United States Patent Office 3,547,804 Patented Dec. 15, 1970

3,547,804

PROCESS FOR PRODUCING HIGH GRADE PETROLEUM COKE

Toshio Noguchi and Masao Furuhashi, Tokyo, Bing Igarashi, Yokohama, Kosaku Yamada, Oita-shi, Noriyoshi Aotsuka, Tokyo, and Mamoru Omori, Omachi-shi, Japan, assignors to Showa Denko Kabushiki Kaisha, and Kyusku Oil Co., Ltd., both of Tokyo, Japan, both corporations of Japan

No Drawing. Filed Apr. 16, 1968, Ser. No. 721,618
Claims priority, application Japan, Aug. 6, 1967, 42/56,762
Int. Cl. C10g 17/00; C10b 55/00
U.S. Cl. 208—46 3 Claims

ABSTRACT OF THE DISCLOSURE

A process for producing premium grade petroleum coke which comprises heating either residual fraction which result when naphtha, kerosene, gas oil or natural gas is pyrolysed for producing unsaturated hydrocarbons, or a mixture of these residual fractions and other petroleum fractions, the overall mass being in a state dilution at a temperature ranging between 380° to 410° C. during this heating step by means of a fraction of 4–35% by volume of said overall mass, the diluent fraction per se being not substantially cokable, raising the mass to the coking temperature to complete the coking, and thereafter recovering the resulting coke.

This invention relates to a process for producing superior premium grade petroleum coke. In general, premium grade petroleum coke is known as needle coke or No. 1 coke and is used for the manufacture of carbon and graphite electrodes. Whereas the structure of the calcined product of regular coke is amorphous and does not have a metallic lustrous appearance, calcined premium grade coke is characterized in that its acicular or stratiform structure is well developed and in that it has a metallic luster. In addition, premium grade coke is characterized in that its graphitized product has a small coefficient of thermal expansion as well as small electric resistance. The premium grade petroleum coke as obtained in accordance with the invention process is of especially high grade and is suitable for the manufacture of graphite electrode, and particularly that of large diameter. The calcined product of this coke has a X-ray index of the (002) crystalline plane by means of the X-ray diffraction method of above 60 and exhibits a great contrast when compared with the numerical values of 20–30 in the case of the calcined regular coke. Further, it has a small electric resistance of such as below 6×10^{-4} Ωcm.

As the starting material for making premium grade coke, it was the usual practice hitherto to use either the cycle oil or residual fraction obtained by the thermal or catalytic cracking at 450–500° C. of gas oil fraction resulting from topping of crude oil, or the residual fraction obtained by thermal cracking of the distillate oil obtained by vacuum distillation of the topped crude.

On the other hand, the industries which produce the unsaturated hydrocarbons such, for example, as ethylene, propylene, butenes, butadiene, etc., by the pyrolysis at 700–900° C. of natural gas or the naphtha and other fractions obtained by topping crude oil are thriving lately. In this case, a considerable amount of a residual fraction

rich in aromatics is produced as a by-product, but it is not being utilized effectively and properly, as this fraction is usually merely being consumed as fuel. For sake of brevity, the term "black oil," as herein used, will hereinafter mean the residual fraction which is formed as a by-product when carrying out the pyrolysis for producing the aforesaid unsaturated hydrocarbons.

It has now been found that superior premium grade coke can be made by treating black oil under specified conditions. Furthermore, it has now been found that coke of comparable, or of higher grade could also be produced from a mixture of black oil and the other petroleum fractions.

The object of this invention is therefore to provide a process for producing superior premium grade petroleum coke suitable for the manufacture of graphite electrodes of large diameter, using as the feed stock either black oil or a mixture of black oil and other petroleum fractions.

It is generally known that when the hydrocarbon fraction of high aromaticity is heated at a temperature of 390–500° C. coke is formed by thermal cracking and thermal polymerization, which are set up via the steps: aromatic hydrocarbons→condensed aromatic hydrocarbons→asphalt→pitch→asphaltic coke→coke. We were able to confirm that when black oil is heated, the foregoing pitch→asphaltic coke step takes place at a temperature about 410–450° C. and that the grade of the final coke product is already decided in the preceding asphalt→pitch step. If premature coking takes place in the asphalt→pitch step and, as a result, minute particles of massy coke are formed locally, amorphous coke is formed with these particles as nuclei, with the consequence that little, if any, coke having acicular crystals is obtained finally.

