

Improving the Bio-Oil Quality via Effective Pyrolysis/Deoxygenation of Palm Kernel Cake over a Metal (Cu, Ni, or Fe)-Doped Carbon Catalyst

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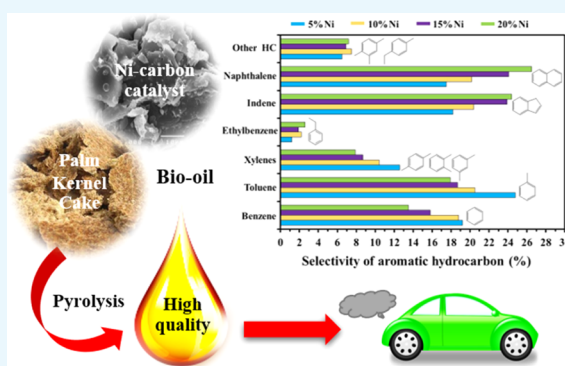


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ABSTRACT: Waste palm kernel cake (WPKC) is being utilized as a biomass feedstock for the sustainable production of catalysts/supports and bio-oil fuels. Herein, metal (Cu, Ni, and/or Fe)-doped carbon catalysts were prepared using conventional impregnation and pyrolysis methods. The physicochemical properties of the as-prepared catalysts were analyzed. According to the obtained results, the catalyst acidity was highly increased with the increase in the metal loading amount on a carbon support, leading to a better performance for deoxygenation/aromatization. A maximum yield of bio-oil from WPKC pyrolysis was achieved up to ~60% under optimum conditions determined via statistical designs. From the results of bio-oil compositions, 15%Ni loading on activated carbon exhibited the best performance of about 72% for the production of hydrocarbon compounds. Monoaromatic hydrocarbons such as benzene, toluene, and xylenes (BTXs) could be reduced via condensation and polymerization with the increase of the Ni-loading amount. Moreover, the catalytic performance of the selected 15%Ni-carbon catalyst was also compared with those of commercial catalysts zeolite and alumina, and the results showed that the 15% metal-doped carbon catalyst presented much better stability/reusability for five times with less reduction of the hydrocarbon yield in the upgraded bio-oil. This research provided an eco-friendly strategy for the low-cost production of bio-oil fuel with a high quality/yield from waste biomass pyrolysis.



1. INTRODUCTION

The sustainable production of renewable energy is now gaining interest due to various environmental problems along with the severe reduction of fossil fuels.^{1,2} Also, CO₂ gas is easily produced in high amounts when fossil fuels are combusted as alternative power sources, leading to an increase in the greenhouse effect and thereby global warming. Thus, it is necessary to find environmentally friendly resources. The utilization of waste biomass or inedible biomass for biofuel production is one of the promising ways with low production cost.³ The transformation of waste biomass into biofuels and green catalysts via a thermal treatment process such as gasification and pyrolysis is widely applied.^{4,5} Here, the biomass pyrolysis might be considered as a clean method for biofuel production because its process is not much complicated. Commercially, the pyrolysis process is performed in the temperature range around 500–700 °C without the presence of oxygen.^{6–8} Unfortunately, even though a high yield of bio-oil of about 30–50% can be obtained from direct pyrolysis of biomass, its quality is still quite low because of the existence of complex oxygen compounds such as acids, furans, phenols, and others.⁹ In order to increase the heating value of the bio-oil, the

oxygenated compounds must be removed via the deoxygenation process.

Hydrodeoxygenation (HDO) has been identified as an effective method for oxygen removal from bio-oil.¹⁰ However, it required a high production cost because the application of external H₂ is needed for catalytic deoxygenation. To avoid using H₂ externally, the use of catalysts having high acidity can be considered. Such catalysts obviously present excellent activity for cracking and deoxygenation processes in bio-oil, leading to an increase in the hydrocarbon yield and a reduction of oxygenated compounds such as acids, ketones, aldehydes, phenols, and other chemicals in upgraded bio-oil. However, undesired products such as polyaromatic hydrocarbons (PAHs) and coke could be further formed from the selective transformation of monoaromatic hydrocarbons (MAHs) such as benzene, toluene, xylenes, and indene via alkylation aromatiza-

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tion and polymerization over catalysts due to the presence of excessive acidity or too strong acid sites, leading to an increase in the viscosity and flash point of bio-oil, making it unsuitable for application as transportation fuel.¹¹ Therefore, we need to consider the properties of a catalyst before utilizing it in the bio-oil upgrading process. Also, the price and the long-term stability of the catalyst must be controlled for specific applications in a practical process. Commercially, alumina and silica have been widely used for catalytic cracking of bio-oil molecules, but the problem is rapid deactivation of the spent catalyst after the first run. To date, commercial zeolites show excellent activity for upgrading bio-oil via various reactions such as cracking, decarboxylation, decarbonylation, dehydration, aromatization, and others, leading to the facile formation of aromatic hydrocarbons as the main components in bio-oil.^{12,13} Many kinds of zeolites have also been tested for bio-oil deoxygenation. Du et al.¹⁴ found that Zeolite Socony Mobil-5 (ZSM-5), an aluminosilicate zeolite in the protonic form with the pore size in the range of about 5.4–5.6 Å, showed better deoxygenation/aromatization activities than others for promoting deoxygenation, resulting in the rich formation of aromatic hydrocarbons in bio-oil. However, due to the limitation of pore size on the zeolite structure, the large components of bio-oil cannot access or disperse to the active site of zeolite.¹⁵ Mesoporous materials are a good choice to solve such a problem. Kaewpengkrow et al.¹⁶ found that mesoporous acid catalysts had high ability for selective conversion of oxygenated compounds into hydrocarbons. To increase the catalytic deoxygenation performance, doping of transition metals such as Ni, Cu, Ga, Fe, Co, and Mo into mesoporous supports has been systematically tried and found that new acid sites are well generated, which can highly promote the bio-oil upgrading process.^{17–20} Among them, Cu, Fe, and Ni, being abundantly available and cheap metals, exhibit the same activity, as compared to noble metals such as Pt and Ru for the bio-oil upgrading process. To date, the main problems during the deoxygenation process are facile formation of coke on commercial catalysts and metal-doped catalysts having too much acidity, which lead to rapid deactivation.²¹

