GASIFICATION IN STEAM OF A BITUMINOUS COAL FROM PEÑARROYA (CORDOBA, SPAIN) AND OF DIFFERENT SAMPLES PREPARED FROM IT

C. Valenzuela Calahorro, A. Bernalte García and *V. Gómez Serrano*

DEPARTAMENTO DE QUÍMICA INORGÁNICA, FACULTAD DE CIENCIAS, UNIVERSIDAD DE EXTREMADURA, 06071 BADAJOZ, SPAIN

The gasification with steam of a bituminous coal from Peñarroya (Cordoba, Spain) (H—O) and of several samples prepared from either by acid treatment (H—H, H—N, H—F and H—F(3)) or by thermal treatment (H—O—C) was studied under both dynamic and isothermal conditions (10 deg/min and 40 min at 1000°).

It was found that only for the samples prepared by hydrofluoric acid treatment, H—F and H—F(3), did the gasification effected under such experimental conditions take place in a complete manner.

Because of the current interest in coal-conversion processes for producing liquid and gaseous fuels, the char-steam reaction has assumed unique importance. The major products of this reaction, CO and H_2, can be used not only as a gas of medium heating value, but also as precursors for the catalytic synthesis of a wide range of products, as well as for the production of substitute natural gas by catalytic methanation.

Most inorganic impurities catalyse the gasification of carbon [1, 2]. The specific catalytic activity of an impurity is determined by its chemical form and degree of dispersion. The effects on the steam-carbon reaction following partial removal of inorganic impurities from a bituminous coal from Peñarroya (Cordoba, Spain) by acid-washing with HCl, HCl—HNO_3 or HCl—HF have been studied under dynamic conditions.

Experimental

The raw coal (H—O) was classified in a previous study [3] according to the ASTM system [4] as a high-volatile bituminous coal. The samples produced from this coal, as starting material, by different treatments are referred to as follows in the text:

5

H—H, produced by refluxing H—O with 5 N HCl solution;

H—N, produced by refluxing H—H with 2 N HNO$_3$ solution;

H—F, produced by treatment of H—H with 48 wt.% HF solution, with evaporation to dryness;

H—F(3), produced by carrying out the HF treatment three times; and

H—O—C, produced by charring H—O at 1000° (10 deg/min) for 2 hours in a flow of nitrogen (200 ml/min, 1 atm.).

The particle size interval between 0.15 and 0.20 mm was chosen for the above treatments.

Proximate analysis of moisture, ash, volatile matter and (by difference) fixed carbon was accomplished for all samples following a thermogravimetric method adapted to the ASTM norms [5].

First, all samples were gasified with steam under dynamic conditions (10 deg-/min) up to 1000°, with subsequently 40 min isothermally at this temperature. A N$_2$—H$_2$O mixture, obtained by bubbling N$_2$ through water at 30°, was used as gasification agent.

Secondly, the above samples were charred, either by heating to 1000°, or by heating to 1000° with a subsequent isothermal period of 50 min. The resulting samples were then gasified with the aim of determining the possible influence of the volatile matter on the gasification process.

About 5 mg of sample was used in each gasification run.

Results and discussion

The results given by the thermogravimetric analysis relative to the moisture, volatile matter, ash and fixed carbon contents for all samples under consideration are listed in Table 1.

As might be expected, the inorganic matter removal was dependent on the acid treatment; this is shown in Table 1 by the variation of the ash yield with the acid treatment. Thus, the HCl treatment had scarcely any effect on the inorganic matter removal from H—O, which suggests that the raw coal has low contents of carbonate and soluble salts. On the other hand, the HF treatment was found to be the most efficient method for removing most inorganic matter from this coal. The latter result agrees with the high SiO$_2$ and Al$_2$O$_3$ contents found by other authors [3] in investigations of the ash obtained from the same raw coal.

Figures 1 to 6 show the results of thermogravimetry applied to study the gasification of our carbonaceous materials in steam. It may be noted that only samples H—F and H—F(3) exhibit constant weight, even after 40 min isothermal heating at 1000°. Moreover, the weight loss percentage progressively decreases from
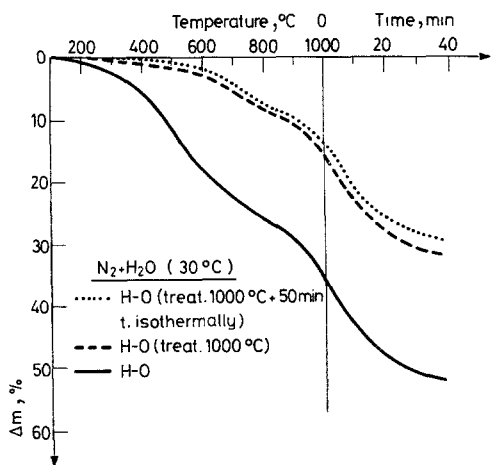
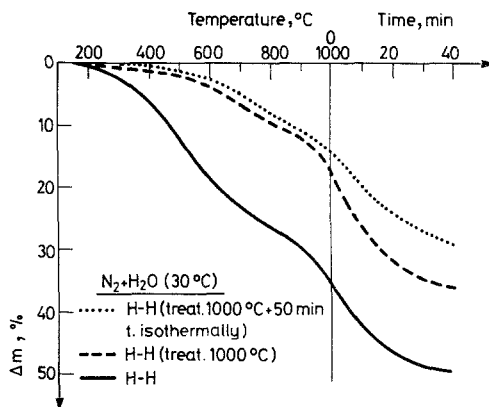Fig. 1 TG curves of H—O and its chars in steam

