Kinetics study of Jatropha oil esterification with ethanol in the presence of tin (II) chloride catalyst for biodiesel production

by Ratna Dewi Kusumaningtyas

Kinetics study of Jatropha oil esterification with ethanol in the presence of tin (II) chloride catalyst for biodiesel production

Cite as: AIP Conference Proceedings **1788**, 030086 (2017); https://doi.org/10.1063/1.4968339

Ratna Dewi Kusumaningtyas, Naomi Ratrianti, Indah Purnamasari, and Arief Budiman

AIP Conference Proceedings **1788**, 030086 (2017); https://doi.org/10.1063/1.4968339

Kinetics Study of Jatropha Oil Esterification with Ethanol in the Presence of Tin (II) Chloride Catalyst for Biodiesel Production

Ratna Dewi Kusumaningtyas[1,a)], Naomi Ratrianti[2], Indah Purnamasari[1], and Arief Budiman[2,b)]

[1]*Chemical Engineering Department, Faculty of Engineering, Universitas Negeri Semarang*
Gunungpati, Semarang 50229, Indonesia
[2]*Chemical Engineering Department, Faculty of Engineering, Universitas Gadjah Mada,*
Yogyakarta 55281, Indonesia

[a)]Corresponding author: ratnadewi.kusumaningtyas@mail.unnes.ac.id
[b)]abudiman@chemeng.ugm.ac.id

Abstract. Jatropha oil is one of the promising feedstocks for biodiesel production. Jatropha oil is non-edible oil hence utilization of this oil would not compete with the needs of food. However, crude jatropha oil usually has high free fatty acid (FFA) content. Due to this fact, direct alkaline-catalyzed transesterification of crude jatropha oil for biodiesel production cannot be performed. FFA in crude jatropha oil will react with a base catalyst, resulting in soap as by product and hindering methyl ester (biodiesel) production. Therefore, prior to a transesterification reaction, it is crucial to run a pretreatment step of jatropha oil which can lower the FFA content in the oil. In this work, the pretreatment process was conducted through the esterification reaction of FFA contained in crude jatropha oil with ethanol over tin (II) chloride catalyst to reduce the acid value of the feedstock. The feedstock was Indonesia crude jatropha oil containing 12.03% of FFA. The esterification reaction was carried out in a batch reactor with a molar ratio of FFA to ethanol was 1:60 and total reaction time was 180 minutes. Tin (II) chloride catalyst was varied at 2.5, 5, 7.5, and 10% wt, whereas the effect of the reaction temperature was studied at 35, 34, 55, and 65 °C. The best reaction conversion was 71.55%, achieved at the following condition: a reaction temperature of 65 °C, catalyst concentration of 10% wt, the reaction time of 180 min, and the molar ratio of FFA to ethanol was 1:60. Kinetics study was also conducted in this work. It was found that esterification reaction of jatropha oil FFA with ethanol catalyzed by tin(II) chloride fitted the first-order pseudo-homogeneous kinetics model. It was also revealed that the frequency factor (A) and the activation energy (Ea) were 4.3864×10^6 min^{-1} and 56.2513 kJ/mole, respectively.

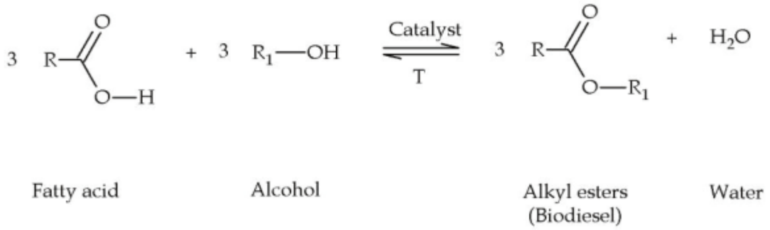
INTRODUCTION

The rapid growth in industrialization and transportation has increased the energy demand all over the world [1]. In accordance with this global trend, fossil fuel is the most used energy source to date. However, recently, there are two important issues related to the fossil fuel utilization. First, fossil fuel depletion has been known as a future challenge of the energy security. Secondly, related to the environmental aspect, fossil fuel burning releases CO_2 emission which is among the primary greenhouse gasses. Greenhouse gasses are the principal contributor to the global warming and climate change [2, 3]. Thus, an efficient strategy is needed to reduce the consumption of fossil fuel as the main CO2 emission source. To overcome this problem, it is essential to develop alternative energy which is renewable and has eco-friendly characteristic. Among the most prospective alternative energy source is biodiesel. Biodiesel is clean energy source which holds many advantages. It has comparable properties to fossil-based diesel fuel, can be produced in large quantity, and it includes to the low carbon energy source. Due to its benefits, biodiesel

International Conference on Engineering, Science and Nanotechnology 2016 (ICESNANO 2016)
AIP Conf. Proc. 1788, 030086-1–030086-7; doi: 10.1063/1.4968339
Published by AIP Publishing. 978-0-7354-1452-5/$30.00

is the top priority of the national biofuel development policy in Indonesia as stated in the Presidential Regulation No/ 2016.

