Sustainable Chemical Engineering
http://ojs.wiserpub.com/index.php/SCE/

Research Article

Valorization of Municipal Solid Wastes and Paper Mill Sludge Through Their Steam Co-Gasification for the Production of Energy Carriers Rich in H_2 and Lean in Greenhouse Gas Emissions

D. Vamvuka*, **N. Papanagiotou**, **A. Ntounta-Marek**

School of Mineral Resources Engineering, Technical University of Crete, Greece
E-mail: dvamvouka@tuc.gr

Abstract: This study aimed to explore the valorization of municipal solid wastes and paper mill sludge through their steam co-gasification, for the production of energy carriers rich in H_2 and lean in CO_2 greenhouse gas emissions. Waste concrete fines and paper sludge ash were investigated as CO_2 sorbents and Na_2CO_3 as a catalyst. The experiments were carried out in a fixed bed reactor coupled with a thermal analysis-mass spectrometer unit. The analysis encompassed various aspects including the composition of the resulting gas and its heating value, H_2 and syngas yield, fuel conversion and energy recovery, under different operating conditions. When quarry dust was used to capture CO_2 at a calcium-to-carbon molar ratio of unity and 750 °C, H_2 in the product gas was 75.7 mol%, molar ratio H_2/CO was 7.19 and syngas yield was 0.65 m^3/kg. When the Na_2CO_3 catalyst was added at a loading of 20%, H_2 in the gas mixture was increased to 81%, the syngas yield to 2.82 m^3/kg and conversion of fuel was complete. When paper sludge ash was used as CO_2 sorbent a higher amount of CO_2 was captured, however the selectivity towards H_2 production was lower. The performance of Na_2CO_3 catalyst was better in the presence of quarry dust sorbent.

***Keywords*:** municipal solid waste, paper sludge, steam gasification, CO_2 capture, catalysts

1. Introduction

The increasing global production of municipal solid wastes (MSW) presents a significant challenge, with current estimates indicating that approximately 24 billion tons of wastes are generated annually, and a rise of 73% in 2050.[1,2] This upward trend is largely driven by factors such as population growth, urbanization and changing consumption patterns, which create pressing needs for effective waste management strategies. The accumulation of MSW is hazardous to the environment and living beings. Soil and water contamination, air pollution and public health risks, associated with landfilling,[2,3] further underscore the urgency of addressing this waste crisis.

In response to these challenges, many countries are actively promoting initiatives aimed at reducing the reliance on landfills. These initiatives include enhanced recycling programs using mainly plastics and metals to produce new products or composting, where after biodegradation of organic waste compost and bricks are produced.[3,4] However, in view of increasing energy demands worldwide and the need for renewable energy sources, MSW which is characterized by a high proportion of organic materials, presents substantial opportunities as a feedstock for sustainable energy production, through waste-to-energy conversion technologies.[4] These technologies, the most common of which are incineration, pyrolysis and gasification, are aligned with the goals of a circular economy with a positive impact on

DOI: https://doi.org/10.37256/sce.6120256123

economic growth.[2-4]

Incineration of MSW is a suitable method for reducing waste, while generating energy and it is economical for large scale applications.[5] However, it has the disadvantages of emitting toxic gases, dioxins and heavy metals.[2,6] On the other hand, gasification stands out as a more environmentally friendly alternative to traditional incineration, due to oxygen-free environment, has lower operational and maintenance costs and diverse use of products.[2,4] During this process MSW can be converted to chemicals and syngas, mainly consisting of H_2 and CO, which can be used in boilers, engines, turbines, fuel cells to produce electricity, or for heating.[2,3,5,7,8] Steam gasification enhances the yield of H_2 gas as compared to air gasification and in combination with pre-pyrolysis techniques increases the reactivity of the resulting char significantly, while also addressing challenges related to tar production, which can hinder the efficiency of the process.[4,6,9]

Despite the promising potential of gasification technologies, research specifically focusing on the gasification of MSW remains relatively limited. Most existing studies have primarily examined the use of air as the gasifying medium, often leading to lower heating values and reduced efficiency in energy recovery. A sorting strategy, based on elemental composition, was proposed to optimize the air gasification process. The yield of syngas, the cold gas efficiency, the lower heating value of syngas and H_2/CO were increased by 37.1%, 39%, 2.2% and 8.8%, respectively.[5] Co-gasification of MSW with agricultural or forest biomass at a blending ratio of 40% MSW increased the H_2 content of product gas, which attained a higher heating value of 6.7 MJ/m.[3,10] In the presence of waste marble powder, H_2 and CO concentrations were promoted to 6.65% and 10%, respectively, whereas the CO_2 concentration was reduced to 0.2%.[2] The gasification of MSW under an atmosphere of carbon dioxide has been studied by several investigators,[7,11,12] including the authors,[13] however research on MSW steam gasification remains scarce. A thermogravimetric-mass spectrometry (TG-MS) analysis and a kinetic study were performed for the thermal decomposition of some representative components of MSW under steam.[6] The use of calcium-based compounds was found to reduce the amounts of CO_2 and tar in the generated gas.[12,14] In the case of a food waste, a significant increase in H_2 production rate from 55 kmol/h to 70.5 kmol/h was observed, as CaO/feedstock ratio increased.[15] On the other hand, when gypsum was added at equal mass portions 1 : 1 to steam gasification of MSW at 800 °C, the syngas yield was found to be reduced by 50%.[16] The production of low-carbon H_2 from MSW is a feasible industrial solution.[17]

Hydrogen is a renewable energy carrier with a high energy content of 122 MJ/kg, making it suitable for various applications, including district heating, power generation and transportation. Hydrogen production reached 97 Mt in 2023[18] and its demand is projected to increase in the coming decades. Renewable, carbon-neutral feedstocks, like biomass, could be a sustainable hydrogen source. On the other hand, global energy-related CO_2 emissions grew by 1.1% in 2023, reaching a new record high of 37.4 billion tonnes.[19] This increase in one of the major greenhouse gases, which presents long-lasting environmental and health effects, motivates the development of renewable energy strategies for sustainable energy forms.

