KINETICS OF CO-PYROLYSIS OF SAWDUST, COAL and TAR

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ABSTRACT

Two coals, sawdust and coal tar were selected to prepare briquettes. Thermogravimetric analyses at three heating rates (i.e. 10, 20 and 30 °C/min) and up to 1000 °C were carried out with the briquette components. Four blends were prepared and the experimental decomposition profiles were compared with the calculated data taking into account the amount of each component in the blend. No interaction was found when comparing the experimental and calculated decomposition profiles of the blends. Isoconversional models OFW (Ozawa-Flynn-Wall) and KAS (Kissinger-Akahira-Sunose) were used to obtain the activation energies of the blend components. The activation energies obtained were introduced in the Coats-Redfern (CR) model to derive the pre-exponential factors. The thermal decomposition profiles calculated using the kinetic parameters were in good agreement with the experimental results in the case of the briquette components, but worse results were obtained in the case of the blends due to their greater complexity.

Keywords: waste sawdust, coal, briquettes, tar, pyrolysis kinetics, OFW, KAS

1. Introduction

Growing international concerns over climate change have been seen accompanied by an increasing interest in global greenhouse gas emissions. The steel industry is becoming more and more concerned about CO₂ emissions resulting from the intensive use of fossil fuels. Primary metal production contributes about 5 % to total world greenhouse gas emissions, and of this, iron and steel production accounts for about 70 %. As a consequence interest in renewable and sustainable energy sources is directing research towards the introduction of biomass-derived carbon into the steelmaking process (Ng et al., 2011; Norgate et al., 2012).

Pyrolysis is a conversion process that allows the transformation of biomass into gas, liquid and solid products. The study of the thermal decomposition of coal and biomass is essential for assessing their applicability and for optimizing the pyrolysis process with a view to scaling up (Ferrara et al., 2014; White et al., 2011). In addition the recycling of wastes is important not only from the point of view of waste treatment and energy recovery but also for upgrading the material. The use of biomass in coking blends could serve to reduce the emission levels due to its carbon neutral content and low ash and sulphur contents (Jung et al., 2014; Montiano et al., 2014a, 2014b).

Thermogravimetric analysis is the most common technique used to evaluate thermal decomposition and perform kinetic studies. A large number of research papers have dealt with thermal decomposition kinetics of coal and biomass with the aim of obtaining kinetic parameters that will serve to predict their behaviour during thermal treatment (White et al., 2011; Solomon et al., 1992). Some studies have revealed significant differences in the kinetic parameters obtained by means of dynamic techniques (experiments performed under non-isothermal conditions) using a single heating rate. Results could be improved by conducting various experiments at different heating rates (Vyazovkin and Wight, 1998).

Isoconversional methods are used to evaluate kinetic parameters based on experiments carried out at various heating rates and provide reliable estimates of the kinetic parameters. These model-free methods are based on an isoconversional premise, the

degree of conversion for a reaction is assumed to be constant and therefore the reaction rate, depends on the reaction temperature (Ferrara et al., 2014; Ceylan and Topçu, 2014; Idris et al., 2010; Wu et al., 2014; White et al., 2011). Another method widely used (Lu et al., 2013; Van der Velden et al., 2010) that is non isothermal is based on the Coats and Redfern equation (Coats and Redfern, 1964). Some authors combine both methods (Kantarelis et al., 2011).

The aims of the present research work are firstly to determine the kinetic parameters of the pyrolysis of components of blends of coal, biomass and tar that are going to be used to prepare briquettes and secondly to determine the existence of synergies during pyrolysis.

2. Experimental

2.1. Materials and methods

Waste chestnut sawdust (SC), a high rank coal (K), a bituminous coal (P) and high temperature coal tar (T) obtained as a sub-product in the coking industry were selected as materials for the experiments. The materials were used to prepare four briquettes of different composition B1: 15 wt.%T + 15 wt.% SC + 70 wt.% K, B2: 15 wt.%T + 15 wt.% SC + 35 wt.% K + 35 wt.% P, B3: 15 wt.%T + 42.5 wt.% K + 42.5 wt.% P, B4: 15 wt.%T + 85 wt.% K. The formulations were selected in order to study the effect of the inclusion of biomass and coals of different rank in the briquettes.

