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Influence of Effective Parameters on Product gas Ratios in Sorption Enhanced Gasification

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Abstract

Biomass steam gasification for the production of syngas is a promising alternative for producing clean energy to substitute fossil fuels and reduce the carbon footprints. Even though the gasification process is not a new technology, there have been limited studies on the process simulation to analyze the gasification behavior. In this research work a mathematical approach was implemented in order to evaluate the effective parameters for steam gasification of palm waste.The final product gas composition was selected as the benchmark to assess the effect of process parameters on gasification behavior. The validated of developed mathematical model was done using the experimental data for steam gasification of biomass along with the experimental data for sorption enhanced steam gasification of biomass.

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*Keywords:*Biomass; Gasification; Kinetics; Syngas; CaO adsorption;

1. Introduction

Gasification is widely known technology allowing varioussolid fuels to be converted into combustible gas or syngas by partial oxidation process. The synthesis gas can be further utilized as a feed stock for the production ofdiverse chemicals or can be used as a fuel after cleaning. Biomass is a sustainable energy resource capable of keeping up with the escalating demand of energy with less environmental impact. The availability of palm waste in Malaysia makes it perfect biomass resource for producing synthesis gas without affecting any agricultural based food

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supply.

Gasification is thermodynamic conversion of biomass occurring at high temperature into gaseous product (syngas). The gaseous product from steam gasification is mainly composed of hydrogen, carbon monoxide, carbon dioxide and methane. Since syngas can be further used for producing many chemicals such as methanol, ammonia, hydrogen, fischer-tropschliquids and synthetic natural gas, so the product gas composition is very important factorfor the further utilization of syngas. Furthermore the use of syngas directly as fuel also require higher heating value gas that is highly dependent on product gas composition. The quality of final product gas from gasification process varies depending upon the gasification agent, gasification reactor, residence time and temperature. Air, oxygen and steam are most commonly used gasification agents. The use of steam as a gasification agent has several advantages over other gasification agents since the use of air dilutes the final composition of product gas and oxygen makes the process more costly. Even though the biomass gasification technology is well recognized worldwide, it is not industrially scaled up extensively. The effect of operating conditions on the process efficiency and energy utilization is still being investigated. Numerous researches have been conducted and reported for palm waste gasification.

In the recent years, several developments have been done in the field of biomass gasification of palm waste to produce syngas and hydrogen. Salleh et al. [1] studied the gasification of empty fruit bunches using air as a gasification agent in a fluidized bed gasifier. They reported the rise in hydrogen composition in final product gas as the temperature was increased over the range of 500-850 °C while similar increasing trend was observed for carbon conversion from 76%-84% over the previously mentioned temperature range. Reza et al. [2] investigated palm kernel shell that was blended with polyethylene prior to catalytic steam gasification and optimized the operating conditions for syngas and H_2 yield. The quality of final product gas from gasifier can be enhanced by using an adsorbent. The adsorbent can be used in a downstream reactor from gasifier and it can also be used within the gasifier. Several studies have been done for the use of adsorbent such as calcium oxide with in biomass gasifier. With the use of calcium oxide in gasifier, the CO_2 produced is continuously adsorbed along with the other gasification reactions occurring reducing the partial pressure of CO_2 in gasifier. Han et al. [3] performed biomass gasification enhanced by in-situ CaO adsorption in a bubbling fluidized bed gasifier for the production of hydrogen. They concluded that the use of CaO improved the WGS reaction, tar cracking and reforming of other higher hydrocarbons in gasifier eventually increasing the production of H_2 in final product gas. In order to evaluate the effect of process parameters,Zakir et al.[4]studied biomass gasification process and asserted that the maximum hydrogen yield was obtained at a temperature of 750 °C and 2.0 w/w of steam to feed stock ratio. There have been limited studies related to kinetics modelling of biomass gasification in order to produce synthesis gas. Giltrap et al.[5]studied the kinetic behaviour of the gasification system and developed a mathematical model to evaluate the syngas constituents in reduction zone assuming the process was isothermal and under steady state conditions. Lu et al. [6]developed a reaction kinetics model and used matlab software to solve equations with the assumptions of isothermal condition, steady state process, instantaneous devolatilization of the process uniform gasifier temperature and instantaneous pyrolysis.Inayat et al. [7] developed a reaction kinetic model to study the influence of effective parameters on the gasification of empty fruit bunches to produce hydrogen rich gas.

