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ANALYSIS OF POLLUTANT EMISSIONS FROM THE BURNING OF BIOMASS PELLETS AND AIR FOR DIFFERENT OPERATING CONDITIONS

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Abstract. *The objective of the present work is to investigate the emissions from the combustion of biomass. This study will be carried out numerically, using pine reforestation biomass, free from the addition of chemicals and in the final format of pellets, with a diameter between 6 and 8 mm. Numerically, the concentrations of volatiles were estimated for different reaction temperatures and the combustion products were determined assuming chemical equilibrium for the same conditions of temperature and equivalence ratio. The estimated volatiles are constituted by* H_2, C_2H_4, C_3H_8, C_2H_6, *CO*, CO_2, CH_4 *and* N_2. *The main combustion products considered are CO,* CO_2, CH_4, H_2, N_2, H_2O *and* O_2. *For equivalence ratios from 0.8 to 3.5, it was numerically observed that increasing the reaction temperature from 650 to 850°C resulted in a variation in the composition of volatiles, increasing the molar concentration of CO present in the combustion products and reducing the concentration of* CO_2*, due to its dissociation, in agreement with the literature.*

Keywords: *biomass combustion, pyrolysis, wood pellets, emissions of pollutants, burner.*

1. INTRODUCTION

Given the high dependence on oil, the effects generated by global warming and the constant concern with the conservation of natural resources, there is a growing need to find alternative, renewable and less polluting sources of energy. Among these sources, Ferreira (2013) highlights solar energy, hydropower, geothermal energy, wind energy, tidal energy and biomass. In this way, studies involving fuels from renewable energy sources, such as biomass, have grown strongly and indicate that this is a promising option for net carbon free combustion process.

Biomass is any renewable, non-fossil resource that has chemical energy in its structure (Omashi et al., 2004). Derived from organic material of animal or plant origin, of natural existence, produced by man or animals, it can be in the form of residues from agricultural, industrial, and urban activities, and can be used as an alternative source of energy (ANEEL, 2005), (Ferreira et al., 2018). It has great possibilities of segmentation and, although inserted in the context of energy generation, this is not an exclusive purpose. As an energy source, it can be converted into solid, liquid or gaseous fuels, this fact being considered an advantage over other energy sources. (Ferreira et al., 2018).

According to the National Energy Balance (BEN, 2022), released by the Energy Research Company (EPE), the Internal Energy Supply (OIE) in Brazil recorded in 2021, an increase of 4.5% compared to the previous year. However, the share of renewable energies in the Brazilian energy matrix was marked by the drop in the supply of hydroelectric energy, associated with water scarcity and the activation of thermoelectric plants. Even so, in 2021, 44.7% of the energy used in the country came from renewable sources, but with a decrease of 7.8% compared to the previous year. Of this percentage, 16.4% refers to sugarcane biomass, 11% to hydraulics, 8.7% to the use of firewood and charcoal and 8.7% to other sources. Of the 55.3% of non-renewable energy used, 34.4% refers only to the use of oil. For comparative purposes, in the world, in 2019, only 14.1% of the energy matrix was renewable.

According to the National Energy Balance (2022), in Brazil, in 2021, total CO_2 emissions reached 445.4 million tons of CO_2 equivalent, an increase of 12.4% over the previous year. Among sectors that use energy, the sector with the highest number of total emissions is transport, causing the country to present an emission rate of 1.5 tons of CO_2 per ton of oil equivalent (toe) consumed.

Observing the decline in renewable energy in Brazil, the increase in CO_2 emissions and the low share of renewable energies that make up the world's energy matrix, greater incentives are needed for the development of research, public and social policies to allow the development of new processes and more efficient equipment, with lower emissions of pollutants.

In this context, despite biomass being a renewable source widely used in Brazil, due to the production of ethanol and sugar, the use of energy from biomass of firewood and charcoal can be further explored. Lora and Venturini (2012) mention that, in addition to being considered a clean, efficient fuel and allowing a combustion with little smoke, the burning of biomass pellets releases less carbon monoxide (CO) when compared to other fuels. Although the combustion of lignocellulosic biomass causes emissions of carbon dioxide (CO_2), these emissions are equivalent to the amount of carbon dioxide captured by the plant in the process of photosynthesis, during its growth process (Manzano-Agugliaro et al., 2013), in other words, it is a carbon neutral process (Callejón-Ferre et al., 2011), (Saidur et al., 2011), (Shen et al., 2015). Then, it is possible to say that the combustion of biomass represents a neutral balance, being less harmful to the environment than the combustion of fossil fuels (Saidur et al., 2011).

