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Valorisation of a Forest Waste (Cistus Seeds) for the Production of Bio-Oils

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Abstract

Biomass is a source of bioenergy, which is the most important renewable energy option, both at present, as well as in the near- and medium-term future. This study aims at valorizing a new forest waste in the Mediterranean region which is never studied by pyrolysis. Slow pyrolysis of *Cistus ladanifer* seeds, available as a natural forest waste product, was carried out in a fixed bed reactor to determine the effect of temperature, heating rate and particle size on the process performance. Pyrolysis experiments were thus carried out at different temperatures, ranging from 300 to 500°C, with heating rates varying from 7 to 28°C.min^{-1}. Samples with particle dimensions from 0.075 to 0.3 mm, 0.15 to 0.3 mm, 0.3 to 0.6 mm and 0.6 to 1.2 mm were examined. The highest yield of liquid products (52.2%) was obtained at a pyrolysis temperature of 450°C, with particle size of 0.3 to 0.6 mm and heating rate of 21°C.min^{-1}. The functional groups and chemical compound present in the bio-oil obtained under optimal conditions were identified by Fourier transform infrared (FTIR) spectrometry. The calorific value of bio-oil was equal to 37.93 MJ.kg^{-1}. The results obtained show that the bio-oil issued from pyrolysis of Cistus seeds could be used as a renewable fuel or a source of pharmaceutical and cosmetic products.

1. Introduction

The world's oil reserves are not eternal and their exploitation for fuel increases emissions of greenhouse gases that contribute to climate change. Renewable biomass can be directly used as a font of energy and is also a promising source of fuels and chemicals, alternative to petroleum-based products [1]. In particular, condensed biogas, or bio-oil, obtained from thermal anaerobic decomposition (pyrolysis) of biomass materials is considered to be an attractive option over conventional fossil fuel resources in terms of sustainability and reduced environmental pollution [2].

In our ongoing effort to promote the use of currently unexploited natural resources, we recently became interested in the valorisation of *Cistus ladanifer*, known as cistus or rockrose, a wild plant that grows extensively in Northern Africa, in the Iberian Peninsula and in Southern France [3]. This shrub tolerates both long summer droughts and cold weather and it is a dominant element in the Mediterranean scrublands [4]. Erstwhile attempts to valorise cistus raw materials were mainly aimed at the production of activated carbon from trunks [5, 6], and of bioethanol from plants previously subjected to steam explosion and extraction with alkali [7]. In the present study, we focus our attention on the pyrolysis of cistus seeds that generates a carbon-rich solid residue (char), a non-condensable gaseous fraction rich in hydrocarbons and, most important, condensable gaseous products (tar or bio-oil). The pyrolysis process thus provides the benefits of a liquid fraction which can be easily stored, transported and used as a fuel, or as an energy vector and a source of chemicals. Indeed, bio-oils have been successfully tested in engines, turbines and boilers, and were also upgraded to high quality hydrocarbon fuels, although at a currently excessive energy and financial cost [8].

