COKER FEEDSTOCK CHARACTERISTICS AND CALCINED COKE PROPERTIES

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Abstract

Commercial delayed coker feedstocks and corresponding green cokes were obtained from four refineries. The feedstock materials were characterized by infrared, chromatographic, and solvent extraction techniques in addition to the conventional physical tests and chemical analyses. The green cokes were calcined in a laboratory induction furnace at 1100, 1200, 1300 and 1400°C. The properties of the resulting calcined cokes were related to the feedstock characteristics. The results indicated significant effects of the feedstock materials which should be taken into account during the control of commercial calcination operations.

Introduction

Variations in the composition of refinery coker feedstocks have significant effects on the properties of electrode-grade calcined petroleum coke. In a previous paper the effects on coke structure and bench-scale anode performance were discussed (1). This paper deals with the effects of feedstock on the properties of calcined coke with particular emphasis on those properties which are predominantly indicative of the degree of calcination.

Materials

Commercial coker feedstocks and corresponding green delayed cokes were used from four different refineries. A catalytic cracker slurry oil and a coal-tar pitch were included for comparison. These two materials were coked in the laboratory under a nitrogen atmosphere at 500°C to obtain the corresponding green cokes.

The feedstocks are designated as follows:

Source	Symbols Used in Figures 2 and 3
1 Vacuum Tower Bottom	○
2 Vacuum Tower Bottom	●
3 Vacuum Tower Bottom	△
4 Vacuum Tower Bottom	▲
5 Catalytic Cracker Bottom	□
6 Coal Tar Pitch	■

Experimental

Feedstocks. The feedstocks were characterized by elemental analysis, density (2), viscosity over a range of temperatures using a Brookfield viscometer, coke yield as determined by the Alcan coking value test, asphaltenes content (3), refractive index (4), and infrared spectroscopy, using a NICOLET 7000 series FTIR spectrometer. The infrared parameters reported were obtained by integrating the area under the peak of the spectra over the 670 to 920 cm^{-1} wave number region and multiplying this by the absorbance units. The aromatic/non-aromatic components were determined by silica gel solvent elution technique (5).

Density-refractivity intercept was calculated from refractive index and density (refractivity intercept = refractive index at 20°C −0.5 × density at 20°C, g/mL) (6). The viscosity-gravity constant (VGC) was derived from Saybolt viscosity at 210°F and specific gravity, 60/60°F (7).

Green Cokes. The green cokes were analysed for volatile matter content, carbon, hydrogen, sulphur, and vibrated bulk density.

