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GASIFICATION STUDY OF EUCALYPTUS WOOD BASED ON THERMODYNAMIC CHEMICAL EQUILIBRIUM

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Abstract. *Biomass is considered an important energy source worldwide. Gasification is one of the options for conversion of biomass into gaseous fuel for both heat and power generation in distributed plants. The present study evaluates the gasification of eucalyptus wood based on computational simulations using a thermodynamic equilibrium model. The open-source program Chemical Equilibrium with Applications (CEA) developed by NASA is applied in this work. Favorable operating parameters are identified by evaluating the syngas composition in terms of* CH_4*,* CO*,* CO_2*,* H_2*,* H_2O*,* N_2*, and unconverted carbon. In addition, cold gas efficiency, carbon conversion, and heating value are evaluated. Gasification temperatures between 400-1000 ºC and equivalence ratios between 1.0 and 8.75 are evaluated by using air as gasifying agent, while pressure is kept constant at 100 kPa. Significant values of CO and* H_2 *concentration in the syngas are reached at temperatures above 550 ºC which is agreement with the occurrence of homogenous and heterogeneous gasification reactions, i.e., Boudouard, water-shift and steam reforming reactions. Optimum values of cold gas efficiency and carbon conversion are identified in terms of gasification temperature and equivalence ratio. In turn, presence of unconverted carbon is identified as a crucial factor for reducing the quality of syngas and consequently the heating value.*

Keywords: *gasification, chemical equilibrium, eucalyptus wood*

1. INTRODUCTION

Biomass energy has been widely explored worldwide due its lower costs, availability, and environmentally friendly aspects. Thermal conversion takes place usually in furnaces and boilers, which has several advantages such as simple technology and low costs. The major issue to convert biomass into electrical power is the scalability, requiring medium or large-scale power plants. One of options for chemical conversion of biomass is gasification technology. Basically, it is a thermochemical process of conversion hydrocarbons into synthesis gas (syngas), rich in H_2 and CO, besides other components such as CO_2, CH_4, N_2, and other minor non-combustible species. The syngas can be either applied to generate electrical-power using internal combustion engines or heat within furnaces. It also can be upgraded for natural gas replacement as synthetic natural gas (SNG), according to Schildhauer and Biollaz (2016).

Production of syngas derivate from solid fuels requires at least three basics processes: drying, pyrolysis (reduction), and gasification. The reactions usually take place within a gasifier which can be equipped with fixed-grate or fluidized bed technology. The gasifiers are usually classified as updraft and downdraft configurations (Figure 1). In updraft gasifiers, biomass inlet and syngas outlet are placed at top, while the air supply occurs at bottom, resulting in a combustion zone near the grate. The major issue in this gasifier is the high tar content in the syngas, which in turn demands purification steps prior the combustion in internal combustion engines. Downdraft gasifiers solves this issue by injecting air above the oxidation zone while the syngas outlet is positioned at bottom. In this arrangement, the combustion products are forced to pass through a reduction zone before the grate, promoting an early conversion of tar into permanent gas species. The major disadvantages are reduced range of feedstock and lower heat efficiency in comparison to updraft gasifier (Quadros, 2013).

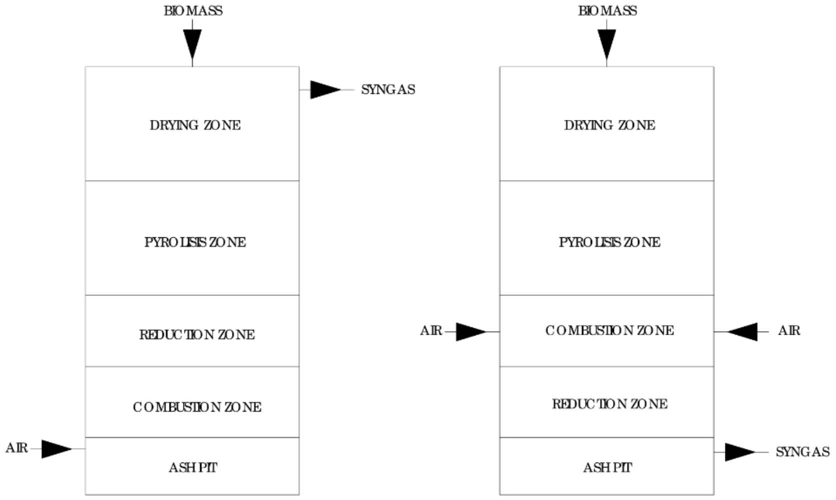


Figure 1. Updraft (left) and downdraft (right) gasifiers.

