

A thermal analysis calculation of pharmaceutical wastewater sludge

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Abstract Thermal pyrolysis of pharmaceutical wastewater sludge, brown coal, and sludge-coal blends were studied by TG dynamic runs carried out at 20 °C min^{-1} in the temperature range from 25 to 850 °C. Different possible kinetic models of thermal decomposition have been considered. The best models of mechanism function for brown coal, pharmaceutical wastewater sludge, and coal–sludge blends are a first-order reaction, a N -dimensional nucleation, and growth reactions with $N = 2$ and 4, respectively. The Arrhenius kinetic parameters for brown coal, pharmaceutical wastewater sludge, and coal–sludge blends are proposed.

Keywords Thermal pyrolysis · Coal–pharmaceutical wastewater sludge blends · Thermogravimetric analysis · Kinetic models · Thermal decomposition

Introduction

Sludge has been landfilled, incinerated, placed in the ocean, or used in agriculture [1]. The disposal of sludge on reclaimed land is no longer a viable solution because farmland sludge applications are limited by the uptake capacity of the soil in addition to the potential pollution by heavy metals [2]. Sludge incineration, however, enjoys a combination of several advantages, including a large reduction of sludge volume to a small stabilized ash and thermal destruction of toxic organic compounds and pathogens. Further, the calorific value of dry sludge may be

recovered through incineration [3]. Pyrolysis is an alternative thermal process in which decomposition of the organic matter takes place without air. The production of carbon, tar, and gases may be useful raw material for chemical industries. In order to increase the quality of gases, the possibility of a joint pyrolysis of sewage sludges and coal in reactors can be an interesting option. In this sense, it is important to ascertain the thermal behavior of sludges not only in conditions of mono-pyrolysis but also of co-pyrolysis with coal, so the process can be controlled and streamlined. Igarashi et al. [4] used a dual-fluidized bed reactor to pyrolyze municipal solid waste. Piskorz et al. [5] studied the flash pyrolysis of sewage sludge considering the formation of organic liquids and char in a bench-scale fluidized bed reactor. Kaminsky et al. [6] pyrolyzed digested sewage using the Hamburg process. Caballero et al. [7] analyzed the formation of primary and secondary products in the pyrolysis of sewage sludge considering the formation of hydrocarbons and carbon oxides measured by the combination of a primary pyrolyzer and a secondary reactor. Kasakura and Hasatani [8] studied the processes of drying and pyrolysis of sludges considering the economics of different alternatives. Co-pyrolysis of coal–sewage sludge mixtures was investigated using an electrically heated entrained flow reactor [9]. The composition and tar yield of pyrolysis gas were determined. The pyrolysis process of oil sludge and sewage sludge in fluidized bed reactor were studied in fluidized bed reactor [10, 11]. They found that the distribution of products depended on the feed material and the pyrolysis conditions. Pyrolysis of activated sewage sludge was investigated under inert conditions in a fluidized bed [12, 13]. The effects of temperature and gas residence time on the product distribution and composition were studied. Koch and Kaminsky pyrolyzed refinery sewage sludge,

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using the products obtained in the plant (oil and gas), and reduced the waste disposal [14].

