

# Effect of Pyrolysis Temperature and Thermal Conditioning on the Coke-Forming Potential of Bio-oils

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**ABSTRACT:** Bio-oil from the pyrolysis of pine sawdust was subjected to a thermal conditioning process aimed at inducing changes in its composition and physicochemical properties. The objective was to facilitate the coprocessing of bio-oil together with conventional feedstocks in catalytic cracking of hydrocarbons (FCC). The pyrolysis was performed at different conditions (heating ramp 15 °C/min, final temperatures from 300 to 650 °C), yielding varying proportions of gases, tar, char, and bio-oil. The maximum bio-oil yield (43.7 wt %) was obtained at 550 °C. Bio-oil showed a high concentration of oxygenated compounds (about 48 wt %) including acids, esters, aldehydes, ketones, furans, alcohols, sugars, phenols, and ethers, together with hydrocarbons and close to 50 wt % of water. The thermal treatments included different conditions (final temperatures from 350 to 550 °C and heating ramps from 8 to 12 °C/min), and the most important consequences were that the concentrations of compounds believed to be coke precursors, such as phenols decreased significantly (between 30 and 50% and particularly some phenolic ethers, up to 90%), and high molecular weight compounds (between 50 and 65%). Some physicochemical properties in the bio-oil changed positively, the CCR decreasing from 4.8 wt % to about 1.5 wt %, and the effective hydrogen index increasing by 30%. Most of the carbon and the hydrogen remained in the liquid phase after the thermal treatment, while about 40% of the oxygen was removed. The byproduct in the thermal process (tar, gases, and pyrolytic lignin), represented an overall yield of about 5 wt %, and the overall yield of conditioned liquid was 38.7 wt % based on the sawdust raw material.

## INTRODUCTION

The low cost of lignocellulosic forest, crop, or industrial residua makes their pyrolysis into liquid products an attractive option to produce sustainable renewable liquid fuels. The most direct use of these liquid products is as fuels in boilers<sup>1</sup> and emulsified in diesel fuels.<sup>2,3</sup> However, the typically high content of oxygen (40–50 wt %) and water (15–30 wt % and more),<sup>1</sup> impedes their direct use as transportation fuels, and some of the oxygenated compounds present, such as aldehydes, ketones, and acids, make them unstable during storage. The H/C ratio and heating values, lower than those of traditional fuels, are also to be considered. However, it has been postulated that the catalytic upgrading into gasoline-range hydrocarbons is feasible.<sup>4–8</sup>

According to their solubility in water, two fractions can be obtained from biomass pyrolysis liquid products. Tar, the water insoluble fraction, is viscous and denser than the water-soluble fraction, which is designated as bio-oil.

Coprocessing in conventional refinery processes, taking part of standard feedstocks, is an interesting option to upgrade bio-oils.<sup>9,10</sup> Among different options, the catalytic cracking of hydrocarbons (FCC) is an appropriate process to convert bio-oil components into light and gasoline range hydrocarbons. The FCC process converts high molecular weight feedstocks, usually heavy vacuum gas oils, VGO, into lighter and much more valuable products such as LPG, gasoline, middle distillates;<sup>11</sup> a delicate heat balance is obeyed in the commercial units, where the heat required by the endothermic cracking reactions in the riser reactor is provided by coke burning off in the regenerator section. The proposed approach could be put at risk by the

expected increase in coke yield when coprocessing bio-oils. Samolada et al.<sup>12</sup> reported that during the catalytic cracking of bio-oil over commercial FCC catalysts in a fixed bed laboratory reactor at temperatures in the range of 500–550 °C, coke yield was about 20 wt %. At lower temperatures (300–400 °C), Adjaye et al.<sup>4</sup> and Srinivas et al.<sup>8</sup> observed that coke yield decreased to the 4–15 wt % range. Even considering that catalytic cracking in this type of laboratory reactors would yield higher amounts of coke, these figures are still excessively high when compared to those observed in commercial or pilot plant FCC units,<sup>13</sup> or fluidized bed laboratory reactors.<sup>14</sup> Other possible drawbacks in the approach are the high content of water in bio-oil and the fact that it may be not possible to dissolve it into VGO; some options were discussed by Corma et al.<sup>15</sup>

In order to coprocess bio-oils in standard FCC units, then, it would be necessary to reduce their coke-forming potential, which could be mainly due to the significant concentration of phenolic compounds and other heavy molecular weight oxygenated species.<sup>16,17</sup> Aromatic ethers and some compounds derived from cellulose and hemicellulose, such as furanes and cyclic ketones, could also be coke precursors. Figure 1 shows a proposed scheme to coprocess pyrolysis liquid products in FCC with a previous conditioning (e.g., a thermal treatment) to reduce the concentration of coke precursors that would be converted into pyrolytic lignin; the resulting liquid would be more adequate to be added to the typical VGO feedstock. The thermal treatment of bio-oil, previous to a catalytic upgrading, was studied by different

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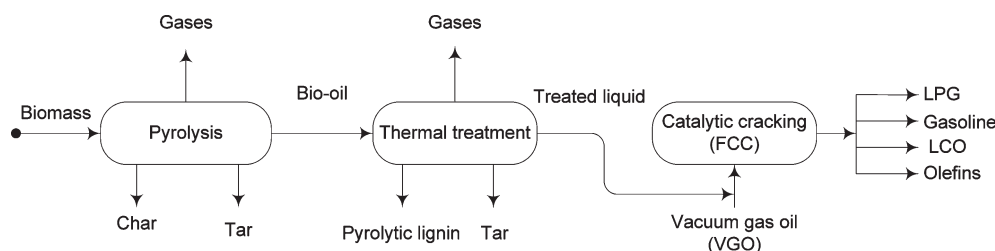


Figure 1. Valorization of bio-oil through coprocessing in FCC with previous thermal conditioning.

