Hydrogen Production from Mixture of Biomass and Polyethylene Waste in Fluidized Bed Catalytic Steam Co-Gasification Process

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Energy from renewable source is expected to complement the energy derived from fossil fuel resources. In current research, an efficient method to produce hydrogen by blending palm kernel shell (PKS) with polyethylene (PE) waste via catalytic steam gasification is studied at pilot scale fluidized bed gasifier. This paper reports the results obtained from a series of experiment that have been performed to improve the hydrogen production efficiency. By mixing the PE waste with biomass and using those as feedstock revealed an increase in the product gas volume percent and hydrogen yield. The highest H_2 content 76.18 vol% achieved at 800 ºC using 25 wt% of PE mixed with PKS. A fuel gas with a calorific value up to 15.98 MJ/Nm^3 was produced which has the potential to be used in engines.

1. Introduction

In view of increasing population the energy consumption and demand increased. With an increased in environmental pollution has urged researchers to seek for renewable alternative. There is also a concern about the environmental pollution caused by the use of fossil fuels. Referring to a recent study, the world CO_2 emission that is the main cause of global warming increased by 3 % in 2011, reaching an all-time high of 34·Gt in 2011 (Olivier et al., 2012). According to the Global Climate Change Initiatives (GCCI), the greenhouse gas intensity should be decreased by 18 % by the year 2012 (Granite and O'Brien, 2005). In addition, it is mandated in the Kyoto Protocol that industrial countries should reduce greenhouse gas emission to 6 percent which is below 1990 levels by the year 2012.

Nowadays one of the serious problems related to environment is an increasing amount of plastic waste that is growing year by year. Today, just a small percentage of plastic waste is recycled and disposal is mainly by landfill or incineration that both are associated with environmental problems. The production of energy from polyethylene waste has been expected to be an effective solution of disposal for this type of waste.

In Malaysia, the agricultural sector has been growing rapidly over the years (Ng et al., 2012) . This has led to significant number of different sources of biomass to be applied as feedstock for the purpose of energy production. Currently, more than 3.88 million hectares of Malaysia land are under oil palm plantation (Idris et al., 2010). PKS is one of by product waste from palm oil during its post-processing. For every ton of oil-palm fruit bunch fed to the palm-oil refining process, about 0.1 tons of palm shell, 0.146 t of palm fiber and 0.2 t of EFB are produced as the solid wastes (Azlina et al., 2009).

From the above perspective, there is an urgent need of exploiting the huge quantities of wastes generated from municipal and oil palm industry to produce more valuable fuels. A promising option is by converting these wastes into bio-fuel. Among the various types of bio-fuels that can be produced, hydrogen is considered as the most important fuel that is expected to become a major source of energy and plays an

important role in the economic development. The thermo-chemical conversion methods are effectively applied in hydrogen production using wide range of biomass feedstock. Among the thermo-chemical conversion technologies, catalytic steam gasification is an interesting process and a promising solution for utilization of biomass blended with PE waste, and not much study has been done at pilot plant scale. The interest in production of hydrogen-rich gas from mixed feedstock on a large scale in developing country like Malaysia can provide many environmental, economical and social objectives. These advantages include mitigating the carbon emission to environment and preventing further global warming, ensuring sustainability source of fuel and reducing the country dependence on fossil fuel. In present work, a mixture of palm kernel shell and polyethylene waste was applied as the feedstock with the aim to produce hydrogen rich gas at pilot plant scale gasifier.

