Dec. 8, 1959 J. H. McNAMARA 2,916,432

UTILIZATION OF LOW-TEMPERATURE TARS

Filed Dec. 12, 1957 2 Sheets-Sheet 1

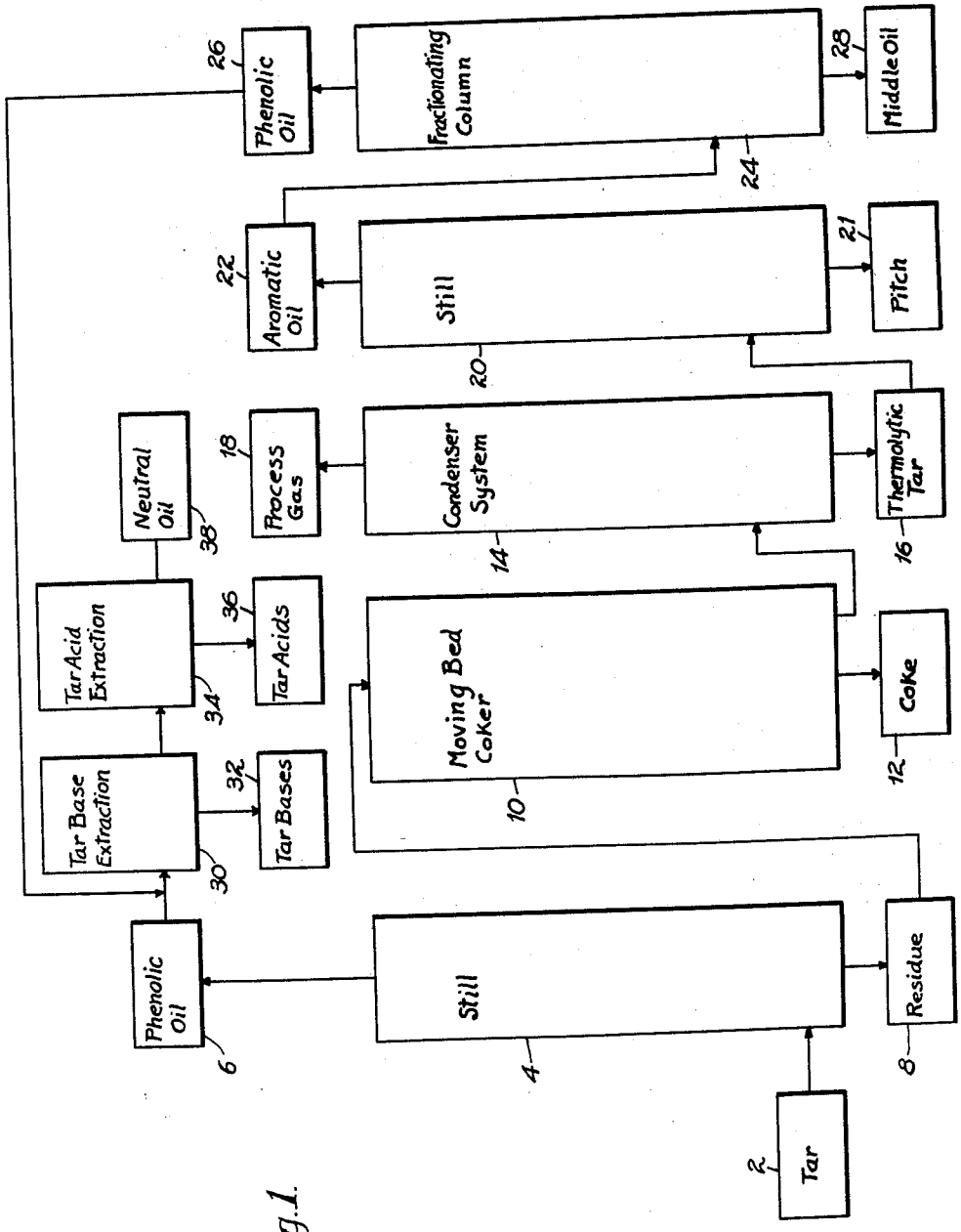


Fig. 1.

