Sustainable Chemical Engineering
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Research Article

Sustainable Management of Forest and Building Wastes for Hydrogen-Rich Syngas from Catalytic Steam Gasification with Minimum CO_2 Emissions

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Received: 25 March 2024; **Revised:** 17 May 2024; **Accepted:** 24 May 2024

Abstract: The current study aimed at the exploitation of forest residues and their industrial waste for biofuel production, together with the exploitation of building demolition wastes (BDW) for CO_2 capture from the gasification process. Selected materials were gasified by steam in a fixed bed unit, using BDW as sorbent and CeO_2 and K_2CO_3 as catalysts. The effects of sorbent/biomass ratio, catalyst loading and temperature on final conversion, product gas composition and heating value, syngas and hydrogen yield and energy recovery were examined and optimum conditions were determined. Analysis of gases was performed in a thermogravimetric-mass spectrometric (TG-MS) system. At a ratio of Ca/C = 1, the amount of CO_2 captured at 750 °C was 73.2-76%, the concentration of hydrogen in the product gas was 56.2-59.3% mol and the higher heating value was 13.1 MJ/m^3. An increase of catalyst loading up to 20% wt resulted in higher conversion and syngas and hydrogen yields. K_2CO_3 catalyst showed a better overall performance. In this case, conversion ranged between 80.7% and 84.8%, the molar fraction of hydrogen in the product gas was 67-80.5%, syngas yield varied from 1.9 m^3/kg to 2.6 m^3/kg, with a heating value of 13.1-13.8 MJ/m^3 and energy recovery was higher.

Keywords**:** forest wastes, building wastes, steam gasification, CO_2 capture, catalysts

1. Introduction

Hydrogen is a clean and efficient energy carrier that can be utilized in transport, industrial and district applications.[1,2] Currently, hydrogen production technologies are water electrolysis, microbial, or photo fermentation and fossil fuels processing, such as gasification of coal, or reforming of natural gas.[2-5] However, the high cost of water electrolysis, the inefficiency of biological methods and the emission of toxic and greenhouse gases in combination with the depletion of fossil fuels reserves, make the use of renewable, sustainable, carbon-neutral feedstocks, such as biomass, a very promising alternative for versatile hydrogen applications in the near future.[1,3-6]

One of the most effective ways for hydrogen generation on a large scale is considered the thermochemical conversion of biomass via steam gasification. This process leads to syngas with elevated hydrogen content and high energy density, as well as less tar production, in comparison to air gasification.[7-8] In order to eliminate tar, which affects the purity of syngas and causes severe operational problems, in situ catalytic treatment, or a two-stage pyrolysis/gasification process, is usually applied. The latter offers additional advantages of higher gasification efficiency, through

DOI: https://doi.org/10.37256/sce.5220244643

the use of a higher reactivity bio-solid and liquid and gaseous energy sources from pyrolysis.[5,9-12]

A byproduct of steam gasification is however the greenhouse gas CO_2. If this is continuously removed from the system, then the steam gasification of char and hydrocarbons reforming are favored and the water-gas shift reaction proceeds forward, leading to an increase in hydrogen yield.[1,8,13-14] Calcium-based sorbents are gaining increased attention lately for CO_2 capture, due to their natural abundance and low cost.[3,8] The exothermic carbonation of CaO can compensate to a great extent for the heat required by the endothermic gasification reactions. Regeneration of CaO can be achieved by calcination of $CaCO_3$ formed, providing heat from the combustion of unconverted char from the process.[3,13]

The concentration of hydrogen in the product gas was found to vary between 47% and 80% mol during the gasification of some agricultural residues, using calcined limestone or dolomite, or mixtures of CaO and MgO sorbents.[14-15] CaO sorption-enhanced gasification is limited though to temperatures up to 700 °C, due to the decomposition of carbonates above this value, resulting in reduced hydrogen yield. Therefore, the addition of catalysts should be considered, in order to improve the efficiency of the process. Combinations of Ni-based catalysts with calcined limestone or dolomite, such as NiO[16], $NiO/\gamma\text{-}Al_2O_3$[14], Ni/Fe[3] and Ni/Ca_2SiO_4[17], used during the steam gasification of pine, corn stalk, cellulose and sawdust, respectively, exhibited a hydrogen concentration in the product gas of 68-90% mol. CeO_2 catalyst has been used as a promoter for tar reforming,[5,18] as an additive of iron catalysts in redox processes for improving their thermal stability and oxidative ability,[5,19] or for doping of CaO materials to capture CO_2 in post-combustion processes[1]. Very few studies reported enhanced hydrogen production in the presence of CeO_2 during the steam gasification of biomass. A Ce-doped CaO material achieved 70% mol hydrogen content in the syngas from algae gasification at 650 °C[1], whereas a Ca-Al-Ce bi-functional material exhibited 81% mol hydrogen concentration in the syngas from wood residue gasification.[20] Also, a Ce/Fe 3:7 catalyst, used to promote hydrogen production from cellulose steam catalytic reforming at 800 °C, generated 28.6% mol hydrogen.[5] On the other hand, alkali salts of K and Na have been used in several investigations for the production of high-quality syngas, from the steam gasification of agricultural residues at temperatures 900-950 °C.[4,16,21] For corn cob, a molar fraction of hydrogen in the gas mixture of 61.5% was obtained, with a total gas yield of 3 m^3/kg[4].

