May 16, 1944. E. T. LAYNG ET AL 2,349,045

DEHYDRO-AROMATIZATION

Filed Sept. 18, 1939

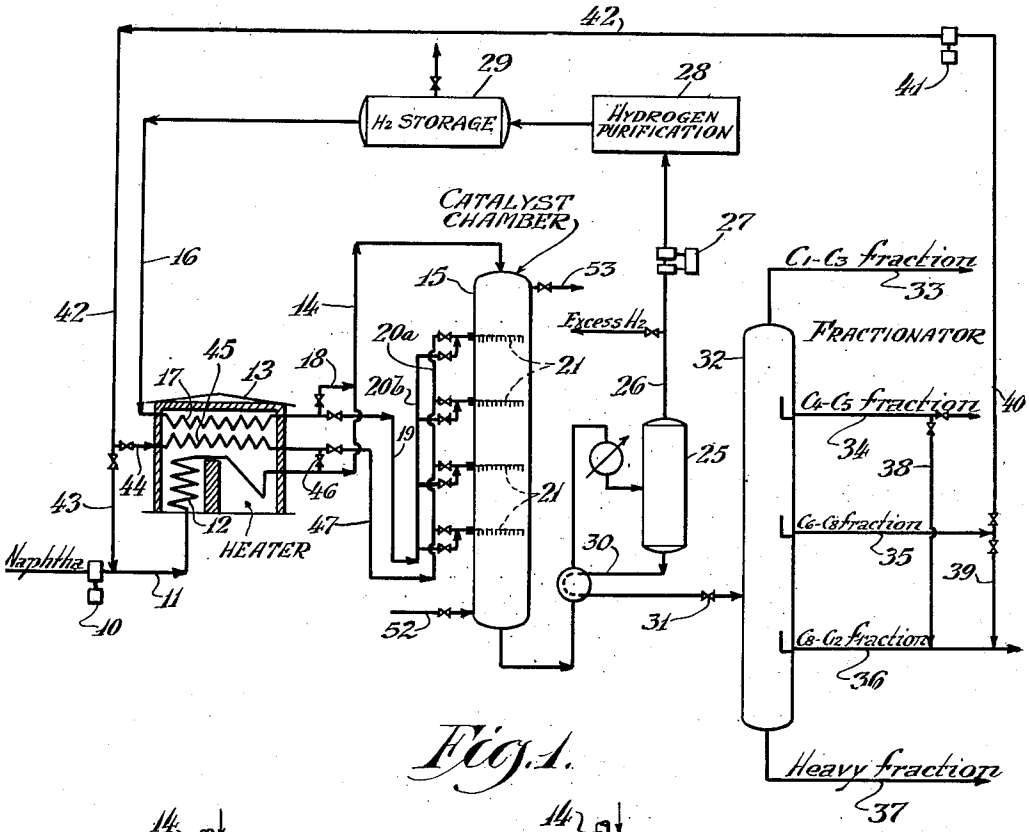

Fig. 1.

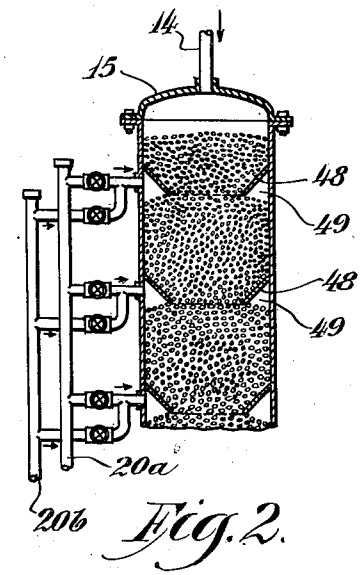

Fig. 2.

