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Catalytic Conversion of Municipal Waste into Clean Energy: Optimizing Hydrogen and Syngas Production with Acid-Functionalized Bottom Ash

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Abstract
Municipal Solid Waste (MSW) management presents a critical environmental challenge. This study investigates a transformative approach: the catalytic steam gasification of MSW using acid-functionalized bottom ash. Employing Response Surface Methodology (RSM) within a modified TG-MS setup enriched with steam, we meticulously analyze key parameters, including temperature, particle size, and catalyst content. Temperature proves the most influential factor in hydrogen and syngas production, revealing a crucial avenue for efficiency enhancement. Acid-treated incineration ash, with active sites and the SO_3H functional group, exhibits remarkable catalytic prowess, promising sustainable waste-to-energy conversion. Through rigorous experimentation, we establish optimal conditions for hydrogen and syngas yields: 684°C temperature, 0.84 mm particle size, and 0.65 wt% catalyst content. This parametric study advances our understanding of MSW gasification and offers a promising route to sustainable energy generation from waste. Our research underscores the pivotal role of catalysis in waste management, addressing environmental concerns while unlocking the latent energy within municipal waste. The outcomes have profound implications for sustainable fuel production, emission control, and our broader mission to create a greener, more energy-efficient future. This study pioneers a sustainable approach to MSW management, demonstrating the potential to transform waste into valuable energy resources, contribute to emission control, and shape a more sustainable future

Keywords: Municipal solid waste, Gasification, Syngas, Hydrogen, Incineration ash

Introduction

The global rapid and continuous increase in industrialization over the last few decades has made environmental pollution to emerged as one of the world's most challenging issues in recent years (Khan et al., 2022). Just like in the developed world, metropolitan cities in sub-Saharan Africa are fast becoming the producer of large quantities of municipal solid waste (MSW), causing significant environmental problems such as water, air, and soil contamination (Muheirwe et al., 2022; Debrah et al., 2022; Ayeleru et al., 2020). The large quantities of unprocessed MSW accruing from very poor management system has aggravated the problem of waste management in sub-Saharan Africa to a great extent, thus causing metropolises to experiencing "trash siege" concerns (Awasthi et al., 2022; Ayeleru et al., 2020). While inappropriate MSW management poses a major threat to humans and the environment, it is increasingly being recognized as an essential renewable resource (Orhorhoro & Oghoghorie, 2019; Awasthi et al., 2022; Yang et al., 2021). It is generally known that the socioeconomic status and local weather conditions have a substantial impact on the MSW composition, which varies greatly from location to location. In most sub-Saharan African countries, the physical composition of MSW is majorly plant remains, food wastes and plastics of various types. These are well known materials that have been successfully utilized in thermochemical conversion for production of fuels of various kinds. Furthermore the utilization of these waste for energy application will go a long way in mitigating pollution due to incineration, which is very commonly used as a way of managing the MSW generated in most sub-saharan countries (\Sege, 2021; Orhorhoro & Oghoghorie, 2019).

Municipalities and residents employ various methods, regulations, and practices to minimize the negative impacts of garbage and identify valuable recyclables. Waste management is typically organized into six key functions: waste

generation, waste handling at the source, collection, transportation, processing and transformation, and disposal (Muheirwe et al., 2022; Debrah et al., 2022). These functions remain consistent, although their implementation may vary in different locations. Waste is initially generated by individuals or entities, and they can dispose of it in one of two ways: either by placing it in a designated container or by breaking it down into its basic components. Following waste generation, formal or informal actors, such as waste management companies or individuals involved in recycling activities, may collect and transport the garbage to another location. This area is often a facility where the waste can undergo processing, such as sorting, separation, or conversion into reusable materials or energy. Finally, the waste that cannot be effectively processed or recycled is disposed of, typically in designated landfills or through other appropriate methods (Orhorhoro & Oghoghorie, 2019; Khan et al., 2022). Overall, these functions and activities are fundamental to waste management, and their specific implementation can vary depending on local regulations, infrastructure, and available resources. Municipal solid waste disposal and treatment can produce substantial greenhouse gas (GHG) emissions. Incineration releases carbon dioxide and nitrous oxide, whereas anaerobic decomposition of waste in landfills emits methane. To mitigate these emissions, thermal and biological treatments are commonly employed to convert solid waste into biofuel and recover valuable resources (Awasthi et al., 2022).

Thermochemical conversion processes, such as gasification and pyrolysis, have gained increasing significance over the past two decades for the production of syngas, char, and bio-oil (Ali et al., 2023). Gasification involves the thermal treatment of carbonaceous materials like biomass, waste, and plastics at temperatures between 500-800°C in the presence of a gasification agent, such as air or steam. This process converts the materials into producer gas, which primarily consists of H_2, CO_2, CO, and CH_4 (Shahbaz et al., 2017; Zhang et al., 2023).

Syngas, derived from gasification, serves not only as a fuel in existing facilities but also as a source of power generation. Additionally, H_2 obtained from syngas serves as a raw material for the production of various compounds, including ammonia, methane, methanol, and ethanol (Shahbaz et al., 2016). These thermochemical conversion processes offer versatile options for utilizing carbonaceous materials and have the potential to contribute to the production of energy and valuable chemical compounds (Sajid et al., 2022). Gasification of municipal solid waste (MSW) provides an integrated solution for waste management and energy recovery. Various studies have been performed for the gasification of MSW and various blends in order to design a sustainable solution. Several gasifier designs have been proposed for the efficient gasification process. Chemical reaction as summarized in below are principal reactions that occur during gasification in all process schemes (Yang et al., 2021; Sajid et al., 2022).

