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Article

Biomass Steam Gasification with *In-Situ* CO_2 Capture for Enriched Hydrogen Gas Production: A Reaction Kinetics Modelling Approach

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Abstract: Due to energy and environmental issues, hydrogen has become a more attractive clean fuel. Furthermore, there is high interest in producing hydrogen from biomass with a view to sustainability. The thermochemical process for hydrogen production, *i.e.* gasification, is the focus of this work. This paper discusses the mathematical modeling of hydrogen production process via biomass steam gasification with calcium oxide as sorbent in a gasifier. A modelling framework consisting of kinetics models for char gasification, methanation, Boudouard, methane reforming, water gas shift and carbonation reactions to represent the gasification and CO_2 adsorption in the gasifier, is developed and implemented in MATLAB. The scope of the work includes an investigation of the influence of the temperature, steam/biomass ratio and sorbent/biomass ratio on the amount of hydrogen produced, product gas compositions and carbon conversion. The importance of different reactions involved in the process is also discussed. It is observed that hydrogen production and carbon conversion increase with increasing temperature and steam/biomass ratio. The model predicts a maximum hydrogen mole fraction in the product gas of 0.81 occurring at 950 K, steam/biomass ratio of 3.0 and sorbent/biomass ratio of 1.0. In addition, at sorbent/biomass ratio of 1.52, purity of H_2 can be increased to 0.98 mole fraction with all CO_2 present in the system adsorbed.

Keywords: hydrogen; biomass; steam gasification; CO_2 adsorption; kinetics modelling

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Nomenclature

C = Concentration (mol/m^3)
k = Arrhenius kinetic constant (s^{-1})
r = Rate of reaction (mol/m^3 s)
K_w = Equilibrium constant (dimensionless)
R = Volumetric rate of component (mol/m^3 s)
n = No of moles
y_i = Mole fraction of component i
N = Total number of data points

Subscripts

e = Experimental
m = Modeling

1. Introduction

Currently the main energy sources are fossil fuels. However, due to the energy crisis and environmental issues, renewable and clean energy sources are now under focus as sustainable supplies of energy in the future. One of the main renewable energy sources is biomass, which can be used for the production of hydrogen as a clean and environment friendly fuel [1,2]. The potential for production of hydrogen from biomass in Malaysia is high due to the availability of agricultural land and consequent abundant availability of agricultural wastes. Biomass can be used to produce enriched hydrogen gas via two thermochemical processes: pyrolysis and gasification. For hydrogen production, the gasification process is reported to be more economical than the pyrolysis process due to its more competitive production costs [3]. The quality of hydrogen and product gas varies with the different gasifying agents, *i.e.* air, oxygen-steam and pure steam, used for the gasification process [3]. Several attempts have been done for hydrogen production in Malaysia via biomass gasification using conventional gasification methods [4,5]. Previous research reported that pure steam resulted in higher yields of hydrogen compared to other gasification agents [6]. Moreover, the production of hydrogen can be increased to more than 80% by using CO_2 adsorption technique in the steam gasification process [7].

Several attempts have been carried out to evaluate the H_2 production from biomass in the presence of a CO_2 sorbent. A new approach proving that H_2 production can be increased by using CaO as CO_2 sorbent has been introduced by Kinoshita and Turn [8]. By coupling two fluidized beds, they have reported that hydrogen yield in the product gas can be increased from 70% to 85% using the *in-situ* adsorption technique. Furthermore, Mahishi and Goswami [9] studied pine bark steam gasification in the presence of CaO as sorbent. Their results showed a high hydrogen yield (70%) in the product gas. Additionally, Florin and Harris [7] discussed the effect of the presence of CaO in biomass gasification and observed that CaO acted as a catalyst as well, leading to two-fold increment in the H_2 yield. They also mentioned that maximum yield of H_2 achievable was increased from 57% to 80% when using a CO_2 sorbent.