Biodiesel can be produced from vegetable oils, both edible and non-edible oils, as raw material. However, due to the competition of edible oil for food and biofuel production, utilization of non-edible vegetable oil as biodiesel feedstocks is more favorable [4]. In this work, biodiesel production using jatropha oil was carried out. Jatropha oil is non-edible oil which is available in Indonesia. Biodiesel is generally produced via alkaline-catalyzed transesterification reaction of vegetable oil. However, jatropha oil contains a high amount of free fatty acid (FFA) which is not suitable for a direct transesterification. The high content of FFA will react with the base catalyst, resulting in soap byproduct and hindering methyl ester (biodiesel production). Therefore, pretreatment step to reduce the FFA content in the feedstock is necessary. The pretreatment process can be performed through the esterification reaction of FFA using alcohol in the presence of acid catalyst [5]. In this work, esterification reaction of jatropha oil was conducted using ethanol over tin (II) chloride catalyst. Tin (II) chloride is solid Lewis acid catalyst which has many benefits. It is cheap, active, less corrosion, easy to separate with the reaction product of the reaction, but it acts alike a homogeneous catalyst during the reaction [6]. The esterification reaction of jatropha oil with alcohol is depicted in Equation (1). In this research, the effects of main parameter of the reaction were evaluated. Kinetics study was also carried out to obtain the kinetics constants of the reaction.



(1)

EXPERIMENTAL METHOD

The feedstock used in this work was jatropha oil with FFA content of 30.57, which was obtained from PT Pura Energi Kudus, Indonesia and absolute ethanol (Merck). The catalyst was tin (II) chloride ($SnCl_2.2H_2O$) was purchased from Merck. The esterification reaction was conducted in a 250 mL batch reactor equipped with a condenser and magnetic stirrer. Initially, 65.5 g jatropha oil was introduced to the reactor and heated up to 35°C. In the same time, 100 mL ethanol was heated separately until it reached the identical temperature, and subsequently, it was discharged to the reactor to react with the jatropha oil. Tin (II) chloride as much as 3.3 g (5% wt) was then added to the reactor. Samples of the reaction were withdrawn at following reaction time: 0, 15, 30, 45, 60, 90, 120, and 180 minutes. The experiments were conducted at various temperature and catalyst concentration. Estimation of the reaction conversion was conducted based on the FFA content in the reaction mixture by using standard NaoH titration [7]. The data obtained was then utilized for kinetics study and kinetics parameter evaluation. Determination of the FFA content was carried out using the following formula:

$$\%\ \text{acid} = \frac{(Mr)(N\ KOH)(V\ KOH)}{(W)(1000)} \times 100\% \qquad (2)$$

$$\%\ FFA = \%\ \text{acid of the sample} - \%\ \text{acid of tin (II) chloride} \qquad (3)$$

Where, % acid of the sample = acid content of (FFA+ tin (II) chloride) in the sample, %wt
% acid of tin (II) chloride = acid content of tin (II) chloride in the sample, %wt
% FFA = The fatty acid content resulted in the esterification reaction, %wt
Mr = molecular weight of oleic acid, g/mol
N KOH = normality of KOH solution used as titrant, N
V KOH = volume of KOH solution used for sample titration, mL
W = weight of oil sample, g

FFA conversion was determined using the following equation:

$$X_A = \left|\frac{\%\,FFA\ initial - \%\,FFA\ sample}{\%\,FFA\ initial}\right| x\ 100\% \tag{4}$$

Where, X_A is reaction conversion, %.

RESULTS AND DISCUSSION

In this work, esterification reaction of jatropha oil with ethanol was carried out in a batch reactor in the presence of tin (II) chloride catalyst. The molar ratio of FFA to ethanol was 1:60. Variables studied in this work were reaction temperature and catalyst concentration.

