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Bio-oil Quality Based on Coconut Carbon Biomass Using Pyrolisis Method

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Abstract

Coconut shells are biomass composed of carbon, hydrogen, oxygen, nitrogen, and other components in small quantities. Biomass can be converted into bio-oil via the pyrolysis method. Bio-oil resulting from pyrolysis has poor quality because it contains oxygen, acid compound, ketone, and ester. To improve the quality of Bio-oil, the pyrolysis process is carried out through a catalytic esterification reaction using a sulfonated H_2SO_4 coconut shell charcoal catalyst. Bio-oil synthesis is carried out at a temperature of 300–500 °C. Coconut shell acid catalyst preparation was carried out by activation using HCl and followed by sulfonation of H_2SO_4 at a temperature of 150°C for 12 hours. The catalyst was characterized using XRD, FTIR, and SEM. The bio-oil obtained was tested for density, kinematic viscosity, water content, pH, ash content, acid value, Bio-oil composition using GCMS, and metal content using ICP-OES. The results of catalyst characterization show that the formed solid carbon-based catalyst from coconut shells has a graphite crystal structure with a densely porous surface and contains sulfonate functional groups. The yield of bio-oil produced was 6.4%. The results of comparing the characteristics of bio-oil before and after improving the quality using a catalyst show that there is a decrease in the kinematic viscosity, water content, ash content, and acid value, as well as an increase in the heating value and pH. The main compounds produced in Bio-oil are esters, ethers, ketones, phenols, alcohols, and carboxylic acids.

Keywords: bio-oil, catalyst, coconut shell, pyrolisis

INTRODUCTION

Coconut shells are biomass containing hemicellulose, cellulose, and lignin, which will be oxidized into phenol in the thermochemical conversion process into bio-oil through pyrolysis (Fardhyanti et al., 2018). Pyrolysis bio-oil consists of a mixture of organic compounds that show various chemical functional groups, contain water, have high viscosity and low calorific value, and are acidic, corrosive, and unstable. This is because bio-oil contains organic acids such as formic acid, acetic acid, and propionic acid (Sutrisno, B., & Hidayat, 2016). Bio-oil can be obtained by pyrolysis. Pyrolysis is a process that produces liquid hydrocarbons (liquid smoke) and charcoal (carbon black) (Lombok & Anom, 2023). Bio-oil belongs to liquid hydrocarbons. Pyrolyzed bio-oil is poorly quality because it contains oxygen and compounds such as acids, ketones, and esters(Lee et al. 2016). The pyrolysis product of coconut shell has a lower pH (Sa'diyah et al., 2018) than commercial fuels, which causes corrosiveness, so it cannot be applied directly as a fuel because it can cause engine damage (Fardhyanti et al., 2020). Therefore, using solid acid catalysts necessary to improve the quality of bio-oil from coconut shells. Theoretically, this catalyst can reduce the temperature during the reaction and provide a reaction pathway with a lower activation energy value (Kauwo et al., 2021).

Esterification is the best method to convert reactive organic acids in bio-oil into more stable esters. The reaction condition for acid esterification in bio-oil is the presence of an acid catalyst in the mixture of bio-oil and alcohol, which is also suitable for many other reactions (Sondakh et al., 2019). Esterification is a heating process involving an acid catalyst mixed with a polar solvent. (Sondakh et al., 2019) We have upgraded bio-oil through an esterification reaction using commercial acid catalysts such as H_2SO_4 and HCl. The results showed that the H_2SO_4 catalyst with 1% catalyst concentration had a better impact on bio-oil characteristics, which were able to reduce viscosity,

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reduce water content, and increase the highest heating value compared to other concentrations and types of catalysts.

Esterification reactions require acid catalysts. The catalytic activity of the catalyst is determined by the type and number of active sites and the surface area of the catalyst. Different types of catalysts have different active sites, numbers of active sites, and surface areas, so other types affect the difference in the esterification reaction rate.

Commercial acid catalysts such as sulfuric acid are homogeneous acid catalysts widely used for catalysts in esterification reactions. Still, weaknesses include difficult to separate, corrosive, toxic, and cause environmental problems. Therefore, a carbon-based solid acid catalyst using coconut shells was developed as a solution to the issues of commercial acids. Carbon-based solid acid catalysts offer the advantage of being easily separated, having low corrosivity and toxicity, and not causing environmental problems. Carbon-based solid acid catalyst from coconut shells has been used for the esterification reaction of Palm Fatty Acid Distillate (PFAD) with methanol (Hidayat et al., 2015). Therefore, carbon-based solid acid catalysts from coconut shells can potentially be an alternative acid catalyst in efforts to improve bio-oil quality, which has been studied in this research.

METHODOLOGY

Instrumentals and Materials

The Instrumentals used were Scanning Electron Microscope (SEM) Zeis Evo 50, Fourier Transform Infra Red (FTIR) Bruker Alpha, X-Ray Difractometer (XRD) Panalytical Empyrean DY 2384, Gas Chromatography-Mass Spectroscopy (GCMS) Shimadzu, Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) Agilent 5110A, set of pyrolysis apparatus, glassware, reflux apparatus, 200 mesh sieve, oven, thermometer, pH meter, densitimeter, magnetic stirrer, hotplate, and centrifugator.

The materials used were coconut shell, H_2SO_4 98% (Merck), HCl 0.1 M, distilled water, phenolphthalein, NaOH 0.01 M, HCl 0.01 M, Methanol p.a, Whatman filter paper No. 41.

Procedure

Coconut Shell Pyrolysis.

As shown in Figure 1, the chopped coconut shells were put into container A in the pyrolysis equipment scheme that had been installed. The container was closed tightly, and the fire source was turned on to 300-500 °C for 3 hours. The bio-oil obtained was collected in container C.

