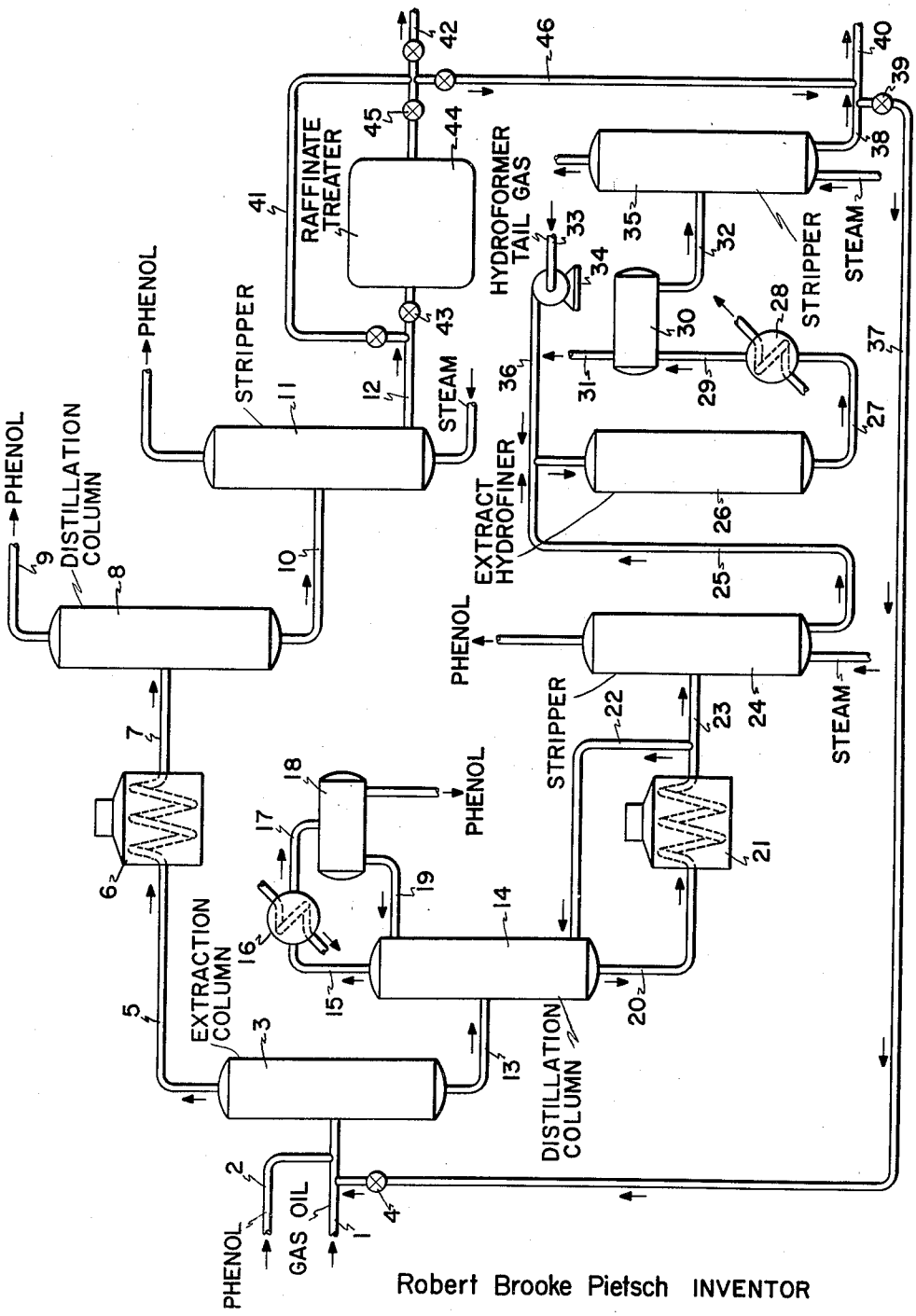
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TREATMENT OF HYDROCARBON OILS

