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Article Review: An Exploration of the Potential of Biochar-Based Bifunctional Catalysts as A Renewable Energy-Based Fuel Innovation

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Abstract. Palm oil shells, as biomass waste, have great potential to be used as raw material for biochar-based bifunctional catalysts. The aim of this research is to assess the potential of palm shell-based biochar as a bifunctional catalyst carrier in the conversion of biomass into renewable fuel. The method used is a literature review of various related articles, with a focus on the characteristics of biochar, the incorporation of bimetallic metals, and catalyst performance. The results of the discussion show that biochar from palm oil shells has textural properties that support the distribution of the catalyst metal, with a high surface area and optimal pore volume at a certain pyrolysis temperature. Incorporation of bimetallic metals on the biochar surface increases catalytic activity through synergy between metals, which has the potential to increase efficiency in catalytic reactions such as hydrogenation and deoxidation. In conclusion, palm shell-based biochar can be an effective and environmentally friendly alternative catalyst in converting biomass into renewable fuel, by selecting the right metal composition to optimize catalyst performance and prevent clumping of active components.

Key words: Biochar, Biomass, Palm Kernel Shell, Renewable Energy, Catalysts

INTRODUCTION

According to data from Badan Pusat Statistik (2016), there are 25 oil palm-producing districts, and it is predicted that for every ton of fresh fruit bunches processed, 5% of oil palm shell waste will be produced [1]. In reference to the sustainable development goals, numerous efforts can be made to increase the benefits of the palm oil industry by designing a circular economy pathway. In addition to the utilization of palm oil waste and sludge, there is a need to intensify the utilization of solid waste [2]. Oil palm shell waste is a potential material for making activated carbon due to its abundant availability and low production costs, and the products it produces have high economic value. Oil palm shells contain 51.6% carbon C and low ash content, making it a potential material in making activated carbon [3]. Oil palm shells contain 26.16% hemicellulose, 6.92% cellulose, and 53.85% lignin, indicating their potential as a raw material for biochar production [4].

Biomass has been identified as a potential resource for the production of biochar catalysts, which have been shown to address the challenges currently facing modern society, such as the need to meet growing energy demands while reducing environmental degradation [5]. The use of biochar-based catalysts has been demonstrated to be advantageous due to the presence of inorganic groups, such as potassium (K) and iron (Fe), on their surface. These groups can be utilized in processes such as tar cracking. Additionally, biochar catalysts contain functional groups that facilitate the adsorption of metal precursors, further enhancing their utility. The production of biochar can be achieved through lignocellulosic biomass, non-lignocellulosic biomass, and lignin-based biomass [6].In addition to these advantages, biochar exhibits several benefits when compared to conventional catalysts, including: Firstly, biochar is characterized by its ease of processing. Secondly, the raw materials required for its production are renewable. Thirdly, biochar can be produced either as the primary byproduct of biomass carbonization or as a byproduct of fast pyrolysis or biomass gasification. Finally, the physicochemical characteristics of biochar can be readily tailored to suit specific applications. Consequently, biochar's advantageous properties position it as a highly effective heterogeneous catalyst [7].

Catalysts play a significant role in various fields, including the chemical industry and petrochemicals. These agents have been shown to enhance process efficiency, expedite reaction rates, and augment the quantity of products generated [8]. The judicious selection of catalysts is paramount to prevent the agglomeration of metal active components during the catalytic process. One solution to this challenge is the use of a metal catalyst carrier.

The metal-bearing catalyst is prepared by reducing the metal that has been charged or incorporated into the carrier material. The metal is then heated and calcined to modify its chemical composition. The metal is subsequently oxidized and reduced. The incorporation of metal oxides on the biochar surface has been demonstrated to enhance the active sites of the catalytic process, thereby presenting a novel catalyst model for hydro-cracking and isomerization processes. The incorporation of bimetallic oxides on the biochar surface has garnered attention as a model heterogeneous catalyst [10].

The objective of this article is to evaluate the capacity of palm kernel shell-based biochar to function as a multifunctional catalyst carrier material. This review concentrates on the properties of biochar, the incorporation of bimetallic metals, and the performance of catalysts in facilitating the conversion of biomass into renewable fuels.

METHODS

The methodology employed entails a comprehensive literature review, encompassing a diverse array of pertinent articles that delve into the potential of bio-char-based bifunctional catalysts in the hydrocracking process for biofuel production. The discourse in the article is structured in a narrative format, with the objective of elucidating the outcomes obtained from the utilization of bio-char-based bifunctional catalysts.