Among the different types of lignocellulosic materials, cellulose, hemicellulose and lignin are found in different proportions; these values vary between 40 and 60%, 15 and 50% and 10 to 30%, respectively (Gelleti et al., 2006). As for their formation, Wang et al. (2017) mentions that the grouping of cellulose macromolecules forms the resistant microfibers that make up the skeleton of the cell wall, while the space between the molecules is filled with hemicellulose and lignin.

Lignocellulosic materials are known to have different decomposition profiles, according to their chemical composition, with cellulose showing greater thermal stability than hemicellulose and lignin (MOHAN et al., 2006). Grønli et al., (2002) reported that, during the thermal decomposition process of lignocellulosic biomass, cellulose and hemicellulose are decomposed first, followed by lignin, at higher temperatures. Therefore, this structure, at an appropriate temperature level, forms a viscoelastic compound, ensuring that the pellet manufacturing process does not require the use of additives (Gelleti et al., 2006).

As for the characterization of biomass, Freitas (2020) mentions that the physical and chemical properties are fundamental to determine the main constituents, since they are the ones that determine the energetic efficiency of the material. The analysis of the biomass is classified in proximate analysis (percentage in mass of moisture, ash, volatile material and fixed carbon) and ultimate analysis (mass percentage of carbon, hydrogen, nitrogen and oxygen).

Tables 1 and 2 show the technical characteristics of different types of biomasses on a dry basis, according to different authors. Analyzing Tab. (1), it can be seen that the content of volatile material in biomass is very high; it is a fuel rich in volatiles, which constitute almost ¾ of its weight. In Tab. (2), it is observed that the components in greater quantity in the biomass are carbon and oxygen.

Table 1. Proximate analysis (db,wt%)

Source	Biomass Type	Volatile Matter	Fixed Carbon	Ashes	Moisture	HHV (MJ/Kg)
Tsamba, 2006	Cashew nut shells	81.80	17.30	0.90	N/A	24.05
Tsamba, 2006	Coconut shells	74.90	24.40	0.70	N/A	20.51
De Sales, 2017	Eucalyptus spp. wood	72.86	15.18	0.79	11.17	19.74
Galindo, 2014	Eucalyptus wood	83.01	15.66	1.34	12.23	N/A
Bandara, 2021	Grass pellet	69.50	12.60	9.49	8.40	16.70
García, 2014	Olive wood	78.30	20.40	2.48	10.60	17.88
García, 2014	Peach wood	75.60	23.90	1.53	9.80	19.59
García, 2014	Pine wood	81.60	17.80	2.07	9.00	19.43
Jayah, 2003	Rubber tree	80.10	19.20	0.70	15.5 ± 3.0	19.60
Islam, 2010	Sugarcane bagasse	75.85	20.01	4.14	11.60	16.81
Bandara, 2021	Wood chips	74.80	13.50	0.58	11.10	18.80
Kim, 2013	Wood pellet	72.70	16.70	0.80	9.80	18.00
Bandara, 2021	Wood pellet	77.80	14.00	0.30	7.90	18.90
Stanisławski, 2022	Wood pellet	87.10	12.69	0.21	5.74	19.35
Campoy, 2014	Wood pellet	81.10	18.40	0.70	6.30	19.60
Tsamba, 2006	Wood pellet	81.30	18.10	0.60	N/A	20.26

Table 2. Ultimate analysis (db, wt%)

Source	Biomass Type	C	H	N	O

Tsamba, 2006	Cashew nut shells	58.30	7.00	0.70	32.05
Tsamba, 2006	Coconut shells	53.90	5.70	0.10	39.44
De Sales, 2017	Eucalyptus spp. wood	49.00	6.30	0.20	44.40
Galindo, 2014	Eucalyptus wood	46.78	5.92	0.32	45.55
Bandara, 2021	Grass pellet	46.90	5.70	3.19	33.70
Pedroso, 2005	Olive wood	46.43	5.63	0.55	44.91
Pedroso, 2005	Peach wood	48.06	5.83	0.55	44.03
Pedroso, 2005	Pine wood	48.18	5.71	0.15	43.89
Jayah, 2003	Rubber tree	50.60	6.50	0.20	42.00
Islam, 2010	Sugarcane bagasse	48.67	6.70	0.45	44.10
Bandara, 2021	Wood chips	51.00	6.10	0.70	42.20
Kim, 2013	Wood pellet	51.02	7.16	0.09	41.73
Bandara, 2021	Wood pellet	50.90	6.00	0.50	42.60
Stanisławski, 2022	Wood pellet	50.88	6.95	0.15	36.03
Campoy, 2014	Wood pellet	49.80	5.80	2.00	42.20
Tsamba, 2006	Wood pellet	50.90	6.20	0.20	42.06