The amount and characteristics of the various materials obtained by pyrolysis of biomass are influenced by the nature of the feedstock, but are also dependent on the process conditions. Thus, slow pyrolysis processes tend to produce higher amounts of char and carbon-rich products, while fast pyrolysis processes boost the production of bio-oil [9]. Heating rate, final temperature, and particle size of the feedstock are three major factors that determine the outcome of the process, as documented by various literature reports. For instance, fast pyrolysis of safflower seeds (*Carthamus tinctorius* L.) of particle size between 0.85 to 1.25 mm was investigated in a fixed-bed reactor under nitrogen flow [10]. The yields of solid, liquid and gas products were evaluated in function of the heating rate (ranging from 100 to 800°C.min^{-1}), the final temperature (from 400 to 700°C) and the flow rate (from 50 to 400 cm^3.min^{-1}). The maximal bio-oil yield (54%) was achieved at the pyrolysis temperature of 600°C, with heating rate of 300 cm^3.min^{-1} and flow rate of nitrogen of 100 cm^3.min^{-1}. The influence of final temperature, particle size and heating rate was assessed in the case of the slow pyrolysis of apricot kernel shell [11]. At the slower heating rate tested (10°C.min^{-1}) the char yield decreased from 35.2 to 29.4% as the final pyrolysis temperature was raised from 400 to 550°C. In the same temperature range, the gas yield increased from 38 to 43%, while the yield of bio-oil slightly improved from 20.6 to 21.4%, reaching a maximum value of 22.6% in the case of a final temperature of 500°C. This trend was in agreement with the one described by Gerçẹl who studied the effects of different pyrolysis temperatures and heating rates on the production of bio-oil from thistle (*Onopordum acanthium* L.) [12]. For slow pyrolysis processes carried out at a heating rate of 7°C.min^{-1}, the char yield declined from 38.3 to 24.1% when the final temperature was brought from 350 to 700°C. The observed drop of carbonization yields upon increasing pyrolysis temperatures has been tentatively ascribed either to a greater extent of primary thermal decomposition of biomass or to secondary decomposition of the char [11, 13, 14].

Other relevant examples of the role played by the operational conditions have been recently reported by Mohammed et al. who demonstrated the viability of pyrolysis processes on castor shell and castor seeds at temperatures ranging between 400 to 600°C with a constant heating rate of 70°C.min^{-1} and particle size of 0.5 to 1 mm [15, 16]. The highest yield of liquid was obtained at a pyrolysis temperature of 550°C, with particle size of 0.5 to 1 mm. The yields of liquid, gas and solid products were found to be in the range of 36.8 to 41.5%, 30.7 to 35.5% and 22.5 to 32%, respectively. This approach is here extended to another abundant forestal waste source of great potential such as cistus.

2. Materials and methods

2.1. Raw material - Cistus ladanifier seeds.

Cistus seeds were collected between July and August 2014 in the North of Morocco (Tangiers and Al Hoceima). The seeds were removed from the plant and then dried in the sun for a month, cleaned by removing all debris and stored in plastic containers.

Figure 1: (a) Cistus bush with fruit (b) Cistus flower (c) Cistus seeds

The raw material was characterized by proximate and ultimate analysis. Ultimate analysis was performed using an analyzer CHNOS (TruSpec micro) to determine the elemental compositions. The content of trace elements was determined by Wavelength Dispersive X-ray Fluorescence Spectrometry (WDXFS) using an Axios instrument. The results obtained are summarized in Tables I and II.

Table I: Components and elemental analysis of the raw material (cistus seeds)

Components	**Wt%**
Proximate Analysis	
Volatiles	69.76
Fixed Carbon	7.64
Ash	9.60
Moisture content	13
Elemental Analysis	
Carbon	68.70
Hydrogen	4
Nitrogen	0.74
Oxygen	26.40
Sulphur	0.16
Calorific value	25.12 MJ / kg

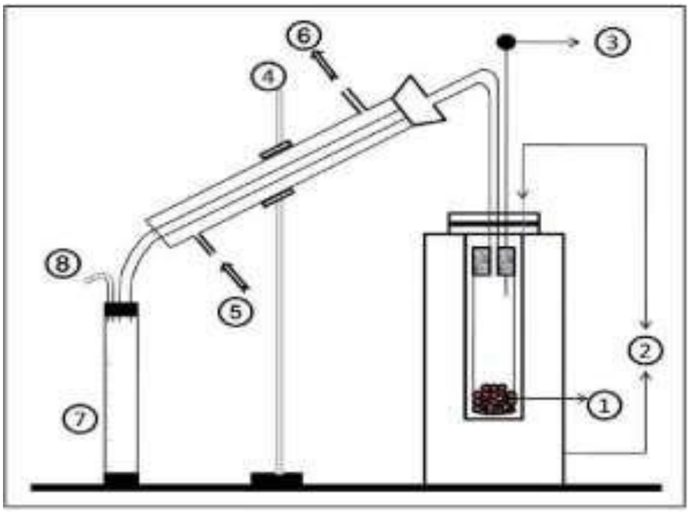
Table II: Trace elements in the cistus seeds raw material determined by Wavelength Dispersive X-ray Fluorescence Spectrometry