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TREATMENT OF HYDROCARBON OILS

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This invention relates to a new and better process for hydrofining hydrocarbons boiling in the gas-oil range to improve their catalytic cracking characteristics and lower sulfur content in the oil and relates more particularly to a process in which aromatics in the hydrocarbon feed are separated from naphthenes by extraction with a suitable solvent and the aromatic fraction is hydrofined to convert a substantial portion of the aromatics to naphthenes. It is thus possible to greatly increase the total conversion of aromatics to napthene ring compounds, a very desirable conversion since much lower carbon and dry gas yields are obtained in cracking napthene ring compounds than in cracking aromatics. It is also desirable to treat kerosene, jet fuel or diesel fuel fractions in this manner to lower the aromatics content and thus improve their burning characteristics.

Hydrofining is defined as an operation in which petroleum hydrocarbons are contacted with hydrogen in the presence of a catalyst usually cobalt molybdate on alumina or molybdenum oxide on alumina at pressure of less than about 1600 p.s.i.g. and temperatures of less than about 800° F. in order to improve their quality or to prepare them for further processing. The reactions taking place under these conditions are desulfurization, removal of nitrogen and/or oxygen and hydrogenation of unsaturated compounds. The combined results of all these reactions and a characteristic of the hydrofining process is the net consumption of hydrogen occurring therein.

In the hydrofining of hydrocarbon fractions boiling in the gas oil boiling range it is known that one of the most important reactions that occurs is the conversion of aromatics to napthenes. As large a conversion as possible is desirable because of the much lower carbon and dry gas yields obtained in the catalytic cracking of a low aromatic content gas oil. Unfortunately, the amount of aromatics conversion is quite low with most feedstocks. Consequently, conventional gas oil hydrofining frequently resorts to rather severe reaction conditions in order to reach low product sulphur levels and thereby realize process credits from lower sulphur content of the products from cracking the hydrofined gas oil. In fact, with some gas oil feeds regeneration of the catalyst every several weeks, rather than not at all as is the case ordinarily in hydrofining, is practiced to reach low sulphur levels. If it were possible to achieve a higher degree of aromatics conversion, such an operation would not only have direct process credits but in addition there would be less need to reach low sulphur levels and hence less severe reaction conditions might be employed.

According to the present invention it has been found experimentally that at any given pressure the product from hydrofining has the same naphthene/aromatic ratio regardless of the naphthene/aromatic ratio of the feed stock. The following table presents laboratory data obtained with a small hydrofining unit operating at 725° F.

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PRODUCT NR/AR REACHES EQUILIBRIUM

[HDS pressure, p.s.i.g.]

Feedstock	Feed NR/AR	400	800	1600
		Product NR/AR		
Bachaquero	1.10	0.68		1.04
West Texas Gas Oil	1.05	0.83	0.94	1.05
Hawkins Vir. Gas Oil	0.84	0.65	0.76	1.00
Hawkins Coker G. O	0.30	0.69	0.86	1.07

It can thus be seen that the aromatic naphthene reaction in hydrofining gas oils, which can be represented as $Ar+H_2=NR$, is reversible and that it reaches an equilibrium value determined by the pressure on the system. By the present invention the desirable hydrofining conversion of aromatics to naphthenes is increased by minimizing the concentration of naphthenes in the feed to the hydrofining reactor. This is accomplished by extracting the aromatics in the feed with a suitable solvent such as phenol, furfural, propane, etc., and feeding only the aromatic extract after removal of the solvent, to the hydrofining step. The untreated raffinate may then be recombined with the hydrofinate and the combined stream subjected to catalytic cracking or the raffinate and the hydrofinate can be separately treated and/or used. The overall aromatics conversion by this operation is substantially higher than would be obtained by the conventional hydrofining of the entire gas oil feed. In one embodiment of this invention the combined stream is then passed to a catalytic cracking process in which the heavy feed relatively low in aromatics is converted into desirable lighter components, i.e. high octane gasoline and fuel oils.

