Sept. 5, 1967 J. ENG ET AL 3,340,184

PROCESS FOR REMOVING SULFUR FROM PETROLEUM
OILS AND SYNTHESIZING MERCAPTANS
Filed Oct. 30, 1964

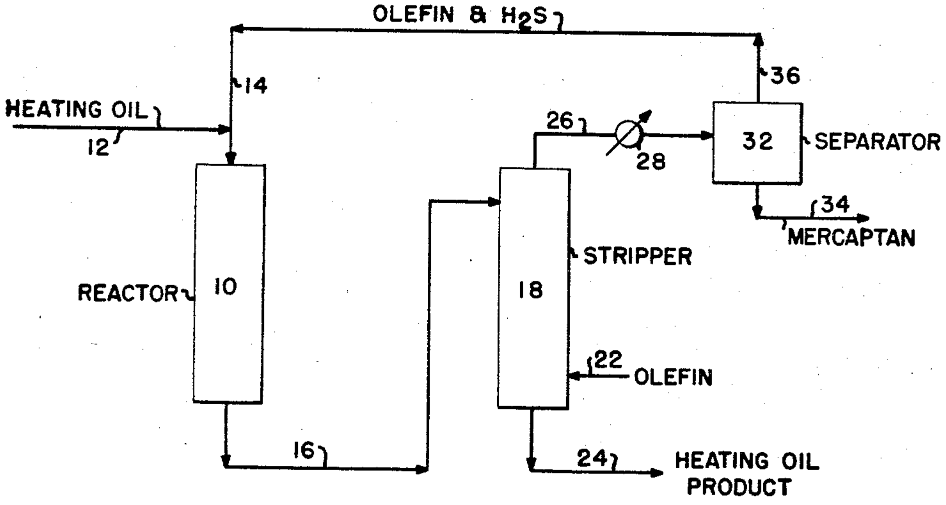

FIG.-1

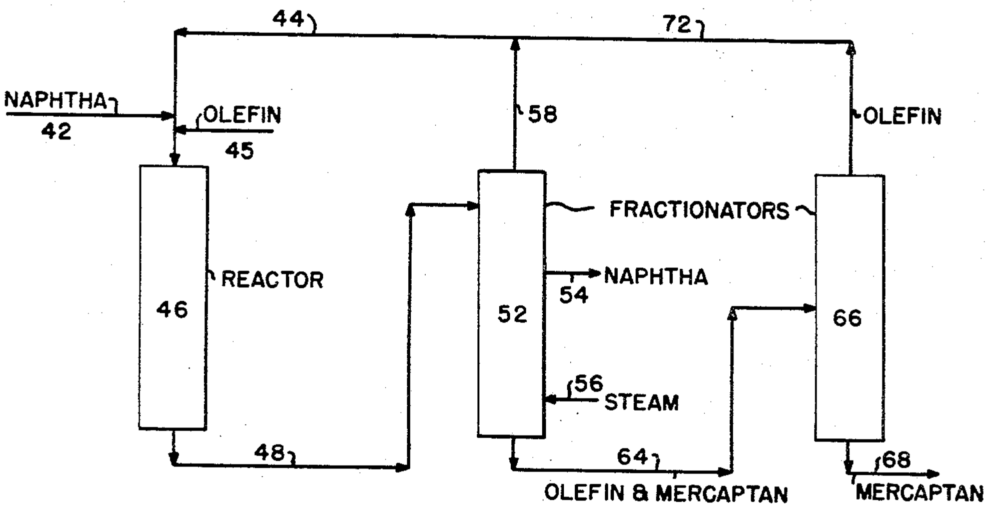

FIG.-2

Jackson Eng
John L. Tiedje

Inventors

By

Patent Attorney

United States Patent Office

3,340,184

Patented Sept. 5, 1967

3,340,184

PROCESS FOR REMOVING SULFUR FROM PETROLEUM OILS AND SYNTHESIZING MERCAPTANS

Jackson Eng and John L. Tiedje, Sarnia, Ontario, Canada, assignors to Esso Research and Engineering Company, a corporation of Delaware

Filed Oct. 30, 1964, Ser. No. 407,731
10 Claims. (Cl. 208—238)

ABSTRACT OF THE DISCLOSURE

Process for desulfurizing hydrocarbon distillates boiling in the range of 90–800° F. and for recovering mercaptans including the steps of passing the distillate and an olefin over a sulfided cobalt molybdate catalyst and separating and recovering desulfurized distillate and mercaptan.

