

A CHEMICAL EQUILIBRIUM BASED MODEL FOR BIOMASS GASIFICATION

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Abstract. *The gasification technology has been object of study of many researchers, especially those involved in promoting large-scale electricity generation in sugarcane mills. This paper presents a simplified model for biomass gasification based on chemical equilibrium considerations. The model consists in the minimization of the Gibbs free energy of the produced gas, constrained by mass and energy balances for the system. Despite the simplicity of the model, its results are reliable in identifying the tendencies of the working parameters for the system. Biomass composition, gasification temperature (air supplied), moisture content, air temperature, and heat losses are parameters that may be varied in order to evaluate different operational points. Results obtained are compared to those found in real operation of gasification processes, aiming the determination of lower heating values (LHV). A discussion on how to adequate the model to real operation is done.*

Keywords: *sugarcane bagasse, gasification*

1. Introduction

Gasification is a thermo-chemical process in which a solid/liquid fuel is converted, due to the addition of heat in a sub-oxidizing atmosphere, into a mixture of gases (produced gas) with low calorific value. The gasification technology has been object of study of many researchers, especially those involved in promoting large-scale electricity generation in sugarcane mills. However, few of these studies focused on the process itself (Souza-Santos, 1999), being more concerned about the application of the produced gas in combined cycles and/or co-firing systems (Consonni and Larson, 1996 and Rodrigues, Walter and Faaij, 2003).

Most recently, many works have been published in the field of gasification modeling by chemical equilibrium and its analysis. A non-stoichiometric model, which uses empirical relations in order to come closer to real operation of gasification of biomass, based on the operation of a circulating fluidized bed, was proposed by Li et al. (2004). Gasification and combustion processes for CHO systems are analyzed based on first and second law analysis, following a stoichiometric approach (Prins and Ptasinski, 2005). These studies provided a fairly comparison between gasification and combustion, showing the principal irreversibilities associated with each process, and the advantages of one and another. The gasification of different biomass materials in an equilibrium model based on equilibrium constants for methane formation and shift reaction is, also, available in Zainal et al. (2001).

This paper presents a simplified model for the gasification based on chemical equilibrium considerations. The model consists in the minimization of the Gibbs free energy of the produced gas, constrained by mass and energy balances for the system.

2. Chemical Equilibrium Modeling

It has been adopted the non-stoichiometric approach to find the chemical equilibrium, in which:

- ✓ Only gaseous species (CH_4 , CO , H_2 , H_2O , CO_2 and N_2) have been considered in equilibrium;
- ✓ The produced gas was modeled as a mixture of ideal gases;
- ✓ No nitrogen pollutants were presented (NO_x , N_2O).

The approach for the equilibrium calculations consists in solving a system of non-linear equations given by (Modell and Tester, 1997):

- N equations related to equilibrium conditions:

$$\mu_j + \sum_{k=1}^w \lambda_k a_{jk} = 0, \text{ for } j = 1, 2, \dots, N \quad (1)$$

- w equations related to material balances:

$$\sum_{j=1}^N (n_j \cdot a_{jk}) = A_k, \text{ for } k = 1, 2, \dots, w \quad (2)$$

where: λ_k – Lagrange multiplier; n_j – number of mols of component j ; a_{jk} – number of atoms of element k in the molecule of component j ; A_k – total number of elements k .

As it was considered a mixture of ideal gases, Eq. (1) can be re-arranged (Abbot, Smith and Van Ness, 2001):

$$\Delta G_j^0 + RT \ln(y_j) + \sum_{k=1}^w \lambda_k a_{jk} = 0, \text{ for } j = 1, 2, \dots, n \quad (3)$$

In order to moderate the system, an energy balance was imposed to the problem:

$$\left(\sum \dot{H}_i \right)_{in} = \left(\sum \dot{H}_j \right)_{out} + \dot{Q}_{losses} \quad (8)$$

$$\left(\sum \dot{H}_i \right)_{in} = \dot{H}_{air} + \dot{H}_{dry \text{ biomass}} + \dot{H}_{biomass \text{ moisture}} + \dot{H}_{steam} \quad (9)$$

$$\left(\sum \dot{H}_j \right)_{out} = \dot{H}_{produced \text{ gas, dry}} + \dot{H}_{steam} \quad (10)$$

$$\dot{Q}_{losses} = f \cdot \left(\sum \dot{H}_i \right)_{in} \quad (11)$$

where: f – loss percentage of the initial total enthalpy.

