EQUILIBRIUM MODELING OF HEMP HURD GASIFICATION

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ABSTRACT: The aim of this work is modeling a gasification process where a non-conventional biomass is used as fuel: hemp hurd residues. An equilibrium model of the gasification reaction was implemented in the Phyton^{TM} software environment. Syngas composition, syngas higher heating value, tar production and gasification cold gas efficiency were evaluated at different value of biomass moisture starting from biomass ultimate analysis and reaction equivalence ratio (ER) value. The model is able to predict char and tar production as function of biomass composition, moisture and ER. A comparison with experimental data obtained from hemp hurd gasification was done to validate equilibrium model results. Gasification tests were performed using a low capacity lab-scale gasification reactor designed to use about 1 kg per hour of dry biomass fuel. Results show small errors between model results and experimental result. Several simulations were performed to assess the gasification dependency on selected boundary conditions like biomass moisture and ER of the gasifier.

Keywords: bioenergy, gasification, hemp, residues, syngas

1 INTRODUCTION

Hemp global sector is a fast growing market, it is projected to grow from USD 4.6 billion in 2019 to USD 26.6 billion by 2025 thanks to the large variety of possible applications hemp is involved into [1,2]. Textile industries as well as sustainable building companies are increasing the demand for hemp fiber [3].

The main by-products of hemp fiber production is hemp hurd: a lignocellulosic residues fragmented in small flakes with a variable length of 1-5 cm. The amount of this biomass is not negligible: literature reports an annual productivity in cold climate conditions of about 10 ton per hectare of dry matter including flowers and seeds that represent a small fraction of the whole plant. Hurd is commonly used as filler for construction material like tiles of bricks and it has a marker value of about 200 €/ton [3]. An alternative way to valorize hemp hurd is the utilization as fuel for combustion biomass facility [3].

This work investigates the use of hemp hurd as fuel for gasification reactor. Gasification is a thermo-chemical reaction that converts a solid or liquid fuel into a gaseous fuel (syngas) using a gasifying agent and heat in sub-stoichiometric environment [4]. Gasification has several advantages compared to other thermochemical processes like pyrolysis and combustion. First, gasification is the most efficient way to convert biomass to electrical energy [5,6], second, it covers a wide range of electrical power output requirement (from 1 kW to 1 MW) [4,6]. Gasification uses not-conventional biomass fuels thanks to some peculiar reactor designs and architectures [7-16]. Furthermore, commercial gasification systems not only convert solid biomass (usually wood chips) into electrical energy and heat but also produce biochar. Biochar consists of charcoal that is disposed from gasification and pyrolysis reactor. It is a highly recalcitrant form of carbon, for this reason its use as soil amendment as also the effect to convert the soil into an effective carbon sink [17,18].

The main problem that afflicts gasification systems is the uncontrolled tar production. Tar is mix of polycyclic aromatic hydrocarbons (PAHs) and it is a pollutant of the syngas stream because it can be dangerous for mechanical components of the gasification power plants. High is the tar amount high is the filtering effort needed to purify the syngas, however a low tar production below 1 g/Nm^3 is difficult to reach with biomass residues because of high moisture, low higher heating content and high ash of the residue [4].

In this paper an equilibrium model based on a general biomass gasification reaction was implemented in Phyton^{TM} software environment. The model was validated using experimental data obtained from hemp hurd gasification test performed with a lab-scale fixed bed gasifier. Furthermore, several simulations were done considering different gasification conditions varying biomass moisture and gasifier equivalence ratio.

2 MATERIAL AND METHODS

2.1 Biomass characterization

Biomass moisture content was calculated according to UNI EN ISO 18134-1. Chemical composition of the organic part of a dried biomass sample were performed using the FLASH 2000 Organic Elemental CHNS-O Analyzer [19]. Biomass ash content was determined weighing a died sample before and after 8 hours muffle furnace calcination at 600 °C. Biomass higher heating value HHV [kJ/kg] were estimated through the Channiwala and Parikh correlation (Eq.1) [20] and biomass lower heating value LHV [kJ/kg] was determined using Eq. 2 [4].

