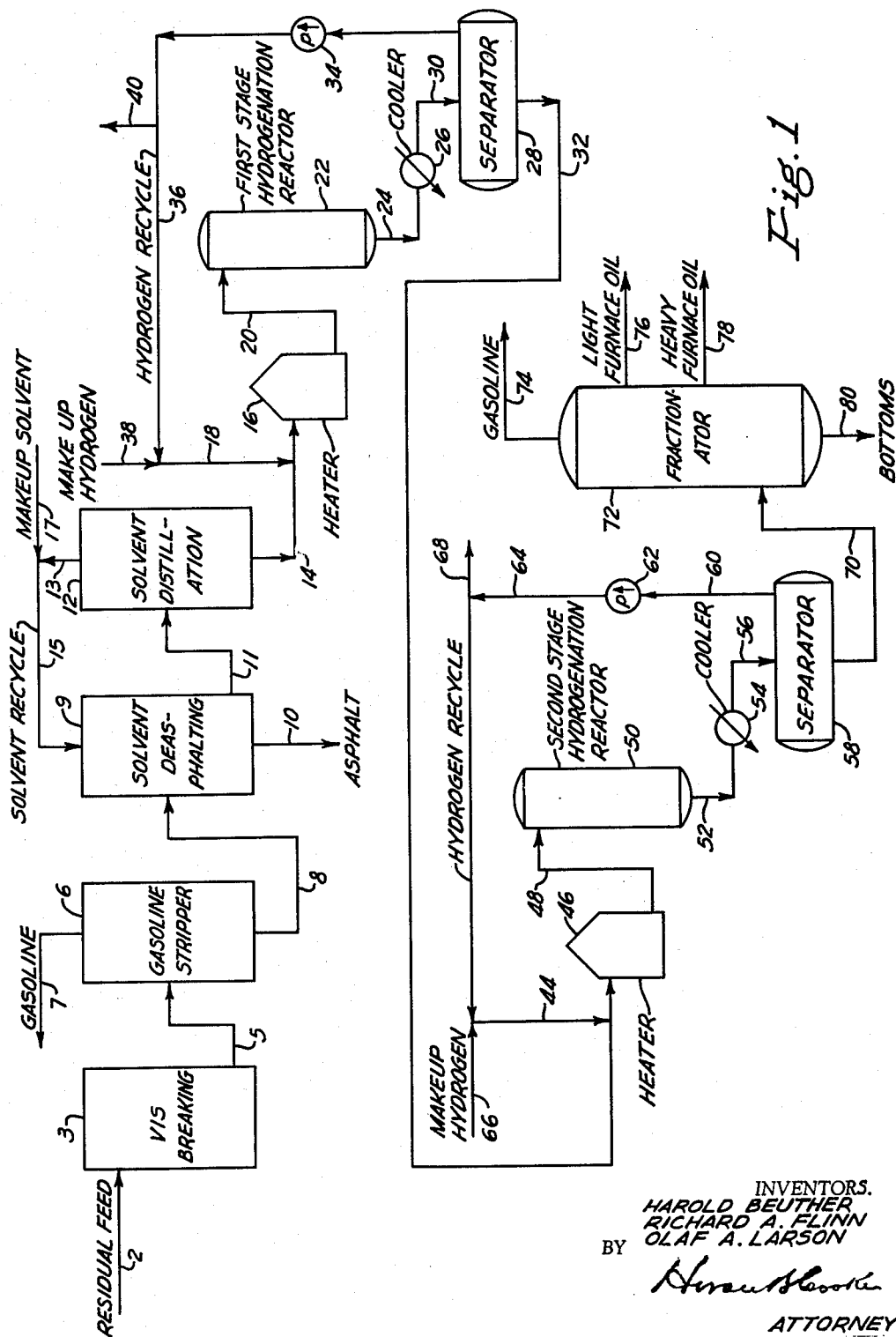


3,132,088

2 Sheets-Sheet 1



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VISBRAKING, DEASPHALTING AND HYDROGENATION OF CRUDE OILS

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2 Sheets-Sheet 2

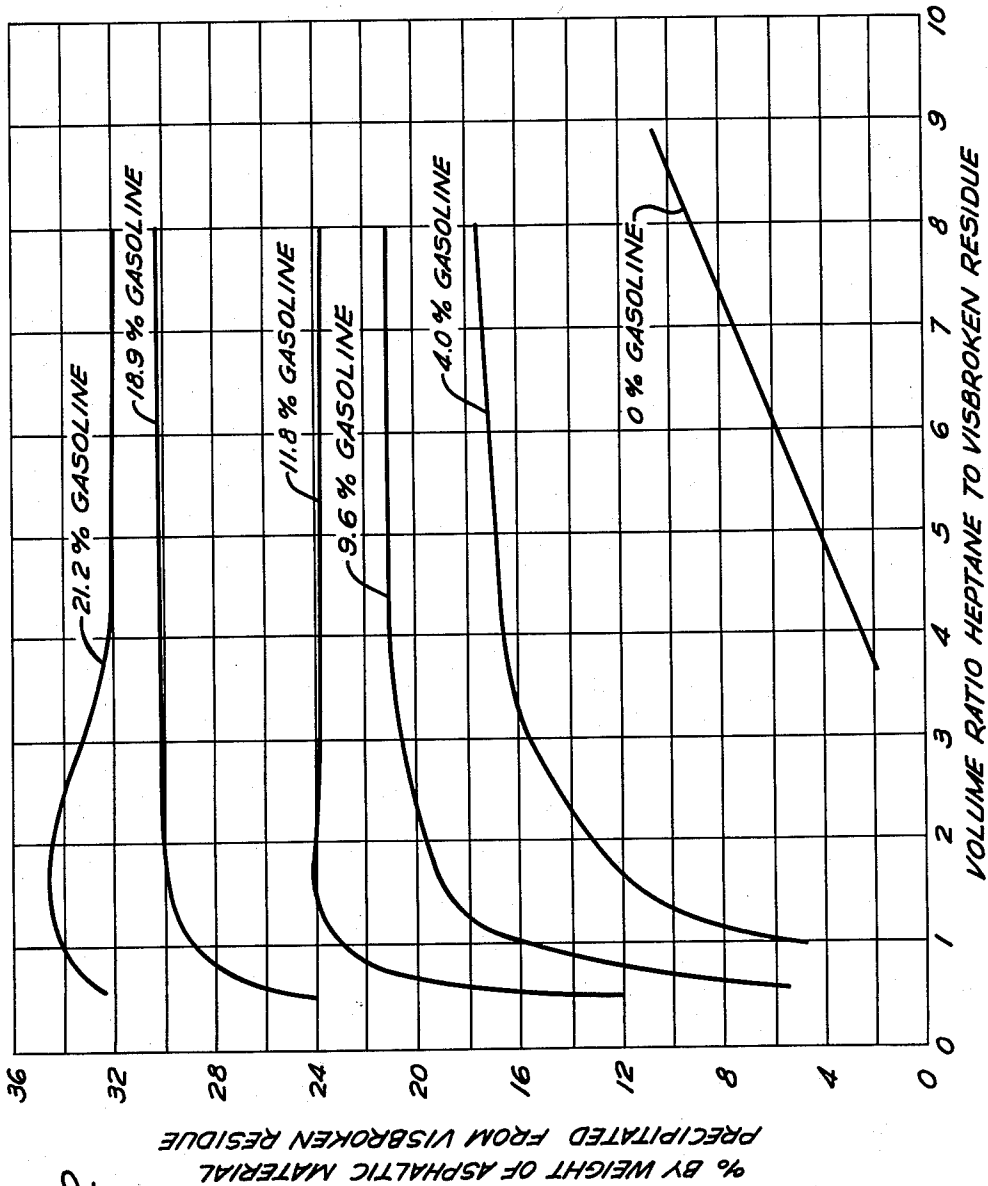


Fig. 2

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3,132,088

VISBREAKING, DEASPHALTING AND HYDROGENATION OF CRUDE OILS

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1 Claim. (Cl. 208—67)

This invention relates to the treatment of heavy hydrocarbons and in particular to the preparation of more valuable hydrocarbons from heavy hydrocarbon stocks which contain asphaltic materials.