This balance is responsible for the determination of the temperature of the system for a given air-to-fuel ratio, or the other way round. It is important to state that the model proposed only deals with atmospheric gasification.

3. Thermodynamic Properties Modeling

In what follows, the main relations for determining the thermodynamic properties of the streams are shown. Gibbs free energies were evaluated by (temperature range considered was 800 – 1600 K):

- Methane (CH_4):

$$\Delta G_{\text{CH}_4}^0 = 108.41 \cdot T - 88635 \quad (12)$$

- Carbon Dioxide (CO_2):

$$\Delta G_{\text{CO}_2}^0 = -1.3503 \cdot T - 394,353 \quad (13)$$

- Carbon monoxide (CO):

$$\Delta G_{\text{CO}}^0 = -88.381 \cdot T - 111,713 \quad (14)$$

- Steam ($\text{H}_2\text{O}_{(v)}$):

$$\Delta G_{\text{H}_2\text{O}}^0 = 55.186 \cdot T - 247,676 \quad (15)$$

These relations were obtained through an analysis of the forming reactions of each component. Gibbs free energies for H_2 and N_2 are zero, because they are considered in their standard state (Modell and Tester, 1997).

Enthalpies (molar basis) for biomass (CH_yO_z) were determined by the following relations (Fock and Thomsen, 2000):

$$\bar{h}_{f_{\text{biomass}}} = \bar{h}_{\text{CO}_2}(25^\circ\text{C}, 1 \text{ bar}) + \frac{y}{2} \cdot \bar{h}_{\text{H}_2\text{O}_{(v)}}(25^\circ\text{C}, 1 \text{ bar}) + \text{LHV}_{\text{biomass}} \quad (16)$$

$$\Delta h = \frac{0.003867 \cdot (T_{\text{biomass}}^2 - T_0^2)}{2} + 0.1031 \cdot (T_{\text{biomass}} - T_0) \quad (17)$$

Enthalpies and entropies for all other components presented in the model were evaluated using the software EES (Klein and Alvarado, 2004). All equations shown above were solved using EES software.

Biomass composition, gasification temperature (air supplied), moisture content, air temperature, and heat losses are parameters that may be varied in order to evaluate different operational points.

4. Results

Aiming to evaluate the model, it was considered a reference case, so that no moisture is presented in the biomass nor steam is added. For the analysis of the gasification process in the reference case, it was considered that the reduced molecular formula of sugarcane bagasse was: $\text{CH}_{1.61}\text{O}_{0.7}$. Fig. (1) shows the molar fractions for different equivalence ratios.

