Energy 94 (2016) 171–179

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

# Immediate catalytic upgrading of soybean shell bio-oil

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## ARTICLE INFO

*Article history:*
Received 20 February 2015
Received in revised form
3 June 2015
Accepted 25 October 2015
Available online 21 November 2015

*Keywords:*
Soybean shell
Pyrolysis
Immediate catalytic upgrading
Fuels
FCC

## 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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http://dx.doi.org/10.1016/j.energy.2015.10.114
0360-5442/

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.

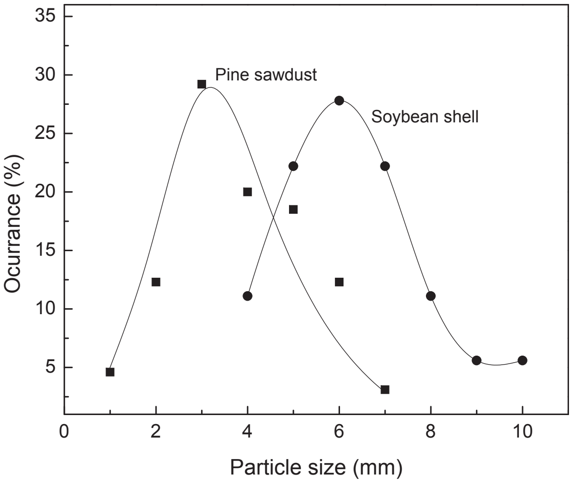

**Fig. 1.** Particle size distribution of the raw biomasses.

### 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

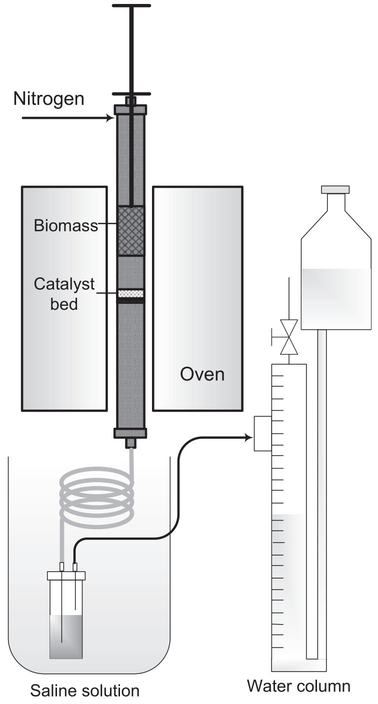

**Fig. 2.** Experimental setup for integrated pyrolysis – immediate catalytic upgrading of bio-oils experiments.

factors specific for each chemical group, which were assessed after analyzing mixtures of standards and a reference compounds (tetralin for liquids adn methane for gases), whose factors were considered equal to one. Each unknown peak, which represented less than 0.5% of the total area, was assigned a response factor which was the average of the other factors.

The content of water in the liquid products was determined by titration with a Karl-Fischer method (IRAM 21320). The amount of coke on the catalytic bed was assessed by thermal programmed oxidation and further methanation of the carbon oxides formed on a Ni catalyst bed; methane was quantified with and FID detector. The yields of the various products in the gas and liquid effluents and the yield of solids were calculated as the relationship between the mass of product and the mass of dry biomass used in the experiment.

## 3. Results and discussion

### 3.1. Composition of raw materials

Table 1 shows the typical composition of the biomasses raw materials used, where it can be seen that the soybean shell contains much more cellulose and hemicellulose and less lignin than the pine sawdust. In the case of soybean shell, about one third of the reported amount of lignin corresponds to cutin [29]. Other biomass raw materials, such as wood sawdusts and agriculture wastes, contain between 60 and 70% of cellulose and hemicellulose and between 23 and 30% of lignin [2].

**Table 1**
Composition of soybean shell and pine sawdust (%wt.).[a]

| | Soybean shell | Pine sawdust |
|---|---|---|
| Water | 9.1 | 9.0 |
| Ash | 4.7 | 0.3 |
| Lignin | 4.3 | 28.0 |
| Cellulose | 40.3 | 35.0 |
| Hemicellulose | 29.4 | 29.0 |
| Lipids | 4.3 | |
| Proteins | 7.9 | |
| Elemental composition | | |
| C | 45.4 | 51.6 |
| H | 6.7 | 5.2 |
| O | 46.9 | 43.2 |
| N | 0.9 | <0.1 |
| S | 0.1 | n.d. |

[a] Adapted from Castro et al. [27], Olguin et al. [21] and Werther et al. [28].

Cellulose and hemicellulose are linear polymers from glucose molecules, in the case of cellulose, and from different monosaccharides (xylose, glucose, galactose and fructose, among others), in the case of hemicellulose, linked by β-1,4-glucosidic bonds. Lignin and cutin are structurally rigid polymers with tridimensional ramifications. Lignin is formed by substituted phenylpropane units (derived from p-coumaryl, coniferyl and sinapyl alcohols) which are linked by carbon-oxygen and carbon–carbon bonds [2], and cutin by long chain fatty acids (C16:0 and C18:1), linked by ester bonds, with hydroxyl or epoxy groups internal to the chain [30]. The content of proteins and ash in soybean shell [29] is relatively high, similar to other fruit and cereal shells (for example 5.4% in wheat shell [23] and 6.4% in white palm fruit [24]). Also the content of lipids is noteworthy, due to the oleaginous character of soybean, where oleic, linolenic and palmitoleic are most important components [29,31].

### 3.2. Product distributions

Table 2 show the yields of the various products, in the pure pyrolysis and the immediate catalytic upgrading of bio-oil vapors over E-Cat, for both soybean shell and pine sawdust (Table 2). It can be seen, in general terms, that liquid products were formed at a higher proportion in the pyrolysis and that the catalyst increased

**Table 2**
Product yields and distributions in the pyrolysis and in the pyrolysis – immediate catalytic upgrading of bio-oils of soybean shell and pine sawdust on catalyst E-Cat (% wt., dry biomass).

