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Semarang, April 8th, 2022

Dear the editors of the journal

"Trends in Sciences"

I would like to submit the manuscript entitled "**The Catalytic Activity of TCA-Modified Indonesian Natural Zeolite during the Esterification of Sengon Wood Bio-oil**" for publication as an original research paper in the Trends in Sciences journal.

The utilisation of typical Indonesian natural materials such as Indonesian natural zeolites for the production of liquid fuels is very beneficial for the future energy research. In this manuscript, we highlighted that the TCA-modified Indonesian natural zeolite was a promising catalyst during the bio-oil upgrading through an esterification technique. A significant decrease in the total acid number of the esterified bio-oil was achieved, by keeping the coke formation and the change in the physical properties low. We believe that these findings could be of interests the readers of the journal.

We declare that the manuscript is original, has not published before, and is currently not being considered for publication elsewhere.

We know of no conflict of interest associated with this publication. As the corresponding author, I confirm that the manuscript has been read and approved for submission by all named authors in the manuscript.

Yours sincerely,

Sri Kadarwati

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The Catalytic Activity of TCA-Modified Indonesian Natural Zeolite during the Esterification of Sengon Wood Bio-oil

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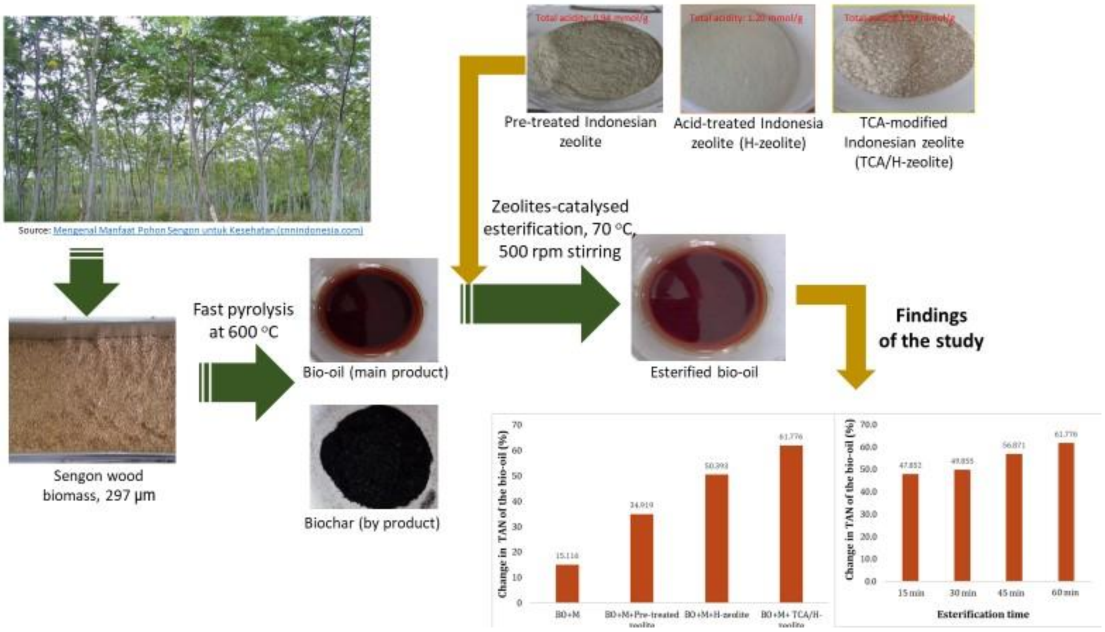
Highlights

- The TCA-modified Indonesian natural zeolite was a promising catalyst for the bio-oil esterification.
- A decrease in the total acid number of the esterified bio-oil was significant.
- The esterified bio-oil was stable while keeping the coke formation low.
- The esterification of the bio-oil using TCA/H-zeolite catalyst took place in a fast rate.

Graphical abstract



Abstract

The bio-oil produced from the pyrolysis of biomass is highly corrosive due to the high content of organic acids. These organic acids could be removed through an appropriate upgrading process, i.e., esterification using alcohols to form less polar esters. In this study, the bio-oil used as the feedstock in the esterification was produced from the pyrolysis of Sengon wood with a particle size of 297 µm at 600 °C. The esterification was performed at 70 °C in the presence of a TCA-modified Indonesian zeolite catalyst with various weight ratios of bio-oil-to-methanol and reaction times under a constant stirring rate of 500 rpm. The esterification progress was indicated by the decrease in the total acid number of the bio-oil after esterification. No significant coke formation (< 0.05wt%) was observed indicating that the suppression of repolymerisation could be achieved. This study showed that the esterification underwent in a fast rate, indicated by the decrease in the total acid number of the bio-oil by 47.85% only over a 15-min esterification.

Compared to the uncatalysed esterification, the TCA/zeolite-catalysed esterification showed a higher decrease in the total acid number of the bio-oil up to 65.83%, due to the conversion of the carboxylic acids to esters.

Keywords: Esterification, Sengon wood bio-oil, TCA-modified Indonesian zeolite, total acid number.

Introduction

The fossil fuel depletion has promoted the exploration of new renewable energy resources. Biomass has been considered as a promising renewable energy resource due to its high availability, its environmentally friendly properties and its zero competition with food sector [1]. A liquid fuel could be produced as the main product from the fast pyrolysis of biomass [2] that is well known as bio-oil or pyrolysis oil. Sengon wood, as an abundantly available feedstock in Indonesia was used in this study for bio-oil production. Sengon wood contains lignin, cellulose, and hemicellulose of 26.1%, 45.4%, and 21.0% and respectively [3], allowing a sustainable starting material for liquid fuel production.

The bio-oil produced from the pyrolysis of biomass could be used as a fuel for boilers, stationary as well as sterling engines [4]. However, the bio-oil cannot be directly used as a fuel for transportation due to several unfavourable properties such as high water content leading to low calorific value and high oxygen content resulting in highly instable properties [5]. In addition, the bio-oil contains high amount of organic acids making it highly corrosive and causing a big challenge during its use as a fuel or its compatibility during further processing in the biorefinery [6]. A bio-oil upgrading is required for the bio-oil to meet the requirements as liquid transportation fuels [7].

Esterification has been reported to show a great potential as bio-oil upgrading technique to reduce the acids content of the bio-oil [8]. It converts the organic acids in the bio-oil to e.g., esters in the presence of alcohols and acid catalysts [9]. The use of solid acid catalysts during the esterification of bio-oil has been considered more beneficial in comparison with that of homogeneous catalysts due to the easy separation resulting in a more efficient and cost-effective process [10]. Several solid acid catalysts such as ion exchange resins [11], modified zirconia [12, 13], Amberlysts [14-16], solid acid catalyst from rice husk ash [17], and heteropoly acids [18] have been used as a catalyst in the esterification of the "real" bio-oil as well as model compounds mimicking bio-oil. In addition, zeolite-based catalysts have been reported to show a great potential as a catalyst for esterification of bio-oil [19-23].

A special attention has been paid to Indonesian natural zeolite primarily in related to its application as a catalyst for bio-oil upgrading. It has a good porosity and modifiable Brønsted acid sites [24] at its surface to anticipate the complicated compositions and behaviour of the bio-oil during the esterification. The modification of Brønsted acid sites at the Indonesian zeolite surface to improve the Brønsted acidity could enhance the catalytic activity of Indonesian zeolite during the esterification of the bio-oil.

The Brønsted acidity of the Indonesian zeolite could be improved by strong acid modification, e.g., trichloroacetic acid (TCA) resulting in the zeolite with a better Brønsted acidity [25]. However, the application of TCA-modified Indonesian natural zeolite as a catalyst for esterification of bio-oil produced from the fast pyrolysis of Sengon wood was rare. More studies to investigate the activity of the TCA-modified Indonesian natural zeolite are necessary to evaluate its potential as a catalyst for the bio-oil esterification. This study focused on the esterification of the bio-oil produced from the fast pyrolysis of Sengon wood sawdust with various weight ratios of bio-oil-to-methanol and reaction times to investigate the esterification behaviour of organic acids in the bio-oil primarily acetic acid in the presence of methanol and TCA-modified Indonesian natural zeolite as a solid acid catalyst.

Materials and methods

Preparation and characterisation of a TCA-modified Indonesian natural zeolite catalyst

The Indonesian natural zeolite from Wonosari, Yogyakarta, Indonesia was used as a starting material of the zeolite catalyst. It was purchased from CV. SSGT Zeolite, Indonesia. The natural zeolite was prepared as previously reported [23]. Briefly, the natural zeolite with a particle size range of 100-120 μm was activated using sequent chemical and physical activation method. Prior to activation process, the natural zeolite was washed in distilled water and dried at 110 ^oC for 3 h to allow the physical contaminant removal. "Pre-treated zeolite" corresponds the natural zeolite from this pre-treatment step.

The natural zeolite was chemically treated using 1% HF, 6 N HCl and 1 N NH_4Cl solutions (prepared from 50% HF, 37% HCl, and solid NH_4Cl, obtained from E. Merck, respectively) in a sequence. This chemical activation was followed with a physical activation, i.e., calcination of the natural zeolite sample at 500 ºC under nitrogen atmosphere to produce “H-zeolite” catalyst.

The modification of the “H-zeolite” catalyst with chloroacetic acid was carried out as reported by Ávila *et al.* [5] with some adjustment. A 5 g of trichloroacetic acid (TCA) was dissolved in 9 mL of demineralised water in an Erlenmeyer flask. A 10 g of “H-zeolite” was added in the TCA solution. The mixture was then heated at 80 °C under a continuous stirring with a low stirring rate of 100 rpm until no water left. The solid obtained was dried in an oven at 110 °C for 2 h resulting in the “TCA/H-zeolite” catalyst.

The formation of the “TCA/H-zeolite” catalyst was confirmed based on the appearance of characteristics vibration peaks at wavenumbers of 830 and 680 cm-1 (the stretching vibration of C-Cl bonds) [25] in the IR spectrum. The IR spectrum of the “TCA/H-zeolite” catalyst was obtained using a Perkin-Elmer Frontier Spotlight 200 type-Fourier transform infrared spectrophotometer. In addition, the possible change in the crystalline structure of Indonesian natural zeolite was evaluated using a PANalytical Xpert’3 Powder X-ray diffractometer.

The surface properties of the “TCA/H-zeolite” catalyst were characterised using a Quantachrome Nova 1200e surface area analyser. The specific surface area, total pore volume and average pore radius were determined using a BET-BJH isotherm adsorption. Moreover, the acidity of the “TCA/H-zeolite” catalyst was determined using an ammonia adsorption. The amount of ammonia adsorbed at the catalyst surface was assigned as the total acidity of the catalyst in mmol ammonia per gram catalyst. This quantitative measurement of the catalyst acidity was combined with the analysis of the chemical functionalities of the catalyst to confirm the presence of the new bonds of ammonia with the Lewis and Brønsted acid sites at the catalyst surface at wavenumbers of 1640, 1550, and 1450 cm^{-1}.

Catalytic esterification of Sengon wood bio-oil

The esterification of the bio-oil with methanol in the presence of “TCA/H-zeolite” catalyst was carried out in a batch reactor system equipped with a temperature monitor and magnetic stirrer. The esterification was conducted at 70 ºC, with a catalyst loading of 10 wt%, a stirring rate of 500 rpm, and various weight ratios of bio-oil-to-methanol of 1:1, 2:1, 1:2 and 1:3. The Sengon wood bio-oil used in the esterification process was produced from the pyrolysis of Sengon wood sawdust with a particle size of 297 μm at 600 °C using a fixed-bed pyrolyser as previously reported [23]. The esterification with a weight ratio of bio-oil-to-methanol which gave the highest decrease in the total acid number of the bio-oil after esterification underwent that with various esterification times of 15, 30, 45 and 60 min.

After each experiment, the mixture of liquid esterification products and possible remaining reactants was recovered and designated as the esterified bio-oil. The coke formation was determined based on the weight difference of solid catalyst before and after the esterification. The yield of coke was calculated using Equation (1) to close the mass balance.

$$Coke\ yield = \frac{W'_{cat} - W^{0}_{cat}}{W_{bio-oil\,fed}} x100\% \qquad (1)$$

Characterisation of the bio-oil after esterification

The esterified bio-oil after each esterification experiment was characterised, including the density, viscosity and total acid number. The density and viscosity of the esterified bio-oil were determined using a gravimetric method by means of a pycnometer and an Ostwald viscometer, respectively.

The total acid number (TAN) of the esterified bio-oil was measured using an SNI 01-3555-1998 procedure as follows. The bio-oil sample was dissolved in acetone to 96 wt% clear solution of bio-oil. A 2.5 g of the bio-oil solution was heated to boil and added with 2-3 drops of phenolphthalein solution. The titration of the bio-oil solution was conducted using 0.1 N KOH solution until a light red colour appeared. The total acid number of the esterified bio-oil was calculated using Equation (2).

$$TAN = \frac{MW_{KOH} \times N_{KOH} \times V_{KOH}}{W_{sample}} \times dilution \qquad (2)$$

Results and discussion

The characteristics of TCA/H-zeolite catalyst

The important properties of the TCA/H-zeolite catalyst prepared in this study was investigated, including the chemical functionalities, the possible change in the crystalline structure, the surface porosity, and the total acidity. The chemical functionalities of the TCA/H-zeolite catalyst were represented by the spectra in Figure 1. The general featured functionalities of the zeolite with aluminosilicate framework were shown by the appearance of a vibration peak –OH groups at 3200-3600 cm^{-1}. In addition, bending vibrations of Al-OH/Si-OH were observed at 1650-1400 cm^{-1}, while stretching vibrations of Si-O/Al-O were observed at wavenumbers of 1250-950 cm^{-1} and 820-650 cm^{-1}.

The success of the zeolite modification with TCA was confirmed by the appearance of stretching vibrations of C-Cl bonds at wavenumbers of 840 and 690 cm^{-1} [25] at the IR spectrum of the TCA/H-zeolite catalyst (Figure 1c). These vibrations indicated the chemical interaction between TCA and the –OH groups of the zeolite.

The change in the crystalline structure of the zeolite over subsequent chemical and physical treatment as well as TCA modification was evaluated through the XRD patterns of the pre-treated zeolite, H-zeolite and the TCA/H-zeolite catalysts, as shown in Figure 2. The similar XRD patterns and peak intensity in Figure 2 indicated that the zeolite did not undergo a significant change in the crystalline structure over the subsequent treatments. Moreover, the intensity of the three highest peaks denoted that the mordenite mineral structure was predominant in the zeolite catalysts.

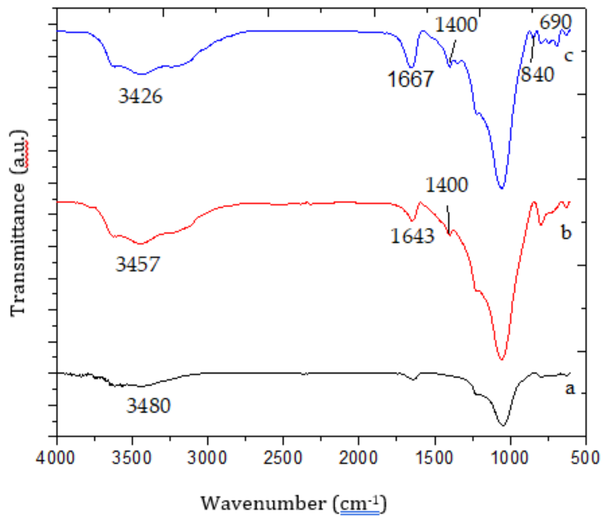


Figure 1. IR spectra of a) pre-treated zeolite, b) H-zeolite and c) TCA/H-zeolite.

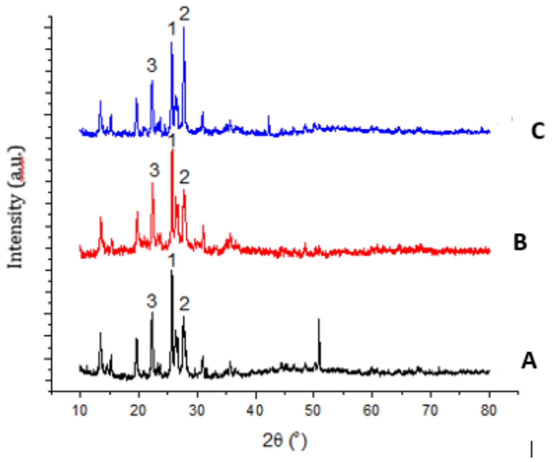


Figure 2. The diffraction patterns of a) pre-treated zeolite, b) H-zeolite and c) TCA/H-zeolite.

The measurement of the total (Lewis and Brønsted) acidity of the TCA/H-zeolite catalyst was performed to support the data of IR spectra indicating the success of the zeolite modification with TCA. The significant increase of the total acidity of the TCA/H-zeolite catalyst would further evidence of the success modification in this study. In addition, the enhanced total acidity of the TCA/H-zeolite catalyst would promote a better esterification process as this acid active sites would play important roles in catalysing the esterification of bio-oil with methanol [12].

The total acidity of the TCA/H-zeolite catalyst was conducted through ammonia adsorption in combination with a gravimetric method. The amount of ammonia adsorbed at the catalyst surface would provide the data the number of acid active sites interacting with the adsorbed ammonia [26, 27].

The total acidity of the TCA/H-zeolite catalyst in comparison with the pre-treated and H-zeolite is presented in Table 1. A significant increase in the total acidity of the TCA/H-zeolite catalyst was observed, 1.7 folds from that of H-zeolite. It was most likely due to the modification of the zeolite with TCA resulting in the chemical interaction of carbonyl oxygen or hydroxyl oxygen of TCA with the Brønsted acid sites of H-zeolite [28].

Table 1. The total acidity of the TCA/H-zeolite measured through ammonia adsorption.

Type of catalyst	Total acidity (mmol NH_3/g)
Pre-treated zeolite	0.94
H-zeolit	1.20
TCA/H-zeolit	3.28

Furthermore, the interaction between ammonia Lewis's base and the Brønsted and Lewis sites of the catalyst was evaluated through the IR spectra of the TCA/H-zeolite catalyst in Figure 3. The interaction of ammonia with the Lewis and Brønsted active sites was designated by the vibrations at wavenumbers of 1450 cm^{-1} and 1550-1640 cm^{-1}, respectively [29].

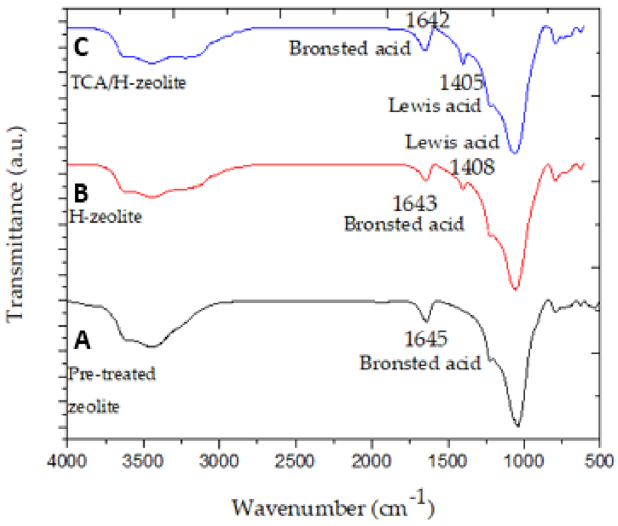


Figure 3. IR spectra of a) pre-treated zeolite, b) H-zeolite and c) TCA/H-zeolite after NH_3 adsorption.

The surface porosity of a catalyst is an important property of the catalyst in supporting the catalytic performance. It was due to the presence of active sites at the catalyst surface including the catalyst pores [30]. The surface porosity of the TCA/H-zeolite catalyst determined in this study included specific surface area, total pore volume and average pore radius of the catalyst as presented in Table 2.

Table 2. The surface porosity of the TCA/H-zeolite determined by BET and BJH adsorption isotherms.

Type of catalyst	Surface area (m^2/g)	Total Pore Volume (cm^3/g)	Average Pore Radius (Å)
Pre-treated zeolite	12.82	0.077	119.96
H-zeolit	22.26	0.065	588.35
TCA/H-zeolit	28.41	0.075	526.31

The surface porosity data in Table 2 showed that chemical and physical treatment towards the pre-treated zeolite caused a significant increase (73.63%) in the surface area of the H-zeolite catalyst. It was might due to the impurity removal and the formation of new pores during the treatment [31]. A further increase (27.63%) in the specific surface area was also observed in the TCA/H-zeolite catalyst, probably due to the surface modification using a strong acid TCA at the solid H-zeolite surface [32, 33].

A significant increase of the average pore radius of the H-zeolite catalyst in comparison with the pre-treated zeolite catalyst (3.9 folds) was also observed. The acid treatment followed with calcination at high temperature of 500 °C probably could cause impurity removal resulting in an increase in the pore size of the zeolite [32]. Moreover, the growth of the pore structure might take place due to the chemical treatment during the preparation of the H-zeolite catalyst [34]. However, a slight decrease (~10%) of the average pore radius was observed after the zeolite modification with TCA. The TCA introduction with a quite high concentration (ca. 35%) at the H-zeolite surface followed with a low drying temperature (80 °C) might promote the pore occupation by the TCA molecules, resulting in the decrease of the average pore size of the zeolite [35].

Unlike the considerable changes in the specific surface area and average pore radius, the total pore volume of the zeolite catalysts was almost unchanged; only ~15% of change was observed. The insignificant change in the total pore volume accompanied with the increase in the average pore radius might be probably attributed to the reduction of the pore depth at the zeolite surface. This would allow the easier interaction between the surface-active sites and the reactants during the esterification of the bio-oil.

Production and Characterisation of the Bio-oil from the Pyrolysis of Sengon Wood Sawdust

The bio-oil used as the feedstock during the esterification in this study was produced from the fast pyrolysis of Sengon wood sawdust with a particle size of 297 µm at 600 oC using a fixed-bed pyrolyser. The yield of the bio-oil was considerably high of 45.66 wt%, as presented in Table 3. Such high temperature would help the lignocellulose macromolecules to undergo good decomposition during the pyrolysis [36]. Lignocellulose composes of lignin, cellulose and hemicellulose with specific decomposition temperatures. Lignin would decompose at 300-550 °C, while hemicellulose and cellulose would decompose at 250-350 °C and 325-400 °C, respectively [37]. The rate of decomposition of lignocellulose macromolecules would increase with increasing the pyrolysis temperature, resulting in more condensable light fractions [38], thus high bio-oil yield. However, extremely high temperature would promote the production of the non-condensable fractions resulting in higher yield of gaseous pyrolysis product [39].

Table 3. The yield of pyrolysis products produced from the pyrolysis of Sengon wood sawdust with a particle size of 297 µm at 600 °C using a fixed-bed pyrolyser.