This invention relates to a process for desulfurizing hydrocarbon distillates and at the same time synthesizing mercaptans.

Many processes are known for desulfurizing hydrocarbon oils such as fuels and lubricating oils. The sulfur compounds in hydrocarbon liquids are objectionable because they are corrosive and have an objectionable odor. In gasolines, high sulfur is undesirable because it reduces the effectiveness of tetraethyl lead. Also, such gasolines have undesirable odor and gum formation tendencies. In fuel oils the sulfur burns to sulfur dioxide which is highly corrosive and foul smelling. Mercaptan sulfur in gasoline, fuel oil, lubricating oils, etc., is bad but mercaptan compounds are useful compounds.

The conventional process for manufacturing mercaptan comprises a separate unit for producing H_2S and a separate reactor system for reacting H_2S and an olefin.

According to the present invention, high sulfur hydrocarbons are mixed with an olefin or olefins (C_nH_{2n}) and this mixture is passed at an elevated temperature and superatmospheric pressure over a catalyst to remove sulfur by converting it to hydrogen sulfide which in the presence of the catalyst combines or reacts with the added olefin or olefins to produce a mercaptan or mercaptans. These two reactions take place in one stage or in one reactor. No H_2S recovery step is required. The molecular specie of the mercaptan produced is controlled by the selection of the olefin type and molecular weight. The present invention is a one-step process which combines desulfurization of a hydrocarbon distillate and the synthesis of mercaptans. The catalyst is sulfided cobalt molybdate on alumina.

The process for desulfurizing hydrocarbon oils is carried out with an olefin which is preferably selected to have a boiling point different from that of the hydrocarbon oil to be treated and desulfurized so as to form a mercaptan from the olefin and the released sulfur material which mercaptan has a boiling point different from that of the oil to be desulfurized so that the mercaptan may preferably be easily separated and recovered in a single fractionation. The olefin selected always has a boiling point lower than the mercaptan formed which facilitates separation of the olefin and mercaptan formed. Where the oil fractiton to be desulfurized is a relatively narrow fraction, the selection of an olefin to be added is relatively easy as the olefin is selected to form a mercaptan having a boiling point which is higher or lower than the boiling range of the fraction. For example, when desulfurizing a heavy naphtha having a boiling range of about 300° F. to 410° F., a C_5 olefin may be used to form amyl mercaptans having a boiling point range below that of the heavy naphtha. Instead of a heavy naphtha, the C_5 olefin may be added to a light naphtha fraction having a lower boiling range than about 200° F. which is lower boiling than the amyl mercaptans formed during desulfurization.

In the drawings:

FIG. 1 represents one form of apparatus for carrying out the invention in a process wherein the treated oil has a higher boiling point than the mercaptan produced; and

FIG. 2 represents another form of apparatus for carrying out the invention in a process wherein the mercaptan produced has a higher boiling point than the treated hydrocarbon distillate.

Referring now to FIG. 1 of the drawing, the reference character **10** designates a reactor vessel containing a fixed bed of catalyst which is sulfided cobalt molybdate and is made by passing H_2S gas over cobalt molybdate catalyst on an alumina base for about 2 to 16 hours at a temperature of about 600° F. at 200 p.s.i.g. pressure. Sulfiding may be carried out in other ways. The amount of sulfur added during sulfiding may vary from about 200% up to about 1500% of the stoichiometric quantity necessary to convert the cobalt oxide and molybdenum oxide to the corresponding sulfides. The catalyst may contain 5–25 wt. percent of cobalt oxide and molybdenum oxide with the ratio of cobalt oxide to the molybdenum oxide in the range of from about 1:5 to about 5:1 supported on adsorptive or activated alumina which may contain up to 25 wt. percent silica. The alumina forms about 50 to 95 wt. percent of the unsulfided cobalt molybdate catalyst.

