Oxy-combustion of corn, sunflower, rape and microalgae bioresidues and their blends from the perspective of thermogravimetric analysis

R. López, C. Fernández, J. Fierro, J. Cara, O. Martínez, M.E. Sánchez[*]

Chemical Engineering Area, Institute of Natural Resources (IRENA), University of León, Avenida de Portugal, 41, 24071 León, Spain

ABSTRACT

Thermogravimetric analysis was used to study and compare the oxy-combustion of different blends of corn bioresidues with sunflower, rape and algae bioresidues. Non-isothermal thermogravimetric data were used to obtain the oxy-combustion kinetics of these bioresidues. This paper reports on the application of the Vyazovkin and Ozawa-Flynn-Wall isoconversional methods to evaluate the kinetic parameters (energy activation, pre-exponential factor and reaction order) in the oxy-combustion of the bioresidues studied.

The activation energy obtained from corn oxy-combustion (E~168.9 kJ mol^{-1}) was lower than that from the blends (corn-sunflower, E~189.0 kJ mol^{-1} and corn-microalgae, E~201.9 kJ mol^{-1}) whereas the activation energy obtained from the corn-rape blend was the lowest (E~155.9 kJ mol^{-1}).

Both the Vyazovkin and Ozawa-Flynn-Wall methods yielded similar results.

1. Introduction

Nowadays, the demand for electric power continues to increase due to population growth, and technological and economic development. Energy production from fossil-fuels combustion, including coal, oil, oil shale and natural gas, results in the emission of greenhouse gasses, being CO_2 the dominant contributor [1].

The growing problem dealing with the increase of greenhouse gas emissions and their potential impact on climate change requires further investigations of alternative technologies to reduce CO_2 emissions. There is a wide range of ways of carbon-free or reduced-carbon sources of energy and combustion with CO_2 capture [2].

In an oxy-combustion process, the fuel is burned in either pure oxygen or a mixture of oxygen and a CO_2 rich recycled flue gas instead of air. Although it is theoretically possible to burn fuel in pure oxygen, the recycled flue gas is generally used for control flame temperature and make up the volume of N_2 to ensure there is enough gas to carry the heat through the boiler [3].

The presence of CO_2 as an important component in the combustion atmosphere has been demonstrated to report differences in thermodynamic of the reactions compared to air atmosphere;

having an influence on the chemical reactions and the heat transfer that takes place during oxy-combustion [4]. Moreover, due to only small amounts of nitrogen enter the combustion chamber or the fuel burns directly in a mixture without nitrogen, the exhaust gas will consist mainly of CO_2 and steam, leading to smaller formation of NO_x than the corresponding to other alternatives.

Biomass is the term used for all organic material that stems from plants including algae, trees and crops that are susceptible to be converted into energy [4]. Among biomass, algae seem to be promising because of their high photosynthetic efficiency, high biomass production, and fast growth. Biomass can be burned directly in waste-to-energy plants without any chemicals processing to produce steam and generate electricity. [5]

The use of oxy-combustion is among the alternative post and pre-combustion capture concepts, a strategy to achieve power production from fuels with CO_2 capture.

Oxy-combustion can, in principle, be applied to any type of fuel utilized for thermal power production. The combination of oxy-combustion with biomass could be used as a CO_2 sink, contributing to reduce the greenhouse effect [6]. This is the reason why oxy combustion is considered to be one of the most promising CO_2 capture technologies since it can be adapted to both existing and new steam power plants [7].

Several works have been performed co-firing coal with biomass [6–10] although limited works are published related to single biomass oxy-combustion.

The aim of this study was to investigate the oxy-combustion of corn and several blends (corn–sunflower, corn–rape and corn–algae) by thermogravimetric analysis. The thermogravimetric results are used to perform a kinetic assessment of the oxy-combustion of these materials using the Vyazovkin model [11,12] for the treatment of non-isothermal TG (mass loss) data. The kinetic parameters (energy of activation, preexponential factor and order of reaction required for the oxy-combustion of these bioresidues) were calculated and compared with those obtained by application of the Ozawa–Flynn–Wall [13,14] model for non-isothermal TG data for the same bioresidues and blends.

2. Materials and methods

2.1. Samples

In this study, four untreated residual biomasses (corn, sunflower, rape and microalgae) and several mixtures (50% by wt.; corn-sunflower, corn-rape and corn-microalgae) were used to investigate the oxy-combustion kinetics under a mixture of 21% O_2/79%CO_2 atmosphere. The composition of 50% by wt. was chosen in order to discuss the effect of blending, but not the effect of the amount blended. The atmosphere composition was chosen to study the effect of CO_2 instead of N_2, that will be reported in a future work.