He et al. (2009) researched on catalytic steam gasification of waste polyethylene and influence of temperature on gas yield and composition. They achieved highest H_2 component of 36.98 mol% at temperature of 900 ºC. Another study by He et al. (2009) performed on MSW via catalytic steam gasification process that resulted in H_2 content of produced gas raised to 53.29 mol% and the highest H_2 yield achieved was 38.60 mol H_2/kg MSW at 950 ºC. Pinto et al. (2009) investigated co-gasification of coal and waste at pilot plant scale. Two fixed bed catalytic reactor were employed and they reported effective reduction in tar and increasing in H_2 content of more than 50 %. Kwak et al. (2006) investigated gasification of solid waste and obtained syngas at 1200ºC which contained 25-34 vol% of CO and 28-34 vol% of H_2. High heating value of produced gas was reported in the range of 10.88-14.65 MJ/Nm^3. Chang et al. (2011) studied on biomass gasification for hydrogen production. In optimized condition, equivalence ratio of 0.2 and 1000 ºC was achieved to produce maximum yield of H_2 and CO of 29.5 mol% and 23.6 mol% respectively. Lv et al. (2007) employed downdraft gasifier to convert biomass to hydrogen rich gas by applying air and oxygen/steam gasification of pine wood block in laboratory scale self-heated downdraft gasifier. The study found that air gasification yields 0.82-0.94 Nm^3/kg biomass of fuel gas with 21.18%-35.39% mol of H_2, 4.76-5.44 MJ/Nm^3 of LHV and 21.18-29.70 g H_2/kg biomass of hydrogen yield. In biomass oxygen/steam gasification, it was reported that LHV and H_2 of fuel gas reached up to 11.11 MJ/Nm^3 and 63.27 % respectively. Hanaoka et al. (2005) studied the effects of woody biomass components on air-steam gasification. They reported that carbon conversion of cellulose, xylan and lignin were raised to 97.9 %, 92.2 % and 52.8 % respectively. The product gas composition in cellulose was 35.5 % mol CO, 27 % mol CO_2 and 28.7 % mol H_2. In contrast, from the conversion of xylan and lignin, the product gas composition was approximately 25 % mol CO, 36 % mol CO_2 and 32 % mol H_2. It can be concluded that the final products composition depends on the fraction of the main components of biomass feedstock. As stated, base on researches study increasing the temperature in presence of catalyst and steam has an advantage for gasification process since it favoured the steam methane reforming and the water gas reaction that caused decreased in the gaseous hydrocarbons and tar content that increased the hydrogen composition.

The purpose of this research is to optimize the catalytic steam gasification process at pilot scale utilizing the mixture of biomass and polyethylene waste as the energy source to produce hydrogen-rich gas.

2. Experimental Section

2.1 Feedstock

The biomass feedstock (PKS) was obtained from local palm oil factory. The PE waste was from high density polyethylene (HDPE) plastic waste grade 2. Samples were pulverized and sieved into a specific particle size between 1-2 mm. The proximate and ultimate analyses of feed stock are reported in Table 1.

Table 1: Proximate and ultimate analysis

Proximate Analysis (wt% wet basis)	PKS	HDPE	Ultimate analysis (wt.% dry basis)	PKS	HDPE
Moisture content	12.00	0.00	C	49.23	85.71
Volatile matter	30.53	99.67	H	5.04	14.29
Fixed carbon	48.50	0.00	O	44.94	0.00
Ash	8.97	0.33	N	0.74	0.00
Holocellulose	54.30	-	S	0.05	0.00
Alpha-cellulose	29.60	-	Density (kg/m3)	733	1194
Lignin	59.30	-	HHV (MJ/kg)	24.97	45.98

2.2 Pilot plant gasifier and experimental procedure

Figure 1 shows the process flow diagram of catalytic steam gasification unit. The pilot plant consists of cylindrical reactor made of (Inconel 625). The fluidized bed gasifier has the height of 2500 mm and internal diameter of 150 mm and 200 mm in gasification and free board zone respectively. The reactor has four individual electrical heaters and the temperature is controlled by temperature controllers. Pressure differential indicator is installed in the reactor and mounted on top of the reactor. Eight thermocouples are installed across the gasifier, two in the dense bed, four in the gasification zone and two in the free board zone.

