Esterification of Bio-Oil Produced from Sengon (*Paraserianthes falcataria*) Wood Using Indonesian Natural Zeolites

Sri Kadarwati*, Evalisa Apriliani, Riska Nurfirda Annisa, Jumaeri Jumaeri, Edy Cahyono, Sri Wahyuni

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Semarang, Indonesia

ABSTRACT. The bio-oil produced from pyrolysis of woody biomass typically shows unfavourable characteristics such as high acidity, hence it becomes highly corrosive. An upgrading process, e.g., esterification, is necessary to improve the bio-oil quality prior to its use as a transportation fuel. In this work, the bio-oil was produced through a fast pyrolysis of Sengon wood in a fixed-bed pyrolyser at various temperatures. The characteristics (density, viscosity, total acid number, relative concentration of acetic acid, etc.) of the bio-oil were evaluated. The bio-oil with the highest acidity underwent an esterification catalysed by Indonesian natural zeolites at 70 °C for 0-180 min with a ratio of bio-oil to methanol of 1:3. The catalytic performance of the Indonesian natural zeolites during the esterification was investigated. A significant decrease in the total acid number in the bio-oil was observed, indicating the zeolite catalyst's good performance. No significant coke formation (0.002-3.704 wt.%) was obtained during the esterification. An interesting phenomenon was observed; a significant decrease in the total acid number was found in the heating up of the bio-oil in the presence of the catalyst but in the absence of methanol. Possibly, other reactions catalysed by the Brønsted and Lewis acids at the zeolite catalyst surface also occurred during the esterification.

Keywords: esterification, Sengon, bio-oil, Indonesian natural zeolite.

1. Introduction

Biomass has great potential as a renewable energy source. Apart from not competing with the food sector, biomass-based energy is carbon neutral, hence environmentally friendly (Ahamed *et al.,* 2020). Biomass can be converted into bio-oil through a pyrolysis technique (Foong *et al.,* 2020; Papari & Hawboldt, 2015). In this study, Sengon wood was used as the feedstock in the bio-oil production. Sengon wood is abundantly available in Indonesia with a sawdust waste availability of up to 5 m³ per day (Saputro *et al.*, 2012). Its high content of cellulose, hemicellulose and lignin (45.4%, 21.0% and 26.1%, respectively) (Hartati *et al.*, 2010) has made a great potential in the bio-oil production through pyrolysis technique. Pyrolysis is thermal decomposition of macromolecular lignocellulose without (or with little) oxygen (Bridgwater, 1999).

Despite of its direct use as a fuel for boiler engines, stationary diesel engines, and sterling engines (Mortensen *et al.,* 2011), as well as gas turbines for electricity production (Chiaramonti *et al.*, 2007), the bio-oil produced from the pyrolysis of lignocellulosic biomass cannot directly be used as a transportation fuel. Bio-oil is corrosive due to its high acidity, low heating value due to its high water content (Hu *et al*., 2017; Bridgwater, 2012),

and unstable during storage at room temperature due to its high content of oxygen-containing compounds (Wang *et al.*, 2013; Prasertpong *et al.*, 2017). Bio-oil upgrading quality is required to increase its compatibility for storage and further processing into liquid fuels.

Esterification is one of bio-oil upgrading techniques for the bio-oil quality and stability improvement. It takes place through the formation of e.g., esters resulting in the bio-oil with higher stability during storage and compatibility with further refining processes (Ciddor *et al.*, 2015). Solid acid catalysts are of promising catalysts for bio-oil esterification. Amberlyst catalysts such as Amberlyst-15 (Weerachanchai *et al.,* 2012), Amberlyst-70 (Wu *et al*., 2016; Hu *et al*., 2012), rice husk ash-based catalyst (Sutrisno & Hidayat, 2016), ion exchange resin (Wang *et al*., 2010), heteropoly acids (Prasertpong & Tippayawong, 2019), modified zirconia (Kim *et al*., 2012; Thitsartarn & Kawi, 2011), and zeolite-based catalysts (Milina *et al*., 2014; Nandiwale *et al*., 2013). Zeolite-based catalysts including natural zeolites have a great potential as a catalyst for esterification (Fattahi *et al.,* 2019; Osatiashtiani *et al.*, 2017). Indonesian natural zeolite showed a good surface porosity (Kadarwati & Wahyuni, 2015). Moreover, the great potential of Indonesian natural zeolite as a catalyst for bio-oil esterification was also

*Corresponding author: srika@mail.unnes.ac.id

indicated by the existence of modifiable Brønsted acid sites at the zeolite surface (Müller *et at.*, 2014). However, the esterification of bio-oil catalysed by Indonesian natural zeolites is rarely found. In addition, studies on the esterification of bio-oil have focused on model compounds such acetic acid and phenol (Prasertpong & Tippayawong, 2019), acetic acid and ethanol (Liu *et al.*, 2015), oleic acid and methanol (Fauzi *et al.*, 2014) and certain fractions of bio-oil e.g., water-phase bio-oil (Wei *et al.*, 2015). Therefore, this study focused on the esterification of real bio-oil catalysed by natural zeolite in Indonesia.

2. Materials and Methods

2.1 Production and characterisation of bio-oil produced from pyrolysis of Sengon wood

Sengon wood sawdust obtained from a sawmill in Wonosobo Regency, Central Java, Indonesia was used as the biomass feedstock. The sawdust was sieved with a size of ± 300 microns and dried in two stages; under direct sunlight and using an oven at 110 °C for 7 h to obtain a biomass feedstock with a maximum moisture content of ca. 10 wt.%.

The bio-oil production from Sengon wood was carried out through fast pyrolysis in a fixed-bed pyrolyser at temperatures of 500-650 °C without any carrier gas as previously reported (Kadarwati *et al.*, 2020). The pyrolysis experiment at 600°C was performed two times to ensure a reproducible data. The bio-oil and biochar produced during the pyrolysis were collected and quantified. The yields of bio-oil and biochar were determined by dividing the weight of bio-oil and biochar produced respectively by the weight of biomass feedstock used in the pyrolysis, as shown by equation (1) and (2). The yield of the gaseous product was determined by difference. The produced bio-oil was stored in dark-coloured glass bottles at ~-5 °C to avoid re-polymerization. This bio-oil was used in the Indonesian natural zeolites-catalysed esterification in this study.

$$\text{Yield of bio-oil} = \frac{\text{Weight of bio-oil}}{\text{Weight of biomass}} \times 100\% \qquad (1)$$

$$\text{Yield of biochar} = \frac{\text{Weight of biochar}}{\text{Weight of biomass}} \times 100\% \qquad (2)$$

