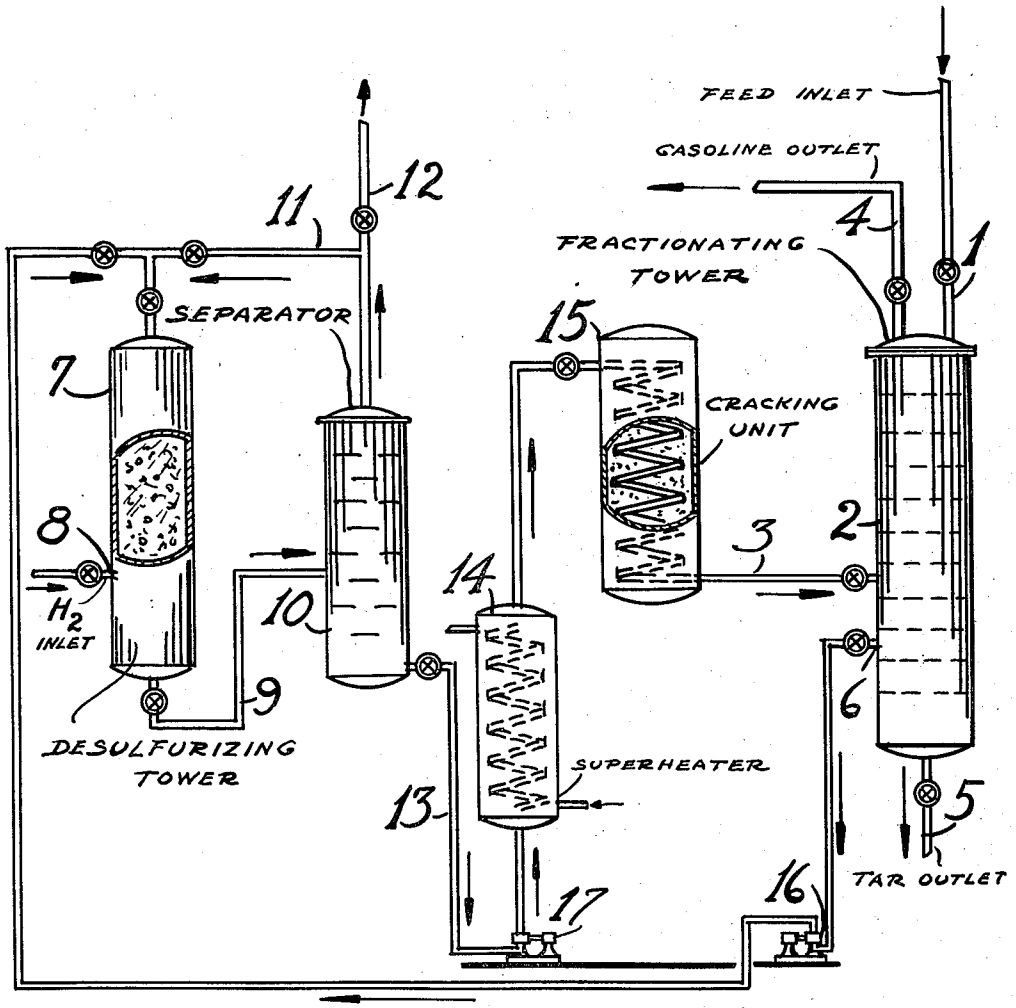
May 12, 1942. B. T. BROOKS 2,282,451

DESULPHURIZING AND CRACKING PROCESS

Filed Dec. 29, 1938



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Patented May 12, 1942 2,282,451

UNITED STATES PATENT OFFICE

2,282,451

DESULPHURIZING AND CRACKING PROCESS

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Application December 29, 1938, Serial No. 248,158

4 Claims. (Cl. 196—24)

This invention relates to the production of superior substantially sulphur-free gasoline in high yields from sulphur-containing heavier hydrocarbon raw materials.

In the present cracking art, feed stocks such as gas oil containing a small amount of sulphur are generally cracked by the usual thermal decomposition processes wherein a portion of the sulphur is liberated as hydrogen sulphide and is drawn off with the fixed gases, while some of the sulphur compounds present in the feed stock, for example as organic sulphur, tends to polymerize and react with other hydrocarbons, especially the unsaturated materials, thereby increasing the amount of coke and tar formed. These organic sulphur compounds are also cracked to some extent, giving volatile sulphur compounds which are exceedingly refractive and difficult to remove from the heavier fractions obtained by the distillation of the cracked product. A considerable portion of this type of sulphur may be removed from the rectified products by costly methods, such as caustic treatment, doctor sweetening, sulphuric acid and the like.