$C + CO_2 \leftrightarrow 2CO$	ΔH = - 172 kJ/mol	(1)
$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	ΔH = + 247 kJ/mol	(2)
$C + 2H_2 \rightarrow CH_4$	ΔH = - 75 kJ/mol	(3)
$H_2 + {}^1/_2\, O_2 \rightarrow H_2O$	ΔH = - 242 kJ/mol	(4)
$C + {}^1/_2\, O_2 \rightarrow CO$	ΔH = - 111 kJ/mol	(5)
$C + O_2 \rightarrow CO_2$	ΔH = - 394 kJ/mol	(6)
$C + HO_2 \rightarrow CO + H_2$	ΔH = - 131 kJ/mol	(7)
$C + 2HO_2 \rightarrow CO_2 + 2H_2$	ΔH = - 90 kJ/mol	(8)
$CH_4 + H_2O \rightarrow CO + 3H_2$	ΔH = + 206 kJ/mol	(9)
$CO_2 + H_2 \rightarrow CO + H_2O$	ΔH = - 41 kJ/mol	(10)

Gasification of MSW involves the conversion of the waste constituents into various products using gasifying agents such as air, steam, CO_2, and oxygen. These gasifying agents play a crucial role in facilitating several important reactions during the gasification process. Combustion Reaction: The gasifying agents, particularly air and oxygen, support the combustion reaction in which the biomass reacts with oxygen to produce carbon dioxide (CO_2), water (H_2O), and heat. This exothermic reaction releases energy and is responsible for the initial conversion of biomass into gaseous products. Methane Reforming: Methane reforming is another reaction that can occur during gasification. In the presence of steam (H_2O), methane (CH_4) can undergo a reforming reaction, typically referred to as steam reforming. This reaction produces hydrogen gas (H_2) and carbon monoxide (CO). Methane reforming is desirable as it yields hydrogen, which can be utilized as a valuable fuel or raw material in various industries. Water Gas Shift Reaction: The water gas shift reaction is an important chemical reaction in gasification. It involves the interaction of carbon monoxide (CO) with steam (H_2O) to produce hydrogen gas (H_2) and carbon dioxide (CO_2). This reaction helps in increasing the hydrogen content in the gas stream, making it a desirable reaction for hydrogen production. Overall,

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these reactions, including combustion, methane reforming, and water gas shift reactions, contribute to the conversion of biomass into a mixture of gases, including hydrogen, carbon monoxide, carbon dioxide, and water vapor, during the gasification process (Shahbaz et al., 2017).

Steam stands out as a distinct gasifying agent for hydrogen (H_2) and syngas production due to several advantageous attributes. First, steam allows for the removal of excess steam in the form of condensate during the gasification process. This helps in controlling the steam-to-biomass ratio and optimizing the gasification conditions. Furthermore, the use of steam as a gasifying agent avoids the dilution of the product gas by nitrogen (N_2) as seen with the use of air. This is significant because it allows for a more concentrated and higher-quality syngas output. Steam gasification is applicable both at small and large scales, making it a potential choice, especially in situations where the use of oxygen as a gasifying agent is not economically viable on a small scale. In addition to its gasification role, steam also simulates the water gas shift reaction, which enriches the product gas with hydrogen (H_2) and carbon monoxide (CO). This reaction is favourable for increasing the hydrogen content in the gas stream (Shahbaz et al., 2017).

The use of catalysts in gasification plays a crucial role. Catalysts not only enhance the desired product yield but also contribute to the reduction of tar and unwanted byproducts, making the process more economical. Different catalysts, such as dolomite, nickel, and alkaline earth metals, have been used in gasification. Each catalyst type has its advantages and disadvantages, such as tar reduction, short active life span, regeneration issues, sintering, carbon deposition, agglomeration, and cost. Researchers are continuously exploring effective and cost-efficient catalysts for gasification processes. Recent studies have highlighted the potential of coal bottom ash (CBA), a byproduct of coal combustion in power plants, as a catalyst in biomass gasification. CBA contains alkaline metals, particularly calcium (Ca) and aluminum (Al), which have shown catalytic activity and can enhance gas yield and reactivity (Patrick et al., 2017). The use of CBA as a bed material in coal gasification has demonstrated better tar reduction compared to silica bed material. However, the gas yield with CBA as a bed material is relatively lower than that with silica bed material. The utilization of ash, including wood ash and CBA, in gasification processes has been investigated (Xiong et al., 2010; Hauserman 1994). These studies have shown increased reactivity and catalytic activity, but the specific application of CBA in biomass gasification is still under investigation and has not been extensively discussed in the literature. The utilization of acid treated CBA has also been reported in literature with resultant functionalization of the ash and significant improvement in product yield for pyrolysis and gasification of biomass (Patrick et al., 2020; Patrick, 2022).

Response Surface Methodology (RSM) is a systematic approach used to design experiments and analyze the results using Analysis of Variance (ANOVA) analysis (Shahbaz et al., 2017). RSM helps establish a relationship between process variables and the desired response. It also provides tools for process optimization. In the context of biomass gasification for H_2 and syngas production, there have been limited studies utilizing RSM experimental design in the literature. For instance, (Yong, 2009) investigated syngas production from palm oil waste gasification using hot compressed water and optimized the process using RSM based on the Central Composite Rotatable Design. In another study, RSM was employed to examine the impact of process factors and their interactions on syngas production from lignite coal steam gasification in a fluidized bed reactor (Karimipour et al., 2013). The researchers evaluated the effects of coal flow rate, particle size, and steam-to-oxygen ratio on CH_4/H_2 ratio, gas yield, and gasification efficiency. These studies highlight the application of RSM in optimizing biomass gasification processes and exploring the effects of various parameters on H_2 and syngas production. However, there is still room for further research utilizing RSM in this field. This study focuses on the utilization of Response Surface Methodology (RSM) to optimize the production of hydrogen and syngas from municipal solid waste (MSW) using functionalized pyrolysis bottom ash catalyst. By employing RSM, the researchers aim to maximize the efficiency and yield of hydrogen and syngas during the gasification process of MSW. The use of functionalized pyrolysis bottom ash catalyst suggests that the researchers are exploring novel catalyst materials to enhance the gasification process. Catalysts play a crucial role in promoting desired reactions, improving yields, and reducing unwanted byproducts in gasification. By utilizing MSW as a feedstock for gasification, the study also highlights the potential of gasification as an effective approach to manage municipal solid waste. Gasification offers a simultaneous solution for waste management and energy generation, allowing for the conversion of MSW into valuable energy products. Overall, this study contributes to the understanding of MSW gasification and demonstrates the potential of RSM and functionalized catalysts in optimizing the production of hydrogen and syngas from MSW.

Methodology

Waste collection and preparation

Municipal waste used in the study was collected from the waste dump site located in Shinko area of Jimeta, Yola metropolis in Nigeria. This was sun dried for 4 days then further dried in an oven set at 105°C for 24 hours to ensure removal of fry bond moisture. The dried waste was crushed then milled and sieved to obtain 0.1-0.1 mm particle sized samples for the experiment (Patrick et al., 2017).

