Properties of Bio-Oil and Bio-Char Produced by Sugar Cane Bagasse Pyrolysis in a Stainless Steel Tubular Reactor

M. Y. GUIDA[1,2*], A. HANNIOUI[1,2]

Abstract. In this study, compositional analysis of the products obtained by thermal degradation of sugar cane bagasse at various pyrolysis temperatures (300, 350, 400, 450, 500, 550, 600, 650, 700, 750 and 800 °C) and heating rate (5, 10, 20 and 50 °C/min) was studied. Sugar cane bagasse was pyrolyzed in a stainless steel tubular reactor. The aim of this work was to experimentally investigate how the temperature and heating rate affects liquid and char product yields via pyrolysis and to determine optimal condition to have a better yield of these products. Liquid product (bio-oil) obtained under the most suitable conditions were characterized by elemental analysis, FT-IR, C-NMR and H-NMR. In addition, column chromatography was employed to determine the aliphatic fraction (Hexane Eluate); gas chromatography and FT-IR were achieved on aliphatic fractions. For char product (bio-char), the elemental chemical composition and yield of the char were determined. The results of our work showed that the amount of liquid product (bio-oil) from pyrolysis of sugar cane bagasse increases with increasing the final temperature and decreases with increasing the heating rate. The highest yield of liquid product is obtained from the samples at 550 °C and at the heating rate of 5°C/min, the maximal average yield achieved almost 32.80 wt%. The yield of char generally decreases with increasing the temperature, the char yield passes from 39.7 wt% to 21 wt% at the heating rate of 5°C/min and from 32 wt% to 17.2 wt% at the heating rate of 50 °C/min at the same range of temperature (300–800 °C). The analysis of bio-oil showed the presence of an aliphatic character and that it is possible to obtain liquid products similar to petroleum from sugar cane bagasse waste. The solid products (bio-char) obtained in the presence of nitrogen (N_2) contain a very important percentage of carbon and high higher heating values (HHV).

Keywords: energy, biomass, sugar cane bagasse, pyrolysis, bio-oil, bio-char

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1. Introduction

In recent years, several researches and projects were focused and led, with the purpose of minimizing the demand of fossil fuels and their replacement by renewable and sustainable alternative energy sources [1, 2]. The increase of oil prices and the big problems engendered by its combustion, concentrated the efforts to find efficient solutions to remedy these international problems [3]. Besides, fuel processing technologies which are applied to obtain high and clean performance products that are consistent with the existing systems have been in demand. Biomass for producing energy has a special place among all other renewable energy sources and it's estimated to contribute with more of 20% to the world's total energy supply [1, 4–6].

Biomass is a mixture of structural constituent (cellulose, hemicellulose and lignin) and minor amounts of extractives [5]. Sugar cane bagasse and other forms of biomass (e.g. olive residue, sunflower shell, almond shell, cottonseed, straw, musk, birch, etc.) are some of the main renewable solid energy resources available and provide the only source of solid (bio-char), liquid (bio-oil) and gaseous product fuels [7–9]. Sugar cane bagasse is a fibrous residue of sugar cane stalks left over after crushing and extraction process of the juice from sugar cane (*Fig. 1*), it consists of approximately 50% cellulose, 25% hemicellulose and 25% lignin (that varies and depends on several factors, which influence the composition of sugar cane bagasse). About 55 million dry tons of bagasse is produced annually all through the world [3, 10–12].

Among all technologies connected to renewable energy, used in the past, studied and used in the present, we find thermochemical conversion of biomass. Different thermochemical treatment processes include pyrolysis, gasification, combustion and liquefaction [13]. Although pyrolysis is still in the developing stage during existing energy scenario it has received special attention as it can convert biomass directly into liquid (bio-oil), solid (bio-char) and gaseous products by thermal decomposition of biomass in the absence of oxygen [14].

Biomass pyrolysis with a long history of use, initially for the production of charcoal (bio-char), has emerged as a limited research domain [2, 4]. Biomass pyrolysis is a thermochemical decomposition process in which organic material such as biomass (containing: cellulose, hemicellulose and lignin) is converted into a carbon rich solid and a volatile matter by heating in the absence of oxygen [15–17]. The solid product of this
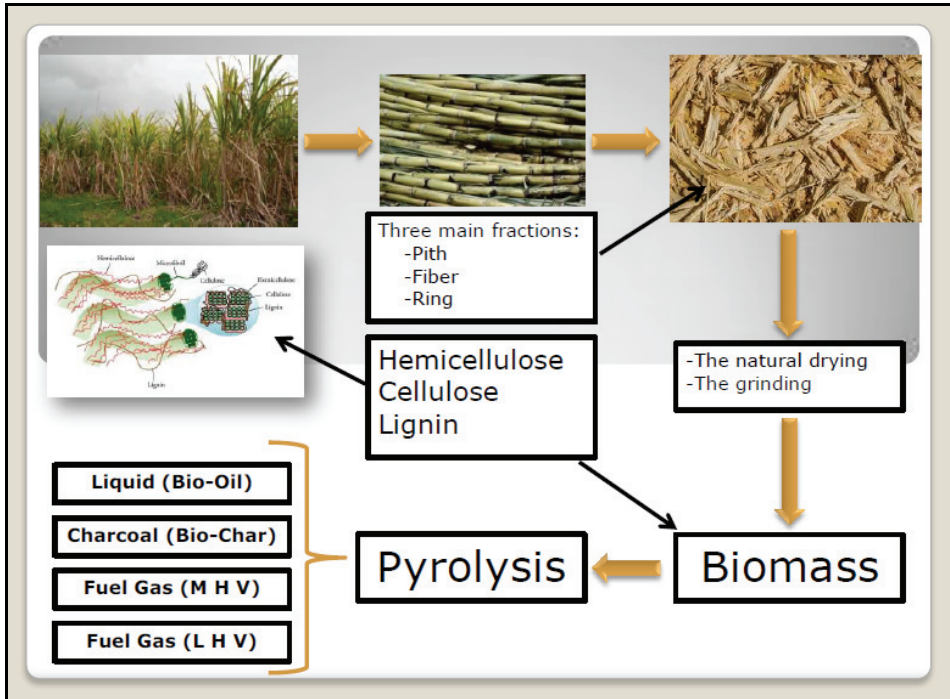
Figure 1. The valuation of sugar cane bagasse