In view of the current advancement in biomass steam gasification, the major focus of this study is to develop a mathematical model incorporating the kinetics of biomass steam gasification reactions toinvestigate the operating parameters in syngas production from sorption enhanced steam gasification of palm waste. The H_2:CO and H_2:CO_2 ratios and hydrogen yield were selected as criterion of efficiency to evaluate the effect of operating conditions. Since the product gas ratios are very much important relative to further utilization of syngas, as syngas based methane production require syngas that is very much high in H_2 content. Similarly the synthesis of other chemicals also require H_2:CO ratio to be varied. In that case a setup is required at the downstream of the gasifier to adjust the product gas composition prior to chemical and fuel synthesis.

2. Technical Approach

The modelled system is based on syngas production from CaO sorption enhanced steam gasification of palm waste. Thermochemical gasification is a complex process involving biomass devolatilization followed by pyrolysis and several heterogeneous and homogeneous chemical reactions so certain assumptions were taken into consideration for

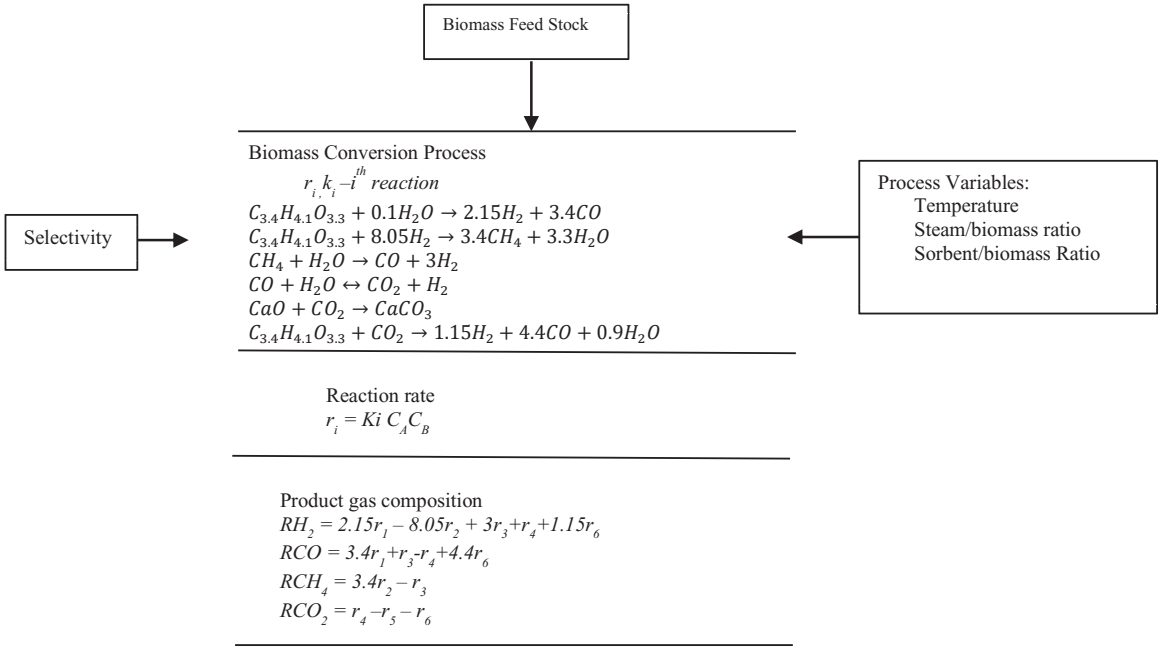

Figure 1Algorithm for mathematical model for syngas production.

processmodelling (1) The ash and tar formation in gasification process are negligible (2) Biomass devolatilization took place instantaneously (3) Steam required for gasification was provided from an external source.

