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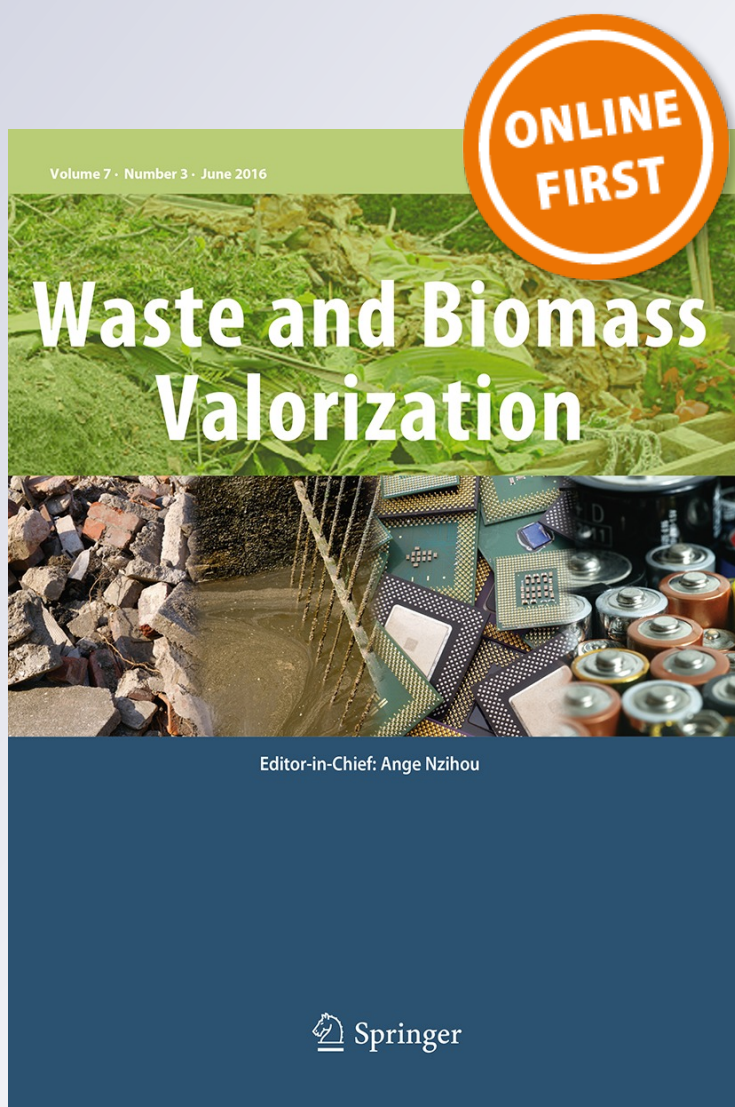
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Hydrocarbons from Bio-oils: Performance of the Matrix in FCC Catalysts in the Immediate Catalytic Upgrading of Different Raw Bio-oils

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Abstract Matrices of FCC catalysts with different content of alumina and the compound catalysts prepared with them including Y zeolite were used to upgrade bio-oils from pine wood sawdust and soybean shell. The biomasses were selected according to their different lignin content which results in very different proportions of phenolic compounds (coke precursors) in the respective bio-oils. The bio-oils were produced by fast pyrolysis and the vapours were immediately upgraded over a fixed bed of catalyst at 550 °C using a mass catalyst/bio-oil relationship of 3.5. In terms of hydrocarbon yield, the matrices were more effective in deoxygenating pine wood sawdust bio-oil and the compound catalysts in deoxygenating soybean shell bio-oil. These differences can be the consequence of the different compositions of the bio-oils which, in the case of pine wood sawdust, includes a significant concentration of phenolic ethers which form coke on the matrix and the external surface of the zeolite, thus preventing lighter compounds from accessing the micropore system of the compound catalysts. Pine sawdust bio-oil produced more coke than soybean shell bio-oil; in the case of compound catalysts, coke deposited preferentially on the catalyst matrix, thus decreasing its mesopore specific surface area up to 65 %.

Keywords Bio-oil · Silica–alumina · Fuels · FCC · Biomass

Introduction

Fossil fuels are the main energy source in present days, but given their naturally limited availability and non renewable character, there exist a growing need for developing new renewable sources. Pyrolysis is a process which permits producing liquid fuels from waste lignocellulosic biomass from agriculture, forestry or industrial wastes. This approach does not compete with food production and the raw materials are inexpensive. The liquid product from pyrolysis processes, which is generically named bio-oil, is a freely flowing, very dark brown liquid with a distinctive smoke smell, its composition being completely different from those of oil derivatives. Bio-oils are very complex mixtures of, mostly, oxygenated species derived from depolymerization and fragmentation reactions of the three main components in biomass: cellulose, hemicellulose and lignin. For example, bio-oils obtained from woods contain about 35–40 % of oxygen, 55–60 of carbon, 15–30 % of water, acidic pH, and density about 1.2 g/cm³ [1].

Bio-oils could be given additional value if they are subjected to catalytic processing in order to be transformed into transportation fuels and valuable chemical products. In this sense, they could be incorporated to standard schemes in oil refining refineries, where they could be co-processed with fossil feedstocks, not requiring large additional investments in infrastructure. Two refining processes showed to be potential receptors of these oxygenated feedstocks; hydrocracking [2–4] and catalytic cracking of hydrocarbons (FCC) [5–7]. Hydrotreating bio-oils over usual catalysts such as sulfided CoMo and NiMo supported on γ -alumina under processes conditions (high hydrogen pressures in the 30–140 bar range and temperatures between 250 and 400 °C) allows obtaining between 30 and 40 % of liquid products with very small amounts of

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oxygen, but consuming the large amount of 2300 STP m³ of hydrogen per feedstock barrel [2–4].

The conversion of bio-oils over FCC catalysts is particularly interesting because the production of hydrocarbons occurs at low pressures and without consuming hydrogen [8]. Consequently, this option has been studied following different approaches: direct conversion over equilibrium catalysts [9] or Y zeolite alone [10–12] (which is the main component in FCC catalysts), or co-processing with fossil feedstocks (vacuum gas oil, light cycle oil and fuel oil) [6, 13, 14]. Moreover, the catalytic upgrading of bio-oils over other acidic zeolites, particularly ZSM-5, which showed to be more efficient in deoxygenation, producing more aromatic hydrocarbons than other zeolites, was also studied, but its use requires the development of new processes [15, 16].

In FCC co-processing of bio-oils, coke yields are a main issue to be considered, particularly if coke yield increases significantly, because it is mandatory to preserve the delicate heat balance in industrial units, based on the heat production in the regenerator section. If too much coke is produced, temperature in the regenerator would increase, affecting catalyst properties and also impacting on catalyst circulation in the unit. Moreover, the characteristics of the coke deposits (degree of condensation, content of hydrogen and/or oxygen) and their location in the catalyst particles could change in co-processing bio-oils together with conventional hydrocarbon cuts. For example, Gueudré et al. [17] showed that the extra coke derived from bio-oil, produced in the co-processing of wood sawdust bio-oils and vacuum gas oil, deposited preferentially on the catalyst matrix.

FCC catalysts are composed by Y zeolite deposited on a matrix, binders and various additives [18]. The matrix provides appropriate shape and size to the particles in order to facilitate circulation in the unit, act as a heat sink to transport energy between the regenerator and reactor sections and easy the diffusion of hydrocarbon molecules to the active sites [19]. Active matrices, which are composed by alumina or silica–alumina, can pre-crack bulky hydrocarbon molecules in the feedstocks to facilitate the diffusion of smaller units to the zeolite active sites; although not exclusively, they are used in the formulation of catalysts which can process resids. The physicochemical properties of these matrices depend strongly on the content of alumina, the method of preparation and, particularly, on the content of tetrahedrally coordinated aluminum atoms [20, 21]. According to reports by Scherzer [18] and Carlson et al. [22], the silica–alumina matrices in FCC catalysts show both Lewis and Brønsted acidic sites; Lewis-type sites increase their number following the alumina content, while Brønsted-type sites show a maximum at about 30 % alumina and then decrease.

Numerous studies were performed on the catalytic cracking of bio-oils aimed at finding catalysts which are selective to the products of interest, in turn minimizing the yield of coke, as shown by Rezaei et al. [8]. They show that the properties of both micro and mesopore catalysts, such as pore size, pore volume, specific surface area and acidity, as well as the main process parameters, such as temperature, catalyst to reactant relationship and contact time, impact significantly on the product distribution.