process is known as the bio-char or char, and is generally high in carbon content. The volatile fraction of this process is partly condensed to a liquid fraction called tar or bio-oil along with a mixture of the non-condensable gases. The bio-oil is stored and further used for energy production. The gases can be utilized for providing heat energy to the pyrolysis reactor [18]. The pyrolysis products are formed from both primary decomposition of the solid biomass as well as secondary reactions of volatile condensable organic products into low-molecular weight gases, secondary tar and char [19–22]. One of the significant benefits of pyrolysis is that it can be conducted at temperatures lower (normally in the range of 400–700°C) than those required in gasification (>700°C) and combustion (>900°C) processes. Numerous studies have been devoted to pyrolysis of biomass [23–27]. 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 they can be used as feedstocks to prepare activated carbons. The liquid product, bio-oil, is also useful as a fuel, it may be added to petroleum refinery feedstocks or upgraded by catalysts to produce premium grade refined fuels, or may

have a potential use as chemical feedstocks. The third product, gas, having high calorific 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 produce 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 and al [28], 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 cutting and kernels olive bagasse 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 and al [29], 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 500–550 °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 have been recently employed to produce bio-oil, gaseous products and solid products as activated carbons. A.E. Putun and al [30], 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% and 18 wt%, respectively, at different nitrogen flow rates [27–30]. V. Minkova and al [31] 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 bagasse waste, he obtained almost ≈28 wt% in pyrolysis of the biomass in nitrogen flow. There exist other works on other biomass pyrolysis. Most of the researches [31–34], 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 500 °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 types of biomass (olive, straw, cane bagasse,

walnut shell, sunflower shell, hazelnut shell, almond shell, etc), have indicated that bio-oils, char and gas yields of pyrolysis may be changed by altering temperature and heating rate [35–40].

In this work, sugar cane bagasse wastes were chosen as the renewable energy source. Their pyrolysis was studied for determining and optimizing the role of these parameters on yield of char and liquid products, and to determine the characteristics of the bio-char and bio-oil. This present work focuses on three aspects of sugar cane bagasse pyrolysis: (1) effect of pyrolysis conditions on the product yields of bio-char and bio-oil; (2) bio-oil product characterization; and (3) bio-char yield analysis and quality.

2. Material and Method

2.1. Sample preparation

The sugar cane bagasse samples were obtained from a sugar factory (sugar mill) which is located about 8 km of Béni-Mellal, Morocco. Bagasse consists of three main fractions: ring, fiber and pith. The samples received in the laboratory contained a big percentage (wt%) of moisture (43 wt%). The moisture content was lowered after a few days of natural drying (to 7–9 wt%) in ambient atmosphere. Air-dried samples were being crashed with the aim of obtaining a uniform material of an average particle size (0.2–0.4 mm).

Table 1. Main characteristics of sugar cane bagasse

	Sugar Cane Bagasse (SCB)
Proximate Analysis	
Moisture	7.9
Volatile matter	78.4
Ash	2.5
Fixed carbon	11.20
Elemental Analysis	
C	47.50
H	5.48
N	0.51
O	46.51
Chemical Analysis	
Hemicellulose	29.68
Cellulose	35.20
Lignin	21.70

The characterization of the samples is given in *Table 1*. Proximate analysis of the raw material having average size was performed according to the standard methods of (ASTM) procedure. The ultimate analysis was performed on sugar cane bagasse samples to determine the elemental composition. A Carlos Erba, EA 1108 elemental analyzer was used to determine the weight fractions of carbon, hydrogen and nitrogen and the weight fraction of oxygen was calculated by the difference. Cellulose, hemicellulose and lignin, being the main constituents of sugar cane bagasse, were also determined.

