March 13, 1962 D. D. MacLAREN 3,025,230

HYDROGENATION OF SHALE OIL

Filed Nov. 9, 1959 2 Sheets-Sheet 1

EFFECT OF FEED VAPORIZATION ON NITROGEN REMOVAL
825°F., 1 V/V/HR. LIQUID SPACE VELOCITY OF SHALE OIL

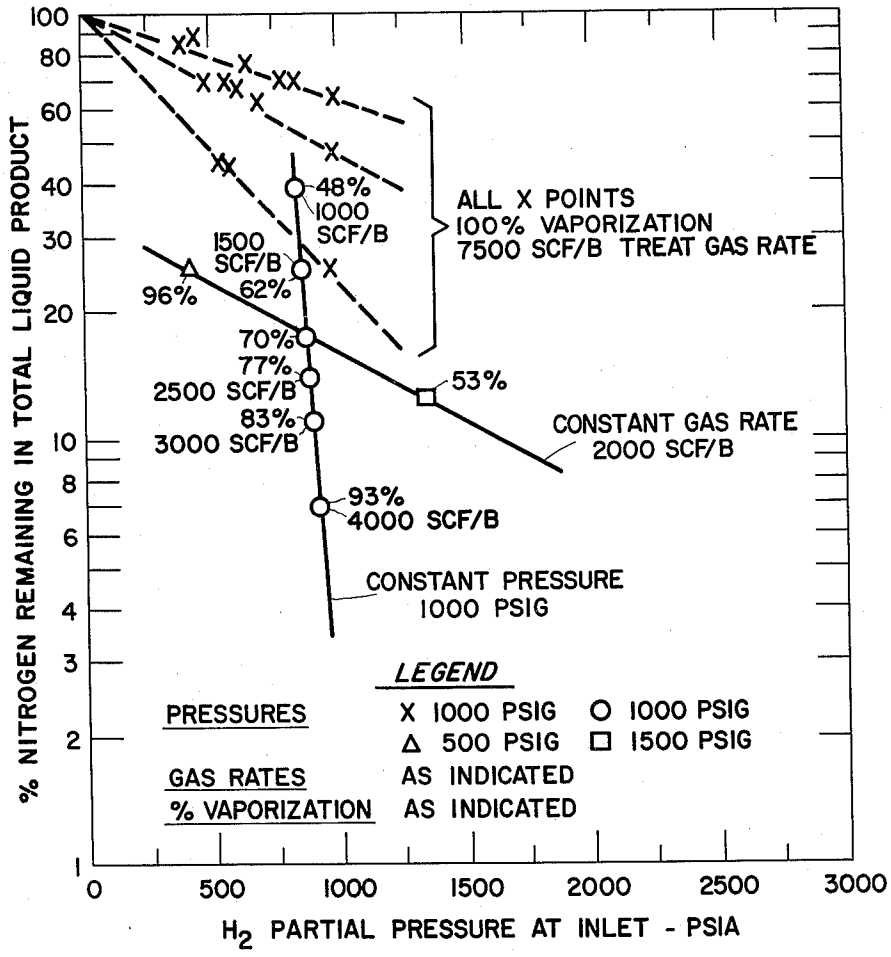


FIGURE 1

Donald D. MacLaren Inventor

By Henry Berk
Attorney

March 13, 1962 D. D. MacLAREN 3,025,230

HYDROGENATION OF SHALE OIL

Filed Nov. 9, 1959 2 Sheets-Sheet 2

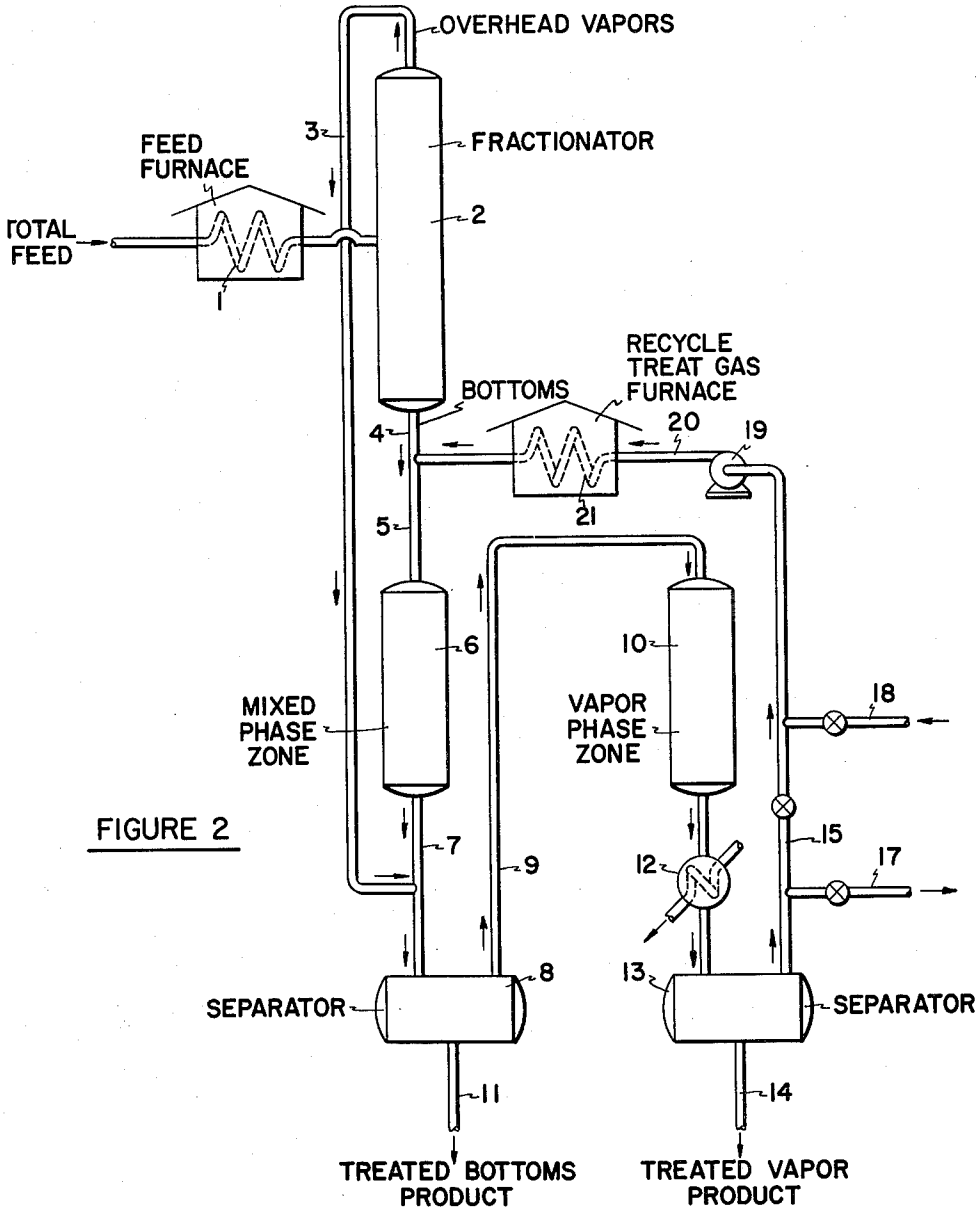


FIGURE 2

Donald D. MacLaren Inventor

By Henry Berk

Attorney

United States Patent Office

3,025,230

Patented Mar. 13, 1962

3,025,230

HYDROGENATION OF SHALE OIL

Donald D. MacLaren, Scotch Plains, N.J., assignor to Esso Research and Engineering Company, a corporation of Delaware

Filed Nov. 9, 1959, Ser. No. 851,595
4 Claims. (Cl. 208—210)

The present invention relates to a process and system for effecting removal of nitrogen from shale oil which distills in the range of 350° F. to 1000° F.+ by catalytic hydrogenation treatment.

