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THERMOCHEMICAL CHARACTERIZATION OF SUGARCANE BAGASSE FOR THE PRODUCTION OF COMBUSTIBLES VIA PYROLYSIS USING N₂ AS CARRIER GAS

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ABSTRACT

Global warming is a large-scale issue that has led humanity to seek for renewable energy sources. Thermal gasification of biomass is a new technology used to produce clean fuels using biomass as feedstock. The resultant products are renewable neutral carbon fuels. Experimental results obtained from the pyrolysis of sugarcane-bagasse ($CH_{1.581}O_{0.671}N_{0.00306}S_{0.00117}$) carried out in a static batch reactor with nitrogen as carrier gas for temperatures ranging between 400°C and 900°C and a heating rate of 4.30 °C /min ±7.8% are discussed. Sugarcane bagasse samples were thermo-chemically characterized in order to determine thermodynamic properties such as enthalpy of formation, high heating value, empirical formulas of biomass, volatile matter, among others. The chemical formula of the bio-oil was estimated using gas composition, given by a gas analyzer, and atom balance on components (char, gas, and bio-oil). The effect of temperature on both the HHV of the syngas and yield of products, which include, bio-oil, gaseous fuels, and char are discussed in detail. As pyrolysis temperature increases, bio-oil production increases, whereas char and syngas production reduces. Chemical empirical formulas for biomass and volatile matter were $CH_{1.581}O_{0.671}N_{0.00306}S_{0.00117}$ and $CH_{1.807}O_{0.767}N_{0.00349}S_{0.00133}$ respectively, whereas, the high heating values (DAF basis) of biomass and volatile matter were 18925.08 kJ/kg and 17472.77 kJ/kg, respectively. The average chemical empirical formula of the bio-oil was $CH_{2.145}O_{0.268}N_{0.268}S_{0.002}$.

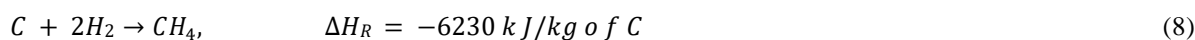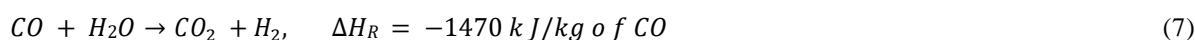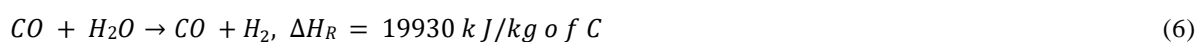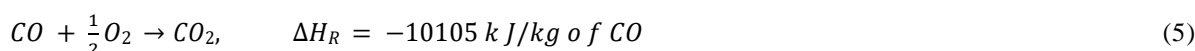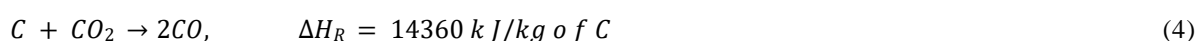**KEYWORDS**: Pyrolysis, sugarcane bagasse, static batch pyrolysis reactor, empirical formula, syngas.
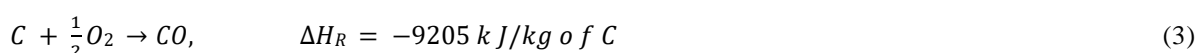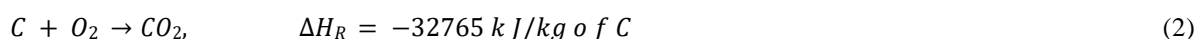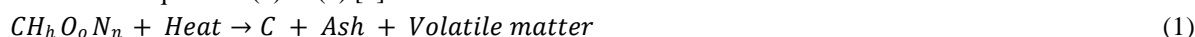
1. INTRODUCTION

Global warming is a large-scale issue that has led researchers to seek for renewable clean energy sources. The increasing greenhouse emissions and other hazardous gases as NO_x and SO_x are mainly due to the dependence of humanity activities on fossil fuels. Energy requirements have increased since the industrial revolution in the twentieth century, when primary energy sources of modern industries were based on petroleum, coal and natural gas. In Colombia, 75.6% of the primary energy supply depends on fossil fuels (natural gas, coal and oil) [1] [2]. Thermal gasification of biomass, including pyrolysis, is a renewable technology to produce liquid and gaseous fuels which mitigates the dependence on fossil fuels.

Modern sugarcane industries around the world produce large quantities of bagasse wastes that can be used for power co-generation or to produce alternative fuels such as bio-diesel. Colombia produces more than 9 million tons of sugarcane and around 6 million tons of sugarcane bagasse waste per year [3] [4]. Massive sugar industries use part of this bagasse to supply heat requirements of their industrial process, while the remaining part, which is not used for heat production, is used as fuel for power co-generation. Small sugar industries do not have an appropriate technology for power co-generation, therefore the surplus bagasse is a by-product that, in most cases, becomes a contaminant of natural resources. Alternatively, those sugarcane bagasse wastes (SCBW), yielded as by-products in small industries, can be used as feedstock for pyrolysis gasification processes to produce a bio-oil for the mitigation of the dependence of these industries on fossil liquid fuels. Gases generated by pyrolysis processes are used as a heating resource, while bio-oil can be chemically processed to produce gasoline, ethanol, etc. [5].

In thermal gasification processes, biomass undergoes four basic sub-processes: drying, pyrolysis, reduction, and oxidation [5] [6]. Typically, there are four global gasification processes known as partial oxidation, pyrolysis,

partial reforming, and reforming. Pyrolysis is the process in which biomass releases its volatile matter by thermal degradation in an inert medium (reaction 1). This global endothermic reaction requires heat addition to be able to produce light volatiles, liquid fuels, and charcoal. The first process, known as partial oxidation, uses oxygen or air as oxidizing source to produce a syngas composed basically of CO, CO_2, CH_4, H_2O, H_2 and traces of light hydrocarbons. Partial reforming uses air-steam mixtures to produce a syngas rich in H_2. The last process, known as reforming, is globally endothermic (requires heat addition) and uses steam as oxidizer to produce a mixture of H_2 and CO_2. During biomass gasification processes, several multiple chemical reactions occur; these can be consecutive or competitive parallel. However, any gasification process can be reduced into a set of global reactions as shown in equations (1) to (8) [6].

$$CH_hO_oN_n + Heat \rightarrow C + Ash + Volatile\ matter \tag{1}$$

$$C + O_2 \rightarrow CO_2, \qquad \Delta H_R = -32765\ kJ/kg\ of\ C \tag{2}$$

$$C + \frac{1}{2}O_2 \rightarrow CO, \qquad \Delta H_R = -9205\ kJ/kg\ of\ C \tag{3}$$

$$C + CO_2 \rightarrow 2CO, \qquad \Delta H_R = 14360\ kJ/kg\ of\ C \tag{4}$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2, \qquad \Delta H_R = -10105\ kJ/kg\ of\ CO \tag{5}$$

$$CO + H_2O \rightarrow CO + H_2, \Delta H_R = 19930\ kJ/kg\ of\ C \tag{6}$$

$$CO + H_2O \rightarrow CO_2 + H_2, \qquad \Delta H_R = -1470\ kJ/kg\ of\ CO \tag{7}$$

$$C + 2H_2 \rightarrow CH_4, \qquad \Delta H_R = -6230\ kJ/kg\ of\ C \tag{8}$$

Reaction (1) corresponds to the release of volatile matter contained in any biomass (pyrolysis), reactions (2) and (3) show oxidation processes, and reactions (4) to (8) present reduction processes.

