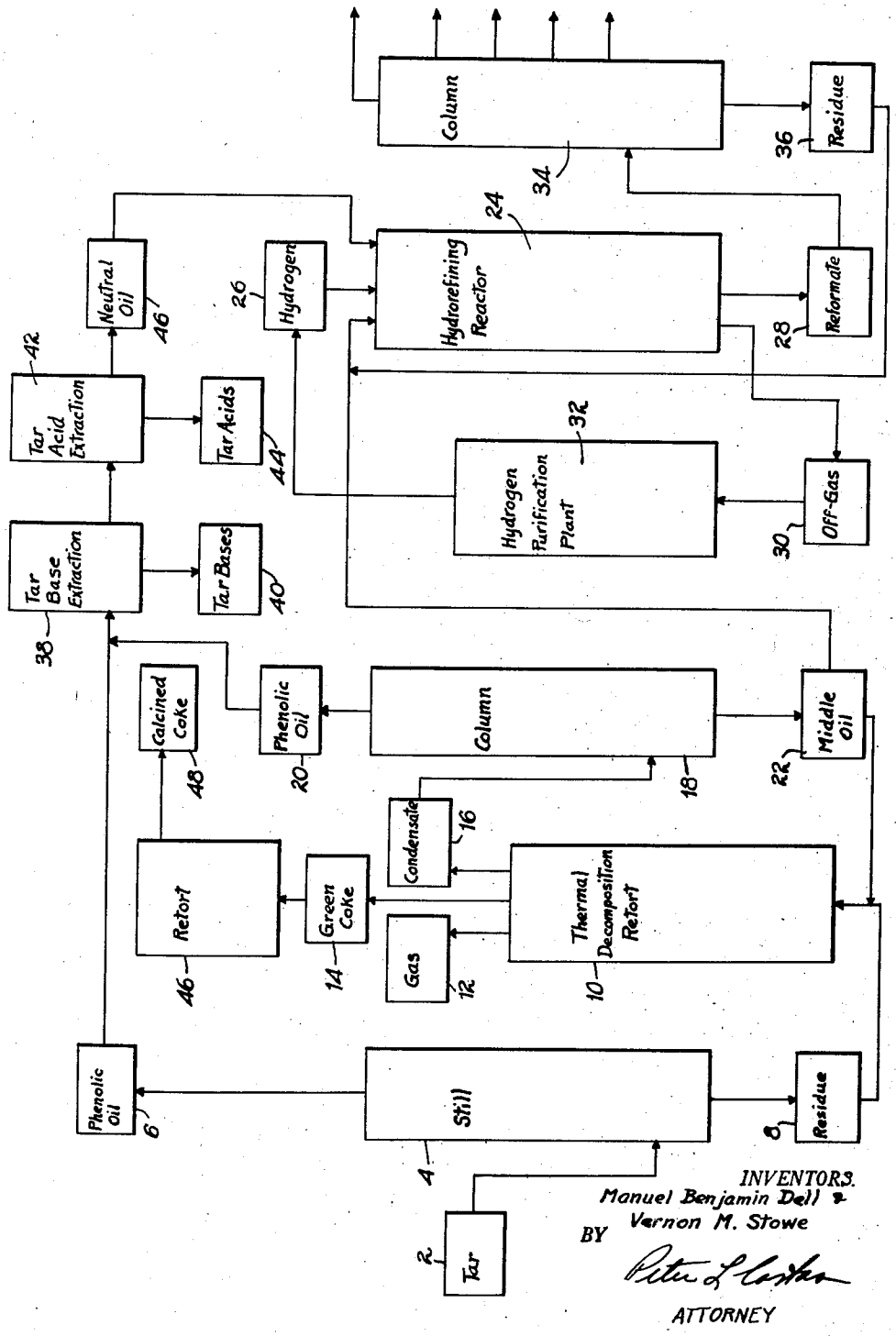
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UTILIZATION OF LOW-TEMPERATURE TARS

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UTILIZATION OF LOW-TEMPERATURE TARS

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This invention relates to the utilization of tars produced in the low-temperature carbonization of bituminous materials. More particularly, it is directed to a method wherein low-temperature tars, or fractions thereof, are thermally decomposed to high-quality coke suitable as an electrode aggregate and to liquid products which are then hydrorefined to hydrocarbon liquids suitable as solvents.