Preparation of Coconut Shell Charcoal

The pyrolyzed coconut shell charcoal was mashed and sieved with a 200-mesh sieve. A total of 10 grams of sieved charcoal was washed with 60 mL of 0.1 M HCl for one hour and then washed with distilled water until neutral. The neutral coconut shell charcoal was oven-dried for 2 hours at 105 ºC. (Sutrisno & Hidayat, 2016).

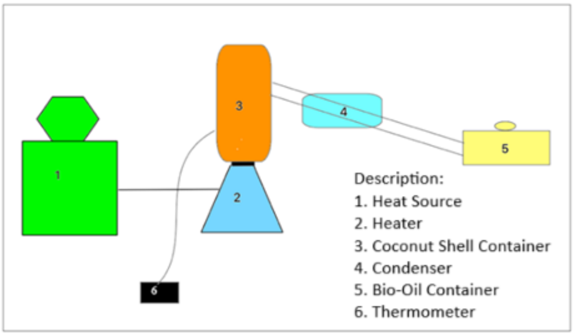

Figure 1. Schematic of the Pyrolysis Equipment Set

Coconut Shell Acid Catalyst Synthesis

The coconut shell acid catalyst was synthesized by sulfonating coconut shell charcoal. A coconut shell-activated charcoal catalyst was prepared with concentrated sulfuric acid. 100 mL of 98% concentrated sulfuric acid was added to 10 g of activated charcoal in a three-neck flask. The mixture was heated to 150 °C for 12 hours. After heating, it was placed into cold distilled water to lower its temperature and filtered. The activated charcoal catalyst was washed with 80 °C distilled water until the pH of the filtrate was neutral. After filtration, the activated charcoal was dried in an oven at 70 °C for approximately 1 hour (Hidayat et al., 2015).

Characterization of Coconut Shell Charcoal Catalysts

The coconut shell charcoal catalyst was characterized by X-ray diffraction (XRD) at 2θ between 10º and 90º and Cu Kα wavelength = 1.54060 Å to determine the structure of the catalyst. Diffractogram results were compared or matched with the Joint Committee on Powder Diffraction Standard (JCPDS) standard data. Characterization using Fourier Transform Infra-Red (FTIR) to identify the functional groups of the sample was carried out at wave numbers 500 - 4000 cm^{-1}. Each functional group of a compound has vibrations at different wave numbers in the FTIR spectra so that the vibrational peaks of the FTIR spectra can be used to identify the functional groups of compounds in the catalyst. We used a Scanning Electron Microscope (SEM) to determine the surface morphology of the catalyst. The characterization was also carried out on coconut shell charcoal and activated coconut shell charcoal for comparison.

Bio-oil Esterification

250 mL bio-oil and 10 grams of coconut shell charcoal catalyst were put into a three-neck flask, then heated to a temperature of 60 ºC, and 50 mL of methanol was added. Then, stir continuously for 90 minutes. After the reaction, it was cooled at room temperature and then separated the solid and liquid phases through filtration; the liquid phases was centrifuged for 2-4 hours to separate the organic and the water phase. The organic phases obtained is bio-oil, which has been upgraded.

Bio-oil before and after upgrading was analyzed using GCMS to determine the composition of chemical compounds contained in and ICP-OES to determine the metal content in bio-oil. In addition, the chemical-physical characteristics of bio-oil were analyzed, including color, density, kinematic viscosity, calorific value, water content, pH, ash content, and acid number (Sutrisno & Hidayat, 2016).

Density was measured using a Densitimeter based on the ASTM D 4052 procedure. Kinematic viscosity was measured on samples measured at 40 °C using a cross-arm viscometer based on the ASTM D 445 procedure. Water content was measured by Karl Fischer titration method based on the ASTM E203 procedure. The pH measurement was carried out based on the ASTM E70 procedure.

Ash Content

Ash content was measured based on ASTM D 482 for petroleum products. A total of 1 gram of Bio-oil was heated at 750 °C for 4 hours.

Acid Numbers

The acid number was measured based on the FBI-A01-03 procedure. One gram sample was put into a 250 mL Erlenmeyer flask. Then, 100 mL of neutralized solvent mixture was added to the Erlenmeyer flask. After that, all solutions in the Erlenmeyer flask were stirred vigorously and titrated with KOH in alcohol until the color changed. The pink color returned to pink with the same intensity as in the neutralized solvent mixture. The pink color obtained should last up to 15 minutes.

Data Analysis

Bio-oil yield was calculated with the equation reported by (Li et al. 2018) :

$$Yield\ (\%) = \frac{Volume\ of\ bio-upgraded\ oil}{Volume\ of\ bio-Initial\ oil}\ x\ 100\%$$

The following formula can calculate kinematic viscosity:

$$V = C\ x\ t$$

Description:

V = Kinematic viscosity (cSt/(mm^2/sec))

C = Viscometer calibration constant (cSt/sec)

t = flow time (second)

Calculation of ash content is done using the formula:

$$Ash\ Content\ (\%) = \frac{(W_o - W)}{W_1}$$

Description:

Wo = weight of sample and weight of constant cup before ignition (g)

W1 = sample weight (g)

W = weight of the sample and the cup after ignition (g)

Acid number calculation using the formula:

$$Acid\ Number\ \left(mg\frac{KOH}{g}\right) = \frac{(A-B)x\ M\ x\ 56.1}{W}$$

Description:
A = KOH volume required during titration (mL)
B = Blank volume
M = Molarity of KOH
W = Sample weight (g)

RESULT AND DISSCUSION

Coconut Shell Charcoal

Pyrolysis of coconut shell produced a yield of 28.4% coconut shell charcoal and 30% bio-oil. The components in the bio-oil produced depend on the time and temperature of the process. In this research, the pyrolysis process uses a simple tool with a heating temperature of 300 - 500 °C, which is included in low-temperature carbonization. This result is explained by Fardhyanti et al., (2018) found that at these heating temperatures, there is a break in the aliphatic carbon bonds (at low temperatures) in coconut shells, then followed by the elimination of heterocomplex rings and the breaking of C-H bonds. The maximum product of the decomposition process occurs at temperatures between 300-350 °C. This study was conducted at heating only up to 500 °C. According to (Sasikumar et al., 2019) the yield of liquid from pyrolysis of coconut shell is reported to increase up to 450 °C and decrease at 600 °C.

