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# Valorization of Forest Waste for the Production of Bio-oils for Biofuel and Biodiesel

*Hammadi el Farissi*

## Abstract

Biomass is a renewable energy source to generate heat and electricity through the enhancement of various organic materials. Cistus slow pyrolysis of seeds and shells was carried out in a fixed bed reactor to determine the effect of pyrolysis temperature, heating rate, and particle size on the performance of pyrolysis. Therefore, pyrolysis experiments were performed at different temperatures, ranging from 300 to 500°C, with heating rates varying from 10 to 70°C.min<sup>-1</sup> for shells and 7 to 28°C.min<sup>-1</sup> for seeds. The particle sizes of samples range from 0.3 to 3.5 mm for shells and 0.075 to 1.2 mm for seeds. The highest yield of liquid products (53.31% for shells; 52.24% for seeds) was obtained at a pyrolysis temperature of 450°C and a heating rate of 40°C.min<sup>-1</sup> for shells and 21°C.min<sup>-1</sup> for seeds. The functional groups and chemical compounds present in the bio-oil obtained under optimal conditions were identified by FTIR. The calorific value of the bio-oil was equal to 37.05 and 37.93 MJ.kg<sup>-1</sup> for shells and seeds, respectively. The obtained results show that the bio-oil from the pyrolysis of Cistus shells and seeds could be used as a renewable fuel or a source of pharmaceutical and chemical raw material.

**Keywords:** bio-oil, bio-fuels, renewable energy, fixed bed pyrolysis, seeds of *Cistus Ladaniferus*, rockrose, green energy, viscosity

## 1. Introduction

The world's oil reserves are not eternal. Exploitation for fuel increases emissions of greenhouse gases that contribute to climate change. Renewable biomass is a promising alternative to petroleum-based products as a source of bio-energy and other bio-products [1], as the chemical value. The condensed Biogas is a type of liquid fuel made from biomass materials. As a kind of new cheap bio-energy, clean, green, bio-oil is considered an attractive option instead of conventional fuel in the aspect of reducing environmental pollution [2].

This study is motivated by a desire for development of natural resources to begin we take as cistus products. The study consisted of pyrolysis byproducts cistus

ladanifer [3]. The cistus pyrolysis regenerates solid carbon-rich products (char) and condensable gaseous products (tar) and non-condensable (hydrocarbons). The process of pyrolysis is the newest part of renewable energy, has been set up and provides the benefits of a liquid product—bio-oil—which can be easily stored and transported and used as a fuel, vector energy and a source of chemicals. Bio-oils have been successfully tested in engines, turbines and boilers, and were up graded to high quality hydrocarbon fuels but currently unacceptably energy and financial cost [4].

The slow pyrolysis is often linked to coal production and fast pyrolysis has been linked to the production of bio-oil. The slow pyrolysis of biomass produces a high content of carbon [5]. Pyrolysis safflower seeds (*Carthamus tinctorius L.*) of particle size between 0.85 and 1.25 mm with a heating rate between 10 and 100°C.min<sup>-1</sup> and the flow rate of nitrogen equals 100 cm<sup>3</sup>.min<sup>-1</sup>, the maximum yield was at 600°C for bio-oil and expensive parallel 53 and 17%. The effect of pyrolysis temperatures, the particle size and the rate of heating on the yield of the apricot kernel shells to pyrolysis temperatures range from 350 to 700°C with a heating rate ranges from 7 at 10°C.min<sup>-1</sup>. For the lower heating rate of 10°C.min<sup>-1</sup>, the carbonization yield is increased from 35.2 to 29.4%, as the final pyrolysis temperature was raised from 400 to 550°C. Same results were also observed by Gerc el [6], who studied the effects of different pyrolysis temperatures and heating rates on pyrolysis (*acanthium Onopordum L.*) When the temperature pyrolysis increased from 350 to 700°C the carbonization yield was increased from 38.3 to 24.1% with a rate of 7°C.min<sup>-1</sup> heating. The decrease in the carbonization yield with increase in temperature could be due to either a larger primary decomposition of biomass at a temperature above or in the secondary decomposition of the tank [7–10]. The gas yield increased from 38 to 43%, with the same amount of increase in temperature. When the temperature increases [11]. *Yorgun et al* studied the fast pyrolysis of sunflower cakes in a tubular reactor. The effect of the final temperature, nitrogen flow rate and particle size on the performance of pyrolysis products were studied. The maximum yield of oil 45% by weight was obtained in the pyrolysis temperature of 550°C, with a flow rate of 1–300 cm<sup>3</sup>.min<sup>-1</sup> sweep gas and the particle size of 0425 to 0850 mm [12, 13].

After a series of studies of characterization of the seeds and shells of cistus by the different techniques of analysis, the determination of the percentages in carbon, oxygen, hydrogen, and nitrogen as well as the determination of the percentages in humidity, ash, fixed carbon, and volatile products, by the elementary analysis of the biomass, we give a clear idea on the pyrolysis of the used biomass. The knowledge of the above-mentioned data creates a good ground for the study of the different factors that influence the yield of bio-oil obtained by pyrolysis. In this chapter, we will study three main parameters that are: the effect of temperature, the effect of granulometry, and the effect of the heating speed on the yield of the two biomasses used.

## 2. Materials and methods

### 2.1 Raw materials

Biomass is the whole of the organic products, plants, and animals used for energy or agronomic purposes. The term biomass covers a very broad field: forestry waste, industrial waste, agricultural waste, the fermentable fraction of household waste and food industries, landfill biogas, or methanization products (sewage sludge, landfills, etc. ...). In this chapter, the different experimental campaigns were carried out using two types of biomass:

We took the initiative to study two types of biomass (**Figure 1**), one with little ash and the other with a lot more ash, in order to compare the different results and to be able to provide solutions for each type of biomass exploited. The main characteristics of the biomasses used are presented below.

## 2.2 Sample characterization

### 2.2.1 Determination of the moisture content

The moisture or water content designated by  $W$  of a sample is the ratio between the mass of water contained in the sample to its anhydrous mass, if we use its total mass this: This ratio will be designated by  $W$ .

$$W = \frac{(m_0 - m_a)}{m_a} * 100 \quad (1)$$

Moisture is determined by subjecting a sample of known mass to oven drying (103°C) for 24 hours until the mass becomes constant. The humidity can be expressed as a percentage.