In this study, the feedstock is mixed with commercial Ni catalyst and is used in the gasification process. Series of experiments were performed in order to investigate the influence of varying different parameters on hydrogen production. The feedstock is fed to the fluidized bed gasifier with feeding rate of 1.2 kg/h via a variable speed screw feeder and two swing lock hopper which was pressurized with nitrogen. The feeding system was cooled by water to avoid any clogging due to the pyrolysis of PE waste in the feedstock. Steam is supplied by the boiler and heated to 270 ºC through a super-heater. The flow rate of super-heated steam is controlled by mass flow controller and steam was applied as the gasifying agent. The produced gas passed through a cyclone and scrubber to remove any fly ash and any tar residual respectively. A multi stage condenser removed all condensable components. An online gas analyzers (Teledyne 7500, 7600 and 4060) were used to determine the amount of H_2, CO, CO_2, CH_4, N_2, O_2, H_2S and NO_2 in the product gas. The main process parameters such as gas composition, temperatures, gas flow rate and pressure were recorded by data acquisition system.
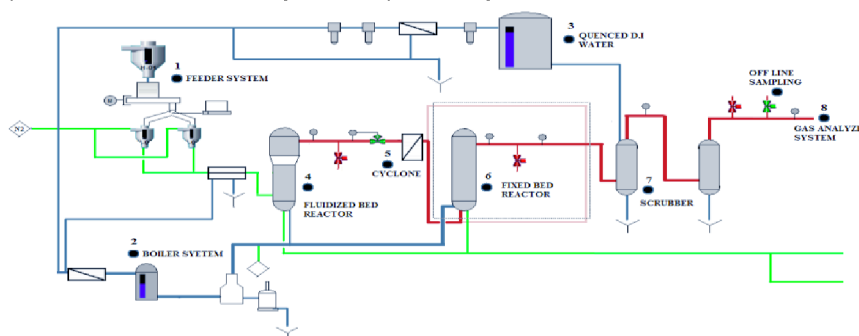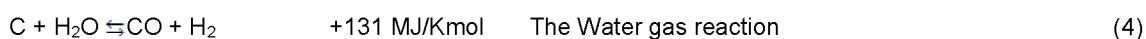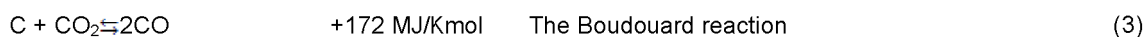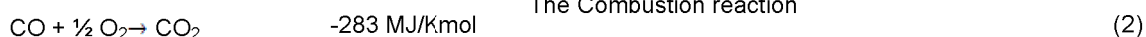

Figure 1. Process flow diagram of pilot plant catalytic steam gasification system. 1-Feeding system 2-Boiler system 3-Quenched D.I. water system 4-Fluidized bed gasifier 5-Cyclone 6-Fixed bed gasifier 7-Scrubber system 8- Gas Analyzer system

3. Results and discussion

3.1 Effect of temperature

According to Xiao et al. (2007), process of biomass gasification occurs in following main three steps. First step; initial pyrolysis or devolatilisation, that occurs at low temperature and produces volatile matter and char. Second step; tar-cracking that favours high temperature reactions. Third step; char gasification that is enhancing by the boudouard reaction. Pinto et al. (2002) stated for PE there is no devolatilisation step and increasing temperature caused decomposition of PE to small molecular radicals and atom that may participate in gasification reactions. In presence of Ni catalyst hydrocarbons molecules and oxygen molecules from dissociation of steam adsorbed on active surface of catalyst and steam methane reforming (7) or steam gasification reaction take place. CO is produced due to catalytic reaction of active site of catalyst (Weil et al., 2006).