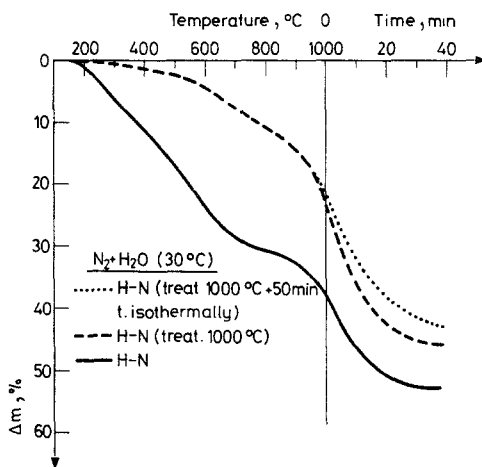Fig. 2 TG curves of H—H and its chars in steam

Fig. 3 TG curves of H—N and its chars in steam

the thermally non-treated sample to the char produced at 1000° for 50 min which is clearly explained by the almost complete removal by thermal treatment of the volatile components and by the fact that the ash yield is more significant when the weight fraction of volatile matter is decreased.

The weight loss percentage for the other samples is lower than the sum of the fixed carbon and volatile matter contents (Table 1); this can be considered as an indication that the gasification process was not completed and that residual carbonaceous matter remained ungasified.
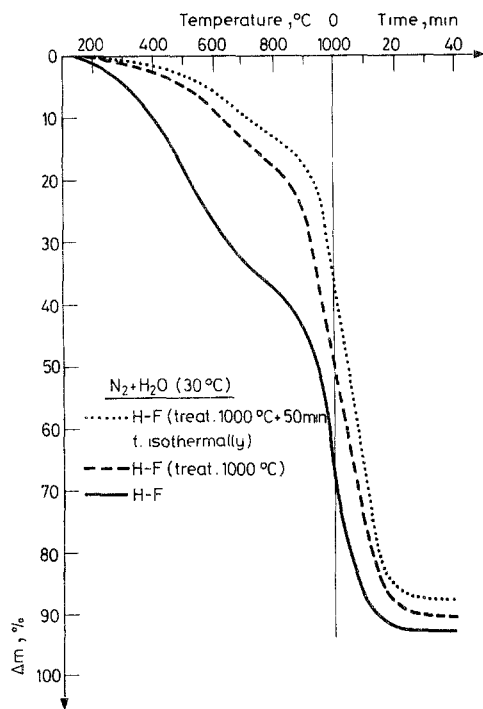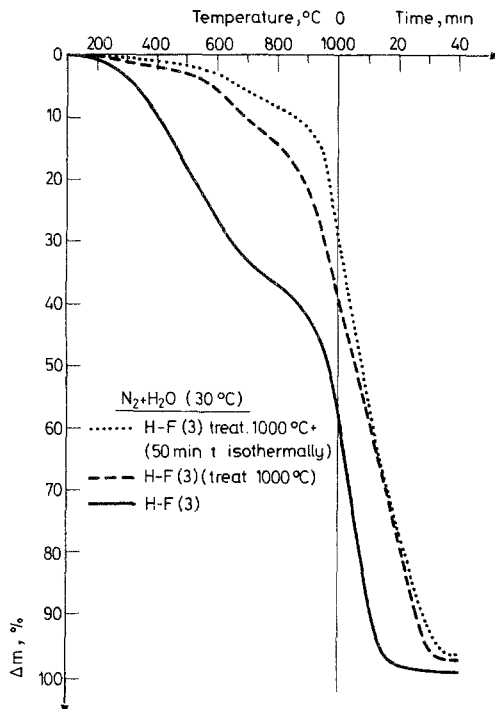
Fig. 4 TG eurves of H—F and its chars in steam