Proximate analyses were performed following the ISO562 and ISO1171 standard procedures for the volatile matter and ash content, respectively (www.iso.org). An elemental analysis was carried out using a LECO CHN-2000 for C, H and N, a LECO S-144 DR for S following the ASTM D5373 and D4239 standards respectively (www.astm.org) and a LECO VTF-900 for the direct determination of O. The inorganic matter composition of each sample was analysed by X-Ray fluorescence (XRF) in a SRS 3000 Bruker spectrometer in accordance with the ASTM D4326-04 standard procedure.

2.2. Thermogravimetric analysis

The pyrolysis experiments were carried out in a TA Instruments SDT 2960 thermoanalyser. A Pt crucible of 110 µl was used for the experiments. A sample of 2-5 mg of

SC, K, P and T with a particle size of < 0.212 mm was employed for each pyrolysis experiment. The temperature was increased between 25 and 1000 at three heating rates: 10, 20 and 30 °C/min. The use of a small particle size and low heating rate was necessary to avoid heat transfer limitations (White et al., 2011). Nitrogen with a purity higher than 99.9997 % was used to maintain an inert atmosphere at a flow rate of 100 ml/min. From the data obtained from the thermogravimetric analysis (TG), the derivative of the weight loss curve (DTG curve) was calculated. The thermobalance was calibrated periodically using standard weights and pure metals such as Zn, Al, and Ag. The tests were carried out at least two times in order to ensure the repeatability of the results.

The briquettes had an ellipsoidal shape, axes of lengths 46 and 42 mm and a weight of around 23 g (Montiano et al., 2014b). Blends resembling the composition of the briquettes were pyrolyzed up to 1000 °C at a rate of 10 °C/min in order to investigate the degree of interaction between the components of the blends. In the case of the blends, samples of 10 mg with a particle size of less than 0.212 mm were used. The experimental mass loss curve was compared to the calculated profile by applying the additivity law, taking into account the composition of the blend and the mass loss curves of the briquette components.

2.3. Pyrolysis kinetics

Kinetic parameters were determined by applying two isoconversional models: Ozawa - Flynn - Wall (OFW) and Kissinger-Akahira-Sunose (KAS) and a combination of these with the Coats- Redfern (CR) model (White et al., 2011).

Isoconversional methods (KAS and OFW) make it possible to determine the activation energy without any knowledge of the reaction mechanism. These methods are usually referred to as “model-free” and assume that the conversion (α) for a reaction is constant and that the reaction rate depends on the reaction temperature. An advantage of these methods is that the systematic error resulting from the kinetic analysis of Arrhenius parameters is eliminated (Brown et al. 2000).

The general kinetic model that describes the degradation process during pyrolysis is expressed by Eq. 1:

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \quad (1)$$

where $f(\alpha)$ is a function that represents the reaction model and will depend on the reaction mechanism, t is time, α is the conversion and $k(T)$ is the reaction constant that depends on the temperature.

The conversion in a pyrolysis process can be written as:

$$\alpha = \frac{w_0 - w_t}{w_0 - w_\infty} = \frac{\Delta w}{\Delta w_0} \quad (2)$$

The rate constant can be expressed by the Arrhenius law as:

$$k(T) = A \cdot e^{-\frac{E_a}{RT}} \quad (3)$$

where A is the pre-exponential factor and E_a the activation energy, R is the universal gas constant and T the absolute temperature, taking into account that the heating rate (β) is constant:

$$\beta = \frac{dT}{dt} = \frac{dT \cdot d\alpha}{d\alpha \cdot dt} \quad (4)$$

Introducing Eqs 3 and 4 into Eq. 1 gives:

$$\int_0^\infty \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T e^{-\frac{E_a}{RT}} dT \quad (5)$$

