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Conversion of Cellulose From Palm Oil Middle Waste (Elaeis Guineensis) Into Bio-oil Products As Alternative Fuel

Adistya Fadhilah Husna[a], Fitria Febrianti[a], Habibie Helminan Syah[a], Rabiatul Adawiyah Pangaribuan[a], Tia Aulia Surbakti[a], Junifa Layla Sihombing[a], Ahmad Nasir Pulungan[a]*

[a]Department of Chemitsry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Medan, Jl. Willem Iskandar Pasar V Medan Estate, Medan 20221, Indonesia

Abstract

Oil palm midrib are very abundant waste, especially in the North Sumatra, Indonesia. Lignocellulose contained in oil palm midrib can be used as a source of alternative energy raw materials. The purpose of this research is to produce bio-oil that can reduce the use of fossil fuels. Natural zeolite (ZAS) as a catalyst was activated by mineral acid and calcination with nitrogen gas. Impregnation of Ni and Fe into ZAS followed by calcination and oxidation process to obtained Ni-Fe/ZAS catalyst. The conversion of oil palm midrib powder into cellulose was carried out by delignification process with NaOH and bleaching. Then, the conversion of bio-oil is carried out by pyrolysis using the HDO process. Based on the results of the catalyst characterization and activity test showed that the Ni-Fe/ZAS catalyst had good characteristics and activity. Bio-oil from fiber is dominated by lignin derivatives, meanwhile cellulose bio-oil is dominated by furan derivatives. Hydrodeoxygenation using a Ni-Fe/ZAS catalyst on fiber produced slightly different compounds from bio-oil in HDO without a catalyst, especially in the reduction percentage of phenol area from 52.91% to 39.58%. Meanwhile, in HDO bio-oil from cellulose, there was an increase in the percent area of phenol from 27.45% to 35.59%.

1. Introduction

The rapid population growth accompanied by industrial progress causes the need for fuel to increase, so that it has an impact on the lack of fossil fuel supplies in nature [1]. Therefore, there is a need for alternative fuels to replace fossil fuels. One of the alternative renewable energy sources is bio-oil. Bio-oil is an oxygenated liquid that has a high density used as a substitute for fuel. Bio-oil can be used as a substitute for fuel in diesel engines, turbines or boilers, although it still requires long-term durability tests, and besides that it can also be used for the production of certain other chemicals such as diesel substitutes, heavy fuel oil, fuel light oil and natural gas fuel for various boilers [2].

Bio-oil can be generated from various lignocellulosic-containing biomass wastes through two main routes: Flash pyrolysis and hydrothermal liquefaction (HTL). Flash pyrolysis involves the rapid thermal decomposition of organic compounds at temperatures between 450-600°C in the absence of oxygen to produce liquids, gases, and charcoal. From this process, organic steam, gas and charcoal are obtained. The organic vapor is condensed into bio-oil with a yield of up to 68% by weight of the feed introduced. While the HTL process involves the reaction of biomass in water at high temperature and pressure with or without a catalyst [3].

One of the biomass that has not been utilized at this time is palm frond waste, which is abundant in North Sumatra. Judging from the chemical composition of oil palm fronds, the compositions of cellulose, hemicellulose, and lignin from palm fronds were 34.89%, 27.14%, and 19.87%. This content is bio-oil energy which is a renewable and environmentally friendly alternative to fossil fuels (petroleum) [1]. Santi *et al* [4] have carried out hydrocracking of pyrolyzed α-cellulose to hydrocarbon over mesoporous carbon catalyst and

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reported that Co/MC72 and Mo/MC72 catalyst improved quantity and quality of bio-oil.

In order for bio-oil to be used as a fuel, its physical and chemical properties need to be improved [5-6]. One method that has been used to improve the quality of bio-oil is the hydrodeoxygenation (HDO) process [7-8], where this process is a way to reduce oxygen under high pressure of hydrogen gas which can be done together to increase the concentration of bio-oil. To speed up the reaction, a catalyst is needed. The catalyst chosen is a carrier metal system catalyst, namely a combination of nickel (Ni) and iron (Fe) which is embedded in a zeolite (Ni-Fe/ZAS). As the carrier, natural zeolite is chosen, which is quite abundant in Indonesia. The use of a combination of Ni and Fe as a catalyst because this metal has good catalytic activity and the price is relatively cheap when compared to precious metals [9].

Therefore, in this research, the pyrolysis of cellulose from palm frond waste into bio-oil products will be carried out, together with the HDO process using a NiFe/ZA catalyst with hydrogen gas flow. The physical and chemical properties of the produced bio-oil were determined to evaluate its potentiality as alternative fuels.

