



Synthesis of palm oil-based trimethylolpropane ester as potential biolubricant: Chemical kinetics modeling

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H I G H L I G H T S

- ▶ Chemical transesterification of palm oil methyl esters (POMEs) was investigated.
- ▶ The possible effect of reversible reactions was considered.
- ▶ A comparison with other kinetic models obtained was conducted.
- ▶ Extended kinetic model has been reinforced using a new set of experimental data.
- ▶ The approaches using numerical simulation provided congruent information.

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A B S T R A C T

The environmental impact of large amounts of lubricants from mineral oils has become an increasingly important issue. The use of rapidly biodegradable lubricants, vegetable products as well as modified vegetable oil esters, could significantly reduce the environmental pollution compared to mineral oils. A kinetic/mathematical model describing chemical transesterification of palm oil-based methyl esters (POMEs) with trimethylolpropane (TMP) to polyol esters has been developed. The kinetics of the transesterification reaction was modeled as three distinct elementary reversible series-parallel reaction mechanisms. The model considers the transesterification reaction to take place in both forward and reverse directions. The resulting kinetics equations were solved using *ode45* solver function in MATLAB, where the rate constants of the proposed kinetic model were determined by minimization of errors based on the optimum criteria of statistical analysis and by comparing the component concentrations at maximum and at equilibrium. The forward and reverse rate constants of all three steps involved in the transesterification reaction were reported. The validity of the model was tested by comparing the observed experimental values with the theoretical calculated data. A good correlation between simulated results and experimental data was observed, confirming that the model was able to predict the rate constants with plausible accuracy. The new proposed kinetic model would facilitate the design of a pilot-scale chemical reactor for the transesterification of POME with TMP to obtain palm oil-based polyol esters as a potential biolubricant.

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1. Introduction

In recent years, worldwide concern about the environmental issues and energy savings are demanding an urgent need for development in research to discover increasingly advanced lubricants as the alternatives to mineral base oils, a non renewable natural source [1]. Lubricants are used in all aspects of manufacturing industry, transport and domestic life such as in automotive, avia-

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tion, metalworking and refrigeration. Among the most used lubricants, the engine oils of automotive industry are the most important. The alternatives to conventional engine oil must be environmentally acceptable, economically improved, excellent low-temperature fluidity and cold starting, high-temperature oxidation resistance, renewable and technically feasible [2]. Many of these basic requirements are satisfied by biolubricant that could be derived from various plant oils sources by chemical modification. Biolubricant has many advantages over mineral oil such as being renewable with higher lubricity, viscosity indices, shear stability, dispersancy, lower volatility and biodegradable which decreased environmental hazards [3].

Plant oils will compete for a share of the emerging biolubricants market with mineral oil-based lubricants based on a number of market reports [4–6]. Several studies showed the improved performance of the chemically modified vegetable oil-based synthetic esters for lubrication purposes [7–12]. The native oils have obviously some drawbacks such as poor oxidative stability, sensitivity to hydrolysis and low-temperature fluidity. Biolubricants derived from branched neopentyl polyols such as trimethylolpropane (TMP), neopentyl glycol (NPG) or pentaerythritol have received wider acceptance due to its much improved performance where the glycerol as the alcohol component in native oils has been replaced by polyols. Moreover, polyol esters have a good resistance from attacks by water molecules [13]. Among three polyols, TMP have a moderate price level, relatively low melting point and hence it is being used extensively to produce environmental acceptable lubricants.

In Malaysia, palm oil methyl esters (POMEs) and TMP are used as the raw materials in the synthesis of vegetable-oil synthetic esters to produce biolubricant. Malaysia is one of the world's major producers of oils and fats and has been the second largest palm oil producer, after Indonesia, since 2006 [14]. With the advantage of being at the highest position in the world in terms of oils and fats production, palm oil products such as POME have been utilized as green biodiesel with positive results that are competitive with petroleum diesel [15]. This would provide an additional advantage to the biolubricant industry, because the POME is readily available from the biodiesel industry. Furthermore, the polyol esters that are produced would have improved lubrication properties compared to the original palm oil. A published study has shown that a batch scale up production of palm oil-based synthetic lubricant in a mini pilot reactor was successful and could be used to a full scale biolubricant production [16].