To solve the above problems, we developed a green, cheap, and stable mesoporous acid catalyst by eco-friendly production from waste biomass derived from industry. Activated carbon is found to be an effective catalyst/support material because it has good ability to improve the bio-oil quality.²² Herein, waste palm kernel cake (WPKC) derived from the palm oil industry was applied as feedstock for the sustainable production of catalysts and bio-oil. In this study, metal (Cu, Ni, or Fe)-doped activated carbon catalysts were prepared from WPKC using impregnation and pyrolysis methods. The activity of the as-prepared catalysts was systematically tested for deoxygenation of bio-oil derived from WPKC pyrolysis. The physical and chemical characteristics of catalysts were characterized to support the catalytic results. A statistical experiment was systematically performed to obtain the highest yield of bio-oil. The product distributions in the upgraded bio-oils from biomass feedstock were investigated by using metal-doped activated carbon with different metal-loading amounts. The catalytic performance and reusability without further regeneration of Ni-carbon were also compared with those of commercial materials such as zeolite and alumina. It is expected to provide higher-performance, longer-stability, and lower-cost green catalysts for the bio-oil deoxygenation process.

2. RESULTS AND DISCUSSION

2.1. Characterization of Catalysts. As shown in Table 1, the pure activated carbon without metal doping exhibited a

Table 1. Physicochemical Properties of the As-Prepared Catalysts

catalysts	surface area (m ² /g)	pore volume (cm ³ /g)		pore size (nm)	crystallite size of metal (nm)	acidity (mmol/g)
		meso	micro			
pure carbon	356	0.15	0.12	2.44		0.087
5%Cu	334	0.15	0.11	2.41	3.8	0.187
10%Cu	315	0.13	0.09	2.37	12.8	0.229
15%Cu	287	0.10	0.08	2.18	18.9	0.341
20%Cu	242	0.09	0.07	2.08	30.7	0.335
5%Ni	341	0.16	0.10	2.42	5.2	0.221
10%Ni	328	0.15	0.10	2.35	15.4	0.379
15%Ni	305	0.15	0.06	2.30	22.8	0.408
20%Ni	288	0.14	0.05	2.21	35.8	0.397
5%Fe	311	0.12	0.11	2.32	2.1	0.175
10%Fe	286	0.08	0.10	2.19	5.9	0.249
15%Fe	253	0.06	0.09	2.01	9.3	0.313
20%Fe	207	0.04	0.07	1.87	15.6	0.384
zeolite	408	0.33	0.42	5.52		0.768
alumina	257	0.75	0.14	10.8		0.205

higher surface area (356 m²/g) than metal (Cu, Ni, or Fe)-doped activated carbon with various loading amounts of 5–20 wt % (207–341 m²/g). The surface area and the pore volume significantly decreased to some extent with the increase in the metal-loading amount, suggesting that the surface and pore structures of the supports are partly covered and occupied by the dispersed metal species.²³ Meanwhile, the mesopore volume in Fe-doped activated carbon severely decreased when compared with those of the others, indicating that the iron oxide formed during thermal treatment was easily distributed into the porous structure, resulting in the facile occurrence of mesopore blockage. Here, an average pore size of around 2.2 nm was clearly observed for all carbon catalysts.

Figure 1 shows the XRD patterns of metal-loaded activated carbon catalysts. One can see weak diffraction peaks appearing at 5 wt % loading amount, corresponding to the metal (Cu, Ni, or Fe) crystalline phase. This indicates that metals with a small particle size were highly distributed on the carbon support without accumulation and sintering effects.^{23,24} Unlikely, the strong diffraction peaks of the Cu, Ni, and Fe crystalline phases were clearly observed at a loading amount of 20 wt %, indicating that this loading amount might not be appropriate. To support these data, the crystallite sizes calculated using Scherrer's equation are also presented in Table 1. As predicted, the crystallite size of metal oxides doped on activated carbon increased with the increase of the metal loading amount. These XRD analysis results were also in good agreement with the BET analysis results.

Figure 2 shows the morphologies of 15%Cu-carbon, 15%Ni-carbon, and 15%Fe-carbon. As is observed, no bulk metal particles were formed on the carbon structure, indicating that metals (Cu, Ni, or Fe) with 15 wt % loading amount were still homogeneously distributed on the support surface. The metal elemental maps and energy-dispersive X-ray (EDX) spectra of each catalyst are also shown in Figure 2. The Cu, Ni, and Fe

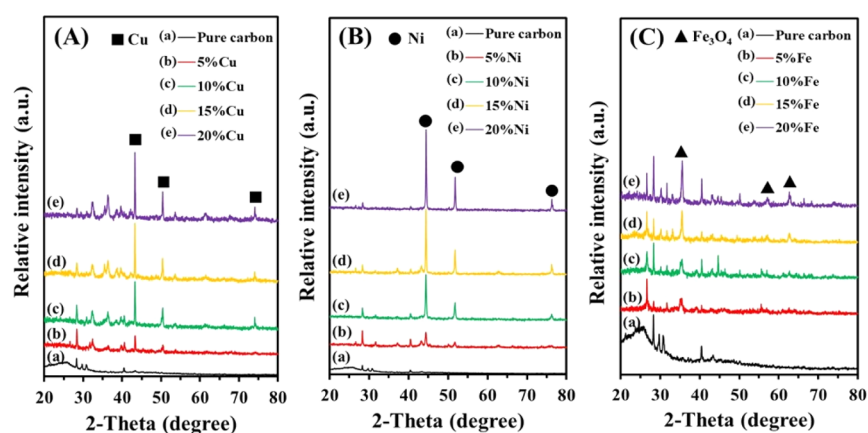


Figure 1. XRD patterns of (A) 0–20%Cu-carbon, (B) 0–20%Ni-carbon, and (C) 0–20%Fe-carbon.

