FCC Matrix Components and Their Combination with Y Zeolite to Enhance the Deoxygenation of Bio-oils

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Abstract

The immediate catalytic conversions of pyrolytic bio-oils from pine sawdust and soybean shell over mesoporous catalysts (silica, alumina, and silica-alumina) and their combinations with Y zeolite, were studied. The effect of mesoporosity and acidity on the bio-oil deoxygenation and conversion into hydrocarbons was investigated. Pyrolysis and immediate catalytic conversion of bio-oil were performed in an integrated pyrolysis–upgrading reactor, for 7 min under a 30-ml/min flow of nitrogen at 550 °C. Important differences were observed in the conversion of the bio-oils, according to the composition of the raw biomasses. Pine sawdust bio-oil produced more coke and less hydrocarbons in the range of gasoline than soybean shell bio-oil over all the catalysts. Mesoporous catalysts showed conversion and deoxygenation between 14 and 29 percentage points higher with the more acidic solid (SiO_2-Al_2O_3) in the case of pine sawdust bio-oil and between 2 and 10 percentage points higher with the solid having the highest specific surface area (SiO_2) in the case of soybean shell bio-oil. Among the compound catalysts, the best performance for the case of pine sawdust corresponded to the catalyst with the highest mesoporosity (Y/SiO_2), while for soybean shell corresponded to the most acidic catalysts (Y/Al_2O_3 and Y/SiO_2-Al_2O_3). Soybean shell bio-oil showed more low molecular weight compounds (less than 130 g mol^{-1}), which diffuse more easily in the zeolite channels, thus favoring conversion and deoxygenation mechanisms. On the contrary, for pine sawdust bio-oil, the surface area contributed by the mesopores in the matrix played a key role in pre-cracking bulky molecules.

Keywords Bio-oil · FCC catalyst · Hydrocarbons · Deoxygenation

Introduction

Fossil fuels are the main energy source at present, but considering limitations in their availability and lack of renewability, as well as the negative impact derived from their consumption, there exists a growing need to develop new sources of renewable energy. Lignocellulosic biomasses, particularly the residual ones, composed of polymeric carbohydrates and lignin, are the most abundant and lowest cost materials that can be employed, among other uses, to produce second-generation biofuels, one of the most important advantages being that they are not food sources.

Lignocellulosic biomass can be transformed into fuels by means of thermo-chemical processes, among which pyrolysis and gasification show higher technical and economic feasibility [1]. Pyrolysis is particularly interesting, given that it can yield liquid products (bio-oils) which can be transformed into transportation fuels and raw materials for the chemical industry by means of catalytic processes, e.g., hydrotreating [2] or conversion over acidic zeolites [3]. Both approaches have been the subject of extensive research [4–6], but studies are still needed to reformulate processes and catalysts or to develop new views using consolidated processes, such as the catalytic cracking of hydrocarbons (FCC).

Bio-oils could play in FCC the role of non-conventional feedstocks, similarly to residual hydrocarbon cuts [4], in partial replacement of conventional feedstocks, usually vacuum gas oils, VGO, and be co-processed. This option has shown promising results from research [4–9]. Coke produced in FCC co-processing preferentially deposits on the catalyst matrix, according to Gueudrè et al. [10], who co-processed bio-oil from pine sawdust and VGO.

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Acid catalysts that have pores in the range of mesopores, such as alumina and silica-alumina, providing better accessibility to active sites to bulky molecules, in combination with acid zeolites, which have stronger acid sites but their micropores impose severe diffusion restrictions to most bio-oil molecules, were shown to be more efficient to upgrade bio-oil than zeolites alone. Thus, the yields of coke are reduced and the yields of products of interest are increased [11, 12]. Y and ZSM-5 were the most studied zeolites under this concept [13, 14]. García et al. [15] showed that better performances in the deoxygenation of pine sawdust bio-oil were produced with hierarchical Y zeolites in comparison with the parent zeolite, the hydrocarbon yields being up to 38% higher; those zeolites had an internal mesoporous structure generated by means of alkaline lixiviation, which produced a more effective conversion of most voluminous compounds in bio-oil. Eschenbacher et al. [16] studied the ex situ deoxygenation of straw fast pyrolysis bio-oil, showing that the generation of mesopores by desilication of the HZSM-5/Al2O3 catalyst extrudates used produced a more important recovery in bio-oil of the energy and the carbon content of the raw biomass.

FCC catalysts are composed of Y zeolite supported on a matrix (active or inactive), binders, and various additives [17]. The matrix provides size, shape, and density to the particles so they can circulate properly between the reactor and regenerator units and may facilitate pre-cracking of most bulky molecules and diffusion to the active sites [18].

Some of the molecules in bio-oils, such as acids, alcohols, and aldehydes and some ketones and furans, do not suffer from important diffusion restrictions in the structure of Y zeolite. Oppositely, bulkier molecules, mainly phenolic ethers such as guaiacol, syringol, and derivatives, react initially on the matrix and/or the external surface of zeolite crystals, thus contributing to pore blocking and catalyst deactivation [3, 14]. Nevertheless, certain compounds in bio-oils with particular chemical structures, such as some ketones and branched furans, showed to be refractory on some zeolites besides not being too voluminous [19–22].

In order to validate decisions about co-processing bio-oils in FCC units, it is necessary to know about the mechanisms of bio-oil deoxygenation over FCC catalysts, particularly considering that its composition is essential to understand the distribution of products.

The conversion of bio-oils obtained from different raw materials, with very different compositions, was studied in this work separately over the main components of FCC catalysts: microporous Y zeolite and mesoporous matrix materials (silica, alumina, and silica-alumina). The performance of these solids was also studied when taking part, at the usual commercial proportions, in compound FCC catalyst prototypes. In both cases, an integrated approach of bio-oil generation and immediate conversion was used.

Emphasis was given to the catalyst's ability to deoxygenate bio-oils. Moreover, information was produced about the behavior of all the chemical types composing bio-oils, both bulky and refractory compounds, and easier to deoxygenate compounds, considering that the reaction mechanisms for the various chemical groups, when taking part in a complex mixture, are different from those observed when pure.

Materials and Methods

Biomass

Raw biomasses used were pine (*Pinus elliotti*) sawdust, with particle size between 1 and 6 mm (70% between 4 and 6 mm), and soybean (*Glycine max*) shell, with particle size between 3 and 10 mm (70% between 5 and 7 mm). Before use, the biomasses were dried for 24 h at 100 °C in an oven. Both raw materials were provided by regional mills, their main characteristics being shown in Table 1.

Properties of the biomasses were determined following ASTM D317 (humidity), ASTM D3173 (volatiles), and ASTM D3174 (ashes) standards. Fixed carbon was calculated by difference from the previous properties. The biomass compositions were determined by means of acid detergent lignin (ADL), following PROMEFA V2 protocol for ANKOM equipment, acid detergent fiber (ADF, ISO 13,906:2008), and neutral detergent fiber (NDF, ISO 16,472:2006). The elemental composition was determined in a CHON-CHN 628 Series Elemental analyzer (LECO

Table 1 Properties of biomasses (%wt. dry basis)

	Pine sawdust	*Soybean shell*
Moisture (%wt.)	9.5	10.0
Proximate analysis		
Volatile matter	76.3	77.2
Fixed carbon	22.9	18.4
Ash	0.8	4.3
Composition		
Lignin	28.0	4.3
Cellulose	35.0	40.3
Hemicellulose	29.0	29.4
Lipids		4.0
Proteins		7.9
Elemental composition		
C	51.6	45.4
H	5.2	6.7
O	43.2	46.9
N	0.1	0.9
S	n.d	0.1
HHV (MJ kg^{-1})	19.7	18.8

Corporation). The heating value was calculated based on the elemental composition [22].

Catalyst Preparation

Table 2 shows the nomenclature and nominal composition of the catalyst used. Six catalysts were prepared: three of them were mesoporous with different porosities and acidities (SiO_2, Al_2O_3, and SiO_2-Al_2O_3) and the other three were compounded with Y zeolite (Y/SiO_2, Y/Al_2O_3, and Y/SiO_2-Al_2O_3). SiO_2 (chromatographic grade, Merck) and Al_2O_3 (Sasol, dispersal pseudoboehmite) were commercial. SiO_2-Al_2O_3 was prepared with 50% kaolin, 38% alumina and 12% silica based on the method described in Magee and Blazek [23], with minor modifications, using sodium silicate as the silica source and aluminum sulfate as the aluminum source.

Y/SiO_2, Y/Al_2O_3, and Y/SiO_2-Al_2O_3 compound catalysts were prepared using Y zeolite (H-USY, Zeolyst CBV 760), the corresponding mesoporous matrix and colloidal silica (Ludox AS-40, Aldrich) as a binder. Before catalyst preparation, in order to stabilize the zeolite, it was steamed (100% steam, flow rate of 2.0 g min^{-1}) in a fixed-bed quartz reactor at 788 °C for 5 h. In all the cases, the zeolite, matrix, and binder components were mixed to form the catalysts at 30, 50, and 20%wt., respectively, thus reproducing typical formulations of commercial FCC catalysts [17]. The three components were mixed at zeolite/matrix/binder: 30/50/20 nominal proportion, adding a mass of water equal to that of the binder, to produce a homogeneous paste. The paste was dried at 110 °C for 16 h. Once calcined (heating ramp of 12 °C min^{-1} up to 550 °C, and then maintained at 550 °C during 4 h), the catalysts were ground and sieved, and the 75–125-µm fraction was used.

