



Kinetics of pyrolysis and combustion of pine needles and cones

R. Font*, J.A. Conesa, J. Moltó, M. Muñoz

Department of Chemical Engineering, University of Alicante, Apto 99, E-03080 Alicante, Spain

ARTICLE INFO

Article history:

Received 30 June 2008

Received in revised form 30 October 2008

Accepted 6 November 2008

Available online 25 November 2008

Keywords:

Pine needle

Pine cone

Pyrolysis

Combustion

Kinetics

ABSTRACT

A wide kinetic study has been carried out under different conditions in TG and TG–MS for each material, at different operating conditions. Runs were carried out at three different atmospheres: N₂, N₂:O₂ 4:1 and N₂:O₂ 9:1. In addition to the dynamic runs carried out at constant heating rate, other runs were performed in an isothermal regime (constant heating rate until the set temperature is reached and then the set temperature is maintained constant).

In addition, a study of the thermal decomposition for both materials was also carried out in a dynamic run using TG–MS in order to observe the evolution of the major compounds and to discuss the information that could be obtained.

From the overall analysis of the data, schemes of reactions and kinetic values were calculated by integration of the differential equations and minimizing the squared differences between the experimental and calculated values. It is important to emphasise that the same set of parameters is proposed for the runs for each material, and depends on neither the heating rate in dynamic runs nor whether the run is carried out in a dynamic or isothermal mode.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Pine needles and cones are biomass that can be of use as fuel themselves or forming fuel briquettes. On the other hand, thermal decomposition takes place under poor combustion conditions in forest fires, and every year wildfires damage vast areas.

Thermal degradation of pine cone and pine needle was the subject of interest of research, focusing on some aspects considered as follows; there are some studies concerning the influence of additives on the pyrolysis of pine needles. Liodakis et al. [1] tested the influence of several fire retardants on the pyrolysis of cellulose and pine needles on DSC, whereas Pappa et al. [2] studied the effects of retardants with TG–MS, and Statheropoulos et al. [3] determined some volatile compounds with the same materials using several analytical methods including Py–GC–MSD.

Lee et al. [4] determined the optimum conditions for the analysis of volatile component pine needles by double-shot pyrolysis–gas chromatography.

Leoni et al. [5] studied the dehydration kinetics of Pinus Pinaster needles from DSC curves using different known mathematical methods in nitrogen and in air.

On the other hand, Senneca [6] studied the pyrolysis kinetics of pine seed shells from TG and DTG data, considering only one reaction and proposing values for the activation energy, reaction order and pre-exponential factor.

Haykiri-Acma and Yaman [7] studied the gasification of pine cone and other biomass material, obtaining the gasification yields at different temperature intervals and proposing a value for the apparent activation energy of 33.8 kJ/mol with a 1:1 nitrogen:–steam ratio of the atmosphere.

Leoni et al. [8] studied the kinetics of the combustion of pine needles by DSC and considered two fractions in the decomposition.

No other kinetic models have been found in literature for combustion at normal conditions and in poor oxygen concentration when pyrolysing or burning pine needles or cones.

The objective of this study has been the proposal of kinetic models valid in different operating conditions, both in pyrolysis and combustion. These kinetic models are useful for understanding the behavior of the materials in reactors and furnaces, and also when burning these materials in different atmospheres and temperature conditions.

2. Experimental

2.1. Raw material

The samples employed in this study were cone and needle of Mediterranean Pine. Prior to the runs, the samples were milled to an average size of 1 mm. Table 1 presents the elemental and

* Corresponding author at: Chemical Engineering Department, University of Alicante, P.O. Box 99, 03080 Alicante, Spain. Tel.: +34 96 590 3546; fax: +34 96 590 38 26.

E-mail address: rafael.font@ua.es (R. Font).

Table 1
Characteristics of the materials used.

	Pine needles	Pine cones
Moisture (wt. %)	12	8.9
Analysis on dry basis		
C (wt.%)	50.4	54.2
H (wt.%)	6.5	6.8
N (wt.%)	0.8	0.3
S (wt.%)	0.01	–
Ash content (wt.%)	4.5	0.8
O% by difference (wt.%)	37.9	38.7
Cl (wt.%)	0.22	0.17
Net calorific value (kJ kg ⁻¹)	20,138	18,782
Ethanol extracts	18.2	7.3
Hemicellulose	17.7	21.7
Cellulose	38.7	39.3
Lignin	20.1	30.9

moisture analysis of the materials studied. Elemental analysis of the major components was carried out in a Perkin-Elmer 2400, the calorific value was determined in an AC-350 calorimetric bomb from Leco Corporation and the ash residue was obtained by calcinations at 850 °C. Moisture was determined by the weight loss at 105 °C for 12 h. Chlorine was measured using an automatic sequential spectrometer X-ray Fluorescence model TW 1480 that gives semi-quantitative results. Ethanol-solubilized, hemicellulose, cellulose and lignin contents were determined for both materials [9–12]. It can be observed that the ultimate analysis (C, H, S, N, Cl) gives similar results for both compounds, although there is a considerable ash percentage in the case of pine needles, probably due to the presence of inert material in the sample which causes a net calorific value lower than that of pine cones. On the other hand, the content of lignin in the pine cones is higher than that of pine needles, which is logical considering the cementing properties of lignin. On the contrary, the ethanol extract content of pine needles is higher than that of pine cones due to the different nature of both materials.

