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EFFECT OF TEMPERATURE AND HEATING RATES ON PYROLYSIS PRODUCTS FROM OLIVE MILL SOLID WASTE (OMSW) AND OLIVE MILL WASTEWATER (OMWW)

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Abstract: *The oil extraction industry generate two by-products, an aqueous effluent, olive mill wastewater (OMWW) and a solid residue, olive mill solid waste (OMSW). Both are considered as a major pollutant in the Mediterranean area causing severe environmental threats. Actually, the main problem regarding is to find an environmental and economical viable solution for this situation. With respect to the conversion technologies for energy use, pyrolysis has been widely used for converting biomass into liquids and solids among the thermo-chemical technologies. Pyrolysis is generally described as the thermal decomposition of the organic components in biomass waste in the absence of oxygen at mediate temperature to yield tar, char and gaseous fractions. This article deals with fast pyrolysis of two olive mill wastes, such as olive mill solid waste (OMSW) and concentrated olive mill wastewater (COMWW) at the range of temperature 400-600 °C in a stainless steel tubular reactor. The aim of this work was to experimentally investigate how the temperature and heating rate affects char, liquid and gaseous (+ losses) product yields from different olive mill via pyrolysis and to determine optimal condition to have a better yield of these products. The amount of liquid "bio-oil" from pyrolysis of olive mill samples decreases with increasing the heating rate and the highest yields were obtained from the samples between 450 °C and 500 °C. For OMSW the maximal average yield achieve almost ≈ 33.41 wt % at 500 °C and 5°C/min, whereas for COMWW it achieve 31.29 wt % at 450 °C with the same heating rate. The yield of char generally decreases with increasing the pyrolysis temperature, beginning with the temperature of 400 °C arriving at a temperature of 600 °C. Concerning the yield of Gaseous product and losses, we notice that, the efficiency increase with increasing the heating rate from 5 °C/min to 50 °C/min. The results show that final temperature (400 °C, 450 °C, 500 °C, 550 °C and 600 °C) and heating rates (5 °C/min, 10 °C/min, 20 °C/min and 50 °C/min) have a remarkable effect on the yields of products. Liquid products obtained under the most suitable and optimal conditions were characterised by elemental analysis, ^{1}H'RMN, FT-IR and CG-MS. Column chromatography was employed and yields of sub-fractions were calculated. Gas chromatography was achieved on aliphatic fractions. The results show the presence of an aliphatic character and that it is possible to obtain liquid products similar to petroleum from olive mill wastes if the pyrolysis conditions are chosen accordingly.*

Keywords: *Olive mill solid waste; Olive mill wastewater; Pyrolysis; Char; liquid (Bio-oil); Gas.*

1. Introduction

Fossil fuel shortage and severe environmental problems have attracted great attention on the exploitation of clean renewable energies. Several types of renewable energies are destined to play an important role in future energy systems [1-4]. Biomass for one has great potential by offering annually renewable sources to replace the liquid hydrocarbons mainly for transportation, for producing energy it has a special place among all other renewable energy sources and it is estimated to contribute with 10-14 % to the world's total energy supply, It is a mixture of structural constituents (hemicelluloses, celluloses and lignin) and minor amounts of extractive which each pyrolyze at different rates and by different mechanisms and pathways. It is believed that as the reaction progresses the carbon becomes less reactive and forms stable chemical structure, and consequently the activation energy increases as the conversion level of biomass increases. There are various conversion technologies to produce liquid fuels, among which fast pyrolysis of biomass has been experiencing rapid development in recent years, because it can offer an alternative way to solve liquid fuel shortage problems and to reduce the environmental problems [5-8].