2.2. Experimental apparatus and procedure

2.2.1. Apparatus

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

2.2.2. 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 an electrically heated tubular furnace. 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 products 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 (bio-char) was removed and weighed. The liquid phase (bio-oil) was collected in cold traps maintained at about 0°C using salty ice. Pyrolysis of sugar cane bagasse was carried out three times (experimental error of <0.5 wt%) to improve the profitability and producibility of the results of experiments to investigate the effect of pyrolysis conditions (sweeping gas nitrogen, final temperature and heating rate) 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 sugar cane bagasse 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 (300 °C, 350 °C, 400 °C, 450 °C, 500 °C, 550 °C, 600 °C, 650 °C, 700 °C, 750 °C and 800 °C). The experiments were conducted under nitrogen (N_2) gas with a flow rate of 100 mL/min. The product obtained from the pyrolysis was recovered in two collectings with dichloromethane as solvent. To improve the yield of the liquid product we used some salt and ice in a bath of water, where there was oily product collecting. The bio-oils obtained were evaporated, spilt and separated in column, with the objective of havng the aliphatic fraction (hexane eluate).
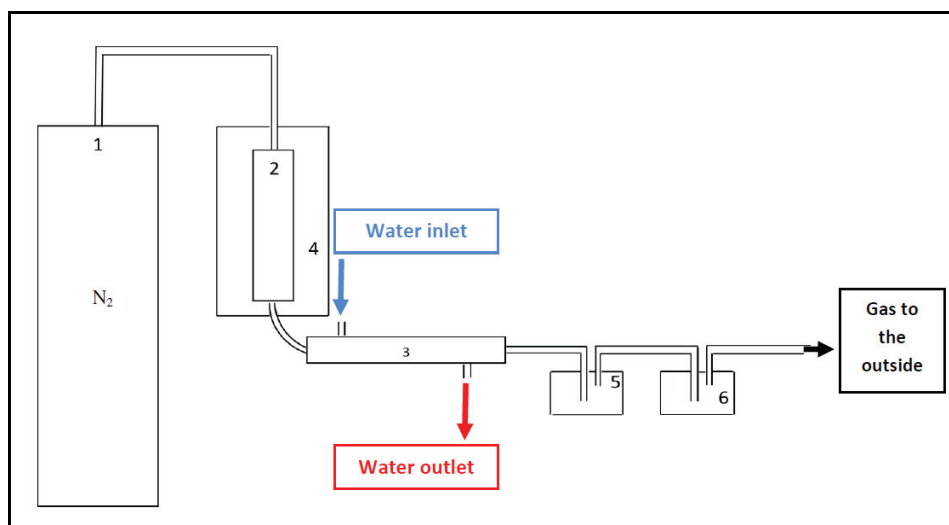
Figure 2. Simple diagram of pyrolysis: (1) Nitrogen tube; (2) stainless steel reactor; (3) condenser; (4) electrical furnace; (5) and (6) oily products collecting

3. Result and Discussion

3.1. Effect of temperature and heating rate on pyrolysis product

The first series of experiments was performed to establish the effect of final temperature on the pyrolysis product yields (bio-oil, bio-char and gas). The plot for effect of temperature on the yield of bio-oils from the sugar cane bagasse waste is given in *Fig. 3.* The yields of bio-oil products from bagasse

wastes generally increased with the increase in pyrolysis temperature from 300 to 550 °C, then decreased with increasing the pyrolysis temperature up to 800 °C. The highest liquid yields were 32.80 wt% for SCB. The highest bio-oils yield was obtained from the bagasse waste samples at 550 °C. The liquid products from the bagasse pyrolysis are dark brown viscous oils. Combustion tests have demonstrated the pyrolysis liquid (bio-oil) products could be burnt efficiently in standard or in slightly modified burners. The liquid products from the bagasse pyrolysis obtained at lower temperature (300–550 °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 resulting in a greater heating value [31, 32]. For sugar cane bagasse waste, organic content allows the thermal decomposition of hemicellulosic and cellulosic compounds at higher temperature, this result can be explained by the characteristics of the organic compounds present in SCB. Several authors [14, 36] confirmed that degradation of lignin containing polyphenol structure starts at a lower temperature. At elevated temperatures, the amount of char from pyrolysis of the bagasse wastes decreases. The char yield at 300 °C was 39.7 wt% and 21 wt% at 800 °C. These results are consistent with the literature [30, 36]. It is known that pyrolysis temperature plays an important role on product distribution. As bagasse wastes 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 50 and 160 °C, bagasse waste loses its moisture, generates noncombustible gases like CO_2 and undergoes depolymerisation reactions involving no significant carbohydrate loss [30]. Chemical bonds preconditioned in the main constituents of biomass sample begin to break at temperatures higher than approximately 200 °C. Breakdown of hemicellulose, which is a thermally less stable constituent, takes place at lower temperatures up to 300 °C forming gases like carbon monoxide. At temperatures between 350 and 550 °C cellulose breaks down 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 place forming hydrogen enriched gaseous products and char undergoes further degradation by being oxidized to CO_2, CO and H_2O [28]. According to these reactions it can be said that relatively low pyrolysis temperatures around 400 °C favors char formation. Temperatures up to 550 °C maximize the production of bio-oils

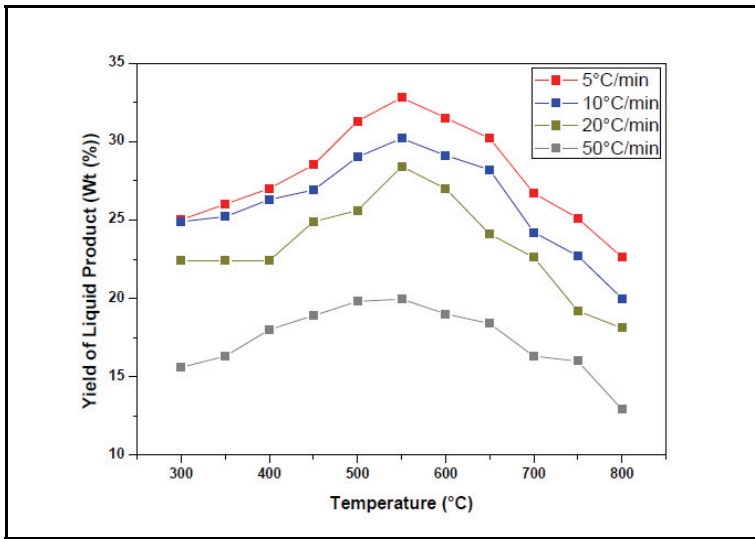and temperatures above 800 °C maximize gaseous products while minimizing char formation.