Type of product	Yield (wt.%)
Bio-oil	45.66
Biochar	29.97
Gaseous product*	24.37

*by difference

The physical and chemical properties of the Sengon wood bio-oil produced through fast pyrolysis technique were measured, including the density, viscosity, and total acid number as shown in Table 4. The density of the bio-oil was not directly related to the quality of the bio-oil. However, this property could provide an indication whether heavy or light molecules were predominant in the bio-oil [40]. The low density of the bio-oil produced in this study (1.07 g/mL) indicated that light molecules with relatively low molecular weight were predominant due to severe decomposition process at 600 °C during the pyrolysis resulting in more condensable light fractions.

Table 4. The characteristics of the bio-oil produced from the pyrolysis of Sengon wood sawdust with a particle size of 297 µm at 600 °C using a fixed-bed pyrolyser.

Property (unit)	Value (wt.%)
Density (g/mL)	1.07
Viscosity (cP)	2.40
TAN (mg KOH/g)	0.73

Another parameter evaluated in this study for the bio-oil quality is viscosity. This parameter is affected by the liquid temperature, the strength of intermolecular forces, and the molecular weight and the amount of the soluble components in the liquid bio-oil [41]. The pyrolysis temperature of 600 °C has resulted in the bio-oil with light components (short carbon chains, low molecular weight) in the considerable amount, resulting in the bio-oil with a low viscosity of 2.40 cP (see Table 4) [42].

The total acid number of the Sengon wood bio-oil was determined by using an aliquot method, as presented in Table 4. This parameter provided an estimation of the content of organic acids in the bio-oil

[43]. The high content of organic acids in bio-oil or liquid fuels would lead to corrosion to engines and/or the equipment used in the further processes such as biorefinery [7]. The high total acid number (0.73 mg/g) of the Sengon wood bio-oil used as the feedstock in the esterification process suggested the high organic acid content in the bio-oil. It was likely due to the presence of organic acids such as carboxylic acids as a result of the decomposition of the lignocellulose macromolecules at higher pyrolysis temperature [44]. The acid removal from the bio-oil is extremely important to minimise the corrosiveness of the bio-oil prior to its use as a fuel or its further processes in the biorefinery through an appropriate upgrading technique. A bio-oil upgrading through an esterification technique using TCA/H-zeolite was investigated with different weight ratios of bio-oil-to-methanol over various reaction times.

Bio-oil upgrading through TCA/H-zeolite-catalysed esterification over different weight ratios of bio-oil-to-methanol

The esterification of the Sengon wood bio-oil in the presence of the TCA/H-zeolite catalyst was carried out with various weight ratios of bio-oil-to-methanol of 2:1, 1:1, 1:2 and 1:3. The liquid and the possible formed coke after each esterification experiment were recovered to close the mass balance, as presented in Table 5. The mass balance closure was higher than 90 wt% indicating a proper experimental execution [45]. The coke yield in all experiments was very low of < 1 wt%. This indicated that the possible repolymerisation between the reactive components in the bio-oil leading to the formation of coke could be prevented during the bio-oil esterification [46] in the presence of the TCA/H-zeolite catalyst.

Table 5. The mass balance closure during the esterification of the Sengon wood bio-oil in the presence of TCA/H-zeolite catalyst at 70 °C with various weight ratios of bio-oil-to-methanol, a catalyst loading of 10 wt%, 60-min reaction time, and stirring rate of 500 rpm.

Weight ratio of BO-to-methanol	Recovered liquid (wt%)	Coke yield (wt%)	Total recovery (%)
2:1	94.11	0.0407	94.15
1:1	91.90	0.0404	91.94
1:2	91.88	0.0394	91.92
1:3	97.79	0.0334	97.82

The density, viscosity and total acid number of the liquid obtained after the TCA/H-zeolite-catalysed esterification with various weight ratios of bio-oil-to-methanol were measured as presented in Table 6. The density of the esterified oil insignificantly changed with relatively abundant addition of methanol compared to the original mixture of the bio-oil and methanol before reaction in the case of the experiments with a weight ratio of bio-oil-to-methanol of 1:2 and 1:3. The relatively unchanged density indicated the relatively similar molecular weight of components in the bio-oil after esterification. The esterification would allow the change in the bio-oil microstructure through the formation of esters or acetals [47]. The similar trend was observed for the viscosity of the esterified oil; the more the methanol added during the esterification, the lower the change in the viscosity of the bio-oil. The presence of methanol could enhance the bio-oil stability [48] and further decrease the rate of aging during storage [49].

Table 6. The density, viscosity and total acid number of the bio-oil after esterification in the presence of TCA/H-zeolite catalyst at 70 °C with various weight ratios of bio-oil-to-methanol, catalyst loading of 10 wt%, 60-min reaction time, and stirring rate of 500 rpm.

Bio-oil property	Weight ratio of bio-oil-to-methanol							
	2:1		1:1		1:2		1:3	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Density (g/mL)	1.0227	1.0252	0.9861	0.9866	0.9415	0.9417	0.9153	0.9186
Viscosity (cP)	2.1094	2.2316	1.9417	2.0283	1.7896	1.8521	1.5643	1.6034
TAN (mg/g)	0.6921	0.3498	0.5852	0.2939	0.5316	0.2031	0.4132	0.1813

Unlike the insignificant changes in the bio-oil density and viscosity, a considerable change in the total acid number of the esterified oil was observed after the esterification in the presence of the TCA/H-zeolite catalyst, as presented in Table 6. The decrease in the total acid number of the bio-oil after esterification was 49.46%, 49.78%, 61.79% and 56.12% for the TCA/H-zeolite-catalysed esterification with a bio-oil-to-methanol weight ratio of 2:1, 1:1, 1:2 and 1:3 respectively. The addition of extra methanol in the esterification with a 1:2 weight ratio could promote the decrease in the total acid number of the bio-oil by ca 25% in comparison with that with a 2:1 and 1:1 weight ratio. The decrease in the total acid number of the bio-oil after esterification could be an indication of the formation of esters as a result of the reaction between carboxylic acids in the bio-oil feedstock and methanol in the presence of the TCA/H-zeolite catalyst [50]. In addition, aldehydes in the bio-oil feedstock could also react with methanol in the presence of acid catalysts, such as TCA/H-zeolite catalyst, to form acetals [51]. The extra addition of methanol in the esterification system (in the case of that with a 1:2 and 1:3 weight ratio) could promote the equilibrium shift to the products, resulting in the increase in the production of products, i.e., esters or acetals [52].

A further increase in the methanol addition in the esterification with a 1:3 weight ratio did not cause a higher decrease in the total acid number of the bio-oil after esterification in the presence of the TCA/H-zeolite catalyst. It might indicate that the equilibrium was not disturbed by the extra addition of methanol in the 1:3 esterification experiment. The weight ratio of bio-oil-to-methanol of 1:2 was then chosen as the condition in the further experiments with various reaction times.

Bio-oil Upgrading through TCA/H-zeolite-catalysed Esterification over Different Reaction Times

The esterification of the Sengon wood bio-oil in the presence of the TCA/H-zeolite catalyst over different reaction times was carried out with a total recovery of > 90%, as listed in Table 7, indicating a proper experimental execution. The recovered liquid contained the esterification products and possible remaining reactants. Tabel 7 shows that the coke yield coke was very low (< 1 wt%), indicating that the coke formation during the bio-oil esterification in the presence of the TCA/H-zeolite could be avoided [52].

Table 7. The mass balance closure during the esterification of the Sengon wood bio-oil in the presence of TCA/H-zeolite catalyst at 70 °C with a catalyst loading of 10 wt%, a weight ratio of bio-oil-to-methanol of 1:2, stirring rate of 500 rpm, for 15-60 min reaction times.

Reaction time (min)	Recovered liquid (wt%)	Coke yield (wt%)	Total (%)
15	92.95	0.0354	92.98
30	95.34	0.0370	95.38
45	92.92	0.0375	92.96
60	91.88	0.0394	91.92

Over prolonged reaction times, the density of the bio-oil after esterification underwent a negligible change, only by < 1%, possibly due to the enhanced stability of the bio-oil during the esterification as is shown in Table 8. The susceptibility of the reactive components of the bio-oil towards re-polymerisation has lowered resulting in the bio-oil with similar compositions of molecular weight [53].

Table 8. The density, viscosity and total acid number of the bio-oil after esterification in the presence of TCA/H-zeolite catalyst at 70 °C with a catalyst loading of 10 wt%, a weight ratio of bio-oil-to-methanol of 1:2, stirring rate of 500 rpm, for 15-60 min reaction times.

Bio-oil property	Esterification time (min)							
	15		30		45		60	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Density (g/mL)	0.9394	0.9399	0.9393	0.9401	0.9393	0.9406	0.9415	0.9417
Viscosity (cP)	1.7748	1.7908	1.7789	1.8040	1.7704	1.8308	1.7896	1.8521
TAN (mg/g)	0.5074	0.2646	0.5161	0.2588	0.5196	0.2241	0.5316	0.2032

The similar trend was observed for the viscosity of the bio-oil after esterification in the presence of the TCA/H-zeolite over various reaction times. Insignificant changes in the bio-oil viscosity by 3-5% were observed, indicating the prevention of the formation of heavy molecules during the catalysed esterification, possibly by the formation of esters and acetals [47].

Alike the change in the total acid number of the bio-oil after esterification with various weight ratios of bio-oil-to-methanol, the total acid number of that after the esterification over various reaction times decreased considerably. Over a 15-min reaction time, the total acid number of the bio-oil after the catalysed esterification decreased by 47.85%. A prolonged esterification of 30 min only caused a further decrease in the total acid number of the bio-oil by 4% (with a 49.85% decrease). A further prolonged reaction times of 45 and 60 min caused a bit higher decrease in the total acid number of bio-oil by 13% and 8%, respectively (with 56.78% and 61.78% decrease, respectively). These data suggested that carboxylic acids in the bio-oil feedstock were converted to esters in a quite fast rate at the beginning of the esterification of the bio-oil in the presence of TCA/H-zeolite catalyst [50]. The rate of esterification became slower by longer reaction times (30-60 min). Probably, the components of the bio-oil feedstock competed to attach to the active sites of the catalysts over time resulting in the high surface coverage [54]. However, not all of these reactants adsorbed at the catalyst surface could be accommodate to react with methanol as the co-adsorbed alcohol-acids intermediates at the catalyst surface were required to allow the reactions to take place [9].

Comparing the Activity of Zeolite Catalysts during the Esterification of Sengon Wood Bio-oil

The activity of the TCA/H-zeolite catalyst during the esterification of the Sengon wood sawdust was confirmed by comparing to that of the pre-treated zeolite and H-zeolite catalysts. The study was performed using the following condition: a temperature of 70 °C, a weight ratio of bio-oil-to-methanol of 1:2 and a reaction time of 60 min. A blank experiment in the absence of any catalyst was also carried out to support the justification on the performance of the TCA/H-zeolite catalyst. The liquid after esterification as well as the possible formed coke was recovered and weighed to close the mass balance as presented in Table 9.

Table 9. The mass balance closure during the esterification of the Sengon wood bio-oil in the presence of TCA/H-zeolite catalyst at 70 °C with a catalyst loading of 10 wt%, a weight ratio of bio-oil-to-methanol of 1:2, stirring rate of 500 rpm for a 60-min reaction time.

Type of catalyst	Recovered liquid (wt%)	Coke Yield (wt%)	Total (%)
NA	94.42	0.016	94.44
Pre-treated zeolite	93.18	0.043	93.23
H-zeolite	94.90	0.041	94.94
TCA/H-zeolite	91.88	0.039	91.92

The data in Table 9 suggested that negligible coke formation (< 1%) was observed. The presence of methanol during the heating up bio-oil was significant in preventing the re-polymerisation of reactive components in the bio-oil feedstock. The good mass balance closure in Table 9 indicated that the experiments were carried out properly. The properties of the bio-oil after the esterification of the bio-oil in the presence of various zeolite catalysts were investigated as listed in Table 10.

The density of the bio-oil after the esterification in Table 10 showed an insignificant change even in the absence of a catalyst. It suggested that the addition of methanol gave a significant effect in stabilising the reactive component of the bio-oil [53]. In contrast, the viscosity of the bio-oil after esterification in the presence and absence of a catalyst has increased in a different level ranging from 3.94% to 39.97%. The lowest increase in the viscosity of the bio-oil after esterification was observed for that in the presence of the TCA/H-zeolite catalyst (3.94%), while the highest increase was observed for that in the presence of the pre-treated zeolite catalyst (39.97%). The blank experiment in the absence of a catalyst did not show a significant increase in the viscosity of the bio-oil after esterification possibly due to the limited interaction of the reactive components in the bio-oil feedstock with methanol [55]. On the other hand, the presence of the zeolite catalysts might promote the interaction between reactive components themselves or with methanol [22]. The pre-treated zeolite might facilitate the interactions between reactive components to polymerise and form bigger molecules with higher molecular weight. As a result, the viscosity of the bio-oil increased significantly after esterification in the presence of the pre-treated zeolite catalyst.

Table 10. The density, viscosity and total acid number of the bio-oil after esterification in the presence of TCA/H-zeolite catalyst at 70 °C with a catalyst loading of 10 wt%, a weight ratio of bio-oil-to-methanol of 1:2, stirring rate of 500 rpm for a 60-min reaction time.

Bio-oil property	Reaction time (min)	Type of catalyst			
		NA	Pre-treated zeolite	H-zeolite	TCA/H-zeolite
Density(g/mL)	0	0.9176	0.9101	0.9140	0.9415
	60	0.9179	0.9347	0.9392	0.9417
Viscosity (cP)	0	1.7336	1.7257	1.7373	1.7896
	60	1.8367	2.3055	2.1174	1.8521
TAN (mg/g)	0	0.7006	0.6515	0.5731	0.5316
	60	0.5947	0.4240	0.2843	0.2032

The bio-oil esterification in the presence of zeolite catalysts (pre-treated, H-zeolite and TCA/H-zeolite catalysts) showed a significant decrease in the total acid number of the bio-oil after esterification by

34.92%, 50.39% and 61.78%, respectively. It was clear that the modification of Indonesian zeolite using TCA could enhance its activity in catalysing the esterification of the Sengon wood bio-oil. It was possibly due to the increase in the acid active sites at the catalyst surface as the result of the TCA modification over the zeolite catalyst [56].

Conclusions

This study investigated the activity of the TCA/H-zeolite catalyst during the bio-oil esterification in the presence of methanol over various weight ratios of bio-oil-to-methanol and reaction times. The presence of TCA/H-zeolite catalyst during the esterification of the bio-oil could suppress the formation of coke. In the presence of TCA/H-zeolite, the weight ratios of bio-oil-to-methanol significantly affected the decrease in the total acid number of the bio-oil after the esterification. Moreover, the esterification of Sengon wood bio-oil in the presence of the TCA/H-zeolite catalyst took place in a fast rate, indicated by the decrease in the total acid number of the bio-oil by 47.85% over a 15-min esterification. Compared to the uncatalysed esterification, the presence of the TCA/H-zeolite catalyst could further enhance the decrease in the total acid number up to 65.83%.

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Good

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Good

Technical accuracy

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Excellent

Use of Tables and Figures

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Referee’s Comments

Abstract
TCA should be defined before using the abbreviation.
TCA/H-zeolite was reported in the body of the work not TCA/zeolite.
Introduction
3rd paragraph: ‘solid acid catalyst from’ change to ‘acid modified rice husk’ or any other expression except the current one in the draft
Materials and Methods
Preparation and characterisation of TCA-modified Indonesian natural zeolite catalyst
2nd paragraph: What is the reason behind the use of percentage in diluting HF and moles for HCl and NH4Cl? Also why did the author use different concentration of the three acids used for treatment? The last sentence should be cited (calcination of zeolite to H-zeolite).
3rd Paragraph: First sentence: Is the author using chloroacetic acid of trichloroacetic acid? TCA was defined in the introduction section, subsequently, the abbreviation should be used, there is no need to redefine it again.
Catalytic esterification of Sengon wood bio-oil
Ist sentence: Define TCA/H-zeolite before the use of the term in the body of this draft
The terms in equation 1 and 2 should be defined.
Page 5:
Table 1 and 2 should be merged for ease of discussion.
Last paragraph in Page 5: Clearly there is change in compounds present in the zeolite depending on the treatment imposed and clearly average pore radius reduced for TCA/H-zeolite. The presence of XRF result would have provided an insight into the extent of treatment on the change in compounds present in zeolite and I will suggest that the author see how XRF can be added or any analysis that will show the quantitative change in the compounds/elements present in zeolite upon modification.
Page 6.
The author did not state the standard properties of the oil in existence or give an indication of this oil. Understanding the standard property that current bio-oil will complement or replace will guide in following subsequent experiments.
Page 7.
Last sentence: The author insinuated that ester was formed after esterification, how do we know for sure that ester was formed? There is no conclusive analysis that pointed in that direction. Which ester dominates this oil? What is the change in functional group ini bio-oil and esterified oil?
It is expected that the author should conduct FTIR and ester profile on his oil. FTIR will give an insight into the change in functional group. Clearly ester peaks will be seen in the spectra. Also, ester profile will give an insight into the dominant ester in the oil formed.
Tables: The table captions are too long. The author should use simple English for his caption while a full description of the table should be done in the body of the draft.
The property of the oil formed was not compared with previous research.

Reviewer E:
Recommendation: Revisions Required

Originality of the work

Excellent

Experimental design and methodology

Good

Adequacy of the discussion

Good

Technical accuracy

Good

Suitability of references

Good

Use of Tables and Figures

Excellent

Standard of English

Good

Clarity and conciseness

Excellent

Referee’s Comments

There are some questions regarding material selection that have not been discussed, the reasons for the different weight ratios of bio-oil-to-methanol have not been explained. as well as research deficiencies and suggestions for further researchers need to be added

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Reviewer G:
Recommendation: Revisions Required

Originality of the work

Good

Experimental design and methodology

Good

Adequacy of the discussion

Good

Technical accuracy

Good

Suitability of references

Adequate

Use of Tables and Figures

Good

Standard of English

Good

Clarity and conciseness

Good

Referee’s Comments

This paper investigated the catalytic activity of TCA-modified Indonesian natural zeolite during the esterification of Sengon wood bio-oil, the results showed that the TCA-modified Indonesian natural zeolite was a promising catalyst for the bio-oil esterification. The results of this paper contribute to the efficient use of bio-oil. However, the following questions need to be carefully considered before publishing.

1. The coke yield of the bio-oil at 70 °C during the esterification cannot represent the coking tendency of bio-oil. It is suggested to measure the coke yield during the utilization of bio-oil at higher temperatures.

2. What is the coke yield of bio-oil when heated at 70 °C, this data should be compared with the data in Table 5.

3. The heavy components affect the viscosity of bio-oil, which is also suggested to discuss in this paper. See the references: Fuel Processing Technology 199 (2020) 106299； Energy Fuels 2019, 33, 11292−11301.

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2 attachments

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3. Bukti konfirmasi *submit* revisi pertama, respon kepada *reviewer*, dan artikel yang di-*resubmit*

(3 Juni 2022)

Dear the editor of Trend in Sciences Journal,

Herewith we submit the revised version of the manuscript based on the reviewers' comments along with the reply to the comments.

The authors have worked hard to revise the manuscript. Please refer to the following detail to justify the revision. The revision regarding the Reviewer A's comments is yellow-highlighted; Reviewer E's comments are blue-highlighted; and Reviewer G's comments are green-highlighted.

In addition to the revision based on the reviewers' comments, the authors have ensured that the manuscript has strictly followed the guideline and the journal template.

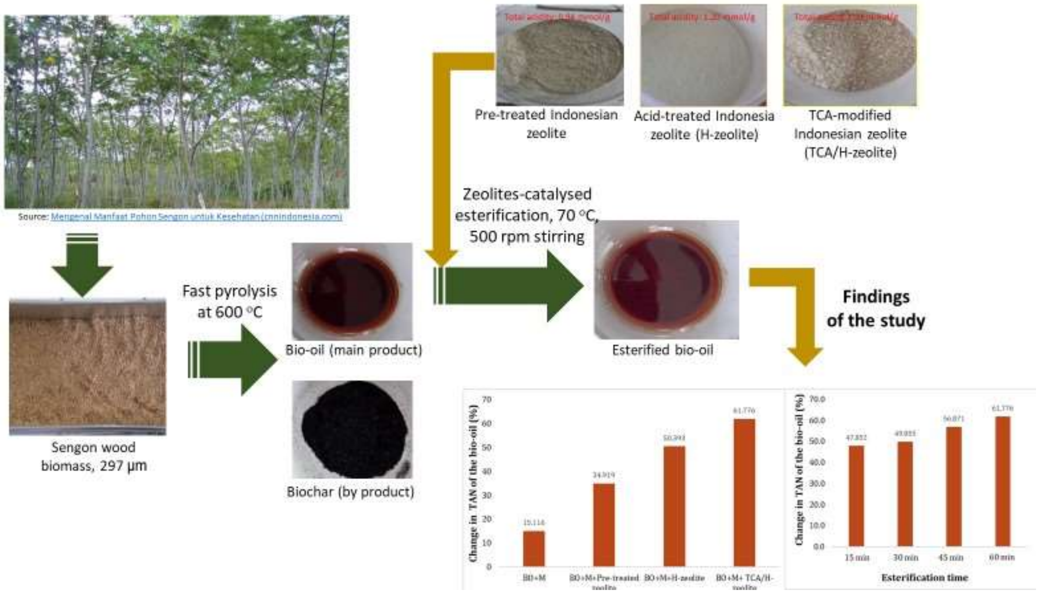
We do hope that the revision is satisfactory and this revised manuscript could be further considered to be published in Trend in Sciences journal.

Thank you very much.

Sincerely yours,

Sri Kadarwati

Graphical abstract



Highlights

- The TCA-modified Indonesian natural zeolite catalyst has been successfully prepared.
- The presence of the TCA/Indonesian natural zeolite during the esterification of bio-oil produced from the pyrolysis of Sengon wood could greatly suppress the severe repolymerisation leading to coke formation
- The TCA/Indonesian natural zeolite-catalysed esterification of Sengon bio-oil underwent in a fast rate.
- The TCA/Indonesian natural zeolite catalyst showed a good performance in this study in comparison with the uncatalysed esterification.

