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Full Length Article

Air- and oxygen-blown characterization of coal and biomass by thermogravimetric analysis

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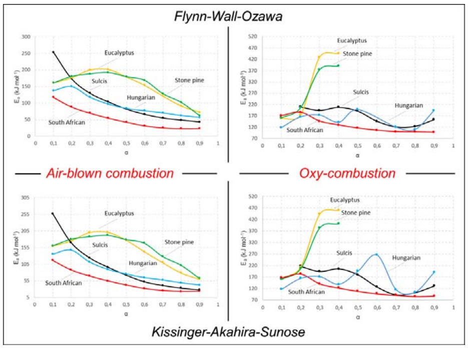
GRAPHICAL ABSTRACT



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ABSTRACT

This paper reports on the results of air-blown combustion and oxy-combustion kinetic characterization (comparing two different isoconversional methods: Flynn-Wall-Ozawa and Kissinger-Akahira-Sunose) of different kinds of coal (from Italy, South Africa and Hungary) and biomass (pine and eucalyptus chips) by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) together with the assessment of different characteristic combustion parameters. It can be observed that the burning rate of fuels can be improved by the oxy-combustion process, shortening the burning time (a mean reduction of the burnout time of 14% and 22% can be observed for coal and biomass samples, respectively). Moreover, biomass shows better ignition performance than coal and enhances combustibility indexes (S and H_f), especially in oxy-combustion conditions. For example, the S index, which reflects combustion properties, increases by an order of magnitude for biomass combustion and oxy-combustion with respect to coal values, thus indicating a higher combustion activity for biomass; an opposite trend can be observed for the H_f index, which describes the rate and intensity of the process and is lower for biomass than for coal, thus indicating better performance for wood chips combustion. Kinetic analysis shows that the activation energy E_a varies with conversion values, reflecting the kinetic complexity in both the processes. Moreover, with the same range of heating rates ($10 \le \beta \le 50$ °C/min) and for the overall range of conversion ($0.1 \le \alpha \le 0.9$), both of the models used fit the experimental data in combustion regime, whereas the increase of the oxygen concentration makes the results reliable for coal samples and more sensitive to weight loss for biomass samples.

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Nomenclature

Acronyms

CCUS	carbon capture, utilization and storage
DSC	differential scanning calorimetry
DTG	derivative thermogravimetry
FWO	Flynn-Wall-Ozawa model
HHV	higher heating value
KAS	Kissinger-Akahira-Sunose model
TG	thermogravimetry
TGA	thermogravimetric analysis

Symbols

D_f	Burnout index (wt.%/min^4)
D_i	ignition index (wt.%/min^3)
DTG_{max}	maximum combustion rate (wt.%/min)
DTG_{mean}	mean combustion rate (wt.%/min)
E_a	activation energy ($kJ\,mol^{-1}$)
H_f	combustion index (°C)
k(T)	reaction rate (function of the kinetic model expression)
A	pre-exponential factor (function of the kinetic model expression)
m_f	residual mass of samples (mg)
m_i	initial mass of samples (mg)
m_α	actual mass of samples (mg)
R	gas constant (J/(mol ∗K))
R^2	correlation coefficient (non-dimensional)
S	combustion index (wt.%/(min^2 ∗°C^3))
T	temperature (K)
T_f	burnout temperature (°C)
t_f	burnout time (min)
T_i	ignition temperature (°C)
t_i	ignition time (min)
T_p	maximum peak temperature (°C)
t_p	maximum peak time (min)
α	conversion degree (non-dimensional)
β	heating rate (°C/min)
$\Delta t_{1/2}$	time range of $DTG/DTG_{max} = 0.5$ (min)
t	time (s)
f(α)	kinetic model (function of the kinetic model expression)
g(α)	integral form of kinetic model (function of the kinetic model expression)

