HYDROCARBON CONVERSION PROCESS WITH SUBSEQUENT REFORMING OF SELECTED HYDROCARBON FRACTIONS

Vladimir Haensel, Hissisdale, and George R. Donaldson, North Riverside, Ill., assignors, by mesne assignments, to Universal Oil Products Company, Des Plaines, Ill., a corporation of Delaware

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This invention relates to the catalytic conversion of hydrocarbon boiling within the gasoline range. It is more specifically concerned with a novel combination of solvents extraction, fractionation, and catalytic reforming. The refining industry has been deeply concerned with recent trends in both the automotive and refining fields which give rise to predictions of unprecedented increases in gasoline quality in the near future. In recognition of these trends, research efforts have been directed toward the development of a practical method for the production of such "super quality" gasoline.

One process that has recently received commercial attention is the catalytic reforming process. The term "reforming" is well known in the petroleum industry and refers to the treatment of gasoline fractions to improve the anti-knock characteristics thereof. A highly successful and economical reforming process that has achieved wide commercial acceptance is described in U.S. Patent No. 2,479,110, issued to Vladimir Haensel. However, the present reforming processes are all limited by decreasing yields at increasing octane numbers. There are also other limitations. For example, when a full boiling range straight-run gasoline or a relatively wide boiling range naphtha is reformed in the presence of a catalyst that promotes dehydration of napthenes and hydrocracking of paraflins, relatively poor yields at considerable power and considerable fouling of the catalyst are obtained when the operating conditions are all used to obtain large octane number improvement. This is in part due to the fact that the relatively severe operating conditions that must be maintained in order to satisfactorily upgrade the higher boiling paraflinic constituents of the feed are too severe for some of the other constituents. The result is that an unacceptable part of the feed stock is undesirably converted to gases and to catalyst carbon.

Therefore, under the usual conditions of operation the yield of liquid product and catalyst life are limited to a considerable extent and primarily dependent on the decomposition and carbon forming tendencies of the higher boiling paraflinic constituents and the aromatic constituents. The higher boiling paraflinic constituents may decompose to form coke on the catalyst and the aromatic constituents also deposit coke or carbonaceous material on the catalyst by reacting with each other and forming polymers or aromatics which are the carbonaceous materials that foul the catalyst. We have invented a method of reforming which largely overcomes these objectionable features of the prior art reforming processes.

It is an object of the present invention to treat a full boiling range straight-run gasoline or a fraction thereof in such a manner that increased yields of high octane number gasoline and aromatics and longer catalyst life are obtained.

In one embodiment the present invention relates to a process for effecting an improved yield of high octane number gasoline which comprises subjecting hydrogen and a gasoline fraction to reforming in a first reforming zone, effecting the separation of at least a portion of the resultant reformed stream into a predominantly paraflinic fraction and a predominantly aromatlc fraction, fractionating at least a portion of said predominantly paraflinic fraction into a low boiling fraction and a high boiling fraction and subjecting at least a portion of said low boiling fraction to reforming in a second reforming zone.

In another embodiment the present invention relates to a process for effecting an improved yield of high octane number gasoline which comprises subjecting hydrogen and a gasoline fraction to reforming in a first reforming zone in the presence of a catalyst that promotes dehydrogenation of the napthenes and hydrocracking of paraflins, subsequently cooling the resultant reformed stream and effecting the separation thereof to provide a gaseous hydrogen-containing stream and an aromatic-rich hydrogen stream, passing the latter to a fractionating zone and removing normally gaseous components therefrom, treating the remaining fraction in a separation zone, withdrawing from said separation zone a predominantly paraflinic fraction and separately withdrawing a predominantly aromatic fraction, subjecting at least a portion of said predominantly paraflinic fraction to fractionation in a fractionation zone, separately withdrawing from said fractionation zone a low boiling fraction and a high boiling fraction, subjecting at least a portion of said low boiling fraction to reforming in a second reforming zone in the presence of a catalyst that promotes dehydrocyclization of paraflins, and recycling at least a portion of said high boiling fraction to said first reforming zone.

In a specific embodiment the present invention relates to a process which comprises subjecting a gasoline fraction to reforming in a first reforming zone, at a temperature of from about 600° F. to about 1000° F., a pressure of from about 200 to about 1000 p.s.i., with hydrogen at a hydrogen to hydrocarbon mol ratio of from about 0.5 to about 20 mols of hydrogen per mol of hydrocarbon, in the presence of from about 0.01% to about 1% by weight of platinum and from about 0.1% to about 3% by weight of combined halogen, subsequently cooling the resultant reformed stream and effecting the separation thereof to provide a gaseous hydrogen-containing stream and an aromatic-rich hydrogen stream, introducing said aromatic-rich hydrogen stream to a fractionation zone to remove normally gaseous components therefrom, passing an aromatic-rich hydrogen stream from said first fractionation zone to an extraction zone wherein said stream is countercurrently contacted with a selective solvent containing diethylene glycol and from about 1% to about 20% by weight of water, separately removing from said extraction zone an extract containing said solvent and a substantial amount of aromatics and a raffinate containing a substantial amount of paraflinic hydrocarbon, introducing said extract to a stripper, removing overhead from said stripper an aromatic-containing stream, removing as bottoms from said stripper a solvent stream and recycling said solvent stream to said extraction zone, subjecting said raffinate to fractionation in a second fractionation zone, separately withdrawing from said second fractionation zone a low boiling fraction and a high boiling fraction, subjecting at least a portion of said low boiling fraction to contact in a second reforming zone with a reforming catalyst at a pressure lower than in said first reforming zone, and recycling at least a portion of said high boiling fraction to said first reforming zone.

