



Effect of acid pretreatment and process temperature on characteristics and yields of pyrolysis products of peanut shells



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ABSTRACT

Pyrolysis of acid pretreated peanut (*Arachis hypogaea*) shells was examined in order to improve the yield of liquids (bio-oils) and the characteristics of the three kinds of pyrolysis products. Also, pyrolysis of the pristine shells was comparatively investigated. The acid pretreatment was carried out employing a dilute HCl solution and it successfully diminished the ash content of the shells. Pyrolysis assays were performed in a fixed-bed reactor at different process temperatures (400 °C, 500 °C, and 600 °C). The maximum bio-oil yield was obtained at a temperature of 500 °C for both the pretreated and the pristine shells, but pyrolysis of the formers yielded more bio-oils than the untreated ones (42 wt% vs. 33 wt%). The increase of the process temperature resulted in a reduction of the solid (bio-char) generation for both samples. Demineralization also led to a further reduction of the bio-char yield. Regarding the products characteristics, neither the pretreatment nor the temperature had a noticeable influence on the elemental composition of the bio-oils. However, water content of the bio-oils was lower for the ones arising from pyrolysis of the demineralized shells although it increased with growing process temperature. Likewise, pyrolysis of the demineralized shells resulted in bio-chars with less ash, improving their potentialities as bio-fuels. Also, the bio-chars arising from the treated shells at the higher temperatures (500 °C and 600 °C) resulted in higher BET surface areas (up to 300 m²/g), pointing to their possible use as rough adsorbents or for further upgrading to activated carbons.

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1. Introduction

A huge amount of lignocellulosic residues are usually generated as by-product by agro-industrial activity [1]. Most of these wastes are disposed in landfills or incinerated increasing air and soil pollution [2]. On the other hand, depletion of fossil fuel forces to find alternative ways of generating energy. Recently, the employment of biomass to generate green, sustainable energy has increased [3]. Unlike fossil fuels, biomass is a renewable energy source with a great availability. Combustion of biomass or of biomass related fuels is considered carbon neutral as plants absorb carbon dioxide

through photosynthesis during growth. Moreover, biomass has less sulphur than fossil fuels and, thus, would emit less SO₂, one of the major sources of acid rain [4].

There are several routes to convert biomass into energy. The selection of the best process depends on the plant composition. High-oil crops are more suitable to be converted to bio-diesel by means of transesterification, while plants with great contents of sugars or starch are usually processed to generate bio-ethanol [5,6]. On the other hand, biomass with high amount of lignin is a good candidate for thermochemical conversion since this biopolymer could be partially degraded at high temperatures. Also, thermochemical conversion is characterized by higher reaction rates than those of biochemical processes [7,8]. Among thermochemical processes, pyrolysis has the benefit of producing liquid biofuels, namely bio-oils, whose storage and pumping are economically more competitive than gases produced by gasification. Despite bio-oil has been successfully employed in diesel engines and gas

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turbines, it presents some disadvantages, compared with fossil fuels [9]. Particularly, the high water content in bio-oils leads to diminutions of energy density and flame temperature [10].

Some researchers have informed that the pyrolysis of demineralized biomass led to bio-oils with a lower water content. Moreover, this pretreatment conducted to an increase in bio-oil production at expenses of bio-char and gases yields [11–16]. Mineral removal could also improve bio-oil processing since the existence of cationic metals in the liquids is undesirable. They could poison catalysts employed in their further upgrading [17]. In addition, as pyrolysis leads to enrichment in ash content in bio-char, demineralization should reduce possible fouling and corrosion problems when it is burnt [18]. Thus, demineralization of lignocellulosic biomasses with high ash content may be an appealing pretreatment in order to improve pyrolysis products performance. In particular it could be interesting for peanut shells, the main by-product of peanut industrial processing, since they are one of the most common wastes generated in the world [19]. To the best of our knowledge, the effect of demineralization on the yields and characteristics of the products arising from the pyrolysis of peanut shells has not been investigated.

Within this background, the present article deals with the pyrolysis of peanut (*Arachis hypogaea*) shells. First, the effects of demineralization on the physicochemical properties of the shells were studied. Afterwards, the pyrolysis of acid treated and pristine peanut shells was performed in a fixed bed reactor. Since process temperature is an important variable with respect to bio-oil yields and water generation [20,21], the pyrolysis of the both samples was investigated at three different temperatures: 400 °C, 500 °C and 600 °C. The influence of the temperature and demineralization on yields distribution as well as on the characteristics of the three kinds of pyrolysis products was systematically investigated.

2. Materials and methods

2.1. Acid pretreatment and characterization of peanut shells

Commercial peanuts (*Arachis hypogaea*) were obtained from a local market. The shells were cleaned, milled, and screen-sieved in order to obtain samples of particle diameter from 250 µm to 500 µm. In order to remove the mineral matter, the shells were treated with a 10 wt% HCl acid solution (20 mL/g of sample) at 80 °C for 1 h. Afterwards, the treated shells were rinsed with distilled water until a pH of 5.5 in washing water was reached. Finally, they were filtered and dried at 60 °C for 24 h. The untreated and demineralized shells were tagged as US and DS, respectively.

Proximate analysis of both types of samples was performed by thermogravimetric analysis (TA Instruments SDT Q600), according to American Society of Testing and Materials (ASTM) standards 5142. Their elemental composition was determined using an automatic elemental analyzer (Carlo Erba model EA 1108). Van Soest analysis was carried out in order to assess the content of main biopolymers (cellulose, hemicellulose and lignin) constituting the pristine and demineralized shells [22]. Ash composition of both samples was analyzed by atomic absorption spectrophotometry using a Perkin Elmer Analyst 200 instrument supplied with hollow cathode lamps for each element. Prior to the analysis, the ashes were dissolved in a 1:1 HNO₃ solution. Si content of ash was quantified by fusion with Na₂CO₃.

Thermal behavior of US and DS was investigated in a TG–DSC/DTA TA Instruments SDT Q600 thermal analyzer. The samples were heated from ambient temperature up to 600 °C under flowing nitrogen. Experiments were performed for samples' masses of 10 mg, fractions of 44–74 µm particle diameter, and heating rate of 100 °C/min.

