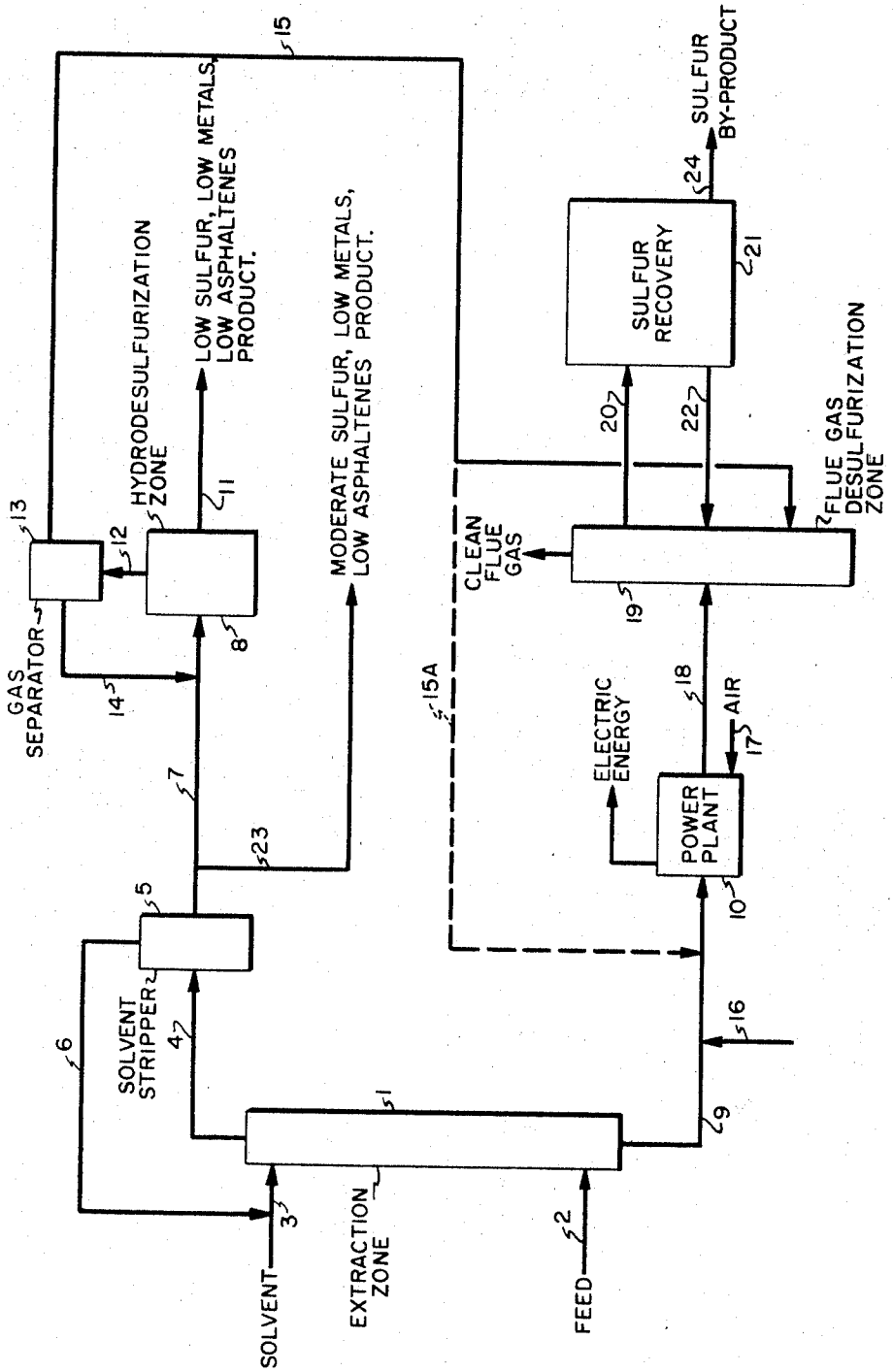
June 24, 1969 A. B. WELTY, JR., ET AL 3,451,923

PROCESS FOR THE UTILIZATION OF HIGH SULFUR HEAVY OIL STOCKS

Filed July 1, 1966



Inventors ALBERT B. WELTY, JR.
STEWART H. HULSE

By C. W. Grady Jr.

