

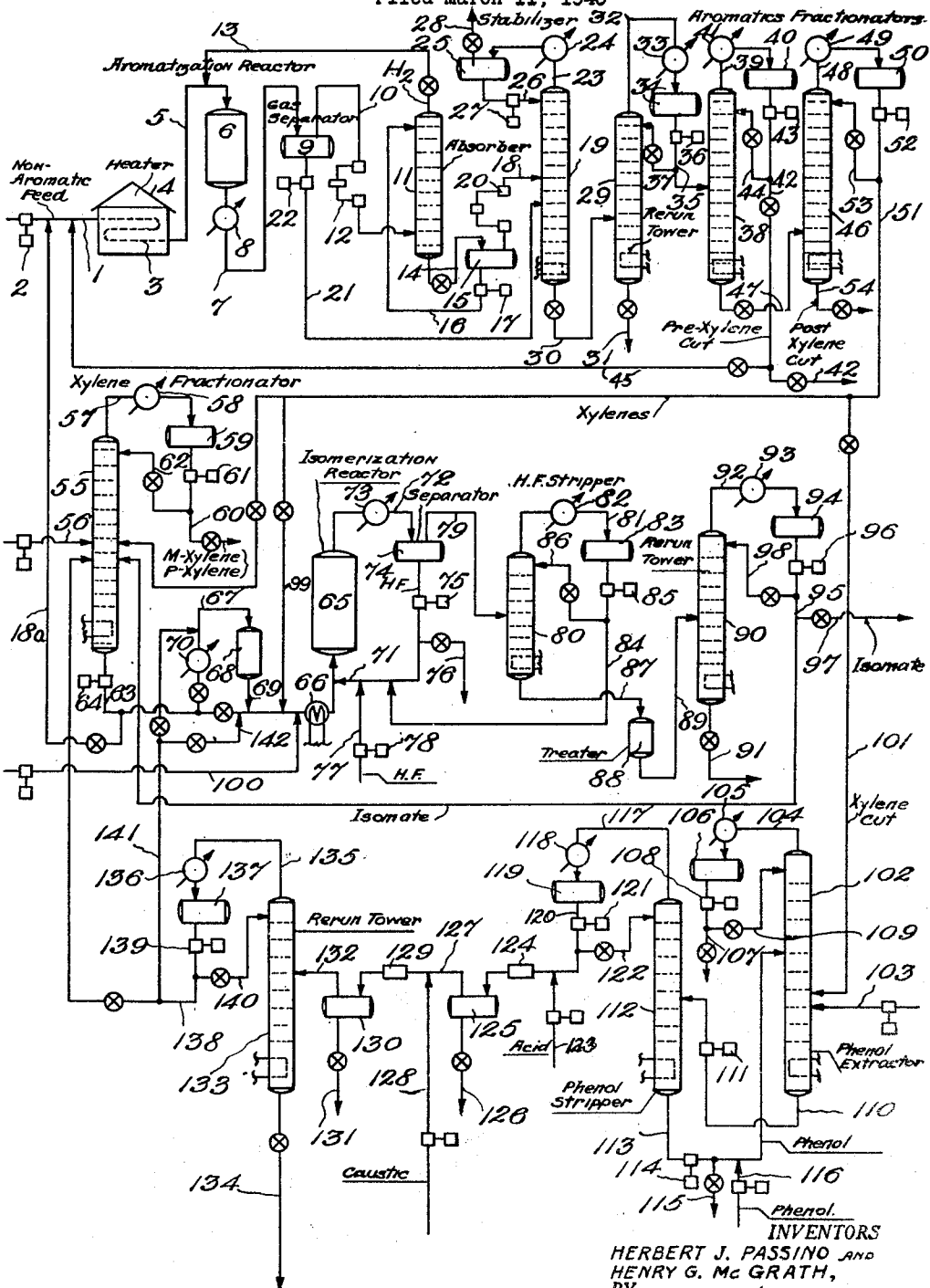
Aug. 12, 1947.

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2,425,559

CATALYTIC CONVERSION OF ALKYL AROMATIC HYDROCARBONS

Filed March 11, 1943



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UNITED STATES PATENT OFFICE

2,425,559

CATALYTIC CONVERSION OF ALKYL AROMATIC HYDROCARBONS

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Application March 11, 1943, Serial No. 478,814

14 Claims. (Cl. 260-668)

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This invention relates to improved methods for the production of motor fuel of the highest anti-knock value. More particularly the invention relates to the production of cyclic hydrocarbon motor fuel constituents, or fractions rich in such constituents, which are of the highest anti-knock value. Still more particularly the invention relates to an improved process for the production of aviation motor fuel constituents of high anti-knock value by selective isomerization of poly-alkylated aromatic hydrocarbons. The invention relates also to improved methods for the isomerization of poly-alkylated cyclic hydrocarbons, such as aromatic and naphthenic hydrocarbons, for any purpose whatever.

In the preparation of aviation motor fuel, particularly for military use, it is desirable to restrict the hydrocarbon constituents which are included in the motor fuel to those of the highest anti-knock value because of the necessity for producing composite fuel of the highest value and because the variations in anti-knock value of the various hydrocarbons increase in degree under the severe operating conditions in which military aviation motor fuel is employed. Necessarily these considerations are important in the preparation of motor fuel for general use, if to a lesser degree.

It is an object of this invention to provide an improved process for the production of motor fuel constituents of the highest anti-knock value. It is a further object of the invention to provide a process for isomerizing poly-alkylated cyclic hydrocarbons which is an improved process by reason of the employment therein of an isomerizing catalyst of superior qualities. It is a further object of the invention to provide an improved process for the treatment of a mixture of poly-alkylated aromatic hydrocarbons to produce therefrom, in the most expeditious and efficient manner, aviation motor fuel constituents of the highest anti-knock value. Other objects include the provision of improved methods for the isomerization of poly-alkylated cyclic hydrocarbons in general for any purpose.

Aromatic hydrocarbons boiling below approximately 400° F. are in general valuable ingredients of motor fuel. However, there is considerable variation in the anti-knock value of these compounds, within a relatively high range, particularly among the members of each group of isomers. In the preparation of aromatic motor fuel constituents for use in aviation gasoline these variations in anti-knock value, particularly in the poly-alkylated aromatic hydrocarbons boil-

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ing within the range of 250° F. to 350° F., are highly important considerations.

The invention will be described with particular application to the treatment of poly-alkylated aromatic hydrocarbons containing 8 to 10 carbon atoms per molecule since these include the poly-alkylated aromatic hydrocarbons boiling within the aviation motor fuel boiling range. It is to be understood, however, that the invention is applicable to the treatment of any mixture of poly-alkylated aromatic hydrocarbons or any individual poly-alkylated aromatic hydrocarbon. Furthermore the invention is applicable to the treatment of any poly-alkylated cyclic hydrocarbon for the production of motor fuel or for other purposes. For example poly-alkylated naphthenes may be isomerized.

The invention will be described also with reference to the accompanying drawing which represents diagrammatically apparatus suitable for carrying out a specific embodiment of the invention which involves the treatment of xylenes. It is to be understood, however, that the process of the invention which is thus illustrated is applicable in the treatment of other poly-alkylated cyclic hydrocarbons which may require somewhat different arrangements of apparatus than are thus provided for the treatment of the xylenes.

Aside from the relatively small amounts of aromatic hydrocarbons which are obtainable in coal tar and certain aromatic petroleum oils, the principal sources of such hydrocarbons are the conversion of cyclic non-aromatic hydrocarbons, such as cyclo-paraffins and cyclo-olefins, to the corresponding aromatic hydrocarbons by dehydrogenation and the conversion of aliphatic hydrocarbons to aromatic hydrocarbons by catalytic cyclization and dehydrogenation reactions, and the thermal and catalytic cracking of higher boiling oils, such as gas oil and reduced crude.

