A study of coal-solid waste blend reactivity

Estudio de reactividad de mezclas de residuos sólidos - carbón

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ABSTRACT

The Flynn-Wall-Ozawa method was used for analysing coal-solid waste blend reactivity in an oxidising atmosphere. The presence of biomass strongly affected coal combustion kinetics when the blend contained more than 30% of it. Activation energy values (evaluated by different blends) were 28.7495 kJ/mol for 0% biomass, 31.3915 kJ/mol for 30% biomass, 39.0365 kJ/mol for 50% biomass, 102.431 kJ/mol for 70% biomass and 107.8075 kJ/mol for 100% biomass; these values were close to those reported in the literature. First-order kinetics correlated the data very well for the 100% coal sample and the blend having 30% biomass and 70% coal. Eighth-order kinetics were more suitable for correlating the experimental data for the 70% biomass-30% coal blend and the 100% biomass sample. Combustion was done without previous pyrolysis of the blends; however segregation of phenomena could be appreciated. This seems to indicate that combustion and devolatilisation are independent processes which should be taken into account when building equipment using these kinds of blend.

Keywords: co-combustion, coal, biomass, reactivity, thermal analysis.

RESUMEN

La reactividad de mezclas de residuos sólidos y carbón en atmósfera oxidante fue analizada usando el método de *Flynn Wall Ozawa*. La cinética de la combustión es fuertemente afectada por la presencia de biomasa, cuando la relación en la mezcla es superior al 30%. Los valores de la energía de activación evaluados para diferentes mezclas fueron: 28.7495 kJ/mol para 0% de biomasa, 31.3915 kJ/mol para 30% de biomasa, 39.0365 kJ/mol para 50% de biomasa, 102.431 kJ/mol para 70% de biomasa y 107.8075 kJ/mol para 100% de biomasa. Estos valores son cercanos a los reportados en la literatura. Se encontró también que para la muestra de carbón al 100% y la mezcla de 30% biomasa y 70% de carbón una cinética de primer orden correlaciona muy bien los datos; mientras que para la mezcla de 70% biomasa 30% carbón y la muestra de 100% biomasa, una cinética de orden 8 es más adecuada para correlacionar los datos experimentales. La combustión se hizo sin la pirólisis previa de las muestras; sin embargo, es posible apreciar una división del fenómeno. Esto parece indicar que la combustión y la devolatilización son procesos independientes, lo cual es importante en la construcción de equipos para este tipo de mezclas.

Palabras clave: co-combustión, carbón, biomasa, reactividad, análisis térmico.

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Introduction

Solid waste from human activities has caused environmental deterioration and poor health for communities living around sanitary landfills. Governments and the scientific community have thus proposed several alternatives for resolving this problem, such as the direct controlled combustion of organic waste solids mixed with coal as energy source (Defeche *et al*., 1980).

Controlled combustion of organic waste solids is a method which is widely used around the world as these residuals are transformed into inert material (ashes) and hot gases; a 70% reduction in weight and 80%-90% in total biomass volume may be achieved (Folgueras *et al*., 2003). A large amount of pollutants emitted by traditional incineration systems such as flying ash, sulphates, chlorhydric acid and substances such as dioxins and furans have made their use become restricted in many countries, especially European ones.

Coal and different types of biomass blends, like urban, forest and industrial solid waste, have being researched as being clean and economic energy alternatives allowing the substitution of traditional fossil fuel, thereby mitigating both the environmental impact brought by its use and partially resolving waste management. This blend reduces polluting gases such

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as nitrogen oxides and sulphur (Romero, 2002), improving combustion efficiency at the same time (Gayana *et al.*, 2004).

Folgueras *et al.,* (2003) carried out TGA and DSC analysis of coal and sewage sludge co-combustion. They studied bituminous coal combustion, three types of sewage sludge and their blends, in static air atmosphere using a 10°C/min heating rate constant from room temperature to 800°C. The process was considered as a series of consecutive first-order reactions in this study using Arrhenius' law for kinetic constant determination.

