

SIMULATION OF BIOMASS COFIRING WITH COAL BY ADICTION OF CELLULOSE AND LIGNIN

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ABSTRACT

Oxidation kinetics of cellulose, lignin, brown coal, and their mixtures were investigated. Using non-linear regression method kinetic parameters from thermogravimetric curves were calculated for oxidation of volatile matter and fixed carbon (char). The presence of the cellulose in the mixture affects the rate constant of lignin and brown coal oxidation which was determined by means of Arrhenius plots.

KEYWORDS: thermogravimetry, coal cofiring, cellulose, lignin

1. INTRODUCTION

The biomass and coal cofiring has got economical and environmental advantages compared to the coal combustion alone (Demirbas, 2003, Kolát et al. 2004). The biomass can be combusted directly in proper devices without an access of oxygen in order to crack lignin and cellulose macromolecules. The coal and the biomass are completely different in their composition and properties. For all biomass applications it is important to know its chemical composition and thermal behavior at oxidizing and inert conditions. Thermal analysis and thermogravimetry in particular allow to acquire the needed information in an easy and rapid way. In the study (Ghetti et al., 1996), a correlation between lignin content in biomass, a thermal behavior, and a quality of produced pyrolysis product is presented. Because the standardized lignin content determination is complicated, there has been suggested a method (Ghetti et al., 1996) using the thermal analysis for this assessment. The method allows a simultaneous characterization of the biomass samples from a variety of sources. The plant fuel basically contains two major compounds: a cellulose and a lignin. The cellulose structure is formed from high-molecular polysaccharides, whose long and fibred molecules arose by a formation of glycosidic bonds between saccharide molecules. The lignin structure consists of aromatic compounds mainly, which are bonded via an oxygen into the carbon skeleton. As a result of considerable structural differences between the compounds mentioned above, the thermoreactivity is fully distinct as well.

The objective of the study was to perform kinetic parameters measurement of a brown coal, cellulose, lignin, and their mixtures cofiring by using thermogravimetry method.

2. EXPERIMENTAL

Brown coal Dresden (HU) (moisture – 19.7%, volatile matter – 42.15%, fixed carbon – 32.64% and ash – 5.46%) was crushed, ground in the segmental mill, sieved and fractions below 100 µm were used for the measurements. Samples were prepared as a mixture of additives, cellulose powder Fluka (FC) and lignin Aldrich (AL).

The thermal analysis was carried out using simultaneous TG-DTA apparatus NETZSCH STA 409 EP. All experiments were conducted under the identical conditions: the simplex (10 mg in weight) were heated up to 1000°C in the crucibles (aluminum oxide) in a dynamic atmosphere of dry air (with a flow rate of 100 cm³ min⁻¹) at a heating rate of 10 deg min⁻¹.

A method of direct non-linear regression (Slovák, 2001) was used for calculation of apparent kinetic parameters of oxidation processes from thermogravimetric (TG) curves.

The calculation is based on the kinetic equation (1).

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) (1-\alpha)^n \quad (1)$$

If the time step is set small enough, the derivatives in Eq (1) may be replaced by differences. We assume that the TG curve is composed of very small linear segments of the length Δt , in which the reaction rate is constant:

$$\Delta\alpha = A \exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \Delta t \quad (2)$$

Where: α - the degree of conversion,
 t - time (s),
 T - absolute temperature
 R - molar gas constant (8.314 J K⁻¹ mol⁻¹),
 A - frequency factor (s⁻¹),
 E - activation energy (J mol⁻¹),
 N - the reaction order.

Assuming the α_0 and t_0 at the beginning of the α vs. t curve, further points of the curve can be calculated from the recurrence relation

$$\alpha_i = \alpha_{i-1} + A \exp\left(-\frac{E}{RT_{i-1}}\right)(1-\alpha_{i-1})^n (t_i - t_{i-1}) \quad (3)$$

If the TG curve consists of p various processes with kinetic parameters A_j , E_j and n_j ($j=1$ to p), Eq. (3) can be used for calculation of extent of conversion for individual reactions. In this case, the equation describing the whole curve can express as a sum of particular equations:

$$\alpha_i = \sum_j \alpha_{j,i-1} + \sum_j A \exp\left(-\frac{E_j}{RT_{i-1}}\right)(1-\alpha_{j,i-1})^{n_j} (t_i - t_{i-1}) \quad (4)$$

Last equation enables the determination of apparent kinetic parameters of multistep reactions by non-linear optimization.

