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Utilization of Bottom Ash as Catalyst in Biomass Steam Gasification for Hydrogen and Syngas Production

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Coal bottom ash is used as the catalyst for biomass gasification of palm kernel shell using thermogravimetric analyzer coupled with mass spectrometer at operating temperature ranging from 650 °C to 750 °C. The objective of this study is to evaluate the gas composition of the biomass gasification using coal bottom ash as the catalyst. The produced hydrogen gas content is 36.57 vol% at temperature of 700 °C while the gas composition of carbon monoxide, carbon dioxide and methane are 24.73, 1.40 and 37.30 vol % respectively. In addition, it is found that the minerals exist in the coal bottom ash help to reduce the formation of carbon dioxide gas while promote the formation of methane in the product gas.

1. Introduction

Malaysia is the world's second largest palm oil producer behind Indonesia and the largest exporter of the crude palm oil in the world (Sumathi et al., 2008). The palm oil production continues to increase from 2000 to 2014 with total production of 19.67 Mt in 2014 (Awalludin et al., 2015). The rapid growth of palm oil production in Malaysia gives huge profit to the country's economy and also leaves behind various type of biomass residue. Abundant availability of the palm oil biomass in Malaysia has potential as source for clean and efficient fuel production. Biomass is the only renewable source that can be converted into both liquid and gaseous fuel through biological and thermochemical conversion (Saxena et al., 2009). One of the most promising way to convert palm oil waste into energy is through gasification. Generally, gasification is a partial oxidation process to convert biomass into gaseous product mainly hydrogen (H_2), carbon dioxide (CO_2), carbon monoxide (CO) and methane (CH_4) at high temperature using oxidizing agent such as steam, oxygen and air (McKendry., 2002). The quality of these gases depends significantly on the operating parameters, including catalyst. Thus, catalytic gasification is considered as the most promising method for biomass gasification and numerous efforts have been made to develop most effective ways to produce gaseous products from gasification with the presence of steam which the most preferred oxidizing agent compared to oxygen and air (He et al., 2009).

Generally, the catalyst used in biomass gasification can be divided into three main categories which are natural mineral catalyst, alkali metal catalyst and transition metal catalyst (Sutton et al., 2001). The catalyst used in biomass gasification must effectively reduce or remove the tar, reform methane in the case of hydrogen and syngas production, achieve desired gas ratio formation of different fuel and chemicals, have long active life and resist carbon deposition to avoid sintering, be strong enough to maintain it property at high temperature and have capacity for low cost regeneration (Chan et al., 2014). The effective utilization of catalyst depends on the placement of catalyst within the process. Primary catalyst is placed in the first reactor to enhance the gasification process. This type of catalyst enhanced carbonation, combustion, methanation and reforming reaction, and reduced tar formation for effective conversion of organic compounds into gases (Devi et al., 2003). On the other hand, some catalysts are placed in the downstream reactor to enhance the reaction involved in the formation of desired products like hydrocarbon and methane. These are known as secondary catalyst. The operating conditions for primary catalyst are same as gasification. Whereas secondary catalysts are operated at different condition than the gasification operating conditions (Sutton et al., 2001).

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Coal Bottom ash is a type of waste material that is produced, yet discarded continuously from the thermal power plant and it is made from the ash particles that is too heavy to be carried away in the flue gas then fall into the ash hopper at the bottom of the boiler (Meawad et al., 2010). The chemical characterization of the bottom ash shows the presence of metals that have been used as catalyst in biomass gasification such as iron (Fe), calcium (Ca), aluminium (Al) and magnesium (Mg). Previously, coal bottom ash was used as bed material in coal gasification while wood ash was used in coal steam gasification (Baker et al., 1985)..They concluded that wood char can be used to produce methanol synthesis gas, methane – rich gas, hydrogen – rich gas and ammonia synthesis gas directly by steam gasification of biomass while (Xiong et al., 2010) concluded that the usage of coal topping in gasification decreased the yields of tar and gas. There is limited research on the use of coal bottom ash as the catalyst in biomass gasification with PKS as the biomass feedstock. The purpose of this study is to investigate the gasification of PKS utilizing the coal bottom ash as the catalyst in TGA-MS. The optimum results from the experiment are presented and compared with previous research reported for H_2, syngas and CH_4 production.

2. Experimental

2.1 Materials and Sample Preparation

The PKS used in this research as feedstock was collected from the Felcra Nasaruddin Palm Oil Mill Sdn Bhd located in Perak, Malaysia. The PKS was sun dried for 2 to 3 days before it was further dried in an air oven to remove the remaining moisture in the PKS. The PKS then grinded and sieved to particle size of 0.71 mm prior to the characterization test. The proximate and ultimate analysis of the PKS were performed using thermo gravimetric analyzer EXSTAR TG/DTA 6300 (Seiko Instrument Inc) and LECO CHNS-932 elemental analyzer while the heating value of the PKS was determined using IKA C5000 oxygen bomb calorimeter respectively. The proximate, ultimate analysis and heating value of the PKS are shown in Table 1, 2 and 3 respectively.