Peat, brown coal, lignite, sub-bituminous and bituminous coals are bituminous materials which have been proposed as feedstocks 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 directed to the utilization of such low-temperature tars and to the hydrogen-treatment of fractions thereof to produce refined hydrocarbon liquids suitable for use as solvents.

The term "hydrorefining," as used herein, refers to the catalytic treatment of low-temperature tar fractions comprising, at least in part, organic compounds containing combined heteroatoms such as sulfur, nitrogen and oxygen, at high temperatures and medium pressures in the presence of hydrogen to produce the corresponding hydrocarbons, and removable hydrogen compounds of the heteroatoms such as hydrogen sulfide, water and ammoniacal substances. Saturation of olefins generally accompanies the removal of the heteroatoms, and other reactions may incidentally occur such as cyclization, dehydrogenation and dealkylation.

The term "low-temperature carbonization," as used herein, refers to a process for the carbonization of bituminous materials at temperatures lower than about 1300° F. Representative of such a process 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	0.35
Specific gravity, 60°/60° F.	0.9867

Moisture, weight percent	2.9
C–I (quinoline-insolubles), weight percent	1.41
Distillation ASTM D20–52, dry basis, weight percent:	
To 170° C.	2.2
170–235° C.	18.4
235–270° C.	12.6
270–300° C.	12.8
300° C. to decomposition temperature	31.3
Residue at decomposition temperature	19.7
Loss	3.0
Decomposition temperature, ° C.	329
Analysis of distillate, vol. percent:	
Tar bases	4.3
Tar acids	23.9
Neutral oil	71.8
Hydrocarbon types [1]:	
Saturates	14
Olefins	40
Aromatics	46

[1] Method disclosed in article by G. U. Dinneen et al., "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 completely aromatic and about 90 percent consists of 3 to 7 ring aromatic compounds with molecular weights up to 400, the remainder consisting of higher molecular weight carbonaceous compounds; in addition, the percentage of phenolic constituents is only about 5 to 12 percent, but substantially all of these are low-boiling tar acids. Low-temperature tar is only partially aromatic, i.e. about 10–45 percent. 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.

The by-product recovery treatment of such tars may involve a distillation process to recover low-boiling oils from which tar acids are recovered. These phenolic constituents are usually a readily marketable commodity and constitute a definite enhancement to the value of the products obtainable from the process. Tar bases may also be extracted from the distillate, although they are of less commercial significance. Heretofore, the neutral oils remaining after such extraction have been considered generally only as fuel oils because of the high content of sulfur and other heteroatoms. The pitch residue, which constitutes about 25 to 80 percent of the original tar, has generally been considered of poor economic value and used as a briquetting binder.

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

Another object is to provide a method for the treatment of low-temperature tars whereby refined hydrocarbon liquids and other valuable products are obtained.

It is also an object to provide a method wherein low-temperature tars are utilized to produce high-quality coke suitable for carbon electrodes and other valuable products.

A further object is to provide a method for cracking the high-boiling tar acids in low-temperature tars to the more valuable low-boiling tar acids.

Further objects and advantages of the present invention will be evident from the attached drawing and following detailed description.

It has now been found that low-temperature tars may be substantially completely utilized by a method in which the tar, or a fraction thereof, is thermally decomposed into coke suitable for carbon electrodes, gas and condensible oils comprising at least in part organic compounds containing combined heteroatoms such as sulfur, nitrogen and oxygen. The condensible oils, or fractions thereof, are then catalytically treated with hydrogen at high temperatures and medium pressures to convert the heteroatom-containing organic components into hydrocarbons and easily removable hydrogen compounds of the heteroatoms, thus removing sulfur, nitrogen and oxygen; simultaneously, olefinic material is saturated.

