Pyrolysis technologies for Pomegranate (*Punica granatum* L.) peel wastes. Prospects in the bioenergy sector

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Abstract:

An unpublished low-cost industrial biomass waste, pomegranate peel, as alternative and sustainable fuel source was studied. A horizontal tubular furnace of original design for conventional and flash pyrolysis was carried out. The bio-char yields from both processes were similar, but the bio-oil and bio-gas yields were higher in flash pyrolysis, depending on the temperature. The bio-char obtained show that it could be used as a fuel (higher heating values ≥ 28.0 MJ/kg) and as a potential precursor of activated carbon. It was also found that the lower temperature of the flash pyrolysis was, the greater the bio-oil yield (~53%) and that the higher was, the greater the biogas yield (~50%). The bio-oil from conventional pyrolysis has a predominantly furanic nature and contained significant amounts of the phenols and benzenes. In contrast, the bio-oil from flash pyrolysis is similar to that of "anthracene oil",

both of them being composed mainly of polycyclic aromatic hydrocarbons. The bio-gas obtained by flash pyrolysis is of a higher quality than that obtained by conventional pyrolysis because it has a lower CO₂ content (32.4% vs 66.6%) and higher syngas content (CO + H₂) (50.8% vs 26.8%). Flash pyrolysis is better in CH₄ production (11.6% vs 4.6%).

Keywords: Bio-char; bio-fuels; conventional pyrolysis; flash pyrolysis; industrial biomass waste; pomegranate peels.

1. Introduction

The evolution and development that is taking place in modern society requires new sources of energy and environmentally friendly techniques.

Energy demand is increasing daily and in the world of the future, the different ways of obtaining energy will play a fundamental role. Although traditionally fossil fuels such as coal, petroleum and natural gas have been used, global CO₂ emissions due to the use of such fuels now pose a serious problem with levels which they have quadrupled between 1960 and 2014 [1]. This has led to the growth of the number of research studies into energy sources that favor a more ecological outcome. Renewable sources such as solar, wind, hydroelectricity, biomass and geothermal power [2] are currently used to supply the needs of our society to the detriment of other less advisable.

One of the alternative sources of energy that has emerged in recent years is biomass. This has led to several studies on its use and impact on the economy and development of different countries and on CO₂ emissions [3], [4]. Moreover it is considered to have a net zero CO₂ impact and it is appropriately referred to as bioenergy [5]. There are different thermochemical processes of biomass conversion. One of them, pyrolysis, is able to process a wide variety of residues including urban waste [6], agricultural residues [7], [8], industrial waste [9], [10], etc. and represents a renewable and alternative energy source to combustion [11].

The pyrolysis process is defined as the thermal decomposition of a material in the absence of oxygen or any other oxygen-containing reagent (air, water, carbon dioxide). This process leads to the production of a volatile fraction consisting of bio-gases, a condensable liquid fraction (bio-oils) and a carbon rich solid residue (bio-char). Pyrolysis is seen as a highly versatile process in which it is possible to optimize a variety of experimental variables, such as the final pyrolysis temperature, heating rate, annealing time, etc., depending on whether the desired aim is to maximize the bio-char that can be used as fuel and as a potential precursor for activated carbons [12], [13], or the bio-oils and bio-gases for multiple applications [14], [15].

The present work has focused on pomegranate peels (PP), a low-cost industrial biomass waste, as a possible alternative source of energy. The pomegranate, botanical name *Punica granatum L*, has been cultivated since ancient times throughout the Mediterranean region reaching a significant world production, level of about 1 million tons [16]. Tunisia is one of the largest producers of pomegranates (higher than 60,000 tons) which is concentrated in the south of the country (more than 60% in Gabes) [17]. Most of the pomegranates are destined for local consumption and for the food industry, which generates a large amount of biomass waste (PP). Despite the socio-economic importance of the pomegranates in this country, few works have been published on the chemical composition of pomegranate leaves, flowers, juice and peels [18].

Although some pyrolysis studies have been devoted to pomegranate seeds or pulp [19], [20], none have been focused on PP.

The main objective of this research work is to study the using of a low-cost industrial biomass waste, PP, through conventional and flash pyrolysis, into a possible source of energy and to evaluate its potential as a fuel in the bioenergy sector. To this end, the comparison, characterization and analysis of the PP pyrolysis fractions (bio-char, bio-oil and bio-gas) obtained from the two thermochemical processes were also reported.

2. Materials and methods

2.1. Biomass

Pomegranate is a tropical and subtropical fruit with extensive crop cultivation in Tunisia. It is destined for multiple uses and is consumed in desserts, juices, etc., or as fresh fruit. Its consumption generates a large amount of waste in the form of the peel of the fruit.

Pomegranate peels are generated in a local industry from the fruit processing (coast of Tunisia, Gabès). The total sample of the biomass wastes (4 kg) was cleaned and dried at 40°C. The total sample was subdivided into amounts of 1 kg and then crushed and sieved to obtain particle sizes of between 1.5 and 5 mm for subsequent treatment in a series of experiments. The particle size was adapted to appropriate sizes for a possible industrial use.

