United States Patent Office 3,310,485
Patented Mar. 21, 1967

3,310,485

HYDROGENATION OF OLEFINIC GASOLINE

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No Drawing. Filed May 4, 1964, Ser. No. 364,762
10 Claims. (Cl. 208—143)

Our invention relates to a process for hydrogenating olefinic containing light distillate stocks employing a hydrocracking catalyst.

In the operation of a refinery wherein a significant portion of the total gasoline pool is produced as light, fluid catalytically cracked (FCC) gasoline, it is quite often found that the octane sensitivity (Research Octane Number minus Motor Octane Number at the same level of TEL addition) of the gasoline pool is not sufficiently low to meet the increasingly more stringent demands of the market. As is known in the art, gasolines containing considerable quantities of olefinic hydrocarbons, such as, for example, light FCC gasolines, have poor octane sensitivity and it follows from this that blending such stocks into the refinery gasoline pool tends to increase the octane sensitivity of the total pool. To construct and maintain a hydrogenating unit and also to purchase and maintain large inventories of hydrogenating catalysts tailored to hydrogenate these stocks of high octane sensitivity in order to saturate the deleterious olefinic components is in most instances economically unfeasible or at least undesirable. To effect such hydrogenation quickly and with the least expense, it would appear advantageous to attempt the hydrogenation in an existing facility such as a hydrocracking unit employing a hydrocracking catalyst. It has been found, however, that such an operation causes side reactions, mainly polymerization and alkylation, resulting in the production of heavy materials having final boiling points or endpoints significantly greater than the endpoint of the charge stock. Thus, the production of this heavy material not only raises the endpoint of the gasoline but also lowers the Research Octane Number of the gasoline at any given level of Motor Octane, and, as will be realized, any lowering of the Octane Number is, of course, undesirable.

We have discovered a method whereby gasoline containing olefinic components can be hydrogenated in order to saturate, at least partially, such olefinic components without the production of any significant quantity of heavy materials, that is, materials having an endpoint substantially higher than the endpoint of the gasoline charge.

Our invention includes a process for hydrogenating the gasoline or other light distillate stock containing olefinic components by contacting the charge stock with hydrogen in the presence of a hydrocracking catalyst under hydrogenating conditions of pressure, space velocity and hydrogen feed rate and at an initial operating temperature above about 500° F. A temperature in this range is maintained until at least about 500 volumes of charge per volume of catalyst have been passed through the catalytic reaction zone. The temperature is then reduced to below 500° F. while the hydrogenation is continued.

Charge stocks suitable for employment in the process of our invention include petroleum distillates, particularly light distillate stocks, which contain any considerable amount of olefinic hydrocarbons. By "considerable amount" is meant any petroleum distillate fraction containing from about 25 to about 75 percent by volume olefinic constituents. The process of our invention is particularly suitable for the treatment of light FCC gasolines generally boiling from the C_5 range up to about 350° F.

The hydrocracking catalysts which can be employed in our invention include any of the well-known two-component hydrocracking catalysts wherein a minor amount of a hydrogenating catalyst is composited with a major amount of a cracking catalyst, e.g., acidic hydrocracking catalysts. For example, such catalysts include the oxides and sulfides of the Group VI and the Group VIII metals either alone or in admixture distended on an acidic support. The acidic supports include, among others, silica-alumina, magnesia-alumina, silica-zirconia-alumina and the particular alumina made in accordance with the methods described in applications S.N. 118,240, now Patent No. 3,188,174; 118,241, now Patent No. 3,151,939, and 118,279, now Patent No. 3,151,940, of Kehl and Stewart, filed June 20, 1961, when combined with tungsten together with either nickel or palladium. Hydrocracking catalysts of this type are also suitable when promoted with a halogen. The hydrocracking catalysts employed in our invention can also be either fresh catalysts or can be catalysts which have previously been employed in hydrocracking operations and then regenerated.