1. Introduction

The utilization of fossil fuels (coal, oil and natural gas) has led an outstanding era of prosperity and advancement for human development. Nevertheless, carbon dioxide concentration in the atmosphere has consequently risen from about 280 ppm (by volume) before the industrial revolution to about 400 ppm in 2016 [1]. A further increase up to about 570 ppm could be expected by the end of this century [2]. The increase in CO_2 emissions can contribute to global warming and climate changes due to the enhanced greenhouse effect. The increasing attention towards climate changes and the recent strategic policies to stabilize and reduce CO_2 emissions has spurred the development of technologies for the use of renewable energy sources. In particular, the European Commission has agreed to reduce their carbon emission by 20% by 2020, by 40% by 2030 and by 80–95% by 2050, with reference to 1990 levels [3]. This is also promoting research in the field of carbon capture, utilization and storage (CCUS) technologies, whereby CO_2 is captured from industrial flue gas and reused (for example for the production of liquid fuels) or permanently stored in geological formations, such as depleted oil and gas fields or saline aquifers [4].

After fossil fuels, biomass is the most important source of energy, which can supply about 14% of the world's energy consumption [5,6]. Among renewable sources, biomass can be considered almost carbon-neutral and presents the lowest risk and capital required to be used in energy generation [7]. Moreover, whereas power generation from sun and wind cannot be programmed, biomass can be used instead of fossil fuels for base-load power generation.

In this context, Sotacarbo is engaged in several theoretical and experimental studies on the potential use of coal and/or biomass for distributed power generation. The aim is the development of CO_2-free power generation technologies for small-scale commercial applications, including the feeding of smart grids in integration with other renewable energy sources. Several experimental campaigns have been carried out in a pilot fixed-bed up-draft gasifier [8,9] and a new bubbling fluidized-bed gasifier is currently under construction in the Sotacarbo Research Centre in Carbonia (Sardinia, Italy) [10].

The fine optimization of both the previously mentioned gasification technologies requires, among other issues, an extensive knowledge of the thermochemical processes occurring in the gasifier (i.e. devolatilization, pyrolysis, gasification and combustion reactions). In particular, it is well known that the knowledge of thermal decomposition of coal and biomass is essential to assess the performance of carbonization, combustion and gasification processes [11]. Non-isothermal thermogravimetric analysis (TGA) is the most simple, the least expensive and the most effective technique to observe both the pyrolysis and combustion profiles of a fuel [12]. Fuel samples are typically heated up to 800–1000 °C in a predefined atmosphere and sample weight losses are measured continuously. Pyrolysis behaviour is typically assessed by performing the analysis in an inert (nitrogen or argon) atmosphere, whereas combustion profiles are determined by feeding the thermogravimetric analyser with an oxidant gas (air or oxygen). Detailed combustion features of the fuels, in terms of characteristics combustion parameters, can also be evaluated, including the ignition, peak and burnout temperatures and combustion rate [13]. This information is of great importance to enhance the knowledge of this process and to estimate its efficiency; it can be successfully used to establish the optimum process conditions.

Several studies have been recently published on combustion performance assessment of different kinds of fuel (coal, biomass, waste, etc.) by thermogravimetric analysis. Table 1 shows a brief summary of the most interesting ones.

As shown in Table 1, many investigations have been conducted and published on combustion (and sometimes co-combustion) of biomass and coal under air atmosphere. Several studies consider oxy-combustion by operating TGA in a O_2/CO_2 atmosphere [14,17], where CO_2 shifts the equilibrium of several reactions, with a significant impact on the process. But it can be noticed that there is a real shortage of published data on oxy-combustion assessment [19,33].

So far, to the best of the present authors' knowledge, only a few papers dealing with the use of oxygen at high concentration in oxy-combustion have been published. The study of oxy-combustion of coal and microalgae in O_2/N_2 or O_2/CO_2 atmosphere at an oxygen concentration of 70–80% by volume is reported by Chen et al. (2013 and 2015) [25,34], respectively. Only for one of these mentioned works has the kinetic study with different models been performed. Only Liu et al. (2016) [19] assess the combustion performance indexes up to an oxygen concentration of 100%.

In this light, a detailed investigation on the oxygen-enriched behaviour of coal and biomass, including both the evaluation of the