Effect of Reaction Temperature

The reaction temperature was varied at 34, 45, 55, and 65 °C. On the other hand, molar ratio of FFA: ethanol and catalyst concentration were maintained at 1:60 and 5%, respectively. Effect of the reaction temperature on the reaction conversion is shown in Fig. 1.

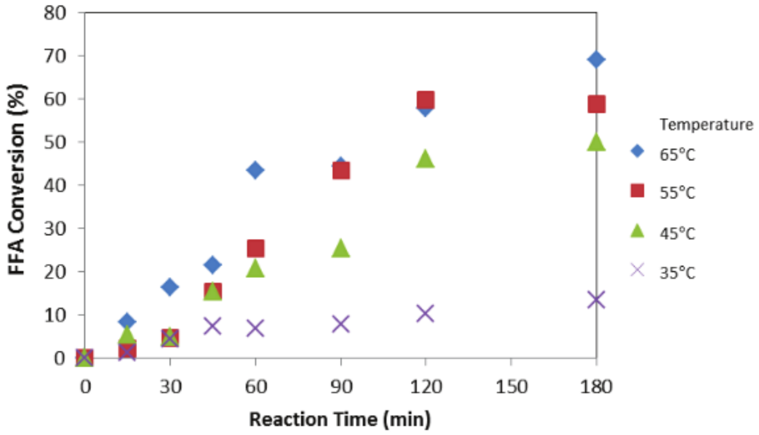


FIGURE 1. Effects of Temperature on the FFA Conversion at Different Reaction Temperatures

Figure 2 revealed that the FFA conversion increased with the increasing of the temperature. It was due to the fact that esterification reaction is an exothermic reaction. Based on the Arrhenius equation, the higher reaction temperature will enhance the value of the reaction rate coefficient, causing the higher reaction rate and conversion. Among the experiments conducted at various temperature and reaction time, the best conversion was 68.96%, which was obtained at the temperature of 65°C with the reaction time of 180 minutes. The optimal reaction temperature obtained was in accordance with the result reported in the literature for FFA esterification using acid catalyst [8]. Therefore, this temperature was employed for the subsequent experiments which studied the influence of catalyst concentration.

Kinetic Study

The data of reaction conversion at different reaction time and temperature were utilized for the reaction kinetics determination. To develop the kinetics model of the reaction, Equation (1) was rewritten to Equation (5).

$$\underset{\text{(FFA)}}{A} + \underset{\text{(Ethanol)}}{E} \rightleftharpoons \underset{\text{(Methyl Ester)}}{D} + \underset{\text{(Water)}}{W} \tag{5}$$

At stoichiometric condition, esterification reaction is usually considered as a second-order reversible reaction, which can be formulated as demonstrated in Equation (6).

$$-r_A = k_1 C_A C_E - k_2 C_w C_D \tag{6}$$

However, in this work, a far excess of alcohol was applied, indicated by the molar ratio of FFA to alcohol of 1:60. Hence, it could be assumed that the reaction equilibrium shifted to the completion of product formation and the reverse reaction could be neglected. Furthermore, since ethanol in the reaction system was great excess with respect to FFA, its concentration could be considered to remain constant throughout the reaction time. Therefore, the ethanol concentration could be included in the rate constant, resulting in a pseudo-first-order reaction rate model [6]. The reaction rate thus can be abridged to one exhibited in Equation (7).

$$-r_A = k\ C_A \tag{7}$$

To obtain the parameters of the reaction rate, mass balance of A (FFA) in batch reactor was developed:

Rate of mass A in – Rate of mass A out – Rate of A consumed in the reaction = Rate of accumulation of A (8)

$$N_{A0} - N_A - (-r_A)\ V = -\ \frac{dC_A.V}{dt} \tag{9}$$

$$0\ -\ 0\ -\ (-r_A)\ V = -\ \frac{dC_A.V}{dt} \tag{10}$$

$$(-r_A) = -\ \frac{dC_A}{dt} \tag{11}$$

Substitution of Equation (7) to Equation (11) resulted in Equation (12):

$$k\ \ C_A = -\ \frac{dC_A}{dt} \tag{12}$$

Based on the stoichiometric equation, C_A can be expressed is the function of reaction conversion:

$$C_A = C_{A0}\ (1 - \frac{X_A}{100}) \tag{13}$$

Substitution of Equation (13) to Equation (12) resulted in the following equation:

$$k.C_{A0}\ (1-\frac{X_A}{100}) = -\ \frac{d\,C_{A0}(1-\frac{X_A}{100})}{dt} \tag{14}$$

