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REMOVAL OF OXYGEN AND WATER FROM HYDRO-CONVERSION FEED STOCKS

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2 Sheets-Sheet 1

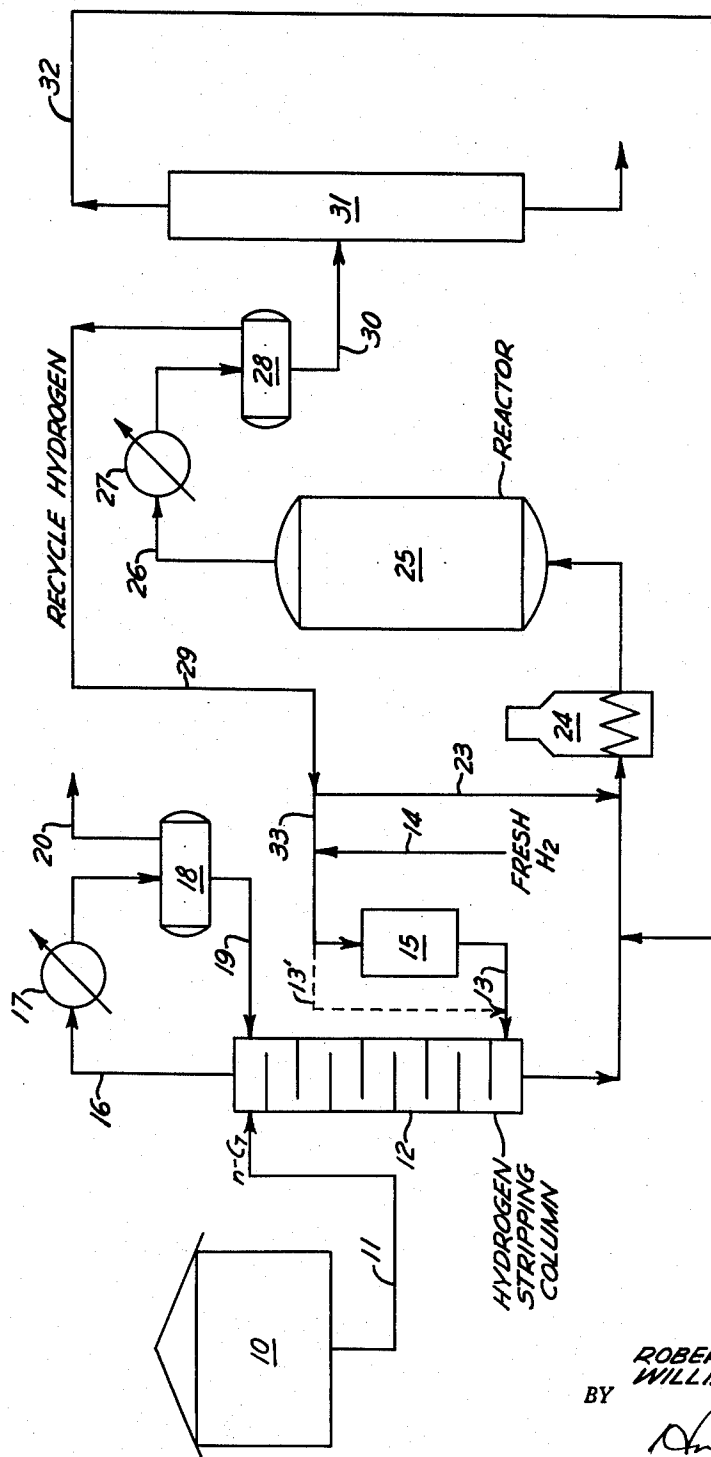


Fig. 1

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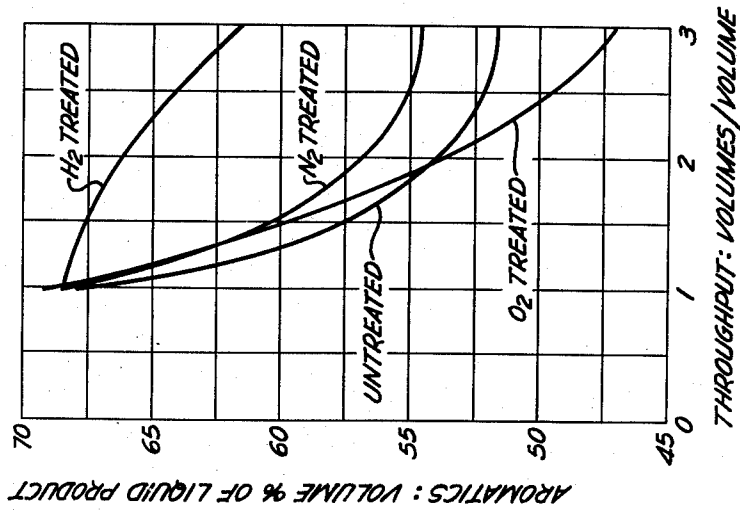
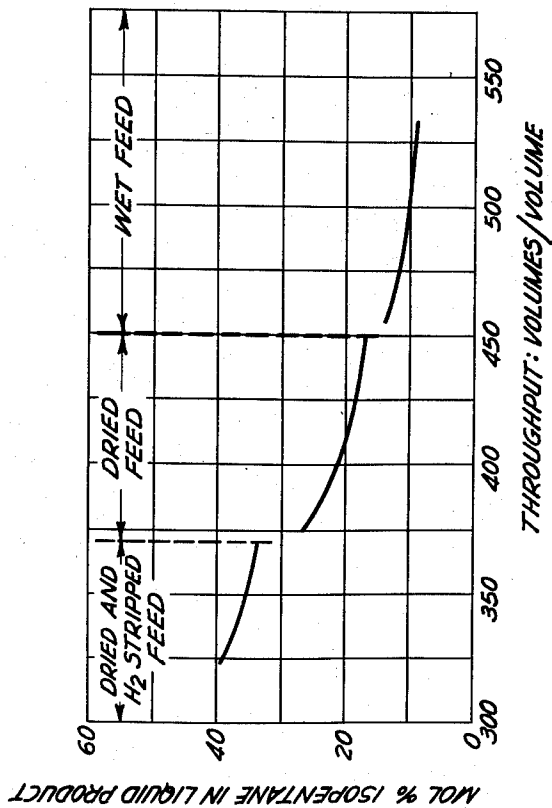
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**REMOVAL OF OXYGEN AND WATER FROM
HYDRO-CONVERSION FEED STOCKS****Robert E. Kline, Verona, and William C. Starnes, Cabot,
Pa., assignors to Gulf Research & Development Com-
pany, Pittsburgh, Pa., a corporation of Delaware****Filed Dec. 28, 1959, Ser. No. 862,196****5 Claims. (Cl. 208—89)**