The major reactions occurring in biomass gasification include biomass gasification reaction, water gas, methane formation reaction and methane reforming reaction along withboudouard reaction andCaO sorption reaction. A mathematical model is developed based on the first order reaction kinetics that is used to analyse the product gas ratios and cold gas efficiency.The overall biomass gasification reaction and carbonation reaction are given along with the algorithm developed for gasification is shown in Figure 1.

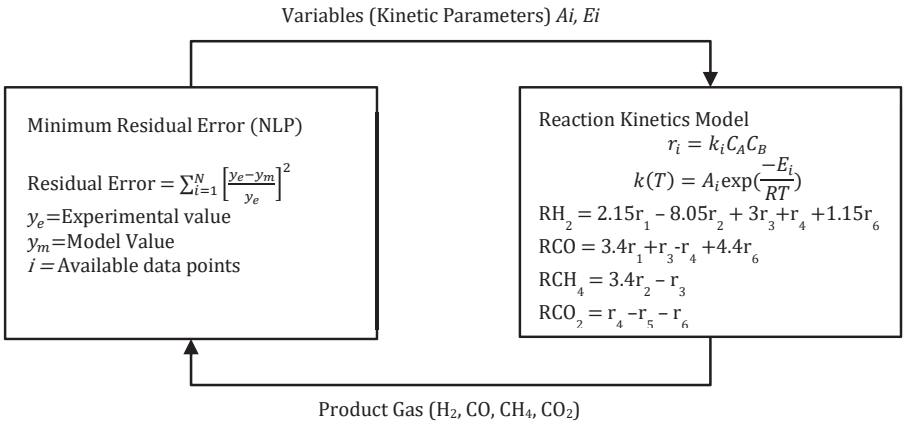

Figure 2: Flow chart for residual minimization approach in parameter fitting approach.

The evaluation of reaction kinetics parameter for each of the reaction was done by minimizing the residual error between experimental results and model predictions. The experimental data was used from literature. The non-linear

programming (NLP) constrained minimization was performed using Matlab*fmincon* solver. Experimental results for syngas yield obtained from literature were used as equation constraints for optimization calculations. The flow chart for minimum residual approach for kinetic model parameter fitting is shown in Figure 2.

Cold gas efficiency is an important benchmark in order to study the biomass gasification process. The cold gas efficiency is determined from the formula described as follow[8];

$$\eta_{CG}(\%)=\frac{m_{gas}LHV_{gas}}{m_{biomas}LHV_{biomass}} \tag{1}$$

Where *m* represents the number of moles of subsequent stream and *LHV* is the lower heating value. In order to calculate the lower heating value of the biomass feed stock and that of product gas the following equations are used;

$$LHV_{gas}=(30\times CO+25.7\times H_2+85.4\times CH_4)\times 0.0042 \tag{2}$$

$$LHV_{biomass}=4.187\times(81C+300H-26(O-S)-6(9H+m)) \tag{3}$$

In Equation(2), CO, H_2 and CH_4 are the volumetric percentage of subsequent component in product gas stream. In equation 3, *C, H, O,* and *S* denote the carbon, hydrogen, oxygen and sulphur contents in biomass while *m* is for moisture content. These values are obtained from ultimate and proximate analysis biomass. Abdullah et al.[9] performed the characterisation of empty fruit bunches (EFB) of oil palm and the proximate and ultimate analysis from their study was used to calculate lower heating value of biomass so that cold gas efficiency of the process can be calculated.

3. Results and discussion

Table 1 lists the kinetic parameters i.e. Arrhenius constant (A) and activation energy (E_a) that were evaluated from mathematical model using the minimization of the residual approach.

