

[54] PURGING AND WASHING COAL NAPHTHA TO REMOVE DIHYDROGEN SULFIDE AND BASIC NITROGEN

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[56] References Cited

UNITED STATES PATENTS

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FOREIGN PATENTS OR APPLICATIONS

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[57] ABSTRACT

Coal-derived naphtha boiling within the range from 80° F. to 450° F. has been found to contain sulfur as H₂S and nitrogen as basic nitrogen compounds, particularly after the extract has been hydrocracked. By the present invention, the H₂S is removed by purging the naphtha with an inert gas such as nitrogen, C₁–C₃ hydrocarbons, hydrogen, flue gas, CO₂, and mixtures thereof. Purging conditions may include a temperature from about 40° F. to about 200° F., a pressure from about 0 psig to about 150 psig, and a treat rate from about 50 SCF/B to about 300 SCF/B.

The basic nitrogen compounds are removed by washing the naphtha with water or with a dilute aqueous solution of strong acids. A concentration of 0 to 10 weight percent of acids, such as sulfuric acid, hydrochloric acid, phosphoric acid, and acetic acid, are suitably employed. Washing conditions are generally the same as those to be employed in the purging step and may include a temperature from about 40° F. to about 200° F., a pressure from about 0 psig to about 150 psig, and a treat rate from about 0.01 volume of acid per volume of naphtha to about 1.0 volume of acid per volume of naphtha.

4 Claims, No Drawings

PURGING AND WASHING COAL NAPHTHA TO REMOVE DIHYDROGEN SULFIDE AND BASIC NITROGEN

CROSS REFERENCE TO RELATED APPLICATION

This application is a Continuation-in-Part of our copending application, Ser. No. 747,798, filed July 26, 1968, and entitled "Process for Producing Coal Naphtha", now abandoned.

The present invention relates to the production of a naphtha by liquefaction of coal. More particularly, the present invention relates to the removal of sulfur and nitrogen compounds from a coal-derived naphtha by a sequence of steps immediately following the fractionation of the product of liquefaction.

According to the present invention, it has been found that in naphtha produced by the liquefaction of coal (for example, by solvent extraction of coal) the nitrogen and sulfur compounds are easily removable by simple steps. The process is based upon the discovery that essentially all of the sulfur content of the freshly prepared naphtha is attributable to H_2S sulfur and that the total nitrogen content of the freshly prepared naphtha contains about 20 percent ammonia nitrogen atoms, about 40 percent of pyridine homologue nitrogen atoms and basic nitrogen atoms in compounds other than pyridine homologues, and 40 percent in gaseous non-basic nitrogen compounds.

The process of the present invention involves two steps: (1) purging the naphtha with an inert gas to remove H_2S , ammonia, and non-basic nitrogen gaseous compounds, leaving in the naphtha the pyridine homologues and basic nitrogen compounds other than pyridine homologues, and (2) washing the stripped naphtha with water or a dilute acid so as to remove the basic nitrogen compounds. By this simple sequence of steps, substantially all of the nitrogen and sulfur is removed from the coal-derived naphtha without the use of expensive treating facilities.

It is important that the coal-derived naphtha be treated by the present invention within 72 hours (preferably within 36 hours) after the fractionation of the total liquefied coal product, since H_2S sulfur is prone to oxidize readily in the presence of the basic nitrogen compounds to produce elemental sulfur or polysulfide sulfur, which is relatively difficult to remove from naphtha. The fractionation is usually carried out immediately (i.e., within about 1 hour) after completion of the extraction step. Once the elemental or polysulfide sulfur has been formed, it can react with basic nitrogen compounds and other oxygenated compounds which may be present in trace amounts in the naphtha to produce thiocarbonates and thiocarbonates which are also very difficult to move. Exemplary of the oxygenated compounds are CO_2 , carboxyl sulfide, carboxylic acids, phenols, and organic carbonyl compounds. Thus, removal of the H_2S at an early stage not only eliminates the sulfur but also tends to prevent the nitrogen from being converted into materials which are difficult to remove. Since the presence of oxygen promotes formation of polysulfides, exclusion of oxygen (e.g., by use of an inert gas blanket) may make it possible to delay treatment by the present invention for periods up to at least a week or 10 days after fractionation.

