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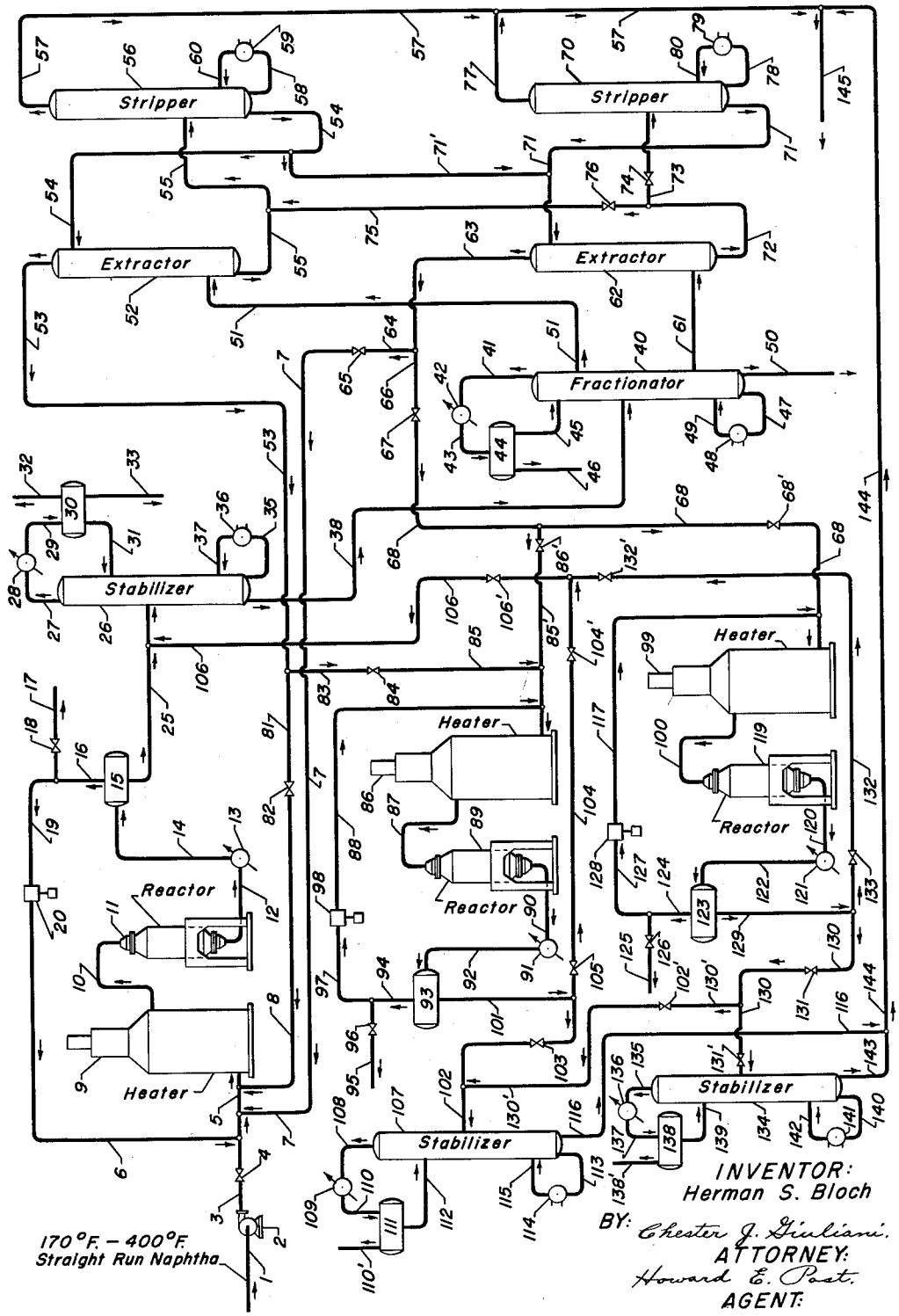

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PRODUCTION OF AN AROMATIC FUEL BY SOLVENT EXTRACTION OF THE REFORMATE FRACTIONS

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This application is a continuation-in-part of my copending application Serial Number 551,127, filed December 5, 1955, now abandoned.

This invention relates to a method of converting a gasoline fraction into aromatics and/or high octane number gasoline. The invention more particularly relates to a combination process in which the steps of catalytic reforming, fractionation and solvent extraction are combined in a novel manner to produce high yields of aromatic hydrocarbons and high octane number gasoline.

The demand for high octane number gasoline in the automotive industry has been increasing steadily, with no indications of a reversal in this trend. As each year arrives the new automobiles have higher compression ratios and higher horsepower outputs which require high octane fuel for satisfactory performance. The refining industry has accordingly developed new processes to meet the ever increasing demand of higher and higher octane number gasolines.

One process that has recently received 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 that has achieved wide commercial acceptance is described in U.S. Patent No. 2,479,110. 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 naphtha is reformed in the presence of a catalyst that promotes dehydrogenation of naphthenes 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 some of the 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 undesirably converted to gases and to carbon deposited on the catalyst. In accordance with the process of the invention a method of reforming is provided which largely overcomes these objectionable features of the prior art reforming processes.

It is an object of the present invention to produce aromatics and a high octane number gasoline from a hydrocarbon charge stock of low octane number boiling within the gasoline range.

