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ScienceDirect
Renewable Energy 33 (2008) 1629–1636
RENEWABLE ENERGY
www.elsevier.com/locate/renene

Biodiesel fuels from palm oil via the non-catalytic transesterification in a bubble column reactor at atmospheric pressure: A kinetic study

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Received 2 January 2007; accepted 15 August 2007
Available online 24 October 2007

Abstract

Biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources. Transesterification of vegetable oils with short-chain alcohol has long been a preferred method for producing biodiesel fuel. A new reactor was developed to produce fatty acid methyl esters (FAME) by blowing bubbles of superheated methanol vapor continuously into vegetable oil without using any catalysts. A kinetic study on the non-catalytic transesterification of palm oil was made in a reactor without stirring at atmospheric pressure. The effects of reaction temperatures (523, 543, and 563 K) on the rate constant, conversion, yield of methyl esters (ME) and composition of the reaction product under semi-batch mode operation are investigated. The activation energy and the frequency factor values of the transesterification reaction obtained in this experiment are 31 kJ/mol and 4.2, respectively. The optimum reaction temperature which gives the highest ME content (95.17% w/w) in the reaction product is 523 K, while the rate constant of the total system increased with reaction temperature.

Keywords: Biodiesel; Palm oil; Non-catalytic transesterification; Kinetic study; Superheated methanol

1. Introduction

Recent increases in petroleum price and uncertainties in its availability have increased the interest in renewable fuels [1]. One of the most interesting alternatives of the renewable fuels, among others, is the vegetable oil fuel for diesel engine. Considerable efforts have been made to develop vegetable oil derivates that approximate the properties and performance of the hydrocarbon-based diesel fuels.

The problems with substituting vegetable oil for diesel fuels are mostly associated with their high viscosities, low volatilities and polyunsaturated character. These characteristics of vegetable oil can be changed in at least four ways: pyrolysis, microemulsification, dilution and transesterification [2]. Here, only transesterification reaction can lead to the products commonly known as biodiesel, i.e., alkyl esters of oil and fats [3].

Transesterification is a reaction in which triglycerides (TG), the main component of vegetable oils or animal fats, be reacted with short-chain alcohols, mainly methanol (MeOH) to form fatty acid methyl esters (FAME), now popularly known as biodiesel fuel. There are three stepwise reactions with intermediate formation of diglycerides (DG) and monoglycerides (MG) resulting in the production of 3 mol of methyl esters (ME) and 1 mol glycerol (GL) [4].

Most of the currently known methods for biodiesel production are using alkaline or acid catalyst. However, there are at least two problems associated with this process. The first problem is due to the two phase nature of

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0960-1481/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.renene.2007.08.011

vegetable oil/MeOH mixture that requires vigorous stirring to proceed in the transesterification reaction. The second problem is products purification from residual catalyst which is left in the reaction product due to unreacted MeOH and saponified products [5]. Transesterification reaction without catalyst utilization will solve those problems.

The non-catalytic transesterification has several advantages. The removal of free fatty acids (FFA) from oil by refining or preesterification is not required [5]. In non-catalytic process, two types of reaction for ME formation will exist, namely TG transesterification and methyl esterification of fatty acids. Consequently, a higher yield can be obtained if compared to that produced by the alkaline-catalyzed method [6,7]. In addition, because of a catalyst free process, separation and purification become much simpler and environmentally friendly. The disadvantages of the non-catalytic process are the necessity of larger molar excess of MeOH (the required molar ratio of MeOH to oil was 24–42) and higher operating temperature (513–623 K) than the catalytic one [5,8,9]. Optimum temperature for the catalytic transesterification is 333 K while molar ratio of MeOH to oil is 6 [10].

