HEAT TREATMENT OF CARBONS: EFFECTS ON GASIFICATION REACTIVITY, ORGANIC AND INORGANIC STRUCTURE

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Introduction

In spite of the large body of evidence that heat treatment of carbons reduces their reactivity towards gaseous reactants via the reordering of the turbostratic structure and the modifications of inorganic matter, the relative importance of these contributions is not yet clear.

Carbonaceous solid materials, such as coals, contain crystalline domains (crystallites) of the order of nanometers, composed of graphite-like layers arranged turbostratically. The primordial crystallites of carbons are already present or are formed in the earliest stages of carbonization and do not change much up to 600°C. Further carbonization does not create new crystallites, but induces the growth of the already existing ones [2]. The rate of carbonization is strongly increased by heat treatment temperature and decreases very rapidly with time [1, 3].

For graphitizing carbons Murty et al [1] suggest that the same extent of transformation can be attained by different combinations of time and temperature [1]: only the rate of the transformation changes, depending on temperature, time and original material. The scenario becomes more complicated in the case of non-graphitizing carbons, and even more so when the transformations of the inorganic matter in coal are taken into account. Under such circumstances it is unlikely that the same extent of transformation can be attained with different combinations of time and temperature, because temperature will reasonably affect not only the rate of transformation, but also its very nature.

Experimental

The carbon materials used in the experimental work were a Pet Coke (PC), a high-inertinite South African (SA) and a high-vitrinite Ruhr (Ru) coal. Coal samples were heat treated in inert atmosphere at different temperatures (T_{HT} between 900 and 1400°C) and for different times (t_{HT} between 1 and 100min). Subsequently they were characterized by means of TGA (using CO_2 as reactant), XRD, TPD, and porosimetric analysis (He-pycnometry and CO_2 adsorption at 273K).

Results and discussion

XRD and porosimetric analysis reveal that, even though untreated PC already presents a rather ordered structure, heat treatment induces a further increase in structural order, in terms of the (10) band of graphite and of He-density, and a reduction of micropore volume. On the contrary, transformations of minerals are very limited. Reactivity profiles relative to different heat treatments progressively merge with each other as gasification proceeds (fig.1). Once it is recognized that burn-off implies further exposure of samples to the reaction temperature, the trends of fig.1 suggest the possibility for PC to attain the same extent of transformation with different combinations of time and temperature. This is interpreted as a proof of a minor role of mineral deactivation versus changes in the organic matrix of coal.

Physical transformations induced by heat treatment in SA involve both the organic structure and the inorganic matter. Untreated SA has a very disordered structure and contains a considerable amount of calcium as a crystalline phase. Heat treatment increases structural order in terms of the (002) and (10) bands, moreover it induces transformations of the inorganic material. Major transformations of calcium occur when T_{HT} is raised from 1200 to 1400°C. In the same temperature range micropore volume and He-density remain unchanged. Reactivity profiles of samples heat treated up to 1200°C overlap at burn-off > 0.5 (fig.2), but when the temperature is further raised up to 1400°C the loss of reactivity becomes sharper, and curves diverge throughout burn-off. It is concluded that the effect of mineral transformations on char deactivation becomes dominant at 1400°C.

Data relative to Ru show that structural order increases only up to T_{HT}=1200°C. Moreover inorganic material as crystalline phases could hardly be observed by XRD, whatever the pretreatment conditions. Transformations of metals like Fe, Ti, Mn and of silico

aluminates, if any, occur at a level which can not be detected by XRD. Micropore volume decreases up to 1400°C. This is consistent with results of TPD experiments, which show a marked reduction in the ratio of CO/CO_2 desorbed with increasing T_{HT}. Moreover reactivity curves relative to different carbonization conditions diverge up to the very final stages of reaction (fig.3), indicating that different transformations (not only in extent, but also in "nature") are attained with different combinations of time and temperature.

Conclusions

Results relative to Pet Coke indicate that deactivation can be entirely ascribed to changes in the organic matrix of coal and that it is possible to attain the same extent of deactivation with different combinations of time and temperature. Results are consistent with findings of Murty et al. [1].