The influence of the matrix composition (high alumina silica–alumina, above 25 wt% alumina) on the overall product distribution in the conversion of bio-oils from different raw biomasses on FCC catalysts and the matrices alone is studied in this work. Particularly, the reactivity of the most refractory oxygenated compounds in bio-oils (phenols) was observed. The behavior of lighter compounds in bio-oils, such as acids, esters, aldehydes, ketones, and furans, which are easier to deoxygenate, although they have different reaction mechanisms when reacted alone or taking part of a mixture [23], is also studied. This information is crucial to the cases of co-processing. Two different raw biomasses were used [24]: pine sawdust (bio-oil with more than 16 wt% of phenolic compounds) and soybean shell (bio-oil with less than 5 wt% of phenolic compounds).

Experimental

Materials

The matrices were silica–alumina microspherical particles also including kaolin, prepared with conventional methods, particle size being in the range 75–125 µm. They were prepared with 50 % kaolin, changing the amount of silica and alumina to produce the different Si/Al relationships. They were prepared based on the method described in Magee and Blazek [25], with minor modifications, using sodium silicate as the silica source and aluminum sulfate as the aluminum source. They were named M-32, M-38 and M-45, following their alumina content. The matrices were subjected to hydrothermal treatment with 100 % steam at 788 °C during 5 h.

The FCC catalysts were prepared with the steamed matrices and Y zeolite (H-USY, Zeolyst CBV 760) and colloidal silica (Ludox AS-40, Aldrich) as a binder. The zeolite, the matrix and the binder were mixed to form the catalysts at 30, 50 and 20 wt%, respectively, reproducing typical formulations of the commercial FCC catalysts [26]. Finally, the catalysts were dried at 110 °C during 16 h and calcined in an oven at 550 °C during 4 h in air. The solids were grounded and sieved to the 75–125 µm range. The catalysts were named C-32, C-38 and C-45, in consistency with the corresponding matrices.

The raw biomasses were soybean (*Glycine max*) shell and pine (*Pinus elliotti*) wood sawdust, which were obtained from regional industries. Their most important characteristics in relation to lignocellulosic and elemental composition were detailed in Bertero and Sedran [24]. Moreover, it is to point out that pine sawdust contains six times more lignin (28 wt%) than soybean shell. The particle size of the raw biomasses was between 2 and 4 mm (pine sawdust) and between 7 and 10 mm (soybean shell); these sizes are the consequence of previous processing in mills. The water content (10 wt% in both cases) was determined by weight difference before and after drying during 18 h at 100 °C.

Catalyst Characterization

The composition of the matrices was determined by means of X ray fluorescence analysis. X ray diffraction patterns were obtained with a Shimadzu XD-D1 diffractometer in the range $5^\circ < 2\theta < 60^\circ$, and the unit cell size of the zeolite was determined following the ASTM D 3942 technique. Micropore size in Y zeolite is 7.4 Å [18].

The textural properties were determined by means of the adsorption of nitrogen at -196°C in a Quantachrome Autosorb-1 sorptometer. The specific surface area was assessed following the BET method in the $0.15 < P/P_0 < 0.30$ range, the total pore volume was estimated at $P/P_0 \sim 0.98$ and the micropore volume and the specific surface area of the mesopores were estimated with the *t*-plot method in the $3.5 \text{ \AA} < t < 5.0 \text{ \AA}$ range. The average mesopore size was assessed with the help of the Barrett–Joyner–Halenda (BJH) model. The content of zeolite material in the compound catalysts was assessed according to the method by Johnson [27].

Acidity in the various solids was determined by means of the TPD temperature programmed desorption of pyridine. The solids were pretreated in situ under N_2 flow at 400°C during 1 h and after cooling to room temperature the saturation with pyridine was performed with a saturator at 80°C with N_2 flow. Then, temperature was increased to 150°C and maintained at this value during 1 h with N_2 flow. The TPD experiments were carried out by heating at $12^\circ\text{C}/\text{min}$ in the $150\text{--}800^\circ\text{C}$ range, pyridine being detected with a FID detector after methanation.

Conversion Experiments

The experiments of biomass pyrolysis and immediate catalytic conversion of the bio-oil were performed in an integrated pyrolysis–catalytic upgrading fixed bed reactor. The reactor, which was described extensively in García et al. [28], has two zones which are heated electrically; the first one where the purely thermal pyrolysis occurs and the

second one where the pyrolysis vapors (bio-oil) are contacted with a catalytic bed. Before each experiment, the catalysts were only heated up to the reaction temperature with a $20^\circ\text{C}/\text{min}$ heating ramp under a $30 \text{ ml}/\text{min}$ nitrogen flow and maintained at this temperature during 5 min. The experiments were carried out at 550°C during 7 min, under a $30 \text{ ml}/\text{min}$ flow of nitrogen. The biomass (0.8 g) was located in a stainless steel basket which was introduced instantly in the pyrolysis zone after the target reaction temperature was reached, thus minimizing secondary polymerization and condensation reactions of the pyrolysis products, which decrease the yield of bio-oil. Pyrolysis vapors were then immediately converted, without intermediate condensation, on the catalytic bed supported on a porous metal plate. The reactor effluents passed through a condenser immersed in a saline solution at -5°C , where liquids were retained, and the gases were collected in a water column and quantified by displacement. After the reaction time was completed, the reactor was swept with nitrogen during 7 min. Mass balances (recoveries) were higher than 90 % in all the cases.

The cumulative Cat/Oil relationship in the experiments (3.5) was calculated based on the organic compounds present in the bio-oil, which were typically about 30 wt% of the dry biomass. Purely thermal pyrolysis experiments were also performed with both raw biomasses in order to produce background information. The performance reported for the various samples are cumulative and the length of the tests was determined experimentally to assure the complete thermal pyrolysis of the biomass (no catalyst).

Product Characterization

Both the liquid and gas product streams were analyzed by means of conventional capillary gas chromatography. Liquids were analyzed in a Varian GC 450 gas chromatograph with a 30 m long, $250 \mu\text{m}$ diameter and $0.25 \mu\text{m}$ film thickness, non-polar, dimethylpolysiloxane HP-1 column and FID. Gases were analyzed in an Agilent 6890N gas chromatograph with a 30 m long, $530 \mu\text{m}$ diameter and $3.0 \mu\text{m}$ film thickness, bonded monolithic carbon-layer GS-CARBONPLOT column, with TCD detection. Products were identified with the help of standards and GC/MS technique. Peak areas were calibrated using response factors specific for each of the chemical groups, in turn determined with mixtures of standards and reference compounds (tetralin for liquids and methane for gases). Unidentified peaks, which were assigned a response factor which was the average of the factors for the other groups, represented less than 0.5 % of the total chromatographic area in all the cases.

The concentration of water in the liquid products was determined by means of Karl-Fischer titration (IRAM

21320). The amount of coke on the catalyst was assessed with a thermal programmed oxidation (TPO; initial temperature, 250 °C during 15 min; heating ramp, 16 °C/min; final temperature, 700 °C, during 16 min) and methanation of the carbon oxides formed (Ni catalyst, methane quantified with FID detection) combined method.

The yield of a given product was calculated as the relationship between the mass of the product and the mass of dried biomass used. The mass selectivity of an individual compound in a group of products was calculated as the relationship between its yield and the sum of all the yields in the group.

Results and Discussion

Matrix and Catalyst Properties

The overall chemical composition of the catalyst matrices, kaolin being included, is shown in Table 1, where the various contents of alumina used in their preparation can be observed. Table 2 shows the more important properties of the matrices and the compound catalysts prepared using them; it can be seen that the specific surface area, pore volume, average mesopore size and acidity increase with the alumina content in the matrices. In the case of the catalysts, some of the properties which depend exclusively on the zeolite component (micropore specific surface area and volume), which were similar in all the cases, are consistent with the catalyst formulation method (see “Materials” section).

According to the pore size distributions shown in Fig. 1, the matrices have pore diameters which are mostly in the 20–200 Å range. The specific surface area belonging to macropores over 500 Å can be neglected in all the cases. The volume of mesopores in matrix M-45 was significantly higher than those in matrices M-38 and M-32; moreover, they were larger pores. It can be seen in Fig. 2 that the XRD patterns of the matrices and the catalysts indicate the existence of alumina in the matrices and the peaks which are typical of Y zeolite in the catalysts. The Y zeolite is the most active component in FCC catalysts, its pores exhibiting strong diffusion resistances which make that

bulky molecules hardly reach internal acidic sites. The parent USY zeolite used in this work has a unit cell size of 24.23 Å.

Catalytic Activity of the Prepared Catalysts

All the experiments of bio-oil production (pyrolysis) with immediate catalytic conversion of the vapours generated four types of products: liquid containing hydrocarbons, oxygenated products and water, gases containing mainly carbon dioxide and light hydrocarbons, and two solids (pyrolytic char, which remained in the basket containing the raw biomass and coke, the solid product of the thermal and catalytic conversion of the bio-oil, deposited on the catalyst surface).

