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Article

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Research paper

Optimization of process variables for esterification of bio-oil model compounds by a heteropolyacid catalyst

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ABSTRACT

In this work, the catalytic upgrading of a bio-oil model compound via esterification with ethanol was studied using 12-tungstosilicic acid as the catalyst. The response surface method was used to investigate and optimize the process variables, which include the ethanol to acid molar ratio, catalyst loading, reaction temperature, and reaction time for maximum conversion of the organic acid for esterification under atmospheric conditions. The effect of high He pressure on acid conversion for esterification was also studied. The maximum acid conversion was almost 90%, which can be achieved at reaction temperature of 77 °C, ethanol to acid molar ratio of 5:1, catalyst loading of 4.0% w/w, and reaction time of 8.3 h. Pressurizing the reaction with inert He did not have any effect for acid conversion at this optimum condition and had a slight negative effect under the studied conditions. After upgrading, the esterified products were found to improve the heating value from 17.6 to 23.2 MJ/kg and appeared to enhance fuel properties.

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1. Introduction

Biomass resources are among the most promising renewable energy sources. They have great potential to improve environmental quality, contribute to rural development, and reinforce the energy security in Thailand and other countries devoid of abundant fossil fuel sources. Energy from biomass is widely used as a source of heat and power. Recently, much of the attention on biomass energy sources has focused on liquid biofuels, which can be derived by various conversion processes. Flash or fast pyrolysis is a promising method for converting biomass into liquid fuels (Pattiya et al., 2006; Jaroenphasemmesuk and Tippayawong, 2015). The resulting biomass pyrolysis oil or bio-oil is a multi-component organic mixture of oxy-compounds, including acids, aldehydes, ketones, esters, phenols, alcohols, and ethers (Lian et al., 2017; Prasertpong et al., 2017). Direct use of bio-oil is hampered by its high viscosity, high water and ash contents, high corrosiveness, low heating value, and oxidative instability (Bridgwater, 2012).

There are various methods to enhance bio-oil quality. Improvement of bio-oil properties via catalytic cracking and hydrotreatment are considered to have great potential to satisfy fuel

oil requirements. However, there are still some challenging issues such as tar, coking, catalyst stability, and hydrogen consumption that need to be overcome (Song et al., 2010; Jaroenphasemmesuk et al., 2017; Xu et al., 2014). Alternatively, catalytic esterification (converting the organic acids in bio-oil into their corresponding esters) may be adopted as a simple and effective upgrading method. This method can also be used as a midway step prior to hydrotreatment.

The use of phosphoric and sulfuric acids has recently acquired a lot of interest in industrial esterification reactions (Lu et al., 2013). Despite the fact that these mineral catalysts have high catalytic activity and selectivity, there remain some concerns about their utilization with regards to equipment corrosion and toxic effluent hazards to the environment (Zhang et al., 2009). Alternative catalysts have been in development for the green esterification process. Lately, it has been demonstrated that heteropolyacids (HPAs) are prospective catalysts for esterification because they have good properties including low corrosiveness, high catalytic activity, and non-toxicity (Timofeeva, 2003; Öztürk et al., 2002; Cardoso et al., 2008).

For chemical reactions, response surface methodology (RSM) in conjunction with central composite design (CCD) of experiments can potentially be used to both study the effects of operating parameters and optimize them for maximum yield. The benefits of these methods include a sufficiently small number

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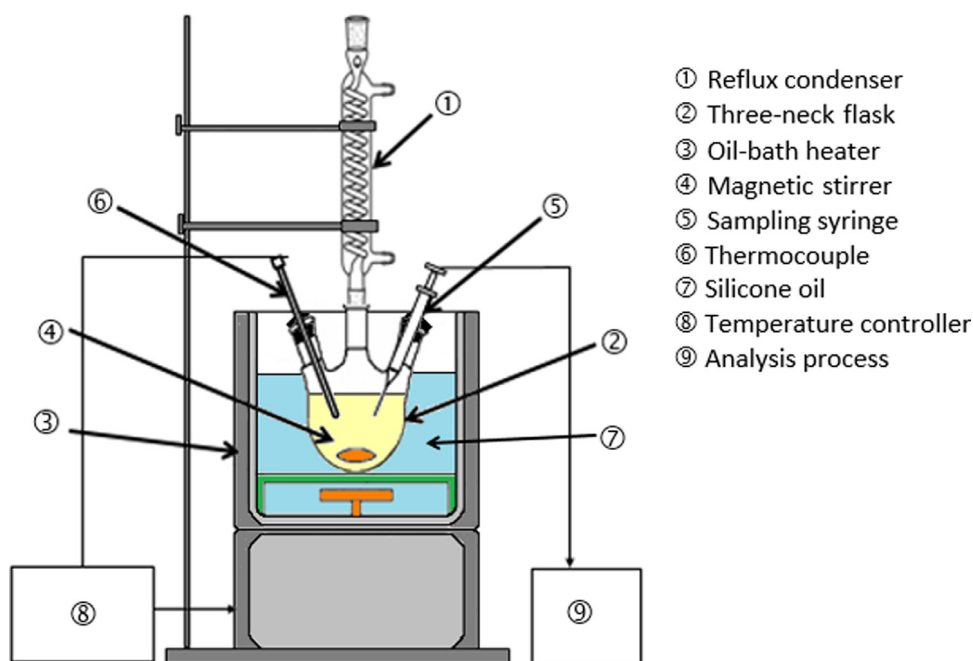


Fig. 1. Experimental setup for the esterification reaction of the bio-oil model compound with ethanol over the HPA catalyst.

