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HYDROREFINING OF LOW-TEMPERATURE TAR FRACTIONS

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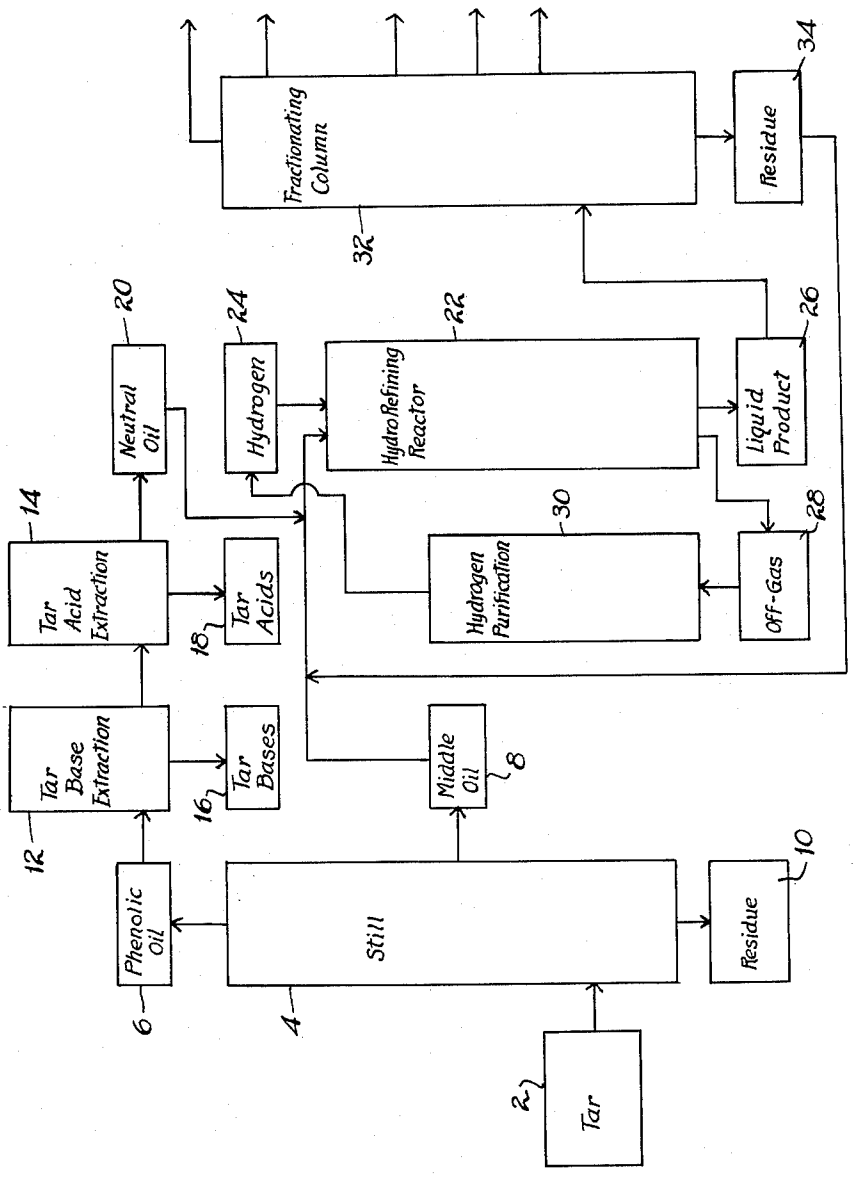

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HYDROREFINING OF LOW-TEMPERATURE TAR FRACTIONS

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This invention is related to the treatment of low-temperature tar fractions with hydrogen to produce refined hydrocarbon liquids and other valuable products. More particularly, it is directed to a method for the production of hydrocarbon liquids suitable for use as solvents by hydrorefining fractions of tars 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 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 in the presence of hydrogen under medium pressure to produce ammoniacal compounds, hydrogen sulfide, water and the corresponding hydrocarbons. 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

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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 Napthas: 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 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 low, 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 a great percentage of the original tar, about 25 to 80 percent, has generally been considered of poor economic value, and used as a fuel or a briquetting binder.

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 refined hydrocarbon liquids and other valuable products are obtained.

It is also an object to provide a method for the hydrorefining of low-temperature tar fractions to produce hydrocarbon solvents substantially free from sulfur, nitrogen, oxygen and other undesirable impurities.

