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Hydrogen Product of Gasification of Sawdust

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Abstract: A theoretical experimental work is developed for the production of gas rich in hydrogen content, based on a model of isothermal gasification of sawdust pellets in a reactor in a fluidized bed regime, simulated through an application in Matlab environment, analyzing in particular the influence of the operating temperature in the range 750 °C-850 °C, oxidizing / fuel ratio (for air and steam) and obtaining kinetic parameters. The simulation model presents good agreement with the experimental values, showing the increase of the hydrogen content with the increase of the temperature as with the greater reducing atmosphere and with the introduction of steam in the process.

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1. INTRODUCTION

Due to the rapid fossil energy consumption and involved environmental contamination, it is urgent to find renewable sources of alternative energy partly or completely, (Mcelroy, 2011). Between these sources the vector hydrogen receives importance, finding its difficulties in the transport, liquefying and sure manipulation, configuring what is known as hydrogen economy (Li et al., 2013) and (Ming et al., 2016).

The hydrogen production for biomass gasification can provide a sustainable renewable energy source like a bearer of clean energy, turning out to be suitable to study how to raise the level of yield of hydrogen during the biomass gasification, although the direct biomass combustion brings prepared problems as deposition of ashes and damage in the combustion device, (Li et al., 2013) and (Chan and Tanksale, 2014).

The biomass gasification qualifies in the gasification with air, with oxygen, with steam, with hydrogen and the compound gasification, according to agent of gasification used in the process (Evans and Milne, 1997). When steam is adopted like gasification agent, not only there are reduction reactions between steam and carbon, but also reform reactions between the steam and the gas product as CH_4 and unsaturated hydrocarbons. In the process, the gas product consists principally of H_2, CO, CO_2. As the content of H_2 and alkanes gases is high in the gas product, the heating value of the product gas is also relatively high, (Ming et al., 2016). The design of the gasifier plays an important role in the process, being a desirable high reaction speed and adapted so that the profiles of temperature and conversion are uniform along the reactor, typical characteristics of the fluidized bed regime. Although a significant work has been realized to investigate the effect of the main parameters of gasification in the valuation of production of hydrogen, there exists little information published about the efficiency of thermodynamic conversion, (Gil et al., 1999) and (Milne et al., 1998).

All the thermal processes of conversion (pyrolysis - gasification) involve the formation of particulates and tars, a complex miscellany of aromatic and polyaromatic condensable hydrocarbons, (Dascomb et al., 2013), (Thin et al.,1996).

This work is of experimental theoretical characteristic based on a model of the gasification of pellets of sawdust in a reactor in fluidized bed regime, simulated across an application in Matlab environment and comparing with the obtained experimental values, analyzing particularly the influence of the temperature of operation and the oxidizing / combustible relation (for air and steam) principally the hydrogen gas content in the miscellany product.

2. MATERIALS AND METHODS

2-1: Gasification model:

The used model, (Matiauda and Benítez 2015) bases on the theory of two phases (bubble – emulsion),in fluidized bed regime. For the simulation of the model there is included a set of ordinary differential equations for the mass balances, adopting isothermal conditions. The model is completed by study and calculation of hydrodynamic parameters participants in the process.

The differential equations of balance of mass are referred to the components C, CO, CO_2, H_2O, O_2, H_2 and CH_4, in two phases, bubble and emulsion, Petersen and Werther (2005).

The reactions of gasification and heats of formation to 25 ºC representative:

$C + O_2 \rightarrow CO_2$ -408.4 kJ/mol (exotermic) (1)

Reaction of gasification of the char
$C + CO_2 \rightarrow 2CO$ +172.0 kJ/mol (endotermic) (2)
Reaction of Boudouard
$C + H_2O \leftrightarrow CO + H_2$ +131.0 kJ/mol (endotermic) (3)
Water gas primary reaction (WG)
$CO + H_2O \leftrightarrow CO_2 + H_2$ -41.1 kJ/mol (exotermic) (4)
Water gas shift reaction (WGS)
$CH_4 + H_2O \leftrightarrow CO + 3H_2$ +206.3 kJ/mol (endotermic) (5)
Methane reforming reaction

The first three reactions are heterogeneous, they happen in the emulsion phase; the last two reactions are homogeneous and bubble and emulsion happen in the phases.