One object of this invention is to remove the sulphur from the cracking feed stock prior to the cracking operation, thereby giving a substantially sweet cracked product and a higher yield of cracked gasoline with low accompanying yields of tar and coke. Another object is to provide for a mild cracking operation prior to the main cracking step to produce antiknock gasoline from the less refractory hydrocarbons and to remove them from the feed stock to the cracking unit so as to prevent over-cracking. Another object is to substantially eliminate the production of hydrogen sulphide in the main cracking unit so as to prevent recombination of the hydrogen sulphide with the unsaturated products, thereby producing sulphur compounds which must necessarily be further removed after separation of the cracked product. Further objects will become apparent as the description proceeds.

The present invention involves the use of three steps, i. e. a desulphurization step which may or may not be carried out under mild cracking conditions, a separation step wherein the hydrogen sulphide produced by the desulphurization operation is removed possibly together with some cracked hydrocarbons, if they are formed, from the main body of the uncraked oil to be fed to the third step which is the cracking unit.

It is essential that the first desulphurization step be carried out in the presence of hydrogen and at a pressure of about 5–50 atmospheres, using a temperature of about 250–350° C. It is also desirable that a metal sulphide hydrogenating catalyst be present, such as the sulphides of molybdenum, tungsten, chromium or uranium. If the feed stock employed is fairly low in sulphur (i. e. about 0.1–1%), it is desirable to carry out the preliminary desulphurization operation under mild cracking conditions, whereby some of the less refractive hydrocarbons are converted into antiknock gasoline, and likewise the organic sulphides and other sulphur compounds present in the feed stock are converted into hydrocarbons and hydrogen sulphide. When the feed stock is fairly low in sulphur, it may be necessary to recirculate some hydrogen sulphide with the feed in order to maintain the catalyst activity, due to the fact that there is an equilibrium relationship between the catalyst and the hydrogen as exemplified by the following equation:

$$Mo_2S_3 + 2 \rightleftarrows 2MoS_2 + 3H_2S$$

In the above example if the Mo_2S_3 is completely reduced to MoS_2, the catalyst becomes inactivated. Hence, it is essential that some Mo_2S_3 be present during the desulphurization operation.

With feed stocks containing higher amounts of sulphur, say above about 1%, it is desirable to carry out this desulphurization operation without substantial cracking of the hydrocarbons. In this case the hydrogen sulphide produced is withdrawn from the product in a separating vessel, since it is desirable that the desulphurization operation be carried out in the liquid phase.

After the removal of the hydrogen sulphide and possibly cracked hydrocarbons from the desulphurization unit, the desulphurized oil is fed into a cracking unit which may be of the conventional thermal cracking type, such as the Dubbs, tube and tank, Gyro, true vapor phase, and the like, or a catalytic cracking process which employs activated bentonites, synthetic gels and other masses as catalysts for the cracking operation.

Referring to the accompanying drawing which presents one embodiment of the present invention in diagrammatic sectional elevation, numeral 1 denotes the introduction of a sulphur-containing fresh feed such as reduced crude pumped into fractionating tower 2 into which enters a hot cracked product 3. In this fractionating tower tar or other heavy product may be drawn off at 5, while the main portion of the

feed (i. e. the heavier portion) together with cycle stock is drawn off by pump 16 at approximately point 6 of the tower and led into desulphurizing tower 7 containing a catalyst in lump form suitable for desulphurizing the entering petroleum hydrocarbon, such as molybdenum sulphide, hydrogen being admitted into this chamber by line 8. The thus desulphurized hydrocarbon together with the sulphur-containing gases are drawn off at line 9 and introduced into chamber 10 wherein a separation is accomplished between the gas and liquid phase materials, some of the gas being recycled into the desulphurizing chamber by line 11, if desired. The sulphur-containing gases and other lighter materials are drawn off through vent 12, while the remaining liquid material is removed from separator 10 through line 13 and forced into super-heating coil 14 by pump 17 wherein the hydrocarbon raw materials are heated up to cracking temperature. Thence the material is forced into the cracking unit 15 which may be a coil or chamber containing catalyst, the unit being operated for optimum gasoline conversion. After the cracking operation, the cracked product is withdrawin into the bubble tower or fractionating tower 2, wherein the gasoline recovery takes place. Although the desulphurizing chamber 7 may be operated at the same pressure as the cracking unit, it is desirable to maintain a pressure of about 5–50 atmospheres in this particular vessel. It is also possible to employ a cracking coil which is merely an extension of superheater 14, if desired. Provision may likewise be made for inserting a vessel in line 3 for removing tar prior to the distillation operation.