Bottom ash preparation and analysis

Bottom ash was obtained from the incineration site of the Shinko municipal waste dumpsite in Jimeta, Yola metropolis, Nigeria. The ash was oven dried at 110°C for 24 hours and milled in preparation for treatment. Treatment of ash was carried out in sulfuric acid solution to ensure a partial dissolution of oxides encapsulated in the glass phase thus releasing them from the silicate/slag matrix. A 50 g bottom ash sample was added to 150 mL of 1 M H_2SO_4 solution earlier heated to 30°C. The mixed was stirred continuously while maintaining the temperature for 3 h. Afterwards, the mixtures were allowed to cool down, washed in deionised water, filtered and dried in an oven at 120°C for 24 h to ensure complete removal of moisture.

The bottom ash samples were characterised by X-ray fluorescence (XRF) to determine their physicochemical properties hence their quality and usability in biomass gasification. The X-Ray Fluorescence (XRF) (Siemens D-500, 100 KV X-Ray diffraction was utilized to analyze the composition of the ash.

Design of experiment

In the existing literature, hydrogen and syngas production through gasification have often been studied using the classical "one factor at a time" approach. However, this method has certain limitations due to its low number of experiments. It does not allow for a comprehensive evaluation of multiple factors, making it difficult to obtain a complete understanding of the gasification process. Additionally, this method does not provide precise information about the effects of operating variables and their interactions on the system being investigated (Li et al., 2023). To overcome these deficiencies, researchers have turned to Response Surface Methodology (RSM) based statistical designs. RSM enables a comprehensive study of operating factors and their interactions. It involves developing a statistical relationship between the input (operating variables) and the output (response). A response surface is generated to identify stable responses and optimize the factors involved. The response surface is created by fitting the data from the experimental design points within the designated parameter space, ensuring that variations in the number of experiments do not impact the analysis and optimization of factors. In RSM, a functional relationship is developed using first-order and second-order polynomials. The coefficients of the model are determined using the least square fit method. These coefficients play a vital role as they indicate the significance of the model and the interactions between variables. By employing RSM, researchers can overcome the limitations of the classical one factor at a time approach and obtain a more comprehensive understanding of the gasification process. RSM enables a thorough investigation of operating variables and their interactions, leading to optimized conditions for hydrogen and syngas production.

In the current study, three operating factors were selected to investigate their influences on the response variables of hydrogen and syngas production (vol%). The selected factors and their operating ranges were as follows:

1. Temperature (A): 500-700 °C
2. Particle size (B): 0.1-1 mm
3. Acid treated Ash (ATA) (C): 0.1 – 1%

The ranges of these operating variables were determined based on previous literature and a series of preliminary experimental runs to ensure a smooth gasification process. To design the experimental array, the researchers utilized Design Expert 10 software package, which is commonly used for statistical analysis. The central composite design (CCD) was employed to fit second-order polynomials, allowing for the study of non-linear interactions between the parameters. In total, 20 design points (experiments) were generated. These included 5 axial runs, 10 factorial runs, and 5 central runs. The central runs were replicated at the center points of the variables to minimize experimental error. The higher number of factorial runs was used to investigate the interactive effects of the variables. By conducting this experimental design and utilizing the CCD, the researchers aimed to understand the complex interactions between the operating factors and their effects on hydrogen and syngas production during the gasification process.

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Catalyst activity test

Steam catalytic gasification of MSW with the bottom ash was carried out using a modified thermogravimetric analyser (Exstar TG/DTA 3200) with mass spectrometer/gas analyser (ThermoStar™ GSD 320 T1) and fitted with a mini steam generator. The entire system (TG-MS setup) is linked to a computer which analyses the data capture from the setup. Process flow diagram of the setup is shown in Figure 1. The steam generator fitted to the TG-MS setup of an adjustable micro pump which supply water at a regulated rate to a heater through which steam is generated and supplied to the TGA section. The ash was added to 10 mg of the municipal waste and heated to 700°C at 25 °C/min after initially maintaining it at 50°C for 1 mins (while purging with N_2) to remove all entrapped gases. The N_2 and steam supply was maintained throughout the experiment. A Schematic diagram of the modified TG-MS setup is shown in Figure 1.

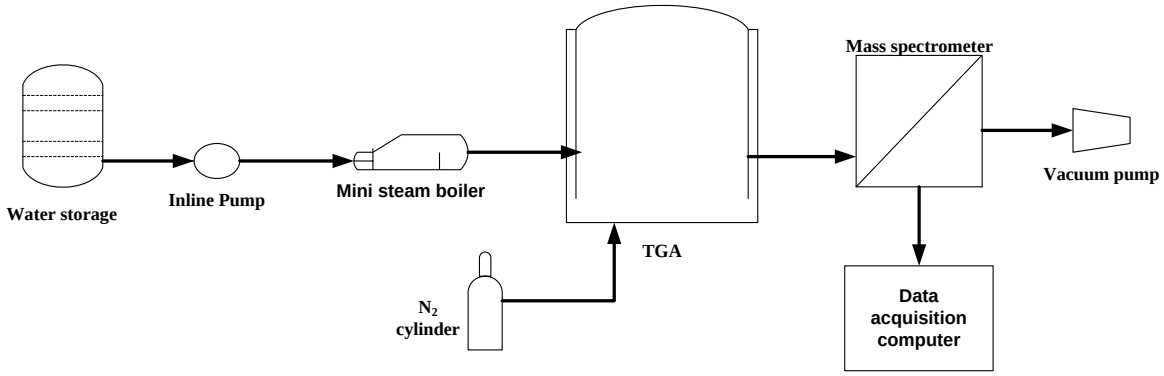

Fig. 1. Schematic diagram of TG-MS setup with attached mini steam generator.

Results

Chemical Properties of the acid treated ash and municipal solid waste

Table 1 portrays the analysis results of the MSW and the acid treated incineration ash. The XRF result shows that ATA has significant content of oxide known to catalyze gasification (Shahbaz et al., 2019). SiO_2, Fe_2O_3, Al_2O_3, CaO, K_2O, and MgO have been reported to effectively catalyze gasification and pyrolysis (Patrick et al., 2017; Zhang et al., 2013). Furthermore the presence of SO_3, indicates that the ash has been functionalized with the incorporation of -SO_3H and formation of anhydrite ($CaSO_4$) with the SO_4^{-2} functional group (Russo et al., 2014; Lathiya et al., 2019). This was also confirmed by FTIR spectra analysis (Patrick, 2020).

Table 1: Analysis of the municipal solid waste and acid treated incineration ash.