2-2: Simulation:
The mathematical model is simulated across an application in environment Matlab like a graphic user interface (GUI).
The text boxes request the initial values of concentrations of O_2, CO_2, CO, H_2O, H_2, CH_4, all in mol/m^3, C (value of volatile carbon, according to the biomass and its composition), y14 and y15 (^oC) there represent the temperatures (isothermal model), diameter of particle (solid bed), volume of the gasifier, the value of porosity of minim fluidization, the time adopted for the simulation (in seconds) and the errors for the numerical technique ODE 45 (Matlab, 2015). The vector of Kbe, coefficient of transference of mass bubble - emulsion, is calculated for the process conditions in accordance with the hydrodynamic model. Chosen the time for the experience, in seconds, are obtained the final concentrations of O_2, CO_2, CO, H_2O, H_2, CH_4, all in % v/v, C (coal), information also available in individual graphs for each of the species of O_2, CO_2, CO, H_2O, H_2, CH_4, in % v/v and C, as its expression in percentages.

2-3: Experimental procedure:
As soon as there was reached the regime temperature of the gasifier reactor , selected by means of the controller, the feeding of the biomass (pellets of sawdust) it is carried out on the top part of the reactor. In the tubes of exit of the gas product is available sample point, located in the section after the solid separator cyclone. The capture of the samples is realized by on-line method and its collection in bags Tedlar for its chromatographic analysis. For the analysis of the products of the gasification of the carried out experiences, there is used a gases cromatograph SRI GC 310C, with detector of thermal conductivity and packed column RESTEK ShinCarbon ST 80/100 GO 2,00mm, length 2m, with gas carrier (He), being used gas mixture pattern provided by the firm Air Liquide.

2-3-1: Laboratory equipment:
Figure 1 shows scheme of the set equipment used where they are indexed according to Controller gasifier (1), Control board (2), Gasifier reactor (3), Biomass feeder (4), Oxidant income (5), Cyclone (6), Sampling device(7)

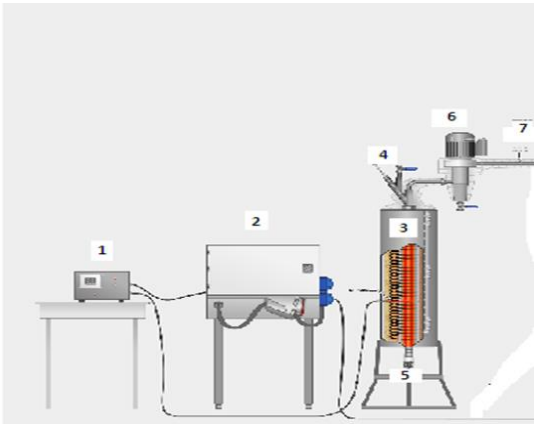


Figure (1): Equipment scheme

The air feeding is carried out in the low part of the reactor through an impeller, variable speed. To handle the mixture air - steam, there is mounted a secondary system of generation of steam. The gasification reactor is a stove pipe of 45mm of diameter, in stainless steel, (high 1 m), thermal camera of isolation of ceramic, covered fibre of sheet DDN 18 finished with epoxi. The termocouples connected to a programmable controller temperatures, are of type K annoyed, the controler is PID-Programador, allowing the potency control by modulation of pulse width.
The raw material biomass consists in pellets of sawdust, provided by commercial company , with advantages like high calorific value (19.23 MJ/kg), content of more uniform moisture (10-15 % bs), compactness and homogeneity (diameter 6.2 mm).
The solid adjuvant is silica sand, classified under the status 20, 35, 40 and 45 M, choosing the fraction of 35M for its suitable behavior in the tests fluid dynamics carried out.

For the experimental activities there were selected certain operative levels of the process of gasification, including the necessary ones to execute the simulation.
• Biomass feed: up to 0.4 kg biomass / h. Moisture of the biomass: 10-15 % d.b.
• Diameter of particle of biomass (pellets): 6.2 mm.
• Bed sand: up to 2 cm high, sieve size 35. Porosity of the bed: 0.3-0.4
• Gasifier agent speed (air): 0.06-0.12 m/s superficial velocity, steam flow 0.1-0.4 kg/h. Minimum fluidization velocity: 0.02-0.04m/s
• Reactor temperature gasifier: 750-800-850 ºC

3. RESULTS AND DISCUSSION

The results obtained experimentally and by means of the simulated process they are detailed next, in format of tables and graphs.

