Research article

Pyrolysis process using a bench scale high pressure thermobalance

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A B S T R A C T

The influence of the pressure and other operating conditions such as particle size, sweep gas flow and initial sample weight on the cellulose pyrolysis process using a bench scale plant high pressure thermobalance was evaluated. The particle size and the sweep gas flow did not have a great influence on the pyrolysis process. Nevertheless, initial sample weight altered the thermochemical behavior of the pyrolysis process. Moreover, a comparison of the values of the kinetic parameters obtained from pyrolysis experiments performed at lab and bench scale was established. On the other hand, the morphology, the presence of functional groups, the surface area, the proximate analysis and elemental analysis of the chars obtained were studied. Moreover, the evolved gases from the pyrolysis performed at different pressures were also analyzed. An increase of pressure led to both a decrease in the temperature at which pyrolysis took place and an increase in the char yield. Furthermore, the higher the pressure, the higher the porosity, the lower the pores size and the higher the occurrence of alkanes and carbonyl components in the resulting chars were. Finally, the gas released analysis from the pyrolysis process by mass spectrometry showed that high pressures promoted the CH_4 and CO_2 formation, the H_2 yield being practically negligible.

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1. Introduction

The climate change, which is mainly attributed to the massive use of fossil fuels for power generation, is one of the main problems that humanity is facing. The energy consumption increases by 1.1% per year due to fast-growing society and the need of improving the world wide social and economic development [1]. On the other hand, the diminution of world fossil fuel reserves is causing an increasing attention towards renewable energies [2]. In this sense, timescales for depletion of oil, coal and gas are projected around 35, 107 and 37 years, respectively [1].

Although energy resources such as solar, wind, geothermal and nuclear are an alternative to generate heat and power, they do not lead to the direct production of gaseous, liquids or solids fuels. In this context biomass should be considered a viable alternative for being used as fossil fuels [3]. In fact, biomass is nowadays one of the major energy sources, contributing approximately to 14% of the world annual energy consumption [4].

Biomass pyrolysis is one of the existing thermochemical conversions process for producing liquid, solid or gas fuels. It can be defined as the biomass degradation by heat in the absence of oxygen under a temperature range (300–600 °C) in an inert atmosphere [5].

Several studies have been carried out to investigate the thermal degradation of cellulose [6–13]. It was found that its pyrolysis process was characterized by a high yield of liquid and low yield of char [14]. It has been reported that an increase of pressure improves the char yield. In particular, the formation and evolution of the char structure at different pressures is an important step to describe the pyrolysis chemistry and the total product distribution [8]. Moreover, the high carbon content and microporous structure of the biochar is useful for several industrial applications [15]. In this sense, optimal operation variables are essential for modeling industrial processes and maximizing the production of each product [16]. For that reason, the analysis of the main pyrolysis operation variables such as temperature, pressure, particle size or initial sample weight should establish which operational conditions are needed to avoid internal-thermal and external-mass transfer limitations, diffusion resistance or secondary reactions.

The design of industrial processes where biomass feedstock is used to produce direct power, fuels, high-value chemicals and other useful products requires the knowledge of the kinetic processes involved in the thermal transformations [17], which in turn allows to define the best operational conditions [18]. Since the kinetic models that define the chemical conversion of the raw biomass with the temperature are usually obtained at lab scale (thermobalance) [11,19–21], they should be validated at bench and pilot scale conditions before being used for design purposes [22].

In this sense, high pressure thermogravimetric analyzer (at a bench plant scale) coupled with a mass spectrometer (HP-TGA-MS) could be a useful technique to obtain information of mass loss and evolved gases during thermochemical conversion. In addition, since the amount of biomass, the temperature and the pressure that can be used are higher

than those used in conventional lab scale TGA, the results obtained from the bench plant device could be valuable for simulating industrial conditions. However, fewer studies have been reported about the effects of the pressure on biomass pyrolysis by means of HP-TGA-MS. In that way, the effect of the pressure on cellulose pyrolysis was studied by William et al. [23]. Fermoso et al. [24] reported the effect of the pyrolysis temperature, the total pressure and the CO_2 concentration on the gasification of biomass char using a pressurized thermogravimetric analyzer. Bhargava et al. [25] studied the partial oxidation of German brown coal under carbon dioxide atmosphere by means of HP-TGA. The effect of the pressure and heating rate on the devolatization behavior of different biomass species was studied by Agrawal [26]. Chan et al. [27] demonstrated that the pressure had a positive effect in enhancing char combustion reactivities using similar equipment. Liu et al. [28] studied the combined effects of surface area, pore structure, degrees of graphitization and graphite crystallites on the char gasification kinetics by means of HP-TGA. Liu et al. [29] also reported the reaction mechanisms and kinetics of high-pressure char CO_2 gasification. Finally, Soreanu et al. [30] studied the CO_2 gasification process of a marine biomass.

The aim of the present study was to analyze the effects of different operation conditions on the cellulose pyrolysis process using a bench plant HP-TGA. Once the pyrolysis conditions were optimized, the kinetic study performed at bench plant scale was compared to a similar one performed at lab scale. Moreover, evolved gases during the thermochemical conversion of cellulose using the MS technique were analyzed. Finally, the effect of pressure on the morphology of char was also evaluated.

