

Hydrotreatment of Cellulose-Derived Bio-Oil Using Copper and/or Zinc Catalysts Supported on Mesoporous Silica-Alumina Synthesized from Lapindo Mud and Catfish Bone

Fahri Swasdika, Wega Trisunaryanti*, and Iip Izul Falah

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Sekip Utara, Yogyakarta 55281, Indonesia

* **Corresponding author:**

email: wegats@ugm.ac.id

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Abstract: Catalysts comprising copper and/or zinc supported on mesoporous silica-alumina (MSA) with a high Si/Al ratio were prepared by wet impregnation method. This study investigated the preparation, characterization, and catalytic application of the prepared catalysts for hydrotreatment of cellulose-derived bio-oil. The wet impregnation was performed by dispersing $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and/or $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ aqueous solution into MSA, followed by calcination and reduction under H_2 gas stream. The acidity test revealed that metal addition on MSA support increases the acidity of catalysts. During hydrotreatment of cellulose-derived bio-oil CuZn/MSA with total acidity, copper loading, zinc loading, and specific surface area of $24.86 \text{ mmol g}^{-1}$, 5.23 wt.%, 3.15 wt.%, and $170.77 \text{ m}^2 \text{ g}^{-1}$, respectively, exhibited the best performance compared to other prepared catalysts with 90.49 wt.% conversion of liquid product.

Keywords: hydrotreatment; bio-oil; catalysis; bifunctional catalyst; mesoporous silica-alumina

■ INTRODUCTION

Lignocellulose biomass is a promising alternative source of petroleum for fuels and chemicals production due to its abundance, non-edible, and relatively low cost [1]. It mainly consists of cellulose (40–60 wt.%), hemicellulose (15–30 wt.%), and lignin (10–25 wt.%) [2]. It could be converted to fuels via a thermochemical process such as pyrolysis. Pyrolysis of biomass usually involves a thermal decomposition of organic materials under an inert atmosphere. Products of biomass pyrolysis mainly consist of bio-oil, char, and gases. Bio-oil produced by biomass pyrolysis has demonstrated as a suitable fuel for heat generation in boiler systems and power generation in some diesel engines [3-4]. However, the produced bio-oil is unusable in internal combustion engines due to its high oxygen content, low heating value, and high acidity [5]. Therefore, an upgrading process to improve the quality of bio-oil is needed.

One of the commonly employed methods for bio-oil upgrading is a hydrotreatment [6-7]. This method

selectively removes oxygen from bio-oil through a catalytic reaction using hydrogen in the presence of a heterogeneous catalyst. Conventional hydrotreating catalysts such as sulfided NiMo and CoMo have been widely used for upgrading bio-oil. However, the sulfided catalysts have problems with sulfur usage and product contamination [8]. Pt-based catalysts have been considered as alternatives due to their high activity for hydrotreatment of bio-oil [9-10]. However, scarcity and the high price of noble metals are the main problems for industrial-scale applications [7]. Other transition metals such as Cu and Zn have attracted considerable attention as hydrotreatment catalysts due to their unique performance in the hydrogenation of esters to alcohol [11-13] and CO_2 [14-15]. However, there is a limited report of Cu-Zn based catalysts for hydrotreatment of bio-oil. The previous study showed that the catalyst containing Cu and Zn metals have good activity in the conversion of cyclic esters into hydrocarbon [16].

Copper-based catalysts exhibit excellent catalytic performance for hydrogenation of esters to alcohols

because they can catalyze selective hydrogenation of carbon-oxygen bonds and are relatively inactive for carbon-carbon bond hydrogenolysis [17]. Copper by itself is usually not active enough, resistant to sintering, nor mechanically stable enough for industrial use [11]. Therefore, promoters such as Zn are needed to improve it. The presence of Zn can promote the dispersion of Cu particles and enhance the reducibility of the copper oxide phase [12].

