

# Pyrolysis of Red Eucalyptus, Camelina Straw, and Wheat Straw in an Ablative Reactor

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**ABSTRACT:** The purpose of this study is to produce and characterize biomass pyrolysis liquids obtained in an ablative bed reactor at laboratory scale. The feedstocks selected include eucalyptus (*Eucalyptus tereticornis*) chips, camelina (*Camelina sativa*) straw pellets, and wheat (*Triticum aestivum*) straw pellets. Pyrolysis experiments were carried out at 550 °C and atmospheric pressure with a nitrogen flow rate of 2.24 N L/min and an average solids feeding rate of 2.5 g/min, yielding 42.4, 48.8, and 41.0 wt % liquids for eucalyptus, camelina straw pellets, and wheat straw pellets, respectively. Such liquids, also known as bio-oils, were characterized using gas chromatography–mass spectrometry and complemented with water content, pH measurements, higher heating values, viscosity, and proximate, and ultimate analyses. The distribution of products and their properties were influenced by both the raw materials characteristics (chemical composition and structure) and the operating conditions used in the experimental setup. With regard to raw material characteristics, features such as fixed carbon content in raw biomass seemed to impact the amount of solid products obtained as in the case of eucalyptus chips, which was the sample with higher fixed carbon content and the one that yielded a greater amount of solids. On the other hand, the experimental setup conditioned the results in the sense of how devolatilization of the materials took place, which in turn influenced the yield to liquid products obtained from the process. Wheat straw yielded a bio-oil with a significant number of unknown molecules in the organic phase (~32.8 wt %), most likely produced from the protein fraction of this biomass. On the other hand, eucalyptus resulted in a larger fraction of carbonaceous residues (~37.1 wt %), while wheat and camelina straw produced around 28.1 and 25.5 wt %, respectively. Finally, camelina presented interesting characteristics as feedstock for pyrolysis due to its low nitrogen content (0.4–0.5 wt %) and lower char yields (~25.5 wt %).

## ■ INTRODUCTION

Biomass is the most abundant source of renewable carbon on the planet. However, large scale conversion processes to transform this raw material into either valuable chemicals or energy in an economic and sustainable manner remains unsolved. Finding alternatives that can overcome this issue is essential in the long term as environmental concerns and more stringent regulations arise around the utilization of fossil-derived feedstocks. For instance, lignocellulosic biomass and its residues are especially important in the strategic roadmap for the production of renewable fuels and chemicals. These feedstocks can be produced in large quantities using non-agricultural land, avoiding the issues of food versus energy.

Lignocellulosic biomass can be converted into more valuable commodities, in the form of energy and/or chemicals, via a number of thermochemical processes, such as gasification, carbonization, and pyrolysis. In the past 30 years pyrolysis technologies at moderate temperatures of around 500 °C and short reaction times have gained considerable interest, primarily because of the advantageous energy densification achieved in the process, which yields a major liquid fraction known as pyrolysis liquids or bio-oil. These liquids can be used directly or processed for heat, power, biofuels, and chemicals.<sup>1–3</sup> The uses and applications of bio-oil and its fractions have been periodically reviewed and discussed.<sup>3,4</sup> For example, the complex mixture of carbohydrates and oxygenated compounds in the aqueous fraction of bio-oil includes valuable aldehydes

(particularly glycolaldehyde), carboxylic acids, and phenolic compounds that have great interest from an industrial point of view. It is particularly noteworthy mentioning the current industrial use of the aqueous fraction of bio-oil for the production of a series of commercial food flavoring and meat browning agents by companies such as Red Arrow (Manitowoc, WI, USA).

In 2012–2013, two large scale biomass catalytic pyrolysis and fast pyrolysis plants were commissioned in Mississippi (USA) and Joensuu (Finland) by the companies Kior and Fortum Power-Heat Oy, respectively.<sup>5</sup> These two plants are envisaged to produce 180,000 and 50,000 tonnes/year of biomass pyrolysis liquids, respectively. Other numerous efforts at demonstration and full scale are currently under development by various companies, as can be checked in recent news, publications, and reports from IEA Bioenergy—Task 34 on Pyrolysis.<sup>6,7</sup> In this context, the current scenario necessarily imposes the implementation of a biorefinery strategy to make biomass an economically feasible and sustainable business. Therefore, apart from developing integrated processes for producing a whole set of valuable products and commodities from the different process streams, it is essential to explore alternative raw materials and resources for the development of

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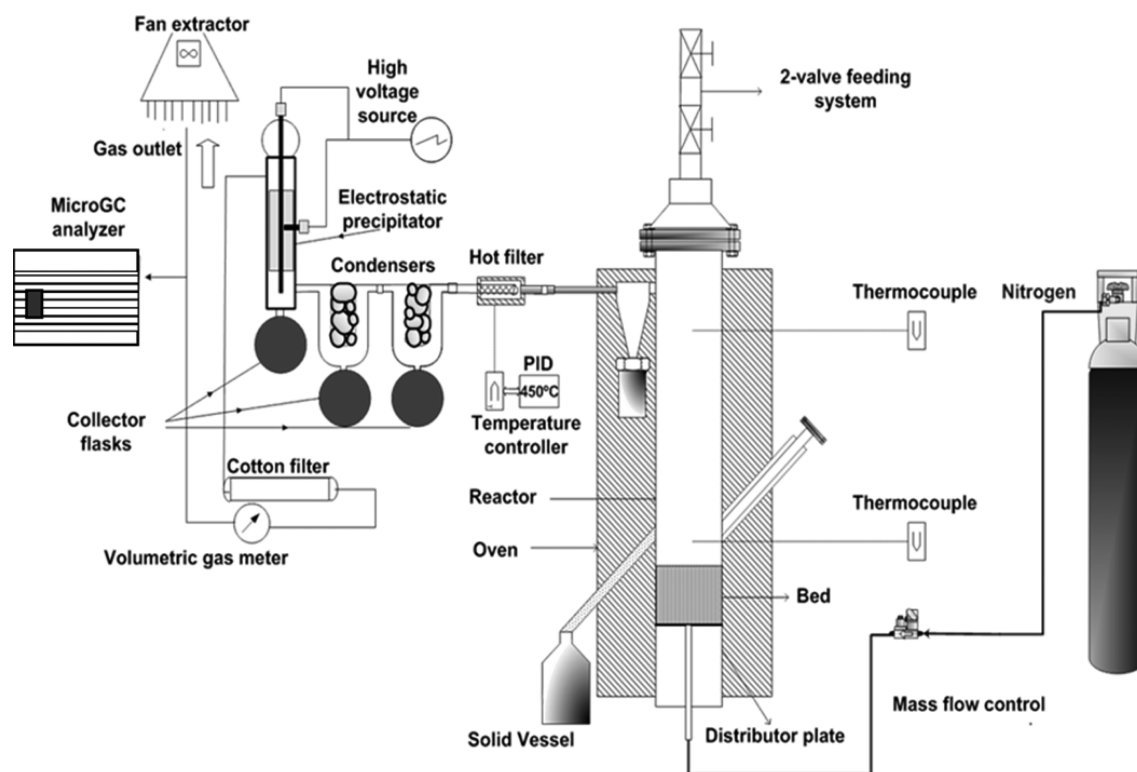