Table 1. Properties of the Biomass Raw Material

property (wt %, dry basis)	
moisture content	10.2
ash	0.3
elemental composition	
C	51.0
H	5.3
O <sup>a</sup>	43.6
N	<0.1
lignocellulosic material composition <sup>b</sup>	
cellulose	35
hemicellulose	29
lignin	28
higher heating value (HHV, MJ/kg)	15.4

<sup>a</sup> Calculated by difference. <sup>b</sup> From the work of Westerhof.<sup>50</sup>

authors,<sup>8,18–20</sup> who observed coke yields up to 30% lower in the catalytic upgrading.

Temperature is one of the key parameters in biomass pyrolysis impacting bio-oil composition.<sup>21,22</sup> The thermal degradation of the three main components of biomass (lignin, cellulose, and hemicellulose) leads to different products, mainly oxygenated. Lignin, which is biosynthetically produced by copolymerization of three phenylpropane monomers, decomposes mainly into various phenolic compounds during pyrolysis,<sup>23</sup> while the carbohydrates yield aldehydes, ketones, acids, esters, and alcohols.

The effect of pyrolysis temperature on bio-oil yield, composition, and coke potential was studied on pine sawdust as the raw material, with the aim of coprocessing it in standard FCC units. Emphasis was placed on phenolic and other oxygenated compounds, considered as potential coke precursors. A comparison was performed with the liquid product from the thermal conditioning of the bio-oil under different conditions, aimed at decreasing the concentration of coke precursors.

## EXPERIMENTAL SECTION

**Bio-oil Production and Thermal Conditioning.** Pine (*pinus elliottii*) sawdust was used to produce bio-oil; it was dried at 100 °C during 18 h to assess the water content by weight difference.

The conventional pyrolysis of approximately 6 g of sawdust was performed in a stainless steel fixed bed reactor of 21.0 cm length and 1.9 cm diameter, heated electrically in a furnace. The heating ramp was 15 °C/min from room temperature up to 300, 350, 550, and 650 °C as the final temperature, that was maintained constant during 60 min. According to previous reports<sup>21</sup> and own results, the heating rate in the range from 5 to 80 °C/min has moderate influence on the product distribution in pyrolysis

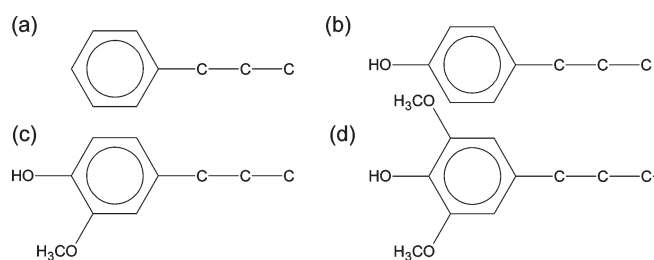


Figure 2. Typical lignin building units (a) phenylpropane, (b) 4-hydroxyphenylpropane, (c) guaiacylpropane, and (d) syringylpropane.

Table 2. Yields in the Pyrolysis Process (wt %)

	temperature, °C			
	300	350	550	650
pyrolysis liquid	24.1	31.2	50.3	44.7
bio-oil	24.1	31.2	43.7	43.5
Tar-P			6.6	1.9
char	63.3	56.2	28.9	32.0
gases	12.6	12.6	20.8	22.6

oils. In order to remove vapors from the reaction zone and minimize secondary reactions, a nitrogen flow of 20 mL/min was circulated through the reactor. Effluents moved through a water–ice condenser where liquid products were collected and gases were vented to the atmosphere.

The liquid pyrolysis product was centrifuged at 3200 rpm during 8 min to separate bio-oil and tar (named Tar-P). The bio-oil obtained at 550 °C (maximum yield, minimum solid residue) was subjected to a thermal conditioning process in a glass reactor of 5.0 cm length and 2.5 cm diameter, under a flow of nitrogen of 5 mL/min. Again products were passed through a water–ice condenser and condensed liquid products were centrifuged to separate a tar fraction (named Tar-T) and the so-called treated liquid, TL. Heating ramps in the conditioning process were 8, 10, and 12 °C/min from room temperature to 350, 400, 450, 500, and 550 °C as final temperature, that was kept constant during 10 min.

Product yields in the pyrolysis process were assessed on the basis of dry raw material and product yields in the thermal conditioning process were assessed on the basis of the bio-oil fed.

**Product Characterization.** Gaseous and liquid products were analyzed by conventional capillary GC in a Agilent 6890N gas chromatograph with a flame ionization detector (FID) and an HP-1 column of 30 m length, 0.25 mm i.d., and 0.25 μm phase thickness. Gases were also analyzed with thermal conductivity detection and a GS-CARBON-PLOT column 30 m length, 0.53 mm i.d., and 3 μm phase thickness. Product identification was performed with the help of standards and mass spectrometry. The calibration of the chromatographic areas was performed with response factors representative of each of the different types of compounds present. Each unidentified peak accounted for less

**Table 3.** Yields in the Thermal Conditioning of Bio-oil (wt %)

	final temperature (°C), heating ramp 12 °C/min				
	350	400	450	500	550
liquid	89.2	90.0	92.8	92.5	92.3
treated liquid	85.2	85.9	89.0	88.7	86.9
Tar-T	4.0	4.1	3.8	3.8	5.4
pyrolytic lignin	5.4	4.9	4.4	4.2	4.5
gases	5.4	5.1	2.8	3.3	3.2

	heating ramp (°C/min), final temperature 500 °C		
	8	10	12
liquid	89.6	92.1	92.5
treated liquid	86.1	88.4	88.7
Tar-T	3.5	3.7	3.8
pyrolytic lignin	5.5	4.3	4.2
gases	4.9	3.6	3.3

than 0.5% of the total chromatographic area, and they were grouped into "unknown components", independently of the elution order.

