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Conversion of pine sawdust bio-oil (raw and thermally processed) over equilibrium FCC catalysts



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HIGHLIGHTS

- ▶ Bio-oil and liquid product from thermal conditioning were converted over FCC catalyst.
- ▶ The conditioned liquid produced more hydrocarbons and less coke than the bio-oil.
- ▶ A model bio-oil yielded less hydrocarbons and more coke than the biomass feedstocks.
- ▶ The products from thermal cracking were also assessed.

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ABSTRACT

A raw bio-oil from pine sawdust, the liquid product from its thermal conditioning and a synthetic bio-oil composed by eight model compounds representing the main chemical groups in bio-oils, were converted thermally and over a commercial equilibrium FCC catalyst. The experiments were performed in a fixed bed reactor at 500 °C. The highest hydrocarbon yield (53.5 wt.%) was obtained with the conditioned liquid. The coke yields were significant in all the cases, from 9 to 14 wt.%. The synthetic bio-oil produced lesser hydrocarbons and more oxygenated compounds and coke than the authentic feedstocks from biomass. The previous thermal treatment of the raw bio-oil had the positive effects of increasing 25% the yield of hydrocarbons, decreasing 55% the yield of oxygenated compounds and decreasing 20% the yield of coke, particularly the more condensed coke.

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1. Introduction

The liquid product from the pyrolysis of lignocellulosic biomass, commonly named bio-oil, could be co-processed with conventional hydrocarbon feedstocks in refineries, where the process of catalytic cracking of hydrocarbons (FCC) is a potential recipient (Corma et al., 2007; Lappas et al., 2009; Fogassy et al., 2010; de Miguel Mercader et al., 2010). This is an attractive alternative for biomass use as fuels and petrochemical raw materials, which could be produced by taking advantage of existing processes and structure, without the need for high capital investments. Other options for upgrading bio-oils exist, such as steam reforming (e.g. Chen et al., 2011) and hydro-deoxygenation (e.g. Yu et al., 2011) processes.

Bio-oils are very complex aqueous mixtures of mostly oxygenated compounds with different chemical structures and a much extended range of molecular weights. In the case of bio-oils from different sawdusts, for example, they contain phenols, furans, acids, esters, alcohols, aldehydes and ketones, which account for

an elemental composition of approximately 35–40% of oxygen and 55–60% of carbon (Czernik and Bridgwater, 2004). Water is always present, with concentrations representing from 15% to 60% of bio-oil (Gayubo et al., 2010; Bertero et al., 2012).

If the approach described above is followed, then, it is necessary to consider that in comparison to conventional FCC feedstocks, that is, vacuum gas oils (VGO), bio-oils have a more important coke forming potential, since their components tend to polymerize at high temperatures (Adjaye and Bakhshi, 1995b; Williams and Horne, 1995; Srinivas et al., 2000; Gayubo et al., 2010). However, FCC technologies exist that can process resid hydrocarbon feedstocks having Carbon Conradson Residue (CCR, an indication of coke forming potential) higher than two, which form more coke. The problems derived from high coke yields in FCC are solved by means of particular innovations such as catalyst coolers, two stage regeneration and more efficient strippers, among others (Wilson, 1997).

Bio-oil co-processing in FCC can be eased by a previous thermal treatment of the bio-oils, which induces an important reduction between 30% and 50% in the concentration of the main coke precursors, such as phenols, aldehydes and ketones (Valle et al., 2007; Gayubo et al., 2010; Bertero et al., 2011). As a consequence, the yield of coke

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over ZSM-5 zeolite was observed to decrease up to 30% in the conversion of previously treated bio-oils as compared to raw bio-oils (Srinivas et al., 2000; Valle et al., 2007). Other possible obstacle in the approach is the significant content of water in bio-oils and the insolubility with hydrocarbon mixtures; however, steam is used in many sections of the FCC process with different purposes, and some options for injecting bio-oils were discussed by Corma et al. (2007).

A synergetic effect between bio-oil and VGO feedstocks during the catalytic cracking, associated to hydrogen transfer from hydrocarbons to oxygenated compounds in the bio-oil has been proposed (Corma et al., 2007; Fogassy et al., 2010; de Miguel Mercader et al., 2010). Some key details in co-processing bio-oils, such as the contribution to the FCC product slate from the various chemical species present, particularly to coke, could be predicted with observations of the intrinsic reactivity of bio-oils and/or individual model compounds over actual (equilibrium) FCC catalysts. In this sense, the use of single model compounds could result in oversimplifying some facts in high complexity systems such as bio-oils, and the use of a mixture of model compounds could be more responsive (Fuhse and Bandermann, 1987; Adjaye and Bakhshi, 1995a; Samolada et al., 2000; Gayubo et al., 2005). Up to the present, the information gathered in this way about bio-oil co-processing is scarce.

It is the objective of this work to analyze the distribution of products obtained in the conversion of a raw bio-oil from the pyrolysis of pine sawdust, of the liquid product after thermal treatment of the same bio-oil and of a mixture of eight model compounds representing the most important chemical groups present in bio-oils, over a commercial equilibrium FCC catalyst. Results were compared to those from the thermal cracking of the same reacting mixtures and from the conversion of the individual test reactants in the synthetic bio-oil.

2. Experimental

The raw bio-oil was produced by means of the conventional pyrolysis of pine sawdust in a fixed bed reactor during 60 min at 550 °C, with a heating ramp of 15 °C/min starting from room temperature. The liquid product from the pyrolysis was centrifuged at 3200 rpm during 8 min to separate an aqueous fraction, named bio-oil, and a tar-like fraction. The raw bio-oil was subjected to a thermal treatment to improve its processing characteristics during 10 min at 500 °C, with a heating ramp of 12 °C/min starting from room temperature. The liquid product from the thermal conditioning process was also centrifuged under the same above mentioned conditions to separate an aqueous fraction named treated liquid and tar. A more detailed description of the equipments and procedures used in the pyrolysis and the thermal treatment can be found in Bertero et al. (2011).

