



Turnitin Originality Report

SUPFLU2610 by Suryadi Ismadji

From paper 2 (Hippo-hippo 02)

Processed on 16-Feb-2018 14:53 WIB

ID: 916903483

Word Count: 8653

Similarity Index 16%	Similarity by Source	
	Internet Sources:	9%
	Publications:	14%
	Student Papers:	4%

sources:

- 1 2% match (student papers from 06-Nov-2016)
[Submitted to University of Oklahoma on 2016-11-06](#)

- 2 1% match (publications)
[Kaur, Navjot, and Amjad Ali. "One-pot transesterification and esterification of waste cooking oil via ethanolysis using Sr:Zr mixed oxide as solid catalyst", RSC Advances, 2014.](#)

- 3 1% match (publications)
[Li, Hao, Shuqian Xia, and Peisheng Ma. "Upgrading fast pyrolysis oil: Solvent-anti-solvent extraction and blending with diesel", Energy Conversion and Management, 2016.](#)

- 4 1% match (Internet from 18-Nov-2016)
http://ir.lib.hiroshima-u.ac.jp/files/public/3/37620/20150618115411753332/k6594_3.pdf

- 5 1% match (publications)
[Sarve, Antaram N., Mahesh N. Varma, and Shriram S. Sonawane. "Response surface optimization and artificial neural network modeling of biodiesel production from crude mahua \(Madhuca indica\) oil under supercritical ethanol conditions using CO2 as co-solvent", RSC Advances, 2015.](#)

- 6 1% match (publications)
[Ong, L.K., A. Kurniawan, A.C. Suwandi, C.X. Lin, X.S. Zhao, and S. Ismadji. "A facile and green preparation of durian shell-derived carbon electrodes for electrochemical double-layer capacitors", Progress in Natural Science Materials International, 2012.](#)

- 7 1% match (publications)
["Contents", The Journal of Supercritical Fluids, 2013.](#)

- 8 1% match (publications)
[Soetaredjo, Felycia Edi, Alfin Kurniawan, Ong Lu Ki, and Suryadi Ismadji. "Incorporation of selectivity factor in modeling binary component adsorption isotherms for heavy metals-biomass system", Chemical Engineering Journal, 2013.](#)

1% match (Internet from 21-Nov-2017)

9

<http://www.redalyc.org/pdf/3032/303250905015.pdf>

10

< 1% match (Internet from 08-Apr-2016)

<http://www.tdx.cat/bitstream/handle/10803/123967/TPOC.pdf?sequence=1>

11

< 1% match (publications)

[Ang, Gaik Tin, San Nee Ooi, Kok Tat Tan, Keat Teong Lee, and Abdul Rahman Mohamed. "Optimization and kinetic studies of sea mango \(Cerbera odollam\) oil for biodiesel production via supercritical reaction", Energy Conversion and Management, 2015.](#)

12

< 1% match (publications)

[Trentin, C.M.. "Continuous production of soybean biodiesel with compressed ethanol in a microtube reactor using carbon dioxide as co-solvent", Fuel Processing Technology, 201105](#)

13

< 1% match (Internet from 07-Dec-2012)

<http://143.225.201.161/pdf/12532.pdf>

14

< 1% match (publications)

[Lou, Shengfeng, Lihua Jia, Xiangfeng Guo, Wenwang Wu, Lianbing Gao, Hongyuan Wu, and Jianjun Wang. "Synthesis of ethylene glycol monomethyl ether monolaurate catalysed by KF/NaAlO₂ as a novel and efficient solid base", RSC Advances, 2016.](#)

15

< 1% match (Internet from 03-Nov-2017)

https://hal-univ-rennes1.archives-ouvertes.fr/hal-01004642/file/Levels_of_dechloranes_and_polybrominated_diphenyl_ethers_accepted.pdf

16

< 1% match (publications)

[Shin, H.Y.. "Statistical optimization for biodiesel production from rapeseed oil via transesterificaion in supercritical methanol", Fuel Processing Technology, 201206](#)

17

< 1% match (Internet from 14-May-2015)

<http://atlas-mts.com/technical-information/sunspots/current-issue/>

18

< 1% match (publications)

[Hanifa Taher. "A Review of Enzymatic Transesterification of Microalgal Oil-Based Biodiesel Using Supercritical Technology", Enzyme Research, 2011](#)

19

< 1% match (publications)

[Adewale, Peter, Marie-Josée Dumont, and Michael Ngadi. "Recent trends of biodiesel production from animal fat wastes and associated production techniques", Renewable and Sustainable Energy Reviews, 2015.](#)

20

< 1% match (publications)

[Palacios-Nereo, Francisco Javier, Pilar Olivares-Carrillo, Antonia Pérez de los Ríos, and Joaquín Quesada-Medina. "High-yield non-catalytic supercritical transesterification of](#)

[soybean oil to biodiesel induced by gradual heating in a batch reactor](#)", *The Journal of Supercritical Fluids*, 2016.

21

< 1% match (publications)

[Punsuvon, V., R. Nokkaew, P. Somkliang, M. Tapanwong, and S. Karnasuta. "The Optimization of Esterification Reaction for Biodiesel Production from Animal Fat", *Energy Sources Part A Recovery Utilization and Environmental Effects*, 2015.](#)

22

< 1% match (publications)

[Fan, Rui, Nan Li, Honggao Xu, Jun Xiang, Lei Wang, and Yanxiang Gao. "The mechanism of hydrothermal hydrolysis for glycyrrhizic acid into glycyrrhetic acid and glycyrrhetic acid 3-O-mono- \$\beta\$ -d-glucuronide in subcritical water", *Food Chemistry*, 2016.](#)

23

< 1% match (Internet from 10-Sep-2013)

http://wormlab.biology.dal.ca/pressmaterial/catches_exploitation/content/Worm_etal_EMBARGOED.pdf

24

< 1% match (Internet from 29-Dec-2017)

[http://www.sphinxesai.com/2015/ch_vol7_no3_ICONN/10/NF59%20\(1108-1117\).pdf](http://www.sphinxesai.com/2015/ch_vol7_no3_ICONN/10/NF59%20(1108-1117).pdf)

25

< 1% match (publications)

["Green Fuels Technology", *Springer Nature*, 2016](#)

26

< 1% match (Internet from 13-Jul-2016)

<https://www.scribd.com/doc/250968236/The-Proceedings-of-TIChE-2014-International-Conference>

27

< 1% match (publications)

[Gunawan, Farrel, Alfin Kurniawan, Iwan Gunawan, Yi-Hsu Ju, Aning Ayucitra, Felycia E. Soetaredjo, and Suryadi Ismadi. "Synthesis of biodiesel from vegetable oils wastewater sludge by in-situ subcritical methanol transesterification: Process evaluation and optimization", *Biomass and Bioenergy*, 2014.](#)

28

< 1% match (publications)

[Vladimir Valerievich Ivchenko. "Accounting for the influence of temperature interval of the transients thermodynamic processes on gas laws", *European Journal of Physics*, 2017](#)

29

< 1% match (Internet from 18-Jan-2018)

http://ijc.iaush.ac.ir/article_11246_d578cf80045d0059b7827e5545e88a9f.pdf

30

< 1% match (Internet from 10-Mar-2016)

<http://cdn.intechopen.com/pdfs-wm/23011.pdf>

31

< 1% match (publications)

[Stacey Lowery Bretz, Natalie Foster, Thomas R Gilbert, Rein V Kirss. "Chemistry: An Atoms Focused Approach, Second Edition", W. W. Norton & Company, 2016](#)

