

Calcination – The Effect of Maximum Heat Treatment Temperature on the Properties of Coke (Part II)

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Introduction

Calcination completes thermal degradation of green coke formed by carbonisation of hydrocarbons. The content of volatile matter is sharply reduced during the calcination process leading to a shrinkage of the coke and the development of the final pore system.

In part I of this study [1] it has been shown, that neither real density nor hydrogen content alone are sufficient indicators for the severity of calcining as the process is influenced by the sulfur content of green coke. Here we will study the effects of sulfur evolution on the development of the pore system for temperatures from 1200 to 1700 °C; this temperature range, preceding the puffing temperature, where macroscopic expansion of the coke grains is observed, will be called prepuffing range.

Experimental

Five petroleum cokes and a coal tar pitch needle coke were calcined in a tunnel kiln to maximum heat treatment temperatures (HTT) between 1000 and 1700 °C. Green coke properties are summarized in table 1. Details of the experimental procedures have been reported in part I [1].

Results and Discussion

As demonstrated in fig. 1, hydrogen release is affected by sulfur content of coke: at constant HTT, hydrogen content for low sulfur cokes is higher than for high sulfur cokes, the differences being more pronounced on the low sulfur side.

Table 1. Green Coke Data

Coke	Sulfur	Volatile Matter %
A	0.18	5.8
B	0.68	7.5
C	1.34	7.5
D	1.12	5.3
E	0.51	5.2
F	1.70	8.3

Densities (as measured by xylene and helium) as well as sulfur and nitrogen content as a function of HTT are shown in figs. 2 to 5 for petroleum cokes A, D and F and pitch needle coke E. For practical reasons, helium densities were measured on coarse grain (0.3 - 0.5 mm and 3 - 4 mm) and xylene density on powder (<0.063 µm).

