



INFLUENCE OF COAL BOTTOM ASH TREATMENT PARAMETERS ON METHANE AND CARBON DIOXIDE YIELD FROM PALM KERNEL SHELL GASIFICATION



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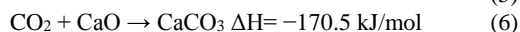
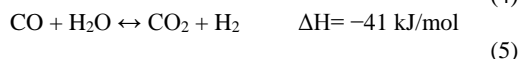
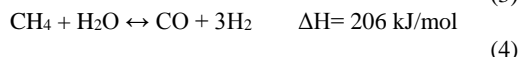
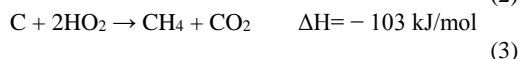
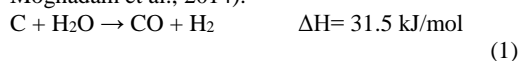
Abstract:

Utilization of coal bottom ash (CBA) as catalyst in biomass gasification is an effective and promising route that will provide alternative ways for utilizing the waste and reducing the cost of gasification process. This study optimised the leaching of CBA in water and performed gasification of palm kernel shell with the treated waste. Response surface methodology (RSM) of central composite design (CDD) was used to design the leaching experiment and to vary the ratio of volume of water to mass of CBA (L/s ratio), leaching time and temperature. This was applied to determine the influence of the parameters on the physicochemical properties of the ash and the yield of CH₄ and CO₂ in steam gasification of palm kernel shell in a thermogravimetric analyser setup incorporated with mass spectrometer and a steam generator (TG-MS). Field Emission Scanning Microscopy/Energy Dispersive X-ray (FESEM-EDX) micrograph of the ash samples show that the pore of the treated ash are clearer and free of debris which may clog the pores and cause fusion and agglomeration easily. Chemical analysis from Energy Dispersive X-ray (EDX) spectra indicated a fall in carbon content (38.76 to 20.60 wt%) and a rise in Fe, Ca, and Al increased from 6.78 to 10.63 wt%, 6.92 to 15.03 wt% and 2.37 to 5.21 wt%, respectively. The increase in metal content increased the catalytic potential of the treated ash. Response surface 3D plots were used to analyse the results. The yields of CH₄ and CO₂ in the gasification process carried out in a thermogravimetric analyser attached to a mass spectrometer and a steam generation setup are as low as 27.5 and 0.94 vol% with an optimum of 29.65 ± 0.06 and 1.02 ± 0.01 vol%, respectively. Syngas yield at optimum condition is 69.35 ± 0.05 vol%. This was obtained using L/s ratio 3, 10 hours leaching time and 56°C temperature as optimized CBA leaching parameters. The most influential variables on CH₄ and CO₂ yields as indicated are L/s ratio and temperature, respectively. Result of the study shows that water-leached CBA can be used effectively in gasification and it reduces the yield of CH₄ and CO₂ thus potentially increasing syngas (H₂ and CO).

Keywords: Coal bottom ash; Treatment; Gasification; Palm kernel shell; TGA

Introduction

Catalytic gasification is one of the most effective ways of converting biomass waste to energy-dense gases with minimal environmental pollution. This process is the thermochemical conversion of carbonaceous substances to gaseous fuel (Khan *et al.*, 2014c) at high temperature (above 600°C) in the presence of catalysts and gasifying agent (oxygen, air, steam, carbon dioxide or a combination of any) (Dai *et al.*, 2015, Shahbaz *et al.*, 2017). Major gasification products include H₂, CO, CH₄, CO₂ and tar. Gasification is represented by the following reactions when CO₂ sorption by CaO is involved (Khan *et al.*, 2014c, Moghadam *et al.*, 2014).



