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DESULFURIZATION PROCESS

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Sheet 1 of 2

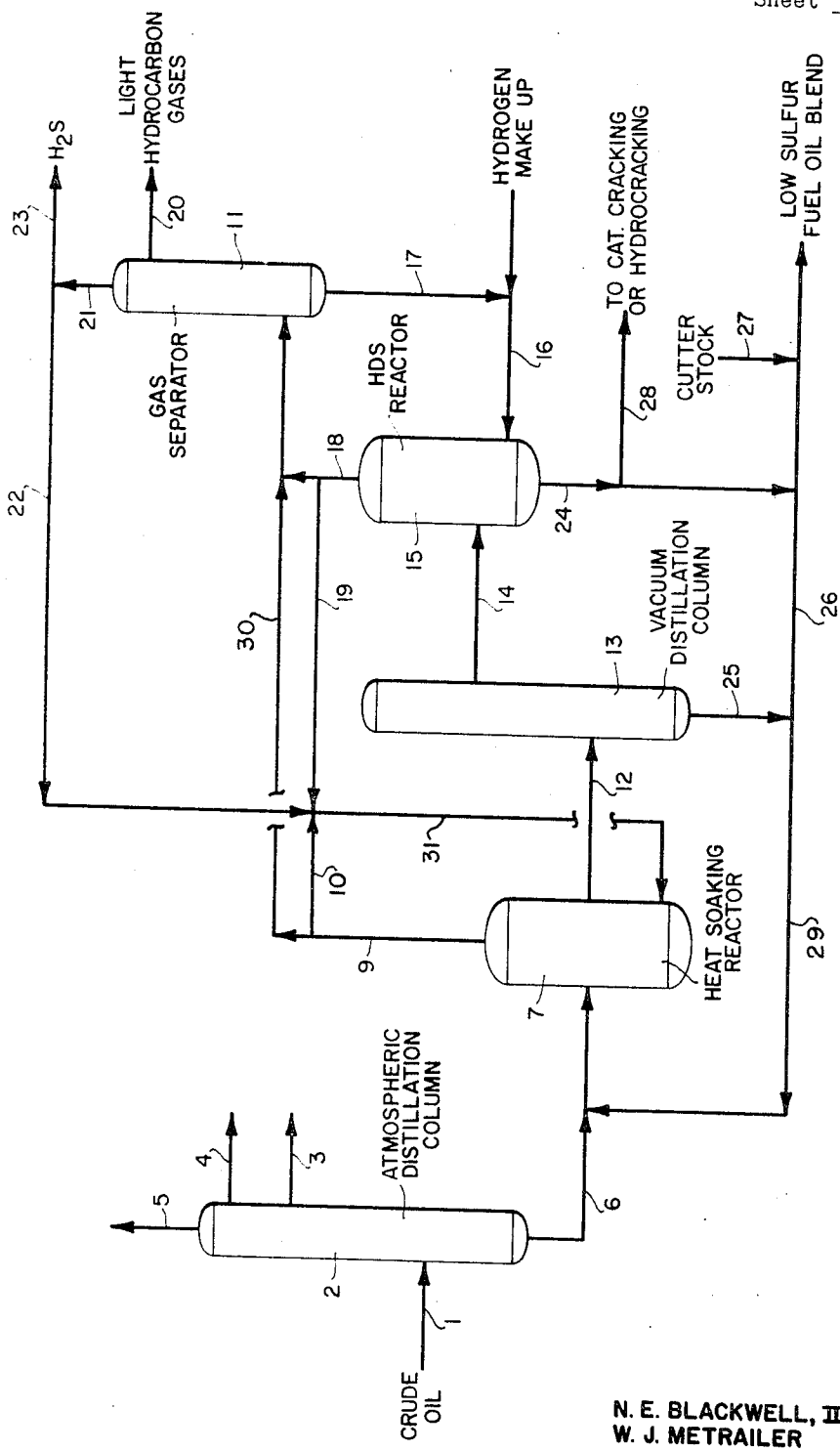


FIGURE I

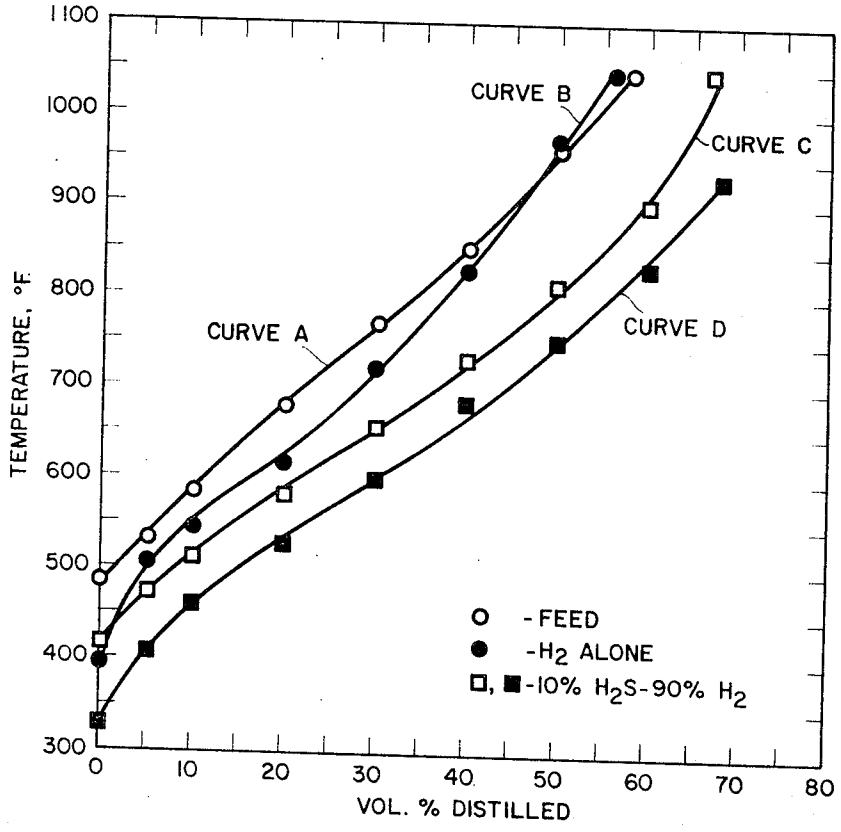
N. E. BLACKWELL, III
W. J. METRAILER
INVENTORS

BY C. W. Grady Jr.

PATENT ATTORNEY

FIGURE 2

BATCH HEAT SOAKING TESTS
BACHAQUERO TOPPED CRUDE



N. E. BLACKWELL, III
W. J. METRAILER INVENTORS

BY C. W. Grady Jr.

PATENT ATTORNEY

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DESULFURIZATION PROCESS

Noah E. Blackwell III, and William J. Metrailer, Baton Rouge, La., assignors to Esso Research and Engineering Company, a corporation of Delaware

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6 Claims

ABSTRACT OF THE DISCLOSURE

The disclosure relates to a process for the production of low sulfur fuel oil comprising the sequential steps of heat soaking in the presence of hydrogen and H_2S, distilling to recover a treated vacuum gas oil fraction, hydrodesulfurizing the vacuum gas oil in the presence of a catalyst, recovering the desulfurized oil, blending the desulfurized oil with vacuum bottoms and recovering a low sulfur fuel oil.

This invention relates to an improved desulfurization process. More particularly the invention relates to an improved desulfurization process characterized by unique pretreatment steps which provide a greater quantity of gas oil for hydrodesulfurization.

Hydrodesulfurization has long been recognized as a means of removing sulfur from residual oils and other heavy petroleum fractions such as gas oils. Many techniques and many catalysts have been suggested in the literature and in patents for reducing the sulfur content of feedstocks for catalytic cracking and other petroleum refining processes and also for reducing the sulfur content of fuel oil components.

The problem which has not been solved to date is the problem of producing a fuel oil containing about 1–2% sulfur from a petroleum residuum containing more than 2–3% sulfur. Fuel oil users are unwilling to pay any significant premium for low sulfur fuel oil and thus desulfurization must be accomplished at a minimum cost. Where the gravity and sulfur content of the feedstock is not too high, vacuum distillation followed by hydrodesulfurization of the vacuum gas oil and blending of the desulfurized gas oil with the vacuum bottoms is the least expensive way of making low sulfur fuel oil. However, when the topped crude or petroleum residuum contains a large proportion of materials boiling above 1030–1100° F. vacuum distillation provides an overall sulfur reduction of only 20–30% which is or soon will be unsatisfactory from a sulfur reduction standpoint. It is probable that the local regulations will require a fuel oil sulfur content of 1.5% or less within the next ten years.

