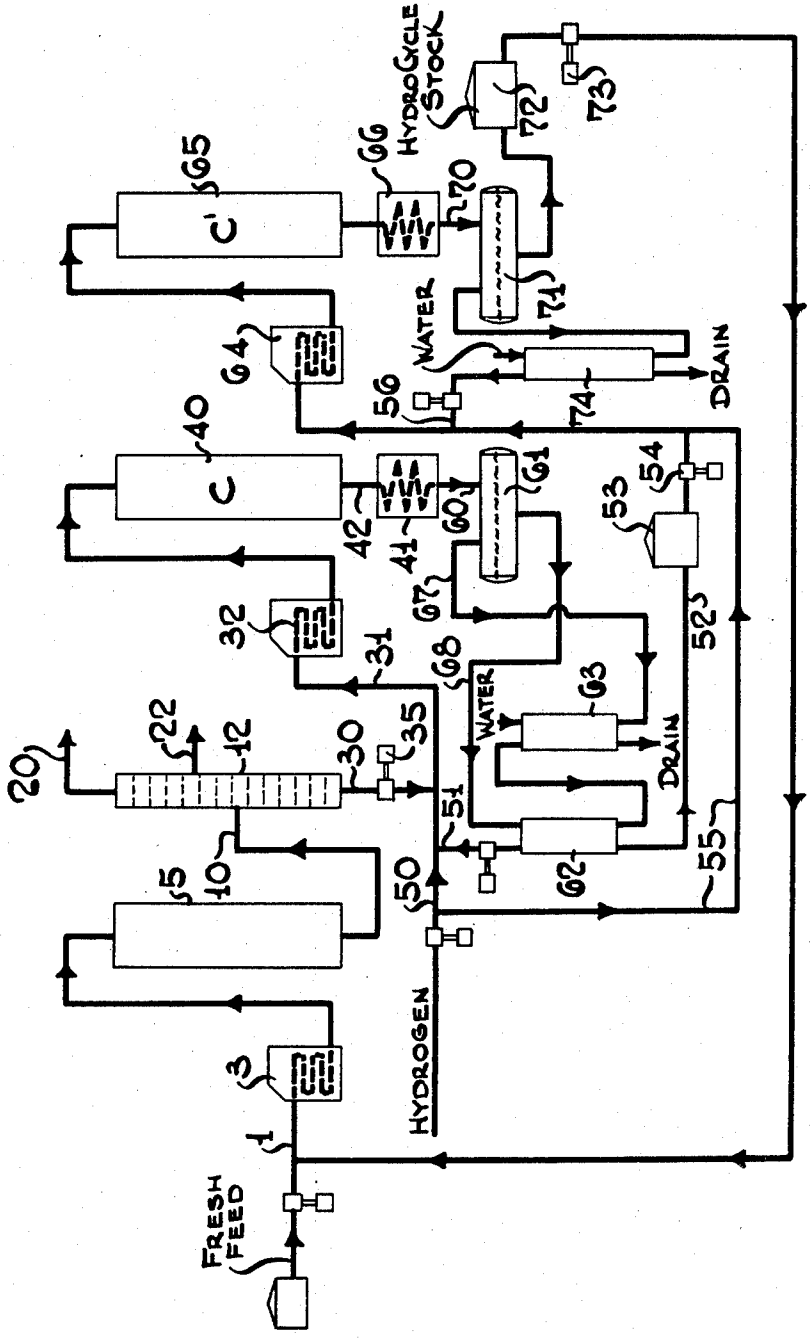
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TWO-STAGE HYDROGENATION TREATMENT FOR HYDROCARBON OILS

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TWO-STAGE HYDROGENATION TREATMENT FOR HYDROCARBON OILS

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The object of my invention is to hydrogenate a hydrocarbon oil so as to saturate aromatic hydrocarbons, and at the same time to hydrogenate olefins, without causing cracking in any substantial degree.

As is known to those who are familiar with the petroleum art, and particularly the catalytic cracking art, it becomes desirable to hydrogenate a hydrocarbon oil such as the gas oil remaining unconverted from a cracking operation before it is recycled to the cracking zone. The reason it is necessary and/or desirable to hydrogenate this material is that the aromatics therein, particularly the aromatics containing two benzene rings in a condensed nucleus, are extremely refractory towards further cracking and possess a strong tendency to produce relatively large quantities of coke on the cracking catalyst when rerun through the cracking zone. It is also desirable to saturate olefins in the cycle oil for substantially the same reason, namely, that the paraffins thus formed have a lesser propensity to form coke on the catalyst.