The reason why coke of high grade is formed by the invention method to be hereinafter fully described is believed to be based on the fact that premature coking is prevented as a result of the coke-forming component in the feed stock being in a state of suitable dilution by means of another fraction during a specified temperature range and that during this period crystal nuclei of acicular structure are formed, following which the coke crystals are developed about these nuclei as centers.

The process for producing superior premium grade petroleum coke according to the present invention comprises heating a feed stock consisting of either a residual fraction which is formed as by-product when pyrolysis of naphtha, kerosene, gas oil or natural gas is carried out for producing unsaturated hydrocarbons, or a mixture of the foregoing residual fraction and a petroleum fraction selected from heavy gas oil and residual fraction obtained from topping crude oil and the residual fraction resulting from the catalytic or thermal cracking of the gas oil fraction, it being provided that the overall mass is in a state of dilution at a temperature ranging from 380° C. to 410° C. during this heating step by means of a fraction of 4–35% by volume of said overall mass, the diluent fraction per se being not substantially cokable and having a boiling point of 380–410° C. under operating pressure; raising the mass to the coking temperature to complete the coking; and thereafter recovering the resulting premium grade coke.

The hereinabove mentioned fractions, which are to be used as the feed stock in this invention, are all well known in the petroleum industry. The black oils all abound in aromaticity. On the other hand, the other petroleum frac-

tions which are used mixed with the black oil are either aliphatic or aromatic depending upon their area of production. These fractions contain in all cases a fraction which per se does not substantially coke. According to this invention, the feed stock must be such that a temperature range of 380–410° C. during the step it is being heated to the coking temperature it is in a state of dilution by means of 4–35% by volume of the feed stock, of the aforesaid fraction which per se does not substantially coke. The accomplishment of this state can be very readily achieved either by suitably incorporating such a fraction in the feed stock or by a suitable choice of an operating pressure in accordance with the distillation characteristics of the feed stock, or by combining these two procedures.

Thus, the cokable component in the feed stock is provided a chance to form acicular crystal nuclei in a state in which it is diluted by the aforesaid fraction which per se does not substantially coke, during the period it is in the temperature range of 380–410° C. Hence, if the hereinbefore prescribed conditions are not satisfied, the object of the invention cannot be achieved. For example, even if black oil is just submitted to a coking treatment without taking these conditions into consideration, high grade petroleum coke cannot be obtained.

The pressure to be employed in the invention process is so chosen that the foregoing conditions are satisfied in accordance with the composition of the feed stock used. On the other hand, when it is intended to employ a predetermined specific pressure, a composition of the feed stock which will satisfy this condition will be chosen.

For sake of brevity, the fraction which is copresent in the feed stock treated at a temperature range of 380–410° C. under operating pressure will hereinafter be referred to as the "diluent fraction." The relationship between the operating pressure and the boiling point of the diluent fraction at atmospheric pressure can be readily computed. Several examples are shown in Table I.

TABLE I

Operating pressure (atm. gauge):	Boiling point of diluent fraction at atmospheric pressure (° C.)
0	380–410
1	355–375
2	320–350
5	290–315
10	250–275
20	210–235

Thus, if the distillation characteristics of the feed stocks to be used are measured in advance, the choice of the operating pressure and the composition of the feed stocks is greatly simplified.

The amount of the diluent fraction to be incorporated in the feed stock should be at least 4% by volume based on the total amount of the feed stock. If less than this amount, the formation and development of the crystal nuclei of acicular coke cannot be promoted. While there is no particular upper limit, an amount in great excess also does not bring about any difference in the results desired and, moreover, since it is a disadvantage from the standpoint of operating period and equipment, it is preferable that the upper limit be placed at about 35% by volume. In general, black oil, depending upon the conditions of the pyrolysis, includes those which contain or do not contain the diluent fraction in an amount such as to satisfy the foregoing conditions. However, it is possible, if necessary, in accordance with the desired operating pressure to use a residual obtained by cutting the black oil at a proper boiling point, or instead a mixture of the black oil with the hereinbefore mentioned other petroleum fractions.