| | | Cat/Oil | | |
|---|---|---|---|---|
| | Pyrolysis | 3.5 | 4.2 | 8.5 |
| **Soybean shell** | | | | |
| Liquids | 54.7 | 47.6 | 46.6 | 45.5 |
| Gases | 17.5 | 22.2 | 22.7 | 22.6 |
| Char | 27.8 | 27.0 | 27.2 | 27.5 |
| Coke | | 3.1 | 3.5 | 4.3 |
| **Product distribution liquid and gaseous** | | | | |
| Hydrocarbons | 2.2 | 7.9 | 6.7 | 4.7 |
| Oxygenated compounds | 33.7 | 17.4 | 17.0 | 18.1 |
| Hydrogen | 1.4 | 1.4 | 2.1 | 2.0 |
| $CO_2$ | 13.7 | 17.8 | 18.2 | 19.0 |
| CO | 0.1 | 0.1 | Traces | Traces |
| Water | 19.8 | 23.9 | 24.7 | 23.0 |
| Unknown | 1.3 | 1.1 | 0.6 | 1.0 |
| **Pine sawdust** | | | | |
| Liquids | 61.4 | 41.9 | 43.6 | 46.3 |
| Gases | 17.2 | 31.3 | 28.4 | 27.0 |
| Char | 21.4 | 21.8 | 22.6 | 20.9 |
| Coke | | 5.0 | 5.4 | 5.8 |
| **Product distribution liquid and gaseous** | | | | |
| Hydrocarbons | 1.3 | 2.6 | 5.0 | 11.7 |
| Oxygenated compounds | 28.1 | 11.7 | 9.3 | 3.7 |
| Hydrogen | 1.7 | 2.6 | 2.4 | 3.3 |
| $CO_2$ | 14.6 | 26.9 | 23.3 | 22.6 |
| CO | 0.1 | Traces | 0.1 | Traces |
| Water | 24.9 | 28.5 | 29.6 | 31.5 |
| Unknown | 7.9 | 0.9 | 2.3 | 0.5 |

the yield of gases. This effect was more important in the case of pine sawdust. The yield of gases was higher when the catalyst bed was present because the cracking reactions on the oxygenated compounds in bio-oil are increased. Similar observations were reported by Olazar et al. [32] and Atuxta et al. [33], in comparing the results from the catalytic (HZSM-5) and non catalytic sawdust pyrolysis at 400 °C in a conical spouted bed reactor.

Important differences in the products distributions from each biomass can be noticed. For example, soybean shell produced more char and less liquid products than pine sawdust in pyrolysis and less gases and coke in the pyrolysis-conversion experiments. These observations about the pyrolysis could be associated to the impact of the particle size on the process, which may impose restrictions on the heat transfer, and also to the composition of each raw material. For example, Shen et al. [34] observed that the yield of bio-oil increased when the particle size of mallee wood sawdust decreased, and Yang et al. [35], who studied different conditions in the pyrolysis of three residual biomasses with very different particle size in a fluidized bed reactor, explained the observed differences in the depolymerization and cracking temperatures based on the changes in the heat conduction due to the different particle sizes. Given the importance of this parameter on various issues of the process, the scaling up of pyrolysis processes aimed at using different biomasses requires further and sounder studies. In relation to the composition of the raw biomass, Yang et al. [35] observed higher bio-oil yields in the cases of biomass containing more lignin and more char in the cases of the biomasses with more cellulose and hemicellulose.

Though no reports were produced about the distributions of products in soybean shell pyrolysis, some studies about the pyrolysis of other soybean byproducts, such as straw and cake, can be found; liquid yields were between 26 and 43%wt., char between 25 and 30%wt. and gases between 20 and 23%wt. in fixed bed reactors at temperatures between 400 and 750 °C [36–38]. When a fluidized bed reactor was used in the pyrolysis of soybean straw, higher yields of liquids up to 70%wt. and lower yields of char about 22%wt. were observed at 500 °C [39]. On the contrary, the pyrolysis of pine sawdust has been extensively studied, showing liquid yields between 40 and 70%, depending on heating rate and final temperature (see, e.g., [2,23]).

When the catalyst is present, the lower content of phenols and high molecular weight oxygenated compounds in soybean bio-oil may be the reason for the lower coke yields which are observed in comparison to those with pine sawdust (see Section 3.3). These compounds (particularly phenolic ethers, cyclic ketones, furans and high molecular weight aldehydes) are considered among the main coke precursors in the catalytic cracking of bio-oils over zeolites [8,9]. Moreover, for both biomasses, coke yield increased when the Cat/Oil relationship increased.

The extent of bio-oil catalytic conversion can be estimated by observing the total yield of oxygenated compounds, which decreased to about half of the yield in the thermal-only pyrolysis when the catalyst was present at Cat/Oil 3.5, for both biomasses, thus suggesting high conversions. In the case of pine sawdust, the yield of oxygenated compounds decreased much further when the Cat/Oil was increased. It is to be noted that some of the compounds which initially compose the bio-oils, such as methanol, acetone and alkylated phenols, are also products in the catalytic conversion of other oxygenated compounds, such as phenolic ethers, furans and cyclic ketones [8,26,40,41], thus impeding to define conversion in the usual way.

The experiments of immediate catalytic upgrading of the bio-oils yielded much more carbon dioxide (40% and more than 50% increases for soybean shell and pine sawdust respectively) and more water (about 20% increase for both raw materials) than the pyrolysis. Carbon monoxide was observed at very low levels with both raw biomasses, both in the pyrolysis and the immediate catalytic upgrading of the bio-oils. Hydrogen was produced at higher levels when the catalyst was present. Other authors obtained water yields similar to those in soybean cake pyrolysis (20%wt., [38]), soybean straw (15%wt. [39]) and pine sawdust (21.4%wt. [42]). Particularly, Stefanidis et al. [42] observed that water yield was increased about 20% in the immediate catalytic cracking of bio-oil from pine sawdust over a FCC catalyst. Olazar et al. [32] and Atuxta et al. [33] observed important increases in the yield of water when HZSM-5 zeolite was added to the standard pyrolysis of pine sawdust, which did not depended significantly on the amount of catalyst.

The yields of hydrocarbons in both cases increased significantly when the catalyst was present, particularly in the case of soybean shell, with a yield four times the one in the pyrolysis. However, in the case of soybean shell, hydrocarbon yield decreased at higher Cat/Oil relationships, while the yields of oxygenated compounds and carbon dioxide increased slightly, while water yield remained stable, thus suggesting that the higher amount of acidic sites does not increase the deoxygenation of bio-oil components. Among oxygenated compounds, the selectivity to those such as formic acid and acetone, which are products of the conversion of other components in bio-oils (see Section 3.6), increases notably. This is probably due to the fact that the compounds in bio-oils which are present at the highest concentrations in soybean shell bio-oil (acids, esters and ketones with molecular weights under 130 g/mol, see Section 3.3) do convert easily over acidic zeolites [8,26,40,43], but form oxygenated compounds instead of hydrocarbons. Considering that in the case of soybean shell the yield of coke increased as a function of Cat/Oil, it is possible that the hydrocarbons produced (which are mainly aromatic hydrocarbons, their selectivity increasing with the Cat/Oil relationship, as discussed in Section 3.4) participate in condensation reactions since more actives sites are available [44]. The opposite effect, that is, the increase in hydrocarbons yield as a function of Cat/Oil, was observed for pine sawdust bio-oil, where carbon dioxide and water yields increased and oxygenated compound yield decreased with the catalyst load. These observations are coincident with other reports about the conversion of bio-oils derived from different sawdusts over acidic zeolites such as Y and ZSM-5 [8,45,46].