The mixture of bio-oil model compounds ("synthetic" bio-oil) was composed of acetic acid (5.7 wt.%), methyl acetate (3.4 wt.%), furfural (4.1 wt.%), 2-hydroxi-3-methylcyclopentenone (6.4 wt.%), methanol (7.3 wt.%), phenol (1.7 wt.%), 2,6-dimethoxyphenol, (syringol, 2.8 wt.%) and 1,2,4-trimethoxybenzene (0.5 wt.%), representing acids, esters, aldehydes/furans, cyclic ketones, alcohols, phenols, phenolic ethers and aromatic ethers, respectively. Water was included at 68.1 wt.%. All the reactants were purchased from Sigma–Aldrich, having purities higher than 98%.

The catalyst used was an equilibrium commercial FCC catalyst (E-Cat) of the octane-barrel type. It was provided by a refinery and showed the following characteristics: particle size, sieved to 100–120 µm; unit cell size, 24.26 Å; rare earth oxides, 1.19 wt.%; zeolite content, 18.0 wt.%; specific surface area, 158 m²/g; micro-pore volume, 0.046 cm³/g; iron, 0.35 wt.% and nickel, 0.06 wt.%.

The conversion experiments were performed in a stainless steel MAT (ASTM D-3907/03)-type fixed-bed reactor of 15.6 mm diameter and 400 mm length, which has a porous metal plate in its mid

position to support the 2 g catalyst bed. The reactor was heated in an electrical furnace up to the reaction temperature of 500 °C under a nitrogen flow of 30 mL/min. The reactants were fed by means of a Cole Parmer Model 75900-05 syringe pump, with flows between 0.5 and 0.7 mL/min to insure W/F₀ values of 0.1 h. Reactor effluents were passed through an ice-water condenser where most of the liquid product was retained, and gases were collected and quantified by displacement of water in a glass column. In all the cases the time on stream was 60 s, after which a sweeping flow of 30 mL/min of nitrogen was passed during 7 min. Mass, carbon and oxygen balances (recoveries) were higher than 90% in all the cases. Thermal cracking reactions were performed with a bed of inert SiC occupying the same volume as the catalytic bed, all the other conditions being the same.

Liquid and gas products were analyzed by conventional capillary gas chromatography in an Agilent 6890 N gas chromatograph equipped with a 30 m length, 0.25 mm i.d. and 0.25 µm phase thickness HP-1 column and FID detection. Gases were also analyzed with a 30 m length, 0.53 mm i.d. and 3.0 µm phase thickness GS-CARBONPLOT column and TCD detection. Products were identified by means of the use of standards and the GC–MS technique. The calibration of the chromatographic areas was performed by using separate response factors for each of the chemical groups, as assessed from mixtures of standards and a reference compound (tetralin for liquids and methane for gases). Unidentified peaks, each representing less than 0.5% of the total chromatographic area were assigned an average response factor. The selectivities to hydrocarbons products were assessed considering the total mass of hydrocarbons, and the selectivities to oxygenated products were assessed considering the total mass of oxygenated compounds.

The amount of water in the liquid products was determined by means of the Karl–Fischer method (IRAM 21320). The amount of coke on the catalyst was assessed with a combined method of thermal programmed oxidation (initial temperature, 250 °C during 15 min; heating ramp, 16 °C/min; final temperature, 700 °C, during 16 min) and further conversion of the carbon oxides formed to methane on a Ni catalyst, which was quantified with a FID detector. The various product yields were calculated in a water free basis as the relationship between the corresponding mass of product and the mass of reactants. Deoxygenation was calculated by comparing the amount of oxygen in the feedstocks and the amount of oxygen in carbon dioxide, carbon monoxide and water in the products.

3. Results and discussion

Pyrolytic bio-oils from lignocellulosic biomass typically contain about 30% of acids and esters, 7% of ketones, 3% of aromatic ethers, 2–6% of alcohols, 2–20% of aldehydes, and more than 12% of

Table 1
Composition of the bio-oil and the liquid resulting from the thermal conditioning (wt.%).

	Bio-oil	Treated liquid
Water	49.6	62.2
Acids	9.1	8.4
Esters	4.0	2.2
Linear aldehydes and ketones	8.6	6.6
Cyclic ketones	3.0	1.7
Furans	2.9	2.6
Alcohols and sugars	4.8	3.3
Phenols	7.7	5.6
Alkylated phenols	2.6	2.2
Phenolic ethers	5.1	3.4
Ethers	0.4	0.3
Other cyclic oxygenated compounds	1.4	1.1
Hydrocarbons	0.4	0.2
Nitrogen compounds	0.7	0.5
Unknown	7.4	5.2

phenols and phenolic ethers (Adjaye and Bakhshi, 1995b; Bertero et al., 2011). Table 1 shows the compositions of the raw bio-oil from pine sawdust and the liquid product of the thermal treatment of this bio-oil, where components were grouped according to the various chemical functionalities. Phenols were classified into alkylated phenols and phenolic ethers, according to the units of molecular substitution. It can be seen that both liquid mixtures contain mainly acids, aldehydes, ketones, alcohols and phenols.

