Thermal and catalytic pyrolysis of sisal residue

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Abstract: In this study residue of sisal biomass was processed by fast pyrolysis in the presence of Ni/Al-MCM-41 catalysts to evaluate the reaction products. The presence of nickel impregnated catalyst provided a higher yield in acetic acid.

Keywords: Sisal biomass, pyrolysis, Ni/Al-MCM-41 catalysts.

1. Introduction

Pyrolysis is an interesting process to convert biomass residues in more valuable products. The use of catalysts in biomass pyrolysis processes promotes the conversion of the reactants forming the majority of the desired products. Mesoporous catalysts as MCM-41 substituted with aluminum have considerable industrial potential as acid catalysts and applicability in biomass pyrolysis. In this work biomass sisal residue was studied by its relevance and availability in Bahia - Brazil, to be processed by fast pyrolysis in the presence of nickel supported on Al-MCM-41 catalysts.

2. Experimental

Al-MCM-41 was prepared with the molar composition: $0.05Al_2O_3:0.1Na_2O:0.3CTMA:26H_2O$. The NaOH solution and sodium aluminate were added to the solution of CTMA until the dissolution of the aluminate was complete. The silica and water were mixed and reserved. The suspensions were mixed and kept under vigorous stirring for half an hour. The product was then placed in an autoclave and heated without stirring at 150 °C for 48 hours. Then the precipitate was filtered and washed. The solid was then dried at 120 °C and calcined at 550 °C under nitrogen atmosphere and after synthetic air. The Ni/Al-MCM-41 catalyst was prepared by wet impregnation. The Ni was impregnated using nickel nitrate to obtain 3 wt% NiO. The solid was dried at 120 °C and calcined in air flow at 450 °C (5 °C min^{-1}) for 3 h.

The pyrolysis tests were conducted in a fixed bed reactor under nitrogen flow and temperature of 550 °C. The biomass (11 g of) was coupled to the top of the reactor and catalyst (5.5 g) was located at the base of the system used, and the gases produced in the pyrolysis were directed to the bed. Gas phase was analyzed by a micro-GC Themo and liquid products were analyzed using a gas chromatograph with a mass spectrometer coupled and equipped with an autosampler (Agilent, G4513A model). The identification of the chromatographic peaks was carried out according to the NIST MS library. Thermogravimetric analysis of biomass was performed using Shimadzu equipment TGA-60, under 50 mL min^{-1} of nitrogen flow.

3. Results and discussion

Accordingly sisal residue thermogravimetric analysis the first weight loss up to about 170 °C is associated with dehydration reactions involving the -OH groups present in saccharide molecules. A second mass loss (170-340 oC) corresponds to hemicellulose degradation step and the beginning of the cellulose decomposition. A third mass loss (340-550 °C) is the degradation of cellulose and lignin. Lignin degradation occurs at higher temperatures and the process ends. To the sisal residue it is possible to observe a wider range associated to lignin degradation being responsible to the formation of about 50% of carbon in the solid material [1].

It is possible to observe in table 1 the diversity of compounds with high applicability and commercial value obtained in the pyrolysis test [2]. The percentage area of acetic acid was higher for all three tests when compared to the literature [3]. This may be associated with the cracking of the side chains of the lignin. In addition, the acetic acid production may be related to the mechanism of the rupture of cellulose rings and subsequent rearrangement of the molecules formed, and the deacetylation of hemicellulose. The acetic acid and 1-hydroxy-2-propanone are associated with decomposition of the hemicellulose. By comparing the thermal pyrolysis in the presence of Al-MCM-41 catalyst (20) was observed a reduction in the percentage area of the acetic acid 41.79 to 38.16. The production of acid was increased with 50.09 area in the presence of the nickel confirming the importance of the metal interaction in the step of hemicellulose decomposition.

Table 1. Major compounds present in bio-oil sisal residue identified by GC / MS.

Pyrolysis	t_R (min)	Mayor compounds (higher 3% of total peak area)	Area (%)
Sisal residue (Thermal)	3.46	Acetic acid	41.79
	3.87	1-hydroxy-2-propanone	6.02
	4.65	Propylene glycol	3.60
	6.86	2,3-butanediol, [R-(R*,R*)]-	9.66
	7.36	2,3-butanediol	10.36
Sisal residue + Al-MCM-41 (20)	2.79	2-butanone	3.60
	2.94	Ethyl acetate	9.48
	3.46	Acetic acid	38.16
	4.94	1,1- diethoxyethane	12.18
	8.35	2-cyclopenten-1-one	10.36
	10.99	2-methyl, 2- cyclopenten-1-one	3.59
	13.76	Phenol	3.08
Sisal residue + Ni/Al-MCM-41 (20)	2.79	2-butanone	10.59
	3.46	Acetic acid	50.09
	6.83	Cyclopentanone	3.77
	8.35	2-cyclopenten-1-one	8.21
	10.99	2-methyl, 2-cyclopenten-1-one	4.16

During the process of conversion of biomass can occur hydrogenolysis, decarboxylation, decarbonylation, hydrocracking and polymerization which give rise to products such as esters, ketones, phenols, aldehydes, alcohols, ethers and hydrocarbons [4]. Figure 2 shows the chemical classes present in bio-oil. The nickel metal presence in pyrolysis promoted ketone and acid formation, while the formation of aldehydes was limited.

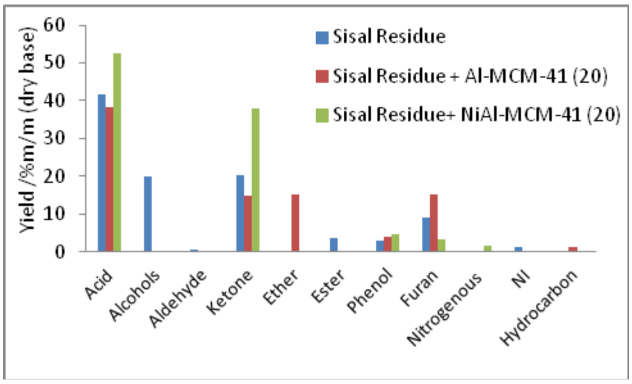

Figure 2. Yield of the classes of compounds present in bio-oil obtained from thermal cracking and catalytic pyrolysis.

4. Conclusions

Thermogravimetric analysis permited to identify the mass loss of regions associated with the composition of lignocellulosic materials. Although the pyrolysis temperature was lower than the decomposition of biomass the same was chosen due to present higher yield of liquid phase. The main groups of compounds formed were acids, ketones and phenols. The significant production of acetic acid was associated to deacetylation of hemicellulose, split of cellulose rings mechanism and cracking of the lignin side chains.The presence of catalysts, especially nickel impregnated provided a higher yield of acetic acid.

References

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