Table 1: Proximate analysis for PKS in weight % (dry basis)

Sample	Moisture Content	Volatile Matter	Ash Content	Fixed Carbon
PKS	4.69	74.27	1.23	19.81

Table 2: Ultimate analysis for PKS in weight % (dry basis)

Sample	C	H	N	S	O
PKS	47.56	5.68	1.25	4.45	41.05

Table 3: Heating Value of the PKS in HHV (MJ/Kg)

Sample	High Heating Value
PKS	19.05

Table 4: XRF analysis of the coal bottom ash

Compound	SiO	Fe_2O_3	CaO	Al_2O_3	MgO	K_2O_3
Concentration (wt%)	44.11	24.31	13.01	9.21	1.88	1.25

Table 5: Coal bottom ash surface properties

Surface Properties	Value
Mean Pore Size	3.01 nm
Pore Volume (BJH)	0.04 cm^3g^{-1}
BET Surface Area	58.01 m^3g^{-1}

The coal bottom ash used in this research as catalyst was collected from TNB Janamanjung Sdn Bhd, a coal power plant situated in Perak, Malaysia. The bottom ash was grinded to the size of 0.25 mm and subjected to X-Ray fluorescence (XRF) and surface properties test. The XRF characterization was performed using Bruker AXS XRF S4 Pioneer while the surface properties test was performed using Micromeritics ASAP 2020

Accelerated Surface Area and Porosimetry analyzer. The chemical composition of the bottom ash and its surface properties are shown in Table 4 and 5 respectively. Quicklime (CaO) was collected from the Universal Lime Sdn Bhd near Batu Gajah, Perak, Malaysia. CaO is very important material which serves well as an adsorbent for carbon dioxide (CO_2) adsorption in biomass gasification (Yusup et al., 2014).

2.2 Experimental Apparatus and Procedure

The experiment was performed using the thermogravimetric analyzer (TGA), EXSTAR TG/DTA 6300 (Seiko Instrument Inc.) coupled with mass spectrometer (MS), (Pfeiffer Vacuum Thermostar). The TGA was used to gasify the biomass while the MS was used to measure the gaseous product such as H_2, CO, CH_4 and CO_2 during the catalytic gasification process. The process flow diagram of the experimental set up of the TGA-MS is illustrated in Figure 1. About 5 mg of biomass was placed in the ceramic crucible together with the coal bottom ash and adsorbent at predetermined percentage ratio. The experiment starts with injecting nitrogen gas into the system at 100 mL min^{-1} for 20 min at 25 °C to remove any entrapped gas inside the system. The TGA then was heated up from 25 °C to the desired temperature at constant heating rate of 25 °C/min and the temperature is maintained for 30 min. The steam is injected into the system at 110 °C to avoid any occurrence of condensation within the system. The steam is generated by a superheater at 110 °C and injected into the system at a flowrate of 300 μLh^{-1} (Chin et al., 2014).