Generally, in gasification processes mixture of endothermic and exothermic reactions occurs and they often take place simultaneously. The principal reactions that take place in gasification process are mentioned below;
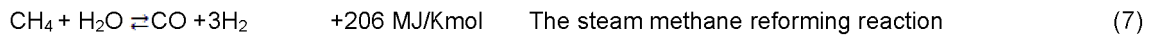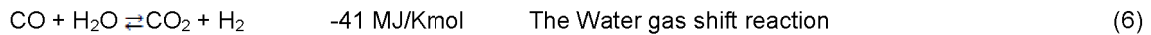
$C + ½ O_2 \rightarrow CO$	-111 MJ/Kmol	The Combustion reaction	(1)
$CO + ½ O_2 \rightarrow CO_2$	-283 MJ/Kmol		(2)
$C + CO_2 \leftrightharpoons 2CO$	+172 MJ/Kmol	The Boudouard reaction	(3)
$C + H_2O \leftrightharpoons CO + H_2$	+131 MJ/Kmol	The Water gas reaction	(4)

$C + 2H_2 \leftrightarrows CH_4$	-75 MJ/Kmol	The Methanation reaction	(5)
$CO + H_2O \rightleftarrows CO_2 + H_2$	-41 MJ/Kmol	The Water gas shift reaction	(6)
$CH_4 + H_2O \rightleftarrows CO + 3H_2$	+206 MJ/Kmol	The steam methane reforming reaction	(7)
$CH_4 + CO_2 \rightleftarrows 2CO + 2H_2$	+260 MJ/Kmol	The Dry reforming reaction	(8)

Figure 2 shows that increasing temperature caused increased in hydrogen yield. Temperature exhibits the most crucial effect on catalytic steam gasification. Increasing the temperature leads to enhancement of secondary cracking and shift reactions thus lead to higher hydrogen yield. According to Le Chatelier's principle, higher temperature favours the products in endothermic reaction. Hydrogen production is favoured at high temperature. At higher temperature reforming reactions $C_nH_m + nH_2O \rightleftharpoons nCO + (n+m/2)H_2$ and $C_nH_m + nCO_2 \leftrightarrows 2nCO + (m/2)H_2$ becoming dominant and cause an increased in hydrogen composition and decreased of hydrocarbons and CO_2 content.

Lv et al. (2004) stated that the steam methane reforming is an endothermic reaction at increasing temperature of gasifier above 700 ºC, which resulted in an increase of H_2 concentration. As illustrated in Figure 3 and 4, H_2 production was found to be highest at 800ºC, S/F: 3 kg/kg and P/B: 0.25 kg/kg, while CO concentration decreased. Also, the Boudouard reaction that favoured temperature higher than 700 ºC caused a decline in CO_2 content. The H_2/CO molar ratio increased with an increase of gasifier temperature. On the other hand, increasing the temperature decreased the LHV from 15.98 to 13.2 MJ/Nm^3 due to conversion of hydrocarbons component, mainly CH_4. It was reported that the gas composition would be dominated by water-gas shift and steam methane reforming reaction at higher temperature > 700 ºC in biomass gasification process. Franco et al. (2003) found that the operating temperature has strong influence on the gas composition. As expected, increased temperature in gasifier led to higher gas yield with reduction in the amounts of char and liquid product that was further cracked to enhanced the gasification process. Over the temperature range of 650 to 800 ºC, the H_2 concentration increased from 54.86 to 76.18 vol%, whilst CO and CO_2 decreased to 8.53 and 4.389 vol%, respectively as illustrated in Figure. 3-5.
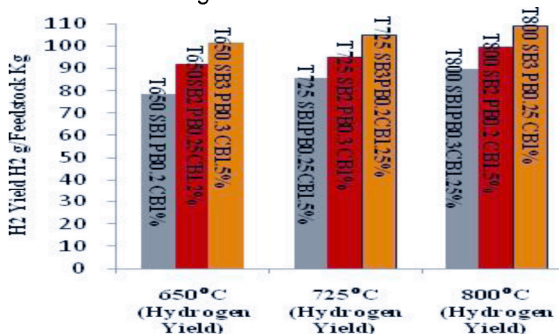

