



Characterization of the liquid products in the pyrolysis of residual chañar and palm fruit biomasses



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HIGHLIGHTS

- Bio-oils and tars from residual chañar and white palm fruits were characterized.
- The bio-oils had high concentration of phenolic eters and heavy oxygenated compounds.
- Chañar fruit bio-oil had more phenols and aromatic hydrocarbons.
- Palm fruit (pericarp and waste seeds) bio-oil had more acids and nitrogen compounds.
- These biomasses are a good source for energy and chemical raw materials.

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ABSTRACT

The endocarp in the chañar (*Geoffroea decorticans*) fruit, the pericarp in the white palm (*Copernicia alba Morong*) fruit and the exhausted white palm seeds from the extraction of oil are all residual lignocellulosic biomasses from the food processing of these fruits. The pyrolysis was performed at 550 °C in a fixed bed reactor during 30 min under N₂ flow with a 15 °C/min heating ramp from room temperature. In all the cases a liquid product (bio-oil and tar) with yields from 35 to 50 wt.%, a gas product and a solid product (char), were produced. The tar represented from 5 to 20 wt.% of the liquid product. The highest bio-oil yield (47 wt.%) was obtained with the chañar fruit endocarp and the highest tar yield (8.8 wt.%) was obtained with the white palm seeds. The bio-oils contained mainly acids (from 6 to 18 wt.%), aldehydes and ketones (from 2 to 10 wt.%) and phenols (from 4 to 13 wt.%), with a high water content (from 44 to 81 wt.%). Their pH was acidic and the densities ranged from 0.97 to 1.24 kg/dm³. The tars had mainly phenols and oxygenated compounds of high molecular weight. After these results, these residual biomasses can be considered as a potential source for energy or fuels and valuable chemical products.

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1. Introduction

The lignocellulosic biomass represents a sustainable choice for the production of fuels and raw materials for the chemical process industry. Its renewable character, low cost and essentially nil balance in terms of carbon dioxide emissions are among the most important advantages from its utilization. In this sense, the growing interest in the production of liquid biofuels could be satisfied through pyrolysis and further upgrading or co-processing of the bio-oils [1].

The pyrolysis of biomass is produced by the thermal degradation of the raw material at high temperature in the absence of oxygen, yielding between 30 and 70 wt.% of a liquid product composed by a large number of compounds, mostly oxygenated, which can be

easily separated into two fractions according to their water solubility [1]. The water insoluble fraction (tar) is viscous, and denser than the water soluble, organic fraction, usually named bio-oil.

Among possible uses, the bio-oils are potential fuels for diesel engines [2], gas turbines and boilers [1] and raw materials to obtain hydrocarbons in the gasoline boiling range by catalytic transformation [3,4] or hydrotreating [5]. They could also be raw materials for the production of resins [6] and cooking and pharmaceutical products [1]. Some chemicals with high demand, such as methanol, acetic acid, acetone and particularly phenols, could be obtained from bio-oils by means of, for example, liquid–liquid extraction [7] or vacuum distillation [8]. Some of these uses could be hindered by certain properties of the bio-oils, such as high acidity, high water content, or store instability, but thermal [9,10] or physical or chemical [2,11] upgradings could improve them.

The use of lignocellulosic residual raw materials from various food industries such as production of vegetable oils (olive [12],

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soybean [13], palm [14]), and fruit shells and grains (peanut [14], pistacho [15], rice [17]), among others, has been extensively studied. The results, which were strongly dependent on the raw materials and the process conditions, showed that liquid yields were from 30 to 50 wt.%, with a high oxygen (between 25 and 40 wt.%) and water (between 20 and 50 wt.%) content.

The white palm (*Copernicia alba Morong*) and the chañar (*Geoffroea decorticans*) are very abundant, native trees in northern Argentina and limiting countries. Their fruits have nutritional characteristics that make them potentially proper for human and animal nutrition [18–21]; however, they are not used extensively in daily foods. If these fruits are used for producing foods, lignocellulosic residua such as the endocarp of the chañar fruit, the pericarp of the white palm fruit and the exhausted white palm seeds in oil extraction occur, which could be subjected to pyrolysis processes to produce bio-oils.