Attorney

United States Patent Office 3,451,923
Patented June 24, 1969

3,451,923

PROCESS FOR THE UTILIZATION OF HIGH SULFUR HEAVY OIL STOCKS

Albert B. Welty, Jr., and Stewart H. Hulse, Westfield, N.J., assignors to Esso Research and Engineering Company, a corporation of Delaware

Filed July 1, 1966, Ser. No. 562,312
Int. Cl. C10g 31/14, 23/02
U.S. Cl. 208—211
11 Claims

ABSTRACT OF THE DISCLOSURE

An integrated process utilizes heavy oil stocks containing at least 1 wt. percent sulfur by separating them into 2 fractions: (1) a lower boiling fraction of low sulfur, low asphaltene and low metal content and (2) a higher boiling fraction of high sulfur, asphaltene and metal content. The lower boiling fraction is hydrodesulfurized to recover a premium fuel oil or cat cracking stock and H_2S. The higher boiling fraction is burned as fuel and the flue gas from the combustion of this fraction contains a high concentration of SO_2. The SO_2 is reacted with the H_2S from the hydrodesulfurization step to produce elemental sulfur and thus avoiding sulfur oxide air pollution.

This invention relates to a process for the utilization of high sulfur heavy oil stocks. More particularly the process relates to a process in which a heavy oil stock containing at least 1 wt. percent sulfur is separated into two fractions which are treated or employed in a manner most suitable and efficient for the processing characteristics of each fraction. Still more particularly the processing of the two fractions is interconnected in a unique way.

Conventional petroleum refining technique begins with crude fractionation to separate the lighter and more valuable components from the crude oil. All or part of the heavy bottoms from this fractionation is usually sold as low priced fuel. Depending on the application, such fuels have practical limitations in use. For example, in certain compact boilers, certain metallurgical furnaces, and in large diesel engines and gas turbines, ash-forming metals and slow burning asphaltenes are undesirable, and in all cases high sulfur content is undesirable, especially from an air pollution point of view. Due to public and governmental concern about air pollution fuel oils containing sulfur are becoming less acceptable on the market. The allowable level depends on the local situation. But, for example, fuel oils with more than 0.5% sulfur cannot be burned in Los Angeles County, and after April 1971, burning of fuels containing more than 1.0% sulfur will be banned in New York City. The SO_2 in flue gas resulting from the combustion of high sulfur fuel oil can be removed by any of several known processes, but at the present time these processes are judged to be generally not economically justified. Hence lower sulfur fuels are increasing in economic importance. And where the fuel is used directly in sensitive devices such as compact boilers, gas turbines or diesel engines, lower metals-content and lower asphaltene-content fuels have important practical and economic advantages.

Because of the expanding market for gasoline, jet fuel, desulfurized fuel oil and other light products, refiners are giving more thought to methods of refining a wider cut of the crude oil, thereby converting more of the bottoms fraction. Since more sulfur, metals and asphaltenes are found in these bottoms fractions, methods must be employed to remove such materials prior to catalytic treatments. It is well known that heavy oils rapidly coke hydrodesulfurization catalysts and increase hydrogen consumption; however, most separation treatments are considered to add too much incremental cost to the products, particularly to residual fuel oil, which can compete with other forms of energy for heating and electricity generation only if the price is low.

It is the object of this invention to provide a process for the utilization of high sulfur heavy oil stocks in which the interconnected steps provide the required benefits which make the process atttractive.