Figure 3. Plot of effect of temperature and heating rate
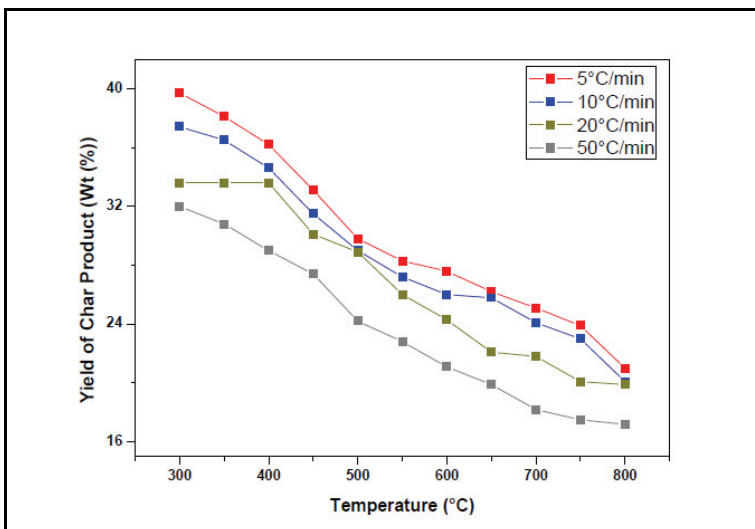on yield of liquid product

Figure 4. Plot of effect of temperature and heating rate
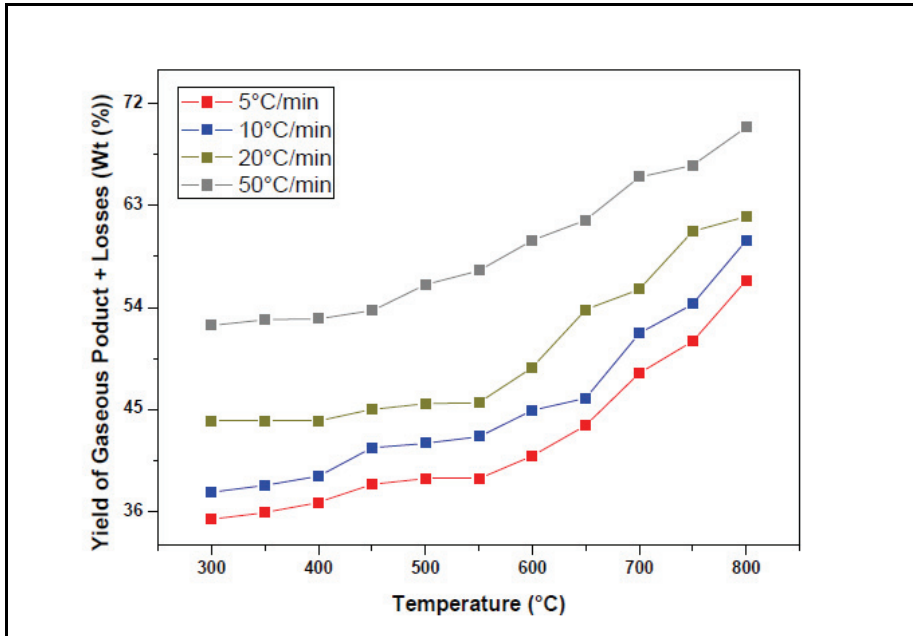on yield of char product

Figure 5. Plot of effect of temperature and heating rate
on yield of gaseous product and losses

Figures 3–5 and *Table 2* show plot of effect temperature and heating rate on yield of liquid, char, gas products and the yield of conversion degree from the pyrolysis of sugar cane bagasse waste, in relation to heating rate (from 5 to 50 °C/min) to a final temperature of 300 to 800 °C in a tubular reactor. 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 is 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. One can say that 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 yields of gaseous products and lower yields of tar. When the pyrolysis temperature was increased the gaseous yield increased. 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 [41–44].

Table 2. Degree conversion of sugar cane bagasse

Conversion Degree (X)		Heating rate (°C/min)			
		5 °C/min	10 °C/min	20 °C/min	50 °C/min
Temperature (°C)	300	64.17	63.46	63.15	62.45
	350	65.11	64.90	63.88	63.14
	400	70.86	70.39	70.10	69.66
	450	71.07	71.01	71.20	70.06
	500	75.24	71.77	71.32	70.89
	550	75.40	74.57	73.40	72.12
	600	75.43	75.23	74.85	73.05
	650	75.65	75.22	74.85	73.29
	700	76.05	75.68	74.88	73.40
	750	76.11	76.54	74.89	74.06
	800	76.80	76.81	74.89	74.90

The second series of experiments was performed to establish the effect of sweeping gas flow rate (nitrogen) on pyrolysis yields of bio-oil. Due to the maximum bio-oil yield obtained in the first series of experiments, the heating rate and particle size were held constant at 5°C/min and 0.2–0.4 mm at different temperatures ranging from 400 to 600 °C. The role of sweeping gas during pyrolysis is to affect the residence time of the gas produced as a result of pyrolysis reactions by removing the products from the hot zone to minimize secondary reactions such as thermal cracking repolymerisation and recondensation and to minimize the liquid yield. The liquid product yields of pyrolysis of sugar cane bagasse waste in relation to the nitrogen flow rate are given in *Fig. 6,* for the heating rate of 5°C/min and pyrolysis temperature varies from 400 °C to 600 °C. It was observed that pyrolysis conversion has increased in small amounts and there was no great obvious influence on the yield of liquid as the rate of nitrogen increased. The highest bio-oil yield was achieved with a nitrogen flow rate of 100 mL/min.
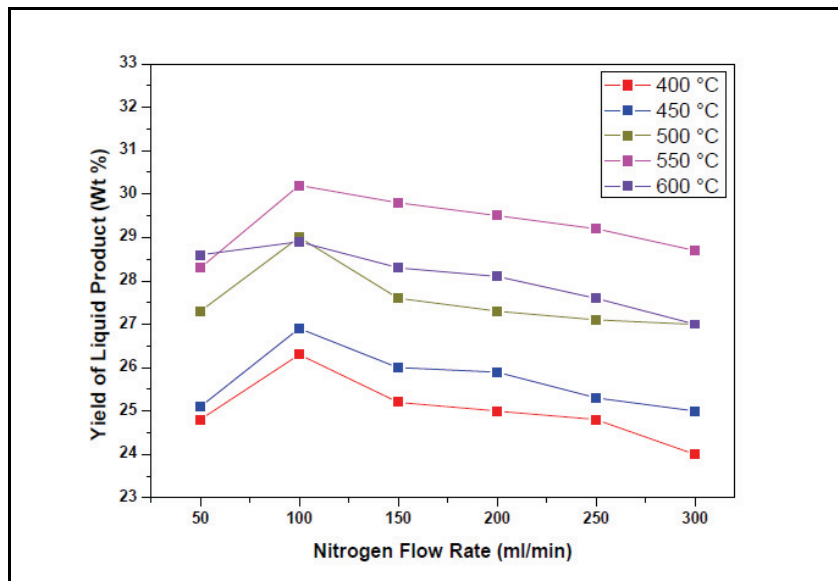
Figure 6. Pyrolysis of sugar cane bagasse at different nitrogen flow rate

