

UNITED STATES PATENT OFFICE

2,404,902

HYDROCARBON CONVERSION

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Application July 21, 1942, Serial No. 451,748

10 Claims. (Cl. 260—673.5)

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This invention pertains to the production of aromatic rich hydrocarbon liquids from petroleum distillates and is directed more particularly to the production of substantially pure aromatics from selected hydrocarbon distillates by means of a novel combination sequence of catalytic and distillation steps.

Various methods have hitherto been proposed for extracting, by means of selective solvents, the aromatic compounds occurring in certain natural petroleum. Methods have also been disclosed for converting a portion of the non-aromatic materials in petroleum distillates to aromatics, which may then be separated by means of selective solvents, just as in the case of the originally occurring aromatics.

While the aromatic compounds present or produced in petroleum fractions may be substantially concentrated through the use of known methods of solvent extraction, it is, however, unfortunately a fact that no known solvent is sufficiently selective to recover by a simple operation all of an aromatic compound from admixture with the associated paraffinic and naphthenic materials in a petroleum distillate and at the same time to recover it in a state of sufficiently high purity that it may be subjected directly to nitration as, for instance, in the preparation of explosives, or may be used directly as raw material in other specific chemical processes.

In our earlier filed copending application Serial No. 434,994 we disclosed a particular method of operating catalytic steps, which are already more or less well known in connection with the reforming of gasolines and naphthas for their antiknock improvement, by means of which it is possible to produce substantially pure aromatic compounds, such as benzene, toluene, ethyl benzene and xylene, from appropriately chosen fractions of petroleum. No complicated solvent extraction procedure is employed in our process, the appropriate steps of catalytic conversion properly related to simple distillation processes being adequate to produce aromatics of better than 99% purity. For instance, it has been found possible by means of the particular combination of process steps which constitutes our invention to convert a "toluene cut," boiling from about 180° to about 240° F., from a California straight-run petroleum distillate, simply and directly into nitration grade toluene with yields of the order of 40% by weight. Our present invention comprises a specific modification of such operation particularly adapting it to the treatment of highly paraffinic stocks.

It is the object of the present invention to pro-

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vide a relatively simple catalytic process by means of which it is possible to prepare low boiling aromatic compounds from highly paraffinic petroleum fractions with a higher degree of purity and in substantially improved yields over hitherto known processes.

It is a more specific object of the present invention to provide a catalytic process wherein catalytic conversion steps are correlated with simple distillation operations in a manner such that selected paraffinic petroleum distillates may be converted to substantially pure aromatic compounds with relatively high yield.

It is a still more specific object of the present invention to provide a catalytic process for converting selected paraffinic petroleum fractions substantially to aromatic compounds wherein two coordinated stages of catalytic treatment are employed in series with a fractionation step interposed between them.

It is another specific object of the present invention to provide a method for converting a selected fraction of paraffinic petroleum to substantially pure aromatic compounds by catalytically preparing an aromatic rich distillate, separating it from non-aromatic compounds so far as practical by fractional distillation and subjecting the so separated fraction to a second catalytic treatment for conversion of the residual non-aromatic compounds.

It is a more specific object of the present invention to provide a process for preparing substantially pure toluene from a petroleum hydrocarbon fraction boiling between about 180° and 235° F. and containing a substantial proportion of paraffinic compounds.

Other and more specific objects of the invention will be apparent from the following description and the appended claims.

While it is conventional practice in most chemical reactions, and particularly in the catalytic processing of hydrocarbons such as in catalytic cracking and catalytic reforming operations, to separate from the product unreacted components of the charge for return to the reaction in order that the highest possible yield of the desired product may be realized from each unit of charge, the present operation differs significantly from such conventional recycle operation in that it is the desired product that is subjected to a second catalytic treatment rather than unreacted components of the initial charge. Our present process further differs from the usual recycle operation in that the once-through material is separated as far as possible from components of the

original charge before being subjected to the second stage of catalytic treatment whereas in recycle operation the recycled material is added to fresh feed prior to being passed over the catalyst. Conditions maintained in the second stage of our present process are also significantly different than prevail in the first stage. It is believed that these elements of novelty are highly significant and are in large part responsible for the peculiar advantages of the process of the present invention.