Figure 1. Schematic diagram of the pyrolysis experimental installation.

economically viable biobased industrial processes. In addition, it is expected that biomass will contribute with around two-thirds of the renewable energy requirements by 2020. Achieving this goal requires the identification of feedstocks that can be readily produced in nonagricultural land and require low irrigation and reduced downstream refinement, i.e., contain lower concentrations of nitrogen, phosphorus, and sulfur. In the field of pyrolysis for the production of liquid, significant efforts have been directed to the study of woody biomass due to its consistency and comparability between tests. Nevertheless, any type of biomass could be used as feedstock for this purpose.<sup>8,9</sup> Hence, in addition to woody biomass, fast growing crops with low cost and high productivity are interesting candidates. In this study eucalyptus, camelina straw, and wheat straw were selected due to their relatively easy production in considerable amounts in nontropical weather.

On the one hand, short rotation woody crops such as eucalyptus have been regarded as materials with great potential for energy production. Eucalyptus is a fast growing source of wood largely used in the paper and pulp industry, producing residues that are potential candidates for pyrolysis.<sup>10–12</sup> On the other hand, camelina is a spring annual oilseed plant of the genus *Cruciferae* that grows well in temperate climates. The grains of camelina are crushed to obtain oil, which is rich in polyunsaturated fatty acids (16.9% linoleic, 35.2%  $\alpha$ -linolenic, and 1.6% erucic acid).<sup>13,14</sup> The residual cake from the oil extraction process is used as nutritional supplement for animal feed due to its high content in protein and omega-3 fatty acids.<sup>15,16</sup> The stalk and straw account for 70% of the total plant and are considered agricultural waste. This stream, however, is composed primarily of lignocellulose that can be liquefied via pyrolysis to bio-oil for the production of fuels upon catalytic upgrading.<sup>17</sup>

Wheat straw is primarily used in the production of livestock blending for animal feed in combination with protein-rich feeds.<sup>18–20</sup> More recently, the development of chemical and thermal revalorization strategies have drawn attention from the scientific community due to its large availability in nontropical climates.<sup>9,21,22</sup> For instance, pyrolysis conversion of this feedstock has been explored in several studies to determine the suitability of wheat straw by comparing its yields and product characteristics to other biomass feedstocks.<sup>8,23,24</sup> However, very few efforts have been made in analyzing the effect of the biomass structure and composition (proteins content) on the characteristics of pyrolysis oil.

The present contribution is aimed to produce and characterize biomass pyrolysis liquids from three different feedstocks: eucalyptus, camelina straw, and wheat straw. Having in mind a potential industrial application for the process, the raw materials were subjected to the least number of necessary pretreatments or preconditioning steps in order to successfully feed them into the reactor.

In order to identify possible differences between pyrolysis oil properties and biomass characteristics obtained, an ablative bed reactor at laboratory scale was employed. It is anticipated that composition and structural properties of the different biomasses will have a direct effect on the characteristic of the pyrolysis oil, which will be critical in the selection and optimization of downstream upgrading processes.

## EXPERIMENTAL SECTION

**Raw Materials.** Three different types of biomass were selected as feedstocks for this study: red eucalyptus (*Eucalyptus tereticornis*), camelina (*Camelina sativa*) straw, and cereal straw (wheat, *Triticum aestivum*). Eucalyptus samples were received in the form of chips of 1–6 cm long which were directly fed to the pyrolysis system. In the case of camelina and wheat straw the received samples were first milled to reduce its size under 2 cm in an industrial hammer mill. The obtained

Table 1. Ultimate and Proximate Analyses and HHV of Feedstocks, Confidence Interval at 90%

analysis	eucalyptus chips <sup>b</sup>	camelina straw <sup>b</sup>	wheat straw <sup>b</sup>	camelina straw pellets	wheat straw pellets
ultimate analysis (wt %)					
C	[42.1, 43.7]	[39.6, 41.8]	[39.1, 40.6]	[41.9, 44.3]	[41.5, 43.1]
H	[5.5, 6.0]	[5.5, 5.8]	[5.3, 5.5]	[5.4, 5.9]	[5.4, 5.6]
N	[0.0, 0.1]	[0.4, 0.5]	[0.5, 0.6]	[0.0, 0.5]	[0.0, 1.4]
S	[0.0, 0.1]	[0.1, 0.2]	[0.1, 0.2]	[0.0, 0.1]	[0.1, 0.2]
O <sup>a</sup>	[50.1, 52.4]	[51.7, 54.4]	[53.1, 55.0]	[49.2, 52.7]	[49.7, 53.0]
proximate analysis (wt %)					
moisture	[10.2, 11.1]	[10.4, 11.1]	[8.7, 8.8]	[6.0, 9.2]	[4.2, 6.7]
volatile matter	[71.5, 73.6]	[72.1, 75.8]	[66.5, 70.9]	[82.9, 84.8]	[76.6, 85.1]
ash	[1.1, 1.8]	[5.8, 6.2]	[7.7, 8.6]	[2.1, 2.8]	[4.2, 4.9]
fixed carbon <sup>a</sup>	[13.5, 17.2]	[6.9, 11.7]	[11.7, 17.1]	[3.2, 9.0]	[3.3, 15.0]
HHV (MJ/kg)	[17.1, 17.6]	[15.1, 15.5]	[15.3, 15.7]	[16.6, 17.1]	[16.2, 16.9]

<sup>a</sup>Calculated by difference. <sup>b</sup>As received.

material was sieved, and the fraction of particles above 500  $\mu\text{m}$  was further milled in the laboratory with a hammer mill and sieved afterward to separate the fraction with a particle diameter between 250 and 500  $\mu\text{m}$ . This fraction was used to produce camelina and wheat straw pellets, which were obtained by mixing the straws with a solution of starch in water (starch content, 16.6 wt %) in a proportion of 1:8, respectively. Pellets were molded to 3.5 cm long and 2.5 cm of diameter in order to successfully feed these materials into the experimental system while aiming at minimizing the influence of biomass particle size. After forming the pellets using the starch solution, these were dried overnight in an oven at 104 °C and contained a final starch content of approximately 22% for camelina pellets and 27% for wheat straw pellets, respectively.