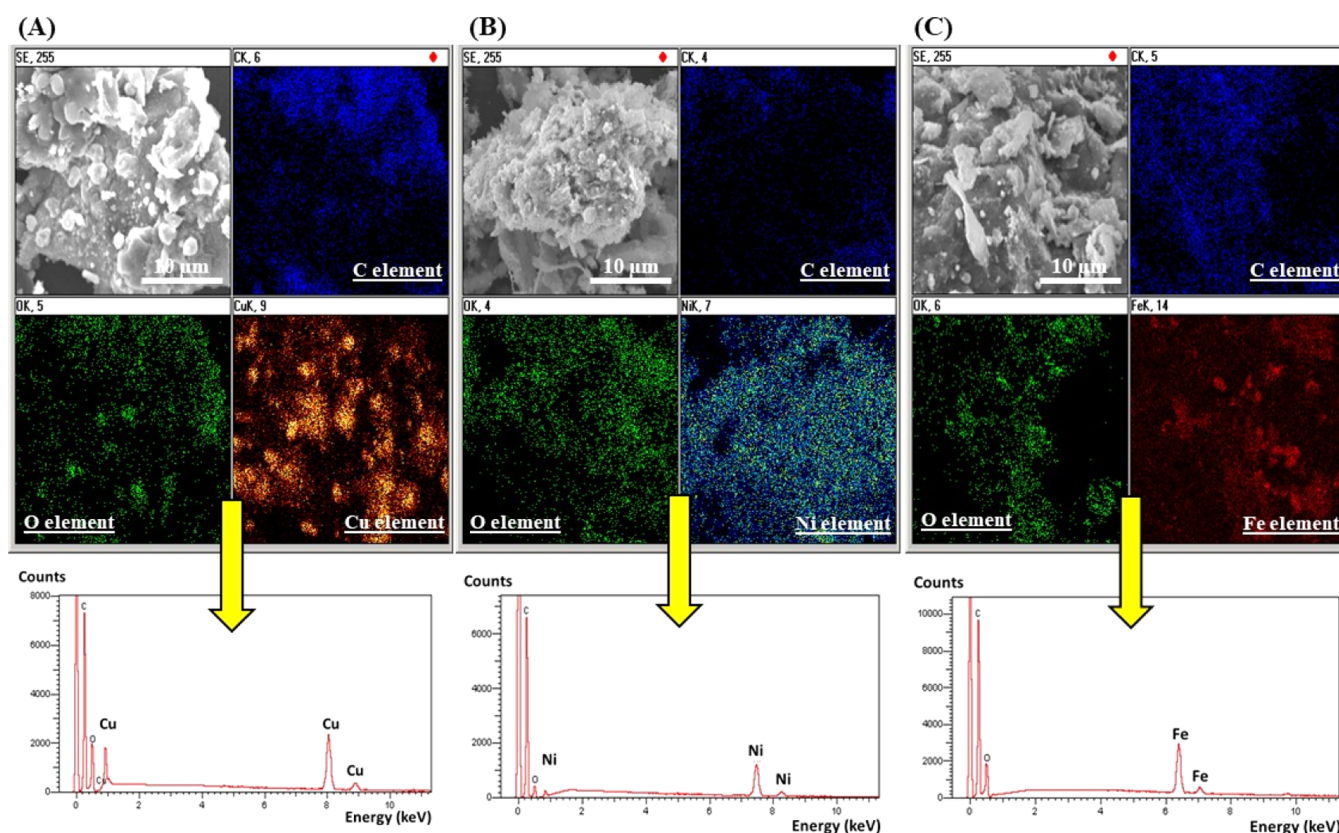


Figure 2. SEM–EDX images and EDX spectra of (A) 15%Cu-carbon, (B) 15%Ni-carbon, and (C) 15%Fe-carbon.

species were found to be well distributed on the surface of the carbon support. The acidity of catalysts was analyzed by the NH_3 -TPD technique, and the results are shown in Figure 3 and Table 1. As shown in Figure 3, two NH_3 desorption peaks were clearly observed in the temperature ranges of 100–450 and 450–650 °C, corresponding to weak acid sites and strong acid sites, respectively. The various patterns of NH_3 desorption peaks should be attributed to the different interactions of the metal proton sites on the carbon structure.^{25,26} Interestingly, strong acid sites of Cu-carbon and Ni-carbon obviously appeared while those of Fe-carbon were quite low, indicating that doping of the Fe metal might not be so good for application as an active catalyst for deoxygenation. It should be noted that the existence of strong acid sites on a catalyst favors the main reactions for bio-oil upgrading such as deoxygenation, alkylation, and aromatiza-

tion. However, it should also be appropriately controlled because the polymerization and polycondensation may also occur during the reaction process in the presence of excessive acidity on catalysts. As shown in Table 1, the acidities of metal-doped carbon catalysts successfully increased with the increase of metal-loading amounts. A small reduction of acidity for 20% Cu-carbon and 20%Ni-carbon should be due to the formation of larger metal particles on the support. Therefore, higher acidities and stronger acid sites on catalysts were more beneficial for improving the bio-oil quality derived from pyrolysis/deoxygenation of WPKC.