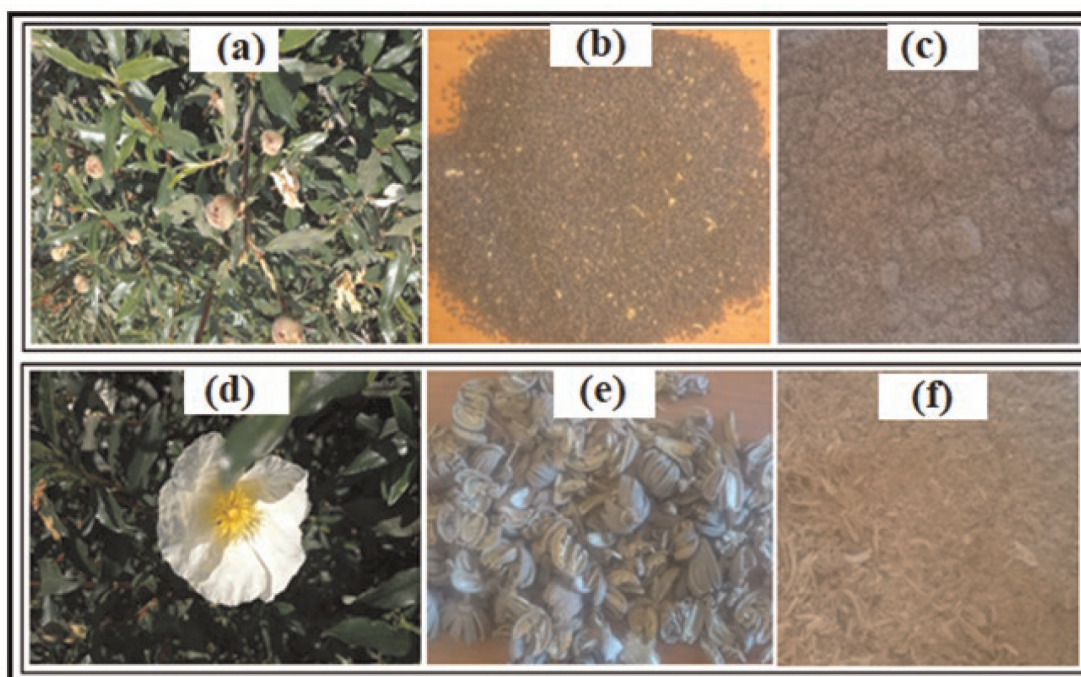
Relative to the anhydrous mass:

$$W_0 = \frac{(m_0 - m_a)}{m_a} * 100 \quad (2)$$

Or  $m_0$ : Total wet mass of the sample in (g); and  $m_a$ : Anhydrous mass in (g).

### 2.2.2 Determination of ash

The cistus seeds and these shells are impregnated samples were incinerated at 600° C, to a constant mass in a muffle furnace.



**Figure 1.**  
(a) Plant with fruit; (b) seeds; (c) seed powder; and (d) plant with flower; (e) shells; and (f) shell powder.

The ash content, expressed as a percentage, is given by the equation:

$$\text{Ash (\%)} = \frac{(m_1 - m_{cr})}{(m_2 - m_{cr})} * 100 \quad (3)$$

Where,  $m_{cr}$ : Mass of the empty crucible (g);  $m_1$ : Mass of the crucible and the ashes (g); and  $m_2$ : Mass of the crucible and the biomass intake (g).

### 2.2.3 Determination of volatile matter and fixed carbon

The volatile matter represents the vapors of organic compounds and gases released by the biomass during pyrolysis, while the carbonaceous matter is the solid residue of carbon that remains after volatilization. Determination of volatile matter and fixed carbon for each sample was performed at  $21^\circ\text{C}.\text{min}^{-1}$  under an inert atmosphere for seeds and  $40^\circ\text{C}.\text{min}^{-1}$  for shells in a fixed bed pyrolysis reactor.

The volatile matter is determined by the formula:

$$\text{Mat.Vol (\%)} = \frac{(m_a - m_v)}{m_0} * 100 \quad (4)$$

Where:  $m_0$ : Initial mass of the sample;  $m_a$ : Mass of the dry sample (g);  $m_v$ : Mass of the devolatilized sample (g);  $m_c$ : Mass of ash (g).

The difference between the mass of the devolatilized sample ( $m_v$ ) and that of the ash ( $m_c$ ) represents the fixed carbon, designated by C. Fixed, whose mass percentage is given by the equation.

$$\text{(\% C.Fixed)} = \frac{(m_v - m_c)}{m_0} * 100 \quad (5)$$

The results of the various analyses are summarized in **Table 1**.

### 2.2.4 Elementary analyses

The values measured are comparable to the results obtained by the pyrolysis of olive stones [1, 2] and those obtained by the pyrolysis of castor oil [14–17]. The contents of sulfur and nitrogen obtained by the different samples are low compared to the other references. **Table 2** presents the elemental composition of pyrolysis by-products in the literature and the values obtained from different samples in this study.

According to the results obtained our biomass presents a significant percentage in C which is higher compared to other biomasses such as olive seed, and castor for

|                 | Seeds (%) | Shells (%) |
|-----------------|-----------|------------|
| Moisture        | 13        | 7.3        |
| Ash             | 9.6       | 2.94       |
| Volatile matter | 69.76     | 74.82      |
| Fixed carbon    | 7.64      | 14.94      |

**Table 1.**  
*Characterization of different samples studied.*

| Literature                                     | C     | H    | O     | N    | S    |
|--|-------|------|-------|------|------|
| Olive Seeds ( <i>Mehmet et al</i> )            | 47.36 | 6.04 | 45.52 | 0.96 | 0.12 |
| Olive Kernel ( <i>Elena Fernandez Ibañez</i> ) | 49.9  | 6.2  | 43.3  | —    | —    |
| Castor seeds ( <i>T.Hassan, R.Lakhmiri</i> )   | 59.25 | 7.15 | 29.94 | 3.20 | 0.46 |
| Castor shells ( <i>T.Hassan, R.Lakhmiri</i> )  | 49.8  | 5.3  | 43.9  | 0.9  | 0.1  |
| Karanja Seeds [18]                             | 53.04 | 7.32 | 35.53 | 3.94 | 0.18 |
| Cistus Seeds                                   | 68.7  | 4    | 26.4  | 0.74 | 0.16 |
| Cistus Shells                                  | 69.03 | 3.75 | 26.49 | 0.68 | 0.05 |

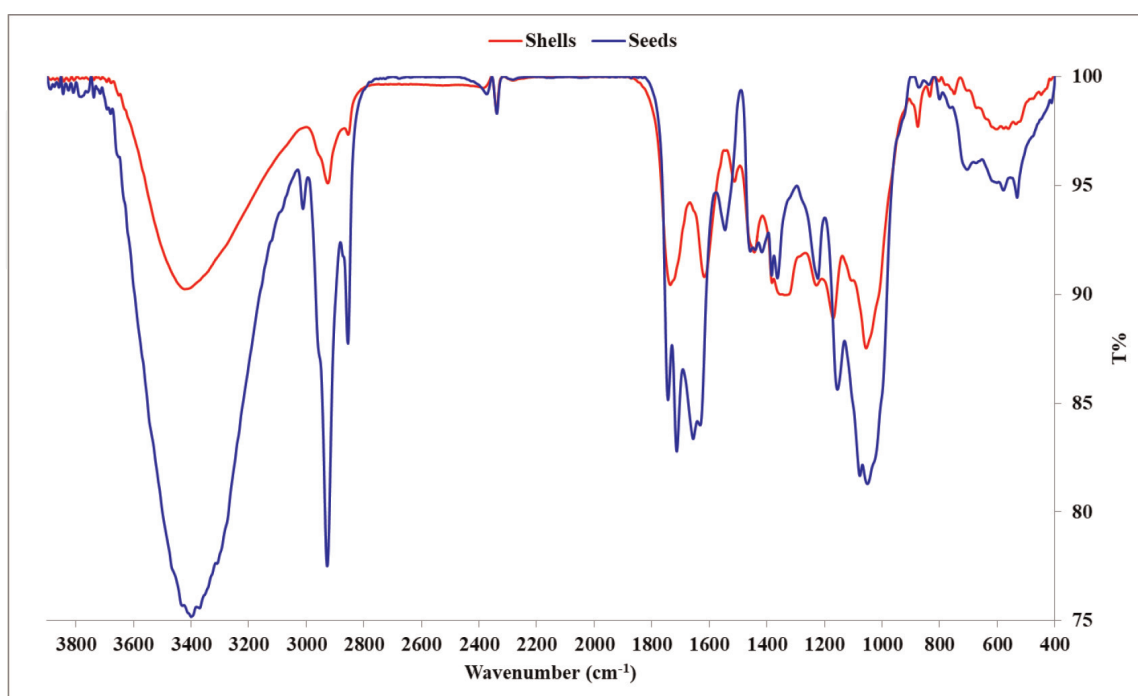
**Table 2.**  
 Elemental composition of same biomass compared with cistus seeds and shells.

