Effect of zeolite matrix over products distribution of catalytic pyrolysis of biomass waste

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Thermo-chemical conversion of biomass has become a promising technology for fuel and platform molecules production. In Argentina, peanut (*Arachis hipogaea*) industry leaves about 200,000 tons of biomass waste per year, all concentrated in the central area of the country causing serious environmental issues. In this sense, pyrolysis (thermochemical process in absence of oxygen) is an adequate technique to process rich in lignin materials. Three types of zeolites, namely ZSM-11, Beta and Y have been tested as heterogeneous catalysts in biomass pyrolysis in order to evaluate the effect of the zeolite type over bio-oil yield and products selectivity.

While ZSM-11 and Beta zeolites were obtained by the traditional hydrothermal crystallization method[1,2], Y zeolite was commercially acquired from Sigma Aldrich. The formers, after synthesized were exchanged with an NH_4Cl solution, desorbed in N_2 flow and further calcined at 500 °C to obtain the protonic forms. The catalysts were named H-ZSM-11, H-Beta and H-Y. Fresh and used materials were widely characterized by XRD, FTIR, ICP and BET techniques.

Peanut shells provided by "Lorenzati, Ruetsch y Cia" (Ticino, Córdoba, Argentina) were washed, grinded and sieved to obtain particle size less than 3.35 mm (ASTM E-11/95) prior to be evaluated. Grinding diminishes heat transfer problems associated with solids[3].

Pyrolysis reactions were done in a quartz fixed bed reactor (23 mm I.D., 290 mm length) at 500 °C under 60 mL/min of N_2 flow for 10 min. Biomass was located in a porous base glass basket inside the reactor and over the catalyst bed. Condensable products were collected in a liquid trap submerged in a refrigerant bath (-15°C) and further analyzed and quantified by GC and GC/MS. Both catalytic and non-catalytic runs were performed for comparison purpose.

Three different products are obtained from the pyrolysis process, called: bio-oil, bio-gas and bio-char. In terms of products yields, while bio-char yield was similar in the three cases studied, bio-oil yield varied in the range of 30-50%. The maximum throughput was achieved with H-ZSM-11 zeolite and the minimum was observed when H-Y catalyst was utilized. Bio-gas yield was comparable in the cases of H-ZSM-11 and H-Beta (around 20%), but it was much higher with H-Y zeolite. This result indicates that H-Y matrix produces higher cracking of the organic molecules after pyrolysis.

Higher concentration of desired products namely, toluene, furfural, xylene, 5-hydroxymethyl furfural (5-HMF), and trimethyl benzene (TMB), among others was observed when H-ZSM-11 catalyst was employed. Moreover, selectivity towards xylene and 5-HMF was 10% and 5% respectively, compared to the 1.5% reached when H-Beta zeolite was used and 0% with H-Y.

The use of zeolites in biomass pyrolysis is beneficial for interesting chemical production, particularly H-ZSM-11 zeolite. This catalyst has proven to generate not only higher bio-oil yields than the others studied, but also a liquid with higher concentration of desired products.

References

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