Fast pyrolysis is a thermal decomposition process that occur in the absence of oxygen to convert biomass into liquid products (bio-oils) together with non-condensable gases and solid char [9-11]. Numerous studies have been devoted on pyrolysis of biomass [12-20]. The solid products such as the char can be used as a fuel either directly as briquettes or as char-oil or char-water slurries or it can be used as feedstocks to prepare activated carbons. The liquid product, bio-oil, is also useful as a fuel, may be added to petroleum refinery feedstocks or upgraded by catalysts to produce premium grade rafined fuels, or may have a potential use as chemical feedstocks. The third product gas having high calorfic value may also be used as a fuel. There are a number of benefits to produce and use bio-oils. The most important one is that bio-oils produces fewer harmful emissions such as SO_x , NO_x gases during production and combustion and they contribute virtually no CO_2 to the atmosphere which accelerates the green house effect. Cottonseed cake was taken as the biomass simple by Ozbay et al [19], to determine the effects of reactor geometry, pyrolysis atmosphere and pyrolysis temperature on the product yields and chemical composition of the liquid product. The maximum oil yield was attained under nitrogen atmosphere at a pyrolysis temperature of 550 °C with a heating rate of 7 °C/min in tubular reactor. Pyrolysis of olive residues (cutting and kernels) in a captive sample reactor at atmospheric pressure under helium with a heating rate of 200 °C/s to a temperature range from 300 to 600 °C has been carried out by Zabaniotou et al [20], to determine the yields of products in relation to pyrolysis temperature, their results showed that as the final temperature increased the percentage of liquid and gaseous products increased and oil products reached a maximum value of ≈ 30 % of dry biomass at about 450 – 550 °C. Having low content of sulfur (0.05 – 0.1 %) and ash (2-3 %), olive residue is a clean and renewable energy source. These by-products with a high content of lignocellulosic materials from olive plantation and have been recently employed to produce bio-oil, gaseous products and solid products as activated carbons. A.E. Putun and al [9], studied the pyrolysis of olive under different conditions to determine the role of final temperature (between 400 °C and 700 °C), sweeping gas flow rate on the product yields and liquid product composition with a heating rate of 7 °C/min, he found that the oil yield was 28.7 wt % at the pyrolysis temperature of 400 °C and it appeared to go through a maximum of 32.7 wt % at the final temperature of 500 °C. For char and gas yields they were approximately 28 wt %, 18 wt % respectively, at different nitrogen flow rates [21, 22]. V. Minkova and al [11] studied the effect of water vapour and biomass nature on the yield and quality of the pyrolysis products from biomass (olive, straw, misk, birch, and bag). For olive residue, he obtained almost ≈ 20 wt % in pyrolysis of the olive in nitrogen flow. It exists other works on other biomass pyrolysis. Most of researches [23-30], show that biomass degradation takes place between 150 °C and 700 °C, the maximum yield of liquid product (Bio-oils) occurs at the average temperature 450 °C – 550 °C, and do not forget the influence of heating rate on yield pyrolysis because it is among the factors which improves the product yield of biomass pyrolysis. Recent studies on different type of biomass (olive, straw, cane bagasse, walnut shell, sunflower shell, hazelnut shell, almond shell... etc), has indicated that bio-oils, char and gas yields of pyrolysis may be changed by altering temperature and heating rate.

In the present work, the pyrolysis of two olive mill samples, olive mill solid waste (OMSW) and concentred olive mill wastewater (COMWW) was studied for determine and optimizing the role of these parameters on yield of liquid, char and gaseous products, and to determine the characteristics of the yield (efficiency) optimal.

2. Experimental

2.1. Materials and samples preparation

The olive mill samples, such as, olive mill solid waste (OMSW) and olive mill wastewater (OMWW) were obtained from Béni-Mellal area which located about 15km of Fkih-Ben-Saleh, Morocco. They were obtained from the solid product of traditional olive oil process (Mâasra in morocco). The samples received contained a big percentage (Wt %) of moisture. The moisture content was lowered after a few days of natural drying in ambitient atmosphere, then they were be crashed with the aim of obtain a uniform material of an average particle size (0.4-1.8 mm). The characterization of the samples is given in Table 1 and Table 2. Proximate analyses of the raw material having average size were performed according to the standard methods of American society for Testing and Materials (ASTM) procedure. Ultimate analyses were performed on olive mill waste (OMSW and OMWW) samples to determine the elemental composition. A Carlo Erba, EA 1108 Elemental Analyser was used to determine the weight fractions of carbon, hydrogen and nitrogen and the weight fraction of oxygen was calculated by the difference. Cellulose , hemicelluloses, lignin and protein, being the main constituents of olive mill wastes such as olive mill solid waste and olive mill wastewater, were also determined. Protein content was determined by the Kjeldahl method using Labconco Rapid still-2.

Table 1. Main characteristics of OMSW and COMWW

	OMSW /%	COMWW /%
Proximate analysis		
Moisture	8.3	3.8
Volatile matter	73.5	61.4
Ash	4.5	25.1
Fixed carbon	13.7	9.7
Elemental analysis		
C	45.5	39.7
H	5.3	4.6
N	1.8	1.7
O	47.4	46
Chemical analysis		
Hemicellulose	21.6	17.4
Cellulose	30.4	23.3
Lignin	43.5	34.2

Table 2. Physical-chemical determination of the raw OMWW

Parameters	Values
pH (25 °C)	5.15
Electrical conductivity Ms/cm à 20 °C	6.73
Total phenols g/L	13.35
Total COD gO_2/l	70.40

2.2. Apparatus

The biomass samples are pyrolysed in a stainless steel tubular reactor, heated with a furnace tubular compact of type R 50/ 250/ 12. Figure 1. This compact tubular furnace provided with cupboard of power and integrated regulation of temperature.