This invention relates to catalytic conversion of gasoline range hydrocarbons in the presence of hydrogen and a solid catalyst. More particularly, it relates to a novel method for preparing or pretreating feed stocks for such a process.

In some operations of processes for catalytic conversion of gasoline range hydrocarbons the charge stock passes directly from a fractionating column to the catalytic reactor without contacting air. In other operations the charge stock is stored in tanks before being charged to the reactor. It appears that oxygen and/or water dissolve in the gasoline range feed stocks when the latter are contacted therewith during storage or during transfer to the reactor and we have found that such dissolved oxygen and water have an adverse effect on certain processes for catalytic conversion of gasoline range hydrocarbons. The present invention is based on our discovery that certain catalytic conversions of gasoline range hydrocarbons can be improved by pretreating the hydrocarbon feed stock to remove dissolved oxygen and water and our discovery of a particularly effective method for removing such oxygen and water from hydrocarbons of the gasoline boiling range.

Our feed stock pretreatment is applied to certain processes in which a gasoline range hydrocarbon or hydrocarbon mixture is contacted in the presence of hydrogen at elevated temperature with a solid hydroactive catalyst to obtain a chemically converted product of about the same average molecular weight as the feed but of greater value, for example, of improved octane rating. Processes which can be improved by our feed stock pretreatment include two main types of processes for catalytic conversion of gasoline range hydrocarbons at elevated temperature and in the presence of hydrogen with a solid hydroactive catalyst composed of certain metals or metal oxides composited with a major amount of a porous catalytic support or carrier.

In one type of such processes a gasoline range hydrocarbon or hydrocarbon mixture is catalytically converted in the presence of hydrogen and of a catalyst composed of a noble metal or platinum group metal, such as platinum or palladium, on an acidic support, such as halogen-promoted alumina, silica-alumina, silica-zirconia, silica-boria, silica-magnesia, and the like. This type of process includes hydroisomerization of aliphatic paraffins, dehydrogenation of naphthenes, and catalytic reforming of low octane gasolines to form high octane products through a combination of reactions such as paraffin isomerization, naphthene dehydrogenation and dehydrocyclization of paraffins.

The other type of process in which our pretreatment is valuable is the type in which a gasoline range hydrocarbon or hydrocarbon mixture is contacted in the presence of a low partial pressure of hydrogen with a catalyst comprising an oxide of a metal of group VI-A of the periodic table on a non-acidic support. This type of catalyst can also be composited with an iron group metal or metal oxide. A process of this type is dehydrocyclization in which an aliphatic hydrocarbon fraction of the C_6 to C_{10} range is contacted at high temperature, i.e., 950° to 1125° F., and at low hydrogen partial pressure, i.e., less than 150 pounds per square inch gauge, with a solid catalyst such as chromic oxide on a non-acidic alumina support

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which promotes dehydrogenation before carbon-carbon scission can occur. This process is used for converting n-hexane, heptanes, octanes, etc., to benzene, toluene, xylenes, etc. Other processes of this type include dehydrogenation of naphthenes to aromatics and of paraffins to olefins and cyclization of paraffins to naphthenes.

The described processes form a class having certain features in common and each of these processes can be improved at least to some extent by the method of our invention, although not necessarily for the same reason. For instance, in the conversion of gasoline range hydrocarbons in the presence of catalysts composed of noble metals on acidic supports it appears that water is chemisorbed by the catalyst and decreases its acidity. The activity of the dual-function catalyst is thus decreased for the types of reactions for which they are used.

In processes employing non-acidic supported group VI-A metal oxide catalysts at low hydrogen partial pressure, the mechanism of the harmful effect of oxygen or water is not as well understood and may be different from the effect with catalysts having highly acidic supports. One possible explanation is that at the high temperatures employed with such catalysts, free oxygen present in the reaction zone may react with the hydrocarbons to produce oxygen-containing fragments which tend to propagate free radical reactions, the products of which can cause rapid catalyst deactivation when the hydrogen partial pressure is low, i.e., below about 150 pounds per square inch gauge. In this connection it should be noted that in catalytic reforming with group VI-A metal oxide catalysts, especially molybdenum oxide, the presence of water or oxygen can be highly beneficial. However, such processes operate at high total pressure and high hydrogen to hydrocarbon ratios so that the hydrogen partial pressure is very high. Under such conditions a molybdenum oxide catalyst can become excessively reduced, with resulting loss of catalyst selectivity for the desired reforming reactions. Apparently, water and oxygen prevent the catalyst from becoming over-reduced in a high concentration of hydrogen and thus maintain or improve its selectivity. However, in processes such as dehydrocyclization and dehydrogenation which operate at low total pressure and low hydrogen concentration we have found that the introduction of oxygen into the reaction zone is harmful, thus distinguishing such processes carried out at a partial pressure of hydrogen less than about 150 pounds per square inch gauge from catalytic reforming carried out with similar catalysts but at high hydrogen partial pressure.

