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HYDROGEN IN SAWDUST GASIFICATION AND THE EQUILIBRIUM MODEL

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ABSTRACT

The objective of this work was to study a stoichiometric equilibrium model for the prediction of the hydrogen content in the gas mixture resulting from the gasification of pine sawdust, analyzing the effects of the variables and parameters in a fixed bed gasifier on a pilot plant scale. The main variable studied was temperature, the parameters considered in the gasification process included the oxygen rate and the presence of steam in the gasifying agent. The theoretical-experimental study compared the compositions obtained by the stoichiometric equilibrium model with the experimental values obtained. The results showed an acceptable concordance of the experimental values of the compositions of the hydrogen content in the producer gas with respect to that obtained through the software simulation of the equilibrium model, in the range of 750-850ºC and values of oxygen rate between 0.2 and 0.3 and with the presence of steam.

INTRODUCTION

Renewable energy sources represent the foundations of the energy policies of developed countries to achieve that the total emissions of greenhouse gases (TGGE) by human action, decrease significantly by the year 2050. Among these renewable energy sources, biomass energy sources have received significant attention due to their sustainability characteristics, environmental and economic impact, adding to their natural abundance. In the Argentine Republic, the energy matrix is still highly dependent on fossil fuels. As of May 2020, according to data from the General Mosconi Argentine Institute of Energy, it is divided into thermal with 62.2%, hydraulic with 21.2%, renewables with 8.3% and nuclear is positioned with 8.3%.

In the case of the province of Misiones, the total potential of feasible biomass generators is 4,725,000 tons/year, forest plantations contribute 64% and the indirect supply for power generation is estimated at 1,721,000 tons/year. year, with 88% of the contributions from the forestry sector. The biomass balance shows a surplus of 3,940,068 tons / year, leaving room for power generation projects from biomass (Martiarena *et al*., 2019). Biomass gasification has the advantage of allowing biomass residues and other similar biodegradable wastes to be converted into valuable fuel. The synthesized gas produced through the gasification of biomass is suitable for multiple applications, as its own fuel, use in fuel cells and production of hydrogen (energy vector of the future) and methanol, among other applications. In a similar direction, its by-products (biochar, tars) are also potentially usable.

The biomass gasification process consists of theconversion of a solid/liquid organic compound into a gas/vapour phase and a solid pase. The synthesis gas generated is a mixture of carbon monoxide (CO), hydrogen (H2), methane (CH4), carbon dioxide (CO2), light hydrocarbons and heavy hydrocarbons (tars). Hydrogen production by biomass gasification can provide a sustainable renewable energy source as a clean energy carrier. The thermochemical gasification process is a technology of vast development even with technological limitations (Ramzan *et al*., 2011; Wu *et al*., 2014; Kirsanovs *et al*., 2019; Matiauda *et al*., 2015) such as the handling of the biomass input, biomass variability, physical properties of the raw material, high moisture content of the biomass (decreases the energy efficiency of the process), the generation of particulates and tar in the final products. The mathematical models for the biomass gasification process include thermodynamic equilibrium models, kinetic models (mathematical description of the kinetics of the main reactions and the hydrodynamic study between the phases), computational fluid dynamics models -CFD (provide the temperature profiles gasifier, solid and gas phases as well as a complete chemical and mechanical analysis of reactor bed fluids), generally applicable for optimizing gasifier design and artificial neural network (ANN) models, fully simulation and do not need mathematical description of the phenomena that occur in the process. Thermodynamic equilibrium models assume that the system of chemical reactions involved in the process reaches a state of thermochemical equilibrium within the gasifier reactor. The equilibrium models can predict the composition of the producer gas, the maximum yield for the optimal conditions of energy efficiency and calorific value of the syngas, considering the

specific biomass and its properties. The components react under conditions of complete mixing at steady state, in an isothermal condition. Equilibria model is suitable for fixed bed reactors and elevated temperaturas. The general assumptions are the steady state; homogeneous and invariable properties, constant and uniform temperature process, local thermodynamic equilibrium and complete chemical reactions. These equilibrium models can be stoichiometric, based on the equilibrium constants and need the reactions and species involved in the process or those known as non-stoichiometric, based on minimizing the Gibbs free energy, requiring only the elementary formula of biomass at process. Various studies and publications treat the stoichiometric and non-stoichiometric equilibrium approach (Melgar *et al*, 2007; Jayah *et al*, 2003; Khadse *et al*, 2006).

