

Kinetic Modeling of Biomass Gasification with Carbon Dioxide Sorption

¹Basil Issac Mathew, ²S. Rupesh, ³C. Muraleedharan, ⁴Arun P

^{1,2,3,4}Mechanical Engineering, National Institute of Technology Calicut, India.

Received February 2016; Accepted 18 April 2016; Available 25 April 2016

Address For Correspondence:

Basil Issac Mathew, Mechanical Engineering, National Institute of Technology Calicut, India.
E-mail: basilmathu@gmail.com

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ABSTRACT

The present work deals with kinetic modelling of air-steam gasification of rice husk in the presence of calcium oxide as sorbent. This model accounts pyrolysis as a function of temperature and air - steam gasification of the pyrolysis product considering Arrhenius reaction kinetics. The developed model is used to study the effect of temperature, steam to biomass ratio, sorbent to biomass ratio and equivalence ratio on product gas composition. An increase in hydrogen concentration by 60% is observed at a temperature of 1000 K, steam to biomass ratio of unity and equivalence ratio of 0.25 when sorbent to biomass ratio is increased.

KEYWORDS: Gasification, CaO sorbent, kinetic model, pyrolysis, syngas.

INTRODUCTION

Systems and processes utilising renewable fuels with limited CO₂ content have significance in the context of green environment and global warming. Biomass gasification is a pro-environmental energy conversion technique which utilises renewable fuels for heat and power generation. Biomass gasification is an energy efficient process to produce gaseous mixture, known as product gas or syngas [1]. This gaseous mixture mainly consists of carbon monoxide, hydrogen, carbon dioxide and traces of methane. Carbon dioxide being an incombustible gas, its capture improves the quality of product gas and reduces emission. CaO is identified as a potential sorbent to capture CO₂ from syngas [2]. This technique improves the prospect of biomass in gasification from carbon neutral emitter to carbon negative emitter. The removal of carbon dioxide from producer gas is done either at the downstream side of the gasifier or by applying CaO sorbent in the gasifier itself. For in-situ CO₂ capture, the sorbent may be mixed either with powdered biomass or with bed material. A parametric study on hydrogen enriched gas production, via steam gasification, in the presence of CaO, was performed by Inayat *et al.* [3]. They investigated the effects of temperature and steam to biomass ratio on the hydrogen concentration, gas yield and gasification efficiency. A kinetic model to study the effect of CaO in air - steam gasification of biomass was developed by Sreejith *et al.* [4]. They used the model to analyse the effect of CaO on gasification performance. The concentration of H₂ in the producer gas was found to increase in the range of 14-16% for air - steam gasification with the addition of CaO. A steady state model of downdraft gasifier was developed by Giltrap *et al.* [5] based on published values of reaction kinetics in the reduction zone. Mass and energy balance was applied to develop differential equations for change in concentration and temperature along the gasifier height. Florin *et al.* [6] developed a thermodynamic equilibrium model to investigate the fundamental reaction parameters influencing the output of H₂- rich gas. A maximum hydrogen concentration of 83% (dry basis) was predicted using the developed model. A method to regenerate the CaO was also proposed. Acharya *et al.* [7] developed a Gibbs free energy minimization model to study the effect of

To Cite This Article: Basil Issac Mathew, S. Rupesh, C. Muraleedharan, Arun P., Kinetic Modeling of Biomass Gasification with Carbon Dioxide Sorption. *Advances in Natural and Applied Sciences*. 10(4); Pages: 472-477

steam to biomass ratio, temperature and sorbent to biomass ratio on product gas composition. They found that an increase in CaO to biomass ratio greatly increased the yield and concentration of hydrogen in product gas. A kinetic model to simulate biomass steam gasification with in-situ CO₂ capture for enriched hydrogen gas production was developed by Inayat *et al.* [8]. The model predicted an increase in hydrogen mole fraction in the product gas from 0.65 to 0.85 using CaO. The evaluation of kinetic parameters for hydrogen production in integrated catalytic adsorption (ICA) steam gasification of palm kernel shell was carried out by Khan *et al.* [9]. They found that the H₂ content in the syngas was gradually increased by increasing steam to biomass and adsorbent to biomass ratios. The present work deals with the kinetic modelling of air - steam gasification of rice husk in the presence of CaO sorbent.

