



Chicken litter: A waste or a source of chemicals? Fast pyrolysis and hydrothermal conversion as alternatives in the valorisation of poultry waste

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ABSTRACT

Poultry production is one of the main and fastest developing branches of the agri-food industry in the world. Chicken litter (ChL) is the most abundant waste from this industry and requires alternative treatments to help mitigate the environmental impacts of improper disposal. Fast pyrolysis and hydrothermal conversion are two recognized thermochemical approaches for the transformation of different types of biomasses, including agro-industrial waste. Fast pyrolysis takes place at atmospheric pressure or under vacuum at moderate to high temperatures (400–800 °C) in the absence of oxygen and requires drying of the feedstock, whereas hydrothermal conversion is a low temperature (180–300 °C) and high pressure (up to 30 MPa) process that takes place in liquid water and particularly suited for moist materials. In this work, we present experimental results that provide a comparison of bio-oils produced by fast pyrolysis and hydrothermal conversion of ChL. In addition, the composition of the pyrolytic oils from ChL is compared with the data obtained from rice husk (the main component of ChL), studied previously. Fast pyrolysis experiments were carried out in a bed reactor at temperatures ranging from 400° to 700°C and at two reaction times of 20- and 40-min. Phenols and other oxygenated compounds were the main families of chemicals present in the bio-oils. Among oxygenated derivatives, fatty acids were predominant. Hydrothermal conversion experiments were performed between 220 and 240 °C for 20- and 40- min and the oil fraction was obtained by evaporation of water from the reaction mixture followed by freeze-drying. These bioliquids were found to be concentrated in fatty acids, especially palmitic acid.

1. Introduction

Rice is among the three most important grain crops in the world, and it has a major contribution to fulfilling food needs across the globe. The role of the rice crop is unavoidable in the current and future worldwide food security. At the global level and according to the world rice outlook, the share of rice in total cereal production did not change significantly between 1961 and 2007. Moreover, the rice-harvested area in 2015–2016 is likely to be 160 million hectares (Mha), and it is not going to change much by 2021–2022 [1,2]. This global and almost constant rice production is making a high amount of inedible vegetable waste (residues after harvest) around the world, and therefore it has partially provided the problem of rural system sustainability. These waste streams, known as rice husk (RH), are lignocellulosic materials

that are normally burnt and used for energy production through direct combustion or gasification. However, RH can become a source of pollution without adequate treatment, leading to several environmental and health issues [3,4]. In Argentina, rice husks are commonly used for the preparation of chicken litter (ChL). This is the most common waste in terms of volume obtained from broiler chicken farming. In addition to RH, and during broiler chicken production, sawdust or shavings of eucalyptus are often mixed. It is common to reuse the litter in two or more than one rearings, even four or five rearings are frequently carried out without completely cleaning the farm. During poultry fattening, droppings, urine, feathers, and spilled feed are deposited on the base material, which contributes a high nutrient content to the final composition of the ChL. This residue is highly appreciated as fertilizer by agricultural and livestock producers in the region and by other regional

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economies. However, continuous application without some care increases environmental contamination. Despite the usual agronomic use of ChL, it is important to explore new alternatives for its management that reduce environmental pollution and give us advantages in its uses.

Poultry farming is one of the main agricultural productions in the northeastern region of Argentina. In terms of poultry meat production (broilers or broiler chickens), the departments of Uruguay, Colón, Gualeguaychú, and Paraná of the province of Entre Ríos have the largest number of farms and slaughterhouses, approximately 50% of the country's total [5]. The management of livestock production residues is a subject of growing interest for the government, farmers, producers, and the population at large. This is because urban-rural interfaces are becoming increasingly complex and society's environmental awareness is evolving more and more relevant. This has been moving upwards the interest in different processes that allow the reusing of agricultural wastes and give them added value. Hence, among the strategies for transforming wastes, pyrolysis is a promising technique that consists of thermal treatment of biomass in absence of oxygen that can generate biochar, bio-oil, and gaseous products for different applications [6]. The quantities, features, and applications of these three main products are determined by the initial conditions of the feedstock from these thermal processes [7]. According to the range of operating conditions, pyrolysis can be classified into three classes: flash, fast and slow. Generally, each of these classes favors the production of one kind of product [8–10]. The bio-oil, a dark brown liquid that is viscous and rich in oxygenated compounds, has been the subject of much research due to its important organic platform compounds with a wide variety of applications. Bio-oils can be used to produce energy by direct combustion, can be refined to produce high calorific value synthetic fuels and can also be applied to produce specific chemicals [11]. In this way, pyrolytic processes may be employed to reuse almost any biomass residue and thus reduce the environmental impact produced by wastes as well as generate high value-added products contributing to the circular economy [12].

On the other hand, hydrothermal conversions have been shown to be more cost-effective as compared to conventional thermochemical processes to upgrade lignocellulosic biomass into fuels and valuable chemicals [13,14]. In recent years, many studies on the hydrothermal product compositions and their distributions have been of great significance in lignocellulose up-gradation. Water develops into an exceptional reaction environment, reactant, and solvent for a diverse range of reactions, including those transformations in other thermal processes that require the presence of acidic or basic catalysts. The initial reaction that takes place when lignocellulosic biomass is heated up in the water is the hydrolysis of cellulose to glucose, which is the crucial difference from dry thermochemical transformation. In the same way, the degradation of lignin occurs to give phenols, among other derivatives [15–17]. With increasing temperature, water ionizes into H^+ and OH^- , favoring transformations in both acidic and basic media. Several studies have proposed that lignocellulosic macromolecules are first broken down into water-soluble molecules, and then partial water-soluble molecules are further degraded into small molecular products like aldehydes, organic acids, and gasses, or condensed into organic-soluble fractions or carbonaceous products [18–22].

Even though many studies have explored the valorization of RH for applications such as fuels, syngas, adsorbents, soil conditioner, source of anhydrosugars and silicon precursor, among others, there is not enough information on the valorization of ChL. [23] In recent years, it has been explored as a raw material for biofuels and industrial chemicals [24]. In addition, biochar produced from chicken litter pyrolysis was evaluated as an organic soil amendment, using gima kalmi (*Ipomoea aquatica*), radish (*Raphanus sativus* var. long Scarlet), soybean (*Glycine max*), corn (*Zea mays*) and winter wheat (*Triticum aestivum*), among others, as a study model [25–27]. In general, the application of biochar from ChL shows significant changes in plant growth promotion and soil biology in terms of microbial biomass. Weldekidan et al., [11] have studied the chicken-litter waste and rice husk pyrolysis at different temperatures to

investigate the thermal behavior and energy recovery potential of the feedstocks. In addition, in this work, the authors report computer-aided thermal analysis and thermogravimetric analysis to study the pyrolysis properties of each biomass in a temperature-controlled regime.