Numerous models were developed to describe gasification processes without and with an integrated CO_2 adsorption technique. Corella *et al.* [10] presented a mathematical model based on the hydrodynamic and kinetic parameters for a circulating fluidized bed biomass gasifier using an air-steam. In their work, the reaction network has been solved using heat and mass balances. They reported that temperature and other parameters can be calculated to optimize the design and operation of the gasifier. Furthermore, Melgar *et al.*, [11] developed a model in MATLAB based on equilibrium Gibbs free energy minimization for a biomass gasification process. The model predicted the changes in the product gas compositions with respect to temperature. In addition, Mahishi and Goswami [12] presented a thermodynamic equilibrium model that predicted the optimum temperature, pressure, steam/biomass ratio and equivalence ratio with respect to the composition profiles of the product gas. Sharma [13] also used a modeling technique to predict the reaction temperatures, unconverted char, equilibrium constants for reduction reactions and optimal energy conversion for a downdraft fixed bed biomass gasifier. Meanwhile, Nikoo and Mahinpey [14] published their ASPEN PLUS simulation work based on reaction kinetics and hydrodynamic parameters for biomass gasification with an air-steam in a fluidized bed reactor. This work investigated the effects of temperature, steam/biomass ratio and biomass particle size on the product gas. Similarly, Shen *et al.* [15] simulated hydrogen production from biomass in interconnected fluidized beds. The purpose of the second fluidized bed is to act as a combustor to achieve the heat required for the gasification process. Proll and Hofbauer [16] proposed their modeling approach consisting of mass balances, energy balances and thermodynamic equilibrium states for a dual fluidized bed gasification in the presence of CaO. The results were used to predict the thermodynamic limits for the dual integrated fluidized bed reactor. Corella *et al.* [17] reported that there are 12 variables that can affect the performance of biomass gasification process including temperature, steam/biomass ratio, pressure, sorbent/biomass ratio, residence time, particle size, *etc.* Florin and Harris [18] and Mahishi *et al.*, [19] reported that most important parameters for biomass steam gasification with CO_2 capture are temperature, steam/biomass ratio and sorbent/biomass ratio. It is also noted that the H_2/CO ratio is also important to investigate the hydrogen production and water gas shift reaction [20]. The objective of this study was to investigate via a reaction kinetics modeling approach the technical feasibility of hydrogen production from steam gasification of wood with *in-situ* CO_2 adsorption. The variables under investigation were temperature, steam/biomass and sorbent/biomass ratio.

2. Model Formulation

2.1. Assumptions

The following assumptions are considered in the kinetics modeling approach:

- the gasifier operates under steady state conditions [10,12,14,15,19,21,22].
- biomass is represented by char [23,24].
- six reactions occur simultaneously in the gasifier including char gasification, Boudouard, methanation, methane reforming, water gas shift and carbonation [21].
- the reactions proceed isothermally and occur at constant volume [14,15,21].
- product gas consist of H_2, CO, CO_2 and CH_4 [14,18,19,23].

- tar and ash formation in the process are negligible. As the calculation of tar content will lead to an increasing amount of error for final product gas composition [14,15,21,23,25–27].

2.2. Reaction Kinetics

The kinetic schemes and heat of reactions occurring in the gasifier are listed in Table 1 [15,28].

Table 1. Reactions occurring in the integrated steam gasification process [16,18].

Reaction no, *i*	Name	Kinetics Scheme	Heat of Reaction, ΔH (kJ/mol)
1	Char Gasification	$C + H_2O \rightarrow CO + H_2$	+131.5
2	Methanation	$C + 2H_2 \rightarrow CH_4$	−74
3	Boudouard	$C + CO_2 \rightarrow 2CO$	+172
4	Methane Reforming	$CH_4 + H_2O \rightarrow CO + 3H_2$	+206
5	Water Gas Shift	$CO + H_2O \leftrightarrow CO_2 + H_2$	−41
6	Carbonation	$CO_2 + CaO \rightarrow CaCO_3$	−178.3

There are numerous possibilities for the rate equations to represent the kinetics behavior of reactions 1–4 and 6. However the simplest model of first order with respect to reacting species' concentrations is selected, as given in Equation 1, due to its applicability [10]:

$$r_i = k_i C_A C_B \tag{1}$$

Here r is the rate of reaction i, C_A is the concentration of reactant A, and k_i is the rate constant for reaction i.

