Patented Apr. 27, 1954 2,676,907

# UNITED STATES PATENT OFFICE

2,676,907

## CATALYTIC CONVERSION OF HYDROCARBONS IN THE PRESENCE OF HYDROGEN

Alex G. Oblad, Springfield, Thomas H. Milliken, Jr., Chester, and Heinz Heinemann, Drexel Hill, Pa., assignors to Houdry Process Corporation, Wilmington, Del., a corporation of Delaware

No Drawing. Application December 17, 1949, Serial No. 133,676

12 Claims. (Cl. 196—53)

1

The present invention relates to an improved process for the production of lower boiling oils, particularly gasoline, from higher boiling hydrocarbons by reaction in the presence of hydrogen at elevated pressure and in the presence of certain catalysts. The invention is particularly concerned with catalytic methods for converting higher boiling paraffin hydrocarbons in mineral oils or fractions thereof, such as crude petroleum oils, gas oils, top crude oils, and in other hydrocarbon fractions from any source, into high yields of gasoline of good anti-knock properties.

It has previously been proposed to subject solid and liquid carbonaceous materials boiling above gasoline to conditions favoring so called destructive hydrogenation, in the presence of catalysts selected for their comparatively high hydrogen adsorption capacity. Such operations are usually conducted at high pressures in the order of about 200 atmospheres and above. Hydrogenation of oils at lower pressures have also been suggested, primarily for the purpose of altering or improving the properties of the oil without substantial splitting of C—C linkages, such as for the removal of sulfur compounds therefrom. Under typical conditions favoring hydrogenation in the presence of such catalysts having comparatively high hydrogenating activity, there are ordinarily obtained hydrocarbon conversion products relatively low in aromatics and having a comparatively high proportion of normal paraffins; the octane ratings of the obtained liquid fractions in the gasoline boiling range are quite low. When applied at higher temperatures (above about 925° F.) to certain selected charge stocks, from among those higher boiling than gasoline, particularly those of high naphthene content, gasoline of higher octanes can be obtained than in the usual lower temperature hydrogenation processes, but only at the expense of considerable reduction in gasoline yields.

Light liquid hydrocarbon fractions such as those boiling in the range of gasoline and naphtha, have also been treated with catalysts generally similar to those used in hydrogenation, and under conditions favoring dehydrogenation of naphthenes present in such fractions. Under the conditions typically employed, hydrogenation of olefins to paraffins is obtained but cyclization

2

of the paraffins does not occur to any significant extent. In these processes, hydrogen may be and usually is recycled to the process but for the purpose only of maintaining catalyst activity, since the process is essentially one of dehydrogenation and results in substantial net hydrogen production.

The catalytic cracking of hydrocarbon oils, particularly at normal or slightly elevated pressure and in the presence of hydrogen, has been extensively employed on a commercial scale. The known commercial processes generally utilize siliceous cracking catalysts of natural or synthetic origin, the more widely used among these being acid-activated clays and synthetic silica-alumina gels. In such catalytic cracking operations the rate of formation of carbonaceous or hydrocarbonaceous deposit, called "coke," limits the severity of conditions that can be employed for efficient and economic operation, so that the extent of conversion of the oil is maintained below that obtaining highest gasoline yields per pass. In these customary cracking processes, as applied for instance to the cracking of gas oils, there can be obtained in a once-through cracking operation, by proper choice of catalyst and conditions, liquid products in the gasoline boiling range amounting to over 40% and even as high as 50% by volume of the oil charged. At these conversion levels the quantity of coke produced generally amounts to in the order of about 10% or more by weight of the quantity of gasoline produced; or stated otherwise, at conversion levels of such gas oils corresponding to about 40–50% by volume gasoline, the coke production amounts to about 3 to 5% or more by weight of the oil charged. At lower conversion levels, producing less than about 40% gasoline by volume of oil charged, the coke production is generally more than proportionately lower, and the gasoline to coke ratios are therefore correspondingly higher; such lower conversion levels are generally favored in commercial operations.

