Case Studies in Thermal Engineering 4 (2014) 42–52

Contents lists available at ScienceDirect

Case Studies in Thermal Engineering

journal homepage: www.elsevier.com/locate/csite

Attempts on cardoon gasification in two different circulating fluidized beds

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ARTICLE INFO

Article history:
Received 30 March 2014
Received in revised form
10 June 2014
Accepted 10 June 2014
Available online 26 June 2014

Keywords:
Cardoon
CFB
Defluidization
Tackling agglomeration problems

ABSTRACT

Few tests have been carried out in order to evaluate the use of cardoon in gasification and combustion applications most of the researchers dealt with agglomeration problems. The aim of this work is to deal with the agglomeration problem and to present a solution for the utilization of this biofuel at a near industrial application scale. For this reason, two experiments were conducted, one in TU Delft and one in Centre for Research and Technology Hellas (CERTH), using fuel cardoon and 50% w/w cardoon blended with 50% w/w giant reed respectively. Both experimental campaigns were carried out in similar atmospheric circulating fluidized bed gasifiers. Apart from the feedstock, the other differences were the gasification medium and the bed material used in each trial. The oxidizing agent at TUD's run was O_2/steam, whereas CERTH's tests used air. When experiments with the cardoon 50% w/w–giant reed 50% w/w blend were performed no agglomeration problems were presented. Consequently, gasification could be achieved in higher temperature than that of pure cardoon which led to the reduction of tar concentration.

1. Introduction

Biomass fuels such as agricultural or agro-industrial residues together with energy crops are considered promising renewable energy sources [1]. To reduce CO_2 emissions, part of the power production can be substituted by using biomass in thermochemical technologies. In a gasification process, solid fuel is converted into a product gas, allowing its more efficient use in combined power cycles or for transportation fuel or chemicals production. Gasification of biomass is a first step of converting biomass into biosyngas which in return can be converted to 2nd generation biofuels [2]. The mostly investigated plant for these thermochemical processes is willow. Willow has low ash content; as a result, it is regarded as a very promising feedstock for fluidized bed applications [3,4]. The main drawback of this biomass fuel is its high cultivation cost [5,6]. For this reason a crop, for which the corresponding costs are much lower, will be examined on gasification trials.

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http://dx.doi.org/10.1016/j.csite.2014.06.004

Nomenclature

CCE	carbon conversion efficiency (%)
CERTH	Centre for Research & Technology Hellas
CFB	circulating fluidized bed
CGE	cold gas efficiency (%)
HHV	high heating value (MJ/kg)
KTH	Royal Institute of Technology
LHV	low heating value (MJ/kg)
SBR	steam to biomass ratio
TUD	Delft University of Technology
u_s	superficial velocity (m/s)
WGSR	water–gas shift reaction

Cynara cardunculus, commonly known as cardoon, is a thistle like plant in the aster family Astaraceae, and is considered by few works as a promising fuel for thermochemical possessing (combustion, gasification) [2]. This has led into a recent rush of changing plantations to this plant for the production of biomass in Mediterranean regions. Nevertheless, there is very little positive evidence from applications of this fuel that it is trouble free.

Cardoon is a perennial herbaceous species native to the Mediterranean region climate which is characterized by dry and hot summer conditions. The factors that influence the properties of cardoon are the chemical soil characteristics, the fertilizers, the harvesting method and the different climatic conditions and rain distribution. One of the major advantages of cardoon crops is the reduced irrigation demands, thus its cultivation costs are lower compared to other crops [7–11]. The plant has an annual development cycle, native to the Mediterranean region, mainly localized in Spain, Italy and Greece (typical conditions are mild winters, hot dry summers and low irregularly distributed annual rainfalls). Foti et al. [12] report that in the year 2000 cardoon cultivation in countries of southern Europe varied between 51,000 ha (in Italy) and 24,000 ha (in Spain). Fernadez et al. [13] conducted several cardoon cultivations and reported that cardoon can survive the summer drought by growing a very deep rooting (up to 7 m) and drying the aboveground plant part during the summer. Angelini et al. [14] reported that the minimum air temperature that the plant can tolerate is -10 °C. Christou et al. [15] reported that cardoon needs four times lower irrigation than other energy crops. The plant's height can reach up to 2 m depending on climate and soil conditions [16]. The reproductive cycle is completed during the summer so the harvest period can start in August when the aboveground part is dried. As a result, the crop leads to a high yield of dried solid biomass [16].

Nevertheless, cardoon can have a very negative effect in a local agricultural system, especially when farmers decide to change the cultivated crop. Cardoon has long been recognized as a horrific pest plant and can also become a serious invasive species [16]. This is mainly because of its perennial tap-root, capable of vigorously regenerating unless the entire root system is destroyed. This task is very difficult and sometimes impossible even if plowing, chaining, scraping and bulldozing are employed [17–19].

Farmers should take into account the abovementioned characteristics of cardoon before deciding to engage in its cultivation due to the benefits of its high dry mass yields [17]. It should be used only into non-irrigated and certainly marginal quality land and without any irrigation if the reported low costs are to be achieved [20].