The bio-oil produced from the pyrolysis of Sengon wood was characterized its density, viscosity, and total acid numbers using a pycnometer, Oswald viscometer and aliquot method, respectively. A characterization using a Perkin-Elmer Frontier Spotlight 200 type-Fourier transform infrared spectrophotometer was also conducted to investigate the chemical functionalities of the bio-oil. The relative concentration of acetic acid in the bio-oil was used as prioritized parameter due to its abundance (ca. 13 wt.%) in the as-prepared bio-oil produced from the pyrolysis of woody biomass as reported earlier (Kadarwati, 2017). The relative concentration of acetic acid in the bio-oil was semi-quantitatively determined by using an Agilent 6820 gas chromatograph. The relative concentration was proportional to the peak area of acetic acid in the corresponding bio-oil. The acetic acid standard has been injected to the gas chromatograph prior to sample injections to confirm the acetic acid peak in the total ion chromatogram of each bio-oil sample. The bio-oil with the highest acetic acid relative concentration was

used as the bio-oil feedstock in the esterification of the bio-oil.

2.2 Preparation and Characterisation of Indonesian natural zeolite catalysts

The Indonesian natural zeolite used in this study was a Wonosari-type zeolite purchased from CV. SSGT Zeolite, Indonesia. The Indonesian natural zeolite catalyst was prepared through multiple steps of chemical activation followed by physical activation as previously reported (Kadarwati & Wahyuni, 2015). The raw zeolite was ground and sieved to a particle size of 100-120 microns. The zeolite was soaked in distilled water (produced by University laboratory) for an hour, rinsed and dried at 110 °C in an oven for 3 h. The catalyst produced in this step is referred as the Z catalyst.

A two-step acid treatment on the Z catalyst was conducted using 1% HF and 6 N HCl solutions (prepared from HF 50% and HCl 37% purchased from Merck, respectively) in a sequent technique for 30 min each. The latter acid treatment was done at 50 °C. A drying using an oven at 110 °C for 3 h at the end of each step of the acid treatment was employed. The sample then underwent a modification process using a 1 N NH_4Cl solution (prepared from NH_4Cl 99% purchased from Merck) through a cation exchange technique to form a H-zeolite catalyst after drying. The sample was soaked in the NH_4Cl solution for seven days under a low-speed stirring. Upon washing and drying, the sample was calcined under nitrogen atmosphere at a temperature of 500 °C. The catalyst produced in this step is referred as the HZ catalyst.

The surface properties (surface area, total pore volume and average pore radius) were characterized using a Quantachrome Nova 1200e surface area analyser. The surface properties were determined using the BET-BJH isotherms. In addition, the change in the crystalline structure of the Indonesian natural zeolite during preparation to form the HZ catalyst was evaluated using a PANalytical Xpert'3 Powder X-ray diffractometer with Cu-Kα (λ of 1.54 Å). Moreover, the acidity of the catalyst was measured based on the adsorption capacity of the zeolite catalysts towards ammonia (as an adsorbate). The weight of ammonia adsorbed on the catalyst surface was determined by a gravimetric method, as reported earlier (Kadarwati *et al.*, 2013). The measurement was conducted in duplo. As the interaction between ammonia and the acid sites at the zeolite surface gave a typical pattern of spectrum, the existence of Brønsted and Lewis acid sites (at wavenumbers of 1650-1620 cm^{-1} and 1401.25 cm^{-1}, respectively) was confirmed by the IR spectra recorded using a Per-kin-Elmer Frontier Spotlight 200 type-Fourier transform infrared spectrophotometer.

2.3 Esterification of bio-oil catalysed by Indonesian natural zeolite catalysts

The bio-oil feedstock used in the esterification experiments was that with the highest relative concentration of acetic acid indicated by the peak area in the corresponding bio-oil. The esterification process was carried out in a batch system using a reflux reactor equipped with a ball cooler and a magnetic stirrer. The esterification of the bio-oil was studied in the presence of methanol (99% obtained from Merck) and catalysed by the Indonesian natural zeolite catalysts i.e., the Z and HZ

catalysts (10 wt.%) at a temperature of 70 °C for various reaction times (0-180 min). The two types of experiments were labelled as "BO+M+Z" and "BO+M+HZ" experiments. An experiment without a catalyst (labelled as "BO+M") and that without adding methanol (labelled as "BO+HZ") was also carried out for a comparison.

After each experiment, the liquid was separated from the solid catalyst and recovered. The solid catalyst was properly washed using acetone and dried. The coke formed during the esterification was quantified. The yield of coke was determined by dividing the weight of coke formed during the esterification by that of the bio-oil used in the corresponding esterification experiment.

The characteristics of the esterified bio-oils i.e., density, viscosity and total acid numbers were measured using the aforementioned methods. Those three characteristics were measured two times to achieve a good reproducibility. The changes in the chemical functionalities of the bio-oil after esterification in the presence (and absence) of methanol and the zeolite catalysts were also investigated using a Perkin-Elmer Frontier Spotlight 200 type-Fourier transform infrared spectrophotometer.

3. Results and Discussion

3.1 Production of the bio-oil through pyrolysis of Sengon wood

3.1.1. Yields of the pyrolysis products produced from pyrolysis of Sengon wood at various temperatures

The pyrolysis parameters showed a significant effect on the yield and the properties of the bio-oil produced. In this study, the pyrolysis of Sengon wood with a particle size of 300 microns was conducted at various temperatures of 500-650 °C. No carrier gas was used during the pyrolysis.

The recovered products i.e., bio-oil and biochar were quantified, and the yields are presented in Figure 1. The yield of the gaseous product was determined by difference. No quantification of the gases produced during the pyrolysis of Sengon wood was carried out. The yield of the bio-oil produced from the pyrolysis of Sengon wood increased with increasing the pyrolysis temperature until 600 °C. It was possibly due to the more decomposition of the lignocellulose macromolecules to form condensable light fractions (Zaman *et al.,* 2017). This was in line with the decrease in the yield of biochar by increasing pyrolysis temperature. However, a decrease in the bio-oil yield was observed at temperatures higher than 600 °C. Severe cracking resulting in more incondensable gases possibly took place at temperatures higher than 600 °C. This was indicated by the increase in the yield of the gaseous product at the higher temperature.

Table 1
Physical and chemical properties the bio-oil produced from the pyrolysis of Sengon wood at pyrolysis temperatures of 500-650 °C.