2.2. Pyrolysis experiments

A fixed bed reactor was employed to perform the pyrolysis assays. The equipment mainly consisted of an AISI 316 stainless steel pipe (2.5 cm I.D., 110 cm total length) with a special device which enabled to support a basket built in stainless steel mesh. The latter was used as a container of the samples. The basket with the sample, constituting the solid fixed-bed, was centrally placed in the heated bottom zone of the reactor, which was externally heated by an electrical furnace driven by a Yokogawa UT350 temperature controller. A chromel–alumel thermocouple was located at the geometrical center of the basket to record the process temperature. At the reactor outlet, a series of flasks immersed in a cooling bath, using isopropyl alcohol at –10 °C as solvent, enabled condensation and collection of the condensable volatiles generated with the pyrolysis course. Non-condensable gases, after passing through the condensation system, were sampled periodically using Teflon gas bags for further analysis by gas chromatography, as detailed in the next subsection.

The pyrolysis assays were carried out according to the following steps. At the beginning of the experiment, all the installation was purged by flowing N₂ (300 cm³ min^{–1}) for 1 h in order to avoid partial combustion of the samples. Afterwards, the heating system was connected and the desired temperature was set. Once the pre-established temperature was attained, the basket containing the sample was displaced to the heated zone of the reactor. Thus, a heating rate of approximately 300 °C min^{–1} was achieved. After the holding time, heating was cut off and the basket was immediately shifted towards the upper non-heated part of the reactor, keeping the N₂ stream. Once ambient temperature was reached, the basket was removed from the reactor. The residual solid and the accumulated liquid products contained in the flasks were weighed to determine product yields. These products were then carefully stored in closed containers for further characterization. Percent yields were calculated as weight of product per total weight of raw sample. Gas yields were obtained by difference from overall mass balances.

From preliminary experiments, it was found that the process temperature was the variable that had the greatest influence on the products yields. Also, it was determined that after 30 min the volatiles generation was negligible, indicating almost complete conversion. Other conditions, such as the particle size or the N₂ flow rate, had a weak influence on the process yields. Therefore, the following pre-established operating conditions were selected to conduct the pyrolysis experiments: temperature = 400–600 °C, N₂ flow rate = 300 cm³ min^{–1}, particle diameter = 250–500 µm; samples' masses = 10–15 g, holding time = 30 min.

2.3. Characterization of the pyrolysis products

Water content of the liquid samples was measured by volumetric Karl-Fischer titration (Metrohm Herisau Karl Fisher Automat E 547) following ASTM E 203. The samples' pH was determined with an Orion 290A portable pH meter. Additionally, total sugar and phenols contents of the bio-oils were evaluated using the phenol-sulphuric and the Folin-Ciocalteu methods, respectively [23]. Also, methylene chloride was used to extract the organic phase from the bio-oils (volume ratio solvent/bio-oil of 2:1) in order to determine their elemental composition by ultimate analyses, as depicted above. The extracted samples were analyzed after methylene chloride had been evaporated. FT-IR analyses of the organic fractions of the bio-oils were carried out employing a Perkin-Elmer IR Spectrum BXII spectrometer with an attenuated total reflection (ATR) accessory made of SeZn in order to identify functional groups within the range 600–4000 cm^{–1}. Furthermore, higher heating value (HHV) was also determined following ASTM D 240 and using a Parr 1341 oxygen bomb calorimeter.

Elemental composition and ash content of the bio-chars were determined using the same instruments and standards detailed above. HHV of bio-chars was measured following ASTM E 711 and employing the equipment depicted above. FT-IR spectra of the solid biofuels were recorded employing the KBr pellet method (sample/KBr ratio of 1:200). In addition, N₂ adsorption isotherms at –196 °C were determined for the bio-chars using an automatic Micromeritics ASAP-2020 HV volumetric sorption analyzer. Prior to gas adsorption measurements, the samples were outgassed at 120 °C for two hours. Textural properties were assessed from the isotherms, according to conventional procedures depicted in detail in previous studies [24]. The Brunauer-Emmett-Teller (BET) surface area (S_{BET}) was determined by the standard BET procedure and total pore volumes (V_t) were estimated from the amount of nitrogen adsorbed at the relative pressure of 0.95 ($p/p_0 = 0.95$). The mean pore widths (r) were calculated from $r = 2 V_t/S_{\text{BET}}$.

Non-condensable gases, after flowing through the condensation system, were sampled periodically using Teflon gas bags, and further analyzed with a Shimadzu GC-8 gas chromatograph supplied with a thermal conductivity detector and a concentric packed Altech CTR I column (6 ft x 1/8 in). Argon as carrier gas and a temperature of 25 °C were employed.

All the experiments were performed at least three times. Differences between replicates were less than 5% in all cases. Average values are reported.

3. Results and discussion

3.1. Influence of the acid pretreatment on peanut shells

Results of the proximate and elemental analyses and the biopolymer composition of the untreated and demineralized peanut shells are displayed in Table 1. The proximate analysis of US agreed with others reported in the literature [25]. It can be seen that the acid pretreatment was successful to remove mineral matter since the ash content of DS was much lower than that of US. The higher volatile content of DS could be attributed to a reduction of the interlinking degree of the biopolymers which constitute the sample and, thus, they became more labile [26,27]. Regarding the elemental analysis results, the mineral removal led to enhance the carbon content and to diminish the nitrogen content. The latter is beneficial from the environmental viewpoint as the combustion of these samples would generate less NO_x [28]. On the other hand, the acid pretreatment resulted in an important increase of the lignin content. This change was in agreement with the higher carbon content,

as lignin has higher carbon content than either the cellulose or the hemicellulose. This alteration in the biopolymer composition may be due to the acid hydrolysis of the cellulose and hemicellulose, with the latter being probably almost completely decomposed into soluble sugars by the acid treatment [12]. Degradation of cellulose and hemicellulose and mineral removal led to a mass loss of approximately 30 wt%.

Table 2 shows the results of the analyses performed in order to determine the ash elemental composition of US and DS. As pointed out in the literature, the alkali metals (Na and K) which are present as soluble salts are easily removed employing distilled water. By contrast, the alkaline earth metals which are predominately bonded to the organic part of the biomass require more severe conditions, such as high temperature or strong acid solutions [14]. It can be seen that the acid pretreatment applied in this work was able to considerably reduce both alkali and alkaline earth metals content of ashes of DS. A relative increase of Si content was found as this element was practically not removed by means of this treatment.