The yields of the various product streams of the purely thermal pyrolysis of both soybean shell and pine sawdust, as well as the detailed composition of the bio-oils, were reported in Bertero and Sedran [24]. Overall, soybean shell produced more char (27.8 wt%), oxygenated compounds (33.7 wt%) and gas hydrocarbons (2.2 wt%) than pine sawdust, which produced more bio-oil (61.4 wt%) and water (24.9 wt%). Soybean shell bio-oil showed a much lower concentration of phenolic compounds (about one-fourth) and other heavy molecular weight products (five times less) than the pine sawdust bio-oil. These experiments can be considered as a blank in order to analyze the effect of different catalysts in the catalytic upgrading of bio-oils. It is to be stressed that the experimental setup used in this work allows immediately converting the bio-oil from the pyrolysis over the catalyst bed, thus contributing to decrease the process energy requirements and to avoid additional heat losses in condensation-heating-evaporation steps if liquid bio-oils are used.

In the experiments with the compound catalysts, more liquid products were obtained, about 54 wt% for the two raw materials, as compared to the matrices, which yielded from 48.4 to 51.5 wt% for the case of soybean shell and from 45.3 to 47.1 wt% for the case of pine sawdust. With both raw materials and catalyst type, the higher the alumina content in the matrix, the higher the yield of liquids. It had been reported that zeolites yielded more liquid products than mesopore acidic solids in the catalytic upgrading of bio-oils; for example, Stefanidis et al. [29] converted beech sawdust bio-oil at 500 °C to observe liquid yields from 48.5 to 53.5 wt% over ZSM-5 zeolite and from 35.4 to 45.7 wt% over alumina. Similar reports were produced by Adjaye and Bakhshi [10], who observed liquid yields in the range from 20.6 to 28.4 wt% and from 8.1 to 16.9 wt% in the cases of upgrading maple wood bio-oil over Y zeolite and silica–alumina, respectively. Under the same conditions, these authors [30] studied the combined effect of

Table 1 Composition of the matrices (wt%)

	M-32	M-38	M-45
SiO ₂	45.95	40.50	34.19
Al ₂ O ₃	51.84	56.94	63.11
TiO ₂	0.79	0.77	0.75
Fe ₂ O ₃	1.29	0.49	1.27
Na ₂ O	<0.05	<0.05	<0.05
SO ₄	0.13	1.30	0.68

Table 2 Properties of the matrices and catalysts

	M-32	M-38	M-45	C-32	C-38	C-45
<i>Textural properties</i>						
BET specific surface area (m ² /g)	74	93	113	207	218	222
Mesopore surface area (m ² /g)	74	92	106	96	114	110
Micropore surface area (m ² /g)	–	1	7	111	104	112
Total pore volume (cm ³ /g)	0.097	0.125	0.174	0.259	0.277	0.303
Mesopore volume (cm ³ /g) ^a	0.097	0.125	0.171	0.204	0.226	0.248
Micropore volume (cm ³ /g)	–	–	0.003	0.055	0.051	0.055
Average mesopore size (Å)	76.0	77.4	83.3	113.2	107.0	109.0
Acidity (μmol Py/g)	148.6	155.6	178.1	90.9	94.4	105.7
Zeolite content ^b	–	–	–	17.0	15.9	17.1

^a Mesopore volume = Total pore volume – micropore volume

^b Zeolite content was estimated by method of Johnson [27]

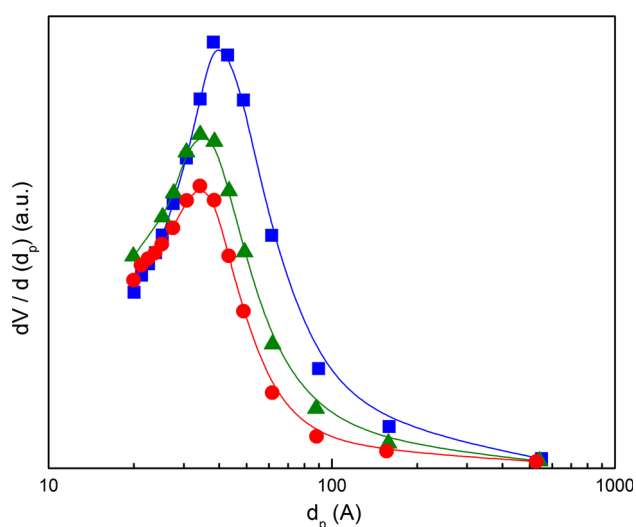


Fig. 1 Pore size distributions in the matrices. Symbols: Circle M-32; triangle M-38; square M-45

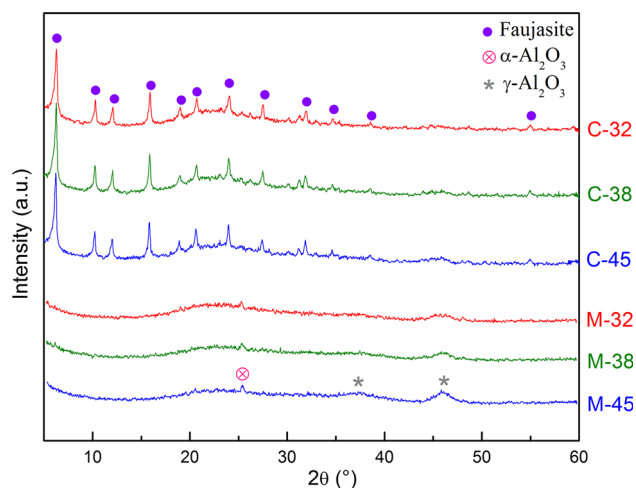


Fig. 2 XRD patterns of the matrices and catalysts

both micro and mesopores in the conversion of the same bio-oil and observed that the yield of liquid hydrocarbons was higher when mixtures of silica-alumina and HZSM-5 zeolite were used as compared to the mesoporous solid alone.

Figure 3 shows the yields of the main products in the pyrolysis-upgrading combined experiments as a function of the alumina content in the matrices. The products which were not included (for example, carbon monoxide) had very low yields less than 0.2 wt% or are not the object of this study, case of pyrolysis char. However, it is interesting to note that the pine sawdust produced more hydrogen (from 1.3 to 1.9 wt%) than soybean shell (from 0.9 to 1.6 wt%) and that for both raw biomasses the yield of hydrogen increased with the concentration of alumina in the matrix both when used alone or in combination with the Y zeolite, in consistency with the increase in the amount of acidic sites. Huber and Corma [31] proposed that in the conversion of bio-oils over zeolite catalysts hydrogen is produced by steam reforming, water gas shift, dehydrogenation and decarbonylation of the hydrocarbons and oxygenated compounds in the bio-oils. Moreover, hydrogen can also be formed by dehydrogenation and decarbonylation on the acidic sites of the matrices in FCC catalysts, even though the amount of strong acid sites is lower [32].

The yield of char was between 26.8 and 27.8 wt% in the experiments of pyrolysis and immediate catalytic upgrading with soybean shell, and between 19.8 and 21.4 wt% in those with pine sawdust, in consistency with previous reports about the pyrolysis of these biomasses [24]. It is to be considered that the yield of char is independent from the type of catalyst, since it is the only result of thermal processes in the pyrolysis step, which remains contained in the basket where the biomass was placed, without contact with the catalyst.

