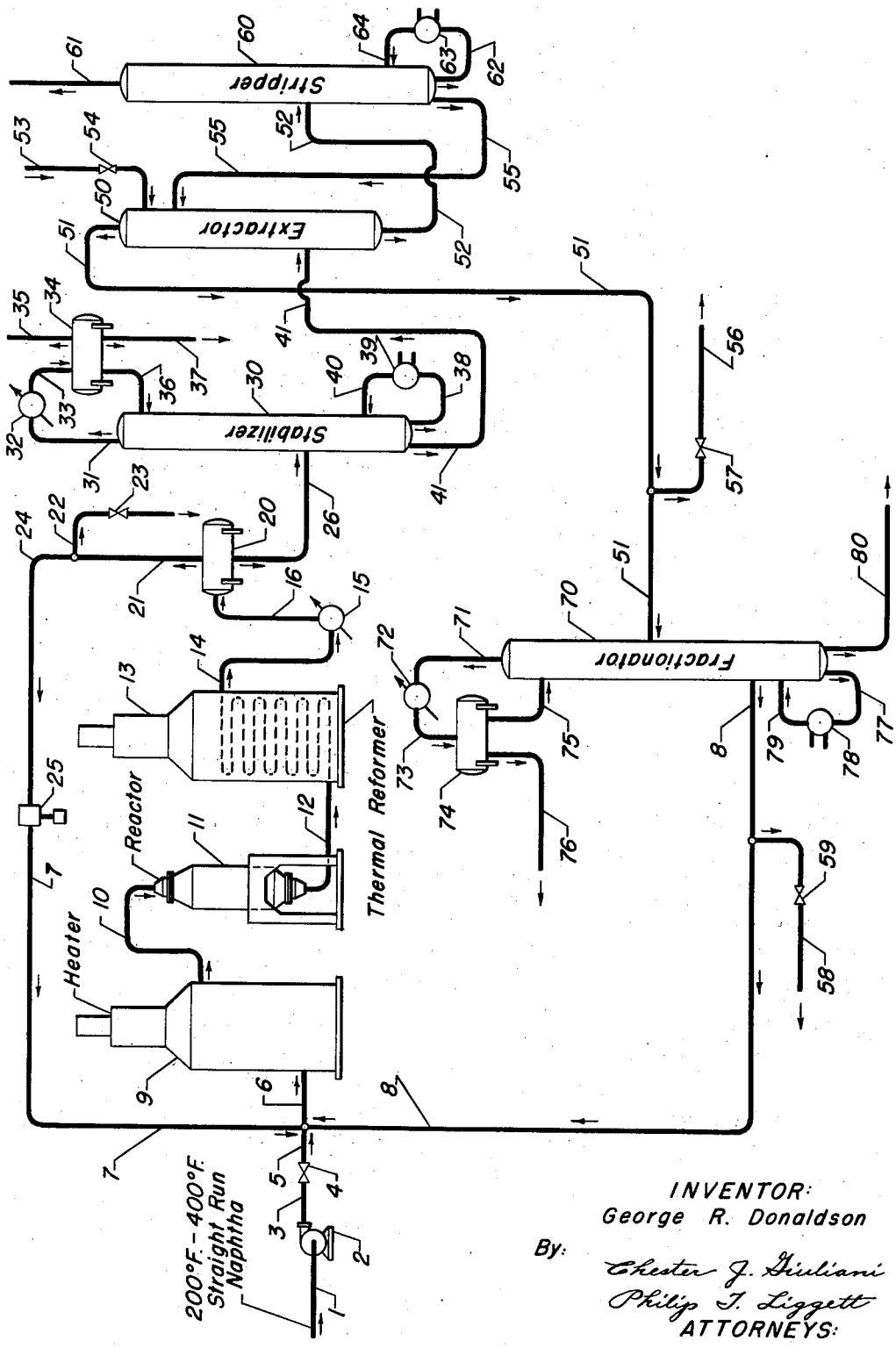
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COMBINATION CATALYTIC REFORMING-THERMAL REFORMING-FRACTIONATION PROCESS

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COMBINATION CATALYTIC REFORMING-THERMAL REFORMING-FRACTIONATION PROCESS

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This invention relates to the catalytic conversion of hydrocarbons boiling within the gasoline range. It is more specifically concerned with a novel combination of catalytic reforming, thermal reforming, solvent extraction and fractionation.