Due to the pollution problems associated with the handling of ChL and the need to valorize this waste, this work aims to evaluate its transformation by means of two thermochemical techniques, fast pyrolysis and hydrothermal conversion. An exhaustive analysis of the composition of products in the liquid phases has been carried out comparing both methodologies in order to find chemical compounds of importance for further applications.

2. Materials and methods

2.1. Chicken Litter properties

Chicken litter material (hereinafter referred to as ChL) was collected by the National Institute of Agricultural Technology (INTA) on November 18, 2020, from a broiler chicken fattening shed located in Concepción del Uruguay, province of Entre Ríos. Sampling was carried out throughout the entire shed in a zig-zag manner, taking representative sub-samples from each possible rearing situation (between lines and under the feeder and drinker lines). The total of sub-samples was mixed in a composite sample, which was refrigerated in the field and then frozen, until it was sent to the university laboratory for further processing. This material received a 44-days-old single broiler upbringing, which was loaded on November 11, 2020, i.e., one week before sampling. On November 16, 2020, the producer ground the litter. During the first 20 days of raising, some antibiotics were administered to the chicks via drinking water (with "Microflud f" florfenicol at 7 days old and "Floxagen" enrofloxacin 10% at 14 days old). The chicken litter consisted of rice husk (~55 wt%) and with what in this work we call "waste from chicken" (WCh), made by chicken droppings, urine, feathers, and spilled feed mixed as bedding material (~45 wt%). Once in the laboratory, the sample was again homogenized by mechanical mixing.

2.2. Characterization of Chicken Litter

For ChL pH determination, a Thermo Scientific OrionStar A211 model pH meter equipped with a combined electrode Orion system Ross was utilized. Instrumental calibration was performed employing 4.014, 6.994 and 9.155 pH standard buffers (Hach) at $(25.0 \pm 0.1) ^\circ C$. The starting and dried material were homogenized (with a mixer for 5 min). Then, 2.0 g were weighed, and 20 mL of Milli Q-water was added. Subsequently, the mixture was moderately stirred for 4 h, allowed to decant for 30 min, filtered (with cellulose filter paper), and finally measured with a pH meter. The obtained value was 8.392 ± 0.02 ($n = 2$).

The proximate, ultimate and inorganic ion analysis of raw ChL in comparison with RH are shown in Table 1. Carbon, Hydrogen, and Nitrogen were measured using an elemental analyzer (CHN 628 LECO corporation, Saint Joseph, Michigan USA) following the AOAC 993.13 method. This instrument uses the combustion technique to simultaneously quantify all 3 elements. The pre-weighed and encapsulated sample is placed in the carrier of the instrument and from there it passes into the main furnace containing pure oxygen for rapid and complete combustion of the sample. C, N and H present in the sample are oxidized to CO_2 , H_2O and NO_x , respectively. Through the oxygen carrier they are led to a secondary furnace for further oxidation. The combined gasses are then collected in a container known as a ballast, and a non-dispersive infrared sensor (or NDIR sensor) is used to detect the C and H. The NO_x gasses are passed through a reduction tube to reduce them to Nitrogen and it is detected by thermal conductivity. Each assay was performed in triplicate and oxygen was calculated by difference.

For ash content determination, 3.5 g of ChL was weighed and kept in an incineration oven at $500 ^\circ C$ for 2 h ($5 ^\circ C/min$) in the first step, and

Table 1
Properties of chicken litter (ChL) and its comparison with rice husks (RH).

Analysis		ChL (%) ^a	RH (%) ^b
Proximate analysis (wt%) ^c	Ash	16.8	15.5
	Fixed carbon	18.9	14.9
	Volatile matter	64.3	69.6
Ultimate analysis (wt%) ^c	C	26.5	42.1
	H	8.5	6.1
	O ^d	45.6	34.9
	N	2.6	1.2
Inorganic ions (wt%) ^e	Sodium	0.32	Nd ^f
	Magnesium	0.34	0.08
	Aluminum	0.05	0.03
	Potassium	2.54	0.46
	Calcium	0.11	0.12
	Manganese	0.04	Nd
	Iron	0.05	0.06
	Nickel	0.0007	Nd
	Copper	0.005	Nd
	Zinc	0.02	Nd

^a Chicken litter.

^b Rice husk, data extracted from Téllez et al. [23].

^c Dry basis.

^d Calculated by difference.

^e Determined by ICP analysis.

^f Not determined

then to 700 °C for 4 h (5 °C/min). Furthermore, 2.0 g of sample was weighed and placed in a hermetically sealed quartz reactor. It was heated for 6 min at 600 °C and then for 6 more minutes at 750 °C. The solid residue obtained was weighed, and the difference in weight corresponded to the Volatile Matter (VM) fraction. Finally, fixed carbon (FC) was determined on a dry basis as the difference between 100 and the sum of ash and volatile matter (VM) percentage yields, as can be seen in Eq. 1 [28–32].

$$FC (\%) = 100 - (\% \text{ Ash} + \% \text{ VM}) \quad (1)$$

The content of Na, Mg, Al, K, Ca, Mn, Fe, Ni, Cu, and Zn were determined by an Agilent 7500cx ICP-MS, equipped with an autosampler (Agilent ASX-500). Argon of quality 5.0 and Alphagaz liquid air were used. Samples were analyzed with Agilent ICP-MS Chemstation B.04.00 (G1834B) software.

ChL sample (0.1008 g) was placed in the Teflon sample holder (Berghof DAP+60) and 6.5 mL of nitric acid (Merck Suprapure 65%, Lot K50394956 825) was added. Then, it was heated to sub-boiling temperature (64–66 °C) for 24 h. The same procedure was followed for the blanks (n = 3), with empty sample holders (no sample). After reaching room temperature, the digested samples (1 mL) were diluted with 9 mL of distilled nitric acid supplemented with scandium and germanium (30 µg/L each), indium and rhenium (10 µg/L each) as internal standards, on the same day of measurement.

Calibration curves for the elements were prepared using the following commercial mixtures: Multi-Analyte Custom Grade Solution Inorganic Ventures IV-60407 and S2-MEB707330.

For data processing, the average value for each element of these blanks was subtracted from each reported sample. The limit of detection (LOD) of the reported method corresponds to 3.3 times the standard deviation of the blank values, while the limit of quantification corresponds to a value equal to 10 times the standard deviation.

