PREDICTION OF HYDROGEN PRODUCTION OF A DOWNDRAFT GASIFIER USING EQUILIBRIUM MODELING FOR DIFFERENT MOISTURE CONTENT FOR SOLID OXIDE FUEL CELL ACTION (SOFC).

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Abstract: Equilibrium modeling has been used to predict the hydrogen production in a downdraft gasifier. The composition of syngas (synthesis gas), the lower heat value (LHV), hence, the cold efficiency of gasifier (▯cg) have been determined. The effects of moisture content (MC) have been investigated for temperature of gasification 800 °C. The predicted values compare reasonably well with experimental data available in literature. The amount of hydrogen and CH4 increase with increase in the range of moisture content in the biomass (eucalyptus) investigated. The LHV and cold efficiency of gasifier decreases with increase in the range of moisture content. Keywords: Hydrogen, SOFC, Prediction, Gasification, Moisture Content.

1. INTRODUCTION

Concern over the depletion of fossil fuels in the near future and an increasing awareness of energy conservation have drawn worldwide attention. Present energy resources, such as coal, oil and gas, are being used at an accelerating rate with fear of depletion in the next century, although coal might be an exception. Apart from this fear, there is also an increasing awareness about environmental pollution and ways of minimizing the same. There are nine general sources of energy on Earth. They are: solar, biomass, wind, wave, hydro, geothermal, nuclear and fossil. Except of the last three the remaining six are generally called renewable sources of energy, as they are not depleted with time. One of the most promising renewable sources of energy is the energy from biomass; utilization of biomass is very important source of energy in many parts of the world, especially for rural zones. Biomass gasification treats the solid feed material in a reactor such that virtually all of it is converted into fuel gas with lower heat calorific values typically 3-6 MJ/Nm3 with most of the energy available from H2 and CO. After cleaning, this gas can be used to run gas turbine, internal combustor motors, fuel cells, etc. In a biomass gasifier, a reaction occurs through a partial combustion with air (less than stoichiometric) to produce a mixture of combustible gases (CO, H2, CH4) diluted in other inert gases (CO2, N2, H2O), some of which are undesired and accompanied with other hydrocarbons of high molecular weight (tars) and inter solid particles. The equilibrium model has been used by many researchers for the analysis of the gasification process. Those models were based on the minimization of Gibbs free energy. This is a constrained optimization problem that generally uses the Lagrange multiplier method. An understanding of some mathematical theories is necessary for solving optimization and no-linear equationsproblems. The other kind of equilibrium model is based on equilibrium constant. Zainal et al (2001) used the latter type of equilibrium model to predict composition of the syngas for different biomass materials. The amount of oxygen in that model was eliminated by defining it in terms of some components in the syngas. S. Jarungthammachote et al (2007) have used a equilibrium model to predicted a reaction temperature by knowing the amount of oxygen, and vice versa. Fuel cells are electrochemical devices that directly convert the chemical energy of a fuel to electricity, water vapor and surplus heat.