During pyrolysis, hydrocarbons are broken down into smaller and simpler molecules resulting in the production of gases e.g. CO_2, H_2O, CO, C_2H_2, C_2H_4, C_2H_6, C_6H_6, among others, bio-oil, and charcoal. Conventional pyrolysis consists in a slow and irreversible thermal degradation of organic components of biomass such as lignocellulose content. Biomass pyrolysis undergoes process such as dehydration, dehydrogenation, aromatization, coke production, condensation of chemical reactions, and reorganization. Products obtained from this process are mostly water, carbon oxides, coal, organic compounds, tar, and polymers. At temperatures between 100°C and 120°C, biomass dehydrates; at T ~ 250°C, a molecular dissociation of water and carbon dioxide occurs (biomass releases sulfur and hydrogen); then at T ~ 340°C, production of methane and light aliphatic begins; when T ~ 380°C, carbonization stage initiates; at T ~ 400°C, $C-O$ and $C-N$ bonds are broken down; at temperatures between 400°C and 600°C, production of tar and oil starts; at T ~ 600°C, cracking and gaseous hydrocarbons are produced, and at T > 600°C volatile aromatic compounds appear [7].

Usually, pyrolysis processes take place under different specific parameters which include a carrier gas (nitrogen or argon), heating rate, pressure, particle size and time of residence. The carrier gas provides an inert medium to transport the volatile matter out of the pyrolysis reactor. Previous researchers suggest that the heating rate strongly affects the yield and quality of the gaseous and liquids products. Slow pyrolysis uses heating rates ranging between 0.1 K/s and 1K/s, and flash pyrolysis reaches heating rates close to 1000 °C/s. Slow pyrolysis favors the production of solid and liquid fuels, while fast pyrolysis favors gaseous fuels [8].

Previous studies on pyrolysis gasification of different types of biomass have been published. In 2001, Bonelli et al., [9] reported changes in the chemical and surface characteristics of Brazil nut shells, pyrolyzed at different temperatures. Also, pyrolysis kinetic results based on non-isothermal thermo-gravimetric (TGA) analysis were reported. In 2002 García-Perez et al. [10], performed vacuum pyrolysis tests of sugarcane bagasse and characterized the bio-oil, charcoal, gas, and aqueous phase produced. They found that for bio-oil between 30 and 40 wt%, low ash content (0.05 wt %) and relatively low viscosity (4.1 cSt at 90 °C), a high calorific value (22.4 MJ/kg), and low content of methanol insoluble materials (0.4 wt%) can be recovered. The yield of charcoal comprises between 20 and 26 wt %. In 2006, Tsai et al. [11] presented results on fast pyrolysis of rice straw, sugarcane bagasse and coconut, using induction heating in an externally heated fixed-bed reactor. Effects of the process parameters such as pyrolysis temperature, heating rate, and holding time on the yield of the pyrolysis

products and their chemical composition were analyzed. They performed a chemical characterization by elemental ($CHNO$), calorific, Fourier transform infrared (FT-IR) spectroscopy, and a gas chromatography/mass spectrometry (GC-MS). The pyrolysis liquid product contains large amounts of water (> 65 wt %) and fewer contents of oxygenated hydrocarbons. In 2009 Sánchez et al. [12] presented results from the sewage sludge pyrolysis in a quartz reactor at different temperatures. They characterized the pyrolysis oil by means of gas chromatography-mass spectrometry (GC-MS). In 2010, Al Arni et al. [13] reported results on pyrolysis of Brazilian sugarcane bagasse. The effect of moisture content of biomass during the pyrolysis process was analyzed. Results show that water added to the biomass before the pyrolysis process resulted in the decrease of power and quantity of the syngas. Also, a simulation tool of a molten carbonate fuel was used in order to estimate the feasibility of the entire process in terms of operating conditions and electrical performance. Rofiqul Islam et al. [14] pyrolyzed sugarcane bagasse in a fixed-bed fire-tube heating reactor under different pyrolysis conditions to determine the effect of pyrolysis temperature (375 °C < T < 575 °C), sweeping glass flow rate and input particle size on the product yields. They also characterized the liquid obtained from the most suitable conditions by physical properties, elemental analyses, GCV, FT-IR, H NMR analysis and distillation. In 2012, Pattiya et al. [15] reported results of fast pyrolysis of agricultural residues from sugarcane and cassava plantations by a free-fall reactor unit. In 2014, Jankovic [16] presented results on pyrolysis process of coffee cup samples in a flow stream of nitrogen at different heating rates; Guidicianni et al. [17] obtained results on slow steam pyrolysis of Arundo donax for the recovery of a solid material suitable to be used as bio-char; Kim et al. [18] elucidated the pyrolysis characteristics of Korean pine nut shells waste. They performed a thermo-gravimetric analysis in order to analyze the pyrolysis kinetics and analyzed the products distribution through a pyrolyzer-gas chromatography/mass spectrometry. In 2015, Montoya et al. [19] reported experimental results of fast pyrolysis of sugarcane bagasse in a fluidized-bed reactor. They evaluated variables such as temperature, biomass feed rate, carried gas flow, biomass and effects of inert material particle size on global product distribution. Borel Lidja et al. [20] studied the resultant products of the pyrolysis of brewer's spent grain (BSG). They analyzed their physicochemical properties and thermal degradation behavior. The BSG was provided by microbrewery in Minas Gerais State, Brazil. The average sieve diameter of dried BSG was 3.23 mm. Different tests were performed using (8 mg) samples at temperatures ranging from 298 to 1173 K, heating rates of 5, 10, 20, 30, 40 and 50 K/min and using nitrogen as purge gas at a flow rate of 50 mL/min. It was found an 83.3% of volatile matter content. Results showed a reduction in oxygen compounds and an increase in the number of hydrocarbons for higher temperatures.

