



## 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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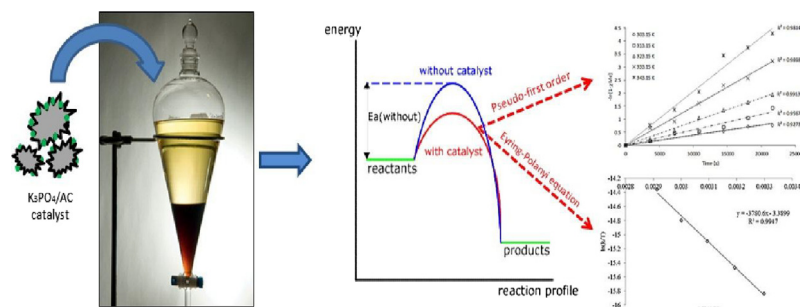
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## GRAPHICAL ABSTRACT



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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 ( $\Delta G$ ) were calculated as  $34.2 \text{ kJ mol}^{-1}$  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 Seriting 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<sup>-1</sup> [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].

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

**Table 1**  
Characterization of feedstock oil.

Parameter	Unit	Content
Moisture	%	3.67
FFA (as Oleic)	wt%	0.98
Saponification value	mgKOH/g	202.69
Molecular weight	g/mol	830.33

### 3. Results and discussion

#### 3.1. Characterization of feedstock oil

Characterization of waste cooking oil was conducted to measure acid value, moisture, and average molecular weight; the results are presented in Table 1. In transesterification process, high amount of FFA leads to saponification, thereby reducing the biodiesel quality and reaction yield [16]. However, according to the result, FFA value did not exceed the limit of 1 wt%, which not exceeding the requirement of preliminary esterification. Repeated usage of cooking oil increased the moisture content, which must be removed, as it could cause saponification [17]. Prior to transesterification, the waste cooking oil was dried at 378.15 K for 1 h to remove the residual moisture. Meanwhile, the saponification value obtained was 202.69 mg KOH/g and, therefore, the molecular weight calculated was 830.33 g/mol. This value of molecular weight was used to calculate the amount of alcohol required for transesterification as it is based on the pre-determined molar ratio (number of mole of methanol to number of mole of feedstock oil).

#### 3.2. Calcination temperature

Calcination temperature affects the catalyst performance and restores its catalytic activity [18]. Calcination of catalyst was carried out in limited supply of oxygen, achieved by flushing with N<sub>2</sub> flow. Temperatures ranging from 324.15 to 1272.15 K were experimented, which pre-determined using thermogravimetric analysis (TGA). As shown in Fig. 1, thermal degradation behavior of the sample was recorded in 4 stages. First degradation slope indicates loss of water absorbed by the sample. Second decomposition slope is likely the depolymerization of hemicellulose, α-cellulose, and lignin. A thermal stable condition at 673.15–973.15 K demonstrates the absence of decomposition behavior, which is suitable for calcination [19]. The third degradation slope indicates the decomposition of the catalyst compound.

#### 3.3. Kinetic studies

##### 3.3.1. Pseudo-first order model

Kinetic of transesterification reactions are well studied by many researchers [20]. Instead of measuring the rate of reaction, it could also describe the phenomena in molecular level [20]. Therefore, by applying the data obtained by Ahmad Farid et al. [12] as baseline values, the rate of methyl esters synthesis using K<sub>3</sub>PO<sub>4</sub>/AC catalyst has been analyzed by considering the controlling factors of the reaction. Transesterification using homogeneous catalyst is described as first and second-order reaction mechanisms. By neglecting side-reactions such as saponification and FFA neutralization, conversion of TGs to methyl esters is the controlling step of the reaction [21]. Application of heterogeneous catalyst is defined by a different type of reaction mechanism whereby the controlling step is dependent on adsorption of reactant (alcohol) and desorption of product (glycerol) from the surface of solid catalyst; this is known as mass transfer. Eley–Rideal (ER) and Langmuir–Hinshelwood–Hougen–Watson (LHHW) are the mechanisms that apply theoretically for heterogeneously catalyzed transesterification [22]. Nevertheless, it only applies to solid catalysts that experience no catalyst leaching. In this work, the K<sub>3</sub>PO<sub>4</sub>/AC catalyst lost its catalytic activity by leaching of the catalyst's active species, which made the reaction partially homogeneous. Since the reaction used excess amount of methanol to ensure the right direction of reaction towards completion and prevented from backward reaction, thus the proposed model of pseudo-first order mechanism shall be followed. In this work, the pseudo-first rate constant is derived from these following equations (Eqs. (4)–(11)).