The most widespread process for the thermochemical conversion of biomass is combustion (Maldonado, 2018). Woody biomass is a widely used resource at industrial, commercial and residential levels, and its most common use is in combustion processes, in thermoelectric plants, residences, cogeneration systems (production of energy and heat simultaneously), pyrolysis and gasification. (Martins and Nunes, 2018).

According to Lora and Venturini (2012), the biomass combustion process occurs in six stages, which are drying, emission of volatiles, ignition of volatiles, burning of volatiles in flame, extinguishing the flame of the volatiles and combustion of the carbon residue. The drying, pyrolysis and gasification steps are the first steps in the combustion process of a solid fuel. During drying, moisture evaporates at low temperatures, between 50 and 100 °C, while the process of pyrolysis or devolatilization of wood begins to happen at approximately 200 °C. In this first moment, there is the decomposition of the hemicellulose of the wood and, at slightly higher temperatures, the decomposition of the cellulose. Then, at temperatures between 400 and 500 °C, the emission and ignition of volatiles occurs, in which it is possible to observe a low rate of devolatilization, due to the decomposition of lignin. Only then, the burning and extinction of the flame of the volatiles take place, at temperatures between 600 and 800 °C, respectively. Finally, at temperatures higher than 800 °C, the combustion of carbon residues, also called fixed carbon or coke, occurs.

In recent years the manufacture and commercialization of wood pellets has been in expansion, and its use as an alternative energy source has shown a constant growth. As a result, the demand for more efficient combustion equipment and fuels that have less environmental impact has grown strongly. In this context, the objective of the present work is to investigate numerically the pollutant emissions from the biomass combustion in presence of air.

2. METHODS

The analytical solution is being developed to estimate the products from the combustion of wood pellets in the presence of air. This model consists of two steps. In the first step, the composition of the volatiles that are released due to the heating of the pellets by pyrolysis and gasification is estimated, being composed of H_2, C_2H_4, C_3H_8, C_2H_6, CO, CO_2, CH_4, N_2. In this way, the reagents will be composed of volatiles, fixed carbon, moisture and air. In the second step, the combustion products are estimated by applying chemical equilibrium and considering only the major species, composed of CH_4, CO, CO_2, N_2, H_2O and H_2. The reaction temperature, equivalence ratio and composition of the biomass will be the input data provided in the model.

The composition of volatiles is estimated based on the atomic mass balance of the pellet, considering carbon, nitrogen, oxygen and hydrogen, obtained from elemental analysis of a set of samples. In this case, the ash was discarded due to its low concentration (less than 0.3%). As the values corresponding to the compositions of carbon (C), hydrogen (H), nitrogen (N), oxygen (O) and ash are represented in mass percentage, it was necessary to convert these data to moles, to leave both sides of the equation with the same unit of measure. The atomic balance can be visualized below, in Equations (1) to (4).

$$2nr_{C2H4} + 3nr_{C3H8} + 2nr_{C2H6} + 1nr_{CH4} + 1nr_{CO} + 1nr_{CO2} + 1nr_{CF} = a \tag{1}$$

$$2nr_{H2} + 4nr_{C2H4} + 8nr_{C3H8} + 6nr_{C2H6} + 4nr_{CH4} = b \tag{2}$$

$$1nr_{CO} + 2nr_{CO2} = c \tag{3}$$

$$2nr_{N2} = d \tag{4}$$

The terms *a*, *b*, *c*, and *d*, correspond to the ultimate analysis reported in Tab. 2, nr_i corresponds to the moles number of volatiles and fixed carbon (*CF*) present in the biomass.