The use of catalyst and adsorbents increase H₂ concentration to over 60 vol% while reducing CO₂ and CH₄ contents (Khan *et al.*, 2014c). Sun *et al.* (2013) gasified corn stalk using industrial sand mixed with silica gel, zeolite and activated alumina as bed material and catalyst. They obtained 36.06 vol% H₂, and reduced CO₂ (26.66 to 19.15 vol%) and CH₄ in the process. When CaO was used with pure Ni powder as catalyst in a pilot scale fluidised bed gasifier at 675°C, the gas produced contained 82.11 vol% H₂, less than 10 vol% CH₄ and no trace of CO₂ (Khan *et al.*, 2014b). A similar study (Inayat *et al.*, 2010) showed an

increase of H₂ from 0.65 to 0.85 mole fraction and a decrease of CO₂ from 0.95 to 0.32 mole fraction for kinetic modelling of steam biomass gasification without CaO and with CaO, respectively. Al-Rahbi and Williams (Al-Rahbi and Williams, 2017) produced hydrogen-rich syngas (over 50 vol%) with low CH₄ and close to 20 vol% CO₂ from biomass gasification using HCl demineralised tyre char. They concluded that ash minerals (metal in tyre char) have significant effect on water gas shift reaction (equations 4 and 5). This was evident in the high H₂ and CO₂ content of the gas produced. Shahbaz *et al.* (Shahbaz *et al.*, 2016b) pointed out from their study that high yield of methane produced in steam catalytic gasification of biomass with coal bottom ash was due to limited steam supply and, Fe and Mg in the coal ash.

Coal bottom ash contains metal oxides including CaO (Shahbaz *et al.*, 2016a) which is a good CO₂ adsorbent in gasification (Khan *et al.*, 2014a). The presence of Al, Fe, Mg, CaO and several other metal oxides make coal bottom ash an attractive gasification catalyst like many other ashes. Various ashes and chars have been used successfully in gasification with good results. Rice husk ash (Shen *et al.*) and char (Shen, 2015) used as catalyst support achieved significant tar conversion (Shen *et al.*, 2014). Coal boiler ash was used to decrease tar yield in coal topping gasification (Xiong *et al.*, 2010). Ashes from brown sea weed, eel grass and rice straw were also used to gasify low rank coal (Rizkiana *et al.*, 2014). Coal bottom ash used with adequate amount of steam reduced the production of CH₄ by encouraging the water gas shift reaction (Shahbaz *et al.*, 2016b). Temperatures between 800 and 850°C favour CH₄ production by enhancing process of CO and CO₂ hydrogenation to CH₄ (Król and Poskrobko, 2016). On the other hand, coal gasification at 700°C using Ca(OH)₂

catalyst generated syngas with 10.1 vol% CH₄ (Chen *et al.*, 2017).

Water-washed ash added in catalytic gasification of coal in pressurised fluidized bed gasifier effectively prevented agglomeration in the process (Lu *et al.*, 2015). It was observed in the study that reduction in K₂CO₃ by leaching significantly reduced the fusion of the coal ash hence reducing agglomeration of ash. On heating, potassium combines with silica to form low-melting temperature silica compound (Zevenhoven-Onderwater *et al.*, 2001) hence causing agglomeration. This could be eliminated or reduced by leaching (Arvelakis *et al.*, 2002).

The present research work examines the influence of various coal bottom ash leaching parameters (liquid/solid ratio, time and temperature) on CH₄ and CO₂ composition of syngas in TGA gasification using water-leached ash as catalyst with a view to reducing them and maximizing H₂ and CO content. Response surface methodology was used to show the effect of these variables and their interaction on the gas composition.

Methodology

Materials

Coal bottom ash (CBA) waste sample was collected from TNB Janamanjung Sdn Bhd power plant, Manjung, Malaysia. The sample was leached in water in order to modify its properties for catalytic application. The CBA sample was oven dried for 24 hours at 105°C to reduce its moisture content.

Palm kernel shell (PKS) for the gasification process was collected from Kilang Sawit Felcra Nasarudin Sdn. Bhd., Bota, Malaysia. The sample was sun dried and then further dried in an oven adjusted to 105°C for 24 hours to ensure the complete removal of moisture. The dried sample was crushed then further milled using a ball mill. CBA particles with size ranging from 0.5-0.75 mm was recovered by sieving and used in the experiment. The particle size range chosen was based on an optimised result from an earlier study (Shahbaz *et al.*, 2016a).

