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Devolatilization and Combustion Kinetics of Low-Rank Coal Blends from Dynamic Measurements

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The aim of this work was to investigate the devolatilization and combustion behavior of some low-rank coals and their blends to gather data useful for the development of the coprocessing of these fuels. Nonisothermal thermogravimetry experiments were carried out in inert and air atmospheres, over the temperature range of 25−850 °C, at a heating rate of 20 °C/min, and with a material particle size of −100 μm. Four blending ratios were used. The samples presented similar thermochemical reactivities. The differential thermogravimetric data for devolatilization were fitted successfully to an independent, first-order parallel reactions model, while those for combustion were fitted to a power law model. Blending did not cause any significant interactions during devolatilization in the solid phase, so that the thermal conversion of blends could be sufficiently predicted based on the thermogravimetric data of the individual fuels. However, this was not true in the case of char combustion.

Introduction

The rational use of coals is of most importance because this energy source is widely distributed around the world. Brown coals constitute the major energy resource in Greece. Of the 6.7 billion tons of proven reserves, 3.85 billion tons are mineable, while indicated reserves amount to 1.6 billion tons and inferred reserves are estimated at 2.3 billion tons. The annual lignite production is over 63.5 million tons, which makes Greece the second-largest lignite producer in the European Community market.[1] This amount covers 70% of the demand for electricity production; however, it is characterized by high ash contents (30−50%), which results in a lower availability and a higher running cost of the plants as well as in environmental pollution.

A key to the confident use of lower quality coals is probably blending. Coals can be blended to provide a fuel that possesses better combustion properties and behavior than those of the component coals by themselves. They are also blended to help solve existing problems at power stations, improve boiler performance, meet emission limits, and reduce costs. On the other hand, a blended product, closely resembling the design coal specification, may not burn in the same way. Interactions can occur between the component coals, which may or may not be beneficial.[2,3] Thus, the compatibility of the alternate coal with respect to the combustion performance has to be properly evaluated.

A deep knowledge of the thermal behavior and the reactivity of the blends during devolatilization and combustion is necessary for developing predictive models for these processes. However, because these involve a complex set of reactions, accurate kinetics is not easy to obtain. Thermal analysis techniques, such as thermogravimetric analysis (TGA), have been widely used in recent years[4−15] because they provide a rapid quantitative method for the examination of these processes under nonisothermal conditions and enable the estimation of the effective kinetic parameters for the various decomposition reactions.

Several methods are available for the evaluation of TGA data for kinetic purposes, with the great majority being referred to individual coals. Very few studies deal with the kinetics of coal blends.[11,16] The most common approach approximates the overall process as a first-order decomposition occurring uniformly throughout the particle.[4−6,8−10,14,15,17] However, for many authors, a simple first-order model is inadequate, and the coal pyrolysis or combustion is described as a series of consecutive or parallel first-order/nth-order processes occurring in different time and temperature intervals.[12,18−23] The differences in the kinetic parameters reported by these studies are related to the experimental methods, operating conditions, data analysis, and chemical composition of the raw materials used.

In this work, TGA data from different low-rank coals and their blends have been investigated in nitrogen and air and kinetic models have been developed. The aim was to obtain some information on the pyrolysis and combustion of these fuels, as a first step necessary for the evaluation of their cofiring, in an effort for the rational use of poor coals.

Experimental Section

Materials. A lignite from the Ptolemais basin, a dry lignite from the briquetting plant of Ptolemais−Amynteon, and one peat from the Phillipous basin, in northern Greece, as well as blends of the lignite with each of the other coals in proportions 80:20, 60:40, 40:60, and 20:80, were used in this work. After air-drying, the samples were milled and sieved to the desired particle size. The characterization of these samples is shown in Table 1. The proximate analysis was carried out according to the ASTM standards (D3172-89), the ultimate analysis was performed using a LECO CHN-600 type analyzer, and the calorific value was determined using a LECO AC-300 type calorimeter.

TGA. The experimental system used was a TGA/differential thermogravimetry (DTG) Perkin-Elmer thermobalance (precision of temperature measurement ±2 °C; microbalance sensitivity <5 μg), with which the sample weight loss and rate of weight loss as functions

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Table 1. Proximate Analysis, Ultimate Analysis, and Calorific Values of Pure Samples, on a Dry Basis

sample	volatile matter (%)	fixed carbon (%)	ash (%)	C (%)	H (%)	N (%)	O (%)	S (%)	HHV (MJ/kg)
Ptolemais lignite	45.19	25.95	28.86	40.60	4.11	1.57	24.02	0.84	14.9
Ptolemais dry lignite	45.24	39.96	14.80	51.21	5.13	1.68	26.50	0.68	20.0
Phillipous peat	50.55	23.26	26.19	37.92	4.56	2.45	28.05	0.83	13.8

Table 2. Reproducibility of Experiments

sample	atmosphere	deviation between two identical experiments (%)
Ptolemais lignite	nitrogen	0.08
	air	0.11
Ptolemais dry lignite	nitrogen	0.06
	air	0.37
Phillipous peat	nitrogen	0.08
	air	0.29

of time or temperature were recorded continuously, under dynamic conditions, in the range 25–850 °C. The experiments were carried out at atmospheric pressure, under a nitrogen/air atmosphere, with a flow rate of 45 mL/min, at a linear heating rate of 20 °C/min. Preliminary tests with different sample masses and sizes and gas flow rates were carried out to check the influence of heat and mass transfer. Small masses (20–25 mg) of each material, thinly distributed in the crucible, and particle sizes of −100 μm were found proper to be used in the experiments to eliminate the effects of eventual side reactions and mass- and heat-transfer limitations.