2.2. Characterization of the samples

2.2.1. Chemical characterization

The ash content was determined by calcining the sample in a muffle at 815°C for 1h in the presence of oxygen, according to the UNE 32004 norm [21] and the moisture of the sample was obtained following the UNE 33002 norm [22], on the basis of the weight loss at 105°C over a period of 1 h. The carbon, hydrogen and nitrogen contents of the samples were determined using LECO CHN-2000 equipment while determination of the sulphur content was carried out on a LECO S-144-DR instrument (LECO Corporation, Groveport, Ohio, United States). The oxygen content was calculated by difference. The high heating values (HHV) were determined on an adiabatic IKA-calorimeter C4000 (IKA, Germany).

2.2.2 X-Ray Diffraction (XRD)

X-ray diffraction was performed on the low temperature ashes (LTA) obtained from the industrial biomass waste by using an oxygen plasma asher, EMITECH K1050X (EMITECH Ltd, Ashford, Kent, England), equipped with a RF generator (13.56 MHz) working at 75 W. A Bruker D8 Advance diffractometer (BRUKER, Germany) equipped with a graphite monochromator and an internal silicon powder pattern and connected to a CuK α radiation source was used to obtain diffraction data. The

diffraction data were collected by step scanning using a step size of 0.02° and a step-time of 3 s. The scan range was from 5 to 80 (2θ).

2.2.3 *Thermogravimetric analysis*

The TGA curves for the PP were obtained using a TGA-Q5000IR thermobalance (TA Instruments, New Castle, DE, EE.UU.). Samples weights of approximately 16-25 mg were heated up to 900°C at a heating rate of 5, 10, 15, 20, 25, 35, $50^\circ\text{C}/\text{min}$ under a nitrogen flow of 25 ml/min. With the data obtained from the analysis a kinetic study of the thermal behavior of the sample was carried out.

2.2.4 *SEM-EDX*

The PP and the bio-char obtained from the conventional and flash pyrolysis were examined using a scanning electron microscope, ZEISS Model DMS-942 (ZEISS, United States), equipped with an energy-dispersive X-ray analysis system (Link-Isis II). Prior to examination, the samples were covered with gold to decrease the charging of the samples and to improve the SEM pictures.

2.2.5 *Chromatographic analysis*

An Agilent 7890A chromatograph combined with a 5975C mass spectrometer (Agilent Technologies, Wilmington, DE, USA) was used for the bio-oil chromatographic analysis. An HP-5MS capillary column (Agilent Technologies, Wilmington, DE, USA) (5% phenyl-methylpolysiloxane) with dimensions of 30m x 0.25mm ID x $0.25\ \mu\text{m}$, was employed to separate the compounds. The column was subjected to the following heating program: an initial temperature of 50°C , no dwell time, a heating rate of $4^\circ\text{C}/\text{min}$ up to 300°C . 1 μl (splitless) of the sample was injected into the equipment. The mass spectral libraries used for identifying the compounds included NIST08, Wiley7n and Wiley275. The mass spectrometer was operated in full scan mode (50-550 uma, 3.21 scans/s, 70 eV ionization voltage). Prior to the analysis, the water in the condensable fraction was separated from the organic fraction; according to a procedure described in detail in published works of our research group [9], [10].

Chromatographic analysis of the gaseous fraction was performed on a Hewlett-Packard 5890 Series II chromatograph (Agilent Technologies, Wilmington, DE, USA) equipped with a thermal conductivity detector (TCD). Stainless steel columns packed with Porapak N and a molecular sieve were used to

separate the compounds. The sample injection procedure is described in previous works of our research group [9], [10]. To quantify the gas composition calibration lines obtained from standard mixtures of defined composition were used.

2.3. *Pyrolysis process*

The methodology is based on previous experience of our research group with biomass pyrolysis processes using both conventional and microwaves heating, as reported in the following published works [9], [10], [12], [23], adapting it to an oven of original design. For the pyrolysis the experimental set-up used consisted of a horizontal tubular furnace of original design connected to a N₂ mass flow controller, a series of cooling condensers for capturing the condensable phase and Tedlar sample bags (Supelco Analytical, USA) for retaining the gaseous phase, Fig. 1. The nitrogen gas used in the experiments is ALPHAGAZ 1 (Air Liquide, Spain).

The amount of sample used in each pyrolysis experiment was about 11-12 g of PP. The conventional pyrolysis experiment was conducted employing a flow of N₂ of 100 ml/min, a heating rate of 25°C/min rate, a pyrolysis temperature of 750°C and a time at the final temperature of 1 h. The sample obtained was labelled PP-P750.

On the other hand, in the flash pyrolysis the sample was introduced instantaneously into the furnace when it reached the desired temperature (750 and 850 °C). To this end, a mechanical device which isolates the sample from the outside was employed. During this thermochemical process a N₂ flow of 100 ml/min was used. The samples obtained were labeled PP-PF750 and PP-PF850 respectively.

In both the flash and the conventional pyrolysis, the sample to be analyzed was placed in an alumina crucible (Sigma-Aldrich, USA). A detailed plan of the set up is shown in Fig. 1.

FIG. 1

3. Results and discussion

153 3.1. *Chemical characterisation of the biomass waste (PP)*

154 The ash content and the results of the ultimate analysis of the PP are shown in [Table 1](#).

155

156 **TABLE 1**

The chemical analysis of the PP showed high carbon and hydrogen contents (46.48% and 4.91, respectively). In this work, the waste displays a higher carbon percentage than other organic residues [8], [9], similar to the pomegranate seeds [19] although there is variation in the percentages of the rest of the elemental components: H, N, S and O. The low ash and sulphur contents (3.13% and 0.05%, respectively) of PP, make this waste a potential precursor of adsorbent materials [24], [25], [26]. The heating value of the PP was 17.1 MJ/Kg (Table 2).