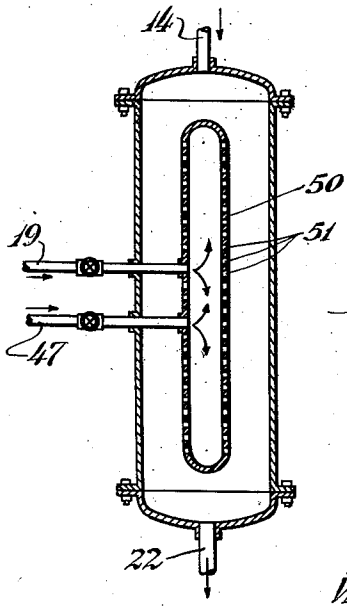

Fig. 3.

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Patented May 16, 1944

2,349,045

UNITED STATES PATENT OFFICE

2,349,045

DEHYDRO-AROMATIZATION

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Application September 18, 1939, Serial No. 295,500

14 Claims. (Cl. 260—673.5)

This invention relates to aromatization of naphtha to produce aromatics for high quality motor fuels by means of an improved catalytic dehydro-aromatization process.

An object of our invention is to produce aromatics from aliphatic hydrocarbons such as hexane, heptane, etc. and a further object is to increase the yield and quality of such aromatics and to decrease the amount of coke, gas and heavy polymers formed in catalytic aromatization. A further object is to convert low knock rating naphtha, preferably a naphtha having a knock rating of 50 or lower, to high knock rating motor fuel, preferably with an octane number of 85 to 90 or higher, by the use of catalysts such as molybdenum oxide on alumina, chromium oxide on alumina and other catalysts having dehydrogenation and ring closing properties. A further object is to increase the yields and quality of motor fuel thus produced and to obtain a motor fuel of desired volatility characteristics.

A still further object is to provide a catalytic conversion system operating in the presence of hydrogen, wherein no hydrogen is consumed but instead hydrogen is actually produced in the system. A further object is to utilize the hydrogen which is recycled in the system as a heat carrier for supplying at least a part of the endothermic heat of the aromatization reaction. A further object is to provide a new and improved method and means for introducing preheated hydrogen into a catalytic conversion system whereby the heat imparted to said system by said hydrogen prevents the temperature drop in said system which would otherwise occur.

Another object of the invention is to provide a method and means for obtaining a maximum degree of aromatization with relatively high space velocities, whereby a given unit can convert a maximum amount of naphtha into aromatic hydrocarbons. A further object is to utilize a specific fraction of the reaction products as a heat carrier to supply at least a part of the required endothermic heat. A further object is to insure maximum conversion of difficultly aromatizable C_6 and C_7 straight chain hydrocarbons into aromatics. A further object is to provide a method and means for obtaining maximum yields of specific types of aromatic compounds. Other objects will be apparent as the detailed description of the invention proceeds.

In practicing the invention we employed catalysts of the type illustrated by molybdenum oxide on alumina, chromium oxide on alumina, etc. and we contact hydrocarbon vapors with such catalyst at temperatures of about 875 to 1075° F. under pressures of about 30 to 450 pounds per square inch and in the presence of about 0.4 to 8 mols of hydrogen per mol of hydrocarbon feed stock. One of our improvements in this process is the recycling of C_6 to C_8, particularly C_6 hydrocarbons from reaction products back through the conversion system. We have found that these particular hydrocarbons are more difficult to aromatize than hydrocarbons of higher molecular weight and that if the space velocity of the naphtha charge is sufficiently low to effect complete aromatization of the C_6 hydrocarbons there will be an undue degradation of hydrocarbons of higher molecular weight. We avoid this degradation by using a space velocity which will produce minimum gas, carbon and polymer formation, and we continuously recycle the C_6 fraction of the final products in such amounts that its conversion is likewise substantially complete.

The invention is applicable to many different processes. For instance, when charging a relatively pure C_6 aliphatic hydrocarbon cut for the manufacture of benzol or when charging a substantially pure C_7 aliphatic hydrocarbon cut for the manufacture of toluol the maximum concentration of the specific fraction is maintained in the reactor at all times and there is a minimum tendency for alkylation or other side reactions because of the absence of C_2 and C_3 hydrocarbons. In such processes the recycling of the C_6 or C_7 fractions respectively not only provides a highly efficient method of introducing heat into the reactor at those points where heat is most necessary, but makes possible the use of greater linear velocities than could be employed in the absence of such recycling, and at the same time a longer catalyst life and greater catalyst activity is obtained.