The content of phenolic ethers (guaiaicol, syringol and their derivatives) was high, representing about 65% of phenols. These compounds are considered as the main precursors for coke formation from bio-oils (Valle et al., 2007). After thermal conditioning, the content of esters and cyclic ketones decreased about 45%, and that of phenols and alcohols about 30%. This decrease was more significant on the compounds with higher molecular weight in the corresponding groups; for example, γ -heptylbutyrolactone in the case of ketones, 4-ethoxy-3-anisaldehyde in the case of aldehydes, and 4-vinylguaiaicol, isoeugenol and 4-ethoxymethylguaiaicol in the case of phenolic ethers. The amount of water in the treated liquid was higher than in the raw bio-oil due to dehydration occurring during the thermal treatment (Bertero et al., 2011).

A synthetic bio-oil was prepared by mixing eight different model compounds which represented the most important chemical groups which can be found in typical bio-oils and water (see Section 2). In this case, most of the model compounds were those present in higher amounts in their corresponding groups, such as, for example, acetic acid, furfural, 2-hydroxi-3-methylcyclopentenone, methanol and 1,2,4-trimethoxybenzene (Bertero et al., 2011, 2012).

The use of individual model compounds to study reactivities and product distributions from the conversion of bio-oils, as well as the reaction mechanisms of the various chemical groups, has been very extended on, particularly, acidic zeolites (Fuhse and Bandermann, 1987; Adjaye and Bakhshi, 1995a; Gayubo et al., 2004a,b). However, even though a mixture of model compounds would represent the behaviour of the different chemical species in bio-oils in a more realistic manner than single model compounds, for example showing eventual interactions between them and their products, their conversion over acidic zeolites has been scarcely reported in the literature (Fuhse and Bandermann, 1987; Samolada et al., 2000; Gayubo et al., 2005). Moreover, up to the present, the use of model mixtures over commercial FCC catalysts has not been reported. In general, the reactivity of a given model compound is higher when incorporated into a mixture as compared to its only conversion, a fact that has been assigned to synergy effects between the different species (Adjaye and Bakhshi, 1995a; Samolada et al., 2000).

The Effective Hydrogen Index (EHI) of the oxygenated feedstock, which is defined by Eq. (1) (Chen et al., 1986), denotes the neat H/C of a feedstock containing heteroatoms

$$\text{EHI} = \left(\frac{\text{H}}{\text{C}} \right)_{\text{ef}} = \frac{(\text{H} - 2\text{O} - 3\text{N} - 2\text{S})}{\text{C}} \quad (1)$$

There H, C, O, N and S are the molar percentages of the corresponding elements on dry basis. The index could be an useful comparative parameter in co-processing bio-oils together with conventional hydrocarbon feedstocks, since the higher the EHI the more efficient the conversion in FCC. In general terms, EHI values in feedstocks from fossil sources range from 1 in aromatic cuts to 2 in paraffinic cuts (Letzsch and Ashton, 1993). The EHI of the raw bio-oil used in this work was 0.79 and that of the liquid product after the thermal conditioning was 1.04 (Bertero et al., 2012). On the other hand, the EHI of the mixture of model compounds was 0.54.

3.1. Catalytic and thermal conversions of the three reacting mixtures

The contact of the three reactant mixtures with the equilibrium FCC catalyst (catalytic conversion) and over inert SiC (thermal conversion) produced solid, liquid and gaseous products in all the cases. It is to be noted that the conversion cannot be assessed strictly, because some of the initial components of the mixtures are in turn products of the conversion of other components (Adjaye and Bakhshi, 1995a). This can be easily verified with, e.g. methanol, acetone, phenol and alkylphenols. However, most of the oxygenated compounds initially present in the feedstocks decreased significantly their concentration in the catalytic experiments, thus suggesting high conversions. Then, yields and product distributions will be used to show the degree of transformation of the reactant mixtures.

Table 2 shows the overall distribution of products in the experiments, that is, including the three product streams, where significant differences can be noticed among the results corresponding to each of the reactants. It is very important to see that dehydration, as shown by the concentration of water among the products, is very important over the catalyst and much more extensive than in the thermal cracking, the most significant being obtained with the synthetic bio-oil. The yields of carbon dioxide in the catalytic experiments were similar in all the cases and larger than the ones observed in the thermal cracking experiments. Carbon monoxide was observed at very low levels and the yield of hydrogen had the same magnitude with all the reactants in both types of experiments. The yield of hydrocarbons and oxygenated compounds had opposite behaviours: in the catalytic experiments hydrocarbons formed much more significantly than in the thermal experiments, while the opposite was observed with the oxygenated compounds. In the catalytic experiments, the highest yields of oxygenated compounds, including unconverted reactants, were observed with the raw and the synthetic bio-oils, and the hydrocarbon yield was higher (as much as 53.5 wt.%) with the treated liquid, as expected from previous reports (Srinivas et al., 2000; Valle et al., 2007; Gayubo et al., 2010; Bertero et al., 2011). In these reports it was

Table 2

Overall product distributions (wt.%, dry basis) in the thermal and catalytic conversions of the raw and synthetic bio-oils and the treated liquid. Reaction temperature: 500 °C.

	Synthetic bio-oil		Bio-oil		Treated liquid	
	SiC	E-Cat	SiC	E-Cat	SiC	E-Cat
Hydrocarbons	16.4	26.8	11.7	42.3	23.9	53.5
Oxygenated	71.1	19.3	71.9	9.6	59.8	5.5
Hydrogen	0.2	1.3	0.9	0.9	0.9	0.7
CO ₂	0.3	3.6	1.6	4.2	1.8	2.0
CO	Traces	Traces	Traces	0.1	Traces	0.1
Water	9.3	34.8	4.6	31.4	4.2	28.4
Coke	0.2	14.0	0.1	11.1	0.1	9.1
Unknown	2.5	0.2	9.2	0.5	9.3	0.7

observed that the previous thermal conditioning of bio-oil induces changes in its composition which favour the yield of hydrocarbons during its catalytic cracking over acidic zeolites; for example, for the particular case of the bio-oil used in this work, the Effective Hydrogen Index (a comparative parameter showing efficiency in FCC conversion) increased up to 30% after thermal treatment (Bertero et al., 2011).