In our calculations we assumed, that the coal and additives oxidation is the first-order reaction and that the effect of diffusion can be neglected under used experimental conditions.

3. RESULTS AND DISCUSSION

Thermal analysis of pure components (cellulose – FC , lignin – AL), and their mixture ($FCAL$ 4:1) was carried out according to the conditions described in the chapter 2.

The DTG results are presented in Figure 1.

These curves are called „burning profiles“, and enable to obtain preliminary information regarding the combustion of carbonaceous materials (Norton 1993). The IT_{vm} values (volatile matter initiation temperature), PT_{vm} (peak temperature at which the maximum combustion of volatile matter occurs) and analogically PT_{fixC} for fixed carbon were determined from the DTG curves. The burnout temperature (BT) is the temperature at which the rate of weight loss becomes less than 1% per minute. This temperature

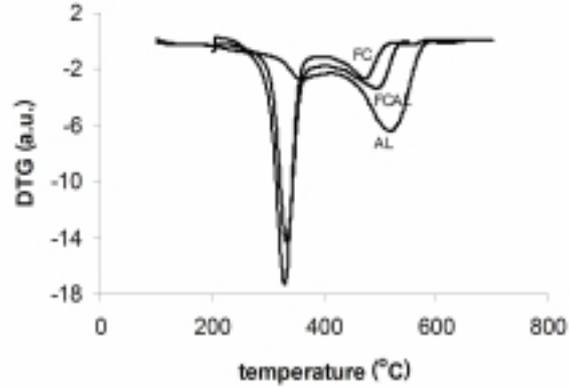


Fig. 1 DTG curves of oxidation of cellulose (FC), lignin (AL), and their mixtures ($FCAL$ 4:1)

can also have important combustion implications relating to the residence time and the furnace temperature. The values of the parameters mentioned above for two steps are presented in Table 1.

Table 1 Temperature parameters of studied samples (°C)

SAMPLE	IT_{vm}	PT_{vm}	PT_{fixC}	BT
AL	333	358	519	553
FC	314	330	475	491
$FCAL_{exp}$	312	333	494	518
$FCAL_{calc}$	317	335	484	503

The $FCAL_{calc}$ values were calculated by the linear addition rule:

$$IT_{vm}(FCAL_{calc}) = x_1 IT_{vm}(FC) + x_2 IT_{vm}(AL) \quad (5)$$

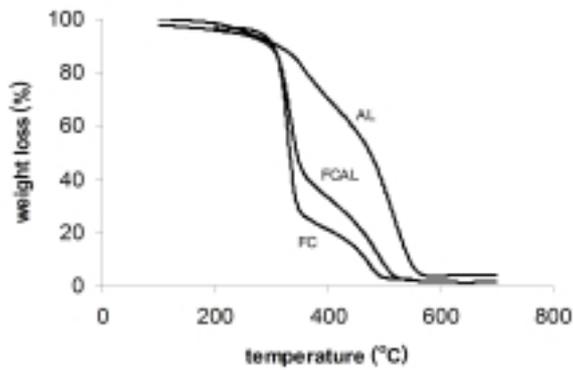
Where x_i is the weight fraction of each material in the blend. According to the results shown in Table 1 it is apparent, that the best consistency is for PT_{vm} , where the difference between experimental and calculated values is 2 °C only.

Within the context of the biomass DTG curves, Ghetti 1996 proposed a method of lignin content determination from the height of second step peak. However, these results may be incorrect, because the peak represents rather of fixed carbon oxidation.