In another embodiment a relatively narrow boiling range fraction, i.e. 325°–550° F., 350°–650° F., 350–675° F. or 350°–800° F. cut is treated with a suitable solvent to extract a major proportion of the aromatics to give a low aromatics raffinate suitable, with or without additional treatment such as the usual chemical treatments or hydrofining, for use as a premium diesel or jet fuel and an aromatics-rich extract which is hydrofined to convert a substantial proportion of the aromatics to naphthenes. The hydrofinate may then be charged to a catalytic cracking unit or, if desired, recycled in whole or in part to the extraction step.

The invention will be more fully understood by reference to the accompanying drawing in which the extractive hydrofining process is illustrated diagrammatically. Gas oil feed or a narrow boiling cut within the gas oil boiling range is introduced through line 1 and phenol through line 2 to extractive column 3, valve 4 being closed. From the top of column 3 the naphthene-rich raffinate is passed through line 5, furnace 6 and line 7 to distillation column 8. From column 8 the major part of the phenol in the raffinate passes overhead through line 9 to phenol recovery and the naphthene-rich gas oil raffinate passes through line 10 to steam stripper 11. The raffinate is discharged from stripper 11 via line 12 and may be passed via line 41 to outlet line 42 and thence to raffinate product storage (not shown). If further treatment of the raffinate is desired, it may be passed from line 12 via valved connection 43 to raffinate treater 44 where it can be subjected to any desired chemical treat-

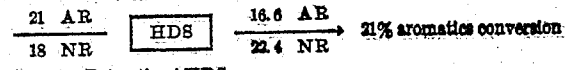
ment such as further extraction with the same or a different solvent, acid or caustic-washing or to hydrofining. The treated raffinate is discharged via line 45 to raffinate outlet line 42. If treated or untreated raffinate is to be combined with the hydrofined extract as described below, outlet line 42 can be closed and the raffinate transferred through line 46 to line 40.

From the bottom of extractive column 3 the aromatic-rich extract passes through line 13 to separation column 14. A heavy reflux is maintained in the upper part of the column and a heavy reboil is maintained on the lower part of the column so that operating temperatures of about 200° F. in the upper section and 600° F. in the lower section of the column are obtained. Phenol passes from the top of the column through line 15, condenser 16 and line 17 to phenol receiving drum 18 from which reflux is maintained through line 19 and from which phenol is returned to line 2 through means not shown. From the bottom of column 14 the aromatic-rich gas oil passes through line 20 to furnace 21 from which part of the stream is returned to column 14 through line 22 and the remainder is passed through line 23 to steam stripper 24 where traces of phenol are stripped from the oil and passed overhead and the stripped aromatics-rich gas oil is passed from the bottom of the column through line 25 to hydrofiner reactor 26. Hydrofiner reactor 26 contains a cobalt molybdate on alumina or a molybdenum oxide on alumina catalyst. The cobalt molybdate on alumina catalyst may contain about 1 to 8% cobalt oxide, 5 to 20% molybdenum oxide, and the remainder alumina. The hydrofining reaction is conducted at temperatures of 600° F. to 900° F., preferably 650° F. to 750° F., pressures of from 200 p.s.i.g. to 1600 p.s.i.g., preferably 400 p.s.i.g. to 800 p.s.i.g., and in the presence of recycle gas supplied at rates of from 200 to 6000 s.c.f./barrel of liquid oil feed, preferably 500 to 1500 s.c.f./barrel. If it is desired to also hydrofine the raffinate the reaction can be carried out in treater 44 under the same general conditions outlined but at somewhat lower temperatures, i.e. as low as about 500° F., and preferably at about 550° F.–650° F.