Coal Bottom Ash Characterisation

The raw and water-leached coal bottom ash samples were characterised to determine their physico-chemical properties. The characterisation includes field emission scanning electron microscopy and physisorption analysis.

Field emission scanning electron microscopy and energy dispersion x-ray analysis (FESEM/EDX)

The FESEM micrographs of the samples were obtained for the samples at a magnification of 5000X using a Zeiss Supra 55 VP instrument. FESEM/EDX spectra were also obtained for each of the samples to determine their chemical compositions.

Physisorption analysis

The physisorption analysis of the ash samples was done using Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry. The pore size and surface area were determined by Branauer-Emmett-Taylor (BET) method while the pore volume was measured using Barret-Joyner-Halenda (BJH) method (Patrick *et al.*, 2017).

Design of Experiment

Response surface methodology (RSM) was used for the experimental design in the Design Expert 8® software. Three level central composite design (CCD) was chosen to develop a relationship between inputs and desired responses. A 3D response surface plot was developed to analyse the interaction between the input variables and responses thereby finding the optimum values for the variables and desired responses. The CBA leaching parameters, volume of water/mass of CBA (L/s) ratio (A), leaching time (B) and temperature were inputted as the variables while the various percentages of product gas components (vol% CH₄ and vol% CO₂) were specified as the response variables to be observed. The ranges of variable chosen for A, B and C were 3 – 5 mL/mg, 3 – 10 hours and 30 – 60°C, respectively were adopted from an earlier study (Patrick *et al.*, 2017). Details of the design is depicted in Table 1.

Leaching of Coal Bottom Ash

Various 100 g samples of CBA were mixed with appropriate quantities of deionized water based on the L/s ratio in the experimental design. The mixtures were heated to temperatures ranging from 23.75 – 66.20°C and simultaneously stirred for 1.55 – 11.45 hours while maintaining the temperature. The leached CBA samples were filtered and dried at 105°C for 24 hours in an oven. The heating and weighing process were repeated until constant masses were attained to ensure that drying was completed. The procedure was adopted from an earlier study (Patrick *et al.*, 2017).

Table 1: Experimental design for leaching of CBA

Run No.	A: Liquid/Solid (L/S) Ratio (mL/mg)	B: Time (h)	C: Temperature (°C)
1	4.00	6.50	45.00
2	5.41	6.50	45.00
3	4.00	6.50	45.00
4	2.59	6.50	45.00
5	5.00	10.00	30.00
6	4.00	6.50	45.00
7	4.00	6.50	45.00
8	5.00	3.00	60.00
9	3.00	3.00	30.00
10	3.00	10.00	60.00
11	4.00	1.55	45.00
12	4.00	6.50	45.00
13	4.00	11.45	45.00
14	4.00	6.50	23.80
15	4.00	6.50	66.20

Gasification of Palm Kernel Shell with Coal Bottom Ash

Thermogravimetric analyser, 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 milled palm kernel shell using the treated CBA. Detailed description and schematic diagram of the setup is given in an earlier work (Shahbaz *et al.*, 2016a). 10 mg samples containing 7 wt% water-leached CBA in palm kernel shell were used throughout the experiment. Nitrogen used as inert carrier gas was supplied at 100 mL/min and steam was supplied at 350 µL/min. The experiments were carried out at 700°C. The gasification parameters were selected based on optimum value obtained in previous work using untreated coal ash (Shahbaz *et al.*, 2016a). The biomass-CBA mixture was heated to 50°C and maintained at the temperature for 20 min to remove all entrapped gases from the sample. It was then heated at a rate of 25 °C/min until the 700°C temperature was attained. This temperature was maintained for 30 mins to ensure complete gasification.

Steam supply to the system was initiated when the temperature reached 500°C.

Results and Discussion

Physico-chemical properties

The FESEM micrograph in Figures 1 gives the image of the untreated and leached ash samples from Run No. 4 and 15. The untreated sample shows surface pores with smaller particles clogging them (Figure 1a). On the other hand, Figures 1b and c show that the leached samples have clearer and wider pores with less particle clogging. No small-scattered particles are seen in this case. The leaching process opened up blocked pores. The result shows close agreement with morphological properties of the ashes presented in an earlier study (Herman *et al.*, 2016). The pore width of the samples generally increased after leaching. Sample obtained from Run No. 15 has the highest pore width (81.23 Å) follow by sample from Run No. 15 (50.01 Å). The untreated sample has the least value of 33.66 Å.

