

Simulation of the Pyrolysis of Biomass Based on Ultimate and Proximate Characterizations

Yurany Camacho Ardila^{*a}, Jaiver E. Jaimes Figueroa^b, Pablo M. Cocha Vesga^c

^aSchool of Environmental Engineering, Universidad Pedagógica y Tecnológica de Colombia, 150003 Tunja, Boyacá, Colombia

^bSchool of Chemical Engineering, Federal University of Maranhão, Av. do Portugueses, 1966. Cidade Universitária "Dom Delgado", CEP 65080-805.. São Luis-MA, Brazil.

^cSchool of Metallurgical Engineering, Universidad Pedagógica y Tecnológica de Colombia, 150003 Tunja, Boyacá, Colombia
yurany.camacho01@uptc.edu.co

Knowledge of the qualitative and quantitative composition of biomass is essential for designing energy conversion processes such as pyrolysis or gasification. Among the various types of analyses used to characterize biomasses, the most important are the thermogravimetric analysis, scanning calorimetry, proximate analysis, ultimate analysis and biochemical analysis. Pyrolysis and gasification of biomass are processes that can be considered as flexible for a variety of biomasses. However, the type of biomass used significantly affects the overall composition of the syngas, char, tar and potential operational issues. In this sense, the proximate analysis categorizes biomasses based on the parameters of moisture content, volatile content, fixed carbon and ash content. One of the most important characterizations of the biomass is the ultimate analysis, which presents the main elements found in it, such as carbon, hydrogen and oxygen. This paper presents a simulation in Aspen PlusTM, based on the ultimate and proximate characterization of the biomass, was modeled a pyrolysis unit for fixed bed (FB) and fluidized bed (FDB) reactors. In the simulation at a temperature of 700 °C, gas yields of 63%, liquid yields of 21% and solids yields of 16% were found for the FDB, while in the case of the FB they were 42%, 30% and 28% respectively. The lowest yield of solid wastes found for FB at high temperatures found was 27%, while in FDB it was 15%. The simulation allows the finding of the main products of the pyrolysis, such as char, tar and gases, in addition to an ultimate and proximate characterization of tar and char.

1. Introduction

The products formed in the devolatilization process, considering the pyrolysis of biomass or coal, are divided into three groups, which depending on their state of aggregation, at room temperature, are called: solid, known as char; liquid, a mixture of tar and water; and gaseous products, referred to as simply gas. According to Xu et al. (2011), Fagbemi et al. (2001), Rodriguez et al. (1987) and Tsai et al. (2006) the content of char after pyrolysis of different biomasses decreases as temperature increases, since the yield of gas in the pyrolysis increases as temperature increases in the reactor. Figueroa et al. (2014) and Rodriguez et al. (1987) demonstrated the content of tar increases as temperature increases, reaching a peak of 70% at a temperature close to 450 °C, yield begins to decrease because of the decomposition of the components present in the tar. The closest results were found in the biomasses researched for sugarcane bagasse and wood; the greatest differences were found when compared with cotton straw, rice straw and coconut shell. Evidently, the use of different biomasses or different devices present different results during pyrolysis for the main products: gases and char. The behavior of the various results presented for a variety of biomasses, is caused, basically, by the difference in the structure of the biomasses (Ardila et al., 2024), which causes a more or less volatile or char content, as well as by the reaction method and the equipment used. The conversion of agricultural residues into renewable energy not only contributes to the reduction of greenhouse gas emissions but also enhances the economic value of by-products from the agricultural industry. Among these residues, sugarcane bagasse — a by-product abundantly generated in sugar and ethanol production — stands out for its high potential in biofuel generation through pyrolysis, owing to its favourable composition and availability.

