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THERMAL ANALYSIS OF AGRICULTURAL RESIDUES WITH APPLICATION TO PRODUCTION FUELS

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An important application of agricultural residues is as fuels for combustion processes. This paper shows how thermal analysis can be used for characterization of different kinds of cereals with a view to increasing efficiency in combustion processes. Results are in good agreement with those derived from standard ASTM methods.

Keywords: agricultural residues, lignocellulose fuels

Introduction

Agricultural residues are very abundant in Spain (Table 1).

These consist mainly of cellulose, hemicellulose, and lignocellulose (Table 2).

Cellulose and hemicellulose can be converted into energy when used as fuels. This can be effected in two ways: (i) by thermochemistry at high temperatures, through combustion, pyrolysis and gasification; (ii) by biochemistry at low temperatures.

Combustion of agricultural residues is an increaslingly common means of obtaining heat and power although thermal performance is low, 20% to 30%, and depends on the water content of the biomass [3]. Already there are twelve thermal power plants in the USA yielding from 10 to 50 MW that burn waste biomass in mixtures with gasoil [4]. Thermal analysis of such waste materials would be expected to yield information that could be used to enhance their thermal effectivity.

This paper describes the thermal characterization of some lignocellulose fuels, straw wheat, straw rye, straw barley and straw six-row barley, by conven-

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tional thermal analysis and standard ASTM methods and compares results derived from these two approaches.

Table 1 Production of agricultural residues in Spain, 1991 [1]

Residues	Million tonnes
Haulm sunflower	2.3
Olive tree	3.5
Cereal straw	6.3
Hault grapes	3.3
Haulm cotton	0.5

Table 2 Composition of agricultural residues [2]

Residues	Cellulose	Hemicellulose	Lignocellulose
Haulm sunflower	28.10%	38.72%	10.53%
Olive tree	41.06%	28.05%	17.55%
Cereal straw	32.47%	39.84%	16.13%
Hault grapes	35.61%	39.20%	23.43%
Haulm cotton	36.84%	36.02%	21.45%

Experimental

Characterization of wheat, rye, barley and six-row barley was carried out by dynamic thermogravimetry (TG) using a Perkin–Elmer TGS–2 and DTA system 7/4 with indirect DSC instruments coupled to a system 4 Microprocessor Controller and a 3600 Thermal Analysis Data Station.

Experiments were conducted in air and nitrogen atmospheres at a flow rate of 50 ml/min using a sample mass of 1 to 4 mg. Measurements were performed in the temperature range 30° to 900°C at a heating rate of 20 deg·min^{-1}.

Peak integration on DSC curves, and subsequent enthalpy calculations, were performed by using the Perkin–Elmer System 7/4 partial area integration program.

The melting endotherm of pure $AgNO_3$, $K_2Cr_2O_7$, $CuCl_2$ and indium metal were used for calibration.

Results following the ASTM method were obtained using the Calorimetric Pump (Prolabo Adiabatic 350) together with the Leco CHN–600 and SC–132 systems.

Results and discussion

Figures 1 to 8 show TG, DTG and DSC curves for straw wheat, straw rye, straw barley and straw six-row barley.

The TG curves can be divided into four stages. The first stage covers dehydration of the samples (30°–110°C). The second stage covers combustion of volatile components (110°–320°C). The third stage covers the temperature interval 320°–530°C and represents combustion of lignocellulosic components. The fourth stage (530°–900°C) does not show any significant weight losses (ash).

Figure 9 compares thermal stability as a function of temperature for all four cereals. At lower temperatures rye has the best thermal stability whereas at higher temperatures wheat is more stable.

DSC curves were recorded in dynamic air and strong exothermic peaks occur at temperatures corresponding to the maximum decomposition rate from TG.

