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Thermochemical conversion of *C. cardunculus* L. in nitrate molten salts

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HIGHLIGHTS

- Nitrate solar salt as heat transfer medium for thermochemical conversion of biomass.
- Solid carbonaceous materials promotes the molten salt degradation.
- Shift from endothermicity to exothermicity process due to solid carbonaceous material.
- Higher gas yield is obtained when using molten salt as heating medium.
- Less complex bio-oil composition compared with fixed bed pyrolysis.

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ABSTRACT

The use of a binary mixture of solar molten salts (60 wt% NaNO₃ and 40 wt% KNO₃) as a heat transfer medium for the production of a solar fuel by the thermochemical conversion of biomass is investigated in the present paper. Thermochemical conversion can be a route for converting the surplus solar irradiation via the direct contact of nitrate molten salts and biomass into storable chemical fuel. Traditional fixed-bed pyrolysis and molten salts pyrolysis have been carried out under an inert atmosphere at a temperature of 500 °C. The composition of the permanent gases and the bio-oil produced has been analyzed along with the temperature profiles inside the reactor. Two distinctive pathways have been observed: an endothermic process in the case of traditional fixed-bed pyrolysis and an exothermic process in the case of molten salt pyrolysis. An attempt has been made to identify possible causes for such differences.

1. Introduction

The development of solar energy technologies is one of the main routes to reduce greenhouse gas emissions. However, solar energy conversion faces the main challenge of energy storage. A solar power plant employing solar salt (60 wt% NaNO₃ and 40 wt% KNO₃) both as a heat transfer fluid and as a thermal energy storage medium is the current state-of-the art of concentrated solar power (CSP) technology. However, the highest thermal energy storage capacity system in operation to date (Gemaspolar thermosolar plant) is a two-tank direct storage system located in the molten salt tower with a thermal energy storage capacity of 15 h. Direct thermal energy storage systems that employ the same fluid in the solar receiver and in the storage system allow for solar energy collection to be decoupled from electricity generation yielding higher capacity factors with solar-only or low hybridization [1]. However, despite the increase of the annual capacity

factor, concentrated solar power plants present a power surplus in the periods of peak irradiation and a power deficit in the periods of reduced irradiation. This surplus energy may be used to sustain endothermic reactions such as biomass pyrolysis or gasification with an aim to produce storable and transportable biofuels that can be used in existing equipment such as turbines or engines [2]. The use of solar energy to assist in the thermochemical conversion of biomass offers some additional advantages over traditional methods [3,4]: (i) the partial combustion of the fuel to generate the heat (20–30% of the fuel energy value) consumed during the endothermic pyrolysis or gasification reactions is avoided; (ii) the CO₂ production from the combustion process is reduced; and (iii) permanent gases are free of combustion products.

Thermochemical conversion of biomass can be carried out by different technologies: combustion, gasification or pyrolysis depending on the desired products. Pyrolysis is a thermochemical decomposition of an organic fuel in an inert atmosphere. The principal pyrolysis products

Abbreviations: CSP, concentrated solar power; CSR, central solar receiver; GC-MS, gas chromatography and mass spectrometry; GY, gas yield; LHV, lower heating value; SPA, solid phase adsorption

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can be divided into three groups: (1) condensable vapors, also recognized as pyrolysis oil or bio-oil; (2) non-condensable or permanent gases such as H_2 , CO, CO_2 , and CH_4 ; and (3) solid product also known as char. Specifically, fast pyrolysis is a pyrolysis process conducted at high heating rates of the fuel, temperatures of approximately 500 °C, and short vapor residence times (< 2 s), generating bio-oil as a main product [5]. Although different reactor designs have been proposed to maximize bio-oil yield (ablative, fixed bed, fluidized bed or vacuum reactors), most of them facilitate a fast pyrolysis regime utilizing nitrogen as the inert carrier gas. Pyrolysis vapors are recovered via condensation methods or by electrostatic precipitators [6]. Gasification is a thermochemical process in which organic material reacts with a controlled amount of oxygen, CO_2 and/or steam at temperatures of 750–900 °C. The main product of gasification is a syngas (mainly H_2 , CO and CO_2), with a minor production of char and tar. Various types of gasifiers have been developed such as fixed-bed gasifiers (including updraft or counter-current and downdraft or co-current gasifiers), fluidized bed gasifiers and entrained flow gasifiers [7].