In accordance with the present invention increased nitrogen removal from shale oil is attained by fractionating the shale oil into a vaporized overhead fraction and a bottoms fraction, hydrogenating the bottoms fraction in a first catalytic reaction zone employing total recycle treat gas to effect as much vaporization as possible in said zone, then admixing with the effluent from said first reaction zone the vaporized overhead fraction to obtain a gas-vapor mixture which is passed through a second catalytic hydrogenation zone.

In the first reaction zone the bottoms fraction is treated in a mixed liquid-vapor phase passed downwardly through a bed of hydrogenation catalyst. In forming the gas-vapor mixture by commingling the treated bottoms and gas with the vaporized overhead fraction of the shale oil, condensation of the treated bottoms takes place, and the condensate is withdrawn as product to prevent forming a mixed phase in the second reaction zone.

The desirability of removing nitrogen from shale oils is known and various methods for accomplishing the removal by hydrogenation have been described, as in an article of W. M. Smith et al. in "Ind. Eng. Chem.," 44, 586 (1952). However, in conventional hydrogenation of a total crude shale oil or wide boiling distillate thereof high boiling components, e.g., those boiling above 800° F., high reaction temperatures are required with resulting high coke formation and rapid catalyst deactivation. Alternatively, large volumes of catalyst are required at lower temperature levels.

In the accompanying drawings:

FIG. 1 shows plotted data regarding the effect of vaporization through varied treat gas rates on the removal of nitrogen of a shale oil.

FIG. 2 is a simplified flow diagram illustrating a preferred system for practicing the invention.

The amount of nitrogen removal from shale oil at a given set of operating conditions is found to be considerably increased by increasing the amount of vaporization. This is clearly indicated in FIG. 1. Two sets of data on hydrogenating a shale oil are shown. The first, obtained with varying activity poor quality catalysts, were under conditions which gave 100% vaporization of the feed by using fixed high amounts of treat gas, 7500 s.c.f./b. (these are the data points represented by X's on the broken lines). Under these conditions a linear relationship between the log of wt. percent nitrogen remaining in the final liquid product and the hydrogen partial pressure in the reaction is indicated. However, with a more active catalyst this relationship no longer holds. With more active catalyst, using varied treat rates, it was observed that at a given total pressure (1000 p.s.i.g.) there was a marked decrease in the amount of nitrogen remaining as the gas rate was increased from 1000 to 4000 s.c.f./b. (These are the points represented by circles on the unbroken line, with the percent vaporization indicated.) This different relation with change of treat gas rate held despite the fact that hydrogen partial pressure changed very little over this range. This is contrary to data obtained at a constant gas rate of 2000 s.c.f./b. where increasing hydrogen pressure from 500 to 1500 p.s.i.g. caused a relatively small decrease in percent nitrogen in the liquid product. This apparent discrepancy can be explained on the basis of the percent vaporization occurring under each set of conditions as indicated in FIG. 1. The greater the percent vaporization, the smaller the quantity of nitrogen remaining in the liquid product at a given hydrogen partial pressure. This clearly indicates that maximum nitrogen removal is obtained by maximizing the percent vaporization. Conversey, a reduced amount of catalyst is required to obtain a given amount of nitrogen removal by maximizing the percent vaporization.

Unfortunately, maximizing vaporization by increasing gas rate is expensive because of the large quantities of recycle gas which must be pumped through the reactor. However, the need for such high gas rates to maximize vaporization can be avoided. This is accomplished by splitting the feed into vapor and liquid fractions with relation to the amount of treat gas being used in the process and conditions under which each fraction is to be treated. The heavy nonvaporized portion of the feed is contacted in a mixed liquid-vapor phase with the total treat gas. Since the nonvaporized portion represents only a small fraction of the total liquid, the effective treat gas rate on this fraction is increased several-fold thereby vaporizing a considerable portion of normally liquid material. This mixture of vapor and liquid is passed through a first reaction zone where the advantage of having the larger amount of vaporization results in greater nitrogen removal.

Since the normally liquid portion is treated to remove nitrogen to an acceptable extent in the first zone, there is no need to pass the liquid portion through a second reaction zone. Consequently, at this point the remaining vapor portion of the feed is combined with the first reactor effluent under conditions for condensing high boiling components undesired in the feed to the second reaction zone. The condensate and unvaporized liquid from the first zone is withdrawn from the system and leaves a completely vapor mixture of feed and treat gas to be passed to the second zone for nitrogen removal.