Fig. 1 shows the thermogravimetric curves of the thermal degradation of US and DS under flowing N₂. The weight fractions were calculated as the ratio m/m_0 , where m and m_0 are the dry mass of the sample at time t and the initial dry mass, respectively. The pretreated sample started to decompose at a higher temperature than the raw one. Also, the temperature where the reaction rate attained a maximum was higher for DS (380 °C) than for US (330 °C). This trend might be due to the catalytic action of the minerals which favors degradation of biomass at lower temperatures [11,29]. It could also be related to the reduction of hemicellulose content (Table 1), whose degradation begins at lower temperatures than those of cellulose and lignin [30]. Furthermore, degradation of DS was more abrupt than that of US, and the residual weight fraction (m/m_0 at 600 °C) for the former was lower (0.22 for DS vs. 0.29 for US).

3.2. Yields of the pyrolysis products

In Fig. 2(a and b) there are represented the yields of bio-oils, bio-chars and gases for the pyrolysis of US and DS at the three process temperatures. As can be appreciated, there was a maximum in the bio-oil yield at a process temperature of 500 °C, for the pyrolysis of both US and DS. At a lower temperature (400 °C), biomass volatilization would not be completed, while, at a higher temperature (600 °C), secondary reactions that convert pyrolysis vapors into non-condensable gases would occur [20,31]. Regarding the bio-char yield, it declined with temperature rising since volatilization reactions would be favoured. This could also explain the increment in gas generation when the temperature was increased.

Results in Fig. 2b also indicate that pyrolysis of DS yielded more bio-oil than US (Fig. 2a) in the studied temperature range. Moreover, although at the higher temperatures (500 °C and 600 °C) pyrolysis of DS yielded less bio-char than US, the reverse trend was observed at 400 °C. These results would be due to the fact that at this lower temperature the catalytic action of minerals would favor volatile generation. Contrarily, at higher temperatures the minerals would promote condensation reactions among volatiles leading to a higher solid yield [32]. Moreover, the relative high yield of bio-char arising from pyrolysis of DS at 400 °C could be due to the

Table 1
Characterization of the untreated (US) and demineralized (DS) peanut shells.

Sample	US	DS
<i>Proximate Analysis [wt %, dry basis]</i>		
Volatile matter	73.6	81.2
Ash	5.9	0.6
Fixed carbon ^a	20.5	18.2
<i>Ultimate Analysis [wt % dry and ash-free basis]</i>		
Carbon	49.6	54.3
Hydrogen	6.5	6.6
Nitrogen	1.8	0.7
Oxygen ^a	42.1	38.4
<i>Biopolymer composition [wt %, dry and ash-free NDF basis]</i>		
Lignin	30.9	42.7
Cellulose	54.6	56.3
Hemicellulose	14.5	1.0

^a Estimated by difference.

Table 2
Ash composition of the untreated (US) and demineralized (DS) peanut shells.

Content [g/kg]	Na	K	Mg	Ca	Al	Fe	Si
US	27	95	144	245	65	35	149
DS	6	19	3	1	76	11	357

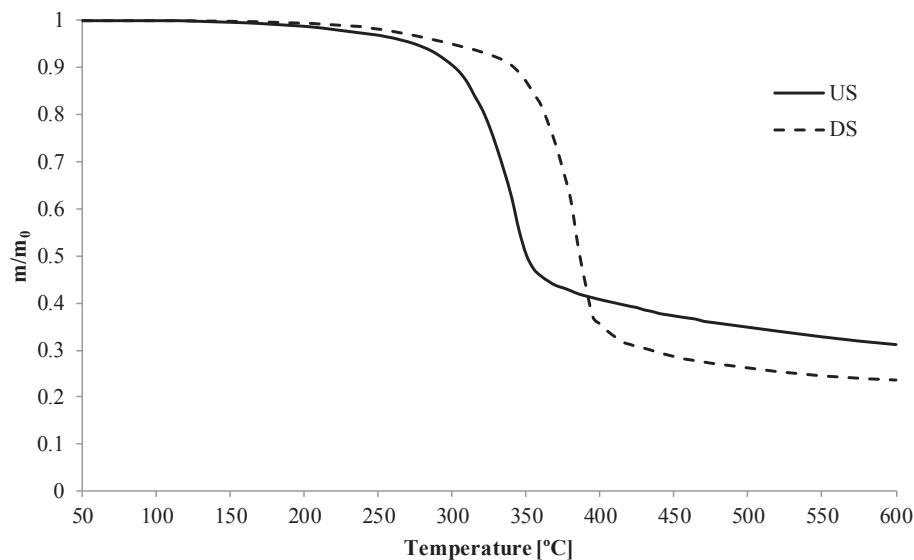


Fig. 1. Thermogravimetric curves for the pyrolysis of the untreated (US) and demineralized (DS) peanut shells.

higher content of lignin, which decomposes at higher temperatures. Furthermore, mineral removal could decrease crosslinking degree among biomass biopolymers reducing their resistance to thermal degradation and generating more volatiles at higher temperatures [26].

On the other hand, bio-char yields obtained in the fixed bed experiments performed at higher temperatures for US and DS (Fig. 2a and b) presented the same trend as those determined from TGA curves (Fig. 1). However, the latter showed that the weight fraction for US degradation at 400 °C was higher than that of DS, in contrast with fixed bed results. This behavior could be due to the higher heating rate achieved in the fixed bed assays, which could shift the degradation start to higher temperatures [31]. Thus, the decomposition of DS at 400 °C could have been less complete than that of US. It has also to be taken into account that the temperature varied throughout the TGA dynamic measurements, whereas it was kept constant for 30 min in the reactor experiments. This could have also contributed to differences in the solid yields.