Various studies have reported kinetics of the non-catalytic transesterification for vegetable oil. Kinetic studies quantify the effect of operating conditions on the efficiency of the process. Diasakou et al. [11] studied the effects of reaction condition (493 K, 5.5 MPa and 508 K, 6.2 MPa) and molar ratios of MeOH to soybean oil (6, 12, 21) on rate constants and ME content in the reaction mixture. Kusdiana and Saka [5] investigated the effects of molar ratio of MeOH to rapeseed oil (3.5, 4.5, 6, 21 and 42) and reaction temperature (473–773 K, pressure 7–105 MPa) on ME formation. Dasari et al. [12] studied non-catalytic alcoholysis kinetics of soybean oil using metal reactor (316 stainless-steel) to obtain surface catalyze effect. Their study focused on reaction rate of MeOH at 393, 423, and 453 K and reactivity of higher alcohols such as ethanol and isopropanol. Most of these studies were conducted under pressurized conditions, i.e., supercritical or subcritical conditions of methanol. However, the safety aspect of the process becomes more critical for real application due to the high-pressure condition. In addition, there is still question about the energetic aspect of the process, and requirement for further study on the economic evaluation of the total system.

Yamazaki et al. [13] studied the non-catalytic alcoholysis of sunflower oil for biodiesel fuel production in a bubble column reactor under atmospheric pressure. Effects of reaction temperature, MeOH feed flow rate, operating pressure, stirring rate and initial oil volume on the outflow rate of FAME were investigated. The study suggested the optimum temperature of 563 K, based on the maximum outflow rate of FAME. However, kinetic studies which quantify the effect of operating conditions on the efficiency of the non-catalytic alcoholysis process under atmospheric pressure have not been conducted.

This paper is aimed to study the kinetics of non-catalytic transesterification reaction of palm oil under atmospheric pressure. Palm oil is used because of its readiness to be the main feedstock for biodiesel program, especially in Indonesia, which has great opportunity to expand its oil plantation [14]. Transesterification experiments were made in a semi-batch mode reactor in which bubbles of superheated MeOH vapor were blown into the oil containing reactor. The effects of reaction temperature on the rate constant, conversion, yield of ME and composition of the reaction product are investigated.

2. Materials and methods

2.1. Materials

Refined palm oil was obtained from Spectrum Chemical Mfg. Corp., Gardena, New Brunswick, with the following characteristic: Iodine Value 50–55, FFA (as oleic) 0.1% w/w, myristic acid, 0.5–5.9% w/w; palmitic acid, 32–47% w/w; stearic acid, 2–8% w/w; oleic acid, 34–44% w/w; linoleic acid, 7–12% w/w. High performance liquid chromatography (HPLC) grade MeOH and molecular sieves 4A 1/16 for transesterification experiment were purchased from Wako Pure Chemical Industries, Ltd., Japan.

Benzene and hexane (all HPLC grade) used in the thin layer chromatography/flame ionization detector (TLC/FID) analysis were purchased from Wako Pure Chemical Industries, Ltd., Japan. Benzene was used as developing solution, and hexane as solvent. Squalane ($C_{30}H_{62}$) as internal standard used in the TLC/FID analysis was purchased from Sigma-Aldrich Japan, Tokyo, Japan. Triolein, diolein, monoolein, oleic acid and methyl oleate used as standards were obtained from Sigma Chemical, St. Louis, MO. Acetonitrile (HPLC grade) as solvent and GL as standard compound used in the HPLC analysis were purchased from Wako Pure Chemical Industries, Ltd., Japan.

2.2. Reactor for non-catalytic transesterification

Schematic flow diagram of reactor used in the experiment is shown in Fig. 1. The bubble column reactor was a 500-mL four-necked flask equipped with a condenser, a pipe for methanol vapor feed and a temperature controller (TC). The reactor was placed in a mantle heater. The glass dehydration column was filled with the molecular sieves. A pump with a variable speed motor (model NPD-461, Nihon Seimitsu Kagaku Co., Ltd., Japan) was used to control charging rate of MeOH. The tin bath was placed on an electric stove. Temperature of tin bath was monitored by a temperature indicator (TI). Temperatures of superheated methanol supplied to the reactor and liquid in the reactor were controlled with the TC.