2.3. Procedure

The pyrolysis experiments were performed in a device designed for this purpose. The main element of this device was a tubular reactor of height 60 cm, i.d. 3.8 cm and o.d. 4.2 cm inserted vertically into on electrically heated tubular furnace. Fig.1. The effective temperature in the electrically heated tubular furnace was controlled automatically (integrated regulation) and the reactor temperature was regulated to reach the temperature desired. Figure 2 shows the flow diagram of pyrolysis. Pyrolysis product yields were determined gravimetrically by weighing the three products. After reaching the final pyrolysis temperature the reactor was set to cool to room temperature. Solid product, char, was removed and weighed. The liquid phase was collected in cold traps maintained at about 0 °C using salty ice. Pyrolysis of olive mill solid waste and olive mill wastewater was carried out three times to improve the profitability and productibility of the results of experiments to investigate the effect of pyrolysis conditions on the product yields and liquid product composition and to determine the pyrolysis condition that gives the maximum bio-oil yield. For the experiments, almost 40 g sample of olive mill waste (OMSW and OMWW) was placed into the reactor and the experiments were carried out with a series of heating rates of 5 °C/min, 10 °C/min, 20 °C/min and 50 °C/min to the final temperature (400 °C, 450 °C, 500 °C, 550 °C and 600 °C). The experiments were conducted under nitrogen gas with a flow rate between 0.6 and 1 cm/min. The product obtained from the pyrolysis was recovered in two collecting which there is a solvent it is dichloromethane. To improve the yield on the liquid product, we used some salt and ice in a bath of water, which there is oily product collecting.


(a) **(b)**

(c)

Figure 1. (a): tubular reactor inserted in a furnace; (b): condenser; (c): two collecting.

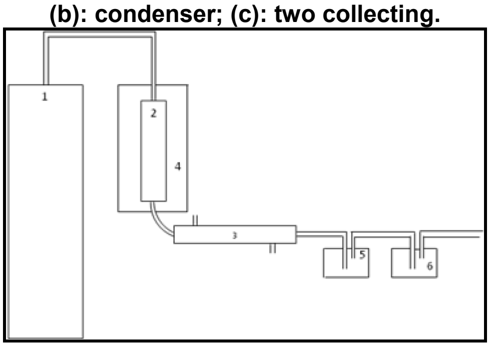

Figure 2. Simple diagram of pyrolysis: (1) Nitrogen tube; (2) stainless steel tube; (3) condenser; (4) electrical furnace; (5) and (6) oily products collecting.

3. Results and discussion

3.1. Effect of pyrolysis temperature on product yields

The plot for effect of temperature on the yield of bio-oil (product liquid) from the Olive mill Solid Waste and Concentred olive mill wastewater are given in Figure 3 and 4. The yields of liquid products from olive mill wastes generally increased with the increase in pyrolysis temperature from 400 to 500 °C for OMSW, and from 400 to 450 °C for COMWW. Then decreased with increased the pyrolysis temperature up to 600 °C. The highest liquid yields were 33.41 and 31.29 Wt % for OMSW and COMWW respectively (Table 3). The highest bio-oil yields were obtained from the olive waste samples between 450 °C and 500 °C. The liquid products from the olive pyrolysis are dark brown viscous oils. Combustion tests have demonstrated the pyrolysis liquid products could be burnet efficiently in standard or in slightly modified burners [31]. The liquid products from the olive pyrolysis obtained at lower temperature (300-450 °C) contain many highly oxygenated polar components that help dissolve the phenolic fractions in water. At elevated carbonization temperature, the amount of these oxygenated organic components decreased which result in a greater heating value [32]. For COMWW organic content allows the thermal decomposition of cellulosic compounds at lower temperature, this results can be explained by the characteristics of the organic compounds present in COMWW. Several authors confirmed that degradation of lignin containing polyphenol structure starts at a lower temperature, the initial temperature of degradation in higher in OMSW, which present a high amount of cellulose in comparison with COMWW. It should be reported that a fuel with a higher percentage of Ashes and impurities in this composition, presents a lower initial temperature of degradation, this effect takes place in the case of COMWW, due to the high amount of ashes. We can say that concentred olive mill wastewater has a high inorganic salts content which may explain the high amount of ashes in the impregnated samples.

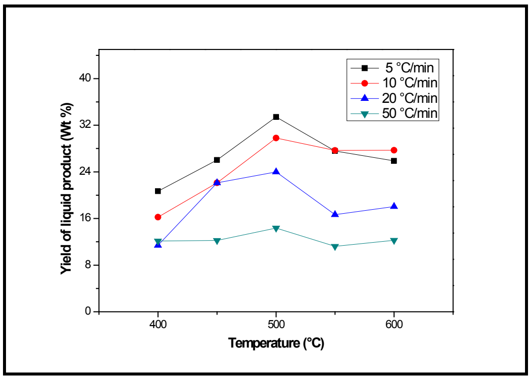

Figure 3. Plot for effect of temperature and heating rate on yield of liquid product from Olive mill solid waste.