The yield of coke deserves special consideration if the co-processing of bio-oil is to be intended in FCC units, due to their high coking trend and the need to obey the delicate heat balance which controls the operation of the commercial units. Phenols, cyclic ketones, aldehydes and aromatic ethers had been pointed as the most important coke precursors, and it has been shown that the conditioning of the bio-oils with a thermal treatment can help to reduce their coking potential (Valle et al., 2007; Gayubo et al., 2010; Bertero et al., 2011, 2012). In the case of the bio-oil used in this work the CCR decreased up to 70% after the thermal conditioning (Bertero et al., 2011). This positive effect can be confirmed with the lowest coke yield being observed in the case of the treated liquid (see Table 1). However, even though coke yield is important, particularly with the raw and synthetic bio-oils, present FCC technologies allow the processing of very high molecular weight feedstocks (resids) with improvements specially designed for dealing with high coke yields, such as catalyst coolers, two stage regeneration and more efficient strippers, among others (Wilson, 1997).

All the feedstocks showed that during their catalytic conversions, decarboxylation and dehydration are the main routes to deoxygenation, which was very high in the cases of the bio-oil (93%) and the treated liquid (95%) and somewhat lower for the synthetic bio-oil (about 86%). Other reports mention deoxygenations from 73% to 90% in the conversion of wood sawdust bio-oils and mixtures of oxygenated model compounds over zeolites Y and ZSM-5 (Adjaye and Bakhshi, 1995a,b; Williams and Horne, 1995; Srinivas et al., 2000; Samolada et al., 2000).

The thermal conversion of all the reactants generated product distributions that were very different from those over the catalyst. The yields of oxygenated compounds were between four and nine times higher than the catalytic ones, the maximum being 19.3 wt.%, with the synthetic bio-oil. On the contrary, the yield of hydrocarbons was from two to four times lower (maximum 23.9 wt.%, treated liquid). The thermal dehydration of the synthetic bio-oil was two times those of the other reactants, but decarboxylation was much smaller. In all the cases, deoxygenation as a result of the thermal effect was low, the highest being about 20% for the synthetic bio-oil and lower than 15% for the other reactants. Overall, these results agree with observations about the thermal conversion of wood sawdust bio-oils (Sharma and Bakhshi, 1993; Williams and Horne, 1995; Adjaye and Bakhshi, 1995b; Gong et al., 2011) and mixtures of oxygenated model compounds over α -alumina, where probably the most important contribution is from thermal sources (Samolada et al., 2000).

The mixtures of oxygenated compounds used to simulate bio-oils which were reported in the literature were very different, including, for example, acetic acid, ethyl butyrate, methanol, cyclopentanol, pentanal, hexanal, heptane-4-one, methyl isopropylketone, tetrahydrofuran and dipropyl ether (Fuhse and Bandermann, 1987); propanoic acid, methyl acetate, methylcyclohexanol, methylcyclopentanone, eugenol and ethoxybenzene (Adjaye and Bakhshi, 1995a); acetic acid, furfural, cyclohexanone, guaiacol, vanillin and water (Samolada et al., 2000); or acetic acid, acetone, methanol, 2-butanol, phenol, guaiacol and water (Gayubo et al., 2005). The conversions of these mixtures over zeolite ZSM-5 were over 90% (Fuhse and Bandermann, 1987; Adjaye and Bakhshi, 1995a; Samolada et al., 2000; Gayubo et al., 2005), with hydrocarbon (mainly aromatics and C4-olefins) and oxygenated compound yields being significant: between 20 and 40 wt.% and between 9

and 17 wt.%, respectively. Deoxygenation proceeded through dehydration and decarboxylation. Conversion over ReUSY zeolite (Samolada et al., 2000) was considerably lower (63%), as well as hydrocarbon yield (about 9 wt.%) and oxygenated compound yield (about 4 wt.%). Some of these observations could be taken into account and compared to results with FCC catalysts. It was observed in this work that the degree of representation of bio-oils by means of a mixture of model compounds is limited, as also stated by Adjaye and Bakhshi (1995a), who used a mixture of six model compounds over HZSM-5. These observations suggest that this issue is not depending on the acidic catalyst used.

The catalytic conversion of bio-oils derived from various sawdusts has been extensively studied over different acid zeolites (Sharma and Bakhshi, 1993; Adjaye and Bakhshi, 1995b; Williams and Horne, 1995; Srinivas et al., 2000; Valle et al., 2007; Gayubo et al., 2010) and mesoporous materials (Antonakou et al., 2006), normally over fixed bed reactors. Adjaye and Bakhshi (1995b) and Williams and Horne (1995) compared the catalytic performances of zeolites Y and ZSM-5 at temperatures between 290 and 500 °C, and reported hydrocarbon yields between 6 and 26 wt.%, which were mainly aromatics in the case of ZSM-5 and aliphatic in the case of Y zeolite, as well as oxygenated compound yields between 6 and 18 wt.%, mainly phenols, alcohols, acids, ketones and furans. With both catalysts dehydration and decarboxylation were important, between 11–33 and 22–39 wt.%, respectively. Coke yields were extremely high (10–30 wt.%), particularly in the case of Y zeolite.

