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Thermogravimetric and mass spectrometric (TG-MS) analysis of sub-bituminous coal-energy crops blends in N_2, air and CO_2/O_2 atmospheres

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ABSTRACT

During oxy-fuel combustion, the gas composition inside the boiler differs from that of conventional combustion in air, which affects to different aspects in combustion processes. Besides, the need to increase the efficiency in energy production in a sustainable way leads to increasingly extreme conditions imposing more demanding performances on materials such as higher temperatures and pressures in more corrosive environments.

The scope of this work is to understand the thermal behaviour and the kinetic of an energetic crop with high chlorine content blended with a Spanish coal at different atmospheres with special attention to oxyfuel combustion conditions and to determine the formation of those compounds which may induce corrosion, by means of mass spectrometry analysis.

The addition of biomass to the fuel mixture seems to increase the reactivity of the samples. The rate maximum of mass change increases with the oxygen content reaching values from 13.6, 16 and 17.7%/min with N_2, air and oxyfuel atmosphere respectively using 100% of cynara as fuel. The greater reactivity of the oxygen decreases the peak temperature being about 325 °C with N_2, 309 °C with air and 304 °C at oxyfuel conditions.

The activation energy increased when the biomass share in the blend independently of the atmosphere and the heating rate. The activation energy is similar to combustion and oxyfuel combustion conditions but about 5–7 kJ/mol higher than pyrolysis atmosphere for all biomass mixture studied. The optimal blend based on the lowest activation energy is 20:80% of cynara/coal.

HCl presence is higher when the percentage of biomass increased. However, SO_2 presence is more related with coal presence. It is important to stand out that any percentage of cynara in the mixture shift to lower temperatures the SO_2 emission profile, from 500 °C to 300 °C. This fact is also observed in the curves of the weight loss derivative.

1. Introduction

In 2015, coal involved the 28.6% of total primary energy supplies, being China the principal producer with the 45.7% of the world production. In 2014, coal was responsible of 45.9% of CO_2 emissions from energy [1]. More efficient processes and new technologies are being researched because of this importance of coal in the global energy panorama. To mitigate these effects on the atmosphere, biomass appears as an important solution due to the fact that it can be considered as CO_2-neutral fuel and contributes to the reduction of SO_2 and NOx emissions [2]. Biomass is regarded as a renewable and CO_2 neutral energy resource, with a high potential for utilization in the future for purposes of heat and electricity generation.

There is growing interest in alternative, non-edible biomass resources such as fast growing trees and perennial grasses (miscanthus, switch grass, reed canary grass), because of their high yield potential, appropriate biomass characteristics, loss input demand and positive environmental impact. However, slagging and fouling are two problems of concern in combustion processes which employ herbaceous and some kinds of agroindustrial biomasses, of high alkaline content in their ashes. Cynara cardunculus, commonly known as cardoon, cynara or thistle in the contest of the energy crops, is a native herb of the Mediterranean area [3] that exhibits suitable characteristics for the production of biomass capable of producing 15–25 tonnes of biomass per hectare and year [4].

Therefore, cofiring biomass with coal entails a promising alternative which may lead to an environmentally friendly use of coal, reducing emissions and providing utilization of biomass residues. In the last years, some works have been made in order to study the co-combustion characteristics of biomass-coal blends [5–12].

Another strategy which is being developed to mitigate CO_2 emissions is oxy-combustion, which consists in employing an oxygen

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enriched atmosphere for combustion, where nitrogen is shifted by CO_2. In the most interesting processes this carbon dioxide comes from combustion flue gas (recirculation of flue gas), allowing concentrating more the dioxide carbon in the flue gas, thus making more efficient the carbon capture and storage processes.

However, biomass fuels vary widely in composition, particle size and chlorine content, which can make utilization of these fuels challenging, suggesting that further research may be useful for improving the blending and cofiring of a selected biomass with coal.

The need to increase the efficiency in energy production in a sustainable way as well as reducing the environmental impact has become evident. This leads to increasingly extreme conditions imposing more demanding performances on materials such as higher temperatures and pressures in more corrosive environments. Chlorine and sulphur are two products of flue gases that can damage materials from the installation, even more when biomass is used [13,14].

Understanding the kinetics of pyrolysis, combustion and oxyfuel conditions of indigenous subbituminous coal and energetic crops and its blends is vital to the design, optimization and scaling up of systems for the conversion of coal-biomass blends to energy by thermochemical processes. The relationship between the extents of reaction as it proceeds with the temperature can be determined by Arrhenius equation. Activation energy (E) and pre-exponential factor (ko) are the two important parameters in Arrhenius equation which are determined by thermal analysis. These parameters can be further used in numerical simulation models such as computational fluid dynamics (CFD) tools to investigate the behaviour of the feedstock under different operating conditions.

