Analyzing esterification kinetics of model bio-oil with ethanol catalyzed by a green catalyst

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Abstract
Fast pyrolysis of biomass is a potential method for the production of bio-oils as a renewable liquid fuel. Bio-oils contain a large number of organic compounds, particularly carboxylic acids, which cause corrosiveness and instability that are troublesome for storage and for the transportation of fuel. Upgrading is an important process to transform bio-oils into high-quality biofuels. Contained organic acids are treated with alcohol to convert them into esters by esterification which may be considered as a good intermediate bio-oil upgrading method. This work presents a kinetic study for 12-tungstosilicic acid (a type of heteropoly acid, HPA) catalyzed esterification of a model bio-oil with ethanol. The main compound of the agro-residue-derived bio-oil was illustrated by oleic acid. The kinetic study was investigated under the molar ratio between ethanol to oleic acid of 9.11:1 and catalyst loading of 10 wt% condition with the varied reaction temperature in the range of 35-75°C. The result showed that a pseudo-first-order was suitable to represent the kinetic model for esterification of the model bio-oil. By fitting between the experimental results and kinetic model, the activation energy (Ea) and the pre-exponential factor (A) were found to be 31.5 kJ/mol and 432 min⁻¹, respectively. This comparatively low activation energy equated to other catalytic esterification proved that the HPA catalyst (12-tungstosilicic acid) considered here was an assured green catalyst for esterification in the bio-oil upgrading process.

Keywords: Bioenergy, Bio-oil upgrading, Catalytic esterification, Chemical conversion, Renewable energy

1. Introduction
In recent times, global attention is attracted to biomass as an important source for alternative renewable energy, particularly in developing countries [1] due to the advantages of its profusion, reproducibility, economic potential, and environmental friendliness [2]. Jatropha curcas is an energy plant that is widely cultivated and considered as one of the inherent feedstocks for the production of biodiesel by transesterification of jatropha oil obtained from seed extraction [3-4]. This generated waste from the...
jatropha seed oil extraction process, jatropha cake, can be further transformed into biofuel as a value-added product [5-6]. Fast pyrolysis is one of the potential techniques for transforming such biomass waste into liquid fuel or bio-oil through a thermochemical process [7-9]. In general, bio-oils consist of water and various oxygenated compounds including acids, alcohols, aldehydes, ketones, and phenols [10-11], which are responsible for unappropriated properties of bio-oil that limited its economical utilization as the fuel in ether stationary and transportation applications including low heating capacity, high water, and oxygen content, instability, high viscosity and corrosiveness [12-13]. The composed acid compounds in bio-oil were considered as the inclined reactive compound, which can cause the viscosity change and instability in bio-oil [14]. Moreover, a large amount of the contained acid compound is responsible for the corrosiveness of bio-oil that limits the direct use of bio-oil in storage and transportation of fuel without upgrading [15]. One of the effective bio-oil upgrading techniques is esterification, which can transform contained acid in bio-oil into ester by treating this compound with alcohol that can reduce the acidity and improve the heating capacity of bio-oil [16]. For esterification investigation, the bio-oil derived from different biomass feedstock such as mallee eucalypts [17], silver grass [18], and risk husks [19] was represented by acetic acid, which was found as the major acid component composed in bio-oil. However, oleic acid was found to be the major acid component composed in bio-oil derived from jatropha cake [20-21] which was rare and few works of literature have reported about it.

Mineral acid catalysts are widely studied and applied for the esterification reaction in the industrial sector due to their high activity and selectivity [22]. However, the equipment corrosion and wastes of the toxic hazardous are still considered as a concerning problem for mineral acid catalyst utilization [23]. In recent times, heteropoly acid (HPA) has gained attention as an interesting and effective catalyst group for esterification through its advantages of low toxicity, volatility, and corrosiveness, while remaining a selectivity and high activity from the high Brønsted acid strength, which can provide fast reaction under mild conditions [24]. The successful HPA catalyzed esterification was reported from Nowakowski et al. [25] for bio-oil upgrading with n-butanol, Prasertpong et al for the upgrading of model bio-oil with ethanol using acetic acid [22] and oleic acid [26] as the model bio-oil.