In fluidized bed pyrolysis reactors, the heat is directly supplied to the fluidizing gas or the bed of solid particles. This type of reactors presents some advantages, such as the high heat transfer rate, good mixing of solids and ease of scaling them up [6]. In contrast, in ablative reactors, the particles are pressed against a heated surface, and they can employ larger fuel particles and do not need a carrier gas. However the scale-up is limited due to the presence of moving parts at high temperatures. Luo et al. [8] compared the pyrolysis of pine wood chips of 10×20 mm size in an ablative reactor and the pyrolysis of wood chips sieved to a particle size < 1 mm in a fluidized bed reactor at a temperature of 500 °C, showing that the bio-oil yields achieved were of 60 wt% and 64 wt%, respectively. Screw and auger reactors have also been employed as pyrolysis reactors for liquid production, although the liquid product yield tends to be somewhat lower than in fluidized beds due to the longer residence times and contact with char [5]. For example, Puy et al. [9] tested pine wood chips sieved to a particle size < 20 mm in an auger pyrolysis reactor at 500 °C and a solid residence time of 5 min. Product distribution comprised a liquid yield of 58.7 wt%, a gas yield of 24.7 wt% and a char yield of 25.8 wt%.

Cynara cardunculus L., cardoon or thistle, is an herbaceous perennial energy crop native to the Mediterranean region that is widely utilized as a fuel for thermochemical conversion processes due its high content of volatile matter and moderate ash content as well as environmental benefits during its cultivation [10,11]. Encinar et al. [12] studied the pyrolysis of *C. cardunculus* L. in a fixed bed reactor. The yields of permanent gases, bio-oil and char were studied for different operating conditions (i.e., temperature, particle size, initial batch feeding weight and residence time). The temperature was proven to be dominant parameter, promoting maximum bio-oil yields of approximately 56 wt % achieved at temperatures between 400 °C and 500 °C, together with a permanent gas yield of approximately 20 wt%. On the other hand, at temperatures between 600 °C and 700 °C, the char heating value increased, and the yield reached 20%, while bio-oil and permanent gas yields reached approximately 50 and 30 wt%, respectively. Serrano et al. [13] studied the gasification of *C. cardunculus* L. in a bubbling fluidized bed using air as the gasifying agent, magnesite and olivine as bed materials, and temperatures in the range of 700–800 °C. The hydrogen content in the product gas was in the range between 13 and 16 % v/v for both magnesite and olivine. Gas yield and lower heating value (LHV) were augmented when operating the reactor at 800 °C, reaching values of 2 Nm^3 per kg of biomass feed (dry ash-free) and 7 MJ/Nm^3 of gas, respectively.

Different approaches have been carried out to integrate solar energy and biomass, including theoretical models [14] as well as experimental studies [15,16]. There are different types of solar reactors that use solar energy as a source of process heat for the endothermic pyrolysis or gasification reactions. Among them, molten salt reactors convert the

biomass or coal particles in a molten salt medium. These reactors, with direct contact between the molten salts and biomass, ensure a uniform temperature distribution inside the reactor and increase the biomass heating rate due to enhanced heat transfer within the molten salts [3]. Adinberg et al. [17] proposed a novel reactor design where cellulose tablets were immersed in a bath of hot molten salts made of eutectic mixture of sodium carbonate and potassium carbonate with a melting point of 710 °C. Small amount of helium was introduced downstream the reactor in order to dilute and cool the evolved volatile products. Carbonate molten salts were tested between 800 and 915 °C, with the aim of maximizing the permanent gas production. At 850 °C, they obtained a syngas yield of 94 wt%, with a high hydrogen fraction (26 vol %) and 6 wt% of char. Relevant tests without molten salt in the reactor yielded 72 wt% of syngas, 18 wt% of liquid fraction and 10 wt% char. A similar reactor concept was proposed by Hathaway et al. [3], who studied both the pyrolysis and steam gasification of cellulose and activated wood charcoal in carbonate molten salts (a blend containing lithium, potassium and sodium carbonate with a melting point of 397 °C). In that work, it was concluded that the presence of molten salt increased the rate of pyrolysis by 74% while gasification rates increased by more than one order of magnitude. It was also found that the alkali metal carbonates catalyzed steam gasification reactions, while the enhancement observed in the pyrolysis rate was solely attributed to the enhanced heat transfer within the salt. Similar conclusions were given by Rizkiana et al. [18], who studied the pyrolysis of coal in ternary eutectic mixture of alkali carbonate salts (Li_2CO_3 , Na_2CO_3 and K_2CO_3). According to their results, the addition of molten salt to the reactor increased the pyrolysis conversion by a 16% at 600 °C, due to the catalytic activity of the alkali species in the salt. Moreover, the bio-oil yield increased in the presence of molten salt over the studied temperature range (450–600 °C). The hydrocarbon content in the bio-oil increased while the oxygenated compounds such as phenols and alcohols decreased compared to the pyrolysis without molten salt.