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RESULTS AND DISCUSSION

The Potential of Oil Palm Shell-Based Biochar

Oil palm shells represent a promising source of biomass for the production of biochar catalysts. Palm kernel shells are a suitable fuel or char material due to their high lignocellulose content. Research on the utilization of char from oil palm shells is currently expanding. For instance, Endriani et al. (2013) employed char from oil palm shells to mitigate soil acidity in planting media [11]. Similarly, Santi's research (2017) examined the utilization of char, derived from the pyrolysis of oil palm shells, to enhance nutrient uptake and carbon sequestration in soil media, demonstrating positive outcomes for oil palm plant productivity [12]. Sukmawati's (2020) study examined the chemical characteristics of biochar derived from diverse biomasses, including corn cobs, shells, and empty palm bunches. The findings indicated that oil palm shells exhibited the most substantial mass loss of 32.02%, concurrently generating the highest volatile substances at 27.74%. This observation underscores the correlation between enhanced mass loss and volatile content with augmented adsorption properties and catalytic activity.

The pyrolysis of palm kernel shell-derived char resulted in a bio-char yield of up to 89 wt%. Furthermore, the investigation revealed that catalysts derived from palm kernel shell bio-char exhibited a remarkable methane conversion efficiency, reaching up to 43%, with a catalyst product yield of approximately 22%. These findings suggest that palm kernel shell bio-char is a promising catalyst support material [13].

Table 1. The textural properties of biochar derived from oil palm shells, measured at various temperatures during the pyrolysis process.

	600ºC	**650ºC**	**700ºC**	**750ºC**	**800ºC**	**850ºC**
Surface Area (m^2/g)	36,70	365,52	300.92	269,87	248,27	87,52
Radius Pori (nm)	4,72	1,97	2,08	2,13	2,28	3,06
Total pore volume	0,09	0,18	0,16	0,14	0,14	0,067
Pore Size	1325,13	3,69	3,29	3,71	3,69	14,83

(Wang *et al*., 2018)

As demonstrated in Table 1, bio-char with optimal textural properties was obtained at a temperature of 6500C, exhibiting a substantial surface area of 365.52 m2/g, a diminutive pore radius of 1.97 nm, and a maximum pore volume of 0.18 cm3/g [14]. This condition is ideal as a catalyst support, as it allows for optimal distribution of the active catalyst metal.

Bimetallic Metal Incorporation on Biochar

Bimetallic metals have the potential to enhance catalytic activity through a unique synergistic effect. Two methodologies are employed to synthesize metal catalysts/biochar from biomass: the two-stage method and the in-situ carbonization method. The two-stage method commences with the conversion of biomass into porous carbon materials through a high-temperature activation process, followed by the loading of metals onto the carbon materials through a calcination method. The in-situ carbonization method, on the other hand, commences with the carbon precursor mixed with active metal salts, followed by calcination at a specific temperature in an inert atmosphere [15]. Sadjadi et al. (2019) utilized halloysite (Hal) and biochar derived from eggplant as supporting materials to produce two types of Pd-based catalysts with equivalent metal loadings: Pd/Hal and Pd/char. In the aniline hydrogenation test at 25°C and 1 bar H2 pressure for 1 hour, the aniline conversion reached 30% for Pd/Hal and 40% for Pd/char. This discrepancy can be attributed to the significantly larger particle size of Pd in Pd/Hal (4.8 ± 1.3 nm) compared to Pd/bio-char (3.6 ± 1.1 nm) [16].

In a study by Jiang et al. (2018), the hydrogenation of p-nitrobenzene was conducted at 25 °C using a catalyst composed of 1.58 wt% Pd@Fe3O4-C and NaBH4 as a hydrogen donor. The resultant conversion reached 100% within a mere three minutes, a feat that surpassed the performance of the 5 wt% Pd/C catalyst commonly used in commercial settings. This enhancement was attributed to the increase of oxygen groups in the biochar following the addition of iron salts, which improved the dispersion of Pd metal and reduced the particle size of Pd.The selectivity of hydrogenation is influenced by the particle size of the metal on the catalyst.Generally, stronger interactions between the metal and the support improve the dispersion of active sites, although in some cases the opposite is true [17].