Generally speaking, the process of the invention comprises separating the heavy oil into a low sulfur low asphaltene, low metals content fraction representing a major proportion of the oil and a high sulfur, high asphaltene fraction representing a minor proportion of the oil. The contaminant-free fraction is wholly or partly subjected to hydrodesulfurization in the presence of a catalyst and recovered as a premium fuel oil or as cat cracking stock or both. The contaminated fraction is used as fuel for selected industrial furnaces or utility power stations. The flue gas from the combustion of this fraction contains a relatively high concentration of SO_2. The SO_2 is reacted with H_2S from the hydrodesulfurization process to produce elemental sulfur, thereby desulfurizing the flue gas and avoiding sulfur oxide air pollution. The sulfur is sold as a by-product or may be used, for example, to make sulfuric acid for fertilizer or other uses. Alternatively, the recovered H_2S may be burned in the industrial furnace or power plant, thereby recovering in a useful way its heat of combustion, the SO_2 formed therefrom being removed from the flue gas by suitable means after combustion. It should be noted that the final sulfur removal from the system occurs in the flue gas desulfurizer. The economics of flue gas desulfurization are sensitive to the sulfur content of the flue gas. The cost of desulfurization depends strongly on the volume of flue gas to be handled and only slightly on its sulfur content, but by-product credit is directly proportional to sulfur content. Thus the net cost of flue gas desulfurization is less the higher the sulfur. One of the advantages for our process is the concentration of sulfur at the flue gas desulfurizer and the consequent improvement in the economics of the flue gas desulfurizer itself.

The invention will be more completely described below in connection with the drawing which is a diagrammatic flow sheet of one embodiment of the process.

The high sulfur heavy oil feedstock is brought into extraction zone 1 by line 2. Suitable feeds include heavy residuum fractions or bottoms fractions derived from the initial separation of the lighter and more valuable fractions from the heavy less valuable fractions of petroleum crude oil. The heavy petroleum oil will have an initial boiling point ranging from 400–1100° F. depending on the characteristics of the original crude oil and the type of initial processing. The feed will contain

from 1–12 wt. percent sulfur, from 2–30 wt. percent asphaltenes, from 10–10,000 p.p.m. metals and may contain nitrogen compounds, arsenic, ash or other catalyst contaminants. Specific feeds include atmospheric residuum, vacuum residuum, visbreaker bottoms, thermal cracker bottoms, cycle stocks, shale oil and mixtures of these. These stocks usually contain 1.5 to 6 wt. percent sulfur. In the extraction zone the feed is countercurrently contacted with a selective solvent added by line **3**. Suitable solvents include HF, BF_3, HF–BF_3 complexes, phenols, propane, butane, pentane, heptane, hexane, naphtha and mixtures of C_2–C_8 paraffinic hydrocarbons. Extraction conditions include pressures of 5–200 p.s.i.a. and temperatures of 20–500° F. Solvent to oil ratios of 1:5 to 5:1 are employed. The extraction is carried out in any known manner with conventional contacting equipment. The solvent extract is carried overhead by line **4** to stripper **5** and stripped solvent is recycled by lines **6** and **3** to the extraction zone. The solvent free oil is passed by line **7** to the hydrodesulfurization zone **8**, and, depending on market requirements, some may be withdrawn via line **23** for certain uses such as for large gas turbines or diesel engines in ships at sea or which are in locations where the moderate sulfur content is acceptable from an air pollution point of view. The bottoms from the extraction zone is passed by line **9** to the large industrial boiler or power plant **10**.

Using as an example a feedstock containing 3% sulfur and about 5 wt. percent asphaltenes, when a solvent such as pentane is used, the overhead comprises about 95% of the feed and contains about 2.5 wt. percent sulfur and the bottoms material rejected by the solvent is very viscous, contains essentially all the asphaltenes and metals, and contains 6–8 wt. percent sulfur. This bottoms material as such is generally unacceptable as a fuel, and requires dilution with distillate to reduce its viscosity so that it can be shipped to the customer and to reduce the sulfur, metals and asphaltenes content to acceptable levels. Distillate is relatively expensive and its use for this purpose is an economic burden. But in our procedure this fuel need not be diluted with distillate, and another economic advantage ensues. Since the fuel need not be shipped, viscosity is no problem. And in a properly operated large industrial furnace or power plant where close attention can be applied to the combustion process, as distinct from diverse, perhaps intermittent small scale operations, the effects of asphaltenes and metals can be satisfactorily controlled while the sulfur is handled by the flue gas desulfurizer. Hence the use of distillate as a mere diluent is avoided and the distillate is saved for more valuable purposes.