Equilibrium model formulation: The proposed model seeks to predict the concentrations of the gases of the non-condensable components of the producer gas CH4, H2O, N2, CO, CO2, H2, in the thermal gasification of pine sawdust, for different ratios of oxygen (ratio between the mass of air introduced in the reactor and the stoichiometric air mass required for complete combustión) and steam rates. The global biomass gasification equation is formulated neglecting the sulfur content and without considering the presence of tar in the producer gas. The molecule $CH_x\,O_y N_z$ is formed from the coefficients *x, y, z*, which are estimated by the stoichiometry of the reaction and respective atomic weights.

$$CH_xO_yN_z+w(H_2O)+a(O_2+3,76N_2)\rightarrow x_1H_2+x_2CO+x_3CO_2+x_4H_2O+x_5CH_4+(z/2+3,76a)N_2 \quad \text{........(1)}$$
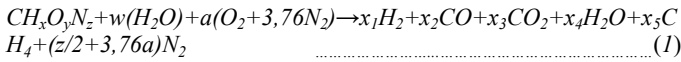
Accordingly, the molecule $CH_{1,35}\,O_{0,54}N_{0,0141}$ is obtained. The percentages given by the final analysis are represented by H, N, C, O; Accordingly, *w, a, x_1, x_2, x_3, x_4* and x_5 represent the number of moles of each component, $(z/2+3.76a)$ corresponds to the number of moles of N2 in the reaction, the moles of water are determined from the moisture content of the sawdust (obtained from proximate analysis).

$$\%moisture = \frac{wMH_2O}{MCH_xO_yN_z+MH_2O} \quad \text{..............(2)}$$

Which allows to obtain *w*.

The atomic balances of equation 1 are carried out, the nitrogen in equation 1 is balanced

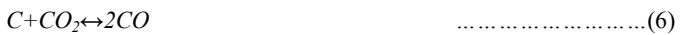Carbon balance: $1 = x_1 + x_2 + x_3$ ....(3)

Hydrogen balance: $2w + x = 2x_1 + 2x_4 + 4x_5$ ....(4)

Oxygen Balance: $y + w + 2a = x_2 + 2x_3 + x_4$ ....(5)

The resolution of these equations implies having more equations, the following reactions of the gasification process are considered.

Boudouard reaction

$C+CO_2\leftrightarrow2CO$ ....(6)

Water gas reaction

$C+H_2O\leftrightarrow CO+H_2$ ....(7)

Methanation reaction

$C+2H_2\leftrightarrow CH_4$ ....(8)

The Boudouard and water gas reactions can be combined to obtain the water gas shift reaction.

$CO+H_2O\leftrightarrow CO_2+H_2$ ....(9)

Equilibrium constants must be calculated for the reactions given by equations 8 and 9, in terms of the Gibbs energy and temperature. For

this, the energy balance is carried out, assuming that the reactants enter under standard conditions (25ºC and 1.0 atm) and that the products leave at an assumed temperature T and 1.0 atm. The energy balance is made from the enthalpies of reactants and products, under the assumption of complete combustion. In addition, the calculation equations of the pertinent entropies are included, to find the Gibbs energy values for the components of interest, which allow finding the equilibrium constants and thus completing the system of non-linear equations.

$$K_8 = e^{\int -(2g^*_{H2}+2g^*_{CH4})/RT} = \frac{x_5}{x_1^2} \quad \text{..................(10)}$$

$$K_9 = e^{\int -(2g^*_{co}-2g^*_{H2O}+g^*_{CO2}+g^*_{H2})/RT} = \frac{x_1\,x_3}{x_5x_4} \quad \text{.............(11)}$$

K_8 and K_9 are the equilibrium constants of the reactions shown in equations 8 and 9,
g^* is the Gibbs energy, *R* is the ideal gas constant and T is the temperature.