$$-r = -\frac{d[TG]}{dt} = k[TG][ROH]^3 \quad (4)$$

$$K' = k[ROH]^3 \quad (5)$$

$$-r = -\frac{d[TG]}{dt} = k'[TG] \quad (6)$$

$$\ln[TG]_0 - \ln[TG] = k't \quad (7)$$

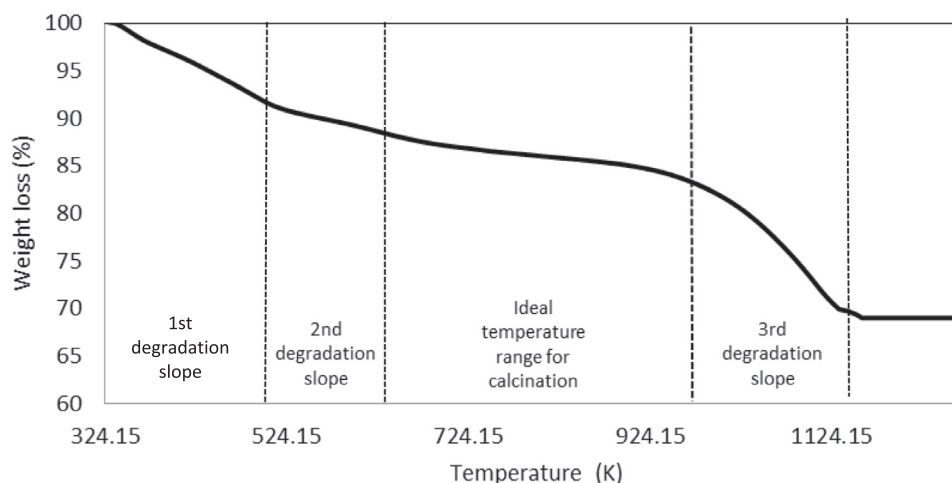
$$\chi_{ME} = 1 - [TG]/[TG]_0 \quad (8)$$

