Preparation of biochar catalyst from coconut shell impregnated with nickel metal as a heterogeneous catalyst

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DOI: 10.2478/9788368412017-053

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Abstract. *Considering its many resources and ecologically favorable characteristics, biochar has gained attention as a potentially heterogeneous catalyst for a variety of chemical processes. To increase its catalytic activity, nickel metal (Ni) was injected into biochar constructed from coconut shells. This study's primary goal is to create a catalyst based on charcoal that contains nickel. The coconut shells were pyrolyzed at high temperatures while under nitrogen flow to create biochar. A nickel solution with nitrates was then used for impregnation. FTIR, XRD, as well as XRF, were among the analytical methods used to characterize the resultant catalyst. While XRD revealed the existence of the nickel oxide stages on the biochar, FTIR measurements demonstrated alterations in the functional elements on the surface of biochar following nickel impregnation. The effectiveness of the impregnation with a consistent nickel concentration across the charcoal surface was validated by XRF measurements. The study's findings show that coconut shell biochar has the potential to be a useful and sustainable heterogeneous catalyst for waste and energy processing.*

Keywords: *Pyrolysis, Coconut Shell, Biochar, Nickel Impregnation, Heterogeneous Catalyst*

Introduction

The use of renewable raw materials is crucial for sustainable development because of the issues of energy demands and environmental contamination [1,2]. Heat, electricity, liquid fuels, hydrogen, as well as high-value chemicals can all be produced from biomass, a plentiful natural resource comprised of lignocellulose, plants, microalgae, and biowaste of the household, urban, and agricultural sectors, including animal fats [3,4]. Biomass can be broken down into solid carbon residues called biochar and biofuels like syngas and bio-oil using thermochemical decomposition methods like pyrolysis or gasification [5–7]. The thermal breakdown of biomass at moderate temperatures (350–700°C) with little to no oxygen results in the production of biochar, a carbon-rich porous solid [8,9]. The thermochemical procedure employed, and the qualities of the biomass feedstock have a significant impact on the chemical and physical properties of biochar [10–12]. In addition to having an enormous area and high porosity, biochar's customized porosity and functional surfaces allow it to be readily modified as a platform for the manufacture of different functionalized carbon materials owing to its numerous functional surface groups (C-O, C=O, COOH, and OH) [6,13]. These characteristics make biochar an effective adsorbent for soil amendment, activated carbon synthesis, and air and water pollution [14,15].

Given its extensive availability, low cost, enormous surface area (which promotes significant dispersion along with stability for metal phases), durability in basic and acidic media, and other advantageous physical/chemical surface characteristics, biochar (BC) has recently been

used extensively in heterogeneous catalysis systems, particularly as a metal support [6]. In numerous applications involving a broad range of reactions, such as trans-esterification/esterification, contributing reforming/cracking, gasification/pyrolysis, hydrolysis, electrochemical and photocatalytic reactions, and persulfate/carboxymethyl sulfate oxidation, among others, biochar materials have demonstrated exceptional activity as a catalyst or catalyst support.

Plantation trash and other abundant sources can be used as feedstock for BC [16], bamboo [17], corn straw rice husk [18], and so on which are quite abundant. A natural resource for creating porous carbon, coconut shell serves as one of the possible feedstocks generated from plant waste which is frequently found in tropical regions. Furthermore, KOH, which is present in coconut shell ash, helps to activate the carbon-containing substrate [19]. Finally, it is highly advantageous for the economy and environment to produce catalysts with exceptional performance from low-value waste [20]. The primary issue with employing carbon as a metal support involves the high propensity for metal sintering brought on by the high-temperature breakdown of the oxygen functional groups that comprise the BC surface [21,22]. Conversely, Kim, et al. [23] noted that the structure of activated carbon derived from coconut shells had a low oxygen content, suggesting that it can inhibit metal sintering onto carbon supports. The choice of metals in a heterogeneous catalyst is crucial to the catalytic process providing support. Exceptional catalytic performance and cheap cost have been demonstrated for nickel (Ni) metal [24]. According to Yang et al. [25], Ni-doped biochar generates syngas and hydrogen at 78.2% by weight, 26 mmol H2/g-biomass, and a biomass conversion efficiency of 73%. Ni-based catalysts also perform well in hydrogen gas production applications when it comes to breaking C-C and C-H bonds [26]. Therefore, the goal of this research is to create BC catalysts of coconut shells by modifying them with the inclusion of Ni metal, then characterize them to determine their properties that are utilized in the procedure of steam reforming to produce hydrogen gas.