T (°C)	Density (g/mL)	Viscosity (cP)	Total acid number (mg KOH/g bio-oil)	Relative concentration of acetic acid (%)
500	1.11	1.95	0.73	48.45
550	1.10	1.91	0.79	49.43
600	1.07	2.04	0.94	79.00
650	1.11	2.02	0.71	72.40
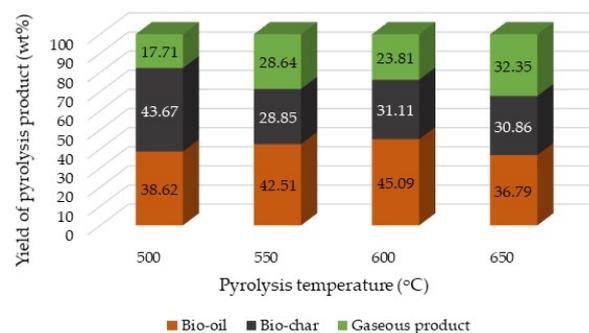
Fig. 1 Yields of bio-oil, biochar and gaseous product produced through the pyrolysis of Sengon wood at temperatures of 500-650 °C.

3.1.2. Characteristics of the bio-oil produced from pyrolysis of Sengon wood at various temperatures

The bio-oils produced from the pyrolysis of Sengon wood underwent some characterisations, i.e., the measurement of density and viscosity, and the determination of the total acid number, as listed in Table 1. A semi-quantitative analysis of the concentration of acetic acid in the bio-oils was also performed to determine the relative concentration of acetic acid in the bio-oils, as shown in Table 1. This was used as the main consideration to select the bio-oil used in the esterification experiments.

As the bio-oils produced from the pyrolysis of Sengon wood in this study was aimed to be used as a fuel candidate, the density and viscosity of the bio-oil should be considered the main properties to be measured. It would be related to the fluidity of the liquid fuel in the engines. Despite of other drawbacks, the bio-oil should have a good fluidity to meet the minimum requirement as a liquid fuel. The density and viscosity of the bio-oils produced through the pyrolysis of Sengon wood at temperatures of 500-650 °C showed a quite good fluidity (Chukwuneke *et al.,* 2019) indicated by the values of density and viscosity listed in Table 1. However, the value of the bio-oil density was higher than that of commercial (diesel and gasoline) fuels, i.e., 0.85 mg/L and 0.70-0.75 mg/L, respectively (Speight, 2011). While, the viscosity of the bio-oil was in the range of that of diesel fuel, i.e., 1.9-4.1 cP (Paar, 2021). With increasing temperature, there was no significant change in the density and viscosity of the bio-oils produced from Sengon woody biomass. It could indicate that the bio-oils had similar content of light fractions formed during the thermal decomposition in the pyrolysis.

The total acid number would roughly represent the amount of organic acids dissolved in the bio-oil. At a lower pyrolysis temperature, the acids were possibly from the breakdown of the side chains of cellulose and hemicellulose as these two biomass components decomposed at a lower temperature; 220–315 °C for hemicellulose and 300–400 °C for cellulose (Yang *et al.*, 2007; Várhegyi *et al.*, 1997). At a higher temperature up to 600 °C, the decomposition of cellulose and hemicellulose was more severe resulting in more acids (Özşen, 2020) as indicated by the relative concentration of acetic acid in Table 1. In addition, the acidic property indicated by the total acid number (Table 1) could also come from the phenolic compounds as a result of the decomposition of lignin (Yang *et al.*, 2007). As the pyrolysis temperature

went higher (T of 650 °C), the non-condensable fractions could form leading to a decrease in the amount of acids as well as the relative concentration of acetic acid in the bio-oil acids (Özşen, 2020). Based on the value of total acid number and relative concentration of acetic acid in Table 1, the bio-oil produced from the pyrolysis of Sengon wood at 600 °C was selected as the feedstock for esterification in the presence of methanol and the zeolite catalysts.

3.2 The characteristics of the zeolite catalysts

The zeolite catalysts prepared in this study was from Wonosari-type zeolite. It was a typical Indonesian natural zeolite rich in mordenite and clinoptilolite minerals (Atikah, 2017). Upon multiple steps of treatment, Indonesian natural zeolite used as a raw material of the zeolite catalysts showed a consistent crystalline structure as is presented in Figure 2. Upon an acid treatment using a 1% HF solution (Figure 2b) followed by that using a 6 N HCl solution (Figure 2c), as well as the modification using ammonium chloride solution to form HZ catalyst (Figure 2d), no significant change in the intensity of the diffraction peaks was observed. It indicated that the crystalline structure of the zeolite catalysts upon acid treatment and modification was perfectly fine, and no damage could be justified. This would suggest that the zeolite catalysts would show a good performance (Phatai *et al.,* 2020) in the esterification of the Sengon wood bio-oil.

To evaluate the required properties for catalysing the esterification of the bio-oil, the surface properties of the zeolite catalysts were determined, and the results are listed in Table 2. The surface area, total pore volume and total surface acidity of the HZ catalyst were significantly higher than those of the Z catalyst. It suggested that the acid treatments and surface modification towards the Z catalyst could promote an impurity removal from the catalyst surface (Burris & Juenger, 2016). In addition, re-arrangement of surface structure during calcination at high temperature (500 °C under nitrogen atmosphere in this study) was possible, resulting in the zeolite with high surface area and pore volume (Menad *et al.*, 2016; Kunkeler *et al.*, 1998). As a consequence, the acid sites were more open and could easily interact with reactants, indicated by the increase in the total surface acidity.
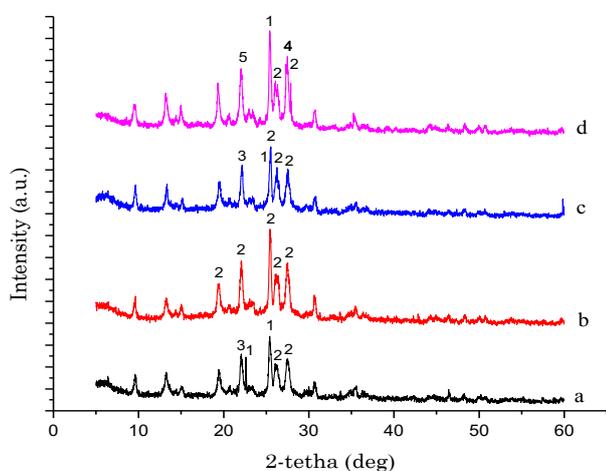
Fig. 2 XRD patterns of the zeolite catalysts (a) Z catalyst, (b) Z catalyst after first acid treatment, (c) Z catalyst after second acid treatment, and (d) HZ catalyst. (1=clinoptilolite; 2=mordenite; 3=cloverite; 4=leonhardite; 5=gmelinite)
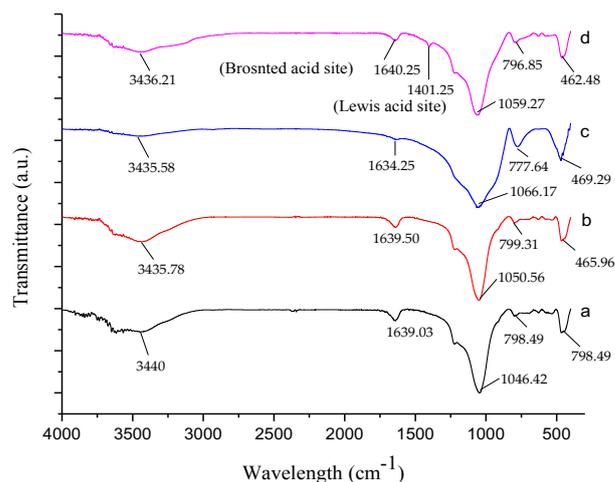
Fig. 3 IR spectra of the zeolite catalysts (a) Z catalyst, (b) Z catalyst after first acid treatment, (c) Z catalyst after second acid treatment, and (d) HZ catalyst.

