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3,451,921

COKE PRODUCTION

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6 Claims

ABSTRACT OF THE DISCLOSURE

Heavy high boiling fractions obtained in the cracking of petroleum distillates in the presence of steam and at essentially atmospheric pressure and termed "pyrolysis fuel oil" can be employed as the charging stock in a delayed coking operation to give a high yield of coke, which after calcining to remove volatile matter and stabilize shrinkage thereof can be employed to manufacture graphite electrodes having an unusually low coefficient of thermal expansion.

This invention relates to a process for manufacturing coke from pyrolysis fuel oil. More particularly, the invention is concerned with methods for producing so-called "delayed" coke.

Delayed coking is a process which employs a pre-heating treatment and a coking chamber designed to accumulate substantial quantities of coke between cleanings. Generally two vertical coke drums are employed, one being in service while the other is decoked. Reaction temperatures from 700° F. to 900° F. are employed in the chamber.

"Delayed coke" usually is large particled, and has a high density. For this reason it has been employed extensively in the production of graphite electrodes.

It is known that many of the phenomena taking place during processing as well as the final properties of graphite electrodes depend upon the coke used as the filler component in combination with a binder such as coal tar pitch. The effect of variations in the coke used is particularly important in the production of large diameter graphite electrodes for use in electric furnaces. This is especially true since in addition to increasing the size of the electrodes, the operators of electric furnaces are employing higher current densities to shorten the furnace cycle.

Electrodes carrying current into a furnace become hotter in the center than on the outside. Because of this temperature gradient the center expands more than the outside of the electrode, thereby generating stresses which tend to produce ruptures. Another temperature gradient exists at the arc tip of the electrode; here again an unequal expansion produces stresses which cause spalling. In order to minimize these stresses and keep them within the limit of the breaking strength of the electrode material, the coefficient of thermal expansion, therefore, should be kept as low as possible.

The thermal expansion of graphite electrodes depends upon three main factors: (1) the kind of coke base material, (2) the method of forming, and (3) the size of the carbonaceous particles employed. Actually there are two values for the coefficient of thermal expansion of graphite articles, since graphite articles are anisotropic. One value of expansion is parallel to the length; the other parallels the diameter of the article. The longitudinal coefficient of thermal expansion is a fundamental property of the coke from which the electrode is manufactured. The importance of this coefficient is that it directly determines the thermal strains to which an electrode may be subjected during use.

It has now been found in accordance with this inven-

tion that heavy high boiling fractions obtained in the cracking of petroleum distillates in the presence of steam and at essentially atmospheric pressure and termed "pyrolysis fuel oil" can be employed as the charging stock in a delayed coking operation to give a high yield of coke, which after calcining to remove volatile matter and stabilize shrinkage thereof can be employed to manufacture graphite electrodes having an unusually low coefficient of thermal expansion.

It has also been found that thermal cracking in the pyrolysis furnaces brings about a considerable degree of thermal desulfurization. As a result, the coke produced by the process of the invention is characterized by a relatively low sulfur content. This feature is also advantageous in the manufacture of graphite electrodes. High sulfur cokes generally are not suitable for the manufacture of large graphite electrodes because of an expansion phenomenon exhibited by such electrodes during graphitization. In addition, cokes prepared in accordance with the invention are characterized by low ash content. In particular, the vanadium content of cokes so prepared is less than 20 parts per million, also as a result of the thermal cracking.

It is the main object of the present invention to provide coke material having a very low coefficient of thermal expansion, which coke is eminently suitable for use in the manufacturing of carbon electrodes for electric furnaces.

The process by which the raw material employed in the present invention is obtained is the following: Petroleum distillate fractions are cracked in a tubular furnace in the presence of steam or other inert diluent gas such as methane under severe conditions of thermal cracking, in a range of temperature from 550° C. to 800° C. with the preferred range being from 650° C. to 775° C. The purpose of this process is generally to produce olefinic gases, such as ethylene, propylene and butylene. A heavy high-boiling fraction-pyrolysis fuel oil is condensed from the effluent from the cracking furnace as a by-product. Preferably before being charged to a delayed coking furnace, the pyrolysis fuel oil is rendered substantially anhydrous by distillation. The oil is characterized by a high content of high molecular weight (above 250) condensed polycyclic hydrocarbons containing at least four condensed rings and having a boiling point in excess of 315° C. In general the higher the content of polynuclear aromatic carbon compounds in the charging material, the higher the quality of the coke.

The charge produced and collected as indicated above is fed to a delayed coker of conventional design, having means for the regulation of temperature, pressure and rate of recycling. Raw coke is produced in the coke drum of the delayed coker under a pressure of 30 to 50 pounds per square inch, and calcined at about 1350° C. The end product then may be sized and employed, for example, in the fabrication of graphite electrodes.

As illustrative examples of the successful practice of the present invention, a number of petroleum distillate fractions were cracked at various temperatures to give pyrolysis fuel oils, which were feed to delayed cokers. Graphite rods were fabricated from the resultant coke, in conventional manner. These examples are tabulated in Tables I and II, and labeled samples numbers 2313 to 2368.

Thus in Table I below appear data showing the percentage of coke obtained with various samples, the compositions of some of which are given in Table II. Also appearing in Table I are the mean coefficients of thermal expansion (CTE) measured over the temperature range of 15 to 100° C., and specific electrical resistance of graphite rods fabricated from the given cokes, together with the same properties observed in graphite produced from con-

ventional coke obtained from vacuum tower bottoms (listed as sample 2318 in the tables). It will be noted from Table I that the sulfur and vanadium content of sample 2318 greatly exceeded that in the samples treated in the manner of the invention.

