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Original Research Article

Optimization of the upgrading process of bio-oil from palm fronds: The effect of temperature, catalyst mass ratio, and reaction time

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ABSTRACT

The lignocellulosic component contained in palm frond waste has potential as an alternative fuel by converting it into bio-oil through a pyrolysis process. However, bio-oil has poor quality when compared to conventional fuels. Therefore, the Hydrodeoxygenation (HDO) process has been widely developed as a promising way to improve the poor physicochemical properties of bio-oil. In this study, a bimetallic CuO-ZnO catalyst loaded on mordenite zeolite was used as a catalyst for HDO bio-oil from palm fronds. Optimization efforts were made on several parameters that affect the reaction including temperature, catalyst mass, and reaction time. This study aims to improve the quality of bio-oil and determine the effect of variations in reaction parameters on the physicochemical properties of upgraded bio-oil. The optimum condition found was the HDO process with a catalyst mass of 3.5 wt% at 325 °C for 120 min. The physicochemical properties of bio-oil after the upgrading process were successfully improved from those of raw bio-oil. The result is a decrease in water content and total acid number, an increase in C and H content accompanied by a reduction in oxygen content with a degree of deoxygenation reaching 72.9%, and an increase in higher heating value (HHV).

Introduction

The depletion of fossil fuel supplies is a problem for future energy availability. Therefore, the search for alternative renewable fuel sources is inevitable. Currently, the development of lignocellulosic-based biomass waste as a source of fuel is widely carried out. In addition to its abundant availability, the use of biomass waste as a raw material can reduce the population of waste in the environment. Palm oil as the main commodity in Indonesia is of course supported by the vast area of oil palm plantations it owns with the production of fresh palm fruit of 246 million tons in 2019. Palm oil mills produce a large amount of different waste including palm kernel shells (1.1 tons/ha), palm fruit fiber (2.7 tons/ha), empty fruit bunches (4.4 tons/ha), and frond waste (10–34 tons/ha/year) (Chantanumat et al., 2022). In general, this waste is not utilized optimally or is only burned, thereby contributing to an increase in CO2 emissions. The waste contains cellulose, hemicellulose and lignin which can be converted into bio-oil products (Husna et al., 2022). Converting palm oil waste into bio-oil can solve disposal problems, reduce waste treatment costs, and increase the added value of waste.

Even though it has a high content of organic compounds, bio-oil cannot be used directly as fuel because its physicochemical properties do not meet standards (Zhong et al., 2021). The high content of acids and oxygenic compounds in bio-oil can cause low pH, increase acidity, lower HHV, cause corrosion, make the product unstable and result in high viscosity (Gea et al., 2022a). Therefore, improving the quality of bio-oil is important to make bio-oil more compatible for storage and subsequent processing into liquid fuel.

Hydrodeoxygenation (HDO) is a hydrotreating process that aims to remove oxygen contaminants bound to hydrocarbon compounds using a catalyst and hydrogen gas. In addition to removing the oxygen content, the HDO process also produces more stable hydrocarbons with a higher energy content (Gea et al., 2022). Therefore, the HDO process has been developed as a promising way to improve the physicochemical properties of bio-oil.

The most widely developed catalyst in the HDO reaction is a heterogeneous catalyst with a combination of active metal sites and supporting materials such as alumina, silica, activated carbon, and zeolite. Effective zeolites are developed taking into account their large surface area, good thermal stability, high selectivity, non-toxicity and controlled acidity (Sihombing et al., 2023). Meanwhile, metal active centers provide high activity for various reaction pathways. In bifunctional catalysts, the acid sites on the zeolite play a role in promoting the breaking of the C-O bond, while the metal sites affect the hydrogenation of the benzene ring. The combination of two metals into a bimetallic catalyst can increase the adsorption ability of the adsorbate on the surface as well as allow selectivity for more reaction pathways (Wang et al., 2018).

In this study, the catalyst used was a bimetallic CuO-ZnO catalyst loaded on mordenite zeolite as a support material (Si/Al ratio= 10, surface area= 438 m2/g, pore diameter= 3.76 nm). This refers to our previous research in Pulungan et al. (2023) which obtained this catalyst as the catalyst with the best material characteristics and activity for the same sample under moderate operating conditions. However, the hydrocarbon components and physicochemical properties of the resulting product are not optimal. Therefore, in this study optimization efforts were made on several parameters that affect the reaction including temperature, catalyst mass, and reaction time. The aim of this study is to gain a better understanding of the factors affecting the performance of the catalytic system for the bio-oil upgrading process. Upgraded bio-oil with the most optimal amount of liquid product yield was then analyzed for its physicochemical properties and components of the compounds contained to be compared with the characteristics of raw bio-oil.