The kinetic of esterification catalyzed by several catalysts were reported. For HPA catalyzed esterification, a kinetic study was reported for tungstophosphoric acid [27], tungstophosphoric acid/SBA-15 [28], tungstosilicic acid/MCM-41 [5] catalyst for biodiesel production, while the tungstosilicic acid catalyzed esterification was reported for esterification of model bio-oil represented by acetic acid [25]. The pseudo-first-order kinetic model was proposed by Jiang et al. [29] as a suitable model for describing the kinetic for a sulfonated cation exchange resin catalyzed esterification reaction, as well as for a kinetic parameter investigation. Moreover, the evaluation of a kinetic parameter using the fitting of a proposed kinetic model and experimental results were reported by Ilgen [30] for the kinetic study of Amberlyst 46 catalyzed esterification of oleic acid with methanol.

2. Materials and Methods

2.1 Materials

In this work, model bio-oil was represented by oleic acid, which was found as the major component composed in bio-oil derived from the jatropha cake fast pyrolysis process provided by TISTR [21]. Oleic acid (purity ≥ 99%) and 12-tungstosilicic acid (H4SiW12O40•nH2O) were supplied from QRec Co., Ltd, and Sigma Aldrich Co LLC, respectively. Ethanol (purity ≥ 99.5%), pure potassium hydroxide (KOH), isopropanol (purity ≥ 99.8%), and toluene (purity ≥ 99.5%) were provided by RCI Labscan Co., Ltd. The solution of phenolphthalein in ethanol (0.1 M) was purchased from Vechavit Part., Ltd. All chemicals were of analytical reagent grade and were utilized as a received condition without further purification.
2.2 Esterification experiments
The esterification reactions were performed in a 250 mL three-necked flask batch reactor connected with thermocouple and refluxed condenser under 500 rpm continuous mechanical stirring and atmospheric pressure. The initial reacting mixture for the typical experimental run was included oleic acid 40 g, a certain amount of 12-tungstosilicic acid, and ethanol to obtain the catalyst loading of 10 wt% and the molar ratio between ethanol to oleic acid of 9.11:1 condition, which was selected according to the previous work antecedent to this work [26]. A constant temperature oil bath equipped with a temperature control system was used for heating the whole reaction system to maintain the desired reaction temperature in a range of 35-75 °C to obtain sufficient experimental data for the analysis of the kinetic profile [31]. The reaction time was started when the reaction temperature reached the expected value. The samples of reacting mixture were taken every 15 minutes for the first hour of reaction time, then every 1 hour for the last 3 hours to observe the change in conversion of oleic acid during the reaction.

2.3 Analytical methods
The collected samples were analyzed with an acid-base color-indicator titration method according to ASTM D974-04 to determine the acid value (AV) [32]. The approximate 0.1 g of sample was dissolved in 100 mL of 100: 99: 1 solution of toluene, isopropanol, and deionized water, and 0.5 mL of the 0.1M phenolphthalein indicator solution, then titrated with 0.1 M KOH standard solution until the color change of the sample mixture was observed. The acid value of the sample was calculated by Eq 1, where AV is the acid value of the sample (mg of KOH/ g), V is the used volume of KOH solution (mL), M is the concentration of the KOH solution (M), MWKOH is the molecular weight of KOH (56.1 g/mol), and Wsample is the weight of the sample (g).

\[ AV = \frac{V \times M \times MW_{KOH}}{W_{sample}} \]  

(1)

After the determination of the acid value of the samples, the oleic acid conversion was calculated from Eq (2), where AV_i is the acid value of the initial sample and AV_t is the acid value of the taken sample, respectively.

\[ \text{Conversion} = \frac{AV_i - AV_t}{AV_i} \times 100\% \]  

(2)