32

< 1% match (student papers from 06-Jul-2014)

[Submitted to Asian Institute of Technology on 2014-07-06](#)

33

< 1% match (Internet from 19-Jul-2017)

<http://mdpi.com/2073-4344/7/3/73/htm>

34

< 1% match (publications)

[Sakdasri, Winatta, Ruengwit Sawangkeaw, and Somkiat Ngamprasertsith. "Response surface methodology for the optimization of biofuel production at a low molar ratio of supercritical methanol to used palm olein oil : Biofuel Production at a Low Molar Ratio of SCM", Asia-Pacific Journal of Chemical Engineering, 2016.](#)

35

< 1% match (publications)

[Food Engineering Series, 2015.](#)

36

< 1% match (publications)

[Shin, H.Y.. "Biodiesel production from waste lard using supercritical methanol", The Journal of Supercritical Fluids, 201201](#)

paper text:

1(This is a sample cover image for this issue. The actual cover is not yet available at this time.) This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues. Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited. In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit: <http://www.elsevier.com/copyright> J. of Supercritical Fluids 75 (2013) 11–20 Contents lists available at SciVerse ScienceDirect The Journal of Supercritical Fluids journal homepage: www.elsevier.com/locate/

supflu

7 **Transesterification of leather tanning waste to biodiesel at supercritical condition: Kinetics and thermodynamics studies** L.K. Onga,¹, A. Kurniawana,¹, A.C. Suwandia,¹, C.X. Lin^b, X.S. Zhaob,^{*}, S. Ismadjia,^{**} **a Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia b School of Chemical Engineering, The University of Queensland, St. Lucia 4072, Qld, Australia**

23 **article info Article history: Received 11 October 2012 Received in revised form 20 December 2012 Accepted 22 December 2012 Keywords:**

Leather tanning waste Supercritical condition Kinetics Thermodynamics ACT abstract Catalyst-free transesterification of leather tanning waste with high free fatty acid (FFA) content at super- critical condition was reported

8 **in this work. The experiments were performed in**

batch system at various temperatures (250–325

4 **°C) under constant pressure of 12 MPa and methanol/fatty oil molar ratio of**

40:1 for

34 **reaction time of 2–10 min.**

Kinetic modeling of formation of fatty acid methyl esters (FAMES) that incorporate reversible esterification and non-reversible transesterification simultaneously was verified. The proposed semi-empirical model was fitted against kinetic experimental data over temperature range studied. The kinetic parameters (i.e. k^{TE} , k^{E} , and $k^{\text{E}'}$) were determined by nonlinear regression fitting. Thermodynamic activation parameters of the reactions

14 **were evaluated based on activation complex theory (ACT) and the following results are obtained: $\Delta G^{\ddagger} > 0$, $\Delta H^{\ddagger} > 0$, and $\Delta S^{\ddagger} < 0$. The**

activation energy (E_a) of transesterification,

11 **forward and reverse esterification** reactions was **36.01 kJ/mol, 28.38 kJ/mol, and 5.66 kJ/mol, respectively.**

© 2012 Elsevier B.V. All rights reserved. 1. Introduction The rising market price and the depleting reserves of world crude oil have become the main reasons behind the search and development of alternative fuels, particularly for transportation and industrial purposes. Biodiesel (BD) is regarded as a promising alternative liquid biofuel to displace petro-diesel fuel that will be fully exhausted in near future. It is biodegradable, low toxicity, and produces much cleaner combustion compared to petro-diesel fuel with significant reduction of carbon monoxide, unburned hydrocarbons, and particulate matters (e.g., aldehydes, fume, and suspension particles) emissions about 50%, 70%, and 50%, respectively [1]. Biodiesel can be also blended with petro-diesel fuel in various proportions to provide similarity in terms of energy density and kinematic viscosity for direct use in the existing engines without extensive modifications. Because of its benefits, the development of biodiesel worldwide has rapidly grown annually [2].

5 **Biodiesel is composed of a mixture of alkyl esters that mostly produced by esterification and/**

or transesterification (or alcohol-ysis) of

5 **various lipid feedstocks such as vegetable oils [3–5] and**

*

6 **Corresponding author. Tel.: +61 7 3346 9997; fax: +61 7 3365 4199. ** Corresponding author. Tel.: +62 31 389 1264; fax: +62 31 289 1267.**

E-mail addresses:

6 **george.zhao@uq.edu.au** (X.S. Zhao), **suryadiismadji@yahoo.com,**

a1f1n kwn@yahoo.com (S. Ismadji). 1 These authors contributed equally to this work.

13 **0896-8446/\$ – see front matter © 2012 Elsevier B.V. All rights reserved. <http://dx.doi.org/10.1016/j.supflu.2012>.**

12.018 animal fats [6,7] with methanol or ethanol as the reacting alcohol.

18 **However, the use of vegetable oils** and animal fats **as biodiesel**

feedstocks causes economic issues for industrial and commercial practices, associated with the market price of these feedstocks that accounts for 75–85% from the overall production cost [8]. Moreover, some of vegetable oils (e.g., palm oil, coconut

18 **oil, and soybean oil) and animal fats** (e.g., beef **tallow**, lamb, **and**

chicken fats) are edible hence causes an intense competition with the food industries. Recently, researches have been directed toward the utilisation of non-edible and low cost feedstocks with high lipid content for biodiesel production such as leather tanning waste. The availability of tannery waste is huge in several countries with total production in Indonesia reached 0.15 million tons annually. The disposal and accumulation of this waste in the environment are of great concerns due to its unpleasant odor and adverse impacts on the soil fertility and water quality. Therefore, there is of interest to manage leather tanning waste properly and one advantageous way is by converting them to biodiesel. The most extensively used methods to produce biodiesel from leather tanning waste are through one-step and/or two-step transesterification using acid and alkaline catalysts [9–11]. In the case of the former, the process is usually conducted using

21 **an alkaline catalyst to** directly **convert triglyceride** into alkyl **ester**. However, **the** alkali-catalyzed **transesterification**

is very sensitive to

26 **high free fatty acid (FFA) and water contents** because **the**

catalyst can saponify FFA to soap that prevents separation of biodiesel from the mixture and lowers biodiesel yield. Therefore, this method only appropriately used for refined feedstocks with low levels of FFA and water, preferably lower than 1 wt.% and 0.06 wt.%, respectively [12]. For acid-catalyzed method, the process was performed in two-step where triglyceride contents in the feedstock are firstly hydrolyzed into monoglycerides, followed by esterification of monoglycerides into alkyl esters. However, this process is time-consuming because the reaction proceeds very slow and requires acid-resistant equipments. Recently, supercritical transesterification

5 **(SC-TE) has been highlighted as an emerging technology for biodiesel** production **from various feedstocks**

including leather-tanning waste.

5This method is able to completely convert fatty acids in feedstock to alkyl ester

in a relatively short time with- out

5involving any catalyts and offers simple product separation from the mixture.