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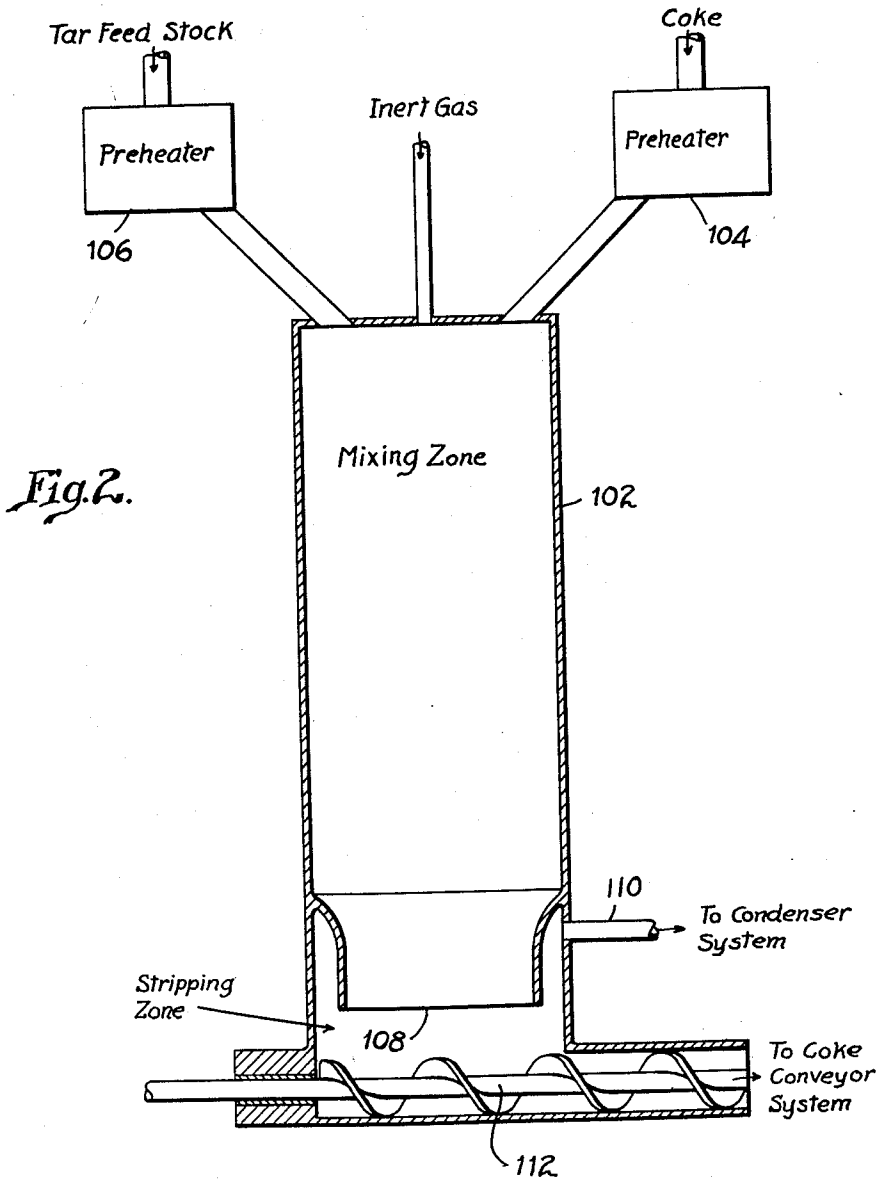


Fig. 2.

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UTILIZATION OF LOW-TEMPERATURE TARS

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6 Claims. (Cl. 208—2)

This invention is related to the treatment of low-temperature tars and tar fractions to produce high-quality coke, aromatic pitch, and other valuable products. More particularly, it is directed to a method for producing electrode-quality coke and aromatic pitch suitable as a binder for carbon electrodes wherein a moving bed of coke is employed to thermally crack tars and tar fractions produced by low-temperature carbonization of bituminous materials.

Peat, brown coal, lignite, sub-bituminous and bituminous coals are bituminous materials which have been proposed as feedstock for low-temperature carbonization processes to secure chars or cokes for use as fuel and tars from which valuable products might be obtained. The present invention is related to utilization of such low-temperature tars for processing to electrode-quality coke, highly aromatic pitches suitable as electrode binders, and other valuable products.