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

In accordance with the present invention, a low-temperature tar fraction is 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 specifically, the hydrorefining conditions include a pressure between 100 and 1000 p.s.i.g., a temperature be-

tween 800° F. and 1150° F., 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 crude or whole tar is initially distilled to to recover phenolic oil and middle oil, and the phenolic oil is desirably processed to recover tar acids and tar bases, leaving a neutral oil. The middle oil is employed as the feed to the hydrorefining reactor, and the neutral oil may also be treated therein, either separately or in admixture with the middle oil. The residue from the distillation may be returned to the carbonizer or treated in accordance with other proceses.

The term "phenolic oil," as used herein, refers to a tar distillate relatively rich in valuable low-boiling phenolic components, 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, and may encompass phenolic oil or middle oil, or both.

The term "low-temperature tar fraction," as employed herein, refers to a distillate from low temperature tar, either whole or extracted, and may encompass middle oil, phenolic oil, oils obtained by caustic-washing of phenolic or middle oils, neutral oils obtained by extraction of phenolic or middle oils, and mixtures thereof.

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

A low-temperature tar **2** is subjected to distillation or topping in a still **4** to recover phenolic oil **6** and middle oil **8**, leaving residue **10**. The middle oil **8** is subjected to hydrorefining in reactor **22**, wherein it is treated with hydrogen-rich gas **24** to remove undesirable impurities, such as sulfur, nitrogen and oxygen, as well as to saturate olefinic constituents. The resultants are liquid product **26** and off-gas **28** which is desirably processed in the hydrogen-purification plant **30** to recover hydrogen or hydrogen-rich gases which then may be recycled as the reactant gas **24**.

The liquid product **26** is 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 **32** into several fractions and a relatively high-boiling residue **34**, which may be recycled for further processing in the reactor **22**.

The higher-boiling fractions from the column **32** may desirably be subjected to a further refining step, such as by treatment with 70 percent sulfuric acid or by filtration.

The phenolic oil **6** is desirably subjected to a conventional treatment **12** to recover the tar bases **16**, which treatment may be of the type utilizing dilute acid, and to a second treatment **14** to remove the tar acids **18**, such as by washing with caustic solution or solvents, leaving a low-boiling neutral oil **20**.

The neutral oil **20** is conveniently processed in the reactor **22** 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 desired.

The residue **10** is preferably subjected to a delayed coking operation such as is described in the copending application of M. B. Dell, "Delayed Coking of Low-Temperature Tars," Serial No. 791,615, filed February 6, 1959.

Temperatures between about 800° F. and 1150° F are employed for the hydrogen treatment, the specific temperatures depending upon the nature of the low-temperature fraction treated. Temperatures above 1150° F. tend to reduce the yield of liquid product, whereas temperatures below 800° F. do not effect sufficient removal of the heteroatoms. Generally, it is preferred to use temperatures between 900 and 950° F. for neutral oil boiling below about 235° C., and temperatures between 950 and 1000° F. 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 aromatic 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 and amounts less than this fail to provide sufficient purification, and quantities above 6000 cubic feet per barrel become prohibitive both from 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.

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

TABLE 2

Distillation of crude lignite tar

PHENOLIC OIL	
Maximum temp., ° C.	235
Phenolic oil, percent by wt. of feed	27.8
Composition, vol. percent:	
Tar bases	3.8
Tar acids	22.6
Neutral oil	73.6
Hydrocarbon types:	
Saturates	9
Olefins	44
Aromatics	47
Neutral oil characteristics:	
Specific gravity, 60°/60° F.	0.8803
Refractive index n^{20} D	1.4908
Sulfur, percent	1.09
Nitrogen, percent	0.37
MIDDLE OIL	
Temp., ° C.	235–335
Product yield, percent by wt. of feed:	
Middle oil	42.3
Residue	29.9
Middle oil composition, vol. percent:	
Tar bases	4.2
Tar acids	21.1
Neutral oil	74.7
Hydrocarbon types:	
Saturates	11
Olefins	28
Aromatics	43
Others	18
Middle oil properties:	
Specific gravity, 60°/60° F.	0.9382
Refractive index n^{20}D.	1.5255
Sulfur, percent	0.89
Nitrogen, percent	0.53

Several fractions produced by distillation of low-temperature lignite tar were hydrorefined in accordance with the present invention. Feedstock A is a mixture of phenolic and middle oils which have been caustic-washed. Feedstock B is a mixture of middle oil and caustic-washed phenolic oil. Feedstock C is middle oil. Analyses of the feedstocks, data on hydrorefining conditions and analyses of the products of hydrorefining are given in the tables below.