Element	Si	K	P	Ca	S	Mg	Cl
Wt%	0.02	0.95	0.40	0.31	0.16	0.11	0.07
Element	Fe	Zn	Cu	I	Al	Ni	Mn
Wt%	0.01	0.01	0.01	0.01	0.01	-	0.02

2.2. Experimental procedure

Pyrolysis experiments were performed in an apparatus with a semi-batch reactor comprising of a cylindrical shaped container made of stainless steel, inserted vertically in an electrically heated furnace. The temperature was controlled by a PID controller (Figure 2).

15 g of cistus seeds were introduced in the reactor. During pyrolysis, vapors generated from the reactor were condensed in a double condenser cooled with iced water at a temperature of 6°C; the experimental configuration is shown in Figure 2. After each experiment, the condensed liquid was collected in the cylinder measuring device and the solid residues (charcoal), remaining in the reactor were collected and weighed using an electronic scale to an accuracy of ± 0.01 g in order to determine their mass yield.



(1)- Biomass Sample
(2) - Furnace & Reactor
(3)- Temperature Controller (PID)
(4)- Condenser
(5)- Water In
(6)- Water Out
(7)- Liquid Collector
(8)- Gas release

Figure 2: Schematic diagram of the experimental pyrolysis set-up

2.3. Analysis of bio-oil

Elemental analysis of carbon, hydrogen and nitrogen present in the bio-oil was determined using a Micro TruSpec instrument. The calorific value of bio-oil was determined using a calorimeter bomb Leco Acetanilide 501-053. The presence of significant functional groups in the bio-oil was detected using Fourier Transform Infrared (FTIR) spectrometry.

3. Results and discussion

3.1. Effect of temperature on the yield of pyrolysis.

Figure 3 shows the yields of pyrolysis products of cistus seeds with particle size of 0.3-0.6 mm as a function of the final temperature, obtained with a constant heating rate of 21°C.min^{-1}. Pyrolysis experiments performed at 300°C afforded charcoal, bio-oil and gas in fairly similar amounts. When the temperature was raised from 300°C to 400°C the oil yield increased from 34.7% up to 51.8%. At the same time the gas yield dropped to 18.2%, while charcoal yield diminished only slightly. In the temperature interval of 400 to 425°C the oil yield increased further, accompanied by gas yield reduction. The yields of oil, solid and gas levelled at temperatures ranging from 425°C and 475°C, with maximum performance in oil product (52.2%) at 450°C. This step was followed by a sharp, parallel decrease of both char and oil yields when temperature was brought from 475 to 500°C, matched by an augmented gas yield [17].

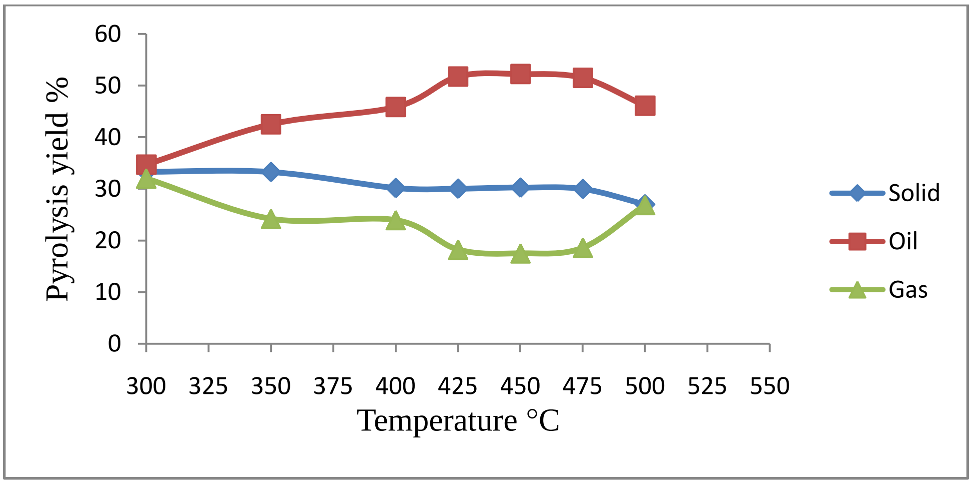


Figure 3: Yield of pyrolysis products at various pyrolysis temperatures

3.2. 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 21°C.min^{-1}. Results are summarized in Figure 4.

