

THE CONSTRUCTION OF AN ISOTHERMAL BALANCE WITH TWO SYMMETRICAL PANS FOR DIRECT HYDROGENATION OF COALS

M. GHODSI and C. NEUMANN-TILTE

Service de Chimie Industrielle et de Chimie des Solides, Université Libre de Bruxelles, Bruxelles (Belgium)

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ABSTRACT

Previously, we constructed an isothermal balance with two symmetrical pans for operation under pressure [1] in which we studied the hydrogenation kinetics of coal chars under pressures up to 5 MPa [2]. The modified version of this balance, makes it possible to study the direct hydrogenation of coals without any preliminary treatment. The balance was tested on an Italian coal, "Sulcis", with a high sulfur content.

INTRODUCTION

Thermogravimetry is a method suiting particularly well the study of the gasification kinetics of coals. This was the method used by Johnson and Nandi [3,4] for chars, and Makino and Toda [5], and Arendt and Van Heek [6] for coals with one-pan balances.

Cyprés et al. [2,7] studied the hydrogenogasification of graphite, pitch carbon and lignite char first in a microbalance under atmospheric pressure and then in a thermobalance under pressure [8]. In order to investigate further in this field, we constructed a pressure thermobalance with two pans, connected to a minicomputer, which makes possible the direct hydrogenation of coals up to 1000°C and under 5 MPa.

The main causes of error in thermogravimetry under pressure, namely Archimedes' forces, viscosity forces arising from the gas flow along mobile parts, and thermal gradient forces, may be avoided, or at least minimized, in a two-pan balance.

DESCRIPTION OF THE BALANCE

The balance previously described [1] could only treat chars. Direct coal gasification yields an important proportion of condensable liquid, the tars,

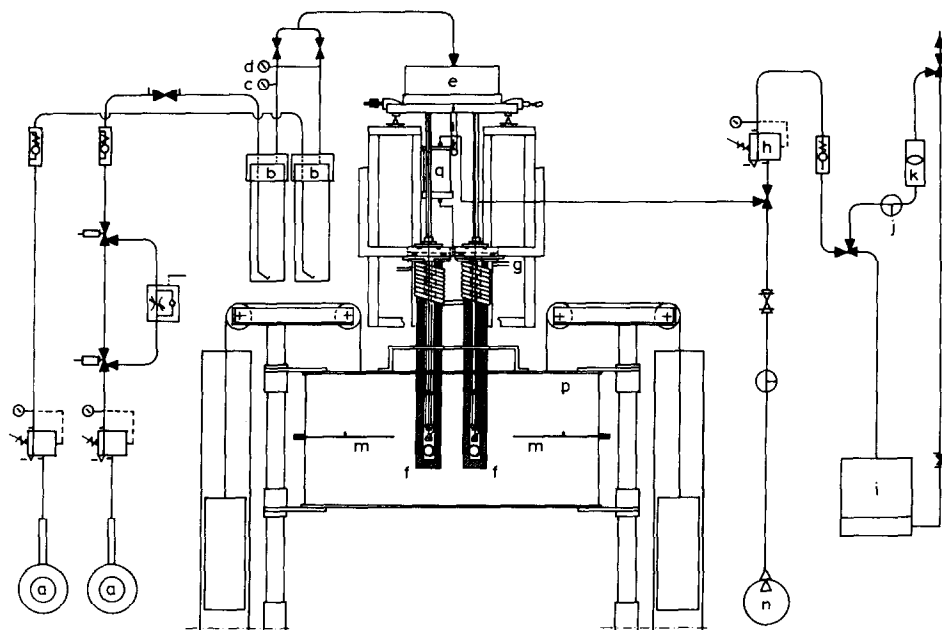


Fig. 1. Schematic diagram of the installation. (a) Gas cylinders; (b) liquid nitrogen traps; (c) manometer; (d) differential manometer; (e) balance head; (f) vessels; (g) flange cooling circuits; (h) expansion valve; (i) chromatograph; (j) flow regulator valve; (k) flow meter; (l) regulation thermocouples; (m) security thermocouples; (n) vacuum pump; (o) crucibles (tare + sample holder); (p) furnace; (q) tar trap.

that could hinder the normal working of the balance. This led us to construct a new balance with some basic changes (fig. 1).