Broadly considered, our process for producing substantially pure aromatic compounds from selected paraffinic petroleum distillates may be divided into four significant and critically related steps, namely, a first stage low-pressure catalytic step, an interstage separation step, a second stage higher pressure catalytic step and a final separation step.

In the first catalytic stage we have found the oxides of metals of the left-hand columns of groups IV, V and VI of the periodic system, and particularly the oxides of chromium, vanadium and molybdenum to be effective cyclizing agents. These oxides may be impregnated in or supported on activated alumina or the active metal components may be coprecipitated with the alumina as when a solution containing a compound of the metal together with aluminum ion is treated with aqueous ammonia.

In the second catalytic stage substantially the same group of catalysts may be used, the result obtained being, qualitatively at least, more dependent upon the conditions maintained than upon the specific catalyst employed. Specific combinations and sequences of catalysts may nevertheless possess certain quantitative advantages. It has for instance been found that greater yields of aromatics with less loss to coke and gas may be secured when a chromium compound catalyst, as described above, is employed in the first stage with a molybdenum containing catalyst in the second stage than when any other catalyst sequence is used.

In a preferred embodiment of the process of the present invention a catalyst in which a chromium compound such as a chromate or dichromate is coprecipitated with or supported on alumina is employed in the first stage while a catalyst in which a molybdenum component coprecipitated with alumina from a solution containing soluble compounds of the two metals is used under appropriately different conditions, described hereinafter, in the second stage. This combination of catalysts has been found to give the smoothest operation and the most desirable results of any combination yet tried.

In carrying out the process of the present invention, when it is applied to the production of pure toluene for nitration or use as a raw material in other chemical processes, we prepare a distillate from naturally occurring, essentially paraffinic petroleum by close fractionation to give a cut boiling from about 180° to 235° F. This stock is charged to an appropriate first catalyst stage employing one of the above-mentioned catalysts and is subjected therein to a temperature between about 800° and 1050° F. in the presence of a carrier gas containing a substantial proportion of hydrogen and at a total pressure in the neighborhood of atmospheric and preferably not over about 50 pounds per square inch for a time sufficient to give the desired conversion to aromatics, as will be explained in detail in a later section. The product from said first catalytic

stage is then separated by distillation into a light gas fraction consisting largely of hydrogen and methane, which may be employed directly as the carrier gas already mentioned or further separated to give a butane fraction which may be removed from the process for other well known uses, a liquid fraction boiling above butane up to about 180° F., which may be either recycled for further processing or removed from the process for use elsewhere, as may be desired, a higher boiling liquid fraction from 180° F. to about 227° F. which is recycled to the first catalyst stage for further processing, a liquid fraction boiling between about 227° F. and 232° F. which is charged to the second catalyst stage, and a bottoms fraction boiling above about 232° F. which may be used as a source of higher boiling aromatics or otherwise disposed of as desired. The narrow boiling cut from 227° F. to 232° F. is charged to the second stage catalyst system together with a carrier gas containing hydrogen and under substantially the same conditions as already described for the first stage operation except that a higher pressure is maintained and the rate of charge, and hence the time of reaction in the second stage, may be varied somewhat to accommodate the particular stock which is undergoing treatment so as to produce a final toluene rich product of the desired characteristics. This crude toluene can then be separated by ordinary good fractional distillation with the production of a toluene product that may directly, or after a slight acid treatment, be satisfactorily subjected to nitration or such other chemical use as desired.

While the process as described herein contemplates two separate catalyst stages arranged in series with an efficient fractional distillation stage between them, it will be apparent to those skilled in the art that by providing adequate storage facilities the same ultimate result can be obtained by preparing and storing the toluene rich 227° to 232° F. cut and substantially passing it through the same catalyst stage in which it was prepared but under the conditions for second stage operation, as already described. This second stage treatment is in no sense equivalent to a recycle treatment through the first stage since it is critically and positively a treatment of the desired product separated as far as possible from all other materials instead of being added to fresh feed as in a typical recycle operation.