The effect of different type of molten salts (FLiNaK, $(LiNaK)_2CO_3$, $ZnCl_2$ -KCl, and KNO_3 - $NaNO_3$) on the thermal behavior of wood particles in pyrolysis process was studied by Nygård and Olsen [19]. Tests were conducted over temperature range of 400–600 °C. During pyrolysis tests including nitrate molten salts they observed a sudden increase in the reaction temperature, exceeding reactor-set temperature. This effect was attributed to the exothermic reaction between the salt and the carbon present in the wood sample. In contrast, other types of salts, did not show such thermal behavior. Maximum heating rates measured in the cylindrical wood particle (30 mm length and 3.5 mm diameter) were observed in FLiNaK salt (46–56 °C/s). Maximum heating rate in wood particles of different diameters [20] was compared to heating rates measured in a fluidized bed reactor [21]. The authors observed that for wood cylindrical particles with a diameter smaller than 4 mm, the maximum heating rate in molten salt pyrolysis was significantly higher than that in a fluidized bed. Jiang et al. [22] studied the effect of different molten salts on the pyrolysis of biomass and found that the maximum yield of bio-oil was achieved for the pyrolysis of cellulose in $ZnCl_2$ at a temperature of 450 °C using N_2 as inert gas. The reported yield of bio-oil was 35 wt%, with a water content of 46%. On the other hand, a mixture of $ZnCl_2$ and KCl as the pyrolysis media at 520 °C, resulted in a bio-oil yield of 20 wt%, with a water content of 40%, while the gas and solid yields were 50% and 30%, respectively. The same molten salt mixture was used by Ai et al. [23] as the medium for the pyrolysis of raw rice stalk at 450 °C. Product yield distribution was 61.7% for solids, 12.1% for liquids and a 22.2% for permanent gases. Among permanent gases H_2 was the dominant product (43.2 vol %) followed by CH_4 (10.8 vol%) and CO_2 (46.0 vol%).

An important aspect that should be considered when using nitrate molten salts at high temperature is the corrosion that may deteriorate the metal parts of the installation. Depending on the process temperature, various alloys are able to resist corrosion. Low carbon content steel sustains low temperature applications while high Cr stainless steel

(SS) is required for high temperatures [24]. The presence of chlorides or water in the nitrate molten salt can promote the corrosion in 304 and 316 SS [25,26]. However, Pacheco [27] hardly observed any corrosion in a 316 SS solar receiver during the operation of the Solar Two Plant. Kruijenga and Gill [28] tested 321 and 347 SS for more than 1000 h. Corrosion affected the 347 SS 30–40% less than 321 SS at temperatures of 600 °C or below, with a metal loss of 16 $\mu\text{m}/\text{year}$. These two SS have been also recommended by Kelly due to the low metal loss [26]. Other alloys such as 321H and 316 T SS, Inconel 718 and 624, or A516 Gr70 carbon steel performed with negligible corrosion deterioration in the temperature range of nitrate molten salts [24,29]. This aspect is out of the scope of this work, although it should be considered in further developments.

This paper investigates the potential of solar molten salts (60 wt% NaNO_3 and 40 wt% KNO_3), which is the fluid employed as the heat transfer fluid and storage medium in the modern and commercial CSP plants, to be used as the direct heat transfer medium for the thermochemical conversion of biomass. This concept would allow using the surplus of solar irradiation stored in the hot tank (565 °C) of a thermosolar power plant operating with molten salts to heat the biomass in a reactor and convert it thermochemically into a fuel that could be stored for a later usage in the electricity generation. Although the conversion of biomass in a molten salt reactor has been considered in the past, no results of this process when employing nitrate salt have been published before. Moreover, the conversion of biomass in the nitrate molten salt reactor has been compared to its conversion in a traditional fixed-bed reactor.

2. Experimental setup

2.1. Materials

C. Cardunculus L. is selected as the pyrolysis fuel. Cylindrical pellets of 6 mm in diameter and 5–25 mm in length are carefully crushed and sieved to a particle size in the range of 1.25–4.75 mm with a bulk density of $442.82 \pm 9.14 \text{ kg/m}^3$ prior to pyrolysis tests in order to enable uninterrupted continuous feeding. Biomass elemental analysis is carried out by means of a CHN analyzer (Leco TruSpec). The proximate analysis is determined in a thermogravimetric analyzer (TA Instruments QA500), using an inert atmosphere for moisture and volatile content and an oxidative atmosphere for ash content. The higher heating value is measured using an isoperibolic calorimeter pump (Parr 6300). Table 1 shows the composition of *C. cardunculus* in terms of proximate and elemental analysis as well as the higher heating value.

A solar molten salt used as a heat transfer medium for pyrolysis tests is manually blended from pure NaNO_3 and KNO_3 salts (purity > 99.5%), as they were received. Binary mixture consisted of these two salts in a mass ratio of 60/40 w/w %. According to Bradshaw and Meeker [30], the melting point of this binary mixture occurs at 238 °C. At temperatures above 560 °C, the molten salt loses its chemical stability by the degradation of nitrates into nitrites and various forms of oxide ions [31].

Table 1

Biomass property characterization.

Proximate analysis [wt.% ar]		Elemental analysis [wt.% db]	
Moisture	7.03	Carbon	48.11
Volatile matter	72.29	Hydrogen	5.58
Fixed carbon	15.01	Nitrogen	0.80
Ash	5.67	Oxygen ^a	39.42
Higher heating value [MJ/kg db]	17.80		

ar: as received, db: dry basis,

^a By difference.