Method

Materials

Coconut shell (*Cocos nucifera L.*) as raw material, nitrogen gas, KOH (p.a Merck), HCl (p.a Merck), Ni $(NO_3)_2 \cdot 6H_2O$ (p.a Merck), $Fe(NO_3)_3 \cdot 9H_2O$ (p.a Merck), Aquades and Aquabides.

Coconut Shell Biomass Preparation

After being sliced into small pieces, the shell of the coconut is left to dry in the heat of the sun for two days or for 24 hours in the oven at 110 ^oC. The coconut shell pieces are then obtained by drying them in an oven to eliminate the water content.

Coconut Shell Pyrolysis Process

A fixed-bed reactor is used to carry out the pyrolysis process. After inserting the coconut shell, the reactor is placed inside a furnace and heated to 500℃ for two hours while nitrogen gas flows at a rate of ± 5 ml per second. A cooling hose is used to circulate the reaction product. Weighing is done on the obtained biochar and liquid product.

Biochar Catalyst Preparation

A 100-mesh sieve is used to grind and filter the pyrolysis biochar. The amount of 100 g for pyrolysis biochar is neutralized by distilled water after being cleaned with 0.1 M HCl. After that,

it is dried for 12 hours at 110 °C in an oven. After that, it is activated using 250 ml of distilled water and KOH at a 4:1 (w: w) ratio. Dehydrated for 24 hours at 110 °C in an oven.

Biochar/ Ni (II) Preparation

The wet impregnation approach was used to modify the Pulungan et al. [27] process, which is followed in the catalyst synthesis. The metal loaded has a 1% (w/w) concentration. 10 g of biochar material has been heated at 500 ºC for an hour into nitrogen-gas flow as an average velocity of ± 5 ml/sec is loaded with the metal precursor. After five hours of refluxing and stirring at 80 ºC, the combination of precursors of metal, and biochar is dried in an oven set to 120 ºC. Additionally, this metal-impregnated biochar underwent oxidation for two hours at 500 ºC using oxygen gas flowing at a flow rate of ±5 ml/sec until Ni (II) biochar was produced.

Characterization of Biochar/ Ni (II)

The catalysts with a Fourier-transform Infrared spectroscopy (FT-IR, Shimadzu IR Prestige-21), X-ray diffraction equipment (XRD Shimadzu 6100), and X-ray fluorescence (XRF) were used to analyze the catalyst structure.

Results and Discussion

Structural Analysis

The catalyst molecule structure BC is examined using XRD analysis both before and subsequent modification. The diffractogram of the XRD test results is shown in Figure 1. according to the study [28]. A clear carbon deposit peak at $2\theta = 22.6^{o}$ appeared in all catalysts. Graphite formation is indicated by the diffraction peak at approximately $2\theta = 43.12°$ [29,30]. Further supporting the prevalent minimal graphitization along with the regularity degree of biochar are two broad, low-intensity diffraction peaks found at 22.6 and 43.12° corresponding to the (002) and (100) crystal planes being part of the graphite structure [30,31]. In contrast, the Ni metal peak was detected at $2\theta = 43.5^{o}$ in the BC/Ni catalyst [32]. Nickel (ii) nitrate hexahydrate was broken down during the calcination process, as evidenced by the identification of NiO nanoparticles as the Ni metal that developed on the surface of the biochar [33].