Coconut shell charcoal from pyrolysis was activated using HCl to dissolve impurities and open the pores of the charcoal. This result is the same as stated Alfiany & Bahri (2013) that HCl is used as an activator because it has better absorption. HCl can dissolve impurities so that more pores are formed. This result is in line with the research showing that activating coconut shell charcoal with the addition of an HCl solution can open and increase the number of pores in coconut shell charcoal and increase its surface area (Nurdin et al., 2022).

Coconut shell charcoal that has been activated is washed with distilled water. This washing is done so that the coconut shell charcoal has a neutral pH and removes the remaining acid activator (Kartika, V., Ratnawulan, 2016). The neutral coconut shell charcoal was then dried at 105 ºC with the aim of removing the water content. According to Adriati et al. (2013), drying aims to remove freely trapped water molecules. The dried coconut shell charcoal was sulfonated to produce a catalyst.

Coconut Shell Acid Catalyst

The synthesis of coconut shell acid catalyst is done by sulfonation. The sulfonation process is carried out by adding H_2SO_4, which is carried out with a reflux process using a three-neck flask with a temperature at 150 °C for 12 hours. The process aims to react coconut shell charcoal with H_2SO_4. The reaction can form an active group $-SO_3H$ on the polycyclic carbon of coconut shell charcoal. Thus, the catalyst will be acidic and can be used for esterification reactions.

The reflux was then cooled and filtered to separate the residue from the reagent solution. The catalyst formed was washed with 80°C distilled water until neutral to remove the remaining sulfate ions that did not react with coconut shell charcoal. The catalyst was dried at 70 °C for approximately 1 hour to remove the water in it. The coconut shell charcoal catalyst formed is solid and black as shown in Figure 2.

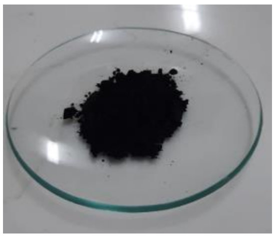

Figure 2. Coconut Shell Charcoal Catalyst

The coconut shell charcoal catalyst formed is a heterogeneous acid catalyst. Sulfonation makes the catalyst insoluble in acids and bases and easily separated when used to catalyze reactions to reuse it. A sulfonated carbon catalyst has a stable carbon group so that it does not dissolve in acidic or basic conditions (Kang et al., 2013).

Characterization of Coconut Shell Acid Catalyst

Coconut shell charcoal acid catalyst was characterized by X-ray diffraction (XRD). Diffractogram results were compared or matched with standard data on the tool to obtain the crystal structure. The coconut shell charcoal catalyst was also characterized by a Scanning Electron Microscope (SEM) to observe its surface morphology. In addition, FTIR analysis was carried out to determine the functional groups and bond interactions in the catalyst formed. The results obtained in the form of diffractograms are presented in Figure 3.

Diffractogram results of HCl-activated coconut shell charcoal and sulfonation show diffraction peaks with high intensity at 2θ = 10º-30º. In coconut shell charcoal without activation, diffraction peaks appear at 2θ = 15º. The diffraction pattern with a broadened peak indicates that the carbon present in coconut shell

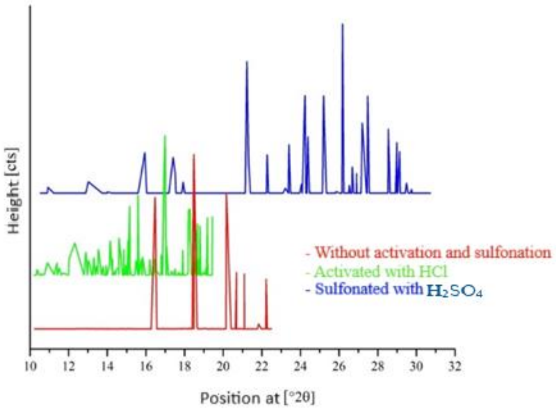

Figure 3. Difractogram of Coconut Shell Charcoal Catalyst

charcoal is amorphous. According to da Luz Corrêa et al. (2020), the diffraction peak that appears at 2θ = 15°-30° is the C of the amorphous carbon structure containing randomly oriented aromatic carbon sheets. In coconut shell charcoal that has been activated with HCl, it can be seen that the intensity of the diffraction peaks at 2θ = 10°-30° starts to decrease, and peaks appear at 2θ = 12.32°, 13.54°, 15.16°, and 16.99°. The decreasing diffraction peaks indicate the irregularity of the carbon structure due to HCl entering the active charcoal structure, causing damage to the bonds in the carbon sheet. This result is based on da Luz Corrêa et al. (2020), who reported that a decrease in the intensity of the widened peak can weaken the carbon sheet due to bond breaking so that it can increase the irregularity of the carbon structure.

The sulfonated coconut shell charcoal catalyst has a decreasing intensity at the diffraction peak of 2θ = 10º-30º, and a peak with the highest intensity appears at 2θ = 26.17º. This number shows that the carbon sheets are weakening their bonds and experiencing bond breakage to form a graphite crystal structure. Based on JCPDS 41-1487, the diffraction peak at 2θ = 26.0° is designated as graphite-structured carbon (002) from the hexagonal graphite diffraction plane.