Calcined Cokes. To obtain the calcined cokes, green cokes (minus 830 plus 420 micrometers, 20 × 35 Tyler mesh) were calcined in a laboratory induction furnace shown in Figure 1 at 1100, 1200, 1300, and 1400°C. The furnace was purged with nitrogen. The heating rate was 50°C/min and the
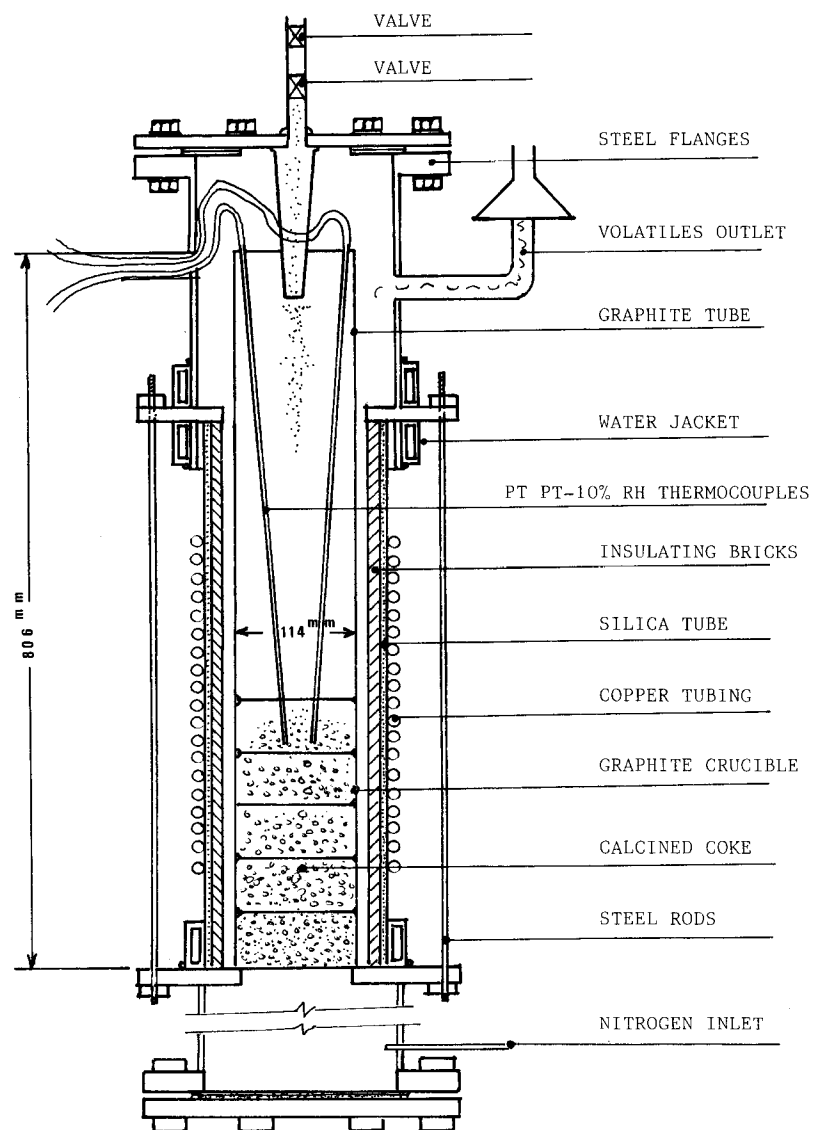
Fig. 1 – Laboratory Induction Furnace Used for Calcination.

Labels: VALVE, VALVE, STEEL FLANGES, VOLATILES OUTLET, GRAPHITE TUBE, WATER JACKET, PT PT-10% RH THERMOCOUPLES, INSULATING BRICKS, SILICA TUBE, COPPER TUBING, GRAPHITE CRUCIBLE, CALCINED COKE, STEEL RODS, NITROGEN INLET, 806 mm, 114 mm

holding time at the final temperature was 30 minutes.

One sample of each green coke was also flash calcined (heating rate: approximately 1000°C/min) to 1200°C in a nitrogen atmosphere and then held at this temperature for 30 minutes.

The properties determined on calcined coke were sulphur, mean crystallite thickness by X-ray diffraction method, kerosene density (minus 40 micrometers, 400 Tyler mesh) and vibrated bulk density (minus 830 plus 420 micrometers, 20 × 35 Tyler mesh).

Results and Discussion

The elemental analysis of the feedstocks is given in Table I. Source 3 exhibits relatively high sulphur content. The C/H atomic ratio does not reveal significant differences between feedstocks 1 through 4. For sources 5 and 6 it is in agreement with values expected for slurry oil and coal tar pitch, respectively.

Other properties are given in Table II. Of significance here is the low value of infrared parameter for feedstock 2 indicating the lowest number of low molecular weight benzene ring compounds (less than 5 to 7 rings) for this material.

The results of further characterization of the feedstocks are given in Table III. Non-aromatic and aromatic compounds are reported as determined by chromatographic separation using silica gel absorbent and three selective solvents: n-heptane, benzene, and pyridine. The non-aromatics include paraffins, olefins, and naphthenes which can be removed from silica gel with n-heptane. The aromatic compounds are not removed with n-heptane, but are easily eluted with benzene. The polar compounds which are eluted with pyridine include materials containing oxygen, sulphur, and nitrogen. The not recovered fraction represents volatile, low molecular weight hydrocarbons, as well as pyridine insoluble compounds.

Composition by carbon-type is also given in Table III. These results were obtained by the density-refractivity intercept method which has been shown to be suitable for the characterization of a wide range of viscous petroleum fractions (6).