It has now been found, in accordance with the present invention, that exceptionally high yields of high octane liquid products in the gasoline boiling range are obtained with unusually low coke production, by conversion of higher boiling hydrocarbons, and even such as are predominantly paraffinic, in the presence of hydrogen and in contact with certain catalysts under

specially selected conditions. The catalysts employed are composed of a siliceous mass of acid reaction active in catalytic cracking and containing intimately associated therewith a very small but critical quantity of molybdenum oxide, such quantity being advantageously selected with reference to the "acidity" of the siliceous mass. The operating conditions for effecting the described catalytic conversion of said hydrocarbons include temperatures in the range of 700–900° F. and pressures in the preferred range of 1000–3000 pounds per square inch gauge, there being added to the reaction at least 3 mols hydrogen gas per mol of oil charged. Advantageously also, the quantity of oil contacted per pass with a particular quantity of catalyst, or conversely the so called catalyst to oil ratio, are maintained within certain selected limits, these limits for any given catalyst being determined by the activity potential of the catalyst, as will hereinafter appear.

In general, the catalysts used in accordance with the present invention comprise a siliceous cracking component of moderate cracking activity, that is a siliceous component having a stabilized activity adapted to customary catalytic cracking, such as one characteristically producing in the cracking of a gas oil at least 25% by volume gasoline. The siliceous cracking component has initially incorporated therewith a small amount of molybdenum oxide, providing less than 1% $MoO_3$ by weight of the catalyst, or from about 0.05% up to about 0.9% $MoO_3$. For superior to optimum results in the described conversion process, catalysts should be employed containing a controlled quantity of molybdenum oxide bearing a definite relation to the acidity of the siliceous cracking component with which the molybdena is incorporated, as is further described below. The acidity of the siliceous component is determined by its capacity for chemisorption of quinoline by contact with quinoline vapors.

As a result of fundamental research carried out in the same laboratories in which the present invention was developed (certain aspects of which are described in the Journal of the American Chemical Society, 1950, volume 72, page 1554) it was found that only a relatively small fraction of the total surface of oxide type cracking catalyst is responsible for the catalytic activity displayed by such catalyst, and that certain definite chemical properties are associated with this part of the catalyst identifying the active principle as an "acid," capable of reacting with bases at high temperatures. It was further found that a general correlation existed between catalyst acidity and activity, such that the chemisorption characteristics of the catalyst for certain bases could be employed as a dependable measure of cracking activity. A method of characterizing catalysts in terms of their capacity for adsorption and retention of quinolines was thereupon established. The following procedure may be employed in determining the quinoline number of the catalyst, involving a highly accurate direct weighing technique:

The catalyst is suspended in a perforated glass basket by a glass wire attached to one end of the beam of an analytical balance. Nitrogen at a constant pressure is then passed through a series of saturators containing liquid quinoline maintained at a constant temperature by a jacket containing boiling liquid. The nitrogen gas saturated with quinoline is passed through preheated vapor transfer lines into contact with the catalyst sample. Flow is continued until a relatively constant weight is observed, and a stream of preheated nitrogen gas is then passed over the catalyst to remove physically held quinoline until a substantially constant weight is observed. The difference in weight before contact with quinoline and after the nitrogen purge is taken as the amount of quinoline chemisorbed.

To obtain the desired superior results in a hydrocarbon conversion process in accordance with the present invention, the catalyst employed must contain a quantity of molybdenum oxide (calculated as $MoO_3$) in millimols equal to approximately 0.2 to 1.2 times the quinoline chemisorption capacity, expressed in milliequivalents of the siliceous mass in which the molybdena is incorporated, optimum results being obtained at about 0.7 millimols $MoO_3$ per milliequivalent of quinoline chemisorbed. Thus a siliceous catalyst having prior to impregnation with molybdenum oxides a quinoline number of 0.06 milliequivalents per gram, gave optimum results in the described hydrogenative hydrocarbon conversion reactions, at a content of molybdenum oxides equal to 0.6% by weight of the catalyst, corresponding to about 0.7 millimols $MoO_3$ per milliequivalent of acidity. In the same manner siliceous catalyst masses having a quinoline number of about .04 milliequivalent per gram prior to impregnation with molybdenum oxides, should preferably be impregnated with 0.4% by weight molybdena, and siliceous masses of lower quinoline number, such as those having a quinoline number of about .02 milliequivalent per gram should be impregnated with approximately 0.2% molybdenum oxides, to obtain optimum results in the present hydrocarbon conversion processes. Superior results short of the optimum are obtained, however, over a limited range of $MoO_3$ content related to the quinoline chemisorption capacity as indicated above. Thus, for the catalyst base of lowest activity mentioned above, that is one having a quinoline number of about .02 milliequivalent per gram prior to incorporation of molybdenum oxides, there may be employed between about 0.06 and 0.35% of molybdenum oxides; while for a catalyst having a quinoline number of .04 milliequivalent per gram the content of molybdenum oxides may lie between about 0.12 and 0.7% by weight. The preferred catalysts, comprise silica alumina gels of stabilized activity having a quinoline number of about .06±.01 me./gm. and containing about 0.6% or from about 0.4% to about 0.9% of molybdenum oxide.