By setting $u = \frac{E_a}{RT}$, Eq. 5 can be expressed as Eq. 6

$$\int_0^\infty \frac{d\alpha}{f(\alpha)} = \frac{AE_a}{\beta R} \int_x^\infty u^{-2} e^{-u} du = \frac{AE_a}{\beta R} P(x) \quad (6)$$

If $g(\alpha) = \int_0^\infty \frac{d\alpha}{f(\alpha)}$, Eq. 6 can be written as:

$$g(\alpha) = \frac{AE_a}{\beta R} P(x) \quad (7)$$

$P(x)$ can be solved using various approximations depending on the method used (White et al., 2011). Depending on the approximation chosen various methods can be derived that allow the activation energy to be determined as a function of the conversion. These methods assume that the kinetics of the reaction does not vary with the heating rate and that the reaction rate depends only on the temperature (Kantarelis et al., 2011; Ceylan and Topçu, 2014; White et al., 2011; Starink, 2003). For instance, the KAS method employs the following empirical approximation (Doyle, 1962; Kissinger, 1957; Sbirrazzuoli et al., 1999):

$$P(x) = x^{-2} e^{-x} \quad (8)$$

which transforms Eq. 7 into:

$$g(\alpha) = \frac{AE_a}{\beta R} x^{-2} e^{-x} \rightarrow \ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AE_a}{Rg(x)}\right) - \frac{E_a}{RT} \quad (9)$$

By plotting $\ln\left(\frac{\beta}{T^2}\right)$ vs $1/T$ for various heating rates, it is possible to calculate the

activation energy for different conversion values.

The OFW method is also commonly employed to determine kinetic parameters, using the Doyle approximation (Kantarelis et al., 2011; Doyle, 1962, 1965; Flynn, 1983):

$$\log(P(x)) \cong -2.315 + 0.457x \quad (10)$$

Then Eq. 7 transforms to:

$$\log(\beta) = \log\left(\frac{AE_a}{Rg(x)}\right) - 2.315 - 0.457 \frac{E_a}{RT} \quad (11)$$

By plotting $\log(\beta)$ vs $1/T$ it is possible to obtain the activation energy corresponding to each conversion step.

Although OFW and KAS are useful for calculating the apparent activation energy, to determine the pre-exponential factor (A) the Coats-Refern method (CR) will be used. The CR model derives from the Arrhenius equation and is useful for calculating the E_a , A and reaction order (Kantarelis et al., 2011). The function $f(\alpha)$ in eq. 1 must first be simplified to obtain a solution to the differential equation. An excellent review by White (White et al., 2011)

summarizes the most common reaction mechanisms in solid state reactions. For chemical control and the reaction order N, $f(\alpha)$ can take the form:

$$f(\alpha) = (1 - \alpha)^N \quad (12)$$

By combining this with equation [1] the following expression is obtained:

$$\frac{d\alpha}{dt} = A \cdot e^{\frac{-E_a}{RT}} (1 - \alpha)^N \quad (13)$$

Taking into account eq. 4 and given that the heating rate is constant the following expression is obtained:

$$\frac{d\alpha}{(1 - \alpha)^N} = \frac{A}{\beta} e^{\frac{-E_a}{RT}} dT \quad (14)$$

Using the approximation of Taylor and assuming that $2RT/E \ll 1$, Eq. 15 and 16 are obtained for $N=1$ and $N \neq 1$, respectively, allowing A and E_a to be calculated. For the present research work N is considered to be 1, and Eq. 15 is used to calculate the frequency factor (A) using the E_a obtained by the isoconversional methods (OFW and KAS).