Other authors tested different approaches to diminish the high coke yields in the catalytic conversion of bio-oils over acidic zeolites. For example, the elimination of precursors, mainly phenols, by thermal conditioning in a mode similar to the one used in this work (Srinivas et al., 2000; Valle et al., 2007; Gayubo et al., 2010), or by means of the selective liquid–liquid extraction (Sharma and Bakhshi, 1993). Bio-oils were also diluted with solvents such as methanol (Valle et al., 2007; Gayubo et al., 2010) and tetralin (Sharma and Bakhshi, 1993), in order to increase hydrocarbon yield and decrease coke yield. This last option is less attractive, since the solvents can mask results due to their reactivity and, moreover, are petrochemical products. After these various strategies, coke yields decreased about 30–50%.

Studies on the conversion of bio-oils over real, equilibrium FCC catalysts are scarce, and normally limited to co-processing with hydrocarbon feedstocks but after having hydrotreated the bio-oils (Samolada et al., 1998; Lappas et al., 2009; Fogassy et al., 2010; de Miguel Mercader et al., 2010). This view about catalysts and approaches on the subject is also seen in a recent review by Al-Sabawi et al. (2012). Most important observations by those authors were that C1–C2 hydrocarbons increased and that C3–C4 hydrocarbons decreased their yields. Gasoline and LCO yields were not affected significantly, although the proportion of aromatics in gasoline increased and some oxygenated aromatic compounds such as phenol and alkylphenols were observed in this boiling range. As expected, coke yield was higher when bio-oil was present (up to 30% increase), and bio-oil deoxygenation lead to significant amounts of water and carbon dioxide. According to various authors, co-processing bio-oils together with fossil feedstocks favors hydrogen transfer from hydrocarbons to oxygenated compounds (Corma et al., 2007; de Miguel Mercader et al., 2010; Fogassy et al., 2010). The various aspects of the conversion of the three feedstocks in the catalytic and thermal experiments are shown in the following sections.

The catalytic cracking of bio-oils and the catalytic pyrolysis of biomass over acids catalysts follow similar reaction pathways (Adjaye and Bakhshi, 1995a; Zhang et al., 2009b). In the fast catalytic pyrolysis of corncob over FCC catalysts in a fluidized bed reactor at 550 °C, Zhang et al. (2009a) obtained between 12 and 18 wt.% of

Table 3
Thermal and catalytic conversions of synthetic bio-oil compounds (wt.%).

	Synthetic bio-oil		Individual	
	SiC	E-Cat	SiC	E-Cat
Acetic acid	^a	100.0	45.0	50.4
Methyl acetate	65.3	98.4	95.3	95.1
Furfural	42.9	100.0	21.6	78.2
2-Hydroxy-3-methylcyclopentenone	63.9	98.2	37.7	84.5
Methanol	3.6	79.2	22.6	60.8
Phenol	0.8	^a	8.2	54.9
Syringol	95.0	100.0	56.7	75.0
1,2,4-Trimethoxybenzene	78.6	88.7	97.1	95.7

^a Recovered mass higher than fed mass.

oil, about 27 wt.% of water, between 15 and 22 wt.% of gases (mainly carbon oxides, methane, ethylene and propylene), about 20 wt.% of char and between 6 and 14 wt.% of coke. Ioannidou et al (2009) obtained less oil (about 10 wt.%) and gases (12.3 wt.%) than Zhang et al. (2009a), but the same yield of water (27 wt.%) and 33 wt.% of solid products (char and coke) in a fixed bed reactor using the same raw material at 500 °C. Adam et al. (2006) reported similar results for the fast catalytic pyrolysis of miscanthus and spruce wood in a fixed bed reactor over equilibrium FCC catalysts. In all the cases the oil product contained mainly alkylated phenols (between 25 and 32 wt.%), ketones (between 10 and 15 wt.%), furans (close to 30 wt.%) and hydrocarbons (between 5 and 16 wt.%), the contents of acids being very low, less than 5 wt.%.

Zeolite HZSM-5 has shown to be efficient in the catalytic upgrading of bio-oils. Moreover, when used under the same conditions as FCC catalysts in the fast catalytic pyrolysis of corn cob (Zhang et al., 2009b), the product distributions were similar but with lower oxygen content, hydrocarbon yields being slightly higher.

3.2. Reactivity of the synthetic bio-oil

The distribution of products in the catalytic conversion of the synthetic bio-oil can be compared to those obtained in the conversion of some of the individual components in the mixture (the model compounds). Table 3 shows the conversions of the components of the synthetic bio-oil observed in the thermal and catalytic experiments (conversions cannot be assessed strictly in the cases of compounds that are also formed from other mixture components), as compared to those obtained in individual experiments under the same conditions, diluted in water at 5 wt.%, or in ben-

zene (case of 1,2,4-trimethoxybenzene) (Bertero, 2012). It can be seen that in some cases the amount of reactant recovered was higher than the amount fed, which confirms interconversions; for example, acetic acid, methanol and phenol are produced in the conversion of methyl acetate, furfural, 2-hydroxy-3-methylcyclopentenone and syringol. Moreover, in the case of acetic acid, its conversion in the mixture was complete. For the rest of the reactants, their conversion over the catalyst was much higher in the mixture, mostly over 90%, than when fed alone. This suggests different behaviours of the model compounds when pure or taking part of a mixture, and some authors postulated that a synergy effect is present between the different species in a mixture and the reaction products in the conversion of oxygenated model compounds over Y and ZSM-5 zeolites (Adjaye and Bakhshi, 1995a; Samolada et al., 2000; Gayubo et al., 2005).