Due to the direct conversion of chemical to electrical energy, fuel cells have a minimum environmental intrusion and the potential for high electrical efficiencies (35–55%), significantly higher than that of conventional power generation systems, which are Carnot limited and lose efficiency because of thermodynamic and mechanical limitations in the system (Dayton DC et al, 2001; EG-G Services, 2002; Larminie J et al, 2002; Lymperopoulos N, 2002). A single fuel cell consists of three parts: the anode, the cathode, an electrically insulating electrolyte or membrane separating the two electrodes. At the anode (negative electrode), fuel gas (H2, CO, CH4) is fed and then diffuses towards the anode/electrolyte boundary, while an oxidant (air or oxygen) is fed continuously to the cathode (positive electrode). In the three-phase boundary (TPB) where anode, electrolyte and fuel gas coexist, the fuel components are oxidized liberating electrons as a result. Since the electrolyte is not electron conducting, electrons travel through an external circuit to the cathode, where they are accepted by oxygen atoms. Hydrogen is the most commonly used fuel in the fuel cell technology, but natural gas, biomass gasification synthesis gas, petroleum-based fuel can also be used. The hydrogen electrochemical reaction used to produce electricity in a fuel cell produces water as the only ‘‘waste’’. This chemical energy then can be converted to electricity through an electrochemical reaction that involves the oxidation of hydrogen with oxygen ions transferred from the electrolyte (anode side), obtained from the reduction of oxygen at the cathode side. The overall electrochemical reaction produces electrons and water as a waste product. SOFC operate at temperatures between 600 and 1000 °C. The electrolyte material in an SOFC is yttrium-stabilized zirconia (YSZ), a solid with a stable cubic structure and high oxide conductivity at SOFC operating temperatures. The anode material is a Ni cermet (ceramic and metal composite) (Dayton DC et al, 2001; EG-G Services, 2002; Larminie J et al, 2002; Lymperopoulos N, 2002). It contains metallic Ni for catalytic activity in an YSZ support, which adds mechanical, thermal and chemical stability and thermal. The cathode consists of mixed oxide with a perskovite crystalline structure, typicallytrontium-doped lanthanum manganite (LSM). The high operating temperatures allow higher fuel flexibility, because in the presence of enough vapor and oxygen complete oxidation is achieved, without catalytic materials being present. The operation of an SOFC fuelled with biomass gasification gas is defined by the following reactions:

$$\text{Anode:}\quad \begin{array}{l} H_2 + O^{2-} = H_2O + 2e- \\ CO + O^{2-} = CO_2 + 2e- \end{array} \tag{1}$$

$$\text{Cathode:}\, O_2 + 4e- = 2O^{2-} \tag{2}$$

2. THE MODEL

The equilibrium model assumes that all reactions are in thermodynamic equilibrium. It is expected that the pyrolysis product burns and achieves equilibrium in the reduction zone before leaving de gasifier, hence an equilibrium model can be used in the downdraft gasifier. The reactions are as follows:

$$C + CO_2 = 2CO \tag{3}$$

$$C + H_2O = CO + H_2 \tag{4}$$

$$C + 2H_2 = CH_4 \tag{5}$$

Eqs (1) and (2) can be combined to give the shift reaction

$$CO + H_2O = CO_2 + H_2 \tag{6}$$

The equilibrium constant for methane formation (K_1) (Eq. (7)) is

$$K_1 = \frac{P_{CH_4}}{(P_{H_2})^2} \tag{7}$$

And the equilibrium constant for the shift reaction (K_2) is

$$K_2 = \frac{P_{CO_2} P_{H2}}{P_{CO} P_{H_2O}} \tag{8}$$

The typical chemical formula for eucalyptus, based on a single atom of carbon, is $C_1H_{1,44}O_{0,67}$

Table 1. Ultimate analysis of eucalyptus (dry bases, weight percentages, molar fraction).

Weight Percentages						
Biomass	C	H	N	S	O	Ash
Eucalyptus	49	5,87	0,3	0,01	43,97	0,72
	Molar Fraction					
	4,08	5,87	0,02	0,0001	2,75	

The global gasification reaction can be written as follows:

$$C_1H_{1.44}O_{0.67} + wH_2O + mO_2 + 3.76mN_2 = x_1H_2 + x_2CO + x_3CO_2 + x_4H_2O + x_5CH_4 + 3.76mN_2$$

$$w = \frac{24{,}28MC}{18(1-MC)} \tag{10}$$

Where w is the amount of water per kmol of eucalyptus, m, the amount of oxygen per kmol of eucalyptus, x1, x2, x3, x4, and x5, the coefficients of constituents of the products.

$$MC = \frac{M_{H_2O}}{M_{eucalyptus}} \tag{11}$$

From the global reactions, there are six unknowns x1, x2, x3, x4, x5, m, representing the five unknowns species for the product and the oxygen content for reaction. Therefore, six equations are required, which are formulated based on the following:

Carbon balance:

$$1 = x_2 + x_3 + x_5 \tag{12}$$

Hydrogen balance:

$$2w + 1{,}44 = 2x_1 + 2x_4 + 4x_5 \tag{13}$$

$$w + 0{,}72 = x_1 + x_4 + 2x_5 \tag{14}$$

Oxygen balance:

$$w + 0{,}66 + 2m = x_2 + 2x_3 + x4 \tag{15}$$

$$K_1 = \frac{x_5}{x_1^2} \tag{16}$$

Shift reaction:

$$K_2 = \frac{x_1 x_3}{x_2 x_4} \tag{17}$$

The equation for the heat balance for the gasification process, assumed to be adiabatic, is:

$$\begin{aligned} &H^0_{feucalyptus} + w(H^0_{fwater(l)} + H_{(vap)}) = x_2 H^0_{fCO} + x_3 H^0_{fCO2} + x_4 H^0_{fH2O(vap)} + x_5 H^0_{fCH4} \\ &+ \Delta T(x_1 cp_{H2} + x_2 cp_{CO} + x_3 cp_{CO2} + x_4 cp_{H2O} + x_5 cp_{CH4} + 3.76 m cp_{N2} \end{aligned} \tag{18}$$

Where $H^0_{feucalyptus}$, is the heat of formation of eucalyptus, $H^0_{fwater(l)}$, the heat of formation of liquid water, H_{vap}, the heat of vaporization of water, $H^0_{fH2O(vap)}$, the heat of formation of water vapor, H^0_{fCO}, H^0_{fCO2}, H^0_{fCH4}, are heats of formation of the gaseous products, cp_{H2}, cp_{CO}, cp_{CO2}, cp_{H2O}, cp_{CH4}, cp_{N2}, are specific heats of the gaseous products, T_2, the gasification temperature at the reduction zone; T_1, the ambient temperature at the reduction zone.

Eq. (18) can be simplified to be:

$$\begin{aligned} &dH_{eucalyptus} + wdH_{H_2O(l)} = x_1 dH_{H_2} + x_2 dH_{CO} + x_3 dH_{CO_2} + x_4 dH_{H_2O(vap)} + x_5 dH_{CH_4} \\ &+ 3{,}76 m dH_{N_2} \end{aligned} \tag{19}$$

The system equations (12), (14), (15), (16), (17) and (19) is solved using The Newton-Raphson Method. The lower calorific value for any biomass material can be determined if the ultimate analysis Is known. The heating value can be determined experimentally by a bomb calorimeter, and according to Channiwala et al, 2002, the LHV for eucalyptus can be calculated from the following equation:

$$LHV = 0{,}3491C + 1{,}1783H + 0{,}1005S - 0{,}1034O - 0{,}0151N - 0{,}0211ASH \tag{20}$$

$$dH_{(gas)} = H_f^0 + \Delta H \tag{21}$$

Where dH, is the heat of formation and ΔH, is enthalpy change

$$\Delta H = \Delta T C_{p(g)} \tag{22}$$

$$dH_{H_2O(l)} = H^0_{f\,H_2O(l)} + H_{(vap)} \tag{23}$$

$$dH_{eucalyptus} = H^0_{feucalyptus} \tag{24}$$

At constant pressure, the specific heat can be written as:

$$C_p = (\frac{\partial H}{\partial T})_p \tag{25}$$

$$\Delta H = C_{pmh}(T_2 - T_1) \tag{26}$$

The dependence of average specific heat on temperature is given by an empirical equation and the most simplified version is (Robert HP et al, 1984):

$$C_{pmh} = R(A + BT_{am} + \frac{C}{3}(4T_{am}^2 - T_1T_2) + \frac{D}{T_1T_2} \tag{27}$$

Where $T_{am} = (T_1+T_2)/2$ is the arithmetic mean temperature and A, B, C and D are the constants for the properties of the gases concerned, C_{pmh}, is the average specific heat over temperature change.

