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Performance of Water-Leached Coal Bottom Ash as Catalyst in Thermogravimetric Analyser (TGA) Biomass Gasification

David O. Patrick, Suzana Yusup*, Noridah B. Osman, Haslinda Zabiri, Muhammad Shahbaz

Biomass Processing Lab, Centre for Biofuel and Biochemical Research, Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610, Perak, Malaysia.
drsuzana_yusuf@utp.edu.my

The catalytic gasification of palm kernel shell in Thermogravimetric Analyser (TGA) with a mass spectrometer setup using water-leached coal bottom ash (CBA) is presented in this research work. The leaching temperature, time and liquid volume to solid (L/s) ratio were varied in the design of experiment using response surface methodology (RSM). Effects of the interaction between these parameters were plotted in 3D surface plots. Maximum H_2 and syngas contents obtained in the steam gasification at 700 °C were 40.78 vol% and 70.94 vol%. CBA leached for 6.5 h at 66.20 °C and L/s ratio of 4 with 81.26 Å pore width, 0.004 cm^2/g pore volume and 1.90 m^2/g BET surface area produced the highest H_2 content while that treated for 6.5 h at 45 °C and L/s ratio of 2.59 with 50.01 Å pore width, 0.004 cm^2/g pore volume and 3.0583 m^2/g BET surface area produced the highest syngas content. The CO_2 content of the gas produced was less than 2 vol%. L/s ratio is the most influential of the leaching parameters affecting H_2 and syngas production.

1. Introduction

The increasing global demand for energy has necessitated the search for economically viable alternative sources that are environmentally friendly and energy intensive. Biomass is one of the most abundant energy sources with a potential for significant contribution to the energy requirement around the globe despite its low contribution of about 10 % to the world's current energy supply of approximately 45 EJ/y (Giron, 2016).

Catalytic gasification involves thermal conversion of carbonaceous substances into various gaseous products, mainly H_2, CO, CO_2 and CH_4 in an environment with controlled supply of air, oxygen, steam or CO_2 and in the presence of catalyst. The product commonly called syngas consists of H_2 and CO with some quantity of CO_2, CH_4 and negligible tar. Catalytic gasification of biomass is an efficient way of producing clean fuel (Nanda et al., 2016). Catalysts used in gasification affect the composition of the products consequently improving the quality of fuels produced since it determines the target product (Herman et al., 2016).

Nickel, dolomite and alkaline metals are commonly used as catalysts in biomass gasification (Khan et al., 2014). Recent researches concentrated on using low-cost catalyst in gasification of biomass (Shahbaz et al., 2016a). Biomass ash and char have been used by several researchers to catalyse gasification (Shen et al., 2014). Xiong et al. (2010) reported that coal boiler ash used as bed material in gasification reduced tar yield due to the presence of the oxides of aluminium, calcium, iron and magnesium which are effective gasification catalysts. Fly and bottom ashes from gasification have been used as sources of CaO catalyst in biodiesel production (Maneerung et al., 2015). Coal bottom ash (CBA) is reported to have been used in combination with CaO in a two-stage pilot fluidised bed gasifier with good results for hydrogen (Shahbaz et al., 2016a) and methane production (Shahbaz et al., 2016b). Shahbaz et al. (2017) concluded from a review that coal bottom ash has the potential for catalytic application in biomass steam gasification considering its cost, composition and physical properties.

Coal bottom ash (CBA) contains oxides which are active catalysts in gasification (Long et al., 2012). X-ray Fluorescence (XRF) analysis of bottom ash obtained from TNB Janamanjung Sdn Bhd power plant, Selangor, Malaysia showed significant amount of oxides like CaO, Al_2O_3, Fe_2O_3, MgO and K_2O_3 (Shahbaz et al., 2016b).

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It has potential for used as gasification catalyst (Herman et al., 2016). Ash used in gasification have shown problems of agglomeration at high temperatures (Llorente et al., 2006), consequently it needs to be treated to improve its performance. Researchers have used various method to control or reduce the extent of agglomeration of ash in gasification (Lin et al., 2003). Lu et al. (2015) observed that washed coal ash used in coal gasification effectively raised the agglomeration temperature. This was due to more than 50 % in K_2O content of the ash. CaO and Fe_2O_3 also reduced by about 50 % but SiO_2 and Al_2O_3 contents, pore size and surface area were higher. The process also resulted to 98.7 % carbon conversion (Lu et al., 2015). Pre-treatment of CBA could significantly improve its catalytic properties. So far only untreated CBA have been used in biomass gasification. There are no reports on the influence of ash treatment parameters on the composition gaseous products. This work is aimed at investigating the production of gaseous fuel from palm kernel shell gasification in TGA, using treated coal bottom ash as catalyst. The effects of CBA treatment parameters (liquid to solid ratio, leaching temperature and time) on the composition of gas were also studied using response surface methodology (RSM).