Bhattacharjee N. [21] used a semi-batch pyrex glass reactor to maximize the pyrolysis oil yield of orange bagasse at different operating conditions. The samples were dried in order to remove the excess of moisture, then grinded up and sieved to 425 µm. 15 mg samples were tested at heating rates ranging between 25 and 100 °C/min, temperatures from 50 °C to 700 °C and a constant N_2 gas flow rate of 0.1 L/min. It was found a volatile matter composed mainly of CO, CO_2, H_2, CH_4, C_2H_2, C_2H_6 and C_3H_8 with variable concentrations depending on the operating conditions. The HHV of the pyrolysis gas at different operating conditions lied in the range of 4.08 to 5.92 MJ/m^3. A pyrolysis study of soybean hulls was performed by Toro J. et al. [22]. The experiments were performed at five different temperatures (from 300 to 600 °C) and a constant heating rate (10 °C /min) in a vertical scale tubular reactor with a nitrogen atmosphere. Resultant gases were mainly composed of CH_4, H_2, CO, CO_2 and light hydrocarbons such as C_2H_6, C_2H_4, C_3H_8, and C_3H_6. Methane generation was relevant at temperatures higher than 300 °C and it maximum value was achieved at 500 °C, while light hydrocarbons were formed only at temperatures between 400 to 500 °C. The HHV of the gas mixture increased with temperature reaching values up to 24.3 MJ/m^3. Barry D. et al. [23] evaluated the economic and environmental impact of implementing the sewage sludge pyrolysis process under different scenarios at the Greenway Wastewater Treatment Plant in London, Ontario. Different scenarios were evaluated: 1) incineration with no energy recovery and landfilling of ash, 2) slow pyrolysis at 500 °C with application of bio-char to agricultural land or 3) with char used as coal substitute in cement kiln and ash used as a cement filler. Results in terms of global warming potential in kg CO_2 showed that incineration without energy recovery is the worst scenario, while pyrolysis of sewage sludge, with the use of bio-char as a substitute fuel in a cement kiln, had the least impact on global warming. For a plant capacity of 2.1 t/h with 8000 operational hours per year, a total capital investment of 13.5 million CAD was estimated. An annual cost of 1.32 million CAD was considered and, for a 20 years lifetime project with a discount rate of 10%, the Net Present Value calculated was 23.5 million CAD.

Literature review evidences that there are not previous studies on the effect of temperature on yield and quality of products (bio-oil, gas, and char) obtained from a sugarcane bagasse slow-pyrolysis process carried out in a static batch pyrolysis reactor heated at very low heating rates and using N_2 as carrier gas. The current research discusses the results obtained from sugarcane bagasse slow-pyrolysis carried out in a static batch pyrolysis reactor heated at a low heating rate (4.30°C /min) and using nitrogen as carrier gas. Parametric results of the pyrolysis temperature (400°C < T < 900°C) on yields and quality of products are discussed. Also, thermochemical properties based on the characterization of the biomass are presented. These properties include biomass enthalpy of formation, empirical formulas of the biomass and volatile matter as well as high heating values of biomass and volatile matter.

2. MATERIALS AND METHODS

Sugarcane bagasse samples were obtained from a Colombian raw sugarcane agro-industry. They were partially dried to reduce moisture content; then, they were grinded up and sieved to obtain a specific particle size as required for proximate and ultimate analyses. Proximate and ultimate analyses were performed under the following standards: ASTM D3173-03 for moisture content, ASTM D3174-04 for ash content, ASTM D3175-02 for volatile matter, ASTM D3172-89 for fixed carbon, ASTM D5865-04 for HHV, ASTM D129-00 (2005) for the percentage of weight of sulfur, ASTM D5373-08 for nitrogen, carbon and hydrogen. Afterwards, particle size distribution of samples was determined by using a sieve analysis. This analysis was carried out based on the standard ASTM C136-0; samples were sieved as-received (including moisture content). Pyrolysis experiments were performed under conditions listed in table 1 (2 repetitions per test) and experimental setup presented in figure 1.

Table 1. Pyrolysis processes protocol

Test	Final Pyrolysis Temperature	Pressure [atm]	Biomass [gr]	Medium	Carrier Gas Flow [L/min]	Particle Size Distribution	Heating Rate [°C/min]
1	400 °C	1	200	Inert (N_2)	1	Figure 2	4.30±7.8%
2	500 °C	1	200	Inert (N_2)	1	Figure 2	4.30±7.8%
3	600 °C	1	200	Inert (N_2)	1	Figure 2	4.30±7.8%
4	700 °C	1	200	Inert (N_2)	1	Figure 2	4.30±7.8%
5	800 °C	1	200	Inert (N_2)	1	Figure 2	4.30±7.8%
6	900 °C	1	200	Inert (N_2)	1	Figure 2	4.30±7.8%

Experimental assembly uses an oven (Thermolyne Thermo Scientific) which reaches temperatures up to 1000 °C and a gas analyzer (Wuhan Cubic Optoelectronics co. Ltd) which analyzes mole fractions of CO, CO_2, CH_4, H_2, O_2 and C_nH_m, as well as the energy density of the gas. Biomass used as feedstock in the pyrolysis process was weighed out and placed inside the reactor. Then, the reactor was placed in the oven and the system was sealed and purged in order to prevent a gas leak and ensure an inert medium. Consecutively, the oven was turned on at the heating rate required (4.30 °C/min). Gases released during the process passed through a condensation system where the bio-fuel was collected. The no-condensable gases, leaving the condensation system, were analyzed by the gas analyzer every 10 minutes. Temperature was recorded every 10 minutes until the oven reaches the final pyrolysis temperature specified for each test. Experiments were carried out until gas composition, recorded by the gas analyzer, showed only N_2 i.e. the volatilization of the volatile matter had ended. Thus, the total time required for each experiment depends on the parametric temperature.
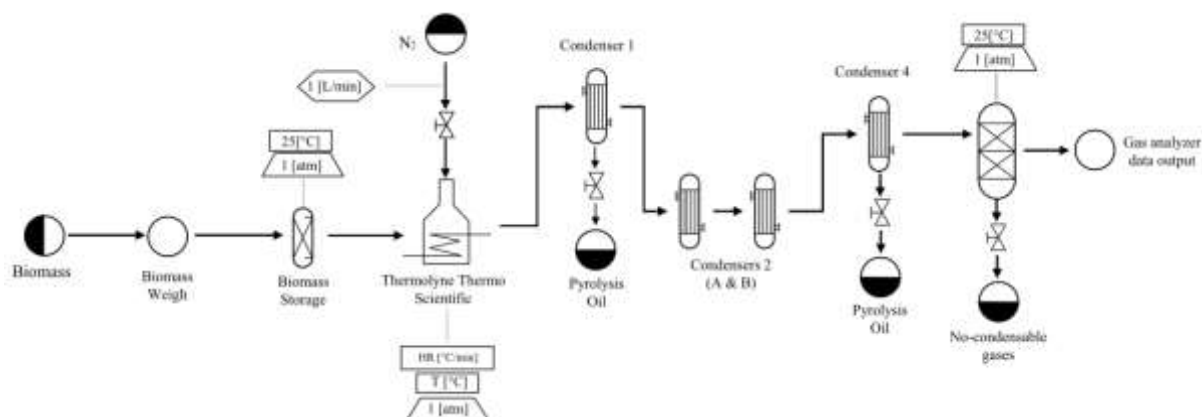
Fig. 1   Flux diagram of the experimental process and equipment