The calculated viscosity-gravity constant given in Table III is another indicator of hydrocarbon composition. Petroleum hydrocarbons with a VGC near 0.800 are of paraffinic character while those with VGC close to 1.000 are of aromatic nature. It should be noted that the precision of the VGC is very good; repeatability at the 95 percent confidence limit is 0.001 unit.

Inspection of the results in Tables II and III indicates that the aromaticity of vacuum bottom feedstocks increases from source 1 through 4. The significantly higher aromaticity found for the catalytic cracker bottom, source 5, is as expected. The coal-tar pitch shown for comparison exhibits the highest aromaticity based on infrared analysis results and VGC value which is in agreement with published information for coal asphaltenes.

The properties of the green cokes are given in Table IV. Of considerable significance is the low bulk density of the coke from source 2.

Table I. Elemental Analysis of Coker Feedstocks

Source (see "Materials")		1	2	3	4	5	6
Carbon	%	83.8	85.8	84.7	85.8	88.4	93.1
Hydrogen	%	11.5	11.4	10.4	11.2	8.4	4.2
Nitrogen	%	0.43	0.45	0.42	0.31	ND	ND
Oxygen	%	3.61	2.01	2.66	1.82	ND	ND
Sulphur	%	0.66	0.88	1.48	0.87	0.90	0.55
C/H (Atomic Ratio)		0.61	0.63	0.68	0.64	0.88	1.84

ND = Not Determined

Table II. Properties of Coker Feedstocks

Source (see "Materials")		1	2	3	4	5	6
API Gravity		14.4	14.4	10.0	13.0	2.0	ND
Density at 20°C	g/mL	0.970	0.970	1.000	0.979	1.060	1.315
Density at 100°C	g/mL	0.923	0.924	0.964	0.930	1.007	ND
EVT-10 (1)	°C	77	76	105	84	36	165
EVT-1000 (1)	°C	32	33	55	40	14	112
Coke Yield	%	13.1	12.8	18.3	18.2	6.7	58.6
N-Heptane Insoluble	%	7.8	10.1	7.8	13.4	1.0	72.0
Refractive Index		1.544	1.542	1.558	1.553	1.642	ND
Infrared Parameter (2)		0.591	0.474	0.593	0.549	1.547	2.650

(1) Equiviscous temperature at 10 and 1000 poises
(2) Integrated area under peak in 670-920 cm^{-1} wave number region × absorbance units
ND = Not Determined

Table III. Characterization Data for Coker Feedstocks

Source (see "Materials")		1	2	3	4	5	6
Chromatography							
Non-aromatics (oils)	%	88.5	81.2	85.1	70.8	51.0	ND
Aromatics (asphaltenes)	%	8.8	13.1	13.2	18.9	34.0	ND
Oxy (polar) compounds	%	0.9	0.5	1.4	9.7	5.0	ND
Not recovered	%	1.8	5.2	0.3	0.6	10.0	ND
Density – Refractivity Intercept							
Aromatic ring carbons	%	25	24	29	30	66	ND
Naphthene ring carbons	%	18	20	27	14	–	ND
Paraffin chain carbons	%	57	56	44	56	34	ND
Viscosity-Gravity Constant		0.854	0.858	0.862	0.863	1.042	1.550

ND = Not Determined

Table IV. Properties of Green Cokes

Source (see "Materials")		1	2	3	4	5	6
Volatile Matter	%	11.1	10.6	11.2	9.6	5.8	6.1
Carbon	%	92.0	91.2	90.4	91.4	93.4	94.8
Hydrogen	%	3.5	3.6	3.8	3.8	3.6	3.0
Sulphur	%	1.07	1.86	3.82	2.55	1.84	0.34
Bulk Density	g/mL	0.762	0.687	0.732	0.721	ND	ND

ND = Not Determined

This is attributed to the high value of "not recovered" fraction found in feedstock 2 as shown in Table III. It is postulated that the presence of volatile, low molecular weight hydrocarbons is responsible for the low green coke bulk density. These compounds are expected to have a reduced coke yield and create a higher porosity of the solidifying material in the drum during coking.