$$k.C_{A0}\ (1-\frac{X_A}{100}) = -\ C_{A0}\ \frac{d(1-\frac{X_A}{100})}{dt} \tag{15}$$

$$k.dt\ \ = -\frac{1}{(1-\frac{X_A}{100})}\ d\ (1-\frac{X_A}{100}) \tag{16}$$

$$k\int_0^t dt\ \ = -\int_0^{X_A} \frac{1}{(1-\frac{X_A}{100})}\ d\ (1-\frac{X_A}{100}) \tag{17}$$

$$k\ .\ t\ \ = -\ln\ (1-\frac{X_A}{100}) \tag{18}$$

The value of reaction rate constant can be obtained using linear regression method. The values of Sum of Square Error (SSE) were also measured. The calculation was solved numerically using Matlab program. The values of reaction rate constant (k) obtained are demonstrated in Table 1. It was revealed that the SSE value for each temperature was small, indicating that the calculation was accurate.

TABLE 1. Reaction Rate Coefficient at Various Reaction Temperatures

Temperature (K)	$k.10^3$(1/min)	$SSE.10^2$
308	0.9066	0.19528
318	3.9716	1.2979
328	5.4821	3.6370
338	6.9330	1.3651

Furthermore, the fitting of the reaction kinetics model to the experimental data is exhibited in Fig. 2. It is shown that the calculated values estimated based on the kinetic model were closed to the experimental data. It means that the kinetic model proposed (pseudo-first order model) was appropriate for this esterification reaction system.

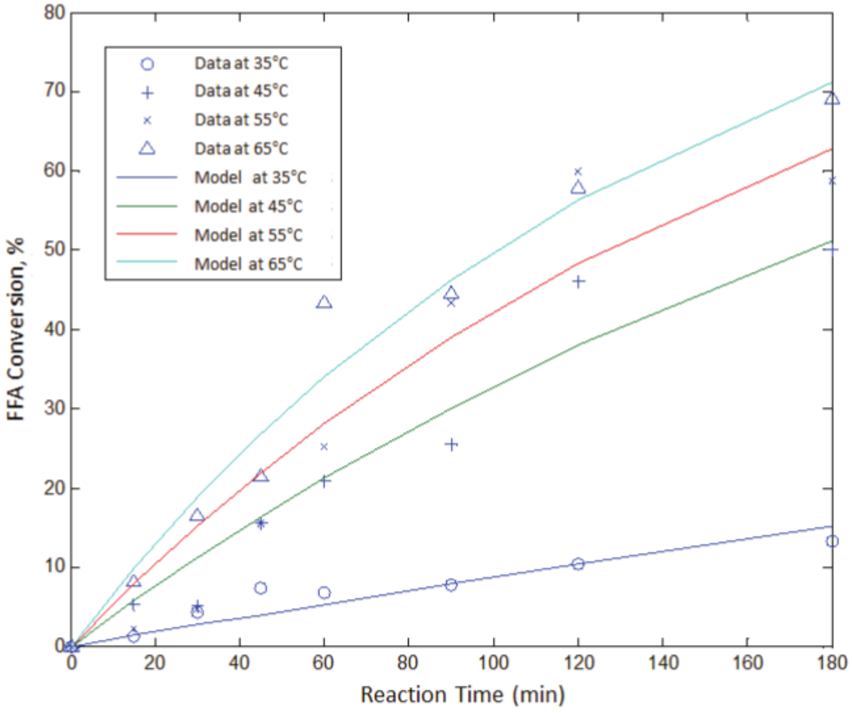


FIGURE 2. Comparison of the Calculated Value Resulted from the Model and the Experimental Data

The reaction rate constant obtained was then utilized to find the activation energy (Ea) and frequency factor (A) values in the Arrhenius equation using linear regression method. Arrhenius stated that correlation between reaction rate and temperature is written as:

$$k = A\exp\left(-\frac{E}{RT}\right) \quad (19)$$

By composing correlation of ln k and (1/T) using linear graph fitting as shown in Fig. 3, it was found that the value of A was 4386414.8912 min^{-1} and the activation energy (E) was 56.2513 kJ/mol. This value of activation energy was comparable to those reported in the literature for acid catalyst esterification, which starting 46.69 kJ/mol [6], 50.74 kJ/mol and 42.76 kJ/mol [9]. The result of this research was considered accurate since the coefficient of determinant (R^2) was 0.8427, which was closed to 1. The relative error in this modeling was 5.088%, and correlation of reaction rate coefficient and the reaction temperature was formulated in the Equation (20).