### 3.3. Bio-oil compositions

In order to study the effect of the catalyst on the oxygenated compounds in bio-oils, it is necessary to know their compositions. Bio-oils are very complex mixtures of organic compounds derived from depolymerization and fragmentation of main components in lignocellulosic biomass (cellulose, hemicellulose and lignin). The pyrolysis of the carbohydrates (cellulose and hemicellulose) produces mainly acids, esters, aldehydes, ketones and furans, as well as minor amounts of ethers and hydrocarbons [42,47]. Furthermore, the pyrolysis of lignin leads to, mainly, phenolic compounds and smaller amounts of methanol, acetic acid, hydrocarbons [42,48] and some furanic compounds by recombination of fragments [47]. Collard et al. [49] reviewed various pyrolysis mechanisms, focusing on the different biomass components, showing that interactions exist between the products from each of them.

Soybean shell also contains some other components at sizeable levels, such as cutin, triglycerides, proteins and ashes (see Table 1), their pyrolysis contributing to the final products. The decomposition of cutin has not been studied extensively and, according to reports from Tegelaar and Leeuw [30], its main products are acids, alcohols and phenols (predominantly vinylphenol). The pyrolysis of lipids produces acids, aldehydes and hydrocarbons (paraffins, aromatics, olefins) within the range of eleven and fifteen carbon atoms per molecule [31,50]. In a similar manner, the pyrolysis of soy proteins produces acids, aldehydes, ketones, alcohols, phenols and hydrocarbons, according to Pütün et al. [36] and Uzun et al. [38], who pyrolyzed soybean cake, a material containing about 45% of proteins. Minerals in the biomass, which are part of ash, impact on the pyrolysis process, catalyzing some deoxygenation and cracking secondary reactions and favoring the fragmentation of monomers of the main polymeric chains (cellulose, hemicellulose and lignin), a fact which contributes to the formation of low molecular weight organic compounds, such as acetic acid and hydroxyacetaldehyde [2].

Table 3 shows the composition of the bio-oils derived from both raw biomasses. It was possible to identify more than 125 compounds, which were grouped according to their chemical functionalities into acids, esters, aldehydes, ketones, furans, alcohols, phenols, ethers, other cyclic oxygenated compounds, hydrocarbons and nitrogenated compounds. Less unknown compounds were observed in the case of soybean shell bio-oil, being about one fourth part of the amount present in pine sawdust bio-oil. Significant differences can be observed between bio-oils from the two raw biomasses. In effect, the bio-oil from soybean shell contains much more acids, esters, ketones, furans and alcohols than the bio-oil from pine sawdust, due to the higher content of cellulose and hemicellulose in soybean shell (refer to Table 1). For both raw biomasses, most important compounds in these groups were acetic, propanoic and 3-hydroxybutanoic acids; methyl acetate and vynil acetate and butanoate (esters); 2-pentanone, 3-penten-2-one, 2,3-pentadione, acetone and alkylated cyclopentenones (ketones); furfural, 3-methylfuran and 5-methylfuranone (furans) and methanol (alcohols).

The most significant difference between bio-oils was the content of phenols, bio-oil from pine sawdust having three times the content in bio-oil from soybean shell, due to the large difference in lignin (see Table 1). Inside the group, the distribution was also different: while in the bio-oil from soybean shell 67% of the phenols were phenol and their derivatives alkylated (especially methylphenol and dimethylphenol), in the bio-oil from pine sawdust predominated phenolic ethers such as guaiacol, syringol and their derivatives, which represented about 85% of the total. In the pyrolysis of pine wood at temperatures between 400 and 600 °C, Amutio et al. [3] also observed guaiacols and catechols as the most important phenols. Also the content of oxygenated compounds with high molecular weight over 130 g $mol^{-1}$ (no distinction between chemical types) in the bio-oil from pine sawdust (20%wt.) was five times larger than in soybean shell bio-oil (4%wt.). Both phenolic ethers and heavy oxygenated compounds are considered among the main coke precursors in the conversion of bio-oils over acidic zeolites [8,9].

**Table 3**
Composition of bio-oils (%wt., dry basis).

| | Soybean shell | Pine sawdust |
|---|---|---|
| Acids | 21.0 | 18.9 |
| Esters | 13.4 | 7.2 |
| Aldehydes | 2.9 | 4.8 |
| Ketones | 24.7 | 18.9 |
| Furans | 5.2 | 3.3 |
| Alcohols | 19.8 | 10.3 |
| Phenols | 5.1 | 16.2 |
| Alkylated phenols | 3.4 | 2.2 |
| Phenolic ethers | 1.7 | 14.0 |
| Ethers | 2.1 | 1.8 |
| Other cyclic oxygenated | 1.1 | 1.0 |
| Hydrocarbons | 0.2 | 0.4 |
| Nitrogenated compounds | 0.7 | 0.2 |
| Unknown | 3.7 | 16.8 |

The differences in the composition of the bio-oils could be somehow associated to the particle size of the raw biomasses, which may influence the results. For example, Shen et al. [34] showed that the content of volatile organic compounds in the pyrolysis of mallee wood sawdust (hydroxyacetaldehyde, methanol and formic acid) increased and the content of heavier compounds (phenols, furans, polyaromatics and olegomeric compounds) decreased when the particle size of the biomass increased. Smaller particle size (case of pine sawdust) favors faster heating rates, thus allowing the release of bigger fragments in the bio-oil.

Soybean shell produced much more nitrogenated compounds (1100 ppm) than pine sawdust (320 ppm) in the bio-oils, which were derivatives from pyrrol and pyridinol, respectively. It should be considered that the occurrence of basic nitrogen compounds (270 ppm in soybean shell and 109 ppm in pine sawdust bio-oils, respectively) may be a hazard for the FCC catalysts, which are acidic in nature [51]. However, some catalyst matrices can act as nitrogen traps, adsorbing these molecules selectively and partially preventing poisoning effects [44]. FCC hydrocarbon feedstocks are very diverse, but they may include up to 4000 ppm of total nitrogen and up to 1000 ppm of basic nitrogen 1000 ppm los [44,52,53]; then, these concentrations in bio-oils would not represent a severe risk if co-processed in FCC.

Both bio-oils contained important concentrations of water (49.5%wt. in pine sawdust and 47.0%wt. in soybean shell bio-oil, respectively). Even though lower contents were reported (e.g., 20–25%wt., [2], these values are typical for woods [9,54]).