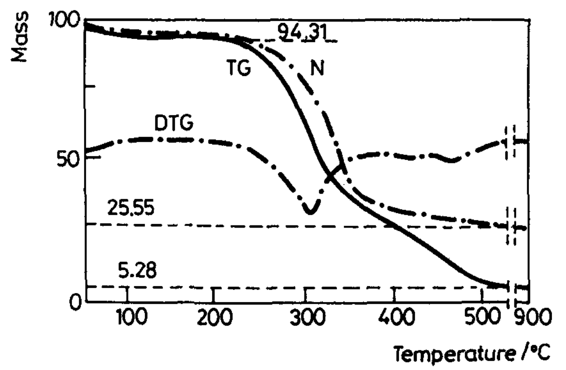

Fig. 1 TG and DTG of straw wheat in air and nitrogen

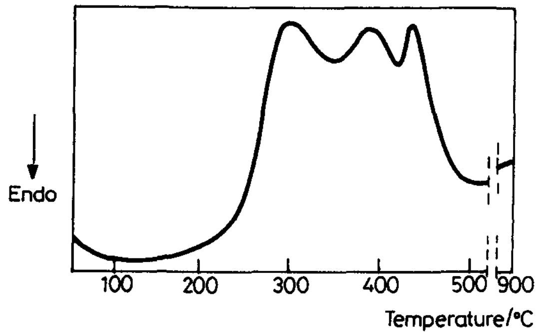

Fig. 2 DSC of straw wheat in air

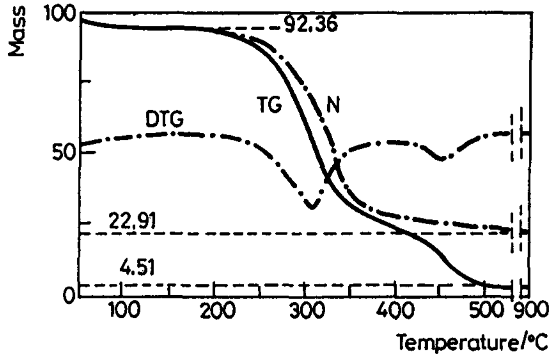

Fig. 3 TG and DTG of straw barley in air and nitrogen

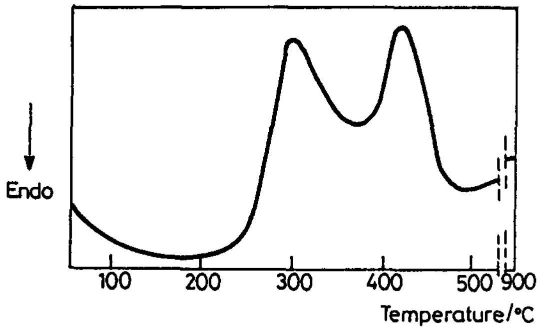

Fig. 4 DSC of straw barley

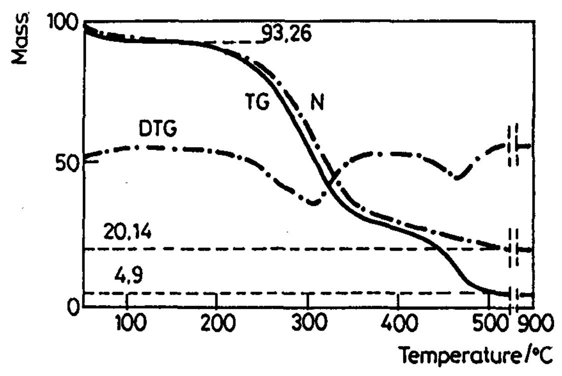

Fig 5 TG and DTG of straw six-row barley in air and nitrogen

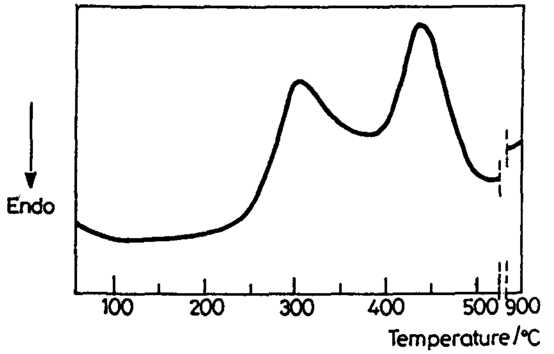

Fig. 6 DSC of straw six-row barley in air

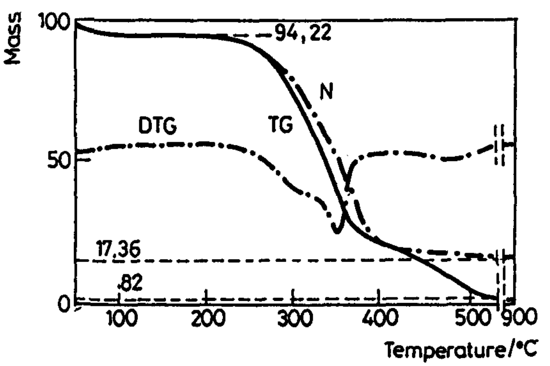