For the reversible reaction of water gas shift, the rate of reaction is represented by Equation 2 [10]:

$$r_5 = k_5 (C_{CO} C_{H_2O} + \frac{C_{CO_2} C_{H_2}}{K_w}) \tag{2}$$

Here k_5 is the rate constant for water gas shift reaction and K_w is equilibrium constant.

The overall volumetric rate of each component i, R_i, is determined according to Chemical Reaction Engineering rules using Equations 3–6:

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

$$R_{CO} = r_1 + 2r_3 + r_4 - r_5 \tag{4}$$

$$R_{CH_4} = r_2 - r_4 \tag{5}$$

$$R_{CO_2} = -r_3 + r_5 - r_6 \tag{6}$$

Several modelling and simulation studies have been carried out for biomass and coal gasification based on a selection of the literature kinetics data [10,22,29–39]. The kinetics parameters for the reactions in Table 1 are referred from the literature listed in Table 2.

Table 2. Kinetics parameters of the reactions.

Reaction no, *i*	Kinetics Parameters, (mol/m^{3}s)	References
1	2.0×10^5 exp (−6,000/T)	[10]
2	4.40 exp (-1.62×10^8/T)	[34]
3	0.12 exp (−17,921/T)	[34]
4	$3\text{x}10^5$ exp (−15,000/T)	[10]
5	10^6 exp (−6,370/T) K_w = 520 exp (−7,230/T)	[10]
6	10.20 exp (−44.5/T)	[40]

The mole fraction for each component is calculated using Equations 7 and 8 below:

$$n_t = \sum n_i \tag{7}$$

$$Mole\ \ fraction_{(i)} = \frac{n_i}{n_t} \tag{8}$$

where n_t the is the total number of moles and n_i is the moles of each component.

The carbon conversion is calculated as the percentage of carbon converted into product gasses, shown as Equation 9 [15]:

$$Carbon\ \ conversion\ \ (\%) = \frac{gasified\ \ carbon\ in\ the\ \ product\ \ (g)}{carbon\ of\ biomass\ \ feed\ \ (g)} \times 100 \tag{9}$$

A residual sum squared (RSS) deviation method was used to calculate the mean error between the model prediction, y_e, and experimental data from literature, y_m, for hydrogen concentration in product gas. The mean error was calculated using mean residual sum squared (MRSS) by Equations 10–12 [14,41]:

$$RSS = \sum_{i=1}^{N} \left(\frac{y_e - y_m}{y_e}\right)^2 \tag{10}$$

$$MRSS = \frac{RSS}{N} \tag{11}$$

$$Mean\ error = \sqrt{MRSS} \tag{12}$$

3. Results and Discussion

3.1. Effect of Temperature

Figure 1 illustrates the effect of gasification temperature on the product gas composition in the range between 800 and 1,100 K. The mole fraction of hydrogen is higher than 0.8 in the product gas due to the usage of pure steam and the CO_2 adsorption technique. Based on Figure 1, the amount of CO is increasing with the increase in temperature. This observation results from the cumulative effect of the exothermic and reversible behavior of water gas shift reaction and the endothermic behavior of the Boudouard, char gasification and methane reforming reactions.

On the other hand, the amounts of CH_4 and CO_2 are found to be decreasing with increasing temperature. The decreasing amount of CO_2 may be due to the exothermic nature of water gas shift reaction and carbonation reaction. The closer view of hydrogen production at different temperatures is clear in Figure 2. From the figure, it can be concluded that the maximum hydrogen mole fraction in product gas composition occurs at 950 K. It is also observed that beyond 950 K, the hydrogen mole fraction in the product gas decreases due to the exothermic and reversible behavior of the water gas shift reaction.

Figure 1. Effect of temperature on product gas composition. Biomass feed rate: 0.072 kg/h; Steam/biomass ratio: 3.0; Sorbent/biomass ratio: 1.0, H_2 (■), CO (●), CO_2 (▲), CH_4 (×).

