Structure and Synthesis of Shot Coke

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Structural characteristics of shot coke were revealed by an optical and an electron microscopes to be coagulated spheres of fine mosaic cokes of high density, the optical units in periphery of a sphere being stacked concentrically. Its synthesis was examined by the carbonization of heavy residues in a tube bomb.

Introduction

Shot coke is a hard coke produced in a delayed coker drum from certain petroleum residues. Difficulty of its grinding deteriorating the value of delayed coke as a solid fuel attracts recent researchs on its structure and mechanism of formation. Marsh et al. [1] and Debyeshise et al.[2] observed its fine mosaic texture and discussed the mechanism for the development of such mosaic texture.

In the present paper, the authors are going to describe the structure of shot by the techinique of montage photographs [3] to discuss the origin of its hardness and its formation mechanism. Some heavy residues famed to give shot cokes were carbonized in the tube bomb to prepare them in the laboratry according to the mechanism estimated from its structure.

Experimental

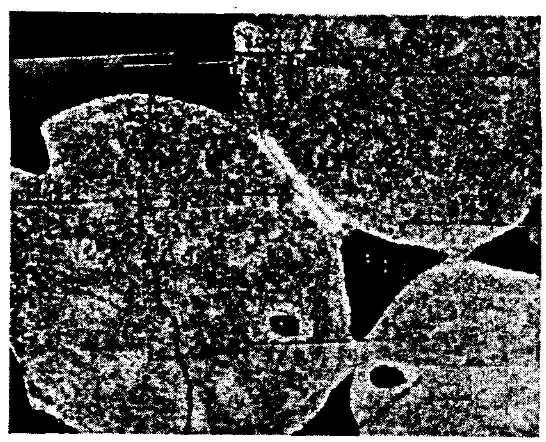
Shot coke and petroleum residues were provided by major US petroleum industries. Structure of coke was examined by means of optical microscopes after the conventional polishing. The montage photographs were taken using point counting stage. The carbonization of petroleum residue was performed with a tube bomb heated in a molten tin bath or fluidized sands. Prior to the carbonization the residues were pretreated under varialble conditions to imitate the preheattreatment in the delayed coking process.

Results

Structure

Fig. 1. shows montage photographs of shot cokes and the sponge coke obtained from the same residue. There are several characteristic features of shot coke observed in the montage photographs. First of all, a shot coke was very dense, with very limited numbers of pores and fissures. Shot coke consisted principally of finer mosaic texture than sponge coke as already reported [1,2]. Some

SPONGE COKE



SHOT COKE

0.5mm

Fig. 1 Montage photographs of sponge and shot cokes details are revealed by the montage. The fine mosaic units at the center of the sphere were arranged in complete randomness, whereas they were oriented concentrically in its periphery. The large units of mosaic texture distributed around the pores, suggesting a different mechanism of carbonization there from that of other areas. The conjunction areas of spheres consisted of partial flow textures which were found often in the sponge coke. Some parts of sponge cokes exhibited quite similar feature to that of shot coke.

Analyses of residues

Chemical analyses of residues 1 and 2 are summarized in Table 1. The residues consist commonly of heavy paraffins and heavy aromatics. When the shot and sponge cokes were compared, larger content of oxygen in the shot coke was noted as Marsh et al. recognized [1].

Carbonization product

Microphotographs of cokes prepared from the residues 1 and 2 in the laboratory are shown in Fig. 2. The carbonizations under atmospheric conditions gave porous coke of masaic and flow textures (Fig. 2a and c). A pressurized carbonization increased the density although no spherical shape was obtained. The carbonization under reduced pressure after the preheat-treatment gave porous and dense cokes separately according to the location in the tube. The texture of the dense coke shown in Fig. 2b was very similar to that of shot coke, although some coarse mosaic texture was present.

Scheme

A scheme for the formation of shot coke can be deduced from the structure, analyses and preparation of shot coke.