The mineral species present in the PP were determined in the ashes obtained at low temperature (LTA). Identification of the crystalline species was carried out by X-ray diffraction (XRD). Fig. S1 (in Supplementary material) shows XRD spectrum corresponding to the pomegranate peel waste ashes (LTA). X-ray diffraction of the PP ashes showed the main mineral phases of the sample to be lime (free CaO), MgO, larnite ($2\text{CaO}\cdot\text{SiO}_2$), calcium carbonate (CaCO_3), quartz (SiO_2), Brownmillerite ($4\text{CaO}\cdot\text{Al}_2\text{Fe}_2\text{O}_6$), and calcium aluminosilicate ($2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$) between $25\text{--}35^\circ$ (2θ) [27].

3.2 Thermal behavior of the biomass waste (PP)

Fig. 2 shows the mass loss (%) and the derivatives of the mass loss ($\%/^\circ\text{C}$) curves obtained during the pyrolysis of PP under an inert atmosphere (N_2 at 25 ml/min) at different heating rates (5, 10, 15, 20, 25, 35, $50^\circ\text{C}/\text{min}$) and several peaks can be observed.

FIG. 2

Generally, biomass devolatilization occurs in three stages: water evaporation, active and passive pyrolysis [28].

The pyrolysis of the PP shows an initial weight loss at temperatures lower than 120°C due to the elimination of water and the more volatile compounds in the sample. After this stage, a substantial weight loss between $200\text{--}600^\circ\text{C}$, which corresponds to the second stage, is due to an

intense structural fragmentation of the biomass and the formation of condensable hydrocarbons and gas emissions; this is due to the decomposition of the major constituents of the lignocellulosic materials (hemicellulose, cellulose and lignin). In contrast with the findings of most studies [9], [10], [29], in the present work three consecutive peaks are observed between 200-380°C as opposed to just one. Between 200-240°C the protruding peak seems to correspond to the degradation of lignin monomers or hemicellulose. This peak also reflects the contribution of pomegranate peel pectin decomposition, as also reported in the work of Yang et al. [30], where a centered weight loss is observed at 237 °C; this peak can be assigned to the pyrolytic de-polymerization and decomposition of the pectin molecules [31]. From 240°C to 380°C, hemicellulose and cellulose decomposition is apparent with peaks frequently overlapping with that of lignin which decomposes over a wide range of temperatures through the entire pyrolysis process. According to Słopiecka et al. [28] the decomposition of hemicellulose takes place at 200-380°C and that of cellulose in the range of 250-380°C although Kilzer and Broido [32] report that the beginning of decomposition of the cellulose occurs at around 220°C. Cellulose is a well-known compound and several models have been formulated to explain its decomposition [33], [34]. As mentioned in the literature [28], lignin decomposes at 180-900°C but without producing any pronounced peaks. Lignin can be defined as an irregular polymer of phenylpropane units [35]. In this work, at 380-570°C a peak can be appreciated as in the thermogravimetric study of biocollagenic wastes of vegetable tanning [10]. The stage between 600°C and the final temperature of the experiment is dominated by thermal stability, passive pyrolysis, except for another soft peak between 600-700°C that might represent the decomposition of inorganic material such as metal carbonates [9]. This stage is characterized by the regrouping of aromatic rings and the breakage the solid fractions or bio-chars formed [29].

As the pyrolysis curves obtained from the thermogravimetric analysis of the PP show (Fig. 2), the percentage of the final weight loss depends only minimally on the heating rate. Interestingly it can be observed that as the heating rate increases, the DTG curves are displaced to the right. This can be attributed to the limitations of heat transfer as the heating rate increases, the time required for the gas purge to reach the temperature required by the process also

increases [10], [36]. On the other hand, the DTG (Derivative Thermogravimetry) curve allows the critical points, such as the instants of maximum speed of mass loss and the kinetics of the process to be determined while a kinetic study based on a simulated differential curve can be obtained from the extracted kinetic parameters [9], [10], [37]. In the light of these data and the decomposition temperatures, the pyrolysis temperature and the heating rate were adjusted to 750 °C and 25 °C/min, respectively, to carry out the pyrolysis in the furnace of original design.

Thus, thermogravimetric analysis (TG-DTG) was employed to study the thermal and kinetic decomposition of PP waste in order to select the most suitable conditions for obtaining the three pyrolysis fractions (solid, condensable liquid and gas).

3.3 *Pyrolysis technologies*

Three products were obtained during the pyrolysis under selected experimental conditions: bio-char, condensable and gas phases. In the case of conventional pyrolysis process the heating is gradual and the proportions obtained from the three fractions are similar, Fig. 3. The solid fraction (bio-char) yield was similar in both pyrolysis technologies, around 30%, although considerable differences were observed in the yields of the other two fractions (bio-oil and bio-gas) (Bio-oils: P750 ~35%, PF750 ~53%, PF850 ~24%. Bio-gas: P750 ~36%, PF750 ~16%, PF850 ~50%). In the flash pyrolysis, at 750°C, the liquid fraction predominated over the rest, whereas at 850°C gas fraction was predominant.

The yields of the three fractions obtained by the conventional pyrolysis of PP with this furnace of original design are similar to those obtained by the previously reported conventional pyrolysis of an industrial macroalgae waste in a Carbolite furnace of larger dimensions [9]. These results were expected as in both cases the biomass waste is of a lignocellulosic nature.

