

AGGLOMERATION PROBLEMS DURING CARDOON FLUIDIZED BED GASIFICATION

by

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Cynara Cardunculus, commonly known as cardoon is a potential energy crop native to the Mediterranean region with high production yields reported. The aim of this work is to present an overview on the contradicting agronomic data available for cardoon and its potential exploitation in industrial thermochemical (i. e. combustion and gasification) applications. Moreover, experimental work on cardoon gasification is presented, focusing on the agglomeration problems it causes when using it in fluidized bed gasifiers. Cardoon cultivated in Greece was gasified in a 100 kW thermal atmospheric circulating fluidized bed gasifier. Due to high ash content (rich in potassium) defluidization was observed at low temperatures (780 °C) during the first 30 minutes after the fuel feeding begun. The agglomerates are investigated with SEM/EDS in an effort to determine the gluing mechanism. The particular cardoon was rich in calcium, and this was apparent in the rich in silicates re-solidified melt.

Keywords: *Cynara Cardunculus*, cardoon, biomass, gasification, fluidized bed, agglomeration

Introduction

Biomass fuels such as agricultural or agro-industrial residues together with energy crops are considered promising renewable energy sources [1]. To reduce CO₂ 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 use more efficiently in combined power cycles. Gasification of biomass is a first step of converting biomass into biosyngas which in return can be converted to 2nd generation biofuels [2]. Nevertheless, biomass gasification of many promising biomass plants suffers agglomeration technical problems prohibiting the economical and trouble-free operation of such systems. *Cynara Cardunculus*, commonly known as cardoon, is a thistle like plant in the aster family *Asteraceae*, and is considered by few works as a promising fuel for thermochemical processing (combustion, gasification) [2].

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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 condition 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 [3-7]. 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). Cardoon can survive the summer drought by growing a very deep rooting (up to 7 meters) and drying the aboveground plant part during the summer [8-12]. The height of plant can reach up to 2 m depending on climate and soil conditions. The reproductive cycle is completed during the summer so the harvest period can start in August when the ground part is dried. As a result, the crop leads to a high yield of dried solid biomass [13-17].

Because of all the above qualities, Cardoon can also 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 can also become a serious invasive species [18]. 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 or impossible even if plowing, chaining, scraping, and bulldozing are employed [19].

Farmers should take into account the abovementioned character of Cardoon before deciding to engage its cultivation due to benefits of its high dry mass yields. 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 [18-21]. The following section, reports the potential uses of this energy crop followed by the main findings of severe agglomeration problems in the fluidized bed facility it was tested.

Non-thermochemical utilization of cardoon

Cardoon seed oil

One of the first industrial uses of this crop waste oil extraction from its seeds, which represent a significant percentage of the total harvested dry biomass (13.2%), *i. e.* about 0.26 ton/ha [13]. Cardoon oil can be easily extracted by cold pressing (~20 °C). Comparing cardoon to rapeseed and sunflower, the seed of cardoon has a 25% of oil content; sunflower and rapeseed have 44% and 36%, respectively. The cardoon seed oil content is lower than that of the other two crops; nevertheless they all exhibit a similar fatty profile [22, 23]. A low cost biodiesel can be produced by esterification of these oils, provided cardoon growing has a low cost [24-26]. Because of its high cetane number, cardoon oil can be as well used in either indirect injection diesel motors or in normal diesel motors as a mixture of diesel oil [15, 16, 27, 28].

Cardoon as a raw material for pulp/paper industry

The possibility of using cardoon for paper pulp production has been investigated in the past [15, 16]. The most important properties of any papermaking lignocellulosic raw material are the content in cellulose and the length of fibers [29]. The amount of cellulose determines the

pulp yield. On the other hand the length of fibers is an important parameter for the quality of the pulp; it is directly related to the strength which dictates the final use. The length is proportional to lignin [27, 29-31]. Cardoon fibers compared to trees such as Eucalyptus' have a similarity in cellulose amount which means an ease of pulping and low cost production. However, the length of eucalyptus' fiber is longer because it contains more lignin than cardoon's fibers. Therefore, a proposed pulp recipe would be to blend cheap cardoon fibers with plants which are used for years in pulp paper industry [29].