Product from the second zone is condensed and may be combined with that from the first zone to produce the total denitrogenated product. In this way a maximum total vaporization is obtained thereby increasing the amount of nitrogen removal under a given set of process conditions.

Typical inspections of a total crude shale oil and of a 70% overhead crude shale oil distillate are given in the following table.

TABLE I

Hydrogenation Operations Shale Oil Feed Inspections Averaged Values

Feed	Total Shale Oil	70% O.H. Shale Oil
Gravity, ° API	19.6	23.3
Conradson Carbon, Wt. percent	4.3	0.7
Nitrogen, Wt. percent	1.88	1.47
Sulfur, Wt. percent	0.68	0.53
Carbon, Wt. percent	84.3	82.7
Hydrogen, Wt. percent	11.3	11.5
H/C Atomic Ratio	1.61	1.67
Pour, ° F		60
Distillation, D-1160:		
Init., ° F	360	358
5%	478	456
10%	535	501
20%	604	563
30%	664	618
40%	730	664
50%	785	711
60%	831	752
70%	879	792
80%	941	822
90%		858
95%		876

It is to be noted that the shale oil feeds to be treated contain from about 1.5 to 2.0 wt. percent nitrogen. The total shale oil feeds can be fractionated at temperatures up to about 875° F. to take overhead at least 75% of the shale oil feed and leave a 25% bottoms fraction. The bottoms fraction and residue contain components difficult to vaporize below 875° F. These figures are averaged values since there are some variations in the distillation characteristics of the various shale oils.

The catalysts used for the hydrogenation are known catalysts that resist poisoning, particularly by the non-hydrocarbon constituents. These catalysts are typified by nickel sulfide-tungsten sulfide, molybdenum sulfide, molybdenum oxide, and combinations of metal oxides, e.g., ferric oxide, molybdenum oxide, and cobalt oxide. A preferred catalyst, known as cobalt molybdate on alumina, is represented by the formula:

$$CoMoO_4 \text{ on } Al_2O_3$$

The temperature and pressure conditions used in this invention are similar to those for hydrogenating shale oil in conventional mixed phase operation. The pressure range can be 200–3000 p.s.i.g., the preferred level being about 800 p.s.i.g. The treat gas rates can vary from 1000 to 10,000 s.c.f./b., the preferred rate ranging from 2000 to 6000 s.c.f./b. depending on the boiling range of the feed stock. The temperature of operation is in the range of 700–900° F., the preferred range being about 775°–825° F. to maximize nitrogen removal while minimizing the rate of catalyst deactivation and need for regeneration. Catalyst space velocity requirements are in the range of 0.1–5 v./v./hr. in terms of liquid feed. The exact quantities will depend on the feed boiling range in question as will be described later.

The liquid hourly space velocity (v./v./hr., i.e., volume of liquid feed/volume of catalyst/hour) required in vapor phase operation for a given nitrogen removal is markedly lower than in liquid phase operation. For instance, in vapor phase operation a space velocity of 1 v./v./hr. might suffice. On the other hand, in liquid phase operation a space velocity as low as 0.2–0.3 v./v./hr. would be required for equivalent nitrogen removal.

Because of this difference in the relative reaction rates in liquid and vapor phase, the catalyst distribution in the two zones of this invention is not in proportion to the amount of feed passed through the zone. For example, in the first reaction zone where a liquid phase will be present, a greater relative quantity of catalyst will be required to achieve a given percent nitrogen removal. Conversely, in the second all vapor phase operation, a lesser quantity of catalyst can be used to obtain this level of nitrogen removal. Accordingly, the catalyst between the two zones is split so that about ½ to ⅔ of the catalyst is included in the first reactor, and ½ to ⅓ in the second zone when treating a feed in which about 25% bottoms would normally be in the liquid phase. The exact split of catalyst will depend on the relative quantities of liquid and vapor in the particular feed stock.

