Environ Res Tec, Vol. 6, No. 3, pp. 189–195, September, 2023

Environmental Research and Technology
https://ert.yildiz.edu.tr - https://dergipark.org.tr/tr/pub/ert
DOI: https://doi.org/10.35208/ert.1210384

Research Article

Evaluating compost for hydrogen and methane rich gas production via supercritical water gasification

Eyup YILDIRIR[1,*], Nihal CENGİZ[2], Levent BALLICE[2]

[1]Department of Chemical Engineering, Faculty of Engineering, University of Uşak, Uşak, Türkiye
[2]Department of Chemical Engineering, Faculty of Engineering, Ege University, İzmir, Türkiye

ARTICLE INFO

Article history
Received: November 26, 2022
Revised: June 12, 2023
Accepted: August 1, 2023

Keywords:
Supercritical Water Gasification; Compost; Hydrogen; Methane

ABSTRACT

The compost produced from organic wastes (MSW, city market's wastes and wood dust) was selected to be processed via supercritical water gasification (SCWG) in order to produce gas product consisting of hydrogen and methane mainly. The effects of parameters such as temperature, reaction time and KOH as an additive were determined and around 55 vol.% of H_2 and CH_4 in the gas product was found after 30 min reaction time together with KOH, at 500 °C. The red mud catalysts did not improve the gasification yields even though they increased the calorific value of the product gas.

Cite this article as: Yildirir E, Cengiz N, Ballice L. Evaluating compost for hydrogen and methane rich gas production via supercritical water gasification. Environ Res Tec 2023;6(3):189–195.

INTRODUCTION

Utilizing organic wastes as a resource for clean energy and chemical feedstock production has been gaining much attention recently since the global municipal solid waste (MSW) production was recorded as 2.01 billion tonnes per year according to a report published in 2018 by Worldbank. Unfortunately, around 33% of this waste is not managed properly and creating risks to the environment [1]. Currently the main disposal method of wastes is landfilling, as 37% of waste produced is landfilled globally. 33% of total waste is managed by open dumping which is commonly seen in economically low developed countries. The share of recovery through recycling and composting remains at 33% and 11% of the waste is incinerated for energy production [1]. Turkey as a developing country produced 32.2 million tons of MSW and 67.2% of it was landfilled to controlled sites, and 20.2% was delivered to open dumping sites in 2018. While the recovered waste amount had a share of 11.9%; 0.38% was composted showing that Turkey needs new routes to deal with the MSW to maintain an environmentally and economically more sustainable waste management [2].

Composting is a biological process to convert organic wastes such as sewage sludge, municipal solid waste etc., into soil amendments. By definition, it is homogenization of mixed organic wastes by means of thermophilic process at a temperature range of 45 to 65 °C [3,4]. The final products after the process have nutrients for the soil, humic acid and metals together with high moisture content around 40 to 60 wt.% [5]. There are reports in the literature criticizing the usage of compost as soil amendment since it has pathogens and heavy metals which are hazardous for the humans. Although vermicomposting, which is the stabilizing the

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***Corresponding author.**
*E-mail address: eyup.yildirir@usak.edu.tr

This paper has been presented at Sixth EurAsia Waste Management Symposium (EWMS 2022)/İstanbul, Türkiye / 24–26 October 2022.

Published by Yıldız Technical University Press, İstanbul, Turkey

organic wastes or compost by the digestion of earthworms and micro-organisms at 35°C reduce somewhat human pathogens, regulations by the governments limit the usage of compost and vermicompost due to their hazard to human health [6]. Therefore, if new evaluation methods were suggested, compost as a cheap product gathered from the MSW could be a valuable feedstock and a new route for waste management.

As a thermo-chemical conversion method, supercritical water gasification process could be applied to compost to produce H_2 and CH_4 rich gas fuel. The high-water content of the compost, therefore could participate in the production of gas products since water undergoes tremendous changes when the conditions reach critical point (374°C, 22.1 MPa). This will prevent a costly pre-drying process which will be required for a pyrolysis or conventional gasification of compost to produce gas fuel.