Table 1
Experimental coded levels and range of the independent parameter.

Independent parameters	Symbols	Range and coded levels of parameter				
		$-\alpha = -2$	-1	0	$+1$	$+\alpha = +2$
Temperature ($^{\circ}\text{C}$)	X_1	40	50	60	70	80 ^a
Alcohol to acid (mol/mol)	X_2	1	2	3	4	5
Catalyst loading (% w/w)	X_3	1	2	3	4	5
Reaction time (h)	X_4	2	4.5	7	9.5	12

^aMaximum temperature was adjusted to 77 $^{\circ}\text{C}$ and α was changed to +1.7 due to the limitation from boiling point of the reaction mixture.

of test cases, considerable amounts of information for the user and determination of the effect of variables and their combinations of interactions on the response (Zhang et al., 2008). Hence, these methods are considered to be effective statistical techniques for optimizing multifactor experiments, developing models, and evaluating the effects of several factors for desirable responses (Liu et al., 2014).

According to the current literature, increasing acid conversion in the esterification process was achieved with the reaction at high pressure and temperature conditions (Peng et al., 2009). Some studies reported that the properties of bio-oil were improved through esterification process under high pressure and temperature by reacting with ethanol (Zhang et al., 2015, 2016), methanol (Hu et al., 2013) and supercritical- CO_2 (Cui et al., 2010).

This work focused on the esterification of a bio-oil model compound with ethanol over 12-tungstosilicic acid. The effects of ethanol to acid mole ratio, catalyst loading, reaction temperature, and reaction time were investigated and optimized. High-pressure esterification was studied and compared. The properties of original and upgraded bio-oil model compounds were also analyzed.

2. Materials and methods

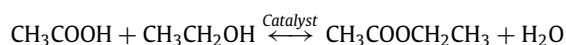
2.1. Materials

A bio-oil model compound was made from a mixture of acetic acid (85% w/w) and phenol (15% w/w) to simulate the bio-oil that is produced from fast pyrolysis of jatropha cake in a fluidized bed

pyrolyzer at 500 $^{\circ}\text{C}$, and that is provided by the Thailand Institute of Scientific and Technological Research (Prasertpong et al., 2017). Pure acetic acid, phenol 15 (99.5% purity), pure ethanol, pure potassium hydroxide, toluene (99.5% purity), isopropyl alcohol (99.8% purity) and pure dioxane in analytical reagent grade were purchased from RCI Labscan Co., Ltd. The 0.1 phenolphthalein solution in ethanol was obtained from Vechavit Part., Ltd. The 12-tungstosilicic acid ($\text{H}_4[\text{Si}(\text{W}_3\text{O}_{10})_4] \cdot \text{H}_2\text{O}$) was purchased from Sigma-Aldrich Co. LLC.

2.2. Esterification experiment

The experimental setup for the esterification process is shown in Fig. 1. It consisted of a three-neck flask with a thermocouple, reflux condenser, and magnetic stirrer - all heated in a constant temperature bath. A typical reaction mixture contained about 20 g of the bio-oil model compound, ethanol, and the HPA catalyst. Effects of the ethanol to acid mole ratio (between 1:1 and 5:1), catalyst loading (between 1 and 5% w/w), reaction temperature (between 40 and 77 $^{\circ}\text{C}$), and reaction time (between 2 and 14 h) were investigated. The esterification reaction between acetic acid and ethanol can be represented with the following formula:



The conversion of acetic acid to ethyl acetate was determined by titration with a 0.1 M potassium hydroxide (KOH) standard solution (Zhang et al., 2006), according to the following equation:

$$Y = \left(\frac{A_f - A_p}{A_f} \right)$$

where Y is the conversion of acetic acid, and A_f and A_p are the acid values of the feed and the final products, respectively.

The properties of the original model bio-oil and upgraded product at optimum condition were analyzed for pH, total acid number (TAN), heating value (HHV), viscosity, density, flash point, pour point, and composition.

2.3. Experimental design

RSM in conjunction with CCD was used to examine linear and interaction effects of the reaction parameters and to analyze the operating condition of esterification to obtain a high conversion of acetic acid. Minitab (Minitab Inc., USA) software was utilized to generate test conditions, execute the statistical analysis and develop the regression model. The process variables in this study comprised of four factors: temperature (X_1), alcohol to acid mole ratio (X_2), catalyst loading (X_3), and reaction time (X_4). The ranges of independent variables and experimental levels used in this study are shown in Table 2.

The RSM and CCD determine the minimum number of test runs that are required to produce a reliable measurement of the desired response (Aslan, 2008). In this work, the desired response to be optimized was the conversion of acid. Using RSM and CCD, the number of test cases needed was found to be 31, based on 16 factor points, eight axial points, and seven center point replications. The complete design matrix and corresponding value of acid conversion for each of the experiments is shown in Table 2. Two axial points on the axis of each design variable were positioned at a distance, α of 2.0. The data were then plotted to the following second-order polynomial equation:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i < j} \beta_{ij} x_i x_j + \varepsilon$$

where Y represents the response variable (conversion of acid); X_i and X_j are decoded independent process variables; β_0 is the interception coefficient; β_i and β_{ii} are the first- and second-order quadratic model coefficients, respectively; β_{ij} is the linear model coefficient for the interaction between variables i and j ; and ε is the standard error.

