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Gasification Reactivity and Mass Spectrometric Analysis of Gases of Energy Crop Chars under a CO₂ Atmosphere

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ABSTRACT: Aiming to investigate the possibility of exploitation of perennial crops for energetic uses, five sustainable energy plants, previously devolatilized, were gasified by carbon dioxide up to 950 °C in a thermobalance system, coupled with a quadrupole mass spectrometer. The gasification reactivity, thermal decomposition characteristics, and products of gasification were determined, and the effect of inherent inorganic matter of these fuels on process parameters was examined. The bulk of the gasification process occurred above 800 °C, with main products CO and lesser amounts of H₂ and H₂O. Gasification reactivity was highly correlated to the specific surface area of the chars. Inherent mineral species K, P, S, and Cl influenced the temperature sensitivity of the process and reduced the gasification rate and H₂ production. However, a lower pyrolysis temperature of char generation increased the gasification reactivity and greatly enhanced H₂ production.

1. INTRODUCTION

Gasification of solid fuels is a most promising and flexible process, generating a fuel gas basically containing CO, H₂, and CH₄, that is suitable for feeding efficient gas engines and gas turbines, co-firing with coal in existing boilers and the synthesis of gaseous or liquid biofuels.¹ It is economical in a wide range of capacities and has superior environmental performance, especially with regard to CO₂ capture and sulfur removal.²

In this process, one step is the devolatilization of the fuel forming char and volatiles and the other step is the reaction of the char with the gasifying agent (air, steam, and carbon dioxide). These steps may be sequential or contemporary; however, the gasification stage is the rate-controlling step, because the reaction is slower. A two-stage process, whose basic principle is to separate the pyrolysis zone from the reduction zone, could be an advantageous method, because of the lack of tar production and the higher reactivity of biocarbons.³ When carbon dioxide from a residual stream is the reactant gas, CO₂ recycling through this technique gives a potential solution associated with the greenhouse gas environmental problem.

The European Union (EU) directive on renewable energy set the target for all member states to obtain 20% of its energy needs from renewable sources by 2020.⁴ Market needs for fuel diversification, price fluctuations, and financial incentives have renewed the interest in biomass fuels, widening the range of materials being investigated. The introduction of plant species in addition to residuals could fully meet the EU Agricultural Policy,⁵ with a million hectares being expected to be allocated to dedicated energy crops in the short term.⁶ Thus far, much effort has been addressed to evaluate the productivity of these crops, while there is little information concerning fuel quality and even less on technological research, especially the research related to the gasification process.^{6,7}

To achieve high gasification efficiency, a high conversion of char is required, at the lowest possible temperature. Thus, char reactivity is of prime importance for the proper design of gasification reactors. Several factors, such as pyrolysis conditions for char preparation, type and partial pressure of the gasifying agent, gasification temperature, pore structure and active sites on char, ash content, and composition, influence the reactivity of

chars.^{8–10} The reactivity of carbon dioxide toward carbonaceous materials has been found to be lower than that of air or steam,¹¹ so that catalysts are used to improve conversion. Alkali (K and Na), alkaline earth (Ca and Mg), and transition (Fe) metals have been found to accelerate the gasification rates of woody and waste biomass chars.^{11–13} Also, the catalytic effect of these metals inherently present in biomass ashes has been verified; however, research is limited to the pyrolysis process or to steam gasification of residual biomass chars.^{9,13–19} Different pretreatments have been suggested^{14,17,20,21} for removing alkaline components from ashes, affecting positively or negatively the char structure, and thus complicating the overall effect on reactivity.

The reactivities of carbonaceous materials have been extensively studied by thermoanalytical techniques, which allow this information to be obtained in a simple and straightforward method. Thermogravimetric analysis (TGA), coupled to mass spectrometry (MS) for detection of evolved gases, has been commonly used for the study of pyrolysis or combustion processes.^{22,23} Some data have been reported on steam gasification too.¹⁸ Carbon dioxide gasification reactivity of woody and agricultural waste materials has been determined under both isothermal^{24,25} and non-isothermal²⁶ conditions. The effect of mineral matter or metal catalysts by acid treatment (which, as stated above, affects the char structure) was investigated as a function of either the reaction rate or peak temperature. However, to the authors' knowledge, there is a lack of information throughout the literature on carbon dioxide gasification of energy crops addressing char reactivity in terms of several factors, such as the temperature, rate, fuel structure, and composition. Also, there is a lack of data on the analysis of their gaseous products and the effect of pyrolysis conditions and inherent inorganics on both gasification rates and gas product distribution.

On the basis of the above, this work aimed to investigate the possibility of exploitation of five sustainable energy crops to

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Table 1. Proximate Analysis, Ultimate Analysis, and Calorific Values of the Fuels (% , Dry)

sample	volatile matter (%)	fixed carbon (%)	ash (%)	C (%)	H (%)	N (%)	O (%)	S (%)	GCV ^a (MJ/kg)
jatropha	69.1	20.8	10.1	48.5	5.8	5.6	29.5	0.5	18.5
cardoon	64.7	17.4	17.9	44.1	4.8	2.0	31.5	0.2	14.7
willow	75.5	20.4	4.1	53.2	5.7	0.5	36.5		18.1
miscanthus	80.6	15.0	4.4	49.7	4.4	0.2	41.3		17.2
helianthus	67.2	15.1	17.7	45.7	4.9	2.6	28.9	0.2	15.2
cardoon leached	64.5	25.5	10.0	41.1	5.5	2.1	41.2	0.05	

^aGCV = gross calorific value.

energetic uses, combining the recycling of CO₂ streams to mitigate greenhouse gas emissions. The objective was to evaluate the gasification reactivity of these fuels under non-isothermal thermogravimetric conditions and analyze gaseous effluents by means of MS, to obtain useful data for the development of practical systems, and to determine the effect of pyrolysis conditions and inherent inorganic matter on thermal conversion characteristics, reactivity, and products of gasification.