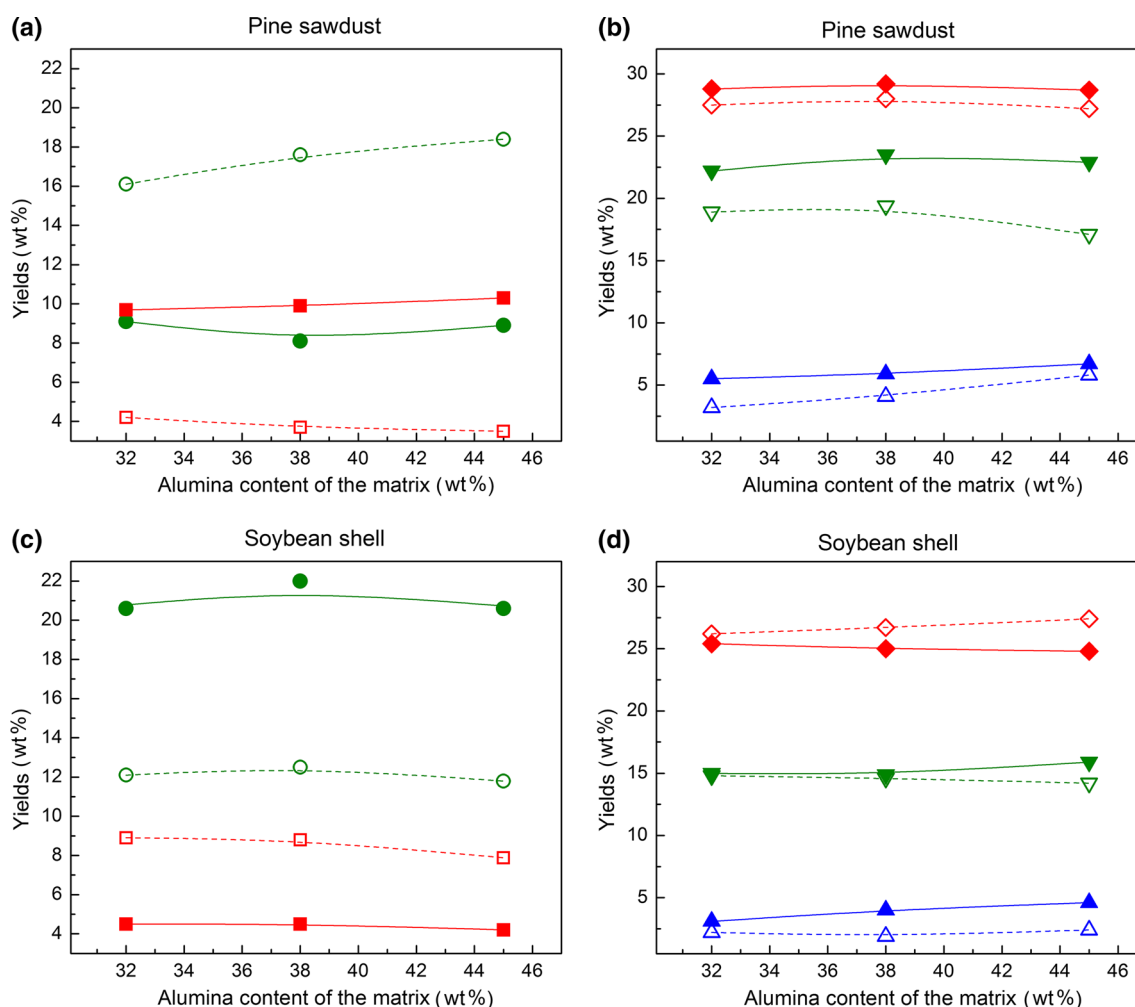


Fig. 3 Product distributions in the conversion of bio-oils on the matrices and catalysts. Symbols: closed, matrices; open, catalysts. *Square* hydrocarbons; *circle* oxygenated compounds; *triangle* coke; *inverted triangle* carbon dioxide; *diamond* water

When the matrices were the upgrading catalyst, the degree of deoxygenation of the bio-oils and, consequently, the yield of hydrocarbons, was different for each of the raw materials (see Fig. 3; Table 3): pine sawdust produced more hydrocarbons than oxygenated compounds, while soybean shell produced up to five times more oxygenated compounds than hydrocarbons. These observations are consistent with the yields of carbon dioxide and water, which indicate the degree of bio-oil deoxygenation; they were 10 and 30 % higher, respectively, in the case of pine sawdust. The effect of the acidity in the matrices was not

significant for both raw biomasses, as shown by the amount of hydrocarbons, which was essentially constant as a function of the alumina content.

Data in Table 3 corresponding to the content of oxygen in the products of the catalytic upgrading of bio-oils show their degrees of conversion and complement results shown in Fig. 3; they demonstrate that the matrices were more efficient in deoxygenating the bio-oil from pine sawdust, while the compound catalysts converted more efficiently the bio-oil from the soybean shell.

In the experiments with the compound catalysts the biomasses also showed opposing trends in relation to their deoxygenation degrees: pine sawdust bio-oil produced up to two times the amount of oxygenated compounds produced by the matrices alone and about half the amount of hydrocarbons, while soybean shell bio-oil doubled its hydrocarbon yield and decreased the yield of oxygenated compounds up to 40 %. The yields of water and carbon dioxide were consistent with the deoxygenation degrees

Table 3 Content of oxygen in the products of the conversion of bio-oils (wt%)

	M-32	M-38	M-45	C-32	C-38	C-45
Pine sawdust bio-oil	4.4	5.2	5.8	11.8	12.5	12.8
Soybean shell bio-oil	11.4	12.8	13.7	5.5	5.9	6.9

Water, carbon oxides and coke not considered

observed with the two biomasses and the two types of solids: the higher the deoxygenation, the higher the yields of these products (see Fig. 3).

These facts can be rationalized in the light of the composition of the bio-oils: that from pine sawdust has 16.2 wt% of phenolic compounds (14.0 wt% are phenolic ethers such as guaiacol, syringol and their derivatives) and 20 wt% of high molecular weight oxygenated compounds, while that from soybean shell contains 5.1 wt% of phenols (1.7 wt% are phenolic ethers) and 4 wt% of high molecular weight oxygenated compounds [24]. Many studies showed that both phenolic ethers and high molecular weight compounds in bio-oils are the main coke producers during their catalytic conversions over acidic zeolites [33, 34] and that these bulky compounds are subjected to severe diffusion restrictions in the zeolite micropore systems [28, 35], thus reacting on the crystal's external surface area to produce smaller molecules which can diffuse more easily and continue their conversion [36]. These bulky reactants produce an important amount of coke derived from polymerization reactions which deposits on the external surface areas of the zeolite and the matrix in compound catalysts. Then, this coke would block micropores in the zeolite, thus impeding the access of small molecules and oxygenated fragments to the inner surface of channels which, then, would not deoxygenate and convert them into hydrocarbons. This would justify why the deoxygenation process of pine sawdust bio-oil over the compound catalysts is not as intense as that of soybean shell. Consistently with these observations, Stefanidis et al. [29] reported that the content of oxygen in the liquid fraction obtained in the immediate catalytic upgrading of beech wood bio-oil, having a high content of phenolic compounds, was between 32 and 35 wt% in the case of using zeolite ZSM-5 and 25 wt% only in the case of using alumina. Simultaneously, the yields of the liquid fraction were between 37 and 45 wt% with the aluminas and between 48 and 53 wt% with the zeolite.

It was also shown in previous reports [8, 28] that if intracrystalline mesoporosity is produced in the crystals of zeolites, then this will facilitate the conversion of bio-oils derived from wood sawdusts, because they improve the accessibility of bulky compounds to the active sites. Particularly, the deoxygenation of the same pine sawdust bio-oil as the one used in this work under the same experimental conditions was up to three times more extended when intracrystalline mesoporosity induced by desilication was present in the zeolite, the effect being more noticeable when the severity of the desilication treatment, and consequently the mesoporosity, were higher [28].

Given these facts, it is possible to accept that in order to deoxygenate bio-oils with a high level of phenolic compounds over a certain catalyst, it is convenient that active

mesopores are present. This condition does not contribute significantly to the performance of microporous catalysts in the conversion of bio-oils with a high concentration of compounds with molecular weights lighter than 130 g/mol (aldehydes, furans, acids, esters and ketones), such as soybean shell bio-oil [24], since smaller molecules will diffuse more easily in the zeolite channels.

Oxygenated Compounds in the Conversion of Bio-oils

The selectivities to the main groups of oxygenated compounds observed in the immediate catalytic upgrading of bio-oils are shown in Fig. 4, where it can be seen that when the matrices alone were used, phenolic compounds were produced more selectively with pine sawdust than with soybean shell as the raw biomass, and the opposite was observed in the case of the compound catalysts. On the contrary, the other oxygenated compounds (acids, esters, aldehydes, ketones, furans and alcohols) all showed a behavior different from that of phenols.

It was observed for both raw biomasses that phenolic compounds were majorly represented by phenol and alkylated phenols, which are the products from the conversion of other components in bio-oil (mainly phenolic ethers and some derivatives from cellulose and hemicellulose, such as ketones) [23, 37, 38]. However, some phenolic ethers derived from guaiacol and syringol, such as methylguaiacols, methoxycatechols, acetoguaicone and 4-vinylguaiacol, among others, were observed in the group.

These evidences confirm that, overall, the soybean shell bio-oil went further in the reaction mechanism (according to the proposal by Adjaye and Bakhshi [37]) over the compound catalysts, while pine sawdust bio-oil did the same over the matrices, consistently with the global yields of hydrocarbons and oxygenated compounds, discussed in the previous section.

Following these observations, Adjaye et al. [30] reported that the phenolic compounds obtained in the catalytic conversion of maple wood bio-oil (which had low phenols content, 6.9 wt%) over silica-alumina decreased considerably when zeolite HZSM-5 was added to the amorphous solid (for example, they decreased from 11 wt% to less than 4.8 wt% at 370 °C), thus confirming the hypothesis that catalysts with micropores are more effective when the amount of phenols in the bio-oil is low.