In our study, we have calculated the kinetic parameters and the weight ratio of both steps on the TG curve (Fig. 2) for samples FC , AL , and $FCAL$ 4:1. The results are presented in Table 2 also including calculated values for mixture of cellulose and lignin with coal. The mass ratios of FC (75.13%) and AL (44.27%) were employed for calculation of mass ratio $(FCAL)_{calc} = 66\%$, and experimental value for the first step was determined to be 60%. We can assume that

Table 2 The kinetic parameters of studied samples

Sample	Step	E (kJ mol ⁻¹)	A (s ⁻¹)	W (%)
AL	1	44	$6.64 \cdot 10^0$	44.27
	2	165	$3.92 \cdot 10^8$	55.73
FC	1	273	$5.55 \cdot 10^{21}$	75.13
	2	106	$1.64 \cdot 10^5$	27.87
FCAL 4:1	1	192	$3.01 \cdot 10^{14}$	59.34
	2	84	$3.14 \cdot 10^3$	40.66
HU	1	86	$1.79 \cdot 10^4$	62.21
	2	132	$1.34 \cdot 10^7$	37.79
HUAL 3:1	1	47	$1.49 \cdot 10^1$	50.86
	2	55	$7.45 \cdot 10^{-1}$	49.14
HUFC 3:1	1	117	$1.57 \cdot 10^8$	86.13
	2	157	$2.11 \cdot 10^{10}$	13.87

**Fig. 2** TG curves of oxidation of cellulose (FC), lignin (AL), and their mixtures (FCAL 4:1)

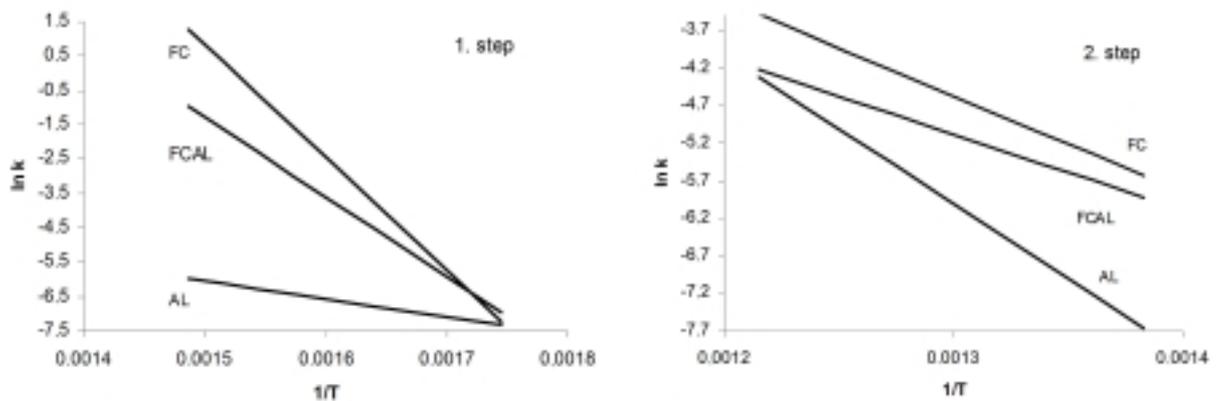
the weight losses in the first step fulfil the addition rule as well.

The Arrhenius plots were calculated for oxidation of cellulose, lignin, and their mixtures by means of the activation energy and the frequency factor values. The results are shown in Figure 3.

It is obvious that the oxidation of the volatile matter and the fixed carbon proceed analogically for pure components in the both steps. The rate constants of mixtures oxidation occur between the Arrhenius plots of lignine and cellulose. In the first step, the difference between the rate constants of components and mixture is very small at low temperatures and as the temperature increases, the difference increases as well.

Further, the thermal analyses of brown coal (HU) and its mixtures (HUFC 3:1, HUAL 3:1) were carried out and the results are presented in Figure 4.