An innovative approach proposed in this study is the utilization of waste materials, generated in high quantities around the world, for capturing CO_2 emissions from the thermochemical conversion of MSW to energy carriers rich in H_2. Thus, the study aims to fill the research gap in the steam gasification of untreated MSW, which is associated with environmental risks worldwide, as well as to explore the valorization of paper sludge produced from paper mills, through its co-gasification with MSW for energetic uses, in order to contribute to the reduction of energy consumption and carbon emissions of the papermaking industry.[20] This process has not been studied before. Only mixtures of paper-mill sludge with sewage sludge have been reported to produce syngas with low H_2 percentage of 2.6-4.1% after gasification in air.[21] Waste concrete fines, a byproduct of construction and demolition activities from all modern economies, primarily composed of calcium carbonate, were selected as CO_2 sorbent, given the limited space available for landfills and the environmental impacts of waste disposal. For example, in Greece about 10 Mt of quarry dust is annually produced.[22] Also, another waste, paper sludge ash resulting from the thermochemical processing of paper sludge, which is rich in calcium carbonate (due to its high content naturally occurring in wood from which paper sludge is generated), was investigated for its potential as another novel in situ CO_2 adsorbent from the gasification process. Additionally, the work focused on the effect of sodium carbonate as a catalyst, based on previous results by the authors,[23] showing improved system performance and enhancement of H_2 yield. The experiments were carried out in a fixed bed reactor coupled with a thermal analysis-mass spectrometer unit. The analysis encompassed various aspects including the composition of the resulting gas and its heating value, H_2 and syngas yield, fuel conversion and energy recovery, under different operating conditions, such as temperature, type of CO_2 sorbent and sorbent-to-fuel ratio and catalyst loading. Through these investigations, the goal is to gain a deeper understanding of how MSW can be effectively transformed into valuable energy resources. Ultimately, these findings will contribute to the development of more sustainable waste management practices and energy recovery strategies, aligning with global efforts to promote environmental sustainability and reduce reliance on fossil fuels.

2. Experimental section

2.1 *Preparation of raw materials and gasification feedstocks*

The raw materials used in this study included MSW sourced from the DEDISA solid waste management company in West Crete and paper mill sludge (PMS), provided by a private company in Northern Greece. MSW was collected monthly over a one-year period from the facility, after metals, plastics and glasses were removed. The composition of MSW consisted of approximately 50% food waste, 30% paper, 12% wood and 8% inert materials. Both materials were dried at 110 °C in an oven and then processed using a Pulverisette 15 cutting mill, to reduce the particle size to under 1 mm.

Quarry dust (QD), which was collected after drying and removing fine aggregates from mortar production, was selected for CO_2 capture during the gasification tests. This material was provided by Finomix AE in West Crete. Additionally, PMS ash was also used as CO_2 adsorbent (specific surface area 5,172 cm^2/g and 3,110 cm^2/g, for QD and PMS ash respectively, as determined by the industry, according to the Blaine method). Both materials with particle size smaller than 100 μm were heated in air to 950 °C for 2 h in a muffle furnace. After calcination, they were placed in a glass container in an atmosphere saturated with water and left for at least one week to convert the CaO component into the active CO_2 sorbent $Ca(OH)_2$.[24] Na_2CO_3, sourced from Sigma-Aldrich, was used as a catalyst. The catalyst was mixed with the gasification feedstocks in weight ratios of 10 : 90 and 20 : 80, varying between 0.1 gMe/gC and 0.5 gMe/gC in char.[25] These mixtures were stirred at room temperature for 24 h, using the incipient wetness method, in order to improve catalyst dispersion on char surface, and subsequently dried at 110 °C in an oven.

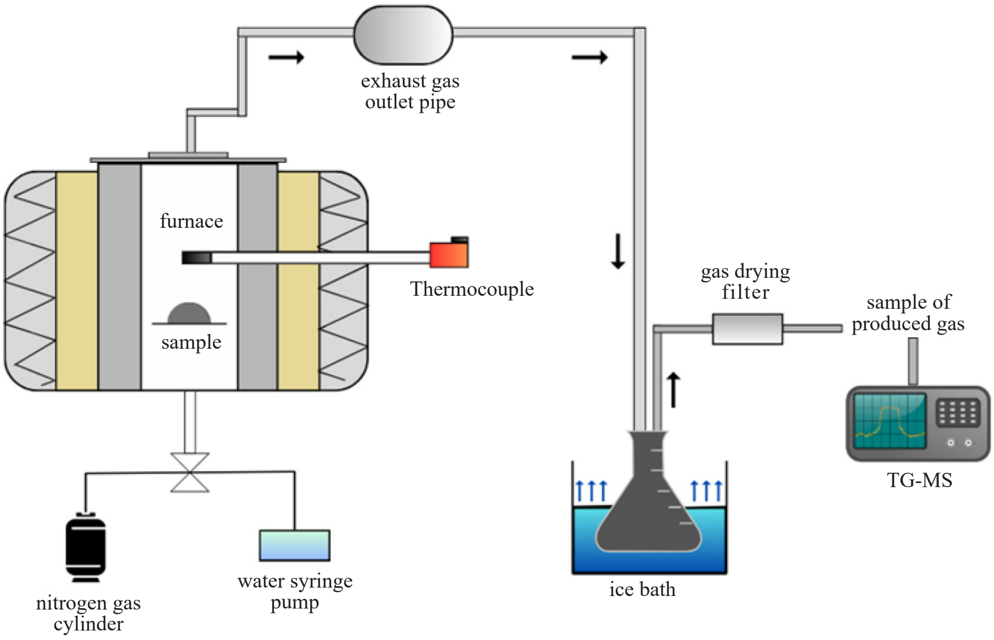

Figure 1. Scematic diagram of experimental set up

Before conducting gasification experiments, the MSW and PMS samples were devolatilized up to 600 °C in a fixed bed reactor system, as illustrated in Figure 1. Pyrolysis gases were analyzed using a thermogravimetric/differential thermogravimetric-mass spectrometry (TG/DTG-MS) unit, whereas condensates were centrifuged to separate bio-oil. Quantification was carried out using high-purity standard gases in argon and the average heating value of the gaseous mixture was determined. The solid pyrolysis products, biochars, were weighed at the end of the experiment, and a mass balance was conducted. Biochars were stored for subsequent analyses and testing.

2.2 *Characterization of materials*

Chemical analyses of both raw fuels and biochars were performed in accordance to the CEN/TC335 European standards. For the determination of moisture, volatile matter and ash content, high-temperature programmable furnaces were utilized. Ultimate analysis was conducted using a Flash 2000 CHNS analyzer, while a Leco AC-300 bomb calorimeter was employed to measure calorific value. The specific surface area was measured with an Autosorb 1Q-C-MP analyzer from Quantachrome, using the Brunauer-Emmett-Teller (BET) method, for relative pressures ranging from 0.015 to 0.32.

Elemental analysis of the bio-oil obtained from pyrolysis experiments was carried out using the CHNS analyzer. The higher heating value (*HHV*) of the oil was deduced using the following equation.[26]

$$HHV_{\text{bio-oil}} = 0.3383C + 1.422\left(H - \frac{O}{8}\right)\ (\text{MJ/kg}) \tag{1}$$

MSW and PMS ashes, along with the QD sorbent, were analysed for their mineralogical and chemical compositions. Mineralogical phases were identified using a D8 Advance X-ray diffractometer (XRD), from Bruker X-ray analysis systems and phase identification was performed with the Crystallography Open Database (COD), in combination with DIFFRAC plus software. The inorganic elements present in the materials were determined with a S2 Ranger/Energy Dispersive X-ray Spectroscopy fluorescence spectrometer (XRF), from Bruker X-ray analysis systems and the results were expressed as oxides.

All the above analyses were the average of at least two replicates, which were conducted in order to assure the reproducibility of the results.