2.4. High-pressure esterification

The experimental setup used for high-pressure esterification is presented in Fig. 2. It consisted of a 100 mL EZE-Seal Stirred reactor (Parker-Autoclave) made from 316 stainless steel and equipped with a ceramic band heater, gas inlet, thermocouple, sample outlet, and mechanical stirrer (MagneDrive®). Typically, 10 g of acetic acid, 1 mL of dioxane as the internal standard, ethanol (measured to give the desired alcohol to acid molar ratio), and 12-tungstosilicic acid (measured to give the desired catalyst wt%) were loaded into the reactor at room temperature. The reactor was then sealed and purged with helium at room temperature 5 times to displace the air left in the reactor. After purging, the reactor was heated to the desired temperature. Once the desired temperature was stable, the reactor was pressurized with helium at pressures of 1, 5, and 10 MPa. The reaction was then conducted for the desired time with a stirring speed of 500 rpm. After the reaction the reactor was cooled to room temperature. Three different test conditions were examined: (i) Optimum Condition: alcohol to acid molar ratio = 5:1, HPA = 4 wt%, $T = 77^\circ\text{C}$, time = 8.3 h, (ii) Lowest catalyst loading: alcohol to acid molar ratio =

Table 2

Experimental range, level of independent variables, and responses.

Test	Process variables (coded values)				Conversion, Y (%)
	X_1	X_2	X_3	X_4	
1	−1	−1	−1	−1	38.3
2	+1	−1	−1	−1	62.8
3	−1	+1	−1	−1	43.4
4	+1	+1	−1	−1	67.5
5	−1	−1	+1	−1	49.3
6	+1	−1	+1	−1	72.7
7	−1	+1	+1	−1	52.8
8	+1	+1	+1	−1	81.3
9	−1	−1	−1	+1	43.0
10	+1	−1	−1	+1	68.1
11	−1	+1	−1	+1	46.3
12	+1	+1	−1	+1	75.7
13	−1	−1	+1	+1	56.9
14	+1	−1	+1	+1	77.7
15	−1	+1	+1	+1	70.3
16	+1	+1	+1	+1	84.8
17	−2	0	0	0	45.8
18	+1.7	0	0	0	81.3
19	0	−2	0	0	60.8
20	0	+2	0	0	74.0
21	0	0	−2	0	50.4
22	0	0	+2	0	74.8
23	0	0	0	−2	47.9
24	0	0	0	+2	59.7
25	0	0	0	0	70.9
26	0	0	0	0	67.0
27	0	0	0	0	65.2
28	0	0	0	0	66.9
29	0	0	0	0	71.0
30	0	0	0	0	72.6
31	0	0	0	0	66.6

3:1, HPA = 1 wt%, $T = 60^\circ\text{C}$, time = 7 h, and (iii) Shortest time: alcohol to acid molar ratio = 3:1, HPA = 3 wt%, $T = 60^\circ\text{C}$, time = 2 h

Both the feed and product reaction mixture were analyzed using an HP 5890 series II gas chromatograph equipped with a flame ionization detector (FID) and using a Restek™ Stabilwax™ column (30 m × 0.25 mm × 0.25; μm film thickness) and autosampler. The GC injector and detector temperatures were set at 250 and 270 $^\circ\text{C}$, respectively. The column temperature was programmed from 40 $^\circ\text{C}$ (holding for 5 min) to 280 $^\circ\text{C}$ (holding for 10 min) at a heating rate of 10 $^\circ\text{C}/\text{min}$. The integrated acetic acid peak was normalized to the integrated dioxane peak to reduce deviation in sampling sizes. The reported conversion of each sample was reported as the average conversion of four independent GC measurements (Ye et al., 2014). The conversion of acetic acid to ethyl acetate was calculated from the following equation:

$$Y = \left(\frac{AC_f - AC_p}{AC_f} \right)$$

where Y is the conversion of acetic acid, and AC_f and AC_p are the acid amount of the feed and the final products, respectively.

2.5. Characterization of bio-oil model compounds

Both original and upgraded bio-oil model compounds (upgraded under the obtained optimum condition) were characterized. Gas chromatography (GC Agilent 7890A) – mass spectrometry (MSD Agilent 5975C) was used to analyze the compositions and the relative concentrations of the model compounds. The US National Institute of Science and Technology (NIST) and Wiley mass spectral libraries were used to identify the chemical compounds. The chromatographic separation was performed using a DB5-MS column (30 m × 0.25 mm × 0.5 μm film thickness). The injector and detector temperatures were set at 250 and 280 $^\circ\text{C}$,