In the first reactor where the bottoms fraction from the prefractionator is treated in mixed liquid-vapor phase with the total H_2-containing treat gas, the preferred reaction temperature should be generally somewhat higher than in the second reactor in which vapors from the treated bottoms and uncondensed overhead vapors from the prefractionator are treated under a lower partial pressure of hydrogen in the vapor phase.

For instance, in the first reactor the reaction temperature is preferably in the range of 800° to 875° F. with approximately 50% of the bottoms (¼ of initial feed to the prefractionator) vaporized in the first reactor, the H_2 partial pressure is in the range of 600 to 650 p.s.i.a. using 3000 to 6000 s.c.f./b. of treat gas based on the initial feed to the prefractionator.

While conditions in the second reactor have some dependence on those in the first reactor, there is room for variations, e.g., by changing the volume rate of flow through the second reactor. The conditions in each reactor can thus be brought to an optimum for any given starting feed and for a given catalyst in attaining the objective of producing a gas oil (430° to 900° F.) of improved quality in lowered nitrogen content for use as a catalytic cracking feed with minimum formation of degradation products, such as coke. In line with obtaining this treatment, the present invention essentially provides for more treatment of the oil in vapor phase and shorter time of heating at high temperaures under conditions that lead to degradation. It provides more efficient fast heat exchange where the vaporized fraction from the prefractionator commingles with higher temperature effluent from the first reactor to act as a quench. In this commingling the highest boiling components, e.g., boiling above 800° F., are condensed and the heat evolved from the condensation is quickly absorbed by the remaining vapors and gases that flow to the second reactor.

In the second reactor uncondensed vapors of the prefractionator overhead and of the treated bottoms effluent from the first reactor are treated as a vapor at a temperature level equal or lower than that in the first reaction zone, e.g., 450°–800° F. The hydrogen partial pressure in this second zone is somewhat lower than in the first because of the increase in hydrocarbons present. The exact level will depend on the split between liquid and vapor in the original feed stock. The lower temperature in this zone is preferred to reduce catalyst deactivation at the reduced treat gas rate.

In FIG. 2 of the drawing, the shale oil feed boiling from about 350° to 1000° F. is heated in a preheating furnace coil **1** to a temperature of 850° F. or in the range of 750° to 850° F. then passed into the flash vaporizing drum **2**, wherein more than 60% of the preheated oil is vaporized. The vaporized oil is rapidly taken overhead at a vapor temperature of 800° F., or in the range of 700° to 825° F., through line **3**. The unvaporized oil bottoms at 825° F. is withdrawn continuously and rapidly from the bottom of drum **2** by line **4**. Drum **2** may be in the form of a fractionating column with one or a few plates and preferably imposing little holdup time as in a flash vaporization.

The hot liquid bottoms at 825° F. is passed by line **4** to a feed inlet **5** of the first reactor **6** which contains the hydrogenation catalyst that amounts to from ½ to ⅔ of total catalyst used in the system.

Hydrogen-rich treat gas preheated in furnace coil **7** to a temperature suitable for reaction, e.g., 825° F., is admixed with the bottoms entering at the top of reactor **6**. This gas is the total treat gas recirculated through the system and may amount to from 1000 to 10,000 standard cubic feet per barrel (s.c.f./b.) of total oil feed to the prefractionator, depending on the amount of treating required. Considering that the bottoms from drum **2** is 25 vol. percent of the total oil feed to drum **2** and the total treat gas used is 6000 s.c.f./b., then ¼ of the total oil is admixed with 24,000 s.c.f./b. of treat gas.

The reaction mixture of oil in liquid and vapor phase with treat gas is passed preferably downflow through reactor **6** at an average temperature of 825° F. and under suitable pressures, e.g., 800 p.s.i.g. with adjusted rate of flow of the liquid vapor and gas for the amount of catalyst in the reactor **6**, a suitable space velocity, e.g., 1 v./v./hr., is maintained.