The characterization of the bio-oil and TL products was completed with elemental microanalysis (Carlo Erba EA 1108), CCR analysis (IRAM 6542), water content (IRAM 21320), density, and pH determinations. The higher heating values of bio-oil, char, and gaseous products were calculated with the Dulong formula;<sup>24</sup> in the case of bio-oil, it was corrected considering the amount of water present.

## RESULTS AND DISCUSSION

**Biomass Composition.** The properties of the pine sawdust raw material are shown in Table 1. The high proportion of lignin is typical of softwoods.<sup>23</sup> Lignins in softwoods are polymers of phenylpropane units with substitutions by hydroxy and methoxy groups, particularly guaiacylpropane (see Figure 2c).

Cellulose is a linear polymer of D-glucose units, linked by  $\beta(1 \rightarrow 4)$ -glycosidic bonds. The hemicellulose fraction is a mixture of various polymerized monosaccharides such as glucose, mannose, galactose, xylose, arabinose, 4-O-methyl glucuronic acid, and galacturonic acid residues.

**Yields in the Pyrolysis Process.** The pyrolysis of pine sawdust produced a residual solid phase (char), a liquid phase, and a gas phase. The liquid phase can be fractionated by centrifugation into bio-oil and Tar-P, which are essentially soluble and insoluble in water, respectively.

The product yields from the pyrolysis at different temperatures are shown in Table 2. These results are in line with previous reports by other authors about the three product streams obtained under similar conditions.<sup>21,22,24,25</sup>

Bio-oil yield was maximum at the highest temperatures used, and the highest yield of Tar-P was obtained at 550 °C. At lower temperatures (300 and 350 °C), Tar-P was not formed, but bio-oil yields were very low. Char yield was very high at 300 °C, but it decreased significantly at 550 °C. These values suggest that the raw material was not completely pyrolyzed at the lowest temperatures. The yield of gases increased steadily as a function of pyrolysis temperature, reaching 22.6 wt % at 650 °C.

**Yields in the Thermal Conditioning Process.** Bio-oil was subjected to a thermal conditioning treatment in order to check possible drops in the concentrations of some compounds in bio-oil considered as coke precursors.<sup>8,18–20</sup> Products were

**Table 4.** Chemical Composition of Pine Sawdust Bio-oil under Different Pyrolysis Temperature (wt %)

	temperature (°C)			
	300	350	550	650
water	53.7	48.4	49.6	41.0
acids	11.8	13.2	5.6	8.1
esters	2.9	3.0	2.8	2.3
linear aldehydes and ketones	8.5	10.6	5.5	7.2
cyclic ketones	1.9	2.2	1.7	1.9
furans	3.3	4.4	3.2	2.7
alcohols and sugars	4.8	7.2	7.2	11.2
phenols	3.0	3.7	8.2	7.3
alkylated phenols	1.0	0.8	2.2	2.2
phenolic ethers	2.1	2.9	6.0	5.1
ethers	0.3	0.3	0.4	1.4
other cyclic oxygenated compounds cyclicos	1.2	1.1	1.9	2.8
hydrocarbons	0.2	0.2	0.6	0.4
nitrogen compounds	0.5	0.6	0.8	0.8
unknown <sup>a</sup>	7.9	4.9	12.5	12.9

<sup>a</sup> Individual peaks smaller than 0.5%.

distributed into three phases; a solid phase retained in the reactor walls (pyrolytic lignin), a liquid phase, and gaseous effluents. The liquid phase was separated by centrifugation into the so-called treated liquid TL, and Tar-T. The different yields as a function of the heating ramp and final temperature in the conditioning are shown in Table 3. It can be seen that liquid yield increased slightly as a function of temperature, while gases and pyrolytic lignin decreased. In most of the cases, the yield of TL was over 88 wt %. Overall, the heating ramp had a low impact on yields, liquid yield being the highest with the fastest ramp.

## CHEMICAL COMPOSITION OF BIO-OIL

Bio-oil is a very complex mixture of different species derived from depolymerization and fragmentation of the three main components in biomass. Carbohydrate pyrolysis, which occurs between 220 and 380 °C approximately, with maximum conversion at 300 °C in the case of cellulose, and 350 °C in the case of hemicellulose, leads to aldehydes, ketones, acids, esters, and alcohols, and lower amounts of ethers and hydrocarbons.<sup>26</sup> On the other hand lignin decomposition, starting at about 230 °C with the rupture of the bonds of the propanoic chains and ending at about 650 °C,<sup>27</sup> leads mainly to phenolic compounds and smaller amounts of methanol, acetic acid, and hydrocarbons.<sup>26,28,29</sup> Water comes from dehydration during the thermal conversion of biomass.

Table 4 shows the composition of the bio-oils obtained at different pyrolysis temperatures, where products were grouped according to their chemical type; phenols were classified as alkyl phenols and phenolic ethers, following the substituting groups. It is possible to observe an elevated concentration of oxygenated compounds, mainly acids, linear aldehydes and ketones, alcohols and sugars, and phenols, that usually represent between 55 and 68 wt % of total products. The most important individual products were formic, acetic, propanoic and butanoic acids, light linear alcohols, pentanones, guaiacols, cresols, and catechols. Water contents were similar to those reported in other publications, that

