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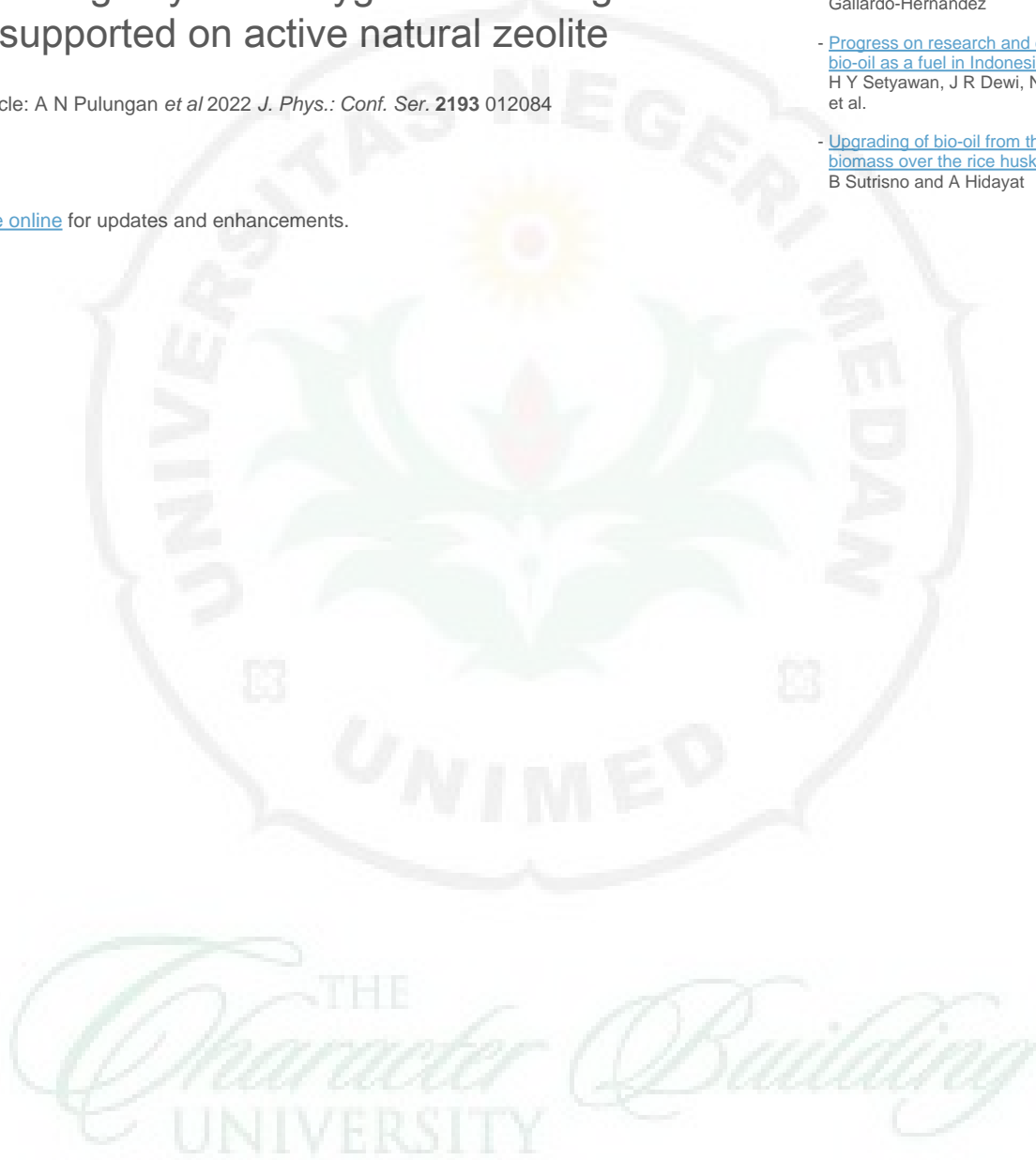# The stabilization of bio-oil as an alternative energy source through hydrodeoxygenation using Co and Co-Mo supported on active natural zeolite

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The stabilization of bio-oil as an alternative energy source through hydrodeoxygenation using Co and Co-Mo supported on active natural zeolite