3.   RESULTS AND DISCUSSION

This section discusses the thermo-chemical characterization and particle size distribution of the sugarcane bagasse used as co-product. Results from tests of sugarcane bagasse pyrolysis and TGA are discussed.

Fuel Properties

Table 2 presents the results given by proximate and ultimate analyses (as received and DAF bases) of the sugarcane bagasse samples. Besides, the empirical formula and enthalpy of formation are shown. The empirical formula was derived via atom balance (DAF basis) on compounds, whereas the enthalpy of formation was obtained based on conservation of energy between reactants and products for the theoretical reaction of one kmol of sugarcane bagasse ($CH_{1.581}O_{0.671}N_{0.00306}S_{0.00117}$).

The dry-ash-free high heating value (HHV_{DAF} 18 925.08 kJ/kg) presented in table 2 corresponds to a 41.81% of the gross heating value of diesel fuel and 55.52% of coal. The HHV of sugarcane bagasse presented in this study is lower than the value reported by [19] (20 500 kJ/kg), but higher than the reported by [24] (17 975 kJ/kg). The difference between those results may be due to sugarcane variety. Comparison between results presented here and values reported by other authors for different biomasses shows that the HHV_{DAF} of the sugarcane bagasse is lower than those (20 129.22 kJ/kg and 19 469 kJ/kg) reported by [18] and [25] for Korean pine nut shell and sugarcane bagasse respectively, but higher than those reported by [24] (18 387 kJ/kg) for oil-palm fiber, [15] (18 300 kJ/kg) for sugarcane tops and (18 400 kJ/kg) for sugarcane leaves, [13] (18 170 kJ/kg) for Brazilian sugarcane bagasse, [26] (18 000 kJ/kg) for sugarcane straw, and [14] (16 810 kJ/kg) for sugarcane waste. Volatile matter content (90.4%) presented in Table 2 is higher than values reported by [27] (82.9%) and [25] (87.8%) for sugarcane bagasse, [15] (74.9%) for sugarcane tops, [18] (73.5%) for Korean pines nut shell, [28] (70.28%) for oil-palm fiber, [14] (75.85%) for sugarcane waste, [26] (74.0%) for sugarcane straw and [13] (84.0%) for Brazilian sugarcane.

Particle size distribution of sugarcane bagasse

Figure 2 illustrates the particle size distribution of the sugarcane bagasse samples with 95% of certainty. Results tend to behave as a normal distribution, however there is a reduction of the percentage of mass when size ranges between $425 - 500$ µm. This is due to the fact that sugarcane bagasse is a fibrous organic material with a non-homogeneous shape which is retained on the larger sieves when being sieved. Nevertheless, particles smaller than 425 µm tend to have a uniform shape and are able to pass through the mesh to the bottom of the system.

Table 2. Results obtained from proximate and ultimate analysis for sugarcane bagasse

Component	As received basis	DAF Basis
Moisture [%]	6.7	
Ash [%]	2.11	
VM [%]	90.4	
FC [%]	0.75	
S [%]	0.14	0.154
C [%]	44.83	49.161
H [%]	5.95	6.525
N [%]	0.16	0.175
O [%]	40.11	43.985
HHV [kJ/kg] Biomass	17 251.78	
HHV_{DAF} [kJ/kg] Biomass		18 925.08
$HHV\ VM_{DAF}$ [kJ/kg]		17 472.77
$HHV\ OIL_{DAF}$ [kJ/kg]		20 252
Empirical Formula Biomass	$CH_{1.581}O_{0.671}N_{0.00306}S_{0.00117}$	
Molar Mass Biomass [$kg/Kmol$]	24.432	
Enthalpy of formation Biomass [$kJ/Kmol$]	-122 859	
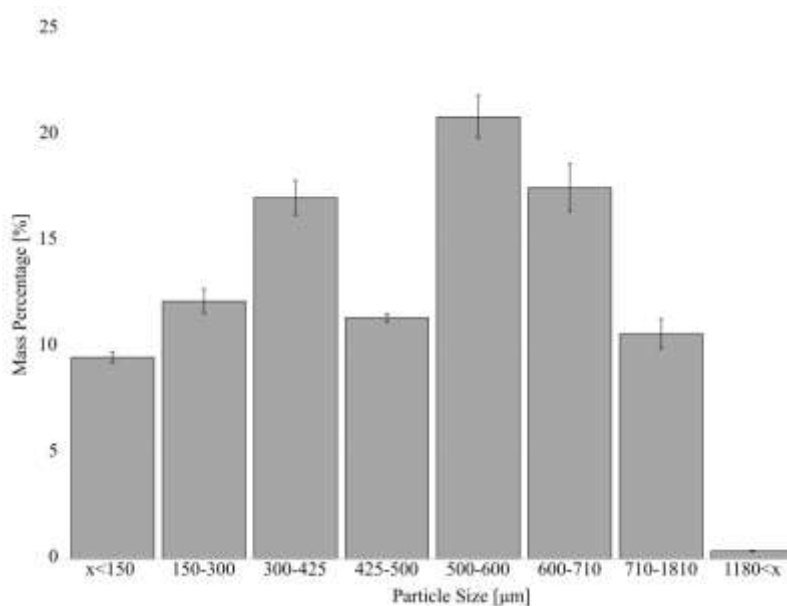
Fig. 2   Particle size distribution for sugarcane bagasse.

