Editorial Corner

Biochar as a Catalyst in Biorefineries: A Sustainable Recovery of Waste Materials

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The concept of biorefinery has gained significant attention in recent years to tackle the challenges of climate change and resource depletion faced by the world [1], [2]. Biorefineries have the potential to transform naturally abundant biomass into an array of valuable products, including biofuels, biochemicals, and biomaterials [1], [3].

Biochar is a carbon-rich material typically produced from biomass through pyrolysis. Owing to its unique characteristics, such as large surface area, tunable porous structure, mechanical and thermal stability, and acid/alkali resistance, it is recognized as a promising catalyst for various biorefinery processes [4]–[6]. Moreover, biochar produced from biomass can reduce the carbon footprint and help to achieve sustainability of the entire biorefinery process [7].

In pyrolysis, the biomass is subjected to high temperatures (300–900 °C) in an oxygen-free atmosphere to produce solid, liquid and gaseous fractions [4], [8]. The porous and highly stable solid fraction obtained is called biochar [9], [10]. Traditionally, biochar is used as a soil conditioner to improve soil fertility and carbon sequestration. In recent years, its applications have extended to various industrial and environmental fields, including biorefinery processes [11], [12].

Biochar based catalysts are widely used in several refining processes including hydrothermal liquefaction of biomass [4], [7], isomerization and dehydration [12], catalytic pyrolysis and gasification [4], [7], transesterification of vegetable oils for biodiesel production [4], [12], biogas production [12], hydrogenation [12], catalytic cracking [4], catalytic reforming [4], and upgradation of biomass [12].

To improve the performance, the biochar is subjected to physical and/or chemical modification depending on the intended applications [4]. Steam and CO_2 are typically used to activate the biochar produced by pyrolysis. Steam and CO_2 activation results in an increase in surface area and porosity of the biochar. It is reported that the surface area increases up to 200 times after gas activation [12]. Additionally, CO_2 activation introduces surface defects and oxygen-containing functional groups. In chemical modification, NaOH, KOH, sulfuric acid, phosphoric acid, chlorosulfonic acid and $ZnCl_2$ are commonly used for biochar activation. The loading ratio of the activating agent, impregnation time, activation temperature and activation temperature influence the activation efficiency [4], [12]. Depending on the activating agent used, surface functional groups such as -OH, -SO_3H, -COOH, etc., are added to the biochar. Introducing these functional groups particularly favors acid catalyst reactions, such as esterification and hydrolysis. It has been reported that $ZnCl_2$ results in swelling of biochar during activation and, hence results in the expansion of pores.

Alternatively, loading of biochar with metals (Ag, Cu, Fe, Ni, Sn, Tn, Zn, Zr), functional materials (carbon nanotubes, graphene, graphene oxide, and zero valent iron) and few heteroatoms (B, N, P and S) can improve the catalytic performance of the biochar [4]. Metal impregnation increases the active sites (for ex. Lewis acid sites) on biochar [12]. Introducing Lewis acidity and Bronsted acidity improves the catalytic efficiency of the biochar in heterogeneous reactions, such as transesterification reactions and hence activated biochar is popular in biodiesel production. In biomass valorization, Bronsted to Lewis acid ratio and hydrophobicity play significant role in controlling the reaction rate kinetics [12]. These properties of biochar are tailored during their production. Thus, biochar has the potential to replace the commonly used solid acid catalysts [13]. Also, for certain metal catalysts biochar acts as a stable support.

Another important operation in biorefinery is biomass upgradation. Biochar can be used as a catalyst for biomass valorization by facilitating processes like deoxygenation and decarboxylation [4], [7]. Owing to the carbonaceous nature of biochar, it acts as a reducing agent and enables the removal of oxygen-containing functional groups from biomass to enhance the quality and value of the generated products.

Thus, due to the versatile roles of biochar in biorefinery applications, it is emerging as a valuable catalyst in the transition towards more sustainable and environmentally friendly resource recovery. As the biorefinery industry evolves continuously, the innovative use of biochar catalysts offers a promising avenue for the creation of wealth from waste, reducing carbon emissions, and promoting circular and sustainable bioeconomy.

References

[1] M. Sriariyanun, M. P. Gundupalli, V. Phakeenuya, T. Phusamtisampa, Y. Cheng, and P. Venkatachalam, "Biorefinery approaches for production of cellulosic ethanol fuel using recombinant engineered microorganisms," *Journal of Applied Science and Engineering*, vol. 27, pp. 1985–2005, 2023.