Table 4 shows the selectivities to some oxygenated compounds in bio-oils which were selected as a function of their molecular sizes; those with kinetic diameter larger than 7.4 Å (pore size in zeolite Y) are probably pre-cracked on the acidic sites in the matrix or the external surface of the zeolite crystals in the compound catalysts, or as a consequence of the thermal level in the gas phase and only

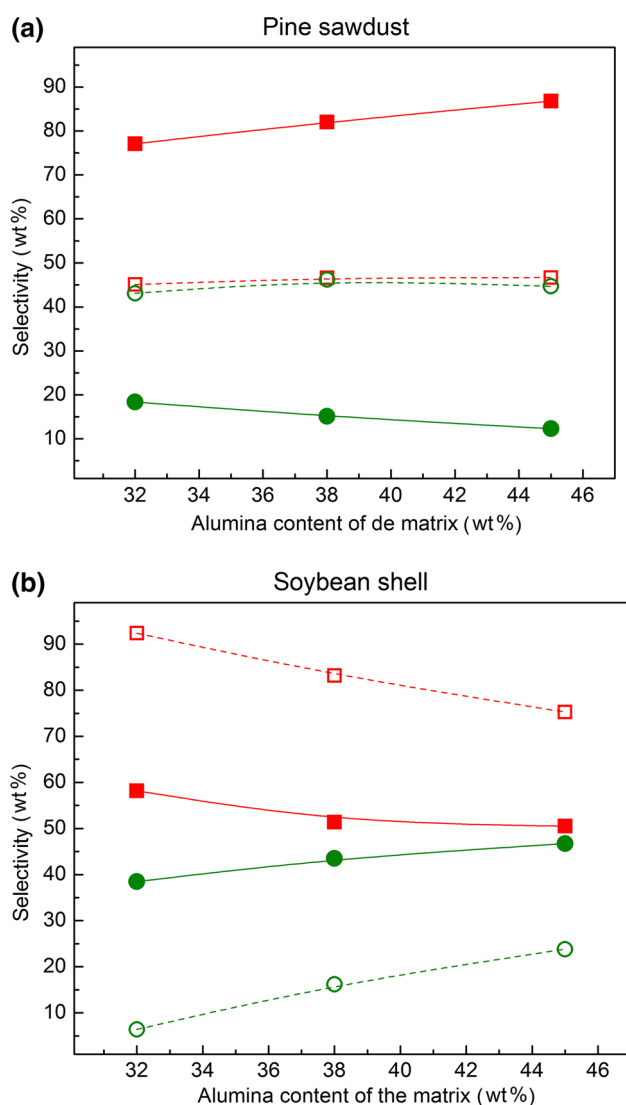


Fig. 4 Selectivity to the main groups of oxygenated compounds in the conversion of bio-oils. Symbols: closed, matrices; open, catalysts. *Square* phenolics compound; *circle* acids, esters, aldehydes, ketones, furans and alcohols

then allowed to diffuse into the zeolite's pore system. Consequently, its conversion will be affected directly by the mesopore specific surface area and the available acidic sites. Data in Table 4 are grouped in the same way as those in Fig. 4. Some minor groups in bio-oils, such as cyclic ethers and nitrogen-containing compounds, were not included because they were converted completely over all the solids or showed very low selectivities. For both raw biomasses the selectivities to phenol and alkylated phenols (cresols, dimethylphenols and trimethylphenols) increased as a function of the content of alumina in the matrices, either alone or taking part of the compound catalysts, thus showing higher conversion of the phenolic ethers which are their precursors. In the reaction mechanisms of bio-oils

over alumina and HY zeolite respectively proposed by Adjaye and Bakhshi [10] and Corma et al. [39], heavier oxygenated compounds (such as phenolic ethers) are cracked to yield lighter, still oxygenated compounds, which are later deoxygenated to yield hydrocarbons. Phenol, while being one of the compounds most refractory to deoxygenation over acidic catalysts because of the high stability of the OH group in its molecule [37, 38, 40–43], is one of these light compounds, which produces hydrocarbons after deoxygenation [43].

When the Y zeolite-matrix catalysts were used with both pine sawdust and soybean shell, the selectivity to phenol decreased to about half the value on the matrices alone. In the case of soybean shell, this is due to the more extended progress in the reaction mechanism on the compound catalysts, since it was observed that the yield of hydrocarbons (see “Catalytic Activity of the Prepared Catalysts” section) and the selectivity to alkylated phenols (cresols, dimethylphenols and trimethylphenols) increased. HY zeolite is much more effective in deoxygenating phenol than amorphous oxides due to the stronger acidic sites [32].

In opposition to observations with soybean shell, the decrease in the selectivity to phenol when the compounds catalysts were used with pine sawdust bio-oil is in line with the lower deoxygenation degree (and lower hydrocarbon yield) observed (see “Catalytic Activity of the Prepared Catalysts” section, Fig. 2; Table 3). In the case of this raw biomass the selectivities to alkylated phenols were much lower in the compounds catalysts than in the matrices alone (refer to Table 4) because of the lower accessibility of heavy, bulky compounds and phenolic ethers to the zeolite channels. It is to be stressed that phenolic ethers in this bio-oils were converted almost completely over the matrices, while selectivities from 3 to 7 wt% among oxygenated were determined over the compound catalysts. It should be noted that pine sawdust bio-oil had three times more total phenols than soybean shell bio-oil, which were about 87.5% phenolic ethers (guaiacol, syringol and their derivatives) [24].

The selectivities to the other compounds analyzed in Table 4 (which are derived mainly from the pyrolysis of cellulose and hemicelluloses) decreased significantly with the concentration of alumina in the matrix, independently of their kinetic diameters, for both raw biomasses in both series of catalysts. It is an expected result, since the amount of acidic sites increases with the content of alumina in the matrix. In the case of soybean shell bio-oil, when the compound catalysts were used, the selectivities to all these compounds decreased, thus confirming that these molecules, or their smaller derivatives, can access freely the acidic sites in the zeolite, which has a stronger deoxygenation effect than the matrix [32]. Particularly, those compounds which showed high selectivities when the

Table 4 Selectivities (wt%) of individual oxygenated products in the conversion of the bio-oils

	Kinetic diameter (Å)	Catalyst					
		M-32	M-38	M-45	C-32	C-38	C-45
Pine sawdust							
<i>Phenols</i>							
Phenol	5.2	22.1	33.6	33.1	13.2	16.5	21.2
Cresol	5.5	13.1	17.0	22.5	10.5	11.1	15.5
Dimethylphenol	6.0	11.2	13.3	23.6	5.5	14.9	14.6
Trimethylphenol	7.6	1.5	1.5	2.5	0.0	1.8	1.1
<i>Other oxygenated compounds</i>							
Acetaldehyde	4.8	4.1	3.3	1.3	1.9	0.6	–
Acetic acid	5.0	1.1	0.5	0.0	0.3	0.1	–
Vinyl acetate	5.5	2.0	1.6	0.8	1.6	0.3	–
2-propenyl butanoate	6.5	3.3	3.8	4.4	0.2	0.3	0.5
Acetone	5.2	–	–	–	2.5	1.0	0.1
Methanol	4.4	–	–	–	3.8	2.8	2.3
Furfural	5.6	5.2	0.6	–	8.3	6.4	5.0
Cyclopentenone	4.7	–	–	–	4.3	8.1	8.3
Methylcyclopentenone	5.5	–	–	–	0.5	0.6	5.3
Soybean shell							
<i>Phenols</i>							
Phenol	5.2	29.0	30.1	30.2	14.2	17.0	17.0
Cresol	5.5	9.9	11.2	15.8	19.2	28.9	30.5
Dimethylphenol	6.0	2.9	4.5	7.3	9.3	14.4	14.0
Trimethylphenol	7.6	0.2	0.8	1.0	14.2	17.2	16.6
<i>Other oxygenated compounds</i>							
Formic acid	4.2	28.6	12.6	3.7	1.0	0.8	–
Acetone	5.2	7.3	3.6	3.0	0.1	0.1	–
Methanol	4.4	1.8	1.3	0.0	0.3	0.3	0.4
Furfural	5.6	5.5	1.9	0.7	1.4	1.2	1.0
Cyclopentenone	4.7	1.0	0.6	0.7	0.3	0.3	0.3
Methylcyclopentenone	5.5	2.3	1.6	1.0	1.4	1.0	0.6

matrices alone were used, such as formic acid, were converted almost completely when the zeolite was added to the matrix. Formic acid, a major product in soybean shell bio-oil, is also produced by the conversion of the furanic compounds which are derived from the pyrolysis of cellulose and hemicelluloses [23, 44, 45].

However, in the case of pine sawdust, when the compound catalysts were used, the behaviors were different and according to the molecular size of the compounds analyzed: those with smaller kinetic diameter (such as acetaldehyde, acetic acid and vinyl acetate) decreased their selectivities in comparison to the matrices alone, because these molecules can easily enter zeolite pores and react, while other, bulkier compounds (such as furfural and methylcyclopentenone), increased their selectivities notably.

A particular case can be defined for acetone and methanol which, besides being small molecules, were

produced more selectively over the compound catalysts. This can be understood based on the fact that they are also produced from the conversion of other oxygenated compounds, especially phenolic ethers [28, 37, 38, 43]. Acetone and methanol were produced with high selectivity in the conversion of bio-oils from pine sawdust over FCC catalysts [9] and maple wood over HZSM-5 zeolite, silica-alumina and their mixtures [30].

Another factor which could influence the different observed individual behaviors of the oxygenated compounds is the interaction and competition for the active sites between them in the complex mixture, as discussed in Bertero and Sedran [9].

Hydrocarbons in the Conversion of Bio-oils

One of the main benefits from the upgrading of bio-oils is their conversion into hydrocarbons, aimed at allowing their

use as fuels or as source of petrochemical raw materials. In this sense, the production of aromatic and olefin hydrocarbons, with various and valuable applications, has been the object of many publications which involved different catalysts and processes [22, 46].

It can be seen in Fig. 5, which shows the selectivities among hydrocarbons, that for both biomasses the selectivities to gaseous hydrocarbons increased as a function of matrix activity (which is directly related to acidity and aluminum content), those to the heaviest hydrocarbons (more than eleven carbon atoms per molecule, mostly aromatic) decreased, while those to gasoline range hydrocarbons were independent of the alumina content in the matrix. Increasing the content of alumina increases acidity

in the matrices (see Table 2), thus favoring cracking and deoxygenation reactions of bio-oil components, leading to light hydrocarbons, particularly olefins [36, 39]. Gas hydrocarbons in these experiments were composed mainly by methane and olefins up to four carbon atoms per molecule, whose selectivity increased notably as a function of the alumina content in the matrix, and decreased when the compound catalysts were used. For example, in upgrading pine sawdust bio-oil, the selectivity to ethylene, which was the most important olefin, increased from 7.9 wt% (M-32) to 13.7 wt% (M-45) and from 2.4 wt% (C-32) to 6.8 wt% (C-45). In the case of soybean shell bio-oil, the selectivity to propylene (now the most important olefin) increased from 6.6 wt% (M-32) to 9.0 wt% (M-45), and from 1.1 wt% (C-32) to 1.3 wt% (C-45). Adjaye and Bakhshi [30] had reported that ethylene and propylene were the main gas hydrocarbons in the conversion of maple wood bio-oil over silica-alumina and HSZM-5 mixtures.

In a mixture of hydrocarbons, aromatics can be formed from olefins through classical cyclization and aromatization mechanisms and from naphthenics through hydrogen transfer reactions [47]; they can also be formed in bio-oils from Diels–Alder reactions from cellulose and hemicellulose derivatives [8] and from deoxygenation and cracking of phenolic compounds. Hydrogen transfer reactions require paired acidic sites and, then, it is expected that they are favored if the alumina content in the matrix is increased or, certainly, if the zeolite is present. de la Puente et al. [21] studied the impact of the composition of the matrix in FCC catalysts using cyclohexene as a test reactant under typical FCC conditions and concluded that the higher the alumina content, the more important the cyclization and hydrogen transfer reactions in comparison to cracking and isomerization. However, in the present cases, aromatic hydrocarbons decreased with increasing alumina content and acidity in the matrix, thus indicating that a more important role is possible from the other mechanisms leading to aromatics besides hydrogen transfer [8], such as decarbonylation, dehydration and hydrolysis of phenolic ethers [48], or aldol condensation of aldehydes and ketones via α - β -unsaturated carbonyl compounds and further cyclization [49].

When the compound catalysts were used, with both raw biomasses, the selectivity to gasoline increased up to two times the values observed with the matrices alone, but for the other hydrocarbon groups, these catalysts showed different performances according to the nature of the corresponding bio-oils. In effect, in the case of pine sawdust bio-oil, they were more selective to gas hydrocarbons than the matrices, which produced heavier hydrocarbons, particularly aromatics in the range of diesel fuel. The opposite was observed with soybean shell, where the compound catalysts produced up to 50 % more aromatics in the range of diesel

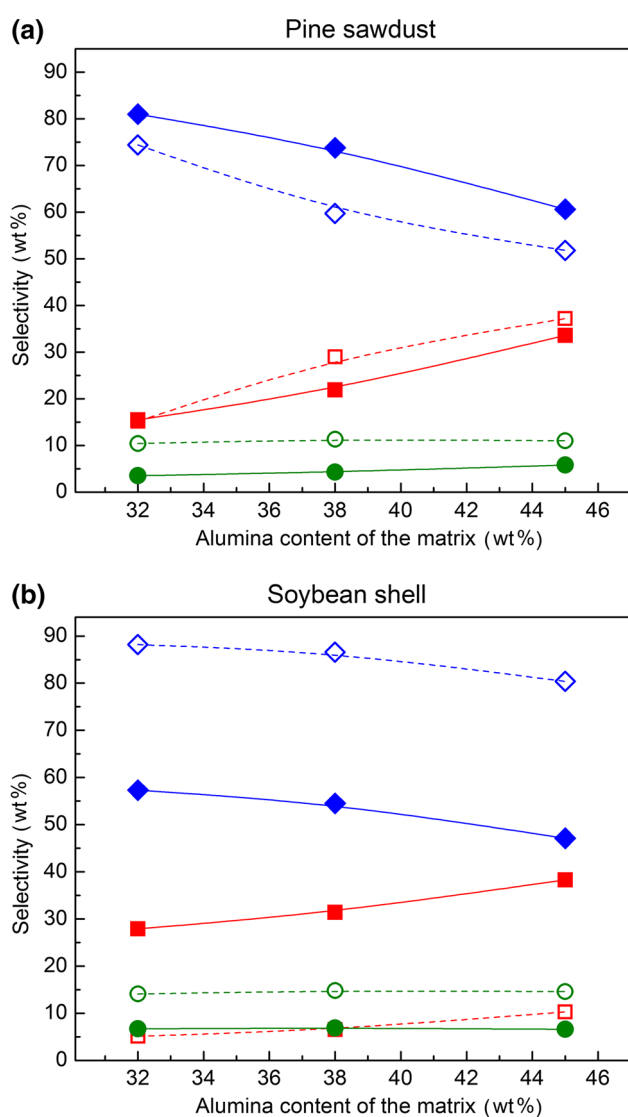


Fig. 5 Selectivity to hydrocarbon groups in the conversion of bio-oils. Symbols: closed, matrices; open, catalysts. *Square* gaseous hydrocarbons (C1–C4); *circle* gasoline; *diamond*, C11+ hydrocarbons

and up to 75 % less gas hydrocarbons than the corresponding matrices. Again these differences are based on the fact that, overall, soybean shell bio-oil is composed by lighter oxygenated compounds which, consequently, can diffuse more easily into the zeolite channels, than those in pine sawdust bio-oil. In this way the reaction mechanism can proceed further and secondary reactions such as oligomerization, cyclization and aromatization prevail. These hypothesis are sustained on the reaction mechanism proposed by Carlson et al. [22], which states that when cellulose and other carbohydrates such as glucose, xylitol and cellobiose convert on zeolites and silica-alumina, they first produce furans by means of thermal effects in the homogeneous phase or dehydration on the catalytic surface, and then furans diffuse into the zeolite to be converted into aromatics, carbon oxides and water through dehydration, decarbonylation, decarboxylation, isomerization, oligomerization and hydrogenation. Moreover, according to results from Iliopoulou et al. [50], the high yield of propylene in the catalytic upgrading of bio-oils is related to the high yields of aromatic hydrocarbons, given the role it plays in aromatic-forming reactions. It is to be noted that the bio-oil from soybean shell produced more propylene than the bio-oil from pine sawdust, which produced more ethylene.

Previous studies with these same bio-oils, using equilibrium commercial FCC catalysts under the same conditions [24], showed higher yields of hydrocarbons with more than eleven C atoms per molecule when soybean shell was used and of gaseous hydrocarbons when pine sawdust was the raw biomass. Foster et al. [35], who compared the yields of aromatic hydrocarbons in the catalytic pyrolysis of maple wood, its bio-oil having phenolic compounds, and glucose, which can be considered representative of compounds derived from cellulose and hemicellulose, reported similar results using HZSM-5 and mesoporous crystalline materials (desilicated HZSM-5). They observed that in the case of maple wood the mesoporous material produced more aromatic hydrocarbons than the zeolite, while in the case of glucose, the observations were the opposite. Stefanidis et al. [29], who studied the catalytic pyrolysis of beech wood over silicalite (high Si/Al relationship over 1000 and very few, though strongly acidic active sites) and Al-MCM-41 (low Si/Al relationship close to 30 and many, but weak, active sites), reported a higher selectivity to aromatic hydrocarbons on silicalite.

Gasoline

Hydrocarbons in the boiling range of gasoline are one of the main objectives of the catalytic upgrading of bio-oils, and aromatic hydrocarbons are the most important

hydrocarbons in this range [11, 51]. Then, it is central to analyze their yield and fuel quality and determine the factors controlling these issues.

As discussed in “Hydrocarbons in the Conversion of Bio-oils” section, the selectivity to gasoline obtained in the conversion of both bio-oils over the compound catalysts was about twice that over the amorphous matrices. It can be seen in Table 5, where the compositions of the gasoline cuts are shown, that the proportion of olefins increased and the proportion of aromatic hydrocarbons decreased with the alumina content in the matrix. Moreover, on the compound catalysts, the selectivities to olefins and to aromatic hydrocarbons significantly decreased and increased, respectively, as compared to the matrices. In the group of aromatic hydrocarbons, light compounds such as benzene and toluene decreased their proportion and heavier compounds such as alkylated benzenes and naphthalenes increased it. This can be explained as the consequence of both strong acidity and shape selectivity effects in the Y zeolite component in the catalysts (see Table 2), factors which are not present in the matrices. The primary cracking and deoxygenation reactions prevail in the matrices, while the zeolite in the compound catalysts facilitates the conversion of intermediate compounds such as olefins into aromatic hydrocarbons. Many studies of the conversion of bio-oils over zeolites and mesoporous acidic materials produced results which are consistent with these observations. For example, Williams and Horne [51] reported more aromatic hydrocarbons, particularly naphthalene and its alkylated homologous compounds, in the conversion of poplar wood bio-oil over Y zeolite than over alumina, and Adjaye and Bakhshi [31] reported significant increases in the yield of aromatic hydrocarbons and decreases in the yields of olefins and paraffins when HZSM-5 zeolite was added to silica-alumina in the conversion of maple wood bio-oil. Later, Ranzei et al. [8] concluded that zeolites

Table 5 Composition of hydrocarbons in the gasoline range cut in the catalytic upgrading of pine sawdust and soybean shell (wt%)

	Catalyst					
	M-32	M-38	M-45	C-32	C-38	C-45
<i>Pine sawdust</i>						
Olefins	52.1	58.2	60.4	23	32.3	33.7
Paraffins	7.1	5.9	4.6	8.4	11.5	14.6
Naphthenics	2.7	1	1.3	0.5	1.1	0.6
Aromatics	38.1	34.9	33.7	68.1	55.1	51.1
<i>Soybean shell</i>						
Olefins	59.6	58	58.9	12.5	14.3	17.9
Paraffins	14.6	22	21.5	16.1	19.1	28.8
Naphthenics	2.5	0.9	1.2	0.4	0.3	0.4
Aromatics	23.3	19.1	18.4	71	66.3	52.9

produce more aromatic hydrocarbons than mesoporous acidic catalysts, either crystalline such as MCM-41 or amorphous such as alumina, in the conversion of phenols derived from lignin, which are the most refractory compounds in bio-oils. Acid strength is also controlling the yield of aromatic hydrocarbons from bio-oils, as demonstrated by Carlson et al. [52] in the conversion of glucose over HZSM-5 zeolite and silicalite, which have the same structure but very different acid properties, which produced 30 wt% and only 8 wt% of aromatic hydrocarbons, respectively.

Most important olefins were pentenes and hexenes, pentenes being more abundant in the experiments with the matrices alone and hexenes on the compound catalysts. Previous studies showed that these olefins were also the most important ones in the gasoline boiling range in the conversion of pine sawdust [9] and soybean shell [24] bio-oils on equilibrium FCC catalysts.

The aromatic hydrocarbons in the gasoline boiling range included benzene, toluene and methyl and trimethyl naphthalenes; the proportion of these naphthalenes being up to 80 % higher in the experiments with the compounds catalysts. Aromatic hydrocarbons with one ring, which represented up to 60 % of the gasoline cut in the case of the matrices, are the products of the deoxygenation and the primary cracking of the phenols in bio-oils, and are also formed from the dehydration of the derivatives from the cellulose and the hemicellulose, following classical oligomerization, cyclization and aromatization mechanisms [8]. Carlson et al. [22] obtained mainly light aromatic hydrocarbons (benzene, toluene, xylenes and ethylbenzene) in the conversion of cellulose and its derivatives (glucose, xylitol and cellobiose) over silica-alumina, which was more selective, and HY zeolite.

The main paraffins in the range were pentane, isopentane (kinetic diameter 5.9 Å), 2,4-dimethylpentane (kinetic diameter 5.83 Å) and decane (kinetic diameter 4.85 Å) [53], the last two prevailing in the compound catalysts. Adjaye and Bakshi [10] obtained mainly aliphatic hydrocarbons (alkylpentanes, alkylhexenes, decane) in the C5–C10 range, and aromatic hydrocarbons (alkylbenzenes, methyl-substituted indene and naphthalene) to a lower extent in the conversion of maple wood bio-oil over silica-alumina and Y zeolite at temperatures between 290 and 410 °C. Particularly in the case of the zeolite observed heavier aromatic hydrocarbons, such as phenantrene and indacene.

The oxygenated compounds remaining in the range of gasoline (mainly phenol and alkylated phenols, see “Oxygenated Compounds in the Conversion of Bio-oils” section), could contribute to increase the octane rating of the cut. Some authors proposed that these compounds could increase octanes even more in reacting with

methanol to form methyl aryl ethers [54]. Indeed, the formulation of older gasoline octane booster additives included phenolic compounds (e.g. phenol, cresol, and dimethylphenol), ethers (methylmethoxypropane and methoxybenzene) [55, 56], furans (dimethylfuran) and ketones (4-methyl-2-pentenone) [57].

Coke

The yield of coke in the catalytic upgrading of bio-oils by acidic catalysts constitutes a significant problem, since it is one of the main reasons of catalyst deactivation. Particularly, both co-processing bio-oils together with conventional FCC feedstocks and their catalytic upgrading face an important challenge in minimizing the yield of coke leading to catalyst deactivation or compromising the heat balance in FCC units. It can be mentioned in that sense that contradictory results were reported; for example, Gueudré et al. [17] observed that the yield of coke increased up to 4 percentage points in co-processing 10 wt% hydrotreated pine sawdust bio-oil with VGO over FCC catalysts and USY zeolite (fixed bed reactor, 500 °C, Cat/Oil 6) which, according to their view, would induce important increases in the regenerator temperatures in FCC if scaled up to commercial scale. However, other studies [14] showed that coke yields did not increase significantly when pine sawdust bio-oils (both raw and after thermal conditioning) were added in quantities from 5 to 20 wt% under the same approach with an equilibrium FCC catalysts at the typical process conditions (fluidized bed reactor, 500 °C, Cat/Oil 1.7). These differences can be explained on the basis of, among other issues, the different compositions of the bio-oils. Gueudré et al. [17] used the non aqueous fraction of hydrotreated bio-oils, while both raw or conditioned bio-oils in [14] contain water at about 50 wt%; water molecules may directly compete with organic compounds (either oxygenated or hydrocarbons) for adsorption sites, thus impacting negatively on coke formation [39]. In order to design robust strategies (catalyst formulation, operating conditions) aimed at co-processing various bio-oils in refinery processes such as FCC, or bio-oil upgrading, it is necessary then to identify the nature and location of the carbonaceous deposits formed during the conversion of these feedstocks, as well as to understand the associated reaction mechanisms.

As it can be seen in Fig. 3, the matrices produced more coke than the compound catalysts, where the shape selectivity from the zeolite component decreases the magnitude of coke-forming reactions during the conversion of bio-oils [30]. It has been shown that catalysts with high mesopore volumes promote the formation of coke [8, 28]. Studies performed with bio-oil model compounds such as glycerol [39] and γ -valerolactone [58] over zeolites (ZSM-5, beta,

Y), mesoporous materials (MCM-41, alumina), and compound mesopore-micropore catalysts such as FCC catalysts, showed that the smaller the pores, the lower the coke yields, because the formation of polyaromatic coke precursors is not favored. Other authors reported results which are in line with those shown in this work; for example, Carlson et al. [22] obtained up to 50 % more coke on silica-alumina than on Y zeolite in the catalytic conversion of cellulose and other carbohydrates such as glucose, xylitol and cellobiose at 600 °C. Moreover, Adjaye and Bakhshi [36] reported coke yields from 10.3 to 28.6 wt% over silica-alumina and from 8.8 to 21.6 wt% on HY zeolite in upgrading maple wood sawdust bio-oil at temperatures from 290 to 410 °C.