Biagini *et al.,* (2002) studied the devolatilisation behaviour of several coals, biomasses and blends of rhem through thermogravimetrical analysis in a nitrogen atmosphere using isothermal and non-isothermal conditions. First-order kinetic mode was assumed for one reaction. The distribution of activation energy model was also used; thermal decomposition is considered to be an independent chemical reaction series in this model.

Calvo *et al.*, (2004) studied rice-husk reactivity in N_2, O_2 atmospheres and blends of them by using TG analysis. They observed three main stages when they worked with the two gases. They used a first reaction model for finding out kinetics' parameters and the Coast Redfern Model for determining the reaction order.

Vuthaluru *et al.*, (2004) also used thermogravimetrical analysis for studying wood residuals with coal blend kinetics. It was found that there were no interactions in blends having a low proportion of biomass and it was proven that a first-order model reaction was suitable for correlating blend kinetics. This work was aimed at studying coal-biomass blend behaviour by using TG, DTG and DSC analysis and calculating kinetic parameters for combustion process, frequency factor A and activation energy E.

Experimental method

Sample preparation

Domestic solid waste from the metropolitan area of Valle de Aburrá in Medellín, Colombia, was gathered then dried in a forced convection oven at 50°C and 60°C. It was then milled until reaching mesh size 200 (particle diameter less than 0.074 mm) and then mixed with the same size coal from the Amagá region.

Characterisation

Tables 1 and 2 show proximate and ultimate analysis for coal and biomass.

Blend preparation

Five different coal–biomass blends were prepared with the following size ratios: 0% biomass-100%coal, 30% biomass-70% coal, 50% biomass-50%coal, 70% biomass-30% coal and 100% biomass-0%coal.

Combustion

Every blend was heated from 30°C to 900 °C in an oxidising atmosphere using a pure oxygen stream in a thermogravimetrical analyser (STA 409 CD Nestzch). Three heating rates were used: 5, 10 and 20°C/min. An additional assay used a 100% biomass-0% coal sample blend in an inert atmosphere at 10°C/min as heating rate to observe behaviour during pyrolysis.

Kinetic model

Decomposition may happen when a sample is being heated; moreover, a kinetic study must be carried out for determining the kinetic parameters characterising such change.

The conversion is defined as:

$$\alpha = \frac{m_i - m}{m_i - m_f} \qquad (1)$$

The kinetics of any solid material's decomposition can be represented in the following way (Kristiansen *et al.*, 1996):

$$A_{solid} \rightarrow B_{solid} + B'_{gaseous} \qquad (2)$$

and its kinetics can be described as:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \qquad (3)$$

Temperature dependence was described by Arrhenius' equation:

$$k(T) = A\exp(-E/RT) \qquad (4)$$

Equations 3 and 4 were obtained in non-isothermal conditions, using the Chain rule:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(\frac{-E}{RT}\right)f(\alpha) \qquad (5)$$

to integrate it is obtained :

$$\int_{\alpha_0}^{\alpha_p} \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{A}{\beta}\int_{T_0}^{T_p} \exp\left(\frac{-E}{RT}\right)dT \qquad (6)$$

where: $\beta = dT/dt$ is the heating rate.

The model proposed by Flynn–Wall– Ozawa was used for finding the kinetic parameters (Fraga *et al.*, 2001); this method has the advantage that activation energy can be calculated without making any assumption about the reaction model. This method also allows activation energy to be obtained as a function of temperature and /or conversion (Vyazovkin *et al.*, 1999).

An attempt was made to integrate as follows in Flynn–Wall–Ozawa's model:

$$g(\alpha) = \frac{A}{\beta}\int_{T_0}^{T_p} \exp\left(\frac{-E}{RT}\right)dT \qquad (7)$$

α_0 = 0 was assumed when temperature was low and no reaction between T = 0 and $T_{0.}$ Doyle's approach (Johannes et al, 2000, Sima *et al.*, 2005) was used for obtaining the following expression:

$$Ln\beta = Ln\frac{AE}{Rg(\alpha)} - 5.3305 - \frac{1.052E}{RT} \qquad (8)$$

A first-order reaction was supposed for finding *A* in the following expression:

$$-\frac{d\alpha}{dt} = A\exp\left(\frac{-E}{RT}\right)f(\alpha) \qquad (9)$$

The following was obtained after algebraic manipulation:

$$\ln A = \ln\left(-\frac{d\alpha / dt}{f(\alpha)}\right) - \frac{E}{RT} \qquad (10)$$

Several *f*(α) should be supposed and which function and frequency factor best correlate the data should be statistically determined (10).