Tar content is certainly one major issue in the gasification process; it is a complex hydrocarbon with high calorific heat which is formed mainly at low temperatures in fuel-rich regions . Condensation of tar at low temperature sections of facilities leads to blocking and fouling in pipelines and other equipment such as filters, combustion engines, turbines, and burners. Tar reduction techniques are divided into primary and secondary methods. The first approach consists in treatments within the gasifier, optimizing tar conversion into non-volatile gas species, such as CO, CO_2, and H_2. The reaction is endothermic and requires high temperature zones as in downdraft gasifiers. Gas treatment downstream the gasifier is the second approach and it consists of filters, cyclones, and catalytically methods. Even though secondary methods are very effective in removing tar content, the primary methods have low operating costs and provide high quality syngas (Valderrama Rios et al., 2018).

Numerical modeling of gasification process is widely used to provide theoretical gasifier favorable operating conditions in order to reduce tar formation. Gasification modeling is usually performed by chemical kinetics and equilibrium calculations. Chemical kinetics is able to predict the gasification behavior by using kinetic parameters which are obtained by experimental methods; it is a most recommended approach for comparison of gasification technologies. Equilibrium calculations predict the thermodynamic limit of the gasification reaction, which is more suitable for evaluating the influence of operating parameters, e.g., temperature, equivalence ratio, oxygen excess, etc. According to Rodrigues et al. (2016), chemical equilibrium approach showed good agreement with experimental data in fixed bed gasifiers at high temperatures, except in updraft gasifiers which normally require more detailed models.

In order to understand the impact of operating parameters of a eucalyptus wood gasification in a 174 kW_{th} gasifier, simulations based on thermodynamic chemical equilibrium are performed. The simulations are carried out with help of the open-source program Chemical Equilibrium with Applications distributed by NASA (National Aeronautics and Space Administration). Among the investigated gasification parameters, temperature and equivalence are compared against species, cold gas efficiency, carbon conversion, and heating value.

2. OVERVIEW OF TEST FACILITY

A large-scale gasification test facility installed at Londrina State University (UEL) is applied as reference for the theoretical studies presented in the presented work. Further information on this test facility is found elsewhere (Figueiredo et al., 2012 and Quadros, 2013). Figure 2 provides an overview of the main components of the test facility while Figure 3 depicts the gasifier. It consists basically of a fixed bed downdraft gasifier with a rated capacity of 174 kW_{th} and an internal combustion engine (nominal power of 45 kW) coupled to an electrical power generator. The fixed bed downdraft gasifier is vertically oriented and equipped with two-staged air admission inlets. A blower provides air to the gasifier which is preheated and divided into two streams upstream of the gasifier. This technique allows to spread out the heat provided by the biomass combustion and reduce tar content in syngas. At the bottom of gasifier, a rotating grate allows the ashes removal while syngas outlet was placed below the grate. A cyclonical separator removes large particles from syngas upstream the heat exchangers. Filters and a trap are also applied upstream the engine to remove the remaining tar and water content; a gasometer keeps the pressure at similar levels during operation. Finally, the syngas is burned in an internal combustion engine connected to an electrical power generator. The engine consists of an originally diesel engine modified to include a spark-ignition system. A security flare is also installed to burn the excess of generated syngas and avoid emission of CH_4 and CO to atmosphere. This test facility operates primarily with eucalyptus wood. A typical composition of eucalyptus wood including high heating value (HHV) and low heating value (LHV) is detailed in Table 1.

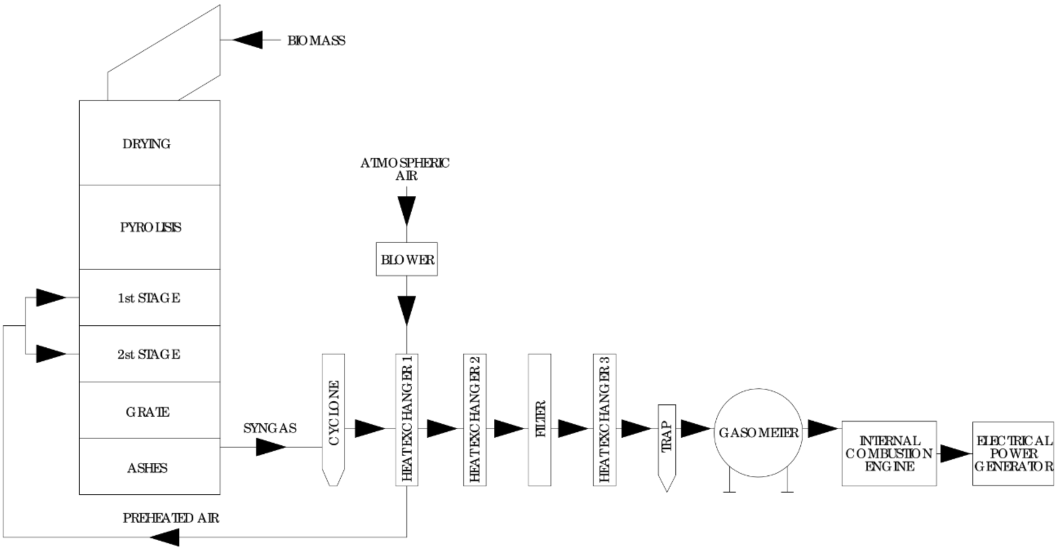


Figure 2. Schematics of gasification test facility according to Figueiredo et al. (2012).

