

THE CONSTRUCTION OF A DIFFERENTIAL THERMAL ANALYSER FOR STUDYING THE GASIFICATION OF COAL UNDER HYDROGEN PRESSURE

R. CYPRÈS, C. BRAEKMAN-DANHEUX, D. PLANCHON and F. GOOSSENS

Service de Chimie Générale et Carbochimie, Faculté des Sciences appliquées (C.P. 165), Université Libre de Bruxelles, Avenue F.D. Roosevelt, 50, 1050 Brussels (Belgium)

(Received 24 April 1985)

ABSTRACT

A differential thermal analysis (DTA) device has been constructed for use up to 1000°C and 5 MPa in parallel with a two-pan thermobalance described previously. The calibration has been realised under pressure and in two different gases. A computer program leads to quantitative measurements of the heats of reaction during direct hydrogenation of coal and chars. Examples are given for hydrogasification of a Beringen Belgian coal.

INTRODUCTION

Differential thermal analysis (DTA) is a useful technique for investigating reactions between solids and gases at elevated temperatures. It is an especially powerful method, when coupled with thermogravimetry, for studying the thermal behaviour of coal during gasification under hydrogen pressure. Makino et al. [1,2] reported DTA results for coal and various catalysts under hydrogen pressure. Tanabe et al. [3] examined the activities of 14 catalysts on a Taiheyo coal by DTA under 15 MPa static hydrogen. They concluded that DTA could be a rapid and convenient method to evaluate catalytic activity. Recently, Rogers [4] reported DTA results on the influence of various cations on lignite hydrogenation.

A thermobalance with two symmetrical pans, which makes possible the direct hydrogenation of coals up to 1000°C and under 5 MPa, has been built in our laboratory [5]. In the present paper, we describe the construction of a simple, under-pressure DTA device, coupled with the thermobalance, which is able to withstand pressures up to 5 MPa of reactive gas and temperatures up to 1000°C. Its calibration and the first results obtained on a Beringen Belgian coal are also presented here.

DESCRIPTION OF THE DTA

Figure 1 gives the schematic diagram of the installation. An alumina crucible (17), made of two identical 0.4-ml compartments, is maintained in the isothermal zone of an HT 3Y1 steel reactor (ID, 36 mm; OD, 60 mm; length, 500 mm). Two chromel–alumel thermocouples are inserted in the centre of each compartment and their signals are analysed by a variable-gain voltmeter (419 A.D.C. null Volt. H.P.). A third thermocouple measures the temperature inside the reactor. The temperature regulation, and the data acquisition and treatments are performed by a microprocessor (29) (IMSAI PCS 42) following specific programs. The whole installation can be evacuated by means of a roughing pump (27). Off-gases pass through a tar trap (19) and are analysed by gas chromatography.

PROCEDURE

A coal sample (~ 1 g), dried, ground and sifted to $500 \mu\text{m}$, is weighed in one of the crucible compartments. The second compartment is filled with the reference compound (alumina). The thermocouples are then adjusted. The

