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Estimation of Producer Gas from Low-grade Coal and Biomass Using Mathematical Modelling

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Abstract

Sustainable energy and reduction in greenhouse gases (GHG) are the challenging issues of the world. Due to the increase in globing warming concern, the industrial world has already reduced the use of fossil fuels to the status of minimal source of energy. Biomass is now believed to be an economically competitive with the fossil fuels, which can be subsequently used for the production of producer or syngas using appropriate technology of thermal conversion. The low energy contents of biomass are compensated by blending with a higher energy content coal.

The major objective of this study is to better understand the effect of Temperature change on the producer gas composition in circulating fluidized bed gasifier (CFBG). Primarily the current work is experimental, but supplemented by the mathematical modeling that explains different steps in terms of existing scientific knowledge. The validation results showed that the model predicted the molar ratio of H_2/CO in the producer gas in the range 0.97, 0.96, 0.93, 0.92, 0.927 and the measured values 0.83, 0.79, 0.78, 0.73 and 0.74 at temperature degree (°C) 750, 800, 820, 850 and 875 respectively. Similarly the molar ratio of CO/CO_2 predicted by the model was; 0.81, 0.84, 0.86, 0.89 and 0.85 against the experimental molar ratio 0.86, 0.91, 0.75, 0.66 and 0.59 respectively at fixed feed and ER value.

Keywords: modeling, furnace, gasification, producer gas,

1. INTRODUCTION

Producer gas from the co-gasification of coal-bagasse blend is a mixture of carbon monoxide (CO), hydrogen (H_2), methane (CH_4), carbon dioxide (CO_2), water (H_2O) and nitrogen (N_2). From many other options of gasification (like steam, oxygen, carbon dioxide), air gasification is considered to be more mature technology compared to other conversion processes. Stable gasification conditions are usually achieved between 700°C and 1100°C temperature and equivalence ratio (ER) between 0.2 and 0.4 [1]. Taking into account from the available technologies of thermal conversion, the circulating fluidizing fluidized bed (CFB) is considered to be the most suitable for medium and large scale gasification, due to the efficient hydrodynamic characteristics of fluidized bed furnace [2,3,4 &5]. Producer gas composition is unknown until the gasification work is conducted, while the experimental work

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is often resource-intensive. Therefore mathematical modeling is one of the inquisitive tools for predicting the producer gas composition using elemental analysis of fuel. Even though the combustion and gasification of coal have been focused since last many decade, at present, there are still many unexplored issues [6, 7].

Mainly, the models can be categorized into three groups: Kinetic models, equilibrium models (stoichiometric and non-stoichiometric) and neural network models. Some hybrid models that linked both aspects i. e. Equilibrium and kinetic have also been developed [8, 9].

Kinetic models are described on account of the reactions mechanism of the process. As it play an important role in designing, evaluating and improving gasifiers because of sensible description and prediction of the gasification process. These models can be very precise but complex in calculations. Several models have been developed in these years based on the kinetic approach, i.e. [10-14].

The limitation of the kinetic model is that their simulations cannot be generalized. They are sternly linked to the shape and specific configuration of the gasifier. Whereas, thermodynamic equilibrium models (TEM) are more wide-ranging. Thermodynamic equilibrium model is considered the simplest of all type as it gives producer gas composition with reasonable accuracy for different feed stocks at some selected gasification temperatures. The composition of a mixture using thermodynamic equilibrium model (TEM) can be studied using different approach. One of the main approaches is called “Gibbs energy minimization method”. It involves evaluating the concentrations of the species present that minimize the total Gibbs energy of the products, in accordance with the constraints imposed by the principle of conservation of mass and of the elements conservation [15-21].

However, the thermodynamic equilibrium model provides a better prediction of the composition of producer gas when the reaction temperature is sufficiently high. Therefore, the entrained bed gasifier due to high operating temperature gives the best prediction; where as a lower degree of accuracy is expected in predicting the producer gas composition for fluidized bed and moving bed gasifiers [22]. As such the equilibrium conditions are difficult to achieve in practical operating conditions, therefore results obtained from thermodynamic equilibrium modeling can serve as the maximum limit on producer gas composition.