While the invention, in certain aspects, is applicable to the treatment of poly-alkylated hydrocarbons from any source an important modification of the invention involves its use in combination with methods for the conversion of aliphatic and cyclic hydrocarbons to aromatic hydrocarbons by dehydrogenation. Consequently the following description of the invention includes the application of the invention to the treatment of poly-alkylated aromatic hydrocarbons produced by dehydrogenation and cyclization of charging stocks which are carefully selected with reference to boiling characteristics.

Referring to the drawing a non-aromatic charging stock is introduced into the system

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through line 1. While this material is referred to as "non-aromatic," in a relative sense, it may contain a substantial proportion of aromatic hydrocarbons since these are not detrimental to the cyclization process. The non-aromatic hydrocarbons to be cyclized may be cyclic or aliphatic, unsaturated or saturated. Ordinarily the charging stocks available will contain all these materials, differing only in the relative proportions. For the production of poly-alkylated aromatic hydrocarbons it is necessary that the charging stock comprise aliphatic hydrocarbons containing at least eight carbon atoms per molecule and which are convertible to aromatic hydrocarbons, or poly-alkylated hexacarbo-cyclic hydrocarbons, such as dimethyl cyclohexane.

The non-aromatic feed is transferred through line 1 by pump 2 to the entrance of a heating coil 3 suitably located in heater 4. In heating coil 3 the hydrocarbon feed is heated to an outlet temperature, generally within the range of 850 to 1050° F., which is selected with reference to the character of the feed and the degree of conversion desired. The outlet of heating coil 3 connects by line 5 with reactor 6 whereby the heated hydrocarbon feed is introduced into the reactor at the desired temperature.

Reactor 6 is provided with suitable dehydrogenating catalytic material for effecting the desired aromatization reactions which may involve dehydrogenation of cyclic hydrocarbons or cyclization and dehydrogenation of aliphatic hydrocarbons, or both. A representative catalyst for such reactions is one comprising principally the "activated alumina" of commerce and containing, as an activating ingredient, 6 to 12 weight per cent of molybdenum oxide. Other dehydrogenating catalysts, such as chromium oxide, alone, or mounted on a suitable support such as alumina, also may be used.

The modification of the invention illustrated by the drawing includes the use of the catalyst as a stationary consolidated granular mass through which the hydrocarbon reactants are passed at the reaction temperature. In this method of operation the passage of the heated hydrocarbons through the reactor is continued until the catalyst is deactivated for further effective use, after which the hydrocarbon stream is diverted to another reactor while the catalyst in the first reactor is regenerated or replaced. This method of operation is continuous with respect to the hydrocarbons but is discontinuous or intermittent with respect to the catalyst. The invention includes, however, the use of dehydrogenation processes in which the catalyst is moved continuously through the reaction zone. In such methods of operation the catalyst is dropped by gravity through the reaction zone in contact with the vaporized hydrocarbon reactants or is suspended as a finely divided powder in the hydrocarbon stream passing through the reaction zone. By another method of operation the catalyst may be maintained in the reactor as a fluidized mass with continuous withdrawal and replacement of a portion of the mass to maintain the activity of the whole mass at a uniform level.

During the passage of the hydrocarbons through reactor 6 aliphatic hydrocarbons having six or more carbon atoms per molecule are converted to aromatic hydrocarbons having corresponding numbers of carbon atoms per molecule, such as benzene, toluene, xylenes, ethyl benzene, propyl benzenes, methyl ethyl benzenes, trimethyl benzenes, methyl propyl benzenes, di-

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methyl ethyl benzenes, and butyl benzenes. In addition cyclic non-aromatic hydrocarbons, such as cyclohexane, methyl cyclohexane, ethyl cyclohexane, dimethyl cyclohexanes, propyl cyclohexanes, trimethyl cyclohexanes, methyl ethyl cyclohexanes, butyl cyclohexanes, methyl propyl cyclohexanes, dimethyl ethyl cyclohexanes, diethyl cyclohexanes, and the corresponding cyclo-olefins and cyclo di-olefins, are converted to corresponding aromatic hydrocarbons by dehydrogenation. Aromatic hydrocarbons which may be present in the mixture apparently do not react undesirably to an appreciable extent in reactor 6 and these may be present in substantial proportions.

The degree of conversion of the non-aromatic hydrocarbons to aromatic hydrocarbons in reactor 6 is controlled by suitable regulation of temperature and space velocity. Substantial conversion of non-aromatic hydrocarbons to aromatic hydrocarbons, particularly the conversion of aliphatic to aromatic hydrocarbons, is associated with high temperatures and relatively low space velocities. Within the temperature range of 850 to 1050° F. space velocities of 0.1 to 3.0 volumes of liquid per volume of catalyst space per hour are employed advantageously. For example, at an operating temperature of 950° F. a space velocity of 0.5 volume of liquid per volume of catalyst space may be employed.

The reactants are withdrawn from reactor 6 through line 7 which passes through cooling means 8 and connects with a separator 9. Cooling at 8 is sufficient to condense the normally liquid constituents of the reaction mixture. In separator 9 the uncondensed gases, which consist principally of hydrogen, are disengaged from the liquid condensate and are withdrawn through line 10. It is desired ordinarily to recycle hydrogen to the reaction zone in the amount of 0.5 to 9, preferably 3.0, mols of hydrogen per mol of hydrocarbon reactants. The recycling of hydrogen in this manner is advantageous, particularly when reactor 6 is maintained under a hydrogen pressure of 30 to 450 pounds per square inch, in maintaining the activity of the catalyst in reactor 6.

The gas passing through line 10 contains a small proportion of low boiling hydrocarbon gases, such as methane and ethane, which are substantially inert in the process. To avoid the accumulation of such materials in the gas product it is desirable to remove at least a portion of such gases from the hydrogen stream prior to recycling it to the reaction zone. Consequently line 10 is connected to the lower portion of an absorber 11. Since it is desirable to maintain absorber 11 at relatively high pressure a compressor 12 is provided in line 10.

In absorber 11 the gases pass upwardly through and around gas and liquid contact elements and are contacted with a hydrocarbon absorber oil, such as naphtha or gas oil, which flows downwardly through absorber 11. Such gas oil or naphtha selectively absorbs a sufficient proportion of the light hydrocarbon gases from the gases passing upwardly through absorber 11. Preferably absorption is sufficiently complete to include in the absorber oil substantially all the hydrocarbon gas and hydrogen gas in an amount equal to the excess which is not used for recycling.

The hydrogen gas is withdrawn overhead from absorber 11 through line 13 which connects

either with line 5, as shown, or with line 1 to permit passage of the hydrogen to reactor 6.

The mixture of absorbent and absorbed gases is withdrawn from the bottom of absorber 11 through line 14 which connects with separator 15. In separator 15 the absorbed hydrocarbons are flashed from the absorbent which is passed through line 16, provided with pump 17, to the upper portion of absorber 11, for re-use.

The gases separated at 15 are withdrawn therefrom through line 18 which connects with stabilizer 19. Since stabilizer 19 is maintained ordinarily at a higher pressure than separator 15 a compressor 20 is provided in line 18 to bring the gases to the desired stabilizer pressure.

The liquefied product separated in gas separator 9 is withdrawn therefrom through line 21, which is provided with a pump 22, and connects with stabilizer 19.

In stabilizer 19 the liquid introduced through line 21 and the compressed gases introduced through line 18 are subjected to fractionating conditions of temperature and pressure to separate overhead substantially all normally gaseous constituents of the mixture. The gases pass overhead through line 23, are cooled at 24 to condense a portion thereof sufficient for refluxing stabilizer 19 and the resulting mixture is delivered to separator 25. Reflux liquids are returned from separator 25 to stabilizer 19 through line 26 and pump 27. Uncondensed gases are withdrawn from separator 25 and from the system through line 28.

