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Developing alternatives to hydrocarbon via pyrolysis and gasification of industry residual biomass

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Abstract: Pyrolysis and gasification are thermal treatment processes using biomass to produce biofuels that can replace fossil fuels in industrial boilers and furnaces. This paper discusses the potential utilization of four types of residual biomass highly produced in the Argentina Northeast (NEA) region, i.e., rice husk, an agricultural waste rich in cotton husk, carob sawdust, and spent red quebracho sawdust, as raw material. Pyrolysis liquid product yields were 34–51 wt% and char yields were 29–40 wt%; tar represented 16–23 wt%. For gasification, gas yields were between 45.6 wt% and 65.7 wt%; as for tar, it represented 2.4–14.1 wt% of initial biomass, and char yields were 31.4–40.3 wt%. Characterization of all products was performed to clarify their potential applications. Bio-oils, i.e., aqueous fractions of pyrolysis liquid products, have high water content (77–88 wt%), that is why they have lower density and viscosity than tars, oil fractions of pyrolysis liquids. However, chemical stability of bio-oils may vary, and their heating values are much lower than the heating values from tars. Based on these, it is possible to concluded that tar is the product with increased added value and higher energy properties. Efficiency of gasification and heating values of the gases obtained were high for waste rich in cotton husk and spent red quebracho sawdust, suggesting a good potential for the utilization in gasification processes. Additionally, char composition and properties for all biomasses, from both process, show that it is feasible to use them in several new applications.

Keywords: lignocellulosic residues; pyrolysis; bio-oil; tar

1. Introduction

The depletion of fossil fuels and negative environmental impact caused by the utilization of these fuels foster the development and usage of renewable energies. Biomass (non-fossilized and biodegradable organic material originating from plants, algae and animals) is one of the most promising sources due to its carbon-neutral balance, high availability, abundance, sustainability and versatility being the only source capable of replacing liquid fossil fuels. However, biomass has a lower heating value than carbon, and it is difficult to transport as solid material, so it is necessary to convert it to higher energy-density fuels.

Especially, from a technological and socio-economic point of view, lignocellulosic residues are an outstanding raw material to obtain chemical and fuel products. In addition, industries facing environmental problems related to the treatment and disposal of wastes require sustainable and eco-friendly technological

solutions. On this point, in recent years, many types of agro-industrial, forestry and urban waste, as well as herbaceous plants and regional invasive shrubs from different parts of the world have been object of several studies for these purposes[1–8].

Some research on waste originating from large-scale industries should be carried out to identify the feasibility of its utilization as an energy source to be used in fuel and raw material production for the chemical industry. For example, rice husk, which is the main by-product in the rice industry, representing 22 wt% of rice production, and today the utilization of this waste has no significant value[9,10]; in Argentina, the annual production of rice residual biomass is 600,000 t[11]. Cotton residue is the main waste from harvesting and industrialization of such fiber. In Argentina, this activity is mainly centered in the Chaco region and the production in the 2018–2019 period was 876,000 t[12]. Red quebracho and carob wood is used for tannin production (one of the most used native extracts in the world). The two most important timber companies in Argentina produce more than 850 t per day of spent red quebracho sawdust as waste[13,14]. Besides, carob timber is widely used for manufacturing furniture, flooring and roofing; in 2008, the production of carob sawdust as waste from the furniture sector was more than 1500 t[15].

Thermochemical treatments such as pyrolysis and gasification for the conversion of residual biomass into biofuels are seen as interesting waste recovery alternatives[2–6]. During pyrolysis, biomass is converted into liquids, solids and gases in an inert atmosphere or with very low oxygen content. Yields of each fraction are dependent on the process variables, as well as the distribution of products within each phase. There are three types of pyrolysis: slow, conventional and fast; the most studied is the conventional pyrolysis (characterized by 5–30 min residence time and heating rates of 20–100 °C min^{-1})[2,3,7].

This research studies the utilization of residual lignocellulosic biomass from large-scale

industrial processes in Argentina for energy generation and chemical production as an alternative to hydrocarbon to support the development of greener products allowing for the utilization of waste material which currently has no relevant applications.

The main goal is contributing to adding value to production chains producing this waste. For this purpose, research has been carried out on production and characterization of appropriate liquid (bio-oil) and solid (char) products which can then be used in different applications using both pyrolytic processes of such wastes and gasification of "producer gas" to feed internal combustion engines for electric power generators. The main goal is to contribute to the creation of added value in production chains generating these types of waste. Therefore, research has been carried out on production and characterization of bio-oil and char using pyrolytic processes of such wastes which should be appropriate for later using them in different applications. Research has also been carried out on gasification of those wastes for obtaining "producer gas" which can be used to feed internal combustion engines and maintain electric power generator. The characterization of the products obtained included the chemical composition and their physical-chemical and combustion properties to identify potential applications.

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2. Materials and methods

2.1. Raw material for biomass

For thermochemical processes, the raw material used included rice husk (Oryza sativa) (RH), cotton straw (Gossypium) (CS), detanninized carob sawdust (Prosopis nigra) (DCS) and detanninized red quebracho sawdust (Schinopsis balansae and Schinopsis lorentzii)

(DQS).

Raw material was provided by regional companies, and its conditioning was performed by drying the material at room temperature until it reached a humidity less than constant 10 wt%. Then, grinding and separation took place to get 0.142 and 0.841 mm particles. Conditioned material was stored in an enclosed container and kept in a controlled environment until its utilization.

DQS had a relative humidity higher than 50 wt% due to the treatment that it undergoes for tannin extraction. Carob sawdust was from sawmills in the city of Machagai, Chaco Argentina. The relative humidity content of carob sawdust was 17–22 wt%. Carob sawdust was laboratory-washed using deionized water at 100 °C under continuous stirring for 2 min, then using a 100 µm sieve it was separated from liquid, and dried at room temperature for 48 h, to represent the waste from the tannin industries. CS and RH were provided by a cotton-gin company and a rice mill, respectively, with less than 10 wt% of moisture content. CS is a mixture of cotton fiber and husk, so it underwent mechanical separation until residues rich in cotton husk (CS-A) and in cotton fiber (CS-B) were obtained. In this paper, CS-A was studied, while CS-B was kept for other uses and recovery treatments.

2.2. Biomass characterization

Biomass was characterized in terms of their water, volatile matter and ash contents, according to ASTM D3173, D3175 and D3174, respectively. The amount of fixed carbon was determined by difference. The elemental compositions of the biomass were determined in a CHN628 Series Elemental Determinator (LECO) equipment. The higher heating values (HHV) were determined following Dulong's formula[16].

