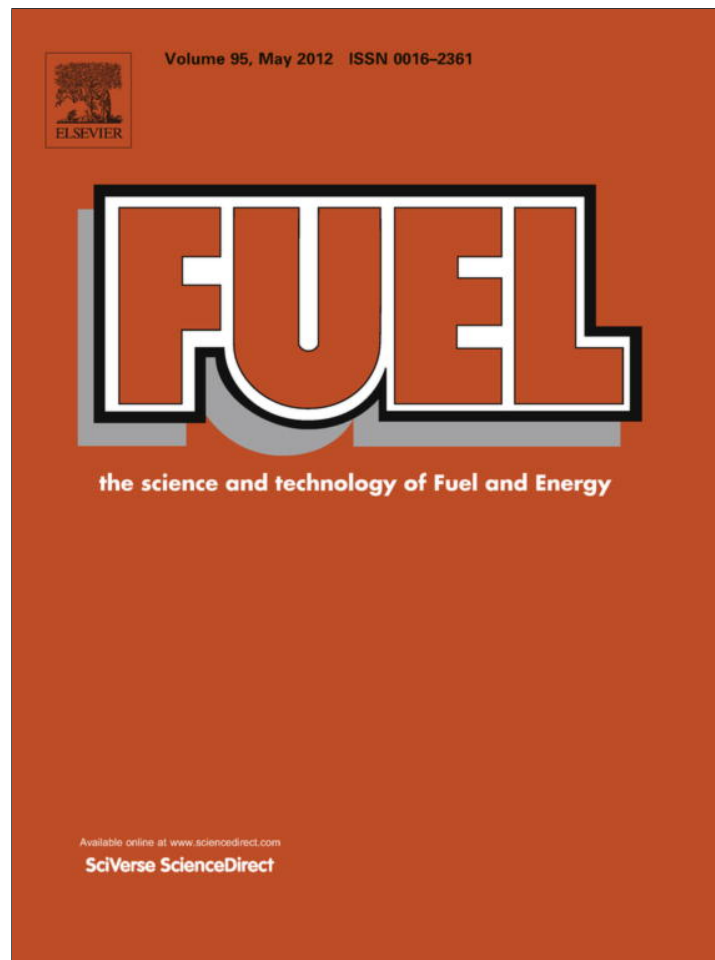


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Fuels from bio-oils: Bio-oil production from different residual sources, characterization and thermal conditioning

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ABSTRACT

Bio-oils from different residual biomass raw materials (pine wood, mesquite wood and wheat shell) were produced by means of conventional pyrolysis at a temperature of 550 °C during 60 min. Bio-oils were separated from gases, tar and char, to show yields between about 30 wt.% and 45 wt.%, and fractionated into water- and ether-soluble fractions in order to know their compositions. Gas chromatography–mass spectrometry was used to identify compounds and complemented with elemental analysis and Conradson carbon residue (CCR), together with water content, density and pH assessments. The composition of the bio-oils varied according to the source biomass. Compounds were considered in eleven main groups: acids, esters, linear aldehydes and ketones, cyclic ketones, furans, alcohols and sugars, phenols, other oxygenated cyclic compounds, hydrocarbons, ethers and nitrogen compounds. The physicochemical properties of bio-oils suggested that it is necessary to upgrade them before co-processing in conventional refining units such as those of catalytic cracking of hydrocarbons. Thermal pre-treatments were conducted with the aim of reducing the CCR of the bio-oils, resulting in a significant average 70% reduction. The concentration of coke precursor phenolic compounds, mainly phenolic ethers, was reduced between 7% and 25%. Another important consequence was the increase in the effective hydrogen index of the mixture, suggesting higher processability in FCC.

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1. Introduction

Fossil fuels are the main energy sources at present, but considering their natural limitation in availability and the fact that they are not renewable, there exists a growing need of developing new and renewable energy sources. Fuels can be obtained from the pyrolysis of lignocellulosic biomass from forest, crop and industrial wastes, a fact that is attractive mainly because of the low cost of the raw materials. Oils from biomass pyrolysis (bio-oils) are free flowing liquids, usually very dark brown in color, with a neat “smoke” smell, its composition being very different from that of petroleum derived fuels. Bio-oils are very complex mixtures of compounds derived from the depolymerization and fragmentation reactions of the main three components in biomass: cellulose, hemicellulose and lignin. It was reported that bio-oils contain approximately 35–40 wt.% of oxygen, 55–60 wt.% of carbon, an acidic pH, density close to 1.2 g cm⁻³ and 15–60 wt.%, or more, of water [1,2]. As a consequence, combustion properties are different from those of conventional fuels.

Upgrading bio-oils into transportation fuels requires the removal of oxygen. This has been attempted by means of hydrotreatment or cracking in the gas phase. Hydrotreating the bio-oils with catalysts

at high temperature and high hydrogen pressure, similarly to processes in petroleum refining, leads to the release of oxygen as water and to the hydrogenation and hydrocracking of heavy molecular weight compounds [3]. The resulting product could then be subjected to catalytic cracking over acidic catalysts such as zeolites [4,5]. However, one of the inconveniences of these processes is their high cost. On the other hand, cracking untreated bio-oils over acidic zeolites produces deoxygenation leading to a mixture of hydrocarbons with a high concentration of aromatics, following a reaction mechanism similar to that of the conversion of alcohols and other oxygenated compounds into hydrocarbons (MTG [6]). The deactivation of the catalysts produced by the high yield of coke could be solved by means of a continuous regeneration process, like in the catalytic cracking of hydrocarbons, FCC.

Among the various options for upgrading bio-oils, the co-processing with hydrocarbon feedstocks in a conventional refining scheme, where they can play the role of non-conventional feedstocks [7,8], deserves consideration. In that sense, two types of processes are potential receivers: the FCC and the thermal processes.