The diluting or carrier gas may, as mentioned above, be the gas produced in the process or a more or less similar gas derived from any other convenient source. We have found, however, that it should contain at least 40% by volume of hydrogen and preferably above 50% in order that the most efficient use of the catalyst may be realized. It has also been found desirable to employ this carrier gas in quantities up to about 3,000 cubic feet, measured under standard conditions of temperature and pressure, per barrel of the liquid hydrocarbon charged. The ratio of gas to hydrocarbon charge on a molecular basis is then from zero to about three to one, which, when the carrier gas contains 50% or more of hydrogen, would thus give a molecular ratio of hydrogen to hydrocarbon of up to about one and one-half to one. Higher ratios may, of course, be employed but without substantial improvement in results.

In addition to the significant ratio of diluent gas to naphtha just explained, we have also found that in the second stage the proportion of hydro-

gen in the diluting gas at any given total pressure or, more broadly, its partial pressure in the reaction mixture, is extremely significant to the satisfactory completion of the conversion of non-aromatic components into aromatics or into compounds that are readily separable from the aromatic compound by fractional distillation. The over-all effect of a substantial partial pressure of hydrogen is to lower the loss of charge to coke and simultaneously to increase the period of operation between catalyst regeneration treatments for the removal of coke deposited thereon. We have found that the major part of this benefit to catalyst life is realized between about two and twenty atmospheres (30 and 300 pounds per square inch) partial pressure of hydrogen and usually between about three and ten atmospheres (45 and 150 pounds per square inch). While the total pressure on the second stage system does not appear to be particularly critical, it will be seen, from what has already been said, to be substantially fixed by the limits of dilution prescribed and by the desirable partial pressures of hydrogen, to a range between about 50 and 500 pounds per square inch and usually to between about 100 and 400 pounds per square inch.

With the hydrogen rich stocks consisting substantially of paraffins and only minor quantities of naphthenes and low boiling aromatics which are preferred for the process of the present invention, it has been found that the process gas as produced in the first catalyst stage usually contains sufficient hydrogen that it may be employed without further adjustment as the diluent gas. When, however, it is desirable to recover from the first stage gas butanes, and possibly also propane for use in other processes, the concentration of hydrogen in the remaining gas is, of course, increased and the gas is therefore rendered even more suitable for use as the diluent or carrier agent in our process. With the temperature, total pressure, partial pressure of hydrogen and degree of dilution of hydrocarbon charge by inert gas regulated substantially within the ranges just specified, the extent of conversion in the catalyst stages may be varied as desired by adjusting the time of the reaction or, more directly, the rate at which the hydrocarbon charge is fed to the process.

We have found that in producing toluene from a paraffinic straight-run gasoline, the toluene cut should be charged to the first catalyst stage at such a rate as will give a debutanized product containing approximately 40% of aromatic compounds in order that the highest over-all yield of toluene from a given amount of charge may be produced with best efficiency and the least operating difficulty. With the more active physical modifications of the above-mentioned catalysts and the conditions of operation as already given, this degree of conversion is realized by charging from about 0.7 to 3.0 volumes of hydrocarbon (measured as liquid) per volume of catalyst (including voids) per hour. While it is true that with a lower conversion in the first stage a slight increase in the over-all yield of toluene may be realized, this is possible only with a substantial reduction in the capacity of any given plant. With a conversion in the first catalyst stage to give more than about 40% of aromatics in the debutanized product, the ratio of toluene to gas and light liquid, boiling below about 180° F., is found to decrease rapidly and hence the yield of toluene per unit of charge is reduced

proportionally by such higher conversion in the first stage.

While it is possible that this optimum conversion in the first stage for highest plant efficiency and highest ultimate yield of toluene might be slightly different for charging stocks varying widely in the nature and relative proportions of the components in the 180° to 250° F. boiling range, such variations will be found to be readily determinable and hence are believed to be comprehended by our invention.