$$[TG] = [TG]_0[1 - \chi_{ME}] \quad (9)$$

$$\frac{d\chi_{ME}}{dt} = k'[1 - \chi_{ME}] \quad (10)$$

$$-\ln[1 - \chi_{ME}] = k't \quad (11)$$

where



**Fig. 1.** Thermal degradation behaviour of K<sub>3</sub>PO<sub>4</sub>/AC catalyst.

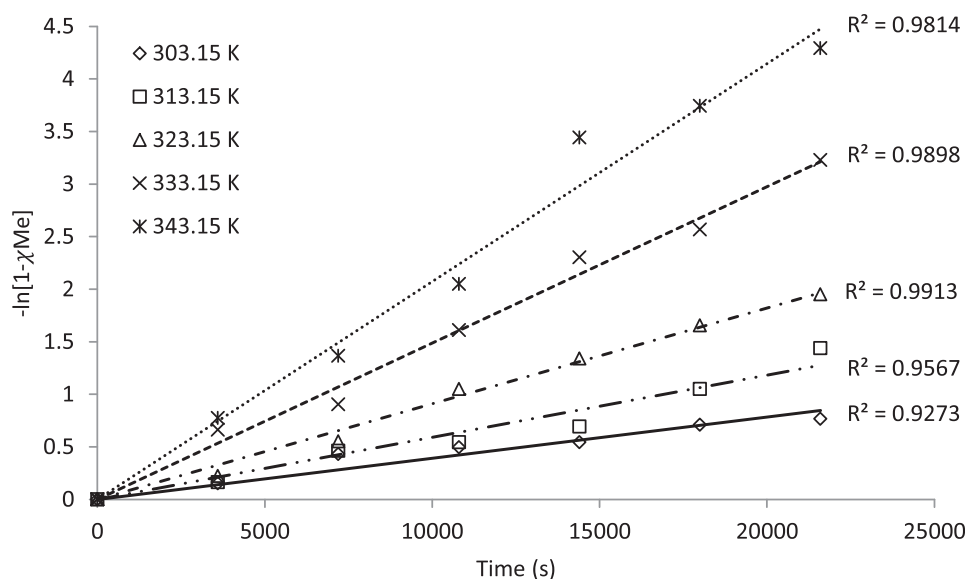


Fig. 2. Plots of  $-\ln(1 - \chi_{ME})$  vs time (s) at different temperatures. The experiment was conducted under reaction condition of 12:1 methanol to oil molar ratio and 5 wt%  $K_3PO_4$ /AC catalyst loading for 6 h.

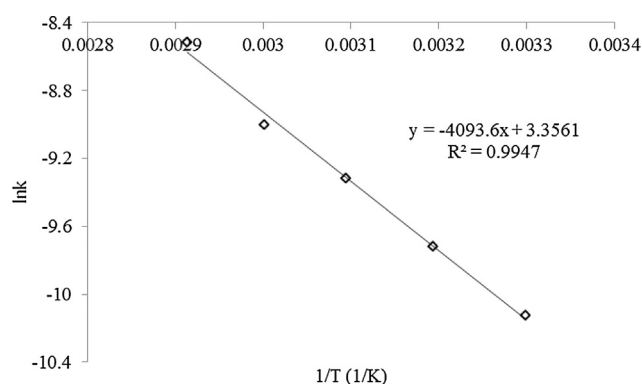


Fig. 3. Plot of  $\ln k$  (1/s) against  $1/T$  (1/K) for transesterification using  $K_3PO_4$ /AC catalyst.

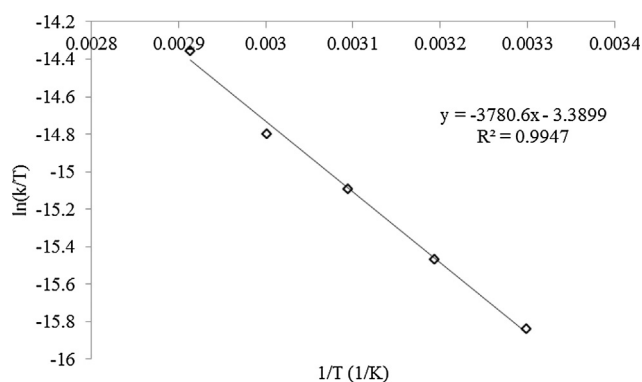


Fig. 4. Erlying-Polanyi plot ( $\ln(k/T)$  against  $1/T$  (1/K)) for Gibbs free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) determination.

[TG]<sub>0</sub> = initial triglyceride concentration  
 [TG] = final triglycerides concentration  
 [ME] = methyl esters concentration  
 [ROH] = methanol concentration  
 $x_{ME}$  = conversion degree of methyl esters  
 $k$  = rate constant  
 $t$  = time

### 3.3.2. Rate constant, activation energy and pre-exponential

The concentrations of esters produced hourly were calculated according to the equations (Eqs. (4)–(11)). By substituting these values into Eq. (12), the rate constant ( $k$ ) was obtained by plotting  $-\ln(1 - \chi_{ME})$  versus reaction time at different temperatures, as shown in Fig. 2. Rate constants ( $k$ ) of 303.15, 313.15, 323.15, 333.15 and 343.15 K were determined to be  $4.0 \times 10^{-5}$ ,  $6.0 \times 10^{-5}$ ,  $9.0 \times 10^{-5}$ ,  $1.0 \times 10^{-4}$  and  $2.0 \times 10^{-4}$ , respectively. Pre-exponential factor ( $A$ ) and activation energy ( $E_a$ ) was obtained by plotting the logarithm of the rate constants ( $k$ ) versus  $1/T$  of absolute temperature using the Arrhenius equation as shown below.