The object of the invention is to provide a method of making vacuum distillation applicable to high gravity, high sulfur feeds employing a minimum of pretreatment of the feeds. We have found that this object can be achieved by heat soaking the feed in the presence of a gas comprising a major amount of hydrogen and a minor amount of H_2S prior to vacuum distillation.

The process of the invention will be more fully described in conjunction with the drawings in which FIGURE 1 is a diagrammatic flow sheet of a preferred embodiment of the process and FIGURE 2 is a graph showing the distillation curves of Bachaquero topped crude after heat soaking.

Referring to FIGURE 1 a petroleum crude oil is fed by line **1** to atmospheric distillation column **2** for separation of the light fractions boiling at less than 500–650° F. The fractions are removed from the column by lines **3**, **4** and **5**. This separation provides a reduced crude or petroleum residuum comprising about 50–90 vol. percent of the crude oil. Suitable crude oils are those having a sulfur content of 1.0–5.5 wt. percent sulfur. These crudes provide atmospheric residuums containing 1.5–6.5 wt. percent sulfur. The process of the invention is most beneficial for oils which have a large proportion of residual components, i.e., 30–70 vol. percent of the oil boils above 700° F. The sulfur in this portion of the oil is present in the less reactive forms such as sulfides and as ring compounds such as substituted thiophenes. The oil is also characterized by metal contents of 50–1000 p.p.m. and often by a high content of coke forming hydrocarbons and nitrogenous contaminants.

The reduced crude is passed by line **6** to heat soaking vessel **7**.

Heat soaking is a non-catalytic thermal treatment characterized by retention of the oil in the heat soaking vessel for an extended period of time whereby 10–50% of the 1100° F. components are converted to material boiling between 700–1100° F. Conditions are selected to avoid any substantial amount of cracking and consequent production of C_1–C_5 hydrocarbons thus heat soaking is intrinsically different from short residence time treatments such as thermal cracking and visbreaking. Heat soaking is carried out at a temperature of 600–900° F., preferably 700–850° F. and a pressure of 100–1000 p.s.i.a. Residence times of 0.5 to 5.5 hours are used. The heat soaking step of the invention differs from conventional heat soaking in the employment of a stream of gas comprising a major amount of hydrogen and a minor amount of H_2S. The gas is passed continuously through the heat soaking vessel at the rate of 400 to 2000 cu. ft. per bbl. of oil in the vessel. Heat soaking can be carried out as a batch process with two or more heat soaking drums being used on an alternating basis but preferably continuous operations are carried out in vessels internally arranged to provide the desired hold time of 0.5 to 5.5 hours. The hydrogen-H_2S gas comprises 80 to 95 vol. percent hydrogen and 5 to 20 vol. percent H_2S. The treat gas is continuously cycled through the heat soaker by lines **9**, **10** and **31**. When required, contaminants are removed by passing a side stream of the gas by line **30** to gas separator **11**. Makeup hydrogen-H_2S mixture is supplied from the hydrodesulfurization reactor overhead by lines **19** and **31** and makeup H_2S is supplied by lines **22** and **31**.

Heat soaked material is passed by line **12** to vacuum distillation column **13**. If desired, light hydrocarbons boiling below about 500–650° F. can be separated by a flash vessel, not shown, located in line **12**. The vacuum column is operated at temperatures ranging from 550 to 700° F. and pressures ranging from 1 to 100 mm. Hg. The cut point of the column ranges from 900–1150° F. (atmospheric equivalent temperature), providing the maximum amount of vacuum gas oil boiling in the range of 600–1150, preferably 700–1100° F. for hydrodesulfurization. Vacuum distillation of atmospheric residual stock which has been heat soaked in the manner described yields about 65–70% gas oil as compared to about 50% without heat soaking.