As the number of unknowns (nr_{c2h4}, nr_{c3h8}, nr_{c2h6}, nr_{ch4}, nr_{co}, nr_{co2}, nr_{h2}, nr_{n2}) is greater than the number of equations available, 4 more equations were added to complement the calculation. Equations (5), (6) and (7) represent the ratios of the mass fractions (*Y*) of the volatile components obtained from the work presented by (Neves et al., 2017), for different reaction temperatures (650 – 850 ºC).

$$R1 = \frac{Y_{C3H8,Neves}}{Y_{C2H4,Neves}} \tag{5}$$

$$R2 = \frac{Y_{CO2,Neves}}{Y_{CO,Neves}} \tag{6}$$

$$R3 = \frac{Y_{C2H6,Neves}}{Y_{CO,Neves}} \tag{7}$$

Equation (8) was also obtained through the work presented by (Neves at al., 2017), for different reaction temperatures, between (650 – 850 °C). It represents a linear adjustment of the mass fractions (*Y*) of the volatile components C_2H_4, C_2H_6, C_3H_8 and CH_4, as a function of the mass fraction of the CH_4 component.

$$Y_{C2H4} + Y_{C2H6} + Y_{C3H8} + Y_{CH4} = 0.00100296 + 2.62577Y_{CH4} - 18.0396Y_{CH4}^2 + 71.8122Y_{CH4}^3 \tag{8}$$

These mass fractions were obtained on a dry basis and free of ash. Also, the higher calorific value (HHV) was determined through the expression presented by Channiwala and Parikh (2002), according to Eq. (9). This equation relates the HHV with the mass fractions of the chemical elements (C, H, S, O, N and ash) present in the pellets, where the term (S) represents sulfur.

$$HHV = 34.91Y_C + 117.83Y_H + 10.05Y_S - 10.84Y_O - 1.51Y_N - 2.11Y_{ASH} \tag{9}$$

In the second stage of the model, after determining the composition of volatiles, the combustion products were estimated by applying the chemical equilibrium considering the formation of the majority species in the combustion products, according to the overall reaction presented in Eq. (10).

$$nr_{H2}H_2 + nr_{C2H4}C_2H_4 + nr_{C3H8}C_3H_8 + nr_{C2H6}C_2H_6 + nr_{CO}CO + nr_{CO2}CO_2 + nr_{CH4}CH_4 + nr_{N2}N_2 + nr_{CF}C_S + nr_{H2O}H_2O + nr_{air}(O_2 + 3.76N_2) \rightarrow np_{CO}CO + np_{CO2}CO_2 + np_{H2}H_2 + np_{N2}N_2 + np_{H2O}H_2O + np_{O2}O_2 + np_{CH4}CH_4 \tag{10}$$

The term np_i represents the moles number of each chemical species (*i*) present in the combustion products. Equations (11) to (14) represent the atomic balance of the overall reaction.

$$2nr_{C2H4} + 3nr_{C3H8} + 2nr_{C2H6} + 1nr_{CO} + 2nr_{CO2} + 1nr_{CH4} + 1nr_{CF} = 1np_{CO} + 1np_{CO2} + 1np_{CH4} \tag{11}$$

$$2nr_{H2} + 4nr_{C2H4} + 8nr_{C3H8} + 6nr_{C2H6} + 4nr_{CH4} + 2nr_{H2O} = 2np_{H2} + 2np_{H2O} + 4np_{CH4} \tag{12}$$

$$1nr_{CO} + 2nr_{CO2} + 1nr_{H2O} + 2ar_{real} = 1np_{CO} + 2np_{CO2} + 1np_{H2O} + 2np_{O2} \tag{13}$$

$$2nr_{N2} + 2ar_{real}3.76 = 2np_{N2} \tag{14}$$

Chemical equilibrium was applied considering the water-gas displacement reaction (K_{H2O}), the CO_2 dissociation reaction (K_{CO2}) and the CH_4 oxidation reaction (K_{CH4}), as presented in Equations (15) to (20). The parameter *P* is the working pressure, which in this case is 101325 Pa, P_{ref} is the reference pressure (101325 Pa), and T_K is the temperature in Kelvin.

$$K_{CO2} = \left(\frac{np_{CO} * np_{O2}^{0.5}}{np_{CO2}}\right)\left(\frac{P}{P_{ref} * np_{total}}\right)^{0.5} \tag{15}$$

$$K_{CO2} = 7.07248\,.\,10^{-109}\,.\,{T_K}^{32.64} \tag{16}$$

$$K_{H2O} = \frac{np_{CO2}\cdot np_{H2}}{np_{CO}\cdot np_{H2O}} \tag{17}$$

$$K_{H2O} = 1.17843\,.\,10^{12}\,.\,{T_K}^{-3.97} \tag{18}$$

$$K_{CH4} = \left(\frac{np_{CO2} \cdot np_{H2O}^2}{np_{CH4} \cdot np_{O2}^2}\right) \tag{19}$$

$$K_{CH4} = 4.70554 \,.\, 10^{3.19} \,.\, T_K{}^{-92.60} \tag{20}$$

The Equations (16), (18) and (20) were obtained through linear adjustment for different temperatures in order to simplify the number of equations present in the model. The software used for this simulation was Engineering Equation Solver (EES).