Non-isothermal thermogravimetric analysis (TGA) is proved to be one of the best methods for the study and understanding of the kinetic of pyrolysis and it has been extensively used at low heating rates and temperatures up to 900 °C. TGA measures the weight loss as a function of reaction temperature. Before cofiring test in fluidized bed combustion (FBC), the characteristics of the parent fuels and their blends need to be determined under oxy-fuel combustion by using non-isothermal thermogravimetric analysis (TGA) technique and then compare with the results obtained using conventional air fired combustion. Besides, it will be determined the flue gases evolved by mass spectrometry making special attention to the compounds which may present corrosion problems about the materials used in the boiler.

The scope of this work is to understand the thermal behaviour and the kinetic of sub-bituminous coal, energy crops and their blends at different atmospheres with special attention to oxy-fuel combustion conditions, and analyse the generation of compounds by mass spectrometry capable of causing corrosion problems.

2. Materials and methods

2.1. Materials

The fuels selected for the study consisted in a sub-bituminous coal, from Puertollano, Spain (PT) and a biomass, Cynara cardunculus, (CC)) an energetic crop in the Mediterranean area. Fuels were air dried and crushed under 100 μm size using Retsh ZM100 mill. Coal and biomass blends were defined by different biomass content shares (0, 20, 40, 60, 80 and 100 biomass wt%). The proximate and ultimate analyses of the fuels were conducted by utilizing LECO Truspec equipment and calorific values were measured by using AC-500 bomb calorimeter. Proximate and ultimate analyses of fuels together with its calorific value are summarized in Table 1 The sub-bituminous coal presents medium sulphur content while the cardoon is characterized by its high chlorine content.

2.2. Experimental set up

Thermogravimetric analysis was carried by thermobalance Mettler TGA 851, which can reach up to 1100 °C/min. About 20–25 mg sample was placed in a platinum pan and then heated from an ambient temperature up to a maximum temperature of 900 °C at a heating rate of 10, 20 and 40 °C/min. The total gas flow was set to 50 ml/min for all experiments. The first set of experiments was conducted using N_2 to analyse the effect of heating rate on the pyrolytic kinetics of the blends PT/CC. The second set of experiments were carried out with air to study the combustion kinetic and finally was used a gas mixture 30% O_2-70% CO_2, to create an oxy-fuel combustion atmosphere.

Table 1
Fuels analysis.

Sample	PT	CC
Proximate analysis (% by mass.)		
Moisture	3.6	7.1
Ash	37.3	9.3
Fixed carbon	35.5	17.7
Volatiles	23.6	65.9
Ultimate analysis (% by mass, d.b.)		
C	44.0	42.3
H	3.5	6.2
N	1.2	0.7
S	0.8	0.2
O	11.6	39.8
Cl	0.08	0.7
HHV (kcal/kg)	4466	3641
LHV (kcal/kg)	4278	3308

The evolved gases from TGA were transferred to a mass spectrometer (MS) Balzers Qualdstar with an electro ionization voltage of 70 eV and mass spectra up to 150 a.m.u. The temperature of the sample transferring line was maintained at 150 °C to prevent condensation of exhausting gas. The MS was operated in a peak jump mode by scanning and identifying ions of mass to charge ratios (m/z) in the range 1–150 a.m.u. the masses 36 and 64, which correspond with HCl and SO_2 respectively, are analysed in detail later.

2.3. Kinetic analysis

Data from TGA and DTG were used to determine the kinetic parameters. The chosen method is Coats & Redfern method [15]. The temperature dependency of reaction rate constant was represented by the Arrhenius law

$$k = k_0 \cdot exp^{-(E/RT)} \tag{1}$$

k, ko, E, R and T denote the reaction rate constant, pre-exponential factor, activation energy, gas constant and temperature in Kelvin, respectively.

The conversion rate was written as a function of temperature (T) and the instantaneous conversion ratio (x):

$$dx/dt = k_0 \cdot exp^{-(E/RT)} (1-x)^n \tag{2}$$

where n is the reaction order.

The instantaneous conversion ratio was calculated by

$$x = (w_0 - w)/(w_0 - w_f) \tag{3}$$

where w_o is the initial mass of the sample, w is the residual mass at given time, and w_f is the final mass at the end of the process.

With the definition of the heating rate as $\beta = dT/dt$, Eq. (2) can be re-written as:

$$dx/dt = k_0/\beta \cdot exp^{(-E/RT)} \cdot (1-x)^n \tag{4}$$

Re-arranging and integrating Eq. (4), the following expression can be obtained:

$$(1-x)^{1-n}/1-n = k_0/\beta \int_0^T exp^{(-E/RT)} dT \quad n \neq 1 \tag{5a}$$