The conditions to be maintained in the second catalyst stage are, as already indicated, substantially different in several respects from those employed in the first stage. These differences may vary slightly with the sequence of catalysts used but should in general fall within the ranges specified. In addition to the possible slight variation in hydrogen concentration in the carrier gas and in the other conditions mentioned above, it may also be desirable to alter the feed rate to the second stage slightly to produce the absolute maximum yields of toluene with minimum loss of charge to gas and coke.

Instead of making adjustments in the feed rate, while maintaining a constant average temperature of reaction, in order to secure the desired degree of conversion in either first or second catalyst stages, it has been found more desirable under certain circumstances to maintain a fixed feed rate and to adjust the inlet temperature to the catalyst chamber to give the desired conversion, the temperature being readjusted as may be necessary to compensate for fluctuations or changes in catalyst activity in order to maintain the extent of conversion constant throughout the operation. Ordinarily it will be found most convenient to fix the point of operating temperature control at the inlet to the catalyst chamber, the temperature there being adjusted to that which is found, with a given apparatus and stock, to give the desired degree of conversion. This point of temperature control is chosen since the temperature at any point within the catalyst chamber is a much less definite quantity due to the rather large temperature drop through the catalyst due to endothermic heat of reaction.

One preferred embodiment of the process of the present invention will now be explained with reference to the figure of the attached drawing. It will be appreciated that this figure is a schematic representation or flow diagram of the apparatus in which the process may be effected. All valves, condensers, heaters and like conventional items of equipment have been accordingly omitted.

For the production of toluene the liquid hydrocarbon charge to the first stage of the process is preferably a closely fractionated cut from a paraffinic petroleum having a boiling range from about 180° to 235° F. This charge may be passed through line 1 to the first stage heating zone 5 to which are also passed recycle gas from line 3, light recycle liquid from line 13, heavy recycle liquid from line 31 and extraneous hydrogen from line 2 when necessary. The preferred ratio of recycle gas to total liquid feed to the catalyst chamber is of the order of 1500 cubic feet per barrel. At this ratio it is desirable that the recycle gas should contain at least 40%, and preferably above 50%, of hydrogen and that the molecular ratio of hydrogen to liquid hydrocarbon charge be of the order of 0.75:1. The extraneous hydrogen added through line 2, as already mentioned, is thus em-

ployed whenever necessary to bring the hydrogen content of the carrier gas entering the heating zone within this desired range.

The heated mixture from zone 5 is passed through line 6 to the first catalyst stage represented by drums I and I' which contain a pelleted, coprecipitated, chromium-aluminum catalyst. A pressure of about 15 pounds per square inch absolute is maintained in the reaction zone with an inlet temperature of between 900° and 1025° F. Under these conditions and with the charging material indicated, the desired extent of reaction can be effected at a charging rate of about 0.2 to 0.3 volumes of liquid charge per volume of catalyst containing space per hour. The reaction mixture is passed from the catalyst zone through line 7 (7') to a first stage liquid stabilizer 3 wherein the butane and lighter components of the charge may be separated from the normally liquid components, the light fraction being passed through line 8 for subsequent treatment, as described later herein, while the normally liquid product is passed through line 10 to a first stage still, 11. This first stage still may in fact consist of one or several separate stills as may be found more convenient and economical in the preparation of the desired close-cut fractions. A low boiling fraction from start to about 180° F. will usually be taken off and removed from the system. A side stream boiling from 180 to about 227° F. may be returned through line 13 as a light recycle stock to the first heating zone 5. A crude toluene fraction boiling from about 227° to 232° F. will be recovered for use as the charging material to the second stage of the process while the fraction boiling above 232° F. may be removed through line 15 and sent forward to a xylene still for the recovery of the higher boiling aromatics.