Furthermore, supercritical transesterification method can tolerate

34FFA and water contents in the feedstock up to 30 wt.% and 36 wt.%, respectively

[13]. In general, the production of biodiesel

4from vegetable oils or animal fats by supercritical alcohol transesterification

was conducted at temperatures of

4250–400 °C, pressures of 10– 45 MPa, and molar ratio of

25alcohol to oil ranging from 40 :1 to 50 :1,

as reported by Sawangkeaw et al. [14] in their review paper. However, the major drawbacks of this method are the extreme reaction condition concerning the use of high operating pressures and temperatures that require a specialized reactor design and considerable high alcohol/lipid molar ratio used in the process, which may pose technical and economical constraints for practical applications. Several innovative technologies have been suggested by Sawangkeaw et al. [14] in order to conduct supercritical transesterification reaction at milder condition and make this technique more feasible for industrial practice such as using co-solvents (e.g. CO₂ or propane) or acid and base catalysts or modifying the SC-TE reaction system involving the use of two-step (subcritical hydrolysis–supercritical methanol esterification) [15] or dual-reactor process [16]. Although catalyst-free biodiesel production by supercritical alcohols has been well researched over past few years, the kinetics of reaction still needs to be studied in conjunction with several controversies in modeling the reaction kinetics by different approaches and the lack of available kinetic data over wide range of pressures and temperatures for industrial process operation and optimization. Several studies have reported the kinetic modeling of supercritical transesterification in batch, semi-batch, or continuous mode from various kinds of feedstocks [17–21]. Kusdiana and Saka [19] studied the batch

12 transesterification of rapeseed oil to biodiesel by supercritical methanol and proposed the reaction

kinetics by ignoring intermediate reactions (i.e. formation of diglyceride and monoglyceride). He et al. [20] also deal with the kinetics of transesterification of soybean oil by supercritical methanol under the same approaches used by Kusdiana and Saka [19], i.e. single step transesterification of triglycerides to fatty acid methyl esters (FAMES) and the reaction is non-reversible and first-order with respect to triglyceride concentration. The transesterification kinetics of refined sunflower oil in supercritical methanol at various pressures and temperatures has been studied by Glisic and Orlovic [21]. They report that transesterification of sunflower oil to biodiesel takes place as three stepwise and parallel reversible reactions. However, most of the previous studies including the aforesaid investigate the kinetics of supercritical transesterification reaction using refined vegetable oils where esterification of free fatty acids (FFAs) to monoalkyl esters is not taken into account. For unrefined (or low-grade) feedstocks with high FFA content, esterification reaction should be incorporated in modeling the kinetics with respect to the formation of monoalkyl esters. In the present work, we develop semi-empirical kinetic model of formation of fatty acid methyl esters at supercritical condition that incorporates non-reversible transesterification and reversible esterification simultaneously. Leather tanning waste and methanol Fig. 1. Fatty acid compositions of leather tanning waste. were employed as the model compound representing unrefined feedstock and reacting alcohol, respectively. The effects of temperature on the kinetic parameters (i.e. rate constants) were discussed. A simple technique for determining rate constants by nonlinear regression fitting was applied. Furthermore, thermodynamics of the reactions (i.e. ΔG^\ddagger , ΔH^\ddagger , and ΔS^\ddagger) were evaluated on the basis of activation complex theory (ACT).

132. Materials and methods 2.1. Materials The

pre-fleshing fat waste as the raw material to produce biodiesel in this work was collected from a leather-tanning factory located at Bogor, West Java, Indonesia. Prior to use, the waste was repeatedly washed with deionized water to remove unwanted components including dirt, blood, preservative salt, etc. Subsequently, the waste was heated at 100

21°C for 1 h to remove water and then filtered to remove remaining flesh. **The**

fatty acid compositions of fatty oil were analyzed by a Shimadzu GC-2014 equipped with a Restek Rtx-65TG fused silica

33 capillary column (30 m × 0.25 mm × 0.10 μm) and a flame ionization detector (FID) and the

result are

4 shown in Fig. 1. The free fatty acid

content of fat waste was 14.9%, as determined by ASTM D5555-95 method. Anhydrous methanol (99.8%) and heptane (99%) were purchased from Merck, Germany. N-methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA) silylation reagent was purchased from Fluka as derivatization grade. The commercial stock solutions of triolein, 1,3-diolein, monoolein, and standard kit of Supelco® 37 component FAME-mix were supplied from Sigma–Aldrich, Singapore and used for the preparation of calibration curves for the quantification of acylglycerides and FAME contents, respectively. Methyl heptadecanoate (99.5%, Fluka) and tricaprin (Sigma–Aldrich) were used as internal standards for the analysis of fatty acid methyl esters and acylglycerides,

16 respectively. 2.2. Supercritical methanol transesterification The schematic of apparatus set-up for

supercritical transesterification experiments is displayed in Fig. 2.

36 The reaction system consists of a

50 ml high pressure batch reactor, fittings and tubings, which made from

16 316-grade stainless steel, a K-type thermocouple for sensing temperature, a pressure gauge, and an external electric

heater. The

6 reactor was also connected to a cylinder gas containing nitrogen

(99.99%) at 15 MPa. Fig. 2. The schematic of apparatus set-up for supercritical transesterification experiments. (N₂ cylinder

27 (1); relief valve (2); electric heater (3); RPM controller (4); magnetic bar (5); reactor (6); and release valve (7)).

The procedure was described as follows: a certain proportion of methanol and fatty oil was loaded to the reactor to give methanol/fatty

10 oil molar ratio of 40:1. A specified amount of

nitro- gen was then purged to the system. The reaction was conducted by rapidly heating methanol–fatty oil mixture from room temperature (around 30 °C) to desired temperatures

24(250 °C, 275 °C, 300 °C, and 325 °C).

After temperature and pressure in the system reached the desired values, the reaction was held for a prescribed time (2 min, 4 min, 6 min, 8 min, and 10 min). During this period, the pres- sure

36was monitored by a pressure gauge and the temperature was

adjusted within ± 2 °C from the set-value by a PID-type controller for maintaining isobar and isothermal conditions. The reactor was then immersed in a water bath to stop the reaction immediately. The mixture was removed from the vessel and settled in a sep- aration funnel overnight for phase separation between biodiesel (fatty acid methyl esters) and glycerol. The methyl ester-rich phase (top layer) was taken and underwent vacuum evaporation for 3 h. The resulted product was analyzed to determine the concentra- tions of residual

30free fatty acids and acylglycerides and fatty acid methyl esters.

All experimental data were reproduced by triplicate experiments with average used as the results. 2.3. Biodiesel analyses Biodiesel analyses in this work were addressed to determine fatty acid methyl ester contents and concentrations of acylglyc- erides (tri-, di-, and monoglycerides) and FFA after the reaction completed. The free fatty acid content in the biodiesel samples was determined by titration against standardized KOH solution by fol- lowing ASTM D5555-95 procedure. The acylglycerides and

26methyl ester contents in the sample were quantified by

gas chromato- gra- phy technique, as described below. 2.3.1. Analysis of fatty acid methyl esters The fatty acid methyl esters in biodiesel were analyzed by a Shi- madzu GC-2014 equipped with an Agilent narrowbore DB-Wax

10capillary column (30 m \times 0.25 mm \times 0.25 μ m) and a FID. Helium was used as carrier gas at pressure of