Forest residues are generated in huge quantities around the world, with an energy potential of 10-16 EJ/y.[22] Particularly, woody waste materials, having high calorific value, are an attractive option as energy sources. There is limited research in the literature on the steam gasification of such wastes for the production of a hydrogen-rich gas. Past studies focused on pine sawdust, or its mixture with sewage sludge, in the presence of various catalysts.[23] The volume fraction of hydrogen was found to increase from 28.7% to 66% using a Fe-Ni catalyst[24] and from 47.7% to 64.8% using iron ore powder at 700-750 °C.[25] Also, a catalytic system $K_2CO_3\text{-}\gamma\ Al_2O_3$ increased the percentage of hydrogen in the product gas from 37.8% to 59.6% mol at 840 °C.[26] Moreover, in past investigations limestone or dolomite materials were principally used for the absorption of CO_2 from product gas.[2,14] To our knowledge, only one study used waste marble powder for the gasification of municipal solid wastes, reporting a high amount of CO_2 though at lower temperatures (750 °C).[8]

Based on the above discussion, the novelty of current work lies in the exploitation of forest residues, obtained from the land restoration activities of coal mines and their industrial waste from wood manufacturing, for biofuel production, together with the exploitation of building demolition wastes for CO_2 capture from the thermochemical process. The aim was to investigate the potential of renewable carbon-neutral feedstocks, such as forest wastes, for hydrogen-rich gas generation, as well as the sustainable management of construction wastes, leading to economic and environmental benefits in the context of the circular economy. Accordingly, selected materials were gasified by steam in a fixed bed unit, using building demolition wastes (BDW) as CO_2 sorbent and CeO_2 and K_2CO_3 as catalysts. The effects of sorbent/biomass ratio, catalyst loading and temperature on final conversion, product gas composition and heating value, syngas and hydrogen yield and energy recovery were examined and optimum conditions were determined. Analysis of gases was performed in a thermogravimetric-mass spectrometric (TG-MS) system.

2. Experimental section

2.1 *Raw materials preparation and characterization*

Acacia pruning (AP) was provided by the Public Power Corporation of Greece. It was collected during the land restoration activities of the open-pit mines in the region of Ptolemais, in North Greece. Acacia sawdust (AS) was provided by a private wood processing company in the nearby area. Pruning was ground to a particle size below 1 mm using a cutting mill, Pulverisette 15. Sawdust was just sieved to the same particle size to remove dirt.

Building demolition wastes (BDW), used as CO_2 adsorbent, were collected from sites around the Technical University of Crete in West Crete, where the experiments took place. These wastes were excavated during the construction of new facilities and consisted mainly of limestone of bedrock and concrete/plaster from previous buildings in the area. The material was ground in a planetary ball mill, model Pulverisette 5 and sieved to a particle size lower than 100 μm. Then it was calcined at 950 °C for 2 h in a muffle furnace and placed in a quartz glass vessel, the bottom of which was filled with water, so that the CaO component would be transformed to $Ca(OH)_2$. The Ca/C molar ratios used in the experiments, according to the stoichiometry of adsorbent material and each fuel biochar, were 0.5, 1 and 2, respectively.

The cerium catalyst was prepared as follows. A certain amount of calcined BDW was immersed in glacial acetic acid (purchased by Sigma-Aldrich) and calcium acetate formed, $Ca\ (C_2H_3O_2)_2$, was dried in the oven at 110 °C for 4 h. A pre-determined amount of calcium acetate was impregnated with cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$)) in distilled water and agitated for 1 h. The weight ratios of CeO_2 to CaO were 10:90, 20:80 and 30:70, respectively. The solution was dried in the oven at 110 °C and then heated at 700 °C for 2 h in the muffle furnace, before use. The K_2CO_3 catalyst (also purchased by Sigma-Aldrich) was mixed with each biochar at mass ratios 10:90, 20:80 and 30:70 and impregnated with distilled water in a glass vessel. After stirring for 3 h, the solution was left to stand for 24 h at room temperature and in continuation it was dried at 105 °C in the oven.

Acacia pruning and sawdust fuels were characterized in terms of volatiles, ash content, CHNOS elemental concentration and calorific value, by adopting the CEN/TC 335 European standards for biomass materials.

Chemical analysis of fuel ashes and BDW material was conducted by an X-ray fluorescence spectrometer (XRF), type S2 Ranger/EDS of Bruker AXS. Mineralogical analysis of fuel ashes, BDW and CeO_2-CaO catalyst were performed by an X-ray diffractometer (XRD), type D8 Advance of Bruker AXS. Crystallography Open Database (COD) and software DIFFRAC Plus were used for mineral phase identification.

Prior to the gasification tests, raw samples were pyrolyzed in nitrogen (flow rate 200 mL/min) up to 600 °C (heating rate 10 °C/min), in a high-temperature fixed bed unit, described in a past investigation by the authors[27]. The specific surface area of biochars produced, as well as of CO_2 adsorbent material, were measured by a BET analyser type Autosorb 1Q-C-MP of Quantachrome, for relative pressures 0.015-0.32. Samples were out-gassed under vacuum at 200 °C, for 1 h, before testing.

2.2 *Steam gasification experiments-apparatus and procedure*

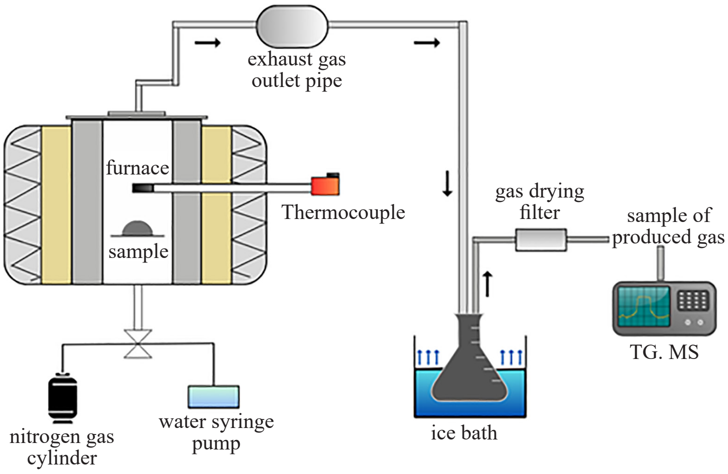


Figure 1. Scematic diagram of experimental set up

A schematic diagram of the experimental set up is illustrated in Figure 1. The stainless steel reactor (ID = 70 mm, H = 140 mm) was surrounded by a 2 m pipe, to enable a uniform steam flow and it was equipped with a grid sample holder and a Ni-Cr-Ni thermocouple, in contact with the sample bed. The furnace temperature controller had an accuracy of ± 3 °C.