The recent developments in the automotive industry have increased the demand for high octane numbered gasolines and the petroleum industry has been striving to keep up with these demands. One process that has achieved great commercial acceptance 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 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 dehydrogenation of naphthenes, dehydrocyclization of paraffins and hydrocracking of paraffins, relatively poor yields and considerable fouling of the catalyst are obtained when the operating conditions are selected to obtain large octane number appreciation. This apparently is due to the fact that the relatively severe operating conditions that must be maintained in order to satisfactorily upgrade the higher boiling paraffinic constituents of the feed are too severe for some of the other constituents. The result is that an appreciable part of the feed stock is unnecessarily converted to gases and to catalyst carbon. I have invented a process which largely overcomes these objectionable features of the prior art reforming processes.

It is an object of the present invention to reform a full boiling range straight-run gasoline, or a relatively wide boiling fraction thereof, in such a manner that increased yields of reformate and longer catalyst life are obtained while producing a liquid product of the desired quality.

It is another object of the present invention to provide an improved-combined operation which will effect an improvement in octane number from the straight chain or branched chain paraffins in the charge stock.

In one embodiment the present invention relates to a process which comprises subjecting hydrogen and a gasoline fraction to reforming in a catalytic reforming zone, introducing at least a portion of the effluent from said reforming zone to a thermal treating zone to convert a substantial portion of the paraffins to olefins, introducing at least a portion of the effluent from said thermal reforming zone to a separation zone, separately withdrawing from said separation zone an aromatic-rich-olefin-rich fraction and a predominantly paraffinic fraction, introducing at least a portion of said predominantly paraffinic fraction to a fractionation zone, separately

withdrawing from said fractionation zone at least a low boiling fraction and a high boiling fraction and recycling at least a portion of said high boiling fraction to said catalytic reforming zone.

In another embodiment the present invention relates to a process which comprises subjecting hydrogen and a mixture of a gasoline fraction and an intermediate boiling paraffinic recycle stock, prepared as hereinafter specified, to catalytic reforming in a catalytic reforming zone, subjecting at least a portion of the effluent from said catalytic reforming zone to a thermal treatment to convert a substantial portion of the paraffins in said portion to olefins, stabilizing the effluent from said thermal treating zone by removing normally gaseous components therefrom, introducing at least a portion of the stabilized hydrocarbon to a separation zone, separately withdrawing from said separation zone an aromatic-rich-olefin-rich fraction and a predominantly paraffinic fraction, introducing at least a portion of said predominantly paraffinic fraction to a fractionation zone, separately withdrawing from said fractionation zone at least a low boiling fraction, an intermediate boiling paraffinic recycle stock and a high boiling fraction, and recycling at least a portion of said intermediate boiling paraffinic recycle stock to said catalytic reforming zone.

In a specific embodiment the present invention relates to a process which comprises subjecting hydrogen, a gasoline fraction and an intermediate boiling raffinate fraction, prepared as hereinafter set forth, to reforming in a catalytic reforming zone at a temperature of from about 600° F. to about 1000° F., in the presence of a reforming catalyst, passing at least a portion of the effluent from said catalytic reforming zone to a thermal reforming zone and therein subjecting said effluent, in the absence of a catalyst, to a temperature within the range of from about 800° F. to about 1200° F., a pressure within the range of from about 50 to about 2000 pounds per square inch and for a period of time sufficient to convert a substantial portion of the paraffins in said effluent to olefins, introducing at least a portion of the effluent from said thermal reforming zone to a stabilization zone to remove normally gaseous components therefrom, introducing the stabilized effluent to a separation zone, separately withdrawing from said separation zone an aromatic-rich-olefin-rich fraction and a predominantly paraffinic raffinate fraction, introducing at least a portion of said predominantly paraffinic fraction to a fractionation zone, separately withdrawing from said fractionation zone at least a low boiling fraction, an intermediate boiling raffinate fraction and a high boiling fraction and recycling at least a portion of the intermediate boiling raffinate fraction to said catalytic reforming zone.