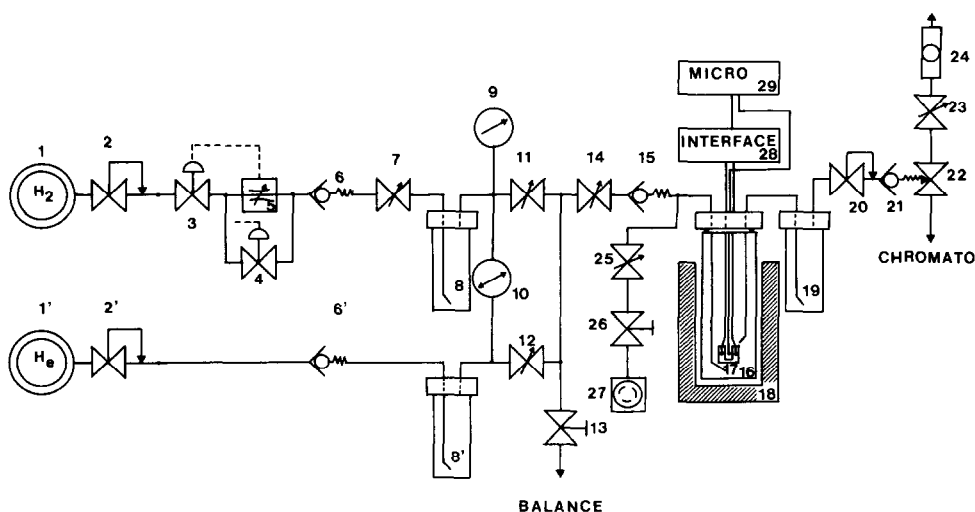


Fig. 1. Schematic diagram of the installation: (1) gas cylinders; (2) pressure regulator valve; (3, 4) electromagnetic valve; (5) safety device; (6, 15, 21) non-return valves; (7) flow regulator valve; (8) liquid nitrogen trap; (9) manometer; (10) differential manometer; (11, 12, 14, 25) flow-regulator valves; (13, 26) throttle valves; (16) reactor; (17) crucible with thermocouples; (18) furnace; (19) tar trap; (20) outside-pressure regulator valve; (22) two-way valve; (23) outside-flow regulator valve; (24) flow-meter; (27) vacuum pump; (28) interface; (29) micro-processor.

TABLE 1

Characteristics of the standards used for calibration

Standards	Reaction temp. ^a (°C)		Reaction ^b	$\Delta H(\text{cal g}^{-1})$
	0.1 MPa H ₂	4 MPa H ₂		
KNO ₃	159	154	T	12.86
Sn	267	257	F	14.4
Pb	346	354	F	5.9
Zn	444	444	F	24.4
Quartz	584	586	T	2
Al	673	675	T	95.25
BaCO ₃	823	818	T	18

^a Reactor temperature at the top of the peak.^b T = polymorphic transition, F = fusion.

reactor and its oven are fixed on the flanges, and after evacuation, the reactive gas is admitted at the required pressure and the system is heated at a rate of 10°C min⁻¹ up to the required temperature. The thermobalance coupled with the DTA system can operate in parallel at the same pressure and temperature.

CALIBRATION

The determination of the heat of reaction from the area of the curve peak is a widely used procedure in DTA [6]. Expressed very simply, $\Delta Hm = KA$,

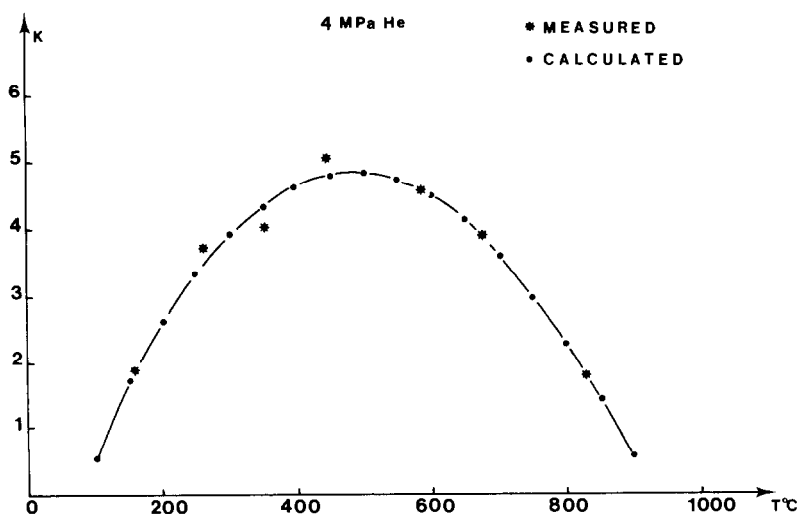


Fig. 2. Calibration coefficient as a function of the reactor temperature, $P = 4$ MPa He.