$$k = 4386414{,}8912\exp\left(-\frac{56{,}2513}{RT}\right) \quad (20)$$

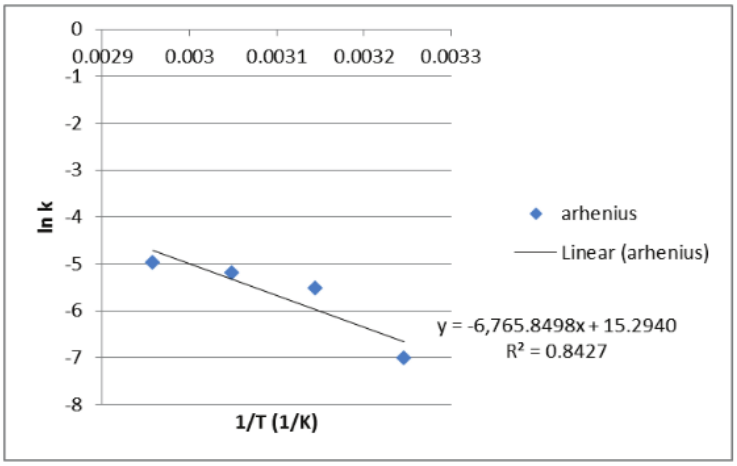


FIGURE 3. Correlation of Reaction Rate Coefficient and Reaction Temperature

Effect of Catalyst Concentration

To evaluate the effect of a catalyst on the reaction conversion, the concentration of the catalyst employed was varied at 2.5, 5, 7.5, and 10% wt. Reactions were conducted at the fixed molar ratio of FFA to ethanol and reaction temperature of 1:60 and 65 °C, respectively. The result is presented in Fig. 4. This Figure has shown that the increasing of the catalyst concentration brought the higher FFA conversion. It is because catalyst can provide an alternative route of the reaction which requires a lower activation energy to result in the product. It consequently brought about the higher reaction rate and higher conversion. Figure 4 demonstrated that the reaction conversion enhanced significantly when the catalyst concentration was increased from 2.5 to 5% wt. However, the addition of the catalyst concentration to the higher amount than 5% resulted in a relatively constant conversion. It is due to the fact that at 5% wt of catalyst, the amount of catalyst has almost reached the maximum amount of catalyst which is required to activate the carbonyl group of the FFA. The best reaction conversion was 71.55% provided by the catalyst concentration of 10% wt. This result is comparable to the reaction performed using a homogeneous sulfuric acid catalyst which yielded reaction conversion of around 77% [8]. On the other hand, in this work, 5% wt of catalyst provided 68.96%. Therefore, the employment of 5% wt of the catalyst is considered more efficient.

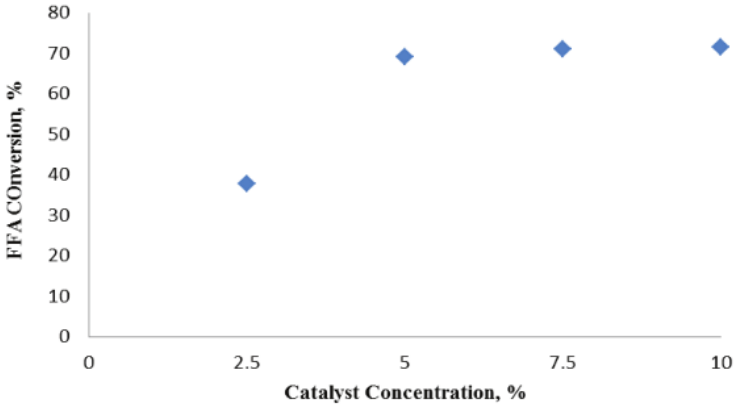


FIGURE 4. FFA Conversion at Different Catalyst Concentration

CONCLUSIONS

Based on the result of the research, it can be concluded that the higher reaction temperature, the higher value of reaction rate coefficient was obtained, resulting in the higher conversion of FFA. On the other hand, the increasing of catalyst concentration employed in the reaction led to the higher reaction conversion achieved. The study on the reaction kinetics showed that the reaction fit the first order pseudo-homogeneous model. Parameter values obtained in this works were: frequent factor (A) was 4.3864 x 10^6 min^{-1}, activation energy (E) was 56.2513 kJ/mol. The highest reaction conversion achieved in the experiments of jatropha oil esterification with ethanol over tin (II) chloride catalyst was 71.55% at the reaction temperature of 65°C using 10% concentration of catalyst at the molar ratio of FFA to ethanol of 1:60.