In a heterogeneous catalyst, a catalyst support also plays an important role in improving the efficiency of hydrotreatment processes. Because the hydrotreatment of aromatics and/or oxygen-containing compounds over bifunctional catalysts involves (de)hydrogenation on metallic centers and isomerization/cracking on acid centers [18]. Porous materials such as zeolite have been widely used as catalyst or catalyst support in the industry due to its unique characteristics such as high surface area, acidity, and thermal stability [19]. However, the application of zeolite is limited to small molecules due to its microporosity. Therefore, porous material with a relatively larger pore would be necessary. Mesoporous silica-alumina (MSA) has received great attention for replacing zeolite as support [9,20-21]. The MSA as catalyst support can be successfully synthesized from natural resources such as Lapindo mud and catfish bone gelatin [22-23]. The high content of Si and Al in Lapindo mud makes great attention to utilize Lapindo mud as a source to produce Si and Al precursor [22-24]. Catfish bone constitutes one of the primary waste associated with industry by-products and is considered as a raw material for gelatin production. Meanwhile, gelatin can be used as an organic template due to its high content of N-H groups which tend to strongly interact with xylanol (Si-OH) group on the silicate species via multiple hydrogen bonding. However, research on the use of gelatin from catfish bone as a template for synthesis of MSA is still rare. Moreover, the utilization of natural resources in the manufacture of MSA may reduce the production cost.

In the present work, the MSA with a high Si/Al molar ratio was synthesized using precursor derived from Lapindo mud and catfish bone. Lapindo mud was used as the source to produce Si and Al precursors, while the

catfish bone was used as the source to produce gelatin as the template precursor. The MSA was used as a support material of copper and/or zinc metals as catalysts for hydrotreatment of bio-oil. α -Cellulose was used as a model of biomass.

■ EXPERIMENTAL SECTION

Materials

Catfish bone waste was collected from Tegalorejo Village, Central Java, Indonesia. Lapindo mud was collected from Sidoarjo Regency, East Java, Indonesia. Hydrochloric acid (HCl 37%) was purchased from Mallinckrodt. Copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, purity 99%), zinc nitrate tetrahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, purity 98.5%), ammonia (NH_3 25%) and sodium hydroxide (NaOH, purity 99%) were purchased from Merck. α -Cellulose was purchased from Sigma-Aldrich. Hydrogen (H_2) and nitrogen (N_2) gas were supplied by PT. Samator Ltd.

Procedure

Extraction of silica and alumina from Lapindo mud

Silica (SiO_2) and alumina (Al_2O_3) extraction had been conducted by the following procedure. The Lapindo mud was dried and sieved up to 100 mesh. 100 g of dried mud was refluxed in 400 mL of 6.0 M HCl (1:4, w/v) at 90 °C and kept under magnetic stirring for 5 h. The Al ions and other soluble metals would be dissolved in the HCl solution. Therefore, it will treat further by adding 150 mL of 6.0 M NaOH (2:3, v/v) up to pH of 8.0, then filtrated to remove the unneeded metals. The Al ions were then precipitated by injecting CO_2 gas into the filtrate. The precipitate was filtered, followed by washing using demineralized water. The slurry was dried at 50 °C and then calcined at 500 °C for 5 h to obtain Al_2O_3 material. Meanwhile, the silica was extracted from Lapindo mud by refluxing the mud residue of aluminium extraction in 400 mL of 6.0 M NaOH (1:4, w/v) at 90 °C and kept this under magnetic stirring for 5 h. The filtrate was then treated by adding a 2.0 M HCl solution to give the solution with a pH of 8. The precipitate was filtered followed by washing using demineralized water. The slurry was dried at 100 °C to obtain solid SiO_2 material.

The chemical composition of silica and alumina was then analyzed using X-Ray Fluorescence (XRF, PANalytical Minipal4).

Extraction of gelatin from catfish bone

Gelatin extraction was carried out according to Marsuki et al. [22] and Kusumastuti et al. [23] with a slight modification. The extraction was prepared by immersing 100 g of catfish bone in 500 mL of 0.1 M NaOH solution (1:5 w/v) for 24 h to remove non-collagenous proteins, then washing with demineralized water to remove the remaining non-collagenous protein until the washed water reached neutral pH. The residue was then immersed with 500 mL of 1.5 M HCl solution (1:5 w/v) for 1 h for demineralization, followed by washing with demineralized water until the wash water reached neutral pH. To produce gelatin, the bone was refluxed with 400 mL of demineralized water (1:4 w/v) at 90 °C for 5 h then evaporated at 50 °C. The dry gelatin was characterized using Fourier Transform-Infrared (FT-IR, Thermo Nicolet iS10).