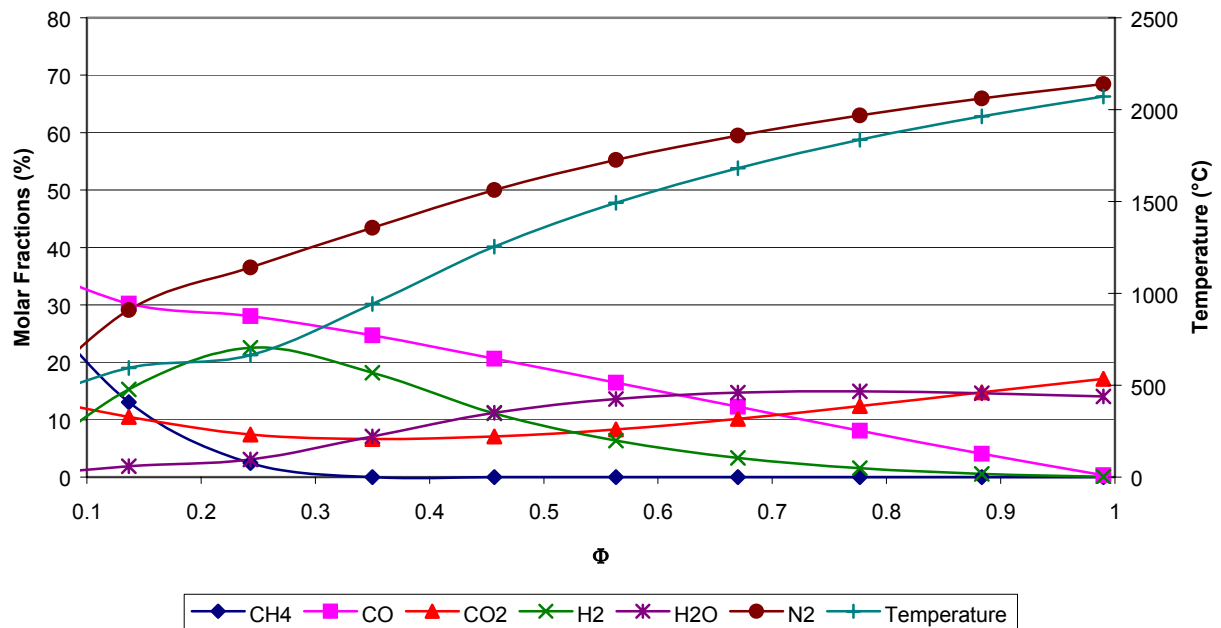


Figure 1 – Molar fractions for various equivalence ratios (pressure: 1 bar)

As more air is added to the system, less CO is formed. This represents that the gasification reactions become less favorable as the equivalence ratio increases, and combustion reactions start to take place. Fig. (1) shows that the H_2 content increases up to 22%, and then decreases to 0%. The point where the H_2 is maximized is the operation condition in which the LHV of the produced gas is a maximum.

As stated by Ruggiero and Manfrida (1999), equilibrium models, which assume perfect gas behavior, cannot describe pyrolysis processes, due to the presence of liquid hydrocarbons as pyrolysis products. So, values for very low equivalence-ratio (below 0.10) should not be considered.

It is also important to notice that for equivalence ratios greater than 0.3, no CH_4 is formed.

In order to confront the model with experimental results, 3 experiments made at IPT (Ushima, 2004) with eucalyptus chips were used. These chips were fed to a downdraft gasifier. According to Reed and Gaur (2001), downdraft gasifiers operate very close to equilibrium conditions. However, fluidized bed gasifiers operate far away from equilibrium conditions.

Table 1 illustrates the operational conditions of the three tests:

Table 1 – Operational Parameters of the Tests

	Test 1	Test 2	Test 3
Chip flow rate (kg/h)	19.3	17.1	15.9
Moisture content (%)	8.0	8.2	20.8
Air flow rate (kg/h)	33.1	31.8	28.7
Temperature of the produced gas after the cleaning system (°C)	14.6	11.0	10.3
Ashes flow rate (kg/h)	1.24	0.6	0.6
Difference between inflow and outflow rates (kg/h)	3.5	2.5	3.8

These conditions were set in the model, and the results are shown in the following tables.

Table 2 – Results for Test 1

Molar Fraction (% wet basis)	Test 1	Model	Relative Deviation
CO	21.7%	24.8%	14.3%
H ₂	17.1%	23.1%	35.1%
CH ₄	2.0%	0.1%	-95.0%
CO ₂	11.0%	8.7%	-20.9%
N ₂	47.0%	41.6%	-11.5%
H ₂ O	1.2%	1.6%	33.3%
LHV (MJ/kg)	5.1	5.5	7.8%
Produced gas flow rate (kg/h)	47.7	50.5	5.9%