Proximate analysis	**wt%**	**Ultimate analysis,**	**wt%**
Moisture content	3.86	C	43.2
Ash content	2.87	H	7.1
Volatile matter	76.92	N	1.3
Fixed carbon	15.6	S	0.1
		O (By difference)	48.3

XRF analysis of Incineration Bottom ash (wt%)

SiO_2	SO_3	Al_2O_3	CaO	Fe_2O_3	MgO	K_2O	TiO_2	Na_2O	P_2O_5	Others
50.77	4.55	13.29	11.65	5.17	3.88	2.82	1.85	1.81	1.5	2.7

XRF analysis of Acid Treated Ash (wt%)

SiO_2	SO_3	Al_2O_3	CaO	Fe_2O_3	MgO	K_2O	TiO_2	Na_2O	P_2O_5	Others
36.14	32.24	9.46	8.29	3.68	2.76	2.01	1.32	1.29	1.07	1.92

Chemical Properties of the acid treated ash and municipal solid waste

Table 2 shows the experimental design and results for hydrogen (H_2) and syngas (H_2 + CO) production.

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Production of hydrogen

Central composite design (CCD) was used to create the correlation between actual values of process variables and hydrogen vol% in steam gasification. To evaluate an appropriate model, regression analysis was performed. The results showed that quadratic model is the best for fitting experimental data. Quadratic models have been employed to predict the performance of gasification with high degree of accuracy. Equation (11) represents the quadratic equation derived by the model in terms of coded factor. This equation explains the interaction of process factors and their effect on hydrogen production (vol%).

Table 2: Experimental design and results for hydrogen and syngas (H_2 + CO) production in TG-MS

Run	A:Temperature (℃)	B:Particle size (mm)	C:ATA content (%)	Hydrogen (vol%)	H_2 + CO (vol%)
1	800	0.1	0.2	32.73	63.28
2	500	0.1	1	23.13	62.3
3	800	1	1	36.94	65.73
4	650	0.55	0.6	28.23	65.4
5	500	1	0.2	22.65	62.1
6	805	0.55	0.6	31.33	61.7
7	650	0.55	0.6	28.22	65.94
8	650	0.55	1.3	29.2	67.3
9	700	0.55	1	38.53	67.3
10	650	0.1	0.6	28.3	65.95
11	800	0.1	1	34.35	64.32
12	800	1	0.2	36.92	64.95
13	650	0.55	0.1	29.8	66.7
14	650	1.3	0.6	27.97	66.1
15	650	0.55	0.6	28.21	65.94
16	700	0.55	0.6	37.25	66.54
17	650	0.55	0.6	28.22	65.94
18	490	0.55	0.6	22.83	61.69
19	500	0.1	0.2	22.33	61.7
20	500	1	1	24.26	63.7

$$\text{Hydrogen} = 29.83 + 6.00\text{A} + 0.8038\text{B} + 0.5853\text{C} + 0.6663\text{AB} + 0.1430\text{AC} - 0.0987\text{BC} - 0.6483A^2 - 0.7738B^2 + 0.3925C^2 \quad (11)$$

The statistical variance analysis in Table 3 was conducted to examine the impact of process variables on the hydrogen (vol%) in steam gasification. The analysis revealed that the model developed, based on the quadratic equation, is statistically valid and significant. This conclusion is supported by the low p-value of 0.0142 and a higher F-value of 4.47. The F-value of 36.76 for temperature is far greater than that for particle size and ATA content. This indicates that temperature is far more influential on the production of hydrogen than either particle size or ATA content. This is also confirmed by the slope of factors A, B and C in Figure 2B. The coefficient of determination (R-squared value) is 0.89, which indicates that the model closely approximates the experimental data and can effectively predict the response variable. The adjusted R-squared value, which is very close to the R-squared value, further confirms the good agreement between the experimental and predicted values. Figure 2(A) illustrates a strong correlation between the experimental and predicted values, supporting the significance of the model and indicating the influence of the terms on the response variable. The lack of fit, which refers to the discrepancy between the model and experimental data, is non-significant. This result suggests that there is minimal random and systematic error within the model, indicating its accuracy in representing the experimental activity. Overall, these findings demonstrate the reliability and suitability of the quadratic model in explaining the relationship between the process variables and hydrogen (vol%) in steam gasification.

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Table 3: ANOVA analysis for hydrogen production

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	408.95	9	45.44	4.47	0.0142	significant
A-Temperature (°C)	373.61	1	373.61	36.76	0.0001	
B-Particle size (mm)	6.77	1	6.77	0.6659	0.4335	
C-ATA content (%)	4.21	1	4.21	0.4140	0.5344	
AB	3.55	1	3.55	0.3494	0.5676	
AC	0.1655	1	0.1655	0.0163	0.9010	
BC	0.0780	1	0.0780	0.0077	0.9319	
A^2	1.87	1	1.87	0.1838	0.6772	
B^2	4.84	1	4.84	0.4766	0.5057	
C^2	1.60	1	1.60	0.1576	0.6997	
Residual	101.64	10	10.16			
Lack of Fit	101.64	7	14.52	0.0217	0.0501	
Pure Error	0.0002	3	0.0001			
Cor Total	510.59	19				
R^2	0.89		Adjusted R^2	0.86		

In Figure 2(B), the perturbation plot is also utilized to assess the sensitivity of process variables on hydrogen (vol%). The perturbation plot illustrates the impact of each operating factor at their mid-values on the response variable. By analyzing the perturbation plot, it becomes possible to understand the individual influence of each process variable on the hydrogen (vol%) production. The plot highlights how changes in a specific factor, while keeping the other variables at their mid-values, affect the response variable. This analysis helps in identifying which factors have a substantial impact on hydrogen (vol%) production and provides insights into optimizing the process conditions for maximizing hydrogen yield. The slope of the temperature plot indicates that it has a much greater influence on the production of hydrogen compared to particle size and ATA content.