While the separation treatment described above is a solvent extraction treatment several other separation treatments are suitable for splitting the feedstock into a relatively low sulfur fraction comprising 50–95 vol. percent of said stock and a relatively high sulfur fraction comprising 5–50 vol. percent of said stock. For example, vacuum distillation of Middle East topped crude can be carried out to provide an approximately 50–50 split. If desired, the separation step can be applied to a heavy whole crude by distilling to produce one or more light distillate fractions, i.e., gas, gasoline, kerosene, light fuel oil and two sulfur containing fractions for treatment in accordance with the invention. Or, residuum from an atmospheric or vaccum distillation may be coked by any of the well-known means and the coke used as fuel in the industrial furnace or power plant much as coal would be. The thermal reactions involved in coking do not selectively remove sulfur from the high boiling fractions. Hence the sulfur content of the coke is higher than that of the overhead much as the sulfur content of the high boiling oil from deasphalting is greater than that of the overhead. In the preferred embodiment a petroleum residuum fraction intended for use as fuel oil and containing more than one percent sulfur is split for processing and use as a premium fuel having a lower sulfur content than the starting material and a residual fraction having a higher sulfur content than the starting material which produces a flue gas which must be treated to remove the SO_2.

Returning to the drawing, the relatively low sulfur oil, i.e., containing about 0.5–3.5 wt. percent S, from the separation step is treated in hydrodesulfurization zone **8** in the conventional manner with known catalysts. Desulfurized product is removed by line **11**. Suitable process conditions are:

Feed rate, v./v./hr.	0.2–3.0
Hydrogen rate, s.c.f./bbl.	500–6000
Pressure, p.s.i.g.	300–3000
Temperature, ° F.	550–850

Preferred catalysts are 5–15 wt. percent molybdena on porous alumina and mixtures of cobalt oxide (3–6 wt. percent) with molybdenum oxide (6–12 wt. percent) on adsorptive alumina. Catalysts containing nickel, chromium, platinum, and tungsten in the form of metals, oxides and sulfides either alone or in combination with cobalt and/or molybdenum, on alumina, silica stabilized alumina, charcoal, kieselguhr and bauxite can be used as well.

A gas comprising H_2 and H_2S is carried overhead from zone **8** by line **12** and the H_2S is removed by a conventional gas separation unit **13**. Hydrogen is recycled by lines **14** and **7**. H_2S is removed by line **15** for subsequent use in the process.

The relatively high sulfur fraction comprising 5–50 vol. percent of the feedstock and also containing a high percentage of sulfur, i.e., about 2.5–10 wt. percent S, and most of the catalyst contaminants is passed by line **9** to power plant **10** for burning in a furnace. When the material is a solid as from a coking operation it may be conveyed to the furnace and charged thereto by any of the well-known means. This material can be blended with other fuel oil or comminuted solid fuel such as coal fed by line **16**. The method of combustion in power plant **10** is conventional and constitutes no part of the invention. Line **17** provides air for combustion.

Flue gas containing a relatively high concentration of SO_2 is passed by line **18** to flue gas desulfurization zone **19**. In one embodiment the flue gas is mixed with H_2S from line **15** at a temperature in the range of 200–300° F. to produce sulfur and water. The reaction is usually conducted in the presence of a catalyst or solid adsorbent such as alumina. The sulfur is removed from the catalyst by heating to 900° F. to vaporize the sulfur. This reaction is conventional and details are available in published literature, e.g., Doumani, et al Ind. Eng. Chem. vol. 36, April 1944, pp. 329–332, and Gamson, et al., Chem. Eng. Progress, vol. 49, April 1953, pp. 203–215. Line **20** denotes a line carrying vaporized sulfur or sulfur on a catalyst or adsorbent to sulfur recovery zone **21**. Line **24** denotes a line for removal of the sulfur produced. Line **22** denotes the catalyst or adsorbent return line.

In another embodiment, H_2S is passed by line **15** and the dotted line **15A** to the power plant fuel input line and passed into power plant **10** as fuel. The H_2S is burned to produce SO_2 and water. The flue gas containing an increased quantity of SO_2 is desulfurized by the best process for the situation at hand. For example, the Alkalized Alumina process of the U.S. Bureau of Mines or the Reinluft process or the Catalytic Oxidation process (Journal of the Air Pollution Control Association, vol. 15, No. 10, pp. 459–64 (1965)), or any other of several processes known to be effective may be used. The exact nature of the sulfur containing by-product will, of course, depend on the process chosen.