Catalyst Characterization

The catalyst textural properties were assessed after the adsorption of nitrogen at −196 °C in a Micromeritics ASAP 2020 equipment, the samples being previously degassed at 300 °C for 3 h. The BET method was used to determine the specific surface area, the total pore volume was estimated

Table 2 Catalyst nominal composition

SiO_2	100% silica
Al_2O_3	100% alumina
SiO_2-Al_2O_3	50% kaolin, 38% alumina, 12% silica
Y/SiO_2	30% H-USY, 70% silica
Y/Al_2O_3	30% H-USY, 50% alumina, 20% silica
Y/SiO_2-Al_2O_3	30% H-USY, 25% kaolin, 19% alumina, 26% silica

at P/Po ~ 0.98 and the micropore volume and the specific surface area of the mesopores were estimated by means of the t-plot method. The Barrett-Joyner-Halenda (BJH) model was used to determine the mesopore size distribution and the average pore diameter according to Eq. 1

$$\bar{d}_p = \frac{\int_{20A}^{500A} d_p g(d_p) d(d_p)}{\int_{20A}^{500A} g(d_p) d(d_p)} \tag{1}$$

where $g(d_p)$ is the pore size distribution given by $d(\text{Vol})/d(d_p)$ (cm^3 g^{-1} Å^{-1}).

The content of zeolite material in the compound catalysts was assessed according to the method by Johnson [24]. A Shimadzu XD-D1 diffractometer was used to collect the zeolite X-ray diffraction patterns in the $5° < 2\theta < 40°$ range. The zeolite unit cell sizes (UCS) were calculated following the ASTM D 3942 method.

Acidity in the various solids was determined by means of the temperature-programmed desorption (TPD) of pyridine. The solids were pretreated in situ under N_2 flow at 500 °C for 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 for 1 h with N_2 flow. The TPD experiments were carried out by heating at 12 °C min^{-1} in the 150 to 800 °C range, pyridine being detected with a FID detector after methanation on a Ni catalyst.

Catalytic Upgrading of Bio-oil

The experiments of pyrolysis and immediate catalytic conversion of bio-oil were performed in integrated pyrolysis–upgrading reactor, which was comprehensively described in García et al. [15]. Briefly, the reactor consists of two zones electrically heated; in the first zone, the purely thermal pyrolysis occurs while in the second zone the pyrolysis volatiles (bio-oil) are converted into a catalytic fixed bed. A 5-cm-long stainless steel basket containing the biomass (5 g) is suddenly introduced in the first zone once the target reaction temperature is reached. In this manner, the polymerization and condensation reactions of the pyrolysis products, which diminish the yield of bio-oil, are minimized. Then, the pyrolysis volatiles are passed through the catalytic bed with 1 g of a catalyst supported on a porous metal plate.

The experiments were carried out during 7 min under a 3-ml min^{-1} flow of nitrogen at 550 °C in both zones (this temperature was chosen because it maximizes the yield of bio-oil [25]). The outlet gas stream was passed through a chiller at −5 °C, where liquids were condensed and the non-condensable gases were retained and quantified by displacement with the aid of a water column. Once the reaction was completed, a stream of nitrogen (30 ml min^{-1}) was used to

sweep the reactor for 7 min. The experiments were duplicated, showing differences lower than 5% in the observations of product compositions. In all the experiments, the mass balances showed recoveries higher than 90%.

The cumulative catalyst to oil mass relationship (3.5) was calculated based on the organic compounds present in the bio-oil. Purely thermal pyrolysis experiments were also performed with the raw biomasses in order to produce background information.

Product Analysis

Both liquids and gases were analyzed by means of capillary gas chromatography. Liquids were analyzed with the aid of a Varian GC 450 gas chromatograph using a capillary column (30 m long, 250-μm diameter, and 0.25-μm film thickness, non-polar, dimethylpolysiloxane HP-1) and a FID detector. An Agilent 6890 N gas chromatograph with a bonded monolithic carbon-layer GS-CARBONPLOT column (30 m long, 530-μm diameter, and 3.0-μm film thickness) and TCD detection was used to analyze the gases. The specific response factors for each of the chemical groups were evaluated from mixtures of standards and reference compounds (tetralin for liquids and methane for gases).

The concentration of water in the liquid products was determined by means of Karl-Fischer titration (IRAM 21,320). The amount of coke on the catalyst was assessed with thermal programmed oxidation (TPO; initial temperature, 250 °C during 15 min; heating ramp, 16 °C min^{-1}; 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 each compound in the experiments was calculated with Eq. 2, the conversion of bio-oil and their components with Eq. 3, and the degree of deoxygenation of bio-oil (molar basis) with Eq. 4.

$$y_i = \frac{m_i}{m_b} \cdot 100, \tag{2}$$

$$X = \frac{m_{ox,0} - m_{ox}}{m_{ox}, 0} \cdot 100, \tag{3}$$

$$Deoxygenation(\%) = \frac{O_{BO} - O_P}{O_{BO}} \cdot 100, \tag{4}$$

where
y_i: the yield of product i (%wt.)
m_i: the mass of product i
m_b: the mass of biomass
X: the conversion of bio-oil and oxygenated compounds in bio-oil (%)

$m_{ox,0}$: the mass of oxygenated compounds in bio-oil obtained in the purely thermal pyrolysis experiments
m_{ox}: the mass of oxygenated compounds in the pyrolysis-catalytic upgrading experiments
O_{BO}: the moles of oxygen in bio-oil in the purely thermal pyrolysis experiments, excluding water
O_P: the moles of oxygen in reaction liquids products in the pyrolysis-catalytic upgrading experiments, excluding water

The selectivities to gasoline and gaseous products were calculated as the relationship between the yield of the corresponding hydrocarbon group and the total yield of hydrocarbons.

Results and Discussion

Catalyst Properties

All the three synthetic mesoporous oxides studied, SiO_2, Al_2O_3, and SiO_2-Al_2O_3, are conventionally used as the matrix in commercial FCC catalysts, depending on the final application in refineries [18]. It is possible to mention the following functions of a catalyst matrix: (i) binding agent to ensure the correct conformation and mechanical stability of the catalyst particles, (ii) zeolite diluent to control activity, (iii) contaminant metal trap, (iv) heat carrier, (v) diffusion medium for reactants and products, and (vi) bulky molecule pre-cracking catalyst [17]. In the catalytic upgrading of bio-oils, these last two aspects undoubtedly can play a key role in the deoxygenation of phenolic ethers such as guaiacol, syringol, and derivatives, as well as other bulky molecules [13, 26].

Silica is considered a relatively inert material as it does not have acidic OH groups and only slight Lewis acidity can be noticed [27]. However, some controversy exists in the literature regarding the catalytic activity of silica. For example, it has been reported that surface silanols (Si–OH groups) showed certain catalytic activity in the cracking of high-density polyethylene [28]. The cracking activity was attributed to a carbenium ion mechanism over the silanol groups that lie on the walls of the pores [28]. Alumina can show both acidic OH groups (Brönsted acidity) as well as Lewis acid sites [18]. Both Brönsted and Lewis sites have been detected in silica-alumina [17, 18]; according to the preparation method, it is possible to adjust the alumina content and, consequently, acidity.

Table 3 shows the properties of the Y zeolite and the various compound catalysts. SiO_2 exhibited the highest specific surface area, all provided by mesopores and, consequently, the highest mesopore volume among the various catalysts. It is interesting to note that the Y zeolite was steamed before the preparation of the compound catalysts in order to provide

Table 3 Catalyst properties

	H-USY	Mesoporous catalysts			Compound catalysts		
		SiO$_2$	Al$_2$O$_3$	SiO$_2$-Al$_2$O$_3$	Y/SiO$_2$	Y/Al$_2$O$_3$	Y/SiO$_2$-Al$_2$O$_3$
Textural properties							
BET specific surface area (m^2/g)	838	438	139	93	348	260	218
Mesopore surface area (m^2/g)	226	438	136	92	328	156	114
Micropore surface area (m^2/g)	612	-	3	1	20	105	104
Total pore volume (cm^3/g)	0.632	0.751	0.441	0.125	0.531	0.506	0.277
Mesopore volume (cm^3/g)[a]	0.282	0.751	0.438	0.125	0.524	0.453	0.226
Micropore volume (cm^3/g)	0.350	-	0.003	-	0.008	0.053	0.051
Average mesopore size (Å)	19.0	87.9	126.1	77.4	61.0	77.7	40.8
Acidity (μmol Py^{-1})	83.0	51.3	103.3	155.6	68.7	108.0	94.4
Weak acid sites	15.0	51.3	41.3	38.9	68.4	50.7	42.8
Strong acid sites	68.0	0.0	62.0	116.7	0.3	57.3	51.6
Zeolite content[b]	-	-	-	-	9.0	16.1	15.9
UCS (Å)	24.21	-	-	-	24.21	24.21	24.21

[a]Mesopore volume = Total pore volume − Micropore volume.
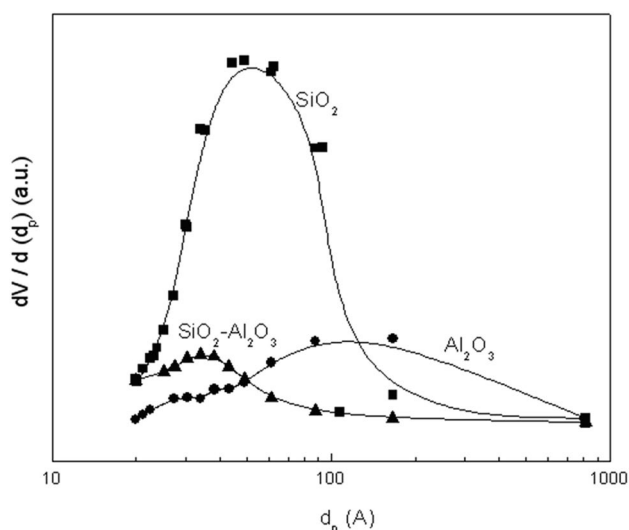
[b]Johnson's method [24]

Fig. 1 Pore size distribution in mesoporous catalysts

hydrothermal stabilization. According to the micropore surface area of the zeolite after steaming, the estimated content of crystalline material is around 61% [24]. If 30%wt. of zeolite is incorporated in the compound catalysts, an upper limit of crystalline material at about 18% is expected in the final catalysts.

