Development of Process Flow Sheet for Syngas Production from Sorption Enhanced Steam Gasification of Palm Kernel Shell

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This study discusses the production of synthesis gas from palm kernel shell via sorption enhanced steam gasification. A flowsheet model that has been presented incorporates the reaction kinetics and mass balance of syngas production process. It was assumed that the reactions involved in steam gasification of biomass with carbon dioxide adsorption, including gasification, methanation, methane reforming, water gas shift, boudouard and carbonation reaction. A parametric study has been performed to investigate the effect of temperature, steam/biomass ratio and sorbent/biomass ratio on the product gas compositions and heating values of the final product. It was concluded that the hydrogen content in product gas increased in the temperature range of 650 - 750 ˚C. The effect of sorbent/biomass ratio was investigated in the range of 0.5 - 1, which showed an increasing trend for hydrogen production while the CO_2 contents reduced in the final product gas. The mass balance has also been presented for each of the equipment in flow sheet developed for synthesis gas production.

1. Introduction

Fossil fuel would not be core energy source in future energy trade due to its depletion and problems related with its usage, including greenhouse gas emissions, global warming, acid rain, torment weather changes and imbalance energy trade (Ahmed et al., 2010). Biomass is accounted as a promising option for alternative and new source due to various benefits such as renewability, CO_2 neutrality, sustainability and weather moderation. The abundant availability of biomass about 200 - 700 EJ/y can increase its global energy share that is 14 % currently and eventually decreased 84 % share of fossil fuel (Shahbaz et al., 2016a). Among two routes of energy extraction from biomass biological and thermochemical conversion processes, thermochemical conversion gasification process is more promising for the extraction of energy in the form of syngas and methane that are currently obtained from fossil sources. Syngas has utter importance due to its various applications in the energy sector and chemical synthesis like hydrogen, synthetic methane, Fisher-Tropsch diesel, methanol, fertilizers and higher hydrocarbon products (Hernández et al., 2016).

Steam gasification of biomass has a distinction among other gasification process by offering advantages like higher heating value of product gas, quality syngas with enrichment of H_2 and applicable both small and large scale (Shahbaz et al., 2016a). The research work has been conducted to convert biomass through gasification with both experimental and modelling approaches. Several studies based on simulations and modelling approach have been reported previously. Two types of modelling approaches have been used for gasification process including kinetic and equilibrium modellings. In equilibrium modelling, thermodynamics of system and reactions have been implemented for the development of model. In kinetic modelling, the kinetics of major reactions are used and a process is modeled to predict the gas composition and yield at given set of operating parameters. The kinetic modelling approach is complex but provides precise outcome compared to equilibrium modelling (Ahmed et al., 2010). Sreejith et al. (2014) used equilibrium modelling approach for gasification of

biomass and predicted hydrogen production of 59.3 vol % at 700 °C and steam/biomass ratio of 1. The removal of CO_2 from the syngas increased the H_2 in the product gas. The utilization of sorbent such as CaO for CO_2 adsorption in gasification process not only enhanced the hydrogen content in syngas but also reduced the energy requirement within system and enabled the gasification process to occur at a lower temperature of 800 °C (Rupesh et al., 2016). To date, very few studies have been reported on CaO sorbent modelling work.

In kinetic modelling, very little work has been made. Sreejith et al. (2014) developed a simulation model for air-steam gasification with enabling CO_2 sorption by using kinetic data from the literature. The modelling approach included different processes during biomass gasification like drying, pyrolysis and char gasification and H_2 content found to be increased with the use of sorbent. In Malaysia, 198 million tons per annum palm oil waste residue are available, which comprises of palm kernel shell (PKS), palm oil fronds (POF) and empty fruit bunches (EFB) (Shahbaz et al.,2016b). Recently, the research has been reported for both experimental and modelling approach to utilize palm oil waste in gasification. In modelling approach, Inayat et al. (2010a) developed a kinetic model for in-situ steam gasification of EFB. The effect of different parameters including temperature and steam/biomass ratio on hydrogen yield has been studied. A flow sheet was also developed for EFB steam gasification with the use of sorption process through the kinetic model approach and system performance was evaluated. It was found that gasification efficiency was increased by 10 % due to the use of CaO (Inayat et al., 2010b). PKS is the major constituent of palm oil residue; it was studied experimentally in an integrated catalytic steam gasification system by Khan et al. (2014).