Heretofore and prior to my invention, although the commercial hydrogention of olefinic material has been achieved both at low and at high hydrogen pressures with catalysts resistant to the deactivating action of such naturally occurring impurities as sulfur- and nitrogen-containing compounds, the non-destructive hydrogenation of aromatic materials to their corresponding naphthenic derivatives has been successfully carried out only at high hydrogen pressure (200 atmospheres) with similar type catalysts. The low pressure hydrogenation of these aromatic materials has been accomplished only with excessive loss in catalyst activity. Since these aromatic materials, when freed from the usual naturally occurring sulfur- and nitrogen-containing compounds, can be hydrogenated at low pressures without excessive loss in catalyst activity, the removal of these impurities will permit this operation to be successfully carried out. Among the advantages of a low pressure hydrogenation process are the lower initial equipment cost per unit of product obtained, the lower process cost for operation of said equipment, and the simpler method of operation.

According to my present invention, the low pressure hydrogenation of aromatic and olefinic type materials may be achieved without excessive loss in catalyst activity with time by means of a two-stage process, wherein the first stage is operated with a sulfur-resistant catalyst at low

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pressures and high temperatures for removal of olefinic materials and sulfur and nitrogen while the second stage is operated with the same type of catalyst or a sulfur-sensitive catalyst at conditions similar to those of the first stage except at lower temperatures for hydrogenation of aromatic materials.

In the accompanying drawing, I have shown diagrammatically a suitable arrangement of apparatus elements in which a preferred modification of my invention may be carried into practical effect.

Referring in detail to the drawing, a gas oil is introduced into the present system through line 1, and thence forced through a heating coil 3, where it is heated to a cracking temperature and thereafter passed through the catalytic cracking zone 5. Since my improvements go to special methods of hydrogenating hydrocarbon oil rather than to cracking it, I shall only refer to the cracking operation without describing it fully, for any cracking operation may be employed that is of the fixed bed or fluid type of process using natural clay or synthetic catalyst, all of which various types of cracking processes are known to petroleum technologists. In the diagram, the cracked products are withdrawn from cracking zone 5 via line 10 and discharged into a fractional distillation tower 12 where the oil is subjected to the usual distillation process in a conventional plate tower to separate the crude hydrocarbon mixture into several cuts of distinct boiling ranges; thus, for example, normally gaseous and/or light ends may be taken off overhead through line 20 while a gasoline fraction may be taken off through line 22. The products from lines 20 and 22 may be processed further in equipment not shown to recover commercial products, according to known means.

Referring to the unconverted gas oil whose treatment goes to the heart of my invention, a sample is withdrawn through line 30 by pump 35 and thence passed to line 31 and through a heating coil 32 into a hydrogenation reactor 40 containing a body of catalyst C which will be more fully identified hereinafter. Simultaneously, hydrogen and hydrogen-containing gas are introduced into the system through lines 50 and 51 and mixed with the gas oil in line 31 before going to heating coil 32. In this first stage of the hydrogenation, the oil feed, which may contain sulfur compounds and nitrogen compounds and which definitely contains olefinic and aromatic materials, is saturated with respect to the olefinic

hydrocarbons; the product which is removed from reactor 40 via line 42 and passed through cooler 41 and line 60 to liquid-gas separator 61 contains paraffinic and aromatic constituents with greatly decreased quantities of sulfur- and nitrogen-containing material impurities. Hereinafter, I have set forth the operating conditions such as catalysts, pressures, temperatures, feed rates, and gas rates to be employed in hydrogenator 40. Since the product in separator 61 may contain some volatile nitrogen compounds and sulfur compounds, it is desirable to pass the material to a scrubber 62 via line 68 for the purpose of removing these compounds. The separator gas which has previously been washed in scrubber 63 is used to remove these volatile compounds from the product in scrubber 62, after which it is returned to the hydrogenation system through line 51. Alternatively, scrubber 62 may be replaced by a conventional liquid phase washing system employing acid and caustic solutions for the removal of any non-volatile nitrogen and sulfur compounds formed during the hydrogenation in reactor 40 and not completely removable by gas blowing. The scrubbed product thence passes through line 52 to storage tank 53 from which it is withdrawn by pump 54 and thereafter mixed with hydrogen and hydrogen-containing gas from lines 55 and 56 and passed to fired coil 64 where it is reheated. The vaporized mixture is thence passed into a second hydrogenation reactor 65, containing a body of catalyst C'. The mixture of hydrogen and hydrocarbons passes through the reactor and a body of catalyst; during this passage through the catalyst, the aromatics are hydrogenated and thereafter the product issuing through cooler 66 and line 70 to liquid-gas separator 71 is released to storage tank 72 from which it may be withdrawn by pump 73 and returned for further processing in cracking zone 5. The separator gas which is washed in scrubber 74 is returned to the hydrogenation system through line 56.