Up till now most of the studies have used the equilibrium model to predict the producer gas composition for various biomass feed stock [23,24].Similarly some others [25] have developed a thermodynamic equilibrium model using coal as feedstock with various types of gasifiers. While little attention has been paid to develop the thermodynamic equilibrium model to predict the composition of producer gas using coal and biomass blends. The objectives of this study are to develop a mathematical model using elemental analysis of coal-biomass blends and to predict the composition of producer gas at different operating conditions. The results of model will be compared with experimental data.

2. Materials and Methods

2.1. Materials

Table-A.1: Material composition used in the modeling

Proximate Analysis (%)			Ultimate analysis (%)		
Parameter	Bagasse	Coal	Element	Bagasse	Coal
Fixed carbon	12.28	51	Carbon	43.07	59.08
Volatile matter	81.33	39.8	Hydrogen	6.6	5.60
Moisture	1.03	0.9	Oxygen	43.41	22.82
Ash	5.35	8.3	Sulphur	0. 16	2.79
HHV MJ/kg	17.88	22.20	Nitrogen	1. 41	1.409

2.2. Methodology

Equilibrium modeling was carried out based on elemental composition of C, H and, O in fuel. Empirical relations were developed for predicting the composition of individual component of producer gas .In spite of the fact that the composition of producer gas affect by several ways ,however it mainly depends on the type of gasifier, feedstock, gasifying medium (air/oxygen/steam) and operating parameters (such as temperature, moisture content and equivalence ratio) [26, 27]. In this study following assumptions has been made for the formulation of the thermodynamic model:

1 Due to high temperature gasification in CFBG, all the product gases assume to behave as ideal gases.

2 All reactions are at thermodynamic equilibrium.

3 Reactions proceed adiabatically, however amount of air is varied to achieve the desired reaction temperature in the gasifier.

4 Nitrogen present in fuel (coal &bagasse) and air is inert. Ash is inert and is not involved in any of the reactions, either as a chemical species or as a catalyst.

5 Carbon conversion efficiency is 100 % .Producer gas comprises only CO_2, CO, H_2, CH_4, N_2 and H_2O. Higher hydrocarbon (tar) other than CH_4 were assume negligible.

6 Sulfur and chlorine content in biomass were also neglected in biomass feed stocks.

Based on elemental analysis of coal and biomass the chemical composition of fuel is taken to be in the form $CH_XO_YN_Z$ and the global gasification reaction can be written as follows:

$$CH_XO_YN_Z + a(O_2 + 3.76\ N_2) \rightarrow CO_2 + H_2O + 3.76\ N_2 \quad (1)$$

Where:"a" is the stoichiometric amount of air required for combustion

$$CH_XO_YN_Z + WH_2O + X_g\ (O_2 + 3.76) \rightarrow X_1H_2 + X_2CO + X_3CO_2 + X_4H_2O + X_5CH4 + 3.76\ N_2 \quad (2)$$

Where: X_g is the actual fuel to air ratio and m_w is the amount of water per kmole of fuel. When moisture content is known, the value of m_w is a constant. The Moisture content mw of the feedstock is calculated as:

$m_w = [M_{fuel} \times m / 18 (1- m)]$ (3)

The major series of reactions that occur inside the fluidized bed reactor are as follows:

Oxidation reaction: $C + O_2 \rightarrow CO_2$ (4)
Boudouard reaction: $C + CO_2 \rightarrow 2CO$ (5)
Steam Gasification: $C + H_2O \rightarrow CO + H_2$ (6)
Water gas shift reaction: $CO + H_2O \rightarrow H_2 + CO_2$ (7)
Methane formation Reaction: $C + 2H_2 \rightarrow CH_4$ (8)