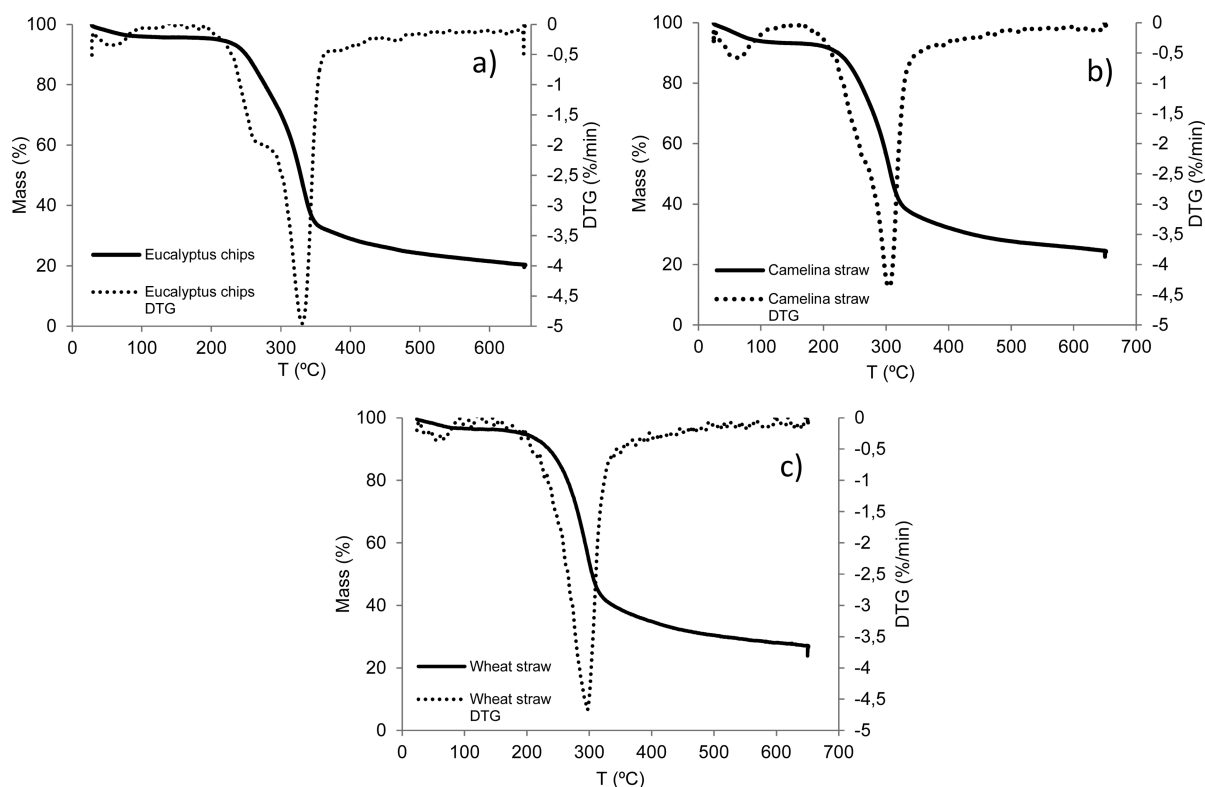
The starch used as binder in the preparation of pellets and washed sea sand utilized as heat transfer material were obtained from Sigma-Aldrich. The calibration of the microGC system was performed employing certified reference gas mixtures containing CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>2</sub>, H<sub>2</sub>S, H<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and CO.

**Experimental Setup.** Pyrolysis experiments were carried out in a pyrolysis installation consisting of a feeding system, reaction zone, condensing system, and online gas analysis setup. Figure 1 shows a schematic diagram of the experimental pyrolysis installation. Eucalyptus chips, camelina straw pellets, and wheat straw pellets were selected as feedstocks and fed into the reactor using a two-valve system installed at the top of the reactor. The feeding system enables a semicontinuous feeding mode, with an average solids feeding rate of 2.5 g/min. The tubular reactor is made of refractory steel (AISI 310) with a total length of 1270 mm. It is composed by two parts, a dense zone with an inner diameter of 40 mm and a freeboard zone with an inner diameter of 70 mm. The reactor also contains a perforated distributing plate situated 340 mm over its bottom, with 1 mm holes in it. In addition, there is a side tube 310 mm over the distributing plate which serves as overflow and collects the unreacted solids from the reactor discharging them into a char pot. The reactor is heated by an electric furnace, and the temperature is controlled in the solids bed with a K-type thermocouple and a proportional-integral-derivative (PID) temperature controller, which allowed the dense zone and freeboard zone to be maintained at 550 and 500 °C, respectively. Sand is laid as a hot fluidized bed in the dense zone, on top of which the devolatilization of the biomass particles takes place. In a typical experiment ca. 180 g of sand (particle size of 250–300  $\mu\text{m}$ ) is placed on top of the distributing plate prior to reaction, in order to obtain a bed height of 10 cm (one-third of the total height of the dense zone). N<sub>2</sub> is used as fluidizing agent, sweeping gas for a rapid evacuation of the pyrolysis vapors from the reactor, and internal standard for online quantification of noncondensable product gases. N<sub>2</sub> flow is controlled using a 10 L/min Bronkhorst mass flow controller, calibrated for the experimental conditions so as to provide a N<sub>2</sub> flow rate of 2.24 N L/min. The vapors and gases produced leave the reactor and flow through a cyclone and a hot filter, at 500 and 450 °C, respectively, in which solid particles swept by the gas are collected. Next, gases and

vapors pass through two ice-cooled condensers and an electrostatic precipitator, in which water and condensable organic compounds are collected. A cotton filter is placed after the precipitator in order to remove small particulates. The volume of the gas produced is measured by a volumetric flow meter.

**Characterization of Raw Materials and Products.** The characterization of the three biomass feedstocks selected included the following analyses: proximate analysis, ultimate analysis, measurement of the heating value, and thermogravimetric analysis (TGA). Ultimate analysis was carried out in an elemental analyzer (Leco TruSpec Micro) in order to determine carbon, hydrogen, sulfur, and nitrogen content in the material, thus calculating oxygen by difference. Proximate analysis was carried out to characterize the material with regard to moisture, ash, volatile matter, and fixed carbon content. Moisture, ash, and volatiles were determined according to the following European standards: UNE-EN 14775:2013 (determination of ash content), UNE-EN 32002:1995 (moisture), and UNE-EN 14774-1:2010 (volatile matter). Fixed carbon content was calculated by difference. The heating value of the feedstocks was measured in a Ika-Werke C2000-basic calorimeter, and TGA was carried out in a thermal analyzer (Netzsch STA 449 F3 Jupiter) using 100 mL/min N<sub>2</sub> as carrier, with heating rate of 5 °C/min, from room temperature to 650 °C, and the temperature was maintained at 650 °C for 1 h.