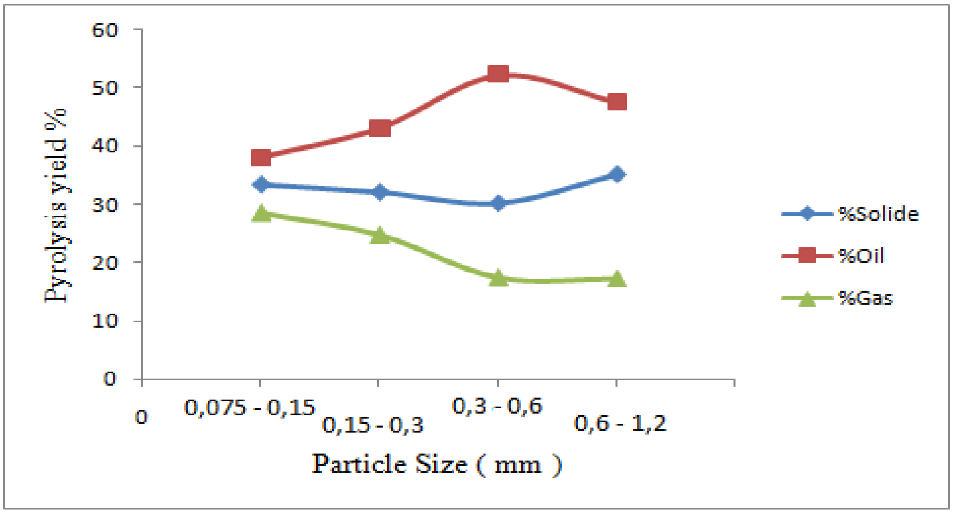


Figure 4: Yield of pyrolysis products for different particle size

The lowest oil yield (38%) was obtained using the feedstock of tiniest particles (0.075-0.15 mm), which conversely afforded the maximal amount of gas products (28.6%) and a charcoal yield equal to 33.4%. When the particle size was increased to 0.15-0.3 mm, the oil yield was incremented to 43.1%, while both gas (24.8%) and char (32.1%) yields decreased. The peak of oil production (yield = 52.2%), in conjunction with a further decline of gas (17.5%) and char (30.2%) yields, was achieved using 0.3-0.6 mm particles. Interestingly, the formation of charcoal (yield = 35.1%) reached a maximum when biggest particles (0.6-1.2 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.

3.3. Effect of heating rate on pyrolysis yields.

Pyrolysis of cistus seeds with particle size = 0.3-0.6 mm was next performed with a final temperature of 450°C and different heating rates. As shown in Figure 5, both oil and char yields evenly grew upon increasing the heating rate from 7 to 14°C.min^{-1}, passing from 43.2 and 29.2%, respectively, at 7°C.min^{-1} to 48.3 and 30.4%, respectively, at 14°C.min^{-1}. The gas yield dropped from 27.6 to 21.2%. This change can be ascribed to the shorter residence time and reduced incidence of cracking for pyrolysis vapours, which also account for the increased yield of tar [18]. At 21°C.min^{-1}, the optimal heating rate for the production of oil (yield = 52.2%), the yields of charcoal and gas underwent a further slight reduction. Finally, for heating rates greater than 21°C.min^{-1}, decreased oil yield against increased solid and gas yields due to the fast pyrolysis of cistus seeds were observed.

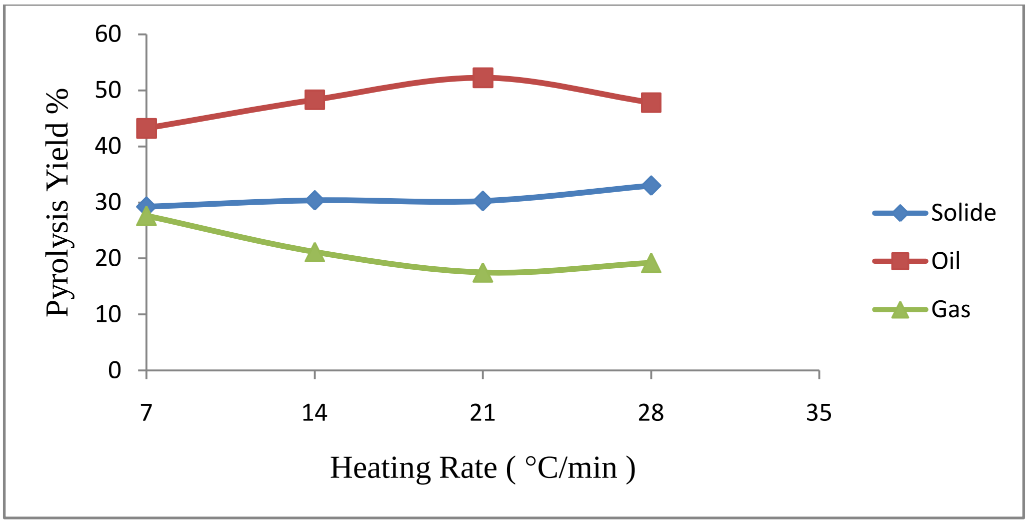


Figure 5: Effect of heating rate on pyrolysis yields

Table III: Properties of bio-oil

Ultimate analysis	**Wt %**
Carbon	71.50
Hydrogen	11.85
Nitrogen	0.63
Oxygen	16.02
H / C molar ratio	1.99
O / C molar ratio	0.17
Calorific value MJ/kg	37.93
Empirical formula	$CH_{1.99}O_{0.17}N_{0.01}$

3.4. Caracterization of bio-oil.

Fourier transform infrared (FTIR) spectrum and elemental analysis of the bio-oil obtained under optimal condition are presented in Figure 6 and Table III, respectively. A summary of the most significant functional groups present in the bio-oil by as detected by FTIR is given in Table IV

Table IV: FTIR Analysis of bio-oil.

Bond type	**Vibration**	**Functional group**	**Wave numbers (cm^{-1})**	
			σ_{th}	σ_{exp}
C-H	νas	cycloalkane	2810-3000	3009.53
C-H	νs	cycloalkane	2810-3000	2955.79
C-H	νas	cycloalkane	2810-3000	2923.09
C-H	νC-sp^{3}as	Aldehyde	2800-2900	2923.02
C=O		aliphatic ketone	1705-1725	1707.85
C=C	νC-sp^2	Two aromatic band in 1600, a band towards 1500	1550-1600	1553.94
				1604.81
			1500-1600	1514.34
C-O	νC-O	Ester	1210-1260	1243.53
C-C		Alkane	1000-1250	1226.33
C-OH	νC-O	Alcool III	1110-1220	1110.79
C-OH	νC-O	Alcool I	1050-1080	1070.35
C-N		Aromatic amine I	1020-1220	1031.53
C-H	δ	cycloalkane	1012-1031	1023.46
=C-H(E)		Alkene	950 - 1010	1012.16
C-H		Aromatic	985 - 910	908.99
C-H	δ C-sp^2-H	Aromatic (disubstituted)	670 – 730	727.29
			750 – 810	---------
			680 – 900	885.05
C-H	δ C-sp^2-H	Aromatic (mono-substitued)	760 – 720	696.33
			730 – 780	743.25
=C-H(Z)		Alkene	650 - 750	660.58

Symmetrical vibration (Vs) antisymmetric vibration (Vas) β deformation and vibration δ