2. EXPERIMENTAL SECTION

2.1. Materials and Characterization. The materials used in this study were two herbaceous energy crops (cardoon and miscanthus) and three short rotation coppice crops (jatropha, willow, and helianthus). Cardoon (*Cynara cardunculus* L.) is a perennial, herbaceous crop of Mediterranean origin that is well-adapted to the xerothermic conditions of southern Europe, with a potential for high yields in such climates.²⁷ Miscanthus (*Miscanthus × giganteus*) is a perennial, C₄ grass of east Asian origin, which is employed in several bioenergy initiatives in Europe.²⁸ Helianthus (*Helianthus annuus* L.) and willow (*Salix* spp.) are two of the most widely cultivated short rotation coppice (SRC) crops, better suited to southern European countries.²⁹ Jatropha (*Jatropha curcas* L.) is a drought-resistant, perennial plant, widely distributed in the wild or semi-cultivated areas in Central and South America, Africa, India, and south Asia. It is capable of achieving high yields under favorable conditions and is gaining importance for the production of biodiesel.³⁰

Characterization of the biomass fuels was performed according to the European standards drawn up by the Technical Committee CEN/TC335. Proximate analysis was carried out using programmable laboratory furnaces following standards EN14774, EN15148, and EN14775. For ultimate analysis, a Thermo Scientific CHNS Flash 2000 type analyzer was used, following standards EN15104 and EN15289, while the calorific value was measured using a Leco AC-300 type calorimeter, following standards EN14918.

Chemical analysis of major elements in ashes was conducted using an inductively coupled plasma mass spectrometer type ICP-MS 7500cx, coupled with an Autosampler Series 3000, both by Agilent Technologies (detection limits of 0.4–34 ppb, depending upon the element). The samples were dissolved by a microwave-assisted digestion with HNO₃ acid. The microwave digestion was carried out using an Anton Paar Multiwave 3000 oven. Phosphorus and chlorine measurements were performed by a spectrophotometer type ultraviolet–visible (UV–vis) Hach 4000 V (detection limit of 200 ppm). For mineralogical analysis, an X-ray diffractometer (XRD) model D8 Advance of Bruker AXS, with application of Cu K α radiation and nickel filter ($U = 35$ kV, and $I = 35$ mA), was used.

Surface areas were determined from N₂ adsorption at 77 K, using an automatic volumetric apparatus, type Nova 2200 of Quantachrome. The Brunauer–Emmett–Teller (BET) model was applied to the N₂ adsorption data at a relative pressure of 0.03–0.3, where monolayer coverage of N₂ molecules is assumed to be complete. Prior to each adsorption measurement, the samples were outgassed overnight at 110 °C, under vacuum of 10^{−6} Torr.

2.2. Leaching Procedure. The energy crops were subjected to washing in double-distilled water, to reduce their metal contents. A total of 100 and 20 mL of water were used for a 1 g sample. The slurries were agitated for 2 h at 80 °C and then filtered in a Buchner funnel. Solid

materials were dried in the oven at 110 °C for 24 h and tested by TGA. Ashes prepared at 560 °C were analyzed using the above-mentioned method.

2.3. Gasification Tests. The carbon dioxide gasification of chars was carried out in a TGA-6/DTG PerkinElmer thermobalance (precision of the temperature measurement at ± 2 °C and microbalance sensitivity of <5 μ g). The sample weight loss and rate of weight loss were recorded continuously under dynamic conditions, as functions of the time or temperature, in the range of 25–950 °C. All experiments were carried out at atmospheric pressure, under a CO₂ atmosphere, with a flow rate of 35 mL/min, at a linear heating rate of 10 °C/min. Argon was used as a purge gas with a flow rate of 45 mL/min. Preliminary tests with different sample masses and sizes and gas flow rates were carried out, to check the influence of heat and mass transfer. Small masses (15–25 mg) of each material, thinly distributed in the crucible, and particle sizes of ≤ 250 μ m were found proper to be used in the experiments, to eliminate the effects of eventual side reactions and mass- and heat-transfer limitations in larger particles. The samples were first devolatilized in argon up to 950 °C at a heating rate of 10 °C/min, as described in a previous work.³¹ Following pyrolysis, the samples were cooled in argon to ambient temperature and the furnace was purged by CO₂ for 30 min. Gasification of the char was carried out up to 950 °C, until a constant weight was reached. The experiments were replicated at least twice to determine their reproducibility, which was found to be very good.