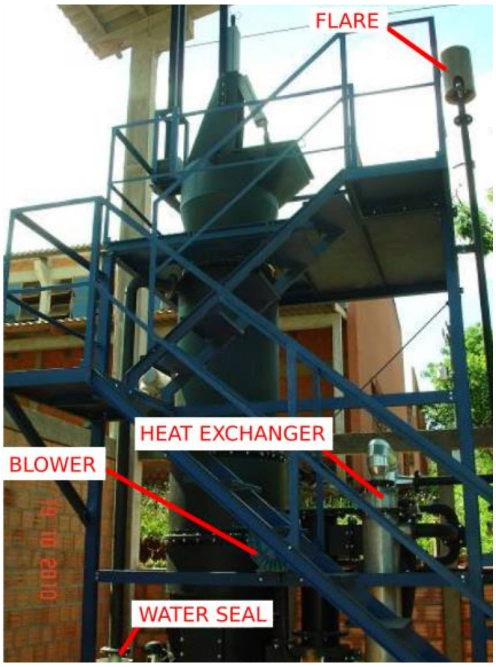


Figure 3. Gasification test facility installed at UEL, according to Figueiredo et al. (2012).

Table 1. Composition of eucalyptus wood, according to Cortez et al. (2008).

Specie	Ultimate analysis (daf %)	Molar weight (kg/kmol)	Total Moles
C	49.420	12	41.183
H	5.920	1	59.203
O	44.347	16	27.717
N	0.303	14	0.216
S	0.010	32	0.003
LHV (MJ/kg)		18.27	
HHV (MJ/kg)		19.42	

3. FUNDAMENTALS OF GASIFICATION

The global gasification reaction for biomass as fuel and atmospheric air as gasifying agent is show in Eq. (1);

$$\begin{aligned} &C_aH_bO_cN_dS_e + n(O_2 + 3.76N_2) \\ &\qquad \rightarrow n_1H_2 + n_2CO + n_3CO_2 + n_3H_2O + n_4CH_4 + n_5N_2 + n_6NO + n_7NO_2 + n_8SO_2 \end{aligned} \tag{1}$$

$C_aH_bO_cN_dS_e$ is the biomass mole composition given by Table 1 while $n(O_2 + 3.76N_2)$ represents the atmospheric air in mole based. The main chemical reactions occurring during a gasification process are shown in Eq. (2) to (8), according to Shayan et al. (2018).

$$C + 0.5O_2 \Leftrightarrow CO - 111\,kJ/mol \text{(partial oxidation)} \tag{2}$$

$$CO + 0.5O_2 \Leftrightarrow CO_2 - 283\,kJ/mol \text{(carbon monoxide combustion)} \tag{3}$$

$$C + O_2 \Leftrightarrow CO_2 - 394\,kJ/mol \text{(carbon combustion)} \tag{4}$$

$$C + CO_2 \Leftrightarrow 2CO + 172\,kJ/mol \text{(Boudouard reaction)} \tag{5}$$

$$C + H_2O \Leftrightarrow CO + H_2 + 131\,kJ/mol \text{(water-gas reaction)} \tag{6}$$

$$CO + H_2O \Leftrightarrow H_2 + CO_2 - 41\,kJ/mol \text{(water-gas shift reaction)} \tag{7}$$

$$CH_4 + H_2O \Leftrightarrow 3H_2 + CO + 206\,kJ/mol \text{(steam reforming)} \tag{8}$$

The carbon conversion into gaseous fuels is modelled by Eq. (4)-(6). Reactions given by Eq. (5) and (6) are endothermic and therefore require heat, which is supplied by the combustion reactions within the same reactor through exothermic reactions detailed above or alternatively supplied by an external source (Schildhauer and Biollaz, 2016).