Carbohydrate (cellulose and hemicellulose) and lignin contents were determined according to NREL/TP-510-42618 and NREL/TP-510-42618 standards, respectively[5–7]. For carbohydrates, biomass hydrolysis was carried out in two stages: the first stage consisted of a treatment with 72 %w/w sulfuric acid at 30 °C for 1 h, and the second stage, consisted of 4% dilution of the acidic solution from the first stage, and 1 h autoclave sterilization at 121 °C. The liquid fraction was analyzed by high-performance liquid chromatography (HPLC) in a Shimadzu equipment on a RezexTM RHM-Monosaccharide H+ (8 %) column (Phenomenex) and refractive index and UV detectors. Structural carbohydrates (glucose for cellulose, and xylan for hemicellulose are quantified, mannose and galactose were not determined because the HPLC chromatographic system used does not quantify these sugars[17], according to the following chromatographic conditions: H_2SO_4 5 mM as mobile phase, 0.6 mL min^{-1}, at 60 °C. For lignin content determination, solid fraction from the previous method was calcined using a muffle at 575 ± 25 °C for 2 h[18].

The thermogravimetry analysis (TGA) of biomass was performed using a Mettler Toledo STARe unit with TGA/SDTA851 module; furnace temperature for TGA was increased from room temperature to 900 °C under a nitrogen flow of 20 mL min^{-1} at a heating rate of 10 °C min^{-1}. The differential scanning calorimetry (DSC) of biomass was made using a Mettler Toledo instrument with a DSC821e module. Samples of 8–13 mg placed inside a 40 µL aluminum crucible were heated from 30 °C to 600 °C under a nitrogen flow of 20 mL min^{-1} at a heating rate of 10 °C min^{-1}.

Biomass composition of ashes was studied using an energy dispersive X-Ray Fluorescence Spectrometer model EDX-720, Shimadzu. Solid samples were mounted in a sample holder with a polypropylene window and were vacuum-dried scanning the Sodium (Na)-Uranium (U) range. Based on ash composition, Base/Acid (B/A) Index, Bed Agglomeration Index (BAI), and the fouling factor (Fu) were determined, following these equations[19,20]:

$$\frac{B}{A} = \left(\frac{Fe_2O_3 + CaO + MgO + Na_2O + K_2O}{SiO_2 + Al_2O_3 + TiO_2}\right) \quad (1)$$

$$\frac{B}{A} = \left(\frac{Fe_2O_3}{Na_2O + K_2O}\right) \quad (2)$$

$$Fu = \left(\frac{\frac{B}{A}}{Na_2O + K_2O}\right) \quad (3)$$

2.3. Pyrolysis experiments

Pyrolysis experiments were carried out in a stainless-steel fixed-bed reactor, which design and construction were previously published[3]. For each experiment, the reactor was loaded with 5–11 g of biomass, which was then heated in an electric furnace from room temperature to 550 °C, for 25 min, that is, with a heating ramp of 20 °C min^{-1}. Once the temperature reached 550 °C, it was maintained for 20 min. A N_2 flow of 30 ml min^{-1} was maintained to create an inert atmosphere adequate for pyrolysis, and to avoid side reactions by removing vapors of the reaction zone. Reaction vapors were sent to a condenser containing a refrigerating mixture of ice-water-sodium chloride at −5 °C where condensable vapors and non-condensable vapors were separated. Part of non-condensable gases, which flow was monitored during the experiment, were sampled for analysis, and the rest, vented to the atmosphere.

Liquid product (called bio-oil) separation into its phases and oil phase (called tar) was made by means of a centrifuge at 3200 rpm for 8 min.

2.4. Gasification experiments

Gasification was carried out using a laboratory-scale moving-bed batch reactor, operating similarly to the continuous processing of a downdraft reactor, in which four reaction zones are observed (drying, pyrolysis, oxidation and reduction). It is a horizontal tubular reactor with a feeding tube where the mesh containing the biomass to be gasified is placed, a resistance-heated tube furnace and an ash collector where the mesh is placed after going through the furnace area.

The transference of the mesh throughout the system is carried out by a piston moved by a motor and controlled by a variable speed drive. There is a nozzle for (controlled) air inlet at the furnace entrance, and a nozzle for gas outlet at the furnace end, thus air and biomass counter flow, like for the downdraft gasifier. Reactions were carried out using an air flow of 600 ml min^{-1}. Reaction gases went through a cleaning cycle, made up of a silica gel cartridge cooled externally with a water-ice-sodium chloride bath, where tar was retained, and a gas scrubber where residual fluids are retained. The flow of gases produced was monitored during the experiment, and sampled for analysis.

Figure 1 shows a diagram of process phases applied to biomass for this research.

2.5. Characterization of solid and liquid products

The pyrolysis and gasification gases were analyzed by gas chromatography in an Agilent 6890N GC unit with a thermal conductivity detector (TCD) and a 0.53 mm i.d. 30 m long GS-CARBONPLOT capillary column with a film thickness of 3 μm. Response factors for each component were determined by creating calibration curves with certified standards (H_2, CO, CH_4, CO_2, N_2, O_2, H_2). Gas heating value was calculated by their composition[21], and gasification efficiency as well as gas heating value-energy ratio obtained when burning initial biomass[22].

Aqueous and oil phases (tar) of bio-oils were analyzed by gas chromatography in an Agilent 6890N GC unit with a flame ionization detector (FID) and a 0.32 mm i.d. 30 m long HP-5 capillary

column with a film thickness of 0.25 µm. For this analysis, the tar was dissolved in methylene chloride. Calibration of chromatographic areas was carried out by determining the response factors for each chemical group, using mixtures of standards and a reference compound (tetralin). Standards and a GC-SM (Shimadzu GCMS-QP2020) were used for component identification.

Elemental composition of both phases of bio-oils was determined in a CHN628 Series Elemental Determinator (LECO) unit, and heating value was calculated from these data, using the Dulong's formula. Density determination was carried out by gravimetry at a controlled temperature and pH of the aqueous fraction of bio-oils was determined with a HANNA HI 8424 pHmeter.

The determination of water content of bio-oils was made according to IRAM 21320 Standard, by titration with a Karl-Fischer unit. This is the recommended technique for bio-oils[18], since other conventional techniques cannot be applied due to the low boiling point (less than 100 °C) of soluble in water organic compounds in bio-oils.

Chars obtained in the pyrolysis and gasification experiments were characterized in terms of their proximal and elemental composition, using the same methodology applied for the analysis of raw material biomass. Their heating values were also calculated by using the Dulong's formula.
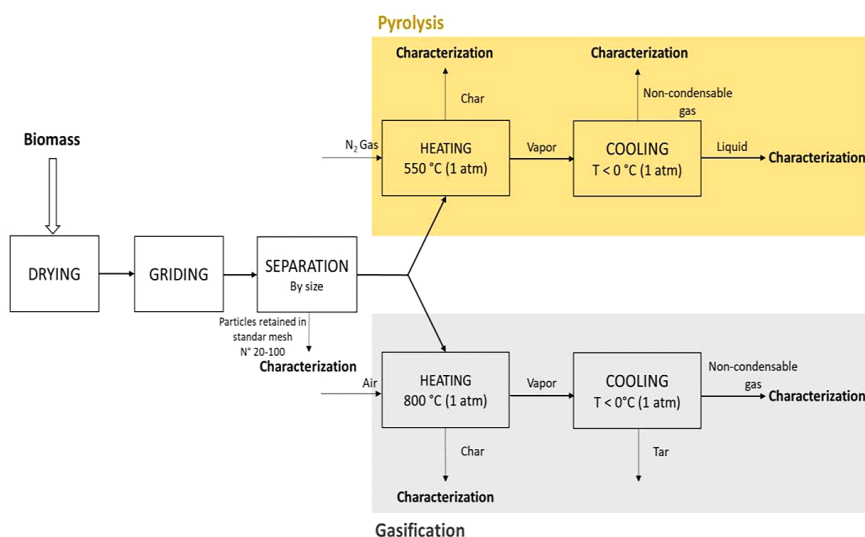

Figure 1. Diagram of biomass thermochemical treatment processes.