Table 2. Heat capacities (constants A, B, C and D) (Robert HP et al, 1984)

Chemical species	tmax	A	10^3B	10^6C	10^-5D	Cp (kJ/kmolK)	ΔH (kJ/kmol)
CH_4	1500	1,702	0,009081	-0,000002164		56,55	43821,29
H_2	3000	3,249	0,000422		8300	29,63	22961,31
CO	2500	3,376	0,000557		-3100	31,16	24146,13
CO_2	2000	5,457	0,001047		-115700	48,33	37448,84
N_2	2000	3,28	0,000593		4000	30,75	23829,66
H_2O	2000	3,47	0,00145		12100	37,43	29001,74
C	2000	1,771	0,000771		-86700	16,87	13068,25

Table 3. Gibbs functions and Heat of formation at 298.15 °K

Chemical species	Phase	ΔG^{o}_{f298} (kJ/kmol)	ΔH^{o}_{f298} (kJ/kmol)	dH (kJ/kmol)
H2O	g	-228572	-241818	-212816,26
H2O	l	-237129	-285830	-256828,26
CO2	g	-394359	-393509	-356060,16
CO	g	-137169	-110525	-86378,87
CH4	g	-50460	-74520	-30698,71
H2	g	0	0	22961,31
O2	g	0	0	
N2	g	0	0	23829,66

The following equation gives the effect of temperature (T) on the equilibrium constant (k). If ΔH^{o} (heat of formation) is negative, that is if the reaction is exothermic, the equilibrium constant will be reduced if the temperature increases. On the contrary, k increases with T for an endothermic reaction.

$$\ln(k) = \frac{-J}{RT} + (\Delta A)\ln(T) + \frac{\Delta B}{2}T + \frac{\Delta C}{6}T^{2} + \frac{\Delta D}{2T^{2}} + I \tag{28}$$

$$J = R\left(\frac{\Delta H^{0}}{R} - (\Delta A)T - \frac{\Delta B}{2}T^{2} - \frac{\Delta C}{3}T^{3} + \frac{\Delta D}{T}\right) \tag{29}$$

$$I = \frac{\Delta G^{0} - J + RT(\Delta A\ln(T)) + RT\left(\frac{\Delta B}{2}T\right) + RT\left(\frac{\Delta C}{6}T^{2}\right) + RT\left(\frac{\Delta D}{2T^{2}}\right)}{-RT} \tag{30}$$

In this paper, two equilibrium equations are required to determinate the equilibrium constants k_1 and k_2. k_1 is the equilibrium constant for the reaction of Eq. (16), ΔA, ΔB, ΔC and ΔD can be obtained from the data of heat capacity and is solved as follows:

$$\Delta = CH_4 - C - 2H_2 \tag{31}$$

$$\Delta A = A_{CH_4} - A_C - 2A_{H_2} \tag{32}$$

$$\Delta B = B_{CH_4} - B_C - 2B_{H_2} \tag{33}$$

$$\Delta C = C_{CH_4} - C_C - 2C_{H_2} \tag{34}$$

$$\Delta D = D_{CH_4} - D_C - 2D_{H_2} \tag{35}$$

For the equilibrium constant k_2:

$$\Delta = CO + H_2O - CO_2 - H_2 \tag{36}$$

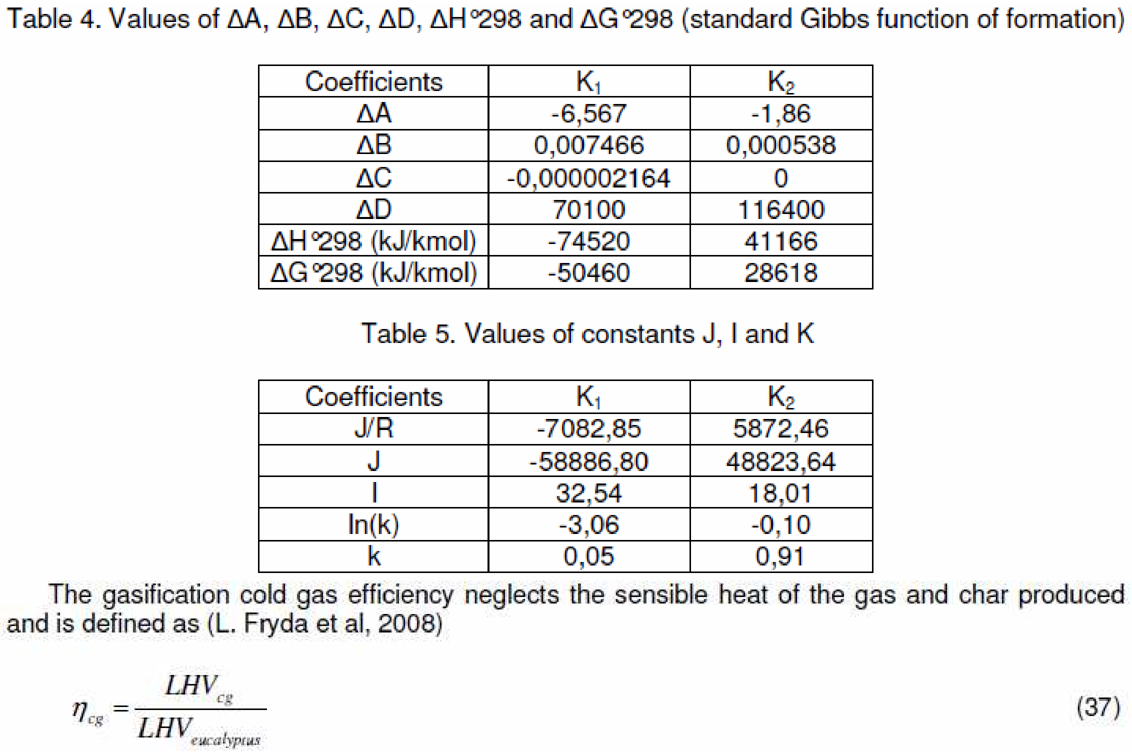

Table 4. Values of ΔA, ΔB, ΔC, ΔD, $\Delta H°298$ and $\Delta G°298$ (standard Gibbs function of formation)

Coefficients	K_1	K_2
ΔA	-6,567	-1,86
ΔB	0,007466	0,000538
ΔC	-0,000002164	0
ΔD	70100	116400
$\Delta H°298$ (kJ/kmol)	-74520	41166
$\Delta G°298$ (kJ/kmol)	-50460	28618

Table 5. Values of constants J, I and K

Coefficients	K_1	K_2
J/R	-7082,85	5872,46
J	-58886,80	48823,64
I	32,54	18,01
ln(k)	-3,06	-0,10
k	0,05	0,91

The gasification cold gas efficiency neglects the sensible heat of the gas and char produced and is defined as (L. Fryda et al, 2008)

$$\eta_{cg} = \frac{LHV_{cg}}{LHV_{eucalyptus}} \qquad (37)$$

3. RESULTS AND DISCUSSION

The equilibrium model described above is used for the gasification of eucalyptus. This model allowed known a syngas composition for moisture content (0,15 and 0,30), and 800 °C of gasification temperature. The model predicted higher amounts of H2, but the predicted amounts of CH4 are lower as shown in table 6. Bacon DW et al, 1982, reported a substantially higher amount of CH4 in the syngas than what was estimated from his equilibrium model calculation. A possible explanation to this is that the state of equilibrium was not met during the experiment. Gumz W, 1950 as cited by Bacon DW et al, 1982, stated that a modified equilibrium constant can be defined as the true equilibrium constant multiplied by the degree of approach to equilibrium.