Trends in Sciences

Responses the referee's comments

Manuscript ID: 3632

Title: The Catalytic Activity of TCA-Modified Indonesian Natural Zeolite during the Esterification of Sengon Wood Bio-oil

Reviewer A

No.	Referee's Comments	Responses
1.	**Abstract** TCA should be defined before using the abbreviation.	The correction has been proceeded as suggested. "The esterification was performed at 70 °C in the presence of a trichloro acetic acid (TCA)-modified Indonesian H-zeolite………"
2.	**Abstract** TCA/H-zeolite was reported in the body of the work not TCA/zeolite.	The correction has been proceeded as suggested. "The esterification was performed at 70 °C in the presence of a trichloro acetic acid (TCA)-modified Indonesian H-zeolite………"
3.	**Introduction** 3rd paragraph: 'solid acid catalyst from' change to 'acid modified rice husk' or any other expression except the current one in the draft	The correction has been proceeded as suggested. "…………..ion exchange resins [11], modified zirconia [12, 13], Amberlysts [14-16], acid modified rice husk ash [17], and heteropoly acids [18] have been used as a catalyst……….."
4.	**Materials and Methods** **Preparation and characterisation of TCA-modified Indonesian natural zeolite catalyst** 2nd paragraph: What is the reason behind the use of percentage in diluting HF and moles for HCl and NH_4Cl? Also why did the author use different concentration of the three acids used for treatment? The last sentence should be cited (calcination of zeolite to H-zeolite).	The use of different chemicals for the zeolite activation was aimed for the different purposes. The different concentration of each used during the chemical activation was chosen based on the previous studies. The use of HF and HCl solution, for example, was aimed to remove the silica and alumina, respectively, outside of the zeolite framework. Meanwhile, the use of the NH_4Cl solution was for the zeolite surface modification, i.e., by exchanging the exchangeable cations at the zeolite surface with NH_4^+ in order to form H-zeolite after calcination. Moreover, a cited references has been added as suggested.
5.	**Preparation and characterisation of TCA-modified Indonesian natural zeolite catalyst** 3rd Paragraph: First sentence: Is the author using chloroacetic acid of trichloroacetic acid? TCA was defined in the introduction section, subsequently, the abbreviation should be used, there is no need to redefine it again.	The correction has been proceeded as suggested. "A 5 g of TCA was dissolved in 9 mL of demineralised water…….."
6.	**Catalytic esterification of Sengon wood bio-oil** 1st sentence: Define TCA/H-zeolite before the use of the term in the body of this draft	The definition of TCA/H-zeolite is stated in the 3rd paragraph of the sub-section '**Preparation and characterisation of TCA-modified Indonesian natural zeolite catalyst**'

7.	**Catalytic esterification of Sengon wood bio-oil** The terms in equation 1 and 2 should be defined.	The definition of the terms in equation (1) and (2) has been added. “W'_{cat} and W^{0}_{cat} are designated as the weight of the “TCA/H-zeolite” catalyst after and before the esterification of the bio-oil, respectively, while $W_{bio\text{-}oil\ fed}$ is the weight of the bio-oil fed in each esterification experiment.” has been added for the equation (1). Meanwhile, “MW_{KOH}, N_{KOH}, and V_{KOH} are designated as the molecular weight, normal concentration and volume of KOH solution, respectively. Meanwhile, W_{sample} and *dilution* are designated as the weight of the sample and the magnitude of dilution employed during the measurement of TAN.” has been added for the equation (2).
8.	**Page 5:** Table 1 and 2 should be merged for ease of discussion.	Table 1 and 2 have been merged and the rest of the tables have been adjusted.
9.	**Page 5:** Last paragraph in Page 5: Clearly there is change in compounds present in the zeolite depending on the treatment imposed and clearly average pore radius reduced for TCA/H-zeolite. The presence of XRF result would have provided an insight into the extent of treatment on the change in compounds present in zeolite and I will suggest that the author see how XRF can be added or any analysis that will show the quantitative change in the compounds/elements present in zeolite upon modification.	The authors are very thankful for the reviewer’s suggestion. Unfortunately, the authors are afraid could not add the XRF data in the manuscript. The manuscript has provided the data on the main requirement of the catalyst, i.e., acid sites on the catalyst surface. The authors think that the current data presented in the manuscript is adequate to support and explain the performance of the TCA/H-zeolite catalyst during the esterification of the bio-oil.
10.	**Page 6.** The author did not state the standard properties of the oil in existence or give an indication of this oil. Understanding the standard property that current bio-oil will complement or replace will guide in following subsequent experiments.	Thank you for the comment. In the authors’ opinion, there is no properties standard of bio-oil. The properties of bio-oil are strongly affected by the feedstocks and pyrolysis conditions, e.g., pyrolysis temperature, particle size of feedstocks, types/configuration of the reactors. In order to achieve the goal of the production of liquid fuels, the comparison of the bio-oil with the commercial fuels is more suitable. While in this study, the authors discussed one of several steps of the process of the liquid fuels production.
11.	**Page 7.** Last sentence: The author insinuated that ester was formed after esterification. How do we know for sure that ester was formed? There is no conclusive analysis that pointed in that direction. Which ester dominates this oil? What is the change in functional group in bio-oil and esterified oil?	The FTIR data and its discussion has been added to discuss the formation of esterification products during the reaction.
12.	**Page 7.** It is expected that the author should conduct FTIR and ester profile on his oil. FTIR will give an insight into the change in functional group. Clearly ester peaks will be seen in the spectra. Also, ester profile will give an insight into the dominant ester in the oil formed.	The FTIR data has been added in each sub-section of **Results and Discussion**.
13.	**Page 7.** Tables: The table captions are too long. The author should use simple English for his	The corrections have been made for the tables with long caption as suggested.

	caption while a full description of the table should be done in the body of the draft.	
14.	**Page 7.** The property of the oil formed was not compared with previous research.	Thank you for the comments. The experiments conducted in this study were different in some extent from those conducted previously, e.g. setting of experiments, focus, feedstock, catalyst, etc. The authors think that the comparison of the oil properties obtained in this study with those conducted previously with different reaction condition is not necessary.

Reviewer E

No.	Referee's Comments	Responses
1.	**Introduction, Paragraph 1** The reasons for choosing sengon wood over other types of wood should also be discussed. Is the content of lignin, cellulose and hemicellulose in sengon wood the highest compared to other types? And is sengon wood a type of local plant that only exists in Indonesia?	The reason for choosing Sengon wood has been added. "The high content of cellulose in Sengon wood would result in the high yield of bio-oil [4]……..".
2.	**<u>Materials and methods</u>** **Preparation and characterisation of a TCA-modified Indonesian natural zeolite catalyst** In this section the heating process is carried out for 3 hours. While this section is 2 hours, is there a reason for the difference in drying time?	The longer drying time for the former process (after soaked in water and rinsed several times) was required to allow water (and other possible moistures) to evaporate. Meanwhile, in the zeolite modification with TCA, the sample itself looked dry (the mixture of H-zeolite and TCA was heated under continuous stirring at 80 ºC until no water macroscopically left). A shorter time of drying is needed to allow all water in the zeolite pores to evaporate.
3.	**<u>Results and Discussion</u>** **Bio-oil upgrading through TCA/H-zeolite-catalysed esterification over different weight ratios of bio-oil-to-methanol** Is there any particular reason why to use this comparison? Why not use a 3:1 ratio for make it balance?	At first, we conducted the experiment with a weight ratio of bio-oil-to-methanol of 2:1 and 1:1. The observed bio-oil properties after esterification were compared. This made us to continue the experiments with higher amount of methanol to prevent the re-polymerisation and to promote the esterification process, as reported in our previous study.
4.	**<u>Conclusions</u>** Can you add to the shortcomings of the research? And suggestions for further researchers what should be done? Because this research is very interesting, to certainly obtain renewable energy in the future	The recommendation has been added after the conclusion as suggested. "The esterification at higher temperatures and using a pressurised reactor would improve the quality of the esterified bio-oil. Furthermore, the combination between hydrocracking and esterification could simultaneously undergo in the presence of hydrogen and hydroprocessing catalysts."

Reviewer G

No.	Referee's Comments	Responses
1.	The coke yield of the bio-oil at 70 °C during the esterification cannot represent the coking tendency of bio-oil. It is suggested to measure the coke yield during the utilization of bio-oil at higher temperatures.	Thank you for the suggestion. The experiments at higher temperatures could not be carried out since the simple reflux reactor was used. A pressurized reactor would be required to allow the esterification at temperatures higher than solvent (methanol) boiling point.

2.	What is the coke yield of bio-oil when heated at 70 °C, this data should be compared with the data in Table 5.	The discussion on the coke formed during the esterification of the bio-oil only in the absence of the TCA/H-zeolite catalyst has been presented in the sub-section **Comparing the activity of zeolite catalysts during the esterification of Sengon wood bio-oil.**
3.	The heavy components affect the viscosity of bio-oil, which is also suggested to discuss in this paper. See the references: Fuel Processing Technology 199 (2020) 106299 ; Energy Fuels 2019, 33, 11292−11301.	The authors did discuss about the relationship between viscosity and heavy components (component with high molecular weight). For an instance, "Insignificant changes in the bio-oil viscosity by 3-5% were observed, indicating the prevention of the formation of heavy molecules during the catalysed esterification, …………..."

TRENDS IN SCIENCES, 202x; xx(xx): xxxxx RESEARCH ARTICLE
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The Catalytic Activity of TCA-Modified Indonesian Natural Zeolite during the Esterification of Sengon Wood Bio-oil

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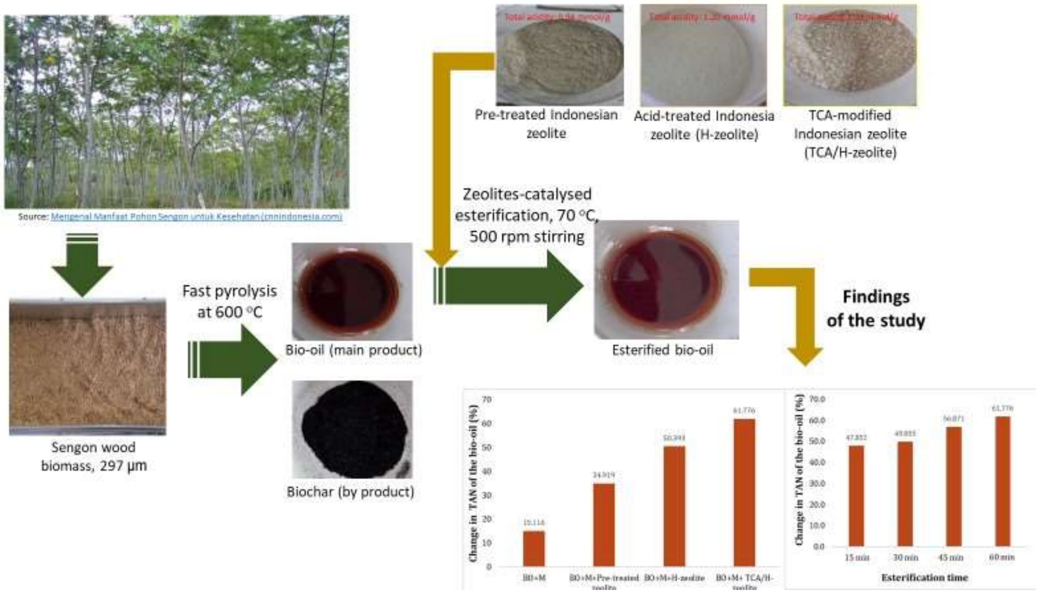
Received: xxx, Revised: xxx, Accepted: xxx

Highlights

- The TCA-modified Indonesian natural zeolite was a promising catalyst for the bio-oil esterification.
- A decrease in the total acid number of the esterified bio-oil was significant.
- The esterified bio-oil was stable while keeping the coke formation low.
- The esterification of the bio-oil using TCA/H-zeolite catalyst took place in a fast rate.

Graphical abstract



Abstract

The bio-oil produced from the pyrolysis of biomass is highly corrosive due to the high content of organic acids. These organic acids could be removed through an appropriate upgrading process, i.e., esterification using alcohols to form less polar esters. In this study, the bio-oil used as the feedstock in the esterification was produced from the pyrolysis of Sengon wood with a particle size of 297 µm at 600 °C. The esterification was performed at 70 °C in the presence of a trichloro acetic acid (TCA)-modified Indonesian H-zeolite catalyst with various weight ratios of bio-oil-to-methanol and reaction times under a constant stirring rate of 500 rpm. The esterification progress was indicated by the decrease in the total acid number of the bio-oil after esterification. No significant coke formation (< 0.05wt%) was observed indicating that the suppression of repolymerisation could be achieved. This study showed that the esterification underwent in a fast rate, indicated by the decrease in the total acid number of the bio-oil by

47.85% only over a 15-min esterification. Compared to the uncatalysed esterification, the TCA/zeolite-catalysed esterification showed a higher decrease in the total acid number of the bio-oil up to 65.83%, due to the conversion of the carboxylic acids to esters.

Keywords: Esterification, Sengon wood bio-oil, TCA-modified Indonesian zeolite, total acid number.

Introduction

The fossil fuel depletion has promoted the exploration of new renewable energy resources. Biomass has been considered as a promising renewable energy resource due to its high availability, its environmentally friendly properties and its zero competition with food sector [1]. A liquid fuel could be produced as the main product from the fast pyrolysis of biomass [2] that is well known as bio-oil or pyrolysis oil. Sengon wood, as an abundantly available feedstock in Indonesia was used in this study for bio-oil production. Sengon wood contains lignin, cellulose, and hemicellulose of 26.1%, 45.4%, and 21.0% and respectively [3]. The high content of cellulose in Sengon wood would result in the high yield of bio-oil [4], allowing a sustainable starting material for liquid fuel production.

The bio-oil produced from the pyrolysis of biomass could be used as a fuel for boilers, stationary as well as sterling engines [5]. However, the bio-oil cannot be directly used as a fuel for transportation due to several unfavourable properties such as high water content leading to low calorific value and high oxygen content resulting in highly instable properties [6]. In addition, the bio-oil contains high amount of organic acids making it highly corrosive and causing a big challenge during its use as a fuel or its compatibility during further processing in the biorefinery [7]. A bio-oil upgrading is required for the bio-oil to meet the requirements as liquid transportation fuels [8].

Esterification has been reported to show a great potential as bio-oil upgrading technique to reduce the acids content of the bio-oil [9]. It converts the organic acids in the bio-oil to e.g., esters in the presence of alcohols and acid catalysts [10]. The use of solid acid catalysts during the esterification of bio-oil has been considered more beneficial in comparison with that of homogeneous catalysts due to the easy separation resulting in a more efficient and cost-effective process [11]. Several solid acid catalysts such as ion exchange resins [12], modified zirconia [13, 14], Amberlysts [15-17], acid modified rice husk ash [18], and heteropoly acids [19] have been used as a catalyst in the esterification of the "real" bio-oil as well as model compounds mimicking bio-oil. In addition, zeolite-based catalysts have been reported to show a great potential as a catalyst for esterification of bio-oil [20-24].

A special attention has been paid to Indonesian natural zeolite primarily in related to its application as a catalyst for bio-oil upgrading. It has a good porosity and modifiable Brønsted acid sites [25] at its surface to anticipate the complicated compositions and behaviour of the bio-oil during the esterification. The modification of Brønsted acid sites at the Indonesian zeolite surface to improve the Brønsted acidity could enhance the catalytic activity of Indonesian zeolite during the esterification of the bio-oil.

The Brønsted acidity of the Indonesian zeolite could be improved by strong acid modification, e.g., trichloroacetic acid (TCA) resulting in the zeolite with a better Brønsted acidity [26]. However, the application of TCA-modified Indonesian natural zeolite as a catalyst for esterification of bio-oil produced from the fast pyrolysis of Sengon wood was rare. More studies to investigate the activity of the TCA-modified Indonesian natural zeolite are necessary to evaluate its potential as a catalyst for the bio-oil esterification. This study focused on the esterification of the bio-oil produced from the fast pyrolysis of Sengon wood sawdust with various weight ratios of bio-oil-to-methanol and reaction times to investigate the esterification behaviour of organic acids in the bio-oil primarily acetic acid in the presence of methanol and TCA-modified Indonesian natural zeolite as a solid acid catalyst.

Materials and methods

Preparation and characterisation of a TCA-modified Indonesian natural zeolite catalyst

The Indonesian natural zeolite from Wonosari, Yogyakarta, Indonesia was used as a starting material of the zeolite catalyst. It was purchased from CV. SSGT Zeolite, Indonesia. The natural zeolite was prepared as previously reported [24]. Briefly, the natural zeolite with a particle size range of 100-120 μm was activated using sequent chemical and physical activation method. Prior to activation process, the natural zeolite was washed in distilled water and dried at 110 °C for 3 h to allow the physical contaminant removal. "Pre-treated zeolite" corresponds the natural zeolite from this pre-treatment step.

The natural zeolite was chemically treated using 1% HF, 6 N HCl and 1 N NH_4Cl solutions (prepared from 50% HF, 37% HCl, and solid NH_4Cl, obtained from E. Merck, respectively) in a sequence. This chemical activation was followed with a physical activation, i.e., calcination of the natural zeolite sample at 500 ºC under nitrogen atmosphere to produce "H-zeolite" catalyst [24].

The modification of the "H-zeolite" catalyst with chloroacetic acid was carried out as reported by Ávila *et al.* [6] with some adjustment. A 5 g of TCA was dissolved in 9 mL of demineralised water in an Erlenmeyer flask. A 10 g of "H-zeolite" was added in the TCA solution. The mixture was then heated at 80 °C under a continuous stirring with a low stirring rate of 100 rpm until no water left. The solid obtained was dried in an oven at 110 °C for 2 h resulting in the "TCA/H-zeolite" catalyst.

The formation of the "TCA/H-zeolite" catalyst was confirmed based on the appearance of characteristics vibration peaks at wavenumbers of 830 and 680 cm^{-1} (the stretching vibration of C-Cl bonds) [26] in the IR spectrum. The IR spectrum of the "TCA/H-zeolite" catalyst was obtained using a Perkin-Elmer Frontier Spotlight 200 type-Fourier transform infrared spectrophotometer. In addition, the possible change in the crystalline structure of Indonesian natural zeolite was evaluated using a PANalytical Xpert'3 Powder X-ray diffractometer.

The surface properties of the "TCA/H-zeolite" catalyst were characterised using a Quantachrome Nova 1200e surface area analyser. The specific surface area, total pore volume and average pore radius were determined using a BET-BJH isotherm adsorption. Moreover, the acidity of the "TCA/H-zeolite" catalyst was determined using an ammonia adsorption. The amount of ammonia adsorbed at the catalyst surface was assigned as the total acidity of the catalyst in mmol ammonia per gram catalyst. This quantitative measurement of the catalyst acidity was combined with the analysis of the chemical functionalities of the catalyst to confirm the presence of the new bonds of ammonia with the Lewis and Brønsted acid sites at the catalyst surface at wavenumbers of 1640, 1550, and 1450 cm^{-1}.

Catalytic esterification of Sengon wood bio-oil

The esterification of the bio-oil with methanol in the presence of "TCA/H-zeolite" catalyst was carried out in a batch reactor system equipped with a temperature monitor and magnetic stirrer. The esterification was conducted at 70 ºC, with a catalyst loading of 10 wt%, a stirring rate of 500 rpm, and various weight ratios of bio-oil-to-methanol of 1:1, 2:1, 1:2 and 1:3. The Sengon wood bio-oil used in the esterification process was produced from the pyrolysis of Sengon wood sawdust with a particle size of 297 µm at 600 °C using a fixed-bed pyrolyser as previously reported [24]. The esterification with a weight ratio of bio-oil-to-methanol which gave the highest decrease in the total acid number of the bio-oil after esterification underwent that with various esterification times of 15, 30, 45 and 60 min.

After each experiment, the mixture of liquid esterification products and possible remaining reactants was recovered and designated as the esterified bio-oil. The coke formation was determined based on the weight difference of solid catalyst before and after the esterification. The yield of coke was calculated using equation (1) to close the mass balance. W'_{cat} and W^0_{cat} are designated as the weight of the "TCA/H-zeolite" catalyst after and before the esterification of the bio-oil, respectively, while $W_{bio\text{-}oil\ fed}$ is the weight of the bio-oil fed in each esterification experiment.

$$Coke\ yield = \frac{W'_{cat} - W^0_{cat}}{W_{bio-oil\,fed}} x100\% \qquad (1)$$

Characterisation of the bio-oil after esterification

The esterified bio-oil after each esterification experiment was characterised, including the density, viscosity and total acid number. The density and viscosity of the esterified bio-oil were determined using a gravimetric method by means of a pycnometer and an Ostwald viscometer, respectively.

The total acid number (TAN) of the esterified bio-oil was measured using an SNI 01-3555-1998 procedure as follows. The bio-oil sample was dissolved in acetone to 96 wt% clear solution of bio-oil. A 2.5 g of the bio-oil solution was heated to boil and added with 2-3 drops of phenolphthalein solution. The titration of the bio-oil solution was conducted using 0.1 N KOH solution until a light red colour appeared. The total acid number of the esterified bio-oil was calculated using Equation (2). MW_{KOH}, N_{KOH}, and V_{KOH} are designated as the molecular weight, normal concentration and volume of KOH solution, respectively. Meanwhile, W_{sample} and *dilution* are designated as the weight of the sample and the magnitude of dilution employed during the measurement of TAN.

$$TAN = \frac{MW_{KOH} \times N_{KOH} \times V_{KOH}}{W_{sample}} \times dilution \qquad (2)$$

Results and discussion

The characteristics of TCA/H-zeolite catalyst

The important properties of the TCA/H-zeolite catalyst prepared in this study was investigated, including the chemical functionalities, the possible change in the crystalline structure, the surface porosity, and the total acidity. The chemical functionalities of the TCA/H-zeolite catalyst were represented by the spectra in Figure 1. The general featured functionalities of the zeolite with aluminosilicate framework were shown by the appearance of a vibration peak –OH groups at 3200-3600 cm^{-1}. In addition, bending vibrations of Al-OH/Si-OH were observed at 1650-1400 cm^{-1}, while stretching vibrations of Si-O/Al-O were observed at wavenumbers of 1250-950 cm^{-1} and 820-650 cm^{-1}.

The success of the zeolite modification with TCA was confirmed by the appearance of stretching vibrations of C-Cl bonds at wavenumbers of 840 and 690 cm^{-1} [26] at the IR spectrum of the TCA/H-zeolite catalyst (Figure 1c). These vibrations indicated the chemical interaction between TCA and the –OH groups of the zeolite.

The change in the crystalline structure of the zeolite over subsequent chemical and physical treatment as well as TCA modification was evaluated through the XRD patterns of the pre-treated zeolite, H-zeolite and the TCA/H-zeolite catalysts, as shown in Figure 2. The similar XRD patterns and peak intensity in Figure 2 indicated that the zeolite did not undergo a significant change in the crystalline structure over the subsequent treatments. Moreover, the intensity of the three highest peaks denoted that the mordenite mineral structure was predominant in the zeolite catalysts.