2.3 *Gasification experiments under a steam atmosphere*

Each biochar produced from the fuels in the previous step was placed in the high-temperature reactor, either alone or mixed with a CO_2 sorbent, at Ca/C molar ratios of 1 or 2 depending on the fuel and adsorbent stoichiometry, as typical ratios used in relevant studies[2,12,14-16] or with a Na_2CO_3 catalyst at specific ratios. The reactor was heated in a nitrogen atmosphere to 600 °C, as described earlier. Once the target temperature was reached, de-ionized water was continuously delivered via an automatic syringe pump and converted into steam, which flowed uniformly in the reactor. The steam-to-biochar mass ratio was maintained at 3 to optimize hydrogen production, as suggested by previous findings.[23] The final gasification temperature ranged from 650 °C to 900 °C, with a holding time of 30 min.

The resulting gaseous products were cooled and dried utilizing a cold trap and a silica gel filter. Sampling was carried out at each temperature using a dedicated Polytetrafluoroethylene (PTFE) Luer Lock gas syringe. Two replicate samples were analyzed both qualitatively and quantitatively using the TG/DTG-MS, with the results averaged. The unit was run under high-purity argon of flow rate 35 mL/min. Gases were introduced into the MS through a transfer line, heated to 200 °C to prevent condensation. The ions separated according to their mass-to-charge ratio were detected by a Secondary Electron Multiplier (SEM). Calibration tests were carried out under the same experimental conditions and calibration factors were calculated using high-purity gases of known concentrations in argon, taking into consideration the intensity of fragments from the compounds analyzed at each mass-to-charge ratio. The operating conditions (high-purity argon and calibration gases, fused silicon capillary heated to 200 °C transfer line, 82 eV of SEM, atomic mass range 1-400, Pyris v3.5 software and Quadstar 422 software) and the methodology are detailed in a previous investigation.[23]

Syngas V_{syn} and hydrogen Y_{H_2} yields were calculated by equations:

$$V_{\text{syn}} = x_{\text{syn}} \times V_{\text{g}} \tag{2}$$

$$Y_{H_2} = x_{H_2} \times V_g \tag{3}$$

where x_{syn}, x_{H_2}, the volume fractions of syngas and hydrogen in product gas and V_g the total volume of gas (m^3).

Energy recovery (ERE) was derived as follows:

$$ERE = \frac{GY \times HHV_g}{HHV_b} \tag{4}$$

where GY the total gas yield (m^3/kg) and HHV_g, HHV_b the higher heating values of gas (MJ/m^3) and biochar (MJ/kg), respectively.

3. Results and discussion

3.1 *Characterization of raw materials and pyrolysis products*

The proximate and ultimate analyses, the calorific value and the specific surface area of MSW and PMS raw fuels are presented in Table 1. MSW was quite rich in volatile matter and its ash content was half the one corresponding to PMS material. The higher carbon and hydrogen contents of MSW sample as compared to PMS, in conjunction with its lower amount of ash, resulted in a higher calorific value. The concentration of nitrogen of both fuels was considerable, revealing some emissions during thermal treatment such as NH_3, however the concentration of sulfur was negligible. The specific surface area, varying between 0.4 m^2/g and 1.6 m^2/g was low and within the range reported for similar materials.[1,4] These low values are most probably associated with the high ash content of these fuels.

Table 1. Characterization of raw fuels (% dry)

Sample	MSW	PMS
Volatile matter	73.1	47.5
Fixed carbon	1.4	1.8
Ash	25.5	50.7
C	38.4	23.2
H	5.8	2.9
N	1.4	1.6
O	28.6	21.5
S	0.3	0.1
HHV (MJ/kg)	16.6	8.4
Specific surface area (m^2/g)	0.4	1.6

The chemical composition of MSW and PMS ashes and that of QD material is illustrated in Figure 2. Both fuel ashes were rich in calcium and silicon compounds. PMS ash presented significantly higher concentrations of CaO, SiO_2 and Al_2O_3 and its CaO content exceeded the value of 53%, due to the high concentration of calcium naturally found in wood from which PMS was generated. Furthermore, Figure 2 shows that 94.5% of QD material consisted of CaO.

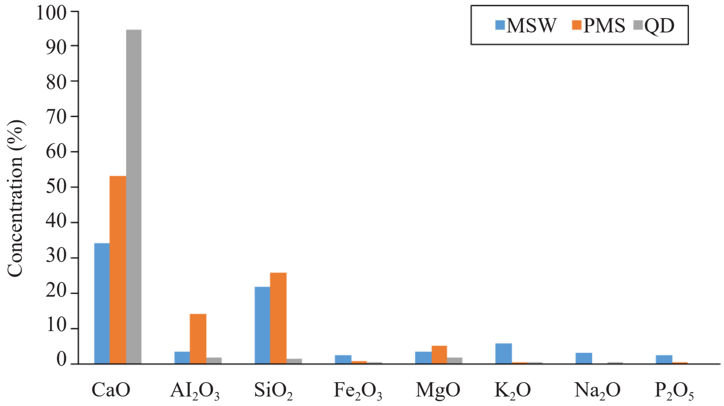

Figure 2. Chemical composition of MSW and PMS ashes and QD material

The mineralogical analyses of the ashes and QD sorbent, presented in Table 2, are in accordance with the chemical analyses. Calcium and silicon in these ashes were mainly incorporated in calcite and quartz minerals. In MSW ash smaller amounts of calcium occurred in the forms of anhydrite, portlandite and hydroxylapatite, whereas in PMS ash silicates talc and clinochlore were identified in low contents. QD after calcination and saturation with water was principally transformed to portlandite, as verified by the XRD analysis. Corresponding XRD spectra are provided in Figure A1.

Table 2. Mineralogical analysis of fuel ashes and QD material

Mineral phases	MSW	PMS	QD
Quartz SiO_2	+++	++	+
Calcite $CaCO_3$	+++	+++	+
Anhydrite $CaSO_4$	+		
Portlandite $Ca(OH)_2$	+		+++
Muscovite $KAl_2(Si_3AlO_{10})(OH)_2$	+		
Microcline $KAlSi_3O_8$	+		
Hydroxyapatite $Ca_5(PO_4)_3OH$	+		
Aphthitalite $NaK_3(SO_4)_2$	+		
Sylvite KCl	+		
Talc $Mg_3Si_4O_{10}(OH)$	+	+	
Clinochlore $(MgAlFe)_6(SiAl)_4O_{10}(OH)_8$		+	
Periclase MgO			+
Magnesite $MgCO_3$	+		

+++ high intensity, ++ medium intensity, + low intensity

A comparison between the yield of solid, liquid and gaseous products after the devolatilization of the fuels and their 50 : 50 w/w mixture at 600 °C is made in Figure 3a and the higher heating value of all pyrolysis products is indicated in Figure 3b. As can be observed, MSW generated the highest amount of biochar (44%), while PMS produced a great amount of liquid condensates (50.5%) and gases (19.5%). The higher heating values of the biochars studied were rather low, due to their high content in ash. However, as Figure 3b shows, the higher heating value of the bio-oils, ranging between 22 MJ/kg and 32 MJ/kg, was high and that of gases significant, between 11 MJ/m^3 and 14 MJ/m^3, with the highest values corresponding to MSW fuel. The higher heating values of the gases produced from the fuel blends were in between those of parent materials. Thus, the liquid and gaseous by-products of the devolatilization step could offer valuable energy for these endothermic processes.