Preparation of mesoporous silica-alumina

In a typical synthesis of MSA, 0.017 g of alumina and 3.0 g of silica was dissolved in 80 mL of NaOH solution (molar ratio NaOH to (SiO₂ + Al₂O₃) of 1:1) under constant stirring at 40 °C. Meanwhile, 3.0 g of gelatin was dissolved in 80 mL of distilled water under constant stirring at 40 °C, and the solution was slowly added into the silica-alumina solution. Afterward, the mixture was adjusted to pH 10 using 1.0 M HCl solution while stirring process was kept for the next 1 h. The formed gel solution was transferred into an autoclave and hydrothermally treated at 100 °C for 24 h. The solid obtained from hydrothermal treatment was filtered, followed by washing with distilled water. The solid was dried at 80 °C for overnight. Finally, the solid was calcined at 550 °C for 5 h and the resulting solid was labeled as MSA. The MSA has a Si/Al molar ratio of 115.34 based on ICP-AES (Shimadzu ICPE-9820) analysis.

Metal impregnation on MSA

Copper and zinc metals were sequentially impregnated onto the prepared MSA by the wet impregnation method, in which Zn metal was firstly

loaded, followed by Cu metals. The mixture of MSA-salt solution was stirred for 24 h at room temperature and dried at 100 °C for overnight. The catalysts were calcined at 500 °C for 3 h under the N₂ gas stream, followed by a reduction under the H₂ gas stream at 450 °C for 3 h. The obtained catalyst was denoted as CuZn/MSA. Further, ZnCu/MSA (Cu metals was firstly loaded followed by Zn metals), Zn/MSA (only zinc metals), and Cu/MSA (only copper metals) catalysts were synthesized following the same method of synthesis CuZn/MSA.

Catalyst characterization

The acidity of the catalyst was determined using the gravimetric method, with NH₃ as the basic adsorbate. The crystallinity of the catalysts was characterized by X-ray diffractometry (XRD, Rigaku Miniflex 600) with CuK α irradiation ($\lambda = 0.154$ nm) in the 2θ range of 2–80°. Pore characteristics of the catalysts were analyzed using a gas sorption analyzer (GSA, Quantachrome Touchwin Series) and evaluated by Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) theories. The metal content of the catalysts was analyzed using an inductively coupled plasma atomic emission spectroscopy (ICP-AES, Shimadzu ICPE-9820). TEM images were determined by a JEOL-JEM-1400 microscope with an electron beam of 120 kV.

Hydrotreatment process

Cellulose was pyrolyzed at 600 °C for 2 h under the N₂ gas stream to produce bio-oil. The liquid product (bio-oil) obtained from the pyrolysis of cellulose was treated at 450 °C for 1 h under the H₂ gas stream in a semi-batch stainless steel reactor (id: 4.5 cm, od: 4.8 cm, length: 30 cm) using catalysts synthesized in this study. The catalyst to feed ratio was 1:30 (w/w). The yield percentage was calculated using Eq. (1), (2), and (3).

$$\text{Coke (wt.\%)} = \frac{W_{\text{coke}}}{W_{\text{feed}}} \times 100\% \quad (1)$$

$$\text{Liquid (wt.\%)} = \frac{W_{\text{liquid}}}{W_{\text{feed}}} \times 100\% \quad (2)$$

$$\text{Gas (wt.\%)} = [100 - \text{Liquid} - \text{Coke}] \% \quad (3)$$

The liquid products obtained from hydrotreatment bio-oil were characterized by using Gas Chromatography-Mass Spectroscopy (Shimadzu QP