3.3. Bio-oils

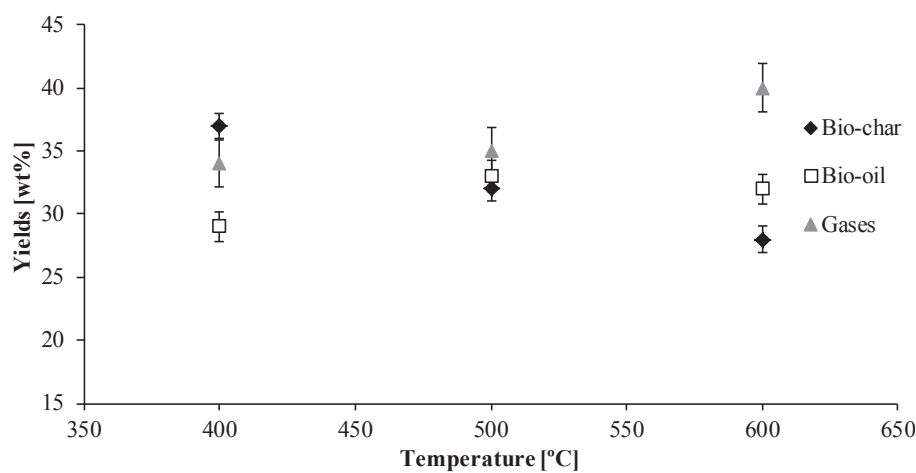
Elemental composition, HHV and pH of the bio-oil generated by the pyrolysis of US and DS are shown in Table 3. These liquids showed a carbon content of 49–56 wt%, an hydrogen content of 6–8 wt%, and an oxygen content of 35–42 wt%. Likewise, the oxygen content of the bio-oils arising from the pyrolysis of DS at 400 °C and 500 °C was lower than the one of the bio-oils produced by the pyrolysis of US at the same process temperatures. Although demineralization reportedly leads to bio-oils with higher oxygen content [15], it has to be taken into account that present analyses were carried out after extraction with methylene chloride. Accordingly, some polar oxygenated compounds, such as short chain carboxylic acids and sugars, could be removed from the bio-oil with the aqueous phase and likely, they were not included in the analyses. Moreover, the bio-oils generated by pyrolysis of DS had less nitrogen content than those produced by pyrolysis of US. This was probably related to the lower nitrogen content of the treated biomass (Table 1). The reduced nitrogen content of the bio-oils is a desirable characteristic as their further combustion would generate less NO_x which subsequently produces acid rain [28]. HHV of the liquids were in the range of 21–24 MJ/kg. Neither the mineral

removal nor the process temperature had a significant influence over the HHV.

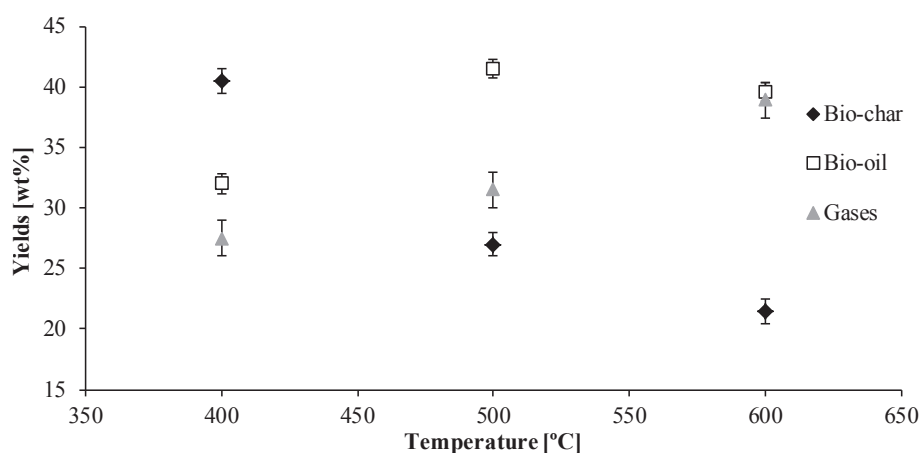
pH values of the bio-oils were in the typical range documented in the literature [9]. Bio-oil acidity is mainly due to carboxylic acids, particularly formic and acetic acids, generated by holocellulose degradation. Patwardhan et al. [33] suggest that the generation of these acids is favoured by the ring scission of glucose catalyzed by the minerals present in the shells. Thus, it would be expected that pyrolysis of DS would produce liquids with a higher pH. However, the inverse trend was found. This behavior could be due to the incomplete removal of HCl after the water washing. In this way, some of the HCl employed in the acid pretreatment could be retained in the shells and, consequently, became part of the generated bio-oil [34].

Fig. 3 shows the water, sugar and phenol contents in the bio-oils arising from the pyrolysis of US and DS. In Fig. 3a, it can be appreciated that the pyrolysis of DS led to bio-oils with less water content than those generated by the thermal degradation of US for the three temperatures investigated. The mineral matter would catalyze several reactions, such as ring scission, that would produce water [13]. Besides, the divalent cations (Ca²⁺ and Mg²⁺) could form carboxylates in the untreated biomass binding different structural fragments of the holocellulose and incrementing the crosslinking. When those ions are replaced by H⁺, after the acid pretreatment, those bonds would break up, reducing the crosslinking and increasing the occurrence of reactions that generate sugar instead of water [26]. Furthermore, it can be seen that increasing the process temperature led to an increment of water content in the bio-oils, suggesting that dehydration reactions were favoured at higher temperatures [21,31].

Regarding the sugar content (Fig. 3b), pyrolysis of DS yielded more of these compounds than that of US in the whole temperature range. As stated before, ring scission of glucose, which makes up cellulose, should be favoured by the presence of mineral matter. This would promote cellulose degradation at temperatures lower than the required for levoglucosan formation. On the other hand, in absence of minerals, cellulose would decompose to produce mainly the aforementioned anhydrosugar. In the case of hemicellulose, if mineral matter is not present, its thermal degradation principally leads to 1,4-anhydro-D-xylopyranose instead of low molecular weight compounds [35]. Since demineralization led to bio-oils with



(a)



(b)

Fig. 2. Effect of the process temperature on products yields for the pyrolysis of the untreated (a) and demineralized (b) peanut shells.

Table 3

Elemental composition, high heating value (HHV) and pH of the bio-oils generated by the pyrolysis of untreated (US) and demineralized (DS) peanut shells at different process temperatures.

Bio-oil	US (400 °C)	US (500 °C)	US (600 °C)	DS (400 °C)	DS (500 °C)	DS (600 °C)
<i>Ultimate Analysis [wt %]</i>						
Carbon	51.8	49.3	54.5	55.9	54.9	55.0
Hydrogen	6.2	8.1	7.3	7.0	6.9	6.5
Nitrogen	2.3	3.7	2.2	1.0	3.1	1.0
Oxygen ^a	39.7	42.1	36.0	36.1	35.1	37.5
HHV [MJ/kg]	21.2	22.5	23.9	24.0	23.7	22.9
pH	3.4	3.1	4.0	2.8	2.9	3.1

^a Estimated by difference.

a higher sugar content, this could be in line with the lower oxygen content of the organic phase of bio-oils arising from pyrolysis of DS (Table 3), as already mentioned. Regarding the process temperature, it had a great effect on the sugar content of the bio-oils derived from pyrolysis of DS. The maximum sugar yield was attained at a temperature of 500 °C. This could be explained considering that at

lower temperatures (400 °C) holocellulose volatilization would not be complete, whereas at higher temperatures (600 °C) secondary reactions would decompose the different sugars into low molecular weight compounds [20]. Instead, the sugar content of the bio-oils arising from US was not significantly affected by the pyrolysis temperature.