In this study, the compost produced from organic wastes (MSW, city market's wastes and wood dust) was selected to be processed via supercritical water gasification (SCWG) in order to produce gas product consisting of hydrogen and methane mainly. Its being waste driven material and its cost around 0.4 €/kg make compost a favourable feed for energy fuel production since composting could be regarded as a homogenization process for the feed. In addition, SCWG process eliminates the costly drying process therefore the high moisture content becomes an advantage. The effects of parameters such as temperature, reaction time, particle size and solid/water ratio were investigated. Red mud as another waste material was activated and used as catalyst together with KOH to determine their effects on the product yields.

EXPERIMENTAL

Samples

Compost sample was purchased from a local company, from Izmir, Turkey. The compost originally contained around 65 wt.% of water, therefore it was air dried, sieved and separated to 3 different mesh sizes for determining the effect of particle size. Red mud was supplied by Alumina Plant in Seydisehir, Turkey, as a sludge and it was filtered and dried at 110 °C. Original red mud contained Fe_2O_3 (37.7%), Al_2O_3 (17.3%), SiO_2 (17.1%), Na_2O (7.1%), CaO (4.5%), and TiO_2 (4.8%). Activated red mud was prepared by placing 600 mL of red mud slurry (~30 % solid content) into a 1 L beaker and heating up to 95 °C while mixing. The pH of the slurry adjusted to be 4-6 by adding 35-37 % of HCl (d=1.18 g/cm^3) dropwise and finally at 95 °C it was held for one hour. NH_3 (25 %, d=0.91 g/cm^3) was added into mixture until obtaining a pH of 8. The mixture was heated further for 1 hour at 95 °C and then filtered and washed. Finally, the filter cake was dried at 110 °C overnight, calcined at 500 °C for 2 hours. KOH was purchased from Sigma-Aldrich.

Experimental Set-up

The supercritical water gasification experiments were performed in a batch autoclave reactor system where the details were given in elsewhere [7]. 1.11 g of compost along with 10 ml of deionized water were fed to the reactor, after the particle size and intended water content of the feed was adjusted. The reactor then purged with nitrogen, sealed and heated with a heating rate of 12 °C/min to the designated temperature. When the set temperature reached, the temperature kept constant for the specified reaction time. After completion of the gasification, the reactor was cooled to room temperature by means of a fan. The gas product was collected with a gas-tight syringe and its volume was measured. The reaction effluent was filtered, washed with deionized water and the remaining char was dried and its weight were determined. A sample from the final gas product was injected to HP 7890 A gas chromatography device which is equipped with TCD, FID, TCD detectors connected in series, after each experiment to determine the gas composition. The gross calorific value of gas products was calculated according to the equation (1)

$$HHV = \sum_{i=1}^{n} X_i HHV_i \tag{1}$$

Where i,.., n=each combustible gas in the product mixture and Xi denotes for mass fraction of each gas in the product mixture. HHVi is the higher heating value of each gas [MJ/kg] (values taken from [8]).

RESULTS

Supercritical water gasification of compost was performed and the resulting gas composed of hydrogen, methane and carbon dioxide mainly. Small amounts of carbon monoxide and hydrocarbon gases (ethane, ethylene, propane and butane) which were referred as C_2-C_4 gases, were also produced during SCWG of compost. The effects of temperature, reaction time, particle size, solid content of feed and catalyst were investigated to determine the optimum reaction conditions in order to produce gas fuel with high calorific value.

FTIR spectrum of compost given in Figure 1 reveal that functional groups originated from carboxylic acids (humic substances) exist in its structure. While broad band observed at 3278 cm^{-1} could be attributed to H bonded OH groups, peak around 2920 cm^{-1} could represent C-H stretch of aliphatic structures within the compost. The peak between 1620 and 1660 cm^{-1} may indicate the C=O vibration of bonded conjugated ketones, carboxylic acids and esters, and the C=C vibration of aromatic components. Finally, broad peak at 1032 cm^{-1} belonging to polysaccharides, can also present Si–O stretch of clay minerals and Si– O–Si vibration of silica since clay minerals are also characterized by a huge band around 1030 cm^{-1} [9,10].