Following air elimination, by purging nitrogen through the system for 30 min, each sample (fuel biochar/BDW/catalyst) was heated up to 600 °C as before, in nitrogen. Distilled water was then injected via an automatic syringe pump, at a flow rate corresponding to steam/sample = 3, in order to enhance the yield of hydrogen produced, according to previous findings.[28] The furnace temperature was raised to 750 °C and held constant for 1 h.

Product gases were cooled down and dried after passing through a cold trap and a silica gel quartz filter, respectively. Sampling was carried out at various temperatures during the tests, using a PTFE Luer Lock gas syringe. Qualitative and quantitative analysis of product gas mixture was performed in a TG-MS (thermogravimetric TG/DTG of Perkin Elmer-mass spectrometer MS QME-200 of Balzers) system, as described in detail in a previous authors report.[27] The conditions were high purity argon (45 mL/min), 200 °C heating of the transfer line, 82 eV electron density, 1-400 atomic mass range, standard gases in argon for calibration and Pyris v3.5/Quadstar 422 software for data processing.

Gasification efficiency GE, syngas V_{syn} or hydrogen Y_{H_2} yield and energy recovery ERE, as a function of temperature, were calculated as follows:

$$GE = \frac{m_g}{m_b} \times 100 \tag{1}$$

where m_g and m_b are the masses of product gas and biochar, respectively.

$$V_{syn} = x_{syn} \times V_g \tag{2}$$

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

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).

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

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 fuels, adsorption material and catalysts*

The characterization of raw fuels and their biochars, in terms of proximate analysis, ultimate analysis and pore structure, is represented in Table 1. Obviously, the composition of the AS sample was very close to that of the AP sample, as AS was a by-product of AP processed from the wood industry. The content of volatile matter was high, whereas that of ash was very low. The higher concentration of carbon and the lower concentration of oxygen in AP fuel resulted in increased calorific value. Biochars were completely devolatilized at 600 °C and were enriched in carbon. As can be seen, the percentages of hydrogen and oxygen in biochars, which were involved in dehydration, dehydroxylation and decarboxylation reactions[11] during thermal treatment, were greatly reduced. These changes in the elemental composition of biochars enhanced their calorific value, in comparison to the raw fuels. Nitrogen and sulphur contents were negligible, implying no emissions during the gasification process. Relevant to the structural characteristics of raw and pyrolyzed materials, Table 1 shows that upon thermal treatment pore volume increased, leading to a specific surface area 112-126 fold higher than the one corresponding to raw samples. This parameter is known to govern the reactivity of the materials during the gasification process.[14,29] The specific surface area of the CO_2 sorbent was found to be 5,012 m^2/g.

Table 1. Proximate, ultimate and structural analyses of raw fuels and biochars (% dry)

	Raw fuels		Biochars	
	AP	AS	AP	AS
	Proximate analysis			
Volatile matter	85.6	85.2	-	-
Fixed carbon	13.4	14.1	96.0	97.1
Ash	1.0	0.7	4.0	2.9
	Ultimate analysis			
C	48.8	46.2	80.0	66.6
H	6.6	6.5	1.7	2.0
N	0.8	-	0.8	-
O	42.8	46.6	13.5	28.5
S	-	-	-	-
HHV (MJ/kg)	19.1	17.5	27.2	21.0
Specific surface area (m^2/g)	2.3	2.5	257.7	315.4
Pore volume x 10^2 (cm^3/g)	0.5	0.7	15.1	20.4
Average pore size (Å)	24.5	24.0	14.1	15.3

The chemical analysis of ashes and BDW material, expressed as oxides of inorganic elements, is indicated in Table 2, whereas the corresponding mineralogical analysis is shown in the XRD spectra of Figure 2. AP and AS ashes were rich in Si and Ca, incorporated in quartz and calcite minerals. Smaller amounts of K and P occurred in the forms of arcanite/sylvite and hydroxylapatite, respectively. On the other hand, BDW material consisted principally of calcite, portlandite and aragonite minerals, accounting for 94.2% of CaO.

Table 2. Composition of fuel ashes and building demolition waste material (% dry)

Sample	CaO	Al_2O_3	SiO_2	Fe_2O_3	MgO	K_2O	Na_2O	P_2O_5
AP	28.9	0.8	46.5	0.3	1.0	7.7	0.6	2.7
AS	32.3	0.9	41.7	0.5	1.1	6.9	0.5	2.5
BDW	94.2	2.0	2.9	0.4	0.2	0.3	-	-