Methods

Materials

The materials used in this study were synthetic mordenite type zeolite (HSZ-640HOA, Tosoh Corporation Japan, SiO_2/Al_2O_3 = 9), $ZnSO_4·7H_2O$ (E. Merck), $Cu(NO_3)2·3H_2O$ (E. Merck), distilled water, ethanol (E. Merck), H_2SO_4 (E. Merck), and KOH (E. Merck). Palm frond waste was obtained from oil palm plantations in North Sumatra, Indonesia. Hydrogen gas, Oxygen gas, and Nitrogen gas were purchased from PT. Aneka Gas, Medan, Indonesia.

Preparation of Bio-oil

Production of bio-oil from palm fronds is carried out using the intermediate pyrolysis method. This process uses a fixed-bed type reactor with nitrogen gas flow. In the early stages, the palm fronds that have been cleaned, then mashed. 50 g of powder was put into the reactor which was set at 500°C with a heating rate of 1.3°C/s. At this stage, the process conditions were carried out at a temperature of 500°C, a pressure of 0.1 MPa, and a residence time of 5 minutes, and N_2 gas was supplied with a flow rate of ±5 mL/s.

Upgrading Process

The bio-oil upgrade stage is carried out in two stages, starting with esterification and then continuing with the HDO process. The esterification procedure follows the method reported by Sondakh et al. (2019), this step begins by mixing bio-oil and ethanol in a ratio of 1:1 (w/w) into the reactor at 60°C for 2 h. After that, followed by the HDO stage in a fixed bed reactor. The reactor has a diameter of 5.5 cm and a height of 25 cm, the catalyst vessel has a diameter of 4.8 cm and a height of 3.5 cm, while the furnace has a diameter of 40 cm and a height of 39 cm. The steam generated from the reaction is flowed through a silicone hose and cooled using a condenser to the product container. Catalyst and bio-oil with a certain ratio are fed into the fixed-bed reactor which had been flowed with N_2 gas for 10 min to remove the oxygen content in the reactor. Next, the reactor was heated to a predetermined temperature and H_2 gas flowed at a flow rate of 10 mL/min. The reaction product is fed into the cooling hose and weighed. In this study, several parameters were varied including temperature (250, 275, 300, 325, and 350°C), catalyst mass (2, 2.5, 3, 3.5 and 4 weight percent, wt%), and reaction time (30, 60, 90, and 120 min).

Characterization of Bio-oil

The physicochemical properties of bio-oil before and after the upgrading process were compared. The tests carried out were elemental analysis (C, H, N, O) using the CHN Analyzer LECO-CHN 628, water content testing using Metrohm 870 KF Titrano Plus, acid number analysis using the titration method, calculating higher calorific value (HHV) using the formula Sheng and Azevedo referred to elemental analysis, density determination using a pycnometer, viscosity determination using an Ostwald viscometer, and component analysis using gas chromatography-mass spectrometry (GC-MS QP2010 Plus Shimadzu).

Results and Discussion

Temperature Effect

The effect of temperature on the HDO process was observed under mild conditions in the temperature range of 250-350°C. The resulting product distribution is shown in Fig-1. Based on Fig-1, there are differences in product distribution at each operating temperature. An increase in temperature from 250-325 °C relatively increases the yield of liquid products, and conversely decreases gas products. Astuti et al. (2020) stated that higher temperatures not only increase C=C hydrogenation but also facilitate C-O hydrogenolysis. However, a different trend occurs when the temperature is increased to 350°C, at which temperature the liquid product decreases and the gas produced increases significantly. What's more, at 350°C, coke yield increases. In this case, the higher temperature promotes a more dominant deoxygenation reaction as a consequence of the higher activation energy. A lot of coke is formed due to the deactivation of the catalyst at higher temperatures because bio-oil repolymerization and poly-condensation reactions increase at high temperatures (Remón et al., 2021). this will affect the hydrogenation path to be slow because of the decreased ability of hydrogen adsorption on the surface (Bjelić et al., 2019). Therefore, the optimum temperature chosen was 325°C with the highest liquid product yield of 93%. Similar results were reported by Madsen et al. (2011) who carried out HDO of waste fat for biodiesel production and obtained an increase in oleic acid conversion from 6% to 100% when the temperature increased from 250°C to 325°C. This condition is then used for operating temperature on various parameters of catalyst mass and reaction time.