example which does not exceed 59%, and for wood and coconut shells it is equal to 53.9 and 57.3% respectively [19]. On the other hand, the other elements like Oxygen, Nitrogen, Hydrogen, and Sulfur are lower than the biomasses quoted in **Table 2**. These values give the advantage to study the seeds and the shells of cistus for the production of bio-oils with the aim of transforming them into biofuels which are the vectors of actuality.

### 2.2.5 Analysis of the functions by FTIR

One introduces 2% of the sample with 98% of KBr then crushes the mixture to prepare pellets. We put the pellet in the support of infrared apparatus we obtain the spectra below.

Fourier transform infrared (FTIR) analysis of the raw material, seeds, and shells of cistus in **Figure 2** shows free -OH bonds at  $3658.07\text{ cm}^{-1}$  and broadband of the bound



**Figure 2.**  
 FTIR spectrum of cistus shells and seeds.

-OH group, =CH<sub>2</sub> groups from 2866 to 3078 cm<sup>-1</sup>, peaks of phosphene from 2280 to 2410 cm<sup>-1</sup>, C=O bonds of the β-lactams with four centers from 1600 to 1720cm<sup>-1</sup>, of aliphatic ketones 1705 to1725 cm<sup>-1</sup>, C=C bonds of aromatics and phenols from 1550 to 1600 cm<sup>-1</sup>, aromatic amines at 1515 cm<sup>-1</sup>, C-O bonds of esters from 1210 to 1260 cm<sup>-1</sup>, P-O-C bonds of phosphene at 1055 cm<sup>-1</sup> and from 530 to 580 cm<sup>-1</sup> of C-N bonds of nitriles, C-H bonds of mono and di-substituted aromatics from 650 to 900 cm<sup>-1</sup> and finally the presence of cyclanes from 415 to 580 cm<sup>-1</sup>. It can be concluded that the infrared spectroscopy confirms the important percentage of oxygen in the biomass by the presence of oxygenated groups like acids, Esters, Alcohols, Ketones, and Ethers.

### 2.2.6 Calorific values

The calorific values are calculated by a calorimetric bomb Leco501–053 Acetani-  
lide. These values obtained are also compared to other biomasses. The results are given in **Table 3**.

According to the results of the **Table 3**, the seeds of cistus and their shells present a better calorific value of 25.12 MJ.kg<sup>-1</sup> and 23.29 MJ.Kg<sup>-1</sup> respectively. To our knowl-  
edge it is the highest in comparison with other biomasses cited in the literature and which are presented in **Table 3**, therefore, the biomass used is a very good source of bio-oil or biofuels of second generation for a sustainable environment and economy.

## 2.3 Experimental setup

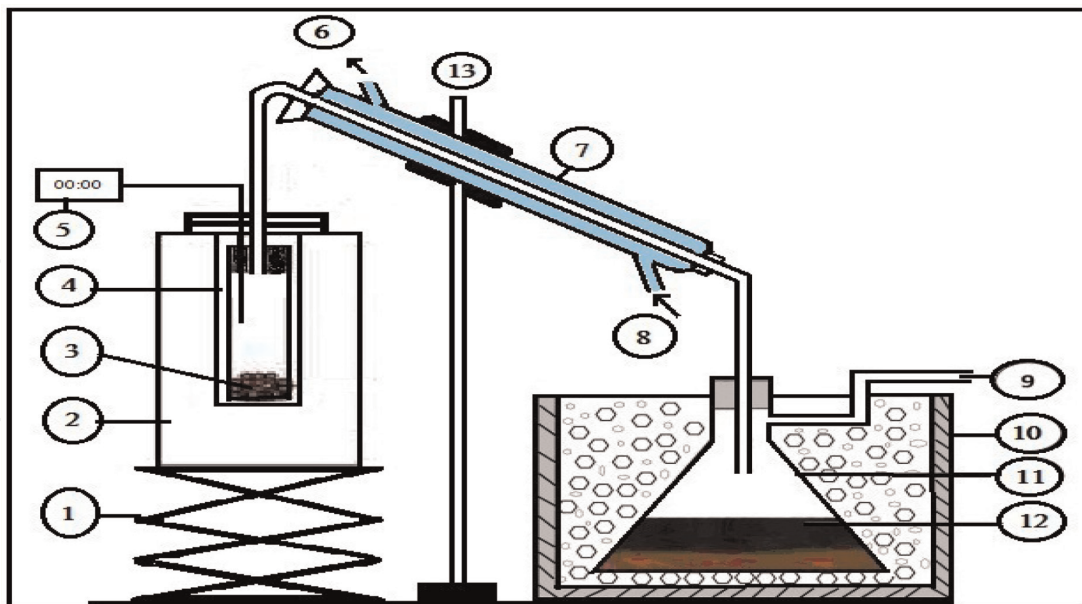
### 2.3.1 Experimental procedure

The experiments were conducted to determine the influence of the pyrolysis temperature at a heating rate varying from 7 to 28°C.min<sup>-1</sup> for seeds and from 10 to 70°C.min<sup>-1</sup> for shells. The experiments were carried out in an apparatus designed with a cylindrical semi-batch reactor, in the shape of a vessel made of stainless steel, inserted vertically into an electrically heated oven (**Figure 3**). The temperature is controlled by a PID controller. The biomass sample (seeds or cistus shells) is intro-  
duced into the reactor during pyrolysis. The vapors generated from the reactor were condensed in a condenser cooled with chilled water. **Figure 3** represents the experimental setup.

After each experiment, the condensed liquid is collected in the cylindrical measur-  
ing device. After pyrolysis, the solid residue was collected and weighed. The sample

| Material               | Calorific Value MJ.kg <sup>-1</sup> |
|------------------------|-------------------------------------|
| Castor seeds [15]      | 24.47                               |
| Castor shells [16]     | 18.9                                |
| Black cumin seeds [20] | 22.46                               |
| Karanja seeds [21]     | 22.38                               |
| Cistus seeds           | 25.12                               |
| Cistus shells          | 23.29                               |

**Table 3.**  
*Calorific values of the raw material.*



**Figure 3.** Pyrolysis experimental set-up. Description: (1) elevator, (2) vertical tube furnace, (3) biomass sample, (4) pyrolysis reactor, (5) temperature controller (PID), (6) water out, (7) condenser, (8) water in, (9) gas release, (10) ice bath, (11) condensate, (12) liquid, and (13) metal support.



