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Pyrolysis of *Cynara cardunculus* L. samples – Effect of operating conditions and bed stage on the evolution of the conversion

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HIGHLIGHTS

- Pyrolysis of *Cynara cardunculus* L. is conducted in a silica sand bed reactor.
- Time evolution of the biomass weight is measured by a high precision scale.
- Increasing either bed temperature or gas velocity enhanced biomass conversion.
- The effect of biomass particle size on pyrolysis depends on the bed stage.
- Heat and mass transfer effects are quantified using an apparent kinetics model.

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ABSTRACT

The effect of different parameters on the pyrolysis of *Cynara cardunculus* L. was studied through an innovative technique based on a precision scale, capable of measuring the time evolution of the biomass samples mass during their thermochemical conversion process while moving freely inside a fluidized bed. A silica sand bed reactor, operated under different values of excess gas velocity and reactor temperature, was employed to hold the pyrolysis reaction of cardoon particles of three different size ranges. The pyrolysis was accelerated for higher excess gas velocities, obtaining pyrolysis times as short as 17.3 s for experiments conducted under bubbling fluidized bed regimes, compared to 185.9 s required to complete the pyrolysis of the same sample in a fixed bed configuration. Similarly, the effect of increasing the reactor temperature promoted faster heating rates across the fuel samples, especially under fixed bed configurations, for which the pyrolysis time is reduced from 321.7 s to 132.0 s when increasing the bed temperature from 450 to 650 °C. Regarding the biomass particle size, small sizes are preferred to minimize the conduction thermal resistance inside the fuel particles and, thus, reduce pyrolysis times and increase volatile yields for the pyrolysis in a bubbling fluidized bed reactor. The opposite result was found when the pyrolysis took place in non-bubbling beds, where the use of larger particles is beneficial to accelerate the biomass pyrolysis reaction.

1. Introduction

Pyrolysis, which consists in the thermal decomposition of solid fuels in a non-oxidative atmosphere at elevated temperatures, is a favorable thermochemical process for biomass conversion, since it enhances the production of a brown-dark liquid called bio-oil, with a lower heating value (LHV) around 14–18 MJ/kg [1]. This bio-oil can be readily stored and transported, permitting its decentralized usage as a fuel in turbines, boilers, and engines or as a source for chemicals production [2,3]. In addition to the bio-oil generated, charcoal and permanent gases are also produced during the pyrolysis of biomass. The physico-chemical properties and the yields of the bio-oil, the permanent gases and the solid residue are strongly affected by the composition of the feedstock, the use of pretreatment techniques for biomass [4,5], and the operating conditions selected for the pyrolysis process, i.e., reactor temperature, heating rate, biomass particle size, or pyrolysis vapor residence time [6,7].

Temperature is considered the most sensitive parameter for pyrolysis, influencing significantly the production of the different pyrolysis products [8]. Previous studies have demonstrated that liquid production can be maximized under certain operating conditions, attaining up to 75 wt% on a dry basis for the pyrolysis of wood in a temperature range of 480–520 °C [6]. Nevertheless, the maximum liquid yield depends not only on the pyrolysis conditions employed, but also on the

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Notation

d_{bm}	particle diameter of the bed material [m]
d_i	inner diameter of the reactor [m]
D_{pellet}	diameter of *Cynara cardunculus* L. pellets [m]
g	gravitational acceleration [m/s^2]
h	height of the reactor [m]
h_b	height of the fixed bed [m]
k	apparent rate coefficient [s^{-1}]
L_{pellet}	length of *Cynara cardunculus* L. pellets [m]
m	mass of the sample at time t [kg]
m_0	initial mass of the sample [kg]
m_{vol}	mass of volatiles in the sample [kg]
t	time [s]
t_{pyr}	pyrolysis time [s]
T	reactor temperature [K]
U	gas velocity [m/s]
U_{mf}	minimum fluidization velocity [m/s]
V_{tot}	percentage of total volatile content released [%]
X	percentage of mass of the sample [%]
X_{res}	percentage of solid residue [%]
ε	void fraction of the bed material [–]
ϕ	sphericity of the dense phase particles [–]
α	conversion factor [%]
μ_g	gas dynamic viscosity at reactor temperature [kg/(m·s)]
ρ_{bm}	particle density of the bed material [kg/m^3]
ρ_g	gas density at reactor temperature [kg/m^3]

feedstock. According to the specific literature, the optimal temperature interval to produce liquid fuel from the pyrolysis of different biomass species ranges from 450 to 650 °C [9–11]. Above this temperature range, the released pyrolysis vapors may undergo secondary cracking reactions, decreasing the liquid yield in favor of permanent gas production [12]. Besides, other research studies have assessed the effect of temperature on the other pyrolysis products, i.e., char and permanent gas. Several authors [13–15] have found a reduction of the solid residue remaining after pyrolysis, i.e., an improvement of the conversion, for increasing reactor temperatures due to the higher thermal energy available.