Fig. 1. Scheme of the experimental setup: (1) mass flow meter; (2) molten salt stopper and collection vessel; (3) electrical furnaces; (4) mesh stainless steel tube for char collection; (5) vibrating biomass feeding system; (6) dry condensation system; (7) wet condensation-impinger; (8) cotton filter; and (9) silica gel.

2.2. Experimental facility

The experiments are performed in a lab-scale reactor as shown in Fig. 1. The reactor consists of a stainless steel tube with a length of 560 mm and an inner diameter of 52.8 mm. A pipe is welded to the bottom side of the reactor, facilitating the discharge of the molten salt after the experiment is finished. At the lower side, the discharge pipe is sealed by a 5 cm stopper made of solidified molten salt. Thus, the reactor content can simply be discharged by heating up the section where the discharge pipe is located. Biomass is top fed by an automatic vibrating system as described in [32]. Nitrogen is introduced through a long pipe stretching to the bottom of the reactor. Inert nitrogen facilitates pyrolysis conditions, mixes the molten salt medium and carries the gaseous products along the experimental set-up. Additional nitrogen is also introduced into the feeding system in order to prevent the backflow of gaseous products from the reactor. The produced gases leave the reactor through its upper part passing through a condensation system prior to on-line gas analysis. To avoid condensation in the transfer line between the reactor and the condensation system, a trace heating and isolation material is used to keep the pipe temperature at 350 °C. The condensation system is a combination of dry and wet principles adapted for the efficient removal of the condensable fraction of gases. Two glass heat exchangers are connected in series to cool down the produced gas stream and remove a major part of the condensable fraction from it. Glass heat exchangers are kept at -5 °C by a flow of chilled ethylene glycol/water (25/75) refrigerant solution. Subsequently, an impinger bottle filled with 2-propanol is employed to wash off tar aerosols. At the end of the condensation system, two filters (cotton wool and silica gel) are used to trap the remaining aerosols and

water vapor prior to gas analysis.

The desired reactor temperature is reached and maintained by two electrical furnaces surrounding the reactor. In this sense, the solar energy collection system has not been included in the experimental facility, but instead electrical resistances melt and heat the molten salt, to simulate the hot fluid coming from the hot tank of a solar power plant. Lower electrical furnaces are only turned on once the experiment is completed to melt down the salt stopper, allowing the discharge of molten salt from the reactor.

The reactor pressure is measured at the reactor bottom by a Kistler 4260A absolute pressure sensor. The temperature is monitored along the reactor using type K thermocouples at the bottom of the reactor (T_{reactor}), in the freeboard ($T_{\text{freeboard}}$) and in the transfer line (T_{transfer}). All of the signals are collected by a National Instruments data acquisition system with analogue input channels.

2.3. Experimental procedure

Two different pyrolysis tests are presented in this work: (1) without molten salt (traditional fixed bed pyrolysis, considered as the reference case in this study) and (2) with molten salt. First, the discharge pipe at the bottom of the reactor is closed in order to seal the reactor. The end of the pipe is immersed into a molten salt bath and kept there until it cools down to ambient temperature when leftover salt around the pipe is removed. Then, the reactor is placed inside the electrical furnaces, and the upper furnace is set to the desired temperature. In cases where the molten salt is used as a heat transfer medium, 220 g of salts are introduced into the reactor by the feeding pipe at the top of the reactor as soon as the temperature inside the reactor reaches 500 °C. The feeding system is immediately reconnected to the reactor along with a steady flow of nitrogen in order to facilitate an inert atmosphere in the reactor. The temperature of the transfer pipe from the exit of the reactor to the condensation system is set to 340 °C, while the temperature of the ethylene glycol/water mixture is set to −5 °C. 0.5 l/min of nitrogen is introduced through the feeding system to prevent the backflow of the produced gases from the reactor. Once the reactor temperature stabilizes, the feeding system is initiated, and all signals are acquired by the PC. Table 2 shows the operating conditions of the experimental tests conducted in this study.

Once the experiment is finished, the furnace located in the lower part of the test rig is turned on in order to melt down molten salt stopper at the end of the discharge tube and collect the molten salt in the discharge vessel. Finally, the whole test rig is cooled down to ambient temperature prior the cleaning of the reactor. The biomass feeding system is also discharged in order to calculate the exact amount of biomass fed.

2.4. Sampling and analysis of pyrolysis products

Non-condensable gases are measured by a modular on-line gas

Table 2
Operating conditions.