As mentioned above, the initial operating temperature employed in the process of our invention must be above about 500° F. and this initial operating temperature can be as high as about 675° F. Preferably, however, the initial operating temperature is maintained in a range from about 500° F. to about 575° F. After a throughput period of at least 500 volumes of charge per volume of catalyst, the operating temperature is then reduced to a level below 500° F. and can be reduced to as low as about 300° F. The actual range to which the operating temperature is reduced is, of course, determined by the extent of hydrogenation which it is desired to be effected. Generally, however, we find that the operating temperature can in most instances be reduced to a range from about 375° F. to about 450° F.

The hydrogen partial pressure employed during the initial period of operation in accordance with our process is in the range from about 100 to about 3000 p.s.i.g. and preferably is from about 300 to about 1000 p.s.i.g. It should be pointed out that a certain decrease in production of the heavy materials during the period of initial operation can also be effected by increasing the hydrogen partial pressure. The extent of this reduction in heavy materials produced, however, is not nearly so great as that effected with employment of temperatures above 500° F.

The space velocity employed during the initial period of the process of our invention can be from about 0.25 to 10 and preferably is from about 0.5 to about 4. We have also found that a hydrogen feed rate from about 1000 to about 10,000 standard cubic feet per barrel (s.c.f./b.), and preferably from 3000 to 6000 s.c.f./b. can be employed.

All of the above operating conditions are those which can be employed during the initial period of operation, i.e., until at least 500 volumes of charge per volume of catalyst have been passed through the reaction zone. After this initial period and when the operating temperature is reduced below 500° F. the other operating conditions can be varied to more conventional ranges.

In order to illustrate our invention in greater detail, reference is made to the following examples.

Example I

In this example a light FCC gasoline having a 330° F. endpoint was hydrogenated over a fixed bed of a fresh, presulfided catalyst. The catalyst comprised 19.2% by weight tungsten, 6.4% by weight nickel and 2.0% by weight fluorine supported on American Cyanamid Triple A silica-alumina (25% Al_2O_3). A series of runs were made employing temperatures in the range from below to just above 500° F. and a hydrogen partial pressure of either 500 or 1000 p.s.i.g. In all of the runs a LHSV

of 1.0 and a hydrogen feed rate of about 4000 s.c.f./b. were employed. The particular temperature and pressure employed in each run together with throughout rate and inspections of the charge and products are shown in Table I below.

TABLE I

	Charge	Run No.				
		1	2	3	4	5
Temperature, ° F.		433	524	429	527	526
Pressure, p.s.i.g.		500	500	1,000	1,000	500
Throughput, vol./vol.		16.5	36.5	48.0	63.0	82.0
Liquid Product:						
Recovery, percent by wt.		95.3	99.4	94.3	97.6	97.9
° API Gravity	66.8	68.2	70.6	69.9	72.3	71.4
Aromatics, percent by vol.	9.9	7.3	6.8	6.9	3.7	6.6
Olefins, percent by vol.	57.7	0.5	0.4	0.5	0.3	0.4
Bromine Number	100.7	Nil	Nil	Nil	Nil	Nil
Knock Rating, +2 cc. TEL:						
Motor	83.5	86.6		86.1	86.3	89.2
Research	98.2	86.9		86.6	[2] 83.6	90.0
Distillation, ASTM D-86:						
90%, ° F.	271	324	277	294	264	277
95%, ° F.	296	392	306	339	290	307
Endpoint	330	455	352	407	318	360
Percent > Charge Endpoint	[1] 0.6	7.9	2.0	4.4	0.6	2.5

[1] Residue remaining after endpoint was recorded.
[2] Appears low.

From the above table it can be seen that essentially all the olefins of the charge stock were hydrogenated in each of the runs; however, it can also be seen that in addition to the hydrogenation of the olefins, some side reaction occurred in almost each run as indicated by an increase in the endpoint of the liquid product in the ASTM D-86 distillation test. It will be noted that the endpoint of the light FCC gasoline charge stock is 330° F. and any material in the products boiling above this figure as shown by the 90%, 95% and endpoint values is, therefore, evidence of heavy material produced by side reactions. (The percentage of this material produced is indicated in the last entry in each column.)