According to the pore size distributions shown in Fig. 1, SiO$_2$ and SiO$_2$-Al$_2$O$_3$ 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 both cases), while the Al$_2$O$_3$ catalyst showed most of its pores in the 80–300-Å range.

The compound catalysts showed higher specific surface areas than mesoporous catalysts, with the exception of Y/SiO$_2$, with an important amount of micropores provided by the zeolite component. The average size of mesopores in the compound catalysts was appreciable smaller than in the parent mesoporous materials; this could be due, in part, to the contribution of mesopores in the zeolite, having an average size of 23 Å, and to the impact of the addition of the ligand agent to conform the particles.

The compound catalysts were more acidic than the corresponding parent mesoporous materials, as contributed by the zeolite, with the exception of Y/SiO$_2$-Al$_2$O$_3$, which was less acidic than the amorphous mesoporous catalyst. Concerning the distribution of acidic sites, the Y zeolite showed more than 80% of strong acid sites (pyridine desorbing at temperatures higher than 200 °C). In the case of the compound catalysts, essentially all the acidity in Y/SiO$_2$ was due to weak acid sites (pyridine desorbing at temperatures lower than 200 °C), while Y/Al$_2$O$_3$ and Y/SiO$_2$-Al$_2$O$_3$ showed slightly more strong than weak acid sites.

It was shown in a previous work with silica-supported Y zeolite that the oxygenated compounds in a pine sawdust bio-oil can also be converted on the support alone, through thermal mechanisms which are promoted by the surface area provided by the silica. However, conversion and hydrocarbon and coke yields were lower than those obtained when the zeolite was present [15]. The catalytic conversion of a bio-oil is conditioned by both the acidic and textural properties of a catalyst; then, higher acidity in the cases of alumina and silica-alumina in these experiments, as compared to silica, would provide higher deoxygenation catalytic activity.

Catalyst Performances: Product Yields

The combined experiments of pyrolysis and immediate catalytic upgrading produced four product streams: liquid products (composed of hydrocarbons, oxygenated compounds, and water), gaseous products (composed mainly of carbon dioxide, hydrogen, and light hydrocarbons), and two solid products (char from pyrolysis, remaining in the biomass basket, and coke from the catalytic conversion of bio-oil, deposited on the catalyst particles). Table 4 shows the product yields, as compared to those corresponding to purely thermal pyrolysis (no catalyst used), where soybean shells produced more gases and char and less liquids than pine sawdust. In both cases, the various yield products were in the ranges reported for different biomasses under similar pyrolysis conditions [29–31].

When silica was used as the upgrading catalyst, the yield of liquids was higher and the yield of gases was lower than the yields observed from the purely thermal pyrolysis, for both raw biomasses. This fact can be attributed to the existence of a contact area favoring thermal reactions [13, 15].

However, when the other two mesoporous solids were used, the yield of liquid products with both biomasses decreased in comparison to those from the thermal process, this difference being more important in the case of SiO_2-Al_2O_3. This could be the consequence of higher amounts of acid sites favoring the cracking of the components of the bio-oil to gas products and coke. Similar observations were reported by Iliopolou et al. [32] in the in situ upgrading of bio-oil from beech sawdust on MCM-41 materials with different acidity; with siliceous MCM-41 (no acidity), they obtained more liquid products than in the case of purely thermal pyrolysis, while higher acidity in the catalysts produced more gases at the expense of lower liquid yield.

In relation to coke yields, the lowest yield with both biomasses was produced on SiO_2, an obvious consequence of having only thermal polymerization and condensation reactions of the oxygenated compounds on the solid surface. The opposite effect was observed on the Al_2O_3 and SiO_2-Al_2O_3 solids with acid sites. It has been postulated that the strong acidic sites promote oligomerization, condensation, and polymerization reactions leading to coke [33].

When micropores and strong acid sites are present on the Y zeolite-mesoporous solid compound catalysts, the liquid yields were lower in most cases. On the contrary, gas yield increased for both biomasses, because the strong acidic sites on the zeolite promote cracking reactions, while coke yield increased in some cases and decreased in others, thus showing the influence of the bio-oil composition. Moreover, as previously reported by García et al. [15], coke formation is also favored in the microporous structure of Y zeolite given, in part, by the restrictions imposed to the diffusion of bulky molecules such as phenolic ethers and substituted cyclic ketones present in bio-oils, which react on the external surface of zeolite particles or on the matrix surface. These results are in line with the report by Lappas et al. [34], who observed increases in the yield of gases in the pyrolysis of a commercial lignocellulose when an inert material (silica sand) was substituted by a FCC catalyst with 10%wt. of a ZSM-5 additive.

The bio-oil from pine sawdust produced much more coke than the bio-oil from soybean shell over all the catalysts. The highest yields were observed with Al_2O_3 among mesopore solids and with Y/Al_2O_3 among compound catalysts in the first case and with SiO_2-Al_2O_3 and Y/SiO_2-Al_2O_3, respectively, in the second case. The higher availability of larger pores in Al_2O_3 and Y/Al_2O_3 permits to localize bulky molecules, such as phenols, which can contact acidic sites [15] and increase coke yield. Phenols are coke precursors [19, 21], which can be found much more extensively in pine sawdust bio-oil than in soybean shell bio-oil. Soybean shell bio-oil produced more coke over the most acidic catalysts, probably due to its high content of low molecular weight furans and ketones, which can be converted more easily on microporous acid catalysts [20, 35].

Table 4 Product yields in the combined experiments of pyrolysis and immediate catalytic upgrading (%wt., dry biomass basis)

	No catalyst	Mesoporous catalysts			Compound catalysts		
		SiO_2	Al_2O_3	SiO_2-Al_2O_3	Y/SiO_2	Y/Al_2O_3	Y/SiO_2-Al_2O_3
Pine sawdust							
Liquid	61.4	64.2	56.2	50.5	54.3	54.3	53.5
Gases	17.2	10.6	17.6	23.5	19.4	18.7	22.6
Char	21.4	23.8	20.0	20.1	23.5	20.1	19.9
Coke	-	1.4	6.1	5.9	2.8	6.9	4.1
Soybean shell							
Liquid	54.3	59.5	54.1	53.3	57.4	56.0	51.2
Gases	17.9	12.2	15.7	15.4	15.4	15.3	20.1
Char	27.8	27.3	27.0	27.3	26.2	27.0	26.8
Coke	-	1.0	3.3	4.0	1.0	1.8	1.9

Bio-oil Conversion and Deoxygenation

In the conversion of the oxygenated compounds in bio-oils, they are initially subjected to dehydration and cracking reactions, the latter proceeding both on the catalyst surface and in the homogeneous gas phase. Dehydrated species, which are smaller than the parent compounds, can diffuse more easily in the zeolite internal channels, if present, and access to the stronger acid sites to be converted into hydrocarbons, carbon oxides, and coke, by means of a complex set of reactions including, mainly, decarbonylation, decarboxylation, isomerization, oligomerization, and dehydrogenation [13, 36].

Table 5 shows conversions and deoxygenation degrees observed in the generation and immediate catalytic upgrading of bio-oils. The contents of oxygen in pine sawdust and soybean shell bio-oil were 45.3 and 47.0%wt., respectively, as shown in Table S1 together with the detailed composition of bio-oils. The detailed list of oxygenated compounds identified in the liquid products of the combined experiments of pyrolysis and immediate upgrading of the bio-oils are shown in Tables S2 and S3 for the cases of pine sawdust and soybean shell, respectively. It is important to recognize that some oxygenated compounds are in turn the products of the conversion of others and, thus, are considered in the calculations of the group conversions. For example, formic acid results from the thermal conversion of methanol [37]; phenol is the product of the conversions of heavier phenolic compounds [38–40] and acids [41]; acetone can be formed from acetic acid [42] and methanol from the demethoxylation of phenolic ethers [43–45].