The reaction mixture product of unvaporized bottoms oil vapors and gas is withdrawn as effluent from reactor **6** through line **7**, e.g., at a higher temperature than the inlet because of the hydrogenation which occurs, e.g., about 875° F., and commingled with vapor from line **3** then passed to the hot separator **8**. In this step a rapid heat exchange takes place. Some of the high boiling vapor components undergo condensation, thereby supplying heat to the remaining vapors and gases which are taken off at about 800° F. from the separator by line **9**

to the second reactor **10**. The liquid oil is withdrawn through line **11** and removed from the system.

In reactor **10** containing the remainder of the total catalyst, e.g., ½ to ⅓ thereof, the oil substantially all in vapor phase is passed with the treat gas at an average of 825° F. under suitable pressure and at a suitable flow rate for the desired refining.

Effluent vapor products and gas from reactor **10** are passed for cooling and condensation by line **11** through condenser **12** to a pressure separator where C_4+ hydrocarbons obtained as liquids, e.g., at 100° F., are withdrawn through line **14**. The remaining treat gas is withdrawn from separator **13** through line **15** for recycling by compressor **19**. Portions of the treat gas are withdrawn by line **17** for separation of undersired nitrogen (NH_3) and sulfur compounds and this gas is replaced by higher purity treat gas from line **18**. The treat gas of sufficient purity is returned by line **20** through the heating coil **21** to the first reactor.

Most of the refined gas oil product, kerosene and gasoline are collected as liquid condensate in **13**. This condensate may then be sent to a stripping column for stripping off hydrocarbons boiling below the gas oil boiling range, e.g., at temperatures below 430° F. Some heavy gas oil components are collected in separator **8** and can be stripped from the heavier oil, e.g., at temperatures in the range of 800° to 900° F. A combined gas oil product having a nitrogen content of less than 0.20 wt. percent is thus obtained, starting with an initial feed that contains 1.6 wt. percent. This is a definite improvement over processes in which more oil in liquid phase is contacted at the same reaction temperatures, with the same amount of catalyst, and with the same amount of treat gas.

Two examples according to the teaching of this invention follow:

EXAMPLE 1

The first is based on data on the effect of treat gas rate on nitrogen removal from a coker distillate containing 1.6 wt. percent nitrogen from a total shale oil when processed over cobalt molybdena on alumina catalyst comparing a conventional procedure (case I) of mixed phase contact throughout with the present invention procedure which gives increased vapor content.

Conditions, overall comparative:

Temp., ° F	825
Pressure, p.s.i.g	1000
Treat gas, s.c.f./b	2000
Space velocity, v./v./hr	1

Results from—	Case I, Conventional	Case II, Increased vapor content
Nitrogen removal, percent	82	90
Wt. percent nitrogen left in liquid product	.29	.16
v./v./hr. for .16 wt. percent nitrogen left	0.7	1.0

Passing all the treat gas and the liquid 30% bottoms through the first zone vaporizes 50% of the bottoms and increases the nitrogen removal from 82 to 90% overall (.16 vs. .29 wt. percent nitrogen remaining). This is a very substantial increase considering that 40% more catalyst would be required in the conventional process to reach the same nitrogen level.

EXAMPLE 2

Similar improved results are shown for a 1000° F. end point shale oil treated according to the method of the present invention which gives maximum contact of vapor with catalyst (case II) with a conventional type procedure (case I) in which a substantial larger amount of liquid contacts the catalyst, as by condensation and internal recycling.

Conditions, overall comparative:

Temp., °F	825
Pressure, p.s.i.g	800
Treat gas, s.c.f./b	6000
Space velocity, v./v./hr	1

Results from—	Case I, Conventional	Case II, Increased vapor content
Nitrogen removal, percent	85	92
Wt. percent nitrogen left in liquid product	0.28	0.15
v./v./hr. for 0.15 wt. percent nitrogen left	0.7	1.0

Steps used in the described process of the invention which aid in obtaining the improvement of better yields of high quality gas oil product and making limited amounts of coke are summed up as follows.

The amount of oil treated in vapor phase is maximized by using all the treat gas on a high boiling fraction with internal recycling of liquid prevented.