The thermogravimetric analysis (TG) is one of the techniques used to study the primary reactions in the decomposition of solids since the heating rate is low and the cracking of primary products is negligible. The interpretation of the experimental data can provide information on the composition of the material, order of reaction, number of different processes that take place in the reaction, and the corresponding kinetic constants. It is also common to find a set of dynamic TG experiments fitted to a kinetic model in which the activation energy and pre-exponential factor were obtained. Hence, TG and differential thermogravimetric profiles (DTG) provide a means for the preliminary assessment of pyrolysis process. This information can then be used to forecast the product of yield and reactor design. The pyrolysis of sewage sludge was examined by thermogravimetric analysis using different heating rates, particle sizes, and final temperatures [2]. Font et al. [15] studied the pyrolysis and combustion of sewage sludge by TG dynamic runs at $15\text{ }^{\circ}\text{C min}^{-1}$. Two different behaviors of pyrolysis of sewage sludges were observed. Otero et al. [16] investigated the behavior of three different sludges and blends mixed with coal by means of a thermogravimetry. The kinetic parameters of drying and pyrolysis of sewage sludges have been determined in an inert gas condition. The activation energy and pre-exponential factor of sludges were determined from mathematical evaluation of TG or DTG curves. The use of TG-MS techniques is established for the characterization of gaseous products arising from thermal degradation of sludges [17, 18]. The reaction kinetics of drying, pyrolysis, and combustion of paper sludge have been determined in a thermogravimetric analyzer at the heating rate of $5\text{--}30\text{ }^{\circ}\text{C min}^{-1}$ [19]. The kinetic parameters of paper sludges were determined. The influence of the different pyrolysis conditions (e.g., temperature and heating rate) on the reactivity, in air and in CO_2 , of municipal sewage sludge was investigated [20]. The pyrolysis and combustion of sewage sludges were studied by TG dynamic runs carried out at $15\text{ }^{\circ}\text{C min}^{-1}$ [21]. The devolatilization of paper and sewage sludges and coals was studied by TG balance, wire mesh reactor, and electrodynamic balance [22]. Thermogravimetric analysis was employed in the investigation of thermal decomposition of sewage sludge. The kinetic parameters of drying, pyrolysis, and gasification of sewage sludge were determined in an argon gas [23]. The first-order kinetic parameters, such as activation energy and pre-exponential factor, were calculated from TG dynamic runs carried out at $10\text{ }^{\circ}\text{C min}^{-1}$ in the temperature range from 25 to $800\text{ }^{\circ}\text{C}$, considering the process as a series of consecutive first-order reactions.

Due to the technological properties of pharmaceutical wastewater sludge (volatile matter, ash and fixed carbon), unlike the coal, significant differences in the pyrolysis profiles must be expected. This may have an important influence on pyrolysis efficiency. Studies on TG and DTG profiles can contribute to enhance the knowledge of this process and, therefore, to establish the optimum operational conditions. The objective of this study was to study the pyrolysis of brown coal and pharmaceutical wastewater sludge, as well as their blends. A kinetic analysis was performed to fit the experimental results and verify the reactivity change when the pharmaceutical wastewater sludge was added to coal. The Arrhenius kinetic parameters were determined from the experimental results. The models of the mechanism function of pharmaceutical wastewater sludge and blends were proposed to determine a kinetic model capable of accounting their thermal decomposition.

Experiments

The pharmaceutical wastewater sludge samples were obtained from a pharmacy wastewater treatment plant located in Harbin of Heilongjiang province. In each test, two kilograms of pharmaceutical wastewater sludge were pretreated. The sample was heated to $105\text{ }^{\circ}\text{C}$ for 24 h and then kept in a desiccator for further use. The pharmaceutical wastewater sludge element contents are listed in Table 1. Every analysis was performed in triplicate. Blends of brown coal and pharmaceutical wastewater sludge were prepared with the content of 33.3 and 46.46 wt%, respectively.

Thermogravimetric analysis was carried out in a ZRY-2P Model TGA equipment. Samples of around 10 mg were used. The experiments were repeated three times to evaluate their reproducibility. The heating rate was $20\text{ }^{\circ}\text{C min}^{-1}$. Pure nitrogen was used as inert gas to prevent the presence of air in the pyrolysis and to remove the gaseous and condensable products evolved during the pyrolysis, thus reducing the secondary reaction effects within the hot solid residue. A constant flow rate of 100 mL min^{-1} was fed in the apparatus. The nitrogen flowrate prevented volatile products to remain close to the devolatilizing particles in the crucible, thus ensuring an inert atmosphere during the runs.

