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GASIFICATION IN AIR AND IN STEAM OF A PARTLY DEMINERALIZED AND HEAT-TREATED COAL

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The gasification in air and in steam of a bituminous coal from Belmez (Cordoba, Spain) (SAO) and of samples resulting either from acid treatment (HCl, SAH; HNO_3 SAN and HF, SAF) or from thermal treatment (SAOC) has been studied under dynamic conditions.

For gasification in air, the sequence of variation of the reactivity is SAN > SAF > SAH > SAO at lower gasification temperatures, and SAF > SAH > SAN > SAO at higher treatment temperatures. In steam, however, the sequence is SAF > SAO, SAH > SAN in the whole interval of gasification temperatures. SAOC shows a reactivity much lower than SAO in both reactant gases. The results are explained by considering the feasible effects of the treatments on the textural characteristics and on the chemical surface of the coal.

Increasing interest in coal gasification processes has led to a need for the investigation of the behaviour of local coal sources in these processes. It is not possible to predict with confidence the gasification behaviour of one coal on the basis of data obtained for another [1], because the reactivity depends not only on the coal quality [2], but also on other factors, such as the presence of catalytic inorganic impurities [3]. A high mineral matter content is a characteristic of Spanish coals, which have mean ash contents in the range 30–45% [4]. It cannot be assumed that the properties of these coals are the same as of coals of similar quality. It might be expected that devolatilization, demineralization and catalytic effects upon reactivity will be modified by the presence of large proportions of mineral matter [5].

The behaviour of Spanish coals in gasification reactions has not been studied sufficiently. The carbon-oxygen [air] reaction is important in the overall gasification scheme because the reaction is rapid and exothermic. Moreover, some chars are reacted with air to produce the heat and temperature required to drive the carbon-water reaction for the production of CO and hydrogen. This paper reports a study

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of the thermal behaviour in oxygen (air) and steam of a Spanish coal from the San Antonio mine (Bélmez, Córdoba, Spain) and of its products of acid treatment and heat treatment.

Experimental

The starting coal (SAO) was obtained from the San Antonio mine which belongs to the Mariánicas Occidentales Subzone in the classification of Spanish coal resources [4]. This coal was classified by following the ASTM norms as high volatile A bituminous [6]. The coal was first ground and sized, and the particle size between 0.15 and 0.20 mm was chosen for subsequent studies.

Ultimate analysis data on the parent coal (Table 1) were obtained in a Perkin–Elmer 240–C elemental analyzer, while the oxygen percentage was calculated by difference. Approximate analysis data (Table 2) were gained by using a Mettler TA–3000 thermogravimetric system [7]. Ash (Table 3) was analyzed following analytical methods described in the literature [8]. The results in Table 3 indicate that the major ash components are silica and alumina.

Table 1 Ultimate analysis of the parent coal (wt%, daf)

C	H	N	S	$O_{(diff)}$
80.9	6.7	1.5	1.9	9.0

Table 2 Approximate analysis of samples (wt%)

Sample	Moisture	Ash	Volatile matter	C_{fixed}
SAO	1.8	52.9	19.9	25.4
SAH	3.4	47.3	21.0	28.4
SAN	3.5	41.7	25.8	29.0
SAF	6.4	4.7	36.7	52.3
SAOC	2.1	56.7	0.6	40.6

Table 3 Ash chemical analysis (expressed as oxides) of the parent coal

Coal	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MgO	CaO	K_2O	Na_2O	SO_3
SAO	58.4	28.7	3.2	1.1	1.7	0.02	5.7	1.3	0.6

The coal was heat-treated in a tubular furnace in flowing nitrogen (99.998 vol%) (flow rate = 100 ml/min) at 5 deg/min up to 1000° and held at this temperature for 2 h. This sample was designated as SAOC.

Removal of inorganic matter from the raw coal (SAO) was accomplished by acid-washing with 5 *N* HCl solution (10 ml per g of coal, at reflux for 30 min) (sample SAH). The removal of inorganic matter was subsequently extended by treating SAH with 2 *N* HNO_3 solution (50 ml per g of coal, at reflux for 30 min) (sample SAN) or with 50 wt% HF solution (4 ml per g of coal, at 85–90° and left to dry) (sample SAF). The acid-treated coals were always washed with distilled water until a negative chloride, nitrate or fluoride ion test was obtained.

The resultant acid and heat-treated coals were then again sized to 0.15–0.20 mm particle size. Approximate analyses of these samples are given in Table 2.

The thermal behaviour of coal chars with oxygen (air) and steam was measured thermogravimetrically (Mettler TA-3000 thermobalance) in the range 300–700° (air) or 900–950° (steam). About 10 mg of sample, in a platinum crucible, was heated in flowing nitrogen (99.998 vol%, flow rate = 200 ml/min) at 50 deg/min to 950° and held at that temperature until constant weight was attained. The temperature in the sample was then changed to the initial reaction temperature and the nitrogen was exchanged for dry air (flow rate = 200 ml/min) or for N_2/H_2O reactant gas prepared by bubbling N_2 (flow rate = 200 ml/min) through water at 30°. Gasification experiments were carried out at a heating rate of 2 deg/min (air) or 1 deg/min (steam); the weight loss during gasification was monitored continuously on the thermobalance.

Data on the adsorption of carbon dioxide (purity >99.998 vol%) at 273 K were obtained by using a conventional volumetric apparatus for gas adsorption. Samples were always first oven-dried at 110° for 24 h and then outgassed at 150° for 12 h, at a pressure of 10^{-6} torr, before adsorption measurements.

Mercury porosimetry data were obtained by using a Carlo Erba 200 porosimeter, which allows pressures in the range 1–2000 kg/cm^2. Samples were always outgassed at a pressure of 10^{-3} torr before dropping mercury from the container to the dilatometer. Helium densities of samples were determined in a Quantachrome Stereopycnometer, following the experimental procedure described elsewhere [9].

Experimental results

Figures 1 and 2 depict the variation of the degree of conversion vs. temperature for the gasification of the samples in air and in steam, respectively. The activity was calculated from the Equation [10]:

$$R = \frac{1}{1-\alpha}\frac{d\alpha}{dt}$$

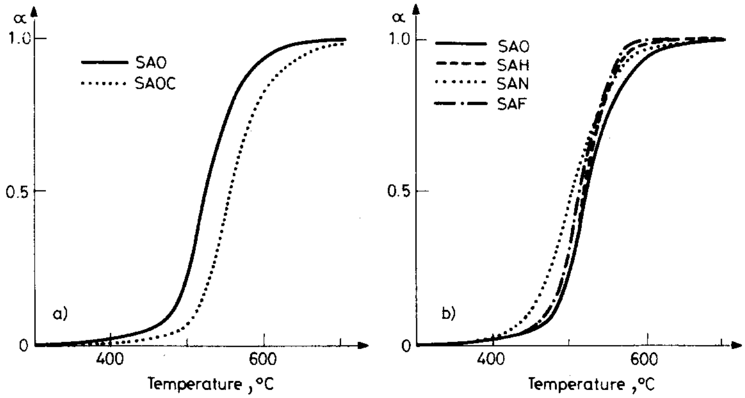

Fig. 1 Variation of degree of conversion with temperature for gasification in air. a) — SAO, ... SAOC; b) — SAO, --- SAH, ... SAN, —.— SAF

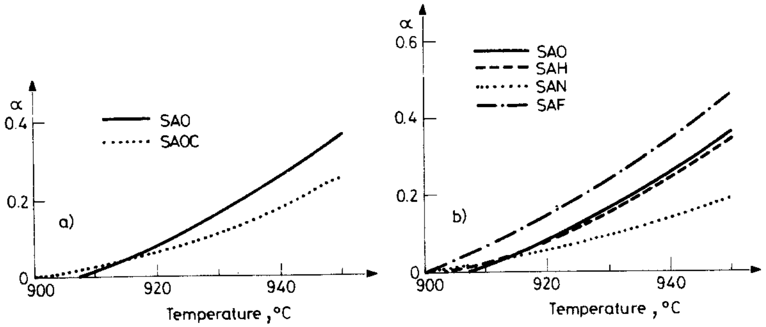

Fig. 2 Variation of degree of conversion with temperature for gasification in steam. a) — SAO, ... SAOC; b) — SAO, --- SAH, ... SAN, —.— SAF

where R = reactivity of the char; α = degree of conversion, referred to the starting sample (dry); $d\alpha/dt$ = variation of the degree of conversion with time (min^{-1}). Reactivities values obtained in this way are given in Tables 4 (gasification in air) and 5 (gasification in steam). In the former case, the sequence of variation of the reactivity is

SAN > SAF > SAH > SAO

at lower gasification temperatures, and

SAF > SAH > SAN > SAO

at higher gasification temperatures. When the gasification is effected in steam, however, the reactivity sequence is

SAF > SAO, SAH > SAN

Table 4 Reactivities of samples in air

Temperature, °C	Reactivity, % min^{-1}				
	SAO	SAH	SAN	SAF	SAOC
350	0.03	0.02	0.04	0.03	0.02
400	0.06	0.04	0.15	0.06	0.03
450	0.21	0.28	0.86	0.34	0.06
500	2.50	2.73	3.80	3.68	0.57
550	5.40	8.96	6.49	9.11	4.58
600	7.31				4.22

Table 5 Reactivities of samples in steam

Temperature, °C	Reactivity, % min^{-1}				
	SAO	SAH	SAN	SAF	SAOC
910	0.50	0.54	0.31	0.78	0.33
920	0.83	0.73	0.38	1.01	0.44
930	1.09	0.91	0.47	1.36	0.67
940	1.32	1.21	0.55	1.78	0.89

Table 6 Apparent surface area (daf) and total open pore volume

Sample	S_{D-R}, m$^2\cdot$g^{-1}	V_T, cm$^3\cdot$g^{-10}
SAO	168	0.13
SAH	246	0.11
SAN	156	0.10
SAF	154	0.15
SAO	206	0.34

in almost the whole temperature interval. SAOC exhibits a reactivity lower than that of SAO in the presence of either reactant gas.

Table 6 gives the values of the apparent specific surface area (daf) as determined from the adsorption of carbon dioxide at 273 K by applying the Dubinin–Radushkevich equation (S_{D-R}) [11]; 0.187 nm^2 was assumed to be the area occupied per molecule of carbon dioxide in the monolayer equivalent. Table 6 also contains the values of the total open pore volume accessible to helium (V_T), as calculated from the equation:

$$V_T = \frac{1}{\varrho_{\mathrm{Hg}}} - \frac{1}{\varrho_{\mathrm{He}}}$$

where ϱ_{Hg} and ϱ_{He} are the densities measured by mercury displacement and by helium displacement, respectively. ϱ_{Hg} and ϱ_{He} were corrected by taking into account the mineral matter content of the coal [12].

Discussion

The above results indicate that the relative sequence of the reactivities of the partly demineralized samples depends on the gasification temperature. At lower gasification temperatures (up to around 500°), SAN proves to be more reactive than any other sample. At temperatures higher than about 500°, however, SAN becomes less reactive than the other acid-treated samples. In an investigation of the reactivity of heat-treated coals in carbon dioxide at 900°, Hippo et al. [13] explained the low reactivity of a coal char in terms of the relative absence of large (feeder) pores in the coal and, hence, the poor utilization of the surface area in the micropores for reaction. In this case, however, the explanation of the reactivity results in terms of the textural characteristics of the samples is not straightforward. Thus, the values of the apparent specific surface area (S_{D-R}) and of the total open volume (V_T) given in Table 6 suggest that the surface area and the porosity of the samples are not the main determinant factors of the extent of coal gasification. SAN, which at lower gasification temperatures shows the highest reactivity, has an S_{D-R} value smaller than that of SAH and a V_T value lower than those of SAH and SAF. Obviously, the porosity distribution in the samples should also be taken into account. In this respect, previous studies on the textural characterization of these samples [6] have shown that all acid-treated samples possess a similar distribution of porosity in the zones of macropores and mesopores, though SAN contains mesopores slightly wider than those in SAH and SAF. The higher reactivity of SAN at the lower gasification temperatures could be due to the formation of carbon-oxygen surface complexes by acid treatment. Thus, it has been reported that charcoals and carbon blacks react with nitric acid or a mixture of nitric and sulphuric acids, giving rise to the formation of such functional groups as carboxylic [14], phenolic [15], quinonic [16] and free radicals [17]. These surface groups could be responsible for the promotion of the gasification reaction in air, the result being an increase in SAN reactivity in relation to those of SAH and SAF. The observed decrease in SAN reactivity at higher gasification temperatures could be due to the depletion of such groups as a result of the gasification of a large amount of coal sample at lower gasification temperatures, together with the partial reactivation of the coal surface.

Different behaviour is observed in the gasification of samples in steam. The results in Table 5 indicate that SAF is the most reactive sample. SAH differs only slightly in its reactivity from SAO, and in almost the whole temperature interval SAN has a reactivity substantially lower than that of SAO. The higher reactivity of SAF is probably a result of the effect on the coal structure of the removal of most of the mineral matter. Thus, when the mineral matter is removed to a large extent from SAH by treatment with hydrofluoric acid, its high content in the coal means that a reorganization of the remaining material would take place, which seems to be responsible for the increase in SAF reactivity. For SAN, the oxygen groups on the coal surface, which probably enhance the reactivity in air, if not active sites for the gasification in steam, will hinder the access of steam molecules to parts of the internal surface, with the result of a decrease in reactivity relative to SAH and SAF. These results could also be explained by assuming the formation of carbon-oxygen surface groups which must be thermally unstable only in the presence of steam. In this way, when the nitric acid-treated sample is heated in steam, such groups would be removed from the coal surface, leaving behind a partly reactivated surface for its gasification.

The results in Tables 4 and 5 also show that the reactivity of SAOC, the sample twice carbonized before being gasified, is in general lower than that for SAO in the presence of either reactant gas. On the other hand, SAOC has a relatively high apparent specific surface area and the largest total open pore volume (Table 6). It seems as if the micropores in SAOC are accessible to carbon dioxide at 273 K and to helium at room temperature, but not to air and to steam at the respective gasification temperatures. We conclude that the extended heat treatment of SAO must affect its porosity in such a way as to bring about a substantial decrease in reactivity. In this respect, it must be noted that SAOC has a mesoporous structure much more poorly developed than that of SAO [6].

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References

1 X. García and L. R. Radovic, Fuel, 65 (1986) 292.

2 R. G. Jenkins, S. P. Nandi and P. L. Walker, Jr. Fuel, 52 (1973) 288.

3 P. L. Walker, Jr., M. Shelef and R. A. Anderson, "Chemistry and Physics of Carbon" (Ed. by P. L. Walker, Jr.), Vol. 4, Marcel Dekker, New York 1968.

4 "Inventario de recursos de carbon en España". Centro de Estudios de la Energía. Ed. Ministerio de Industria y Energía. Madrid 1979.

5 C. Fernández González, A. Linares Solano, B. McEnaney and C. Salinas-Martinez de Lecea, Accepted for publication in Fuel.

6 C. Valenzuela Calahorro, T. Chaves Cano and V. Gómez Serrano, Submitted for publication in Fuel.

7 C. Valenzuela Calahorro and A. Bernalte, Boletín Geológico y Minero, 96 1 (1958) 58.

8 F. Bermejo Martinez, "Química Analítica Cuantativa", Imprenta del Seminario Conciliar, Santiago de Compostela 1963.

9 J. E. Shields and S. Lowell, J. Colloid Interface Sci., 103 (1985) 226.

10 P. Leonhart, A. Sulimma, K. H. van Heek and H. Jüntgent, Fuel, 62 (1983) 62.

11 M. M. Dubinin, "Progress in Surface and Membrane Science (Ed. J. F. Danielli), Vol. 9, Academic Press, New York 1975, p. 1-70.

12 O. P. Mahajan and P. L. Walker, Jr., "Analytical Methods for Coals and Coal Products", Vol. 2, Cap. 32. Academic Press, New York 1978, p. 465–493.

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

14 I. I. A. Kuzin, T. G. Plasheno and V. P. Taushkenov, Izv. Vysshykh. Uchebn. Zavedenii Khim. i Khim. Teknol., 3 (1958) 61.

15 J. B. Donnet, F. Hueber, N. Perol and J. Jaeger, J. Chem. Phys., 60 (1963) 426.

16 V. A. Garten and D. E. Weiss, Rev. Pure Appl. Chem., 7 (1957) 69.

17 B. R. Puri, S. Singh and O. P. Mahajan, J. Indian Chem. Soc., 42 (1965) 427.

Zusammenfassung — Die Vergasung einer bituminösen Kohle von Belmez (Cordoba, Spanien) und von daraus durch Säurebehandlung (HCl, SAH; HNO_3, SAN und HF, SAF) oder thermische Behandlung (SAOC) erhaltenen Proben in Luft und Dampf wurde unter dynamischen Bedingungen untersucht. Bei Vergasung in Luft ist die Reihenfolge der Reaktivität bei niedrigen Temperaturen SAN > SAF > SAH > SAO und bei höheren Temperaturen SAF > SAH > SAN > SAO. In Dampf ist jedoch über den gesamten Temperaturbereich der Vergasung die Reihenfolge SAF > SAO, SAH > SAN. SAOC zeigt in beiden Reaktantgasen eine viel geringere Reaktivität als SAO. Die Ergebnisse werden im Zusammenhang mit den Auswirkungen der Behandlungen auf Textur und Zusammensetzung der Kohleoberfläche erklärt.

Резюме — В динамических условиях в атмосфере воздуха и пара изучена газификация битуминозных углей месторождения Белмез (Кордоба, Испания) (САО) и образцов этих же углей, полученных кислотной обработкой (соляной кислотой — САХ, азотной кислотой — САН и фтористоводородной — САФ) или термической обработкой — САОК. При низкотемпературной газификации углей в воздушной атмосфере реакционная способность их располагается в ряд САН > САФ > САХ > САО, а при высокотемпературной — в ряд САФ > САХ > САН > САО. Однако, в атмосфере пара при тех же самых температурах газификации, реакционная способность располагается в рад САФ > САО, САХ > САН. Реакционная способность САОК в обоих газовых атмосферах несколько ниже по сравнению с САО. Полученные результаты объяснены на основе влияния обработки на текстурные характеристики углей и их химическую поверхность.