The experimental procedure for obtaining a typical thermogram was as follows: The sample under testing was uniformly spread and weighed directly into the crucible. After flushing with nitrogen, the temperature was increased to 110 °C in order to dry the sample. After a drying period of 30 min, the temperature was increased to the desired value of 850 °C at the preselected heating rate and held constant at this value, until steady-state conditions were obtained. The furnace was then cooled to ambient temperature, the nitrogen stream was switched to air at a flow rate of 45 mL/min, and the temperature was again increased to 850 °C, until the coal mass was completely burned.

The experiments were replicated at least twice to determine their reproducibility, which was found to be very good. Some examples are presented in Table 2.

Kinetic Model

The kinetics of thermal decomposition of carbonaceous materials is complicated because it involves a large number of reactions in parallel and in series. In this work, the pyrolysis process was described by the independent, first-order parallel reactions model.[12,20–24] According to this model, the decomposition of coal is described by a number of independent parallel reactions. The overall rate of conversion for N reactions and the thermal decomposition of the individual components can be expressed as

$$-\frac{dm}{dt} = \sum_i c_i \frac{da_i}{dt} \qquad i = 1, 2, 3, ..., N \qquad (1)$$

$$\frac{da_i}{dt} = A_i \exp(-E/RT)(1 - a_i) \qquad (2)$$

where dm/dt = mass loss rate, A_i = preexponential factor, i = component, E_i = activation energy, a_i = conversion rate, R = gas constant, c_i = contribution of

the partial process to the overall mass loss, $m_0 - m_{char}$, and T = temperature.

In the kinetic analysis, the nonlinear least-squares algorithm was used, which identifies kinetic parameters that minimize values of the objective function:

$$OF = \sum\left[\left(\frac{dm}{dt}\right)^{exp} - \left(\frac{dm}{dt}\right)^{calc}\right]^2 \qquad (3)$$

$(dm/dt)^{exp}$ is the experimentally observed DTG curve and $(dm/dt)^{calc}$ is the calculated DTG curve, obtained by numerical solution of the kinetic differential equation with the given set of parameters.

The deviation between the observed and calculated curves at the optimal set of parameters was calculated as follows:

$$deviation\ (\%) = 100 \times \frac{\sqrt{OF(z - N)}}{max(-dm/dt)^{exp}} \qquad (4)$$

where z is the number of data points and N is the number of parameters employed in the model.

Combustion of the coal chars was described by a power law model. Coal chars may be composed of parts with different reactivities, and the reactivity of a unit surface area may vary as the sample is burning out. To include the char heterogeneity in the model, it was assumed that a coal char sample could be a mixture of components with different reactivities:[22]

$$m(t) = \sum_{j=1}^{n} c_j[1 - a_j(t)] + m_\infty \qquad [m(0) = 1] \qquad (5)$$

where m is the sample mass normalized by the initial sample mass, n is the number of components, c_j is the fraction of combustibles in component j, $a_j(t)$ is the reacted fraction of component j in time t, and m_∞ is the normalized amount of the solid residues (minerals) at the end of the experiment.

A separate equation was used for each component to describe the dependence of the reaction rate on the temperature and fractional burnoff:

$$da_j/dt = A_j \exp(-E/RT)g(P_{O_2})\,f(a_j) \qquad (6)$$

where A_j is the preexponential factor of component j, E_j is the activation energy of component j, g expresses the effect of ambient gas composition, and f describes the change of surface reactivity as a function of the fractional burnoff.

Because the function $g(P_{O_2})$ represented the partial pressure of oxygen in air, its value was included in the preexponential factor, while the $f(a_j)$ function was described by

$$da_j/dt = (1 - a_j)^{n_j} \qquad (7)$$

where n_j is the reaction order.