As to operating conditions, in the first or feed purification stage of the hydrogenation process, I propose to use a catalyst consisting of sulfides of metallic elements of group VI or group VIII of the periodic system or mixtures of the same, either as such or supported on an inert carrier which may be composed of alumina, silica, diatomaceous earth, and the like. As examples of the same may be mentioned molybdenum sulfide on activated alumina, mixtures of nickel sulfide and tungsten sulfide or molybdenum sulfide, and so forth. The pressures for this process are in the range of 200 to 1000 pounds per square inch with temperatures of 500 to 900° F. and preferably from 700 to 900° F. Gas rates of 5000 to 10,000 cubic feet per barrel of feed or 10 to 20 moles of hydrogen per mole of feed are used with feed rates in the range of from 0.5 to 4 volumes of feed per volume of catalyst per hour.

In the second or aromatics hydrogenation stage of my process, the conditions employed are similar to those used in the first stage, but the temperatures are maintained somewhat lower, being of the order of 300 to 700° F. The catalysts used in this second stage may be the same as those used in the first stage or they may consist of supported metals and/or metal oxides of group VIII elements of the periodic system. A suitable material is metallic nickel on alumina, silica gel, kieselguhr or similar carrier.

The following example may serve to illustrate

certain of the features of the hydrogenation process:

Feed Stock to Catalytic Cracking	Virgin Paraffinic Gas Oil
Boiling Point, 50% @ °F	570
Sulfur, Weight Percent	1.05
Specific Dispersion	129
Feed Stock to Hydrogenation	**Catalytically Cracked Cycle Stock**
Boiling Point, 50% @°F	590
Sulfur, Weight Percent	1.42
Specific Dispersion	180
Aromatic Hydrogenation Conditions	
Catalyst	{3 Mols Nickel Sulfide, 1 Mol Molybdenum Sulfide.
Pressure, Lbs./Sq. In.	750
Average Temperature, °F.	625
Feed Rate, Vol./Vol. Cat./Hr.	0.5
Gas Rate, CF/Barrel Feed	6,000
Hydrogenated Product	
Boiling Point, 50% @°F	570
Sulfur, Weight Percent	0.06
Specific Dispersion	133

That the hydrogenated product is an improved feed stock for further catalytic cracking is indicated by the much lower specific dispersion. This property is indicative of a lower aromatic content as illustrated in the following tabulation showing the relation between the specific dispersion of hydrogenated catalytically cracked cycle stocks and their ease of cracking as distinguished by their extent of cracking under the same given cracking conditions.

Feed Stock	Virgin Gas Oil	Catalytically Cracked Cycle Stock	Hydrog. Cycle Stock	
Boiling Point, 50% @°F.	570	590	586	570
Specific Dispersion	129	180	146	138
Catalytic Cracking Characteristics				
Conversion to Material Boiling under 400° F., Volume Percent	65.8	44.3	51.0	57.3

From this example it may be seen that hydrogenation of a catalytically cracked cycle stock improves its catalytic cracking characteristics. In addition, as the extent of hydrogenation increases and the content of refractory aromatic material decreases, as indicated by the specific dispersion of the hydrogenated product, its ease of cracking increases.

In the foregoing example, it has been clearly shown that catalytically cracked cycle stocks containing aromatic materials refractory towards further catalytic cracking may be sufficiently improved in catalytic cracking characteristics by low pressure hydrogenation at the represented operating conditions to be comparable with the virgin gas oil feed stock with respect to ease of cracking. Continued successful operation at these conditions requires the use of a feed pretreatment step which may be achieved at conditions similar to those in the aromatics hydrogenation step, but at an elevated temperature.