3. Results and discussion
The HPA catalyzed esterification of oleic acid with ethanol was considered as a reversible reaction. The main products produced from this reaction are ethyl oleate and water, which can be illustrated with Eq. (3)

\[ \overset{\text{Oleic acid}}{\text{RCOOH}} + \overset{\text{Ethanol}}{\text{C}_2\text{H}_5\text{OH}} \xrightarrow{k_1} \overset{\text{Ethyl oleate}}{\text{RCOOC}_2\text{H}_5} + \overset{\text{Water}}{\text{H}_2\text{O}} \]  

(3)

The liquid phase pseudo-second-order kinetic can be used to describe this reaction in the forward and reverse direction [33-34]. The overall reaction rate of this reaction can be represented as Eq. (4) [27, 30, 34], where [A], [B], [C], [D] were the concentration of oleic acid, ethanol, ethyl oleate, and water respectively; X, Y, Z, W denote their reaction order. The reaction rate constant in the forward and reverse direction was denoted by k1 and k2, respectively.
In this work, the molar ratio between ethanol to oleic acid of 9.11:1 was used, which was over the balance value and indicated the higher concentrations of the initial reactant compared with other components. Thus, \( k_1 [B]^y \) can be supposed as the constant [25, 35]. Besides, this esterification reaction was considered as the irreversible reaction since the excess alcohol can push the reaction equilibrium in the forward direction to form the ethyl oleate, which causes the much higher value of the kinetic constant in the forward direction \( (k_1) \) comparing with the kinetic constant in the reverse direction \( (k_2) \) [25, 36].

The reaction rate of this reaction was simplified into Eq. (5), which can be expressed with the pseudo-first-order kinetic model, where \( k = k_1 [B]^y \) [27, 30, 34].

\[
-\frac{d[A]}{dt} = k[A]^n
\]  

(5)

When the initial concentration and conversion of oleic acid are defined as \( [A_0] \) and \( X \), respectively, then the concentration of oleic acid can be defined as Eq. 6 [37]

\[
[A] = [A_0](1 - X)
\]  

(6)

Eq. 5 can be transformed into Eq. 7 [37-38]

\[
-\frac{d[A]}{dt} = -\frac{d\{[A_0](1 - X)\}}{dt} = [A_0] \frac{dX}{dt} = k[A]^n
\]  

(7)

Then:

\[
\frac{dX}{dt} = \frac{k}{[A_0]} \{[A_0](1 - X)\}^n
\]  

(8)

\[
\frac{1}{(1 - X)^n} dX = \frac{k}{[A_0]^{(1-n)}} dt
\]  

(9)

When the reaction order \( (n) = 1 \), Eq. 9 was transformed into Eq. 10 [25, 30, 39]

\[
\frac{1}{(1 - X)} dX = -k dt
\]  

(10)

After the Integrating of Eq. 10, the pseudo-second-order kinetic equation in terms of acid conversion was obtained as illustrated in Eq. 11.

\[
\ln(1 - X) = -kt
\]  

(11)

The obtained experimental data for esterification of oleic acid at various reaction temperatures were fitted with Eq. 11 as displayed in Figure 1 and the reaction rate constant \( (k) \) for the respective reaction temperature was calculated from the slope of the line. The summary of the obtained reaction rate constants and their particular coefficient of determination \((R^2)\) were represented in Table 1.
The reaction rate constant, summarized in Table 1, tended to increase with the increased reaction temperature, which implied that the reaction temperature can increase the rate of the reaction. Since the esterification is an endothermic reaction, the increase of reaction temperature was led to improve molecular motion speed and the mass transfer rate of the reaction system, which can be accelerated the rate of reaction [18, 40]. This result was consistent with the report of Yu et al. [35] for SO$_4^{2-}$/ZrO$_2$ catalyzed wasted cooking oil upgrading, Prasertpong et. al. [25] for HPA catalyzed bio-oil model compound upgrading as well as various studies for biodiesel production [34, 39, 41].