The pyrolysis in the preheating produces from the residue long paraffins, medium aromatics, heavy aromatics through the thermal bond fissions. Rapid stream of heated oil and steam in the drum stripped off the volatile of medium aromatics and kept paraffins and heavy aromatics at the bottom of the drum before the completion of carbonization. Since the medium aromatics behave as a solvent to dissolve the fractions of heavy paraffin and aromatics, its elimination leads to their phase separation. The heavy aromatic fraction of high viscosity and coke yield may precipitate to forms cores of spheres in the paraffins matrix. The oxidized wax found in the sludge may be also expelled. While the spheres, thus precipitated, are carbonized, they move up and down on the stream in the matrix to grow in their diameter by collecting the carbonization substances concentrically. The larger spheres may sediment to the bottom to coagulate without coalscence because of high viscosity. High coking value under the pressure may provide high density. Small amount of medium aromatic occuluded may evolve from the sphere during the carbonization, leaving pores in the coke. Such aromtics may mediate the viscosity to increase the anisotropic unit around pores.

Such a mechanism suggests the formation of shot coke at the wall side of the bottom of the drum. The volatile aromatics which may control the carbonization and phase separation are supplied

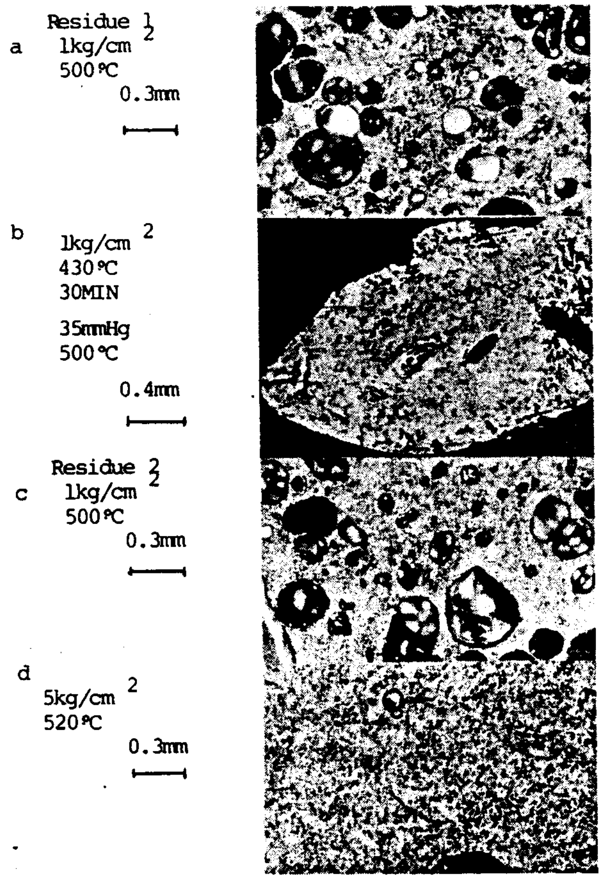


Fig. 2. Microphotographs of Carbonized Products

from the lower carbonization zone at the upper parts of the drum.

Solution proposed

According to the mechanism, some solutions to avoid the formation of shot coke can be proposed. The solution should not lead to the increase of coke yield.

1)Feed adjustment
- a) addition of non-carbonizing aromatic additive to the initial feed (at the time of drum switch)
- b) removal or precracking of paraffins from the initial feed
- c) decomposition of oxidized wax in the initial feed

2)Operational conditions
- a) high recycle rate at the time of drum switch
- b) lower stream rate at the time of drum switch
- c) even stream of oil and stream from the bottom of drum (no dead space)
- d) delicate control of carbonization pressure to suppress the phase separation

References

1. H. Marsh, C. Calvert and J. Bacha. Abstracts of Carbon '84, p128, Bordeux (1984)
2. S.Eser, R.G. Jenkins and F.J. Derbyshir. Abstracts of Carbon '84, p378, Bordeux (1984)
3. H. Marsh and I. Mochida, Fuel 1984, 60, p231

Table 1. Analyses of Residues (1,2)

(wt%)

Sample	C	H	N	S	Satu.	Aroma.	Resin	Asph.
Residue 1	86.9	12.1	-	0.2	43.2	18.9	35.8	3.0
Residue 2	83.0	9.2	0.9	5.7	7.5	24.2	25.8	42.5