Brielly, the present invention provides a method for effecting an improved yield of high octane gasoline from a hydrocarbon stream boiling in the gasoline range which comprises subjecting the hydrocarbon stream to reforming in the presence of hydrogen and a suitable reforming
catalyst. In the first reforming zone naphthenes are dehydrogenated to aromatics and heavy paraffins are hydrogenated to lower boiling paraffins. It is also preferred that the conditions and the catalyst in the first reaction zone be such that there is some paraffin isomerization and some paraffin dehydrocyclization. The resulting reformed stream is cooled and the separation thereof effected to provide gaseous hydrogen-containing stream and an aromatic-rich hydrocarbon stream. The aromatic-rich hydrocarbon stream is fractionated to reject the normally gaseous hydrocarbons produced in the process and the resultant liquid is passed to a separation zone in which the recovery of aromatic hydrocarbons is effected. The resulting non- aromatics or paraffinic hydrocarbon stream is passed to a fractionation zone wherein the raffinate or paraffinic hydrocarbon stream is fractionated into at least a low boiling fraction and a high boiling fraction. The low boiling fraction is passed to a second reforming zone wherein it is contacted with a dehydrocyclization catalyst while in the presence of hydrogen. The second reforming zone is at a pressure at least 75 pounds per square inch lower than the pressure in the first reforming zone and preferably at least 100 pounds per square inch lower than the pressure in the first reforming zone. In the second reforming zone the temperature is preferably higher than the temperature in the first reforming zone. In the second reforming zone the low boiling paraffins are dehydrocyclized to form additional aromatic hydrocarbons. The product from the second reaction zone is passed to the first fractionation zone and from there the stream follows the same route as the effluent from the first reforming zone. The high boiling fraction removed from the second fractionation zone may be further fractionated and in a preferred embodiment of the present invention at least a portion of the high boiling fraction is recycled to the first reforming zone.

A feature of our process is that mild hydrocracking conditions may be employed in the first reforming step. Generally more severe conditions are necessary to dehydrocyclize lower boiling straight chain paraffins to form aromatics than to dehydrogenate a cycloparaffin or naphthene to form an aromatic. Reforming of the low octane number lower boiling paraffins in a separate reaction zone results in their being dehydrocyclized to aromatics and/or their being converted to lower boiling high octane number paraffins without the excessive production of gaseous hydrocarbons that would result were these lower boiling paraffins substantially reformed in the first reforming reactor continued at conditions of high severity. Therefore, a feature of our process is that the conditions in the second reforming zone may be severe enough to convert a substantial portion of the paraffin to aromatics while at the same time minimizing undesirable side reactions which otherwise reduce yields of useful gasoline products. As hereinbefore mentioned, one of the chief reasons for deposit of carbon or carbonaceous material on the catalyst is the reaction of aromatics to form polynuclear aromatics. In our process, however, the aromatics are removed and, therefore, substantially less carbon is formed on the catalyst with resultant longer catalyst life. High severity operation in the presence of aromatics is also not desirable from considerations of chemical equilibria involved, as in such operations the aromatics in the feed limit the extent to which such aromatics can be formed from naphthenes and paraffins. In contrast, however, the use of our process involves the removal of a substantial portion of the aromatics from the charge to the second reaction zone which thus permits the formation of additional aromatics unrestricted by the limitations of chemical equilibria.

Similarly, the isomerization of normal hexane rating straight chain paraffins to the higher octane quality branch chain structure paraffins is an equilibrium reaction. As the isomerization of normal hexane is important to achieve in up-grading gasolines, due to the very limited extent that it undergoes dehydrocyclization at reasonable operating conditions, a feature of our process is that isohexanes may be continuously removed and the normal hexane introduced to the second reaction zone thus obtaining substantially complete conversion of low octane normal hexane to much higher quality isohexanes with almost no restrictions in yield due to chemical equilibrium considerations.

Accordingly, the aromatics are separated from the paraffins and the naphthenes in the reformate from the first reaction zone for several reasons. One reason is that if the aromatics were introduced to the second reaction zone it would be highly undesirable and impractical. Another reason is that the aromatics in the reformate from the second reaction zone tend to result in a greater carbon deposition and consequently a shorter catalyst life. Still another reason, which has hereinbefore been mentioned, is that high concentrations of aromatics in the reaction zone tend to suppress the dehydrogenation of naphthenes to aromatics and to suppress the dehydrocyclization of paraffins to aromatics, said dehydrogenation and said dehydrocyclization being equilibrium processes.

