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Cynara cardunculus L. gasification in a bubbling fluidized bed: The effect of magnesite and olivine on product gas, tar and gasification performance

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HIGHLIGHTS

- *Cynara cardunculus* L. was gasified in a pilot-scale BFB using magnesite and olivine at different temperatures.
- Tar analysis based on total GC detectable, secondary and tertiary tars as well as individual tar compounds was discussed.
- Relatively high hydrogen content due to magnesite, olivine and biomass ash composition was obtained.
- Magnesite leaded to a better gasification performance at low temperature while olivine did at high temperature.
- No agglomeration problems were found due to the addition of kaolin to the raw biomass.

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ABSTRACT

Gasification of *Cynara cardunculus* L. was performed in a bubbling fluidized bed (BFB) using air as gasifying agent and, magnesite and olivine as different bed materials. Temperature was varied during the experiments (700–800 °C) with fixed biomass feeding and air flow rate. The effect of using the magnesite and olivine on gas and tar composition, carbon and biomass conversion, and cold gas efficiency was investigated. The product gas showed high hydrogen content (13–16% v/v) for both magnesite and olivine in the studied temperature range. Higher heating value and gas yield were improved with increasing the temperature from 700 to 800 °C. Biomass and carbon conversion were greater than 75%, obtaining values higher than 90% for both 700 and 800 °C in magnesite and for 800 °C in olivine. Small differences in total tar were observed between materials, although tar composition was very different. BTEX were higher for olivine and similar PAHs was obtained for both magnesite and olivine. A higher catalytic activity at 800 °C was observed for magnesite. Gasification performance was better with magnesite at 700 °C while olivine showed better properties at 800 °C.

1. Introduction

Gasification is a thermochemical process that transforms different carbonaceous materials like biomass into a useful product gas or chemical feedstock [1]. The process needs a small amount of oxygen, less than that required for stoichiometric oxidizing conditions, to produce a combustible gas composed of H_2, CO, CH_4, CO_2, N_2 and light hydrocarbons, with limited formation of dioxins, SO_x and NO_x, being NH_3 and H_2S the main nitrogen and sulphur compounds due to the gasification reduction conditions [2]. The flexibility in terms of feedstock type and size, the good solid–gas mixing and temperature control, and high mass transfer rate, make bubbling fluidized bed (BFB) reactors an advantageous option for biomass gasification [3,4]. However, there are two key considerations to be taken into account in biomass gasification in a BFB reactor: the high alkali content in biomass, and tar production. The high alkali content promotes bed agglomeration changing the operating conditions and leading, in some cases, to

Abbreviations: BFB, bubbling fluidized bed; BTEX, benzene, toluene, ethylbenzene and xylene; CGE, cold gas efficiency; daf, dry-ash free; ER, equivalent ratio; FID, flame ionization detector; GC, gas chromatography; GY, gas yield; HHV, higher heating value; ID, inner diameter; LHV, lower heating value; MSD, mass spectrum detector; NTP, normal temperature and pressure conditions; PAH, polyaromatic hydrocarbons; SPA, solid phase adsorption; TGA, thermogravimetric analyzer.

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defluidization. Tars, previously defined by Milne et al. [5] as the organics produced under thermal or partial-oxidation regimes of any organic material and generally assumed to be largely aromatic, and defined by Kiel et al. [6] as all organic compounds with a molecular weight larger than benzene, excluding soot and char, also need to be considered. Tar related issues can lead to unscheduled stops and may impact the performance of downstream unit processes [7].

The end use of the product gas determines the requirements for tar concentration: compressing and piping needs less than 600 mg/Nm^3; the maximum tar concentration for internal combustion engines is 100 mg/Nm^3, being phenols and cresols corrosive for this engines; less than 0.1 mg/Nm^3 is required for synthesis applications; or, in the case of close-couple combustors, the gas quality is not a major issue. Different cleaning technologies, ranging from cyclones, coolers, filters or catalytic cracking or reforming, are available to adapt the gas characteristics to these requirements [5].

Different bed materials such as dolomite, magnesite, olivine or metal based catalysts are frequently used in order to avoid agglomeration, to reduce tar yield and to improve gas composition [8,9]. Corella et al. [10] compared dolomite and olivine, concluding that dolomite was better for tar reduction but generated more fine particles than olivine. Many authors have studied the performance of olivine as an in-bed catalyst with different types of feedstock such as woody biomass or plastic waste, obtaining improvements in gas composition and tar yield compared to silica sand [11–13]. Rapagnà et al. [14] used olivine particles during steam gasification of almond shells, concluding that it had good catalytic activity at temperatures around 800 °C. Magnesite is another alternative as a bed material in BFB gasification. Siedlecki et al. [7] obtained very promising results using magnesite either as a bed additive or as a bed material. In addition to bed material gasification conditions such as temperature, biomass throughput, type of biomass, gasifying agent or gasifier configuration also affect tar yield and gas composition [15]. Gasification temperatures between 700 and 800 °C are critically important in terms of tar mitigation as they are high enough to produce limited quantities of tar and below the dew point of many tar molecules [16].