It is the objective of this study to report the characterization of the products from the pyrolysis of these residual lignocellulosic materials in order to define their potential as renewable energy sources and raw materials for the chemical industry. Product yields, composition of the liquid products (bio-oils and tars) and the most relevant physicochemical properties were assessed and compared.

2. Experimental

2.1. Materials and characterization

The raw materials used were the endocarp from the chañar fruit (*Geoffroea decorticans*), named CHA, the pericarp from the white palm fruit (*Copernicia alba Morong*), named PAL, and the resid from the extraction of oil from white palm seeds, named ResPAL. CHA, which represented 40 wt.% of the fresh fruits, was obtained by crushing them in a blade mill followed by separation of the seeds in a disc mill. The dried white palm fruits were crushed in a disc mill and the PAL, which represented 51 wt.% of the fresh fruits, was separated from the seeds using a vibrating sieve. The seeds were then pressed in a screw press in order to obtain the oil and the resid from this process, having a yield of approximately 20 wt.%, was the ResPAL [21].

All the raw materials were finally crushed to particles with sizes from 2.4 to 4.8 mm and dried at 100 °C during 6 h. The contents of water, proteins and ashes were assessed by standard AOAC methods (methods 934.01, 984.13 and 9923.03, respectively) [22], and the content of lipids by PET-CO1 method [23]. The mass of lignocellulosic material was determined by difference considering lipids, ashes and proteins [24]. The amount of fibers (mainly lignin) was determined following the procedure by Osborne and Voogt [25].

2.2. Pyrolysis

The bio-oils were obtained from the pyrolysis of a fixed bed of raw material located in a stainless steel reactor of 21.0 cm length and 1.9 cm internal diameter. The masses of biomass varied from 10 to 15 g. The heating ramp was 15 °C/min, from room temperature to the final temperature of 550 °C, which was kept constant during 30 min. A constant flow of 20 ml/min of nitrogen was circulated through the bed during the experiments in order to remove gases from the reaction zone and minimize secondary condensation and carbonization reactions.

The reactor effluents were passed through an ice-water condenser where the liquids were condensed and the gases were sent to the atmosphere after sampling with a Tedlar gas sampling bag.

The masses of solid product in the reactor (char) and condensed liquid product were determined by weighing the reactor and the

condenser, respectively, before and after the experiments. The mass of gases was determined by difference from the overall mass balance.

The liquid product was centrifuged at 3200 rpm during 8 min to separate an aqueous fraction, named bio-oil, and a tar fraction.

2.3. Product characterization

All the liquid and gas fractions were analyzed by conventional capillary gas chromatography in a Agilent 6890N gas chromatograph with a flame ionization detector and a HP-1 column, 30 m long, 0.25 mm internal diameter and 0.25 µm active phase thickness. The tar fractions were dissolved at 10 wt.% in methanol to perform this analysis. The gaseous products were also analyzed with a GS-CARBONPLOT column, 30 m long, 0.53 mm internal diameter and 3 µm active phase thickness and a thermal conductivity detector.

The identification of products was performed by means of gas chromatography–mass spectrometry (GC/MS) and the help of standards. The calibration of the chromatographic areas was done using response factors for each of the chemical groups present, which were previously determined by using mixtures of standards and a reference compound (tetralin for the liquids and methane for the gases) with various concentrations. The unidentified chromatographic peaks, having areas which represented less of 0.5% of the total area, were assigned an average response factor.

The characterization of the liquid products was complemented with elemental microanalysis in a Carlo Erba EA 1108 equipment. In the case of the bio-oils, also density, pH and water content (Karl-Fischer technique, IRAM 21320) were assessed. The heating values of the liquid and gas products, corrected according to the water content, were calculated with the DuLong formula [26].

3. Results and discussion

3.1. Characterization of the raw materials

The properties of the various biomasses are shown in Table 1, where it can be seen that they differ considerably. The amount of lignocellulosic material is high in all the cases (between 83 and 97 wt.%), but CHA has much more lignin than the biomasses derived from white palm fruit, which show higher carbohydrate contents. Moreover, these materials have more proteins than CHA and consequently more nitrogen. The highest lipid content is observed in ResPAL.