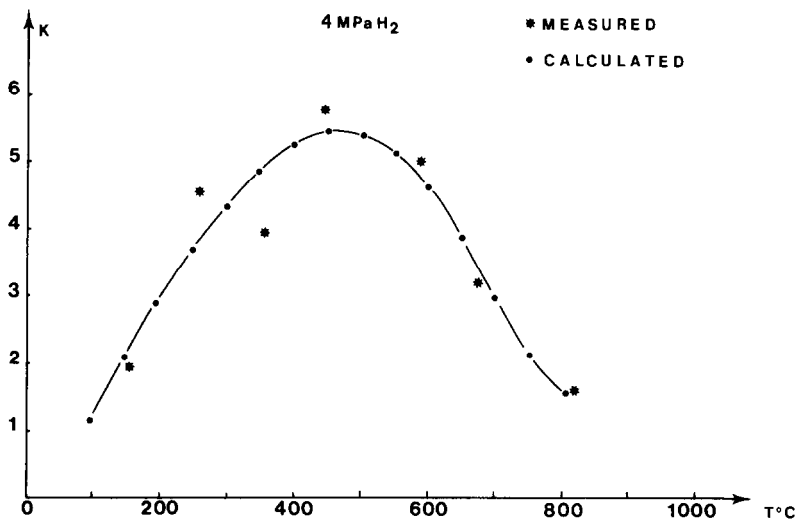


Fig. 3. Calibration coefficient as a function of the reactor temperature, $P = 4 \text{ MPa H}_2$.

where ΔH is the heat of reaction, m is the mass of reactive sample, K is the calibration coefficient and A is the curve peak area. The calibration coefficient has to be determined by use of compounds having known heats of reaction. A series of standards has been used to cover the temperature interval needed (20–900°C). Moreover, several experiments have been performed with the same standard under different pressures (0.1, 2 and 4 MPa) of two different gases (H_2 and He). The characteristics of the standards are given in Table 1. Figures 2 and 3 show the calibration coefficient as a function of the reactor temperature under 4 MPa He and H_2 .

APPLICATION TO COAL

In order to verify the performance of the installation, DTA of a coal has been performed at two different pressures of He and H_2 . A Beringen (Belgian) coal has been used; its characteristics are given in Table 2. Figures 4–7 show the DTA diagrams obtained with this coal, heated from 20 to

TABLE 2

Beringen coal analysis

Proximate analysis (wt%):	moisture, 3.7
	ash (mf), 7.3
	volatile matter (mf), 35.5
Ultimate analysis (wt% mf):	C, 74.4; H, 4.8; N, 1.9; S, 0.6; O, 10.9 ^a

^a Measured.

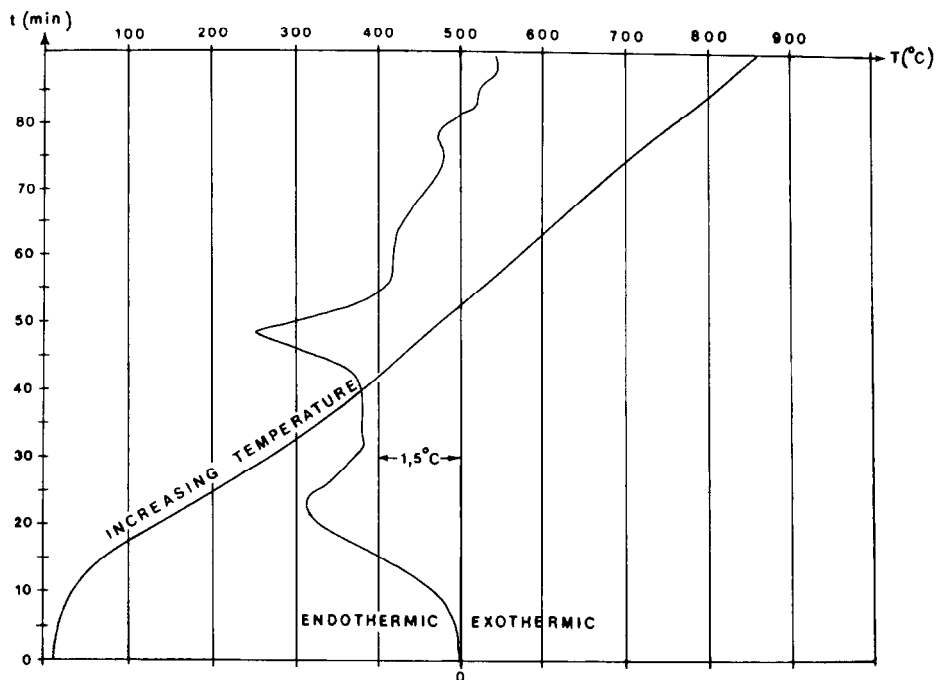


Fig. 4. DTA of Beringen coal, $P = 0.1$ MPa He.