The solid, liquid, and gaseous products were also characterized using different techniques. On the one hand, solid products were characterized following the same procedure and using the same equipment as with raw materials: heating value, ultimate analysis, and proximate analysis were determined. On the other hand, the liquid products recovered from the two ice-cooled condensers and the electrostatic precipitator in each experiment were mixed together, forming the liquid that will be referred to as bio-oil. When centrifuged, bio-oils separated into two main phases (and a third thin and discontinuous upper layer), which were also characterized. The following properties of these bio-oils and separated phases were measured: viscosity at 40 °C, H<sub>2</sub>O content of bio-oil and bio-oil heavier phase, ultimate analysis, heating value, pH, and the composition of the two main phases obtained after centrifugation for each bio-oil. Viscosities were measured in a Cannon-Fenske routine viscometer (Cannon Instrument Co., model 150 T845) at 40 °C following the standard method EN ISO 3104. The water content was determined by means of Karl Fischer titration (Mettler-Toledo V20 volumetric KF titrator) and the pH was measured with a pH meter. The aqueous and organic phases of bio-oil were separated by centrifugation, and afterward they were analyzed by GC-MS (Agilent 7890 GC-system, model G3440A, equipped with a 5975C mass spectrometer detector. The column for the aqueous phase was an Agilent HP-FFAP, with 0.20 mm inner diameter, 50 m length, and 0.33  $\mu\text{m}$  film thickness. The column for the organic phase was an Agilent DB-17 ms, with 0.25 mm inner diameter, 60 m length, and 0.25  $\mu\text{m}$  film thickness).



**Figure 2.** Thermogravimetric analysis of feedstocks (TG and DTG): (a) eucalyptus; (b) camelina straw; (c) wheat straw. Conditions: 100 mL/min  $N_2$ ; heating rate, 5 °C/min, from room temperature to 650 °C, T maintained at 650 °C for 1 h.

Also, the composition of noncondensable gas products ( $N_2$ ,  $H_2$ ,  $CO_2$ ,  $CO$ ,  $CH_4$ ,  $C_2H_2$ ,  $C_2H_4$ , and  $C_2H_6$ ) was analyzed online with a MicroGC gas chromatograph (Agilent M3000 series, model G2801A) equipped with two analysis modules (PlotU and MolSieve 5A) and TCD detectors.

## RESULTS AND DISCUSSION

**Characterization of Raw Materials.** The characterization of the physicochemical properties of the three biomasses was performed in order to identify the relationship of pyrolysis liquid composition and feedstock. Table 1 summarizes the ultimate, proximate, and higher heating value (HHV) analyses of the feedstocks (eucalyptus chips, camelina straw, wheat straw, and the corresponding pellets) with a confidence interval of 90%. It can be noted that the elemental compositions of the three feedstocks selected are fairly similar. If any, it should be pointed out that, in the case of wheat straw pellets, sulfur and nitrogen contents were higher than in the case of the other two materials. In contrast, some differences can be observed in the proximate analysis of the raw materials. While the moisture of the “as received” samples was fairly similar, the procedure followed in the production of pellets (for wheat and camelina straw) included a drying step to remove the excess of water–starch solution used as binder. Therefore, eucalyptus chips had higher moisture than the final straw pellets fed to the pyrolysis reactor.

In addition, eucalyptus presented higher fixed carbon content whereas wheat straw pellets presented a higher content of ash and volatile matter. The former is a known characteristic of several straws when compared to woody biomass,<sup>8,23,25</sup> while the latter is increased in this study with the addition of the starch to prepare the pellets. As for the energy content, herbaceous crops typically present inferior heating values than

woody biomass,<sup>23</sup> which is in agreement with the HHV obtained for the materials as received. Furthermore, it can be observed that pelletizing of the straws can increase HHV, probably due to the use of starch as a binder.

Figure 2 shows the TG analyses of eucalyptus chips, camelina straw, and wheat straw. If DTG curves are analyzed, some differences can be observed. For the wheat and camelina straws the main weight loss occurs at around 300 °C, which can be probably connected to the decomposition of hemicellulose and cellulose.<sup>9,26</sup> In the case of eucalyptus chips, two stages can be distinguished. At approximately 260 °C, a first decomposition in eucalyptus biomass can be observed, followed by a second step at around 330 °C. Eucalyptus is a hardwood with a higher lignin content that renders the structure with higher mechanical strength and chemical stability; thereby this material is more recalcitrant than camelina and wheat straws. This is in agreement with the broader degradation region observed in eucalyptus. The thermal decomposition of lignin in this stream occurs over an extensive temperature range delaying the decomposition of hemicellulose and cellulose.<sup>9,23</sup>

**Pyrolysis Experiments.** The products obtained during pyrolysis experiments can be grouped into liquid, gas, and solid fractions. The liquid one (bio-oil) was collected from the condensation system and further analyzed; gas composition was determined in situ by a microGC analysis system; and a solid residue was obtained.

Product yield, mass balances, and gas composition of the pyrolysis experiments are presented in Table 2. The mass balance closures for the pyrolysis of eucalyptus chips, camelina, and wheat were 93.8%, 94.6%, and 90.5%, respectively. This difference in the balance closures may be due to partial losses during the recovery of the solid and liquid products and to some minor experimental error during mass quantification of

**Table 2. Product Yield of the Pyrolysis Experiments and Gas Phase Composition (N<sub>2</sub> and H<sub>2</sub>O Free)**

product	eucalyptus chips	camelina straw pellets	wheat straw pellets
product yield (wt %)			
liquid	42.4	48.8	41.0
gas	14.3	20.3	21.4
solid	37.1	25.5	28.1
mass balance (wt %)	93.8	94.6	90.5
bio-oil organic phase/aqueous phase mass ratio	15/85	6/94	3/97
mean gas composition (vol %)			
H <sub>2</sub>	5.9	4.2	5.4
CO	35.1	35.9	34.8
CO <sub>2</sub>	39.6	47.1	46.4
CH <sub>4</sub>	16.0	10.1	10.9
H <sub>2</sub> S	0.6	0.0	0.0
C <sub>2</sub> H <sub>4</sub>	1.3	1.4	1.0
C <sub>2</sub> H <sub>6</sub>	1.3	1.4	1.5
C <sub>2</sub> H <sub>2</sub>	0.3	0.0	0.0

the products obtained from the pyrolysis runs, specifically in the liquid phase. The yields to liquid, solid, and gas products were calculated as follows:

$$\text{yield}_{\text{gas}} = \frac{M_g}{M_T}; \quad \text{yield}_{\text{liquid}} = \frac{M_l}{M_T}; \quad \text{yield}_{\text{solid}} = \frac{M_s}{M_T} \quad (1)$$

$M_T$  being the total mass of the biomass fed to the system through the two-valve system;  $M_g$ , the mass of product gas obtained from the experiment (calculated from the data obtained in the microGC online gas analysis);  $M_l$ , the total mass of liquid product collected in the pyrolysis system (condensers and electrostatic precipitator); and  $M_s$ , the total mass of solid product recovered from the system after pyrolysis.