The method of least squares was employed as before, and the deviation between the observed and calculated curves was obtained by eq 4.
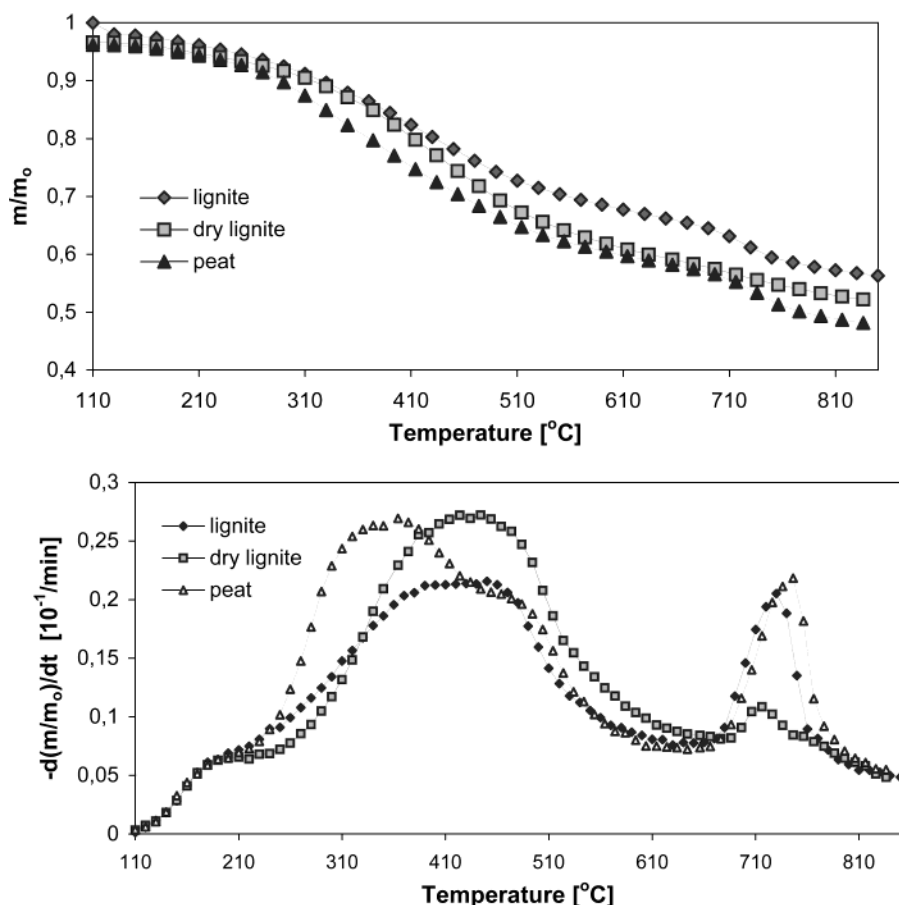
Figure 1. TG and DTG pyrolysis profiles of coal samples.

The component behavior of these chars was well reflected by the shape of their experimental $-dm/dt$ functions. All chars evidenced an additional peak at temperatures above 650 °C, which was attributed to the thermal decomposition of a mineral calcium carbonate component. It is well-known that the thermal decomposition of calcium carbonate is extremely sensitive to the presence of carbon dioxide in the ambient gas;[25] hence, its mathematical modeling should include sophisticated equations for mass transport and backward reactions. The investigation of this problem was beyond the scope of the present study, and this approach is in accordance with that of other researchers.[10,12,14,22]

Results and Discussion

Thermal Decomposition Characteristics. A comparison of the proximate and ultimate analysis results, as well as of the calorific values of the three samples under study, is made in Table 1. As can be seen, the highest amount of volatiles was evolved by the peat (volatiles 50.1%), while the lowest was evolved by the lignite (volatiles 45.2%). The calorific value and the percentages of total C, H, and O were higher for dry lignite. The N content was high in the case of peat (2.45% on a dry basis), while the S content was comparable for all samples and was rather low (between 0.68% and 0.84% on a dry basis).

The TG and DTG curves of the coals, which were obtained in nitrogen, are shown in Figure 1. It can be observed that the initial decomposition temperature was below 200 °C. The DTG curves show three peaks. The first peak, which occurs around 108 °C, is due to the

elimination of water. The second peak, appearing in the temperature range of 350−500 °C, is related to primary devolatilization, during which the bulk of the volatiles in the form of C, H, and O compounds is released. The third peak, occurring at temperatures higher than 650 °C, corresponds mainly to condensation of the carbon matrix, with the evolution of secondary gases leading to the formation of char.[26,27]

A comparison of the burning profiles of the coals, obtained in air, is illustrated in Figure 2. As can be seen, the reaction threshold occurred at about 350 °C for all samples, while the bulk of the process occurred mainly in the 450−600 °C region. Lignite and peat show a bimodal combination of chars with differing reactivity, in this temperature region, whereas dry lignite represents three overlapping peaks and thus a more heterogeneous mixture.