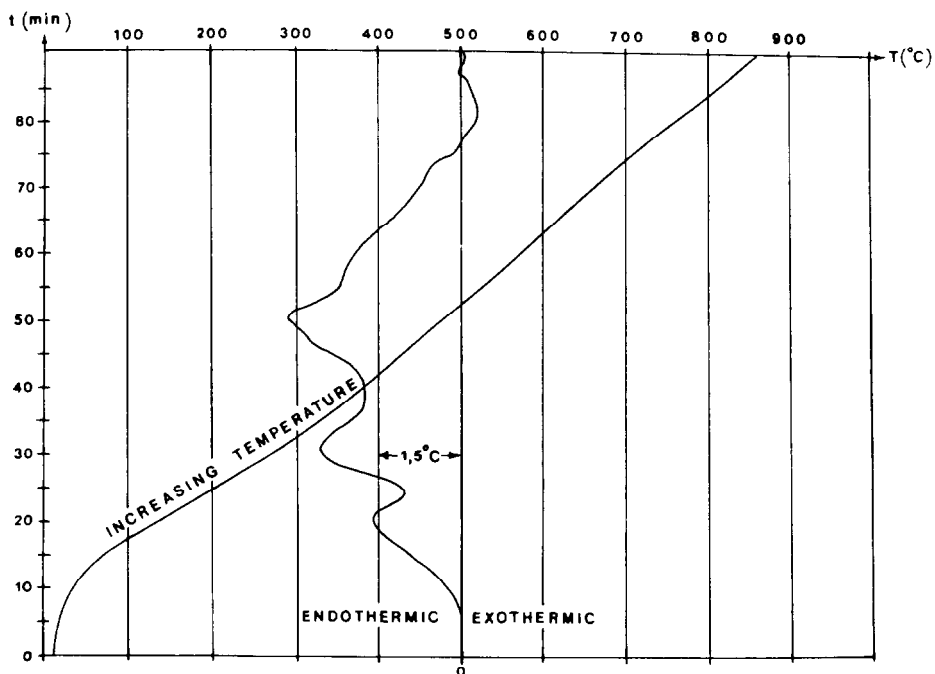


Fig. 5. DTA of Beringen coal, $P = 3$ MPa He.

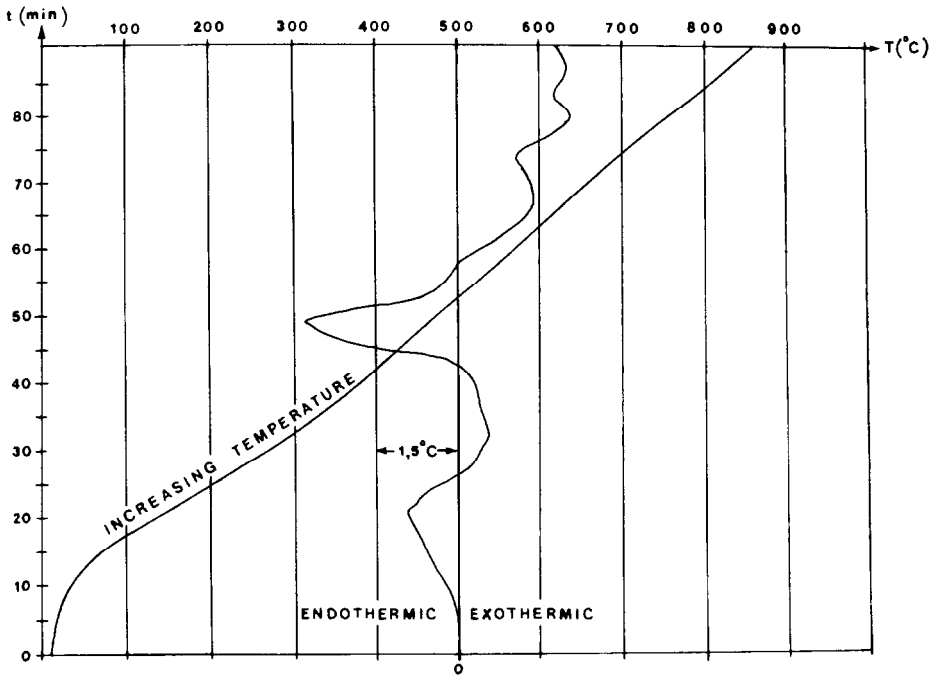


Fig. 6. DTA of Beringen coal, $P = 0.1 \text{ MPa H}_2$.

