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Flowsheet Development and Modelling of Hydrogen Production from Empty Fruit Bunch via Steam Gasification

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Due to the availability of agricultural land and significant production of palm oil in Malaysia, there is abundance of biomass in the form of agricultural wastes. This work reports a mathematical model for the flowsheet developed for hydrogen production from empty fruit bunch from oil palm via steam gasification with in-situ carbon dioxide capture by CaO as sorbent. The flowsheet model incorporates the chemical reaction kinetics, mass and energy balances calculations. Parameter analysis on the influence of the temperature, steam/biomass and sorbent/biomass ratios are performed. It is predicted that more than 70 mole% hydrogen can be produced at 1150 K. In addition, CO_2 are predicted to be fully absorbed from the system at sorbent/biomass ratio of 2.0. It is observed that the thermodynamic efficiency of the gasifier increases with temperature reaching a maximum efficiency of 84 % at steam/biomass ratio of 2.0. It is shown that by using CaO as the sorbent in the gasifier, the efficiency can be increased by 10 % compared to the conventional gasification method.

1. Introduction

The use of hydrogen as clean and sustainable fuel has recently attracted significant attention due to the recent energy crisis and the tightening of environmental regulation. An increasing pattern of hydrogen utilization was observed with world demand: hydrogen usage in 2006 was reported to be 50 MT/y with 10 % increase in the annual projection. Being the world largest producer of palm oil, the potential for hydrogen production in Malaysia is logical due to the abundance of biomass estimated at 21.625 t th^{-1} y^{-1} (Kelly-Yong et al., 2007). Empty fruit bunch (EFB) from oil palm alone constitutes 23 % of this amount. Among the thermo-chemical processes that can convert biomass into hydrogen are pyrolysis and gasification. Between the two, Balat (2008) found that gasification offers lower production cost. It is also reported that the use of pure steam as the gasifying agent is more economical and favor the production of hydrogen more than other conventional agents (Franco et al., 2003). Moreover, hydrogen purity in the product gas can be increased by absorbing CO_2 from the system using CaO as sorbent (Pfeifer et al., 2009). Several works were reported based on experiments and modeling study for the hydrogen production which focuses on the effect of various operating parameters on the hydrogen concentration in the product gas.

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In a study by Florin and Harris (2007), a thermodynamic equilibrium model was proposed for hydrogen production from biomass coupled with CO_2 capture. The results showed that the hydrogen concentration could be increased from 50 to 80 vol% in the product gas using the capture step. Later, Abu-Zahra et al. (2009) introduced a new concept of an integrated process with co-production of hydrogen. Using syngas as the feedstock, the simulation predicted 95 % hydrogen in the product gas. Another equilibrium model was reported by Mahishi et al. (2008) for steam gasification with CO_2 adsorption using CaO as sorbent. Their results showed that the hydrogen concentration was increased by 19 % and the thermodynamic efficiency of the overall process was increased by 10 % with the CO_2 adsorption step. Another flowsheet model with some simplifications was developed in ASPEN PLUS process simulator for a coal gasification process consisted of gasifier, gas cleaning and cooling units (Emun et al., 2008). The thermodynamic efficiency higher than 45 % was observed.

2. Technical Approach

2.1 Process development

The process flow used in the current study is shown in Figure 1. The Empty Fruit Bunch (EFB) is pretreated prior to gasification, i.e. the moisture is removed through drying and the EFB is subsequently grinded. The EFB and sorbent are fed into the gasifier at atmospheric temperature. The steam produced in a steam generator is superheated to 523 K and forward to the system. The gasification process is integrated with CO_2 adsorption step and six major reactions listed in Table 1 are assumed to take place in the gasifier. As the steam gasification process is endothermic, external energy, Q_r, is supplied. Fly ash and other solid particulates are removed from the product gas using a filter. Next the product gas is cooled down by passing it through a scrubber. Finally a pressure swing adsorption unit is used to purify the product gas to achieve 99.99 % pure hydrogen.

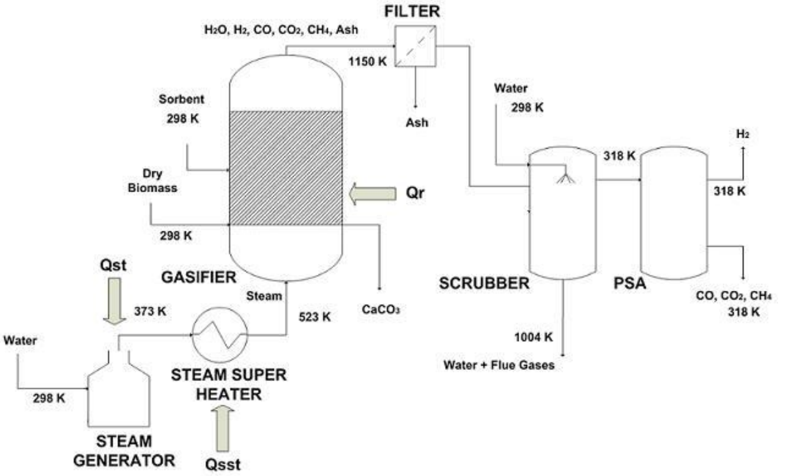

Figure 1: Process flow diagram for the gasification process with in-situ CO_2 adsorption

2.2 Assumptions

The following assumptions are considered in the flowsheet development for the gasification process.