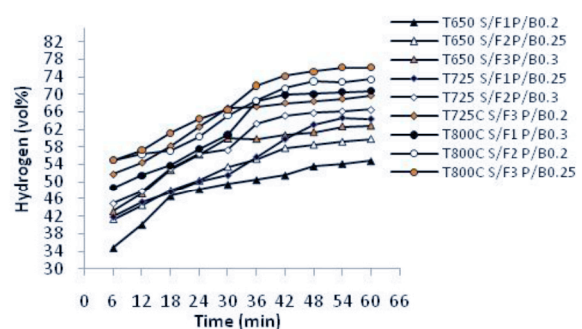Figure 2. Effect of variables on hydrogen yield

Figure 3. Effect of temperature, S/F ratio and P/B ratio on hydrogen production
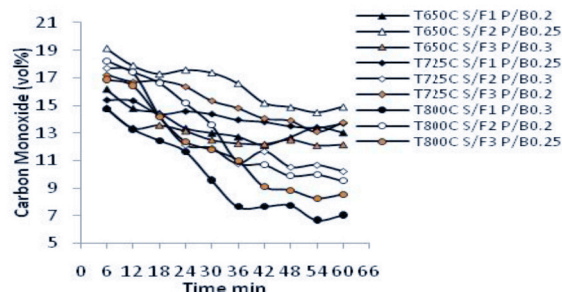

Figure 4. Effect of temperature, S/F ratio and P/B ratio on carbon monoxide production
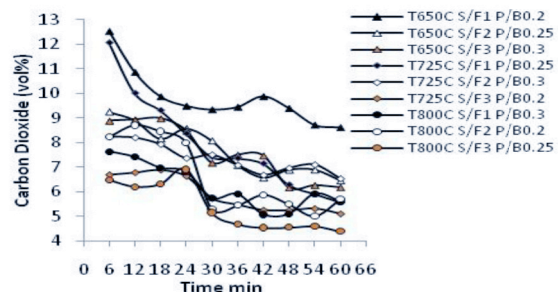

Figure 5. Effect of temperature, S/F ratio and P/B ratio on carbon dioxide fraction

Highest carbon conversion of 88.3 wt% was achieved at 800 ºC. HHV decreased in the range of 17.7 to 14.18 MJ/Nm^3 by increasing the temperature from 650 to 800 ºC respectively. Increasing the temperature caused increase in the hydrogen fraction in gas components and led to slightly decreasing CO content. In an addition CO_2 composition decreased by increasing the temperature. CH_4 and tar composition decreased with increasing temperature and S/F ratio due to cracking and reforming reactions. These obtained results agree with other researchers' findings e.g Gil et al.(1997) display the result of biomass gasification and Pinto et al.(2002) reported on the co-gasification study of biomass mixed with plastic wastes,

3.2 Effect of polyethylene waste blending

To increase the H_2 composition in the gasification process, PE waste was blended with biomass feedstock up to 30 % (kg/kg). Blended PE waste with biomass feedstock caused an increase in the hydrocarbons compositions. The polymer chain decomposes into small molecules which would be mostly CH_4, C_2H_4, H_2 and heavy hydrocarbons. Addition of PE to biomass feedstock caused two processing steps to occur; the initial step is thermo-decomposition of PE waste and biomass that resulted in producing heavy and light hydrocarbons, char and volatiles. The second step consists of reactions that produced hydrocarbons and char with volatiles and steam at high temperature mostly 650-1,000ºC. Therefore the purposes of blending the PE waste with biomass as feedstock were; to increase the light hydrocarbons production; to accelerate steam methane reforming reaction and to enhance the gasification efficiency based on hydrogen yield.
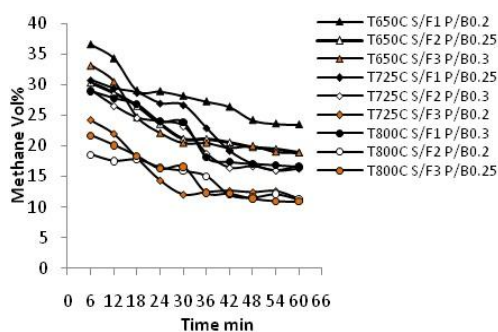