3. Results and discussion

3.1. Biomass composition

The quantity of energy potentially available from a given biomass source is intrinsic, but the actual energy recovered with different methods will be more or less depending on the thermochemical conversion technology used[23].

So, inherent properties of the biomass source will determine both the choice of the thermochemical conversion process and the subsequent processing difficulties that may arise.

They are: Moisture content, heating value, fixed and volatile carbon proportions, ash and alkali metal content, cellulose/lignin ratio.

Table 1 shows the composition and properties of the biomasses studied. After conditioning, raw material have a moisture percentage close to 10 wt%.

Composition of structural carbohydrates, lignin and ash from selected residual biomass was similar to the values reported by other authors for the same-type biomass[3,24–26]. However, significant differences were observed: lignin content from RH

was significantly lower, and from hemicelluloses was higher than other types of biomass. This material also showed high ash content, which was expected due to its characteristic high silica content[27,28]. Both types of wood sawdust (DCS and DQS) presented high lignin values and low ash content, which is consistent with the reports by Demirbas et al.[29] for hardwoods. Çaglar and Demirbas[30] reported 32.6 wt% cellulose, 18.7 wt% hemicellulose, and 48.7 wt% lignin, with 5.8 wt% ash for cotton cocoon shell[30], while Pütün et al.[31] reported content of C = 48.9 wt%, O = 44.7 wt%, and H = 5.2 wt% for a mix of cotton straw and stalk, with 4.7 wt% ash content, 70.1 wt% volatile matter, and 17.1 wt% fixed carbon[31].

Higher Heating Value of biomass, which allows for estimating energy utilization of biomass when directly burned, was almost half the HHV of coal (24–35 MJ kg^{-1}), and similar to HHV of wood (12–21 MJ kg^{-1})[2,32]. A small quantity of nitrogen was found, less than 1 wt% for all biomass types which favors pyrolysis oil and syngas production as reported by Friedl et al.[33], since this component increases pollution in combustion when it is present in the fuel. Wood sawdust (DCS and DQS) showed higher heating value compared to other types of biomass studied, consistent with its higher carbon content[33].

Cellulose/lignin ratio of biomass is an important characteristic in pyrolysis, as it affects yielding and composition of liquid products. For example, biomass with high lignin contents, such as DCS and DQS, tend to produce lower liquid yields but it has a higher energy density than liquid products high in cellulose derivative content[2].

Table 1. Biomass composition (wt%).

-	RH	CS-A	DCS	DQS
Proximate analysis	-	-	-	-
Moisture	8.59	11.29	10.51	9.42
Volatile matter	55.70	63.43	68.09	65.83
Fixed-carbon	14.56	19.89	20.39	22.80
Ash	21.15	5.39	1.01	1.95
Lignocellulosic composition*	-	-	-	-
Lignin	15.81	26.61	39.40	36.47
Cellulose	34.60	38.25	36.10	35.87
Hemicellulose	16.42	13.54	12.95	14.16
Others	3.43	4.92	0.03	2.13
Ultimate analysis**	-	-	-	-
C	35.87	41.76	44.75	45.99
H	4.95	5.59	6.17	5.86
O	37.74	46.47	47.42	45.83
N	0.29	0.79	0.65	0.37
HHV (MJ kg^{-1})	12.48	13.83	15.50	15.75

$^{(*)}$ Lignocellulosic material + Moisture + Ash = 100
$^{(**)}$ C + H + O + N + Ash = 100

3.2. Ash composition

Table 2 shows ash composition from each biomass, stating that for RH, 90.2 wt% of inorganic material was SiO$_2$, then this raw material becomes a significant silica source. Calcination and

pyrolysis of RH is one of the most studied methods for producing nanostructured silica, which has various applications in construction, chemical industries, electronics, glass and ceramics manufacturing, cement doping and composite polymeric material manufacturing, and other potential uses[34,35]. For wood sawdust, a CaO content higher than 85 wt% was evidenced while CS-A showed the highest percentage of K_2O (more than 55 wt%)[36]. Ash content in DSC, DQS and CS-A is low, thus inorganic material for utilization is also low, if applications for oxides in its ashes are considered.

It is important to know ash composition of both biomass and chars from pyrolysis and gasification, this composition will be discussed in Subsection 3.9, if the application as solid fuel is considered as ashes are settled on heating surfaces in industrial boilers, reducing heat transfer, causing equipment corrosion, slagging of radiant surfaces, fouling on exchange surfaces, and obstruction and clogging of gas flow[37].

Table 2. Biomass composition of ashes (wt%).

-	RH	CS-A	DCS	DQS
SiO_2	90.20	-	1.57	1.29
Al_2O_3	3.91	-	-	-
K_2O	2.95	56.5	1.14	0.89
CaO	1.21	38.07	88.18	94.11
P_2O_5	0.51	1.49	-	-
Cl	0.36	1.90	3.24	1.01
MnO	0.33	0.25	-	-
Fe_2O_3	0.30	0.34	3.13	1.08
SO_3	0.17	0.67	0.67	0.17
CuO	0.02	0.1	0.69	0.2
Br	0.02	0.05	-	-
ZnO	0.02	0.12	0.26	-
TiO_2	-	-	0.38	-
SrO	-	0.51	0.57	1.25
Ag_2O	-	-	0.17	-

B/A ratio in organic waste allows identifying the slagging factor, thus ashes low inclination to slag formation when B/A < 0.5, mid-inclination when 0.5 < B/A < 1, high inclination when 1 < B/A < 1.75, and severe inclination when B/A > 1.75[20]. Ashes from RH showed a value lower than 0.5 and therefore a low inclination to slag formation, while wood sawdust ashes (DCS and DQS) evidenced a severe inclination to slag formation, due to the high presence of CaO. Slagging factor could not be determined in CS-A ashes.

BAI is studied for assessing operational problems during fluidized bed combustion which is the type of technology used in power plants. Fluidized bed agglomeration appears when BAI < 0.15[20]. No agglomeration issues were seen in wood sawdust ashes since BAI are 1.25 for DQS and 2.73 for DCS, respectively. This is not the same for RH and CS-A ashes, as BAI values were 0.1 and 0.01, respectively.

Another important parameter, i.e., Fu, is primarily based on B/A ratio. Although the

presence of sodium in biomass ash is generally low or non-existent, it has been shown that one of the main components is potassium (see **Table 2**). When K, together with SO_3 and CaO, is condensed into suspended ash particles there is an increase in stickiness resulting in significant fouling. Low fouling is expected for Fu < 0.6, high fouling for Fu values up to 40, and extremely high fouling for values higher than 40[20]. For RH ashes, a very low Fu (0.14) was seen, while for hardwood ashes, very high Fu values (54.05 for DCS and 66.30 for DQS) were observed, indicating severe likelihood of fouling.