The charge stocks which may be reformed in accordance with my process comprise hydrocarbon fractions that boil within the gasoline range and that contain naphthenes and paraffins. The preferred stocks are those consisting essentially of naphthenes and paraffins, although aromatics and other amounts of oleins may be present. This preferred class includes straight-run gasoline, natural gasoline and the like. The gasoline fraction may be a full boiling range gasoline having an initial boiling point within the range of from about 50°F. to about 100°F. and an end boiling point within the range of from about 350°F. to about 425°F., or it may be a blend of the various gasolines and/or gasoline fractions which may be used and thermally cracked and/or catalytically cracked gasolines may be used as charging stock. However, when these unsaturated gasoline fractions are used, it is preferred that they be used either in admixture with a straight-run, unrefractured natural gasoline fraction, or else hydrogenated prior to use.

In a preferred operation in the first reforming step, wherein the charge is subjected to hydrocracking and aromatization, the contact is made at a pressure of from about 200 to about 1000 pounds per square inch. In the subsequent catalytic contacting step in the second reforming zone, the C₆ aromatics having hydrocarbon fraction contacts the catalyst at a lower pressure, said pressure being at least 75 pounds per square inch and preferably at least 100 pounds per square inch lower than the pressure in the first reforming step. It is also to be noted that since the group of five-membered naphthenes such as methylcyclopentane which are present in the low boiling fraction of the raffinate, are not completely converted to benzene in the first reforming step so that a subsequent contact after removal of aromatics permits further dehydrogenation and conversion of such fractions to benzene and other aromatics without the serious loss of dehydrocyclization to produce aromatics of higher octane number and/or isomerization to branched chain paraffins of higher octane number.

A preferred operation effects the recycle of the hydrogen stream being separated from the reformed gasoline stream into contact with the charge stock in order to provide added hydrogen to the catalytic reforming zone. Similarly, hydrogen separated from the second reforming zone may be recycled to the latter to provide the presence
of additional hydrogen during the catalytic contact of the paraffins. Various types of desirable and suitable catalysts may be used within each stage of the process; however, the preferred operation utilizes platinum-containing catalyst in each of the contact zones. The catalysts that may be used in the first reforming zone of our invention comprise those reforming catalysts that permit dehydrogenation of naphthenic hydrocarbons, hydrocracking of paraffinic hydrocarbons and isomerization of paraffinic hydrocarbons. A satisfactory catalyst comprises a platinum-alumina-silica catalyst of the type described in U.S. Patent No. 2,478,916, issued August 16, 1949. A preferred catalyst comprises a platinum-alumina-combined halogen catalyst of the type described in U.S. Patent No. 2,479,109, issued August 16, 1949. Other catalysts such as molybdena-alumina, chromia-alumina, and platinum on a carrier or support such as a cracking catalyst base may be used. In the second reforming zone as well as in the first reforming zone, the platinum concentration in the catalyst may range up to about 10% by weight or more of the alumina, but a desirable catalyst may be provided to contain as low as from about 0.01% to about 1% by weight of platinum. The halogen ions may be present in an amount of from about 0.1% to about 8% by weight of the catalyst but preferably are present in an amount of from about 0.1% to about 3% by weight of the alumina on a dry basis. Also, all of the halogen ions provide a desirable catalyst, the fluoride ions are particularly preferred and next in order are the chloride ions, the bromide ions and iodide ions. In the second stage of catalyst contact where the non-aromatic C₆₈ fraction undergoes dehydrocyclization there may be a lesser quantity of platinum present in the catalyst.

Except for pressure level, the operating conditions maintained in each of the two reforming stages of our process are essentially the same. The conditions in the first zone should be such that substantial conversion of naphthenes to aromatics and relatively mild hydrocracking of paraffins are induced; and, further, the operating conditions in the second zone should be such that there is a substantial conversion of paraffinic compounds to aromatics by dehydrocyclization as well as isomerization of paraffins such as the isomerization of normal hexane to isohexane. When employing platinum-alumina-combined halogen catalysts in both of the reforming zones, the conditions in each are usually a temperature within the range of from about 600° F. to about 1000° F. and a weight hourly space velocity of from about 0.5 to about 20. The weight hourly space velocity is defined as the weight of oil per hour per weight of catalyst in the reaction zone. It is preferred that the reforming reaction in both of the reaction zones be conducted in the presence of hydrogen. In one embodiment of the process, sufficient hydrogen will be produced in the reaction to furnish the hydrogen required in the process and, therefore, it may be unnecessary to introduce hydrogen from an external source or to recycle hydrogen within the process. However, it will be preferred to introduce hydrogen from an external source generally at the beginning of the operation and to recycle hydrogen within the process in order to be assured of a sufficient hydrogen atmosphere in each of the reaction zones. The hydrogen present in each of the reaction zones will be within the range of from about 0.5 to about 20 mols of hydrogen per mol of hydrocarbon. In some cases, the gas to be recycled will contain hydrogen sulfide introduced with the charge or liberated by the catalyst and it is within the scope of the present invention to treat the hydrogen-containing gas to remove hydrogen sulfide or other impurities before recycling the hydrogen to the reforming zone. The pressure in the first reaction zone is from about 200 to about 1000 pounds per square inch. The pressure in the second reaction zone is lower, and is at least 75 pounds per square inch lower and preferably at least about 100 pounds per square inch lower. The pressure range, therefore, is from about 125 to about 925 p.s.i. The temperature in the second reaction zone is preferably higher than in the first reaction zone. The conditions are such that there are substantially no olefins present in the product streams from the first and the second reaction zones.