Several authors have studied the pyrolysis of sugarcane bagasse in fixed or fluidized bed reactor showing the yields of tar, char and gases at different temperatures (Tsai et al. 2006; Xu et al., 2011; Rodriguez et al., 1987; Figueroa et al., 2013; Hugo, 2010). According to Mothé and De Miranda (2013), the primary pyrolysis of sugarcane bagasse ends at temperatures close to 400 °C, , a yield of char of 30-50% and a yield of liquid of 40-50% (Xu et al., 2011; Tsai et al., 2006). In the final step of the secondary pyrolysis, close to the temperatures of 600 °C Mothé and De Miranda (2013), observe the yields of gas and char in the range of 38-53% and 16-33%, respectively and liquid 35-46%. According to Hugo (2010) the contents of the ultimate analysis for H and O in char decreases as temperature increases, and the content for C is increased, which is why in many simulations found in the literature the char generated at high temperatures is, practically, a ratio of carbon and ash because of what is present in its ultimate analysis. Most of the gases generated during pyrolysis are usually considered as CO, CO₂, H₂, CH₄, C₂H₄ and C₂H₆. The main components within the fraction of gases obtained after the pyrolysis of various biomasses (Fagbemi et al., 2001) are H₂ and CO, and at high pyrolysis temperatures it can be find the largest quantities of these two components and low amounts of CO₂ and CH₄. Different authors have used the Aspen Plus™ process simulator to simulate the pyrolysis process. The equilibrium reactor offers possibilities for calculating the equilibrium constant; it can operate solely as a separator, as a reactor that minimizes the Gibbs free energy without an associated reaction set, or as a reactor that uses equilibrium reactions. Miranda et al. (2019) evaluated the fast pyrolysis of bagasse using an equilibrium reactor to investigate the behavior of temperature, pressure and moisture content on the distribution of pyrolysis products. Liu et al (2022) carried out a simulation of the pyrolysis process using equilibrium reactors seeking the optimization of biochar. Some authors use equilibrium reactors in Aspen Plus seeking to minimize the Gibbs free energy (Hasan et al., 2024); under these conditions, they observed a gas yield of 15-22%. An equilibrium reactor calculates the product distribution assuming thermodynamic equilibrium, while a yield reactor requires predefined output distributions and does not simulate equilibrium conditions.

2. Simulation

For the non-conventional components used in the simulation, the following characterization was considered.

Characterization of the Biomass: Sugarcane bagasse does not appear in the database of Aspen Plus™; therefore, was used the data creation resource for a substance of the "non-conventional solid" type to estimate its properties in the system. For this end, was had to insert actual information on the bagasse, such higher heating value (HHV), heat capacity, heat of formation and composition data obtained in thermal analysis, such as the proximate analysis and ultimate analysis. For the calculation of the properties of the biomass, was used the method of advanced properties (NC); this method is used to specify the models used to calculate the non-conventional properties of solids. Since the non-conventional components are heterogeneous solids that do not participate in chemical or phase equilibrium, the only physical properties calculated for these components are enthalpy and density. The general char model used to calculate the enthalpy in Aspen Plus™ is the HCOALGEN. In this way, the methodology used for the characterization of the biomass was the following: Initially, was chose the HCOALGEN method (Coal Enthalpy model), which basically needs the information of the proximate analysis (PROXANAL), ultimate analysis (ULTANAL) and sulfur content (SULFANAL). The data for sulfur were obtained from the composition of the ULTANAL for sulfur. This complete characterization is shown in Table 1. Within the HCOALGEN method, was chose option 6 for the HHV, into which a value may be added in the simulator. Option 6 within the simulator corresponds to a HHV value inserted as a new characterization; in this case, the correlation developed by Ardila et al. (2024) for HHV based on elemental analysis. This correlation was inserted using a FORTRAN calculation block. For heat of formation, was used option 1 of the simulator, which is based on the assumption of complete combustion of all elements except the ash. For this case, was used the ultimate analysis data. For the calculation of the density of the biomass, was used the DNSTYGEN method, which allows the calculation of the global component and its constituents. In this case, was considered 100% of the general analysis of the biomass and inserted the value of 1490 kg/m³, calculated for sugarcane bagasse by Figueroa et al. (2014). As additional information, was used a characterization of the particle size of the sugarcane bagasse in the PSD option of the simulator. The values used are found in Table 1.

Characterization of char: similarly, to the bagasse, char is not in the database of the simulator, thus requiring a similar characterization to consider it as a non-conventional component. The methodology used for the characterization of the char was the following: was chose the HCOALGEN method (Coal Enthalpy model). For the ultimate, proximate and sulfur analyses, was used, initially, some random values; however, these values are modified as soon as the pyrolyzer model is executed. For heat capacity, was used option 2, named CP2C in the simulator, using the coefficients of the model presented by the simulator Aspen Plus™. The calculation of the heat of formation was considered equal to that presented for biomass. For the calculation of the density of the

char, the correlation of the simulator named DGHARIGT was considered. For the characterization of particle size, was considered the same one as for biomass.

Table 1: Proximate and ultimate analysis of sugarcane bagasse used in the simulation (Figuroa et al. 2014), and particle size analysis of sugarcane bagasse used in the simulation^a.

