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Thermochimica Acta 370 (2001) 91–97

thermochimica acta

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Different approaches to proximate analysis by thermogravimetry analysis

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Received 11 August 2000; accepted 11 December 2000

Abstract

The experimental optimization by the simplex method of the proximate analysis of coal and biomass by thermogravimetry analysis (TGA) is reported. Heating rate, final temperature, holding time, Ar flow rate and sample size were the control variables. The response function used was chosen to minimize the difference in percentage of volatile matter with the ASTM characterization. The relative accuracy of the method was demonstrated by determination of the volatile matter contents of a number of coals in parallel with the ASTM certified method. The method is successfully used with biomass samples.

Keywords: Proximate analysis; Coal; TGA

1. Introduction

Proximate analysis covers the determination of moisture, volatile matter, fixed carbon and ash in coals and cokes, and is used to establish the rank of coals, to show the ratio of combustible to incombustible constituents, or to evaluate coal for various purposes. Thus, it is important to both the suppliers and users of coal to have a rapid, accurate and reliable procedure to obtain the proximate analysis. Traditionally, the various proximate analysis determinations involve heating the sample in furnace under ASTM [1] specific conditions. These determinations, however, are not only time consuming but also they require a significant amount of sample. Quite often in research, samples to be characterized are few milligrams of products from microreactors or fine preparative experiments. This is why several attempts have been focused on finding an alternative method for proximate analysis by thermogravimetry analysis (TGA) [2]. In nitrogen, moisture and volatiles are lost at temperatures up to 900°C, and fixed carbon is burnt in oxygen leaving the ash as a residue. Those studies are in agreement to ASTM results within the experimental error only when samples of very high content of fixed carbon are studied [3] or when experimental conditions as gas flow rates, heating ramps or sample mass are found for a specific type of coal [4]. In fact, ASTM proposes a standard for compositional analysis by thermogravimetry [5], as a general technique to determine the amount of highly volatile matter, medium volatile matter, combustible material, and ash content of compounds. Nevertheless, that standard only gives guidelines of heating ramps or final temperatures, to be adapted to the type of sample to analyze.

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PII: S0040-6031(00)00789-9

Table 1
Proximate analysis of coals determined by ASTM method, dry basis

	%VM[a]	%FC[b]	%A[c]
Sample 49	20.58	69.48	9.94
Sample 53	41.95	52.18	5.87
Sample 55	46.54	47.25	6.21
saca5	28.29	34.97	36.73

[a] Percentage of volatile matter.
[b] Percentage of fixed carbon.
[c] Percentage of ash.

This work presents different approaches to proximate analysis, in an attempt to solve the problem of characterization of small samples (20 mg or less) of different stages of coal combustion obtained in a bench scale entrained flow reactor [6]. On the other hand, one specific problem of characterization of small samples of biomass has been solved as well with thermogravimetry.

2. Experimental

Four coals were used. Three of them (49, 53 and 55) were selected from a group of coals from round robin calibration exercises, so their proximate characterization is certified by a number of laboratories. The other coal used for this work comes from the Institute coal bank, and it was selected due to its high reactivity. Their proximate composition is given in Table 1. Thermogravimetric measurements were performed with a DSC 2960 TA Instruments thermobalance. Ten milligrams of sample were used except for those experiments where sample mass is a variable to optimize. All experiments comprised three different steps: drying, devolatilization in inert atmosphere, and combustion in oxygen. Moisture content was considered as the mass loss when the sample is heated at 20°C/min till 105°C, 90 ml/min Ar, and this temperature was maintained for 5 min. Then, the devolatilization step starts at a variable ramp, Ar flow, final temperature and isothermal time, depending on the series of experiments studied (Table 2).

The first series of experiments were an adaptation of the method proposed by TA Instruments as technical application of the device [7], where the proximate analysis was proposed to be complete in 15 min. Seteram proposed as well a similar method for proximate analysis of coal [2], so the first series of experiments would represent those conditions proposed by thermobalance manufacturers for proximate analysis of coals and fuels. The second series of experiments were an adaptation of the method described in [8], where the devolatilization step described in Table 2 was followed by a cooling step in inert atmosphere until no weight change was detected.