II. Model development:

The model is developed using reaction kinetic approach with rice husk as the feedstock material. The results of proximate and ultimate analyses of the feed stock used in the model are given in TABLE 1.

The following assumptions are made for the formulation of the model,

- Elements other than C, H and O in the feedstock are negligible.
- Nitrogen is considered as inert.
- Char yielded in devolatilisation stage is taken as pure carbon.
- Steam is supplied at 1 bar and 573 K and air at ambient conditions.
- Only the CO₂ sorption property of CaO is accounted, neglecting its catalytic activity.

Table 1: Results of Proximate and Ultimate analyses of rice husk

| Proximate analysis (wt. %) | | Ultimate analysis (wt. %) | |
|----------------------------|----|---------------------------|-------|
| Moisture | 12 | Carbon | 34.35 |
| Volatile matter | 58 | Hydrogen | 5.22 |
| Ash | 18 | Oxygen | 57.66 |
| Fixed Carbon | 12 | Nitrogen | 2.43 |

The model mainly consists of pyrolysis, partial oxidation, gasification and carbonation reactions. The amount of pyrolysis products are determined from the correlations developed by Gomez-Barea *et al.* [10], given by Equations (1) - (6):

$$\text{gas yield} = 311.10 - 351.45 * \left(\frac{T_{\text{py}}}{T_{\text{ref}}}\right) + 121.43 * \left(\frac{T_{\text{py}}}{T_{\text{ref}}}\right)^2 \quad (1)$$

$$\text{char yield} = -15.03 + 50.58 * \left(\frac{T_{\text{py}}}{T_{\text{ref}}}\right) - 18.09 * \left(\frac{T_{\text{py}}}{T_{\text{ref}}}\right)^2 \quad (2)$$

$$\text{CO (vol. \%)} = 240.53 - 225.12 * \left(\frac{T_{\text{py}}}{T_{\text{ref}}}\right) + 67.50 * \left(\frac{T_{\text{py}}}{T_{\text{ref}}}\right)^2 \quad (3)$$

$$\text{CO}_2 \text{ (vol. \%)} = -206.86 + 267.66 * \left(\frac{T_{\text{py}}}{T_{\text{ref}}}\right) - 77.50 * \left(\frac{T_{\text{py}}}{T_{\text{ref}}}\right)^2 \quad (4)$$

$$\text{CH}_4 \text{ (vol. \%)} = -168.64 + 214.47 * \left(\frac{T_{\text{py}}}{T_{\text{ref}}}\right) - 62.51 * \left(\frac{T_{\text{py}}}{T_{\text{ref}}}\right)^2 \quad (5)$$

$$\text{H}_2 \text{ (vol. \%)} = 239.97 - 257.01 * \left(\frac{T_{\text{py}}}{T_{\text{ref}}}\right) + 72.50 * \left(\frac{T_{\text{py}}}{T_{\text{ref}}}\right)^2 \quad (6)$$

The chemical reactions considered in this model are given in TABLE 2. Among the reactions, R₁- R₄ and R₈ are heterogeneous reactions whereas R₅- R₇ are homogeneous reactions. The reaction rate (r_i) is expressed as a function of temperature using Arrhenius constant:

$$r_i = k_i C_A C_B \quad (7)$$

Arrhenius constant is given by:

$$k_i = A \exp\left(\frac{E_a}{RT}\right) \quad (8)$$

where C_A and C_B are the concentrations (mol/m³) of species in the reactant side, A is the pre-exponential factor (s⁻¹), E_a is activation energy (J mol⁻¹) and R is universal gas constant (J mol⁻¹ K⁻¹). The kinetic rate equations for the gasification reactions are given in TABLE 3.