**Figure 4.** Photography of reactor.

inlet of biomass and charcoal were solid measured by the electro weighing machine balance with an accuracy of  $\pm 0.01$  g.

### 2.3.2 Pyrolysis reactor

The reactor is a fixed bed (**Figure 4**). The detailed drawings are provided in part (2.3.1). It consists of a 310 AISI47 refractory stainless steel tube with an internal diameter of 60 mm and a total height of 150 mm. The head of the reactor is removable so that the bed can be introduced and then recovered at the end of the experiment. The whole reaction zone, between the diffuser and the gas outlet at the top of the reactor, has a total height of 150 mm. It includes the bubbling bed and the disengagement zone.



### 3. Results and discussion

To carry out this study we are obliged to fix the other parameters like particle size and heating rate as well as residence time. We introduce 15 g of the cistus seeds into the reactor which is fed with an electric current. The different results will be presented in the following sections. The yields of different pyrolysis products are calculated by the difference between the initial weight and the final weight which is the solid (char) that remains in the reactor. The liquid (Bio-Oil) which is taken in a graduated cylinder and the percentage of gas escaped to the atmosphere were calculated by the following relationship:

$$\%Gas = 100 - (\%Solid + \%Liquid) \quad (6)$$

In this step the particle size is fixed between 0.3 and 0.6 mm, to determine the effect of temperature. Using the results of the first experiments we have done we have found that the best yields in bio-oils are expected at a temperature equal to 450°C. At this stage we have already determined the main factor which is the temperature, and then it only remains the speed of heating that we vary from 7 to 28°C.min<sup>-1</sup>. So, we take this conclusion in hand and we begin the study by the variation of the speed of heating from 7 to 28°C.min<sup>-1</sup> each time, we calculate the yield of the obtained bio-oil. We deduced that for a heating speed lower than 21°C.min<sup>-1</sup> we have yields of bio-oil less than 52.24% the same thing for speeds higher than 21°C.min<sup>-1</sup>. Finally, we find that the optimal speed for this study is equal to 21°C.min<sup>-1</sup>.

The diameter of the particles is fixed between 0.3 and 0.6 mm. 15 g of rockrose seeds are introduced into the fixed bed reactor and the temperature is changed between 300 and 500°C. The yields of the products of pyrolysis are calculated by the difference between the initial weight and the final weight that constitutes the solid (char) that remains in the reactor, the liquid (HP) that is taken in a graduated test tube, and the percentage of the gas that has escaped in the atmosphere were calculated by the relation of Eq. (6).

#### 3.1 Cistus seeds

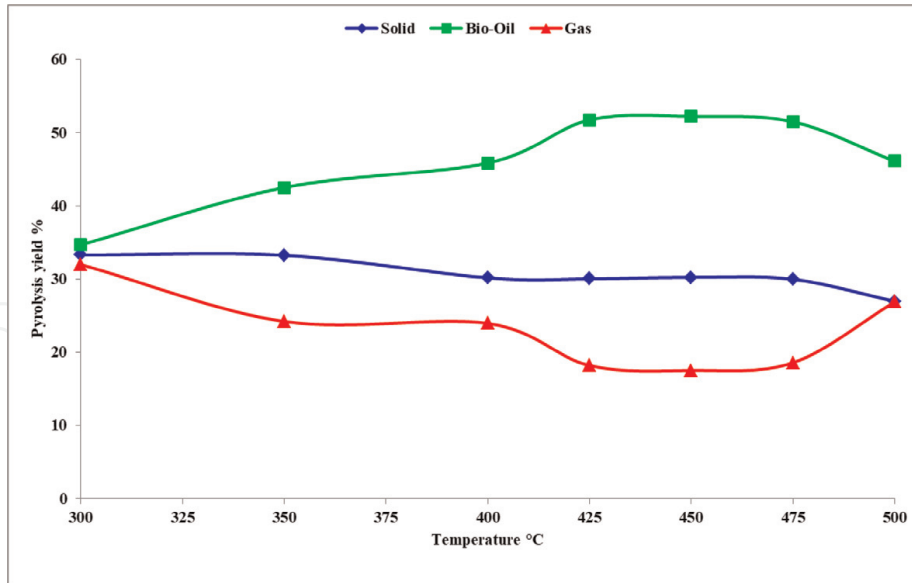
##### 3.1.1 Effect of temperature on pyrolysis yield with $d_p$ ( $0.3 \leq d_p \leq 0.6$ mm)

**Figure 5** represents the pyrolysis yields of cistus seeds with a heating rate of 21°C.min<sup>-1</sup> starting from a temperature of 300°C. The yields of charcoal, pyrolysis oil and gas are quite close. When the temperature increases from 300 to 400°C we observe, on the one hand, an increase of liquid from 34.7 to 51.76%, and on the other hand a slight decrease of coal yield and gas yield down to 18.2%. In the range of 400 to 425°C, the liquid continues to increase along with a decrease in gas yield. At temperatures between 425 and 475°C a plateau of yield for the three (Bio-Oil, solid and gas) was noticed with a maximum yield of liquid at 450°C which is equal to 52.24%. From 475 to 500°C we observe a drop in the yield of solid and liquid in parallel and an increase in the yield of gas.

For the sizes that vary between 0.3; 0.4 and 0.5 mm at the same temperature we notice a small variation in the yield of pyrolysates which is equal to 0.2%. For this reason we have taken the particle size between 0.3 and 0.6 mm to complete the study.

##### 3.1.2 Effect of heating rate on pyrolysis yields

**Figure 6** shows the effect of heating rate on pyrolysate yields. The liquid and gas yields increase from 43.2 to 52.24% and from 27.60 to 17.51%, respectively when the