A hydrocarbon distillate having a boiling range between about 300° F. and 700° F. such as a virgin gas oil is passed through line **12** at a temperature of between about 400° F. and 700° F., preferably 500° F., and into line **14** containing an added olefin and recycle hydrogen sulfide. The olefin may be one selected from the group comprising C_2 olefin to C_6 olefins. The resulting mixture is introduced into the top of the reactor **10** for passage over the catalyst therein. The catalyst is sulfided cobalt molybdate on alumina and before sulfiding it contains 3.5% cobalt oxide (CoO), 12.5% molybdenum oxide (MoO_3) on alumina. The catalyst is in the form of 1/16" diameter extrudate of approximately 1/8" long.

The pressure in the reactor **10** is maintained between about 100 p.s.i.g. and 1000 p.s.i.g. The olefin and heating oil are passed through the sulfided cobalt molybdate-alumina at a rate of 1 volume of liquid olefin-heating oil to 1 volume of catalyst per hour (1 v./v./hr.). The space velocity may vary between about 0.5 and 5 volumes of liquid olefin-hydrocarbon oil per volume of catalyst per hour. The amount of olefin on the heating oil may vary between about 0.2:1 and 1:0.2 by volume (liquid) or about 0.1:1 and 1:0.2 by weight.

Under these conditions, mercaptans, sulfides, disulfides and other reactive sulfur compounds in the heating oil are converted to hydrogen sulfide. The hydrogen sulfide then further reacts with the olefin to form the corresponding mercaptan. Where propylene is the olefin used, propyl mercaptan is formed.

The apparatus shown in FIG. 1 is especially adapted for desulfurizing heating oil and for producing propyl mercaptan at the same time. However, the process used in connection with the apparatus of FIG. 1 is not restricted to the addition of propylene only, as other low boiling olefins up to C_6 olefins may be used instead of propylene or in addition to propylene. In the process used in connection with FIG. 1, a necessary requirement is that the boiling range of the mercaptan product must be below the initial boiling point of heating oil so that the mercaptan may be recovered in high purity by a single fractionation.

The total effluent is withdrawn from the bottom of reactor **10** through line **16** and passed into the upper portion of stripper vessel **18** where the excess olefin, hydrogen sulfide and mercaptan are stripped out overhead. The stripping agent which may be steam is introduced into the lower portion of stripping vessel **18** through line **22** for upward passage countercurrent to the downflowing higher boiling heating oil. The stripping agent is preferably make-up olefin and is the olefin which is used as the reactant in reactor **10** for reaction with the sulfur in the hydrocarbon oil being treated. Where the olefin used as a reactant is a low boiling olefin such as propylene, for example, the stripping gas introduced through line **22** comprises the low boiling olefin or propylene which may be pure propylene or impure propylene containing other compounds or other olefins. However, with an impure olefin stream, the purity of the mercaptan produced will be correspondingly reduced.

The stripping vessel is maintained at a temperature between about 50° F. and 350° F. and under a pressure between about atmospheric pressure and 200 p.s.i.g. The heating oil product substantially lowered in objectionable sulfur compounds and having less than 2 mercaptan number is withdrawn from the bottom of stripping vessel through line **24**.

The stripped out materials comprising olefin, H_2S and mercaptan pass overhead through line **26** into condenser **28** to cool the materials to a temperature between about 50° F. and 200° F. and to condense the mercaptan product while unreacted and make-up propylene or other olefin is recycled through lines **36** and **14** along with any unreacted hydrogen sulfide to reactor **10**. The condensing temperature depends on the mercaptan and is intermediate to that required to condense the mercaptan but not the olefin. The cooled mixture is passed to gas-liquid separator **32** to separate liquid mercaptan which is withdrawn from the bottom of separator **32** through line **34**. The separated gases including olefin or olefins and hydrogen sulfide pass overhead through line **36** for recycle through line **14** to reactor **10**. It is to be noted that here the low boiling olefin such as propylene is used both as a stripping gas in stripping vessel **18** and also as a reactant in reactor **10**. When the olefin and corresponding mercaptan boils at a higher temperature range than the sulfur-containing hydrocarbon oil, steam is used as the stripping gas.