The term "low-temperature carbonization," as used herein, refers to processes for carbonization of bituminous materials at temperatures lower than about 1300° F. Representative of such processes is that described by V. F. Parry in U.S. Patent 2,773,018 and in "Drying and Carbonizing Fine Coal in Entrained and Fluidized State," Bureau of Mines Report of Investigations 4954, U.S. Department of Interior, dated April 1953.

The term "low-temperature tar" as used herein refers to tars produced by low-temperature carbonization of peat, brown coal, lignite, sub-bituminous or bituminous coals. Such tars are generally oily, tarry organic masses ranging from viscous liquids to soft semi-solid materials at room temperature and may contain small quantities of char, ash or other inert material, dissolved gases and water.

A typical analysis of low-temperature tar obtained by carbonization of Texas lignite at 946° F. utilizing the Parry process, supra, is shown in Table 1 below:

TABLE 1

Analysis of crude tar

Ash, weight percent	.37
Specific gravity, 60°/60° F	1.009
Moisture, weight percent (ASTM D95–46)	5.80
C–I (quinoline-insolubles), weight percent	1.37
Infrared index	0.10
Distillation, ASTM D20–52, dry basis, weight percent:	
To 170° C	1.4
170–235° C	14.6
235–270° C	12.8
270–300° C	14.6
300° C.—Decomposition temperature	27.3
Residue at decomposition temperature	27.1
Loss	2.2
Decomposition temperature, ° C	360
Analysis of distillate, vol. percent—	
Tar bases	4.3
Tar acids	23.9
Neutral oil	71.8
Hydrocarbon types, vol. percent: [1]	
Saturates	14
Olefins	46
Aromatics	40

[1] Method described by G. U. Dinneen, "Shale Oil Naphthas: Analysis of Small Samples by Silica Gel Adsorption Method," Analytical Chemistry, vol. 19, p. 992 (1947).

Low-temperature carbonization is generally favored for the production of large quantities of tar as compared to high-temperature processes, thus permitting recovery of considerably greater amounts of tar oils. However, considerable differences exist in the nature of the tars. High-temperature tars are almost completely aromatic, about 90 percent consisting of 3 to 7 ring aromatic compounds with molecular weights up to 400, and the remainder consisting of higher molecular weight carbonaceous compounds; in addition, the percentage of phenolic constituents is low, about 5 to 12 percent, but substantially all of these are low-boiling tar acids. Low-temperature tar is only about 10–45 percent aromatic. It contains relatively large quantities of phenolic constituents, ranging from 20 to 45 percent of the tar; however, these are about evenly distributed in the valuable low-boiling phenolic range and in the higher boiling fraction.

Generally, the product recovery treatment of low-temperature tars involves a distillation process to recover oils from which the tar acids are removed. These phenolic constituents are usually a readily marketable commodity and constitute a definite enhancement to the process. Tar bases may also be extracted from the distillate although of less commercial significance. The neutral oil remaining after such extraction has been proposed as a fuel or as a feedstock for various refining processes, or its components may be separated. The pitch residue which constitutes a great percentage of the original tar, about 25 to 80 percent, has generally been considered of poor economic value. Much experimental work has been devoted to the development of more valuable uses for this pitch, including the preparation of binders for carbon products.

It is an object of this invention to provide a method for substantially complete utilization of low-temperature tar.

Another object is to provide a method for the treatment of low-temperature tar whereby a highly aromatic pitch suitable as a carbon electrode binder and other valuable products are obtained.

It is also an object to provide a method for treating low-temperature tars wherein high-boiling tar acids are cracked to valuable low-boiling tar acids.

It is a further object to provide a method for the production of high-quality coke suitable for carbon electrodes.

Other objects and advantages of the present invention will be evident from the following detailed description and the attached drawings wherein:

Fig. 1 is a diagrammatic flowsheet illustrating a process embodying the invention;

Fig. 2 is a diagrammatic representation of a moving bed coking apparatus, more particularly, of a vertical retort type, which is suitable for use in carrying out part of the process.

Binder pitches for carbon products, especially anodes for the electrolytic production of aluminum, must meet certain minimum standards. Generally, such anodes must have low resistivity and low reactivity, and it has been found that these properties are obtained when the binder is one of high aromaticity and relatively low quinoline-insoluble content. Pitches obtained by distillation of low-temperature tars fail to meet these criteria, especially with respect to aromaticity.