According [28] to out of these above reactions, the oxidation, steam gasification, Boudouard and Methanation reactions are independent. The oxidation reaction is assumed to be very fast as it is completed quickly, where as the water gas shift reaction is considered as the subtraction of the steam gasification and Boudouard reactions,. Therefore, Methanation and water-gas shift reaction could be considered to be in equilibrium and the equilibrium constant for these two reactions as the function of their molar composition can be written as follows:

Equilibrium constant from the shift reaction:

$$K_1 = \frac{P_{C.O_2}.P_{H_2}}{P_{CO}.P_{H_2O}} = \frac{n_{CO_2}.n_{H_2}}{n_{co}.n_{H_2O}} = \frac{x_3.x_1}{x_2.x_4} \tag{9}$$

Equilibrium constant from methane formation reaction:

$$K_2 = \frac{P_{CH_4}}{(P_{H_2})^2} = \frac{n_{CH_4}.n_{tot}}{(n_{H2})^2} = \frac{x_5 * n_{total}}{(x_1)^2} \tag{10}$$

The value of K_1 & K_2 can be determine by Gibbs free energy .The Gibbs free energy is weak function of pressure , while it is strongly dependent on reaction temperature [29]

$$-RT\ell nK = \Delta G_T^0 \tag{11}$$

$$\Delta G_T^0 = \sum_i x_i \Delta \overset{0}{g}_{f,T,i} \tag{12}$$

Where $\Delta g^0_{f,T,i}$ is empirically calculated as given in eq.13

$$\Delta g^{-0}_{f,T,i} = h^0_{f,T,i} - (a)T\ell nT - (b)T^2 - \frac{c}{2T^3} - \frac{d}{3T^4} - \frac{e}{2T} + f + gT \tag{13}$$

Table-A.2: Coefficients of eq-12 and standard heat of formation [30]

Species	a	b	c	d	e	f	g	Δh_f^0 298.15 (KJ/Kmole)
CO	5.62E-3	- 1.19E-5	6.38E-9	-1.85E-12	-4.89E2	0.868	-0.0613	-110
CH_4	-4.6E-2	1.13E-5	1.32E-8	-6.65E-12	-4.89E2	14.1	-0.121	-74.8
CO_2	-1.95E-2	3.12E-5	-2.45E-8	6.95E-12	-4.89E2	5.27	-0.121	-393.5
H_2O	-8.95E-3	-3.67E-6	5.21E-9	-1.48E-12	0	02.87	-0.172	-241.8

From the global reaction Eq.-2, there are six unknowns, x_1, x_2, x_3, x_4, x_5 and m_W, representing the molar composition of five unknown species in the producer gas and the oxygen content for the reaction. Hence, to predict the composition of producer gas, at least six equations are required.

$$C : 1 = x_1 + x_3 + x_5 \tag{14}$$

$$H : 2m_w + x = 2x_2 + 2x_4 + 4x_5 \tag{15}$$

$$O : 2X_g + Y + m_w = x_1 + 2x_3 + x_4 \tag{16}$$

Hence, we have six equations (9, 10 & 13-16) and six unknown variable, solve them simultaneously to determine the value of x1, x 2, x3, x4, and x5. Now as the reaction process is assumed to be adiabatic so, the enthalpy balances inside the gasifier results in the equation shown:

$$h^0_{f-CBB} + m_w(h^0_{f-H2O(l)} + h_{vap}) + x_g(h^0_{f-O2} + 3.76 * h^0_{f-N2}) \tag{17}$$

$$= x_1(h^0_{f-co} + \int_{298}^{Tg} C_{P-CO} dT) + x_2(h^0_{f-H2} + \int_{298}^{Tg} C_{P-H2} dT)$$

$$+ x_3(h^0_{f-co2} + \int_{298}^{Tg} C_{P-CO2}) + x_4(h^0_{P-H20} + \int_{298}^{Tg} C_{P-H2O} dT)$$

$$+ x_5(h^0_{CH4} + \int_{298}^{Tg} C_{P-CH4} dT) + (3.76 \times x_g \int_{298}^{Tg} C_{P-N2})$$

The heating value of the fuel ($\bar{h}^0_{f-CBB}$) was determined experimentally with a bomb calorimeter. Heat of formation of coal-biomass blend (CBB) can also be calculated with accuracy using the following equation [31].

$$h_{f-CBB} = HHV(Kj / Kmole) = 0.2326\left(146.58C + 56.878H - 51.53O - 6.58A + 29.45\right) \tag{18}$$

Where C, H, O and A is the fraction of carbon, hydrogen, oxygen and ash respectively in coal-biomass blends. The ultimate analysis and heating value of these blends are given in Table-III.

Moreover, from the above equation put the heat of formation h^0_{f-o2}, h^0_{f-H2} and h^0_{f-N2} equal to zero at the reference temperature 298 K and pressure of 1 atmospheric and reduce the above equation for further calculation. The Cp at some temperature "T" can be calculated from the following:

$$cp_{(T)} = c_1 + c_2T^1 + c_3T^2 + c_4T^3\left(\frac{kj}{kg}\right) \tag{19}$$

Integration of Eq-17 from the ambient temperature to gasification temperature gave the sensible heat of each gas species. The value of empirical constant C_1-C_4 is taken as reported by [31].

Table A.3: Coefficients of specific heat capacity for various gases.

Gases	C_1	C_2	C_3	C_4
N_2	31.2	-1.36E-2	2.68E-5	-1.17E-8
H_2	29.1	-1.92E-3	4.00E-6	-8.70E-10
CO	30.9	-1.29E-2	2.79E-5	-1.23-8
CO_2	19.8	7.34E-2	-5.60E-5	1.72E-8
CH_4	19.3	5.21E-2	1.20E-5	-1.13E-8
H_2O (g)	32.2	1.92E-3	1.06E-5	-3.60E-9

The standard heat of formation (Δhf°) could also be equated as [32]:

$$\frac{d\ln k}{dT} = \frac{\Delta h_f^o}{RT^2} \tag{20}$$

Heat of formation is basically a function of temperature, and hence Eq. (19) can be integrated as follows [29/14]:

$$\ln k = \int \frac{\Delta h_f^o}{RT^2} dT + I \tag{21}$$

Δhf° could also be equated as [12]:

$$\frac{\Delta h_f^0}{R} = -\frac{j}{RT} + \Delta AT + \frac{\Delta B}{2}T^2 + \frac{\Delta C}{3}T^3 - \frac{\Delta D}{T} \tag{22}$$

Substituting Eq. (21) into Eq. (20)

$$\ln k = -\frac{j}{RT} + \Delta A \ln T + \frac{\Delta B}{2}T + \frac{\Delta C}{6}T^2 + \frac{\Delta D}{2T^2} + I \tag{23}$$

From eq-11 and multiply eq-21 by -RT gives the following:

$$\Delta G^0 = j - RT(\Delta A \ln T + \frac{\Delta B}{2}T + \frac{\Delta C}{6}T^2 + \frac{\Delta D}{2T^2} + I \tag{24}$$

Table A.4: Gibbs function of formation and heat of formation at 298K [32]

Chemical species	Phase	ΔG^0 at 298.15 (KJ/K-mole)	Δh_f^0 298.15 (KJ/K-mole)
CO_2	G	-394359	-393.5
CO	G	-137169	-110
CH_4	G	-50460	-74.8
H_2O	L	-237129	-
H_2O	G	-228572	-241.8
H_2	G	0	-
N_2	G	0	-

Table-A.5: Heat capacity Constant A, B, C and D [32]

Chemical species	Heat capacity coefficient (A)	Heat capacity coefficient (B)	Heat capacity coefficient (C)	Heat capacity coefficient (D)
CO_2	3.376	5.57E-04	-	-3100
CO	5.457	1.05E-03	-	-115700
CH_4	1.702	9.08E-03	-2.164E-06	-
H_2	3.249	4.22E-04	-	8300
H_2O	3.470	1.45E-03	-	12100
C	1.771	0.771		-0.867

Eqns-20-22 will be used to determine the equilibrium constant for any reaction temperature “T”. The value of constant “j” can be determined by Eq-20 at constant temperature 298.15K ,where the value ofΔh_f^0 is known .Similarly ,the integration constant “I” can be determine using Eq-21or 22 at the temperature at which the value of ΔG^0 or ln(k) is known ,normally at 298.15K.

The value of ΔA, ΔB, ΔC & ΔD can be calculated from the data of heat capacity. The equation to determine of ΔA, ΔB, ΔC & ΔD for Methanation reaction using heat capacity data from Table-IV has been reported as [23].

$\Delta A = ACH_4 - AC - 2AH_2$

$\Delta B = BCH_4 - BC - 2BH_2$

$\Delta C = BCH_4 - BC - 2BH_2$

$\Delta D = DCH_4 - DC - 2DH_2$

After calculating the value of constant j and I from Eqns-20 & 22 respectively at 298 K, using the Δh_f^0 and ΔG_f^0 from Table-III, then substitute the value of these constants in Eq. -21 for the determination of equilibrium constant k_1 and $k_2$at any temperature “T”.

2.3. Algorithms and General Formula Derivation

To resolve the systems of nonlinear equations, the algebraic method is one of the most useful tools to solve the equation. The model was run with an elemental composition of coal and coal biomass blends of weight proportion 94/6, and 91/9 as feed stocks. The elemental compositions of the feedstock's coal and coal-biomass blends were used to obtain the producer gas composition by solving six equations (Eqns. 9, 10 & 13-16) in MATLAB [33]. Newton- Jacobi iteration was used for solving these equations. Complete MATLAB coding for these overall equilibrium model were used to predict the gas composition.

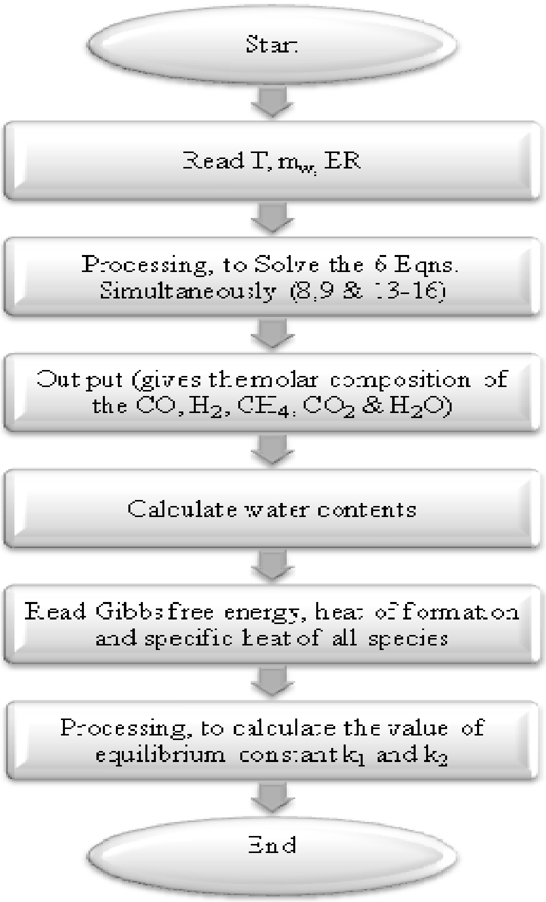

Fig. 1: Flow diagram of Mat lab program used for estimation of producer gas composition

3. Results and Discussion

The model was validated against the experimental run. This experimental run was made for coal-biomass feedstock of weight proportion 91/9 at fixed ER value. The experiment was conducted on an air-blown CFB gasifier. The ultimate and proximate analyses for coal and bagasse given in Table 1 were used as reference data. The input data of experimental run was entered into the model and the predictions were found to be in good agreement with the reported results. For example the model predicted the molar ratio of H_2/CO in the producer gas in the range 0.97, 0 96, 0.92, 0.93 and 0.927 and for the same input, the experimental results were measured 0.83, 0.798, 0.786, 0.73 and

