Fuel 95 (2012) 305–311

Contents lists available at SciVerse ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Kinetic study of lignocellulosic biomass oxidative pyrolysis

Maider Amutio, Gartzen Lopez, Roberto Aguado, Maite Artetxe, Javier Bilbao, Martin Olazar *

Department of Chemical Engineering, University of the Basque Country, P.O. Box 644, E48080 Bilbao, Spain

ARTICLE INFO

Article history:
Received 14 July 2011
Received in revised form 21 September 2011
Accepted 6 October 2011
Available online 20 October 2011

Keywords:
Lignocellulosic biomass
Oxidative pyrolysis
Kinetics
Thermogravimetry
Pinewood

ABSTRACT

Biomass oxidative pyrolysis is of great interest from the point of view of large-scale bio-oil production in autothermal regime. A study has been carried out in thermobalance with different oxygen concentrations (5, 10 and 20 vol.%) in the inlet gas stream in order to analyze the effect of oxygen on the lignocellulosic biomass pyrolysis process and establish a kinetic model for oxidative pyrolysis. The results have been compared with those obtained in inert atmosphere pyrolysis. Firstly, the kinetic pathway has been determined, concluding that pinewood oxidative pyrolysis is the sum of biomass pyrolysis and heterogeneous oxidation plus the combustion of the remaining char. A kinetic model consisting of six simultaneous reactions has been developed, which allows identifying the volatiles released from the joint pyrolysis-combustion of the pyrolyzable and non-pyrolyzable fractions corresponding to hemicellulose, cellulose and lignin.

1. Introduction

The need to find alternative raw materials to petroleum, due to the reduction in reserves and a raising demand for energy, has informed the development of technologies for the valorization of natural gas, coal and biomass [1]. Biomass is considered to be the most promising alternative to fossil fuels, since its rational use does not contribute to a net rise in the level of CO_2 in the atmosphere. Furthermore, it is the only renewable source of fixed carbon that can be converted into liquid, solid and gaseous fuels, in addition to its use for heat and power.

In recent years, an overall valorization of biomass has been suggested under the biorefinery concept in order to obtain transportation fuels and valuable chemicals, by subjecting the biomass to several processes, such as gasification, pyrolysis and hydrolysis [2,3].

Pyrolysis is one of the technologies with best industrial perspectives for biomass valorization, since the process conditions can be optimized to maximize the yields of gas, liquid and char [4,5]. The production of a liquid (bio-oil) from lignocellulosic biomass has received growing interest, as it is possible at moderate scale in rural areas to decouple bio-oil production from its upgrading in a biorefinery, where a suitable acid catalyst can selectively convert it into olefins [6] or aromatics [7]. Bio-oil can also generate H_2 using a bifunctional reforming catalyst [8] and be co-fed into refinery units, such as those for fluidized catalytic cracking (FCC) [9], or mixed with methanol in the methanol to olefins transformation process (MTO) [10].

A wide range of reactor configurations has been used to perform biomass pyrolysis, such as fluidized bed reactors, transport and circulating fluidized bed reactors, ablative reactors, auger reactors, vacuum reactors and conical spouted bed reactors [5]. One of the greatest challenges for scaling-up pyrolysis processes is the energy supply, specifically the energy required to heat the raw material and the fluidizing gas to the process temperature [5,11,12]. This heat can be supplied only partially by the fluidizing gas due to certain limitations, such as gas bypassing in the reactor and a rather low flexibility in the flow-rate and temperature of the inlet gas. Furthermore, the energy supply through the reactor walls has several limitations, since the ratio between the wall surface area and the mass contained in the bed is very low. Finally, internal heat transfer surfaces can be used, but these devices may affect the hydrodynamics of the reactor and increase the complexity of the design. Furthermore, they may undergo quick soiling due to the tar and soot present in the bed during the pyrolysis process.

Accordingly, oxidative pyrolysis, involving the addition of a sufficiently low concentration of oxygen to avoid significant effects by combustion reactions in the process, is the step forward towards adapting this process to industrial scale, given that the energy required is supplied in the pyrolysis process itself by the combustion of part of the pyrolytic products. As a result, an autothermal regime is obtained, which will facilitate energy integration and reduce operating costs, improving process feasibility.

This paper aims to provide information about the kinetics required for the large-scale autothermal operation to be used in the development of a technology based on the conical spouted

---

* Corresponding author. Tel.: +34 946 012 527; fax: +34 946 013 500.
E-mail address: martin.olazar@ehu.es (M. Olazar).