For the proposal and solution of the energy balance, the reagents enter under standard conditions of pressure and temperature, the gaseous products at the temperature according to the experimental gasification schedule, at atmospheric pressure. Under steady conditions, the energy balance is given by

$$Q_{output} = \Sigma_{reactants}\,x_g\,\left(\overline{H}^*_f + \Delta\overline{H}\right)_{reactants} - \Sigma_{products}\,x_p\,\left(\overline{H}^*_f + \Delta\overline{H}\right)_{products} = 0 \quad \text{..................(12)}$$

Where reagents (subscript *g*) includes sawdust biomass, oxygen, water (l), nitrogen with their corresponding molar coefficients (*1,a,w, 3.76a*), while for the products there is x_1 factor of the enthalpy term of H2, x_2 of CO , x_3 of CO2 , x_4 of H2 O(g), x_5 of CH4 , $(z/2+3.76a)$ factor of the enthalpy term of N2 .

$$Q_{out} = \Sigma_{reactants}\,n_R\,\left(\overline{h}^*_f + \Delta\overline{h}\right)_R - \Sigma_{products}\,n_P\,\left(\overline{h}^*_f + \Delta\overline{h}\right)_P \quad \text{....(13)}$$

With $\overline{H}^*_f$ the enthalpy of formation, $\Delta\overline{h}^-$ the enthalpy change.

Table 1. Enthalpies of formation (Perry et al,1992)

	H_2	CO	CO_2	$H_2O(l)$	$H_2O(g)$	CH_4	N_2	O_2
$\overline{H}^*_f(\frac{kJ}{kmol})$	0	-110.530	-393.530	-285.830	-241.820	-74.850	0	0

In the case of sawdust biomass, it is calculated according to the expression

$$\overline{H}^*_{fsawdust} = Lower\ calorific\ value + \Sigma_p\,x_p\,\left(\overline{H}^*_f\right)_p \quad \text{.............(14)}$$

The lower calorific value is of 438417,45 kJ/Kmol, $\left(\overline{H}^*_f\right)_p$ the enthalpy of formation of the *p*(products), in kJ/Kmol. Assuming a complete combustion reaction for sawdust biomass

$$CH_xO_yN_z+ \alpha(O_2+3,76N_2)\rightarrow\beta\ CO_2+\delta H_2O+\gamma N_2 \quad \text{..................(15)}$$
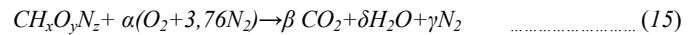
From the balance of this equation, the values for *α, β,δ,γ*.

The enthalpy calculations as a function of temperature are made by the expresión (Perry *et al*, 1992)

$$\Delta\overline{H}(T)=\int_{T_0}^T \overline{c}_p\,(T)dT = \int_{T_0}^T (a + bT + cT^2 + dT^3)\,dT \quad \text{............(16)}$$

With $\overline{c}_p$ specific heat, the coefficients obtained from Perry *et al*,1992, with these values the respective enthalpic terms are calculated for use in (12)

To determine the equilibrium constants K_8 and K_9, equation (*17*) is used to find the Gibbs energy

$$\Delta \bar{g}^* = \Delta H - T \Delta S^* \qquad \qquad \text{.................(17)}$$

Therefore, the entropy of the products at temperature T and at T_0 of the reactants must be calculated through expression (Perry *et al*, 1992).

$$\Delta \bar{S}^*(T) = \int_{T_0}^{T} \frac{c_{p(T)}}{T} dT = a \ln\left(\frac{T}{T_0}\right) + b(T - T_0) + \frac{c}{2}(T - T_0)^2 + \frac{d}{3}(T - T_0)^3 + \bar{S}^* \qquad \text{.................(18)}$$

With $\bar{S}^*$ the standard entropy values, so that the Gibbs energy values can be calculated and therefore the constants K_8 and K_9 to complete the system of nonlinear equations to be solved by software script.