Pyrolysis
This section presents experimental results obtained from sugarcane pyrolysis ($CH_{1.581}O_{0.671}N_{0.00306}S_{0.00117} + heat$) tests.
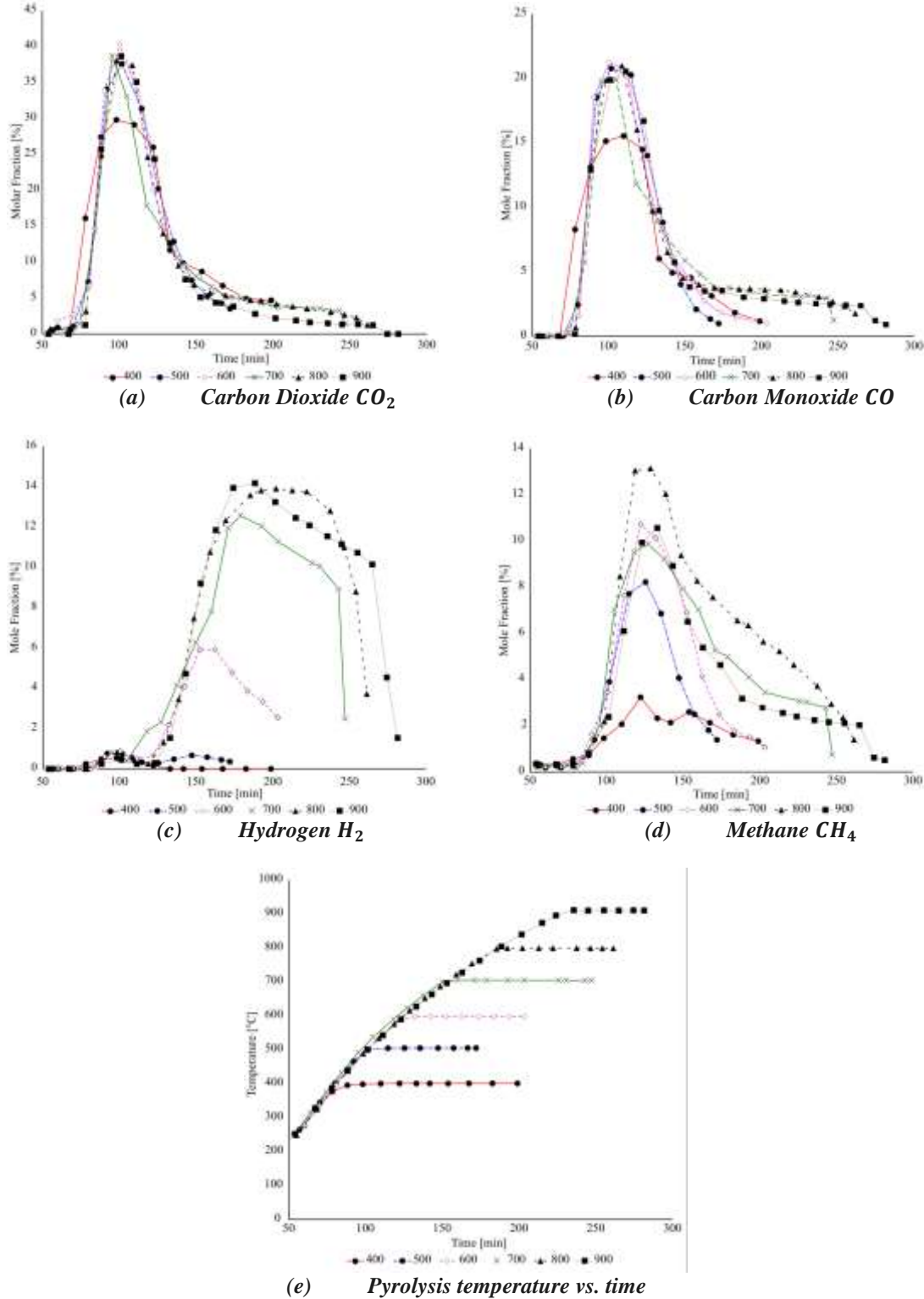
Gas Composition

(a)   *Carbon Dioxide CO_2*

(b)   *Carbon Monoxide CO*

(c)   *Hydrogen H_2*

(d)   *Methane CH_4*

(e)   *Pyrolysis temperature vs. time*
Fig. 3   Mole fraction vs. time for different final pyrolysis temperatures.

Figure 8 shows both, average dry-base molar gas composition and temperatures vs. time, for experiments carried out at temperatures showed in Table 1. The total time of each test varies with temperature. Results of CO_2, CO,

H_2 and CH_4 are presented, although the gas analyzer also reported O_2 and light hydrocarbons; results of those gases are not presented since they were traces. The production of methane initiates approximately at minute 90 and increases until minute 125, where it virtually stabilizes and begins to decrease. The range of time in which methane is produced depends on temperature, i.e. higher temperatures tend to increase time. At 400°C< T < 800°C, the production of methane increases with temperature e.g. at T = 800 °C the maximum methane production is 13% while at 400°C it is only 3%. Hydrogen production starts 30 minutes after methane and increases rapidly for 100 minutes where it reaches its maximum production. At 175 min < t < 250 min the H_2 tends to decrease slightly with time, however, after 250 min there is a strong decrease in the production. Like methane, hydrogen also increases with increments of temperatures, reaching its maximum value (~ 15%) at 900°C. At 400°C < T < 500°C the production of H_2 is negligible, indicating that the production of H_2 is possible for T > 500°C. Carbon monoxide and carbon dioxide production curves show a similar trend: they start at t = 75 min and increase rapidly until approximately 120 min when they reach their maximum value. At t = 120 min, the concentration curves begin to decrease faster until t = 150 min where curves stabilize at very low concentrations. Figures 3a and 3b also show higher content of CO_2 than CO. The maximum content of CO_2 is 40%, while for CO it is only 22%, indicating that the production of CO_2 is almost twice the production of CO.
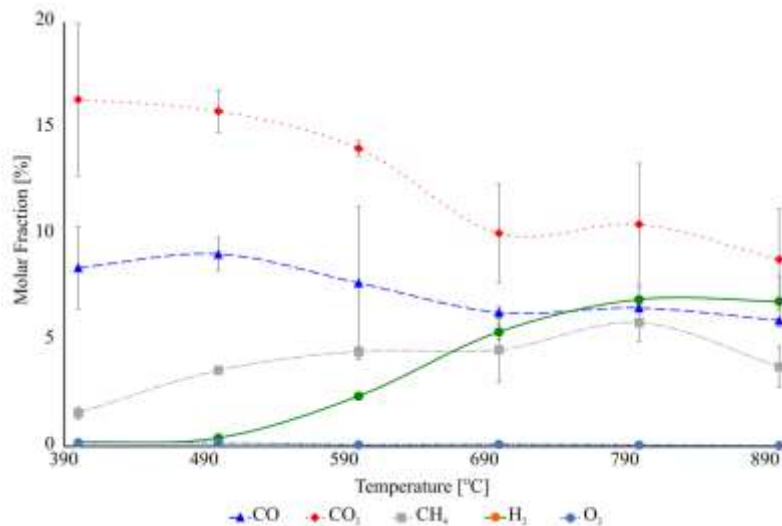

Fig. 4   Effect of final pyrolysis temperature on the average mole fraction of gases.