$$N = 1 \rightarrow \ln\left(\frac{-\ln(1 - \alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E_a}\right) - \frac{E_a}{RT} \quad (15)$$

$$N \neq 1 \rightarrow \ln\left(\frac{(1 - \alpha)^{1-N} - 1}{(1 - N)T^2}\right) = \ln\left(\frac{AR}{\beta E_a}\right) - \frac{E_a}{RT} \quad (16)$$

3. Results and discussion

3.1. Characteristics of the materials used

The elemental and proximate analyses of K, P, SC and T are presented in [Table 1](#). The two coals are of a different rank (VM= 22.7 and 14.6 wt.% db) and have lower volatile matter than SC (VM=78.8 wt.% db) and T (VM=65.9 wt.% db). The highest oxygen content and the lowest C/O atomic ratio correspond to SC. The highest C/H atomic ratio corresponds

to coal K, reflecting its higher degree of aromaticity. The coal tar will be used as binder in the preparation of the briquettes and shows negligible ash content. The sawdust has very low S and ash contents and high volatile matter contents compared to the coals.

3.2. Thermal decomposition of the briquette components and their blends

The variation of conversion (x) and dx/dt with temperature for all the components of the briquettes obtained using three heating rates are shown in [Figure 1](#). The coals present one main decomposition stage with a temperature of maximum rate of devolatilization (T_{max}) between 512 and 534 °C in the case of K and between 477 and 500 °C for coal P depending on the heating rate used. A second stage of decomposition with T_{max} in the range between 739 and 768 °C as a function of the heating rate is especially relevant in relation to the main decomposition stage in the case of the high rank coal.

The pyrolysis of sawdust consists of three decomposition stages: 1. Hemicellulose (200-300 °C) 2. Cellulose (275-350 °C) and 3. lignin (280- >550 °C) ([Yang et al., 2007](#); [Montiano et al., 2013](#)). The tar presents a broad decomposition stage which can be divided into four parts in the range between 115 and 600 °C. Tar is the most volatile of all the materials studied, conversion at 300 °C being around 50 %. Most of the biomass is devolatilized after decomposition of the cellulose, whereas the coals require further treatment at higher temperatures to complete their devolatilization. The temperature ranges of the pyrolysis process are influenced by the heating rate. Increasing the heating rate produces an increase in the values of dx/dt and the temperatures of the maximum rate of volatile matter evolution corresponding to the different stages. At higher heating rates the samples reach the required temperature in shorter times whereas at lower heating rates the heating of the particles occurs more gradually with a more effective heat transfer to the inner parts of the particles ([Barriocanal et al., 2003](#); [Damartzis et al., 2011](#); [Ceylan et al., 2014](#)).

3.3. Pyrolysis kinetics

Preliminary experiments were carried out to determine whether there were any resistances, such as heat and mass transfer, that might affect the thermogravimetric analysis and the results derived from the kinetic study.

The apparent activation energy of the sawdust, the tar and the coals was determined by isoconversional KAS and OFW methods. The KAS is defined by Eq. 9. By plotting $\ln(\beta/T^2)$ vs $1/T$ for different conversion values, it is possible to obtain the activation energy from the slope of the lines (Figure 2). In the case of the OFW method Eq.11 is used and E_a is obtained from the slope of the plot $\log(\beta)$ vs $1/T$ for each conversion degree, as shown in Figure 3. The results of the analysis of Figures 2 and 3 are presented in Table 2. In general the values obtained for R^2 are high, although in the case of the high rank coal K for conversion values of 0.6 and 0.7 and SC and P for a conversion value of 0.7, the correlation coefficient is slightly lower due to the shape of the experimental curves obtained which almost overlap for the different heating rates (Figure 1). The average activation energies obtained for each material using the two model-free models are very similar (Table 2). In the case of the coals, the values obtained were 284.7/282.7 and 213.5/216.2 kJ/mol for coal P and K respectively. Activation energy values of around 270 kJ/mol were obtained by other authors for coal (Idris et al., 2010; Wu et al., 2014). The average activation energy obtained for tar was 184.3 and 183.7 kJ/mol using the KAS and OFW methods respectively. The smallest value was obtained for the sawdust with $E_a=155.2$ and 156.8 kJ/mol using KAS and OFW respectively. In the literature a wide range of E_a values can be found for biomass due to the huge differences between different types of biomass and their heterogeneity. For stone pine wood chips a value of 116.7 kJ/mol has been reported (Ferrara et al., 2014) whereas Ceylan (Ceylan and Topçu, 2014) reported a value of 131.1 kJ/mol for hazelnut husk, using the OFW method. The variations in the activation energy observed using these methods are due to heterogeneity of the samples which experience changes in reactivity as the reaction progresses and also to the complex nature of the reactions (Kantarelis et al., 2011; Ceylan and Topçu, 2014). For the materials studied in the present research work the descending order of activation energy is as follows: $P>K>T>SC$. To satisfactorily explain these results it must be borne in mind that increasing the heating rate will lead to decomposition taking place at higher temperatures. The fact that coal P is a bituminous coal that passes through a plastic stage, which means softening of the coal mass followed by a temperature range