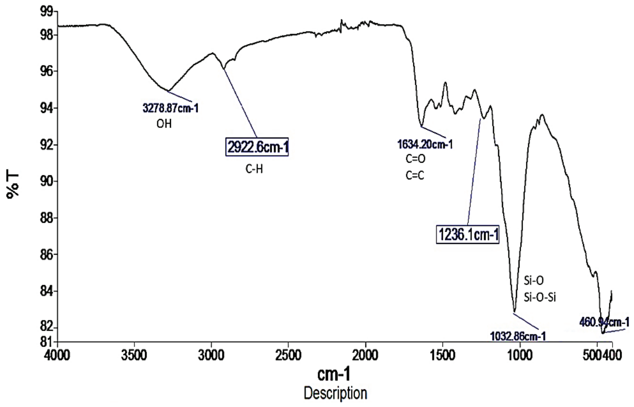
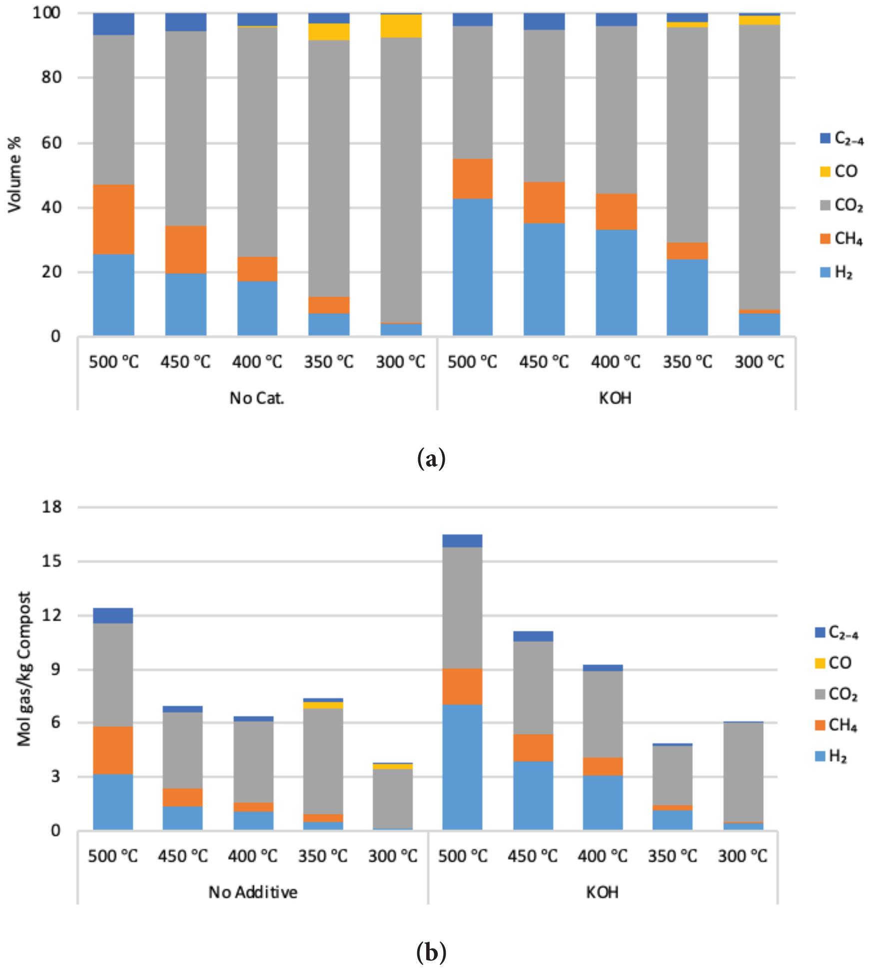


Figure 1. FTIR spectrum of raw compost.

The ash content of compost was determined by oxidizing at 700 °C for 2 hours in a furnace. It was found to be 27.5, 15.4 and 31.1 wt.% for particle sizes of x<1.18, 1.18<x<2.35 and 2.35<x<3.45 mm, respectively.