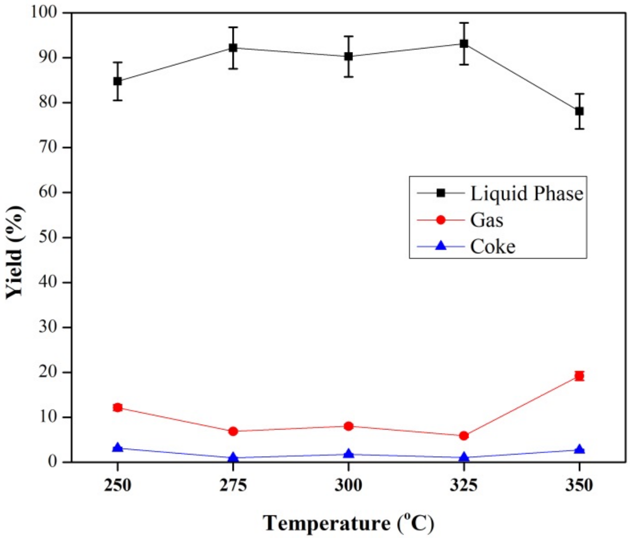

Fig-1. Product distribution produced at various temperatures of 250, 275, 300, 325, and 350°C.

Mass Catalyst Effect

The influence of the mass ratio of the catalyst to the mass of raw bio-oil used in the HDO process was observed at various ratios of 2.0, 2.5, 3.0, 3.5, and 4.0 wt%. The resulting product distribution is shown in Fig-2.

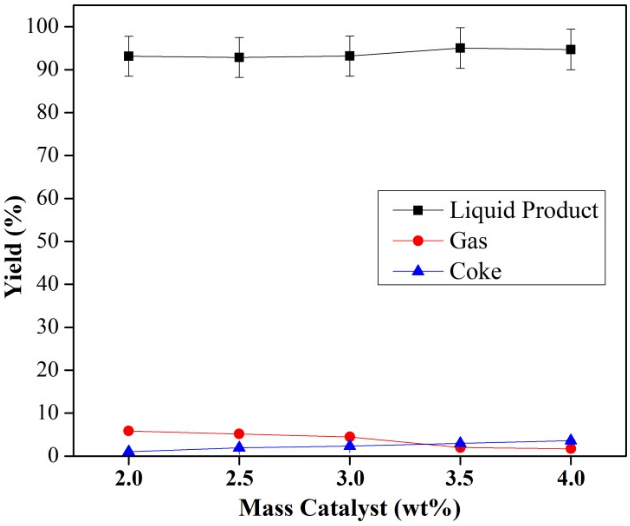

Fig-2. The resulting product distribution on the catalyst mass variation was 2.0, 2.5, 3.0, 3.5, and 4.0 wt%.

Based on Fig-2, it was observed that there was a slight change in the liquid product distribution by varying the mass ratio of the catalyst. The highest yield of liquid product was obtained at a mass ratio of 3.5 wt% catalyst of 95%. Increasing the catalyst mass seems to decrease the gas yield. Increasing the catalyst load helps stabilize the bio-oil, thereby reducing its transformation into gas and solid species. This is in line with the report of Remón et al. who stated that increasing the amount of catalyst from 0 to 0.25 g catalyst/g bio-oil increased the yield of bio-oil and decreased the yield of the water fraction. This result is due to the positive impact of the catalyst on the HDO reaction, which is not only able to prevent the decomposition of bio-oil into gas and solid, but also reduces the formation of water through condensation and water-soluble products with low molecular weight through thermal cracking processes (Remón et al., 2021). Similar results were also reported by Kumar et al., stearic acid conversion increased with increasing catalyst loading. Approximately 75% conversion of stearic acid was achieved for 0.75(w/v)% loading of 15NiAl catalyst after 360 min of reaction compared to using catalyst ratios of 0.1, 0.25, and 0.5(w/v)% (Kumar et al., 2014).

Meanwhile, HDO with a mass ratio of 4 wt% catalyst produced the least gas yield, but the most coke, while the liquid product decreased compared to a mass ratio of 3.5 wt%. Too much amount of catalyst can also have a negative impact leading to susceptibility to deactivation, for example due to sintering at high temperatures. Therefore, a mass ratio of 3.5 wt% was chosen as the optimum condition for the next parameter test.