These experiments revealed a close relationship between the feedstock and the pyrolysis products yields. The gas yield obtained for wheat and camelina straw pellets was higher than that of eucalyptus chips. This increase in the gas products can be attributed to the elevated ash content observed in the wheat and camelina straws (see Table 1), which has been reported to have a catalytic effect on vapors cracking, which may increase the gas yield in pyrolysis.<sup>7</sup> The solid fraction yielded in the pyrolysis eucalyptus chips was the greatest (ca. 37 wt %), while camelina and wheat straw yielded around 25 and 28% solid product, respectively. This can also be related to the differences in the composition of the raw materials (Table 1), as eucalyptus chips are the feedstock with the highest fixed carbon + ash content. On the other hand, pyrolysis of wheat straw, which presents an intermediate fixed carbon + ash content compared to that of eucalyptus and that of camelina straw, also produces an amount of solid residue between the other two feedstocks.<sup>25,27</sup> The biomass particle size could also have an effect on the yields to the different products and on the selectivity to certain compounds. However, depending on the operating conditions, the effect of the particle size on these parameters can be limited, almost negligible, particularly when biomass particle sizes over 2 mm are subjected to pyrolysis.<sup>28</sup>

These results are fairly similar to other results found in the literature for the pyrolysis of woody and herbaceous biomass feedstocks using different technologies. Puy et al.<sup>29</sup> conducted pyrolysis of pine woodchips using an Auger reactor at different

operating conditions. At 550 °C and 3.9 kg/h of solids feeding rate during 3 h, overall results of 51 wt % liquid yield, 23 wt % gas yield, and 26 wt % solid yield were obtained.

Other authors have reported results of pyrolysis of herbaceous materials using a bubbling fluidized bed technology at 500–525 °C.<sup>23</sup> Using wheat straw as feedstock at an average solids feeding rate 0.4 kg/h during 1.8 h at 525 °C, the following yields were reported: 35 wt % liquid yield, 27 wt % gas yield, and 28 wt % solid yield, which are very similar to the results reported here, though the yield to liquid is slightly higher in the present work. Other herbaceous biomass feedstocks (switch grass and miscanthus) were evaluated in that work, using pyrolysis temperatures of 505 and 512 °C, and the liquid yields reported by Greenhalf et al. were somewhat higher in the case of switch grass pyrolysis (58 wt %), but very similar to the results of camelina pyrolysis reported here (Table 2) and the results of miscanthus pyrolysis from that work are compared (49 wt % versus 47 wt %, respectively). However, the comparison of results must be done carefully, always bearing in mind that in all of these works different pyrolysis technologies, raw materials, and operating conditions are used.

On the other hand, as stated before, gas composition was analyzed in situ with a microGC analysis system, obtaining a mean gas composition at steady state which is presented in Table 2 (N<sub>2</sub> and H<sub>2</sub>O free basis). The lower heating values (LHV), calculated from the mean gas composition of these gases, were 1931.2, 1267.3, and 1263.5 kJ/(N m<sup>3</sup>) for eucalyptus chips, camelina straw pellets, and wheat straw pellets, respectively. The presence of most gases was within the same range in the three biomasses; however, it can be observed that CH<sub>4</sub>, H<sub>2</sub>, and C<sub>2</sub>H<sub>2</sub> contents were slightly greater in the pyrolysis gas obtained from eucalyptus. This may explain the higher LHV of gas obtained from eucalyptus pyrolysis.

**Bio-Oils Characterization.** The liquid fractions obtained by ice-cooling condensation and electrostatic precipitation of the pyrolysis vapors were collected, which constituted the bio-oil, and stored under refrigeration for further analysis. The bio-oil produced from eucalyptus became immediately segregated into two phases, whereas camelina straw and wheat straw bio-oils formed a microemulsion. This system usually consists of a continuous phase, formed by water and short oxygenated molecules, and a discontinuous phase, composed of lignin-derived macromolecules.<sup>7</sup> Once H<sub>2</sub>O content, viscosity, and pH of the bio-oil were measured, the samples were centrifuged to separate the different phases for GC-MS analysis. In all three cases, three phases were observed after centrifugation: a thin top organic phase, a middle aqueous phase, and a heavy organic phase. The top organic phase consisted of a thin discontinuous layer formed of small droplets in the surface of the liquid. For this reason it was not possible to separate this phase in any of the bio-oil samples for analysis. In contrast, the aqueous and organic heavy phases were large enough to be separated and analyzed individually. Therefore, the liquid obtained during each experiment was collected, forming the bio-oil. This bio-oil was separated into two main phases upon centrifugation: an aqueous phase (from now on, aqueous phase) and a heavy organic phase (from now on, organic phase). The organic phase/aqueous phase mass ratios obtained for the different bio-oils are presented in Table 2. The H<sub>2</sub>O content of the aqueous and heavy organic phases, viscosity, and pH results obtained for each bio-oil are presented in Table 3, and the GC-MS results are summarized in Figures 3 and 4.

Table 3. Properties of Obtained Bio-Oils<sup>a</sup>

property	eucalyptus chips bio-oil	camelina straw pellets bio-oil	wheat straw pellets bio-oil
viscosity at 40 °C (cSt)	3.0	3.7	n/d
pH	2.6	3.5	3.1
aqueous phase H <sub>2</sub> O content (wt %)	71.6	55.1	68.8
organic phase H <sub>2</sub> O content (wt %)	8.2	7.8	14.4
measured HHV, OP (MJ/kg)	26.9	23.8	25.3
estimated HHV, OP (MJ/kg)	26.9	22.9	24.8

<sup>a</sup>OP, organic phase; n/d, not determined.

As can be observed in Table 3, the aqueous phase H<sub>2</sub>O content was greater for eucalyptus chips than for wheat and camelina straws. Considering that the water concentration in bio-oils is originated from both pyrolysis reactions and from the original moisture of the material,<sup>3</sup> it could be proposed that the higher moisture content of the eucalyptus chips could lead to a higher H<sub>2</sub>O content. Nonetheless, a significant amount of reaction water can be incorporated into the product liquids as a consequence of cracking reactions, which could be catalyzed by metals contained in the ashes of the different raw materials, particularly in the case of wheat straw, because of its characteristic high content in potassium.<sup>23</sup> The relatively high water contents obtained may result in a quick phase separation in pyrolysis liquids,<sup>30</sup> as occurred in the case of eucalyptus bio-oil. This could explain the results obtained.

The viscosity values measured in the three bio-oils are lower than other values found in the literature,<sup>2,28,30</sup> though this can be attributed to the relatively higher water content of the liquids in this work, since an increased water content lowers the viscosity of bio-oils.<sup>2</sup> Also, the liquids obtained showed a pH between 2.6 and 3.5, which are similar to other pH values of bio-oils in previous studies.<sup>3</sup> Regarding the composition of these bio-oils (Table 4), ultimate analyses of both aqueous and organic phases were carried out. If the results obtained for these phases are compared for each material, it can be noticed that C, H, N, and S contents tend to be higher in the bio-oil organic phases while O is present in larger amounts in the aqueous phases. This is related to the type or families of compounds contained in each phase, as can be seen in Figures 3 and 4 and in Table 5.