The effluent from the first reforming zone, along with the effluent from the second reforming zone is usually passed to a stabilizer which effects the separation of normally gaseous material which comprises hydrogen, hydrogen sulfide, ammonia and hydrocarbons containing one to four carbon atoms per molecule from the normally liquid hydrocarbons. In a preferred embodiment of the invention the effluent from the first reaction zone is passed to a stabilizer and the effluent from the second reaction zone is introduced to a common stabilizer since the use of one stabilizer for each of the effluents is of decided economic advantage. The stabilized liquid is then passed to a separation zone to produce a more concentrated aromatic fraction. The separation of a more concentrated aromatic fraction may be accomplished in any conventional manner such as solvent extraction, solid absorption, fractional crystallization, the use of urea adducts, molecular sieves, etc., however, the solvent extraction process is particularly preferred in the present invention since its use generally produces best results.

Solvant extraction processes are used to separate certain components in a mixture from other components thereof by a separation process based upon a difference in solubility of the components in a particular solvent. It is frequently desirable to separate various substances by solvent extraction: when the substances to be separated have similar boiling points, are unstable at temperatures at which fractionation is effected, form constant boiling mixtures, etc. It is particularly desirable to separate aromatic hydrocarbons from a petroleum fraction containing these aromatic hydrocarbons by solvent extraction because a petroleum fraction is normally a complex mixture of hydrocarbons whose boiling points are extremely close together and because the petroleum fraction contains numerous cyclic compounds which tend to form constant boiling or azeotropic mixtures. As hereinbefore stated, the basis of a solvent extraction separation is the difference in solubility in a given solvent of one of the substances to be separated from the other. It may, therefore, be seen that the more extreme this difference the easier the separation will be and an easier separation reflects itself process-wise in less expensive equipment and greater yields per pass in the use of processing equipment as well as in higher purity of product. A particularly preferred solvent for separating aromatic hydrocarbons from non-aromatic hydrocarbons is a mixture of water and a hydrophilic organic solvent.

Such a solvent may have its solubility regulated by adding more or less water thereto. Thus, by adding more water to the solvent, the solubility of all components in the hydrocarbon mixture are reduced, but the solubility difference between the components is increased. This effect is reflected process-wise in less contacting stages required to obtain a given purity of product. However, a greater throughput of solvent must be used in order to obtain the same amount of material dissolved.

As hereinbefore stated, the solvent to be used in this invention is preferably a mixture of a hydrophobic organic solvent and water, wherein the amount diluted in the mixture is selected to regulate the solubility in the solvent of the materials to be separated. Suitable hydrophilic organic solvents include alcohols, glycols, aldehydes, glycerine, phenol, etc. Particular preferred solvents are diethylene glycol, triethylene glycol, dipropylene glycol, tripropylene glycol and substances thereof containing from about 1% to about 20% by weight of water. Other hydrophilic substances such as sulfur dioxide, etc., may be used.
In classifying hydrocarbon type compounds according to increasing solubility in such a solvent, it is found that the solubility of the various classes increases according to the following order: the least soluble are the paraffins followed in increasing order of solubility by naphthenes, olefins, diolefins, acetylenes, sulfur, nitrogen, and oxygen-containing compounds and aromatic hydrocarbons. It may thus be seen that a charge stock which is rich in unsaturated compounds will produce a greater problem in solvent extraction than a saturated charge stock since the unsaturated compounds fall between the paraffins and aromatics in solubility. It may be seen that an ideal charge to solvent extraction is one containing paraffinic and aromatic hydrocarbons exclusively.

The paraffinic compounds also differ among themselves in their relative solubility in the solvent. The solubility appears to be a function of the boiling point of the paraffin with the lower boiling or lighter paraffins being more soluble than the higher boiling or heavier paraffins. Therefore, when heavy paraffins are dissolved in the solvent they may be displaced from the solvent by adding lighter paraffins thereto. In an embodiment of this invention it is preferred to recycle and reform the heavier paraffins in the first reaction zone and, therefore, a light paraffin is charged to the extraction zone to displace the heavier paraffins that are being recovered in the distillation zone from the solvent by flooding the heavier paraffins into the raffinate. The light paraffins which are introduced to the extraction zone are the isohexanes and lighter paraffins which are removed as overhead from fractionation of the raffinate.

It is an essential feature of the present invention that the raffinate from the extraction zone is passed to a fractional distillation zone in which the raffinate is fractionated into at least two fractions, that is, a low boiling fraction and a high boiling fraction. We have discovered and our invention is based on this discovery that when the raffinate is fractionated into at least two fractions that the higher boiling ether paraffins in the low boiling fraction and the lower boiling ether paraffins in the high boiling fraction are recycled to the first reaction zone. The low octane number lower boiling fraction, however, requires a different operating condition for reforming the low octane number higher boiling fraction are those present in the first reaction zone, and, therefore, in a preferred embodiment of the present invention the higher boiling fraction is recycled to the first reaction zone. The low octane number lower boiling fraction, however, requires a different operating condition and the lower boiling fraction is reformed in a second reaction zone in which the catalytic and conditions are such that a maximum product of high octane gasoline is achieved.