More particularly, the thermal decomposition takes place at a pressure between atmospheric and 100 pounds per square inch and at a temperature of about 375° C. to 475° C. The hydrorefining conditions include a temperature between 425° C. and 620° C. a pressure between 100 and 1000 p.s.i.g., a liquid hourly space velocity between 0.25 and 4.0, and a hydrogen feed rate between 1000 and 6000 cubic feet per barrel of feed. Preferably, the whole or crude tar is initially distilled to recover phenolic oil prior to the thermal decomposition; it is also desirable to fractionate the condensible oils from the thermal decomposition so as to recover a second phenolic oil which has resulted from cracking of the higher boiling constituents, the balance of the condensible oils or middle oil being used as the feedstock for the hydrorefining operation. These phenolic oils are desirably processed to recover tar acids and tar bases, leaving a neutral oil which also may be hydrorefined either separately or in admixture with the middle oil. Similarly, the phenolic oils may be caustic-washed only to recover the tar acids alone.

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 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 tar, and may encompass phenolic oil, or middle oil, or both.

For a more detailed description, reference is made to the accompanying drawing, which is a diagrammatic flowsheet illustrating an embodiment of the invention.

Low-temperature tar **2** is subjected to distillation in still **4** to recover phenolic oil **6** and leaving a residue **8**. The residue **8** is subjected to thermal decomposition in retort **10** to yield gas **12**, green coke **14** and condensible oils or condensate **16** which is fractionated in column **18** into phenolic oil **20** and middle oil **22**. The middle oil **22** is then subjected to a hydrorefining treatment in reactor **24** wherein it is treated with hydrogen or hydrogen-rich gas **26** to remove undesirable combined heteroatoms such as sulfur, nitrogen and oxygen, as well as to saturate olefinic constituents. The resultants are liquid product **28** and an off-gas **30** which is desirably processed in the hydrogen purification plant **32** to recover and/or make hydrogen or hydrogen-rich gas which then may be recycled as the reactant gas **26**. A portion of the condensate **16**, or middle oil **22**, is preferably recycled and admixed with the residue **8** prior to the retort **10**.

The liquid product **28** is a refined partially aromatic oil, substantially free from noxious impurities, which may be used as a solvent. The liquid product is preferably fractionated in the column **34** into several fractions and a relatively high-boiling residue **36**, which may be recycled for further processing in the reactor **24**.

The higher-boiling fractions from the column **34** may desirably be subjected to a further refining step, such as by treatment with a solution of sulfuric acid or by percolation through clays.

The phenolic oil **6** is desirably subjected to a conventional treatment **38** to recover the tar bases **40**, which treatment may be of the type utilizing dilute acid, and to a second treatment **42** to remove the tar acids **44**, such as by washing with caustic solution or solvents, leaving a low-boiling neutral oil **46**. The phenolic oil **20** from column **18** is also rich in low-boiling tar acids and tar bases which have resulted from the cracking of high-boiling constituents in the retort **10**, and these are conveniently recovered in extraction plants such as **38** and **42**.

The neutral oil **46** is conveniently processed in the reactor **24** in order to refine it to valuable solvents, separately or in admixture with the middle oil, or it may be used without further treatment, if so desired.

The green coke **14** is desirably calcined in the retort **46** at temperatures above 1000° C. to prepare a high-grade calcined coke **48** suitable as an aggregate for carbon electrodes.

The apparatus for effecting the thermal decomposition may be of any type capable of affording the condition of temperature and pressure herein described. A delayed coker is preferably employed, although other types of coking apparatus, such as a pot still, may be satisfactorily utilized.