FIG. 3

The characteristics of the biomass (moisture, chemical composition, particle size,...) and the experimental parameters (temperature, heating rate, residence time, ...) also influence the

product yield which may display different properties as a result [38]. In fact, several studies have reported that temperature and the longer residence times and slow heating rates cause an increase in gas production and a reduction in the liquid yield [39], [40]. In their pyrolysis investigations on softwood by R. Alén et al. [41], in the temperature range of 400-1000°C a change in the behavior of the wood constituents and a reduction from 70%-20% in char yield were observed when the temperature increased. The temperature used is a determining factor, because at low temperatures some of the material may remain unreacted [40]. Another way to modify the yield of the different pyrolysis fractions is through the addition of other compounds such as clay mineral bentonite [42].

Flash pyrolysis for a short time and a high heating rate are commonly used to obtain bio-oil [43] apart from offering others advantages in the conversion of biomass [44]. Likewise, the production of gas is favored at higher temperatures [38] which explains why in the present study a greater percentage of gas fraction was obtained at 850°C than at 750°C in flash pyrolysis.

3.4 *Characterization of the different pyrolysis fractions*

3.4.1 *Solid fraction: Bio-char.*

Table 1 shows the results achieved by chemical characterization of the industrial biomass waste, PP, and the different bio-chars obtained by conventional pyrolysis: PP-P750 and by flash pyrolysis: PP-PF750 and PP-PF850.

The carbon content of the bio-chars (up to 83.48%) is higher than in industrial biomass waste (46.48%) which is also the case with other wastes [9], [29]. On the other hand, the C content obtained in flash pyrolysis at 850 ° C is greater than at 750°C as reported in other studies [19] due to the influence of temperature. The nitrogen content also experiences a increase in the bio-chars obtained (up to 1.09% vs 0.41% in the biomass waste) by both pyrolysis technologies while there is a decrease in other elements such as hydrogen (up to 1.43% vs 4.91% in the biomass waste) and sulphur, Table 1 . The oxygen content drastically decreases from 45.02% in the biomass waste to values of around 7% in the bio-chars. There are also slight differences in the

chemical characteristics of the materials obtained by the two pyrolysis technologies (carbon content: PP-PF750 81.43% vs PP-P750 82.73%; hydrogen content: PP-PF750 1.43% vs PP-P750 0.70%), [Table 1](#). It is worth noting the low nitrogen and sulphur contents in the bio-chars which would make possible the energetic use by combustion of the bio-chars since very little or no nitrogen and sulphur oxides will be generated.

The heating values of the bio-chars obtained by conventional and flash pyrolysis also improved from 17.1 MJ/kg to ~28.5 MJ/kg ([Table 2](#)). These values are similar to or higher than the results of other bio-chars derived from different wastes [\[10\]](#), [\[23\]](#).

TABLE 2

Although chemical characterization of the bio-chars obtained by flash and conventional pyrolysis showed only slight differences, as just commented, SEM-EDX analysis revealed structures that differed from one char to another, [Fig. 4](#).

FIG. 4

In the biomass waste (PP) a fibrous rigid vegetal structure is observed and remains after the pyrolysis process at 750°C and 850°C but before thermochemical degradation the surface looks smooth and devoid of pores [\[26\]](#), [\[45\]](#). From the images, it can be inferred that when the raw material undergoes thermal degradation its structure changes and pores appear in the bio-chars obtained.

The bio-char generated shows peculiar characteristics depending on the type of pyrolysis technologies carried out and a porous structure appears. In the bio-char obtained by conventional pyrolysis, bubbles are formed and some of them show various fissures, probably because they are about to explode. This is confirmed by an examination of the flash pyrolysis bio-chars where the vacuoles or bubbles formed have already burst and volatile products have

been released into the gas stream. This might explain the large amount of gases and liquids in the samples obtained by flash pyrolysis, [Fig. 3](#). The bubble formation is more active and vigorous in the flash pyrolysis samples. This is also common when the heating rate increases [\[46\]](#).

3.4.2. *Liquid fraction: Bio-oil*

Bio-oil is another fraction whose applications as biofuel are multiple and very useful in various fields, one of which is industrial power generation. The high heating value (HHV) of the bio-oils obtained in the present work was calculated with an empirical equation developed by Friedl et al. [\[47\]](#) about prediction of heating values of biomass fuel from elemental composition:

$$\text{HHV (MJ/kg)} = (3.55 \cdot C^2 - 232 \cdot C - 2230 \cdot H + 51.2 \cdot H + 131 \cdot N + 20,600) \times 10^{-3}$$

The high heating values of the bio-oils obtained in this work are practically the same (~20.4 MJ/Kg) and independent of pyrolysis technologies, [Table 2](#). These results are similar to those obtained by R.R. Gil et al. [\[10\]](#) in his study of the pyrolysis of biocollagenic wastes of vegetable tanning and lower than those of fuel oil, gasoline or diesel (44–46 MJ/kg) [\[48\]](#).

In this study the bio-oils were analyzed by chromatographic analysis. [Fig. S2](#) (in Supplementary material) shows chromatograms of the bio-oils obtained by the two pyrolysis technologies and in [Table S1](#) (in Supplementary material) their chemical compounds are presented.

In this work, flash pyrolysis at 750°C generated the highest percentage of liquid fraction of all, around 53%, 31% of solid residue and 16% of bio-gas.