We have discovered that the harmful effect of dissolved oxygen or water in the gasoline range feed stocks for the described processes can be overcome by stripping the liquid hydrocarbon fraction with a stream of dry hydrogen and charging the stripped fraction to the catalytic reactor without further contact with oxygenic fluids such as air, oxygen or water. We have also discovered that hydrogen is unexpectedly superior to other gases as a stripping gas for removing not only dissolved oxygen or air but also water from hydrocarbons of the gasoline boiling range (i.e., C_4 to about 450° F. endpoint). Based on these discoveries, our process comprises stripping a gasoline range liquid hydrocarbon feed for such a process with a stream of dry hydrogen in a gas to liquid ratio sufficient to reduce the oxygen content of the hydrocarbon fraction to less than 15 milligrams of oxygen per liter of hydrocarbon. The deoxygenated hydrocarbon is then subjected to the appropriate catalytic conversion process, which is either a process for catalytic conversion of gasoline range hydrocarbons by contact in the presence of hydrogen with a catalyst composed of a platinum group metal on an acidic support at elevated temperature and pressure or a process for catalytic conversion of gasoline

range hydrocarbons by contact in the presence of hydrogen with a catalyst comprising a group VI-A metal oxide on a non-acidic support at elevated temperature and at a partial pressure of hydrogen less than about 150 pounds per square inch gauge.

We will describe our process in more detail by reference to the drawings of which:

FIGURE 1 is a flow diagram of one modification of our process;

FIGURE 2 is a plot of data obtained in the dehydrocyclization of n-heptane under varying operating conditions and with different methods of pretreating the n-heptane charge stock; and

FIGURE 3 is a plot of data obtained in hydroisomerization of n-pentane with different pretreatments of the feed stock.

A typical operation of our process as applied to dehydrocyclization of paraffins is illustrated in FIGURE 1. The charge stock is a straight run heptane fraction which is stored in tank 10 with its surface in contact with air. The heptane fraction, containing, for example, 70 milligrams of dissolved oxygen per liter of hydrocarbon, is charged by line 11 to the upper end of stripping column 12.

Column 12 is provided with vapor-liquid contacting means. For example, as shown diagrammatically in FIGURE 1, column 12 is a baffled column having a series of alternately staggered trays or baffles. The liquid hydrocarbon stream enters the upper end of column 12 at a temperature, for example, of 70° F. and at atmospheric pressure. Oxygen-free, dry hydrogen is introduced by line 13 and passes upwardly in countercurrent contact with the downwardly cascading liquid hydrocarbon stream. The hydrogen gas introduced by line 13 can be fresh hydrogen from an outside source as introduced by line 14 or can be a hydrogen-rich recycle gas recovered from the dehydrocyclization product, as we will describe in more detail hereinafter. Preferably, we pass the hydrogen stream through an adsorbent drying means such as a molecular sieve column 15 before passing it into column 12. Both deoxygenation and drying of the hydrogen may be especially necessary if fresh hydrogen from storage is employed. Preferably, we pass the fresh hydrogen over a deoxygenation-type catalyst, e.g., palladium on alumina, prior to passage through an adsorbent such as molecular sieve column 15 and before passing it into column 12. If a mixture of fresh and recycle hydrogen is employed, it may be necessary to dry and deoxygenate only the fresh hydrogen prior to introduction to column 12.

A hydrogen stream containing stripped oxygen or air passes overhead from column 12 by line 16. The gas stream is cooled by condenser 17 to condense any entrained hydrocarbon vapor. Condensate separates from uncondensed gas in separator 18 and returns to column 12 by line 19. The hydrogen passing from the separator by line 20 can be discarded or used for any purpose for which hydrogen containing a small amount of oxygen is suitable.

A hydrocarbon stream essentially free of oxygen and water is recovered from the bottom of column 12 by line 22. The hydrogen-stripped hydrocarbon stream in admixture with hydrogen from line 23 is pumped through a preheater 24 where it is heated to a desired vapor temperature. The charge is introduced at dehydrocyclization reaction conditions, to reactor 25 which contains a dehydrocyclization catalyst such as a fixed-bed of a pelleted, chromia-alumina catalyst. Typical dehydrocyclization conditions for reactor 25 include, for example, an average reactor temperature of 1015° F., a pressure of 10 pounds per square inch gauge (abbreviated hereinafter as p.s.i.g.), a liquid-hourly space velocity (abbreviated hereinafter as LHSV) of 1.0 volume of liquid hydrocarbon per volume of catalyst per hour (abbreviated hereinafter as vol./vol./hr.) and a hydrogen concentration of

2,000 standard cubic feet per barrel of hydrocarbon (abbreviated hereinafter as s.c.f./bbl.).

The reactor effluent withdrawn by line 26 is cooled by the condenser 27 to a suitable temperature for condensing normally liquid components and is passed to a gas-liquid separator 28 where normally gaseous materials are separated from normally liquid hydrocarbons. A hydrogen-rich gas stream, containing, for example, 80 percent hydrogen, is recycled to the reactor charge line 22 by lines 29 and 23. A portion of the hydrogen-rich gas of line 29 can be passed by line 33, alone or in admixture with fresh hydrogen from line 14, to the bottom of stripping column 12 via line 13. As already mentioned, the process hydrogen gas of line 33 can be passed through adsorption drier 15 in advance of the stripping column 12 or, if sufficiently dry, can be passed directly to column 12 by line 13', thus by-passing drier 15. Normally, the recycle hydrogen is sufficiently dry and oxygen-free. Therefore, another possibility is to pass the recycle hydrogen via line 13' to column 12 while passing any fresh hydrogen that contains oxygen or water through drier 15 and/or over a deoxygenation catalyst as mentioned above. The normally liquid portion of the effluent from reactor 25 is passed by line 30 to the product fractionator 31. A bottoms fraction rich in aromatics and an overhead fraction which contains unconverted heptane are recovered. The latter fraction is recycled by line 32 to the reactor charge line 22.

The central element of our new process is the hydrogen stripping of the hydrocarbon fraction to remove dissolved oxygen and water. In discussing the flow sheet of FIGURE 1 we have described countercurrent stripping of a hydrocarbon stream with a stream of dry hydrogen in a stripping column provided with vapor liquid contacting means such as packing or bubble cap trays. However, a simpler method of passing hydrogen through the liquid hydrocarbon can be used. For example, the stripping can be accomplished simply by bubbling hydrogen gas into the bottom of a tank filled with the liquid hydrocarbon. Most suitably, however, the stripping is accomplished by introducing a stream of liquid hydrocarbon charge stock into the top of a simple stripping column, for instance, provided with four or five bubble cap trays, and introducing hydrogen into the bottom of the column in countercurrent contact with the hydrocarbon liquid and hydrogen gas.

We have satisfactorily carried out the stripping of gasoline range hydrocarbon feed stocks with hydrogen at ambient temperature of about 70° F. and at atmospheric pressure. Such conditions are preferred. However, if desired, the hydrocarbon liquid can be heated mildly before stripping it with hydrogen. This lowers the solubility of dissolved oxygen in the liquid hydrocarbons but raises the problem of vaporization of hydrocarbons. The pressure of the gas above the liquid hydrocarbon during the stripping operation can be somewhat below or above atmospheric pressure but the pressure should not be above about 30 pounds per square inch gauge. We will discuss more fully hereinafter the advantages of hydrogen-stripping of gasoline range hydrocarbons at such relatively low pressure and temperature.

We have found that in the stripping operation the hydrocarbon should be contacted with considerably more than an equal volume of hydrogen. Preferably, the hydrocarbon should be contacted with at least 4 gaseous volumes of hydrogen per liquid volume of hydrocarbon. As we will demonstrate and discuss more fully hereinafter, it is possible to reduce the oxygen content of the hydrocarbon charge stock substantially to zero in less time if a rather high volume ratio, e.g., 4:1 to 8:1 ratio of hydrogen to hydrocarbon, is employed.

The efficiency of the stripping operation or, in other words, the removal of substantially all of the oxygen with a relatively small amount of hydrogen in a short time requires thorough mixing or intimate contact between

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the hydrogen and hydrocarbon. Therefore, means contributing to intimate vapor-liquid contact should be employed. As we have indicated a stripping column provided with vapor-liquid contacting means can be employed. However, satisfactory stripping is achieved by bubbling hydrogen through a vessel of hydrocarbon liquid if the hydrogen is uniformly distributed at the bottom of the vessel, for example, by means of a sparger.

The gasoline range hydrocarbon charge stocks applicable for the dehydrocyclization modification of our process include paraffinic hydrocarbons of the C₆ to C₁₀ range. Suitable charge stocks include either single paraffins of this range, such as n-hexane, n-heptane, or n-octane, or hydrocarbon fractions predominating in such paraffins. These charge stocks differ from those employed in catalytic reforming in having a relatively low content of naphthenes. Minor amounts of cyclics, for example, as much as 25 percent naphthenes or even greater amounts of aromatics, can be tolerated in the charge stocks for our process but the conditions for dehydrocyclization are not the proper conditions for upgrading of naphthenes and the aromatics require no upgrading.

Suitable reaction conditions for dehydrocyclization of C₆ to C₁₀ aliphatic hydrocarbons include a temperature of 950° to 1125° F., a pressure from atmospheric to 50 p.s.i.g., a hydrogen concentration of 500 to 5,000 s.c.f./bbl. and a liquid-hourly space velocity of 0.1 to 3.0 vol./vol./hr. Thus, in comparison to conditions conventional for catalytic reforming of naphthenic naphthas, our dehydrocyclization process employs a somewhat lower pressure, a higher temperature, a lower hydrogen concentration, a lower space velocity and employs a dehydrogenation type catalyst having little or no acidity or carbonium ion activity instead of the dual-function catalysts employed for catalytic reforming of naphthenic stocks. Consequently, although minor amounts of components such as naphthenes which are best upgraded under catalytic reforming conditions can be present, our dehydrocyclization charge stocks are preferably composed almost entirely of straight or branched chain paraffins of the C₆ to C₁₀ carbon atom range.