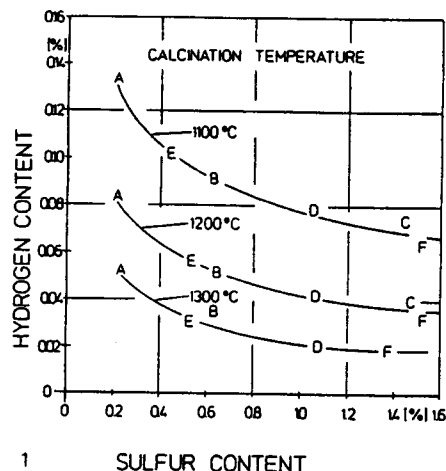


Fig. 1

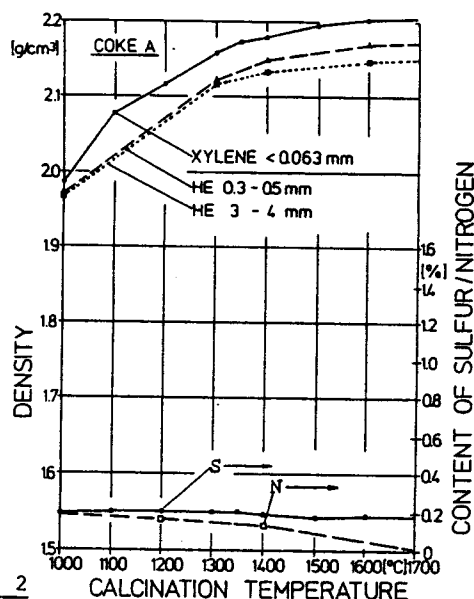


Fig. 2

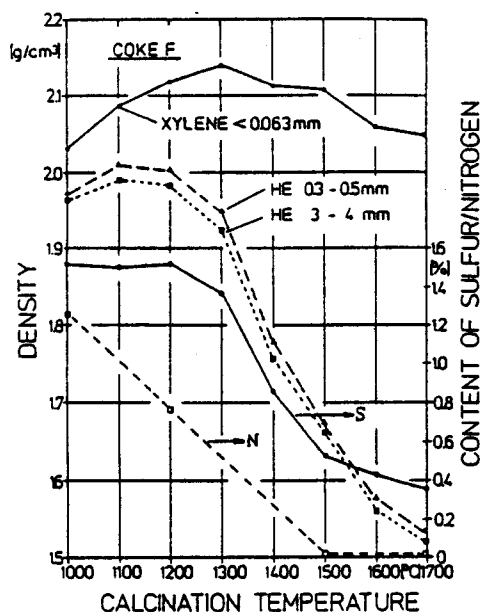


Fig. 3

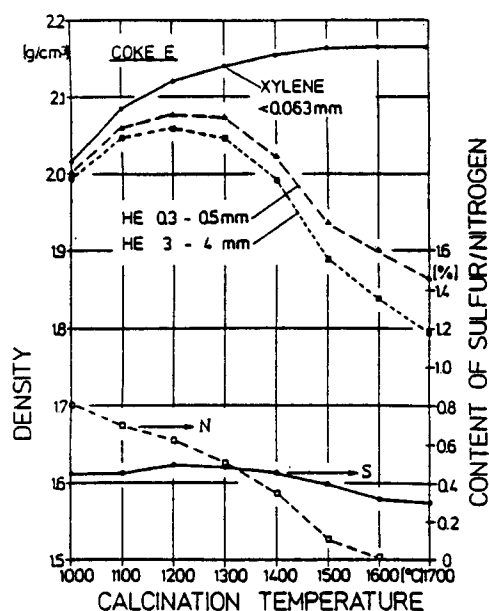


Fig. 4

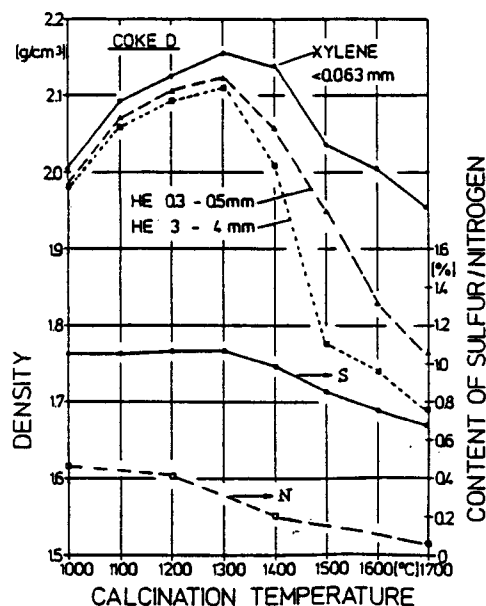


Fig. 5

Coke A is a non-puffing petroleum needle coke with low sulfur and nitrogen content. Densities increase monotonously with HTT. Coke F is a high sulfur/high nitrogen petroleum coke. While nitrogen decreases steadily to about zero at 1500°C, sulfur release starts at 1200°C. Sulfur evolution is closely correlated with a drastic decrease first in helium densities, later followed by a less drastic decrease in xylene density. The cause of this density decrease is the creation of closed porosity by sulfur evolution in the prepuffing range. Puffing effects which can be measured macroscopically by high-temperature dilatometry on coke grains or artifacts, start at 1500 to 1600°C for coke F.

Puffing of pitch needle coke E and petroleum needle coke D is similar in magnitude (without puffing inhibitor) and starts at 1600 to 1700°C. Puffing of pitch coke E is anomalous in the sense that it can not be inhibited by the addition of Fe_2O_3 [2]. Prepuffing starts at 1200 to 1300°C for pitch coke E and 1300°C for petroleum coke D. In both cases, no correlation exists with the decreasing nitrogen content, but a clear correspondence to the starting point of sulfur evolution. There is one important difference in the behaviour of pitch coke E and petroleum coke D: while xylene and helium densities of coke D decrease in the prepuffing range, xylene density (but not helium densities) of pitch coke E increases monotonously with HTT as in the case of low sulfur coke A. This means that prepuffing of pitch coke E leads to larger pores than prepuffing of petroleum coke D.

Conclusions

- It has been shown that
- hydrogen content of coke is affected by sulfur content;
- sulfur evolution of high and medium sulfur cokes starts at 1200 to 1300°C;
- sulfur evolution leads to prepuffing, i.e. formation of closed pores without macroscopic expansion of coke grains;
- prepuffing is not affected by nitrogen evolution;
- prepuffing of pitch coke E is different from prepuffing of petroleum coke D, as pitch coke E develops larger pores on sulfur evolution than petroleum coke D.

From this investigation it may be assumed that the anomalous puffing behaviour of coal tar pitch cokes in comparison to petroleum cokes is due to different coke microstructures.

References

- /1/ M. H. Wagner, H. Pauls, H. Tillmanns, G. Wilhelmi, Proc. 16th Conf. Carbon, San Diego (1983), p. 582.
- /2/ I. Letizia, M.H. Wagner, Proc. 16th Conf. Carbon, San Diego (1983), p. 593.
- /3/ M.H. Wagner, I. Letizia, this conference.