To date, limited research has been reported for steam gasification of palm oil waste with sorbent. Particularly, in the case of PKS steam gasification, no study has been reported on process modelling. The objective of this paper is to develop a flowsheet model with the use of sorption method by using kinetics of reactions. In addition, the effect of parameters ranges such as temperature from 650 °C to 750 °C, sorbent/biomass ratio from 0.3 wt/wt to1 wt/wt and steam/biomass ratio from 1 to 2 are varied to study their effect on syngas production as well as on heating values of the product gas. The predicted results are compared with experimental results that are performed using setup model developed through kinetic modelling approach.

2. Methodology

2.1 Experimental setup

The pilot scale sorption enhanced gasification system was used to validate the developed process through kinetic modelling is shown in Figure 1. The system consisted of feeding system, fluidized bed gasifier, steam generation system, water treatment and gas cleaning system. The biomass used in this study was PKS and its proximate and ultimate analysis is given in Table 1. The PKS was fed into the fluidized bed gasifier through screw feeding system. Steam was generated in the boiler and heated up to 350 °C in the superheater. The steam reacted with biomass in the fluidized bed gasifier. CaO was placed in the fluidized bed gasifier as a bed material. The solid particles were removed from product gas through a cyclone separator and $CaCO_3$ was removed at the bottom of the gasifier. The product gas was cooled down to 25 °C and sent to the gas analyzing system.
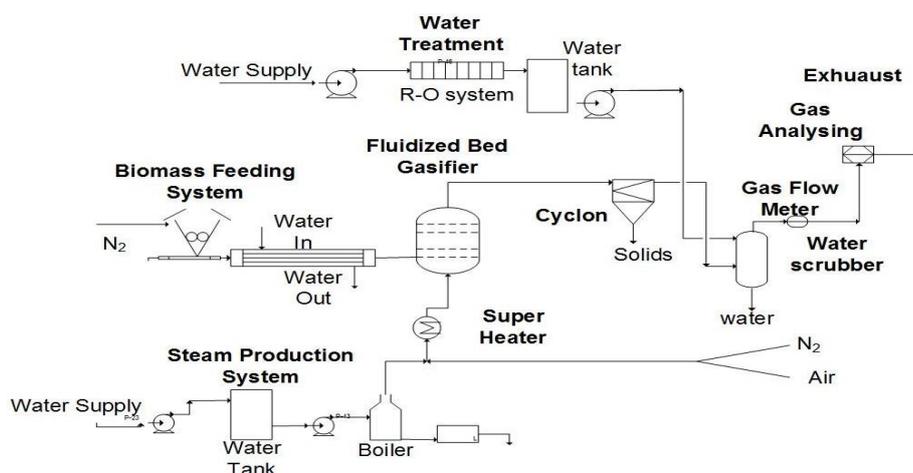
Figure 1: Process flow diagram of sorption enhanced steam gasification process

Table 1: Ultimate analysis and proximate analysis

Ultimate Analysis		Proximate analysis	
Biomass Composition	Wt (%)	Component	Wt (%)
Carbon	48.78	Moisture	9.70
Hydrogen	5.70	(dry mass) fraction basis	
Nitrogen	1.01	Volatile matter	80.81
Sulfur	0.21	Fixed carbon	14.25
Oxygen (by difference)	44.2	Ash	4.94
HHV (MJ/kg)	18.82		

2.2 Technical Approach

The system has been modelled for syngas production through steam gasification of PKS with capturing of CO_2 with the utilization of CaO. The production of syngas through gasification process is the result of a complex set of reactions that occured at different stages of the process including decomposition of biomass, followed by the combustion and pyrolysis. The gasification process is a mixture of exothermic and endothermic reactions. The most influencing reactions in steam gasification are methane formation, water gas shift reaction, methane reformation and boudouard reactions at higher temperature. The CO_2 capturing through carbonation reaction is also an important reaction in which CaO sorbent is used within the process. The reactions that are involved in the gasification process are given in Table 2. By using the reaction kinetics of the mentioned reactions, a mathematical model is formulated.

Table 2 Reaction scheme and kinetic parameters (Inayat et al., 2010a)

No	Reactions	Activation energy	Frequency factor
1	$C_{4.1}H_{5.7}O_{2.8} + 1.3H_2O \rightarrow 4.2H_2 + 4.1CO$	-6,000	2.0×10^5
2	$C_{4.1}H_{5.7}O_{2.8} + 8.1H_2 \rightarrow 4.1CH_4 + 2.8H_2O$	1.62×10^8	4.40
3	$CH_4 + H_2O \rightarrow CO + 3H_2$	15.0×10^3	3.0×10^5
4	$CO + H_2O \rightarrow CO_2 + H_2$	-6.4×10^3	1.0×10^6
5	$CO_2 + CaO \rightarrow CaCO_3$	-44.5	10.20
6	$C_{4.1}H_{5.7}O_{2.8} + CO_2 \rightarrow 2.15H_2 + 4.1CO + 0.18O_2$	1.8×10^{-4}	0.12