Table (1): Simulated and experimental values for temperature of 750 ºC

Products	*Experimental %*	*Simulated %*	*Square chi (χ^2)*
H_2	29.60± 1	26.90	0.246
CO	65.70± 1	65.18	0.004
CO_2	2.10± 0.1	1.05	0.525
CH_4	1.05± 0.2	0.08	0.896
O_2	1.50± 0.2	0.56	0.589

The simulated percentage of water is 0.031 %.
Kbe = [13.6 13.6 13.21 13.21 14.5 14.5 15.9 15.9 26.6 26.6 14.7 14.7] s^{-1}, pairs bubble-emulsion.

Tabla (2): Simulated and experimental values for temperature of 800 ºC

Products	*Experimentals %*	*Simulated %*	*Square chi (χ^2)*
H_2	32.80± 1	32.00	0.019
CO	51.80± 1	53.70	0.069
CO_2	0.62± 0.1	2.50	5.700
CH_4	2.48± 0.2	0.54	1.517
O_2	8.35± 0.2	7.10	0.187

The simulated percentage of water is 0.11 %.
Kbe = [14.4 14.4 12.2 12.2 14.4 14.4 15.9 15.9 26.5 26.5 14.6 14.6] s^{-1}, simulation time: 15 s; air flow: 0.28 m^3/h.

Table (3): Simulated and experimental values for temperature of 850 ºC

Products	*Experimentals %*	*Simulated %*	*Square chi (χ^2)*
H_2	35.60 ± 1	32.5	0.269
CO	56.20± 1	56.9	0.008
CO_2	2.20± 0.2	2.4	0.018
CH_4	1.10± 0.1	0.6	0.227
O_2	4.68± 0.2	6.6	0.829

The simulated percentage of water is 0.11 %, simulation time: 15 s; air flow: 0.28 m^3/h
Kbe = [14.9 14.9 12.6 12.6 14.9 14.9 16.5 16.5 27.4 27.4 15.2 15.2] s^{-1}

The values of the statistician χ2 mark coherence between simulated - experimental values except for CO_2 where there is observed difference between the obtained percentages. The graphs concentration (% v/v) - time (s) for the different gaseous species generated by the application for the temperature of operation of 850 ºC, are shown in figures 2 to 6, with vertical axis in % v/v and horizontal axis in seconds.

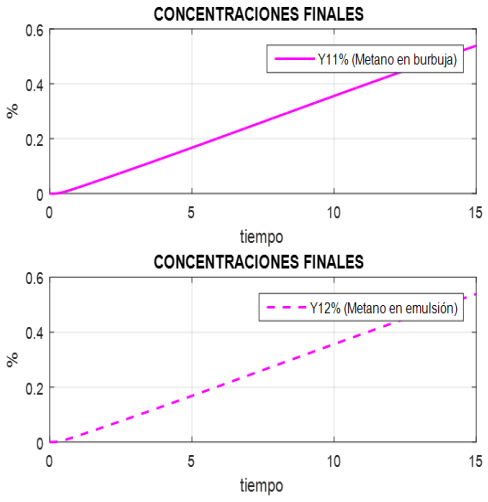


Figure (2): Methane evolution(simulated)