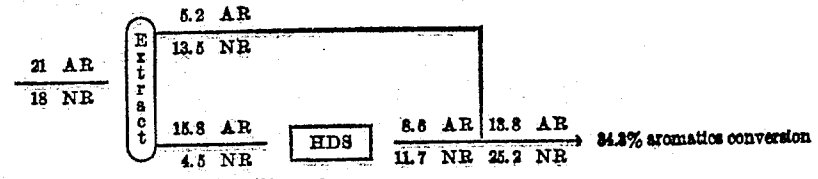
From hydrofiner reactor 26 the products are passed through line 27, cooler 28 and line 29 to separator drum 30 where the hydrofiner tail gas is passed out from the system through line 31. Through line 32 liquid hydrofinate is passed to steam stripper 35. Hydroformer tail gas or other hydrogen-rich treat gas is fed through line 33 to compressor 34 where it is raised to hydrofiner reactor pressure and is then passed through line 36 to the hydrofiner. Liquid hydrofined gas oil leaves the bottom of stripper column 35 and is passed through line 38 past closed valve 39 to outlet line 40 and thence to hydrofined extract product storage. As indicated above, the raffinate may be combined with the hydrofined extract product in line 40 and the mixture then passed to product storage or this combined stream may be passed to conventional catalytic cracking where this heavy feed is converted into desirable lighter components, i.e. high octane gasoline and fuel oils. If desired, hydrofinate may be recycled through line 41, valves 39 and 4 being partially opened, to gas oil feed line 1, thus securing still higher aromatic conversion and, of course, lower sulfur content of the hydrofinate. Ordinarily with or without recycle, sulfur contents of the recombined product will meet specifications required for feeds to cracking especially in view of the lower coke and gas forming properties of this much higher naphthene content-product. However, if it is necessary or desired to lower sulfur content further, this naphthene-rich fraction may be separately hydrofined in treater 44 as described above. The advantage of the present process is not thus lost if it is necessary to hydrofine the raffinate. Lower temperatures and a milder treat are used so that the reversible aromatic conversion reaction does not proceed and force conversion in the wrong direction.

The advantages of the present process can be illustrated by the following comparison of results obtained with a Bachaquero gas oil having an aromatic/naphthene ratio of 21/18. Hydrofining is carried out at 650° F. and 800 p.s.i.g. under which conditions the equilibrium aromatic/naphthene ratio is 1.35. Extraction efficiency is 75%.

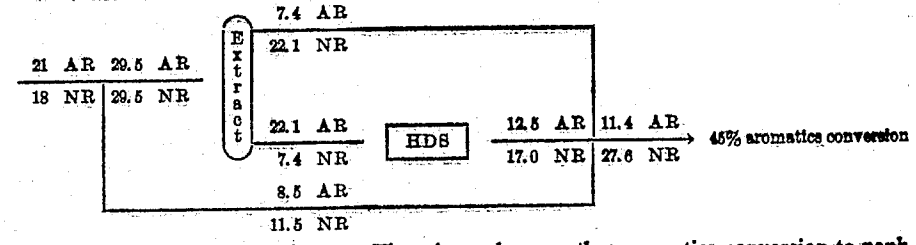
Case 1.—Conventional HDS:



Case 2.—Extraction+HDS:



Case 3.—Extraction+HDS+51% recycle:



Thus, it can be seen that aromatics conversion to naphthenes can be increased by the present process without recycle 63% and with recycle 117.5%. It should further be noted that the same increase in aromatics conversion can also be obtained even if the raffinate is not combined with the hydrofined extract product.

In order to more fully explain the invention, the following examples are set forth with the understanding that they are merely illustrative of the invention and that the invention is not restricted to the specific details enumerated therein.