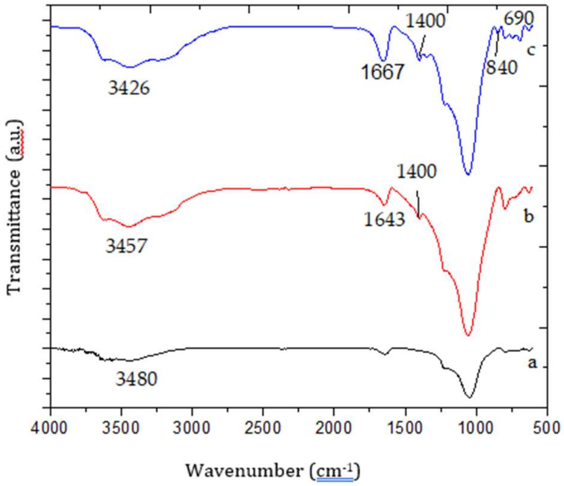


Figure 1. IR spectra of a) pre-treated zeolite, b) H-zeolite and c) TCA/H-zeolite.

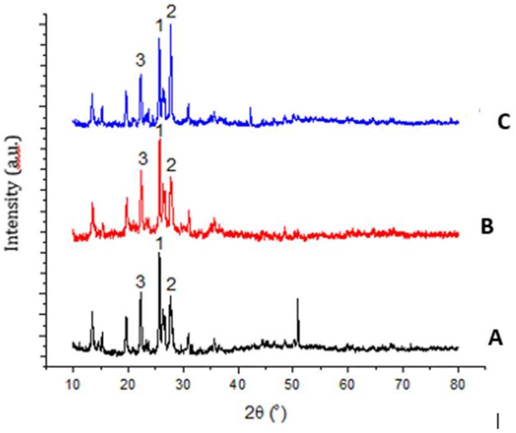


Figure 2. The diffraction patterns of a) pre-treated zeolite, b) H-zeolite and c) TCA/H-zeolite.

The measurement of the total (Lewis and Brønsted) acidity of the TCA/H-zeolite catalyst was performed to support the data of IR spectra indicating the success of the zeolite modification with TCA. The significant increase of the total acidity of the TCA/H-zeolite catalyst would further evidence of the success modification in this study. In addition, the enhanced total acidity of the TCA/H-zeolite catalyst would promote a better esterification process as this acid active sites would play important roles in catalysing the esterification of bio-oil with methanol [13].

The total acidity of the TCA/H-zeolite catalyst was conducted through ammonia adsorption in combination with a gravimetric method. The amount of ammonia adsorbed at the catalyst surface would provide the data the number of acid active sites interacting with the adsorbed ammonia [27, 28].

The total acidity of the TCA/H-zeolite catalyst in comparison with the pre-treated and H-zeolite is presented in Table 1. A significant increase in the total acidity of the TCA/H-zeolite catalyst was observed, 1.7 folds from that of H-zeolite. It was most likely due to the modification of the zeolite with TCA resulting in the chemical interaction of carbonyl oxygen or hydroxyl oxygen of TCA with the Brønsted acid sites of H-zeolite [29].

Table 1. The total acidity and the surface porosity of the zeolite catalysts.

Type of catalyst	Total acidity (mmol NH_3/g)	Surface area (m^2/g)	Total Pore Volume (cm^3/g)	Average Pore Radius (Å)
Pre-treated zeolite	0.94	12.82	0.077	119.96
H-zeolite	1.20	22.26	0.065	588.35
TCA/H-zeolite	3.28	28.41	0.075	526.31

Furthermore, the interaction between ammonia Lewis's base and the Brønsted and Lewis sites of the catalyst was evaluated through the IR spectra of the TCA/H-zeolite catalyst in Figure 3. The interaction of ammonia with the Lewis and Brønsted active sites was designated by the vibrations at wavenumbers of 1450 cm^{-1} and 1550-1640 cm^{-1}, respectively [30].

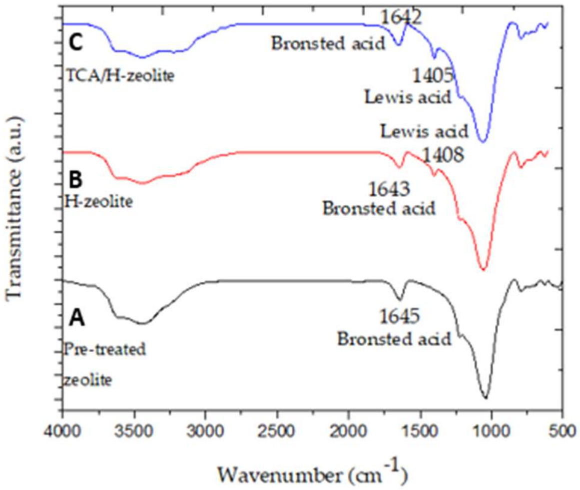


Figure 3. IR spectra of a) pre-treated zeolite, b) H-zeolite and c) TCA/H-zeolite after NH_3 adsorption.

The surface porosity of a catalyst is an important property of the catalyst in supporting the catalytic performance. It was due to the presence of active sites at the catalyst surface including the catalyst pores [31]. The surface porosity of the TCA/H-zeolite catalyst determined in this study included specific surface area, total pore volume and average pore radius of the catalyst as presented in Table 1.

The surface porosity data in Table 1 showed that chemical and physical treatment towards the pre-treated zeolite caused a significant increase (73.63%) in the surface area of the H-zeolite catalyst. It was might due to the impurity removal and the formation of new pores during the treatment [32]. A further increase (27.63%) in the specific surface area was also observed in the TCA/H-zeolite catalyst, probably due to the surface modification using a strong acid TCA at the solid H-zeolite surface [33, 34].

A significant increase of the average pore radius of the H-zeolite catalyst in comparison with the pre-treated zeolite catalyst (3.9 folds) was also observed. The acid treatment followed with calcination at high temperature of 500 ºC probably could cause impurity removal resulting in an increase in the pore size of the zeolite [33]. Moreover, the growth of the pore structure might take place due to the chemical treatment during the preparation of the H-zeolite catalyst [35]. However, a slight decrease (~10%) of the average pore radius was observed after the zeolite modification with TCA. The TCA introduction with a quite high concentration (ca. 35%) at the H-zeolite surface followed with a low drying temperature (80 ºC) might promote the pore occupation by the TCA molecules, resulting in the decrease of the average pore size of the zeolite [36].

Unlike the considerable changes in the specific surface area and average pore radius, the total pore volume of the zeolite catalysts was almost unchanged; only ~15% of change was observed. The insignificant change in the total pore volume accompanied with the increase in the average pore radius might be probably attributed to the reduction of the pore depth at the zeolite surface. This would allow the easier interaction between the surface-active sites and the reactants during the esterification of the bio-oil.

Production and characterisation of the bio-oil from the pyrolysis of Sengon wood sawdust

The bio-oil used as the feedstock during the esterification in this study was produced from the fast pyrolysis of Sengon wood sawdust with a particle size of 297 µm at 600 °C using a fixed-bed pyrolyser. The yield of the bio-oil was considerably high of 45.66 wt%, as presented in Table 2. Such high temperature would help the lignocellulose macromolecules to undergo good decomposition during the pyrolysis [37]. Lignocellulose composes of lignin, cellulose and hemicellulose with specific decomposition temperatures. Lignin would decompose at 300-550 °C, while hemicellulose and cellulose would decompose at 250-350 °C and 325-400 °C, respectively [38]. The rate of decomposition of lignocellulose macromolecules would increase with increasing the pyrolysis temperature, resulting in more condensable light fractions [39], thus high bio-oil yield. However, extremely high temperature would promote the production of the non-condensable fractions resulting in higher yield of gaseous pyrolysis product [40].

Table 2. The yield of pyrolysis products produced from the pyrolysis of Sengon wood sawdust with a particle size of 297 µm at 600 ºC using a fixed-bed pyrolyser.

Type of product	Yield (wt.%)
Bio-oil	45.66
Biochar	29.97
Gaseous product*	24.37

*by difference

The physical and chemical properties of the Sengon wood bio-oil produced through fast pyrolysis technique were measured, including the density, viscosity, and total acid number as shown in Table 3. The density of the bio-oil was not directly related to the quality of the bio-oil. However, this property could provide an indication whether heavy or light molecules were predominant in the bio-oil [41]. The low density of the bio-oil produced in this study (1.07 g/mL) indicated that light molecules with relatively low molecular weight were predominant due to severe decomposition process at 600 °C during the pyrolysis resulting in more condensable light fractions.

Table 3. The characteristics of the bio-oil produced from the pyrolysis of Sengon wood sawdust with a particle size of 297 µm at 600 ºC using a fixed-bed pyrolyser.

Property (unit)	Value (wt.%)
Density (g/mL)	1.07
Viscosity (cP)	2.40
TAN (mg KOH/g)	0.73

Another parameter evaluated in this study for the bio-oil quality is viscosity. This parameter is affected by the liquid temperature, the strength of intermolecular forces, and the molecular weight and the amount of the soluble components in the liquid bio-oil [42]. The pyrolysis temperature of 600 °C has resulted in the bio-oil with light components (short carbon chains, low molecular weight) in the considerable amount, resulting in the bio-oil with a low viscosity of 2.40 cP (see Table 3) [43].

The total acid number of the Sengon wood bio-oil was determined by using an aliquot method, as presented in Table 3. This parameter provided an estimation of the content of organic acids in the bio-oil

[44]. The high content of organic acids in bio-oil or liquid fuels would lead to corrosion to engines and/or the equipment used in the further processes such as biorefinery [8]. The high total acid number (0.73 mg/g) of the Sengon wood bio-oil used as the feedstock in the esterification process suggested the high organic acid content in the bio-oil. It was likely due to the presence of organic acids such as carboxylic acids as a result of the decomposition of the lignocellulose macromolecules at higher pyrolysis temperature [45]. The acid removal from the bio-oil is extremely important to minimise the corrosiveness of the bio-oil prior to its use as a fuel or its further processes in the biorefinery through an appropriate upgrading technique. A bio-oil upgrading through an esterification technique using TCA/H-zeolite was investigated with different weight ratios of bio-oil-to-methanol over various reaction times.

Bio-oil upgrading through TCA/H-zeolite-catalysed esterification over different weight ratios of bio-oil-to-methanol

The esterification of the Sengon wood bio-oil in the presence of the TCA/H-zeolite catalyst was carried out with various weight ratios of bio-oil-to-methanol of 2:1, 1:1, 1:2 and 1:3 at 70 °C, a catalyst loading of 10 wt%, a 60-min reaction time, and a stirring rate of 500 rpm. The liquid and the possible formed coke after each esterification experiment were recovered to close the mass balance, as presented in Table 4. The mass balance closure was higher than 90 wt% indicating a proper experimental execution [46]. The coke yield in all experiments was very low of < 1 wt%. This indicated that the possible repolymerisation between the reactive components in the bio-oil leading to the formation of coke could be prevented during the bio-oil esterification [47] in the presence of the TCA/H-zeolite catalyst.

Table 4. The mass balance closure during the esterification of the Sengon wood bio-oil in the presence of TCA/H-zeolite catalyst with various weight ratios of bio-oil-to-methanol.

Weight ratio of BO-to-methanol	Recovered liquid (wt%)	Coke yield (wt%)	Total recovery (%)
2:1	94.11	0.0407	94.15
1:1	91.90	0.0404	91.94
1:2	91.88	0.0394	91.92
1:3	97.79	0.0334	97.82

The density, viscosity and total acid number of the liquid obtained after the TCA/H-zeolite-catalysed esterification with various weight ratios of bio-oil-to-methanol at 70 °C were measured as presented in Table 5. A catalyst loading of 10 wt%, a 60-min reaction time, and a stirring rate of 500 rpm were employed during each experiment. The density of the esterified oil insignificantly changed with relatively abundant addition of methanol compared to the original mixture of the bio-oil and methanol before reaction in the case of the experiments with a weight ratio of bio-oil-to-methanol of 1:2 and 1:3. The relatively unchanged density indicated the relatively similar molecular weight of components in the bio-oil after esterification. The esterification would allow the change in the bio-oil microstructure through the formation of esters or acetals [48]. The similar trend was observed for the viscosity of the esterified oil; the more the methanol added during the esterification, the lower the change in the viscosity of the bio-oil. The presence of methanol could enhance the bio-oil stability [49] and further decrease the rate of aging during storage [50].

Table 5. The density, viscosity and total acid number of the bio-oil after esterification in the presence of TCA/H-zeolite catalyst with various weight ratios of bio-oil-to-methanol.

Bio-oil property	Weight ratio of bio-oil-to-methanol							
	2:1		1:1		1:2		1:3	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Density (g/mL)	1.0227	1.0252	0.9861	0.9866	0.9415	0.9417	0.9153	0.9186
Viscosity (cP)	2.1094	2.2316	1.9417	2.0283	1.7896	1.8521	1.5643	1.6034
TAN (mg/g)	0.6921	0.3498	0.5852	0.2939	0.5316	0.2031	0.4132	0.1813

Unlike the insignificant changes in the bio-oil density and viscosity, a considerable change in the total acid number of the esterified oil was observed after the esterification in the presence of the TCA/H-zeolite catalyst, as presented in Table 5. The decrease in the total acid number of the bio-oil after esterification was 49.46%, 49.78%, 61.79% and 56.12% for the TCA/H-zeolite-catalysed esterification with a bio-oil-to-methanol weight ratio of 2:1, 1:1, 1:2 and 1:3 respectively. The addition of extra methanol in the esterification with a 1:2 weight ratio could promote the decrease in the total acid number of the bio-oil by ca 25% in comparison with that with a 2:1 and 1:1 weight ratio. The decrease in the total acid number of the bio-oil after esterification could be an indication of the formation of esters as a result of the reaction between carboxylic acids in the bio-oil feedstock and methanol in the presence of the TCA/H-zeolite catalyst [51]. In addition, aldehydes in the bio-oil feedstock could also react with methanol in the presence of acid catalysts, such as TCA/H-zeolite catalyst, to form acetals [52]. The extra addition of methanol in the esterification system (in the case of that with a 1:2 and 1:3 weight ratio) could promote the equilibrium shift to the products, resulting in the increase in the production of products, i.e., esters or acetals [53].

A further increase in the methanol addition in the esterification with a 1:3 weight ratio did not cause a higher decrease in the total acid number of the bio-oil after esterification in the presence of the TCA/H-zeolite catalyst. It might indicate that the equilibrium was not disturbed by the extra addition of methanol in the 1:3 esterification experiment. The weight ratio of bio-oil-to-methanol of 1:2 was then chosen as the condition in the further experiments with various reaction times.

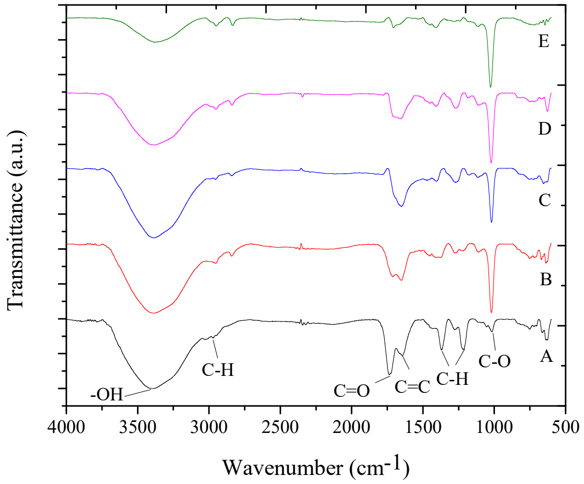


Figure 4. The IR spectra of (A) the fresh bio-oil and the bio-oils after esterification with a weight ratio of bio-oil-to-methanol of (B) 2:1, (C) 1:1, (D) 1:2 and (E) 1:3 in the presence of the TCA/H-zeolite catalyst.

Further observation on the possible formation of esterification products, e.g., esters, an FTIR measurement was conducted towards the fresh bio-oil (the bio-oil before the esterification) and the bio-oils after the esterification with different weight ratios of bio-oil-to-methanol in the presence of the TCA/H-zeolite catalyst. The IR spectra of the fresh and esterified bio-oils are depicted in Figure 4. A considerable increase in the peak intensity of the hydroxyl and C–H alkane groups at wavenumbers of 3350 cm^{-1} and 2950-2800 cm^{-1}, respectively, in the esterified bio-oils (Figure 4(B)-(E)) was observed, possibly due to the formation of esters [54]. In addition, a significant increase in the peak intensity of C–O groups at a wavenumber of 1000 cm^{-1} was observed as an indication of the presence of methanol in the reaction system, as well as the formation of ester [53]. Meanwhile, the decrease in the peak intensity at a wavenumber of 1750 cm^{-1} designated for the carbonyl groups from carboxylic acids, aldehydes and ketones [52], possibly due to its conversion to acetals [55, 56].

Bio-oil upgrading through TCA/H-zeolite-catalysed esterification over different reaction times

The esterification of the Sengon wood bio-oil in the presence of the TCA/H-zeolite catalyst over different reaction times at 70 °C with a catalyst loading of 10 wt%, a weight ratio of bio-oil-to-methanol of 1:2, stirring rate of 500 rpm was carried out with a total recovery of > 90%, as listed in Table 6, indicating a proper experimental execution. The recovered liquid contained the esterification products and possible remaining reactants. Table 6 shows that the coke yield coke was very low (< 1 wt%), indicating that the coke formation during the bio-oil esterification in the presence of the TCA/H-zeolite could be avoided [53].

Over prolonged reaction times, the density of the bio-oil after esterification underwent a negligible change, only by < 1%, possibly due to the enhanced stability of the bio-oil during the esterification as is shown in Table 7. The susceptibility of the reactive components of the bio-oil towards re-polymerisation has lowered resulting in the bio-oil with similar compositions of molecular weight [57].

Table 6. The mass balance closure during the esterification of the Sengon wood bio-oil in the presence of TCA/H-zeolite catalyst for 15-60 min reaction times.

Reaction time (min)	Recovered liquid (wt%)	Coke yield (wt%)	Total (%)
15	92.95	0.0354	92.98
30	95.34	0.0370	95.38
45	92.92	0.0375	92.96
60	91.88	0.0394	91.92

Table 7. The density, viscosity and total acid number of the bio-oil after esterification in the presence of TCA/H-zeolite catalyst for 15-60 min reaction times.

Bio-oil property	Esterification time (min)							
	15		30		45		60	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Density (g/mL)	0.9394	0.9399	0.9393	0.9401	0.9393	0.9406	0.9415	0.9417
Viscosity (cP)	1.7748	1.7908	1.7789	1.8040	1.7704	1.8308	1.7896	1.8521
TAN (mg/g)	0.5074	0.2646	0.5161	0.2588	0.5196	0.2241	0.5316	0.2032

The similar trend was observed for the viscosity of the bio-oil after esterification in the presence of the TCA/H-zeolite over various reaction times at 70 °C with a catalyst loading of 10 wt%, a weight ratio of bio-oil-to-methanol of 1:2, stirring rate of 500 rpm. Insignificant changes in the bio-oil viscosity by 3-5% were observed, indicating the prevention of the formation of heavy molecules during the catalysed esterification, possibly by the formation of esters and acetals [48].

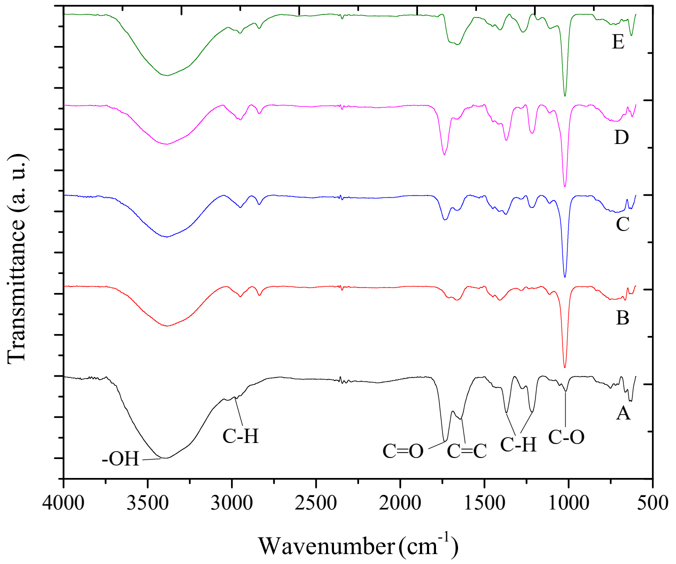


Figure 5. The IR spectra of the bio-oils after a (A) 0-min, (B) 15-min, (C) 30-min, (D) 45-min and (E) 60-min esterification in the presence of the TCA/H-zeolite catalyst.

Alike the change in the total acid number of the bio-oil after esterification with various weight ratios of bio-oil-to-methanol, the total acid number of that after the esterification over various reaction times decreased considerably. Over a 15-min reaction time, the total acid number of the bio-oil after the catalysed esterification decreased by 47.85%. A prolonged esterification of 30 min only caused a further decrease in the total acid number of the bio-oil by 4% (with a 49.85% decrease). A further prolonged reaction times of 45 and 60 min caused a bit higher decrease in the total acid number of bio-oil by 13% and 8%, respectively (with 56.78% and 61.78% decrease, respectively). These data suggested that carboxylic acids in the bio-oil feedstock were converted to esters in a quite fast rate at the beginning of the esterification of the bio-oil in the presence of TCA/H-zeolite catalyst [51]. The rate of esterification became slower by longer reaction times (30-60 min). Probably, the components of the bio-oil feedstock competed to attach to the active sites of the catalysts over time resulting in the high surface coverage [58]. However, not all of these reactants adsorbed at the catalyst surface could be accommodate to react with methanol as the co-adsorbed alcohol-acids intermediates at the catalyst surface were required to allow the reactions to take place [10].

A measurement using an FTIR spectrophotometer was conducted towards the fresh bio-oil and the bio-oils obtained after the TCA/H-zeolite-catalysed esterification over different reaction times. The IR spectra of the bio-oils before and after esterification over different reaction times are presented in Figure 5. A similar observation of the IR spectra with those in Figure 4 was obtained. An increase in the peak intensity of the hydroxyl and C–H groups at wavenumbers of 3350 and 2950-2800 cm^{-1}, respectively, was observed in Figure 5, indicating the formation of water as a side-product of esterification between methanol and carboxylic acids [55, 56]. The formation of esters was also indicated by the increase in the C–O groups at a wavenumber of 1000 cm^{-1} [53]. Moreover, the carbonyl-containing compounds as designated by the peaks at a wavenumber 1750 cm^{-1} [53] in the bio-oil were possibly converted to acetals [55], as indicated by the decrease in the corresponding peak intensity.