Based on these observations on biomass composition, it may be deduced that direct application in boilers could lead to severe operational problems, given the high fouling and slag-forming ability of hardwood sawdust ash (DSC and DQS), and the high inclination to agglomeration of RH and CS-A ashes. Developing new technological alternatives allowing ash utilization and recovery for industrial assets, particularly those replacing hydrocarbons, is key to provide solutions to the productive sector regarding management of these residual biomass.

On this point, alternatives like thermochemical pyrolysis and gasification treatments should be studied.

3.3. Thermal behavior of biomass

Biomass behavior during thermal decomposition is shown in **Figures 2** and **3**, for DCS and TG profiles, respectively. The DSC analysis for the four types of biomass studied, an endothermic peak approx. at 100 ℃ was observed, which is the result from the removal of moisture. According to literature data[38], 280–310 ℃, 355–365 ℃, and 410–430 ℃ exotherms observed correspond to the thermal degradation of hemicellulose, cellulose and lignin, respectively. For non-previously chemically treated biomass (RH and CS-A), these transitions are seen; for RH they are well-marked with maximum at 291 ℃ for hemicellulose, 353 ℃ for cellulose and 415 ℃ for lignin. On the other hand, in detanninized biomass (DCS and DQS) greater lignin degradation is noticed, consistent with the high content of this bio-polymer (see **Table 1**). It is also seen that no differentiation between hemicellulose and cellulose degradation can be made.
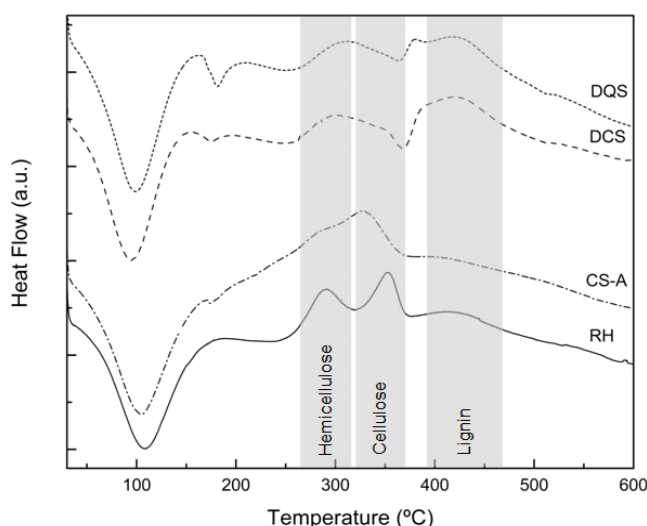

Figure 2. Differential scanning calorimetry (DSC) curves.

Because of the differences in biomass behavior seen in the DSC analysis (i.e., the types of biomass that underwent a previous detanninization treatment, and those that did not),

TG analyzes were carried out for RH (untreated biomass) and DQS (biomass subject to detanninization). For TG profiles, they were the typical profiles as those for lignocellulosic

material[39]. In both cases, the pyrolytic process involved three stages: first, from heating start (room temperature) to 100 ℃ approximately, when there is a loss of moisture and volatile matter; this stage showed a loss of mass of almost 8 wt% for both. The highest loss of mass observed in both cases occurred during the second decomposition stage when temperature ranges from 200–400 °C, and decomposition of approximately 49 wt% of RH, and 59 wt% of sawdust DQS takes place. This stage showed two thermal events: one from 200 °C with a maximum temperature of 300 °C, and another from 325 °C with a maximum from 340 °C to 360 °C, which is consistent with hemicellulose and cellulose decomposition, respectively[40]. The third stage, from 400 ℃ until the end of the analysis, most of the lignin decomposition, as well as partial carbonaceous material residue decomposition occurs. Finally, residual material that remains without decomposing corresponds to ashes and fixed carbon (see values in **Table 1**). These results are consistent with those reported by other authors for pine sawdust and rice husks[41,42].
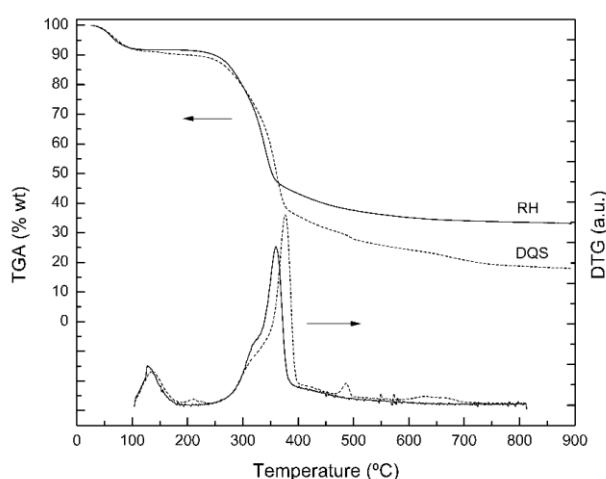

Figure 3. Thermogravimetric (TG) and derived thermogravimetric (DTG) curves.

3.4. Pyrolysis product yields

In biomass pyrolysis, products are a complex mixture of decomposition products from single components (mainly cellulose, hemicellulose and lignin), each of them has its own structural and kinetic characteristics of decomposition. Biomass breaks down into vapors, aerosols, and char. After cooling and condensing vapors and aerosols, a dark brown liquid is formed, called bio-oil, which is easily separated into its aqueous and oil phases (tar) when water content exceeds 30 wt%[2]. Bio-oil yields and properties depend on raw material, the process type and conditions, and the efficiency of collection of the product.

Table 3 shows yields in pyrolysis of the four biomasses studied, which resulted in three types of products: one liquid product (bio-oil), consisting of two phases (aqueous and tar), one solid product (char), and one gaseous product. Char contained inorganic material originally present in biomass. Differences in yields were observed depending on the type of biomass. The maximum yield to liquid products was obtained with RH (41.9 wt%) and the lowest yield with DCS (30.9 wt%). Biomass from DCS resulted in the highest quantity of gases, and biomass from RH produced the highest quantity of char, consistent with its high ash content (see **Table 1**). Yields of pyrolysis products are similar to those published by other authors under similar conditions with lignocellulosic material with similar characteristics[25,43].

Table 3. Pyrolysis yields, composition, and heating value of gas products.