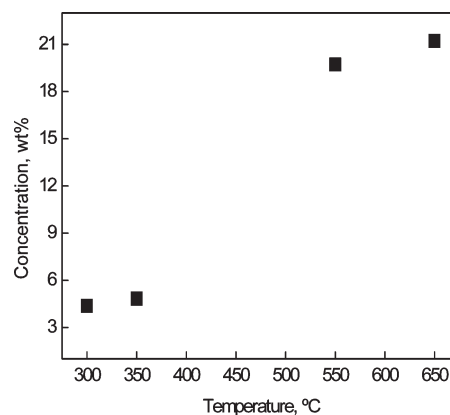
**Table 5. Concentration of Phenolic Compounds in the Bio-oil as a Function of Pyrolysis Temperature (wt %)**

	temperature (°C)			
	300	350	550	650
phenols	3.0	3.7	8.2	7.3
alkylated phenols	1.0	0.8	2.2	2.2
phenol	0.10	0.10	0.19	0.10
cresols	0.61	0.53	0.95	1.16
dimethylphenols	0.16	0.14	0.27	0.39
2-ethylphenol	0.02	0.01	0.08	0.03
4-ethylcatechol	0.05	0.05	0.20	0.15
2-methylhydroquinone	0.02	0.01	0.07	0.05
2,5-dimethylhydroquinone	0.03	0.01	0.15	0.10
2- <i>tert</i> -butyl-4-methyl-6-(1-phenylethyl)phenol			0.15	0.08
2,2'-methylenebis[6- <i>tert</i> -butyl-4-ethylphenol]				0.01
2,6-ditert-butyl- <i>p</i> -cresol			0.11	0.13
phenolic ethers	2.5	2.9	6.0	5.1
methoxycatechol	0.18	0.17	0.44	0.43
guaiacol	0.60	0.96	1.07	0.81
methylguaiacols	0.58	0.99	1.48	1.23
ethylguaiacols	0.15	0.28	0.53	0.62
4-vinylguaiacol	0.15	0.14	0.22	0.20
4-ethoxymethylguaiacol	0.00	0.00	0.05	0.06
eugenol	0.07	0.04	0.14	0.09
isoeugenol	0.22	0.22	0.38	0.19
vainillin	0.06	0.06	0.29	0.10
syringol	0.02	0.01	0.05	0.10
4-propenylsyringol			0.18	0.23
benzoic acid, 4-hydroxy-3-methoxy			0.09	0.07
homosyringic acid			0.27	0.26
acetoguaiacone	0.03	0.02	0.41	0.33
acetosyringone			0.06	0.01
guaiacylacetone			0.20	0.26
3,4-dimethoxyacetophenone			0.08	0.07
3,4-dihydroxyacetophenone	0.01	0.02	0.08	0.07

is, about 50 wt % for a mixture of softwoods<sup>30,31</sup> and 63 wt % for pine sawdust.<sup>32</sup>

The most significant differences in composition were observed at 650 °C, with a lower concentration of water and a higher concentration of sugars, ethers, and other cyclic oxygenated compounds. Particularly, the contents of lactose, levoglucosane, 1-ethoxybutane, 2-ethoxypentane, 2,3-dihydropyran, and propylene carbonate were about 2–4 times higher than in the other conditions. The lower pyrolysis temperatures (300 and 350 °C) produced more acids, especially acetic acid and 2-methylpropanoic acid, linear ketones and furanes; particularly, the concentrations of 2,3-pentadione, 4-hydroxy-4-methylbutanone, furfural, and furanmethanol were much higher than those in bio-oils obtained at higher temperatures.

Phenols are considered as coke precursors during the catalytic cracking of bio-oils over acidic catalysts, a fact that can affect the feasibility of coprocessing them together with conventional FCC hydrocarbon feedstocks. In that sense, when converted over acid zeolites, phenolic ethers showed a stronger trend to form coke than alkylated phenols,<sup>4,17</sup> since they initiate condensation mechanisms at low temperatures between 200 and 250 °C, the

**Figure 3.** Effect of pyrolysis temperature on the concentration of heavy molecular weight compounds in bio-oil.

products leading to polycyclic aromatic hydrocarbons at about 400 °C, in turn producing coke.<sup>29</sup>

The concentrations of phenols in the bio-oil obtained at 300 and 350 °C were much lower than those observed at higher pyrolysis temperatures, the highest one being obtained at 550 °C. The proportion of ethers was always high (between 67 and 77 wt %) among phenolic compounds. Moreover, while more than 80 wt % of the phenolic ethers had high molecular weights over 130 g/mol, more than 85 wt % of the alkylated phenols had low molecular weights below that limit. Table 5 shows the concentrations of phenolic compounds observed in the bio-oils produced at different pyrolysis temperatures. According to their source, they can be classified into those from the direct degradation of lignin and those from secondary reactions. At low pyrolysis temperatures, most important products were alkyl guaiacols (see e.g., guaiacol and methylguaiacols), from the degradation of lignin, and at 550 °C or more, the concentrations of alkyl phenols and benzenediols (see, e.g., cresols, dimethylphenols increased drastically, as a consequence of the high temperature.<sup>27</sup>

The heavy molecular weight components in bio-oil, arbitrarily defined as those with molecular weight higher than 130 g/mol and without discrimination among chemical types, could also be considered as coke precursors, since they participate in polymerization reactions during catalytic upgrading.<sup>8</sup> It can be seen in Figure 3 that the concentration of these compounds, such as 1,2,4-trimethoxybenzene, 4-ethoxy-3-anisaldehyde, or  $\gamma$ -heptylbutyrolactone, increases significantly at higher temperatures.