It is another object of the present invention to provide a novel combination process in which the steps of catalytic reforming, fractionation and solvent extraction of aromatics are combined in a manner that provides high yields of aromatic hydrocarbons and high octane number gasoline.

In one of its embodiments the present invention relates to a process which comprises subjecting a gasoline fraction in the presence of hydrogen to catalytic reforming, fractionating the reforming product and separating thereby a low boiling fraction having an end point of 250° F. and a fraction boiling above about 250° F., subjecting said low boiling fraction to solvent extraction with a solvent consisting of an aqueous diethylene glycol at extraction conditions which effect substantially complete recovery of the benzene and toluene in said low boiling fraction and produce a separate low boiling paraffinic fraction substantially free of aromatic hydrocarbons, separately subjecting the higher boiling fraction to solvent extraction with an aqueous glycol solvent comprising a glycol selected from the group consisting of diethylene glycol and triethylene glycol at selectively more severe extraction conditions than said first mentioned solvent extraction to form thereby a high boiling predominantly paraffinic fraction substantially free of aromatic hydrocarbons and a high boiling predominantly aromatic fraction, and thereafter combining the low boiling aromatic extract with the high boiling aromatic extract to form a motor fuel of high octane number.

Briefly, the present invention provides a method for producing a high octane number gasoline and/or aromatics from a hydrocarbon stock boiling approximately within the gasoline range which comprises subjecting said stock to reforming in the presence of hydrogen and a suitable reforming catalyst in a first reforming zone. In the first catalytic reforming zone naphthenes are catalytically dehydrogenated to aromatics. It is also preferred that the conditions and catalyst composition promote heavy paraffin hydrocracking, paraffin isomerization and paraffin dehydrocyclization. The resulting catalytically reformed stream is cooled and the stream is passed to a first fractionation zone. In the first fractionation zone a separation of the resulting reformed stream is effected to provide a gaseous hydrogen-containing stream and a liquid stream. The separation may be a flash-type separation. The gaseous hydrogen-containing stream may be vented; however, it is preferred to recycle at least a portion thereof to the first catalytic reforming zone or employ it in another reforming zone. The liquid stream is passed to a fractionator or stabilizer and therein fractionated to remove normally gaseous components. In some cases it is desirable to remove isohexane and lighter hydrocarbons from the liquid. The liquid from the fractionator or stabilizer is then passed to a fractionator wherein the liquid is fractionated into at least a low boiling fraction and a high boiling fraction. The removal of the normally gaseous components, which usually comprise C_4 and lighter components, and the fractionation of the liquid into a low boiling normally liquid fraction having an end point of about 250° F. and a high boiling normally liquid fraction boiling above about 250° F. may be accomplished in a single fractionator; however, when desired two or more fractionators may be used. The low boiling fraction is thereafter subjected to solvent extraction with a glycol solvent wherein the aromatics which consist predominantly of benzene and toluene are separated from a substantially aromatic free raffinate. The raffinate is a low boiling predominantly paraffinic fraction and may be recycled to the catalytic reforming zone or to a separate catalytic reforming zone.

The high boiling fraction having an initial boiling point above about 250° F. is separately subjected to solvent extraction, but the extraction conditions required to recover all or substantially all of the aromatic components of the higher boiling fraction are somewhat more severe than the extraction of the low boiling fraction because of the lower degree of solubility of the higher boiling aromatics in the solvent. The more severe extraction conditions also require the use of a different solvent composition in the latter extraction; that is, a solvent having greater selec-

tivity and solvency for higher molecular weight aromatic hydrocarbons. The raffinate recovered from the second extraction zone, comprising a high boiling predominantly paraffinic fraction, may be recycled to the first catalytic reforming zone or it may be reformed in a separate reforming reaction zone, along with or in the absence of the low boiling predominantly paraffinic raffinate fraction.

The present invention is partly based on the discovery that when the reformed gasoline product of the catalytic reforming zone is fractionated into at least two fractions, that is, a low boiling normally liquid fraction and a high boiling normally liquid fraction before subjecting the reformate to solvent extraction, the aromatics may be extracted from each fraction under conditions which will produce optimum yield of extract under extraction conditions best adapted to each fraction but not to the other fraction. The over-all operation will, therefore, be more economical, more selective, and will yield products of better quality and improved yield. If a single extraction is employed, the highly soluble lower boiling aromatics interfere with extraction of the less-soluble higher boiling aromatics; and if conditions are employed which will completely dissolve the higher boiling aromatics, the lower boiling non-aromatics (which have about the same solubility as higher boiling aromatics) are indiscriminately dissolved in the selective solvent. These difficulties are overcome in an economical manner by the improvement herein provided.

Hydrocarbons suitable as feed stocks to the reforming zone of the present process are 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. The preferred feed stocks thus include 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 select fraction thereof, usually 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 various gasolines and/or gasoline fractions may also be used, including thermally cracked and/or catalytically cracked gasolines. In general, however, when the latter 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.