Up to date, comparatively few tests and analyses have been carried out in order to verify the suitability of cardoon in pyrolysis, gasification and combustion [21–34]. Pyrolysis is the initial step in all thermochemical conversion processes of biomass materials, but also in techniques for the production of bio-oil. Cardoon's ash minerals such as potassium slightly affect the reactivity of cardoon; mainly causing the thermal degradation to start at lower temperatures [35]. Furthermore, the pyrolysis of cardoon yields more char compared to other energy crops because of its higher ash content [26]. Regarding combustion, cardoon-fired test runs on lab-scale and pilot-scale have been performed [21,23,25], in which molten ash and slag were observed, creating severe problems to the continuous combustion process, and simultaneously reducing the boiler's load and availability. The effect of leaching the cardoon on its pyrolysis kinetics pyrolysis has been investigated by TGA tests performed by Vamvuka and Sfakiotakis [25]. There are no reported gasification attempts on larger scales.

The work presented in this paper addresses scale-up by conducting air-blown gasification experiments in a pilot-scale circulating fluidized bed gasifier in order to assess the quality of cardoon at a near industrial application scale and report practical problems from its utilization. Two experiments were conducted, one at TU Delft and one at Center for Research and Technology Hellas (CERTH), using as fuel cardoon and 50% w/w cardoon blended with 50% w/w giant reed. Giant reed was chosen mainly due to the fact that it is a fast growing perennial grass, native to the Mediterranean area. Additionally, it has been highlighted as a very promising crop in terms of energy production in southern Europe [36].

The circulating fluidized bed gasifiers had nearly the same thermal capacity (100 kW). As observed in previous studies, cardoon's high ash concentration, along with the presence of mineral elements (K, Si, Ca) in its composition, results in a low ash melting point, which causes agglomeration problems [37]. The following section reports the findings of agglomeration problems when conducting the experiments with cardoon, in contrast with using the cardoon–giant reed blend.

2. Experimental

2.1. Cardoon feedstock used

The cardoon used in the experiments was cultivated, harvested and pelletized grown in the region of central Greece from the Greek company Pavlos N. Pettas S.A [38]. The second fuel used in this campaign (cardoon–giant reed mixture) was

Table 1
Fuel proximate, ultimate and heating value analyses.

	Cardoon	Cardoon 50% w/w/giant reed 50% w/w
Proximate analysis (wt%, dry basis)		
Moisture	13.2	8.9
Volatiles	65.07	70.3
Fixed carbon	5.46	24.4
Ash	15.38	5.2
Ultimate analysis (wt%, dry basis)		
C	42.69	46.6
H	5.30	5.9
N	2.23	0.9
S	0.45	0
O[a]	31.3	46.5
Cl	0.29	0
Ash	17.7	5.7
HHV d.b. (MJ/kg)[b]	17.3	16.9

[a] By subtraction.
[b] higher heating value (HHV) of dry solids (d.b.).

Table 2
Ash composition expressed as elements % ash.

	Cardoon	50% w/w Cardoon/50% w/w giant reed
Elemental ash analysis (% ash)		
Al	2.420	14.90
Ca	45.04	29.40
P	2.040	8.470
K	30.64	19.20
Mg	0.000	0.000
Na	14.45	7.510
Si	6.330	19.70
S	0.000	0.000

provided by the Greek company SAMARAS [39]. Table 1 presents the fuel analyses of cardoon pellets: proximate (according to ASTM E871, D1 102-84) and ultimate analysis (according to ASTM D3176-93, D3177-33). The ash analysis of the major ash species is given in Table 2.

2.2. *Bed material*

The experimental campaign was carried out with two different bed inventories. Magnesite bed was used in the experiment conducted with steam/O_2. The mean chemical composition of this magnesite is 45% MgO and 50% CO_2 with small Fe quantities and it crystallizes in trigonal–hexagonal scalenohedral [40,41,32,33]. In a fluidized bed gasification process, magnesite has been proven to have tar conversion capabilities, mainly due to its Mg and Fe content [42]. The chemical composition of the magnesite used is given in Table 3. The initial bed inventory was 13 kg sieved to narrow particle size range (d=350–500 μm).

In the experiment conducted with the cardoon–giant reed blend, olivine was used as bed inventory. Olivine also has tar conversion capabilities as it also includes Fe and Mg [21]. The initial weight of the bed material was ~7 kg with a narrow particle size range (d=350–500 μm). The chemical composition of olivine is presented in Table 3.

The determination of the fluidization regime during the gasification tests, has been estimated for both reactors by calculating the values U^* and dp^* [43]. Fig. 1 indicates the limit of the bubbling and fast fluidization regimes. The black point corresponds to the test with O_2/steam, whereas the white corresponds to the air experiment. Regarding the gasification with O_2/steam testU^* is 1.9, and 1.8 for air gasification. The dp^* for the test carried out with O_2/steam is 7.1, whereas for the trial performed with air is 8.2.

Table 3
Chemical analysis and density of magnesite and olivine bed material.