It can be seen that conversions were high over all the solids, differences depending on bio-oil nature: when mesoporous catalysts were used, the best performance for pine sawdust in terms of conversion and deoxygenation was obtained with $SiO_2-Al_2O_3$, while SiO_2 was the best choice for soybean shell. Then, according to the raw material, a certain surface area and low acidity is enough to produce deoxygenation reactions. If the catalyst, for example, $SiO_2-Al_2O_3$, has a higher density of acid sites, reaction mechanisms change, and the importance of catalytic reactions such as oligomerization, aromatization, alkylation, and isomerization clearly increase [46], leading to hydrocarbons and coke. On the contrary, if the catalyst majorly provides surface area, thermal dehydration reactions become important; for example, the conversion of soybean shell bio-oil over SiO_2 produced more water and less hydrocarbons (see Table 6 in the "Distribution of Liquid and Gaseous Products" section) and coke (see Table 4 in the "Catalyst Performances: Product Yields" section) than over the other mesoporous catalysts. In this sense, Olazar et al. [47] showed that oxygenated compounds adsorb on inert materials, such as silicon carbide and silica, and that some deoxygenation reactions are produced on not acidic solid areas; for example, the dehydration of ethanol from *Pinus insignis* sawdust pyrolysis to form ethylene and water proceeds on sand. Other authors showed deoxygenation degrees up to 60% when using acid catalysts. For example, Ibarra et al. [48] evaluated the performance of different zeolite-based catalysts (HY, HZSM-5, and HBeta) in the catalytic cracking of bio-oil from the pyrolysis of pine sawdust; they used a fluidized bed reactor at 550 °C and observed deoxygenations between 61 and 80%. Naqvi

Table 5 Bio-oil and group conversions in the immediate catalytic upgrading over the various catalysts

	Mesoporous catalysts			Compound catalysts		
	SiO_2	Al_2O_3	$SiO_2-Al_2O_3$	Y/SiO_2	Y/Al_2O_3	$Y/SiO_2-Al_2O_3$
Pine sawdust						
Bio-oil conversion (%wt.)	69.3	84.6	98.9	91.1	85.1	90.7
Deoxygenation of liquid products (% molar)	82.0	72.7	94.7	83.2	72.5	87.5
Oxygen content of liquid products (%wt.)	7.8	17.0	4.6	8.0	10.0	7.5
Individual conversion (% molar)						
Acids and esters	100.0	100.0	100.0	91.8	98.0	56.9
Aldehydes, ketones, furans and alcohols	79.4	81.9	82.6	77.6	68.1	47.8
Phenolic ethers	66.1	77.1	87.4	72.8	92.9	99.9
Soybean shell						
Bio-oil conversion (%wt.)	96.8	92.2	86.1	88.1	91.0	94.8
Deoxygenation of liquid products (% molar)	88.4	84.0	86.7	87.7	85.1	94.6
Oxygen content of liquid products (%wt.)	9.5	16.0	7.0	6.5	8.0	4.0
Individual conversion (% molar)						
Acids and esters	89.9	76.4	78.9	85.0	81.4	99.0
Aldehydes, ketones, furans and alcohols	94.0	97.2	62.5	91.0	97.5	99.4
Phenolic ethers	100.0	100.0	100.0	100.0	100.0	100.0

Table 6 Liquid and gas yields in the combined experiments of pyrolysis and immediate catalytic upgrading (%wt.)

	No catalyst	Mesoporous catalysts			Compound catalysts		
		SiO_2	Al_2O_3	SiO_2-Al_2O_3	Y/SiO_2	Y/Al_2O_3	Y/SiO_2-Al_2O_3
Pine sawdust							
Hydrocarbons	5.9	15.2	18.8	26.2	17.0	11.6	10.0
Liquid hydrocarbons	1.8	8.5	11.3	11.2	6.3	3.7	4.1
Gaseous hydrocarbons	4.1	6.7	7.5	15.0	10.7	7.9	5.9
Oxygenated compounds	31.2	29.7	13.9	10.1	13.8	20.7	26.6
Oxygenated (liquids)	25.7	29.0	12.4	8.3	10.6	19.0	16.6
Oxygenated (gas)	5.5	0.7	1.5	1.8	3.2	1.7	10.0
Hydrogen	1.6	1.0	2.2	1.7	1.4	2.4	1.8
CO_2	5.2	2.3	6.3	4.9	4.0	6.9	5.1
Water	25.0	26.2	29.5	29.2	30.2	27.8	23.9
Unknown	9.1	0.5	3.2	1.9	7.3	3.7	8.9
Soybean shell							
Hydrocarbons	11.8	12.1	15.9	14.4	13.5	14.6	20.1
Liquid hydrocarbons	7.1	5.3	7.6	4.5	6.4	6.9	11.3
Gaseous hydrocarbons	4.7	6.8	8.3	9.9	7.1	7.7	8.8
Oxygenated compounds	35.6	9.8	10.2	24.0	14.5	11.5	10.6
Oxygenated (liquids)	27.2	9.7	8.1	22.3	12.1	9.1	3.7
Oxygenated (gas)	8.4	0.1	2.1	1.7	2.4	2.4	6.9
Hydrogen	1.2	1.2	1.3	1.0	1.5	1.3	1.1
CO_2	3.4	3.5	3.9	3.0	4.4	3.7	3.5
Water	19.8	31.3	26.0	25.0	26.4	26.7	26.7
Unknown	0.3	12.6	12.4	1.3	12.5	13.4	9.3

et al. [49] studied the catalytic pyrolysis of paddy husk over MCM-22, ITQ-2, and ZSM-5 acid catalysts at 450 °C; the results showed that ZSM-5 removed more oxygen (84.6%), as compared to MCM-22 (72.7%), ITQ-2 (80.6%), and the non-catalytic conversion (46.7%).

Even though SiO_2 is relatively inert, certain oxygenated compounds converted completely on this catalyst: acids and esters in the case of pine sawdust bio-oil and phenolic ethers in the case of soybean shell; see Table 5). It is thus confirmed that the existence of a surface area, in this case, provided exclusively by mesopores, promotes the diffusion of reactants and thermal reactions such as cracking and dehydration of bulky compounds in bio-oils, such as phenolic ethers, when they are at low concentrations in the mixtures. Consistently with these observations, Mochizuki et al. [50] observed that the addition of silica, with properties in the range of those shown here (surface area between 280 and 693 m^2 g^{-1}, pore volume between 0.43 and 1.19 ml g^{-1}, average pore diameter between 2.6 and 16.4 nm), significantly decreased the content of acids, aldehydes, and ketones in bio-oils.

When the compound catalysts were used, the best performance (high conversions and degree of deoxygenation) for the case of pine sawdust corresponded to the catalyst with the highest mesoporosity (Y/SiO_2), while for soybean shell corresponded to the most acidic catalysts (Y/Al_2O_3 and Y/

SiO_2-Al_2O_3). Again, differences in the composition of the bio-oils played a key role: deoxygenation and cracking of phenolic and other high molecular weight compounds prevailing in pine bio-oil require larger pores to improve their diffusion and pre-cracking, while smaller compounds such as acids, aldehydes, ketones, and furans, prevailing in soybean shell bio-oil, depend less on pore size and convert more easily over catalysts with high acidity.

Effect of Raw Biomass Composition on the Conversion of Bio-oil Components

The conversion of the individual components of bio-oils changed depending on the catalysts, probably as the consequence of the nature of the raw biomass and the proportions in which these compounds occurred in each case, besides the intrinsic reactivity given by the corresponding chemical structure. Thus, phenolic ethers converted completely over the three mesoporous catalysts in the case of soybean shell, while they converted more efficiently over SiO_2-Al_2O_3 in the case of pine sawdust. From this latter raw biomass, the conversion of certain bulky phenolic ethers, such as methoxycatechol and ethylguaiacol, was complete over SiO_2-Al_2O_3 and about 30% over Al_2O_3 and SiO_2. Given that these compounds were found less reactive

over acid catalysts than others in bio-oils [19, 20], it could be assumed that the higher acidity of catalysts SiO_2-Al_2O_3 favors its deoxygenation.

The opposite behavior was observed for acids and esters in pine sawdust bio-oil, which converted completely over all the mesoporous catalysts. SiO_2 was more efficient in the case of soybean shell bio-oil. Moreover, the other chemical groups (aldehydes, ketones, furans, and alcohols) bio-oil showed more extended conversion over SiO_2-Al_2O_3 when taking part of pine sawdust bio-oil or over Al_2O_3 when soybean shell was the raw biomass.

The incorporation of Y zeolite to the mesoporous solids increased substantially the conversion of some oxygenated compounds, given the type and amount of acidity contributed by the crystalline solid. For example, phenolic ethers from pine sawdust bio-oil converted much more on the compound catalysts than on the corresponding mesoporous solids and, the more acidic the catalyst, the higher the conversion. It was also noticed that the conversion of some bulky and/or refractory compounds in this bio-oil improved notably; for example, the conversion of methoxycatechol increased from 29% over SiO_2 to 54% over Y/SiO_2, and that of ethyl guaiacol, from 2 to 28% over the same catalysts. These facts reinforce the hypothesis that oxygenated compounds in bio-oil are subjected, mostly, in the first instance, to thermal reactions that convert them into lighter compounds, still oxygenated, which then, adsorbed on the acid sites, follow classical mechanisms of deoxygenation and conversion to hydrocarbons [13, 36]. Then, bulkier compounds in bio-oils require surface area as that provided by mesopores in amorphous materials, for the first steps in their conversion and then acidity to deoxygenate and produce hydrocarbons.

On the contrary, the conversion of acids, esters, aldehydes, ketones, furans, and alcohol in pine sawdust bio-oil notably decreased when Y zeolite was added to the mesoporous solids; in some cases, this effect was very significant, its conversion decreasing from more than 90% over SiO_2-Al_2O_3 to less than 30% over Y/SiO_2-Al_2O_3. The opposite (higher conversion on the compound catalysts) was observed for these compounds when taking part in soybean shell bio-oil. For some of them, it was very important; for example, pentanoic acid increased its conversion 35% when Y zeolite was incorporated to SiO_2, and 65% when added to Al_2O_3, and 3-methylfuran conversion increased from 40.5% over SiO_2-Al_2O_3 to 100% over Y/SiO_2-Al_2O_3.

Ibarra et al. [48] determined the conversion of some components considered representative of the various chemical groups in the bio-oil from pine sawdust, when it was converted over different zeolite-based catalysts (HY, HZSM-5, and HBeta), reporting up to 100% conversion for the cases of acetaldehyde, hydroxyacetone, furfural, levoglucosan,

and 3-methyl-1,2-cyclopentenone, and 60% for the cases of phenolic compounds and acetic acid.