2010 S). The percentage of the product was calculated using Eq. (4).

$$\text{Product} = (\% \text{ Area}) \times (\% \text{ Liquid}) \quad (4)$$

RESULTS AND DISCUSSION

Characterization of Catfish Bone Gelatin

The FT-IR spectrum of the catfish bone gelatin is presented in Fig. 1. Generally, the FT-IR spectrum of gelatin shows five characteristic polypeptide absorption bands called amide A, B, I, II, and III. Amide A observed at 3392 cm^{-1} corresponds to the stretching vibration of N-H group coupled with hydrogen bonding. A free N-H stretching vibration normally occurs in the range of $3400\text{--}3440 \text{ cm}^{-1}$. When the N-H group of a peptide is involved in a hydrogen bond, the position is shifted to lower frequencies [25]. Amide B was observed at 2939 cm^{-1} which corresponds to the asymmetric stretching vibrations of $=\text{C-H}$ as well as NH_3 [25-26].

Amide I which appears at 1652 cm^{-1} is mainly due to C=O stretching vibration coupled to CN contribution, CCN deformation, and in-plane bending modes [25]. The amide II band exhibited at 1537 cm^{-1} corresponds to an out of phase combination of C-N stretching vibration coupled to in-plane NH deformation modes of peptide group [25]. The amide III band at 1242 cm^{-1} represents the combination between CN stretching vibrations and NH deformation from the amide linkage as well as the absorptions arising from wagging vibrations of CH_2 groups [25-26]. Gelatin which contains a lot of NH groups

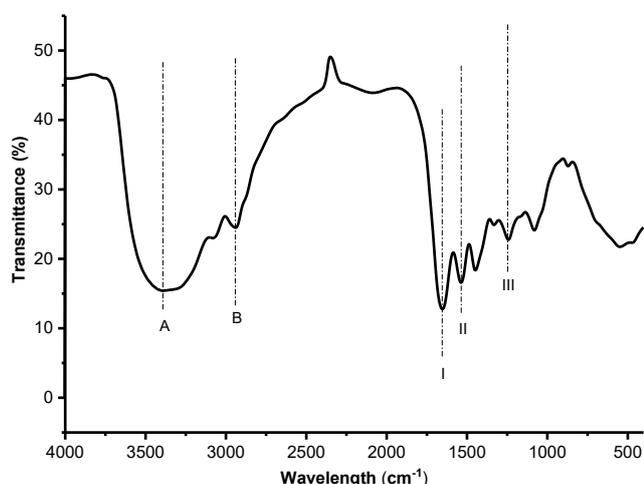


Fig 1. The spectrum of catfish bone gelatin

can be used as a template in preparation of MSA materials. These N-H groups tend to strongly interact with sylanol groups (Si-OH) via multiple hydrogen bonds [27].

Extraction of Silica and Alumina from Lapindo Mud

XRF analysis showed that Lapindo mud contains various kinds of metals such as Fe (36.90%), Si (35.10%), Al (11.00%), Ca (6.95%), K (3.52%), Ti (2.09%), S (1.10%), and others (3.34%). The high content of Si and Al in Lapindo mud makes it one of the resources that can be utilized to produce Si and Al. To produce them, the other metals should be removed by several chemical and physical steps, such as acid leaching and precipitation using an acid or alkaline followed by filtration. In the first step, acid extraction using hydrochloric acid was conducted to destroy the crystalline aluminosilicate phase to release free aluminium ions. Various metals could be dissolved at this condition such as Fe, therefore, the addition of 6.0 M NaOH could be used to remove them. Some impurities will be precipitated into $\text{M}(\text{OH})_n$, while Al remains dissolved in the solution. The Al ions can be precipitated by injecting CO_2 gas into the solution followed by filtration and washing using demineralized water to obtain alumina solid.

The silica was extracted from solid residue alumina extraction by refluxing the solid in 6.0 M NaOH. The silica will be reacted with NaOH to produce $\text{Na}_2\text{SiO}_3(\text{aq})$. The impurities will be removed in the solid residue. By adjusting the pH with the addition of HCl to pH of 8.0, silica could be obtained as the precipitate. In this study, the yield of alumina extraction is 10.83 wt.% with a purity of 84.5 wt.% based on XRF analysis. Meanwhile, the yield of silica extraction is 21.47 wt.% with a purity of 96.3 wt.% based on XRF analysis.