2.2. Catalytic Deoxygenation of Bio-oil from WPKC Pyrolysis. In this study, optimum conditions, that is, a reaction temperature of 550 °C, a heating rate of 1000 °C/min, and an ultrasonic pretreatment time of 200 min, were employed for all

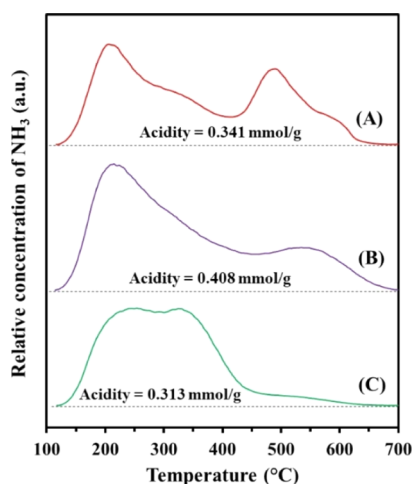


Figure 3. NH_3 -TPD profiles of (A) 15%Cu-carbon, (B) 15%Ni-carbon, and (C) 15%Fe-carbon.

studies so that the highest yield of bio-oil could be obtained. The results and discussion for the optimization process for bio-oil production and biomass characterization are provided in the Supporting Information (Tables S1–S3 and Figs. S1–S5).^{27–31} Figure 4A,D,G shows the chemical compositions of pyrolysis/deoxygenation of pretreated WPKC using 15%Cu-carbon, 15%Ni-carbon, and 15%Fe-carbon. Herein, the chemical compositions were divided into nine types such as (I) aromatic

hydrocarbons, (II) aliphatic hydrocarbons, (III) phenols, (IV) ketones, (V) aldehydes, (VI) furans, (VII) sugars, (VIII) acids, and (IX) others. Here, (I) and (II) types in the bio-oil were identified as indicators to define the deoxygenation efficiency of each catalyst. It is found that the total hydrocarbon yield obtained was about 7% when an acid catalyst was not utilized. After using the Cu-, Ni-, or Fe-carbon catalyst, the hydrocarbon yield highly increased, especially for the formation of aromatic hydrocarbon. Here, 15 wt % metal (Cu, Ni, and Fe)-doped carbon catalysts provided the best results for improving the bio-oil based on the highest yields of total hydrocarbons of around 65–75%. Thereafter, a slight reduction of the total hydrocarbon yield occurred when 20 wt % metal (Cu, Ni, and Fe)-doped carbon catalysts were used. This should be due to further conversion of light hydrocarbons into coke via polycondensation. It should be noted that no sugar compounds existed in bio-oil after 10–20 wt % metal (Cu, Ni, and Fe)-doped carbon catalysts were applied. This indicates that sugar compounds easily transformed into furan via dehydration, followed by decarbonylation for light hydrocarbon formation.³² Meanwhile, the acid compounds in bio-oil such as acetic acid completely decarboxylated into carbon dioxide over 15 wt % metal-doped carbon catalyst, indicating that bio-oil acidity was successfully reduced, leading to a significant reduction in the corrosive rate.

Figure 4B,E,H,C,F,I shows the mass balance of product yields such as bio-oil, water, gas, and coke char and the yields of different gases such as hydrogen, carbon monoxide, carbon dioxide, and methane. As expected, the yields of carbon