Comparison of diffractograms between coconut shell charcoal without activation and sulfonation with HCl-activated coconut shell charcoal and then sulfonated resulted in widened diffraction peaks whose intensity decreased. New single peaks appeared, which shifted to larger 2θ° values. New diffraction peaks that appear after catalyst activation are caused by impurities that the activator has dissolved due to the activation process. The dissolution of impurities will open pores on the surface of coconut shell charcoal (Pranoto et al., 2020). The results of characterization with XRD show that the activation and sulfonation process has occurred, and charcoal with a different structure from arranging has been produced without activation and sulfonation. Increasingly irregular diffraction peaks indicate this condition.

The coconut shell charcoal catalyst was also characterized by a Scanning Electron Microscope (SEM) to observe its surface morphology and the pores formed. The results of the surface morphology of coconut shell charcoal catalyst (a), activated coconut shell charcoal (b), and activated and sulfonated coconut shell charcoal (c) are presented in Figure 4.

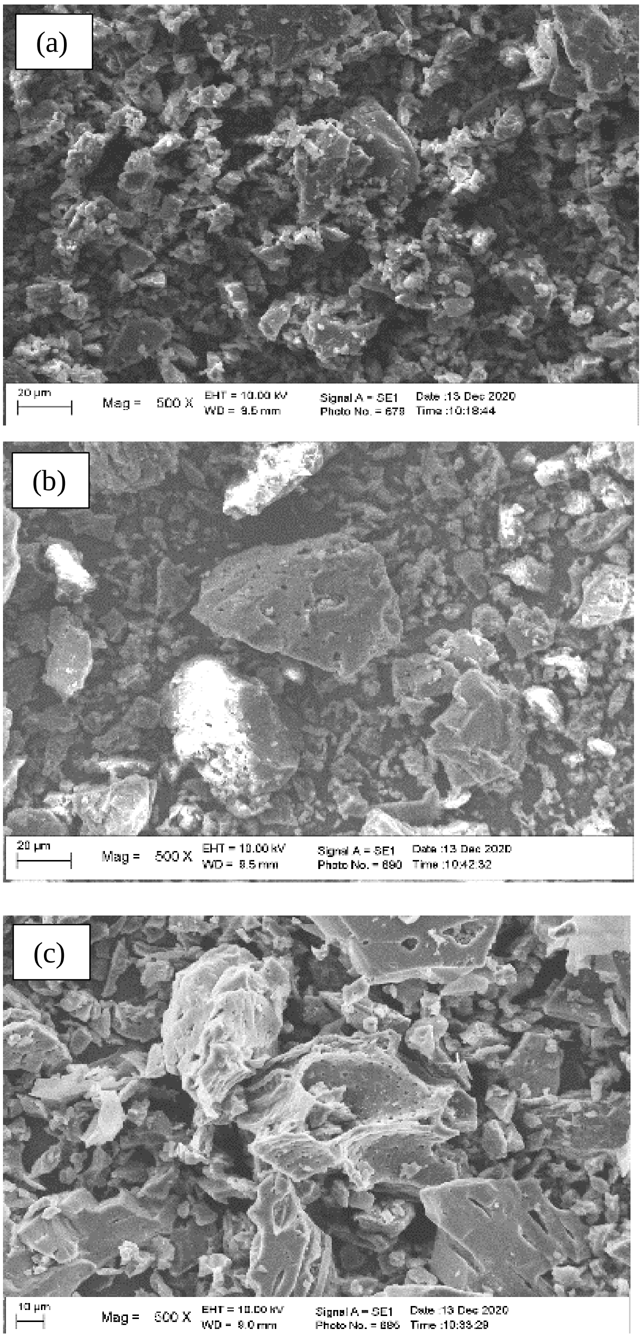

Figure 4. Morphology of (a) Coconut Shell Charcoal, (b) Activated Coconut Shell Charcoal, and (c) Activated and Sulfonated Coconut Shell Charcoal

Figure 4 shows differences in the surface pore morphology of the three types of coconut shell charcoal characterized using SEM. In Figure 4 (a), the results of the surface morphology of coconut shell charcoal formed regular clumps with less clearly visible pores. This is due to impurities on the surface of the charcoal that is not activated. Coconut shell charcoal activated with HCl in Figure 4. (b) has a variety of shapes, regular and irregular. Small pores are increasingly visible on the surface. Figure 4. (c) shows that HCl-activated coconut shell charcoal, then sulfonated, has a sheet-like morphology. The surface pores are more clearly visible with a larger size and more in number when compared to the other two charcoals.

Activated charcoal with HCl has a larger pore morphology than activated charcoal without activation. This is because the pores of charcoal, without activation, are still mostly covered by hydrogen and other organic compounds whose components consist of ash, water, nitrogen, and sulfur (Verayana et al., 2018). The pores found in activated carbon can increase the ability to adsorb adsorbates because the pore is a gap that expands the surface of activated carbon. The activation stage produces a broad outer surface with sufficient pores. The visible pores indicate the activation process of activated charcoal has been successful (Bakti & Gareso, 2018). Carbonization and activation cause volatile compounds to disappear resulting in a fixed carbon mass with a widening of the pore network present in the activated carbon sample. This result is in line with research (Safariyanti et al., 2018) which shows that the effect of activation on carbon causes the number of pores on the surface of the carbon to increase, which creates a lot of space on the surface of the carbon, causing the surface area of the carbon to become large.