Heavy crudes such as those which contain asphaltic materials and which have an API gravity below about 20° or topped or reduced crudes containing asphaltic materials are of low value. Conversion of these heavy asphaltic materials into hydrocarbons of higher value has been accomplished but such procedures are usually expensive or in many cases have undesirable aspects. For instance, it is known to hydrogenate such asphaltic materials to form catalytic cracking stocks. However, thorough conversion of asphaltic components, sulfur and metal compounds etc. is not obtained unless very high pressures are employed. If moderate pressures of about 1,000 p.s.i. are used, the subsequent catalytic cracking is not economical because of rapid deposition of coke on the cracking catalyst from the unconverted asphaltic materials. Also, metalliferous components are unconverted and poison the cracking catalyst. If the product from this moderate pressure process is distilled to obtain a distillate catalytic cracking stock, the yield of this stock is low. It is also known to deasphalt such heavy stocks and then subject them to a mild hydrogenation such as at about 1,000 p.s.i. However the yields of useful products from such procedures have also been relatively low.

This invention has for its object to provide improved procedure for preparing valuable hydrocarbon products from heavy asphaltic containing crudes or fractions thereof. Another object is to provide improved procedure for combined deasphalting and hydrogen treatment of asphalt containing crudes or topped or reduced crudes which have an API gravity below about 20. Another object is to provide improved procedure for preparing a catalytic cracking stock and furnace oils in high yields from asphalt containing crudes, topped or reduced crudes having a gravity below about 20° API. A still further object is to improve the state of the art. Other objects will appear hereinafter.

These and other objects are accomplished by our invention which includes subjecting a crude or a topped or reduced crude having an API gravity below about 20 and containing asphaltic materials, i.e., a residual stock, to a visbreaking operation, deasphalting the visbroken asphalt containing material, and subjecting the visbroken and deasphalted material to treatment with hydrogen at a pressure between about 500 and 3,500 p.s.i. in the presence of a hydrogenation catalyst.

We have found in accordance with our invention that by treatment in this manner the deasphalting step is simplified and a considerable increase in yield of valuable products, especially furnace oil, is obtained. Also, a product is obtained in high yield which constitutes a high quality catalytic cracking charge stock.

The residual feed stock used in our process may be any asphalt containing crude petroleum or any residual fraction thereof which has an API gravity of below about 20. There are many petroleum crudes which are very viscous and high in asphaltic content and we contemplate the treatment of such crudes without removal of any of

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their components when they have a gravity below about 20. On the other hand, most crudes are of higher gravity and with such crudes it is desirable to remove valuable portions thereof in conventional manner and to obtain a residual fraction. This residual fraction may be prepared by atmospheric or vacuum distillation.

The visbreaking operation may be any such operation known in the prior art. Although any degree of visbreaking may be employed it is advantageous to use conditions which form between about 4 and 20 percent gasoline. These visbreaking operations are commonly carried out by passing the charge stock through a heating coil and heating the oil to a mild cracking temperature. The time of heating, the pressure and the temperature of heating control the amount of thermal cracking or conversion into lower boiling components such as gasoline. In general the temperature may be between about 850° and 975° F., the heating time between about 250 and 1,000 seconds, and the pressure between about 50 and 600 p.s.i.g. Procedures of this type are described in standard textbooks and reference is made thereto for further details. See for instance Sachanen, Conversion of Petroleum, Second Edition, Reinhold Publishing Corporation, 1948, pages 252—254.

After visbreaking, the product is preferably subjected to distillation to remove lower boiling components such as gasoline formed during the visbreaking step. The gasoline has an undesirable effect on the subsequent deasphalting step and it is advantageous, but not necessary, to remove it for this reason. Other components such as furnace oil may be removed if desired although we prefer to retain such materials since they are improved by the subsequent hydrogenation.

The deasphalting step is carried out utilizing any known solvent deasphalting procedure. Such procedure is described in standard textbooks. See for instance Kalichevsky, Petroleum Refining with Chemicals, Elsevier Publishing Company, 1956, pages 388—396. Although we may use a conventional deasphalting solvent such as propane, we prefer to employ an aliphatic hydrocarbon having 5 to 18 carbon atoms in the molecule. Thus we have found that hydrocarbons such as heptane or cetane may be added to the visbroken residual fraction and will cause precipitation of the asphaltic material. At the same time these solvents cause a larger amount of hydrocarbon substances to be retained in the oil portion of the feed. These additional hydrocarbons are of a resinous nature but we have found that during the subsequent hydrogenation they are converted into excellent catalytic cracking charge stocks. Therefore by using this particular type of deasphalting solvent the overall yields of high grade products are markedly improved. The previous visbreaking step reduces the amount of deasphalting solvent required. One to four parts solvent to one of visbroken residual stock and preferably a one-to-one ratio is generally used. The deasphalting step may be carried out in the manner described in our application Serial No. 27,955, entitled "Treatment of Petroleum Fractions," filed May 9, 1960, now Patent No. 3,053,750. This application discloses the deasphalting of residual stocks by heating a mixture of residual stock and deasphalting solvent to an elevated temperature and then adding an additional amount of deasphalting solvent to quench the mixture to a lower temperature. This causes improved precipitation and/or settling of asphaltic materials. However as indicated above, any conventional method of carrying out the deasphalting operation may be employed.