The aromatization reaction is endothermic and if the superheat in the charging stock is relied on for furnishing the heat of the reaction the catalyst chamber will become cooler and cooler from the inlet toward the outlet end. An important feature of the invention is the separate heating of the recycled hydrogen or the recycled C_6 fraction or both and the introduction of these hot gases at spaced points in the conversion zone so that the conversion zone may be at a more uniform temperature throughout than would otherwise be possible. Special provision is made for the introduction of these heated gases to prevent local overheating of the catalyst at

the points of introduction. These and many other features of the invention will be more apparent as the detailed description of the invention proceeds.

In the drawing which is annexed hereto, which forms a part of this specification, and in which similar parts are designated by like reference characters in the several figures—

Figure 1 is a simplified flow diagram of our improved dehydroaromatization system;

Figure 2 is a detailed vertical section of the catalyst chamber showing one modification of our means for introducing hot gases; and

Figure 3 is a vertical section of another embodiment of means for introducing hot gases into the catalyst chamber.

The invention is not limited to any particular naphtha, nor to a naphtha of any particular boiling range. The naphtha may be either straight run or cracked or it may be produced by the hydrogenation of carbonaceous materials, by the catalytic conversion of carbon monoxide and hydrogen or by any other known method. The boiling range may be within the range of about 125 to 450° F. Closely cut fractions may be separately treated under optimum conditions. Generally speaking, the charging stocks for the process are aliphatic hydrocarbons consisting chiefly of straight chain paraffins or olefins having from 6 to 14 carbon atoms. Preferably charging stock is a straight run or cracked naphtha and most effective results are obtained by utilizing a stock which initially has an octane number lower than 50.

Various catalysts may be employed for the reforming or conversion step, preferably an oxide of a sixth group metal mounted on active alumina (a form of alumina obtained as a scale in aluminum ore purification). About 2 to 10% of molybdenum oxide on alumina or about 8 to 40% of chromium oxide on alumina have been found to give excellent results. It should be understood, however, that the present invention is not limited to any particular catalyst but is applicable to the use of any dehydro-aromatization catalyst known to the art. The minor ingredient of the catalyst is preferably an oxide or sulfide of molybdenum, chromium, tungsten or uranium or any mixture thereof mounted on bauxite, precipitated alumina, activated alumina or any other suitable catalyst support. Magnesium, aluminum or zinc chromites, molybdenites, etc. may be employed since it has been found that the sixth group metal is particularly active when it is in the anion. Vanadium and cerium oxides have been found to be effective for the conversion. Oxides of copper, nickel, manganese, etc. may be included to facilitate regeneration or for supplementing catalyst activity.

The catalysts may be made by impregnating activated alumina or other support with molybdic acid, ammonium molybdate or any other catalyst compound decomposable by heat. Also, the aluminum and molybdenum oxides may be coprecipitated as a gel or the separate oxides may be mixed together as a paste, dried, extruded under pressure or pelleted and heated to a temperature of about 1000 to 1200° F. Since the preparation of the catalyst forms no part of the present invention it will not be described in further detail.

The catalyst may be employed in fixed beds, in movable beds or as a powder suspended in a gaseous stream, the conversion in all cases being in the vapor phase. The fixed bed catalysts may be positioned in tubes mounted for instance in the convection section of a furnace or they may be positioned in a single bed or plurality of beds in vertical towers or chambers. The moving catalyst may be charged to the top of a tower or tube either continuously or intermittently, the spent catalyst being withdrawn from the base of the tube at substantially the same rate; in this case the reaction takes place continuously and under substantially constant conditions of temperature and pressure, the regeneration being effected outside of the conversion zone. The powdered catalyst may be fed into a rapidly moving stream of vaporized naphtha and hydrogen, separated therefrom after the reaction is completed and separately regenerated by oxygen while suspended in flue gas. Any of these specific catalyst reactors or their equivalents may be used in practicing the invention, but they will not be described in further detail.