Assumptions: Due to the limitation of modelling approach, some assumptions are made for the syngas production with CO_2 capturing system.
   (1)   Steady state process at atmospheric pressure and no temperature gradient within gasifier
   (2)   Tar production is neglected and ash contents are considered to be inert.
   (3)   The degradation of biomass occurs instantaneously through homogenous and heterogeneous gasification reactions.
   (4)   The product gas mixture consists of hydrogen, methane, carbon mono oxide and carbon dioxides.
   (5)   Since the process is continuous, there is no mass accumulation within the system.
   (6)   The first order kinetics is assumed in this kinetic modelling approach.

2.3 Model formulation

Reaction kinetic model approach is used for the formulation of the model. The reactions assumed for the modelling of steam gasification with the enabled CO_2 system are given in Table 2. In kinetic modelling, the rate equations are used for the description of reactions behavior. The first order kinetics is assumed in this kinetic modelling approach. The first order rate equations of mentioned reactions in Table 2 are considered for the formulation of the kinetic-based model using Eq(1).

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

The notations used for rate of reaction are *r* and *k* is the constant of rate equation that is strongly influenced by temperature. In order to calculate the temperature dependence of rate constant *k*, Arrhenius equation is employed as mentioned in Eq(2).

$$k_i = A_i e^{\frac{-E}{RT}} \tag{2}$$

The activation energy and frequency factor described as *E* and *A,* are the main features of Arrhenius equation. In order to determine the production rate of volumetric flow, Eq(3) - Eq(6) are used. The kinetic parameters taken from literature are depicted in Table 2.

$$RH_2 = 4.2r_1 - 8.1r_2 + 3r_3 + r_4 + 2.15r_6 \tag{3}$$

$$RCO = 4.1r_1 + r_3 - r_4 + 4.1r_6 \tag{4}$$

$$RCO_2 = r_4 - r_5 - r_6 \tag{5}$$

$$RCH_4 = 4.1r_2 + r_3 \tag{6}$$

The mass balance is calculated by using general mass balance equation as depicted in Eq(7).

$$\sum m_{in} = \sum m_{out} \tag{7}$$

The performance indicators include gasification efficiency along with higher heating value (HHV$_g$) and lower heating value (LHV$_g$) of syngas produced. The LHV$_g$ and HHV$_g$ are determined by using Eq(8) - (9).

$$LHV_g = (30 \times CO + 25.7 \times H_2 + 85.4 \times CH_4)0.0042 \tag{8}$$

$$HHV_g = (CO \times 30.18 + H_2 \times 30.52 + CH_4 \times 9.5) \times 4.18 \tag{9}$$

The gasification efficiency is determined using correlation mentioned in Eq(10).

$$\eta_G = \frac{\text{Total moles of product gas}}{\text{moles of dry PKS fed}} \tag{10}$$

3. Results and Discussions

The model developed for steam gasification of PKS with CO_2 capturing using CaO is performed in a similar experimental set up for the validation of model in the same range of parameters, including temperature of 650-750 °C, sorbent/biomass ratio of 0.3 - 1 and steam/biomass ratio of 1.0 - 2.0. The gas compositions predicted by the model have good agreement with experimental results in the temperature range as shown in Figure 2. It can be seen that H_2 production is increased with the increase in temperature whereas CO production has the inverse effect. This increase in hydrogen content and the decrease in CO content are also observed which is due to the activity of in water gas shift reaction, methane reforming and carbonation reaction. The deviation of experimental and modelling results is due to the formation of tar that is not considered in modelling approach. A similar trend is also observed by Acharay et al. (2010) for H_2 and CO in the presence of CaO. The CO_2 found to be decreasing from temperature 650 to 700 °C which is due to the carbonation reaction, whereas, the CO_2 content increases above 700 °C due to reverse carbonation reaction. The release of CO_2 from CaO_3 is also reported by Rupesh et al. (2016) at 727 °C and Khan et al. (2014) at 675 °C. Methane formation decreased with an increase in temperature due to methane reformation reaction that was enhanced with the elevation of temperature. The enrichment of H_2-content in syngas at elevated temperature is the result of methane reforming reaction that is responsible for CO/H_2 ratio.
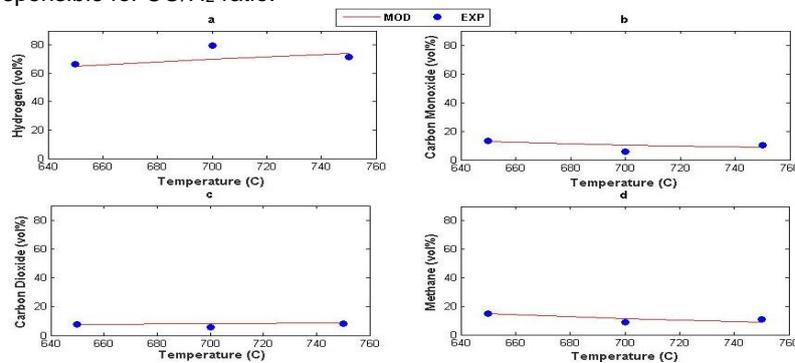
Figure 2: Effect of temperature on syngas composition.