The visbroken-deasphalted residual stock is contacted with hydrogen in the presence of a hydrogenation catalyst such as a group VI left-hand column metal of the periodic system, their oxides and sulfides. Similarly metals of the iron group, their oxides and sulfides may

be employed as catalysts. These group VI and iron group catalysts may be mixed with one another. For instance, an advantageous mixture is a mixture of cobalt and molybdenum oxides. Another advantageous mixture is a mixture of nickel and tungsten oxides. These catalysts are deposited upon a porous catalyst carrier. Typical catalyst carriers are activated alumina, pumice, a silica-alumina cracking catalyst, etc. The pressure during the hydrogenation is maintained between about 500 and 3,500 p.s.i. and preferably is between about 1000 and 2000 p.s.i. The temperature may be between about 550° and 825° F. and preferably between about 650° and 800° F. A space velocity between about 0.3 and 10.0 volumes of charge stock per hour per volume of catalyst and preferably between about 0.5 and 4.0 is utilized. The hydrogen is present during the reaction in a ratio of between about 200 and 20,000 standard cubic feet and preferably between about 2000 and 10,000 standard cubic feet per barrel of visbroken-deasphalted residual charge stock.

A preferred mode of hydrogenation as indicated above is to utilize a pressure of between about 1,000 and 2,000 p.s.i. This pressure is a relatively moderate pressure as compared with pressures heretofore used in destructive hydrogenation. Therefore the cost of the equipment is considerably lower than such destructive hydrogenation equipment. By operating in accordance with our invention, and utilizing a pressure of 2,000 to 3,500 p.s.i., it is possible to obtain thoroughgoing conversion into a catalytic cracking charge stock without using the relatively high pressures of the destructive hydrogenation prior art. Alternatively, if the cost of this higher pressure equipment is prohibitive, it is entirely feasible to obtain high yields of good quality furnace oil and catalytic cracking charge stock by carrying out the hydrogen treatment of our invention at a pressure of between about 1,000 and 2,000 p.s.i. The cost of equipment when operating in this pressure range is much lower and at the same time markedly improved results are obtained as compared with previous operations carried out at similar pressures.

When operating in accordance with this low pressure modification, i.e., 1,000 to 2,000 p.s.i. it is advantageous although not necessary to utilize a two-stage hydrogenation operation since it has been found that with such a two-stage hydrogenation process the yield of distillate products such as gasoline and furnace oil is substantially greater than with a single stage hydrogenation. The catalyst used in both of these two-stage hydrogenations may be the same. For instance, a cobalt-molybdate catalyst may be used in both stages. An advantageous combination of steps for this moderate pressure type of process is to use cobalt molybdate in the first stage in order to take advantage of the high desulfurization and hydrogenation activity of this catalyst and to use a nickel-tungstate catalyst in the second stage in order to obtain a high degree of removal of nitrogen which, of course, has a harmful effect on the catalytic cracking catalyst if the product is subsequently catalytically cracked. The space velocity may be doubled as compared with a single stage process and still obtain greater yields. A space velocity of 1.0 to 6.0 in each reactor is preferred when using this two-stage modification.

The product from the hydrogen treatment may be subjected to a distillation to separate desired components. The type of fractions separated will depend upon the end use. Ordinarily we prefer to subject the product to distillation to separate gasoline and furnace oil fractions and to obtain a residual fraction which may be catalytically cracked.

FIGURE I of the accompanying drawings illustrates diagrammatic apparatus in which our invention may be carried out. Referring to the drawing, a residual feed to be treated in accordance with our invention is introduced through conduit 2 into visbreaking unit 3 where it is subjected to visbreaking in the manner herein described.