-	RH	CS-A	DCS	DQS
Yields (wt%)	-	-	-	-
Aqueous phase	29.3	34.7	24.8	34.6
Tar	12.6	-	6.1	9.2
Char	39.4	31.1	25.6	31.6
Gases	18.8	34.1	43.5	24.6
Gas composition (vol%)	-	-	-	-
Hydrogen	4.2	14.5	30.8	31.0
Carbon monoxide	2.4	8.5	12.3	19.2
Methane	1.1	2.8	7.1	9.9
Carbon dioxide	1.1	3.8	6.6	8.0
Nitrogen	91.3	70.3	37.2	31.8
LHV (kcal Nm^{-3})	249.8	800.5	1790.8	2045.1

Tar represented 30 wt% of the bio-oil obtained in RH pyrolysis, and around 20 wt% in wood sawdust pyrolysis. Tar is mainly obtained from lignin[44], which content was clearly higher in wood sawdust (see **Table 1**); however, higher tar quantities from RH could be associated with greater progress in lignin decomposition, which is evidenced when considering char/ash ratio for each biomass. Thus, considering only the organic fraction of char, RH produced the lowest quantity of char (18.2 wt%), while DQS and DCS produced 25.6 and 29.6 wt%, respectively. In addition, it is known that inorganic components of biomass have a catalytic effect during biomass pyrolysis[45], so recombination of low molecular mass compounds in the vapor phase also provides high molecular mass compounds, tar components. Tar components are particularly prone to be converted into light gases, char, water, and more refractory tar. These reactions result in enriched tar with less oxygenated and probably more stable species[46].

Non-condensable gases from the process are mainly composed of carbon dioxide, methane, carbon monoxide, hydrogen and light hydrocarbons, which are diluted in nitrogen used in the experiment to generate the inert atmosphere for pyrolysis. Gases from sawdust pyrolysis showed high hydrogen and methane concentrations and, consequently, higher heating values than the remaining types of biomass. It was observed that lignin (which content was higher in wood sawdust than in the remaining types of biomass) produces a large quantity of H_2 and methane during pyrolysis process, while cellulose and hemicellulose (major components in RH and CS-A) provide a greater quantity of carbon oxides[32]. The H_2 in the pyrolysis gaseous products comes, in part, from the rupture of the aromatic rings present in the lignin. This is supported by the research of Yang et al.[47], who studied the pyrolysis of the cellulose, hemicellulose and lignin, i.e., the three main polymeric components of biomass. Yang et al.[47] observed that lignin had the highest yield of H_2 and CH_4, which could be attributed to the higher content of aromatic rings and O-CH_3 functional groups in the original lignin sample, since the H_2 from organic pyrolysis came mainly from the cracking and deformation of C=C (aromatic) and C–H (aromatic), while CH_4 was produced mainly by methoxy cracking. The cracking and reforming of the aromatic rings leads to the release of H_2 at higher temperatures (> 400 °C)[47]. Gas stream can be used as industrial fuel and as heat source for the

pyrolysis process itself, or it can be used in gas turbines to produce electricity[48].

3.5. Bio-oil composition

As stated before, bio-oil is composed of two fractions, an aqueous fraction and an oil fraction (called tar). The aqueous fraction is yellow/brown, has a distinctive smoky odor, and is denser than tar. **Figure 4** shows the composition of aqueous fractions from the four bio-oils, grouped by chemical type. A high percentage of acids, aldehydes, ketones, alcohols, and phenols is observed (81–88 wt%, dry matter basis). Acids, ketones and alcohols are mainly obtained from pyrolysis of cellulose and hemicellulose, while phenols are originated from lignin[49,50]. The high content of acetic acid, 2-pentanone and methanol was common to the four biomass under study.

Acetic acid is the most important organic compound in bio-oils, and acetic acid concentrations are similar in all aqueous fractions of biomass[3,51,52]; in this research paper, it represented 88–99% of total acids. Acetic acid is generally produced by removal of acetyl groups from hemicellulose structure at high temperature (425–690 °C), this reaction releases CO_2[53]. RH presented the highest percentage of hemicellulose (see **Table 1**), and consequently of acetic acid in the aqueous fraction obtained in pyrolysis. Finally, for the group of acids, it is important to highlight that formic acid was not observed in bio-oils from the wood sawdust under study; the maximum content of this compound was 2.26 wt% for CS-A. The presence of volatile organic acids such as acetic acid, formic acid and propionic acid makes it difficult to use bio-oils as direct fuel[54,55]. There are several methods for improving bio-oils for this[56], namely, we can reference to catalytic treatments removing acetic acid and improving its properties[54]. Considering these cases, the absence of formic acid in bio-oils from DCS and DQS leads to less efforts to improve the quality of these liquids for potential use as fuel.

2-pentanone was the major component in

ketones in all studied cases. RH had a more significant percentage of this component and of acetol (1-hydroxy-2-propanone) with 34.2% and 4.3% of total ketones, respectively. Acetol is other product found in significant quantities during cellulose pyrolysis[57]. The four types of biomass studied showed a relevant and similar quantity of cellulose content (see **Table 1**), thus the similarity of acetol concentration in bio-oils from those biomass types was expected.

For all cases, methanol was the highest percentage found in the group of alcohols and sugars. This product comes from pyrolysis of lignin and cellulose[50]. RH had the lowest methanol content in its aqueous fraction, which may because composition of this biomass has the lowest lignin content (see **Table 1**). Another component of this group is levoglucosan, a main product from cellulose pyrolysis[57]; its yielding decreases at temperatures higher than 530 °C, which in turn generates decomposition compounds of lower molecular mass. In all the cases under study, levoglucosan content in the aqueous fraction was less than 1.1 wt% Levoglucosan is commonly used as a chemical tracer of biomass burning in atmospheric studies[58,59] and hydrolysis of levoglucosan produces glucose[60,61], a significant monomer used in the biorefinery sector.

Aldehydes and heterocycles content was higher in the aqueous fraction from RH. The main compounds were cinnamaldehyde, octanal and 2-butenal (in the aldehyde group), and 2-acetylfuran, 5-(hydroxymethyl)-furfural and 2-furanmethanol (in the heterocyclic group, the latter compound represented 28–39% of the total). 3,4-dihydro-2H-pyran was also observed, with variable proportions of 3% (CS-A), and 37% (RH) within the group. Pyrans contain oxygen in their ring, so it must be minimized in bio-oils intended to be used as fuels, since oxygen content makes them unstable, reactive and corrosive in nature, with low heating value. Higher oxygen content in bio-oil also means more hydrogen for improving this fuel. Previous studies indicate that pyrans are produced during

11

cellulose pyrolysis (with yields of up to 10 wt% of total cellulose)[62]. It is necessary to remember that cellulose is the least complex and most abundant component in biomass[63] (see **Table 1**), so it is possible to recognize the efficiency of the pyrolysis treatment carried out considering selectivity to pyrans (given that these compounds did not represent more than 0.5 wt% of cellulose).

For esters, the main components found were vinyl-2-butenoate, propyl-butanoate, and propyl-3-butenoate; the latter component was not present in the aqueous fraction from CS-A. As for ethers, they were represented by 1,2,5-trimethoxy-benzene and ethoxybutane in all cases. Small quantities of

isopropylcyclopentene were identified in the hydrocarbon group.

Some authors reported the same compounds and similar distributions for bio-oil from rice husk[64,65], for bio-oil from cotton waste[66], and for bio-oils from hardwood sawdust[3,67].