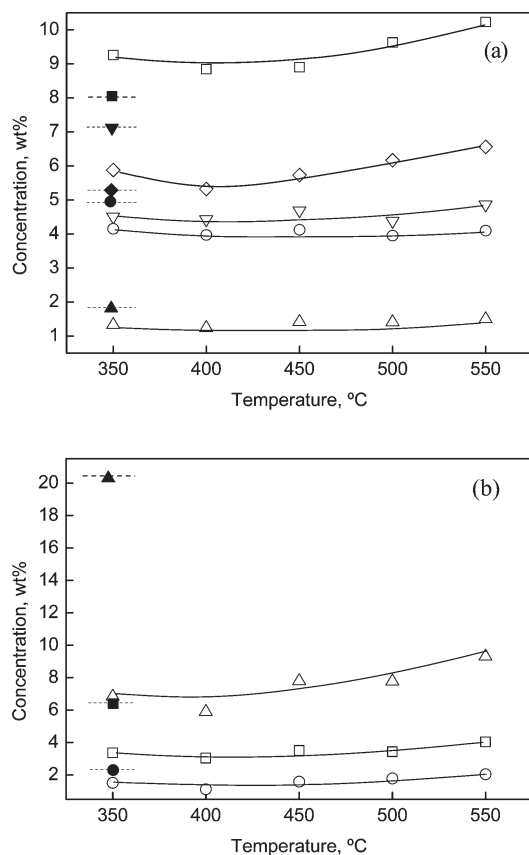
## CHEMICAL COMPOSITION OF TL PRODUCT

The tendency to form coke by bio-oil has been associated particularly to the occurrence of phenolic and high molecular weight oxygenated compounds,<sup>16,17</sup> but also cyclic ketones, furans, and other oxygenated may play an important role in coke yield during the catalytic upgrading of bio-oils.<sup>5,33</sup>

The changes in the concentration of some of the main groups in the product TL as a consequence of the thermal conditioning are shown in Figures 4 and 5 in comparison to the source bio-oil, according to different final temperatures and heating ramps. It can be seen that, independently of the experimental parameters, the thermal conditioning produced similar results on the composition of TL.

The concentration of cyclic ketones, furans, and alcohols decreased between 10 and 30%, although some compounds in these groups, such as cyclopentenone, cyclohexenone, and





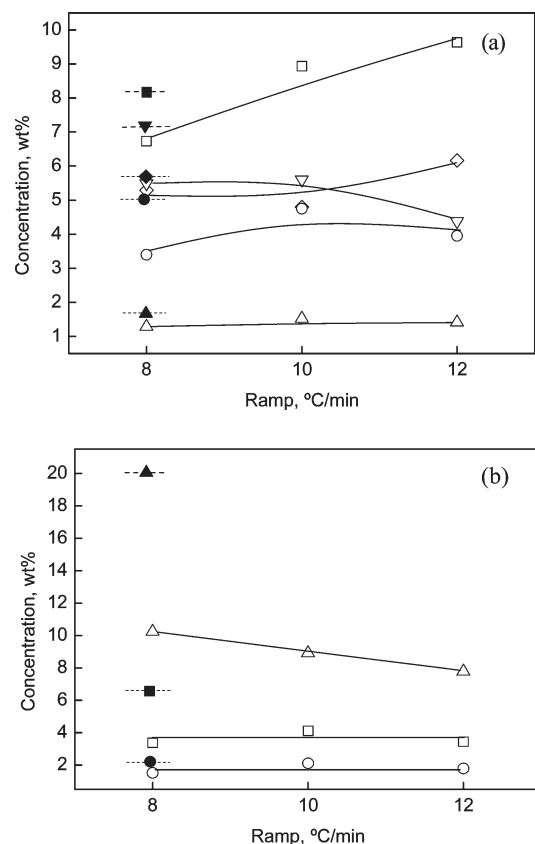
**Figure 4.** Concentration of the main groups in TL product and source bio-oil (550 °C) as a function of final temperature (heating ramp: 12 °C/min): (symbols) open, TL; closed, bio-oil. (a) ■, acids and esters; ◆, aldehydes and linear ketones; ▲, cyclic ketones; ▼, alcohols and sugars; ●, furans and other cyclic oxygenated. (b) ■, phenolic ethers; ●, alkylated phenols; ▲, heavy molecular weights (heavier than 130 g/mol).

5-hydroxymethylfurfural decreased more severely, between 45 and 70%. However, the effect on sugars such as levoglucosane and D-mannoheptulose and other cyclic oxygenated such as trimethoxybenzene and 4-ethoxy-3-anisaldehyde was much more significant, reductions in concentrations being up to 65 and 95%, respectively.

Hydrocarbons are not present in high concentrations in bio-oil; some of them, such as 2-hexene and 1-(1-methylethyl)-cyclopentene, decreased their concentrations in about 50% after thermal treatment.

The concentration of acids and esters, aldehydes, and linear ketones in TL product was slightly higher than in the source bio-oil when the thermal treatment was performed at the highest temperatures and fastest heating ramps. Among these groups, those compounds with low molecular weight, such as formic, acetic, and 3-hydroxybutanoic in the case of acids, methyl, and 2-propenyl acetate in the case of esters, and 2-pentanone and 2,3-pentadione in the case of linear ketones, increased their concentrations between 50 and 100%. On the other hand, the opposite effect was observed on heavy molecular weight compounds, such as 3-propylpentanedioic acid, ethyl tetradecanoate, and 2,6-dimethyl-2,5-heptadien-4-one, that decreased their concentration to about half that in the source bio-oil.

In all the conditions tested, overall, the content of phenols decreased about 30 to 50% from bio-oil to TL. These changes were more important on phenolic ethers, with changes of up to 90% in



**Figure 5.** Concentration of the main groups in TL product and source bio-oil as a function of the heating ramp (final temperature: 500 °C): (symbols) open, TL; closed, bio-oil. (a) ■, acid and esters; ◆, aldehydes and linear ketones; ▲, cyclic ketones; ▼, alcohols and sugars; ●, furans and other cyclic oxygenated. (b) ■, phenolic ethers; ●, alkylated phenols; ▲, heavy molecular weights (heavier than 130 g/mol).

those with high molecular weight, such as 4-vinylguaiacol, acetosyringone, 4-ethoxymethylguaiacol, and 3,4-dimethoxyacetophenone. Low molecular weight alkylated phenols (phenol, methylphenols) increased slightly in comparison to the source bio-oil.