The effect of sorbent on syngas composition can be seen in Figure 3a. It is found that the H_2 production has a direct relationship with sorbent/biomass ratio and an inverse relation with CO_2. The increase in H_2 content is due to water gas shift reaction, as the partial pressure of CO_2 is reduced by adsorption,the equilibrium shift in the forward direction resulting in higher production of H_2 and CO. Khan et al. (2014) also reported the increase of H_2 content with the increase in CaO/biomass ratio from 0.5 - 1.5. Steam is very effective gasifying agent when syngas is required with higher H_2 content. It is clear from Figure 3b that the H_2 content is increased sharply with the increase in steam/biomass ratio of 1-1.5 and then the rise is steeper. The CO and CO_2 contents are also decreased with the increase in steam addition. On the other hand, methane formation decreases from 45 vol % to 10 vol %. The addition of steam enhances the activity of water gas shift reaction and methane reformation reaction, resulting in the enrichment of H_2 content and the reduction in methane content. Rupesh et al. (2016) also reported the enrichment of H_2 content in the presence of CaO by increasing the steam/biomass ratio from 0 - 2 and with the similar justification.
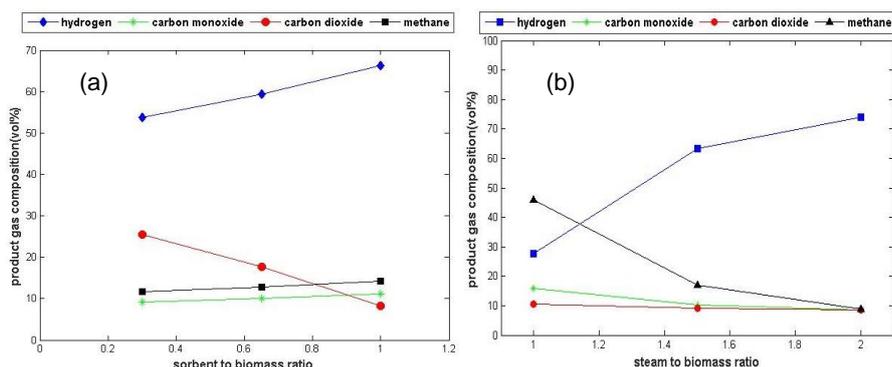
Figure 3: (a) Effect of sorbent/biomass ratio (b) Effect of steam/biomass ratio on syngas production

Figure 4 shows the mass balance of developed sorption enhanced gasification system. It is depicted that H_2 production is 159.6 g/h from 1800 g/h of biomass feed. The productions of other gasses are 833.3 g/h of CO and 203.5 g/h of methane. The production of CO_2 is 407.4 g/h which is very low that shows the activity of CaO sorbent. It can be justified that 1,800 g/h of CaO resulted in 2,476.3 g/h $CaCO_3$ due to the carbonation reaction. It could be concluded that only 18 % of steam is used for hydrogen production and the remaining steam is used to provide fluidization of biomass and $CaCO_3$ is recovered in the form of condensate. A large amount of unreacted steam in steam gasification is a drawback of steam gasification and is discussed by many authors (Inayat et al, 2010a).
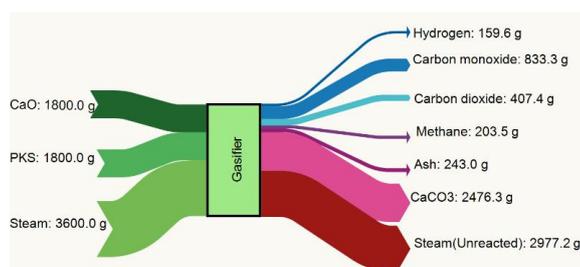
Figure 4: Mass balance of gasification system