Feedstock for thermochemical processes

Thermochemical processes are employed to convert biomass into heat, power, and fuels. Up to date, few tests and analysis have been carried out in order to verify the suitability of cardoon in pyrolysis, gasification, and combustion [32-45].

One of the most important aspects of cardoon is its high ash content as well as the high alkali and chlorine contents. Table 1 shows the main elemental composition of the ash from different European samples and in different forms (chopped, milled, baled and pelletized) as well from different parts of the plant [36, 42, 46, 47]. It also presents the ash composition of the cardoon pellets used for the gasification experiments presented in this work. In most cases cardoon is chopped, milled, baled and pelletized using the entire plant. Table 1 reveals the high ash content and especially the high amounts of K and Ca. The high ash contents are attributed to soil being collected together with the plant harvesting. The high concentration of potassium could be caused by fertilization [44].

Table 1. Ash composition expressed as oxides of the major elements wt.% for different reported cardoon biomasses

Part of plant	Origin*	Si	Ca	Al	Na	K	P	Ref.
Stems	GR	66.6	8.79	2.20	0.38	18.4	3.53	[42]
Stems	GR	71.0	3.33	2.28	0.38	19.3	3.69	[46]
Leaves	GR	52.8	7.98	2.82	0.19	33.7	2.50	[42]
Leaves	GR	47.9	8.51	2.62	0.18	36.7	3.99	[46]
All chopped	GR	9.95	46.7	2.54	14.8	24.6	2.63	[45]
All chopped	SP	5.94	27.0	0.82	14.4	48.3	3.33	[24]
Milled	SP	8.11	24.9	0.80	1.21	61.3	3.52	[57]
Baled	SP	1.05	26.3	0.21	15.5	54.2	2.52	[24]
Pelletised	SP	27.2	24.4	5.71	13.1	27.7	1.81	[24]
All chopped	IT	6.61	31.1	0.96	29.1	28.2	3.07	[24]
Cardoon used in this work	GR	6.33	45.04	2.42	14.45	30.64	2.04	

* GR – Greek, SP – Spanish, IT – Italian

Several works have assessed the cardoon pyrolysis rates, using thermogravimetric analyzers (TGA) in order to determine its thermal decomposition behavior [32, 35, 37, 39-42, 44, 45]. Pyrolysis is the initial step in all thermochemical conversion processes of biomass materials, but also a process to produce biooil, gas, and char. Minerals apparent in cardoon such as potassium, do not greatly affect the reactivity of cardoon, but influence the sensitivity of the reaction, causing the pyrolysis degradation to be able to start at lower temperatures. Furthermore the pyrolysis of cardoon yields more char compared to other energy crops because of its higher ash content [37].

Up to date, combustion is the dominant process for using solid cardoon sources. Cardoon-fired test runs in lab-scale and pilot-scale have been performed in the past [33, 34, 43]. Molten ash and slag were observed in these works which created severe problems to the continuous combustion process, simultaneously reducing the achievable boiler load and availability. These problems were attributed to the high concentration of ash, especially that of Si, K, Ca [33, 37, 38].

Although, there is a high research interest in the possibilities and advantages of cardoon co-fired with coal, cardoon combustion appears to have a great potential [38]. Co-firing with high sulfur lignite [38] has several advantages due to replacing the sulfur burden of lignite with biomass as well as reducing CO₂ emissions and saving on credit costs.

The research performed so far on the use of cardoon in the field of gasification is limited to lab-scale test runs. The produced gas in steam gasification tests has been investigated in [36]. A theoretical model was also run in [34]. There are no gasification attempts in larger scales. The work presented here addresses this issue by conducting air 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.

Table 2. Analyses of the cardoon used

Proximate analysis [wt.%]	
Moisture	13.2
Volatiles	65.1
Fixed carbon	5.46
Ash	15.4
Ultimate analysis [wt.%, dry basis]	
C	42.7
H	5.30
N	2.23
S	0.45
O*	0.45
Cl	0.29
Ash	17.7
HHV d. b. [MJkg ⁻¹]**	17.30

* by subtraction, ** higher heating Value (HHV) of dry solids (d. b.)