TABLE I

Sample No.	Feed to thermal cracker	Temp. of cracking (° C.)	Analysis of calcined coke, percent		
			Coke yield	Ash	Sulfur
2313	Light petroleum dist.	750	28.2	0.29	0.25
2314	do.	775	33.1	0.14	0.21
2304	Wax distillate	750	36.7	0.15	0.78
2312	do.	775	41.0	0.25	0.70
2325	Coker gas oil	750	40.1	0.20	0.92
2355	Vacuum gas oil	650	39.0	0.18	1.07
2357	do.	675	45.5	0.30	0.80
2315	do.	735	47.5	0.30	1.00
2316	do.	760	49.5	0.15	0.97
2326	Combined petroleum distillate.	775	42.8	0.56	0.59
2368	Light gas oil, West Texas crude.	775	31.0	0.24	0.70
2318	Coke from vacuum tower bottoms.		21.5	0.32	1.25

Sample No.	Analysis of calcined coke, parts per million vanadium	Properties of graphite rods	
		CTE (° C.) ¹ ×10 ⁷	Specific resistance ohm-cm. ×10 ⁶
2313	18	6.6	795
2314	9	5.3	783
2304	18	5.6	665
2312	3	5.6	787
2325	6	5.1	808
2355	6	7.1	757
2357	12	5.7	810
2315	8	7.7	813
2316	3	5.7	772
2326	1	5.0	805
2368	4	6.2	765
2318	25.6	19.0	

TABLE II.—ANALYTICAL DATA ON SAMPLES OF PYROLYSIS FUEL OILS AND VACUUM TOWER BOTTOMS

Sample No.	Specific gravity	Analysis of oils, ¹ percent			
		C	H	S	Ash
2304	1.12	91.2	6.2	1.30	0.005
2312	Wax	88.35	5.85	1.14	0.001
2313	1.11	86.3	6.64	0.63	0.052
2314	1.13	92.4	6.06	0.51	0.002
2315	1.17	87.25	5.96	1.44	0.046
2316	1.17	89.2	5.67	1.47	0.024
2325	1.16	91.1	5.92	1.51	0.005
2326	1.16	92.15	5.70	0.96	0.038
2318	0.973	84.4	10.63	0.85	0.018

¹ The analytical data here presented are for samples "dried" to remove water.

Sample No.	Analysis of oils ¹		Analysis of calcined coke		P.p.m. V
	P.p.m. V	Percent conradson carbon	Percent ash	Percent S	
2304	3.7	27.0	0.15	0.78	18.2
2312	3.0	30.4	0.25	0.70	2.6
2313	1.4	20.9	0.29	0.25	18.2
2314	1.5	24.6	0.14	0.21	9.5
2315	3.2	37.3	0.30	1.00	7.6
2316	6.4	38.9	0.15	0.97	3.0
2325	2.3	29.8	0.20	0.92	6.2
2326	2.0	33.6	0.56	0.59	0.3
2318	48.7	16.5	0.32	1.25	25.6

¹ The analytical data here presented are for samples "dried" to remove water.

The pyrolysis fuel oils shown in Table I yield cokes which on the average show a longitudinal (in the direction of extrusion) coefficient of thermal expansion of 6.0×10^{-7} (° C.)⁻¹. Empirically, it has been established that this coefficient of thermal expansion measured on rods will correlate with field experience with full sized graphite electrodes employed in electric arc furnaces. A coefficient of thermal expansion of 6.0 indicates that high quality graphite electrodes can be manufactured from such cokes. In comparison, cokes produced from the residues from distillation of petroleum ("reduced crudes") generally show coefficients of thermal expansion in the range of 12 to 20×10^{-7} (° C.)⁻¹.

It will be obvious to those skilled in the art that under less severe conditions of temperature with longer times of contact, slightly lower temperatures can be utilized to produce highly aromatic cracked stocks suitable for coking to produce coke equivalent to that of the process of the invention. Furthermore, the pyrolysis fuel oils which are generated in the production of olefins by processes other than steam dilution in tubular furnaces as disclosed hereinbefore are suitable for coking in the manner disclosed. For example, the pyrolysis fuel oils from processes for olefin production utilizing recirculating granular or powdered ceramic solids, as disclosed in U.S. Patent 2,432,298 and 2,436,254, or carbonaceous solids (as disclosed in the "Petroleum Refiner," vol. 34, October 1955, pp. 139-140) may also be used.

What is claimed is:

1. A process for producing coke having a low sulfur content and a vanadium content of less than 20 parts per million, comprising feeding to a delayed coker a pyrolysis fuel oil fraction obtained by cracking petroleum distillate fractions in the presence of a diluent gas at essentially atmospheric pressure and at a temperature range of 650° C. to 775° C. so as to produce olefinic gases and said pyrolysis fuel oil fraction, and coking said pyrolysis fuel oil fraction.

2. The process of claim 1 wherein said pyrolysis fuel oil is anhydrous.

3. The process of claim 1 wherein said pyrolysis fuel oil fraction has a molecular weight of above 250 and a boiling point in excess of about 315° C.

4. The process of claim 1 wherein said cracking is effected in the presence of methane.

5. The process of claim 1 wherein said diluent gas is steam.

6. The process of claim 1 wherein said pyrolysis fuel oil is dried prior to feeding to said delayed coker.

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