The third series of experiments comprise the optimization procedure designed by a simplex experimental design. Software used was Multisimplex from Multisimplex AC. Heating rate, final temperature, holding time, Ar flow rate and sample mass were control variables. The response function used was a weighted linear combination of three variables: difference in percentage of volatile matter, run time and Ar flow rate. Obviously the goal of each experiment is to find a point in weight loss curve that clearly signals the volatile matter. For this set of experiment volatile matter is considered as that released before combustion step starts. Run time and Ar flow are included in the optimization equation because they were considered as important parameters to define a routine analysis procedure.

For all the experiments, the combustion step starts with the automatic switch of Ar into 80 ml/min O_2, and final temperature is kept for 20 min to allow complete combustion.

Table 2
Experimental conditions for devolatilization step in TGA for the three methods studied

Experiments	Heating rate (°C/min)	T_{final} (°C)	Time at T_{final} (min)	Ar flow rate (ml/min)	Sample mass (mg)
First series [7]	Jump	900	5	90	10
Second series [8]	20	900	5	90	10
Third series	Variable	Variable	Variable	Variable	Variable

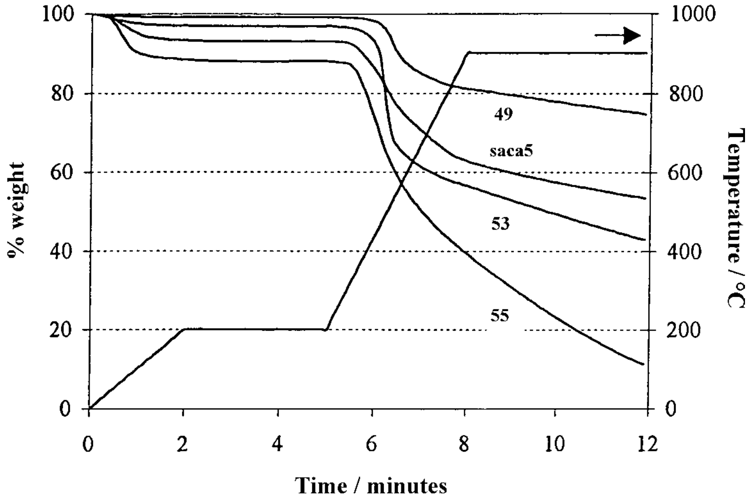

Fig. 1. TGA profile of drying and devolatilization in Ar for the four coals (first series of experiments).

3. Results

Fig. 1 illustrates the TGA profile of drying and devolatilization obtained for the first series of experiments. The first weight loss corresponds to moisture, and constant weight is reached. After the second heating step, there is an isothermal stage of 5 min, where a plateau in weight loss should be reached, as proposed by the technical notes. It is clear from the results that constant weight is not reached, so it is not possible to find a point at which devolatilization finishes. If purge gas is switched to O_2, complete combustion is reached in 5 min, with the remaining weight considered as ash content.

The second series of experiments is illustrated in Fig. 2. The main differences with the first series are: heating ramp during devolatilization is slow (20°C/min), and it is followed by a cooling step. This way, a mass loss plateau is reached for all coals. This method gave a quantification of moisture, volatile matter and

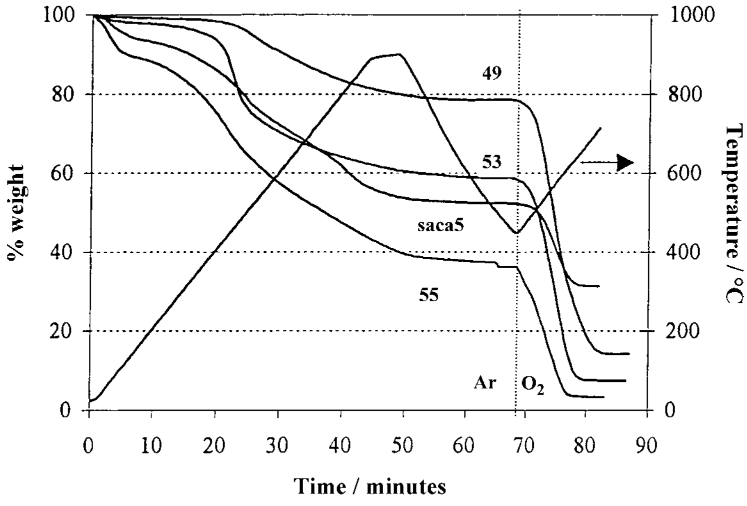

Fig. 2. TGA profile of the four coals obtained at conditions adapted from [7] (second series of experiments).