where the coal becomes fluid and then resolidifies to form a coherent mass, may explain why a higher activation energy is needed for the decomposition of coal P compared to coal K.

Variation in the activation energy with conversion is attributed to the concurrence of various decomposition mechanisms that involve multiple processes during pyrolysis (Kantarelis et al., 2011; Ceylan and Topçu, 2014; López-Vazquez et al., 2013). The lower activation energy values in the case of biomass can be associated to the lineal polymeric structure of the hemicellulose and the initiation of the decomposition process that occurs at the weaker links. The increase in the activation energy is promoted by occurrence of several simultaneous processes during the final degradation of the hemicellulose (Alén et al., 1996). The increase in activation energy in the case of biomass up to conversion values of 0.4 can be assigned to the contribution of the three components of the sawdust (López-Vazquez et al., 2013). A lower activation energy indicates that the volatile materials are more easily decomposed and that the reaction rate is faster than for the materials that need a higher activation energy. In the case of the coal tar (T) the activation energy has been calculated for conversion values ≥ 0.2 , due to the different nature of the processes taking place during first stages of heating which in turn, may have been related to the evaporation of highly volatile compounds present in coal tar. Other authors have also considered that mass loss up to temperatures of 175 °C correspond to the evaporation of light volatiles (Chen et al., 2015).

By using the activation energy obtained with OFW and KAS in Eq. 15 it is possible to obtain the pre-exponential factor (A). The results are presented in Table 3 for the three heating rates studied. By applying the kinetic parameters in Tables 2 and 3 it is possible to calculate the conversion and its derivative with time for all the components of the blends. The simulation was carried out for a conversion interval between 0.1 and 0.7 except for tar that was carried out for a conversion range between 0.2 and 0.7. The results of the simulation are presented in Figure 4. The activation energy and pre-exponential factor used for the calculations are the average of those obtained by means of the KAS and OFW methods and CR method, respectively. A comparison between the experimental and calculated conversions and the derivative of the conversion versus time are in very good agreement.

3.4. Pyrolysis of the blends

The variation of the conversion and its derivative with time of the blends that make up the briquettes are shown in [Figure 5](#). The number of decomposition stages depends on the composition of the briquettes. For B1 and B2 more stages are observed due to the presence of sawdust. The dx/dt curves show the peaks corresponding to the components of the blends. It appears that the decomposition of the biomass and coal occurs independently with little interaction. All the curves evidence dehydration and the presence of highly volatile material in the tar. Blends B1 and B2 show maxima at around 275 and 330 °C due to the presence of sawdust. B1 has a peak at 510 °C while in the case of B2 this peak appears at 492 °C corresponding to the pyrolysis of the higher rank coal. The higher the temperature of the peak, the greater the proportion of coal of higher rank. The decomposition of lignin overlaps that of the coals although it is not easy to appreciate because the value of maximum rate of decomposition in the case of lignin is lower than that of the coal ([Lu et al., 2013](#)). In the case of B3 and B4 because only coal and tar are present in the blend, the dx/dt curve is simpler and only the peaks corresponding to the tar and the coal are apparent. The curves corresponding to the decomposition of coals of different rank, the higher the rank, the higher the temperature of maximum rate of decomposition and the lower the value of this rate. So, for B4 that contains a higher amount of the high rank coal the main peak appears at a higher temperature than for B3 (500 vs 492 °C) and with a lower rate (0.032 min⁻¹ vs. 0.048 min⁻¹).