Table 2
Surface properties of the zeolite catalysts prepared from Indonesian natural zeolite.

Catalyst	Surface area (m²/g)	Total pore volume (cm³/g)	Average pore radius (Å)	Total surface acidity (mmol ammonia/g catalyst)
Z	35.02	0.08	1264.8	0.94
HZ	231.39	0.17	1185.0	1.20

The acid sites were confirmed by the IR spectra presented in Figure 3. The existence of Brønsted acid sites was confirmed by the appearance of peaks at wavenumbers of 1650-1620 cm⁻¹ (Hartanto, 2016). The Brønsted acid site was observed for both Z and HZ catalysts, while the Lewis acid site appeared in the HZ catalyst only. Originally, Indonesian natural zeolite possessed a predominant Brønsted acid as presented in Figure 3a. Upon acids (HF and HCl solutions) treatment, Brønsted acids were still observed. Upon an advanced chemical treatment using NH₄Cl solution followed by calcination at 500 °C, Lewis acids appeared as indicated by the peak at 1400 cm⁻¹ (Figure 3d), possibly due to the extraction of the zeolite framework and/or the dehydroxylation phenomena (Serrano *et al.,* 2012).

In spite of the increase in the surface area, total pore volume and total surface acidity of the HZ catalyst, a significant decrease in the average pore radius was observed. It might be due to the relatively low calcination temperature employed in this study. The calcination at a temperature lower than 800 might lead to the decrease in the pore size of the zeolites (Menad *et al.*, 2016).

3.3 Esterification of bio-oil in the presence of methanol using the Indonesian natural zeolite catalysts

Esterification is a promising upgrading technique in order to improve the quality and stability of bio-oil produced from pyrolysis of biomass (Ciddor *et al.*, 2015; Liu *et al.*, 2015). In this study, the esterification of "real" bio-oil produced from the pyrolysis of Sengon wood at a temperature of 600 °C was carried out at 70 °C with a ratio

of bio-oil to methanol of 1:3 and catalysed by the zeolite catalysts. An experiment without a catalyst in the presence of methanol ("BO+M" experiment) and with the HZ catalyst in the absence of methanol (BO+HZ experiment) was also performed as a comparison. The mass balance of the experiments conducted in this study was carefully determined and the result is presented in Figure 4.

The coke formation was insignificant during the esterification of Sengon wood bio-oil in the presence of the zeolite (Z or HZ) catalyst and methanol. It was possibly due to the esterification occurred between the (carboxylic) acids in the bio-oil with methanol in the presence of the zeolite solid acid catalysts. Moreover, the presence of methanol in the thermal treatment of the bio-oil in the presence of a catalyst could significantly suppress the formation of coke by converting the reactive compounds such as carboxylic acids, aldehydes, C6 sugars and furans into more stable compounds (Hu *et al.,* 2012; Wu *et al.,* 2016). In contrast, the presence of methanol in the bio-oil in the "BO+M" experiment but with the absence of the zeolite catalysts resulted in a low coke formation (3.7 wt.%). In the absence of the Z and HZ catalysts, the interaction between re-active components in the bio-oil such as carboxylic acids, aldehydes and other oxygen containing compounds would partly result in a repolymerized products with higher molecular weight such as coke, even in the presence of methanol. The role of methanol in suppressing coke formation in this case would not be the scope of this study.

The role of the Z and HZ catalysts was likely significant in suppressing the coke formation during the esterification of the bio-oil in the presence of methanol (Wu *et al.,* 2016). It could be observed from the insignificant coke formation in the thermal treatment of the bio-oil with-out adding methanol, only with the HZ catalyst alone (please see "BO+HZ" experiment in Figure 4). A negligible coke formation was observed.
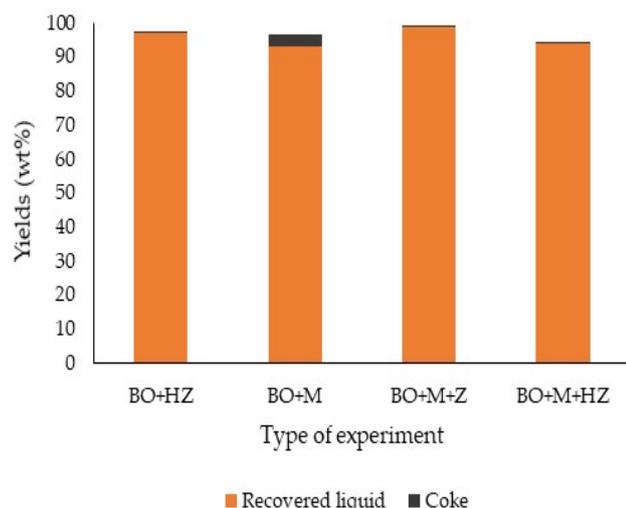
Fig. 4 Mass balance of the esterification products in the esterification of bio-oil in the presence and the absence of methanol and catalysed by the zeolite catalysts at 70 °C with a ratio of bio-oil-to-methanol of 1:3, a catalyst loading of 10 wt.%, a reaction time of 180 min and stirring rate of 500 rpm. (BO=bio-oil, M=methanol).
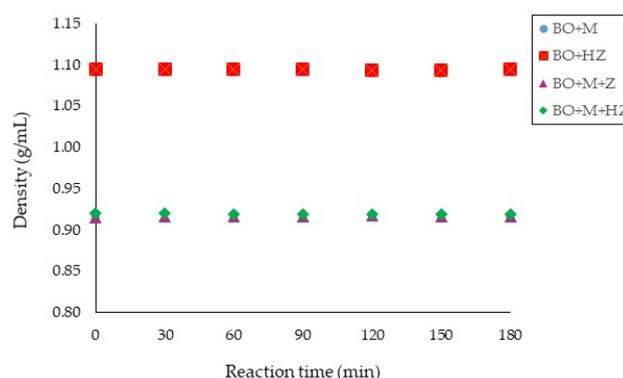
Fig. 5 Density of the esterified bio-oil from the esterification of bio-oil in the presence and the absence of methanol and catalysed by the zeolite catalysts at 70 °C with a ratio of bio-oil-to-methanol of 1:3, a catalyst loading of 10 wt.%, a reaction time of 0-180 min and stirring rate of 500 rpm. (BO=bio-oil, M=methanol).