In some cases the heavy boiling fraction may contain components which are heavier than desirable to recycle to the reforming zone. For example, the raffinate may contain heavy aromatics, that is, aromatics boiling above about 400° F. and upon recycling heavy aromatics to the first reforming zone, these heavier aromatics have a tendency to condense and form carbonaceous material on the catalyst and to deactivate the same. In a preferred embodiment of the present invention the heavy fraction of the raffinate is further fractionated to remove heavy components therefrom, that is, components boiling above about 400° F. The heavy raffinate substantially free of components boiling above about 400° F. is then preferably recycled to the first reforming zone. The exact temperature at which the raffinate is split in general depends upon the character of the components in the raffinate; however, we have found that generally the split may be made at about 250° F., that is, the end point of the low boiling fraction is about 250° F. and the initial boiling point of the heavy paraffin fraction is about 250° F. The low boiling raffinate therefore has an initial boiling point of from about n-hexane to about 200° F. and a preferred end point within the range of from about 240° F. to about 260° F. The heavy raffinate has a preferred initial boiling point within the 240–260° F. range and an end point within the 375–425° F. range.

The light raffinate from the fractionation zone is passed to a second reforming zone in which a dehydrocyclization catalyst and dehydrocyclization conditions are maintained. As hereinbefore mentioned, the use of the second reaction zone is preferred since the conditions in the second zone may be selected so as to produce the highest possible yield of aromatics from the second zone charge stock, which consists almost entirely of all paraffinic hydrocarbons. The effluent from the second reaction zone is recycled to the first fractionation zone or stabilizer and the aromatics present in the effluent from the second reaction zone are ultimately removed in the extractor. It is also preferred that the catalyst in the second reaction zone promotes paraffin isomerization.

Additional features and advantages of our invention will be apparent from the following description of the accompanying drawing which illustrates a particular method for conducting a gasoline reforming operation in accordance with the present invention.

Referring now to the drawing, there is indicated a 150° F. to 400° F. gasoline charge stream being passed by way of line 1 and valve 2 into heater 3 while in admixture with hydrogen being recycled by way of line 4. This gasoline stream may be a straight-run gasoline, natural gasoline or other relatively low octane number stream which is to undergo reforming to provide a high yield of aromatic hydrocarbon to the solvent by passing the heavier paraffins into the raffinate. The light paraffins which are introduced to the extraction zone are the isohexanes and lighter paraffins which are removed as overhead from fractionation of the raffinate.

The reforming reactor 6 contains a bed of spherical catalyst of approximately 1/4 inch average diameter containing 0.3% platinum, 0.5% combined fluorine, and 0.1% combined chlorine. During the passage of the charging stock through the first reactor 6 the bulk of the naphthenes containing six or more carbon atoms per molecule are dehydrogenated to the corresponding aromatics and a portion of the paraffins are hydrocracked to lower boiling paraffins. Some isomerization of the paraffins and some dehydrocyclization of the paraffins in the charge preferably also takes place. The drawing indicates a single conversion zone 6, however, it is to be understood that one or more zones may be utilized in series, with interheaters therebetween if desired, so that there may be accomplished a substantial degree of aromatization of the charge stream.

At the conditions in the reforming zone or reactor 6 and in the presence of hydrogen and the catalyst of this process, olefinic materials will not be produced in any appreciable amount example, the raffinate may contain heavy aromatics boiling above about 400° F. and upon recycling heavy aromatics to the first reforming zone, these heavier aromatics have a tendency to condense and form carbonaceous material on the catalyst and to deactivate the same. In a preferred embodiment of the present invention the heavy fraction of the raffinate is further fractionated to remove heavy components therefrom, that is, components boiling above about 400° F. The heavy raffinate substantially free of components boiling above about 400° F. is then preferably recycled to the first reforming zone. The exact temperature at which the raffinate is split in general depends upon the character of the components in the raffinate; however, we have found that generally the split may be made at about 250° F., that is, the end point of the low boiling fraction is about 250° F. and the initial boiling point of the heavy paraffin fraction is about 250° F. The low boiling raffinate therefore has an initial boiling point of from about n-hexane to about 200° F. and a preferred end point within the range of from about 240° F. to about 260° F. The heavy raffinate has a preferred initial boiling point within the 240–260° F. range and an end point within the 375–425° F. range.

