THERMAL CRACKING OF LOW-TEMPERATURE CARBONIZATION TARS TO PRODUCE ANODE BINDER PITCH

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Introduction

The availability of high-quality binders for carbon anodes has been of increasing concern to the aluminum industry. These binders require high aromaticity, low contaminant content, and suitable rheological and graphitization properties.

Low-temperature carbonization (LTC) of non-coking coals, extensively practiced prior to the dramatic growth of oil refining, has been revisited recently. Several groups including the Institute of Gas Technology (IGT) have developed advanced LTC processes. In the efforts to develop markets for solid and liquid products, IGT studied the potential to obtain anode binders from LTC liquids.

Unmodified LTC tars have not generally been regarded as suitable for anode binders, and conventional heat-treatment has offered limited success in upgrading these materials. Berber *et al*[1,2] investigated the upgrading of Texas lignite LTC tars to anode-binder pitch and recommended flash thermal cracking (FTC) as the most effective of three methods studied. IGT applied a similar approach to Illinois No. 6 LTC liquids, as described below, including the evaluation of test anodes.[3]

Experimental

Materials

LTC liquids were obtained from pyrolysis of Illinois No. 6 coal in a 40-kg/h IGT fluidized-bed reactor at 620°C. The recovered LTC tars were distilled to a 275°C pot temperature, and the distillation bottoms were collected for analysis and upgrading. FTC carrier gas was Matheson extra dry nitrogen, and the FTC quench solvent was a 1:1 (wt) mixture of dichloromethane and tetrahydrofuran.

FTC Equipment and Procedures

FTC tests were conducted in an electrically heated 5-cm-id, 120-cm long stainless steel pipe reactor (Figure 1). Preheated LTC distillation bottoms were pumped into reactor *a* with a cocurrent inert gas via an atomization device. FTC tests were conducted at 650-890°C and an estimated residence time of 1.9-2.4 s. The coal liquids cracked rapidly to form coke, pitch, oil, and gases. Coke accumulated primarily on the reactor inner walls. Most of

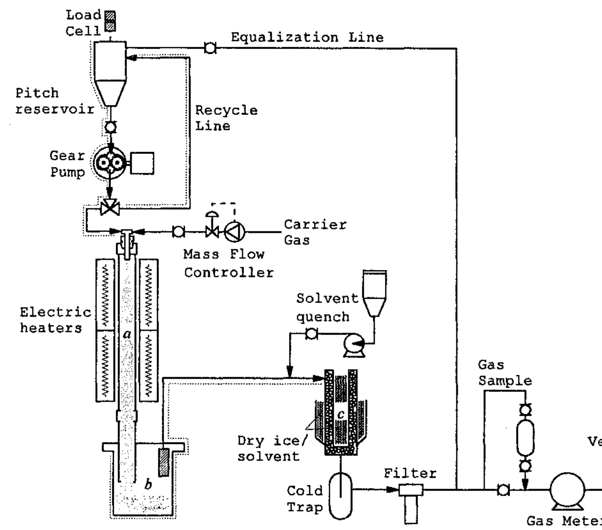

Figure 1. Flash Thermocracking Apparatus Schematic

the pitch product collected in receiver vessel *b*, which was maintained at 180°C. Oils were scrubbed from the gas stream by a solvent quench and cooled in condensation tower *c*. The condensates and vessel washings were combined, strained, analyzed, and distilled to recover a 400°C+ finished pitch.

Test Anode Preparation

Anodes were prepared by blending the FTC pitch with preheated petroleum coke filler at 60°C above the binder softening point, compressing the hot paste in an oil-heated floating mold press at 600 atm, and cooling the 5×12-cm cores to room temperature. The green cores were then packed in fluid coke and baked according to the following schedule: 20-150°C at 100°C/h, 150-300°C at 10°C/h, 300-1100°C at 50°C/h, and a 20-h soak at 1100°C.

Results and Discussion

FTC Yields and Pitch Properties

LTC bottoms were fed to the FTC reactor at 7-9 g/min for 18-40 min. Properties of LTC bottoms, one selected FTC pitch, and typical electrode binder pitches are shown in Table 1. Over the 650-890°C temperature range, the product yields were as follows: pitch, 21-54%; coke, 13-30%; oil, 8-28%; and gas, 3-41%. The pitch and oil yields decreased with temperature while coke and gas yields increased. Pitch quality parameters (QI, TI, coking value, C:H ratio, density) generally improved across the temperature range while sulfur content decreased, but softening point peaked in the 750-800°C range while QI, TI, and coking value leveled off at values near those given in Table 1.