Results and Discussion

It was observed from proximate and ultimate analysis that biomass had a greater amount of volatile matter than coal; it also had a lower high-heat value. These conditions greatly influence designing a combustion chamber. It had also to be taken into account that biomass was dried before any treatment because it had around 60% humidity on a wet base.

Assays carried out with 100% biomass using a 10°C/min heating rate with TGA and DTG equipment led to obtaining a devolatilisation profile (Figure 2). An exothermic process can be observed from the DSC curve when the biomass was subjected to an inert atmosphere, corresponding to biomass devolatilisation.

An additional peak in this process could be noted when the lost weight profile in an inert atmosphere was compared to that in an oxidising one. The first peak (around 260°C) coincided with devolatilisation (as observed in the DSC profile). The first peak was presented in both atmospheres at the same temperature; total mass loss was practically the same. The second peak was due to the combustion process (from 320°C).

Figure 1 shows that devolatilisation and combustion during biomass burn-off in an oxidising atmosphere are separate processes, maybe due to different kinds of volatile material having an ignition point higher than 320°C.

It can be noticed that the curves corresponding to blends having more biomass content (see Figure 2) presented greater bigger peak temperature values (a point where any change inside a sample was occurring); this could have happened due to complexity in biomass composition compared to the composition of the coal.

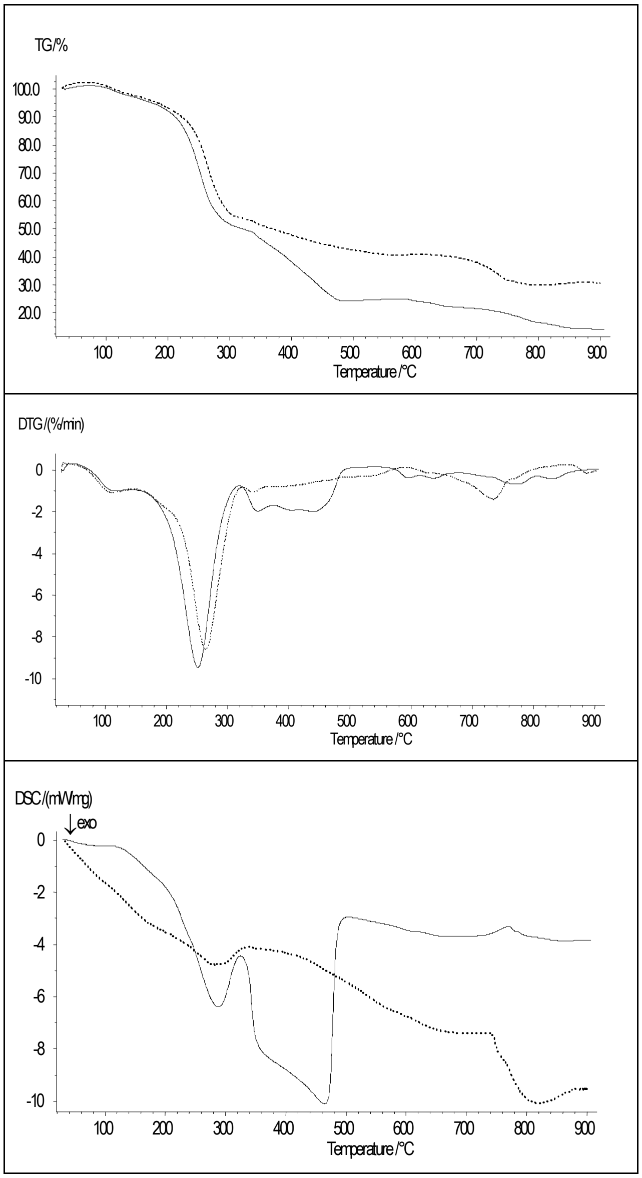

Figure 1. TG, DTB and DSC for 100% biomass in an oxidising (___) atmosphere and in an inert (-----) atmosphere

Displacements were observed toward more weight losses when biomass content was increased in the TG curve, being attributed to larger volatile material biomass content and that volatile material was released from biomass in less time than from coal. A displacement of peaks could be observed toward smaller temperatures in DTG curves and therefore at shorter times, this being attributed to thermal decomposition first beginning in blends having more biomass content.