Compound	**Magnesite**	**Olivine**
	Fraction (wt%)	
Si	1	35.2
Fe	5.5	11.2
Mg	65	47.45
Ca	28.5	4.9
Al	0	1.24
Density (kg/m_N^3)	2980	3200

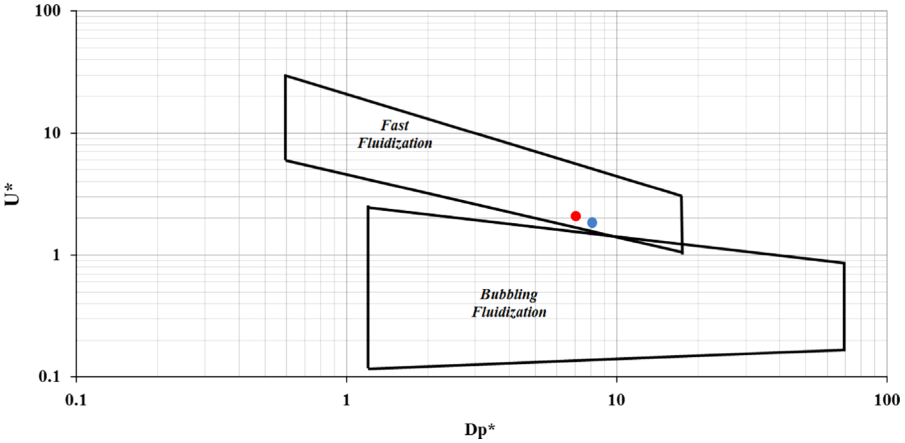

Fig. 1. Map of bubbling and fast fluidization regimes. Blue point: test with air, Red point: test with O_2/steam. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

2.3. Description of test facilities and methodologies employed

2.3.1. Circulating fluidized bed gasifier at TU Delft

The circulating fluidized bed (CFB) reactor is operated under atmospheric pressure, the oxidizer supply is steam–oxygen, and the facility has a thermal input of 100 kW_{th}. Its riser is a cylindrical tube made of stainless steel 310 L, with an inner diameter (ID) of 83 mm and a height of 5.5 m. The main flow of the gasification medium is introduced at the bottom of the riser via nine tuyeres with two holes each. Unconverted char and bed inventory are separated from product gas by means of a 102 mm ID cyclone having a height of 630 mm and return to the riser through a 54 mm ID downcomer tube. Afterwards, syngas is further purified by two high temperature ceramic candle filter units (BWF and Pall filter) connected in parallel downstream of the second cyclone (with the same dimensions as the first cyclone) which can be switched during operation.

The feeding system can supply fuel at a maximum rate of 20 kg/h. The measurement equipment consists of flow meters (Endress and Hauser AT70 thermal flow meters for all primary flows, except for steam, where an Endress and Hauser Prowirl 72 vortex flow meter is used), nine (9) thermocouples (K types), eight (8) differential pressure meters and weighing devices. Table 4 shows the conditions during cardoon gasification.

Syngas was analyzed by means of several analytical instruments which include Hartmann & Braun Uras10P NDIR (online CO_2, CO with a range 0–25% v/v for both species), Hartmann & Braun Magnos 6G PM (online O_2 with a range 0–25% v/v), Varian CP4900 μ-GC (semi-online CO, CO_2, H_2, CH_4, benzene, toluene and xylenes (BTX)). The schematic drawing of the CFB gasifier installation is illustrated in Fig. 2. To avoid the coarsest particles from penetrating the sampling line, the gas analysis probe point is located into the direction of the main gas flow.

During the experiment, a sample flow of the product gas is continuously extracted upstream of the gas outlet of the first cyclone. Additionally, the particle filter vessel is heated by using a heating jacket (Tyco IJ-GL glass silk heating jacket). The temperature of both is maintained at 300 °C using temperature controllers. Then, the sample gas flows through the primary and secondary condenser, which are connected in series, removing the condensables with the highest boiling point, predominantly heavy tar and some water. From there it proceeds to the gaspump and finally to the gas analysis system. Afterwards, a slip stream of the gas passes through a second condenser (in an ice bath) and then followed by two flasks filled with silica gel, hence completely analyzing the product gas (Fig. 2). Tar measurements have been conducted using the Solid Phase Adsorption (SPA) method developed by KTH [44] and the sampling point is located immediately downstream of the filter outlet.

Table 4
Conditions of gasification tests.

	TUD	CERTH
Fuel	Cardoon	50% w/w Cardoon/50% w/w giant reed
Gasification medium (GM)	O_2–steam	Air
Flow of GM in riser [kg/h]	Oxygen flow: 4 Steam flow: 12	11.1
Flow in downcomer [kg/h]	1.2	3.67 (N_2)
Purging flow (N_2) [kg/h]	1.4–1.6	–

