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Immediate catalytic upgrading of soybean shell bio-oil

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ABSTRACT

The pyrolysis of soybean shell and the immediate catalytic upgrading of the bio-oil over an equilibrium FCC catalyst was studied in order to define its potential as a source for fuels and chemicals. The experiments of pyrolysis and immediate catalytic upgrading were performed at 550 °C during 7 min with different catalysts to oil relationships in an integrated fixed bed pyrolysis-conversion reactor. The results were compared under the same conditions against those from pine sawdust, which is a biomass source commonly used for the production of bio-oil. In the pyrolysis the pine sawdust produced more liquids (61.4%wt.) than the soybean shell (54.7%wt.). When the catalyst was presented, the yield of hydrocarbons increased, particularly in the case of soybean shell, which was four time higher than in the pyrolysis. The bio-oil from soybean shell produced less coke (between 3.1 and 4.3%wt.) in its immediate catalytic upgrading than that from pine sawdust (between 5 and 5.8%wt.), due to its lower content of phenolic and other high molecular weight compounds (three and five times less, respectively). Moreover, soybean shell showed a higher selectivity to hydrocarbons in the gasoline range, with more olefins and less aromatic than pine sawdust.

1. Introduction

Worldwide, the increasing shortage and corresponding lower quality of crude oil, the steadily higher demand of transportation fuels and the extra pressure exerted by more severe environmental care legislation, all make it necessary to seriously consider the use of fuels which are less contaminant and, moreover, obtained from renewable sources [1]. Biomass, particularly the lignocellulosic one, has a high potential to produce fuels and chemical raw materials for various uses, one option being the direct production of liquid fuels, which shows an reduction in CO_2 emission, given its reabsorption during biomass growth [2]. Today biomass is transformed into fuels following three main approaches: esterification of vegetable fatty acids (or other raw materials) to biodiesel, fermentation of sugars to bioethanol and thermochemical conversion of lignocellulosic biomass to bio-oils.

Pyrolysis, the thermochemical degradation of biomass by effect of high temperatures without or with limited concentrations of oxygen, is a well known commercial process (see, for example, Dynamotive Energy Systems and Ensyn Technology) which can transform lignocellulosic biomass into gas and liquid (bio-oil) products [1]. The effect of operational variables has been shown in many publications; for example, Amutio et al. [3] studied how pyrolysis temperature impacts on bio-oil yields, while Park and Jang [4] determined its influence on product properties. The addition of small amounts of oxygen to the commercial process facilitates burning char, thus contributing to the autothermal character of the process, a fact which has been described in a kinetic model with six simultaneous reactions by Amutio et al. [5] and Cai et al. [6] reviewed various kinetic models, including kinetic parameters, for various biomasses.

Bio-oils are dark brown, freely flowing liquids which have a strong smoke-like smell and which constitute extremely complex mixtures mainly composed by oxygenated compounds such as acids, esters, aldehydes, ketones, phenols and alcohols [1]. Bio-oils are claimed as fuels for diesel engines, gas turbines and boilers [2], but in order to make them compatible with present technologies it is necessary to upgrade them into hydrocarbons. Possible options are hydroprocessing [7] or conversion over acidic zeolites [8–10].

The catalysts which are used in the process of fluid catalytic cracking of hydrocarbons (FCC) are composed by Y zeolite supported on a matrix, which is either active (alumina, silica-alumina) or inactive (silica), plus a number of additives, binders and fillers [11]. These catalysts showed to be efficient in deoxygenating bio-oils [12–14]. The catalyst particles in the commercial process move between a fluidized bed transport reactor (riser) and a dense

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fluidized regenerator where coke is burnt off; a fraction of the circulating catalyst (named equilibrium catalyst, which is indeed active) is removed in order to avoid an excessive loss of activity and is replaced by fresh catalyst. This waste catalyst has a number of possible uses, such as pozzolanic material in concretes [15] or flushing catalyst in refineries [16]. Then, this catalyst could be used to upgrade bio-oils into hydrocarbons.

Different wood sawdusts, such as pine, poplar, maple, beech and mesquite, among others, have been the most studied raw materials for production of bio-oils by means of pyrolysis [2]. Liquid yields can be as high as 70% in the case of fast pyrolysis [1]. However, it should be considered that residual materials from both forest industry and agriculture activities, such as fruit and grain shells, stover and by-products are potentially good, low cost raw materials for pyrolysis and bio-oil production. Soybean is one of the most important industrial crops in the world. Argentina, as one of the most important producers of soy oil and flour, generates a large amount of soybean shell, about 2.4 million tons per year of this by-product [17], which has very low market price and is habitually used in supplementing animal feed [18]. Soybean shell could also be used to produce microcrystalline cellulose [19], heavy metal adsorbents in liquid effluents [20] and even as a fiber-adding component in human feeding [21]. However, its possible use as a source of fuels and chemicals has not been reported. Soybean shell could be transformed into high value products, such as transportation fuels or chemicals, by means of catalytic processes which would not be competitors to the food market, since soybean shell is a byproduct from soybean processing with very low value, which is not used in human feeding. This approach is opposed to that of first generation biofuels, which are obtained from biomass useful to obtain foods.