In summary, in the case of pine sawdust, compounds which derive mainly from cellulose and hemicellulose pyrolysis (acids, esters, aldehydes, ketones, furans, and alcohols) converted more extensively on the mesoporous catalysts than on the zeolite containing catalysts. Phenolic ethers, which derive from lignin pyrolysis behaved oppositely. However, the conversion of soybean shell bio-oil showed that cellulose and hemicellulose-derived compounds converted more on the compound catalysts, and phenols converted completely over all the catalysts.

These results show that an oxygenated compound in bio-oil can behave very differently when facing a catalyst, depending on the catalyst, its chemical nature, and the composition of the mixture where it is included. Other authors also observed that when zeolite HZSM-5 was added in the pyrolysis of beech wood [51], the oxygenated compounds behaved differently in comparison to the purely thermal process. While the concentration of compounds with $C=O$ bonds (acids, aldehydes, and ketones) decreased, that of compounds with $C-O-C$ bonds (esters, furans) increased; moreover, compounds with $C-OH$ bonds performed differently if aliphatic alcohols, which increased their conversion, or phenols, which decreased their conversion [51].

Distribution of Liquid and Gaseous Products

Given that the major interest in upgrading bio-oils is to convert them into hydrocarbons, minimizing the loss of carbon and hydrogen in the overall balance, it is necessary to analyze the composition of liquid and gas products. The yield of hydrocarbons in the range of transportation fuels and petrochemical raw materials has been the object of extensive research, involving process design and the evaluation of various catalysts [52, 53].

Table 6 shows the distribution of the major groups of liquid and gas products obtained in the experiments of pyrolysis and immediate catalytic upgrading of the bio-oil, where results are compared with the one obtained in the purely thermal pyrolysis. In this case, the soybean shell yielded more hydrocarbons and oxygenated compounds, and less water and carbon dioxide than pine sawdust. These differences are attributed to the substantial differences in the composition of the raw biomasses and to the lower content of oxygen in soybean shell bio-oil. A detailed analysis of the products in the pyrolysis of these biomasses was published in Bertero et al. [29].

As compared to purely thermal pyrolysis, when bio-oil volatiles contact an upgrading catalyst, the yield of oxygenated compounds decreased considerably and the yield of hydrocarbons increased correspondingly in all the cases (both raw biomasses, all the catalysts). The content of water

among liquid products was higher when catalysts were used, thus supporting the view that dehydration is the main deoxygenation route for components of bio-oils. High water yields had also been observed in the catalytic conversion of bio-oils or model compounds, which had been attributed to deoxygenation and cracking of oxygenated compounds (see, for example, Graça et al. [54], who co-processed bio-oil model compounds (phenol, acetic acid, and hydroxyacetone) and vacuum gas oil over equilibrium FCC catalysts). Besides, Lappas et al. [34] compared the pyrolysis of commercial lignocellulose over silica sand and over a FCC catalyst.

Concerning the yields of hydrocarbons, it was observed that the higher acidity increased its conversion over the mesoporous catalysts in the case of pine sawdust (SiO_2-Al_2O_3 > Al_2O_3 > SiO_2). As expected, the yield of oxygenated compounds and deoxygenation products (mostly water) followed opposite trends. Oxygenated compounds from pine sawdust pyrolysis decreased their yields when catalyst acidity increased (SiO_2-Al_2O_3 < Al_2O_3 < SiO_2), while in the case of soybean shell they decreased when the specific surface area was larger (SiO_2 < Al_2O_3 < SiO_2-Al_2O_3).

However, different behaviors were observed with the compound catalysts, depending on the biomass: while soybean shell produced more hydrocarbons and less oxygenated compounds in the order Y/SiO_2-Al_2O_3 > Y/Al_2O_3 > Y/SiO_2, pine sawdust showed the opposite ranking. These facts show again that the composition of the resulting bio-oil substantially impacts on the performance of the catalysts converting them into hydrocarbons. Then, light compounds in soybean shell bio-oil with molecular weights lighter than 130 g mol^{-1}, which represent 96% of all the products, would diffuse more easily in the zeolite channels, leading to a more effective conversion into hydrocarbons on the strong acid sites in the micropore solids. These low molecular weight

compounds indeed have diverse chemical structures, including carbonylic, carboxylic, hydroxylic, esters, and furanic ring functional groups. Thus, the highest hydrocarbon yield was observed with the most acidic solid (Y/SiO_2-Al_2O_3). On the contrary, heavy compounds in pine sawdust bio-oil, which represented 20% of all the products, 85% of phenols being phenolic ethers, are subjected to more severe diffusion restrictions in Y zeolite. Consequently, they were more easily converted into hydrocarbons on the catalyst with larger mesopore specific surface area (Y/SiO_2), which is acid enough and where diffusion restrictions are less significant. In a few words, the efficiency of conversion of oxygenated compounds in bio-oils into hydrocarbons strongly depends on the feasibility of achieving adsorption on the acid sites.

The yield of hydrogen was, in general terms, higher in the conversion of pine sawdust bio-oil than in soybean shell bio-oil. This had been observed previously in using FCC catalysts [29].

Gasoline Yield in the Catalytic Upgrading of Bio-oil Volatiles

Table 7 shows the gasoline (C5–C12) selectivity and the distribution by hydrocarbon types in the cut, observed in the catalytic upgrading of bio-oil volatiles. It can be observed in general for all the catalysts that the selectivity to gasoline was much higher in the upgrading of soybean shell bio-oil. Moreover, in all the cases except for catalyst Y/$SiO_2Al_2O_3$, the gasoline produced from soybean shell included more olefins than the one from pine sawdust, which included more aromatic hydrocarbons. Increased olefinicity in the cut could be the consequence of a higher content of oxygenated compounds derived from cellulose and hemicellulose in the bio-oil and the restricted content of molecular hydrogen in

Table 7 Selectivity to gasoline and group composition (%wt.)

	Mesoporous catalysts			Compound catalysts		
	SiO_2	Al_2O_3	SiO_2-Al_2O_3	Y/SiO_2	Y/Al_2O_3	Y/SiO_2-Al_2O_3
Pine sawdust						
Selectivity	8.0	6.6	6.6	16.6	12.5	3.8
Composition						
Olefins	27.6	44.8	49.1	43.7	49.5	63.8
Paraffins	1.4	10.9	4.7	5.1	13.5	14.6
Naphthenics	1.2	2.9	1.9	1.8	2.3	0.6
Aromatics	69.8	41.4	44.4	49.4	34.5	21.1
Soybean shell						
Selectivity	20.0	15.1	12.3	20.5	17.9	8.0
Composition						
Olefins	53.5	62.1	66.5	51.9	55.7	41.4
Paraffins	13.6	14.2	14.5	13.4	19.1	13.6
Naphthenics	1.7	2.7	2.5	1.5	2.3	1.6
Aromatics	31.3	21.0	16.5	33.1	23.0	43.4

the reacting medium (see Table 6 in the "Distribution of Liquid and Gaseous Products" section) as compared to pine sawdust [54]. Oxygenated compounds such as aldehydes, ketones, and furans, which are produced in the pyrolysis of cellulose and hemicellulose, showed to be olefin precursors in their conversion over acid catalysts [20, 35, 55]. Oxygenated compounds with aromatic basis, such as phenols, which are predominant in pine sawdust bio-oil, could justify the higher proportion of aromatic hydrocarbons in gasoline formed from that biomass.

Aromatic hydrocarbons in gasoline from pine sawdust were mostly C8–C11 alkylbenzenes in the mesoporous catalysts, but benzene and toluene were the most important in the compound catalysts, probably from the cracking of branched aromatics. In the case of soybean shell as the raw biomass, in all the catalysts, benzene, and toluene were prevailing, representing more than 70% of the group in some cases. Carlson et al. [52] pyrolyzed sugars such as glucose, xylitol, and cellobiose (which can be considered representatives of cellulose and hemicellulose) over Y zeolite and SiO_2-Al_2O_3, among others, obtaining benzene plus toluene selectivities up to 40% among aromatics.

The content of olefins in gasoline decreased in the order SiO_2-$Al_2O_3 > Al_2O_3 > SiO_2$ and Y/SiO_2-$Al_2O_3 >$ Y/$Al_2O_3 >$ Y/SiO_2, for both raw biomasses, thus reflecting a clear catalytic effect in their production. On the contrary, the content of hydrocarbons in the cut showed the opposite trend, with the exception of catalyst Y/SiO_2-Al_2O_3 in the case of soybean shell bio-oil. In a previous work, where silica-aluminas with different Al_2O_3 were used [56], the conversion of these bio-oils under similar conditions showed that catalysts with the highest acidities produced less

aromatic hydrocarbons. These observations, which are similar to results shown here, are opposite to those shown in the conversion of hydrocarbon feedstocks such as vacuum gas oils, where aromatic hydrocarbons are produced by means of cyclization and hydrogen transfer reactions [57] reactions which are promoted when the density of acid sites is high. Aromatics hydrocarbons are formed in highly oxygenated feedstocks such as bio-oils by means of mechanisms including decarbonylation, dehydration, and hydrolysis of phenolic ethers [58], or aldol condensation of aldehydes and ketones via α-β-unsaturated carbonyl compounds and further cyclization [59].

Paraffins, mainly isopentane, dimethylpentane, and decane, were produced more selectively from soybean shell over all the catalysts. In the conversion of hydrocarbon feedstocks over FCC catalysts, paraffins are formed mainly from cracking and hydrogen transfer and consumed by cracking [57], taking place particularly on strong acid sites. An analogous behavior can be expected in the conversion of oxygenated feedstocks, considering that for both bio-oils paraffins were produced more extensively on the catalysts containing Y zeolite. Similar observations were reported by Adjaye and Bakshi [13], who obtained aliphatic hydrocarbons (alkylpentanes, alkylhexenes, decane) in the C5–C10 range in the conversion of maple wood bio-oil over silica-alumina and Y zeolite.