Fig. 7 TG and DTG of straw rye in air and nitrogen

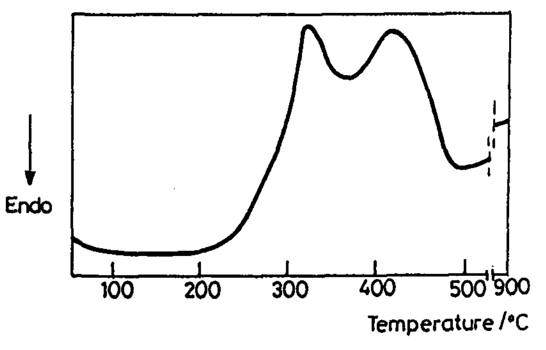

Fig. 8 DSC of straw rye in air

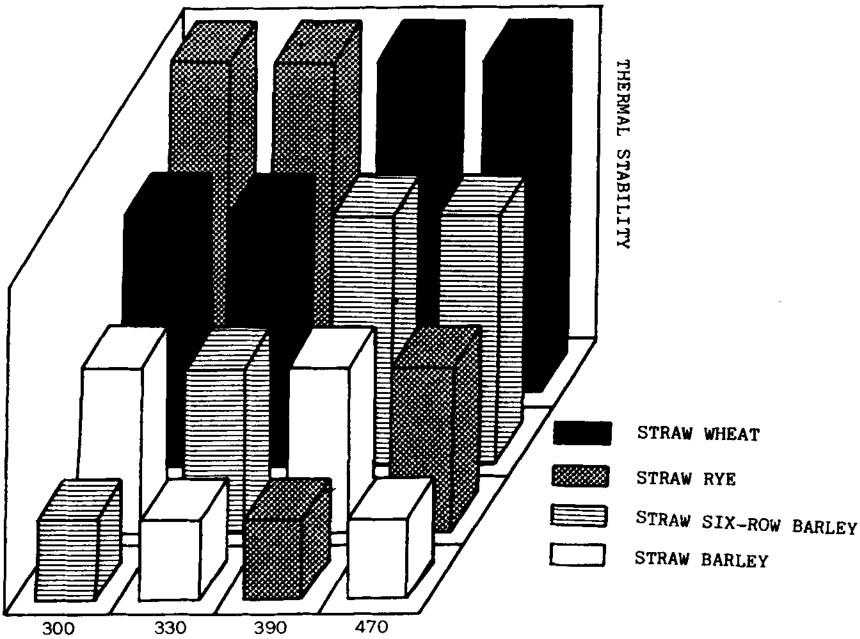

Fig. 9 Thermal stability of samples

TG curves in a nitrogen atmosphere were used to determine amounts of volatile components and those in air to determine amounts of ashes [5]. Table 3 compares the thermal analysis results with those obtained following the conventional ASTM method (LARECOM Laboratorio Regional de Combustible). The data show good agreement.