2.4. Thermogravimetry (TG)–MS Measurement of Gases. The analysis of the gas product distribution from the gasification tests was conducted through a quadrupole mass spectrometer (Balzers QME 200) coupled to the thermobalance system. The transfer line was heated to 200 °C, to prevent the condensation of the gaseous products in it. The ion source was operated at 82 eV electron energy, and the mass detection range was 1–400 atomic mass units (amu). Prior to the tests, the apparatus was purged with the carrier gas (pure Ar) for 1 h. The ions separated according to their mass-to-charge ratio were detected by a secondary electron multiplier (SEM). The collection of the TGA/MS data was performed by the TGA (Pyris, version 3.5) and MS software (Quadstar 422).

About 60 mass spectrometric intensities were recorded in the experiments. The mass-to-charge ratios (m/z), which were chosen with respect to good signals for greater accuracy, were 28, 15, 2, and 18, which account for CO, CH₄, H₂, and H₂O, respectively. For CH₄, m/z 15 was selected, because the intensity was high (85.8%) and there was no contribution from the reactant gas. The mass spectra intensities were normalized by the initial sample mass, so that a comparison between different samples could be made.

3. RESULTS AND DISCUSSION

3.1. Characterization of Fuels. The proximate and ultimate analyses as well as the calorific values of the energy crops studied are represented in Table 1. As seen, all samples are characterized by a high amount of volatiles, ranging from 65 to 80%, that could be considered desirable for a good regulation of gasification processes. Willow and miscanthus are low in inorganic constituents ($\sim 4\%$), while cardoon and helianthus present a rather high ash content ($\sim 18\%$). The percentage of nitrogen of the fuels, with the exception of willow and miscanthus, is high, which might be a problem during their thermal processing. However, the sulfur

Table 2. Chemical Analysis of Ashes in Main Oxides (%)

sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	P ₂ O ₅	MnO	TiO ₂	SO ₃	B/A ^a
jatropha	3.1	0.5	0.1	4.3	3.8	26.5	0.2	2.9	0.1	0.01	3.7	9.6
cardoon	3.9	1.0	0.6	16.8	3.7	23.7	1.7	4.9	0.03	0.03	7.5	9.4
willow	3.6	0.6	0.3	16.8	10.0	13.3	6.6	8.9	0.1	0.03	5.1	4.1
miscanthus	59.3	1.2	0.8	4.5	2.2	10.3	0.4	3.7	0.1	0.02	3.9	0.2
helianthus	5.0	0.5	0.3	14.6	10.6	12.4	7.5	12.6	0.04	0.03	6.6	0.6
cardoon leached	7.5	2.4	5.5	45.3	7.1	8.4	1.0	2.0	0.07	0.04	3.3	6.7

$$^a \text{B/A} = (\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{K}_2\text{O} + \text{Na}_2\text{O})/(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2).$$

content of all samples is very low or practically null, implying that sulfur emissions are not of concern for these energy crops, when used for power production. Finally, the highest calorific value corresponds to willow, because of its lower ash and higher volatiles and fixed carbon contents.

The concentrations of the main inorganic constituents of the ashes, expressed in the typical way as oxides, are presented in Table 2. Cardoon, willow, and helianthus ashes were rich in Ca, Mg, K, and P, which are essential plant nutrients and soil improvement agents. For miscanthus, silica appeared to be the main ash-forming element. Alkalis, in the form of potassium oxide, were present in large concentrations in all samples, with jatropha having the highest content, ~27%. Sodium was found in significant amounts in willow and helianthus. On the other hand, the low concentrations of Al and Fe in these ashes suggest that their origin was mostly inherent rather than adventitious material from sands, clays, and soil.

3.2. Gasification Reactivity of Chars. The reactivity of the chars and the thermal decomposition characteristics in a CO₂ atmosphere are compared in Figure 1, which illustrates reaction rates as a function of the temperature, and in Table 3, respectively. These results confirm that gasification reactivity is dramatically

influenced by the temperature. Char gasification was slow until about 800 °C, reaching only about 10–15% of the complete conversion, after which the bulk of the process occurred. The curves, with the exception of the curve corresponding to cardoon, showed single peaks, with their maxima centered between 870 and 950 °C. Cardoon char reacted about 2 times slower than the other chars, and its peak temperature was displayed to a lower value. As Table 3 shows, this crop together with jatropha decomposed at a lower temperature (<700 °C) in comparison to the rest of the fuels. This behavior could be explained by the higher lignin content of these two materials, as shown in an earlier work by the author.³¹ On the other hand, it is clearly observed that willow char displayed the highest gasification rate and conversion. Also, the higher cellulose content in this crop and miscanthus (as previously shown³¹) elevated the peak temperature of gasification, agreeing with previous investigations.¹⁵ The order of the reaction rate sequence for the various chars studied can be ranked as willow > miscanthus > helianthus > jatropha > cardoon. By defining as mean reactivity the ratio of peak rate/peak temperature ($R_{\text{max}}/T_{\text{max}}$), according to Ghetti et al.,³² as a means of comparing the reactivity of the samples, Table 3 shows that the mean reactivity sequence order is willow > jatropha > helianthus > miscanthus > cardoon.

There are several factors affecting char reactivity, such as the chemical composition and structure of the parent fuel, inorganic constituents, pyrolysis conditions, and concentration of the gasifying agent. The char gasification process is more complex than the solid devolatilization process, because the former is a heterogeneous process, where the chemical reactions are located over the surface of the material.^{9,33} In the present work, the experiments were conducted under identical conditions, so that a direct comparison between the gasification behaviors of the crops could be made. The pyrolysis temperature, retention time, and concentration of CO₂ were kept constant throughout the tests. Thus, the role of indigenous mineral matter and structure of the biomass samples in the gasification process were examined.