Fig. 5 TG curves of H—F(3) and its chars in steam

Table 1 Proximate analysis of samples

Sample	Moisture	Volatile matter	Fixed carbon	Ash
		%		
H—O	4.74	18.88	38.56	42.56
H—H	4.73	18.58	38.86	42.56
H—N	7.06	24.28	37.05	38.67
H—F	8.36	31.17	60.62	7.91
H—F(3)	9.18	33.22	65.37	1.41
H—O—C	4.14	2.14	40.23	57.58

Moisture: Weight loss from room temperature to 120° and after five minutes of isothermal treatment at this temperature. (N_2-atmosphere)

Volatile matter: Weight loss from 120° to 950° (80 deg/min) and seven minutes of isothermal treatment at this temperature (N_2-atmosphere)

Fixed carbon and ash: After the seven minutes at 950° under N_2, a switching valve is used to change N_2 by O_2 for the combustion of the fixed carbon. The weight loss represents the fixed carbon content and the residue then represents the ash content.

For samples H—O and H—H, the difference between the weight loss percentages corresponding to the thermally treated and non-treated samples is very close to the volatile matter content. This suggests that the removal of such volatile matter by thermal treatment does not have a significant effect on the subsequently fixed carbon gasification.

In contrast, for sample H—N the difference between the weight loss percentages for the thermally treated and non-treated samples is somewhat smaller than the
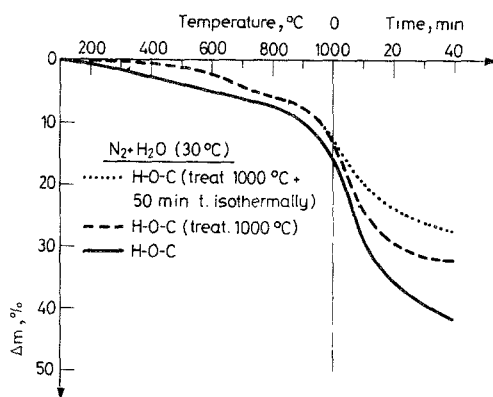

Fig. 6 TG curves of H—O—C and its chars in steam

volatile matter content of this latter material. This result can be explained by assuming the formation during HNO_3 treatment of carbon-oxygen surface complexes; once decomposed by thermal treatment, these give rise to a more porous carbonaceous material, with active sites of easier attack by steam.

Finally, for sample H—O—C the difference between the weight loss percentages is always greater than the volatile matter content. The decrease in the weight loss percentage when the thermal treatment intensity is increased must be due to the formation of progressively larger and more perfect graphitic microcrystallites as a result of the thermal treatment. These more ordered microcrystallites will possess a less accessible surface area for the steam molecules, and they will therefore be rather more difficult to gasify with the reactive agent.

The results given above indicate that the greater weight loss percentage for each sample corresponds to the lower ash yield. It is likely that part of the carbonaceous matter occurs occluded in the mineral matter and that, consequently, it must be only slightly accessible to the steam molecules under the experimental conditions in which the gasification process was carried out. A lowering of the inorganic impurity content in chars resulted in increases in reactivity [6]. The effect was attributed to

the presence of additional macropores and transitional pores in these chars as a result of the removal of inorganic constituents. That is, the accessibility to the active carbon sites was enhanced.

* * *

References

1 P. L. Walker, Jr., F. Rusinko and L. G. Austin Adv. Catal., 11 (1959) 221.

2 P. L. Walker, Jr., M. Shelef and R. A. Anderson—Chemistry and Physics of Carbon., Vol. 4., Marcel Dekker, N.Y., (1968).

3 M. C. Fernandez Gonzales, Thesis Doctoral. Fac. Ciencias. Univ. Extremadura, Badajoz, Spain, 1984.

4 L. Grainger and J. Gibson, Coal utilisation: Technology Economics and Policy, Graham & Trotman, London, 1981.

5 The model TGS-2 Thermogravimetric System. Folleto N° L-508. Perkin-Elmer Co., 1978.

6 E. Hippo and P. L. Walker, Jr., Fuel, 54 (1975) 245.

Zusammenfassung — Die Dampfvergasung von bituminöser Kohle (H—O) (Penarroya, Cordoba, Spanien) und von daraus durch Säurebehandlungen (H—H, H—N, H—F und H—F(3)) oder thermische Behandlung (H—O—C) hergestellten Proben wurde unter dynamischen und isothermen Bedingungen (10 °/min und 40 min bei 1000°) untersucht. Es wurde festgestellt, daß nur die durch Flußsäurebehandlung hergestellten Proben (H—F und H—F(3)) unter den experimentellen Bedingungen vollständig vergasbar sind.

Резюме — В динамических и изотермических условиях (10°/мин и 40 мин для 1000°) ихучена газификация водяным паром битуминозных углей месторождения Пенароя (Испания) и некоторых образцов, полученных из них кислотной или термической обработкой. Установлено, что только в случает образцов, полученных обработкой фтористоводородной кислотой, газификация протекает полностью при данных экспериментальных условиях.