Kinetics of transesterification to produce palm oil-based lubricants is similar to the kinetics of the vegetable oils to methyl esters since the reaction mechanism involves three consecutive competitive reversible reaction steps [17]. Since transesterification reactions have been studied for many vegetable oils such as soybean, rapeseed, sunflower, palm and safflower seed [18–20] there are many published reports on the reaction kinetics of vegetable oils to methyl esters. This will provide parameters, primarily concentrations distributions as the key of interest in this study that is capable to estimate the extent of the reaction at any time in selective conditions. Modelling and simulation of chemical kinetics is essential in the design of a scale-up experiment in order to analyze the details of the reaction kinetics rather than running several prototype experiments for optimization of the product yield that would incur additional costs such as raw material costs, equipments costs and maintenance costs. Thus, it is simpler to assess and study the kinetics of this complex reaction system with a suitable numerical simulation that can predict the products distribution for the palm oil-based synthetic lubricants to ensure the economic viability for production of the lubricants.

An attempt made by Yunus et al. [17] to simulate a kinetic model using an integral method was acceptable, but the approach was only valid if all the reactions involved were irreversible. An alternative approach was to use a nonlinear regression method via MATLAB [21], a modified reversible kinetic model based from literature [22], where Laplace transformation was used to solve the rate equations and compute the rate constants. Nevertheless, the model proposed by Kamil and Yusup [21] was only validated using the literature data [17] and only applicable during the initial stages of the reaction (1–15 min). This is not satisfactory because the transesterification between POME and TM took 1 h to complete the reaction. The main problem with the kinetics models developed so far is their inability to predict the concentration profiles towards the end of reaction (equilibrium). Hamid et al. [23]

proposed another approach, where a non-stiff solution of a Runge–Kutta method of order 4 and 5 in MATLAB was used to predict the product concentrations versus time profiles. The aim of this work was to provide more information about the transesterification kinetics to extend the range of the previously published kinetic model [23]. The approach was validated using a new set of experimental data and the experimental data from the literature. In addition, comparisons were also made, with the available kinetic models [17,21].

2. Materials and methods

2.1. Raw materials

Palm oil methyl esters (POMEs) were obtained from Carotech (Malaysia) Sdn. Bhd. Trimethylolpropane, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol was purchased from Fluka Chemie GmbH (Switzerland) and alkaline catalyst, liquid sodium methoxide was obtained from Merck-Schuchardt (Germany). Other chemicals such as ethyl acetate and N, O-Bis (trimethylsilyl) trifluoroacetamide (BSTFA) were purchased from Fluka Chemie GmbH.

2.2. Fractionation

Approximately 50% of the original palm oil methyl esters (POMEs) were fractionated via vacuum distillation at temperatures of 170–180 °C under vacuum pressures of 1.0–1.5 mbar. The bottom product, which contains high-oleic POME, was dried overnight in an oven at 105 °C to decrease the moisture content, and 200 g of it was used as the starting material in the synthesis of high-oleic palm oil-based polyol esters.

2.3. Transesterification

Transesterification reactions were performed in a 500 mL three-neck flask equipped with a thermometer, a sampling port and a reflux condenser. The condenser was connected to a vacuum line equipped with a relief valve, accumulator and vacuum trap. The reactor was filled with a known amount of TMP at a molar ratio of high-oleic POME to TMP of 10:1 as reported in our previous study [17]. The reactant was then heated and stirred with a magnetic stirrer in the temperature-controlled oil bath while under vacuum until the TMP melted at about 60 °C. Then the anhydrous high-oleic POME was added to a flask, and the mixture was heated to the operating temperature of 110 °C under vacuum pressure of 1–1.5 mbar. The liquid sodium methoxide catalyst was then added at a fixed 2% w/w based on the total mass of reactants. The vacuum was applied gradually to avoid spillover of the reaction materials. Samples were taken at specific time intervals, where each sample was collected in a small, capped vial and was immediately refrigerated at 2 °C for products analysis. Finally, the reaction mixture was cooled to room temperature and vacuum filtered to remove the catalyst and solid materials formed during the reaction.

2.4. Analysis

In this study, gas chromatography (GC) analysis was used to analyze the products of transesterification of high-oleic POME and TMP to polyol esters, because it provides distinct separation of polyol esters and dissolution according to carbon number. Briefly, 0.2 mL of the reaction sample was added to an auto-sampler vial. The sample was diluted with 1 mL of ethyl acetate and then swirled for several minutes. BSTFA (0.5 mL) was added to the mixture and swirled again for several minutes. These steps were repeated for the other reaction samples. The prepared sam-

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