Furthermore, through study of the DTG curves, it can be observed that the peaks differ in position and height. Taking into consideration that the peak height is directly proportional to the reactivity, while the temperature corresponding to the peak height is inversely proportional to the reactivity,[28] the peat that also has the highest volatiles content is the most reactive among the species studied in nitrogen, followed in sequence by dry lignite and lignite. However, the lignite seemed to be the most reactive among the species studied in air, followed in sequence by dry lignite and peat. Table 3, which represents the devolatilization and combustion characteristics of the samples studied, shows that the maximum pyrolysis rates increased as the volatiles
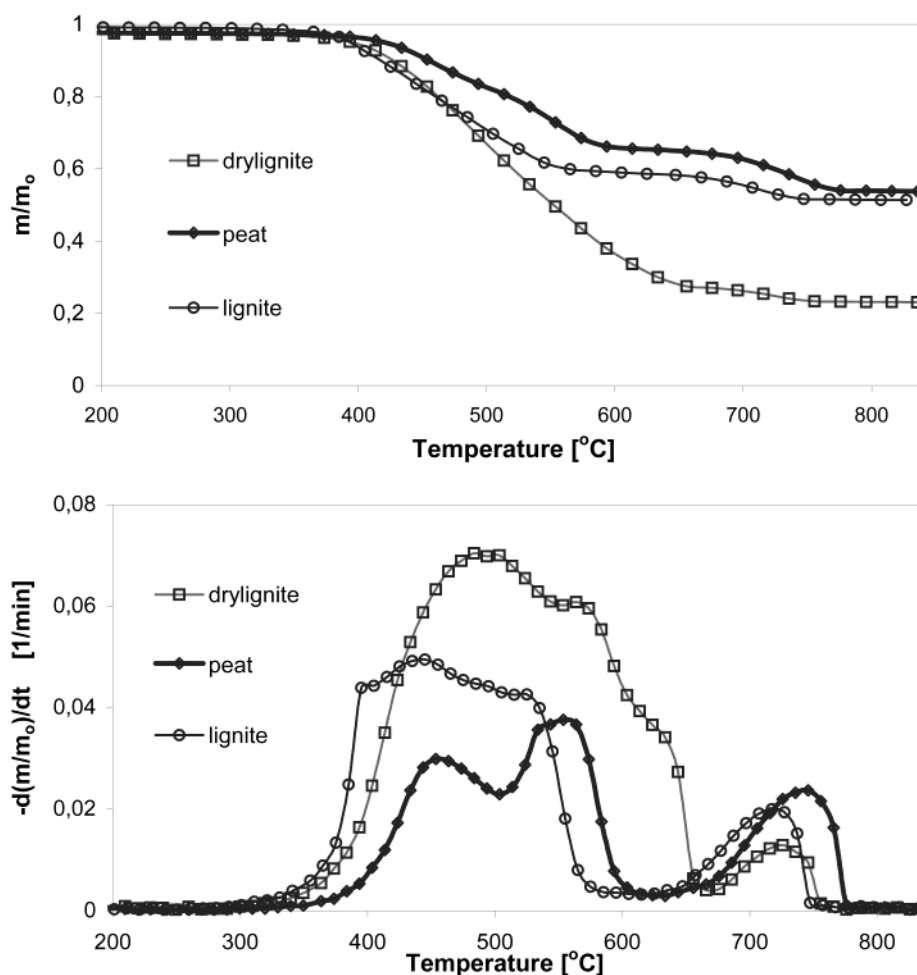
Figure 2. TG and DTG burning profiles of coal samples.

Table 3. Devolatilization and Combustion Characteristics of Pure Samples

sample	atmosphere	initial dec temp (°C)	max dec rate × 10² (min⁻¹)	temp at max dec rate (°C)	volatiles content (% dry)	fixed carbon content (% dry)	char convn up to 650 °C (% dry)
Ptolemais lignite	nitrogen	179	2.05	443	43.84	26.74	
	air		4.93	460			85.3
Ptolemais dry lignite	nitrogen	183	2.76	427	47.39	41.42	
	air		7.15	486			93.9
Phillipous peat	nitrogen	181	2.79	366	51.72	23.25	
	air		3.75	555			77.6

content of the samples increased, while the maximum combustion rates increased with char conversion.

Because the temperature and shape of the third DTG peak, in all thermograms, seemed to be characteristic of calcium carbonate powders and the peak height seemed to vary in proportion to the amount of calcium carbonate in each coal sample (lignite contained 18.9%, dry lignite 9.8%, peat 25.6%, as calculated by X-ray diffractometry, X-ray fluorescence spectroscopy, and proximate analysis), it was decided to undertake some further tests in order to prove this event. Thus, the materials were acid washed to remove the inorganics and then tested by TGA, under the same experimental conditions. The results, such as those illustrated in Figure 3, verified that the peak appearing above 700 °C in the combustion thermograms represented the decomposition of calcium carbonate. The procedure of acid washing is described in detail elsewhere.[29]

The behavior of blends made of lignite and each of the other coals was studied under the same experimen-

tal conditions. Maximum pyrolysis and combustion rates and peak temperatures for blending ratios 0:100, 20:80, 40:60, 80:20, and 100:0 are compared in Table 4. As shown, volatile and char yields were almost proportional to the contribution of each individual coal in the blend. As the dry lignite or peat percentage in the blend with the lignite was increased, an increase in the volatile yields and a decrease in the char yields were attained for devolatilization, while there was an increase in char conversion for combustion. Furthermore, from the DTG pyrolysis curves of lignite/dry lignite mixtures, such as those illustrated in Figure 4, it is clear that the position of the peaks was shifted to lower temperatures, as the percentages of dry lignite and peat were raised. These temperatures varied in proportion to the contribution of each component, revealing that the presence of these coals in the blends improved their reactivity. However, the height of the DTG peaks did not change appreciably with increasing amounts of each coal in the blend because the volatiles content and maximum devolatil-
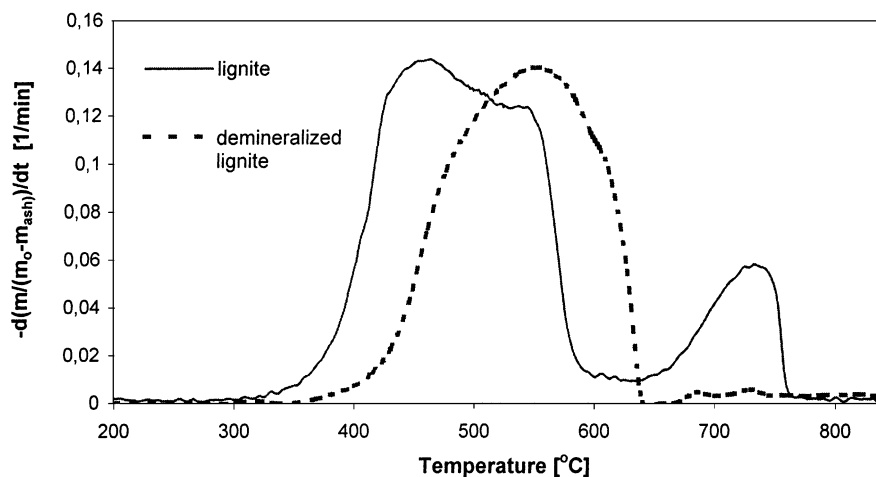
Figure 3. DTG burning profiles of raw and demineralized samples of Ptolemais lignite.