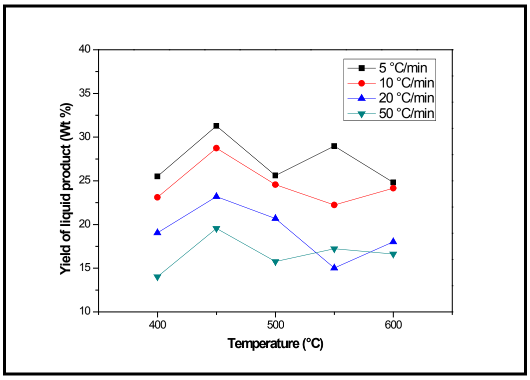

Figure 4. Plot for effect of temperature and heating rate on yield of liquid product from Concentred Olive mill wastewater.

The plots of effect of temperature on the yield of char product from the olive wastes are given in figure 5 and 6. At elevated temperatures, the amount of char from pyrolysis of the olive wastes decreases. The char yields at 450 °C were 27.4 Wt % and 26.82 Wt % for OMWS and COMWW respectively. And at 500 °C were 27.18 Wt % and 26.82 Wt % for OMSW and COMWW respectively in the same heating rate (5 °C/min).

As indicated in table 4 and in Figure 7 and 8, the yields of gaseous products generally increases with increased the pyrolysis temperature, except some value which is due to the loss during experiment.

These results are consistent with literature [33]. It is known that pyrolysis temperature plays an important role on product distribution. As olive oil residue reaches elevated temperature, the different chemical components undergo thermal degradation that affects the conversion yields and product quality. The extent of the changes depends on the temperature and length of pyrolysis time. At relatively lower temperature, between 65 and 180 °C, olive oil residue loses its moisture, generates non-combustible gases like CO_2 and undergoes depolymerisation reactions involving no significant carbohydrate loss. Chemical bonds preconditioned in the main constituents of biomass sample begin to break at temperatures higher that approximately 200 °C. Breakdown of hemicelluloses, which is less thermally stable constituent, takes place at lower temperatures up to 300 °C forming gases like carbon monoxide. At temperatures between 350 and 500 °C cellulose breakdowns and lignin starts to decompose resulting in charcoal, water and heavier tars. Between these temperatures tar also undergoes cracking to lighter gases and repolymerisation to char. At higher temperatures, gasification reactions take places forming hydrogen enriched gaseous products and char undergoes further degradation by being oxidized to CO_2, CO and H_2O. According to these reactions it can be said that relatively low pyrolysis temperatures around 400 °C favours char formation. Temperatures up to 600 °C maximise the production of bio-oils and temperatures above 700 °C maximise gaseous products while minimising char formation.

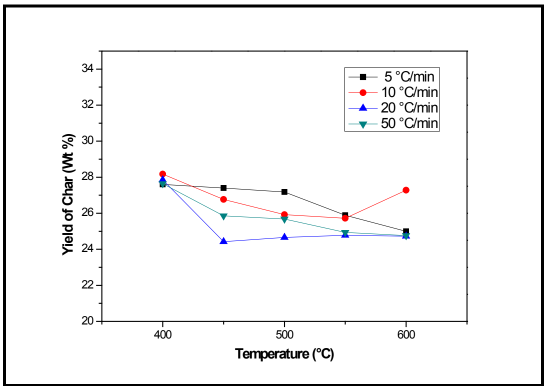

Figure 5. Plot for effect of temperature and heating rate on yield of Char from Olive mill solid waste.

3.2. Effect of the heating rate on product yields

Table 3, 4, 5 and 6 shows the yield of conversion degree, oil, gases and char product from the pyrolysis of the olive mill wastes such as olive mill solid waste and concentred olive mill wastewater in relation to heating rate from 5 to 50 °C/min to a final temperature of 450 and 500 °C in a tubular reactor. For olive mill solid waste and olive mill wastewater, there was a decrease in oil yield from 5 to 50 °C/min. The conversion degree and yield of gases increased from 5 to 50 °C/ min, while there was a corresponding progressive decrease in derived residual coke.

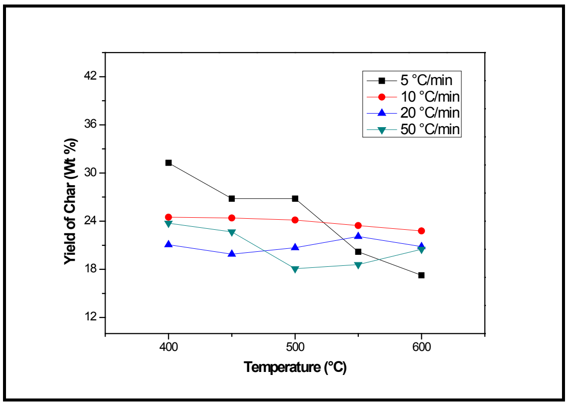

Figure 6. Plot for effect of temperature and heating rate on yield of Char from Concentred Olive mill wastewater.