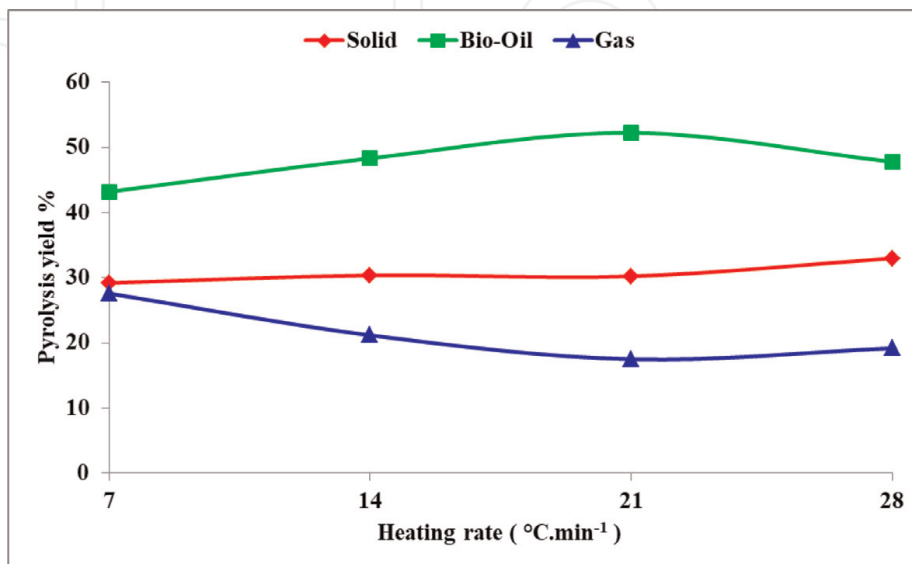


**Figure 5.**  
Yield of pyrolysis products at various pyrolysis temperatures of seeds.

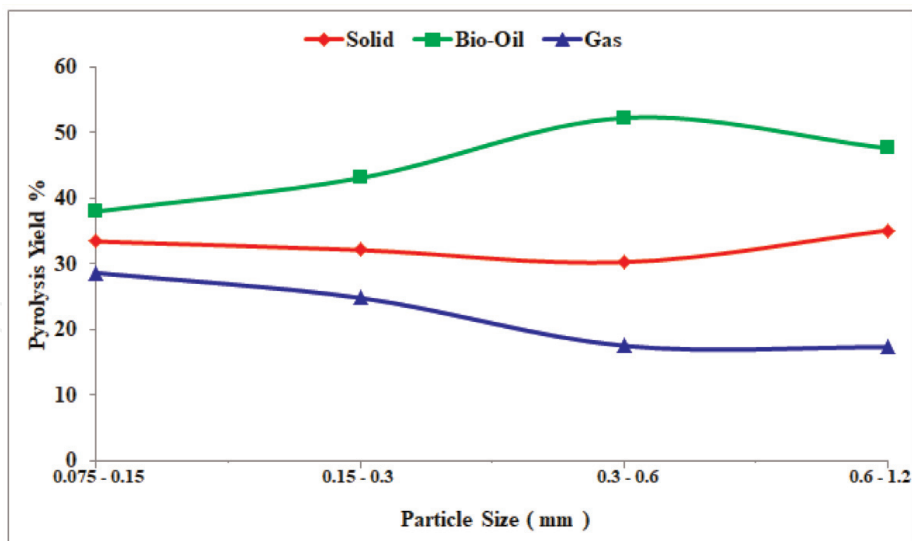
heating rate is increased from 7 to 21°C.min<sup>-1</sup>. The increase in liquid yield with increasing heating rate may be due to higher heating rates breaking thermal barriers and mass transfer in the particles. The gas yield also increases with increasing heating rates due to the cracking of pyrolysis vapors at higher heating rates. The solid yield was increased slightly from 29.2 to 30.24 wt% when the heating rate was increased from 7 to 21°C.min<sup>-1</sup>.

### 3.1.3 Effect of particle size on pyrolysis yields

The effect of particle size on the yields of pyrolysis products is shown in **Figure 7**, under the temperature of 450°C and the heating rate equal to 21°C.min<sup>-1</sup>. Oil yield increased from 38 to 43.07% followed by a slight decrease in solid yield from 33.4 to



**Figure 6.**  
Effect of heating rate on pyrolysis yields of seeds.



**Figure 7.**  
Yield of pyrolysis products with different particle size seeds.

32.11 wt% and gas yield decreased from 28.6 to 24.82 wt% when the particle size increased from less than 0.075 to 0.15 mm and from 0.15 to 0.3 mm. And for particle sizes from 0.3 to 0.6 mm, the bio-oil yield follows a progressive increase until the maximum yield of 52.24%.

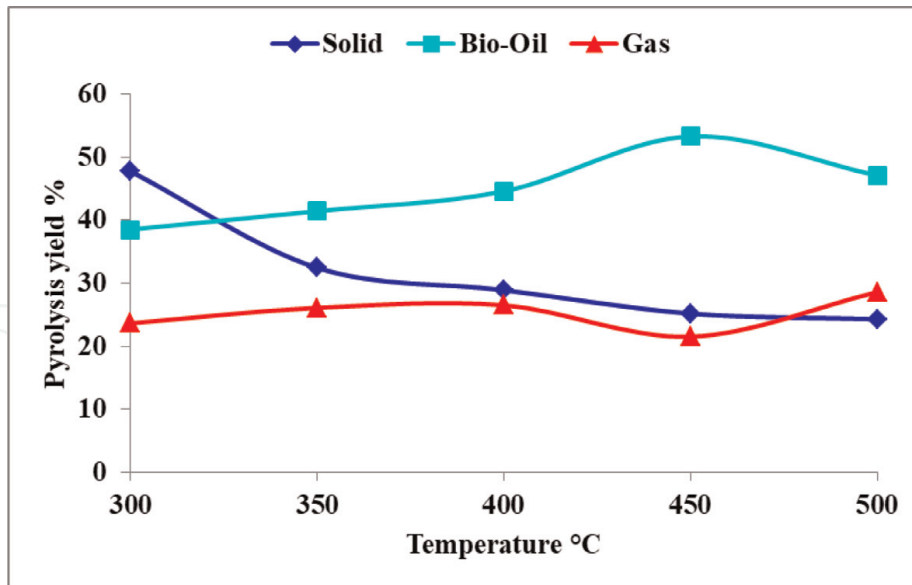
On the other hand the yield of gas and solid decreases from 24.82 to 17.51% and from 32.11 to 30.24% respectively. For particle sizes from 0.6 to 0.9 mm, the solid yield increases to 35.1%, and the gas and bio-oil yields decrease from 17.51 to 17.3% and from 52.24 to 47.6% respectively. For smaller particle sizes, the yield favors cracking hydrocarbons. The increases in solid yield with increasing particle size for the biomass sample could be due to a greater temperature gradient, within the particles. Thus at some point, the core temperature is lower than the surface temperature, this eventually gives rise to an increase in solid yield.

### 3.2 Cistus shells

#### 3.2.1 Effect of temperature on the pyrolysis yield

**Figure 8** shows the slow yields of pyrolysis products of cistus shells with the particle size of 2–3 mm at different temperatures from 300 to 500°C. The liquid yields and gas increased 38.53 to 44.6% by weight and 23.64 to 26.49%, respectively, while the solid yield decreased from 47.82 to 28.91% when the pyrolysis temperature is increased from 300 to 400°C.

In the temperature range of 400 to 450°C, it is observed a small decrease in solid and gas pass yield of 28.91 to 25.18% and from 26.49 to 21.51%, respectively, and the yield of bio-oil follow the increase maximum yield which was 53.31%. The low yield of liquid and low temperature gas is due to the incomplete decomposition of the shell. The decrease in the bio-oil yield and the increase in the gas yield of 47.11 and 28.6% respectively were observed at 500°C could be due to secondary cracking pyrolysis vapor and solid char. Similar results were observed in the study slow pyrolysis fixed bed of *Carpinus Betulus* residues (*U. Morali et al*), the same trend was predicted by other researchers (*Kar Yakup and Ilknur Demiral*) different Pyrolysis of the liquid could be due to different biomass components.