Briefly stated, my process comprises catalytically reforming a gasoline in the presence of hydrogen. It is a feature of my invention that an intermediate boiling paraffinic recycle stock, prepared as hereinafter set forth, be recycled to the catalytic reforming zone. At least a portion of the effluent from the catalytic reforming zone is introduced to a thermal conversion zone in the absence of a catalyst. The resulting thermally reformed stream may be cooled and a separation thereof effected to provide a gaseous hydrogen-containing stream and an aromatic-rich-olefin-rich hydrocarbon stream. In another embodiment the effluent from the catalytic reforming zone is cooled and a hydrogen-rich gas separated therefrom and recycled to the catalytic reaction zone and the liquid is passed to a thermal conversion zone. The effluent from the catalytic reforming zone is subjected to a thermal treatment at an elevated temperature and pressure to convert a substantial portion of the straight chain

or slightly branched chain paraffins in the effluent from the catalytic reforming zone to olefins. In the thermal reforming zone additional aromatics are also formed, however, in low amounts. Hydrogen is separated from the thermal reforming zone effluent and recycled to the catalytic reforming zone. As hereinbefore mentioned, the hydrogen may be separated from the effluent from the catalytic reforming zone. The remaining liquid products are fractionated to stabilize the liquid, that is to reject normally gaseous components produced in the process, and the resulting stabilized liquid is separated to separate the aromatics and the olefins from the paraffins. A fraction containing the major proportion of the aromatics and the major proportion of the olefins is separately removed from the separation zone and a highly paraffinic fraction is also removed from said separation zone. Usually, however, the highly paraffinic fraction contains olefinic hydrocarbons. The highly paraffinic fraction is introduced to a fractionation zone. The olefins present in the highly paraffinic fraction are low boiling and therefore may be removed as overhead from the fractionator. Any aromatics in the highly paraffinic fraction are high boiling aromatic hydrocarbons and, therefore, these may be removed as bottoms from the fractionator. The intermediate or heart-cut fraction is removed from an intermediate portion of the fractionator and is substantially free of olefinic and aromatic hydrocarbons. This heart-cut fraction, therefore, is predominantly paraffinic and I have discovered that this heart-cut fraction may be recycled to the catalytic reforming zone. As a result of this recycling, the final products of the process produce a gasoline of extremely high octane number having excellent yield-octane number relationships.

It is preferred that the reforming operation in the first reforming zone be an operation in which a catalyst having a relatively long life is used. A platinum-containing catalyst is preferred for use in the first reforming zone. These catalysts are hereinafter described in greater detail. A fixed bed reforming operation is preferred for the first reforming zone because the preferred catalysts to use in this zone comprise platinum-containing catalysts, and a fixed bed operation prevents loss of the relatively expensive catalyst. Further, it has been found that at the relatively mild conditions necessary in the first reforming zone to convert the naphthenes in the charge to aromatics, that the preferred catalysts, which are hereinafter described, may be employed for extended periods of time without regeneration or replacement; that is, an essentially non-regenerative process may be employed. This is of great economic advantage since fixed bed operations employ apparatus which is relatively simple compared to that employed in fluidized operations, and further the maintenance problems when using fixed bed operations are markedly less than when using a fluidized operation. Further, it has been found that fixed bed operations in the first reforming zone give better results. This may be due to the temperature profile, that is temperature drop or rise through the catalyst bed, which may be such that the desired reactions are promoted to a greater extent than when a uniform temperature is maintained throughout the catalyst bed. While a fixed bed operation is preferred in the first catalytic reforming zone it is to be understood that fluidized, fluidized-fixed bed, moving bed and/or slurry types of operations may also be used, however, not necessarily with equivalent results.

The effluent from the catalytic reforming zone may be cooled and a hydrogen-rich gas stream separated therefrom and recycled to the catalytic reforming zone. However, it is preferred that the entire effluent from the catalytic reforming zone, without the intermediate cooling and hydrogen gas separation, be passed to the thermal reforming zone.

In the thermal reforming zone the pressure is within the range of from about 50 to about 2000 pounds per square inch and preferably within the range of from about 500 to about 1000 pounds per square inch. The temperature in the thermal reforming zone is within the range of from about 800° F. to about 1200° F. and preferably within the range of from about 900° F. to about 1100° F. At these operating conditions and in the absence of a catalyst olefins are produced from the straight or slightly branched chain paraffins. At these operating conditions the aromatics are unchanged and in fact additional aromatics may be formed. I have discovered that a thermal treatment of the catalytically reformed gasoline produces a gasoline of unexpectedly high octane number and excellent starting characteristics. The thermal treatment is performed in the absence of a catalyst since it has been found that olefins are produced in sufficient amounts in the absence of a catalyst and, further, if a catalyst were to be used the olefins would tend to polymerize and deposit carbonaceous material on the catalyst and, therefore, the catalyst would be rapidly deactivated.

A feature of my process is that mild operating conditions may be employed in the catalytic reforming zone. Reforming of the low octane number paraffins, that is the conversion of these paraffins to olefins, in a separate thermal reaction zone results in their being converted to lower boiling olefins without the excessive production of gaseous hydrocarbons and catalyst deactivation that would result were it attempted to convert the rest of the charge and these lower boiling paraffins in the first reforming reactor continued at conditions of high severity. Therefore, a feature of my process is that the conditions in the second or thermal reforming zone may be severe enough to convert a substantial portion of the paraffins to olefins. By eliminating low octane number, high boiling paraffins from the final product, the end product becomes a gasoline of high quality.

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 minor amounts of olefins 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 selected fraction thereof, which usually is a higher boiling fraction commonly referred to as naphtha and having an initial boiling point within the range of from about 150° F. to about 250° F. and an end boiling point within the range of from about 350° F. to about 425° F. Mixtures of the various gasolines and/or gasoline fractions may also 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 or natural gasoline fraction, or else hydrogenated prior to use.

In a preferred operation, in the first reforming step, wherein the charge is subjected to aromatization, the contact is made at a pressure of from about 200 to about 1000 pounds per square inch. In the subsequent non-catalytic contacting step the hydrocarbon fraction is contacted at a pressure within the range of from about 50 to about 2000 pounds per square inch and preferably from about 500 to about 1000 pounds per square inch. The effluent from the first reaction zone may be separated into a hydrogen-rich gas stream which is recycled to the first reforming zone and an aromatic-rich hydrocarbon stream which is passed to the thermal reforming zone.

A preferred operation effects the recycle of hydrogen into contact with the charge stream in order to provide added hydrogen to the catalytic reforming zone. The

hydrogen may be provided by cooling the effluent from the catalytic reforming zone and separating the cooled effluent into a hydrogen-containing gas phase and a liquid phase. The hydrogen-rich gas phase may be recycled to the catalytic reforming zone. In another embodiment of the present invention the effluent from the catalytic reforming zone is not separated into a hydrogen-rich gas stream and an aromatic-rich hydrocarbon stream, but the entire catalytic reactor effluent is passed to the thermal reforming zone. Generally the conditions in the first reforming zone and in the thermal reforming zone are such that there is a net production of hydrogen.

Variations of desirable and suitable catalysts may be utilized within the first stage of the process, however, the preferred operation utilizes the improved platinum-alumina-combined halogen catalyst in the first reaction zone. The catalyst that may be used in the first reforming zone of my invention comprises those reforming catalysts that permit dehydrogenation of naphthenic hydrocarbons. It is also preferred that the catalyst promote 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 an inert or relatively inert or cracking catalyst base may be used.

The platinum concentration on the catalyst in the first reforming zone 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, while any of the halogen ions provides a desirable catalyst, the fluoride ions are particularly preferred and next in order are the chloride ions, the bromide ions, and the iodide ions.

The conditions in the first catalytic zone should be such that substantial conversion of naphthenes to aromatics is induced, and it is also preferred that relatively mild hydrocracking of paraffins is induced. The operating conditions in the second non-catalytic zone should be such that there is a substantial conversion of paraffinic hydrocarbons to olefins. The temperature in the first reforming zone is usually a temperature within the range of from about 600° F. to about 1000° F. The weight hourly space velocity in the catalytic zone is usually within the range 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 the first reaction zone be conducted in the presence of hydrogen. In one embodiment of the process sufficient hydrogen will be produced 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 in the process. However, it usually is 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. The hydrogen present in the first reaction zone may 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 same to the reforming zone.