Characterization of MSA and Catalysts Prepared

Fig. 2 shows the FT-IR spectra of MSA before and after calcination. The spectra before calcination indicate the characteristics of the gelatin template. The bands observed around 1547 and 2949 cm^{-1} are corresponding to the amide II and B from the gelatin structure, respectively. This result is in agreement with the previous

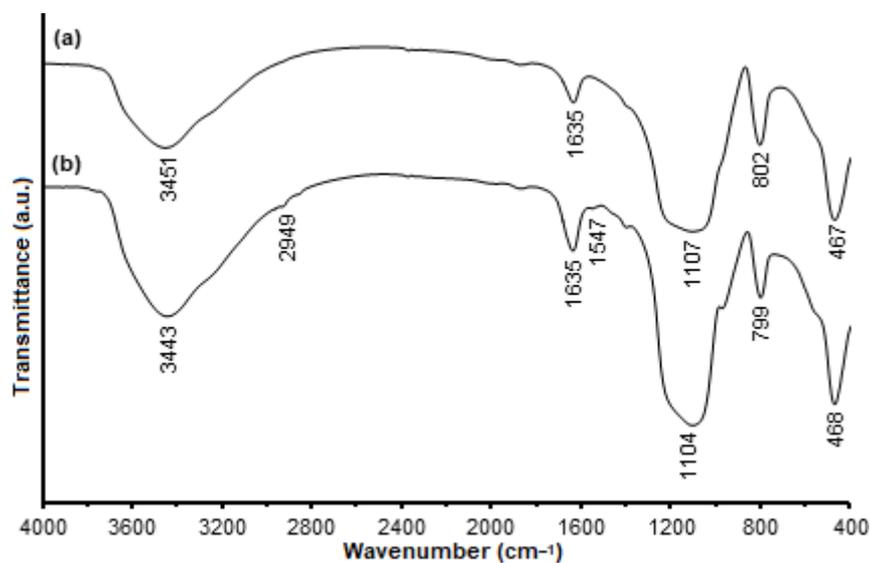


Fig 2. FT-IR spectra of MSA (a) before calcination and (b) after calcination

study that after hydrothermal MSA still contains gelatin [23]. In Fig. 2(b), the bands which correspond to gelatin were not observed. It is proven that the calcination process is effective to eliminate gelatin from the MSA framework. The characteristics of the silica-alumina material were observed in MSA material before calcination as well as after calcination. There are strong bands around at 1100 and 799, which correspond to stretching asymmetric, symmetric stretching of T-O, respectively [28]. The absorption band at 468 cm^{-1} refers to the bending vibration of T-O-T [29]. The band at 3400 cm^{-1} corresponds to OH stretching vibration bound to Si or Al, as well as the adsorbed H_2O molecule on the MSA surface [23]. The molecular vibration of water molecules is confirmed by the presence of an absorption band at 1635 cm^{-1} which corresponds to the bending vibration of O-H.

Fig. 3 shows the XRD patterns of the synthesized MSA and impregnated catalysts. It was observed that MSA is amorphous, as indicated by the single broad peak at 2θ of 21° that arises from the lack of an ordered crystalline structure [30]. The XRD patterns of modified MSA are also presented in Fig. 4. The XRD pattern of Cu/MSA shows peaks at 2θ of 36.2° due to the formation of CuO crystallite. In contrast, ZnCu/MSA and CuZn/MSA show a peak at 2θ of 36.0° indicating the presence of the ZnO phase together with the peaks at 2θ of

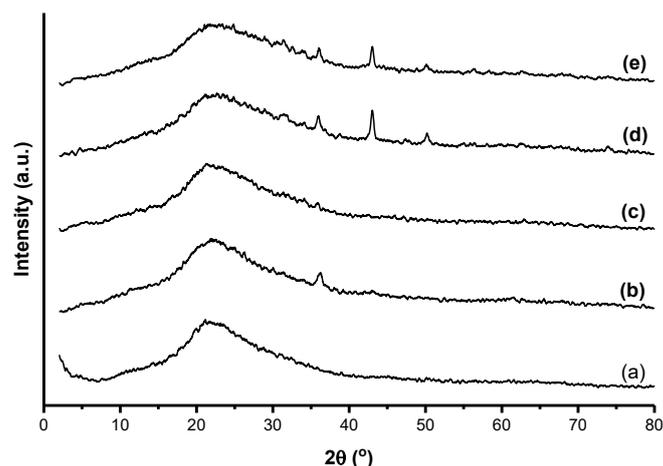


Fig 3. XRD pattern of (a) MSA, (b) Cu/MSA, (c) Zn/MSA, (d) ZnCu/MSA, and (e) CuZn/MSA