2. Methodology

2.1 Materials

CBA obtained from TNB Janamanjung Sdn Bhd power plant, Manjung, Malaysia was used as catalyst in this study. The sample was dried in an oven at 105 °C for 24 h to reduce its moisture content.

Palm kernel shell (PKS) obtained from Kilang Sawit Felcra Nasarudin Sdn. Bhd., Malaysia was used for the gasification. The sample was oven dried for 24 h at 105 °C to reduce the moisture content. This was milled in a ball mill and sieved to obtain 0.5 – 0.75 mm particle size range which was used in the experiment. The choice of 0.5 – 0.75 particle size was based on earlier optimized results (Shahbaz et al., 2016a).

2.2 Design of experiment

Experimental design was based on response surface methodology (RSM) in the Design Expert 8® (Shahbaz et al., 2016a). Three level central composite design (CCD) was selected to develop a relationship between input variables and the desired responses, while quadratic model was used for the model development. A response surface plot was developed to analyse the interaction between the input variables and the responses. The CBA leaching parameters, volume of water/CBA mass (L/s) ration (A), leaching time (B) and leaching temperature were specified as the input variables while the various percentages of product gas components (vol% H_2 and vol% syngas) were specified as the responses to be observed. The ranges for A, B and C were 3 – 5 mL/mg, 3 – 10 h and 30 – 60 °C. Each factor was varied over 5 levels to obtain 15 experimental runs as shown in Table 1. The array of experiments has 5 centre point runs and, 10 non-centre points. The factorial and axial point were repeated once each, to reduce experimental error.

2.3 Leaching of coal bottom ash

100 g samples of CBA were mixed with an equivalent amount of deionized water based on the L/s ration in the experimental design. The mixtures were then heated to temperatures ranging from 23.75 – 66.20 °C and stirred for 1.55 – 11.45 h while maintaining the temperature based on the experimental design. The leached coal was filtered, and oven dried at 105 °C for 24 h. It was weighed and heated until constant weight was achieved.

2.4 Surface properties determination

The pore size, pore volume and surface area of the best performing samples for H_2 and syngas production were studied by the Brunauer-Emmett-Taylor (BET) technique in a Physisorption Analyzer Micromeritics ASAP 2020.

2.5 TGA gasification of palm kernel shell with coal bottom ash

Thermogravimetric analyzer, Exstar TG/DTA 3200 fitted with a mini steam generation setup and a mass spectrometer/ gas analysis system (ThermoStar™ GSD 320 T1) was used to carry out the gasification of the palm kernel shell using the previously treated coal bottom ash. Detailed description and schematic diagram of the setup were given in earlier work (Shahbaz et al., 2016a). A constant mass of 10 mg of palm kernel shell was used throughout the experiment. Inert carrier gas (100 mL/min N_2) and steam (350 µL/min) rates were maintained throughout. 7 wt% coal bottom ash and 700 °C temperature were chosen for all the runs base on optimum obtained in previous work using untreated coal ash (Shahbaz et al., 2016a). The biomass sample was heated and maintained at 50 °C for 20 min while being purged with N_2 gas to remove all entrapped gas from the system. It was then heated at a rate of 25 °C/min and kept constant for 30 min at 700 °C to ensure complete gasification. Steam was injected to the system at 500 °C.

Table 1: Experimental design and results

Run No.	A: Volume/ Mass (L/s) Ratio (mL/mg)	B: Time (h)	C: Temperature (ºC)	Vol% H_2	Vol% Syngas
1.00	4.00	6.50	45.00	30.56	69.11
2.00	5.41	6.50	45.00	39.84	66.76
3.00	4.00	6.50	45.00	30.56	69.10
4.00	2.59	6.50	45.00	29.09	70.94
5.00	5.00	10.00	30.00	37.13	65.27
6.00	4.00	6.50	45.00	30.56	69.09
7.00	4.00	6.50	45.00	30.55	69.14
8.00	5.00	3.00	60.00	27.56	69.42
9.00	3.00	3.00	30.00	38.45	65.96
10.00	3.00	10.00	60.00	40.50	67.34
11.00	4.00	1.55	45.00	39.76	66.10
12.00	4.00	6.50	45.00	30.56	69.02
13.00	4.00	11.45	45.00	40.31	67.23
14.00	4.00	6.50	23.80	40.61	67.61
15.00	4.00	6.50	66.20	40.78	65.62