Generally, the temperature of the thermal decomposition is between 375° C. and 475° C. and preferably between 380° C. and 420° C. The pressures employed may vary between atmospheric and 100 pounds per square inch. The pressure selected will depend largely upon the character of the feedstock, but about 40 to 60 pounds per square inch is preferable.

A portion of the condensible oils, such as the middle oil fraction, may be recycled and mixed with the tar feedstock prior to the preheater. By so doing, especially in the case of topped tar, the feedstock is more easily transported and premature coking is substantially eliminated. Generally, this recycle ratio may be between 0.3 and 3.0 times the feedstock, and preferably between 0.5 and 1.5.

The ash content of the coke produced by the process will be dependent upon that of the feedstock. Especially for the production of 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 been found desirable to reduce the solids contained in the feed tar 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.

Temperatures between about 425° C. and 620° C. are employed for the hydrogen treatment, the specific tempertures depending upon the nature of the low-temperature tar fraction treated. Temperatures above 620° C. tend to reduce the yield of liquid product, whereas temperatures below 425° C. do not effect sufficient removal of the heteroatoms. Generally, it is preferred to use temperatures between 425° C. and 510° C. for neutral oil boiling below about 235° C., and temperatures between 510° C. and 540° C. for middle oil.

The hydrorefining proceeds satisfactorily at total pressures between 100 and 1000 pounds per square inch gauge. Pressures above 1000 p.s.i.g. cause excessive cracking of the molecules and hydrogenation of the aro-

matic nuclei, while pressures below 100 p.s.i.g. result in increased deposits of carbonaceous materials on the catalyst. Generally, a pressure between 500 and 800 p.s.i.g. is preferred for treatment of both neutral oil and middle oil.

The liquid hourly space velocity may be between 0.25 and 4.0 volumes per volume of catalyst per hour. Generally, lower space velocity rates decrease the liquid product yield, whereas higher rates do not provide sufficient purification of the feed. Preferably a rate of between about 0.5 and 1.3 is employed for treatment of all tar fractions.

The hydrogen feed should be in excess of stoichiometric requirements as amounts less than this do not provide sufficient purification, and quantities above 6000 cubic feet per barrel become prohibitive from both cost and handling standpoints. Generally, about 3000 cubic feet per barrel has been preferred for treatment of the various tar fractions.

The catalyst employed may be any of the contact agents generally employed to promote desulfurization. Found especially suitable were oxides of cobalt and molybdenum on alumina, molybdenum oxide on alumina, and oxides of nickel and tungsten on alumina. Specifically, the following catalysts have been satisfactorily employed: 2.55 percent cobalt oxide and 15.45 percent molybdenum oxide on alumina; 5 percent cobalt oxide and 11 percent molybdenum oxide on alumina; 11 percent molybdenum oxide on alumina; 3 percent cobalt oxide on alumina; and 4 percent nickel oxide and 7 percent tungsten oxide on alumina.

In accordance with this invention, crude or whole lignite low-temperature tar, as substantially described in Table 1, was distilled to recover phenolic oil. Data on this distillation are shown in Table 2 below:

TABLE 2

Initial distillation of crude lignite tar

Max. temp., ° C.	235
Products, wt. percent:	
Phenolic oil	27.8
Residue	72.2
Residue properties:	
Specific gravity, 60°/60° F.	1.07
C–I (quinoline-insolubles), wt. percent	0.42
Ash, wt. percent	0.92
Moisture, wt. percent	1.3
Sulfur, wt. percent	0.99
Phenolic oil composition, vol. percent:	
Tar bases	3.8
Tar acids	22.6
Neutral oil	73.6
Hydrocarbon types, vol. percent:	
Saturates	7
Olefins	44
Aromatics	47

A low-temperature lignite tar residue, substantially as described in Table 2, was thermally decomposed in a delayed coker to obtain green coke, process gas and condensate as shown in Tables 3 and 4.