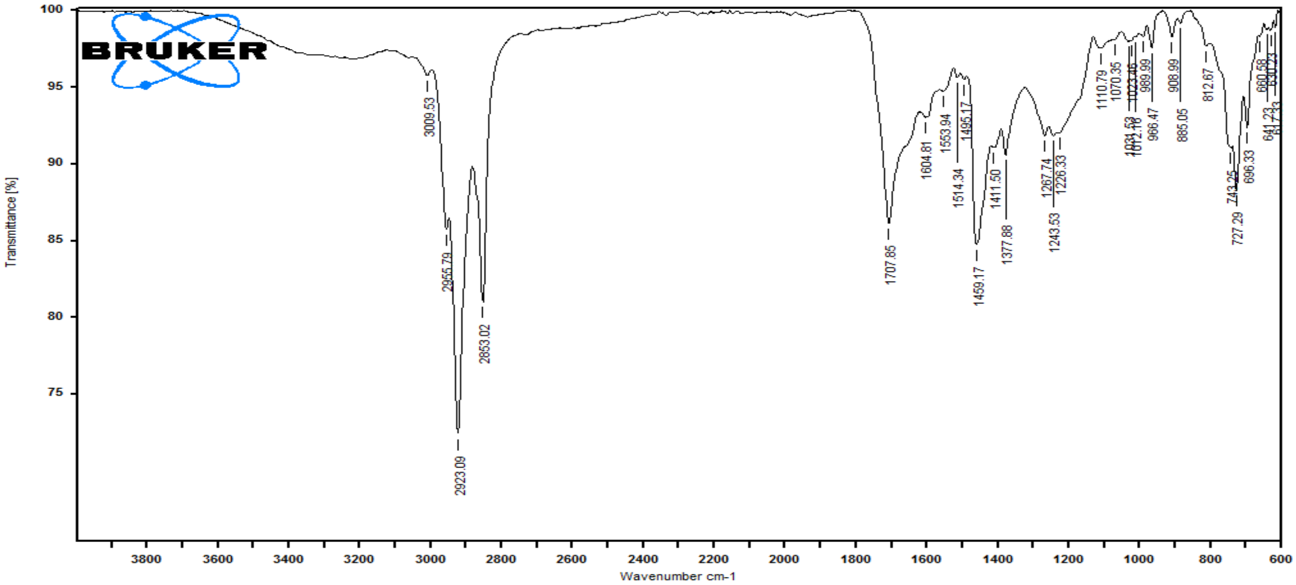


Figure 6: FTIR spectrum of bio-oil

FTIR analysis of the bio-oil obtained by pyrolysis of cistus seeds showed the presence of C-H bonds of cycloalkane symmetric and antisymmetric vibration between 2800-2900 cm^{-1}, aliphatic ketones from 1705 to 1725 cm^{-1}, C= C bonds of aromatic phenols between 1550 - 1600 cm^{-1}, C-O esters between 1210-1260 cm^{-1}, C-OH bonds in primary and secondary alcohols between 1050 to 1080 cm^{-1} and between 1110 to 1220 $cm^{- 1}$, connections C-N aromatic amines between 1020-1220 cm^{-1}, C-H bonds the mono aromatic and disubstituted between 650-900 cm^{-1} and finally the presence of the isomers (Z) and (E) alkenes between 650-750 cm^{-1} and 950-1010 cm^{-1}.

Conclusion

Cistus seeds represent a potentially useful feedstock for the production of bio-oil, as shown by a series of pyrolysis experiments performed in a semi-batch reactor, in which three major parameters affecting the outcome of the thermochemical process have been systematically varied. The highest yield of liquid products (52.2%) was obtained at a pyrolysis temperature of 450°C, with particle size of 0.3 to 0.6 mm and heating rate of 21°C.min^{-1}. The functional groups and chemical compound present in the bio-oil obtained under optimal conditions were identified by FTIR spectrometry. The calorific value of the oil is 37,93 MJ kg^{-1}, which is close to that of petroleum fractions.

The bio-oil obtained from cistus seeds holds suitable properties as a substitute for fossil fuels and it could be used either directly or in combination with other conventional products. An important advantage of its application as a fuel is that it virtually contains no sulfur. Therefore, it would emit almost no sulfur oxides into the atmosphere. In addition, it has potential as a feedstock for the chemical and material industries.