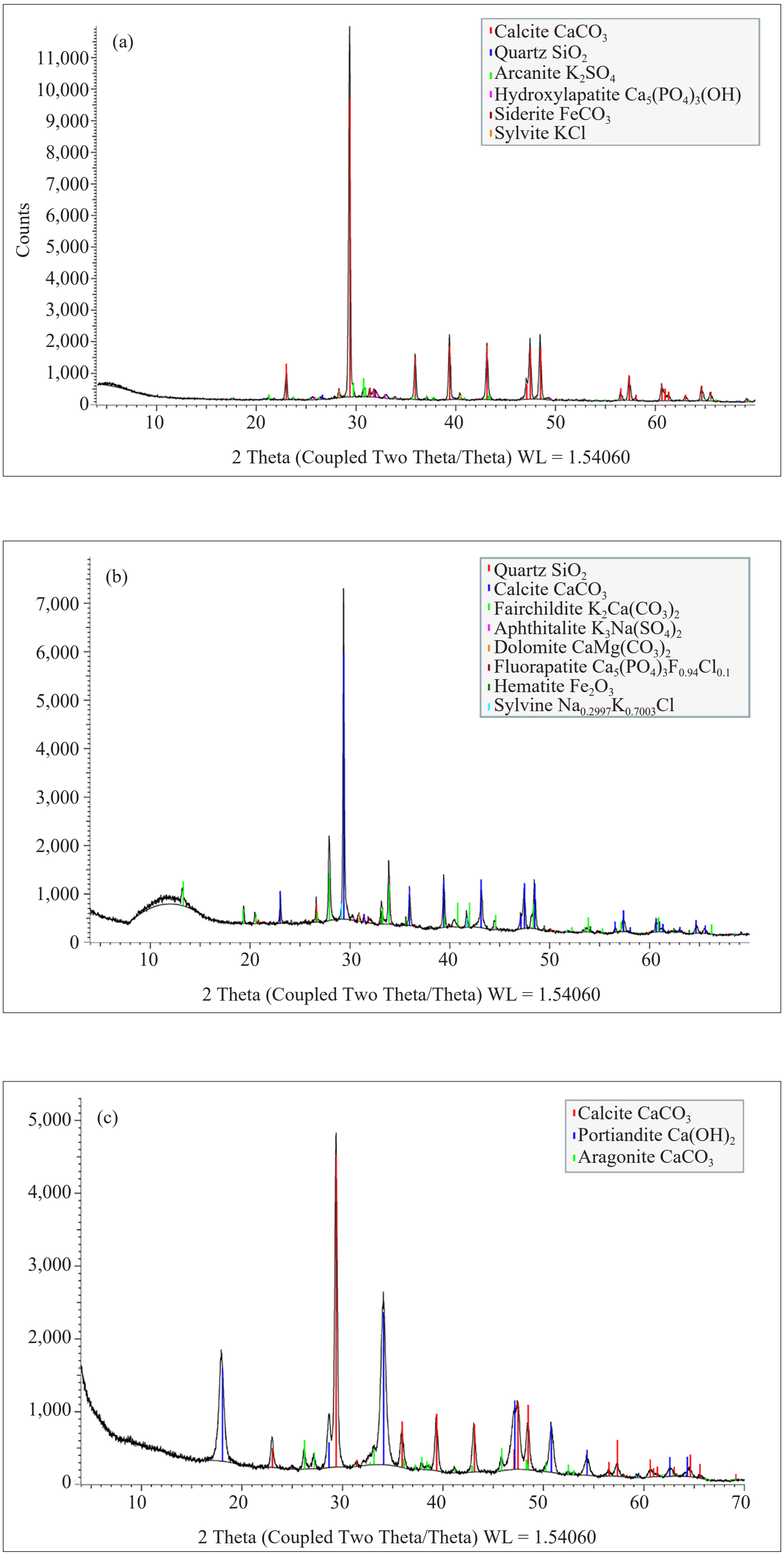


Figure 2. XRD spectra of AP ash (a), AS ash (b) and BDWsorbent (c)

3.2 *Effect of CO_2 sorbent on gasification performance*

Process conversion, product gas composition and its higher heating value, without the addition of BDW material for CO_2 capture, for the two fuels examined, are summarized in Table 3 as a function of gasification temperature. As can be seen, as the temperature was raised, the endothermic gasification reactions presented below were favored, increasing drastically the conversion from about 11% at 650 °C to about 66% at 750 °C. The extent of increase was about the same for the two samples, due to their similarity, however, the final conversion of AS fuel was somehow higher, due to its greater specific surface area than AP fuel (Table 1), which is directly related to fuel reactivity.

Table 3. Conversion and gas composition as a function of temperature without sorbent (% dry)

Sample	Temperature (°C)	Conversion GE (%)	Composition of gas (mol %)					HHV (MJ/m^3)
			H_2	CO_2	CO	CH_4	C_xH_y	
AP	650	11.3	15.2	13.1	70.9	0.7	0.1	11.3
	700	37.6	33.1	20.3	40.1	6.4	0.1	11.9
	730	51.1	33.6	22.2	37.3	6.8	0.1	11.8
	750	64.2	42.2	23.0	26.8	7.9	0.1	12.0
AS	650	11.8	16.6	4.2	78.7	0.5	-	12.3
	700	39.6	34.1	16.9	46.7	2.3	-	11.2
	730	53.8	40.5	18.7	38.0	2.8	-	11.1
	750	67.5	55.4	19.0	21.6	4.0	-	11.4

Primary reactions of char steam gasification:

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

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

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

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

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

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

The composition of generated gas was also slightly influenced by process temperature. At lower temperatures, the main product was CO with lower amounts of H_2. Under these conditions, the principal reactions taking place were reactions (5), (7) and reverse water-gas shift (9). When the temperature was increased up to 750 °C, Table 3 clearly shows that the concentration of H_2 in product gas was significantly enhanced, those of CO_2 and CH_4 were also increased, whereas the concentration of CO was lowered. Therefore, at higher temperatures endothermic reactions (5), (6), reforming reaction (9) and reverse reaction (10) were promoted. Although the Boudouard reaction (7) is also favored above 700 °C, any CO formed could have been consumed in the gas phase. The maximum content of H_2 in the gas mixture was 42.2% for AP biochar and 55.4% for AS biochar. As concerns the higher heating value of gas, although the percentage of H_2 was increasing with temperature, the balance between CO and CO_2 resulted in a nearly constant heating value of gas for both fuels. For comparison, steam gasification of cellulose at 750 °C was reported to produce about 40% mol H_2,[3] whereas for wood chips at 900 °C it was found to be 54% mol,[12] agreeing with current values.