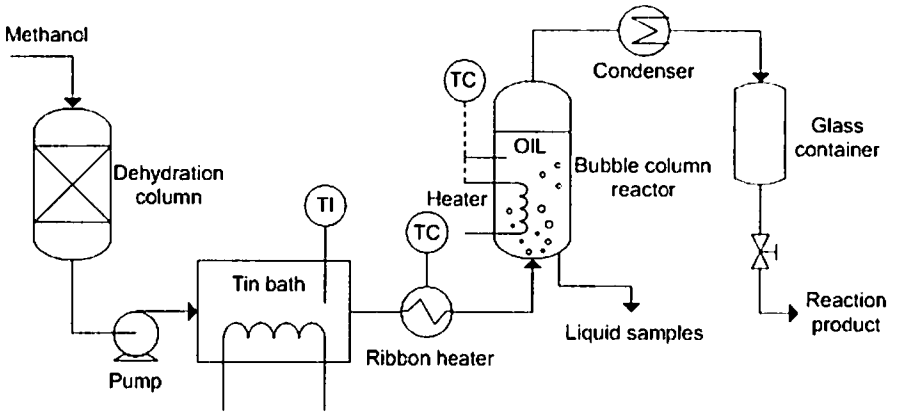

Fig. 1. Schematic flow diagram of reactor used in non-catalytic transesterification experiment.

2.3. Transesterification reaction procedure and conditions

The reactor was initially charged with 200 g of the refined palm oil and heated to the desired temperature. Reactions were conducted at 523, 543, and 563 K under atmospheric pressure. Liquid MeOH was pumped out of the dehydration column to the tin bath for vaporization. The MeOH vapor was taken through a ribbon heater and the reaction started by blowing the bubbles of superheated MeOH (0.1 MPa, 503–533 K) continuously into the reactor at fixed flow rate of 4 g/min. Reacted products in gas phase were condensed and collected using a glass container. The reaction products were taken from the glass container every 20 min and then weighed (samples A). During the reaction course (300 min), 15 samples were collected. Liquid samples in the reactor were taken every 20 min to analyze TG, DG, MG and ME contents using TLC/FID.

2.4. Analysis

The fatty acid composition of palm oil was analyzed by gas chromatography using a GC-2010AF (SPL/FID) Series Gas Chromatograph System equipped with a split/splitless injection system, a FID, an auto injector AOC-20i and a LabSolution GSsolution software from Shimadzu Co. Japan. The column was a 30 m × 0.25 mm, 0.25 μm DB-Wax capillary column (J&W Scientific from Agilent Technologies USA) with He at 40 cm/s as the carrier gas and a split ratio of 5.0:1. Injector and detector temperatures were 573 K, oven temperature started at 323 K for 3 min, increased to 523 K at a rate of 10 K/min, and held at this temperature for 8 min. About 1 mL of prepared sample was put into GC auto sampler vials and 1 μL of sample was injected into the column. The calculation of mass percentage for each fatty acid was based on ratio of peak area of each component to total peak area.

The GL contents in the samples A were analyzed by an HPLC (JASCO, Tokyo, Japan), equipped with a model 880-PU pump, a degasser DG-2080-53, a column oven CO-965, an intelligent sampler 855-AS, a recorder Borwin Software version 1.50 and a refractive index detector (GL Science, RI Model 408, Tokyo, Japan). A column (CAPCELL PAK NH_2 UG80, 25 cm in length × 4.6 mm in inner diameter, Shiseido, Tokyo, Japan) was used for separation. Samples A (0.5 mL) which had been filtered by using advantec filter (DISMIC-13 JP, PTFE 0.20 μm, Toyo Roshi Kaisha, Ltd., Japan) were diluted with 1.5 mL solvent (acetonitrile: water = 85:15 vol) and then were put into the intelligent sampler. Mass of the samples was measured before and after dilution. The HPLC mobile phase consisted of a 85:15 volumetric mixture of acetonitrile and water was used as a carrier solvent. The HPLC pump was operated at 1 mL/min solvent, and the column temperature was kept at 313 K. The sample injection volume was 10 μL. Based on the results of the preliminary experiment, the GL contents in the liquid samples taken from the reactor were very small so it can be ignored.

