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Energy Procedia 160 (2019) 317–323

Energy Procedia

www.elsevier.com/locate/procedia

2nd International Conference on Energy and Power, ICEP2018, 13–15 December 2018, Sydney, Australia

# Biomass gasification in a fixed bed downdraft reactor with oxygen enriched air: a modified equilibrium modeling study

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**Abstract**

Biomass conversion by gasification process is increasingly becoming attractive, especially for ceramic making industry, to transform biomass materials into combustible fuel gas called producer gas. This producer gas can then be used to fully or partially substitute liquefied petroleum gas in ceramic firing process. However, air gasification is known to generate low calorific value of gaseous fuel (3-6 MJ/Nm$^3$) which may not be able to generate sufficiently high temperature (> 1200 $^o$C) flame required by ceramic firing process. Use of oxygen enriched air is therefore of great interest if medium to high calorific value producer gas is required. In this work, a modified equilibrium model of global gasification reactions is developed to predict the resultant distribution of combustible gas species in the producer gas and to study the effect of operating parameters (oxygen content in air, and equivalence ratio) in a gasification process of agro-residues in a fixed bed downdraft gasifier at a fixed temperature. The modified equilibrium model of global gasification reactions developed in this work is based on thermodynamically stoichiometric approach due to its simplicity and reduced computational time. Model predictions of reaction kinetic constants for gasification reactions and gas concentration are validated by comparing with available experimental data. Simulation of influence of oxygen content in air (21-50%) and equivalence ratio (0.15-0.35) on composition of combustible gas and its heating value is carried out. The preliminary model simulation is found to give good qualitative prediction of experimental results. For maximum calorific value of producer gas generated, oxygen content in air should be 50%, and the equivalence ratio should be 0.15, respectively. For better accuracy of this modified equilibrium model, unconverted char and tar should be further considered.



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1876-6102 
10.1016/j.egypro.2019.02.163

*Keywords:* Chemical kinetcis; producer gas; renewable energy; stoichiometry; thermochemical conversion

## 1. Introduction

Biomass has gained enormous interests with widespread utilization. Conversion by gasification process is increasingly becoming attractive, especially for ceramic making industry, to transform biomass materials into combustible fuel gas called producer gas [1]. It is a mixture of combustible gases consisting mainly of $H_2$, CO, $CH_4$, $CO_2$ and $N_2$. This gas can be used to fully or partially substitute liquefied petroleum gas in ceramic firing process. Gasification process occurs in temperature range of 750°C to 1300°C with different gasifying agents such as air, oxygen, steam or mixture of them [2]. However, air gasification is known to generate low calorific value of gaseous fuel (3-6 MJ/Nm$^3$) which may not be able to generate sufficiently high temperature (> 1200°C) flame required by ceramic firing process. Oxygen gasification can produce high calorific value gas around 10-20 MJ/Nm$^3$ but the oxygen production cost is quite expensive for industrial utilization. Use of oxygen enriched air is therefore of great interest if producer gas with medium to high calorific values can be generated with viable cost. Production of 30-50% $O_2$ enriched air based on membrane separation technology is becoming competitive [3].

Gasification process id affected by gasifier type, feedstock composition, gasifying agent, equivalence ratio, reaction temperature, etc. Study of operating condition and its effects on gasification process is often derived through trials by experiments. But the limitation of laborious process, time and high cost in experiments makes mathematical modeling attractive. It can be used to investigate biomass gasification especially when large scale experimental study seems to be difficult and uneconomical. Generally, biomass gasification models are carried out using two techniques; kinetic model and thermodynamic equilibrium model. Requirement of many detailed information on mechanisms, specific gasifier configuration, and numerous mathematical formulas causes the process of kinetic model complicated. Thermodynamic equilibrium model, based on mass balance and chemical balance, is less complicated, and can be applied to various biomass types and reactor types [4, 5]. Thermodynamic equilibrium model can be categorized into two approaches; stoichiometric (on the basis of equilibrium constant) and non-stoichiometric (on the basis of minimizing the Gibbs free energy). Stoichiometric approach is usually less complex, and has been widely used to study the effect of process parameters [6, 7]. Various researchers, such as Shama [8], Huang and Ramaswamy [9], Atnaw et al. [10], Loha et al. [11], Koroneos and Lykidou [12] used this approach to predict gasification performance. Their studies showed reasonable agreement with experimental data. However, some predictions remain still inaccurate. Many researchers have tried to develop their models to improve the accuracy [13, 14]. Ramanan al. [15] developed an equilibrium model to predict the gas composition under varying operating parameters of equivalence ratio, reaction temperature, and moisture content. Jarungthammachote and Dutta [13] developed a model by multiplying equilibrium constants with coefficients for predicting the gas composition from solid waste in downdraft gasifier. Barman et al. [14] considered tar as a product in the equilibrium model.