The reforming zone which receives the gasoline boiling range feed stock, herein referred to as the first reforming zone, is maintained at hydroforming reaction conditions which effect substantial conversion of the naphthenes to aromatics and also induce hydrocracking of the heavy paraffin components. The reforming reaction proceeds at a temperature within the range of from about 600° F. to about 1000° F. and more preferably, from about 750° to about 950° F. The weight hourly space velocity, defined as the weight of oil per hour per weight of catalyst in the reaction zone, is preferably within the range of from about 1 to 1 to about 10 to 1. It is preferred that the reforming reaction in the first reforming reaction zone be conducted in the presence of hydrogen at pressures of from about 100 to about 1000 pounds per square inch. In the normal operation of the reforming zone, sufficient hydrogen will be produced in the reaction zone via dehydrogenation and dehydrocyclization reactions, to furnish the hydrogen required in the process and, therefore, a net production of hydrogen takes place, making it 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 provide sufficient hydrogen in the reaction zone to inhibit carbon deposition on the reforming catalyst. Thus, sufficient hydrogen is supplied to maintain the hydrogen to hydrocarbon mol ratio in the reforming zone within the range of from about 0.5 to 1 to about 10 to 1. It is to be noted that by virtue of the present method of operation the conditions in the first reforming reaction zone are substantially milder than if it were attempted to reform the charge stock to high octane levels in a once-through operation.

The reforming reaction in the first reforming zone is preferably catalyzed in order to promote the rate and extent of total conversion. One of the preferred catalysts for the reforming reaction is a platinum-alumina-combined halogen composite in which the halogen component is selected from chlorine and fluorine. The catalyst utilized in the one or more reforming zones provided in the present combination process may vary in composition from one catalytic reforming zone to the other; however, it is generally preferred to utilize catalysts of the same composition in each of the reaction zones in order to facilitate catalyst loading and catalyst reclaiming projects. Particularly preferred catalysts for use in the reforming stages of the present process are the platinum-alumina-silica catalyst composites of the type described in U.S. Patent No. 2,478,916 issued August 16, 1949, and the platinum-alumina-combined halogen composite catalysts of the type described in U.S. Patent No. 2,479,109 issued August 16, 1949. Other suitable catalysts include the platinum-alumina, and platinum supported on a modified cracking catalyst base.

The aforementioned platinum-containing composite catalysts may contain up to about 10% by weight of platinum, although very effective catalysts contain from about 0.01% to about 1% by weight of platinum. Catalysts containing combined halogen are effective hydrocracking-reforming catalysts when they contain from about 0.1% to about 8% halogen by weight of the catalyst, particularly preferred catalysts containing from about 0.1% to about 3% by weight of halogen which is preferably made up of both chlorine and fluorine.

A fixed bed reforming operation is preferred for each of the catalytic reforming zones, the feed stock being passed through the fixed bed of catalyst at the specified reforming conditions in liquid phase. It has been found that at the relatively mild conditions maintained in each of the reforming zones the above preferred catalysts may be employed for extended periods of time without regeneration or replacement. This is of great economic advantage to the refiner because fixed bed operations employ apparatus which is relatively inexpensive compared with that employed for fluidized operations, and, in addition, the maintenance of fixed bed reactors is markedly less than the maintenance of fluidized reactors. Further, it has been found that fixed bed operations in the catalytic reforming zone generally produce better yields. This effect may be the result of a more desirable temperature profile in the fixed bed system; that is, the temperature drop or rise through the catalyst bed may be such that the desired reactions are promoted to a greater extent in a fixed bed reactor than when a uniform temperature is maintained throughout the catalyst bed. While a fixed bed operation is preferred in each of the catalytic reforming zones, it is to be understood that fluidized, fluidized-fixed bed, moving bed and/or slurry types of operation may also be used, however not necessarily with equivalent results.

In accordance with the process of the present invention the product of the reforming stage is fractionated to separate the total reformate into (1) a low boiling fraction having an end boiling point of about 250° F., containing benzene and toluene which are recovered therefrom by solvent extraction at relatively mild extraction

conditions, and (2) a higher boiling fraction boiling above about 250° F. containing xylene, ethylbenzene and higher alkyl aromatic hydrocarbons which are recovered therefrom by means of solvent extraction effected at more severe extraction conditions. It is thus the essence of this invention to provide a process in which the extraction stages of the process are operated at the particular optimum conditions of extraction especially adapted to recover the aromatics from each fraction. In contrast to such selective extraction, when the entire reformate is subjected to solvent extraction at conditions which will ensure the maximum recovery of all of the aromatics in the entire reformate product, the extraction conditions must be sufficiently severe to accommodate the least readily extracted higher alkyl aromatic hydrocarbons and at such conditions, the extraction results in the recovery in the extract of a large proportion of the light non-aromatic hydrocarbons which, in effect, contaminate the extract with non-aromatics of low octane number having less desirable blending qualities for motor fuel use. On the other hand, utilizing the process of the present invention wherein the reformate is first fractionated into low and higher boiling fractions and each of the resulting cuts are separately subjected to solvent extraction at extraction conditions tailor-made for the aromatics contained in each fraction, the extracts recovered in each extraction are substantially pure aromatics having high motor fuel blending qualities because of the absence of contaminating low octane number aliphatics.