Table 1: Kinetic Parameters optimized for gasification reactions

Reaction no.	Arrhenius Constant (A)	Activation Energy (E_a)
1	6008.309	2126.279
2	287.642	-4648.334
3	203.766	5981.961
4	852.326	-1572.436
5	21.827	-289.315
6	62.785	-745.037

Two case studies were performed using the kinetics model developed: one with CaO adsorption and other one without CaO adsorption. The developed model was first validated with data from literature[9]without the use of adsorbent.Figure 3 shows the temperature profiles of palm waste gasification over the temperature range of 1023 K-1073 K for product gas composition. The results evaluated form developed model were in agreement with the experimental data. The increase in gasification temperature, increased the hydrogen contents in product gas and also at the same time production of carbon dioxide increased over the increase in gasification temperature. On the other hand, carbon monoxide contents in product gas decreased along with methane with the rise in temperature. About 15 % increase in hydrogen production was seen over the specified temperature range. It was due to the fact that the increase in gasificationtemperature shifted the equilibrium for water gas shift reaction consequentlyraising the amount of hydrogen and carbon dioxide in product gas whereas the carbon monoxide contents were reduced. The rise in gasification temperature also enhanced the methane reforming reaction that reduced the methane in final product gas.

Han et al. [3] studied biomass gasification using fluidized bed gasifier integrated with sorption enhanced biomass steam gasification process CaO as an adsorbent. Figure 4 depicts the temperature profile for biomass gasification over the temperature range of 873 K to 973 K. The production of hydrogen is higher and that of carbon dioxide is lower with calcium oxide adsorption in this case. This effect is due to carbonation reaction. The calcium carbonate continuously adsorbed the CO_2 being produced through water gas shift reaction. According to le-chatlier'sprinciple,

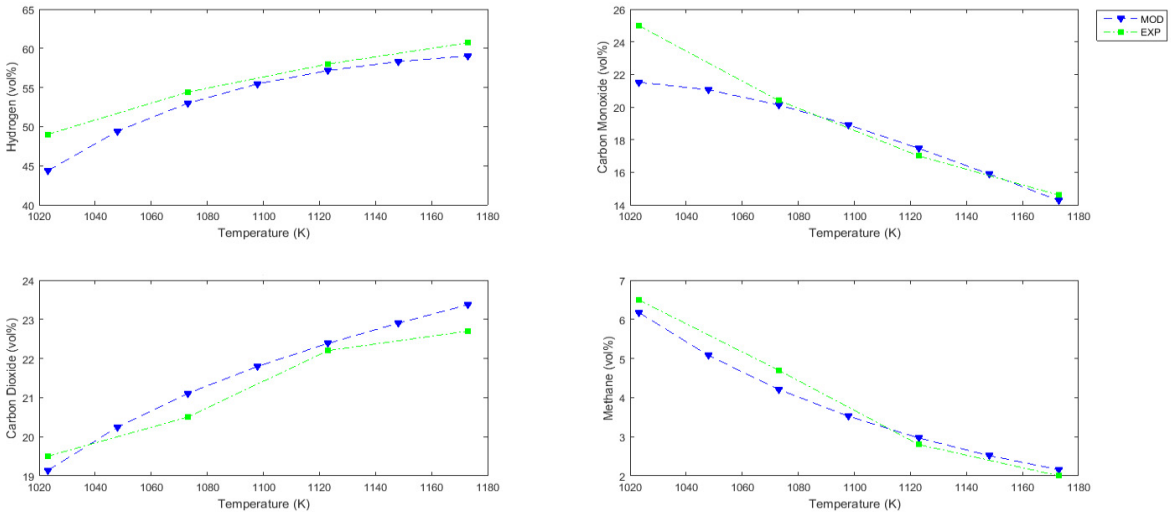

Figure 3: Effect of Temperature on syngas composition from Biomass Steam Gasification [8].