The visbroken feed is then introduced via conduit 5 into gasoline stripper 6 where gasoline formed during visbreaking is removed through conduit 7. Gasoline-free bottoms are withdrawn from stripper 6 through conduit 8 and introduced into deasphalting unit 9 where it is subjected to a deasphalting treatment as described above. Asphalt is removed from deasphalting unit 9 through conduit 10. The deasphalted feed is then introduced via conduit 11 into solvent distillation unit 12 where deasphalting solvent is removed through conduit 13 and recycled through conduit 15 together with make-up solvent introduced through conduit 17. The visbroken and deasphalted feed is then introduced via conduit 14 into heater 16 in conjunction with a mixture of recycled and make-up hydrogen introduced through conduit 18. This mixture is heated to approximately reaction temperature in heater 16 and is then introduced via conduit 20 into hydrogenation reactor 22 which is filled with hydrogenation catalyst. In this first stage hydrogenation reactor, the hydrocarbon is subjected to hydrogenation under the conditions described, and the hydrogenated feed is then withdrawn through conduit 24, cooled in cooler 26 and then introduced into separator 28 via conduit 30. Hydrogen treated hydrocarbon is removed from separator 28 via conduit 32 and separated hydrogen is recycled by pump 34 through conduit 36. Make-up hydrogen is introduced through conduit 38 and a part of the hydrogen recycle is bled off through conduit 40 to maintain hydrogen purity.

The first stage product removed through conduit 32 from separator 28 is mixed with hydrogen introduced through conduit 44 and is introduced into heater 46. The heated mixture flows through conduit 48 into second stage hydrogenation reactor 50 which is also filled with a bed of hydrogenation catalyst. Hydrogen treatment takes place in this second stage reactor in the manner described above, and the hydrogen treated product flows through conduit 52, cooler 54 and conduit 56 into separator 58. Hydrogen separated in separator 58 flows through conduit 60 into pump 62 and is recirculated via conduit 64. Make-up hydrogen is introduced through conduit 66, and a portion of the recycle hydrogen is bled off through conduit 68 in order to maintain hydrogen purity.

The two-stage hydrogen treated product flows from separator 58 through conduit 70 and is introduced into fractionator 72 where it is subjected to fractionation to separate desired fractions. Thus gasoline is removed through conduit 74, light furnace oil through conduit 76, heavy furnace oil through conduit 78 and a bottom extraction through conduit 80.

The following example illustrates the benefits obtained by a mild visbreaking, i.e., such as to form between about 4 and 20 percent gasoline, and especially between about 8 and 12 percent gasoline, as well as other advantages of our invention.

EXAMPLE

Five samples of a residual fraction having the properties given in Table I were visbroken by heating to a temperature between 875° and 980° F. and at a pressure of about 200 p.s.i.g. The time of heating was kept constant at about 370 seconds while temperature was varied in order to vary the thermal cracking and obtain gasoline formation varying from about 4 to 21 percent. The gasoline formed was removed. These gasoline-free products and a sample of the original unvisbroken charge stock were then deasphalted utilizing heptane as a deasphalting solvent. The deasphalting was accomplished by adding various amounts of heptane to the visbroken product at a temperature of 80° F. and permitting the asphalt to settle. After removal, the asphalt was washed with heptane, dried and weighed. The amounts of asphaltic material removed for each visbroken product with various amounts of heptane are set forth in Table II, and are presented graphically in the accompanying drawing.

Table I

PROPERTIES OF RESIDUES AFTER VISBREAKING

Visbreaking conditions:					
Temperature, ° F.	875	900	920	950	980
Residence time, seconds	370	370	370	370	370
Debutanized gasoline yield (percent by volume)	0	4.0	9.6	11.8	18.9
Properties of Gasoline-free Visbroken Residue:					
° API Gravity	6.8	7.0	6.3	5.9	4.1
Carbon Residue, Conradson, percent	19.73	23.28	24.33	24.07	28.07
Viscosity, SUV at 210° F., sec.	8,620	1,440	1,230	1,060	1,310
Vanadium, p.p.m.	136	155	162	168	185
Nickel, p.p.m.	40.1	44.4	46.5	45.3	50.7