Gaseous Hydrocarbons in the Catalytic Upgrading of Bio-oil Volatiles

Table 8 shows the selectivity to gaseous products C1–C4 and the distribution for all the cases. It was observed that with

Table 8 Selectivity to gas hydrocarbons and product composition (%wt.)

	Mesoporous catalysts			Compound catalysts		
	SiO_2	Al_2O_3	SiO_2-Al_2O_3	Y/SiO_2	Y/Al_2O_3	Y/SiO_2-Al_2O_3
Pine sawdust						
Selectivity	43.9	40.1	57.4	63.2	67.8	59.4
Composition						
Methane	41.9	48.8	23.7	26.9	41.0	50.1
Ethane + ethylene	31.8	21.5	48.8	39.2	27.3	19.5
Propane + propylene	15.1	19.5	18.0	18.8	20.4	19.3
i-Butane	3.0	4.5	2.4	3.4	4.5	4.7
Butenes	7.9	5.2	6.4	10.3	6.3	5.8
Soybean shell						
Selectivity	55.9	51.9	68.5	52.6	52.9	43.9
Composition						
Methane	35.9	33.2	23.2	35.9	35.2	31.1
Ethane + ethylene	30.4	28.8	38.1	30.4	28.0	26.5
Propane + propylene	19.5	23.9	23.5	19.5	22.6	37.6
i-Butane	5.1	6.9	4.9	5.1	6.7	4.0
Butenes	8.8	6.9	9.6	8.8	7.2	4.9

the mesoporous catalysts the gas products were produced more selectively in the upgrading of soybean shell bio-oil. If the catalysts contained Y zeolite, the selectivity was higher with pine sawdust bio-oil. This could be due, in part, to the higher conversion of phenols, which are present at higher concentrations in pine sawdust bio-oil, over compound catalysts (see the "Effect of Raw Biomass Composition on the Conversion of Bio-oil Components" section); these compounds produce methane and light olefins when cracked on acidic catalysts [19, 21, 60]. Similar facts had been noticed in the conversion of these bio-oils over SiO$_2$-Al$_2$O$_3$ and FCC catalysts [29, 56], where the amorphous matrices were more selective to gases than the corresponding catalysts with Y zeolite in the case of soybean shell and the opposite was confirmed with pine sawdust.

For all the catalysts, the highest proportion of methane among gases was observed with pine sawdust raw biomass. Soybean shells corresponded to the highest yields for olefins, thus following the same trend observed with olefins in gasoline (see the "Gasoline Yield in the Catalytic Upgrading of Bio-oil Volatiles" section). In cracking phenols over FCC catalysts, To and Resasco [60] showed that methane was produced in significant amounts after cracking side chains in phenolic rings such as those occurring in guaiacol, syringol, and homologous alkylated molecules, which are the most prevalent phenols in pine sawdust bio-oil. According to their view, these molecules condense to form a kind of oligomeric cover on the catalytic surface, named phenolic pool, which then cracks to form fragments which follow classical mechanisms leading to hydrocarbons. Moreover, Gong et al. [55] showed that light olefins are produced considerably in the conversion of cellulose and hemicellulose derivatives, which are prevailing in soybean shell bio-oil, and to a lesser extent in the conversion of lignin and sawdust. These authors studied the potential of various biomasses in the selective production of light olefins in the catalytic pyrolysis over 6%wt. La/HZSM-5 at 600 °C in a packed-bed reactor, observing that the selectivity to C2–C4 olefins (% wt. in relation to feedstock biomass), decreased in the order cellulose (16.2%) > hemicellulose (14.7%) > sugarcane bagasse (12.1%) > rice husk (10.5%) > sawdust (7.9%) > lignin (5.3%).

Coke Yields

Coke deposition in the catalytic upgrading of bio-oils has been studied on acid catalysts, mainly HZSM-5 zeolites [14, 52, 61, 62]. In the process, coke can be formed from homogeneous gas-phase thermal decomposition reactions and from heterogeneous reactions on the catalyst, starting from the volatile oxygenated compounds, the dehydrated species, or the aromatic hydrocarbons [52]. Results from these researches show the importance of process conditions and reaction media in the yield and composition of coke, as well as in its distribution in the porous structure of the catalysts. It was shown, for example, that water, both originally present in bio-oil and also as the product of different reactions, attenuates the acid strength of the acid sites, impacting on overall adsorption and, consequently, on coke precursors condensation [14, 52, 61, 62].

The yield of coke is shown in Table 4 and discussed in the "Catalyst Performances: Product Yields" section. Coke on SiO$_2$ from both bio-oils is mostly formed from the condensation and polymerization of oxygenated compounds; in this sense, it should be considered that phenolic compounds derived from the pyrolysis of lignin are highly reactive and strongly tend to condensate as a consequence of the thermal level when temperature is between 500 and 550 °C [63]. Condensation reactions compete with the cracking of intermediate compounds for the acid sites available on the catalyst surface [64].

Table 9 shows how much carbon from the bio-oils is captured by coke over the various catalysts. This amount was much lower, for all the catalysts, from 20 to 40% in mesoporous catalysts and about 50% in compound catalysts, in the case of soybean shell as compared to pine sawdust. As already mentioned, pine sawdust contributed much more phenolic and heavy molecular compounds, which are main coke precursors, to bio-oil (see sections "Catalyst Performances: Product Yields" to "Effect of Raw Biomass Composition on the Conversion of Bio-oil Components").

Coke combustion profiles in Fig. 2 show a peak at temperatures between 550 and 600 °C for the mesoporous catalysts for both bio-oils, while compound catalysts exhibited a peak at 700 °C, thus showing a more extended degree of coke condensation and, consequently, a lower H/C relationship [33, 54]. Numerous authors [33, 54, 60] showed that in the conversion of bio-oils over zeolites supported on mesoporous catalysts, two types of coke were produced: one with a lower degree of condensation, mainly derived from oxygenated species, and the other one, more condensed, derived from classical hydrocarbon conversion mechanisms [14, 61]. The mesoporous catalysts showed for both

Table 9 Proportion of carbon in bio-oil deposited as coke in the immediate catalytic upgrading of bio-oils (%wt.)

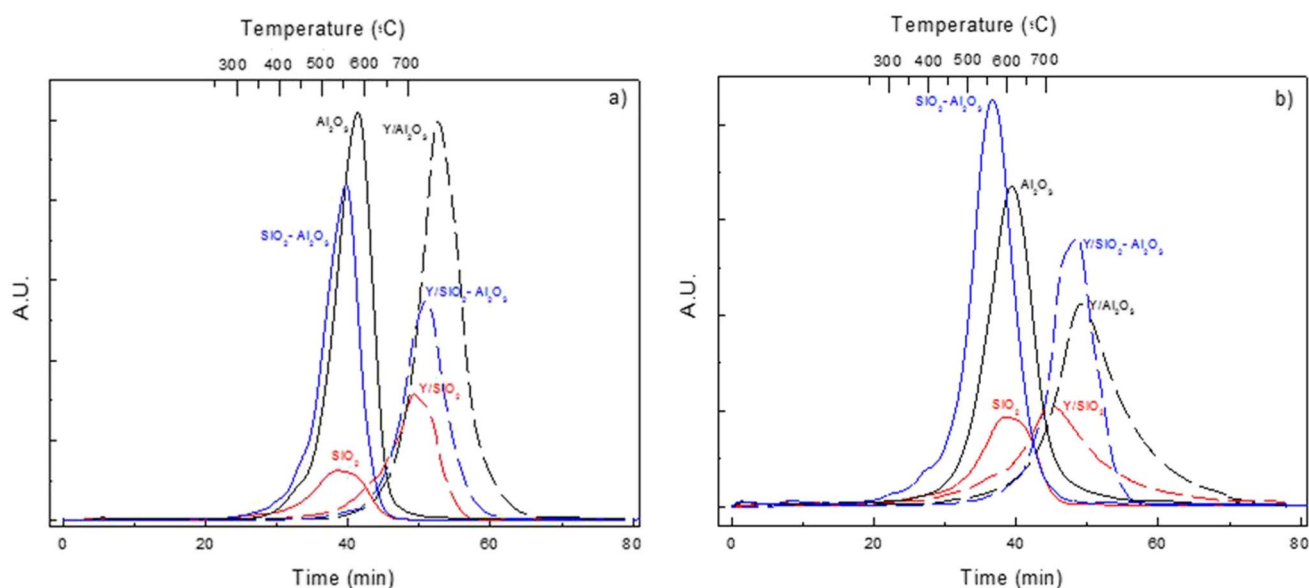|	Carbon from bio-oil in coke	
	Pine sawdust	Soybean shell
SiO$_2$	4.9	3.9
Al$_2$O$_3$	21.7	13.0
SiO$_2$-Al$_2$O$_3$	23.4	16.0
Y/SiO$_2$	8.9	3.9
Y/Al$_2$O$_3$	24.4	9.5
Y/SiO$_2$-Al$_2$O$_3$	14.3	7.6

Fig. 2 Combustion profiles of coke formed in the immediate catalytic upgrading of bio-oil vapors. a pine sawdust; b soybean shell

raw biomasses that the coke was more condensed if catalysts acidity was higher, in consistency with higher hydrocarbon yields (see the "Distribution of Liquid and Gaseous Products" section). According to To and Resasco [60], less condensed coke, deposited on the matrix of FCC catalysts during the conversion of phenolic compounds, is produced from the oligomerization of adsorbed phenolate ions.