In the conversion of pure components, the highest hydrocarbon yield was observed with 1,2,4-trimethoxybenzene (47.1 wt.%) and the lowest with methyl acetate (0.9 wt.%), and the opposite was observed with the yield of oxygenated compounds (maximum for methyl acetate, 54.5 wt.%; minimum for 1,2,4-trimethoxybenzene, 0.2 wt.%) (Bertero, 2012).

The deoxygenation effects observed when the components of the mixture were reacted pure (decarboxylation from 12% to 36%; dehydration from 5% to 27%) were contrary to those observed with the mixture (see Table 2; mainly, dehydration, and some decarboxylation).

All these significantly different evidences suggest that individual model compounds constitute an over simplified approach to represent bio-oils and study their reactivity. Furthermore, the comparison between results with the synthetic bio-oil and the raw and conditioned feedstocks show that important differences are apparent in, for example, the magnitude of deoxygenation. These facts suggest that a mixture of model compounds is not completely adequate to study the intrinsic behaviour of bio-oils over FCC catalysts.

3.3. Oxygenated products in the thermal and catalytic conversions

Table 4 shows the distributions of oxygenated products obtained in the thermal and catalytic conversions of the different reactant mixtures. In all the cases the conversion over catalyst E-Cat produced mainly phenols and alcohols, phenol and cresols being the most important among phenols, and methanol among alcohols. Acetone was produced in significant amounts in the case of the raw bio-oil and the treated liquid. It is to be noted that, even though the high concentrations of phenolic ethers in the feedstocks, particularly in the cases of the raw and conditioned bio-

Table 4
Distribution of oxygenated products (wt.%) in the thermal and catalytic conversions of the raw and synthetic bio-oils and the treated liquid. Reaction temperature 500 °C.

	Synthetic bio-oil		Bio-oil		Treated liquid	
	SiC	E-Cat	SiC	E-Cat	SiC	E-Cat
Oxygenated compounds yields (wt.%)	71.1	19.3	71.9	9.6	59.8	5.5
Selectivity (wt.%)						
Acids	28.2		33.3	2.3	38.6	0.9
Esters	5.3	0.9	8.1		4.7	
Linear aldehydes and ketones	0.2	0.9	20.6	25.1	25.3	32.5
Cyclic ketones	11.7	1.9	4.1		3.9	
Furans	10.7	1.2	4.3	4.5	3.2	2.7
Alcohols	31.5	25.0	15.8	16.3	13.2	18.2
Phenols	10.8	69.2	10.5	51.0	8.4	45.2
Alkylated phenols	9.5	69.2	4.9	51.0	4.0	45.2
Phenolic ethers	1.3		5.6		4.4	
Ethers			1.0		0.7	
Other cyclic oxygenated compounds	1.6	0.9	1.4	0.8	1.4	0.5
Nitrogen compounds			0.9		0.6	

oil, these compounds were not observed among the products of the catalytic conversions, thus suggesting a high reactivity. This was also observed on zeolite ZSM-5 (Chantal et al., 1985).

The thermal conversions generated similar distributions of products with all the reactants, showing acids, alcohols and phenols as the main products. Most of the products were the same as those in the reacting mixtures, though with a different distribution, consistently with the observations by Williams and Horne (1995) and Srinivas et al. (2000).

In the case of the synthetic bio-oil, the selectivity of the main oxygenated compounds over catalyst E-Cat (e.g. phenol, cresols and methanol) was higher than in the other reactant mixtures. Other products, such as acetone and dibenzofuran showed much lower selectivities. These observations are similar to reports from the conversion of different mixtures of oxygenated compounds over zeolites REUSY and HZSM-5 (Adjaye and Bakhshi, 1995a; Samolada et al., 2000).

The distribution of oxygenated products in the catalytic conversion of the synthetic bio-oil can be compared with those in the individual conversion of the model compounds. For example, phenol and cresols were the most important oxygenated products in the conversion of methanol, syringol and 1,2,4-trimethoxybenzene on this type of catalyst, and methanol was also an important product in the conversion of methyl acetate, furfural, 2-hydroxi-3-methylcyclopentenone and syringol (Bertero, 2012).

The main oxygenated products in the thermal conversion of the synthetic bio-oil were acetic acid and methanol (selectivities about 30 wt.%), and furfural and 2-hydroxi-3-methylcyclopentenone (selectivities about 10 wt.%). Other oxygenated compounds were also observed, such as cresols and methylcyclopentenone (selectivities of 1.3 wt.%), and acetone, ethylfuranone and dimethylphenol (selectivities lower than 1 wt.%). Methanol and acetone are products from the thermal conversion of most of the components in the synthetic bio-oil (Bertero, 2012) and, particularly, acetic acid is produced by the hydrolysis of methyl acetate (Morrison and Boyd, 1985). Moreover, methylcyclopentenone is the main oxygenated product in the conversion of 2-hydroxi-3-methylcyclopentenone, and phenols (mainly phenol and cresols) are the main

oxygenated products in the conversion of syringol and 1,2,4-trimethoxybenzene (Bertero, 2012).

In the catalytic conversion of the authentic feedstocks from pine sawdust, the conditioned liquid produced less phenols and more acetone and methanol than the bio-oil. Some acids, such as acetic and pentanoic, and furans such as furfural and benzofurans, were produced with both feedstocks with low selectivity. These results are similar to reports over zeolites Y and ZSM-5 (Sharma and Bakhshi 1993; Adjaye and Bakhshi, 1995b; Williams and Horne, 1995; Srinivas et al., 2000).