Time Reaction Effect

The effect of reaction duration during the HDO process was observed at 30, 60, 90 and 120 min. The resulting product distribution is shown in Fig-3.

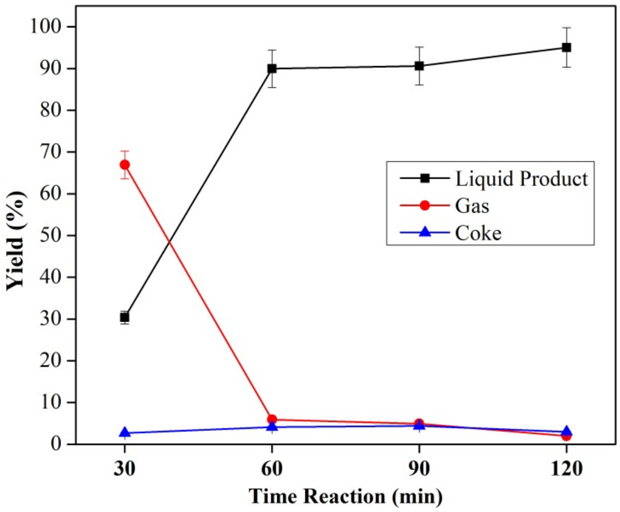

Fig-3. The distribution of the products produced at various reaction times of 30, 60, 90, and 120 min.

Based on Fig-3, extending the reaction time has a significant effect on the distribution of the resulting product. The longer the reaction time, the higher the liquid product obtained, while the less gas produced. Liu et al. (2023), reported that the variation in product distribution at different reaction times is another evidence to prove the HDO reaction pathway, where almost 98% guaiacol conversion was achieved when the reaction time reached 2 h and increased to 100% when the time was extended to 4 h.

Physicochemical Properties of Upgraded Bio-oil

The bio-oil obtained from the HDO results which had the highest yield of liquid products was then analyzed for its physicochemical properties. Some of these properties are summarized in Table 1.

Table 1. Physicochemical properties of raw bio-oil and upgraded bio-oil with a catalyst mass ratio of 3.5 wt% at 325°C for 120 min.

Properties	Raw bio-oil	CuO-ZnO/Mor
Water content (%)	88.87	55.25
Density (g/cm3)	0.92	0.84
Viscosity (cP)	0.71	0.79
TAN (mgNaOH/g oil)	61.41	16.57
Elemental analysis (wt%)		
C	7.59	22.59
H	10.27	11.03
N	0.19	0.07
O[a]	81.95	66.31
H/C	16.17	5.82
O/C	8.12	2.20
DOD (%)	-	72.90
HHV (MJ/kg)[b]	10.82	15.56

[a] calculated based on the difference.

[b] calorific value is calculated based on the following formula: HHV (MJ/ kg) = -1.3675 + (0.3137 C) + (0.7009 H) + (0.0318 O)

Based on the data in Table 1, it appears that there has been an increase in the physicochemical properties of the upgraded product to be better than raw bio-oil. among others, a decrease in water content and total acid number, an increase in C and H content accompanied by a reduction in oxygen content with a degree of deoxygenation reaching 72.9%, and an increase in heating value (HHV). The water content contained in bio-oil is reduced to 55% compared to raw bio-oil. Although the water content of the upgrading product is still high, this decrease has an impact on other physical properties. For example, the density of bio-oil after HDO decreases to a close to the fuel density range. In addition, as a result of the release of oxygen as water and gas molecules, the heating value also increases from 10.82 to 15.56 MJ/kg. The total acid number was successfully reduced by almost a quarter of the total raw acid number of bio-oil. This shows that the pre-treatment process with the esterification method is able to reduce the acid content in the bio-oil (Gea et al., 2022b).

Constituent of Raw Bio-oil and Upgraded Product

Raw bio-oil and upgraded bio-oil were analyzed for their compound content using GC-MS. Bio-oil which is the result of pyrolysis of lignocellulosic based biomass, reduces various components to produce a complex product mixture. The compound components that appear are grouped into several groups of compounds, namely the groups of acids, furfural, ketones, phenols, cresols, guaiacol, catechol, and cycloalkenes, which have been summarized in Fig-4.