In the case of FCC, its versatility and operative flexibility are important advantages that support the process as a candidate for co-processing bio-oils. Moreover, the typical FCC catalyst (acidic Y zeolite on a matrix plus various additives) seems appropriate. This approach can be considered as opposite to direct biomass gasification into H₂ and CO, which can be later subjected to

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Fischer–Tropsch synthesis and converted into liquid fuels. It is assumed that biomass pyrolysis products contain molecular construction units proper to be processed in FCC and converted into products in the gasoline and diesel boiling ranges, and even into petrochemical raw materials in the range of LPG [7,9]. One of the key points to be studied is the high coke yield expected, that could affect catalyst performance and the delicate heat balance in FCC units. The main coke precursors in bio-oils are phenolic compounds [10,11] that could be selectively removed by means of, for example, conditioning thermal pre-treatments [11–16].

Sawdust is the main waste in forest industries, that is normally incinerated [17], while wheat shell is a low value by-product from cereal milling industry, which is incorporated into animal feedstocks. It is the objective of this work to determine the composition of bio-oils obtained by conventional pyrolysis of various residual lignocellulosic biomasses, such as pine and mesquite sawdust and wheat shell, and to study the effect of pre-conditioning thermal treatments over different physicochemical parameters that might impact negatively on the potential of co-processing bio-oils in refineries.

2. Experimental

2.1. Materials

Bio-oils were obtained from lignocellulosic residual biomass feedstocks: sawdust from pine (*Pinus elliottii*) and mesquite (*Prosopis juliflora*) trees, and wheat (*Triticum vulgare*) shell. Pine wood is soft, with long fibers, while mesquite wood is hard, with short fibers. Wheat shell represents about 14–19 wt.% of the whole grain, and it includes the shell, the aleurone layer and parts of the endosperm. The water content of the raw materials was assessed after drying at 100 °C in an oven during 18 h. The composition of the biomasses in terms of cellulose, hemicellulose and lignin was taken from average values in the literature [18–20]. The main properties of the different raw materials are shown in Table 1.

2.2. Bio-oil production and thermal treatment

Bio-oils were produced by conventional pyrolysis of the raw materials placed in a fixed bed in a 21 cm long and 1.9 cm diameter stainless steel reactor, heated in an electrical oven. A mass of 7–11 g of biomass was used in each experiment, performed with a heating ramp of 15 °C/min from room temperature to 550 °C; finally this temperature was maintained during 60 min. During

Table 1
Properties of the biomass raw materials.

Property (% dry basis)	Pine sawdust	Mesquite sawdust	Wheat shell
Moisture content	10.2	12.5	18.8
Ash	0.3 ^a	0.6 ^b	5.4 ^c
<i>Elemental composition</i>			
C	51.6	53.0	46.8
H	5.2	4.8	6.0
O ^d	43.2	41.6	43.8
N	–	0.6	3.4
<i>Lignocellulosic material composition</i>			
Cellulose	35 ^a	40–45 ^b	10–15 ^c
Hemicellulose	29 ^a	25–30 ^b	30 ^c
Lignin	28 ^a	11–28 ^b	4–8 ^c
Higher heating value (HHV, MJ/kg)	15.4	15.4	14.1

^a From Ref. [18].

^b From Ref. [19].

^c From Ref. [20].

^d Calculated by difference.

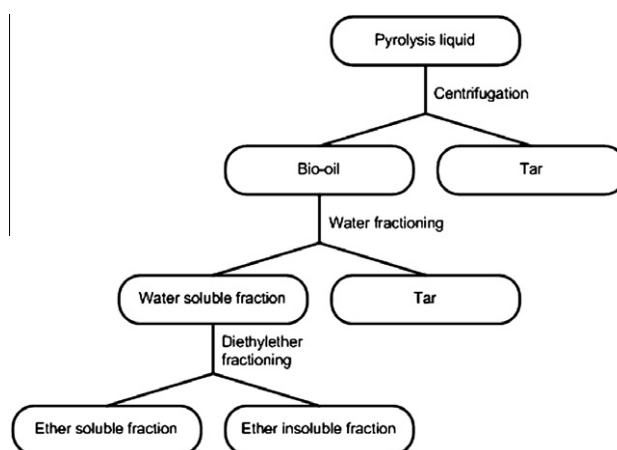


Fig. 1. Fractioning of bio-oil.

pyrolysis the reactor was swept with a flow of 20 ml/min of N₂ in order to remove vapors from the reaction zone and to minimize secondary reactions. The effluents from the reactor were sent to a water–ice condenser where liquids were separated and gases vented to the atmosphere; samples were taken from both portions. The masses of char and pyrolysis liquids were assessed by weighing the reactor and the condenser, respectively, before and after the experiments. The mass of gases was assessed by difference.

The pyrolysis liquids, which included two phases, were centrifuged at 3200 rpm during 8 min to separate bio-oil and a tar fraction. After that, the bio-oil was separated into fractions by means of the following specific procedure, based on that developed by Sipilä et al. [21], leading to four fractions according to their solubility in water and diethylether. One volume of bio-oil was mixed with ten volumes of water added drop by drop under constant stirring, and the mixture was then filtered to separate more tar and a water soluble (WS) fraction. This WS fraction was mixed with the same volume of diethylether, stirred vigorously, and after 5 min of settling the ether soluble (ES) and insoluble (EI) fractions were separated. The different steps are shown in Fig. 1.

The thermal treatments of the bio-oils were performed in a reactor heated in an electrical oven. The 5 cm long and 2.5 cm diameter glass reactor was swept with a flow of 5 ml/min of N₂ during the experiments. Liquid effluents were collected like in the pyrolysis experiments, gases were vented, and samples were taken from both portions. Three to five grams of bio-oil were used in each experiment. The heating ramp used was 12 °C/min from room temperature to 500 °C and this temperature was kept during 10 min. The liquid products from the thermal treatment, which included two phases, were centrifuged to yield a treated liquid and tar.