Table 2: Chemical reactions considered in the model

| Reaction number | Reaction | Reaction name |
|-----------------|---|-------------------------|
| R ₁ | C + H ₂ O → CO + H ₂ | Char gasification |
| R ₂ | C + 2H ₂ → CH ₄ | Methane formation |
| R ₃ | C + CO ₂ → 2CO | Boudouard reaction |
| R ₄ | CH ₄ + H ₂ O → CO + 3H ₂ | Steam methane reforming |
| R ₅ | CO + H ₂ O → CO ₂ + H ₂ | Water gas shift |
| R ₆ | 2C + O ₂ → 2CO | Char partial oxidation |
| R ₇ | 2CO + O ₂ → 2CO ₂ | CO combustion |
| R ₈ | CaO + CO ₂ → CaCO ₃ | Carbonation reaction |

Pyrolysis products react with gasifying agents to yield hydrogen, carbon monoxide, carbon dioxide and methane. The net rate of appearance ($R_{N,i}$) of a species is obtained from adequate addition (Equations 8-11), according to rules of chemical reaction engineering.

$$R_{H_2} = r_1 - 2 * r_2 + 3 * r_4 + r_5 \tag{9}$$

$$R_{CO} = r_1 + 2 * r_3 + r_4 - r_5 + 2 * r_6 - 2 * r_7 \tag{10}$$

$$R_{CH_4} = r_2 - r_4 \tag{11}$$

$$R_{CO_2} = -r_3 + r_5 + 2 * r_7 - r_8 \tag{12}$$

Lower heating value (LHV) of the product gas is given by [10]:

$$LHV = 10.79 Y_{H_2} + 12.26 Y_{CO} + 10.79 Y_{CH_4} \tag{13}$$

The developed model is used to analyse the effect of various operating parameters like gasification temperature, steam to biomass ratio (SBR), equivalence ratio (ER) and sorbent to biomass ratio (SOBR) on product gas composition.

Table 3. Kinetics of the reactions

| Reaction number | Reaction rate |
|-----------------|--|
| R ₁ | $r_1 = \frac{K_1 * C_{H_2O}}{1 + K_2 * C_{H_2O} + K_3 C_{H_2}}$ $K_1 = 4.93 * 10^3 * \exp\left(\frac{-18522}{T}\right), K_2 = 1.11 * 10 * \exp\left(\frac{-3548}{T}\right)$ $K_3 = 1.53 * 10^{-9} * \exp\left(\frac{-25161}{T}\right)$ |
| R ₂ | $r_2 = 4.4 * \exp\left(\frac{-1.62 * 10^8}{T}\right) * C_C * C_{H_2}$ |
| R ₃ | $r_3 = 4364 * \exp\left(\frac{-29844}{T}\right) * C_{CO_2}$ |
| R ₄ | $r_4 = 3.3 * 10^{10} * \exp\left(\frac{2.4 * 10^5}{R * T}\right) * C_{CH_4}^{1.7} * C_{H_2}^{-0.8}$ |
| R ₅ | $r_5 = 10^6 * \exp\left(\frac{15000}{T}\right) * \left(C_{CO} * C_{H_2O} + \frac{C_{H_2}}{520 * \exp\left(\frac{-7230}{T}\right)}\right)$ |
| R ₆ | $r_6 = 3.98 * 10^{20} * \exp\left(\frac{-20129}{T_p}\right) * C_{CO} * C_{O_2}^{0.25} * C_{CO_2}^{0.5}$ |
| R ₇ | $r_7 = 3.98 * 10^{20} * \exp\left(\frac{-20129}{T_p}\right) * C_{CO} * C_{O_2}^{0.25}$ |
| R ₈ | $r_8 = 10.2 * \exp\left(\frac{-44.5}{T}\right) * C_{CO_2} * C_{CaO}$ |

RESULTS AND DISCUSSION

3.1. Effect of temperature on product gas composition:

The effect of temperature on product gas composition is shown in Fig. 1. It is found that hydrogen and carbon dioxide concentrations increased and that of carbon monoxide decreased with temperature, respectively. This is mainly due to the effect of water gas shift reaction.