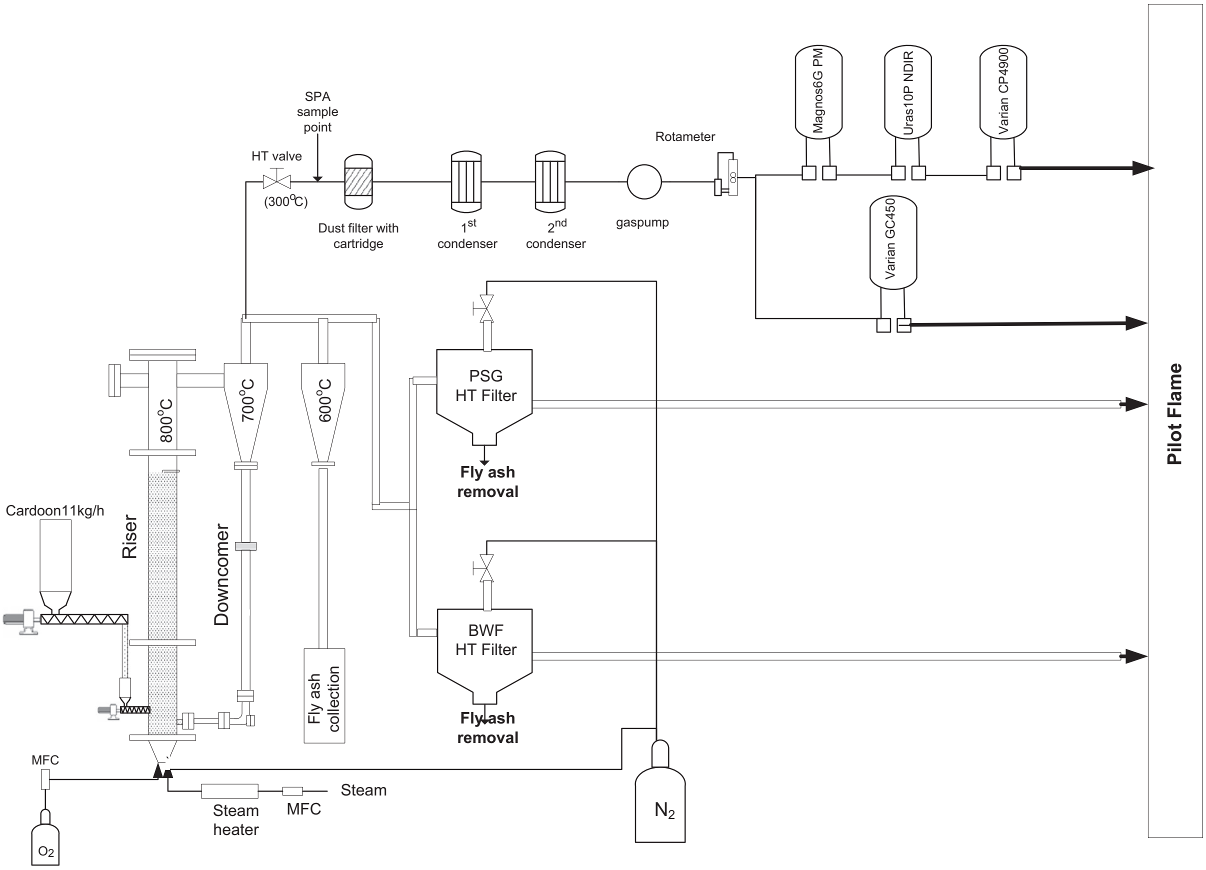

Fig. 2. A schematic of the CFB gasifier installation at TU Delft.

2.3.2. Circulating fluidized bed gasifier at CERTH

The circulating fluidized bed gasifier is an atmospheric pressure, air-blown gasifier with a thermal input of 100 kW_{th}. It consists of a stainless steel 316 L cylindrical tube with 78 mm internal diameter (ID) and 6.0 m in height (Fig. 3). Fluidization air is also preheated and introduced into the bed through a distributor, which has six (6) tubes with bubble-caps at the end, located at the bottom of the riser. The biomass fuel mixture is fed into the bed, at about 265 mm above the distributor. The feeding system consists of two hoppers for the initial storage of the solid fuel and a volumetric silo whose flow rate is adjusted by a dosimetric screw feeder. The second silo serves to feed the fuel inside the gasifier using a second screw feeder which rotates faster than the first one. Special attention was given to the design of the feeding system, as the temperature in the final feeding tube (near the reactor) was very high. A cooling jacket was necessary to avoid pyrolysis prior to the reactor in that part between the silo and the reactor. In order to avoid the product gas back flow, a minor air flow was also added through the top of the silo. The air flow was regulated by mass flow controllers. The particulate matter was removed from the produced syngas by means of a cyclone which has an internal diameter 260 mm and height 800 mm. This unreacted char and bed material return to the riser, through the downcomer tube which has an internal diameter of 68 mm.