The content of oxygen is relatively high in all the cases, thus determining heat powers (higher heating value, HHV) which are not too high. Other lignocellulosic biomasses, such as wood

Table 1

Composition of the raw material biomasses (wt.%, dry basis) and higher heating value (HHV, MJ/kg).

	CHA	PAL	ResPAL
Water	3.9	4.7	6.4
Lipids	0.0	1.9	5.2
Proteins	2.3	8.6	6.6
Ashes	0.4	6.7	4.7
Lignocellulosic material	97.2	82.8	83.5
Lignin	48.7	24.3	10.8
Celullose + hemicelulose	48.5	58.5	72.7
<i>Elemental composition</i>			
C	46.4	46.5	43.3
H	6.5	6.0	6.9
O	46.7	43.9	48.5
N	0.4	3.6	1.3
HHV	16.7	16.5	15.9

sawdusts, pericarps from various fruits and bagasse from sugar cane, have HHV which range from 15 to 19 MJ/kg [26,27].

3.2. Product yields in the pyrolysis

The yields of the various products in the pyrolysis processes mainly depend on the raw material and the reaction temperature. According to reports from other authors and own results, there exists a maximum in the bio-oil yield which is located at about 550 °C [23,28,29]. On the other hand, the heating rate, in the range from 5 to 80 °C/min, has not a significant effect on the product distributions [26].

Table 2 shows the various yields obtained with the different biomass raw materials. In all the cases, three types of products are obtained: solid (which remains in the reactor, named char), liquid and gaseous. Two liquid fractions were obtained by centrifugation: one is soluble in water (bio-oil) and the other is insoluble (tar).

The highest bio-oil yield was obtained with CHA (47 wt.%), and the highest tar yield with ResPAL (8.8 wt.%). The biomasses from white palm fruit yielded more char than CHA, and the yield of gases was from 20 to 26 wt.% in all the cases. Other authors reported similar values for the three product streams in the conventional pyrolysis of various raw materials, such as wood sawdusts, fruit pulps, crop residua and fruit shells [7,12,13,16,17,26].

3.3. Composition of the bio-oils

The bio-oils are aqueous mixtures made up of a large number of compounds representing various chemical species derived from the complex conversion network of the three main components in biomass: cellulose, hemicellulose and lignin [1]. Table 3 shows the composition of the bio-oils obtained from the three biomasses, grouped according to chemical types. Phenols were classified into alkylated phenols and phenolic ethers. Unidentified products were arbitrarily separated into three groups according to their molecular weight, which was estimated from the chromatographic elution order. It was possible to identify 111 compounds, most of them oxygenated, their molecular weights ranging from 32 to more than 350 g/mol. Full details of the composition of bio-oils can be found in Supplementary Data.

Some observations were common to all the bio-oils; for example, that the main chemical groups were acids, aldehydes, ketones, alcohols and phenols. The most important products in each of the groups were light carboxylic acids with up to five carbon atoms per molecule (acids), linear and cyclic pentanones (aldehydes and ketones), methanol (alcohols), and guaiacols, cresols and catechols (phenols).

Acetic acid, which derives mainly from the deacetylation of hemicellulose [30], was the main compound in the group of acids. The bio-oils derived from the white palm fruit showed from two to three times more acetic acid than that coming from the chañar fruit, as expected due to the higher content of carbohydrates in white palm fruit biomass (see Table 1). Bio-oils typically contain high amounts of acetic acid; for example, between 15 and 59 wt.% in the cases of various wood sawdusts and fruit shells

Table 2
Yields (wt.%) in the pyrolysis of the various biomasses at 550 °C and heating ramp 15 °C/min.

	CHA	PAL	ResPAL
Liquids	49.4	34.9	43.7
Bio-oil	47.0	31.8	34.9
Tar	2.4	3.1	8.8
Char	29.2	38.5	36.0
Gases	21.4	26.6	20.4

[31,32]. Acetic acid could be recovered from bio-oils by means of liquid–liquid extraction with aliphatic tertiary amines [33].