Equivalence ratio, given by Eq. (9), is an important operating parameter during gasification and is defined as the mass ratio of air and fuel by the mass ratio of air and fuel at stoichiometric conditions.

$$\phi = \frac{\frac{m_{air}}{m_{fuel}}}{\left(\frac{m_{air}}{m_{fuel}}\right)_{stoichiometric}} \tag{9}$$

The theoretical cold gas efficiency (CGE) determines the gasification efficiency by comparing the biomass and syngas high heating value as given by the following equation, as suggested by Rodrigues et al. (2016):

$$CGE = \frac{\frac{\dot{m_{syngas}}}{MW_{syngas}} \sum_{i=1}^{N} y_i\, HHV_i VM_i}{\dot{m_{biomass}} HHV_{biomass}} \tag{10}$$

where $\dot{m_{syngas}}$ and $\dot{m_{biomass}}$ are the mass of syngas and biomass, MW_{syngas} is the molar weight of syngas, y_i, HHV_i and VM_i is the molar concentration, high heating value, and molar volume of specie *I*; $HHV_{biomass}$ is the biomass high heating value.

The carbon conversion (CC), calculated by Eq. (11), gives reaction efficiency in converting the biomass carbon into permanent gaseous species (i.e., CO, CO_2, and hydrocarbons). Values of carbon conversion below 100% mean the presence of tar and other undesirable compounds in syngas. The gas yield given by Eq. (12) is also an important parameter to be determined during gasification and represents the amount of gas released per each kilogram of biomass (Rodrigues et al., 2016).

$$CC = \frac{12Y(CO + CO_2 + CH_4 + 2C_2H_4 + 2C_2H_6)_{kmol,syngas}}{24.79C_{kg,biomass}} \tag{11}$$

$$Y = \frac{\frac{\dot{m}_{syngas}}{MW_{syngas}} 24.79}{\dot{m}_{biomass}} \tag{12}$$

4. CHEMICAL EQUILIBRIUM

The gasification reactions are modelled using a chemical equilibrium approach. The simulations are performed using the NASA Chemical Equilibrium with Applications (CEA) program. CEA calculates products concentration, thermodynamics, and transport properties of any mixtures through chemical equilibrium approach using minimization of Gibbs energy ("NASA Chemical Equilibrium with Applications (CEA)"). The Gibbs energy per kilogram of mixture *g* is given by the following equation, according to Gordon; J. McBride (1994):

$$g = \sum_{j=1}^{NS} \mu_j \, n_j \tag{13}$$

where NS refers to the number of species in the mixture and $n_i$is the number of kilogram-moles of specie *j*. The chemical potential per kilogram-mole n_j of specie *j* is defined by Eq. (14).

$$\mu_j = \left(\frac{\partial g}{\partial n_j}\right)_{T,P,n_{i\neq j}} \tag{14}$$

The minimization of Gibbs free energy is usually subject to certain constrains, such as mass-balance constrains, given by Eq. (15).

$$\sum_{j=1}^{NS} a_{ij} - b_i^0 = 0 (i = 1,\ldots,l) \tag{15}$$

$$b_i - b_i^0 = 0 (i = 1,\ldots,l) \tag{16}$$

where $a_{ij}$are the number of kilograms-atoms of element *i* per kilogram-mole of specie *j*, b_i^0 is the assigned number of kilogram-atoms of element *i* per kilogram of total reactants, $b_i$is the number of kilogram-atoms of element *i* per kilogram of mixture (Eq. 17), given by Eq. (13) and the index *l* is the number of chemical elements.

$$b_i = \sum_{j=1}^{NS} a_{ij} \, n_j (i = 1,\ldots,l) \tag{17}$$

Defining a term *G* by Eq. (18):

$$G = g + \sum_{i=1}^{l} \lambda_i \left(b_i - b_i^0\right) \tag{18}$$

Where λ_i are Lagrangian multipliers, the equilibrium condition is given by:

$$\delta G = \sum_{j=1}^{NS} \left(\mu_j + \sum_{i=1}^{l} \lambda_i \, a_{ij}\right) \delta n_j + \sum_{i=1}^{l} \left(b_i - b_i^0\right) \delta \lambda_i = 0 \tag{19}$$

The modeling of chemical equilibrium approach is based in solve the set of λ_i multiplier which minimizes δG at constant temperature and pressure. In the present study, gasification reaction between 400 ºC to 1000 ºC and equivalence ratios ranging from 1 to 8.75 are studied; these conditions are usually applied to simulate a downdraft gasifier according to Rodrigues et al. (2016). Pressure weakly influence in gasification reactions according to Schildhauer and Biollaz (2016) and for this reason atmospheric pressure (100 kPa) was set in all investigated cases.

5. RESULTS

Figure 4 shows the effect of equivalence ratio in the gasification products at temperatures between 400 ºC and 1000 ºC. At stoichiometric conditions (equivalence ratio close to 1), CO_2 and H_2O formation occurs at entire temperature range because of oxidation reactions. This condition is undesirable because fuel chemical energy is converted into thermal energy within the gasifier and reducing the syngas heating value. An increase in the equivalence ratio encourages formation of CO, H_2, and other minor species at all temperature range. This effect occurs due the absence of oxygen (O_2) in the reaction, displacing the chemical equilibrium towards partially oxidized species. As temperature increases, formation of CO and H_2 is encouraged in parallel to a decrease of CH_4 and CO_2 concentration. Endothermic reactions including Boudouard, water-gas, and steam reforming explain this behavior.