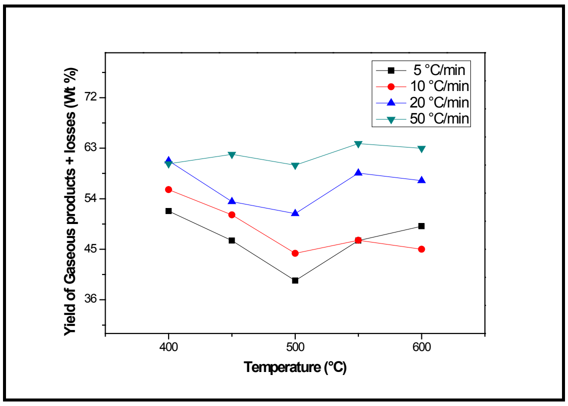

Figure 7. Plot for effect of temperature and heating rate on yield of Gaseous product and losses from Olive mill solid waste.

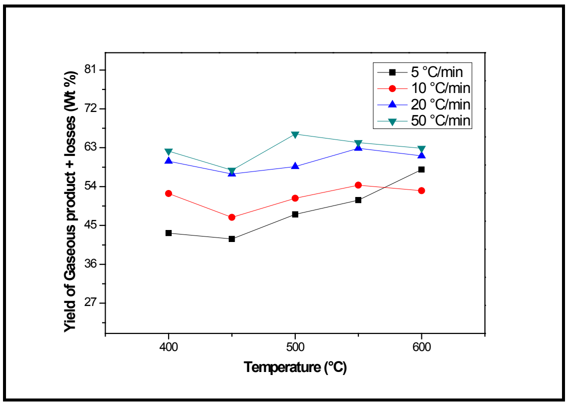

Figure 8. Plot for effect of temperature and heating rate on yield of Gaseous product and losses from Concentred Olive mill wastewater.

The heating rate has a big influence on product distribution, a rapid heating rate increases volatiles yields and decreases char yield. A rapid heating leads to a fast depolymerisation of the solid material to primary volatiles while at a lower heating rate dehydration to more stable anhydrocellulose is limited and very low. The result is that very small amounts of char produced in the primary reactions at rapid heating. Our experiments have demonstrated this theory. The char yields for a heating rate of 50 °C/min were lower than yields achieved at the lower heating rate of 5 °C/min. At optimal temperature, the char yield decreased from 26.39 % to 25.68 % and from 26.82 % to 22.66 %, for olive mill solid waste and olive mill wastewater respectively, as the heating rate was raised from 5 °C/min to 50 °C/min. The higher treatment temperature has led to more tar cracking resulting in higher yield of gaseous products and lower yield of tar. When the pyrolysis temperature was increased the gaseous yield increased.

At high temperatures both the rate of primary pyrolysis and the rate of thermal cracking of tar to gaseous products are high. The temperature markedly influences the heating rate. The heat flux is proportional to the driving force, the temperature difference between the particle and the environment. At higher temperature, the heat flux and the heating rate are higher.

