

Dec. 24, 1968

M. C. CHERVENAK ET AL
HIGH CONVERSION HYDROGENATION
Original Filed Dec. 16, 1964

3,418,234

FIG. 1

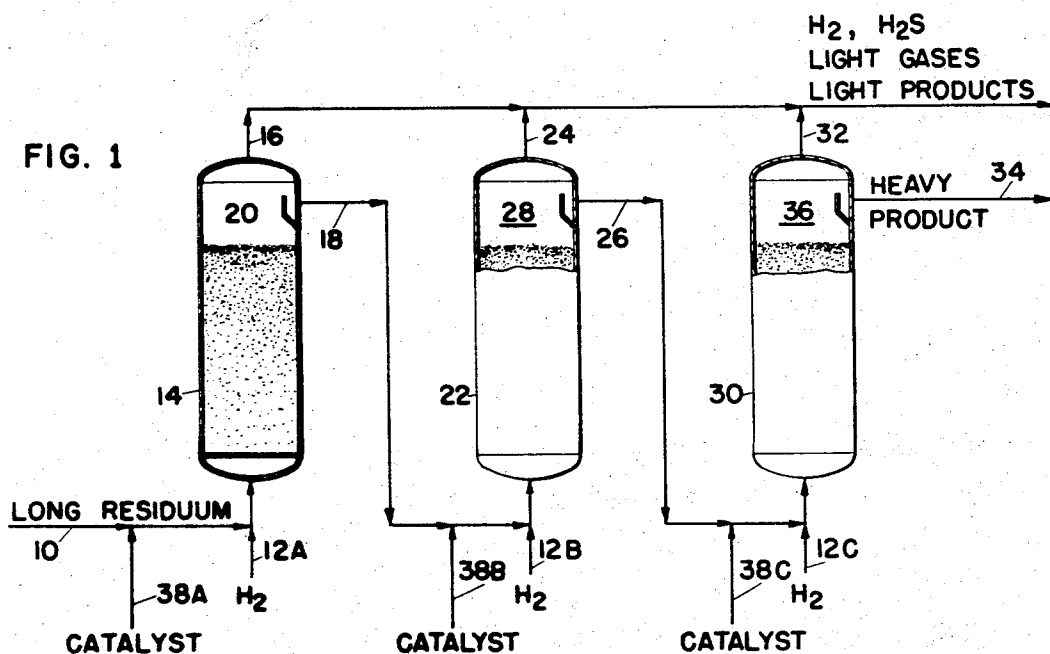
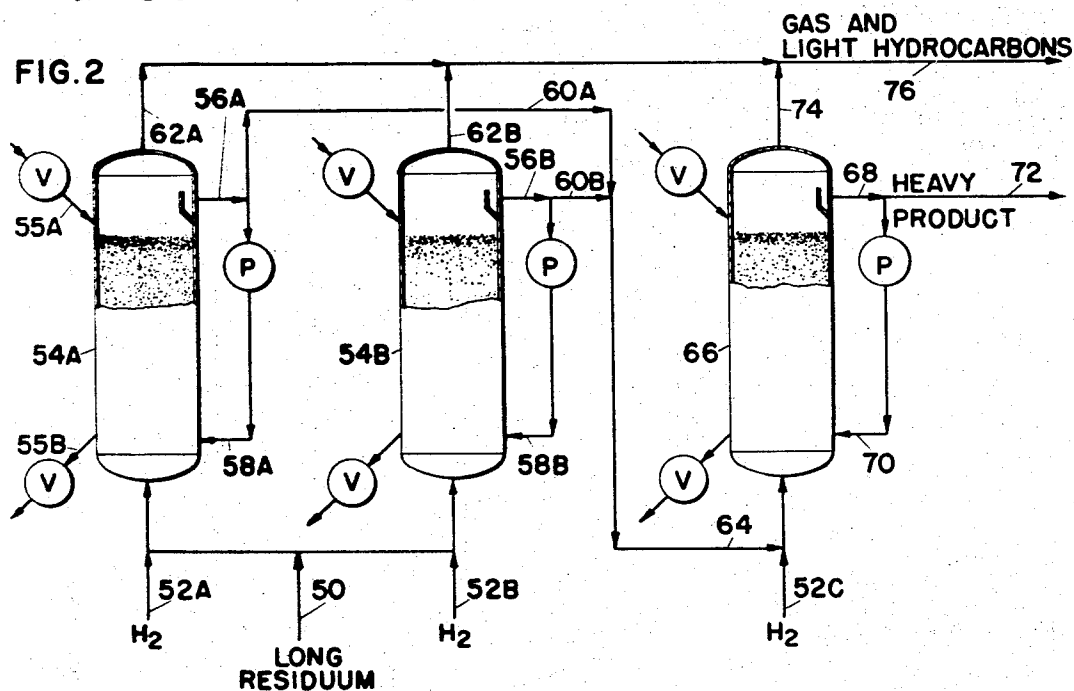