We employ for dehydrocyclization a catalyst having little or no carbonium ion activity and, as we have indicated, the preferred catalyst is composed of a minor amount of chromic oxide distended on a substantially non-acidic alumina support. Other types of catalysts which promote dehydrogenation before carbon-carbon scission can occur are also suitable. They include the platinum group metals and the oxides of the metals of group VI-A of the periodic table. The catalyst metal or metal oxide is normally distended on a support or carrier which has little or no acidity or carbonium ion activity. A preferred support is alumina which is free of or substantially free of substances such as halogens which contribute to acidity. Other suitable supports include silica gel and composites of alumina and silica which contain more than 75 percent alumina. Supports which normally have acidity, for example, composites of silica-alumina, silica-magnesia, silica-zirconia, etc., can be employed if they are impregnated or base exchanged with an alkali metal or alkaline earth metal salt or hydroxide to reduce the acidity of the support.

We have carried out a series of heptane dehydrocyclization runs, in certain of which runs the hydrocarbon feed stock was pretreated either in accordance with our invention or with other stripping gases. The results demonstrate the unexpected advantages which are obtained in dehydrocyclization by our novel procedure. The following example describes procedures followed in the series of runs.

EXAMPLE 1

Separate batches of a pure grade n-heptane dehydrocyclization charge stock were stripped at ambient temperature and atmospheric pressure with hydrogen, nitrogen or oxygen before being subjected to dehydrocycliza-

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tion. We will refer specifically to the procedure used in hydrogen - stripping but the procedure with the other stripping gases was substantially the same. In each stripping operation the n-heptane and the stripping gas were first dried by percolation through a column of Linde Type 4A molecular sieve pellets. The apparatus employed for gas contacting or stripping was a vertically elongated, cylindrical vessel provided with lines for introducing and withdrawing liquid hydrocarbons and gas streams. The vessel was first purged with dry hydrogen and then the dried n-heptane feed stock was introduced in an amount which almost filled the vessel. The stripping gas, metered through a rotameter at a desired rate, was then charged into the bottom of the stripping vessel, passing through a fritted disc to assure good distribution through the liquid heptane. The hydrogen was charged in a ratio of 4 volumes of gas per volume of liquid per hour for a period of at least 2 hours. A gaseous stream was withdrawn from the top of the vessel and was passed through a condenser to condense any heptane carried as vapor by the gas and to return the liquid heptane to the vessel. After stripping for a period of at least 2 hours the liquid heptane was withdrawn from the bottom of the stripping vessel for passage to the dehydrocyclization unit while introducing hydrogen into the top of the vessel. In this manner, a hydrogen blanket was maintained in contact with the stripped feed stock to avoid contact with air. Thereafter, in a series of dehydrocyclization runs the various gas-treated heptane charge stocks were subjected to dehydrocyclization. The dehydrocyclization runs employed a fixed-bed of pelleted chromia-alumina catalyst which had a previously measured lined-out dehydrocyclization activity. In order to obtain a dry catalyst condition for each run a minimum two-hour hydrogen pretreatment of the catalyst at run temperature was completed immediately before charging of the hydrocarbon stock. Each dehydrocyclization run was followed by a 950°-1100° F. regeneration of the catalyst with dry air. Each of the variously treated n-heptane charge stocks were subjected to dehydrocyclization at an average temperature of 1015° F., a pressure of 10 pounds per square inch gauge, a liquid-hourly space velocity of 1 volume of hydrocarbon per volume of catalyst per hour and a hydrogen to hydrocarbon ratio of 1,500 standard cubic feet per barrel of hydrocarbon. The liquid product was collected hourly for a total throughput of 3.0 volumes of charge per volume of catalyst and then analyzed for hydrocarbon-type distribution by an FIA analysis. The results obtained in this series of runs are summarized in the following table and are illustrated in FIGURE 2. Also included are the results obtained with an adsorbent-dried n-heptane charge stock which had not been subjected to gas-stripping.

Table I

DEHYDROCYCLIZATION OF ADSORBENT-DRIED PURE GRADE n-HEPTANE

Stripping Gas	None	Hydrogen	Nitrogen	Oxygen
Oxygen Content of Dehydrocyclization Charge Stock After Stripping, Mg./Liter	~70	3(±1)	15(±1)	~300
Liquid Product:				
Yield, Wt. Percent of Charge	70.9	72.1	~71	70.4
Aromatics Content, Vol. Percent—				
Total Product	57.6	65.5	60.2	56.1
Products for Throughput Intervals:				
0-1	67.4	68.5	69.3	67.8
1-2	53.8	66.3	56.8	53.7
2-3	51.7	61.8	54.5	47.0

The data in the above table show that treating dry n-heptane with hydrogen reduced the dissolved oxygen content of the hydrocarbon from about 70 to less than 5 milligrams per liter. Contacting with nitrogen was

not as successful; the oxygen content was reduced to about 15 milligrams per liter. Saturation of n-heptane with oxygen has been found to be accomplished at a dissolved oxygen level of about 480 milligrams per liter. However, this saturation condition is not retained unless gaseous oxygen-liquid hydrocarbon mixing is continued. An equilibrium oxygen level of about 300 milligrams per liter of liquid was found to result within a short time after mixing was stopped and an oxygen (or air) blanket contact was established. An untreated sample of n-heptane was found to contain about 70 milligrams of dissolved oxygen per liter.

From the standpoint of conversion of the paraffinic charge to aromatics, a particular advantage exists for the use of a dehydrocyclization feed stock pretreated with hydrogen. As shown in Table I, this feed stock yields a liquid product under identical processing conditions which contains the maximum yield of aromatics. Furthermore, FIGURE 2 of the drawing, which plots the data of Table I, reveals that this higher yield is obtained concomitantly with a minimum amount of deactivation during the cycle. The aromatic yield obtained during the throughput interval, 0-1, was equivalent for every run, indicating that each run was made with the catalyst at an equivalent initial activity. However, with the hydrogen-treated charge a loss of less than 7 percent aromatics in the liquid product was experienced during the run. Losses of 15-20 percent in aromatic yield were sustained in the runs made with the feeds of higher oxygen content. These data show the value of reducing the dissolved oxygen content of the dehydrocyclization feed to less than about 5 milligrams per liter. A concentration of about 15 milligrams per liter is the maximum limit for acceptable operation in accordance with our invention.

In the above example the liquid hydrocarbon charge stocks were dried by contact with molecular sieves before the gas stripping or at least before being charged to the dehydrocyclization reactor. This contact of a liquid hydrocarbon fraction with molecular sieves is effective for removing water, but not dissolved oxygen from the liquid hydrocarbon fraction. In contrast, our procedure of hydrogen stripping the liquid hydrocarbon fraction is effective for removing both water and dissolved oxygen. This is demonstrated by operations that we have carried out in molecular sieve contacting and hydrogen stripping of heptane fractions that contain water and/or dissolved oxygen.

We have contacted with molecular sieves a liquid n-heptane fraction containing a few parts by weight of water per million parts of hydrocarbon and 33.4 milligrams of oxygen per liter of hydrocarbon. The heptane fraction was percolated through a column of pelleted Linde Type 4A molecular sieves at a liquid-hourly space velocity of 2 volumes of hydrocarbon per volume of adsorbent per hour. This reduced the water content of the fraction but the oxygen content remained at 32.7 milligrams per liter. The dried fraction was stored for 24 hours in contact with dry air. At the end of this time the water content had not changed but the oxygen content increased to 72.8 milligrams per liter. This demonstrates that although solid adsorbent contacting removes water it does not effectively remove dissolved oxygen and also that the oxygen content of a gasoline range liquid hydrocarbon fraction increases if the liquid is exposed to air.

In another operation the same n-heptane fraction containing less than about 5 parts per million of water and 33.4 milligrams per liter of oxygen was dried with Linde Type 4A molecular sieves and then stripped with dry hydrogen at a ratio of 6 volumes of hydrogen per volume of liquid hydrocarbon. The water content was markedly reduced and the oxygen content was reduced to 4.3 milligrams per liter. This demonstrates that our hydro-

gen stripping procedure effectively removes water and oxygen from gasoline range hydrocarbons.

We have discussed results obtained in dehydrocyclization of an n-heptane fraction. We have also practiced our process with a wider boiling range mixture, namely, a paraffin fraction of the C₇ to C₉ range and have obtained results which demonstrate the effectiveness of our process for various types of dehydrocyclization charge stocks. Specific details of the operation with the C₇-C₉ fraction are given in the following example.

EXAMPLE 2

Separate batches of a C₇ to C₉ molecular weight range Kuwait straight-run gasoline fraction were stripped at ambient temperature and atmospheric pressure with hydrogen or air and then subjected to dehydrocyclization. The stripping and dehydrocyclization were carried out substantially as described in Example 1. The yield and aromatics content for the total liquid product obtained in the dehydrocyclization runs from start-up to a throughput of 3.0 volumes of charge per volume of catalyst are given in the following table.

Table II

DEHYDROCYCLIZATION OF C₇-C₉ KUWAIT GASOLINE

Stripping Gas.....	None	Hydrogen	Air
Oxygen Content of Dehydrocyclization Charge Stock After Stripping, Mg./Liter.	83	11	88
Liquid Product:			
Yield, Wt. Percent of Charge.....		62.2	66.0
Aromatics Content, Vol. Percent.....		67.3	59.1

The dissolved oxygen in the charge stock analyzed 83 mg./liter. After treatment with air, it increased only to 88 mg./liter. This indicates that the charge stock as received was essentially saturated with oxygen content of the atmosphere (air). Treatment with hydrogen lowered its oxygen content to 11 mg./liter. The advantage of our hydrogen stripping of the charge for dehydrocyclization is again illustrated by the 8.2 volume percent greater aromatic content of the product obtained from the hydrogen treated charge stock.

The examples above have described the use of substantially pure hydrogen as the stripping gas. We have indicated that impure hydrogen streams can also be used, but such streams should contain about at least 75 mol percent hydrogen. The following example describes the procedure and results of stripping n-heptane with platformer off-gas, which is an impure hydrogen stream recovered from the reactor effluent of a catalytic reforming process.