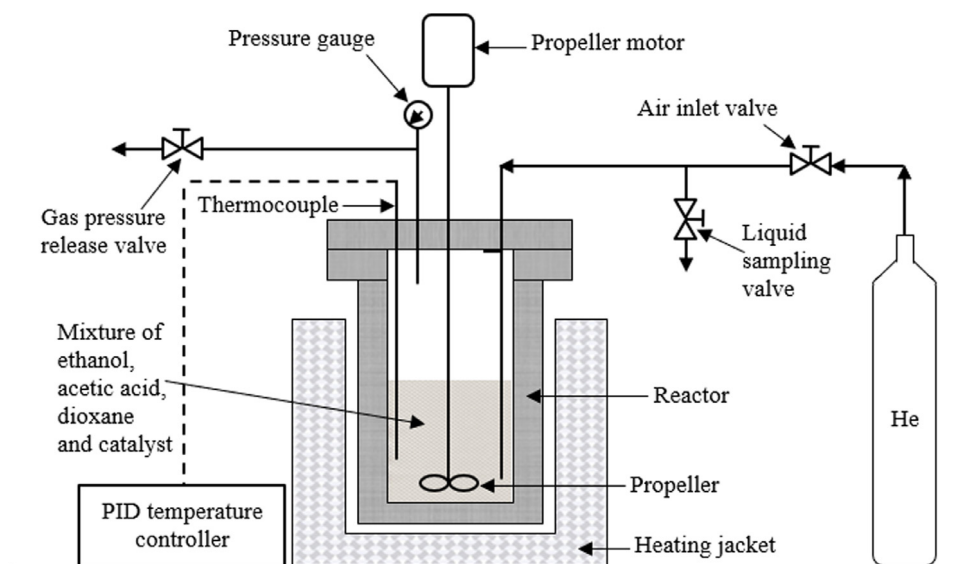


Fig. 2. Experimental setup for the high-pressure esterification reaction of the bio-oil model compound with ethanol over HPA catalyst.

respectively. The column temperature was programmed from 40 °C (holding for 5 min) to 280 °C (holding for 10 min) at a heating rate of 10 °C/min.

The calorific value was evaluated using an oxygen bomb calorimeter in accordance with ASTM D8409. The viscosity was measured using a Saybolt viscometer in accordance with ASTM D88. The pH value was determined using a Mettler Toledo pH meter. The flash point was evaluated using a Cleveland open cup tester (ASTM D92). The pour point and density were determined in accordance with ASTM D79 and D369. The acid number measurement was based on ASTM D974 with the modification of using 0.34 M KOH in isopropyl alcohol and phenolphthalein for the indicator.

3. Results and discussion

3.1. Acid conversion and model fitting

The experimental results obtained after running the 31 cases for the statistical design are shown in Table 2. The acid conversion was found to vary between 38 to 85%, depending on the experimental conditions. The multi-regression was used to determine the best-fitting model. The model adequacy was justified by an analysis of variance (ANOVA) (Ye et al., 2014). The ANOVA result for the quadratic model of conversion of acid by esterification is given in Table 3. It was found that the value of R^2 for the acid conversion model was 0.972, where an R^2 value of 1.0 is used to represent the complete agreement between experimental and predicted response (Montgomery, 2013). Based on the R^2 obtained, 97.2% of the sample variation for the esterification reaction can be attributed to the independent variables investigated.

To determine the significance of each term at a specified level of confidence, each term's respective p -value and F -value were examined. The p -value is used to reject the null hypothesis, where a small p -value represents the more significant its corresponding coefficient and the contribution towards the response variable (Mohammad Fauzi et al., 2014). In the ANOVA analysis in Table 3, the variables that were highly significant are indicated by a high F -value. For analysis at the 95% confidence level, a low p -value (<0.05) and high F -value were used to indicate the factors that have a large effect on the response (Istadi and Amin, 2006). It can be seen that four linear terms (X_1 , X_2 , X_3 , X_4) and two quadratic terms (X_3^2 ; X_4^2) showed significant effects on the conversion of

Table 3
ANOVA analysis for the conversion of acid as the desired response (unreduced model).

Source	Sum of squares	Mean square	F-value	p-value
Model	4806.53	343.32	40.02	0.000*
X_1	2792.10	2792.10	325.44	0.000*
X_2	265.73	265.73	30.97	0.000*
X_3	934.00	934.00	108.87	0.000*
X_4	254.02	254.02	29.61	0.000*
X_1^2	16.81	16.81	1.96	0.181
X_2^2	2.94	2.94	0.34	0.567
X_3^2	67.15	67.15	7.83	0.013*
X_4^2	399.83	399.83	46.60	0.000*
X_1X_2	0.48	0.48	0.06	0.815
X_1X_3	15.72	15.72	1.83	0.195
X_1X_4	7.08	7.08	0.82	0.377
X_2X_3	8.91	8.91	1.04	0.323
X_2X_4	5.62	5.62	0.65	0.430
X_3X_4	9.73	9.73	1.13	0.303
R^2	0.9722		Adj. R^2 : 0.9479	

*Significant effect.

acid at 95% confidence level. Based on the p -values and F -values, the order of significance for each of the model terms was given as follows: X_1 (temperature), X_2 (alcohol to acid mole ratio), X_3 (catalyst loading), X_4 (reaction time), X_3^2 ([catalyst loading] 2); and X_4^2 ([reaction time] 2).

To improve the experimental model, the insignificant model terms were eliminated, and the reduced model was re-analyzed with the statistical method to ultimately produce a new model. The new reduced model equation for the conversion of acetic acid was analyzed by ANOVA and the analysis result is shown in Table 4. The R^2 value of 0.959 for the conversion of acid indicated an excellent agreement between the experimental and the predicted acid conversion.

The model adequacy was further justified by ANOVA. It was observed that the R^2 value of the new reduced model was less than the R^2 value of the unreduced model due to decreasing variable number in the regression model. However, an increase in the adjusted R^2 value was obtained from the elimination of the insignificant model terms that improved the new model (Mazaheri et al., 2010). In addition, the F -value of 93 with an extremely low p -value (0.000) for the overall model of acid conversion and

Table 4
ANOVA for the conversion of acid as the desired response (reduced model).