Referring now to FIG. 2, which is especially adapted for desulfurizing naphtha and producing, for example, a mercaptan such as dodecyl mercaptan at the same time but not restricted thereto, the reference character **42** designates a line for feeding a hydrocarbon distillate such as high sulfur naphtha or the like having a boiling range between about 90° F. and 400° F. into recycle line **44** containing a high boiling recycled olefin, such as C_{12} olefin. Other olefins can be utilized to produce other mercaptans, as long as the olefin boils above the high sulfur hydrocarbon oil. Olefin make-up is introduced into line **44** through line **45**. The resulting mixture is introduced into the top of reactor **46** containing sulfided cobalt molybdate on alumina catalyst. The same catalyst is used here as described above in connection with reactor **10**. The temperature in reactor **46** is between about 400° F. and 700° F., the pressure is between 100 p.s.i.g. and 1000 p.s.i.g., the liquid space velocity is between about 0.5 and 5 parts by volume of liquid fed to reactor **46** per part by volume of catalyst per hour.

The reaction products are withdrawn from the bottom of reactor **46** through line **48** and passed into the upper portion of fractionating column **52** for fractionating the reaction products into desulfurized naphtha which is withdrawn as a side stream through line **54**. The pressure in the fractionator **52** can be between about 0 p.s.i.g. and 200 p.s.i.g. Steam as as stripping means is introduced as the bottom portion of the fractionator **52** through line **56** to strip out hydrogen sulfide which leaves the fractionator **52** overhead through line **58** and is recycled through line **44** to reactor **46**. The bottom of the fractionator **52** is at a temperature between about 300° F. and 600° F. and the top of the fractionator is between about 50° F. and 250° F.

The bottoms from fractionator **52** contain relatively high boiling unreacted olefin or olefins and the mercaptan corresponding to the olefin. Use of an olefin mixture will produce a mixture of different mercaptans. The boiling range of the olefins must not overlap the boiling rang of the mercaptans as otherwise low purity mercaptans will be produced. The mercaptan in the bottoms fraction is higher boiling than the naphtha feed and hence is taken off from a lower region than naphtha from the fractionator **52**.

The bottoms fraction is withdrawn from the bottom of fractionator **52** through line **64** and introduced into the intermediate region of a second fractionator **66** to separate the high boiling mercaptan from the unreacted olefin or olefins. Here also the olefin has a lower boiling point than the mercaptan formed to permit easy separation of the olefin from the mercaptan. Fractionator **66** is at a pressure between about 0 p.s.i.g. and 200 p.s.i.g. The temperature at the bottom of fractionator **66** is between about 400° F. and 600° F. and the temperature at the top of the fractionator **66** is between about 300° F. and 500° F.

In the fractionator **66** the mercaptan such as dodecyl mercaptan is separated from gaseous material and is withdrawn from the bottom of fractionator **66** through line **68**. The separated gaseous material comprising the unreacted olefin or olefins is passed overhead through line **72** and is recycled through line **44** to reactor **46**. When higher than C_{12} olefins are used, such as C_{14} olefins, the corresponding mercaptans will be produced such as C_{14} mercaptans.

Laboratory experiments have been carried out with a 50–50 volume mixture of C_5 olefins and heavy naphtha feed containing 0.7 wt. percent sulphur in the form of ethyl disulphide. The ethyl disulphide was added because the initial mixture was almost sulphur free. The feed mixture was processed over sulphided cobalt molybdate catalyst which initially before sulfiding was comprised of 3.5 wt. percent cobalt oxide, 12.5% molybdenum oxide and 84% alumina. The reactor effluent was analyzed for total sulfur and mercaptan sulphur contents to determine the conversion of ethyl disulphide to mercaptans. A reaction temperature of about 500° F. is preferred. At this temperature, 64% conversion to mercaptans was obtained.

The heavy naphtha feed had a boiling range of about 300° F. to 410° F. and was a virgin stream derived from atmospheric distillation of crude oil. The C_5 olefins were produced by fractionating (15 theoretical plates, 10 reflux ratio) a C_4 to C_6 olefinic stream from the catalytic cracker to yield a 65 to 98° F. VT (vapor temperature) fraction. The composition of this C_5 olefin concentrate is as follows:

	Wt. percent
Isopentane	28.6
N-pentane	5.6
Pentene-1	6.5
2-methyl butene-1	16.5
Trans-pentene-2	12.9
Cis-pentane-2	6.0
2-methyl butene-2	22.0
Unidentified	1.9
	100.0

In this experiment, the mercaptan product was not recovered quantitatively. The amount of mercaptan in the reactor effluent was measured by titration with silver nitrate solution. A sample of the reactor effluent, was treated with 30 Baumé NaOH solution to extract the mercaptans. After neutralizing the caustic with hydrochloric acid, an oily substance was produced which was analyzed on the chromatograph. N-amyl mercaptan and isoamyl mercaptan were positively identified. (Other C_5 mercaptans also existed but could not be confirmed due to lack of suitable standards.)