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Abstract. In this study, hydrodeoxygenation (HDO) process of bio-oil from coconut shell waste was catalyzed by active Sarulla natural zeolite (ZAS) supported by Co metal and a combination of Co-Mo metal. The resulting bio-oil HDO product is expected to have good physicochemical stability during the storage period so as to increase its potential as an alternative source of hydrocarbon energy. Preparation and activation of ZAS catalyst with 3M HCl and calcination with N2 gas flow. Impregnation of Co and Co-Mo into ZAS was carried out by wet impregnation method followed by oxidation and reduction with O2 and H2 gas flow. Several important properties of the catalyst were characterized by XRD, SEM, FTIR, and BET methods. Bio-oil HDO process is carried out in fixed bed reactor with H2 gas flow at a certain temperature for two hours. Analysis of physicochemical properties and stability of bio-oil products includes analysis of acid number, viscosity, elementary content, HHV, and component analysis using GC-MS. The data obtained showed that the loading of two metals increased the spesific surface area, volume and pore size, but decreased the crystallinity of the catalyst. Based on the distribution of HDO products, it indicates that monometal catalysts tend to produce more liquid phase, coke, and gas while bimetallic catalysts tend to produce more organic phase. Viscosity and acid number of bio-oil catalyzed by Co-Mo/ZAS is lower than that of Co/ZAS. Co/ZAS catalyst showed high selectivity towards the aqueous phase. The bio-oil catalyzed by Co/ZAS has a higher HHV and a higher viscosity and lower oxygen content as a result of the release of hydrogen bound oxygen into water molecules. Thus, it can be assumed that the deposition of Co and Co-Mo on zeolite has a different effect on the characteristics of zeolite and its activity as a catalyst.

1. Introduction

The need for energy in the world continues to increase, while the supply of fossil fuels is running low and cannot be renewed. On the other hand, Indonesia is rich in lignocellulosic biomass which has the potential as an alternative energy source. Lignocellulosic conversion of foodstuffs such as cassava [1], sugarcane [2], and maize [3] have been converted into bioethanol, biomethanol and biodiesel fuels in the past few decades. However, in its development it is considered less effective because it can lead to an increase in food prices and a food crisis. For this reason, the use of lignocellulosic from agricultural and plantation waste can be used as a smart solution. Bio-oil as a condensation product from the combustion of lignocellulosic materials has the potential to be a renewable and environmentally

friendly alternative fuel source. The content of organic compounds in bio-oil can also be converted into fuel fractions or chemicals that have added value [4]. From the environmental point of view, CO from lignocellulosic combustion is biogenic so that it can be used by plants as photosynthetic material to reduce the greenhouse effect, and the energy produced is free from the issue of NO_2 pollutants.

The content of bio-oil compounds such as guaiacol, anisole, phenol, phenolic monomer, furan, dimer, and carboxylic acid can be further increased to obtain hydrocarbons by using various upgrading methods. Compared to the content of fossil fuels, bio-oil has the potential to be an alternative fuel. However, bio-oil cannot be used directly as fuel because of the high oxygen content (35-40%) so that the energy density (HHV) is still low (~20 MJ/kg) far compared to fossil fuels for transportation (~45MJ/kg). In addition, the water content is still high (15-30%), very acidic, and high viscosity [5][6]. This is because the bio-oil component is unstable during storage as a result of being easily oxidized, polymerized and condensed by heavy molecular oxygenate compounds [7][8]. Therefore, stabilization or stabilization methods need to be carried out in order to maintain component stability and improve the quality of bio-oil.

Efforts to stabilize bio-oil can be done by reducing the oxygen content and cutting compounds that have heavy molecules through the HDO process [9]. The HDO process is carried out with the help of a catalyst and hydrogen gas to convert compounds into products [10] [11]. Zeolite has become one of the most studied as HDO catalysts [12][13] this is due to the presence of Bronsted acid sites, large pore size and thermal stability [14][15]. The combination of metal active centers and acid sites in a carrier produces a bifunctional catalyst that can significantly influence the reaction pathway to increase phenolic conversion in the HDO process [16]. Metal incorporation significantly increased the total acidity as confirmed by NH-TPD analysis and FTIR pyridine analysis. The presence of metal greatly increased the conversion of n-dodecane compared to the parent sample in the catalytic cracking reaction using BEA zeolite supported by Ni and Ni/Co [17].