There is significant evidence in the literature that some indigenous inorganic compounds, such as the oxides and salts of

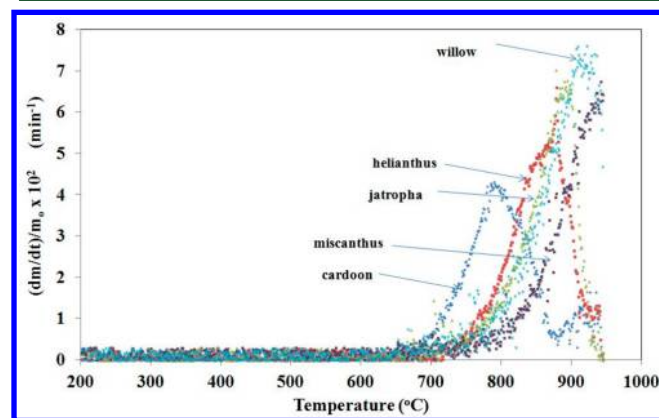


Figure 1. DTG gasification profiles of the energy crops.

Table 3. Gasification Characteristics of Energy Crop Chars

sample	initial reaction temperature (°C)	maximum reaction rate ($\times 10^2$, min ⁻¹)	temperature at maximum reaction rate (°C)	$R_{\text{max}}/T_{\text{max}}$ ($\times 10^4$, min ⁻¹ /°C)	conversion (% daf)	alkali index (Al)	O/C (mol/mol)
jatropha	680	6.82	893	0.763	67.7	0.98	0.45
cardoon	600	4.52	781	0.578	66.2	1.68	0.52
willow	709	7.48	919	0.813	86.8	0.45	0.51
miscanthus	710	6.77	943	0.717	84.6	0.01	0.62
helianthus	705	6.68	876	0.762	70.5	1.46	0.47
cardoon-600 ^a	593	5.67	798	0.710	81.5	1.68	0.52
cardoon leached	730	6.94	841	0.825	74.2	0.67	0.75

^aPyrolyzed at 600 °C.

alkaline (K and Na) and alkaline earth (Ca and Mg) metals, act as catalysts and improve the reactivity of biomass gasification.^{11,15,18,24,33,34} The alkali index (AI), describing the ratio of the sum of the basic compounds to the acidic compounds in ash (base/acid ratio), is commonly used to estimate the catalytically active species within the ash.

$$AI = \text{ash (wt\%)}(B/A)$$

Generally, the higher the AI, the higher the catalytic activity. As Table 3 shows, the order of the AI sequence for the energy crop chars studied is cardoon > helianthus > jatropha > willow > miscanthus. This trend is not in accordance with the reaction rate and the gasification conversion of char. In contrast to other findings,³⁵ the high silicon content in miscanthus char, which lowered the AI, did not seem to have an inhibiting effect on the rate. Furthermore, Figure 2 illustrates that there is no correlation

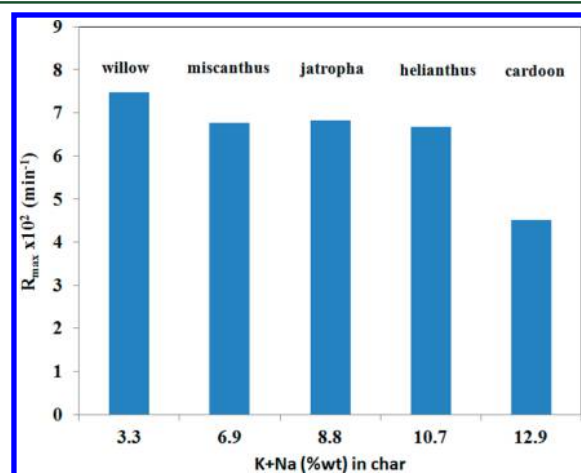


Figure 2. Gasification rate of fuels as a function of the alkali metal (K and Na) content in the chars.

between the alkali metal (K and Na) content in the chars and the reaction rate. Cardoon, which had the highest concentration in alkalis, presented the lowest rate. These results agree with those obtained by previous researchers³⁴ for different biomass fuels. Therefore, it can be concluded that inorganic matter was not the main factor that affected the gasification reactivity of the crop samples.

It is known that the heterogeneous rates of char conversion are also determined by surface area, porosity, and carbon active sites. These properties might be influenced by the cellulose, hemicellulose, and lignin content of lignocellulosic biomass materials, as found from the experimental results of this study shown above. The specific surface areas (S_{BET}) and pore volumes of the raw biomass samples and their chars, as calculated from N_2 adsorption data via the BET method, are presented in Table 4. It can be observed that the surface area is greatly enhanced after the pyrolysis process. The increase in the surface area is associated with a decrease in the average pore size, suggesting the development of microporosity with thermal treatment. The total pore volume of the samples is closely related to their specific surface area. For willow char, the surface area is 117 times higher, for miscanthus char, the surface area is 115 times higher, for helianthus char, the surface area is 56 times higher, for jatropha char, the surface area is 9.5 times higher, and for cardoon char, the surface area is 7.6 times higher than that of the original crop materials. A comparison between Tables 3 and 4 and Figure 3 clearly shows that there is a direct relationship between