Instrumental and procedural blanks were determined together with samples, and the average of five runs was obtained for each sample. Quantitative analysis was performed against calibration standards for each element. Precision (% CV) was below 3% counting five measures on the same sample.

Powder X-ray diffraction patterns (PDRX) were carried out in a diffractometer Panalytical X'Pert Pro, using a Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation with current conditions at 40 mA and voltage at 40 kV. The patterns were recorded using a pixel 1D detector with 230 canals; each

pattern was recorded between 10° and 60° in 2 θ with a step of 0.026° and with a time for a step of 92.95 s at r.t. Samples were ground into a fine powder in an agate mortar and measurements were performed on a single-crystal silicon sample holder. The patterns of ChL biomass were recorded and compared with rice husk.

FT-IR spectra of ChL were recorded as a powder sample in a KBr pellet (ThermoFisher Scientific) in the range of 4000–400 cm⁻¹. The pellet was prepared by grinding potassium bromide 99 + % FT-IR grade (Sigma- Aldrich) in an agate pestle mixing with the sample and testing different concentrations. Measurements were obtained from 32 scans with a resolution of 4 cm⁻¹. OMNIC software was used for data analysis.

2.3. Fast pyrolysis procedure

The fast pyrolysis reactions were carried out in a tubular quartz reactor under a nitrogen atmosphere. The reactor was heated externally with a tubular furnace and the temperature was regulated by a thermocouple and a controller. The reactor had a length of 25 cm and an inner diameter of 2.5 cm, which was connected to a vacuum line, where a vacuum pump gave vacuum conditions inside the reactor with pressures around the 1–5 Torr. Likewise, Nitrogen flow was circulated inside the reactor during and after the pyrolysis process at a flow of 0.1 mL/s to ensure Oxygen absence. The residence times were short (approximately 0.1 s). At the end of the hot zone in the reactor there was a condensation trap refrigerated with liquid nitrogen where the liquid products were collected. The biomass was placed in a quartz boat and a typical reaction was carried with 3–3.5 g of biomass located inside the reactor in a cool zone until the vacuum line reached the desired conditions of pressure and temperature. The reaction time was recorded from the moment in which the material was placed in the center of the high-temperature zone. When each pyrolysis reaction ended, the solid residue remaining in the boat was recovered and weighed. Likewise, the bio-oil was removed from the trap with acetone or methanol, and later evaporated, weighed and analyzed by GC-MS. The gas fraction was calculated by the weight difference between the initial mass of RH and the solid and liquid fractions. The pyrolysis reaction took 20 or 40 min and the temperatures tested were 400, 500, 600, and 700 °C.

2.4. Hydrothermal conversion procedure

The experiments were carried out in a tubular reactor which was made of stainless steel (25 mL nominal capacity, internal diameter = 30 mm; height = 70 mm) and placed in an oven fitted with an internal thermocouple. The hydrothermal processes were carried out using 11.8% wt. of biomass using a volume of 15 mL of distilled water. The reactor was purged two times with nitrogen flow to remove the inside air. Then the mixture was heated up to the designated temperature (220, 230, and 240 °C) and maintained at this temperature for 20 or 40 min. The pressure in the reactor, which was measured with a manometer connected to the reactor, was equal to the saturated vapor pressure of water at the operating temperature, between 10 and 12 MPa. Upon completion of the reaction, the reactor was cooled down and then immersed in cold water. The reaction mixture consisting of a yellowish liquid and a brownish solid was separated by filtration, using acetone in the rinsing of the solid. To obtain the oily liquid from each hydrothermal conversion, the amount of water was first reduced by evaporation under reduced pressure and then freeze-dried to constant weight. Finally, each sample was redissolved in acetone or methanol for GC-MS characterization. To determine the yield of each fraction, the solid residue and the oily liquid were directly weighed while the gaseous fraction was calculated by difference. The experiments were repeated three times.

2.5. Bio-oils characterization

Approximately 0.05 g of each bio-oil was dissolved in 3 mL of solvent (acetone or methanol) and the mixture was homogenized. The

samples were filtered with filter paper (cellulose) and transferred to 1.5 mL vials. Finally, 0.5 μL of supernatant was analyzed by GC-MS, using a QP-2020 ULTRA Shimadzu spectrometer, with a single quadrupole mass analyzer (2–1090 u.m.a) and an automatic sample injector AOC-20i. The injector temperature was 250 $^{\circ}\text{C}$ and the separation was performed using a Mega 5-ms capillary column (30 m \times 0,25 mm \times 0,25 μm). Helium was used as a carrier gas with a split injection mode, pressure as a flow control mode (65.2 kPa), and a total flow rate of 7.5 mL/min (column flow: 1.00 mL/min; linear velocity: 36.8 cm/sec; purge flow: 1.5 mL/min, split ratio: 5.0). The oven temperature was programmed from 80 $^{\circ}\text{C}$ (3 min) to 280 $^{\circ}\text{C}$ (7 min) with a heating rate of 10 $^{\circ}\text{C}/\text{min}$. The temperature of the GC-MS interface was held at 280 $^{\circ}\text{C}$ and the mass spectrometer was operated at 70 eV under electron ionization. The area corresponding to each compound is proportional to the amount of that compound in the ChL bio-oil sample. Consequently, the peak area percentage of a compound was used to compare the change in the relative amount in the different bio-oils. Different databases available in the GC-MS software solution, such as Wiley and NIST, were used to identify the compounds from the chromatographic peaks (> 85% match).

3. Results and discussion

3.1. Characterization of ChL

The composition of dried chicken litter (ChL) and rice husk (RH) as reference material [27] is shown in Table 1. Ash and fixed carbon are slightly higher in ChL (16.8 wt% and 18.9 wt%) than in RH (15.5 wt% and 14.9 wt%, respectively), while the volatile matter is larger in RH.

The ultimate analysis shows that the O and C content was dissimilar in the ChL and RH samples, ChL had a lower carbon content and a higher oxygen content relative to raw RH. Moreover, an increase in N and H content was observed for ChL. The higher content of N was due to the presence of protein-derived material in ChL.

The analysis of inorganic species showed significant differences in the amount of potassium from ChL (2.54 wt%) concerning RH (0.46 wt%). Another important variation was found in the higher magnesium content present in ChL (0.34 wt% compared to 0.08% in RH). On the contrary, slight changes in calcium, aluminum, and iron content could be observed when both biomasses were compared. The differences in the properties of these two materials could be attributed to the presence of a wide variety of organic, such as nitrogenated compounds, and inorganic components in the poultry litter (droppings, urine, feathers, and spilled feed).