In an actual plant unit, the amyl mercaptans would be recovered by apparatus such as shown in FIG. 1. Amyl mercaptans have boiling points ranging from 210 to 260° F., which are intermediate and do not overlap the boiling range of the C_5 olefins and heavy virgin naphtha.

The catalyst is that above described.

Results of the experiments are given in the following Table 1.

TABLE 1.—SYNTHESIZING MERCAPTANS

Feed: Equivolume mixture of C_5 olefins and heavy naptha containing $(C_2H_5)_2S_2$
Treat Conditions: 300 p.s.i.g.; 1.1 liquid volume of feed/volume of catalyst/hr.; temp. as ind.
Catalyst: Sulphided CoMo on Al_2O_3 (See above)

	Effect of treat temp.			Effect of feed sulphur concentration		
Treat Temp. ° F	400	500	600	500	500	500
Feed:						
Total sulphur wt. percent	0.74	0.74	0.74	2.4	3.5	7.4
Mercaptan sulphur wt. percent	Nil	Nil	Nil	Nil	Nil	Nil
Total Product: [1]						
Total sulphur wt. percent	0.70	0.72	0.71	2.2	3.1	7.0
Mercaptan sulphur wt. percent	0.20	0.47	0.27	0.69	1.00	1.48
Difference [2]	0.50	0.25	0.44	1.51	2.10	5.52
Conversion, percent: Disulphide to mercaptan	27	64	36	29	28	20
LV percent $C_5H_{11}SH$ on feed [3]	0.6	1.3	0.8	2.0	2.8	4.2

[1] Include mercaptans that were formed.

[2] After removal of mercaptans from product (C_5 olefins and heavy naphtha after treatment) sulphur level is estimated to be difference between total and mercaptan sulphur.

[3] Calculated from mercaptan sulphur analysis on rotal product and assuming only amyl mercaptans were formed.

Additional experiments were carried out in which sour gas oil was passed in admixture with propylene through a fixed bed of sulfided cobalt molybdate on alumina catalyst such as described above.

These experiments were run to sweeten the gas oil by catalytically converting sulfur compounds such as mercaptans to hydrogen sulfide and also concurrently produce propyl mercaptan by reacting propylene and the hydrogen sulfide produced in situ.

The hydrocarbon feed in the experiments reported in Table 2 was a 300–640° F. sour gas oil which had an extremely high mercaptan number of 120 and would not be marketable unless it was sweetened. Other sour gas oils having other boiling point ranges such as 300° to 725° F. and other mercaptan numbers such as 10 to 150 may be used. Obviously, with lower mercaptan number gas oils, lesser amount of propyl mercaptan would be produced. In these experiments the treat temperature was varied from 300° F. to 700° F. while maintaining other variables such as space velocity, pressure and proylene to gas oil ratio constant. In these runs the preferred temperature is between about 500° F. and 600° F. The mercaptan number of the 300° F.+ gas oil fraction was reduced from 117 to 9 and 5, respectively, as to 500° F. and 600° F., a reduction of approximately 95%. Concurrently, low boiling propyl mercaptans were produced. (N-propyl mercaptan boils at 154° F. and isopropyl mercaptan at 126.6° F.)

About 2.4 LV percent (liquid volume percent) of the initial to 225° F. fraction was produced in the 500° F. treat. This fraction contained mercaptan sulphur to the extent of 8.35 weight percent. Since pure propyl mercaptan would have a sulfur content of 42 weight percent, the purity of our product is about 20% propyl mercaptan. The concentration of the mercaptans can be raised by improved fractionation efficiency.

Although 2.4 LV percent of a 20% mercaptan concentration solution does not appear considerable, it should be noted that processing units built for sweetening gas oils are generally in the range of 5000 to 10,000 b./d. capacity. On this basis, about 25 to 50 b./d. of pure mercaptans could be produced and this would be quite an appreciable amount.