Experimental

Cardoon feedstock used

The cardoon fuel used in the experiments was supplied from an agricultural company in the region of central Greece that cultivated and brought the crop into pelletized form. Table 2 presents the fuel analyses of cardoon pellets: proximate (ASTM E871, D1 102-84) and ultimate analysis (ASTM D3176-93, D3177-33). The ash analysis of the major ash species is given in tab.1. The cardoon used for the tests had significantly high calcium ash content, as well as sulfur and chlorine content.

Description of test facility and methodology

The circulating fluidized bed gasifier (CFBG) consists of a stainless steel 316L cylindrical tube with 78 mm internal diameter (ID) and 6.0 m in height. Fluidisation air is also preheated and introduced to the bed through a distributor, which has six tubes with bubble-caps at the end. 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: its flow rate is adjusted by a dosimetric screw feeder. The second silo serves to feed the fuel into the gasifier. 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. A minor air flow was also added through the top of the silo, in order to avoid the product gas back flow. The air flow was regulated by mass flow controllers based on the thermal mass flow sensing technique. The particulate matter was removed from the produced syngas by means of a cyclone which has an internal diameter of 260 mm and height of 800 mm. The unburned char and bed material return to the riser, through the downcomer tube which has an internal diameter of 68 mm. A second cyclone (70 mm ID) removes the fine particles that were not collected in the first cyclone (fig.1).

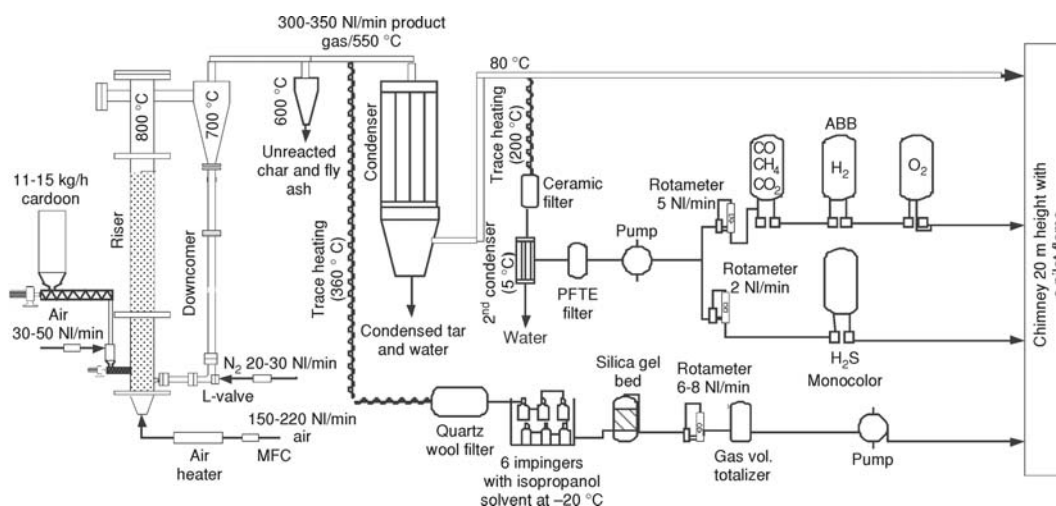


Figure 1. A schematic of the CFB gasifier installation and product gas analyser systems

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 CO₂ (0-25% v/v), CH₄ (0-15% v/v), a thermal conductivity detector for H₂ with a range 0-15% v/v, while O₂ is determined using a paramagnetic sensor with a range of 0-25% v/v. Furthermore, there is the possibility for detecting hydrogen sulfide (H₂S). The Monocolor 2Ex analyzer operates semi-continuously according to a colometric measuring principle. The determination of H₂S is based on a reaction on a test paper strip which is saturated with a chemically selective color indicator (lead acetate or silver nitrate). All data are displayed and acquired on a PC *via* a data acquisition system (fig. 1).