Source	Sum of squares	Mean square	F-value	p-value
Model	4740.22	790.04	93.14	0.000*
X ₁	2887.55	2887.55	340.42	0.000*
X ₂	265.73	265.73	31.33	0.000*
X ₃	934.00	934.00	110.11	0.000*
X ₄	254.02	254.02	29.95	0.000*
X ₃ ²	60.82	60.82	7.17	0.013*
X ₄ ²	387.77	387.77	45.71	0.000*
R ²	0.9588		Adj. R ² : 0.9485	

*Significant effect.

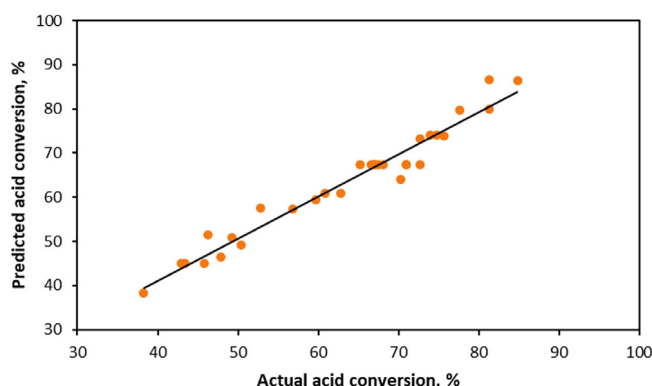


Fig. 3. Comparison between the predicted and actual response values obtained from the model for the conversion of acetic acid.

the insignificance of the lack of fit to the model indicated the sufficiency of the model for the response variables tested. From the ANOVA and the statistical parameters, the simplified regressive polynomial model considering only the significant terms for the conversion of acetic acid is given as follows:

$$Y = -79.33 + 1.1233X_1 + 3.324X_2 + 14.90X_3 + 9.47X_4 - 1.444X_3^2 - 0.5832X_4^2$$

where Y = conversion of acid (%), X₁ = temperature (°C), X₂ = alcohol to acid mole ratio, X₃ = catalyst loading (% w/w), and X₄ = reaction time (h).

The acid conversions of the predicted response value are compared against those from the actual response values obtained from experiment in Fig. 3. The plotted points are close to the diagonal line, which demonstrates the close similarity between the predicted and actual values as well as the excellent capturing of the correlation between the reaction variables and acid conversion in the model (Talebian-Kiakalaie et al., 2013).

The esterification process was optimized to obtain the highest conversion of acid using RSM. To obtain the optimum condition of the process, the polynomial model equation was solved using Minitab software. The optimum condition for the bio-oil model compound esterification with ethanol over the HPA catalyst was predicted to be as follows: temperature (X₁) = 77 °C, alcohol to acid mole ratio (X₂) = 5:1, catalyst loading (X₃) = 4.0% w/w, and reaction time (X₄) = 8.3 h. The theoretical conversion is above 99% for this optimum condition, which is larger than the experimental conversion value of 89. However, this difference is considered to be quite acceptable.

3.2. Main effect of the process variables

The individual effect of the reaction variables on the esterification process is shown in Fig. 4. Temperature significantly affected the acid conversion, showing a monotonic increase in the acid conversion with increasing temperature, as shown in Fig. 4(a). This was because increasing temperature considerably accelerated the speed of molecular motion and mass transfer rate (Jiang et al., 2013). Moreover, the mass transfer limitation between the reactant and the catalyst was improved at high temperature (Liu et al., 2014).

Alcohol to acid mole ratio is one of the important parameters affecting the conversion of acid. The higher acid conversion was achieved by increasing the molar ratio of alcohol to acid, as presented in Fig. 4(b). Since esterification is reversible, the excess alcohol may contribute to pushing the equilibrium in the forward direction (Liu et al., 2015). However, catalyst deactivation with increasing alcohol concentration was reported as a result of alcohol adsorption on the catalyst surface (Ding et al., 2011). Moreover, Jiang et al. (2013) reported that increasing the molar ratio of alcohol to acid may lead to a reduction in conversion in a fixed catalyst reaction system due to decreasing catalyst concentration in the system.

The effect of catalyst loading on esterification was investigated and the result is shown in Fig. 4(c). The increasing acid conversion was observed with increasing catalyst loading in the range of 1.0 to 4.03% w/w because the increase in catalyst loading favored the dispersion of active sites (Jermy and Pandurangan, 2005). However, excessive catalyst (more than 4.03% w/w) appeared to decrease the acid conversion. This may have been due to the fact that the excess catalyst contributed to an increase in viscosity of the reaction mixture which limited the mass transfer in the system (Saha and Goud, 2014; Piang-Siong et al., 2012). The effect of reaction time on the conversion of acid is shown in Fig. 4(d). An increase in acid conversion was observed with increasing reaction time in the range of 2 to 8.26 h. The acid conversion was decreased for the reaction time beyond 8.26 h because the excess reaction time led to a faster reaction in the reverse direction and increased the formation of acid (Eevera et al., 2009; Saha and Goud, 2014).