The invention may be more clearly understood from the following examples by which it is not intended to limit the invention in any particular respect:

Example 1.—A West Texas gas oil containing 2½% sulphur is passed over a molybdenum sulphide catalyst at 35 atmospheres pressure and at 265° C. in the presence of hydrogen which is fed into the system in the proportion of one mole of hydrogen to five moles of feed stock. The products issuing from this desulphurizing unit are led under pressure into a small fractionating tower wherein the fixed gases containing hydrogen sulphide, hydrogen and small amounts of hydrocarbons are led off the top and the hydrogen is recovered for further reuse. The liquid removed from the bottom of the tower is then fed into a tube and tank cracking unit wherein the stock is cracked under ordinary cracking conditions for the maximum yield of gasoline, giving a stable, low sulphur gasoline in high yields.

Example 2.—A reduced crude containing 0.8% sulphur is passed into a heated tower containing chromium sulphide and alumina, together with hydrogen in the proportion of one mole of hydrogen to one mole of oil, the temperature being 360° C. The time of contact is adjusted so that about 2–5 of the feed stock is converted into gasoline. The reaction mixture is then led into a distillation tower wherein the fixed gases and gasoline are removed, the gasoline, hydrogen and hydrogen sulphide being separated by subsequent operations, and at least a portion of the hydrogen-hydrogen sulphide mixture is recirculated back to the desulphurizing unit. The liquid removed from the fractionating tower is then led into a heated vessel at atmospheric pressure and at about 565° C., in presence of an activated clay such as "Super-Filtrol," the time of cracking being adjusted so that about 40% of the feed stock to this unit is converted into gasoline. The gasoline produced is especially low in sulphur and the amount of coke produced on the catalyst is fairly low.

By the present method it has been found possible to remove more of the sulphur from the feed stock than is possible by a straight cracking operation. Furthermore, the preliminary desulphurization operation acts as a means for preheating the feed stock for the subsequent cracking operation so that there is no substantial loss of heat throughout all of the operations. If the hydrogen sulphide is not removed after the desulphurization step and prior to the cracking operation, it tends to combine with the unsaturates produced by the final cracking operation, giving sulphur-containing products which must then subsequently be removed. Furthermore, by eliminating subsequent treatment of the cracked products to a great extent, high yields of gasoline are possible with minimum production of coke and tar. The amount of hydrogen which may be employed with the feed stock to the desulphurizing unit may vary from one mole of hydrogen to twenty moles of oil, to one mole of hydrogen to one-half mole of oil, depending upon the amount of sulphur present in the feed stock, the pressure employed, and other conditions of operation in the desulphurizing unit.

This invention is not limited to any specific examples or to any theory of operation, but merely by the following claims in which it is intended to cover the invention as broadly as the prior art permits.

I claim:

1. A process for making cracked gasoline which comprises subjecting a feed stock of relatively heavy hydrocarbons containing about .1 to about 1% sulphur to mild cracking conditions at a temperature of about 360° C. and in the presence of hydrogen, hydrogenating catalyst and added hydrogen sulphide to remove sulphur from the feed stock and to produce about 2% to 5% of gasoline, thereafter removing hydrogen sulphide, hydrogen and gasoline from the product, and then subjecting the remainder of the product to more severe cracking conditions than employed in the first cracking operation to produce the maximum yield of gasoline.

2. The process of making an anti-knock gasoline from a gas oil of sulphur content about .1 to about 1% which comprises subjecting said gas oil to mild cracking conditions at a temperature of about 360° C. and in the presence of hydrogen, added hydrogen sulphide and a hydrogenating catalyst to remove sulphur from the feed stock and to produce from about 2% to 5% of gasoline, thereafter removing hydrogen sulphide, hydrogen and cracked gasoline from the product and then subjecting the remainder of the product to catalytic cracking and in the presence of a cracking catalyst to produce about 40% of gasoline on the feed to the second cracking step.

3. A process for making gasoline which comprises mixing a crude oil with cracked products leaving a cracking zone to heat the crude oil and remove volatile constituents therefrom and to provide a heated fraction comprising relatively heavy hydrocarbons and containing from about .1 to 1% of sulphur, passing the heated fraction

to a desulphurizing zone without further heating it and subjecting it to mild cracking conditions at a temperature of about 360° C. in the presence of hydrogen, hydrogen sulphide and a metal sulphide catalyst to form a relatively small amount of gasoline and to form hydrogen sulphide from the sulphur in the oil, thereafter removing hydrogen, hydrogen sulphide and gasoline from the cracked products, then subjecting the remaining hydrocarbons to more severe cracking conditions than employed in the first cracking operation and in the absence of substantial amounts of added hydrogen and using the cracked products from said last mentioned cracking operation for preheating and stripping the crude oil.

4. A process according to claim 3 wherein the removed hydrogen sulphide is returned to the mild cracking step.

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