In the experiment, the whole mixture of gas oil feed and propylene in equal volume ratio was passed through the catalyst bed. The product from the treatment went into a separator maintained at about 30° F. to 40° F. range where the propylene was allowed to flash off through a knockout trap maintained at 32° F. and a condensing trap maintained at minus 100° F. The first trap prevented any loss of propyl mercaptans and the second trap served to condense the unreacted propylene. The contents from the first trap were combined with the liquid product from the separator and fractionated (15 theoretical plates, 5 reflux ratio) to produce the fractions indicated in Table 2.

TABLE 2.—MERCAPTAN PRODUCTION CONCURRENTLY WITH GAS OIL SWEETENING

Feed: 300/640° F., gas oil (120 RSH No.)
Propylene/feed: 0.29 liquid vol. propylene/vol. gas oil
Operating conditions:
  1 v./v./hr. on combined propylene and gas oil feed
  200 p.s.i.g.
  Unconverted propylene recycled
  CoMo-Al_2O_3 catalyst; sulphided

	Gas oil feed	Depropanized liquid product					Pure C_3H_7SH
Experiment No	----------	5	4	2	3	8	----------
Treat temp., ° F	----------	300	400	500	600	700	----------
Init./225° F. cut:							
LV, percent	Nil	Nil	Nil	2.4	1.7	0.7	----------
RSH No.[1]	----------	-------	-------	5,679	6,458	3,017	----------
RSH–S Wt. percent [2]	----------	-------	-------	8.35	8.51	4.29	42.0
225/300° F. cut:							
LV, percent	1.8	2.2	2.9	5.4	4.3	2.4	----------
RSH No	189	269	1,543	58	138	309	----------
300° F. plus cut:							
LV, percent	98.2	97.8	97.1	92.2	94.0	96.9	----------
RSH No	117	98	89	9	5	11	----------
Total S. wt. percent	0.84	0.79	0.76	0.67	0.57	-------	----------

[1] These figures are calculated from mercaptan numbers $\frac{\text{RSH No.}}{\text{Spec. grav. of fraction}} \times \frac{100}{1,000}$ wt. percent.

[2] Mercaptan sulphur wt. percent on init./225° F. cut.

Mercaptan sulphur on the various fractions was determined by silver nitrate titration and total sulfur on the 300° F. plus cut by the method described by ASTM D 1552–58 T.

The pressure in carrying out experiments similar to those reported in Table 2 can be varied between about 100 and 1000 p.s.i.g. (pounds per square inch gage). The space velocity can be varied between about 0.5 and 5 v./v./hr. (volumes of liquid feed per volume of catalyst per hour). The propylene to gas oil feed ratio can vary between about 0.2:1 and 1:0.2 on a liquid volume basis. Instead of propylene, other olefins or olefin mixtures such as ethylene, butenes, pentenes and hexenes may be used.

In addition, a few experiments have been carried out on a blend consisting of 10 LV percent C_{12} olefins (C_3 tetramer) and 90 LV percent of an acid treated paraffinic oil. The C_{12} olefins possess a distillation range of 375–425° F. and the paraffinic oil, a distillation range of about 500–700° F. Carbon disulfide was added to this blend to the extent of 1 weight percent sulfur and the total mixture was passed through a heated reactor packed with sulfided cobalt molybdate on alumina catalyst. Operating conditions were 600° F., 300 p.s.i.g. and 1 LHSV (liquid hour space velocity for the mixture).

Dodecyl mercaptans were identified but were not recovered from the product by distillation. From the mercaptan numbers of the total products, it was estimated that about 0.2 to 0.6 LV percent on feed of dodecyl mercaptan were produced.

On the process associated with FIG. 2, the C_{12} olefin has a lower boiling point than the C_{12} mercaptan and so the mercaptan can be separated by fractionation and removed as a bottoms product. The separated olefin passes overhead and is recycled to the reactor.

In other experiments, a paraffinic oil having a boiling range of 500–700° F. was used rather than naphtha. The paraffinic oil boiling range is above that of C_{12} mercaptans which have a boiling range of about 440 to 480° F. In the laboratory experiment, the total product (C_{12} mercaptan plus unreacted C_{12} olefins plus paraffinic oil) was actually fractionated under vacuum to yield a 400–500° F. (atmospheric pressure cut). Chromatograph analyses on this cut positively identified normal and tertiary C_{12} mercaptans.