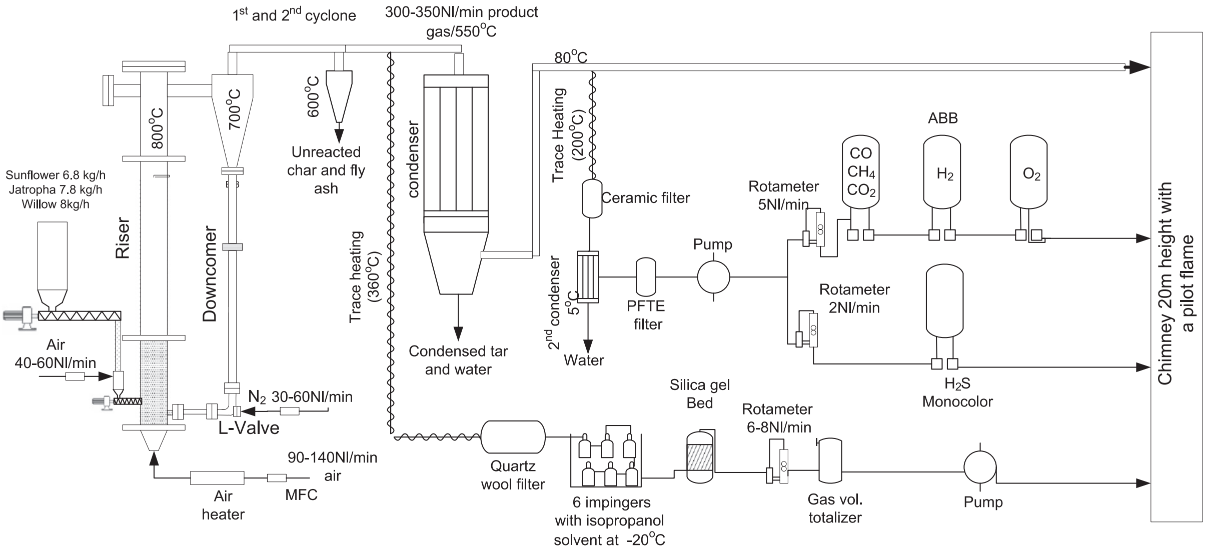

Fig. 3. A schematic of the CFB gasifier installation and product gas analyzer systems at CERTH.

A nitrogen flow is used to assist recirculation and prevent char accumulation at the bottom of downcomer. A second cyclone (70 mm ID and 600 mm) removes unburned char and fly ash which are not captured during the first separation. Afterwards, syngas is cooled by a water cooled condenser (Fig. 3).

The main components of the product gas are analyzed from a slip-stream by means of a multi-component gas analyzer instrument (ABB AO2000) equipped with IR measurement of CO (0–25% v/v) and CO_2 (0–25% v/v), CH_4 (0–15% v/v), a thermal conductivity detector for H_2 with a range 0–15% v/v, while O_2 is determined using a paramagnetic sensor with a range of 0–25% v/v. Furthermore, there is the possibility for detecting hydrogen sulfide (H_2S). The Monocolor 2Ex analyzer operates semi-continuously according to a colorometric measuring principle. The determination of H_2S is based on a reaction on a moving test paper strip which is saturated with a chemically selective color indicator (lead acetate). In addition, the measurement equipment consists of three (3) mass flow controllers, 11 K-type thermocouples, nine (9) absolute pressure transmitters and weighting devices. Temperature, pressure, mass flow and gas composition, are displayed and acquired on a PC via a data acquisition system (Fig. 3)

3. Results and discussion

Table 5 presents the gasification conditions and the composition of the product gas and tar concentration obtained from the tests conducted in the two gasification systems.

3.1. Effect of temperature on gas composition

In Table 5, it can be seen that the mean hydrogen concentration is higher at 750 °C than at 700 °C, when net cardoon was used as fuel; that the values increase from 34.5 vol% to 36.5 vol% (dry gas basis). The opposite behavior is observed in the cardoon blend where hydrogen concentration was reduced from 22.3 vol% to 22.1 vol%. H_2 to CO ratio is used to present the correlation between the predominant species of the product gas. In the experiments conducted with steam/O_2 mixtures (TUD) at 700 °C and 750 °C, the average ratio was 5.1, and 4.3 respectively. Contrary, in the experiments conducted with air, as the gasification medium (CERTH), the average H_2/CO ratio was significantly lower (0.76 at 750 °C and 0.64 at 800 °C). By increasing the operating temperature, the rate of the endothermal reactions is enhanced (methane reforming reaction, steam char reaction, Boudouard reaction). As a result, the reactions' products are favored [45].

When the gasification medium is steam the slightly exothermic reaction of water–gas shift (WGSR) reaction (R.1) is enhanced, as a result the content of carbon dioxide is too high in the syngas [46]

$$CO+H_2O \leftrightarrow H_2+CO_2 \quad \Delta H^0{}_{298} = -41\ \mathrm{kJ/mol} \qquad (R.1)$$

The other reason is the necessary low operating temperature, due to which a large proportion of carbon is not converted to the gas phase. Increasing the temperature of the reactor, the CO_2 concentration decreases. For the gasification experiment at 700 °C of cardoon with giant reed the mean CO_2 concentration was 55.4 vol%, and at 750 °C it was 50.4 vol%. These values were reduced down to 38.5 vol% when gasification was performed at 750 °C and further down to 34.1 vol% when the

Table 5
Experimental data for gasification tests.