Figure 4. (b), shows that activated charcoal that has not been sulfonated has a pore surface with small voids. The small cavity size is caused by the previous activation process that is less than optimal, so that the pore opening process is not perfect. The pore size will affect the amount of H_2SO_4 absorbed in the sulfonation process.

In Figure 4. (c), it can be seen that the surface structure of coconut shell charcoal that has been sulfonated has more open pores compared to coconut shell charcoal and activated coconut shell charcoal. Sulfonation can damage the catalyst's pore structure so that the catalyst's surface area will be reduced. Large catalyst pores will cause reactants to diffuse more easily to the inside of the catalyst. This can lead to more intensive contact between the reactants and the acid center of the catalyst, and the catalyst will produce better activity (Kang et al., 2013)

The more open surface morphological structure allows reactants to enter the catalyst surface so that it is expected to interact with H^+ groups bound to the catalyst surface (Amelia et al., 2019). The sulfonation process affects not only the sulfonic acid site but also the oxygenated acid site. The $-SO_3H$ group is expressed as the main catalytically active site of sulfonation results, and the carboxyl group also increases the inherent activity of the $-SO_3H$ group, resulting in esterification (da Luz Corrêa et al., 2020). Thus, increasing the number of sulfonated coconut shell charcoal pores can increase the surface area and active groups of hydroxyl (-OH) and carboxyl (-COOH). This causes these active groups to interact with the adsorbate when acting as a catalyst (Pranoto et al. 2020). The results of catalyst characterization with SEM showed the success of activation and sulfonation, which increased the number of pores and pore size.

The coconut shell charcoal catalyst was characterized using FTIR to determine the functional groups in the catalyst that can be used as active groups in the catalytic process. The results of the FTIR spectra of the coconut shell charcoal acid catalyst formed from sulfonation results compared to those of coconut shell charcoal and activated coconut shell charcoal are presented in Figure 5.

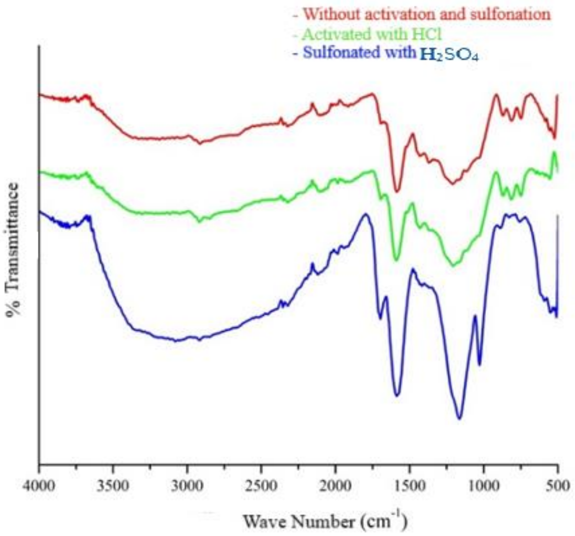

Figure 5. FTIR spectra of coconut shell charcoal catalysts

The FTIR spectra of coconut shell charcoal in Figure 5, which is colored red, show vibrations at wave number 3187.97 cm^{-1}, which are vibrations of aromatic groups (C-H), indicating the presence of alkane and alkene compounds. The vibration that appears at wave number 2913.29 cm^{-1} is the vibration of C-H methylene (-CH_2-). Vibrations at wave number 1692.77 cm^{-1} are vibrations of carbonyl compounds in the form of conjugated ketones. Vibration at wave number 1585.53 cm^{-1} appears C-C absorption on the aromatic ring. Vibrations at wave number 1208.61 cm^{-1} are vibrations of stretching C-O phenol, and at wave number 1369.85 cm^{-1}, methyl vibrations (-CH_3) appear.

In Figure 5, the green spectra show the FTIR spectra of coconut shell charcoal activated with HCl. The comparison with the FTIR spectra of coconut shell charcoal shows that in the FTIR spectra of activated coconut shell charcoal, vibrations at wave number 1369.85 cm^{-1} do not appear, which is the vibration of methyl (-CH_3), and an increase in the intensity of vibrations at wave number 1693.45 cm^{-1} which is the vibration of carbonyl compounds in the form of conjugated ketones. In addition, vibrations also appear at wave number 3305.04 cm$^{-1,}$ which is the vibration of the -OH hydroxyl group. The disappearance of the -CH_3 group on the activated carbon is in line with the study of Bakti & Gareso (2018) because in the carbon activation process, there is evaporation of volatile compounds.

In Figure 5, the blue spectra show the FTIR spectra of sulfonated coconut shell charcoal compared to the FTIR spectra of activated coconut shell charcoal, showing that the FTIR spectra of sulfonated coconut shell charcoal disappear at wave number 2913.29 cm^{-1} which is the vibration of C-H methylene (-CH_2-) and also at wave number 1429.88 cm^{-1} which is the bending vibration of C-H methyl group. Sulfonated coconut shell charcoal increases the intensity of vibrations at wave number 1693.45 cm$^{-1,}$ which is the vibration of carbonyl compounds in the form of conjugated ketones, and vibrations appear at wave number 1028.59 cm-1, which is the vibration of sulfonate functional groups. The vibrations on the sulfonate functional group indicate that the sulfonation reaction of coconut shell charcoal has been successfully carried out. This result aligns with research (da Luz Corrêa et al., 2020) that the sulfonated catalyst was identified from the vibration at 1032 cm^{-1} wavelength, which is the stretching of the O=S=O group of the sulfonate group. Similar results were reported by (Hu et al., 2015) that the vibrations associated with the O=S=O and SO_3H groups appear at a wave number of 1038 cm^{-1} (Hidayat et al., 2015) reported the presence of SO3H groups on the sulfonated activated carbon catalyst characterized by the appearance of a peak at 1040 cm^{-1} which is a symmetrical stretching vibration of S=O.