METHODOLOGY

Process equipment: The gasification unit, Figure 1, is made up of the main reactor and its material storage, dosing and transport system as well as handling devices and accessories for the measurement and control of variables. The sawdust storage container, to feed the reactor, is a cone-shaped hopper with a diameter of 188.6 mm and a height of 484.6 mm, built with 1 mm thick AISI 310 stainless steel sheet. The transport to the gasifier is carried out by means of endless screws connected to the outlet of the hopper, which lead the sawdust to a vertical tube (transparent closed). The sawdust slides gravitationally until it enters the reactor, a mechanical action carried out by a feeding piston inserted in an inclined stainless steel tube. The dosing motor is of the stepper type, governed by an Arduino system that regulates the motor pulses to control the feeding speed. The gasifier has two differentiated parts: the bed and the free zone. The bed (reaction zone) is 536 mm high and has an internal diameter of 56 mm, limited at the bottom by a grid where the sawdust falls. The free zone is a widening of the primary tube with an internal diameter of 90 mm and a height of 217 mm and fulfills the function of avoiding the entrainment of the particles in the bed and favoring the mixture of the gas, increasing the residence time, which represents the possibility of a post gasification chamber, with secondary air inlet.
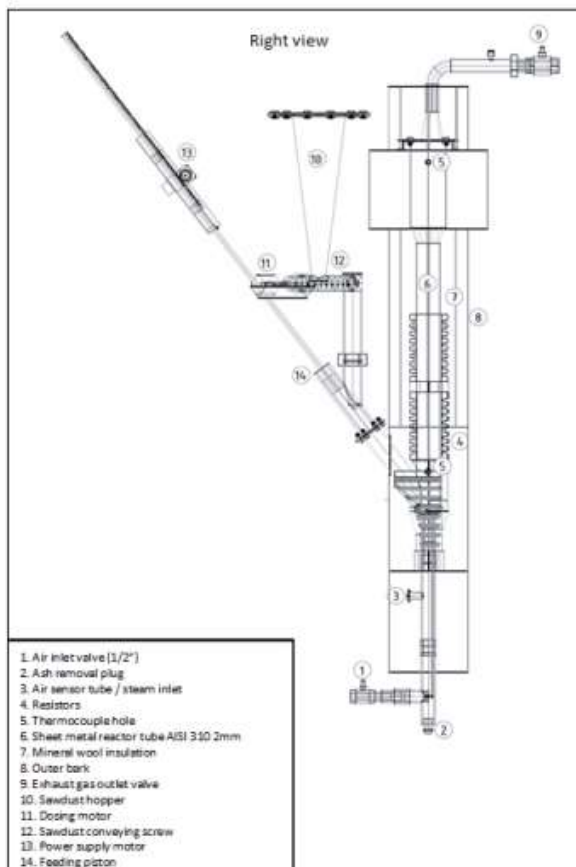

1. Air inlet valve (1/2")
2. Ash removal plug
3. Air sensor tube / steam inlet
4. Resistors
5. Thermocouple hole
6. Sheet metal reactor tube AISI 310 2mm
7. Mineral wool insulation
8. Outer bark
9. Exhaust gas outlet valve
10. Sawdust hopper
11. Dosing motor
12. Sawdust conveying screw
13. Power supply motor
14. Feeding piston