Condition	**TUD**		**CERTH**	
	1	**2**	**1**	**2**
Fuel	Cardoon		50% w/w Cardoon/50% w/w Giant reed	
Feeding rate [kg/h]	10.7		7.8	
Steady state [min]	60	45	60	70
Bed material	Magnesite		Olivine	
Gasifier temperature [°C]	700	750	700	800
Gasification medium	O_2–steam		Air	
Flow of gasification medium [m^3_N/h]	7.8	7.8	6	6
u_s (during gasification)	3.3	3.4	3.2	3.3
SBR	1.2	1.2	–	–
Equivalence ratio [λ or ER]	0.3	0.3	0.3	0.3
Gas composition [%]	**Nitrogen free**		**Nitrogen free**	
H_2	34.56	36.56	22.3	22.1
CO_2	55.44	50.42	38.5	34.1
CO	6.78	8.5	29.3	34.6
CH_4	4.1	4.54	9.9	9.3
H_2/CO	5.1	4.3	0.76	0.64
Tar content [g/m^3_N]	**134.1**	**122.3**	5.9	2.8
Water content [kg/h]	4.1	5.9	2.79	2.7
H_2 in moisture of fuel [kg/h]	0.15	0.15	0.07	0.07
H_2 in fuel (d.b.) [kg/h]	0.5	0.5	0.4	0.4
H_2 in tar/incoming H_2 [%]	1.9	0.6	1.6	0.55
C in tar/incoming C [%]	5.3	1.3	3.1	1.2
C in fly ash/incoming C [%]	1.1		0.8	
CCE [%]	**64.1**	**69**	**75.5**	**78**
LHV [MJ/m^3_N]	5.3	5.5	3.44	3.69
CGE [%]	67	72.2	59.3	62.3
Product gas [kg/h]	17.2	18	16.2	17.3

cardoon blend with giant reed was gasified at 800 °C. The increase of temperature slightly impacts the production of methane in both experiments; at 700 °C CH_4 concentration is 4.1 vol% while at 750 °C it is 4.5 vol% for cardoon fuel and at 750 °C is 9.9 vol% while at 800 °C it is 9.3 vol% for the cardoon blend fuel.

The concentration of H_2 is almost 1.5 times higher in the case of the experiment conducted with steam/H_2O mixture (TUD) compared with the experiments with air as the gasification agent (CERTH). This is due to the O_2/steam that enhances the reforming of hydrocarbons (R.2), resulting in the production of more H_2, also in combination with the WGSR [46]

$$C_nH_m + nH_2O \leftrightarrow (n+m/2)H_2 + nCO. \tag{R.2}$$

3.2. CCE %, CGE % and heating values of product gas

Generally, higher gasification temperatures lead to higher gas yields. The effects of operational parameters on carbon conversion efficiency (CCE %), cold gas efficiency (CGE %) and heating values obtained from the two fuels gasification are given in Table 5. These results are in agreement with those reported by other researchers [47,48].

As illustrated in Table 5, CCE % was higher for the experiment conducted in CERTH. This is a result of the smaller fuel feeding rate during that experiment, which leads to a better solid (unconverted char) residence time and as a consequence the carbon conversion is enhanced.

On the other hand the *LHV* of the outlet gas was higher for the experiment conducted in TUD. The *LHV* of the product gas is the sum of the *LHV* of each constituent multiplied by its mass fraction in syngas (Eq. (1)) [46]

$$LHV = LHV_{H2}X_{H2} + LHV_{CO}X_{co} + LHV_{CH4}X_{CH4} \tag{1}$$

At 750 °C the hydrogen volumetric percentage in the outlet gas composition (nitrogen included) is 30.6% for the experiment conducted with O_2/steam, while for the experiment with air is almost three times lower (7.9%). So, with the percentages of CO and CH_4 being 7.1%, 3.8% and 10.5%, 3.5% for the experiments in TUD and CERTH, respectively, it is understandable that the LHV of the outlet gas produced with O_2/steam gasification medium is higher compared to that derived from air.

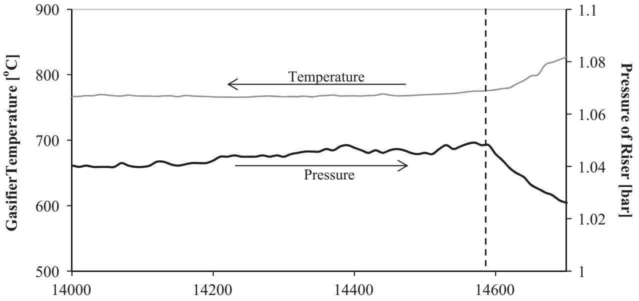

Fig. 4. Typical fluidized bed pressure drop loss during an externally induced defluidization test (rising of temperature).

Fig. 5. Photograph of an indicative agglomerate of olivine joined particles with cardoon ash.

The gas production was also higher when cardoon was used, reaching a rate of 18 kg/h at 750 °C, compared to a rate of 17.3 kg/h at 800 °C for the cardoon blend. This difference is also attributed to the different feeding rate used in the two experiments, resulting in higher product yield for the experiment performed at TUD, where the feeding rate was also higher.

