



# Differences between combustion and oxy-combustion of corn and corn–rape blend using thermogravimetric analysis



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## ABSTRACT

Nowadays, diverse technologies to produce electricity based on bioresidues are investigated in order to reduce the external energy dependence of occidental countries, as Spain.

Thermogravimetric analysis was used to study and compare the combustion and oxy-combustion of corn, rape and a corn–rape blend. Non-isothermal thermogravimetric data were used to obtain the reaction kinetics of these bioresidues. This paper reports on the application of the Vyazovkin and Ozawa–Flynn–Wall isoconversional methods for the evaluation of kinetic parameters (energy activation, pre-exponential factor and order of reaction) for the oxidation of the biomasses studied.

Differences were found in the TG curves in accordance with the proximate analysis results for the cellulose, hemicellulose, lignin, volatile matter and fixed carbon content of biomasses and the atmosphere of the reaction. The presence of CO<sub>2</sub> in the atmosphere instead of N<sub>2</sub> was also discussed.

The activation energy obtained from corn (153.0 kJ/mol) combustion was lower than that obtained from corn oxy-combustion (168.6 kJ/mol). However, corn–rape blend oxidation was more favourable in the presence of CO<sub>2</sub> ( $E \sim 155.3$  kJ/mol) than in N<sub>2</sub> ( $E \sim 155.9$  kJ/mol). Both Vyazovkin and Ozawa–Flynn–Wall methods yielded similar results.

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## 1. Introduction

The use of renewable energies will be increasing in the near future. Amongst them, biomass is recognised as one of the most important because it has no carbon dioxide emissions which may affect the environment, it uses residual feedstocks and it increases employment in rural areas. Biomass combustion to obtain electricity or heating plays an important role in energy production. Moreover, biomass residues contain significantly less sulphur and nitrogen compared to fossil fuels, reducing SO<sub>x</sub> and NO<sub>x</sub> emissions [1,2].

Oxy-combustion is suggested as one of the possible emerging technologies for capturing CO<sub>2</sub> from power plants. The main feature of oxy-fuel combustion is that the fuel burns in either pure oxygen or a mixture of oxygen and a CO<sub>2</sub> 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 makes up the volume of the missing N<sub>2</sub> to ensure that there is enough gas to carry the heat through the boiler [3]. During this process it produced a flue gas consisting mainly of carbon dioxide and water vapour. The water can be easily separated, producing a stream of CO<sub>2</sub> ready for sequestration which can be compressed and transported to a suitable

geological storage site or further utilised [4]. Typically, between 60 and 80% of the flue gas is recycled to the boiler [5]. During oxy-combustion, the gas composition inside the boiler differs greatly from that of conventional combustion with air, and this affects different aspects of combustion. The presence of CO<sub>2</sub> during oxy-fuel combustion affects the heat transfer, flame ignition, emissions, and ash properties [6, 7].

Utilisation of renewable biomass fuels such as wood, straw, and other energy crops in thermal power plants with carbon capture and storage is attracting increased attention. Limited works have been published related to single biomass oxy-combustion [8,9].

Although, most of the works have been performed co-firing coal with biomasses.

Biomass cofiring in coal power plants is in many cases a cost-effective option to substitute coal for biomass in electricity production, due to its ability to produce highly concentrated CO<sub>2</sub> in the flue gas, which in turn allows easier and cheaper CO<sub>2</sub> separation from flue gas [10]. Moreover, according to E. Özgür et al. [11] one of the advantages of co-firing two different fuel types is that the power plant in operation can burn a supplementary fuel, which, depending on the fuel type and combustion system, can result in little or no additional costs for the new fuel. Co-firing with biomass can be friendlier environmentally because of lower emissions of greenhouse gases from carbon-neutral fuel in the blend.

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As was described by Wilk and Magdziarz [12], oxy-combustion is used simultaneously with the process of eliminating nitrogen from air combustion (largely responsible for the formation of NO) and replacing it into exhaust gas (RFG – recycled flue gas). Despite the very high temperatures in the chamber (e.g. 1600 °C in the melting process), the concentration of nitrogen oxides may be lower, due to the elimination of nitrogen from combustion air.

The objective of this work was to compare the behaviour of corn, rape and a blend of corn with rape during combustion and oxy-combustion treatments, using TG and DTG profiles for being the simplest and most effective techniques for observing the burning profile of biomass. Finally the kinetic parameters (energy of activation, pre-exponential factor and order of reaction required for the combustion/oxy-combustion of the bioresidues) were calculated and compared with those obtained by the application of the Vyazovkin model [13,14] and the Ozawa–Flynn–Wall model [15,16] for non-isothermal TG data for the same bioresidues and blends. The kinetic data obtained in this work are highly important due to their contribution to equipment design. The blending of biomasses is also important if it can demonstrate that electricity generation in power plants becomes more economically sustainable than using fossil fuels.