The effect of the Ca/C molar ratio, when BDW material was used as CO_2 adsorbent, on the distribution of final gas at 750 °C and its higher heating value is illustrated in Figure 3. It can be observed that when Ca/C = 1 adsorption of CO_2 was higher, as compared to Ca/C = 2, reaching a value of 76%, implying some saturation of the sorbent. Due to CO_2 reduction in product gas, the percentages of H_2 and CO increased (up to 41% and 64%, respectively in relation to gasification without sorbent), thus raising the higher heating value from 11.4-12 MJ/m^3, without sorbent addition, to 13.1 MJ/m^3 after adsorption of CO_2. It must be mentioned that during the periodic sampling of gas at different temperatures it was found that the maximum amount of CO_2 captured by the sorbent occurred at temperatures below 700 °C (86-95%) because the carbonation reaction (11) was hindered at higher temperatures and decomposition of $CaCO_3$ was initiated. However, at lower temperatures conversion and H_2 mole fraction were also lower, so the optimum temperature was considered to be 750 °C at a Ca/C = 1. Under these conditions, the H_2 content achieved in the gas was 59.3% mol for the AP sample and 56.2% mol for the AS sample.

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

Previous studies using several calcium-based CO_2 absorbents, such as limestone and dolomite, during the steam gasification of corn stalk or citrus residue at 650-750 °C, reported an H_2 concentration in product gas of 47-70% mol and 54.1% mol, respectively and a CO_2 concentration of 3-20% mol.[2,14] Other studies, using waste marble powder (WMP) for the gasification of municipal solid wastes (MSW) at a ratio WMP/MSW = 1 at 750 °C, obtained an H_2 percentage of only 28% mol, with a high amount of CO_2 in the gas mixture[8].

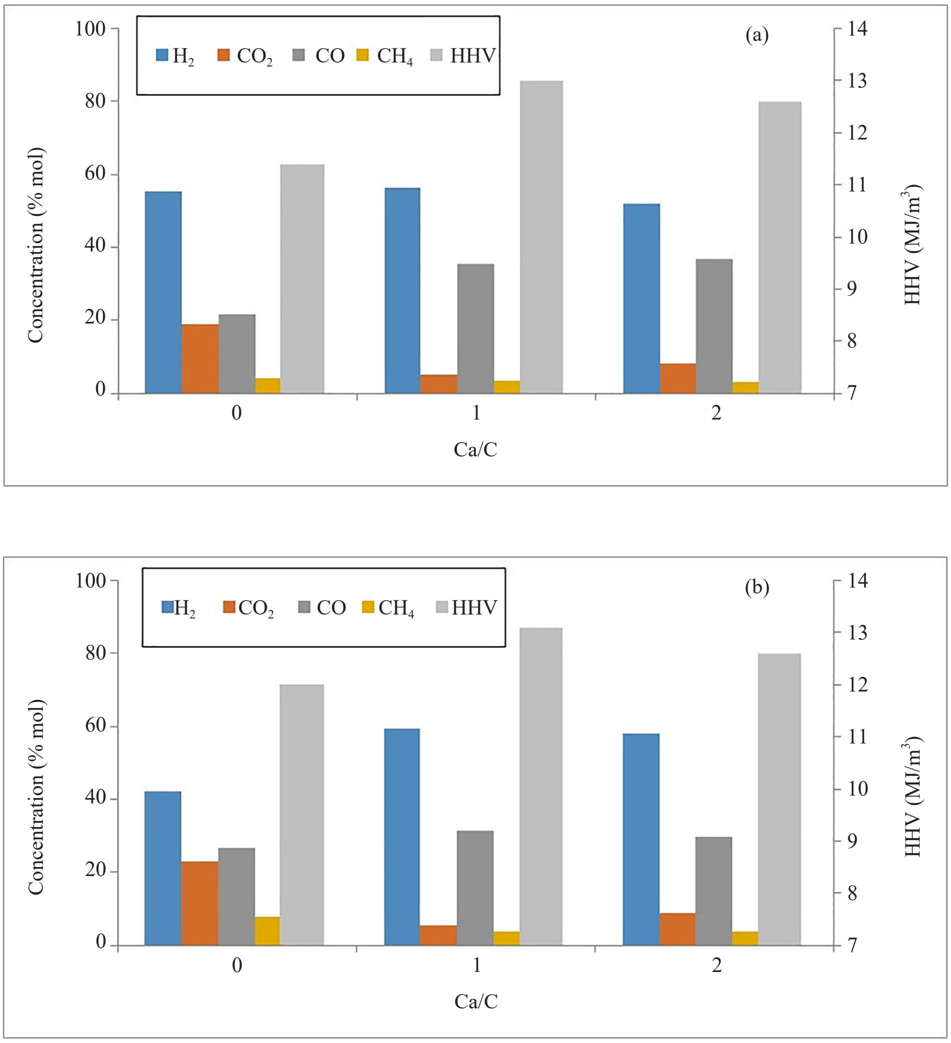


Figure 3. Distribution of gas and higher heating value as a function of Ca/C molar ratio at 750 °C for (a) AP and (b) AS chars

3.3 Effect of catalysts on gasification performance in presence of CO_2 sorbent

The effect of CeO_2-CaO and K_2CO_3 catalyst loading on solid fuel conversion, synthesis of generated gas and higher heating value at 750 °C and Ca/C = 1 is indicated in Tables 4 and 5, whereas the effect of syngas (CO + H_2) yield as a function of temperature is shown in Figure 4. From Tables 4 and 5 it can be noticed that for the CeO_2-CaO catalyst the improvement in conversion was rather small. On the other hand, for K_2CO_3, which is known to produce potassium active intermediates increasing the reactivity of fuels,[4] a higher conversion was achieved at 30% wt catalyst, from 64.2-67.5% to 81-85%, in comparison to non catalyzed reaction. Furthermore, an increased temperature for catalyst loading up to 20% wt resulted in higher amounts of H_2 and CO in the gas mixture, as also seen in Figure 4, leading to a small improvement in the heating value. Thus, reactions (5), (7) and the water-gas shift reaction (9) were promoted in this case. The enhanced conversion, at the higher temperature, contributed to a higher yield of syngas presented in Figure 4. The above results indicate that a higher percentage of catalyst (30% wt) did not exhibit a further positive effect on the composition of final gas, in terms of H_2 or syngas generation. At a catalyst loading of 20% wt the molar fraction of H_2 was about 73% in the case of CeO_2-CaO catalyst for both fuels and the yield of syngas was 1.77 m^3/kg. For K_2CO_3 catalyst the corresponding percentage of H_2 was 80.5% for AP biochar and 67% for AS biochar, while syngas yield was 2.6 m^3/kg and 1.9 m^3/kg, respectively.