Kinetic theory of pyrolysis

According to non-isothermal kinetic models, the kinetic equation of solid thermal decomposition is given as follows:

Table 1 Volatilized and element content of raw sewage sludge and brown coal

	Pharmaceutical sludge	Brown coal
Water content of fresh sludge/%	86.2	13
Volatilized solid content/%	54.23	29.12
Carbon content/%	4.7	36.3
Hydrogen content/%	5.6	30.1
Nitrogen content/%	2.1	0.85
Sulfur content/%	1.7	0.38
Chlorine content/%	<0.01	–
Net heating value/kJ kg ⁻¹	16031	20962

*All calculations were based on the weight of sludge that 105 °C oven dried and at least triplicates were carried out

$$\frac{d\alpha}{dT} = \frac{A}{\beta} f(\alpha) \exp\left(-\frac{E}{RT}\right) \quad (1)$$

where α is the fraction extent of reaction in time t , and is expressed as $(w_i - w_t)/(w_i - w_f)$, where w_i is the initial weight, w_t is the weight at a specific temperature, and w_f is the final weight. β is the heating rate, E is the activation energy, A is the pre-exponential factor, and $f(\alpha)$ is the kinetic differential function. Its integral form is as follows:

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT. \quad (2)$$

Using the experimental data, the pre-exponential factor A can be obtained from the intercept and the energy of activation from the slope of the plot. It can be seen that the Arrhenius kinetic parameters A and E depend upon the function $G(\alpha)$.

In order to obtain the pre-exponential factor and the energy of activation, the difference differential method is used. The calculation procedure is as follows: The first determining mass-loss conversion and rate; reciprocal of temperature at some points on the TG curve; then their differences between two adjacent points can be determined from one thermal analysis curve. Since the activation energy value is dependent on the slope of the plot, the linearity of the plot will affect the accuracy of the determination of this value. The method of least square is used to correlate with TG data. The regressing correlation coefficient, R , can be obtained. Usually, the value of R from the kinetic plot would be indicative of the linearity of the slope of the plot. Its value is generally used to measure the goodness-of-fit of a line when applied to scatter plots. Comparing with values of R using the different mechanism function $G(\alpha)$, a more sound mathematical model of $G(\alpha)$ with highest of R can be determined.

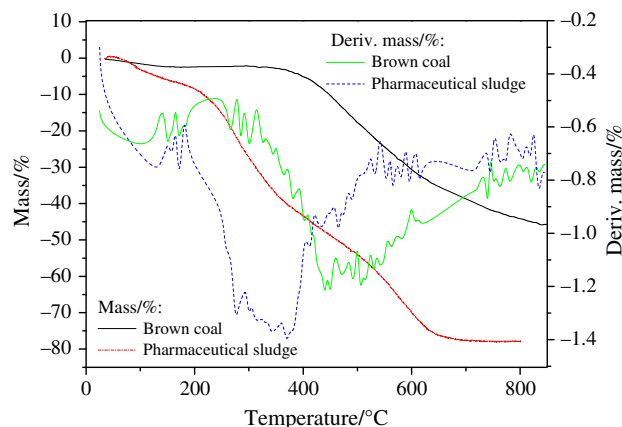


Fig. 1 A plot of TG and DTG signal for brown coal and pharmaceutical wastewater sludge at a heating rate of 20 °C min⁻¹ using an atmosphere of nitrogen at a flow rate of 100 mL min⁻¹

Results and discussion

The experimental variations of the weight fraction versus temperature in the dynamic runs carried out at 20 °C min⁻¹ in an inert atmosphere were obtained. Figure 1 shows the evolution of the TG and DTG of the brown coal and pharmaceutical wastewater sludge as a function of temperature. It can be seen that a peak in the DTG curves at the range from 51.2 to 129.8 °C with a maximum around 98.2 °C for the coal sample, and at the range from 40.1 to 159.3 °C with a maximum around 100.2 °C for the pharmaceutical wastewater sludge. Corresponding decrease can be observed in the TG, which is attributed to the loss of physically adsorbed water. It is obvious that the devolatilization process of pharmaceutical wastewater sludge shifts to higher temperatures than the corresponding ones for coal.

From TG curves, it can be seen that the devolatilization of coal and pharmaceutical wastewater sludge sample undergoes a continuous weight loss. The beginning devolatilization temperature and the maximum weight loss temperature can be evaluated from TG and DTG curves.