Table II

PROPERTIES OF RESIDUES AFTER DEASPHALTENING WITH TWO VOLUMES OF HEPTANE TO ONE VOLUME OF GASOLINE-FREE VISBROKEN RESIDUE

Asphaltene Yield:					
Percent by weight	0	13.8	19.8	24.0	30.6
Deasphalted Residue Yield and Inspections:					
Percent by weight	100.0	86.2	80.2	76.0	69.4
° API Gravity	6.8	8.6	9.6	10.7	10.4
Carbon Residue, Conradson, percent	19.73	19.15	16.85	15.61	15.57
Viscosity, SUV at 210° F., sec.	8,620	256	181	69.3	13.4
Vanadium, p.p.m.	136	85.2	62.4	50.0	26.3
Nickel, p.p.m.	40.1	26.8	19.7	15.5	10.9

A visbroken product containing about 10 percent gasoline prepared and deasphalted as described above was subjected to distillation to remove the gasoline and portions thereof were contacted with hydrogen under the following respective conditions: at a pressure of 1000 p.s.i.g., 2000 p.s.i.g., and 3000 p.s.i.g.; a temperature of 789° F., 787° F. and 791° F.; in the presence of a cobalt molybdate catalyst deposited upon alumina. The space velocity used in these runs were respectively 0.54, 1.90 and 7.74 volumes of oil per volume of catalyst per hour and the hydrogenation recycle rate was 3700, 4300 and 4000 standard cubic feet per barrel of visbroken-deasphalted residual hydrocarbon charge stock, respectively. The properties of the final products are given in Table III.

Table III

	1,000 p.s.i.g.	2,000 p.s.i.g.	3,000 p.s.i.g.
Gravity, ° API	26.1	25.5	21.3
Viscosity, SUV, sec.:			
100° F.	68	110	691
130° F.	50	71	255
Sulfur, percent	0.33	0.38	0.86
Nitrogen, percent	0.14	0.15	0.19
Carbon Residue, Conradson, percent	3.37	2.57	3.74
Vanadium, p.p.m.	0.1	0.1	0.1

It will be noted from Table II that visbreaking to between about 4 and 20 percent gasoline results in a marked improvement in asphalt removal in regard to the amount of solvent required. This effect reaches a maximum at about 10 percent gasoline as shown in the graphical presentation of these data in the drawing (FIGURE 2). It will also be noted that visbreaking to a gasoline yield of above about 20 percent does not improve the deasphalting operation in regard to the amount of solvent required. It will also be noted from the above data that the visbreaking operation, even when only a moderate amount of gasoline is formed such as 4 percent results in a marked improvement as compared with procedures in which no visbreaking is applied to the residual charge stock. The overall procedure of the invention is shown in Table III to yield a product which can be used as a high quality catalytic cracking stock low in metal impurities and nitrogen and having a reasonable carbon residue.

We claim:

The process which comprises subjecting a member of the group consisting of crudes, reduced crudes and topped crudes having an API gravity of below about 20° and containing a substantial amount of asphaltic materials to visbreaking to form about 10 percent gasoline, removing the gasoline, deasphalting the remaining visbroken material with about 2 volumes of heptane to one volume of visbroken material, subjecting the visbroken and deasphalted material to treatment with hydrogen in two separate stages in the presence of a member of the group consisting of sulfides and oxides of group VI left-hand column and of iron group metals, sulfides and oxides deposited upon a porous catalyst carrier, at a pressure between about 1000 and 2000 p.s.i., at a temperature between about 650° and 800° F., at a space velocity between about 0.5 and 4.0, and at a hydrogen recycle rate of between about 2000 and 10,000 standard cubic feet per barrel of visbroken-deasphalted residual hydrocarbon charge stock, removing gasoline-furnace oil and catalytically cracking the remainder of the product.

References Cited in the file of this patent

UNITED STATES PATENTS

2,045,794	Pier	June 30, 1936
2,459,465	Smith	Jan. 18, 1949
2,559,285	Douce	July 3, 1951
2,644,785	Harding et al.	July 7, 1953
2,697,681	Murray et al.	Dec. 21, 1954
2,727,853	Hennig	Dec. 20, 1955
2,848,376	Oettinger	Aug. 19, 1958
2,914,457	Beavon	Nov. 24, 1959
2,926,129	Kimberlin et al.	Feb. 23, 1960
2,943,048	Rust et al.	June 28, 1960
2,953,612	Haxton et al.	Sept. 20, 1960

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,132,088

May 5, 1964

Harold Beuther et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 7, for "bisbreaking" read -- visbreaking
--; column 5, Table I, last column, for "19.97" read -- 29.97
--.

Signed and sealed this 13th day of October 1964.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents