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Effects of Purification on the Hydrogen Production in Biomass Gasification Process

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Energy from renewable sources such as biomass are expected to complement the energy derived from fossil fuel resources due to its abundant reserves and relatively low price compared with other energy sources. These biomass wastes are used to produce hydrogen gas via gasification process. In order to study the gasification process, there have been substantial researches involving gasification using process simulation studies where the most commonly used is Aspen Plus software. The researcher basically often uses different types of gasifier in their studies where the most preferred in the literature are fluidized bed gasifier and downdraft fixed bed gasifier. The previous research did not focus on hydrogen gas purification produced from biomass gasification process. The objective of this research is to evaluate the performance of biomass gasification purification on the hydrogen production. The biomass used in this paper is oil palm frond since it is the most abundant waste produced compared to another oil palm wastes. Both of the fluidized bed gasifier and downdraft fixed bed gasifier models are developed in the Aspen Plus and the performance of the gasifier is determined by focusing on the total amount of hydrogen gas. Based on the gasification-purification simulation results obtained, the fluidized bed reactor produces approximately 7.95 % amount of hydrogen gas compare to only 6.75 % hydrogen gas for fixed bed reactor.

1. Introduction

Oil palm frond is one of the main biomass wastes in Malaysia. In 2009, the amount of oil palm frond waste is counted up to 44.8×10^6 t and it has created a major disposal problem (Ng et al., 2011). Basically, oil palm frond waste is usually retained in the plantations and left to decompose naturally for nutrient replacement or mulching purposes. The high potential value of this waste to be used for more lucrative purposes is often being ignored. Less than 10 % of the biomass wastes have been used for niche downstream application such as gasification (Sun et al., 2014). Biomass gasification process can be applied as one of the solutions in order to utilize of oil palm frond waste.

Biomass gasification is known as a process of incomplete combustion of biomass resulting in production of synthesis gas consisting of carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2) and traces of methane (CH_4). The generated syngas is then applied as a gaseous fuel or serves as an input for fuel cell to produce electricity and heat (Sosnowska et al., 2014). The two most common gasifiers used in the gasification process can be classified into two categories namely fixed bed and fluidized bed. For fixed bed gasifier, it can be divided into updraft (counter-current) and downdraft (co-current) gasifiers which is based on the direction of the flow of the gasifying agent (Basu, 2006). For updraft gasifier, the biomass moves downwards through a bed, while reacting with the gasifying agent that moves in the opposite direction (Konda et al., 2012). Meanwhile for downdraft gasifier, the gasifying agent moves downwards through the bed in the same direction as the biomass feedstock (Figueroa et al., 2013). The main advantage of this gasifier is its ability to produce syngas with low tar content and it does not require extensive clean-up compare to updraft gasifier which requires extensive clean-up to remove high amount of tar before it can be used in the synthesis applications (Kosov et al., 2015). Meanwhile bubbling fluidized bed and circulating fluidized bed gasifiers are the two main types of fluidized bed reactor, which usually operate at temperature between 700 - 900 °C. In the bubbling fluidized bed gasifier, the gasifying agent is injected at the bottom of the reactor at a velocity equal to the minimum fluidization velocity to

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ensure intense mixing of the hot bed material (Ruoppolo et al., 2013). The operation of circulating fluidized bed gasifier is almost similar to the bubbling fluidized bed gasifier, with the main difference is the velocity of the gasifying agent usually exceeds the minimum fluidization point. Due to this high velocity, an entrainment of the particles in the product gas occurs. The particles are separated in a cyclone at the exit of the reactor and the bed material is returned to the reactor (Basu, 2006). The circulating fluidized bed provides lower heat exchange compared to the bubbling fluidized bed gasifier and thus not suitable for a wide range of biomass particle sizes. Bubbling fluidized bed gasifier with air is a relatively simple process for syngas production.

The syngas produced from gasification process can be used to produce energy by using fuel cells. Syngas needs to undergo hydrogen purification process because some syngas such CO is poisoning to the Proton Exchange Membrane Fuel Cell (PEMFC) and it needs to be lower than 10 ppm or it can cause serious damage to the PEMFC membrane layer. There are 3 categories of hydrogen purification which each category has specific techniques and methods. There are: 1) Chemical (catalytic purification), 2) Physical (metal hydride separation, pressure swing adsorption, cryogenic separation) and 3) Selective diffusion (noble metal membrane diffusion, polymer membrane diffusion, solid polymer electrolyte cells). Catalytic purification has been known as the best method since the purity of outcome hydrogen is about 99.99 % and the pure hydrogen act as the best input for PEMFC. Catalytic purification removes oxygen by reaction with hydrogen to form water, and carbon monoxide by oxidation or methanation. This technique is used to upgrade relatively pure hydrogen produced and reduce the concentration of CO since CO can cause serious poisoning to PEMFC membrane. The main methods of catalytic purification are as follows: i) Purification with hydrogen selective membrane, ii) CO methanation, iii) Preferential oxidation (PROX) of CO. For the application of small-scale fuel processor, the selective membrane purification, CO methanation, and the CO-PROX have been considered to be promising. Catalytic preferential oxidation of CO (CO-PROX) is one of the most suitable methods of purification of H_2 because of high CO conversion rate at low temperature range meanwhile the PROX of CO is a reaction to convert CO in a H_2-rich gas mixture to CO_2 with minimal H_2 consumption which all these are preferable for PEMFC operating conditions. This method has the potential to increase the amount of hydrogen in the end of the operation.

Modelling and simulation is progressively becoming a useful tool to investigate the process parameters of the biomass gasification process (Wahid et al., 2016). In terms of the modelling and simulation, Aspen Plus process simulator is widely applied to represent the desired gasification process. In the earlier work carried out by Nikoo and Mahinpey (2008), they used Aspen Plus to simulate pine sawdust gasification in fluidized bed reactor while in the work of Figueroa et al. (2013), they investigated steam gasification process of sugarcane bagasse in a fixed bed reactor. The previous work just focusing on biomass gasification process only without trying to investigate the purification of hydrogen. There is no attempt to compare different gasifiers for hydrogen production in the literature. The objective of this study is to investigate and compare the performance of hydrogen purification on bubbling fluidized bed gasifier and downdraft fixed bed gasifier employing oil palm frond as biomass input for hydrogen production. Here the process design flow sheet for fluidized bed and fixed bed are developed in the Aspen Plus. Then the performances for both gasifiers are analysed and compared in terms of total production of syngas and amount of hydrogen produced after catalytic purification process.

2. Modelling Approach

In this section modelling approach, has been presented in detail, including (i) all the process assumptions used to simplify the physical problem; (ii) properties of the model; and (iii) process modelling using Aspen Plus simulator. Aspen Plus is full-featured software, used by many professional researchers to simulate a model and predict the performance of processes without complex calculations (Nikoo and Mahinpey, 2008).

2.1 Process Assumptions

In this study, there are few assumptions need to be considered in the modelling process. The assumptions used for both gasification models are (i) the processes are in the isothermal and steady state conditions; (ii) the composition of char consists only carbon, void and ash; (iii) all chemical reactions occur under equilibrium state in the gasifier and there is no pressure loss; (iv) all the particles are assumed in the spherical shape, uniform size and the average diameter remains constant during the gasification meaning that no species concentration or thermal gradients exist within the particle; (v) the syngas produced are ideal gases state, including H_2, CO, CO_2, steam (H_2O) and CH_4; (vi) all hydrogen and oxygen contained in the biomass is assumed to be released during devolatilization.

2.2 Models Properties

Both of the fluidized and fixed bed models are simulated as a stand-alone model using the same operating conditions which consists of the feed flow rate of 10 kg/h, temperature of 700 °C and pressure of 1 bar. For gasifying agent, both models have the same air flow rate of 10 kg/h. However only fluidized bed has additional gasifying agent which is steam with flow rate of 1.8 kg/h. The Redlich-Kwong-Soave (RKS) cubic equation of state with Boston-Mathias alpha function (RKS-BM) is used as thermo-physical property method in both gasification processes. In this study, oil palm frond is used as a feed for both gasification process based on the ultimate and proximate analysis as shown in Table 1. The enthalpy and density models selected for both feed and ash are non-conventional components. In this study, feed (oil palm frond) is defined as nonconventional components based on their ultimate and proximate analysis as shown in Table 1. The reactions of both gasification processes are shown below:

Table 1: Proximate and ultimate analysis of oil palm frond (Konda et al., 2012)

Proximate analysis (wt.% dry basis)		Ultimate analysis (wt.% dry basis)	
Moisture content	6.3	C	42.55
Volatile Matter	51.3	H	5.48
Fixed Carbon	41	N	2.18
Ash	6.3	S	0.20
		O	43.38

$$C + O_2 \rightarrow CO_2 \tag{1}$$

$$C + 0.5O_2 \rightarrow CO \tag{2}$$

$$C + CO_2 \leftrightarrow 2CO \tag{3}$$

$$C + H_2O \leftrightarrow CO + H_2 \tag{4}$$

$$C + 2H_2 \rightarrow CH_4 \tag{5}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{6}$$

$$H_2 + 0.5O_2 \rightarrow H_2O \tag{7}$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \tag{8}$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \tag{9}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{10}$$

$$CO + 0.5O_2 \rightarrow CO_2 \tag{11}$$

2.3 Process Modelling using Aspen Plus

Aspen Plus has been selected as a simulation tool to represent the gasification process. The decomposition of the process into its constituent elements for individual study of performance can be evaluated using Aspen Plus. The process characteristics such as flow rates, compositions, temperatures, pressures, properties, equipment sizes can be more easily predicted by using analysis techniques. In this work, Aspen Plus is used to develop the gasification downdraft fixed bed and bubbling fluidized bed gasifiers with catalytic purification reactor.