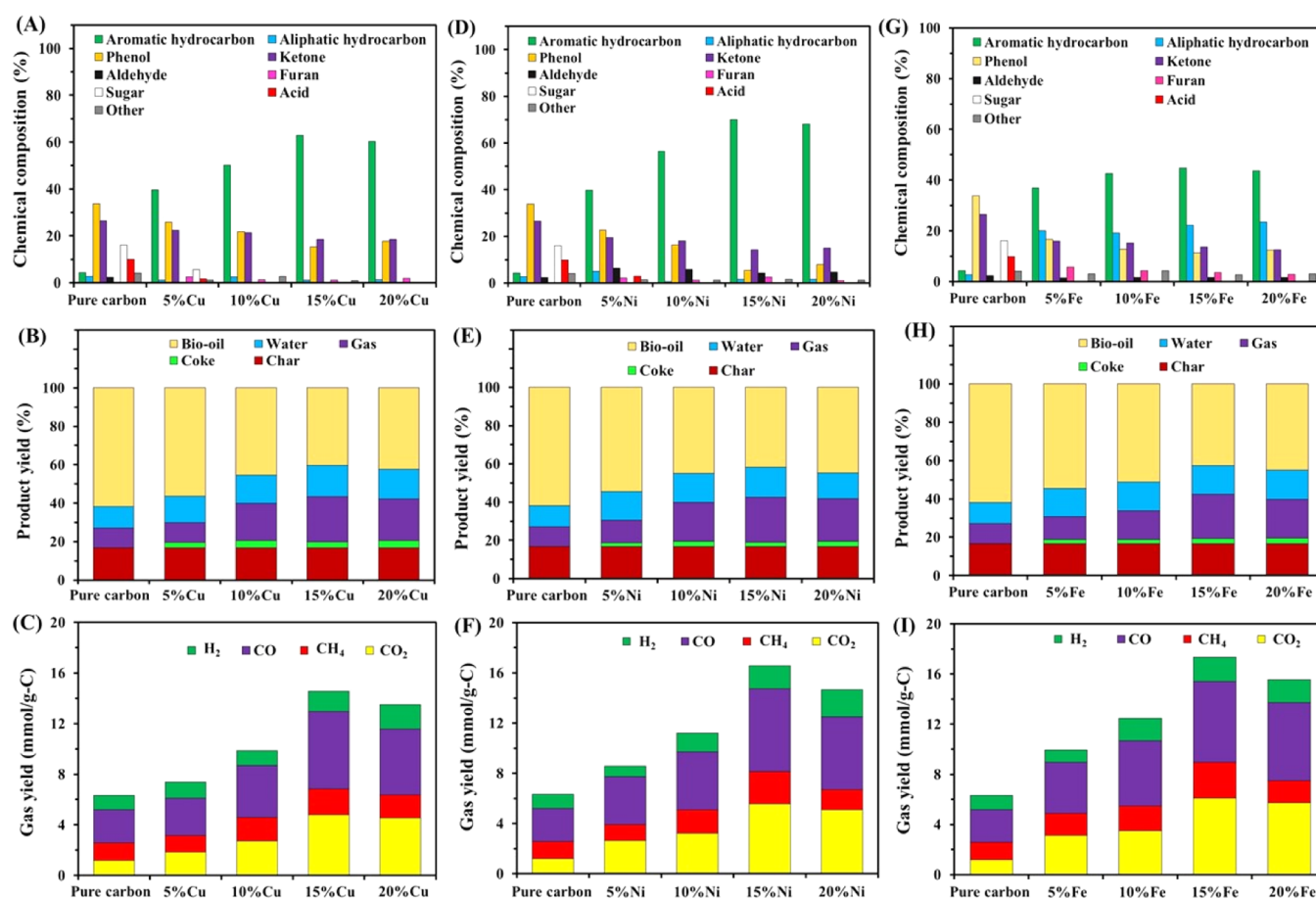


Figure 4. Chemical compositions of bio-oil, mass balance of products, and gas yields obtained from pyrolysis/deoxygenation of pretreated WPKC over (A–C) 0–20%Cu-carbon, (D–F) 0–20%Ni-carbon, and (G–I) 0–20%Fe-carbon.

monoxide, carbon dioxide, and water dramatically increased with the enhancement of the total hydrocarbon yield, while the oxygenated compounds were perfectly removed via the deoxygenation process.³³ This indicates that our prepared catalysts were highly effective for the bio-oil upgrading process. However, the effect of metal loading should be considered because a too high loading amount such as 20 wt % could promote the facile formation of coke on catalysts. Based on these results, 15% Ni-carbon was found to be the best catalyst for improving the bio-oil quality because a total hydrocarbon yield of up to ~72% was achieved, including an aliphatic yield of 2.5% and an aromatic yield of 69.5%. Meanwhile, the lowest quality in upgraded bio-oil was found for 15% Fe-carbon. The best performance of 15% Ni-carbon should be ascribed to the presence of the proper acidity and acid sites via strong interactions between Ni species and the carbon material. This difference was also supported by the results of NH₃-TPD profiles. Therefore, the 15% Ni-carbon catalyst was applied for further studies.

Figure 5 shows the selectivity for aromatic formation in bio-oil catalyzed by 5–20%Ni-carbon catalysts. Herein, aromatic

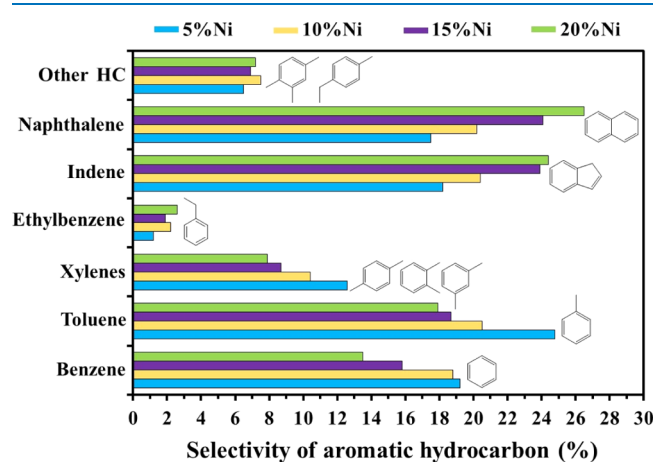


Figure 5. Aromatic selectivity obtained from pyrolysis/deoxygenation of pretreated WPKC over 5–20%Ni-carbon.

hydrocarbons were divided into seven types such as benzene, toluene, xylenes, indene, naphthalene, and others. For 5%Ni-carbon, the aromatic selectivity in the upgraded bio-oil was in the order of toluene > benzene > indene > naphthalene > xylenes > others > ethylbenzene. This selectivity pattern significantly changed upon adjusting the Ni loading amount. PAHs such as naphthalene continuously increased with the increase of the Ni amount from 5 to 20 wt %, confirming that aromatization/alkylation of MAHs into PAHs could be well promoted with a higher amount of Ni. Therefore, the aromatic hydrocarbons produced in this research could be practically applied as fuel additives because their aromaticity was in the range of gasoline.³⁴

Figure 6 shows the effect of the weight ratio of WPKC on 15% Ni-carbon for hydrocarbon production from the pyrolysis process. The hydrocarbon yield continuously enhanced with the increase of the WPKC:15%Ni-carbon ratio from 0.1:0 to 0.1:0.8 and after that no significant change was detected. As is well known, the bio-oil yield reduced with the increase of the catalyst amount, due to further conversion of bio-oil into coke and gases. Nevertheless, it also highly promoted the catalytic deoxygenation because more acid sites were available. From