Experiments were conducted using olivine as bed inventory. In fluidized bed-gasification process, olivine has been proven to have tar cracking capabilities, mainly to its Fe and Mg content [48]. The chemical composition of the olivine used is given in tab. 3. The initial bed material was ~7000 g sieved to a narrow particle size range ($d = 350\text{-}500\ \mu\text{m}$).

Table 3. Chemical analyses and density of the olivine bed material

Compound	Fraction [wt.%]
SiO ₂	42.3
FeO	8.71
MgO	41.2
CaO	4.21
Al ₂ O ₃	2.84
Cr ₂ O ₃ + NiO	0.08
Density	3200 [kgm ⁻³]

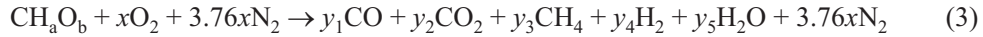
Assuming that the fluidization medium is air and the mean particle diameter (d_p) of olivine is 384 μm with a particle density (ρ_s) 3200 kg/m^3 [48-50], its shape factor assumed (ϕ_s) 0.85 [49, 50] and the corresponding voidage (e_{mf}) for minimum fluidization is 0.5, then the minimum fluidization at 25 °C is 0.2 m/s and is given by eq. (1):

$$\frac{1.75}{\varepsilon_{mf}^3 \phi_s} \left(\frac{d_p u_{mf} \rho_g}{\mu} \right)^2 + \frac{150(1 - \varepsilon_{mf})}{\varepsilon_{mf}^2 \phi_s^2} \frac{d_p u_{mf} \rho_g}{\mu} = \frac{d_p^3 \rho_g (\rho_s - \rho_g) g}{\mu^2} \quad (1)$$

The most important value in order to validate that the fluidization is carried out in a circulation mode is the terminal velocity of a single particle which can be estimated by eq. (2). Using similar assumptions it was calculated at 1.079 m/s:

$$u_t = \sqrt{\frac{4d_p (\rho_s - \rho_g) g}{3\rho_s C_D}} \quad (2)$$

Before the fuel feed in the gasifier the superficial velocity is equal to the flow of air. In contrast, during gasification of biomass much more gas volumes are produced compared to the air used, as a result the superficial velocity is equal with velocity of product gas. The total product gas is the sum of the gaseous products as shown in eq.(3):

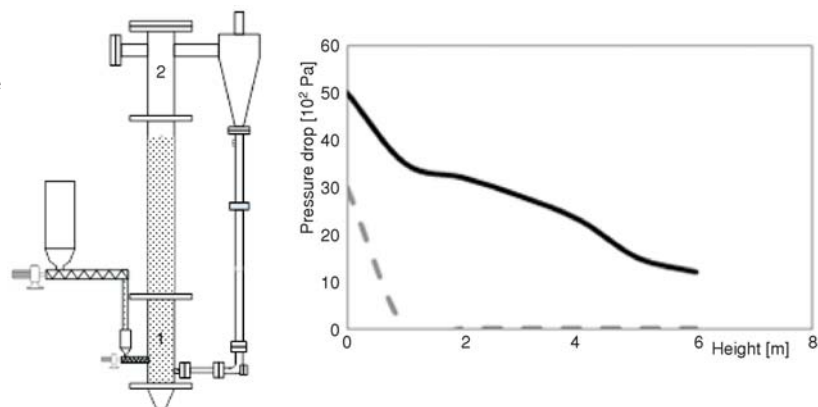


The u_o during gasification was estimated at 4.5 m/s which means that $u_o/u_t = 4.17$.

The feeding rate of cardoon biomass was 11 kg/h. The amount of ash in cardoon is high (15.38% in a. r.). This means that for 11 kg/h feeding rate the ash input (if all amount remained in the bed), would represent 24.16% of the original bed inventory. The amount of air used for the gasification is expressed by the air ratio (λ) *i. e.* the oxidizing agent quantity compared to that required to fully oxidize/combust the biomass carbon and hydrogen. Based on similar works the air ratio (λ) was chosen 0.3 [49, 50].