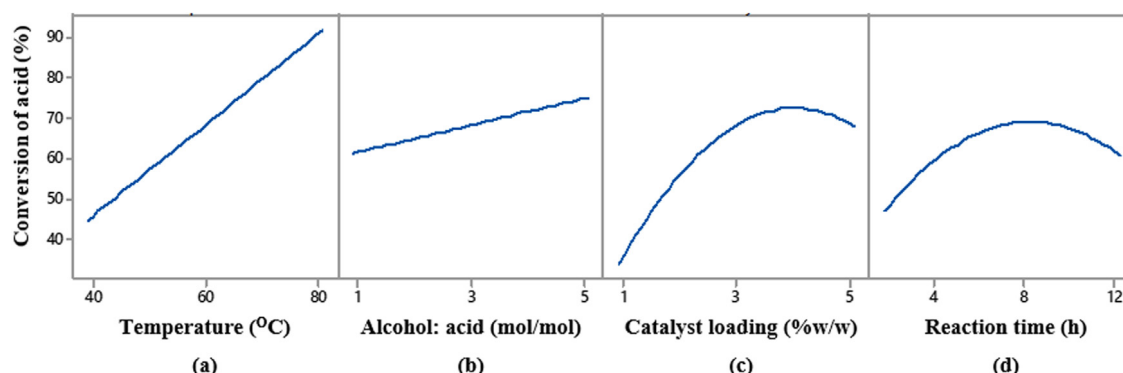


Fig. 4. Main effect plots of temperature (a), alcohol to acid mole ratio (b), catalyst loading (c), and reaction time (d) on the conversion of acid.

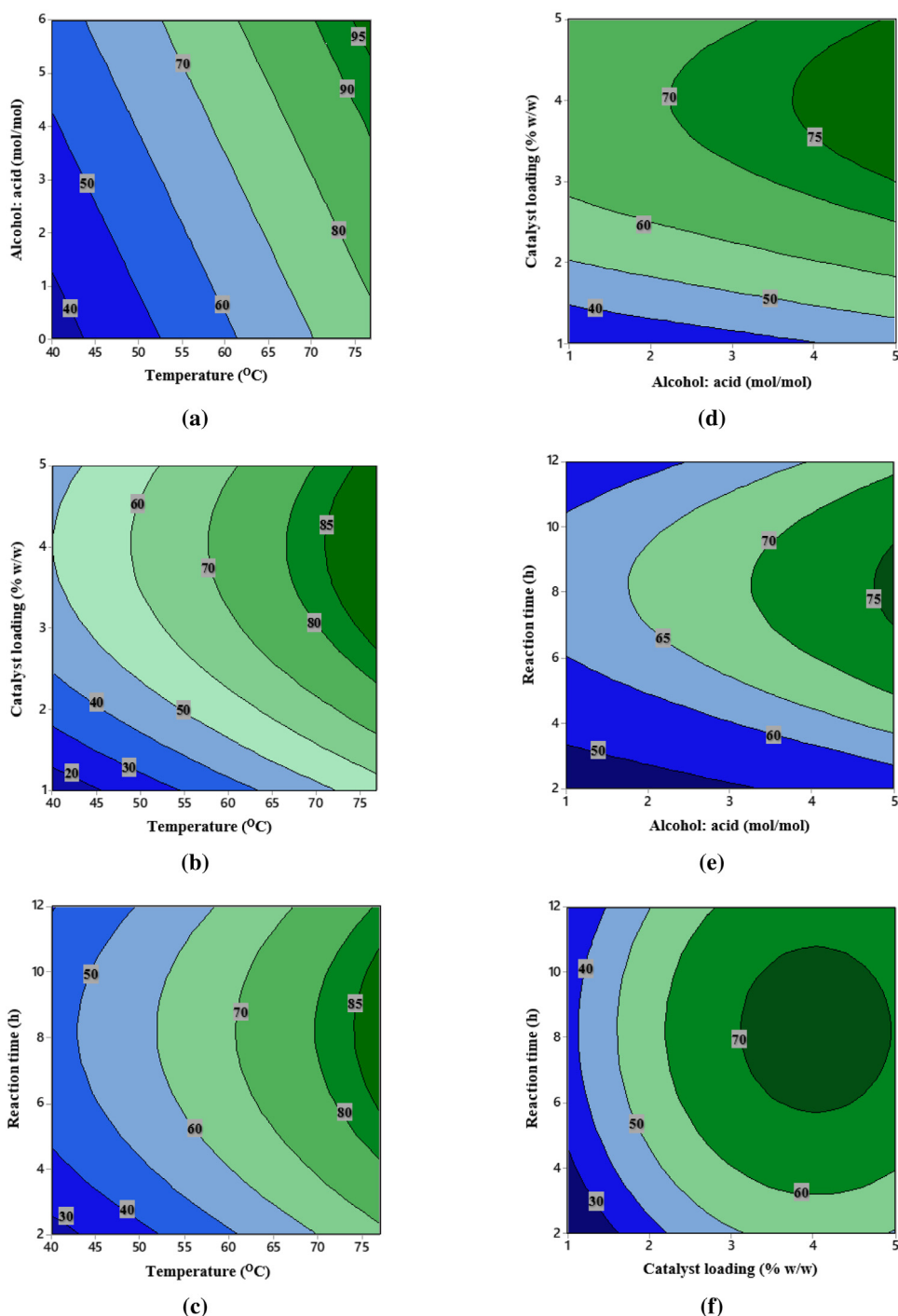


Fig. 5. Contour plots representing the effect on the conversion of acid for the interaction between (a) temperature and mole ratio of alcohol to acid, (b) temperature and catalyst loading, (c) temperature and reaction time, (d) mole ratio of alcohol to acid and catalyst loading, (e) mole ratio of alcohol to acid and reaction time, and (f) catalyst loading and reaction time.