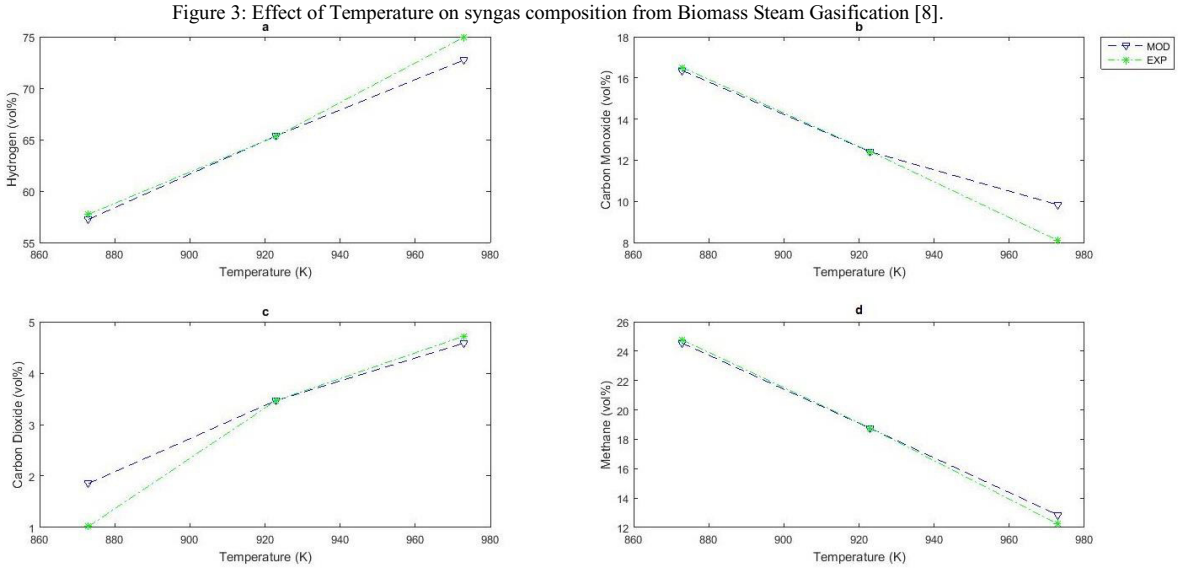

Figure 4: Effect with Temperature on Syngas Production from Sorption Enhance Gasification.

the continuous removal of CO_2 in gasifier reduced the partial pressure of CO_2 eventually affecting the position of the reaction equilibrium of the water gas shift reaction, increasing the hydrogen contents as well as decreasing the carbon dioxide in product gas.

Under the predefined operating conditions including steam/biomass ratios and sorbent/biomass ratios, the effect of temperature on gasification was studied. The temperature profiles in figure 5 demonstrate the effect in terms of

H_2:CO, H_2:CO_2, CO:CO_2 and H_2:CH_4 ratios. Figure 5 shows that model predicts the rise in hydrogen to carbon monoxide ratio with the rise in temperature. At the temperature of 973 K the ratio is predicted to be maximum and was about 7.4. The rise in H_2/CO ratio is due to the fact that with the increase in temperature of steam reforming reaction for both biomass char and methane is enhanced as both of these reactions are highly endothermic. Figure 5 demonstrate that the ratio of hydrogen and carbon dioxide reduces with the rise in gasification temperature. The rise in temperature shifts the water gas shift reaction towards the product side. Similarly the increase in temperature also enhances the hydrogen to methane ratios.

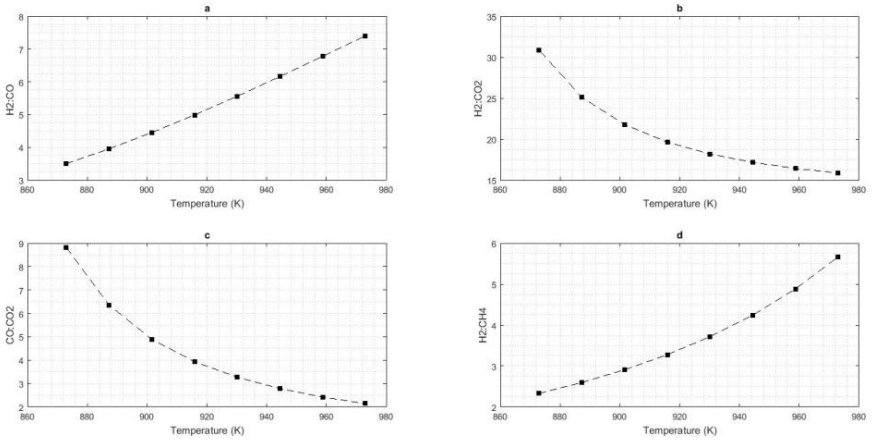

Figure 5: Effect of Temperature on Syngas Ratios.