Conclusions

The pyrolysis and immediate catalytic conversion of bio-oil from pine sawdust and soybean shell on the main components of FCC catalysts (different matrices alone or combined with Y zeolite) showed very different results according to the composition of the raw biomasses. Bio-oil from soybean shell, which includes less phenols and more light molecular weight compounds such as acids, esters, ketones, and furans, showed a lower selectivity to coke and carbon loss during its conversion than bio-oil from pine sawdust. Moreover, bio-oil from soybean shell also exhibited a higher selectivity to hydrocarbons products in the range of gasoline and a more extended degree of deoxygenation as well. These pieces of evidence suggest that all the catalysts were more efficient to upgrade soybean shell bio-oil than pine sawdust bio-oil.

The conversion of high molecular weight oxygenated compounds in bio-oils (> 130 g mol^{-1}), was improved when Y zeolite was added to the various mesoporous solids, thus supporting the hypothesis that zeolite acidity provides the proper medium to transform small oxygenated molecular fragments into hydrocarbons. The surface area provided by mesopores is crucial to increase the

initial thermal cracking, improving the diffusion of bulky molecules which cannot enter into the zeolite micropore system. Thus, fragments from these molecules can access strong acid sites in the zeolite channels.

These significant differences in the performance of the catalysts, both mesoporous or compound, depending on the nature of the raw biomass and the corresponding bio-oil, suggest that in considering options to produce hydrocarbons from biomass sources, it is necessary to clarify the role played by the different components of by means of these studies, which are complementary to process optimization.

Declarations

References

1. Kumar R, Strezov V, Weldekidan H, He J, Singh S, Kan T, Dastjerdi B (2009) Lignocellulose biomass pyrolysis for bio-oil production: a review of biomass pre-treatment methods for production of drop-in fuels. Renew Sust Energy Review 123:109763. https://doi.org/10.1016/j.rser.2020.109763

2. Zacher AH, Elliott DC, Olarte MV, Wang H, Jones SB, Meyer PA (2019) Technology advancements in hydroprocessing of bio-oils. Biomass Bioenergy 12:151–168. https://doi.org/10.1016/j.biombioe.2019.04.015

3. Valle B, Gayubo AG, Aguayo AT, Olazar M, Bilbao J (2010) Selective production of aromatics by crude bio-oil valorization with a nickel-modified HZSM-5 zeolite catalyst. Energy Fuels 24:2060–2070. https://doi.org/10.1021/ef901231j

4. Al-Sabawi M, Chen J, Ng S (2012) Fluid catalytic cracking of biomass-derived oils and their blends with petroleum feedstocks: a review. Energy Fuels 26:5355–5372. https://doi.org/10.1021/ef3006417

5. de Rezende PA, de Almeida MBB, Leal Mendes F, Casavechia LC, Talmadge MS, Kinchin CM, Chum HL (2017) Fast pyrolysis oil from pinewood chips co-processing with vacuum gas oil in an FCC unit for second generation fuel production. Fuel 188:462–473. https://doi.org/10.1016/j.fuel.2016.10.032

6. Fogassy G, Thegarid N, Toussaint G, van Veen A, Schuurman Y, Mirodatos C (2010) Biomass derived feedstock co-processing with vacuum gas oil for second-generation fuel production in FCC units. Appl Catal B 96:476–485. https://doi.org/10.1016/j.apcatb.2010.03.008

7. Bertero M, Sedran U (2015) Co-processing of bio-oil in fluid catalytic cracking. In: Pandey A, Bhaskar T, Stocker M (eds.) Recent advances in thermo-chemical conversion of biomass. Amsterdam: Elsevier, pp 355–381. ISBN: 9780444632890

8. Bertero M, García JR, Falco M, Sedran U (2020) Conversion of cow manure pyrolytic tar under FCC conditions over modified equilibrium catalysts. Waste Biomass Valorization 11:2925–2933. https://doi.org/10.1007/s12649-019-00588-y

9. Thegarid N, Fogassy G, Schuurman Y, Mirodatos C, Stefanidis S, Iliopoulou I, Kalogiannis K, Lappas A (2014) Second generation biofuels by co-processing catalytic pyrolysis oil in FCC units. Appl Catal B Environ. 165:161–166. https://doi.org/10.1016/j.apcatb.2013.01.019

10. Gueudrè L, Milina M, Mitchell S, Pérez-Ramírez J (2014) Coke chemistry under vacuum gasoil/bio-oil FCC co-processing conditions. Adv Funct Mater 24:209–219. https://doi.org/10.1016/j.cattod.2014.09.001

11. Rezaei P, Shafaghat H, Ashri W, Daud W (2014) Production of green aromatics and olefins by catalytic cracking of oxygenate compounds derived from biomass pyrolysis: a review. Appl Catal A Gen 469:490–511. https://doi.org/10.1016/j.apcata.2013.09.036

12. Adam J, Antonakou E, Lappas A, Stöcker M, Nilsen MH, Bouzga A, Hustad JE, Øye G (2006) In situ catalytic upgrading of biomass derived fast pyrolysis vapours in a fixed bed reactor using mesoporous materials. Microporous Mesoporous Mater 96:93–101. https://doi.org/10.1016/j.micromeso.2006.06.021

13. Adjaye J, Bakhshi N (1995) Production of hydrocarbons by catalytic: upgrading of a fast pyrolysis bio-oil. Part II: comparative catalyst performance and reaction pathways. Fuel Process Technol 45:185–202. https://doi.org/10.1016/0378-3820(95)00040-E

14. Valle B, Castaño P, Olazar M, Bilbao J, Gayubo AG (2012) Deactivating species in the transformation of crude bio-oil with methanol into hydrocarbons on a HZSM-5 catalyst. J Catal 285:304–314. https://doi.org/10.1016/j.jcat.2011.10.004

15. García JR, Bertero M, Falco M, Sedran U (2015) Catalytic cracking of bio-oils improved by the formation of mesopores by means of Y zeolite desilication. Appl Catal A Gen 503:1–8. https://doi.org/10.1016/j.apcata.2014.11.005

16. Eschenbacher A, Jensen PA, Henriksen UB, Ahrenfeldt A, Li C, Duus JØ, Mentzel UV, Jensen AD (2019) Deoxygenation of wheat straw fast pyrolysis vapors using HZSM-5, Al_2O_3, HZSM-5/Al_2O_3 extrudates, and desilicated HZSM-5/Al_2O_3 extrudates. Energy Fuels 33:6405–6420. https://doi.org/10.1021/acs.energyfuels.9b00906

17. Scherzer J (1989) Octane-enhancing, zeolitic FCC catalysts: scientific and technical aspects. Catal Rev Sci Eng 31:215–254. https://doi.org/10.1080/01614948909349934

18. Wojciechowski B, Corma A, Dekker M (1986) Catalytic cracking: catalysts, chemistry and kinetics, Meisel SL (ed), New York: AIChE J, 236. https://doi.org/10.1002/aic.690330925

19. Gayubo AG, Aguayo AT, Atutxa A, Aguado R, Bilbao J (2004) Transformation of oxygenate components of biomass pyrolysis oil on a HZSM-5 zeolite. I. Alcohols and phenols. Ind Eng Chem Res 43:2610–2618. https://doi.org/10.1021/ie030791o

20. Gayubo AG, Aguayo AT, Atutxa A, Aguado R, Olazar M, Bilbao J (2004) Transformation of oxygenate components of biomass pyrolysis oil on a HZSM-5 Zeolite. II. Aldehydes, ketones and acids. Ind Eng Chem Res 43:2619–2626. https://doi.org/10.1021/ie030792g

21. Bertero M, Sedran U (2013) Upgrading of bio-oils over equilibrium FCC catalysts. Contribution from alcohols, phenols and aromatic ethers. Catal Today 212:10–15. https://doi.org/10.1016/j.cattod.2013.03.016

22. Channiwala SA, Parikh PP (2002) A unified correlation for estimating HHV of solid, liquid and gaseous fuels. Fuel 81(8):1051–1063. https://doi.org/10.1016/S0016-2361(01)00131-4

23. Magee JS, Blazek JJ (1976) Zeolite chemistry and catalysis, Rabo JA (ed.), ACSM N° 171, Washington, 796 p. ISBN 9780841202764

24. Johnson MFL (1978) Estimation of the zeolite content of a catalyst from nitrogen adsorption isotherms. J Catal 52:425–431. https://doi.org/10.1016/0021-9517(78)90346-9

25. Bertero M, de la Puente G, Sedran U (2012) Fuels from bio-oils. Bio-oil production from different sources, characterization and thermal conditioning. Fuel 95:263–271. https://doi.org/10.1016/j.fuel.2011.08.041

26. Gayubo AG, Valle B, Aguayo A, Olazar M, Bilbao J (2010) Olefin production by catalytic transformation of crude bio-oil in a two-step process. Ind Eng Chem Res 49:123–131. https://doi.org/10.1021/ie901204n

27. Gilbert W, Morgado E, de Abreu M, de la Puente G, Passamonti F, Sedran U (2011) A novel fluid catalytic cracking approach for producing low aromatic LCO. Fuel Process Technol 92:2235–2240. https://doi.org/10.1016/j.fuproc.2011.07.006

28. Seddegi ZS, Budrthumal U, Al-Arfaj AA, Al-Amer AM, Barri SA (2002) Catalytic cracking of polyethylene over all-silica MCM-41 molecular sieve. App Catal A: Gen 225:167–176. https://doi.org/10.1016/S0926-860X(01)00872-9

29. Bertero M, Sedran U (2016) Immediate catalytic upgrading of soybean shell bio-oil. Energy 94:171–179. https://doi.org/10.1016/j.energy.2015.10.114