The gasification performance is assessed on the basis of heating values of product gas. The lower and higher heating values decrease with the increase in temperature as shown in Figure 5a. The reduction of heating values is due to the decrease in methane and CO contents that have more contribution in heating value than H_2. Figure 5b shows the gasification efficiency is increased from 60 to 85 % with the increase in temperature from 650 to 750 ˚C. The increase in gasification efficiency explained an increase in the gas yield.
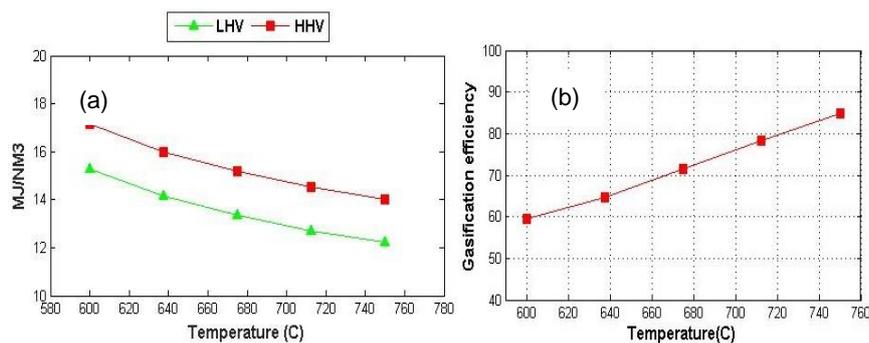
Figure 5: (a) Effect of temperature on LHV_g and HHV_g (b) Effect of temperature on Gasification efficiency

4. Conclusions

In this study, a model was developed for steam gasification of PKS with enabled CO_2 capturing using CaO sorbent. The model predicted results were validated with experimental data performed at the operating conditions of the model. It was predicted that syngas composition was highly influenced by temperature and H_2 content increased from 65 % to 79 % with an increase in temperature. Syngas production was very sensitive to steam/biomass ratio. By increasing the steam/biomass ratio from 1 - 2, the increase of 30 % in H_2 content and the decrease of 50 % in methane content were observed. The use of sorbent/biomass ratio was found very effective for CO_2 sorption. The CO_2 formation dropped about 20 % with an increase in sorbent/biomass ratio from 0.5 to 1. The HHV_g of 17.2 MJ/NM^3 and LHV_g of 15.2 MJ/NM^3 of product gas with a maximum of 85 % gasification efficiency showed the good performance of the system.

References

Acharya B., Dutta A., Basu P., 2010, An investigation into steam gasification of biomass for hydrogen enriched gas production in presence of CaO, International Journal of Hydrogen Energy, 35, 1582-1589.

Ahmed T.Y, Ahmad M.M., Yusup S., Inayat A., Khan Z., 2012, Mathematical and computational approaches for design of biomass gasification for hydrogen production: A review, Renewable and Sustainable Energy Reviews, 16, 2304-2315.

Hernández, J.J., Lapuerta M. Monedero E., 2016, Characterisation of residual char from biomass gasification: effect of the gasifier operating conditions, Journal of Cleaner Production, 138, 83-93.

Inayat A., Ahmad M.M., Yusup S., Mutalib M.I.A., 2010a, Biomass steam gasification with in-situ CO_2 capture for enriched hydrogen gas production: a reaction kinetics modelling approach, Energies, 3, 1472-1484.

Inayat A., Ahmad M.M., Mutalib M.A., Yusup S., 2010b, Flowsheet development and modelling of hydrogen production from empty fruit bunch via steam gasification, Chemical Engineering Transactions, 21, 427-432.

Khan Z., Yusup S., Ahmad M.M., Rashidi N.A., 2014, integrated catalytic adsorption steam gasification for hydrogen production, International Journal of Hydrogen Energy, 40, 3286-3293.

Rupesh S., Muraleedharan C., Arun P., 2016, ASPEN plus modelling of air–steam gasification of biomass with sorbent enabled CO_2 capture, Resource-Efficient Technologies, 2, 94-103.

Shahbaz M., Yusup S., Inayat A., Patrick D.O., Pratama A., 2016a, Application of response surface methodology to investigate the effect of different variables on conversion of palm kernel shell in steam gasification using coal bottom ash, Applied Energy, 184, 1306-1315.

Shahbaz M., Yusup S., Pratama A., Inayat A., Patrick D.O., Ammar M., 2016b, Parametric Study and Optimization of Methane Production in Biomass Gasification in the Presence of Coal Bottom Ash, Procedia Engineering, 148, 409-416.

Sreejith C., Muraleedharan C., Arun P., 2014, Performance prediction of steam gasification of wood using an Aspen plus thermodynamic equilibrium model, International Journal of Sustainable Energy, 33, 416-434.