Taken as a whole, a relative increase in some of the lighter compounds and a decrease in some of the heavier compounds in the conditioning of bio-oil can be seen. It must be considered that some low molecular weight products, such as acetone, formic acid, methanol, phenol, and methyl- and dimethylphenols, are the result of thermal cracking from heavier components in bio-oil, such as syringol and vanillin.<sup>34</sup> Moreover, heavier compounds in bio-oil tend to form pyrolytic lignin, thus being removed from the liquid phase.<sup>8</sup>

Unclassified heavy molecular weight compounds in bio-oil decreased their concentration dramatically after the thermal treatment (between 50 and 65%). Similarly to pyrolysis, the content of these compounds in TL increased with the final temperature, but decreased slightly as the heating ramp was faster.

## CHEMICAL COMPOSITION OF TAR

Tar is composed mainly by derivatives of lignin: monomeric, such as phenols, guaiacols, and chatecols, or dimeric, such as stilbenes, biphenyls, resinol, diphenylether, and phenylcoumaran. It also includes some compounds derived from degradation of polysaccharides.<sup>35,36</sup> The development of tar could be due to the

**Table 6. Composition of Tars (wt %): Tar-P (pyrolysis at 550 °C, 15 °C/min) and Tar-T (thermal conditioning at 500 °C, 12 °C/min)**

	Tar-P	Tar-T
acids	7.3	7.3
esters	5.4	5.5
linear aldehydes and ketones	7.3	12.7
cyclic ketones	4.8	5.0
furans	5.1	4.4
alcohols and sugars	5.0	8.4
phenols	25.8	29.3
alkylated phenols	6.3	10.9
phenolic ethers	19.6	16.4
ethers	0.2	0.1
other cyclic oxygenated compounds	2.6	2.5
hydrocarbons	0.9	0.9
nitrogen compounds	0.9	1.3
unknown <sup>a</sup>	34.8	22.8

<sup>a</sup> Individual peaks smaller than 0.5%.

partial cracking of lignin units during pyrolysis or even to the recombination of low molecular weight compounds in the gas phase.<sup>37</sup> In acidic media at high temperatures, phenolic compounds tend to polymerize together with aldehydes from cellulose and hemicellulose.<sup>27</sup>

Table 6 shows the composition of tars obtained in pine sawdust pyrolysis and in the thermal conditioning of the corresponding bio-oil. It can be seen that the compositions are similar, with the compounds being essentially the same as those in bio-oil distributed dissimilarly. Tars showed some compounds derived from carbohydrates, particularly aldehydes, ketones, acids, esters, and furans. The most important compounds were acetic and 3-hydroxybutanoic acids, acetic anhydride and methyl butanoate esters, 2-butenal, 2-pentanone, 2,3-pentadione, and 2-hydroxy-3-methylcyclopenten-2-one representing aldehydes and ketones, and furfural (furane). The amounts of aldehydes and linear ketones, and of alcohols and sugars in Tar-T, were two and three times those in Tar-P, respectively. In these same groups, the concentration of light compounds such as 1-hydroxy-2-propanone, 3-penten-2-one, 2,3-pentadione, methanol, and 2-butanol was between 2 and 4 times higher in Tar-T.

The concentration of phenolic compounds in Tar-P was three times higher than in bio-oil and five times higher in Tar-T than in TL product. The most important products were phenol, methylphenols, dimethylphenols, guaiacols, methylguaiacols, ethylguaiacols, isoegenol, and 4-hydroxy-3-methoxybenzoic acid.

In both tars, the content of high molecular weight compounds was high (about 53 wt % in Tar-P and 38 wt % in Tar-T). These concentrations represented three and five times, respectively, those of the pair liquids, bio-oil, and TL.

**Elemental Composition of Products from the Pyrolysis Process.** The elemental composition of the products obtained in the pyrolysis of pine sawdust is shown in Table 7. The typical high level of oxygen in the bio-oil is determined by the fact that about 65% of the oxygen in the sawdust concentrated in this product (43% taking part of water, the rest among the various oxygenated compounds). The content of oxygen in Tar-P was significantly lower, as also observed by, e.g., Oasmaa et al.<sup>35</sup>

Gases were composed by CO<sub>2</sub> (86.7 wt %), CO (1.2 wt %), hydrogen (6.5 wt %), oxygenated compounds (2.1 wt %), such as

**Table 7. Elemental Composition of Products from Pine Sawdust Pyrolysis (550 °C, 15 °C/min)**

	elemental composition (wt%)				HHV (MJ/kg)
	C	H	O	N	
bio-oil <sup>a</sup>	45.8	8.7	45.3	<0.1	10.0
Tar-P	59.2	7.2	33.5	<0.1	24.4
char	90.9	1.8	7.3	<0.2	32.0
gases	28.4	17.5	64.1		8.9

<sup>a</sup> Water-free basis.

**Table 8. Elemental Composition of Products from the Thermal Conditioning (500 °C, 12 °C/min) of Bio-oil**

	elemental composition (wt%)				HHV (MJ/kg)
	C	H	O	N	
treated liquid <sup>a</sup>	45.9	9.6	44.3	<0.1	8.1
Tar-T	58.5	6.9	34.5	<0.1	23.5
pyrolytic lignin	66.1	2.0	31.9		19.5
gases	32.7	13.9	53.4		21.4

<sup>a</sup> Water-free basis.

formic acid, methanol and acetaldehyde, and C1–C3 hydrocarbons (3.8 wt %). This observation is consistent with that by Yanik et al.<sup>38</sup> The HHV was similar to that of bio-oil, coincident with previous observations,<sup>39</sup> and even though it is relatively low, gases can be used to provide part of the energy needed in pyrolysis.

