

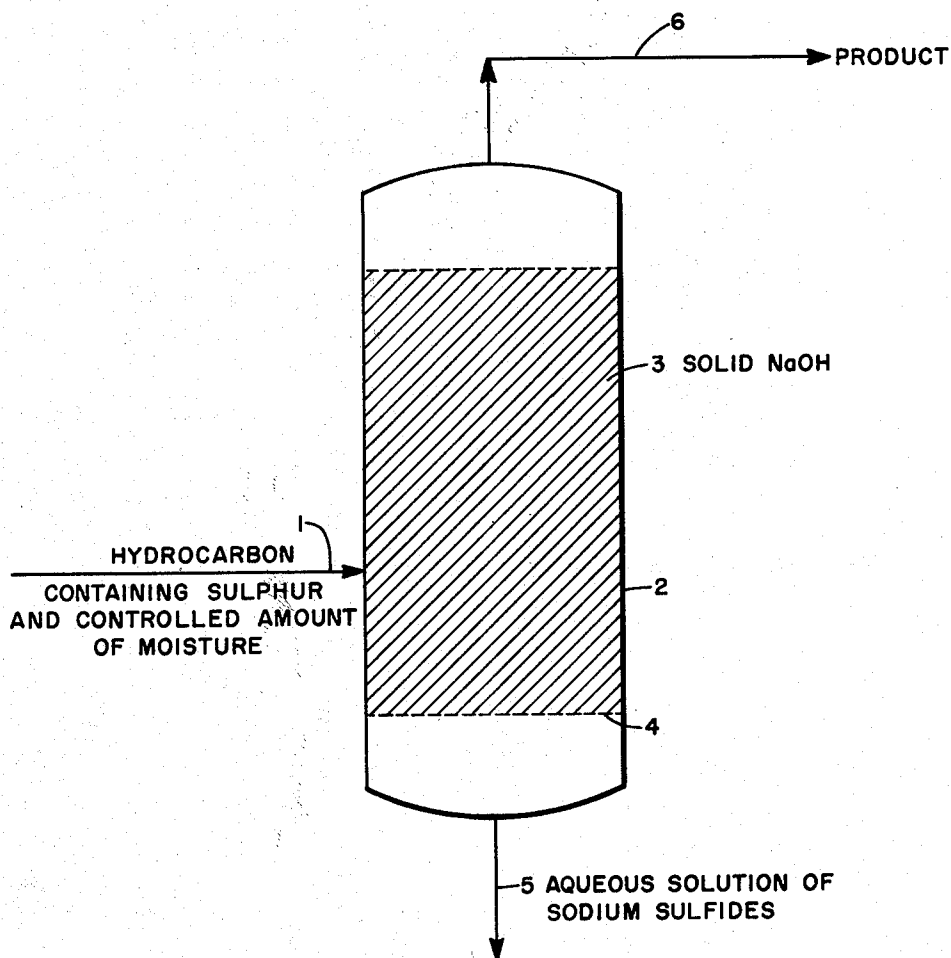
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REMOVAL OF ELEMENTAL SULFUR FROM HYDROCARBONS

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1

2

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REMOVAL OF ELEMENTAL SULFUR FROM HYDROCARBONS

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The present invention is directed to a method for treating hydrocarbons. More particularly, the invention is directed to a method for removing elemental sulfur from hydrocarbons. The method is particularly intended for use in the removal of sulfur from the lighter hydrocarbons, such as gasoline, naphtha, and liquefied petroleum gas.

It is well known that elemental sulfur contained in hydrocarbon streams is corrosive and damaging to metal equipment, particularly copper and copper alloys. In order to avoid damage to such devices as brass valves and gauges, it is necessary to remove elemental sulfur from hydrocarbon streams. It is known that sulfur, hydrogen sulfide, and various acidic substances may be removed from hydrocarbons by treatment with strongly alkaline solutions. Prior investigators have recommended washing hydrocarbons with sodium hydroxide solutions. When washing with sodium hydroxide solution, either in a packed tower or by mixing the liquids directly, the treated hydrocarbon invariably contains considerable water which must then be removed in a subsequent treating step. To avoid a separate drying step, various absorbents impregnated with sodium hydroxide solution have been recommended. Such alkaline absorbents are considerably more expensive than sodium hydroxide itself and are so difficult to regenerate that in practice they must simply be discarded. It would be desirable to treat hydrocarbons with solid sodium hydroxide alone, but in practice, if this is attempted, it is found that within a short time the sodium hydroxide acquires a yellowish surface coating and is no longer effective. I have discovered, however, that sodium hydroxide in solid form can be used without difficulty providing certain variables are controlled within critical limits.

