.5	-	97	96.8	96.6	96.2
Acid Value	mg KOH/g	0.5 max	0.5 max	0.39	0.40	0.38	0.39
Moisture Content	% volume	0.05 max	0.05 max	0.01	0.01	0.02	0.01
Oxidation Stability	Hr	6	-	14.21	13.48	10.54	8.9
Sulphur Content	% mass	0.01 max	0.05 max	0.01	0.02	0.01	0.01
Flash Point	^{o}C	120 min	130 min	153	155	155	153
Heating Value	kJ/g	35 min	-	40.1	39.6	39.9	39.8
Free Glycerine	% mass	0.02 max	0.02 max	0.006	0.008	0.006	0.0053
Total Glycerine	% mass	0.24	0.25	0.05	0.07	0.078	0.080

3.4 Kinetics of Transesterification Process

Kinetics of transesterification reaction of CPO and RSO in the presence of potassium hydroxide (KOH) as homogenous catalyst and methanol was carried out in a single step. Equation 1 expressed the general transesterification reaction.

$$[TG]\ (\text{triglycerides}) + 3\ ROH \longrightarrow \text{FAME} + \text{Glycerol} \quad (1)$$

Catalyst amount with respect to oil is adequate for the reaction to proceed towards forward path to produce methyl esters. The, rate law for forward transesterification reaction of methyl esters production is expressed as,

$$\text{Rate} = -r_{\text{FAME}} = -d[TG]/dt = k^{*}\,[TG]\,[ROH]^3 \quad (2)$$

[TG] = Concentration of triglycerides, [ROH] = Alcohol concentration, k* = rate constant
Current work used methanol as the alcohol. Equation 2 can be rewritten as,

$$\text{Rate} = -r_{\text{FAME}} = -d[TG]/dt = k^{*}\,[TG]\,[CH_3OH]^3 \quad (3)$$

According to Eq. 3, the overall reaction follows the fourth order reaction rate and methanol was used in excess during the reaction. The methanol concentration is assumed to remain constant during the reaction. Thus the reaction follows the pseudo-first order kinetics and the Equation 3 was re-written as;

$$\text{Rate} = -r_{\text{FAME}} = -d[TG]/dt = k\,[TG] \quad (4)$$

$$\text{Rate} = -r_{FAME} = -d[TG]/[TG] = k\,dt \tag{5}$$

Where k is modified reaction rate constant, $k = k^{*}[CH_3OH]^3$,After integration Equation 5 becomes,

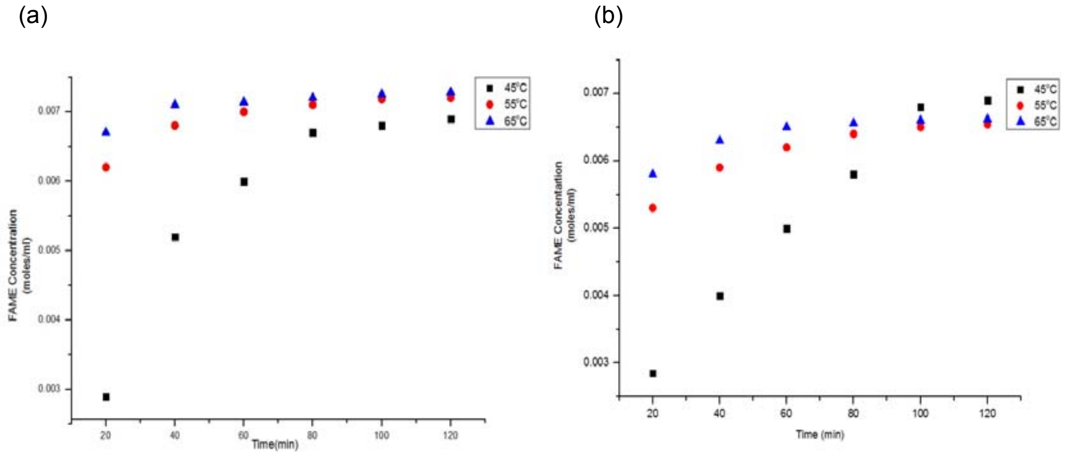
$$\ln[TG_0] - \ln[TG_t] = kt \tag{6}$$

According to mass balance,

$$X_{ME} = 1 - [TG]/[TG_0] \tag{7}$$

$$[TG] = [TG_0](1 - X_{ME}) \tag{8}$$

Where, X_{ME} = Methyl ester conversion .The FAME conversions calculated using GC- FID at different temperatures and time interval are shown in Figure 3 (a) and (b)



(a) (b)