In this study, natural zeolite from Sarulla, North Sumatra was used as a support for Co and Co-Mo metals to produce bifunctional catalysts. The presence of Co and Co-Mo in the zeolite carrier material is expected to increase the catalyst character and catalytic activity of the zeolite as a catalyst in achieving stability and stability of the components of the HDO bio-oil product.

2. Method

2.1. Materials
Bio-oil was obtained from coconut shell pyrolysis, deionized water, natural zeolite from Sarulla Pahae Jae Tapanuli Utara, nitrogen, oxygen and hydrogen gases were from PT Aneka Gas Medan, (NH4)6Mo7O24·4H2O (p.a), Co(NO3)2·6H2O (p.a), HCl (p.a), HNO3 (p.a), NaOH (p.a.), and methanol (p.a) were purchased from Merck.

2.2. Preparation and Activation of Catalyst
At the initial stage, the ZAS preparation process was carried out which included the zeolite refining process, activation process and calcination following the procedure carried out by [13]. Natural zeolite was crushed and sieved with a 100 mesh sieve. The zeolite was then immersed in distilled water for 24 hours at room temperature. The zeolite was filtered and the precipitate was dried at 120 °C. This clean zeolite was activated using 3M HCl at a temperature of 90 °C for 30 minutes, the resulting precipitate was washed with distilled water until the pH was neutral. The precipitate was dried at a temperature of 120 °C. Furthermore, it was calcined at a temperature of 500 °C with nitrogen gas flowing for 4 hours to obtain the active Sarulla natural zeolite.

2.3. Preparation of Co/ZAS and Co-Mo/ZAS
A total of 1,214 grams of cobalt nitrate ($Co(NO_3)_2$·H_2O) was dissolved in 500 mL of deionized water then put in a three neck flask and added 100 grams of active zeolite, then refluxed for 5 hours at 80 °C, then dried at 120 °C followed by the process Oxidation and reduction respectively with oxygen and hydrogen

gas flow at a temperature of 500 ºC for 2 hours to obtain a Co/ZAS catalyst.

A total of 0.92 grams (NH4)6Mo7O24·4H2O) was dissolved in 500 mL deionized water then added 100 grams of active zeolite. Then the mixture was refluxed for 5 hours at 80 ºC, then dried at 120 ºC and Mo/ZAS catalyst was obtained, then the Mo catalyst /ZAS added 0.57 grams of cobalt nitrate (Co(NO3)2·H2O) which had been dissolved in deionized water. The mixture was refluxed for 5 hours at a temperature of 80 ºC, then dried at a temperature of 120 ºC, followed by an oxidation and reduction process at a temperature of 500 ºC for 2 hours to obtain a CoMo/ZAS catalyst. The catalysts were characterized by XRD, SEM-EDX, and BET methods.

2.4 Bio-oil Hydrodeoxygenation

The HDO method of bio-oil stabilization is carried out in a fixed-bed reactor using Co/ZAS and CoMo/ZAS catalysts. In the initial stage, the catalyst and feed (bio-oil) were weighed at 1: 40 ratio.Next,the feed and catalyst were respectively put in the designated container and placed into a stainless steel reactor. After that, the reactor was put into a furnace and heated to temperature at 250 ºC. The vapor produced from the reaction was flowed through a silicon hose and passed through a condenser, where the liquid product, such as HDO bio-oil, was collected. The yields, such as coke, liquid phase and organic phase were calculated. Bio-oilwas characterized for its compound and elementary components (C, H, O, N, S) by using CHN Analyzer LECO-CHN 628, viscosity (Viscometer Ostwald), acid number (titr imetric method), and HHV by Sheng and Azvedo's formula [18]. The degree of deoxygenation (DOD) was estimated as follows:

$$DOD \ (\%) = \frac{MO_{raw \ bio-oil} - MO_{bio-oil \ HDO}}{MO_{raw \ bio-oil}} \ x100\% \qquad (1)$$

Where MO is the atomic O/C ratio of bio-oil.