2. Experimental
2.1 Materials
This research uses oil palm midrib, the chemicals used are Sarulla natural zeolite, hydrochloric acid (HCl), 10% acetic acid (CH_3COOH), 15% sodium hydroxide (NaOH), sodium chloride (NaCl), 10% hydrogen peroxide (H_2O_2), distilled water, precursor of Fe and Ni, gas mixture of H_2/N_2.

The tools used are a set of glassware, beaker glass, oven, measuring cup, hotplate, magnetic stirrer, 100 and 80 mesh filters, analytical balance, stirring rod, mortar and pestle, vacuum apparatus, reflux apparatus, Gas Chromatography and Mass Spectroscopy (GC-MS), X-Ray Difraction (XRD), Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX) and Fourier Transform Infrared Spectroscopy (FTIR).

2.2 Catalyst Preparation
Natural zeolite was ground using a mortar and pestle and sieved through a 100 mesh sieve. Zeolite was activated with 3M HCl at 100 ℃ and homogenized with a magnetic stirrer for 1 h. The result was filtered and the precipitate was washed with distilled water to remove residual HCl, until a neutral pH was reached, then dried in an oven at 120 °C for 5 h. The activated zeolite calcination process was carried out at a temperature of 500 °C with nitrogen gas flowing for 2 h. Natural zeolite that has been active is named ZAS.

The synthesis of the catalyst was carried out at room temperature and the impregnation of Ni-Fe metal on the zeolite was carried out by the wet impregnation method. A total of 6.05 g of Ni metal and 2.9 g of Fe metal were weighed, then dissolved with aquadest. Ni and Fe metal solution was mixed with 100 g of natural Zeolite which had been previously activated, then the mixed solution was refluxed and stirred with a magnetic stirrer at 80 ℃ for 3 h, then dried in an oven at 120 °C for 4 h, then calcined with gas. O_2 and H_2 gas at 500 °C for 2 h [10]. The active zeolite that has been loaded with Ni and Fe metals is named Ni-Fe/ZAS.

The catalysts that have been made are micro-analyzed with XRD and SEM-EDX instruments to be able to see the crystal shape of the catalysts that have been made and see the diffraction peaks of the catalysts.

2.3 Cellulose Production from Oil Palm Midrib
At first, the palm frond was cut about 3-5 cm, then ground using a grinder and sieved to obtain a sieve size of 80 mesh. Then dried at 100 °C for 1 h.

Palm frond flour weighing 35 g was cooked with 700 mL of 15% NaOH solution, temperature of 100 for 3 h aimed at dissolving non-cellulose components. The remaining solids were then washed with clean water until free of NaOH. Furthermore, soaking was carried out with 700 mL of distilled water mixed with 14 g NaCl and 35 mL of 10% acetic acid. It was filtered and the fiber was washed with distilled water so that the pH was neutral [11].

Furthermore, bleaching was carried out by dissolving the sample in 10% H_2O_2 at a temperature of 60 °C for 1 h. The sample obtained was filtered and washed with distilled water until the remaining filtrate was neutral. Then the fibers obtained were dried using an oven at 100 °C for 2 h.

2.4 Bio-oil Production
A total of 5 g of cellulose was put into the pyrolysis reactor and then 3 g of catalyst was added. Next, nitrogen gas was flowed for 10 minutes to remove the air, then the reactor was heated at a temperature of 450 °C with a heating rate of 45 °C /minute. The bio-oil is then continued with the HDO process with a Ni-Fe/ZAS catalyst and hydrogen gas flow for 2 h. The HDO bio-oil product is removed from the flask and then the bio-oil is filtered through filter paper.

2.5 Characterization of Bio-oil
Qualitative analysis was carried out to identify organic compounds in the composition of Bio-Oil samples using GC-MS. Characterization of physical and chem ical properties of bio-oil includes pH and viscosity [12].

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3. Results and Dicsussion

3.1 Catalyst Crystallinity Properties

X-ray diffraction measurements were carried out to identify the crystallinity of zeolite after acid activation, and after deposition of Ni and Fe metals. The comparison of the diffractogram of activated zeolite and metal-loaded zeolite can be seen in Fig.1.
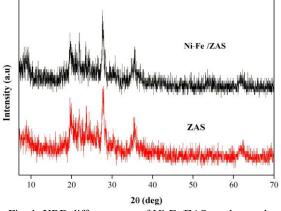

Fig. 1: XRD diffractogram of Ni-Fe/ZAS catalyst and activated zeolite (ZAS)

Based on Fig.1, ZAS diffractogram shows the main peak confirming the presence of natural zeolite at $2\theta = 27.74°$, $19.79°$, $35.48°$. Based on the JCPDS-International Center for Diffraction Data (2001) concluded that the sample is a type of modernite crystal, these results are in agreement with those reported by Sihombing *et al* [13].

