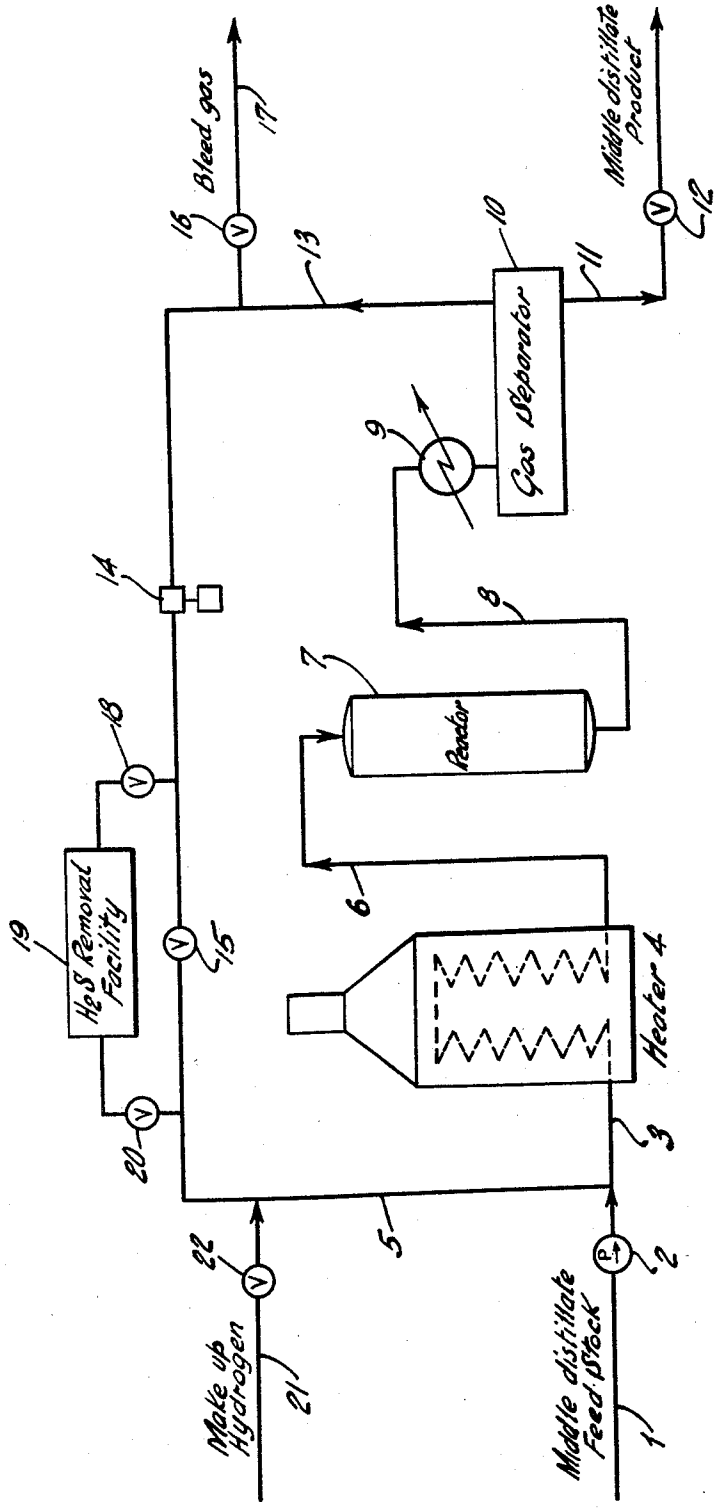
Dec. 8, 1959 M. D. RIORDAN ET AL 2,916,443

PROCESS FOR DESULFURIZING PETROLEUM DISTILLATES USING A SPENT PLATINUM REFORMING CATALYST

Filed Aug. 8, 1955



United States Patent Office

2,916,443

Patented Dec. 8, 1959

2,916,443

PROCESS FOR DESULFURIZING PETROLEUM DISTILLATES USING A SPENT PLATINUM REFORMING CATALYST

Michael D. Riordan, Fishkill, and Herbert E. Vermillion, Wappingers Falls, N.Y., assignors to Texaco Inc., a corporation of Delaware

Application August 8, 1955, Serial No. 526,813

5 Claims. (Cl. 208—217)

This invention relates to a hydrocarbon conversion process. More particularly, it relates to a process for desulfurizing middle distillates by hydrodesulfurization employing a supported platinum catalyst.

Middle distillate is a term applied to petroleum fractions higher boiling than gasoline and lower boiling than lubricating oil fractions. Kerosene, diesel fuel, distillate fuel oil, and gas oil, for example, are included by the term middle distillate. Crude petroleum oils and the middle distillates produced therefrom contain varying types and amounts of sulfur compounds. These sulfur compounds may be objectionable because of bad odor and the harmful effects on stability, corrosiveness and burning characteristics of the products in which they are found. Numerous means have been used to remove sulfur compounds or to convert them to less objectionable forms. These means have included clay treating, acid treating, copper sweetening, doctor sweetening, solvent extraction and mild hydrogenation. The mild dehydrogenation processes heretofore used are commonly carried out by passing the oil to be treated in admixture with hydrogen over a sulfur resistant hydrogenation catalyst at temperatures of 700° F. to 800° F. and at pressures of 500 to 1000 p.s.i. Catalysts commonly used for mild hydrogenation of middle distillates include tungsten-sulfide, nickel-sulfide, cobalt molybdate and chromia alumina.