- The gasifier operates under a steady state condition.
- EFB could be represented by $C_{3.4}H_{4.1}O_{3.3}$ (Ahmad et al., 2009).
- The reactions proceed isothermally and at constant volume.
- There is no tar formation in the process.

2.3 Model formulation

For the modeling for the reaction kinetics, six major reactions listed in Table 1 are assumed to take place.

Table 1: Reactions scheme in the gasifier (Ahmad et al., 2009).

No	Name	Reaction
1	Char gasification	$C_{3.4}H_{4.1}O_{3.3} + 0.1\ H_2O \rightarrow 2.15\ H_2 + 3.4\ CO$
2	Methanation	$C_{3.4}H_{4.1}O_{3.3} + 8.05\ H_2 \rightarrow 3.4\ CH_4 + 3.3\ H_2O$
3	Boudouard	$C_{3.4}H_{4.1}O_{3.3} + CO_2 \rightarrow 4.4\ CO + 0.9\ H_2O + 1.15\ H_2$
4	Methane reforming	$CH_4 + H_2O \rightarrow CO + 3H_2$
5	Water gas shift	$CO + H_2O \leftrightarrow CO2 + H_2$
6	Carbonation	$CO_2 + CaO \rightarrow CaCO_3$

The kinetic models for the gasifier based on these reactions were presented and validated in an earlier work by Ahmad et al. (2009). With the assumption of no heat losses and no work done, the mass and energy balances around the gasifier are represented by equations (1) and (2) respectively (Mahishi and Goswami, 2007).

$$mEFB + mH_2O + mCaO = mH_2 + mCO + mCO_2 + mCH_4 + mH_2O + mCaCO_3 \tag{1}$$

$$H_{EFB} + H_{H_2O} + H_{CaO} + Q_r = H_{H_2} + H_{CO} + H_{CO_2} + H_{CH_4} + H_{H_2O} + H_{CaCO_3} \tag{2}$$

Here m represents the mass, H denoting enthalpy and Q_r represents the external energy required by (or rejected by) the gasifier. The enthalpy for each component is calculated using equations (3) and (4).

$$H = n \times (H_f + \Delta H) \tag{3}$$

$$\Delta H = \int_{T_1}^{T_2} C_p dT \tag{4}$$

where n is the number of moles and H_f is the standard enthalpy of formation for the component. The change in enthalpy, ΔH, are calculated using the heat capacity equation referred from literature (Tang and Kitagawa, 2005) based on the heat capacity, C_p. The thermodynamic efficiency of the system is calculated using equation (5) (Mahishi et al., 2008).

$$\eta = \frac{Lower\ heating\ value\ of\ product\ gas}{Lower\ heating\ value\ of\ biomass + (Q_{ST} + Q_{SST} + Q_r)} \tag{5}$$

Here Q_{ST} and Q_{SST} is the energy required for steam generation and for super steam generation respectively, calculated using equation (6) with respect to temperature change.

$$Q_{ST\ or\ SST} = n_{H_2O} \times \Delta H_{H_2O} \tag{6}$$

Meanwhile Q_r is the energy required for the process and is calculated using the energy balance given as equation (2). The lower heating value (LHV) of the product gas and biomass is calculated using equations (7) and (8) respectively.

$$LHV\ of\ product\ gas = (n_{H_2} \times LHV_{H_2}) + (n_{CO} \times LHV_{CO}) + (n_{CH_4} \times LHV_{CH_4}) \quad (7)$$

$$LHV\ of\ biomass = n_{EFB} \times LHV_{EFB} \quad (8)$$

The values of LHV of the product gas and EFB are taken from literature (Kelly-Yong et al., 2007).

3. Results and Discussion

3.1 Effect of steam/biomass ratio

The effect of the steam/biomass ratio on the product gas composition and thermodynamic efficiency is shown in Figure 2. It is observed that by increasing the steam/biomass ratio, H_2 amount produced increases whilst CO amount decreases. This is due to methane reforming and water gas shift reactions, which are highly dependent on the steam feed and are pushed forward in the presence of excess steam based on Le Chatelier's principle. The amount of CO_2 also increases slightly due to the forward reaction of the water gas shift, resulting from the increased steam/biomass ratio. Meanwhile, by increasing steam/biomass ratio from 1.5 to 2.0, the efficiency increases from 80.8 % to 84.2 % before it decreases at higher steam/biomass ratio. The results demonstrate that although increasing the steam amount has the effect of increasing hydrogen amount in the product gas but beyond a certain limit, it will no longer in favor of the process efficiency: as more steam is supplied to the process, more energy is required to generate steam, hence more heat is lost along with the product gas.