TLC/FID was used to analyze contents of TG, DG, MG and ME in the samples of reaction products without MeOH and the liquid samples in the reactor [15]. MeOH contents in the samples A were evaporated using a rotary evaporator and then the reaction products without MeOH were obtained (samples B). Each of samples B and the liquid samples in the reactor was weighed and its composition was analyzed using TLC/FID. Analyses were performed with an Iatroscan MK-5 Analyzer (Iatron Laboratories, Inc., Japan). The FID used hydrogen and air with flow rates of 160 mL and 2000 mL/min, respectively. Type SIII Chromarods were used as thin layer. Before being spotted, rods were scanned as blank on the instrument to obtain the proper degree of hydration. The samples B and the liquid samples (20–30 mg) were diluted with 1 mL solvent (250 mg squalane in 50 mL hexane) and 1 μL of the solution were spotted on each rod. Five replicates were used for each solution. The rods were developed for 30 min (they were stored in a glass chamber in which the atmosphere was saturated with benzene vapor), oven dried at 383–403 K for 5 min and then analyzed on the Iatroscan. The mass fraction of TG, DG, MG, and ME in the samples B and the liquid samples taken from the reactor was calculated based on the concentration of internal standard.

3. Results and discussion

The fatty acid composition of palm oil used in this experiment was palmitic acid, 34.98% w/w; stearic acid, 13.78% w/w; oleic acid, 41.23% w/w; linoleic acid, 10.01% w/w. Based on the fatty acid composition, the average molecular weight of TG, DG, MG and ME from the palm oil was assumed to be 858, 603, 348 and 287, respectively. Change of component mass versus reaction time of the reaction product without MeOH and liquid in the reactor at 563 K is given in Figs. 2 and 3. A typical curve at other temperatures (523 and 543 K) followed a similar pattern.

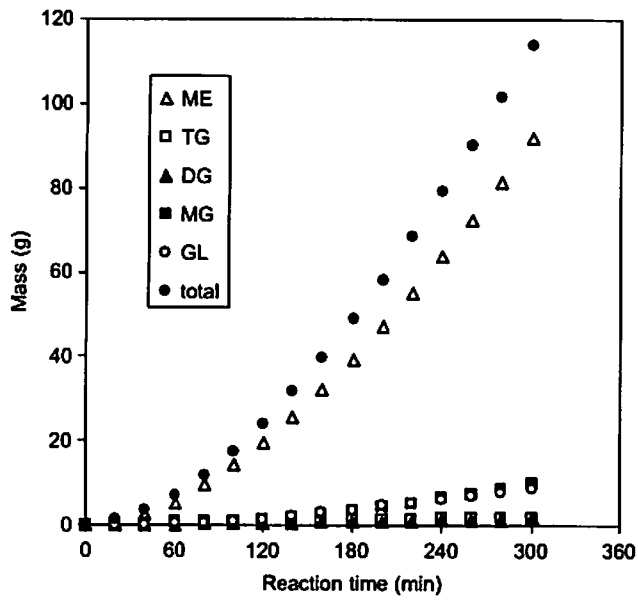

Fig. 2. Change of component mass of the reaction product at 563 K.

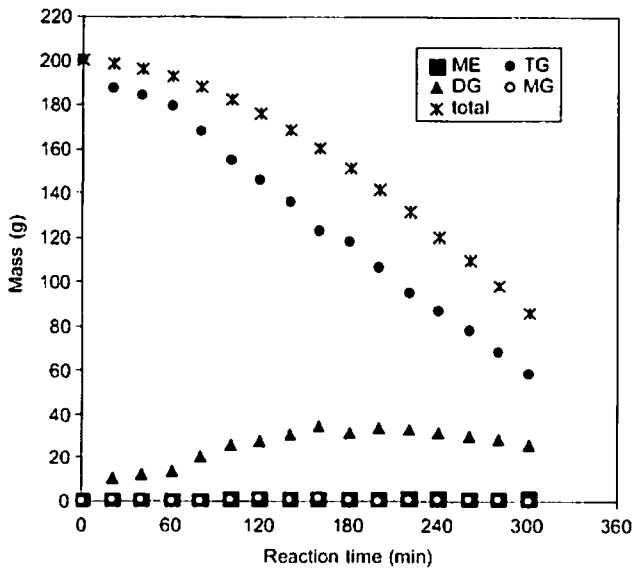

Fig. 3. Change of component mass of liquid in the reactor at 563 K.