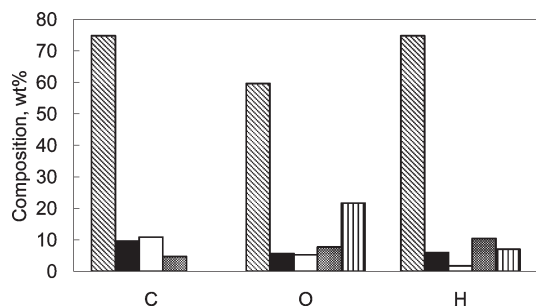
The higher heating values of liquid fractions correlate with the content of water: the more water, the lower the HHV (refer to Table 7).

The solid fraction product (char) contains typically between 70 and 95 wt % of carbon, between 5 and 20 wt % of oxygen, and between 1 and 4 wt % of hydrogen.<sup>25,38,40</sup> Its direct use as fuel is attractive since it has very low levels of nitrogen and sulfur, but it can also be upgraded to activated carbon or chemical products.<sup>40,41</sup> Char from pine sawdust has values that fall in the respective ranges. The loss of volatile compounds (water, light oxygenated, carbon oxides, hydrogen, hydrocarbons) during pyrolysis leads to an increment in the carbon content, and to a decrease in hydrogen and oxygen contents, in the char fraction. Moreover, these changes result in a high HHV value.

## ■ ELEMENTAL COMPOSITION OF PRODUCTS OF THERMAL TREATMENT

The elemental composition of the products obtained in the thermal conditioning of the bio-oil obtained at 550 °C (highest yield, minimum char) is shown in Table 8. The amount of oxygen in the liquid product TL was as high as in the source bio-oil, and its HHV somewhat lower, due to the higher amount of water.

Pyrolytic lignin usually contains between 23 and 26 wt % of oxygen, between 68 and 71 wt % of carbon, and about 4 wt % of hydrogen.<sup>5,8,19</sup> Values in Table 8 are coincident with these ranges. Since this product composition is similar to that of lignins obtained in the production of cellulosic pulps,<sup>42</sup> similar upgrading technologies could be used with this solid product, such as pyrolysis to extract phenols to be used in cosmetic products or in the production of phenol–formaldehyde resins.<sup>20</sup>



**Figure 6.** Elemental balance in the various products in the thermal conditioning (12 °C/min, 500 °C) of bio-oil obtained at 550 °C: (diagonal lines), treated liquid (organic fraction); (closed), Tar-T; (open), pyrolytic lignin; (checked), gases; (vertical lines), water.

**Table 9. Physicochemical Properties of the Bio-oil as a Function of Pyrolysis Temperature**

	temperature, °C			
	300	350	550	650
pH	3	3	3	2
density (kg/dm <sup>3</sup> )	1.10	1.17	1.07	1.10
CCR (wt %)	3.0	3.0	4.8	3.5
EHI	n.a.	n.a.	0.8	n.a.

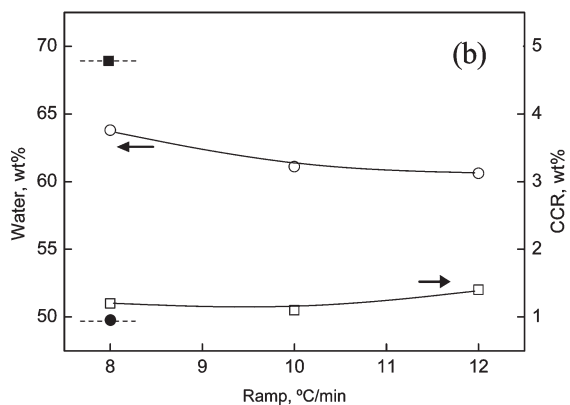
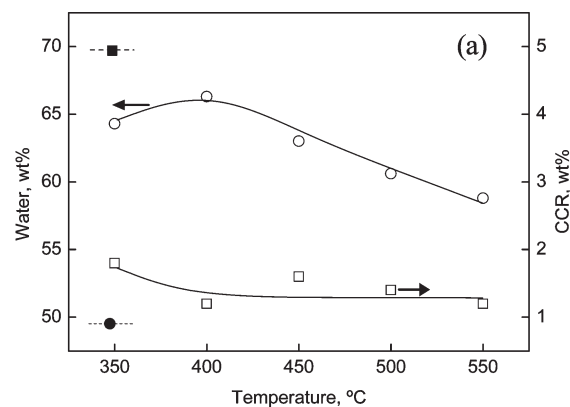
The pyrolytic lignin obtained after the thermal conditioning of bio-oil from pine sawdust is highly dehydrogenated and has a high content of oxygen, close to 30 wt %. It has to be mentioned that the samples of pyrolytic lignin were homogenized before analysis as they may show a different degree of polymerization.<sup>19</sup> The polymerization of cellulose- and hemicellulose-derived compounds in bio-oil (such as aldehydes, ketones, and acids), and of lignin-derived products (such as phenols, chatechols, guaiacols, and syringols) is strongly dependent on bio-oil composition and experimental conditions, mainly temperature.<sup>43,44</sup>

Same as pyrolytic lignin, the production of Tar-T could be due to the polymerization of low molecular weight compounds, mainly derived from lignin.<sup>27,37</sup> The concentration of oxygen in Tar-T was slightly higher than that in pyrolytic lignin, but hydrogen was present in much higher concentration (7 wt %).

Gaseous products in the thermal conditioning were mainly composed of CO (52.4 wt %) and CO<sub>2</sub> (31.5 wt %), hydrogen (13.6 wt %), oxygenated compounds such as acetic acid, acetone, 2-pentanone and butanoic acid (1.3 wt %), and light hydrocarbons (0.9 wt %). The HHV of these gases is much higher than that of obtained in pyrolysis, due to their lower content of oxygen.