In order to determine if there are interactions during the decomposition of the components of the briquettes, the experimental mass loss curves of the four briquettes and those calculated assuming additivity have been plotted in [Figure 6](#). All the calculated curves are very close to the experimental ones; the maximum deviation values being 1.66 % for B1, 1.01 % for B2, 2.75 % for B3 and 1.45 % for B4. Therefore, our results indicate that there is no interaction between the components of the briquettes during pyrolysis. Whether interaction takes place between coal and biomass during co-processing is still a controversial issue. Some authors when studying the devolatilization behaviour of blends of biomass and

coal have concluded that no interaction occurs under inert conditions and that the pyrolysis products yields are related to the amount of biomass and coal in the initial blend (Masnadi et al., 2014; Ferrara et al., 2014; Lu et al., 2013). Other authors, however, have observed the occurrence of interactions between coal and biomass during co-combustion and co-gasification (Wu et al., 2013; Seo et al., 2010) and during the co-pyrolysis of biomass and lignite (Zhang et al., 2007).

The results obtained from thermogravimetric analysis show that the blend components underwent independent thermal degradation. Consequently it should be possible to calculate the decomposition curves corresponding to the blends from the decomposition curves calculated for the briquette components (Figure 4) and the composition of the blends that make up the briquettes. The curves predicted for each briquette component and the percentage of the component in each briquette were used for the calculation. Table 4 presents a comparison of the experimental and calculated solid residues obtained for the four briquettes and includes the relative error. Although the differences are not very great it has to be taken into account that the pyrolysis experiments for the individual briquette components and the briquettes were performed using different amounts of mass (2 mg in the case of the briquette components vs 10 mg in the blends) which could be a source of error. Clearly therefore more work is needed to be able to predict the decomposition of the blends that make up the briquettes bearing in mind that the blends contain up to four components.

Conclusions

The pyrolysis of coal, sawdust, tar and four blends was studied by means of thermogravimetry. Kinetic parameters: activation energy and pre-exponential factor, associated with their thermal decomposition were obtained by means of the OFW, KAS and Coats-Refren method. The variation of the conversion and its derivative with time calculated using the kinetic parameters obtained are in agreement with the experimental curves for all

the blend components. The blend components underwent independent thermal degradation without apparent synergism. A comparison of the experimental solid yield and that calculated using the predicted curves of the briquette components indicated the need for further investigation.

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Table 1. Elemental and proximate analysis of the materials.

	P	SC	K	T
VM (wt.% db) ¹	22.7	78.8	14.6	65.9 ³
Ash (wt.%db)	7.8	1.3	8.4	--
C (wt.%db)	83.7	50.2	83.0	90.3
H (wt.%db)	4.8	5.7	3.9	4.7
N (wt.%db)	1.5	0.5	2.1	0.8
S (wt.%db)	0.75	0.00	0.48	0.38
O (wt.%db)	2.6	43.0	2.6	2.8
C/H ²	1.5	0.7	1.8	1.6
C/O ²	42.9	1.6	42.6	43.0

¹VM, volatile matter content on a dry basis (db). ² Atomic ratio. ³: From thermogravimetric analysis.

Table 2. Kinetic parameters of biomass, coals and tar, obtained using the OFW and KAS methods.