The liquid product separated as a condensate in the bottom of stabilizer 19 is transferred to rerun tower 29 by means of line 30. In rerun tower 29 the liquids are fractionated to separate high boiling condensation products.

The hydrocarbons vaporized in tower 29 pass overhead through line 32 which is provided with cooling means 33 and connects with reflux drum 34. At 33 the vapors are cooled to effect condensation thereof and the condensate thus obtained is withdrawn from drum 34 through line 35 by means of pump 36 for transfer to subsequent fractionating means for the separation of a narrow boiling cut suitable for further treatment. A portion of the condensate flowing through line 35 is diverted through line 37 and returned to the upper portion of tower 29 as reflux.

Since the modification here illustrated relates specifically to the treatment of xylenes the subsequent fractionation of the liquids flowing through line 35 is conducted in a manner effective to separate a narrow boiling fraction including xylenes and to separate the remainder of the liquids in a manner which may be desired for the further handling of such material. In the specific modification illustrated in the drawing these liquids are fractionated, in two separate fractionators, to separate a xylene cut, a pre-xylene cut containing the lower boiling hydrocarbons and a post-xylene cut containing the higher boiling hydrocarbons.

In carrying out this separation line 35 is connected to a fractionator 38 which is maintained under fractionating conditions of temperature and pressure effective to separate overhead, as vapors, the hydrocarbons lower boiling than xylene. The overhead vapors are withdrawn from fractionator 38 through line 39 which connects with reflux drum 40 and is provided with cooling means 41. At 41 the vapors are cooled sufficiently to effect condensation thereof. The condensate which accumulates at 40 is withdrawn

therefrom through line 42, provided with pump 43, as the pre-xylene cut. A part of this cut is returned to the upper portion of fractionator 38 as reflux through line 44 which connects line 42 with fractionator 38. The pre-xylene cut flowing through line 42 may be withdrawn thereby from the system or all or a portion of this material may be recycled to the aromatization treatment for further conversion thereof. Such recycling may be effected conveniently by line 45 which connects line 42 with line 1.

The bottoms in fractionator 38, which include the xylenes, are transferred from fractionator 38 to fractionator 46 by means of line 47. In fractionator 46 fractionating conditions of temperature and pressure are maintained effective to separate overhead vapors containing the xylenes and substantially free from higher boiling aromatic hydrocarbons. These vapors, which constitute the xylene cut, are withdrawn through line 48 which is provided with cooling means 49 and connects with reflux drum 50. The vapors are cooled at 49 to effect condensation thereof and the condensate is withdrawn from drum 50 through line 51 which is provided with pump 52. A portion of the condensate is returned to fractionator 46 as reflux by passage through line 53 which connects line 51 with the upper portion of fractionator 46. The bottoms separated in fractionator 46, which constitute the post-xylene cut, are withdrawn from fractionator 46, and from the system, through line 54.

The further treatment of the xylene cut flowing through line 51 in accordance with this invention depends upon the proportion of non-aromatic hydrocarbons contained therein and upon the character of the isomerizing treatment to be employed. Since certain isomerizing catalysts react with paraffinic and naphthenic hydrocarbons it is desirable, when employing such catalysts to isomerize the poly-alkylated aromatic hydrocarbons, to restrict the proportion of such paraffinic and naphthenic hydrocarbons in the aromatic fraction as much as possible. Other isomerizing catalysts are not subject to this disability so that a larger proportion of nonaromatic hydrocarbons can be tolerated.

In operations which require an aromatic cut which is free, or substantially free, from non-aromatic hydrocarbons the isomerization feed may be prepared by suitable regulation of the charging stock to the aromatization process, by solvent extraction of non-aromatic hydrocarbons from the aromatized product or other mixture of aromatic and non-aromatic hydrocarbons by a combination of these two methods, or by any other suitable means. For example in the preparation of a xylene cut which is to be substantially free from non-aromatic hydrocarbons it is advantageous to fractionate the non-aromatic feed introduced through line 1 to eliminate substantially constituents higher boiling than approximately 260° F. As a result of such preliminary fractionation the constituents of the aromatized product boiling above 260° F. will consist substantially entirely of aromatic hydrocarbons from which a xylene fraction can be fractionally separated.

Since it is an object of this invention to produce hydrocarbon fractions of the highest octane value the elimination of non-aromatic hydrocarbons from the product by such control of the feed to the aromatization operation is desirable as a relatively simple method of excluding such hydrocarbons from the product. Consequently

it is a preferred modification of this invention to regulate the end boiling point of the non-aromatic feed passing through line 1 at about 260° F., when the production of xylenes of the highest anti-knock value is an object of the process. This method of operation may be employed advantageously in connection with the production of toluene by aromatization operations, in which case the toluene product is included in the pre-xylene cut passing through line 42. In such a method of operation the post-xylene cut withdrawn at line 54 is relatively small in quantity and comprises principally high boiling alkylated aromatic hydrocarbons resulting from alkylation reactions occurring during the aromatization treatment.

The further handling of a xylene cut produced by the above described preferred modification depends upon the relative proportions of the various xylenes therein and the proportion of ortho-xylene which is tolerable in the product of the process. If the xylene cut flowing through line 51 predominates in meta-xylene and para-xylene preliminary fractionation to separate a cut predominating in ortho-xylene is desirable, if only for the purpose of reducing the load on the isomerization operation. However, if the xylene cut flowing through line 51 predominates in ortho-xylene, or if the amount of ortho-xylene which is tolerable in the product of the process is greater than the equilibrium amount of this constituent, it may be desirable to pass the xylene cut flowing through line 51 directly to the isomerization treatment. The relative proportions of the xylene isomers in the aromatization product depend primarily on the composition of the feed stock. For example, if the xylenes are formed by dehydrogenation of dimethylated cyclic hydrocarbons, their structures apparently govern those of the xylenes formed therefrom. Similarly the location of methyl groups on aliphatic starting compounds appears to affect the structure of the poly-alkylated aromatic hydrocarbon formed therefrom.

As it is a preferred modification of the invention to produce a product containing less than the equilibrium proportion of ortho-xylene, which is about 10% at room temperature, it is preferable to subject the xylene cut to a preliminary fractionation to recover meta- and para-xylenes therefrom without further treatment, since this can be effected in the same fractionation equipment which is required to separate excess ortho-xylene from the isomerized product. In accordance with this preferred modification line 51 is connected with a xylene fractionator 55.

It is the function of fractionator 55 to provide a product which is free, or substantially free, from ortho-xylene and at the same time prepare a feed for the isomerization treatment which predominates in ortho-xylene. The feed to fractionator 55 may be supplied entirely from the source to which it is connected by line 51 or it may be supplied, from any suitable source of xylenes, with a similar relatively narrow boiling range xylene cut through line 56, or xylenes may be introduced into fractionator 55 from both of lines 51 and 56.

In xylene fractionator 55 fractionating conditions of temperature and pressure are maintained which are effective to separate overhead a vapor mixture comprising meta-xylene and para-xylene and substantially free from ortho-xylene. The degree of fractionation necessary in fractionator 55 depends somewhat upon the amount of ortho-

xylene which may be tolerated in the xylene product of the process. Somewhat greater latitude is permissible in the constitution of the bottoms separated in fractionator 55 since any mixture of the xylenes containing more than the equilibrium proportion of the ortho-xylene may be employed as feed to the isomerization treatment. However, efficient use of the isomerization apparatus indicates the desirability of an isomerization feed predominating in ortho-xylene. It is desired ordinarily to take overhead a xylene product substantially free from ortho-xylene while withdrawing a bottoms which contains an appreciable, if minor, amount of meta- and para-xylenes. The reduction in cost of the fractionation operation which results from permitting inclusion of meta- and para-xylenes in the bottoms may justify the increased size of the isomerization apparatus made necessary by the inclusion of these relatively inert materials in the feed thereto.