In this work, a modified equilibrium model of global gasification reactions is developed to predict the distribution of combustible gas species in the producer gas and to study the effect of operating parameters (oxygen content in air, and equivalence ratio) in a gasification process of agro-residues in a fixed bed downdraft gasifier.

## 2. Methodology

Thermodynamic equilibrium approach was used to develop a mathematical model to predict producer gas composition. The model is based on biomass composition that can be applicable to any biomass type. The feedstocks in the prediction were corn cobs and corn stovers which ultimate analysis results are shown in Table 1.

Table 1. Ultimate analyses of corn cob and corn stovers.

| Biomass type | Ultimate analysis (*wt.%*) | | | |
|---|---|---|---|---|
| | C | H | O | N |
| Corn cobs | 45.5 | 6.2 | 47.0 | 1.3 |
| Corn stovers | 47.4 | 5.9 | 38.1 | 0.7 |

Effects of equivalence ratio (0.15-0.35) and oxygen enriched air with oxygen content of 21-50% based on membrane technology were predicted and the predicted results are compared with the experimental data. While the gasification temperature was fixed at 800 °C, all other operation conditions were varied for the gasification in a fixed bed gasifier.

### 2.1. Model formulation

The thermodynamic equilibrium model was developed based on the following assumptions:

- The reactor is considered to be steady state and uniform temperature with zero dimension.
- The residence time is high enough to achieve equilibrium state.
- All carbon content in biomass is converted into gaseous form. The gaseous compounds formed are only $H_2$, CO, $CH_4$, $CO_2$, $N_2$ and $H_2O$. Tar is assumed to be negligible.
- Ash is assumed as inert in all reactions.
- All product gases behave as ideal gases.

The chemical composition of biomass is taken to be $CH_xO_yN_z$. It is gasified in m moles of air, the global gasification reaction can be written as follows:

$$CH_xO_yN_z + m\left(O_2 + \frac{\%N_2}{\%O_2}N_2\right) = x_{H_2}H_2 + x_{CO}CO + x_{CH_4}CH_4 + x_{CO_2}CO_2 + x_{H_2O}H_2O + \left(\frac{z}{2} + 3.76m\right)N_2 \quad (1)$$

where $x_{H_2}$, $x_{CO}$, $x_{CH_4}$, $x_{CO_2}$, and $x_{H_2O}$ are mole ratio of $H_2$, CO, $CH_4$, $CO_2$, and, $H_2O$ respectively. x, y, and z are mole ratio (H/C, O/C, and N/C) determined from ultimate analysis of the biomass. Balancing carbon, hydrogen and oxygen moles of the global reaction can be written as

$$\text{C: } x_{CO} + x_{CO_2} + x_{CH_4} = 1 \quad (2)$$

$$\text{H: } x + 2w = x_{H_2} + 2x_{H_2O} + 4x_{CH_4} \quad (3)$$

$$\text{O: } y + 2m + w = x_{CO} + 2x_{CO_2} + x_{H_2O} \quad (4)$$

The major reactions that occur inside the gasification process are as follows:

$$C + CO_2 \rightarrow 2CO \quad (5)$$

$$C + H_2O \rightarrow CO + H_2 \quad (6)$$

$$C + 2H_2 \rightarrow CH_4 \quad (7)$$

The first two reactions shown above (eqs. 5 and 6) can be combined into eq. (8) known as water-gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (8)$$

So, eqs. (7) and (8) are used to represent the major reactions that occur in the gasification process. The equilibrium constant for these equations as the function of their molar composition can be written as follows:

$$K_1 = \frac{x_{CH_4}}{(x_{H_2})^2} \quad (9)$$

$$K_2 = \frac{x_{CO_2}x_{H_2}}{x_{CO}x_{H_2O}} \quad (10)$$

The value of $K_1$ and $K_2$ can be determined by Gibbs free energy as presented in eqs. (11) and (12)

$$\ln K = -\frac{\Delta G^{\circ}}{\bar{R}T} \tag{11}$$

$$\Delta G = \sum_i x_i \Delta \bar{g}_{T,i} \tag{12}$$

The change in Gibbs free energy for an individual gas is given by:

$$\Delta \bar{g}_{T,i} = \bar{H}_{f,i} - aTlnT - bT^2 - \frac{c}{2}T^2 - \frac{d}{3}T^4 + \frac{e}{2T} + f + gT \tag{13}$$

where a-g are coefficients at standard reference state of 298 K and 1 atm pressure. It can be seen that the Gibbs free energy is function of the reaction temperature. Zainal et al. [16] simplified eq. (11) for ln K as

$$\ln K_1 = \exp\left(\frac{4276}{T}\right) - 3.961 \tag{14}$$

$$\ln K_2 = \frac{7082.848}{T} + (-6.567)lnT + \frac{7.466\times10^{-3}}{2}T + \frac{-2.164\times10^{-6}}{6}T^2 + \frac{0.701\times10^{-5}}{2(T)^2} + 32.541 \tag{15}$$