Coal Extract

The coal extract from which the naphtha of the present invention is obtained can be produced by a number of well-known methods, such as the extraction of coal by hydrogen-donor solvents, the catalytic hydrogenation of coal in a liquid solvent, etc. Exemplary processes for obtaining the naphtha of the present invention are disclosed in U.S. Pat. Nos. Re. 25,770; 2,018,241; and 3,117,921. Preferably, the naphtha will be obtained by contacting coal with a hydrogen donor solvent at a temperature of about 700° F. to about 850° F. and a pressure of about 350 psig to about 1,000 psig, either in the presence of or in the absence of extraneously added molecular hydrogen. An extraction period of from about 1 hour to about 2 hours is preferred. An extraction zone product is obtained which comprises a liquid extract phase and a solid, undissolved residue. The extract may be first flashed to remove naphtha and lighter materials, or may be charged directly into a hydrocracking zone. In either event, the heavier constituents are hydrocracked to produce additional naphtha, which can be separately treated according to the present invention or which can be combined with the flashed naphtha before such treatment. The naphtha cuts hereinabove mentioned will boil within the range from about 80° F. to about 450° F., preferably within the range from about 125° F. to about 400° F. Suitable hydrocracking conditions include (e.g.) contact with a cobalt-molybdate catalyst and hydrogen at a temperature of about 750° F., a pressure of about 2,000 psig, a weight hourly space velocity of 0.8 pound of liquid per pound of catalyst per hour (lb./lb./hr.), and a hydrogen treat rate of about 5,000 SCF/B.

A suitable hydrocracked naphtha obtained by the process hereinabove discussed will have the following inspection data.

TABLE I

Inspections on Typical Coal-Derived Naphtha Sample*	
Specific Gravity 60/60	0.874
Elemental Analysis:	
Carbon	88.70 Wt. %
Hydrogen	11.19 Wt. %
Nitrogen	0.04 Wt. %
Sulfur	0.02 Wt. %
Oxygen	0.05 Wt. %
ASTM Distillation:	
IBP	160° F.
5%	227° F.
10%	250° F.
20%	280° F.
30%	308° F.
40%	333° F.
50%	350° F.
60%	366° F.
70%	373° F.
80%	394° F.
90%	406° F.
91%	423° F. final

(1% loss, 8% solids in condenser)

*Obtained by hydrogen-donor solvent extraction at about 750° F. and 350 psig, residence time about one hour; extract hydrocracked, and naphtha recovered by distillation.

As will be seen above, the coal-derived naphtha contains nitrogen and sulfur compounds. The naphtha will contain from about 20 to about 1,000 parts per million of basic nitrogen (expressed by weight) and from 20 to 1,000 parts per million of sulfur (expressed by weight), usually from 100 to 200 wppm of sulfur and from 200

to 300 wppm of nitrogen will be typical. Some variation will be experienced with different coal sources and with operation of the distillation and extraction steps, so that the sulfur and nitrogen contents may not fall within the ranges above stated. The present invention is applicable nonetheless if the naphtha contains at least 20 wppm of sulfur and 20 wppm of nitrogen. Since the sulfur begins to form an appreciable amount of elemental sulfur and polysulfide within about 72 hours after distillation if oxygen is not rigorously excluded, it is essential that the treatment of the present invention be carried out on the distilled naphtha within 72 hours after the distillation step.

Purging

After removal of the naphtha from the fractionator, it is sequentially treated by two steps: purging and washing. Although the order of treatment is not critical, it is preferred that the naphtha first be purged with an inert gas so as to remove H₂S, ammonia and non-basic gaseous compounds. When the acid wash is employed first, ammonia is extracted into the acid, thereby reducing its capacity to remove other basic nitrogen compounds.