The resulting reformed stream passes from the first reaction zone 6 by way of line 7, cooler 8 and line 9 and subsequently enters receiver 10. A resulting hydrogen-containing gaseous stream is discharged from the upper portion of receiver 10 by way of line 11 and a portion of this stream may be vented or withdrawn as fuel gas or process gas by way of lines 12 and 46 and valve 47 while the remaining portion passes by way of valve 14 into compressor 15. In a preferred operation all of the excess gas in line 12 passes through lines 12 and 45 to provide a hydrogen atmosphere in reactor 116. In such an operation valve 47 would be in a closed position. The latter provides for compressing and recycling a portion of the hydrogen-containing stream by way of line 4 into heater 3 and again into conversion zone 6. A condensed hydrocarbon stream is passed from receiver 10 by way of line 16 and valve 17 and enters a first fractionation zone or stabilizer 18. In accordance with this invention, normally gaseous hydrocarbons are removed overhead through line 20. In stabilizer the normally gaseous material, which includes hydrogen, ammonia, hydrogen sulfide, and hydrogen carbon gases containing from one to four carbon atoms per molecule is separated from the hydrocarbon liquid comprising aromatic hydrocarbons and paraffinic hydrocarbons.
The gaseous material passes overhead through line 20 into cooler 21, wherein a portion of the material is condensed and the entire stream passes through line 22 into reactor 15. In reactor 23 the liquid phase and the gaseous phase of the overhead material separate; the gaseous material passes through line 25 from which it may be vented to the atmosphere or used as fuel or may be further used in the present process or other processes. The stabilizer has heat provided thereto by reboiler 27 and connecting lines 26 and 27. It is contemplated that the stabilizer and reboiler will operate at a sufficient pressure to liquefy at least a portion of the overhead material so that a liquid reflux stream may be available to improve the separation in stabilizer 18. The liquid reflux is removed from receiver 23 through line 24 and passes into an upper portion of stabilizer 18. A portion of the liquid phase in receiver 23 may be removed through line 23.

The stabilizer bottoms, which as hereinbefore stated, comprises substantially paraffinic and aromatic hydrocarbons, is withdrawn from stabilizer 18 through lines 26 and 29 and passed into an intermediate section of extractor 30. In extractor 30 the hydrocarbon material rises and is countercurrently contacted at an elevated temperature with a descending stream of selective solvent. In the embodiment diethylene glycol is used with the latter entering the upper portion of extractor 30 through line 32. Water may also be introduced into extractor 30 through line 33 containing valve 34 which is shown as being added to the glycol stream. Water may also be added to extractor 30 independently of line 32, if it may be separately fed into extractor 30. As hereinbefore mentioned, the water is added to increase the selectivity of the solvent.

As a result of the countercurrent contact of the selective solvent and the hydrocarbon charge to be produced according to line 29, the aromatic hydrocarbons contained in the charge to the extractor are selectively dissolved in the solvent thereby forming an extract stream 35 containing the solvent and aromatic hydrocarbons, and a raffinate stream 31 containing the paraffinic hydrocarbons. The raffinate stream passes from the upper portion of extractor 30 through line 31 while the extract stream passes through the lower portion of extractor 30 through line 35. Line 35 passes to flash drum 36. Flash drum 36 is maintained at a pressure lower than the extractor in order to keep the aromatic mixture from being flashed overhead and are removed through line 38. The remainder of the liquid is withdrawn from flash drum 36 through line 37 and introduced to stripper 41 wherein the dissolved aromatic hydrocarbons and dissolved paraffins are separated from the selective solvent. Line 37 is preferably connected to the stripper 41 at a point in the upper half of the column. The separation in the stripper 41 is not difficult as the aromatic hydrocarbons are substantially different in nature from the selective solvent as well as having a substantially different boiling point. The aromatic hydrocarbon stream along with some light paraffins passes overhead from the stripper 41 through line 40 and combines with the overhead from the flash drum in line 38 and the combined stream in line 39 is recovered as product or may be further bleached and as such other products. Heat is provided for the stripping operation by reboiler 43. In the embodiment of the present invention, the material is separated into lines 42 and 44. The solvent stream, which is taken from the bottom of stripper 41 through lines 42 and 32, and is passed into the upper portion of extractor 30 as hereinbefore mentioned.

The raffinate stream from extractor 30, which is withdrawn through line 31 is fractionated into at least two fractions. The raffinate also contains dissolved and entrained solvent and the raffinate may be washed to remove the solvent before recycling any fraction of the raffinate to the reforming zone. In the drawing the raffinate in line 31 is introduced into fractionator 50. Fractionator 50 is preferably operated as a deisohexanizer. The conditions in deisohexanizer 50 are maintained so that the components lighter than those which it is preferred to reform are removed as an overhead fraction. In the embodiment of the drawing, the overhead is shown as comprising components boiling below normal hexane, that is, the overhead fraction contains isohexane and lighter components. These components are removed from fractionator 50 through line 51 and pass into cooler 52 wherein the material is condensed and the entire stream passes through line 53 into receiver 54. The liquid in receiver 54 splits up into several streams. A portion of the liquid in receiver 54 is withdrawn through line 55 and introduced into the upper portion of deisohexanizer 50 as reflux. A portion of the liquid in receiver 54 may be withdrawn through line 56 as product and in some instances may be combined with the product in line 39. As illustrated in the drawing only a portion of the liquid product in receiver 54 is withdrawn through lines 56 and 56' while the remainder of the light fraction is withdrawn through line 56 and passed to a lower portion of extractor 30. This use of the isohexane and lighter fraction in line 56, that is as reflux to extractor 30, is a preferred feature of the invention. The use of this isohexane and lighter fraction enables more of the heavier paraffins to be recycled to the reforming reactor and this combined operation provides a greater utilization of the product streams and ultimately increases the yield and octane number of the final product.