The various chemical reactions concurrently taking place during the described catalytic conversion of a hydrocarbon oil are quite complex and involve a number of different individual reactions on the different components of the oil. The results obtained in applying the process to oil fractions which have not been previously subjected to dehydrogenation or to catalytic cracking, or to oils otherwise having a low olefin content (less than 5% olefins), indicate that transformation of paraffins in the oil contribute substantially to the quality of the obtained gasoline. It appears that the principal and characteristic reactions going on include in addition to removal of side chains from alkyl aromatic compounds and the transformation of naphthenes in the oil, the splitting of carbon-carbon paraffin linkages, aromatization by ring closure of resulting $C_6$ and higher paraffins, and isomerization of normal paraffins to branched chain compounds. The overall balance of the process with the usual

cracking charges results in a net consumption of hydrogen, and with such charges addition of heat is ordinarily not required to maintain the overall reaction. The resulting products obtained from the conversion of a gas oil, for instance, are relatively highly saturated and low in olefinicity; the liquid portion thereof, however, has an adequate content of aromatics and is relatively high in the proportion of branched chain compounds, so that the motor gasoline fraction as a whole is of high anti-knock quality, equal or superior to that typically obtained in the usual cracking of the same oils with synthetic silica-alumina or other catalysts. The yields of desired liquid products, including gasoline, are markedly higher than in customary catalytic cracking, while the production of coke is greatly reduced.

To obtain the superior results characteristic of the present invention, including high rates of conversion and the production of large yields of gasoline of good octane quality, it is important that the oil be contacted with a sufficient quantity of the catalyst, the required quantity depending upon the acidity of the cracking component of the catalyst; that is the acidity of the siliceous catalyst mass prior to molybdena incorporation. In general, catalyst to oil ratios furnishing at least one equivalent of acid prior to molybdena incorporation (as determined by quinoline chemisorption) per 1000 mols of oil to be contacted per pass, must be used. Higher catalyst to oil ratios such as those furnishing approximately an equivalent or more of acid for each hundred mols of oil, in general give increasingly superior results up to certain limits. No particular advantage has been found for very high catalyst to oil ratios, as in excess of about 3 equivalents of acid per 100 mols of oil.

The small amounts of coke produced in the process enable the use of comparatively long on stream periods exceeding one or two hours, or longer periods if desired, without necessitating regeneration of the catalyst. Regeneration may be carried out by contacting the coke-containing catalyst with oxygen-containing gas at elevated temperature not exceeding about 1000° F., for a sufficient period to burn off the coke to desired extent.

Although the process may be carried out in moving catalyst systems comprising separate zones or vessels for the hydrocarbon conversion reaction and for regeneration of the catalyst, it is preferred to employ fixed catalyst bed reactors, and to regenerate the catalyst periodically in situ as required when the activity or selectivity of the catalyst falls below that desired. The operation may be carried out in known manner employed with fixed bed catalytic conversion systems, by diverting the flow of hydrocarbons at the end of a fixed on stream period, preferably to another reactor of a series, while the used coke-containing catalyst is being prepared for and subjected to regeneration. Such regeneration may be effected at the pressure prevailing in the reaction vessel or preferably at a lower pressure; in the latter instance after first depressuring the vessel to desired extent. Intermediate the on stream reaction and regeneration of the catalyst, the reaction vessel and contents are purged by passing an incompatible gas therethrough. Thus, after the hydrocarbon conversion step, the vessel may be purged with hydrogen and the hydrogen swept out with an inert gas, such as nitrogen or spent flue gas, followed by the admission of oxygen-containing gas to effect regeneration. After regeneration has been carried out to the required extent, excess oxygen-containing gas may be swept from the vessel with an inert gas such as nitrogen, carbon dioxide or spent flue gas, and hydrogen again admitted for a short period prior to returning the flow of hydrocarbons to the reactor. The admission of hydrogen prior to returning on-stream is desirable in order to restore the catalyst to the lower state of oxidation desired for the hydrocarbon conversion reaction, since oxidation of the catalyst during the regeneration period may convert the same to higher oxidized state.