The ultimate analyses (Table 4) revealed that eucalyptus bio-oil contained more C in the organic phase than in the aqueous phase when compared to camelina straw pellets and wheat straw. The inverse distribution of contents occurs for O in these bio-oils, being that the rest of the elements contents are fairly similar for the aqueous and organic phases. In contrast, the N-content in both phases of wheat straw bio-oil was significantly higher than that in eucalyptus and camelina straw. Wheat straw is known for its noticeable protein content,<sup>31,32</sup> which explains its use in blends for animal feeding as commented before and can be the cause for higher N-content in this raw material. Moreover, the differences in composition are connected to the distinct values of higher heating value (HHV) obtained for each organic phase sample, so that the eucalyptus chips organic

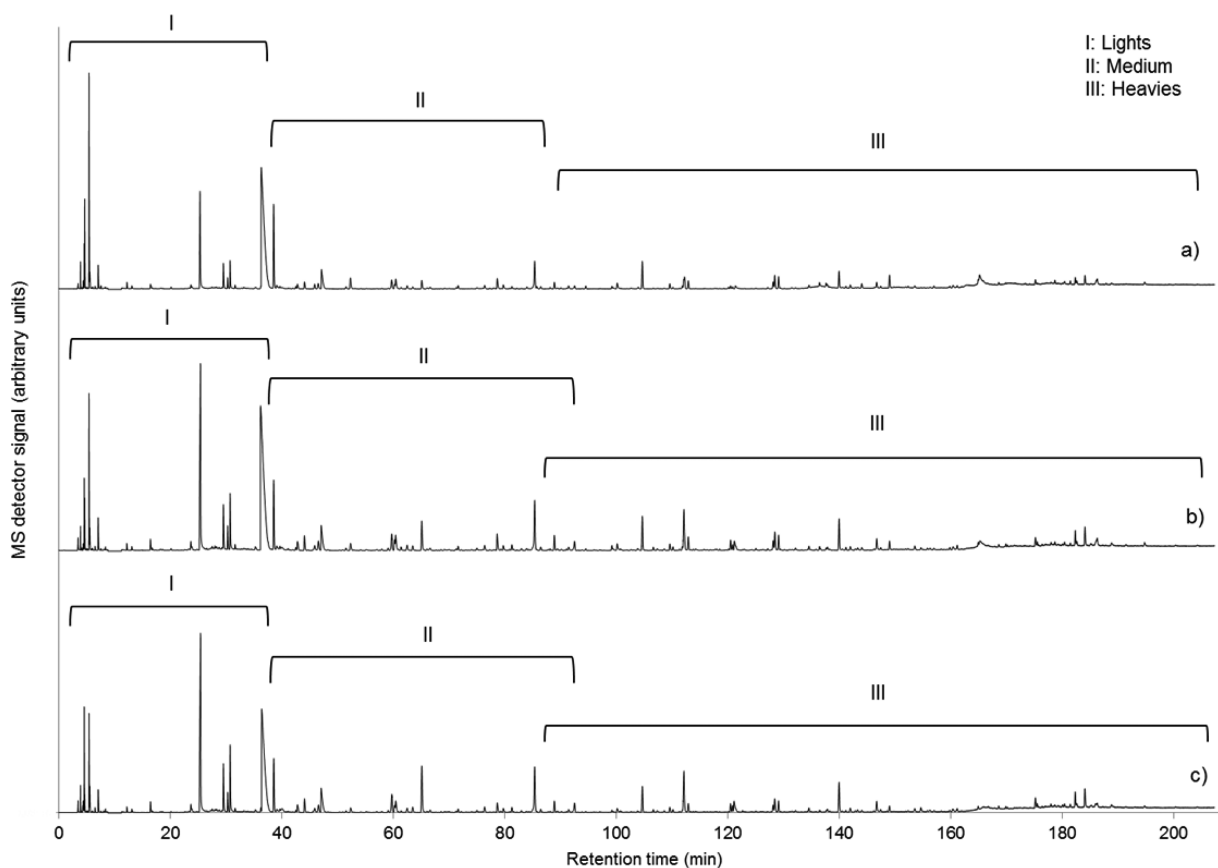
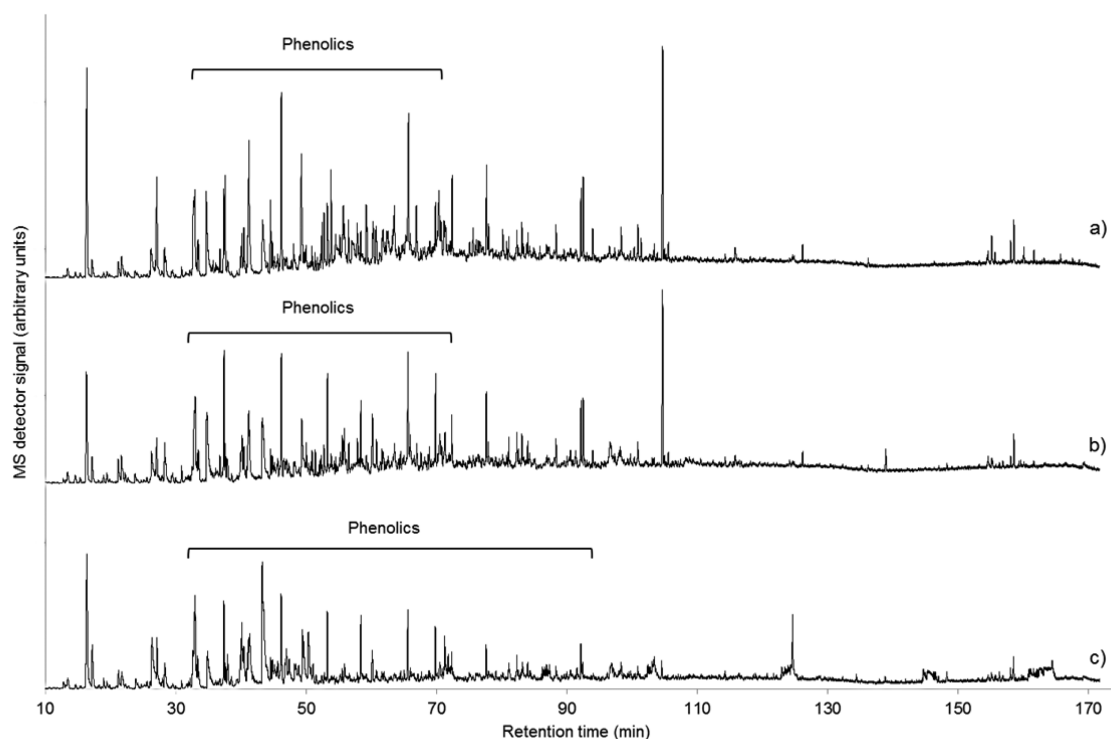


Figure 3. GC-MS analysis of aqueous phase of bio-oils: (a) eucalyptus bio-oil aqueous phase; (b) camelina straw pellets bio-oil aqueous phase; (c) wheat straw pellets bio-oil aqueous phase.