As already mentioned, no reports are known about the composition of bio-oil from soybean shell. Some studies about pyrolysis of soybean byproducts, such as soybean cake [36–38] and soybean straw [39] reported the composition of the respective bio-oils, but they were limited. In the case of soybean cake, carboxylic acids and esters were identified but not quantified, as well as phenols, alcohols, aldehydes and ketones, and a big concentration of nitrogen (between 7 and 10.8%wt., a consequence of the high content of proteins in soybean, close to 45%wt.). In the case of soybean straw, Boateng et al. [39] observed a larger amount of compounds produced from carbohydrates (25%wt., specially acetic acid, acetol, levoglucosan and furfural) than from lignin (about 2% wt., mainly phenol, methylphenol, guaiacol, methylguaiacol and eugenol).

The pyrolysis of soybean shell was performed by Galletti and Reeves [55] at 600 °C in order to characterize the lignin component, the final objective being to provide a better digestibility by cattle. They identified four main compounds: guaiacol, 4-vinylguaiacol, guaiacylpropanone and syringylpropene and observed that the proportion of phenolic compounds in organic components was 9.2% of the chromatographic area. They also noted the occurrence of furanic compounds. It is to be noted that the distribution of products was not determined, but pyrolysis was used as an analytical tool to characterize the lignin fraction in soybean shell.

On the contrary, pine sawdust bio-oil has been extensively studied [2,56]. The main chemical groups composing the bio-oil were coincidently reported to be the same as these observed in this work; for example, acids and esthers between 4 and 15%, aldehydes and ketones between 10 and 20 and phenols more than 20%.

According to these results, the bio-oil from soybean shell is potentially useful for the production of hydrocarbons by upgrading over acidic zeolites, particularly by reason of its low contents of phenolic and high molecular weight oxygenated compounds as compared to other bio-oils.

### 3.4. *Hydrocarbons in the pyrolysis and immediate catalytic upgrading of the bio-oils*

Fig. 3 shows, for both raw biomasses, the selectivities of the different hydrocarbon groups in the pyrolysis and the immediate catalytic upgrading of the bio-oil vapors, where it is possible to note important differences between the two processes. In effect, in the pyrolysis, C1−C4 gases and particularly methane, ethylene and propylene, were the main hydrocarbon products, while in the case of the catalytic upgrading of bio-oil vapors, hydrocarbons with more than eleven atoms per molecule were the most important.

In these cases the selectivity to aromatics increased following the Cat/Oil relationship, especially with pine sawdust bio-oil, where these compounds represented up to 95% of the hydrocarbons produced. Among gases, ethylene and propylene had the highest yields with soybean shell, and propylene and butenes with pine sawdust. In increasing the mass of catalyst, the selectivity to gases decreased considerably, particularly with pine sawdust. Olazar et al. [32] and Atuxta et al. [33], reported that light C2−C3 hydrocarbons, which are final products in cracking oxygenated bio-oil components, increased after higher loads of HZSM-5 catalyst were used, while C4+ olefins (intermediate products), decreased.

C5−C9 non aromatic hydrocarbons were produced with low selectivity in all the cases, but their distribution changed according to the type of experiment. Most important compounds in this range in the pyrolysis were cyclooctane, decane and 1-(1-methylethyl)-cyclopentene, which are generally present in bio-oils from various sources [23], while the catalytic bed lead to C5 and C6 olefins to represent between 70 and 95% in the group, as also observed by these authors in preliminary studies about pine sawdust bio-oil conversion over FCC catalysts [12]. The selectivity to these hydrocarbons, which was about two times higher for soybean shell, decreased slightly when the Cat/Oil relationship was increased.

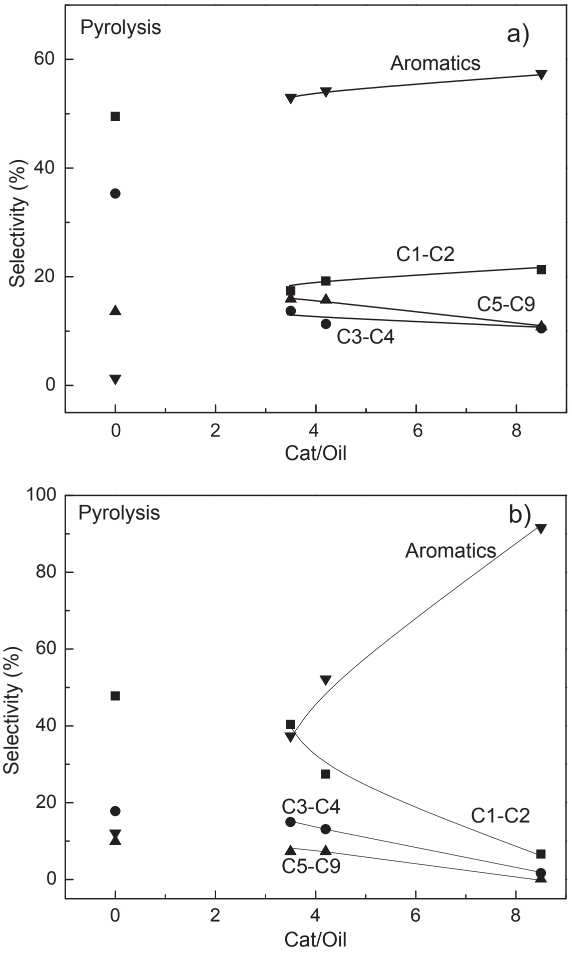

**Fig. 3.** Selectivity to hydrocarbon groups in the pyrolysis and the pyrolysis − immediate catalytic upgrading of bio-oils processes. a) soybean shell; b) pine sawdust. Symbols: ■, C1−C2; ●, C3−C4; ▲, C5−C9 non aromatic hydrocarbons; ▼ aromatics.

In the scarce studies about pyrolysis of the various biomasses derived from soybean (soybean cake, stover), the analysis of the hydrocarbons produced lacked detail. Uzun et al. [38] observed some n-paraffins in the C17−C21 range, branched paraffins (mainly pristane), olefins and aromatics. Sensöz and Kaynar [37] reported hydrocarbons in the C9−C33 range, particularly olefins and aromatics, and lower amount of naphthenics. Pütün et al. [36] observed paraffins and olefins in the C10−C29 range, the highest concentrations corresponding to C14−C18 hydrocarbons. However, in all these works, gaseous products from the pyrolysis were not analyzed. Soybean shell has much more cellulose and hemicellulose than lignin (see Table 1); then, the observations about the responses of these pure carbohydrates to pyrolysis and catalytic conversion could be helpful to explain product distributions obtained with the biomass. Stefanidis et al. [42] studied the pyrolysis and immediate catalytic upgrading over ZSM-5 of cellulose, xylan and lignin, observing that carbohydrates produced less aromatic hydrocarbons tan lignin. Most important aromatic hydrocarbons were toluene, xylenes and other alkyl substituted benzenic compounds. On the contrary, lignin produced a higher amount of heavier aromatic compounds, such as naphthalene and methylnaphthalene. It can be seen in Fig. 3 that the selectivity to aromatic hydrocarbons was much more important in the case of pine sawdust, which is a biomass with high lignin content.