The following example describes an embodiment of the process which is similar to the embodiment disclosed

in the drawing except that vacuum distillation is used as the initial separation step rather than solvent extraction.

EXAMPLE 1

50,000 bbl./day of Venezeulan atmospheric residuum containing 2.85% sulfur, 10.5% asphaltenes and 475 w.p.p.m. metals, mostly vanadium, is subjected to vacuum distillation to provide 27,200 bbl./day of distillate containing 1.98% sulfur, 0.3% asphaltenes and 3 w.p.p.m. metals and 22,800 bbl./day of vacuum bottoms containing 3.56% sulfur, 22.7% asphaltenes and 1050 w.p.p.m. metals. The distillate is hydrodesulfurized using cobalt molybdate on alumina catalyst at 800 p.s.i.g., 700° F., a hydrogen recycle gas rate of 2500 standard cubic feet/bbl. and at a space velocity of 1.0 v./v./hr. Sulfur is reduced from 1.98% to 1.19% by this treatment and the H_2S produced, amounting to 2.12% sulfur based on vacuum bottoms is used in the flue gas desulfurization step or is added to the power plant fuel. Thus the amount of sulfur going to the flue gas desulfurization step is 5.68% based on the vacuum bottoms. In the case where this H_2S goes directly to flue gas desulfurization it is desired to carry out the well known Claus reaction between SO_2 and H_2S to give sulfur: $2H_2S+SO_2 \rightarrow 2H_2O+3S$. Actually about 3% of the sulfur oxides in the flue gas are SO_3 and about 97% are SO_2. The SO_3 reacts in an analogous way, but more H_2S is required to satisfy stoichiometric requirements: $SO_3+3H_2S \rightarrow 3H_2O+4S$. The net result is that 2.03 moles of H_2S are required for each mole of (SO_2+SO_3) in the flue gas. In this example, the flue gas contains 3.56 wt. percent sulfur as (SO_2+SO_3) in a concentration of about 2000 w.p.p.m. as (SO_2+SO_3) depending on the amount of air excess used in combustion. Therefore, $3.56 \times 2.03 = 7.24\%$ sulfur in the form of H_2S, based on vacuum bottoms, is required to react with all the (SO_2+SO_3). In this example, then, some of the H_2S required, amounting to 5.12% based on vacuum residuum (i.e. 7.24%–2.12%), is supplied extraneously by reacting some of the sulfur finally recovered with hydrogen. The amount of H_2S which must be made depends on the sulfur contained in the distillate and bottoms fractions. In certain cases as in deasphalting or coking where the overhead is large compared to the bottoms no extraneous H_2S is required and indeed the H_2S made in desulfurization is split, some going directly to flue gas desulfurization and the rest to the combustion, but always in such a proportion as to give the desired stoichiometric balance in the flue gas desulfurization operation.

In this example, the H_2S may all be burned in the furnace, in which case flue gas desulfurization processes depending on other principles than the Claus reaction may be employed. In this case, the flue gas is cleaned of solids by known means and then passed at about 850° F. over a standard vanadium SO_2 oxidation catalyst to convert 95% of the SO_2 to SO_3. Continued cooling of the flue gas to 220° F. condenses dilute 75% sulfuric acid, thus removing most of the sulfur oxides from the flue gas. The 75% sulfuric acid is concentrated to 93%, a standard grade used in commerce, and utilized for fertilizer and other purposes. The sulfuric acid recovered amounts to 680 tons/day. At a price of $25/ton, for example, this amounts to $17,000/day of 75¢/bbl. of bottoms fed to the furnace, which helps to defray the cost of the entire desulfurization and fuel oil improvement process described.