Aromaticity of binder pitch as measured by the infrared index [1] is considered to be a substantially reliable guide to the suitability of a binder. Analysis of various data on binders when related to the properties of the electrode have indicated that the aromaticity of the binder pitch is one of the most significant factors in producing electrodes having low resistivities and low reactivities. Indicative of this is Table Two in which properties of various pitches and the anodes produced therewith are listed.

sis is subsequently calcined; the tar is distilled to a pitch having the required physical properties while obtaining a highly aromatic oil from which low-boiling phenolic constituents may be recovered.

The amount of tar feedstock introduced into the moving bed of coke is maintained at a weight ratio of 1 part feed per 6 to 10 parts of coke; expressed inversely, the coke to feedstock weight ratio is in the range of 6–10:1. An effective means of controlling this is by the rate of coke withdrawal from the thermolysis zone. Greater amounts of feed produce a wet coke and the tar is not sufficiently stripped; in addition, the wet coke tends to agglomerate and produce mechanical difficulties. If lesser amounts are introduced, there is an increase in the amount of carbon products (quinoline-insolubles or C–I) found in the product tar.

The terms "low-temperature tar feedstock" or "tar feedstock" as used herein refer to crude or whole low-temperature tars, or to fractions thereof, such as the residues upon topping, or distillates.

The term "phenolic oil," as used herein, refers to a tar distillate relatively rich in valuable phenolic constituents, such as phenol, cresols, xylenols, and ethyl

TABLE 2

Properties of anodes prepared with various binders

Binder	S.P.,[1] °C.	C-I[2], Percent	C-II,[3] Percent	Coking[4] Value	IR Index	Anode Properties		
						Baked[5] Apparent Density	Resistivity,[6] Ohm-in.	Sulfate Reactivity,[7] Percent
Coke-Oven	109	16.5	33.0	44.1	1.38	1.46	0.0028	2.4
Coke-Oven	109	7.6	32.0	----	1.37	1.43	0.0029	4.7
Unknown Foreign	104	11.5	24.8	35.2	1.08	1.41	0.0030	5.7
Petroleum Oil-Gas	116	13.3	37.2	42.8	1.01	1.41	0.0028	7.0
Straight Distillation of Bituminous Low-Temperature Tar	87	0.2	4.6	11.1	0.47	1.39	0.0031	80.0
Straight Distillation of Lignite Low-Temperature Tar	111	17.7	28.4	29.3	0.29	1.37	0.0042	100.0

[1] Softening point is determined by the cube-in-air test (Barrett method).
[2] Quinoline-insolubles content.
[3] Acetone insolubles—C-I (quinoline insolubles).
[4] ASTM D271-48 (paragraph 14c).
[5] The anode is weighed dry, then soaked for 24 hours in water containing few drops of a detergent solution. It is suspended in water and weighed; then it is removed, dried with towel and weighed while wet. The difference between the weight in water and wet weight is determined and then this figure is divided into the dry weight to give the baked apparent density.
[6] A current of known amperage is passed through a cylindrical anode and a set of probes is used to determine the voltage drop along the longitudinal axis. Resistivity is then calculated by the formula:

$$\rho = \frac{(E)}{(I)} \frac{(A)}{(D)}$$

where ρ=resistivity in ohm-inches
E=average voltage drop across probes
A=cross-sectional area of sample (square inches)
I=current passed through samples (amperes)
D=distance between probes (inches)

[7] Sulfate reactivity is the loss in weight of a carbon specimen, 1 inch in diameter by ½ inch, when immersed in molten sodium sulfate at 940° C. It is considered an excellent measure of the reactivity of an anode in a bath for the production of aluminum by the Hall process.

It has now been found that low-temperature tar feedstocks can be utilized for the production of high quality coke, aromatic pitch suitable as a binder for carbon electrodes, and other valuable products by a method wherein such tar feedstocks are thermolytically cracked on a moving bed of coke preheated to a temperature between about 700° C. and 900° C. to yield gaseous and liquid products including a thermolytic tar, the coke or non-volatile product forming on the surface of the heated coke. The green coke produced by the thermoly-

phenols. It is preferred to use about 235° C. as the end point for this distillate although variations may be made dependent upon the compounds desired in this fraction.

The term, "middle oil," as used herein, refers to a tar distillate boiling above the phenolic oil range.