In accordance with the present invention at least a portion of the catalytic reactor effluent is subjected to a thermal treatment, at a temperature, pressure and time sufficient to convert a substantial portion of the paraffins in the effluent to aromatics. The pressure is within the range of from about 50 to 2000 pounds per square inch and preferably of from about 500 to about 1000 pounds per square inch. The temperature is within the range of from about 800° F. to about 1200° F. and preferably within the range of from about 900° F. to about 1100° F. The aromatic-rich hydrocarbon stream is subjected to these pressures and temperatures for a time sufficient to convert a substantial portion of the paraffins in the catalytic reactor effluent to olefins and the exact time is dependent upon the particular temperature and pressure selected. At higher temperatures less time is necessary than at lower temperatures. The thermal treatment or thermal reforming is conducted in a thermal treating zone. The zone may be a reactor or two or more reactors in parallel or in a series. In a preferred method the conversion zone is a thermal coil or thermal reforming coil in a heater so that the reactants may be more easily maintained at conversion temperature. The actual residence time of a particular molecule in the thermal reforming zone usually is from about ten seconds to about five hundred seconds or more depending upon the temperature and pressure as hereinbefore mentioned.

At least a portion of the effluent from the thermal reforming zone is usually passed to a stabilizer. The stabilization effects the separation of the normally gaseous material which comprises hydrogen, hydrogen sulfide, ammonia, and hydrocarbons containing from one to about four carbon atoms per molecule, from the normally liquid hydrocarbons. The effluent from the stabilizer is then passed to a separation zone. An olefin-rich-aromatic-rich stream is removed from the separation zone and a predominantly paraffinic stream is also removed from the separation zone. The predominantly paraffinic stream, however, contains low boiling olefins and high boiling aromatic hydrocarbons.

The separation of an aromatic-rich-olefin-rich fraction may be accomplished in any conventional manner such as solvent extraction, solid absorption, extractive crystallization, fractional crystallization, molecular sieves, mechanical separation, etc. However, the solvent extraction process is particularly preferred in the present invention since its use generally produces a raffinate most suitable for catalytic reforming.

Solvent 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 by solvent extraction because a petroleum fraction is normally a continuous 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. 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 processwise 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 hydrophilic organic solvent and water, wherein the amount of water contained in the mixture is selected to regulate the solubility in the solvent of the materials to be separated. Suitable hydrophilic organic solvents include alcohol, glycols, aldehydes, glycerine, phenol, etc. Particularly preferred solvents are diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, tripropylene glycol, and mixtures thereof containing from about 1% to about 20% by weight of water. Other hydrophilic substances as sulfur dioxide, etc. may be used.

In classifying hydrocarbon and hydrocarbon type compounds according to increasing solubility in such a solvent, it is found that the solubility of the various classes increases in the following manner: 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.

The solubility difference between paraffins and olefins is greater than the solubility difference between olefins and aromatic hydrocarbons, that is when comparing components of approximately equal boiling points. It therefore is possible to separate the solvent extraction process so that the olefins and aromatics are dissolved in the solvent while the paraffins remain in the raffinate phase. The extract phase from the separation process therefore will be olefin-rich and aromatic-rich.

The paraffinic compounds also differ 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 the heavier paraffins to the catalytic reforming zone and therefore a light paraffin or a light olefin is charged to the extraction zone to displace the heavier paraffins from the solvent into the raffinate phase.

The predominantly paraffinic fraction from the separation zone, preferably the raffinate from the selective solvent extraction zone, is subjected to a fractionation zone to fractionate the raffinate into at least a high boiling portion and a low boiling portion. In a preferred embodiment of this invention the raffinate is fractionated into a low boiling fraction, an intermediate boiling fraction, and a high boiling fraction. The high boiling paraffins in the charge to the catalytic reforming zone are more easily cracked than the lower boiling paraffins and, therefore, the lower boiling fraction of the raffinate will contain the major amount of the olefins produced in the thermal reforming zone. The higher and intermediate boiling fraction accordingly will be substantially free of olefinic hydrocarbons. The raffinate may also contain components which are high enough in octane number and low enough in boiling point so that they need not be enhanced in octane number and it is, therefore, preferred that a light fraction be recovered from the raffinate and recovered as product. Usually the isohexane and lighter fraction is not improved in octane number when subsequently reformed and, therefore, it is preferred that the isohexane and lighter fraction be removed from the raffinate. The end point of the light material removed as overhead from the fractionator therefore preferably is about 156° F., the boiling point of normal hexane. Generally the end point of the low boiling fraction is within the range of from about 150° F. to about 250° F.