Corn, sunflower and rape were taken from the region of Leon, Spain, while microalgae was supplied from Almeria, Spain. Microalgae (*Scenedesmus almeriensis*) is often used in aquiculture and energy improvement research. Microalgae were grown in a closed tubular photobioreactor. Sampling was carried out carefully to represent the original biomass as well as possible. The selected terrestrial bioresidues were dried, crushed and sieved under 90 µm [15,16]. The microalgae sample was a green powder with a 90 µm average particle size. The mixtures were prepared by mixing 100 mg of each bioresidue to maintain reproducibility after sieving. Once blended, a sample of 10 ± 0.1 mg was taken for the experiments.

Before thermogravimetric analysis, the bioresidues were analysed to determine their proximate and elemental characteristics and corresponding heating values, which are known to affect thermal conversion. The moisture content was determined gravimetrically using the oven drying method. The HHV (higher heating value) at a constant volume was measured by an adiabatic oxygen bomb calorimeter. Proximate determinations were made in accordance with modified procedures from E 870 (Standard Methods for Analysis of Wood Bioresidues), D 1102 (ash in wood) and E 872 (volatile matter). For the elemental determination, a LECO model CHN-600 instrument was used to determine the carbon, hydrogen and nitrogen content. Sulphur was determined using a LECO model SC-132 instrument. The results of the elemental and proximate analyses for corn, sunflower, rape and microalgae are listed in Table 1. Because corn, sunflower and rape are lignocellulosic bioresidues, the cellulose, hemicellulose and lignin compositions of the bioresidues were determined by duplicate analyses of NDF (neutral detergent fibre), ADF (acid detergent fibre) and crude fibre [17] in ground samples using an Ankom 200 fibre analyser. The results are shown in Table 2. A proximate lignocellulose analysis was taken into account [5] for the results discussion.

2.2. TG analysis

The oxy-combustion was studied in terms of the thermal behaviour of the bioresidues in a TA Instruments SDTQ600 analyser. The TG (mass loss) and DTG (differential mass loss) were

Table 1
Proximate analysis, elemental analysis and calorific values corresponding to the corn, sunflower, rape and microalgae used in this study.

Material	Corn	Sunflower	Rape	Microalgae
Proximate analysis				
Moisture(%)	8.0	7.4	9.2	5.4
Volatile matter[a](%)	76.8	77.4	80.4	73.1
Ash[a](%)	5.7	2.8	2.6	20.0
Fixed carbon[a,c](%)	17.5	19.8	17.0	6.9
Elemental analysis				
C[b](%)	48.8	49.4	49.7	54.8
H[b](%)	6.2	6.1	6.3	7.6
N[b](%)	0.5	0.2	0.2	8.5
S[b](%)	0.1	0.2	0.2	0.4
O[b,c](%)	44.4	44.1	43.6	28.7
Calorific value				
HHV(MJ/kg)	18.45	18.84	19.49	20.91

HHV = high heating value.

[a] Dry basis.
[b] Dry ash free basis.
[c] Calculated by difference.

recorded continuously as a function of time and temperature from room temperature to 1173 K using four temperature ramps ($\beta = dT/dt$): 10, 20, 30 and 40 K min^{-1}. This heating speed was chosen because it is low enough to favour homogeneous ignition [18] and minimise mass transfer effects. High heating rates cause large temperature gradients throughout the sample, affecting kinetics [19,20]. For each sample and heating rate, the TG curves were obtained in triplicate to verify the reproducibility of the results. All dynamic runs were carried out in a pan containing 10 ± 0.1 mg of the sample. The oxidising atmosphere inside the furnace during temperature-programmed combustion was determined by a continuous flow of 100 cm^3 min^{-1} of a mixture 79% CO_2, 21% O_2, at atmospheric pressure based on the literature conditions for these processes [15,16,21].

2.3. Determination of oxy-combustion indexes

2.3.1. Ignition temperature (t_e) and ignition index (D_i)

As described by Ma et al. [22] and shown in Fig. 1 the ignition temperature (T_e) was defined as follows [22,23]: first, through the DTG peak point, a vertical line was drawn downward to intersect the TG oblique line at point C. Second, a tangent line to the TG curve was made at point A, which intersected the extended TG initial level line at point B. Third, another vertical line was made downwards through point B, which met the cross axis at point D. The temperature corresponding to point D was defined as T_e. The ignition index D_i was determined by the following equation [24]:

$$D_i = \frac{\left(\frac{dw}{dt}\right)_{max}}{t_p t_e} \tag{1}$$

where $(dw/dt)_{max}$ is the maximum oxy-combustion rate, t_p is the time corresponding to the maximum oxy-combustion rate and t_e is the ignition time.

Table 2
Composition of principal components in no-marine biowastes [5].

Material	Cellulose(%)	Hemicellulose(%)	Lignin(%)
Corn	18.6	29.7	12.0
Sunflower	40.5	15.2	16.6
Rape	25.7	21.6	7.4