2.3.1 Fixed Bed Gasification Model

For fixed bed reactor, the main process in the gasification process is classified into four stages which consist of the drying of the feed, the decomposition of the feed, char gasification and combustion and separation process. The gasification flow sheet for fixed bed reactor is shown in Figure 1. The first stage is the drying of the feed in order to remove water content in the feed. Next is the RSTOIC reactor which is used to simulate the decomposition of the feed. Here the extent of the reaction (Feed: 0.0555 H_2O) is used in the RSTOIC to transform some part of the inlet feed to water. When the dry feed enters the RYIELD reactor, the decomposition of the feed is taken place and the feed is then converted into the atoms of carbon, hydrogen, oxygen, sulphur, nitrogen and ash. The decomposed feed and air enter the RGIBBS block and will undergo combustion and gasification reaction in the RGIBBS reactor which employing all the reactions from Eq(1) to Eq(9). Subsequently, the SEPARATOR block is used in order to separate the ash from the mixture of the syngas. The syngas produces from the gasifier model are then entering the hydrogen purification process or CO-PROX. Afterwards the syngas will go to HTS (high-temperature water gas shift reactor) and LTS (low temperature water gas shift reactor). In the HTS and LTS reactors, the water gas shift reaction between CO and steam occurs as shown in Eq(10). The HTS (high-temperature water gas shift reactor) is operated at temperature of 300 °C and the LTS (low temperature water gas shift reactor) is operated at temperature of 200 °C. After HTS, the exit CO concentration is expected to be in the range of 2 % to 4 % and 1 % for LTS. The CO-selective oxidation reaction (Eq(11) takes place in the preferential oxidation reactor, represented by the unit PROX. This reactor is operated at temperature of 150 °C. At this stage, the remaining CO in the H_2 feed is reduced to an acceptable level for PEMFC applications (less than 10 ppm).