Referring specifically to Figure 1—naphtha, for instance a C_6–C_{12} cut, is introduced by pump 10 through line 11 to coils 12 in pipe still furnace 13 and thence through transfer line 14 to the catalyst chamber or converter 15. Hydrogen from line 16 may be introduced into line 11 or into line 14 but it is preferably passed through separate heating coil 17 and thence through line 18 into line 14 or through line 19 and header 20b into all or any of distributing lines 21.

We will first describe the process of making high quality motor fuel from a naphtha cut of relatively wide boiling range. This naphtha is introduced into the catalyst chamber maintained at an average temperature of about 875 to 1075° F., preferably at about 950 to 1000° F. at a pressure of about 30 to 450 and preferably about 200 to 250 pounds per square inch. About 0.4 to 8 mols of hydrogen, for example 3 mols, are employed per mol of naphtha charged and the hydrogen may be heated to a temperature considerably higher than the temperature of the naphtha.

The catalyst is preferably about 2 to 6% of molybdenum oxide on alumina, although it should be understood that any dehydro-aromatization catalyst as hereinabove described may be used. The space velocity may be about 0.04 to 10 volumes, for example 0.6 of liquid naphtha feed plus recycle per volume of catalyst space per hour. The space velocity will, of course, depend upon the nature of the catalyst, the nature of the charging stock and the temperature. As the catalyst becomes more and more spent the space velocity must be lowered or the temperature must be increased to maintain the same activity. Generally speaking, the larger space velocities go with the higher temperatures. For instance, a space velocity of about 0.5 at 950° F. may give substantially the same amount of conversion with the same catalyst as a space velocity of 1 at 1000° F.

Hot gases and reaction products are withdrawn from chamber 15 through line 22 and passed through heat exchanger 23 and cooler 24 to hydrogen separator 25, which is preferably at substantially reaction pressure and at a temperature of about 35 to 105° F. Hydrogen is withdrawn through line 26 and forced by compressor 27 through suitable scrubbers or purifying means 28 and thence into storage tank 29 from whence it is returned to the system through line 16. Excess hydrogen may be vented from the system either from line 26 through valved line 26a or from storage tank 29 through valved line 29a.

The liquid from the bottom of separator 25 is withdrawn through line 30 to heat exchanger 23 and thence through pressure reducing valve 31 to fractionating column 32. For simplicity we have shown a single column and it should be understood that any number of fractionating columns with stripping means and/or stabilizers may be employed for effecting the desired separation of specific hydrocarbon fractions.

Any C_1–C_3 hydrocarbon gases are withdrawn from the system through line 33, although a portion of such hydrocarbons may be recycled with the hydrogen in line 16 for the alkylation of benzol.

The C_4 and C_5 hydrocarbons are preferably withdrawn as a separate stream through line 34. The C_6 fraction (which may be broadened out to include the C_5 to C_8 hydrocarbons) is withdrawn through line 35. The heavy naphtha fraction, i. e. C_8 to C_{12} hydrocarbons, is withdrawn through line 36. Heavy hydrocarbons may be withdrawn through line 37.

In order to obtain a motor fuel of the desired volatility we prefer to blend the C_4 and C_5 hydrocarbon fraction with the heavy naphtha fraction by closing the valve in line 34 and opening the valve in line 38. Similarly, a part of the C_6 fraction may be blended with the heavy naphtha through line 39, but a substantial portion of the C_6 fraction which may vary from about 0.5 to 4 times the amount withdrawn through line 39, is passed by line 40 to pump 41 and line 42 either through line 43 to inlet line 11 or through line 44 and heater coil 45. This heater coil 45 may discharge through line 46 into transfer line 14 but it is preferably discharged through line 47 into header 20*a* from which it passes to any or preferably all of distributing lines 21.