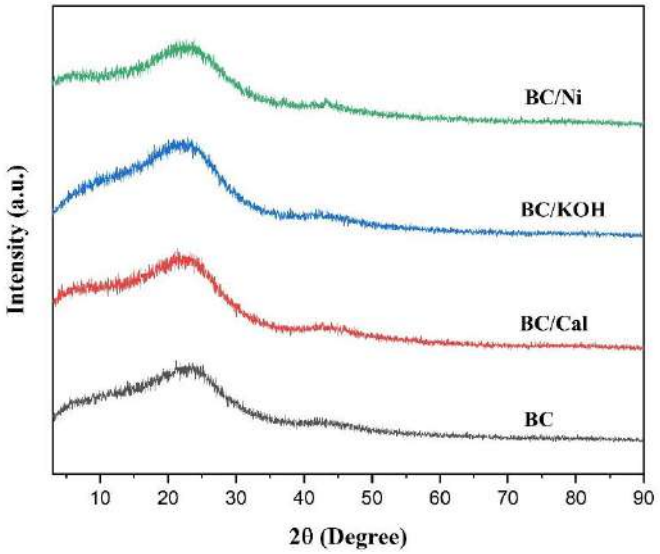

Figure 1. XRD diffractogram analysis of BC, BC/Cal, BC/KOH, and BC/Ni.

Functional Group Analysis

Changes in the BC catalyst's functional groups preceding and following modification are detected using FTIR analysis. The absence of distinctive OH peaks in all catalysts, as seen in Figure 2, indicates the pyrolysis process effectively inhibited the development of the water-based phase in the final biochar. Vibrations from C-H bonds from alkyl and acryl groups were detected by the BC catalyst peak around 2900-3000 cm^{-1}, suggesting the existence of aliphatic components of the biochar structure [34]. Following modification with the inclusion of Ni metal, the vibration associated with the C=O stretching peak was detected at 1690 cm^{-1}. Changes in the BC catalyst's functional groups before and after modification are detected using FTIR analysis. The C=C (aromatic ring) from the lignin structural vibration and the C-O-C vibration from stretching are linked to the peaks at 1579 and 1002 cm^{-1} [35]. Aromatic CH and benzene rings are identified by the peaks at 746, 808, and 860 cm^{-1} [36–38]. The percentages of -C-O-C and C-C bonds increased whereas the content of other functional groups that included oxygen decreased following KOH modification. This suggests that KOH activation dehydrated and decarboxylated the biochar, improving aromatization [39]. Furthermore, upon KOH activation, the strength of the absorption peaks rose, suggesting the creation of additional chemical groups [36]. A large peak at 1224 cm^{-1}, linked to C-O vibrations, and at 594 cm^{-1}, linked to the production of Ni-O-C bonds created by NiO and support by oxygen bridges, were seen in the BC/Ni catalyst enhanced with Ni metal support. Electrostatic attraction and polarization cause cations to interact with components that have π-rich electron configurations in the Ni^{2+}-π association process. The formation of a broad C-O peak in BC/Ni can be seen following the metal adsorption process because the aromatic organization in biochar is the primary π donor in the Ni^{2+} process. The cation-π communication is a strong intermolecular relationship among cations and aromatic systems [34,40].