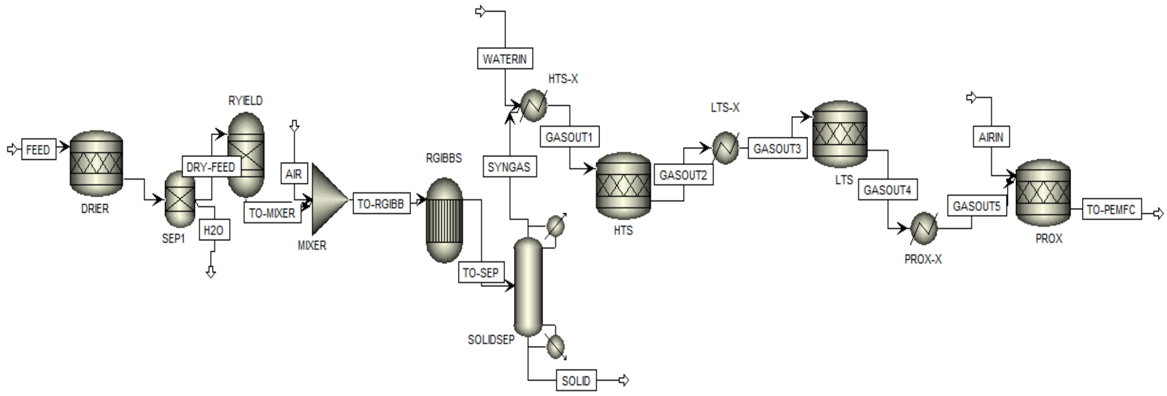

Figure 1: Fixed bed gasification with hydrogen purification flowsheet

2.3.2 Fluidised Bed Gasification Model

For fluidised bed, the gasification process basically is classified into 4 stages which consist of decomposition of feed, volatile reactions, char gasification and the separation of gas and solid. The Aspen Plus flow sheet gasification process using fluidised bed is shown in Figure 2. Based on Figure 2, the first stage of the gasification process is represented by RYIELD which is the yield reactor. After the biomass enters the yield reactor, it is decomposed and converted into its components. In the case of oil palm frond, the atoms of carbon, hydrogen, oxygen, sulphur, nitrogen and ash were converted into their specific yield for each syngas by using the yield distribution based on the ultimate analysis. For volatile reactions, it involves two units which are the SEPARATOR and RGIBBS. The SEPARATOR will separate the products from the yield reactor into volatile matter and solids. The amount of volatile matter is specified in Aspen Plus based on the information from Table 1. The complete separation of volatile matter from SEPARATOR is then fed into to the Gibbs reactor (RGIBBS). In the Gibbs reactor, the volatile matter will undergo combustion process and the reaction is assumed to follow the Gibbs equilibrium which employing all the Eq(6) to Eq(9). The steam and air will mix with the syngas in the MIXER and then undergo char gasification process in the RGIBBS. All the Eq(1) to Eq(9) will take place in the process. The syngas product is then separated in the SEPARATOR into gas and solid products. The syngas then will undergo catalytic purification as similar as the catalytic purification process in the fixed bed gasification.

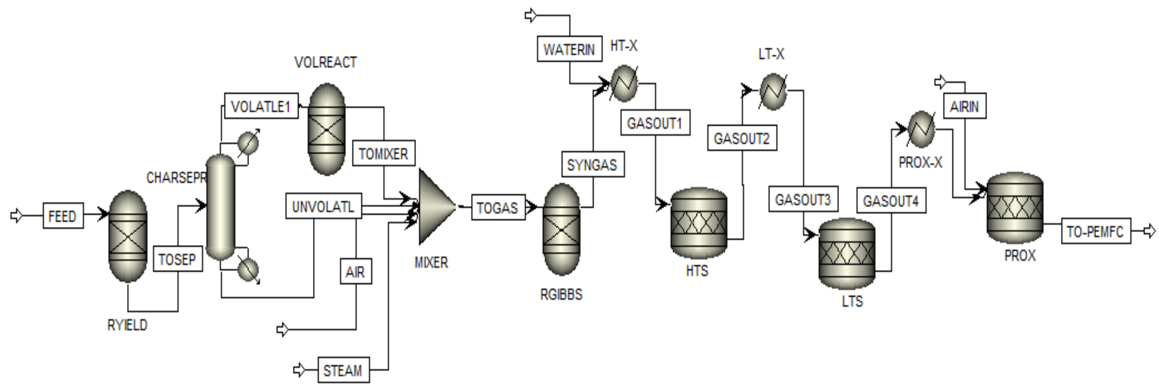

Figure 2: Fluidised bed gasification process with hydrogen purification flowsheet

3. Results and Discussions

The simulation results of the biomass gasification without purification process are shown in Table 2. Based on Table 2, the hydrogen gas produced by fluidised bed (6.69 %) shows more percentage compared to fixed bed reactor (4.91 %). This is due to the presence of steam flow inside of the fluidised bed gasification which increases the hydrogen production. The solid fuel particles from biomass are brought into contact with a restricted supply of oxygen by feeding them into oxygen or air starved fluidised bed. The fuel particles are quickly heated to the bed temperature and undergo rapid drying and pyrolysis (Basu, 2006). Besides, the small amount of methane produced (1.36 % for fixed bed and 1.21 % for fluidised bed) also caused by the hydrogasification reaction (see Eq(5)) during the gasification. This reaction produces methane, but its amount usually relatively low, especially at low pressures, compared to the pyrolysis which produces more amounts of other syngas (Karimipour et al., 2012). Some of the methane is decomposed which resulting into the increment of CO_2 amount as indicated by Eq(8). The higher content value of CO caused by Boudouard reaction which is determined by Eq(2). At high temperature, the endergonic reaction will cause more C and CO_2 to be converted into CO. The fluidised bed reactor provides excellent biomass mixing compared to the fixed bed reactor (Wahid et al., 2016). This specification trigger the process inside of the gasification to have high tendency to gain high amount of heating value and this is also improved the mass and heat transfer from biomass leading to the more hydrogen production.