3.2. Effect of ER on product gas composition:

Fig. 2 gives the variation of product gas composition with ER. It is found that concentration of all the product gas constituents except carbon dioxide decreases with increase in ER. This is because as ER is increased, the product gas becomes more diluted with air and the process is shifted more from gasification to combustion.

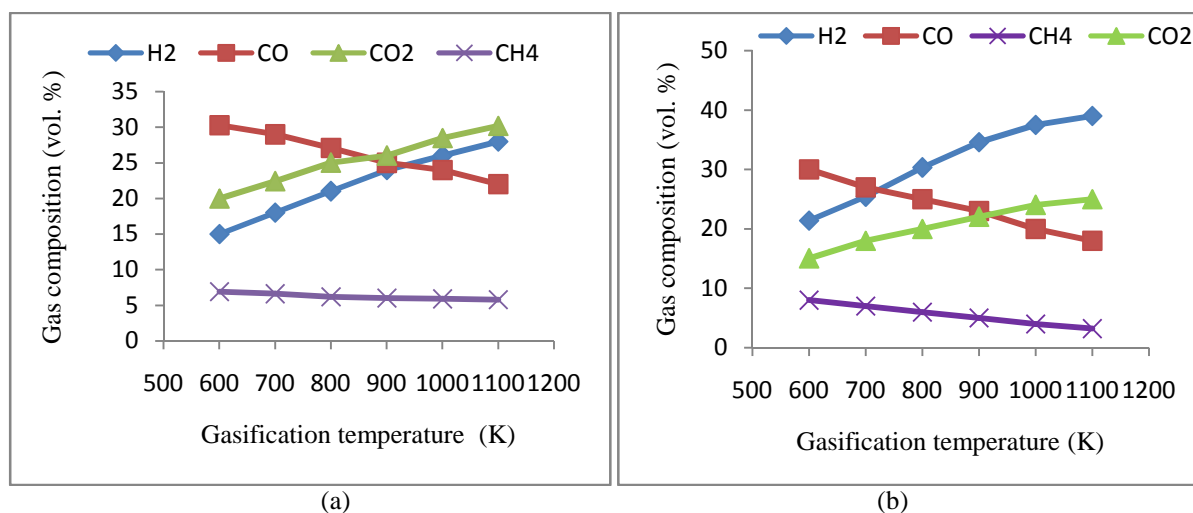


Fig. 1: Effect of temperature on product gas composition (a) without (b) with sorbent (SOBR=1). (ER=0.25, SBR=1)

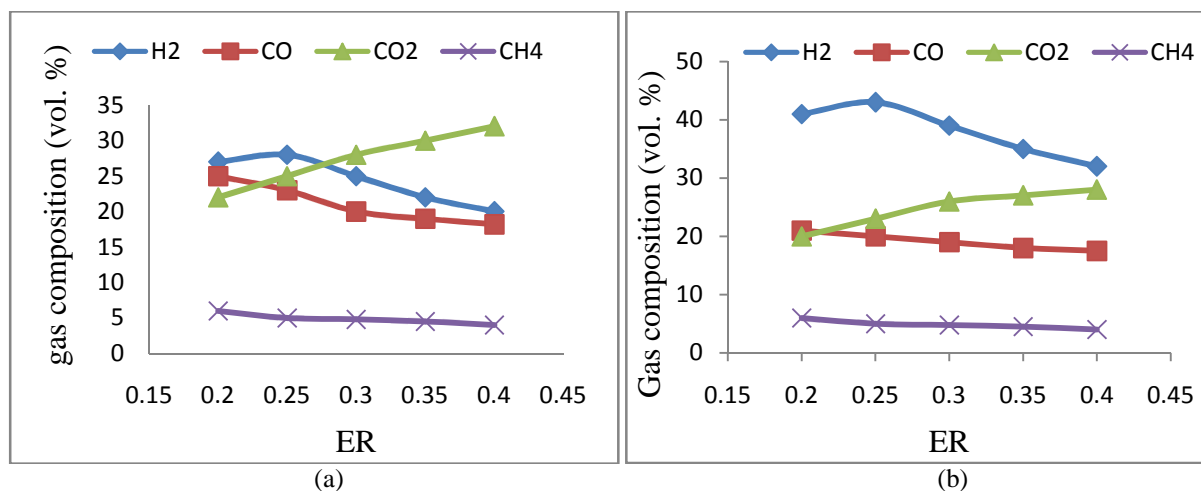


Fig. 2: Effect of ER on product gas composition (a) without (b) with sorbent (SOBR=1). (T=1000 K, SBR=1)