Although the experiments were carried out in an atmosphere oxidising, two peaks defined in the curves having greater biomass content (above 30%) could be clearly noticed when comparing the results obtained with those reported in the literature and with the assay carried out in an inert nitrogen atmosphere for the 100% biomass-0% coal blend. One of them (200°C-350°C) could have been due to the volatilisation stage while the other one (400°C-600°C) could have been attributed to the blends' combustion stage which appeared in the assay with O_2.

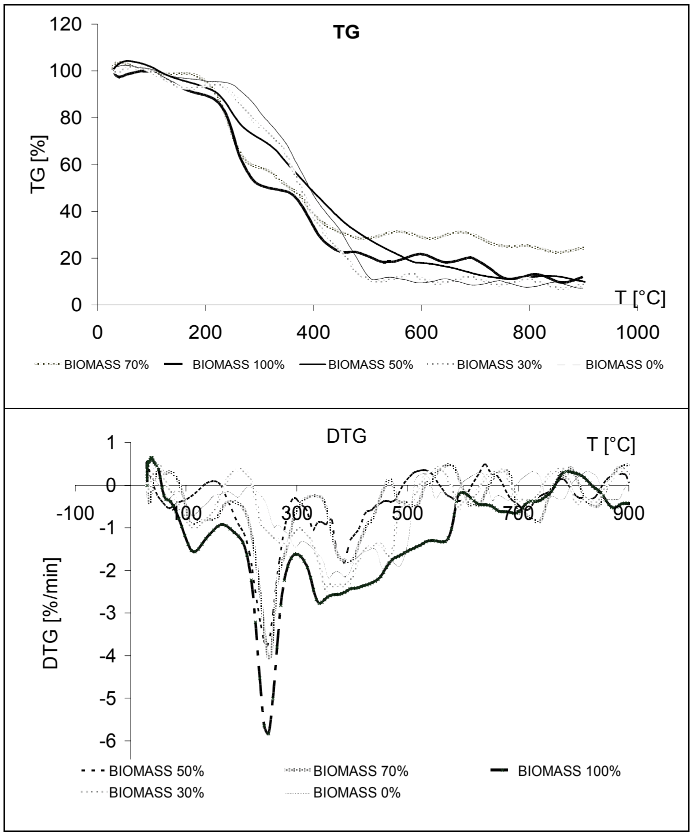

Figure 2. TG, TGA and DTG Results

Only a thermal event was observed for blends having 0%-30% biomass content (i.e. a complete combustion stage). This was more exothermal than the largest biomass proportion (Figure 3c: DSC profile). Similar behaviour was observed to the coal in blends having a low biomass ratio; it could be said that the behaviour of coal was rarely modified by adding small amounts of biomass (up to 30%).

Changing the heating rate did not present changes in the blends' overall behaviour since they conserved the same tendency in thermal analysis curves for 5°C/min, 10°C/min and 20°C/min rates. This factor's effect on analysis was that the exothermal peaks moved toward higher temperatures with increased heating rate in the case of DTG and DSC while this factor had no clear influence on TG. However, it should be noted that the 10°C/min rate allowed the events being the object of our study to be observed more clearly (Figure 3).

The activation energy given from Flynn-Wall–Ozawa's method was given by taking the slope of each straight line shown in Figure 4. This figure shows that although the lines are not completely parallel (due to the amount of reactions), activation energy was constant and almost the same for each conversion. The latter did not happen when biomass ratio exceeded 50% where two clearly differentiated areas appeared (respectively corresponding to volatilisation and combustion).