The low boiling fraction separated from the total reformate is subjected to a first solvent extraction utilizing a solvent which is selective for the aromatic components contained in the lower boiling cut, while at the same time, the higher boiling cut of the reformate product is separately subjected to a second solvent extraction utilizing a solvent selective for the aromatic components of the latter cut. In general, each extraction zone is also operated at temperatures and solvent to feed ratios particularly adapted to the recovery of the particular aromatics in each cut. By more severe operating conditions in the extraction zone for the solvent extraction of the higher boiling cut is meant those process variables which had they been maintained in the first extraction zone would cause more extract (including more of the less readily extracted hydrocarbons) to be present in the solvent phase from the extractor. More severe operating conditions may be achieved by using a higher solvent to feed ratio, or a solvent of higher solvent power, or a higher temperature, or an extractor of more stages or less water in the solvent, or any combination of these. Similarly, in the stripping stage of the process for recovery of the aromatic extract from the rich solvent, a higher temperature, or more stripping steam, or both may be employed. It should be noted that these more severe operating conditions often result in a more expensive extraction separation, but that in the present process the more costly conditions are applied to only a small proportion of the effluent stream, rather than to the total reformate. In thus separately extracting the low and high boiling fractions to recover more completely the aromatic components of each fraction, it necessarily follows that the non-extracted raffinates of each extraction are more predominantly paraffinic and when these are recycled to the reforming step or separately subjected to individual reforming reactions, a greater net yield of aromatic product is realized because of the absence of aromatics in the recycle fractions which inhibit the conversion of the non-aromatic components in these recycle fractions to their aromatic analogs.

A particularly desirable solvent for separating aromatic hydrocarbons from non-aromatic hydrocarbons is a mixture of water and a polyalkylene glycol which may have its solvency (or solvent capacity) regulated by adding more or less water. Thus, by adding more water to the solvent, the solubilities of all components of the hydrocarbon mixture are reduced, but the solubility difference between the components is increased. This effect is reflected process-wise in that fewer contacting stages are 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.

Aromatic compounds differ in their relative solubility in glycol solvents; that is, the solubility appears to be a function of the boiling point of the aromatics, with the lower boiling or lighter aromatics being more soluble than the higher boiling or heavier aromatics. With respect to the non-aromatic hydrocarbons, solubility in glycol solvents also decreases with increasing molecular weights. As a consequence, the lighter paraffins have solubilities comparable with those of the heavier aromatics, making separation difficult without the double extraction method herein described.

The solvents employed in both of the solvent extraction stages of the present process are polyalkylene glycols, the compositions of which are specifically adjusted to provide a solvent composition especially adapted to effect substantially complete recovery of the aromatic components of each of the low and higher boiling reformate cuts and simultaneously produce substantially aromatic-free raffinate streams. It has been found that for the extraction of the low boiling reformate fraction (i.e., the reformate cut boiling up to about 250° F.) an aqueous diethylene glycol solution containing from about 5 to about 10 percent by weight of water constitutes a highly selective solvent composition for the extraction of such fractions, utilizing a solvent to feed (*S/F*) ratio of from 3 to 1 to about 8 to 1 at a temperature of extraction within the range of from about 225° to about 275° F. Since the aromatic components of the higher boiling reformate cut (i.e., boiling above about 250° F.) are less readily extracted and more severe extraction conditions are required to effect recovery of the aromatics in the latter higher boiling cut, the temperature of extraction utilizing the same glycol may be increased for extraction of the higher boiling cut, the *S/F* ratio may be increased, or the water content of the solvent composition may be decreased for the same glycol; alternatively, a solvent composition comprising diethylene glycol or triethylene glycol (which may incorporate varying proportions of dipropylene glycol to increase its solvency) may be provided. Thus, with diethylene or triethylene glycol and water mixtures as sovent, the water content of the solvent supplied to the extraction zone is maintained at from about 1 to about 5 percent by weight and the extraction temperature is increased to from about 350° to about 425° F. and the solvent to feed ratio is maintained at from about 5 to 1 to about 15 to 1. With a solvent composition containing a significant proportion of dipropylene glycol in admixture with diethylene glycol or triethylene glycol, the water content of the mixture is maintained at from about 2 to about 10 percent water, the extraction is effected at temperatures of from 250° to about 375° F. and the *S/F* ratio is maintained within the range of from about 5 to 1 to about 15 to 1.

The low boiling fraction of the aromatic reformate, therefore, is extracted into a low boiling predominantly paraffinic fraction (raffinate) and a low boiling aromatic fraction (extract). Likewise the high boiling fraction of the reformate is separated into a high boiling predominantly paraffinic fraction and a high boiling aromatic fraction. These aromatic streams may be separately recovered as product or in a preferred embodiment the low boiling aromatic fraction and the high boiling aromatic fraction are blended to produce the motor fuel blending agent, which is the product of the present process. At least a portion of the low boiling predominantly paraffinic fraction may be recycled to the first catalytic reforming zone, or in another embodiment of this invention the low boiling predominantly

paraffinic fraction may be separately reformed in a separate or second catalytic reforming zone. Likewise at least a portion of the high boiling predominantly paraffinic fraction may be recycled to the first catalytic reforming zone, or in another embodiment of this invention the high boiling predominantly paraffinic fraction and the low boiling predominantly paraffinic fraction may be reformed together in a second catalytic reforming zone. In still another embodiment of this invention the high boiling predominantly paraffinic fraction is separately reformed in a third catalytic reforming zone. The product from the second and/or third catalytic reforming zones may be recovered as product or they may be fractionated into low boiling and high boiling fractions and solvent extracted so as to recover the aromatics therefrom.

When a second and/or third catalytic reforming zone are used, the catalyst and conditions therein may be selected from the catalyst and conditions hereinbefore described for the first catalytic reforming zone.