43.1 and 50.3° corresponding to the metallic Cu phase [31]. No diffraction of zinc species was found in Zn/MSA samples. This indicates that zinc species are well dispersed at the surface and/or in the channel of MSA [12,32]. The proposed structure of Cu and/or Zn supported on MSA was depicted in Fig. 4. MSA has unbalance charge due to the presence of Al atoms in the structure, therefore naturally it was neutralized with the cation such as Na, Ca, Mg, etc. In this case, the Zn and Cu cation was impregnated on the MSA structure and it can act to balance the charge by binding with the O atom closest to the Al atom.

in each metal act as Lewis acid, which contributes to the total acidity of the catalysts. Herein, it should be noted that CuZn/MSA exhibits higher acidity than other catalysts.

Fig. 7 shows the TEM micrograph of the MSA. The TEM micrograph shows that the MSA has a wormhole-like structure. This result is similar to those of the TEM micrograph of MSA that were synthesized on previous reports [22-23]. The homogeneity of the MSA pore size is relatively low due to the use of a gelatin template which has a wide molecular weight distribution range. The dark spots as shown by the arrow in Fig. 7 were observed in CuZn/MSA, indicating that metal particles are dispersed well in the MSA matrix.

Catalytic Performance

To examine the catalytic properties of synthesized and modified MSA, all samples were tested in the hydrotreatment of bio-oil. Bio-oil was obtained from the pyrolysis of cellulose. Cellulose-derived bio-oil is physically dark brown, thick, and smoke-smell. GC-MS data show that bio-oil contains various oxygenated compounds including ether, aldehyde, ketone, acid, ester, furan, anhydride, and other miscellaneous oxygenates (Table 2). The major product in bio-oil is 1-hydroxy-2-propanone, which is about 20.14%.

Hydrotreatment of cellulose-derived bio-oil was carried out with and without a catalyst. Fig. 8 shows the

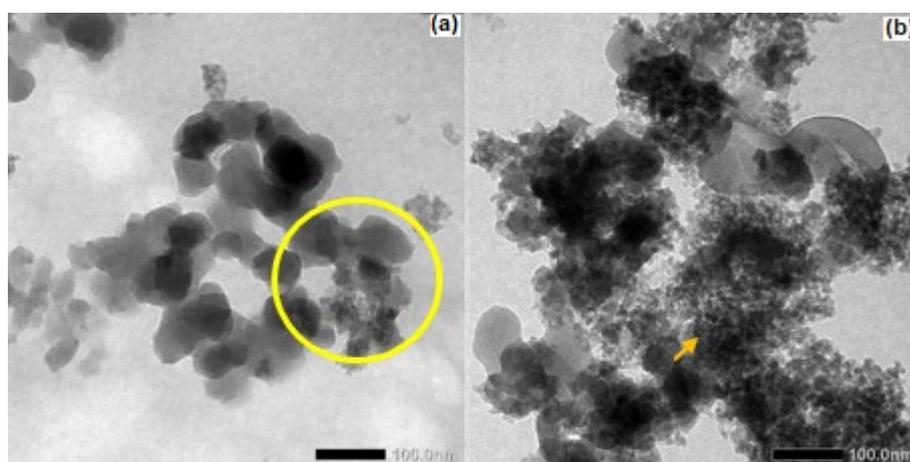


Fig 7. TEM micrograph of MSA (a) and CuZn/MSA (b)

