Structure in Shot Coke

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Abstract. A series of shot cokes and sponge cokes from industrial delayed cokers was examined by scanning electron microscopy (SEM) and optical microscopy (OM) of external, fractured internal and polished surfaces. Calcined cokes were etched with chromic acid solution and etching behaviour related to the optical texture of the cokes. The shot coke spheres have an inner structure of fine-grained mosaic and a smooth external skin, ~50 μm thick, of coarse-grained mosaic and small domains. Structure of cokes from delayed cokers is strongly dependent upon the composition of the feedstock PLUS the associated manipulation of the system by the volatile evolution within the coker.

Introduction

Delayed coking is one of the commercial coking processes used to convert petroleum residues to solid coke (1). It is a semi-continuous process operating at about 480 to 500°C which produces a mixture of gases, distillate liquids and carbonaceous solids (2). The operator of the delayed coker has limited control over the final properties of the coke. Overall chemical composition of the feedstock and initial chemical reactions are important factors determining the type or texture of coke formed on carbonization.

Selected aromatic feedstocks may be used in the delayed coking process to produce high-quality needle-cokes for graphite production. These feedstocks are usually of high aromaticity and are low in sulphur, mineral matter and quinoline-insoluble material. These needle-cokes are characterised by their large-sized (up to 500 μm diameter) optical texture units (isochromatic areas), as studied by optical microscopy.

Cokes more usually produced by the delayed coking process are the more porous carbonaceous solids or sponge cokes. These are used mainly as solid fuels or in the manufacture of carbon anodes for the electrolysis of aluminium. The optical texture of sponge coke is smaller than that of the needle-cokes.

An undesirable product of the delayed coker which is sometimes produced along with the sponge coke is shot coke. This type of coke has the appearance of lead shot i.e. exists as spheres 1-10 mm diameter. Individual spheres can aggregate into large clusters of 15 cm diameter or more, or may occur dispersed with the sponge coke to various extents (3). Shot coke is undesirable because on opening the delayed coker it may pour out in an uncontrolled way from the drum, it is of relatively low electrical conductivity and it usually contains large amounts of sulphur and metals.

The processes which occur in the delayed coker are not fully understood.

Objectives

1. To examine structure in shot cokes by optical and scanning electron microscopy.
2. To comment on shot coke formation in the delayed coker.

Materials Used

A series of shot cokes and sponge cokes from industrial delayed cokers were examined.

Experimental

External, fractured-internal and polished surfaces of the cokes were examined by scanning electron microscopy (SEM) and optical microscopy (OM). Calcined cokes were etched with chromic acid solution and etching behaviour related to the optical texture of the cokes. The calcining to 1273 K was undertaken to enhance the etching behaviour. Etching with chromic acid allows preferential gasification of the more ordered parts of the anisotropic carbon and is useful to demonstrate the extent and direction of orientation of anisotropic carbon within a carbonaceous material (4, 5).

Results and Discussion

Point-counting analyses of the shot cokes indicate that mosaics constitute about 91 to 96% of the optical texture. Overall the sponge coke has larger optical texture than shot coke.

All shot cokes had the morphology of Figure 1, i.e. almost spheroidal, with a smooth external skin. The surfaces of the spheres were pitted with pores, 100-200 μm dia. entering into the sphere. The fracture surface across an equational plane is seen in Figure 2. Pores originate 0.5 mm from the surface and have smooth surfaces. Inner shot coke structure is of fine-grained mosaics, the external skin consisting of coarse-grained mosaic and small domains. These observations suggest that the spheres were plastic/fluid prior to their formation and that volatile matter was being released in significant quantities to create the macroporosity which did not collapse after the passage of the bubble.

Figure 3 shows the morphology of clustered shot coke. The external surface is again smooth and continuous over the surface, even where particles are fused. The internal structural constituents of fracture surface of the fusion bridge are similar in texture to the bulk particles i.e. mosaics. The evidence suggests that the individual particles were formed first, followed by fusion to clusters towards the end of the coking process. The sponge coke structure of Figure 4 represents a half-way stage between the non-porous fluid phase and the individual spheres of Figure 1.

It would appear, that at a critical stage of the coking process within the delayed coker, the fluid petroleum residue feedstock, because of the formation of relatively viscous growth units of liquid crystals (mesophase) has assumed a "paste-like" quality. It would appear that these feedstocks produce significant proportions of volatile matter, which forces its way through this paste-like, plastic matrix. Inclusions observed in sponge-coke may arise from a lack of total miscibility of feedstock components. The distinct components apparently carbonize separately and their individual resultant cokes become incorporated into the sponge coke as distinct entities.

Conclusions

1. The feedstock leading to shot coke in the delayed coker forms a high viscosity fused pitch/mesophase system which is subject to disturbance by volatile evolution.
2. Fragments of "shot coke" are too viscous to permit coalescence and reform to a continuous system.
3. Structure is dependent upon the chemical composition of the feedstock e.g. N, S, O, asphaltene content and aromaticity, plus the associated manipulation of the system by the volatile evolution within the coker.

References

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0.5 mm

Figure 1. SEM micrograph of external fracture surface of shot coke.


2 mm

Figure 3. SEM micrograph of external surface of clustered shot coke.

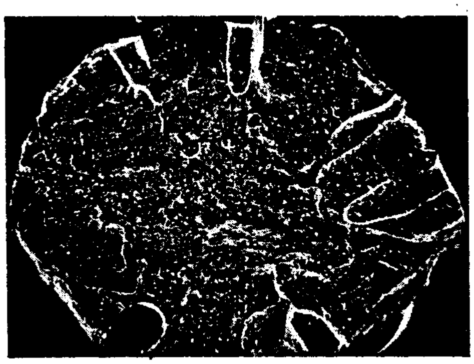
0.5 mm

Figure 2. SEM micrograph of internal fracture surface of shot coke.

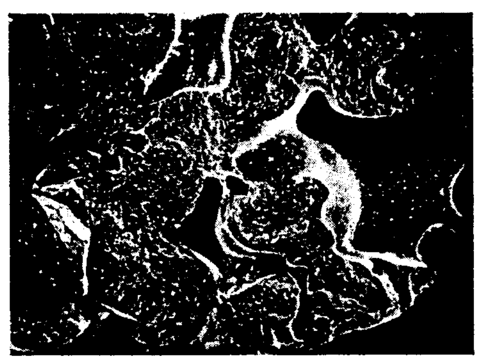
0.5 mm

Figure 4. SEM micrograph of internal (fracture) surface of sponge coke.