Table 3
Comparison of proximate analysis of coals by ASTM analysis and by the second series of experiments

	ASTM			Second series		
	%VM[a]	%FC[b]	%A[c]	%VM	%FC	%A
49	20.58	69.48	9.94	20.41	69.27	10.32
53	41.95	52.18	5.87	39.46	52.92	7.62
55	46.54	47.25	6.21	57.60	38.76	3.65
saca5	28.29	34.97	36.73	43.71	22.61	33.67

[a] Percentage of volatile matter.

[b] Percentage of fixed carbon.

[c] Percentage of ash.

fixed carbon content by constant weight lines, with the results shown in Table 3. The method seemed to be suitable for two of the coals studied (49 and 53), whereas for the other two, the mass evolved during the heating and cooling periods was higher than the volatile matter after ASTM.

Since the way in which volatile matter releases coal matrix can be monitorized by the shape of weight loss, the first derivative of weight loss curve versus time can give useful information; the end of the first derivative peak is easily seen when the heating ramp (i.e., the speed of mass loss) is high (Fig. 3). The four coals were tested at a ramp of 80°C/min in Ar till 1020°C, and 10 min isothermal in O_2, and the first derivative of weight is shown as a function of temperature in Fig. 4. For all coals, the maximum rate of loss of mass is around 500°C. None of the coals reached zero slope in the range of temperatures studied; moreover, coals 55 and saca5 have a second peak of mass loss in inert atmosphere at 700–800°C. As these results indicate, the real behavior of coal volatilization, as seen in thermobalance is not comparable to proximate analysis by ASTM method.

From these TGA scans, different criteria can be agreed to fix a point at which volatile matter can be considered as completely released. Provided that profiles of the first derivative do not reach the zero value even at high temperatures, the second derivative was calculated for each run. The end of devolatilization could be considered at that point at which the second derivative reaches zero. The mass loss measured after the drying step till the end of the second derivative of weight (versus time), as a function of heating ramp, gives the results shown in Table 4, expressed as

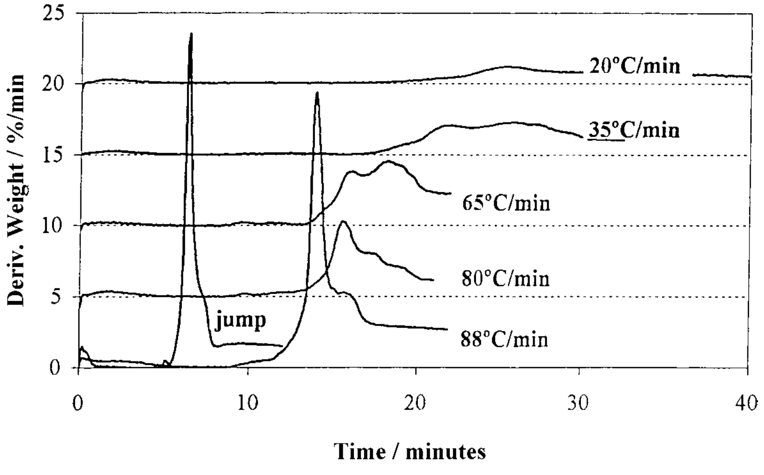

Fig. 3. Derivative of weight loss versus time as a function of heating ramp for coal 49.

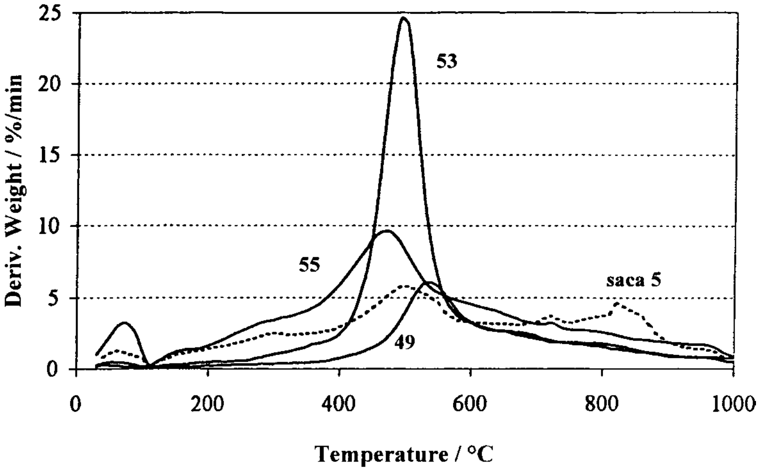

Fig. 4. Derivative of weight loss versus temperature at a heating ramp of 80°C/min for the four coals.

difference with volatiles percentage ASTM. The standard for compositional analysis proposes that if a distinct mass plateau is not observed, the atmosphere change into O_2 can be made based upon some agreed temperature [5]. Suggested temperature for coal is 900°C, and heating ramps from 10 to 150°C/min. Table 4 shows the results calculating volatile matter as that loss at 900°C at 20 and 80°C/min. The great disagreement with ASTM values is clear.

