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2,723,946

HYDROCARBON CONVERSION PROCESS

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No Drawing. Application May 29, 1950,
Serial No. 165,107

8 Claims. (Cl. 196—50)

This invention relates to the catalytic conversion of hydrocarbons. It is more specifically concerned with a method of reforming hydrocarbon fractions boiling approximately within the gasoline range.

Recently, a superior reforming catalyst has been developed, said catalyst comprising palladium or, preferably, platinum and alumina as the principal constituents and frequently containing minor amounts of a halogen, particularly fluorine or chlorine. Catalysts of this type are capable of increasing the octane number of hydrocarbon stocks such as straight-run gasolines and naphthas to values that are substantially higher than those that ordinarily can be reached by thermal reforming. In addition, the yield-octane number relationship is much better than are the corresponding relationships obtained in either thermal reforming or in most of the prior catalytic reforming processes. It has been found that by an appropriate selection of operating conditions and by charging a feed stock of relatively low end point, these catalysts can be used for a number of weeks or months without regeneration. However, if the end point of the charge stock is relatively high, or if the charging stock contains minor traces of impurities, such as nitrogen compounds, which tend to deactivate or poison the catalyst, the rate of catalyst deactivation is greatly accelerated. In order that this process be economically attractive it is desirable that it be substantially nonregenerative. I have invented a process by means of which greatly increased catalyst life is obtained with poor stocks as well as with good stocks.

It is an object of this invention to convert gasoline boiling range hydrocarbons to more valuable products.

Another object of this invention is to reform low octane number hydrocarbon fractions to products of higher octane number.

Still another object of this invention is to reform in substantially nonregenerative operation in the presence of platinum- or palladium-containing catalysts gasoline fractions that tend to relatively rapidly deactivate said catalyst.

In one embodiment my invention relates to an improvement in the conversion of a hydrocarbon charge stock in the presence of a catalyst selected from the group consisting of platinum- and palladium-containing catalyst at conversion conditions at which the charge stock tends to deactivate the catalyst, said improvement comprising processing said stock until the catalyst has lost a measurable amount of activity, discontinuing the processing of said charge stock and substituting therefor a hydrocarbon charge stock which exhibits less tendency to deactivate the fresh catalyst, processing said latter stock until at least a part of the lost activity has been restored, and thereafter discontinuing the processing of said latter stock and resuming the processing of said first stock.

In a more specific embodiment my invention relates

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to an improvement in the reforming of a hydrocarbon charge stock boiling approximately within the gasoline range and having a relatively high end point in the presence of hydrogen and a platinum-containing catalyst at reforming conditions at which the charge stock exhibits a substantial tendency to deactivate the catalyst, said improvement comprising reforming said stock until the catalyst has lost a measurable amount of activity, discontinuing the reforming of said charge stock and substituting therefor a normally liquid hydrocarbon charge stock of lower end point which exhibits less tendency to deactivate the fresh catalyst, reforming said latter stock until at least a part of the lost activity has been restored, and thereafter discontinuing the reforming of said latter stock and resuming the reforming of said first stock.

In another specific embodiment my invention relates to an improvement in the reforming of hydrocarbon charge stocks boiling approximately within the gasoline range and having an appreciable nitrogen compound content at reforming conditions at which the charge stock exhibits a substantial tendency to deactivate the catalyst, the improvement which comprises reforming said stock until the catalyst has lost a measurable amount of activity, discontinuing the reforming of said charge stock and substituting therefor a normally liquid hydrocarbon charge stock substantially free from nitrogen compounds which exhibits less tendency to deactivate the fresh catalyst, reforming said latter stock until at least a part of the lost activity has been restored, and thereafter discontinuing the processing of said latter stock and resuming the processing of said first stock.

In the hydrocarbon reforming processes employing a catalyst comprising platinum and alumina or palladium and alumina, the hydrocarbon reactant to be converted is preheated and, together with hydrogen, is contacted with the catalyst. As is usual in catalytic processes of this type, the hydrocarbon conversion reaction ordinarily is accompanied by a fouling reaction which causes deposition of carbonaceous material, hereinafter called carbon on the catalyst. The presence of the deposit lowers the activity of the catalyst and in the usual operation a point is reached at which the effectiveness of the catalyst is so low that it must either be discarded and replaced with fresh catalyst, or the activity of the catalyst must be restored by the removal of the carbon by combustion. Both methods are expensive, and it can be readily seen that substantial economic and operating advantages would accrue if it were possible to hinder or retard carbon formation, or remove carbon formed during the processing of the hydrocarbon.