37.3 kPa and column flow of 2.30 ml/min. The temperatures of injector and FID were operated at 250 °C and 300 °C, respectively. The oven was programmed at 50 °C for 2 min, ramped at 10 °C/min to 250 °C and hold isothermally for 8 min. The sample injection volume was 1 μ l in splitless mode. Prior to injection, the sample was mixed with a certain amount of 100 mg/ml methyl heptadecanoate internal standard solution and diluted with heptane. The resulted methyl ester peaks in the sample were identified by comparing their retention time with the reference standards. 2.3.2. Analysis of acylglycerides The concentrations of residual

acylglycerides in biodiesel were determined by GC analysis, using an Agilent widebore DB-5HT (15 m × 0.32 mm × 0.1 μm) high temperature capillary column by adopting ASTM D6584 method. The calibration solutions were prepared based on the ASTM D6584 procedure. Prior to injection, a known amount of tricaprins internal standard solution was added to the sample, derivatized with MSTFA, and diluted in heptane. The gas chromatography conditions for analysis of acylglycerides were as follows: Carrier gas: helium at column flow of 3 ml/min and pressure of 169.4 kPa; injector and FID temperatures were 360 °C and 380 °C, respectively; The column

15oven temperature was set at 50 °C for 1 min, ramped at 15 °C/min to 180 °C, then elevated to 230 °C at 7 °C /min, and finally ramped to 380 °C at 30 °C/min and maintain for 10 min. The

injection volume of sample was 1 μl with a split ratio of 30:1. Identification of acylglycerides peaks was performed by the same manner as those of methyl ester peaks. The mass percentage of individual glycerides in the sample was calculated by following equation: Acylglycerides (wt.%) = $100 (a_0 \times AAG/A_{int} + b) \times V_{int} \times C_{int} / m$ (1) where a_0 and b are the slope and the intercept of calibration curves of mono-, di-, and triglycerides, respectively, V_{int}

11is the volume of tricaprins solution added to the sample (ml), C_{int} is the concentration of tricaprins solution (mg/

ml), and m is the mass of the sample (mg). The peak areas of acylglycerides and tricaprins internal standard were symbolized as AAG and A_{int} , respectively and designated as the response ratio (AAG/A_{int}) in Eq. (1) based on the ASTM D6584 method. 3. Results and discussion 3.1. Kinetic modeling Transesterification is a transformation reaction of fatty acid esters (e.g. oil or fat) to monoalkyl esters through an interchange of alkyl group between triglycerides and short-chain alcohol (e.g. methanol or ethanol) that occurs in three consecutive steps: (i) transformation of triglyceride (TG) to diglycerides (DG) and monoalkyl esters, (ii) transformation of DG to monoglyceride (MG) and monoalkyl esters, and (iii) transformation of MG to monoalkyl esters and glycerol. In this work, the kinetic evaluation of transesterification of leather tanning waste in batch system was performed using experimental data over

4temperature range of 250–325 °C and reaction time of 2–10 min

at constant methanol

4/oil molar ratio of 40:1 and pressure of 12 MPa. The

existence of single phase of methanol–fatty oil mixture

35strongly depends on the applied pressure and temperature to the system

hence it is necessary to verify

35the critical point of the mixture.

For this purpose, Lee–Kesler method was used to estimate the critical properties (i.e. P_c and T_c) of pure fatty oil due to the unavailability of thermophysical data of this substance. For simplification purpose, the mixture of saturated and unsaturated triglycerides in fatty oil was assumed as a single pseudo-triacylglyceride with equal molecular weight and degree of unsaturation of the original oil based on the approach taken in some previous studies [22–24]. The critical properties of methanol–fatty oil mixture were estimated by constructing phase diagram using Phase Envelope feature in ChemCAD software (Version 6.2.0, Chem- stations Inc.) with Predictive Soave–Redlich–Kwong (PSRK) as the thermodynamic model. This group contribution equation of state was recommended by ChemCAD Wizard for the estimation of Fig. 3. Phase diagram and critical point of supercritical

20mixture of methanol– fatty oil with a molar ratio of 40:1.

thermophysical properties of a mixture containing supercritical components [25]. It can be seen from a phase diagram in Fig. 3 that the critical pressure and critical temperature of methanol–fatty oil mixture with a molar ratio of 40:1 are 7.49 MPa and 244.04 °C, respectively. Hence, it is verified that pressure of 12 MPa and temperatures ranging from 250 °C to 325 °C used in this study are sufficient to generate supercritical

20mixture of methanol and fatty oil with a molar ratio of 40:1.

In order to simplify the complex behavior of transesterification reaction, several approaches were applied in modeling the reaction kinetics with respect

9to the formation of fatty acid methyl esters: i. The

overall supercritical transesterification reaction is irreversible according to the work reported by Marulanda et al. [26] hence the three consecutive steps of transformations of triglycerides to fatty acid methyl esters were indeed to be irreversible. ii. The concentration change of methanol was ignored because methanol/fat molar ratio loaded to the system (40:1) is sufficiently high relative to the stoichiometric amount of methanol consumed by triglycerides (3:1) to undergo methanolysis reaction. Under this assumption, the overall supercritical trans-

25esterification reaction is presumed to be pseudo -first order with respect to

triglyceride concentration alone. iii. The extent of glycerol–methanol reactions was ignored relative

9 to the formation of fatty acid methyl esters. The

kinetic representations of transesterification based on several approaches above were presented as follows: $TG + MeOH \xrightarrow{k_1} DG + FAME$ (2) $DG + MeOH \xrightarrow{k_2} MG + FAME$ (3) $MG + MeOH \xrightarrow{k_3} 3FAME + \text{glycerol}$ (4) The overall transesterification reaction (summation of Eq. (2) to Eq. (4)): $TG + 3MeOH \xrightarrow{k_{TE}} 3FAME + \text{glycerol}$ (5) Because leather tanning waste used in this work contains high portion of FFA (14.9%), esterification reaction of FFAs to fatty acid methyl esters was taken into account: $FFA + MeOH \xrightleftharpoons{k_E} FAME + H_2O$ (6) k_E From Eq. (6), it is apparent that water is accumulated in the system during the reaction hence hydrolysis reactions of TG and FAME species are expected to be occurred. However, the extent of these reactions can be presumed to be minor regarding the steric hindrance factor, which defined as the retardation of chemical reaction due to large size or overcrowded groups in the reacting molecules. Because triglycerides have more complex molecular structure than methyl esters, higher value of steric hindrance is expected for such molecules. Therefore, the extent of hydrolysis of triglycerides is neglected relative to that of hydrolysis of methyl esters, owing to higher steric hindrance in the former reaction. The rate equation forms of Eqs. (2)–(6) can be written as follows: $-r_{TG} = k_1[TG][MeOH]$ (7) $-r_{DG} = k_2[DG][MeOH] - k_1[TG][MeOH]$ (8) $-r_{MG} = k_3[MG][MeOH] - k_2[DG][MeOH]$ (9) Since DG and MG are intermediate species, which immediately reacted with methanol, the notations of $-r_{DG}$ and $-r_{MG}$ can be presumed to be zero (i.e. quasi steady-state assumption). This assumption was supported from GC analysis results that show no considerable change on the concentrations of mono- and diglycerides at the initial and the end of reaction time. $-r_{DG} = 0 = k_2[DG][MeOH] - k_1[TG][MeOH] \Rightarrow k_1[TG][MeOH] = k_2[DG][MeOH]$ (10) $-r_{MG} = 0 = k_3[MG][MeOH] - k_2[DG][MeOH] \Rightarrow k_2[DG][MeOH] = k_3[MG][MeOH]$ (11) The rate of formation of methyl esters (r_{FAME}) from transesterification reaction: $r_{FAME} = -r_{MeOH} = k_1[TG][MeOH] + k_2[DG][MeOH] + k_3[MG][MeOH]$ (12) Substitutes the term of $k_2[DG][MeOH]$ and $k_3[MG][MeOH]$ in Eq. (12) with $k_1[TG][MeOH]$ as expressed in Eqs. (10) and (11) give: $r_{FAME} = -r_{MeOH} = 3k_1[TG][MeOH]$, with $3k_1 = k_{TE}$ and $[TG] = [TG]_{init} - XTG$ (13) where XTG is the amount of triglycerides converted to methyl esters (mol l⁻¹). The rate of formation of methyl esters (r'_{FAME}) from esterification reaction: $r'_{FAME} = -r_{MeOH} = k_E[FFA][MeOH] - k'_E[FAME][H_2O]$ (14) The term of $[FFA]$ and $[H_2O]$ in Eq. (14) can be expressed as $[FFA] = [FFA]_{init} - XFFA$ and $[H_2O] = [H_2O]_{init} + XFFA$, respectively, where $XFFA$ is the amount of FFA converted to FAME (mol l⁻¹). The concentration of FAME in the system can be stoichiometrically expressed as $[FAME] = [FAME]_{init} + XFFA + 3XTG$ regarding esterification and transesterification reactions. The validity of stoichiometric equation above was assessed through comparison between calculated (represented as lines) and experimental FAME (represented as symbols) concentrations, as depicted in Fig. 4. It was found that the experimental and theoretical FAME values were slightly different (with average errors about 5% at all temperatures), revealing the validity of equation to be used for kinetic modeling. At initial reaction time ($t = 0$) or immediately after the system reached the desired pressure and temperature, the concentrations of fatty acid methyl esters ($[FAME]_{init}$) and water ($[H_2O]_{init}$) in the system were analyzed to investigate the extent of transesterification and esterification reactions during heating time. From GC analysis results (see Fig. 5), it can be seen that the extent of FAME formation was not significant.