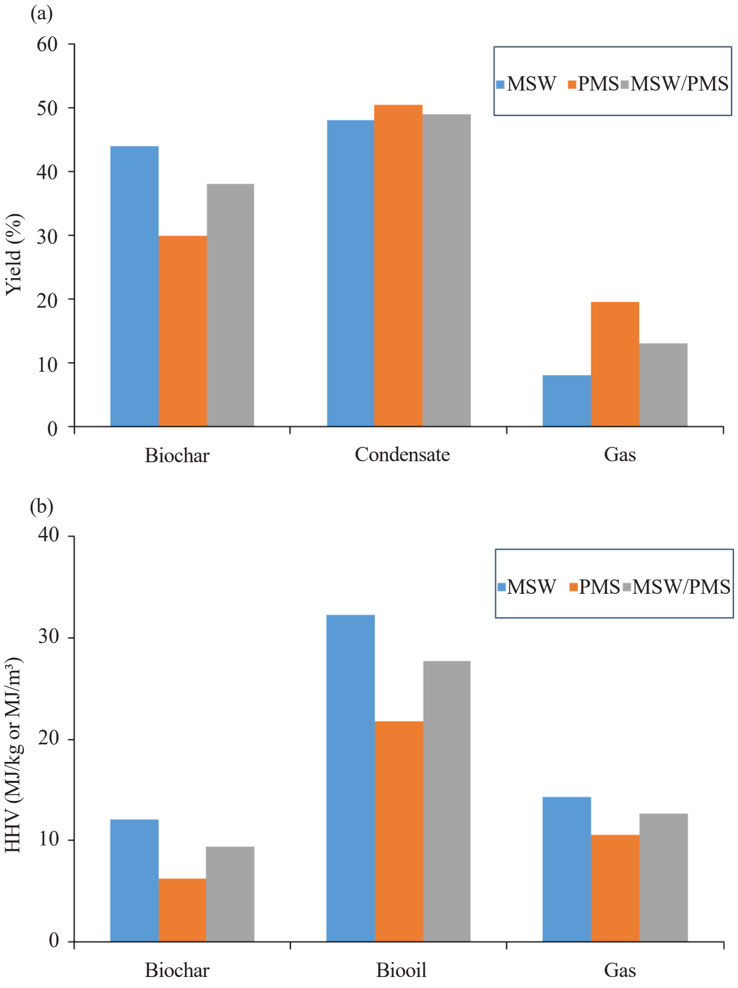

Figure 3. Yield of pyrolysis products and their higher heating value

3.2 *Gasification performance of fuels without the addition of CO_2 sorbent or catalyst*

The composition of the product gas mixture, the higher heating value of gas and fuel conversion, as a function of temperature during the gasification of the two fuels and their blend, without the addition of QD or Na_2CO_3 catalyst, are summarized in Table 3. Also, the principal reactions taking place simultaneously during the steam gasification of chars are presented below, in order to assist in the explanation of the results:

$$C + H_2O \rightarrow CO + H_2 \qquad \Delta H = 131 \text{ kJ/mol} \tag{5}$$

$$C + 2H_2O \rightarrow CO_2 + 2H_2 \qquad \Delta H = 90\ \text{kJ/mol} \tag{6}$$

$$C + CO_2 \rightarrow 2CO \qquad \Delta H = 172\ \text{kJ/mol} \tag{7}$$

$$C + 2H_2 \rightarrow CH_4 \qquad \Delta H = -75\ \text{kJ/mol} \tag{8}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H = -41\ \text{kJ/mol} \tag{9}$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H = 206\ \text{kJ/mol} \tag{10}$$

Table 3. Gasification performance of fuels without addition of sorbent or catalyst (% dry)

Sample	Temperature (°C)	Composition of gas (mol%)					*HHV* (MJ/m^3)	Conversion (% dry)
		H_2	CO_2	CO	CH_4	C_xH_y		
MSW	650	10.8	14.7	74.3	0.2	0.09	12.2	8.7
	700	32.8	29.1	37.0	0.9	0.05	9.3	22.3
	750	39.0	34.9	24.8	1.2	0.05	8.6	33.5
	800	39.8	41.8	14.2	1.2	0.04	7.4	40.2
	850	40.1	37.0	24.4	0.5	0.04	8.5	46.3
	900	51.6	20.8	27.3	0.2	0.04	10.2	47.5
PMS	650	4.2	1.8	93.8	0.1	0.08	12.5	9.9
	700	18.8	6.1	73.8	1.1	0.08	12.2	28.1
	750	32.6	11.4	54.0	1.9	0.07	11.8	46.2
	800	43.6	19.7	33.9	2.7	0.08	11.8	49.8
	850	51.9	32.1	13.9	2.0	0.06	9.2	60.6
	900	52.2	34.0	11.9	1.7	0.06	8.9	62.5
MSW/PMS	650	7.0	8.4	84.4	0.1	0.09	11.7	9.4
	700	20.8	18.6	59.5	1.0	0.07	10.7	25.8
	750	34.8	23.5	40.1	1.5	0.06	10.2	40.1
	800	39.7	31.1	26.6	2.5	0.06	9.5	45.7
	850	45.3	35.0	21.1	1.4	0.05	9.1	53.7
	900	51.2	26.7	21.0	1.0	0.05	9.6	55.0

It is obvious from this table that temperature is a critical parameter for this endothermic process, promoting the conversion rate and the generation of H_2. At low temperatures, below 700 °C, the main gas product was CO produced from reactions (5, 7) and reverse (9), whereas conversion of fuels was very low 22-28%. As the temperature was gradually increased up to 900 °C, it can be observed that the concentration of H_2 in the gas mixture was greatly enhanced, from 32.8 mol% to 51.6 mol% for MSW char and from 18.8 mol% to 52.2 mol% for PMS char. At the same time, the concentration of CO was reduced from 37 mol% to 27.3 mol% for MSW char and from 73.8 mol% to 11.9 mol% for PMS char, while that of CO_2 was raised, reaching values up to 41.8 mol% for MSW fuel and 34 mol% for PMS fuel. CH_4 was produced in small amounts, because reaction (8) was not favored in current tests, as it requires a high pressure to proceed. These results suggest that at higher temperatures reactions (5, 6, 9) and reverse (10) were promoted. The Boudouard reaction (7) was also taking place above 700 °C, however the drop in CO concentration with temperature reveals that this was consumed in the gas phase through equations (9) and reverse (10).