Further, the density and viscosity of the esterified bio-oil in all experiments were measured, and the results are presented in Figure 5 and Figure 6. No significant change in the density of the esterified bio-oil samples was observed. It might indicate that no heavy molecular fraction was formed during the esterification of the bio-oils (Sondakh *et al.,* 2019), in the presence and absence of the zeolite catalysts and methanol. Please note that the density of the esterified bio-oil from the "BO+HZ" experiment that seemed higher than that of other experiments was due to no methanol addition. The density of the esterified bio-oil from this experiment was the same as the density of the bio-oil alone.

A similar trend was observed on the viscosity of the esterified bio-oil from all experiments, as is shown in Figure 6. An insignificant change was also observed. This data supported the density data in Figure 5. However, a considerable decrease in the viscosity of the esterified bio-oil from the "BO+M+HZ" experiment was observed at a 90-min reaction time. Further decrease in the viscosity of the esterified bio-oil was observed at a longer reaction time of 180 min. It was possibly due to the formation of light fractions as a result of the reaction between methanol and reactive components in the bio-oil (Sondakh *et al,* 2018) at a low temperature of 70 °C in the presence of the HZ solid acid catalyst.
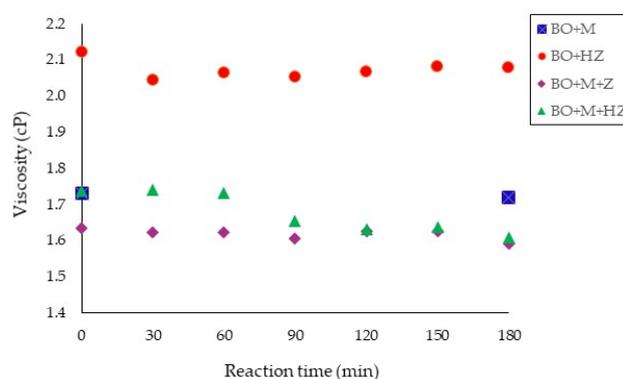
Fig. 6 Viscosity of the esterified bio-oil from the esterification of bio-oil in the presence and the absence of methanol and catalysed by the zeolite catalysts at 70 °C with a ratio of bio-oil-to-methanol of 1:3, a catalyst loading of 10 wt.%, a reaction time of 0-180 min and stirring rate of 500 rpm. (BO=bio-oil, M=methanol).
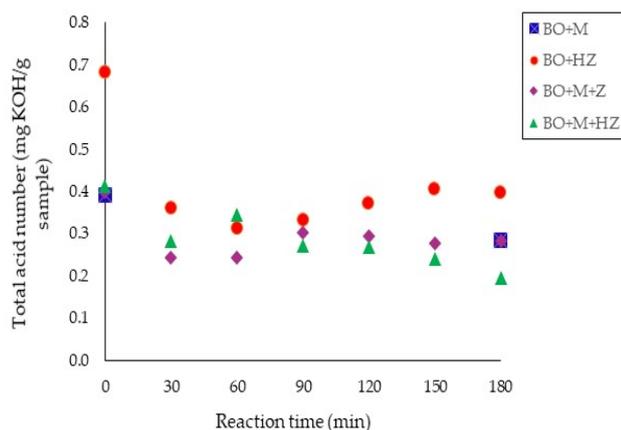
Fig. 7 Total acid number of the esterified bio-oil sample from the esterification of bio-oil in the presence and the absence of methanol and catalysed by the zeolite catalysts at 70 °C with a ratio of bio-oil-to-methanol of 1:3, a catalyst loading of 10 wt.%, a reaction time of 0-180 min and stirring rate of 500 rpm. (BO=bio-oil, M=methanol).

To evaluate the performance of the zeolite catalysts prepared in this study, the determination of total acid number of the esterified bio-oil in the presence of methanol and the zeolite catalysts over 0-180 min reaction time was carried out, as is presented in Figure 7. Overall, the esterified bio-oil from "BO+M+HZ" experiment showed a highest decrease in the total acid number (~53%), followed by that from the "BO+HZ" experiment (~42%). The latter indicated an interesting phenomenon, suggesting that other reactions might take place between the reactive components in the bio-oil during heating up at 70 °C in the presence of the HZ catalyst. Despite of the slight increase (6-11%) in the total acid number of the esterified bio-oil from 60 to 120 min was probably due to the reverse reaction resulting back in the initial acids. This reverse reaction could be promoted by the saturated zeolite surface by the absorbed products, leading to the equilibrium shift to the left (reactant side). A further investigation seemed required to study the behaviour of the bio-oil alone in the presence of a solid acid catalyst such as HZ catalyst. This would be a part of our future work.
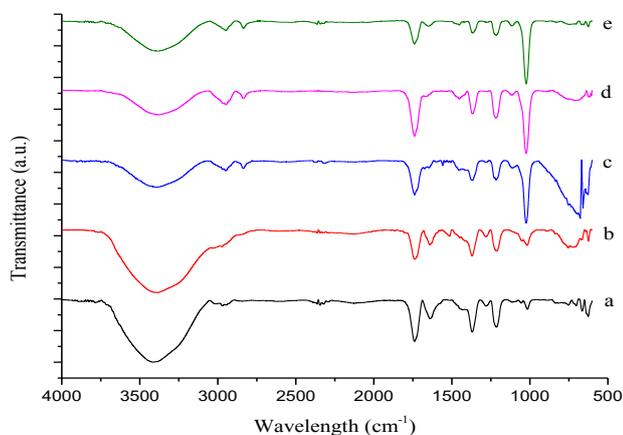
The role of the zeolite catalysts during the esterification of the bio-oil was further explained by the changes in the IR spectra of the esterified bio-oil from all experiments in the presence and absence of the catalysts for a 180-min reaction time, as is presented in Figure 8. The content of water, carboxylic acids, phenols and polyols in the "fresh" bio-oil (Figure 8a) considerably decreased when methanol and the zeolite catalysts were employed (Figure 8d and 8e). This change was indicated by the decrease in the intensity of the broad intense absorption at a wavenumber of 3200 and 3600 cm⁻¹ designated to hydrogen bonded O–H stretching absorption (Zhang *et al.*, 2013). A strong carbonyl stretching band at a wavenumber of 1650-1780 cm⁻¹ was observed in the "fresh" bio-oil (Figure 8a) and the esterified bio-oil with the Z catalyst (Figure 8d). A lower band was observed for the bio-oils from other experiments (Figure 8b, 8c, and 8e). The formation of esters and ethers in the esterified bio-oil from "BO+M" (Figure 8c), "BO+M+Z" (Figure 8d), and "BO+M+HZ" (Figure 8e) experiments was confirmed by the strengthening of C–O stretching vibrations at wavenumbers between 900 and 1300 cm⁻¹ (1240, 1070, 1044, 1022, and 950 cm⁻¹) (Jiang *et al.*, 2011). The presence of molecules with sp³ aliphatic bonds was confirmed at a wavenumber of 2850-2950 cm⁻¹ designated to a C–H stretching vibration and a wavenumber of 1375-1475 cm⁻¹ designated to the C–H deformation vibrations (Pokorna *et al.*, 2009). The relative intensity in these two regions significantly increased in the esterified bio-oil in the presence of methanol and the zeolite catalysts possibly due to the formation of esters, ethers and acetals (Zhang *et al.*, 2014).