The TG curve of HU is similar to the curve of the mixture HUAL and therefore the HU curve is not

**Fig. 3** The Arrhenius plots for oxidation of cellulose (FC), lignin (AL), and their mixtures (FCAL 4:1)

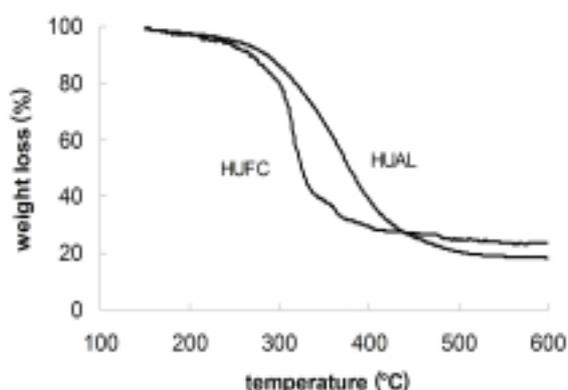


Fig. 4 TG curves of oxidation of the mixtures (HUFC 3:1, HUAL 3:1)

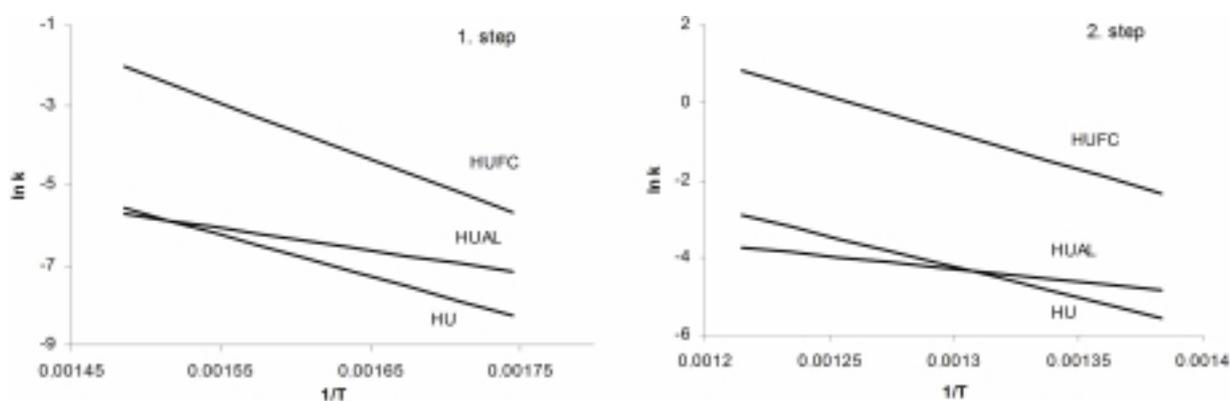


Fig. 5 The Arrhenius plots for oxidation of brown coal (HU) and its mixtures (HUFC 3:1, HUAL 3:1)

presented in Figure 4. The kinetic parameters were calculated from the TG curves of HU, HUFC, and HUAL samples (see Table 2). The corresponding Arrhenius plots are presented in Figure 5.

From the Figure 5, it is apparent that the oxidation course of the mixtures HUFC and HUAL is similar to the oxidation of the cellulose and the lignin. The rate constants of HUFC oxidation are higher than the constants of HUAL oxidation for entire temperature range. This finding is true for the oxidation of volatile matter and fixed carbon as well.

3. CONCLUSIONS

Characteristic thermal parameters (IT_{vm} , PT_{vm} , PT_{fixC} , BT) of oxidation of cellulose, lignin, and their mixtures were determined by the DTG curves (burning profiles). The parameters fulfil the addition rule, mainly in case of the peak temperature (PT_{vm}) at which the maximum combustion of volatile matter occurs. Determined kinetic parameters (activation

energy and frequency factor) enabled the calculation of the Arrhenius plots for cellulose, lignin, brown coal, and their mixtures oxidation. According to these plots of mixtures: cellulose + lignin, coal + cellulose, and coal + lignin resulted following findings: (a) the cellulose affects oxidation rate of volatile matter from lignin and oxidation of fixed carbon, significantly, (b) same conclusion can be made for oxidation of the mixture containing brown coal and cellulose, (c) the oxidation rate of brown coal and lignin mixture differs from coal oxidation rate slightly.

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