Length of heating and its intensity affect the rate and extent of pyrolytic reactions, the sequence of these reactions, and composition of the resultant products. Pyrolytic reactions proceed over a wide range of temperatures; hence, products formed earlier tend to undergo further transformation and decomposition in a series of consecutive reactions. Further, various products are formed as secondary reactions to continuous heating of the initial products. Long heating periods allow the sequence of these reactions to take place whereas rapid heating tends to reduce these secondary reactions and the further degradation of the earlier formed products. If heat is supplied fast enough during flash pyrolysis, little or no char results and subsequent processing is greatly simplified. There could be substantial difference between the reactor temperature and that of the biomass. Hence, at higher temperatures, the rate of reaction may be controlled by the rate of heat transfer rather than the kinetics of the reactions. The main products of biomass pyrolysis are char, tar, pyroligneous acid, and gas. At low temperature, char is the dominant product followed by H_2O. Hardwoods yield less char but more acids than softwoods. The yield of volatile products (gases and liquids) increases with increasing heating rate while solid residue decreases. The effect of heating rate can be viewed as the effect of temperature and residence time. As the heating rate is increased, the residence time of volatiles at low or intermediate temperatures decreases. Most of the reactions that favor tar conversion to gas occur at higher temperatures. At low heating rates, the volatiles have sufficient time to escape from the reaction zone before significant cracking can occur. Heating rate is a function of the feedstock size and the type of pyrolysis equipment. The rate of thermal diffusion within a particle decreases with increasing particle size, thus resulting in lower heating rate. Liquid products are favored by pyrolysis of small particles at high heating rates and high temperature, while char is maximized by pyrolysis of large particles at low heating rates and low temperatures as mentioned earlier. Scott and al [26] have reported over 60% wt (of moisture-free wood) liquid products and 10% char below 600°C in fast pyrolysis of maple wood (120 µm). Aarsen et al [32] reported that the pyrolysis of 1 µm wood particles in a fluidized bed at 800°C is nearly complete within 2 seconds. They estimated the heating rate to be about 500°C/s. Small quantities (<10%) of char were produced. Fast and flash pyrolysis processes have recently attracted considerable attention as a means of maximizing gaseous and liquid products from biomass. Ayll'on and al [7] studied pyrolysis of meat and bone meal in a fixed bed reactor and investigated the influence of the final pyrolysis temperature and heating rate on the product (char, tar and gas) distribution and composition as well as char characterization. Two sets of experiments were performed at different final pyrolysis temperatures between 300 and 900 °C and heating rates from 2 to 14 °C/min. Their results showed that the effect of the final pyrolysis temperature is more important than the effect of the heating rate. The analysis of pyrolysis product distribution showed that the major products obtained at any temperature or heating rate were bio-oil and char. Most of the decomposition takes place at temperatures lower than 500 °C, and no more significant decomposition is produced above 750 °C. The chars obtained present a low specific surface area, less than 45 m^2/g. The bio-oil obtained is mainly composed of more than 60% nitrogenated aliphatic compounds (such as nitriles, amides and cyclic compounds), 15% aliphatic hydrocarbons (such as alkanes and alkenes), 10% oxygenated aliphatic compounds (mostly carboxylic acids) and about 8% oxygenated aromatic compounds (mainly phenolics).

3.3. Bio-oil characterisation

Previous studies have shown that biomass pyrolysis oils countain a very wide range of complex organic chemicals.

Table 3. Influence of heating rate on product yield from pyrolysis of OMSW and COMWW at 450 °C.

Heating rate (°C/min)		**5**	**10**	**20**	**50**
OMSW	**bio-oil**	**26.05**	**22.12**	**22.11**	**12.24**
	char	**27.4**	**26.77**	**24.42**	**25.86**
	Gas + losses	**46.55**	**51.11**	**53.47**	**61.90**
COMWW	**bio-oil**	**31.29**	**28.74**	**23.19**	**19.55**
	char	**26.82**	**24.40**	**19.90**	**22.66**
	Gas + losses	**41.89**	**46.85**	**56.91**	**57.79**

Table 4. Influence of heating rate on product yield from pyrolysis of OMSW and COMWW at 500 °C.

Heating rate (°C/min)		5	10	20	50
OMSW	bio-oil	33.41	29.81	23.98	14.36
	char	27.18	25.92	24.66	25.68
	Gas + losses	39.41	44.27	51.35	59.96

COMWW	bio-oil	25.6	24.56	20.69	15.77
	char	26.82	24.13	20.69	18.09
	Gas + losses	47.58	51.30	58.62	66.14

Table 5. Degree of conversion of olive mill solid waste.

		Heating rate (°C/min)			
	Conversion degree	**5**	**10**	**20**	**50**
Temperature (°C)	**400**	72.39	71.82	72.14	72.35
	450	72.59	73.22	75.57	74.13
	500	73.71	74.07	75.33	74.31
	550	74.10	74.27	75.21	75.05
	600	75	72.71	75.26	75.23

Table 6. Degree of conversion of concentrated olive mill wastewater.

		Heating rate (°C/min)			
	Conversion degree	**5**	**10**	**20**	**50**
Temperature (°C)	**400**	69.05	75.49	78.92	76.24
	450	73.17	75.59	79.15	77.33
	500	73.17	75.86	79.3	81.9
	550	79.8	76.54	77.9	81.4
	600	82.74	77.2	79.15	79.49

FT-IR spectra of bio-oils under optimum conditions (optimal temperature and heating rate) for olive mill solid waste (OMSW) and concentrated olive mill wastewater (COMWW) at 450 °C and 500 °C respectively are given in Figure 9-10. From Figure 9 and 10, we notice that there is a resemblance between both curves of olive mill solid waste in both conditions, for OMSW, the stretching vibrations between 1044 and 1462 cm^{-1} indicate the presence of alkanes (C-C, $-CH_3$, $-CH_2$). The figure show the presence of two peaks at 1709 cm^{-1} and 2853 cm^{-1} what shows the presence of compounds aliphatic like Aldehyde and Carboxylic acid respectively. The =C-H, $-CH_2$ stretching vibrations at 736 cm^{-1} and 1515 cm^{-1} indicate the presence of Alcène and compounds unsaturated of nitrogen. The only difference which exists between both curves, it is that the curve of olive mill solid waste at 500 °C and 5°C/min, show a small vibration at 3369 cm^{-1} what shows the presence of natural compounds of N-H Amide.