For the pharmaceutical wastewater sludge, the devolatilization starts at 179.7 °C, and the weight loss at the final temperature is 44.6%. The peak of the devolatilization rate has a maximum value of 0.02167 mg s⁻¹ at a temperature of 370.6 °C. For brown coal, the devolatilization starts at 325 °C, and a higher peak occurs between 443 and 606 °C with a maximum devolatilization rate of 0.00665 mg s⁻¹ at 513 °C. After the devolatilization, the global weight loss is 46.1%.

Table 2 shows the values of the energy of activation, pre-exponential factor, and regressing correlation coefficients using the different models of mechanism function $G(\alpha)$. The values of R vary with models of mechanism function. It can be seen that for brown coal the best

Table 2 Calculated correlation coefficient using 25 models of mechanism function

	Pharmaceutical sludge			Brown coal			Coal–sludge blend No. 1			Coal–sludge blend No. 2		
	$E/\text{kJ mol}^{-1}$	$\lg A/\text{s}^{-1}$	R	$E/\text{kJ mol}^{-1}$	$\lg A/\text{s}^{-1}$	R	$E/\text{kJ mol}^{-1}$	$\lg A/\text{s}^{-1}$	R	$E/\text{kJ mol}^{-1}$	$\lg A/\text{s}^{-1}$	R
1	34.589	-1.330	0.8988	57.542	2.614	0.9252	45.564	-1.040	0.9318	48.351	-0.939	0.9657
2	38.123	-1.250	0.9216	49.663	2.689	0.8509	49.181	-0.996	0.9466	52.279	-0.875	0.9752
3	40.407	-1.310	0.9339	59.887	2.718	0.8373	51.823	-1.050	0.9545	55.155	-0.918	0.9799
4	42.645	-1.430	0.9435	51.995	2.798	0.6648	54.554	-1.150	0.9606	58.130	-1.000	0.9831
5	39.776	-1.730	0.9295	46.559	2.602	0.4566	52.170	-1.390	0.9516	55.536	-1.250	0.9776
6	31.661	-2.620	0.8750	55.258	2.803	0.6832	45.620	-2.080	0.9125	48.429	-1.970	0.9472
7	28.596	-2.970	0.8483	50.324	2.518	0.7241	43.186	-2.350	0.8925	45.786	-2.250	0.9295
8	2.223	-3.110	0.3420	60.491	2.663	0.8941	11.797	-2.570	0.6599	13.076	-2.500	0.6945
9	5.014	-2.920	0.6513	64.063	2.680	0.9690	14.544	-2.410	0.7583	15.972	-2.330	0.7905
10	13.388	-2.340	0.9146	48.357	2.553	0.2145	22.784	-1.930	0.9109	24.662	-1.840	0.9368
11	30.136	-1.180	0.9568	42.537	2.541	0.1013	39.263	-0.973	0.9663	42.041	-0.854	0.9858
12	46.884	-2.880	0.9583	51.268	2.773	0.7546	55.743	-1.500	0.9622	59.421	0.135	0.9787
13	80.379	2.284	0.9561	76.883	2.778	0.6644	88.702	1.902	0.9453	94.180	2.114	0.9589
14	113.870	4.597	0.9544	58.334	2.633	0.8431	121.660	3.819	0.9338	128.930	4.094	0.9461
15	7.241	-2.990	0.6863	69.982	2.719	0.7369	17.694	-2.440	0.7877	19.127	-2.380	0.8278
16	20.915	-2.160	0.8740	62.116	2.696	0.8916	31.629	-1.740	0.9137	33.739	-1.660	0.9515
17	34.589	-1.330	0.8988	74.553	2.769	0.4266	45.564	-1.040	0.9318	48.351	-0.939	0.9657
18	11.866	-3.100	0.8550	70.469	2.759	0.4986	22.997	-2.550	0.8526	24.898	-2.460	0.8811
19	11.269	-3.040	0.8439	79.367	2.840	0.8725	22.189	-2.500	0.8493	24.017	-2.410	0.8794
20	11.089	-2.580	0.8633	60.112	2.722	0.9007	20.856	-2.120	0.8758	22.561	-2.040	0.9082
21	10.150	-2.980	0.8150	79.627	2.861	0.1589	20.823	-2.450	0.8382	22.529	-2.370	0.8712
22	10.036	-2.690	0.8282	74.273	2.849	0.3741	19.982	-2.210	0.8553	21.611	-2.130	0.8904
23	2.903	-3.160	0.3240	69.998	2.844	0.8347	13.471	-2.560	0.6658	14.549	-2.510	0.7116
24	21.816	-1.460	0.9576	68.572	2.799	0.8896	30.000	-1.220	0.9482	32.552	-1.090	0.9517
25	7.241	-2.990	0.6863	45.753	2.754	0.4026	17.694	-2.440	0.7877	19.127	-2.380	0.8278