Table 4. Conversion and gas composition as a function of catalyst loading at Ca/C = 1 and 750 °C for AP biochar (% dry)

Catalyst	Catalyst loading (wt %)	Conversion GE (%)	Composition of gas (mol %)					HHV (MJ/m^3)
			H_2	CO_2	CO	CH_4	C_xH_y	
-	-	64.2	59.3	5.5	31.3	3.8	0.09	13.1
CeO_2-CaO	10	65.6	72.0	5.2	16.5	6.2	0.06	13.8
	20	66.8	73.0	5.1	15.6	6.2	0.09	13.9
	30	67.1	70.9	5.7	16.1	6.4	0.09	13.7
K_2CO_3	10	72.8	79.1	5.9	11.5	3.5	0.02	13.0
	20	80.7	80.5	5.1	10.8	3.6	-	13.1
	30	81.0	80.0	5.2	11.3	3.5	-	13.0

Table 5. Conversion and gas composition as a function of catalyst loading at Ca/C = 1 and 750 °C for AS biochar (% dry)

Catalyst	Catalyst loading (wt %)	Conversion GE (%)	Composition of gas (mol %)					HHV (MJ/m^3)
			H_2	CO_2	CO	CH_4	C_xH_y	
-	-	67.5	56.2	5.1	35.3	3.3	0.07	13.0
CeO_2-CaO	10	68.0	72.0	5.2	16.8	6.0	0.05	13.8
	20	69.1	72.7	5.0	16.4	5.9	0.05	13.8
	30	70.0	55.5	5.4	34.2	4.8	0.09	13.4
K_2CO_3	10	76.6	65.0	5.6	23.3	6.0	0.1	13.7
	20	84.8	66.6	5.3	21.8	6.2	0.1	13.8
	30	85.0	67.0	5.4	21.4	6.1	0.1	13.7

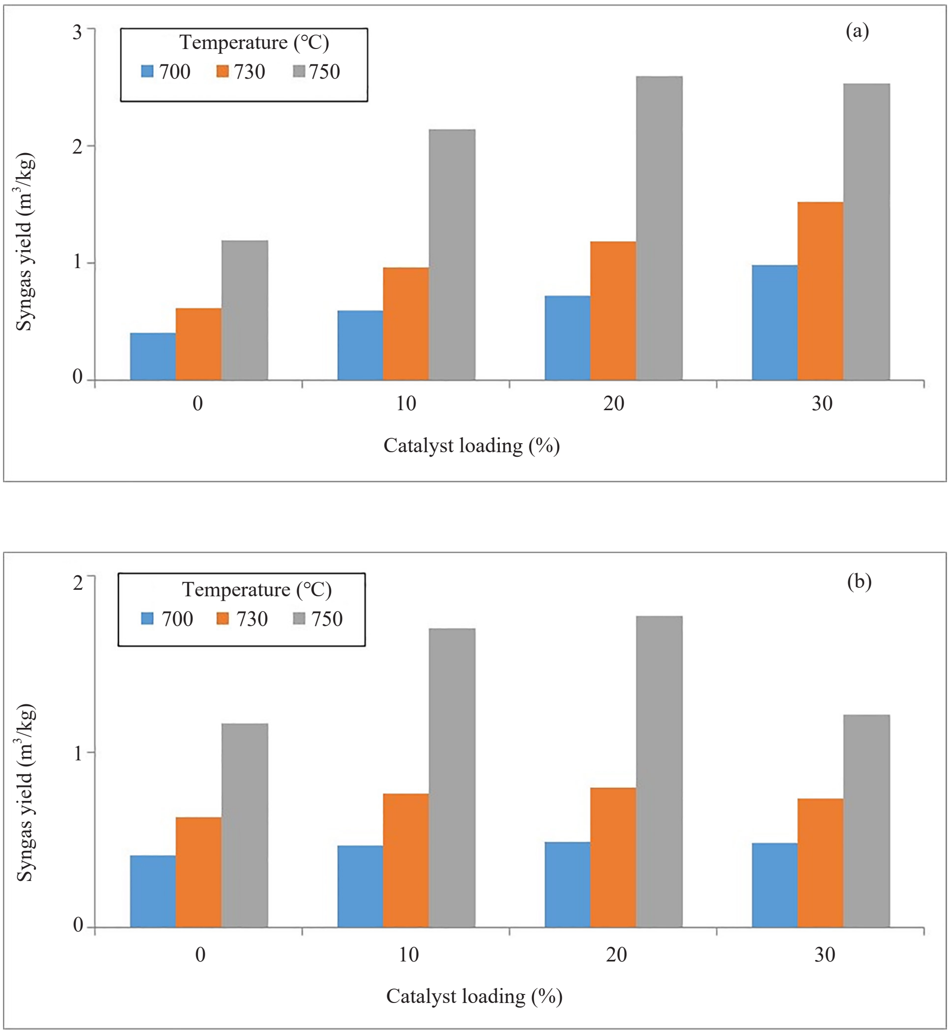


Figure 4. Effect of catalyst loading and temperature on syngas yield at Ca/C = 1 for (a) K_2CO_3 and AP char and (b) CeO_2 and AS char