3. RESULTS AND DISCUSSIONS

The results and discussions section was divided into two sessions, results of volatiles used in the analytical solution, which refers to combustion reactants and results of combustion products.

3.1 Determination of volatiles

The volatiles released by burning the pellets and obtained through the analytical solution by the equations (1) to (8) described previously, are estimated based on the ultimate analysis of (Jayah et al., 2003). The same, are shown in Tab. (3), where, *X* refers to the molar fraction of each chemical component *i* of the fuel, and, *T* to the temperature, which was varied between 650 – 850 °C.

Table 3. Molar fraction (*X*) of fuel chemical components *i* for different temperatures

T (ºC)	X_{C2H4}	X_{C2H6}	X_{C3H8}	X_{CH4}	X_{CO2}	X_{CO}	X_{H2}	X_{N2}
650	0.006711	0.004010	0.008544	0.030380	0.078560	0.243700	0.383000	0.002035
675	0.006620	0.004544	0.007032	0.028500	0.073020	0.250900	0.386600	0.002016
700	0.006685	0.004864	0.005642	0.027800	0.068920	0.256300	0.388800	0.002001
725	0.006787	0.004916	0.004387	0.028130	0.065770	0.260300	0.390100	0.001990
750	0.006805	0.004706	0.003280	0.029380	0.063310	0.263500	0.390400	0.001981
775	0.006625	0.004278	0.002336	0.031460	0.061350	0.266100	0.390000	0.001975
800	0.006157	0.003705	0.001572	0.034240	0.059750	0.268400	0.389000	0.001970
825	0.005374	0.003084	0.001000	0.037450	0.058430	0.270400	0.387500	0.001966
850	0.004399	0.002532	0.000624	0.040510	0.057310	0.272200	0.385900	0.001964

Through Tab. (3), it is possible to observe that the molar fractions of C_3H_8 (X_{C3H8}), CO_2 (X_{CO2}) and N_2 (X_{N2}) decreased with increasing temperature, different from the molar fractions of CH_4 (X_{CH4}) and CO (X_{CO}), which increased by 25 and 10%, respectively. In turn, the molar fraction of C_2H_6 (X_{C2H6}), C_2H_4 (X_{C2H4}) and H_2 (X_{H2}) had a slightly different behavior from the others, increasing until temperatures of 725, 750 and 775 °C, respectively, and decreasing from then on. The molar fraction of N_2 varied little with the increase in temperature, less than 5%.

3.2 Determination of combustion products

Figures 1 and 2 show the molar fraction of CO (X_{CO}) and CO_2 (X_{CO2}) present in the combustion products as a function of the equivalence ratio and temperature. In Figure 2 it is possible to observe an increase in the CO_2 molar fraction up to the equivalence ratio close to stoichiometry. Then, the X_{CO2} decreases due to CO_2 dissociation and CO formation. This behavior is consistent with the literature (Turns, 2013). For $\varnothing = 3.5$ the increase of reaction temperature from 650 to 850 °C resulted and decreasing from then on in the molar fraction of CO_2 by approximately 65%. This effect is a result of increases of the equilibrium constant of the CO_2 dissociation reaction at higher reaction temperatures.

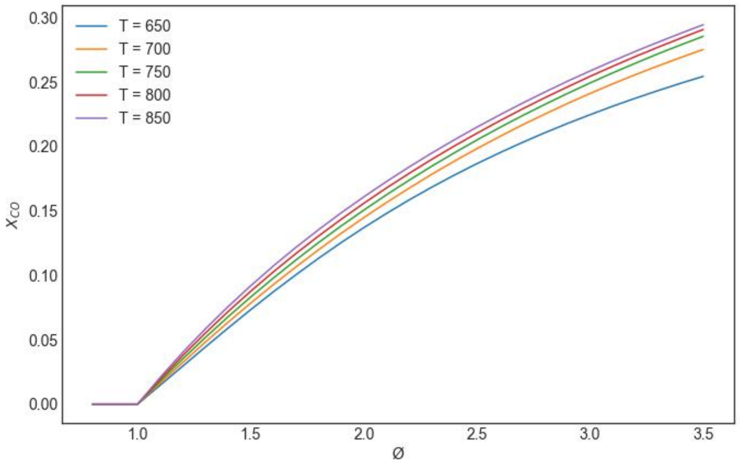

Figure 1. Molar fraction of CO (X_{CO}) as a function of the equivalence ratio (Ø) and temperature.