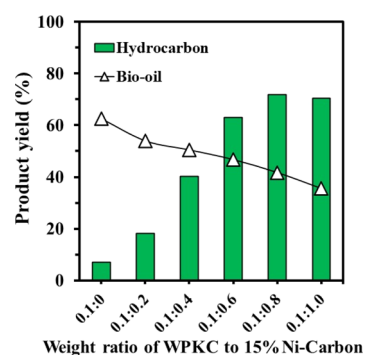


Figure 6. Effect of the weight ratio of WPKC to 15%Ni-carbon on hydrocarbon production in upgraded bio-oil from pyrolysis/deoxygenation of pretreated WPKC.

these results, a WPKC:15%Ni-carbon ratio of 0.1:0.8 was selected as the optimal condition. The bio-oil properties were tested by comparing with the ASTM standard D 7544-12 (Table S4). As expected, the bio-oil quality derived in this study met the ASTM standards, indicating that it may be possibly applied as transportation fuel.

The principal mechanisms for catalytic pyrolysis/deoxygenation of biomass are shown in Figure 7. As is known, the main compositions of biomass were classified into three types such as (I) cellulose, (II) hemicellulose, and (III) lignin. In the first step, cellulose and hemicellulose were depolymerized into sugar compounds and furans, respectively.^{35,36} Then, these compounds were further converted into oxygenated compounds with smaller molecules such as acetic acid, propanone, butanal, and others via a thermal cracking process. In the presence of heterogeneous acid catalysts with strong acid sites, the deoxygenation reactions such as dehydration, decarbonylation, and decarboxylation should occur, leading to the selective conversion of oxygenated compounds into light hydrocarbons, carbon monoxide, carbon dioxide, and water. Meanwhile, light hydrocarbons were further converted into aromatic compounds such as benzene, toluene, xylenes, indene, and naphthalene via alkylation, oligomerization, cyclization, and aromatization processes. In the case of lignin pyrolysis, it was initially depolymerized at positions of C–C and C–O bonds to form the phenol compounds, followed by aromatic compounds via thermal cracking/deoxygenation processes at high reaction temperatures.³⁷ Char was obtained after the completion of pyrolysis via repolymerization. It should be noted that the yield of char depends on the reaction temperature and the ash amount present in biomass. In this study, strong acid sites or Lewis acid sites were successfully generated after Cu, Ni, and Fe were loaded on the carbon support. The presence of these active sites including electron pair acceptors favors the aromatization reaction. That was why aromatic compounds were easily produced in bio-oil after catalytic pyrolysis/deoxygenation of biomass. However, PAHs and coke could be coproduced via polymerization and polycondensation when a catalyst with too high acidity of was applied, leading to simultaneous reductions of the total hydrocarbon yield and catalyst stability.³⁸

2.3. Comparison of Catalyst Reusability. Figure 8 shows the comparison results for reusing the 15%Ni-carbon, zeolite, and alumina for five cycles without any regeneration. Herein, commercial zeolite (74.65% SiO₂–25% Al₂O₃–0.35% Na₂O) and γ -alumina were purchased from Alfa Aesar and Saint-Gobain, respectively. In the first cycle, one can see that commercial zeolite exhibited a better catalytic performance than

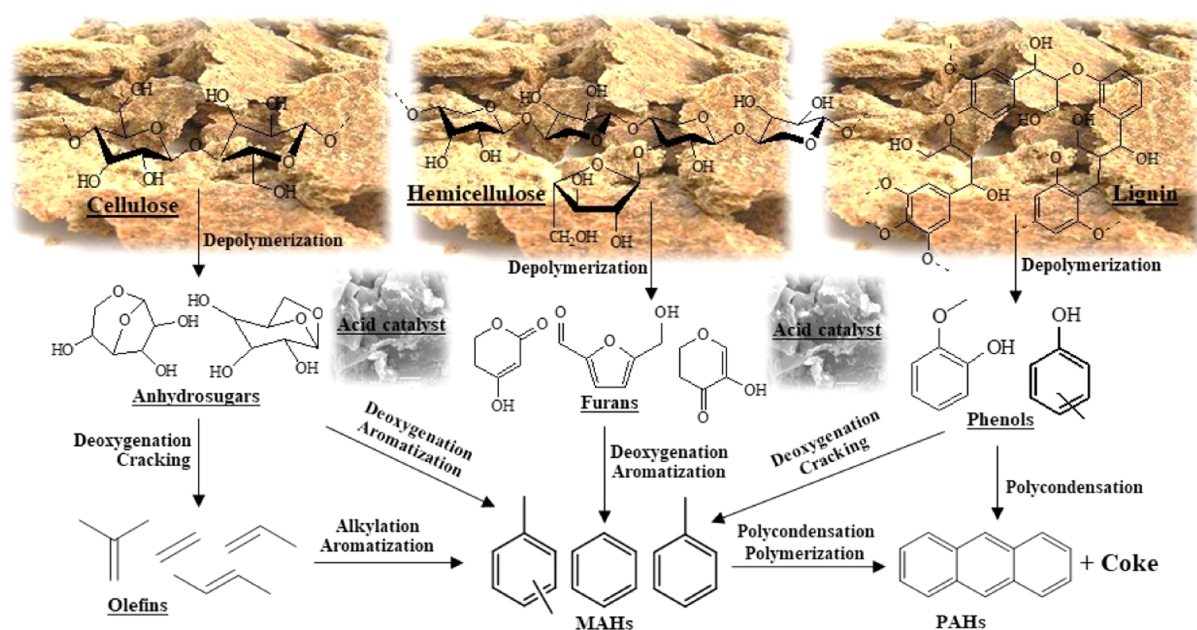


Figure 7. Reaction pathways for catalytic pyrolysis/deoxygenation of biomass into bio-oils with rich aromatic hydrocarbons.