The variety of feedstocks tested in previous investigations, the different experimental conditions and the interpretation of the results make a direct comparison of present findings with literature data. As concerns CeO_2 catalyst, some researchers reported that Ce-doped CaO material at 650 °C and CaO/C = 1.5 improved the H_2 production from Enteromorpha prolifera, by steam gasification, achieving 79% mol H_2 in the syngas, with a yield of 0.07 m^3/kg.[1] Also, a Ce/Fe = 3:7 catalyst, used to promote H_2 production from cellulose steam catalytic reforming at 800 °C, generated 28.6% mol H_2.[5] On the other hand, concerning the K_2CO_3 catalyst, char conversions between 90% and 95% were found,[4,30] whereas for steam gasification of corn cob H_2 content in the product gas of 61.5% mol was obtained at 900 °C, with a total gas yield of 3 m^3/kg.[4]

The performance of the two catalysts studied, at the optimum conditions previously discussed (750 °C, Ca/C = 1, catalyst loading 20% wt), is compared in Table 6 and Figure 5. As can be observed, the effect of the CeO_2-CaO catalyst on AP and AS fuels was about the same. The concentration of hydrogen in the gas mixture, from a value of 56.2-59.3% mol without catalyst addition increased to 73% mol in the presence of CeO_2-CaO, enhanced up to about 30%. This hydrogen increase was accompanied by a reduction of CO, implying that the water-gas shift reaction (9) proceeded to the right. On the other hand, the effect of the K_2CO_3 catalyst on the fuels was different. For AP biochar the content of hydrogen increased from 59.3% mol with no catalyst to 80.5% mol with K_2CO_3 addition, i.e. enhanced by 36%, while for AS biochar the corresponding values were from 56.2% mol to 66.6% mol, i.e. an enhancement of 18.5%. A possible mechanism in this case could be the transfer of oxygen by potassium catalyst from CO_2 to the carbon surface and subsequent release of CO, or promotion of reverse reaction (9), as also confirmed by Table 5 (CO in the gas mixture was 21.4-23.3% for AS char, whereas 11.3-11.5% for AP char). However, although the selectivity of the K_2CO_3 catalyst towards hydrogen production was lower than that of CeO_2-CaO for AS fuel, conversion was significantly higher (84.8% vs. 69.1%) as Table 6 shows, leading finally to a higher syngas yield and a similar hydrogen yield (Figure 5). Therefore, when K_2CO_3 was used as a catalyst, syngas and hydrogen yields were maximized for both fuels, ranging from 1.9-2.6 m^3/kg to 1.3-2.1 m^3/kg, respectively, as also seen in Figure 5. Accordingly, energy recovery was greater in the presence of a K_2CO_3 catalyst, in comparison to the CeO_2-CaO catalyst (Table 6). The improved performance of the K_2CO_3 catalyst has been assigned to its ability to increase the number of active sites on char or to form reactive surface intermediates. Suggested mechanisms are:[31-32]

$$\text{I. } K_2CO_3 + 2C \rightarrow 2K + 3CO \tag{12}$$

$$2K + 2H_2O \rightarrow 2KOH + H_2 \tag{13}$$

$$2KOH + CO \rightarrow K_2CO_3 + H_2 \tag{14}$$

$$\text{II. } K_2CO_3 + H_2O \rightarrow KHCO_3 + KOH \tag{15}$$

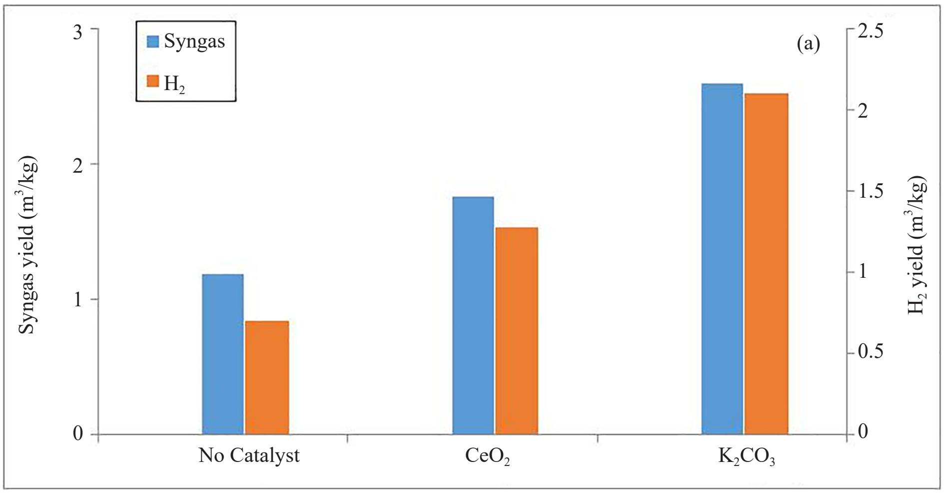
$$KOH + CO \rightarrow HCOOK \tag{16}$$

$$HCOOK + H_2O \rightarrow KHCO_3 + H_2 \tag{17}$$

$$2KHCO_3 \rightarrow H_2O + K_2CO_3 + CO_2 \tag{18}$$

Table 6. Comparison of catalysts for the two fuels at loading 20 % wt, Ca/C = 1 and 750 °C (% dry)

Sample	Catalyst	Composition of gas (mol %)					HHV (MJ/m^3)	GE (%)	ERE
		H_2	CO_2	CO	CH_4	C_xH_y			
AP	CeO_2-CaO	73.0	5.1	15.6	6.2	0.09	13.9	66.8	0.95
	K_2CO_3	80.5	5.1	10.8	3.6	-	13.1	80.7	1.25
AS	CeO_2-CaO	72.7	5.0	16.4	5.9	0.05	13.8	69.1	1.16
	K_2CO_3	66.6	5.3	21.8	6.2	0.1	13.8	84.8	1.24