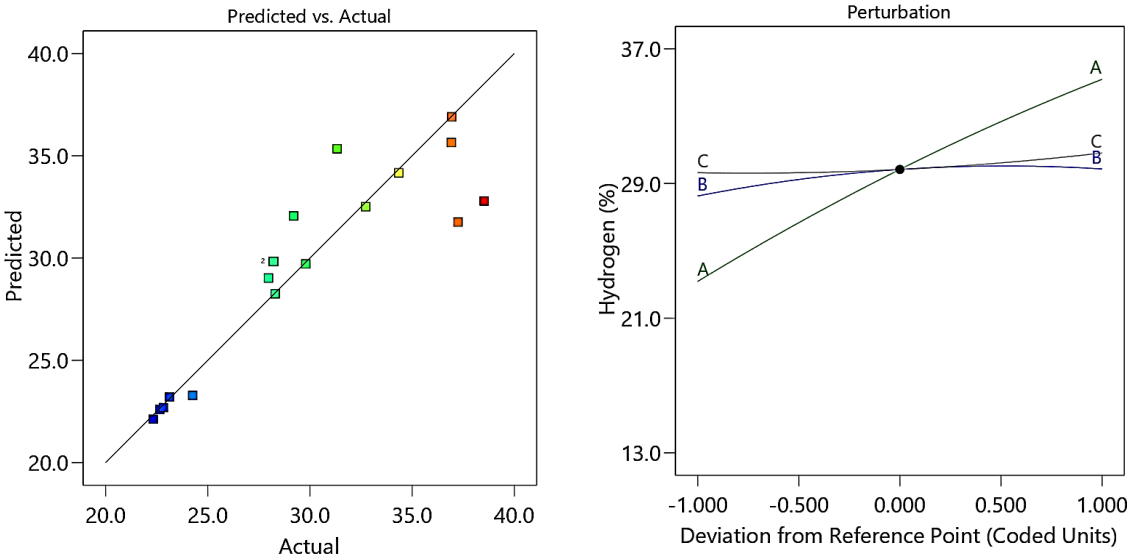

Figure 2: (A) Predicted response values vs Actual values. (B) Perturbation plot of effecting factors on hydrogen (vol%).

The three-dimensional graph, shown in Figure 3, was developed to study the effects of variables on hydrogen (vol%). The results indicate response of hydrogen (vol%) production to the interaction of temperature, particle size and ATA content. Initially, hydrogen production increases from about 21 vol% at 500°C to 37 vol% at 800°C, for the interaction

between temperature and particle size (Figure 3A). Higher temperature increase the production of hydrogen since the rate of reaction increases with increase in temperature of reaction (Li et al., 2009). Furthermore, there was a slight increase in hydrogen production. The trend was also reported in literature (Khan et al., 2014). Small particle size leads to a larger surface area, which enhances heat transfer. This increased heat transfer promotes the production of light gases, such as hydrogen, resulting in higher yields (Li et al., 2009).

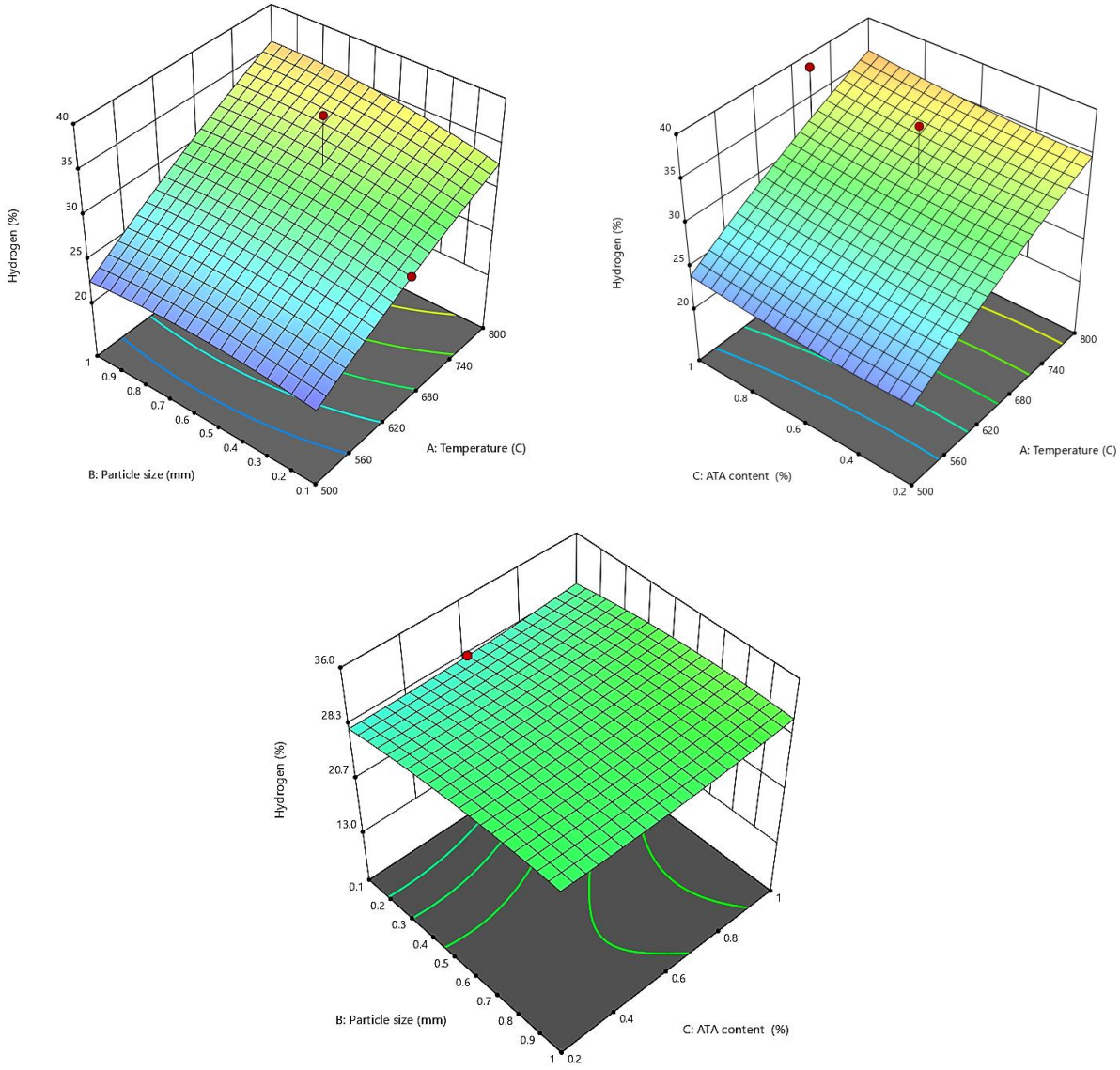

Figure 3: Surface plot showing response of hydrogen (vol%) production to the interaction of temperature (500–750°C), particle size (0.1–1 mm) and ATA content (0.2–1%).

The effect of interaction of temperature and catalyst content is depicted in Figure 2B. It is observed that there is generally an increase in hydrogen production with increase in catalyst production. An increase in catalyst content from 0.2 to 1% resulted in an increase in hydrogen production of about 3 vol%, from 34 to 37 vol%. The increase in catalyst content also increase the metal oxides and acid sites available for gasification, thus promoting tar cracking and hydrogen-rich gas yield (Li et al., 2009; Tang et al., 2023; Ahamed et al., 2021; Patrick, 2020).