In initially starting up a run the reactor is filled with catalyst and brought to reaction temperature, preferably at ordinary pressure, by circulation of a preheated gas or vapor therethrough, which is not substantially reactive in the presence of the catalyst. Hydrogen from a separate reservoir maintained under constant pressure is then admitted to the reactor to bring the same up to desired operating pressure or somewhat below that pressure, followed by the admission of the hydrocarbons until the desired operating pressure conditions are established, at which time the flow of hydrocarbons and hydrogen is maintained in the required proportions and the regular cycle of operations including purging and regeneration set up.

## EXAMPLE I

The following example is typical of a preferred operation:

A light East Texas gas oil of 35.5 API gravity containing less than 15% aromatics and boiling in the range of about 413° to 712° F. was passed over a catalyst prepared from silica-alumina gel (87.5 $SiO_2$/12.5 $Al_2O_3$ by weight) in the form of cylindrical pellets having an apparent bulk density of 600 grams per liter, 4 mm. in diameter and of like length. These pellets had a quinoline number of 0.06 milliequivalent per gram and were impregnated with 0.6% by weight molybdenum oxides (determined as $MoO_3$). The conversion of the oil was carried out under the following average operating conditions: temperature of 800° F., pressure of 1500 p. s. i. gauge, at a liquid space velocity of 2 volumes of oil per volume of catalyst per hour and a catalyst to oil volume ratio of 0.5, hydrogen being added at the rate of 6 mols $H_2$ per mol of oil (average molecular weight 240), operating for an on stream period of one hour. Other runs were made under approximately the same conditions at catalyst/oil ratios of 0.25 and 1.0, the respective on stream periods being 2 hours and one-half hour.

The yields obtained are shown in the following table.

*Table 1*

| | At catalyst/oil volume ratio | | |
|---|---|---|---|
| | 0.25 | 0.5 | 1.0 |
| Conversion, Wt. percent | 68.2 | 68.1 | 87.0 |
| Gasoline, ($C_4$+) Volume percent of feed oil | 75.1 | 77.9 | 84.4 |
| Coke, Wt. percent of Feed Oil | 0.4 | 0.6 | 0.8 |
| Dry Gas, Wt. percent of Feed Oil | 6.2 | 5.7 | 16.3 |
| Gasoline Octane No. (to 410° F.): | | | |
| CFR-M straight | | 78.4 | |
| CFR-M+1 cc. TEL | | 83.6 | |
| CFR-M+3 cc. TEL | | 90.1 | |
| CFR-R straight | | 80.4 | |
| CFR-R+1 cc. TEL | | 85.5 | |
| CFR-R+3 cc. TEL | | 93.4 | |

The ratio of normal to iso compounds in the $C_4$ fractions obtained was about 1:3 while in the $C_5$ fraction the ratio of normal to iso compounds was about 1:10. The gasoline produced contained about 28–30% aromatics and 1% or less olefins.

The catalyst employed in the above example was prepared by dissolving an appropriate amount of ammonium molybdate in that quantity of water which would be taken up by the catalyst while appearing dry (approximately 50 cc. $H_2O$ per 100 grams of catalyst) and impregnating the catalyst with the solution until the water was completely soaked up. The impregnated catalyst was then dried and heated to 1000° F. in a muffle furnace for 3 hours. The initial silica-alumina pellets subjected to impregnation were of the commercial type prepared by coprecipitation of sodium silicate and sodium aluminate in the presence of ammonium sulfate solution furnishing an amount of sulfate anion equal to the stoichiometric equivalent of the total alkali metal content of the silicate and aluminate solutions, and under conditions resulting in the formation of a coagulum having a pH of approximately 9.7 and containing about 3.9% by weight of Na (water washed and dried basis). The product was steamed, dried at 240–260° F. and coarse ground. The obtained coarse granules were treated in a countercurrent system with ammonium nitrate solution and water to remove sodium, then freed of excess water on a filter press. About ⅓ of the filter cake was dried and pulverized, then mulled with the remaining wet filter cake to form a paste which was molded into cylindrical pellets of the required size and the pellets dried at 220 to 240° F. Prior to treatment with ammonium molybdate solution the pellets were treated in air at 1400° F. for four hours. The heat-treated catalyst pellets thus prepared, and prior to impregnation with molybdena, had a quinoline number of .06 milliequivalent per gram.