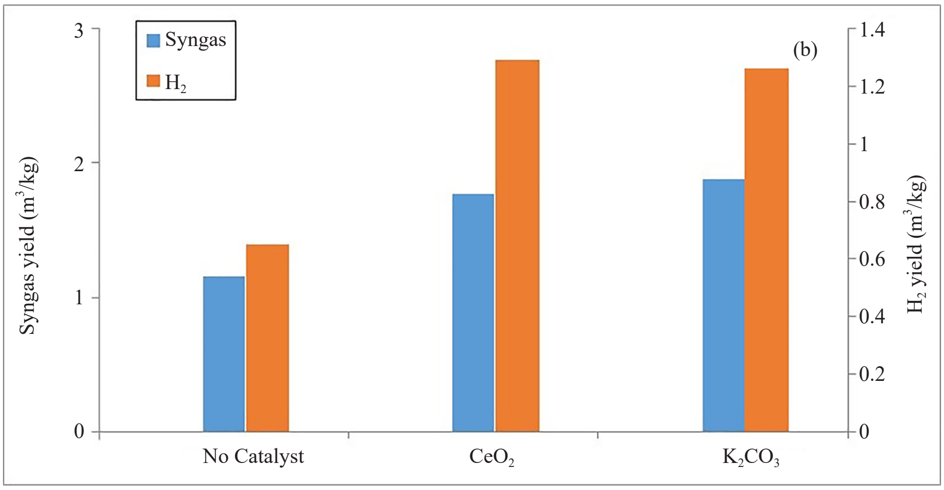


Figure 5. Comparison of catalysts (20% wt) on syngas and hydrogen yields at 750 °C and Ca/C = 1 for (a) AP and (b) AS chars

3.4 *Factorial analysis*

A full factorial experimentation was conducted for acacia pruning fuel in the presence of a potassium carbonate catalyst, which showed the best performance. This enabled the investigation of how changes in the calcium-to-carbon molar ratio (Ca/C) and catalyst loading (% K_2CO_3) affect the percentage of H_2 in the gas mixture (mol %), the syngas yield (m^3/kg) and the conversion factor (%). The calcium-to-carbon ratio and the percentage of catalyst were studied in three and four levels, respectively, resulting in 12 different combinations. The estimation of the effects (main and higher order), as well as the interactions of Ca/C and catalyst loading on the molar fraction of H_2, the syngas yield and the conversion were evaluated according to the factorial analysis methodology described by Myers and Montgomery.[33] The effects of Ca/C and % K_2CO_3 on these parameters are presented in Table 7.

Table 7. Effects of Ca/C and K_2CO_3 loading on H_2 content in the mixture, syngas yield and conversion, from factorial analysis

Process factors	H_2 (mol %)	Syngas yield (m^3/kg)	Conversion (%)
A: Ca/C	19.65	0.62	0
B: % K_2CO_3	16.95	1.14	17.49
AA	-23.60	-0.91	0
AB	2.40	0.19	0
BB	-20.29	-0.98	-9.34

The results indicate the strong positive main effects of Ca/C (A) and % K_2CO_3 (B) on H_2 percentage and syngas yield. Furthermore, the interaction (AB) and the higher order effects of Ca/C (AA) and % K_2CO_3 (BB) on H_2 percentage and syngas yield are also significant, indicating their non-linear relations. Concerning conversion, it is evident from Table 7 that only the % K_2CO_3 has a significant effect on conversion, as both its main (B) and higher-order (BB) effects are important.

3.5 *Environmental and economic aspects*

Carbon dioxide is one of the major greenhouse gases contributing to global warming. Recently, emissions reached

36.3 Gt/y from industrial processes.[34] Therefore, a great effort is made worldwide to adopt negative-CO_2 emission technologies, especially in the energy sector. As such, biomass feedstocks, considered CO_2-neutral, when integrated with CO_2 capture systems during gasification or other processes could meet the goal of carbon-negative applications.

The production cost of H_2 through biomass gasification has been reported to range between 1.2 $/kg and 2.4 $/kg.[35-36] Operating cost is highly influenced by feedstock characteristics and price, process conditions mainly temperature, CO_2 capture technology and catalyst cost. Biomass prices are expected to decrease in the following decades,[36] particularly for waste materials that are globally generated in huge quantities, while novel cheap catalysts are being developed. Previous investigations have shown that when using Ca-based sorbents for CO_2 capture the cost was 16-44 $/t CO_2, which is about half the cost of amine scrubbing technologies.[37] If waste materials are used as sorbents, such as building demolition wastes used in the current study and the concentrated CO_2 stream is recycled in the gasification process, then the above cost could be minimized.

The results herein are promising, suggesting the production of H_2 exclusively from waste materials and the reduction of carbon footprint to the environment. Obviously, the materials are new and further tests optimizing the parameters involved are necessary to establish the feasibility of the process. Computational modeling, larger application scale and techno-economic assessments are important issues in building a sustainable economy based on hydrogen use.

4. Conclusions

Endothermic gasification reactions were favored at higher temperatures. Conversion and higher heating value of gas at 750 °C were 64.2% and 12 MJ/m^3 for acacia pruning and 67.5% and 11.4 MJ/m^3 for acacia sawdust. When building demolition waste material was used as CO_2 sorbent at a ratio Ca/C = 1, the amount of CO_2 captured at 750 °C was 73.2-76%, the concentration of hydrogen in the product gas was 56.2-59.3% mol and the higher heating value was 13.1 MJ/m^3. An increase of catalyst loading up to 20% wt resulted in higher conversion and syngas yield, as well as greater amounts of H_2 in the mixture, leading to higher hydrogen yields. K_2CO_3 catalyst showed a better overall performance at a loading of 20% wt than CeO_2-CaO catalyst, considering also its lower cost. In this case, conversion of the solid waste studied ranged between 80.7% and 84.8%, the molar fraction of hydrogen in the product gas was 67-80.5%, syngas yield varied from 1.9 m^3/kg to 2.6 m^3/kg, with a heating value of 13.1-13.8 MJ/m^3 and energy recovery was higher.

Acknowledgements

The authors kindly thank Prof. G. Xiroudakis for providing the BDW material, 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

Authors declare there is no conflict of interest at any point with reference to research findings.

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