The xylene vapors passing overhead in fractionator 55 are withdrawn therefrom through line 57 which is provided with cooling means 58 and connects with reflux drum 59. The vapors are condensed at 58 and the condensate accumulates in drum 59 from which it is withdrawn through line 60 provided with pump 61. The poly-alkylated hydrocarbons flowing through the 60 consists essentially of meta-xylene and para-xylene and represent motor fuel constituents of the highest anti-knock value, particularly for use in military aviation. A portion of the material flowing through line 60 may be returned to the upper portion of fractionator 55 as reflux by line 62 which connects line 60 with fractionator 55.

The bottoms separated in fractionator 55 predominate in ortho-xylene but may include appreciable amounts of meta-xylene and para-xylene and are withdrawn through line 63 provided with pump 64. Line 63 connects with isomerization reactor 65 and is provided, if necessary, with heating or cooling means 66 to bring the isomerization charge to the desired reaction temperature. If the isomerization charge flowing through line 63 contains an amount of water which is detrimental in the isomerization reaction zone or other subsequent parts of the apparatus it may be diverted from line 63 through line 67 which connects with drier 68. Drier 68 suitably is filled with granular drying medium, such as alumina, for absorbing the water contained in the hydrocarbon mixture passing therethrough. The dried mixture is withdrawn from drier 68 by line 69 which connects with line 63. To prevent injury to the drying medium and to assist that operation it may be necessary of desirable to provide cooling means 70 in line 67.

In accordance with a preferred modification of the invention the ortho-xylene is isomerized by contact thereof with a catalyst comprising hydrogen fluoride as the essential ingredient. Preferably the isomerization treatment is effected by a liquid phase contact of the hydrocarbons and liquefied hydrogen fluoride at the desired isomerization reaction temperature. The xylene fraction passing through line 63 is intimately mixed with liquefied hydrogen fluoride which may be introduced into line 63 by means of line 71, by which it is recycled from a subsequent point in the process. The resulting mixture passes through reactor 65 in contact with suitable mixing means (not shown) and is maintained therein for the desired length of time.

In reactor 65 the mixture of hydrocarbons and hydrogen fluoride is maintained for a length of

time which depends upon the degree of conversion desired and the operating temperature. At relatively low temperatures, such as room temperature or lower, relatively long contact times of an hour or more are necessary to achieve substantial conversion of the ortho-xylene to its isomers. At higher temperatures, for example within the range of 100 to 250° F. which are preferred in the present invention shorter reaction times may be employed. While substantially equilibrium proportions of the xylenes can be achieved in relatively short reaction times at relatively high temperatures and under pressures sufficient only to maintain the liquid phase conditions it may be desirable to limit the reaction time to produce a xylene product containing more than the equilibrium proportion of the ortho-xylene especially if the isomerized product is to be fractionated for the separation of ortho-xylene from its isomers.

The isomerized product is withdrawn from reactor 65 through line 72 which is provided with cooling means 73 and which connects with separator 74. In separator 74 the mixture of hydrogen fluoride and hydrocarbons is permitted to separate into an upper, or hydrocarbon, layer and a lower, or hydrogen fluoride, layer. The hydrogen fluoride is withdrawn through line 71 which, as mentioned above, connect with line 63 for recycling the hydrogen fluoride for further use. Line 71 is provided with a pump 75 to facilitate recycling the hydrogen fluoride and withdrawing a portion thereof through line 76 which connects with line 71. A portion of the hydrogen fluoride may be withdrawn intermittently or continuously through line 76, and replaced by fresh or regenerated hydrogen fluoride which is introduced through line 77 provided with pump 78. The hydrogen fluoride may react with certain portions of the hydrocarbon reactants with the formation of complexes which are absorbed in the hydrogen fluoride and tend to lower its activity. The effect of the formation of such complexes is compensated for by withdrawing a portion of the recycled hydrogen fluoride at 76 and replacing it at 77. The complex withdrawn at 76 may be treated to regenerate the hydrogen fluoride.

The hydrocarbons separated as the upper layer in separator 74 are withdrawn therefrom through line 79 which connects with a hydrogen fluoride stripper 80. In stripper 80 the hydrocarbon mixture is subjected to fractionating conditions of temperature and pressure effective to separate overhead hydrogen fluoride vapors. The hydrogen fluoride vapors are withdrawn overhead through line 81 which is provided with cooling means 82 and connects with accumulator 83. The hydrogen fluoride is condensed at 82 and the liquefied material thus obtained is returned for re-use through line 84, provided with pump 85, which connects accumulator 83 with line 71. A portion of the liquefied hydrogen fluoride may be returned to the upper portion of stripper 80 as reflux by means of line 86.

The isomerized product, or isomate, which collects in the bottom of stripper 80 is withdrawn therefrom through line 87 which connects with treater 88. Treater 88 is a suitable receptacle containing granular treating material such as bauxite for absorbing residual quantities of hydrogen fluoride from the isomate. The treated isomate is then withdrawn from treater 88 through line 89 which connects with rerun tower 90.

In tower 90 the isomate is subjected to fractionating conditions of temperature and pressure effective to pass overhead the xylene product as a vapor while retaining as a bottoms any heavy constituents which may be formed in reactor 65 by alkylation reactions. These bottoms are withdrawn from tower 90, and from the system, through line 91.

The vapors passing overhead in tower 90, which comprise the isomate, are withdrawn through line 92 which is provided with cooling means 93 and connects with accumulator drum 94. The vapor is cooled at 93 to effect complete condensation and the condensate thus obtained collects in drum 94. The isomate is withdrawn from drum 94 through line 95 provided with pump 96. Preferably line 95 is connected to xylene fractionator 55 in order to include the para-xylene and meta-xylene formed in the isomerization treatment in the overhead product of fractionator 55, as described, and to permit recycling the unconverted ortho-xylene to the isomerization treatment. However, if the proportion of ortho-xylene left in the isomate is not greater than the amount which is tolerable in the desired product the isomate flowing through line 95 may be withdrawn from the process, as a product thereof, through line 97. A portion of the liquid flowing through line 95 may be returned to tower 90 as reflux through line 98.

In connection with the operation of xylene fractionator 55 on a feed from a source indicated by line 51 it may be desirable to divert a portion of the bottoms in line 63 to prevent the accumulation in the isomerization system of paraffinic and naphthenic hydrocarbons boiling approximately in the boiling range of ortho-xylene. Hydrocarbons of this character which may be included in the aromatization products supplied through line 51 or which may be included in the xylene stream supplied through line 56 are largely unaffected by the isomerization treatment. Consequently these materials may tend to accumulate in the system when all, or substantially all, of the isomate in line 95 is recycled to fractionator 55. Since some of these paraffinic and naphthenic hydrocarbons may be convertible to aromatic hydrocarbons the hydrocarbons to be diverted from line 63 conveniently may be recycled to the aromatization process for further treatment therein. Line 100, which connects line 63 with line 1 is provided for this purpose.

In the foregoing description of the isomerization treatment the feed to the isomerization treatment is prepared in fractionator 55, as bottoms. However, it may be desirable to pass the feed to the isomerization reaction without preliminary fractionation particularly if it contains a predominating amount of ortho-xylene. Indeed it may be desirable to eliminate the use of xylene fractionator 55 altogether if the feed predominates in ortho-xylene and if the proportion of ortho-xylene left in the isomate is no more than the maximum amount thereof which is tolerable in the product. In accordance with this modification the xylenes passing through line 51 may be diverted wholly or partly through line 99 which connects line 51 with line 63. Likewise mixtures of aromatic hydrocarbons which are susceptible to the isomerization treatment may be introduced from an external source through line 100 which connects with line 63 near the entrance of heater or cooler 66. In this method of operation the isomate may be further fractionated at 55 to separate a highly purified prod-

uct and an ortho-xylene fraction for recycling or the isomate may be employed as such without further fractionation.