Example 1

A 13.4° API specific gravity 870/1100° F. vapor temperature normal cut range Bachaquero gas oil feed containing 2.67 wt. percent sulfur is combined with 70 volume percent of phenol based on the gas oil feed, and the mixture is supplied to an extractive distillation column operating at 150° F. and 10 p.s.i.g. All of the towers in the extraction system are maintained at a common 10 p.s.i.g. pressure 75% of the gas oil feed to the column passes overhead and 25% of the gas oil is separated or removed with the phenol and passes from the bottom of

the column. By this separation 75% of the total aromatics in the gas oil feed are concentrated in the extract.

The raffinate from column 3 containing 1.49% sulfur and having a specific gravity of 20° API is passed to column 8 at a temperature of 600° F. In column 8 phenol is separated overhead and the gas oil passes from the bottom of the column, is steam stripped in column 11, and then is passed through line 12 to rejoin the hydrofinate. The extract from column 3 containing 5.65 wt. percent sulfur and having a specific gravity of −3.3° API is passed to separation tower 14 wherein reflux and reboil ratios are maintained so that a temperature at the top of the tower of 220° F. and a temperature at the bottom of the tower of 600° F. are obtained. Steam stripper 24 is operated at a temperature of 600° F. Hydrofining is conducted at 650° F. and 800 p.s.i.g. with a cobalt oxide-molybdenum oxide catalyst. This catalyst contains 3% cobalt oxide and 12% molybdenum oxide supported on granular gamma alumina in the form of ⅛" pills. A 0.5 volume of oil/volume of catalyst space velocity is employed, and 770 s.c.f. of hydroformer tail gas per barrel of feed are supplied as treat gas. The steam stripper 35 operates at a pressure of 100 p.s.i.g., and a temperature of 410° F. Leaving the steam stripper, the hydrofined product contains 0.5 wt. percent sulfur, a 45.6% conversion of aromatics to naphthenes having been obtained. The hydrofinate when recombined with the naphthene-rich raffinate separated out in the extraction column 3 contains 1.23 wt. percent sulfur and contains only 13.8% aromatics.

Example 2

A 350°–550° F. boiling range kerosene fraction is combined with 70 volume percent of phenol and supplied to an extractive distillation column. The raffinate is taken overhead and after steam stripping to remove residual phenol is suitable for use directly as a low smoke point fuel. The extract removed from the bottom of the column is stripped of phenol and then hydrofined at about 650° F. and 800 p.s.i.g. in admixture with about 800 cu. ft. of hydrogen-rich treat gas per barrel of aromatics-rich extract and in contact with a cobalt oxide-molybdenum oxide (cobalt molybdate) catalyst at about 0.5 space velocity to convert about 35–45% of the aromatics to naphthenes.

Example 3

A lubricating oil stock is subjected to solvent extraction under conventional conditions. The raffinate, freed of residual amounts of solvent is blended to motor oil. The extract is freed of solvent and subjected to hydrofining under the conditions as described in Example 1. The hydrofined extract is suitable for charging to a catalytic cracking unit for conversion to high octane number gasoline and fuel oil without yielding excessive amounts of coke and dry gas as would be the case if the untreated extract was charged to the catalytic cracking unit.

This application is a continuation-in-part of my application Serial No. 631,784, filed December 31, 1956, on "Improved Treatment of Hydrocarbon Oils."

It is to be understood this invention is not limited to the specific examples above which have been offered merely as an illustration and that modifications may be made without departing from the spirit of this invention.

What is claimed is:

1. An improved method for upgrading hydrocarbons boiling in the gas oil boiling range which comprises extracting aromatics in the gas oil boiling range feed with a suitable solvent, stripping residual solvent from the raffinate to produce a low aromatics content raffinate stream, removing and recovering solvent from the aromatics-rich extract, passing the solvent-free extract into a hydrofining zone charged with an active hydrofining catalyst operating under conditions so as to obtain substantial conversion of aromatics to naphthenes of temperatures of from 600° to 900° F., pressures of from 200 p.s.i.g. to 1600 p.s.i.g. and in the presence of hydrogen-rich treat gas supplied at rates of from 200 to 6000 s.c.f./barrel of liquid oil feed.