![Figure 1](image.png)

**Figure 1.** The kinetic modeling curve for the HPA catalyzed esterification reaction under different reaction temperatures.

| T (°C) | k (min$^{-1}$) | R$^2$ |
|--------|----------------|-------|
| 35     | 0.0019         | 0.9754|
| 45     | 0.0030         | 0.9929|
| 55     | 0.0041         | 0.9523|
| 65     | 0.0062         | 0.9734|
| 75     | 0.0077         | 0.9364|

A good correlation between the experimental data and the calculated value was observed from Table 1 with the above 0.93 of the coefficients of determination (R$^2$) [34]. These results proved that the pseudo-first-order kinetic model had justified describing the esterification reaction catalyzed by the HPA catalyst. The literature was also reported the pseudo-first-order kinetic model for bio-oil upgrading with the catalytic esterification [25] and biodiesel production via Amberlyst 46 [30], F-SO$_4^{2-}$/MWCNTs [34], HPA catalyst [27, 42], and TPA$_3$/SBA-15 [28] catalyzed esterification.

After the reaction rate constants under different reaction temperatures were determined. The Arrhenius equation (Eq. 12) was applied to model the relation between the reaction temperature and the rate coefficient, which can be used for kinetic parameter calculation, where $E_a$, $A$, $R$, and $T$ were the activation energy (J/mol), pre-exponential factor (min$^{-1}$), gas constant (J/K mol) and reaction temperature (K), respectively. The logarithms of the reaction rate constant (ln k) were plotted versus 1/T
as illustrated in Figure 2, while the value of $E_a$ and $A$ can be determined from the slope and interception on the y-axis of this plot [18, 25].

\[
\ln k = \frac{E_a}{RT} - \ln A
\]  

The linear relationship between the logarithms of the reaction rate constant and the reverse of temperature demonstrated the ratification of the Arrhenius equation to explain the esterification reaction catalyzed by the HPA catalyst with the $R^2$ value of 0.99 [34]. The activation energy and pre-exponential factor for this reaction were calculated and compared with the result obtained from the literature, which was summarized in Table 2.

![Figure 2. Arrhenius plot for HPA catalyzed esterification reaction.](image)

The pre-exponential factor of 432 min$^{-1}$ and apparent activation energy of 31.5 kJ/mol were gained for the HPA catalyzed esterification of oleic acid as the model bio-oil with ethanol. This activation energy related to the HPA catalyst was observed to be lowest comparing with the results obtained from the other comparable esterification reaction catalyzed by ether homogeneous and heterogeneous catalysts shown in Table 2. This low activation energy implied that this reaction with the HPA catalyst required lower energy to make the reaction occurred. Hence, the HPA catalyst can be considered as a promising catalyst with a high catalytic performance for bio-oil upgrading via esterification due to its relatively low activation energy. The higher frequency of collisions between the reactant molecules of the esterification reaction catalyzed by the HPA catalyst was indicated by the higher pre-exponential factor related to the HPA catalyst comparing with other catalysts.

| Catalyst | $E_a$ (kJ/mol) | $A$ (min$^{-1}$) | Reference |
|----------|----------------|-----------------|-----------|
| H$_2$SO$_4$ | 51.6 | - | [43] |
| H$_2$SO$_4$ | 46.0 | $1.8 \times 10^5$ | [44] |
| TPA3/SBA-15 | 44.6 | 12.7 | [28] |
| F-SO$_2^2$/MWCNTs | 32.7 | - | [34] |
| zinc acetate | 32.6 | 120 | [36] |
| HPA; tungstosilicic acid | 31.5 | 432 | This work |
4. Conclusion
The kinetic behavior of HPA (tungstosilicic acid) catalyzed esterification of oleic acid as the model bio-oil with ethanol was investigated in the batch condition under atmospheric pressure. The results showed that tungstosilicic acid is an effective catalyst for the esterification process. The kinetic of this esterification reaction was appropriately described with the pseudo-first-order kinetic model. The experimental data were fitted with the kinetic model to obtain the pre-exponential factor (A) of 432 min⁻¹ and the apparent activation energy (Ea) of 31.5 kJ/ mol for this esterification reaction. The tungstosilicic acid was expected to be an assuring catalyst for upgrading of bio-oil with the esterification process with the comparatively low activation energy comparing with other related catalytically esterification reaction.

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