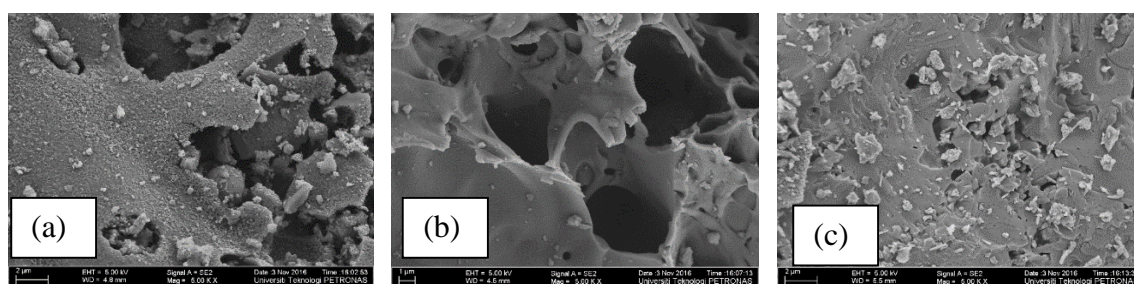


Figure 1: FESEM micrograph of CBA samples (a) untreated, (b) water-leached CBA from Run No. 9 and (c) water-leached CBA from Run No. 15.

Results of EDX analysis of three different points on both the untreated and leached ash samples are shown in Tables 2 and 3. The detailed numerical values of the chemical composition of the spectral points are given. The untreated sample has large amount of carbon in two of the points analysed. Carbon content of the untreated sample is higher than that for the treated sample. Spectra analysis obtained

for the leached sample indicates a significant increase in metal content. Si and Fe are the most available metals on the leached sample with up to 36.21 and 16.47 wt%, respectively on one of the mapping sites. Invariably, leaching improves the metal percentage content of the CBA.

Table 2: EDX result for different points on the raw ash

Element	Spectrum 1		Spectrum 2		Spectrum 3		Average	
	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
O K	23.67	20.07	14.26	15.34	49.61	64.17	29.18	33.19
Na K	-	-	-	-	0.51	0.46	0.17	0.15
Mg K	1.26	0.70	-	-	0.35	0.30	0.54	0.33
Al K	0.86	0.43	0.97	0.62	5.28	4.05	2.37	1.70
Si K	1.63	0.79	5.43	3.33	38.26	28.19	15.11	10.77
Ca K	2.67	0.90	13.93	5.98	4.15	2.14	6.92	3.01
Fe K	1.63	0.39	16.89	5.21	1.83	0.68	6.78	2.09
C K	67.77	76.52	48.51	69.52	-	-	38.76	48.68
Cl K	0.50	0.19	-	-	-	-	0.17	0.06
Totals	100.00		100.00		100.00		100.00	

Table 3; EDX results for different points on the ash from Run No. 4

Element	Spectrum 1		Spectrum 2		Spectrum 3		Average	
	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
O K	-	-	48.22	65.12	29.16	46.08	25.79	37.07
Na K	-	-	0.63	0.59	-	-	0.21	0.20
Mg K	-	-	2.68	2.38	1.23	1.28	1.30	1.22
Al K	-	-	9.13	7.31	6.50	6.09	5.21	4.47
Si K	1.43	0.84	21.18	16.30	36.21	32.59	19.61	16.58
K K	-	-	1.36	0.75	1.76	1.14	1.04	0.63
Ca K	30.83	12.67	6.52	3.52	7.73	4.88	15.03	7.02
Ti K	-	-	0.81	0.36	0.93	0.49	0.58	0.28
Fe K	5.96	1.76	9.46	3.66	16.47	7.45	10.63	4.29
C K	61.79	84.74	-	-	-	-	20.60	28.25
Totals	100.00		100.00		100.00		100.00	