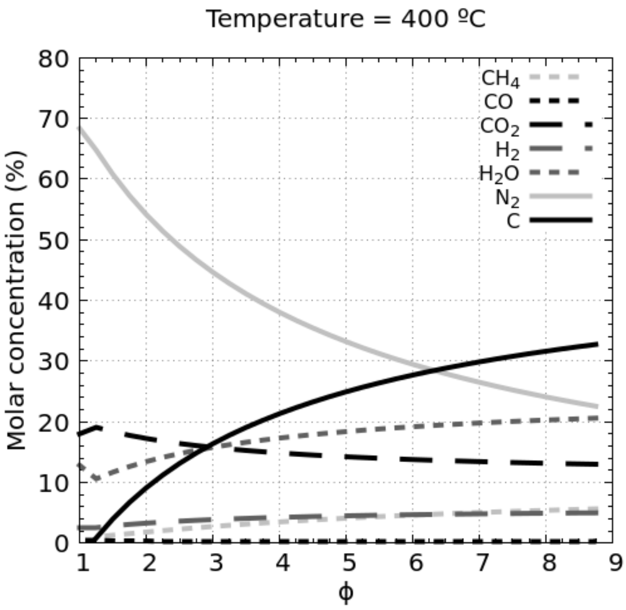
At temperatures lower than 550 ºC no significant differences among the results are noted due to insufficient thermal energy to activate the reactions; limitation of chemical equilibrium modeling at lower temperatures has been reported in the literature Rodrigues et al. (2016). Peak of CO concentration (almost 20 mol%) occurs at equivalence ratios between 2.50 and 2.75 at 550 ºC. It is worth to note that CO concentration is negligible (less than 5 mol%) at temperatures below 550 °C while presence of unconverted carbon (C) is noted for the entire range of equivalence ratio.

As temperature increases, the presence of unconverted carbon shifts to higher values of equivalence ratio while formation of CO is reduced. At 550 °C unconverted carbon is noted at equivalence ratios around 2.5, while at temperatures between 900-1050 ºC it occurs at values higher than 6.0. Even though there are specific conditions for CO formation, the conversion of hydrocarbons and water into hydrogen occurs almost in all range of temperature and equivalence ratio. A more pronounced presence of hydrogen occurs at temperatures higher than 550 ºC as a consequence of endothermic reactions; a similar effect is also noted for CO.

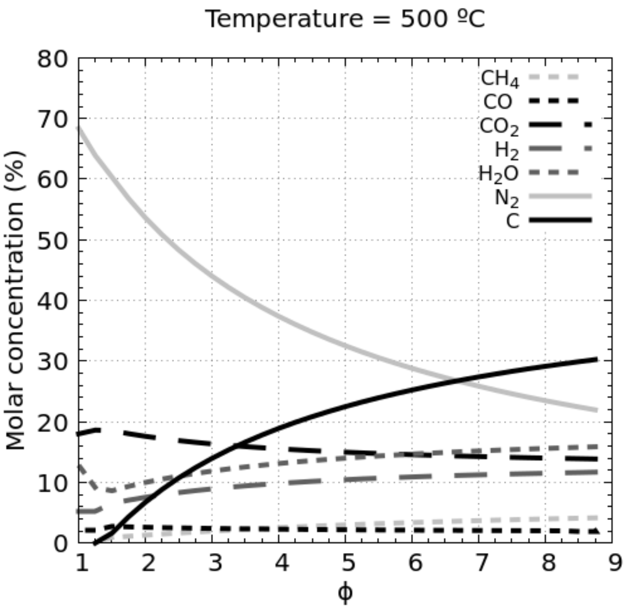
As expected, molar concentration of N_2 decreases as the equivalence ratio increases while temperature has no influence on the concentration. The presence of N_2 is almost exclusively due to air applied gasifying agent whereas the fuel-N (0.303% daf) is almost negligible in the eucalyptus wood.