TABLE 3

Feedstock analysis

Type of feedstock	A	B	C
Specific gravity, 60°/60° F	0.8803	0.9262	0.9382
Refractive index, n^{20} D	1.4908	1.5135	1.5255
Sulfur, percent	1.09	0.94	0.89
Nitrogen, percent	0.37	0.37	0.53
Mixed aniline point, ° C	43.3	49.0	49.5
Distillation, ASTM D 158-41, ° C.:			
Initial boiling point	151	99	187
5%	178	170	225
10%	184	197	238
20%	198	220	260
30%	206	245	276
40%	219	264	290
50%	234	275	306
60%	247	289	316
70%	262	308	339
80%	278	333	-------
90%	304	-------	-------

TABLE 4

Hydrorefining conditions

	A	B	C
Contact agent	$CoO.MoO_3.Al_2O_3$	$CoO.MoO_3.Al_2O_3$	$MoO_3.Al_2O_3$
Temperature, ° C	512	512	493
Pressure, p.s.i.g	500	500	200
Liquid hourly space velocity	1.0	1.0	0.67
H_2 feed, cu. ft. per bbl	3,000	3,000	3,475

TABLE 5

Reformate products

	A	B	C
Product yield, vol. percent feed:			
Organic	92	91	88.2
Inorganic	5.7	4.6	0.4
Gas—			
H_2 consumed, cu. ft./bbl	992	761	1,132
H_2 recoverable from methane in off-gas, cu. ft./bbl	1,136	1,239	1,662
Organic Product:			
Specific gravity, 60°/60° F	0.8230	0.8877	0.8636
Refractive index n^{20}D	1.4724	1.4962	1.5050
Sulfur, Percent	nil	0.014	0.12
Nitrogen, Percent	nil	-------	0.14
Mixed aniline point, ° C	48.3	46.0	45.5

The reformate or hydrorefined product is a partially aromatic oil which may be distilled into several fractions which may be employed as commercial solvents. The properties of these several fractions indicate good solvent characteristics by reason of their aromaticity and low sulfur and nitrogen contents. Data for various fractions obtained by distilling a hydrorefined liquid product from middle oil and caustic-washed phenolic oil (B in Tables 3–5) are given in Table 6 below. The fractions boiling above 93° C. were washed with 70% sulfuric acid.

Having thus described the invention, I claim:

1. In the utilization of low-temperature tars containing combined heteroatoms to prepare refined hydrocarbon liquids suitable as solvents, the method comprising distilling said tars to recover phenolic oil and middle oil; extracting the tar acids from said phenolic oil; and hydrorefining a mixture of the oil from which tar acids have been extracted as aforesaid and said middle oil by catalytic treatment with hydrogen at a temperature between 800° F. and 1150° F., a pressure between 100 and 1000 pounds per square inch gauge and a liquid hourly space velocity between 0.25 and 4.0.

2. In the utilization of low-temperature tars containing combined heteroatoms to prepare refined hydrocarbon liquids, the method comprising distilling said tars to recover phenolic oil and middle oil; extracting the tar acids and tar bases from said phenolic oil to leave a neutral oil; hydrorefining said middle oil and said neutral oil in admixture by catalytic treatment with hydrogen at a temperature between 800° F. and 1150° F., a pressure between 100 and 1000 pounds per square inch gauge and a liquid hourly space velocity between 0.25 and 4.0.

TABLE 6

Solvent data

Fraction, ° C	93	93–135	135–279	179–216	216–288	288–Decomp.
Yield, vol. percent, hydrorefined organic Product	9.3	8.9	12.3	17.5	30.8	7.4
Specific gravity, 60°/60° F	.6878	.7672	.8076	.8448	.8959	.9285
Mixed aniline point, ° C	[1] 49.4	48.89	43.33	42.22	42.78	47.22
Sulfur, percent	.003	Nil	.008	0.016	0.03	0.06
Refractive index, n^{20}D	1.4052	1.4318	1.4553	1.4772	1.5131	1.5368

[1] Straight aniline point, ° C.

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