As shown in Figs. 2 and 3, almost all of ME and GL could be obtained in the reaction product. On the other hand, mass of TG in the reaction product was very small. After 300 min of reaction time, the mass of ME, GL and TG in the reaction product at 563 K were 91.94, 8.91 and 1.67 g, respectively.

3.1. Kinetics of the non-catalytic transesterification under semi-batch mode process

Diasakou et al. [11] proposed the thermal transesterification reaction to be divided into three steps. TG reacts with methanol to produce DG which in turn reacts with MeOH to produce MG. Finally, MG reacts with MeOH to give GL. At each reaction step, one molecule of ME is produced for each molecule of MeOH consumed. This kinetics mechanism can be represented by the following:

$$\mathrm{TG} + \mathrm{MeOH} \xrightarrow{k_1} \mathrm{DG} + \mathrm{ME}, \quad (1)$$

$$\mathrm{DG} + \mathrm{MeOH} \xrightarrow{k_2} \mathrm{MG} + \mathrm{ME}, \quad (2)$$

$$\mathrm{MG} + \mathrm{MeOH} \xrightarrow{k_3} \mathrm{GL} + \mathrm{ME}, \quad (3)$$

where k_1, k_2, k_3 are the reaction rate constants of Eqs. (1), (2) and (3), respectively.

Kusdiana and Saka [5] defined a simpler mathematical model for the overall reaction in the transesterification reaction by ignoring the intermediate reactions of DG and MG, so the three steps can be simplified to be one step as follows:

$$\mathrm{TG} + 3\mathrm{MeOH} \xrightarrow{k} \mathrm{GL} + 3\mathrm{ME}, \quad (4)$$

where k is the rate constant of the overall reaction in the transesterification reaction.

Diasakou et al. [11] and Kusdiana and Saka [5] made the experiments of transesterification reaction in a batch reactor. In semi-batch mode operation where one fluid (MeOH) is continuously passed through a reactor containing a second fluid (TG), the concentration of MeOH in the gas does not change appreciably. Also reactant MeOH is absorbed and reacts slowly with component TG of the liquid. With the passage of reaction time (t) the concentration of TG (C_{TG}) will fall but the concentration of MeOH (C_{MeOH}) will remain unchanged [16]. If the kinetics is first order with respect to both MeOH and TG for the overall reaction, the reaction rate based on the decreased concentration of TG (r_{TG}) can be given by

$$-r_{\mathrm{TG}} = -\mathrm{d}C_{\mathrm{TG}}/\mathrm{d}t = kC_{\mathrm{MeOH}}C_{\mathrm{TG}}. \quad (5)$$

Rearranging, integrating, and noting that C_{MeOH} is constant, the equation will become

$$-\ln(C_{\mathrm{TG},t}/C_{\mathrm{TG},0}) = k't \quad \text{where } k' = kC_{\mathrm{MeOH}}. \quad (6)$$

In this experiment, three species were defined as ME, GL and unmethyl esterified compounds (uME) which include TG, DG and MG. Therefore, Eq. (6) can be modified to [5]

$$-\ln(C_{\mathrm{uME},t}/C_{\mathrm{uME},0}) = k't. \quad (7)$$

Based on the results shown in Figs. 2 and 3, concentration (% mol/mol) of each component in the total system (liquid in the reactor and reaction product) during the first 5 h at 563 K was calculated and shown in Fig. 4. A typical concentration curve at other temperatures (523 and 543 K) followed a similar pattern.

The increase in ME concentration was followed by an increase in GL concentration as it was liberated from TG molecules. Following an initial increase, the DG concentration decreased and after 300 min (5 h) concentration of DG at 563 K was 8.12% mol/mol. Similar to DG, concentration of MG was initially increased, reached a maximum value, and decreased very slowly.