3.3. Effect of SBR on product gas composition:

The variation of product gas composition with SBR is shown in Fig. 3. As SBR increases, the concentration of hydrogen and carbon dioxide increases whereas that of carbon monoxide decreases. This is because when more steam is supplied, the forward water gas shift reaction is favoured as per Le-Chatelier's principle.

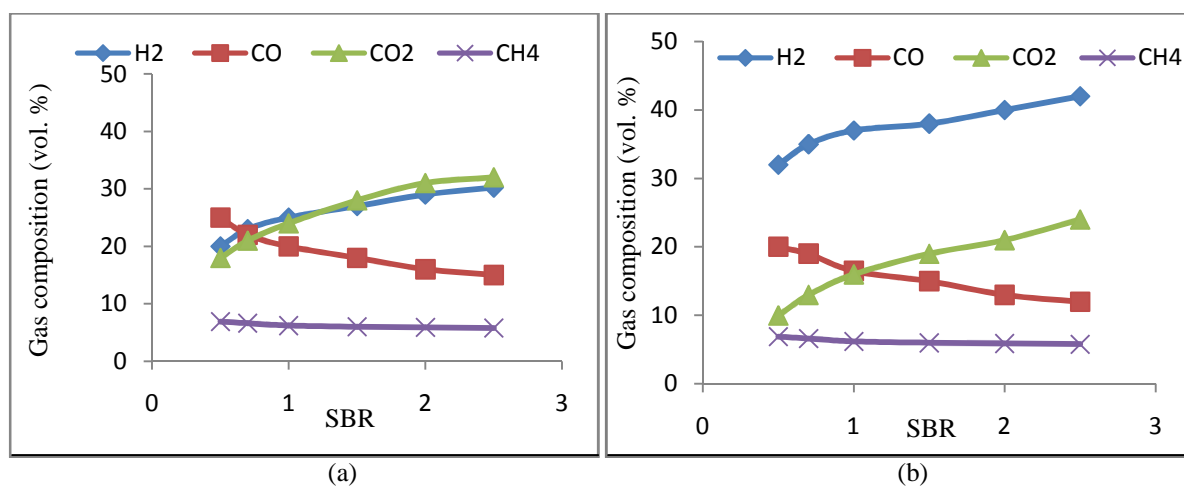


Fig. 3: Effect of SBR on product gas composition (a) without (b) with sorbent (SOBR=1). (T=1000 K, ER=0.25)

3.4. Effect of SOBR on product gas composition:

Fig. 4 gives the variation of product gas composition with SOBR. It is found that with an increase in SOBR, hydrogen concentration increases whereas that of carbon monoxide and carbon dioxide decreases. This decrease in carbon dioxide is due to the effect of carbonation reaction ($\text{CaO}_{(s)} + \text{CO}_{2(g)} \rightarrow \text{CaCO}_{3(s)}$) whereas the decrease in carbon monoxide is due to effect of forward water gas shift reaction. As CO₂ is captured using CaO, the partial pressure of carbon dioxide in the product side of water gas shift reaction decreases. This promotes the water gas shift reaction in forward direction and results in more hydrogen yield.