Table 4. Structural Characteristics of Raw and Thermally Treated Energy Crops

sample	specific surface area (m^2/g)	micropore volume ($\times 10^2, \text{cm}^3/\text{g}$)	average pore size (\AA)
jatropha-r ^a	6.7	0.88	46.6
jatropha-d ^b	63.5	6.60	36.3
cardoon-r	6.9	0.87	50.2
cardoon-d	52.6	5.21	41.3
cardoon leached-r	7.5	0.90	42.9
cardoon leached-d	55.2	5.59	36.3
willow-r	1.8	0.16	37.2
willow-d	210.6	12.30	19.2
miscanthus-r	1.7	0.16	36.5
miscanthus-d	195.8	11.98	24.5
helianthus-r	1.8	0.20	43.1
helianthus-d	98.2	9.80	34.7

^ar = raw. ^bd = devolatilized.

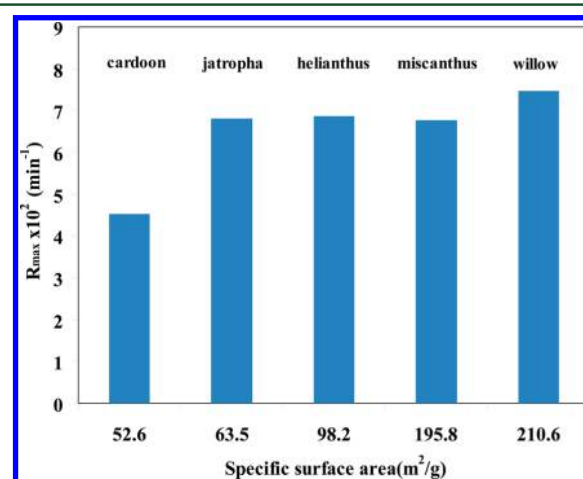


Figure 3. Gasification rate of fuels as a function of the specific surface area of chars.

gasification reactivity and S_{BET} . The char with a larger S_{BET} possesses higher gasification reactivity, and the order of the S_{BET} sequence for the various chars tested can be ranked as cardoon < jatropha < helianthus < miscanthus < willow.

Additionally, the effect of the crystalline structure, expressed by the O/C mole ratio of each char, is considered an important factor in evaluating gasification reactivities.^{10,35} A lower O/C indicates a higher order crystalline structure, tending to decrease the gasification reactivity. From Table 3, it can be observed that there is a positive correlation between the O/C in char and its gasification rate and conversion, implying that miscanthus char had a less graphitic structure than the rest of the chars tested.

3.3. Gaseous Products of Gasification. The evolution profiles of the main gaseous products released during the gasification of cardoon (raw sample) up to 950 °C, i.e., CO , H_2O , and H_2 , as monitored by the TG–MS system, are illustrated in Figure 4. Sulfur compounds were not detected, because cardoon had a very low sulfur content. Also, any release of nitrogen compounds cannot be related to the evolution of NH_3 and HCN , because the signal of these ions (m/z 17 and 27, respectively) has a great contribution from H_2O and hydrocarbons ($\text{C}_2\text{--C}_4$), respectively.

To evaluate these mass spectra, the predominant reactions taking place simultaneously during the CO_2 gasification process must be presented. Thermal cracking is not considered, because no peaks related to hydrocarbons were detected during the tests.

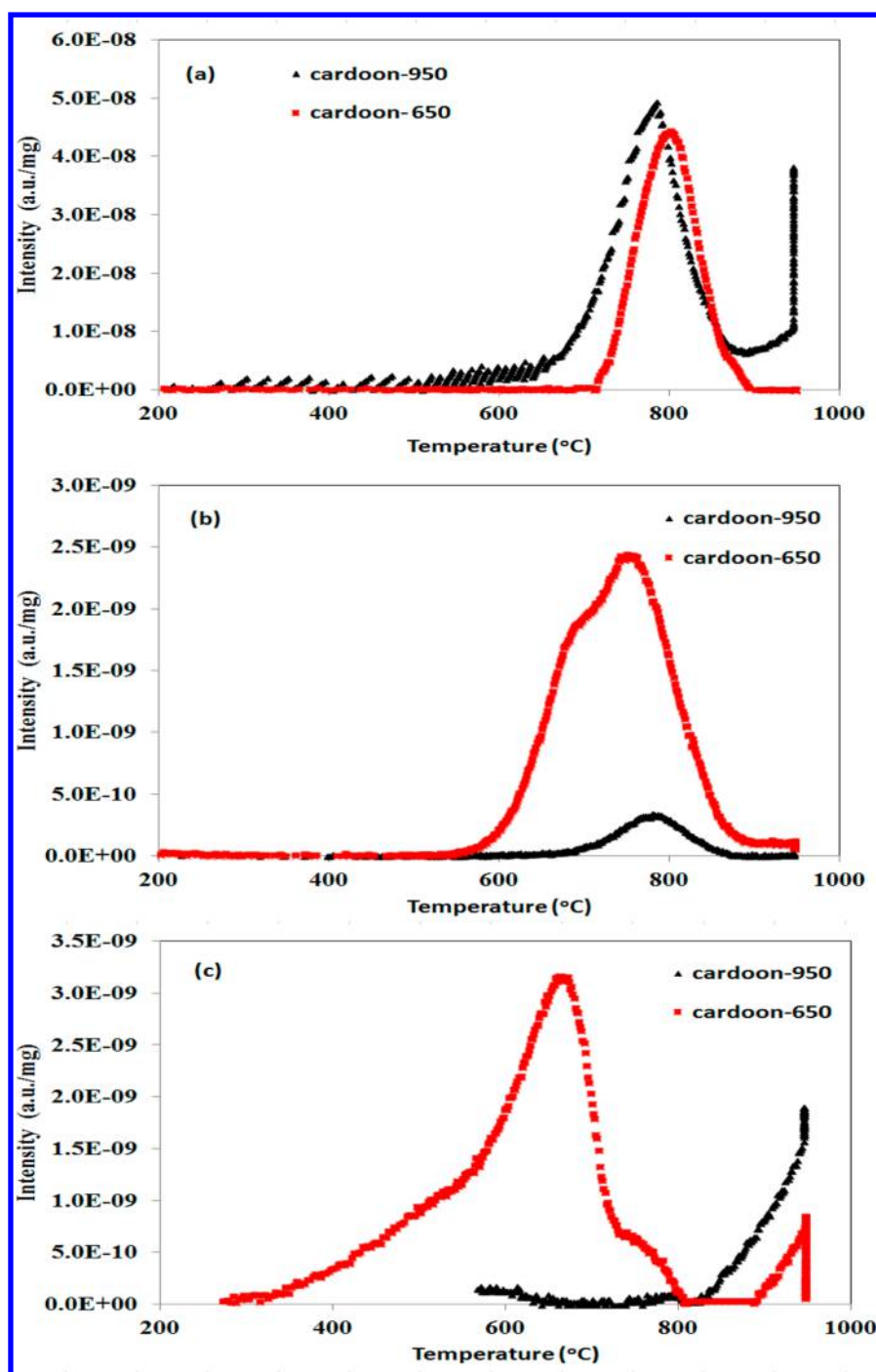
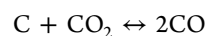