Six pressure transmitters (WIKA, S-10) were used for monitoring of pressures at different riser heights (every 1 m). These measured the pressure with a range 0-0.16 MPa and an accuracy of 10 kPa their signal was logged at a frequency of 10 Hz. and was averaged in post signal processing at 1 Hz. In a normal operation of gasifier the pressure drop profile across the riser is show in fig. 2 (solid line). Several experimental works examine agglomeration during fluidized bed combustion/gasification of biomass and/or coal are available on lab- or pilot-scale fluidized systems [48, 51-53]. These works provided the methodology of determining the defluidization as soon as the pressure drop across the riser, and especially between bottom and top of the gasifier (points 1-2 in fig. 2) significantly dropped because of the creation of openings and channels in the bed after this event (fig. 2 – dashed line). This allows the defluidization temperature determination at the onset of ΔP (pressure drop) with an accuracy of ± 5 °C.

Figure 2. The pressure drop profile across the CFB riser: the solid line represents the normal operation whereas the dashed line when defluidization occurs



Results and discussion

After a 15 minute operation without heat addition from the external electric system at around 740 °C, a temperature increase rate of approximately 1.5 °C/min was established. This led to severe agglomeration few minutes later, when the gasification temperature reached 780 °C (fig. 3). In fig. 4 the volume fraction of the major product gas species until the onset of defluidization is

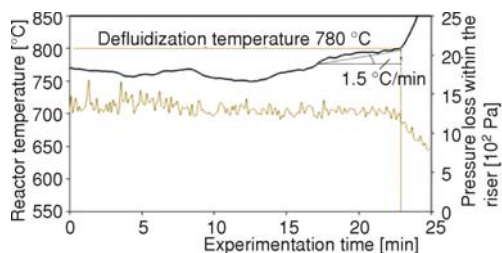


Figure 3. Typical fluidized bed pressure loss during an externally induced defluidization test (rising of temperature)

presented. Once defluidization started, poor bed mixing caused an inhomogeneous bed temperature profile apart from the significant pressure drop. After defluidization fuel was not fed anymore to the gasifier and the air flow was switched to nitrogen, so as to cool the system without any further reactions. The bed material was collected and sieved to determine any changes in the particle size distribution.

Figure 5 shows a real photograph of an agglomerated bed material piece, indicate how severe the effect was. Numerous scan electron microscopy/energy dispersive spectrometry analyses (SEM/EDS) were performed on agglomer-

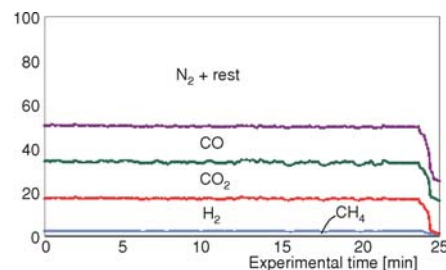


Figure 4. Volume fraction of the major product gas species until the onset of defluidization (followed by purging with N₂)