It may be desirable, or necessary, to subject the hydrocarbon mixture containing the poly-alkylated hydrocarbons to an extraction treatment designed to remove therefrom aliphatic and naphthenic hydrocarbons. This preliminary treatment of the feed to the isomerization process may be necessary when employing a catalyst which is highly susceptible to the deactivating effect of such aliphatic and naphthenic hydrocarbons. Ordinarily the preliminary separation of non-aromatic hydrocarbons is necessary in the treatment of the product of the aromatization of a feed stock having an end boiling point within the boiling range of the desired aromatic hydrocarbons. For example, the charge to the aromatization treatment may be fractionated to an end boiling point of approximately 300° F. to produce a mixture containing poly-alkylated hydrocarbons having 8 and 9 or more carbon atoms per molecule. Under these circumstances it is necessary ordinarily to remove accompanying aliphatic and naphthenic hydrocarbons and other non-aromatic hydrocarbons from the mixture containing the poly-alkylated aromatic hydrocarbons prior to isomerization treatment thereof.

When employing the preliminary extraction treatment of the feed to the isomerization process the xylene cut flowing through line 51 is diverted therefrom through line 101 which connects with a suitable extraction apparatus such as phenol extractor 102. Likewise mixtures containing poly-alkylated hydrocarbons from an external source may be introduced into phenol extractor 102 by means of line 103.

The hydrocarbon mixtures from lines 101 or 103 are introduced into extractor 102 at a point approximately one-third the length of the extractor 102 from the bottom thereof. In extractor 102 the hydrocarbon mixtures are mixed with downwardly flowing liquid phenol and the aromatic hydrocarbons are absorbed thereby. In addition a portion of the non-aromatic hydrocarbons are also absorbed by the phenol. The mixture flows downwardly in extractor 102 and is heated by contact with hot vapors and by suitable re-boiling means in the bottom of extractor 102 to vaporize unabsorbed non-aromatic hydrocarbons and to strip from the extract non-aromatic hydrocarbons previously absorbed. Such heat treatment ordinarily strips the extract of a portion of the absorbed aromatic hydrocarbons also and these are continuously contacted with the downwardly flowing phenol solvent as the vapors flow upwardly from the bottom of tower 102, or from points adjacent the bottom thereof, to the point, approximately two-thirds the distance up tower 102, at which the phenol solvent is introduced. In this manner aromatic hydrocarbons which are stripped from the bottoms are reabsorbed. The unabsorbed vapors rise above the point of introduction of the phenol in the approximately upper one-third of tower 102 in which they are refluxed under suitable conditions to effect condensation of phenol and absorbed hydrocarbons.

The non-aromatic hydrocarbons which pass overhead in extractor 102 as vapors are withdrawn therefrom through line 104 which is provided with cooling means 105 and connects with accumulator drum 106. The vapors are cooled at 105 to effect condensation thereof and the condensate is collected in drum 106. Condensate is withdrawn from line 106 through line 107 pro-

vided with pump 108. Hydrocarbons thus obtained may be withdrawn through line 107 from the process and may be wholly or partly recycled, by means not shown, from line 107 to the entrance of the aromatization process. A portion of this condensate also is returned to the upper portion of extractor 102 as reflux through line 109 which connects line 107 with extractor 102.

The extract collected in the bottom of extractor 102 is withdrawn therefrom through line 110, provided with pump 111 and transferred to phenol stripper 112. In stripper 112 the extract is heated to a temperature sufficiently high to strip absorbed hydrocarbons from the phenol solvent. The latter is withdrawn from the bottom of stripper 112 through line 113 provided with pump 114, which connects with extractor 102, at a point approximately two-thirds the way up, as described above. A portion of the phenol solvent which circulates through line 113 may be withdrawn intermittently or continuously, through line 115, and replaced with fresh phenol, through line 116, to maintain the quality of the solvent at the desired level.

The hydrocarbon vapors which are substantially entirely aromatic in character are withdrawn overhead from stripper 112 through line 117 which is provided with cooling means 118 and connects with accumulator drum 119. At 118 the vapors are cooled to effect condensation thereof and condensate thus obtained is collected in accumulator 119. This condensate is withdrawn from accumulator 119 through line 120 provided with pump 121. A portion of the liquids flowing through line 120 may be returned to the phenol stripper 112 as reflux by means of line 122 which connects line 120 with the upper portion of stripper 112.

To remove residual quantities of phenol which may be entrained in the aromatic liquids flowing through line 120 the liquids may be treated with an acid to absorb such phenol. For example a suitable acid may be introduced into the system through line 123 which connects with line 120. The resulting mixture is further mixed by passage through mixer 124 which is interposed in line 120 and the mixture is then permitted to settle in a suitable drum 125, to which line 120 is connected.

In drum 125 the acid containing absorbed phenol settles out as a lower phase and is withdrawn through line 126. The acid treated hydrocarbons pass overhead from drum 125 through line 127. To remove acid entrained in such liquids caustic may be introduced into line 127 through line 128. The resulting mixture may be mixed further by passage through mixer 129 and then permitted to separate in settler 130, to which line 127 connects. In settler 130 the caustic containing absorbed acid separates as a lower phase and is withdrawn through line 131. The treated hydrocarbons pass overhead from settler 130 through line 132 which connects with rerun tower 133.

In rerun tower 133 the treated aromatic hydrocarbons are fractionated to separate as bottoms high boiling hydrocarbons resulting from polymerization of unsaturates by means of the acid treating agent. Such bottoms are withdrawn from tower 133 and from the system through line 134. The rerun tower 133 is operated under fractionating conditions of temperature and pressure to separate overhead a vapor mixture containing the aromatic hydrocarbons to be isomerized. Such vapors are withdrawn through line 135

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which is provided with cooling means 136 and connects with reflux drum 137. The vapors are cooled at 136 to effect condensation thereof and the condensate collects in drum 137. The condensate is withdrawn from drum 137 through line 138 which is provided with pump 139. A portion of this condensate may be returned through line 140, to the upper portion of tower 133 as reflux.

If it is desired to subject the aromatic hydrocarbons flowing through line 138 to preliminary fractionation prior to isomerization, line 138 is connected to fractionator 55 in the manner shown. However, for certain reasons which have been discussed above it may be desired to subject the whole mixture of aromatic hydrocarbons directly to isomerization prior to any fractionation thereof. For example, a portion of the hydrocarbons flowing through line 138 may be diverted through line 141. Since the hydrocarbon mixture flowing through line 141 may contain water as a result of the treatments at 125 and 130 it is preferred ordinarily to connect line 141 with line 67 as shown in order to pass the hydrocarbons through drier 68. However, if such drying is not necessary the hydrocarbons may be introduced from line 141 directly into line 63 by means of line 142.

In the above description of the invention there are numerous references for illustration to the treatment of the polyalkylated aromatic hydrocarbons having 8 carbon atoms per molecule, that is, the xylenes. The invention is applicable, however, to the production of gasoline constituents of high anti-knock value having 9, 10 and 11 carbon atoms per molecule.

The aromatization treatment of a feed stock fractionated to an end boiling point of approximately 300° F. permits the recovery by fractionation, of an aromatized product, of a substantially pure aromatic fraction boiling above 300° F., and consisting essentially of aromatic hydrocarbons having 9 carbon atoms per molecule. These apparently consist principally of the trimethyl benzenes. Furthermore that portion of the aromatized product boiling between 260 and 300° F. is highly aromatic in character and contains the xylenes. This fraction is treated in accordance with the method outlined above, preferably after an extraction treatment to remove non-aromatic hydrocarbons.