3.2. Analysis of the bio-oil and bio-char from pyrolysis *of SCB*

Previous studies have shown that biomass pyrolysis oils contain a very wide range of complex organic chemicals. The elemental compositions and the average chemical composition of bio-oils characterized under nitrogen gas are listed in *Tables 1* and *3*. The results showed that composition of samples of sugar cane bagasse, moisture and ash percentage play a very important role in the composition of bio-oils produced by pyrolysis. From the elemental analysis of samples, sugar cane bagasse contains high percentage of hemicellulose, cellulose, lignin and moisture (water vapour or steam). During pyrolysis the water vapour plays a reactive agent role that reacts with the pyrolysis products. Water vapour may stabilize the radicals obtained by the thermal decomposition of fuel increasing the yield of volatiles. By comparing H/C ratios of pyrolysis oils with conventional fuels indicates that the H/C ratios of oil obtained in this study were between those of light and heavy petroleum products.

H-NMR and C-NMR spectra of bio-oils indicate the presence of an aliphatic character of bio-oils obtained at 5°C/min and 550°C, from pyrolysis of sugar cane bagasse. From *Figs 7* and *8* the domain of movement, which varies between 0.5 and 4 ppm, shows the presence of
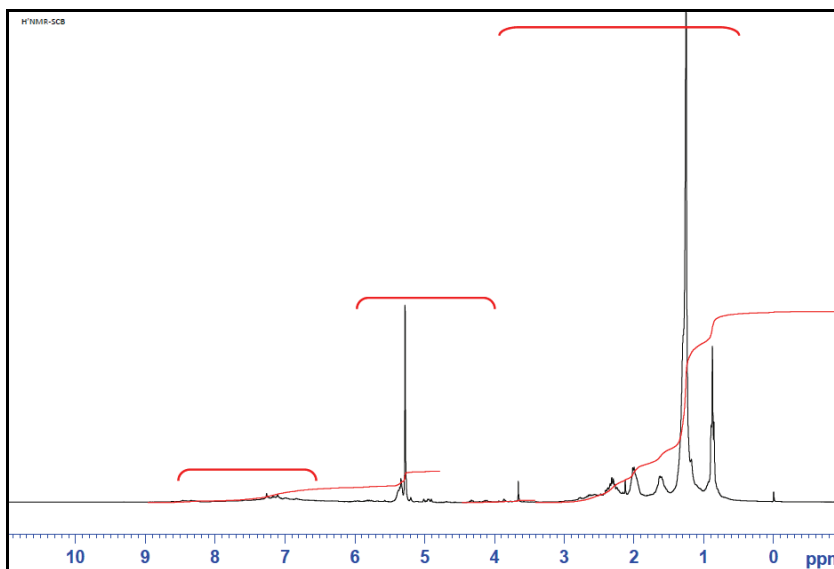
Figure 7. H-NMR spectra for bio-oils at 550 °C and 5 °C/min of sugar cane bagasse
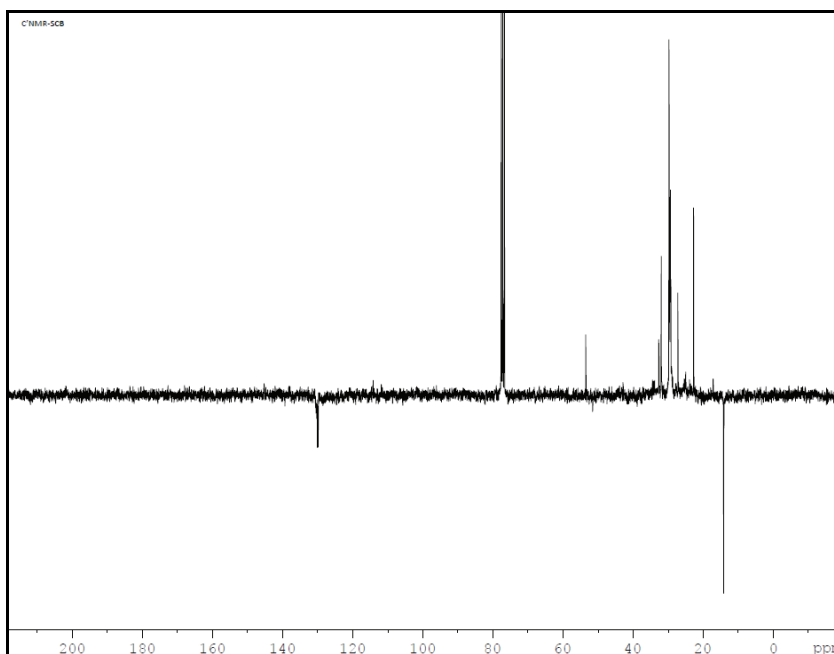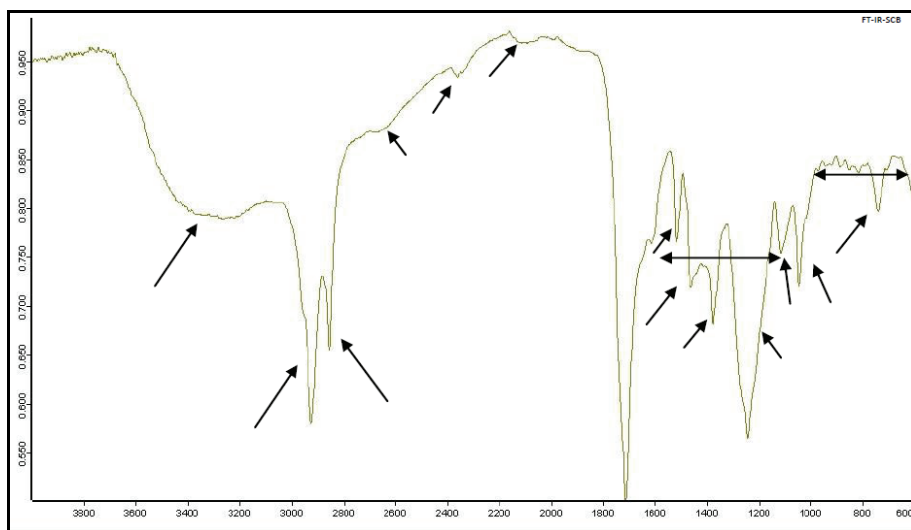