Upgrading Bio-Oil Through Bio-Oil Esterification

Esterification of bio-oil is carried out using coconut shell acid catalyst and the addition of methanol, which is then heated at 60 ºC. Esterification is basically useful for removing carboxylic acids from bio-oil to form esters (Panwar & Paul, 2021).

Catalysts in the esterification process are useful for accelerating the reaction process. Solid acid catalysts are used in this study because solid acid catalysts produce H+, which forms monomolecular carboxyation with oxygen on the carbonyl group in the acid structure. Then, the hydroxyl group on methanol attacks the carbonyl group on oleic acid, resulting in a nucleophilic addition reaction. The intermediates obtained are highly unstable. After a reversible rearrangement stage, the water molecule is lost as a leaving group, and finally methyl oleate is formed. (Lu et al., 2019).

This study was conducted by adding methanol solvent into bio-oil to help homogenize, prevent phase separation, and increase the rate of esterification reaction. In the esterification reaction mechanism, the strong acidic nature of the -SO3H group makes the protonation of methanol molecules difficult. However, when a weak acidic group -COOH is added to methanol, the deprotonated form of -COOH can generate hydrogen bonds with the -OH group in the methanol molecule, giving a fraction of the negative charge to the oxygen in the methanol molecule. Furthermore, the negative charge increases the Nucleophilicity of the methanol molecule and thus positively affects the reaction rate and conversion of esterification (da Luz Corrêa et al., 2020).

The addition of methanol can also affect the chemical properties of the bio-oil produced. Bio-oil consists of highly active oxygen-containing compounds, and the high viscosity can hinder the application of bio-oil as a fuel. Bio-oil viscosity generally increases over time due to condensation and polymerization of the water-soluble fraction. Adding solvents such as methanol to bio-oil helps in homogenization by preventing phase separation, lowering the viscosity and density, and increasing the higher heating value of Bio-oil (Panwar & Paul, 2021). (Oasmaa et al., 2004) She has conducted research on the addition of methanol, ethanol, and isopropanol to bio-oil. Methanol was the most effective in reducing the viscosity and increasing the stability of Bio-oil. Adding methanol to Bio-oil reduces viscosity by decreasing polymerization and aging reactions.

Bio-oil quality improvement (upgrading) is done through bio-oil esterification reactions with a volume of 250 mL, producing 16 mL of upgraded bio-oil. Bio-oil yield from esterification at 60º for 90 minutes using coconut shell charcoal acid catalyst was calculated using the equation reported by Li et al. (2018) and obtained at 6.4%. This result is not much different compared to the results from (da Luz Corrêa et al., 2020), which showed that the yield of bio-oil esterification using a sulfonated acid catalyst was 7.3%. Research results by Sondakh et al. (2019) Bio-oil yield from esterification at 60º for 240 minutes using commercial acid catalysts in sulfuric acid and hydrochloric acid was more than 70%. The difference in reaction time can be one of the reasons for the difference in the results of this study; Sondakh conducted an esterification reaction for up to 240 minutes, while this study was only 90 minutes.

Figure 6. Color of Bio-oil Before Upgrade (Right) and After Upgrade (Left)

Physical and Chemical Characteristics of Bio-oil

Bio-oil before and after upgrading was analyzed for chemical-physical properties such as color, density, kinematic viscosity, heating value, moisture content, pH, ash content, acid number, chemical composition, and metal content. The results of chemical-physical properties such as color, density, kinematic viscosity, heating value, moisture content, pH, ash content, and acid number are presented in Table 1.

Table 1. Physical and Chemical Characteristics of Bio-oil

Characteristics	Value Limit (ASTM D7544)	Method	*Bio-oil*	*Bio-oil Upgraded*
Color	-	-	Dark brown	Light brown
Density 20° Kg/dm^3	1.1 – 1.3	ASTM D 4052	1.052	0.945
Kinematic viscosity 40°C, mm^2/s (cSt)	125 max	ASTM D 445	1.475	0.968
Caloric MJ/kg	15 min	ASTM D 240	5.481	19.376
Water content %	30 max	ASTM E 203	35.11	27.21
pH	-	ASTM E70	2.706	4.042
Ash content %	0.25 max	ASTM 482	4.31	3.59
Acid number	0.8	FBI-A01-03	57.75	23.95

The results of the comparison of bio-oil characteristics before and after upgrading showed a decrease in viscosity, kinematic viscosity, moisture content, ash content, and acid number, as well as an increase in calorific value and pH.

Bio-oil Composition Identification by GCMS

GCMS was used to identify the composition of Bio-oil compounds before and after upgrading. The results of GCMS analysis of bio-oil are presented in Table 2.

Table 2: GCMS Analysis Results of Bio-oil

Senyawa	Kandungan (%)	
	Bio oil awal	Bio-oil *upgrade*
Sulfur dioksida	-	1,4
2-propanone, 1-hydroxy	1,23	2,51
1-hydroxy-2-butanone	-	1,34
Asam asetat	56,25	21,28
Butanoic acid, 2-propenyl ester	-	1,5
L-Serine, O-methyl-, methyl ester	-	1,15
2-Cyclopenten-1-one, 2hydroxy-3-methyl	-	1,84
Phenol, 2-methoxy	2,91	5,23
Creosol	1,1	1,54
Phenol	23,73	39,15
Phenol, 4-ethyl-2methoxyphenol	-	1,1
p-Creosol	-	1,36
Phenol, 2,6-dimethoxyphenol	-	6,23
propanoic acid, 2-methyl-, 2-methylpropyl ester	1,24	1,27
3,5-Dimethoxy-4-hydroxytoluene	-	1,35
Gallacetopenone, 4'-methylether	-	1,2
n-Hexadecanoid acid	-	1,51
6-Octadecenooic acid	-	4,36
Methyl isocyanide	1,28	-