Comparing the activity of zeolite catalysts during the esterification of Sengon wood bio-oil

The activity of the TCA/H-zeolite catalyst during the esterification of the Sengon wood sawdust was confirmed by comparing to that of the pre-treated zeolite and H-zeolite catalysts. The study was performed using the following condition: a temperature of 70 °C, a weight ratio of bio-oil-to-methanol of 1:2 and a reaction time of 60 min. A blank experiment in the absence of any catalyst was also carried out to support the justification on the performance of the TCA/H-zeolite catalyst. The liquid after esterification as well as the possible formed coke was recovered and weighed to close the mass balance as presented in Table 8.

Table 8. The mass balance closure during the esterification of the Sengon wood bio-oil in the presence of various catalysts.

Type of catalyst	Recovered liquid (wt%)	Coke Yield (wt%)	Total (%)
NA	94.42	0.016	94.44
Pre-treated zeolite	93.18	0.043	93.23
H-zeolite	94.90	0.041	94.94
TCA/H-zeolite	91.88	0.039	91.92

The data in Table 8 suggested that negligible coke formation (< 1%) was observed. The presence of methanol during the heating up bio-oil was significant in preventing the re-polymerisation of reactive components in the bio-oil feedstock. The good mass balance closure in Table 8 indicated that the experiments were carried out properly. The properties of the bio-oil after the esterification of the bio-oil in the presence of various zeolite catalysts at 70 °C with a catalyst loading of 10 wt%, a weight ratio of bio-oil-to-methanol of 1:2, stirring rate of 500 rpm for a 60-min reaction time were investigated as listed in Table 9.

Table 9. The density, viscosity and total acid number of the bio-oil after esterification in the presence of the zeolite catalysts.

Bio-oil property	Reaction time (min)	Type of catalyst			
		NA	Pre-treated zeolite	H-zeolite	TCA/H-zeolite
Density(g/mL)	0	0.9176	0.9101	0.9140	0.9415
	60	0.9179	0.9347	0.9392	0.9417
Viscosity (cP)	0	1.7336	1.7257	1.7373	1.7896
	60	1.8367	2.3055	2.1174	1.8521
TAN (mg/g)	0	0.7006	0.6515	0.5731	0.5316
	60	0.5947	0.4240	0.2843	0.2032

The density of the bio-oil after the esterification in Table 9 showed an insignificant change even in the absence of a catalyst. It suggested that the addition of methanol gave a significant effect in stabilising the reactive component of the bio-oil [53]. In contrast, the viscosity of the bio-oil after esterification in the presence and absence of a catalyst has increased in a different level ranging from 3.94% to 39.97%. The lowest increase in the viscosity of the bio-oil after esterification was observed for that in the presence of the TCA/H-zeolite catalyst (3.94%), while the highest increase was observed for that in the presence of the pre-treated zeolite catalyst (39.97%). The blank experiment in the absence of a catalyst did not show a significant increase in the viscosity of the bio-oil after esterification possibly due to the limited interaction of the reactive components in the bio-oil feedstock with methanol [59]. On the other hand, the presence of the zeolite catalysts might promote the interaction between reactive components themselves or with methanol [23]. The pre-treated zeolite might facilitate the interactions between reactive components to polymerise and form bigger molecules with higher molecular weight. As a result, the viscosity of the bio-oil increased significantly after esterification in the presence of the pre-treated zeolite catalyst.

The bio-oil esterification in the presence of zeolite catalysts (pre-treated, H-zeolite and TCA/H-zeolite catalysts) showed a significant decrease in the total acid number of the bio-oil after esterification by 34.92%, 50.39% and 61.78%, respectively. It was clear that the modification of Indonesian zeolite using TCA could enhance its activity in catalysing the esterification of the Sengon wood bio-oil. It was possibly due to the increase in the acid active sites at the catalyst surface as the result of the TCA modification over the zeolite catalyst [60].

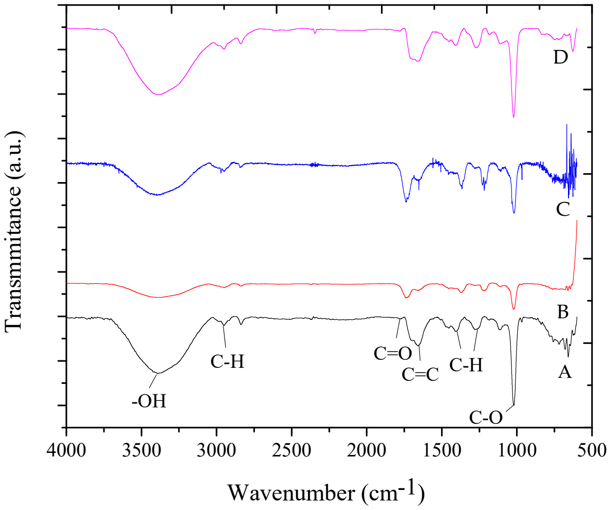


Figure 6. The IR spectra of the esterified bio-oils in the presence of (A) no catalyst, (B) pre-treated zeolite, (C) H-zeolite and (E) the TCA/H-zeolite catalysts.

The change in the functionalities of the bio-oils before and after the esterification of the bio-oils in the absence and presence of a catalyst was investigated using an FTIR spectrophotometer, as presented in Figure 6. The high peak intensity of the C–O groups in the esterified bio-oils in Figure 6 indicated the formation of esters [53]. The presence of the TCA/H-zeolite did promote the formation of esters (and possibly other esterification products, e.g., acetals [56]) in comparison with that of other zeolite catalysts.

Conclusions

This study investigated the activity of the TCA/H-zeolite catalyst during the bio-oil esterification in the presence of methanol over various weight ratios of bio-oil-to-methanol and reaction times. The presence of TCA/H-zeolite catalyst during the esterification of the bio-oil could suppress the formation of coke. In the presence of TCA/H-zeolite, the weight ratios of bio-oil-to-methanol significantly affected the decrease in the total acid number of the bio-oil after the esterification. Moreover, the esterification of Sengon wood bio-oil in the presence of the TCA/H-zeolite catalyst took place in a fast rate, indicated by the decrease in the total acid number of the bio-oil by 47.85% over a 15-min esterification. Compared to the uncatalysed esterification, the presence of the TCA/H-zeolite catalyst could further enhance the decrease in the total acid number up to 65.83%.

The esterification at higher temperatures and using a pressurised reactor would improve the quality of the esterified bio-oil. Furthermore, the combination between hydrocracking and esterification could simultaneously undergo in the presence of hydrogen and hydroprocessing catalysts.

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2 messages

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To: Sri Kadarwati <srika@mail.unnes.ac.id>, Riska Annisa <riskana40@gmail.com>, Evalisa Apriliani <evalisaapriliani@gmail.com>, Cepi Kurniawan <kurniawan.cepi@mail.unnes.ac.id>, Samuel Budi Kusuma <samuelbudi@mail.unnes.ac.id>

Dear Professor Sri Kadarwati, Riska Annisa, Evalisa Apriliani, Cepi Kurniawan, Samuel Budi Kusuma:

We have reached a decision regarding your submission to Trends in Sciences, "The The Catalytic Activity of TCA-Modified Indonesian Natural Zeolite during the Esterification of Sengon Wood Bio-oil". The reviewers have no further comment. We are pleased to inform that your manuscript is accepted and scheduled to publish in Trends in Sciences (TiS) in Volume 19, 2022.

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Thank you for submitting your work to this journal.

Regards,
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TRENDS IN SCIENCES 2023; 20(xx): xxxxx RESEARCH ARTICLE
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The Catalytic Activity of TCA-Modified Indonesian Natural Zeolite During the Esterification of Sengon Wood Bio-Oil

**Sri Kadarwati[*1], Riska Nurfirda Annisa[2], Evalisa Apriliani[3],
Cepi Kurniawan[4] and Samuel Budi Wardhana Kusuma[5]**

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Abstract

The bio-oil produced from the pyrolysis of biomass is highly corrosive due to the high content of organic acids. These organic acids could be removed through an appropriate upgrading process, i.e., esterification using alcohols to form less polar esters. In this study, the bio-oil used as the feedstock in the esterification was produced from the pyrolysis of Sengon wood with a particle size of 297 μm at 600 °C. The esterification was performed at 70 °C in the presence of a trichloro acetic acid (TCA)-modified Indonesian H-zeolite catalyst with various weight ratios of bio-oil-to-methanol and reaction times under a constant stirring rate of 500 rpm. The esterification progress was indicated by the decrease in the total acid number of the bio-oil after esterification. No significant coke formation (< 0.05 wt%) was observed indicating that the suppression of repolymerisation could be achieved. This study showed that the esterification underwent in a fast rate, indicated by the decrease in the total acid number of the bio-oil by 47.85 % only over a 15-min esterification. Compared to the uncatalysed esterification, the TCA/zeolite-catalysed esterification showed a higher decrease in the total acid number of the bio-oil up to 65.83 %, due to the conversion of the carboxylic acids to esters.

Keywords: Esterification, Sengon wood bio-oil, TCA-modified Indonesian zeolite, Total acid number

Introduction

The fossil fuel depletion has promoted the exploration of new renewable energy resources. Biomass has been considered as a promising renewable energy resource due to its high availability, its environmentally friendly properties and its zero competition with food sector [1]. A liquid fuel could be produced as the main product from the fast pyrolysis of biomass [2] that is well known as bio-oil or pyrolysis oil. Sengon wood, as an abundantly available feedstock in Indonesia was used in this study for bio-oil production. Sengon wood contains lignin, cellulose, and hemicellulose of 26.1, 45.4 and 21.0 % and respectively [3]. The high content of cellulose in Sengon wood would result in the high yield of bio-oil [4], allowing a sustainable starting material for liquid fuel production.

The bio-oil produced from the pyrolysis of biomass could be used as a fuel for boilers, stationary as well as sterling engines [5]. However, the bio-oil cannot be directly used as a fuel for transportation due to several unfavourable properties such as high water content leading to low calorific value and high oxygen content resulting in highly instable properties [6]. In addition, the bio-oil contains high amount of organic acids making it highly corrosive and causing a big challenge during its use as a fuel or its compatibility during further processing in the biorefinery [7]. A bio-oil upgrading is required for the bio-oil to meet the requirements as liquid transportation fuels [8].

Esterification has been reported to show a great potential as bio-oil upgrading technique to reduce the acids content of the bio-oil [9]. It converts the organic acids in the bio-oil to e.g., esters in the presence of alcohols and acid catalysts [10]. The use of solid acid catalysts during the esterification of bio-oil has been considered more beneficial in comparison with that of homogeneous catalysts due to the easy separation resulting in a more efficient and cost-effective process [11]. Several solid acid catalysts such as ion exchange resins [12], modified zirconia [13,14], Amberlysts [15-17], acid modified rice husk ash [18], and heteropoly acids [19] have been used as a catalyst in the esterification of the "real" bio-oil as well as model compounds mimicking bio-oil. In addition, zeolite-based catalysts have been reported to show a great potential as a catalyst for esterification of bio-oil [20-24].

A special attention has been paid to Indonesian natural zeolite primarily in related to its application as a catalyst for bio-oil upgrading. It has a good porosity and modifiable Brønsted acid sites [25] at its surface to anticipate the complicated compositions and behaviour of the bio-oil during the esterification. The modification of Brønsted acid sites at the Indonesian zeolite surface to improve the Brønsted acidity could enhance the catalytic activity of Indonesian zeolite during the esterification of the bio-oil.

The Brønsted acidity of the Indonesian zeolite could be improved by strong acid modification, e.g., trichloroacetic acid (TCA) resulting in the zeolite with a better Brønsted acidity [26]. However, the application of TCA-modified Indonesian natural zeolite as a catalyst for esterification of bio-oil produced from the fast pyrolysis of Sengon wood was rare. More studies to investigate the activity of the TCA-modified Indonesian natural zeolite are necessary to evaluate its potential as a catalyst for the bio-oil esterification. This study focused on the esterification of the bio-oil produced from the fast pyrolysis of Sengon wood sawdust with various weight ratios of bio-oil-to-methanol and reaction times to investigate the esterification behaviour of organic acids in the bio-oil primarily acetic acid in the presence of methanol and TCA-modified Indonesian natural zeolite as a solid acid catalyst.

Materials and methods

Preparation and characterisation of a TCA-modified Indonesian natural zeolite catalyst

The Indonesian natural zeolite from Wonosari, Yogyakarta, Indonesia was used as a starting material of the zeolite catalyst. It was purchased from CV. SSGT Zeolite, Indonesia. The natural zeolite was prepared as previously reported [24]. Briefly, the natural zeolite with a particle size range of 100 - 120 μm was activated using sequent chemical and physical activation method. Prior to activation process, the natural zeolite was washed in distilled water and dried at 110 °C for 3 h to allow the physical contaminant removal. “Pre-treated zeolite” corresponds the natural zeolite from this pre-treatment step.

The natural zeolite was chemically treated using 1 % HF, 6 N HCl and 1 N NH_4Cl solutions (prepared from 50 % HF, 37 % HCl, and solid NH_4Cl, obtained from E. Merck, respectively) in a sequence. This chemical activation was followed with a physical activation, i.e., calcination of the natural zeolite sample at 500 °C under nitrogen atmosphere to produce “H-zeolite” catalyst [24].

The modification of the “H-zeolite” catalyst with chloroacetic acid was carried out as reported by Ávila *et al.* [6] with some adjustment. A 5 g of TCA was dissolved in 9 mL of demineralised water in an Erlenmeyer flask. A 10 g of “H-zeolite” was added in the TCA solution. The mixture was then heated at 80 °C under a continuous stirring with a low stirring rate of 100 rpm until no water left. The solid obtained was dried in an oven at 110 °C for 2 h resulting in the “TCA/H-zeolite” catalyst.

The formation of the “TCA/H-zeolite” catalyst was confirmed based on the appearance of characteristics vibration peaks at wavenumbers of 830 and 680 cm^{-1} (the stretching vibration of C-Cl bonds) [26] in the IR spectrum. The IR spectrum of the “TCA/H-zeolite” catalyst was obtained using a Perkin-Elmer Frontier Spotlight 200 type-Fourier transform infrared spectrophotometer. In addition, the possible change in the crystalline structure of Indonesian natural zeolite was evaluated using a PANalytical Xpert’3 Powder X-ray diffractometer.

The surface properties of the “TCA/H-zeolite” catalyst were characterised using a Quantachrome Nova 1,200e surface area analyser. The specific surface area, total pore volume and average pore radius were determined using a BET-BJH isotherm adsorption. Moreover, the acidity of the “TCA/H-zeolite” catalyst was determined using an ammonia adsorption. The amount of ammonia adsorbed at the catalyst surface was assigned as the total acidity of the catalyst in mmol ammonia per gram catalyst. This quantitative measurement of the catalyst acidity was combined with the analysis of the chemical functionalities of the catalyst to confirm the presence of the new bonds of ammonia with the Lewis and Brønsted acid sites at the catalyst surface at wavenumbers of 1,640, 1,550 and 1,450 cm^{-1}.

Catalytic esterification of sengon wood bio-oil

The esterification of the bio-oil with methanol in the presence of “TCA/H-zeolite” catalyst was carried out in a batch reactor system equipped with a temperature monitor and magnetic stirrer. The esterification was conducted at 70 °C, with a catalyst loading of 10 wt%, a stirring rate of 500 rpm, and various weight ratios of bio-oil-to-methanol of 1:1, 2:1, 1:2 and 1:3. The Sengon wood bio-oil used in the esterification process was produced from the pyrolysis of Sengon wood sawdust with a particle size of 297 μm at 600 °C using a fixed-bed pyrolyser as previously reported [24]. The esterification with a weight ratio of bio-oil-to-methanol which gave the highest decrease in the total acid number of the bio-oil after esterification underwent that with various esterification times of 15, 30, 45 and 60 min.

After each experiment, the mixture of liquid esterification products and possible remaining reactants was recovered and designated as the esterified bio-oil. The coke formation was determined based on the weight difference of solid catalyst before and after the esterification. The yield of coke was calculated using Eq. (1) to close the mass balance. W'_{cat} and W^0_{cat} are designated as the weight of the "TCA/H-zeolite" catalyst after and before the esterification of the bio-oil, respectively, while $W_{bio\text{-}oil\ fed}$ is the weight of the bio-oil fed in each esterification experiment.

$$Coke\ yield = \frac{W'_{cat} - W^0_{cat}}{W_{bio-oil\,fed}} x100\% \tag{1}$$

Characterisation of the bio-oil after esterification

The esterified bio-oil after each esterification experiment was characterised, including the density, viscosity and total acid number. The density and viscosity of the esterified bio-oil were determined using a gravimetric method by means of a pycnometer and an Ostwald viscometer, respectively.

The total acid number (TAN) of the esterified bio-oil was measured using an SNI 01-3555-1998 procedure as follows. The bio-oil sample was dissolved in acetone to 96 wt% clear solution of bio-oil. A 2.5 g of the bio-oil solution was heated to boil and added with 2-3 drops of phenolphthalein solution. The titration of the bio-oil solution was conducted using 0.1 N KOH solution until a light red colour appeared. The total acid number of the esterified bio-oil was calculated using Eq. (2). MW_{KOH}, N_{KOH}, and V_{KOH} are designated as the molecular weight, normal concentration and volume of KOH solution, respectively. Meanwhile, W_{sample} and *dilution* are designated as the weight of the sample and the magnitude of dilution employed during the measurement of TAN.

$$TAN = \frac{MW_{KOH} \times N_{KOH} \times V_{KOH}}{W_{sample}} \times dilution \tag{2}$$

Results and discussion

The characteristics of TCA/H-zeolite catalyst

The important properties of the TCA/H-zeolite catalyst prepared in this study was investigated, including the chemical functionalities, the possible change in the crystalline structure, the surface porosity, and the total acidity. The chemical functionalities of the TCA/H-zeolite catalyst were represented by the spectra in **Figure 1**. The general featured functionalities of the zeolite with aluminosilicate framework were shown by the appearance of a vibration peak −OH groups at 3,200 - 3,600 cm^{-1}. In addition, bending vibrations of Al-OH/Si-OH were observed at 1,650 - 1,400 cm^{-1}, while stretching vibrations of Si-O/Al-O were observed at wavenumbers of 1,250 - 950 and 820 - 650 cm^{-1}.

The success of the zeolite modification with TCA was confirmed by the appearance of stretching vibrations of C-Cl bonds at wavenumbers of 840 and 690 cm^{-1} [26] at the IR spectrum of the TCA/H-zeolite catalyst (**Figure 1(c)**). These vibrations indicated the chemical interaction between TCA and the –OH groups of the zeolite.

The change in the crystalline structure of the zeolite over subsequent chemical and physical treatment as well as TCA modification was evaluated through the XRD patterns of the pre-treated zeolite, H-zeolite and the TCA/H-zeolite catalysts, as shown in **Figure 2**. The similar XRD patterns and peak intensity in **Figure 2** indicated that the zeolite did not undergo a significant change in the crystalline structure over the subsequent treatments. Moreover, the intensity of the 3 highest peaks denoted that the mordenite mineral structure was predominant in the zeolite catalysts.

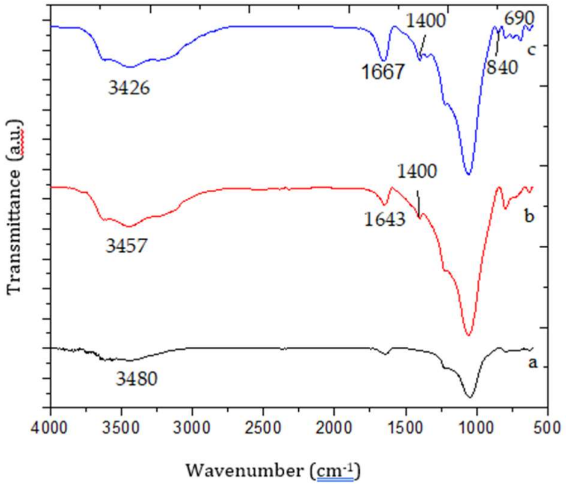

Figure 1 IR spectra of a) pre-treated zeolite, b) H-zeolite and c) TCA/H-zeolite.

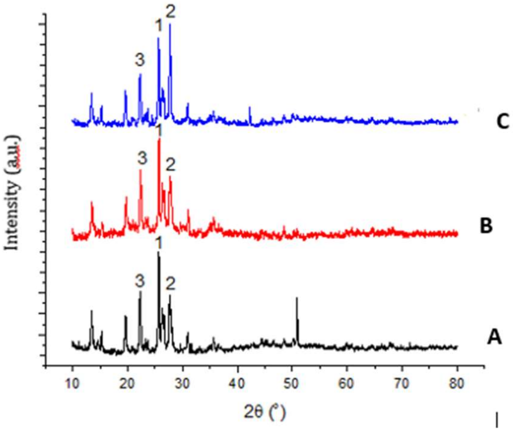

Figure 2 The diffraction patterns of a) pre-treated zeolite, b) H-zeolite and c) TCA/H-zeolite.

The measurement of the total (Lewis and Brønsted) acidity of the TCA/H-zeolite catalyst was performed to support the data of IR spectra indicating the success of the zeolite modification with TCA. The significant increase of the total acidity of the TCA/H-zeolite catalyst would further evidence of the success modification in this study. In addition, the enhanced total acidity of the TCA/H-zeolite catalyst would promote a better esterification process as this acid active sites would play important roles in catalysing the esterification of bio-oil with methanol [13].

The total acidity of the TCA/H-zeolite catalyst was conducted through ammonia adsorption in combination with a gravimetric method. The amount of ammonia adsorbed at the catalyst surface would provide the data the number of acid active sites interacting with the adsorbed ammonia [27,28].

The total acidity of the TCA/H-zeolite catalyst in comparison with the pre-treated and H-zeolite is presented in **Table 1**. A significant increase in the total acidity of the TCA/H-zeolite catalyst was observed, 1.7 folds from that of H-zeolite. It was most likely due to the modification of the zeolite with TCA resulting in the chemical interaction of carbonyl oxygen or hydroxyl oxygen of TCA with the Brønsted acid sites of H-zeolite [29].

Table 1 The total acidity and the surface porosity of the zeolite catalysts.

Type of catalyst	Total acidity (mmol NH_3/g)	Surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore radius (Å)
Pre-treated zeolite	0.94	12.82	0.077	119.96
H-zeolite	1.20	22.26	0.065	588.35
TCA/H-zeolite	3.28	28.41	0.075	526.31

Furthermore, the interaction between ammonia Lewis's base and the Brønsted and Lewis sites of the catalyst was evaluated through the IR spectra of the TCA/H-zeolite catalyst in **Figure 3**. The interaction of ammonia with the Lewis and Brønsted active sites was designated by the vibrations at wavenumbers of 1,450 cm^{-1} and 1,550 - 1,640 cm^{-1}, respectively [30].