2.3. Product characterization

The various liquid fractions and the gases from biomass pyrolysis and from bio-oil thermal treatments were analyzed by conventional capillary gas chromatography in a Agilent 6890 N gas chromatograph equipped with a FID detector and a 30 m long, 0.25 mm internal diameter and 0.25 μm phase thickness non-polar HP1 column. Product identification was done with the help of standards and gas chromatography–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 than 0.5% of the total chromatographic area, and they were grouped into three groups of “unknown components”, according to their elution order.

The characterization of the bio-oil and the treated liquid was complemented with elemental microanalysis (Carlo Erba EA 1108), Conradson Carbon analysis (CCR, IRAM 6542), moisture content (Karl Fischer titration, IRAM 21320), density and pH measurements. The higher heating values of bio-oils, char and gaseous products were calculated with the DuLong formula [22]; in the case of bio-oils and the treated liquids, they were corrected considering the amount of water present.

3. Results and discussion

3.1. Biomass properties

As shown in Table 1, the compositions of the three raw materials differ considerably. The amounts of nitrogen, moisture and ash in the wheat shell are much higher than those in the sawdusts. The difference in nitrogen can be explained because the protein content in wheat shell is much higher than in sawdusts. On the contrary, the cellulose and lignin contents in wheat shell are significantly lower.

3.2. Product yields in the pyrolysis process

Product distribution in the pyrolysis depends on the reaction parameters such as temperature, heating rate and reactant particle size, as well as on the starting biomass. Different authors studied the impact of pyrolysis temperature on the yield of the liquid product [22–25], who reported that there exists a maximum in the yield of bio-oil at 450–550 °C; secondary reactions are more significant and decrease liquid yield at higher temperatures, while carbohydrate and lignin depolymerizations are incomplete at lower temperatures. A pyrolysis temperature of 550 °C, which resulted optimum for maximum bio-oil from pine sawdust, was used for all the biomasses.

Table 2 shows the product yields in biomass pyrolysis. Three main products were observed in all the cases: a solid product phase (char), a liquid product with two phases, and a gas product phase, with some differences in yields according to the starting biomass. As described previously, two fractions can be separated by centrifuging the liquid pyrolysis product: bio-oil and tar. Maximum bio-oil yield was obtained with pine sawdust (43.7 wt.%), and tar was similar in all the cases, in the range of 3–6 wt.%. Char production was important in all the cases, over 28 wt.%; gases were most important in the case of wheat shell (25.9 wt.%). It is to be noted that comparable product distributions were reported when using other different raw materials such as wood pine, fruit pulp and bagasse under similar conditions [22,23,25].

3.3. Compositions of bio-oils

Bio-oils are very complex mixtures of different chemical species derived from depolymerization and fragmentation of biomass main components, covering a wide range of molecular weights. Due to the large amount of oxygen in the various functional groups, bio-oils are thermally unstable and can not be fractionated by means of conventional techniques such as distillation. The water–ether separation technique leads to four fractions.

The compositions of the three bio-oils are shown in Table 3 grouped according to chemical types: acids, esters, linear aldehydes and ketones, cyclic ketones, furans, alcohols and sugars, phenols, other oxygenated cyclic compounds, hydrocarbons, ethers and nitrogen compounds. Phenols were divided into phenolic ethers and alkylated phenols, according to the substitution units. Some observations apply similarly to all the bio-oils. For example, it is possible to note a high proportion of oxygenated compounds,

Table 2
Yields of the main pyrolysis products (wt.%).

	Pine sawdust	Mesquite sawdust	Wheat shell
Pyrolysis liquid	50.3	38.7	38.0
Bio-oil	43.7	35.9	31.8
Tar	6.6	2.8	6.2
Char	28.9	36.6	36.1
Gases	20.8	24.7	25.9

the most important ones being acids, aldehydes, ketones and phenols, representing between 50 and 60 wt.% of the products. These groups were mainly composed by acetic, 2-hydroxy-butanoic and 4-methyl-pentanoic acids, linear chain and cyclic pentanones, guaiacols, cresols and catechols.

The composition of these complex mixtures can be associated to some extent to the composition of the starting biomass raw materials. The liquid phase obtained from cellulose and hemicellulose pyrolysis is mainly composed by aldehydes, ketones, furans, acids and esters, and smaller amounts of hydrocarbons, ethers and alcohols [26]. Phenolic compounds in bio-oil are originated during the pyrolysis of lignin, which is a complex aromatic structure composed by substituted phenyl propane units, linked by hydroxy and methoxy groups. Lignins from softwoods do not present large differences from various species, being composed mainly by guaiacyl units and smaller amounts of syringyl and p-hydroxyphenyl units. On the contrary, lignins from hardwoods have similar proportions of guaiacyl and syringyl units [27]. These facts can explain the higher concentrations of compounds like syringol in the bio-oil produced from mesquite sawdust as compared to those from pine sawdust and wheat shell. Moreover, lignins from hardwoods have a much higher amount of methoxy groups than those from softwoods and grass biomass [28], thus explaining the much higher concentration of phenolic ethers in bio-oil from mesquite sawdust. This is an important fact, because phenolic ethers yielded more coke than phenols when cracked as test reactants over acidic zeolites [11,29].

The high molecular weight oxygenated compounds present in bio-oils (arbitrarily defined as those with molecular weight over 130 g/mol) could also be precursors for coke, since they participate in polymerization reactions during their catalytic upgrading processing [13]. The content of these compounds was very high, over 40 wt.%, in mesquite and wheat shell bio-oils, and about 20 wt.% in the case of pine sawdust bio-oil.