Some research studies contain an analysis of the condensable fraction obtained from pyrolysis of biomass waste and a possible classification of the compounds present in the bio-oil is provided by some authors [\[9\]](#), [\[10\]](#), [\[14\]](#). In [Fig. 5](#) of the present work, the relative abundance of the compounds detected by GC-MS for the conventional and flash pyrolysis pomegranate peel bio-oils are presented. It can be seen that the bio-oil compounds obtained from these two pyrolysis technologies differ greatly. Conventional pyrolysis favours the formation of oxigenated

organic compounds (furan and their derivatives ~54%, phenol and their derivatives ~25%); the main organic compounds characteristic of conventional pyrolysis bio-oil (furan and their derivatives) are not obtained by flash pyrolysis in appreciable amounts (less than 7%). On the other hand, organic compounds with several aromatic rings (PAH) such as phenanthrene, anthracene, fluorene, fluoranthene, pyrene and naphthalene, are present in the flash pyrolysis bio-oils. These organic compounds are absent in the conventional pyrolysis bio-oils, [Fig. 5](#).

FIG. 5

The thermal degradation of cellulose and hemicellulose generates a large amount of furan derivatives [\[49\]](#) which can be used as solvents for resins and for the synthesis of chemical products such as insecticides, stabilizers and pharmaceutical products.

Benzenes and phenol compounds originate from lignin which is a rich source of phenolic compounds, phenols and alkylbenzenes [\[19\]](#). The formation of the benzene ring structure is produced by a polycondensation reaction between aldehydes and ketones, or by the decomposition of amino acids [\[50\]](#). The benzenes and phenolic compounds can be used for the preparation of products such as synthetic resins, dyes, pesticides, lubricating oils, solvents, etc.

Despite the high heating values of the bio-oils obtained in the PP flash pyrolysis, its high content in PAH compounds (greater than 60%) greatly restricts its use for energy purposes (combustion). The substance "anthracene oil" is composed of phenanthrene, anthracene, acenaphthene, fluoranthene, fluorene, pyrene and carbazole and many of these compounds are found in the bio-oils obtained in PP flash pyrolysis. Anthracene oil is used as a raw material for the production of carbon black, pitches [\[51\]](#), etc. Most PAHs like phenanthrene are used to make dyes, plastics, pesticides, explosives and are also employed in clinical research and for drug synthesis. In the plastic industry, synthetic tanning agents and phenanthrene, when subjected to high temperatures and high pressure, may undergo hydrogenation to produce hydrophenanthrene, which is an essential component of the fuel used of senior jet aircraft [\[52\]](#).

Russell et al. [42] in their work about the increase of charcoal yield in the slow pyrolysis of biomass observed that the clay mineral bentonite addition led to the improvement of the charcoal and gas yield at the expense of heavy oils during biomass pyrolysis. The increasing pyrolysis temperature and clay mineral content lead to a greater degree of the cracking reactions with the decomposition of heavy pyrolysis oils into lighter oils.

In this work, it can be seen the absence of nitrogen compound in the bio-oils. This fact is contrary to happens in the pyrolysis of other similar industrial biomass waste, such as macroalgae waste from the Agar–Agar industry [23], where the pyrolysis bio-oil present significant quantities of nitrogen compounds (higher than 35%) such as pyrroles, pyrazoles, pyridines. This fact can be due to the high nitrogen content (5.21%) present in the macroalgae waste versus to the small amount of nitrogen content (0.41%) present in the pomegranate peel wastes. Something totally similar happens in the pyrolysis of an other industrial waste, leather waste, whose pyrolysis bio-oils present a 37.1% of nitrogen compounds (the leather waste present a 7.5% nitrogen content) [10].

3.4.3 Gaseous fraction: Bio-gas

The high heating values of the gas fractions are shown in Table 2. Flash pyrolysis produces gas fractions with HHV values higher than that obtained with conventional pyrolysis. Flash pyrolysis at 850°C produced a gas fraction with highest HHV (11.5 MJ/Kg). The heating values of the pyrolysis gases are lower than those of other gaseous fuels, such as natural gas (56 MJ/kg) but they are higher to those of blast furnace gas (2.74 MJ/kg).

The pyrolysis of biomass produces a gas rich in carbon oxides due to the high carbon and oxygen content of industrial biomass waste, Table 1. The formation of the gaseous compounds is a consequence of cracking reactions and the reactions between the species formed during pyrolysis.

Fig. 6 shows the different compounds contained in the bio-gas fraction obtained from the different pyrolysis technologies of PP.

FIG. 6

The main gases produced are: CO₂, CO, H₂, CH₄, and in a lesser proportion oxygen and other hydrocarbons as C₂H₄, C₂H₆, C₃H₆, C₄H₆ .

The origin of CO₂ is mainly dependent on the carboxy groups present in the biomass waste. It is important to note that less CO₂ is produced in flash pyrolysis than in conventional pyrolysis (~35% vol. vs ~65% vol.). CO is mainly formed from the secondary cracking of volatiles and by a reduction of CO₂ [9], [10], and its generation is favored in flash pyrolysis (higher than 30% vol.) in this study. The formation of methane is due to release of methyl radicals. Flash pyrolysis produces more CH₄ than conventional pyrolysis (higher than 10% vol. vs lower than 5% vol.). This gas compound is favored by the low temperature in conventional pyrolysis [42], as occurs in the flash pyrolysis in the present work (Fig. 6), while high temperatures favor the production of hydrogen [38]. The hydrogen is probably caused by the polycondensation of free radicals generated during the pyrolysis process and by dehydrogenation reactions in the char and oil, such as aromatization, condensation and the formation of alkenes. Most of the H₂ production (nearly 20% vol.) takes place in flash pyrolysis at the highest temperature.