Phenolic compounds were the group with the largest number of components (21 compounds), which are detailed in **Table 4**, grouped according to the substitution units of the phenolic ring into alkylated phenols and phenolic ethers. These latter compounds represented 57% of the total for RH, and approximately 65% for the remaining types of biomass under study.
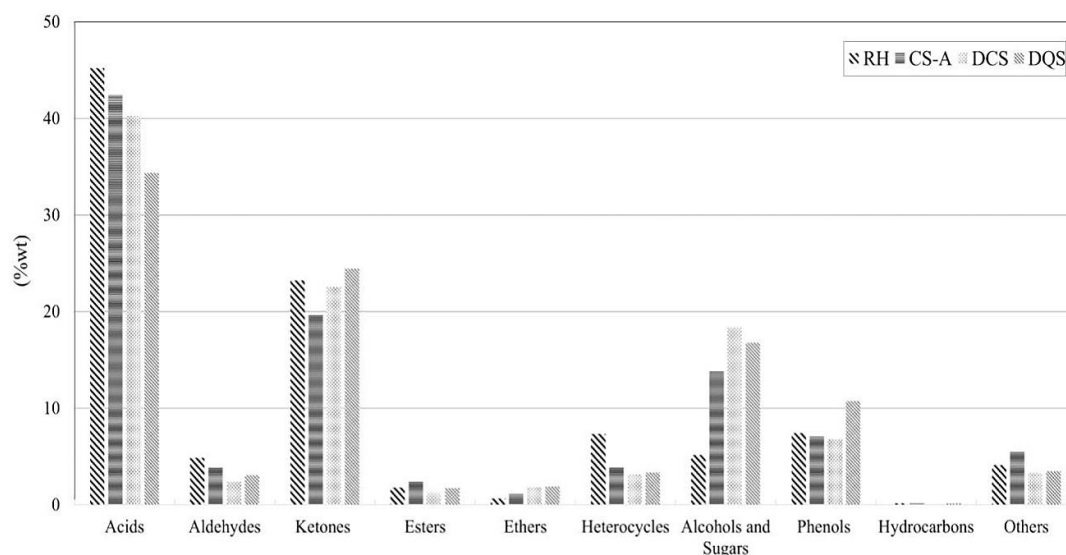

Figure 4. Distribution of aqueous fraction compounds from bio-oil in chemical types.

Cresols (methylphenols) were the major compounds in the alkylated phenols, in all cases, representing a quarter of the total for CS-A and DQS, half for DCS, and 40% for RH. The presence of xylenols (dimethylphenols) and ethylphenol should also be highlighted. Methylguaiacol was the most relevant component in the phenolic ether subgroup for all cases, representing from a quarter to a third of this subgroup. Methylguaiacol is one of the free phenols related to smokey, rough wood,

clove, spicy and phenolic flavors in wines stored in wooden containers[68]. Among the types of biomass studied, bio-oil from DQS presented the highest percentage of this compound, where the aforementioned organoleptic characteristics were mostly perceived. The presence of 3-methoxhyphenol, syringol and guaiacol in the phenolic ether subgroup in the aqueous fractions of bio-oils in all types of biomass studied should be highlighted.

Table 4. Concentration of phenolic compounds in the bio-oil aqueous phase (wt%).

-	RH	CS-A	DCS	DQS
Phenol	1.22	0.56	0.86	0.72
Alkylated phenols	1.97	2.01	1.56	3.10
Cresols (methylphenol)	0.80	0.49	0.78	0.73
Dimethylphenol	0.76	0.57	0.14	0.72
Ethylphenol	0.14	0.18	0.22	0.3
Trimethylphenol	0.02	0.16	0.04	0.31
1,3-Benzenediol, 4-ethyl-	0.08	0.10	0.13	0.10
2-Methylhydroquinone	0.02	0.16	0.05	0.03
1-(4-hydroxy-3-methylphenyl)-2-propanone(guaiacyl acetone)	0.05	0.17	0.08	0.54
2,6-Di-tert-butyl-p-cresol	0.11	0.18	0.13	0.38
Phenolic ethers	4.23	4.54	4.41	6.93
Guaiacol	0.17	0.17	0.35	0.24
Methylguaiacol	1.46	1.19	1.39	2.57
3-methoxyphenol	1.31	1.03	1.00	1.24
4-ethyl-3-methoxyphenol	0.18	0.35	0.30	0.50
4-ethylguaiacol (4-ethyl-2-methoxy-phenol)	0.15	0.24	0.20	0.23
4-propylguaiacol	0.09	0.12	0.14	0.14
4-vinylguaiacol (2-methoxy-4-vinylphenol)	0.12	0.16	0.12	0.30
4-methoxycatechol (4-methoxy-1,2-benzenediol)	0.32	0.25	0.22	0.32
4-hydroxy-3-methoxybenzaldehyde (vainillin)	0.03	0.06	0.03	0.04
Acetosyringone	0.02	0.04	0.03	0.08
Eugenol	0.05	0.11	0.09	0.17
Syringol	0.34	0.81	0.54	1.09
Total phenolics compounds	7.42	7.11	6.84	10.75

Phenolic compounds found in bio-oils derive from lignin pyrolysis, which is a biopolymer mainly constituted by three repeating units: cumaryl (H), guaiacyl (G) and syringyl (S), linked together by ester, ether and carbon-carbon bonds. Lignins with fewer of these bonds are less condensed (and therefore easier to break down); for example, husk rice lignin, which, like any herbaceous species, also has a greater quantity of H units than wood lignins, and a higher degree of acylation[69]. That is why its structure is more linear than the structure of wood lignins.

As shown in **Table 4**, phenols derived from pyrolysis of lignin G units, such as guaiacol, 4-methylguaiacol, 4-ethylguaiacol and 4-vinylguaiacol[70] were found in significant amounts in the aqueous fractions of all the types of biomass under study. Phenolic compounds derived from H units -such as phenol, 4-methylphenol, 4-ethylphenol- and S units -such as syringol, 4-methylsyringol, 4-ethylsyringol, and 4-vinylsyringol, etc. were present in higher amounts in bio-oils from RH and hardwoods (DCS and DQS), respectively. These observations are consistent with formation of the respective lignins. Lignin from husk rice is formed mainly by G units, with an H:G:S ratio of 7:81:12[70], while the ratios of S-units and G-units of hardwood pyrolytic lignin are in the range of 58–79% and 21–41%,

respectively[71,72].

3.6. Physical and chemical properties of bio-oils

Table 5 shows elemental composition and properties of the aqueous fractions of bio-oils obtained in the pyrolysis process. Water content was very high for all cases, and consistent with other reports found in literature for wood sawdust and cereal husks; for example, 84.4 wt% for wheat husk[3], 85 wt% for soybean husk[73], 60 wt% for cellulose and 75 wt% for lignin isolated from pine

sawdust[74]. High water content in these fractions reduces heating values and increases their oxidative properties as fuel, but viscosity and allows for atomization and combustion[49].

Density of the aqueous fractions of bio-oils are similar to regular densities found this type of liquids[2]; typical density of fuel-oil is 0.94 kg dm^{-3}. pH of bio-oils was low, due to high content of acids present in their composition (see **Figure 4**, Section 3.5); these values were also typical for these liquids[75].

Table 5. Elemental composition and properties of aqueous fractions from bio-oils.