GCMS analysis results in Table 2 detected seven bio-oil compounds, mostly acetic acid and phenol compounds. The results of bio-oil upgrading detected 18 compounds that had a decreasing acetic acid content while the phenol content increased. The compounds detected in the bio-oil upgrading results include 1-hydroxy-2-butanone, 2-cyclopentene-1-on, and 2-hydroxy-3-methyl, including ketone compounds; butanoic acid, 2-propenyl ester and L-Serine, O-methyl-, methyl ester including ester compounds; phenol, 4-ethyl-2 methoxyphenyl, phenol, and 2,6-dimethoxy phenol belong to the phenol compound group; p-Creosol belongs to the ether group; 3,5-dimethoxy-4-hydroxytoluene and galaacetophenone belong to the ketone compound group; 4'-methylether belongs to the ether compound group; and 6-octadecanoic acid belongs to the carboxylic acid compound group. The results show that the main compounds in bio-oil that have been upgraded are ether, ester, ketone, phenol, alcohol, and carboxylic acids. These results align with research (Sondakh et al., 2019) that shows the main chemical compounds in upgraded bio-oil are esters, ethers, ketones, phenols, and alcohols.

Esterification reactions are generally reactions between carboxylic compounds using alcohol to produce esters. The decrease in the content of acetic acid compounds between bio-oil before and after upgrading and the identification of several ester compounds indicate that esterification reactions have occurred in the bio-oil upgrading process using coconut shell charcoal acid catalyst.

Bio-oil Metal Content

The metal content in bio-oil was analyzed by ICP-OES and is presented in Table 3. The results of this study show that bio-oil contains metals Ca, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ini, Si, Sn, Ti, V, Zn, Ag, Al, and Ba. The highest levels of metals are Ca, Zn, and Mo, respectively. Upgrading bio-oil causes a decrease in metal content.

Table 3. Metal Content in Bio-oil

Metal	*Bio-oil* (mg/L)	*Bio-oil upgrade* (mg/L)
Ca	73.6	71.17
Cr	0.22	0.14
Cu	0.25	0.23
Fe	3.1	2.94
Mg	1.27	1.01
Mn	0.17	0.52
Mo	4.49	0.27
Na	3.3	4.97
Ni	0.3	0.21
Si	1.34	1.75
Sn	3.94	1.21
Ti	0.07	0.07
V	1.03	0.66
Zn	28.16	24.71
Ag	0.16	0.76
Al	0.22	4.46
Ba	0.26	0.27

The research held by Saravana et al. (2020) about bio-oil from pyrolysis contains metals Mg, Ini, Ca, Na, K, Ag, and P, where the largest metal content is Na, Ca, then Mg in a row from the largest. The amount of metal content affects the bio-oil yield. The higher the metal content, the lower the bio-oil yield. This is explained by Chouhan and Sarma (2013) that higher bio-oil yields in bio-oils with lower biomass ash content will be obtained. Higher amounts of alkali and other metals such as Na, K, Ca, and Mg resulted in higher ash content and decreased bio-oil yield.

CONCLUSION

The characterization results show that the carbon-based solid catalyst formed by the coconut shell has a graphite crystal structure with dense and porous surfaces. The catalyst contains sulfonate groups, indicating that the sulfonation reaction of coconut shell charcoal was successful. The bio-oil yield from upgrading through an esterification reaction using a carbon-based solid catalyst from coconut shells is 6.4%. The comparison of bio-oil characteristics before and after upgrading using a carbon-based solid catalyst from coconut shell showed a decrease in kinematic viscosity, water content, ash content, acid number, and an increase in calorific value and pH. The main compounds in the upgraded bio-oil were ether, ester, ketone, phenol, alcohol, and carboxylic acid. The largest metal contents are Na, Ca, and then Mg in a row from the largest, and the levels decrease after upgrading the bio-oil.

REFERENCES

Adriati, M., Suseno, A., & Taslimah, T. (2013). Modifikasi Zeolit Alam Menggunakan Besi (Fe) dan Kobalt (Co) untuk Katalis Degradasi Fenol. *Jurnal Kimia Sains Dan Aplikasi*, *16*(1), 1.

Alfiany, H., Bahri, S., & N. (2013). Kajian Penggunaan Arang Aktif Tongkol Jagung sebagai Adsorben Logam Pb dengan Beberapa Aktivator Alam. *Jurnal Natural Science*, *2*(3), 75–86.

Amelia, R., Pandapotan, H., & Purwanto. (2019). Pembuatan Dan Karakterisasi Katalis Karbon Aktif Tersulfonasi Sebagai Katalis Ramah Lingkungan Pada Proses Hidrolisis Biomassa. *Jurnal Teknologi Kimia Dan Industri*, *2*(4), 146–156.

Bakti, A. I., & Gareso, P. L. (2018). Characterization of Active Carbon Prepared from Coconuts Shells using FTIR, XRD and SEM Techniques. *Jurnal Ilmiah Pendidikan Fisika Al-Biruni*, *7*(1), 33–39.

Sasikumar, C., Sundaresan, R., Nagaraja, M., Shankar MS, & Karthikeyan, S. (2019). Bio-Oil from Coconut Shells. *International Journal of Recent Technology and Engineering (IJRTE)*, *8*(4), 657–659.