30. Yang S, Wu M, Wu C (2014) Application of biomass fast pyrolysis part I: pyrolysis characteristics and products. Energy 66:162–171. https://doi.org/10.1016/j.energy.2013.12.063

31. Pütün A, Apaydin E, Pütün E (2002) Bio-oil production from pyrolysis and steam pyrolysis of soybean cake: products yields and composition. Energy 27:703–710. https://doi.org/10.1016/S0360-5442(02)00015-4

32. Iliopoulou E, Antonakou E, Karakoulia S, Vasalos I, Lappas A, Triantafyllidis K (2007) Catalytic conversion of biomass pyrolysis products by mesoporous materials: effect of steam stability and

acidity of Al-MCM-41 catalysts. Chem Eng J 134:51–57. https://doi.org/10.1016/j.cej.2007.03.066

33. Cerqueira H, Caeiro G, Costa L, Ramôa Ribeiro F (2008) Deactivation of FCC catalysts. J Molec Catal A: Chemical 292:1–13. https://doi.org/10.1016/j.molcata.2008.06.014

34. Lappas AA, Samolada MC, Iatridis DK, Voutetakis SS, Vasalos IA (2002) Biomass pyrolysis in a circulating fluid bed reactor for the production of fuels and chemicals. Fuel 81:2087–2095. https://doi.org/10.1016/S0016-2361(02)00195-3

35. Bertero M, de la Puente G, Sedran U (2013) Products and coke from the conversion of bio-oil acids, esters, aldehydes and ketones over equilibrium FCC catalysts. Renew Energy 60:349–354. https://doi.org/10.1016/j.renene.2013.04.017

36. Corma A, Huber G, Sauvanaud L, O'Connor P (2007) Processing biomass-derived oxygenates in the oil refinery: catalytic cracking (FCC) reaction pathways and role of catalyst. J Catal 247:307–327. https://doi.org/10.1016/j.jcat.2007.01.023

37. Moldoveanu SC (2019) Pyrolysis of organic molecules with applications to health and environmental issues - techniques and instrumentation in analytical chemistry. 2nd Edition https://doi.org/10.1016/B978-0-444-64000-0.00001-9

38. Adjaye JD, Bakhshi NN (1995) Catalytic conversion of a biomass-derived oil to fuels and chemicals I: model compound studies and reaction pathways. Biomass Bioenergy 8:131–149. https://doi.org/10.1016/0961-9534(95)00018-3

39. Chantal P, Kaliaguine S, Grandmaison JL (1985) Reactions of phenolic compounds over HZSM-5. Appl Catal 18:133–145. https://doi.org/10.1016/S0166-9834(00)80304-8

40. Wang S, Cai Q, Chen J, Zhang L, Zhu L, Luo Z (2015) Co-cracking of bio-oil model compound mixtures and ethanol over different metal oxide-modified HZSM-5 catalysts. Fuel 160:534–543. https://doi.org/10.1016/j.fuel.2015.08.011

41. Wang S, Guo Z, Cai Q, Guo L (2012) Catalytic conversion of carboxylic acids in bio-oil for liquid hydrocarbons production. Biomass Bioenergy 45:138–143. https://doi.org/10.1016/j.biombioe.2012.05.023

42. Chen G, Zhang R, Ma W, Liu B, Li X, Yan B, Cheng Z, Wang T (2018) Catalytic cracking of model compounds of bio-oil over HZSM-5 and the catalyst deactivation. Sci Total Environ 631–632:1611–1622. https://doi.org/10.1016/j.scitotenv.2018.03.147

43. Chen G, Liu J, Li X, Zhang J, Yin H, Su Z (2020) Investigation on catalytic hydrodeoxygenation of eugenol blend with light fraction in bio-oil over Ni-based catalysts. Renew Energy 157:456–465. https://doi.org/10.1016/j.renene.2020.05.040

44. Chen W, Luo Z, Yu C, Yang Y, Li G, Zhang J (2014) Catalytic conversion of guaiacol in ethanol for bio-oil upgrading to stable oxygenated organics. Fuel Process Technol 126:420–428. https://doi.org/10.1016/j.fuproc.2014.05.022

45. Venkatesan K, Krishna JVJ, Anjana S, Selvam P, Vinu R (2021) Hydrodeoxygenation kinetics of syringol, guaiacol and phenol over H-ZSM-5. Catal Commun 148:106–164. https://doi.org/10.1016/j.catcom.2020.106164

46. Adjaye JD, Katikaneni SPR, Bakhshi NN (1996) Catalytic conversion of a biofuel to hydrocarbons: effect of mixtures of HZSM-5 and silica-alumina catalysts on product distribution. Fuel Proc Tech 48:115–143. https://doi.org/10.1016/S0378-3820(96)01031-4

47. Olazar M, Aguado R, Barona A, Bilbao J (2000) Pyrolysis of sawdust in a conical spouted bed reactor with a HZSM-5 catalyst. AIChE J 46:1025–1033. https://doi.org/10.1002/aic.690460514

48. Ibarra A, Hita I, Azkoiti MJ, Arandes JM, Bilbao J (2019) Catalytic cracking of raw bio-oil under FCC unit conditions over different zeolite-based catalysts. J Ind Eng Chem 78:372–382. https://doi.org/10.1016/j.jiec.2019.05.032

49. Naqvi SR, Uemura Y, Yusup S, Sugiur Y, Nishiyama N, Naqvi M (2015) The role of zeolite structure and acidity in catalytic deoxygenation of biomass pyrolysis vapors. Energy Procedia 75:793–800. https://doi.org/10.1016/j.egypro.2015.07.126

50. Mochizuki T, Atong D, Chen SY, Toba M, Yoshimura Y (2013) Effect of SiO2 pore size on catalytic fast pyrolysis of Jatropha residues by using pyrolyzer-GC/MS Cat. Comm 26:1–4. https://doi.org/10.1016/j.catcom.2013.02.018

51. Stefanidis SD, Kalogiannis KG, Iliopoulou EF, Lappas AA, Pilavachi PA (2011) In-situ upgrading of biomass pyrolysis vapors: catalyst screening on a fixed bed reactor. Biores Tech 102:8261–8267. https://doi.org/10.1016/j.biortech.2011.06.032

52. Carlson T, Tompsett G, Conner W, Huber G (2009) Aromatic production from catalytic fast pyrolysis of biomass-derived feedstocks. Top Catal 52:241–252. https://doi.org/10.1007/s11244-008-9160-6

53. Park H, Dong J, Jeon J, SeunYoo K, Yim J, Min Sohn J, Park Y (2007) Conversion of the pyrolytic vapor of radiata pine over zeolites. J Ind Eng Chem 13:182–189

54. Graça I, Ramôa Ribeiro F, Cerqueira HS, Lam YL, de Almeida MBB (2009) Catalytic cracking of mixtures of model bio-oil compounds and gasoil. App Catal B: Env 90:556–563. https://doi.org/10.1016/j.apcatb.2009.04.010

55. Gong F, Yang Z, Hong C, Huang W, Ning S, Zhang Z, Xu Y, Li Q (2011) Selective conversion of bio-oil to light olefins: controlling catalytic cracking for maximum olefins. Bior Tech 102:9247–9254. https://doi.org/10.1016/j.biortech.2011.07.009

56. Bertero M, García JR, Falco M, Sedran U (2017) Hydrocarbons from bio-oils: performance of the matrix in FCC catalysts in the immediate catalytic upgrading of different raw bio-oils. Waste Biomass Valor 8:933–948. https://doi.org/10.1007/s12649-016-9624-z

57. de la Puente G, Falabella E, Sousa-Aguiar M, Figueiredo Costa A, Sedran U (2003) The influence on selectivity of the aluminum content in the matrix of FCC catalysts. Appl Catal A: General 242:381–391. https://doi.org/10.1016/S0926-860X(02)00526-4

58. Samolada M, Papafotica A, Vasalos I (2000) Catalyst evaluation for catalytic biomass pyrolysis. Energy Fuels 14:1161–1167. https://doi.org/10.1021/ef000026b

59. Fuhse J, Bandermann F (1987) Conversion of organic oxygenated compounds and their mixtures on H-ZSM5. Chem Eng Technol 10:323–329. https://doi.org/10.1002/ceat.270100139

60. To AT, Resasco D (2014) Role of a phenolic pool in the conversion of m-cresol to aromatics over HY and HZSM-5 zeolites. Appl Catal A: Gral 487:62–71. https://doi.org/10.1016/j.apcata.2014.09.006

61. Gayubo AG, Aguayo A, Atutxa A, Prieto R, Bilbao J (2004) Deactivation of a HZSM-5 zeolite catalyst in the transformation of the aqueous fraction of biomass pyrolysis oil into hydrocarbons. Energy Fuels 18:1640–1647. https://doi.org/10.1021/ef040027u

62. Ibáñez M, Valle B, Bilbao J, Gayubo AG, Castaño P (2012) Effect of operating conditions on the coke nature and HZSM-5 catalysts deactivation in the transformation of crude bio-oil into hydrocarbons. Catal Today 195:106–113. https://doi.org/10.1016/j.cattod.2012.04.030

63. Zhou S, Garcia-Perez M, Pecha B, Kersten SRA, McDonald AG, Westerhof RJM (2013) Effect of the fast pyrolysis temperature on the primary and secondary products of lignin. Energy Fuels 27:5867–5877. https://doi.org/10.1021/ef4001677

64. Bai X, Kim KH, Brown RC, Dalluge E, Hutchinson C, Lee YJ, Dalluge D (2014) Formation of phenolic oligomers during fast pyrolysis of lignin. Fuel 128:170–179. https://doi.org/10.1016/j.fuel.2014.03.013