The recycled C_6 fraction, which in the present example may include also C_7 and perhaps C_8 hydrocarbons, may be heated to a higher temperature than the original charging stock without appreciable thermal cracking. Thus while the original naphtha cannot be safely heated to temperatures very much above 1075° F. the recycled C_6 fraction may be heated to temperatures of 1100° F. or higher without danger of substantial thermal decomposition. When these hot and partially converted gases are introduced into the reaction chamber at spaced points through lines 21 a substantial part of the endothermic heat of the aromatization reaction is supplied, thus tending to keep the catalyst chamber more nearly at a uniform temperature throughout. Furthermore, in each pass the C_6 fraction undergoes further aromatization until with what amounts to about 3 to 5 recycling steps this aromatization may be substantially complete.

Since the recycled hydrogen and the recycled C_6 fraction may be at a much higher temperature than that prevailing in the catalyst chamber care must be taken to prevent overheating of the catalyst at the point of hot gas introduction. We have found that this problem may be effectively solved by providing the catalyst chamber with a series of frustro conical baffles 48, the outer edges of which are welded or otherwise secured to the catalyst chamber in such a manner that the inclined sides thereof act as a hopper for delivering the catalyst from zone to zone. By introducing the hot gases from lines 21 into the annular spaces 49 between the baffle walls and the catalyst chamber these hot gases are tempered by the gases in the catalyst chamber itself, so that the total gas stream is effectively reheated without overheating the adjacent catalyst material.

In another modification, as illustrated in Figure 3, we may introduce the hot hydrogen or hot C_6 vapors into a centrally located tube 50 having perforations 51 therein. These perforations may be so spaced that the hot gases are distributed throughout the catalyst chamber to maintain a substantially uniform temperature therein. Thus in the modification shown in Figure 3 the catalyst chamber remains full of catalyst material, the naphtha vapors flow from top to bottom (although upward flow may be used), and the superheated hydrogen or C_6 hydrocarbons are injected throughout the length of the catalyst bed for preventing undue cooling of the catalyst on account of the endothermic heat of the reaction.

For the sake of simplicity we have shown only a single catalyst chamber 15 but it should be understood that a plurality of such chambers will be used, certain of said chambers being on stream while others are undergoing purging and regeneration. The chambers may be purged with flue gas, steam, low-grade hydrogen or other inert gas which may be introduced through line 52 and withdrawn through line 53. Regeneration may be effected by burning with regulated amounts of oxygen in a flue gas stream, conditions being so regulated that the hot spot or combustion zone will not exceed a temperature of about 1200°. The specific method of regeneration forms no part of the present invention and it will not be described in further detail.

The modification shown in Figures 2 and 3 may be used for moving bed catalysts as well as for fixed bed catalysts and this means of introducing superheated gases into the reaction zone is particularly important when concurrent flow of catalyst material and hydrocarbon vapors is employed. When powdered catalyst is used and is carried through the reactor by the gaseous stream then the expedients illustrated in Figures 2 and 3 are, of course, not necessary.

When the invention is applied to relatively close-cut naphtha fractions for the manufacture of substantially pure benzol or pure toluol, the recycled benzol is thermally extremely stable so that it may be heated to very high temperatures and then used for supplying the endothermic heat of aromatization. This recycling expedient cuts down materially the amount of heat which would otherwise have to be supplied by expensive heat transfer media.

When making substantially pure benzol from C_6 hydrocarbons there will be no necessity for withdrawing any side stream through line 34, and the C_6 open chain hydrocarbons will be withdrawn through line 35 for recycling while benzene is withdrawn through line 36. Benzol itself boils at a slightly higher temperature than open chain C_6 hydrocarbons and it is thus possible to recycle the incompletely converted hydrocarbons while withdrawing at least the major part of the benzene produced.

Similarly, when making toluol from C_7 hydrocarbons the open chain C_7 hydrocarbons are withdrawn through line 35 and the major part of the toluol is withdrawn through line 36. In the case of benzol, toluol and similar aromatics, it is not essential that these products be closely fractionated in column 32 since the recycling of some of the benzol or toluol helps to maintain a more even temperature in the conversion system.