4. Conclusion

The production of the bio-oil produced from the pyrolysis of Sengon woody biomass was carried out at temperatures of 500-650 °C. The highest yield of bio-oil was achieved at 600 °C (i.e., 45 wt.%). The produced bio-oils were highly flowing with a density and viscosity of ~1.1 g/mL and ~2.0, respectively. The total acid number and the relative concentration of acetic acid in the bio-oil were ranging from 0.71 to 0.94 mg/g and from 48.45 to 79%, respectively. The bio-oil with highest total acid number and relative concentration of acetic acid was esterified in the presence of methanol using the zeolite catalysts prepared from Indonesian natural zeolite through two-step acid treatment and surface modification. The zeolite catalysts showed a good performance in catalysing the esterification of bio-oil in the presence of methanol indicated by the decrease in the total acid number of the esterified bio-oil. In the presence of methanol, the HZ catalyst showed the highest performance in reducing the total acids in the bio-oil up to 52.94 %. The formation of esters and ethers was confirmed by the IR spectra of the esterified bio-oil. A considerable decrease in the total acid number was also observed for the reaction of the bio-oil in the absence of methanol but in the presence of the HZ catalyst. Other reactions catalysed by the zeolite solid acid catalyst might also take place between the reactive components in the bio-oil even without an extra addition of methanol. This would be another part of our study.

Fig. 8 IR spectra of (a) fresh bio-oil, and the esterified bio-oil from (b) "BO+HZ", (c) "BO+M", (d) "BO+M+Z", and (e) "BO+M+HZ" experiments of the esterification of bio-oil at 70 °C with a ratio of bio-oil-to-methanol of 1:3, a catalyst loading of 10 wt.%, a reaction time of 180 min and stirring rate of 500 rpm. (BO=bio-oil, M=methanol).

Acknowledgments

References

Ahamed, T.S., Anto, S., Mathimani, T., Brindhadevi, K. & Pugazhendhi, A. (2020). Upgrading of bio-oil from thermochemical conversion of various biomass – Mechanism, challenges and opportunities. *Fuel,* 287*,* 119329; doi: 10.1016/j.fuel.2020.119329.

Atikah, W.S. (2017). Potensi zeolit alam gunung kidul teraktivasi sebagai media adsorben pewarna tekstil. *Arena Tekstil*, 32(1), 17-24.

Bridgwater, A.V. (1999). Principles and practice of biomass fast pyrolysis processes for liquids. *Journal of Analytical and Applied Pyrolysis*, 51(1–2), 3-22; doi: 10.1016/S0165-2370(99)00005-4.

Bridgwater, A.V. (2012). Review of fast pyrolysis of biomass and product upgrading. *Biomass & Bioenergy*, 38, 68–94; doi: 10.1016/j.biombioe.2011.01.048.

Bridgwater, A.V., Meier, D. & Radlein, D. (1999). An overview of fast pyrolysis of biomass. *Organic Geochemistry*, 30(12), 1479-1493; doi: 10.1016/S0146-6380(99)00120-5.

Burris, L.E. & Juenger, M.C.G. (2016). The effect of acid treatment on the reactivity of natural zeolites used as supplementary cementitious materials. *Cement and Concrete Research*, 79, 185-193; 10.1016/j.cemconres.2015.08.007.

Chiaramonti, D., Oasmaa, A. & Solantausta, Y. (2007). Power generation using fast pyrolysis liquids from biomass. *Renewable and Sustainable Energy Reviews,* 11(6), 1056-1086; doi: 10.1016/j.rser.2005.07.008.

Chukwuneke, J.L., Ewulonu, M.C., Chukwujike, I.C. & Okolie, P.C. (2019). Physico-chemical analysis of pyrolyzed bio-oil from swietenia macrophylla (mahogany) wood. *Heliyon*, 5(6), e01790, 1-7; doi: 10.1016/j.heliyon.2019.e01790.

Ciddor, L.A., Bennett, J.A., Hunns, J.A. & Wilson, K. (2015). Catalytic upgrading of bio-oils by esterification. *Journal of Chemical Technology & Biotechnology*, 90(5), n/a-n/a; doi: 10.1002/jctb.4662.

Fattahi, N., Triantafyllidis, K., Luque, R. & Ramazani, A. (2019). Zeolite-Based Catalysts: A Valuable Approach toward Ester Bond Formation. *Catalysts,* 9(758), 1-23; doi: 10.3390/catal9090758.

Fauzi, A.H.M., Amin, N.A.S. & Mat, R. (2014). Esterification of oleic acid to biodiesel using magnetic ionic liquid: Multi-objective optimization and kinetic study. *Applied Energy*, 114*,* 809–818; doi: 10.1016/j.apenergy.2013.10.011.

Foong, S.Y., Liew, R.K., Yang, Y., Cheng, Y.W., Yek, P.N.Y., Mahari, W.A.W., Lee, X.Y., Han, C.S., Vo, D.-V. N., Le, Q.V., Aghbashlo, M., Tabatabaei, M., Sonne, C., Peng, W., & Lam, S.S. (2020). Valorization of biomass waste to engineered activated biochar by microwave pyrolysis: Progress, challenges, and future directions. *Chemical Engineering Journal*, 389, 124401; doi: 10.1016/j.cej.2020.124401.