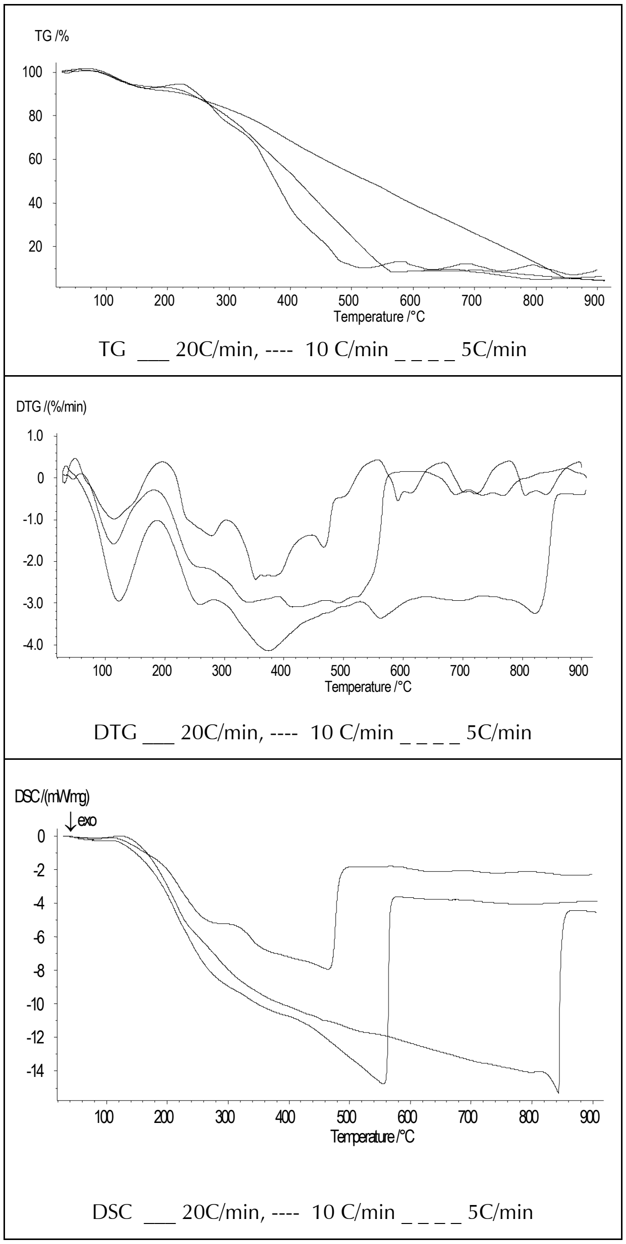

Figure 3. Comparison between three heating rate for 30% biomass

The values obtained for activation energy, evaluated using different blends, were 28.7495 kJ/mol for 0% biomass, 31.3915 kJ/mol for 30% biomass, 39.0365 kJ/mol for biomass 50%, 102.431 kJ/mol for 70% biomass and 107.8075 kJ/mol for 100% biomass. These values were close to those reported in the literature.

Equation (10) was used for calculating the frequency factor, finding that first-order kinetics correlated the data very well for the 100% coal sample and 30% biomass-70% coal blend, while eighth-order kinetics correlated the data better for 70% biomass-30% coal blends and the 100% biomass sample (see Figure 5).

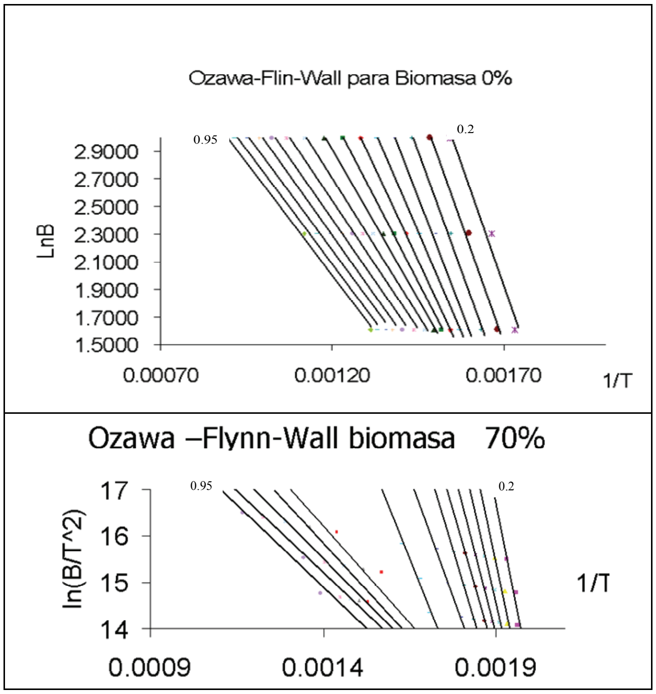

Figure 4. Results according Ozawa-Flynn-Wall Model.