The powder X-ray diffraction (PXRD) patterns acquired from samples

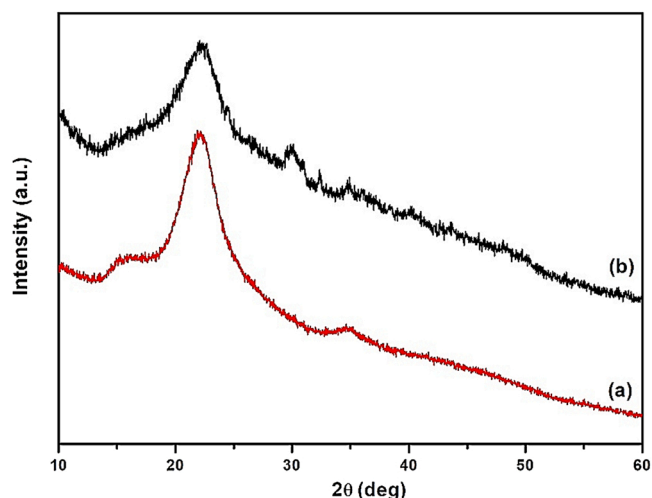


Fig. 1. PXRD profiles were obtained from: a) RH and b) ChL.

of RH and ChL are displayed, as shown in Fig. 1. A general amorphous profile could be predominantly observed in both samples, which was evidenced by the absence of well-defined peaks. Despite this, both patterns showed the same broad peak, with a maximum intensity at 22 $^{\circ}$ at 2 θ . This peak indicates that solids have mainly an amorphous structure, which can be attributed to amorphous silica and other inorganic compounds in the amorphous state, such as MgO and K₂O, in agreement with the ICP-MS analysis. On the one hand, it is known that amorphous silicon dioxide is present in rice husk [33–35], and it is an important component of the ChL material. On the other hand, a few sharp peaks appeared in ChL without being observed in the RH pattern. Although inorganic potassium and magnesium compounds are present in small quantities in RH [36], they are higher in ChL. It is known that chicken feathers present high amounts of K and Mg [37], and therefore would be one of the main ones responsible for ChL. In addition, unpublished results from our research group indicate the presence of inorganic compounds derived from K and Mg in ChL ash samples.

Concerning FT-IR analyses, ChL exhibited broad bands due to extensive overlapping of individual transmissions. The comparison between spectra of ChL and RH samples is shown in Fig. 2. The most pronounced bands in the spectrum of ChL were at 3411 (a); 2925 (b); 1655 (c); 1547 (d); 1410 (e); 1056 (f) and 770 cm^{-1} (g). The broad and intense signals associated with O-H and C-H stretching were observed in both samples between 3700 and 3000 cm^{-1} . The signal corresponding to the asymmetric stretching of the -OH group of adsorbed water molecules was slightly shifted around 1655 cm^{-1} in ChL, concerning that observed around 1633 cm^{-1} in RH. This shift could be due to the C=O stretching from the acid group or primary amides in WCh (1646 cm^{-1}). CH-stretching of aliphatic CH/CH₂ signals can be noticed at 2919 and 2925 cm^{-1} in RH, and ChL, respectively. For ChL, the C=C stretching vibration of aromatic rings (derived from lignin) also appeared at slightly displaced values (1547 and 1410 cm^{-1}) about rice husks (1510 and 1424 cm^{-1}) [38]. The stretching and bending vibrations of bonds O-Si-O were at 1056 and 770 cm^{-1} , while they were at 1023 and 798 cm^{-1} in RH. It was observed that the signal at 770 cm^{-1} was lower in ChL than in RH.

3.2. Fast pyrolysis

Fast pyrolysis of ChL was performed at different times (20 and 40 min) and temperatures (400, 500, 600, and 700 $^{\circ}\text{C}$). The yields of the products (biochar, bio-oil, and gas) are shown in Fig. 3 as a function of temperature at both reaction times (20 and 40 min). Since heat rate, pressure, and residence times remained constant, gaseous products turned out to be the main fraction (40–61 wt% yield) regardless of the evaluated pyrolysis conditions (time and final temperature). Overall, an increase in the gaseous fraction was observed with increasing temperature, both at 20 min and 40 min of reaction (from 40 to 51 wt% and 48–61 wt%, respectively). On the contrary, the solid fraction (biochar) decreased with increasing temperature (from 38 wt% to 28 wt% at 20 min, and 30–17 wt% at 40 min). For the two evaluated times, the yield of the liquid fraction reached its maximum value at 500 $^{\circ}\text{C}$ (27–28 wt%). Although the temperature range agrees with reported works on pyrolysis of ChL, e.g., Weldekidan et al. [11] obtained 37 wt% at 500 $^{\circ}\text{C}$ and Simbolon et al. [39] obtained 33 wt% of oil at 400 $^{\circ}\text{C}$ from a mechanical mixture of chicken manure and rice husk, in our case the yields were slightly lower. Compared with the results previously obtained in the research group concerning the pyrolysis of rice husks [23], it was observed that the gaseous fraction remains the largest one, with yields of between 37 and 54 wt%. In agreement with the pyrolysis of other lignocellulosic biomasses (including rice husks), ChL reactions showed that the formation of gaseous products increased with increasing conversion temperature at the expense of the liquid and solid fractions. Regarding bio-oils formation, the maximum value was achieved at 400 $^{\circ}\text{C}$ for RH giving a 34 wt% yield, a value greater than that obtained for ChL. The lower bio-oil formation observed in the ChL