The Effects of Temperature

Temperature was the most influential parameter during SCWG process, as the gas composition and product yield greatly changed with the increasing temperature as shown in Figure 2a and 2b. At 300 °C and 350 °C, 89 vol.% and 79 vol.% of the product gas consisted of CO_2, respectively. In hydrothermal medium, at low temperatures initially decarboxylation reactions of intermediates resulting from hydrolysis of organics occur, which is the main source of CO_2 [11]. H_2 and CH_4 yields increased to 3.2 mol/kg and 2.6 mol/kg compost, respectively, as the temperature reached 500 °C. Methanation of CO_2 and CO, and water-gas shift reactions become dominant when the supercritical conditions of water achieved [12]. Although CO in the product gas was found at lower temperatures, with the aforementioned reactions' increasing selectivity at higher temperatures, CO was not detected at temperatures above 450 °C. KOH additions further increased H_2 yields as it was 7 mol/kg compost at 500 °C, since alkalis promote water-gas shift reaction. In addition, above critical point, free-radical reaction mechanism governs the decomposition of biomass so more H_2 production is observed [13].



(a)

(b)

Figure 2. (a) Product gas composition and (b) yield during SCWG of compost at various temperatures.

The Effects of Reaction Time, Particle Size and Water Content of the Feed

The effect of time on the gas composition and yield was investigated at 0, 30, 60 and 90 minutes of reaction times at 500 °C, and the results are given in Figure 3a and 3b.

The amount of total produced gas during SCWG of compost ascended with the increasing reaction time. At 0-minute reaction time, 7.6 moles of gas was obtained per kg of compost processed while it increased almost thrice the amount and reached 21.5 moles at 90 minute reaction time. The gas composition was improved with the increasing reaction time as well, since CO_2 was dropped to 38.1 vol.% yielding 61.9 vol.% combustible gases at the end of 90 minutes. The CH_4 yield increased gradually until the 60 minute of reaction time while it boosted to 6.7 from 2.3 moles when the time increased to 90 minutes. H_2 too, increased steadily with the increasing reaction time, which could be the results of methanation of CO_2 (1) and water-gas shift reaction (2);

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{2}$$

The effect of particle size was also investigated at 500 °C and the results represented in Figure 4a and 4b.

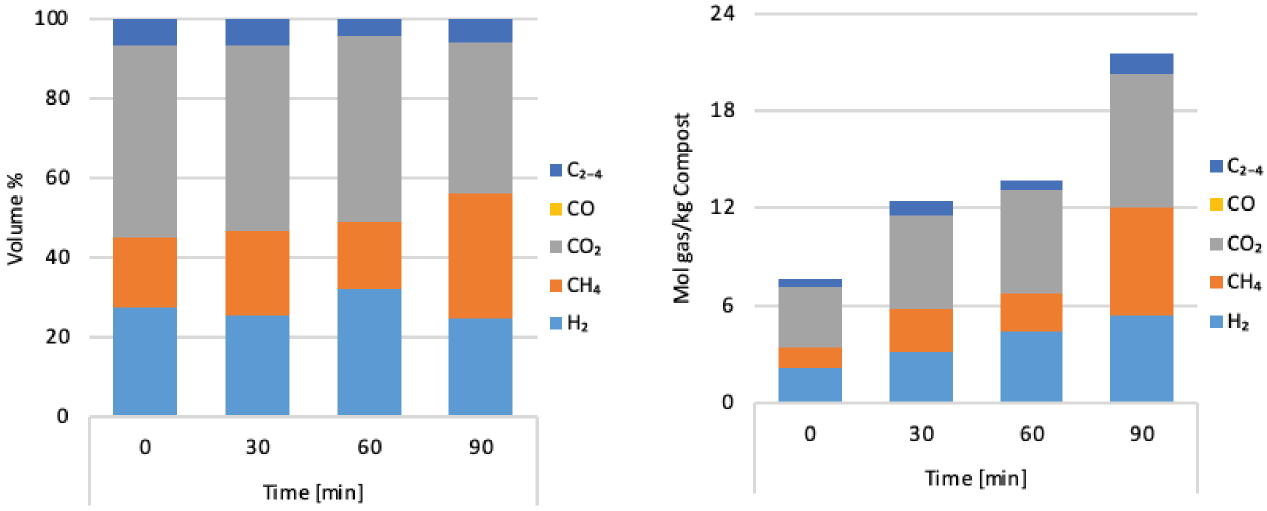
The results revealed that mid-sized particles experienced slightly higher product yields and gas composition. The ash content of mid-sized particles was determined to be the lowest, therefore it contained more volatiles compared to other particle sizes. As a result, total gas production was slightly increased. Nevertheless, this could be an indication of the homogeneous structure of compost consisting of various kinds of wastes and biomass, even though in general the studies revealed that the changing the particle size affects less during SCWG process compared to other parameters [14].

