

Delayed Cokes from Solvent Refined Coals

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With potentially decreased availability of petroleum resids for coker feedstocks, solvent refined coal (SRC) with its low sulfur and low ash could be a good feed candidate. However, little is known about how the properties of calcined delayed cokes are affected by the type of SRC used as coker feed.

For calcined coke used in carbon anodes for aluminum smelting cells the vibrated bulk density (VBD) is the most important physical property affecting anode consumption, electrical resistivity, flexural strength and baked apparent density (1,2). In 1974 a program was begun to determine how VBD is affected by variations in SRC feedstocks to a delayed coker.

Materials. The SRC-1 feeds (Table 1) were obtained from the 6 t/d pilot plant at Wilsonville, AL. They were produced from high-volatile bituminous Kentucky coals. The chief variables were extent of hydrogenation, separation process and after-treatment by LC-fining. Separation processes included filtration, critical solvent deashing (CSD) and solvent flocculation. Each SRC was characterized by amounts of oils, asphaltenes and preasphaltenes determined from differential solubilities in pentane, toluene and pyridine. Hydrocarbon type analysis was by NMR. Real density was determined in He. Preasphaltenes of the oil-free SRC was calculated from:
100 (Preasphaltenes, %)/(100-Oil, %).

Apparatus and Procedure. SRC diluted with condensate from a previous run to simulate recycle oil was pumped through a preheater into the bottom of a vertical steel coke drum at 460-470°C and about 0.34 MPa. The drum was 200 mm dia. by about 1.2 m high and had a capacity of about 13 kg green coke. Runs lasted 2-1/2 to 4 hours. Coke yields were 68 to 91%. The green coke was calcined by heating under nitrogen at 25°/hour and soaking 10 hours at 1100°C. VBD of the -0.59+0.30 mm (Tyler screen -28+48) fraction of the calcined coke was determined on a 100 gm sample using an early version of ASTM D 4292. Because of faster upheat rate, coke from a commercial rotary kiln would have a VBD lower by about 0.3 Mg/m³.

Discussion. VBD of the calcined coke increased sharply with preasphaltenes of the oil-free SRC (Figure 1). This agrees with observations that in pitch, preasphaltenes form less graphitizable cokes than asphaltenes (3). VBD was not related to aromatic or naphthenic carbon.

While microstructures were not examined, presumably the high VBD cokes had the mosaic structure. This structure resulted from hindered coalescence after flocculation of the mesophase emulsion in the active liquid zone of the coke drum (4). Generally, coalescence is hindered by (a) high viscosity of residual continuous phase, (b) presence of a finely divided solid emulsifier, (c) absence of physical force promoting coalescence or (d) electric charge on the dispersed phase.

Table 1. Properties of SRCs and Cokes

Run	33	35	39	42	43	45
Feed						
Separation	Filter	CSD	CSD	CSD & LC	?	Solvent Flocc.
Preasph., %	39.8	24.1	25.6	25.1	31.8	36.7
Asphalt., %	56.9	68.4	68.6	59.8	63.7	52.7
Oil, %	3.3	6.7	5.8	12.1	4.3	10.4
Aromatic C, %	72.2	78.5	71.0	78.1	71.3	75.6
Naphth. C, %	23.3	--	22.0	19.9	24.5	19.7
Ash, %	0.10	0.25	0.14	-	-	0.17
Preasph. oil-free, %	41.1	25.8	27.1	28.5	33.3	40.9
Calcined coke properties						
VBD, Mg/m ³	1.00	0.92	0.96	0.98	1.00	1.00
Real density, Mg/m ³	--	--	2.00	2.06	2.10	2.11

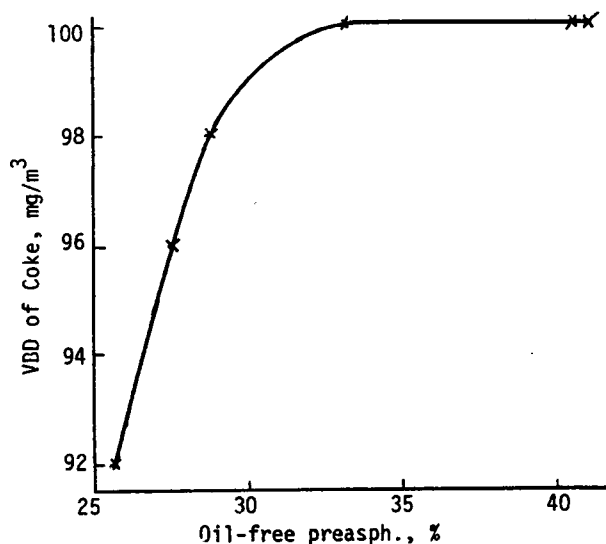


Figure 1. Effect of oil-free preasphaltenes on VBD of coke.

In SRC cokes high viscosity (a) is the predominant factor favoring the mosaic microstructure (and high VBD). Viscosity of the continuous phase increases with increasing preasphaltenes because of their higher initial molecular weight (5). Viscosity increases greatly on carbonization because of greater condensation and cross-linking reactions of preasphaltenes which contain more reactive functional groups as shown by higher O, S and/or N (6). Murakami et al. (7) stated that for SRCs with decreased atomic O/C, flow structure was favored over mosaic. This is confirmed by plots of their data (Figure 2) which show that for SRCs with decreased O/C, (O+S)/C or (O+S+N)/C the graphitization of cokes heated to 2800°C increased. C/H correlated poorly and (O+S)/H did not correlate with graphitization.

Colloidal or finely divided solids (b) not removed during the separation step could prevent coalescence. However, assuming suspended matter was unconverted coal with 10% ash the maximum amount of suspended coal would be 2.5%, too small an amount to hinder coalescence (8). Factor (c) was probably constant in these runs and factor (d) has not been evaluated for this non-aqueous system.

Conclusion. The type of coke prepared can be controlled by adjusting the preasphaltenes in the feed SRC.

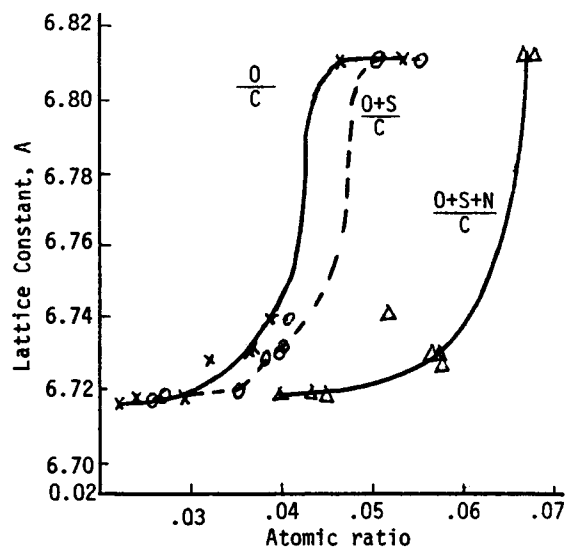


Figure 2. Variation of 2800°C lattice constant with atomic ratio of feed.

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