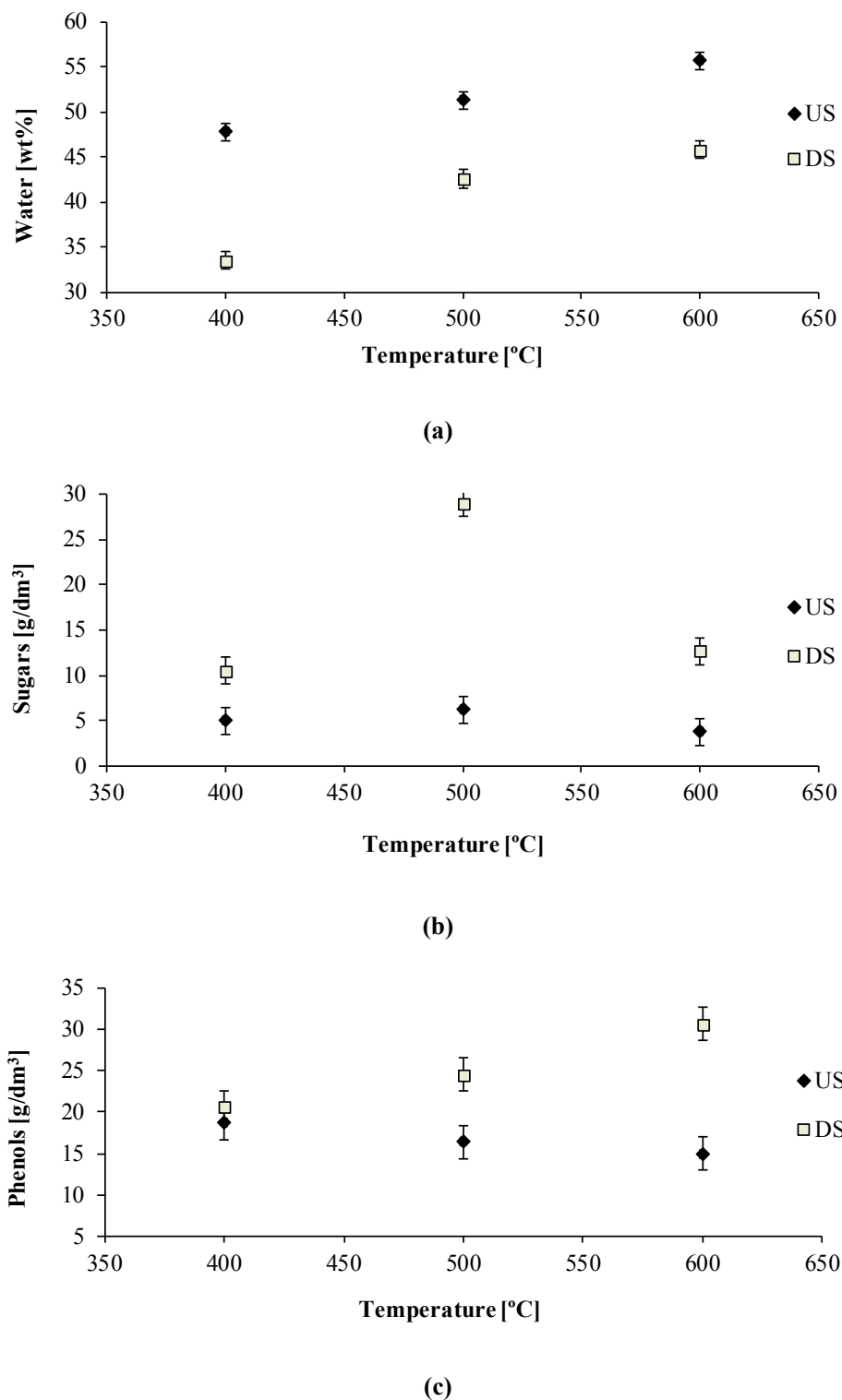


Fig. 3. Contents of water (a), sugars (b), and phenols (c) in the bio-oils generated from the pyrolysis of the untreated (US) and demineralized (DS) peanut shells, at different temperatures. Sugars and phenols were determined in the aqueous phase.

Demineralization also led to bio-oils with higher phenol content (Fig. 3c). This result could be a consequence of the decrease of the degree of crosslinking of lignin due to the mineral removal, considering that lignin is the main source of phenols since it is constituted by 4-hydroxypropane, guaiacylpropane and syringilpropane units [30,35]. Moreover, DS had higher lignin content than

US (Table 1). For the pyrolysis of DS, the increase of temperature promoted a rise in phenol content, while this variable had no noticeable effect on the US phenol content.

The FTIR spectra of the investigated bio-oils are displayed in Fig. 4. All the samples exhibited similar spectra characterized by a strong absorption band at 3400 cm⁻¹, corresponding to O-H