Heat is provided for the fractionating in fractionator 50 by reboiler 58 and connecting lines 57 and 59. The bottoms, which are substantially free of components boiling below normal hexane, are removed from deisohexanizer 50 through lines 57 and 60. A portion of the liquid in line 60 may be withdrawn as product through line 61, however, it is preferred that all the liquid in line 61 passes through line 62 into fractionator 70. Fractionators 70 and 90 operate so as to provide a low boiling predominantly paraffinic fraction and a high boiling predominantly paraffinic fraction with the low boiling fraction reformed in second reaction zone 116 while the heavier fraction is recycled to reforming reactor 6, all of which is hereinafter described in detail.

The normal hexane and heavier fraction in line 62 is introduced into fractionator 70. Fractionator 70 has heat provided thereto by reboiler 89 and connecting lines 79 and 81. A light fraction is withdrawn overhead through line 71 and the fraction passes through cooler 72 and line 73 into overhead receiver 74. Some of the liquid is withdrawn from receiver 74 through line 75 and introduced into an upper portion of fractionator 70 as reflux. In the embodiment herein illustrated the fractionator is operated so that the end point of the liquid in receiver 74 is about 250° F. The liquid fraction in receiver 74 therefore contains components boiling from normal hexane to about 250° F. A portion of the normal hexane-250° F. fraction is withdrawn from receiver 74 through line 76. A portion of the liquid in line 76 may be withdrawn as product through line 77, however, it is preferred that all the liquid be withdrawn through lines 76 and 78 and subjected to reforming in reactor 116. The normal hexane-250° F. fraction in line 78 is picked up by pump 111 and discharged into line 112 and combined with other product streams. Heat is provided for the stripping operation by reboiler 113. In the embodiment of the present invention, the mixture of light raffinate and hydrogen in line 113 passes into heater 114 wherein the combined stream is heated to a temperature of the order of about 920° F. The pressure in the second reaction zone is in the order of 400 pounds per square inch. As hereinbefore mentioned, the pressure in the second reaction zone 116 is at least 75 pounds per square inch lower than the pressure in the first reaction zone 6 and preferably is at least 100 pounds per square inch lower. The combined stream is heated in heater 114 and...
passes through line 115 into reactor 116. Reforming reactor 116 contains a bed of spherical catalyst of the same composition of the catalyst in reactor 6. During the passage of the charge stock through the second reactor 116 a substantial portion of the paraffins containing six or more hydrocarbons per molecule are dehydrocyclized to the corresponding aromatics and a portion of the paraffins are hydrocracked to lower boiling paraffins. A substantial portion of the paraffins are also isomerized, for example, normal hexane is isomerized to isohexane. The drawing indicates a single conversion zone 116, however, it is hereby understood that one or more zones may be utilized in series with inter heaters between as desired so that there may be accomplished a substantial degree of dehydrocyclization of the charge stream. The conditions in the reforming zone of reactor 116 are selected so that there is substantial dehydrocyclization and isomerization of paraffins and so that there are substantially no olefinic substances produced. At the conditions hereinbefore specified, and in the presence of hydrogen and the catalyst of this invention, olefinic materials will not be produced in any appreciable amounts. The effluent stream from reactor 116 passes by way of line 117, cooler 118, line 120 and subsequently enters another heater. The resulting hydrocarbon-containing gaseous stream is discharged from the upper portion of receiver 121 by way of line 125 and a portion of this stream may be vented or withdrawn as fuel gas or process gas by way of line 128 and a portion may be recycled by means of a compressor to the reaction zone 116. Sufficient hydrogen may be introduced through line 45 so that recycling of the hydrogen in line 125 may be unnecessary. The condensed hydrocarbon stream is withdrawn from separator 121 by way of line 126. The liquid in line 126 is introduced to stabilizer 18 through line 16. A heavy predominantly paraffinic fraction is withdrawn from fractionator 70 through lines 79 and 82. A portion of the liquid in line 82 may be withdrawn as product through line 83, however, it is preferred that all of the liquid in line 82 pass through line 84 into fractionator 90. Fractionator 90 is operated so that components that are heavier than are desirable to recycle to reforming reactor 6 are removed as bottoms. We have discovered that the fraction boiling above about 400°F. is predominantly aromatic and, therefore, no benefits can be obtained in recycling the 400°F. + fraction to the reforming 6 fact, recycling the 400°F. + fraction to the first reactor 6 may cause excessive deactivation of the catalyst by coking of the same. In a preferred embodiment of the present invention the extractor 30 is operated at rather moderate conditions so that a considerable amount of the heavy aromatics are present in the raffinate and these heavy aromatics are subsequently removed as bottoms in fractionator 90. The economics of the operation are definitely in favor of operating extractor 30 at moderate conditions and removing the aromatics in fractionator 90 instead of in the extract in line 35. Fractionator 90 has been provided hereto by rebolber 99 and connecting lines 98 and 100. The 400°F. F. and heavier fraction may be removed from fractionator 90 through lines 98 and 110. The heavy product in line 110 may be combined with other product streams. The overhead material from fractionator 90 is withdrawn through line 91, passes into cooler 92, line 93 and enters receiver 93'. A portion of the liquid in receiver 93' is withdrawn as reflux through line 94 and introduced into an upper portion of fractionator 90 to aid in the separation of the hydrocarbons. The material in line 93, in the embodiment herein illustrated, comprises hydrocarbon boiling between 250°F. and 400°F. A portion of the 250°F. to 400°F. F. fraction in receiver 93' is withdrawn through line 95. A portion of the heavy fraction in line 95 may be withdrawn through line 96 as product, however, a portion of the liquid in line 95 passes through line 97 and is recycled to line 1 to eventually pass into the reactor 16. Additionally, the process illustrated in the drawing represents one of the preferred forms of our invention, it is to be understood that our invention is not limited thereby. A number of variations may be introduced into the process without departing from the spirit and scope of said invention in reforming zone 6. The following example is given to further illustrate our invention, but it is not given for the purpose of unduly limiting the generally broad scope of said invention. Example A naphtha fraction having an initial boiling point of 189°F. and an end boiling point of 395°F. is passed through a bed of platinum-alumina-hydrogen catalyst comprising alumina containing 0.3% by weight of platinum and 0.2% by weight of fluorine, at a pressure of 700 pounds per square inch, a hydrogen to hydrocarbon molar ratio of 7, a feed rate. The effluent from the reaction zone is cooled and the C8 and lighter components removed by fractional distillation. The remaining liquid is countercurrently contacted in a sieve deck tower with a descending stream of 97% diethylene glycol and 3% water. The contact is effected at 210°F. and approximately 175 pounds per square inch pressure. The raffinate is removed from the top of the tower and the extract is removed from the bottom of the tower. The aromatics are recovered from the extract by fractional distillation. The raffinate is fractionated to form a low boiling fraction having an initial boiling point of 150°F. and an end boiling point of 248°F. and a high boiling fraction having an initial boiling point of 248°F. and an end point of 400°F. The low boiling fraction is passed through a bed of platinum-alumina-hydrogen catalyst comprising alumina containing 0.3% by weight of platinum and 0.2% by weight of fluorine at a pressure of 400 pounds per square inch, a hydrogen to hydrocarbon molar ratio of 7, a weight hourly space velocity of 3, and an initial average catalyst temperature of 910°F. 291545
fraction boiling in the range between said end point and about 400 °F., reforming said light fraction in a second reforming zone in the presence of at least a portion of said hydrogen-containing gas and at a pressure at least 75 pounds per square inch lower than the pressure in said first reforming zone, and recycling said heavier fraction to said first reforming zone.