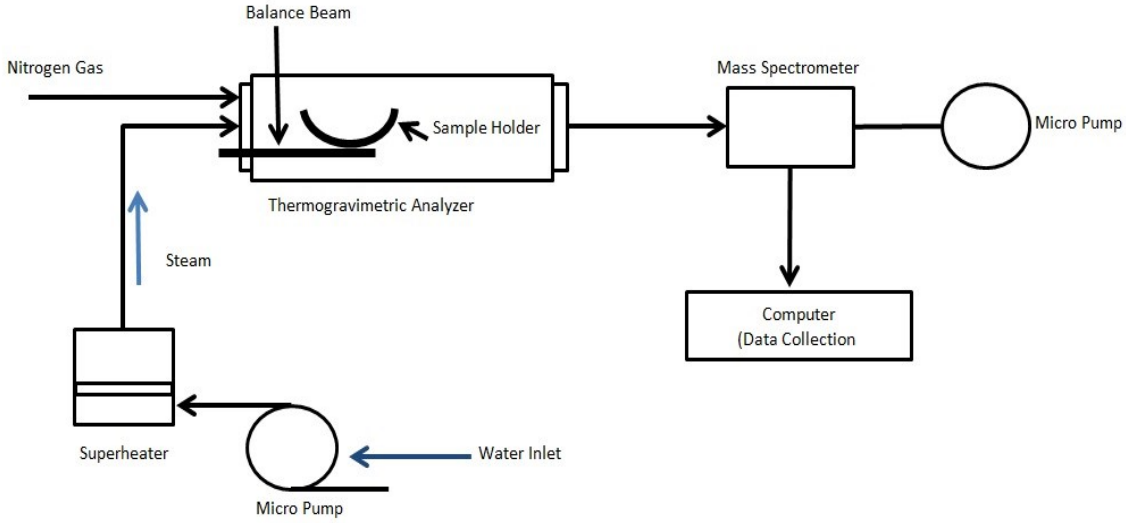

Figure 1: Process flow diagram of TGA-MS experimental set up

3. Result and Discussion

The gaseous products from the experiment were analyzed by MS and were mainly consist of H_2, CO_2, CO and CH_4 on nitrogen free basis as shown in Figure 2. It was observed that the hydrogen content increases from 33.36 vol % at 650 °C to 36.57 vol % at temperature of 700 °C and then decreases to 34.68 vol % at temperature of 750 °C. However, reverse trend was observed for the CH_4 content in the product gas with the highest gas content of CH_4 was at 650 °C with 41.49 vol % then decreased to 37.30 vol % at 700 °C and then increased again to 37.81 vol % at 750 °C respectively. There was almost no changes in CO trend with the amount of CO generated in this study are maintained at 24 vol %. Initially the CO content was 24.10 vol % at 650 °C and increased slightly to 24.73 vol % at 700 ^{o}C and then decreased to 24.24 vol % at temperature of 750 °C. There was no significant effect on the CO_2 content in the product gas with composition range of 0.96 to 3.27 vol % within the temperature studied. This justified that the water gas shift reaction favoured the H_2 formation rather than CO_2 formation as the temperature increased from 650 to 700 °C but slightly decreased at 750 °C respectively.