Figure 4. Evolution profiles of gases (a) CO, (b) H₂, and (c) H₂O released during the gasification of cardoon char pyrolyzed at 600 or 950 °C.

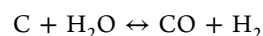
Primary reaction:

Boudouard

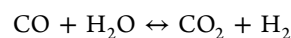


Secondary reactions:

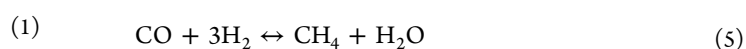
water gas



water-gas shift



methanation



The CO evolution profile closely resembled the corresponding differential thermogravimetry (DTG) curve (Figure 1), presenting two peaks: a higher peak in the range of 700–850 °C and a second lower peak at 950 °C. This indicates that most of the char was consumed by the Boudouard reaction (reaction 1). Furthermore, panels b and c of Figure 4 show that, between 700 and 850 °C, H₂ and H₂O were also released in small amounts. This points out to the occurrence of reactions 2 and 3.

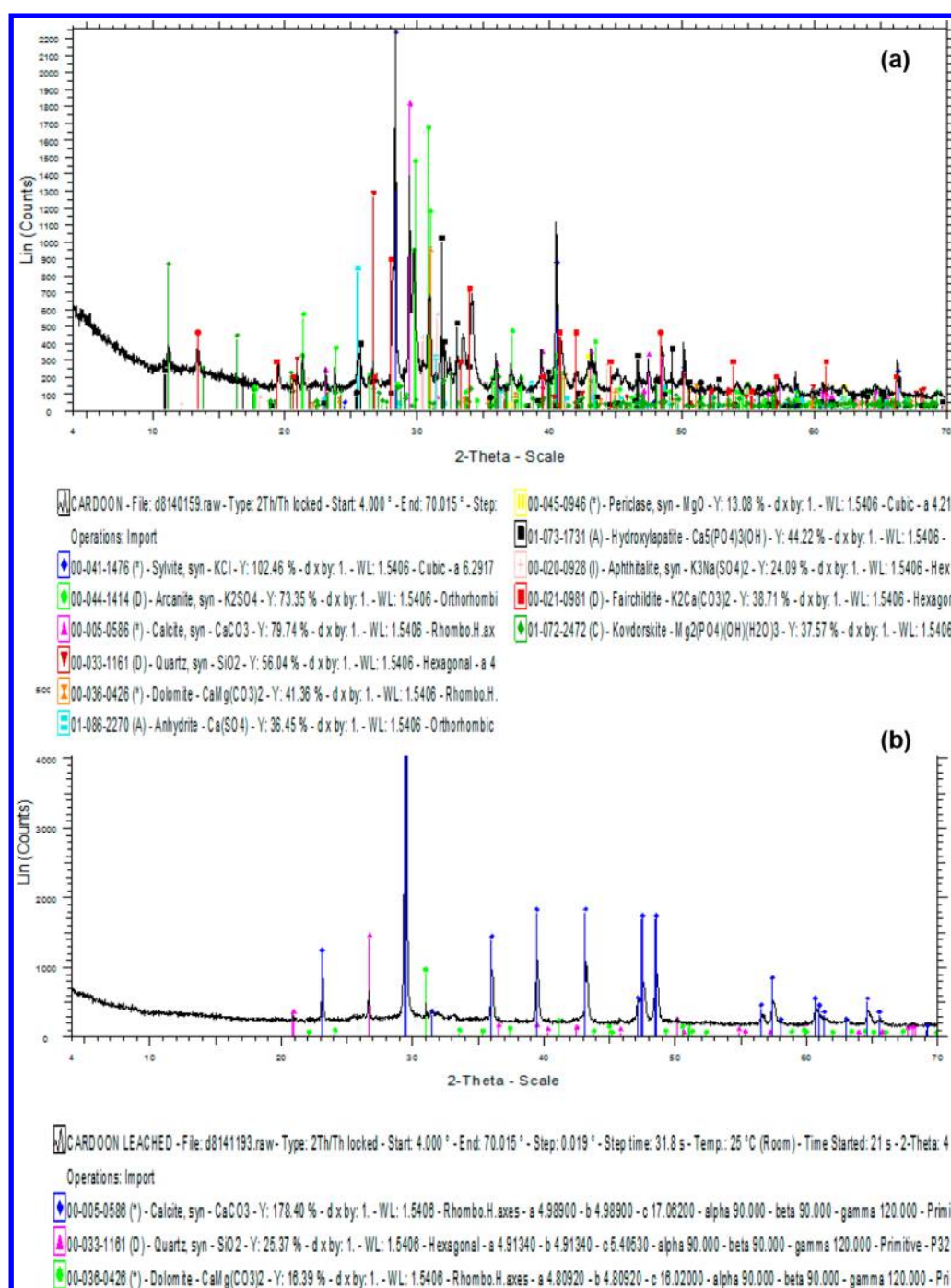


Figure 5. XRD diagrams of (a) cardoon and (b) cardoon-leached ashes.

In the present study, no CH₄ was formed, because it is known that reaction 4 requires high pressure to proceed and hydrogen production was small for the methanation reaction (reaction 5) to take place. At temperatures above 850 °C, it can be observed that H₂ evolution ceased, the concentration of CO was increased, and the H₂O concentration peaked to its maximum value. CO and H₂O formation can be attributed to the Boudouard (reaction 1) and the reverse water-gas shift (reaction 3) reactions.

As previously discussed, one of the objectives of this study was to investigate the influence of pyrolysis conditions on conversion performance, reactivity, and products of gasification. Thus, the cardoon sample was also devolatilized up to 600 °C, instead of

950 °C, and then gasified with CO₂, as before. The results are presented in Table 3 and Figure 4. Table 3 shows that, when the fuel was pyrolyzed at a lower temperature, its reactivity in a CO₂ atmosphere was increased, the reaction rate peaked at a higher value, and a final conversion of 81.5% was achieved, which was considerably higher than the conversion obtained when pyrolysis was conducted up to 950 °C (i.e., 66%). This behavior can be explained through examination of Figure 4. As observed, for the low-temperature pyrolyzed sample, H₂O formation was greatly enhanced, even at low temperatures, the amount of H₂ released was about 7 times higher, and the concentration of CO was reduced, as compared to the high-temperature pyrolyzed sample. Evolution of chemical H₂O showed an additional peak at