The development of Ni and Fe on zeolite resulted in a decrease in the intensity of three main peaks, namely at $2\theta = 27.74°$ from 713 intensity changed to $2\theta = 27.71°$ intensity 634, at $2\theta = 19.79°$ from 436 intensity changed to $2\theta = 19.66°$ intensity 305 and at $2\theta = 35.48°$ from intensity 366 changed to $2\theta = 27.71°$ intensity 151. However, the diffractogram of Ni-Fe/ZAS catalyst showed that metal impregnation into zeolite did not damage the crystal structure of zeolite. It can be observed from the peaks that is still in the same 2θ region, although it has decreased in intensity at several peaks.

3.2 Surface Mophology of Catalyst

From the SEM results obtained information on the physical morphology of the surface, while from the EDX obtained the chemical composition on the surface of the sample. The SEM imaging and EDX of the catalyst is shown in Fig. 2.
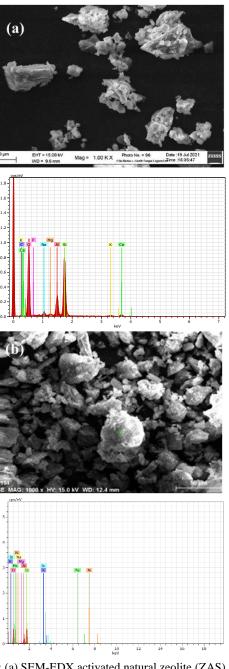

Fig. 2: (a) SEM-EDX activated natural zeolite (ZAS) and (b) SEM-EDX of t Ni-Fe/ZAS catalyst.

Fig 2 (a) shows the surface morphology of the ZAS. However, due to the poor shooting angle technique, because not much can be analyzed from the surface of ZAS. However, the SEM-EDX data showed a fairly high Si content. This can be understood because in ZAS there are still a lot of impurities which are crystalline and amourpus. Fig 2 (b) shows the SEM results showing the surface morphology of the Ni-Fe/ZAS catalyst, which shows the surface of small grains on the surface caused by the attached metal and based on the EDX results it can be seen that the Ni-Fe metal has attached to the natural zeolite but the concentration is not according

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to theory (calculation). It is suspected that the presence of Ni-Fe metal is not only present on the ZAS surface but mostly enters the ZAS pore.

3.3 Functional Group Analysis

The FT-IR analysis serves to identify the presence of functional groups based on the bonds contained in one compound. The comparison of the IR spectra of palm fiber and cellulose is presented in Fig. 3.
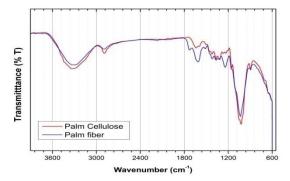

Fig. 3: FTIR Spectra of palm fiber and palm cellulose.

Fig 3 shows that there is an absorption shift in some wavenumber, observed at the number of carbonyl groups (C=O) in the range 1600-1800 cm^{-1}. This is as a result of the delignification process, the termination and removal of lignin compounds. The results of the FTIR spectrum analysis for cellulose and palm midrib fiber can be seen in the Table 1.

Table 1. Cellulose FT-IR Spectrum Analysis

Wave number (cm^{-1})	Functional groups	Compound Type
1000-1200	Ester	C-O
1300-1500	Aliphatic	-CH$_2$
1600-1800	Carbonyl	C=O
2800-2900	Aldehyde	C-H
3200-3500	Carboxylic Acid	O-H

Table 2. Oil Palm Fibers FT-IR Spectrum Analysis

Wave number (cm^{-1})	Functional groups	Compound Type
1000-1300	Eter	C-O-C
1349-1470	Alkane	C-H
2800-2900	Aldehyde	C-H
2850-2960	Alkane	C-H
3000-3600	Carboxylic Acid	O-H

The results of the FTIR spectroscopy analysis showed that -Cellulose and oil palm fibers provide a spectrum that describes the structure of cellulose.