When the recycled material is separately heated it may act as a heat carrier for the reaction.

Instead of making pure benzol or pure toluol we may employ an open chain hydrocarbon mixture for the preparation of high solvency naphtha and different grades of solvency naphtha may be made by using a C_7—C_8 fraction, a C_8—C_9 fraction, a C_9—C_{10} fraction, etc. and in such cases the lighter components of the charge may be recycled for the purposes hereinabove described.

While we have described in detail preferred embodiments of our invention, it will be understood that we do not limit ourselves to any of such details except as defined by the following claims.

We claim:

1. The method of producing increased yields of toluene from a naphtha charging stock which method comprises contacting said charging stock with a catalyst consisting essentially of a group VI metal oxide on alumina in a conversion zone at a temperature of approximately 950° F. to 1000° F., under a pressure in the general vicinity of 250 pounds per square inch in the presence of about 3 mols of hydrogen per mol of naphtha charge and at a space velocity of approximately 0.5 to 1 liquid volume of naphtha per hour per volume of catalyst in the conversion zone, separating hydrogen from the products leaving the conversion zone, heating at least a part of said separated hydrogen and returning said heated hydrogen to the conversion zone, fractionating the products after the hydrogen separation step to recover a toluene fraction and an aliphatic C_7 hydrocarbon fraction, heating said separated aliphatic C_7 hydrocarbon and returning the heated aliphatic C_7 hydrocarbon fraction to the conversion zone.

2. The method of claim 1 wherein the catalyst consists essentially of approximately 6% of molybdenum oxide on an active alumina support.

3. The method of producing increased yields of toluene from a petroleum naphtha which comprises contacting said naphtha with a catalyst consisting essentially of a group VI metal oxide on alumina at a pressure of about 30 to 450 pounds per square inch and a temperature of about 875 to 1075° F. in the presence of about 0.4 to 8 mols of hydrogen per mol of naphtha with a space velocity of about 0.04 to 10 volumes of liquid naphtha per hour per volume of catalyst space, separating from aromatization products a gas fraction rich in hydrogen, purifying at least a part of said gas fraction to remove hydrocarbon contaminants from said hydrogen, heating said purified hydrogen to a temperature above that at which the aromatization reaction takes place, introducing the heated hydrogen into the zone of the aromatizing reaction to supply a part of the exothermic heat of aromatization, separating from aromatization products a liquid fraction consisting essentially of C_7 hydrocarbons and again contacting said liquid fraction consisting essentially of C_7 hydrocarbons with said catalyst under substantially the conditions recited for said first contacting step.

4. The method of producing toluene from a petroleum naphtha which comprises vaporizing and heating a close cut C_7 naphtha fraction to aromatization temperature, contacting said naphtha in a contacting zone with a catalyst consisting essentially of active alumina containing molybdenum oxide deposited thereon, effecting said contacting at a space velocity, temperature and pressure for producing large yields of toluene and substantial amounts of hydrogen, recycling at least a part of the produced hydrogen through a heating zone whereby it is returned to the contacting zone at a temperature which is substantially higher than the temperature of the vapors with which it is to be admixed in said contacting zone, fractionating the normally liquid products from the contacting zone to separate a C_7 hydrocarbon product fraction from other conversion products, heating at least a substantial portion of said C_7 hydrocarbon product fraction and returning said heated fraction to the contacting zone.