Table 2. Chemical composition of cellulose-derived bio-oil

Compounds	Formula	Content (%)	Compounds	Formula	Content (%)
1-Hidroxy-2-propanone	C ₃ H ₆ O ₂	20.14	1-Acetyloxy-2-propanone	C ₄ H ₆ O ₂	1.16
2,3-Butanedione	C ₄ H ₆ O ₂	13.53	3-Pentanone	C ₅ H ₁₀ O	0.85
Methanoic acid	CH ₂ O ₂	12.72	2-Butanone	C ₄ H ₈ O	0.69
Etanolic acid	C ₂ H ₄ O ₂	12.34	3-Methyl-1,2-cyclopentadione	C ₆ H ₈ O ₂	0.68
2-Furancarboxaldehyde	C ₅ H ₄ O ₂	10.61	2-Methyl-2-cyclopenten-1-one	C ₆ H ₈ O	0.43
Ethanal	C ₂ H ₄ O	6.34	3-Methyl cyclopentanone	C ₆ H ₁₀ O	0.42
Ethenyl Propanoic	C ₅ H ₈ O ₂	2.58	2-Butenal	C ₄ H ₆ O	0.32
1-Hidroxy-2-propanone	C ₄ H ₈ O ₂	2.56	2,3-Dihydro-1,4-dioxine	C ₄ H ₆ O ₂	0.27
Acetic acid anhydride	C ₄ H ₆ O ₃	2.31	3-Penten-2-one	C ₅ H ₈ O	0.18
Propanal	C ₃ H ₆ O	2.19	2-Pentanone	C ₄ H ₁₀ O	0.17
2,3-Pentanedione	C ₅ H ₈ O ₂	2.16	2,5-Hexanedione	C ₆ H ₁₀ O ₂	0.17
Acetylfuran	C ₆ H ₆ O ₂	1.52	Tetrahydropyran-3-one	C ₅ H ₈ O ₂	0.15
Propanoic acid	C ₃ H ₆ O ₂	1.28	Tetrahydrofuran	C ₄ H ₈ O	0.12
1-Acetyloxy-2-butanone	C ₆ H ₁₀ O ₃	1.20	Methyl succinic anhydride	C ₅ H ₄ O ₃	0.11
2(5H)-Furanone	C ₄ H ₄ O ₂	1.17	2-etoxy propane	C ₅ H ₁₂ O	0.10

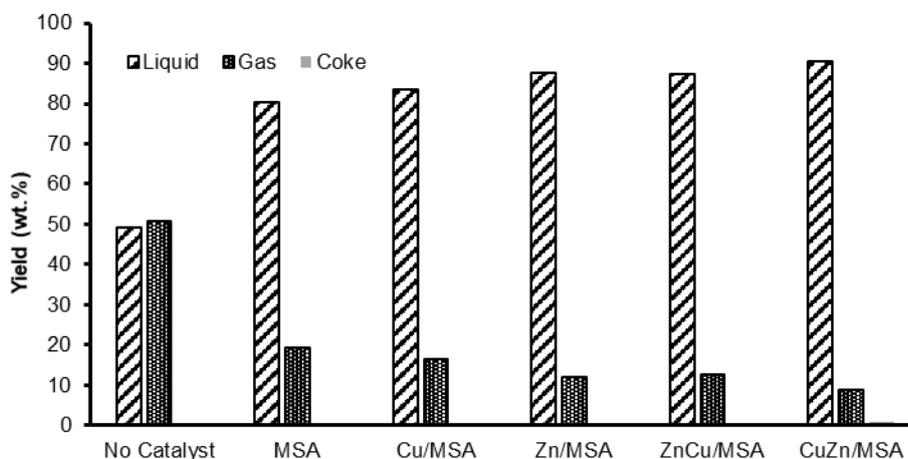


Fig 8. The product distribution of cellulose-derived bio-oil hydrotreatment

product distribution of bio-oil hydrotreatment. It can be shown that many liquid products could be obtained using catalysts more than without catalysts, while gas products could be obtained more without a catalyst. This phenomenon is expected to occur because of the differences in the reaction mechanism involved. Without a catalyst, the reaction occurs through the formation of radical ion triggered by high temperature to produce short-chain carbon compounds, while in the presence of a catalyst, the reaction takes place via the formation of the carbocation to produce longer chain carbon compounds [33]. The short-chain carbon compounds would tend to be in the gaseous phase, while the longer chain carbon compounds would tend to be in the liquid phase.