The effect of increased catalyst to oil ratios is apparent from the comparative results reported in the above table; higher conversion and more gasoline is obtained as the catalyst/oil ratio is increased, accompanied by a relatively small increase in coke production. Even at the higher conversion levels the gasoline to coke ratios in all instances approach or exceed an order of magnitude above that obtained in customary catalytic cracking. The gas oil employed in the above example has a density of approximately 843 grams per liter and a determined average molecular weight of about 240, corresponding to a content of 3.6 mols per liter. The employed catalyst to oil volume ratios of 0.25, 0.5 and 1.0 therefore, correspond to an equivalent of acid provided by the catalyst for each 400, 200, and 100 mols of oil respectively.

No particular advantage has been found for increasing temperature beyond about 800° F. Lower pressures than that of the example, as down to 1000 p. s. i. gauge and otherwise at the same operating conditions tend toward some decrease in conversion rates and increased coke; below 1000 p. s. i. the conversion rate falls off more rapidly and coke production is increasingly favored.

Decreasing the hydrogen to oil molar ratio as down to about 3:1 results in lowering of gasoline production by about 20% or more of the quantity of gasoline obtained at 6:1 mol ratio. Space velocities of 2 or more (volumes of oil per hour per volume of catalyst) are generally favored, since at space velocities of about one the gasoline yields are considerably reduced and coke make approximately doubled, while at higher space velocities of 3 or above, coke production shows a progressive decrease often accompanied by increase in gasoline yields over that obtaining at lower space velocity.

The results obtained under the described operating conditions with the particular catalysts according to the invention are particularly surprising, since at comparatively high pressure and in the presence of hydrogen the usual cracking catalysts furnish yields and products largely similar to those obtained with the same catalyst under customary cracking conditions (normal pressures and no added hydrogen). The molybdena-containing catalysts of the invention, on the other hand, used under such customary cracking conditions show up considerably poorer than cracking catalysts free from molybdena, producing very low gasoline yields and exceedingly large quantities of coke.

The exceptional adaptability of the catalysts employed in the described conversion operations of the invention is further evident from a comparison of results obtained with typical hydrogenating catalyst under the same conditions. Thus, under the operating conditions of the invention a typical hydrogenating catalyst comprising $MoO_3$ on activated alumina produces only an insignificant yield of gasoline from gas oil. The composition of the gas produced in the process is indicative of a different mechanism of reaction than that obtaining in the process of the present invention, as evidenced by the high predominance of $CH_4$ and comparatively low content of $C_3$ and higher hydrocarbons in the gas obtained with typical hydrogenating catalyst, whereas the content of branched chain compounds is quite low as compared with typical gas compositions obtained when using the described catalysts of the present invention.

Among the various siliceous cracking catalysts suitable as components for impregnation with the described quantities of molybdenum oxide in the preparation of catalysts for use in accordance with the invention, there are included synthetic gels of silica-alumina and silica-alumina gels containing a refractory third metal oxide active in combination therewith, such as zirconia, beryllia, magnesia, thoria; composites prepared from hydrous silica with one of these specified refractory oxides. Also useful, but not necessarily equivalent to these synthetic composites are the natural hydrosilicates of aluminum and/or magnesium having adequate cracking activity, including acid-activated clay, particularly of the sub-bentonite type. There also come into consideration active composites of clay with added synthetic metal oxides, such as alumina. The quantity of molybdenum oxide incorporated in the catalyst will depend upon the acidity of the siliceous component in which the molybdena is to be incorporated, determined by quinoline chemisorption capacity as hereinbefore described. As the cracking activity of siliceous catalysts may vary with the method of preparation as well as with the proportions of its components, so does the quinoline adsorption capacity of such catalyst compositions vary. The activity of catalysts can be stabilized and adjusted by calcination under selected conditions in steam, air, and selected mixtures of these; change in activity thus produced will also be reflected in the quinoline chemisorption capacity.