Recycle gas is charged to the second heating zone 18 from line 16, additional hydrogen, when required, from line 17 and second stage recycle liquid from line 26. The recycle or carrier gas to the second stage need not be quite so rich in hydrogen as the gas in the first stage but in any event it should contain at least 20% of hydrogen, and preferably at least 30%. The rate of charging gas to the second stage will usually be substantially higher than to the first stage, that is, about 6,000 cubic feet per barrel of crude toluene charged from line 14 as compared to less than about 3,000 cubic feet to stage one. A pressure of about 215 pounds per square inch absolute and an inlet temperature between about 950° and 1025° F. are maintained in the second stage of the process. The liquid feed rate is of the order of 1.0 vol./vol./hr. when an active coprecipitated molybdenum-aluminum catalyst is employed.

The product from the second catalyst stage II (II') is passed through line 20 (20') to the second stage liquid stabilizer 21 wherein the butane and lighter gases are separated from the normally liquid components, the former being discharged from the system or passed through line 22 to line 9 for treatment together with the gaseous product from the first stage, while the normally liquid fraction is discharged through line 23 to toluene still 24. The toluene still 24 may, as in the case of the first stage still, actually consist of one or more stills conveniently arranged to most efficiently prepare the desired close fractionated cuts. A start to about 220° F. cut may be taken overhead from this still through line 15 to line 10 and still 11. A 220° to 230° F. fraction may be prepared for return through line 16 as second stage recycle liquid to the second

stage heating zone 18. In some instances it may be preferable to include this latter cut with the light cut, whereupon the combined start to 230° F. fraction would be passed through line 25 as already described. A 230° to 232° F. fraction, which will now contain 99%+ toluene, is discharged through line 27 while the bottoms boiling above 232° F. may be discharged from the system or sent through line 28 to the xylene still 29 for recovery of such higher boiling aromatics as may be present.

The xylene still 29, in which the bottoms fractions from first stage still 11 and toluene still 24 are combined, will usually be operated to give three fractions: A 235° to 275° F. cut which is removed at 30 and discharged from the system, sent to the absorber 32 or sent by line 31 as heavy recycle liquid to the first heating zone 5, a 275° to 295° F. cut removed at 33 which will contain a mixture of the three isomeric xylenes and ethyl benzene, and a bottoms cut boiling above 295° F. which is removed at 34 and discharged from the system or sent through line 35 to absorber 32.

The absorber 32 is employed for separating the butane and sometimes also the propane fractions from the gases produced in the first and second stage treatments. These heavier gaseous hydrocarbons are absorbed in a sponge liquid which may be a hydrocarbon liquid provided especially for that purpose or may, as already herein indicated, be the intermediate and/or heavy liquid fractions produced during the reaction, such as the bottoms cut from the first stage or toluene stills or the outside fractions from the xylene still. The saturated sponge liquid from absorber 32 may be removed through line 36 and sent to a recovery system, not shown, or sent through line 31 to the first heating zone 5 as heavy recycle liquid. The gases leaving the absorber at 37 are passed by line 16 to the second heating zone 18, by lines 16 and 3' to the recycle gas holder 38, or by lines 16 and 3 to the first heating zone 5.

While, for convenience, the drawing has shown both the first and second catalyst stages as composed of two catalyst drums, so arranged that the catalyst in one drum may be regenerated while the other is on stream, it will be appreciated that any more convenient number of drums may be employed. For instance, when on stream periods shorter than about one hour are desirable, it may be found necessary to provide three or more drums for each catalyst stage in order that the complete cycle of on stream and regeneration steps may proceed without interruption. The inert gases necessary for purging the catalyst drums prior to their regeneration, and necessary also for diluting the air used in reburning the catalyst, are stored in purge gas holder 39 which is shown with appropriate connections to the catalyst drums of both stages of the process. In general, it is desirable in regenerating catalysts of the class employed in the present process to dilute the air employed in regeneration sufficiently that temperature in the catalyst may be held below the point at which appreciable inactivation of the more sensitive catalysts may occur. This temperature is about 1200° F. Instead of effecting this temperature control by flue gas recycle, it may equally well be effected by the now well known method of building into the catalyst chamber heat dissipating means such as fins, flues and tubes for circulating a cooling fluid.