The raffinate from the extraction zone may also contain components which are heavier than are suitable for reforming and which may be removed from fractionation. For example, components boiling above about 425° F., and frequently above about 350° F. are generally not suitable for catalytically reforming since they tend to readily deactivate the catalyst. This heavy fraction also contains a large proportion of aromatic hydrocarbons and these may be satisfactorily removed from the process by withdrawing them from the bottom of the fractionator. The intermediate fraction removed from the fractionation zone therefore preferably has an initial boiling point within the range of from about 150° F. to about 250° F. and an end point within the range of from about 350° F. to about 425° F. This intermediate fraction contains only slight amounts of olefins and aromatics and is predominantly paraffinic and is, therefore, most suitable for reforming, and in accordance with the present invention this intermediate or heart-cut fraction is recycled to the catalytic reforming zone.

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

Referring now to the drawing a straight-run gasoline fraction having an initial boiling point of 200° F. and an end point of 400° F. is passed through line 1, is picked up by pump 2, and discharged through line 3 containing valve 4 and then through line 5. The intermediate boiling raffinate recycle stream in line 8, prepared as hereinafter specified, and a hydrogen-rich gas stream in line 7 mix with the charge in line 5 and the mixture in line 6 is passed into heater 9 wherein the combined stream is heated to a temperature of 900° F. The heated combined stream is withdrawn from heater 9 by way of line 10 and passes into reforming reactor 11.

Reforming reactor 11 contains a bed of cylindrical catalyst of approximately ⅛ inch average diameter containing 0.5% platinum, 0.5% combined fluorine, and 0.1% by weight of combined chlorine. The pressure in the reactor is 700 pounds per square inch, the weight hourly space velocity is 3.0 and the hydrogen to hydrocarbon mol ratio is 10 to 1. During the passage of the charge stock through reactor 11 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, especially the higher boiling paraffins, are hydrocracked to lower boiling paraffins. Some isomerization of the paraffins also takes place, this reaction being of particular importance in the isomerization of normal hexane as this hydrocarbon is of relatively low octane number and is not readily dehydrocyclicized. The important octane number increasing reaction of dehydrocyclization also occurs in reactor 11 at these conditions. By this reaction a substantial portion of the paraffins are converted to aromatics. This reaction is extremely important in increasing the octane number of the paraffins which are recycled to the reforming reactor through line 8. The conditions in the reforming zone or reactor 11 are such that there are substantially no olefinic substances produced.

The effluent from reactor 11 passes through line 12 and into thermal reformer 13. As hereinbefore mentioned, a hydrogen-rich gas stream may be separated from the catalytic reactor effluent in line 12; however, in the embodiment illustrated, the entire effluent is passed directly into thermal conversion zone 13. Thermal conversion zone 13 is herein illustrated as a heater in which tubes or a coil is located. In the thermal heating zone 13 the material is heated to an elevated temperature and the time, temperature, and pressure are correlated to pro-

duce a substantial amount of olefins. In the operation described a temperature of 1070° F. and a pressure of 550 pounds per square inch are employed. At these conditions the average residence time of the charge stream is about ninety seconds.

The effluent from thermal reformer **13** passes through line **14**, cooler **15**, line **16**, and into receiver or separator **20**. Hydrogen is withdrawn from the top of receiver **20** through line **21**. Excess hydrogen may be withdrawn through line **22** containing valve **23**. At least a portion of the hydrogen in line **21** passes through line **24**, is picked up by compressor **25** and discharged into line **7**.