Table 3 Chemical components of samples

Samples	% Wet		% Volatiles s/d		% Ashes s/d		% Coal s/d	
	TG	ASTM	TG	ASTM	TG	ASTM	TG	ASTM
Straw wheat	5.69	4.26	73.11	75.85	5.60	6.52	21.29	17.63
Straw barley	7.64	6.89	75.57	78.26	4.88	5.25	19.55	16.49
Straw six-row barley	6.74	4.43	78.53	78.54	5.25	4.18	16.22	17.28
Straw rye	5.78	3.82	81.57	83.59	1.93	1.93	16.50	14.48

DSC curves in air were used to obtain the enthalpy ΔH over a fixed temperature interval that we term the thermobalance heat value (THV). The enthalpy of combustion at 298 K that we term the high heat value (HHV), was measured in an adiabatic calorimeter following the ASTM method. Table 4 compares HHV and THV data for the four materials.

Table 4 Experimental results for HHV and THV

Sample	HHV/kcal· kg^{-1}	THV/kcal· kg^{-1}
Straw wheat	4398	1850.3
Straw barley	4478	2050.4
Straw six-row barley	4458	2102.5
Straw rye	4382	1683.5

Both energy parameters are quite different, but the purpose of this work was to obtain the HHV parameter through the THV parameter measured by thermal analysis methods.

We have proposed a correlation [6] based on the following equation:

$$HHV_c = THV + A\ \%\ \mathrm{C} + B\ \%\ \mathrm{H} + C$$

where HHV_c: high heat value, calculated
TVH: thermobalance heat value
%C: carbon in sample
%H: hydrogen in sample
A,B,C: constants

Table 5 Chemical components of standard samples and experimental HHV

Sample	% C	% H	%O	% A	HHV/kcal· kg^{-1}	THV/kcal· kg^{-1}
Graphite	95	--	--	5.0	7831.1	4882.0
D-Glucose	40.002	6.714	53.284	0.5	3735.0	1547.4

The A and B constants were calculated from DSC using standard samples of graphite and D-glucose (Table 5). Table 6 lists other data used. The results obtained were: A = 32.5, B = 154.4. The C constant was calculated according to Sancho *et al.* [2].

$$C = -150\left(1 + \frac{\%\,Ash}{100}\right)$$

Table 6 Chemical components of straws

Samples	% C	% H	% N	% S	% O	% Ash
Straw wheat	47.87	6.91	0.72	0.053	44.447	6.52
Straw barley	48.40	7.28	0.92	0.058	43.342	5.25
Straw six-row barley	47.98	7.15	0.85	0.056	43.964	4.18
Straw rye	50.08	6.99	0.46	0.024	42.446	1.93

Table 7 Energy parameters of straws

Samples	*HHV* exp/kcal· kg^{-1}	*THV*/kcal· kg^{-1}	*HHV calc.*/kcal· kg^{-1}	% A
Straw wheat	4398	1850.3	4331.4	- 1.51
Straw barley	4478	2050.4	4604.7	+ 2.83
Straw six-row barley	4458	2102.5	4623.7	+ 3.72
Straw rye	4382	1683.5	4253.2	- 2.94

Table 7 shows the *HHV* data calculated from this equation for all the samples. Results show good agreement with the experimental data obtained by ASTM methods.

Conclusions

TG and DTG curves show differences in thermal stability between the samples (Fig. 9) and are in good agreement with results given by Corlateanu [7]. Following similar expresions for coal through thermal analysis by Sancho [6], we have proposed a new correlation for biomass and calculated the *HHV* according to experimental data *THV* obtained from DSC curves.

The calculated *HHV* data from thermal analysis methods are in good agreement with the experimental *HHV* data from the ASTM method. Thermal analysis methods can therefore be a good alternative for rapid and quantitative characterization of agricultural residues under consideration as fuels in combustion.

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Zusammenfassung — Eine wichtige Anwendung von agrarwirtschaftlichen Restbeständen ist die Verwendung als Brennstoff für Verbrennungsprozesse. Es wird hier gezeigt, wie die Thermoanalyse zur Charakterisierung verschiedener Getreidearten angewendet werden kann, um eine höhere Effektivität der Verbrennungsprozesse zu erreichen. Die erhaltenen Resultate stehen in guter Übereinstimmung mit den mittels Standard-ASTM-Methoden ermittelten Ergebnissen.