It is, accordingly, an object of this invention to provide a method of removal of sulfur from hydrocarbons in which solid sodium hydroxide is the treating agent. A further object of this invention is the elimination of the steps of treating solution preparation and drying of the treated hydrocarbon. Other objects and advantages will be apparent on reading the following description.

Briefly, the present invention may be described as a method for removing elemental sulfur from a liquid hydrocarbon which comprises contacting with solid sodium hydroxide a hydrocarbon stream having included therein at least 7.60 parts by weight of water per part of sulfur contained therein to yield both a hydrocarbon phase and an aqueous phase containing removed sulfur and recovering said hydrocarbon phase. The method is particularly suitable for treatment of liquefied petroleum gas and gasoline range hydrocarbons.

The removal of elemental sulfur from a hydrocarbon stream by means of solid sodium hydroxide is accomplished through a series of chemical reactions of which those listed below are probably the most important. The final products possess very little solubility in hydrocarbons and are easily separated.

- (1) $4\text{NaOH} + 6\text{H}_2\text{O} + 12\text{S} \rightarrow 8\text{H}_2\text{S} + 2\text{Na}_2\text{S}_2\text{O}_5$
- (2) $\text{NaOH} + \text{H}_2\text{S} \rightarrow \text{NaHS} + \text{H}_2\text{O}$
- (3) $\text{NaHS} + \text{NaOH} \rightarrow \text{Na}_2\text{S} + \text{H}_2\text{O}$
- (4) $\text{Na}_2\text{S} + 3\text{S} \rightarrow \text{Na}_2\text{S}_4$
- (5) $\text{Na}_2\text{S}_4 + \text{S} \rightarrow \text{Na}_2\text{S}_5$

If the hydrocarbon stream is absolutely dry, all reaction ceases almost immediately, because the sodium hydroxide becomes coated over with the products of reaction. The coating formed is yellow in color and consists of sodium disulfides and polysulfides, probably derived mainly from traces of H_2S in the hydrocarbon and traces of moisture in the NaOH . If an uncontrolled amount of water is added to the hydrocarbon, the bed of solid sodium hydroxide is quickly washed away, resulting in considerable waste. For practical, economical reasons, the quantity of water in the hydrocarbon should be limited to only the necessary amount. For any except those streams of extremely high sulfur content, all of the necessary water will dissolve in the hydrocarbon. The sodium sulfides formed by the series of chemical reactions are water soluble only to the extent of about 25 percent by weight. (There is some variation from one compound to another, so that it is difficult to set a fixed solubility figure.) With a water solubility of about 25 percent, it is necessary that the hydrocarbon feed contain at least 7.6 parts by weight of water per part of free sulfur contained therein. The table below contains conditions for 1 p.p.m. sulfur-contaminated butane. Each of the numbers, when multiplied by the number of p.p.m. sulfur, determines actual conditions for a specific contaminated stream.

TABLE

	Pounds/1000 barrels per p.p.m. free sulfur
Sulfur contaminant	0.204
NaOH consumed by reaction	0.255
Salts formed	0.402
Water formed	0.057
Additional water required (minimum)	1.55

The method is effective and convenient for treating gasoline containing from a trace to more than 25 p.p.m. sulfur, employing temperatures as high as about 140° F. For treating liquefied petroleum gases, it is preferred to operate at ambient temperatures and pressures up to about 200 p.s.i., so that it is feasible to remove more than 15 p.p.m. sulfur, if desired. The capabilities of the method are more than adequate, so far as ordinary petroleum refinery streams are concerned.

The hydrocarbon stream preferably flows downward through a bed of sodium hydroxide pellets or flakes. There should be sufficient space beneath the supporting grid of the sodium hydroxide bed to permit gravity separation of the aqueous phase and removal of this aqueous solution of sodium sulfides from the bottom of the vessel. The preferred cross sectional area of the treating bed is about 1 square foot for each 500 barrels per throughput. The depth of the bed may vary, a deep bed requiring less frequent replacement. In practice, a depth of about 8 feet has been found to be very satisfactory.

The sulfur content of the hydrocarbon stream should be determined by a reliable analytical technique. It is desirable to determine sulfur content of an entire tank of hydrocarbon and redetermine sulfur content before beginning treatment of another tank. Thus, errors introduced by variation of sulfur content in a continuous

3

stream are eliminated without the necessity for frequent periodic sampling and analysis.

The invention will be further illustrated by reference to the drawing. Referring now to the drawing, number 1 designates the feed line through which the hydrocarbon stream containing sulfur and a controlled amount of moisture enters the treating vessel 2. The vessel contains a bed of sodium hydroxide pellets or flakes 3, supported on grid 4. During treatment, an aqueous phase containing the removed sulfur in the form of sodium sulfides descends to the bottom of the vessel and is removed through line 5. The hydrocarbon product phase which is free of elemental sulfur rises to the top of the vessel and is removed through line 6. For a better understanding of my invention, reference should be had to the following examples, which are given by way of illustration and not limitation.