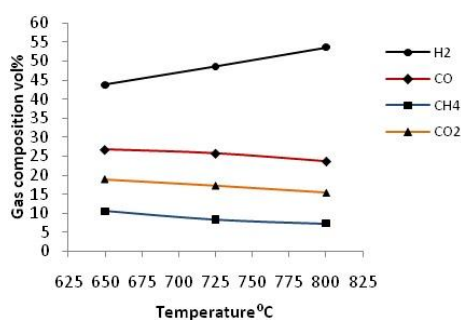Figure 6. Effect of varying of PE component in biomass feedstock on methane concentration

Figure 7. Gas composition of gasifying PKS in non presence of PE waste, S/F ratio 3(kg/kg)

As shown in Fig.6, by blending PE waste to biomass feedstock caused the concentration of CH_4 to be varied in the range of 30.4 to 36.6 vol%. When similar experiment was conducted without PE waste the CH_4 concentration reached to a maximum value of 10.54 vol%. Adding PE waste to biomass feedstock caused an increase in CH_4 concentration in the product gas composition and by increasing the temperature and steam/feedstock ratio, the CH_4 concentration observed is due to the reforming reactions (7 and 8) that is becoming dominant and caused further conversion of CH_4 to H_2 and CO.

3.3 Effect of steam/feedstock ratio

Steam to feedstock (S/F) ratio can be an influential parameter on the gasification process. The introduction of steam to gasification is favourable for improving gas quality. There was significant decreased in CO concentration with maximum value of H_2 up to S/B ratio of about 2-3(w/w). Moreover, the carbon conversion and LHV reached to maximum and minimum values respectively at the same S/F ratio.

Gao and Quan (2009) concluded that an optimum S/B ratio existed for the conversion process as introducing too large a S/B ratio to the gasifier does not always favour the hydrogen production and will not be cost effective to produce such a large amount of super heated steam. However, excessive steam would lower gasification temperature and consequently degrade product gas quality (Lv et al., 2004).

Effect of S/F ratio has been studied over the range of 1-3 (w/w). From the results it was found that the steam reforming reaction (7) and water gas shift reaction (6) are the main conversion reactions in catalytic steam gasification process that increased the hydrogen production. As shown in Fig. 3 and 6, at lower S/F ratio, CH_4 fraction produced is higher due to lower flow rate of gasifying agent and mild reforming reactions. By enhancement of the quantity of injected steam to the process, the steam methane reforming (7) became dominant and caused an increase in the hydrogen concentration in produced gas. The produced CO contributes in water gas shift reaction (6) and caused an enhancement of the H_2 production. CO_2 was consumed by CO_2 methane reforming (8) and Boudouard reaction (3). These reaction (6, 7 and 8) becoming strongly effective with an increasing S/F ratio and temperature. Eventually, hydrogen

composition is increased to 76.18 vol%, CO and CO_2 compositions decreased to 8.53 vol% and 4.39 vol% respectively.

4. Conclusion

Blending the PE waste with biomass favours enhancement of hydrogen production. Mixing 30 % of PE waste with biomass feedstock led to an increase in H_2 and syngas content to 76.18 % (v/v) and 84.71 % (v/v), respectively. Highest LHV and carbon conversion efficiency are obtained at 15.6 (MJ/Nm^3) and 88.3 wt% respectively. Feedstock conversion and hydrogen production are mostly effected by temperature. Tar conversion during co-gasification of PKS blended with PE waste favoured high temperature. In addition 70 %-80 % decreased in tar content was observed. PE waste feedstock produced higher hydrogen yield approximately 108.8 g H_2/ kg feedstock.

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