Hartanto, D., Yuan, L.S., Sari, S.M., Sugiarso, D., Murwarni, I.K., Ersam, T., Prasetyoko, D. & Nur, H. (2016). The use of the combination of FTIR, pyridine adsorption, ^{27}Al and ^{29}Si MAS NMR to determine the Brönsted and Lewis acidic sites. *Jurnal Teknologi,* 78(6), 223-228; doi: 10.11113/jt.v78.8821.

Hartati, N.S., Sudarmonowati, E., Fatriasari, W., Hermiati, E., Dwianto, W., Kaida, R., Baba, K. & Hayashi, T. (2010). Wood characteristic of superior Sengon collection and prospect of wood properties improvement through genetic engineering. *Wood Research Journal,* 1(2),103–107; doi: 10.51850/wrj.2010.1.2.103-107.

Hu, X., Gunawan, R., Mourant, D., Hasan, M.MD., Wu, L., Song, Y., Lievens, C. & Li, C-Z. (2017). Upgrading of bio-oil via acid-catalyzed reactions in alcohols — A mini review. *Fuel Processing Technology*, 155, 2–19; doi: 10.1016/j.fuproc.2016.08.020.

Hu, X., Gunawan, R., Mourant, D., Lievens, C., Li, X., Zhang, S., Chaiwat, W. & Li, C-Z. (2012). Acid-catalysed reactions between methanol and the bio-oil from the fast pyrolysis of mallee bark. *Fuel*, 97, 512-522; doi: 10.1016/j.fuel.2012.02.032.

Hu, X., Wu, L., Wang, Y., Mourant, D., Lievens, C., Gunawan, R. & Li, C.-Z. (2012). Mediating acid-catalyzed conversion of levoglucosan into platform chemicals with various solvents. *Green Chemistry*, 14, 3087–3098; doi: doi.org/10.1039/C2GC35961H.

Jiang, X.X., Naoko, E. & Zhong, Z.P. (2011). Fuel properties of bio-oil/bio-diesel mixture characterized by TG, FTIR and ^{1}H NMR. *Korean Journal of Chemical Engineering*, 28, 133–137; doi: 10.1007/s11814-010-0328-y.

Kadarwati, S. & Wahyuni, S. (2015). Characterization and Performance Test of Palm Oil Based Bio-Fuel Produced Via Ni/Zeolite-Catalyzed Cracking Process. *International Journal of Renewable Energy Development*, 4(1), 32-38; doi: 10.14710/ijred.4.1.32-38.

Kadarwati, S., Hu, X., Gunawan, R., Westerhof, R., Gholizadeh, M. Hasan, M.D.M., & Li, C.-Z. (2017). Coke formation during the hydrotreatment of bio-oil using NiMo and CoMo catalysts. *Fuel Processing Technology,* 155, 261-268; doi: 10.1016/j.fuproc.2016.08.021.

Kadarwati, S., Qurrochman, T., Kurniawan, C., Jumaeri, J. & Kasmui, K. (2020). Feasibility study on the utilization of mahogany (Swietenia macrophylla King) wood as a raw material in the bio-oil production. *Journal of Physics Conference Series*, 1567, 022029; doi: 10.1088/1742-6596/1567/2/022029.

Kadarwati, S., Rahmawati, F., Rahayu, P.E. & Supardi, K.I. (2013). Kinetics and Mechanism of Ni/Zeolite-Catalyzed Hydrocracking of Palm Oil into Bio-Fuel. *Indonesian Journal of Chemistry*, 13(1), 77–85; doi: 10.22146/ijc.21330.

Kim, M., DiMaggio, C., Salley, S.O. & Simon, Ng.K.Y. (2012). A new generation of zirconia supported metal oxide catalysts for converting low grade renewable feedstocks to biodiesel. *Bioresource Technology,* 118, 37-42. doi: 10.1016/j.biortech.2012.04.035.

Kunkeler, P.J., Zuurdeeg, B.J., van der Waal, J.C., van Bokhoven, J.A., Koningsberger, D.C. & van Bekkum, H. (1998). Zeolite Beta: The Relationship between Calcination Procedure, Aluminum Configuration, and Lewis Acidity. *Journal of Catalysis*, 180, 234-244; doi: 10.1006/JCAT.1998.2273.

Liu, Y., Li, Z., Leahy, J.J. & Kwapinski, W. (2015). Catalytically upgrading bio-oil via esterification. *Energy & Fuels*, 29(6), 3691–3698; doi: 10.1021/acs.energyfuels.5b00163.

Menad, K., Feddag, A. & Rubenis, K. (2016). Synthesis and study of calcination temperature influence on the change of structural properties of the lta zeolite. *Rasayan Journal of Chemistry*, 9(4), 788–797.

Milina, M., Mitchell, S. & Pérez-Ramírez, J. (2014). Prospectives for bio-oil upgrading via esterification over zeolite catalysts. *Catalysis Today*, 235, 176-183; doi: 10.1016/j.cattod.2014.02.047.

Mortensen, P.M, Grunwaldt, J.D., Jensen, P.A., Knudsen, K.G. & Jensen, A.D. (2011). A review of catalytic upgrading of bio-oil to engine fuels. *Applied Catalysis A: General*, 407(1–2), 1-19; doi: 10.1016/j.apcata.2011.08.046.

Müller, J.M., Mesquita, G.C., Franco, S.M., Borges, L.D., de Macedo, J.L., Dias, J.A., & Dias, S.C.L. (2014). Solid-state dealumination of zeolites for use as catalysts in alcohol dehydration. *Microporous and Mesoporous Material*, 204, 50–57; doi: 10.1016/j.micromeso.2014.11.002.

Nandiwale, K.Y., Sonar, S.K., Niphadkar, P.S., Joshi, P.N., Deshpande, S.S., Patil, V.S. & Bokade, V.V. (2013). Catalytic

upgrading of renewable levulinic acid to ethyl levulinate biodiesel using dodecatungstophosphoric acid supported on desilicated H-ZSM-5 as catalyst. *Applied Catalysis A: General*, 460–461, 90-98; doi: 10.1016/j.apcata.2013.04.024.

Osatiashtiani, A., Puértolas, B., Oliveira, C.C.S., Manayil, J.C., Barbero, B., Isaacs, M., Michailof, C., Heracleous, E., Pérez-Ramírez, J., Lee, A.F. & Wilson, K. (2017). On the influence of Si:Al ratio and hierarchical porosity of FAU zeolites in solid acid catalysed esterification pretreatment of bio-oil. *Biomass Conversion and Biorefinery, 7*, 331–342; doi: 10.1007/s13399-017-0254-x.

Özşen, A.Y. (2020). Conversion of biomass to organic acids by liquefaction reactions under subcritical conditions. *Frontier in Chemistry,* 8(24), 1-14; doi: 10.3389/fchem.2020.00024.