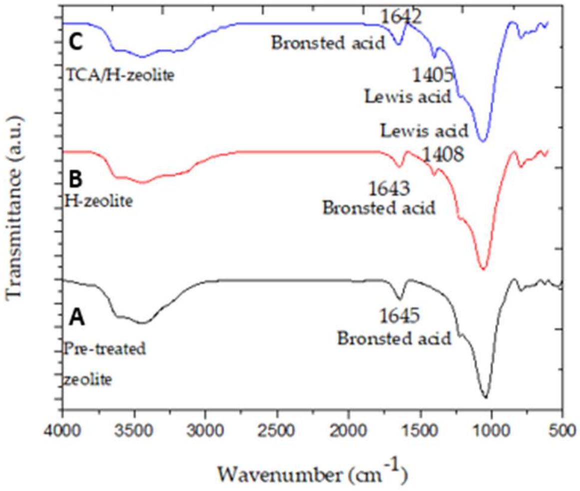

Figure 3 IR spectra of a) pre-treated zeolite, b) H-zeolite and c) TCA/H-zeolite after NH_3 adsorption.

The surface porosity of a catalyst is an important property of the catalyst in supporting the catalytic performance. It was due to the presence of active sites at the catalyst surface including the catalyst pores [31]. The surface porosity of the TCA/H-zeolite catalyst determined in this study included specific surface area, total pore volume and average pore radius of the catalyst as presented in **Table 1**.

The surface porosity data in **Table 1** showed that chemical and physical treatment towards the pre-treated zeolite caused a significant increase (73.63 %) in the surface area of the H-zeolite catalyst. It was might due to the impurity removal and the formation of new pores during the treatment [32]. A further increase (27.63 %) in the specific surface area was also observed in the TCA/H-zeolite catalyst, probably due to the surface modification using a strong acid TCA at the solid H-zeolite surface [33,34].

A significant increase of the average pore radius of the H-zeolite catalyst in comparison with the pre-treated zeolite catalyst (3.9 folds) was also observed. The acid treatment followed with calcination at high temperature of 500 °C probably could cause impurity removal resulting in an increase in the pore size of the zeolite [33]. Moreover, the growth of the pore structure might take place due to the chemical treatment during the preparation of the H-zeolite catalyst [35]. However, a slight decrease (~10 %) of the average pore radius was observed after the zeolite modification with TCA. The TCA introduction with a quite high concentration (ca. 35 %) at the H-zeolite surface followed with a low drying temperature (80 °C) might promote the pore occupation by the TCA molecules, resulting in the decrease of the average pore size of the zeolite [36].

Unlike the considerable changes in the specific surface area and average pore radius, the total pore volume of the zeolite catalysts was almost unchanged; only ~15 % of change was observed. The insignificant change in the total pore volume accompanied with the increase in the average pore radius might be probably attributed to the reduction of the pore depth at the zeolite surface. This would allow the easier interaction between the surface-active sites and the reactants during the esterification of the bio-oil.

Production and characterisation of the bio-oil from the pyrolysis of sengon wood sawdust

The bio-oil used as the feedstock during the esterification in this study was produced from the fast pyrolysis of Sengon wood sawdust with a particle size of 297 µm at 600 °C using a fixed-bed pyrolyser. The yield of the bio-oil was considerably high of 45.66 wt%, as presented in **Table 2**. Such high temperature would help the lignocellulose macromolecules to undergo good decomposition during the pyrolysis [37]. Lignocellulose composes of lignin, cellulose and hemicellulose with specific decomposition temperatures. Lignin would decompose at 300 - 550 °C, while hemicellulose and cellulose would decompose at 250 - 350 and 325 - 400 °C, respectively [38]. The rate of decomposition of lignocellulose macromolecules would increase with increasing the pyrolysis temperature, resulting in more condensable light fractions [39], thus high bio-oil yield. However, extremely high temperature would promote the production of the non-condensable fractions resulting in higher yield of gaseous pyrolysis product [40].

Table 2 The yield of pyrolysis products produced from the pyrolysis of Sengon wood sawdust with a particle size of 297 µm at 600 °C using a fixed-bed pyrolyser.

Type of product	Yield (wt.%)
Bio-oil	45.66
Biochar	29.97
Gaseous product*	24.37

*by difference

The physical and chemical properties of the Sengon wood bio-oil produced through fast pyrolysis technique were measured, including the density, viscosity, and total acid number as shown in **Table 3**. The density of the bio-oil was not directly related to the quality of the bio-oil. However, this property could provide an indication whether heavy or light molecules were predominant in the bio-oil [41]. The low density of the bio-oil produced in this study (1.07 g/mL) indicated that light molecules with relatively low molecular weight were predominant due to severe decomposition process at 600 °C during the pyrolysis resulting in more condensable light fractions.

Table 3 The characteristics of the bio-oil produced from the pyrolysis of Sengon wood sawdust with a particle size of 297 µm at 600 °C using a fixed-bed pyrolyser.

Property (unit)	Value (wt.%)
Density (g/mL)	1.07
Viscosity (cP)	2.40
TAN (mg KOH/g)	0.73

Another parameter evaluated in this study for the bio-oil quality is viscosity. This parameter is affected by the liquid temperature, the strength of intermolecular forces, and the molecular weight and the amount of the soluble components in the liquid bio-oil [42]. The pyrolysis temperature of 600 °C has resulted in the bio-oil with light components (short carbon chains, low molecular weight) in the considerable amount, resulting in the bio-oil with a low viscosity of 2.40 cP (see **Table 3**) [43].

The total acid number of the Sengon wood bio-oil was determined by using an aliquot method, as presented in **Table 3**. This parameter provided an estimation of the content of organic acids in the bio-oil [44]. The high content of organic acids in bio-oil or liquid fuels would lead to corrosion to engines and/or the equipment used in the further processes such as biorefinery [8]. The high total acid number (0.73 mg/g) of the Sengon wood bio-oil used as the feedstock in the esterification process suggested the high organic acid content in the bio-oil. It was likely due to the presence of organic acids such as carboxylic acids as a result of the decomposition of the lignocellulose macromolecules at higher pyrolysis temperature [45]. The acid removal from the bio-oil is extremely important to minimise the corrosiveness of the bio-oil prior to its use as a fuel or its further processes in the biorefinery through an appropriate upgrading technique. A bio-oil upgrading through an esterification technique using TCA/H-zeolite was investigated with different weight ratios of bio-oil-to-methanol over various reaction times.

Bio-oil upgrading through TCA/H-zeolite-catalysed esterification over different weight ratios of bio-oil-to-methanol

The esterification of the Sengon wood bio-oil in the presence of the TCA/H-zeolite catalyst was carried out with various weight ratios of bio-oil-to-methanol of 2:1, 1:1, 1:2 and 1:3 at 70 °C, a catalyst loading of 10 wt%, a 60-min reaction time, and a stirring rate of 500 rpm. The liquid and the possible formed coke after each esterification experiment were recovered to close the mass balance, as presented in **Table 4**. The mass balance closure was higher than 90 wt% indicating a proper experimental execution [46]. The coke yield in all experiments was very low of < 1 wt%. This indicated that the possible repolymerisation between the reactive components in the bio-oil leading to the formation of coke could be prevented during the bio-oil esterification [47] in the presence of the TCA/H-zeolite catalyst.

Table 4 The mass balance closure during the esterification of the sengon wood bio-oil in the presence of TCA/H-zeolite catalyst with various weight ratios of bio-oil-to-methanol.

Weight ratio of BO-to-methanol	Recovered liquid (wt%)	Coke yield (wt%)	Total recovery (%)
2:1	94.11	0.0407	94.15
1:1	91.90	0.0404	91.94
1:2	91.88	0.0394	91.92
1:3	97.79	0.0334	97.82

The density, viscosity and total acid number of the liquid obtained after the TCA/H-zeolite-catalysed esterification with various weight ratios of bio-oil-to-methanol at 70 °C were measured as presented in **Table 5**. A catalyst loading of 10 wt%, a 60-min reaction time, and a stirring rate of 500 rpm were employed during each experiment. The density of the esterified oil insignificantly changed with relatively abundant addition of methanol compared to the original mixture of the bio-oil and methanol before reaction in the case of the experiments with a weight ratio of bio-oil-to-methanol of 1:2 and 1:3. The relatively unchanged density indicated the relatively similar molecular weight of components in the bio-oil after esterification. The esterification would allow the change in the bio-oil microstructure through the formation of esters or acetals [48]. The similar trend was observed for the viscosity of the esterified oil; the more the methanol added during the esterification, the lower the change in the viscosity of the bio-oil. The presence of methanol could enhance the bio-oil stability [49] and further decrease the rate of aging during storage [50].

Table 5 The density, viscosity and total acid number of the bio-oil after esterification in the presence of TCA/H-zeolite catalyst with various weight ratios of bio-oil-to-methanol.

Bio-oil property	Weight ratio of bio-oil-to-methanol							
	2:1		1:1		1:2		1:3	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Density (g/mL)	1.0227	1.0252	0.9861	0.9866	0.9415	0.9417	0.9153	0.9186
Viscosity (cP)	2.1094	2.2316	1.9417	2.0283	1.7896	1.8521	1.5643	1.6034
TAN (mg/g)	0.6921	0.3498	0.5852	0.2939	0.5316	0.2031	0.4132	0.1813

Unlike the insignificant changes in the bio-oil density and viscosity, a considerable change in the total acid number of the esterified oil was observed after the esterification in the presence of the TCA/H-zeolite catalyst, as presented in **Table 5**. The decrease in the total acid number of the bio-oil after esterification was 49.46, 49.78, 61.79 and 56.12 % for the TCA/H-zeolite-catalysed esterification with a bio-oil-to-methanol weight ratio of 2:1, 1:1, 1:2 and 1:3 respectively. The addition of extra methanol in the esterification with a 1:2 weight ratio could promote the decrease in the total acid number of the bio-oil by ca 25 % in comparison with that with a 2:1 and 1:1 weight ratio. The decrease in the total acid number of the bio-oil after esterification could be an indication of the formation of esters as a result of the reaction between carboxylic acids in the bio-oil feedstock and methanol in the presence of the TCA/H-zeolite catalyst [51]. In addition, aldehydes in the bio-oil feedstock could also react with methanol in the presence of acid catalysts, such as TCA/H-zeolite catalyst, to form acetals [52]. The extra addition of methanol in the esterification system (in the case of that with a 1:2 and 1:3 weight ratio) could promote the equilibrium shift to the products, resulting in the increase in the production of products, i.e., esters or acetals [53].

A further increase in the methanol addition in the esterification with a 1:3 weight ratio did not cause a higher decrease in the total acid number of the bio-oil after esterification in the presence of the TCA/H-zeolite catalyst. It might indicate that the equilibrium was not disturbed by the extra addition of methanol in the 1:3 esterification experiment. The weight ratio of bio-oil-to-methanol of 1:2 was then chosen as the condition in the further experiments with various reaction times.

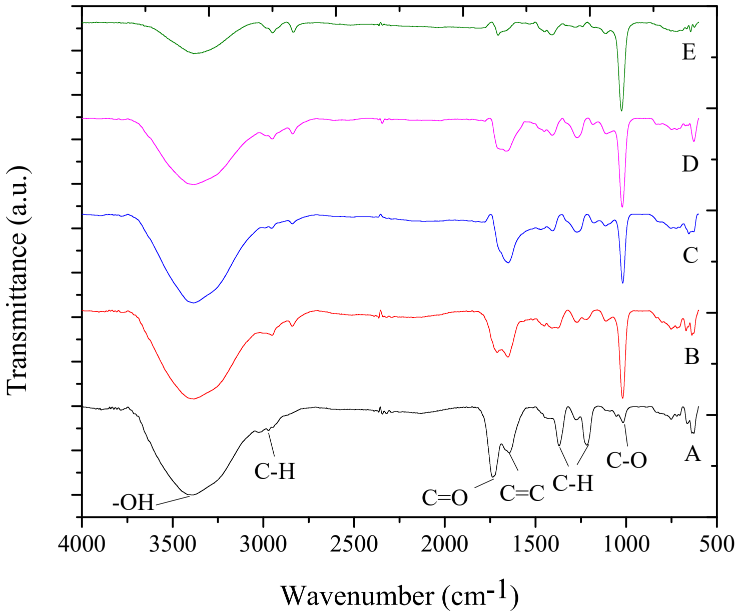

Figure 4 The IR spectra of (A) the fresh bio-oil and the bio-oils after esterification with a weight ratio of bio-oil-to-methanol of (B) 2:1, (C) 1:1, (D) 1:2 and (E) 1:3 in the presence of the TCA/H-zeolite catalyst.

Further observation on the possible formation of esterification products, e.g., esters, an FTIR measurement was conducted towards the fresh bio-oil (the bio-oil before the esterification) and the bio-oils after the esterification with different weight ratios of bio-oil-to-methanol in the presence of the TCA/H-zeolite catalyst. The IR spectra of the fresh and esterified bio-oils are depicted in **Figure 4**. A considerable increase in the peak intensity of the hydroxyl and C-H alkane groups at wavenumbers of 3,350 cm^{-1} and 2,950 - 2,800 cm^{-1}, respectively, in the esterified bio-oils (**Figures 4(B) - 4(E)**) was observed, possibly due to the formation of esters [54]. In addition, a significant increase in the peak intensity of C-O groups at a wavenumber of 1,000 cm^{-1} was observed as an indication of the presence of methanol in the reaction system, as well as the formation of ester [53]. Meanwhile, the decrease in the peak intensity at a wavenumber of 1,750 cm^{-1} designated for the carbonyl groups from carboxylic acids, aldehydes and ketones [52], possibly due to its conversion to acetals [55,56].

Bio-oil upgrading through TCA/H-zeolite-catalysed esterification over different reaction times

The esterification of the Sengon wood bio-oil in the presence of the TCA/H-zeolite catalyst over different reaction times at 70 °C with a catalyst loading of 10 wt%, a weight ratio of bio-oil-to-methanol of 1:2, stirring rate of 500 rpm was carried out with a total recovery of > 90 %, as listed in **Table 6**, indicating a proper experimental execution. The recovered liquid contained the esterification products and possible remaining reactants. Table 6 shows that the coke yield coke was very low (< 1 wt%), indicating that the coke formation during the bio-oil esterification in the presence of the TCA/H-zeolite could be avoided [53].

Over prolonged reaction times, the density of the bio-oil after esterification underwent a negligible change, only by < 1 %, possibly due to the enhanced stability of the bio-oil during the esterification as is shown in **Table 7**. The susceptibility of the reactive components of the bio-oil towards re-polymerisation has lowered resulting in the bio-oil with similar compositions of molecular weight [57].

Table 6 The mass balance closure during the esterification of the Sengon wood bio-oil in the presence of TCA/H-zeolite catalyst for 15 - 60 min reaction times.

Reaction time (min)	Recovered liquid (wt%)	Coke yield (wt%)	Total (%)
15	92.95	0.0354	92.98
30	95.34	0.0370	95.38
45	92.92	0.0375	92.96
60	91.88	0.0394	91.92

Table 7 The density, viscosity and total acid number of the bio-oil after esterification in the presence of TCA/H-zeolite catalyst for 15 - 60 min reaction times.

Bio-oil property	Esterification time (min)							
	15		30		45		60	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Density (g/mL)	0.9394	0.9399	0.9393	0.9401	0.9393	0.9406	0.9415	0.9417
Viscosity (cP)	1.7748	1.7908	1.7789	1.8040	1.7704	1.8308	1.7896	1.8521
TAN (mg/g)	0.5074	0.2646	0.5161	0.2588	0.5196	0.2241	0.5316	0.2032

The similar trend was observed for the viscosity of the bio-oil after esterification in the presence of the TCA/H-zeolite over various reaction times at 70 °C with a catalyst loading of 10 wt%, a weight ratio of bio-oil-to-methanol of 1:2, stirring rate of 500 rpm. Insignificant changes in the bio-oil viscosity by 3 - 5 % were observed, indicating the prevention of the formation of heavy molecules during the catalysed esterification, possibly by the formation of esters and acetals [48].

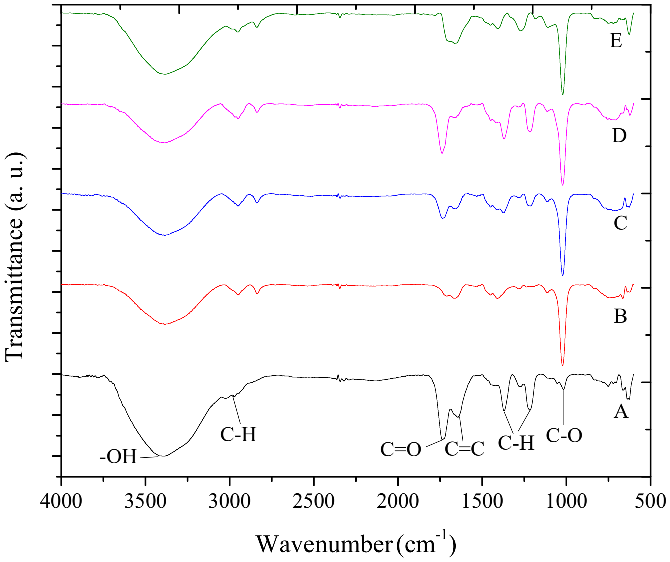

Figure 5 The IR spectra of the bio-oils after a (A) 0-min, (B) 15-min, (C) 30-min, (D) 45-min and (E) 60-min esterification in the presence of the TCA/H-zeolite catalyst.

Alike the change in the total acid number of the bio-oil after esterification with various weight ratios of bio-oil-to-methanol, the total acid number of that after the esterification over various reaction times decreased considerably. Over a 15-min reaction time, the total acid number of the bio-oil after the catalysed esterification decreased by 47.85 %. A prolonged esterification of 30 min only caused a further decrease in the total acid number of the bio-oil by 4 % (with a 49.85 % decrease). A further prolonged reaction times of 45 and 60 min caused a bit higher decrease in the total acid number of bio-oil by 13 and 8 %, respectively (with 56.78 and 61.78 % decrease, respectively). These data suggested that carboxylic acids in the bio-oil feedstock were converted to esters in a quite fast rate at the beginning of the esterification of the bio-oil in the presence of TCA/H-zeolite catalyst [51]. The rate of esterification became slower by longer reaction times (30 - 60 min). Probably, the components of the bio-oil feedstock competed to attach to the active sites of the catalysts over time resulting in the high surface coverage [58]. However, not all of these reactants adsorbed at the catalyst surface could be accommodate to react with methanol as the co-adsorbed alcohol-acids intermediates at the catalyst surface were required to allow the reactions to take place [10].

A measurement using an FTIR spectrophotometer was conducted towards the fresh bio-oil and the bio-oils obtained after the TCA/H-zeolite-catalysed esterification over different reaction times. The IR spectra of the bio-oils before and after esterification over different reaction times are presented in **Figure 5**. A similar observation of the IR spectra with those in **Figure 4** was obtained. An increase in the peak intensity of the hydroxyl and C-H groups at wavenumbers of 3,350 and 2,950 - 2,800 cm^{-1}, respectively, was observed in **Figure 5**, indicating the formation of water as a side-product of esterification between methanol and carboxylic acids [55,56]. The formation of esters was also indicated by the increase in the C-O groups at a wavenumber of 1,000 cm^{-1} [53]. Moreover, the carbonyl-containing compounds as designated by the peaks at a wavenumber 1,750 cm^{-1} [53] in the bio-oil were possibly converted to acetals [55], as indicated by the decrease in the corresponding peak intensity.

Comparing the activity of zeolite catalysts during the esterification of sengon wood bio-oil

The activity of the TCA/H-zeolite catalyst during the esterification of the Sengon wood sawdust was confirmed by comparing to that of the pre-treated zeolite and H-zeolite catalysts. The study was performed using the following condition: a temperature of 70 °C, a weight ratio of bio-oil-to-methanol of 1:2 and a reaction time of 60 min. A blank experiment in the absence of any catalyst was also carried out to support the justification on the performance of the TCA/H-zeolite catalyst. The liquid after esterification as well as the possible formed coke was recovered and weighed to close the mass balance as presented in **Table 8**.

Table 8 The mass balance closure during the esterification of the Sengon wood bio-oil in the presence of various catalysts.

Type of catalyst	Recovered liquid (wt%)	Coke Yield (wt%)	Total (%)
NA	94.42	0.016	94.44
Pre-treated zeolite	93.18	0.043	93.23
H-zeolite	94.90	0.041	94.94
TCA/H-zeolite	91.88	0.039	91.92

The data in **Table 8** suggested that negligible coke formation (< 1 %) was observed. The presence of methanol during the heating up bio-oil was significant in preventing the re-polymerisation of reactive components in the bio-oil feedstock. The good mass balance closure in **Table 8** indicated that the experiments were carried out properly. The properties of the bio-oil after the esterification of the bio-oil in the presence of various zeolite catalysts at 70 °C with a catalyst loading of 10 wt%, a weight ratio of bio-oil-to-methanol of 1:2, stirring rate of 500 rpm for a 60-min reaction time were investigated as listed in **Table 9**.

Table 9 The density, viscosity and total acid number of the bio-oil after esterification in the presence of the zeolite catalysts.

Bio-oil property	Reaction time (min)	Type of catalyst			
		NA	Pre-treated zeolite	H-zeolite	TCA/H-zeolite
Density(g/mL)	0	0.9176	0.9101	0.9140	0.9415
	60	0.9179	0.9347	0.9392	0.9417
Viscosity (cP)	0	1.7336	1.7257	1.7373	1.7896
	60	1.8367	2.3055	2.1174	1.8521
TAN (mg/g)	0	0.7006	0.6515	0.5731	0.5316
	60	0.5947	0.4240	0.2843	0.2032

The density of the bio-oil after the esterification in **Table 9** showed an insignificant change even in the absence of a catalyst. It suggested that the addition of methanol gave a significant effect in stabilising the reactive component of the bio-oil [53]. In contrast, the viscosity of the bio-oil after esterification in the presence and absence of a catalyst has increased in a different level ranging from 3.94 - 39.97 %. The lowest increase in the viscosity of the bio-oil after esterification was observed for that in the presence of the TCA/H-zeolite catalyst (3.94 %), while the highest increase was observed for that in the presence of the pre-treated zeolite catalyst (39.97 %). The blank experiment in the absence of a catalyst did not show a significant increase in the viscosity of the bio-oil after esterification possibly due to the limited interaction of the reactive components in the bio-oil feedstock with methanol [59]. On the other hand, the presence of the zeolite catalysts might promote the interaction between reactive components themselves or with methanol [23]. The pre-treated zeolite might facilitate the interactions between reactive components to polymerise and form bigger molecules with higher molecular weight. As a result, the viscosity of the bio-oil increased significantly after esterification in the presence of the pre-treated zeolite catalyst.