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Production of syngas

The central composite design was employed to establish the functional relationship between syngas production and process parameters in the steam gasification of MSW. This relationship provides insights into the combined and interactive effects of variables on the response. In a similar manner to the hydrogen (vol%) response, the quadratic model is found to be a better fit for the syngas production data. The equation representing the model is developed in terms of coded factors, excluding insignificant terms that do not negatively impact the model. This equation, given in Equation (12), captures the relationship between the process parameters and syngas production.

$$\mathrm{H2} + \mathrm{CO} = 65.93 + 0.8528\mathrm{A} + 0.4240\mathrm{B} + 0.3357\mathrm{C} + 0.1600\mathrm{AB} - 0.0232\mathrm{AC} + 0.0925\mathrm{BC} - 3.16A^2 + 0.0417B^2 + 0.5288C^2 \quad (12)$$

Table 4 presents the ANOVA analysis for syngas production in the catalyzed steam gasification study. The low p-value of 0.0005 indicates that the model is statistically significant. This suggests that the model can effectively predict the production of syngas based on the given process parameters. The higher F-value of 11 for temperature compared to 2.75 and 2.02 for particle size and catalyst content, respectively indicates that temperature has greater influence on the yield of syngas than particle size and catalyst content. This observation is also confirmed by the perturbation plot in Figure 4B, in which the curve of factor A is much steeper than that of B and C. The slope of factors B and C are almost the same (Figure 4B) as also indicated by their values in Table 4.

Table 4: ANOVA analysis for syngas production

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	66.52	9	7.39	10.78	0.0005	significant
A-Temperature (°C)	7.54	1	7.54	11.00	0.0078	
B-Particle size (mm)	1.88	1	1.88	2.75	0.1285	
C-ATA content (wt%)	1.38	1	1.38	2.02	0.1858	
AB	0.2048	1	0.2048	0.2986	0.5967	
AC	0.0044	1	0.0044	0.0064	0.9380	
BC	0.0685	1	0.0685	0.0998	0.7586	
A^2	44.47	1	44.47	64.84	< 0.0001	
B^2	0.0141	1	0.0141	0.0205	0.8890	
C^2	2.91	1	2.91	4.24	0.0665	
Residual	6.86	10	0.6859			
Lack of Fit	6.64	7	0.9486	13.01	0.0595	
Pure Error	0.2187	3	0.0729			
Cor Total	73.38	19				
R^2	0.9065		Adjusted R^2	0.8224		

The model exhibits a strong estimation capability, as evidenced by the high R-squared value of 0.9065. The goodness of the model in predicting response data is further supported by the Adj-R-squared coefficients. The small difference between the R-squared and Adj-R-squared values indicates a close agreement between the actual and predicted values. Figure 4(A) depicts the relationship between the actual and predicted values and shows that they are closely aligned. This indicates that the predicted data is very close to that actual, hence the model will effectively predict the experimental results. Additionally, the nonsignificant result of the lack of fit test is favorable, indicating that the model can accurately predict syngas production within the investigated range of variables.

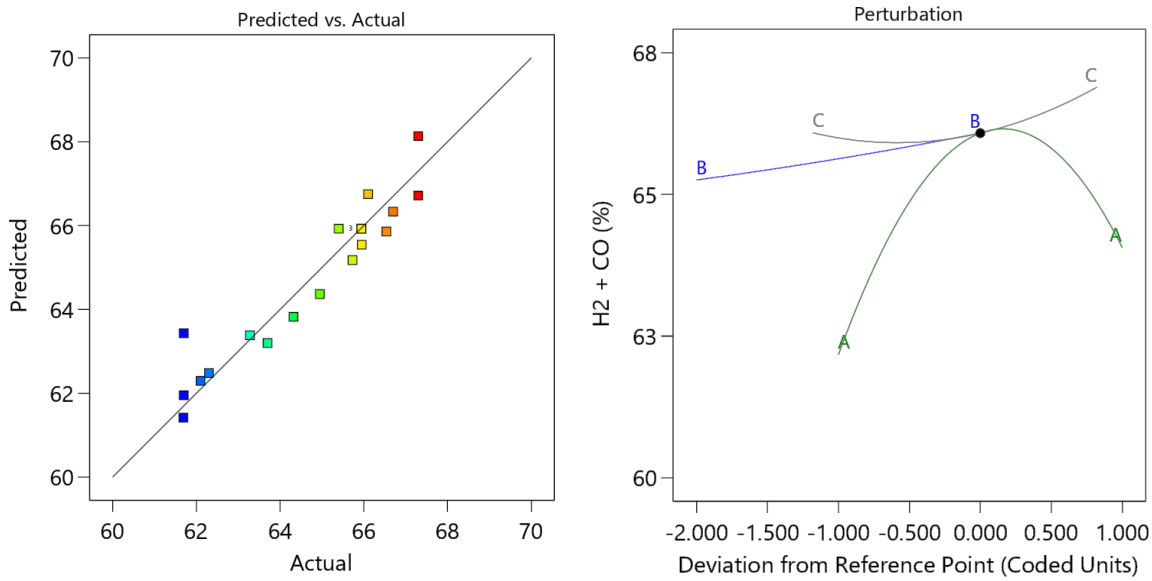

Figure 4: (A) Predicted response values vs Actual values. (B) Perturbation plot of effecting factors on syngas (vol%).

The results of parametric study and effect of interaction of the variables on the production of syngas is portrayed in Figure 5. The highest syngas yield was observed. Around 700℃. After an initial increase in syngas production from 500 to 680℃, further increasing the temperature leads to a decline in syngas production. The reactions in Equation 1to 10 are mostly exothermic and higher temperatures could impact them negatively and cause a reversal in the case of reversible reactions (Sajid et al., 2022). An optimum temperature of about 700℃ was also reported for catalytic steam gasification in literature (Shahbaz et al., 2017; Khan et al., 2014). The effects of particle size and catalyst content exhibit a similar trend as observed for hydrogen production. The interaction of particle size and catalyst content at a fixed temperature has very little impact on changes in syngas production. However, there was an increase in syngas production from 66.3 to 67.5 vol%, when catalyst content was increase from 0.2 to 1 wt% at a fixed particle size of 1 mm. The increase in syngas production was due to increase in catalyst active site available for reaction occasioned by the larger quantity of catalyst in the system (Tang et al., 2023; Patrick, 2020).