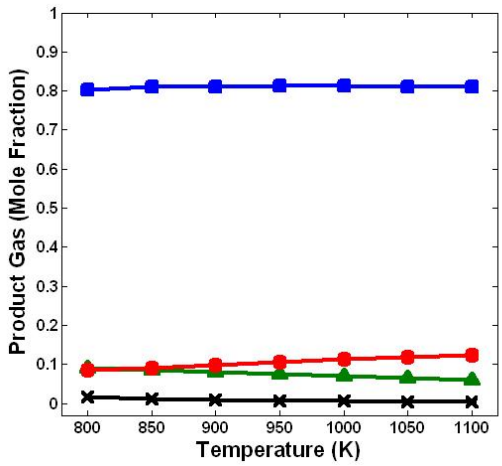
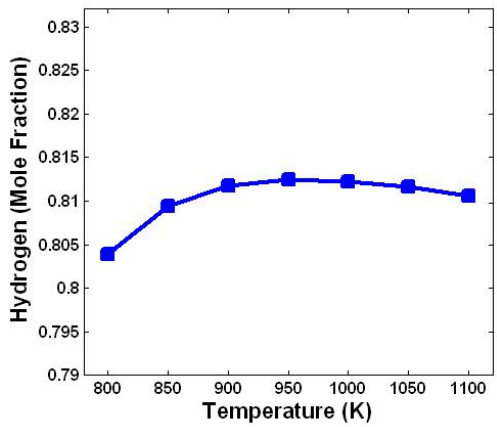


Figure 2. Effect of temperature on hydrogen production. Biomass feed rate: 0.072 kg/h; Steam/biomass ratio: 3.0; Sorbent/biomass ratio: 1.0.

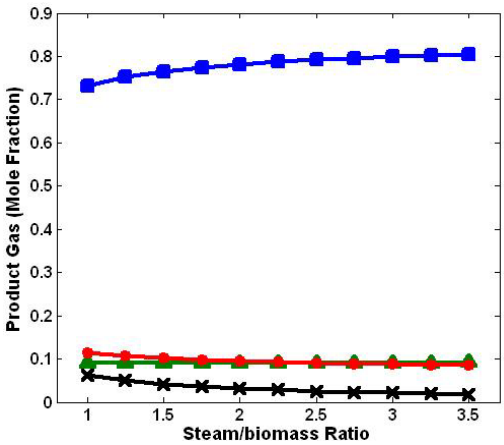


3.2. Effect of Steam/Biomass Ratio

Steam/biomass ratio is also important in steam gasification process. It is predicted that when the the steam/biomass ratio increases, the H_2 mole fraction increases and the amount of CO and CH_4 decreases. Figure 3 shows the change in the product gas composition by increasing the steam/biomass ratio.

Steam is the only gasification agent used, hence the reactions involving steam, especially methane reforming and water gas shift reaction are highly dependent on steam feed rate. Therefore, at higher steam/biomass ratio, the hydrogen yield increases to a high extent.

Figure 3. Effect of Steam/biomass ratio on product gas. Biomass feed rate: 0.072 kg/h; Temperature: 800 K; Sorbent/biomass ratio: 1.0, H_2 (■), CO (●), CO_2 (▲), CH_4 (×).



3.3. Three Dimensional Results Based on the Effect of Temperature and Steam/Biomass Ratio

Figures 4 and 5 show the surface plot for the effect of both temperature and steam/biomass ratio on H_2 mole fraction and H_2/CO ratio. Figure 4 shows that hydrogen production increases by increasing temperature and steam/biomass ratio. These results can be explained by the effect of Le Chatelier's principle on the endothermic reforming reactions of biomass and CH_4 that are promoted by the increasing temperature. At 800 K with a lower steam/biomass ratio of 1.0, the hydrogen mole fraction is observed to be 0.73, and at 1,100 K and high steam/biomass ratio, *i.e.* 3.5, the hydrogen mole fraction is almost 0.81. Furthermore, the surface plot shows that the highest hydrogen mole fraction of 0.814 occurs at 950 K at a steam/biomass ratio of 3.0.

Figure 4. Surface plot of hydrogen for different temperatures and steam/biomass ratios. Biomass feed rate: 0.072 kg/h; Sorbent/biomass ratio: 1.0.