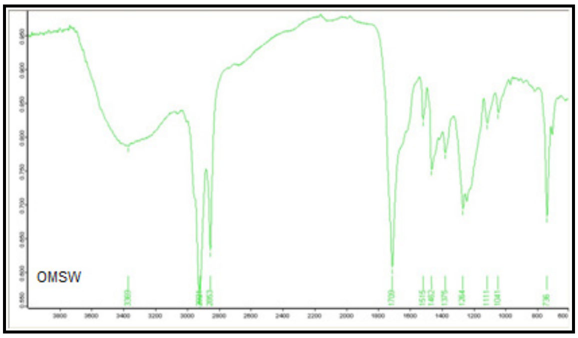

Figure 9. FT-IR spectra of bio-oil at 500 °C and 5 °C/min of olive mill solid waste.

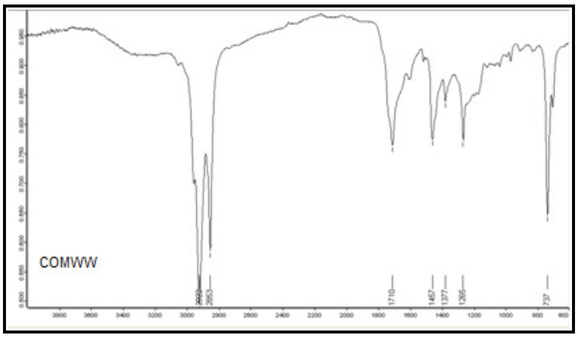

Figure 10. FT-IR spectra of bio-oil at 450 °C and 5 °C/min of concentrated olive mill wastewater.

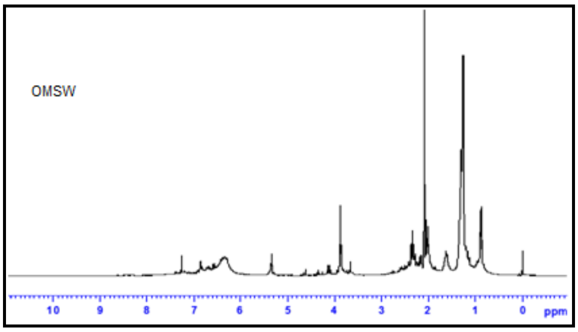

Figure 11. [1]H-NMR spectra for bio-oils at 500 °C and 5 °C/min of olive mill wastewater.

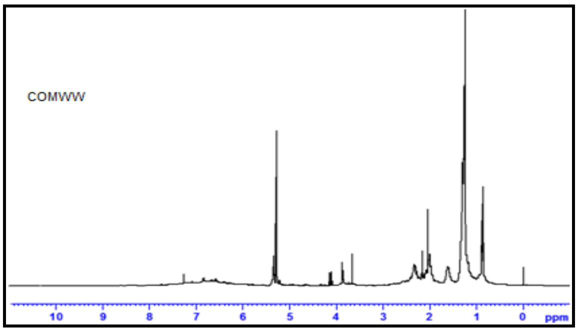

Figure 12. [1]H-NMR spectra for bio-oils at 450 °C and 5 °C/min of concentrated olive mill wastewater.

Table 7. Results of the column chromatography for the two bio-oils.

	OMSW	COMWW
Bio-oil (%)	33.41	31.29
Asphaltene + losses (%)	49.9	51.4
Maltene (%)	50.1	48.6
Aliphatic (%)	40.2	38
Aromatic (%)	21.4	27.5
Polar + losses (by difference) (%)	38.4	34.5

Table 8. Elemental compositions of bio-oils obtained from OMSW and COMWW.

Sample	%C	%H	%N	%O	H/C
OMSW	67.11	8.61	1.3	22.98	1.50
COMWW	66. 3	6.78	1.56	25.36	1.38

Table 9. Percentage of Protons contained in bio-oil obtained from pyrolysis of OMSW and COMWW.

Sample	HA %	HO %	HS %
OMSW	31.5	10.9	57.6
COMWW	28.3	19.30	52.4

For concentrated olive mill wastewater, we notice that both curves in both conditions are largely similar. From figure 9 and 10, we find the aromatic compounds existence; one can see it in the stretching vibration at 737 cm^{-1}. The vibration stretching between 1265 cm^{-1} and 1710 cm^{-1} (containing the values of stretching vibrations at 1377 cm^{-1} and 1457 cm^{-1}) show the presence of alkane compounds, aldehyde and ethers or amine. The vibration stretching at 2853 cm^{-1} and 2922 cm^{-1} indicate the presence of aldehyde and alkane compounds respectively. If we make a small comparison between olive mill solid waste and concentrated olive mill wastewater, one can say that olive mill solid waste contains many compounds than concentrated olive mill wastewater. Figures 11-12, shows the H-NMR spectra of bio-oils obtained at optimum conditions for olive mill solid waste and concentrated olive mill wastewater.