The main target of the third series of experiments was to establish a point in mass loss curve to determine volatile matter content and fixed carbon content. For that, a set of experimental conditions (heating rate, Ar flow, final temperature, time at final temperature, sample mass) were optimized by the Multisimplex program. The conditions are described in Table 5: trials 1–6 were the first experiments designed to cover the complete range of variables. With the results obtained in those six trials, new experimental conditions were proposed by the simplex program. As the results were produced, the program conducted the experimental conditions to a clear trend: heating rates of around 80°C/min, final temperature of around 780°C and high Ar flow rates. Several of the best adjustments are shown in Table 5 as the difference between the percentage in volatile matter ASTM and the obtained for each trial. As can be seen, after 50 trials, the values failed to converge in a complete agreement for all coals with the ASTM characterization. This lack of success in convergence is caused by the different behavior among coals: two of them seemed to be less reactive and differences of volatile matter with ASTM values were negative, while one of the coals was very reactive at every condition studied and volatilization at inert atmosphere seemed to be higher than the ASTM value. On the other hand, coal 55 was easily adjusted.

These results confirm the trend observed in the first and the second series of experiments: coals do not behave in the same way under devolatilization conditions, no matter the heating ramp or final temperature. This is clearly seen in Fig. 5 for trial 46.

Coals 49 and 53 devolatilize as temperature increases, reaching constant weight during the isothermal step. On the other hand, coals 55 and saca5 seem to have a volatile fraction even at high

Table 4
Difference of volatile matter percentage with that calculated at the end of the second derivative, and at 900°C reached at two different heating ramps

	$\%VM - \%VM_{ASTM}$[a]		
	At the end of the second derivative	At 900°C (80°C/min)	At 900°C (20°C/min)
49	−2.7	−2.7	−1.1
53	−6.4	−2.8	−1.4
55	−2.7	−1.2	5.2
saca5	8.0	6.2	13.7

[a] Percentage of volatile matter.

Table 5
Experimental conditions for the third series of experiments, proposed by the Multisimplex program

Third series	Heating rate (°C/min)	T_{final} (°C)	Time at T_{final} (min)	Ar flow rate (ml/min)	Sample mass (mg)	%VM − $\%\mathrm{VM_{ASTM}}$[a]			
						49	53	55	saca5
Trial 1	35	825	2.5	65	12.5	3.5	12.2	7.5	23.3
Trial 2	65	825	7.5	35	12.5	19.0			35.6
Trial 3	35	675	7.5	65	7.5	5.0	4.6	11.4	21.8
Trial 4	65	675	2.5	35	12.5	9.7	−10.2	1.8	11.9
Trial 5	65	825	2.5	65	7.5	5.7	−2.2	12.0	18.4
Trial 6	35	825	2.5	35	7.5	26.0		31.6	
Trial 29	83	705	8.4	114	7.7	−2.7	−2.4	−2.5	2.4
Trial 34	84	811	6.9	107	13.2	−1.8	−2.2	−0.3	2.2
Trial 39	79	783	6.9	88	11.5	−1.8	−2.4	2.9	2.4
Trial 46	77	817	6.7	119	10.3	−1.4	−2.1	2.5	4.6
Trial 47	77	769	5.7	96	10.6	−3.5	−3.5	0.2	2.7
Trial 49	76	780	5.7	105	10.3	−2.8	−3.8	0.1	2.6

[a] Percentage of volatile matter.

temperatures, and go on loosing mass during the isothermal step. So, the results show that two of the coals would need higher temperatures and higher holding times to reach ASTM values, whereas those extreme conditions would imply an excess in mass loss for the other two.