The opposite is true for the case of pine sawdust, with numerous reports about the hydrocarbons produced in the pyrolysis of pine sawdust (e.g., Refs. [2,23,54,56]), which showed that methane is the main gaseous product and aromatics, linear paraffins and olefins with up to 30 carbon atoms per molecule predominated in the liquid products.

No studies about the catalytic cracking of bio-oil from soybean shell over acidic catalyst have been published; however, those where bio-oil from pine sawdust was used showed that light olefins and aromatics with two or more rings are the main hydrocarbonated products from deoxygenation and cracking of the bio-oil components over zeolites, mainly Y and ZSM-5 [8,41,42]. Moreover, a small number of reports about the conversion of pine sawdust bio-oil over FCC catalysts were published [12,42,57] and limited to the option of co-processing in refineries with conventional feedstocks [14,58,59]. The main conclusions from these authors were that the yield of gaseous hydrocarbons increases and the yield of gasoline and LCO (light cycle oil) decrease when the oxygenated bio-oil feedstock is added.

Observations in the conversion of model compounds and bio-oils from various wood sawdusts over zeolite catalysts can be taken into account to rationalize the results over the behavior of FCC catalysts, particularly for the case of soybean shell, with no previous reports. In a general view, it was observed that alcohols dehydrate producing olefins which further oligomerize, cyclization and transfer hydrogen to produce aromatics [60]. However, aromatics alcohols such as phenol, are much less reactive than linear alcohols such as methanol, and generate, mainly, light C1−C4 hydrocarbons [40]. Phenolic ethers, which are considered as some of the main coke producers in bio-oils, also yield aromatic hydrocarbons [8,41]. Acids and esters produce specially C1−C4 hydrocarbons over HY zeolite and aromatics over ZSM-5, while aldehydes, ketones and furans produce liquid hydrocarbons, particularly C5+ olefins and aromatics [26,43,61].

### 3.5. Hydrocarbons in the gasoline range

It is particularly attractive if hydrocarbon products from the conversion of biomass correspond to the boiling range of gasoline (C5-216 °C), due to both the high value of this oil product and the renewable option opened to replace fossil fuels.

In both cases (sawdust pine and soybean shell) the selectivity to hydrocarbons in the gasoline range was poorer in the pyrolysis-only process and increased as a function of Cat/Oil relationship, as it can be seen in Table 4, where the composition of the cut is also shown. Soybean shell biomass produced more hydrocarbons in this range than pine sawdust, a fact which is positive if fuels are considered as a final objective.

In all the cases olefins were the main hydrocarbons in the range of gasoline. Moreover, as already discussed in the previous section, some paraffins with six to ten carbon atoms per molecule were present in the pyrolysis-only process, while aromatic hydrocarbons were predominant when the catalyst was used. The impact of the Cat/Oil relationship on the selectivity to olefins and aromatics was the opposite: the concentration of olefins decreased and that of aromatics increased significantly, suggesting a more extended reaction progress, when the Cat/Oil was higher, as shown in Table 4. According to the reaction mechanism proposed by Corma et al. [51] for the conversion of bio-oils over acidic zeolites, olefins are subjected to oligomerization, cyclization, aromatization, hydrogen transfer and alkylation to produce aromatic hydrocarbons; these reactions being favored if more acidic sites are provided.

Other differences can be noticed in the composition of hydrocarbons in the gasoline range in the pyrolysis-conversion scheme, which can be attributed to the differences in the source biomass: pine sawdust produced mainly C5 olefins, as noted in the conversion of that bio-oil over FCC catalyst [12], while soybean shell produced mainly C6 olefins. Considering that ketones are among the most important components in soybean shell bio-oil (refer to Table 3), it is to be noted that C5+ olefins were reported among the chief products in the conversion of ketones over HZSM-5 [26].

Benzene and toluene increased their proportion among aromatics in hydrocarbons in the gasoline range when the Cat/Oil relationship was increased in the case of soybean shell, representing up to 85% of the aromatic hydrocarbons. Oppositely, heavier aromatics such as naphthalene and methylnaphthalene were much more concentrated, representing more than 97% of aromatics, in hydrocarbons in the gasoline range in the case of pine sawdust at the highest Cat/Oil. This difference could be explained as the consequence of the content of phenolic compounds in the respective bio-oils (refer to Table 3). Phenolic ethers, which are particularly abundant in pine sawdust bio-oil, convert into aromatic hydrocarbons with more than ten carbon atoms per molecule and more than two rings when converted over zeolites [8] and FCC catalysts [14,41]. Alcohols, aldehydes, ketones, acids and esthers, which are present at higher concentration in soybean shell bio-oil, produce monoaromatics such as benzene, toluene and xylenes [8,26,43]. Olazar et al. [32] had observed yields of highly aromatic hydrocarbons in the gasoline range up to 8.2%wt. in the catalytic pyrolysis of pine sawdust with HZSM-5.

**Table 4**
Selectivity to hydrocarbons in the gasoline range and composition of the cut in the pyrolysis and pyrolysis – immediate catalytic upgrading of bio-oils of soybean shell and pine sawdust (%wt.).

| | | Cat/Oil | | |
|---|---|---|---|---|
| Soybean shell | Pyrolysis | 3.5 | 4.2 | 8.5 |
| Selectivity | 15.2 | 19.2 | 23.6 | 24.1 |
| Composition | | | | |
| Olefins | 53.5 | 78.2 | 64.6 | 61.9 |
| Paraffins | 37.9 | 4.4 | 6.7 | 5.4 |
| Naphthenics | – | 0.2 | 0.3 | 0.1 |
| Aromatics | 8.7 | 17.2 | 28.5 | 32.6 |
| Pine sawdust | | | | |
| Selectivity | 11.3 | 15.6 | 20.8 | 23.2 |
| Composition | | | | |
| Olefins | 68.7 | 39.5 | 30.3 | 0.4 |
| Paraffins | 18.7 | 5.8 | 3.7 | – |
| Naphthenics | – | 1.3 | 0.8 | – |
| Aromatics | 12.6 | 53.5 | 65.2 | 99.5 |

### 3.6. Oxygenated compounds in the pyrolysis and the immediate catalytic upgrading of the bio-oils

Fig. 4 shows the selectivities to the main groups of oxygenated compounds in the pyrolysis and pyrolysis-conversion experiments (yields were shown in Table 2), where it can be seen for both raw biomasses that phenols, and particularly phenol, cresol, dimethylphenol and trimethylphenol increased significantly and that acids and esthers, aldehydes, ketones and furans decreased. Similar facts were noticed in the conversion of various bio-oils from wood sawdusts over Y and ZSM-5 zeolites [8,62] and commercial FCC

