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## OPTIMIZATION OF THE SYNTHESIS GAS MODELING OBTAINED FROM A FLUIDIZED BED GASIFIER USING THE KUHN-TUCKER MULTIPLIERS

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**Abstract.** The objective of this work was to develop a chemical equilibrium model for the syngas obtained from fluidized bed gasifiers using air, steam or oxygen as gasification agents. The developed method uses a chemical equilibrium model modified by chemical disequilibrium factors. These factors are determined using an optimization method that uses the Kuhn - Tucker multipliers. The modified chemical equilibrium model uses the three most commonly used chemical reactions in the syngas modeling, which are the methane formation reaction, the homogeneous water-gas reaction, and the methane reforming reaction. It was considered 7 experimental compositions of the syngas for which the parameter  $ER$  varies between 0 and 0.36, the parameter  $S/B$  varies between 0 and 1.32, volumetric oxygen flow rate of  $1.5 \text{ Nm}^3/\text{h}$ , and the gasification temperature ( $T_{\text{Gas}}$ ) varies between  $650 \text{ }^\circ\text{C}$  and  $808 \text{ }^\circ\text{C}$ . The RMS error obtained for the different estimates of the composition of the syngas was considered admissible.

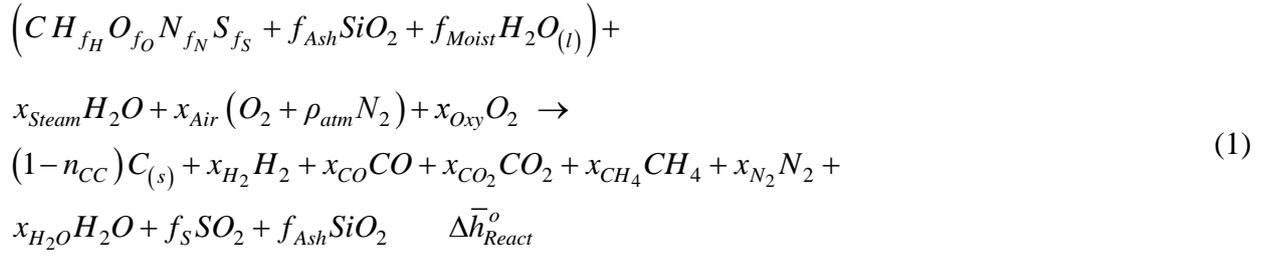
**Keywords:** Gasification, fluidized bed, Kuhn – Tucker multipliers.

### 1. INTRODUCTION

In gasification there are several reasons (non-homogeneous product mix, gasification time, gasifier heat loss, etc.) where in fluidized bed and fixed bed gasifier the products never reach a state of chemical equilibrium, which is why many authors correct their chemical equilibrium (chemical equilibrium constant) models with chemical disequilibrium factors (also known as adjustment factors), these quantities being empirically calculated (trial and error). These factors are multiplied to the equilibrium constants, thus giving rise to a new chemical equilibrium model capable of better predicting the composition of the syngas. Consequently, a smaller, and therefore more acceptable, RMS (root mean square) error is thus achieved. But so far, there is no proposed method for calculating such disequilibrium factors for fluidized bed gasification modeling (Loha, *et al.*, 2011) or for fixed bed gasifier (Zainal, *et al.*, 2001). In this work, a simple method is proposed that responds to such a requirement, which consists in calculating such chemical disequilibrium factors analytically, thus providing a very small RMS error.

### 2. MATERIAL AND METHOD

In the overall reaction of the gasification process presented in Eq. (1) both air, vapor and pure oxygen are considered as gasification agents. This was established to cover the largest number of studies in articles related to fluidized bed gasification. The overall gasification reaction presented in Eq. (1) is similar to that used by Mendiburu, *et al.*, 2014.



In this study it is considered  $\rho_{atm}=3.76$ , and the conversion efficiency of carbon represented as  $n_{CC}$ . To find the molar amounts and thus the percentage compositions of the components of the syngas, a mass balance of all the chemical elements present in the overall reaction was first carried out. For the use of the molar masses, enthalpies and Gibbs free energies of the different chemical substances were used the data provided by McBride, *et al.*, 2002. By performing the mass balance for carbon, hydrogen and oxygen, Eq. (2) - (4) were obtained.

$$x_{CO} = n_{CC} - x_{CO_2} - x_{CH_4} \tag{2}$$

$$x_{H_2} = C_{H_2} + n_{CC} + x_{CO_2} - 3x_{CH_4} \tag{3}$$

$$x_{H_2O} = C_{H_2O} - n_{CC} - x_{CO_2} + x_{CH_4} \tag{4}$$

$$x_T = C_T + n_{CC} - 2x_{CH_4} \tag{5}$$

In Eq. (5) the total molar amount of gases ( $x_T$ ) in the products of the overall gasification reaction was presented. The constants  $C_{H_2}$ ,  $C_{H_2O}$  and  $C_T$  are defined in Eq. (6) - (8), respectively.