In the rest of the groups, significant differences could be observed according to the biomass raw material: bio-oils from white palm fruit have more nitrogenated compounds than the bio-oil from chañar fruit, in consistency with the higher content of proteins in those biomasses (see Table 1). Moreover, the main ketones in the bio-oils from PAL and ResPAL were acetone and 3-penten-2-one, while in the bio-oil from CHA they were 2-pentanone and 2,3-pentadione.

The yield of aromatic hydrocarbons such as trimethylnaphthalene, fluorene and fluorene was from three to six times higher in the bio-oil from CHA than in those from palm fruit, possibly due to the higher lignin content, which is an aromatic biopolymer. The aromatic hydrocarbons are the products from the thermal transformation of phenols and from Diels–Alder type reactions between phenolic compounds and products from the degradation of polysaccharides [34,35].

Heavy products in bio-oils, in this case defined arbitrarily without chemical discrimination as those with molecular weight over 130 g/mol, are considered as coke precursors during the catalytic conversion over acidic zeolites [36]. Their concentration was much higher in the bio-oil from CHA (31.6 wt.%), as compared with the cases from PAL (13.5 wt.%) and from ResPAL (20.9 wt.%). Other bio-oils from wood sawdust showed contents between 20 and 40 wt.% [10].

3.3.1. Phenolic compounds in the bio-oil

The lignin portion in biomass is made up of substituted phenyl propane units, linked by means of hydroxyl and methoxy groups, the proportions of the most important monomers (guaiacyl, syringyl and p-hydroxyphenyl units) changing widely between the different biomass types [37]. The pyrolysis of lignin involves depolymerization, homolysis and cracking reactions [35] and generates mainly phenolic compounds together with minor amounts of methanol, acetic acid and hydrocarbons [30,38].

One of the main characteristics of bio-oils is the important concentration of phenolic compounds, from 8 to 22 wt.% [39], a fact which can hinder some potential applications. For example, the use as a raw material to be transformed into transportation fuels over acidic zeolites could be impeded by this high content of phenols (particularly phenolic ethers), which are precursors of coke leading to catalyst deactivation [3,4]. On the contrary, this property (particularly concerning the high concentrations of some phenolic ethers such as vainillin, guaiacol and syringol) favors the use of bio-oils as raw materials to separate some phenolic compounds which are intermediary in the synthesis of pharmaceutical and polymeric compounds, or aimed at producing adhesives [1,6,8]. Guaiacol and its alkylated homologous compounds are usually the most important phenolic ethers present in bio-oils, which are thermally unstable and can be transformed through secondary reactions in the pyrolysis, producing alkylated phenols and aromatic hydrocarbons [35,40].

The content of phenols in bio-oil from CHA (23 wt.%) was much higher than those in bio-oils derived from palm fruits, due to the higher content of lignin (refer to Table 1). Particularly, phenolic ethers were present at two times the concentration in the other bio-oils. In all the cases the main phenolic ethers were guaiacol, methylguaiacol and methoxycatechol, representing between 40% and 70% of the group, in consistency with previous observations on bio-oils derived from various wood sawdusts and wheat shell [10]. In the bio-oil from CHA, syringol, acetoguacone and guaiacetylacetone were also important.

Cresol and dimethylphenol, which are products from the deep cracking of the lignin and from secondary reactions of the primary products such as guaiacols [41], were the most important alkylated

Table 3
Composition of bio-oils and tars from the various raw materials (wt.%, dry basis).

	CHA		PAL		ResPAL	
	Bio-oil	Tar	Bio-oil	Tar	Bio-oil	Tar
Acids	17.1	6.6	51.4	5.8	33.6	11.0
Esters	6.6	8.0	4.7	11.6	6.2	4.4
Linear aldehydes and ketones	10.8	7.2	5.8	2.8	9.2	2.5
Cyclic ketones	3.5	5.1	2.8	9.8	5.6	5.8
Furans	8.1	7.6	5.3	6.7	9.8	5.9
Alcohols and sugars	8.3	–	10.6	–	3.6	–
Ethers	0.6	–	0.5	–	0.3	0.3
Other oxygenated cyclic compounds	4.2	6.4	1.3	6.9	2.9	1.7
Phenols	22.7	39.8	11.4	38.9	17.4	33.7
Alkylated phenols	5.3	5.1	2.8	12.6	8.1	10.8
Phenolic ethers	17.7	34.7	8.7	26.3	9.4	22.9
Hydrocarbons	5.0	4.7	0.8	2.6	1.4	16.6
Nitrogen compounds	0.3	0.9	1.6	2.3	2.2	1.0
Unknown	12.5	13.7	4.5	12.6	8.0	17.1

phenols in all the cases, representing from 50% to 70% of the phenols. The highest proportion of alkylated phenols was observed in the bio-oil from ResPAL (8.1 wt.%).

3.4. Chemical composition of tars

Tar is the water-insoluble fraction from the liquid product in the pyrolysis of lignocellulosic biomass, which is viscous and denser than the bio-oil. It is mainly composed by derivatives from lignin; monomeric compounds such as phenols, guaiacols and catechols, or dimeric compounds such as stilbenes, biphenyl, resinol, diphenyl ether and phenylcumarane; compounds derived from the degradation of polysaccharides, such as aldehydes and ketones are also present [42,43]. The thermal conversion of low molecular weight compounds (for example, polymerization of phenols and aldehydes) could also contribute to products in tar [35,44].

Table 3 shows the compositions of tars obtained in the pyrolysis of the various biomasses, grouped according to the chemical types; they can be compared with the corresponding bio-oils to observe that the most important compounds were essentially the same in both cases, distributions being significantly different. The tars included some compounds from the degradation of carbohydrates, mainly acids, esters, ketones and furans. Most important acids were acetic, isocrotonic, 4-methylpentanoic and 3-propylethanedioc, most important esters were vinyl and 2-propenyl acetates, most important ketones were dimethylcyclopentanone and 2-hydroxy-3-methylcyclopentenone, and most important furans were furfural, 5-methylfurfural and 3-methylfuran.

Similarly to bio-oils, important differences could be observed according to the raw material. For example, the tar from CHA contains about three times more aldehydes and linear ketones than tars derived from palm fruits. Moreover, the content of the most important compounds, such as 1-hydroxy-2-propanone and 2,6-dimethyl-2,5-heptadien-4-one, was particularly higher. The tar from PAL showed the highest content of esters, particularly allyl acetylacetate and 2-propenylbutanoate, and of nitrogen-containing compounds, in consistency with the higher protein content in this raw material. The tar from ResPAL showed two times the concentration of acids than the other tars, and a small amount of other cyclic oxygenated compounds.

The amount of phenolic compounds in the tars was 75% higher than in the bio-oil in the case of CHA and two to three times higher in the cases of white palm fruit raw materials. The concentration of phenolic ethers in the group was particularly high in the case of CHA tar (87%) and relatively lower in tars derived from white palm fruit (about 68%). In all the cases the most important compounds

were phenol, cresol, guaiacol and its alkylated homologous compounds, isoeugenol and syringol.

The content of compounds with molecular weights over 130 g/mol in the tars was very high (about 50% in the cases of CHA and PAL and 70% in the case of ResPAL), that is, much higher than in the corresponding bio-oils (see Section 3.3.1). This is consistent with previous observations by Scholze et al. [44] on bio-oils and tars from various wood sawdusts.

It is to be noted that the tar obtained from ResPAL showed a small amount of compounds which are not soluble in methanol (the solvent used to perform the chromatographic analysis), which could include polymeric species with elevated molecular weights [8]. This characteristic was observed by other authors in the tar from exhausted oil palm fruit bunches [14]. This tar from ResPAL showed a higher content of aromatic hydrocarbons (mainly methylfluorene, dityolymethane and tetramethylnaphthalene) than the other tars. 95% of the aromatic hydrocarbons produced during the pyrolysis of ResPAL were concentrated in the tar, while this proportion was only between 30% and 35% in the other cases.

Due to the high concentration of phenols, pyrolytic tars are potential raw materials in the chemical process industry to produce adhesives or as phenol substituting agent in phenol-formaldehyde resins [6]. A mixture of phenolic compounds could be recovered from tars by means of liquid-liquid extraction or vacuum distillation [7].

3.5. Physicochemical properties of bio-oils and tars

The storage and direct utilization of the liquid products from the pyrolysis is difficult due to their nature, which is acidic, strongly reactive and unstable. Moreover, bio-oils contain large amounts of water. The elemental composition and higher heating value of bio-oils and tars derived from the various raw materials are shown in Table 4, where the contents of water and the densities of the bio-oils are also included. These properties show values similar to those in bio-oils from various biomasses, as reported in the literature; for example, the concentration of water in bio-oil was 63 wt.% for pine sawdust [4], 40 wt.% for soybean cake [13], and 84 wt.% for wheat shell [10]. Water in bio-oil reduces its heating value but improves fluidity in reducing its viscosity, thus helping in atomization and combustion if used directly as a fuel [11].

The pHs of the bio-oils were 3 in all the cases. The low pHs, which is one of the characteristics of the bio-oils, are consistent with the high concentration of acids [39]. This acidity, which makes bio-oils corrosive, particularly at high temperatures, is one of the reasons conditioning their direct use as fuels [11].

Density is an important property in relation to transportation; all the bio-oils showed values in the typical range from 0.9 to 1.3 kg/dm³ [39].

The elemental compositions of bio-oils show approximately between 35% and 40% of oxygen and 55% and 60% of carbon [1].

Table 4
Composition (wt.%, dry basis), physicochemical properties and higher heating value (HHV, MJ/kg) of bio-oils and tars from the various raw materials.

	CHA		PAL		ResPAL	
	Bio-oil	Tar	Bio-oil	Tar	Bio-oil	Tar
Water (wt.%)	44.3		62.4		81.5	
Density (kg/dm ³)	1.24		0.97		1.02	
<i>Elemental composition</i>						
C	56.7	35.5	42.3	37.5	59.5	59.2
H	7.1	7.8	8.2	9.0	5.6	8.2
O	35.9	56.6	48.5	53.3	32.2	31.9
N	0.2	<0.1	1.1	0.2	2.7	0.7
HHV	23.0	13.1	17.3	16.1	22.5	26.0

Bio-oil from PAL showed the highest oxygen content (48.5%), while those from CHA y ResPAL had concentrations close to 35%, and the opposite was observed in relation to carbon, which was higher in bio-oils from CHA and ResPAL, close to 60%. The high content of nitrogen in bio-oils from white palm fruit is due to the important concentration of proteins in that raw material biomass.

The heating value of bio-oils is decreased as a consequence of the high oxygen and water contents; they typically range from 15 to 22 MJ/kg [39], which represents about 50% of the value corresponding to fuel oil (40 MJ/kg [45]). Various bio-oils showed similar values; for example, 13.9 MJ/kg (bio-oil de residual biomass from soybean oil extraction, with 40 wt.% of water [13]), and between 13 and 16 MJ/kg (bio-oil from pine and poplar, with 18 wt.% of water [46]). The highest higher heating value value in this work, 23 MJ/kg, corresponded to bio-oil from CHA.

Tars from CHA and PAL showed less carbon and more oxygen than the respective bio-oils, thus determining lower HHVs. In all the cases the amount of nitrogen in tars was much lower than in the bio-oils. According to previous reports [39,43], the tars from the pyrolysis of wood sawdusts typically contain between 65% and 70% of C, 5% and 7% of H and 23% and 30% of O.

3.6. Composition of the pyrolysis gases

The flow of gaseous products during the pyrolysis was the highest for all the raw materials in the 250–350 °C range. A second peak in the gas flow was observed at approximately 500 °C. These maxima could correspond to the decomposition of the carbohydrate and lignin portions of the biomasses, respectively [45].

The compositions of the gas streams are shown in Table 5. The main compounds were carbon dioxide (between 70 and 73 wt.%), hydrogen (between 4 and 19 wt.%), hydrocarbons with up to 5 carbon atoms per molecule (between 6 and 15 wt.%) and oxygenated compounds such as methanol, acetone, formic acid, acetic acid and methyl acetate (between 2 and 5 wt.%). Most important hydrocarbons were methane, ethylene and propylene. When using palm fruit biomasses, the yield of hydrogen was up to five times higher and the yield of hydrocarbons was up to three times lower than those from CHA. These results are consistent with reports from other authors for various biomasses such as pine sawdust [27,47], corncob and oregano stalks [48].