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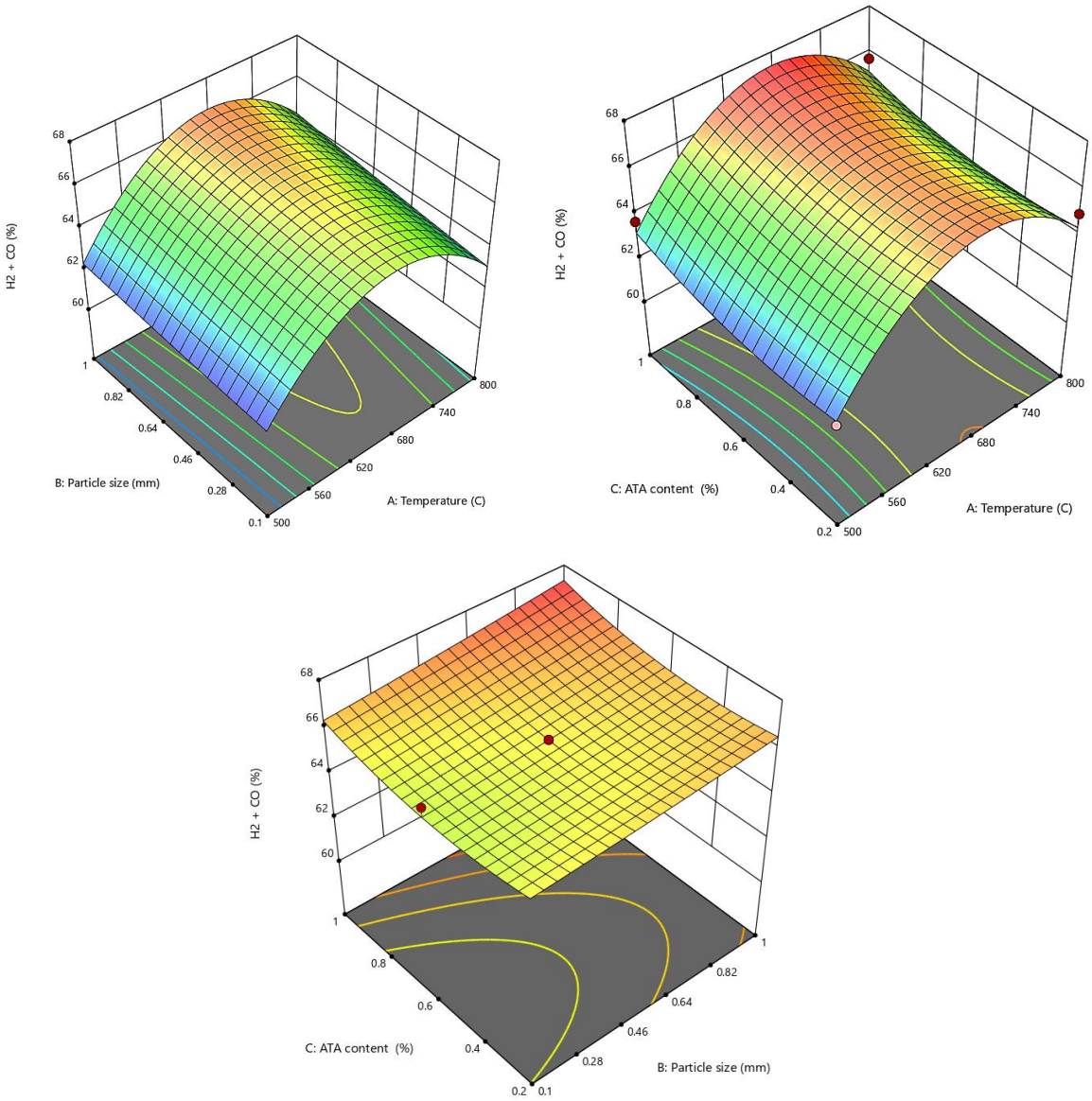

Figure 5: Surface plot showing response of syngas (vol%) production to the interaction of temperature (500–750°C), particle size (0.1–1 mm) and ATA content (0.2–1%).

Optimization studies

Figure 5 displays the results of the optimization of the process for hydrogen and syngas obtained using a numerical optimization tool incorporated in the response surface methodology (RSM). The optimized operating conditions obtained from the numerical optimization tool are 684°C temperature, particle size of 0.84 mm, and 0.65 wt% catalyst content. These optimized conditions yielded hydrogen and syngas production of 38.35 vol% and 66.96 vol%, respectively. Three confirmation experiments were conducted using these optimized conditions. To assess the reliability of the results, the standard deviation was calculated. The result of optimization confirmatory runs was 38.23 ± 0.007 vol% and 66.91 ± 0.003 vol%.

Comparative studies on performance of BA and ATA

The performance of the incineration ash (BA) and the acid functionalized ash was conducted at the optimum particle size and catalyst content to ascertain the effect on the acid treatment on the performance of the ash. The comparative effect of temperature on performance of ash samples for hydrogen and syngas production is displayed in Figure 6.

Slight increases were observed for both hydrogen and syngas production when ATA was used. The functionalized ash has more active site for reactions to take place, thus resulting in higher hydrogen and syngas production. Increasing the temperature has a positive impact on the production of both syngas and hydrogen for both types of ashes. Higher temperatures result in increased kinetic energy of the molecules, leading to more frequent collisions and ultimately promoting the production of gaseous products. (Su et al., 2015; Su et al., 2015). Beyond 700℃, a slight decrease in the production of gaseous products is observed. This decrease is likely due to the inhibition of exothermic reactions caused by the higher temperatures. (Sajid et al., 2022).