Typical cracking catalysts with their corresponding quinoline adsorption capacity (prior to $MoO_3$ incorportion) and the preferred quantities of $MoO_3$ to be added thereto in accordance with the invention are illustrated in the following table:

*Table 2*

| Catalyst base | Heat Treated | Quinoline No. | Wt. Percent $MoO_3$ | | |
|---|---|---|---|---|---|
| | | | Range | | Optimum |
| 1. 87.5% $SiO_2$; 12.5% $Al_2O_3$; gel coprecipitated at pH 9 to 10. | 1,350° F., 12 hrs.; 92% air, 8% steam | 0.06 | 0.2 | 0.9 | 0.6 |
| 2. Same as 1 above | 1,300° F., 4 hrs.; 100% steam | 0.03 | $0.08_5$ | 0.50 | 0.3 |
| 3. Same as 1 above | 1,225° F., 10 hrs.; 100% steam | $.04_4$ | 0.12 | 0.75 | 0.4 |
| 4. $SiO_2$ gel + 1.0%; $Al_2O_3$; gel dipped in Al $(NO_3)_3$ sol'n. and heated. | 1,050° F., 2 hrs.; air | 0.02 | 0.06 | 0.35 | 0.2 |
| 5. Commercial acid-activated clay (Filtrol) freed of sulfate. | 1,550° F., 2 hrs.; air | $0.01_8$ | 0.05 | 0.30 | 0.2 |
| 6. 90.5 $SiO_2$; 9.5 $ZrO_2$; gel coprecipitated at pH 6. | 1,400° F., 10 hrs.; 95% air, 5% steam | $0.03_3$ | 0.09 | 0.55 | 0.3 |

The values in the above table showing a figure in the last decimal place by subscript indicate non-significance of that figure, in accordance with the usual practice in such notation.

In using catalysts containing about 0.6% $MoO_3$ and above, the preferred operating conditions for conversion of light gas oils include liquid space rates of about 1 to 4 volumes of oil per hour per volume of catalyst, and hydrogen to oil molar ratios of not less than 3/1 and to as high as 8/1 and above. For fixed bed operation the catalyst to oil ratio will be determined by the length of the on stream period in the operating cycle, and may lie between about 0.1/1.0 to 3/1 volumes of catalyst per volume of oil. For heavier charging stocks, less severe conditions should be employed, which are preferably obtained by employing higher space rates in charging the oil or using lower catalyst to oil ratios within the defined range. Decrease of severity of conversion by reduction of temperature below about 700° F. is not advised in the present operations.

Approximately the same conversion can be obtained with catalyst of lower activity by increasing the severity of processing conditions. For example, in using catalysts having a low quinoline capacity, such as those containing as an optimum about 0.2% $MoO_3$, space rates of about 0.7 to about 1.3, and catalyst to oil ratios preferably of about 6/1 or generally in the range of about 0.3/1 to 9/1 may be employed, consistent with furnishing the described acid equivalent per mol of oil. With catalysts of high quinoline number, on the other hand, less catalyst for a given volume of oil and higher oil charging rates are required.

The more important advantages of the present process lie in the conversion of oils which are not predominantly aromatic; such as in general, charge stocks containing less than about 50% aromatics. Although applicable to characteristically naphthenic charge stocks, the results obtained by the present process in the conversion of oils relatively rich in paraffins as those containing 40% or more paraffins, are particularly surprising, since in known processes of destructive hydrogenation paraffin components of the oil are not converted to high octane products in the gasoline boiling range, except at the sacrifice of yields.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim as our invention:

1. The method of converting predominantly non-aromatic hydrocarbon oils of higher boiling range into liquid products of lower boiling range including gasoline, which comprises subjecting such an oil together with a least 3 molar equivalents of added hydrogen to contact with a catalyst consisting of a small quantity of molybdenum oxide intimately incorporated with an adsorptive siliceous acidic material having hydrocarbon cracking activity, said contact being effected at a pressure of 1000 to 3000 pounds per square inch and at a temperature of 700 to 900° F., the quantity of molybdenum oxide in said catalyst being correlated with the acidity of said adsorptive siliceous material and corresponding to 0.2 to 1.2 millimols of molybdenum oxide determined as $MoO_3$ per milliequivalent of quinoline chemisorption capacity of said siliceous material, and the ratio of cataylst to oil during such contacting being that at least sufficient to furnish one equivalent of acid per thousand moles of oil.

2. The method of converting paraffins and naphthenes in hydrocarbon oil fractions substantially free of catalytic cracked gasoline into gasoline of high octane value, which comprises subjecting a predominantly non-aromatic distillate fraction of a virgin crude oil together with at least 3 molar equivalents of added hydrogen gas to contact with a catalyst consisting of an adsorptive acidic siliceous mass having incorporated therewith less than 1% by weight of molybdenum oxide considered as $MoO_3$, said contact being effected at a pressure of 1000 to 3000 pounds per square inch and at a temperature of 700–900° F., employing at least 0.1 volume of catalyst per volume of such oil.