$$C_{H_2} = \frac{f_H}{2} - f_O - 2x_{Oxy} - 2x_{Air} + 2f_S \tag{6}$$

$$C_{H_2O} = f_O + f_{Moist} + 2x_{Oxy} + x_{Steam} + 2x_{Air} - 2f_S \tag{7}$$

$$C_T = \frac{f_H}{2} + f_{Moist} + x_{Steam} + \frac{f_N}{2} + \rho_{atm} x_{Air} + f_S \tag{8}$$

The method proposed in this work consists in the minimization of a certain objective function which is derived from the RMS error calculation (Devore and Berk, 2012). To develop the method it is indispensable to calculate the amount of total reference mol of the syngas composition ( $x_{TR}$ ). This amount is defined as the sum of the equivalent molar amounts of each of the component gases of the syngas present in the volumetric base used to express the syngas. To establish the objective function was represented as  $EP_i\%$  the experimental percentage of the component  $i$  of the syngas, which can be  $H_2$ ,  $CO$ ,  $CO_2$ ,  $CH_4$  or  $N_2$ . The amount  $x_{TR}$  present in the volumetric base corresponding to the composition of the syngas is presented in Eq. (9) and Eq. (10) for a dry nitrogen-containing (DNCB) and nitrogen-free (DNFB) volumetric base, respectively.

$$x_{TR} = \frac{100 \left( \frac{f_N}{2} + \rho_{atm} x_{Air} \right)}{EP_{N_2}} \quad (9)$$

$$x_{TR} = C_{H_2} + 2n_{CC} + x_{CO_2} - 3x_{CH_4} \quad (10)$$

The objective functions for the composition of the syngas in DNCB or in DNFB are presented in Eq. (11) and Eq. (12), respectively.

$$F_{Obj}(n_{CC}, x_{CO_2}, x_{CH_4}) =: F_{Obj} = \sum_{i=H_2, CO, CO_2, CH_4} (EP_i x_{TR} - 100x_i)^2 \quad (11)$$

$$F_{Obj}(n_{CC}, x_{CO_2}, x_{CH_4}) =: F_{Obj} = \sum_{i=H_2, CO, CO_2, CH_4} (EP_i x_{TR} - 100x_i)^2 x_{TR}^{-2} \quad (12)$$

The Eq. (13) - (15) were used to calculate the chemical disequilibrium factors ( $f_{des,1}$ ,  $f_{des,2}$  and  $f_{des,3}$ ), and these equations were obtained from the equilibrium constant corresponding to the methane formation reaction (MFR), homogeneous water-gas reaction (HWGR), methane reforming reaction (MRR), respectively.

$$f_{des,1} = \frac{x_{CH_4} x_T \left( \frac{P_{Gas}}{P_o} \right)^{-1}}{K_{MFR} (T_{Gas}) x_{H_2}^2} \quad (13)$$

$$f_{des,2} = \frac{x_{CO_2} x_{H_2}}{K_{HWGR} (T_{Gas}) x_{CO} x_{H_2O}} \quad (14)$$

$$f_{des,3} = \frac{x_{CO} (x_{H_2})^3 \left( \frac{P_{Gas}}{P_o} \right)^2}{K_{MRR} (T_{Gas}) x_{CH_4} x_{H_2O} x_T^2} \quad (15)$$

The chemical equilibrium constant of the methane formation reaction, the homogeneous water-gas reaction and the methane reforming reaction are  $K_{MFR}$ ,  $K_{HWGR}$  and  $K_{MRR}$ , respectively. The gasification pressure and the normal pressure were represented by  $P_{Gas}$  e  $P_o$ , respectively, and the gasification temperature was represented by  $T_{Gas}$ .

For simplicity of working with the following equations, the notational changes of  $n_{CC}$ ,  $x_{CO_2}$  and  $x_{CH_4}$  by  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_3$ , respectively, were established. In Eq. (16) we present the Lagrangian expression for the optimization using the Kuhn-Tucker multipliers ( $\mu$ ).

$$L = F_{Obj} + \sum_{i=1}^3 \mu_i (\alpha_i - 1) - \sum_{i=1}^3 \mu_{i+3} \alpha_i \quad (16)$$

Applying the conditions of Karush-Kuhn-Tucker, we obtain the following system of equations presented in Eq. (17) - (19).