The same framework fails to interpret the experimental behaviour of the two bituminous coals used in this work. Thermo-deactivation of South African coal, indeed, involves both the organic and the inorganic fractions. In particular at 1400°C the transformations of crystalline Ca seem to become the dominant factor. Correspondingly the difference in reactivity between samples treated at temperatures below and above 1400°C can no longer be compensated by parallel changes of treatment times.

Also in the case of Ruhr coal different heat treatment temperatures result in reactivity plots which diverge up to the very final stages of reaction. In this case XRD analysis is not helpful in providing a key for deactivation. Future work will be directed to identify the nature of organic versus inorganic matter transformations. In particular the relevance of catalyst dispersion and sintering will be investigated. The role of inertinite versus vitrinite ratio also needs to be better clarified.

References

1. H.N. Murty, D.L. Biedermann, E.A. Heintz, *Carbon*, 1969, 7, 667 ;
2. Emmerich, F.G., *Carbon*, 1995, 33, 1709
3. Fair, F.V. and Collins, F.M. in *Proc. 5th Carbon conference*, Pergamon Press, Oxford, 1962, 503.

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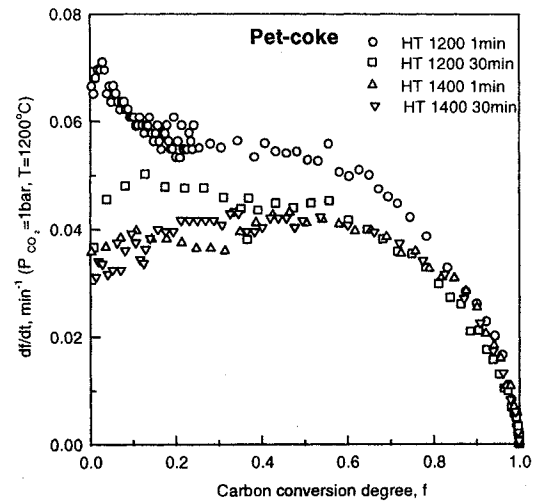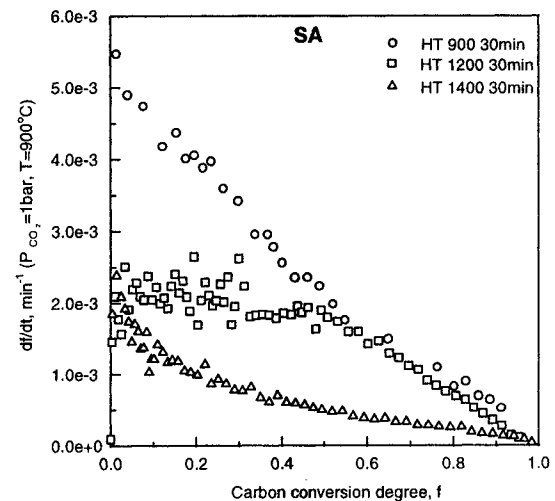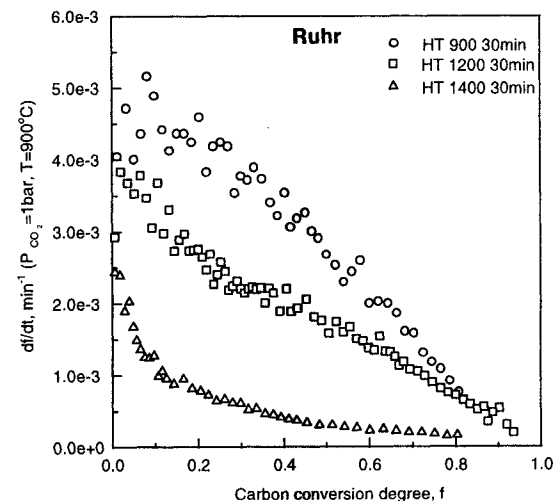Fig.1 CO_2 reactivity of Pet-Coke at 1200°C

Fig.2 CO_2 reactivity of South African coal at 900°C

Fig.3 CO_2 reactivity of Ruhr coal at 900°C

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