Figure 8. C-NMR spectra for bio-oils at 550 °C
and 5 °C/min of sugar cane bagasse

aliphatic compound, between the domains of 4–6 ppm, we have a peak appear for SCB, which justifies the presence of olefinic compounds (HO). The peak which has a value between 6.5–7.2 ppm indicates the presence of aromatic compounds (HA) for the specter of bio-oil of sugar cane bagasse. We can say that peaks which are situated in the domain of 4–8 ppm are not particularly clear and that can be due to the overlapping of peaks during the recording of H-NMR analysis.

FT-IR spectra of the bio-oils and aliphatic fraction of the pyrolysis of sugar cane bagasse under nitrogen atmosphere are given in *Figs 9* and *10*. The results obtained shape with the results obtained in H-NMR analysis. The C-H stretching vibrations between 2800 and 3000 cm^{-1} and C-H deformation vibrations between 1350–1475 cm^{-1} indicate the presence of alkanes. The C=H stretching vibrations between 1650–1750 cm^{-1} indicate the presence of ketones or aldehydes. The absorbance peaks between 1575–1675 cm^{-1} represent C=C stretching vibrations indicative of alkenes and aromatics.

A gas liquid chromatogram of the aliphatic subfraction (hexane eluate) of bio-oils obtained under nitrogen atmosphere is shown in *Figure 11*. The results of this chromatogram have showed that aliphatic subfraction of the bio-oil has similar distribution of straight chain alkanes and alkenes with standard diesel.

Figure 9. FT-IR spectra for bio-oils at 550 °C and 5 °C/min
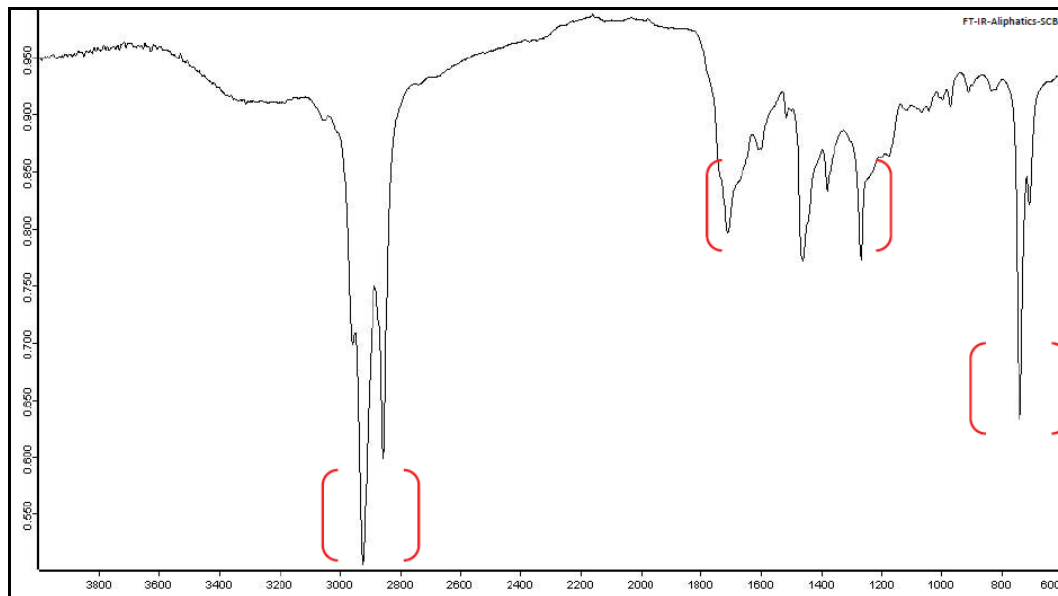of sugar cane bagasse