Additional features and advantages of the present 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. Although the process illustrated in the drawing represents one or more of the preferred forms of this invention, it is to be understood that the invention is not limited thereby. For simplification, many valves, pumps, heat exchangers, etc. have been eliminated from the drawing as their illustration is not essential to an understanding of the invention.

Referring now to the drawing, the present process is illustrated with respect to a feed stock comprising a straight run naphtha having an initial boiling point of 170° F. and an end point of 400° F. being passed through line **1**, picked up by pump **2** and discharged through line **3** containing valve **4**. A hydrogen-rich gas stream in line **6** mixes with the charge in line **3** and the combined stream in line **5** is passed into heater **9** wherein the mixture is heated to a temperature of 905° F. A high boiling predominantly paraffinic fraction, derived from the process as hereinafter described, may be introduced into the process flow through line **7** and mixed with incoming feed stock. A low boiling predominantly paraffinic fraction, derived from the process as hereinafter described, may also be mixed with the incoming feed stock, being charged into line **5** from line **8**.

The heated combined stream is withdrawn from heater **9** through line **10** and passes into catalytic reforming reaction zone **11**. Reforming reactor **11** contains a bed of spherical catalyst particles of approximately ⅛" average diameter containing alumina, 0.5% platinum and 0.4% combined chlorine. The pressure in the reactor is 600 p.s.i., the weight hourly space velocity is 3.0 and the hydrogen to hydrocarbon mole ratio is 6 to 1. During the passage of the charge stock through reactor **11**, the bulk of the naphthenes containing 6 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 also takes place. The important octane number increasing reaction of dehydrocyclization also occurs in reactor **11** at these conditions. By means of this reaction a substantial portion of the paraffins, especially the higher boiling paraffins, are converted to aromatics, a major factor in increasing the octane number of the non-aromatic portion of the fraction.

The effluent from reactor **11** passes through line **12**, cooler **13**, line **14** and into separator **15**. Hydrogen is withdrawn from the top of receiver or separator **15** through line **16**. Excess hydrogen may be withdrawn through line **17** containing valve **18**. At least a portion of the hydrogen in line **16** passes through line **19**, is picked up by compressor **20** and discharged into line **6**.

The liquid hydrocarbons, comprising the reformate and the bulk of the normally gaseous hydrocarbons produced in the process, are withdrawn from receiver **15** through line **25** and passed into fractionator or stabilizer **26**. Line **106** which connects with line **25** is provided to transfer unstabilized reformate from reactors **89** and/or **119** into stabilizer **26** for stabilization of the effluent from these reactors. Separate stabilization systems may also be provided, as is hereinafter described.

In stabilizer **26** normally gaseous components comprising C_4 and lighter hydrocarbons are removed overhead through line **27**. Since isohexanes are high in octane number and are not increased in octane number by subsequent reforming, the isohexane and lighter components are preferably removed overhead through line **27**, passed through cooler **28** wherein a portion of the material is condensed, and the entire stream passed through line **29** into receiver **30**. In receiver **30** the liquid phase and the gas phase of the overhead material separate; the gas passes through line **32** from which it may be vented to the atmosphere or otherwise used. Liquid may be withdrawn from receiver **30** through line **33**. Stabilizer **26** is operated at a sufficient pressure to liquefy at least a portion of the overhead material so that a liquid stream is available to improve the separation in stabilizer **26**. The liquid reflux passes from receiver **30** through line **31** and into an upper portion of fractionator **26**. Stabilizer **26** is supplied with heat by reboiler **36** and connecting lines **35** and **37**.

The stabilized liquid is withdrawn from the bottom of stabilizer **26** through line **38** and introduced into fractionator **40**. In fractionator **40** the stabilized reformate is separated into a low boiling fraction having an end point of about 250° F. and a high boiling fraction boiling above about 250° F., to the end point of the reformate. The overhead comprising the low boiling fraction from fractionator **40** passes through line **41**, cooler **42**, line **43** and into receiver **44**. Fractionator **40** and receiver **44** are operated at a temperature and pressure sufficient to liquefy the overhead material in line **41**. The liquid in receiver **44** may be withdrawn from the system through line **46**. However, generally at least a portion of the liquid material is used as reflux and passes from receiver **44** through line **45** into an upper portion of fractionator **40**. The fractionator has heat provided thereto by reboiler **48** and connecting lines **47** and **49**. The low boiling fraction having an initial boiling point of about 160° F. and an end point of about 250° F. is withdrawn from an upper section of fractionator **40** through line **51** and charged into extractor **52**. A fraction having an initial boiling point of about 250° F. and an end point of about 400° F. is withdrawn from fractionator **40** through line **61** and charged into separate extractor **62**. Components boiling above 400° F. are withdrawn from fractionator **40** through line **50**.

The low boiling fraction is introduced in liquid phase into the lower portion of extractor **52** through line **51**, and thereafter rises and is countercurrently contacted at a temperature of about 250° F. with a descending liquid stream of a solvent selective for benzene and toluene at a solvent/feed ratio of 5:1. The pressure maintained in extractor **52** is 150 p.s.i. Aqueous diethylene glycol containing 7.5% water is used as the solvent. The solvent enters the upper portion of extractor **52** through line **54**. As a result of the countercurrent liquid-liquid contact of the selective solvent and the hydrocarbon stock, the aromatic hydrocarbons contained in the low boiling fraction are selectively dissolved in the solvent, thereby forming a rich solvent stream containing the solvent and substantially all of the benzene and toluene present in the low boiling fraction. A predominantly paraffinic raffinate stream containing substantially all of the paraffinic hydrocarbons present in the low boiling fraction is removed from extractor **52** through line **53**. The rich solvent

phase is removed from the lower portion of extractor 52 through line 55.