The 300-350° F. fraction of the aromatized product of a feed having an end point of 300° F., or a similar mixture from any source, may be treated to produce fractions of improved anti-knock value. This fraction is substantially entirely aromatic and contains poly-alkylated aromatic hydrocarbons which are principally trimethyl benzenes. If this fraction predominates in the 1,2,3 and 1,2,4 trimethyl benzenes it may be subjected to isomerization treatment to improve its anti-knock value by converting these compounds to 1,3,5 trimethyl benzene which is of superior anti-knock value. If the fraction already contains an appreciable amount of 1,3,5 trimethyl benzene it is further sub-divided into a fraction boiling between 300 and 333° F., and a fraction boiling above 333° F. The higher boiling fraction is then subjected to isomerization treatment in the manner described above after which it may be combined with the low boiling fraction or may be subjected to further fractionation to separate the lower boiling 1,3,5 trimethyl benzene as a product. For example, in the apparatus illustrated in the drawing a frac-

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tion boiling between 300 and 350° F. may be obtained in the fractionation of the aromatized product and passed through line 51, instead of the xylenes. In fractionator 55 the C₈ aromatic hydrocarbons are fractionated to separate an overhead product boiling between 300 and 333° F. as described above. The bottoms thus obtained are subjected to isomerization, in the manner described for ortho-xylene, and the isomerized product is refractionated in fractionator 55 to separate the low boiling isomer, 1,3,5 trimethyl benzene. In this manner an aviation motor fuel fraction of high anti-knock value is obtained as the overhead product of fractionator 55.

By fractionating the feed to the aromatization process to an end point between 300 and 350° F. more or less aromatic hydrocarbons having 10 or more carbon atoms per molecule are obtained in the aromatized product. By fractionating the aromatized product to separate hydrocarbons boiling above the point of the feed an aromatic fraction free, or substantially free, of non-aromatic hydrocarbons is obtained. That portion of this product boiling between 333° F. and 350° F. may be subjected to isomerization in the manner described above to produce a product of improved anti-knock value. This fraction contains 1,2,4 trimethyl benzene and 1,2,3 trimethyl benzene as described above and may include also the methyl isopropyl benzenes, as well as 1,2 diethyl benzene, isobutyl benzene and secondary butyl benzene. Isomerization of this fraction converts trimethyl benzenes contained therein to 1,3,5 trimethyl benzene which is lower boiling and can be separated from the product by fractionation if desired. Isomerization of this fraction also converts 1,2 diethyl benzene to its isomers which are higher boiling and substantially superior in anti-knock value. While the isomers of 1,2 diethyl benzene boil above the aviation gasoline boiling range they are valuable ingredients in ordinary motor fuel and the conversion permits the removal of a constituent of relatively low anti-knock value from the fraction being isomerized. The isomerization of this fraction also establishes equilibrium proportions among the methyl isopropyl benzenes. Since the equilibrium proportion of ortho methyl isopropyl benzene is rather low, and since the anti-knock value of this compound is substantially lower than that of its isomers, any change in the proportions of the methyl isopropyl benzenes ordinarily represents a substantial improvement in the anti-knock value of the mixture.

Conveniently the isomerization of this fraction may be carried out in the presence of a substantial proportion of benzene or toluene in order to effect, simultaneously, isomerization of poly-alkylated benzenes and transfer of alkyl groups from the poly-alkylated benzenes, such as the trimethyl benzenes to the benzene or toluene molecules to produce alkylated benzenes of lower boiling point. For example, trimethyl benzenes of low anti-knock value, such as 1,2,3 trimethyl benzene may be reacted with toluene in the alkylation reaction zone to produce xylenes which may be treated, in the manner described above, in a subsequent operation, or with benzene to produce toluene and xylenes. Also benzene may be reacted with methyl isopropyl benzenes to produce toluene and isopropyl benzene, or with toluene to produce xylenes and isopropyl benzene. In carrying out such alkylation-dealkylation treatments relatively high temperatures, within the range suitable for the isomerization

reaction, are desirable. For example, temperatures in the range of 200 to 400° F. may be employed. Substantial pressure, within the range of 300 to 1000 pounds per square inch, also is a desirable operative condition.

The isomerization treatment of poly-alkylated aromatic hydrocarbons may be carried out, with or without the presence of benzene or toluene, at relatively high temperatures which effect cracking in the alkyl groups of relatively high boiling aromatic hydrocarbons particularly in alkyl groups of more than two carbon atoms. For example, in the 333-350° F. fraction mentioned above there may occur methyl isopropyl benzenes, secondary butyl benzene, isobutyl benzene and tertiary butyl benzene. These compounds may be cracked advantageously by the removal of a methyl group from a side chain to produce lower boiling hydrocarbons of high anti-knock value. This modification of the invention thus provides for simultaneous isomerization of poly-alkylated hydrocarbons to isomers of maximum anti-knock value and treatment of either poly-alkylated or mono-alkylated hydrocarbons having side chains of two or more carbon atoms to produce lower boiling products of high anti-knock value. In addition there may be effected simultaneous transfer of alkyl groups from a poly-alkylated aromatic hydrocarbon to a mono-alkylated or non-alkylated hydrocarbon with beneficial results. To effect cracking of side chains in the manner described, or the removal of side chains entirely, while isomerizing in the presence of hydrogen fluoride, temperatures of 300 to 800° F. may be employed. The foregoing specific application of the invention is directed particularly to the treatment of aromatic hydrocarbons boiling up to 350° F. since higher boiling hydrocarbons ordinarily are not included in aviation motor fuel intended for military use. However, the invention may be employed with advantage in the preparation of aromatic hydrocarbons of high anti-knock value for use in motor fuel for non-military aviation use or for non-aviation use. For example, isomerization of the ortho diethyl benzene to its isomers has been mentioned above. The meta and para forms of this compound boil above the end point of military aviation fuel but represent valuable high boiling ingredients of motor fuel for other purposes. In addition the compounds boiling within the range of 350 to 400° F. include other poly-alkylated hydrocarbons which may be isomerized to forms of maximum anti-knock value. For example, ortho methyl propyl benzene may be isomerized to the meta or para forms which are of higher value. In addition the tetra-methyl benzenes and the dimethyl ethyl benzenes also may be subjected to isomerization treatment, with suitable fractionation if desired, to obtain the isomers of highest anti-knock value. In the last-mentioned groups of isomers those which are free of ortho relationships of the side chains are of superior anti-knock value.

The 350-400° F. fraction also may be treated with advantage to obtain lower boiling aromatic hydrocarbons by the methods, described above, which include dealkylation and cracking in the alkyl groups. For example, the tetramethyl benzenes and the dimethyl ethyl benzenes may be dealkylated with advantage, preferably in the presence of benzene or toluene to obtain transfer of methyl groups to the lower boiling hydrocarbons. The methyl propyl benzenes may be treated likewise or may be subjected to cracking in the manner described to obtain lower boiling

products. Similarly diethyl benzenes may be cracked or dealkylated. Butyl benzene, boiling at 361° F., preferably is cracked in the alkyl groups. The lower boiling products obtained by these various treatments may be subjected to isomerization and fractionation in the manner described above, if necessary, to obtain products of maximum anti-knock value. The residual hydrocarbons boiling in the original boiling range may be recycled for further treatment or may be taken as a motor fuel constituent of improved anti-knock value by reason of the isomerization reactions.