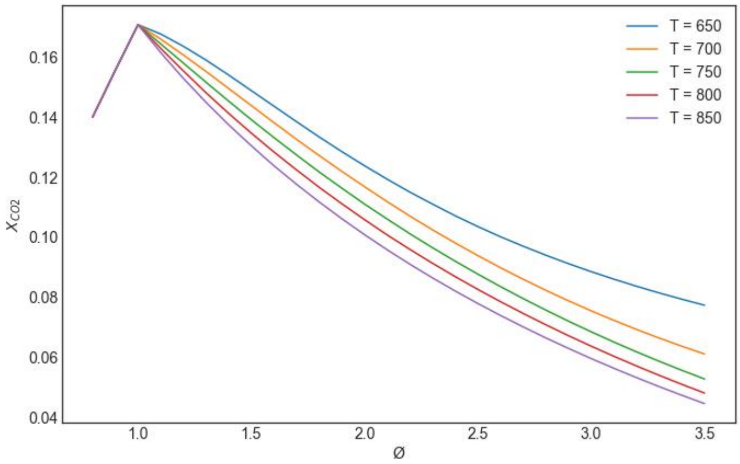

Figure 2. Molar fraction of CO_2 (X_{CO2}) as a function of the equivalence ratio (Ø) and temperature.

Figure 3 shows the variation of the molar fraction of H_2 (X_{H2}), as a function of the variation of the equivalence ratio and temperature. In Fig. 3, increasing the temperature from 650 to 850 °C and changing the equivalence ratio from 0.8 to 3.5 resulted in an increase in the molar fraction of H_2 by approximately 12%. For equivalence ratios below stoichiometry, the molar fraction of H_2 becomes negligible. The increase in X_{H2} with increasing Ø is a result of the water-gas displacement reaction, which in turn promotes the conversion of CO and H_2O into CO_2 and H_2.

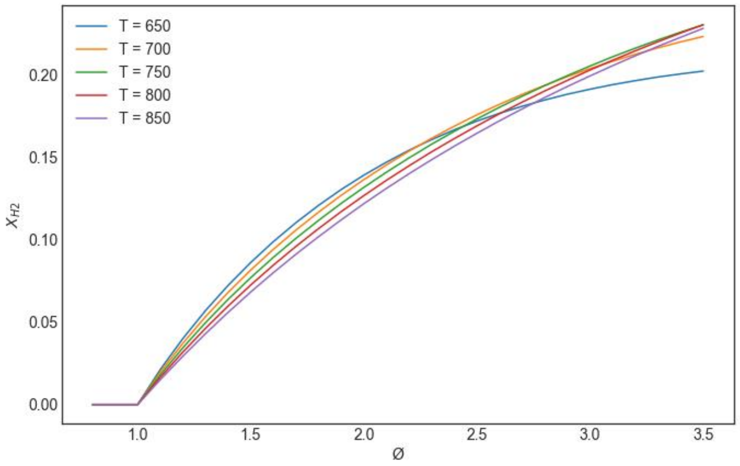

Figure 3. Molar Fraction of H_2 (X_{H2}) as a function of the equivalence ratio (Ø) and temperature.

Figure 4 shows the variation of the molar fraction of CO_2 (X_{CO2}), CO (X_{CO}), O_2 (X_{O2}), H_2O (X_{H2O}) and H_2 (X_{H2}) as a function of the variation of the equivalence ratio from 0.8 to 3.5 and temperature from 650 °C.