The bio-gas fraction of sample PP-PF850 was the largest one: around 48%. Furthermore, the highest production of syngas corresponds to this sample. However, other authors have reported that the production of syngas is favored more by conventional pyrolysis than by the flash process [38].

3.5. Kinetic study

The kinetic study of PP by dynamic thermogravimetry is based on reactions of thermal decomposition of the biomass waste from room temperature to 900°C and sample weight loss speed is analyzed.

Kinetics calculations involve a knowledge of the reaction mechanisms and the behavior when the raw material is subjected to thermal degradation. Pyrolysis of the organic materials generates a large number of reactions some of which are very simple. However pyrolysis kinetics and mechanism reactions are not fully known because of the complex nature of the reactions.

The use of dynamic experiments at different heating rates generates more kinetic data and is more useful for the study of pyrolysis at higher temperatures than isothermal experiments at low preheating rates [53].

The Arrhenius equation is used by many researchers [9], [10], [54], for calculating kinetic parameters:

$$K(T) = Ae^{-E/RT}$$

where $K(T)$ expresses the variation in the reaction speed as a function of temperature; A is the preexponential constant; E is the apparent activation energy (Jmol^{-1}); R is the universal gas constant ($8.314 \text{ Jmol}^{-1}\text{K}^{-1}$) and T is the temperature (K).

The methods for calculating the activation energy are based on several mathematical models: Friedman, Horowitz-Metzger, Van Krevelen, Coats-Redfern, Flynn-Wall...) [10], [37], [55]. In this study Coats-Redfern has been used [28], [37]. The kinetic parameters values (average activation energy (E) and the preexponential factor (A)) and the reaction order (n) are shown in Table 3 and the simulated differential curve in Fig. 7.

TABLE 3

FIG. 7

The kinetic study has been divided into 5 steps for the PP waste heated at $25^\circ\text{C}/\text{min}$, as we can see in Table 3, as against less steps in other works [9], [10]. The main difference to other studies is to be found in the three differentiated DTG curves obtained for the lignocellulosic

biomass compounds (cellulose, hemicellulose and lignin) during the thermal decomposition [10], [34], [36]. In other works, [9], [10], [55], the curves overlap whereas in this work three distinct stages are observed between 200-380°C corresponding to the decomposition of the lignocellulosic compounds.

Table 3 shows that the first order model is suitable for all the steps except the last one, which requires a third order model. The stage after 900°C because of the slow rate of weight loss is considered a passive pyrolysis zone.

4. Conclusions

Based on the thermogravimetric analysis, at higher temperatures than 750°C the PP does not present a significant decomposition. The variation in heating rate (5-50 °C/min) did not seriously affect the degradation of the PP. Moreover, in the DTG curves, hemicellulose and cellulose decomposition was observed to overlap with lignin, although in this case, the three peaks corresponding to these lignocellulosic compounds, were clearly differentiated between 200-380°C. The peak between 200-240°C also reflects the contribution of pomegranate peel pectin decomposition, which can be assigned to the pyrolytic de-polymerization and decomposition of the pectin molecules.

The amounts of bio-char obtained by the conventional and flash pyrolysis of PP was more or less the same (~30 %) while the bio-oil and bio-gas fractions obtained were higher in the flash pyrolysis, depending on the temperature.

The bio-chars obtained from the conventional and flash pyrolysis of PP, are suitable for use as fuel (higher heating values (HHV) ≥ 28.0 MJ/Kg) and as activated carbon precursors due to their high carbon (higher than 81.43 %) and low ash (lower than 9.12 %) contents.

Conventional pyrolysis favors the production of bio-oil with oxygenated organic compounds (furan and their derivatives ~54%, phenol and their derivatives ~25%). Furan and their derivatives are not produced in appreciable amounts in flash pyrolysis (less than 7%). Organic compounds belonging to PAH (phenantrene, anthracene, fluorene, fluoranthene, pyrene and

naphthalene) are present in the flash pyrolysis bio-oils but they are absent in the bio-oil obtained by conventional pyrolysis. Due to the low nitrogen content in the pomegranate peel waste the pyrolysis bio-oils do not present nitrogen organic compounds. The sample that contains the largest bio-oil fraction is PP-PF750. Pyrolysis bio-oils can be used in several applications such as organic industrial synthesis and in a possible energy production.

The gases produced in these pyrolysis processes were CO₂, CO, H₂, CH₄, and to a lesser extent oxygen and other hydrocarbons such as C₂H₄, C₂H₆, C₃H₆, C₄H₆. The gas fraction of the flash pyrolysis process carried out at 850°C was the largest comprising around 48% of the total products. It was found that the production of CO₂ was lower in the flash pyrolysis than in conventional pyrolysis (35% vol. vs 65% vol.). Flash pyrolysis is better than conventional one in the CH₄ production. The highest H₂ yield (nearly 20% vol.) and syngas yield (higher than 50% vol.) were obtained in flash pyrolysis at the highest temperature.

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FIGURE CAPTIONS

Fig. 1. Pyrolysis set up

Fig. 2. TG and DTG data for the pyrolysis of Pomegranate Peels

Fig. 3. Product yields from conventional and flash pyrolysis

Fig. 4. SEM micrograph of the biomass waste and the bio-chars.