Among the oxygenated products, the thermal cracking of the conditioned liquid and the bio-oil produced mainly acids, aldehydes, ketones, alcohols and phenols. The selectivity to acids, mainly formic and acetic, was over 30 wt.% with both feedstocks, similarly to observations from Srinivas et al. (2000). The main aldehydes and linear ketones were 2-butenal, 2-pentanone, 2,3-pentadione and acetone, and the main alcohols were methanol and ethanol. The selectivity to phenols was higher with the bio-oil, about 10%, than with the conditioned liquid. The proportion of phenolic ethers among phenol derivatives in the products (53% in both cases, see Table 4) was lower than in the respective feedstocks (66% in bio-oil and 60% in the conditioned liquid, see Table 1). These remarks are in line with some known facts; for example, it is known that guaiacol and its derivatives, which are the prevailing phenolic ethers in bio-oils, react easily as a consequence of temperature, leading to phenol and its alkylated homologous compounds (Hosoya et al., 2008).

3.4. Hydrocarbon products in the thermal and catalytic conversions

It has been postulated that the occurrence of water in this reacting system could help in the production of hydrocarbon products on acidic zeolites, since it can act as a hydrogen donor (Samolada et al., 2000). This may be positive to co-process bio-oils in FCC. Table 5 shows the distributions of hydrocarbon products from the thermal and catalytic conversions of the various feedstocks. It can be seen that C1–C4 gases, particularly methane and olefins, were the main products in all the cases. Light olefins had been proposed as impor-

Table 5

Selectivity of hydrocarbon products (wt.%) in the thermal and catalytic conversions of the raw and synthetic bio-oils and the treated liquid. Reaction temperature 500 °C.

	Synthetic bio-oil		Bio-oil		Treated liquid	
	SiC	E-Cat	SiC	E-Cat	SiC	E-Cat
Hydrocarbons yield (wt.%)	16.4	26.8	11.7	42.3	23.9	53.5
Selectivity (wt.%)						
Hydrocarbons C1–C2	31.5	47.7	57.3	59.6	57.5	55.4
Methane	25.8	39.0	30.3	28.1	29.3	27.3
Ethane	1.3	2.6	6.0	4.6	4.2	3.6
Ethylene	4.4	6.1	21.0	26.9	24.0	24.5
Hydrocarbons C3–C4	37.4	17.5	35.9	28.5	33.4	32.0
Propane				0.5		0.7
Propylene	8.9	9.2	15.9	15.8	14.8	19.1
1,3-Propadiene	0.1	0.1	0.1	Traces	0.1	0.1
<i>n</i> -Butane		0.4		3.7		3.1
Isobutane	0.1	0.8	7.3	4.8	6.5	4.5
Butenes	28.3	7.0	12.9	3.7	12.0	4.5
Hydrocarbons C5–C9	25.1	8.3	6.8	4.6	8.1	5.7
<i>i</i> -Pentane		0.2		0.5		0.7
<i>n</i> -Pentane		2.8	0.5	0.1	0.4	0.3
Pentenes	23.0	3.8	4.0	3.3	5.6	3.9
C6+ Aliphatics	1.3	0.7	2.0	0.7	2.0	0.8
C6+ Cycloparaffins and naphthenics	0.8	0.8	0.3		0.1	
Aromatics	6.0	26.5		7.3	1.0	7.0
Benzene	0.1	5.4		1.3	1.0	2.3
Toluene	0.1	0.1				
Xylenes	0.7	1.0				0.2
Ethylbenzene	0.2	0.1				
Aromatics C9	0.4	4.0		0.2		0.3
Aromatics C10	1.7	8.7		1.1		0.7
Aromatics C11+	2.8	7.2		4.7		3.6

tant products from deoxygenation and cracking reactions of the bio-oil components (Adjaye and Bakhshi, 1995b). Liquid hydrocarbon products in the C5–C15 range were also obtained in the catalytic conversions, particularly for the synthetic bio-oil.

When the synthetic bio-oil was converted on catalyst E-Cat, the selectivity to gasoline was 35 wt.%, with a high content of aromatics (76 wt.%), benzene and alkylated monoaromatics being the main hydrocarbons. One third of the aromatic hydrocarbons were naphthalene and its alkylated derivatives. The conversion of the individual components of the synthetic bio-oil under the same conditions showed that acetic acid, methyl acetate, phenol and syringol yielded mainly C1–C4 hydrocarbons (selectivities between 75 and 100 wt.%), with a high content of olefins, while furfural, methanol and 1,2,4-trimethoxybenzene, produced almost exclusively liquid hydrocarbons in the range C5–C15, with a high content of C5 olefins in the case of furfural, and of aromatics in the case of methanol and 1,2,4-trimethoxybenzene (Bertero, 2012). The cyclic ketone 2-hydroxy-3-methylcyclopentenone produced similar proportions of gaseous and liquid hydrocarbons, with a complex distribution of products in each range of molecular weights (Bertero, 2012).

The thermal conversion of the synthetic bio-oil produced mostly methane (25.8 wt.% selectivity) and C4–C5 olefins (51.3 wt.% selectivity), and, to a lower extent, aromatic hydrocarbons in the C6–C12 range. This product distribution can be compared to the results in the conversion of the individual components of the mixture, where it had been observed that acetic acid, methyl acetate, methanol, phenol and syringol produced exclusively C1–C4 hydrocarbons, highly olefinic. Furfural produced mainly C5 olefins (selectivity 70 wt.%), and 1,2,4-trimethoxybenzene, exclusively aromatic hydrocarbons, where polyaromatics such as naphthalene, fenantrene and alkylated homologous represented 11 wt.%. When fed individually, 2-hydroxy-3-methylcyclopentenone showed the same selectivity to C4 olefins and aromatic hydrocarbons (Bertero, 2012).