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

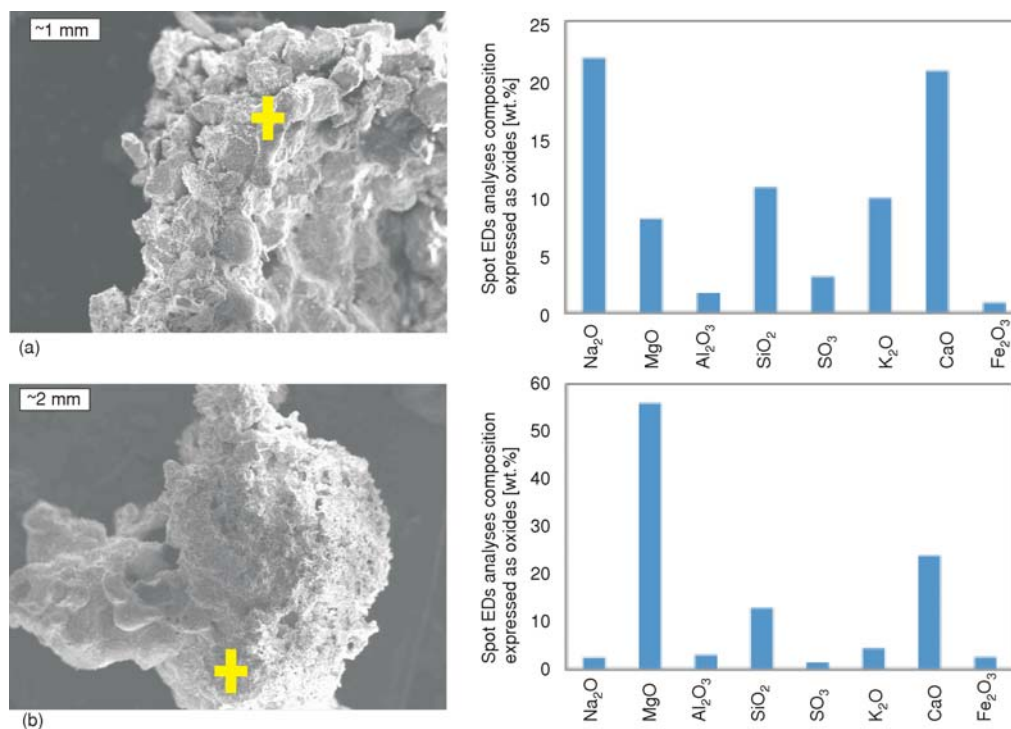


Figure 6. SEM and EDS spot analyses of two agglomerates (a) (b) collected after the defluidization during the gasification of cardoon in olivine bed

ates and their cross-sections. Some of the most representative and explanatory SEM are discussed in the following paragraphs.

A typical SEM of a cluster-like formed during cardoon gasification in olivine is shown in fig. 6, revealing the mechanism of its formation: Cardoon has a very high alkali and silicate ash content that easily melted at elevated temperatures of a reacting char particle. This makes the char very adhesive and prone to capture bed material particles.

EDS spot analyses is given in the accompanying bar graphs at the marked points. The gluing melt are found rich in sodium, potassium, calcium, magnesium, and silicon. Calcium based melt is apparent in fig. 7 which is a SEM elemental mapping cross-section of agglomerate from the controlled defluidization tests of cardoon. Several numbers of hollow calcium based large particles were also observed during gasification tests (fig. 8). The char high temperatures

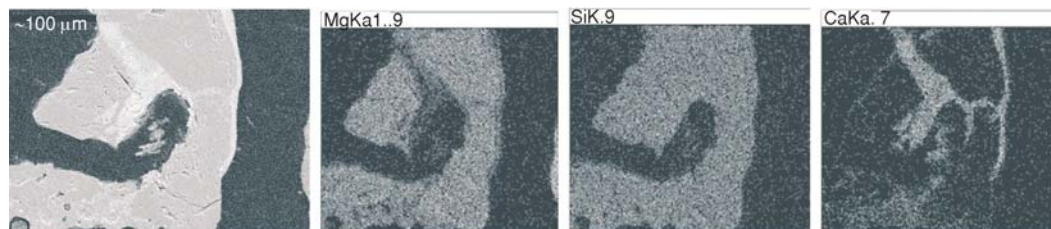


Figure 7. SEM/EDS elemental mapping of an agglomerate cross-section (Si, Mg, and Ca)

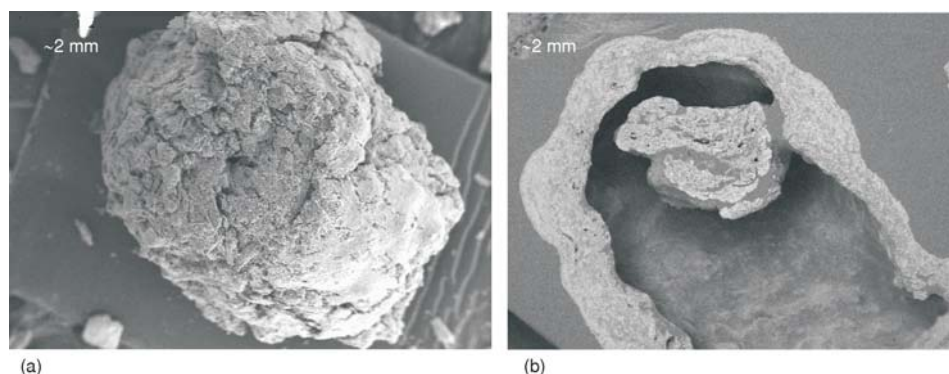


Figure 8. (a) SEM of calcium based ash particles; (b) SEM of their cross-section, which shows their hollow nature