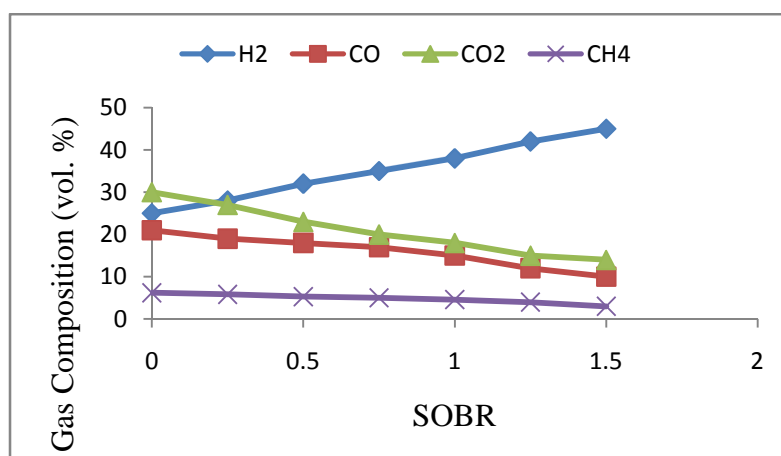


Fig. 4: Effect of SOBR on product gas composition (T=1000 K, ER=0.25, SBR=1)

3.5. Effect of ER and SBR on LHV:

The effect of ER and SBR on lower heating value of the product gas is given by Figs. 5(a) and 5(b), respectively. It is found that LHV of syngas increases with SBR and decreases with ER. This is attributed to the increase and decrease in hydrogen yield with SBR and ER, respectively.

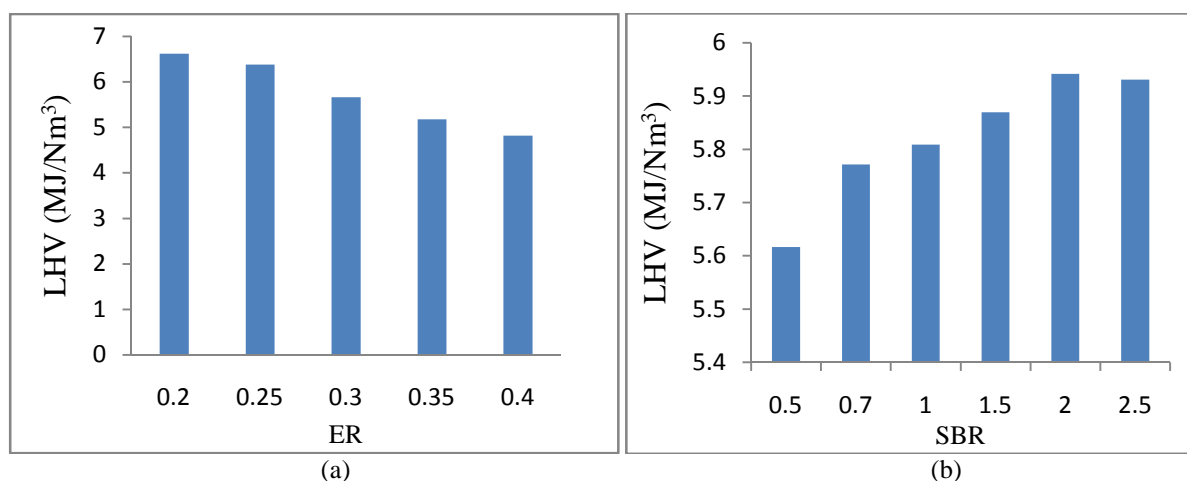


Fig. 5: Effect of (a) ER and (b) SBR on LHV ($T=1000$ K, $SOBR=1$)

Conclusions:

A kinetic model for air–steam gasification with CO_2 capture using CaO sorbent was developed. The developed model was used to analyse the effect of CaO sorbent in product gas composition. It was observed that addition of CaO increased hydrogen concentration under all operating conditions. It was also found that at a temperature of 1000 K, SBR of unity and ER of 0.25, the concentration of H_2 and CO_2 in the product gas was increased and decreased by 60% and 50%, respectively, when SOBR was increased up to 1.5.

ACKNOWLEDGEMENT

Authors gratefully acknowledge the financial support provided by MNRE through R&D project on “Investigation on bio-hydrogen production by thermo chemical method in fluidised bed gasifier under catalytic support and its utilization” (no. 103/181/2010-NT).

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