In lab-scale systems char conversion is underestimated, as some amount of char leaves the cyclone in form of fine particles. This is attributed mainly to the small height of these facilities. In the present work the mean particle size of the escaped char was approximately 20 μm. Additionally, in both facilities (TUD, CERTH), this char was collected from the second cyclone.

Generally, since the higher the residence time is, the more char conversion increases, a bubbling fluidized bed could be better utilized in such trials. One reason for such a choice is the fact that in BFB reactors the solids remain in the bed for hours. Apart from that, the same solids stay longer in the BFB freeboard than they do in a CFB riser. Dual fluidized bed reactors could provide another solution to the problem of low carbon conversion [49].

3.3. Agglomeration problems

In the test carried out with O_2/steam using magnesite as bed material, after 2 h of operation at circa 750 °C, a temperature increase rate of approximately 0.8 °C/min was induced. This fact led to severe agglomeration few minutes later, when the gasification temperature reached a temperature of 760 °C (Fig. 4). Once defluidization started, poor bed mixing caused an inhomogeneous bed temperature profile apart from the significant pressure drop loss. After that point, fuel was not fed to the gasifier anymore and the oxygen–steam flow was switched to nitrogen, in order to cool down the system without any further reactions.

Fig. 5 illustrates a real photograph of an agglomerated bed material piece, which indicates how severe the effect was. Numerous Scan Electron Microscopy/Energy Dispersive Spectrometry (SEM/EDS) analyses were performed on these collected agglomerates and cross-sections made by embedding into resin. Some of the most representative and explanatory SEMs are discussed in the following paragraphs.

A typical SEM picture of a cluster-like formed during cardoon gasification in magnesite is presented in Fig. 6. Cardoon has a very high alkali and silicate ash content that is easily moltenat elevated temperatures of a reacting char particle. This makes the char very adhesive and prone to capture bed material particles. EDS spot analysis is presented in the accompanying bar graphs at the marked points. The gluing melt is rich in magnesium, calcium and silicon. Magnesium as element causes a relatively high melting point, while MgO–CaO–SiO_2 is a eutectic structure. This phenomenon was also reported elsewhere [50].

This particular cardoon sample used for the O_2/steam gasification tests had a significantly high calcium ash content (Table 2) which reacts with potassium and silica. As a result the presence of these inorganic decreases the melting point temperature of the ash [51]. Consequently, calcium derived from cardoon's ash together with the magnesium of the bed material, create a fusible structure. On the contrary, the ash of giant reed contains a significant amount of aluminum. When alumina-rich compounds are present, the solid-solid reactions may result in the formation of alkali-aluminum silicates

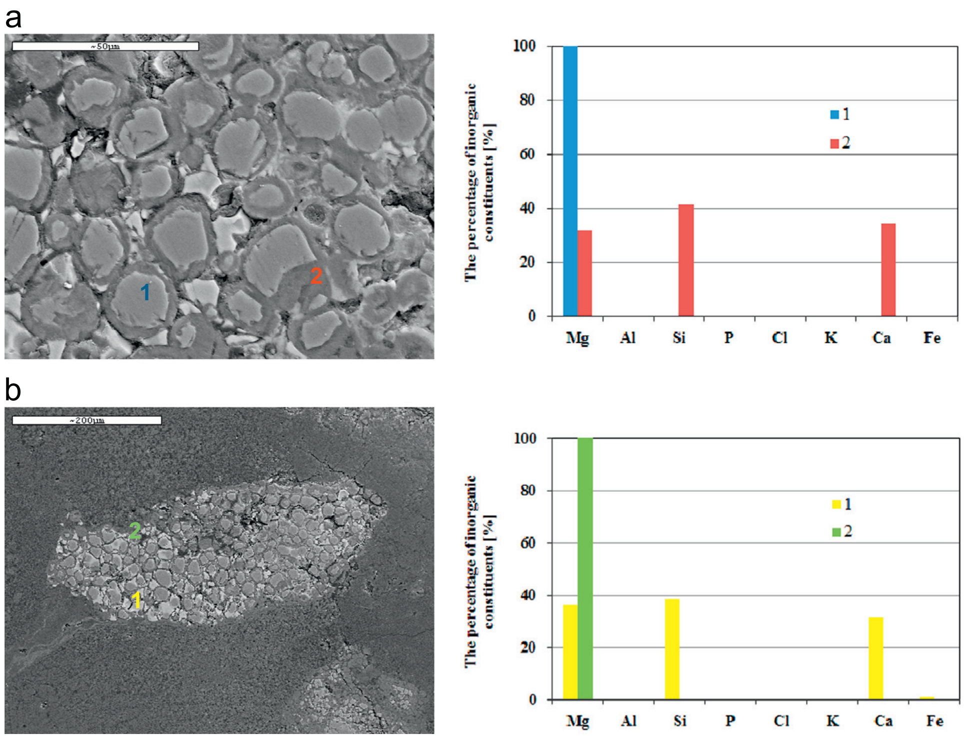

Fig. 6. Agglomerates obtained from cardoon gasification using magnesite as bed material.