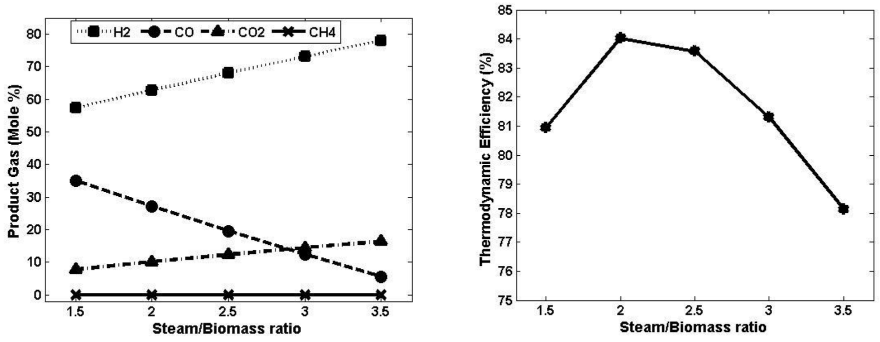

Figure 2: Effect of steam/biomass ratio on product gas composition and thermodynamic efficiency. Temperature: 1150 K, Sorbent/biomass ratio: 1.0.

3.2 Effect of temperature

Based on the profiles in Figure 3, by increasing the temperature of the gasification process, the yield for methane and CO decreases but the total gas and hydrogen produced increase. This can be explained by the endothermic nature of char gasification and methane reforming reactions that are promoted by heat. In addition, the CO_2

adsorption step promotes the water gas shift reaction forward, consistent with the Le Chatelier's principle. The thermodynamic efficiency of the process is also observed to be increasing with temperature, due to the increased hydrogen content in the product gas. By 1150 K, the efficiency of the process is observed to be more than 80 %.

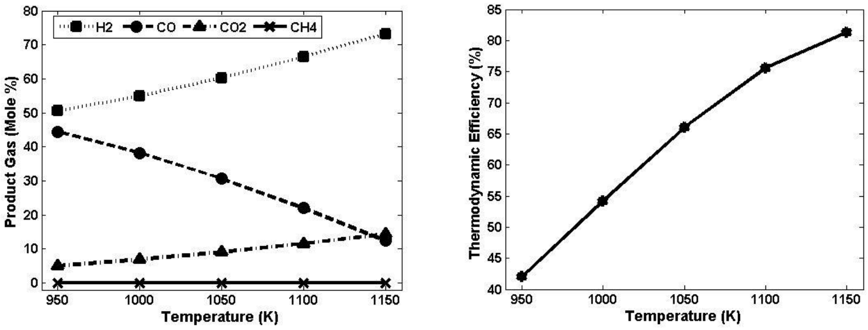

Figure 3: Effect of temperature on product gas composition and thermodynamic efficiency. Steam/biomass: 3.0, Sorbent/biomass ratio: 1.0.

3.3 Effect of sorbent/biomass ratio

Figure 4 shows the profiles of the product gas composition and the thermodynamic efficiency of the steam gasification system based on the influence of the sorbent amount. Without the presence of CaO, i.e. at sorbent/biomass ratio of 0.0, the amount of H_2 and CO_2 predicted is 55 and 28 mole% respectively. At sorbent/biomass ratio of 2.0, it shows that all the CO_2 was absorbed by the absorbent thus leaving no CO_2 in the product gas. The hydrogen amount increases to reach 74 mole%. The CO_2 absorption by the sorbent removes the CO_2 from the system and hence promote of the forward reaction of water gas shift. In addition, it also observed that the thermodynamic efficiency of the process increases with the increase in the sorbent/biomass ratio. The comparison between the efficiency at sorbent/biomass ratio of 0.0 with that at 0.5 shows increment by more than 10 %.

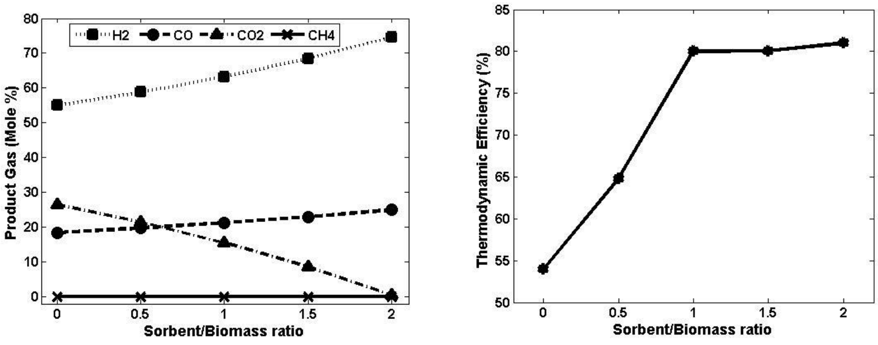

Figure 4: Effect of sorbent/biomass ratio on product gas composition and thermodynamic efficiency. Steam/biomass: 3.0, Temperature: 1150 K.

This can be explained as the CO_2 absorption step removes CO_2 with zero LHV from the product gas and increases the amount of hydrogen with high value of LHV in the product gas. As the sorbent/biomass ratio is increased to 1.0, the efficiency reaches 80 %. Beyond this point, further increase in the sorbent/biomass ratio no longer lead to significant increase in the efficiency.

Acknowledgements

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