2. The process as defined in claim 1 in which the raffinate is further treated to improve its characteristics by acid washing.

3. The process as defined in claim 1 in which the raffinate is further treated to improve its characteristics by caustic washing.

4. The process as defined in claim 1 in which the raffinate is further treated to improve its characteristics by treatment in contact with a hydrofining catalyst at temperatures of about 500 to 650° F., pressures of from 200 to 1600 p.s.i.g. and in the presence of hydrogen-rich treat gas supplied at rates of from 200 to 6000 s.c.f./barrel of liquid oil feed.

5. An improved method for upgrading hydrocarbons boiling in the gas oil boiling range which comprises extracting aromatics in the gas oil boiling range feed with a suitable solvent, stripping residual solvent from the raffinate to produce a low aromatics content raffinate stream, removing and recovering solvent from the aromatics-rich extract, passing the solvent-free extract into a hydrofining zone charged with an active hydrofining catalyst operating under conditions so as to obtain substantial conversion of aromatics to naphthenes of temperatures of from 600° to 900° F., pressures of from 200 p.s.i.g. to 1600 p.s.i.g. and in the presence of hydrogen-rich treat gas supplied at rates of from 200 to 6000 s.c.f./barrel of liquid oil feed, separating the liquid hydrofined material from the normally gaseous materials and recycling at least a portion of the liquid hydrofined products to the solvent extraction step.

6. The process as defined in claim 5 in which the raffinate is further treated to improve its characteristics by acid washing.

7. The process as defined in claim 5 in which the raffinate is further treated to improve its characteristics by caustic washing.

8. The process as defined in claim 5 in which the raffinate is further treated to improve its characteristics by treatment in contact with a hydrofining catalyst at temperatures of about 500 to 650° F., pressures of from 200 to 1600 p.s.i.g. and in the presence of hydrogen-rich treat gas supplied at rates of from 200 to 6000 s.c.f./barrel of liquid oil feed.

9. An improved process for the hydrofining of hydrocarbons boiling in the gas oil range which comprises extracting aromatics in the gas oil feed with a suitable solvent, recovering the solvent from this extract, passing this solvent free extract into a hydrofining zone charged with an active hydrofining catalyst operating under conditions so as to obtain substantial conversion of aromatics to naphthenes of temperatures of from 600° to 900° F., pressures of from 200 p.s.i.g. to 1600 p.s.i.g., and in the presence of treat gas supplied at rates of from 200 to 6000 s.c.f./barrel of liquid oil feed, and recombining the raffinate from solvent extraction with the hydrofined solvent free extract thus obtaining an increased conversion of aromatics to naphthenes for the total feed processed.

10. An improved process for the hydrofining of hydrocarbons boiling in the gas oil range which comprises extracting aromatics in the gas oil feed with a suitable solvent, recovering the solvent from this extract, passing this solvent free extract into a hydrofining zone charged with an active hydrofining catalyst operating under conditions so as to obtain substantial conversion of aromatics to naphthenes of temperatures of from 650° to 750° F., pressures of from 400 p.s.i.g. to 800 p.s.i.g., and in the presence of treat gas supplied at rates of from 500 to 1500 s.c.f./barrel of liquid oil feed, and recombining the raffinate from solvent extraction with the hydrofined solvent

free extract thus obtaining an increased conversion of aromatics to naphthenes for the total feed processed.

11. The process as in claim 9 in which the solvent used for extraction is phenol.

12. The process as in claim 9 in which the solvent used for extraction is furfural.

13. The process as in claim 9 in which the solvent used for extraction is propane.

14. The process as in claim 9 in which the gas oil is contacted with about 70 volume percent of phenol based on the feed at a temperature of about 150° F., and a pressure of about 10 p.s.i.g. to produce a raffinate containing about 75% of the feed and an extract fraction containing about 25% of the feed in which about 75% of the aromatics in the total feed are concentrated.

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