After heating the feed stock at 380–410° C. in the presence of the aforesaid diluent fraction, the overall mass is heated to coking temperature to complete the coking. For completion of the coking, it is required to reach the final temperature of 450–550° C. Thus, the intended high grade acicular coke is obtained, its crystals having been developed about the already formed acicular crystal nuclei.

In practicing the invention process, any apparatus will do so long as the hereinbefore stated conditions are satisfied. For example, the conventional delayed coking apparatus can be used.

The following examples and comparisons are given for further illustration of this invention. It is understood, however, that these examples are not to be construed as limiting the invention in any way whatsoever.

The black oil used in the examples was the residual fraction obtained by pyrolysis of naphtha for the purpose of producing unsaturated hydrocarbons and the residual oils which resulted by cutting the foregoing residual oil at respectively 220° C. and 240° C. The properties and the distillation characteristics at normal atmospheric pressure of these black oils are shown in Table II. On the other hand, the properties and distillation characteristics at normal atmospheric pressure of the other petroleum fractions which are to be used mixed with these black oils are shown in Table III.

TABLE II.—PROPERTIES OF THE BLACK OIL USED

	Black oil	Black oil, 220° C. residue	Black oil, 240° C. residue
Specific gravity (15° C./4° C.)	1.047	1.093	1.185
Conradson residual carbon	8.60	14.93	22.10
Viscosity (centistoke)	[1] 6.64		[2] 81.2
Distillation characteristics, ° C.:			
5%	206	224	246
10%	210	226	252
20%	215	235	295
30%	222	239	342
40%	232	260	400
50%	240	323	415
60%	299	408	
70%	405	417	

[1] 30° C.
[2] 100° C.

TABLE III.—OTHER PETROLEUM FRACTIONS

	Minas 280° C. residue (rich in non-aromatics)	Seria heavy gas oil (300–350° C.) (rich in aromatics)
Specific gravity (15° C./4° C.)	0.883	0.875
Conradson residual carbon (wt. percent)	3.5	
Distillation characteristics, ° C.:		
IBP	276	300
5%	298	305
10%	327	307
20%	365	308
30%	402	309
40%	434	311
50%	[1]	312
60%		313
70%		315
80%		317
90%		325

[1] Decomposed.

EXAMPLE 1

A 2-liter reaction tower having a vent was charged with 1.5 liter of a feedstock enumerated in Table II, following which the feed stock was heated from the outside until a temperature of 500° C. was finally attained.

In Table IV are shown the respective conditions and the properties of the resulting cokes. In Table IV the diluent fraction used was that having a boiling point 380–410° C. and the amounts thereof were values calculated from the distillation curve of the feed stock and the relationship between operating pressure and the boiling range of the diluent fraction (Table I).

Runs 2 and 3 are controls which do not satisfy the conditions of the present invention.

TABLE IV

Run	Feed stock	Coking Conditions: Operating pressure (kg./cm.²g.)	Diluent fraction (vol. percent)	Heating period to 410° C. (hr.)	Heating period at 410–500° C. (hr.)	Properties of resulting coke: Yield (wt. percent)	X-ray index [1]	Specific resistance [2] (Ω cm.)	Coefficient of thermal expansion [2] (per ° C.)
1	Black oil	20	32.3	8	8	25	74	6.0×10^{-4}	5.8×10^{-7}
2	do	2	1.5	4	8	22	30	8.2×10^{-4}	7.7×10^{-7}
3	Mixture of 90 vol. percent black oil and 10 vol. percent 210–230° C. fraction of black oil	20	39.9	9	8	14	75	5.9×10^{-4}	5.6×10^{-7}
4	Black oil 220° C. residue	20	13.5	7	8	33	80	5.6×10^{-4}	5.5×10^{-7}
5	do	2	4.1	4	8	31	63	6.0×10^{-4}	6.2×10^{-7}
6	Black oil 240° C. residue	10	9.0	6	8	53	86	5.8×10^{-4}	5.4×10^{-7}
7	do	5	5.2	5	8	47	71	5.9×10^{-4}	6.0×10^{-7}
8	Mixture of black oil 240° C. residue and 20% of 290–315° C. fraction of black oil	5	24.1	7	8	44	76	5.8×10^{-4}	6.0×10^{-7}
9	Mixture of 90% black oil and 10% 290–315° C. fraction of black oil	5	13.5	6	8	19	79	5.9×10^{-4}	5.6×10^{-7}
10	Commercial regular petroleum coke					25	84	8.5×10^{-4}	10.2×10^{-7}