	#1	#2	#3	#4	#5	#6	#cell
Biomass feeding rate [kg _{ar} /h]	0.23	0.23	0.23	0.22	0.22	0.22	20.3 ^a
N ₂ flow rate [l/min]	10	10	10	10	10	10	12
N ₂ feeding flow rate [l/min]	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Mass of molten salts [g]	–	–	–	220.1	220.7	221.4	220.0
Reactor temperature [°C]	512	500	504	505	473	510	495
Freeboard temperature [°C]	510	500	515	495	500	475	517
Transfer temperature [°C]	325	345	325	345	360	350	370
Ethylene glycol/water temperature [°C]	−4.8	−5.1	−6.2	−5.6	−6.0	−6.1	−2.6
Maximum residence time [s]	2.96	2.96	2.96	2.96	2.96	2.96	2.46
Experiment duration [min]	60.0	60.0	36.8	15.5	18.5	25.4	4.0

^a Batch experiment with pure cellulose, in [g].

analyzer to detect CO, CO₂, CH₄ and O₂ (Ultramat 23, Siemens); H₂ (Calomat 6, Siemens); and C₂H₄ and C₂H₆ (Ultramat 6, Siemens). Analyzers are fitted with infrared, paramagnetic cell, and thermal conductivity detectors. Before each experiment, modular detectors are calibrated by a certified gas calibration mixture. The nitrogen concentration is calculated by difference.

The condensable fraction of the product gas is sampled by the solid phase adsorption (SPA) method [33,34], using pre-packed Discovery® DSC-NH₂ SPA cartridges with polymerically bonded aminopropyl sorbent. For each experimental condition, two parallel SPA samples are taken manually using a 100 ml syringe. Bio-oil compounds are immediately extracted from the SPA sorbent by the addition of 1.8 ml of dichloromethane. Separation and analysis of bio-oil samples is carried out by a Varian 431-GC gas chromatograph coupled with a Varian 210-MS (ion trap) mass spectrometer instrument. A constant helium flow of 1.2 ml/min is passed through a non-polar VF-5MS capillary column (30 m × 0.25 mm, 0.25 μm film thickness). Additional details with regards to the analysis of the condensable fraction can be found in [32]. The most abundant bio-oil compounds are identified using the NIST 2.0 library. However, due to the inadequate matching of the unknown mass spectra against library mass spectra, it is not possible to identify all of the major compounds with a good level of certainty. Only a match probability higher than 30% is considered to be adequate to identify the compounds with their structural formula. Due to the complex composition of the bio-oil and lack of suitable calibration standards [35,36], bio-oil yields are presented in a semi-quantified manner (i.e., presenting only relative values of the chromatogram integration area).

3. Results and discussion

3.1. Yield and composition of permanent gases

The reference pyrolysis tests (traditional fixed-bed pyrolysis) with continuous biomass feeding is compared with pyrolysis tests employing a molten salt as a heat transfer medium. Only the results from tests number #2 and #4 (Table 2) are shown in the present paper. Those results show good reproducibility between the different tests with acceptable deviations due to biomass heterogeneity, around 10% from the mean value. Fig. 2 shows the permanent gas composition for both tests. The reference tests without salts generate a pyrolytic gas that mainly consists of CO₂ around 2.5% v/v (53% v/v N₂ free), and CO around 1.5% v/v (32% v/v N₂ free), with CH₄, C₂H₄, and C₂H₆ yields typically under 0.5% v/v (9% CH₄, 3% C₂H₄ and 3% C₂H₆ % v/v N₂ free). Nitrogen is the dominant gas species (~95% v/v) since it is the carrier gas for the pyrolysis process. A negligible amount of H₂ is found in the pyrolytic gas. At pyrolysis temperatures lower than 500 °C, negligible yields of H₂ were also found by Strezov et al. [35]. They stated that hydrogen is released after the secondary thermal cracking of bio-oil vapors promoted by elevated temperature. Carbon conversion into gas results in values of approximately 16%, which is in agreement with a pyrolysis process, being the rest of the carbon from the biomass collected as char and bio-oil. These findings are in agreement with those obtained by Encinar et al. [12] for the fixed bed pyrolysis of cardoon. Pyrolysis tests with molten salts result in the depletion of N₂ yields (~81% v/v) due to a higher production of CO, around 8% v/v (44% v/v N₂ free) and CO₂ around 5.5% v/v (29% v/v N₂ free). The H₂ yield also increases up to around 3% v/v (15% v/v N₂ free). No remaining char has been visually found after pyrolysis tests employing molten salts, obtaining a carbon conversion into gas of 60%. Instead, a larger quantity of shoot and a substantial aqueous condensable fraction are observed in the condensation system. These results indicate higher heating rates in the molten salt pyrolysis compared to traditional fixed-bed pyrolysis. Higher heating rates increase carbon conversion efficiency and improve the pyrolytic gas composition.

Along with the permanent gases, both the gas yield (GY) and lower heating value (LHV) calculated for the pyrolysis test employing molten

Fig. 2. Permanent gas composition (including nitrogen) and carbon conversion: (a) traditional fixed-bed pyrolysis and (b) molten salt pyrolysis.