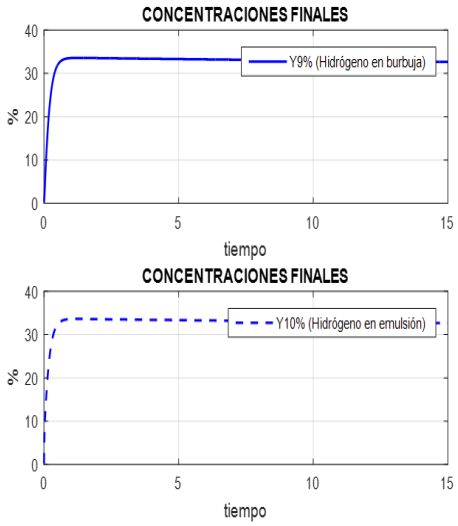
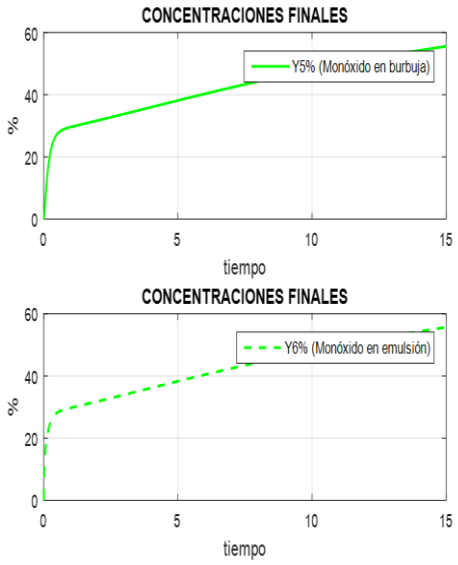


Figure (3): Hydrogen evolution(simulated)



Figure(4): Monoxide evolution (simulated)

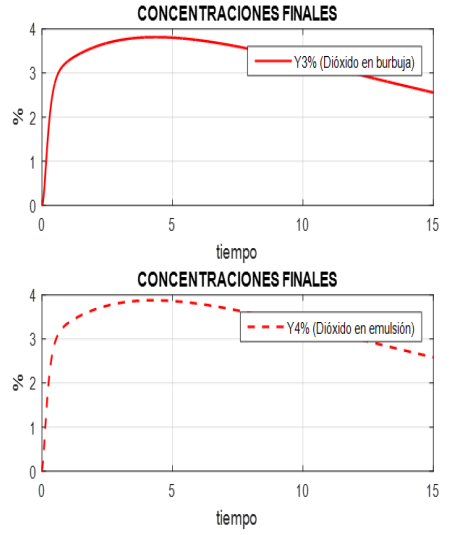


Figure (5): Dioxide evolution (simulated)

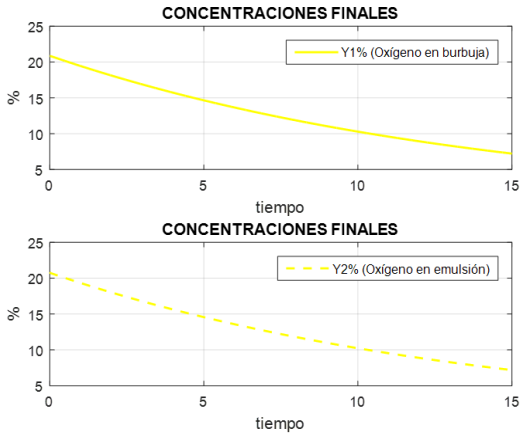


Figure (6): Oxygen evolution (simulated)

Of the results obtained (stage 1,2 and 3) hydrogen highlights the increase in the gas content with the temperature, representing the temperature of 850 ºC the thermal operative level adapted by the biggest content in gas hydrogen as in the best operative behavior in the experiences carried out in plant.

3-1: Influence of the valuation of oxygen in the gasification stage:

A considered importance parameter in the biomass gasification with air is the rate oxygen, which reflects the air deposited with regard to the stoichiometric value necessary for the finished combustion of the biomass fed to the gasifier. Oxygen rate levels are achieved by varying the temporary mass input of the biomass. The obtained results are indexed at the level of temperature of 850 ^{o}C employee in the gasification experiences. Using a routine of the interface for a speed of the air of 0.12 m/s and elementary composition of the biomass given for $CH_{1.61}O_{0.68}$, there are generated the results expressed in the Table 4.

Table (4): Influence of oxygen rate

Air velocity (m/s)	*Biomass (kg/h)*	*H_2%*	*CO%*	*CO_2%*	*CH_4%*	*Oxygen rate*
0.12	0.010	35.6	56.2	2.2	1.1	0.195
0.12	0.006	34.5	55.5	2.8	0.9	0.44
0.12	0.008	33.7	54.1	3.1	0.8	0.324

From the table it is displayed that in the range oxygen rate studied, to major value of rate of oxygen (less reductive condition), descending order in the column of the table 4, decreases the content of the gases H_2, CO and CH_4, increasing the content of CO_2, since the increase in the oxygen content of the oxidizer favors oxidized species.