A tar trap was placed in the gas circuit just after the vessels. Although the gas flow enters at the balance head, tar deposits also occurred against the stream; accordingly, the length of the vessels in the area outside the furnace was significantly extended and water cooled. A heating system maintained the balance head (Sartorius 4406) at temperature above 100°C . Tar deposits appeared, in the main, where we thought they would. However, a pitch deposit on the suspension wires in the cooled area necessitated regular cleaning. A minicomputer, integrated to the system, made it possible, with two programs, to regulate the temperature and to analyse the experimental data.

The system was protected in three ways.

(a) An electrostatic valve stopped the hydrogen flow in case of leaks and started an alarm.

(b) The computer stopped the experiment if the cooling water flow was insufficient.

(c) Thermocouples in the hottest area of the furnace were linked to regulators set at 1000°C .

THERMOGRAVIMETRY OF THE SULCIS COAL

Coal analysis (wt. %)

Sulcis coal is a young coal from Italy with high sulfur and calcite contents:

Proximate analysis.

Moisture			6.0%
Volatile	matter	(m.a.f.) *	56.4%
	ash	(m.f.) *	12.9%
Reduced	ash	(m.f.)	7.5%

ultimate analysis (m.f.). C 63.2%; H 3.7%; N 1.8%; O 14.1%; S 4.3%; ash 12.9%.

Sulfur distribution (m.f.). Sulfate 0.32%; pyritic 0.36%; organic 3.63%.

Mineral matter (m.f.). CaCO₃ 7.3%; MgCO₃ 2.9%; CaSO₄ · 2 H₂O 1.7%; SiO₂ 0.6%; Al₂O₃ 0.2%; Fe₂O₃ 0.6%; FeS₂ 0.7%.

Procedure

The coal was dried, ground, sifted to less than 106 μm , compacted and kept under vacuum. The samples (± 100 mg) were placed in alumina crucibles. After evacuation, the apparatus was purged with helium and the zero stability checked. Then the pure and dry experimental gas was admitted at the experimental pressure from 20°C upwards. The installation was then heated up to the desired temperature at 12°C min⁻¹ followed by soaking at that temperature. Off gases were analyzed by gas chromatography.

STUDY OF DIFFERENT PARAMETERS

Pressure

Figure 2 shows the gasification yield under hydrogen pressure from 0.1 to 5 MPa as well as that under 0.1 MPa of helium. It was found that, whatever the pressure, the gasification yield reaches about 50% at 600°C, approximately equivalent to the volatile matter of the coal. This suggests that the gasification yield of this fraction is little influenced by pressure. In contrast, the gasification of the hydrogenable fraction depends markedly on pressure as Makino and Toda [5] and Cochran [9] had previously reported. At 900°C under 5 MPa, the gasification yield is over 95%.

* m.a.f. = moisture and ash free; m.f. = moisture free.

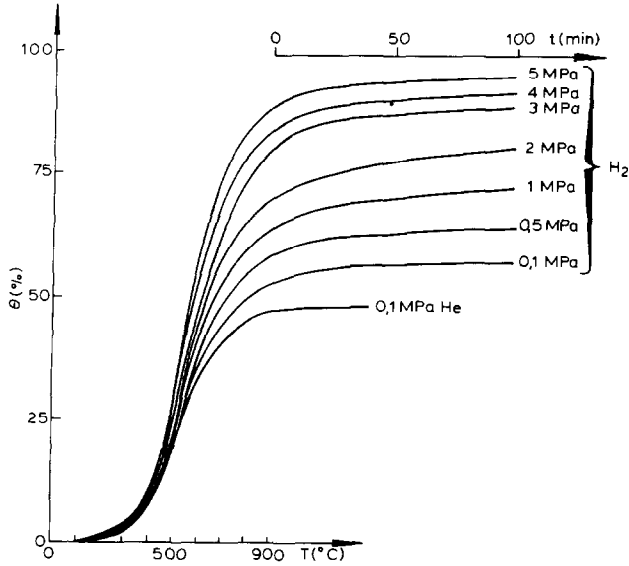


Fig. 2. Thermogravimetry of Sulcis coal under different hydrogen pressures and under helium.