formulation of mechanism function $G(\alpha)$ is a first-order reaction

$$G(\alpha) = -\ln(1 - \alpha). \quad (3)$$

For the pharmaceutical wastewater sludge, the optimum model is a N -dimensional nucleation and growth reactions with $N = 4$:

$$G(\alpha) = -\ln(1 - \alpha)^4. \quad (4)$$

In the gasification processes, the heating value of the blend should be considered. In the present case, the pharmaceutical wastewater sludge has a heating value of only 11 MJ kg^{-1} and should be considered unstable in a direct gasification process. Therefore, this allows pharmaceutical wastewater sludge fuels to be co-fired with a coal, thus recovering the pharmaceutical wastewater sludge energy content. Blending up to 50 wt% of pharmaceutical wastewater sludge with coal, the net heating value of blend with a 15.6 MJ kg^{-1} can be obtained. This blend is considered suitable for a gasification process.

The thermogravimetric analysis has been conducted for the coal–pharmaceutical wastewater sludge blends

prepared. The TG and DTG curves of the coal–pharmaceutical wastewater sludge blends are reported in Figs. 2 and 3 with 54.54 and 66.7 wt% of coal as a function of temperature. The net heating values of the blends are 16.1 and 17.4 MJ kg^{-1} , respectively. Comparing with Fig. 1,

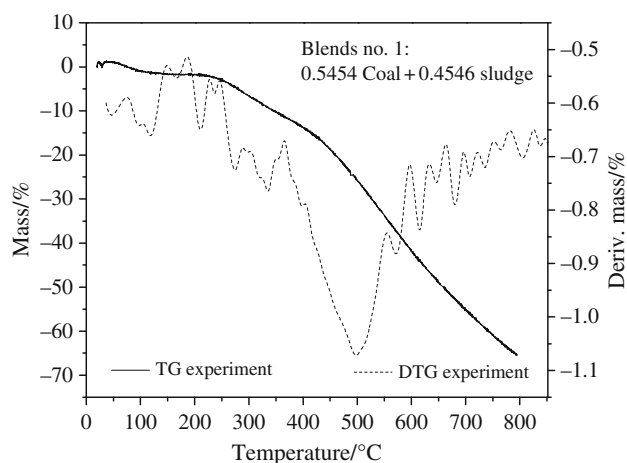


Fig. 2 TG and DTG profiles of blends sample 1 at a heating rate of 20 °C min^{-1} in an atmosphere of nitrogen

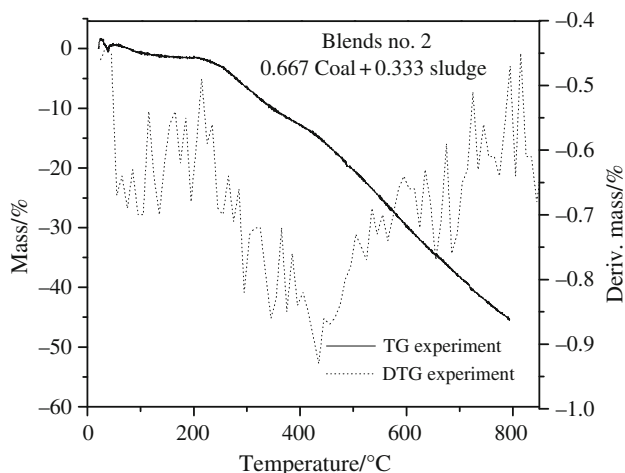


Fig. 3 TG and DTG profiles of blends sample 2 at a heating rate of 20 °C min⁻¹ in an atmosphere of nitrogen