Fig. 5. Relative abundance of the compounds detected by GC-MS in the bio-oils.

Fig. 6. Composition (vol. (%)) of gases produced from conventional and flash pyrolysis of the pomegranate peels.

Fig. 7. Comparison between the observed (solid line) and simulated differential curve (symbols) for PP at 25°C/min.

Table 1. Chemical composition of the biomass waste (PP) and the chars obtained in conventional and flash pyrolysis

SAMPLE	Ash (%)*	C (%)*	H (%)*	N (%)*	S (%)*	O (%)**	H/C	H/O
PP	3.13	46.48	4.91	0.41	0.05	45.02	0.11	0.11
PP-P750	8.52	82.73	0.70	0.87	0.03	7.15	0.01	0.10
PP-PF750	9.12	81.43	1.43	1.00	0.04	6.98	0.02	0.20
PP-PF850	8.35	83.48	0.75	1.09	0.04	6.29	0.01	0.12

*Dry basis

**Determined by difference

Table 2. Heating values of the pomegranate peel (PP) and pyrolysis fractions from conventional (PP-P750) and flash pyrolysis (PP-PF750 and PP-PF850)

SAMPLE	HHV (MJ/Kg)		
	Bio-char	Bio-oil	Bio-gas
PP-P750	28.0	20.4	3.6
PP-PF750	28.6	20.3	10.3
PP-PF850	28.5	20.3	11.5
HHV of PP is 17.1 MJ/Kg			

Table 3. Kinetic parameters during pyrolysis of pomegranate peels

Heating rate (25°C/min)				
T(°C)	n	A (min ⁻¹)	E (KJ/mol)	R ²
50-120	1	9.07E+06	39.93	0.98
120-230	1	4.12E+09	78.89	0.99
230-290	1	2.46E+12	116.43	0.99
290-380	1	1.46E+13	137.11	0.99
380-750	3	1.84E+06	72.54	0.98

- 1- N_2
- 2- Mass flow controller
- 3- Stick with mechanical device
- 4- Horizontal tubular furnace

- 5- Alumina crucible
- 6- Quartz tube
- 7- Cooling condensers
- 8- Tedlar sample bag

Figure 1.

Figure 2

Figure 3.

Figure 4

Figure 5.

Figure 6

Figure 7

Supplementary data for:

**Pyrolysis technologies for Pomegranate (*Punica granatum L.*)
peel wastes. Prospects in the bioenergy sector.**

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Figure S1. XRD spectrum corresponding to the ashes of the pomegranate peels

Figure S2. GC-MS chromatogram of the bio-oils obtained from the pomegranate peels by conventional and flash pyrolysis.

Table S1. Bio-oils chemical compounds

Conventional pyrolysis: BIO-OIL PP-P750			
Peak	Retention time (min)	Percentage quantified area	Compound
1	3.390	28.23	Furfural
2	3.736	2.49	Dimethylfuran
3	4.802	0.44	Methyl-Cyclopenten-one
4	4.916	4.80	Furanyl-Ethanone
5	5.227	2.62	Dimethyl-Pentene
6	6.238	11.73	Methyl-Furancarboxaldehyde
7	6.798	4.04	Phenol
8	8.058	2.15	Hydroxy-methyl-Cyclopenten-one
9	8.965	1.12	Methyl-Phenol
10	9.693	1.18	Methyl-Phenol
11	9.986	5.62	Methoxy-Phenol
12	10.982	1.50	Maltol
13	13.396	1.29	Methoxy-methyl-Phenol
14	13.988	6.52	Benzenediol
15	15.002	2.63	Hydroxymethyl -Furancarboxaldehyde
16	15.729	1.69	Methoxy-Benzenediol
17	16.244	1.69	Ethyl-methoxy-Phenol
18	17.39	2.37	Acetoxymethyl-Furaldehyde
19	18.627	4.66	Dimethoxy-Phenol
20	20.42	3.49	Propenyl-Cyclopentane
21	21.656	2.74	Methoxy-propenyl-Phenol
22	24.188	2.08	Hydroxy-Methoxy-Benzeneacetic acid
23	28.972	1.88	Dimethoxy-propenyl-Phenol
24	56.939	0.84	Stigmastan-diene
25	60.374	2.19	.gamma.-Sitosterol

Flash pyrolysis: BIO-OIL PP-PF750			
Peak	Retention time (min)	Percentage quantified area	Compound
1	6,899	11,10	Phenol
2	8,929	0,64	Methyl-Phenol
3	9,609	2,58	Methyl-Phenol
4	14,181	0,51	Dihydro-benzofuran
5	14,449	0,75	Dihydro-benzofuran
6	20,854	0,37	Biphenyl
7	21,401	1,13	Biphenylene
8	23,427	0,35	Dibenzofuran
9	24,259	0,33	Dibenzofuran
10	24,813	0,62	Fluorene derivate
11	24,995	0,20	Fluorene derivate
12	25,249	1,22	Naphthalenol. acetate
13	25,361	2,85	Fluorene
14	25,815	0,45	Naphthalenol. acetate
15	25,922	1,66	Fluorene derivate
16	26,344	1,19	Fluorene derivate
17	26,534	1,85	Fluorene derivate
18	26,831	0,49	Methyl-Dibenzofuran
19	27,528	0,61	Acenaphthylenone