FIG. 2



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HIGH CONVERSION HYDROGENATION

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Continuation of application Ser. No. 418,702, Dec. 16, 1964. This application Feb. 16, 1967, Ser. No. 632,851
5 Claims. (Cl. 208—59)

ABSTRACT OF THE DISCLOSURE

A multiple stage, ebullated bed hydrogenation of a residuum feed material with relatively low conversion per stage and interstage removal of reaction effluent vapors to produce a high yield of low sulfur fuel oil.

Cross references to related applications

This application is a continuation of our application, Ser. No. 418,702, filed Dec. 16, 1964, now abandoned.

Background of the invention

As is well known to those in the art, furnace oil is the broad middle fraction of an oil comprising kerosene, No. 2 fuel, and diesel fuel; the initial boiling point of this fraction may be about 300° F. and the final boiling point may be about 800° F. Naphtha is the lighter fraction which may be incorporated or reformed into gasoline; this fraction generally has an initial boiling point of about 100° F. and a final boiling point of about 400° F. Under normal conditions of hydrogenation of a long residuum at a conversion of 90%, for example, the ratio of furnace oil to naphtha produced is about one to one. In many geographical areas, such amounts of naphtha are undesirable. In Europe, for example, market conditions are such that the possible production of 25,000 B/D (barrels per day) of naphtha from 50,000 B/D of long residuum would completely eliminate such a plant from consideration. Operation at a lower conversion of residuum is no solution to this problem since then larger quantities of objectionable heavy products will be obtained, leading to excess production of No. 6 fuel oil that has very low value.

In recent years, there has been increasing concern over the presence of industrial waste gases and automobile exhaust fume in the air. This "air pollution" has grown to alarming proportions, especially in the larger, metropolitan areas. One of the causes of the pollution is the high concentration of sulfur compounds in the air due to combustion of industrial fuels. Special emphasis is now being placed on the use of low sulfur fuel oils. Our invention is specifically drawn to a process of producing high yields of such a "low sulfur" fuel oil.

Summary of the invention

This invention is a process of production from a high sulfur residuum feed material, a high yield of low sulfur fuel oil. The purpose of this invention is achieved by carrying out the conversion in a series of hydrogenation steps, each of which is at relatively mild conditions and removing the product vapors overhead between stages while passing the liquid effluent onto the next stage for further treatment.

The use of several stages produces a significant improvement in desulfurization level of the product over

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that which would be obtained from a single stage and the removal of the effluent vapor prevents the further cracking of the desired fuel oil to naphtha.

However, we have now found that low naphtha yields can be obtained with high overall conversion of the residuum feed if the conversion is carried out in a series of steps, each of which is at relatively mild conditions, and if after each conversion stage, the vapors are removed overhead and only the unconverted heavy material is thus further treated.

It should likewise be noted that removal of the vapors between stages is readily accomplished by separating the vapor from the liquid at the top of the reactor at reactor conditions of temperature and pressure. Such a practice is simple and inexpensive. However, we do not wish to be restricted to this possibility and for certain cases may prefer to remove the total reactor effluent to another vessel where the separation may be made. In all cases, however, the separation is made substantially at reactor conditions of temperature and pressure.

It is important to understand that this invention is applicable to a given special market situation extant at a given time in a particular part of the world. In this sense it should not be held in conflict or in contraction to other patent applications and issued patents wherein hydrogenation of heavy hydrocarbons is taught with catalyst in random motion with other objects and objectives. For example, where a reasonably good heavy fuel oil market exists, another type of apparatus may be best employed to operate at residuum conversions much below those taught here. Similarly, in the U.S.A., it would be desirable to produce naphtha for gasoline in relatively large quantities and a still different form of apparatus might be used. However, where markets are poor for both fuel oil and naphtha or gasoline, we have found that the apparatus described herein confers the unexpected benefits and advantages as described.