2. Materials and methods

2.1. Cellulose sample

Dry biomass of cellulose was purchased from Acros organics. It was presented in a microcrystalline form with an average particle size of 50 μm. The ultimate analysis and proximate analysis was performed following the standard UNE 15104:2011, UNE–EN ISO18123, UNE 32-004-84 and UNE 32002-95. Table 1 shows the proximate and ultimate analysis of the cellulose sample.

2.2. Experimental set-up

Pyrolysis experiments were carried out using a HP-TGA bench plant coupled with a MS (Fig. 1). This experimental set up consisted of the following units: supply, condensate separation, reaction and analysis systems. The reaction system was constituted by a high pressure thermobalance *LINSEIS L81PT High Pressure TGA-DTA/DSC* that measured weight changes (TGA) in a sample as a function of temperature or time in a controlled atmosphere. The analysis system was formed by a mass spectrometer ThermoStar-GSD320 quadrupole mass analyzer (PFEIFFER VACCUM), which allowed the identification of the compounds released during the thermal degradation of the sample.

Table 1
Proximate and ultimate analysis of the cellulose sample.

Proximate analysis (wt%)*daf				
	Moisture	Ash	VM*	FC*diff
Cellulose	3.0	0.8	90.7	6.0

Ultimate analysis (wt%)*daf				
	C	H	N	S	O*diff
Cellulose	42.18	6.15	0.01	0.06	51.61

*daf: dry and ash free basis; O*diff*: % of oxygen calculated from difference of C, H, N and S; VM: Volatile matter; Fixed carbon*diff*: % of fixed carbon was calculated from difference from moisture, ash and volatile matter.

2.3. Pyrolysis experiments

Pyrolysis experiments were carried out in the HP-TGA apparatus described above. Each experiment was repeated at least three times, being the average value recorded. The experimental errors determined for the measurement of the temperature and the weight loss were ± 0.2 °C and ± 0.8%, respectively. The initial sample weight, the particle size of the sample and the pressure were varied in order to evaluate their effect on the pyrolysis process of the cellulose used in this study.

2.3.1. Effect of particle size

Pyrolysis of cellulose was carried out at different particle size ranges (<25, 25–50, 50–100, 100–150 and 150–200 μm) with an initial mass of 100 mg were pyrolyzed at atmospheric pressure in a N_2 flow rate of 200 Nml/min. For this purpose, samples were heated from 25 °C to 720 °C at a heating rate of 10 °C/min.

2.3.2. Effect of nitrogen gas flow

Pyrolysis of the cellulose at atmospheric pressure was carried out at two nitrogen gas flow rates: 200 Nml/min and 500 Nml/min (initial mass: 100 mg, and particle size range: 100–150 μm). Samples were heated from 25 °C to 720 °C at a heating rate of 10 °C/min.

2.3.3. Effect of the initial sample weight

Pyrolysis of the cellulose at atmospheric pressure was performed using different initial sample weights: 10, 30, 100, 600, 800 and 1000 mg (particle size range: 100–150 μm, and nitrogen flow rate: 200 Nml/min). Samples were heated from 25 °C to 720 °C at a heating rate of 10 °C/min.

2.3.4. Effect of pressure

Pyrolysis of the cellulose was carried out at different pressures:1, 9, 17, 25 bar (initial sample weight: 800 mg, particle size: 100–150 μm). N_2 flow rate was varied as a function of the pressure set point in order to keep this variable in a steady value during the experiment: 200 Nml/min, 400 Nml/min, 750 Nml/min and 1100 Nml/min, respectively. The sample was heated from 25 °C to 720 °C at a heating rate of 10 °C/min.

2.4. Kinetic analysis

Kinetic data obtained in a previous study performed at lab scale thermobalance [11] were compared to those obtained in this study carried out at bench plant scale. The model used in this research for describing the pyrolysis process was similar as that reported elsewhere [11]. The following equations represent the kinetic rates of the thermal decomposition of a material, considering n pyrolizable compounds, independent parallel n^{th}-order reactions and an Arrhenius dependence of the rate constants.

$$\frac{d\alpha}{dt} = \sum_{i=1}^{n} c_i k_{io} \, exp\left(-\frac{E_{ia}}{RTs}\right)(1-\alpha_i)^{ni} \tag{2.1}$$

$$\frac{d\alpha}{dt} = k_{io} \, exp\left(-\frac{E_{ia}}{RTs}\right)(1-\alpha_i)^{ni} \tag{2.2}$$

where α is the degree of conversion of the material, k_{io} and E_{ia} are the pre-exponential factor and the activation energy for the individual components, respectively; R is the gas constant; n, is the reaction order; and α_i, is the degree of conversion for the individual component define by:

$$\alpha_i = \frac{m_{io} - m_{ip}}{m_{io}} \tag{2.3}$$

In this equation, m_{io} and m_{ip} represent the mass at $t = 0$ and $t = t$ for each component, respectively. c_i is a constant related to the initial composition of the different components. Finally, Ts is the actual sample