8 A plausible explanation to this point is that during the

heating time, the mixture still existed in two 1.1 1.0 FAME (mol/L) 0.9 0.8 0.7 0.6 0.5 2 4 6 8 10 Reaction Time (min) Fig. 4. Comparison plots between calculated (lines) and experimental (symbols) FAME concentrations in the reaction system

24((?)250°C;(?)275°C;(×)300°C;and (?)325°C).

phases due to poor miscibility of methanol in the fatty oil and the absence of stirring action. Accordingly, the formation of methyl esters was restricted and it only took place in the interface area between methanol and fatty oil. Besides, a rapid heating rate also minimized the time available for the occurring reactions. Hence, the notations of $[FAME_{init}]$ and $[H_2O_{init}]$ can be presumed to be zero. Substituting the term of $[FFA_{init}] - XFFA$ into $[FFA]$; $[H_2O_{init}] + XFFA$ into $[H_2O]$; and $[FAME_{init}] + XFFA + 3XTG$ into $[FAME]$ in Eq. (14), the following equation was obtained: $rF'_{AME} = -r_{MeOH} = kE[FFA_{init} - XFFA][MeOH] - k'E[XFFA + 3XTG][XFFA]$ (15) By combining the rate of formation of FAME in Eqs. (13) and (15) give: $rF'_{AME} - r_{MeOH} = kTE[TG][MeOH] + kE[FFA_{init} - XFFA][MeOH] - k'E[XFFA + 3XTG][XFFA]$ (16) Because the concentration change of methanol was neglected, Eq. (16) can be simplified to: $rF'_{AME} = -r_{MeOH} = k'TE[TG_{init} - XTG] + k'E[FFA_{init} - XFFA]k'E[XFFA + 3XTG][XFFA]$ (17) where $[TG_{init}]$ and $[FFA_{init}]$ are the initial concentrations of triglyceride and free fatty acid, respectively, in the unit of mol l⁻¹. The reaction rate constants of $k'TE$ and $k'E$ (min⁻¹) were designated as the rate constant of transesterification and forward esterification multiplied by concentration of methanol. The rate equation in Eq. (17) was proposed as semi-empirical kinetic model that incorporates reversible esterification and non-reversible transesterification reactions simultaneously. The molar concentration of fatty acid methyl esters (mol l⁻¹) was calculated by dividing the peak area of each fatty acid methyl ester species with its corresponding molecular weight then multiplied by the density of product. The values of r_{FAME} were calculated by differential method. The kinetic parameters (i.e. $k'TE$, $k'E$, and kE')

8 were determined by nonlinear regression fitting using SigmaPlot software (Version 12.3, Systat Software Inc.) and the results are

listed in Table 1. The experimental data are fitted by successive approximation method until convergence and tolerance satisfied. The step size and the number of iterations were designed to reduce Table 1 The fitted values of rate constants of transesterification, forward and reverse esterification at supercritical condition.

30T (°C) k' TE (min⁻¹) k' E (min⁻¹)

kE' (min⁻¹) kE a R² 250 0.32 275 0.42 300 0.52 325 0.96 1.90 0.58 2.97 0.60 3.55 0.64 4.42 0.68 3.28 0.99 4.95 0.99 5.55 0.98 6.50 0.97 a The equilibrium constant of esterification reaction, defined as $kE = k'E/k'E$ unnecessary computation without affecting the accuracy of predictions. The initial values of the fitted parameters (i.e. rate constants) were determined for starting the calculation. The constraints for all fitted parameters were greater than zero. The following objective function was applied for minimizing the standard error of estimate (also known as the sum of squares error (SSE)) between actual and predicted values: $(Y - Y')^2_{est} = \sqrt{\sum N}$ (18) Here est is the standard error of estimate, N is the number of experimental data points, Y is the actual or experimentally measured values, and Y' is the predicted values. In Table 1, it was found that the values of $k'TE$ increase with increasing temperature, indicating that higher temperature favors transesterification of triglycerides to methyl esters. An explanation to this point is that high temperature weakens the degree of hydrogen bonding in hydroxyl group of methanol so it becomes less polar compared

to liquid methanol at ambient pressure and temperature. As the result, methanol and fatty oil molecules collide more frequently as a result of increased homogeneity in the reaction mixture that facilitated the formation of methyl esters. Increasing temperature also causes the molecules to move around faster because of

8 **greater kinetic energy in the system that increases the**

number of collisions per unit time. Moreover, the increasing value of k_{TE} with temperature also reflects the Arrhenius behavior of transesterification reaction. The values of k_E and $k_{E'}$ rate constants were also enhanced with increasing temperature, revealing the Arrhenius behavior of forward and reverse esterification reactions. Interestingly, the rate constant of forward esterification is greater than reverse esterification in all temperatures, indicating that the formation of methyl esters is more favorable than hydrolysis reaction. By comparing the values of k_{TE} and k_E , it can be concluded that the rate of formation of methyl esters from esterification is faster than transesterification. This may be ascribed to the reaction mechanism involved in the transformation of FFA and TG to FAME that follows S_N2 mechanism. In the latter case, the transformation of TG to FAME proceeds in three consecutive steps, which expected to be more energy- and time-consuming during structural orientation and conformation of the reactants and intermediate species on the reaction pathway hence the rate constant of transesterification is slower than esterification with respect to the formation of fatty acid methyl esters. Further evidences of this explanation from thermodynamic consideration will be discussed in the next section. As comparison, the recently proposed kinetic models of non-catalytic transesterification and esterification and their rate constants are summarized in Table 2 [17,19,27,28]. The magnitude of transesterification rate constants in this work comparable to that of Kusdiana and Saka [19] but considerably higher than that of Song et al. [27] for similar reaction system and the approaches taken in proposing the model. By comparing the rate constants of forward esterification (i.e. methanolysis of FFA to FAME), the values in this work differ greatly to those obtained by Cho et al. [17] and Alenezi et al. [28]. In their studies, Cho et al. [17] and Alenezi et al. [28] Fig. 5. The chromatograms of methyl ester peaks with variation of reaction time at 12 MPa and 325 °C. only consider esterification of free fatty acids to model the kinetics of FAME formation while this work also incorporates transesterification of fatty acid esters where simultaneously occurring ester- and transesterification were responsible in the FAME formation. Additionally, the composition of feedstock may act as a determining factor toward the rate constants, as confirmed by Rathore and Madras [29]. While high temperatures favored for increasing the conversion efficiency of FFA and TG, it should be known the temperature limit of the process to avoid thermal decomposition of methyl ester species. The dependency of decomposition of methyl esters on temperature has been recently studied by Shin et al. [30] and Quesada-Medina and Olivares-Carrillo [31]. In their studies, it was known that thermal decomposition of polyunsaturated