Example 1

In a laboratory experiment liquid butane containing approximately 20 p.p.m. elemental sulfur was allowed to flow at the rate of 0.5 cc. per minute through a bed containing 0.5 pound of sodium hydroxide flakes. The treatment was continued over a period of 24 hours. The NGAA copper strip test was used to determine the quantity of the product. In this test a polished copper strip is exposed to a sample of the hydrocarbon in a closed tubular pressure container for a period of time, after which the appearance of the copper surface is compared with a series of standard corroded copper strips for both surface texture and color. The standard strips are arranged in increasing extent of corrosion numbered in groups from 1 through 4, each group subdivided by the letters A, B, C, etc. The appearance of the strip must be rated in group 1 in order to pass. (See NGAA Liquefied Petroleum Gas Specifications and Test Methods, Pub. No. 2140-60, Natural Gasoline Association of America, 421 Kennedy Building, Tulsa 3, Oklahoma.) The A.S.A. Method No. Z11.21-1956 or A.S.T.M. Method D130-56 may also be used. The experiment was started at 2 p.m. and concluded at 2 p.m. the following day. Below are the results of the copper strip tests before and after treatment at three different times during the course of the experiment.

Time	C.S.T. before treater	C.S.T. after treater
3:00 p.m.-----	4-A	1-A
8:00 p.m.-----	4-A	1-B
2:00 p.m.-----	4-A	1-B

Example 2

In a larger scale experiment, 1000 barrels of butane containing 10-15 p.p.m. elemental sulfur was treated by contacting with a bed of 50 pounds of sodium hydroxide flakes at the rate of 50 to 60 barrels per hour. Below are the results of copper strip tests taken before and after treatment during and at the time of the experiment.

Treated vol. (bbls.)	C.S.T. before treater	C.S.T. after treater
500-----	4-A	0
1,000-----	3-B	1-A

Example 3

In this example, 2000 barrels of liquid butane with an elemental sulfur content varying from 6 to about 20 p.p.m. was treated by contacting with a bed of 50 pounds of solid sodium hydroxide. Below are the results of copper strip tests made during the course of the

4

treatment, both on streams preceding and following the treating vessel.

Treated vol. (bbls.)	C.S.T. before treater	C.S.T. after treater
500-----	4-A	1-A
1,000-----	2-C	1-A
1,500-----	3-A	0
2,000-----	4-A	0

In the above three examples the sulfur content of the liquid butane was determined prior to treatment and the water content of the hydrocarbon was maintained at approximately 7.6 pounds of water per pound of sulfur contained therein.

Example 4

In a continuous operation a hydrocarbon stream made up of a mixture of propane, butane, and natural gasoline averaging about 35 p.p.m. elemental sulfur was treated by contacting with a bed containing 800 pounds of sodium hydroxide flakes. The hydrocarbon stream was too dry for the desired chemical reaction to take place. The proper amount of moisture was added to the stream by mixing therewith a controlled amount of straight run gasoline which was saturated with water. The sulfur content of the mixed hydrocarbon stream was monitored by periodic sampling and analysis. The treating method was operated for a period of several months under these conditions without failure or malfunction.

From the foregoing description, taken with the drawing and the several examples, it will be clear that an advantageous process has been provided for removing elemental sulfur from hydrocarbon streams.

The invention having been fully described and illustrated, what I wish to claim as new and useful and secured by Letters Patent is:

1. A method for removing elemental sulfur from a liquid hydrocarbon which comprises contacting with a treating agent consisting of solid sodium hydroxide a hydrocarbon stream having included therein at least a trace of elemental sulfur and at least 7.6 parts by weight of water per part by weight of sulfur contained therein to yield a hydrocarbon phase and an aqueous phase containing removed sulfur, and recovering said hydrocarbon phase.

2. A method according to claim 1 in which the liquid hydrocarbon is a mixture of propane, butane, and gasoline.

3. A method according to claim 1 in which the liquid hydrocarbon is liquefied petroleum gas.

4. A method according to claim 1 in which the liquid hydrocarbon is butane.

5. A method for removing elemental sulfur from a hydrocarbon containing at least a trace of elemental sulfur which comprises adjusting the water content of said hydrocarbon so as to contain at least about 7.6 parts by weight of water per part by weight of elemental sulfur, contacting the thus-adjusted hydrocarbon in liquid phase with a treating agent consisting of solid sodium hydroxide, and removing from the thus-contacted hydrocarbon an aqueous phase containing removed sulfur.

6. The method of claim 5 wherein said hydrocarbon comprises a liquefied normally-gaseous hydrocarbon.

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