By integrating the steps of the process, applicants have provided an efficient and economical basis for the processing of high sulfur stocks which are presently being marketed at marginal prices. Depending on the feed to the process the lower sulfur product is a premium grade fuel oil suitable for use in gas turbines, diesel engines and other sensitive devices or a low sulfur stock for further refining treatments such as cat cracking or hydrocracking. Depending on how the H_2S is used, the flue gas from the combustion of the high sulfur fraction yields elemental sulfur or H_2SO_4 or other valuable commercial products. A very important beneficial aspect of the process is the production of a clean flue gas which can be vented in populated areas without sulfur oxide air pollution. In summary, then, this process converts heavy residual hydrocarbon oils into premium fuels or stocks suitable for further refining while at the same time generating low cost heat, recovering valuable elemental sulfur, sulfuric acid or other valuable sulfur-containing by-products, and while venting only flue gas which will not contaminate the air with sulfur oxides.

What is claimed is:

1. A process for the utilization of high sulfur heavy oil stocks containing at least one wt. percent sulfur comprising steps of:
   - (A) subjecting a high sulfur heavy oil stock boiling 400–1100° F. to a separation treatment in which said stock is separated into a relatively low sulfur and low boiling fraction comprising 50–95 vol. percent of said stock and a relatively high sulfur and high boiling fraction comprising 5–50 vol. percent of said stock;
   - (B) subjecting said low sulfur fraction to hydrodesulfurization in the presence of a catalyst at hydrodesulfurization conditions;
   - (C) recovering a desulfurized product oil and H_2S;
   - (D) burning said high sulfur fraction under conditions in which SO_2 is produced in the flue gas;
   - (E) reacting said H_2S and said SO_2 to produce elemental sulfur and recovering said sulfur.

2. Process according to claim 1 in which said separation treatment is solvent extraction.

3. Process according to claim 2 in which the solvent is a C_3–C_8 paraffinic hydrocarbon.

4. Process according to claim 2 in which the solvent is propane.

5. Process according to claim 2 in which the solvent is a propane-butane mixture.

6. Process according to claim 2 in which the solvent is pentane.

7. Process according to claim 1 in which said separation treatment is vacuum distillation.

8. A process for increasing the utilization of heavy residual hydrocarbon oil containing at least one wt. percent sulfur comprising the steps of:
   - (A) subjecting heavy residual hydrocarbon oil boiling 400–1100° F. and containing at least one wt. percent sulfur, 2–30 wt. percent asphaltenes and from 10–10,000 p.p.m. metals to a separation treatment in which the oil is separated into a first low boiling fraction comprising 50–95 vol. percent of the oil having a sulfur content less than the sulfur content of the heavy residual fuel oil and a second high boiling fraction comprising 5–50 vol. percent of the oil having a sulfur content greater than the sulfur content of the heavy residual oil and essentially all of the asphaltenes and metals;
   - (B) subjecting said first fraction to hydrodesulfurization in the presence of a sulfur sensitive catalyst at hydrodesulfurization conditions;
   - (C) recovering a hydrodesulfurized premium fuel oil containing less than one wt. percent sulfur and H_2S;
   - (D) burning said second fraction and said H_2S in the furnace of an electric power plant whereby an increased quantity of SO_2 is present in the flue gas;
   - (E) removing SO_2 and any SO_3 from the flue gas by means of an absorbent;
   - (F) recovering a valuable sulfur by-product therefrom;
   - (G) venting substantially sulfur free flue gas to the atmosphere.

9. Process according to claim 8 in which asphaltenes are separated by extracting said heavy residual hydrocarbon oil with pentane.

10. Process according to claim 8 in which said separation treatment is vacuum distillation.

11. Process according to claim 8 in which a portion of said first fraction is recovered as a product and the remainder of said fraction is subjected to hydrodesulfurization.

References Cited

UNITED STATES PATENTS

2,697,064	12/1954	Brown	23—225
2,717,855	9/1955	Nicholson	208—211
2,889,207	6/1959	Eliot	23—225
2,992,076	7/1961	Thompson et al.	23—225
3,001,932	9/1961	Pietsch	208—211
3,027,317	3/1962	Reeg et al.	208—211
3,193,495	7/1965	Ellor et al.	208—211

DELBERT E. GANTZ, *Primary Examiner.*

G. J. CRASANAKIS, *Assistant Examiner.*

U.S. Cl. X.R.

23—225