5. The method of obtaining large yields of relatively pure aromatics from a naphtha charging stock containing aliphatic hydrocarbons boiling within the range of about 125 to 450° F. which method comprises contacting said naphtha with an aromatizing catalyst in a contacting zone at a temperature within the approximate range of 875 to 1075° F. under a pressure within the approximate range of 30 to 450 pounds per square inch in the presence of about 0.5 to 8 mols of hydrogen per mol of naphtha charged and at a space velocity within the approximate range of 0.04 to 10 volumes of liquid naphtha per volume of catalyst space per hour such that substantial aliphatic cyclization is effected, separating from the products of the contacting step a hydrocarbon fraction consisting essentially of hydrocarbons having at least 6 carbon atoms per molecule but not more than 7 carbon atoms per molecule, heating said fraction to a temperature above the average temperature in the contacting zone and subsequently contacting said fraction with said catalyst at a temperature within the approximate range of 875 to 1075° F. under a pressure within the approximate range of 30 to 450 pounds per square inch and at a space velocity within the approximate range of 0.04 to 10 volumes of liquid hydrocarbon fraction per hour per volume of catalyst space to obtain an increase in the yield of relatively pure aromatics.

6. The method of claim 5 wherein the hydrocarbon fraction is a C_8 hydrocarbon fraction.

7. The method of claim 5 wherein the hydrocarbon fraction is a toluol fraction.

8. The method of claim 5 wherein the hydrocarbon fraction consists chiefly of non-aromatic hydrocarbons containing 7 carbon atoms per molecule.

9. The method of claim 5 wherein the heating of the hydrocarbon fraction prior to its introduction into the second contacting step is to a higher temperature than the temperature to which the original naphtha could be heated without thermal decomposition.

10. The method of preparing valuable cyclic hydrocarbons from petroleum naphtha which comprises contacting said naphtha with an aromatizing catalyst in a contacting zone at a pressure within the approximate range of 30 to 450 pounds per square inch and a temperature within the approximate range of 875 to 1075° F. in the presence of about 0.4 to 8 mols of hydrogen per mol of naphtha with a space velocity of about .04 to 10 volumes of liquid naphtha per volume of catalyst space per hour, separating a hydrogen-rich gas from aromatization products, heating at least a part of said separated gas and returning it to the contacting step, separating from aromatization products a fraction consisting essentially of hydrocarbons having at least 6 carbon atoms but not more than 7 carbon atoms per molecule which fraction is thermally more stable than said naphtha, heating the separated fraction to a tempera-

ture above that at which the aromatization reaction takes place and returning the heated fraction to the contacting zone to supply a part of the endothermic heat of aromatization.

11. The method of increasing the toluene concentration in a C_7 hydrocarbon fraction obtained by fractionating products produced from the aromatization of aliphatic hydrocarbons of the light naphtha boiling range with an aromatizing catalyst under aromatizing conditions, which method comprises heating said C_7 hydrocarbon fraction to a temperature above aromatization temperature and again contacting it with an aromatizing catalyst at a temperature within the approximate range of 875 to 1075° F. under a pressure within the approximate range of 30 to 450 pounds per square inch in the presence of about 0.4 to 8 mols of hydrogen per mol of C_7 hydrocarbon charged and at a space velocity sufficiently low to effect further aromatization, and separating a relatively pure toluene fraction from lower boiling and higher boiling products.

12. The method of producing increased yields of toluene from a naphtha charging stock containing C_7 hydrocarbons which method comprises contacting said charging stock with an aromatizing catalyst in a conversion zone under conditions for effecting aromatization and hydrogen production, separating hydrogen from the products leaving said conversion zone, heating at least a part of said separated hydrogen and returning said heated hydrogen to the conversion zone, fractionating the products after the hydrogen separation step and recovering a toluene fraction and a C_7 hydrocarbon fraction which is lower boiling than toluene, heating said last-named C_7 hydrocarbon fraction and returning said heated C_7 hydrocarbon fraction to the conversion zone as a part of the naphtha charging stock introduced thereto.

13. The method of claim 12 wherein the aromatizing catalyst consists essentially of alumina and molybdenum oxide.

14. The method of claim 12 wherein the contacting is effected at a temperature within the approximate range of 875 to 1075° F. under a pressure of about 30 to 450 pounds per square inch in the presence of about 0.4 to 8 mols of hydrogen per mol of naphtha charged and at a space velocity within the approximate range of 0.04 to 10 volumes of liquid naphtha charged per hour per volume of catalyst space in the conversion zone.

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