Figure 4 reports the effects of pyrolysis temperature on the average mole fraction (dry basis) of the gases leaving the condensation system. The average gas production was calculated by integrating the curves presented in figure 8 for each specie and each temperature over time. The production of CH_4 begins at about 500 °C and increases as the pyrolysis temperature rises, reaching its maximum value (5.85%) at 800°C. At 400°C < T > 700°C, the carbon monoxide and carbon dioxide curves show a decreasing trend for increased pyrolysis temperatures. They reach their maximum (CO_2 : 16.35% and CO : 8.43%) and minimum (CO_2 : 8.82% and CO : 5.95%) concentration values at 400°C and 900°C respectively. At T ~ 690°C, CO and CO_2 production show an inflection point where they tend to increase for higher temperatures. The production of H_2 starts at 500°C and increases with temperature. Its maximum average mole fraction (6.93%) is reached at 800°C. Results show that at 400°C < T < 500°C the syngas leaving the condensation system is mostly composed of CO, CO_2, and CH_4. Typically, this syngas is used as fuel to produce the heat required in the pyrolysis process which is globally endothermic and requires heat addition.

Figure 5 displays the effect of pyrolysis temperature on the energy density applying equation (9) to the syngas produced. The energy density ranged from 1 720 kJ/m³ to 4 038 kJ/m³. The maximum value (4 038 kJ/kg) is reached at T = 800 °C where the production of CH_4 is the highest. The maximum experimental energy density value reported here corresponds to the 11.21% of the natural gas energy density (36 MJ/m³). Whenever the CH_4, CO and H_2 production increases, the HHV grows as these gases provide high heating values to the mixture.
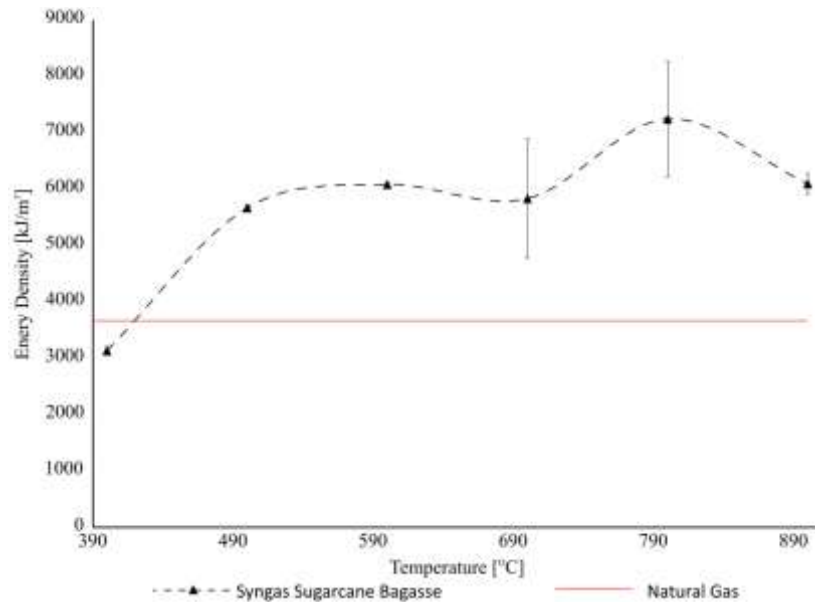
Fig. 5   *Effect of pyrolysis temperature on the energy density of the gases (dry basis) produced via pyrolysis.*

$$HHV_{gases} = \sum_{i=1}^{n}(X_i * HHV_i) \tag{9}$$

Where X_i and HHV_i are the mole fractions and high heating values for CH_4, H_2, and CO produced respectively. The HHV value reported corresponds to the energy density of the syngas mixture produced via pyrolysis.

Products from Pyrolysis
Products obtained from the pyrolysis process of sugarcane bagasse were char, oil and gases. Solid residues (char) were recovered by cleaning the reactor once the experiments finished and the oven cooled off. Pyrolysis oil was obtained by a continue condensation in the condenser for each experiment. Char and bio-oil obtained were stored in plastic bags and glass containers, respectively. The flow rate of the gases leaving the condensers and entering to the gas analyzer was measured by a flowmeter and analyzed by the gas analyzer every 10 min.

Figure 6 presents the effect of temperature on yields of char, bio-oil and gases. Since the mass of gases varies with time in each experiment, the average mass of gases reported here was determined using a mass balance. i.e. the mass of the gases was determined by the difference between the initial mass of biomass and bio-oil final mass. The highest value of mass of the pyrolysis oil ranges between $40 - 50\%$ of the initial mass of the sugarcane bagasse samples, while char presents the smallest values. At T = 400°C, the production of tar reaches values close to $80\ gr$ and remains almost constant as equilibrium temperature rises. At T ~ 650°C, tar develops an inflection point and the curve increases until it reaches a maximum value at T = 700 °C. Then, tar slope acquires a negative value leading the production to slightly decrease to $93\ gr$. This information suggests that at slow heating rates and high pyrolysis temperatures, the chemical reactions favor the production of condensable volatiles resulting in an increased production of pyrolysis oil. If compared with the values obtained by [29] for the African oil palm, char production follows a similar tendency, though the values are higher for the palm. The difference of the average gas production at different pyrolysis temperatures between both biomasses is $5\ gr$.
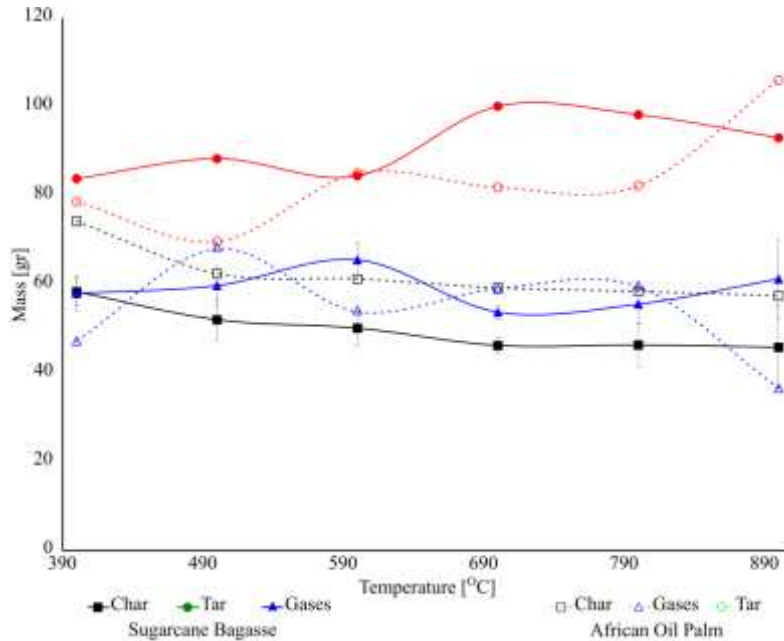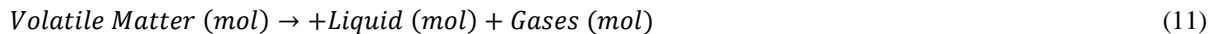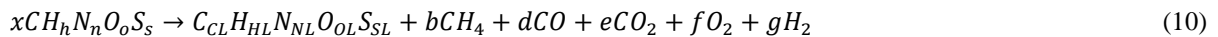
Fig. 6 *Effect of equilibrium temperature on the production of char, tar and gases. Values for African Oil Palm adapted from [29].*