Fig. 3. Gas yield and gas lower heating value (including nitrogen): (a) traditional fixed-bed pyrolysis and (b) molten salt pyrolysis.

salt seem to be higher with respect to fixed bed pyrolysis test. As shown in Fig. 3, the GY is approximately 17% higher, whereas the LHV is observed to be approximately 247% higher than values derived from the reference pyrolysis tests. This agrees with the higher concentration of combustible gases such as CO, H₂, and CH₄ as well as light hydrocarbons, which are the main species affecting the LHV [37]. The calculated LHV of the permanent gases (10.7 MJ/Nm³, N₂ free) are higher than the values obtained by Encinar et al. [12], who reported a LHV of

8.2 MJ/Nm³ for the gas from the fixed bed pyrolysis of *C. cardunculus* L. at 500 °C, while the GY is similar when given per kg of cardoon (0.13 Nm³/kg vs 0.14 Nm³/kg). 23.7 wt% of biomass fed (dry ash-free) converts into permanent gas during fixed bed pyrolysis. This value increases up to 89.9 wt% during molten salt pyrolysis. These results correlates with negligible char production which is not visually observed in molten salt after the experiments.

Fig. 4. Chromatograms of bio-oil (identification numbers correspond to those in Table 3): (a) traditional fixed-bed pyrolysis and (b) molten salt pyrolysis.

3.2. Bio-oil analysis

Fig. 4 shows mass spectrometry chromatograms of bio-oils sampled by means of an SPA method. Bio-oil derived from traditional fixed-bed pyrolysis is a complex product with regards to its molecular diversity. The structural formulas of the 23 identified organic compounds are presented in Table 3. Pyrolysis bio-oil predominantly consists of five and six carbon aromatic structures, which are rich in oxygen while possessing functional groups such as alkyl, alkenyl, hydroxyl, carbonyl, and methoxy. Additionally, a number of saturated and unsaturated aliphatic hydrocarbons are also identified in bio-oil. Similar types of compounds were detected during the batch-fed fixed bed pyrolysis of elephant grass [35,36] and miscanthus [38]. Strezov et al. [35] conducted lab scale pyrolysis tests at heating rates of 10 and 50 °C/min up to a maximum temperature of 500 °C. Compound identification was possible by a flash pyrolysis GC/MS technique applied to the collected bio-oil. The major bio-oil compounds derived from the test at a heating rate of 10 °C/min were classified in the following groups: phthalate esters, benzene compounds, phenols, octadecanoic acid, hexadecanoic acid, and pyrans, together accounting for 50% of the bio-oil weight. Lee et al. [36] studied the pyrolysis products in the range of heating rates between 50 and 150 °C/min with a reaction temperature of approximately 500 °C. The most abundant bio-oil compounds identified by GC-MS were acetic acid, 2-methyl-2-cyclopenten-1-one, 2-hydroxy-3-methyl-2-cyclopenten-1-one, phenol, and 1,2-benzenediol, which resemble the bio-oil composition of the present work. Park et al. [38] analyzed the bio-oil composition from pyrolysis carried out at temperatures between 400 and 500 °C. The main products identified by GC-MS were acetic acid, 2-furancarboxaldehyde, 4-vinylphenol, 2,6-dimethoxy-phenol, and levoglucosan.

According to Fig. 4, the complexity of chromatograms obtained from the test with molten salt is reduced. Eighteen bio-oil compounds are identified with adequate probability. With respect to the bio-oil produced in the traditional fixed-bed pyrolysis, it seems that oxygenated compounds are greatly reduced when thermochemical conversion is carried out in molten salts. By comparison of the integrated chromatographic areas, increased yields of benzene and toluene, 6.5-

fold and 2.5-fold, respectively, are observed in favor of molten salt pyrolysis. The total integrated chromatographic area is considered as the total GC detectable bio-oil, which encompasses all compounds eluted between 2 and 40 min. The yield of the total GC detectable bio-oil from molten salt pyrolysis was 25% less than that generated during traditional fixed-bed pyrolysis. A notable difference is also found with the presence of naphthalene in the bio-oil from molten salt pyrolysis. According to Strezov et al. [35], Lee et al. [36], and Chen et al. [39], a higher heating rate results in higher yields of bio-oil. A higher heating rate was found to shift the reactions towards a higher temperature range but also reduce the occurrence of secondary reactions as a result of the faster devolatilization of biomass particles.

3.3. Effect of molten salt on the biomass pyrolysis

The possible causes for the differences between traditional fixed-bed pyrolysis and molten salt pyrolysis are investigated through the temperature evolution during the experimental tests shown in Fig. 5. The temperature profile of the reference test declines as soon as biomass is introduced into the reactor. This observation is in accordance with the absence of oxygen inside the reactor, leading to endothermic pyrolysis reactions [5]. On the other hand, the temperature profile of the molten salt pyrolysis increases as soon as biomass feeding commences. Nygård and Olsen [19] also reported this behavior during the pyrolysis of wood particles in a KNO₃-NaNO₃ molten salt reactor. The elevated reactor temperature suggests that exothermal oxidation reactions occur inside the reactor, probably due to degradation of the molten salt. This degradation can be induced either by the feedstock constituents, pyrolysis products, or by any other impurity.