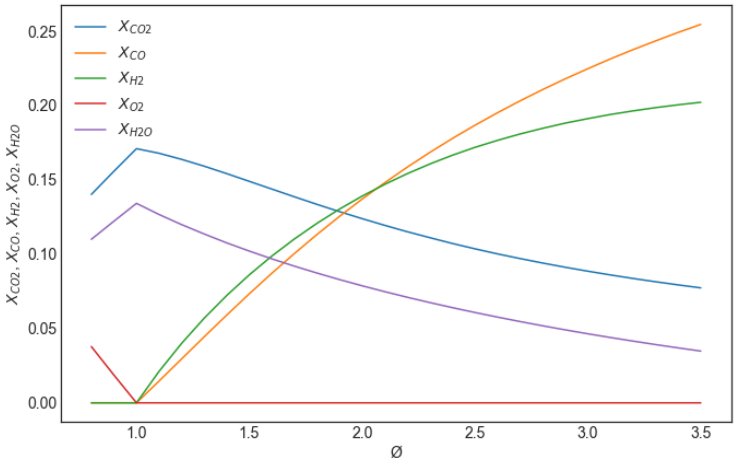

Figure 4. Molar Fraction of CO_2 (X_{CO2}), CO (X_{CO}), O_2 (X_{O2}), H_2O (X_{H2O}) and H_2 (X_{H2}) as a function of the equivalence ratio (Ø) and temperature 650 °C.

It is possible to observe the curves of CO_2, CO, O_2, H_2O and H_2 for different equivalence ratios and temperature of 650 °C. By uniting these five curves in a single graph, it is possible to see more clearly what happens to the molar fractions of these chemical components simultaneously. For $Ø = 1$, there is the highest molar fraction of CO_2 ($X_{CO2} = 0.17$) and H_2O ($X_{H2O} = 0.1342$) that decrease with the increase of the equivalence ratio, until 0.08 and 0.03482 in $Ø = 3.5$, respectively. However, CO and H_2, as mentioned earlier, for equivalence ratios smaller than the stoichiometric one, are negligible. They start to grow, from $Ø = 1$, as CO_2 dissociation and water-gas displacement reactions take place.

The chemical species O_2 is present in higher concentration for smaller equivalence ratios than the stoichiometric one, different from CO. As the molar concentration of CO increases, the molar concentration of O_2 decreases, until it reaches stoichiometry and becomes negligible. For Turns (2013), it is possible to say that both CO and O_2 species become main products as the combustion becomes rich or lean. Still, Turns (2013) mentions that under conditions of complete combustion ($Ø = 1$), that is, without dissociation, the chemical species of O_2, CO and H_2 would be zero.

3.3 Validation of the analytical solution

For validation of the analytical solution, it was necessary to provide some input data to the program. These data were obtained through other articles, where the authors presented the necessary information, such as the composition of the biomass used, reaction temperature and equivalence ratio. The results obtained experimentally by Pedroso et al., (2005), Galindo et al., (2014) and De Sales et al., (2017) are compared to those obtained analytically, through the software.

Pedroso et al., (2005) gasifies three different types of biomass, olive wood, peach wood and pine wood, chopped into small pieces of 2x1x1cm. Biomass is introduced from the top of the gasifier and has an air inlet at the bottom. Galindo et al., (2014) studied the gasification of biomass in a two-stage downdraft gasifier with air supply. The biomass used in the research was eucalyptus wood in cubic format with a size smaller than 6 cm and fed by the upper part of the gasifier. De Sales et al. (2017) studied the gasification of woody biomass (eucalyptus spp.) in a two-stage downdraft reactor using different gasifying agents. Despite other gasifying agents studied, data were extracted only from gasification with air. The biomass used was cut into small pieces of 5x5x5 cm, in order to avoid the formation of empty spaces in the bed and, as in the previous cases, the biomass feed into the gasifier is from the upper.

The data referring to the characterizations of the biomass cited by each author are presented in Tab. (1) and (2). Pedroso et al., (2005) did not inform the amount of fixed carbon, volatile materials and higher calorific value of the fuel, therefore, they were used as data of entry in the program, the information referring to the informed biomass, but from the authors García et al., (2014).

Pedroso et al., (2005) investigated the emissions of CO, H_2, CO_2, CH_4, O_2 and N_2 for three different types of wood. The equivalence ratios used by the authors were 2.06, 2.03 and 2.85, for olive wood, peach wood and pine wood, respectively. The temperatures used are in accordance with those listed in Tab. (4).

Table 4. Working temperatures used by Pedroso et al., (2005)

T (°C)	Olive	Peach	Pine

T_1	240	200	230
T_2	258	218	248
T_3	607	507	580
T_4	920	900	870
T_5	850	880	830
T_6	152	144	135

In the program, the lowest temperatures did not show good agreement with the data presented, since the analytical solution use as a basis for fuel determination, the emissions reported by Neves et al., (2017) and, the authors presented the emissions for temperatures between 650 – 850 °C.

Table 5 presents the CO, H_2, CO_2 and N_2 emissions reported by the authors (Pedroso et al., 2005), for the three different types of wood.