**Figure 4.** GC-MS analysis of organic phases of bio-oils: (a) eucalyptus chips bio-oil organic phase; (b) camelina straw pellets bio-oil organic phase; (c) wheat straw pellets bio-oil organic phase.

**Table 4.** Ultimate Analysis of the Obtained Bio-Oils, Dry Basis

	composition (wt %)				
	S	H	C	N	O <sup>a</sup>
eucalyptus chips					
organic phase	0.0	6.3	69.5	0.3	23.8
aqueous phase	0.0	1.8	34.9	0.0	63.3
camelina straw pellets					
organic phase	0.1	5.9	60.8	0.3	32.9
aqueous phase	0.1	4.3	38.4	0.1	57.1
wheat straw pellets					
organic phase	0.1	5.4	69.4	9.0	16.1
aqueous phase	0.1	0.8	40.4	0.8	57.8

<sup>a</sup>Calculated by difference.

phase, with the highest C- and H-contents, is the one with the highest HHV, as reflected in Table 3. For comparison purposes, the HHV values were also estimated using a correlation for liquid, solid, and gaseous fuels.<sup>33</sup> This correlation calculates (eq 2) heating values from the ultimate analysis of materials, providing HHV for the studied samples which are in agreement with the ones obtained experimentally, as can be seen in Table 3.

$$\text{HHV}/(\text{kJ/g}) = 0.3491\%C + 1.1783\%H - 0.1034\%O - 0.0151\%N + 0.1005\%S \quad (2)$$

The higher heating value of the organic phases presented in Table 3 are in the range of other results found in the literature for the organic phases of pyrolysis liquids obtained from woody and herbaceous biomass feedstocks.<sup>23,34</sup>

The two main bio-oil phases were analyzed separately, and the results obtained are presented in Table 5 together with

**Table 5.** GC-MS Semiquantitative Analyses of Aqueous/Organic Phases from Bio-Oil Samples

family	% relative area		
	eucalyptus chips bio-oil	camelina straw pellets bio-oil	wheat straw pellets bio-oil
aqueous phase			
acids and esters	44.7	39.3	33.5
ketones	19.9	30.8	37.2
aldehydes	0.8	0.5	0.5
alcohols	11.3	4.3	3.6
furans	9.0	7.5	9.1
phenolics	7.3	7.2	7.2
sugars	2.9	3.8	4.2
nitrogenated	0.0	0.3	0.0
others	4.1	6.4	4.7
organic phase			
furans	12.8	11.2	5.4
ketones	4.6	4.6	5.1
aldehydes and ethers	1.8	1.4	0.0
esters	8.4	9.0	0.0
alcohols	2.3	0.0	0.0
phenolics	60.5	60.8	51.2
aromatics—no oxygen	1.9	2.2	1.4
nitrogenated	0.0	0.0	4.0
others cycles	2.5	10.2	0.0
others	5.0	0.0	32.8

Figures 3 and 4. The abundance of the different compounds could be calculated by doing a semiquantitative analysis of the peaks from the GC-MS analyses, by assuming identical response factors for all of the compounds analyzed. The compositions were thus determined as area percentages with

Table 6. Main Components in Bio-Oil Samples Determined by Semiquantitative Analysis

	compound by abundance, % relative area)		
	eucalyptus chips	camelina straw pellets	wheat straw pellets
aqueous phase			
first	acetic acid, 41	acetic acid, 35	acetic acid, 28
second	methyl alcohol, 8	1-hydroxy-2-propanone, 12	1-hydroxy-2-propanone, 14
third	1-hydroxy-2-propanone, 7	furfural, 4	furfural, 4
fourth	furfural, 6	methyl alcohol, 3	1-hydroxy-2-butanone, 3
organic phase			
first	2,4-dimethylfuran, 9	2,5-dimethylfuran, 8	4-ethylphenol, 13
second	methyl ester 9-octadecenoic acid, 7	methyl ester 9-octadecenoic acid, 7	others, 7
third	3,4-dimethylphenol, 7	2-methylphenol, 7	2-methylphenol, 5
fourth	2,3,5-trimethylphenol, 5	4-Methylphenol, 7	2-methoxy-4-methylphenol, 4

respect to the total sum of areas of all of the identified compounds.

On one hand, the characterization of the liquid samples by GC-MS showed that the aqueous phases were primarily composed of small acids, ketones, aldehydes, and alcohols (58–65% of the total sample depending on the material corresponding to region I in Figure 3), with smaller proportions of furans and other five-C cycles (region II in Figure 3) and some phenols and sugars (region III in Figure 3), in agreement with other analyses reported by other authors.<sup>29</sup> From Figure 3, it can be observed that the resultant chromatograms are similar for the three samples, with only minor differences. In all cases, according to the semiquantitative analysis, acetic acid was the main component in the aqueous phase. In addition, the detected compounds were grouped in families attending to their functional groups as shown in Table 5. It should be pointed out that for all samples the predominant functional groups are acids, esters, and ketones, with also an important proportion of simple alcohols and phenolic compounds. Specifically, the aqueous phase of eucalyptus bio-oil is the one with the highest content in the first family group, mainly composed of acids, which supports the results obtained in pH measurements reported in Table 3 showing that eucalyptus chips bio-oil presents the greater acidity of all three bio-oils. In contrast, wheat straw pellets bio-oil, which presented a slightly higher acidity according to results shown in Table 3, does not contain a higher proportion of acids than camelina straw bio-oil. Nevertheless, it should be remarked that the amount of ketones, which are weak acids, is noticeably greater in the case of wheat straw bio-oil, which may explain the difference in acidity between these bio-oils.

GC-MS semiquantitative analysis of the organic phases (Table 5 and Figure 4) showed that phenolics are the most abundant type of compound in them, mainly derived from the depolymerization of the structure of lignin, followed by furans. The chromatograms obtained are similar for the three organic phases although some differences can be noticed. The clearest difference is that in the case of eucalyptus chips and camelina straw pellets a peak appeared at a retention time of around 104.6 min, identified as methyl ester 9-octadecenoic acid, which was not detected in wheat straw pellets bio-oil. Conversely, a peak identified as 1-docosene can be observed at 124.6 min for wheat straw organic phase, which was not detected for the other two samples. In addition, nitrogenated compounds were detected in the organic phase of wheat straw pellets bio-oil, the one containing the greatest proportion of N of all aqueous and organic phases according to ultimate analysis reported in Table 4. In addition, it should be noticed the considerable amount of

compounds grouped under “others” in the organic phase of wheat straw, which is also related to N-content in this sample. GC-MS signal indicated the presence of compounds with N-substituents, but the identification of them was not clear enough to elucidate the specific compound represented. Moreover, it can be observed that the second most abundant compound (Table 6) in this phase was identified with lower matching probability.