In another modification a 333-400° F. aromatic fraction, which may contain 75 or more possible aromatic hydrocarbons, may be subjected to treatment at relatively high temperature in the presence of an isomerizing catalyst to effect isomerization, cracking of alkyl groups and dealkylation. Aromatic hydrocarbons having less than eight carbon atoms per molecule may be added to effect simultaneous alkylation of these hydrocarbons. The product of this treatment is fractionated to separate material boiling below 350° F. for including in aviation motor fuel or for further treatment in the manner described above. The remainder, boiling in the range of 350-400° F., may be retreated or employed as motor fuel.

In the isomerization treatments it is a general objective to convert poly-alkylated benzenes having alkyl groups attached to adjacent carbon atoms in the benzene ring, such as ortho-xylene, 1,2,3 trimethyl benzene, 1,2,4 trimethyl benzene, and ortho methyl isopropyl benzene, to isomers thereof having no alkyl groups attached to adjacent carbon atoms in the benzene ring, such as the meta and para forms of the xylenes and methyl isopropyl benzene, and mesitylene. Necessarily the extent of such conversion is limited to the equilibrium proportion. This may represent a substantial degree of conversion in the case of di-alkylated benzenes and a lesser degree of conversion in the case of benzenes having attached thereto more than two alkyl groups. The former are represented by the xylenes, which may be treated without fractionation, as described, and the latter are represented by the trimethyl benzenes which may require fractionation to obtain a product of high anti-knock value.

In treatments involving cracking and dealkylation the isomerizing effect of the catalyst may be exerted on poly-alkylated aromatic hydrocarbons in the charge stock, or on poly-alkylated products, or both. For example, 1,2,3 trimethyl benzene may be converted to lower boiling products by isomerization or by dealkylation to xylenes which are then subjected to the isomerizing effect of the catalyst. Similarly methyl isopropyl benzene may be isomerized and also reacted with toluene to produce cumene and xylenes, the latter also subject to isomerization. Also the trimethyl benzenes and methyl isopropyl benzenes may be isomerized beneficially while close-boiling compounds such as butyl benzenes are cracked or dealkylated. Similarly tetramethyl benzenes are reacted with toluene to produce xylenes which are then isomerized to form a product having the equilibrium proportion of the isomers.

In the foregoing description of the process reference is made specifically to the isomerization of poly-alkylated hydrocarbons in which the alkyl groups are located adjacent each other to produce poly-alkylated hydrocarbons on which

the alkyl groups are more widely spaced. For example, ortho-xylene is converted to its isomers and 1,2,3 and 1,2,4 trimethyl benzenes are to be converted to 1,3,5 trimethyl benzene. Such transformations are for the purpose of producing materials of improved anti-knock value. However, it may be desirable to produce poly-alkylated hydrocarbons for uses other than as motor fuel, in which case the isomerization reaction may be employed with equal advantage to produce other desired types of isomers. For example, it may be desirable to convert either meta-xylene or para-xylene, or both, to ortho-xylene. This is accomplished readily since the ortho-xylene product is separated as a bottoms, from the isomerized product, while the meta-xylene and para-xylene are recycled. On the other hand it may be desired to produce para-xylene from meta-xylene or ortho-xylene. This is accomplished by isomerization in the manner described above since the para-xylene isomer is separated from the others by freezing, in which operation the meta-xylene and ortho-xylene may be recycled. The hydrogen fluoride catalyst employed in this invention is highly active in promoting the conversion of any poly-alkylated cyclic hydrocarbons or group of isomers to the equilibrium proportions of such hydrocarbon and its isomers. For example, it may be desired to isomerize poly-alkylated naphthenes and cyclo-olefins having no alkyl groups attached to adjacent carbon atoms in the ring to those having that arrangement, since the latter are superior in anti-knock value. By suitable fractionation in a manner analogous to the method described above in connection with the treatment of xylenes hydrogen fluoride isomerizing catalyst may be employed to produce almost any poly-alkylated cyclic hydrocarbon substantially free from its isomers.

As was indicated above the isomerization of the polyalkylated hydrocarbons by means of hydrogen fluoride can be effected at temperatures ranging from 32° F. to substantially higher temperatures at which decomposition reactions occur. However, the optimum temperatures for effecting a maximum rate of conversion with minimum decomposition are in the range of 100 to 250° F. When cracking or dealkylation is desired higher temperatures may be employed.

The proportion of hydrogen fluoride in the reaction zone should be substantially high. Ordinarily a volumetric ratio of one part of liquid hydrogen fluoride to one part of liquid hydrocarbons is satisfactory. In general a range of volumetric ratios of liquefied hydrogen fluoride to hydrocarbons in the reaction zone between 1:20 and 2:1 and may be employed with advantage.

While the isomerization with hydrogen fluoride is best carried out with both catalyst and hydrocarbon reactants in the liquid phase, vapor phase or mixed phase conditions may be employed. For example both hydrocarbons and hydrogen fluoride may be in the vapor phase if the temperature required is not so high as to produce excessive decomposition. Alternatively liquid hydrocarbons may be contacted with vaporized hydrogen fluoride. However, it is preferred to maintain both hydrocarbons and hydrogen fluoride in the liquid phase since this reduces the size of the apparatus necessary.

The pressure on the isomerization reaction zone when employing hydrogen fluoride is without substantial effect except as it may be required to maintain the desired liquid phase conditions.

When dealkylating in the presence of benzene or toluene higher pressures may be desired.

The time of contact of the hydrocarbons and hydrogen fluoride in the isomerization reaction zone depends upon the temperature, the degree of conversion desired, the ratio of catalysts to hydrocarbons and the efficiency of mixing. At relatively low temperatures a rather long time of contact, i. e., of an hour or more, may be required to achieve equilibrium proportions of the poly-alkylated aromatic hydrocarbons. At higher temperatures within the preferred range and with efficient mixing of the hydrocarbons with a substantial proportion of catalyst a contact time of a few minutes is sufficient to achieve substantial isomerization.

While the preferred isomerization catalyst comprises hydrogen fluoride as the essential ingredient, and while hydrogen fluoride alone is an effective catalyst for isomerizing poly-alkylated hydrocarbons, the catalyst may be promoted by the incorporation therein of a small amount of boron trifluoride. The addition of boron trifluoride to the catalyst is advantageous since it permits the isomerization treatment of paraffin hydrocarbons at the same time that the poly-alkylated aromatic hydrocarbons are isomerized. A small proportion of boron trifluoride can be handled in the catalyst in apparatus of the type illustrated in the drawing if sufficient pressure is maintained on the isomerization system, as liquid hydrogen fluoride will dissolve a small proportion of boron trifluoride. The use of larger proportions necessitates the employment of additional apparatus for recovering and recycling the boron trifluoride in excess of the amount which remains dissolved in the hydrogen fluoride.

Other catalytic material may be employed in the process to isomerize the poly-alkylated aromatic hydrocarbons. These include activated clays, activated charcoals, dihydroxyfluoboric acid, boron fluoride and fluorosulfonic acid. In general any solid selective catalytic material which is capable of promoting cracking of hydrocarbons may be employed at non-cracking temperatures to isomerize the poly-alkylated aromatic hydrocarbons and at higher temperatures to effect both cracking and isomerization. These include siliceous materials such as activated clays, metal silicates, such as aluminum silicate, and silica-alumina catalysts, such as silica gels activated with alumina. Other suitable materials include alumina promoted with a non-metallic oxide, such as boron oxide.

The use of hydrogen fluoride, alone or in combination with a boron fluoride promoter, is, however, a preferred modification of this invention because of its superior activity, its physical properties, and the fact that it is active at relatively low temperatures. The last-mentioned fact is important in connection with conversion of ortho di-alkylated benzenes since the equilibrium proportion of the latter appears to increase with temperature.