TABLE 3

Thermal decomposition

Conditions:	
Temp., ° C.	425
Pressure, p.s.i.g.	50
Product yields:	
Coke, green, wt. percent of feed	26.1
Gas, cu. ft. per lb. of feed	1.18
Condensate, wt. percent of feed	62.8
Phenolic oil (to 235° C.), vol. percent of condensate	32.0
Middle oil (over 235° C.), vol. percent of of condensate	68.0

TABLE 4

Product analysis

Gas, mol percent:	
Hydrogen	4.9
Methane	46.3
Ethane	15.4
Propane	7.7
Ethylene	2.5
Propylene	3.8
Carbon monoxide	5.6
Carbon dioxide	5.7
Others	7.1
Condensate composition, vol. percent:	
Tar bases	2.6
Tar acids	18.7
Neutral oil	78.7
Hydrocarbon types, vol. percent:	
Saturates	25
Aromatics	40
Olefins	35
Condensate distillation, ASTM D–86:	
Initial, ° C.	51
10 ml.	167
20 ml.	207
30 ml.	231
40 ml.	251
50 ml.	260
60 ml.	284
70 ml.	331
85.8 ml.	337
Decomposition, ° C.	337
Residue, percent	10.8

The middle oil from the thermal decomposition described in Table 3 was hydrorefined in accordance with the present invention; neutral oil obtained by extraction of the tar acids and tar bases of the phenolic oil described in Table 3 was also hydrorefined. The catalyst employed was one containing 2.55 percent cobalt oxide and 15.45 percent molybdenum oxide on alumina. Analyses of the feedstocks, data on hydrorefining conditions and analyses of the hydrorefined products are given in the following tables.

TABLE 5

Feedstock analysis

	A	B
Type of Feedstock	Middle Oil	Neutral Oil
Specific gravity, 60°/60° F.	0.9365	0.8241
Refractive index, n_D^{20}	1.5168	1.4594
Sulfur, wt. percent	0.81	0.83
Nitrogen, wt. percent	0.40	Nil
Mixed aniline point, ° C.	52.8	47.2
Distillation, ASTM D158–41, ° C.:		
Initial boiling point	109	72
5%	230	117
10%	239	131
20%	249	151
30%	258	166
40%	268	179
50%	277	191
60%	289	203
70%	301	215
80%	316	227
90%	337	246
91%	339	
95%		262
98%		281

TABLE 6

Hydrorefining conditions

	A	B
Temperature, ° C.	511	491
Pressure, p.s.i.g.	500	500
Liquid hourly space velocity	1.0	1.0
H_2, cu. ft. per bbl. of feed	3,000	3,000

TABLE 7

Reformate products

	A	B
Product yield, vol. percent feed:		
Organic	91	94
Inorganic	7.4	4.4
Gas—		
H_2 consumed, cu. ft./bbl	1,096	753
H_2 recoverable from methane in off-gas, cu. ft./bbl	1,150	688
Organic product:		
Specific gravity, 60°/60° F	0.8693	0.7959
Refractive index $n^{20}D$	1.5018	1.4524
Sulfur, percent	0.050	0.010
Nitrogen, percent	0.09	Nil
Mixed aniline point, ° C	47	53
Kauri butanol	61.5	48.8

The reformate or hydrorefined product is a partially aromatic oil which may be distilled into several fractions suitable as commercial solvents. The properties of these several fractions, as given in Table 8, indicate good solvent characteristics by reason of their aromaticity and low sulfur and nitrogen contents. The fractions boiling above 93° C. were washed with 70% sulfuric acid.