$$k = A \cdot \exp\left[-\frac{E}{RT}\right] \quad (12)$$

$$\ln k = \ln A - \frac{E_a}{RT} \quad (13)$$

where

$$R \text{ (universal gas constant)} = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

Fig. 3 shows a plot of  $\ln k$  vs  $1/T$  that displays a straight line with  $R^2$  value obtained at 0.9947. This signifies the reaction is well fitted to pseudo-first order model. The  $E_a$  and  $A$  were calculated as  $34.20 \text{ kJ mol}^{-1}$  and  $28.68 \text{ s}^{-1}$ , respectively. The activation energy ( $E_a$ ) for transesterification is usually reported between  $33.6$  and  $84 \text{ kJ mol}^{-1}$  [20]. Therefore, in this work, the value of  $E_a$  obtained is in agreement with the reported range.

### 3.3.3. Kinetic model accuracy

In order to estimate the accuracy of the kinetic model, the experimental data were subjected to mean relative errors (MRE) analysis [28,24]. As mentioned in Section 3.2.2, the activation energy ( $E_a$ ) and pre-exponential factor ( $A$ ) calculated were  $34.2 \text{ kJ mol}^{-1}$  and  $28.68 \text{ s}^{-1}$ , respectively, which can be simplified as Eq. (14). By substituting Eq. (14) into Eq. (11), the methyl ester conversion was exemplified as a function of temperature (K) and time (h) in Eq. (15). At different temperatures and times of methyl esters conversion, the projected data using Eq. (15) were in good agreement with the experimental data measured, accounting the MRE calculated only at 2.99%.

$$k = 28.68 \exp\left(-\frac{3.42 \times 10^4}{T}\right) \quad (14)$$

**Table 2**

Previous studies on kinetic and thermodynamic of transesterification.

Feedstock	Catalyst	Activation energy ( $E_a$ ) ( $\text{kJ mol}^{-1}$ )	Gibbs free energy ( $\Delta G$ ) ( $\text{kJ mol}^{-1}$ )	Mean relative errors (MRE) (%)	Reference
WCO	$\text{K}_3\text{PO}_4/\text{AC}$	34.20	$-33.68^a$	2.99	This study
Sunflower oil	Al-Sr nanocatalyst	72.86	$-9.26^b$	–	[20]
Waste cotton seed oil	Zn/CaO	43.00	na	–	[23]
Corn oil	$\text{CaO}/\text{SiO}_2$	49.91	na	5.36	[24]
Jatropha oil	Molybdenum impregnated calcium oxide	66.02	43.62	–	[25]
Algae	$\text{H}_2\text{SO}_4$	14.52	$92.71^c$	–	[26]
Waste cotton seed oil	Li/NiO	74.20	na	–	[27]
WCO	Waste mussel shells (CaO)	79.83	na	11.68	[28]

<sup>a</sup> At optimal reaction temperature of 333.15 K.<sup>b</sup> At optimal reaction temperature of 338.15 K.<sup>c</sup> At optimal reaction temperature of 328.15 K.

$$\chi ME = 1 - \exp\left(28.68 \exp\left(-\frac{3.42 \times 10^4}{T}\right)t\right) \quad (15)$$

### 3.3.4. Thermodynamic

Gibbs free energy ( $\Delta G$ ) of a system plays an important role in understanding the spontaneity of a reaction process. Changes in enthalpy and entropy describe the reaction either through endothermic or exothermic reaction pathways. In this work, Eyring-Polanyi equation was applied to calculate the  $\Delta G$ . By substituting  $\Delta G = \Delta H - T\Delta S$  into Eq. (16), the derived equivalence can be written as Eq. (17) [26].

$$= \frac{k^b T}{h} \exp\left(-\frac{\Delta G}{RT}\right) \quad (16)$$

$$\ln\left(\frac{k}{T}\right) = -\left(\frac{\Delta H}{RT}\right) = \left[\ln K + \ln\left(\frac{k^b}{h}\right) + \frac{\Delta S}{R}\right] \quad (17)$$

where

k = rate constant ( $\text{min}^{-1}$ )

T = absolute temperature (K)

R =  $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$  (universal gas constant) $k^b = 1.38 \times 10^{23} \text{ J K}^{-1}$  (Boltzmann constant)h =  $6.63 \times 10^{-34} \text{ J s}$  (Planck's constant)

K = 1 (transmission coefficient)

By referring to Fig. 4, values of enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) can be calculated according to Eq. (17). Value of  $\Delta G$  was then calculated by substituting the data into  $\Delta G = \Delta H - T\Delta S$ . It was found that  $\Delta H$  and  $\Delta S$  were  $31.43 \text{ kJ mol}^{-1}$  and  $195.45 \text{ J mol}^{-1} \text{ K}^{-1}$  respectively. A positive value of  $\Delta H$  emphasizes the reaction experienced the endothermic pathway whereby the heat energy is absorbed to bring the reactants to transition state towards the products. A negative value of  $\Delta S$  indicates that the system was less disordered, meaning that most of the energy inputs were channeled into the reaction rather than dispersing out. With increment in temperatures, the equilibrium constants increased too, which led to more negative Gibbs free energy obtained. At optimal temperature of 333.15 K, the  $\Delta G$  was calculated at  $-33.68 \text{ kJ mol}^{-1}$ . This signified that the reaction was exergonic in nature and spontaneous at high temperature.

### 3.4. Kinetic and thermodynamic comparison with other catalysts

Several studies were reported on kinetic and thermodynamic of biodiesel production that was calculated via pseudo-first order, as shown in Table 2. From these data, variation in catalysts influenced the kinetic and thermodynamic parameters [20]. Activation energy ( $E_a$ ) is well-defined as the minimum energy for a chemical reaction to initiate whereby the utilization of  $\text{K}_3\text{PO}_4/\text{AC}$  catalyst was found the lowest

compared to other catalysts. However, there were fewer studies carried out on the thermodynamic. The higher the  $\Delta G$ , the more favorable the reaction to be spontaneous. In this present work, it was found that the reaction using  $\text{K}_3\text{PO}_4/\text{AC}$  catalyst experienced an exergonic phase. This type of reaction refers to phenomenon where energy is released as the reaction proceed, making the reaction certainly spontaneous and thermodynamically favorable. Owing to this, Gibbs free energy ( $\Delta G$ ) resulted was negative value ( $\Delta G^\circ < 0$ ).

## 4. Conclusion

The reaction kinetic was in line with pseudo-first order model due to excess of methanol employed and catalyst leaching. The rate constants, activation energy and pre-exponential factor were found to be  $1.0 \times 10^{-4}$  (at optimal temperature of 333.15 K),  $34.2 \text{ kJ mol}^{-1}$  (in agreement with the reported range of  $33.6\text{--}84 \text{ kJ mol}^{-1}$ ) and  $28.68 \text{ s}^{-1}$ , respectively. For thermodynamic parameters, via Eyring-Polanyi equation, the results of  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$  were obtained at  $-33.68 \text{ kJ mol}^{-1}$ ,  $31.43 \text{ kJ mol}^{-1}$  and  $195.45 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively. These signified the reaction was spontaneous at high temperature and exergonic in nature. It was found that the use of the  $\text{K}_3\text{PO}_4/\text{AC}$  catalyst in biodiesel production has the lowest  $E_a$  and the highest  $\Delta G$  in comparison to previous studies.

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