I have found that the useful life of the catalyst can be greatly increased if a charging stock that exhibits a low tendency to foul or carbonize the catalyst is periodically substituted for the normal hydrocarbon charging stock that exhibits a greater tendency to foul the catalyst.

It has been observed that hydrocarbon fractions possessing relatively high end boiling points produce a considerably larger amount of carbon in a given amount of time than do hydrocarbon fractions having lower end boiling points. Thus, for example, the catalyst carbon production rate with a 300–400° F. straight-run naphtha is many times higher than is the carbon production rate at equivalent conditions with a 100–300° F. straight-run naphtha.

I have found that if I reform a relatively high boiling hydrocarbon fraction in the presence of a palladium- or platinum-containing catalyst, thereby depositing an appreciable amount of carbon on the catalyst, and thereafter

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reform a lower boiling fraction with the same catalyst, that there is not merely a decrease in the rate at which carbon is deposited during the processing of the last-named fraction, but that there is an actual decrease in the amount of carbon on the catalyst. This decrease in the carbon content of the catalyst results in at least a partial restoration of the catalyst activity. Consequently, it is possible to again switch back to the higher boiling fraction and obtain an appreciable further amount of conversion therewith. Briefly then, it can be seen that I am able to process a greater amount of higher boiling charging stock with a given amount of catalyst by alternately processing higher boiling and lower boiling stocks, than would be possible if I processed only the higher boiling fraction.

A particularly useful application of my invention involves separating a normal wide boiling hydrocarbon reforming stock into, for example, a higher boiling fraction and a lower boiling fraction and alternately subjecting said fractions to reforming in the presence of a catalyst comprising palladium- or platinum-alumina. Each fraction can then be processed under the conditions most favorable for a good yield-octane number relationship for that particular fraction. In addition, the processing of the lower boiling fraction removes a certain amount of the carbon deposited on the catalyst during the processing of the higher boiling fraction. With this type of operation I can obtain markedly increased overall catalyst life as well as a superior yield-octane number relationship.

Another type of hydrocarbon reforming charge stock that tends to deactivate catalysts of the type herein described are those hydrocarbon fractions that possess an appreciable nitrogen compound content. The nitrogen compounds appear to temporarily poison the catalyst, thereby deactivating the same. The deactivation does not appear to be due to deposition of carbonaceous material on the catalyst, since the rate of carbon formation with such stocks frequently is appreciably lower than it is with nitrogen-free stocks. I have found that if a catalyst that has become at least partially deactivated through the reforming of a hydrocarbon stock containing nitrogen compounds, is used for the reforming of a nitrogen-free charging stock, the activity of the catalyst is largely restored. Therefore, when it is necessary to process a hydrocarbon stock containing an appreciable nitrogen compound content, such as a straight-run gasoline from the Los Angeles Basin, I alternately process a stock that is substantially free from nitrogen compounds. In this way I am able to process a much larger amount of the nitrogen-containing stock than would otherwise be possible.

The hydrocarbon stocks that may be converted in accordance with my process comprise hydrocarbon fractions containing saturated hydrocarbons, particularly naphthenes. The preferred stocks are those consisting essentially of naphthenes and paraffins, although in some cases aromatics and/or olefins also may be present. This preferred class includes straight-run gasolines, natural gasolines, and the like. On the other hand, it frequently is advantageous to charge thermally or catalytically cracked gasolines, particularly higher boiling fractions thereof to my reforming process. If a cracked gasoline or fraction is charged, it often will be processed in admixture with a straight-run fraction. The gasoline may be full boiling range gasoline having an initial boiling point of from about 50° to about 100° F. and an end boiling point within the range of from about 325° to about 425° F., or it may be a selected fraction thereof which usually will be a higher boiling fraction, commonly referred to as naphtha, and generally having an initial boiling point within the range of from about 125° to about 250° F. and an end boiling point within the range of from about 350° F. to about 425° F.

The hydrocarbon stock that I use to at least partially restore the activity of the used catalyst should be one that exhibits less tendency than the first-used stock to deactivate the catalyst at substantially the same operating con-

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ditions or, preferably, at conditions to give substantially the same octane number, when employing fresh catalyst. For example, if stock A is reformed over platinum-alumina-combined halogen catalyst until there has been an appreciable loss in catalyst activity, stock B can be used to restore at least a portion of said lost activity if stock B causes less deactivation of fresh platinum-alumina-combined halogen catalyst than is brought about by stock A at conditions to give reformates of approximately the same octane number.