The liquid hydrocarbons comprising the reformate and the bulk of the normally gaseous hydrocarbons produced in the process are withdrawn from receiver **20** through line **26** and passed into fractionator or stabilizer **30**. Normally gaseous hydrocarbons are removed overhead through line **31**. In stabilizer **30** the normally gaseous material, which includes hydrogen, ammonia, hydrogen sulfide, and hydrocarbon gases containing from 1 to about 4 carbon atoms per molecule, is separated from the hydrocarbon liquid comprising aromatic hydrocarbons, olefinic hydrocarbons, and paraffinic hydrocarbons.

The gaseous material passes overhead through line **31** into cooler **32** wherein a portion of the material is condensed and the entire stream passes through line **33** into overhead receiver **34**. In receiver **34** the liquid phase and the gas phase of the overhead material separate. The gases pass through line **35** from which they may be vented to the atmosphere or otherwise used. The gases removed through line **35** are highly olefinic and by suitable treatment they may be used as polymerization or alkylation charge stocks. The stabilizer has heat provided thereto by reboiler **39** and connecting lines **38** and **40**. The conditions in the stabilizer **30** are usually such that C_4 and lighter components are removed as overhead, however, the gasoline therein may be cut deeper, that is C_5 and/or C_6 hydrocarbons may be removed overhead through line **31**. It is contemplated that the stabilizer **30** and reeciver **34** will operate at a sufficient pressure to liquefy at least a portion of the overhead material so that a liquid stream may be available to improve the separation in stabilizer **30**. The liquid reflux passes from receiver **34** through line **36** into an upper portion of stabilizer **30**. Liquid in receiver **34** may also be withdrawn through line **37**.

The stabilizer bottoms, which comprise paraffinic, olefinic, and aromatic hydrocarbons, are withdrawn through line **41** and introduced into a lower portion of extractor **50**. In extractor **50** the hydrocarbon material rises and is countercurrently contacted at an elevated temperature in the liquid phase with a descending stream of a selective solvent. In this embodiment 96% diethylene glycol and 4% water is used as the solvent. Water is introduced through line **53** containing valve **54**. The diethylene glycol enters the upper portion of extractor **50** through line **55**. As hereinbefore mentioned, the water is added to increase the selectivity of the solvent in line **55**. The average temperature in the extractor is maintained at about 305° F. The pressure is maintained at 175 pounds per square inch.

As a result of the countercurrent contact of the selective solvent and hydrocarbon stock, the aromatic hydrocarbons and the olefinic hydrocarbons maintained in the charge stock introduced through line **41** are selectively dissolved in the solvent thereby forming an extract stream **52** containing the bulk of the aromatic hydrocarbons and the bulk of the olefinic hydrocarbons and a predominantly paraffinic raffinate stream **51** containing the bulk of the paraffinic hydrocarbons. The raffinate stream passes from the upper portion of extractor **50** through line **51** while the extract phase stream passes from the lower portion of extractor **50** through line **52**.

The extract phase in line **52** is introduced to stripper **60** wherein the dissolved aromatic hydrocarbons and olefinic hydrocarbons and minor amounts of dissolved paraffins are separated from the selective solvent. The aromatic-rich-olefin-rich stream along with some light paraffins passes overhead through line **61** and may be recovered as product or subjected to a further rectification or purification step. Heat is provided for the stripping operation by reboiler **63** and connecting lines **62** and **64**. The solvent stream is taken from the bottom of stripper **60** through line **55** and is passed into the upper portion of extractor **50**.

The raffinate stream in line **51** is introduced into fractionator **70**. A portion of the stream in line **51** may be withdrawn as product through line **56** containing valve **57**. A light fraction having an end point of 225° F. is removed overhead through line **71**, passes through cooler **72**, line **73**, and into receiver **74**. A portion of the liquid material in receiver **74** is used as reflux and is passed through line **75** into an upper portion of fractionator **70**. Another portion of the liquid material in receiver **74** is withdrawn through line **76**.

A heavy fraction, that is a fraction boiling above 350° F. is withdrawn from the bottom of fractionator **70** through line **80**. Heat is provided for the fractionation by reboiler **78** and connecting lines **77** and **79**. An intermediate boiling raffinate fraction having an initial boiling point of 225° F. and an end point of 350° F. is withdrawn at an intermediate portion of fractionator **70** through line **8** and this heavy raffinate fraction is recycled through line **8** and eventually passes through reforming reactor **11**. A portion of the intermediate fraction in line **8** may be withdrawn as product through line **58** containing valve **59**.