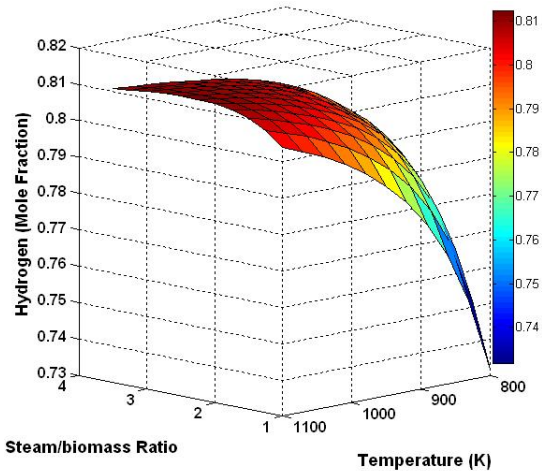


Figure 5 shows that a lower temperature and higher steam/biomass ratio produces a higher value of the H_2/CO ratio due to the faster water gas shift reaction. The H_2/CO ratio is predicted to be 6.6 at a temperature of 1,100 K and steam/biomass ratio of 3.5. However, at a lower temperature of 800 K and steam/biomass ratio of 3.5, the H_2/CO ratio is at the maximum value, *i.e.* 9.3. Hence, the results shows

that a high temperature does not favor the gasification process using steam for hydrogen production due to the exothermic and reversible behavior of water gas shift reaction which also causes an increase in carbon monoxide production. The H_2/CO ratio is observed to be higher at lower temperatures of 800–950 K. The ratio decreases with the increase of temperature due to the increase of CO and decrease of H_2, as the forward reaction of water gas shift is unfavorable at high temperature.

Figure 5. Surface plot of H_2/CO for different temperatures and steam/biomass ratios. Biomass feed rate: 0.072 kg/h; Sorbent/biomass ratio: 1.0.

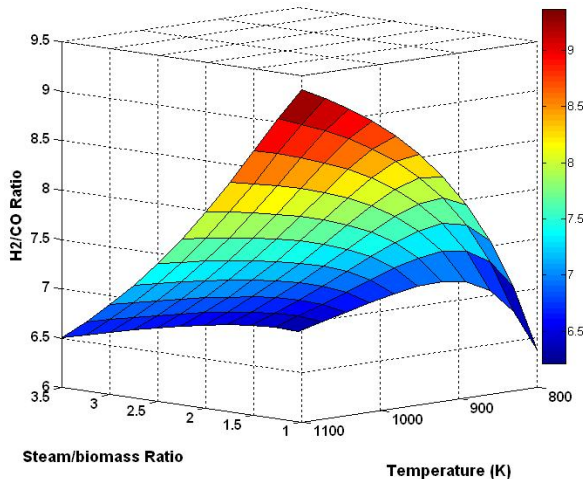
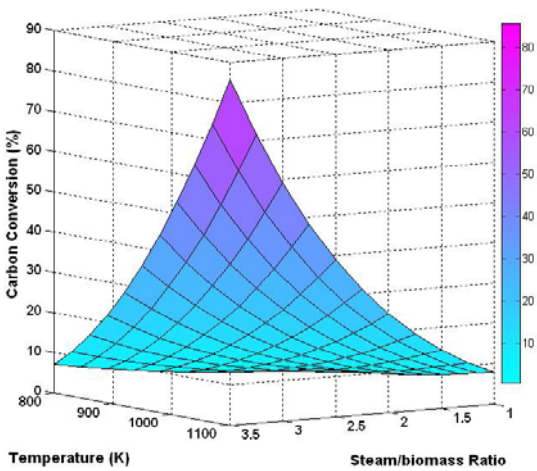


Figure 6 shows the surface plot for carbon conversion with respect to changes in temperature and steam/biomass ratio. The figure shows that carbon conversion increases by increasing both temperature and steam/biomass ratio. High temperature and high steam/biomass ratio favor carbon conversion. At 1,100 K and steam/biomass ratio of 3.5 the carbon conversion is more than 80%.

Figure 6. Surface plot of carbon conversion for different temperatures and steam/biomass ratios. Biomass feed rate: 0.072 kg/h; Sorbent/biomass ratio: 1.0.



