Influence of the solid catalyst porosity on the products yields and composition from peanut shells pyrolysis

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Argentine is the first worldwide peanut (*Arachis hypogaea*) exporter, with around 600,000 tons per year of commercialization. Nevertheless, peanut production leaves around a 25 vol% of shells as residue of the process. This low density waste (0.10 kg/dm^3) is actually burned or buried, causing serious environmental problems, or stored in silos but with an auto ignition risk characteristic of this kind of material.

As an alternative in order to solve this issue and to obtain interesting chemical products, a catalytic pyrolysis process is proposed. In this sense, two type of porous solid materials were studied as catalysts for the reaction: a traditional microporous ZSM-11 zeolite (H-ZSM-11 micro) and a hierarchical form of the same class of MEL zeolite (H-ZSM-11 micro/meso).

From the pyrolysis reaction three products lines are obtained: a liquid fraction, called bio-oil; a solid one, known as bio-char, and gases. The bio-oil is a high energy density liquid fuel, which could be used as substitute of fuel-oil [1]. However, high oxygen compounds concentration is obtained from the thermal process that makes this product of reduced stability and poor heating value. We propose the use of the above mentioned zeolites as catalysts for the *in situ* cracking reactions for the deoxygenation of the components and to obtain high value chemical products.

Experimental

ZSM-11 zeolites were obtained from the traditional hydrothermal crystallization method [2]. To obtain the hierarchical material, the obtained solid was further desilicated with aqueous NaOH at 65 °C for 30 minutes. Both materials, as synthesized and desilicated, were finally exchanged with a NH_4Cl solution, desorbed in N_2 flow and further calcined at 500 °C. The obtained solids were called H-ZSM-11 micro and H-ZSM-11 micro/meso, respectively. The fresh and used materials were widely characterized.

The pyrolysis reactions were done in a fixed bed reactor at 500 °C with a 30 mL/min N_2 flow for 10 min. For comparison purpose, thermal and catalytic process were done. Condensable products were collected in a bath with refrigerant mixture and then analyzed and quantified in a GC and GC/MS chromatographs.

Results

Bio-char yields were quiet similar with both studied catalysts, but bio-oil production was a 7 % higher when hierarchical material was employed. Besides, the liquid composition presented higher toluene, styrene, 5-hydroxymethylfurfural concentrations, that are chemical compounds of interest for the fine chemical industry, not presented when thermal pyrolysis was done.

Conclusions

Better bio-oil yields were obtained when H-ZSM-11 micro/meso was employed as catalyst for peanut shell pyrolysis. Moreover, higher concentrations of desired products on the liquid fraction of products were achieved when the hierarchical zeolite catalyzed the reaction. In

this sense, the use of zeolites is beneficial for interesting chemical production, particularly the desilicated H-ZSM-11.

References

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