Estimation of pyrolysis oil composition
Composition of the liquid fuel was estimated by using atom balance and mass conservation on components (equations (10) and (11)).

$$xCH_hN_nO_oS_s \rightarrow C_{CL}H_{HL}N_{NL}O_{OL}S_{SL} + bCH_4 + dCO + eCO_2 + fO_2 + gH_2 \qquad (10)$$

$$Volatile\ Matter\ (mol) \rightarrow +Liquid\ (mol) + Gases\ (mol) \qquad (11)$$

Where, $CH_hN_nO_oS_s$ is the empirical formula of volatiles, $C_{CL}H_{HL}N_{NL}O_{OL}S_{SL}$ empirical formula of the bio-oil, and x, b, d, e, f, g are the molar (dry and N_2 free basis) average gas molar coefficients obtained from the average syngas composition shown in figure 4. Equation (10) shows the molar balance of volatiles supplied producing liquid fuel (dry basis), and gases. The balance was carried out by measuring the masses of the biomass supplied and their respective products. Table 3 shows the effect of pyrolysis temperature on the normalized empirical formula of the bio-oil along with their respective HHV, which was estimated using energy balance between volatile matter and products (bio-oil and gases) by means of equation (12) and (13) [30]. As pyrolysis temperature increases, hydrogen and nitrogen atoms decreases, while oxygen increases. Chemical reactions at low pyrolysis temperatures lead to the production of oil fuel containing higher values of hydrogen. Instead, higher temperatures result in an oil with a higher content of O_2. Increased values of nitrogen and sulfur are due to the thermal degradation of molecules and reorganization into nitrogenized aromatic compounds [12]. It is desirable to obtain small percentages of oxygen because its presence results in a low HHV, non-miscible with petroleum liquid, corrosive to common materials and thermal and chemical instability [30]. Moreover, the HHV of the pyrolysis oil (dry basis) calculated by equation (12) takes values between 17 638 kJ/kg and 23 606 kJ/kg, while those values calculated by Boie equation range between 10 620 kJ/kg and 17 633 kJ/kg as show by figure 7. This difference indicates that Boie equation is not appropriate to calculate the HHV of liquids. The HHV (22.4 MJ/kg) reported by [10] for liquid oil, obtained from vacuum pyrolysis of sugarcane bagasse, fits in the HHV range (17 638 kJ/kg to 23 606 kJ/kg) presented in this study.

$$HHV_{volatile} = x * HHV_{oil}[Dry\ Basis] + y * HHV_{gases}[N_2\ Free] \quad (12)$$

$$HHV_{oil} = 35160 * Y_c + 116225 * Y_h - 11090 * Y_o + 6280 * Y_n + 10456 * Y_s \quad (13)$$

Table 3. Effect of equilibrium temperature on the normalized empirical formula of pyrolysis oil

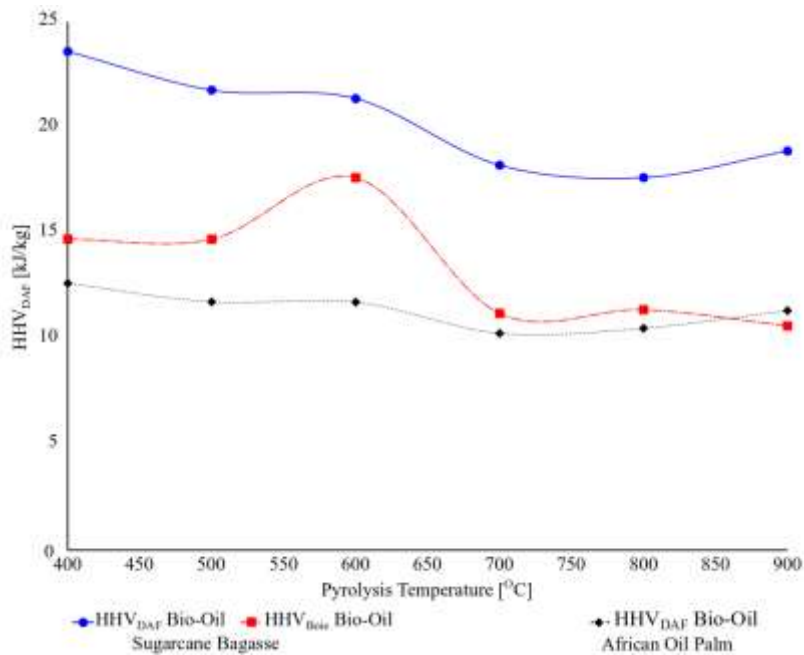| Pyrolysis Temperature [°C]	Normalized Empirical Formula (pyrolysis oil)				
	C	H	N	O	S
400	1	2.139	0.00435	0.567	0.00174
500	1	2.187	0.00453	0.566	0.00197
600	1	2.088	0.00453	0.453	0.00197
700	1	1.883	0.00410	0.681	0.00145
800	1	1.853	0.00427	0.668	0.00169
900	1	1.839	0.00392	0.704	0.00116

Fig. 7   Difference on the effect of equilibrium temperature on the HHV (DAF basis) calculated by mass balance and Boie's Equation. Values for African Oil Palm adapted from [29].

Figure 7 also presents the *HHV* for the african oil palm gases generated by pyrolisis under the same experimental conditions. It is possible to see a similar tendency between both biomasses except for T = 700 °C where the highest value is reached for sugarcane bagasse (23 606 kJ/kg); the *HHV* peak for the african oil palm is 12 626 kJ/kg at 400°C. At 700°C and 800°C the *HHV* of the syngas is similar.