Typically, the heating value of pyrolysis gases is relatively low and they are used as fluidizing agents in the reactors and as fuels to provide part of the energy needed to carry out the pyrolysis [47].

3.7. Pyrolysis process

Decarboxylation reactions yielding CO₂, decarbonylation reactions yielding CO and dehydration reactions occur during the pyrolysis of biomass, which contribute to remove oxygen from the solid

Table 5
Composition (wt.%) and higher heating value (MJ/kg) of the pyrolysis gases.

	CHA	PAL	ResPAL
Carbon dioxide	72.7	70.1	72.2
Carbon monoxide	3.7	0.1	1.1
Hydrogen	4.0	19.0	13.0
Hydrocarbons	14.7	5.6	8.6
C1–C2	10.9	4.1	6.7
C3–C4	3.0	0.8	1.5
C5	0.8	0.2	0.4
Oxygenated compounds	2.3	5.7	5.0
Unidentified	2.6	0.3	0.9
HHV	13.1	28.2	22.1

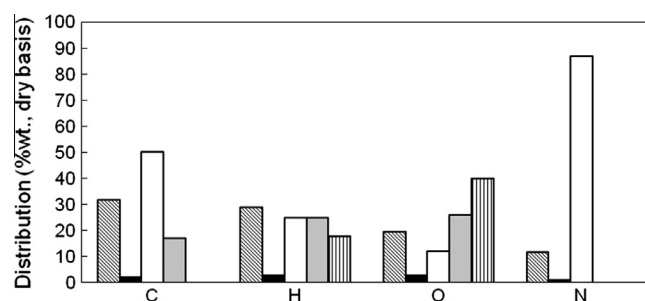


Fig. 1. Elemental balance in the products of the pyrolysis of CHA. Symbols: ▨, bio-oil (organic fraction); ■, tar; □, char; ▒, gases; ▤, water.

raw material. As a consequence, approximately 70% of the oxygen present in all the biomasses studied was removed by these routes.

Fig. 1 shows the overall elemental balance in the pyrolysis products for the example of CHA. It can be seen that 60% of the oxygen and 47% of the hydrogen in the biomass ended in the bio-oil taking part of both water and the oxygenated products. In relation to carbon, 50% of the source carbon concentrated in char. In the cases of white palm fruit derived products, the observations were similar, with approximately 55% of the oxygen and 30% of the hydrogen in the biomass concentrating in the bio-oil, mainly as water, and about 70% of the carbon appearing in the char. Similar results were reported for the pyrolysis of pine sawdust [29].

4. Conclusions

The pyrolysis of residual lignocellulosic biomass derived from unexploited plants, such as chañar fruit endocarp and white palm pericarp and exhausted seeds, produced liquid fractions with yields from 34.9 to 49.4 wt.%, gas fractions with yields from 20.4 to 26.6 wt.% and solid fractions with yields from 29.2 to 38.5 wt.%. Each liquid product was composed of an aqueous phase (bio-oil) with, mainly, acids, aldehydes, ketones and phenols covering up to 73 wt.% of the fraction, and an alquitranous phase (tar), mainly composed by phenols (up to 40 wt.%) and oxygenated compounds with high molecular weight.

The highest bio-oil yield (47 wt.%) was obtained with the chañar fruit endocarp and the highest tar yield (8.8 wt.%) was obtained with the white palm exhausted seeds. Significant differences were observed in the composition of the bio-oil according to the raw material: the endocarp of the chañar fruit induced a higher content of phenols (23 wt.%) and of aromatic hydrocarbons due to its higher lignin content, while the white palm fruit pericarp and exhausted seeds lead to more acids (33.6 y 51.4 wt.%, respectively, particularly acetic) and nitrogen containing compounds due to their high carbohydrate and protein content. The lowest concentration of water in bio-oils was observed in the case of chañar endocarp (44 wt.%).

After these results, these residual biomasses can be considered as potential sources for energy or fuels and valuable chemical products. The full utilization of white palm and chañar fruits could be performed commercially by using edible portions for the production of human food such as oils and jams, as well as cattle feedstock, and resids submitted to this pyrolysis – bio-oil approach.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.fuel.2013.08.027>.

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