3.4 Bio-oil Production Results

A total of 10 g of each sample, namely cellulose and palm midrib fiber, were put into the pyrolysis reactor and then a certain number of 2 g of catalyst was added. Furthermore, the pyrolysis process is carried out, which produces liquid smoke products. Then continued the HDO process with Ni-Fe/ZAS catalyst and hydrogen gas flow for 2 hours. The HDO bio-oil product was removed from the flask and then the bio-oil was filtered through filter paper.

Table 3. Results of Bio-oil in the Pyrolysis-HDO process

Sample	Catalyst	Massa (g)	Bio-oil (%)
Fiber	Catalyst Ni-Fe/ZAS	10	45
Fiber	-	10	38
Cellulose	Catalyst Ni-Fe/ZAS	10	40
Cellulose	-	10	37

From the data above, the sample conversion results for oil palm midrib fiber with Ni-Fe/ZAS catalyst is 45%, uncatalyzed coconut midrib fiber is 38%, cellulose with Ni-Fe/ZAS catalyst is 40% and cellulose without catalyst is 37%. It can be concluded that the most produced Bio-oil products in the HDO process are samples that use a catalyst. The metallic NiFe catalyst used for the pyrolysis of cellulose proved that Ni$_2$Fe$_3$ catalyst powder has excellent catalytic activity to increase the bio-oil produced from the sample.

3.5 Analysis of Physical and Chemical Properties of Bio-Oil
3.5.1 Analysis of GC-MS

The GC-MS chromatogram of all bio-oil product conditions is shown in Fig 4. The GC-MS chromatogram of Bio-oil powdered palm fronds without a catalyst showed the 3 highest peaks, namely phenol compounds with an area of 52.91%, and 2-furancarboxaldehyde with an area of 13.66% and 2-cyclopenten-1-one with an area of 5.31%. Chromatogram of GC MS bio-oil of palm midrib powder with Ni-Fe/ZAS catalyst showed 3 highest peaks, namely phenol compounds with an area of 39.58%, 2-furancarboxaldehyde with an area of 14.12% and 2-cyclopenten-1-one with an area of 6.40%. Chromatogram of GC-MS bio-oil from cellulose from palm fronds without a catalyst showed the 3 highest peaks, namely phenol compounds with an area of 27.45%, 2-cyclopenten-1-one with an area of 11.52% and 2-furancarboxaldehyde with an area of 11.09 %. The GC-MS chromatogram of bio-oil cellulose from palm fronds with Ni-Fe/ZAS catalyst showed 3 highest peaks, namely phenol compounds with an area of 35.59%, 2-furancarboxaldehyde with an area of 16.04% and 1-acetoxy-2-propionoxyethane with an area of 8.48%.
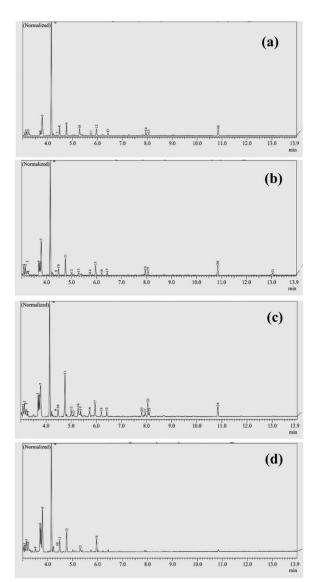
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Fig . 4: GC-MS- Chromatogram of (a) Bio-Oil from fiber with Ni-Fe/ZAS Catalyst; (b) Bio-Oil from fiber without Catalyst; (c) Bio-Oil from cellulose with Ni-Fe/ZAS Catalyst, and (d) Bio-Oil from cellulose without Catalyst.

Based on the peaks that appear in the GC-MS spectra, it is known that bio-oil from fiber has fewer compounds than bio-oil from cellulose. This is because the lignin that is still present in the fiber is more difficult to decompose because it contains a benzene ring [14-15]. In addition, there are several compounds that are more dominant in each pyrolysis raw material. Bio-oil from fiber is dominated by lignin derivatives, namely phenol compounds, guaiacol, syringol, and pyrocatechol. Meanwhile, cellulose bio-oil is dominated by aldehydes, ketones, furan derivatives, and phenols [14]. According to Graca *et al* [16], components of bio-oil such as oxygenate compounds consisting of phenol, acetic acid, and hydroxy acetone can reduce the quality of bio-oil. Phenol compounds have the effect of

increasing viscosity, decreasing pH, increasing acidity, and decreasing calorific value [17].