The influence of sorbent to biomass feedstock in biomass steam gasification is shown in Figure 6. It can be seen from the figure that Calcium oxide sorbent in gasifier highly effect the final gas composition. With the rise in sorbent to biomass ratio the hydrogen in product gas increases while carbon monoxide decreases. The hydrogen contents varies from 47% to 72% over the sorbent range of 0-1. The carbon dioxide contents decrease from 38% - 6%.

The use of calcium oxide in biomass steam gasification as an adsorbent highly affect the final product gas composition. As this step advances the water gas shift by continuously removing the carbon dioxide from the product gas.

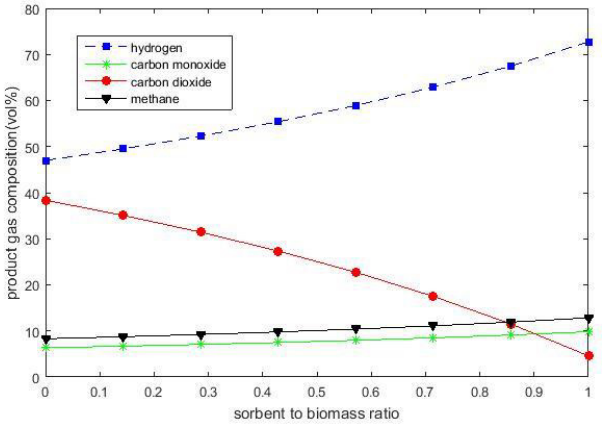

Figure 6: Effect of Sorbent/Biomass ratio on Product Gas Composition.

Figure 7 depicts the trend for the cold gas efficiency with the variation of temperature and steam to biomass ratio over the range of 873-973K and 1.3-2.0 respectively. The decrease in cold gas efficiency can be seen in the figure

with the rise in temperature and it can also be observed that efficiency also decreases as the steam to biomass ratio over range of 1.3-2.0. At the steam to biomass ratio of 1.3, the cold gas efficiency is 39.8% decreased over the temperature range of 873 to 973K. On the other hand this decrease in cold gas efficiency is observed to be 19.7% when steam to biomass ratio is increased from 1.3 to 2.0.

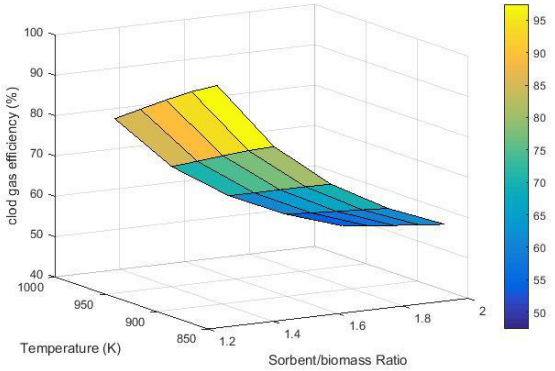

Figure 7: Surface plot for the influence on cold gas efficiency.

4. Conclusion

In this study a reaction kinetic model was discussed to check the influence of process parameters on the production of syngas from biomass steam gasification. The parametric study showed that the final product gas composition is highly affected by temperature and also the influence of adsorption reaction is high. The results showed that the rise in gasification temperature increase the hydrogen contents in syngas increasing the hydrogen to carbon monoxide ratio up to 7.4. The use of calcium oxide as a sorbent increased the hydrogen and carbon monoxide contents while decreasing the carbon dioxide simultaneously.

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