The purging step can be carried out with any gas which is inert with respect to the naphtha. Exemplary gases are nitrogen, C₁-C₃ hydrocarbons, hydrogen, flue gas, CO₂ etc. The purging step should be carried out at a temperature from 40° F. to 200° F., preferably ambient temperature (about 77° F.). The pressure is not critical, but may range from 0 to 150 psig, preferably 0 psig. The pressure is chosen to reduce volatilization of hydrocarbon components of the naphtha. It is also desirable to use a condenser on the off-gas stream to recover any hydrocarbons which might be carried over. The amount of gas which is passed in contact with the naphtha is sufficient to strip the H₂S, ammonia and gaseous non-basic nitrogen compounds from the naphtha. In general, at ambient temperature, the treat rate will total about 50 to 300 SCF of gas per barrel of naphtha, preferably about 175 SCF/B. The rate at which the gas is passed through the naphtha generally is not critical, and about 200 to 400 SCF/B per hour will be suitable. The purging step may be terminated when the off-gas is substantially free of H₂S. Usually, the purging step is carried out for 0.1 to 1.0 hour.

Washing

The purged naphtha is next treated to remove water-soluble basic nitrogen compounds. The washing step can be carried out with water or with dilute solutions of acids. Preferably, a dilute acid will be employed. Suitable acids are sulfuric acid, hydrochloric acid,

long as undesirable side reactions are not experienced. The washing step is carried out in suitable liquid/liquid contacting apparatus, such as a packed column, bubble-cap tower, a mixing zone (e.g., orifice mixer or centrifugal pump) followed by a settling zone, etc. Preferably, the washing step will be carried out in an orifice mixer or centrifugal pump followed by a settling zone.

Conditions under which the washing step is carried out may vary widely, but the use of ambient temperatures and pressures is preferred for simplicity. The temperature can range from 40° F. to 200° F. (preferably about 77° F.), the pressure from 0 to 150 psig (preferably 0 psig), and the treat rate from about 0.01 volume of aqueous wash liquid per volume of naphtha to about 1.0 vol/vol, preferably 0.05 vol/vol. Higher ratios can be employed but are not economically attractive. The preferred wash liquid is 0.25N H₂SO₄. Several washing stages may be employed, if desired. Preferably, three countercurrent stages will be used.

EXAMPLES

In order to illustrate the present invention, the following examples are presented.

Example 1

A naphtha obtained by hydrogen-donor solvent extraction and having the inspection data shown in Table I was purged with nitrogen for 30 minutes at 77° F. The results of this treatment are shown hereinafter in Table II, compared with the other examples.

Example 2

The naphtha having an inspection data of Table I was subjected to extraction with 0.25N aqueous H₂SO₄ at a temperature of about 77° F. and a treat rate of 1 volume of the dilute acid per volume of naphtha. After settling, the acid extract was separated from the raffinate and each phase was analyzed for sulfur and nitrogen. The results of this example are also shown in Table II.

Example 3

The naphtha shown in Table I was extracted with a sodium hydroxide solution having a concentration of 5 weight percent; a treat rate of 1 volume of caustic solution per volume of naphtha was used. The results of this extraction are shown in Table II.

Example 4

The treatment of the naphtha shown in Table I in Examples 1 and 2 was done sequentially. That is, it was first purged with nitrogen and then washed with the 0.25N H₂SO₄. The results of this example are also shown below in Table II.

TABLE II
Summary of Examples

	Naphtha feed	Example 1		Example 2	Example 3	Example 4	
		Off-gas	Naphtha	Naphtha raffinate	Naphtha raffinate	Off-gas	Raffinate
Total nitrogen, p.p.m. ¹	209	105	103	1	73	Present	2
Basic nitrogen, p.p.m.....	141	44	97	<2	do	do	<13
Total sulfur, p.p.m.....	171	² 17	46	do	do	do
H ₂ S sulfur, p.p.m.....	155	Present ³	0.0	Present ³	do	do	do

¹ All p.p.m. are expressed by weight, based on naphtha feed.

² Not measured quantitatively.

³ Lower limit of analytical accuracy. May be less than 17 p.p.m.

phosphoric acid, and acetic acid. The concentration of the acid in the aqueous wash liquid can range from 0 percent to 10 percent by weight. Higher may be used so

By reference to Table II it is seen that in Example 1 the gas purge reduced total nitrogen in the naphtha from 209 ppm to 103 ppm, reduced the total sulfur

from 171 to 17 ppm and eliminated entirely the sulfur attributable to H₂S.