3. Result and discussion

3.1 Crystallinity of catalyst

The crystallinity of the catalyst was observed through XRD analysis. Based on the diffractogram in Figure 1, there are peaks with high intensity in the $2\theta= 20-30°$ region. Both Co/ZAS and Co-Mo/ZAS catalysts have almost the same diffractogram pattern. The peak with high intensity indicates the crystalline phase and conversely the peak with low intensity indicates the amorphous phase. The difference in intensity at the peak can provide information about the crystallinity of the catalyst so that the degree of crystallinity can be calculated. From the results of the calculation of the degree of crystallinity, it is known that the Co-Mo/ZAS catalyst has a degree of crystallinity of 42%, higher than that of Co/ZAS of 36%.
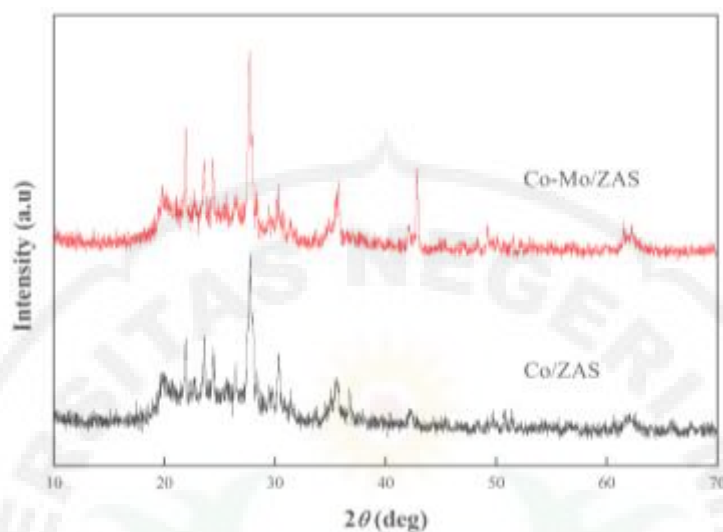
Figure 1. Diffractogram comparison of Co/ZAS and Co-Mo/ZAS.

3.2 Surface Morphology

The surface morphology of Co/ZAS and Co-Mo/ZAS catalysts was observed using SEM (Fig 2). The surface of the Co/ZAS catalyst tends to be more tenuous with better particle size homogeneity, while the Co-Mo/ZAS catalyst is denser and the grain size of the particles tends to be more diverse. This result is correlated with the catalyst crystallinity data which indicates that the denser catalyst surface gives a higher degree of crystallinity.
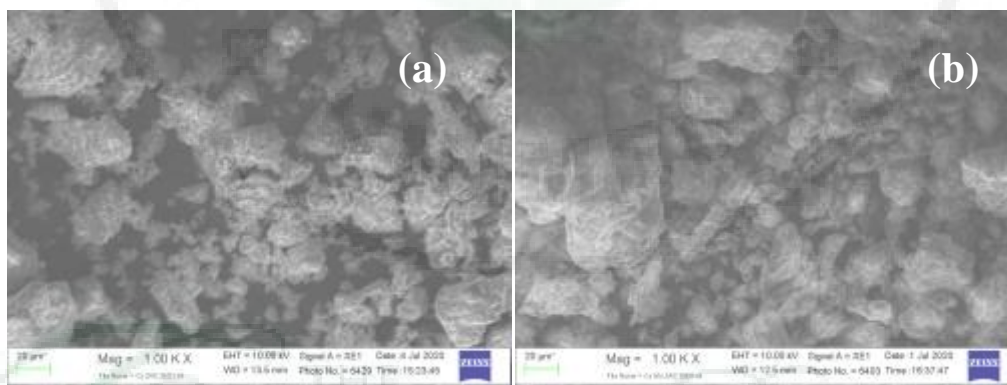

Figure 2. Surface morphologyof catalysts (a) Co/ZAS and (b) Co-Mo/ZAS magnification of 1000x.