The effect of water content of compost was studied at three different concentrations of 10, 20 and 30 wt.% dry compost and Figure 5a and 5b reveals the results. The sum of H_2 and CH_4 in total in the product gas was around 42 vol.% in all concentrations while the share of H_2 increased with the increasing concentration. This might be due to water-gas reaction, since CO composition was 0 vol.% at 10wt.% while it was increased to 6.8 vol.% at higher concentrations. Water-gas shift reaction is an equilibrium reaction, therefore the increase in CO composition was balanced with the less water content of the feed, as a result the increase in H_2 composition was limited. In addition, less moles of gas per kg of feed was produced, indicating that the higher feed concentration decreased the gasification efficiency. This might be a result of "cage effect", creating a limitation in the reaction rates caused by the water molecules [15].

The Effects of Catalysts

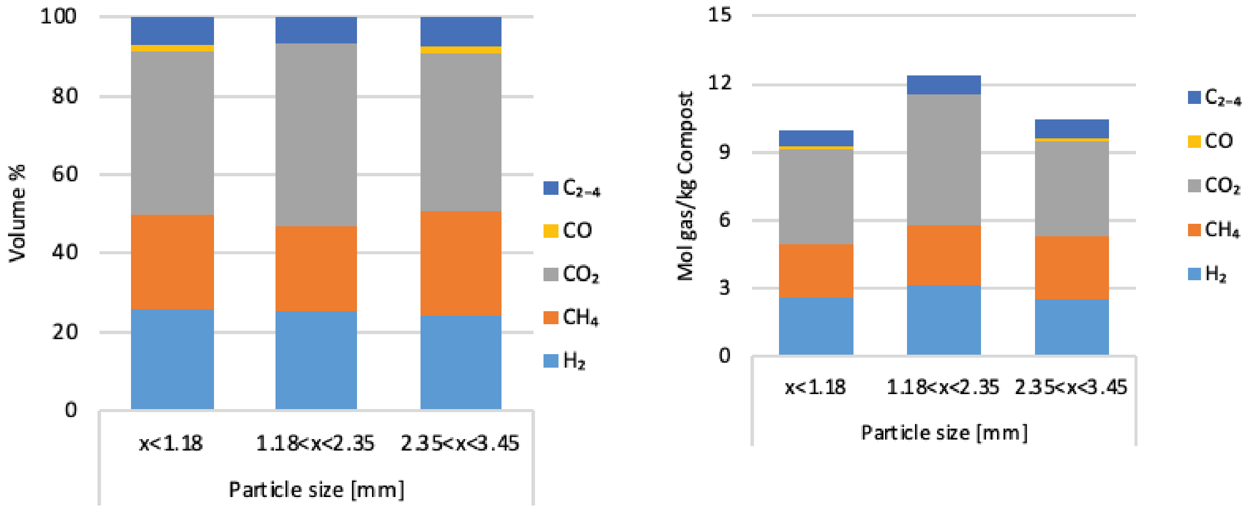
The catalytic effects of original red mud (ORM), activated red mud (ARM) and KOH were investigated and the results are shown in Figure 6a and 6b. The red mud catalysts yielded more C_2-C_4 and CO, whereas CO was not detected in the presence of KOH. The red mud contains metal oxides which are affective in oxidation of biomass in hydrothermal medium [16]. CO would be a partial oxidation product of compost gasification, while the red mud catalysts slightly reduced H_2 composition and increased CO_2 composition in the product gas.

The addition of KOH promoted the water-gas shift reaction, hence H_2 increased from 25.5 vol.% to 42.6 vol.%.