Statistical analysis

The analysis of variance (ANOVA) of the effect of CBA leaching parameters and their interactions on the CH₄ and CO₂ content of the gas produced are shown in Tables 4 and 5, respectively. The p-value for CH₄ (0.0029) and CO₂ (0.0494) yields indicate that the models generated are significant, thus they are valid for the analysis of the system within the range of the leaching parameters used. The F value gives an idea of the relative extent of influence of the leaching parameters on the yield of CH₄ and CO₂ in the process. The order of influence of the variables on CH₄ and CO₂ production is L/s ratio > time > temperature and temperature > L/s ratio > time, respectively as indicated by

their F values. This is also confirmed by the perturbation curves depicted in Figures 2a and b. The steepness of the plot indicates the comparative influence of each of the variables. The R² for both CH₄ and CO₂ production (0.9690 and 0.8962, respectively) approach unity, showing close agreement with ideal model. The close agreement of the adj-R² values (0.9132 and 0.7095, respectively) with their respective R² values. This indicates that there is a close relationship between the interacting parameters and the responses. Second order polynomial regression models developed in terms of coded factors are given in Equations 7 and 8 for CH₄ and CO₂ yields, respectively.

Table 4: ANOVA for CH₄ production.

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F
Model	61.57	9	6.84	17.37	0.0029
A- L/s ratio	9.86	1	9.86	25.04	0.0041
B-Time	0.73	1	0.73	1.86	0.2306
C-Temperature	0.66	1	0.66	1.66	0.2535
AB	6.39	1	6.39	16.22	0.0100
AC	2.35	1	2.35	5.97	0.0585
BC	8.85	1	8.85	22.47	0.0051
A ²	1.21	1	1.21	3.07	0.1400
B ²	22.76	1	22.76	57.80	0.0006
C ²	17.81	1	17.81	45.24	0.0011
Residual	1.97	5	0.39		
Lack of Fit	1.97	1	1.97		
R ²	0.9690				
Adj. R ²	0.9132				

Table 5: ANOVA for CO₂ production.

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F
Model	5.64	9	0.63	4.80	0.0494
A- L/s ratio	0.035	1	0.035	0.27	0.6258
B-Time	2.849E-003	1	2.849E-003	0.022	0.8883
C-Temperature	0.36	1	0.36	2.75	0.1580
AB	0.18	1	0.18	1.36	0.2962
AC	1.687E-004	1	1.687E-004	1.293E-003	0.9727
BC	0.16	1	0.16	1.20	0.3237
A ²	1.20	1	1.20	9.23	0.0288
B ²	3.00	1	3.00	22.98	0.0049
C ²	1.23	1	1.23	9.41	0.0279
Residual	0.65	5	0.13		
Lack of Fit	0.65	1	0.65		
R ²	0.8962				
Adjusted R ²	0.7095				

$$\text{CH}_4 \text{ Yield} = 28.5 + 1.57A - 0.43B + 0.4C + 1.79AB - 1.08AC + 2.10BC + 0.4A^2 + 1.72B^2 + 1.52C^2 \quad (7)$$

$$\text{CO}_2 \text{ Yield} = 2.47 - 0.094A + 0.027B + 0.3C + 0.3AB - 9.18 \times 10^{-3}AC - 0.28BC - 0.4A^2 - 0.62B^2 - 0.4C^2 \quad (8)$$