Table 3 – Results for Test 2

Molar Fraction (% wet basis)	Test 2	Model	Relative Deviation
CO	20.6%	24.4%	18.4%
H ₂	16.5%	21.2%	28.5%
CH ₄	2.0%	0.0%	-100.0%
CO ₂	11.2%	8.6%	-23.2%
N ₂	47.8%	44.5%	-6.9%
H ₂ O	1.3%	1.3%	0.0%
LHV (MJ/kg)	4.9	5.1	4.1%
Produced gas flow rate (kg/h)	45.8	46.5	1.6%

Table 4 – Results for Test 3

Molar Fraction (% wet basis)	Test 3	Model	Relative Deviation
CO	17.5%	19.5%	11.4%
H ₂	17.5%	20.7%	18.3%
CH ₄	2.0%	0.0%	-100.0%
CO ₂	13.1%	11.6%	-11.5%
N ₂	48.9%	47.1%	-3.7%
H ₂ O	1.0%	1.2%	20.0%
LHV (MJ/kg)	4.7	4.3	-8.5%
Produced gas flow rate (kg/h)	40.2	40.7	1.2%

These tables show that, despite the great differences among the molar concentrations, LHV values are quite close to those found in the tests. The model over predicts the molar concentrations of CO, H₂ and H₂O, but the low concentrations of CH₄ allow for the system to calculate good LHV values.

The model developed predicts produced gas flow rates greater than the ones observed as a result of, mainly:

- Kinetic aspects of gasification reactions;
- Presence of nitrogen, sulphur and ashes in the biomass composition (not considered in the model);
- Existence of unconverted carbon in the ashes (not considered in the model);

- Errors resulting from the measures during the experiments, as these differences account for over 15% of the inflow rate.

The great differences between calculated values and experimental values for CH₄ molar fractions are a result of the sudden cease of gasification reactions at the bottom of the reactor. This cease is a consequence of the temperatures at the bottom, which are too low to start-up the reactions. In an equilibrium model, it is assumed that all reactions achieve a steady-state condition, thus no kinetic effects (such as sudden cease) are considered.

To overcome the difference in the molar fraction values, and to take into account non-equilibrium conditions, Fock and Thomsen (2000) imposed a fixed CH₄ molar fraction to the system, as well a quantity of unconverted carbon. The same idea was implemented in the model, and the results are shown in the next tables (all the ash was considered as unconverted carbon, following the approach proposed by Fock and Thomsen, 2000).

Table 5 – Results for Test 1

Molar Fraction (% wet basis)	Test 1	Modified Model I	Relative Deviation
CO	21.7%	21.2%	-2.3%
H ₂	17.1%	16.0%	-6.4%
CH ₄	2.0%	2.0%	0.0%
CO ₂	11.0%	10.5%	-4.5%
N ₂	47.0%	48.7%	3.6%
H ₂ O	1.2%	1.6%	33.3%
LHV (MJ/kg)	5.1	4.6	-9.8%
Produced gas flow rate (kg/h)	47.7	46.8	-1.9%

Table 6 – Results for Test 2

Molar Fraction (% wet basis)	Test 2	Modified Model I	Relative Deviation
CO	20.6%	21.9%	6.3%
H ₂	16.5%	15.2%	-7.9%
CH ₄	2.0%	2.0%	0.0%
CO ₂	11.2%	10.1%	-9.8%
N ₂	47.8%	49.6%	3.8%
H ₂ O	1.3%	1.3%	0.0%
LHV (MJ/kg)	4.9	4.5	-8.2%
Produced gas flow rate (kg/h)	45.8	44.5	-2.9%

Table 7 – Results for Test 3

Molar Fraction (% wet basis)	Test 3	Modified Model I	Relative Deviation
CO	17.50%	16.7%	-4.6%
H ₂	17.50%	13.7%	-21.7%
CH ₄	2.00%	2.0%	0.0%
CO ₂	13.10%	13.1%	0.0%
N ₂	48.90%	53.3%	9.0%
H ₂ O	1.00%	1.2%	20.0%
LHV (MJ/kg)	4.7	3.4	-27.7%
Produced gas flow rate (kg/h)	40.2	38.6	-3.9%

Although, the differences among molar fractions do decrease with the modifications proposed, LHV values are jeopardized in relation to those of pure equilibrium model. This might be explained by the decrease in the CO and H₂ concentrations, lowering the presence of combustible gases (the increase in CH₄ concentration is not sufficient to offset this decrease).