2.2. Thermobalance

Runs for pyrolysis were carried out on a Mettler Toledo thermobalance model TGA/SDTA851e/LF/1600. This equipment has a horizontal furnace and a parallel-guided balance. In this way, positioning of the sample has no influence in the measurement,

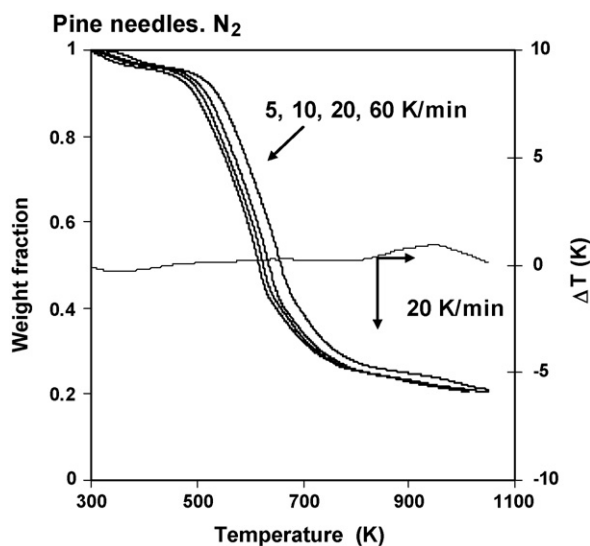


Fig. 1. Pine needle pyrolysis at several heating rates: 5, 10, 20 and 60 K min⁻¹. Experimental curves (the calculated curves overlap the experimental ones).

and flow gas perturbation and thermal buoyancy are minimized. The sample temperature was measured with a sensor directly attached to the sample holder.

For the pyrolysis runs, the atmosphere used was nitrogen. Two atmospheres were used for the combustion runs: N₂:O₂ 4:1 and N₂:O₂ 9:1. The flow rate was 100 ml min⁻¹.

Dynamic experiments were carried out at different heating rates between 5 and 60 °C min⁻¹, from the initial temperature up to 1073 K, including in this way the entire range of decomposition. Isothermal experiments started with a constant heating rate until the desired temperature was reached, the final temperature was maintained constant throughout the pyrolysis or combustion process and the experiment was considered to be finished when the weight loss rate was very small. The mass of sample used was around 5 mg, and under these conditions the heat transfer limitations can be neglected.

A pyrolysis run with a heating rate of 5 °C min⁻¹ using Avicel PH-105 microcrystalline cellulose was done. The kinetic values obtained showed good agreement with the results presented by Grønli et al. [13] in their round-robin study of cellulose pyrolysis kinetics by thermogravimetry. This experiment was used to check the good performance of the thermobalance.

The TG-MS runs were carried out in a TGA/SDTA851e/LF/1600 with TG-ATD coupled to a Thermostat GSD301T Pfeiffer Vacuum MS apparatus using helium as carrier gas and with the following operating conditions: mass sample around 10 mg, heating rate 30 °C/min, ionization 70 eV, SIR detection of several ions: 4, 13–18, 25–32, 35–46 in one run and the following ions in another run: 4, 32, 43–46, 50–52, 55–58, 60, 65, 68, 73, 78, 91, 96, 105, 106. It was tested that the very small oxygen concentration in the helium used can cause a small oxidation of the sample and/or the volatiles evolved in the pyrolysis run. The response of the different ions was divided by that of helium ($m/z=4$) and subtracted from that corresponding to the beginning of the run.

3. Pyrolysis: results and discussion

3.1. Pyrolysis: experimental results

Fig. 1 shows the experimental TG plots for pine needle pyrolysis (nitrogen) at heating rates of 5, 10, 20 and 60 K min⁻¹. In the figures, the weight fraction represents the residual mass fraction of the solid (including residue formed and non-reacted initial solid). The value of increment of temperature, corresponding to the DTA,

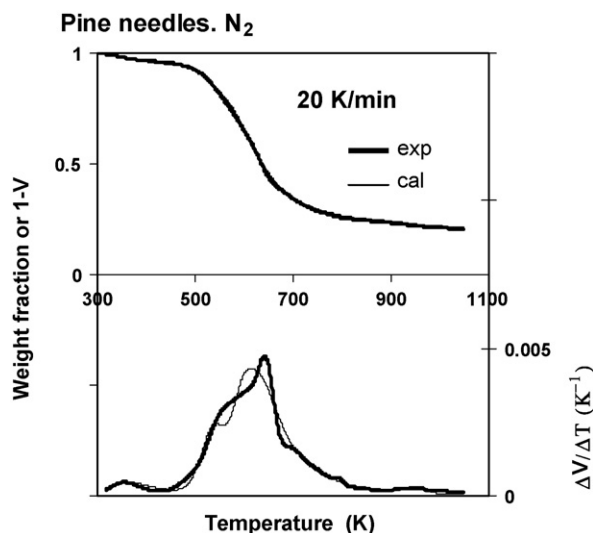


Fig. 2. Weight fraction and its derivative from a pine needle pyrolysis run.

Download English Version:

<https://daneshyari.com/en/article/1197522>

Download Persian Version:

<https://daneshyari.com/article/1197522>

[Daneshyari.com](https://daneshyari.com)