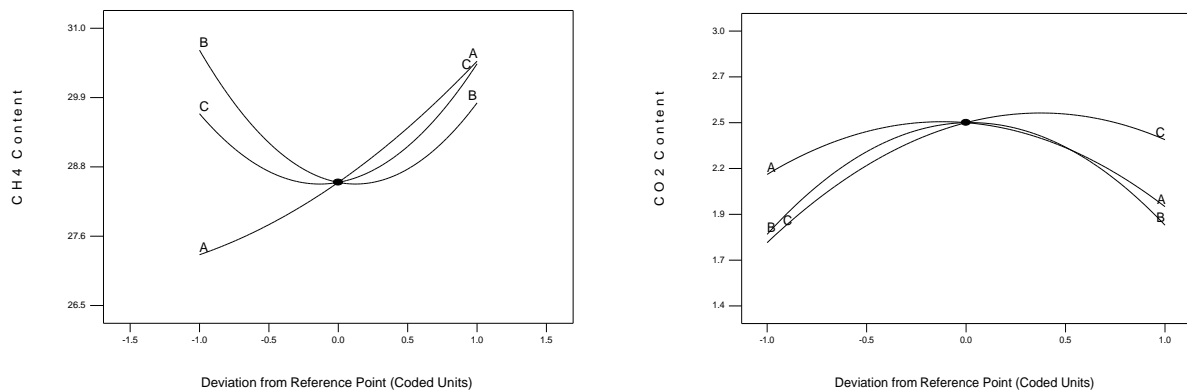


Figure 2: Perturbation chart for (a) CH₄ and (b) CO₂ yield.

The 3D surface plot in Figures 3 depicts the effect of interactions of the CBA leaching time, temperature and L/s ratio on the CH₄ and CO₂ content of gas produced during the gasification process. Figure 4 on the other hand gives the predicted and actual yield of the gases for all the experimental runs. An increase in time tend to cause a fall in CH₄ yield for L/s ratio below 4 (Figure 3a). For L/s ratios between 4 and 6, CH₄ yield decreases with increase in time from 3 to 6 hours and then increases up to the highest value (33.5 vol%) obtained for this interaction at 10 hours leaching time. This is likely because higher leaching time increased the pore width while not significantly reducing the oxide, which catalysed the gasification reaction. The effect of interactions of L/s ratio and temperature at 6.5 hours leaching time (midpoint) is given in Figure 3b. An increase in L/s ratio cause an increase in the CH₄ yield for all temperatures. The highest CH₄ yield for this interaction is 32.5 vol% obtained at 30°C and an L/s ratio of 3. This is likely because the loss in water-soluble oxides was higher at higher temperatures even though the pore width also increased. The quantity of metal oxides that catalyse the reaction is lower in sample leached at higher temperatures thus causing a lower of yield CH₄. The influence of interaction of leaching temperature and time on CH₄ production is depicted in Figure 3c. CH₄ yield increased with an increase in leaching temperature and time except for temperature below 42°C, which shows a reversal in the trend. The highest predicted and actual CH₄ yields (33.64 and 33.21 vol% respectively) were obtained from experimental run number 1 (Figure 4). These are lower than

the predicted and actual CH₄ yields (40.79 and 40.73 vol%) obtained by Shahbaz et al. (Shahbaz et al., 2016b) using untreated ash in the same process. This indicates that the Yield. Experimental run number treated ash has better capacity to reduce CH₄ production, which invariably increases the syngas yield. Experimental run number 5 resulted in the lowest predicted and actual yields of CH₄ (27.07 and 27.5 vol%, respectively). This is 32.48% lower than actual yield obtained from use of untreated CBA.

The effect of interaction on L/s ratio, time and temperature on CO₂ yield shown in Figures 3c, d and e follow the same pattern. The CO₂ yield rises with increase in each of the variable, reaches its maximum around the centre of the interaction points and the falls. Adsorption of CO₂ is due to the presence of CaO in the CBA which is not depleted by the leaching process, instead its comparative proportion the adsorption of CO₂. Figure 4 shows that the highest predicted and actual yield of CO₂ obtained (2.47 and 2.57, respectively) from Run numbers 11 to 15 are much lower than that obtained for gasification using untreated CBA and many other catalyst. Sun et al. (Sun et al., 2013) obtained 19.15 vol% CO₂ while Al-Rahbi and Williams (Al-Rahbi and Williams, 2017) had close to 20 vol% CO₂. The least predicted and actual yield of CO₂ for the process were 0.83 and 0.94, respectively. This is obtained using water-leached CBA used in Run numbers 4 and 7, respectively. It shows the treated CBA has the capacity of to reduce CO₂ production in biomass gasification significantly.