The reforming catalyst that may be used in my process is selected from those catalysts, comprising at least one refractory oxide composited or associated with platinum or palladium, that are capable of promoting hydrocracking of paraffins and dehydrogenation of naphthenes. A preferred type of catalyst that falls in this category is described in U. S. Patent No. 2,479,109, issued August 16, 1949. These catalysts comprise alumina, platinum, and combined halogen, especially combined fluorine and combined chlorine. They are prepared by forming a mixture of alumina and a halogen compound, the halogen being in an amount of from about 0.1% to about 1.0% by weight of said alumina on a dry basis, and thereafter compositing about 0.1% to about 1.0% platinum with the mixture, and subsequently heating the composite.

Another group of catalysts that may be used in the present process comprises a cracking component and a metal selected from the group consisting of platinum and palladium. The cracking component ordinarily will comprise silica and at least one other metal oxide, usually selected from the group consisting of alumina, zirconia, magnesia, and thoria. Another type of cracking component that may be used in these catalysts comprise alumina-boria composites. These catalysts are made, for example, by drying a composite of silica hydrogel and alumina hydrogel and thereafter incorporating into the dry composite a metal selected from the group consisting of platinum and palladium in an amount of from about 0.1% to about 1.0%. Further details concerning the preparation of catalysts of this type will be found in U. S. Patent No. 2,478,916.

Hydrocarbon reforming operations carried out in accordance with my invention ordinarily will be conducted at temperatures of from about 600° F. to about 1000° F. if the catalyst comprises a cracking component and a metal selected from the group consisting of platinum and palladium. If the catalyst comprises platinum-alumina-combined halogen, the temperature ordinarily will lie within the range of from about 750° F. to about 1000° F.

The pressures at which my process will be conducted will lie within the range of from about 50 to 1200 p. s. i., a total pressure of at least 250 lbs. ordinarily is preferred. The weight hourly space velocity, defined as the weight of hydrocarbons charged per hour per weight of catalyst in the reaction zone, should lie within the range of from about 0.2 to about 40. The amount of hydrogen charged along with the hydrocarbons usually will be from about 0.5 to about 15 mols per mol of hydrocarbon. However, with certain types of charging stocks and in certain types of operations, sufficient hydrogen is produced in situ so that there is no necessity for charging external hydrogen.

The following example is given to illustrate my invention, but it is not given for purposes of limiting the generally broad scope of said invention.

A Mid-Continent straight-run gasoline was fractionated into a lower and a higher boiling fraction. The lower boiling fraction had a boiling range, in the ASTM distillation, of 190° to 350° F. The higher boiling fraction had a distillation range of from 350° to about 400° F. The low end point material was processed for 65 hours over a catalyst comprising 0.3% platinum, 0.3% fluorine, and 0.3% chlorine on alumina. The higher boiling fraction was processed in three different runs over three separate batches of catalyst of the composition given above, said runs being 22, 65, and 192 hours in duration.

The operating conditions and results are shown in the following table:

Table I

Run No.			1	2	3	4
Catalyst			Fresh	Fresh	Fresh	Fresh
	190°-350° FEP	350°-400° FEP	190°-350° FEP	350°-400° FEP	350°-400° FEP	350°-400° FEP
Length of Run, Hours			65	65	22	192
Operating Cond.:						
Average Cat. Temp., ° C			456	457	456	456
Pressure, p. s. i. g			500	500	500	500
Liquid Hr. Space Velocity			2.0	2.0	2.0	2.0
H ₂ /Chg. Mol Ratio			3.2	3.6	3.5	3.4
Reformate Yield, Vol. Percent			92.2-93.8	91.9-93.3	92.2	93.9-94.9
Reformate Octane Nos.:						
F-2 Clear	40.5	19.0	78.0-76.2	76.4-69.2	75.8	66.2-65.8
F-2+3 cc. TEL/gal	66.8	47.1	86.7	82.5		74.4
F-1 Clear	43.2	24.0	84.7	81.7-75.4	81.7	71.1-70.8
F-1+3 cc. TEL/gal	67.4	46.5	94.7	91.9-87.7	92.2	85.7-85.2
Carbon on Catalyst:						
As Charged, Wt. Percent			0	0	0	0
As Removed, Wt. Percent			0.78	4.99	3.44	8.42

The longer runs were divided into periods and reformate inspections and yield data were obtained for the various periods, which accounts for the ranges given in the table. However, complete analytical data were not always obtained for each period, hence such values as were determined are reported.

A comparison of the results of run No. 1 with those of run No. 2, shows that the higher boiling stock produced more than 6 times the amount of carbon that was produced by the lower boiling charge stock in the same length of time. A comparison of runs 2, 3 and 4 shows that the amount of carbon deposited on the catalysts increases with increase in processing time. The activity decline of the catalyst is shown by the absolute octane numbers of the reformate as well as the variations during the run. The variations or ranges are not strictly comparable because the time intervals in each run during which reformate was collected and the octane number thereof determined varied somewhat from run to run. However, in general, it can be seen that not only is the quality of the reformate produced from the higher boiling charging stock lower than that produced from the lower boiling charging stock, but also that the rate of decline in quality, which is a measure of the rate of decline of catalyst activity, was greater in the runs in which the higher boiling material was reformed.

