



Full Length Article

Kinetic and thermodynamic of heterogeneously K_3PO_4/AC -catalysed transesterification via pseudo-first order mechanism and Eyring-Polanyi equation



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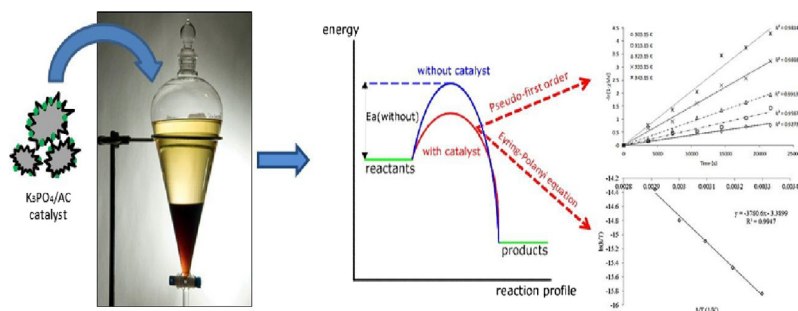
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GRAPHICAL ABSTRACT



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ABSTRACT

The use of carbon-based catalysts has drawn so much interest in biodiesel production due to improved reaction performance. However, there was lack of comprehensive studies in term of its kinetic and thermodynamic perspective. Therefore, a methodical study is essential to uncover the influence of the carbon catalyst with respect to reaction rate and yield. This study represents kinetic and thermodynamic of heterogeneously K_3PO_4/AC -catalysed transesterification. It was done correspondingly via pseudo-first order mechanism and Eyring-Polanyi equation, whereby, under the optimal reaction temperature of 333.15 K, all data have fitted satisfactorily in both models with resulted R^2 of 0.99, respectively. Activation energy (E_a) and Gibbs free energy (ΔG) were calculated as 34.2 kJ mol^{-1} and $-33.68 \text{ kJ mol}^{-1}$, indicating the reaction was exergonic and spontaneous at high temperature.

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1. Introduction

In the search for new energy sources, biodiesel has been a standout among potential biofuels that could reduce our reliance on non-renewable fuels, as it is suitable as a substitute for petroleum diesel due to its guaranteeing offers such as low carbon emission, excellent lubricity, and biodegradability [1]. Transesterification is the reaction where a molecule of triglyceride reacts with methanol to form a structure of methyl esters and by-product glycerol [2]. The utilization of homogeneous catalysts such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) dominate the biodiesel industry due to its enhanced production process, high availability and cheap prices [3]. However, as reported in recent works, the uses of heterogeneous catalysts are gaining interest among researchers for its desirable qualities such as reusability and improved catalytic activity [4,5]. The catalyst exists in an alternate phase of the reaction mixture, making it easier to be recovered and produce higher esters content. Industrial synthesis reactions for biodiesel have generally been carried out over homogeneous catalysts but the use of solid catalysts instead of homogeneous liquid catalysts reduce the cost of biodiesel synthesis.

Generally, in biodiesel development, carbon is adopted as catalyst-support and serves as an adsorbent for purification [6,7]. According to Konwar et al. [8], use of carbon-based catalyst produces a high fuel yield for low alcohol usage at a short period and mild reaction temperature, which, however, involved intricate synthesis procedure compared to homogeneous catalyst and, in some cases, expensive to be made due to costly chemicals used. Recently, development of catalyst using biomass as carbon precursor for more economical biodiesel production has been gaining attraction [9]. During its early development, researchers focused on the synthesis of the acid catalyst for high FFA-contained oils [9]. Yet, use of the acidic catalyst led to time-consuming reaction for triglycerides-predominated feedstocks (low FFA-contained oils), which were carried out at high temperature using a substantial amount of alcohol [10]. These difficulties, however, can be overcome by employing base catalysts, which offer outstanding catalytic activity and stability, also produce higher yield at shorter and milder conditions [11].

A great deal of research has been conducted on heterogeneous catalyst development, but only few were carried out to comprehend reaction's kinetic and thermodynamic. As previously studied by Ahmad Farid et al. [12], K_3PO_4/AC catalyst was successfully developed, characterised and optimised for biodiesel production from waste cooking oil. By using these data obtained as baseline values, a further investigation concerning kinetic and thermodynamic was carried out. In this research, kinetic (rate constant, activation energy and pre-exponential) and thermodynamic (Gibbs free energy) of the heterogeneous reaction was calculated according to pseudo-first order mechanism and Eyring-Polanyi equation, respectively. Comparison with other reported solid catalysts for biodiesel production was also discussed.