Based on Fig-4, the product distribution obtained consists of a mixture of different compounds, which shows the existence of a step-by-step mechanism through the formation of various intermediates. The furfural group is the compound with the highest percentage contained in raw bio-oil, followed by phenol. On the other hand, after the upgrading process, ketones, phenols, and cycloalkenes were found as the most dominant components. These results prove that there is a change in the content of a compound or the conversion of one compound into another. Observations of these compounds can then provide information regarding possible reaction pathways. In this study, we will discuss two groups of compounds that were significantly reduced in raw bio-oil, namely the furfural and guaiacol groups.

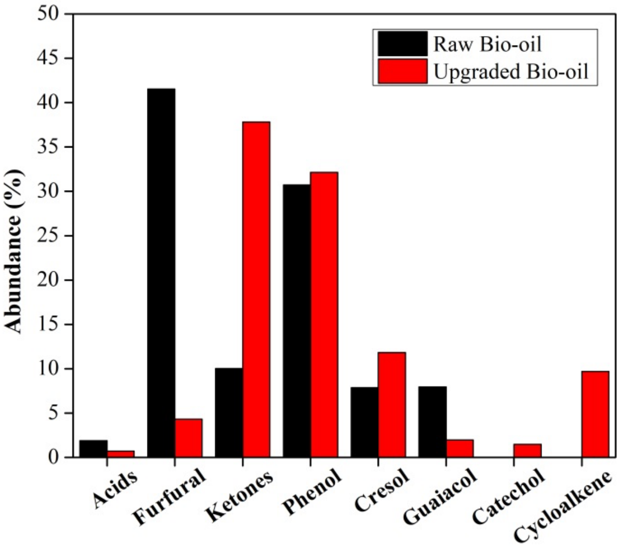

Fig-4. Composition of compounds in raw bio-oil and upgraded product catalyzed by CuO-ZnO/Mor at an optimum temperature of 300°C with a catalyst mass ratio of 3.5 wt% at 325°C for 120 min.

Furfural ($C_5H_4O_2$) is an oxygenated compound obtained by dehydration of hemicellulose constituents derived from lignocellulosic biomass. These compounds are potentially important as components of fuels and chemical production, but require some improvement to reduce their reactivity (Luo et al., 2016). During deoxygenation, the furfural adduct undergoes hydrogenation, ring-opening and dehydration reactions, yielding many intermediate products based on various reaction pathways (Fig-5) (Ramos et al., 2016; Dohade & Dhepe, 2018; Tian et al., 2021). Shao et al. reported that alloying Ni with Cu and Zn can weaken the adsorption of C═C bonds on furan furfural rings, while increasing the activation of C═O and C–O–C bonds, avoiding deep hydrogenation of furan rings, thereby facilitating the rearrangement of furfuryl alcohol. to cyclopentanone (Shao et al., 2022). Besides that, ketones can be obtained from the rearrangement of furfuryl alcohol in the presence of hydrogen or could also be obtained from the ring opening of methylfuran to form open chain ketones (Pulungan et al., 2023). This pathway may have occurred due to the large increase in the percentage of ketones contained after HDO, while the furfural content decreased drastically.

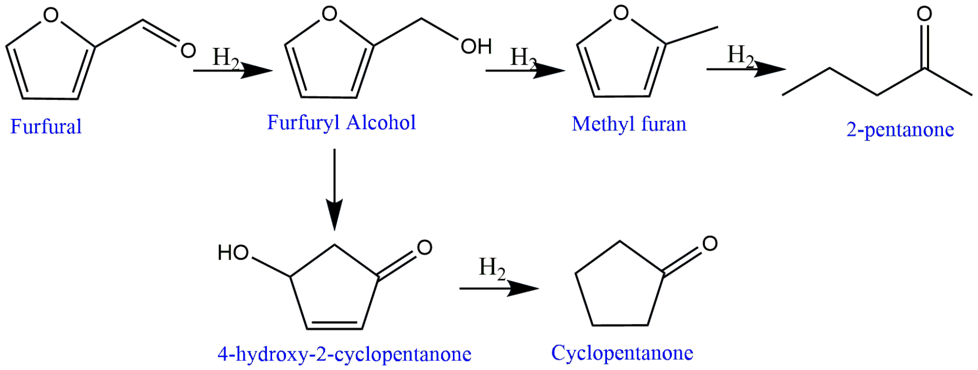

Fig-5. Possible reaction pathways for HDO furfural (Ramos et al., 2016; Dohade & Dhepe, 2018; Tian et al., 2021).