Summarizing, the release of volatile matter depends strongly on the type of coal, so that it is extremely difficult to find a temperature program with TGA to resemble the ASTM analysis. The method for proximate characterization with TGA can be adapted for each type of sample. In this way, after a short series of trials to follow devolatilization, a method can be established and used routinely. As an example, TGA can be of great help for research in combustion and gasification of biomass as clean fuels. In this case, the solid residue of olive after exhaustive oil extraction was characterized by three standard methods: ASTM, the method proposed by the instrument technical note [7], and the method proposed in [8]. Results are compared in Table 6. From ASTM characterization, this sample is highly volatile. The slow heating ramp till 900°C of [8] involves a loss of mass beyond the volatile matter. On the other hand, ash percentage is overestimated when the fast method is used. The experimental conditions were optimized: 11.5 mg,

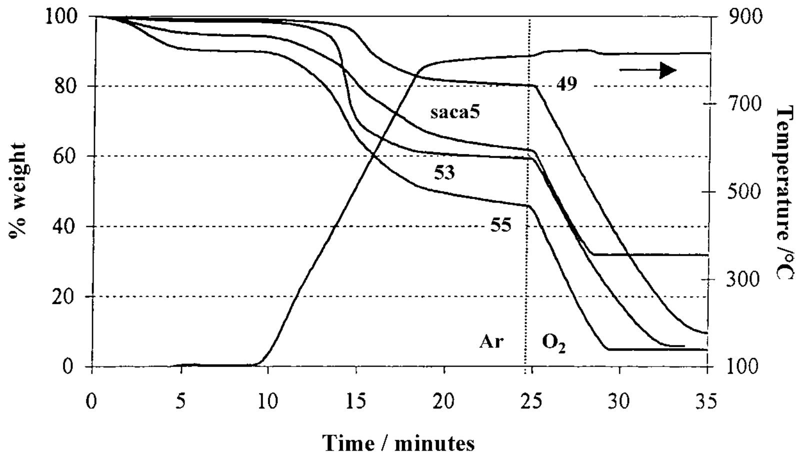

Fig. 5. TGA profile of the four coals obtained at trial 46 of simplex optimization.

Table 6
Comparison of proximate analysis of coals by ASTM analysis and by the first and the second series of experiments of biomass samples obtained of oil extraction from olives

	Extraction residue			Stone			600–710 mesh fraction of stone		
	%VM[a]	%FC[b]	%A[c]	%VM	%FC	%A	%VM	%FC	%A
ASTM	73.3	21.0	5.7	79.3	19.9	0.7	75.6	20.7	3.6
First series	74.1	19.3	6.5						
Second series	83.8	11.1	5.0						
Simplex	73.2	21.4	5.3	78.9	20.2	0.9	77.2	21.2	1.5

[a] Percentage of volatile matter.
[b] Percentage of fixed carbon.
[c] Percentage of ash.

heating ramp of 54°C/min in 92 ml/min Ar, 4.6 min at 800°C. The proximate characterization was of high agreement with the ASTM values. The experimental conditions were checked with two other samples, previously characterized by ASTM: olive stone and a size fraction of stone (Table 6). The method was accepted and used for routine analysis of samples of 10 mg (different particle size fractions, different density fractions, etc.), each run lasting 30 min. Those results were successfully used in [9].

It is worthwhile to comment on the performance of TGA in ash percentage determination. High heating ramp of first series of experiment involves an overestimation of ash content, due to the residual presence of unburned material. On the other hand, the high temperature and long time of combustion in second series imply low ash percentages, that can be due to the devolatilization of light inorganics and changes in mineral matter. Although the third series of experiments were designed to optimize the volatile content, ash percentages were in good agreement with ASTM values as well, within an error of ±1%. The method can be adapted and optimized to minimize differences between ash determination and ash content by ASTM method. The optimization gave the following parameters: drying at 20°C/min till 105°C, 3 min isothermal, switching inert gas into O_2, and 50°C/min till 850°C. This method gave an ash quantification of an error of ±0.5%. It is used routinely when the target is an accurate quantification of ash content of small samples (20 mg or less) of different stages of coal combustion obtained in a bench scale entrained flow reactor. The values obtained are used successfully in research to develop predictive tools to the fouling/slagging phenomena throughout the influence of well controlled operating conditions and coal properties [6].

Acknowledgements

Authors acknowledge the European Commission for the financial support by contract No. ECSC 7220-PR/048. M.C.M. and M.T.I. are thankful to the Ministry of Science and Technology.

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