The amount of oil treated in liquid phase and subjected to high temperatures is minimized, particularly by preventing internal recycling of highest boiling components through the reaction zones, since these components pass only once down through the first reactor, and by commingling the prefractionator vapors as a quench with effluent from the first reactor, thus giving an efficient direct heat exchange through condensation of the highest boiling components which are prevented from going to and condensing in the second reactor.

The invention described is claimed as follows:

1. In a process of hydrofining a shale oil boiling in the range of about 350° F. to 1000° F.+, the improvement which comprises preheating the shale oil feed to an elevated temperature high enough to vaporize a major proportion thereof, separating a resulting vaporized fraction from a remaining liquid fraction of the feed oil, passing the said liquid fraction at elevated temperature mixed with total hydrogen-rich treat gas down through a hydrogenation catalyst contained in a first reaction zone under hydrogenation conditions for nitrogen removal which cause vaporization of a part of said liquid fraction, commingling said vaporized fraction of the feed oil with effluent gas, vapor and liquid from the first reaction zone for heat exchange of thus commingled substances and condensation of highest boiling components of the effluent from the first reaction zone, passing remaining vapors and gases substantially free of liquid from said commingling through a second reaction zone containing hydrogenation catalyst under hydrogenation conditions for nitrogen removal.

2. In hydrogenating a shale oil to remove nitrogen and sulfur containing contaminants, 60 to 80 vol. percent said oil boiling to about 800° F. and 20 to 40 vol. percent boiling above 800° F., the improvement which comprises vaporizing a lower boiling 60 to 80 vol. percent fraction of said shale oil feed at about 750° to 850° F., passing a resulting higher boiling unvaporized fraction of said feed oil in mixed liquid-vapor phase under hydrogenation conditions for nitrogen removal with hydrogen-containing treat gas in sufficient proportion to vaporize part of the oil mixed with the gas passed down through a hydrogenation catalyst-filled first reaction zone, mixing said vaporized fraction of the feed oil with higher temperature effluent liquid oil, vapor, and gas from said first reaction zone to condense out highest boiling vapors in said first reaction zone effluent which boil substantially above 800° F. and impart heat to remaining oil vapors and gas, passing said remaining oil vapors and gas free of liquid oil and of said condensed vapor into contact with a hydrogenation catalyst in a second reaction zone under nitrogen removing conditions to hydrotreat said remaining oil vapors.

3. In the hydrogenation of claim 2, said higher boiling unvaporized fraction of the shale oil feed mixed with

the treat gas being hydrogenated in mixed liquid-vapor phase at about 800° to 850° F. in flowing downwardly in the first zone, the vaporized lower boiling fraction of the feed oil being at a temperature in the range of about 750° to 800° F. on mixing with the higher temperature effluent of the first reaction zone, and said remaining oil vapors and gas being contacted with the hydrogenation catalyst in said second reaction zone at lower hydrogen partial pressure, lower average reaction temperature, and higher space velocity than used in the first reaction zone.

4. In hydrotreating a hydrocarbon oil feed boiling in the range of 350° F. to 1000° F.+ having nitrogen-containing contaminants and using a hydrogenation catalyst, hydrogen-containing treat gas and hydrogenating conditions for nitrogen removal, the improvement which comprises heating the hydrocarbon oil feed to an elevated temperature high enough to vaporize a major proportion thereof, separating the resulting vaporized portion from the higher boiling liquid portion of the feed, passing the latter in admixture with all of the hydrogen-containing treat gas through a first reaction zone containing part of the catalyst under hydrogenating conditions capable of effecting substantial vaporization of said liquid feed, mixing a lower boiling portion of said feed in vapor phase with hot total effluent from said first reaction zone to quench the effluent from the first reaction zone and condense at least a portion of the vaporous components that were formed therein separating the liquid components from the hot mixture of vapors and gases formed so that these liquid components are not brought further into contact with the catalyst in said reaction zones and passing the hot mixture of vapors and gases through a second reaction zone containing hydrogenation catalyst under hydrogenating conditions.

References Cited in the file of this patent

UNITED STATES PATENTS

2,844,517 Inwood ---------- July 22, 1958