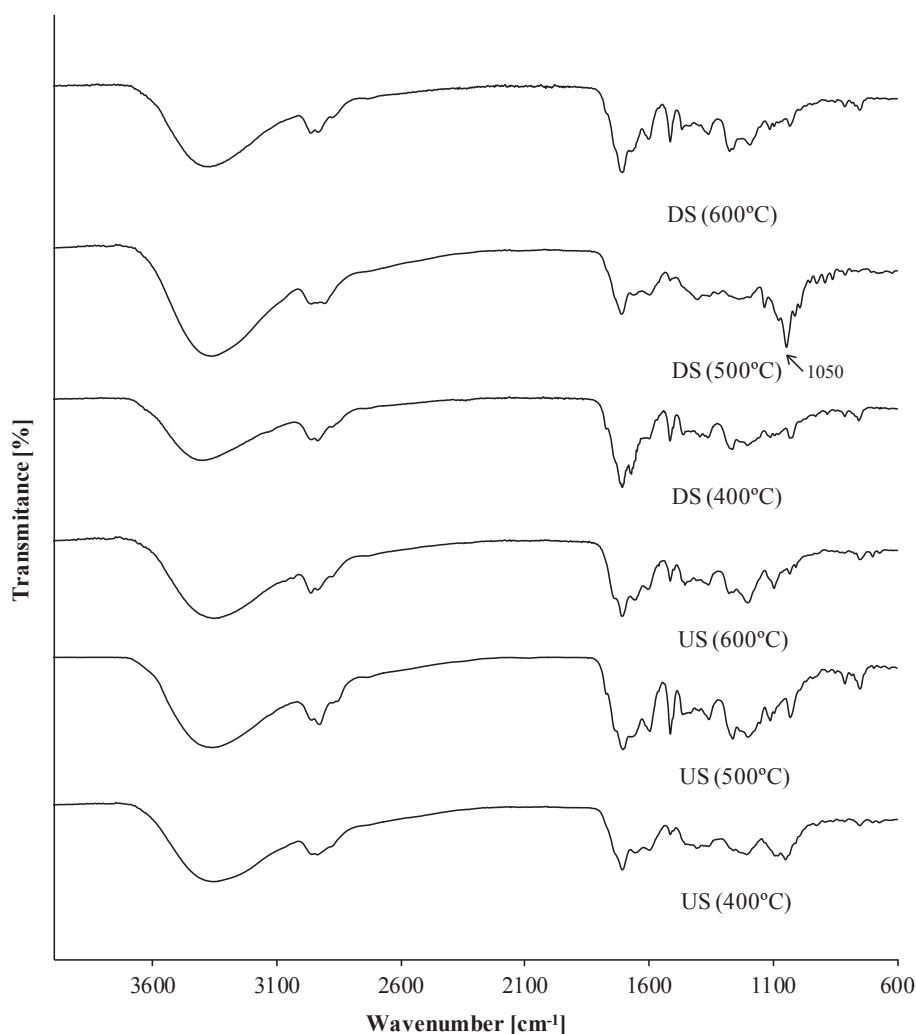


Fig. 4. FT-IR spectra of the bio-oils derived from the pyrolysis of the untreated (US) and demineralized (DS) peanut shells, at different temperatures.

stretching indicating the presence of phenols and alcohols. It can also be recognized absorption peaks at 3000 to 2800 cm^{-1} , attributable to C-H stretching of methyl and methylene groups [36]. The absorption band at 1750 cm^{-1} would be mainly due to the presence of carboxylic acids, ketones and aldehydes, and the absorption bands at 1595 cm^{-1} and at 1500 cm^{-1} may be due to the presence of aromatic compounds. The main difference among the spectra corresponded to the more noticeable peak at 1050 cm^{-1} for the bio-oil generated from the pyrolysis of DS at $500\text{ }^{\circ}\text{C}$. This band, which would correspond to aliphatic ethers, could have been caused by

the ether group of the levoglucosan, in accordance with the high content of sugars of this bio-oil (Fig. 3b).

3.4. Bio-chars

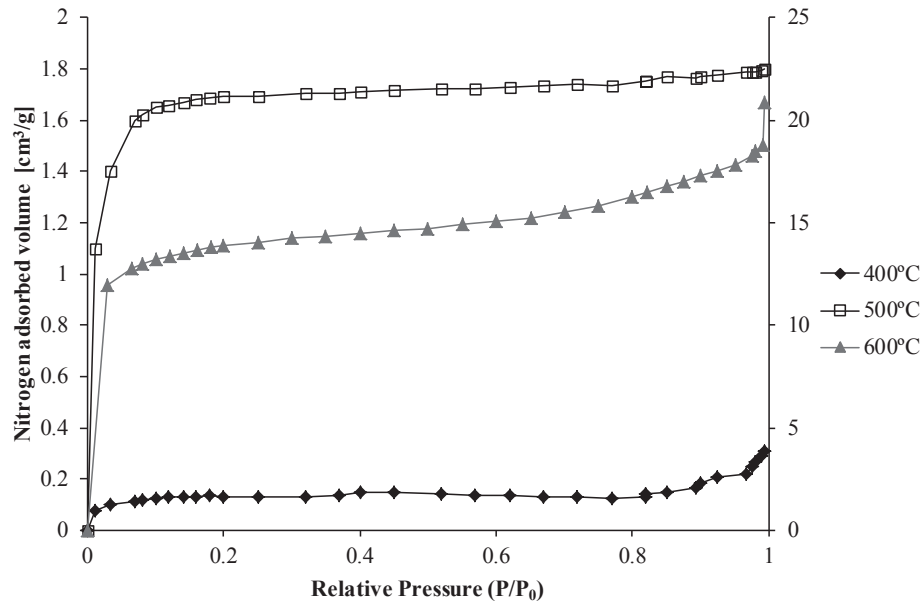
Ash content, elemental composition, and HHV of the bio-chars arising from the pyrolysis of US and DS are displayed in Table 4. In line with the minor ash content of the treated biomass (Table 1), bio-chars derived from pyrolysis of DS presented much lower ash contents than those generated from US. Therefore, combustion of the

Table 4

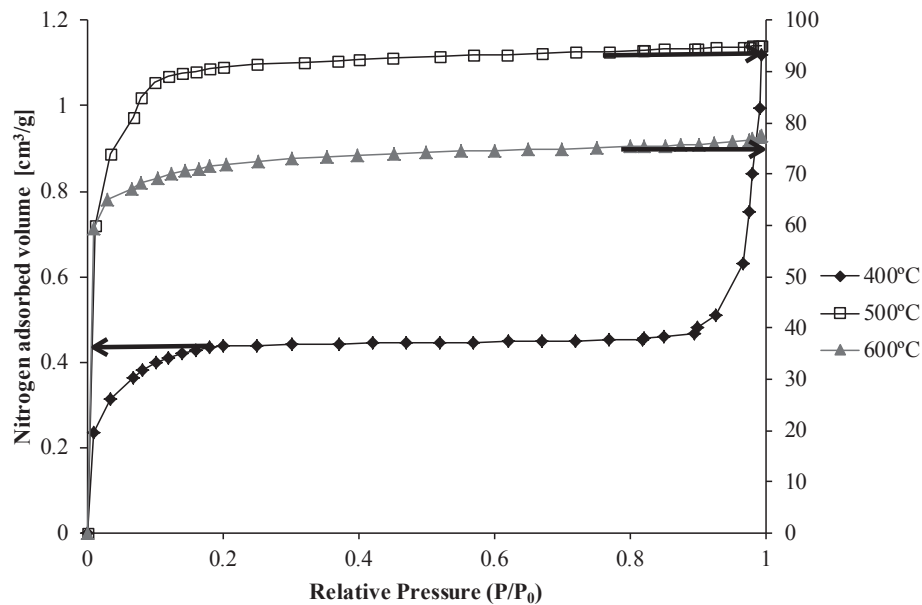
Ash content, elemental composition and high heating value (HHV) of the bio-chars generated by the pyrolysis of untreated (US) and demineralized (DS) peanut shells at different process temperatures.