Further objects and advantages of our invention will appear from the following description of a preferred form of embodiment thereof when taken with the drawing attached, such drawing being illustrative thereof.

Brief description of the drawing

FIG. 1 is a schematic view of a multiple stage hydrogenation process.

FIG. 2 is a schematic view of a modified type of multistage hydrogenation process.

Description of the preferred embodiment

In accordance with our invention, a heavy hydrocarbon charge such as Kuwait long residuum at 10, together with hydrogen at 12A, is introduced into a reactor 14 such as shown in the Johanson patent, 2,987,465. Such a reactor will be suitably charged with a catalyst such as cobalt molybdenum oxide on alumina, the particles being of an average size between about 60 mesh and 270 mesh. A small makeup of fresh catalyst is entered with the feed at 38A.

The liquid and gas upflow through the bed of catalyst is such that it will tend to expand the catalyst bed at least 10% based on the bed volume without fluid flow, and such that the particles are all in a random motion in the liquid. In such condition, they are described as "ebullated" in the said Johanson patent.

As stated therein, it is a relatively simple matter to operate any particular process so as to cause the mass of contact material employed to become ebullated and

to calculate the percent expansion of the ebullated mass for any given set of reaction conditions. In most processes carried out in accordance with this invention, the expanded volume of the ebullated mass will exceed by 10% but not more than about 100% the volume of the settled mass.

Under the preferred conditions of temperature, pressure and throughput as hereinafter set forth, a vapor effluent is removed at 16 and a liquid effluent is removed at 18 from the upper portion of the reaction zone 20. The liquid is then conducted to the second stage reactor 22.

Similar operations are carried out in the second stage reactor. The liquid feed at 18 joins with additional hydrogen at 12B and passes upwardly through the same or a similar type of catalyst. Small amounts of additional makeup catalyst may also be added at 38B. A gaseous effluent is removed at 24, and a liquid at 26 from the upper portion of the reaction zone 28.

In FIG. 1, we have also shown a third reactor 30 which similarly is filled with catalyst through which the liquid 26 from the second reactor and added fresh hydrogen in line 12 may pass upwardly at "ebullated" bed conditions. Similarly, makeup catalyst is added at 38C, a vapor effluent is removed overhead at 32 and a heavy product 34 is removed from the upper part of the reaction zone, generally designated 36.

Usually, three stages of conversion are preferred; at least two are required, and normally not more than four are helpful.

From the last stage, in this case reactor 30, the vapor effluent removed at 32, joins with the other vapor effluents at 16 and 24 and passes in a well known manner (not shown) to recovery apparatus in which the hydrogen is separated from the light hydrocarbons and from the other gases such as hydrogen sulfide, such hydrogen being available as recycle. The light hydrocarbons may be then distilled or treated by conventional means to recover light products.

The heavy liquid product at 34 is the reacted, desulfurized liquid. This, in turn, will pass to suitable fractionation equipment for further treatment if necessary, to meet specification products.

FIG. 2 is a second possible embodiment of our invention in which the contact particles are approximately of a size passing through $\frac{1}{4}$ " mesh openings but retained by $\frac{1}{32}$ " mesh openings (i.e., between about 3 and 20 mesh screens on the Tyler scale). In this case, the quantity of feed is sufficiently large that parallel first stage reactors are employed. About half of the feed (again, for example, Kuwait long residuum) is fed from 50 into reactor 54A, with the remaining half into reactor 54B. Hydrogen is fed with the feed through lines 52A and 52B, respectively. The catalyst beds in reactors 54A and 54B are ebullated as described previously for FIG. 1. However, in this case, the larger sized particles of nickel molybdate catalyst required a higher liquid velocity than can be obtained from the feed alone to effect ebullating conditions; such liquid velocities are obtained by recycle of the hot reactor liquid effluent as shown by lines 56A and 58A for reactor 54A, and 56B and 58B for reactor 54B, respectively. In each reactor, the liquid velocities are controlled to obtain the 10% to 100% bed expansion as previously obtained in the example of FIG. 1.

The net liquid effluent from reactor 54A proceeds through line 60A, is joined with the net liquid effluent from reactor 54B issuing through line 60B, and then passes through line 64 to enter reactor 66. Hydrogen is also supplied to reactor 66, through line 52C. Reactor 66 is filled with beads of nickel molybdate catalyst of about 0.03" diameter. The catalyst bed is again ebullated with liquid velocities again augmented by use of a hot liquid recycle pumped as shown from line 68 through line 70 and then back into the reactor. The net effluent from reactor 66 is again separated at the top of the

reactor into a vapor effluent which issues through line 74 and a liquid effluent issuing through line 72.