The bio-oil esterification in the presence of zeolite catalysts (pre-treated, H-zeolite and TCA/H-zeolite catalysts) showed a significant decrease in the total acid number of the bio-oil after esterification by 34.92, 50.39 and 61.78 %, respectively. It was clear that the modification of Indonesian zeolite using TCA could enhance its activity in catalysing the esterification of the Sengon wood bio-oil. It was possibly due to the increase in the acid active sites at the catalyst surface as the result of the TCA modification over the zeolite catalyst [60].

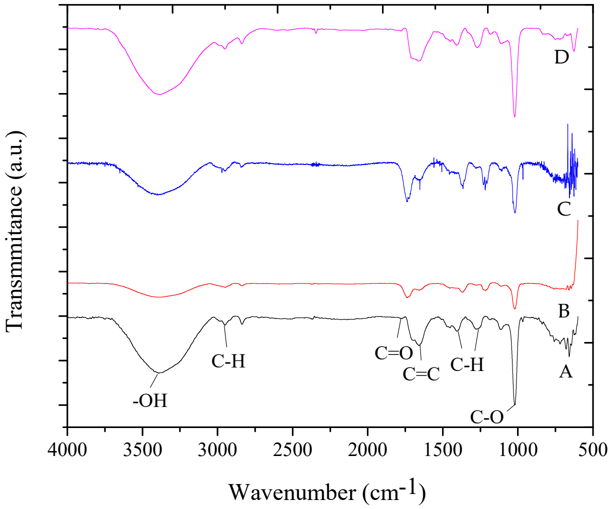

Figure 6 The IR spectra of the esterified bio-oils in the presence of (A) no catalyst, (B) pre-treated zeolite, (C) H-zeolite and (E) the TCA/H-zeolite catalysts.

The change in the functionalities of the bio-oils before and after the esterification of the bio-oils in the absence and presence of a catalyst was investigated using an FTIR spectrophotometer, as presented in **Figure 6**. The high peak intensity of the C-O groups in the esterified bio-oils in Figure 6 indicated the formation of esters [53]. The presence of the TCA/H-zeolite did promote the formation of esters (and possibly other esterification products, e.g., acetals [56]) in comparison with that of other zeolite catalysts.

Conclusions

This study investigated the activity of the TCA/H-zeolite catalyst during the bio-oil esterification in the presence of methanol over various weight ratios of bio-oil-to-methanol and reaction times. The presence of TCA/H-zeolite catalyst during the esterification of the bio-oil could suppress the formation of coke. In the presence of TCA/H-zeolite, the weight ratios of bio-oil-to-methanol significantly affected the decrease in the total acid number of the bio-oil after the esterification. Moreover, the esterification of Sengon wood bio-oil in the presence of the TCA/H-zeolite catalyst took place in a fast rate, indicated by the decrease in the total acid number of the bio-oil by 47.85 % over a 15-min esterification. Compared to the uncatalysed esterification, the presence of the TCA/H-zeolite catalyst could further enhance the decrease in the total acid number up to 65.83 %.

The esterification at higher temperatures and using a pressurised reactor would improve the quality of the esterified bio-oil. Furthermore, the combination between hydrocracking and esterification could simultaneously undergo in the presence of hydrogen and hydroprocessing catalysts.

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The Catalytic Activity of TCA-Modified Indonesian Natural Zeolite During the Esterification of Sengon Wood Bio-Oil

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Abstract

The bio-oil produced from the pyrolysis of biomass is highly corrosive due to the high content of organic acids. These organic acids could be removed through an appropriate upgrading process, i.e., esterification using alcohols to form less polar esters. In this study, the bio-oil used as the feedstock in the esterification was produced from the pyrolysis of Sengon wood with a particle size of 297 µm at 600 °C. The esterification was performed at 70 °C in the presence of a trichloro acetic acid (TCA)-modified Indonesian H-zeolite catalyst with various weight ratios of bio-oil-to-methanol and reaction times under a constant stirring rate of 500 rpm. The esterification progress was indicated by the decrease in the total acid number of the bio-oil after esterification. No significant coke formation (< 0.05 wt%) was observed indicating that the suppression of repolymerisation could be achieved. This study showed that the esterification underwent in a fast rate, indicated by the decrease in the total acid number of the bio-oil by 47.85 % only over a 15-min esterification. Compared to the uncatalysed esterification, the TCA/zeolite-catalysed esterification showed a higher decrease in the total acid number of the bio-oil up to 65.83 %, due to the conversion of the carboxylic acids to esters.

Keywords: Esterification, Sengon wood bio-oil, TCA-modified Indonesian zeolite, Total acid number

Introduction

The fossil fuel depletion has promoted the exploration of new renewable energy resources. Biomass has been considered as a promising renewable energy resource due to its high availability, its environmentally friendly properties and its zero competition with food sector [1]. A liquid fuel could be produced as the main product from the fast pyrolysis of biomass [2] that is well known as bio-oil or pyrolysis oil. Sengon wood, as an abundantly available feedstock in Indonesia was used in this study for bio-oil production. Sengon wood contains lignin, cellulose, and hemicellulose of 26.1, 45.4 and 21.0 % and respectively [3]. The high content of cellulose in Sengon wood would result in the high yield of bio-oil [4], allowing a sustainable starting material for liquid fuel production.

The bio-oil produced from the pyrolysis of biomass could be used as a fuel for boilers, stationary as well as sterling engines [5]. However, the bio-oil cannot be directly used as a fuel for transportation due to several unfavourable properties such as high water content leading to low calorific value and high oxygen content resulting in highly instable properties [6]. In addition, the bio-oil contains high amount of organic acids making it highly corrosive and causing a big challenge during its use as a fuel or its compatibility during further processing in the biorefinery [7]. A bio-oil upgrading is required for the bio-oil to meet the requirements as liquid transportation fuels [8].

Esterification has been reported to show a great potential as bio-oil upgrading technique to reduce the acids content of the bio-oil [9]. It converts the organic acids in the bio-oil to e.g., esters in the presence of alcohols and acid catalysts [10]. The use of solid acid catalysts during the esterification of bio-oil has been considered more beneficial in comparison with that of homogeneous catalysts due to the easy separation resulting in a more efficient and cost-effective process [11]. Several solid acid catalysts such as ion exchange resins [12], modified zirconia [13,14], Amberlysts [15-17], acid modified rice husk ash [18], and heteropoly acids [19] have been used as a catalyst in the esterification of the "real" bio-oil as well as model compounds mimicking bio-oil. In addition, zeolite-based catalysts have been reported to show a great potential as a catalyst for esterification of bio-oil [20-24].

A special attention has been paid to Indonesian natural zeolite primarily in related to its application as a catalyst for bio-oil upgrading. It has a good porosity and modifiable Brønsted acid sites [25] at its surface to anticipate the complicated compositions and behaviour of the bio-oil during the esterification. The modification of Brønsted acid sites at the Indonesian zeolite surface to improve the Brønsted acidity could enhance the catalytic activity of Indonesian zeolite during the esterification of the bio-oil.

The Brønsted acidity of the Indonesian zeolite could be improved by strong acid modification, e.g., trichloroacetic acid (TCA) resulting in the zeolite with a better Brønsted acidity [26]. However, the application of TCA-modified Indonesian natural zeolite as a catalyst for esterification of bio-oil produced from the fast pyrolysis of Sengon wood was rare. More studies to investigate the activity of the TCA-modified Indonesian natural zeolite are necessary to evaluate its potential as a catalyst for the bio-oil esterification. This study focused on the esterification of the bio-oil produced from the fast pyrolysis of Sengon wood sawdust with various weight ratios of bio-oil-to-methanol and reaction times to investigate the esterification behaviour of organic acids in the bio-oil primarily acetic acid in the presence of methanol and TCA-modified Indonesian natural zeolite as a solid acid catalyst.

Materials and methods

Preparation and characterisation of a TCA-modified Indonesian natural zeolite catalyst

The Indonesian natural zeolite from Wonosari, Yogyakarta, Indonesia was used as a starting material of the zeolite catalyst. It was purchased from CV. SSGT Zeolite, Indonesia. The natural zeolite was prepared as previously reported [24]. Briefly, the natural zeolite with a particle size range of 100 - 120 μm was activated using sequent chemical and physical activation method. Prior to activation process, the natural zeolite was washed in distilled water and dried at 110 °C for 3 h to allow the physical contaminant removal. "Pre-treated zeolite" corresponds the natural zeolite from this pre-treatment step.

The natural zeolite was chemically treated using 1 % HF, 6 N HCl and 1 N NH_4Cl solutions (prepared from 50 % HF, 37 % HCl, and solid NH_4Cl, obtained from E. Merck, respectively) in a sequence. This chemical activation was followed with a physical activation, i.e., calcination of the natural zeolite sample at 500 °C under nitrogen atmosphere to produce "H-zeolite" catalyst [24].

The modification of the "H-zeolite" catalyst with chloroacetic acid was carried out as reported by Ávila *et al.* [6] with some adjustment. A 5 g of TCA was dissolved in 9 mL of demineralised water in an Erlenmeyer flask. A 10 g of "H-zeolite" was added in the TCA solution. The mixture was then heated at 80 °C under a continuous stirring with a low stirring rate of 100 rpm until no water left. The solid obtained was dried in an oven at 110 °C for 2 h resulting in the "TCA/H-zeolite" catalyst.

The formation of the "TCA/H-zeolite" catalyst was confirmed based on the appearance of characteristics vibration peaks at wavenumbers of 830 and 680 cm^{-1} (the stretching vibration of C-Cl bonds) [26] in the IR spectrum. The IR spectrum of the "TCA/H-zeolite" catalyst was obtained using a Perkin-Elmer Frontier Spotlight 200 type-Fourier transform infrared spectrophotometer. In addition, the possible change in the crystalline structure of Indonesian natural zeolite was evaluated using a PANalytical Xpert'3 Powder X-ray diffractometer.

The surface properties of the "TCA/H-zeolite" catalyst were characterised using a Quantachrome Nova 1,200e surface area analyser. The specific surface area, total pore volume and average pore radius were determined using a BET-BJH isotherm adsorption. Moreover, the acidity of the "TCA/H-zeolite" catalyst was determined using an ammonia adsorption. The amount of ammonia adsorbed at the catalyst surface was assigned as the total acidity of the catalyst in mmol ammonia per gram catalyst. This quantitative measurement of the catalyst acidity was combined with the analysis of the chemical functionalities of the catalyst to confirm the presence of the new bonds of ammonia with the Lewis and Brønsted acid sites at the catalyst surface at wavenumbers of 1,640, 1,550 and 1,450 cm^{-1}.

Catalytic esterification of sengon wood bio-oil

The esterification of the bio-oil with methanol in the presence of "TCA/H-zeolite" catalyst was carried out in a batch reactor system equipped with a temperature monitor and magnetic stirrer. The esterification was conducted at 70 °C, with a catalyst loading of 10 wt%, a stirring rate of 500 rpm, and various weight ratios of bio-oil-to-methanol of 1:1, 2:1, 1:2 and 1:3. The Sengon wood bio-oil used in the esterification process was produced from the pyrolysis of Sengon wood sawdust with a particle size of 297 μm at 600 °C using a fixed-bed pyrolyser as previously reported [24]. The esterification with a weight ratio of bio-oil-to-methanol which gave the highest decrease in the total acid number of the bio-oil after esterification underwent that with various esterification times of 15, 30, 45 and 60 min.

After each experiment, the mixture of liquid esterification products and possible remaining reactants was recovered and designated as the esterified bio-oil. The coke formation was determined based on the weight difference of solid catalyst before and after the esterification. The yield of coke was calculated using Eq. (1) to close the mass balance. W'_{cat} and W^0_{cat} are designated as the weight of the "TCA/H-zeolite" catalyst after and before the esterification of the bio-oil, respectively, while $W_{bio\text{-}oil\ fed}$ is the weight of the bio-oil fed in each esterification experiment.

$$Coke\ yield = \frac{W'_{cat} - W^0_{cat}}{W_{bio-oil\,fed}} x100\% \tag{1}$$

Characterisation of the bio-oil after esterification

The esterified bio-oil after each esterification experiment was characterised, including the density, viscosity and total acid number. The density and viscosity of the esterified bio-oil were determined using a gravimetric method by means of a pycnometer and an Ostwald viscometer, respectively.

The total acid number (TAN) of the esterified bio-oil was measured using an SNI 01-3555-1998 procedure as follows. The bio-oil sample was dissolved in acetone to 96 wt% clear solution of bio-oil. A 2.5 g of the bio-oil solution was heated to boil and added with 2-3 drops of phenolphthalein solution. The titration of the bio-oil solution was conducted using 0.1 N KOH solution until a light red colour appeared. The total acid number of the esterified bio-oil was calculated using Eq. (2). MW_{KOH}, N_{KOH}, and V_{KOH} are designated as the molecular weight, normal concentration and volume of KOH solution, respectively. Meanwhile, W_{sample} and *dilution* are designated as the weight of the sample and the magnitude of dilution employed during the measurement of TAN.

$$TAN = \frac{MW_{KOH} \times N_{KOH} \times V_{KOH}}{W_{sample}} \times dilution \tag{2}$$

Results and discussion

The characteristics of TCA/H-zeolite catalyst

The important properties of the TCA/H-zeolite catalyst prepared in this study was investigated, including the chemical functionalities, the possible change in the crystalline structure, the surface porosity, and the total acidity. The chemical functionalities of the TCA/H-zeolite catalyst were represented by the spectra in **Figure 1**. The general featured functionalities of the zeolite with aluminosilicate framework were shown by the appearance of a vibration peak −OH groups at 3,200 - 3,600 cm^{-1}. In addition, bending vibrations of Al-OH/Si-OH were observed at 1,650 - 1,400 cm^{-1}, while stretching vibrations of Si-O/Al-O were observed at wavenumbers of 1,250 - 950 and 820 - 650 cm^{-1}.

The success of the zeolite modification with TCA was confirmed by the appearance of stretching vibrations of C-Cl bonds at wavenumbers of 840 and 690 cm^{-1} [26] at the IR spectrum of the TCA/H-zeolite catalyst (**Figure 1(c)**). These vibrations indicated the chemical interaction between TCA and the –OH groups of the zeolite.

The change in the crystalline structure of the zeolite over subsequent chemical and physical treatment as well as TCA modification was evaluated through the XRD patterns of the pre-treated zeolite, H-zeolite and the TCA/H-zeolite catalysts, as shown in **Figure 2**. The similar XRD patterns and peak intensity in **Figure 2** indicated that the zeolite did not undergo a significant change in the crystalline structure over the subsequent treatments. Moreover, the intensity of the 3 highest peaks denoted that the mordenite mineral structure was predominant in the zeolite catalysts.

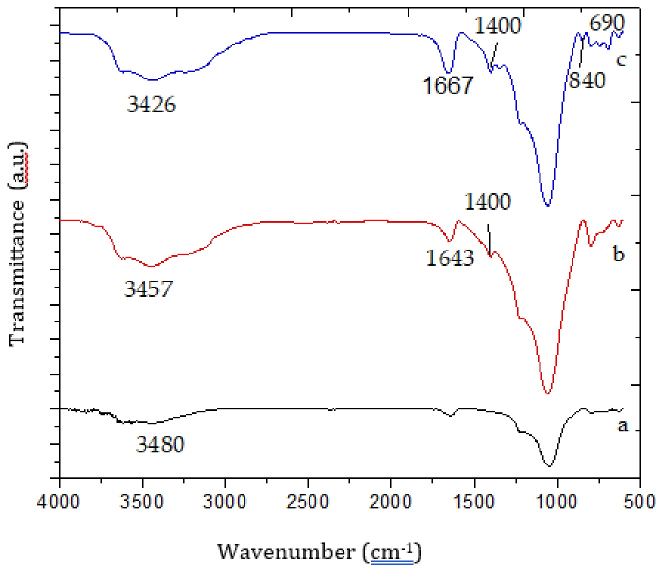

Figure 1 IR spectra of a) pre-treated zeolite, b) H-zeolite and c) TCA/H-zeolite.

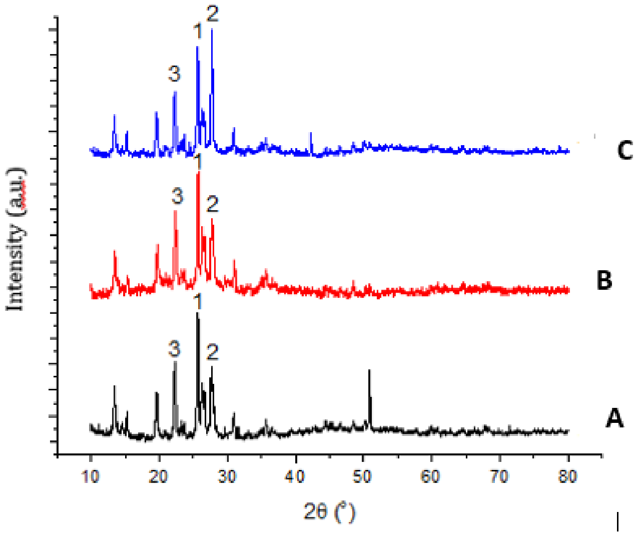

Figure 2 The diffraction patterns of a) pre-treated zeolite, b) H-zeolite and c) TCA/H-zeolite.

The measurement of the total (Lewis and Brønsted) acidity of the TCA/H-zeolite catalyst was performed to support the data of IR spectra indicating the success of the zeolite modification with TCA. The significant increase of the total acidity of the TCA/H-zeolite catalyst would further evidence of the success modification in this study. In addition, the enhanced total acidity of the TCA/H-zeolite catalyst would promote a better esterification process as this acid active sites would play important roles in catalysing the esterification of bio-oil with methanol [13].

The total acidity of the TCA/H-zeolite catalyst was conducted through ammonia adsorption in combination with a gravimetric method. The amount of ammonia adsorbed at the catalyst surface would provide the data the number of acid active sites interacting with the adsorbed ammonia [27,28].

The total acidity of the TCA/H-zeolite catalyst in comparison with the pre-treated and H-zeolite is presented in **Table 1**. A significant increase in the total acidity of the TCA/H-zeolite catalyst was observed, 1.7 folds from that of H-zeolite. It was most likely due to the modification of the zeolite with TCA resulting in the chemical interaction of carbonyl oxygen or hydroxyl oxygen of TCA with the Brønsted acid sites of H-zeolite [29].

Table 1 The total acidity and the surface porosity of the zeolite catalysts.

Type of catalyst	Total acidity (mmol NH$_3$/g)	Surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore radius (Å)
Pre-treated zeolite	0.94	12.82	0.077	119.96
H-zeolite	1.20	22.26	0.065	588.35
TCA/H-zeolite	3.28	28.41	0.075	526.31

Furthermore, the interaction between ammonia Lewis's base and the Brønsted and Lewis sites of the catalyst was evaluated through the IR spectra of the TCA/H-zeolite catalyst in **Figure 3**. The interaction of ammonia with the Lewis and Brønsted active sites was designated by the vibrations at wavenumbers of 1,450 cm^{-1} and 1,550 - 1,640 cm^{-1}, respectively [30].

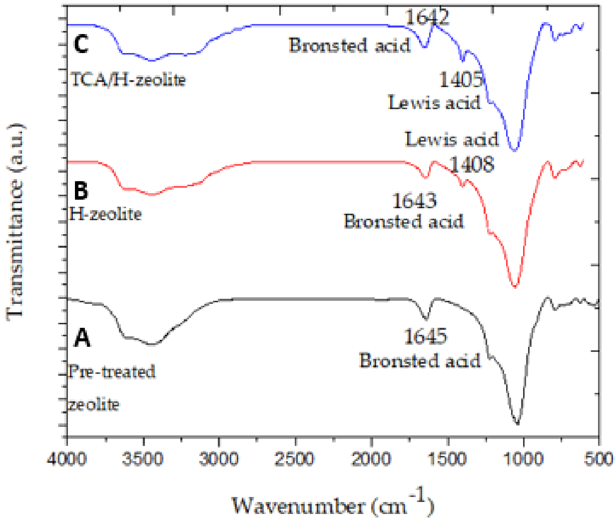

Figure 3 IR spectra of a) pre-treated zeolite, b) H-zeolite and c) TCA/H-zeolite after NH$_3$ adsorption.

The surface porosity of a catalyst is an important property of the catalyst in supporting the catalytic performance. It was due to the presence of active sites at the catalyst surface including the catalyst pores [31]. The surface porosity of the TCA/H-zeolite catalyst determined in this study included specific surface area, total pore volume and average pore radius of the catalyst as presented in **Table 1**.

The surface porosity data in **Table 1** showed that chemical and physical treatment towards the pre-treated zeolite caused a significant increase (73.63 %) in the surface area of the H-zeolite catalyst. It was might due to the impurity removal and the formation of new pores during the treatment [32]. A further increase (27.63 %) in the specific surface area was also observed in the TCA/H-zeolite catalyst, probably due to the surface modification using a strong acid TCA at the solid H-zeolite surface [33,34].

A significant increase of the average pore radius of the H-zeolite catalyst in comparison with the pre-treated zeolite catalyst (3.9 folds) was also observed. The acid treatment followed with calcination at high temperature of 500 °C probably could cause impurity removal resulting in an increase in the pore size of the zeolite [33]. Moreover, the growth of the pore structure might take place due to the chemical treatment during the preparation of the H-zeolite catalyst [35]. However, a slight decrease (~10 %) of the average pore radius was observed after the zeolite modification with TCA. The TCA introduction with a quite high concentration (ca. 35 %) at the H-zeolite surface followed with a low drying temperature (80 °C) might promote the pore occupation by the TCA molecules, resulting in the decrease of the average pore size of the zeolite [36].

Unlike the considerable changes in the specific surface area and average pore radius, the total pore volume of the zeolite catalysts was almost unchanged; only ~15 % of change was observed. The insignificant change in the total pore volume accompanied with the increase in the average pore radius might be probably attributed to the reduction of the pore depth at the zeolite surface. This would allow the easier interaction between the surface-active sites and the reactants during the esterification of the bio-oil.

Production and characterisation of the bio-oil from the pyrolysis of sengon wood sawdust

The bio-oil used as the feedstock during the esterification in this study was produced from the fast pyrolysis of Sengon wood sawdust with a particle size of 297 μm at 600 °C using a fixed-bed pyrolyser. The yield of the bio-oil was considerably high of 45.66 wt%, as presented in **Table 2**. Such high temperature would help the lignocellulose macromolecules to undergo good decomposition during the pyrolysis [37]. Lignocellulose composes of lignin, cellulose and hemicellulose with specific decomposition temperatures. Lignin would decompose at 300 - 550 °C, while hemicellulose and cellulose would decompose at 250 - 350 and 325 - 400 °C, respectively [38]. The rate of decomposition of lignocellulose macromolecules would increase with increasing the pyrolysis temperature, resulting in more condensable light fractions [39], thus high bio-oil yield. However, extremely high temperature would promote the production of the non-condensable fractions resulting in higher yield of gaseous pyrolysis product [40].