The analysis of the catalyst composition was carried out using EDX which is summarized in Table 1. Co/ZAS catalyst has a lower Si/Al ratio when compared to the Si/Al ratio of Co-Mo/ZAS catalyst, this is related to the amount of outer Al that decays during activation process with mineral acids [19]. A high Si/Al ratio is also linear to a high degree of crystallinity. In addition, Co-Mo/ZAS catalyst also has fewer impurities. This will affect the surface morphology of the catalyst which is neater and cleaner so that the crystallinity of the catalyst is higher. The absence of Co metal observed in the Co/ZAS catalyst gives the possibility that very little metal is deposited on the zeolite or it could be that the metal that is absorbed into the pores of the zeolite and is not on the surface of the zeolite. This indication is supported by the surface area and pore data of the catalyst in Table 3.

Table 1. Composition of Co/ZAS and Co-Mo/ZAS catalysts.

Component	Co/ZAS	Co-Mo/ZAS
Si	47.78	22.36
Al	8.61	3.53
O	36.97	68.17
Co	0.00	0.49
Mo	0.00	0.19
Impurities	6.64	5.26
Si/Al	5.55	6.33

3.3 Adsorption-Desorption Isotherm Analysis

The graph of the adsorption-desorption isotherm of the Co-ZAS and Co-Mo/ZAS catalysts is shown in Fig 3. Based on the IUPAC classification, the graph of the isotherm is classified as type IV with a hysteresis loop at P/P_0 between 0.4-0.9. The presence of a hysteresis loop on the isotherm graph indicates that the zeolite material has micro and mesopores.
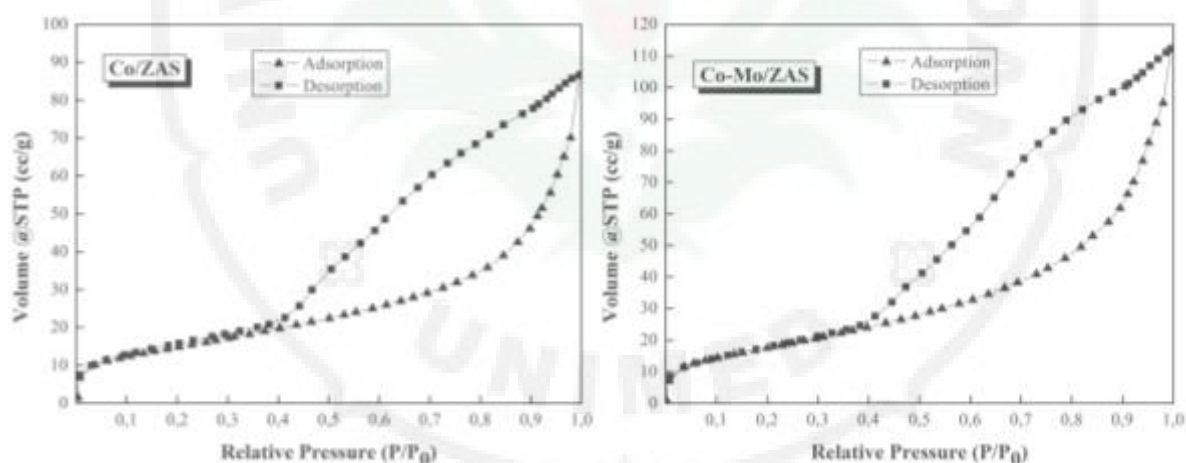
Figure 3. Adsorption-desorption isotherm graphs of Co/ZAS and Co-Mo/ZAS.

The results of measurements of surface area, pore diameter, and total volume of the catalyst are summarized in Table 2. The pore sizes of the two catalysts are included in the mesoporous size (2-50 nm). The bearing of two metals generally has an effect on the characteristics of the zeolite. Co-Mo/ZAS has a specific surface area, pore diameter and total pore volume which is larger than zeolite which is only carried by Co metal. If two metals enter the zeolite pore, it can widen the pore diameter so that the pore size increases, the pore volume increases, and the specific surface area increases.

Table 2. Surface area, pore diameter, and total volume of Co/ZAS and Co-Mo/ZAS.