Vacuum gas oil is passed by line **14** to hydrodesulfurization reactor **15**. Any suitable type of hydrodesulfurization reactor and a conventional catalyst are employed. Suitable hydrogenating components include mixtures of a member of the group consisting of Group VI oxides and sulfides with a member of the group consisting of iron, cobalt and nickel oxides and sulfides deposited on a porous carrier. Mixtures of the oxides and sulfides of cobalt, nickel, tungsten and molybdenum on supports containing alumina, bauxite, silica, magnesia, zirconia are preferred catalysts. Cobalt molybdate, nickel molybdate or tungsten sulfide with nickel sulfide are the most preferred metal salt combinations and alumina and silica

alumina are the most preferred supports. The reaction conditions are those known for catalytic hydrodesulfurization and will ordinarily involve a temperature of 600 to 850° F., a pressure in the range of 200 to 2000 p.s.i.a., a hydrogen partial pressure of 100 to 1800 p.s.i.a., a space velocity of 0.5 to 5.0 v./v./hr., and a hydrogen to oil ratio of 500 to 5000 s.c.f. per bbl. of feed. Makeup hydrogen for desulfurization is passed by line **16** to reactor **15**. Recycle hydrogen is supplied by lines **17** and **16**. Unreacted hydrogen and H_2S leave the reactor by line **18**. Part of this gas mixture can be passed by line **19** to line **31** for use in heat soaking. The remainder of the gas mixture passes from line **18** to line **30** and thence to gas separator **11**. Gas separator **11** is shown schematically and it may comprise one or more vessels arranged to separate hydrocarbons as liquids or gases or both and to separate hydrogen and H_2S. Light hydrocarbon gases are removed from the separator by line **20**. H_2S is removed from the separator by lines **21** and **23** and when required a part of the H_2S is passed by lines **22** and **31** to heat soaker **7** to adjust the H_2S content of the heat soaker gas. The balance of the H_2S is passed by line **23** to a sulfur recovery zone not shown. The streams of H_2S, hydrogen and mixtures thereof are directed and proportioned in the system by suitable valves and instrumentation not shown.

Desulfurized gas oil is removed from reactor **15** by line **24**. Preferably this oil is blended with vacuum tower bottoms from lines **25** and **26** to provide a low sulfur blended fuel oil. Cutter stock can be added by line **27** to adjust the viscosity of the fuel oil. If desired all or part of the desulfurized gas oil can be recovered by line **28** for use as catalytic cracking stock or hydrocracking stock. In another embodiment all or part of the vacuum bottoms can be recycled to the heat soaking zone by line **29**.

FIGURE 2 shows plots of the vacuum distillation curves (ASTM D–1160) for heat soaked Bachaquero topped crude. Heat soaking was carried out at 750° F. and 800 p.s.i.g. employing 1000 s.c.f. of gas per barrel of feed. The feed was on temperature for 4 hours. Curve A shows the distillation curve for feed, curve B shows the distillation curve for heat soaking with hydrogen and curves C and D show the distillation curves when the heat soaking is conducted in the presence of a gas containing 10% H_2S and 90% hydrogen.

If it were desirable to use a cut point of 1050° F. in vacuum distillation it will be seen from FIGURE 2 that 56–58% of vacuum gas oil would be obtained for hydrodesulfurization from the feed or from heat soaking with hydrogen. In contrast at least 66% vacuum gas oil is distilled when the H_2S-hydrogen gas is passed through the heat soaking zone. Furthermore the percentage distilled at any temperature is 10–20% greater in the case of heat soaking according to the invention with the result that this material is more easily hydrodesulfurized.

The following example discloses the operation of the process.

Example

The charge stock employed is a Venezuelan crude having a gravity of 26.3° API at 60° F., a sulfur content of 1.39% by weight, a metals content of 156 p.p.m. nickel by weight, and it contains 6% by weight asphaltenes. The residuum from the crude is not a suitable stock for direct hydrodesulfurization because of its high metals and asphaltene content.

When 100 bbl. of this charge stock is topped by atmospheric distillation to produce fuel oil of 175 S.S.F. @ 122° F. viscosity, a yield of 65.6 bbl. with a sulfur content of 1.82% by weight is obtained. Of this 65.6 bbl. residuum, 52.4 bbl. boils above 700° F.+ and 24.0 bbl. boils above 1100° F. The material boiling between 700° F. and 1100° F. has a sulfur content of 1.36% by weight. A 700–1100° F. heavy vacuum gas oil is prepared by vacuum distillation without previous heat soaking. The 28.4 bbl. of heavy vacuum gas oil so produced is subjected to hydrodesulfurization over a cobalt molybdate catalyst at 700° F., 800 p.s.i.g., and 1500 s.c.f./b. of 80% H_2 treat gas at a feed rate of 1.0 vol. feed per hour per vol. of catalyst. At these conditions 85% of the sulfur present in the feed is converted to hydrogen sulfide and is separated from the product to yield a product containing 0.2% sulfur by weight in a volumetric yield of 100%. The hydrodesulfurized product is blended back with the 24.0 bbl. of 1100° F.+ bottoms and the 13.2 bbl. lighter material (700° F.—) originally present in the topped crude to produce 65.6 bbl. fuel oil with a sulfur content of 1.31% by weight. Operating in this manner it is possible to obtain an overall sulfur reduction of only 28%.