Figure 10. FT-IR spectra of aliphatic fraction at 550 °C and 5 °C/min
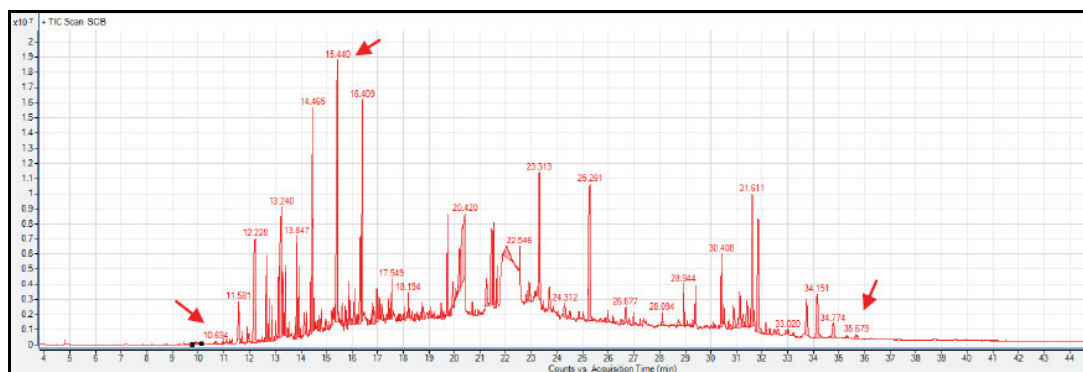of sugar cane bagasse

Figure 11. Chromatogram of aliphatic fraction (hexane eluate) at 550 °C
and 5 °C/min of sugar cane bagasse

Elemental analysis of bio-chars obtained by pyrolysis of sugar cane
bagasse is presented in *Table 3*. One can notice that the percentage of the
carbon content is higher for bio-char. *Figures 12–16* present the percentage
of the carbon, hydrogen, oxygen and HHVs in relation to the carbonization

temperature. We notice that carbon content increased as the final temperature was raised from 300 °C to 800 °C, while hydrogen and content decreased, they showed the HHVs of bio-chars at 5 °C/min. As can be seen from the figures, the HHV increased as the final temperature was raised from 300 °C to 800 °C.

Table 3. Elemental composition of bio-oils and bio-char obtained under nitrogen atmosphere at 550 °C and 5 °C/min for sugar cane bagasse

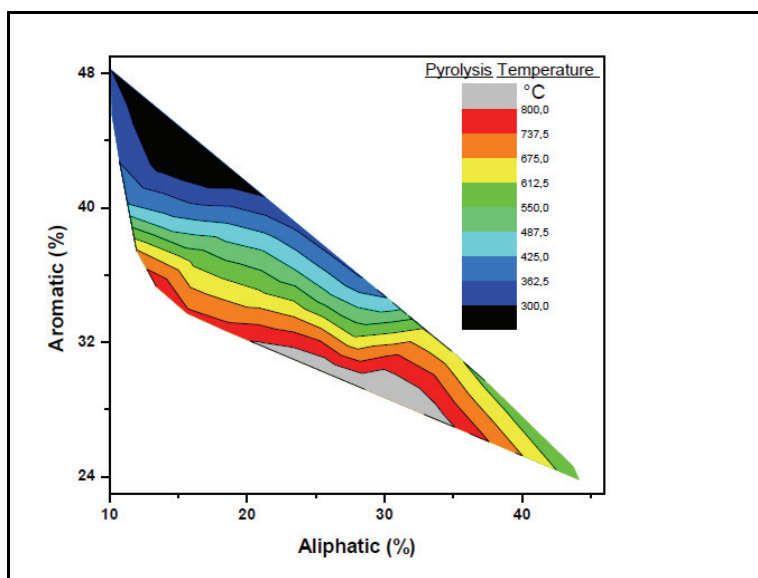| Ultimate Analysis (w/w %)	Sugar cane bagasse (SCB)	
	Bio-oil	Bio-char
Carbon	68.23	71.5
Hydrogen	9.70	2.80
Oxygen	20.75	22.2
Nitrogen	1.32	3.50
H/C	1.70	0.46
O/C	0.22	0.23

Figure 12. Evolution of aromatic and aliphatic compounds according to the pyrolysis temperature at 5 °C/min
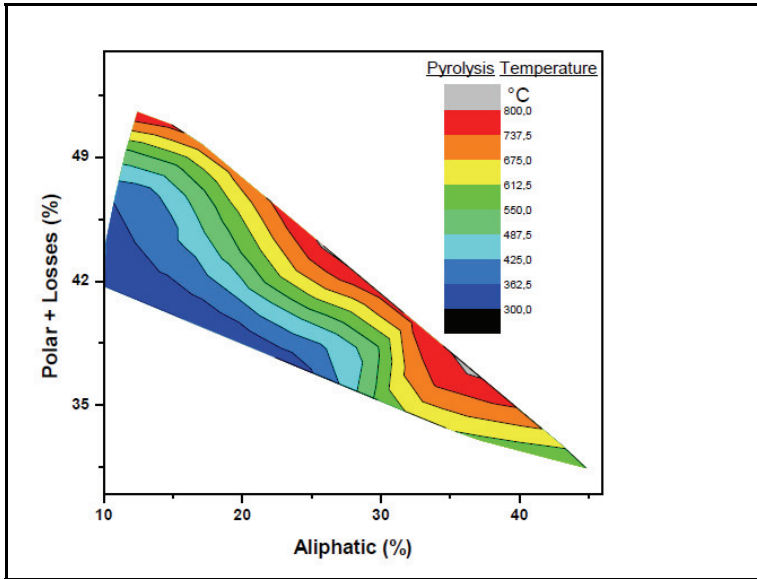
Figure 13. Evolution polar (+losses) and aliphatic compounds according to the pyrolysis temperature at 5 °C/min
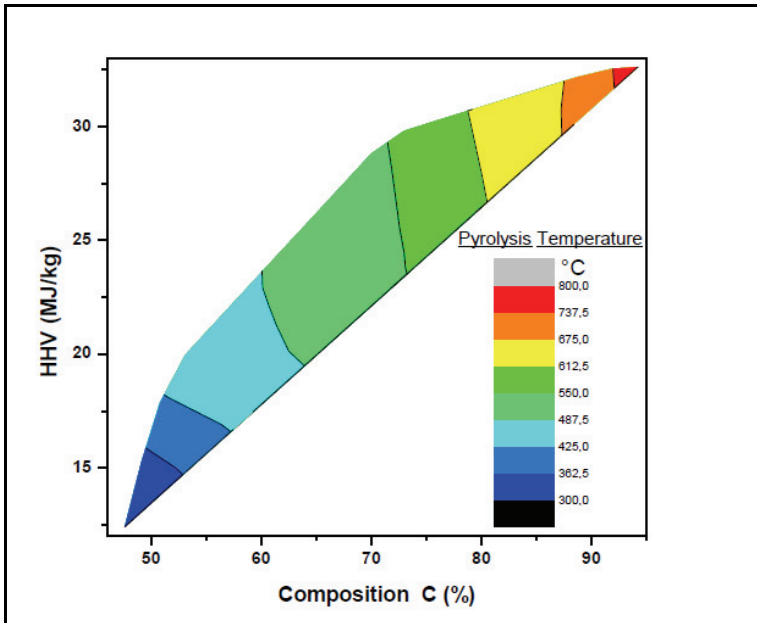