In order to find out if the presence of a permanent gas in contact with the molten salt is responsible of the molten salt degradation a test is performed flowing a gas mixture with a certified composition (Table 4) through the molten salt reactor. Certified gas mixture is composed of the same compounds as found in the real pyrolytic gas.

The permanent gas composition does not change by passing through the molten salt at temperatures from 300 to 550 °C. The measured process parameters such as the reactor temperature and pressure also

Table 3
Identified bio-oil compounds.

Traditional fixed-bed pyrolysis			Molten salt pyrolysis		
	Compound name	Structural formula		Compound name	Structural formula
1	2-Methylfuran		1	Benzene	
2	Benzene		2	1,4-Cyclohexadiene	
3	Toluene		3	Toluene	
4	Hexane		4	3,4,5-Trimethyl-1-hexene	
5	2,5-Dimethylfuran		5	Ethylbenzene	
6	2-Furanmethanol		6	o/m/p-Xylene	
7	Ethylbenzene		7	3-Ethylhexane	
8	o/m/p-Xylene		8	3-Ethyltoluene	
9	2-Methyl-2-cyclopenten-1-one		9	2-Propenylbenzen	
10	3-Methyl-2-cyclopenten-1-one		10	2-Ethynyltoluene	
11	Phenol		11	2-Propylheptanol	
12	2-Hydroxy-3-methyl-2-cyclopentene-1-one		12	Naphthalene	
13	o/m/p-Cresol		13	n-Tetradecane	$\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$
14	2-Methoxyphenol		14	Methenamine	
15	o/m/p-Xylenol		15	Benzocycloheptatriene	
16	2-Methoxy-4-methylphenol		16	Tetradecane,2,6,10-trimethyl	
17	2,4-Dimethoxytoluene		17	2-Hexadecenoic acid	
18	2-Methoxy-4-vinylphenol		18	2-Hexadecanol	
19	2,6-Dimethoxyphenol				
20	2-Methoxy-4-propenylphenol				

(continued on next page)

Table 3 (continued)

Traditional fixed-bed pyrolysis		Molten salt pyrolysis	
Compound name	Structural formula	Compound name	Structural formula
21	3- <i>tert</i> -Butyl-4-hydroxyanisole		
22	Cis-Vaccenic acid		
23	2-Hexadecanol

Fig. 5. Temperature profiles: (a) traditional fixed-bed pyrolysis and (b) molten salt pyrolysis.

do not change throughout the conducted tests. This indicates the chemical stability of the molten salt while in direct contact with permanent gas from a thermochemical conversion of biomass.

The dominant biomass polymer cellulose is pyrolysed in order to investigate if the elemental constituents or any other impurity in the biomass can cause the molten salt degradation. High purity cellulose powder (DS-0, Sigma-Aldrich) manually compressed into pills of approximately 0.5 g is used in this case. 20.3 g of cellulose pills, are manually fed from the top of the reactor with a two-minute period (#cell test in Table 2).

Fig. 6a shows the permanent gas composition evolved during molten salt pyrolysis using cellulose as a fuel. The permanent gas is mainly composed of CO₂, CO and H₂. Due to the manual feeding, an unstable gas concentration is observed. Fig. 6b shows the temperature

Table 4

Composition of the certified gas mixture [% v/v].

H ₂	CO	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	N ₂
7.69	14.75	13.03	3.53	1.99	0.58	58.43

profiles of T_{reactor} and $T_{\text{freeboard}}$ measured during the cellulose pyrolysis experiment. It can be observed that both temperatures increase soon after cellulose is introduced into the reactor. Elevated temperatures indicate an exothermic reaction inside the reactor instead of an endothermic pyrolysis process, similar to the observation during *C. cardunculus* molten salt pyrolysis.

As cellulose is only composed of carbon, hydrogen and oxygen, these results indicate that the presence of carbon in contact with the molten salts may promotes the degradation of the molten salt, according to the mechanism proposed by Bauer et al. (Eq. (1)) [31]. This can explain the exothermic reactions in the molten salt pyrolysis, shifting the pyrolysis towards a gasification process and delivering higher yields of CO, CO₂, H₂ and CH₄. Gimenez and Fereres [40] studied the influence of different impurities on the thermal degradation of nitrate-based molten salt. Their results showed that the addition of 5% Na₂CO₃ to a solar salt sample decreased the maximum temperature or stability limit of the sample (temperature at which the sample has lost 3% of its initial weight) by 8%. In addition, the small amount of O₂ observed in the permanent gas measured at the reactor exit, in the pyrolysis of *C. cardunculus* in molten salts (Fig. 2b), might be attributed

Fig. 6. Molten salt pyrolysis using cellulose as a fuel: (a) permanent gas composition (including nitrogen) and (b) temperature profiles.

this effect and to the limited mixing inside the reactor. Then, this can explain the exothermic reactions in the molten salt pyrolysis, shifting the pyrolysis towards a gasification process and delivering higher yields of CO, CO₂, H₂ and CH₄.