As one of the main depolymerization products, guaiacol has three types of C–O bonds, namely C(sp3)-OAr (247 kJ/mol), C(sp2)-OMe (356 kJ/mol) and C(sp2)–OH (414 kJ/mol) (Liu et al., 2023). The catalytic hydrodeoxygenation reaction can selectively break the C–O bond in guaiacol and remove the oxygen functional group (Gea et al., 2022). In a bifunctional catalyst system, the acid support on the one hand increases the adsorption strength of the phenolic monomer. The acidic sites around the metal lead to an increase in the rate of hydrogenation and hydrogenolysis. This increase is thought to be due to a combination of higher concentrations of the reacting substrates and additional hydrogen transfer via protons from the nearby Brønsted strong acid site (Song et al., 2015).

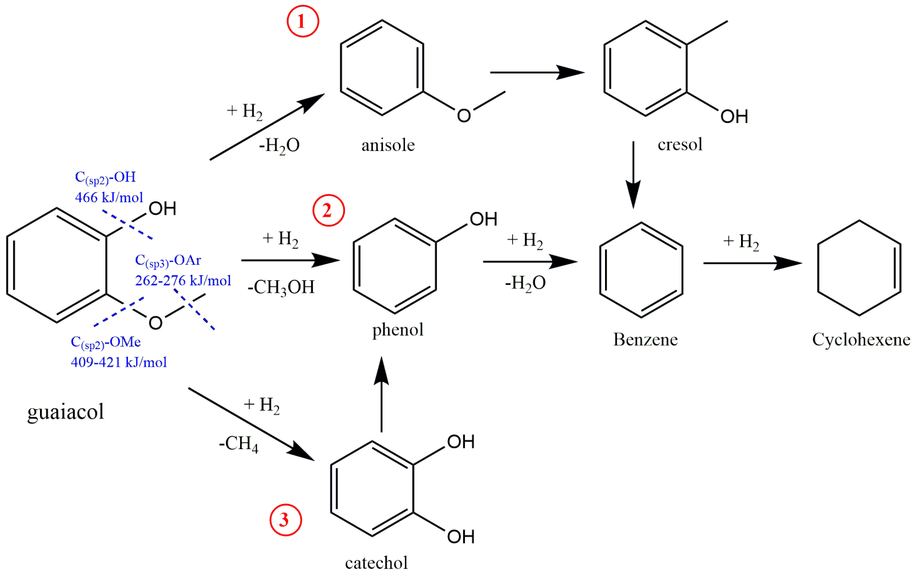

Fig-6. Possible reaction pathways for HDO guaiacol (Gea et al., 2022).

Guaiacol during the HDO process can go through several reaction pathways (Fig-6). Judging from the intermediate compounds formed, it can be predicted that the path traversed by guaiacol. The hydrogenolysis pathway (pathway 1) which involves the release of oxygen in the form of water provides an intermediate compound in the form of anisole which can then be transformed into cresol. Pathway 2 is guaiacol demethoxylated to phenol. This can be proven by increasing the percentage of phenol in the upgraded bio-oil. Pathway 3 is demethylation to form catechol. The occurrence of this pathway is also evidenced by the detection of catechol in the upgraded product. However, methoxy termination in the second pathway tends to be preferred even though it has a greater bond dissociation energy than C-aliphatic termination in pathway 3. This is related to less steric hindrance in C-aromatic so that bond breaking becomes easier. Methoxy group removal is easier than aromatics, compared to aliphatic species and also compared to the hydroxyl group removal (Bjelić et al., 2019). The phenolic compounds can then undergo further deoxygenation to form benzene. Benzene then undergoes hydrogenation to obtain cyclohexene as a fuel hydrocarbon component.

Conclusion

Optimization efforts have been made on several parameters that affect the reaction, including temperature, catalyst mass, and reaction time. The optimum condition found was the HDO process with 3.5 wt% catalyst mass at 325°C for 120 min. The physicochemical properties of bio-oil after the upgrade process have been successfully improved from raw bio-oil. Based on the results of GC-MS analysis, the most dominant components that underwent changes were furfural and guaiacol compounds where it was explained that furfural might undergo conversion to ketones while guaiacol was converted to phenol and cycloalkane. The effort to improve the quality of bio-oil that have been carried out in this study are quite promising for further development because they have been proven to improve the physicochemical properties of bio-oil so that its application in various fields will be more effective.