3. Results and discussion

3.1 Parametric study

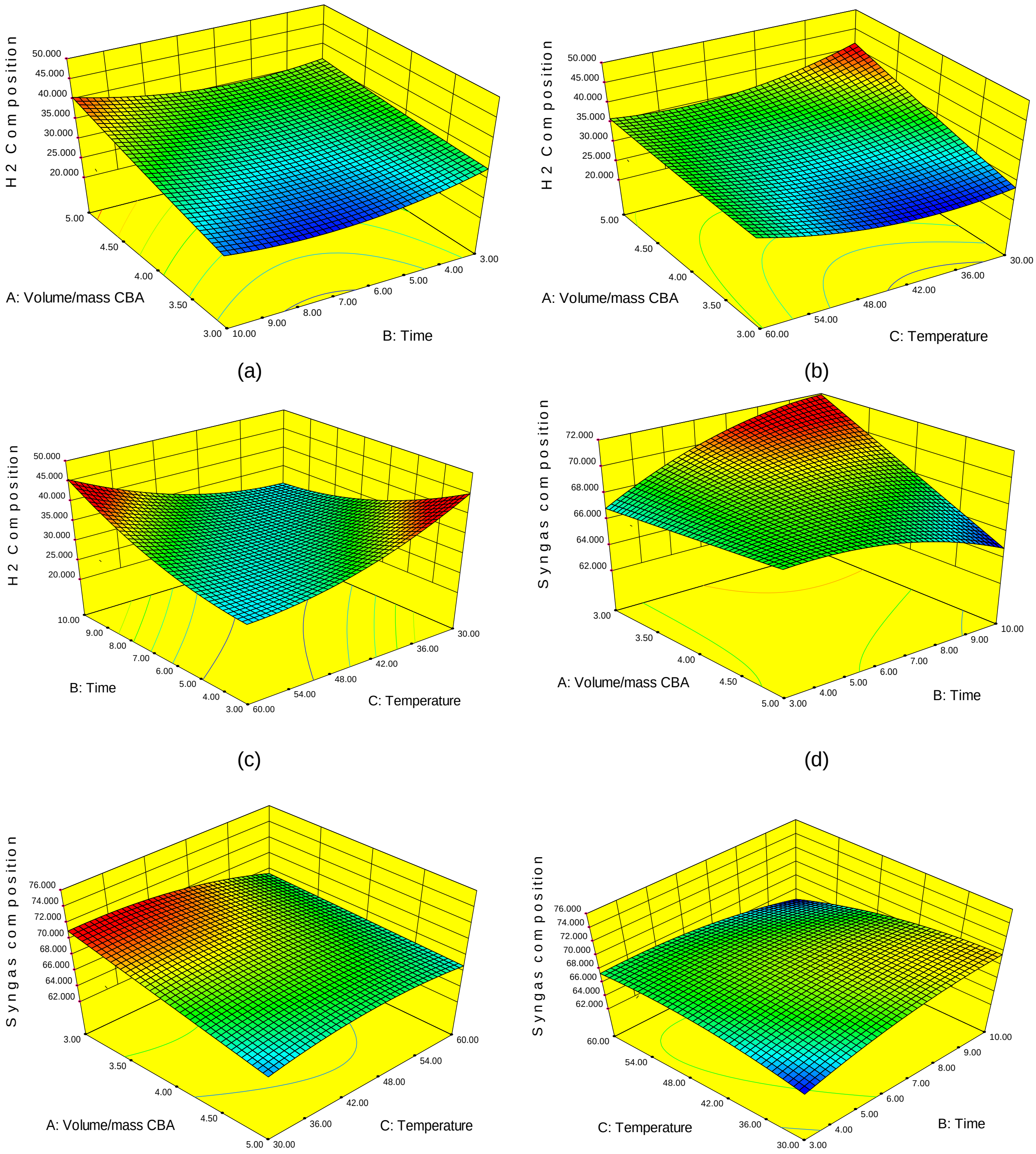
The effect of CBA leaching parameters and the effect of their interaction on gasification products is shown on the 3D surface plot in Figure 1. Figure 1a, b and c give the effect of interaction of leaching time, L/s ratio and temperature on H_2 composition while Figures 1d, e and f give their effect on syngas composition.