Chouhan, A., & Sarma, A. (2013). Critical Analysis of Process Parameters for Bio-oil Production via Pyrolysis of Biomass: A Review. *Recent Patents on Engineering*, *7*(2), 98–114.

da Luz Corrêa, A. P., Bastos, R. R. C., Rocha Filho, G. N. da, Zamian, J. R., & Conceição, L. R. V. da. (2020). Preparation of sulfonated carbon-based catalysts from murumuru kernel shell and their performance in the esterification reaction. *RSC Advances*, *10*(34), 20245–20256.

Fardhyanti, D. S., Chafidz, A., Triwibowo, B., Prasetiawan, H., Cahyani, N. N., & Andriyani, S. (2020). Improving the Quality of Bio-Oil Produced from Rice Husk Pyrolysis by Extraction of its Phenolic Compounds. *Jurnal Bahan Alam Terbarukan*, *8*(2), 90–100.

Fardhyanti, D. S., Megawati, Kurniawan, C., Sigit Lestari, R. A., & Triwibowo, B. (2018). Producing Bio-Oil from Coconut Shell by Fast Pyrolysis Processing. *MATEC Web of Conferences*, *237*, 0–4.

Hidayat, A., Rochmadi, Wijaya, K., & Budiman, A. (2015). Esterification of Free Fatty Acid on Palm Fatty Acid Distillate using Activated Carbon Catalysts Generated from Coconut Shell. *Procedia Chemistry*, *16*, 365–371.

Hu, L., Lin, L., Wu, Z., Zhou, S., & Liu, S. (2015). Chemocatalytic hydrolysis of cellulose into glucose over solid acid catalysts. *Applied Catalysis B: Environmental*, *174–175*, 225–243.

Kang, S., Ye, J., & Chang, J. (2013). Recent Advances in Carbon-Based Sulfonated Catalyst Preparation and Application. *Internatioal Review of Chemical Engineering*, *5*(2), 133–144.

Kartika, V., Ratnawulan, & G. (2016). Karbon Aktif Kulit Singkong sebagai Bahan Dasar GDL (Gas Diffusion Layer). *Pillar of Physics*, *7*(April), 105–112.

Kauwo, F. A. G., Anom, I. D. K., & Lombok, J. Z. (2021). Pyrolysis Reaction Kinetics of Styrofoam Plastic Waste. *Indo. J. Chem. Res.*, *9*(1), 57–62.

Lee, H., Kim, Y.-M., Lee, I.-G., Jeon, J.-K., Jung, S.-C., Chung, J., Choi, W., & Park, Y.-K. (2016). Recent advances in the catalytic hydrodeoxygenation of bio-oil. *Korean Journal of Chemical Engineering*, *33*.

Li, J., Lv, X., Wang, Y., Li, Q., & Hu, C. (2018). Hydrotreatment Upgrading of Bio-oil from Torrefaction of Pubescens in Alcohol over Pd/NbOPO4. *ACS Omega*, *3*(5), 4836–4846.

Lombok, J. Z., & Anom, I. D. K. (2023). Characterization and Identification Compounds of Liquid Smoke from Used Tire Waste Pyrolysis. *Indo. J. Chem. Res.*, *11*(1), 15–22.

Lu, P., Wang, K., & Gong, J. (2019). Optimization of salix carbonation solid acid catalysts for one-step synthesis by response surface method. *Applied Sciences (Switzerland)*, *9*(8).

Nurdin, A., Iriani, I., Harahap, H., & Fahmi, A. (2022). Production Process of Large Pore Size Activated Carbon from Palm Kernel Shell using Sodium Chloride as An Activator. *Indo. J. Chem. Res.*, *10*(1), 8–13.

Oasmaa, A., Kuoppala, E., Selin, J. F., Gust, S., & Solantausta, Y. (2004). Fast Pyrolisis of Forestry Residue and Pine for Improvement of The Product Quality by Solvent Addition. *Energy and Fuels*, *18*(5), 1578–1583.

Panwar, N. L., & Paul, A. S. (2021). An overview of recent development in bio-oil upgrading and separation techniques. *Environmental Engineering Research*, *26*(5), 0–1.

Pranoto, P., Martini, T., & Maharditya, W. (2020). Uji Efektivitas dan Karakterisasi Komposit Tanah Andisol/Arang Tempurung Kelapa Untuk Adsorpsi Logam Berat Besi (Fe). *ALCHEMY Jurnal Penelitian Kimia*, *16*(1), 50.

Sa’diyah, K., Rohman, F., Harsanti, W., Nugraha, I., & Febrianto, N. A. (2018). Pyrolysis of Coconut Coir and Shell as Alternative Energy Source. *Jurnal Bahan Alam Terbarukan*, *7*(2), 115–120.

Safariyanti, S. J., Rahmalia, W., & Shofiyani, A. (2018). Sintesis dan Karakteristik Karbon Aktif dari Tempurung Buah Nipah (Nypa fruticans) Menggunakan Aktivator Asam Klorida. *Jurnal Kimia Khatulistiwa*, *7*(2), 41–46.

Saravana Sathiya Prabhahar, R., Nagaraj, P., & Jeyasubramanian, K. (2020). Promotion of bio oil, H2 gas from the pyrolysis of rice husk assisted with nano silver catalyst and utilization of bio oil blend in CI engine. *International Journal of Hydrogen Energy*, *45*(33), 16355–16371.

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*(1).

Sutrisno, B., & Hidayat, A. (2016). Upgrading of bio-oil from The Pyrolisis of Biomass Over the Rice Husk Ash Catalysts. *IOP Conference Series : Materials Science and Engineering*, *162*(1), 8–15.

Verayana, Ppautungan, M., & Iyabu, H. (2018). Pengaruh Aktivator HCl dan H3PO4 terhadap Karakteristik (Morfologi Pori) Arang Aktif Tempurung Kelapa serta Uji Adsorpsi pada Logam Timbal. *Jurnal Entropi*, *13*(1), 67–75.