Conflict of Interests

The author(s) declares that there is no conflict of interest in this research and manuscript.

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References

Astuti, M. D., Kristina, D., Rodiansono, R., & Mujiyanti, D. R. (2020). One-pot selective conversion of biomass-derived furfural into cyclopentanone/Cyclopentanol over TiO2 supported bimetallic Ni-M (M = Co, Fe) catalysts. *Bulletin of Chemical Reaction Engineering & Catalysis*, 15(1), 231–241. https://doi.org/10.9767/bcrec.15.1.6307.231-241

Bjelić, A., Grilc, M., Huš, M., & Likozar, B. (2019). Hydrogenation and hydrodeoxygenation of aromatic lignin monomers over Cu/C, Ni/C, Pd/C, Pt/C, Rh/C and Ru/C catalysts: Mechanisms, reaction micro-kinetic modelling and quantitative structure-activity relationships. *Chemical Engineering Journal*, 359(July 2018), 305–320. https://doi.org/10.1016/j.cej.2018.11.107

Chantanumat, Y., Phetwarotai, W., Sangthong, S., Palamanit, A., Abu Bakar, M. S., Cheirsilp, B., & Phusunti, N. (2022). Characterization of bio-oil and biochar from slow pyrolysis of oil palm plantation and palm oil mill wastes. *Biomass Conversion and Biorefinery*, 13(15), 13813–13825. https://doi.org/10.1007/s13399-021-02291-2

Dohade, M., & Dhepe, P. L. (2018). Efficient method for cyclopentanone synthesis from furfural: Understanding the role of solvents and solubility in a bimetallic catalytic system. *Catalysis Science and Technology*, 8(20), 5259–5269. https://doi.org/10.1039/c8cy01468j

Gea, S., Hutapea, Y. A., Piliang, A. F. R., Pulungan, A. N., Rahayu, R., Layla, J., Tikoalu, A. D., Wijaya, K., & Saputri, W. D. (2022). A comprehensive review of experimental parameters in bio-oil upgrading from pyrolysis of biomass to biofuel through catalytic hydrodeoxygenation. *BioEnergy Research*, 16(1), 325–347. https://doi.org/10.1007/s12155-022-10438-w

Gea, S., Irvan, I., Wijaya, K., Nadia, A., Pulungan, A. N., Sihombing, J. L., & Rahayu, R. (2022a). Bio-oil hydrodeoxygenation over acid activated-zeolite with different Si/Al ratio. *Biofuel Research Journal*, 9(2), 1630–1639. https://doi.org/10.18331/brj2022.9.2.4

Gea, S., Irvan, Wijaya, K., Nadia, A., Pulungan, A. N., Sihombing, J. L., & Rahayu. (2022b). Bio-oil hydrodeoxygenation over zeolite-based catalyst: the effect of zeolite activation and nickel loading on product characteristics. *International Journal of Energy and Environmental Engineering*, 13(2), 541–553. https://doi.org/10.1007/s40095-021-00467-0

Husna, A. F., Febrianti, F., Syah, H. H., Pangaribuan, R. A., Surbakti, T. A., Sihombing, J. L., & Pulungan, A. N. (2022). Conversion of cellulose from palm oil middle waste (Elaeis Guineensis) into bio-oil products as alternative fuel. *Egyptian Journal of Chemistry*, 65(11), 61–67. https://doi.org/10.21608/ejchem.2022.96526.4517

Kumar, P., Yenumala, S. R., Maity, S. K., & Shee, D. (2014). Kinetics of hydrodeoxygenation of stearic acid using supported nickel catalysts: Effects of supports. *Applied Catalysis A: Genera*l, 471, 28–38. https://doi.org/10.1016/j.apcata.2013.11.021

Liu, T., Tian, Z., Zhang, W., Luo, B., Lei, L., Wang, C., Liu, J., Shu, R., & Chen, Y. (2023). Selective hydrodeoxygenation of lignin-derived phenols to alkyl cyclohexanols over highly dispersed RuFe bimetallic catalysts. *Fuel*, 339(100), 126916. https://doi.org/10.1016/j.fuel.2022.126916

Luo, J., Monai, M., Yun, H., Arroyo-Ramírez, L., Wang, C., Murray, C. B., Fornasiero, P., & Gorte, R. J. (2016). The H2 pressure dependence of hydrodeoxygenation selectivities for furfural over Pt/C catalysts. Catalysis Letters, 146(4), 711–717. https://doi.org/10.1007/s10562-016-1705-x