3.4. Effect of Sorbent/Biomass Ratio

The presence of sorbent (CaO) in the system increases the hydrogen mole fraction in the product gas by absorbing the CO_2 produced. The difference in H_2 and CO_2 mole fractions in the product gas

using CaO as sorbent is shown in Figure 7; that hydrogen amount can be increased from 0.65 to 0.83 mole fraction and CO_2 amount can be decreased from 0.31 to 0.09 by using CaO.

The amount of sorbent used in the system also influences the production of H_2, as illustrated in Figure 8. As observed in the figure, by increasing the sorbent/biomass ratio, the H_2 amount increases and CO_2 amount decreases. Figure 8 shows the effect of amount of sorbent on product gas of gasification process. By increasing sorbent/biomass ratio, the H_2 increases and CO_2 decreases.

Figure 7. Effect of CaO on hydrogen and carbon dioxide. Biomass feed rate: 0.072 kg/h; Sorbent/biomass ratio: 1.2; Temperature: 950 K; Steam/biomass ratio: 3.0.

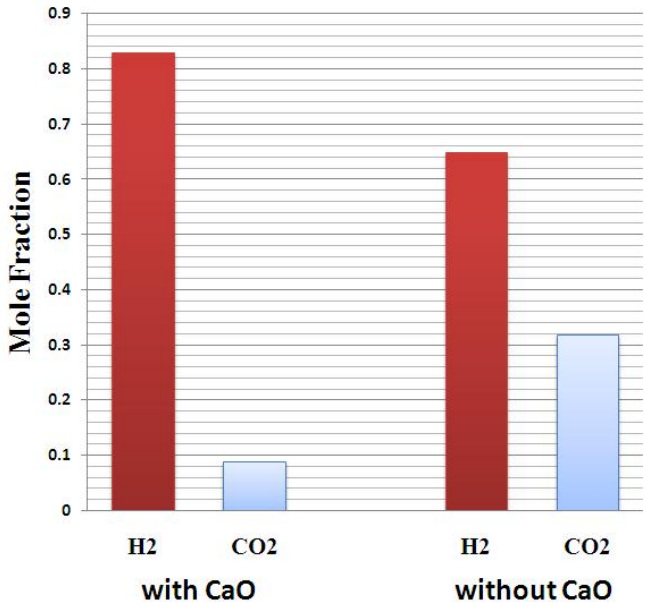
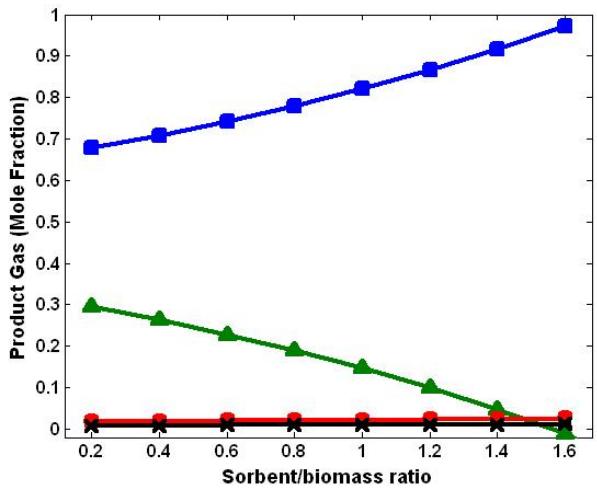


Figure 8. Effect of sorbent/biomass ratio on product gas. Biomass feed rate: 0.072 kg/h; Temperature: 950 K; Steam/biomass ratio: 3.5. H_2 (■), CO (●), CO_2 (▲), CH_4 (×)



It is also predicted that at sorbent/biomass ratio of 1.56 all CO_2 produced is absorbed by the sorbent and no CO_2 in the product gas. In addition, the maximum hydrogen mole fraction achieved is 0.98. The increase in hydrogen production with the use of sorbent CaO is because CaO captures CO_2 and further pushes the water gas shift reaction forward, based on Le Chatelier's principle.