	P				K				SC				T			
	KAS		OFW		KAS		OFW		KAS		OFW		KAS		OFW	
x	Ea (kJ/mol)	R ²	Ea (kJ/mol)	R ²	Ea (kJ/mol)	R ²	Ea (kJ/mol)	R ²	Ea (kJ/mol)	R ²	Ea (kJ/mol)	R ²	Ea (kJ/mol)	R ²	Ea (kJ/mol)	R ²
0.1	319.8	0.995	315.2	0.995	174.6	0.998	177.8	0.998	132.0	0.987	134.1	0.988	--	--	--	--
0.2	300.0	0.993	296.8	0.994	200.9	0.984	203.2	0.986	146.8	0.999	148.4	0.999	221.0	0.992	217.5	0.992
0.3	249.2	0.991	248.7	0.992	207.2	0.974	209.5	0.978	172.5	0.999	173.1	0.999	179.4	0.978	178.4	0.980
0.4	271.4	0.986	270.0	0.987	208.1	0.949	210.8	0.955	178.2	0.969	178.7	0.972	168.1	0.996	168.0	0.997
0.5	296.0	1.000	293.6	1.000	195.4	0.858	199.3	0.874	157.1	0.911	158.8	0.920	172.6	0.989	172.7	0.990
0.6	261.3	0.968	260.9	0.971	223.0	0.739	226.3	0.764	160.6	0.910	162.3	0.920	178.3	0.980	178.6	0.982
0.7	295.2	0.840	293.6	0.852	285.3	0.685	286.4	0.708	139.3	0.843	142.1	0.891	186.6	0.989	186.9	0.990
Average	284.7	0.968	282.7	0.970	213.5	0.884	216.2	0.895	155.2	0.945	156.8	0.956	184.3	0.987	183.7	0.989

Table 3. Frequency factor A (s⁻¹) of biomass, coals and coal tar, using isoconversional and CR methods.

Material	10°C/min		20 °C/min		30 °C/min		R ²	
	KAS	OFW	KAS	OFW	KAS	OFW	KAS	OFW
P	7.52E+19	3.41E+19	3.76E+19	3.76E+19	7.72E+19	3.55E+19	0.968	0.970
K	3.90E+12	4.54E+12	7.08E+12	8.22E+12	4.98E+12	5.77E+12	0.884	0.895
SC	8.61E+12	9.78E+12	1.02E+13	1.15E+13	8.47E+12	9.58E+12	0.945	0.956
T	6.38E+38	3.39E+37	6.78E+38	3.67E+37	6.37E+38	3.50E+37	0.989	0.990

Table 4. Comparison between the experimental and calculated solid residues for the four briquettes.

Briquette	T (°C)	Residue exp (wt.%)	Residue calc. (%)	Relative Error (%)
B1	200	92.3	99.0	7.3
	300	86.0	95.3	3.2
	500	73.7	85.0	7.8
	620	69.1	76.4	17.2
B2	200	93.3	99.0	7.3
	300	87.5	95.5	3.4
	500	72.8	81.4	11.8
	620	67.8	70.9	23.2
B3	200	96.0	99.6	7.9
	300	94.1	98.7	7.0
	500	87.2	91.4	1.0
	620	81.4	83.1	10.0
B4	200	94.7	99.4	7.7
	300	91.6	98.1	6.3
	500	85.4	93.4	1.2
	620	81.1	86.4	6.3

Figure 1. Variation of x and dx/dt with temperature (T) at three heating rates (10, 20 and 30 °C/min) for the briquette components.

Figure 2. Determination of the activation energy by means of the KAS method for the components of the briquettes.

Figure 3. Determination of the activation energy by means of the OFW method for the components of the briquettes.

Figure 4. Comparison between experimental and calculated data using KAS-OFW-CR method for the coals (K and P), biomass (SC) and tar (T) at 10, 20 and 30 °C/min.

Figure 5. Variation of the conversion and its derivative versus time for the briquettes at 10 °C/min.

Figure 6. Variation of mass loss with temperature for the four briquettes. Experimental and calculated values.