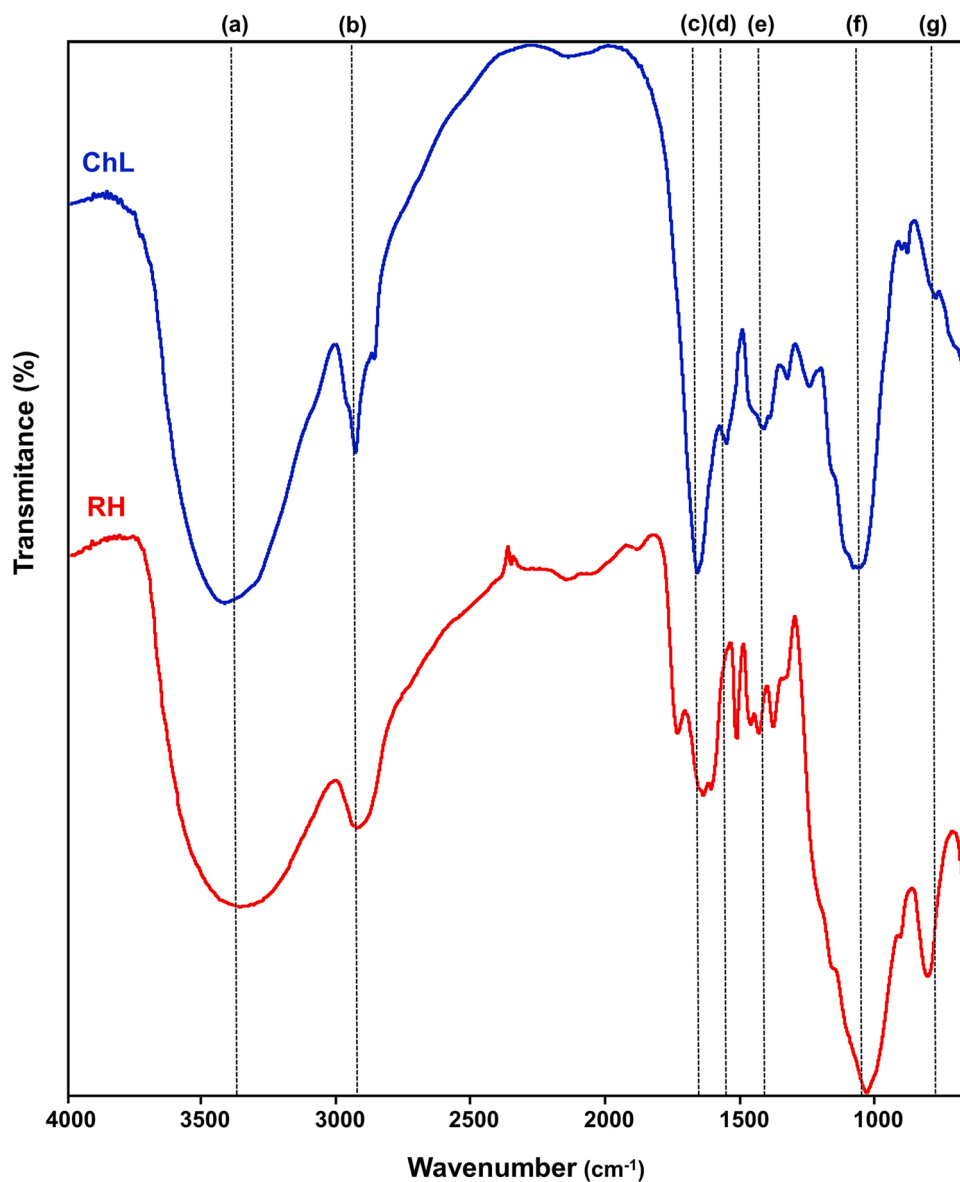


Fig. 2. FT-IR spectra of ChL (blue) and RH (red). FT-IR spectral bands (cm^{-1}): RH: 3355; 2919; 1728; 1633; 1510; 1424; 1371; 1023 and 798. ChL: (a) 3411; (b) 2925; (c) 1655; (d) 1547; (e) 1410; (f) 1056 and (g) 770.

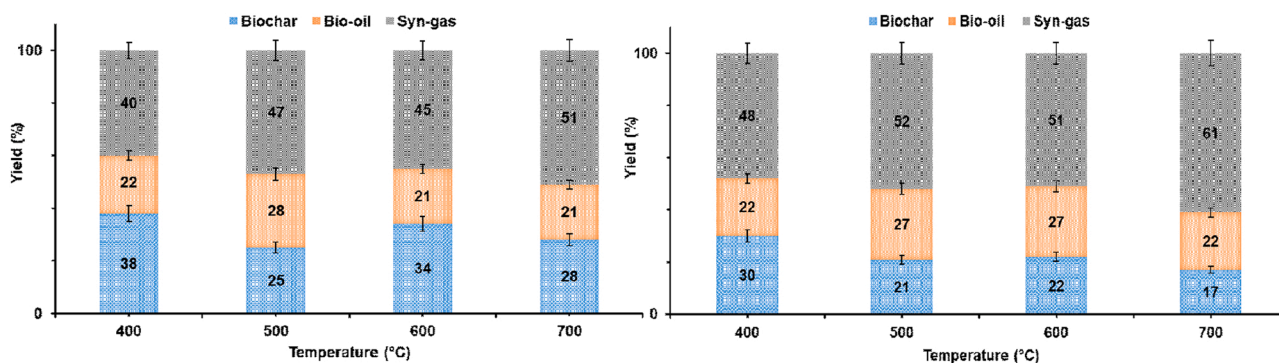


Fig. 3. Product yields from pyrolysis reactions of chicken litter at (a) 20 and (b) 40 min.

pyrolytic transformations can be attributed to the characteristics of the biomass itself. ChL had a lower C content, a higher O content, and a higher ash content than RH. Alkali metals in ash biomass catalyze

cracking reactions of pyrolytic vapors and have a considerable effect on fast pyrolysis product distribution, including the chemical composition of bio-oil [40]. It is known that inorganic compounds found naturally

within biomass favor the formation of char and gas at the expense of pyrolysis liquid yield [41]. In this case, ChL had a high content of K, Na, and Mg which may have contributed to the decrease in oil production. Thus, and according to the results obtained, the best conditions for generating bio-oil were 500 °C and 20 min experiment duration.

The composition of bio-oils from the pyrolysis of ChL was analyzed using GC-MS. When the bio-oils were extracted with acetone for analysis, it was observed that a proportion of these oils was not soluble in acetone. For this reason, we proceeded to solubilize the pyrolysates with methanol and compare both GC-MS analyses. For this purpose, the acetone extracts were evaporated to remove the solvent, and methanol was added for further analysis.

In accordance with the ion chromatograms and the main families of compounds in each bio-oil, the following groups could be categorized: aromatic (AR), oxygenated (OXY), nitrogenated (NIT), and anhydrosugar (ANH) compounds. Fig. 4 illustrates the variation of these groups of compounds with pyrolysis temperature and reaction times in acetone and methanol solutions.

Overall, aromatic and oxygenated compounds were the major product families, at all evaluated temperatures and pyrolysis experiments times. The difference in the proportion of these compounds (AR and OXY) according to the solvent used in the extraction of the pyrolysate was remarkable. Aromatics predominated at 20 and 40 min and at temperatures above 600 °C when the pyrolysate was extracted with acetone; while a predominance of oxygenated compounds was observed when methanol is used as the extractive solvent.