In the foregoing description of the invention reference is made specifically to the separation of aromatic hydrocarbons from non-aromatic hydrocarbons by absorption of the latter in phenol. It is to be understood, however, that any method for obtaining such separation may be employed. For example, other solvents may be employed instead of phenol and other methods, such as azeotropic distillation, may be employed. For example, the xylene cut flowing through line 101 can be mixed with methanol or other agents capable

of forming a low boiling azeotrope with the non-aromatic constituents. The resulting mixture is then distilled in tower 102 to separate a bottoms rich in aromatics while passing overhead a mixture of low boiling azeotropes of methanol with the non-aromatic constituents of the mixture.

We claim:

1. A method for improving the motor fuel value of a mixture of poly-alkylated aromatic hydrocarbons which comprises separating a portion of said mixture in which the ratio of poly-alkylated aromatic hydrocarbons having alkyl groups attached to adjacent carbon atoms in the benzene ring to those having alkyl groups attached to non-adjacent carbon atoms is greater than in the original mixture, and subjecting said separated portion to isomerization treatment with a catalyst comprising hydrogen fluoride as the essential ingredient to convert said poly-alkylated aromatic hydrocarbons to isomers thereof having no alkyl groups attached to adjacent carbon atoms in the benzene ring.

2. A method for improving the motor fuel value of a mixture of poly-alkylated aromatic hydrocarbons which comprises separating a portion of said mixture in which the ratio of poly-alkylated aromatic hydrocarbons having alkyl groups attached to adjacent carbon atoms in the benzene ring to those having alkyl groups attached to non-adjacent carbon atoms is greater than in the original mixture, subjecting said separated portion to isomerization treatment with a catalyst comprising hydrogen fluoride as the essential ingredient to convert said poly-alkylated aromatic hydrocarbons to isomers thereof having no alkyl groups attached to adjacent carbon atoms in the benzene ring, and recombining said isomerized hydrocarbons with the remainder of said mixture.

3. A method for improving the motor fuel value of a mixture of poly-alkylated aromatic hydrocarbons which comprises separating a portion of said mixture in which the poly-alkylated aromatic hydrocarbons predominate in those having alkyl groups attached to adjacent carbon atoms in the benzene ring, and subjecting said separated portion to isomerization treatment by contact thereof with an isomerization catalyst comprising hydrogen fluoride as the essential ingredient to convert said poly-alkylated aromatic hydrocarbons to isomers thereof having no alkyl groups attached to adjacent carbon atoms in the benzene ring.

4. A method for improving the motor fuel value of a mixture of aromatic hydrocarbons which comprises separating a portion of said mixture containing poly-alkylated aromatic hydrocarbons and aromatic hydrocarbons having attached thereto alkyl groups of more than two carbon atoms, and subjecting said separated portion to simultaneous isomerization and cracking treatment in the presence of hydrogen fluoride at a temperature above 250° F. to isomerize poly-alkylated aromatic hydrocarbons and to effect cracking in said alkyl groups of more than two carbon atoms.

5. A method for improving the motor fuel value of a mixture of hydrocarbons containing poly-alkylated aromatic hydrocarbons which comprises contacting said mixture with hydrogen fluoride at a temperature of 200-400° F. in the presence of aromatic hydrocarbons having less than eight carbon atoms per molecule to convert said poly-alkylated hydrocarbons to lower boiling poly-alkylated hydrocarbons in which no

alkyl groups are attached to adjacent carbon atoms in the benzene ring, said treatment being carried out in the substantial absence of other reactive hydrocarbons and for a length of time whereby the formation of said last mentioned poly-alkylated hydrocarbons constitutes the principal reaction.

6. A method for isomerizing poly-alkylated aromatic hydrocarbons which comprises contacting said aromatic hydrocarbons with hydrogen fluoride at a temperature of 100-250° F. and in the substantial absence of other reactive hydrocarbons whereby isomerization of said poly-alkylated aromatic hydrocarbons is the principal reaction.

7. A method for isomerizing xylenes which comprises contacting said xylenes with hydrogen fluoride at a temperature of 100-250° F. and in the substantial absence of other reactive hydrocarbons whereby isomerization of xylenes is the principal reaction.

8. A method for isomerizing ortho-xylene which comprises contacting said ortho-xylene with hydrogen fluoride at a temperature of 100-250° F. and in the substantial absence of other reactive hydrocarbons whereby isomerization of ortho xylene is the principal reaction.

9. A method for improving the motor fuel value of a mixture of xylenes including ortho-xylene which comprises contacting with hydrogen fluoride a portion of said mixture containing said ortho-xylene in a proportion greater than in said mixture and greater than the proportion of ortho xylene in a mixture of the xylenes in molecular equilibrium at the temperature of contact, said treatment being carried out at a temperature of 100-250° F. and in the substantial absence of other reactive hydrocarbons whereby isomerization of xylenes constitutes the principal reaction.

10. A method for improving the motor fuel value of a mixture of xylenes including ortho-xylene which comprises separating from said mixture a portion thereof containing ortho-xylene in a proportion greater than the proportion thereof in said mixture, contacting said separated portion with hydrogen fluoride at a temperature of 100-250° F. to isomerize ortho-xylene to the isomers thereof, and recombining the isomerized xylenes with said mixture.

11. A method for producing poly-alkylated aromatic hydrocarbons of high anti-knock value which comprises preparing a feed stock containing non-aromatic hydrocarbons having eight carbon atoms per molecule and convertible to xylenes and substantially free of hydrocarbons boiling in the boiling range of the said xylenes, subjecting said feed stock to aromatizing treatment in the presence of a dehydrogenating catalyst to effect conversion thereof to xylenes, fractionating the aromatized product to separate a fraction boiling above the end point of the feed stock and including said xylenes, and subjecting xylenes thus obtained to isomerization treatment in the presence of a hydrogen fluoride catalyst to effect conversion of xylenes having alkyl groups attached to adjacent carbon atoms in the benzene ring to isomers thereof having no alkyl groups attached to adjacent carbon atoms in the benzene ring.

12. A method for producing motor fuel constituents of high anti-knock value which comprises subjecting non-aromatic hydrocarbons having at least eight carbon atoms per molecule to aromatization treatment in the presence of a dehydrogenating catalyst to effect conversion

thereof to aromatic hydrocarbons having a corresponding number of carbon atoms per molecule including poly-alkylated aromatic hydrocarbons, separating from said aromatized product a fraction including the xylene products of aromatization, further fractionating said xylene fraction to separate an overhead product comprising meta-xylene and para-xylene and substantially free from ortho-xylene and a bottoms product predominating in ortho-xylene, subjecting a portion of said bottoms product to isomerization treatment in the presence of a hydrogen fluoride catalyst to convert ortho-xylene to its isomers, combining at least a part of the isomerized product with the xylene fraction for fractionation as described, and recycling to the aromatization treatment a portion of said bottoms product.

13. A method for producing aviation motor fuel of high anti-knock value from a mixture of aromatic hydrocarbons boiling below and above 333° F. which comprises separating from said mixture a fraction comprising aromatic hydrocarbons boiling between 333° F. and approximately 400° F., subjecting said last-mentioned fraction to treatment in the presence of a hydrogen fluoride catalyst at elevated temperature to effect simultaneous isomerization of poly-alkylated benzenes and cracking of other aromatic constituents of the said fraction in the alkyl groups thereof, separating from the products of said treatment a fraction boiling below 350° F. and combining said last-mentioned fraction with constituents of said first-mentioned mixture boiling below 333° F.

14. A method for isomerizing poly-alkylated aromatic hydrocarbons which comprises contacting said aromatic hydrocarbons with hydrogen fluoride promoted with boron trifluoride at a temperature of 100-250° F. and in the substantial absence of other reactive hydrocarbons

whereby isomerization of said poly-alkylated aromatic hydrocarbons is the principal reaction.

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