The term, "tar distillate," as used herein, refers to any distillate from low-temperature tars or from tars formed in the thermal treatment of low-temperature tars, and may encompass phenolic oil, middle oil, or both.

To prevent combustion of the coke and thermolysis products, a substantially inert or non-combusting atmosphere is provided. Such gases as carbon monoxide, hydrogen, methane and nitrogen may be employed. More desirably, the process gas resulting from the thermolysis may be stripped of the olefins and recycled to provide the inert atmosphere. By so doing, the C–I or carbon

[1] The infrared index of the various pitches indicated herein was determined by a method in which 0.250 gram of pitch is dissolved in 10 ml. of carbon disulfide and allowed to stand for two hours. The infrared spectrum of the supernatant liquid is determined using a cell width of 0.50 mm. in a (Perkin-Elmer Model 112) spectrometer. After correcting for absorption of the solvent, the infrared index is taken as the ratio of the transmittance at the 3.4 microns aliphatic absorption range divided by the transmittance at the 3.3 microns aromatic absorption range.

content of the tar can also be reduced. Another alternative is to strip the gas of both methane and hydrogen, as well as the olefins, since these gases may be desirably employed in hydrogen treatment plants. Also the gas can be recycled without treatment; however, in either of the latter two alternatives, the beneficial effect of increasing liquid product yield and decreasing the C–I content will be substantially reduced.

The ash content of the coke produced by the process will be dependent upon that of the feedstock. Especially for the production of consumable anodes for electrolytic reduction cells, it is desirable that the coke contain as little ash as possible, and generally less than about 0.8 percent. Thus, when employing low-temperature tars which usually contain considerable quantities of ash, it has often been found desirable to reduce the solids content of the feedstock prior to the thermal decomposition. For this purpose, several methods may be employed such as, for example, those disclosed in U.S. Patents 2,631,982 to Donegan and 2,774,716 to Kulik.

Referring now to Fig. 1, diagrammatically illustrated is a process embodying the invention, wherein a low-temperature tar **2** is topped in still **4** to recover phenolic oil **6**, leaving a residue **8**. The residue **8** is preheated and introduced into the moving bed coker **10** wherein it is cracked to coke **12** and a volatile stream which is passed through the condenser system **14** to remove the condensible materials which are recovered as thermolytic tar **16** (a light oil fraction may be recovered separately if so desired). The process gas **18** may be stripped of the olefins and recycled to the coker **10**, or its components may be separated, or it may be used as fuel. The thermolytic tar **16** is topped in still **20** to an aromatic pitch **21** of the desired physical properties and a highly aromatic oil **22** which may be fractionated in the column **24** into phenolic oil **26** and middle oil **28**.

The phenolic oil **6**, as well as the phenolic oil **26**, are desirably subjected to a conventional treatment **30** to recover the tar bases **32**, which treatment may be of the type utilizing dilute acid, and to a second treatment **34** to remove the tar acids **36**, such as by washing with caustic solution or solvents, leaving a low-boiling neutral oil **38**.

Coke in excess of that required for the coking apparatus may be calcined to produce a high-quality material suitable for carbon electrodes.

As an alternative process, the low-temperature tar may be distilled to recover a middle oil in addition to the phenolic oil, and the middle oil fraction may be employed as the feed to the moving bed coker.

Figure 2 is a diagrammatic representation of a vertical retort type of moving bed coking apparatus which can be used as the coker **10** of Fig. 1. Generally, the unit consists of well-insulated or heated retort **102** in combination with a furnace **104**, for preheating the coke to cracking temperatures and, desirably, a heating coil or furnace **106** for heating the tar feedstock to a temperature of about 150–300° C. The preheated coke and tar feedstock are fed into the retort **102** and admixed by any suitable means, such as a stirrer, or by agitation or rotation of the retort Coke is withdrawn through outlet **108** where it passes through a heated stripping zone in which the volatile products are driven off and pass out through the discharge **110** to the condenser system. The amount of coke withdrawn and fed is easily controlled by gravity and the screw conveyor **112**. Inert gas is supplied to the top of the retort **102** or through the coke preheater **104**. The conveyor **112** may return the coke directly to the preheater **104** (less the excess amount formed by thermolysis).