Table 4 shows the compositions of the WS, ES and EI fractions from all the bio-oils: it can be seen that the same compounds were present in all the fractions, thus showing that a solubility equilibrium between fractions was established. However, the concentrations of each of the groups in each of the fractions were different according to the raw material. The WS fractions, that were light yellow in color in all the cases, represented more than 90 wt.% of bio-oil. The product distributions in these fractions were very similar to those in the corresponding bio-oils, the main groups being acids, aldehydes, ketones and phenols. Most important compounds were pentanones (2-pentanone, 2-hydroxy-3-methyl-cyclopentanone and 2,4-dimethyl-cyclopentanone) among ketones and 2-butenal among aldehydes, and guaiacol, methylguaiacol, cresol, dimethylphenol and methoxycatechol among phenols; the amount of acids in the WS fractions were higher than those in the bio-oils, particularly for lighter compounds in the group, such as formic, acetic and propanoic acids.

The ES fractions from bio-oils contain low-molecular weight compounds. Their compositions carry information about the raw materials and the degree of thermal degradation achieved [21]. The main groups of the ES fractions were furans, phenols, aldehydes and ketones. The most important furans were furfural,

Table 3
Chemical composition of the bio-oil.

Compounds (wt.%, dry basis)	Raw material		
	Pine sawdust	Mesquite sawdust	Wheat shell
Acids	18.71	16.99	18.91
Formic acid	0.95	1.07	1.86
Acetic acid	5.58	4.33	6.18
Propanoic acid	0.30	0.19	0.97
Isocrotonic acid	1.01	0.39	1.17
Propanoic acid, 2-methyl-	0.60	0.66	0.95
Butanoic acid	0.68	0.30	0.44
Pentanoic acid	0.96	1.27	2.22
Butanoic acid, 2-hydroxy-	2.62	2.04	1.26
Pentanoic acid, 4-methyl-	5.26	2.51	1.76
Pentanedioic acid, 3-propyl-	0.74	4.25	2.09
Esters	8.29	7.62	8.62
Methyl acetate	0.65	0.20	0.17
2-Propenyl acetate	0.99	0.55	0.53
Acetic anhydride	1.40	1.17	1.06
Vinyl acetate	0.74	2.34	1.64
Methyl butanoate	2.25	1.04	1.22
Vinyl butanoate	0.61	0.23	0.87
2-Propenyl butanoate	0.26	0.39	1.43
Allyl acetylacetate	0.89	1.45	1.11
Isobutyl isobutanoate	0.49	0.25	0.59
Linear aldehydes and ketones	17.52	9.12	7.34
Acetaldehyde	0.13	0.06	0.35
Acetone	1.69	0.82	0.47
2-Butenal	2.23	2.02	1.38
2-Butanone	1.03	0.37	0.15
2-Pentanone, 1-hydroxy-	1.35	0.52	0.78
3-Penten-2-one	0.86	0.70	0.19
2-Pentanone	2.17	1.48	1.14
2,3-Pentadione	4.80	0.15	0.14
2-Butanone, 4-hydroxy-3methyl-	1.07	0.97	0.80
2-Pentanone, 4-hydroxy-4-methyl-	0.15	0.05	0.16
4-Heptanone, 2-methyl-	0.10	0.06	0.34
Octanal	1.64	1.56	0.80
2-Butanone, 1-(acetyloxy)-	0.10	0.19	0.15
2,5-Heptadione, 2,6-dimethyl-	0.20	0.16	0.47
Cyclic ketones	6.11	5.77	6.06
Cyclopentenone	0.72	0.63	0.20
Cyclopentanone	1.03	0.87	1.25
Cyclopentenone, 2-methyl-	0.53	0.34	1.09
Cyclopentenone, 3-methyl-	0.43	0.60	0.17
Cyclopentanone, 2-methyl-	0.11	0.03	0.26
Cyclohexenone	0.21	0.11	0.14
Cyclohexanone	0.27	0.20	0.17
Cyclopentenone, 2,4-dimethyl-	0.69	0.87	0.11
Cyclopentenone, 3,4-dimethyl-	0.27	0.15	0.48
Cyclohexanone, 1-methyl-	0.21	0.10	0.12
1,2-Cyclopentanedione, 2-methyl-	0.04	0.31	0.11
Cyclopentenone, 2-hydroxy-3-methyl-	1.30	1.24	0.70
Cyclopentenone, 2-hydroxy-3-ethyl-	0.28	0.31	1.25
Furans	5.95	6.25	3.44
Furan, 3-methyl-	0.62	0.14	0.20
Furfural	2.76	3.43	0.72
2-Furanone, 2-methyl-	0.18	0.23	0.03
2-Furanmethanol	0.43	0.69	0.94
Furfural, 5-methyl-	0.89	0.56	0.24
Furfural, 5-(hydroxymethyl)-	0.14	0.15	0.40
2-Acetyl furan	0.25	0.83	0.74
γ -Heptylbutyrolactone	0.69	0.21	0.17
Alcohols and Sugars	9.81	8.06	6.04
Methanol	8.19	5.65	3.22
Ethanol	0.96	0.76	0.55
Levoglucosane	0.66	1.65	2.27
Lactose	0.35	0.43	0.89
Ethers	0.31	1.22	1.38
Propane, 1-ethoxy-2-methyl-	0.80	0.25	0.40

Table 3 (continued)