Utilization of Metal-embedded Biochar Catalysts in Various Catalytic Processes

Biochar possesses physicochemical properties that facilitate its role in various catalytic reactions. In a seminal study, Shen and Yoshikawa (2014) examined biochar-based catalysts derived from nickel-embedded rice husk, exploring their application in biomass hydro-enhancement. Hail's findings indicated that biochar possesses the capacity to deoxidize, resulting in the formation of nickel-based catalysts. The high oxygen content and the ideal pore structure of biochar facilitate the combination of non-precious metals, resulting in the production of non-precious

metal/biochar catalysts that show considerable promise for future development [18].

In non-precious metal catalytic systems, nitrogen-containing carbon supports are typically selected to achieve optimal catalytic performance through the synergistic effect of N atoms and non-metal elements. Yuan et al. (2018) synthesized carbalt-based catalysts on nitrogen-doped carbon. The resulting Co@NC catalyst exhibited remarkable catalytic efficiency for the hydrogen transfer reaction of various functional nitroarene compounds with formic acid (FA) as a hydrogen donor in an aqueous solution. This reaction produced aniline with a conversion rate of more than 99.9% for 6 hours at 90°C. The nitrogen-carbon layer divides the cobalt nanoparticles in space, effectively avoiding agglomeration, sintering, and loss of Co. In addition, the strong interaction between the cobalt nanoparticles and the carbon-nitrogen layer enhances the metalloid properties of the carbon-nitrogen layer surface. Nitrogen atoms, which possess high electronegativity, function as basic sites to absorb protons from FA, thereby enabling the capture of H1 ions as opposed to basic substances within the reaction system. Concurrently, cobalt can interact with HCOO- to form an intermediate in the form of cobalt formate, ensuring a synergistic effect in the catalytic process [19].

Bimetallic catalysts possess the capacity to amalgamate the properties of two metals, thereby enhancing their catalytic performance. De et al. (2015) utilized a Cu-Ru/C catalyst, leveraging the hydrogenolysis properties of Cu and the chloride resistance of Ru. This catalyst has been shown to hydrogenate HMF in n-butanol at 6.8 bar H2 pressure, achieving a DMF selectivity of up to 71% [20,21]. Sun et al. (2013) observed that a Pd-Fe/C catalyst could completely decarboxylate phenolic compounds at 450 °C, yielding an 83.2% yield of aromatic compounds, which is significantly higher than the 43.3% yield achieved with Fe/C. The presence of palladium (Pd) facilitates the reduction of FeO to Fe, resulting in the formation of a Pd-Fe alloy. This phenomenon enhances phenol adsorption and weakens the C-O bond, thereby making Fe the primary active site, while Pd plays a supportive role through H2 dissociation during hydrogenation [22]. In a related study, Zhu et al. (2019) synthesized a 5 wt% Cu-15 wt% Ni/BC catalyst, prepared by loading Cu and Ni on biochar via wet impregnation, resulting in complete conversion and 91.3% selectivity for 2,5-dimethylfurfuryl alcohol from HMF at 220°C and 3 MPa H2 pressure for 6 h [23]. However, it was observed that excessive Cu loading led to a decline in catalyst efficiency. This is attributed to the fact that the CuO active site, which functions as an electron acceptor to dissociate hydrogen, was occluded. Consequently, this resulted in a decrease in the turnover rate (TOF). Conversely, an augmentation in Ni charge has been demonstrated to enhance the quantity of hydrogenation sites, fortify the interaction between Ni and Cu, impede metal sintering, and diminish metal particle size, thereby enhancing catalyst reactivity. However, it should be noted that the utilization of an excess of the second metal can result in the agglomeration of the active constituents, thereby diminishing the dispersion of the metal and consequently reducing the efficacy of the catalyst's active sites [24]. Consequently, the optimization of metal composition emerges as a pivotal strategy to ensure the maximization of the performance of bimetallic catalysts.

CONCLUSIONS

A comprehensive review of the extant literature reveals that palm kernel shells possess considerable promise as a source of raw materials for the production of bio-char-based bifunctional catalysts. The distribution of catalyst metals is favored by optimal physicochemical properties at specific pyrolysis temperatures. The incorporation of bimetallic metals in bio-char has been demonstrated to enhance catalytic activity through the synergistic effect between the metals and the carbon support. It is therefore imperative to select the most appropriate metal composition to optimize catalyst performance and prevent sintering.

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