The catalytic conversion of the conditioned liquid yielded about 25 % more hydrocarbons than the raw bio-oil. The selectivity to hydrocarbons in the boiling range of gasoline in the conversion of raw bio-oil was low (10 wt.%), with highly aromatic (54.9 wt.%) and C5 olefinic (26.1 wt.%) contents. The most important aromatic hydrocarbons in the range were naphthalene and alkylated homologous (68 wt.%). These characteristics were similar to those reported on zeolites Y and ZSM-5 (Sharma and Bakhshi, 1993; Adjaye and Bakhshi, 1995b; Williams and Horne, 1995).

The catalytic conversion of the conditioned liquid lead to a gasoline selectivity of 12.3 wt.%, that is, about 25% higher than that of the bio-oil, showing a higher content of C5 olefins (32.6 wt.%) and similar of aromatic hydrocarbons (52.7 wt.%). Benzene and naphthalene and its alkylated derivatives were the main aromatic hydrocarbons in the range, but the proportion of two ring aromatics was about one third lower than in the case of the raw bio-oil. The selectivity to C1–C2 was slightly lower than that of bio-oil, and the selectivity to C3–C4 hydrocarbons slightly higher. In this group of hydrocarbons, the content of olefins observed with the conditioned liquid (74 wt.%) was higher than with bio-oil (68 wt.%).

The thermal conversions of the raw bio-oil and the conditioned liquid showed similar distributions of hydrocarbon products, with methane (30 wt.% selectivity) and C2–C4 olefins (selectivity 50 wt.%), being the most important products, as also observed by other authors in the thermal conversion of bio-oils derived from different wood sawdusts (Sharma and Bakhshi, 1993; Williams and Horne, 1995; Adjaye and Bakhshi, 1995b; Srinivas et al., 2000; Gong et al., 2011).

In general terms, the conversion of the synthetic bio-oil over catalyst E-Cat, lead to hydrocarbon product distributions that were

very different to the ones observed with true bio-oils, a fact which is consistent with published reports (zeolite HZSM-5, Adjaye and Bakhshi, 1995a). With all the feedstocks the main hydrocarbons in the boiling range of gasoline were aromatics, but their selectivity was much higher with the synthetic bio-oil. Moreover, the synthetic bio-oil produced mainly monoaromatic hydrocarbons, while two-rings aromatics were predominant in products from bio-oil and the conditioned liquid.

3.5. Analysis of the coke yields in the thermal and catalytic conversions

It has been postulated that coke in the acid catalyzed conversion of bio-oil has both thermal and catalytic sources (Sharma and Bakhshi, 1993; Williams and Horne, 1995; Srinivas et al., 2000; Gayubo et al., 2004a,b; Valle et al., 2007). In the case of compound catalysts such as those used in FCC, where the main component (Y zeolite) is supported on a matrix, the coke from thermal sources will in general deposit on the matrix, thus exerting a less severe deactivation effect on the active sites than coke from catalytic sources (Gayubo et al., 2005).

Coke yield in the catalytic conversions was high in all the cases, being maximum for the synthetic bio-oil (14 wt.%, see Table 2). When the components of the synthetic bio-oil were converted alone, 2-hydroxy-3-methylcyclopentenone and 1,2,4-trimethoxybenzene showed the highest coke yields (12.8 and 16 wt.%, respectively), and acetic acid the lowest (1.6 wt.%). The other oxygenated compounds produced between 4.4 and 8.5 wt.% (Bertero, 2012). The treated liquid yielded less coke in its catalytic conversion (yield 9.1 wt.%), which resulted about 20% lower than in the case of the raw bio-oil. In all the cases in the thermal conversions, coke yields were much lower than in the catalytic conversions, as also observed by Williams and Horne (1995) with pine sawdust bio-oil. Different bio-oils from sawdusts converted over Y and ZSM-5 zeolites produced very high yields of coke, between 10 and 22 wt.% (Sharma and Bakhshi, 1993; Adjaye and Bakhshi, 1995b; Williams and Horne, 1995), while the yields from mixtures of model oxygenated compounds representing the main chemical groups in bio-oils over the same catalysts were lower, between 4 and 12 wt.% (Adjaye and Bakhshi, 1995a; Samolada et al., 2000).

The combustion profile of the coke deposits from the synthetic bio-oil showed a single peak with its maximum at 700 °C, thus insinuating a very high condensation, which could be the consequence of the high yield of aromatic hydrocarbons observed in its conversion (see Table 5). In the cases of the raw bio-oil and the treated liquid, two peaks were observed, the first one located at about 630 °C, which corresponded to a less condensed coke, and the second one at 700 °C., which corresponded to a more condensed coke. The results of a deconvolution exercise of the combustion profiles (Lorentzian curves, fitting degree 0.995) showed that after thermal treatment of the raw bio-oil, the contribution of the second peak to the total amount of coke was decreased in about 45%.

The combustion profiles corresponding to the coke formed on the SiC particles showed a very small peak, consistent with the very low yields, located at about 450 °C.

4. Conclusions

The conversion of the raw bio-oil from pine sawdust, the liquid product from its thermal conditioning and a synthetic bio-oil over an equilibrium FCC catalyst produced hydrocarbons (mainly C4-olefins), oxygenated compounds and coke.

The synthetic bio-oil produced lesser hydrocarbons and more oxygenated compounds and coke than the feeds from sawdust. The positive effects of the thermal treatment of the raw bio-oil

were shown in increasing the yield of hydrocarbons and decreasing the yield of coke, particularly the more condensed portion.

The prediction of the behavior of bio-oils over acidic catalysts by means of mixtures of model compounds is limited.

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