10 **methyl esters containing two or more double-bond (e.g. methyl linoleate and methyl linolenate)**

start to appear at temperatures about 300 °C while saturated methyl esters (e.g. methyl palmitate and methyl stearate) hardly decomposed even at temperatures above 350 °C. Table 2 A summary of recently reported kinetic models of non-catalytic transesterification and esterification. Kinetic model Approaches Rate constants Solution Reference In $[[uuMMEE,,0t]] = -kt$ $r_{TG} = -(4.3376 \times 10^5) \exp - 1.052R7T \times 10^5$

32 **methyl myristate; (?) methyl palmitate; () methyl palmitolein; () methyl heptadecanoate; () methyl stearate; () methyl oleate; () methyl linoleate; () methyl linolenate; and () methyl arachidate).**

The effect of pressure may not be crucial toward the rate constants of supercritical transesterification and esterification.

28 **According to the Le Chatelier's principle, the increase of pressure shifts the chemical equilibrium in a direction that**

lowers the pressure, in other means, to the direction that exhibits less number of moles and vice versa. Because esterification and transesterification reactions have the same

31 **number of moles of reactants and products** (stoichiometrically equal in both reaction sides), **the**

change of pressure would not

31 **affect the chemical equilibrium of the reaction. This**

effect also applies to supercritical fluid reaction system because of its behavior that resembles gases (i.e. fills and takes the shape of the container). Hence, it can be concluded that the rate constants of esterification and transesterification were unaffected by the change of pressures regarding: (1) the law of action–reaction above and (2) the role of pressure that only serves for tuning the density of fluid (i.e. methanol) in the mixture. 3.2. Thermodynamic analysis

2 **Thermodynamic analysis was addressed for evaluating the enthalpy (ΔH^\ddagger), entropy (ΔS^\ddagger), and the Gibb's free energy of activation (ΔG^\ddagger), which are the important features for interpreting**

the behavior of transesterification and esterification

2 **reactions. In this regard, ACT (activation complex theory), which developed by Eyring in 1935 [32] was applied to evaluate thermodynamic parameters**

above in conjunction with temperature-dependent rate constant. This theory proposes that any particular chemical reaction proceeded via a transitory energized species of intermediate structure between

reactants and products called the activated complex and this complex is in quasi-equilibrium state with the reactants [33], as described below: $X + Y \leftrightarrow [X \dots Y]^\ddagger \rightarrow \text{product}$ (19) where X and Y are the reactants and the superscript notation \ddagger refers to the activation-state complex. The

29 **mathematical relation between rate constants and temperature can be expressed by the following Arrhenius equation:** $E_a k = A \exp$

– RT (20) Taking the natural logarithm of equation above gives: ()

9 **$\ln k = \ln A - E_a / RT$** Here **k** is the **rate constant** (min **-1**), **A** is the frequency factor or **pre-exponential** coefficient (min **-1**),

17 **R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), T is the absolute temperature (K), and E_a is the activation energy (kJ /mol). The**

plot of 1/T as abscissa and ln k as ordinate in Eq. (21) gives a straight line with slope and intercept $2.0 \ln k$ (min -1) -2 -4 -6 0.0014 0.0016 0.0018 0.0020 0.0022 1/T (K⁻¹) Fig. 7. Overlay of regressed lines (– – –) of Arrhenius plots for supercritical transesterification of (?) tannery waste, () rapeseed oil [19], () Karanja and () Jatropha oils [27], and esterification of leather tanning waste (?) forward, (x) reverse, () PFAD [17], and () oleic acid [35]. of $-E_a/R$ and $\ln A$, respectively. The value of

22 **Gibb's free energy of activation**

(ΔG^\ddagger) can be calculated from Eyring–Polanyi equation [34], which is analog to Arrhenius equation: $k = k_B T \exp(-\Delta G^\ddagger / RT) h$ (22) Taking the natural logarithm of equation above and inserting $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$ gives: $\ln k = -\Delta H^\ddagger / R T + \ln k_B h + \Delta S^\ddagger / R$ (23) where k_B and

2h **are the Boltzmann (1.38 × 10⁻²³ J K⁻¹) and Planck () () [()] (6.63 × 10⁻³⁴ J s) constants, respectively. Eq. (23) resembles van't Hoff's equation describing the mathematical relation between enthalpy and entropy of activation with rate constant. The values of**

enthalpy (ΔH^\ddagger) and entropy of activation (ΔS^\ddagger) can be obtained

14 **from the slope and the intercept of linear plot of 1/T vs. ln (k/T).**

The prefactor refers to the transmission coefficient and this value is usually taken to be unity in most cases. Originally, Eyring–Polanyi equations (Eqs. (22) and (23)) were developed for kinetic theory of gas phase reaction, but it can be applied to supercritical phase because this phase retains the gas-like transport properties and behaves like a gas. The Arrhenius plots of transesterification and esterification are displayed in Fig. 7 while the values of corresponding thermodynamic parameters (A and E_a) are given in Table 3. The frequency factors of transesterification and forward esterification were higher than reverse esterification, indicating the formation of methyl esters is more predominant than its hydrolysis. In chemical kinetics, the frequency factor (A) describes how often the molecules collide at concentration of 1 mole/l and on whether the molecules are properly oriented during the collisions. Hence, higher value of frequency factor means higher probability of successful collisions (i.e. the collisions that cause chemical change). By comparing the frequency factor between transesterification and forward esterification, it can be concluded that the formation of methyl esters from esterification of free fatty acid is more feasible than transesterification of triglycerides. The activation energy (E_a) of transesterification,

11 forward and reverse esterification was 36.01 kJ/mol, 28.38 kJ/mol, and 5.66 kJ/mol, respectively.

Higher activation energy for transesterification caused a slower formation rate of methyl esters compared to esterification. This is likely due to greater steric interactions -9.0 -9.5 $\ln(k/T)$ -10.0 -10.5 -11.0 -11.5 0.00165 0.00170 0.00175 0.00180 0.00185 0.00190 0.00195 $1/T$ (K⁻¹) Fig. 8. The Eyring plots of (?) transesterification, (?) forward and (x) reverse esterification

9 of leather tanning waste to biodiesel at supercritical condition. (i.e. intra- and

intermolecular van der Waals repulsion) that retard nucleophilic attack on the carbocation of triglyceride by methoxide radicals. Another factor that caused the increase of activation energy is the structural conformation of the transition state involving the changes of bond lengths and bond angles. These two factors were found to be more prominent in triglycerides than FFA due to more complex molecular structure of the former. As comparison, several reported values of activation energy and frequency factor for non-catalytic transesterification and esterification of various feedstocks with methanol as the reacting alcohol are included in Table 3 and Fig. 7 [17–19,27–29,35–37]. In Table 3, it can be seen that the value of activation energy in this work was much lower than those reported by Kusdiana and Saka [19] and Song et al. [27] for single-step transesterification of rapeseed oil and RBD palm oil, respectively, but comparable to that of

12 Varma and Madras [35] for supercritical transesterification of castor oil

4 at temperature range of 200–350 °C and pressure of 20 MPa.