The presence of oxygen in the pyrolytic gas also affects bio-oil composition, shifting the process towards the gasification process, where benzene, toluene and naphthalene are found to be dominant tar compounds [41,42]. With respect to the tar yields, Kinoshita et al. [41] observed a reduction in the total tar yield and an increase in the yields of benzene and naphthalene over the equivalence ratios between 0.22 and 0.32 in the air blown fluidized bed gasifier. A steady toluene yield was observed up to an equivalence ratio of 0.27, followed by a decrease as the equivalence ratio increased. More recently, Horvat et al. [42] found that at a constant temperature, the equivalence ratio has relatively little impact on the yield or composition of tar from the air blown fluidized bed gasification of grassy biomass. Thus, the effect of molten salt on the bio-oil composition and yield shall be explained by a combination of two factors. Due to the higher heating rate, the yield of bio-oil shall increase, but the oil acidity may decrease. However, in the present study, the yield of bio-oil decreased with respect to the higher heating rate, which could be attributed to the presence of oxygen released due to molten salt thermal degradation. Mitigation of oxygenated bio-oil compounds along with enhanced yields of benzene, toluene and naphthalene can be associated with the synergistic effect of a higher heating rate and oxygen presence during molten salt pyrolysis.

To support these findings, a final test is carried out in a thermogravimetric analyzer (TGA Q500, TA Instruments), using pure cellulose and molten salt. Both pure cellulose and molten salt are separately subjected to the same heating program as well as blend of cellulose and molten salt in a mass ratio 1 mg:20 mg. The oven program is specified by the following segments: heating to 105 °C at 20 °C/min; isothermal during 20 min; equilibrate at 50 °C; heating to 550 °C at 50 °C/min; and

isothermal during 30 min.

Fig. 7 shows the curves of thermogravimetric experiments. During pyrolysis of pure cellulose (Fig. 7a) around 95% of the initial mass (0.95 mg) is lost in the process. In the case of molten salt (Fig. 7b), around 3.7% of the initial mass (0.74 mg) is lost, indicating a high thermal stability. However, when the blend of cellulose and molten salt is thermo-gravimetrically analysed (Fig. 7c), the weight loss accounts for about 14% of the initial weight (3.1 mg). This value is higher than the sum of losses of the two materials separately (0.95 mg + 0.74 mg). Evidently, the presence of the cellulose degrades the molten salt, leading to an additional weight loss of molten salt of around 1.4 mg. Moreover, Fig. 7, shows the derivative of the weight loss where it can be observed that the decomposition of cellulose takes place at 340 °C while the main weight loss of molten salt occurs at 550 °C. In the cellulose and molten salt blend (Fig. 7c), two distinctive peaks are observed: one at 340 °C and a second one at 430 °C. The first one corresponds to the decomposition of the cellulose while the second peak may correspond to the molten salt degradation catalyzed by the presence of cellulose.

4. Conclusions

The feasibility of using nitrate molten salts from a concentrated solar power plant as a heat transfer medium for the thermochemical conversion of biomass, in direct contact, is addressed in this study. The thermochemical conversion of *C. cardunculus* L. is experimentally studied in a reactor where the biomass particles are immersed in a bath of nitrate molten salts at 500 °C aiming to produce a solar fuel. The results of molten salt pyrolysis are compared to traditional fixed-bed pyrolysis using nitrogen as the carrier gas, obtaining the following conclusions:

- The biomass pyrolysis in direct contact with a molten salt shifts the process towards an exothermic reaction due to the degradation of molten salts.
- Molten salt degradation is probably induced by the presence of solid carbonaceous material, which may promote the molten salt

Fig. 7. TGA pyrolysis curves: (a) pure cellulose, (b) molten salt and (c) blend of pure cellulose and molten salt. (solid blue: weight; dashed red: der. weight). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

degradation while releasing oxygen. Oxygen reacts with the biomass shifting the endothermic pyrolysis process towards an exothermic process.

- The permanent gas produced during molten salt pyrolysis contains higher yields of CO, CO₂ and H₂, compared to that produced during traditional fixed-bed pyrolysis.
- The gas yield and the gas lower heating value are also higher in the molten salt pyrolysis.
- The molten salt pyrolysis tests evolve the process condition rather typical in gasification than pyrolysis process.
- The yield of total GC-detectable bio-oil from molten salt pyrolysis decreases by approximately 25% with respect to the fixed bed pyrolysis.
- The oxygen content as well as the complexity of bio-oil also decreases and this effect might be associated with the synergistic effect of a higher heating rate and oxygen presence during molten salt pyrolysis.
- According to the TGA experiments, the presence of cellulose in contact with the molten salt leads to a weight loss of 10% of molten salt compared to 4% that is loss when the molten salt is heated in the absence of biomass.

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