EFFECT OF NbZn CATALYST ON PRODUCTION OF ALDEHYDE-RICH BIO-OIL

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ABSTRACT

This work evaluates the influence of NbZn catalysts prepared at different temperatures on the composition of bio-oil from babassu residue. Faced with the demand for renewable sources of fuels and chemicals, biomass pyrolysis has stood out due to its great production potential of both, biofuels and chemicals. Catalytic pyrolysis has proven to be of great relevance in the production of bio-oil composed of chemicals with high-added value given the selectivity of the catalysts. In this work, it was possible to observe that the use of NbZn in the pyrolysis of babassu residue increased the production of high-added value aldehydes, such as acetaldehyde and hydroxyacetaldehyde.

Keywords: Pyrolysis. Catalyst. NbZn. Bio-oil. Babassu.

1 INTRODUCTION

In recent years, biomass has gained increasing prominence as a raw material for various chemical products due to its environmentally friendly nature.[1] Among the biomass transformation processes, pyrolysis has stood out given the versatility of products, generating solid, liquid (bio-oil) and gases that can be applied to energy production or even to the production of chemical products.[2] Pyrolysis is a complex, multi-step thermoconversion process where the raw material is degraded through heating without oxygen.[3] Bio-oil produced from pyrolysis is an interesting alternative to replace fossil fuels once it comes from renewable sources, although its undesired properties to application as biofuel such as high oxygen and water content, high viscosity and corrosivity[4].However, bio-oil can also be applied as a renewable source of high-value chemicals such as hydrocarbons, aromatics and phenolics[5,6].

Given that the properties of pyrolysis products are influenced by operating conditions[2], catalytic pyrolysis can be an available technology for producing chemicals with high added value.[1] The association of catalytic pyrolysis with biomass can be promising for high-value organic compounds production once biomass, as raw material can make the production of these chemicals cheaper and more sustainable.[1] Among catalysts already studied, niobium-based catalysts, such as Nb_2O_5, stand out for their high selectivity and stability[7,8].

To evaluate the effect of NbZn catalysts prepared, from niobium oxide and zinc oxide, at different temperatures on the composition of bio-oil, in this work pyrolysis tests were carried out using babassu residue (BB) as biomass. In Brazil, babassu is the source of income for many rural families, mainly from the northeast of Brazil.[9] The figure of the women breakers (summed more than 300 thousand workers) is a cultural symbol of this agroextractivist activity[10]. This work aims to show the production of high-value chemicals from babassu residue and the influence of NbZn catalysts on this production.

2 MATERIAL & METHODS

NbZn catalysts were synthesized from a mechanical mixture of niobium oxide and zinc oxide. The resulting solid was separated into three samples that were calcined at different temperatures, respectively (600, 800 and 1000 °C). The solids were characterized by X-ray diffraction.

Pyrolysis essays were carried out in a pyrolysis reactor coupled to a gas chromatograph with mass spectroscopy detection (Py-GC-MS). The samples were the raw biomass (sample BB), and the biomass mixed with the catalysts in a proportion of 50%:50% (w/w): sample BB+NbZn600 (babassu + NbZn calcined at 600 °C); sample BB+NbZn800 (babassu + NbZn calcined at 800 °C); sample BB+NbZn1000 (babassu + NbZn calcined at 1000 °C).

Pyrolysis was carried out at 550 °C using a pyrolysis apparatus Frontier®, model EGA-PY-3030D, coupled to a GC-MS Shimadzu®, model QP-2020 NX (column RTX1701 60 m, 0.25 mm, 0.25 µm at 20 to 280 °C). Helium was the inert gas. Identification of the peaks with a minimum of 80% similarity.

3 RESULTS & DISCUSSION

The X-ray diffraction showed that the catalysts mainly presented crystalline structures of the O-$Zn_3Nb_2O_8$ type. The increase in temperature promoted the crystallinity of the solids without significant phase segregation.

The pyrolysis products of the samples were separated into nine functional groups as shown in Figure 1. Among the functional groups in the bio-oil from raw biomass (BB), the production of aldehydes, sugars and N-components (here included in the group entitled others) stands out. The association of biomass with catalysts increased the production of aldehydes.

The use of the NbZn600 catalyst promoted a 71% increase in aldehyde production, while the NbZn800 and NbZn1000 catalysts promoted a 43% and 33% increase, respectively. Aldehydes are mainly products of the degradation of hemicellulose and cellulose[11] and N-components are mainly generated from proteins[12].