Madsen, A. T., Ahmed, E. H., Christensen, C. H., Fehrmann, R., & Riisager, A. (2011). Hydrodeoxygenation of waste fat for diesel production: Study on model feed with Pt/alumina catalyst. *Fuel*, 90(11), 3433–3438. https://doi.org/10.1016/j.fuel.2011.06.005

Pulungan, A. N., Goei, R., Harahap, F., Simatupang, L., Suriani, C., Gea, S., Hasibuan, M. I., Sihombing, J. L., & Tok, A. I. Y. (2023). Pyrolysis of palm fronds waste into bio-oil and upgrading process via esterification-hydrodeoxygenation using Cu–Zn metal oxide catalyst loaded on mordenite zeolite. *Waste and Biomass Valorization*, 15(1), 187–206. https://doi.org/10.1007/s12649-023-02153-0

Pulungan, A. N., Goei, R., Kembaren, A., Nurfajriani, N., Sihombing, J. L., Gea, S., Wong, H. R., Hasibuan, M. I., Rahayu, R., & Tok, A. I. Y. (2023). Two stages upgrading of bio-oil through esterification and hydrodeoxygenation reactions using Fe2O3-CoO supported catalyst. *Biomass Conversion and Biorefinery*, 0123456789. https://doi.org/10.1007/s13399-023-04237-2

Ramos, R., Tišler, Z., Kikhtyanin, O., & Kubička, D. (2016). Towards understanding the hydrodeoxygenation pathways of furfural-acetone aldol condensation products over supported Pt catalysts. *Catalysis Science and Technology*, 6(6), 1829–1841. https://doi.org/10.1039/c5cy01422k

Remón, J., Casales, M., Gracia, J., Callén, M. S., Pinilla, J. L., & Suelves, I. (2021). Sustainable production of liquid biofuels and value-added platform chemicals by hydrodeoxygenation of lignocellulosic bio-oil over a carbon–neutral Mo2C/CNF catalyst. *Chemical Engineering Journal*, 405, 126705. https://doi.org/10.1016/j.cej.2020.126705

Shao, Y., Sun, K., Fan, M., Gao, G., Wang, J., Zhang, L., Zhang, S., & Hu, X. (2022). Synthesis of a thermally and hydrothermally stable copper-based catalyst via alloying of Cu with Ni and Zn for catalyzing conversion of furfural into cyclopentanone. *ACS Sustainable Chemistry & Engineering*, 10(27), 8763–8777. https://doi.org/10.1021/acssuschemeng.2c01082

Sihombing, J. L., Herlinawati, H., Pulungan, A. N., Simatupang, L., Rahayu, R., & Wibowo, A. A. (2023). Effective hydrodeoxygenation bio-oil via natural zeolite supported transition metal oxide catalyst. *Arabian Journal of Chemistry*, 16(6), 104707. https://doi.org/10.1016/j.arabjc.2023.104707

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

Song, W., Liu, Y., Baráth, E., Zhao, C., & Lercher, J. A. (2015). Synergistic effects of Ni and acid sites for hydrogenation and C-O bond cleavage of substituted phenols. *Green Chemistry*, 17(2), 1204–1218. https://doi.org/10.1039/c4gc01798f

Tian, H., Gao, G., Xu, Q., Gao, Z., Zhang, S., Hu, G., Xu, L., & Hu, X. (2021). Facilitating selective conversion of furfural to cyclopentanone via reducing availability of metallic nickel sites. *Molecular Catalysis*, 510(March), 111697. https://doi.org/10.1016/j.mcat.2021.111697

Wang, C., Luo, J., Liao, V., Lee, J. D., Onn, T. M., Murray, C. B., & Gorte, R. J. (2018). A comparison of furfural hydrodeoxygenation over Pt-Co and Ni-Fe catalysts at high and low H2 pressures. *Catalysis Today*, 302, 73–79. https://doi.org/10.1016/j.cattod.2017.06.042

Zhong, M., Huang, J., Yuan, J., Rong, S., Ou, P., Chen, X., Zhang, B., Ke, Q., & Zhu, Z. (2021). Solvothermal synthesis and characterization of porous co microspheres. *Materiali in Tehnologije*, 55(5), 663–666. https://doi.org/10.17222/MIT.2021.160