The catalyst from each of the foregoing runs was used, without regeneration or further treatment, in the reforming of a 110°-350° F. end point Pennsylvania straight-run gasoline. The operating conditions and results of these runs are shown in the following table: The catalysts from runs 1, 2, 3, and 4 were used in runs 5, 6, 7, and 8, respectively.

Table II

Run No.		5	6	7	8
Catalyst		Fresh	Fresh	Fresh	Fresh
Charge Stock	110°-350° FEP	110°-350° FEP	110°-350° FEP	110°-350° FEP	110°-350° FEP
Length of Run, Hrs		72	72	72	74
Operating Conditions:					
Catalyst Av., ° C		466	466	465	464
Pressure, p. s. i. g		700	700	700	700
Liquid Hr. Space Vel.		4.0	4.0	4.0	4.1
H ₂ /Chg. Mol Ratio		4.9	5.4	5.1	5.2
Reformate Yield, Vol. Percent		94.7	96.1	95.8	95.8
Reformate Octane Nos.:					
F-2 Clear	51.3	71.2	66.3-69.0	67.0-69.4	60.2-64.2
F-2+3 cc. TEL/gal	69.7	85.0	83.1-84.6	83.1	80.8
F-1 Clear	49.5	73.4-75.0	70.3	71.0-74.2	63.3-66.8
F-1+3 cc. TEL/gal	70.3	89.5	86.3	87.0-87.6	80.8-84.2
Carbon on Catalyst:					
As Charged, Wt. Percent		0.78	4.99	3.44	8.42
As Removed, Wt. Percent		0.76	4.37	2.96	7.07

It can be seen that the reforming of the lower boiling straight-run gasoline fraction over the used catalyst low-

ered the carbon content of said catalysts. The restoration of the activity accompanying the decrease in the carbon content is shown by the increase in the octane numbers in the reformate during the runs.

The data in the foregoing tables show that platinum-alumina-combined halogen catalyst that has been substantially deactivated during the processing of the relatively high end point reforming charge stock, can be reactivated at least in part by further reforming with said catalyst of a lower boiling charging stock. When such partially reactivated catalyst, as was recovered from runs 5, 6, 7 and 8, is used for the additional processing of higher boiling fractions, it is found that the catalyst exhibits increased activity in such operation.

I claim as my invention:

1. In the reforming of a hydrocarbon charge stock boiling approximately within the gasoline range and having a relatively high end point in the presence of hydrogen and a catalyst containing a metal of the group consisting of platinum and palladium, the method which comprises reforming said stock until the catalyst has lost activity, discontinuing the reforming of said charge stock and substituting therefor a normally liquid hydrocarbon charge stock of lower end point, reforming said latter stock in the presence of hydrogen until at least a portion of the lost activity has been restored, and thereafter discontinuing the reforming of said latter stock and resuming the reforming of said first stock.

2. The process of claim 1 further characterized in that said normally liquid hydrocarbon charge stock comprises a straight-run petroleum fraction.

3. The process of claim 1 further characterized in that said catalyst comprises platinum and alumina.

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4. The process of claim 1 further characterized in that said catalyst comprises alumina containing from about 0.1% to about 1.0% platinum and from about 0.1% to about 1.0% combined halogen.

5. The process of claim 1 further characterized in that said catalyst comprises alumina containing from about 0.1% to about 1.0% platinum and from about 0.1% to about 1.0% combined fluorine.

6. A process for the treatment of relatively light and heavy gasoline fractions, the heavier fraction forming more carbon than the lighter fraction during catalytic reforming, which comprises reforming the heavier gasoline fraction in the presence of hydrogen and a platinum-containing catalyst until the activity of the catalyst has been lowered by the deposition of carbon thereon, then discontinuing the contacting of the heavier fraction with said catalyst and substituting the lighter gasoline fraction therefor, reforming the lighter fraction in contact with said catalyst and in the presence of hydrogen until at least a portion of the carbon deposit has been removed from the catalyst, thereafter discontinuing the reforming of the lighter fraction in contact with said catalyst and

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resuming the reforming of the heavier gasoline fraction in contact with the catalyst.

7. The process of claim 6 further characterized in that said catalyst comprises platinum and alumina.

8. The process of claim 6 further characterized in that said catalyst comprises platinum, alumina and combined halogen.

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