the curve for each blend lies between that of the coal and the pharmaceutical wastewater sludge. The devolatilization starts at 191.1 and 195.2 °C for blend sample 1 and 2, respectively. The temperature at the maximum of weight loss is at 195.23 and 498.36 °C. From these curves, it was possible to verify that the weight loss curve of each blend was the sum of the weight loss curves of the coal and the pharmaceutical wastewater sludge. The weight loss of blends may be written as:

$$Y_{\text{blend}} = x_{\text{coal}} Y_{\text{coal}} + x_{\text{sludge}} Y_{\text{sludge}} \tag{5}$$

Fig. 4 Experimental and calculated curves for blends No. 1 and No. 2 at a heating rate of 20 °C min⁻¹ in an atmosphere of nitrogen

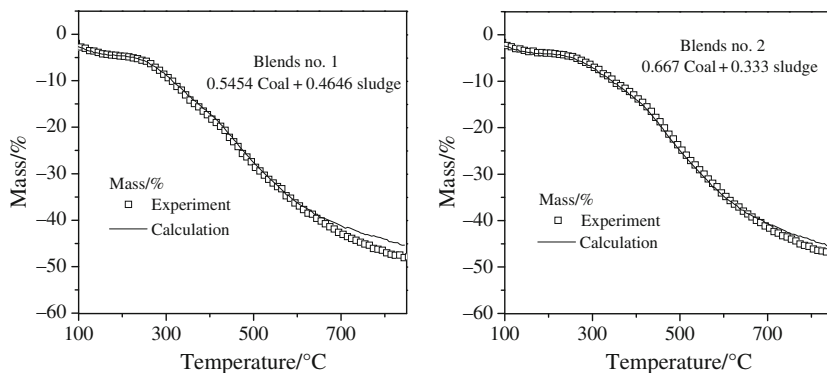
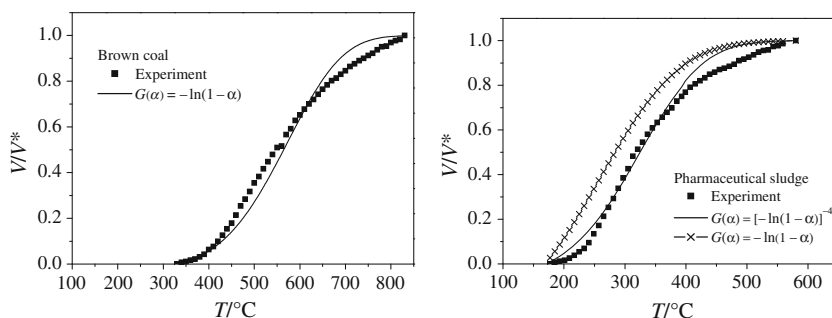


Fig. 5 Predicted volatile of brown coal and pharmaceutical wastewater sludge



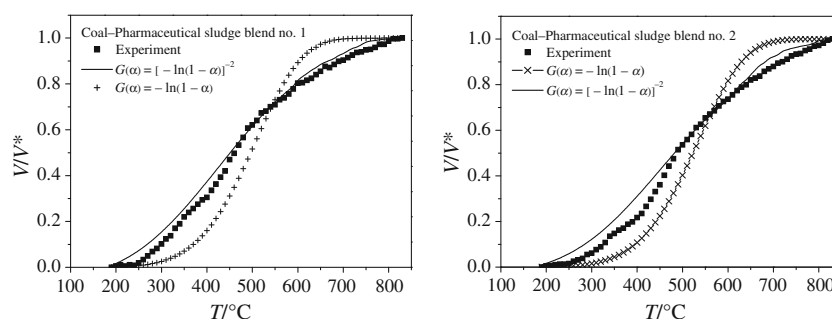
where x is the weight fraction of each material in the blend, Y is the weight loss of each material in the same operative condition.