Compounds (wt.%, dry basis)	Raw material		
	Pine sawdust	Mesquite sawdust	Wheat shell
Butane, 1-ethoxy-	0.31	0.02	0.08
Pentane, 2-ethoxy-	0.40	0.18	0.25
Phenols	15.74	28.23	19.02
Alkylated phenols	5.41	7.26	7.69
Phenol	0.36	0.82	0.37
Cresol	2.48	1.67	1.03
2-Methylhydroquinone	0.06	0.25	0.45
Catechol, 4-ethyl-	0.17	0.53	0.82
Dimethylphenol	1.15	1.79	2.72
Ethylphenol	0.23	0.19	0.31
Trimethylphenol	0.41	0.95	0.98
1,3-Benzenediol, 4-ethyl-	0.24	0.36	0.32
2,5-Dimethylhydroquinone	0.19	0.29	0.18
2,6-Di-tert-butyl-p-cresol	0.09	0.14	0.20
2-Tert-butyl-4-methyl-6-(1-phenylethyl)phenol	0.01	0.12	0.09
2,2'-Methylenbis[6-tert-butyl-4-ethylphenol]	0.00	0.16	0.23
Phenolic ethers	10.33	20.97	11.33
Guaiacol	2.15	2.76	1.05
Cynamaldehyde	0.14	0.35	0.66
Methylguaiacol	2.80	5.57	1.95
Methoxycatechol	0.68	1.41	2.10
Guaiacol, 4-vinyl-	0.47	0.66	0.52
Ethylguaiacol	0.82	1.25	0.80
Vainillin	0.37	0.82	0.41
Acetophenone, 3,4-dihydroxy-	0.21	0.27	0.43
Syringol	0.22	2.26	0.53
Eugenol	0.22	0.35	0.22
Isoeugenol	0.56	0.47	0.27
Acetoguaiacone	0.32	0.89	0.22
Benzoic acid, 4-hydroxy-3-methoxy-	0.37	1.08	0.33
Guaiacylacetone	0.40	0.89	0.36
Acetophenone, 3,4-dimethoxy-	0.07	0.35	0.38
Guaiacol, 4-ethoxymethyl-	0.12	0.11	0.10
Syringol, 4-propenyl-	0.18	0.56	0.52
Acetosyringone	0.02	0.20	0.18
Homosyringic acid	0.22	0.73	0.30
Other oxygenated cyclic compounds	2.91	3.96	2.64
2,3-Dihydropyran	1.49	1.97	0.16
Propylene carbonate	0.95	0.47	0.82
Phenylacetone	0.18	0.24	0.68
1,2,4-Trimethoxybenzene	0.13	0.23	0.24
1,2,5-Trimethoxybenzene	0.05	0.80	0.34
3-Anysaldehyde, 4-ethoxy-	0.12	0.25	0.39
Hydrocarbons and derived	0.80	2.15	3.81
1,4-Pentadiene, 2-methyl-	0.15	0.06	0.42
2-Hexene	0.06	0.05	0.31
Cyclopentene, 1-(1-methylethyl)-	0.11	0.11	0.58
Cyclooctane	0.04	0.05	0.22
Decane	0.18	0.15	0.12
Trimethylnaphtalene	0.16	0.95	0.51
Methylfluorene	0.01	0.14	0.13
Fluorene	0.02	0.28	0.22
Tetramethylnaphtalene	0.03	0.29	0.37
Ditolylmethane	0.03	0.06	0.93
Nitrogen compounds	1.53	1.18	1.48
Aniline	0.14	0.19	0.05
2-Formylpyrrol	0.18	0.19	0.13
2-Pyrimidol	0.15	0.20	0.66
Sec-Butylnitrite	0.33	0.17	0.15
2-Acetylpyrrol	0.13	0.18	0.08
3-Pyrimidol, 2-methyl-	0.06	0.09	0.41
Dibutylformamide	0.53	0.15	0.00
Unknown	11.96	11.32	21.75
UK1	7.32	1.80	3.39
UK2	3.32	2.85	7.77
UK3	1.22	5.78	11.08

Table 4
Chemical composition of the ether soluble (ES), ether insoluble (EI) and water soluble (WS) fractions of the bio-oils.

Compounds (wt.%, dry basis)	Raw material		
	Pine sawdust	Mesquite sawdust	Wheat shell
<i>ES fraction</i>			
Acids	20.48	17.65	17.99
Esters	6.54	6.64	7.06
Linear aldehydes and ketones	11.13	7.69	8.82
Cyclic ketones	6.42	7.49	8.04
Furans	13.35	17.33	11.06
Alcohols and sugars	2.25	3.86	2.65
Ethers	0.22	0.10	0.26
Phenols	25.88	28.55	22.13
Other oxygenated cyclic compounds	1.40	2.20	1.49
Hydrocarbons and derived	0.90	0.83	1.89
Nitrogen compounds	1.20	0.79	0.81
Unknown	9.51	5.97	16.35
<i>EI fraction</i>			
Acids	36.66	46.72	46.42
Esters	5.46	7.01	8.39
Linear aldehydes and ketones	18.12	10.90	8.76
Cyclic ketones	3.31	4.11	2.71
Furans	3.14	4.56	2.58
Alcohols and sugars	8.56	9.43	8.47
Ethers	2.08	1.40	3.94
Phenols	13.40	10.19	13.18
Other oxygenated cyclic compounds	3.00	2.31	1.01
Hydrocarbons and derived	1.35	0.97	1.64
Nitrogen compounds	1.38	0.64	1.32
Unknown	4.97	2.85	4.68
<i>WS fraction</i>			
Acids	22.44	24.42	28.45
Esters	6.74	7.33	9.52
Linear aldehydes and ketones	14.58	10.74	8.94
Cyclic ketones	5.64	5.46	4.74
Furans	7.13	6.29	4.35
Alcohols and sugars	10.46	8.92	8.93
Ethers	1.76	1.88	4.33
Phenols	18.62	24.88	18.70
Other oxygenated cyclic compounds	2.38	3.34	2.05
Hydrocarbons and derived	1.15	1.60	2.42
Nitrogen compounds	1.37	0.95	1.87
Unknown	8.80	5.52	9.06

5-methyl-furfural and 2-furanmethanol, and the most important ketones were 2-hydroxy-3-methyl-cyclopentenone, cyclohexanone and 2,4-dimethyl-cyclopentenone. The ES fraction from the wheat shell bio-oil showed much higher amounts of alkylated phenols; for example, phenol, one of the most important compounds, was about 50% more concentrated than in pine and mesquite sawdust analogous fractions. In contrast, the concentrations of most important phenolic ethers (guaiacol, methylguaiacol, ethylguaiacol and methoxycatechol) were from two to three times higher in pine and mesquite bio-oil ES fractions than in the case of wheat shell.