3-2: Steam effect on content of hydrogen and gaseous products:

The influence of the steam in the feeding with the biomass is studied determining the kinetic constant for the gasification process.

Studied level of temperature: 850 ºC for gasifier reactor.

Feeding biomass: 0.4 kg/h, dry basic moisture: 15 %.

Relations v/b (steam / biomass): 0.4-0.46-0.7-0.9.

RE: stoichiometric yield of hydrogen, obtainable considering the reactions (6) and (7) and its stoichiometry.

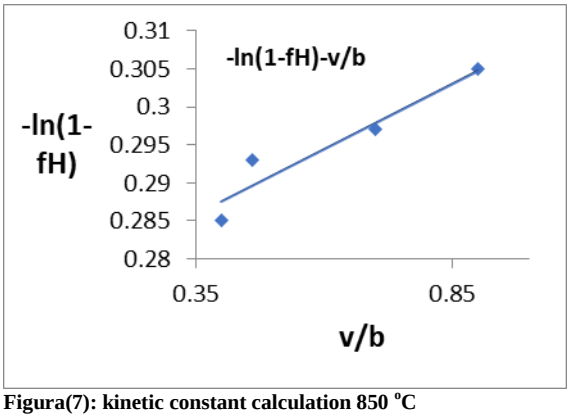
$$CH_{1.61}O_{0.68}+0.32H_20 \rightarrow 1.125H_2+CO \quad (6)$$
$$H_2O+CO \rightarrow H_2+CO_2 \quad (7)$$

In tabla5 the yield is used in hydrogen Yh, for the different relations steam to biomass (v/b) (kg steam/kg biomass); fH (mol hydrogen / biomass / stoichiometric yield of hydrogen calculated according to Yh/RE), shaping the kinetic equation as

Tabla 5. Table of values for constant kinetic calculation

H_2 (%)	*Y_h ($molH_2$/kg biomass)*	*$fH=Y_h/RE$*	*-ln(1-fH)*	*v/b*
36.0	21.60	0.248	0.285	0.40
36.7	22.02	0.254	0.293	0.46
37.2	22.32	0.257	0.297	0.70
38.1	22.86	0.263	0.305	0.90

The figure 7 represents ln graph (1-fH)-v/b for the temperature of 850 ^{o}C, based on the kinetic equation (8), in this case with a value of kH of 0.0345, which gives a measurement of the yield of hydrogen in the gasification with steam, which from the value showed in the table 5 demonstrates a progress (from 36.0 % to 38.1 %) in the content with regard to the oxidizing air (35.6 %) for equal temperature.



Figura(7): kinetic constant calculation 850 ^{o}C

From the optics of the influence of the transference of mass, turn of the simulation demonstrates insignificant change in the concentration of the gases of the gaseous mixture product, fundamentally of that of interest that is the hydrogen content, turning out to be despicable the change in the coefficients of transference of mass, indicating the thermal effect as the gravitating one for the levels of concentration of the gas product in the proposed model.

4. CONCLUSIONS

- The values obtained from the concentrations of the gaseous species in the gas product of the gasification process, by means of the simulation model, are in agreement with them at the experimental level, for the chosen temperature levels (750-800-850 ^{o}C), evidenced through the appropriate statistic, taking into account the broad simplifying assumptions involved in the formulation of the model and the numerical tool for its resolution.

- Biomass gasification, with center in a gas rich in hydrogen, in consonance with the simplified model predictor, turns out to be preponderantly influenced by the levels of temperature, predominant on the transference of mass and of the hydrodynamics.

- The experimental conditions and results indicate like an ideal temperature the level of 850 ^{o}C, attending on the commitment of the increase in content of hydrogen and good functioning of the equipment.

- For the level of temperature of 850 ^{o}C, the hydrogen content in the gas product of the stage of gasification decreases with the increase of the feed of air, that is to say that this increase of content of oxygen in the oxidizing agent diminishes the ambience favoring the enrichment in hydrogen.

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