3.3. Interaction effect of process variables

The interaction effects of the reaction parameters were evaluated from the contours of the polynomial model of acid conversion. The acid conversion was plotted as a function of two variables, while other process variables were kept constant at the coded zero (middle) levels. The effects of the four process variables on the acid conversion are shown in Fig. 5.

The relationship between temperature and the molar ratio of alcohol to acid on conversion is presented in Fig. 5(a). An increase in acid conversion was apparent with both increasing

temperature and molar ratio of alcohol to acid. This observation was in agreement with Shi et al. (2011).

The effect of temperature and catalyst loading on the conversion of acid is illustrated in Fig. 5(b). The conversion clearly increased with increasing temperature at a constant catalyst amount. At a constant temperature, increasing catalyst loading up to 4% w/w (Level + 1) resulted in increased conversion of acid, then the conversion decreased when the catalyst loading further increased to 5% w/w (level + α) due to the increasing viscosity of the reaction mixture as mentioned in Section 3.2.

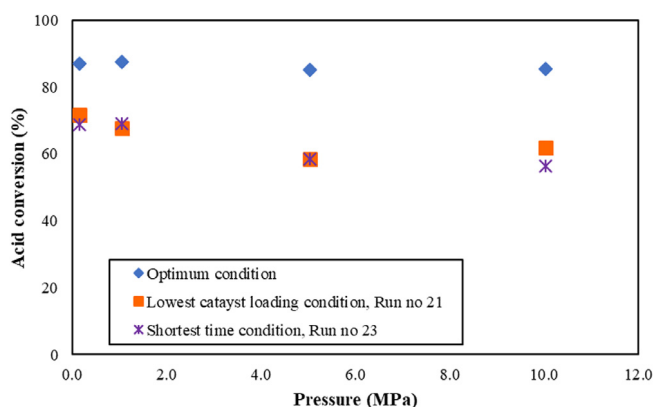


Fig. 6. Effect of pressure to acid conversion in the esterification of acetic acid with ethanol over 12-tungstosilicic acid under optimum Condition (♦): alcohol to acid molar ratio = 5:1, HPA = 4 wt%, $T = 77^\circ\text{C}$, time = 8.3 h, lowest catalyst loading (■): alcohol to acid molar ratio = 3:1, HPA = 1 wt%, $T = 60^\circ\text{C}$, time = 7 h, and shortest time (*): alcohol to acid molar ratio = 3:1, HPA = 3 wt%, $T = 60^\circ\text{C}$, time = 2 h.

The effect of temperature and reaction time on acid conversion is shown in Fig. 5(c). The acid conversion showed a parabolic pattern with the reaction time at fixed temperature. At a constant reaction time, the conversion of acid increased with increasing temperature because it can accelerate the molecular movement and the rate of mass transfer.

Fig. 5(d) depicts the effect of the molar ratio of alcohol to acid and catalyst loading. The conversion of acid showed a parabolic pattern with catalyst loading at a fixed molar ratio of alcohol to acid. An increase in the molar ratio of alcohol to acid increased the conversion of acid at a constant catalyst loading. Because esterification is a reversible reaction, the excess alcohol can push the equilibrium of the reaction to forward direction.

The relationship between the molar ratio of alcohol to acid and reaction time on acid conversion is shown in Fig. 5(e). For a

fixed molar ratio of alcohol to acid, the increasing acid conversion was observed with the reaction time to 8 h, after which the acid conversion decreased. The increasing molar ratio of alcohol to acid resulted in an increased conversion at a fixed reaction time.

The effect of catalyst loading and reaction time on conversion of acid is indicated in Fig. 5(f). For a fixed reaction time (less than 6 h), increase in catalyst loading from 1.0 to 3.2% w/w increased the conversion of acid, at which point it remained almost constant with further increase in amount of catalyst to 5% w/w. For a constant catalyst loading, increasing reaction time from 2 to 6 h increased the conversion of acid. Then, the conversion remained almost constant with further increase in reaction time to 11 h, after which the conversion decreased.

3.4. Effect of pressure on acid conversion

The effect of pressure on acid conversion in the esterification of acetic acid with ethanol over 12-tungstosilicic acid under various conditions is shown in Fig. 6. The increase of pressure in the reaction led to a decrease in the acid conversion for esterification under the lowest catalyst loading (Run no. 21) and shortest reaction time condition (Run no. 23). This is likely because an increase in pressure causes increased reaction mixture viscosity and limits the mobility of molecules (Mezger, 2011; Peng et al., 1938), which may increase mass transfer resistance. For esterification under the optimum condition the pressure did not affect acid conversion, perhaps due to the higher temperature reducing viscosity enough to overcome the effect of pressure. Moreover, the acid conversion was higher with the autoclave reactor than with the flask reactor, as is clearly seen in Table 5. This believed to be because the reaction is weakly catalyzed by the stainless-steel material of the autoclave (Di Mondo et al., 2011).