ES fractions from pine and mesquite bio-oil have similar proportions for all the groups, although furans and phenols are somewhat more concentrated in the case of mesquite, and acids and linear aldehydes and ketones are somewhat more concentrated in the case of pine. Acetic acid is present in similar concentrations in all the ES fractions, being the main compound in the acid group, followed by 4-methyl-pentanoic acid and 3-hydroxy-butanoic acid.

The EI fractions contain mainly products from the defragmentation of polysaccharides in the biomass and show a much higher content of acids, linear aldehydes and ketones and alcohols and sugars than the ES fractions. The main compounds observed were

formic and acetic acids, 2-pentanone, 2-butenal, methanol, levo-glucosane and lactose.

The water insoluble fraction, also named tar, is viscous and denser than the WS fraction. Tar production could be due to the partial cracking of lignin units during pyrolysis, or even to the recombination of low molecular weight compounds in the gas phase [30]. In acidic media at high temperatures, phenolic compounds tend to polymerize together with aldehydes from cellulose and hemicellulose [8]. Tars from the various biomass showed a concentration of phenols which was much higher than that in bio-oils, together with small amounts of acids, esters, alcohols, aldehydes and ketones (results not shown).

3.4. Physicochemical properties of bio-oils

Table 5 shows the physicochemical properties of the bio-oils. Water in the bio-oils comes from dehydration reactions during pyrolysis. The water contents of bio-oils from woods were in the range of reported values (e.g. about 50% from softwoods and 57% from hardwoods [26,31]). On the other hand, wheat shell bio-oil had a very high content of water.

The possible direct use of bio-oil as a fuel must consider the higher heating value (HHV), which is reduced by water; however, water also reduces viscosity and helps in atomization and combustion [32]. The concentration of water was the largest in wheat shell bio-oil. It can be seen that the HHVs were different for each bio-oil; in general terms, they are similar to those of the raw materials and about 45% lower than those of conventional fossil fuels (fuel oil, 40 MJ/kg [26]). This is mainly due to the high water and oxygen concentrations in bio-oil. Other bio-oils have HHVs in the range of 15–22 MJ/kg (apricot and peach pulp, 28 wt.% water [22]), 13.9 MJ/kg (soybean cake, 40 wt.% water [24]), 13–16 MJ/kg (pine, poplar and birch sawdust, 18 wt.% water [33]).

The elemental compositions of the bio-oils were calculated on a water free basis [34]. The large amount of oxygen, which is typical of bio-oils, can be seen in the cases of pine and mesquite woods; the wheat shell bio-oil showed significantly lower amounts of oxygen, but higher amounts of carbon. The much higher amount of nitrogen in this bio-oil as compared to those from woods is due to the proteins in the raw material.

The pH was low in the case of wood bio-oils, due to the elevated amount of acids (average 18 wt.%). The high content of water in the bio-oil from wheat shell, with a similar content of acids, may explain the higher pH.

All the bio-oils showed similar densities, which were typical [35].

If co-processing of bio-oils is intended in refineries, the effective hydrogen index (EHI, [36]) can be a useful comparative parameter. The higher the EHI in the feedstock, the more efficient the FCC conversion [36,37]. The index, which is defined by Eq. (1), denotes the neat H/C of a feedstock containing heteroatoms,

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

where H, C, O, N and S are the molar percentages of the corresponding elements on dry basis.

The values of EHI were lower than 1 for pine and mesquite bio-oil, but considerably higher than 1 for wheat shell bio-oil. These EHI values can be compared to those of petroleum-derived feeds, which range from slightly over 1 for highly aromatic residues to 2 for highly paraffinic feeds [38]; heavy oils such as atmospheric resid, coal oil and shale oil, with high content of polar and aromatic compounds, have EHI values between 1.4 and 1.7 [39]. In this respect, bio-oil can be viewed as a hydrogen-deficient molecule as compared with petroleum-based feedstocks [37].

Table 5
Physicochemical properties of the bio-oil.

	Pine sawdust	Mesquite sawdust	Wheat shell
pH	3	3	6
Density (kg/dm ³)	1.07	1.07	1.06
Water (wt.%)	49.60	67.60	84.40
Conradson carbon residue (CCR, wt.%)	4.80	2.80	0.84
Higher heating value (HHV, MJ/kg)	10.03	7.72	6.02
Elemental composition (wt.%, dry basis)			
C	45.8	59.4	69.9
H	8.7	5.8	9.7
N	<0.2	<0.3	11.5
O ^a	45.3	34.5	8.8
H/C (M)	2.28	1.49	1.90
O/C (M)	0.74	0.45	0.07
Effective hydrogen index (EHI, M)	0.79	0.59	1.30

^a Calculated by difference.

Table 6
Product yields in the thermal treatment of bio-oils (wt.%).

	Pine sawdust	Mesquite sawdust	Wheat shell
Liquid	84.5	86.7	88.5
Treated liquid	83.5	86.1	88.4
Tar	1.0	0.6	0.1
Pyrolytic lignin	7.0	3.5	2.7
Gases	8.5	9.8	8.8

The Conradson carbon residue (CCR) is an indicator of the coke forming potential of the bio-oil. Pine bio-oil showed the highest value (4.8 wt.%) among the cases studied and wheat shell bio-oil the lowest (0.84 wt.%). This is an important issue, because this is a key factor in the delicate heat balance in FCC units. Feedstocks with CCR higher than 2 are considered as residual in FCC processing. In those cases, the higher content of contaminant metals and the higher coke yields, among other issues, make it necessary to use special technologies and catalysts [40].

3.5. Product yields in the thermal treatments

As previously discussed, the high coke forming potential of bio-oils could be reduced if they are subjected to a thermal treatment previous to co-processing [11–16].

Table 6 shows the product yields in the thermal treatment of bio-oil from the different raw materials. In all the cases, and similarly to pyrolysis, solid (pyrolytic lignin retained on the reactor walls), liquid (two phases) and gaseous products were obtained. The yields of liquids, that were composed by the treated liquid and a tar phase, were over 85 wt.% in all the cases, and gases represented approximately 9 wt.%. The yields of treated liquids and the water contents were different according to the source biomass.

Some products undergo thermal cracking, leading to CO₂ and hydrocarbons such as methane and ethane. Most of the light compounds (e.g., formic acid, acetic acid, methanol, 2-furanmethanol, 2-butanone, cyclopentenone, furfural, 2-pentanone, phenol, methylphenol and dimethylphenol) were concentrated in the treated liquid, with recoveries higher than 80%; some of them were also observed in the gas and tar phases.

Most of the high molecular weight compounds probably condense during the thermal treatment to yield tar and pyrolytic lignin. It was observed particularly that some phenolic compounds (e.g., eugenol, isoeugenol, vainillin, 4-ethoxymethylguaiaicol, 2,5-dimethylhydroquinone, guaiacylacetone, 3,4-dihydroxyacetophenone and 2,2'-methylenebis[6-tert-butyl-4-ethylphenol]), and some carbohydrates derivatives (e.g. 5-(hydroxymethyl)-furfural,

2,6-dimethyl-2,5-heptadien-4-one and lactose) were only recovered in the 20–50% range, thus showing a specific trend to form tar and/or pyrolytic lignin.

3.6. Compositions of the treated liquids

The changes in the amounts of the main groups in the treated liquids as compared to the starting bio-oils, are shown in Table 7. It can be seen that variations were similar from the qualitative point of view, with magnitudes that depended on the parent bio-oil. In general terms, the concentration of the group of furans increased slightly, while those of acids increased substantially and the other groups showed less important changes. However, in the group of acids and esters some compounds increased their concentrations over 50%, such as 2-furanmethanol and 5-(hydroxymethyl)-furfural. Considering linear aldehydes and ketones, the most important compounds in the group in each of the bio-oils showed significant rises in their concentrations (for example, 2,3-pentadione, 2-pentanone and 2-butenal).

The concentrations of phenols were affected by the thermal treatment in the expected direction; that is, reductions from 7% in pine bio-oil to 25% in mesquite bio-oil were observed. Low molecular weight phenols in the group, such as phenol and methylphenols, increased slightly, and high molecular weight phenols, such as syringol, 4-propenylsyringol and isoeugenol, decreased significantly. The content of phenols was essentially constant in wheat shell bio-oil. Since these phenolic compounds are considered coke precursors [10,11], this is an important and positive change in pyrolysis liquids to ease their co-processing.

Heavy molecular weight compounds decreased their amounts between 10% and 15% in all the cases. Unknown products were grouped according to their range of molecular weights into three categories. The lighter group (UK1, about approximately less than 130 g/mol) increased its concentration in all the cases, from about 5% to about 40%. On the contrary, the group UK2, with intermediate molecular weights, kept its concentration stable in the cases of mesquite bio-oil and significantly decreased in pine and wheat shell bio-oils. The group UK3 (heaviest compounds, above 160 g/mol) in mesquite bio-oil showed a clear reduction in its concentration after the thermal treatment (27%).

3.7. Physicochemical properties of the treated liquids

The physicochemical properties of the treated liquids, which are reported in Table 8, can be compared with those of the corresponding bio-oils (see Table 5 for comparisons). Most importantly, a significant decrease (average 70%) in the CCR values can be observed

Table 7

Chemical composition of treated liquid and bio-oil.

Compounds (wt.%, dry basis)	Bio-oil			Treated liquid		
	Pine sawdust	Mesquite sawdust	Wheat shell	Pine sawdust	Mesquite sawdust	Wheat shell
Acids	18.71	16.99	18.91	22.60	22.07	26.31
Esters	8.29	7.62	8.62	5.80	6.36	6.43
Linear aldehydes and ketones	17.52	9.12	7.34	17.46	10.50	7.38
Cyclic ketones	6.11	5.77	6.06	4.44	4.82	4.62
Furans	5.95	6.25	3.44	6.98	7.15	4.89
Alcohols and sugars	9.81	8.06	6.04	8.86	6.40	5.12
Ethers	0.80	1.22	1.38	0.72	0.39	0.28
Phenols	15.74	28.23	19.02	14.69	21.58	19.13
Other oxygenated cyclic compounds	2.91	3.96	2.64	3.02	3.51	2.75
Hydrocarbons and derived	0.80	2.15	2.42	0.64	1.92	2.67
Nitrogen compounds	1.53	1.18	1.48	1.27	1.37	0.86
Unknown	11.96	11.32	21.75	13.83	13.72	19.11
UK1	7.32	1.80	3.39	8.51	5.74	4.75
UK2	3.32	2.85	7.77	3.80	3.67	4.90
UK3	1.22	5.78	11.08	1.21	4.52	9.92

Table 8

Physicochemical properties of the treated liquid.

	Pine sawdust	Mesquite sawdust	Wheat shell
pH	3	3	5
Density (kg/dm ³)	1.08	1.17	1.12
Water (wt.%)	60.60	69.60	90.10
Conradson carbon residue (CCR, wt.%)	1.50	0.91	0.20
Higher heating value (HHV, MJ/kg)	8.41	7.64	4.28
Elemental composition (wt.%, dry basis)			
C	45.9	53.6	63.9
H	9.6	9.4	16.0
N	<0.2	<0.3	11.1
O	44.3	36.6	9.2
H/C (M)	2.50	2.15	3.03
O/C (M)	0.72	0.51	0.11
Effective hydrogen index (EHI, M)	1.04	0.72	2.36

Table 9Main products in the gas streams from biomass pyrolysis and bio-oil thermal treatments (CO and CO₂ excluded).