	HR	CS-A	DCS	DQS
Water (wt%)	73.0	83.4	77.7	68.8
pH	3	4	3	3
Density (kg dm^{-3})	1.09	1.07	1.07	1.11
Elemental composition (wt%, dry basis)				
C	44.3	55.2	51.6	46.1
H	9.5	11.2	10.0	8.8
O	45.3	30.9	37.4	43.6
N	1.0	2.8	1.0	1.5
HHV (MJ kg^{-1}, dry basis)	20.5	29.3	25.2	20.4
HHV (MJ kg^{-1}, wet basis)	5.5	4.9	5.2	6.4

Bio-oils are combustible, but not flammable. On account of the high content of non-volatile components, a large amount of energy is required for ignition, but once ignited, flames are stable and self-sustained. HHV is around 16–19 MJ kg^{-1}, depending on the raw material of biomass, resulting in approximately half HHV of hydrocarbons given high oxygen content, the presence of water and having a higher density[2,75]. Fuel oil is a fossil fuel normally used in industrial boilers and furnaces and has an HHV of 40 MJ kg^{-1}; bio-oils from lignocellulosic residues could totally or partially replace fuel oil in boilers, since their HHV on a dry matter basis (see **Table 5**) were only 15–38 % lower than HHV of fuel oil. However, in order to consider this as a relevant property, it is

necessary to apply any methodology for removing water from this fraction; those options are available at a very high cost.

Table 6 shows elemental composition and heating values of tar from biomass of higher yield of the oil fraction, RH (untreated biomass) and DQS (biomass subject to detanninizing process). Tars had more carbon. In addition, tar hydrogen content was similar to biomass from which those tars were extracted (see **Table 1**), thus less oxygen and much higher HHV were observed, showing an evident concentration of energy in this pyrolysis product. Generally speaking, HHVs of pyrolytic tar ranges from 24 to 29 MJ kg^{-1}, which is much higher than HHVs of the aqueous phase[2,75].

Table 6. Elemental composition and properties of tars.

-	HR	DQS
Elemental composition (wt%)		
C	62.6	60.9
H	6.3	8.2
O	28.8	29.5
N	2.3	1.5
HHV (MJ kg^{-1})	25.1	27.1

Viscosity of bio-oils can vary widely (35–1000 cP at 40 °C) depending on raw material and process conditions[2,75], and decreases at higher temperatures. That is why very viscous bio-oils can be easily pumped after moderate pre-heating. These characteristics allow us to consider its potential for using as fuel, partially replacing fossil derivatives.

3.7. Potential uses of bio-oils and their fractions

Characterization of bio-oils from industry residual biomass analyzed in this research allows for determining the potential for bio-oil uses and applications. As mentioned, and discussed in Section 1, the most direct application would be as fuel for diesel engines[76], and for gas turbines and boilers[77]. However, we may consider more sophisticated applications in products with higher added value. For example, using these bio-oils or their fractions, hydrocarbons similar to gasoline may be obtained by hydrodeoxygenation with typical hydrotreating catalysts (i.e., sulfided CoMo or NiMo), or zeolites for catalytic cracking to obtain a highly aromatic product[78]. The latter has been extensively studied by authors in this paper for sawdust from different wood, cereal husks and even cown manure[73,79–82].

In addition, we are currently studying the application of the carbons obtained in pyrolysis and in the gas of different biomasses, including RH, as metal absorbents in industrial effluents.

Alternatively, bio-oils could be converted into hydrogen or syngas by catalytic steam reforming, an option particularly interesting for the aqueous fraction, as shown by Li et al.[83]. It may also be raw material for making chemicals for food additives[84], pharmaceutical products[85], fertilizers[86], pesticides[87] and resins[88]. Some high-demand chemicals, such as methanol, acetic acid, acetone and, particularly, phenols, could be obtained from bio-oils by, for example, liquid-liquid extraction[89] or distillation[90]. However, it is still necessary to develop reliable and low-cost separation procedures, because of the large number of compounds in low concentration, which makes it very difficult to isolate them, as well as to coordinate with potential markets.

Some chemicals produced from bio-oil are already commercial products (such as liquid smoke), or can be available on the market in the short term. To this extent, it is important to note that to be included in this category, liquid smoke shall meet certain requirements, established by the FDA (U.S. Food and Drug Administration), and by country laws. For example, a 2–20% acidity (as acetic acid), 2–25% carbonyl content (as heptaldehyde) and 0.1–16% phenols (as 2,6-dimethoxyphenol). It shall be noted that aqueous fractions from bio-oils in this research need to be subject to treatments for improvement (distillation, condensation and filtering) in order to meet these requirements. Specifically, the aqueous fraction from DQS is in the beginning of the conditioning processes and analytical determinations. The

purpose is the assessment by the National Administration of Drugs, Food and Medical Technology (ANMAT) in Argentina to check whether it is fit for consumption.

Tar can be used in several applications, including as a partial alternative to phenol in the production of phenol-formaldehyde resins, which are widely used as adhesives for composite wood paneling[91,92], and fossil resources for asphalt mixes that are more resistant to aging and elastic deformation[93]; or in the production of adsorbing microspheres[94–96]. Additionally, from this bio-oil fraction, various chemical compounds can be extracted, such as aromatic hydrocarbons and phenols[97]. Considering tar and lignin characteristics and composition are similar, some new applications are being developed by replacing lignin with tar, for example, for the production of carbon fiber by repolymerization[98], and the production of microspheres for agrochemical and biocide release-control, with a slow release of the active component[99]. Particularly, tar from RH has been used for the production of eugenol-encapsulated microparticles as biocide, and it was included in alginate films to develop active packaging materials by the authors of this paper[100].

3.8. Biomass gasification

The final products of biomass gasification are divided into solid phase and gas/vapor phase. The latter, in turn, is composed of a gas phase (non-condensable) and a condensable phase (tar).

In downdraft gasifiers, such as the gasifier used for this research, both gas and solid phases counter flow, creating four reaction zones: drying, pyrolysis, oxidation, and reduction. As gas product travels from the high temperature oxidation zone to the reduction zone, all tar vapors are effectively consumed, providing a much cleaner gas than that obtained in updraft gasifiers. However, for most syngas applications, it is necessary to completely remove tars, particulates, and nitrogen-containing compounds. Hot gas cleaning technology provides for options for removing tar and ammonia by catalytic cracking reactions and decomposition of ammonia into H_2 and N_2[101].

Table 7 shows yielding of gasification of RH, CS-A, DQS (DCS biomass was not gasified as particles were too small and they pass through the equipment retaining mesh), as well as composition and heating value of the stream of gases produced, and the efficiency of the process. In all cases, gas yield was high, and char percentages were like those obtained in pyrolysis for each type of biomass (see **Table 3**, Section 3.3). The heating value of the produced gas, which also contains the nitrogen present in the air used as an oxidizing agent, was similar to the heating value reported for this type of operating configurations[99]. Gas phase produced was a mixture of non-condensables at room temperature: CO, H_2, CO_2 and CH_4, consistent with the results reported by other authors, for example, Yoon et al. who reported gases from husk gasification with 13.6% H_2, 14.9% CO, 12.9% CO_2, and 2.3% CH_4, and a heating value of 1084 kcal Nm^{-3}[102].