**Characterization of Solid Products.** Pyrolysis of the three feedstocks yielded, together with gas and liquid products, a solid residue or char that accumulated inside the stainless steel reactor. This material, which presents a similar size and shape to the biomass fed,<sup>35</sup> was recovered from the reactor in every case, separated from the silica sand used as hot bed on top of which biomasses were devolatilized and characterized.

The results for ultimate and proximate analyses (Table 7) of the aforementioned solids showed that S- and N-contents in

Table 7. Ultimate and Proximate Analyses and HHV of Pyrolysis Chars, Confidence Interval at 90%

analysis	eucalyptus chips	camelina straw pellets	wheat straw pellets
ultimate analysis (wt %)			
S	[0.0, 0.1]	[0.0, 0.1]	[0.1, 0.2]
H	[2.4, 2.8]	[2.3, 2.5]	[2.6, 2.8]
C	[82.6, 82.7]	[77.0, 78.8]	[69.4, 70.4]
N	[0.0, 0.1]	[0.0, 0.1]	[1.2, 1.4]
O <sup>a</sup>	[14.3, 15.0]	[18.5, 20.7]	[25.2, 26.7]
proximate analysis (wt %)			
moisture	[3.9, 4.9]	[3.0, 6.6]	[3.4, 4.2]
volatile matter	19.7 <sup>b</sup>	19.9 <sup>b</sup>	[15.2, 27.6]
ash	[4.2, 4.6]	[8.9, 10.9]	[12.1, 14.1]
fixed carbon <sup>a</sup>	71.32	65.4	[54.1, 69.3]
HHV (MJ/kg)	[30.3, 30.5]	[28.1, 28.6]	[25.9, 26.6]

<sup>a</sup>Calculated by difference. <sup>b</sup>Confidence interval cannot be calculated as only one measurement of the property is available.

wheat straw were higher, while eucalyptus char presented the highest C-content. The amount of fixed carbon in eucalyptus solid residue is also higher than in the other two materials, as occurred with the proximate analysis of these materials. This, along with the fact that eucalyptus char contains lower amounts of ashes, may explain the higher heating value of this solid when compared to the ones obtained from the pyrolysis of both straw pellets. It is noteworthy to mention that C-content and fixed carbon content in solid residues decreases as follows:

eucalyptus chips > camelina straw pellets > wheat straw pellets, whereas ash content increases in this sequence for chars: eucalyptus chips < camelina straw pellets < wheat straw pellets. Subsequently, these differences in composition can explain that heating value of the mentioned solids decreases in the following order: eucalyptus chips > camelina straw pellets > wheat straw pellets, as reported in Table 7.

If these results are compared to other values found in the literature, it can be observed that the ash content of the solid product of the herbaceous feedstocks is similar to others found in the literature,<sup>23</sup> though the HHV values are higher in the present work. The ultimate analyses also indicate a greater C content in the solid products of the pyrolysis of the herbaceous materials in this work. This could indicate an incomplete devolatilization of the carbon-containing compounds in the materials, which could be a consequence of the heat transfer limitations in the experimental setup.

Nonetheless, if the solid product of eucalyptus pyrolysis is compared to other values found in the literature concerning pyrolysis of wood chips,<sup>29</sup> it can be observed that the results are very similar in terms of ash and volatile matter, though the moisture content is a little higher and, accordingly, the fixed carbon content, determined by difference, is a little lower in the case of the solid product from eucalyptus pyrolysis. Furthermore, volatile matter contents in the range of 16% have been reported previously in different char samples obtained from pyrolysis at 550 °C of several biomasses.<sup>36,37</sup>

## CONCLUSION

On the one hand, the distribution of gas, solid, and liquid products obtained for the three materials studied is between the results that would be obtained for fast pyrolysis and the ones produced in a slow pyrolysis or carbonization process. These results are in connection with the experimental conditions in which the pyrolysis runs took place.

On the other hand, with regard to the different feedstocks studied some appreciations can be drawn. Moreover, the bio-oils obtained in the experiments were separated into an aqueous and an organic phase that were characterized by GC-MS. From this analysis it can be established that the aqueous phases were composed principally of acids, esters, and ketones, which contributes to the acid properties of the bio-oils, whereas the organic phases present an important fraction of phenolic compounds, derived from the decomposition of lignin.<sup>38</sup> It was also observed that the nitrogen content of the organic phase of wheat straw bio-oil complicated the identification of compounds detected by GC-MS in this phase.

To summarize, three different biomasses (eucalyptus, camelina straw, and wheat straw) were pyrolyzed at 550 °C in an ablative bed reactor, yielding a mixture of liquid, gas, and solid products. A comprehensive analysis of the physicochemical properties of the raw materials and products was performed. From this analysis it was possible to identify eucalyptus as the material with the highest fixed carbon and moisture content. This feedstock yielded the greater amount of solid product together with the bio-oil with higher H<sub>2</sub>O content. Conversely, both straw pellets contained more volatile matter and ash than eucalyptus. These two materials yielded more liquid and gaseous products (as a whole) than eucalyptus, and bio-oils with less water content and higher viscosity values. In addition, it should be pointed out the noticeable difference in nitrogen content between wheat straw and the other two

feedstocks, especially when it comes to the liquid and solid products obtained from wheat straw pellets pyrolysis.

Finally, the results indicated that camelina presents interesting characteristics as feedstock for pyrolysis. It can grow in arid or marginal lands, and the straw is obtained as a residue from the production of biodiesel. Also, the bio-oil produced from this material presents lower water content than the other pyrolysis oils. In contrast to wheat straw, camelina straw will not compete with animal feed, and its low protein content reduces the nitrogen and sulfur content making less intensive the hydroprocessing required to remove impurities.

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### Notes

The authors declare no competing financial interest.

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## ABBREVIATIONS

DTG = differential thermogravimetry

GC-MS = gas chromatography coupled to mass spectrometry

HHV = higher heating value

LHV = lower heating value

$M_g$  = mass of product gas obtained from the experiment (calculated from the data obtained in the microGC online gas analysis)

$M_l$  = total mass of liquid product collected in the pyrolysis system (condensers and electrostatic precipitator)

$M_s$  = total mass of solid product recovered from the system after pyrolysis

$M_T$  = total mass of biomass fed to the system through the two-valve system

TG = thermogravimetry

yield<sub>gas</sub> = gas yield

yield<sub>liquid</sub> = liquid yield

yield<sub>solid</sub> = solid yield

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