$$\frac{\partial F_{Obj}}{\partial \alpha_i} + \mu_i - \mu_{i+3} = 0 \text{ for } i=1 \text{ to } 3 \quad (17)$$

$$\mu_i (\alpha_i - 1) = 0 \text{ for } i=1 \text{ to } 3 \quad (18)$$

$$\mu_{i+3} \alpha_i = 0 \text{ for } i=1 \text{ to } 3 \quad (19)$$

This system of equations is under the inequality constraints presented in Eq. (17) originated by the domains established for each independent variable.

$$\alpha_i \leq 1, \alpha_i \geq 0, \mu_j \geq 0 \text{ for } i=1 \text{ to } 3 \text{ and } j=1 \text{ to } 6. \quad (20)$$

Solving the system of Eq. (17) - (19), the different molar amounts present in the products of the overall gasification reaction were calculated to finally replace those quantities in Eq. (13) - (15) to calculate the different chemical disequilibrium factors. The fsolve command of the MATLAB program was used as the solution tool of the system (17) - (19).

### 3. RESULTS AND DISCUSSION

The optimization method for modeling the syngas composition was tested for 7 experimental compositions, which are presented in Tab. 1.

Table 1. Syngas experimental compositions

Test	1	2	3	4	5	6	7
Reference	Karmakar, <i>et al.</i> , 2013.		Karmakar and Datta, 2011.		Sethupathy Subbaiah, <i>et al.</i> , 2014.		Campoy, <i>et al.</i> , 2009.
ER	0.25	0.35	0	0	0.18	0.18	0.36
S/B	0	0	1.32	1.32	0.30	0.30	0.32
Oxygen flow rate (Nm <sup>3</sup> /h)	0	0	0	0	0	0	1.5
T <sub>Gas</sub> (°C)	650	725	690	730	650	700	808
H <sub>2</sub>	17.22	15.88	50.50	52.20	20.55	20.70	28.1
CO	24.84	22.89	12.83	15.90	16.45	17.25	32.3
CO <sub>2</sub>	14.92	14.21	28.51	25.65	17.30	17.00	30.2
CH <sub>4</sub>	2.62	0.84	8.16	6.25	4.92	4.85	9.4
N <sub>2</sub>	40.40	46.18	---	---	40.78	40.20	---

In Tab. 2, we present the modeling of the different experimental compositions of the syngas presented in Tab. 1. In this table it can be observed in general, the different theoretical compositions obtained by the modeling are close to the experimental compositions and the RMS error in the range of [0.08, 3.70].

Estimates for components of the syngas such as H<sub>2</sub> and CO are very close to the experimental compositions, but the estimation of N<sub>2</sub> for all modeling of the experimental compositions are the same quantities, which causes the proposed model for the estimation for the syngas composition is optimal.

From the results presented in Tab. 2, the chemical disequilibrium factor  $f_{des,2}$  is the most appropriate disequilibrium factor to approximate the theoretical composition to the experimental composition of the syngas, because the factor  $f_{des,1}$  has very large values (greater than 10) and for the factor  $f_{des,3}$  has very small values (less than 0.001).

Table 2. Modeling of the syngas experimental compositions

Test	1	2	3	4	5	6	7
n <sub>CC</sub> (%)	87.19	95.29	100	100	67.78	69.46	100
H <sub>2</sub>	17.10	15.82	49.71	51.40	21.22	21.41	27.4
CO	24.96	22.95	13.74	16.82	15.78	16.54	34.2
CO <sub>2</sub>	15.17	14.33	30.39	27.55	15.96	15.58	34.6
CH <sub>4</sub>	2.37	0.72	6.16	4.22	6.26	6.27	3.8
N <sub>2</sub>	40.40	46.18	0	0	40.78	40.20	0
RMS	0.18	0.08	1.50	1.52	0.95	1.00	3.70
$f_{des,1}$	3.8192	3.1867	2.7769	2.7410	8.0929	14.2797	30.5924
$f_{des,2}$	0.5115	0.7807	1.0702	1.0076	0.2923	0.3598	0.4940
$f_{des,3}$	0.1578	0.0489	0.0185	0.0126	0.0131	0.0033	0.0003
$\Delta H_{React}^{\circ}$	17.2752	6.1188	130.1976	145.0134	95.7479	102.8030	-75.9620
$\mu_1$	0	0	24.2508	23.7076	0	0	339.9281

#### 4. CONCLUSIONS

From the results it is shown that the components of the syngas are not in chemical equilibrium with reference to the calculated chemical disequilibrium factors. This difference is most noticeable for gasification with air and air with steam.

The advantage of the proposed model was that it considers as output variable the carbon conversion efficiency, thus making a more real equilibrium model. The conversion efficiency of the carbon to the steam gasification is in accordance with the actual carbon conversion data which establishes that it is close to 100%.

All calculated solutions comply with the established inequality constraints of the optimization method. On the other hand, the proposed chemical equilibrium model yields a very small RMS error because the compositions obtained from the syngas modeling are very close to the selected experimental results.

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