The condensable phase, i.e., tar from gasification, is formed from a series of complex reactions, highly dependent on reaction conditions and the type of gasifier (for example, less than 1 wt% of biomass for downdraft gasifiers, 1–5 wt% for bubbling fluidized bed gasifiers, and 10–20 wt% for updraft gasifiers). Tars come from the pyrolysis stage and are subject to recombination and decomposition[103]. Biomass from RH was the biomass producing the greatest amount of tar, as observed by Lin et al.[104].

Table 7. Gasification yields, composition and heating value of gas products.

	RH	CS-A	DQS
Yieds (wt%)	-	-	-
Tar	14.1	4.2	2.4

Table 7. (*Continued*).

	RH	CS-A	DQS
Char	40.3	31.4	31.9
Gases	45.6	64.4	65.7
Gas composition (vol%)	-	-	-
Hydrogen	4.5	19.0	20.2
Carbon monoxide	5.7	21.1	22.3
Methane	1.3	4.2	8.3
Carbon dioxide	20.6	22.3	19.0
Nitrogen	67.9	33.5	30.3
Lower Heating Value (kcal Nm^{-3})	361.1	1357.2	1740.8
Gasification Efficiency (%)	22.6	69.3	49.6

The solid phase is a mixture of unconverted organic fraction (char) and ash. The amount of char mainly depends on the gasification technology used and the operating conditions (for example, 5–10 wt% of biomass for fluidized bed gasifiers, and 20–25 wt% for fixed bed gasifiers), while ash depends on raw material for biomass. The heating value (HHV) of char varies from 25 to 30 MJ kg^{-1}, depending on the amount of unconverted organic fraction[103]. Efficiency of gasification was high for CS-A and DQS; however, low gasification efficiency for RH is due to the high ash content in this type of biomass.

3.9. Char composition and properties

Table 8 shows char composition and properties obtained in the pyrolytic and gasification experiments of the types of biomass studied. All chars were mainly composed of carbon (46–90%) and oxygen (2–38%). As char has high carbon content, it has greater energy value than the original biomass, and can be used to generate heat for the process, and for briquettes as a substitute for traditional coal, which are smokeless, burn 50% longer and are a renewable product because they are made from waste.

These materials are also used for production of activated carbon, or for improving soil fertility serving as pH increaser in acid soils[35,43]. Furthermore, as it has a large surface area, it can be used for contaminant filtration and adsorption, and physical or chemical activation processes can improve this quality[50]. It was determined that carbon adsorbents obtained by pyrolysis have hydrophilic surfaces and are suitable for removing metal ions and other contaminants from water[49].

Table 8. Char composition and properties from pyrolysis (P) and gasification (G).

	HR (P)	HR (G)	CS-A (P)	CS-A (G)	DCS (P)	DQS (P)	DQS (G)
Proximate analysis (wt%)	-	-	-	-	-	-	-
Moisture	5.0	4.7	8.6	17.2	7.3	5.0	10.0
Volatile matter	20.7	9.6	32.4	20.8	22.5	14.9	9.9
Fixed-carbon	31.2	35.3	53.0	57.7	73.3	80.4	84.5
Ash	48.1	55.1	14.6	21.5	4.2	4.7	5.6
Elemental composition (wt%)	-	-	-	-	-	-	-
C	46.4	-	75.7	68.3	90.7	87.8	83.5
H	1.6	-	2.2	2.0	2.0	1.7	1.7

Table 8. (*Continued*).

	HR (P)	HR (G)	CS-A (P)	CS-A (G)	DCS (P)	DQS (P)	DQS (G)
O	3.4	-	5.8	6.8	1.9	5.0	8.7
N	0.5	-	1.7	1.4	1.2	0.8	0.5
HHV (MJ kg^{-1})	17.4	-	27.7	24.8	33.3	31.3	29.1

Residual char from thermochemical processes (especially gasification) of lignocellulosic biomass, which contains ashes from original raw material and a carbonaceous residue forming a single solid material, can also be used for new applications, replacing little commercial materials which are not so environmentally friendly. Examples include using it as absorbent for metals in aqueous solutions[105]. Char from pyrolysis and gasification of RH is under study by the authors of this research paper as RH has a significant content of SiO$_2$. The first results from Scanning Electron Microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDS, EDX, EDXS) studies indicate that RH char washed with 0.1 N HCl solution before pyrolysis, contains high content of silica as a inorganic component, equal amount of oxygen and a small amount of carbon, as organic components. Silica is a material used for several applications. The characteristics of microparticles found in our laboratories show that these microparticles are highly porous; therefore, good catalytic properties can be attributed to it. At the same time, char of RH is being studied as an Al absorbent for sanitation of as industrial effluent coming from an anodized aluminum profile company by authors of this paper.

4. Conclusions

In this research, four residual biomasses highly produced in the NEA region were conditioned and characterized. The values in the analysis of proximal composition, lignocellulosic material and elemental composition were as expected and comparable to those obtained by other authors.

Such biomasses were studied as raw material in pyrolysis and gasification processes. In pyrolysis, yielding values of all products were as expected, rice husk biomass produced more quantity of liquid (44.9 wt%) and char (39.4 wt%) consistent with its high ash content.

Spent red quebracho showed a higher proportion of bio-oil (aqueous phase) in liquid products. This can be due to the treatment at origin of this biomass coming from the tannin extraction process in the industry.

Bio-oil composition indicated high concentration of acids, ketones, alcohols, and phenols for all types of biomass studied. In particular, high content of phenols found in bio-oil from QCA suggests that it can be considered as potential raw material for chemical processing industries, adhesive production and as an alternative agent to phenol used in the production of phenol-formaldehyde resins.

Water content of bio-oils was high which reduced heating value although it would increase fluidity and atomization in its utilization as fuel. The density values of these liquids turned out to be between 0.13 kg m^{-3} and 0.17 kg m^{-3} higher than fuel-oil density values, showing that it would be necessary to modify transportation and supply to existing boilers and furnaces, in case bio-oils are used as an alternative to fuel-oil. Bio-oil pH was low pointing out the need for bio-oils to be treated after conditioning. As for the calorific value of pyrolytic tars, it reached 70% in PCS of fuel oil, suggesting that this fraction of pyrolysis liquids could be more suitable to use as a substitute to fossil fuels.

For the gasification process, the highest efficiencies and the highest heating values found in

the gases obtained were found in CS-A and DQS; in fact, the latter parameter values were far higher than initial biomass values, suggesting a good potential for the utilization of these residues in gasification processes. Regarding the composition and properties of char obtained for all biomasses, both in the pyrolysis and gasification processes, they show that it is possible to use them in a number of new applications.

Author contributions

Conceptualization, TS and BM; methodology, TS and SP; software, BM and FM; validation, TS; formal analysis, TS, BM and CE; investigation, TS and SP; resources, TS and CE; data curation, TS and SP; writing—original draft preparation, TS and SP; writing—review & editing, TS, BM and CE; visualization, FM and CE; supervision, BM and CE; project administration, TS and CE; funding acquisition, TS, BM, FM and CE.

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Conflict of interest

The authors declare no conflict of interest.

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