There are five equations (eqs. (2), (3), (4), (9), and (10)) and five unknowns ($x_{H_2}, x_{CO}, x_{CO_2}, x_{H_2O}, x_{CH_4}$). MATLAB code with Newton-Raphson method is used to solve the nonlinear equations, and LHV is calculated by

$$LHV = 10.78 \times \%H_2 + 12.63 \times \%CO + 35.88 \times \%CH_4 \ \ [\mathrm{MJ/m^3}] \tag{16}$$

*2.2. Model validation and modification*

The gas composition from model calculation is compared with experimental results to check its deviation by root mean square error (RMSE). In actual gasification system, the non-equilibrium conditions are always existent. Therefore, the model is developed by multiplying non-equilibrium coefficients A and B to $K_1$ and $K_2$ to minimize errors. Many researchers applied this method to develop their models and resulted in better prediction [13, 14, 17].

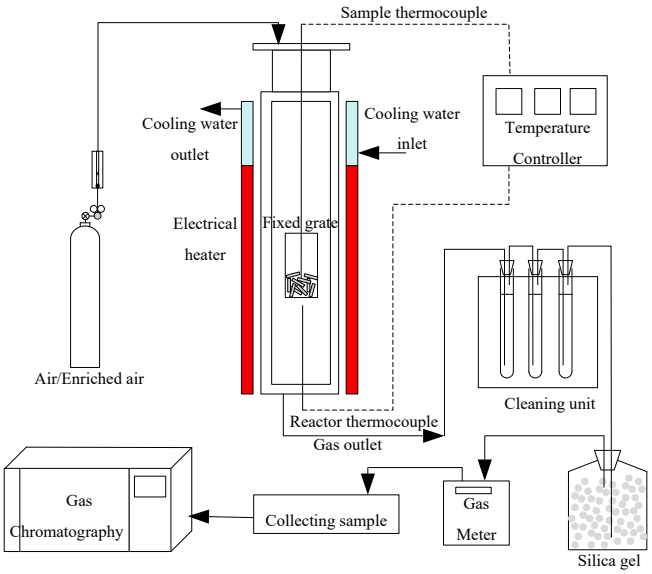


Fig. 1. Experimental setup.

$$RMSE = \sqrt{\frac{\Sigma(x_e - x_p)^2}{N}} \quad (17)$$

### 2.3. Experimental setup

A laboratory scale fixed bed gasifier was used in this study. Schematic diagram of the setup is shown in Fig. 1. The reactor was surrounded and controlled by a 5 kW electrical heater with insulated covering. K-type thermocouples were installed to monitor and control temperature of the reactor and sampling biomass. 15 g of biomass (corn cob pellets and corn stover pellets) was loaded in the heating section with controlling temperature at 800°C. Air and oxygen enriched air were supplied with the same conditions in model calculation. The product gas was cooled, dried, and collected in gas bags. The gas was subsequently analyzed to measure the composition of $H_2$, CO, $CH_4$, $CO_2$, and $N_2$ by a Shimadzu gas chromatography model GC-8A.

## 3. Result and discussion

The predicted gas distributions are calculated using fundamental thermodynamic equilibrium. Figs. 2 and 3 show the gas distributions from model calculation comparing with experimental results. It was found that both biomass materials showed similar results. Corn cobs were found to produce more $H_2$ while stover produced more CO. The model predictions showed similar tendency with the experimental results. The concentrations of $H_2$ and CO were overpredicted, while $CH_4$ was underpredicted. These results agreed with Melgar et al. [18] and Arun et al. [12].