Temperature

The curves in Fig. 3 represent the hydrogenation yields for temperatures between 600 and 1000°C under 4 MPa.

It should be noted that the gasification kinetics of the hydrogenable

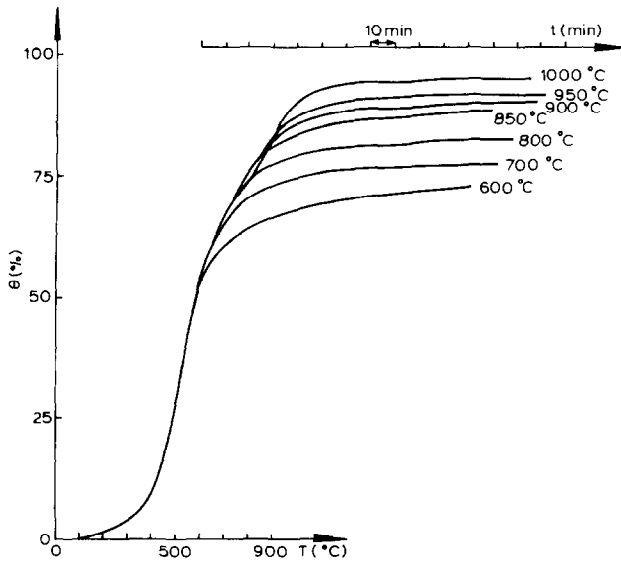


Fig. 3. Thermogravimetry of Sulcis coal under 4 MPa of H_2 at different temperatures.

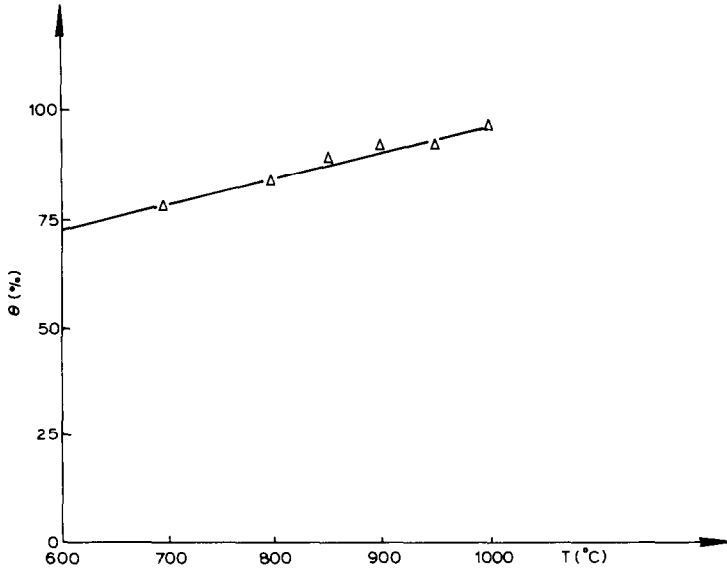


Fig. 4. Gasification yields of Sulcis coal under 4 MPa of H_2 versus gasification temperature.

fraction of the coal is a function of temperature. Figure 4 shows the gasification yield as a function of the temperature of the straight-line portion after 100 min. It yields a linear relation $\theta\% = 0.058 T + 37.79$ ($r = 0.99$).