Figure 5(a) shows the theoretical cold gas efficiency (CGE) as a function of temperature and equivalence ratio. At each temperature level there is an equivalence ratio that maximizes the CGE either due to presence of unconverted carbon or due to presence of fully oxidized species, i.e., CO_2 and H_2O. Overall, high values of equivalence ratio become necessary to maximize the CGE as temperature increases. As depicted in Fig. 5(a), at 600 ºC a maximum CGE of around 57% was achieved at an equivalence ratio close to 2.0, while at 800 ºC a maximum CGE of around 97% at a value of equivalence ratio around 5.0. A CGE of 100% is achieved only at temperatures higher than 800 ºC. Figure 5(b) shows the carbon conversion (CC) as a function of temperature and equivalence ratio. The plot indicates clearly the operating parameters which are less favorable due to presence of unconverted carbon. For instance, presence of unconverted carbon at 600 ºC occurs at equivalence rations close to 2.0, while at 800 ºC unconverted carbon is noted at equivalence ratio higher than 5.

Another important parameter for evaluating the syngas quality is the heating value. Figure 6 shows the values of low heating value (LHV) and high heating value (HHV) as a function of temperature and equivalence ratio. Overall, a more pronounced slope of heating value is noted until a certain value of equivalence ratio which is followed by reduced slope where the curve becomes almost flat. The slope is more significant when CO and H_2 are simultaneously formed and there is absence of unconverted carbon. On the other hand, the slope is less significant in the presence of unconverted carbon although the H_2 conversion still occurs as indicated by Fig. 3. Maximum values of LHV is 9.0 MJ/m³ while HHV reaches values slightly higher, around 9.5 MJ/m³.


Temperature = 400 ºC
Molar concentration (%)
0
10
20
30
40
50
60
70
80
1
2
3
4
5
6
7
8
9
ϕ
CH_4
CO
CO_2
H_2
H_2O
N_2
C

(a)


Temperature = 500 ºC
Molar concentration (%)
0
10
20
30
40
50
60
70
80
1
2
3
4
5
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7
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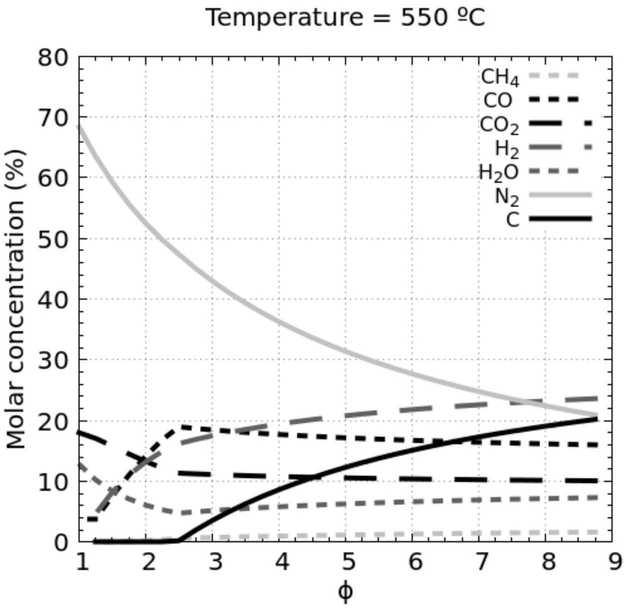
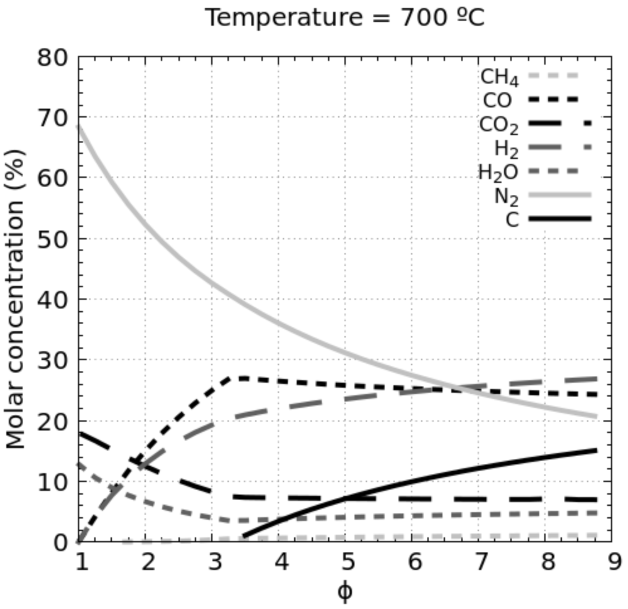
9
ϕ
CH_4
CO
CO_2
H_2
H_2O
N_2
C