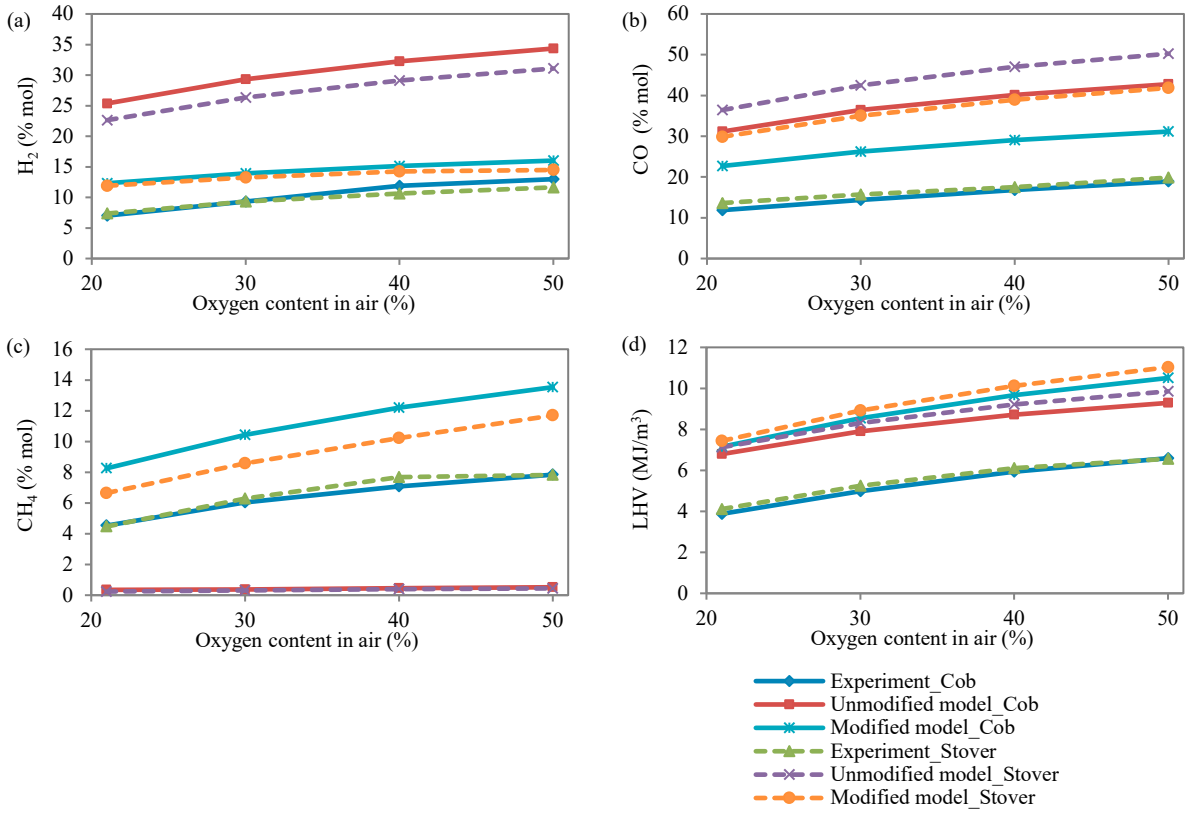


Fig. 2. Effect of oxygen content in air on (a) $H_2$ production; (b) CO production; (c) $CH_4$ production; (d) LHV.