While I have described a two-stage hydrogenation process and used as an illustration the hydrogenation of a catalytically cracked cycle stock, I wish it to be distinctly understood that

the example which I have previously given, relating to the hydrogenation of a catalytically cracked gas oil cycle stock, was purely illustrative and not given for the purpose of imposing any limitation on my invention. My invention applies broadly to any process where it is desired to non-destructively hydrogenate a hydrocarbon oil to saturate the olefins contained therein, and to reduce the aromatics content by their hydrogenation to naphthenes, regardless of the source of the oil or of the use to which it may subsequently be put. I have described the nature and purpose of my invention in the best mode of carrying it into effect.

What I claim is:

1. A two-stage hydrogenation process which comprises feeding a hydrogen-containing gas and a gas oil containing aromatics, sulfur and nitrogen to a reaction zone maintained at a temperature of from 700 to 900° F. under a pressure of from about 200 to 1000 pounds per square inch, and containing a sulfactive catalyst selected from the group consisting of the sulfides of metals of groups VI and VIII of the periodic system and mixtures of such sulfides, permitting the said gas oil to remain resident in the reaction zone for a sufficient period of time to convert the nitrogen and sulfur compounds in the said feed stock to volatile compounds, withdrawing the reaction products from said reaction zone, removing volatile nitrogen and sulfur compounds therefrom, passing the substantially sulfur and nitrogen free product to a second reaction zone where it is contacted with hydrogen and a sulfur-sensitive catalyst at temperatures of from 500 to 700° F. while under pressures of from about 200 to 1000 pounds per square inch for a sufficient period of time to effect simple hydrogenation of olefins and aromatics in the said oil, and recovering from the said second zone a product of lower aromaticity than the original feed stock, but having substantially the same boiling range as the original feed stock.

2. A two-stage hydrogenation process which comprises feeding a hydrogen-containing gas and a gas oil containing aromatics, sulfur and nitrogen to a reaction zone maintained at a temperature of from about 700 to 900° F. under a pressure of from about 200 to 1000 pounds per square inch, and containing as catalyst a mixture of nickel and tungsten sulfides, permitting the said gas oil to remain resident in the reaction zone for a sufficient period of time to convert the nitrogen and sulfur compounds in the said feed stock to volatile compounds, withdrawing the reaction products from said reaction zone, removing volatile nitrogen and sulfur compounds therefrom, passing the substantially sulfur and nitrogen free

product to a second reaction zone where it is contacted with hydrogen and a sulfur-sensitive catalyst at temperatures of from about 500 to 700° F. while under pressure of from about 200 to 1000 pounds per square inch for a sufficient period of time to effect simple hydrogenation of olefins and aromatics in the said oil, and recovering from the said second zone a product of lower aromaticity than the original feed stock, but having substantially the same boiling range as the original feed stock.

3. A two-stage hydrogenation process which comprises feeding a hydrogen-containing gas and a gas oil containing aromatics, sulfur and nitrogen to a reaction zone maintained at a temperature of from 700 to 900° F. under a pressure of from about 200 to 1000 pounds per square inch and containing as catalyst a mixture of nickel sulfide and molybdenum sulfide, permitting the said gas oil to remain resident in the reaction zone for a sufficient period of time to convert the nitrogen and sulfur compounds in the said feed stock to volatile compounds, withdrawing the reaction products from said reaction zone, removing volatile nitrogen and sulfur compounds therefrom, passing the substantially sulfur and nitrogen free product to a second reaction zone where it is contacted with hydrogen and a sulfur-sensitive catalyst at temperatures of from about 500 to 700° F. while under pressures of from about 200 to 1000 pounds per square inch for a sufficient period of time to effect simple hydrogenation of olefins and aromatics in the said oil, and recovering from the said second zone a product of lower aromaticity than the original feed stock, but having substantially the same boiling range as the original feed stock.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,954,993	Gohr	Apr. 17, 1934
1,955,297	Jennings	Apr. 17, 1934
1,957,787	Krauch et al.	May 8, 1934
2,120,715	Seguy	June 14, 1938
2,149,900	Pier et al.	Mar. 7, 1939
2,159,281	Marecaux	May 23, 1939
2,191,157	Pier et al.	Feb. 20, 1940
2,357,741	Howes et al.	Sept. 5, 1944
2,358,879	Redcay	Sept. 26, 1944
2,365,751	Drennan	Dec. 26, 1944
2,376,086	Reid	May 15, 1945
2,417,308	Lee	Mar. 11, 1947