3. A hydrocarbon conversion process which comprises catalytically reforming a gasoline fraction in a first reforming zone, stabilizing the resultant hydrocarbon products in a stabilizing zone to separate normally gaseous hydrocarbons from the reformed gasoline, subjecting substantially all of the stabilized reformed gasoline to solvent extraction to separate the same into a paraffinic raffinate and an aromatic concentrate, recovering said aromatic concentrate as a product of the process, fractionating said raffinate to separate therefrom a relatively light fraction having an end boiling point in the range of about 240–260 °F. and a heavier fraction boiling in the range between said end point and about 400 °F., reforming said light fraction in a second reforming zone in the presence of at least a portion of said hydrogen-containing gas and at a pressure at least 75 pounds per square inch lower than the pressure in said first reforming zone, and recycling said heavier fraction to said first reforming zone, and supplying the reformed products from said second reforming zone to said stabilizing zone for stabilization therein together with said hydrocarbon products from the first reforming zone.

4. A hydrocarbon conversion process which comprises catalytically reforming a gasoline fraction in the presence of hydrogen in a first reforming zone, separating a hydrogen-containing gas from the resultant hydrocarbon products, stabilizing the latter in a stabilizing zone to separate normally gaseous hydrocarbons from the reformed gasoline, subjecting substantially all of the stabilized reformed gasoline to solvent extraction to separate the same into a paraffinic raffinate and an aromatic concentrate, recovering said aromatic concentrate as a product of the process, fractionating said raffinate to separate therefrom a relatively light fraction having an end boiling point in the range of about 240–260 °F. and a heavier fraction boiling in the range between said end point and about 400 °F., reforming said light fraction in a second reforming zone in the presence of at least a portion of said hydrogen-containing gas and at a pressure at least 75 pounds per square inch lower than the pressure in said first reforming zone, recycling said heavier fraction to said first reforming zone, and supplying the reformed products from said second reforming zone to said stabilizing zone for stabilization therein together with said hydrocarbon products from the first reforming zone.

5. A hydrocarbon conversion process which comprises catalytically reforming a gasoline fraction in a first reforming zone, subjecting substantially all of the resultant reformed gasoline products to solvent extraction to separate the same into a paraffinic raffinate and an aromatic concentrate, recovering said aromatic concentrate as a product of the process, fractionating said raffinate to separate therefrom a relatively light gasoline fraction and a heavier gasoline fraction, and reforming said light fraction in a second reforming zone under independently controlled reforming conditions.

6. The process of claim 5 further characterized in that said heavier gasoline fraction is recycled to the first reforming zone.

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