The variation of activation energy values is strongly related to the rate constants, which is inversely proportional to the activation energy. In this context, higher activation energy corresponds to a slower

reaction rate and vice versa. The dependence of activation energy toward rate constants was also revealed in Fig. 7. The slope of the regressed lines of Arrhenius plots for transesterification of leather tanning waste and rapeseed oil [19] is steeper than those of Karanja oil and Jatropha oil [29], indicating greater temperature sensitivity of the rate constants in the former than the latter. In other hand, the slopes of the regressed lines for esterification of leather tanning waste, PFAD [17], and oleic acid [37] are similar. Meanwhile, there is no clear relationship actually between the rate constants and frequency factor, at least theoretically. However, it should be kept in mind that the reacting molecules should be correctly oriented and had enough the internal energy (above the activation energy) to undergo a particular reaction. Fig. 8 depicts the Eyring plots of transesterification and esterification and the values of activation parameters (i.e. ΔG^\ddagger , ΔH^\ddagger , and ΔS^\ddagger) are listed in Table 4. The values of enthalpy of activation of transesterification, forward and reverse esterification were 40.66 kJ/mol, 34.23 kJ/mol, and 10.9 kJ/mol, respectively, indicating that

2energy input (heat) from external source is required to raise the energy level and transform the reactants to their transition state. The values of

entropy of activation (ΔS^\ddagger)

3were negative in all corresponding reactions, which is in conformance with previous studies [17–20]. The negative

values of ΔS^\ddagger

3may arise as a result of associative mechanism, which means that the reactant species joined each other to form transition state along the reaction pathway. Hence, the transition state has more ordered structure Table 3 The

Arrhenius parameters of non-catalytic transesterification and esterification. Reaction model Feedstock T ($^{\circ}\text{C}$)

3Ea (kJ/mol) A (min⁻¹)

R2 References Single-step transesterification Forward esterification Reverse esterification Single-step transesterification Single-step Transesterification Single-step transesterification Single-step transesterification Single-step transesterification Single-step transesterification Esterification Esterification Forward esterification Reverse esterification Tannery waste Palm olein

18oil Rapeseed oil RBD palm oil Jatropha oil Karanja oil Sunflower oil Linseed oil Castor oil

Oleic acid PFADc Free fatty acids 250–325 36.01 28.38 5.66 270–350 81.37 200–500 67.76a 350 105b
 200–400 11.37 10.54 250–350 3.00 200–350 46.50 35.00 200–250 24.80 230–290 17.74 250–320 72 23.2
 1176.67 1372.98 2.11 not reported 3.21 × 10⁵ a Not reported 101.02 78.21 Not reported 4.68 32.4 2.90 2.12
 5.00 × 10⁵ 7.90 0.92 0.97 0.99 0.98 0.89 0.96 0.99 0.99 – 0.99 0.99 0.99 0.97 0.98 0.97 This work [18] [19]
 [27] [29] [36] [35] [37] [17] [28] a Calculated from k values

4 in the temperature range of 270– 487 °C listed in Table

1 of Ref. [19]. b Determined from numerical analysis by Levenberg–Marquardt algorithm. c Palm Fatty Acid Distillate, a by-product from crude palm oil refinery with FFA contents of 87.3%. Table 4 The Eyring activation parameters of transesterification and esterification reactions at supercritical condition. Reaction T (K) ΔG^\ddagger (kJ/mol) ΔH^\ddagger (kJ/mol) ΔS^\ddagger (J/mol K) R² Transesterification 523.15 548.15 573.15 598.15 153.64 159.48 165.32 171.16 31.37 –233.71 0.90 Forward esterification 523.15 548.15 573.15 598.15 145.34 151.15 156.96 162.77 23.74 –232.43 0.95 Reverse esterification 523.15 548.15 573.15 598.15 150.79 157.94 165.10 172.26 1.02 –286.28 0.97 than the reactants in the ground state,

3 accordingly a negative value of entropy of activation. The degree and spontaneity of

chemical reactions can be denoted from the

22 Gibb's free energy of activation

(ΔG^\ddagger) parameter. As denoted in Table 4, the

22 positive values of ΔG^\ddagger were observed in all reactions,

revealing endergonic and unspontaneous characteristics. Furthermore, the positive value of ΔG^\ddagger

3 may be ascribed to the higher energy level in the transition state than in the

reactant species. and endothermic characteristics of transesterification and esterification at supercritical condition.

6 Acknowledgments The Australian Research Council (ARC) is acknowledged for financial support under the ARC Future Fellow Program (FT100100879).