It has now been found that middle distillate oils may be desulfurized by mild hydrogenation efficiently and with high selectivity when employing a supported platinum catalyst. By the process of this invention, middle distillates are desulfurized by mild hydrogenation in the presence of a supported platinum catalyst. Substantial desulfurization may be obtained at temperatures as low as 500° F. Higher temperatures up to about 800° F. may be employed although at this temperature and higher, undesired reactions, such as hydrocracking or dehydrogenation, may become pronounced. These reactions are undesirable in middle distillate processing since they tend to alter the boiling range and increase the aromaticity of the product. These effects in turn may degrade the burning characteristics of kerosene or fuel oil and lower the diesel index or cetane number of diesel fuels. Preferred temperatures for the process of this invention are in the range of 550 to 700° F. The process of this invention may be performed at pressures of about 200 to about 1000 pounds per square inch. Increasing the pressure tends to suppress dehydrogenation of naphthenes to aromatics. Preferred pressures are in the range of about 400 to about 1000 p.s.i. Space velocities of about 0.1 to 10.0 volumes of oil per hour per volume of catalyst may be employed but space velocities of about 0.5 to 3.0 are preferred.

The catalyst employed in the process of this invention is platinum on alumina. It is desirable that the catalyst be substantially free from acidic constituents which tend to promote cracking. The platinum-alumina catalyst contains a small proportion of platinum, for example, 1 to 2% by weight, or less. Usually the amount is less than 1%. A catalyst composed of 0.5% platinum on gamma alumina has proved entirely satisfactory. The surface area of the catalyst does not appear particularly critical and catalyst with both high surface areas and low surface areas may be satisfactorily used.

In a specific example of the invention, a platinum-alumina catalyst is prepared to contain 0.5% platinum by weight on alumina. A solution of 25 grams of $H_2PtCl_6.6H_2O$ in 1200 ccs. of water are saturated with hydrogen sulfide by bubbling the gas through the solution for one-half hour to form a PtS_2. The PtS_2 slurry is mixed with 1990 grams of freshly calcined 8 to 14 mesh alumina having a typical analysis as follows:

	Percent
Al_2O_3	96.00
Fe_2O_3	0.05
SiO_2	0.10
Na_2O	0.10
TiO_2	0.02
H_2O	3.73

and a specific surface of 59.5 $m.^2/g.$ after calcining. 240 cc. of 30% hydrogen peroxide is added to the alumina-platinum sulfide mixture and allowed to stand for one hour, after which the mixture is dried on a steam plate.

Another catalyst which is suitable for the process of this invention, comprises platinum, alumina, and a combined halogen. Such a catalyst may have a composition of 0.3% Pt, 0.6% $AlF_3.\frac{1}{2}H_2O$, 99.1% Al_2O_3. Supported platinum catalysts which have been used for catalytic reforming of gasoline until they have been spent for reforming purposes, have been found to retain desulfurization activity, and may be used for the process of this invention.

An advantage of the process of this invention is that middle distillate petroleum fractions may be efficiently desulfurized with yields of essentially 100%.

Another advantage of this process is that middle distillates may be selectively desulfurized by mild hydrogenation without substantial hydrocracking or reforming of naphthenes to aromatics.

The accompanying drawing diagrammatically illustrates the process of this invention. Although the drawing illustrates one arrangement of apparatus in which the process of this invention may be practiced, it is not intended to limit the invention to the particular apparatus or material described.

A middle distillate feed stock from external storage, not shown, is admitted to the system through line **1** and charged by pump **2** through line **3**. Hydrogen or a hydrogen-containing gas in line **5** is combined with the middle distillate in line **3** and the combined stream passes to heater **4** where it is heated to reaction temperature. Heater effluent passes through transfer line **6** and into reactor **7** which contains a supported platinum catalyst. In reactor **7**, a portion of the hydrogen reacts with sulfur present in the middle distillate feed to form hydrogen sulfide. The reactor effluent flows through line **8**, cooler **9** and is discharged into gas separator **10**. Middle distillate product of reduced sulfur content is withdrawn through line **11** and is discharged through valve **12** to external storage, not shown. The gas separated in gas separator **10** comprises unreacted hydrogen and hydrogen sulfide. This gas is withdrawn from gas separator **10** through line **13** and may be recycled by compressor **14** through valve **15** and line **5**. Hydrogen sulfide produced by the desulfurization reaction may be withdrawn from the system by bleeding gas through valve **16** and line **17**. Hydrogen sulfide may also be removed from the recycle gas by diverting at least a por-

tion of the recycle gas through valve **18**, hydrogen sulfide removal facilities **19** and valve **20**. Hydrogen sulfide removal facility **19** may comprise, for example, amine scrubbing. Make-up hydrogen to supply the hydrogen consumed in the desulfurization reaction, and withdrawn from the system dissolved in the products or in the bleed stream, is supplied from an external source, not shown, through line **21**, valve **22** and is combined with the recycle gas in line **5**.