Figure 1a shows that, an increase in L/s ratio increased the H_2, when temperature is at the midpoint. At this temperature, the surface properties improved (Table 2), increasing the heat and mass transfer and resulting in enhanced ash reactivity (Shahbaz et al., 2016a). Fe_2O_3 (which increases H_2 composition (Shen et al., 2014)) and other alkali and alkali earth metal which improve catalytic activities of the ash (Rizkiana et al., 2014) are significantly retained in the ash because of the low leaching temperature (Lu et al., 2015). This in turn increased the H_2 composition. Increase in leaching time increased H_2 composition at high L/s ratio, but reduced it at lower L/s ratio. Figure 1b gives the relation between L/s ratio and temperature at the mid value of leaching time. It is observed that low temperature and high L/s ratio gave the maximum H_2 composition in this case. At high L/s ratio, increase in temperature reduced the H_2 composition, but at lower L/s ratio, higher temperature favoured increase in H_2 composition. High L/s ratio and temperature combination reduce the alkali and alkali earth metal in the ash substantially (Lu et al., 2015), thereby lowering the H_2 composition due to low Fe content. The interaction of time and temperature at the midpoint of L/s ratio is presented in Figure 1c. The maximum H_2 composition is obtained at the lowest temperature and time, and also at the highest temperature and time. H_2 composition reduces with increase in temperature at lower leaching time but increases with increase in temperature at higher leaching time. The maximum H_2 composition from the model (approximately 45.20 vol%) is obtained using sample treated at 60 °C for 3 hours with L/s ratio of 4, while the actual (40.78 vol%) from experimental work was obtained using ash treated at 66.20 °C for 6.5 h, with L/s ratio of 4 (properties of the ashes are given in Table 2). These values are higher than H_2 yield obtained by Wan Ab Karim Ghani et al. (2009) (31 mol%) using silica beads bed material and comparable to the composition of H_2 (47.41 vol% at 690 °C) obtained by Khan et al. (2011) for palm kernel shell TGA gasification using Fe-Ni bimetallic catalyst on zeolite β support.

Table 2: Surface properties of leached coal bottom ash with highest H_2 and syngas composition.

Parameter	Run 15	Run 9	Run 4	Raw CBA
Pore Width (Å)	81.23	45.05	50.01	33.66
Pore Volume (cm^3/g)	0.004	0.005	0.004	0.020
BET Surface Area (m^2/g)	1.90	4.51	3.06	24.44

The effect of interaction of L/s ratio and time on syngas composition is shown in Figure 1d. The maximum syngas composition is obtained at the highest L/s ratio and least time. The lowest syngas composition was obtained at the highest L/s ratio and time. Syngas composition increased with increase in L/s ratio. At low L/s, it increased with leaching time, but the trend is reversed at higher L/s ratio.



(a) (b) (c) (d) (e) (f)

Figure 1: Effect of CBA leaching parameters interaction on H_2 (a-c) and syngas (d-f) production.

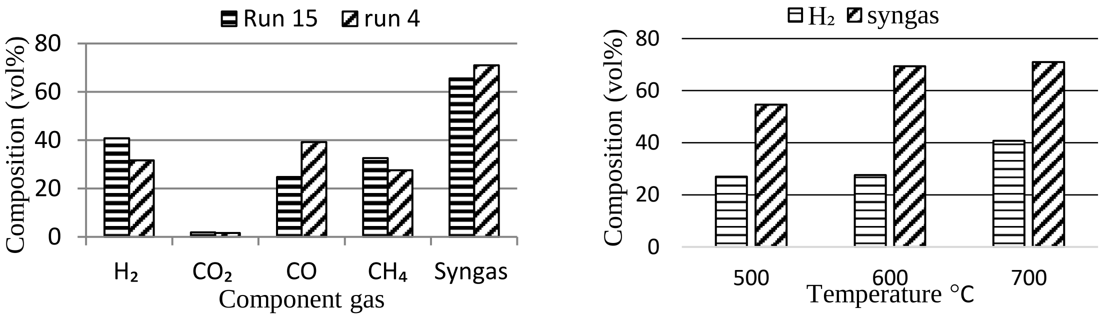
Figure 1e shows the interaction of L/s ratio and temperature for syngas production. Lower temperature and L/s values favoured high syngas composition. The least syngas composition is obtained at the lowest temperature and the highest L/s ratio. The effect of interaction of temperature and leaching time at fixed L/s ratio on syngas composition is depicted in Figures 1f. Maximum syngas composition is obtained at the least temperature and highest leaching time, while a combination of lowest temperature and time, and highest temperature and time gave the least syngas composition. The maximum syngas composition from the model (72 vol%) is obtained using sample treated at 45 °C for 10 h and L/s ratio of 3, while the actual value (70.94 vol%) from experimental work was obtained using ash treated at 45 °C for 6.5 h and L/s ratio of 2.59 (properties of the ash are given in Table 2). The higher gas yield from this sample could be attributed to the higher pore width which allows better mass and heat transfer, thus increasing gasification rate (Sanchez-Silva et al., 2013).