The rich solvent phase in line 55 passes into stripper 56 wherein the dissolved extract hydrocarbons are separated from the selective solvent. The aromatic hydrocarbon extract stream is recovered as an overhead from stripper 56 through line 57 and may be recovered as a portion of the total product through line 145 or subjected to further rectification by means not illustrated on the accompanying diagram. Heat is provided for the stripping operation by reboiler 59 and connecting lines 58 and 60. The lean solvent stream is taken from the bottom of stripper 56 through line 54 and is passed into the upper portion of extractor 52 through line 54. Line 75 which connects with line 55 and which contains valve 76 is provided in order to transfer the rich solvent from extractor 62 into stripper 56 thereby combining the rich solvent phases from both extractors for simultaneous stripping in one vessel.

The higher boiling fraction of the reformate removed from fractionator 40 through line 61 is introduced into a lower portion of extractor 62. As hereinbefore mentioned the conditions in second extractor 62 are more severe than the conditions in first extractor 52. The high boiling fraction of the reformate, in liquid phase, rises and is counter-currently contacted at an elevated temperature with a descending stream of a glycol solvent selective for the higher boiling aromatics in the fraction. A suitable solvent for use in extractor 62 is diethylene glycol containing about 1.5% water or a mixture of diethylene glycol and dipropylene glycol (e.g. a mixture in which the ratio of DEG/DPG is 90/10) and containing about 2% by weight of water. An extraction temperature of approximately 375° F. is maintained in extractor 62 and the pressure is 200 p.s.i. A solvent to feed ratio of 8:1 is employed. The lean solvent composition enters the upper portion of extractor 62 through line 71. As a result of the countercurrent contact with the selective solvent, the aromatic hydrocarbons contained in the high boiling fraction charged into extractor 62 through line 61 are selectively dissolved in the solvent, thereby forming a rich solvent stream containing the solvent and substantially all of the aromatic hydrocarbons and a paraffinic raffinate stream consisting predominantly of the paraffinic hydrocarbons present in the high boiling fraction. The raffinate stream is removed from the upper portion of extractor 62 through line 63. The rich solvent stream is removed from the lower portion of extractor 62 through line 72. The rich solvent may be transferred to a separate stripper 70 or alternatively, charged with the rich solvent from extractor 52 into common stripper 56. When a common stripper is used, valve 74 is maintained in a closed position and valve 76 is maintained in an open position. The extract thereupon passes through line 72 and line 75 containing valve 76. The material in line 75 mixes with the material in line 55 and the mixture is passed into stripper 56. Lean solvent for extractor 62 is removed from the bottom of stripper 56 through line 54 and continues through line 71' and 71 into an upper portion of extractor 62. When a common stripper is not employed valve 76 is maintained closed and valve 74 open. In this operation the extract in line 72 continues through line 73 containing valve 74 and into stripper 70. In stripper 70 the dissolved aromatic hydrocarbons are separated from a lean, regenerated solvent. The aromatic hydrocarbon extract stream is recovered as an overhead distillate through line 77 and discharged from the process flow as product through lines 57 and 145, or subjected to further fractionation by means not illustrated in the accompanying diagram. Heat is provided for the stripping operation by reboiler 79 and connecting lines 78 and 80. The lean solvent stream is taken from the bottom of stripper 70 through line 71 and may be recycled directly into the upper portion of extractor 62.

The low boiling predominantly paraffinic raffinate removed from extractor 52 through line 53 may be recycled to reforming reactor 11 through line 81, valve 82 and line 8 which connects line 3 and thereby mixes with fresh charge stock to the reforming reactor. Likewise, the high boiling predominantly paraffinic raffinate fraction is removed from extractor 62 through line 63 and may be recycled to reforming reactor 11 through line 64, valve 65 and line 7 which connects with line 3, thereby mixing the recycle paraffins with the fresh charge in line 3. In accordance with an alternative embodiment, herein illustrated, valves 82 and 65 may be maintained in a closed position, while valves 84 and 67 are maintained open in order to direct the low and high boiling raffinate streams into separate reforming zones. In this operation the low boiling predominantly paraffinic raffinate fraction in line 53 is transferred through line 83, valve 84 and line 85 into heater 86. In a similar manner the high boiling predominantly paraffinic raffinate fraction in line 63 is transferred through line 66, valve 67 and line 68 into one of two alternative routes. Valve 68' may be maintained closed and valve 86' maintained open. In this alternative the high boiling predominantly paraffinic fraction in line 68 continues its flow through valve 86' and line 85', mixes with the low boiling paraffinic raffinate fraction in line 85 and the mixture thereafter transferred into heater 86 which prepares the mixed paraffins for reforming in reactor 89. In another mode of operation, valve 86' is maintained closed and valve 68' is maintained open. In this operation the material in line 68 continues through valve 68' into heater 99. The latter operation wherein valve 86' is maintained closed and valve 68' is maintained open will be described in the following description.