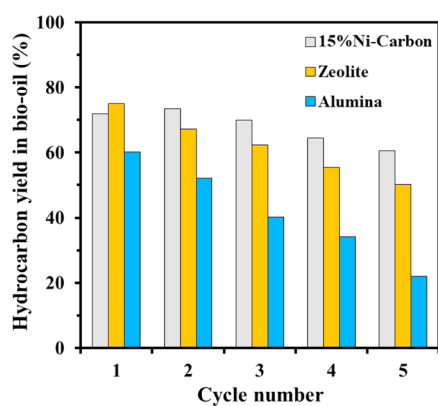
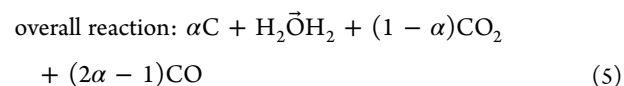
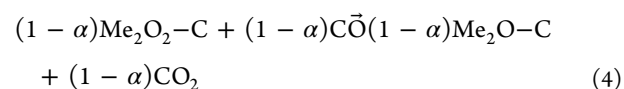
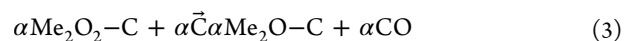
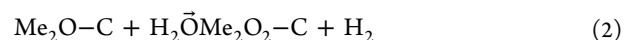


Figure 8. Reusability of 15%Ni-carbon, zeolite, and alumina for catalytic deoxygenation of bio-oil from WPKC pyrolysis.

others, due to the presence of highest acidity and surface areas (Table 1). Unlikely, the activities of zeolite and alumina severely dropped after the first cycle. This phenomenon can be described as coke formation on a highly acidic catalyst via a polycondensation reaction, leading to a significant reduction in the hydrocarbon yield in bio-oil.³⁹ Also, undesirable products such as PAHs were easily formed when a catalyst with a too large pore size was applied, resulting in further conversion of PAHs into coke. These results indicate that the as-prepared 15%Ni-carbon catalyst was not only cheaper and cleaner but also presented a better stability than commercial catalysts. Here, a small reduction of hydrocarbon yield in bio-oil was found for 15%Ni-carbon in each cycle, where the reduction percentage was less than 10% from the first to the fifth cycle. This reduction should be attributed to the coke formation on the surface of the 15%Ni-carbon catalyst, leading to negligible deactivation of the catalyst.^{40–42} Interestingly, the hydrocarbon yield increased a little in the second cycle. This should be attributed to the presence of alkali and alkaline earth metallic (AAEM) species on the spent catalyst derived from biomass decomposition during the pyrolysis process. Interestingly, the ability for coke formation

on the catalyst could be significantly reduced by AAEM species, as shown in eqs 1–5⁴³



As shown in Table S5, the main ash compositions of palm kernel cake were K_2O and CaO or AAEM species. As is known, the presence of AAEM promoted the in situ production of H_2 during biomass pyrolysis, leading to strong enhancement of deoxygenation, especially for the hydrodeoxygenation reaction. That was why the hydrocarbon yield increased to some extent when the spent catalyst was reused in the bio-oil upgrading process.

3. CONCLUSIONS

Upgrading bio-oil derived from palm kernel cake pyrolysis was achieved by using metal (Cu, Ni, and Fe)-loaded activated carbon catalysts. A maximum bio-oil yield of 60.1% was obtained under optimum conditions determined via statistical analysis. It should be noted that the operation cost for ultrasonic pretreatment was still quite high, but it is strongly required for application on a larger scale such as in industrial plants because the bio-oil yield increased up to 10–20%, which could reduce the running time for the production process. The introduction of a transition metal on activated carbon resulted in the regeneration of new acid sites, which was useful for deoxygenation reactions. The 15%Ni-carbon catalyst exhibited the highest catalytic activity for the conversion of oxygenated

compounds to hydrocarbons. The PAH selectivity increased with the Ni loading amount. The catalyst could be reused for five cycles with a slight reduction in the hydrocarbon yield. Overall, this research provided a clean strategy for sustainable production of a stable catalyst and bio-oil with high quality from waste biomass feedstock, which could be applied to replace fossil fuels, leading to a significant reduction of CO₂ emission causing the greenhouse effect and thereby global warming. It is also expected that such a green/cheap catalyst could be further developed for achieving a cleaner process.

4. EXPERIMENTAL SECTION

4.1. Pretreatment of Biomass Feedstock. WPKC collected from Thailand was utilized as a biomass milled to particles with a size of 400 mesh. The proximate analysis of WPKC was carried out using ASTM D5142-04 methods, while its elemental and ash compositions were detected using an elemental analyzer (FLASH 2000, USA) and an EDX spectrometer (XRF-Phillips, PW 2400, Netherlands), respectively (Table S5). Prior to pyrolysis, biomass feedstock was dried at 105 °C overnight. 2 g of biomass powder was moistened with 50 mL of distilled water and heated in an ultrasonic bath at a frequency of 40 kHz and a power of 150 W for 30–240 min. Thereafter, the pretreated biomass was dried by evaporation at 105 °C overnight.