It was noted that AR gradually increased with the increase in temperature. In all cases, the increase in temperature led to a higher AR

formation, reaching a maximum of 49% of the total peak area at 600 °C and 700 °C (acetone extract), at reaction times of 40 min (Fig. 4.b). It is noticeable that a lower number of aromatic compounds was detected in the methanolic extracts, reaching a maximum of 39% of the total ion chromatogram at 700 °C and 20 min (Fig. 4.c).

Among the main AR, phenol and guaiacol were found at all evaluated temperatures. In addition, cresols, 4-vinylguaiacol, and xylenols were found in the pyrolysates. It is known that phenol derivatives are produced from the thermal degradation of lignin at temperatures higher than 400 °C. Several studies of lignocellulosic biomass indicate values of 30–60% peak area determined by GC-MS correspond to phenolic compounds [42–45]. In the case of RH pyrolysis, the amount of AR gradually increased with the increase in temperature, reaching a maximum of 27% of the total area at 700 °C. Based on this background, the formation of AR from ChL would not only come from the degradation of the lignin present in the RH but also the rest of the organic matter in the ChL.

Several oxygenated compounds (OXY) were identified in the bio-oils, due to thermal degradation of cellulose and hemicellulose from rice husk [44,46] and from other components of ChL. As opposed to the aromatics just described, OXY gradually decreased with the increase in temperature, giving area values between 39% and 64% at the lowest evaluated temperature (400 °C). Although this trend was observed in the pyrolysis carried out at both 20 and 40 min and in the chromatograms of both extracts (in acetone and methanol), the decrease in oxygenates was more marked in the reactions carried out for 20 min. Although the type of oxygenated derivatives identified depended on the reaction condition, the main one was palmitic acid, regardless of the experimental setting. Nevertheless, other fatty acids such as oleic acid

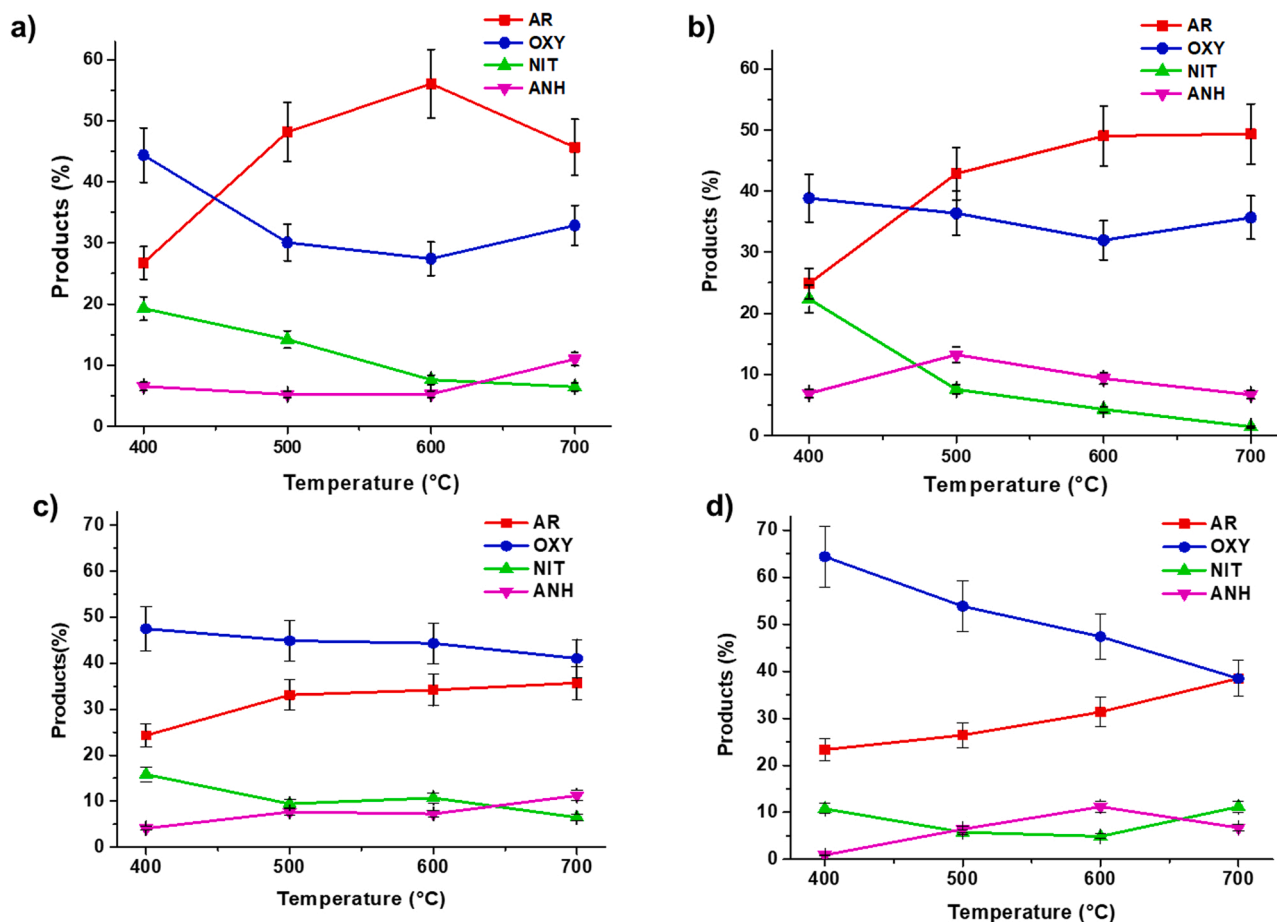


Fig. 4. Composition of bio-oils from ChL pyrolysis, analyzed by GC-MS technique: a) Acetone extract, reaction time: 20 min; b) Acetone extract, reaction time: 40 min; c) Methanol extract, reaction time: 20 min and d) Methanol extract, reaction time: 40 min. AR: aromatic compounds, OXY: oxygenated compounds, NIT: nitrogenated compounds, and ANH: anhydrosugars.

and stearic acid were also present to a considerable extent. The formation of these fatty acids was relevant at 400 °C, obtaining in the chromatograms 35% of the total ion area for these derivatives, 16% of this area corresponding to palmitic acid. When comparing the acetone and methanol extracts, a higher concentration of these acids in methanol could be observed, due to its better solubility properties in alcohols. These fatty acids mainly came from chicken litter's oily secretion product of the uropygial (green) gland [47]. Moreover, recent studies by the research group indicate that both pyrograms obtained from analytical pyrolysis and pyrolytic bio-oils from RH yield fatty acids, although in proportions of less than 5% of the total peak area. Among other oxygenated products, pentanal, *cis*-9-hexadecenal, 2-hydroxy-3-methyl-2-cyclopenten-1-one, and 2,3-dihydro-benzofuran were found in the ChL bio-oil, using both solvents. Many of these oxygenated compounds were also detected in the bio-oils generated in the pyrolysis of RH [23].