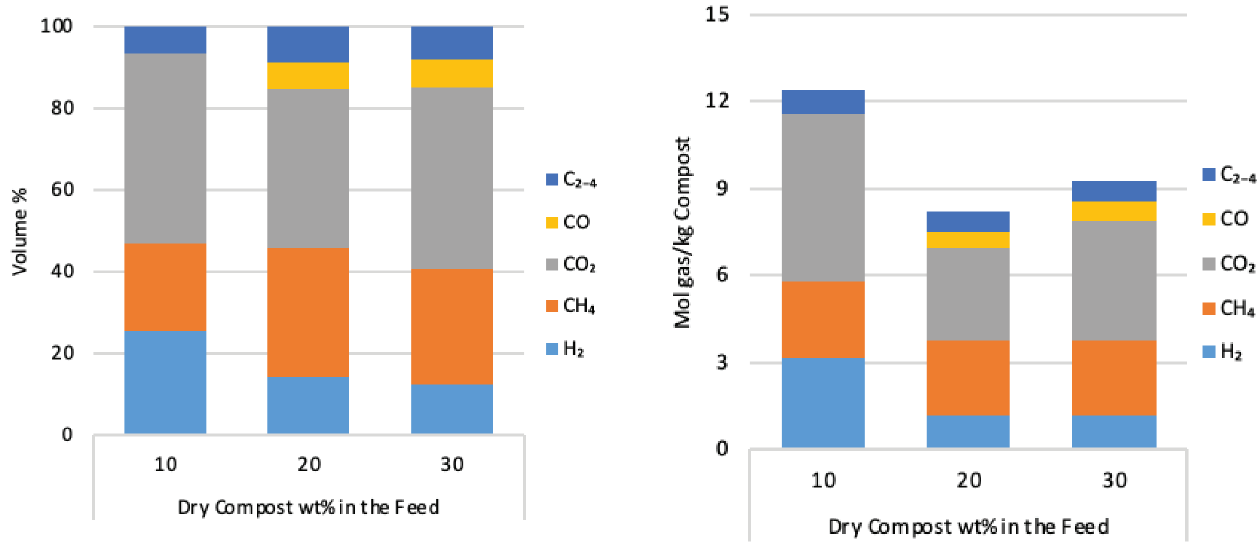
(a) (b)

Figure 3. (a) Product gas composition and (b) yield during SCWG of compost at various reaction times at 500 °C.



(a) (b)

Figure 4. (a) Product gas composition and (b) yield during SCWG of compost at various particle sizes at 500 °C.

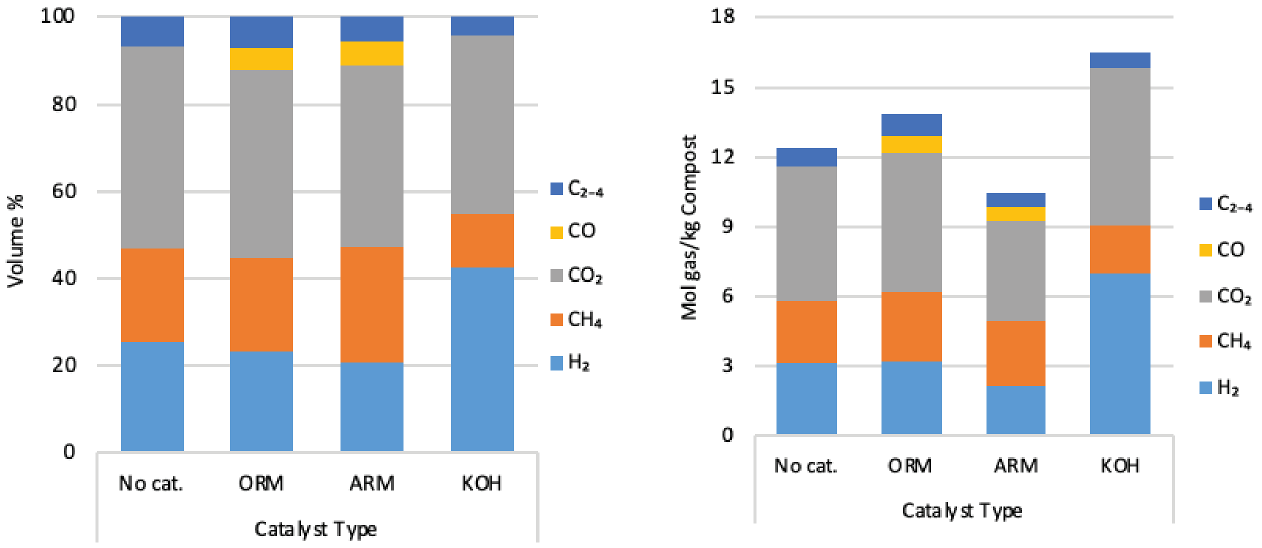


(a) (b)

Figure 5. (a) Product gas composition and (b) yield during SCWG of compost at various dry solid concentrations at 500 °C.