Table 5. Comparison between the molar fraction of emissions obtained by Pedroso et al., (2005) and analytically

Emissions (vol.%)	Olive Wood			Peach Wood			Pine Wood		
	Article	Model	Error	Article	Model	Error	Article	Model	Error
CO	17.40	14.26	22%	17.70	15.47	14%	16.00	14.57	10%
H_2	13.20	13.49	2%	15.00	12.08	24%	12.10	13.72	12%
CO_2	12.40	12.76	3%	13.50	11.21	20%	11.40	12.62	10%
N_2	54.90	49.36	11%	51.70	50.41	3%	59.40	50.22	18%

Through Tab. (5), it is possible to observe that the highest error obtained for CO was 22%, referring to olive wood. On the other hand, the highest error obtained for H_2 and CO_2 emissions was 24 and 20%, respectively, for peach wood. Already, the biggest error obtained for N_2 emissions was 18% for pine wood.

Galindo et al., (2014) investigated the emissions of CO, H_2, CO_2 and CH_4, for three different equivalence ratios and different temperatures in each round. For the exposed data, emissions are expressed at a temperature of 663.71 °C and equivalence ratio 3.58, referring to the second round. The authors emphasize that the reported equivalence ratios are not exact, they are an average and may vary. Tab. (6) presents the CO, H_2 and CO_2 emissions presented by the authors (Galindo et al., 2014) for eucalyptus wood.

Table 6. Comparison between the molar fraction of emissions obtained by Galindo et al., (2014) and analytically

Emissions (vol.%)	Eucalyptus Wood		
	Article	Model	Error
CO	18.59	20.28	8%
H_2	17.71	20.91	15%
CO_2	13.32	12.31	8%

In general, emissions showed good agreement with what was exposed by the authors, since the error obtained for CO, H_2 and CO_2 emissions was 8, 15 and 8%, respectively.

De Sales et al., (2017) investigated CO, H_2 and CH_4 emissions from eucalyptus wood for three different equivalence ratios. These ratios are 2.52, 2.38, and 2.67, arranged in that order in the data that follows. The authors presented the minimum, maximum and average value of each emissions. However, the working temperature was not informed, therefore, the temperatures of 650, 750 and 850 °C were used in the program. The average of each emissions was compared to the average reported by the authors, as shown in Tab. (7).

Table 7. Comparison between the molar fraction of emissions obtained by De Sales et al., (2017) and analytically

Emissions (vol.%)	Eucalyptus Wood								
	Article	Model	Error	Article	Model	Error	Article	Model	Error
CO	17.80	17.69	1%	15.40	16.53	7%	21.00	18.82	12%
H_2	17.20	17.83	4%	16.30	16.80	3%	16.30	18.80	13%

In general, the equivalence ratio that showed the best agreement was for $\varnothing = 2.52$, with errors of 1 and 4% for CO and H_2 emissions, respectively. However, for $\varnothing = 2.38$ the error for H_2 emission was only 3%. If compared with the other authors, the error obtained for the CO with these operating conditions was the best. However, for H_2, the smallest error obtained was 2% for olive wood by Pedroso et al., (2005). CH_4 emissions were not exposed because the molar fraction obtained as a percentage of volume by both authors and analytically was between 1 and 2, a very small value compared to the other emissions.

4. CONCLUSIONS

The analytical solution has been developed and adjusted to determine from volatiles to the end products of the combustion reaction. It was numerically observed that increasing the temperature from 650 to 850 °C resulted in a variation in the volatile composition, increasing the molar concentration of CO present in the combustion products and reducing the concentration of CO_2, due to its dissociation. The CO and H_2 compositions become significant for higher than stoichiometric equivalence ratios, while the CO_2 concentration begins to decrease, due to its dissociation. That is, for equivalence ratios smaller than the stoichiometric one, the molar fraction of these two compounds is negligible.

The validation of the analytical solution was based on the experimental results obtained by three different authors, Pedroso et al., (2005), Galindo et al., (2014) and De Sales et al., (2017). The results obtained analytically for both emissions are in agreement with those presented by the authors. Where, the smallest and largest error obtained for CO emissions are 1 and 22%, respectively. For H_2 emissions, the smallest and largest errors obtained are 2 and 24%, respectively.

Thus, in general, the analytical solution for equivalence ratios greater than the stoichiometric one showed satisfactory results, with errors between 1 and 24%, lower than expected, considering that the solution was obtained through chemical equilibrium, only as a function of working temperature, equivalence ratio and biomass composition. The intention is to continue working on this solution to obtain even better results.

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