Pine sawdust bio-oil produced more coke than soybean shell bio-oil in all the cases, due to its higher content of phenolic and high molecular weight compounds (refer to discussion in “Catalytic Activity of the Prepared Catalysts” section), which are coke precursors [33, 59]. It had been shown in the catalytic pyrolysis over La/HZSM-5 that the raw biomasses which include more lignin, such as wood sawdusts, produce much more coke than others with more cellulose and hemicelluloses, such as cereal shells [60].

In the catalytic conversion of bio-oils, coke is produced by the thermal polymerization of phenolic and high molecular weight compounds [40, 61] and by homogeneous reactions in the gas phase and heterogeneous reactions in the catalyst surface [52, 62]. Coke from thermal sources preferentially deposits on the external surface of zeolite crystals and on the matrix in compound catalysts, while catalytic coke forms inside zeolite channels as the result of the transformation of the oxygenated compounds on the acidic sites through oligomerization, cyclization, aromatization and condensation reactions, among others [59, 63, 64].

Table 6 shows the changes in the textural properties of the catalysts after the immediate upgrading of bio-oils for the example cases of the matrix with intermediate

aluminum content and the compound catalyst prepared using it and Y zeolite. It can be observed that the spent catalysts showed an important decrease (up to 65 %) in the BET specific surface area and total pore volume, which can be attributed to pore blocking. For both solids the specific surface area and mesopore volume were significantly affected with both raw biomasses; on the contrary, the micropore volume in the compound catalyst showed slight changes.

The catalyst pore size distribution also changed after upgrading bio-oils. As it can be seen in Fig. 6, for the case of the matrix included in Table 6 (M-38), most affected pores were those with pore diameter under 100 Å, particularly when pine sawdust was used. Data in Fig. 6 are consistent with the increase in the average size of available pores (see Table 6).

Table 7 shows that about 38–47 % of the total amount of carbon in the bio-oil from pine sawdust deposits as coke

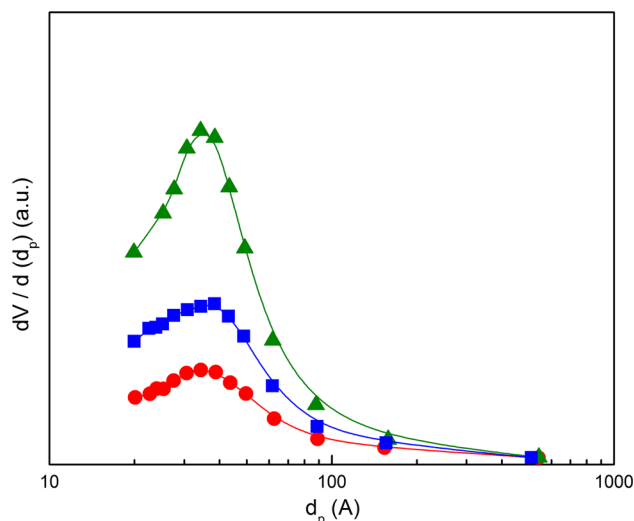


Fig. 6 Pore size distributions in matrix M-38 before (*triangle*) and after (*circle* pine sawdust; *square* soybean shell) the immediate upgrading of bio-oils

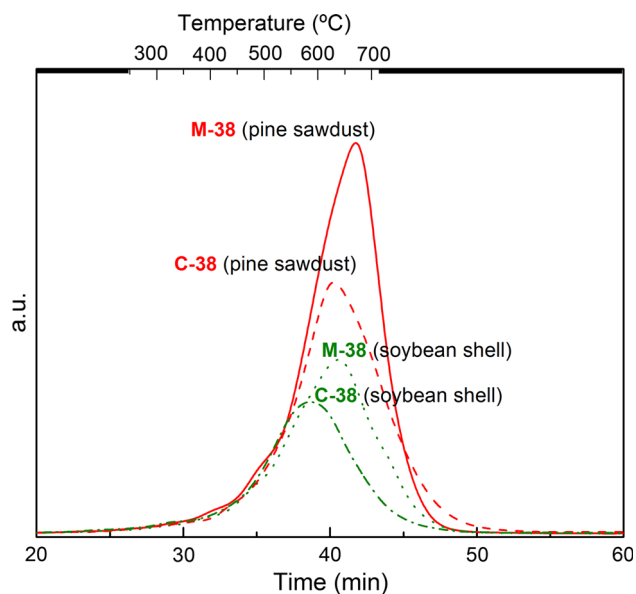
Table 6 Changes in the textural properties of the catalysts before and after the conversion of bio-oils

	M-38			C-38		
	Fresh M-38	Pine sawdust	Soybean shell	Fresh C-38	Pine sawdust	Soybean shell
BET specific surface area (m ² /g)	74	33	55	218	181	176
Mesopore surface area (m ² /g)	74	33	55	114	81	71
Micropore surface area (m ² /g)	–	–	–	104	100	105
Total pore volume (cm ³ /g)	0.0968	0.0627	0.0836	0.2774	0.2342	0.2229
Mesopore volume (cm ³ /g) ^a	0.0968	0.0627	0.0836	0.2263	0.1843	0.1707
Micropore volume (cm ³ /g)	–	–	–	0.0511	0.0499	0.0522
Average mesopore size (Å)	77.4	101.9	89.1	107.0	115.7	116.8

^a Mesopore volume = Total pore volume – micropore volume

Table 7 Amount of carbon in the bio-oils which deposits as coke in the immediate catalytic upgrading [24]

	Catalyst					
	M-32	M-38	M-45	C-32	C-38	C-45
Sawdust pine bio-oil	38.6	41.3	47.1	22.7	28.5	40.8
Soybean shell bio-oil	23.3	30.3	35.2	14.5	16.4	18.0

**Fig. 7** Combustion profiles of the coke on the matrix M-38 and the corresponding catalyst C-38 in the immediate upgrading of the bio-oils

when immediately upgraded over the matrices, while this proportion decreases dramatically, about 40 %, when soybean shell is used. Moreover, when the alumina content in the matrices increases, the amount of carbon going to coke increased. This proportion also reduces (about 50 % in the case of soybean shell) when the zeolite is added to the matrices. As discussed previously, the yield of coke with the matrices alone was higher (refer to Fig. 3), and it is to be mentioned that the combustion of the coke formed on the compound catalysts showed its maxima located at lower temperatures than those of the matrices. As seen in Fig. 7 for the example of matrix M-38, the combustion peaks in the case of pine sawdust and soybean shell bio-oils were located at about 670 and 635 °C and 660 and 620 °C, respectively. Lower temperatures in the combustion profiles indicate a lower degree of condensation in the respective coke and, consequently, a higher H/C relationship [17, 65].

The preferential decrease in the specific surface area and mesopore volume of the matrices and not in the zeolite micropores in the compound catalysts after the immediate

catalytic upgrading of the bio-oils (see Table 6) could be explained based on the observations by Gueudrè et al. [17]. These authors studied the co-processing of hydrotreated pine sawdust bio-oil over equilibrium FCC catalysts and USY zeolite, and postulated that the coke derived from the oxygenated compounds deposits preferentially on the matrix mesopores, while that from VGO hydrocarbons, which is more condensed, deposits on the zeolite component.

Conclusions

The performance of high alumina, silica-alumina matrices of FCC catalysts and the compound catalysts including Y zeolite which were formulated with them was investigated in the immediate catalytic upgrading of bio-oils from different raw biomasses (pine sawdust and soybean shell). The compositions of the bio-oils were very different, particularly in relation to the content of high molecular weight compounds such as phenolic ethers. These compounds are more diffusionally restricted in their conversion over micropore catalysts such as Y zeolite than other components of bio-oils such as acids, esters, aldehydes and linear ketones.

The content of alumina in the matrix has not a major effect on the overall distributions of products, as shown by the results observed with both bio-oils. However, even though the total amount of oxygenated compounds remained essentially constant, those originally present in the bio-oils decreased (that is, reacted) and those which are products, such as phenols, increased when the concentration of alumina increased.

On the contrary, the composition of the bio-oil significantly conditions the performance of the catalyst. It was observed that, in terms of the yield of hydrocarbons, the matrices alone were more efficient in deoxygenating the bio-oil from pine sawdust, while the compound catalysts converted more efficiently the bio-oil from the soybean shell. Lesser hydrocarbons are produced from the pine sawdust bio-oil on the compound catalysts because a significant part of the oxygenated compounds (those with heavy molecular weight) can not enter micropores and form coke which obstructs them, thus preventing lighter compounds from accessing the micropore system and converting into hydrocarbons.

It is possible to accept, then, that in order to deoxygenate bio-oils with a high concentration of phenolic compounds, such as those derived from woods, it is convenient that the catalyst includes mesopores in order to decrease the diffusion restrictions of these compounds and ease their conversion. This fact would be less important in the upgrading of bio-oils from low lignin biomasses, where

the concentrations of aldehydes, furans, acids, esters and ketones of low molecular weight prevail.

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