Bio-char	US (400 °C)	US (500 °C)	US (600 °C)	DS (400 °C)	DS (500 °C)	DS (600 °C)
Ash [wt%, dry basis]	14.2	19.5	19.2	1.8	2.1	2.2
<i>Ultimate Analysis [wt %, dry and ash-free basis]</i>						
Carbon	85.4	88.0	91.1	73.5	86.8	89.0
Hydrogen	3.7	2.3	1.9	5.0	3.0	2.6
Nitrogen	0.6	3.0	0.9	0.5	4.0	1.0
Oxygen ^a	10.3	6.7	6.1	21.0	6.2	7.5
HHV [MJ/kg]	32.7	32.3	33.4	29.3	33.0	33.2

^a Estimated by difference.



(a)



(b)

Fig. 5. Nitrogen adsorption isotherms ($-196\text{ }^{\circ}\text{C}$) for the bio-chars generated from the pyrolysis of the untreated (a) and demineralized (b) peanut shells, at different temperatures.

former bio-chars would cause less fouling and corrosion. Moreover, as expected, the bio-chars had higher carbon content and lower oxygen and hydrogen contents than the biomasses. Volatiles generated during pyrolysis are rich in O and H and, thus, the bio-chars were enriched in C. Increasing the process temperature led to a greater C content of the bio-chars, as decarboxylation and dehydration reactions are favoured at higher temperatures [3]. There were no important differences for the elemental composition of the bio-chars generated from the pyrolysis of US and DS at $500\text{ }^{\circ}\text{C}$ and at $600\text{ }^{\circ}\text{C}$. On the other hand, the bio-char produced by pyrolysis of DS at $400\text{ }^{\circ}\text{C}$ showed a lower carbon content than the one generated

from the pyrolysis of US. As seen in Fig. 1, thermal degradation of the demineralized shells started at higher temperatures and, thus, the oxygen content of the bio-char derived from DS at $400\text{ }^{\circ}\text{C}$ was more similar to that of the acid pretreated shells. This result is in line with the higher yield of the bio-char for pyrolysis of DS at $400\text{ }^{\circ}\text{C}$ (Fig. 2b). The higher oxygen content of this bio-char was responsible for the relatively lower HHV (29.3 MJ/kg) in comparison with that determined for the other five bio-chars, that presented a HHV over 32.0 MJ/kg .

Nitrogen adsorption isotherms of the bio-chars generated by the pyrolysis of US and DS at the different temperatures are presented

Table 5

Textural characteristics of the bio-chars obtained from the pyrolysis of the untreated (US) and demineralized (DS) peanut shells.

Bio-char	US (400 °C)	US (500 °C)	US (600 °C)	DS (400 °C)	DS (500 °C)	DS (600 °C)
S_{BET} [m ² /g]	0.5	5.2	48	1.6	300	248
$V_t \times 10^3$ [cm ³ /g]	1	3	30	2	160	120
r [nm]	4.0	1.7	1.3	1.7	0.9	1.0

in Fig. 5. According to IUPAC classification, all the isotherms presented typical characteristics of type I, pointing out that all the bio-chars were predominantly microporous. The textural properties of these bio-chars are listed in Table 5. At 400 °C, both bio-chars showed almost no porous development as evidenced in negligible BET area. However, at higher temperatures, the pyrolysis of DS conducted to bio-chars with considerable BET area. Acid pretreatment with HCl would wash out minerals that block pores and whose opening would result in porous matrix [12]. Moreover, pore development is generally related to the competition between the amount of volatiles released during pyrolysis and the possibility of condensation reactions that lead to pore blocking. An increase in thermal degradation velocity diminishes the residence time of volatiles inside the pores and, consequently, would reduce the chance of condensation [29,32]. Given that thermal degradation of DS was more abrupt than that of US (Fig. 1), the increase in BET area and total pore volume of the bio-chars arisen from the former sample would be due to the shorter residence time of the volatiles in the pores of these bio-chars.

The FTIR spectra of the developed bio-chars are exhibited in Fig. 6. Compared with the spectra of the bio-oils, these spectra showed less peaks as bio-chars had less functional groups than the liquids. In all

the six spectra, it could be observed a peak at 1600 cm⁻¹, due to C=C bond stretching, and another one at 1370 cm⁻¹, as a result of symmetrical CH₃ group deformation [36]. It can be seen that bio-chars arisen from pyrolysis at higher temperatures exhibited less peaks. The absorption band of the O-H stretching, at 3350 cm⁻¹, was just strong for the bio-chars generated by the pyrolysis of US and DS at 400 °C. For the bio-chars obtained at higher temperatures, this band became faint. The bio-char generated from the pyrolysis of DS at 400 °C was the one which showed more functional groups. Several absorption peaks, such as the ones at 1730 cm⁻¹ (C=O bond stretching of carboxyl/carboxyls), at 1110 cm⁻¹ (corresponding to ketones and esters) and at 1050 cm⁻¹ (C–O bond stretching in alcohols and ethers) were detected. The presence of these groups was in line with the higher oxygen content of this bio-char (Table 4).

3.5. Pyrolysis gases

The yields of the main gases of pyrolysis, calculated on the basis of moles of generated gas per kg of biomass are shown in Fig. 7. At 400 °C, the main generated gas species was CO₂. It would be mainly generated by the decomposition of hemicellulose, which is the less resistant to thermal degradation of the main biopolymer