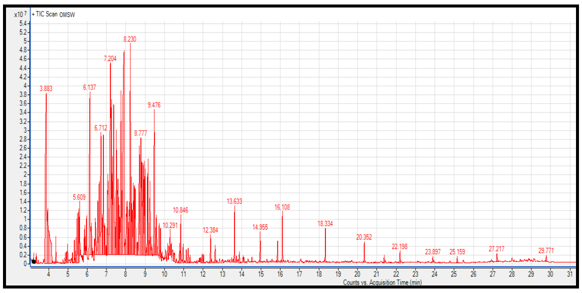

Figure 13. Chromatogram of aliphatic fraction of bio-oil at 500 °C and 5 °C/min of Olive mill wastewater.

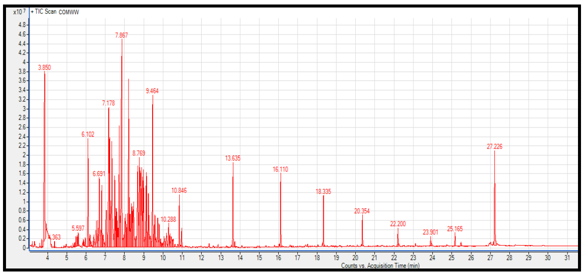

Figure 14. Chromatogram of aliphatic fraction of bio-oil at 450 °C and 5 °C/min of Concentrated Olive mill wastewater.

^{1}H-NMR spectra of the bio-oils indicate the presence of an aliphatic character of bio-oils from the pyrolysis of concentrated olive mill wastewater and olive mill solid waste. From figure 12, the peak which has a value between 6.5 – 7.2 ppm indicate the presence of aromatic compounds (HA) for two specter of concentrated olive mill wastewater. The domain of movement which varies between 0.5 and 4 ppm show the presence of aliphatic subtraction, we notice the presence of aliphatic compounds (HS) in specter of olive mill wastewater (1.1 ppm, 2 ppm, 3.9 ppm). Between the domains of 4 – 6 ppm, we have a peak appear at 5.4 ppm, What justifies the presence of oléfinic compounds (HO). Figure 13 show ^{1}H'NMR specter for bio-oils at 500 °C at 5 °C/min. The specter show that exists tree fractions, first one, propagates between 0.9 ppm and 2.3 ppm what indicates the presence of alkane and alcéne. From table 8 and 9 we notice that the percentage of protons contained in bio-oil obtained from pyrolysis of OMSW and COMWW have an aliphatic character and characterised with a higher H/C ratio, further comparison of H/C ratios of pyrolysis oils with conventional fuels indicates that the H/C ratios of the oils obtained in this study close to those of light and heavy petroleum products. Column chromatography was employed and yields of sub-fractions were calculated, table 7 show the results of the column chromatography for the two bio-oils. For the aliphatic fraction, Gas chromatography was achieved, Figures 14 and 15 shows chromatograms of the aliphatic subfractions of bio-oils obtained under the most suitable conditions for olive mill solid waste and concentrated olive mill wastewater, the distribution of straight chain exhibit one the range of C_4-C_{29} and C_4-C_{27} for oils of OMSW and COMWW respectively, the results of this chromatograms have showed that aliphatic subfraction of the bio-oil has similar distribution of straight chain alkanes with standard diesel.

4. Conclusion

In the present work, the pyrolysis of olive mill waste such as olive mill solid waste and concentred olive mill wastewater was performed in a tubular reactor and the effects of the heating rate and pyrolysis temperature on product yields ware investigated. For OMSW the maximal average yield achieve almost ≈ 33 wt % at 500 °C and 5°C/min, whereas for COMWW it achieve 31 wt % at 450 °C with the same heating rate. The results showed that final temperature and heating rate have a remarkable effect on the yields of products. The purpose of this work it was to determine optimal condition of temperature and heating rate to have a maximal yield via pyrolysis. A temperature between 450 °C and 500 °C at the heating rate of 5 °C/min were the conditions wished and looked to have good one returns on oil. Knowing that there is other works which succeeded almost in same results and in same working condition, what is reflected either what gives a big certainly in works to realize. Bio-oils obtained under optimum conditions were analyzed by elemental analysis, FT-IR, ^{1}H'NMR and CG-MS, the results show that bio-oils contain a large wide of products and it is possible to obtain liquid products similar to petroleum from olive mill wastes if the pyrolysis conditions are chosen well.

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