The effect of heating rate of biomass particles on the pyrolysis reaction has also been studied by many researchers [7]. It is widely accepted that rapid heating of biomass samples is required to enhance liquid production [16–19]. Biomass particle size also influences the pyrolysis process due to heat and mass transfer effects inside the solid particle [20]. The use of biomass particle sizes under 2 mm was recommended by Bridgwater et al. [6] to reduce thermal conduction effects inside fuel particles and enhance bio-oil yields when the pyrolysis occurs in fluidized bed reactors. Regarding experimental works, the most common conclusion is that a decrease in biomass particle size leads to larger conversion degrees and liquid yields [21–23].

Considering the effects of the above-mentioned parameters on the pyrolysis of lignocellulosic biomass, an accurate control of the operating conditions is required to improve the conversion efficiency and maximize liquid yields. Fluidized beds are widely employed in the thermochemical conversion of biomass since they enable an easy control of the operating conditions of the chemical reactions. This technology provides high heat and mass transfer coefficients due to the contact between fuel particles and bed material [2]. In fact, the convection heat transfer coefficient of a fixed bed increases substantially when the gas velocity is increased above the minimum fluidization velocity [24]. In addition, the high thermal inertia of the solid particles that conformed fluidized beds permits the isothermal operation, even when holding exothermic or endothermic chemical reactions.

Thermochemical conversion in fluidized bed reactors requires a proper fuel mixing with the bed material to maximize the heat transfer and, thus, increase the efficiency of the process. The effect of the superficial velocity of the fluidizing gas on this mixing has been studied by several authors. Rowe and Nienow [25], who studied particle mixing and segregation in fluidized beds, reported a better solid mixing as the excess gas velocity was increased. This conclusion was also attained by Bilbao et al. [26], who found more homogenous straw/sand mixtures for higher gas velocities. Soria-Verdugo et al. [27,28], applying digital image analysis to study the motion of fuel particles in a pseudo 2D fluidized bed, concluded that the axial mixing increased with the gas velocity, obtaining homogeneous mixing for gas velocities around three times the minimum fluidization velocity even for low density fuel particles, for which the buoyancy force obtained is overcome by the increase of the drag force for higher gas velocities. This result was confirmed for lab-scale 3D fluidized beds by Soria-Verdugo et al. [29] and Lundberg et al. [30].

This work investigates the effects of variations in reactor temperature, biomass particle size, and excess gas velocity on the pyrolysis of *Cynara cardunculus* L. (cardoon) samples in a silica sand bed reactor using an innovative measuring system. The time evolution of the mass of cardoon remaining inside the reactor during the pyrolysis was measured by a precision scale, capable of detecting the mass released by the sample during its conversion while moving freely inside the reactor. The effects of temperature, excess gas velocity, and biomass particle size were studied, analyzing the synergies between the operating parameters and the reactor bed regime. The optimal excess gas velocity for the conversion of cardoon was also determined based on the measured pyrolysis time.

2. Theoretical background

Biomass pyrolysis is a complex process involving a huge number of reactions which are either parallel or consecutive. Therefore, a detailed model of the biomass pyrolysis kinetics would result in a tedious process. In this regard, Reschmeier et al. [31] proposed a simplified model to describe the apparent kinetics of biomass pyrolysis, for which, assuming a first-order reaction, the variation of mass of the sample, m, with time, t, is proportional to the mass of volatiles remaining in the sample, $m_{vol}(t)$, and the apparent rate coefficient, k:

$$\frac{dm}{dt} = -k \cdot m_{vol}(t). \tag{1}$$

Considering that the mass of the sample, m, can be expressed as the sum of the mass of volatiles, $m_{vol}(t)$, and the mass of solid residue, m_{res}, at any time, i.e., $m = m_{vol} + m_{res}$, Eq. (1) can be integrated obtaining the following expression for the time evolution of the mass of the sample:

$$m = m_{vol}(0) \cdot \exp(-k \cdot t) + m_{res}, \tag{2}$$

where $m_{vol}(0)$ is the total mass of volatiles contained in the sample.

Dividing Eq. (2) by the initial mass of the sample, m_0, and considering that the percentage of solid residue at the end of the pyrolysis process, X_{res}, can be calculated from the total percentage of volatile matter of the sample, V_{tot}, as $X_{res} = 100 - V_{tot}$, the time evolution of the mass percentage of the sample can be determined as:

$$X = 100 + V_{tot} \cdot [\exp(-k \cdot t) - 1]. \tag{3}$$

This expression was found to be accurate to describe the pyrolysis of small particles of dry sewage sludge in a bubbling fluidized bed reactor by Soria-Verdugo et al. [32], provided that the effects of heat and mass transfer in the sample are slight.