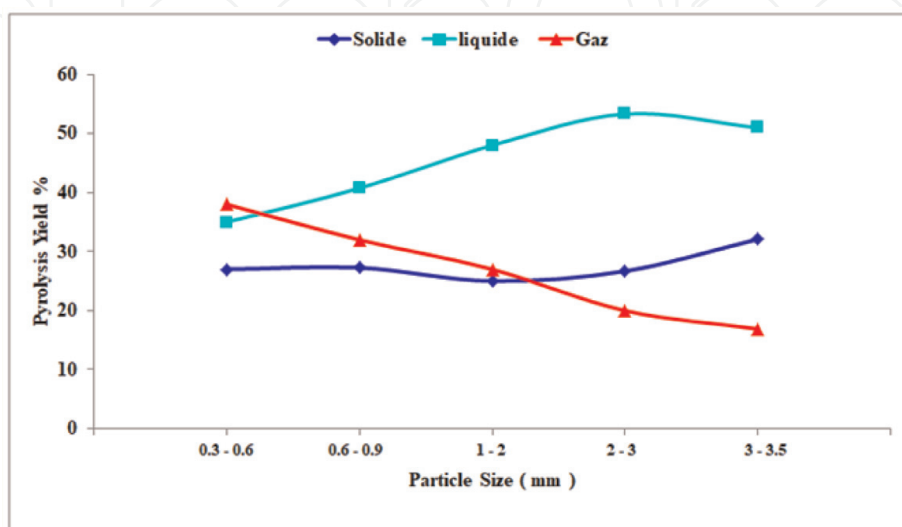


**Figure 8.**  
 Yield of pyrolysis products at various pyrolysis temperatures of shells.

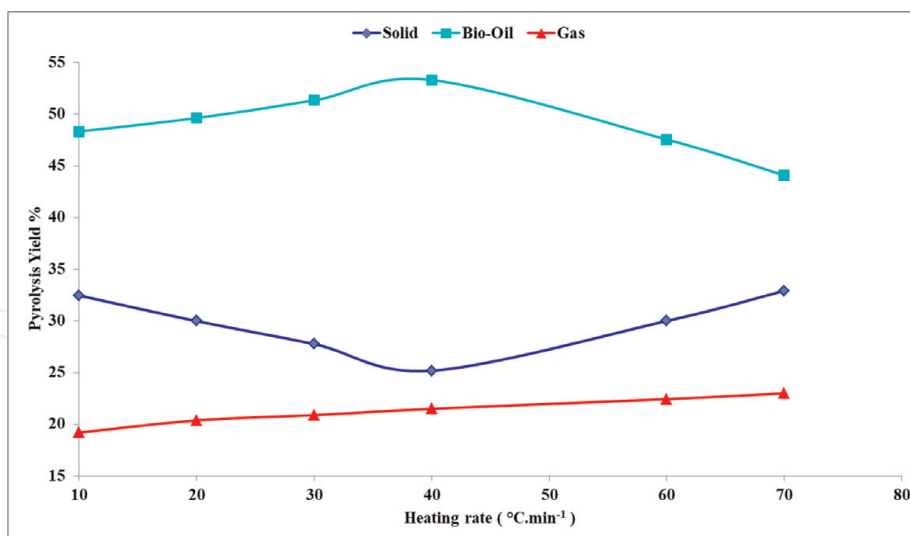
### 3.2.2 Effect of particle size on pyrolysis yields

The effect of particle size on products yields was assessed by running pyrolysis experiments with a final temperature of 450°C and heating rate equal to 40°C.min<sup>-1</sup>. Results are summarized in **Figure 9**. The lowest oil yield (35%) was obtained using the feedstock of tiniest particles (0.3–0.6 mm), which conversely afforded the maximal amount of gas products (38%) and a charcoal yield equal to 27%. When the particle size was increased to 1–2 mm, the oil yield was incremented to 48%, while both gas (27%) and char (25%) yields decreased.

The peak of oil production (yield = 53.31%), in conjunction with a further decline of gas (20%) and char (26.69%) yields, was achieved using 2–3 mm particles. Interestingly, the formation of charcoal (yield = 32.1%) reached a maximum when biggest



**Figure 9.**  
 Yield of pyrolysis products with different particle size shells.



**Figure 10.**  
Effect of heating rate on pyrolysis yields of shells.

particles (3–3.5 mm) were used, showing a significant effect of particle size on the performance of carbonization processes. On one hand, the use of smaller particles could promote the cracking of hydrocarbons, and the longer residence time of volatiles in the reactor would lead to the decrease of liquid yield. On the other hand, the increase of biomass particles size could produce a larger temperature gradient within the particles, so that at some point, the core temperature is lower than the surface, which might possibly lead to an increase in solid products yield.

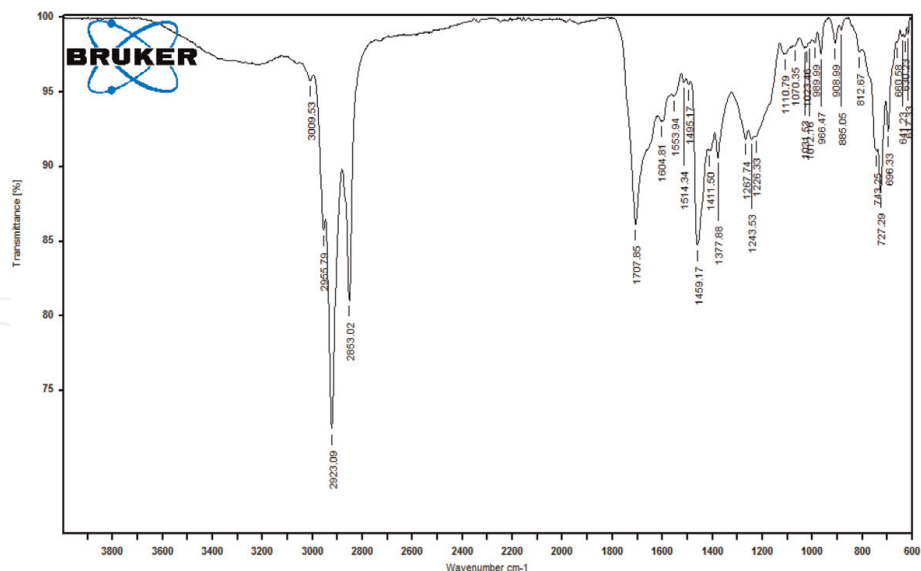
### 3.2.3 Effect of heating rate on pyrolysis yields

Pyrolysis of cistus shells with particle size from 2 to 3 mm was next performed with a final temperature of 450°C and different heating rates. As shown in **Figure 10**, both oil and gas yields evenly grew upon increasing the heating rate from 10 to 40°C.min<sup>-1</sup>, passing from 48.33 and 19.20%, respectively, at 10°C.min<sup>-1</sup> to 53.31 and 21.5%, respectively, at 40°C.min<sup>-1</sup>. The char yield dropped from 32.47 to 25.19%. This change can be ascribed to the shorter residence time and reduced incidence of cracking for pyrolysis vapors, which also account for the increased yield of tar. At 40°C.min<sup>-1</sup>, the optimal heating rate for the production of oil (yield = 53.31%), the yields of charcoal and gas underwent a further slight reduction. Finally, for heating rates greater than 40°C.min<sup>-1</sup>, decreased oil yield against increased solid and gas yields due to the fast pyrolysis of cistus seeds were observed.