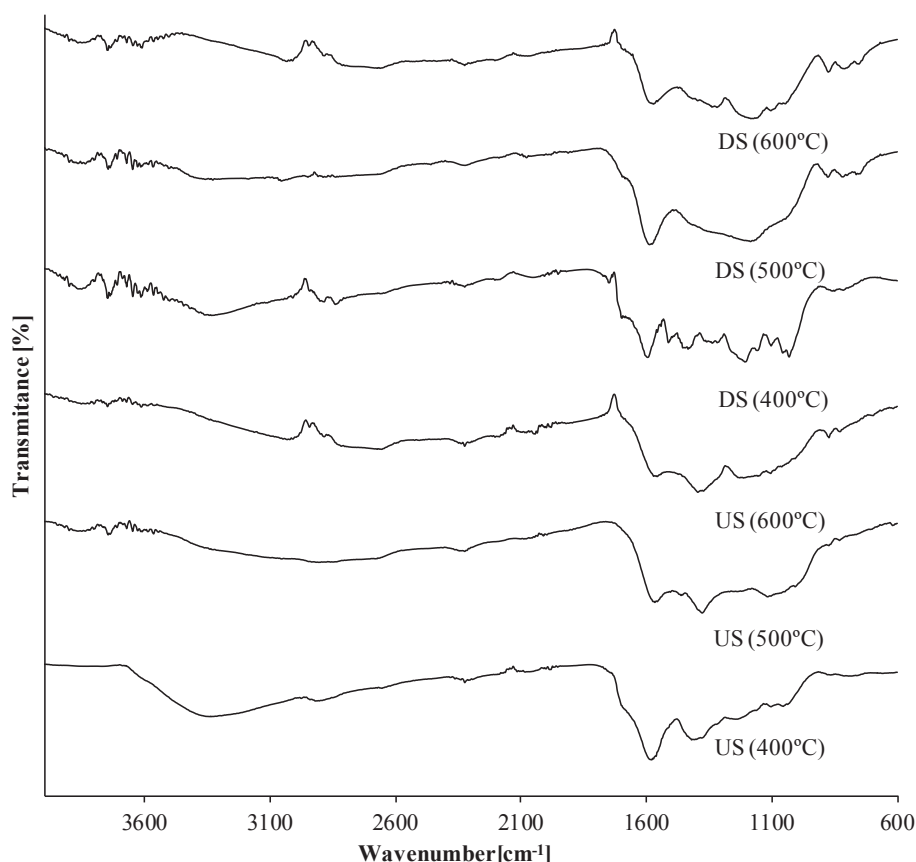


Fig. 6. FT-IR spectra of the bio-chars produced from the pyrolysis of the untreated (US) and demineralized (DS) peanut shells, at different temperatures.

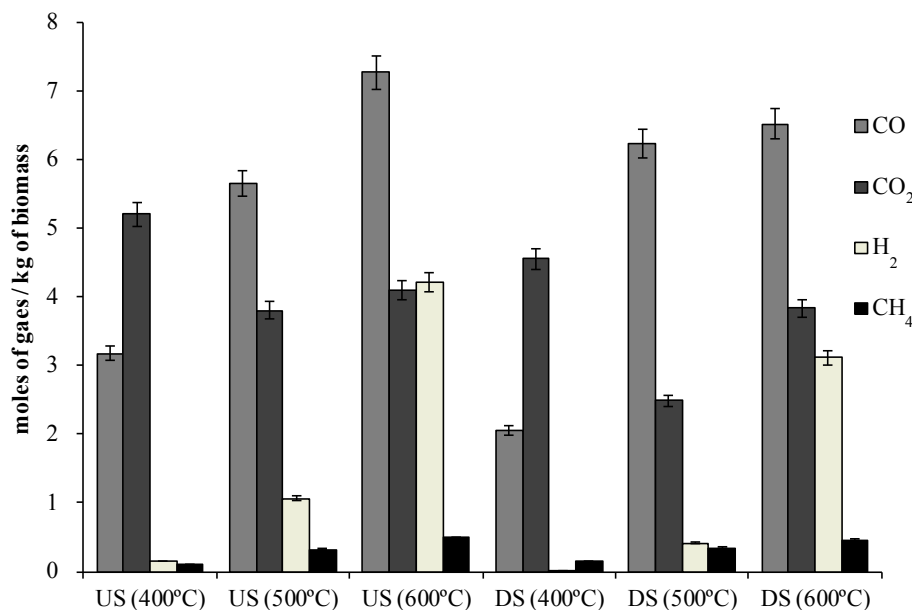


Fig. 7. Production of main gases arising from the pyrolysis of the untreated (US) and demineralized (DS) peanut shells, at different temperatures.

constituents of lignocellulosic biomass [30]. At higher temperatures, CO was the main gas species, likely arising from cellulose decomposition. As both US and DS samples had more cellulose than hemicellulose (Table 1), it was expectable that at higher temperatures more CO than CO₂ would be produced. Moreover, the gasification reaction of the bio-char with CO₂ producing CO could also contribute to the increase of this gas [37]. On the other hand, it can be seen that the pyrolysis of DS at all process temperatures led to a minor generation of CO₂. As alkaline and alkaline earth metals would promote carbonyl and carboxyl rupture, which facilitates CO₂ generation, the pyrolysis of the demineralized sample would produce less of this species [14]. Regarding generation of CH₄ and H₂, the amount of these gases was just significant at 600 °C. Both gases should be mainly due to lignin decomposition. CH₄ would result from the cleavage of the carboxyl groups of lignin, while H₂ would come from the cracking of C–H and C=C aromatic bonds [38]. The HHV of the gaseous products [MJ] per kg of biomass was calculated as the sum of the product of the moles of each gas generated per kg of biomass sample (G_i) and the heat of combustion of each gas [MJ mol⁻¹]:

$$\text{HHV [MJ/kg biomass]} = 0.802 G_{\text{CH}_4} + 0.286 G_{\text{H}_2} + 0.283 G_{\text{CO}} \quad (1)$$

The HHV for the pyrolysis gases arising from US were 1.0, 1.9 and 3.7 MJ/kg biomass for the process temperatures of 400 °C, 500 °C and 600 °C, respectively. In the case of the pyrolysis of DS, the gases had a of 0.7, 2.2 and 2.9 MJ/kg biomass for increasing pyrolysis temperatures. Greater HHV values were due to the higher concentrations of CO, CH₄ and H₂ generated at the higher process temperatures.

4. Conclusions

Pyrolysis of untreated and demineralized peanut shells, an abundant lignocellulosic waste, to generate green energy vectors and other value-added products was comparatively investigated at different process temperatures (400–600 °C). Experiments performed in a fixed bed reactor indicated that the pyrolysis of the acid

pretreated samples led to an increase in bio-oils generation at all process temperatures. Demineralization followed by pyrolysis of the shells resulted in less water generation and in an increase of sugars and phenols contents in the bio-oils. Pyrolysis of the demineralized shells also conducted to bio-chars with a low ash content, which could help to minimize slagging and fouling in furnaces upon their further combustion. The process temperature did not have as much influence as the acid pretreatment on yields and characteristics of the bio-oils. However, it had a strong effect on those of the bio-char and pyrolysis gases. The bio-char generation was reduced and gases production augmented with higher temperature. Furthermore, the carbon content of the bio-chars was greater at higher pyrolysis temperatures. Pyrolysis of the demineralized shells at higher temperatures also conducted to bio-chars with an appreciable BET surface area, pointing to their possible use as rough adsorbents or for further upgrading to activated carbons. On the other hand, rising process temperatures incremented the generation of CO, H₂ and CH₄, in turn leading to enhanced higher heating values of the pyrolysis gases.

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