Figure 1. Sketch of the gasifier system

The heating of the gasifier is carried out by a resistive system, resistances (Kanthal A-1 wire) inserted in cylinders made with a mixture of 70% clay and 30% crushed ceramic. The total power available is 2.1 Kw. The bed and the free zone are thermally insulated with a 25.4 mm thick ceramic blanket. The set (reactor, heating elements, insulation) is wrapped in a steel casing painted with epoxy paint, mounted on a metal ring structure. The speed of the air is measured with an anemometer-flow meter arranged in the lower part of the gasifier, modifying the free sections to adapt the inlet flow. Steam generation is carried out in a container heated by resistances and with an output bypass to the reactor and purge in a PPN pipe, with adequate production capacity for the steam / biomass ratios of the feeding system. Figure 2 shows a schematic picture of the movement of fluids and materials.
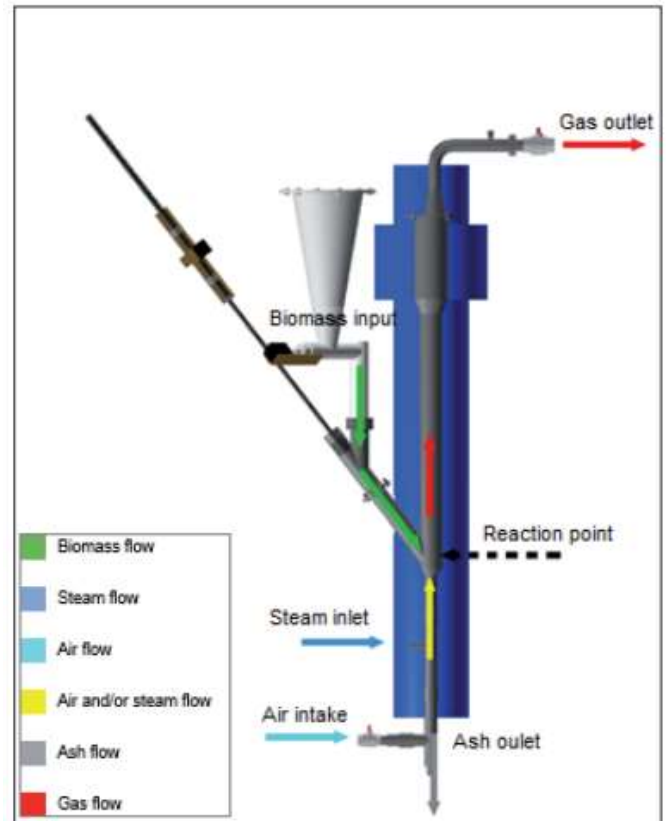

Figure 2. Biomass-fluid flows

For the control system, there is an Eaton Easy 822 DC-TC PLC model to which two Novus TxRail transducers are connected to their respective type K thermocouples, to control the reaction temperature and detect the gas mixture temperature. Gas sampling is carried out with a 500 ml Tedlar bag fitted with a flexible aspirator and a glass rod to access the gas outlet, at a temperature of approximately 350 oC. The bag is in a container that acts as a vacuum chamber.

Experimental procedure: The biomass is obtained from a medium-scale sawmill in the city of Posadas. Sawdust is selected from the twin endless, multiple circular and edger saws, which are part of the log transformation line. The sawdust, before storage, is homogenized outside on a flat surface. The determination of the moisture content of the sawdust is carried out by the weight difference process. With the wet and dry weights, the moisture content on a dry basis of 110% of the original sample is obtained. Sieves No. 8 and No. 5 (2.38-4.00 mm respectively) are used for classification and subsequent oven drying. This fraction represents 65% of the total collected, and the fractions are discarded, which, due to their size, make their handling difficult. The classification is made for a moisture content on a dry basis of 10%. The basic density of the sawdust is determined by the weight / volume ratio, the sample being previously dried at 103 oC for 24 h. Average values of basic density of 370 kg / m^3 are obtained.