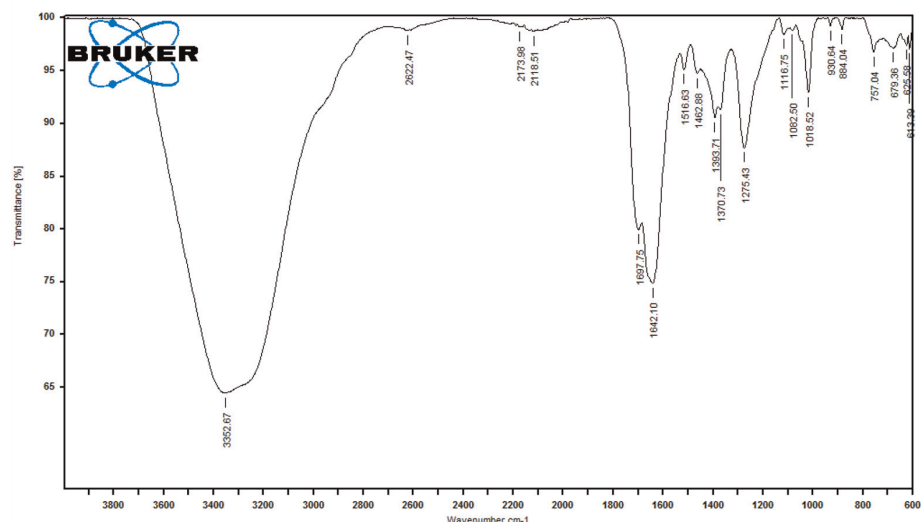
## 3.3 Bio-oil

The obtained bio-oil is characterized by FTIR spectroscopy to determine the different functional groups existing. **Figures 11** and **12** shows the infrared spectrum of the bio-oil of cistus seeds and shells. **Tables 4** and **5** represents the results of elemental analysis of the bio-oil and the calorific values.

The analysis of the bio-oil of cistus seeds by Fourier Transform Infrared (FTIR) (**Figure 11**) shows the C-H bonds of cyclobutane in symmetrical and antisymmetrical vibration between (2800–2900 cm<sup>-1</sup>), the aliphatic ketones (1705–1725 cm<sup>-1</sup>), the C=C bonds of aromatics and phenols between (1550–1600 cm<sup>-1</sup>), the C-O bonds of



**Figure 11.**  
FTIR spectrum of bio-oil (*Cistus seeds*).



**Figure 12.**  
FTIR spectrum of bio-oil (*Cistus shells*).

esters between ( $1210\text{--}1260\text{ cm}^{-1}$ ), C-OH bonds of primary and secondary alcohols between ( $1050\text{--}1080\text{ cm}^{-1}$ ), and between ( $1110\text{--}1220\text{ cm}^{-1}$ ), C-N bonds of aromatic amines between ( $1020\text{--}1220\text{ cm}^{-1}$ ), C-H bonds of mono and disubstituted aromatics between ( $650\text{--}900\text{ cm}^{-1}$ ) and finally the presence of (Z) and (E) isomers of alkenes between ( $650\text{--}750\text{ cm}^{-1}$ ) and ( $950\text{--}1010\text{ cm}^{-1}$ ).

Bio-oil analysis of *cistus shells* by oven transformation (FTIR) (**Figure 12**), shows -OH groups of phenols and acids between at  $3352.67\text{ cm}^{-1}$  and  $2622.47\text{ cm}^{-1}$  respectively, the C=O of acids at  $2173.98\text{ cm}^{-1}$  and aromatic ketones at  $1697.75\text{ cm}^{-1}$ , the C  $\equiv$  C of alkynes at  $2118.51\text{ cm}^{-1}$ , the C=C of alkenes at  $1642, 10\text{ cm}^{-1}$  and, the C-N of amines at  $1516.63\text{ cm}^{-1}$ , the C-H of aldehydes at  $1370.73\text{ cm}^{-1}$ , the C-N of aromatic amides at  $1275.43\text{ cm}^{-1}$ , the C-O of esters and ethers at  $1082.50\text{ cm}^{-1}$ , the nitrile groups -NO<sub>2</sub> at  $930.64\text{ cm}^{-1}$  and finally the C-H bonds of polycyclic and substituted aromatic groups between  $679$  and  $757.04\text{ cm}^{-1}$ .

| Element   | Ultimate analysis (w/w %)                              |             |             |         |       |          |          |
|-----------|--|-------------|-------------|---------|-------|----------|----------|
|           | Cistus seeds [22]                                      | Castor [15] | Sesame [23] | Mustard | Neem  | Jatropha | Rapeseed |
| C         | 71.5   | 70.5        | 45.19       | 47.47   | 42.52 | 59.17    | 45.92    |
| H         | 11.85  | 10.35       | 7.55        | 5.73    | 4.52  | 6.52     | 6.21     |
| N         | 0.63   | 5.1         | 7.26        | 6.16    | 1.87  | 0.38     | 6.90     |
| S         | NI   | NI          | 0.72        | 1.74    | 1.30  | NI       | 0.88     |
| O         | 16.02  | 14.05       | 39.27       | 38.91   | 49.79 | 33.93    | 40.09    |
| H/C       | 1.99   | 1.75        | 0.17        | 1.45    | 1.28  | NI       | 1.62     |
| O/C       | 0.17   | NI          | NI          | NI      | NI    | NI       | NI       |
| HV(MJ/kg) | 37.93  | 36.5        | 19.78       | 20.5    | 18.20 | 13.55    | 19.84    |
| Formula   | CH <sub>1.99</sub> O <sub>0.17</sub> N <sub>0.01</sub> |             |             |         |       |          |          |

**Table 4.**  
Elemental analysis of bio-oil from seeds.

| Element                 | Ultimate analysis (w/w %)                              |             |                     |                        |                    |
|-------------------------|--|-------------|---------------------|------------------------|--------------------|
|                         | Cistus Shells  | Castor [16] | Apricol Kernel [11] | Hornbeam (Charme) [24] | Walnut (Noix) [25] |
| C                       | 71.7   | 74.5        | 64.45               | 66.42                  | 59.89              |
| H                       | 14.87  | 10.76       | 8.24                | 6.93                   | 7.33               |
| N                       | 0.54   | 2.56        | 0.81                | 1.54                   | 0.5                |
| S                       | NI   | NI          | NI                  | NI                     | 0.02               |
| O                       | 12.89  | 11.78       | 26.50               | 25.11                  | 32.26              |
| H/C                     | 2.49   | 1.76        | 1.53                | 1.24                   | 1.74               |
| O/C                     | 0.21   | 0.12        | NI                  | NI                     | NI                 |
| Calorific Value (MJ/kg) | 37.05  | 35.01       | 27.19               | 30                     | 25.01              |
| Formula                 | CH <sub>2.49</sub> O <sub>0.21</sub> N <sub>0.01</sub> |             | NI                  |                        |                    |

**Table 5.**  
Elemental analysis of bio-oil from shells.

The results of **Table 5** shows that our bio-oil extracted by fixed bed pyrolysis contains more carbon compared to Apricol, hornbeam and walnut shells, but the percentage of oxygen in the bio-oil is smaller than Apricol, hornbeam and walnut bio-oils. In addition, we observe a total absence of sulfur in our bio-oil. We do not forget that the energetic value of the bio-oil is the highest compared to the bio-oils quoted in the literature and close to that of the oil which varies from 40 to 44 MJ.kg<sup>-1</sup> (**Table 6**).