By a comparison of the data from runs 1 and 2, the effect of employing a temperature above 500° F. can readily be seen. Thus, in run 1 at 433° F. and 500 p.s.i.g., about 8% of the liquid produced boiled above the endpoint of the charge stock; whereas in run 2 at 524° F. and 500 p.s.i.g. only 2% of the liquid product boiled above the endpoint of the charge stock. Moreover, in run 1 the 90% point was 53° F. greater, the 95% point was 96° F. greater and the endpoint 125° F. greater than the corresponding distillation points for the charge stock, while in run 2 the 90% and 95% distillation points of the hydrogenating gasoline product were nearly the same as that of the charge stock and the endpoint of the product was only 22° F. greater than the endpoint of the charge.

A comparison of the product data from runs 1 and 3 wherein the temperatures employed were substantially the same and below 500° F. a certain reduction in the quantity of heavy materials produced was effected by increasing the hydrogen partial pressure from 500 p.s.i.g. in run 1 to 1000 p.s.i.g. in run 3. Thus, the yield of heavy material was 4.4% at 1000 p.s.i.g. in run 3 compared with 7.9% at 500 p.s.i.g. in run 1. However, when the pressure was held at 1000 p.s.i.g. and the temperature increased to 527° F. (greater than 500° F.) in run 4, the quantity of heavy material decreased to somewhat less than 0.6%, almost identical to the charge stock. Furthermore, the boiling range of the liquid product in run 4 was substantially the same as that of the charge stock. It can be seen, therefore, that increasing the pressure in combination with the employment of a temperature above 500° F. is extremely effective in preventing the production of heavy material during the initial period of operation.

By a comparison of the data of run 5 with the data of run 2, it can be seen that the effect of throughput is not an important factor in the early stages of hydrogenation with a hydrocracking catalyst at temperatures greater than 500° F. in accordance with our invention. In run 5 the temperature and pressure employed were the same as employed in run 2, and yet the yield of heavy material in run 5 after 82 volumes per volume throughout was substantially the same as in run 2 after only 36.5 volumes per volume of throughput.

The effect of operating in accordance with the process of our invention can be further seen by comparing the octane ratings of the gasolines from runs 1 and 3 with the octane rating of the gasoline from run 5. Each of these three gasolines contained about 7% aromatics and yet the 360° F. endpoint gasoline from run 5 has a Research and Motor Octane Number advantage of about 3 over the gasolines from runs 1 and 3 having 445° F. and 407° F. endpoints, respectively.

Example II

In this example a light FCC gasoline having a 239° F. endpoint was hydrogenated over a fixed bed of a regenerated, fluorine promoted nickel-tungsten on silica-alumina catalyst. This particular catalyst had been employed for a substantial period of time in various hydrocracking operations and had substantially the same composition as the fresh catalyst employed in Example I with the exception of a somewhat lower fluorine content. The catalyst of this example comprised 18.7% by weight tungsten, 6.4% by weight nickel and 1.6% by weight fluorine supported on American Cyanamid Triple A silica-alumina (25% Al_2O_3). The regeneration procedure employed consisted of a carbon burnoff stage and a sulfiding stage. In the carbon burnoff stage nitrogen containing about 0.2% oxygen was passed through the catalyst at a bed temperature of 925° F. The oxygen content was gradually increased to 2.0% while maintaining the bed temperature in the range from between 925° and 950° F. When 2.0% oxygen content was reached without further increase in bed temperature, air was gradually added for a period of about 2 hours to complete the carbon burnoff. This regenerated catalyst was then sulfided prior to its use in the runs of this example by contacting it with a hydrogen stream containing about 10% hydrogen sulfide at a catalyst bed temperature of about 600° F. for about 6 hours.