$$HHV = 349.1C + 1178.3H + 100.5S - 103.4O - 15.1N - 21.1ASH \quad (1)$$

$$LHV = HHV - h_g\left[\left(\frac{9H}{20}\right) + \left(\frac{M}{100}\right)\right] \quad (2)$$

where *C*, *H*, *S*, *O*, *N* and *ASH* [% wt.] are respectively the mass percentages of carbon, hydrogen, sulfur, oxygen, nitrogen and ashes of the biomass calculated on a dry basis. h_g [kJ/kg] is the latent heat of vaporization of water at ambient pressure and *M* [% wt.] is the moisture content of the biomass. Table I resumes the results of the previous analysis and Figure 1 show a hemp hurd biomass sample.

Table I: Hemp hurd characterization

Variabile	Value
Biomass moisture M [% wt. ar]	10
Ash amount ASH [% wt. dry]	7.38
Carbon amount C [% wt. dry]	43.00
Hydrogen amount H [% wt. dry]	5.58
Sulphur amount S [% wt. dry]	0
Oxygen amount O [% wt. dry]	3.58
Nitrogen amount N [% wt. dry]	0.45
Higher heating value HHV [MJ/kg dry]	16.94
Lower heating value LHV [MJ/kg dry]	15.72

Figure 1: Hemp hurd biomass sample

2.2 Equilibrium gasification modelling

The following reaction developed by [21,22] is used to model the whole gasification:

$$CH_xO_yN_z + wH_2O + m(O_2 + 3.76N_2) = n_{H_2}H_2 + n_{CO}CO + n_{CO_2}CO_2 + n_{H_2O}H_2O + n_{CH_4}CH_4 + (1 - \alpha_c)C \; + n_{tar}CH_pO_q + \left(\tfrac{z}{2} + 3.76m\right)N_2 \tag{3}$$

where $CH_xO_yN_z$ is the as-received biomass molecular formula, the subscripts x, y and z are evaluated through the following equations:

$$x = \frac{HM_C}{CM_H}; \qquad y = \frac{OM_C}{CM_O}; \qquad z = \frac{NM_C}{CM_N} \tag{4}$$

where C, H, O, N [% wt.] are the weight percentage of the basic elements in the biomass (taken from Table I); M_c [g/mol] is the carbon molar weight; M_H [g/mol] is the hydrogen molar weight; M_O [g/mol] is the oxygen molar weight and M_N [g/mol] is the nitrogen molar weight. Other symbols in the Eq. 3 are: w [mol$_{H2O}$/mol$_{bio}$] is a constant that depends on biomass moisture and it is calculated through Eq. 5; m [mol$_{O2}$/ mol$_{bio}$] is a constant that depends on gasifier equivalence ratio ER and it is evaluated through Eq.6; n_i [mol$_i$/mol$_{bio}$] is the i-th product gas molar amount per mole of inlet biomass (i = H_2; CO; CO_2; H_2O; CH_4); α_c is the carbon conversion factor that it calculated thorugh Eq. 7 fuction of gasification temperatute T [K] and ER [23]; n_{tar}[mol$_{tar}$/mol$_{bio}$] is the molar amount of tar per mole of inlet biomass; CH_pO_q is the tar molecular formula, in this paper we assume p = 1.003 and q = 0.33 as suggested by Tinaut et al. [24]. In the model n_{tar} is back-calculated from the weight pecentage of tar in the total products W_{tar} given by Eq. 8 developed by Sadaka et al. [25]:

$$w = \frac{MW_{bio} \cdot M(100+ASH)}{100 \cdot [MW_{H_2O}(1-{}^{M}/_{100})} \tag{5}$$

$$m = ER \cdot \left(1 + \frac{x}{4} - \frac{y}{2}\right) \tag{6}$$

$$\alpha_c = 0.901 + 0.493(1 - e^{-ER + 0.0003\,T}) \tag{7}$$

$$W_{tar} = 35.98\, e^{-0.00298\,T} \tag{8}$$

From Eq. 3 several element balances can be written:

Carbon:

$$n_{CO} + n_{CO_2} + n_{CH_4} + (1 - \alpha_c) + n_{tar} - 1 = 0 \tag{9}$$

Hydrogen:

$$2n_{H_2} + 2n_{H_2O} + 4n_{CH_4} + n_{tar}p - x = 0 \tag{10}$$

Oxygen:

$$n_{CO} + 2n_{CO_2} + n_{CH_4} + n_{tar}q - y = 0 \tag{11}$$

Furthermore using Eq. (8) the total mass balance can be written as follow:

$$(W_{tar}/100) * \left[n_{H_2}M_{H_2} + n_{CO}M_{CO} + n_{CO_2}M_{CO_2} + n_{CO_2}M_{CO_2} + n_{CH_4}M_{CH_4} + (1 - \alpha_c)M_C + n_{tar}M_{tar} + \left(\tfrac{z}{2} + 3.76m\right)\right] - n_{tar}M_{tar} = 0 \tag{12}$$

In this equilibrium model only two reactions are considered:

Water gas shift: $CO + H_2O \leftrightarrow CO_2 + H_2$ (13)

Methanation: $C + 2H_2 \leftrightarrow CH_4$ (14)

The equilibrium constants for these reactions depend on reaction temperature:

$$K_1 = \frac{n_{CO_2}n_{H_2}}{n_{CO}\,n_{H_2O}} = exp\left\{\frac{4276}{T} - 3.96\right\} \tag{15}$$

$$K_2 = \frac{n_{CH_4} \times n_{total}}{\left(n_{H_2}\right)^2} = exp\left\{\frac{7082.842}{T} - (6.567)\,ln\,T + \frac{(7.467\times10^{-3})\times T}{2} - \frac{2.167\times10^{-6}}{6}T^2 + \frac{0.702}{2T^2} + 32.541\right\} \tag{16}$$

where $n_{total} = \sum_i n_i + n_{tar}$ [mol/mol$_{bio}$] because the tar is considered in vapour phase inside the reactor. Knowing the reaction temperature T and the equivalence ratio ER, the system composed of Eqs. 9-10-11-12-15-16 can be solved to find the gasification products molar amount per mole of inlet biomass. However, reaction temperature can be also calculated from the molar enthalpy conservation equation (Eq. 19) considering the reactants at standard condition (25 °C and 1 atm).

$$h_{reactants} = h^0_{f_{bio}} + wh^0_{f_{H2O}} + m\left(h^0_{f_{O_2}} + 3.76h^0_{f_{N_2}}\right) \quad (17)$$

$$h_{products} = \sum_i n_i \left[h^0_{f_i} + \int_{289}^{T} C_{p_i} dT\right] + n_{tar}\left[h^0_{f_{tar}} + c_{p,tar}(T-298)\right] + (1-\alpha_c)\left[h^0_{f_C} + c_{p,C}(T-298)\right] \quad (18)$$

$$h_{reactants} = h_{products} \quad (19)$$

where $h^0_{f_{bio}}$ [kJ/kmol] is the biomass formation enthalphy at standard conditions calculated through Eq. 20 that takes into account a complete combustion of the biomass [21]; $h^0_{f_i}$ [kJ/kmol] is the i-th gas formation enthalphy at standard conditions [21]; C_{p_i} [kJ/(kmol K)] is the i-th gas specific heat at constant pressure [21]; $h^0_{f_{tar}}$[kJ/kmol] is the tar formation enthalphy at standard conditions calculated through Eq. 20 [21]; $c_{p,tar}$ [kJ/(kmol K)] is the tar specific heat considered as polyatomic perfect gas at constant pressure; $h^0_{f_C}$[kJ/kmol] is the carbon formation enthalphy at standard conditions calculated through Eq. 20 [21]; $c_{p,tar}$ [kJ/(kmol K)] is the carbon specific heat considering carbon similar to graphite.

$$h^0_{f_j} = LHV_j + \sum_k n_k \cdot h^0_{f_k} \quad (20)$$

where j = biomass, tar, carbon; LHV_j [kJ/kmol] is the fuel lower heating value; k = CO_2; H_2O; N_2O is the combustion product; n_k [mol/mol$_j$] is the molar amount of the product per mole of fuel; $h^0_{f_k}$ [kJ/kmol] is the enthalpy of formation of the combustion products at standard conditions.