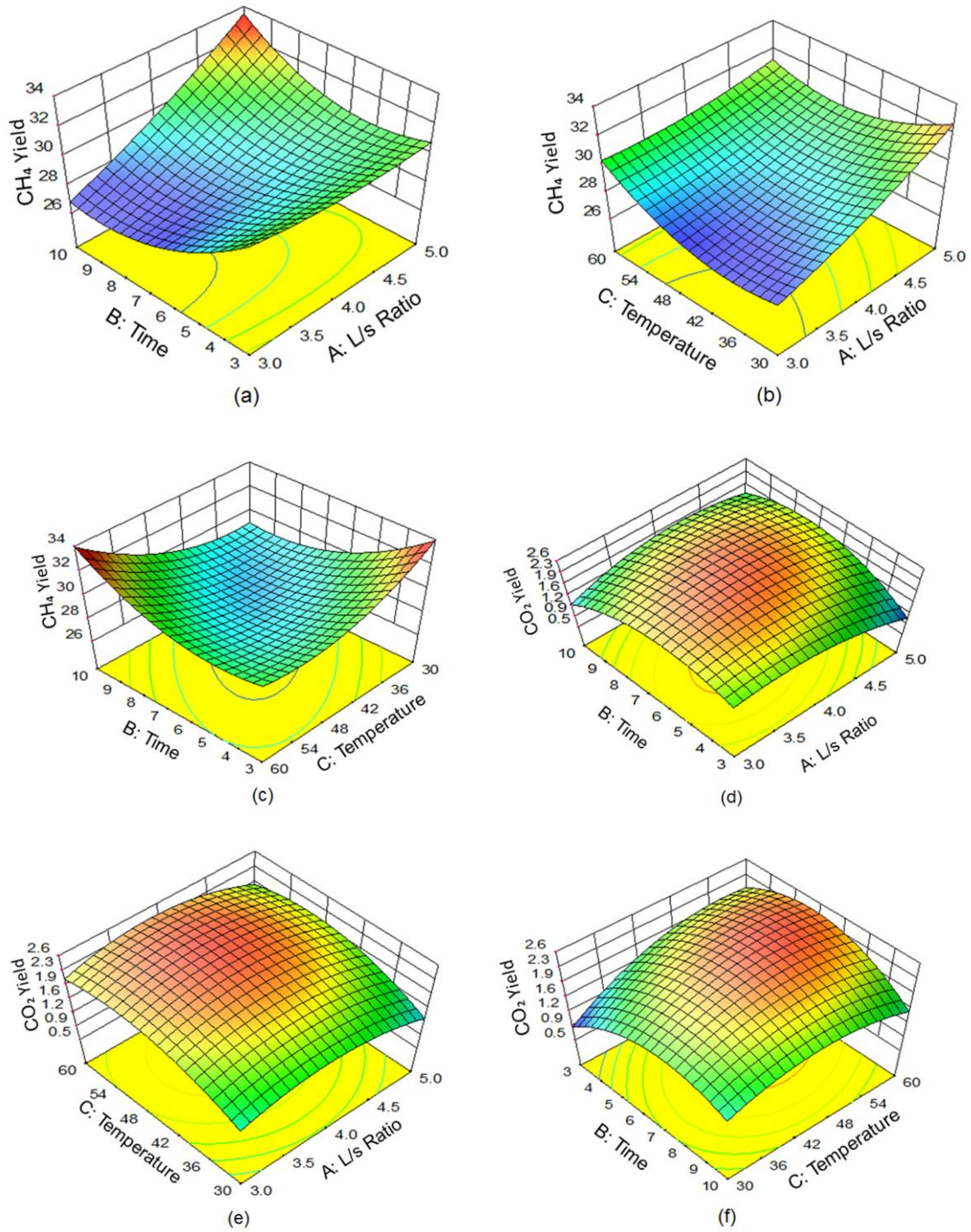


Figure 3: Effect of interactions of CBA leaching parameters on CH₄ and CO₂ yield.