Proximate (w/w%)		Ultimate (dry basis-w/w%)	Average particle diameter (mm)	Mass fraction retained
Moisture (air)	7.8	C 44.52	0.60	0.21
Fixed carbon-FC-(dry basis)	10.81	H 5.90	0.60	0.18
Volatile material-VM-(dry basis)	83.97	N 0.32	0.85	0.22
Ash(dry basis)	5.22	Cl 0.29	1.18	0.11
		S 0.10	2.00	0.05
		O 43.65	2.36	0.06
			4.75	0.01
			6.30	0.16
			9.00	

air: as received. a Characterization obtained from LOPCA/LDPS/BIOEN/FEQ/UNICAMP

Characterization of tar: The tar was characterized free of water. Within the COALGEN method, option 6 was chosen for the HHV, using the correlation proposed by Channiwala and Parikh (2002), which is specific for solids, gases and liquids. It was inserted using a Fortran calculation block. To calculate the tar density, the simulator correlation called DCOALIGT was considered. The other properties were characterized using the same methodology used in the char characterization.

To characterize conventional substances (gas) the simulator database was used.

2.1 Modeling of the Pyrolysis Unit

The components used in the simulations were CO₂, H₂, CH₄, C₂H₆, CO, C₂H₄ as conventional and char, tar and ash as non-conventional. Table 2 describes the operations used in the flowcharts. After reviewing different data from the literature and demonstrated that different product yields can be obtained, depending on the biomass and the process used, in the Table 3 is present the representative correlations for the pyrolysis process of sugarcane bagasse. It is important to highlight that the correlations presented need not be necessarily used in the model; it is simply necessary to disable the calculation block that provides the equations for the analysis of the correlations. The novelty of this work lies in integrating literature-based correlations into a full Aspen Plus simulation process, including biomass drying, pyrolysis, and separation steps. This integration allows the model to simulate not only the decomposition but also the behavior of products under operational parameters, extending typical applications of Aspen Plus in biomass pyrolysis studies.

Table 2: Description of the flowchart for the pyrolysis process presented in Figure 1

ASPEN Plus™ Name	ID Block	Description
RYIELD	SEC-1	Simulation of the biomass drying step. It decomposes the water content of the non-conventional component within the Simulator (BIOMASS).
	PIROLPRI	Simulation of the pyrolysis. In this step, char and tar are formed, as well as non-condensable volatiles, including H ₂ , CO, CO ₂ , CH ₄ , C ₂ H ₄ , and the condensable volatiles are related to tar and water. The correlations presented in Table 2 were used through a calculation block using Fortran.
SEP	SEC-2	Simulation of the biomass drying step (separation).
	CICLONE	The cyclone is used to represent the gas-solid separation.
HEATER	CON-2	It represents the gas-liquid separation.
	CON-1	It simulates the condenser.
HIERARCHY	HHV	Simulation used to represent a calorimetric bomb for the analysis of the higher heating value HHV of the pyrolysis gases.

The correlations found for the pyrolysis studies at various temperatures and, specifically, for sugarcane bagasse are presented in Table 3. The formula considered to describe the composition of the biomass in this model is CH_xO_yN_wS_zCl_p. Figure 1 presents the flow diagram to represent the pyrolysis (or initial decomposition of the biomass in the gasification).

fluidized bed reactor, which provides greater quantities of H₂ and CO. The yields of CH₄ and C₂H₄ reach a maximum value of 9%-FB and 6%-FDB and 4%FB and -2.5%-FDB, respectively, close to the temperature of 750 °C. The model allows us to determine the composition of the char by vary the temperature, giving rise to new non-conventional components (fuels), that can be used in further thermochemical processes within the simulator. The effect of temperature on the composition of the char and of the tar is presented in Table 4. A table summarizing this comparison should be included to support the discussion. Additionally, simulation results should be compared with other studies on fixed bed pyrolysis reactors to strengthen the validation. it can be concluded Moreover, comparative figures with other fixed bed reactor studies should be included to reinforce model validation.

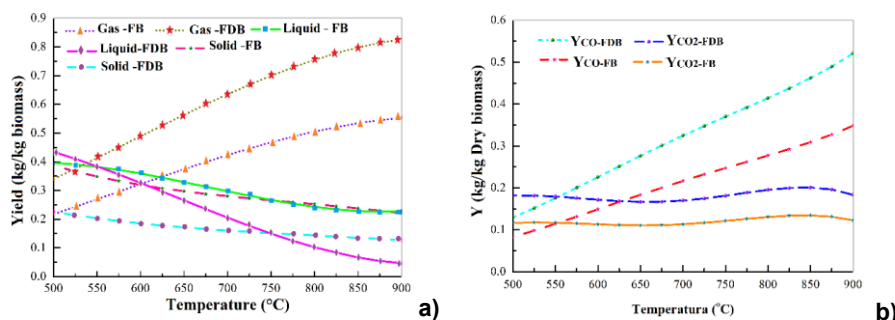


Figure 2: Yields of the pyrolysis products of sugarcane bagasse in fixed bed and fluidized bed (dry basis). a) gas, liquid and solid yield b) CO and CO₂ yield

