FAST PYROLYSIS AND CATALYTIC UPGRADING OF CORNCOB BIOMASS FOR FUEL PRODUCTION

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ABSTRACT: The thermochemical conversion of corncob through fast pyrolysis, follow by catalytic hydrotreatment (HDT) of the fast pyrolysis bio-oil (FPBO), was investigated in this study. The corncob biomass was submitted to the fast pyrolysis treatment at 550 °C with a feeding rate of 10 kg/h for FPBO production. The FPBO underwent catalytic HDT at 250 °C for 50 minutes, using the Pd-Nb catalyst with the goal of reducing the oxygen content of this fraction while improving the overall FPBO properties. The C/O content was 1.23 on the raw corncob 2.11 on the bio-oil and after the HDT treatment, the C/O content increased to 3.17. After the HDT treatment, compounds known to cause FPBO instability, such as aldehydes and carbohydrates were completely converted. Ketones content, on the other hand, was reduced by 54% wt. Therefore, the thermochemical conversion route seems to be a promising alternative for valorization of corn cob, a high lignin content biomass produced in high volumes in emerging countries such as Brazil, with potential to produce renewable fuel if an upgrading step is combined with the fast pyrolysis conversion technology.
Keywords: corncob, fast pyrolysis, catalytic conversion, liquid biofuel

1 INTRODUCTION

Fast pyrolysis and catalytic upgrading of corncob biomass have emerged as promising technologies to produce renewable fuels. Corncob biomass, a largely available agricultural residue in Brazil, offers a sustainable feedstock for fuel production. Fast pyrolysis involves the fast thermal decomposition of corncob biomass to obtain FPBO, while catalytic HDT enhances its quality by modifying its composition and properties. These technologies combined aim to overcome the limitations of FPBO, such as high oxygen content and instability, making it suitable for various fuel applications and platform chemicals obtention. The utilization of corncob biomass for fuel production presents environmental benefits, reduces dependence on fossil fuels, and promotes rural development. This research aims to explore the potential of fast pyrolysis and catalytic upgrading of corncob biomass, contributing to the development of sustainable and environmentally friendly fuel sources, as well as obtain different green platform chemicals.

2 MATERIALS AND METHODS

2.1 Pyrolysis oil obtention

The fast pyrolysis of the corncob was be conducted at the Phyton process development unit located at the Institute of Catalysis Research and Technology, Germany [1]. Dried (moisture content below 10 wt.%) and milled (<1.6 mm) corncob was submitted to fast pyrolysis at 500 °C. The FPBO was obtained by condensation of organic vapors at 90 °C (FPBO) and was further used as feedstock for the catalytic hydrotreatment, described in the section 2.2.

2.2 Catalytic Hydrotreatment of the FPBO

The catalytic hydrogenation was performed in a high pressure inox reactor. An amount of 50g of the FPBO obtained as described in the item 2.1 was used in the reaction, with 2 g of Pd-Ni catalyst. The reactor was pressurized with H_2 until reaches 80 bar. The reactor was heated to 250°C with a heating rate of 3.3°C/min, and maintained at 250°C for 50 minutes. After 02 hours of reaction, the reactor was cooled using compressed air until 50 °C, followed by an ice-cold bath until 10 °C.

From HDT products were collected three phases: the heavy oily phase (upgraded bio-oil - UO), the light aqueous phase and the solids (including the spent catalyst).

2.3 Products characterization

The FPBO and the heavy phase of the catalytic hydrotreatment were characterized by a variety of analytical techniques (elemental analysis, H_2O content and gas chromatography with mass spectrometry (GC-MS) and gas chromatography with flame chromatography ionization detector (GC-FID)) [2].

3 RESULTS

3.1 Fast pyrolysis of corn bob

The table 1 compares the elemental composition of the corncob before the fast pyrolysis treatment, the FPBO obtained from the fast pyrolysis as well as the UO elemental composition and each Higher Heating Value (HHV).