Table 2: Comparison amount of syngas (%) between two gasifiers model

Components	Fixed bed	Fluidised bed
CO_2	29.17	38.33
CO	64.56	53.76
H_2	4.91	6.69
CH_4	1.36	1.21

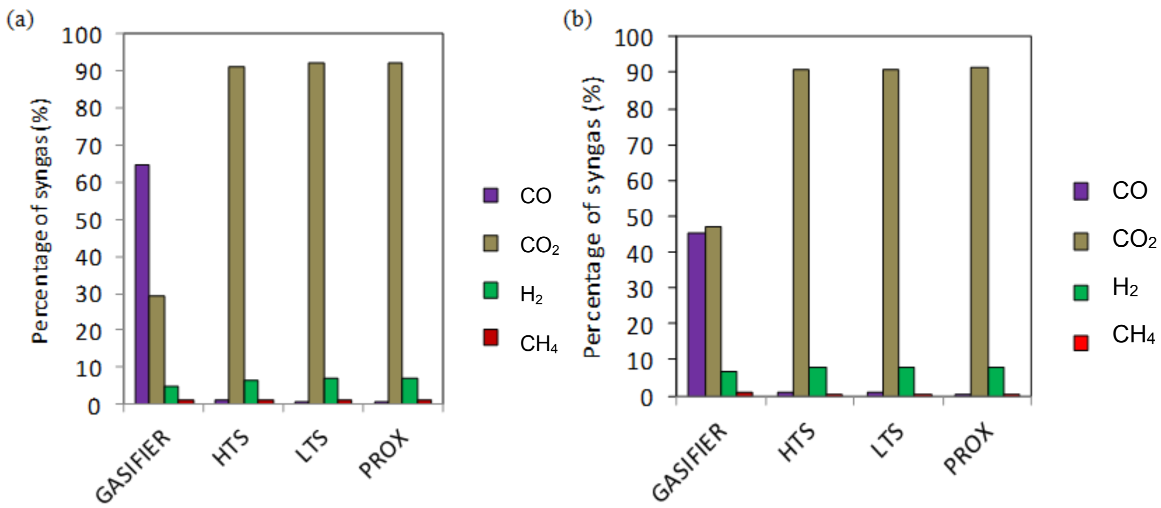

Figure 3: Product gas percentages at the outlets of the gasifier, HTS reactor, LTS reactor and PROX reactor from (a) fixed bed, (b) fluidised bed

Figure 3 shows the amount of product gas composition in terms of percentages at the outlets of the gasifier, high- and low-temperature water gas shift reactors (HTS and LTS) and a preferential oxidation reactor (PROX) from fixed bed and fluidised bed gasifier. The product gases from both biomass gasifier contains high percentage of CO which are 64.56 % for fixed bed gasifier and 53.76 % from the fluidised bed gasifier which exceeding the allowable limit of 1 % for PEMFC application. The PEMFC performance degrades when CO is present in the syngas; this is referred to as CO poisoning. The CO has a strong tendency to be adsorbed into catalyst surface on the PEMFC and blocking the active catalyst sites which are required for hydrogen oxidation reaction. Since this problem happened, the product gas should undergo catalytic preferential oxidation of CO (CO-PROX) flow through HTS and LTS and lastly PROX. The amounts CO_2 and H_2 gases are then increased while the amount of CO is decreased when all of these gases went through HTS and LTS. The conversion of the CO achieved approximately 96 % to 98 %. This is due to the water gas shift reaction Eq(10) occurs in both reactors. The syngas is then fed to the PROX reactor where the O_2 and CO underwent partial oxidation which produces CO_2. Here the CO concentration is reduced to less than 10 ppm and the total hydrogen amount is increased from 4.91 % to 6.75 % for fixed bed gasifier. Meanwhile it has been observed that the total hydrogen amount is increased from 6.69 % to 8 % for fluidised bed gasifier. It can be concluded that the fluidised bed is the most effective gasifier compared to fixed bed gasifier for gasification process since its produce more hydrogen even after PROX reactor has been implemented to both reactors during the gasification-purification process.

4. Conclusions

A purification process has been included for downdraft fixed bed gasification and bubbling fluidised bed gasification in Aspen Plus. Firstly, the gasification process for both gasifiers are conducted and followed by purification of hydrogen steps by using catalytic preferential oxidation of CO (CO-PROX) which consists of high-temperature water gas shift reactor (HTS), low temperature water gas shift reactor (LTS) and lastly preferential oxidation reactor (PROX). For the gasification process, both models are successfully simulated in the Aspen Plus and the hydrogen gas produced by bubbling fluidised bed gasifier (6.69 %) is higher to the downdraft fixed bed reactor gasifier (4.91 %) using the same operating condition. After the catalytic preferential oxidation of CO (CO-PROX) have been applied, the amount of CO for both reactor is reduced to less than 10 ppm and the amount of hydrogen is increased to 6.75 % for fixed bed gasifier and 8 % for fluidised bed gasifier. It can be concluded that the CO-PROX system is able to increase the amount hydrogen for both of the gasifiers and it is also shown that fluidised bed gasifier is the most efficient gasifier in terms of total hydrogen gas produced compared to the fixed bed gasifier.

Acknowledgments

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