Table 4: Effect of the temperature on the composition of C, H, O, N, S, Cl, VM and FC for char generated in the pyrolysis and on the composition of C, H and O for tar generated in the pyrolysis.^a

Composition of the char								Composition of the tar			
T (°C)	% C	% H	% O	% Cl	% N	% S	VM	FC	C	H	O
500	81.82	2.88	13.18	0.87	2.88	0.30	19.11	80.89	53.6	7.7	38.7
550	83.98	2.46	11.17	0.98	2.46	0.34	14.62	85.38	55.6	7.2	37.2
600	85.41	2.07	9.86	1.09	2.07	0.37	11.40	88.60	57.1	6.5	36.4
650	86.35	1.72	9.02	1.18	1.72	0.41	9.08	90.92	59.0	5.7	35.3
700	87.03	1.42	8.43	1.27	1.42	0.44	7.41	92.59	59.6	5.3	35.1
750	87.69	1.14	7.84	1.36	1.14	0.47	6.22	93.78			
800	88.55	0.91	6.99	1.45	0.91	0.50	5.36	94.64			
850	89.85	0.72	5.60	1.56	0.72	0.54	4.74	95.26			
900	91.83	0.56	3.38	1.73	0.56	0.60	4.29	95.71			

^aPyrolysis in fixed bed, ash-free compositions.

As noted in Table 4, an increase in temperature decreases the oxygen and hydrogen content in char, since greater quantities of volatile products are formed, thereby increasing the amount of fixed carbon within the char, thus originating a char that is mainly composed of carbon (as for example at the temperature of 900 °C). The composition of the char, when compared between both types of reactors, is mainly affected by the loss of oxygen content, being greater in the pyrolysis in the fluidized bed reactor. The proportions of N, S, Cl are changed by the loss of oxygen and hydrogen. In this specific pyrolysis case, was considered that N, S and Cl remained in the solids, and nitrogenous components were not formed in the volatiles. The composition of the tar for the fixed bed reactor does not suffer major changes when the temperature increases; however, the hydrogen content seems to decrease slightly, with a slight increase in the oxygen content. Knowing the composition of both char and tar, it can find the HHV (equations previously inserted in the simulator). The HHV of tar, char and gas (simulating a calorimetric bomb) for different temperatures were studied. The HHV of char increases as the temperature of pyrolysis is increased, ranging from 27.21-29.18 MJ/Kg-daf. This increase was also evidenced in the pyrolytic gases, but it was more pronounced than in the char, and was found a value of 8.10 MJ/Nm³ at a temperature of 500 °C; when the temperature was increased to 550 °C, a value of 12.10 MJ/Nm³ was obtained. The results for the gas can be compared to the data reported in the literature for sugarcane bagasse, in which differences in the proportions are found; however, the profile of the results is maintained. The highest HHV obtained from the simulation was 18.52 MJ/Nm³ at 700 °C, while the literature data report a HHV of 16.5 MJ/Nm³ at the same temperature. The HHV of tar and char, when compared to the data reported by Das et al. (2004) for sugarcane bagasse are very close to the value found experimentally. To compare the results of the simulation for the bagasse with other biomasses, at the temperature of 500 °C, was can observe that the HHV of tar from bagasse is lower than for wood pyrolysis and greater than for peanut shell; the HHV of char is greater than for

other biomasses and the HHV of gases is greater for wood. While the simulation yielded results consistent with the experimental data reported by Das et al. (2004), some discrepancies were observed, particularly under high-temperature conditions. These differences may be attributed to variations in the biomass composition used or the accuracy of the thermodynamic models employed in the simulation. Future studies could focus on calibrating simulation models for different types of biomass to improve the accuracy of the results.

4. Conclusions

In this study, correlations for the pyrolysis of sugarcane bagasse in FB and FDB reactors based on experimental data were used and inserted into the Aspen plus simulator using Fortran calculation blocks. In the simulation pyrolytic products (tar, water, char and gases) were characterized in an ash-free and dry basis, and was considered as main gases the H₂, H₂O, CO, CO₂, CH₄ and C₂H₄. The simulation procedure developed predicts the yields of tar, char, water and gases generated during pyrolysis, the compositions of different gases, as well as the proximate and ultimate characterization of the char and tar and their HHV. Higher gas yields were found in the FDB compared to the FB. The char composition in the FB at 700 °C was 87.03% C, 1.42% H, 8.43% O, 1.42% Cl and 0.44% S and the tar composition was 59.6% C, 5.3% H, 35.1% O. The data collected and the pyrolysis simulation procedure, based on the ultimate and proximate analysis of sugarcane bagasse, are useful for simulating the initial steps of gasification and combustion, as well as representing secondary pyrolysis products within the temperature ranges studied.

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