This invention is further described in the following examples.

Example I

A kerosene containing 0.49 weight percent sulfur and having an aniline point of 136.4° F. from a high sulfur crude oil is desulfurized by mild hydrogenation using a catalyst having the composition (by weight) 0.3% Pt, 0.6% $AlF_3.\frac{1}{2}H_2O$, 99.1% Al_2O_3 at a pressure of 250 p.s.i.g. and with a hydrogen flow rate of 2,727 cubic feet per barrel. The results which are obtained at various temperatures and space velocities are given in the following tabulation:

Temp., ° F.	Volumetric Space Velocity	Sulfur, Wt. Percent	Aniline Point, ° F.
602	0.5	0.009	134.9
604	1.0	0.046	138.5
697	0.5	0.014	132.1
699	1.0	0.023	134.6
752	0.5	0.015	120.4
750	1.0	0.016	123.4
804	2.0	0.019	118.7

It will be noted that over 98% of the sulfur is removed from the kerosene by mild hydrogenation with a supported platinum catalyst at a temperature of 602° F. and at a space velocity of 0.5. It will also be noted that at 804° F. with a space velocity of 2, more than 96% of the sulfur is removed. However, the lowering of the aniline point indicates that at this temperature (804° F.) reforming of naphthenes to produce aromatics may occur.

Example II

A kerosene containing 0.49 weight percent sulfur and having an aniline point of 136.4° F. from a high sulfur crude oil is desulfurized by mild hydrogenation using a catalyst having the composition 0.5% platinum on alumina at a pressure of 400 p.s.i.g. and with a hydrogen flow rate of 14,387 cubic feet per barrel. The results which are obtained at various temperatures and space velocities are given in the following tabulation:

Temp., ° F.	Volumetric Space Velocity	Sulfur, Wt. Percent	Aniline Point, ° F.
503	0.5	0.16	142.5
501	1.0	0.13	142.7
548	0.5	0.019	148.8
554	1.0	0.036	143.4
605	0.5	0.004	147.1
604	1.0	0.021	145.0
704	0.5	0.003	143.2
701	1.0	0.002	144.3
752	0.5	0.003	129.9
749	1.0	0.003	135.6

It will be noted that at 501° F. with a space velocity of 1.0, over 73% of the sulfur is removed. At temperatures of about 605° F. and 0.5 space velocity, over 99% of the sulfur is removed. The treatment shown by this example results in an increase in the aniline point of the product at all temperatures below about 750° F. which indicates that substantial dehydrogenation of naphthenes to form aromatics does not occur.

Although this invention has been described in connection with fixed bed catalytic reactors, it is to be understood that the reaction may be carried out in a reactor containing a dense phase fluidized bed of catalyst, or in an entrained catalyst reaction system.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process for desulfurizing a middle distillate which comprises contacting a sulfur containing middle distillate with hydrogen at a temperature between about 500° F. and 800° F., a pressure between about 200 and 1000 p.s.i. and a space velocity between about 0.1 and 10 volumes of distillate per hour per volume of catalyst in the presence of a platinum on alumina catalyst, said catalyst having been conditioned by the catalytic reforming of gasoline stock and having become spent for reforming purposes, said desulfurization being characterized by the substantial absence of cracking or dehydrogenation.

2. The process of claim 1 in which the middle distillate is kerosene.

3. The process of claim 1 in which the middle distillate is a gas oil.

4. The process of claim 1 in which the middle distillate is diesel fuel.

5. A process for desulfurizing a middle distillate which comprises contacting a sulfur containing middle distillate with hydrogen at a temperature between about 500° F. and 750° F., a pressure between about 250 and 400 p.s.i. and a space velocity between about 0.5 and 1.0 volume of distillate per hour per volume of catalyst in the presence of a platinum on alumina catalyst, said catalyst having been conditioned by the catalytic reforming of gasoline stock and having become spent for reforming purposes, said desulfurization process being characterized by the substantial absence of cracking and dehydrogenation.

References Cited in the file of this patent

UNITED STATES PATENTS

2,116,061	Dorrer	May 3, 1938
2,401,334	Burk et al.	June 4, 1946
2,437,532	Huffman	Mar. 9, 1948
2,440,673	Jones	May 4, 1948
2,542,471	Brandon	June 15, 1949
2,542,970	Jones	Feb. 27, 1951
2,547,380	Fleck	Apr. 3, 1951
2,608,534	Fleck	Aug. 26, 1951
2,651,598	Ciapetta	Sept. 8, 1953
2,658,028	Haensel	Nov. 3, 1953
2,722,501	Kassel	Nov. 1, 1955
2,724,683	Nadro	Nov. 22, 1955
2,773,007	Gerhold	Dec. 4, 1956
2,833,698	Patton et al.	May 6, 1958