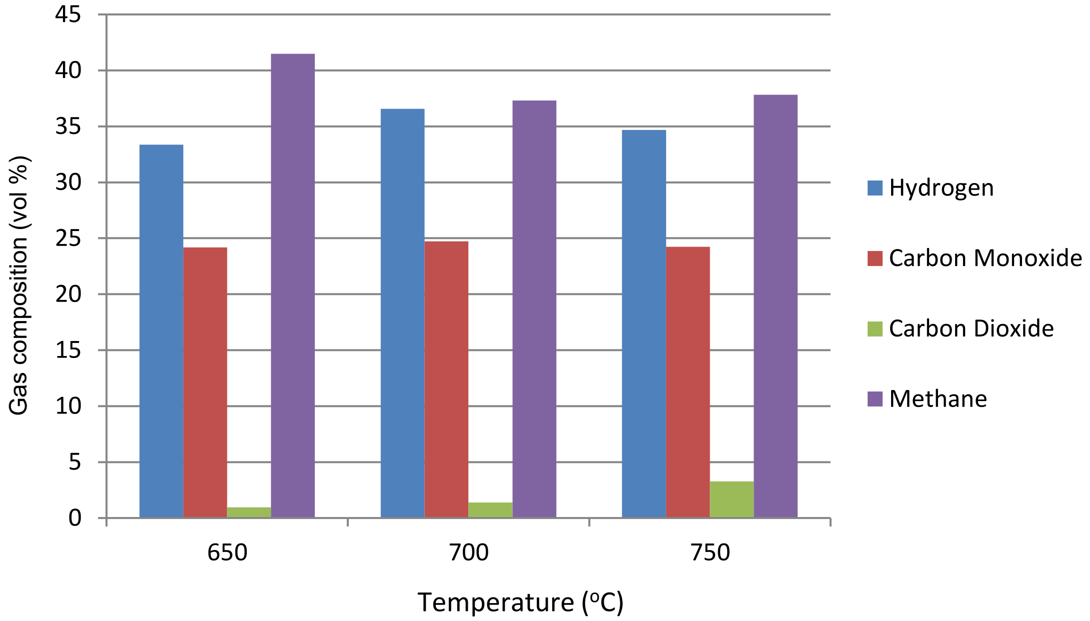

Figure 2: The effect of temperature on the product gas composition

The comparisons of the hydrogen production from previous studies are shown in Figure 3. The highest H_2 production from this study was lower compared with the previous studies but the CH_4 composition was higher. In this study, the H_2 content of the product gas was around 29 to 36 vol %. The highest H_2 content in this study was 36.57 vol % at temperature of 700 °C, particle size of 0.71 mm, biomass to adsorbent ratio of 1.25 and coal to bottom ash percentage of 6 %. Khan and co-worker carried out in-situ catalytic gasification of PKS in pilot scale fluidized bed gasifier (Khan et al., 2014). The optimum parameter yielding the highest H_2 content of 82.11 vol % at 675 °C with the composition of other gas such as CO, and CH_4 were 6.45 and 11.43 vol % respectively. There was no formation of CO_2 at this operating temperature. (Moghadam et al., 2013) carried out research on the catalytic steam gasification of PKS mixture and polyethylene at pilot scale gasification plant. The research was operated at 800 °C, catalyst to feedstock ratio of 10 % and polyethylene to PKS ratio of 0.3. The gas composition of H_2, CO, CO_2 and CH_4 were 70, 7, 5, 18 vol % respectively at the given operating condition. (Pinto et al., 2002) carried out co-gasification of wood pine and polyethylene mixtures in a fluidized bed steam gasifier at temperature of 870 °C and polyethylene to wood pine ratio of 0.1 with the gases content for H_2, CO, CO_2 and CH_4 for this research were 40, 35, 10 and 11 vol % respectively. The highest H_2 composition of 82.11 vol % was reported (Khan et al., 2014). Whereas other researcher and present study has lower H_2 yield as shown in Figure 3. The H_2 composition is lower in non- catalytic gasification process compared to catalytic gasification process. In the present study coal bottom ash is used as a catalyst in similar gasification process used with higher CH_4 composition (Khan et al., 2014).

The coal bottom ash favours CH_4 formation during the catalytic gasification process. The steam methane reforming reaction was not dominant and causing CH_4 formation in the present study to be high. The formation of CH_4 in present study is 37.3 vol %, which is higher compared to previous reported as shown in Figure 3.. The formation of CH_4 in present study is 37.3 vol %, slightly higher compared to the H_2 content while the CO_2 content in present study was relatively low with 1.4 vol % at 700 °C compare with (Moghadam et al., 2013) . The presence of the CaO inside the coal bottom ash helps to capture the CO_2 at lower temperature and similar result also reported in a previous research with the absence of CO_2 in the product gas at relatively low temperature of 675 °C by using CaO as catalyst in PKS steam gasification (Khan et al., 2014). He also suggested that the usage of CaO as catalyst should be operated at temperature below 700 °C to avoid reversed carbonation reaction which will reduce the H_2 production and increase the CO_2 production in the product gas. It confirmed that the coal bottom ash has the catalytic effect in biomass gasification by reducing CO_2 gas and helped to promote the formation of CH_4 in the product gas.

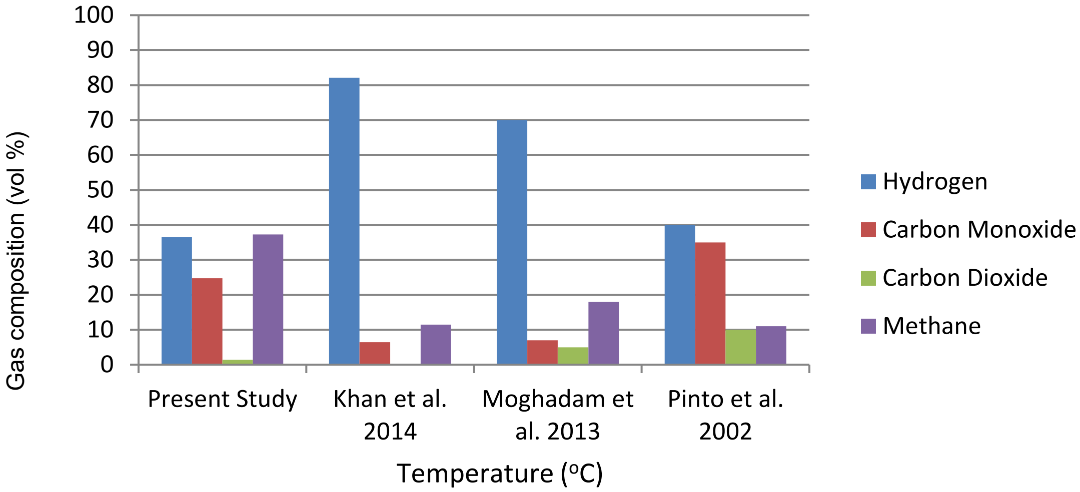

Figure 3: Comparative study of the product gas composition

4. Conclusions

The gasification of the PKS in TGA-MS set up by using coal bottom ash as catalyst was studied at temperature between 650 to 700 °C. From the characterization, coal bottom ash contained minerals that have been used as catalyst such as CaO and Fe_2O_3. It was found that the highest H_2 content obtained at 700 °C is 36.57 vol % while the gas composition of CO, CO_2 and CH_4 are 24.73, 1.4, and 37.3 vol % respectively. The low amount of the CO_2 in the product gas indicated that the presence of CaO in the coal bottom ash can help to capture CO_2 gas while increased the formation of CH_4 gas.

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