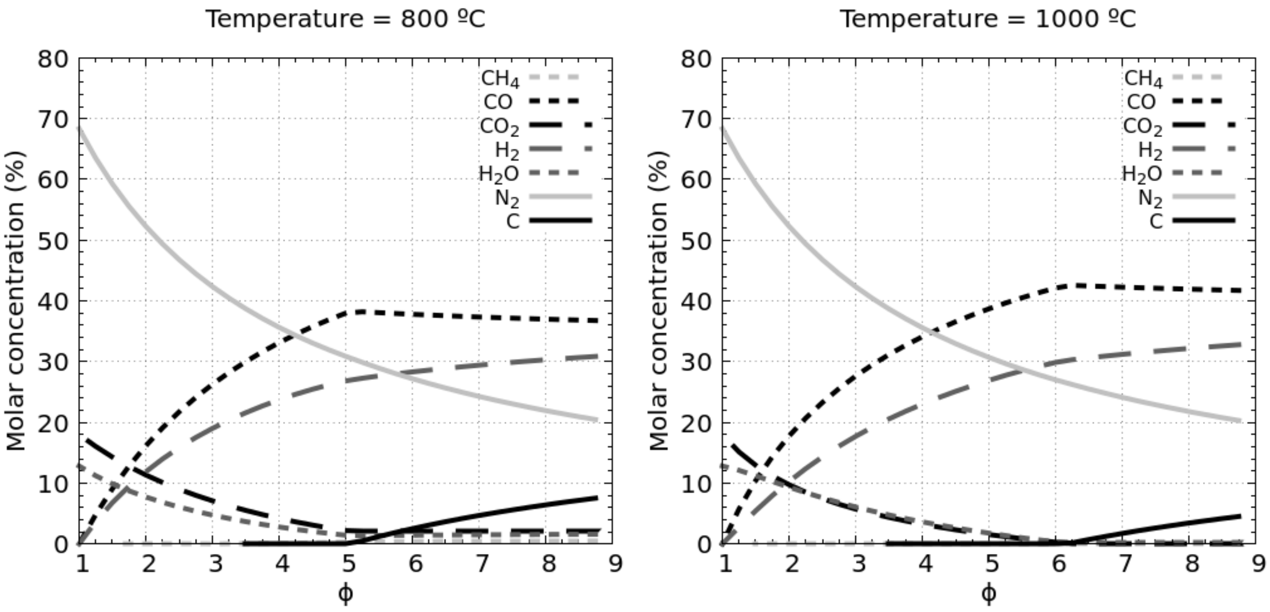
(b)


Temperature = 550 ºC
Molar concentration (%)
0
10
20
30
40
50
60
70
80
1
2
3
4
5
6
7
8
9
ϕ
CH_4
CO
CO_2
H_2
H_2O
N_2
C

(c)

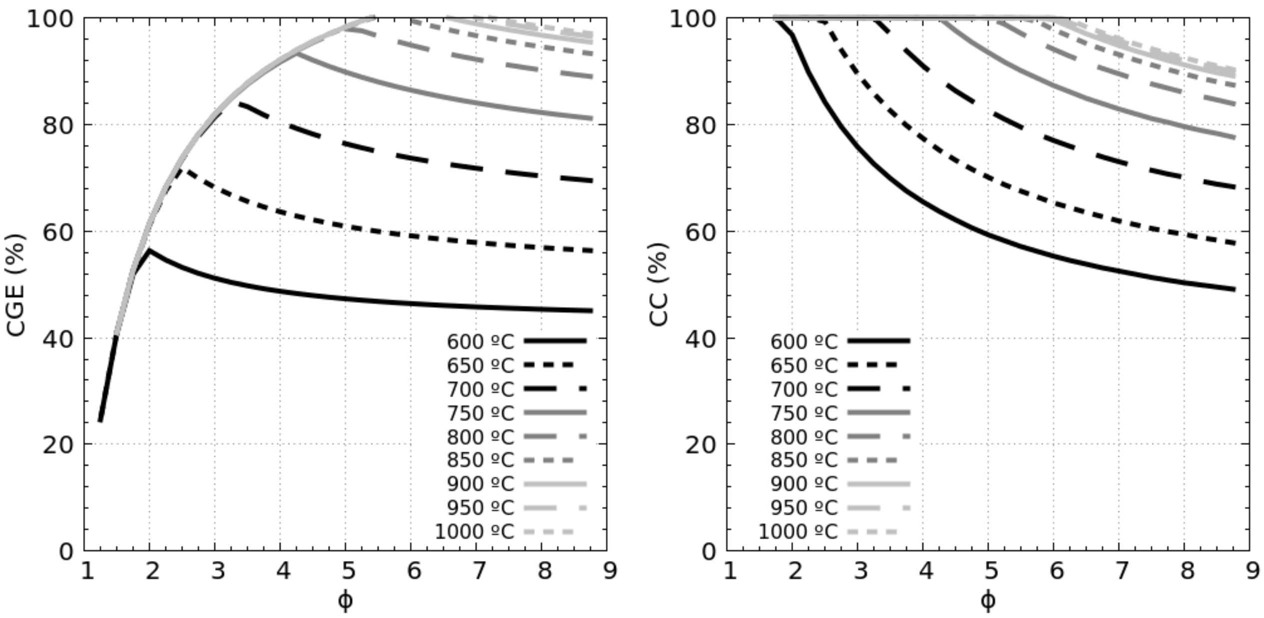

Temperature = 700 ºC
Molar concentration (%)
0
10
20
30
40
50
60
70
80
1
2
3
4
5
6
7
8
9
ϕ
CH_4
CO
CO_2
H_2
H_2O
N_2
C