Process experiences: Once the operating temperature of the gasifier reactor, selected by the controller, is reached, the sawdust stored in the hopper is fed to the reactor at the height of the reaction zone grid. The gaseous product outlet tube has a sampling point, located in the section after the solids separator cyclone. The capture of the samples is carried out by the online method, using Tedlar bags for their chromatographic analysis. To determine the concentration of the producer gas components, a SRI GC 310C gas chromatograph is used, with a thermal conductivity detector and a RESTEK ShinCarbon ST packed column with carrier gas (He).

Table 2. Composition of sawdust

Sawdust composition %weight					
C	H	O	N	S	H_2O
51,80	6,10	41,19	0,30	0,01	10,00

The average operating levels for the experimental activities are as listed:

- Sawdust feeding: up to 0.4 kg of sawdust / h. Sawdust moisture: 10% dry basis.
- Superficial velocity of the gasifier (air): 0.06-0.12 m/s, for different oxygen rates, steam flow: 0.5-1 by weight of steam / sawdust.
- Gasifier reactor temperature: 750 -850 ºC.

The ultimate analysis of the sawdust is shown in Table 2.

RESULTS AND DISCUSSION

The Figures 3,4 and 5 show the concenrations (%V/V) of the gases in the producer gas mixture, varying the gasification temperature and the oxygen rate (OR). The equilibrium values obtained by the model simulation are compared with the experimental results, for identical process conditions.
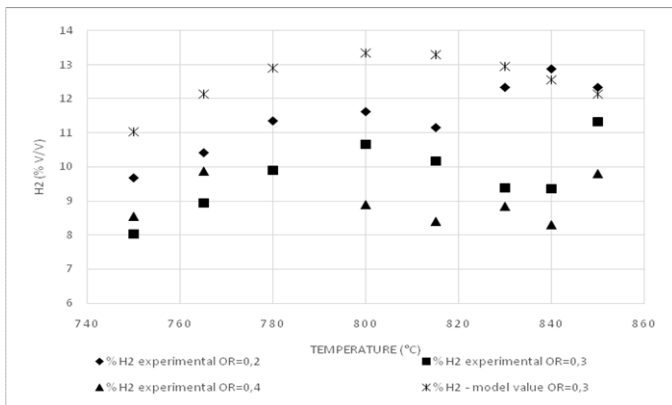

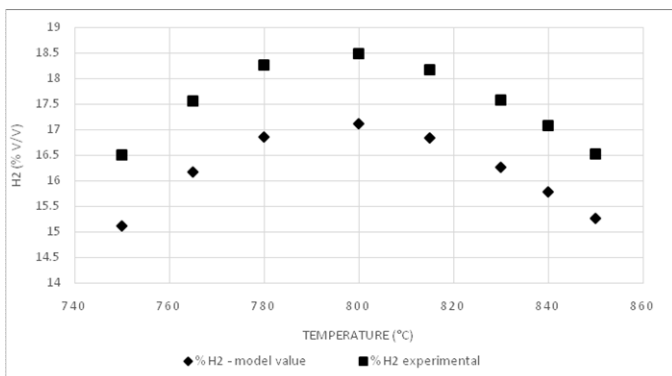**Figure 3. H2 concentrations (in producer gas) at different OR (oxygen ratio)**