A series of runs were made employing this regenerated presulfided catalyst employing temperatures in the range from below to above 500° F., a hydrogen partial pressure of 500 p.s.i.g., a hydrogen feed rate of about 4000 s.c.f./b. and a space velocity of either 1.0 or 2.0. The particular temperature and space velocity employed in each run together with the throughput rate and inspections of the charge and products are shown in Table II below.

TABLE II

	Charge	Run No.					
		1	2	3	4	5	6
Temperature, ° F		425	510	460	422	576	457
Space Velocity (LHSV), vol./hr./vol		2.0	2.0	2.0	1.0	1.0	1.0
Throughput, vol./vol		17.0	106	533.6	84	212.8	499.5
Liquid Product:							
Recovery, percent by wt		98.7	99.4	97.8	98.3	92.3	102.7
° API Gravity	72.4	70.3	75.6	73.7	73.2	76.7	76.1
Aromatics, percent by vol	4.8		7.8	3.6	4.0	5.0	3.7
Olefins, percent by vol	59.7		2.2	35.9	21.1	0.9	15.1
Bromine Number	112.7	38.1	11.0	61.6	37	1.72	27.4
Knock Rating, +2 cc. TEL:							
Motor	84.0	86.4	89.5	85.6	86.7	89.4	87.7
Research	99.2	94.3	89.5	97.9	93.5	90.4	95.4
Distillation, D-86:							
90%, ° F	205	384	218	206	243	212	208
95%, ° F	223	477	250	224	388	254	228
Endpoint	239	491	393	254	393	294	247
Percent > Charge Endpoint	[1] 0.6	18.3	6.2	2.4	8.6	4.4	2.0

[1] Residue remaining after endpoint was recorded.

The advantage in employing a temperature greater than 500° F. during the initial period of operation in order to avoid the production of heavy material can again be seen by comparing run 1 at 425° F. with run 2 at 510° F. Aside from temperature, the operating conditions in both of these runs were substantially the same and yet the amount of heavy material obtained in run 1 was 18.3% as opposed to 6.2% obtained in run 2—a 300% improvement. The greater quantity of heavy material present in the product in run 1 is further emphasized by a comparison of the ASTM D–86 distillations.

A comparison of the data from runs 2 and 3 clearly demonstrates that after a throughput of greater than 500 volumes per volume a reactor temperature greater than 500° F. is not necessary to prevent the formation of heavy materials. Thus, in run 3 operating at 460° F. after 533.6 volumes per volume of throughput the amount of heavy material obtained was only 2.4%, while it was necessary in run 2 to operate at a temperature above 500° F. in order to reduce the formation of heavy material to 6.2%. This data confirms that the formation of heavy material is not a problem at temperatures lower than 500° F. after the catalyst has aged for the minimum period of 500 volumes per volume in accordance with our invention.

Runs 4, 5 and 6, wherein a space velocity of 1.0 rather than 2.0 was employed, are cumulative to the showing of runs 1, 2 and 3. Thus, in run 5 at 576° F. only about one-half as much heavy material was formed as in run 4 at 422° F. Further, run 6 again demonstrates that after a throughput of 500 volumes per volume a temperature below 500° F., i.e., 457° F., can be employed to obtain only 2.0% of heavy material in the product.

Example III

In this example the refinery gasoline pool, which inter alia contained the total refinery output of light FCC gasoline, varied in octane sensitivity in the range of 10 to 10.5. In order to reduce the octane sensitivity of the total pool down to an acceptable level, the fraction of the light FCC gasoline boiling from C_5 to about 260°–280° F. endpoint was selected for hydrogenation in accordance with the process of our invention. This particular fraction was selected since it constituted the larger component of the gasoline pool and also contained a considerable amount of olefinic hydrocarbons (about 58%). The catalyst employed was an aged, presulfided nickel-tungsten promoted with 2% fluorine supported on alumina catalyst similar to the catalysts of Examples I and II. The hydrogenation was carried out at a temperature above 500° F. in an existing hydrocracking unit over the hydrocracking catalyst described above, which is normally contained in such unit. The hydrogenated FCC gasoline obtained from this hydrogenation was added to the refinery gasoline pool and the octane sensitivity of the pool, now containing the hydrogenated FCC gasoline, was reduced to 9.0.

