



Transesterification of leather tanning waste to biodiesel at supercritical condition: Kinetics and thermodynamics studies

L.K. Ong^{a,1}, A. Kurniawan^{a,1}, A.C. Suwandi^{a,1}, C.X. Lin^b, X.S. Zhao^{b,*}, S. Ismadji^{a,**}

^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

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ABSTRACT

Catalyst-free transesterification of leather tanning waste with high free fatty acid (FFA) content at supercritical condition was reported in this work. The experiments were performed in batch system at various temperatures (250–325 °C) under constant pressure of 12 MPa and methanol/fatty oil molar ratio of 40:1 for 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_E') were determined by nonlinear regression fitting. Thermodynamic activation parameters of the reactions 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, forward and reverse esterification reactions was 36.01 kJ/mol, 28.38 kJ/mol, and 5.66 kJ/mol, respectively.

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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].

Biodiesel is composed of a mixture of alkyl esters that mostly produced by esterification and/or transesterification (or alcoholysis) of various lipid feedstocks such as vegetable oils [3–5] and

animal fats [6,7] with methanol or ethanol as the reacting alcohol. 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 vegetables oils (e.g., palm oil, coconut 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 an alkaline catalyst to directly convert triglyceride into alkyl ester. However, the alkali-catalyzed transesterification is very sensitive to 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

* 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: 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.

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 (SC-TE) has been highlighted as an emerging technology for biodiesel production from various feedstocks including leather-tanning waste. This method is able to completely convert fatty acids in feedstock to alkyl ester in a relatively short time without involving any catalysts and offers simple product separation from the mixture. Furthermore, supercritical transesterification method can tolerate FFA and water contents in the feedstock up to 30 wt.% and 36 wt.%, respectively [13]. In general, the production of biodiesel from vegetable oils or animal fats by supercritical alcohol transesterification was conducted at temperatures of 250–400 °C, pressures of 10–45 MPa, and molar ratio of alcohol 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 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

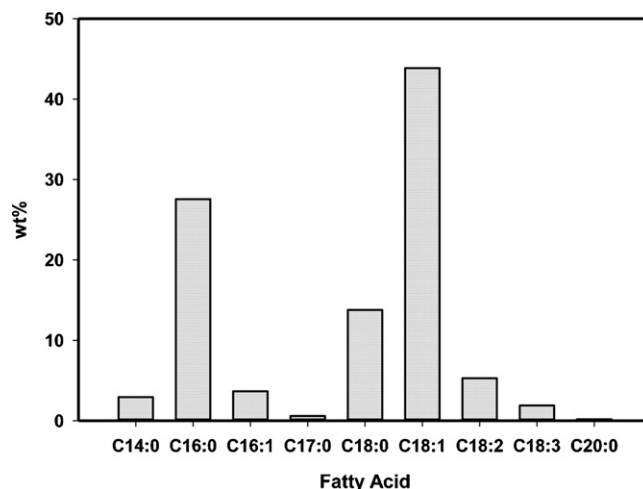


Fig. 1. Fatty acid compositions of leather tanning waste.

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).

2. 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 °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 capillary column (30 m × 0.25 mm × 0.10 μm) and a flame ionization detector (FID) and the result are 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, respectively.

2.2. Supercritical methanol transesterification

The schematic of apparatus set-up for supercritical transesterification experiments is displayed in Fig. 2. The reaction system consists of a 50 ml high pressure batch reactor, fittings and tubings, which made from 316-grade stainless steel, a K-type thermocouple for sensing temperature, a pressure gauge, and an external electric heater. The reactor was also connected to a cylinder gas containing nitrogen (99.99%) at 15 MPa.

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