Figure 3. H2 concentrations (in producer gas) with steam fed

The simulation is carried out using the program in the Octave environment, the graphical user interface for loading data and generating results, is shown in figure 6. The program requests the input of the values (by weight, from the last analysis) of C, H, O,N,S of the sawdust as well as the moisture content of the sawdust, its lower calorific value, for the gasification temperature (isothermal), oxygen rate used in the experience and the possibility of using steam as an oxidizer. The program contemplates the presence or absence of char at the end of the process. Since a system of nonlinear equations is to be solved, the program employs a trust region algorithm. The outputs are the compositions in equilibrium of the gaseous species H2, CO, CO2, H2O, CH4 and N2, generating data files for each combination of variables that are compared with the experimental values obtained, concluding in the calculation of the respective RCM (root mean square error).
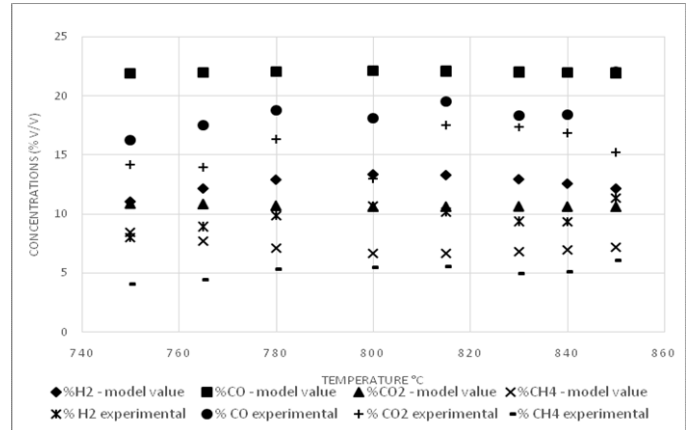

Figure 4. Experimental concentrations and according to the theoretical model of H2, CO, CO2 and CH4 for OR = 0.3

From the results plotted for high temperature values, close to 800º C (1073 K), for example, the equilibrium is shifted in the direction of formation of CO and H2, with less tendency to form CO2 and H2O, with lower values of oxygen rate (only air as oxidizer). This trend is similar to that observed in the experimental values. The differences between model values and experimental values, in the concentrations of the gaseous species of producer gas, are reduced in the temperature range close to 750ºC and 850 ºC with values of root mean square error (RMSE) between 2,9-5,1. The equilibrium model overestimates the formation of CO, CO2, and underestimates that of CH4.
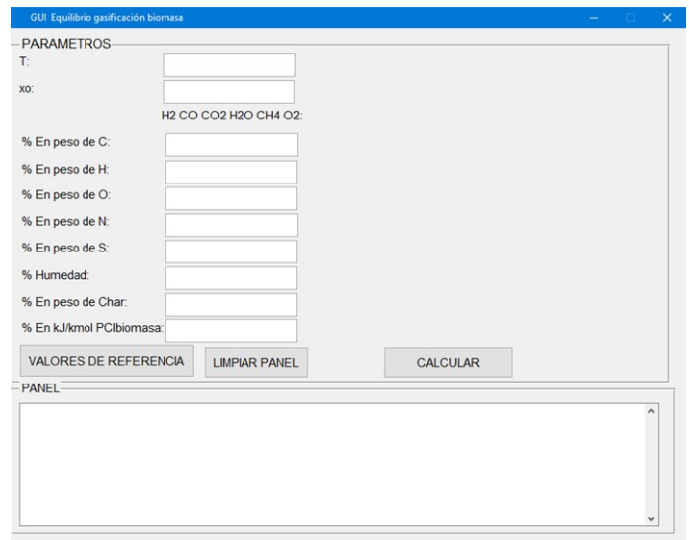

Figure 5. Graphical interface Equilibrio gasificación biomasa

CONCLUSIONS

For the production of gas containing hydrogen, the thermochemical gasification with air and steam of pine sawdust, the stoichiometric

equilibrium model was developed, using air and steam as oxidizing agent, in a fixed-bed reactor on a pilot plant scale, covering suitable OR 8oxygen rate) range for gasification. This model and its simulation showed acceptable predicted values when compared with the experimental values carried out for identical process conditions used. Regarding the scientific literature, these values present greater or lesser agreement, originating from different particular conditions obtained. Resulta oportuno, a próximos trabajos, ampliar el estudio de los modelos de equilibrio, implementando modificaciones y ajustes.

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