Kinetics of the Reaction
The DTG curves of sugarcane bagasse for 10°C/min and 30°C/min heating rate are presented in figure 8a. The behavior of the DTG curves show a gradual thermal decomposition process. The first peak presented at T ~ 300°C corresponds to the degradation of hemicellulose and the second maximum T ~ 350°C to cellulose. The tendency of the curves in figure 8a and the values reported here are close to those reported in reference [31].
Figure 8b shows the TGA (Thermogravimetric Analyses) at two different heating rates (10 and 30°C/min). The initial part of the process represents the moisture content released between 30°C and ~ 200°C and corresponds to

(~ 5%) of the mass. The volatilization (VM) occurs at temperatures from ~ 250°C to ~ 400°C and is represented by the steep slope. For temperatures, higher than 500°C the remaining mass composition is fixed carbon and ash, leading to a small variation on the percentage of mass.
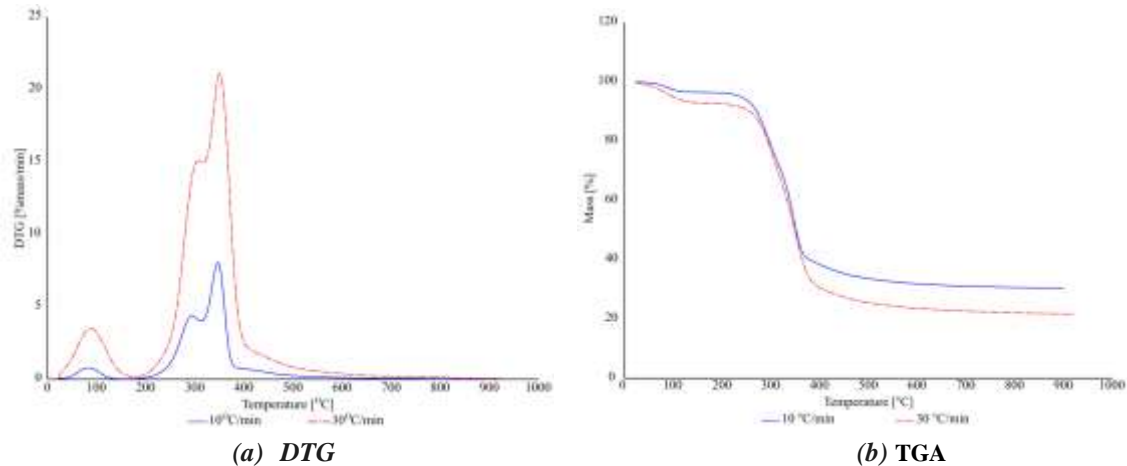

(a) DTG   *(b) TGA*
Fig. 8 Thermogravimetric Analyses of sugarcane bagasse at different heating rates.
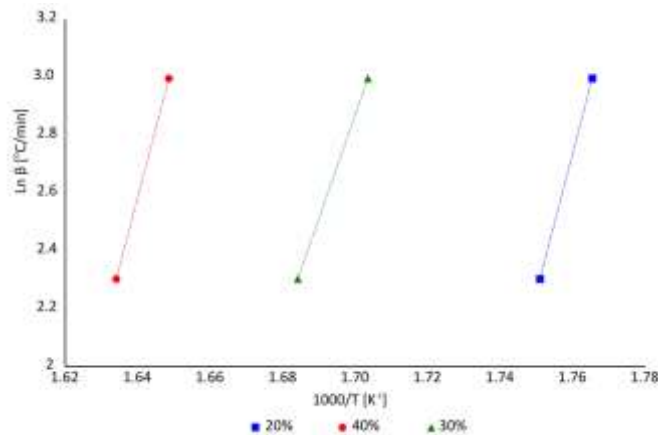
Gas Composition

Fig. 9 Curves to determine the activation energy of the sugarcane bagasse.

Figure 9 displays the $\ln(\beta)$ for two heating rates ($\beta = 10$ and $30°C/min$) as a function of the temperature and for a percentage of conversion $\alpha = 20, 30$ and 40. Using the model proposed by [32], it is possible to relate the slopes of adjusted lines that match the experimental results with the activation energy of the kinetics of the biomass. Table 4 lists the slopes and the activation energies for different percentages of conversion.

Table 4. Slope and activation energy obtained from figure 9

Mass [%]	Slope	$\Delta E_i \left[\dfrac{kJ}{kmol}\right]$	$\Delta E_{Average} \left[\dfrac{kJ}{kmol}\right]$
80	48.01	379.425	
70	35.79	282.849	259.694
60	47.64	376.500	

The average activation energy calculated (259.7 kJ/kmol) is 10% higher than the values reported by Garcia et al. [31] (235 kJ/kmol) for sugarcane bagasse and higher than those calculated for the coffee husk 221 kJ/kmol by [33], whereas values reported here are similar to those calculated by [5] (255.5 kJ/kmol) for the coffee pulp. Values reported by [34] for sugarcane bagasse range between 195 – 213 kJ/kmol. This difference may be due to the method used to calculate E and the number of TGA curves used for its estimation.

4.   CONCLUSIONS

Results in this study show that the pyrolysis of sugarcane bagasse ($CH_{1.581}O_{0.671}N_{0.00306}S_{0.00117}$) carried out in a static batch reactor at 400°C< T< 900°C with nitrogen as carrier gas and using a heating rate of 4.30°C/min ±7.8%, produces a syngas composed mainly of CO, CO_2, H_2, and CH_4. The average mole fraction (dry base) of the species produced varied between 8.82% and 16.35% for CO_2; 5.95% and 8.43% for CO; 1.58% and 5.85% for CH_4; 0.2% and 6.84% for H_2. The highest production of carbon monoxide and carbon dioxide occurred at 400°C< T< 700°C, while hydrogen and methane at 600°C< T< 800°C.

Moreover, the yields of char, bio-oil, and gases per each kilogram of biomass varied between 22.9% and 29.2% for solid residues; 41.9% and 50.1% for liquid; 26.9% and 32.8% for gases. The HHV of the gases range between 1 720 kJ/m³ and 4 038 kJ/m³, whereas the HHV of the bio-oil ranged between 17 638 kJ/kg and 23 606 kJ/kg. The bio-oil HHV (22.4 MJ/kg) reported by [10] is in the range of the HHV reported in this study. The maximum production of char was found at T= 400°C, whereas maximum production of gases was at T = 600 °C and pyrolysis oil at T = 800 °C. The highest HHV of gases was produced at T = 800°C and the HHV of liquid at T = 400°C.

5.   ACKNOWLEDGEMENTS

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