low temperatures (300–700 °C). The fact that CO and CH₄ were not generated in this temperature regime, whereas H₂ increased, suggests that self-gasification of the sample by steam was taking place via reaction 2, followed by the water-gas shift reaction (reaction 3). At temperatures of 700–850 °C, when the Boudouard reaction (reaction 1) commenced, H₂ production reached its maximum through reactions 2 and 3.

At this point, it must be mentioned that similar results were obtained for willow crop, when this was first devolatilized at 600 °C and then gasified (a conversion of 92% was reached). These findings are interesting for practical applications. For instance, when energy crops are used for bio-oil production, where usually pyrolysis occurs between 500 and 600 °C, residual chars could be gasified with a recycled CO₂ stream for heat or power generation or even for the production of a gas rich in H₂ suitable for a fuel cell.

3.4. Effect of Leaching on Reactivity and Products of Gasification. As already mentioned in the Introduction, among the energy crops studied, cardoon is a very promising alternative fuel for south European countries, such as Greece, because it is grown naturally in abundance in uncultivated soils, is well-adapted to the local xerothermic conditions, and has a potential for high biomass yields. For these reasons, it was selected for further investigations and, specifically, for the leaching tests.

The ash content of cardoon was reduced by 44% upon leaching (raw sample at 17.4% and leached sample at 10%). The XRD peaks in Figure 5 clearly illustrate that K, P, S, and Cl elements in ash, mainly incorporated in carbonates, sulfates, and chlorides, were almost completely removed, leaving mainly silicon, because this was present in the stable form of quartz, as well as some calcite and dolomite. The chemical analysis of washed fuel ash (Table 2) showed that K₂O was depleted by 65%, P₂O₅ was depleted by 60%, SO₃ was depleted by 56%, and Cl was depleted by 90%.