Small amounts of makeup catalyst may be added periodically to any of the reactors 54A, 54B, or 54C through appropriate catchpots. Corresponding amounts of spent catalyst may similarly be withdrawn from said reactors. Valved lines 55A and 55B indicate this control.

The vapor effluents from the reactors may be combined as shown in FIG. 2 and withdrawn in line 76. The combined vapor effluent is then treated conventionally to separate out the light normally liquid hydrocarbons as products, light gaseous hydrocarbons which may be used as fuel, hydrogen sulfide which may be converted to elemental sulfur and a hydrogen stream which is recycled back to the reactors.

The net liquid effluent issuing from 72 may likewise be conventionally treated by distillation to recover individual valuable desulfurized products including a high yield of furnace oil, the product most highly desired in the situation satisfied by this invention.

It will, of course, be recognized that the recycle lines 56A, 56B, and 68, which are shown as external lines for clarity, may just as readily be internal within the reactor. It will also be recognized that all of the effluent could be removed from the upper part of the reactor and the liquid-gas separation be accomplished in an external separator.

Preferred operating conditions for this invention are reaction temperatures in the range of 800 to 900° F., a total pressure in the range of 1,000 to 3,000 p.s.i.g., a total space velocity for the several reaction zones of at least 0.25 v./hr./v., in the presence of hydrogen under a partial pressure of at least 1,000 p.s.i. and with a hydrogen rate of less than 6,000 standard cubic feet per barrel of feed entering each reaction stage. Since the removal of vapor between stages likewise removed hydrogen, additional hydrogen must be provided for the after-stages; however, in no case will this exceed 6,000 standard cubic feet per barrel of feed entering the stage.

Most catalysts in the class of those used for hydrogenation or hydrosulfurization will be at least partially effective for this invention. A preferred catalytic composition comprises nickel or cobalt together with molybdenum deposited on a support of alumina. However, as is well known, many other metals, metal oxides and metal sulfides may produce similarly desirable results, as will many other supports, such as clays, bauxites and other natural ores or synthetic compositions including silica, magnesia and the like.

EXAMPLE 1

This example illustrates the use of this invention in accordance with FIG. 1, but with only two stages used instead of the three shown in FIG. 1.

The feed was Kuwait atmospheric residuum corresponding to the bottom 36% of the crude. This feed had a gravity of 10.9° API and a sulfur content of 4.66 weight percent.

The feed was hydrogenated over a catalyst composed of cobalt and molybdenum sulfides supported on alumina. The catalyst was of a size averaging 200 mesh with only very small amounts finer than 325 mesh. The catalyst was ebullated by the feed to obtain a bed expansion of about 50%. The apparatus was operated with the liquid effluent from the first reactor separated from the vapor effluent, with only the liquid (together with added hydrogen) passing to the second stage. Other operating conditions were:

Total pressure	-----p.s.i.g.	2,500
Hydrogen pressure	-----p.s.i.g.	2,000
Reaction temperature	-----° F.	835
Space velocity	-----v./hr./v.	0.75
Gas rate	-----s.c.f./bbl.	8,700
Makeup catalyst rate	-----lb./bbl.	0.12

Operating results were as follows:

	Yield, Percent of Charge	Gravity, ° API	Sulfur, Weight Percent
Light Gas, C ₁ -C ₃ , Weight Percent.....	3.2	-----	-----
Naphtha, C ₄ -392° F., Volume Percent.....	12.9	65.6	0.05
Furnace Oil, 392°-750° F., Volume Percent.....	36.2	32.0	0.48
Heavy Gas Oil, 750°-1,050° F., Volume Percent.....	41.6	20.0	1.07
Tar, 1,050° F.+, Volume Percent.....	13.9	3.0	2.31
Total Liquid Product, C ₄ +, Volume Percent.....	104.6	26.1	0.94

These results showed an excellent yield of kerosene and furnace oil (36.2 volume percent) compared to naphtha (12.9 volume percent). All products were highly desulfurized compared to the feed (4.66 weight percent sulfur) and were of good quality as indicated by their API gravities. The yield of tar was small and the total liquid product yield 104.6% on a volumetric basis. The unexpected result was a gravity of 3° API for the tar, compared to negative API gravities (higher specific gravities) usually obtained without staging of the liquid as practiced in this invention. Such a high API gravity indicates a considerable amount of hydrogen has been consumed to enter the tar and consequently that the tar could be further hydrogenated in a third stage to ultimately yield an even smaller yield of tar and heavy fuel oil (and correspondingly an even higher yield of kerosene and furnace oil) than shown in this example.