The following example is given to further illustrate my invention but is not given for the purpose of unduly limiting the generally broad scope of said invention.

Example

A straight-run gasoline fraction having an initial boiling point of 185° F. and an end point of 395° F. is reformed by passing the fraction through a catalytic reactor tube centrally located in an electrically heated furnace. The tube is filled with a catalyst containing alumina, 0.4% platinum and 0.3% by weight of fluorine. Hydrogen is introduced to the reforming zone in admixture with the charge. An intermediate boiling recycle fraction, prepared as hereinafter described, is also passed along with the charge stock and hydrogen into the reforming zone. The reforming conditions maintained in the reactor are an average catalyst temperature of 890° F. a pressure of 550 pounds per square inch, a weight hourly space velocity of 3.0 and a hydrogen to hydrocarbon mol ratio of 4:1. The effluent from the catalytic reactor is passed directly to a thermal reaction zone. In the thermal reaction zone the temperature of the charge is maintained at approximately 1030° F. and the pressure at 525 pounds per square inch. At these conditions the average residence time of a molecule is approximately seventy seconds. The effluent from the thermal reaction zone is cooled and passed to a receiver in which a hydrogen-rich gas separates from the liquid. The hydrogen-rich gas is vented and the liquid is passed to a stabilizer to fractionate out C_4 and lighter components. The stabilized hydrocarbon stream is passed to the lower portion of an extraction column. The hydrocarbon liquid is pumped into the extractor column, rises and is countercurrently contacted with a stream of 97% diethylene glycol and 3% water. The extractor is maintained at a temperature of 300° F., 200 pounds per square inch pressure and a 6:1 solvent to feed ratio.

The extract phase containing the bulk of the aromatic and olefinic hydrocarbons is removed from the bottom of the extraction column and passed to a stripper in which the aromatics and olefins are separated from the solvent by a steam stripping operation. The raffinate is removed from the top of the extractor and is passed to a

fractionator. The raffinate is fractionated into three fractions: (1) I.B.P.—185° F., (2) 185° F.–360° F., and (3) 360° F.—E.P. The 185° F.–360° F. is recycled directly to the reforming reactor as the intermediate boiling recycle fraction. The I.B.P.—185° F. fraction contains a high proportion of olefins and is suitable as a blending agent in motor fuels since it is very high in octane number. The 360° F.—E.P. fraction is also recovered as product since it is relatively high in aromatic concentration and has a high octane number. One or more of these product streams may be combined with the overhead stream from the stripper and the blend is a motor fuel of high octane number and excellent starting characteristics.

I claim as my invention:

1. A process which comprises catalytically reforming a gasoline fraction, subjecting resultant reformate boiling in the gasoline range to thermal non-catalytic reforming to convert paraffins to olefins, subjecting normally liquid products of the thermal reforming to solvent extraction to separate aromatics and olefins from paraffins, thereby forming a predominantly paraffinic raffinate containing low boiling olefins and high boiling aromatics, fractionating the raffinate to separate therefrom an intermediate fraction having an initial boiling point within the range of from about 150° to about 250° F. and an end point within the range of from about 350° F. to about 425° F., and supplying said intermediate fraction to the catalytic reforming step.

2. A process which comprises catalytically reforming a gasoline fraction at a temperature of from about 600° F. to about 1000° F., subjecting resultant reformate boiling in the gasoline range to thermal non-catalytic reforming at a temperature within the range of from about 800° F. to about 1200° F., a pressure within the range of from about 50 to about 2000 pounds per square inch and for a period of time sufficient to convert a substantial portion of the paraffins in said reformate to olefins, stabilizing the effluent from the thermal reforming step to remove normally gaseous components therefrom, subjecting the stabilized effluent to solvent extraction to separate aromatics and olefins from paraffins, thereby forming a predominantly paraffinic raffinate containing low boiling olefins and high boiling aromatics, fractionating the raffinate to separate therefrom an intermediate fraction having an initial boiling point within the range of from about 150° F. to about 250° F. and an end point within the range of from about 350° F. to about 425° F., and supplying said intermediate fraction to the catalytic reforming step.

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