2. Materials and methods

2.1. Materials

Oil palm empty fruit bunch (OPEFB) sample was collected from FELDA Serting Hilir Palm Oil Mill near Negeri Sembilan, Malaysia. Waste cooking oil was collected from a residential area located around Seri Kembangan Selangor, Malaysia. Potassium hydroxide (KOH) (95.5%) and analytical grade *n*-hexane (99.9%) were supplied by Merck, USA. Methanol (95%) was purchased from Friendemann Schmidt Chemical, Australia. Potassium phosphate tri-basic (K_3PO_4) (98%) was purchased from Sigma-Aldrich, USA. Nitrogen gas (N_2) (99%) and helium gas (He) (99%) were purchased from Malaysian Oxygen Berhad (MOX). Supelco FAME mix standard and methyl heptadecanoate (99%) were purchased from Sigma-Aldrich, Germany.

2.2. Characterization of feedstock oil

Moisture and free fatty acids (FFA) content were determined according to the standard method of MPOB p2.1 (2004) and AOCS Ca 5a-40 (1997), respectively [13,14]. The fatty acids profile of the oil sample was performed according to the International and European Standards ISO 5509 (2000) and EN 14103 (2003) by Hewlett Packard 5890 gas chromatograph equipped with a Hewlett Packard 3396 Series II integrator and 7673 controller, flame ionization detector with split injection (Agilent Technologies Inc., Santa Clara, CA). Supelco capillary column (SP-2560) (100 m × 0.25 mm × 0.20 m) was used to separate the compound in the oil sample. While helium gas was used as the carrier gas at a flow rate of 0.5 ml min⁻¹ [15].

2.3. The molecular weight of feedstock oil

An amount of oil was placed inside the round bottom flask equipped with a reflux condenser. Ethanolic KOH solution was added before refluxed for 1 h. Once completed, titration was carried out using phenolphthalein and HCl. As for blank, titration was conducted without the presence of waste cooking oil in the mixture. The saponification value was calculated according to Eq. (1). (AOCS Method cd 3-25). Meanwhile, the average molecular weight of oil can be estimated according to Eq. (2).

$$SV = \frac{56.1 N (V_b - V_s)}{W} \quad (1)$$

$$\text{Average molecular weight} = \frac{56.1 \times 1000 \text{ mg} \times 3}{SV} \quad (2)$$

where V_b and V_s are the volumes of HCl solution for blank and oil sample respectively. While N is normality of HCl, W is the weight of oil sample and SV stands for the saponification value.

2.4. Synthesis of K_3PO_4/AC catalyst

As mentioned in the earlier study [12], the carbon precursor was prepared using OPEFB through carbonization and KOH-activation at 973.15 K for 2 h under a continuous flow of N_2 . The activated carbon obtained was then neutralized with 0.1 M HCl and hot water until pH of 6–7, and subsequently dried at 378.15 K for 16 h. Following that, impregnation and calcination were conducted with activated carbon to K_3PO_4 weight ratio of 1:1 and calcined for 3 h in an inert environment, respectively. An appropriate calcination temperature was selected according to thermal stability baseline, which was studied via thermogravimetric (TGA) analysis. This is important to avoid decomposition of the impregnated catalyst during calcination, which could lead to the reduction of catalytic strength.

2.5. Transesterification

The reaction was carried out using 1 L three-neck round-bottom flask equipped with a magnetic stirrer bar and reflux condenser on a digital heating mantle (Misung Scientific Co.). Esters content was analyzed using gas chromatography (Shimadzu GC-14C) equipped with flame ionization detector (GC-FID) and polar RTX65 capillary column (30 m × 0.5 mm × 0.25 μm), and the esters content was determined by Eq. (3). The effect of reaction parameters, e.g. varying K_3PO_4 concentration (0.25:1–1:1), methanol to oil molar ratio (3:1–15:1), catalyst loading (1–6 wt%), and reaction temperature (303.15–343.14 K) was investigated by sampling at an hourly interval during 6 h reaction time. The extensive description of the method used and result obtained was well-elaborated in our previous study [12].

$$\text{Methyl esters content (\%)} = \frac{\text{Total mole of methyl esters}}{\left(\frac{\text{Weight of WCO}}{\text{Molecular Weight of WCO}} \right) \times 3} \times 100\% \quad (3)$$

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