TABLE 8

Solvent data

Fraction, ° C	Below 93		93–135		135–179		179–216		216–288		288–Decomp. B
	A	B	A	B	A	B	A	B	A	B	
Yield, vol. percent, hydrorefined organic product	6.7	13.3	9.1	17.1	11.7	27.4	12.0	23.2	40.5	17.2	16.0
Specific gravity, 60°/60° F		0.6814	0.7763	0.7417	0.8224	0.7938	0.8592	0.8291	0.8963	0.8612	0.9159
Mixed aniline point, °C	[1] 36.0	[1] 64.4	45.56	57.78	38.89	51.11	39.44	50.00	43.33	52.22	56.11
Kauri butanol		35.7	58.7	43.5	68.0	49.1	65.0	51.0	59.1	52.0	42.5
Sulfur, percent		Nil	0.01	Nil	0.01	Nil	0.03	Nil	0.09	0.003	0.08
Refractive index, $n^{20}D$	1.4125	1.3965	1.4403	1.4160	1.4645	1.4458	1.4855	1.4660	1.5115	1.4879	1.5265

[1] Straight aniline point, ° C.

The green coke was calcined at a temperature of about 1200° F. for 20 hours. The properties of the calcined material and of anodes prepared therewith were determined, comparison determinations being made for commercially available petroleum coke. As evidenced by the data in Table 9, the coke made in accordance with the present invention produces anodes of greatly improved resistivity; the baked apparent density is superior, and the sulfate reactivity is in the acceptable range and substantially equivalent to that of petroleum coke.

TABLE 9

Coke	Coke			Anode [1]		
	Volatile Matter, Wt. Percent	Ash, wt. Percent	Resistivity,[2] ohms-in.	Baked Apparent Density [3]	Resistivity,[4] ohms-in.	Sulfate Reactivity [5]
Petroleum	0.14	0.45	0.0549	1.50	0.0026	59
Lignite	0.00	4.14	0.0484	1.52	0.0022	69

[1] Cylindrical anodes made with 110° C. softening point coke-oven pitch.

[2] Great Lakes Carbon Company, Procedure No. C-12A.

[3] 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 a 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.

[4] 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:

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

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)

[5] 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 960° 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.

Having thus described the invention, we claim:

1. In the utilization of low-temperature tars to prepare electrode-quality coke, refined hydrocarbon liquids suitable as solvents and other valuable products, the method comprising distilling low-temperature tar to recover phenolic oil; thermally decomposing the residue from said phenolic oil distillation at a temperature between 375° C. and 475° C. and a pressure between atmospheric and 100 pounds per square inch to convert said residue into coke, gaseous products, and condensible oils including phenolic oil and middle oil, said condensible oils being comprised, in part, of organic compounds containing combined heteroatoms; recycling a portion of condensible hydrocarbons in admixture with said residue in an amount between 0.3 and 3.0 to 1 prior to said thermal decomposition step; extracting phenolic constituents from said first-mentioned and second-mentioned phenolic oils; hydrorefining said middle oil by catalytic treatment with hydrogen at a temperature between 425° C. and 620° C., a pressure between 100 and 1000 pounds per square inch and a liquid hourly space velocity between 0.25 and 4.0, thereby obtaining refined hydrocarbon liquids suitable as solvents.

2. The method in accordance with claim 1 in which the oil from which the phenolic constituents are extracted is also hydrorefined.

3. The method in accordance with claim 2 in which the oil remaining after extraction of the phenolic constituents is hydrorefined in admixture with the middle oil.

4. The method in accordance with claim 1 in which the coke is calcined at a temperature above 1000° C. to produce an electrode quality aggregate.

5. In the utilization of low-temperature tars to pre-

pare electrode-quality coke, refined hydrocarbon liquids suitable as solvents and other valuable products, the method comprising distilling low-temperature tar to recover phenolic oil; thermally decomposing the residue from said phenolic oil distillation at a temperature between 375° C. and 475° C. and a pressure between atmospheric and 100 pounds per square inch to convert said residue into coke, gaseous products, and condensible oils including phenolic oil and middle oil, said condensible oils being comprised, in part, of organic compounds containing combined heteroatoms; recycling a portion of condensible hydrocarbons in admixture with said residue to said thermal decomposition step; extracting phenolic constituents from said first-mentioned and second-mentioned phenolic oils; and hydrorefining said middle oil by catalytic treatment with hydrogen thereby obtaining refined hydrocarbon liquids suitable as solvents.

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