0.74 at temperature degree (°C) 750, 800, 820, 850 and 875 respectively. Similarly the molar ratio of CO/CO_2 predicted by the model were as measured; 0.81, 0.838, 0.866, 0.896 and 0.85 against the experimental molar ratio 0.86, 0.917, 0.75, 0.66 and 0.59 respectively. The input data for the said run as given : input coal-biomass blend (91/9) mass flow 3.64 kg hr-1, air for gasification 6 kg hr-1 temperature 750°C – 900°C at atmospheric pressure. Figure 2 & 3 compares the experimental results as measured in experimental run to the model predictions using the input data presented above. The model predictions are in fair agreement with the experimental data. For example the model predicted the decreasing trend of H_2/CO ranging from 0.97 to 0.92 and the experimental values also gave the same decreasing trend (0.83 to 0.74) but with smaller deviation.

However, the molar ratio of CO/CO_2 is over predicted by the model although trend was same for both and molar ratio of CO/CO_2 increased with increasing temperature. The molar ratio of CO/CO_2 was over predicted by the model, this was perhaps due to the complexity of the co-gasification reactions, as order and sequence of the co-gasification can't be predicted accurately.

The product gas of the fluidized bed gasifier contains tar, which is not included in equilibrium models, additionally the amount of other hydrocarbons and diluting impact of inert gases (N_2 and CO_2) and moisture has also ignored in the model. Therefore over-prediction of methane is a quite common reason of the model.

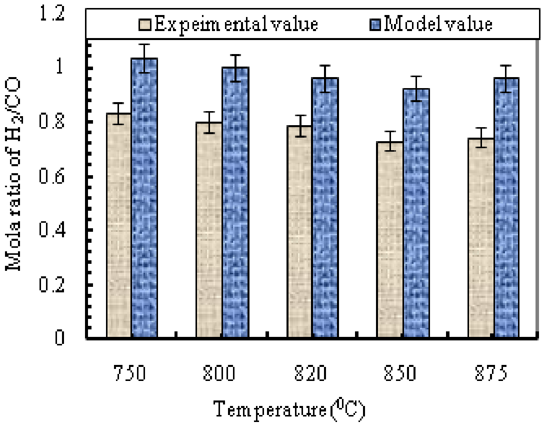

Fig. 2: Shows the comparison of the molar ratio of H_2/CO between experimental and model values for coal-bagasse blend 91/9 at fixed ER=0.30.

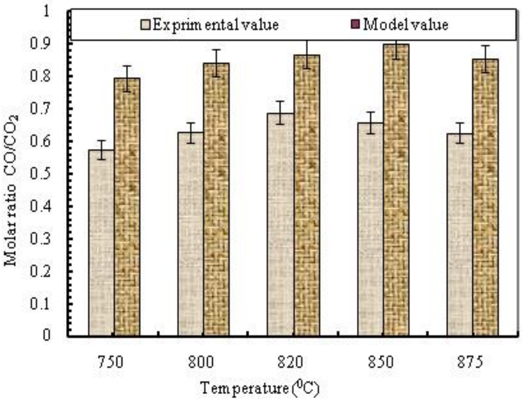

Fig. 3: Shows the comparison of molar ratio of CO/CO_2 for experimental and model values for coal-bagasse blend 91/9 at fixed ER=0.30

4. Conclusions

Product gas composition was predicted using the thermodynamic model. Series of gasification reactions and various co-relations were used to determine the producer gas composition at some specific temperature. The results of the developed model were compared with the experimental data as given in Figure 2& 3 and observations are being summarized as follow.

The molar ratio of H_2/CO found in experimental run and model prediction are almost similar in trend for all temperature range little variation, however it was more pronounced at low temperature.

The molar ratio of CO/CO_2 was over predicted by the model, this was perhaps due to the complexity of the co-gasification reactions as order and sequence of the co-gasification can't be predicted accurately.

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