Figure 14. Evolution of HHV of bio-char according to the composition (C) and the pyrolysis temperature at 5 °C/min
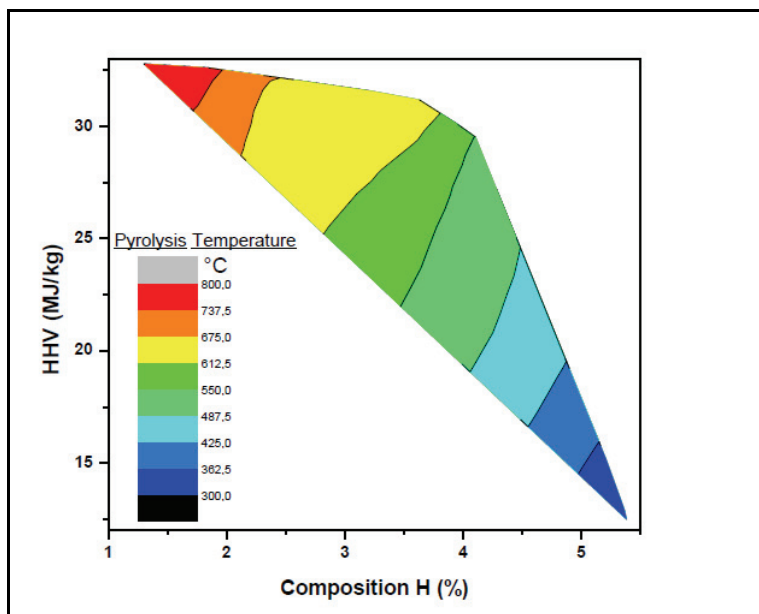
Figure 15. Evolution of HHV of bio-char according to the composition (H) and the pyrolysis temperature at 5 °C/min
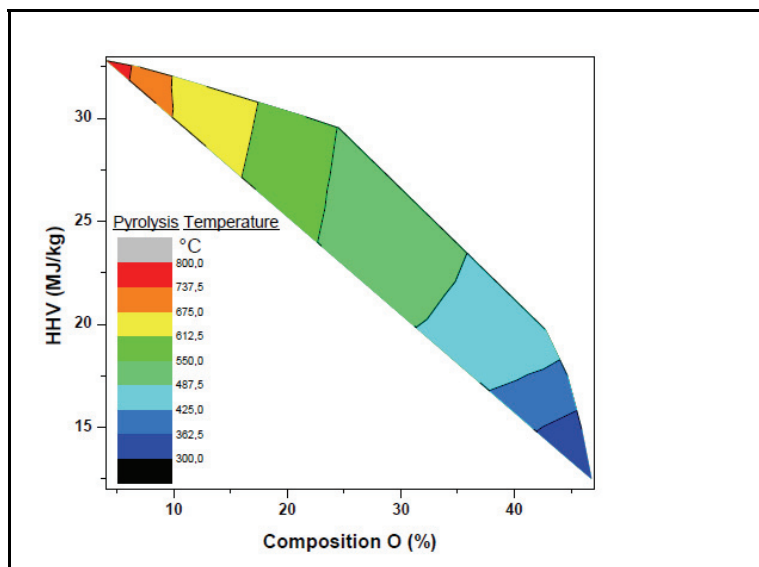

Figure 16. Evolution of HHV of bio-char according to the composition (O) and the pyrolysis temperature at 5 °C/min

4. Conclusions

This study yielded basic information on the thermal decomposition of biomass such as sugar cane bagasse. The results can be used in the development of thermal conversion technologies for biomass, as well as in basic research on combustion, gasification and liquefaction, because the primary valorization mechanism is common to all these applications except that of liquefaction.

Present results showed that both the heating rate and temperature had a significant effect on yields of bio-oil and bio-char resulting from pyrolysis of sugar cane bagasse. Maximum liquid yield of 32.80 wt% was obtained at a final temperature of 550 °C, with a heating rate of 5°C/min and a nitrogen flow rate of 100 mL/min. Bio-oils obtained under optimum conditions were analyzed, the results show that they contain a wide range of products and it is possible to obtain liquid products similar to petroleum from sugar cane bagasse if the pyrolysis conditions are chosen well.

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