Figure 3: Time Vs. FAME concentration plot for (a) CPO (b) RSO

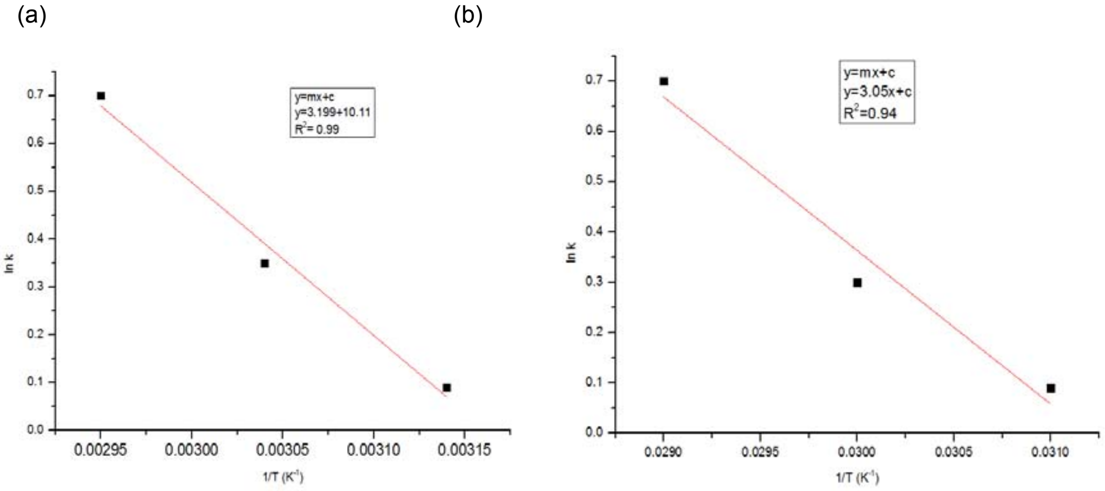
Rate expression can be written in terms of conversion

$$dX_{ME}/(1 - X_{ME}) = k\,dt \tag{9}$$

Integration of the Equation 9 resulted in

$$-\ln(1 - X_{ME}) = kt \tag{10}$$

Figure 4 shows the logarithm plot of reaction rate constant with respect to reciprocal of temperature. The activation energy and frequency factor were calculated using these plots and results as shown in Table2.



(a) (b)

Figure 4: ln(k) Vs. reciprocal plot of temperature for (a) CPO (b) RSO

Table :2 Kinetic parameters for base transesterification process and comparison with literature

Kinetic Parameters	Current Study		Jain et al.(2010)	Rabu et al.(2013)
	CPO	RSO	Jatropha Cucras	Waste Cooking Oil
Activation energy (kJ/mole)	33.2	43.4	8.78	25.4
Frequency Factor (min^{-1})	2.4 x 10^{3}	1.3 x 10^{3}	-	-

4. Conclusions

The contents of fatty acids in both biodiesel, in terms of saturated and unsaturated extensively contributed to the difference in two essential and critical properties of FAME. A signature design of 80 % RSOME (non-edible oil) and 20 % POME (edible oil) conformed to international standards set by ASTM D6751and EN 14214 (Ahmad et al., 2013) and found to be the optimum blend ratio with enhanced oxidation stability and low temperature property. It was found for base transesterification process kinetic studies that it follows the pseudo first reaction order. Activation energy was found to be 33.2 kJ/mol and 43.4 kJ/mol for CPO and RSO transesterification process respectively. While, frequency factor was found to be 2.4 x 10^{3} and 1.3 x 10^{3} for CPO and RSO respectively.

Acknowledgement

Author(s) would like to thank Green Technology, Universiti Teknologi PETRONAS for lab facilities and PRGS (158-200-158) research grant for provided funds.

References

Atabani A.E., Mahlia T.M.I., Masjuki H.H., Badruddin I.A., Yussof H.W., Chong W.T., Lee K.T., 2013, A comparative evaluation of physical and chemical properties of biodiesel synthesized from edible and non-edible oils and study effect of biodiesel blending, Energy, 58, 296-304, DOI:10.1016/j.energy.2013.05.040

Ahmad J., Yusup S., Bokhari A., Ruzaimah N.M.K., 2013, Study of fuel properties of rubber seed oil based biodiesel, Energy Conversion and Management, 78, 266-275, DOI:10.1016/j.enconman.2013.10.056

Jain S., Sharma M.P., 2010, Kinetics of acid base catalyzed transesterification of jatropha curcas oil, Bioresource Technology, 101, 7701-7706, DOI:10.1016/jbiortech.2010.05.034.

Kim J.K., Yim E.S., Jeon C.H., Jung C.S., Han B.H., 2012, Cold performance of various biodiesel fuel blends at low temperature, International Journal of Automotive Technology, 13, 293-300, DOI:10.1007/s12239-012-0027-2.

Martins M.I., Pires R.F., Alves M.J., Hori C.E., Reis M.H.M., Cardoso V.L., 2013, Transesterification of soybean oil for biodiesel production using hydrotalcite as basic catalyst, Chemical Engineering Transactions, 32, 817-822, DOI:10.3303/CET1332137.

Malaysia Rubber Board (MRB) 2012, Natural Rubber Statistics 2011 <www.lgm.gov.my/nrstat/nrstats.pdf>, Accessed 17.08.2012

Ng W.P.Q., Lam H.L., Yusup S., 2012, Supply network design and the utilisation of rubber seed oil as biofuel and biochemicals, Chemical Engineering Transactions, 29, 835-840, DOI:10.3303/CET1229140.

Park J. Y., Kim D.K., Lee J.P., Park S.C., Kim Y.J., Lee J.S., 2008, Blending effects of biodiesels on oxidation stability and low temperature flow properties, Bioresource Technology, 99, 1196-1203, DOI:10.1016/j.biortech.2007.02.017.

Rabu R.A., Janajreh I., Honnery D., 2013, Transesterification of waste cooking oil: Process optimization and conversion rate evaluation, Energy Conversion and Management, 65, 764-769, DOI:10.1016/jenconman.2012.02.031.

Yusup S. and Khan M A., 2010, Base catalyzed transesterification of acid treated vegetable oil blend for biodiesel production, Biomass and Bioenergy, 34, 1500-1504, DOI:10.1016/jbiombioe.2010.04.027.