Properties	Co/ZAS	Co-Mo/ZAS
S_{BET} (m^2/g)	54	65
V_{total} (cc/g)	0.12	0.16
Average pore diameter (nm)	3.14	3.33

3.4 Bio-oil Hydrodeoxygenation

The distribution of bio-oil products that have gone through the HDO process can be seen in Fig 4. The different characteristics of the catalyst give different activities and selectivity to the final bio-oil product [20]. Both catalysts produced a more dominant yield on the water fraction, especially Co/ZAS catalyst with a yield of almost 80% water fraction. The Co-Mo/ZAS catalyst produced an organic fraction of up to 60%, more than the Co/ZAS catalyst which was only 12%.
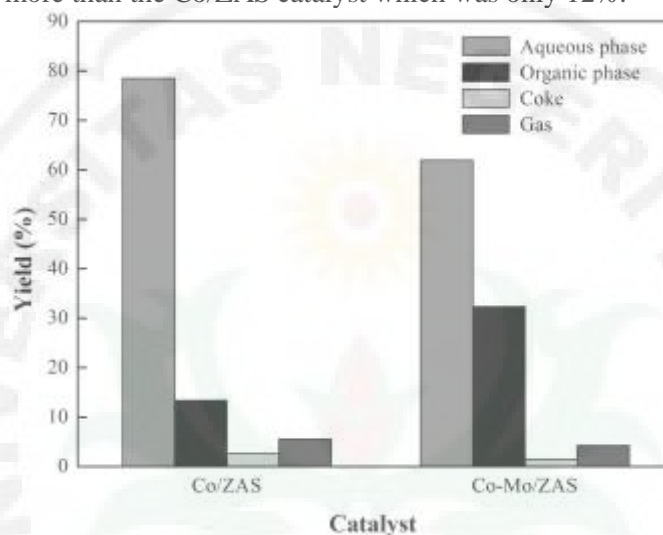

Figure 4. Product distribution of bio-oil catalyzed by Co/ZAS and Co-Mo/ZAS.

Analysis of physicochemical properties of bio-oil products and raw bio-oil were carried out on organic fractions, including elementary content, HHV, viscosity, acid number, and analysis of compound content using GC-MS (Table 4). Bio-oil products have increased carbon content and decreased oxygen content compared to raw bio-oil content. This change is caused by a series of HDO reactions that occur, such as demethylation, hydrogenation, or deoxygenation. Furthermore, it can be observed from the comparison of the molar ratios of H/C and O/C in each bio-oil which can provide information about the route of reaction that may have occured. Both of atomic H/C ratio and O/C ratio decreased after HDO. The lower atomic H/C ratio of bio-oil product may be produced due to decomposition of the organic phase to gas phase [21]. This can be proven from the atomic H/C ratio of bio-oil Co/ZAS which is lower than Co-Mo/ZAS while the gas phase of bio-oil Co/ZAS is more abundant than the gas phase of Co-Mo/ZAS. Meanwhile, the lower atomic O/C ratio is closely related to a direct deoxygenation reaction pathway has occurred [22]. The degree of deoxygenation was calculated from the value of the atomic O/C ratio of raw bio-oil and bio-oil HDO. Bio-oil catalyzed by Co/ZAS catalyst produced much lower oxygen content than bio-oil catalyzed by Co-Mo/ZAS. This decrease in oxygen content resulted in a very high degree of deoxygenation reaching 80%, while the bio-oil Co-Mo/ZAS was only 49%. Oxygen comes out as water molecules, therefore the aqueous fraction increases dramatically compared to other fractions.

Changes in the elementary bio-oil content affect the calorific value (HHV) which is calculated based on the levels of C, H, and O. In general, HHV of bio-oil after HDO has improved compared to HHV raw bio-oil, especially bio-oil Co/ZAS was improved from 12.46 MJ/Kg to 19.40 MJ.Kg. this is linear with the value of bio-oil viscosity which also increases as a result of reduced water content in bio-oil. However, the acid number is still high due to the high acid content in bio-oil.

Table 3. Physicochemical properties of HDO bio-oil.