In Example 2 it is seen that the acid wash reduced the basic nitrogen to 2 ppm. Of this basic nitrogen, the ammonia nitrogen comprised 55 ppm, but the sulfur remained at a high level. It will be noted that the N compounds were found in the acid extract.

Example 3 shows that the use of caustic as an extraction agent is not as effective as water (which can reduce basic nitrogen to 3 ppm) in reducing the total nitrogen.

Example 4 shows that the final raffinate which is produced by first purging with nitrogen and then washing with a dilute acid contains only 2 ppm total nitrogen and less than an indicated 13 ppm (perhaps nil) total sulfur. Example 4 is an illustration of the efficacy of the present invention and shows that by simple purging and washing, the naphtha from coal liquefaction can be treated to reduce substantially the nitrogen/sulfur content thereof.

What is desired to be covered by the present patent application should be judged not by the specific examples herein given, but rather by the appended claims.

We claim:

1. A method of treating a hydrocracked coal extract fraction boiling within the range from about 125° F. to about 400° F., containing at least 20 wppm of sulfur and at least 20 wppm of nitrogen, substantially all of said sulfur being present as H₂S and substantially all of said nitrogen occurring as basic nitrogen, which comprises:

within 72 hours after said fraction is obtained by fractionation, in indifferent order:

1. purging said fraction with a molecular oxygen-free purge gas which is inert to the constituents of said fraction to remove substantially all of the free H₂S in said fraction, and
2. washing said fraction with water to remove substantially all of said basic nitrogen compounds, and recovering a purged and washed product having a substantially lower nitrogen and sulfur content than said fraction,

said purging step being carried out at a temperature from about 40° F. to about 200° F., a pressure from about 0 psig to about 150 psig, and a treat rate from about 50 SCF/B to about 300 SCF/B, and

said washing step being carried out at a temperature from about 40° F., to about 200° F., a pressure from about 0 psig to about 150 psig, and a treat rate from about 0.01 vol/vol to about 1.0 vol/vol.

2. A method of treating a hydrocracked coal extract

fraction boiling within the range from about 125° F. to about 400° F., containing from 100 to 200 wppm of sulfur and from 200 to 300 wppm of nitrogen, substantially all of said sulfur being present as H₂S and substantially all of said nitrogen occurring as basic nitrogen, which comprises:

within 72 hours after said fraction is obtained by fractionation, in indifferent order:

1. purging said fraction with a molecular oxygen-free purge gas which is inert to the constituents of said fraction to remove substantially all of the free H₂S in said fraction, and

2. washing said fraction with water to remove substantially all of said basic nitrogen compounds, and recovering a purged and washed product having a substantially lower nitrogen and sulfur content than said fraction,

said purging step being carried out at a temperature from about 40° F. to about 200° F. a pressure from about 0 psig to about 150 psig, and a treat rate from about 50 SCF/B to about 300 SCF/B, and

said washing step being carried out at a temperature from about 40° F. to about 200° F., a pressure from about 0 psig to about 150 psig, and a treat rate from about 0.01 vol/vol to about 1.0 vol/vol.

3. A method of treating a hydrocracked coal extract fraction boiling within the range from about 80° F. to about 450° F., containing from 100 wppm to 200 wppm of sulfur and from 200 wppm to 300 wppm of nitrogen, substantially all of said sulfur being present as H₂S and substantially all of said nitrogen occurring as basic nitrogen, which comprises:

within 72 hours after said fraction is obtained by fractionation in indifferent order:

1. purging said fraction with nitrogen, and
2. washing said fraction with 0.25 N sulfuric acid, and recovering a purged and washed product having a substantially lower nitrogen and sulfur content than said fraction.

4. A method in accordance with claim 3 wherein the purging conditions are:
a temperature of about 77° F.,
a pressure of about 0 psig, and
a treat rate of about 175 SCF of nitrogen per barrel of fraction,

and the washing conditions include:
a temperature of about 77° F.,
a pressure of about 0 psig, and
a treat rate of about 0.05 volumes of wash liquid per volume of fraction.

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