Illustrative of the efficacy of the present invention are the following tables. A low-temperature lignite tar as described in Table 1 was topped to recover phenolic oil as shown in Table 3. The residue from the topping was thermally cracked on a moving bed of petroleum coke in a vertical retort under the conditions shown in Table 4 (columns A and B). Also, whole or untopped tar was used in columns C and D of Table 4. As shown in Table 5, thermolytic tar produced as described in Table 4 was then distilled to an aromatic pitch of the desired physical properties and an aromatic oil, from which valuable phenolic constituents may be extracted.

TABLE 3

Initial distillation of crude lignite tar

Maximum temp., ° C	250
Products, percent by weight of feed:	
Distillate	30
Residue	70
Residue properties:	
Specific gravity, 60°/60° F	1.07
C–I (quinoline-insoluble), wt. percent	2.1
Infrared index	0.15
S, percent by wt	0.99
C/H weight ratio	9.66
Distillate composition, vol. percent:	
Tar bases	3.8
Tar acids	22.6
Neutral oil	73.6
Hydrocarbon types, vol. percent—	
Saturates	9
Olefins	44
Aromatics	47

TABLE 4

Thermolytic cracking

	A	B	C	D
Tar feedstock	Topped Tar	Topped Tar	Whole Tar	Whole Tar
Operating conditions:				
Temp. coke, ° C	750	870	750	870
Temp. tar feed, ° C	200	200	200	200
Coke stripping temp., ° C	650	650	650	650
Coke/tar feed wt. ratio	7	9	7	8
Product yield, percent by wt.:				
Total gas	39.3	43.7	52.2	65.6
Tar yield (all liquid products)	42.4	28.2	41.0	20.0
Coke	18.3	28.1	6.8	14.4
Product gas composition, mol percent:				
H_2	24.5	32.2	15.5	27.5
CH_4	33.3	35.5	31.3	37.4
C_2H_6	4.1	1.4	4.0	1.4
C_2H_4	14.6	13.4	18.4	14.5
C_3H_6	Nil	0.8	9.0	0.7
CO	10.2	11.8	11.2	12.1
Others	13.3	4.9	10.6	6.4
Heating value, B.t.u./s.c.f.	1,100	825	1,182	931

TABLE 5

Distillation of thermolytic tar

	A	B	C	D
Tar temp., ° C	310	300	310	300
Products, percent by wt.:				
Aromatic oil	44.6	34.6	52.5	48.6
Pitch	55.4	65.4	47.5	51.4
Properties of pitch:				
Softening point, ° C	106	101	108	97
Ash, wt. percent	0.06	0.4	.02	0.6
C-I, quinoline-insoluble, wt. percent	0.26	1.5	.08	0.18
Infrared Index	.96	1.30	1.00	1.32
Aromatic oil composition:				
Tar bases	5.2	9.8	5.6	16.4
Tar acids	21	2.4	16.6	1.4
Neutral oil	73.8	87.8	77.8	82.2
Hydrocarbon types, vol. percent—				
Aromatics	100	100	100	100
Others	Nil	Nil	Nil	Nil
Distillation, ASTM D20-52, percent by wt.:				
To 170° C	16.8	23.5	38.8	45.8
170-235° C	25.4	30.4	23.6	26.0
235°270° C	29.9	28.5	18.7	16.1
270-300° C	27.9	17.6	18.9	12.1

Electrodes made with binders consisting of pitch obtained by straight distillation of lignite, and coke-oven pitch respectively, were compared to those made with the binder or thermolytic pitch produced by the process of the present invention, and the results are tabulated in Table 6.

TABLE 6

Properties of anodes prepared with various binder pitches

Pitch	Pitch Properties		Anode Properties [1]		
	S. P., ° C.	Infrared Index	Baked Apparent Density	Resistivity, ohms-in.	Sulfate Reactivity [2]
Lignite by Straight Distillation	111	0.29	1.37	0.0042	100.0
Lignite Thermolytic Pitch:					
(*a*) 750° C	106	0.96	1.43	0.0030	24.1
(*b*) 870° C	101	1.30	1.55	0.0026	17.4
100% Coke-Oven Pitch	109	1.38	1.46	0.0028	16.5

[1] Anodes prepared from calcined petroleum coke and 17.5 percent by weight of binder pitch and baked at 1080° C.
[2] Sulfate reactivity determined at 960° C.