To correlate experimental data and quantify the temperature and reaction time effects, the experimental results were analyzed further in term of the reaction kinetics, as mentioned earlier. The model is based on overall reaction, and the reaction is assumed to proceed in the first order rate as a function of the uME concentration (C_{uME}), as described by Eq. (7). Fig. 5 shows the relationship between the concentration of uME and reaction times at different temperatures. Gradient of the linear regression of $-\ln(C_{uME,t}/C_{uME,0})$ curve with respect to the reaction time is regarded as the rate constant (k'). The linear regression was calculated after exclusion of the reaction instability during the initial reaction time. The instability could be due to inhomogeneity of temperature in the reactor. This is also shown by the increase of DG and MG concentration during the initial reaction time, as described above. Summary of the rate constant (k') for each reaction temperature is shown in Table 1.

The k' value increased with reaction temperature, according to the Arrhenius equation [17]:

$$\ln k' = \ln A - E_a/RT, \quad (8)$$

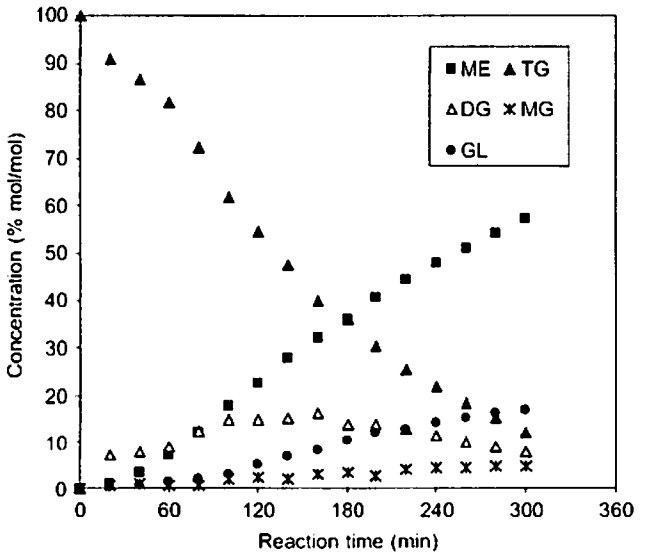

Fig. 4. Change of component concentration in the total system during the transesterification of palm oil at 563 K.

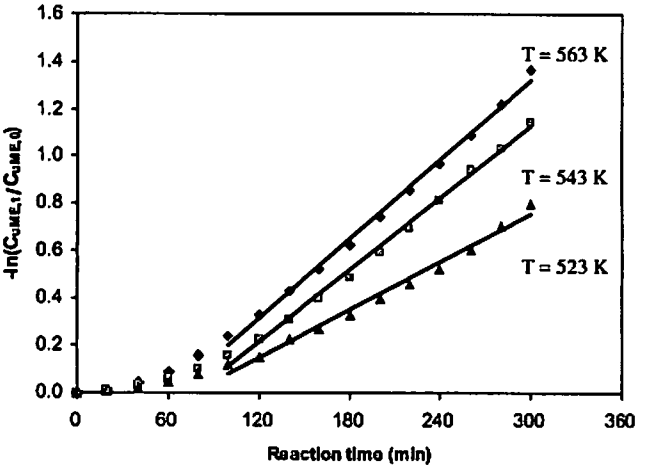

Fig. 5. The concentration of uME in palm oil during transesterification reaction.

Table 1
The rate constant of palm oil transesterification

Reaction temperature (K)	k' (min^{-1})	R^2 (%)
523	0.0034	98.75
543	0.0051	99.43
563	0.0056	99.62

where E_a is the activation energy, R is the molar gas constant (8.314 J/mol K) and A is the frequency factor. The data in the Table 1 were used to determine the activation energy and the frequency factor from a plot of reaction rate constant (k') versus the reciprocal of absolute temperature ($1/T$) as shown in Fig. 6. According to Eq. (8), the activation energy (E_a) was found to be 31 kJ/mol and a frequency factor (A) was 4.2.

The constant of reaction rate for rapeseed oil transesterification in supercritical MeOH, as reported by Kusdiana and Saka, was 0,0007 s^{-1} (0.042 min^{-1}) at 543 K, while the activation energy (E_a) and frequency factor (A) was 69 kJ/mol and 6936, respectively. The rate constant is about eight times higher than the value obtained in this experiment, while the activation energy is about two times larger. These differences are due to the frequency factor which is nearly 1650 times higher than the present experiment. The Kusdiana and Saka's experiment was performed under supercritical condition, where the polarity of MeOH would decrease. As a result, non-polar TG can be solvated with supercritical MeOH to form a single phase of vegetable oil/MeOH mixture.