EXAMPLE 2

Example 2 illustrates the use of this invention as in FIG. 2, however, with two stages in series, rather than in FIG. 2 where there is shown two stages in parallel followed by a stage in series. Thus, the basic difference between Example 1 and Example 2 is the use in Example 2 of a catalyst of 1/32" extrudates of cobalt and molybdenum sulfides supported on alumina which are ebullated to provide a bed expansion of 50% with the assistance of the hot liquid recycle streams shown in FIG. 2 as 56A, 58A and the like.

Employing the same feed stock and other operating conditions as in Example 1, the same results will be obtained without staging of the liquid such as that practiced in this invention. Thus, Example 2 will likewise provide high yields of furnace oil, with low yields of naphtha and tar as obtained in Example 1. The choice whether to use catalyst in the size range from 60 mesh to 270 mesh Tyler (Example 1 and FIG. 1) or 1/4" to 1/32" in major diameter (Example 2 and FIG. 2) will depend on specific commercial circumstances, primarily involving a balance between the lower plant cost when using the finer catalyst, and the higher solids content of the heavy product (tar or heavy fuel oil) when using said finer catalyst.

While we have shown preferred forms of embodiment of our invention, we are aware that modifications within the scope and spirit of our invention will occur to those skilled in the art, and such modifications are contemplated to be within the scope of the claims appended hereinafter.

We claim:

1. In a method for producing a low sulfur fuel oil from a sulfur containing crude petroleum charge containing at least about 25 volume percent of components boiling above about 975° F. wherein the charge, in liquid

phase, is passed upwardly through a reaction zone containing a hydrodesulfurization catalyst and a hydrogen rich gas under conditions in which the catalyst is maintained in random motion in the liquid, and wherein the temperature in the reaction zone is maintained in the range of 800° to 900° F. and the total pressure is in the range of 1,000 to 3,000 p.s.i.g., the improvement which comprises:

- (a) separating a gaseous effluent from the liquid effluent from said reaction zone without substantial temperature or pressure change;
- (b) passing the liquid effluent, without substantial reduction in temperature, to a second reaction zone;
- (c) maintaining reaction conditions in the second reaction zone substantially the same as in the first zone;
- (d) the total space velocity for the several reaction zones being at least 0.25 v./hr./v.;
- (e) separating the gaseous effluent from the liquid effluent from the second reaction zone;
- (f) and recovering from the total effluent of the respective reaction zones a liquid component, which liquid component on fractionation yields a typical naphtha boiling range material, a furnace oil boiling range material, a heavy gas oil boiling fraction and a tar residuum;
- (g) the ratio of the total liquid product to feed exceeding 100% and the ratio of furnace oil to naphtha being at least 2 to 1 by weight;
- (h) the sulfur content of the furnace oil fraction being less than 1.0 weight percent.

2. A method of converting a crude petroleum charge as claimed in claim 1, wherein at least 50 volume percent of the material boiling above 975° F. in the charge stock is converted to material boiling below 975° F.

3. A method of converting a crude petroleum charge as claimed in claim 1, wherein there are at least three reaction zones and not to exceed four reaction zones from each of which except the last the liquid effluent separated from one of the reaction zones is passed to the subsequent reaction zone.

4. A method of converting a crude petroleum charge as claimed in claim 1, wherein the catalyst particles are in the size range of from 60 to 270 mesh Tyler and the velocities of the liquid and gas passing upwardly through said reaction zones are sufficient to expand the catalyst particles in said reaction zones at least 10% over their settled volume.

5. A method of converting a crude petroleum charge as claimed in claim 1, wherein the catalyst particles are in the size range of 1/4" to 1/32" in major diameter, the velocities of liquid and gas sufficient to expand the body of catalyst particles at least 10% over its settled volume, and a part of the reactor liquid effluent is recycled to the lower part of said reaction zones without substantial cooling.

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U.S. Cl. X.R.

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