Among these catalysts, CuZn/MSA catalyst has better performance in producing liquid product than others. This phenomenon was caused by the synergetic effect between Cu and Zn metals. The presence of Zn metals in the bimetallic catalysts electron density on copper and can store or activate hydrogen during the hydrotreatment process [12]. The presence of Zn as the co-promotor can also increase the dispersion of copper particles. The good dispersion of copper particle enhances the effectiveness of the catalyst to produce liquid products.

Comparing to the previous studies, CuZn/MSA catalysts have better performance to produce liquid product. The liquid product that could be obtained using CuZn/MSA catalyst is 90.49 (wt.%). The previous study reported a various hydrotreatments of cellulose-derived

bio-oil using some catalysts, such as Ni/MSA, Mo/MSA, NiMo/MSA, and MoNi/MSA [23]. The highest yield of liquid product of 85.29 (wt.%) could be obtained using MoNi/MSA catalyst. The other previous study also reported hydrotreatment of cellulose-derived bio-oil using Co/MSA, Mo/MSA, and CoMo/MSA catalysts, which the highest yield of liquid product of 82.13 (wt.%) could be obtained using CoMo/MSA catalyst [22].

The chemical composition of the liquid product of bio-oil hydrotreatment was analyzed using GC-MS. It is known that the hydrotreatment of bio-oil involves very complicated reactions, however, the exact mechanism has not been fully understood. These complicated reactions are due to the fact that the bio-oil contains various compounds. Therefore, we focused on the major compounds contained in the liquid product. The major compounds in the liquid product are shown in Table 3. The number of compounds in the upgraded bio-oil was less than in bio-oil. The hydrotreatment of bio-oil significantly reduces several compounds, especially compounds of ketone group such as 2,3-butanedione. Methanoic acid is also reduced during hydrotreatment processes. Reducing the acids could improve the quality of bio-oil because the acids especially formic acid and acetic acid contribute to the acidity of bio-oil [8]. The hydrotreatment process could produce hydrocarbon such as *n*-hexane using MSA catalysts. These results show the MSA catalysts have high selectivity for producing *n*-hexane.

Table 3. Major compounds in bio-oil and upgraded bio-oil

Compound	Product percentage (wt.%)						
	Bio-oil	Catalytic upgrading*					
		No catalyst	MSA	Cu/MSA	Zn/MSA	ZnCu/MSA	CuZn/MSA
<i>n</i> -Hexane	-	-	17.49	-	-	-	-
Ethanal	6.34	4.19	14.41	9.93	9.75	11.28	8.00
2,3-butanadione	13.54	-	-	2.65	-	-	-
Methanoic acid	12.72	-	-	0.45	-	1.15	0.81
Ethanoic acid	12.34	11.90	-	11.23	13.13	12.51	19.79
2-Furancarboxaldehyde	10.61	7.31	13.06	22.51	24.13	18.00	15.07
1-Hydroxy-2-propanone	20.14	11.95	10.78	7.72	6.41	10.73	18.12

■ CONCLUSION

In this study, the preparation of heterogeneous catalysts by a wet impregnation method was successfully carried out. Catalysts comprising Cu and/or Zn supported on MSA denoted as Cu/MSA, Zn/MSA, ZnCu/MSA, and CuZn/MSA were used for hydrotreatment of cellulose-derived bio-oil. The synthesized MSA presented a BET specific surface area of $200.52 \text{ m}^2 \text{ g}^{-1}$, a total pore volume of 0.817 cc g^{-1} , and a pore diameter of 11.44 nm . The acidity of MSA increased after metal loading, which the highest acidity of $24.86 \text{ mmol g}^{-1}$ belonged to CuZn/MSA. During hydrotreatment of cellulose-derived bio-oil CuZn/MSA with total acidity, copper loading, zinc loading, and specific surface area of $24.86 \text{ mmol g}^{-1}$, $5.23 \text{ wt.}\%$, $3.15 \text{ wt.}\%$, and $170.77 \text{ m}^2 \text{ g}^{-1}$, respectively, exhibited the best performance compared to other prepared catalysts with $90.49 \text{ wt.}\%$ conversion of liquid product.

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