The second method for the measurement of the kinematic viscosity is obtained by measuring the time of flow of a given volume of liquid under the effect of gravity (the dynamic viscosity ( $\eta$ ) in (g.cm<sup>-1</sup>.s<sup>-1</sup> or mPa.s) of a fluid is obtained by multiplying its kinematic viscosity ( $\gamma$ ) in (cm<sup>2</sup>.s<sup>-1</sup> or stokes (cSt)) by its density ( $\rho$ )). Experimentally

| Samples             | Density             | Speed limit        | A                  | B               | Dyn. Viscosity | Kin. Viscosity                         |
|---------------------|---------------------|--------------------|--------------------|-----------------|----------------|--|
|                     | $\text{mg cm}^{-3}$ | $\text{cm.s}^{-1}$ | $\text{cm.s}^{-2}$ | $\text{s}^{-1}$ | $\eta$ (mPa.s) | $\eta$ ( $\text{mm}^2.\text{s}^{-1}$ ) |
| Bio-oil (seeds)     | 897.6               | 1.0182             | 6.5487             | 6.4317          | 3.8693         | 4.3107                                 |
| Bio-oil (shells)    | 881.3               | 1.0521             | 6.6078             | 6.2806          | 3.7784         | 4.2871                                 |
| Commercial Diesel 1 | 829.9               | 1.2109             | 6.7947             | 5.6113          | 3.3758         | 4.0677                                 |
| Commercial Diesel 2 | 829.4               | 1.2268             | 6.7965             | 5.5400          | 3.3329         | 4.0185                                 |
| Commercial Diesel 3 | 830.3               | 1.2475             | 6.7931             | 5.4454          | 3.2760         | 3.9454                                 |

**Table 6.**  
 Properties physicochemical experimental obtained by the mechanic study.

| Samples             | Time  | Distance | Dyn Viscosity    | Kin Viscosity                          | Volume              |
|---------------------|-------|----------|------------------|--|---------------------|
|                     | t (s) | d (cm)   | $\gamma$ (mPa.s) | $\eta$ ( $\text{mm}^2 \text{s}^{-1}$ ) | V ( $\text{cm}^3$ ) |
| Bio-oil (Seeds)     | 0.116 | 20       | 3.869            | 4.310                                  | 10                  |
| Bio-oil (Shells)    | 0.118 | 20       | 3.734            | 4.237                                  | 10                  |
| Commercial Diesel 1 | 0.126 | 20       | 3.293            | 3.968                                  | 10                  |
| Commercial Diesel 2 | 0.125 | 20       | 3.318            | 4000                                   | 10                  |
| Commercial Diesel 3 | 0.128 | 20       | 3.243            | 3.906                                  | 10                  |

**Table 7.**  
 Properties physicochemical experimental obtained by the volume study.

not having a viscometer the measurement of the time of flow of a volume  $V = 10 \text{ cm}^3$  of liquid in a graduated burette of length 20 cm, the temperature of 20 °C the results are grouped in **Table 7** gave:  $\eta = \gamma/\rho$  with  $\rho$  in  $\text{g.cm}^{-3}$  [26].

We can deduce from the unit of kinematic viscosity the relationship that links the volume of liquid, the time of decantation and the length of the burette  $\gamma = V/L.t$  These results allow to highlight the small difference in viscosity between the bio-oil of seeds and shells of cistus and biodiesel. So we can improve the density of our bio-oil by

| Physical properties                           | Cistus   |        | Commercial |          |          |
|---|--|--------|------------|----------|----------|
|   | Seeds  | Shells | Diesel 1   | Diesel 2 | Diesel 3 |
| Appearance                                    | Typically a dark brown free flowing liquid     |        | Yellowish  |          |          |
| Odor  | A distinctive smoky smell                      |        | Aromatic   |          |          |
| Calorific value ( $\text{MJ Kg}^{-1}$ )       | 37.93  | 37.05  | 41.50      | 43.20    | 42.35    |
| Density ( $\text{mg cm}^{-3}$ )               | 897.6  | 881.3  | 829.9      | 829.4    | 830.3    |
| Dyn Viscosity (mPa.s)                         | 3.768  | 3.716  | 3.306      | 3.255    | 3.254    |
| Kin Viscosity ( $\text{mm}^2 \text{s}^{-1}$ ) | 4.198  | 4.217  | 3.986      | 3.922    | 3.919    |
| pH  | 3.8  | 4.02   |            |          |          |
| Miscibility                                   | Methanol, Ethanol, Toluene, diesel, and Petrol |        |            |          |          |

**Table 8.**  
 Fuel properties of cistus seeds and shells pyrolysis oil.



adding a percentage of ethanol to increase the calorific value and thus bringing its density closer to the density of commercial fuels. To improve the bio-oil we can refine it by the reactions of trans-esterification to mimic the acids and the methyl esters of the vegetable oils as well as the ethyl ethers.

To confirm the experimental results found in this study concerning viscosity and density, measurements results are obtained at 20°C, were made using an apparatus (Anton paar DMATM4500M) with a (Software Version 2.93.9364.129) (**Table 8**).

#### **4. Conclusion**

A parametric study focused mainly on the impact of temperature, size and heating rate on the yield of pyrolysates. The ex-beech liquids show high solid residue and gas contents, good homogeneity and yields up to 52.24% for seeds and 53.34% for shells at 450°C. Chemical analyses were also carried out to characterize the pyrolysis products obtained in order to determine the oxygen, carbon and hydrogen contents in the solid residues and in the liquids.

So far, the percentage of C, O, N and H of the pyrolysis oils as a whole is high compared to other biomasses located in the literature and also present important and very high calorific powers in comparison with wood and with other biomass as castor, black cumin, karanja, apricol, walnut and hornbeam. The main innovative character of this study lies in the adopted approach which consists in valorizing the bio-oils of pyrolysis, in particular in the production of biofuels in a first time and in a second time the synthesis of chemical products with the aim of use in cosmetic, pharmaceutical and food. The valorization of the solid (charcoal) as a bioadsorbent which will be detailed in another chapter.

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#### **Conflict of interest**

The author declares no conflict of interest.

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### **Author details**


Hammadi el Farissi

Faculty of Sciences, Department of Chemistry, Laboratory of Environment and Applied Chemistry (LCAE), Physical Chemistry of the Natural Resources and Processes, Mohamed First University, Oujda, Morocco

\*Address all correspondence to: [hammadielfarissi04@gmail.com](mailto:hammadielfarissi04@gmail.com)

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