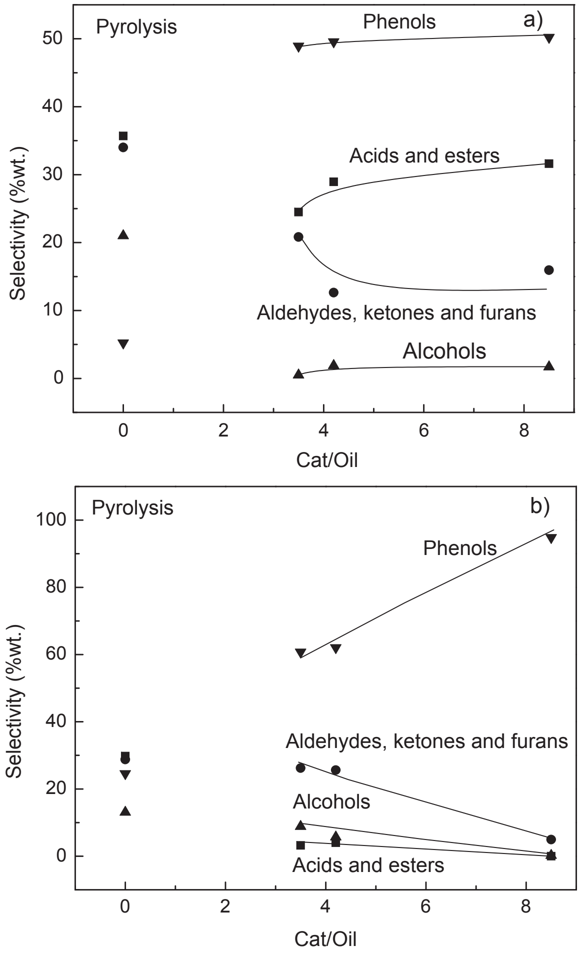

**Fig. 4.** Selectivity to the main groups of oxygenated compounds in the pyrolysis and the pyrolysis – immediate catalytic upgrading of bio-oils processes. a) soybean shell; b) pine sawdust. Symbols: &z.squf, acids and esthers; ●, aldehydes, ketones and furans; ▲, alcohols; ▼ phenols.

catalysts [12]. It is well known that acid catalysts can produce alkylated phenols from phenolic esthers, and that the removal of the hydroxyl group from phenol can be hardly achieved [8,14,40–42]. Alkylated phenols are also produced in the conversion of other components of bio-oils, such as ketones, alcohols, and aromatic ethers [8,41,43].

Atuxta et al. [33] also observed that the effect of the HZSM-5 catalyst in the catalytic pyrolysis of pine sawdust was more important on the deoxygenation of lighter components in bio-oil, such as acetic acid and methanol, increasing as a function of the catalyst load.

As already mentioned, the overall proportion of acids and esters among oxygenated compounds decreased in the catalytic experiments in comparison to pyrolysis. However, some compounds increased; for example, in the case of soybean shell, the selectivity to formic acid increased notably from 0.5% in pyrolysis to 12.2% in pyrolysis-conversion, reaching up to 25% at the highest Cat/Oil. Formic acid may be the consequence of the conversion of some furanic compounds such as furfural and hydroxymethylfurfural, which produce oxygenated fragments of the type HCO [43,63]. Moreover, formic acid was observed by Sitompul et al. [64] as one of the main products of the conversion of cellulose and hemicelluloses over catalysts with Bronsted acidic sites such as those of FCC. This could be considered in view of the higher content of carbohydrates in soybean shell in comparison to pine sawdust (see Table 1). Corbetta et al. [65] studied the effect of particle size on the product distribution in pyrolysis of wood sawdusts, observing that formic acid is produced in the first steps.

On the contrary, most important acids and esters in the pyrolysis, such as acetic, propanoic and pentanoic acids and methyl acetate and vynil butanoate esters, as well as other compounds in the group with higher molecular weight, such as 3-propyl-pentanedioic acid and isobutyl isobutanoate, decreased significantly their concentrations (up to 65% at Cat/Oil 8.5) when the catalyst was present. In the case of pine sawdust a similar behavior was observed for the group, with concentration increases for light compounds (mainly acetic acid) and severe decreases of up to 95%, of heavier compounds at the largest Cat/Oil relationship. Stefanidis et al. [42] also noticed that the acids in bio-oils decreased after the immediate catalytic upgrading over ZSM-5 at 500 °C when cellulose, xylan and lignin, and their mixtures, were the raw materials.

Increases in the concentrations of lighter compounds and decreases in heavier compounds were also observed for the group of aldehydes, ketones and furans. For example, for soybean shell raw biomass, the proportion of acetone was two times larger in the catalytic experiments with the highest Cat/Oil than in the pyrolysis, while heavier furans such as $\gamma$-heptylbutyrolactone and 5-hydroxymethylfurfural, decreased to one third part. In the case of pine sawdust furans and cyclic ketones reacted almost completely on the catalyst (Cat/Oil 8.5), while acetone increased slightly. Acetone is the product of the reaction of many of bio-oil components over acidic catalysts; for example, it can be obtained by dehydrating acetic acid or methyl acetate [26,60,66] and also from the conversion of furans, linear and cyclic ketones, alcohols and phenolic ethers [41,43].

## 4. Conclusions

Two different approaches (pyrolysis-only and pyrolysis plus immediate catalytic conversion of bio-oil vapors over a bed of commercial equilibrium FCC catalyst) of soybean shell biomass were studied comparatively to pine sawdust in the search for proper uses of that residual raw material.

The pyrolysis of soybean shell produced more char and less liquid products (bio-oil) than pine sawdust, but the thermal plus catalytic treatment produced more hydrocarbons, particularly liquid, and less coke and gases.

The yield of oxygenated compounds from soybean shell was larger than from pine sawdust, both in the pyrolysis and the pyrolysis-conversion processes. However, the distribution of these compounds was different: bio-oil from soybean shell showed one third of phenolic compounds and one fifth of heavy molecular weight oxygenated compounds of the amounts obtained with bio-oil from pine sawdust. These facts correlate with the higher coke yields with pine sawdust biomass.

The immediate catalytic upgrading of bio-oils from both raw materials increased significantly the yield of hydrocarbons, thus improving the quality of the liquid products. Hydrocarbons were mainly gaseous in the pyrolysis and aromatic in the pyrolysis-conversion, with soybean shell producing much more non aromatic hydrocarbons in the C5–C9 range. In this way, soybean shell produced selectively more hydrocarbons in the gasoline range with more olefins and less aromatics than pine sawdust.

These results suggest that soybean shell could be used to be produce bio-oil by means of pyrolysis in a way similar to those approaches used with other residual biomasses commonly used. Moreover, the immediate catalytic upgrading of the bio-oil over an equilibrium commercial FCC catalyst is an interesting option, independently from the source biomass, to increase the yield of hydrocarbons, particularly liquid ones. This process is also convenient to avoid successive steps of condensation and evaporation of the bio-oils, thus reducing operative costs.