4. Conclusions References The production of biodiesel from leather tanning waste with high free fatty acid content by methanolysis reaction at supercritical condition has been demonstrated in this work. The supercritical transesterification experiments were conducted at 12 MPa and methanol/fatty oil molar ratio of 40:1 with variation of temperatures from 250 °C to 325 °C. The proposed semi-empirical kinetic model of formation of fatty acid methyl esters incorporating reversible esterification and non-reversible transesterification fitted well with experimental results. Nonlinear regression fitting can be used as an alternative technique for determining reaction rate constants rather than applying numerical analysis with a complex algorithm and an elaborate computation. The activation energy of transesterification, forward and reverse esterification was 36.01 kJ/mol, 28.38 kJ/mol, and 5.66 kJ/mol, respectively. Thermodynamic activation parameters of the reactions (i.e. ΔG^\ddagger , ΔH^\ddagger , and ΔS^\ddagger) were evaluated based on activation complex theory (ACT) and positive values of ΔG^\ddagger and ΔH^\ddagger and negative values of ΔS^\ddagger were obtained, revealing the unspontaneous, endergonic, [1] N.S. Kasim, T.H. Tsai, S. Gunawan, Y.H. Ju, Biodiesel production from rice bran oil and supercritical methanol, *Bioresource Technology* 100 (2009) 2399–2403. [2] F.O. Licht, World ethanol and biofuels report, in: L.S. Brown (Ed.), *World on the Edge: How to Prevent Environmental and Economic Collapse*, W.W. Norton & Co, New York, 2011, p. 265. [3] D.D.C. Barbosa, T.M. Serra, S.M.P. Meneghetti, M.R. Meneghetti, Biodiesel production by ethanolysis of mixed castor and soybean oils, *Fuel* 89 (2010) 3791–3794. [4] R. Chakraborty, S. Bepari, A. Banerjee, Transesterification of soybean oil catalyzed by fly ash and egg shell derived solid catalysts, *Chemical Engineering Journal* 165 (2010) 798–805. [5] A.K. Endalew, Y. Kiros, R. Zanzi, Inorganic heterogeneous catalysts for biodiesel production from vegetable oils, *Biomass and Bioenergy* 35 (2011) 3787–3809. [6] E. Alptekin, M. Canakci, Optimization of pretreatment reaction for methyl ester production from chicken fat, *Fuel* 89 (2010) 4035–4039. [7] J.M. Encinar, N. Sanchez, G. Martinez, L. Garcia, Study of biodiesel production from animal fats with high free fatty acid content, *Bioresource Technology* 102 (2010) 10907–10914. [8] M.J. Haas, T.A. Foglia, Alternate feed stocks and technologies for biodiesel production, in: G. Knothe, J. Krahl, J.V. Gerpen (Eds.), *Biodiesel Handbook*, AOCS Press, Illinois, 2005, pp. 42–61. [9] E. Alptekin, M. Canakci, H. Sanli, Evaluation of leather industry wastes as a feedstock for biodiesel production, *Fuel* 95 (2012) 214–220. [10] K. Kolomaznik, M. Barinova, T. Furst, Possibility of using tannery waste for biodiesel production, *Journal of the American Leather Chemists Association* 104 (2009) 177–182. [11] H. Ozgunay, S. Colak, G. Zengin, O. Sari, H. Sarikahya, L. Yuceer, Performance and emission study of biodiesel from leather industry pre-fleshings, *Waste Management* 27 (2007) 1897–1901. [12] M. Canakci, The potential of restaurant waste lipids as biodiesel feedstocks, *Bioresource Technology* 98 (2007) 183–190. [13] Y. Warabi, D. Kusdiana, S. Saka, Reactivity of triglycerides and fatty acids of rapeseed oil in supercritical alcohols, *Bioresource Technology* 91 (2004) 283–287. [14] R. Sawangkeaw, K. Bunyakiat, S. Ngamprasertsith, A review of laboratory-scale research on lipid conversion to biodiesel with supercritical methanol (2001–2009), *Journal of Supercritical Fluids* 55 (2010) 1–13. [15] E. Minami, S. Saka, Kinetics of hydrolysis and methyl esterification for biodiesel production in two-step supercritical methanol process, *Fuel* 85 (2006) 2479–2483. [16] S.A. D'ippolito, J.C. Yori, M.E. Iturria, C.L. Pieck, C.R. Vera, Analysis of a two-step, noncatalytic, supercritical biodiesel production process with heat recovery, *Energy and Fuels* 21 (2007) 339–346. [17] H.J. Cho, S.H. Kim, S.W. Hong, Y.K. Yeo, A single step non-catalytic esterification of palm fatty acid distillate (PFAD) for biodiesel production, *Fuel* 93 (2012) 373–380. [18] C.S. Choi, J.W. Kim, C.J. Jeong, H. Kim, K.P. Yoo, Transesterification kinetics of palm olein oil using supercritical methanol, *Journal of Supercritical Fluids* 58 (2011) 365–370. [19] D. Kusdiana, S. Saka, Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol, *Fuel* 80 (2001) 693–698. [20] H. He, S. Sun, T. Wang, S. Zhu, Transesterification kinetics of soybean oil for production of biodiesel in supercritical methanol, *Journal of the American Oil Chemists Society* 84 (2007) 399–404. [21] S.B. Glisic, A.M. Orlovic, Modelling of non-catalytic biodiesel synthesis under sub and supercritical conditions: the influence of phase distribution, *Journal of*

Supercritical Fluids 65 (2012) 61–70. [22] K. Bunyakiat, S. Makmee, R. Sawangkeaw, S. Ngamprasertsith, Continuous production of biodiesel via transesterification from vegetable oils in supercritical methanol, Energy and Fuels 20 (2006) 812–817. [23] S. Espinosa, T. Fornari, S.B. Bottini, E.A. Brignole, Phase equilibria in mixtures of fatty oils and derivatives with near critical fluids using the GC-EOS model, Journal of Supercritical Fluids 23 (2002) 91–102. [24] T. Srinophakun, B. Phithakchokchai, Phase equilibrium modeling of triglycerides in supercritical fluids, Journal of Chemical Thermodynamics 43 (2011) 471–478. [25] T. Holderbaum, J. Gmehling, PSRK: a group contribution equation of state based on UNIFAC, Fluid Phase Equilibria 70 (1991) 251–265. [26] V.F. Marulanda, G. Anitescu, L.L. Tavlarides, Investigations on supercritical transesterification of chicken fat for biodiesel production from low-cost lipid feedstocks, Journal of Supercritical Fluids 54 (2010) 53–60. [27] E.S. Song, J.w. Lim, H.S. Lee, Y.W. Lee, Transesterification of RBD palm oil using supercritical methanol, Journal of Supercritical Fluids 44 (2008) 356–363. [28] R. Alenezi, G.A. Leeke, J.M. Winterbottom, R.C.D. Santos, A.R. Khan, Esterification kinetics of free fatty acids with supercritical methanol for biodiesel production, Energy Conversion and Management 51 (2010) 1055–1059. [29] V. Rathore, G. Madras, Synthesis of biodiesel from edible and non-edible oils in supercritical alcohols and enzymatic synthesis in supercritical carbon dioxide, Fuel 86 (2007) 2650–2659. [30] H.Y. Shin, S.M. Lim, S.Y. Bae, S.C. Oh, Thermal decomposition and stability of fatty acid methyl esters in supercritical methanol, Journal of Analytical and Applied Pyrolysis 92 (2011) 332–338. [31] J. Quesada-Medina, P. Olivares-Carrillo, Evidence of thermal decomposition of fatty acid methyl esters during the synthesis of biodiesel with supercritical methanol, Journal of Supercritical Fluids 56 (2011) 56–63. [32] H. Eyring, The activated complex in chemical reactions, Journal of Chemical Physics 3 (1935) 63–71. [33] K.J. Laidler, Chemical Kinetics, 3rd ed., Harper-Collins Publishers, New York, 1987. [34] M.G. Evans, M. Polanyi, Some applications of the transition state method to the calculation of reaction velocities, especially in solution, Transactions of the Faraday Society 31 (1935) 875–894. [35] M.N. Varma, G. Madras, Synthesis of biodiesel from castor oil and linseed oil in supercritical fluids, Industrial and Engineering Chemistry Research 46 (2007) 1–6. [36] G. Madras, C. Kolluru, R. Kumar, Synthesis of biodiesel in supercritical fluids, Fuel 83 (2004) 2029–2033. [37] N.H. Joelianingsih, S. Hagiwara, Y. Sagara, T.H. Soerawidjaya, A.H. Tambunan, K. Abdullah, Performance of a bubble column reactor for the non-catalytic methyl esterification of free fatty acids at atmospheric pressure, Journal of Chemical Engineering of Japan 40 (2007) 780–785. Author's personal copy L.K. Ong et al. / J. of Supercritical Fluids 75 (2013) 11–20 Author's personal copy L.K. Ong et al. / J. of Supercritical Fluids 75 (2013) 11–20 13 14 Author's personal copy L.K. Ong et al. / J. of Supercritical Fluids 75 (2013) 11–20 Author's personal copy L.K. Ong et al. / J. of Supercritical Fluids 75 (2013) 11–20 15 16 Author's personal copy L.K. Ong et al. / J. of Supercritical Fluids 75 (2013) 11–20 Author's personal copy L.K. Ong et al. / J. of Supercritical Fluids 75 (2013) 11–20 17 18 Author's personal copy L.K. Ong et al. / J. of Supercritical Fluids 75 (2013) 11–20 Author's personal copy L.K. Ong et al. / J. of Supercritical Fluids 75 (2013) 11–20 19 20 Author's personal copy L.K. Ong et al. / J. of Supercritical Fluids 75 (2013) 11–20