[1] X-ray index: A specimen prepared by calcining the resulting coke at 1,250° C. and then comminuted to less than 350 mesh is measured for the diffraction peak of its [002] crystal plane by means of the X-ray diffraction method. The height of the peak is designated as h, and the width at half peak height as B. Then h/B is the X-ray index.

[2] The specific resistance and the coefficient of thermal expansion are values obtained by first making the resulting coke into a graphite electrode rod and measuring the foregoing values from this rod.

EXAMPLE 2

To a 4-liter reaction tower having a vent at its top and maintained at 490–500° C. by external heating was introduced from its bottom at the rate of 2.5 liters per hour a feed stock oil mixed in a proportion indicated in Table V. After continuing the introduction of the feed stock oil for 3 hours, the reaction tower was maintained for 4 hours at 490–500° C. Run 8 is the control.

TABLE V

Run	Black oil (vol. percent)	Black oil 240° C. residue (vol. percent)	Minas 280° C. residue (vol. percent)	Seria heavy gas oil 300–350° C. (vol. percent)	Operating pressure (kg./cm.² g.)	Diluent fraction (vol. percent)	Properties of Resulting Coke: Yield (wt. percent)	X-ray index	Specific resistance (Ω cm.)	Coefficient of thermal expansion (per ° C.)
1	90			10	5	9.7	28	104	5.4×10^{-4}	4.7×10^{-7}
2	80			20	5	16.4	21	92	5.7×10^{-4}	4.8×10^{-7}
3		95		5	5	8.9	35	98	5.6×10^{-4}	4.9×10^{-7}
4		90		10	5	12.3	32	101	5.4×10^{-4}	4.8×10^{-7}
5		90	10		2	5.8	38	87	5.6×10^{-7}	5.1×10^{-7}
6	70		30		2	4.3	26	78	5.8×10^{-4}	5.3×10^{-7}
7	50		50		2	5.1	20	84	5.5×10^{-4}	5.1×10^{-7}
8 [1]	70		30		0	3.8	19	50	7.1×10^{-4}	8.5×10^{-7}

[1] Control.

We claim:

1. A process for producing superior premium grade coke which comprises heating to a temperature of 410° C. a black-oil feedstock selected from the group consisting of (a) a residual fraction which is formed as a by-product when naphtha, kerosene, gas oil or natural gas is pyrolyzed at a temperature of 700° to 900° C. in the production of unsaturated hydrocarbons and (b) mixtures of said residual fraction and petroleum fractions selected from heavy gas oil or residual fractions obtained by topping crude petroleum, it being provided that said feedstock is in a state of dilution at a temperature ranging from 380° to 410° C. during said heating step due to the presence of a diluent fraction having a boiling point of 380°–410° under operating pressure and constituting from 4–35% by volume of the total feedstock; heating the feedstock at the coking temperature to complete the coking; and thereafter recovering the resulting premium grade coke.

2. The process of claim 1 wherein said diluent fraction is supplied by said residual fraction (a) itself.

3. The process of claim 1 wherein said diluent fraction is supplied by said petroleum fraction mixed with said residual fraction (a).

References Cited

UNITED STATES PATENTS

2,126,989	8/1938	Engelstein	208—50
2,768,127	10/1956	Kimberlin et al.	208—50
2,775,549	12/1956	Shea	208—50

WILBUR L. BASCOMB, JR., Primary Examiner

D. E. EDWARDS, Assistant Examiner

U.S. Cl. X.R.

201—23; 208—131