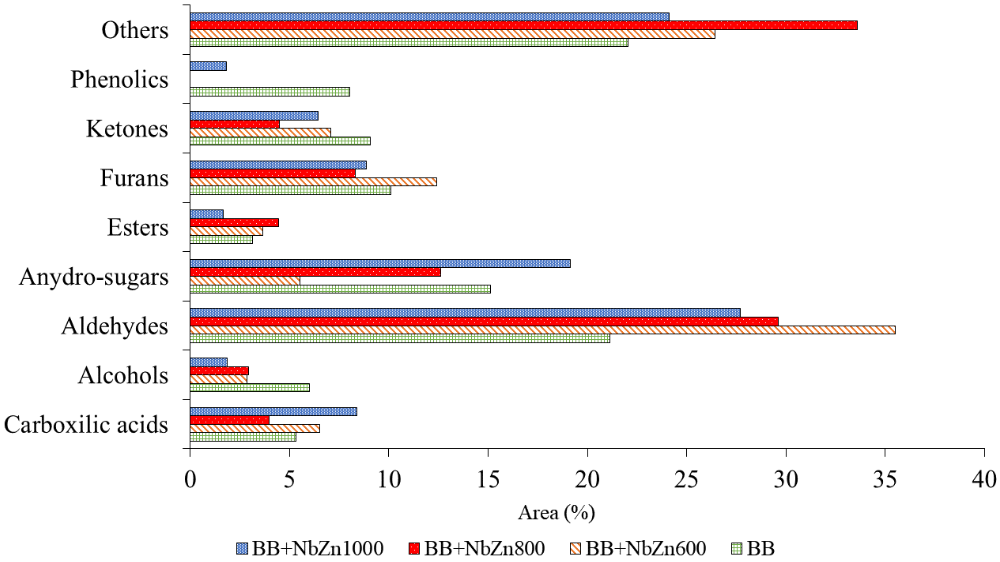

Figure 1 Functional groups of the bio-oil.

Modified niobium is effective in breaking C-O bonds.[13] Calcined under milder conditions, NbZn600 has shown to be more effective in producing bio-oil rich in aldehydes, possibly from breaking this type of bond in hemicellulose and cellulose. The main aldehydes produced are shown in Table 1.

It is possible to notice among the aldehydes produced, the presence of compounds with high added value such as acetaldehyde and hydroxyacetaldehyde. The similarity between the products obtained from pyrolysis highlights the function of accelerating the production of components, without extensively modifying the biomass degradation mechanism.

Table 1 Main aldehydes produced by pyrolysis for each sample.

Sample	%Formaldehyde	%Acetaldehyde	%Methyl glyoxal	%Hydroxyacetaldehyde
BB	3	1	5	11
BB+NbZn600	7	5	11	13
BB+NbZn800	0	3	10	17
BB+NbZn1000	4	2	7	15

4 CONCLUSION

This work shows that NbZn catalysts are potentially effective in increasing the production of aldehydes with high-added value. The results showed that the calcination temperature influenced the bio-oil composition. The catalyst prepared at the lowest calcination temperature promoted the production of aldehydes.

REFERENCES

1 LI, B.-Z., BI, D.-M., DONG, Q., LI, Y.-J., LIU, Y.-Y., HUANG, F.-P. 2020. BioResources. 15(3). 5666–5678.
2 CHENG, S., SHU, J., XIA, H., WANG, S., ZHANG, L., PENG, J., LI, C., JIANG, X., ZHANG, Q. 2019. Appl Therm Eng. 148. 1164–1170.
3 AL-RUMAIHI, A., SHAHBAZ, M., MCKAY, G., MACKEY, H., AL-ANSARI, T. 2022. Renew. Sustain. Energy Rev. 167.
4 SABER, M., NAKHSHINIEV, B., YOSHIKAWA, K. 2016. Renew Sustain Energy Rev. 58. 918–930.
5 KIM, J. Y., MOON, J., LEE, J. H., JIN, X., CHOI, J. W. 2020. Fuel, 279.
6 WANG, H., HAN, H., SUN, E., ZHANG, Y., LI, J., CHEN, Y., SONG, H., ZHAO, H., KANG, Y. 2019. J. Anal. Appl. Pyrolysis. 142.
7 SOUSA, L. F. (2014). Investigação *in situ* do efeito SMSI em catalisadores Ni/Nb_2O_5 e sua influência sobre a reação de oxidação parcial do metano. Universidade Federal do Rio de Janeiro. Rio de Janeiro.
8 ZIOLEK, M. 2003. Catalysis Today.78 (1-4). 47–64. 28.
9 ROCHA, M. R. T. 2004. Agricultura Familiar: Pesquisa, Formação e Desenvolvimento. 4 (4).

10 MATOS, F., SHIRAISHI, J., RAMOS, V. 2015. ActionAid Brasil.
11 ZHANG, L., LIU, J., ZHANG, Z., YANG, Z., WANG, X., LI, D., LIN, R. 2023. Biomass Conv. Bioref.13(13). 11789–11802.
12 SAN-EMETERIO, L. M., LÓPEZ-NÚÑEZ, R., GONZÁLEZ-VILA, F. J., GONZÁLEZ-PÉREZ, J. A. 2021. Appl. Sci. 11(15). 6684.
13 LI, Z., ZHANG, H., YANG, D., HU, Z., WANG, F., ZHANG, Z. 2023. Molecules, 28 (10).

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