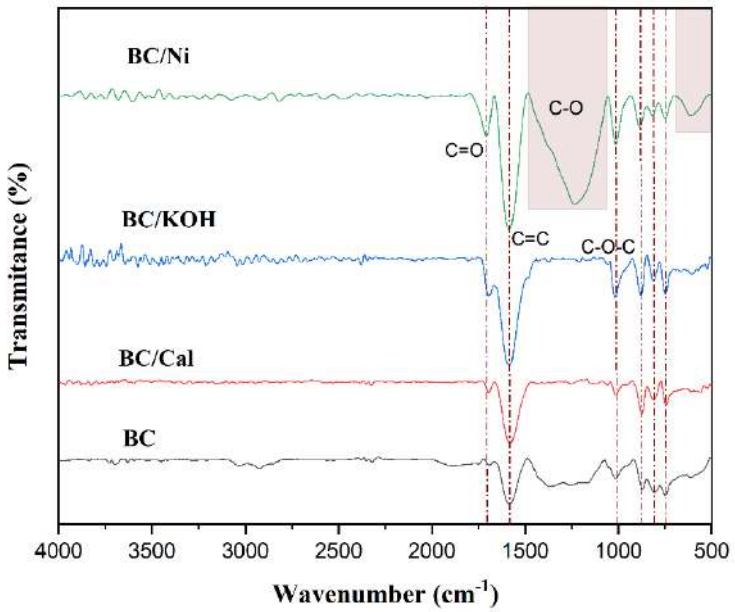

Figure 2. Fourier-Transform Infrared Spectroscopy (FTIR) of BC, BC/Cal, BC/KOH, BC/Ni.

Component Analysis

The elements present in the biochar both before and after alteration were identified by X-ray fluorescence (XRF) analysis, and the results are listed in Table 1. According to Table 1, BC without modification has the highest concentrations of numerous metal minerals, including potassium (2.17%) and aluminum (1.51%). On BC, the metal impregnation procedure has been completed. It is understood that 1.35 % of the BC terrain was made up of metal. The mass achieved is roughly equal to the goal for the metal instilled in BC, which is 1%, and it correlates with the earlier XRD and FTIR data analysis detecting the presence of Ni metal. This indicates that the wet impregnation approach worked in accelerating the metal development process. The abundance of potassium (K), magnesium (Mg), manganese (Mn), to iron (Fe) elements in biochar, in addition to Ni metal, has a beneficial effect on raising the reaction rate to speed up the conversion process and produce gas [41]. Conversely, biochar is regarded as a catalytic support; to a certain degree, it can react with H_2O/CO_2 via the Boundouard reaction or water gas reaction to generate more gas products such as H_2, CO, or CO_2 [32].

Table 1. Component Analysis of the Catalyst

Components	Mass (%)			
	BC	BC-Cal	BC-KOH	BC-Ni
Al	1.51	1.57	1.41	1.02
Si	0.236	0.124	0.0559	0.230
P	0.159	0.158	0.125	0.205
S	0.0740	0.120	0.0709	0.218
Cl	0.0805	0.0723	0.0570	0.0322
K	2.17	2.00	1.69	0.473
Ca	0.0606	0.0596	0.0445	0.0833
Cr	0.0038	0.0091	0.0012	0.0207
Mn	0.0013	0.0024	0.0006	0.0114
Fe	0.0634	0.0781	0.0192	0.365
Ni	0.0004	0.0040	0.0010	1.35
Cu	0.0034	0.0038	0.0027	0.0090
Zn	0.0012	0.0016	0.0009	0.0053
Sr	0.0012	0.0007	0.0006	0.0007
Ag	0.0001	0.0001	0.0001	-
Cd	0.0012	-	-	-
Zr	0.0001	0.0001	0.0001	0.0002
Br	0.0002	-	-	-
Rb	0.0026	0.0001	-	-
Mo	-	0.0002	-	0.0003
Co	-	-	-	0.0048

Conclusion

In the study's findings, biochar treated with nickel (Ni) and activated with KOH exhibited improved catalytic qualities. The biochar's graphitic structure was validated by XRD analysis, and the modified sample showed extra NiO peaks, a sign of effective nickel impregnation. Following pyrolysis, FTIR examination revealed the loss of OH groups and the rise in aromatic and aliphatic structures because of KOH activation, which fortified the C-O-C and C-C bonds. According to XRF measurements, the biochar's nickel loading was 1.35%, and the catalytic activity was supported by components including K, Mg, Mn, and Fe. All things considered, this altered biochar demonstrated a great deal of promise for catalytic uses in gas generation and conversion procedures.

Acknowledgments

We would like to acknowledge the Rector of Universitas Negeri Medan (UNIMED) for the funding support in this study through the Applied Product Research scheme, under grant number 0267/UN33.8/PPKM/PPT/2024.

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