We claim:

1. A process for hydrogenating a gasoline containing olefinic components which comprises contacting the gasoline with hydrogen in the presence of a hydrocracking catalyst under hydrogenating conditions of pressure, space velocity and hydrogen feed rate and at an initial temperature above about 500° F., maintaining the temperature above 500° F. until the catalyst has been contacted by at least 500 volumes of gasoline per volume of catalyst, then reducing the temperature to below about 460° F. while continuing the hydrogenation.

2. A process for hydrogenating a light fluid catalytically cracked gasoline fraction containing olefinic components, which process comprises contacting the gasoline with hydrogen in the presence of a hydrocracking catalyst comprising a minor amount of a hydrogenating component composited with a major amount of an acidic hydrocracking component at an initial temperature above about 500° F., a hydrogen partial pressure from about 100 to about 3000 p.s.i.g., a liquid hourly space velocity from about 0.25 to about 10 volumes of gasoline per volume of catalyst per hour and a hydrogen feed rate from about 1000 to about 10,000 s.c.f./b., maintaining these operating conditions until the catalyst has been contacted by at least 500 volumes of gasoline per volume of catalyst, and then reducing the temperature to below about 460° F. while continuing the hydrogenation.

3. The process of claim 2 wherein the fluid catalytically cracked gasoline fraction boils from the C_5 range up to about 350° F.

4. The process of claim 2 wherein the hydrogen partial pressure is from about 300 to about 1000 p.s.i.g., the liquid hourly space velocity is from about 0.5 to 4 and the hydrogen feed rate is from about 3000 to about 6000 s.c.f./b.

5. The process of claim 4 wherein the hydrogenating component comprises nickel and tungsten and the hydrocracking component comprises silica-alumina.

6. The process of claim 5 wherein the catalyst is promoted with fluorine.

7. A process for hydrogenating a light fluid catalytically cracked gasoline fraction containing olefinic components, which process comprises contacting the gasoline with hydrogen in the presence of a hydrocracking catalyst comprising a minor amount of a hydrogenating component composited with a major amount of an acidic hydrocracking component at an initial temperature of from about 500° F. to about 675° F., a hydrogen partial pressure from about 100 to about 3000 p.s.i.g., a liquid hourly space velocity from about 0.25 to about 10 volumes of gasoline per volume of catalyst per hour and a hydrogen feed rate from about 1000 to about 10,000 s.c.f./b., maintaining these operating conditions until the catalyst has been contacted by at least 500 volumes of gasoline per

volume of catalyst, and then reducing the temperature to below about 460° F. and above about 300° F. while continuing the hydrogenation.

8. The process of claim 7 wherein the initial temperature is from about 500° F. to about 575° F., the hydrogen partial pressure is from about 300 to about 1000 p.s.i.g., the liquid hourly space velocity is from about 0.5 to about 4, the hydrogen feed rate is from about 3000 to about 6000 s.c.f./b., and after the catalyst has been contacted by at least 500 volumes of gasoline per volume of catalyst, the temperature is then reduced to the range from about 375° F. to about 450° F.

9. The process of claim 8 wherein the hydrogenating

component comprises nickel and tungsten and the hydrocracking component comprises silica-alumina.

10. The process of claim 9 wherein the catalyst is promoted with fluorine.

References Cited by the Examiner

UNITED STATES PATENTS

3,125,505	4/1964	Tupman et al.	208—143
3,169,106	2/1965	Lefrancois et al.	208—143
3,203,891	8/1965	Holden	208—143

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