The lower amount of CO in the product gas at higher temperatures, at the expense of CO_2, decreased the higher heating value of the gas mixture. Higher heating values in the case of MSW char were lower, due to the higher CO_2 content in the gas. The promotion of endothermic reactions with temperature raised fuel conversion, attaining values of 47.5% for MSW char and 62.5% for PMS char on a dry basis. The higher conversion of PMS material is attributed to its higher specific surface area in comparison to MSW material, i.e. 76 m^2/g vs. 49.8 m^2/g, as measured by the BET method previously reported, which is directly related to the reactivity of the fuels. Finally, Table 3 shows that when MSW char was mixed with PMS char in equal amounts, the distribution of product gas was slightly affected, while the final conversion increased.

There are limited studies in the literature on the steam gasification of MSW and very rare on the steam gasification of PMS. A variety of experimental equipment and conditions have been used. At temperatures between 800 °C and 900 °C, the concentrations of H_2 and CO in the product gas were found to vary between 32-57 mol% and 15-17 mol%, respectively,[14,24] agreeing with the results of the current work. For the steam gasification of cellulose, which is a main component of paper waste materials, the H_2 content of generated gas at 750 °C was found to be 40 mol%.

3.3 *Gasification performance of fuels in the presence of CO_2 sorbent and Na_2CO_3 catalyst*

The effect of QD material used to capture CO_2 emitted from the steam gasification process of MSW biochar at 750 °C, as expressed by the Ca/C molar ratio, on the composition of generated gas and the H_2/CO molar ratio, is illustrated in Figure 4a. Although the periodic sampling of gas showed that less CO_2 was produced at a temperature of 700 °C, the mole fraction of H_2 in the mixture was lower and conversion too, so that the final temperature was selected to be 750 °C, allowing some decomposition of the calcium carbonate formed through the carbonation reaction (11), as shown below.

Mechanism of CO_2 capture, after reaction of feedstock with steam and $Ca(OH)_2$ from the sorbent:

$$\text{Gasifier} \quad Ca(OH)_2 + CO_2 \leftrightarrow CaCO_3 + H_2O \tag{11}$$

$$\text{Calciner} \quad CaCO_3 \rightarrow CaO + CO_2 \tag{12}$$

$$\text{Sorbent make up} \quad CaO + H_2O \rightarrow Ca(OH)_2 \tag{13}$$

Figure 4a shows that when Ca/C = 1 the amount of CO_2 captured by QD sorbent was 65%, whereas when Ca/C = 2 it was 77%. However, at Ca/C = 1 the percentage of H_2 in the product gas increased by 94.1%, reaching a value of 75.7 mol% and the H_2/CO was very high 7.2. On the other hand, at a Ca/C = 2 the concentration of H_2 was raised by 72.8%, attaining a value of 67.4 mol% in the mixture, with a H_2/CO 2.9. Consequently, when QD was used as CO_2 sorbent, reactions (5, 9) were promoted, while reaction (7) was less favored. In addition, in terms of the enrichment of product gas in H_2, the optimum Ca/C ratio would be 1. The great enhancement of H_2/CO under these conditions suggests that the gasification of MSW char could be used for chemical synthesis or production of biofuels.[27]

The effect of Na_2CO_3 catalyst loading on the distribution of gases in the mixture and the molar H_2/CO ratio at 750 °C in the presence of QD sorbent, at a molar ratio Ca/C = 1, for MSW fuel, is indicated in Figure 4b. These results show that Na_2CO_3 catalyzed the solid-gas endothermic reactions (5-7), thus increasing the amounts of H_2 and CO in the product gas (syngas) and further improving retention of CO_2 by about 55%. The catalytic performance of Na_2CO_3 has been assigned to the increase in the number of active sites on the char surface, and enhancement of physicochemical properties, which leads to a faster conversion or the formation of reactive surface intermediates.[28] Suggested mechanisms are:[29]

$$Na_2CO_3 + 2C \rightarrow 2Na + 3CO \tag{14}$$

$$2Na + 2H_2O \rightarrow 2NaOH + H_2 \tag{15}$$

$$2NaOH + CO \rightarrow Na_2CO_3 + H_2 \tag{16}$$

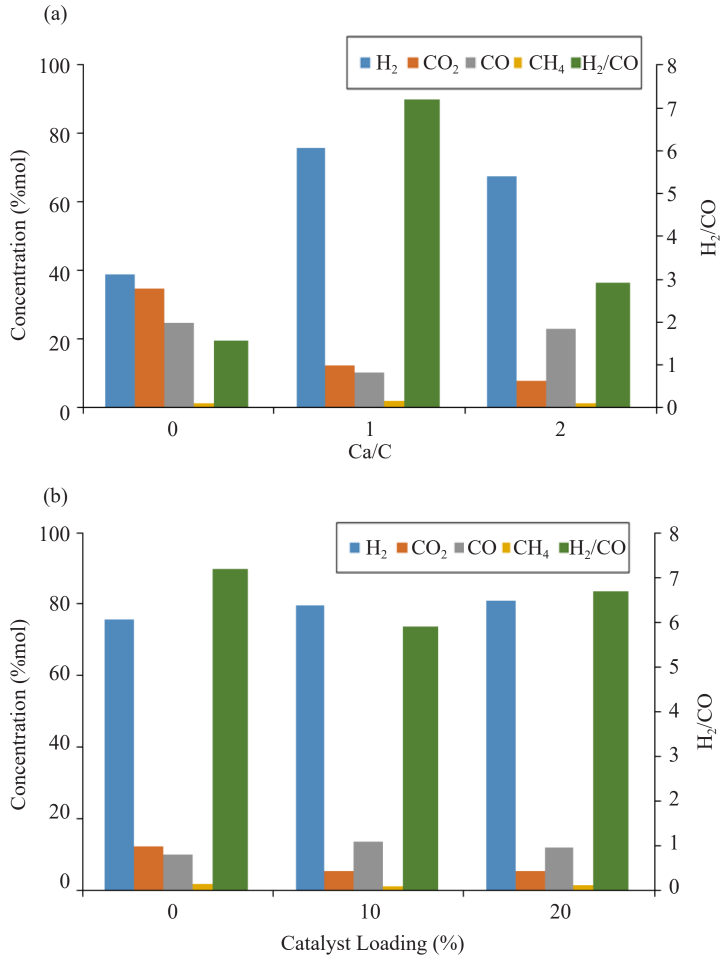

Figure 4. Effect of QD material and catalyst loading on the composition of gas at 750 °C for MSW

These steps promote the formation of H_2 and CO. Alternatively, sodium species may promote CO_2 reduction according to the following reaction scheme:

$$Na_2CO_3 + 2C \rightarrow 2Na + 3CO \tag{17}$$

$$2Na + CO_2 \rightarrow Na_2O + CO \tag{18}$$

$$Na_2O + CO_2 \rightarrow Na_2CO_3 \tag{19}$$

An increase in catalyst loading from 10% to 20% did not influence the results to a great extent, but resulted in a small positive effect on the H_2/CO, which was raised from 5.9 to 6.7. When the percentage of Na_2CO_3 was 20%, a mole fraction of H_2 of 81% was achieved in the mixture.