Table 1: Element composition and Higher Heating Value of the dry samples

	In natura Corncob	FPBO	UO
C (wt.%)	51.3	62.5	68.8
H (wt.%)	7	7.5	7.8
N (wt.%)	0.1	0.4	0.4
O (wt.%)	41.6	29.6	23
Water content (wt.%)	7.10	8.8	8.0
HHV (MJ/kg)	21.9	27.6	30.7

After the fast pyrolysis reaction, the FPBO obtained presented higher carbon and lower oxygen when compared to its *in natura* composition, resulting on an increase of 71% of the HHV. Almost 43% wt. of the *in natura* corncob were converted in FPBO, 6% wt. were converted in aqueous condensate, almost 13% wt. in char and the other 39% wt. were converted in gas. The water content of the FPBO were also 8.8% wt.

3.3 Catalytic Hydrotreatment

As shown in table 1, after the HDT, the carbon content increased while the oxygen content decreased. The increased in the carbon content was around 10% wt., while the oxygen content decreased around 23% wt. after the HDT reaction. The C/O ratio increased approx. 40% after HDT, which contributed to the increase of the higher heating value of the UO by 11%. The reaction to produce the UO obtained a yield of 72% wt., and the water concentration reduced from 8.8% wt. to 8.0% wt. after the upgrade with hydrogen and the Pd-Ni catalyst.

The oxygen reduction on the bio-oil occurs due to the conversion of oxygen compounds present in the bio-oil, such as sugars, ketones, and aldehydes, into other non-oxygen compounds, or into smaller and soluble in water molecules, which can be removed in the light aqueous phase of the hydrotreatment products [3].

Figure 1 has the composition of oxygenated compounds present in the FPBO before and after the HDT.

The reduction of oxygen compounds in the bio-oil by converting or solubilizing in water the aldehydes and other reactive compounds increases the bio-oil storage stability, due to the reduction of the oxidative process that might alter the bio-oil viscosity [3], [4]. The Figure 1 shows that the aldehydens and sugars were completly removed on the heavy oily phase of the upgraded bio-oil, and 54% wt. of the ketones was removed.

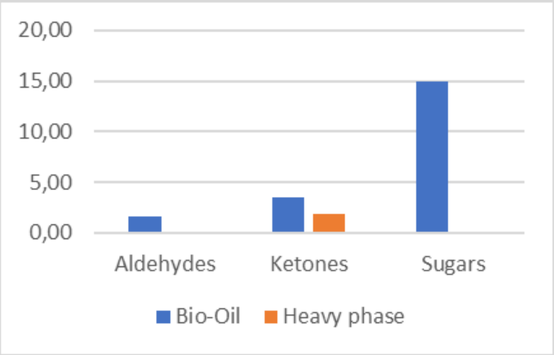

Figure 1: Oxygenated compounds consumption after hydrotreatment

Even though the compounds that caused instability on the bio-oil, mainly aldehydes, ketones and sugars, were converted, the aromatic compounds (phenols, guaiacols and syringols) slightly increased their concentration after the catalytic hydrotreatment, as shown in the figure 2.

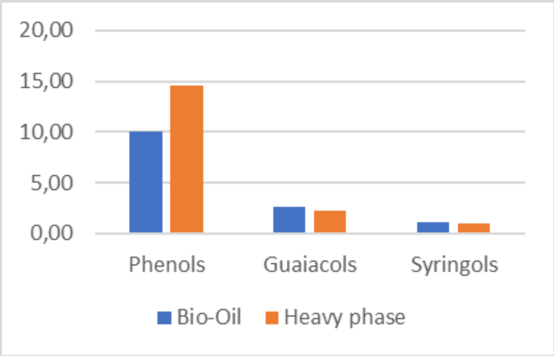

Figure 2: Phenolic compounds concentration before and after the hydrotreatment

The phenols increased its composition on the upgraded bio-oil around 46% wt., and the concentration of guaiacols and syringols was reduced in the upgraded bio-oil by 15% wt. and 17.5% wt., respectively. Phenolic compounds are the ones with higher concentration around the aromatic compounds of this upgraded bio-oil, corresponding to 9.64% wt. of the upgraded bio-oil mass.

4 CONCLUSIONS

The combination of fast pyrolysis and catalytic upgrading presented an increase on the bio-oil's HHV of 11%, as well as reducing all the aldehydes, sugars and 54% of the ketones, as well as reducing the water content, which shows a promising option for the efficient utilization of corn cob, a biomass abundant in Brazil. This approach has the potential to generate renewable fuel and potentially obtain different green platform chemicals by integrating an upgrading process with the fast pyrolysis conversion technology.

5 REFERENCES

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