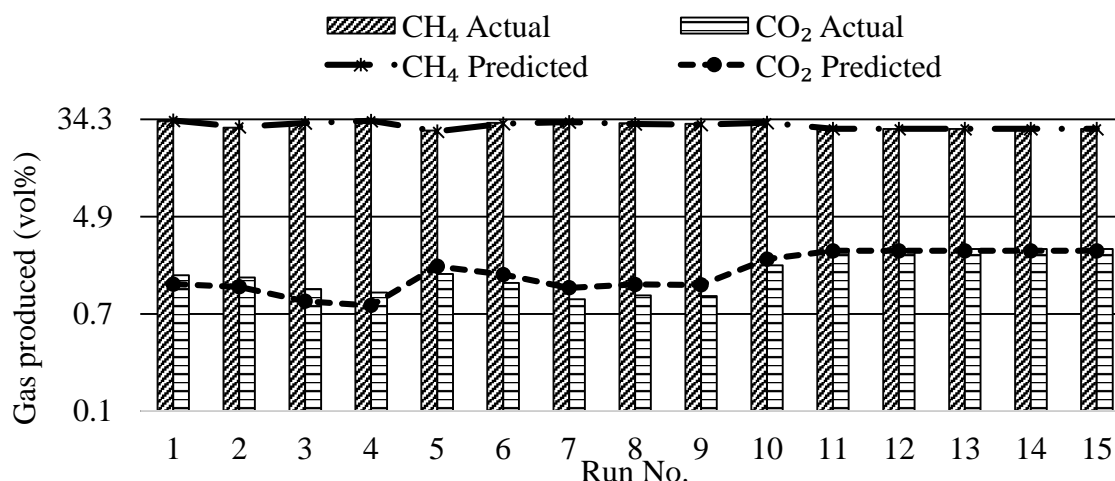


Figure 4: Actual and predicted CH₄ and CO₂ production from the different experimental runs.

Optimization of CBA water leaching parameters

The optimum values of leaching parameters for best performance was determined using response surface optimizer of design expert 8® software. Using the software interface, the leaching parameters were set to remain within earlier selected range of

Values. The Responses, CH₄ and CO₂ yields were set at minimum while syngas yield (H₂ and CO) was set at maximum. These selection minimized CH₄ and CO₂ yields while maximizing syngas yield. The optimum conditions obtained were L/s ratio 3, 10 hours leaching time and 56°C temperature. These conditions resulted in a model predicted CH₄ and CO₂ yields of 30.1 and 1.1 vol%. Three confirmatory runs were conducted with CBA treated using the optimum condition. The actual CH₄ and CO₂ yields obtained using CBA treated at the optimum condition are 29.65 ± 0.06 and 1.02 ± 0.01 vol%, respectively. Syngas yield from the actual experiment at optimum condition is 69.35 ± 0.05 vol%. These values have standard deviations of less than 5% hence there is a close agreement between the predicted and actual values.

Conclusion

CBA has been treated by leaching in water at different L/s ratios, time and temperatures to improve its catalytic properties in gasification. Its influence on the yield of CH₄ and CO₂ in the gasification of palm kernel shell using TGA has also been studied.

CBA pores were cleared of debris that could fuse easily on heating and caused likely agglomeration as seen from FESEM micrograph. This also improved the contact of the reacting gases with the metal oxide required to catalyse the reaction. Leaching also reduced the carbon content of the ash. The average carbon content decreased from 38.76 to 20.60 wt% across different points while Fe, Ca, and Al increased from 6.78 to 10.63 wt%, 6.92 to 15.03 wt% and 2.37 to 5.21 wt%, respectively thus making the metals more available for the reaction.

The actual yields of CH₄ and CO₂ in the process are as low as 27.5 and 0.94 vol% which are predicted to reach 27.07 and 0.83 vol%, respectively. The optimum CBA parameter leaching parameters are L/s ratio 3, 10 hours leaching time and 56°C temperature which resulted in CH₄, CO₂ and syngas yields of 29.65 ± 0.06, 1.02 ± 0.01 and 69.35 ± 0.05 vol%, respectively. The most influential variables on CH₄

and CO₂ yields as indicated by the study are L/s ratio and temperature, respectively. Result of the study shows that water leached CBA can be used effectively in gasification and it reduces the yield of CH₄ and CO₂ thereby increasing syngas yield.

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Conflict of Interest

The author declares no conflict of interest.

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