Table 1. Properties of LTC Distillation Bottoms, FTC Pitch, and Typical Electrode Binder Pitch

	LTC Bottoms	FTC Pitch	Typical Electrode Binder
QI, wt%	0.01	14.9	8-12
TI, wt%	7.0	27.4	26-32
Softening pt, °C (R&B)	40	84	88-121
Coking value, wt%	24.0	51.8	55-60
Specific gravity	1.16	1.26	1.32
Carbon, wt%	82.94	90.28	92.6
Hydrogen, wt%	7.03	4.86	4.4
Nitrogen, wt%	0.74	1.01	0.9
Sulfur, wt%	2.44	2.12	0.6
Oxygen, wt% (by diff)	6.85	1.15	1.0
Ash, wt%	0.00	0.00	<0.5
C:H atomic ratio	0.99	1.56	1.75

Microscopic Analysis

Optical microscopy revealed that a typical FTC pitch sample consisted of 62.3% continuous binder phase, 37.3% solids, and only 0.4% of mesophase. The solids were predominantly normal or natural QI, rounded and 0.2 - 2 μm in diameter (Figure 2).

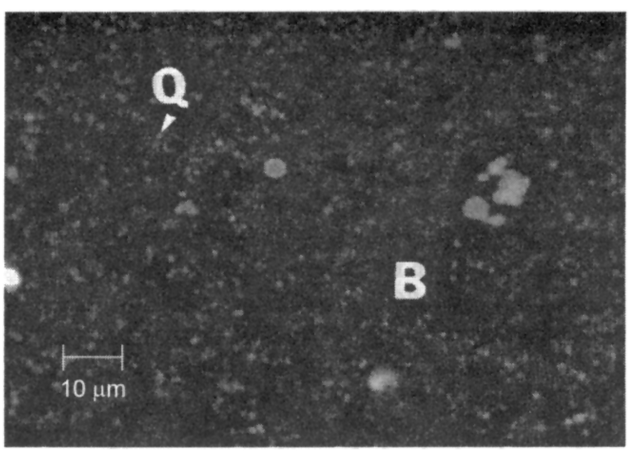

Figure 2. Photomicrograph of Thermally Cracked Pitch (Q=quinoline insolubles, B=binder phase)

Test Anodes

Test anodes were made from 869°C FTC pitch (Table 1) and from conventional coal-tar pitch using 18-20 wt% binder. The FTC-based anodes matched or surpassed the anodes made with conventional binder in all of the 10 key performance properties tested (Table 2), assuring good physical integrity, proper electrical performance, and good resistance to fracture under high-temperature conditions. Anode reactivity was satisfactory in spite of the relatively high sulfur content. The FTC pitch wetted the coke particles well, and there was no significant crack development during baking. Chemical analyses did not show any unusual contaminants, and the sulfur content (1.82 wt%) was within an acceptable range of 1.2-2.4 wt%.

Table 2. Test Anode Properties

Binder	Conventional		FTC Pitch	
Binder wt%	18	20	18	20
Anode density, g/cm^3	1.502	1.501	1.521	1.494
Resistivity, mohm·m	68.5	61.7	62.1	62.1
Coefficient of thermal expansion, 10^{-6}/K	4.1	3.8	4.4	4.1
Thermal conductivity, W/mK	2.2	2.5	2.5	2.9
Flexural strength, MPa	6.0	9.6	8.2	12.0
Compressive strength, MPa	33	36	43	33
Young's modulus, GPa	3	3	3	3
Air permeability, nPm	2.16	2.60	1.64	2.67
CO_2 reactivity, wt% loss	4.7	4.9	4.2	4.5
Air reactivity, wt% loss	19.3	22.5	19.2	21.6

Conclusions

Illinois No. 6 coal liquids from a fluidized-bed LTC process can be upgraded by flash thermal cracking (FTC) at 850-870°C to obtain a satisfactory binder pitch for prebaked anodes. The FTC method using spray atomization of the pitch into the cocurrent flow reactor with an inert carrier gas produces primary QI in the finished pitch with very little mesophase formation, reduces the heteroatom content, and improves the carbonization properties to acceptable levels.

Acknowledgments

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