Nitrogen compounds (NIT) and anhydrosugars (ANH) were found in area values lower than 19% and 11%, respectively. Xanthosine and levoglucosan (LG) were the representative products of each family. Although LG was the main sugar detected, it was found in very small quantities (around 5–8% of the total area). This finding was surprising considering that in bio-oils derived from RH pyrolysis, anhydrosugars were the main products (44% and 47% of the total area between 400 and 500 °C) and LG accounted for about 90% of the total sugars [23]. The results obtained here would indicate that the residual material from chicken farming (organic and inorganic) would inhibit the formation of sugars by degradation of the cellulose of the rice husk constituent of the chicken litter. This is in line with studies that show that the formation of LG from cellulosic biomass is highly dependent on the presence of other components in the biomass, either inorganic (alkaline) ions or other species, which can almost completely inhibit the production of this sugar [48–51].

Finally, other compounds were detected in the bio-oils, although in smaller quantities than 8% of the total area, so they were excluded from Fig. 4. Among them, saturated and unsaturated long-chain hydrocarbons, sterol derivatives, sulfur- and halogen-derived compounds were identified.

To evaluate which products came from the pyrolysis of chicken waste (feces, urine, feathers among others), this material was manually separated from the chicken litter and subjected to pyrolysis conditions. This residue was referred to as WCh (waste from chicken), which was crushed and pyrolyzed at 500 °C for 20 min. These conditions were chosen taking into account the best bio-oil yields obtained for ChL.

The product yields in the pyrolytic transformation of WCh were: 52 wt% of gas fraction, 26 wt% of solid carbonaceous fraction and 22 wt% of bio-oil. These values were very similar to those found in the pyrolysis of ChL, with a slight decrease in the amount of bio-oil (22 wt% for WCh versus 28 wt% for ChL).

The composition of the pyrolytic liquid was analyzed by GC-MS using acetone or methanol to dissolve the liquid fraction, as was done for ChL. Oxygenated compounds were the predominant compounds in both extracts, 56% of the total area for acetone extract and 57% of the total area for methanolic extract. Palmitic acid was the main compound, showing 27% of the total area in the acetone extract and 19% of the total area in the methanol extract. Furthermore, 13% and 9% of oleic acid were found when acetone and methanol were used; while 8% and 6% in the case of stearic acid, in each order. Comparing these results with those obtained for ChL, a higher proportion of these fatty acids was observed in the bio-oils derived from WCh indicating that these compounds came mostly from the WCh portion.

Looking at the aromatics, 19% of the total ion chromatogram was obtained for the acetone extract and 15% for the methanol extract. Compared to ChL, the number of aromatics was much lower, this can be attributed to the fact that the proportion of lignin in WCh is much lower than that found in ChL. Among the major compounds found in WCh, phenol and 2-methyl phenol (from the cresol family) were the major

compounds in the methanol and acetone extracts, respectively. In methanol, other compounds were found in significant amounts such as guaiacol, 4-vinylguaiacol, and cresols; while in acetone, phenol, xylenols, and 4-vinylguaiacol were identified. All these compounds were also detected in ChL.

Nitrogenated derivatives were found in a lower proportion than in ChL-derived bio-oils. The purine nucleoside xanthosine was the major compound detected (12% of the total area in the methanol extract and 10% of the total area in the acetone extract) as in ChL. Anhydrosugars, on the other hand, did not exceed 2% of the total ion chromatogram, which is consistent with the decrease of cellulosic material in WCh compared to ChL. Other main compounds detected in the pyrolytic liquids were sterol derivatives (14% of the total area in acetone) and *N*-methyl glyphosate (8% of the total area in methanol). In the case of sterols, these metabolites are known to be eliminated in bird feces and urine. In the case of the glyphosate derivative, the presence of this compound in the bio-oil was surprising. This result would show that these birds were probably exposed to herbicides of the glyphosate family and have eliminated them through urine. In literature, the presence of glyphosates in the urine of domestic animals has been studied, suggesting widespread exposure of pets through food, drinking water, and outdoor activities [52].

3.3. Hydrothermal conversion of ChL

The hydrothermal reactions were carried out under the following conditions: 220 °C (40 min), 230 °C (40 min), and 240 °C (20 and 40 min). No large variation in the amount of bio-oil was observed with either temperature change or reaction times, as the yields were between 13 and 23 wt% (Table 2). These values were lower than those obtained in fast pyrolysis, perhaps due to the freeze-drying process in which volatile condensable liquids may be lost during water sublimation. Regarding the solid fraction, it was predominant at all evaluated conditions and decreased significantly when the time of reaction was duplicated. The gaseous products were the second most important fraction, with an increase in their formation observed at the highest temperature and time evaluated.

Variations in the compositions of the liquid fractions were observed according to process temperature and time. In addition, it should be noted that the liquid residues resulting from the water extraction by freeze-drying were not completely soluble in acetone, generating complications for the analysis of all the components by GC-MS. For this reason, it was evaluated to completely dissolve the liquid concentrates with methanol and perform the GC-MS analysis again. In these bio-liquids, the main families of compounds were oxygenated (OXY), aromatics (AR), and long-chain hydrocarbons (LCH). Other compounds that did not belong to these families were classified as "Others" (see Fig. 5).

It was observed that in the case of acetone-soluble compounds, long-chain hydrocarbons predominated at 220 °C, 230 °C, and 240 °C (20 min), with aromatic derivatives being the second most important. In the case of the oil from the reaction at 240 °C with a longer reaction time (40 min), aromatics predominated in addition to other types of compounds (sterol derivatives and terpenes). In the case of bio-oils dissolved in methanol, oxygenated compounds were observed to be the majority in all cases, with the highest proportion found at 240 °C at

Table 2
Distribution of products in hydrothermal processes of chicken litter (ChL).