Table 4. Devolatilization and Combustion Characteristics of Ptolemais Lignite/Coal Blends

		Devolatilization			
sample	blending ratio	max dec rate × 10^2 (min^{-1})	temp at max dec rate (°C)	volatiles content (% dry)	char content (% dry)
Ptolemais dry lignite/	0:100	2.05	443	43.84	56.16
Ptolemais lignite	20:80	2.17	440	43.16	56.84
	40:60	2.39	437	45.27	54.73
	60:40	2.38	428	44.12	55.88
	80:20	2.63	421	44.57	55.43
	100:0	2.76	427	47.39	52.61
Phillipous peat/	0:100	2.05	443	43.84	56.16
Ptolemais lignite	20:80	2.10	418	44.73	55.27
	40:60	2.18	402	47.02	52.98
	60:40	2.25	375	48.16	51.84
	80:20	2.33	372	48.46	51.54
	100:0	2.79	366	51.72	48.28

		Combustion			
sample	blending ratio	max dec rate × 10^2 (min^{-1})	temp of the first peak (°C)	temp of the second peak (°C)	char convn up to 650 °C (% dry)
Ptolemais dry lignite/	0:100	4.93	460	534	85.3
Ptolemais lignite	20:80	5.53	474	548	87.9
	40:60	6.19	476	554	90.2
	60:40	6.24	478	554	90.9
	80:20	6.87	479	562	93.1
	100:0	7.15	486	566	93.9
Phillipous peat/	0:100	4.93	460	534	85.3
Ptolemais lignite	20:80	4.66	459	544	82.9
	40:60	4.39	457	548	80.9
	60:40	3.89	456	549	79.5
	80:20	4.05	455	550	78.9
	100:0	3.75	456	555	77.6

ization rates did not vary significantly between the samples studied. Similarly, from Table 4 and Figure 5, it can be observed that blending did not affect significantly the reactivities of the individual coals in air because both the position and the height of the DTG peaks varied almost in proportion to the contribution of each blend component.

Kinetics. The pyrolysis process was modeled, according to the shape of the DTG curves, by a kinetic scheme consisting of five independent, first-order parallel reactions. The combustion of the samples under study was described by the power law model, adjusted to include char heterogeneity. A two-to-three-component behavior was well reflected by the shape of the experimental DTG curves. The calculated DTG curves for dry lignite are plotted together with the experimental curves in Figures 6 and 7. As can be seen, the agreement between the model predictions and the experimental measurements is very good, with a deviation value below 2% for both pyrolysis and combustion. Similar fits were obtained for all samples. The kinetic parameters estimated by means of the model are reported in Table 5. Estimates show that these parameters are very similar among the samples, indicating comparable reactivities of the three feedstocks. In the case of pyrolysis, for the lower temperature region 200−600 °C, the activation energies vary between 19 and 109 kJ/mol, whereas for the higher temperature region 600−850 °C, where the reactions taking place do not result in appreciable weight loss, they are in the range of 116−399 kJ/mol. In the case of combustion, the calculated energy values change in the range of 121−179 kJ/mol between the three chars and the order of the reactions describing the combustion process varies between 0.4 and 2. These data are in reasonable agreement with those reported in the literature,[4,7,9,10,12,21,30] taking into consideration the type
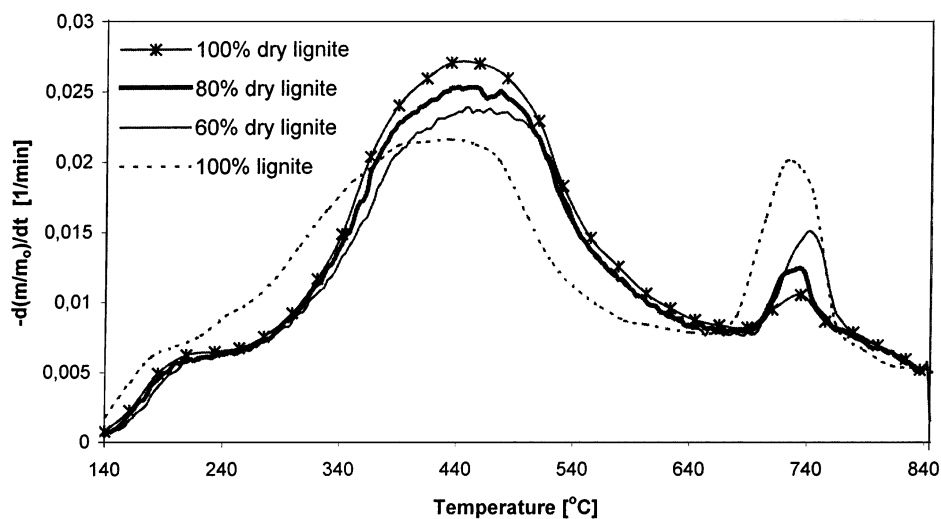
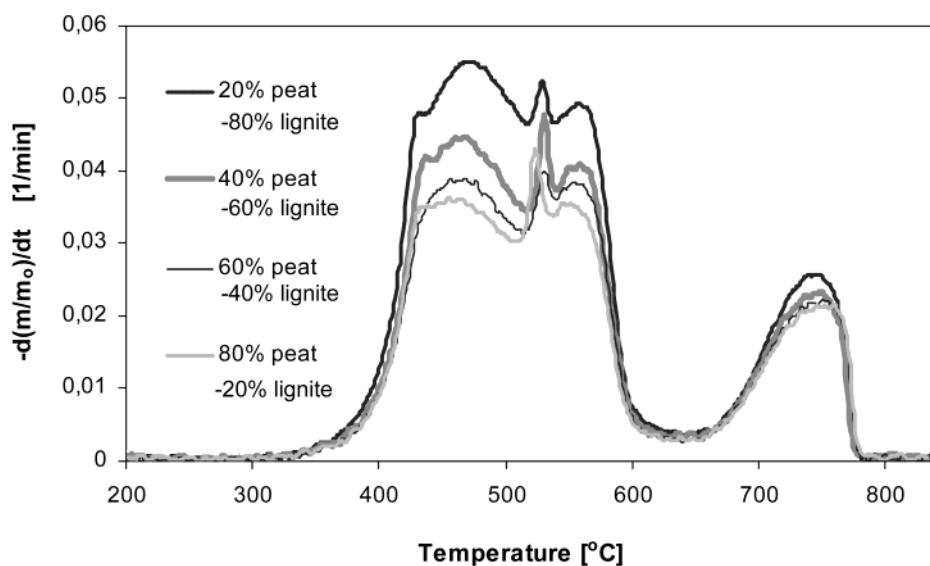**Figure 4.** DTG pyrolysis profiles of lignite/dry lignite blends.