Table V shows selected properties of the cokes calcined in the laboratory at 1200°C while Figures 2 and 3 show the correlation of kerosene density and mean crystallite thickness with calcination temperature, respectively. It can be seen in Table V that the low bulk density of coke from feedstock 2 prevails after calcination in the laboratory. This behaviour of source 2 coke has also been observed and reconfirmed during calcination trials in a commercial rotary kiln.

Table V. Selected Properties of Calcined Cokes

(Laboratory Calcination at 1200°C)

Source (see "Materials")		1	2	3	4	5	6
Sulphur	%	1.05	2.00	3.68	2.48	1.75	0.32
Mean Crystallite Thickness	Å	26.0	26.8	28.4	28.0	27.0	24.0
Kerosene Density	g/mL	2.05	2.05	2.06	2.08	2.06	1.96
Bulk Density	g/mL	1.006	0.839	0.958	0.993	ND	ND
Bulk Density Upon Flash Heating	g/mL	0.844	0.769	0.820	0.833	ND	ND

ND = Not Determined

Figures 2 and 3 reflect two well-known features which will not be discussed here, namely the very different response of coal tar pitch to carbonization and heat treatment when compared to petroleum fractions and the effect of thermal desulphurization on the real density of high-sulphur petroleum coke. Both aspects have been adequately dealt with in the literature (8,9).

In this paper attention is focused on the usefulness of kerosene density and mean crystallite thickness as measures of degree of heat treatment and control tools for commercial calcination.
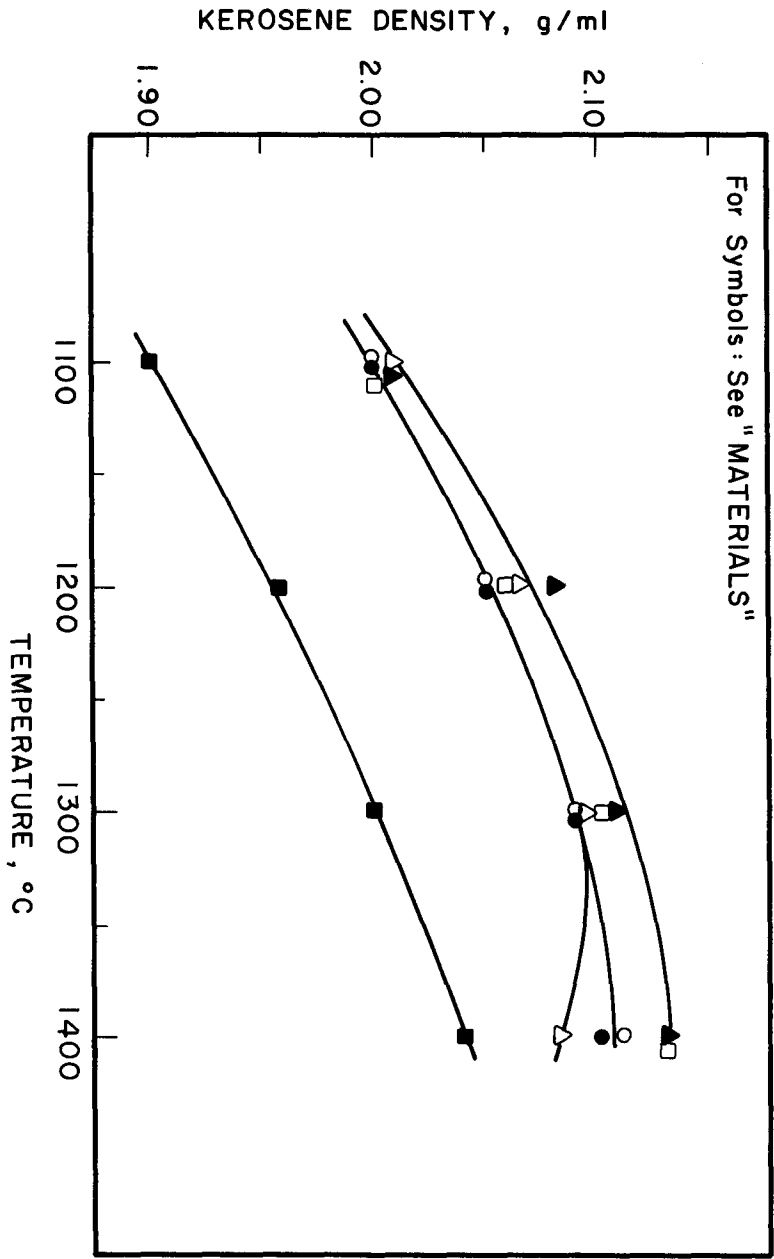
KEROSENE DENSITY, g/ml

Fig. 2 – Correlation Between Kerosene Density and Temperature of Calcination.