## Acknowledgments

This work was performed with the financial assistance of University of Litoral (Santa Fe, Argentina), Secretary of Science and Technology, Proj. CAID 2011 #501-201101-00329LI; CONICET, PIP 1257/09 and the National Agency for Scientific and Technological Promotion, PICT 2010/2123.

## References

[1] Brigdwater A. Review of fast pyrolysis of biomass and product upgrading. Biomass Bioenergy 2012;38:68–94.
[2] Mohan D, Pittman C, Steele P. Pyrolysis of wood/biomasss for bio-oil: a review. Energy Fuels 2006;20:848–89.
[3] Amutio M, López G, Artetxe M, Elordi G, Olazar M, Bilbao J. Influence of temperature on biomass pyrolysis in a conical spouted bed reactor. Resour Conserv Recycl 2012;59:23–31.
[4] Park S, Jang C. Effects of pyrolysis temperature on changes in fuel characteristics of biomass char. Energy 2012;39:187–95.
[5] Amutio M, Lopez G, Aguado R, Artetxe M, Bilbao J, Olazar M. Kinetic study of lignocellulosic biomass oxidative pyrolysis. Fuel 2012;95:305–11.
[6] Cai J, Wu W, Liu R. An overview of distributed activation energy model and its application in the pyrolysis of lignocellulosic biomass. Renew Sust Energy Rev 2013;20:236–46.
[7] Elliott D. Historical developments in hydroprocessing bio-oils. Energy Fuels 2007;21:1792–815.
[8] Adjaye J, Bakhshi N. Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part II: comparative catalyst performance and reaction pathways. Fuel Process Technol 1995;45:185–202.
[9] Gayubo A, Valle B, Aguayo A, Olazar M, Bilbao J. Pyrolytic lignin removal for the valorization of biomass pyrolysis crude bio-oil by catalytic transformation. Ind Eng Chem Res 2010;49:123–31.
[10] Mortensen P, Grunwaldt J, Jensen P, Knudsen K, Jensen A. A review of catalytic upgrading of bio-oil to engine fuels. Appl Catal A General 2011;407:1–19.
[11] Scherzer J. Octane-enhancing, zeolitic FCC Catalysts: scientific and technical aspects. Cat Rev Sci Eng 1989;31:215.
[12] Bertero M, Sedran U. Conversion of pine sawdust bio-oil (raw and thermally processed) over equilibrium FCC catalysts. Bioresour Technol 2013;135:644–51.
[13] Corma A, Huber G, Sauvanaud L, O'Connor P. Processing biomass-derived oxygenates in the oil refinery: catalytic cracking (FCC) reaction pathways and role of catalyst. J Catal 2007;247:307–27.
[14] Graça I, Lopes J, Ribeiro M, Ramoa F, Cerqueira H, de Almeida M. Bio-oils and FCC feedstocks co-processing: Impact of phenolic molecules on FCC hydrocarbons transformation over MFI. Appl Catal B Environ 2011;101:613–21.