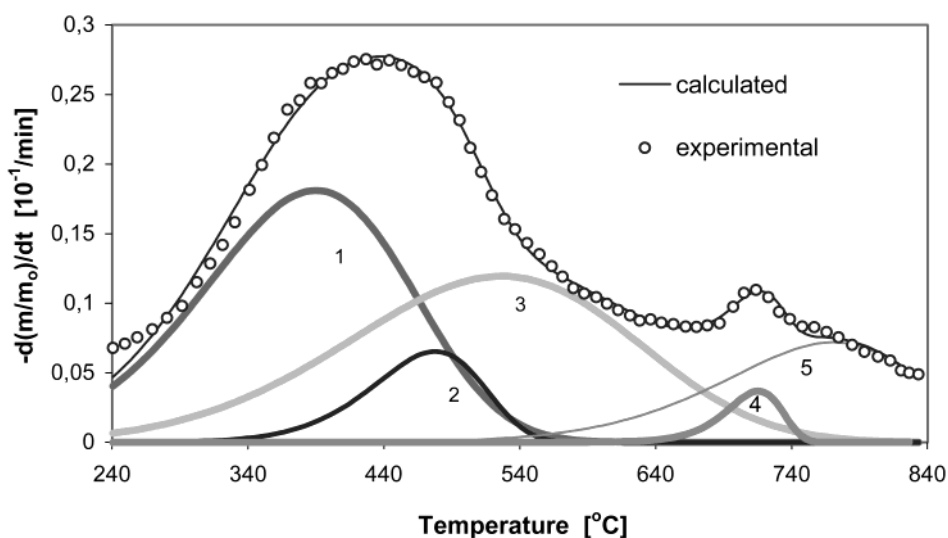**Figure 5.** DTG burning profiles of lignite/peat blends.

Figure 6. Kinetic evaluation of pyrolysis for Ptolemais dry lignite.

of the sample, and they further indicate that both processes were chemically controlled.

To model the kinetics of the blends, theoretical DTG curves, representing the sum of the individual components' behavior in the mixture, were calculated:

$$(\mathrm{d}m/\mathrm{d}t)_{\text{sum}} = x_1 (\mathrm{d}m/\mathrm{d}t)_{\text{lignite}} + x_2 (\mathrm{d}m/\mathrm{d}t)_{\text{coal}}$$
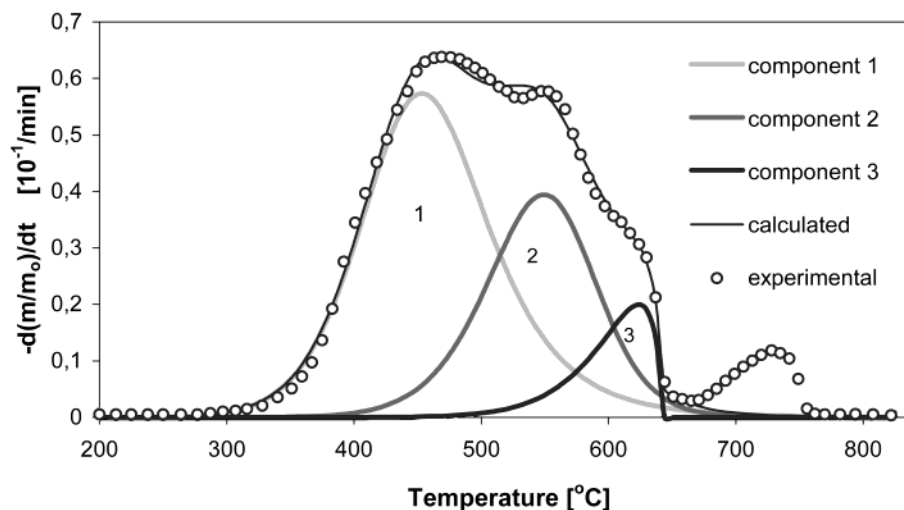
Figure 7. Kinetic evaluation of combustion for Ptolemais dry lignite.