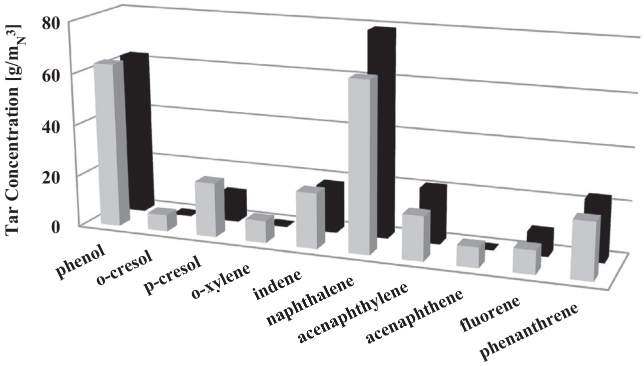

Fig. 7. Tar components from the test conducted in test with O_2/steam and magnesite as bed material.

(K_2O–Al_2O_3–SiO_2), which have a much higher melting temperature [52]. That is a plausible explanation why the blend's ash had higher melting points compared to cardoon's.

3.4. Effect on tar formation/reduction

The measurement of tar was conducted with two different off-line methods. The CEN TF 143 system was used at CERTH, whereas the tests in TUD were carried out using Solid Phase Adsorption (SPA) techniques, which are faster and potentially more flexible as devices. Quantitative tar component measurements were performed at the O_2/steam experiment, and the results are presented in Fig. 7. In this test, cardoon and O_2/steam were used as feedstock and gasification medium respectively. As observed from Fig. 7, at both low and high temperature the two major tar species are phenol and naphthalene. This observation agreed well with the results reported by other researchers. Meng et al. [53] conducted experiments in an atmospheric circulating fluidized bed gasifier with O_2/steam. The concentration of phenol and naphthalene in the produced gas at 730 °C was 1.5 g/m^3 and 2.7 g/m^3, respectively, with a total tar concentration of ~35 g/m^3. An experimental campaign similar (gasification with O_2/steam as oxidizing medium) to other two works was carried out in Vienna University. Tests were conducted in an industrial scale dual fluidized bed using CaO as bed material. Measured tar levels were low compared to the trial which was performed on TUD [49]. Siedlecki [54] performed an experimental campaign with miscanthus as fuel at 750 °C similar to the campaign of Meng. The tar levels for the same

Table 6
Tar concentration in both syngas.

Temperature [°C]	Tar concentration [g/m_N^3 dry basis gas]	
	TUD (O_2/steam)	CERTH (air)
700	134.1	5.9
750	122.3	–
800	–	2.8

temperature were higher (~20 g/m^3 dry nitrogen free). Phenol and naphthalene content in product gas was 2.5 g/m^3 and 12 g/m^3, respectively. The increase of the gasification temperature enhances the formation of non-oxygenated aromatic compounds at the expense of phenols. On the contrary, the total amount of tar in the product gas decreases by increasing the operational temperature. The quality of syngas in the case of O_2/steam gasification is much better than in the tests performed with air as agent (Table 6). Generally, using an O_2/steam gasification medium yields product gas from which liquid fuels can be synthesized after cleaning and upgrading. The main reason is the high concentration of H_2, in comparison with the usage of air as medium. Consequently, the syngas derived from air-blown gasification is preferred for heat generation and electricity production, due to its low heating value [44]. Also the ratio between H_2 and CO is higher when O_2/steam is used, so the conditions for synthesizing liquid biofuels are better [48]. On the other hand, the major drawback of O_2/steam gasification is the high level of tar. It can be seen that for the same operational temperature at 700 °C the tar concentration acquired from the O_2/steam test was 134.1 g/m^3 on a dry gas basis, whereas the experiment carried out with air produced 5.9 g/m^3 on the same basis.

4. Conclusion

Although cardoon is an ideal energy crop for a temperate zone, results arising from this work and previous studies show that it is not possible to achieve long term gasification tests in large scale FBs with this biofuel. This is a result of its ashes' high content of potassium, silica and calcium that causes agglomeration leading to defluidization. The main agglomeration mechanism is the total melting of the silica, calcium and magnesium salts or silica, calcium, potassium, ash forming a highly viscous liquid. Defluidization was observed in two cases, in which different bed materials and gasification media were used (magnesite and an O_2–steam flow using TUDs CFB gasifier and olivine and an air flow using CERTHs CFB gasifier). In the second experiment presented in this work where 50% w/w cardoon was blended with 50% w/w giant reed, no agglomeration problems were observed. So, the main conclusion from this study is that the blending of cardoon with another type of biomass fuel, with properties similar to these of the giant reed, can be a solution for the use of cardoon as feedstock for a long term gasification process in a large scale FB. Also, a big difference was observed in the tar concentration between the two experiments which was 134.1 g/m^3 (dry gas basis) and 5.9 g/m^3 (dry gas basis) for O_2/steam and air as gasification medium, respectively, at a temperature of 700 °C. An even larger reduction of the tar concentration was presented at a temperature of 800 °C for the case of air blown gasification.

Acknowledgments

The research leading to this publication has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 284498 ***BRISK***. The authors would also like to acknowledge TUD students George Klironomos and Siman Tüfekçioglu who assisted in the performance of the experimental campaigns.

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