3.5. Comparison with Literature Data

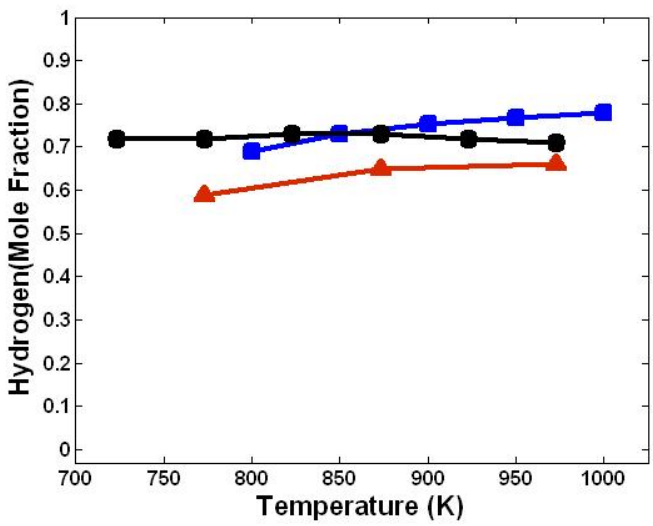
A comparison has been done between the results predicted from the developed model and literatures as shown in Table 3. Mahishi and Goswami [9] performed experiments on steam gasification using CaO as sorbent. On the other hand, Florin and Harris [18] developed an equilibrium model for a similar system. These two experimental and modelling works were selected as a basis of comparison have similar operating conditions as the current study.

Table 3. Operating conditions for comparison.

Parameters	This Model	Mahishi and Goswami [9]	Florin and Harris [18]
Approach	Kinetics Modelling	Experimental Work	Equilibrium Modelling
Gasification agent	Steam	Steam	Steam
Temperature range (K)	800–1,000	773–973	723–973
Pressure (atm)	1	1	4.9
Steam/biomass ratio	2.0	1.0	2.0
Sorbent/biomass ratio	1.0	1.0	0.50

Figure 9 shows the comparison in the hydrogen production with respect to the change in temperature, between the results predicted by this model and the literature data. The kinetics model is suitable to predict the product gas compositions while equilibrium models are used to predict maximum product yield from the process [42]. Figure 9 shows that our model predictions are in good agreement with the literature. Based on Figure 9, the profiles show similar trends with the experimental as well as the modelling results. The model predicts an increment in the H_2 production with increasing temperature. The hydrogen mole fractions are higher than the experimental data due to the use of higher steam/biomass ratio, *i.e.* 2.0, as shown in Table 3. Due to the small deviations observed between the model prediction and published experimental work, *i.e.* a mean error of 0.0871, the model has shown the ability to predict the gasification reaction with reasonable accuracy and therefore can be extended to predict hydrogen production for a specific biomass.

Figure 9. Effect of temperature on hydrogen production. This Model (■), Mahishi and Goswami [9] (▲), Florin and Harris [18] (●).



4. Conclusions

A reaction kinetics model is developed for the prediction of the product gas composition in a steam gasification system integrated with a CO_2 adsorption step. Each reaction captured in the model affects the performance of the biomass gasification process, where water gas shift reaction and methane steam reforming reaction are the main reactions for hydrogen production. In addition, temperature is an important variable, as the hydrogen production is initially increased by increasing the temperature. However, at very high temperature, the hydrogen mole fraction in the product gas decreases due to the exothermic and reversible behavior of the water gas shift reaction. Steam/biomass ratio is also a very important parameter in the steam gasification process. It is predicted that H_2 purity increases by increasing steam/biomass ratio, while the CO and CH_4 mole fractions decrease. Both methane reforming reaction and water gas shift reaction are highly dependent on the steam feed rate. The study shows that a temperature of 950 K and steam/biomass ratio of 3.0 provide maximum hydrogen mole fraction in the product gas of 0.814. The maximum H_2/CO ratio is predicted to accrue at a lower temperature and higher steam/biomass ratio due to the maximum consumption of CO in the water gas shift reaction, as both conditions are in favor of the forward water gas shift reaction. Furthermore, carbon conversion increased by increasing both temperature and steam/biomass ratio. With addition of CaO as sorbent, the hydrogen mole fraction in the product gas can be increased from 0.65 to 0.85. At sorbent/biomass 1.52, this study predicts that H_2 with a purity of 0.98 is obtained with all CO_2 present in the system absorbed. This because by capturing CO_2, the water gas shift reaction is shifted forward increasing the H_2 yield and H_2 purity is increased as CO_2 is removed from the system.

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