Table 5. Calculated Kinetic Parameters for Pyrolysis and Combustion

| | | sample | | | | | | | | | | | |
| | | kinetic param[a] for Ptolemais lignite | | | | kinetic param[b] for Ptolemais dry lignite | | | | kinetic param[c] for Phillipous peat | | | |
reaction	atm	A (min^{-1})(pyr.) (min^{-1} MPa^{-1})(com.)	E (kJ/mol)	c (%)	n	A (min^{-1})(pyr.) (min^{-1} MPa^{-1})(com.)	E (kJ/mol)	c (%)	n	A (min^{-1})(pyr.) (min^{-1} MPa^{-1})(com.)	E (kJ/mol)	c (%)	n
1	nitrogen	1.5×10^3	47.7	12.2		5.5×10^2	42.9	38.1		1.5×10^3	44.4	37.2	
	air	1.2×10^9	150.6	50.2	2	5.3×10^6	121.1	56.2	2	1.2×10^9	152.7	25.8	1
2	nitrogen	2.6	19.1	60.9		1.8×10^7	109.2	8.1		1.8×10^7	108.6	10.6	
	air	2.7×10^6	130.9	35.1	0.75	6.3×10^7	153.7	32.2	1.4	2.7×10^6	133.5	47.6	0.7
3	nitrogen	1.8×10^7	107.0	5.1		1.2×10^2	44.1	36.0		1.5×10^2	44.1	27.3	
	air					3.3×10^8	179.3	9.3	0.4				
4	nitrogen	5.3×10^{20}	398.1	9.9		1.1×10^{21}	398.8	2.4		5.2×10^{18}	363.2	9.4	
	air												
5	nitrogen	1.8×10^5	119.9	11.9		1.7×10^5	116.6	15.5		1.7×10^5	116.1	15.4	
	air												

[a] Nitrogen: Dev = 1.98%. Air: Dev = 3.6%. [b] Nitrogen: Dev = 1.91%. Air: Dev = 1.9%. [c] Nitrogen: Dev = 1.98%. Air: Dev = 3.0%.

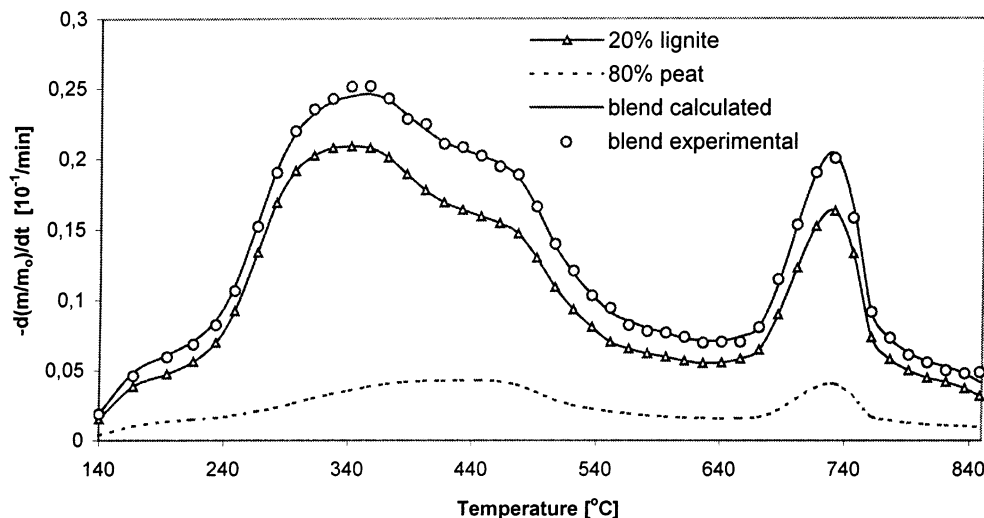**Figure 8.** Comparison between experimental and calculated DTG pyrolysis curves for lignite/peat blends.

where $(dm/dt)_{lignite}$ and $(dm/dt)_{coal}$ are the normalized rates of mass loss, as found from the individual experiments, and x_1 and x_2 are the mass fractions of lignite and alternate coal in the mixture, respectively. In this way, any interactions between the components of each blend would be identified.