In this experiment, MeOH bubbles are dispersed in oil phase, and the system consists of two phases. The reaction rate might be controlled by the mass transfer at the gas–liquid interface. The gas–liquid interfacial area need to be enlarged to increase the frequency factor value of the reaction so that the constant rate and reaction rate can be increased.

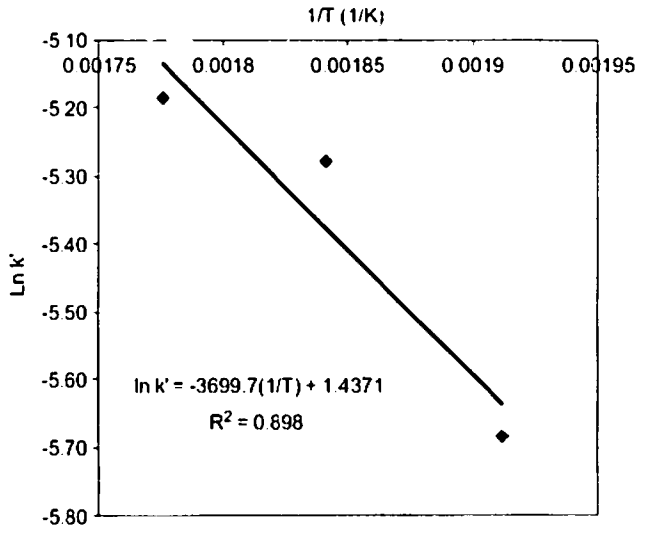

Fig. 6. First order reaction rate constant in Arrhenius plot during the transesterification of palm oil.

3.2. Effect of reaction temperature on the conversion, yield of ME and the reaction product composition

The conversion of reaction, α (%), for the overall reaction in the total system of the transesterification process is defined as in

$$\alpha = (C_{uME,0} - C_{uME,t})/C_{uME,0} \times 100 \quad (9)$$

where $C_{uME,0} = 100\%$ mol/mol.

The yield is defined as the ration of the mass of ME in the reaction product to the mass of initial oil (% w/w). The conversion and yield of ME at 60, 180, and 300 min of reaction time are summarized in Table 2, along with the composition of the reaction product as well as the liquid samples in the reactor.

The conversion of the reaction and yield of ME increased with reaction time and reaction temperature. The ME content (% w/w) in the reaction product increased with reaction time, however the ME content at the end of each experiment (300 min) decreased with reaction temperature. On the other hand, TG content in the reaction product as well as in the liquid in reactor tank decreased with reaction time at all reaction temperatures. Most of the ME was obtained in the reaction product, while most of the TG was contained by liquid in the reactor. These results can be explained by using the steam distillation principle. Steam was used to dissolve a component that has a high boiling point so that the boiling point of component can be decreased and the component can be evaporated at lower temperature by using distillation process. Table 3 shows the boiling point and vapor pressure of components in the transesterification of palm oil to biodiesel [18–21].

TG of long-chain fatty acids have extremely low vapor pressure and can be distilled satisfactory only by molecular or short-path distillation. Therefore, their boiling points can be observed only under very high vacuum condition. Some of these data are shown in the Table 3 [22]. Vapor pressure of ME was much higher than TG at the same reaction temperature so the volatility of ME was higher than TG, therefore the ME could be obtained in the reaction product. The same reason could be applied for GL. Vapor pressure of MG is much higher than TG, therefore MG content in the reaction product increased with reaction temperature.

The quality of the reaction product is very important for market acceptance of biodiesel. As described in Eqs. (1)–(3), during the transesterification process, MG and DG are formed and contained intermediately in the reaction product. These contaminants can lead to severe operational problems, such as engine deposits, filter clogging, or fuel deterioration [23], when used as biodiesel fuel. According to the European Union (EU) standards for biodiesel (EN 14214), the minimum acceptable purity of biodiesel (ME content) is 96.5% w/w using EN 14103 testing procedure [24]. This standard is also used in other non-EU countries such as in Australia, South Africa, and Indonesia.