Li et al. (2004) proposed the use of empirical correlations in order to consider kinetic aspects. Thus, the model should be modified to run as shown in Fig. 2:

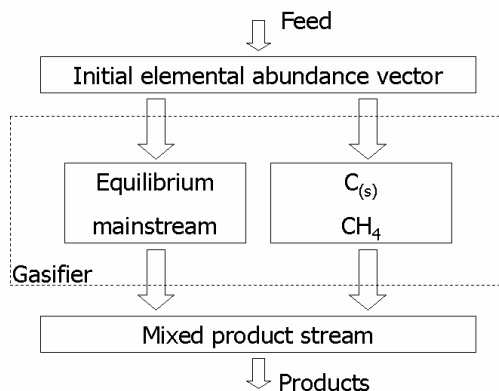


Figure 2 – Schematic representation of the modified model (Li et al., 2004)

Volumes of CH₄ formed and unconverted carbon are found using empirical correlations, and the other quantities are found through equilibrium calculations.

$$\beta_{\text{CH}_4} = 0.11 \cdot (1 - \phi) \quad (18)$$

$$n_{\text{CH}_4} = \beta_{\text{CH}_4} \cdot n_{\text{C}, \text{initial}} \quad (19)$$

$$\beta_{\text{C}} = 0.25 + 0.75 \cdot \exp\left(-\frac{\phi}{0.23}\right) \quad (20)$$

$$n_{\text{C}} = \beta_{\text{C}} \cdot n_{\text{C}, \text{initial}} \quad (21)$$

$$\beta_{\text{H}} = 1 - \frac{4 \cdot \beta_{\text{CH}_4} \cdot n_{\text{C}, \text{initial}}}{n_{\text{H}, \text{initial}}} \quad (22)$$

$$n_{\text{H}} = \beta_{\text{H}} \cdot n_{\text{H}, \text{initial}} \quad (23)$$

These parameters alter the quantity of atoms of C and H sent to equilibrium calculations. Table 8 shows the results of the modified model for Test 1.

Table 8 – Results for Test 1

Molar Fraction (% wet basis)	Test 1	Modified Model II	Relative Deviation
CO	21.7%	8.7%	-59.9%
H2	17.1%	4.5%	-73.7%
CH4	2.0%	3.9%	95.0%
CO2	11.0%	16.6%	50.9%
N2	47.0%	64.7%	37.7%
H2O	1.2%	1.6%	33.3%
LHV (MJ/kg)	5.1	2.3	-54.9%
Produced gas flow rate (kg/h)	47.7	40.4	-15.3%
Unconverted carbon flow rate (kg/h)	1.2	3.9	225.0%

All results are worse than the ones from the model based on Fock and Thomsen (2000). This is quite reasonable since the correlations adopted were derived from a fluidized bed reactor operation, not a downdraft one.

To test the model validity, data from Li et al. (2004) was used for comparison with results of the model. In what follows 2 tests are presented.

Table 9 – Test Cases from Li et al. (2004)

	Test 14	Test 15
<i>Biomass flow rate (kg/h)</i>	41,4	15,6
<i>Moisture content (%)</i>	6,7	4,2
<i>Air flow rate (kg/h)</i>	63,1	38.0

Table 10 – Results for Test 14

Molar Fraction (% wet basis)	Test 1	Modified Model II	Relative Deviation
H ₂	7,3%	12,1%	65,5%
N ₂	55,4%	60,0%	8,4%
CO	17,9%	11,2%	-37,5%
CH ₄	3,2%	4,8%	50,8%
CO ₂	16,3%	11,9%	-27,2%
H ₂	7,3%	12,1%	65,5%
LHV (MJ/kg)	4.6	4.6	0%

Table 11 – Results for Test 15

Molar Fraction (% wet basis)	Test 15	Modified Model II	Relative Deviation
H ₂	5,9	5,8	-1,4%
N ₂	64,6	69,0	6,9%
CO	10	10,0	-0,3%
CH ₄	1,2	2,8	135,2%
CO ₂	18,3	12,4	-32,5%
LHV (MJ/kg)	2,54	2,9	18,1%

Although, some disparities occurred the tests allowed the validation of the correlations used.