A comparison of current results with those from previous investigations is difficult, due to the very limited data in literature. One study using waste marble powder (WMP) as CO_2 sorbent during the gasification of MSW at 750 °C and a molar ratio of WMP/MSW = 1, reported a very low H_2 content in gas 28 mol%, as compared to this work using QD sorbent (75.7 mol%) and a high content of CO_2 up to 30 mol%.[14] Another study indicated that the presence of waste marble powder promoted H_2 and CO to 6.65% and 10%, respectively, during the air gasification of MSW, whereas reduced the CO_2 content to 0.2%.[2] Also, a significant increase was observed in the H_2 production rate from 55 kmol/h to 70.5 kmol/h, as CaO/feedstock ratio increased in the steam gasification of food waste.[15] On the other hand, when gypsum was added at equal mass proportions 1 : 1 to steam gasification of MSW at 800 °C, the syngas yield was found to be reduced by 50%.[16] Concerning the catalytic activity of Na_2CO_3 during the steam gasification process, past research by the authors has shown that for the gasification of a winery waste and helianthus at 750 °C using a CO_2 sorbent and Na_2CO_3 loading of 20%, the molar fraction of H_2 in the gas mixture ranged between 73% and 96% for the two fuels and the syngas yield varied between 1.86-4.94 m^3/kg.[23] Two-stage gasification of refused derived fuel, without CO_2 sorbent and in the presence of a clay catalyst for tar cracking, was reported to increase the content of H_2 in the gas phase from 3.9% in the absence of a catalyst to 24% in the presence of a catalyst at 850 °C.[9] These values are well below the present findings.

Table 4. Comparison of gasification performance of MSW, when using QD or PMS ash as carbon dioxide sorbents at 750 °C, Ca/C = 1 and catalyst loading 20% (% dry)

Sorbent	Catalyst	Composition of gas (mol%)				Conversion (%)	ERE	*HHV* (MJ/m^3)	Syngas yield (m^3/kg)
		H_2	CO_2	CO	CH_4				
QD	-	75.7	12.2	10.1	1.9	33.5	0.73	11.8	0.65
	Na_2CO_3	81.0	5.4	12.1	1.4	100	3.14	12.5	2.82
PMS Ash	-	56.9	6.4	35.2	1.3	87.5	1.52	12.4	1.36
	Na_2CO_3	56.5	3.9	38.8	0.8	100	1.82	12.5	1.67

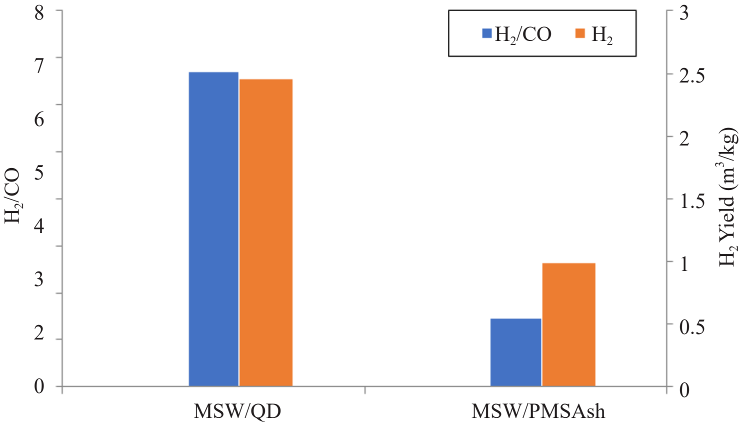

Figure 5. Comparison of QD material and PMS ash on the H_2/CO ratio and hydrogen yield at 750 °C and Ca/C = 1 for MSW

As it was previously presented, when PMS waste material was mixed with MSW and gasified, the H_2 content in the product gas was about the same as that from the gasification of MSW only, whereas the concentration of CO_2 was generally lower. The fact that PMS was very rich in inorganic compounds (Table 1), consisting of over 50% of calcite, gave the trigger to investigate the possibility of using PMS ash disposed from incineration processes as a CO_2 sorbent for the steam gasification process, thus offering environmental and economic benefits. Therefore, Table 4 and Figure 5 compare the gasification performance of MSW fuel, when using QD or PMS ash to capture CO_2 emissions. These results show that although PMS ash adsorbed a higher amount of CO_2 than QD material, further reducing its concentration in the product gas by 48%, its selectivity towards H_2 production was lower, leading to a H_2 yield of 0.99 m^3/kg, as opposed to 2.45 m^3/kg in the case of QD material, and a H_2/CO of 1.46 vs. 6.69, respectively. On the other hand, when PMS ash was used as sorbent the syngas yield and conversion were increased, resulting in a higher energy recovery (1.52) in comparison to QD sorbent (0.73). Accordingly, the higher mole fraction of CO in the generated gas, in the presence of PMS ash (35.2% vs. 10.1%), increased somehow its higher heating value (Table 4) to 12.4 MJ/m^3. The performance of the Na_2CO_3 catalyst was better in the presence of QD sorbent, in terms of H_2 yield, H_2/CO and energy recovery. As previously presented, Na_2CO_3 promoted endothermic reactions (5-7), leading to increased H_2 and CO and reduced CO_2 contents in the generated gas. The lower selectivity of PMS ash towards H_2 generation could be probably assigned to the significant content of PMS ash in silicon and aluminum minerals[11,30] in the forms of quartz, clinochlore and talc, which could decrease the reactivity of steam endothermic reactions.

3.4 *Challenges and prospects*

The environmental and health challenges associated with MSW disposal, including the leaching of harmful pollutants into groundwater and the release of toxic gases and dust into the atmosphere, alongside the high costs of landfilling, are driving the need for more efficient and sustainable waste management practices. These practices serve as alternatives to traditional waste deposition. The constant and readily available nature of MSW, coupled with its zero-cost and rich organic content, makes MSW a promising resource for sustainable energy generation through waste-to-energy technologies, supporting both circular economy objectives and energy security goals.

On the other hand, the growing demand for paper products in recent years, combined with the high energy consumption of the papermaking industry,[20] offers significant potential for energy recovery and a reduction in carbon emissions from paper sludge byproducts, which contain high amounts of organic material.[21] Co-processing these waste materials can enhance the flexibility and economic viability of processing plants, while simultaneously reducing their carbon footprint. Moreover, utilizing paper sludge ash as a carbon dioxide sorbent during the thermal treatment of these materials not only mitigates the environmental risks associated with improper ash disposal, but also contributes to lowering greenhouse gas emissions and the cost of carbon sequestration.

Additionally, the extremely high content of calcium carbonate in waste concrete fines, generated in huge amounts from construction activities, the limited landfill capacity and the environmental impacts of their disposal, are challenging for their valorization as CO_2 sorbents. Regeneration of these materials is simple and feasible. The heat released by the carbonation reaction can compensate to a great extent for the regeneration process.