In order that the progressive increase in toluene content of the hydrocarbon liquid as it

passes through the process of the present invention may be better visualized, the approximate percentage of toluene contained in the liquid passing through lines 10, 14, 23 and 27 has been indicated on the drawing. While these values may vary somewhat with different charging stocks, they may be substantially regulated by controlling the conversion effected in the first stage so that the liquid passing through line 10 will contain about 40% aromatics. With the average paraffinic stock used as a basis for the foregoing description, the crude toluene charge (line 14) to the second stage will then contain approximately 90% total aromatics, the second stage product (line 23) passing to the toluene still will contain about 96% toluene and the final product discharged through line 27 will be substantially pure (99%+) toluene. For convenience in visualizing the process, these figures have been indicated enclosed in circles at the appropriate points on the drawing. The over-all yields of toluene that have thus been obtained vary from about 32 to 42% by volume of the liquid charge.

The process of our present invention may be further illustrated by reference to the following specific example:

Example

A fraction from a paraffinic straight-run gasoline boiling between 180° and 240° F. (true boiling points) was subjected to the two-stage process just described wherein a chromic oxide-alumina composition was used as the catalyst in the first stage and a molybdenum-alumina coprecipitate was employed in the second. The operating conditions and results obtained were as follows:

	1st stage	2d stage
Temperature av., °F.....	950	960
Pressure p. s. i. abs.....	15	215
Feed rate (liq.) v./v./hr.....	0.25	1.0
On stream periods, min.....	60	60
Gas recycle, cu. ft./bbl. feed.....	1,500	6,000
Yield, vol. percent liquid.....	80	96
Coke loss, wt. percent.....	1.0	1.1
Gas loss, wt. percent.....	15.0	3.0
Toluene vol. percent of prod.....	20.0	99.0
Toluene yield vol. percent chg.....		35

While the foregoing discussion and examples have been directed particularly to the production of toluene from a typical paraffinic stock, it is equally possible to produce the other low boiling aromatics, such as benzene, ethyl benzene and xylene, from the appropriate fractions of a similar stock.

Having now described and illustrated our "two-stage catalyst" process comprising a particular combination of catalytic and distillation steps for the production of substantially pure aromatic liquids from selected paraffinic petroleum fractions, we claim:

1. Process for the production of a substantially pure liquid aromatic which comprises subjecting a selected narrow boiling fraction from a paraffinic base petroleum to reforming, dehydrogenation and cyclization over a metal oxide catalyst containing as the active component an oxide of a metal selected from the group consisting of the metals in the left-hand columns of groups IV, V and VI of the periodic system at a temperature between 800° and 1050° F., a pressure of about 15 p. s. i. absolute and in the presence of a hydrogen containing carrier gas in the ratio of about two molecules of gas per molecule of hydrocarbon charge for a time sufficient to produce a liquid

product falling substantially in the same range as the original charge and containing a significantly higher concentration of aromatic compounds than the charge, fractionally distilling this liquid product to produce a cut boiling substantially within the range of the original charge, subjecting said cut to a second treatment with a metal oxide dehydrogenation catalyst containing as the active component an oxide of a metal selected from the group consisting of the metal of the left hand columns of groups IV, V, and VI of the periodic system at a pressure higher than employed in the first stage, collecting the liquid product and sharply fractionating it to separate the desired aromatic in a substantially pure state.

2. Process for the production of toluene which comprises subjecting a fraction from a paraffinic petroleum boiling in the range from about 180° to about 240° F. to the action of a catalyst comprising chromic oxide and alumina at a temperature between about 900° and 1025° F. under a pressure of about atmospheric and in the presence of a carrier gas containing at least 40% hydrogen, said carrier gas being in the ratio of about 1500 cubic feet per barrel of liquid charge for a time sufficient to produce a debutanized liquid product containing about 40% of total aromatics, fractionally distilling said liquid product to produce a sharp cut boiling between about 227° and 232° F., subjecting said cut to a second catalytic treatment over a coprecipitated molybdena-alumina catalyst in the presence of a carrier gas containing free hydrogen at a temperature between about 900 and 1025° F. and under a pressure of about 200 p. s. i. for a time sufficient to produce a debutanized product containing at least 90% aromatics and subjecting said product to an efficient fractional distillation to produce a fraction containing at least 99% toluene.