To evaluate these correlations for other materials than those from Li et al (2004), data from sugarcane bagasse pellet gasification will be used (Baptista et al., 1986). The gasifier used in this experiment is one of atmospheric fluidized bed, similar to the one described in Li et al. (2004). Table 12 shows the operational conditions of three tests from Baptista et al. (1986).

Table 12 – Operational Parameters of the Tests

	Test 9	Test 15	Test 17
<i>Bagasse pellet flow rate (kg/h)</i>	182.2	246.1	226.7
<i>Moisture content (%)</i>	9.2	9.2	9.2
<i>Air flow rate (kg/h)</i>	250.0	253.2	261.8
<i>Steam flow rate (kg/h)</i>	30.7	0.0	0.0

Tables 12 to 14 illustrate the results for these simulations.

Table 13 – Results for Test 9

Molar Fraction (% wet basis)	Test 9	Modified Model II	Relative Deviation
CO ₂	13.1%	20.3%	55.0%
CO	15.6%	6.3%	-59.6%
O ₂	3.3%	0%	-100.0%
CH ₄	4.7%	4.7%	0.0%
H ₂	5.2%	5.6%	7.7%
N ₂	58.1%	63.1%	8.6%
HHV (MJ/kg)	4.5	3.1	-31.2%
Produced gas flow rate (kg/h)	458.1	425.8	-7.0%

Table 14 – Results for Test 15

Molar Fraction (% wet basis)	Test 15	Modified Model II	Relative Deviation
CO ₂	15.2%	21.0%	38.4%
CO	18.8%	6.4%	-66.0%
O ₂	1.2%	0%	-100.0%
CH ₄	5.6%	6.7%	19.6%
H ₂	7.4%	5.2%	-29.7%
N ₂	51.8%	60.7%	17.2%
HHV (MJ/kg)	5.5	4.1	-25.6%
Produced gas flow rate (kg/h)	487.8	441.36	-9.5%

Table 15 – Results for Test 17

Molar Fraction (% wet basis)	Test 17	Modified Model II	Relative Deviation
CO ₂	15.3%	20.2%	32.0%
CO	19.1%	7.1%	-62.8%
O ₂	1.1%	0%	-100.0%
CH ₄	5.1%	5.8%	13.7%
H ₂	5.9%	5.1%	-13.6%
N ₂	53.5%	61.8%	15.5%
HHV (MJ/kg)	5.2	3.9	-25.6%

As those correlations were not derived from bagasse gasification, the results just presented are worse than those of Tab. 10 and 11. However, they are better than those given by pure equilibrium.

5. Conclusions

A chemical equilibrium approach for biomass gasification has been presented, and some modifications were discussed in order to consider non-equilibrium aspects.

The pure equilibrium model results showed good adherence to downdraft gasifier operation, especially for LHV values. These results indicate that equilibrium models might be useful for the evaluation of thermodynamic (energetic) behavior of systems based on gasification processes. The modifications proposed by Fock and Thomsen (2000) made the molar fractions come closer to real operation values, what could be useful for predictive analysis of downdraft gasifiers.

The use of empirical correlations proved to be more efficient to take into account kinetic aspects than the other approaches. Nevertheless, their application is somewhat restricted to models based on the fuel used to derive such correlations, as well as the type of the gasifier.

All in all, modifications proposed by Fock and Thomsen (2000) proved to be the most flexible ones, with good adherence to real operation conditions, and should be integrated to the chemical equilibrium model proposed in the paper.

One last remark should be addressed concerning the experimental results used. The reports used to collect those data did not have any comments or specifications on uncertainties of the measured data.

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