### ■ BIO-OIL DEOXYGENATION DURING THERMAL CONDITIONING

The deoxygenation of bio-oil during the thermal conditioning process is conducted mainly through dehydration, decarbonylation to form CO, and decarboxylation to form CO<sub>2</sub>, accounting for more than 70% of the oxygen removed. Moreover, thermal cracking also occurs, leading to methane and other light hydrocarbons.<sup>8</sup> It is an important fact that decarbonylation and decarboxylation reactions do not impact on the content of hydrogen in bio-oil. The elemental balance among the various



**Figure 7.** Changes in CCR and water content in the thermal conditioning of bio-oil. (a) Effect of final temperature (heating ramp: 12 °C/min). (b) Effect of heating ramp (final temperature: 500 °C): (dotted lines) source bio-oil, (full line) TL product; (symbols) ■, CCR; ●, water content.

products of the thermal treatment shown in Figure 6 details how the carbon, oxygen, and hydrogen originally present in the bio-oil distribute. It can be seen that about 75% of the carbon and the hydrogen remain in the liquid phase (organic fraction). Concerning oxygen, about 40% is removed from the organic fraction in the liquid raw material, 22% taking part of water, 10% ends up in the pyrolytic lignin and tar, and only 8% is removed by decarbonylation and decarboxylation reactions.

### ■ PHYSICO-CHEMICALS PROPERTIES OF BIO-OILS AND TREATED LIQUIDS

The Conradson Carbon Residue index (CCR) is an indicator of coke-forming potential in hydrocarbon feedstocks in refineries, that could also be considered in the case of bio-oil. This a key factor in the analysis of the feasibility of coprocessing bio-oil together with conventional or resid feedstocks in FCC, because any factor altering coke yield may have a severe impact on the delicate heat balance of the process and, consequently, deserves serious consideration. For example, feedstocks with CCR higher than 2 wt % are considered resid; among other factors, they produce additional thermal loads in the regeneration section in comparison to standard VGOs that could affect negatively various issues.<sup>45</sup>

It can be seen in Table 9 (physicochemical properties as a function of pyrolysis temperature) that the bio-oil CCR

increased with the final temperature, a fact that is consistent with the increase in the concentration of phenols and heavy molecular weight oxygenated compounds.

The pH in bio-oils is low due to the high occurrence of acids, while density did not change very much and was close to reported values.<sup>46</sup>

Another important characteristic to be considered in coprocessing is the effective hydrogen index of the feedstock (EHI<sup>47</sup>), which could be a useful comparative parameter. In processes such as FCC, the higher the EHI, the more efficient the conversion. It should be noted that petroleum-derived conventional feedstocks range from slightly higher than 1 in the case of highly aromatic to close to 2 in the case of highly paraffinic feedstocks.<sup>48</sup> Heavy residual feedstocks such as atmospheric resid, coal oil, and shale oil, with high content of polar and aromatic compounds, have EHI values from 1.4 to 1.7.<sup>49</sup> It is in this sense that bio-oils can be considered as feedstock strongly deficient in hydrogen.

pH (close to 3) and density (between 1.07 and 1.09 g/mL) in TL product resulted in being similar to that of the source bio-oil. It is to be noted that another positive effect of the thermal conditioning process was that the EHI increased about 30%, leading to values in the range of commercial FCC feedstocks.

The changes in the amount of water and CCR in TL product as a function of final conditioning temperature and heating ramp are shown in Figure 7a and b, respectively, where they can be compared to those of the source bio-oil. It can be seen that the strong CCR decrease (maximum, about 70%) was more important at the highest temperatures; simultaneously, the content of water in TL was substantially higher than in bio-oil, but this change was less important at the highest temperatures and heating ramps. The CCR value in Tar-T is extremely high (9.73 wt %).

## CONCLUSIONS

It is possible to assist the coprocessing of bio-oils from residual lignocellulosic raw materials with conventional feedstocks in FCC by means of a previous thermal conditioning process, aimed at decreasing the coke-forming potential of the highly oxygenated pyrolysis liquids. The pyrolysis of pine sawdust was chosen as a case example, with bio-oil showing a typical composition that included acids, esters, aldehydes, ketones, furans, alcohols, sugars, phenols, and ethers among most important compounds, together with hydrocarbons and close to 50 wt % of water. The maximum bio-oil yield (43.7 wt %) was obtained at 550 °C.

The different conditions in the thermal treatment (final temperatures from 350 to 550 °C and heating ramps from 8 to 12 °C/min) all yielded 90 wt %, or more, of liquid products, and induced changes in the composition of the bio-oil. The overall yield of liquid to process after the two steps (pyrolysis at 550 °C and thermal conditioning at 500 °C) was 38.7 wt %. Important negative variations were observed among the oxygenated compounds believed to be coke precursors, such as phenols (between 30 and 50% decrease), particularly some phenolic ethers (up to 90% decrease) and high molecular weight compounds (between 50 and 65% decrease).

Changes in some physicochemical properties in the bio-oil induced by the thermal treatment resulted positive, such as the significant decrease in the CCR indicative of coke-forming potential, from 4.8 wt % to about 1.5 wt %, and the 30% increase in the effective hydrogen index, which is related to the efficiency in

catalytic cracking conversion. Most of the carbon and the hydrogen remained in the organic liquid fraction, while about 40% of the oxygen was removed. By-products in both pyrolysis and the thermal process (char, tar, gases, and pyrolytic lignin) could be used as fuels, even in the same process, or subjected to upgrading.

Although the impact of the addition of pyrolysis liquids to a typical VGO FCC feedstock for coprocessing will sensibly depend on the amount added, the water insoluble tar fractions, both in the pyrolysis and the thermal process, which showed much higher concentrations of phenols and high molecular weight compounds, as well as a much higher CCR index, do not represent a proper choice.

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