ACKNOWLEDGMENT

We would like to thank to Directorate Research and Community Service-Indonesian Directorate General of Higher Education, Ministry of Research, Technology, and Higher Education for supporting the research funding through Hibah Bersaing Grant scheme.

REFERENCES

1. Y.M. Sani, W.M.A.W. Daud and A.R.A. Azis, Journal of Environmental Chemical Engineering **1**, 113–121 (2013).
2. M. Hook and X. Tang, Energy Policy **52**, 797–809 (2013).
3. B.H. Tsai, C.J. Chang and C.H Chang, Energy **100,** 416-424 (2016).
4. S. Nitiema-Yefanova, L. Coniglio, R. Schneider, R.H.C. Nebie and Y.L. Bonzi-Coulibaly, Renewable Energy **96**, 881-890 (2016).
5. R.D. Kusumaningtyas, I.N. Aji, H. Hadiyanto and A. Budiman, Bulletin of Chemical Reaction Engineering & Catalysis **11**, 66-74 (2016).
6. A.L. Cardoso, S.C.G. Neves and M.J. da Silva, Energies **1**, 79-92 (2008).
7. D. A.G. Aranda, R.T.P. Santos, N.C.O. Tapanes, A.L.D. Ramos and O.A.C. Antunes, Catal. Lett. **122**, 20-25 (2008).
8. M. Chai, Q. Tu, M. Lu and Y.J. Yang, Fuel Processing Technology **125**, 106-113 (2014).
9. M. Berrios, J. Siles and M.A. Martin, Fuel **86**, 2383-2388 (2007).

Kinetics study of Jatropha oil esterification with ethanol in the presence of tin (II) chloride catalyst for biodiesel production

ORIGINALITY REPORT

12%	6%	13%	5%
SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS

PRIMARY SOURCES

1	Submitted to Universitas Diponegoro Student Paper	1%
2	mafiadoc.com Internet Source	1%
3	Dhoni Hartanto, Asalil Mustain, Febry Dwi Nugroho. "Prediction of vapor-liquid equilibria for the alcohol + glycerol systems using UNIFAC and modified UNIFAC (Dortmund)", AIP Publishing, 2017 Publication	1%
4	Ibtisam M. Kamal, Firas H. Albadran, Fanar M. Bamerni, Danar H. Aziz, Mustafa Alfaize. "Simulation and optimization of Camelina oil fatty acids reaction to produce fatty acid methyl esters in a reactive distillation reactor", IOP Conference Series: Materials Science and Engineering, 2020 Publication	1%
5	BankoviÄ‡-IliÄ‡, Ivana B., Olivera S.	

	StamenkoviÄ‡, and Vlada B. VeljkoviÄ‡. "Biodiesel production from non-edible plant oils", Renewable and Sustainable Energy Reviews, 2012. Publication	1%
6	Madhu Agarwal, Kailash Singh, S. P. Chaurasia. "Kinetic modeling for biodiesel production by heterogeneous catalysis", Journal of Renewable and Sustainable Energy, 2012 Publication	1%
7	www.tandfonline.com Internet Source	1%
8	"Light Metals 2020", Springer Science and Business Media LLC, 2020 Publication	1%
9	"Process Systems Engineering for Biofuels Development", Wiley, 2020 Publication	1%
10	eprints.utp.edu.my Internet Source	1%
11	Avhad, M.R., and J.M. Marchetti. "A review on recent advancement in catalytic materials for biodiesel production", Renewable and Sustainable Energy Reviews, 2015. Publication	1%
12	Anjali Patel, Varsha Brahmkhatri. "Kinetic study	

	of oleic acid esterification over 12-tungstophosphoric acid catalyst anchored to different mesoporous silica supports", Fuel Processing Technology, 2013 Publication	1%
13	Ozbay, N.. "Esterification of free fatty acids in waste cooking oils (WCO): Role of ion-exchange resins", Fuel, 200808 Publication	1%
14	Vasanthakumar Sathyaselvabala, Senthilkumar Ponnusamy, Premkumar Manickam Periyaraman, Dinesh Kirupha Selvaraj et al. "Two step biodiesel production from Calophyllum inophyllum oil: Studies on thermodynamic and kinetic modelling of modified β-zeolite catalysed pre-treatment", The Canadian Journal of Chemical Engineering, 2012 Publication	1%

Exclude quotes	On	Exclude matches	< 1%
Exclude bibliography	On		