The neutral oil remaining after tar acid and tar base extraction of the phenolic oil from the thermolytic tar distillation has been found to contain large percentages of naphthalenic and other polynuclear compounds. It is thus desirable that this oil be processed separately from other streams to preserve its identity and to facilitate recovery of these constituents.

Although a moving bed coker of the vertical type has been illustrated and described, it is obvious that other types of apparatus providing a moving bed of coke may be employed such as, for example, the horizontal type wherein the coke is transported by a moving grate. Other modifications obvious to those skilled in the art may be made within the spirit of this invention.

Having thus described the invention, I claim:

1. In the production of aromatic pitch and other valuable products from low-temperature tars wherein a moving bed of coke is employed for thermal cracking, the method comprising heating said coke to a temperature between 700° C. and 900° C.; introducing into said heated coke a low-temperature tar feedstock at a coke to feedstock ratio of 6–10:1 whereby said feedstock is coked and forms gaseous and liquid products including a thermolytic tar; and distilling said thermolytic tar to obtain aromatic pitch and an aromatic oil.

2. The method in accordance with claim 1 wherein the tar feedstock is the residue after distilling low-temperature tar to recover phenolic oil.

3. The method in accordance with claim 1 wherein the tar feedstock is middle oil obtained by distillation of low-temperature tar.

4. In the production of aromatic pitch and other valuable products from low-temperature tars, the method comprising: heating coke to a temperature between 700° C. and 900° C.; providing within a retort a moving bed of said heated coke, said retort being further provided with an inert atmosphere; introducing a low-temperature tar feedstock into said moving bed of heated coke at a coke to feedstock ratio of 6–10:1; admixing said feedstock and said coke whereby said feedstock is coked with the formation of gaseous and liquid products including a thermolytic tar; condensing said thermolytic tar; distilling said thermolytic tar to an aromatic pitch; recovering from said distillation an aromatic oil; withdrawing coke from said retort; and recycling at least part of said withdrawn coke to said heating step.

5. In the production of aromatic pitch and other valuable products from low-temperature tars, the method comprising: distilling low-temperature tar to recover phenolic oil; heating coke to a temperature between 700° C. and 900° C.; providing within a retort a moving bed of said heated coke, said retort being further provided with an inert atmosphere; introducing into said moving bed of heated coke the residue from said phenolic oil distillation at a coke to residue ratio of 6–10:1, thereby coking said residue to yield gaseous and liquid products including a thermolytic tar; withdrawing the gaseous and liquid products from said retort; condensing said thermolytic tar; distilling said thermolytic tar to an aromatic pitch; recovering from said second-mentioned distillation an aromatic oil containing phenolic constituents; extracting from said phenolic oil and from said aromatic oil phenolic constituents contained therein; withdrawing coke from said retort; recycling at least part of said withdrawn coke to

said heating step; and recycling at least part of said gaseous products to said retort to provide an inert atmosphere therein.

6. In the production of aromatic pitch and other valuable products from low-temperature tars wherein a continuous thermal cracking process is employed in an apparatus provided with a moving bed of heated coke and further provided with an inert atmosphere, the method comprising: distilling low-temperature tar to recover a phenolic oil; heating said coke to a temperature between 700° C. and 900° C.; introducing the residue from said phenolic oil distillation into said apparatus and into said heated coke at a coke to feedstock ratio of 6–10:1; admixing said residue and said coke; stripping from said coke and residue admixture the gaseous and liquid products including a thermolytic tar, the non-volatile product being deposited upon said coke; condensing said thermolytic tar; distilling said thermolytic tar to an aromatic pitch having properties suitable as a carbon electrode binder; recovering from said second-mentioned distillation an aromatic oil containing phenolic constituents; extracting phenolic constituents from said aromatic oil and from said phenolic oil; stripping olefinic material from said gaseous products; recycling said stripped gaseous products to the cracking apparatus to provide the inert atmosphere; withdrawing coke from said apparatus; recycling coke to said heating step and said apparatus; and calcining excess coke formed in the thermal cracking to obtain a coke suitable for carbon electrodes.

References Cited in the file of this patent

UNITED STATES PATENTS

1,622,964	Morgan	Mar. 29, 1927
2,260,071	Wilton	Oct. 21, 1944
2,734,852	Moser	Feb. 14, 1956
2,789,942	Cooper et al.	Apr. 23, 1957