If, however, the 700° F.+ material is subjected to heat treatment in the presence of H_2 and H_2S before vacuum distillation, an enhanced yield of vacuum gas oil is obtained. When the 700° F.+ bottoms (52.4 bbl.) is subjected to heat soaking at 800 p.s.i.g. and 750° F. for four hours holding time and in the presence of 1000 s.c.f. per hour treat gas per bbl. of oil the treatment results in conversion of about 40% of the 1100° F.+ material to material boiling within or slightly below the 700–1100° F. range and this material contains about one-third of the sulfur formerly present in the 1100° F.+ material. Thus, the feed to the hydrodesulfurization step amounts to about 38 bbl. per 100 bbl. crude and it has a sulfur content of about 1.58 by weight. The same conditions as those set forth above are employed in the desulfurization step resulting in a product heavy gas oil containing about 0.24% sulfur. Reblending in a like manner as previously described results in a final volume of 38 bbl. fuel oil per 100 bbl. crude charged and which has a sulfur content of 0.98% by weight. Overall desulfurization is 46% in comparison with the 28% achieved when the heat soaking in the presence of H_2 and H_2S was omitted. Furthermore, the blended fuel oil contains less than 1% sulfur making it an acceptable fuel at locations where most fuel oils cannot be used.

Thus, the process of the present invention provides a means of meeting all foreseen requirements with respect to the sulfur content of industrial fuel oil. Only two uncomplicated and relatively inexpensive processing steps, e.g., heat soaking and vacuum distillation are required prior to catalytic hydrodesulfurization. The process achieves a sulfur reduction of 30–70 wt. percent based on the sulfur content of the petroleum residuum. Petroleum residuums containing 1–2 wt. percent sulfur can be treated according to the invention to provide heavy fuel oil blends containing less than 1.0 wt. percent sulfur.

What is claimed is:

1. A process for the production of low sulfur fuel oil comprising the steps of:

(1) Heat soaking a sulfur-containing topped petroleum residuum fraction for 0.5 to 5.5 hours at a temperature in the range of 600 to 800° F. and a pressure of 100 to 1000 p.s.i.a. while continuously passing 400 to 2000 s.c.f. per bbl. of a gas containing 80 to 95 vol. percent H_2 and 5 to 20 vol. percent H_2S through the residuum in intimate contact therewith.

(2) Passing the heat soaked residuum to a vacuum distillation zone.

(3) Distilling the residuum at a temperature in the range of 550 to 700° F. and a pressure in the range of 1 to 100 mm. Hg.

(4) Recovering a vacuum gas oil fraction and a vacuum bottoms fraction.

(5) Passing the vacuum gas oil fraction to a hydrodesulfurization zone.

(6) Contacting the vacuum gas oil with a stream of hydrogen containing gas at a temperature of 600 to 850° F. and a pressure in the range of 200 to 2000 p.s.i.a. in the presence of hydrodesulfurization catalyst.

(7) Recovering a desulfurized vacuum gas oil.

(8) Blending the desulfurized vacuum gas oil fraction with the vacuum bottoms fraction.

(9) And recovering a low sulfur fuel oil.

2. Process according to claim 1 in which the hydrodesulfurization catalyst comprises a mixture of a member of the group consisting of Group VI oxides and sulfides with a member of the group consisting of iron, cobalt and nickel oxides and sulfides deposited upon a porous carrier.

3. Process according to claim 2 in which the catalyst comprises cobalt molybdate on alumina.

4. Process according to claim 1 in which the vacuum gas oil boils in the range of 700–1100° F.

5. Process according to claim 1 in which the petroleum residuum contains 1–2 wt. percent sulfur and the fuel oil contains less than 1.0 wt. percent sulfur.

6. Process according to claim 1 in which the heat soaking step converts 10–50 wt. percent of the 1100° F.+ components to material boiling between 700–1100° F.

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DELBERT E. GANTZ, *Primary Examiner.*

G. J. CRASANAKIS, *Assistant Examiner.*