The findings of this study are promising, indicating that MSW and paper mill sludge could serve as feedstocks in co-gasification processes to produce low-carbon hydrogen from waste materials, including paper sludge ash and quarry dust from the cement industry as CO_2 sorbents. While the environmental benefits of such processes are evident, further testing to optimize the involved parameters is essential to assess the process's feasibility and scalability. Key areas for investigation include a comprehensive characterization of feed materials, understanding the synergistic behavior of blended wastes, expanding and optimizing operational parameters, exploring different sorbents for CO_2 capture, testing various catalysts to enhance gasification reactivity and their cyclic capacity, managing byproducts such as tar, and conducting computational and techno-economic analyses to evaluate the viability of large-scale implementation.

4. Conclusions

During the steam gasification of MSW and PMS biochars up to 900 °C, a H_2 concentration of 51.6 mol% and 52.2 mol% was achieved in the product gas, respectively, while the content of CO_2 in the gas reached values as high as 41.8 mol%. When quarry dust was used to capture CO_2 at 750 °C, the percentage of H_2 in the product gas was 75.7 mol%, the molar H_2/CO was 7.19 and syngas yield was 0.65 m^3/kg. When the Na_2CO_3 catalyst was added at a loading of 20%, the molar fraction of H_2 in the gas mixture was increased to 81% and the syngas yield to 2.82 m^3/kg. When PMS ash was used as a CO_2 sorbent, a higher amount of CO_2 was captured, however the selectivity towards H_2 production was lower leading to a H_2/CO 1.46 and a syngas yield of 1.36 m^3/kg. The performance of the Na_2CO_3 catalyst was better in the presence of quarry dust sorbent in terms of H_2 yield, H_2/CO and energy recovery.

Overall, and in the context of environmental management of wastes and circular economy, the co-gasification of municipal solid wastes and paper sludge chars was found to be advantageous, producing a gas with a similar composition to each component fuel. Waste concrete fines and paper sludge ash could successfully capture emissions of CO_2 and in the presence of Na_2CO_3 catalyst a H_2/CO and a syngas yield of 6.7 and 2.82 m^3/kg could be achieved.

Acknowledgements

The authors kindly thank the laboratories of Hydrocarbons Chemistry, Applied Mineralogy, Quality Control, Health and Safety in the Mineral Industry, of the Technical University of Crete and Dr. T. Ioannides and Dr. M. Smyrnioti from the Inst. of Chemical Engineering Sciences in Patra, for the various analyses of the samples.

Conflict of interest

The authors declare no competing financial interest.

References

[1] Sipra, A. T.; Gao, N.; Sarwar, H. Municipal solid waste (MSW) pyrolysis for biofuels production: A review of effects of MSW components and catalysts. *Fuel Process. Technol*. **2018,** *175*, 131-147.

[2] Amin, N.; Khan, Z.; Razzaq, A.; Ghauri, M.; Khurram, S.; Inayat, A.; Jaffery, M.; Hameed, Z. Municipal solid waste air gasification using waste marble powder as a catalyst for syngas production. *J. Energy Inst.* **2024,** *113*, 101496.

[3] Kaur, A.; Bharti, R.; Sharma, R. Municipal solid waste as a source of energy. *Materials Today Proc.* **2023,** *81*, 904-915.

[4] Lee, D. J. Gasification of municipal solid waste (MSW) as a cleaner final disposal route: A mini-review. *Biores. Technol*. **2022,** *344*, 126217.

[5] Liang, R.; Chen, C.; Ge, Y.; Tao, J.; Yan, B.; Wang, H.; Wang. K.; Bu, Q.; Chen, G. A conceptual sorting strategy of municipal solid waste towards efficient gasification. *Energy Conver. Manag*. **2024,** *304*, 118209.

[6] Zhang, J.; Chen, T.; Wu, J.; Wu, J. TG-MS analysis and kinetic study for thermal decomposition of six representative components of municipal solid waste under steam atmosphere. *Waste Manag.* **2015,** *43*, 152-161.

[7] Hla, S. S.; Lopes, R.; Roberts, D. The CO_2 gasification reactivity of chars produced from Australian municipal solid waste. *Fuel* **2016,** *185*, 847-854.

[8] Santos, R. G.; Alencar, A. C. Biomass-derived syngas production via gasification process and its catalytic conversion into fuels by Fischer Tropsch synthesis: A review. *Int. J. Hydr. Energy* **2020,** *45*, 18114-18132.

[9] Suhaj, P.; Haydary, J.; Husar, J.; Steltenpohl, P.; Supa, I. Catalytic gasification of refuse-derived fuel in a two-stage laboratory scale pyrolysis/gasification unit with catalyst based on clay minerals. *Waste Manag*. **2019,** *85*, 1-10.

[10] Cao, Y.; Fu, L.; Mofrad, A. Combined-gasification of biomass and municipal solid waste in a fluidized bed gasifier. *J. Energy Inst*. **2019,** *92*, 1683-1688.

[11] Aluri, S.; Syed, A.; Flick, D. W.; Muzzy, J. D.; Sievers, C.; Agrawal, P. K. Pyrolysis and gasification studies of model refuse derived fuel (RDF) using thermogravimetric analysis. *Fuel Process. Technol.* **2018,** *179*, 154-166.

[12] Zheng, X.; Ying, Z.; Wang, B.; Chen, C. Hydrogen and syngas production from municipal solid waste (MSW) gasification via reusing CO_2. *Appl. Therm. Eng.* **2018,** *144*, 242-247.

[13] Vamvuka, D.; Karouki, E.; Sfakiotakis, S. Gasification of waste biomass chars by carbon dioxide via thermogravimetry-Effect of catalysts. *Comb. Sci. Techn*. **2012,** *184*, 64-77.

[14] Irfan, M.; Li, A.; Zhang, L.; Wang, M.; Chen, C.; Khushk, S. Production of hydrogen enriched syngas from municipal solid waste gasification with waste marble powder as a catalyst. *Int. J. Hydr. Energy* **2019,** *44*, 8051-8061.

[15] Ali, A. M.; Shahbaz, M.; Inayat, M.; Shahzad, K.; Al-Zahrani, A. A.; Mahpudz, A. B. Conversion of municipals

waste into syngas and methanol via steam gasification using CaO as sorbent: An aspen plus modelling. *Fuel* **2023,** *349*, 128640.

[16] Burra, K. R. G.; Hernandez, I. F.; Castaldi, M. J.; Mavukwana, A.; Gupta, A. K. Gasification of municipal solid wastes with gypsum wastes under different gasifying environments. *J. Energy Inst.* **2024,** *114*, 101644.

[17] Centi, G.; Perathoner, S. Chemistry and energy beyond fossil fuels. A perspective view on the role of syngas from waste sources. *Catal. Today* **2020,** *342*, 4-12.

[18] International Energy Agency. *Global Hydrogen reviews 2024*. http://www.iea.org/ (accessed 17 January, 2025).