## 2. Materials and methods

### 2.1. Samples

In this study, two untreated biomass bioresidues, corn and rape and a 50% by wt. mixture of both were used to investigate the influence of the atmosphere (combustion: 21% O<sub>2</sub> and 79% N<sub>2</sub>; oxy-combustion: 21% O<sub>2</sub>, 79% CO<sub>2</sub>) on the combustion and oxy-combustion kinetics. Both corn and rape were taken from the region of Leon, Spain. The bioresidues were dried, crushed and sieved under 90 μm [17,18].

Before thermogravimetric analysis, the bioresidues were characterised by the respective analysis to determine their proximate and ultimate characteristics and corresponding heating values, which are known to affect thermal conversion. The moisture content was determined gravimetrically using the oven drying method. The higher heating value (HHV) 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 ultimate analysis, a LECO model CHN-600 instrument was used to determine the carbon, hydrogen and nitrogen

**Table 1**  
Proximate analysis, ultimate analysis and heating value corresponding to the corn and rape used in this study.

Material	Corn	Rape
Proximate analysis		
Moisture (%)	8.0	9.2
Volatile matter <sup>a</sup> (%)	76.8	80.4
Ash <sup>a</sup> (%)	5.7	2.6
Fixed carbon <sup>a,b</sup> (%)	17.5	17.0
Ultimate analysis		
C <sup>c</sup> (%)	48.8	49.7
H <sup>c</sup> (%)	6.2	6.3
N <sup>c</sup> (%)	0.5	0.2
S <sup>c</sup> (%)	0.1	0.2
O <sup>b,c</sup> (%)	44.4	43.6
Heating value		
HHV (MJ/kg)	18.45	19.49

HHV = high heating value.

<sup>a</sup> Dry basis.

<sup>b</sup> Calculated by difference.

<sup>c</sup> Dry ash free basis.

**Table 2**  
Composition of principal components of corn and rape bioresidues.

Material	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Corn	18.6	29.7	12.0
Rape	25.7	21.6	7.4

contents. Sulphur was analysed using a LECO model SC-132 instrument. The results of the proximate and ultimate analyses for corn and rape are listed in Table 1. Because corn and rape are lignocellulosic bioresidues, the cellulose, hemicellulose and lignin compositions of the bioresidues were determined by duplicate analyses of neutral detergent fibre (NDF), acid detergent fibre (ADF) and crude fibre [19] 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 discussion of results. In order to compare the different atmospheres used in the experiments, thermal conductivity and heat capacity, and their dependence on temperature, of N<sub>2</sub> and CO<sub>2</sub> are listed in Table 3.

### 2.2. TG analysis

The co-oxy-combustion and oxy-combustion were analysed in terms of the thermal behaviour of the bioresidues in a TA Instruments SDTQ600 analyser. A schematic diagram of the experimental setup appears in Fig. 1.

The mass loss (TG) and differential mass loss (DTG) were recorded continuously as a function of time and temperature from room temperature to 1173 K using four heating rates ( $\beta = dT/dt$ ): 10, 20, 30 and 40 K/min. These temperature rates were chosen because they are low enough to favour homogeneous ignition [20] and minimise mass transfer effects. High heating rates cause large temperature gradients throughout the sample, affecting kinetics [21,22]. For each sample and heating rate, the TG curves were obtained in triplicate to verify the reproducibility of the results and the experiments showed good repeatability with standard errors  $\pm 1$  °C (within a confidence interval of 95%), according to [23]. All dynamic runs were carried out in a pan containing  $10 \pm 0.1$  mg of the sample. The oxidising atmosphere inside the furnace during temperature-programmed combustion was determined by a continuous flow of 100 cm<sup>3</sup> min<sup>-1</sup> at atmospheric pressure based on the literature conditions for these processes [17,18,24]. In combustion processes, the atmosphere contained 79% of N<sub>2</sub> and 21% of O<sub>2</sub>. In oxy-combustion processes, the atmosphere was adjusted at 79% of CO<sub>2</sub> and 21% of O<sub>2</sub>.

In order to understand the difference between both combustion and oxy-combustion processes, Fig. 2 shows the diverse properties of CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> molecules obtained with ChemDraw® v.12. The most important property to establish difference in the internal molecular diffusion in the particles of biomass is the molecular volume. CO<sub>2</sub> is a triatomic

**Table 3**  
Thermal conductivity  $k$  (W/K) and heat capacity  $C_p$  (J/(molK)) of the N<sub>2</sub> and CO<sub>2</sub> at different temperatures [45].

T (K)	Thermal conductivity $k$ (W/K)		Heat capacity $C_p$ (J/(molK))	
	N <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>
500	38.5	33.5	29.6	44.6
600	44.5	41.6	30.1	47.3
700	50.5	49.3	30.7	49.5
750	53.4	53.0	31.1	50.5
800	56.3	56.7	31.4	51.4

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