This experiment shows that conversion and yield of ME at reaction temperature of 563 K was the highest, but the quality was low due to the ME content in the reaction product (87.47% w/w after 300 min of reaction time). Based on the quality consideration, the reaction temperature of 523 K was considered as the best condition because the ME content in the reaction product was 95.17% w/w after 300 min of reaction time, although the value of the conversion and yield of ME was 55.07% mol/mol and 27.43% w/w, respectively. Therefore, in future research efforts should be continued to increase the ME content in the reaction product, the conversion and the yield of ME.

4. Conclusions

Transesterification of palm oil with superheated MeOH vapor has been carried out at 523–563 K reactor temperature under atmospheric pressure in the absence of a catalyst. Evaluation on the reaction kinetic based on changes of the uME concentration shows that reaction rate constant at 523, 543 and 563 K was 0.0034, 0.0051 and 0.0056 min^{-1}, respectively, activation energy was 31 kJ/mol, and frequency factor was 4.2. The rate constant, conversion and yield of ME showed an increase trend with the reaction temperature, but the ME content in the reaction product decreased as the reaction temperature was increased. The optimum reaction temperature which gives the highest ME content (95.17% w/w) was 523 K, while the rate constant of the total system increased as the reaction temperature was increased. Experimental results indicated that in order to increase process efficiency showed by the value of rate constant, conversion and yield of ME the interfacial area of gas–liquid phase should be enlarged.

Table 2
Summary of transesterification experimental results

T^a (K)	t^b (min)	Composition in the reaction product (% w/w)				Composition of liquid in the reactor (% w/w)				α (%)	Yield (% w/w)
		ME	MG	DG	TG	ME	MG	DG	TG		
523	60	74.67	2.29	4.48	18.56	0.17	0.00	6.76	93.07	4.03	1.25
	180	93.64	1.29	2.26	2.81	1.18	1.34	16.39	81.08	28.04	10.96
	300	95.17	2.19	1.50	1.15	2.52	0.31	18.50	78.67	55.07	27.43
543	60	77.93	4.09	8.27	9.71	0.00	0.33	7.40	92.27	5.52	1.89
	180	92.40	2.55	3.21	1.85	1.09	0.57	20.11	78.23	38.55	16.77
	300	92.61	2.59	3.97	0.84	1.81	0.56	25.93	71.71	68.27	40.36
563	60	80.04	4.35	7.36	10.16	0.00	0.00	7.11	92.89	6.61	2.71
	180	87.35	8.12	7.88	2.94	0.36	0.69	21.04	77.91	46.51	19.73
	300	87.47	8.48	9.39	1.59	1.82	0.00	30.36	67.82	74.53	45.93

[a]Reaction temperature.
[b]Reaction time.

Table 3
The boiling point of components

Component	Boiling point (K)	Vapor pressure (Pa)
Methanol	337.9[a]	101 300
Glycerol	563[a]	101 300
Methyl palmitate	611[b]	101 300
Methyl stearate	625[b]	101 300
Methyl oleate	622[b]	101 300
Methyl linoleate	639[b]	101 300
Tripalmitin	571[c]	6.66
Tristearin	586[c]	6.66
Triolein	508–513[d]	2399
Trilinolein	-	-

[a]Perry's Handbook, 7th ed. [18].
[b]Yuan et al. [19].
[c]Swern, [20].
[d]Weast and Astle [21].

Acknowledgments

This work was conducted between October–December 2005 at the National Food Research Institute, Tsukuba, Japan as a part of the Ph.D. sandwich program between Bogor Agricultural University, Indonesia and The University of Tokyo, Japan. This program was funded by Technological and Professional Skills Development Sector Project (TPSDP) Batch III, the Ministry of National Education of Indonesia, ADB Loan No.: 1792-INO to Chemical Engineering Department of Institut Teknologi Indonesia. A part of this work was supported by a grant-in-aid Study Project of Global Warming from the Ministry of Agriculture, Forestry and Fisheries of Japan.

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