4.2. Catalyst Preparation and Characterization. Metal (Cu, Ni or Fe)-doped activated carbon catalysts with various metal-loading amounts (5–20 wt %) were prepared by the impregnation method. In brief, a certain amount of CuSO₄·5H₂O, NiSO₄·6H₂O, or FeSO₄·7H₂O was dissolved in deionized water and stirred until a homogeneous solution was obtained. Then, the palm kernel cake powder was added to the mixture and stirred at ambient temperature for 2 h. Thereafter, the slurry was dried at 80 °C and pyrolyzed at 600 °C for 30 min under atmospheric pressure. The as-prepared catalysts were characterized using various techniques to support the catalytic activities. The details are as follows: (I) the N₂ sorption isotherm was obtained using a Quantachrome instrument (NOVA 4200e, USA) in order to identify the surface area (BET method) and the pore volume/pore size (BJH method) of catalysts. The type and crystallinity of metal oxide doped into activated carbon as well as the WPKC structure before and after pretreatment were determined using an X-ray diffractometer (XRD, PANalytical, X'Pert PRO, Netherlands), operating in a 2θ range of 20–80° with a scanning step of 0.02° using Cu Kα radiation. The existence of each functional group on WPKC before and after pretreatment was verified by Fourier transform infrared (FT-IR) spectrometry using a PerkinElmer (Spectrum 100, USA) FT-IR spectrometer with the attenuated total reflectance (ATR) technique in the wavenumber range between 4000 and 800 cm⁻¹. The catalyst acidity was quantified with a NH₃-temperature-programmed desorption (NH₃-TPD) technique using a BET-CAT analyzer (BEL, Japan). The morphologies of catalysts and WPKC before and after pretreatment as well as the dispersion rates of Cu, Ni, and Fe species on the catalyst surfaces were investigated by using a scanning electron microscope (JSM-5410 LV, USA) coupled with an EDX detector (OXFORD, England).

4.3. Catalytic Deoxygenation Test. The WPKC pyrolysis was performed on a fixed-bed reactor system (OkWell, Thailand), operating at atmospheric pressure. A schematic diagram of the pyrolytic apparatus is shown in Figure 9. In a typical run, 0.5 g of WPKC and 4.0 g of the catalyst were

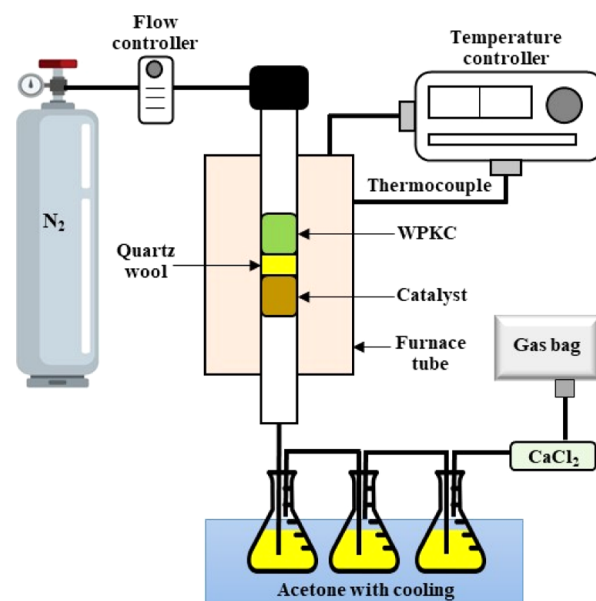


Figure 9. Schematic diagram of the experimental setup for pyrolysis/deoxygenation of biomass/bio-oil.

separately packed with quartz wool in the reactor. During the reaction, N₂ was used as the carrier gas with a flow rate of 50 mL/min. Prior to the experiment, the reactor was purged with N₂ gas flow for approximately 5 min to remove the internal oxygen. The optimal reaction temperature and the heating rate were investigated. The bio-oil products were condensed by trapping with acetone soaked in cooling bath. The gas products were purified with a CaCl₂ filter and collected in a gas bag for further analysis. After the completion of this process, the char yield in the reactor was determined to find the yield by the weighting process. It should be noted that before the catalytic upgrading of bio-oil by using various catalysts, the statistical optimization for fast pyrolysis of biomass was carried out to find the maximum bio-oil yield. The details are provided in the Supporting Information (Tables S1 and S2).

4.4. Analysis of Bio-oil and Other Products. The bio-oil compositions were characterized using an Agilent 6890 gas chromatography/mass spectrometry (GC-MS) system installed with a HP-5MS column (30 m × 0.25 μm × 0.25 mm). Nitrogen with a high purity of 99.99% was used as a carrier gas. The temperature of the GC injector was set at 280 °C for bio-oil vaporization. The heating temperature in the GC oven was started at 60 °C for 1 min, increased to 90 °C for 1 min with a heating rate of 3 °C/min, further increased to 170 °C for 1 min. Finally, the temperature was held at 300 °C for 8 min. Each compound in the bio-oil was analyzed by matching the GC-MS spectra with the National Institute of Standards and Technology (NIST) mass spectral library. The pyrolytic gas was determined using a gas chromatograph (GC-TCD, Agilent7890A, USA) using helium as a carrier gas. Herein, two packed columns are applied as follows: (I) a polymer paraplott U column was kept at 40 °C to detect CH₄ and CO₂ gases and (II) a molecular sieve 5A column was maintained at 60 °C to analyze CO and H₂ gases. The product yield was quantified using an external standard method. The amount of coke deposited on the catalysts was investigated by weighing the catalysts before and after the reactions.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c02999>.

Experimental section; results and discussion on statistical designs for the optimization of pretreated WPKC pyrolysis; characterization results of untreated and pretreated WPKC by XRD, FT-IR, and SEM analyses; bio-oil quality obtained from pyrolysis/deoxygenation of WPKC; and proximate, ultimate, and ash compositions of WPKC (PDF).

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Notes

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