The low boiling predominantly paraffinic fraction in line 85 mixes with hydrogen being recycled through line 88 and the mixture enters heater 86 wherein the mixture is heated to a temperature of 915° F. The heated stream is withdrawn from heater 86 through line 87 into catalytic reforming reaction zone 89 containing a reforming catalyst of the type hereinabove described and the reaction conditions maintained therein are substantially similar to the reforming conversion heretofore described. During the passage of the charge through reactor 89, isomerization and dehydrocyclization of the paraffins occur. The effluent from reactor 89 passes through line 90, cooler 91, line 92 and into separator 93. Hydrogen is withdrawn from the top of receiver or separator 93 through line 94. Excess hydrogen may be withdrawn through line 95 containing valve 96. At least a portion of the hydrogen in line 94 passes through line 97, is picked up by compressor 98 and discharged into line 88.

The liquid hydrocarbons, comprising the reformate and the bulk of the normally gaseous hydrocarbons produced in the process, are withdrawn from receiver 93 through line 101. Valve 103 may be maintained closed and valve 105 maintained open whereby the material in line 101 passes through valve 105, line 104, open valve 104' open valve 106' and line 106 and finally into stabilizer 26. In this manner the effluent from reactor 11 and the effluent from reactor 89 are stabilized in stabilizer 26. In another manner of operation, which operation is herein illustrated and further described, valve 105 is maintained in a closed position and valve 103 is maintained open. The liquid material in line 101 therefore passes through line 101 valve 103 and line 102 into stabilizer 107. Line 130' connects with line 102 and the effluent from reactor 119 may pass through line 130' and line 102 into stabilizer 107. This operation is hereinafter described in greater detail.

In stabilizer 107 normally gaseous components, comprising C_4 and lighter hydrocarbons are removed over-

head through line 108, cooler 109 and pass through line 110 into receiver 111. Stabilizer 107 and receiver 111 are maintained at a pressure sufficient to condense at least a portion of the overhead material. Liquid reflux is therefore withdrawn from receiver 111 through line 112 and passed to an upper portion of stabilizer 107. The gaseous components may be removed from receiver 111 through line 110'. Heat is provided to stabilizer 107 by reboiler 114 and connecting lines 113 and 115. The stabilized reformate is withdrawn through line 116 and may be recovered as product. However, the material in line 115 may also continue through line 144 to be withdrawn as product through line 145, along with other product streams, such as the material in line 57 being withdrawn through line 145.

The high boiling paraffinic raffinate from extractor 62 continues through line 68 and valve 68' into heater 99. A hydrogen recycle gas stream in line 117 combines with this hydrocarbon charge being passed into heater 99 wherein the hydrocarbon charge is heated to a temperature of 920° F. The heated, combined stream is withdrawn from heater 99 through line 100 and passes to catalytic reforming zone 119. Reforming reactor 119 also contains a reforming catalyst of the composition hereinabove described. The pressure in the reactor is also somewhat higher than in reactor 89, preferably at about 500 pounds per square inch. The weight hourly space velocity is 3.0 and the hydrogen to hydrocarbon mol ratio is 8 to 1. During the passage of the charge stock through reactor 119, a portion of the paraffins are hydrocracked to lower boiling paraffins. Isomerization and dehydrocyclization also occurs in reactor 119. The effluent from reactor 119 passes through line 120, cooler 121, line 122 and into separator 123. Hydrogen is withdrawn from the top of receiver or separator 123 through line 124. Excess hydrogen may be withdrawn through line 125 containing valve 126. At least a portion of the hydrogen in line 124 continues through line 127, is picked up by compressor 128 and recycled to reactor 99 through line 117. The liquid hydrocarbons, comprising the reformate and the bulk of the normally gaseous hydrocarbons produced in the process, are withdrawn from receiver 123 through line 129. In an operation in which valve 131 is maintained closed and valve 133 maintained open, the material in line 129 continues through valve 133, line 132, open valve 132', open valve 106', line 106 and into stabilizer 26. In such an operation the effluent from reactor 11 and the effluent from reactor 119 are stabilized in a common stabilizer 26.

In another embodiment herein illustrated and further described, valve 133 is maintained closed, valve 131' maintained closed and valve 102' maintained open, whereupon the reformate in line 129 continues through line 130, valve 131 and line 130' containing open valve 102' into stabilizer 107. In such an operation the effluent from reactor 119 and the effluent from reactor 89 are stabilized in a common stabilizer 107. Valve 102' may be maintained closed and valve 131' maintained open, whereby the reformate in line 129 passes through line 130 containing open valve 131 and through valve 131' into stabilizer 134. In stabilizer 134 the normally gaseous hydrocarbons are withdrawn overhead through line 135, pass through cooler 136, and line 137 into overhead receiver 138. Stabilizer 134 and receiver 138 are maintained at a sufficient pressure to liquefy at least a portion of the overhead material. The liquefied material is withdrawn from receiver 138 through line 139 and charged into an upper portion of stabilizer 134 as reflux. Normally gaseous hydrocarbons are withdrawn from receiver 138 through line 138'. Heat is supplied to stabilizer 134 by reboiler 141 and connecting lines 140 and 142. The stabilized reformate is withdrawn from stabilizer 134 through line 143 and is preferably combined with the hydrocarbon stream in line 116 withdrawn as product through line 145.

The following example is given to further illustrate the operability of the present invention, however, it is not introduced with the intention of unduly limiting the generally broad scope of the invention.