3.2 Gaseous product distribution

The gaseous product distribution for TGA gasification (at 700 °C) of palm kernel shell, using coal ash from runs 4 and 15 is shown in Figure 2a. It shows the highest compositions of H_2 and syngas obtained. In both cases, the composition of CH_4 is below 35 vol% and that of CO_2 is less than 2 vol%. The CO_2 content is far lower than the least CO_2 content (about 25 vol%) obtained in a similar work using Fe-Ni bimetallic catalyst (Khan et al., 2011). The leached coal bottom ash has the potential to reduce the cost of CO_2 removal in gasification due to the presence of CaO which adsorbs the CO_2.

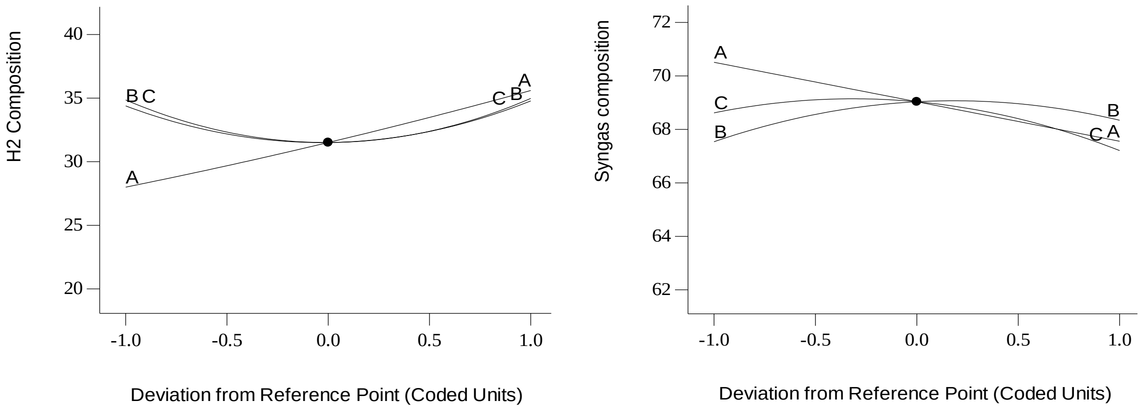
H_2 and syngas profiles for gasification using treated coal ash are shown in Figure 2b. H_2 increased in the product gas from 26.96 vol% at 500 °C to 40.78 vol% at 700 °C. There was a rise in syngas composition from 54.58 vol% at 500 °C to 70.94 vol% at 700 °C. These closely agree with the finding of Shahbaz et al. (2016a) that the optimum temperature for steam gasification of palm shell using coal bottom ash is 692 °C.

Perturbation charts (obtained using Design Expert® software) for H_2 and syngas shown in Figures 3a and b, give the impact of variation of the leaching parameters on the composition of the gases. In Figure 3a, (for H_2) L/s ratio (A) has the highest influence followed by temperature (C), then time (B). For syngas (Figure 3b), L/s ratio (A) was followed by time (B), then temperature (C) in influence ranking.



(a) *(b)*

Figure 2: (a) Gaseous product distribution for the TGA gasification (at 700 °C). (b) Profile of gas production for H_2 (with run 15) and syngas with (run 4).



(a) *(b)*

Figure 3: Perturbation chart for (a) H_2 gas and (b) syngas compositions.

4. Conclusions

The effect of CBA leaching temperature, time and L/s ratio, and their interactions on the composition of H_2 and syngas produced in TGA gasification of palm kernel shell is highlighted in this studied. Treated CBA produced 40.78 vol% H_2 when used as catalyst in TGA gasification of palm kernel shell. The H_2 composition is predicted to increase to a maximum of 45.20 vol%. The highest syngas composition of 70.94 vol% was obtained using

CBA treated at 45 °C for 6.5 h with L/s ratio of 2.59. Model prediction showed an increase to 72 vol% syngas. A low CO_2 composition of less than 2 vol% is obtained in the process. The results suggest that leached CBA could be used successfully for fuel production in biomass gasification.

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