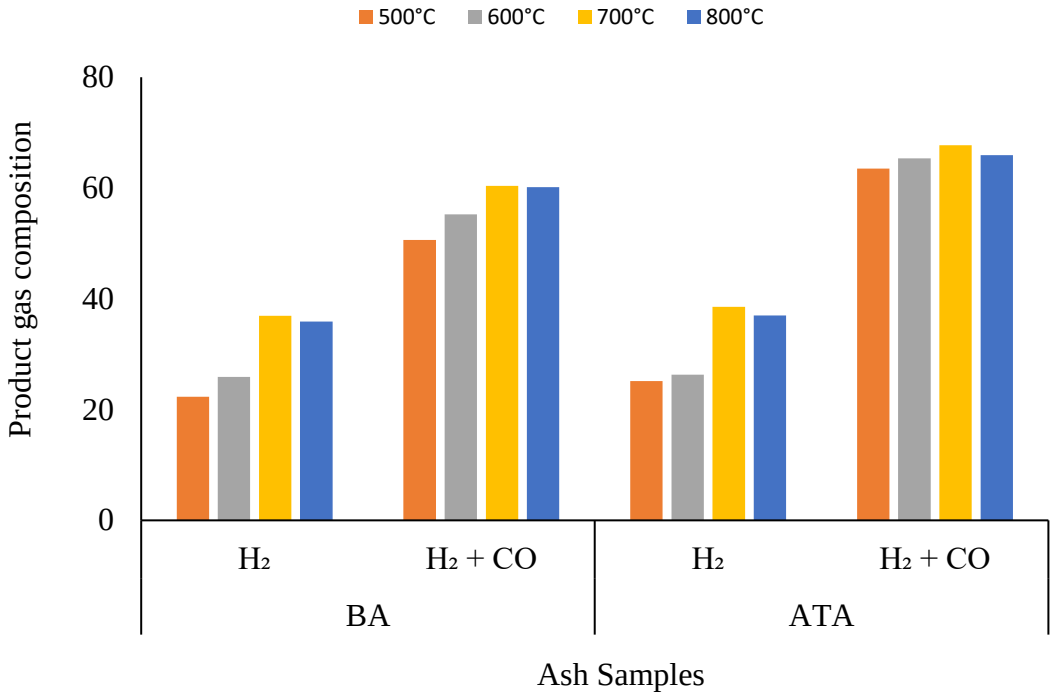

Figure 6: Effect of temperature on product gas composition

The effects of ash content on the production of syngas and hydrogen for both the incineration and acid treated ash are displayed in Figures 7 and 8, respectively. The yields of both hydrogen and syngas are far higher for the acid functionalized ash (ATA) compared to BA. The catalyst content reaches its optimum at about 0.67 wt%. Beyond this quantity there is a slight decrease in production of gaseous products. The result agrees with the findings of other researchers (Khan et al., 2014; Shahbaz et al., 2017). The hydrogen production was 38.53 vol% is slightly higher than that reported (37.13 vol%) for a similar catalytic steam gasification of biomass (Shahbaz et al., 2017) and 33.82 vol% for air gasification of empty fruit bunch (Mohammed et al., 2011). At optimum condition, the carbon conversion efficiencies was evaluated to be 43.76% and is very close to that obtained by Shahbaz et al. (2017). The carbon conversion efficiency is higher than that obtained in other studies; 41.94% (Khan et al., 2014) and 24% (Xu et al., 2005).

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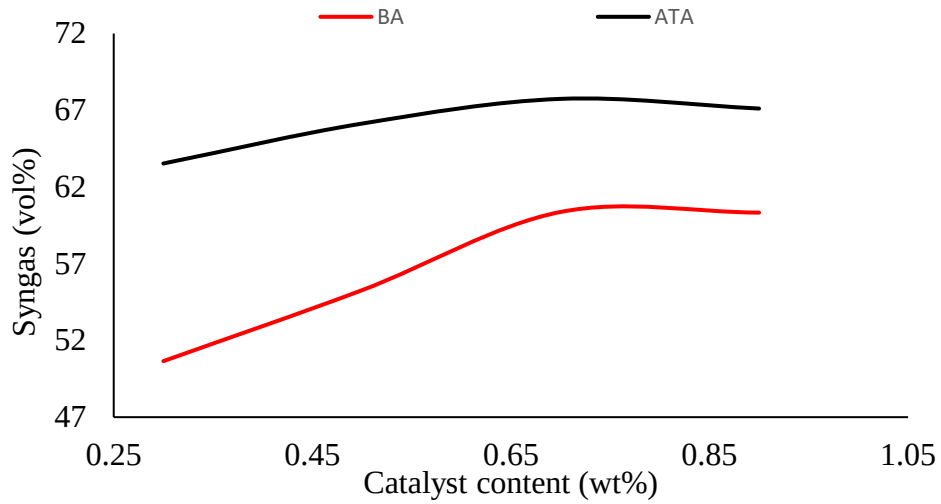

Figure 7: Effect of bottom ash content on syngas production

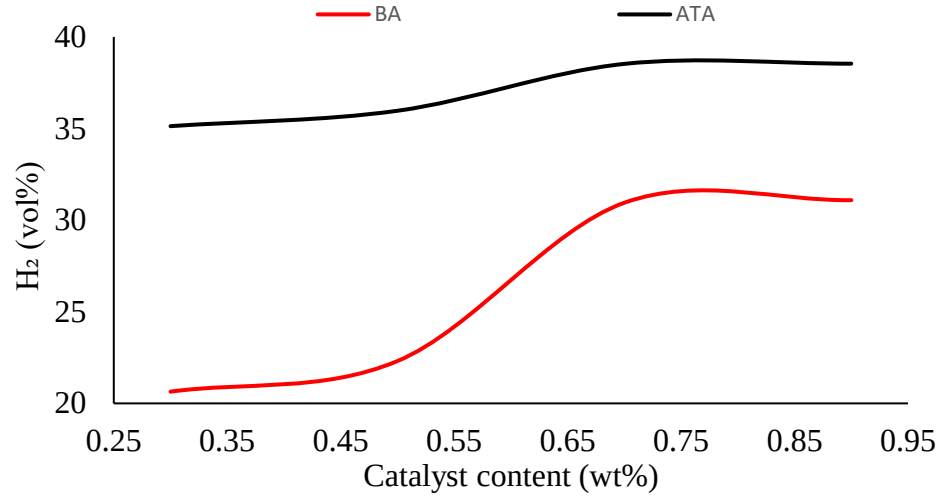

Figure 8: Effect of bottom ash content on hydrogen production

Conclusion

The optimum conditions obtained for the catalytic steam gasification of the MSW with ATA were a temperature of 684C, particle size of 0.84 mm, and 0.65 wt% catalyst content. At these optimized conditions in the TGA-MS setup, the maximum production of hydrogen and syngas is reported as 38.35 vol% and 66.96 vol%, respectively. The acid treated ash performed far beyond the original incineration ash with hydrogen and syngas production of 38.56 vol% and 67.74 vol% compared to 36.95 vol% and 60.37 vol% for the original ash. The process has a good carbon conversion efficiency of 43.76%.

Conflicts of Interest: Authors declare that there is no conflict of interest.

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