Chemical balance and enthalpy balance are then linked togheter in a solution algorithm depicted in Figure 2.

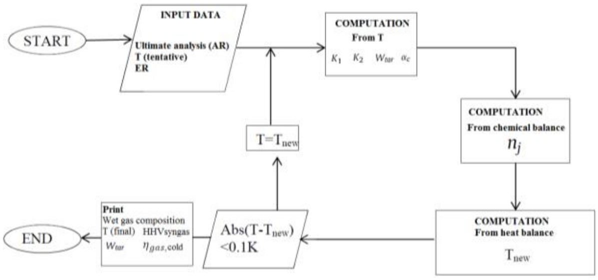

Figure 2: Solution algorithm

The algorithm was implemented in Phyton™ software environment in order to estimate the following outputs: syngas molar composition x_i [% mol. = % vol.] (considering water vapor or not); syngas higher heating value HHV_{syngas} [MJ/Nm^3] using Eq. 21 and considering the syngas as ideal gas; gasifier cold efficiency $\eta_{gas,cold}$ [%] using Eq. 22 and tar volumetric production rate v_{tar} [g/Nm^3] using Eq. 23 considering the syngas as ideal gas.

$$HHV_{syngas} = x_{H_2}HHV_{H_2} + x_{CO}HHV_{CO} + x_{CH_4}HHV_{CH_4} \quad (21)$$

$$\eta_{gas,cold} = \frac{HHV_{syngas}v_{syngas}}{HHV_{bio}M_{bio}} \quad (22)$$

$$v_{tar} = \frac{n_{tar}M_{tar}}{v_{syngas}} \quad (23)$$

where HHV_{H_2} [MJ/Nm^3] is the H_2 volumetric higher heating value; HHV_{CO} [MJ/Nm^3] is the CO volumetric higher heating value; HHV_{CH_4} [MJ/Nm^3] is the CH_4 volumetric higher heating value; $v_{syngas} = 0.022414\, n_i M_i$ [Nm^3/mol$_{bio}$] is the volume of syngas obtained from the gasification of 1 mole of biomass; M_{bio} [g/mol] is the biomass molar weight.

2.3 Experimental gasification facility

The lab-scale gasifier used in the experimental (Figure 3) was the “Femto Gasifier” [26]. During hemp hurd the gasification test the following variables were measured: volume of syngas produced through an indirect method that uses gas totalizer [26]; gas composition though gas chromatographic analysis of 2 gas samples; mass of biomass used through a scale. Gasification cold gas efficiency were calculated using Eq. 24.

$$\eta_{gas,cold} = \frac{HHV_{Syngas}\ X\ Volume\ of\ syngas}{HHV_{bio}\ \ X\ Mass\ of\ biomass} \quad (24)$$

During the test 3 type K thermocouples connected to a Pyco TC-08 datalogger are used to monitor inlet air temperature, average gasification temperature and outlet syngas temperature.

Figure 3: Femto Gasifier [26]

3 RESULTS AND DISCUSSION

Table II resumes the comparison between experimental data and model results concerning hemp hurd gasification. The comparison between syngas composition evaluated through the equilibrium model and through gas cromatography shows small differences probably given by the strong hyphotesis adopted in the equilibrium model and the unstable temperatures measured during the gasification test (Figure 4).

Figures 5,6,7 depict equilibrium model outputs at different ER and M values. The figures show a strong dependency of the gasifier output with the biomass moisture and the equivalence ratio (ER). Lower is the moisture better is the gasifier behavior in term of efficiency, syngas HHV and tar production. However, a moisture value lower than 10% is acceptable in industrial application and do not create sensible inefficiencies. ER value is crucial to have a good cold gas efficiency, in fact for ER = 0.3 the best efficiency of about 59.5 % was estimated. This value is quite common for fixed bed gasifier that are design to work in these precise conditions. In practice, ER is very hard to set during gasification operation, in fact it depends on several factor such as biomass composition, particle dimensions and shape, moisture and syngas flow rate. A good control system should be able to recognize this value during operation and adjust the working parameter in order to achieve ER = 0.3.