T (°C)	Time (min)	Oil fraction	Solid fraction	Gas fraction
220	20	13 ± 1	68 ± 7	19 ± 2
	40	15 ± 1	61 ± 6	24 ± 3
230	20	13 ± 1	65 ± 7	22 ± 3
	40	18 ± 2	56 ± 5	26 ± 4
240	20	15 ± 1	61 ± 6	24 ± 3
	40	23 ± 2	50 ± 5	27 ± 4

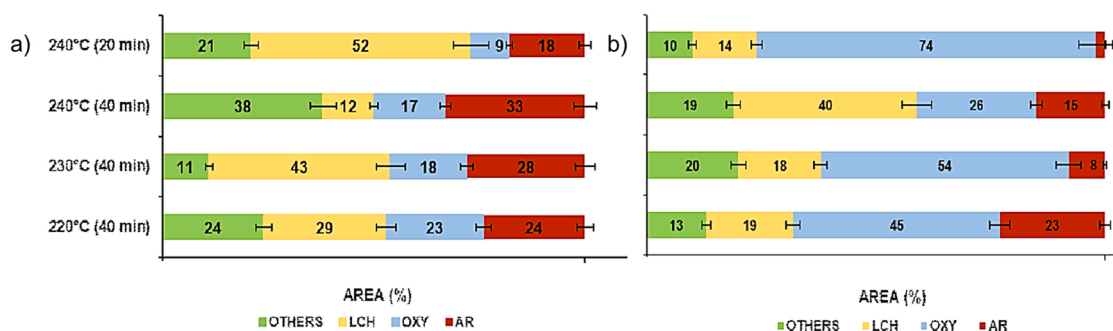


Fig. 5. Composition of bio-oils from ChL hydrothermal conversion, analyzed by GC-MS technique: a) Acetone extract and b) Methanol extract. LCH: long-chain hydrocarbons, OXY: oxygenated compounds, and AR: aromatic compounds.

20 min

Mainly saturated and unsaturated C9-C18 hydrocarbons were found in the oils extracted with acetone and methanol. For example, undecane, nonane, and tridecane were the major compounds in the acetone extract of the reaction at 240 °C (20 min) and in the methanolic extract of the reaction at 240 °C (40 min). It should be noted that LCH were very minor products in the ChL pyrolysates, which would indicate that at lower biomass transformation temperatures, as in hydrothermal conversion, the formation of these hydrocarbons is feasible, whereas under fast pyrolysis conditions LCH can fragment to give low molecular weight compounds.

Among the aromatic compounds, phenols are the major ones, particularly 4-vinyl guaiacol, 3-(2-hydroxyphenyl)-2-propenoic acid and salicylate derivatives (octyl and homomenthyl salicylate). Guaiacols were also detected in the bio-oils from the fast pyrolysis of ChL while salicylate derivatives were only detected in the hydrothermal reactions. In this respect, octyl salicylate has been reported as one of the VOCs in the rice gelatinization process [53].

Looking at the OXY composition, carboxylic acids were predominant, e.g., in the methanol extract of the 240 °C (20 min) reaction, the area corresponding to palmitic acid represented 50% of the total area of all detected compounds. These results show that the formation of palmitic acid was favored in the wet pyrolysis conditions, at moderate temperatures and not very long reaction times. Comparing the proportion of palmitic acid in the reactions carried out at 240 °C for 20 and 40 min, it is observed that the amount of fatty acid decreased drastically with increasing reaction time (18% of the total area at 40 min). Probably the increase in time leads to a degradation of the acid into compounds of lower molecular weight. Moreover, in all the extracts evaluated, oleic and stearic acids and esters of other acids were found in smaller proportions.

Within the 'Others' group, nitrogen-containing compounds were found in the first place of relevance, followed by terpene derivatives and, in much lower proportion, some halogenated compounds.

4. Conclusion

The fast pyrolysis and hydrothermal conversion of chicken litter were extensively studied. The results derived from fast pyrolysis were compared with those obtained from the pyrolysis of rice husk, which is the main component of poultry litter.

Bio-oil production was higher using the dry pyrolysis technique (21–28 wt%) compared to the wet pyrolysis (16–22 wt%). In both cases, the bio-oil yield was lower than that obtained using rice husk as starting material. The optimum conditions to achieve the highest oil yield were 500 °C and 20 min reaction time using fast pyrolysis.

The composition of the bio-liquid was highly dependent on the thermal method used in the biomass conversion and the conditions used in each type of conversion. The liquid fractions obtained from both dry and wet pyrolysis were dissolved in acetone (partially) or in methanol

(totally), and differences were also observed in the composition of these extracts according to GC-MS analysis.

In the fast pyrolysis reactions, phenol derivatives were the major compounds in the experiments carried out for 20 min at 500–700 °C; while oxygenates were the major compounds in the experiments carried out for 40 min at 400–700 °C. Among the oxygenated derivatives, the presence of fatty acids, especially palmitic acid, was highlighted. Although the presence of fatty acids has been detected in the pyrolytic liquid derived from the fast pyrolysis of RH, the amount is significantly lower than that found in the ChL bio-oils. By pyrolysis of chicken waste (WCh), which was separated from rice husk in the ChL, a bio-oil highly enriched in fatty acids was obtained. This could be explained by a high lipid content in WCh.

Furthermore, it was observed that the formation of anhydro-sugars from the lignocellulosic fraction of ChL (mainly RH) was practically inhibited, probably due to the presence of various organic and inorganic species in ChL.

In the case of hydrothermal treatment of ChL, it was possible to obtain bioliquids enriched in fatty acids, mainly palmitic acid, at much lower temperatures than fast pyrolysis. In addition, long-chain hydrocarbons and aromatics were present in the bioliquids in moderate amounts and could be efficiently extracted using acetone.

Both fast pyrolysis and hydrothermal conversion are processes that allow obtaining high value-added products from agro-industrial waste such as chicken litter. Each of the techniques has advantages and disadvantages, for example in dry pyrolysis the bio-oil is obtained without any type of work-up although the conversion temperatures are higher, while in wet pyrolysis the recovery of bio-oil is more complex although the conversion temperatures are lower, reducing the energy cost of the process.

CRedit authorship contribution statement

Erica M. Pachón Gómez: Investigation, Methodology. **Rodrigo E. Domínguez:** Investigation, Methodology, Conceptualization, Writing. **Débora López:** Investigation, Methodology, Validation, Writing. **Jhoan F. Téllez:** Investigation, Methodology, Formal analysis. **Marcos Marino:** Investigation; Methodology. **Natalia Almada:** Methodology, Resources. **Juan M. Gange:** Methodology, Resources. **E. Laura Moyano:** Conceptualization, Visualization, Funding acquisition, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

No data was used for the research described in the article.

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