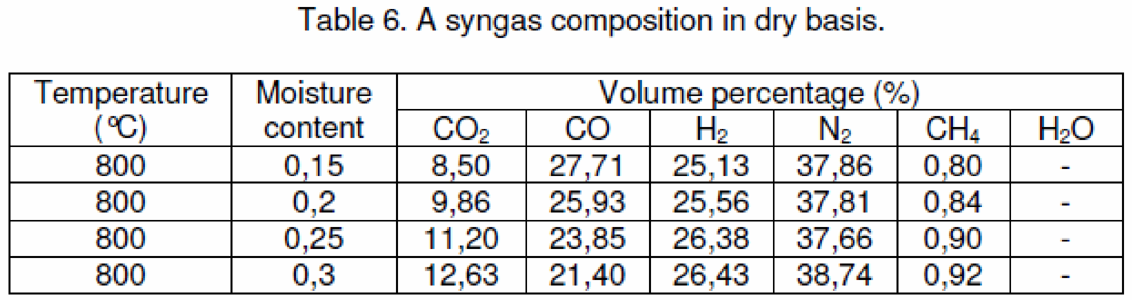

Table 6. A syngas composition in dry basis.

Temperature (°C)	Moisture content	Volume percentage (%)					
		CO_2	CO	H_2	N_2	CH_4	H_2O
800	0,15	8,50	27,71	25,13	37,86	0,80	-
800	0,2	9,86	25,93	25,56	37,81	0,84	-
800	0,25	11,20	23,85	26,38	37,66	0,90	-
800	0,3	12,63	21,40	26,43	38,74	0,92	-

Table 5 shows the effect of moisture content in the eucalyptus on the percentage of H2 in the syngas when the bed is working at 800 °C. The H2 content in syngas tends to increase with increasing of moisture content in the eucalyptus, due to the fact that the water vapor in the gasification reaction was increased. The Eq. (4) describes this important fact to the H2 production process, this H2 as energy carrier for electricity generating by SOFCs. The amount of CH4 produced in the syngas increase with increasing moisture content. The values predicted is found in the range of values available in literature as shows in table 7.

Table 7. Typical properties of product syngas from biomass in dry basis (Handbook of Biomass downdraft Gasifier Engine Systems, 1988).

LHV (MJ/Nm^3)	Volume percentage (%)					
	CO_2	CO	H_2	N_2	CH_4	H_2O
5,8	10,2	22,1	15,2	50,8	1,7	-

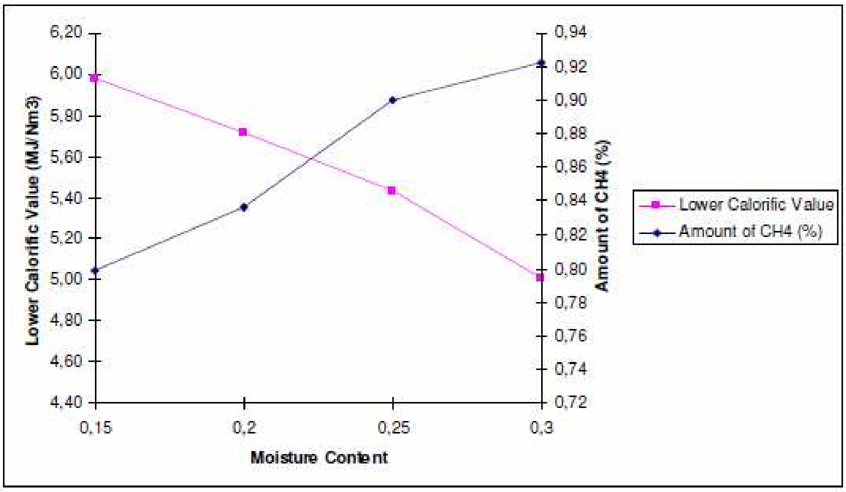

Figure 1 - The effect of moisture content on the lower calorific value and amount of CH_4

Figure 1 shows the effect of moisture content on the lower calorific value and amount of CH4. It can be observed that the lower calorific value gradually decreases from 6 to 5 MJ/Nm3 when varying MC from 0% to 30%. The amount of CH4 increases from 0,80% to 0,92% when varying MC in same range.