As show in Figure 7, tar production is almost constant in the moisture range 0-20%, however tar strongly depends on ER value. A high ER value (i.e. 0.4) decreases tar production, a low ER value (i.e. 0.2) increases tar production. Again, a good compromise is ER = 0.3 where maximum efficiency is reached.

Table II: Model Vs. Experimental results comparison

Syngas composition	**Experimental test (gas chromatography)**			**Model**
Dry basis	**Sample 1**	**Sample 2**	**Average**	**ER = 0.3**
H_2 [% vol.]	13.1	11.9	11.9	20.8
N_2 [% vol.]	49.1	50.1	50.1	46.2
CH_4 [% vol.]	2.3	2.2	2.2	2.1
CO [% vol.]	20.1	18.1	18.1	12.3
CO_2 [% vol.]	11.9	13.4	12.7	18.5
HHV [MJ/Nm^3]	5.1	4.7	4.9	4.4
Cold gas efficiency	**Experiment**			**Model**
$\eta_{gas,cold}$ [%]	65.8			58.1

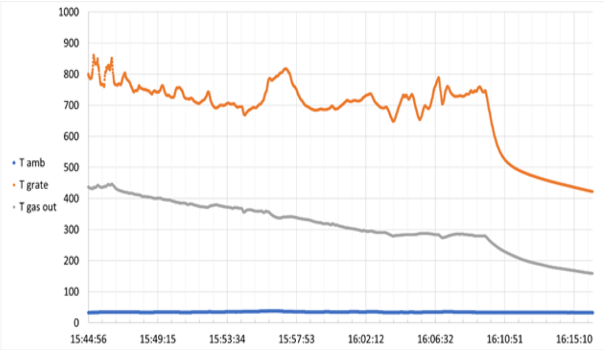

Figure 4: Gasifier temperature trends during the experimental test

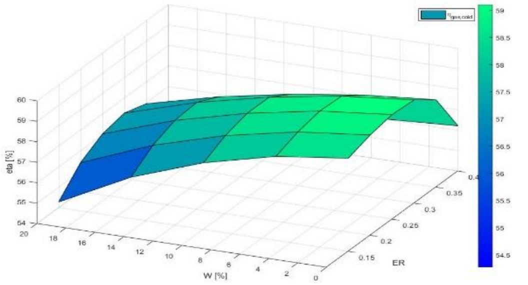

Figure 5: Gasifier cold gas efficiency Vs. moisture and ER

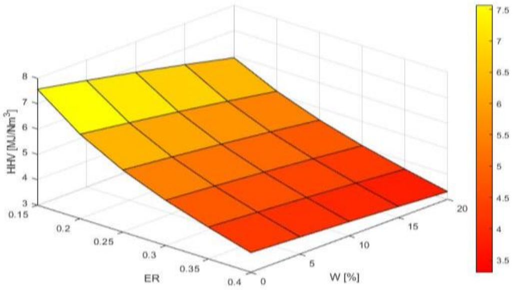

Figure 6: Wet syngas HHV Vs. moisture and ER

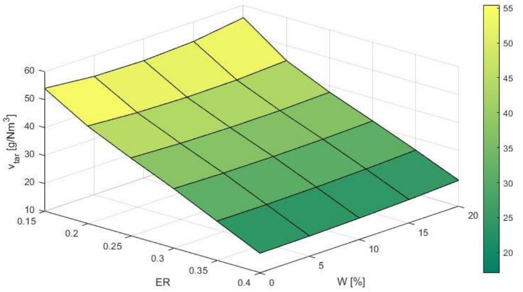

Figure 7: Volume percentage of tar in the syngas Vs. moisture and ER

4 CONCLUSIONS

The developed equilibrium model predicts with good accuracy hemp hurd gasification. In fact, a cold gas efficiency of about 58% and a syngas heating value of about 4.4 MJ/Nm^3 are obtained from the model with 10% of biomass moisture and equivalence ratio ER = 0.3; these values are in line with literature data about fixed bed gasification. Model simulations varying ER in the range 0.2-0.4 and varying M in the range 0-20% showed a good dependency of the gasifier with the ER value.

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