Example

A straight-run naphtha fraction having an initial boiling point of 161° F. and an end boiling point of 401° F. is reformed by passing the fraction through a reactor tube located in an electric furnace. A low boiling predominantly paraffinic fraction, separated as hereinafter described, having an initial boiling point of 153° F. and an end boiling point of 250° F. and a high boiling predominantly paraffinic fraction having an initial boiling point of 248° F. and an end point of 395° F. are also passed through the reactor in admixture with the fresh straight-run naphtha charge. The tube is filled with a catalyst containing alumina, 0.5% platinum and 0.7% fluorine. Hydrogen is also introduced into the reaction zone. The reforming conditions maintained in the reactor are an average catalyst temperature of 900° 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 6:1.

The effluent from the reactor is stabilized in a fractionating column by removing C_4 and lighter components. The stabilized material is then passed to a fractionator. A low boiling fraction having an initial boiling point of 153° F. and an end point of 250° F. and comprising 38% of the reactor effluent, is removed from an upper portion of the fractionator. A high boiling fraction having an initial boiling point of 250° F. and an end boiling point of 403° F. and comprising 48% of the reactor effluent, is removed from a lower portion of the fractionator.

The low boiling fraction is passed to a lower portion of an extraction column. The hydrocarbon liquid is pumped into the extraction column, rises in the column and is countercurrently contacted with a stream of 92.5% diethylene glycol and 7.5% of water. The extractor is operated at a temperature of 250° F. and a 5:1 solvent to feed ratio. The pressure on the column is 150 pounds per square inch. The extract phase is removed from the bottom of the extraction column and passed to a stripper in which the aromatics are separated from the solvent by a steam stripping operation. The raffinate is removed from the top of the extractor and is recycled to the reforming reactor as the low boiling predominantly paraffinic fraction.

The 250 to 430° F. fraction passed to a second extraction column wherein the fraction rises in the column and is countercurrently contacted with a descending stream of solvent comprising 80% diethylene glycol 18% dipropylene glycol and 2% water. The extractor is maintained at a pressure of 200 pounds per square inch, 250° F. and the solvent to feed ratio (volumes/volume) supplied to the extractor was 8:1. A rich solvent phase is removed from the bottom of the extraction column and charged into a second stripper in which the aromatics are separated from the solvent by steam distillation. A paraffinic raffinate containing less than 3% aromatics is removed from the top of the extractor and is recycled to the reforming reactor as the aforementioned high boiling predominantly paraffinic fraction.

The aromatics separated from the first stripper and the aromatics separated from the second stripper are mixed and the mixture is a blending agent for the production of high octane number gasolines. The yield and purity of the aromatic products are exceptionally high. The paraffinic raffinate streams in which the aromatic content is especially low are an excellent source of smokeless jet fuel.

I claim as my invention:

1. A process for the production of an aromatic fuel product which comprises catalytically reforming a gasoline boiling range fraction in the presence of hydrogen,

separating substantially all of the gasoline boiling hydrocarbons from the reforming step into a low boiling fraction having an end boiling point of about 250° F. and a high boiling fraction having an initial boiling point of about 250° F. and boiling within the gasoline range, subjecting said low boiling fraction to solvent extraction with an aqueous polyethylene glycol solvent at extraction conditions selective for the separation of benzene and toluene, substantially free of non-aromatics, from a paraffinic raffinate substantially free of aromatic hydrocarbons, subjecting said high boiling fraction to solvent extraction with an aqueous glycol solvent comprising a polyethylene glycol at extraction conditions selective for the separation of aromatic hydrocarbons boiling above about 250° F. substantially free of non-aromatics, the solvent extraction of said high boiling fraction being effected at extraction conditions at which the solvent has greater solvent capacity for the aromatic components contained in the fraction than the first-mentioned extraction conditions and characterized by at least one of the following conditions compared to the extraction of said low boiling fraction: a lesser amount of water in the solvent, the presence of dipropylene glycol in the solvent, a greater solvent to feed ratio, and a higher temperature of extraction, and thereafter mixing the resulting aromatic extracts recovered from each of said low boiling and high boiling fractions.

2. The process of claim 1 further characterized in that said polyethylene glycol is diethylene glycol.

3. The process of claim 1 further characterized in that said polyethylene glycol is triethylene glycol.

4. The process of claim 1 further characterized in that paraffinic raffinate separated from the high boiling fraction is recycled to said catalytic reforming step.

5. The process of claim 1 further characterized in that said extraction of the low boiling fraction is effected in the presence of an aqueous diethylene glycol containing from 5 to 10 percent by weight of water at a solvent to feed ratio of from 3/1 to 8/1 and at a temperature of from about 225° F. to about 275° F.

6. The process of claim 1 further characterized in that said extraction of the high boiling fraction is effected in the presence of a solvent composition comprising a glycol selected from the group consisting of diethylene glycol and triethylene glycol containing from 1 to 5 percent by weight of water, at a temperature of from about 350° to about 425° F., and at a solvent to feed ratio of from about 5/1 to about 15/1.

7. The process of claim 6 further characterized in that said solvent composition is an aqueous mixture of glycols consisting of a polyethylene glycol selected from the group consisting of diethylene glycol and triethylene glycol and dipropylene glycol containing from about 5 to about 10 percent by weight of water.

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