The yields of gases were affected via catalyst presence, whereas the highest total moles of gas per kg of compost was achieved as 16.5 mol/kg in the presence of KOH. ORM addition did not increase remarkably while ARM addition decreased the total gas produced. The slight or negative effects of red mud catalysts could be attributed to compost structure, since naturally compost may contain some heavy metals [17].

On the other hand, the calorific value of the product gas was the highest when SCWG of compost performed with 10 wt.% dry compost at 500 °C for 30 minutes. However, as mentioned before, when the solid concentration of feed increased, gasification yield decreased due to cage effect. In the end, a product gas with 20.1 MJ/Nm^3 calorific value obtained without any catalysts, at 90 minutes of reaction time. Although KOH increased H_2 yield, since volumetric energy density of hydrogen is low, the calorific value of the



(a) (b)

Figure 6. (a) Product gas composition and (b) yield during SCWG of compost with different catalysts at 500 °C.

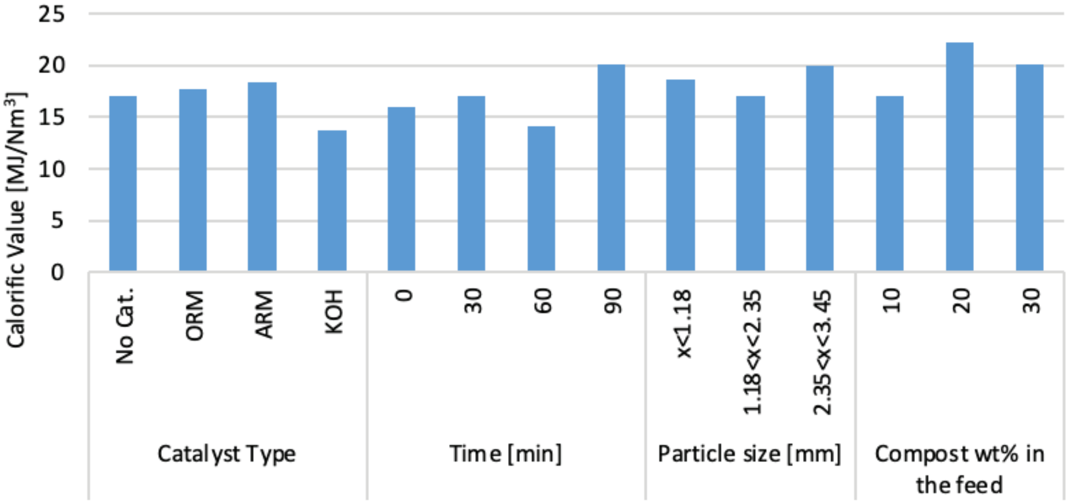


Figure 7. Gross calorific values of product gas obtained during SCWG of compost at different conditions at 500 °C.

product gas was not improved. If the aim is producing a specific gas component, then a catalyst with a high selectivity should be chosen.

CONCLUSION

Supercritical water gasification of compost was evaluated to determine the optimum conditions. High H_2 yield was achieved in the presence of KOH. In addition, around 55 vol.% of H_2 and CH_4 in the gas product was found after 30 min reaction time together with KOH, at 500°C. Although the red mud catalysts increased the calorific value of the product gas obtained, the total gas yield did not improve. The product gas with the highest calorific value was gathered as 20.1 MJ/Nm³ when the reaction time increased to 90 minutes. While the change in particle size did not affect the gasification yields, increasing the amount of dry solid in the feed dramatically decreased the efficiencies.

ACKNOWLEDGMENT

We are thankful to Mr. Gürsel Serin for the assistance during the experiments and analysis.

CONFLICT OF INTEREST

The authors declare no potential conflicts of interest regarding the research, authorship and/or publication of this article.

DATA AVAILABILITY

The data used to support the findings of this study are included within the article.

AUTHOR'S CONTRIBUTIONS

All authors are contributed equally to bring out this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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