[15] Payá J, Monzó J, Borrachero M. Fluid catalytic cracking catalyst residue (FCCR) an excellent mineral by-product for improving early strength development of cement mixtures. Cement Concrete Res 1999;29:1773–9.
[16] Albemarle FCC Manual 5.4 The role of catalyst in FCC troubleshooting. www.albemarle.com (Accessed July 2014).
[17] Franco D. Anuario estadístico oleaginosas. www.alimentosargentinos.gov.ar/oleaginosos. Accessed January 2014.
[18] Ipharraguerre I, Clark J. Soyhulls as an alternative feed for lactating dairy cows: a review. J Dairy Sci 2003;86:1052–73.
[19] Uesu N, Gómez Pineda E, Hechenleitner A. Microcrystalline cellulose from soybean husk: effects of solvent treatments on its properties as acetylsalicylic acid carrier. Int J Pharm 2000;206:85–96.
[20] Blanes P, Sala L, García S, González J, Frascaroli M, Bordon M, et al. Salvado de soja: Potential biosorbente para remediación de aguas contaminadas con cromo, in Quinto Congreso de la Soja del Mercosur, Rosario, Argentina. 2011. p. 1–5.
[21] Olguin M, Posadas M, Revelant G, Labourdette V, Marinozzi D, Elías H, et al. Soybean hull: potential ingredients for functional foods. Rev Chil Nutr 2009;36:239–45.
[22] Bertero M, de la Puente G, Sedran U. Effect pf pyrolysis temperature and thermal conditioning on the coke-forming potential of bio-oils. Energy Fuels 2011;25:1267–75.
[23] Bertero M, de la Puente G, Sedran U. Fuels from bio-oils. Bio-oil production from different sources, characterization and thermal conditioning. Fuel 2012;95:263–71.
[24] Bertero M, Gorostegui H, Orrabalis C, Guzmán C, Calandri E, Sedran U. Characterization of the liquid products in the pyrolysis of residual chañar and palm fruit biomasses. Fuel 2014;116:409–14.
[25] Horne P, Williams P. Reaction of oxygenated biomass pyrolysis model compounds over a ZSM-5 catalyst. Renew Energy 1996;67:131–44.
[26] Gayubo A, Aguayo A, Atutxa A, Aguado R, Olazar M, Bilbao J. Transformation of oxygenate components of biomass pyrolysis oil on a HZSM-5 zeolite. II. Aldehydes, ketones and acids. Ind Eng Chem Res 2004;43:2619–26.
[27] Castro H, Andreo N, Vottero D. Marca Líquida Agropecuaria 2005;15:17–8.
[28] Werther J, Saenger M, Hartge M, Ogada T, Siagi Z. Combustion of agricultural residues. Prog Energy Comb Sci 2000;26:1–27.
[29] Foundation FEDNA. http://www.fundacionfedna.org/node/466. Accessed January 2014.
[30] Tegelaar E, de Leeuw J. Some mechanisms of flash pyrolysis of naturally occurring higher plant polyesters. J Anal App Pyrolysis 1989;15:289–95.
[31] Schwab A, Dykstrab G, Selkeo E, Sorensonb S, Prydeo E. Diesel fuel from thermal decomposition of soybean oil. J Am Oil Chem Soc 1988;65:1781–6.
[32] Olazar M, Aguado R, Barona A, Bilbao J. Pyrolysis of sawdust in a conical spouted bed reactor with a HZSM-5 catalyst. AIChE J 2000;46:1025–33.
[33] Atutxa A, Aguado R, Gayubo A, Olazar M, Bilbao J. Kinetic description of catalytic pyrolysis of biomass in a conical spouted bed reactor. Energy Fuels 2005;19:765–74.
[34] Shen J, Wang X, Garcia-Perez M, Mourant D, Rhodes M, Li C. Effects of particle size on the fast pyrolysis of oil mallee woody biomass. Fuel 2009;88:1810–7.
[35] Yang S, Wu M, Wu C. Application of biomass fast pyrolysis part I: pyrolysis characteristics and products. Energy 2014;66:162–71.
[36] Pütün A, Apaydin E, Pütün E. Bio-oil production from pyrolysis and steam pyrolysis of soybean cake: products yields and composition. Energy 2002;27:703–10.
[37] Sensöz S, Kaynar I. Bio-oil production from soybean (Glycine max L.): fuel properties of bio-oil. Ind Crops Prod 2006;23:99–105.
[38] Uzun B, Pütün A, Pütün E. Fast pyrolysis of soybean cake: product yields and compositions. Bioresour Technol 2002;97:569–76.
[39] Boateng A, Mullen C, Goldberg N, Hicks K, Devine T, Lima I, et al. Sustainable production of bioenergy and biochar from the straw of high-biomass soybean lines via fast pyrolysis. Env Prog Sust Energy 2010;29:175–83.
[40] Gayubo A, Aguayo A, Atutxa A, Aguado R, Bilbao J. Transformation of oxygenate components of biomass pyrolysis oil on a HZSM-5 zeolite. I. Alcohols and phenols. J Ind Eng Chem Res 2004;43:2610–8.
[41] Bertero M, Sedran U. Upgrading of bio-oils over equilibrium FCC catalysts. Contribution from alcohols, phenols and aromatic ethers. Catal Today 2013;212:10–5.
[42] Stefanidis S, Kalogiannis K, Iliopoulou E, Lappas A, Pilavachi P. In-situ upgrading of biomass pyrolysis vapors: catalyst screening on a fixed bed reactor. Bioresour Technol 2011;102:8261–7.
[43] Bertero M, de la Puente G, Sedran U. Products and coke from the conversion of bio-oil acids, esters, aldehydes and ketones over equilibrium FCC catalysts. Renew Energy 2013;60:349–54.
[44] Cerqueira H, Caeiro G, Costa L, Ramôa Ribeiro F. Desactivation of FCC catalyst. J Mol Catal A Chem 2008;292:1–13.
[45] Gong F, Yang Z, Hong C, Huang W, Ning S, Zhang Z, et al. Selective conversion of bio-oil to light olefins: controlling catalytic cracking for maximum olefins. Bioresour Technol 2011;102:9247–54.
[46] Vitolo S, Seggiani M, Frediani P, Ambrosini G, Politi L. Catalytic upgrading of pyrolytic oils to fuel over different zeolites. Fuel 1999;78:1147–59.
[47] Kanaujia P, Sharma Y, Garg M, Tripathi D, Singh R. Review of analytical strategies in the production and upgrading of bio-oils derived from lignocellulosic biomass. J Anal Appl Pyrolysis 2014;105:55–74.
[48] Kawamoto H, Horigoshi S, Saka S. Pyrolysis reactions of various lignin model dimers. J Wood Sci 2007;53:168–74.
[49] Collar F, Blin J. A review on pyrolysis of biomass constituents: mechanism and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignins. Renew Sust Energy Rev 2014;38:594–608.
[50] Lima D, Soares V, Ribeiro E, Carvalho D, Cardoso É, Rassi F, et al. Diesel-like fuel obtained by pyrolysis of vegetable oils. J Anal Appl Pyrolysis 2004;71:987–96.
[51] Corma A, Mocholí F. New silica-alumina-magnesia FCC active matrix and its possibilities as a basic nitrogen passivating compound. Appl Catal A General 1992;84:31–46.
[52] Li X, Zhu J, Wu B. Characterization of basic nitrogen-containing compounds in the products of lube base oil processing by electrospray ionization fourier transform ion cyclotron resonance mass Spectrometry. Bull Korean Chem Soc 2014;35:165–72.
[53] Ng S, Wang J, Fairbridge C, Zhu Y, Yang L, Ding F, et al. Study of Canadian FCC feeds from various origins and treatments. 1. Ranking of feedstocks based on feed quality and product distribution. Energy Fuels 2004;18:160–71.
[54] Garcia-Pérez M, Chaala A, Pakdel H, Kretschmer D, Roy C. Characterization of bio-oils in chemical families. Biomass Bioenergy 2007;31:222–42.
[55] Galletti G, Reeves J. Pyrolysis-gas chromatography/mass spectrometry of lignocellulosics in forages and by-products. J Anal Appl Pyrolysis 1991;19:203–12.
[56] Stas M, Kubicka M, Chudoba J, Pospísil M. Overview of analytical methods used for chemical characterization of pyrolysis bio-oil. Energy Fuels 2014;28:385–402.
[57] Adam A, Antonakou E, Lappas A, Stöcker M, Nilsen M, Bouzga A, et al. In situ catalytic upgrading of biomass derived fast pyrolysis vapours in a fixed bed reactor using mesoporous materials. Microp Mesop Mat 2006;96:93–101.
[58] Fogassy G, Thegarid N, Schurmann Y, Mirodatos C. The fate of bio-carbon in FCC co-processing products. Green Chem 2012;14:1367–71.
[59] Thegarid N, Fogassy G, Schuurman Y, Mirodatos C, Stefanidis S, Iliopoulou I, et al. Second-generation biofuels by co-processing catalytic pyrolysis oil in FCC units. Appl Catal B Environ 2013;165:161–6.
[60] Chang C, Silvestri A. The conversion of methanol and other o-compounds to hydrocarbons over zeolite catalysts. J Catal 1977;47:249–59.
[61] Wang S, Guo Z, Cai Q, Guo L. Catalytic conversion of carboxylic acids in bio-oil for liquid hydrocarbons production. Biomass Bioenergy 2012;45:138–43.
[62] Srinivas S, Dalai A, Bakhshi N. Thermal and catalytic upgrading of a biomass-derived oil in a dual reaction system. Can J Chem Eng 2000;78:343–54.
[63] Moldoveanu S. Pyrolysis de organic molecules with applications to health and environmental. Amsterdam: Elsevier; 2010.
[64] Sitompul J, Simangunsonga R, Asrizala A, Alisyahbanaa H, Leea H, Rasrendra C. Catalytic conversion of empty fruit bunch of palm oil for reducing lactic acid. Procedia Chem 2014;9:88–93.
[65] Corbetta M, Frassoldati A, Bennadji H, Smith K, Serapiglia K, Gauthier G, et al. Pyrolysis of centimeter-scale woody biomass particles: kinetic modeling and experimental validation. Energy Fuels 2014;28:3884–98.
[66] Chang C, Chen N, Koening L, Walsh D. Synergism in acetic acid/methanol reactions over ZSM-5 zeolites. ACS Div Fuel Chem Prepr 1983;28:146–52.