EXAMPLE 3

A batch of pure grade n-heptane dehydrocyclization charge stock was stripped at ambient temperature and atmospheric pressure with a hydrogen-rich platformer off-gas before being subjected to dehydrocyclization. Prior to the stripping operation, the n-heptane was contacted with water and air to obtain high levels of both water and dissolved oxygen in the charge stock. The stripping gas was first dried by percolation through an adsorbent drying column filled with pelleted Linde Type 4A molecular sieves. The apparatus and procedure of the stripping operation were substantially as described in Example 1. The gas to liquid ratio was 5.6 to 1. The analysis of the platformer off-gas used as stripping gas is given in Table III below:

Table III

COMPOSITION OF PLATFORMER OFF-GAS

	Mol percent
Carbon monoxide.....	0.5
Oxygen	0.1
Hydrogen	79.2
Methane	12.0

Table III—Continued

	Mol percent
Ethane	4.5
Ethylene	0.3
Propane	2.3
Butanes	0.8
Butenes	0.1
Isopentane	0.2

The results obtained in stripping with the gas of Table II are summarized in Table IV below:

Table IV

STRIPPING OF n-HEPTANE WITH IMPURE HYDROGEN

Stripping Time, Hours	0.0	0.5	1.0	2.0
n-Heptane Analysis:				
Water, p.p.m.	92	39	1.7	1.7
Oxygen Content, Mg./Liter	107	44	5.7	5.7

The results of Example 3 show that stripping with platformer gas will lower the dissolved oxygen content of n-heptane to less than 15 mg./liter. The length of the treatment should be somewhat greater than one-half hour to meet the specification. However, stripping for more than one hour did not show any further lowering of the dissolved oxygen content of the n-heptane.

The following example demonstrates the value of hydrogen-stripping paraffin feed stocks before subjecting such feed stocks to hydroisomerization over a halogen-promoted, platinum-alumina catalyst.

EXAMPLE 4

Hydroisomerization of n-pentane was carried out in three successive phases which differed essentially only with respect to the pretreatment of the feed stock. The paraffin feed stock was pure grade n-pentane which had been absorbent-dried by contact with molecular sieves. The hydroisomerization was carried out by charging the pentane in admixture with hydrogen to a fixed-bed reactor containing a pelleted catalyst composed of about 0.4 weight percent platinum, 0.6 weight percent fluorine, 0.2 weight percent chlorine and the rest essentially alumina. On-stream reaction conditions were: temperature, 650° F.; pressure, 500 p.s.i.g.; hydrogen concentration corresponding to a mol fraction of hydrocarbon in the reactor charge of 0.7; and LHSV of 4 vol./col./hr. In the first phase of the run the feed stock was pretreated after adsorbent-drying by heating and stripping with hydrogen gas and thereafter was maintained in contact with a hydrogen atmosphere until charged to the reactor. In the second phase the feed stock was adsorbent-dried but was not hydrogen-stripped. The feed was in contact with dry air after being adsorbent-dried. In the third phase, after the feed was adsorbent-dried, an amount of t-butyl alcohol corresponding to 50 parts by weight of water per million parts of hydrocarbon was added to the feed.

FIGURE 3 of the drawing provides a comparison of the results of the three phases of the above example. It shows that at 670° F. the average conversion level obtained in the first phase with the hydrogen-stripped feed corresponded to about 36 percent isopentane in the liquid product. In the second phase, when the feed was dried but not hydrogen-stripped, the average conversion level dropped to about 21 percent. A further drop in conversion occurred in the third phase when the wet feed was substituted, the average conversion level being about 11 percent.

We have discovered that the deoxygenation and drying of gasoline range hydrocarbons by stripping with dry hydrogen can be accomplished with a low ratio of hydrogen gas to hydrocarbon liquid if the pressure and temperature are kept relatively low. We conduct the stripping operation at a temperature below the initial boiling point of the gasoline range hydrocarbon being stripped. In any event, the temperature is below 150° F. and normally the tem-

perature is ambient temperature, for example, 50° to 90° F. The stripping operation preferably is carried out at atmospheric pressure but a somewhat higher pressure can be employed. In any event, the gas pressure in the stripping vessel will be less than about 30 pounds per square inch gauge.

By employing the indicated low temperature and pressure during the stripping operation we effectively remove oxygen and water from the hydrocarbons with a gas to liquid ratio no greater than about 8 standard volumes of stripping gas per volume of liquid hydrocarbon (about 50 standard cubic feet of hydrogen per barrel of hydrocarbon). Larger amounts of hydrogen can be used, e.g., as high as about 25 volumes of hydrogen per volume of hydrocarbon, to obtain slightly improved stripping under some conditions. However, the removal of oxygen and water from gasoline hydrocarbons is essentially completed when stripped with 8 or less volumes of hydrogen per volume of hydrocarbon at atmospheric pressure and 50° to 90° F. The use of higher ratios of hydrogen to hydrocarbon has little or no advantage in increasing the removal of oxygen and water and is usually merely wasteful of hydrogen.

Under some conditions adequate stripping can be accomplished with a ratio of hydrogen to hydrocarbon ratio considerably less than 8:1. However, we have also found in comparing the stripping of gasoline hydrocarbons at different ratios of hydrogen to hydrocarbon, that the time required for complete stripping with low ratios of hydrogen to hydrocarbon is longer than would be expected from the results obtained with higher ratios. Therefore, for reasonably rapid stripping the hydrocarbon fraction should be contacted with a total amount of hydrogen of at least about 4, and preferably 4 to 8, standard volumes per volume of hydrocarbon and the gas should be passed through the hydrocarbon at a rapid rate.

The ratio of hydrogen to hydrocarbon is not the only consideration. The rate at which the hydrogen passes through the hydrocarbon liquid also influences the results. In general, the same ratio of hydrogen to hydrocarbon will accomplish better stripping at a low gas rate than at a higher rate, but the time required to complete the stripping may be excessive. In employing a gas to liquid ratio in the range of 4:1 to 8:1 the rate of hydrogen flow should be sufficient to complete the contact of the 4 to 8 volumes of hydrogen with one volume of hydrocarbon in less than 2 hours, preferably in 15 minutes to 2 hours, whether the stripping is batch or continuous.