References

1. Hornung A., “Transformation of Biomass – Theory to Practice” (2014) John Wiley & Sons, Chichester (UK), ISBN 978-1-119-97327-0.
2. Mohan, D., Pittman, C.U., Steele, P.H., “Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review” *Energy Fuels* 20 (2006), 848.
3. Dentinho M.T.P., Belo A.T., Bessa R.J.B., “Digestion, ruminal fermentation and microbial nitrogen supply in sheep fed soybean meal treated with Cistus ladanifer L. tannins” *Small Rumin. Res.* 119 (2014) 57.
4. Guzmán B., Vargas, P., “Long-distance colonization of the Western Mediterranean by Cistus Ladanifer (Cistaceae) despite the absence of special dispersal mechanisms” *J. Biogeogr.* 36 (2009) 954
5. Pastor-Villegas J., Durán-Valle C.J., Valenzuela-Calahorro C., Gómez-Serrano V. “Organic chemical structure and structural shrinkage of chars prepared from rockrose” *Carbon* 36 (1998) 1251
6. Pastor-Villegas J., Durán-Valle C.J., “Pore structure of activated carbons prepared by carbon dioxide and steam activation at different temperatures from extracted rockrose” *Carbon* 40 (2002) 397
7. Ferro M.D., Fernandes M.C., Paulino, A.F.C., Prozil S.O., Gravitis J., Evtuguin D.V., Xavier A.M.R.B. “Bioethanol production from steam explosion pretreated and alkali extracted Cistus ladanifer (rockrose)” *Biochem. Eng. J.* 104 (2015) 98
8. Guo, M., Song, W., Buhain, J., “Bioenergy and biofuels: History, status, and perspective” *Renew. Sustainable Energy Rev.* 42 (2015) 712.
9. Singh R., Krishna, B.B., Mishra, G., Kumar, J., Bhaskar, T., “Strategies for selection of thermo-chemical processes for the valorisation of biomass” *Renew. Energy* 98 (2016) 226
10. Onay O., “Influence of pyrolysis temperature and heating rate on the production of bio-oil and char from safflower seed by pyrolysis, using a well-swept fixed-bed reactor” *Fuel Process. Technol.* 88 (2007) 523.
11. Demiral I., Kul S.C., “Pyrolysis of apricot kernel shell in a fixed-bed reactor : Characterization of bio-oil and char” *J. Anal. Appl.* 107 (2014) 17.
12. Gerçȩl H.F., “Bio-oil production from Onopordum acanthium L. by slow pyrolysis” *J. Anal. Appl. Pyrol.* 92 (2011) 233.
13. Demiral I., Eryazıcı A., Şensöz S., “Bio -oil production from pyrolysis of corncob (Zea mays L.)” *Biomass Bioenergy* 36 (2012) 43.
14. Horne P.T.W.P.A., “Influence of temperature on the products from the flash pyrolysis of biomass” *Fuel* 75 (1996) 1051.

15. Mohammed T.H., Lakhmiri R., Azmani A., "Bio-oil from Pyrolysis of Castor Seeds" *IJBAS-IJENS* Vol.14 no. 04 (2014) 14.
16. Mohammed T.H., Lakhmiri R., Azmani A., Hassan I.I., "Bio-oil from Pyrolysis of Castor Shell" *IJBAS-IJENS* Vol.14 no. 06 (2014) 1.
17. Elfarissi H., Lakhmiri R., ‘‘Production of Bio-oil from Seeds By Fixed-Bed Pyrolisis" *The 3rd International Workshop on Waste Management and Sustainable Development 7-9 October 2015 ATLAS RIF HOTEL Tanger,"* (2015).
18. Haykiri-Acman H., Yaman S., Kucukbayrak S., "Effect of Heating Rate on the Pyrolysis Yields of Rapeseed" *Renew. Energy* 31(2006) 803.

(2017) ; http://www.jmaterenvironsci.com