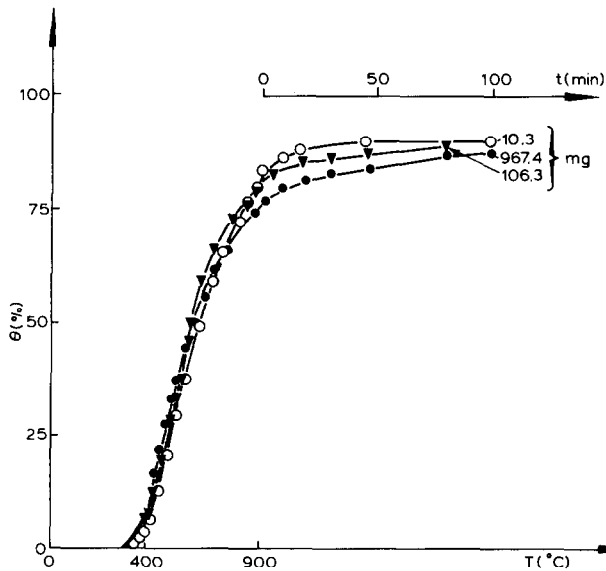


Fig. 5. Thermogravimetry of 10, 100 and 1000 mg Sulcis coal samples under 4 MPa of H_2 .

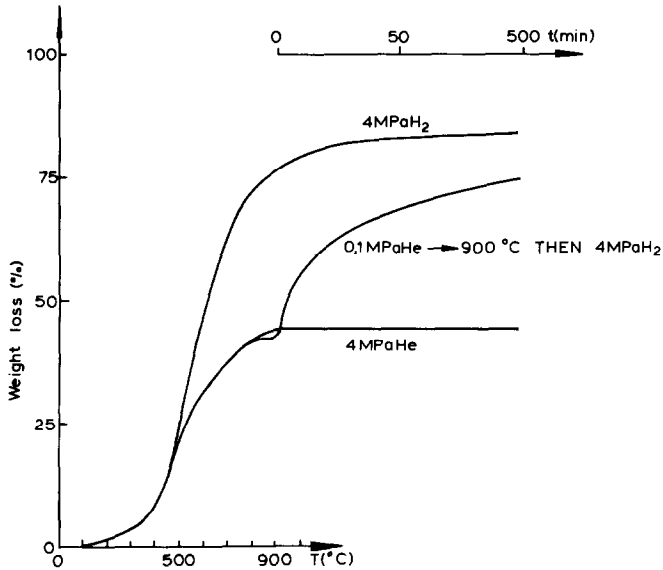


Fig. 6. Thermogravimetry of Sulcis coal under different conditions.

Mass of the sample

Samples of 10, 100 and 1000 mg were treated after pre-heating under 0.1 MPa of helium. The results appear in Fig. 5 and show that the curves are little influenced by this parameter. The limited deviations at 900°C can be accounted for by diffusion processes.

Gas atmosphere

Figure 6 presents three thermogravimetric curves under 4 MPa of He or H₂, and under 0.1 MPa of He up to 900°C (carbonization) followed by gasification under 4 MPa H₂ at 900°C for 100 min. The devolatilization yield is little influenced by pressure in a neutral atmosphere, but the non-gasified fraction of the coal is not lost: it can still be hydrogenated at a slower rate.

Gas analysis

The validity of the results is only qualitative since, on the one hand, gases at the outlet are greatly diluted in hydrogen and, on the other hand, there is a delay between the formation of a compound and its detection.

The detected gases were CH₄, C₂H₆ and CO₂. CO₂ appeared towards 300°C, reached a maximum at 600°C and disappeared around 700°C. C₂H₆ reached a first maximum around 300°C and a second more important one, towards 750°C. It then quickly disappeared. CH₄ was increasingly produced from 650°C up to 900°C. These results corroborate those found in the

literature [2,5,10]. The temperature of the maxima vary according to the type of coal.

CONCLUSIONS

We have constructed a two-pan thermobalance for use up to 1000°C and 5 MPa for the direct hydrogenation of coals without preliminary treatment. The symmetrical pans remove the usual causes of error in thermogravimetry with one-pan balances. The installation was designed so as to protect the balance head against the condensation of the products from the coal pyrolysis (tars, aromatics, water). The experiments on Sulcis coal exhibit clearly the appreciable performance of the balance. It also brings out the marked influence of pressure on the hydrogenation kinetics of coals. At 900°C and under 5 MPa H₂ the gasification is almost complete.

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