As an illustration of suitable ratios and rates, we have accomplished substantially complete removal of oxygen and water from n-heptane fractions by stripping the liquid fraction for 2 hours with dry hydrogen in a ratio of 4 standard volumes of hydrogen per volume of liquid hydrocarbon and at a hydrogen rate of 1 standard cubic foot per hour. On the other hand, when employing a hydrogen to hydrocarbon ratio of 1:1 and a hydrogen rate of 0.25 standard cubic feet per hour for stripping n-heptane, the water content was still high after 4 hours.

Not all combinations of the indicated ranges of ratios and rates will produce the same results, but within these ranges satisfactory results can be achieved. Within the ranges of stripping conditions indicated, assuming efficient contact between the hydrogen and liquid hydrocarbon, we can achieve substantially complete removal of oxygen and water from gasoline range hydrocarbon streams without substantial liquid loss by vaporization and without excessive expense in condensing vaporized hydrocarbons for return to the stripper.

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:

1. The dehydrocyclization process which comprises

stripping a charge stock consisting only of a saturated aliphatic hydrocarbon fraction of the C_6 to C_{10} range in the liquid phase with a stream of dry hydrogen at a pressure below 30 pounds per square inch gauge and at ambient temperature below about 90° F., in a gas to liquid ratio sufficient to reduce the oxygen content of the hydrocarbon fraction to less than 15 milligrams per liter of hydrocarbon, thereafter maintaining the stripped fraction out of contact with oxygenic fluids and contacting the stripped hydrocarbon fraction with a dehydrocyclization catalyst comprising an oxide of a group VI-A metal on a non-acidic support in the presence of hydrogen and at dehydrocyclization reaction conditions, including a partial pressure of hydrogen less than 150 pounds per square inch gauge, and recovering a product enriched in aromatics.

2. The dehydrocyclization process which comprises stripping a normal heptane liquid fraction at atmospheric pressure and a temperature of about 50° to 90° F., with a dry gas stream containing at least 75 volume percent hydrogen, in a gas to liquid ratio of about 4 to 8 volumes of stripping gas per volume of liquid hydrocarbon and at a stripping gas rate sufficient to complete the contact of said 4 to 8 volumes of gas with one volume of liquid hydrocarbon in 15 minutes to 2 hours, recovering a stripped heptane fraction containing less than 5 milligrams of oxygen per liter of hydrocarbon, thereafter maintaining the stripped fraction out of contact with oxygenic fluids and contacting said fraction with a chromia-alumina dehydrocyclization catalyst in the presence of hydrogen at a temperature from 950° to 1125° F., a pressure from atmospheric to 30 pounds per square inch gauge, a hydrogen concentration of 500 to 5000 standard cubic feet per barrel of hydrocarbon and a liquid-hourly space velocity of 0.1 to 3 vol./vol./hr. and recovering a hydrocarbon fraction enriched in toluene.

3. The process which comprises stripping a gasoline range hydrocarbon fraction consisting only of paraffinic hydrocarbons in the liquid phase at atmospheric pressure and at ambient temperature below about 90° F. with a stream of dry hydrogen in a gas to liquid ratio of 4 to 8 standard volumes of gas per volume of liquid hydrocarbon, to reduce the oxygen content of the hydrocarbon fraction to less than 5 milligrams per liter of hydrocarbon, thereafter maintaining the stripped fraction out of contact with oxygenic fluids and subjecting the stripped hydrocarbon fraction to catalytic conversion by contact

in the presence of hydrogen at elevated temperature and at a partial pressure of hydrogen less than 150 pounds per square inch gauge with a catalyst comprising a group VI-A metal oxide on a non-acidic support.

4. The process for pretreating a gasoline range hydrocarbon feed stock consisting only of paraffinic hydrocarbons for catalytic conversion by contact in the presence of hydrogen with a catalyst comprising a group VI-A metal oxide on a non-acidic support at elevated temperature and hydrogen partial pressure less than 150 pounds per square inch gauge, which comprises stripping said gasoline range hydrocarbon feed stock with a stream of dry hydrogen at atmospheric pressure and at ambient temperature below about 90° F., in a gas to liquid ratio of 4 to 8 standard volumes of stripping gas per volume of liquid hydrocarbon and at a gas rate sufficient to complete the contact of said 4 to 8 volumes of hydrogen with one volume of liquid hydrocarbon in less than 2 hours, recovering a stripped hydrocarbon fraction containing less than 5 milligrams of oxygen per liter of hydrocarbon, maintaining the stripped fraction out of contact with oxygenic fluids and charging said fraction to said catalytic conversion process.

5. The process which comprises stripping a charge consisting only of an aliphatic paraffin boiling in the gasoline range in the liquid phase at atmospheric pressure and at an ambient temperature below about 90° F. with a stream of dry hydrogen in a gas to liquid ratio of 4 to 8 standard volumes of gas per volume of liquid hydrocarbon, to reduce the oxygen content of the aliphatic paraffin to less than five milligrams per liter of aliphatic paraffin, thereafter maintaining the stripped paraffin out of contact with oxygenic fluids and subjecting the stripped aliphatic paraffin to catalytic conversion by contact in the presence of hydrogen at elevated temperature and pressure with a catalyst composed of a platinum group metal on an acidic support.

References Cited in the file of this patent

UNITED STATES PATENTS

2,749,287	Kirshenbaum	June 5, 1956
2,766,179	Fenske et al.	Oct. 9, 1956
2,890,165	Bednars et al.	June 9, 1959
2,903,415	Bowles	Sept. 8, 1959