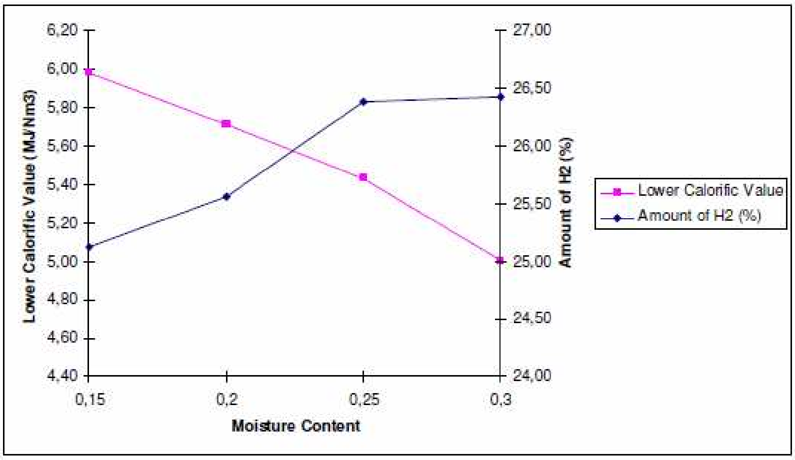

Figure 2 - The effect of moisture content on the lower calorific value and amount of H_2

Figure 2 shows the effect of moisture content on the lower calorific value and amount of H_2. It can be observed that the amount of H_2 increase from 25,13% to 26,43% when varying MC from 0% to 30%.

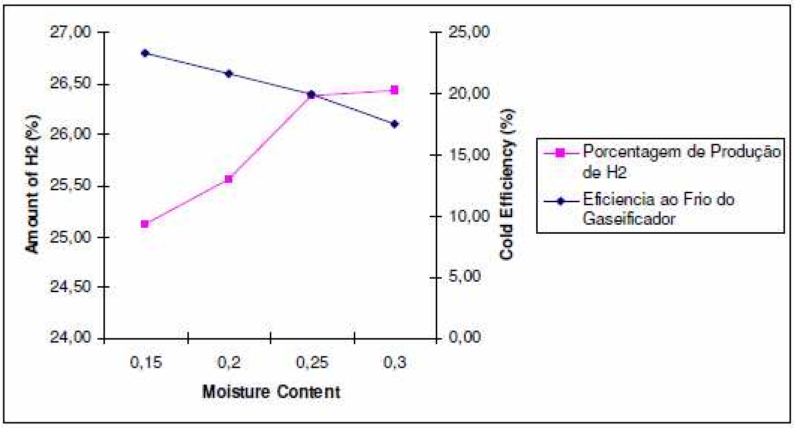

Figure 3 - The effect of moisture content on the cold efficiency gasifier and amount of H_2

Figure 3 shows the effect of moisture content on the cold efficiency gasifier and amount of H_2. It can be observed that cold efficiency gasifier gradually decrease from 23,36% to 17,55% when varying MC from 0% to 30%, due to the fact the lower calorific value gradually decrease in the same range.

4. CONCLUSION

The hydrogen production in a downdraft gasifier is predicted using an equilibrium model. The calculations of the syngas composition, lower calorific value and cold gas efficiency with eucalyptus are illustrated. The predict syngas composition values compare reasonably well with empirical values available in the literature. With known ultimate analysis of eucalyptus and its lower calorific value, the model can predict the syngas composition, a lower calorific value of a syngas and cold gas efficiency of gasifier. From the analysis, the following conclusions are made:

1. The amount of hydrogen in the syngas increases with moisture content, this aspect is important to SOFCs system works.
2. The amount of methane in the syngas increases with moisture content, the value in syngas is quite small and is of the order of 1%.
3. The lower calorific value in the syngas decreases with the increases in moisture content.
4. The cold gas efficiency decreases with the increases in moisture content.

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