In Fig. 4, the experimental and calculated weight loss curves are compared. The slight differences may be explained within the experimental error range at the high temperature. So it is worth noting that during the devolatilization process of the blends studied, no interaction and no effect caused by the different rate of devolatilization or by the different quantity of volatile released were observed. The thermal decomposition of pharmaceutical wastewater sludge is not affected significantly by the presence of coal; coal as well does not seem to be influenced by the release of volatile matter from pharmaceutical wastewater sludge, in the conditions of this study.

In fact, each component of the mixture blends behaves individually, with no interactions with the other material. Further, the nitrogen flowrate present during the TG runs prevents the volatile products to remain close to the devolatilizing material, ensuring an inert atmosphere on the sample during the run.

In other words, the coal pyrolysis, which occurs later than the pharmaceutical wastewater sludge pyrolysis, is not affected by the presence of oxygenated species released from the pharmaceutical wastewater sludge in the early stages of the experiment. From the plot of $\ln[(d\alpha/dt)/f(\alpha)]$ against $1/T$, the energy of activation and pre-exponential factor were obtained for blends sample No. 1 and 2. Table 2 shows the values of energy of activation, pre-

Fig. 6 Predicted volatile of coal–sludge blends No. 1 and 2



exponential factor, and R using the different mechanism function $G(\alpha)$. It can be seen that for the coal–pharmaceutical wastewater sludge blends the best model of mechanism function is a N -dimensional nucleation and growth reactions with $N = 2$:

$$G(\alpha) = [-\ln(1 - \alpha)]^2. \quad (6)$$

Substituting Eqs. 4 and 6 into 1 and integrating, it gives

$$v = v^* \left\{ 1 - \exp \left[\left(-\frac{A}{\beta} \int_{T_1}^{T_2} \exp \left(-\frac{E}{RT} \right) dT \right)^{\frac{1}{2}} \right] \right\} \quad (7)$$

$$v = v^* \left\{ 1 - \exp \left[\left(-\frac{A}{\beta} \int_{T_1}^{T_2} \exp \left(-\frac{E}{RT} \right) dT \right)^{\frac{1}{2}} \right] \right\} \quad (8)$$

For the first-order reaction, the volatile releasing pyrolysis is expressed as follows

$$v = v^* \left\{ 1 - \exp \left(-\frac{A}{\beta} \int_{T_1}^{T_2} \exp \left(-\frac{E}{RT} \right) dT \right) \right\} \quad (9)$$

where v^* is the volatile content at the final temperature.

Figure 5 shows the predicted volatile of brown coal and pharmaceutical wastewater sludge as a function of temperature. It indicates that the predicted volatiles of coal are in good agreement with experiments using the model of first-order reaction.

Figure 6 shows the predicted volatile as a function of temperature for blends sample No. 1 and 2. Using the mechanism function of Eq. 6 the predicted volatile of coal–pharmaceutical wastewater sludge blends coincide with experimental results.

Conclusions

Temperature-programmed pyrolysis has been shown to offer quite relevant information about the pharmaceutical wastewater sludge and the coal–pharmaceutical sludge blends decomposition process. The pyrolysis of pharmaceutical

wastewater sludge was different from that of coal, volatile materials being given off at lower temperatures. The coal–pharmaceutical wastewater sludge blends showed an intermediate behavior between sludge and coal, which might be predicted from the weighted sum of the blend components. The results of kinetic analyses showed that the first-order reactions together with Arrhenius law could not reasonably explain the different stages of weight loss found for pharmaceutical wastewater sludge and blends.

For brown coal, the pyrolysis process could be described using the first-order reaction model. For the pharmaceutical wastewater sludge and coal–pharmaceutical wastewater sludge blends, the best model of mechanism function was a N -dimensional nucleation and growth reactions with $N = 4$ and 2, respectively. The predictions of volatile content of pharmaceutical wastewater sludge and coal–pharmaceutical wastewater sludge blends using the reaction model of $G(\alpha) = -\ln(1 - \alpha)^4$ and $G(\alpha) = [-\ln(1 - \alpha)]^2$ were in agreement with experimental date.

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