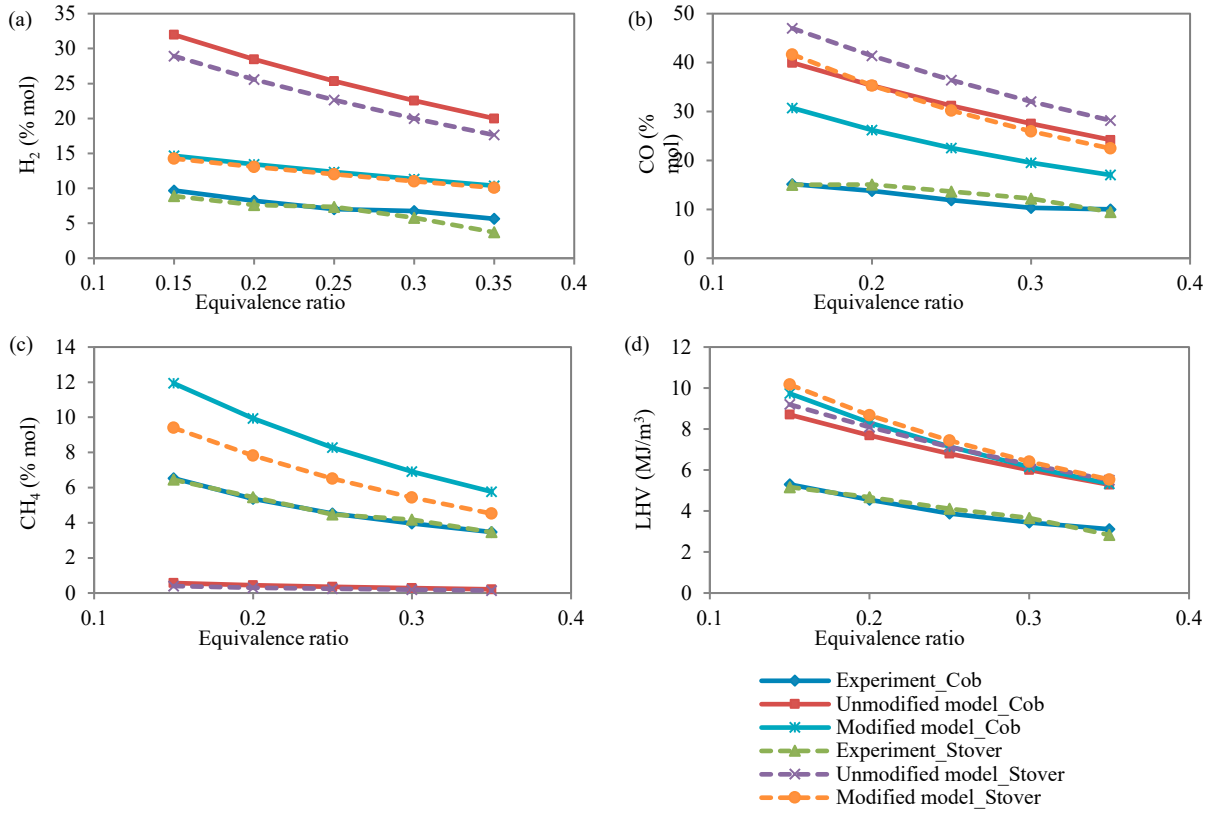


Fig. 3. Effect of equivalence ratio on (a) $H_2$ production; (b) CO production; (c) $CH_4$ production; (d) LHV.

The model was modified by multiplying correction factors called non-equilibrium coefficients A and B to $K_1$ and $K_2$ to minimize errors. In this work, initial RMSE of 12.99 was reduced to a minimum of 6.37 at the coefficients A = 125 and B = 1.01. The modified model predictions resulted in closer values to the experimental data. However, the accuracy of the predictions was still somewhat shortcoming. The difference between the model predictions and experimental results may be attributed to incompatibility in model assumptions such as no tar and solid residues, and reaction time may be insufficient. It was possible that many reactions occurred in the gasification process, hence, only water-gas shift and methanation reactions may not fully represent this study, resulting in some discrepancies between predicted and experimental results. Unconverted char and tar may be further taken into account for better accuracy. However, this modified model was found to give good qualitative prediction of experimental results. It may be used to explain the behavior of gasification process.

Fig. 2 shows the effects of oxygen content in air on combustible gas composition. The increase in oxygen content from 21 to 50**%** increased all of combustible gas concentration**.** This can be explained by the lower nitrogen dilution at the same equivalence ratio. Less nitrogen dilution in the enriched air affected the increase in concentration of the other gases, including $H_2$, CO, and $CH_4$**.** This increasing combustible gas composition also improved LHV. Oxygen enriched air with 50% oxygen content gave the highest LHV.

The composition of $H_2$, CO, and $CH_4$ was found to decrease gradually when the ER was increased from 0**.**15 to 0**.**35, as shown in Fig**.** 3**.** Similar trend was also observed by Htut et al. [20]. An increase in ER increased air flow into the process which may dilute the producer gas**.** The additional oxygen also favoured the oxidation of the solid carbon and combustible gaseous contents, and reduces partial oxidation, $H_2$, CO, and $CH_4$ were consumed and $CO_2$ was formed**.** The increase in ER also reduced contact durations for gasification reactions. The decrease in these combustible gas compositions led to low LHV.

## 4. Conclusion

A modified thermodynamic equilibrium gasification model based on equilibrium constant was developed to predict product gas composition and compared to the experimental data. The predicted gas composition was shown to have similar trend to experimental data, but the prediction was still not quantitatively accurate. RSME was around 6.37. The deviations could be from incompatibility in assumptions made in simulation studies. For better accuracy of this modified equilibrium model, unconverted char and tar may be further taken into account. The use of oxygen enriched air increased LHV as oxygen content contradictory with increasing ER. Oxygen content in air in the range of 50% with equivalence ratio of 0.15 may be used for generating maximum calorific value.

## Acknowledgements

The authors wish to acknowledge the supports from the Energy Policy and Planning Office, Ministry of Energy, Thailand Research Fund (RSA5680011), and Chiang Mai University.

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