Cardoon or thistle can be a good option for biomass gasification compared with other energy crops due to its low cost, nitrate pollution and water consumption, it can be cultivated on land not suitable for food production and enhancement of soil characteristics [17,18]. It is a herbaceous perennial species well adapted to Mediterranean regions with hot dry summers [18]. Among the Mediterranean countries, Spain has ideal conditions for cardoon production [19], moreover, the biomass from this plant has high volatile matter content (more than 75%), which is an important benefit in biomass gasification [20]. The interest in this energy crop is not new, Herguido et al. [21] gasified different biomasses in a BFB with steam, including *Cynara cardunculus* L., and studied the effect of temperature on gas composition, char and tar yields using silica sand as the bed material. Their results showed both low gas yield and carbon conversion, and high char yield. Steam gasification of cardoon was also studied by Encinar et al. [22] and the results were compared with cardoon pyrolysis in a fixed bed reactor under similar conditions [20]. They reported that H_2 yield was better for steam gasification than for pyrolysis at the same temperature. High temperature favoured the generation of H_2 and CO, as well as gas yield and conversion rates. Zabaniotou et al. [19] gasified *C. cardunculus* in a fixed bed reactor for different equivalent ratios and temperatures. They concluded that the product gas obtained by fixed bed air gasification was similar to steam gasification in terms of H_2 and CO, with high H_2 content. As a result they suggested cardoon gasification as a possible route for H_2 production.

Some investigations on combustion and gasification of thistle have recently been carried out with the goal of understanding the role of its high alkali content in bed agglomeration. Abelha et al. [23] employed blends of cardoon and eucalyptus to reduce agglomeration while gasifying with a mixture of air and steam using silica sand as the bed material. Agglomeration decreased and it finally disappeared when 80% w/w of eucalyptus was used. However, higher amounts of H_2 and low tar content were obtained when eucalyptus was not used and cardoon was gasified on its own with air and steam. On the other hand, it was observed that dolomite prevented agglomeration even with low concentrations of eucalyptus. Similar results in terms of bed agglomeration were reported by Christodoulou et al. [24] who used giant reed in combination with *C. cardunculus*, employing magnesite and olivine as bed materials i.e. agglomeration occurred when cardoon only was gasified either with magnesite or olivine. In another study, Christodoulou et al. [25] analyzed the agglomerates obtained from gasifying cardoon in an olivine bed. The agglomerates were found to be formed by a melted phase rich in sodium, potassium, calcium, magnesium and silicon. Serrano et al. [26] used silica sand and an alternative bed material, sepiolite, in order to compare the defluidization time and agglomerates during cardoon gasification at different air velocities and observed that sepiolite delayed the defluidization time by up to an order of magnitude compared with silica sand. These studies show that the use of different bed materials such as magnesite, olivine or sepiolite can delay agglomeration and suggest that dolomite can be used to completely avoid it. Cardoon co-gasification with other types of biomass such as woody biomass (e.g. eucalyptus or giant reed) appears to be a promising strategy to mitigate agglomeration problems. Additionally, kaolin ($Al_2Si_2O_5(OH)_4$) has been proven to be an effective additive to increase the ash melting point/temperature [27–30] and prevent or mitigate agglomeration when gasifying high alkali biomass.

As stated by Kiel et al. [6], tar analyses not only need to be focused on the amount of total tar generation (g/Nm^3) but also on its composition. When tar composition is known the tar dew point which defines its condensation behaviour can be calculated and the water solubility of the tar can be evaluated. In spite of the aforementioned studies based on cardoon gasification, only one of them [24] gives some information about tar generation and speciation. To the authors' knowledge no other studies have been reported regarding this aspect of *C. cardunculus* gasification. The present work focuses on air gasification of this biomass and examines the role of temperature (between 700 and 800 °C), and bed materials, with kaolin amended cardoon on agglomeration. The analysis also includes a discussion of gas composition and gasification performance. A detailed tar analysis is undertaken and the tars are evaluated in terms of total tar and the main individual compounds. Finally, a mass balance was carried out to check the consistency of the results and to obtain information for future work.

2. Experimental methodology

2.1. Biomass and bed materials characterization

The feedstock used in these experiments was *C. cardunculus* L. Proximate and ultimate analyses were carried out using a TGA Q500 thermogravimetric analyzer (TA Instruments) and a Leco TruSpec CHN-S elemental analyser. Higher heating value (HHV) was also measured with a Parr 6300 isoperibolic calorimeter. Finally, inorganic elemental composition analysis using atomic