3. The method of converting paraffin-rich hydrocarbon oils containing less than about 5% olefins and containing components boiling above the range of heavy naphtha, into products comprising predominantly gasoline, which comprises subjecting such paraffin-rich oil together with at least 3 molar equivalents of added hydrogen gas to contact during a fixed reaction period with a catalyst comprising as components thereof a catalytically active silica-alumina acidic mass, and molybdenum oxide intimately associated with said mass in an amount equal to 0.05 to 0.9% by weight of said catalyst, under reaction conditions including temperatures of 700–900° F. and pressure of 1000–3000 pounds per square inch, the quantity of oil contacted with the catalyst during said fixed reaction period being determined by the acidity of the silica-alumina component of the catalyst as measured by the capacity of such component for chemisorption of quinoline, and being not more than 1000 mols of oil per acid equivalent of said component.

4. The method in accordance with claim 3 wherein the quantity of oil per pass contacted with the catalyst does not exceed about 100 mols of oil per acid equivalent of said silica-alumina component.

5. The method in accordance with claim 3 wherein at least 6 mols of added hydrogen are employed per mol of oil charged.

6. The method in accordance with claim 3 wherein the silica-alumina component of the catalyst consists of a calcined synthetic silica-alumina gel having a quinoline adsorption capacity of .06±.01 milliequivalent per gram, and said component is impregnated with at least about 0.4% by weight molybdenum oxide determined as $MoO_3$.

7. The method of catalytic conversion of non-aromatic hydrocarbons in a virgin distillate of higher boiling range into gasoline of high octane value with concomitant formation of relatively small quantities of carbonaceous deposit, which comprises contacting such an oil containing non-aromatic hydrocarbons with a fixed bed of catalyst in a reaction zone at 700–900° F. and at super-atmospheric pressure, together with at least 3 molar equivalents of added hydrogen, said catalyst comprising a catalytically active calcined siliceous gel having intimately incorporated with said calcined gel molybdenum oxide in an amount corresponding to 0.05% to 0.9% by weight of said catalyst, said calcined gel in the absence of molybdenum oxide having an acidity corresponding to a chemisorption capacity for quinoline between about 0.02 to about 0.06 milliequivalent of acid per gram of calcined gel, and wherein further the amount of molybdenum oxide incorporated with said calcined gel is equal to 0.2 to 1.2 millimols $MoO_3$ per milliequivalent of such chemisorption capacity of said calcined gel.

8. The method in accordance with claim 7 wherein the amount of molybdenum oxide incorporated with said calcined gel is equal to approximately 0.7 millimol $MoO_3$ per milliequivalent of the quinoline chemisorption capacity of said calcined gel.

9. The method in accordance with claim 7 wherein the pressure in said reaction zone is at an approximate average of 1500 pounds per square inch.

10. The method in accordance with claim 7 wherein said oil is charged to said reaction zone at a space rate of not less than 2 volumes of oil per hour per volume of catalyst in said zone.

11. The method in accordance with claim 10 wherein said oil is charged continuously to said reaction zone without intermediate regeneration of catalyst therein, for a period of time providing a volume ratio of catalyst to oil of not less than 0.25.

12. The method in accordance with claim 7 wherein said oil is continuously charged to said reaction zone without intermediate regeneration of catalyst in said zone, and flow of oil to said zone is thereafter interrupted before the amount of oil entering such reaction zone exceeds 400 mols per acid equivolent of the calcined gel component of the catalyst in said zone as determined prior to molybdenum oxide incorporation therewith.

References Cited in the file of this patent

UNITED STATES PATENTS

| Number | Name | Date |
|---|---|---|
| 2,331,338 | Michael et al. | Oct. 12, 1943 |
| 2,334,159 | Friedman | Nov. 9, 1943 |
| 2,341,792 | Kanhofer | Feb. 15, 1944 |
| 2,369,009 | Block et al. | Feb. 6, 1945 |
| 2,408,948 | Ocon et al. | Oct. 8, 1946 |
| 2,541,229 | Fleming | Feb. 13, 1951 |
| 2,541,317 | Wilson | Feb. 13, 1951 |
| 2,585,337 | McKinley | Feb. 12, 1952 |