For Symbols: See "MATERIALS"

TEMPERATURE, °C

MEAN CRYSTALLITE THICKNESS, Å
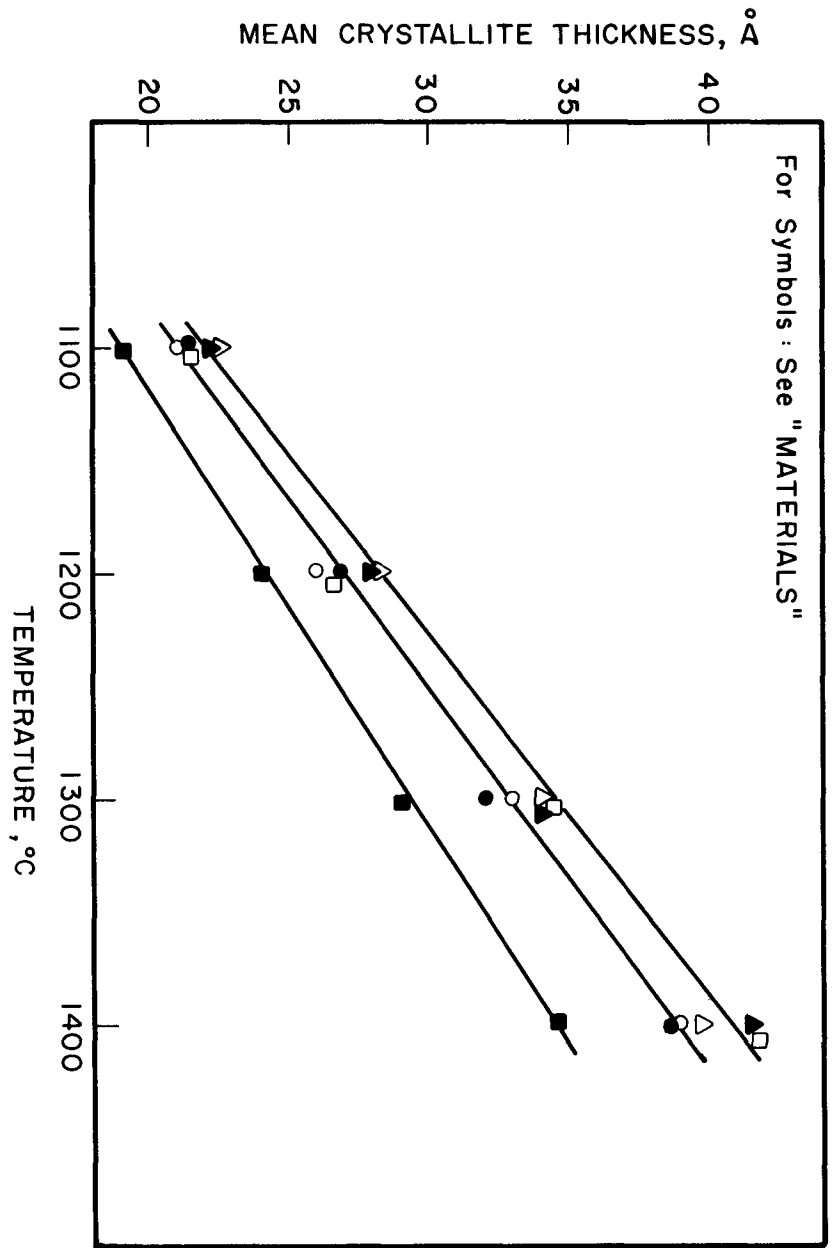
Fig. 3 – Correlation Between Mean Crystallite Thickness and Temperature of Calcination.

For Symbols: See "MATERIALS"

TEMPERATURE, °C