Compounds (wt.%, dry basis)	Pyrolysis			Thermal treatment		
	Pine sawdust	Mesquite sawdust	Wheat shell	Pine sawdust	Mesquite sawdust	Wheat shell
Acids and esters	22.4	21.6	22.3	8.5	25.9	21.1
Formic acid	0.4	0.1	1.2	0.2	0.8	2.0
Acetic acid	14.2	16.3	11.7	7.8	13.9	11.3
Acetic anhydride	0.4	0.9	1.8	0.2	0.9	1.0
Pentanoic acid		1.8	2.1		4.6	4.5
Butanoic acid, 3-hydroxy-	0.7	1.4	0.4	0.3	2.4	0.8
Propanoic acid			1.8			1.5
Methyl butanoate	2.2	0.9	3.3		2.9	
2-propenyl acetate	4.5	0.2			0.4	
Aldehydes and ketones	6.2	3.2	4.7	3.4	10.7	12.7
Acetone	3.3	1.2	2.1	1.5	4.4	7.8
2-Butanone	0.6	0.7	0.2	0.5	0.8	2.1
2-Butanone, 4-hydroxy-3-methyl-	0.3	0.1	0.8	0.2	0.3	
2-Pentanone	1.2	0.7	0.6	1.0	3.6	1.1
3-Penten-2-one	0.4	0.2	0.4	0.1	0.6	0.7
2,3-Pentadione	0.1	0.1	0.2	0.1	0.2	0.6
Cyclopentanone		0.1	0.3		0.7	0.3
2-Butenal	0.3	0.1	0.1		0.1	0.1
Alcohols	8.9	5.9	5.7	29.3	19.5	19.1
Methanol	5.9	4.1	4.1	20.1	13.5	12.6
Ethanol	3.0	1.8	1.6	9.2	6.0	6.5
Ethers	1.0	0.4	0.8	0.5	0.9	1.2
Propane, 1-ethoxy-2-methyl-	0.1	0.1	0.6	0.1	0.2	0.3
Butane, 1-ethoxy-	0.9	0.1	0.1	0.4	0.1	
Pentane, 2-ethoxy		0.2	0.1		0.6	0.9
Hydrocarbons	61.5	68.9	66.5	58.3	43.0	45.9
Methane	48.8	58.9	53.7	45.8	34.8	37.6
Ethane	10.2	5.0	8.6	7.9	4.0	4.9
Propane	1.5	3.1	1.3	1.8	2.0	1.5
Butane	1.0	1.9	2.9	2.8	2.2	1.9

in reference to the starting bio-oil. It can also be seen that the water content increases, as the consequence of the selective loss of volatile products during the thermal treatment; however, this issue could be controlled by changing operative approach and conditions. The higher heating values of the treated liquids show smaller values than those of the corresponding bio-oils, particularly in the case of the wheat shell bio-oil. Most importantly, the EHI increased after the thermal treatment in all the cases, between 30% and 80% as compared to the starting bio-oil, reaching values similar to those in commercial FCC feedstocks.

3.8. Gas products in pyrolysis and thermal treatments

The flow of gas products during the pyrolysis was maximum for the three raw materials in the 250–350 °C range. A second peak in gas flows was observed at approximately 450 °C for the pine and wheat shell biomasses, and at approximately 550 °C for mesquite sawdust. These maxima could correspond to the pyrolysis of carbohydrates and lignin, respectively [26]. The main gaseous products observed, other than carbon oxides, and their concentrations, are shown in Table 9. Hydrocarbons represent about 65 wt.% of the reactor gas effluents (CO and CO₂ excluded), methane being the most important compound in all the cases. The other important groups were acids, esters and alcohols. Carbon oxides are the most important gas products in the pyrolysis of lignocellulosic materials, representing about 80–90% [41]; for example, it has been reported that pyrolysis gases from pine sawdust contained 86.7 wt.% of CO₂, 1.2 wt.% of CO and 6.5 wt.% of H₂ [42].

A similar distribution was observed in the gas products from the thermal treatments of bio-oils (refer to Table 9). It is to be noted that the composition of the gases in the thermal treatments depended more importantly on the raw material. Gases in a thermal treatment process of pine bio-oil contained 52.4 wt.% of CO, 31.5 wt.% of CO₂ and 13.6 wt.% of hydrogen [42].

4. Conclusions

Bio-oil yields from the conventional pyrolysis of mesquite and pine sawdust and wheat shell ranged from about 30 wt.% to about 45 wt.% and showed different compositions. Main compounds could be grouped into acids, esters, linear aldehydes and ketones, cyclic ketones, furans, alcohols and sugars, phenols, other oxygenated cyclic compounds, hydrocarbons, ethers and nitrogen compounds. The physicochemical properties of bio-oils (heating value reduced by high water content, large amount of oxygenated compounds, moderate effective hydrogen index, high Conradson carbon residue indicating high coke forming potential) all suggest that it is necessary to upgrade them before co-processing in conventional refining units such as those of the catalytic cracking of hydrocarbons.

Thermal pre-treatments aimed at reducing the CCR of the bio-oils produced significant positive changes of about average 70% reduction. It was particularly observed that the concentration of phenolic compounds (mainly phenolic ethers), which are considered coke precursors, was reduced between 7% and 25%. The water content in bio-oils after the treatments increased, but it could be controlled up to certain level according to the process. Another important consequence was that the effective hydrogen index of the mixture increased, showing higher processability in FCC.

Bio-oils from pine wood resulted the most convenient for FCC co-processing, because their yields were higher, their content of heavy molecular weight compounds was about half that of the other bio-oils, and the thermal pre-treatment induced important positive changes in CCR and EHI.

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