0016-2361/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.fuel.2011.10.008

Nomenclature

c_i	mass concentration of i pseudocomponent
DTG	differential thermogravimetry
E_i	activation energy of i pseudocomponent (kJ mol^{-1})
$(k_0)_i$	frequency factor of i pseudocomponent (s^{-1})
k_i	kinetic constant for the mass loss of each i pseudocomponent (s^{-1})
L	number of experimental data available
n, m, p, q	reaction orders
P_{O_2}	oxygen partial pressure (bar)
t	time (s)
W, W_0, W_∞	mass of biomass sample at t time, at the beginning of pyrolysis and at the end of pyrolysis, respectively (mg)
W_i, $W_{0,i}$, $W_{\infty,i}$	mass of i pseudocomponent in the sample at t time, at the beginning and at the end (mg)
X	conversion of the biomass sample by mass unit of pyrolyzable mass
X_i, $X_{\infty,i}$	conversion of i pseudocomponent at t time and at the end

bed reactor (CSBR). Although the reaction conditions are very different between a large scale fast pyrolysis device and a thermogravimetric one (in terms of heating rate, gas residence time, biomass particle size, etc.), this study carried out using a thermobalance is suitable for determining the intrinsic kinetics of biomass oxidative pyrolysis. The conical spouted bed reactor is a suitable technology for the production of bio-oil as it has a low production cost, it is simple to operate and several improvements for the scale-up of the process have been carried out in previous studies: (i) Continuous operation [13]; (ii) vacuum operation [14], where the N_2 flow-rate to be heated to the reaction temperature is significantly reduced and bio-oil condensation is simplified; and (iii) the use of internal devices [15].

Biomass pyrolysis kinetics using an inert atmosphere has been extensively studied by means of thermal analytical techniques [16–18], fast heating pyrolysis reactors [19,20], and reactors operating under conditions similar to those of industrial furnaces (fast heating and short residence times for the products) [21–24].

In general, the formation of primary volatile products in biomass pyrolysis has been described using one-component [21–23,25–28] or multi-component mechanisms [16–18,29–36]. The multi-component mechanism generally consists of the devolatilization reactions of biomass main components, i.e., hemicellulose, cellulose and lignin [33], which are considered to be parallel and independent, although there are important interactions between their devolatilization [32].

The oxidation kinetics of biomass [37–57] and other solid fuels, such as coal [58–60], tyres [61,62] and plastic wastes [40,63], has also been the subject of several studies. The kinetic pathway of the oxidation is different for each solid fuel and can be a result of two competitive processes: particle ignition dominated by either burning volatile matter (reactions A–B) or heterogeneous oxidation (reaction C) [40,58–60], Fig. 1.

2. Material and methods

The biomass used in this study is forest pinewood waste (*pinus insignis*), with a particle size smaller than 0.2 mm in order to avoid heat and mass restrictions within the particle [38]. Its main characteristics are summarized in Table 1. Three commercial products have been taken as representative of biomass components: cellulose (435236-250G, Sigma–Aldrich), xylan (X0502-10G, Sigma–Aldrich), which is accepted as a hemicellulose equivalent [31,64], and organosolv lignin (371017-100G, Sigma–Aldrich).

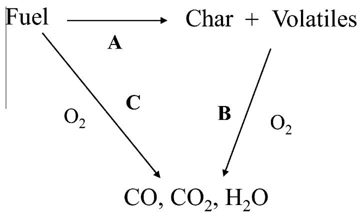

Fig. 1. Possible mechanisms for solid conversion in an oxidative atmosphere [40].

The kinetic study has been carried out by thermogravimetry in a TGA Q5000 thermobalance. The pyrolysis experiments have been carried out by subjecting the sample (approximately 10 mg) to a heating ramp of 15 °C min^{-1} from room temperature to 800 °C. Oxygen concentration in the carrier gas has been 5%, 10% and 20% in volume, with a total flow-rate of 100 ml min^{-1}.

3. Results and discussion

3.1. Kinetic pathway

Prior to proposing the kinetic model for pinewood sawdust oxidative pyrolysis, the reaction pathway of the process must be established in order to determine whether volatile material burning or heterogeneous reaction dominates the oxidation (Fig. 1). According to Senneca et al. [40] the identification of the kinetic pathway can be carried out by analyzing the shape of the DTG curve for solid fuel oxidative pyrolysis and comparing it with the curve for inert pyrolysis. Fig. 2 shows the DTG curves for the inert and oxidative pyrolysis of pinewood sawdust, with 5, 10 and 20 vol.% of oxygen.

As observed in Fig. 2, biomass oxidative pyrolysis records two peaks, the first one is shifted to lower temperatures than that corresponding to inert pyrolysis (0% O_2) and the second peak at higher temperatures is related to char combustion, as has been reported previously by other authors [37–40,42,43,48–54,57]. This shape is typical of a reaction pathway midway between the two extreme cases corresponding to reactions A–B and reaction C in Fig. 1 and evidences a synergistic effect of purely thermal degradation and heterogeneous oxidation, occurring over comparable time scales [40].

The shape and position of both peaks in Fig. 2 depend on the oxygen partial pressure. At higher oxygen concentrations, both peaks appear at lower temperatures, and the peak corresponding to the combustion of char becomes sharper. The temperature values of the DTG peaks for different oxygen concentration are reported in Table 2.

Table 1
Biomass characterization.

Ultimate analysis (wt.%)	
Carbon	49.33
Hydrogen	6.06
Nitrogen	0.04
Oxygen	44.57
Proximate analysis (wt.%)	
Volatile matter	73.4
Fixed carbon	16.7
Ash	0.5
Moisture	9.4
HHV (MJ kg^{-1})	19.8