melt its ash as a result a layer similar with the shape of char was created. Char was gasified but a hollow large particle remained. Alkali-silicates (K_2O-SiO_2) have a eutectic point of about 780 °C, while the eutectic point of $K_2O-CaO-SiO_2$ is even lower [51]. This is a reason why agglomerates rich in calcium were observed. This could be an explanation for the appearance of these hollow particles. This effect is also shown in fig. 9.

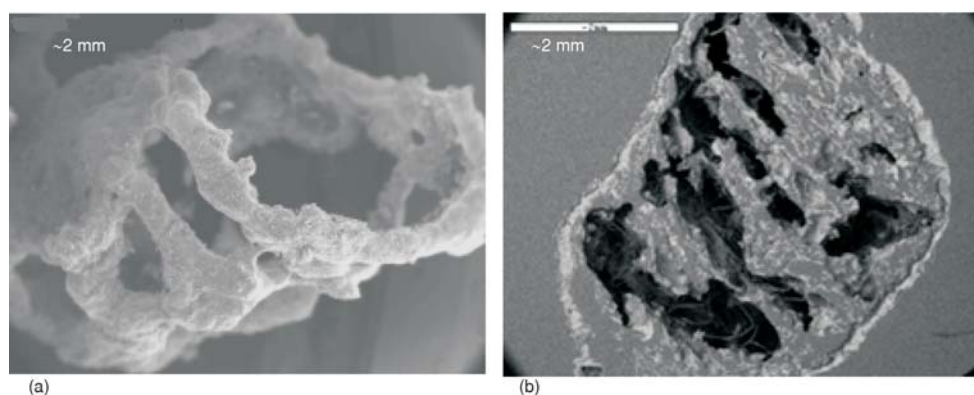


Figure 9. (a) SEM of calcium based ash particles remnant of a pellet; (b) SEM of a cross-section of such a formation

Conclusions

Cardoon is a plant which can survive in Mediterranean climates with minor requirements in irrigation. As a consequence of this, its cultivation is cheaper compared to other species; also it is a promising plant for the pulp paper industry. Although cardoon is an ideal energy crop for temperate zone, results arising from this work show that cardoon is not possible to achieve long term gasification tests in large scale FB without pretreatment (for example leaching). As a result, it is not recommended as it is for such thermochemical process in because its ash high content in potassium, silica, and calcium causes defluidization. The high potassium, silica, and calcium content of cardoon are responsible for total defluidization in the FB gasification

tests at relatively low temperatures (780 °C). The main agglomeration mechanism is total melting of the calcium, potassium, and silica ash forming a highly viscous liquid. Also, several particles rich in calcium derived from the cardoon's ash used.

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Nomenclature

A	– cross-sectional area of riser, [m ²]
C_D	– drag coefficient of a single particle
d	– range of particle diameter of bed material, [μm]
d_p	– mean particle diameter, [μm]
g	– gravitational acceleration, [ms ⁻²]
n_{air}	– molar rate of air into gasifier, [mols ⁻¹]
u_{mf}	– minimum fluidization velocity of the bed inventory, [ms ⁻¹]
u_t	– terminal velocity of the bed inventory, [ms ⁻¹]

u_0	– fluidization velocity, [ms ⁻¹]
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Greek symbols

ε_{mf}	– voidage at minimum fluidization
λ	– air ratio
μ	– fluid viscosity, [Pa·s]
φ_s	– the factor of sphericity of particle
ρ_s	– density of particle, [kgm ⁻³]
ρ_g	– density of fluid, [kgm ⁻³]

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