Properties	Raw Bio-oil	Co/ZAS	Co-Mo/ZAS
Elemental analysis (wt%)			
C	14.31	44.49	24.72
H	9.88	7.57	9.17
N	0.01	0.76	0.21
O[a]	75.8	47.18	65.90
HHV (MJ/kg)[b]	12.46	19.40	14.91
Viscosity (mm^2/s)	5.34	9.25	1.51
Acid number (mg NaOH/g oil)	171	164	141
H/C	8.28	2.04	4.45
O/C	3.97	0.79	1.99
DOD (%)	-	80.10	49.87

[a] Calculated by difference in percentage.
[b] High heating value was calculated by using the following formula: HHV (MJ/ kg) = -1.3675 + (0.3137 C) + (0.7009 H) + (0.0318 O)

Based on the data on the characteristics of the catalyst and the bio-oil analysis that has been done, the two catalysts have different characters and show different activities and product selectivity. This is closely related to the nature and character of each catalyst. Co/ZAS catalyst which has a smaller surface area, pore volume, and pore diameter shows better product selectivity in the water fraction product. Meanwhile Co-Mo/ZAS catalysts which have larger surface area and pores tend to produce products with larger molecules as organic fractions. The higher Si/Al ratio in Co-Mo/ZAS catalyst causes the catalyst to be more hydrophobic so that more organic phase products are produced than bio-oil products catalyzed by Co/ZAS.

The compounds contained in raw bio-oil and HDO bio-oil are summarized in Table 4. Phenol compounds and their derivatives are the largest content in bio-oil. Based on the data in Table 4, the phenol content increased after HDO process. In addition, Phenol, 2,6-dimethoxy were reduced, especially in bio-oil catalyzed by Co/ZAS. Meanwhile, 1,4:3,6-Dianhydro-alpha-d-glucopyranose compounds did not appear again after HDO. In this case, the increase in certain compounds is related to the conversion of other compounds such as, the reduce of Phenol, 2,6-dimethoxy may undergo a demethoxylation reaction to Phenol, 2-methoxy- which then undergoes demethoxylation again to produce a more stable phenolic compound [21].

Tabel 4. Compounds contained in bio-oil HDO

Compound	RT	Area (%)		
		Raw Bio-oil	Co/ZAS	Co-Mo/ZAS
2-Cyclopenten-1-one, 3-methyl-	3.786	-	-	1.34
3-Furanol, tetrahydro-	3.817	1.25	-	-
Phenol	4.148	44.13	46.42	48.22
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	4.757	5.47	4.87	4.72
2-Furanmethanol, tetrahydro-	5.293	2.48	3.42	2.74
Phenol, 2-methyl-	5.389	-	-	1.59
Phenol, 3-methyl-	5.741	2.18	2.07	2.72

Phenol, 2-methoxy-	5.958	1.70	1.67	2.60
3-Ethyl-2-hydroxy-2-cyclopenten-1-one	6.423	-	1.07	1.23
1,4:3,6-Dianhydro-alpha-d-glucopyranose	7.821	1.29	-	-
1,2-Benzenediol	7.948	14.76	13.34	9.80
1,2-Benzenediol, 3-methoxy	9.045	5.00	6.68	5.80
1,2-Benzenediol, 4-methyl-	9.664	3.15	3.61	3.20
Phenol, 2,6-dimethoxy-	10.847	11.99	9.32	10.27
4-ethylcatechol	11.828	1.20	1.25	1.54
1,2,4-Trimethoxybenzene	13.048	2.66	1.48	1.70
Benzoic acid, 4-hydroxy-, methyl ester	13.161	-	1.13	1.21
2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)	14.428	1.34	1.13	1.32

4. Conclusion

The deposition of Co and Co-Mo metals on natural zeolite produces catalysts with different characteristics and catalytic activity. Co-Mo/ZAS catalyst has better crystallinity and surface morphology homogeneity than Co/ZAS catalyst. In addition, the value of surface area, pore diameter, and total pore volume of zeolite with two impregnated metals is greater than the value for zeolite with one impregnated metal. Co/ZAS catalyst showed high selectivity towards the aqueous phase. The bio-oil catalyzed by Co/ZAS has a higher HHV and a higher viscosity and lower oxygen content which is indicated by the degree of deoxygenation reaching 80% as a result of the release of hydrogen bound oxygen into water molecules. phenol compounds have improved due to demethoxylation reaction that occur in methoxyphenol compounds.

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