Table 2 The yield of pyrolysis products produced from the pyrolysis of Sengon wood sawdust with a particle size of 297 μm at 600 °C using a fixed-bed pyrolyser.

Type of product	Yield (wt.%)
Bio-oil	45.66
Biochar	29.97
Gaseous product*	24.37

*by difference

The physical and chemical properties of the Sengon wood bio-oil produced through fast pyrolysis technique were measured, including the density, viscosity, and total acid number as shown in **Table 3**. The density of the bio-oil was not directly related to the quality of the bio-oil. However, this property could provide an indication whether heavy or light molecules were predominant in the bio-oil [41]. The low density of the bio-oil produced in this study (1.07 g/mL) indicated that light molecules with relatively low molecular weight were predominant due to severe decomposition process at 600 °C during the pyrolysis resulting in more condensable light fractions.

Table 3 The characteristics of the bio-oil produced from the pyrolysis of Sengon wood sawdust with a particle size of 297 μm at 600 °C using a fixed-bed pyrolyser.

Property (unit)	Value (wt.%)
Density (g/mL)	1.07
Viscosity (cP)	2.40
TAN (mg KOH/g)	0.73

Another parameter evaluated in this study for the bio-oil quality is viscosity. This parameter is affected by the liquid temperature, the strength of intermolecular forces, and the molecular weight and the amount of the soluble components in the liquid bio-oil [42]. The pyrolysis temperature of 600 °C has resulted in the bio-oil with light components (short carbon chains, low molecular weight) in the considerable amount, resulting in the bio-oil with a low viscosity of 2.40 cP (see **Table 3**) [43].

The total acid number of the Sengon wood bio-oil was determined by using an aliquot method, as presented in **Table 3**. This parameter provided an estimation of the content of organic acids in the bio-oil [44]. The high content of organic acids in bio-oil or liquid fuels would lead to corrosion to engines and/or the equipment used in the further processes such as biorefinery [8]. The high total acid number (0.73 mg/g) of the Sengon wood bio-oil used as the feedstock in the esterification process suggested the high organic acid content in the bio-oil. It was likely due to the presence of organic acids such as carboxylic acids as a result of the decomposition of the lignocellulose macromolecules at higher pyrolysis temperature [45]. The acid removal from the bio-oil is extremely important to minimise the corrosiveness of the bio-oil prior to its use as a fuel or its further processes in the biorefinery through an appropriate upgrading technique. A bio-oil upgrading through an esterification technique using TCA/H-zeolite was investigated with different weight ratios of bio-oil-to-methanol over various reaction times.

Bio-oil upgrading through TCA/H-zeolite-catalysed esterification over different weight ratios of bio-oil-to-methanol

The esterification of the Sengon wood bio-oil in the presence of the TCA/H-zeolite catalyst was carried out with various weight ratios of bio-oil-to-methanol of 2:1, 1:1, 1:2 and 1:3 at 70 °C, a catalyst loading of 10 wt%, a 60-min reaction time, and a stirring rate of 500 rpm. The liquid and the possible formed coke after each esterification experiment were recovered to close the mass balance, as presented in **Table 4**. The mass balance closure was higher than 90 wt% indicating a proper experimental execution [46]. The coke yield in all experiments was very low of < 1 wt%. This indicated that the possible repolymerisation between the reactive components in the bio-oil leading to the formation of coke could be prevented during the bio-oil esterification [47] in the presence of the TCA/H-zeolite catalyst.

Table 4 The mass balance closure during the esterification of the sengon wood bio-oil in the presence of TCA/H-zeolite catalyst with various weight ratios of bio-oil-to-methanol.

Weight ratio of BO-to-methanol	Recovered liquid (wt%)	Coke yield (wt%)	Total recovery (%)
2:1	94.11	0.0407	94.15
1:1	91.90	0.0404	91.94
1:2	91.88	0.0394	91.92
1:3	97.79	0.0334	97.82

The density, viscosity and total acid number of the liquid obtained after the TCA/H-zeolite-catalysed esterification with various weight ratios of bio-oil-to-methanol at 70 °C were measured as presented in **Table 5**. A catalyst loading of 10 wt%, a 60-min reaction time, and a stirring rate of 500 rpm were employed during each experiment. The density of the esterified oil insignificantly changed with relatively abundant addition of methanol compared to the original mixture of the bio-oil and methanol before reaction in the case of the experiments with a weight ratio of bio-oil-to-methanol of 1:2 and 1:3. The relatively unchanged density indicated the relatively similar molecular weight of components in the bio-oil after esterification. The esterification would allow the change in the bio-oil microstructure through the formation of esters or acetals [48]. The similar trend was observed for the viscosity of the esterified oil; the more the methanol added during the esterification, the lower the change in the viscosity of the bio-oil. The presence of methanol could enhance the bio-oil stability [49] and further decrease the rate of aging during storage [50].

Table 5 The density, viscosity and total acid number of the bio-oil after esterification in the presence of TCA/H-zeolite catalyst with various weight ratios of bio-oil-to-methanol.

Bio-oil property	Weight ratio of bio-oil-to-methanol							
	2:1		1:1		1:2		1:3	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Density (g/mL)	1.0227	1.0252	0.9861	0.9866	0.9415	0.9417	0.9153	0.9186
Viscosity (cP)	2.1094	2.2316	1.9417	2.0283	1.7896	1.8521	1.5643	1.6034
TAN (mg/g)	0.6921	0.3498	0.5852	0.2939	0.5316	0.2031	0.4132	0.1813

Unlike the insignificant changes in the bio-oil density and viscosity, a considerable change in the total acid number of the esterified oil was observed after the esterification in the presence of the TCA/H-zeolite catalyst, as presented in **Table 5**. The decrease in the total acid number of the bio-oil after esterification was 49.46, 49.78, 61.79 and 56.12 % for the TCA/H-zeolite-catalysed esterification with a bio-oil-to-methanol weight ratio of 2:1, 1:1, 1:2 and 1:3 respectively. The addition of extra methanol in the esterification with a 1:2 weight ratio could promote the decrease in the total acid number of the bio-oil by ca 25 % in comparison with that with a 2:1 and 1:1 weight ratio. The decrease in the total acid number of the bio-oil after esterification could be an indication of the formation of esters as a result of the reaction between carboxylic acids in the bio-oil feedstock and methanol in the presence of the TCA/H-zeolite catalyst [51]. In addition, aldehydes in the bio-oil feedstock could also react with methanol in the presence of acid catalysts, such as TCA/H-zeolite catalyst, to form acetals [52]. The extra addition of methanol in the esterification system (in the case of that with a 1:2 and 1:3 weight ratio) could promote the equilibrium shift to the products, resulting in the increase in the production of products, i.e., esters or acetals [53].

A further increase in the methanol addition in the esterification with a 1:3 weight ratio did not cause a higher decrease in the total acid number of the bio-oil after esterification in the presence of the TCA/H-zeolite catalyst. It might indicate that the equilibrium was not disturbed by the extra addition of methanol in the 1:3 esterification experiment. The weight ratio of bio-oil-to-methanol of 1:2 was then chosen as the condition in the further experiments with various reaction times.

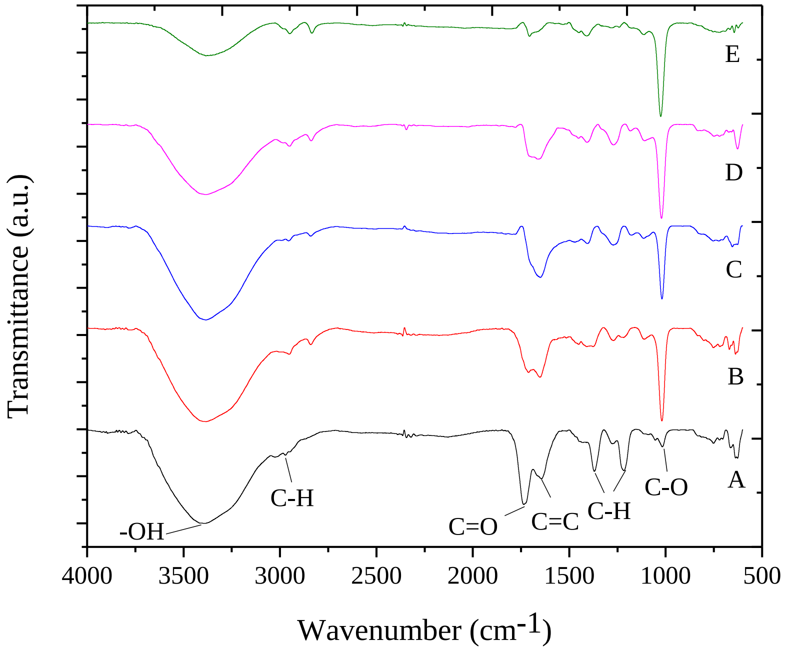

Figure 4 The IR spectra of (A) the fresh bio-oil and the bio-oils after esterification with a weight ratio of bio-oil-to-methanol of (B) 2:1, (C) 1:1, (D) 1:2 and (E) 1:3 in the presence of the TCA/H-zeolite catalyst.

Further observation on the possible formation of esterification products, e.g., esters, an FTIR measurement was conducted towards the fresh bio-oil (the bio-oil before the esterification) and the bio-oils after the esterification with different weight ratios of bio-oil-to-methanol in the presence of the TCA/H-zeolite catalyst. The IR spectra of the fresh and esterified bio-oils are depicted in **Figure 4**. A considerable increase in the peak intensity of the hydroxyl and C-H alkane groups at wavenumbers of 3,350 cm^{-1} and 2,950 - 2,800 cm^{-1}, respectively, in the esterified bio-oils (**Figures 4(B)** - **4(E)**) was observed, possibly due to the formation of esters [54]. In addition, a significant increase in the peak intensity of C-O groups at a wavenumber of 1,000 cm^{-1} was observed as an indication of the presence of methanol in the reaction system, as well as the formation of ester [53]. Meanwhile, the decrease in the peak intensity at a wavenumber of 1,750 cm^{-1} designated for the carbonyl groups from carboxylic acids, aldehydes and ketones [52], possibly due to its conversion to acetals [55,56].

Bio-oil upgrading through TCA/H-zeolite-catalysed esterification over different reaction times

The esterification of the Sengon wood bio-oil in the presence of the TCA/H-zeolite catalyst over different reaction times at 70 °C with a catalyst loading of 10 wt%, a weight ratio of bio-oil-to-methanol of 1:2, stirring rate of 500 rpm was carried out with a total recovery of > 90 %, as listed in **Table 6**, indicating a proper experimental execution. The recovered liquid contained the esterification products and possible remaining reactants. Table 6 shows that the coke yield coke was very low (< 1 wt%), indicating that the coke formation during the bio-oil esterification in the presence of the TCA/H-zeolite could be avoided [53].

Over prolonged reaction times, the density of the bio-oil after esterification underwent a negligible change, only by < 1 %, possibly due to the enhanced stability of the bio-oil during the esterification as is shown in **Table 7**. The susceptibility of the reactive components of the bio-oil towards re-polymerisation has lowered resulting in the bio-oil with similar compositions of molecular weight [57].

Table 6 The mass balance closure during the esterification of the Sengon wood bio-oil in the presence of TCA/H-zeolite catalyst for 15 - 60 min reaction times.

Reaction time (min)	Recovered liquid (wt%)	Coke yield (wt%)	Total (%)
15	92.95	0.0354	92.98
30	95.34	0.0370	95.38
45	92.92	0.0375	92.96
60	91.88	0.0394	91.92

Table 7 The density, viscosity and total acid number of the bio-oil after esterification in the presence of TCA/H-zeolite catalyst for 15 - 60 min reaction times.

Bio-oil property	Esterification time (min)							
	15		30		45		60	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Density (g/mL)	0.9394	0.9399	0.9393	0.9401	0.9393	0.9406	0.9415	0.9417
Viscosity (cP)	1.7748	1.7908	1.7789	1.8040	1.7704	1.8308	1.7896	1.8521
TAN (mg/g)	0.5074	0.2646	0.5161	0.2588	0.5196	0.2241	0.5316	0.2032

The similar trend was observed for the viscosity of the bio-oil after esterification in the presence of the TCA/H-zeolite over various reaction times at 70 °C with a catalyst loading of 10 wt%, a weight ratio of bio-oil-to-methanol of 1:2, stirring rate of 500 rpm. Insignificant changes in the bio-oil viscosity by 3 - 5 % were observed, indicating the prevention of the formation of heavy molecules during the catalysed esterification, possibly by the formation of esters and acetals [48].

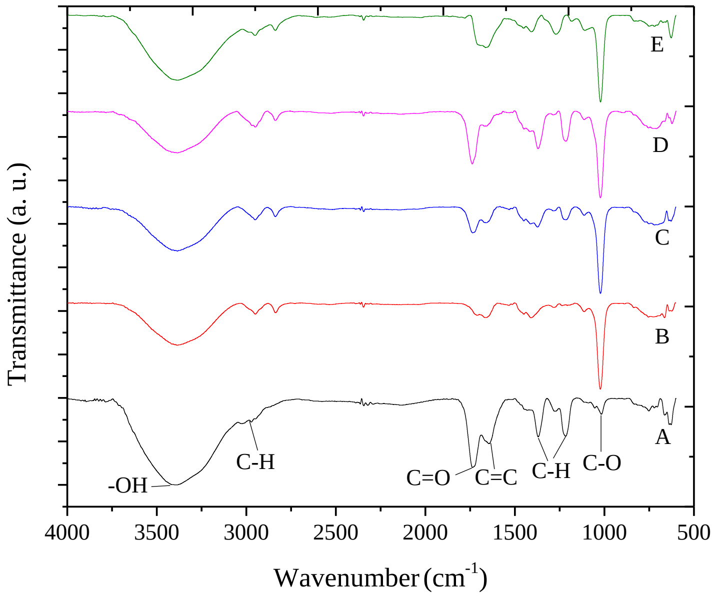

Figure 5 The IR spectra of the bio-oils after a (A) 0-min, (B) 15-min, (C) 30-min, (D) 45-min and (E) 60-min esterification in the presence of the TCA/H-zeolite catalyst.

Alike the change in the total acid number of the bio-oil after esterification with various weight ratios of bio-oil-to-methanol, the total acid number of that after the esterification over various reaction times decreased considerably. Over a 15-min reaction time, the total acid number of the bio-oil after the catalysed esterification decreased by 47.85 %. A prolonged esterification of 30 min only caused a further decrease in the total acid number of the bio-oil by 4 % (with a 49.85 % decrease). A further prolonged reaction times of 45 and 60 min caused a bit higher decrease in the total acid number of bio-oil by 13 and 8 %, respectively (with 56.78 and 61.78 % decrease, respectively). These data suggested that carboxylic acids in the bio-oil feedstock were converted to esters in a quite fast rate at the beginning of the esterification of the bio-oil in the presence of TCA/H-zeolite catalyst [51]. The rate of esterification became slower by longer reaction times (30 - 60 min). Probably, the components of the bio-oil feedstock competed to attach to the active sites of the catalysts over time resulting in the high surface coverage [58]. However, not all of these reactants adsorbed at the catalyst surface could be accommodate to react with methanol as the co-adsorbed alcohol-acids intermediates at the catalyst surface were required to allow the reactions to take place [10].

A measurement using an FTIR spectrophotometer was conducted towards the fresh bio-oil and the bio-oils obtained after the TCA/H-zeolite-catalysed esterification over different reaction times. The IR spectra of the bio-oils before and after esterification over different reaction times are presented in **Figure 5**. A similar observation of the IR spectra with those in **Figure 4** was obtained. An increase in the peak intensity of the hydroxyl and C-H groups at wavenumbers of 3,350 and 2,950 - 2,800 cm^{-1}, respectively, was observed in **Figure 5**, indicating the formation of water as a side-product of esterification between methanol and carboxylic acids [55,56]. The formation of esters was also indicated by the increase in the C-O groups at a wavenumber of 1,000 cm^{-1} [53]. Moreover, the carbonyl-containing compounds as designated by the peaks at a wavenumber 1,750 cm^{-1} [53] in the bio-oil were possibly converted to acetals [55], as indicated by the decrease in the corresponding peak intensity.

Comparing the activity of zeolite catalysts during the esterification of sengon wood bio-oil

The activity of the TCA/H-zeolite catalyst during the esterification of the Sengon wood sawdust was confirmed by comparing to that of the pre-treated zeolite and H-zeolite catalysts. The study was performed using the following condition: a temperature of 70 °C, a weight ratio of bio-oil-to-methanol of 1:2 and a reaction time of 60 min. A blank experiment in the absence of any catalyst was also carried out to support the justification on the performance of the TCA/H-zeolite catalyst. The liquid after esterification as well as the possible formed coke was recovered and weighed to close the mass balance as presented in **Table 8**.

Table 8 The mass balance closure during the esterification of the Sengon wood bio-oil in the presence of various catalysts.

Type of catalyst	Recovered liquid (wt%)	Coke Yield (wt%)	Total (%)
NA	94.42	0.016	94.44
Pre-treated zeolite	93.18	0.043	93.23
H-zeolite	94.90	0.041	94.94
TCA/H-zeolite	91.88	0.039	91.92

The data in **Table 8** suggested that negligible coke formation (< 1 %) was observed. The presence of methanol during the heating up bio-oil was significant in preventing the re-polymerisation of reactive components in the bio-oil feedstock. The good mass balance closure in **Table 8** indicated that the experiments were carried out properly. The properties of the bio-oil after the esterification of the bio-oil in the presence of various zeolite catalysts at 70 °C with a catalyst loading of 10 wt%, a weight ratio of bio-oil-to-methanol of 1:2, stirring rate of 500 rpm for a 60-min reaction time were investigated as listed in **Table 9**.

Table 9 The density, viscosity and total acid number of the bio-oil after esterification in the presence of the zeolite catalysts.

Bio-oil property	Reaction time (min)	Type of catalyst			
		NA	Pre-treated zeolite	H-zeolite	TCA/H-zeolite
Density(g/mL)	0	0.9176	0.9101	0.9140	0.9415
	60	0.9179	0.9347	0.9392	0.9417
Viscosity (cP)	0	1.7336	1.7257	1.7373	1.7896
	60	1.8367	2.3055	2.1174	1.8521
TAN (mg/g)	0	0.7006	0.6515	0.5731	0.5316
	60	0.5947	0.4240	0.2843	0.2032

The density of the bio-oil after the esterification in **Table 9** showed an insignificant change even in the absence of a catalyst. It suggested that the addition of methanol gave a significant effect in stabilising the reactive component of the bio-oil [53]. In contrast, the viscosity of the bio-oil after esterification in the presence and absence of a catalyst has increased in a different level ranging from 3.94 - 39.97 %. The lowest increase in the viscosity of the bio-oil after esterification was observed for that in the presence of the TCA/H-zeolite catalyst (3.94 %), while the highest increase was observed for that in the presence of the pre-treated zeolite catalyst (39.97 %). The blank experiment in the absence of a catalyst did not show a significant increase in the viscosity of the bio-oil after esterification possibly due to the limited interaction of the reactive components in the bio-oil feedstock with methanol [59]. On the other hand, the presence of the zeolite catalysts might promote the interaction between reactive components themselves or with methanol [23]. The pre-treated zeolite might facilitate the interactions between reactive components to polymerise and form bigger molecules with higher molecular weight. As a result, the viscosity of the bio-oil increased significantly after esterification in the presence of the pre-treated zeolite catalyst.

The bio-oil esterification in the presence of zeolite catalysts (pre-treated, H-zeolite and TCA/H-zeolite catalysts) showed a significant decrease in the total acid number of the bio-oil after esterification by 34.92, 50.39 and 61.78 %, respectively. It was clear that the modification of Indonesian zeolite using TCA could enhance its activity in catalysing the esterification of the Sengon wood bio-oil. It was possibly due to the increase in the acid active sites at the catalyst surface as the result of the TCA modification over the zeolite catalyst [60].

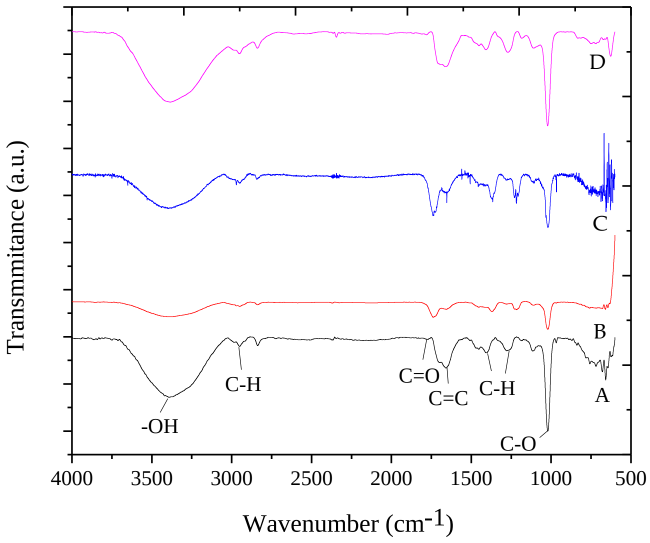

Figure 6 The IR spectra of the esterified bio-oils in the presence of (A) no catalyst, (B) pre-treated zeolite, (C) H-zeolite and (E) the TCA/H-zeolite catalysts.

The change in the functionalities of the bio-oils before and after the esterification of the bio-oils in the absence and presence of a catalyst was investigated using an FTIR spectrophotometer, as presented in **Figure 6**. The high peak intensity of the C-O groups in the esterified bio-oils in Figure 6 indicated the formation of esters [53]. The presence of the TCA/H-zeolite did promote the formation of esters (and possibly other esterification products, e.g., acetals [56]) in comparison with that of other zeolite catalysts.

Conclusions

This study investigated the activity of the TCA/H-zeolite catalyst during the bio-oil esterification in the presence of methanol over various weight ratios of bio-oil-to-methanol and reaction times. The presence of TCA/H-zeolite catalyst during the esterification of the bio-oil could suppress the formation of coke. In the presence of TCA/H-zeolite, the weight ratios of bio-oil-to-methanol significantly affected the decrease in the total acid number of the bio-oil after the esterification. Moreover, the esterification of Sengon wood bio-oil in the presence of the TCA/H-zeolite catalyst took place in a fast rate, indicated by the decrease in the total acid number of the bio-oil by 47.85 % over a 15-min esterification. Compared to the uncatalysed esterification, the presence of the TCA/H-zeolite catalyst could further enhance the decrease in the total acid number up to 65.83 %.

The esterification at higher temperatures and using a pressurised reactor would improve the quality of the esterified bio-oil. Furthermore, the combination between hydrocracking and esterification could simultaneously undergo in the presence of hydrogen and hydroprocessing catalysts.

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