Hydrodeoxygenation using a Ni-Fe/ZAS catalyst on fiber produced slightly different compounds from uncatalyzed HDO, especially in the reduction in the percentage of phenol area from 52.91% to 39.58%. Sumianto *et al* [12] revealed that bio-oil with a phenol content of not more than 50% would be very good if used as fuel. On the other hand, the decomposition rate of lignin continued, indicated by the increase in the percent area of guaiacol and syringol, from 3.75% to 4.21%, and from 3.65% to 4.87%, respectively. In addition to phenolic compounds, this bio-oil also produces furfural compounds although it is not dominant. HDO with Ni-Fe/ZAA catalyst causes less furfural compounds to be produced than bio-oil in HDO without using a catalyst. This is related to the role of Ni-Fe metal embedded in the zeolite as a hydrogenation catalyst. Furfural compounds during the HDO process can undergo hydrogenation to produce furfuryl alcohol compounds which are further converted into tetrahydrofurfuryl alcohol, ketones, and other open ring products [18]. This is reinforced by the increase in the percentage area of several compounds including 2-furyl methyl ketone, 5-methylfurfural, 1-hydroxy-2-butanone acetate, and ethanone,1-(2,3,4-trihydroxyphenyl).

The compounds contained in the bio-oil in HDO from cellulose using a Ni-Fe/ZAS catalyst also have some differences compared to the bio-oil in HDO without a catalyst. These differences include an increase in the percentage area of 2-furyl methyl ketone, 5-methylfurfural, tetrahydrofurfuryl alcohol, 1-hydroxy-2-butanone acetate, and 2,3-hexanedione compounds. In addition, there was an increase in the percentage of phenol and guaiacol area, respectively, from 27.45% to 35.59%, and from 3.71% to 4.34%. The increase in phenol and guaiacol compounds is thought to be due to the absence of conversion of phenol and guaiacol compounds into other compounds during HDO due to interference from furfural compounds [19-20]. Dwiatmoko *et al* [18] reported that the presence of furfural compounds had a significant effect on the conversion of guaiacol. when no furfural compounds, the conversion of guaiacol compounds was 98%, but after adding furfural compounds the conversion of guaiacol decreased drastically to 28%. This indicates that the catalytic activity decreased due to poisoning catalyst by carbon deposition from polymerization and absorption of furfural compounds and their derivatives.

3.5.2 pH Test

Bio-oil of palm bunches has a pH level of ± 3. The results showed that the addition of catalyst did not have a significant effect on the pH of the bio-oil.

High acidity is due to the presence of acetic acid and other acids due to the pyrolysis process that breaks down cellulose and lignin as well as acidic extractive substances. So in general the acidity of bio-oil is quite high between 2.5-3.

3.5.3 Viscosity Test

Viscosity is a measure of the viscosity of a fluid which indicates the size of the friction in the fluid. The greater the viscosity of a fluid, the harder it is for the fluid to flow and the harder it is for an object to move in the fluid. The high viscosity makes it difficult for bio-oil to flow properly and causes a relatively high pressure drop in the piping process during distribution [12]. There is no significant difference in the viscosity obtained from the four samples. The average value of its viscosity is about of 0.8934 Ns/m^2. The low viscosity value is related to the high water content of bio-oil. This indicates that the bio-oil from the palm fronds is easier to flow in the distribution process.

4. Conclusion

Based on the results of the catalyst characterization and activity test on the continuous pyrolysis process with the HDO process showed that the Ni-Fe/ZAS catalyst had good characteristics and activity. Bio-oil from fiber is dominated by lignin derivatives, namely phenol compounds, guaiacol, syringol, and pyrocatechol. Meanwhile, cellulose bio-oil is dominated by aldehydes, ketones, furan derivatives, and phenols. Furfural compounds during the HDO process can undergo hydrogenation to produce furfuryl alcohol compounds which are further converted into tetrahydrofurfuryl alcohol, ketones, and other open ring products. Hydrodeoxygenation using a Ni-Fe/ZAS catalyst on fiber produced slightly different compounds from bio-oil in HDO without a catalyst, especially the reduction in the percentage of phenol area from 52.91% to 39.58%. Meanwhile, in HDO bio-oil from cellulose, there was an increase in the percent area of phenol and guaiacol, respectively from 27.45% to 35.59%, and from 3.71% to 4.34%. Phenol content of less than 50% is reported to be very good if used as a fuel. Therefore, bio-oil catalyzed by Ni-Fe/ZAS catalyst has the potential to be further developed as a fuel in the future.

5. Conflicts of interest

The authors declare no conflict of interest.

6. Acknowledgments

7. References

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