Conclusions

The Flynn–Wall– Ozawa method was used for evaluating the kinetic parameters of biomass and coal blends during combustion, leading to successful results. Biomass in the blends led to segregation: devolatilisation was independent of combustion.

Adding low proportions of biomass to coal did not reveal interactions modifying coal combustion behaviour. However, combustion and devolatilisation were independent processes for blends having more than 30% biomass. The latter could cause a drop in industrial burners' energy efficiency if it were not possible to use additional combustion air to burn-off the volatile material.

Coal-solid waste burner design should consider devolatilisation and combustion separately. A designer must consider a short time-scale for completing the overall process, one time-scale for completing the combustion of all volatile material released first and another time-scale for pyrolysed material. This means that larger combustion chambers must be built for solid waste or that mixed with coal for others which only use coal.

Nomenclature

A pre-exponential factor
E activation energy
m, mass in time t
m_i initial mass
m_f final mass
α conversion
$f(\alpha)$ reaction model
t time
T temperature

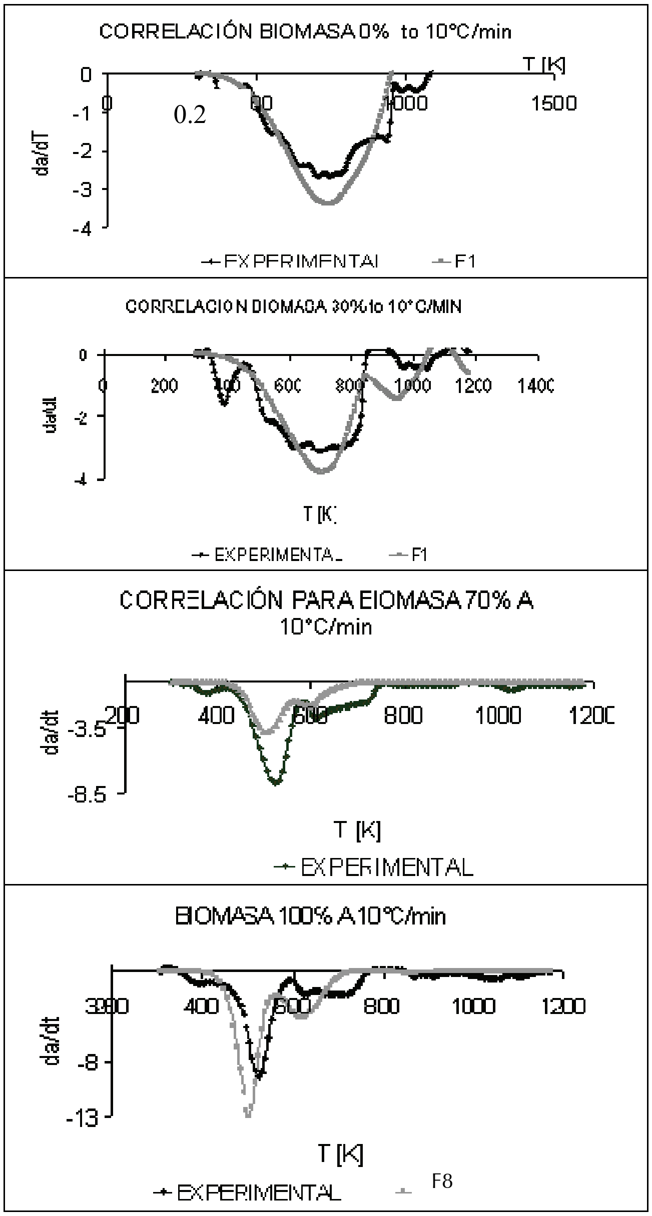

Figure 5. Correlations between experimental and theoretical data for different blends.

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