Paar, A. (2021). Description of diesel fuel. https://wiki.anton-paar.com/en/diesel-fuel/. Accessed on April 4, 2021.

Papari, S. & Hawboldt, K. (2015). A review on the pyrolysis of woody biomass to bio-oil: Focus on kinetic models, *Renewable and Sustainable Energy Reviews,* 52, 1580-1595; doi: 10.1016/j.rser.2015.07.191.

Phatai, P., Loiha, S., Prayoonpokarach, S. & Wittayakun, J. (2020). Effect of Crystallinity of Zeolite Beta on Physicochemical Properties and Performance of Cobalt Catalysts. *Sains Malaysiana,* 49(1), 75-84; doi: 10.17576/jsm-2020-4901-09.

Pokorna, E., Postelmans, N., Jenicek, P., Schreurs, S., Carleer, R. & Yperman, (2009). J. Study of bio-oils and solids from flash pyrolysis of sewage sludges. *Fuel,* 88, 1344–1350; doi: 10.1016/j.fuel.2009.02.020.

Prasertpong, P. & Tippayawong, N. (2019). Energy Upgrading of biomass pyrolysis oil model compound via esterification: kinetic study using heteropoly acid. *Procedia*, 160, 253–259; doi: 10.1016/j.egypro.2019.02.144.

Prasertpong, P., Jaroenkhasemmeesuk, C., Tippayawong, N. & Thanmongkhon, Y. (2017). Characterization of bio-oils from jatropha residues and mixtures of model compounds. *Chiang Mai University Journal of Natural Sciences,* 16, 135–144; doi: 10.12982/cmujns.2017.0011.

Saputro, D.D., Widayat, W., Saptoadi, H., Grafika, J., & Yogyakarta, N. (2012). Karakterisasi briket dari limbah pengolahan kayu sengon dengan metode cetak panas. *Prosiding Seminar Nasional Aplikasi Sains & Teknologi,* Period III (November 2012), 394–400.

Serrano, D.P., García, R.A., Linares, M. & Gil, B. (2012). Influence of the calcination treatment on the catalytic properties of hierarchical ZSM-5. *Catalysis Today,* 179(1), 91-101; doi: 10.1016/j.cattod.2011.06.029.

Sondakh, R.C., Hambali, E. & Indrasti, N.S. (2018). Esterification bio-oil using acid catalyst and ethanol. *International Journal of Engineering and Management Research,* 8(5), 137-141; doi: 10.31033/ijemr.8.5.15.

Sondakh, R.C., Hambali, E. & Indrasti, N.S. (2019). Improving characteristic of bio-oil by esterification method. *IOP Conference Series: Earth and Environmental Science,* 230, 012071, 1-6; doi: 10.1088/1755-1315/230/1/012071.

Speight, J.G. (2011). *2–Production, properties and environmental impact of hydrocarbon fuel conversion.* In: Khan, M.R.

Advances in Clean Hydrocarbon Fuel Processing. Woodhead Publishing Limited.

Sutrisno, B. & Hidayat, A. (2016). Upgrading of bio-oil from the pyrolysis of biomass over the rice husk ash catalysts. *IOP Conference Series: Materials Science and Engineering,* 162, 012014; doi: 10.1088/1757-899X/162/1/012014.

Thitsartarn, W. & Kawi, S. (2011). Transesterification of Oil by Sulfated Zr-Supported Mesoporous Silica. *Industrial & Engineering Chemistry Research*, 50, 7857-7865; doi: 10.1021/ie1022817.

Várhegyi, G., Antal, M.J., Jakab, E. & Szabó, P. (1997). Kinetic modeling of biomass pyrolysis. *Journal of Analytical and Applied Pyrolysis*, 42(1), 73–87; doi: 10.1016/S0165-2370(96)00971-0.

Wang, J-J., Chang, J. & Fan, J. (2010). Catalytic esterification of bio-oil by ion exchange resins. *Journal of Fuel Chemistry and Technology*, 38(5), 560-564; doi: 10.1016/S1872-5813(10)60045-X.

Wang, Y., Hu, X., Mourant, D., Song, Y., Zhang, L., Lievens, C., Xiang, J. & Li, C-Z. (2013). Evolution of aromatic structures during the reforming of bio-oil: importance of the interactions among bio-oil components. *Fuel*, 111, 805–812; doi: 10.1016/j.fuel.2013.03.072.

Weerachanchai, P., Tangsathitkulchai, C. & Tangsathitkulchai, M. (2012). Effect of reaction conditions on the catalytic esterification of bio-oil. *Korean Journal of Chemical Engineering*, 29(2), 182-189; doi: 10.1007/s11814-011-0161-y.

Wei, Y., Lei, H., Zhu, L., Zhang, X., Yadavalli, G., Liu, Y. & Yan, D. (2015). Oxygen-Containing Fuels from High Acid Water Phase Pyrolysis Bio-Oils by ZSM−5 Catalysis: Kinetic and Mechanism Studies. *Energies*, 8, 5898-5915; doi: 10.3390/en8065898.

Wu, L., Hu, X., Wang, S., Mourant, D., Song, Y., Li, T. & Li, C.-Z. (2016). Formation of coke during the esterification of pyrolysis bio-oil. *RSC Advances*, 6, 86485-86493. doi: 10.1039/C6RA14939A.

Yang, H., Yan, R., Chen, H., Lee, D.H. & Zheng, C. (2007). Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel*, 86(12–13), 1781–1788; doi: 10.1016/j.fuel.2006.12.013.

Zaman, C.Z., Pal, K., Yehye, W.A., Sagadevan, S., Shah, S.T., Adebisi, G.A., Marliana, E., Rafique, R.F. & Johan, R.B. (2017). Pyrolysis: A Sustainable Way to Generate Energy from Waste, in Pyrolysis, M. Samer, IntechOpen, doi: 10.5772/intechopen.69036. Available from: https://www.intechopen.com/books/pyrolysis/pyrolysis-a-sustainable-way-to-generate-energy-from-waste.

Zhang, L., Shen, C. & Liu, R. (2014). GC–MS and FT-IR analysis of the bio-oil with addition of ethyl acetate during storage. *Frontiers in Energy Research*, 2(3), 1-6; doi: 10.3389/fenrg.2014.00003.

Zhang, Z., Sui, S., Wang, F., Wang, Q. & Pittman Jr., C.U. (2013). Catalytic Conversion of Bio-Oil to Oxygen-Containing Fuels by Acid-Catalyzed Reaction with Olefins and Alcohols over Silica Sulfuric Acid. *Energies*, 6, 4531-4550; doi: 10.3390/en6094531.