3.5. Effect on bio-oil composition and properties

The analysis results of the compositions of the original and upgraded bio-oil model compounds are illustrated in Fig. 7. It

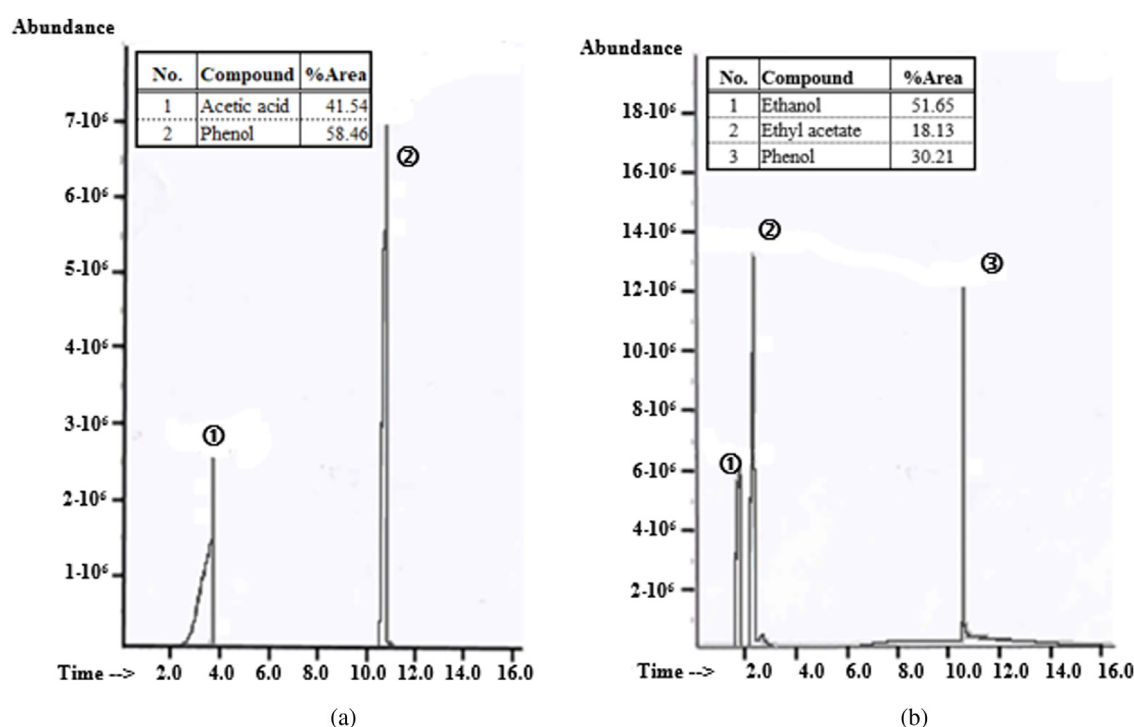


Fig. 7. Typical GC-MS results of (a) original bio-oil compound and (b) upgraded bio-oil model compound.

Table 5

Comparison of acid conversion with autoclave reactor and flask reactor.

Reactor	Acid conversion (%)					
	Lowest catalyst loading		Shortest reaction time		Optimum condition	
	Non-catalyzed	Catalyzed	Non-catalyzed	Catalyzed	Non-catalyzed	Catalyzed
Flask	3	50	0	48	8	87
Autoclave	4	72	1	69	16	88

Table 6

Comparison of original and upgraded bio-oil model compound properties.

Physical properties	Original model oil	Upgraded model oil	Petroleum (Chen et al., 2014)
pH	0.0	1.36	–
TAN (mg _{KOH} /g _{oil})	928	23	–
HHV (MJ/kg)	17.7	23.2	40
Viscosity (cSt @ 40 °C)	0.42	0.18	1.6–5.8
Density (kg/m ³)	1024	812	850
Flash point (°C)	45.7	<25.0	44.0–55.0
Pour point (°C)	3.0	<–13.0	–

can be seen that the composition of the original bio-oil model compound consisted of acetic acid and phenol, which agreed with those used in the preparation of the bio-oil model compound. After upgrading, a significant change in composition was observed. The ethyl acetate was clearly dominant with the excess alcohol, whereas acetic acid was not detected. It was possible that most acetic acid in the original model oil may have been reacted and converted (Montgomery, 2013). Phenol was seen in the upgraded bio-oil model compound because it contains a strongly bound hydroxyl group and its conversion was negligible during esterification (Hu et al., 2012).

The properties of the original and upgraded bio-oil model compounds are shown in Table 6. The original high content of acetic acid led to a low pH value and a high acid number. After upgrading with the esterification process, the upgraded bio-oil model compound had a higher pH and lower TAN than the original compound since the acetic acid was converted to ester during the process. Moreover, an increased heating value from 17.7 to 23.27 MJ/kg was realized, while viscosity, density, flash point, and pour point decreased from 0.42 to 0.18 cSt (at 40 °C), 1024 to 812 kg/m³, 45.7 to 25 °C, and 3 to lower than –13 °C, respectively. These changes indicated that the quality of the bio-oil model compound was improved by esterification process and came closer to the properties of the typical petroleum fuel shown in Table 6.

4. Conclusion

Bio-oil, a promising biomass energy source but with some challenges affecting its utilization, needs upgrading. Esterification is among the most practical approaches. In this work, esterification of a bio-oil model compound with ethanol over a commercial HPA catalyst was investigated. 12-tungstosilicic acid was shown to be effective in the esterification with ethanol of the acetic acid component of a bio-oil model solution. By using RSM and CCD to both investigate and optimize the correlations between the reaction variables and acid conversion, it was found that a maximum acid conversion of nearly 90% can be achieved at reaction temperature of 77 °C, mole ratio of alcohol to acid of 5:1, catalyst loading of 4.0% w/w, and reaction time of 8.3 h. The analysis of composition by GC–MS, pH value, and TAN demonstrated that the acetic acid content was significantly reduced. After upgrading the bio-oil solution, the properties of the esterified product appeared to improve.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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