The reactivity changes in carbon dioxide, brought about by the removal of inorganic constituents, were investigated by performing thermal analysis for leached cardoon, under the same experimental conditions for the raw crop. It was found that washing of the sample did not affect the yield of volatiles (Table 1), slightly reduced the pyrolysis rate, but shifted the peak temperature to a higher value (from 324 to 368 °C). This suggests that K, P, S, and Cl, especially K, which was abundant in the raw sample, influenced the sensitivity of the reaction in argon, causing the degradation of cardoon to start at a lower temperature. On the other hand, from comparison of the DTG curves of gasification in Figure 6, it can be observed that the curve corresponding to deashed char was shifted to a much higher temperature (~60 °C), whereas its peak value was increased by a factor of 1.5. Conversion was also enhanced. Therefore, it seems that minerals, which were removed upon washing, served as diluents in cardoon gasification, inhibiting the reaction rate, and as before influenced the temperature sensitivity of the char in carbon dioxide. Because the gasification rate depends among other factors upon the accessibility of the reactant gas to the interior of the solid particles, the surface areas and the pore volumes of the raw and leached samples were determined via the nitrogen adsorption method. Table 4 shows that cardoon produced from leached biomass presented a higher surface area and pore volume with respect to those of the untreated sample. Therefore, soluble minerals decreased the reactivity of the char. It is possible that inorganic particles form clusters on the char structure, which block the surface pores or access to the adjacent micropores.^{10,13}

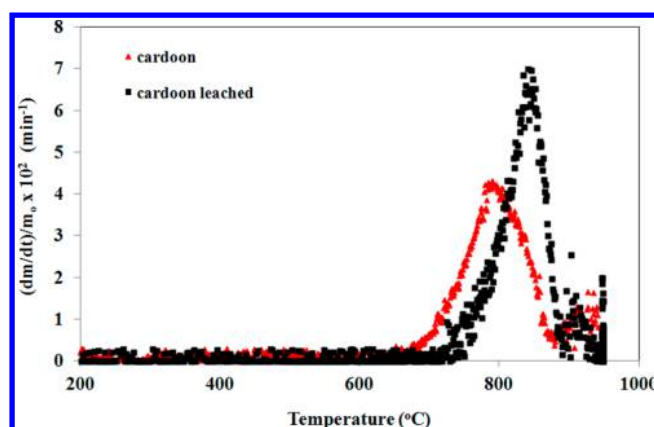


Figure 6. DTG gasification profiles of cardoon and cardoon-leached samples.

The products derived from the gasification of the cardoon-leached sample were evaluated by TG–MS analysis, as for the raw fuel. Previous findings that, for deashed char gasification reactions commenced at a higher temperature and the reaction rate was increased, are reflected in the gaseous yields observed in Figure 7. Thus, CO, H₂, and H₂O exhibited a greater intensity

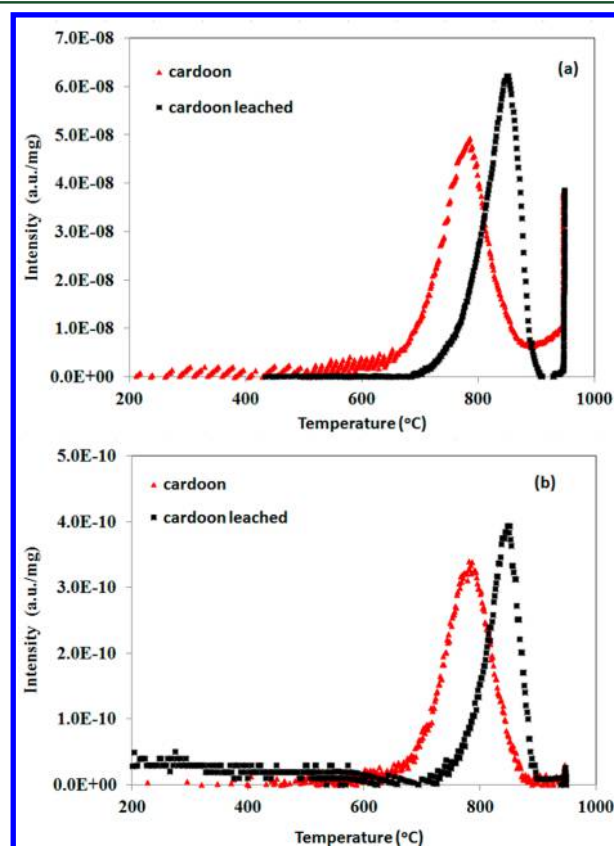


Figure 7. Evolution profiles of gases (a) CO and (b) H₂, released during the gasification of cardoon and cardoon-leached samples.

upon fuel leaching and were released at temperatures about 60 °C higher, as compared to the raw crop.

4. CONCLUSION

The energy crops studied were characterized by high volatile contents, low to medium ash contents, and very low sulfur contents.

The ashes were rich in Ca, Mg, K, and P compounds. For miscanthus, Si was the main ash element.

The bulk of the char gasification process occurred above 800 °C. Gasification reactivity was highly correlated to the specific surface area of the chars, and the sequence order was willow > miscanthus > helianthus > jatropha > cardoon. Inherent inorganic species K, P, S, and Cl, which were leached upon washing as carbonates, sulfates, and chlorides, served as diluents in cardoon gasification, inhibiting the reaction rate, and influenced the temperature sensitivity of the char in CO₂. On the other hand, a lower pyrolysis temperature for char generation increased the gasification reactivity of the char while elevating the peak temperature.

Above 700 °C, the products of gasification were CO and smaller amounts of H₂ and H₂O. Upon cardoon fuel leaching, which delayed the gasification process and increased the reactivity, gas production was higher, as compared to the raw material, whereas when the char was prepared at a lower temperature, evolution of H₂ was greatly enhanced, because of self-gasification of the sample by steam.

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Notes

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