(d)



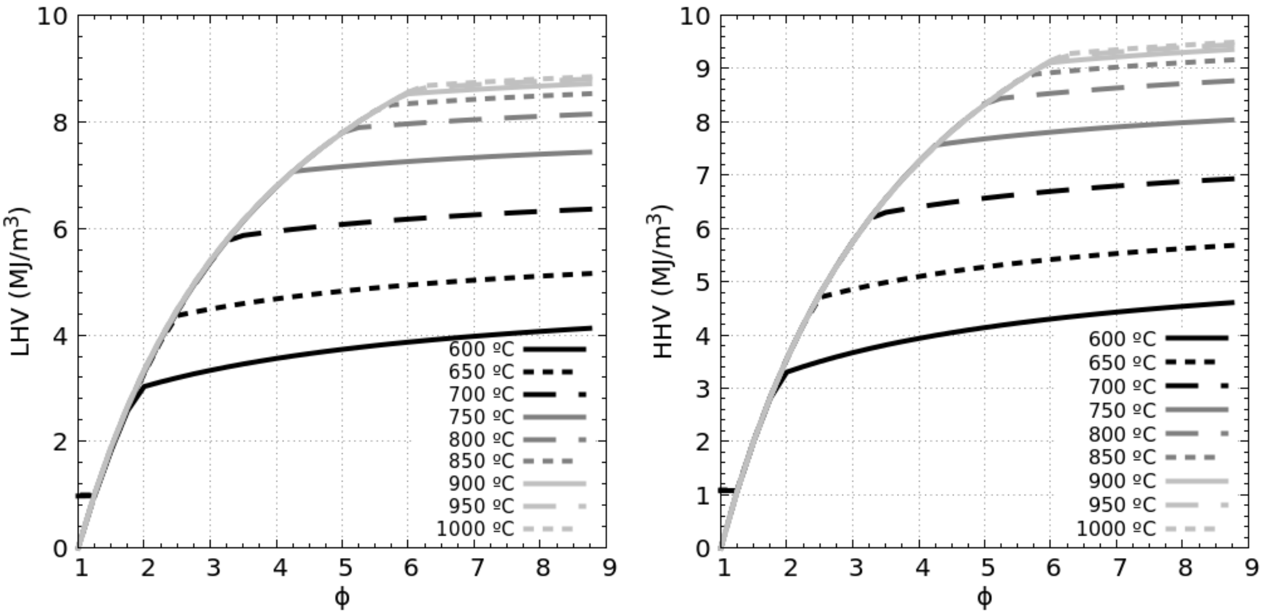
(e) (f)

Figure 4. Gasification products as a function of equivalence ratio for different temperatures.



(a) (b)

Figure 5. (a) CGE and (b) CC for different temperatures.



(a) (b)

Figure 6. Syngas (a) LHV and (b) HHV for different temperatures.

6. CONCLUSION

The present work evaluates the theoretical gasification behavior of eucalyptus wood based on chemical equilibrium calculations. The analysis employed the open-source software Chemical Equilibrium with Applications developed by NASA. The simulations are performed applying air as gasifying agent at operating temperatures between 400 °C and 1000 °C at 100 kPa. The evaluated parameters include syngas composition, cold gas efficiency, carbon conversion, and heating value. The major conclusions are summarized as follows:

i. At temperatures lower than 550 ºC results are similar and no significant deviations are noted among the results mainly due insufficient thermal energy and unconverted carbon presence is more prominent;
ii. Significant values of CO and H_2 (higher than 15 mol%) in the syngas are obtained at temperatures above 550 ºC as consequence of as Boudouard, water-shift and steam reforming reactions
iii. High values of equivalence ratio are necessary to maximize cold gas efficiency as temperature increased;
iv. Cold gas efficiency of 100% is achieved at temperatures higher than 800 ºC and equivalence ratios greater than 5.5;
v. Unconverted carbon and fully oxidized species concentration reduce drastically cold gas efficiency;
vi. Carbon conversion plots indicate non-favorable operating conditions as function of equivalence ratio and temperature which yield for instance unconverted carbon;
vii. Heating values varies as function of temperature and equivalence ratio. Maximum high heating value of 9.5 MJ/m³ is achieved at 900 ºC and equivalence ratio of 6.25;

7. ACKNOWLEDGEMENTS

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