[2] Y.-S. Cheng, P. Mutrakulcharoen, S. Chuetor, K. Cheenkachorn, P. Tantayotai, E. J. Panakkal, and M. Sriariyanun, "Recent situation and progress in biorefining process of lignocellulosic biomass: Toward green economy," *Applied Science and Engineering Progress*, vol. 13, no. 4, pp. 299–311, 2020, doi : 10.14416/j.asep.2020.08.002.

[3] T. Ruensodsai and M. Sriariyanun, "Sustainable development and progress of lignocellulose conversion to platform chemicals," *The Journal of King Mongkut's University of Technology North Bangkok*, vol. 32, no. 4, pp. 1–4, 2022, doi: 10.14416/j.kmutnb.2022.03.001 (in Thai).

[4] R. Shan, J. Han, J. Gu, H. Yuan, B. Luo, and Y. Chen, "A review of recent developments in catalytic applications of biochar-based materials," *Resources, Conservation and Recycling*, vol. 162, Mar. 2020, Art. no. 105036.

[5] F. R. Oliveira, A. K. Patel, D. P. Jaisi, S. Adhikari, H. Lu, and S. K. Khanal, "Environmental application of biochar: Current status and perspectives," *Bioresource Technology*, vol. 246, pp. 110–122, Aug. 2017.

[6] R.-Z. Wang, D.-L. Huang, Y.-G. Liu, C. Zhang, C. Lai, X. Wang, G.-M. Zeng, X.-M. Gong, A. Duan, Q. Zhang , and P. Xu, "Recent advances in biochar-based catalysts: Properties, applications and mechanisms for pollution remediation," *Chemical Engineering Journal*, vol. 371, pp. 380–403, Sep. 2019.

[7] X. Yuan, Y. Cao, J. Li, A. K. Patel, C.-D. Dong, X. Jin, C. Gu, A. C.K. Yip, D. C.W. Tsang, and Y. Sik Ok, "Recent advancements and challenges in emerging applications of biochar-based catalysts," *Biotechnology Advances*, vol. 67, Oct. 2023, Art. no. 108181.

[8] S. Krishnan, S. Sivaraman, S. Jothipandiyan, P. Venkatachalam, S. Ramiah Shanmugam, and N. Paramasivam, "Bioprospecting of aqueous phase from pyrolysis of plant waste residues to disrupt MRSA biofilms," *Biofouling*, vol. 39, no. 2, pp. 231–243, 2023.

[9] S. Subramaniyasharma, S. R. Shanmugam, V. Bhuvaneswari, V. Ponnusami, and S.

Rangabhashiyam, “Pyrolysis of an invasive weed Prosopis juliflora wood biomass for the adsorptive removal of ciprofloxacin,” *Biomass Conversion and Biorefinery*, pp. 1–16, 2023, Art. no. 0123456789.

[10] H. M. Perera, A. Upamali Rajapaksha, S. Liyanage, A. Ekanayake, R. Selvasembian, A. Daverey, and M. Vithanage, “Enhanced adsorptive removal of hexavalent chromium in aqueous media using chitosan-modified biochar: Synthesis, sorption mechanism, and reusability,” *Environmental Research*, vol. 231, Aug. 2023, Art. no. 115982.

[11] Z. Zhang, Z. Zhu, B. Shen, and L. Liu, “Insights into biochar and hydrochar production and applications: A review,” *Energy*, vol. 171, pp. 581–598, 2019.

[12] X. Xiong, I. K. M. Yu, L. Cao, D. C. W. Tsang, S. Zhang, and Y. S. Ok, “A review of biochar-based catalysts for chemical synthesis, biofuel production, and pollution control,” *Bioresource Technology*, vol. 246, pp. 254–270, 2017.

[13] H. I. Mahdi, N. N. Ramlee, J. Leandro da Silva Duarte, Y.-S. Cheng, R. Selvasembian, F. Amir, L. Hadlich de Oliveira, N. I. W. Azelee, L. Meili, and G. Rangasamy, “A comprehensive review on nanocatalysts and nanobiocatalysts for biodiesel production in Indonesia, Malaysia, Brazil and USA,” *Chemosphere*, vol. 319, Apr. 2023, Art. no. 138003.

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