The catalytic upgrading of bio-oils could be implemented in refineries or petrochemical plants, where it would be an external feedstock, but also integrated with the pyrolysis process. The immediate catalytic upgrading of bio-oils in the same reactor, immediately after they are produced by pyrolysis, is very attractive due to the significant energy savings which result from the unification of the steps of bio-oil production, conditioning and upgrading, as can be easily confirmed at the laboratory level.

It is the objective of this work to study the pyrolysis of soybean shell and the immediate catalytic upgrading of bio-oil vapors, that is, without intermediate condensation, over a bed of commercial equilibrium FCC catalyst placed downwards in the same reactor, trying to define the potential of this residual material to produce fuels or chemicals. Results will be compared with those of analogous experiments using pine sawdust, with the catalyst to reactants relationship as the controlling parameter and special emphasis on bio-oil composition and the yield of hydrocarbons in the gasoline boiling range.

2. Experimental

The raw soybean (*Glycine max*) shell and the pine (*Pinus elliotti*) sawdust were obtained from regional industries. The particle size of the biomasses was mostly between 1 and 6 mm in the case of pine sawdust and between 3 and 10 mm in the case of soybean shell; these sizes are the consequence of previous processing in mills. Fig. 1 shows the particle size distributions. The biomasses were stored in hermetic plastic bags in a fresh and dry environment. Before use, they were dried during 18 h at 100 °C in an oven to determine the water content. The catalyst was a commercial, equilibrium FCC catalyst (E-Cat) of the octane-barrel type, with the following main characteristics: particle size 100–120 μm; unit cell size 24.26 Å; rare earth oxides 1.19%wt.; zeolite content 18.0%wt.; total specific surface area 158 $m^2\ g^{-1}$; micropore volume (t-plot) 0.046 $cm^3\ g^{-1}$; iron 0.35%wt., vanadium 0.10%wt. and nickel 0.06% wt.

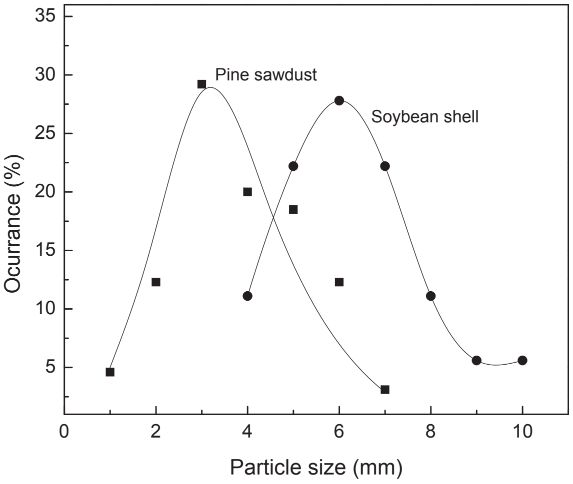

Fig. 1. Particle size distribution of the raw biomasses.

2.1. Pyrolysis and immediate catalytic upgrading of the bio-oils

Biomass pyrolysis and immediate catalytic cracking of bio-oil vapors were performed in a single reactor (refer to Fig. 2) which has two electrically heated zones. The experiments were conducted during 7 min at 550 °C under a 30 ml min^{-1} flow of nitrogen. In previous studies using very different biomasses it was shown that the temperature of 550 °C was optimum to maximize bio-oil yield in most of the cases [18,22–24]. In each test, the biomass was located in a stainless steel mesh basket which was introduced instantaneously in the first zone of the reactor, where the thermal (only) pyrolysis occurs, once the set temperature was reached. Air in the reactor was purged during heating up to the reaction temperature by means of a nitrogen flow. The vapors from the pyrolysis then pass to the second zone, where they convert over the catalyst bed which is supported on a porous plate. The catalyst to oil relationship was calculated in a cumulative way, based on the organic compounds present in the bio-oil, which represented about 30% of the dry biomass. The Cat/Oil parameter was the relationship between the mass of catalyst in each experiment and the mass of organic compounds in bio-oil obtained in the pyrolysis experiments. The products of the reaction passed through a condenser immersed in a saline solution at −5 °C, where condensable products were retained, and the gases were collected in a graduated glass column and quantified by water displacement. After the experiment was finished the reactor was swept with flowing nitrogen at 30 mL min^{-1} (standard pressure and temperature) during 7 min. In all the cases mass balances (recoveries) were better than 90%. The mass loss is due to the adherence of some products to the reactor's wall as a consequence of their polymerization, which has been reported previously [25,26].

2.2. Product characterization

Gas and liquid products were analyzed by capillary gas chromatography in a Varian GC 450 chromatograph with an HP-1 column and FID detection. The gases were also analyzed in an Agilent 6890N gas chromatograph with a GS-CARBONPLOT column and TCD detection. The identification of products was performed with the help of standards and GC/MS technique. The calibration of the chromatographic peak areas was performed by using response