20	28,071	0,48	Methyl-Naphthalenol
21	28,372	0,32	(Ethenediyl)bis-Benzene
22	28,573	1,52	Methyl-Fluorene
23	28,750	0,58	Methyl-Fluorene
24	28,83	0,42	Methyl-Fluorene
25	29,033	1,57	Fluoren-one
26	29,656	1,41	Methyl-Fluorene
27	30,135	0,56	Dihydro- Cyclopropaphenanthrene
28	30,508	0,32	Phenanthrene
29	30,76	10,69	Phenanthrene/Anthracene derivate
30	30,964	4,17	Dibenzofuran
31	32,503	1,25	Dibenzocyclooctene
32	32,740	0,63	Phenyl-Indene
33	32,898	0,92	Methyl-Phenanthrene
34	33,582	1,44	Methyl-Phenanthrene
35	33,735	2,84	Methyl-Phenanthrene
36	33,952	1,81	Cyclopentaphenanthrene
37	34,099	2,10	Methyl-Phenanthrene
38	34,218	1,74	Methyl-Phenanthrene
39	34,315	1,53	Cyclopentaphenanthrene
40	34,636	1,16	Dimetil-Phenanthrene
41	35,122	0,38	Phenylnaphthalene
42	35,474	1,84	Dimethyl-Phenanthrene
43	36,475	0,31	Phenylnaphthalene
44	36,934	1,09	Tricyclohexadeca-octaene
45	37,153	0,85	Dihydro-Indene
46	37,247	0,51	Fluoranthene
47	37,490	3,44	Fluoranthene derivate
48	38,028	2,81	Fluoranthene derivate
49	38,429	0,94	Pyrene
50	38,664	4,69	Ethenyl-Anthracene
51	38,808	0,79	Methyl-Pyrene
52	40,206	0,50	Methyl-Pyrene
53	40,739	0,60	Benzofluorene
54	40,831	1,57	Benzofluorene
55	41,221	2,03	Methyl-Pyrene
56	41,779	0,94	Methyl-Pyrene
57	41,945	0,62	Methyl-Fluoranthene
58	42,144	0,73	Dimethyl-Pyrene
59	43,38	0,58	Dimethyl-Pyrene
60	44,329	0,30	Tetrahydro methoxy-Phenanthrenone
61	44,500	0,47	Cyclopentapyrene
62	45,503	0,86	Benzanthracene
63	45,67	1,65	Triphenylene
64	45,895	1,65	Methyl-Chrysene
65	48,153	0,43	Methyl-Chrysene
66	48,35	0,33	Hexaethylidene-Cyclohexane
67	48,824	0,46	Benzofluoranthene
68	51,568	1,03	Benzofluoranthene
69	52,023	0,24	Benzacephenanthrylene
70	53,026	0,97	Eiconsane

Flash pyrolysis: BIO-OIL PP-PF850			
Peak	Retention time (min)	Percentage quantified area	Compound
1	6.781	7.42	Phenol
2	8.94	0.25	Methyl-Phenol
3	9.635	1.33	Methyl-Phenol
4	12.983	4.10	Naphthalene
5	16.649	1.33	Methyl-Naphthalene
6	17.166	1.13	Methyl-Naphthalene
7	19.378	1.29	Biphenyl
8	20.343	0.40	Ethenyl-Naphthalene
9	20.893	1.62	Ethenyl-Naphthalene
10	21.446	9.64	Biphenylene
11	22.488	0.50	Acenaphthene
12	22.642	0.37	Methyl-Biphenyl
13	23.475	0.94	Dibenzofuran
14	24.297	0.38	Dimethoxy-Benzenemethanol
15	24.844	0.72	Fluorene derivate
16	25.216	0.49	Fluorene derivate
17	25.39	6.11	Fluorene
18	25.95	1.67	Fluorene derivate
19	26.374	1.30	Fluorene derivate
20	26.568	2.15	Fluorene derivate
21	26.887	0.39	Fluorenol
22	28.599	1.33	Methyl-Fluorene
23	28.767	0.37	Methyl-Fluorene
24	29.06	0.61	Methyl-Fluorene
25	29.685	0.53	Fluorenone
26	30.512	0.38	Tetradecahydro-Phenanthrene
27	30.741	14.32	Phenanthrene
28	30.956	6.12	Phenanthrene derivate
29	32.766	0.33	Dibenzocyclooctene
30	32.937	0.20	Phenyl-Indene
31	33.754	1.35	Methyl-Phenanthrene
32	33.968	1.10	Cyclopentaphenanthrene
33	34.095	3.77	Cyclopentaphenanthrene
34	34.314	1.30	Methyl-Anthracene
35	34.676	0.62	Cyclopentaphenanthrene
36	35.499	1.29	Phenyl-Naphthalene
37	36.826	0.27	Tricyclohexadeca-octaene
38	36.939	0.54	Phenyl-Naphthalene
39	37.476	4.50	Fluoranthene
40	38.023	2.69	Fluoranthene derivate
41	38.447	0.69	Fluoranthene derivate
42	38.63	6.52	Pyrene
43	40.867	1.63	Benzofluorene
44	41.256	1.70	Benzofluorene
45	41.807	0.48	Methyl-Fluoranthene
46	41.984	0.40	Methyl-Pyrene
47	44.555	0.65	Tetrahydro-methoxy-Phenanthrenone
48	45.557	0.76	Cyclopentapyrene
49	45.735	1.19	Triphenylene
50	51.673	0.85	Benzopyrene

Graphical abstract