[19] International Energy Agency. CO_2 *Emissions in 2023*. http://www.iea.org/ (accessed 17 January, 2025).

[20] Man, Y.; Hong, M.; Li, J.; Yang, S.; Qian, Y.; Liu, H. Paper mills integrated gasification combined cycle process with high energy efficiency for cleaner production. *J. Cleaner Prod*. **2017,** *156*, 244-252.

[21] Chiang, K. Y.; Lu, C. H.; Liao, C. K.; Ger, R. H. R. Characteristics of hydrogen energy yield by co-gasified of sewage sludge and paper-mill sludge in a commercial scale plant. *Int. J. Hydr. Energy* **2016,** *41*, 21641-21648.

[22] Galetakis, M.; Alevizos, G.; Leventakis, K. Evaluation of fine limestone quarry by-products, for the production of building elements-An experimental approach. *Cnstruct. Build. Mater*. **2012,** *26*, 122-130.

[23] Vamvuka, D.; Afthentopoulos, E.; Sfakiotakis, S. H_2-rich gas production from steam gasification of a winery waste and its blends with industrial wastes. Effect of operating parameters on gas quality and efficiency. *Renew. Energy* **2022,** *197*, 1224-1232.

[24] Zeng, X.; Fang, M.; Lv, T.; Tian, J.; Xia, Z.; Cen, J.; Wang, Q. Enhanced hydrogen production by the catalytic alkaline thermal gasification of cellulose with Ni/Fe dual-functional CaO based catalysts. *Int. J. Hydr. Energy* **2021,** *46*, 32783-32799.

[25] Roncancio, R.; Ulcay, M.; Arango, J.; Gore, J. Experimental study of CO_2 corn stover char gasification using iron nitrate as a catalyst under a high-pressure environment. *Fuel* **2020,** *267*, 117237.

[26] Mateus, M. M.; Gaspar, D.; Matos, S.; Reigo, A.; Motta, C.; Castenheira, I. Converting a residue from an edible source into a bio-oil. *J. Environ. Chem. Eng*. **2019,** *7*, 103004.

[27] Nagy, G.; Dobo, Z. Experimental investigation of fixed-bed pyrolysis and steam gasification of food waste blended with woody biomass. *Biomass Bioenergy* **2020,** *139*, 105580.

[28] Ning, S.; Jia, S.; Ying, H.; Sun, Y.; Xu, W.; Yin, H. Hydrogen-rich syngas produced by catalytic steam gasification of corncob char. *Biomass and Bioenergy* **2018,** *117*, 131-136.

[29] McKee, D. W. Mechanisms of the alkali metal catalyzed gasification of carbon. *Fuel* **1983,** *62*, 170-175.

[30] Elsaddik, M.; Nzihou, A.; Delmas, M.; Delmas, G. H. Steam gasification of cellulose pulp char: Insights on experimental and kinetic study with a focus on the role of silicon. *Energy* **2023,** *271*, 126997.

Appendix A

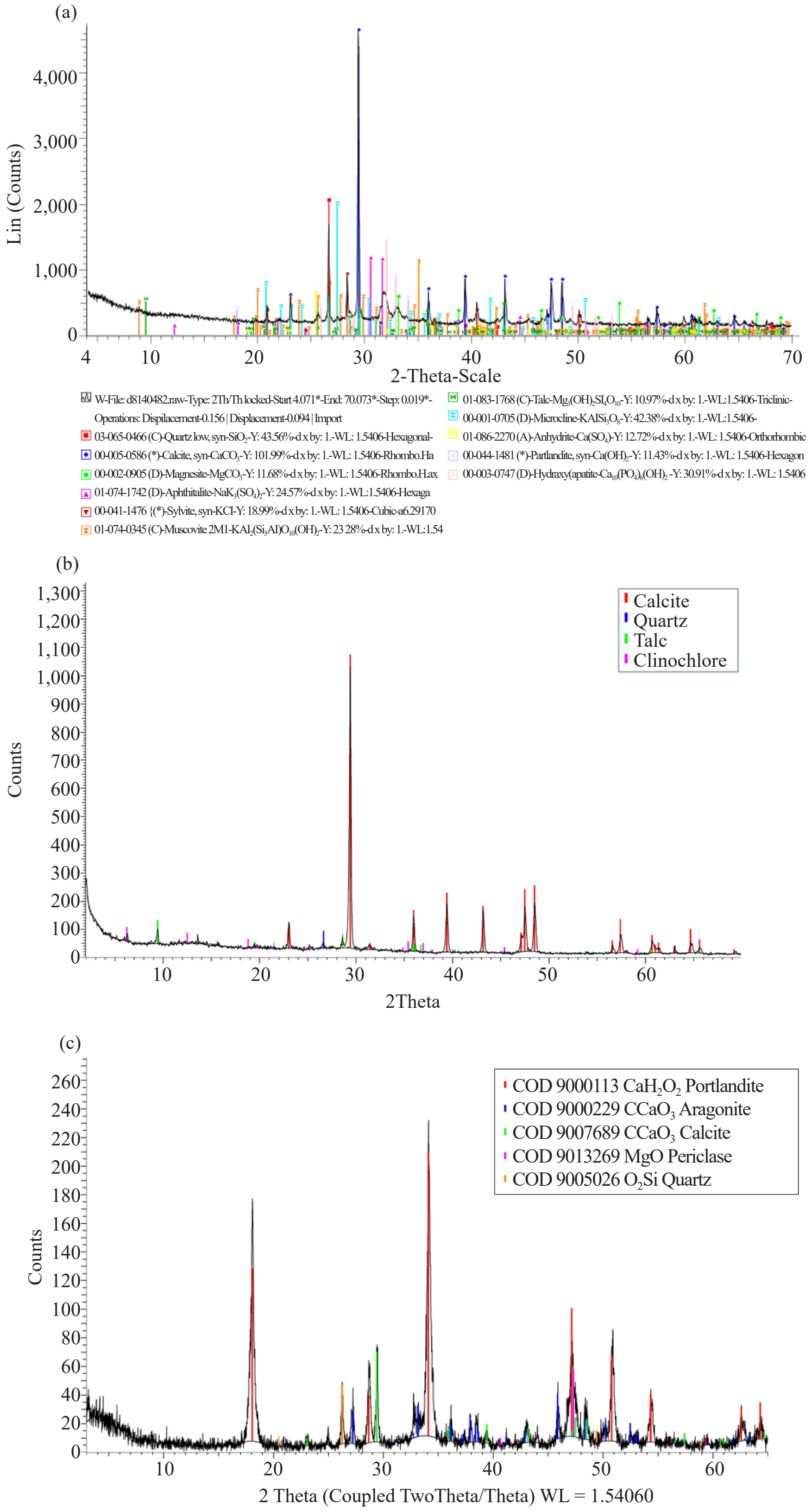

Figure A1. XRD spectra of MSW ash (a), PMS ash (b) and QD (c)