While sulfided cobalt molybdate on alumina is the only catalyst mentioned, other desulfurizing catalysts may be used.

What is claimed is:

1. A method of removing sulfur from paraffinic naphtha as a mercaptan consisting essentially of the steps of admixing at least one C_{12} olefin with the naphtha, passing the mixture over sulfided cobalt molybdate on alumina in a reaction zone at an elevated temperature and pressure, fractionating the reaction products to separate desulfurized naphtha as product from hydrogen sulfide and from a bottoms fraction containing C_{12} olefin and C_{12} mercaptan, recycling at least part of said hydrogen sulfide to said reaction zone, separating said bottoms fraction into a C_{12} mercaptan fraction as product and C_{12} olefin and recycling said C_{12} olefin to said reaction zone.

2. A method according to claim **1** wherein the temperature is between about 400° F. and 700° F. and the pressure is between about 100 p.s.i.g. and 1000 p.s.i.g.

3. A method according to claim **2** wherein the temperature is about 500° F. and the pressure is about 200 p.s.i.g.

4. A method of removing sulfur from paraffinic naphtha as a mercaptan consisting essentially of the steps of admixing an olefin having a higher boiling point than said naphtha, passing the mixture over sulfided cobalt

molybdate on alumina in a reaction zone at an elevated temperature and pressure to form a mercaptan, fractionating the reaction products to separate desulfurized naphtha from a bottoms fraction containing unreacted olefin and a mercaptan and recovering the mercaptan as product.

5. A method of removing sulfur from paraffinic naphtha as a mercaptan which comprises admixing an olefin having a lower boiling point than naphtha, passing the mixture over sulfided cobalt molybdate on alumina in a reaction zone at an elevated temperature and pressure to form a mercaptan, separating desulfurized naphtha from unreacted olefin and mercaptan and recovering the mercaptan as product.

6. A method of desulfurizing virgin heating oil and forming mercaptans consisting essentially of the steps of admixing with a heating oil an olefin having a lower boiling point than said heating oil, passing the mixture over a catalyst comprising sulfided cobalt molybdate on alumina in a reaction zone at an elevated temperature and pressure, to form a mercaptan having a lower boiling point than said heating oil, passing the resulting reaction products to a stripping zone, introducing a stripping gas into the lower portion of said stripping zone for upward flow therethrough and utilizing as at least a part of a stripping gas a lower boiling olefin of the same number of carbon atoms as said admixed olefin, removing desulfurized oil from the bottom of said stripping zone, removing overhead a mixture of olefin, hydrogen sulfide and mercaptan, recovering mercaptan from an olefin and hydrogen sulfide mixture and recycling said last mentioned mixture to said reaction zone.

7. A method according to claim **6** wherein said elevated temperature is between about 400° F. and 700° F. and the pressure is between about 100 p.s.i.g. and 1000 p.s.i.g.

8. A method according to claim **6** wherein said olefin comprises propylene, said temperature is between about 500° F. and 600° F. and the recovered mercaptan comprises propyl mercaptan.

9. A method of removing sulfur from naphtha as a mercaptan consisting essentially of the steps of admixing a C_5 olefin with the naphtha, passing the resulting mixture over sulfided cobalt molybdate catalyst on alumina in a reaction zone at an elevated temperature and pressure, recovering desulfurized naphtha and a C_5 mercaptan as product.

10. A method for desulfurizing virgin hydrocarbon distillates boiling in the range of 90–800° F. and for recovering the sulfur as a mercaptan consisting essentially of the steps of:

(A) admixing an olefin having a boiling range different from that of the distillate with the distillate,
(B) passing the mixture over sulfided cobalt molybdate on alumina catalyst in a reaction zone at a temperature in the range of 400–700° F. and a pressure in the range of 100–1000 p.s.i.g. whereby a mercaptan having a boiling range different from that of the distillate is formed as one of the reaction products,
(C) separating desulfurized distillate and mercaptan, and
(D) recovering the two products.

References Cited

UNITED STATES PATENTS

2,088,500	7/1937	Waterman	208—237
2,739,102	3/1956	Rylander	208—238
3,124,526	3/1964	Butler et al.	208—216
3,162,597	12/1964	Davis et al.	208—216

DELBERT E. GANTZ, *Primary Examiner.*

SAMUEL P. JONES, *Examiner.*