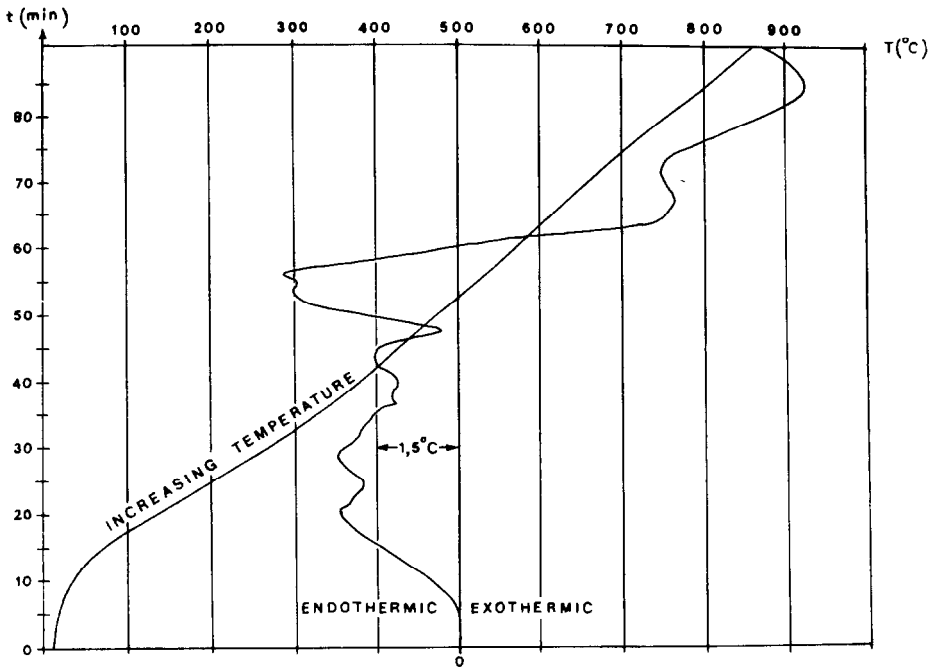


Fig. 7. DTA of Beringen coal, $P = 3 \text{ MPa H}_2$.

900°C at 10°C min⁻¹ under 0.1 and 3 MPa He and H₂. The heats of reaction corresponding to the exothermic curve under hydrogen pressure have been calculated, using the calibration coefficient determined previously. From 146 cal g⁻¹ under 0.1 MPa H₂, the heat of reaction increases to 460 cal g⁻¹ under 3 MPa H₂, confirming the influence of hydrogen pressure on the coal reactivity. The computer program permits the deconvolution of the curve in its individual gaussians. The method will now be used routinely for coal hydrogenation research in parallel with thermogravimetry and analysis of the evolved gases.

ACKNOWLEDGEMENT

The authors wish to thank the European Coal and Steel Community for the financial support for this research.

REFERENCES

- 1 K. Makino, T. Takekawa and K. Ouchi, *Therm. Anal.*, 5 (1977) 52.
- 2 K. Makino, S. Veda and M. Shibaoka, *Fuel*, 57 (1978) 655.
- 3 K. Tanabe, H. Sasaki and H. Hattori, *Fuel Process. Technol.*, 2 (1979) 253.
- 4 D.E. Rogers, *Fuel*, 63 (1984) 1610.
- 5 M. Ghodsi and C. Neumann-Tilte, *Thermochim. Acta*, 62 (1983) 1.
- 6 W.W. Wendlandt, *Thermal Methods of Analysis, Chemistry Series, Vol. 19*, Wiley, New York, 1974.