Indeed, Figure 8, being representative among all samples, shows that the fit between experimental and calculated DTG pyrolysis curves for peat blends is very good, with deviation values below 2%. Therefore, it seems that no significant interactions occurred in the solid phase during devolatilization. This finding, that the devolatilization of the mixture is sufficiently predicted by a simple summation of the individual behavior of its components, provides information on the mixture's behavior based on the experimental data for each fuel. In addition, it allows simulation of the kinetics of the blend, using the kinetic parameters obtained for the
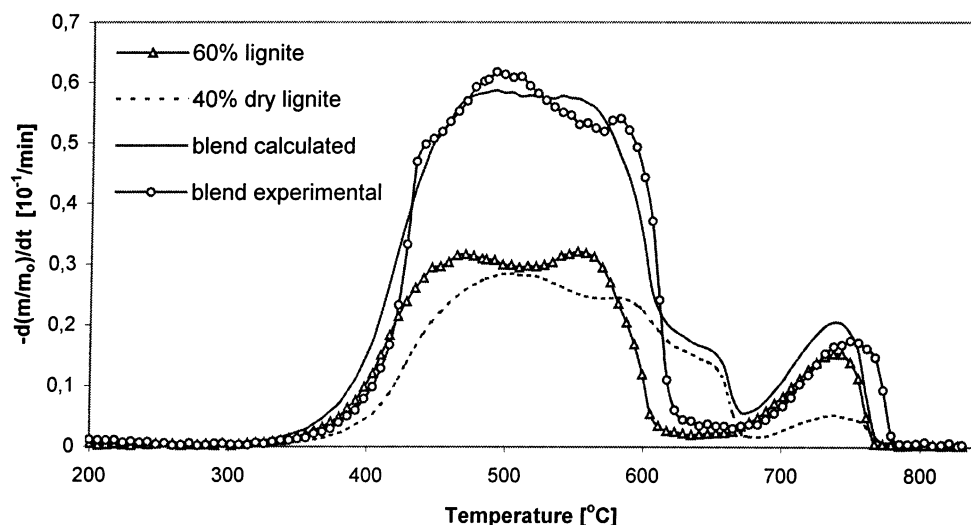
Figure 9. Comparison between experimental and calculated DTG combustion curves for lignite/dry lignite blends.

Table 6. Calculated Kinetic Parameters for the Combustion of Coal Char Blends at a Blending Ratio of 60:40

	sample							
	kinetic param[a] for Ptolemais dry lignite/ Ptolemais lignite				kinetic param[b] for Philippi peat/ Ptolemais lignite			
reaction	A (min^{-1} MPa^{-1})	E (kJ/mol)	c (%)	n	A (min^{-1} MPa^{-1})	E (kJ/mol)	c (%)	n
1	5.3×10^6	118.4	45.9	2	1.2×10^9	156.2	27.7	1.4
2	1.0×10^7	142.5	45.2	2	2.7×10^6	136.0	31.5	0.7
3	1.4×10^8	181.7	8.4	0.5				

[a] Dev = 3.6%. [b] Dev = 3.2%.

isolated compounds and taking into account the percentages of the fuels in the mixture. Thus, for devolatilization, cumulative models were proposed, involving a number of independent parallel reactions, which are the sum of the reactions representing the decomposition of each coal sample.

On the other hand, for char combustion, Figure 9 shows that by a simple summation of the burning profiles of the component coals the fit between experimental and calculated DTG curves was not so good. Similar fits were obtained for all mixtures, with deviation values ranging between 6.4% and 17.5%. This finding reveals that some interactions between the individual fuels occurred when these were blended, because of their different chemical composition. Such interactions have also been reported by other investigators.[2,31,32] To determine to which extent this nonadditivity of the DTG curves complicates the prediction of the combustion reactivity of the blends, the power law model, previously described, was also used to model the kinetics of the mixtures. Some of the calculated results, at a blending ratio of lignite to alternative coal of 40: 60, are represented in Table 6. From the estimated values of the kinetic parameters A, E, and n, it is clear that these did not change significantly in comparison to those calculated for the individual fuels; however, they were closer to the values corresponding to the alternative coal (dry lignite and peat). This information will be useful for the cofiring of these low-rank coals. It appears that, although the pyrolytic behavior of the blends can be predicted accurately from the behavior of the component coals, this is not quite true in the case of chars' combustion and some complications arise.

Conclusions

The TG/DTG thermograms of the coals studied under a nitrogen atmosphere showed that their thermochemical reactivity was similar, while the burning profiles presented a two-component combination of chars with differing reactivity, depending on the type of the sample and the temperature region. Blending of lignite with dry lignite or peat did not affect the devolatilization or combustion reactivities of the individual coals significantly.

A independent, parallel first-order reactions model was found to reproduce devolatilization mass loss with high accuracy, for all coal samples. For the primary devolatilization region, activation energy values ranging from 19 to 109 kJ/mol were calculated. The kinetic model for the blends was performed successfully based only on the kinetic parameters obtained for the individual fuels.

In the case of char combustion, a power law model, adjusted to include char heterogeneity, fitted the experimental results with great accuracy. Activation energy values and reaction orders ranged from 121 to 179 kJ/mol and from 0.4 to 2, respectively, among the three chars under study. The kinetic parameters of the blends, although similar to those of the isolated fuels, could not be predicted accurately by a simple summation of the individual components' behavior in the mixture. It seems that some interaction between the component coals occurred because of their different chemical compositions.

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