3. Process as in claim 2 wherein the catalyst in the second stage is a coprecipitated vanadium oxide-aluminum oxide composition.

4. Process for the production of an aromatic rich stock which comprises subjecting a selective narrow boiling paraffinic distillate to the action of a cyclization catalyst containing as the active component an oxide of a metal selected from the group consisting of the metals of the left-hand columns of groups IV, V and VI of the periodic system at substantially atmospheric pressure and a temperature between about 900 and 1025° F. in the presence of a carrier gas containing a substantial proportion of free hydrogen, collecting the liquid product, fractionally distilling said collected liquid product for the removal of components boiling both above and below the original charge and subjecting the so segregated liquid boiling within the range of the original charge to a second catalytic treatment with a catalyst containing as the active component an oxide of a metal selected from the group consisting of the metals of the left hand columns of groups IV, V, and VI of the periodic system in the presence of a carrier gas containing free hydrogen and at a pressure substantially higher than that employed in the first stage for the conversion of non-aromatic compounds to render the aromatic compound separable by fractional distillation.

5. Process for the production of substantially pure toluene from a paraffinic petroleum distillate which comprises subjecting a fraction from said distillate boiling within the range from about 180° to about 240° F. to the action of a catalyst comprising chromium oxide and alumina in a first stage at a temperature between about 900° and

1050° F. and a pressure of substantially atmospheric in the presence of a recycle gas containing between about 45 and 90% free hydrogen, said gas being present in quantity less than about 3000 cubic feet per barrel of liquid charge, collecting the liquid product formed, separating from said liquid product by extreme fractionation a toluene rich fraction containing substantially only hydrocarbon impurities that are inseparable from toluene by said fractionation, subjecting said crude toluene fraction to the action of a coprecipitated catalyst comprising molybdenum oxide and alumina at a temperature between about 900° and 1050° F. and a pressure between about 50 and 300 p. s. i. in the presence of a carrier gas containing free hydrogen in the ratio of between 2000 and 12,000 cubic feet of gas per barrel of liquid charge whereby the hydrocarbon materials associated with the toluene are converted to substances that are separable from the toluene by fractional distillation and effecting said separation to produce toluene of nitration grade.

6. Process for producing a substantially pure relatively low boiling aromatic compound from a paraffinic hydrocarbon fraction containing constituents boiling within the gasoline boiling range, which comprises aromatizing said paraffinic fraction by subjection to the action of a dehydrogenation catalyst comprising coprecipitated alumina and an oxide of a metal selected from the group consisting of the metals in the left-hand columns of groups IV, V and VI of the periodic system at a temperature from about 800° to 1050° F. in the presence of a carrier gas containing at least 40% by volume of hydrogen, at a total pressure from about atmospheric to about 50 pounds per square inch, with a molecular ratio of hydrogen to hydrocarbon up to one and one-half to one, and at a space velocity of about 0.2 to about 3.0 volumes of liquid hydrocarbons charged per volume of catalyst space per hour, separating from the resulting product by fractional distillation a relatively narrow cut containing essentially only the desired aromatic compound and other constituents inseparable therefrom by fractional distillation, subjecting said narrow cut to the action of a catalyst comprising coprecipitated alumina and an oxide of a metal selected from the group consisting of the metals in the left-

hand columns of groups IV, V and VI of the periodic system in the presence of a carrier gas containing at least 20% by volume of hydrogen, at a total pressure higher than that maintained in said aromatizing zone and being of the order of from 50 to 500 pounds per square inch and at a partial pressure of hydrogen from about 30 to 300 pounds per square inch to transform said cut and render said aromatic compound separable therefrom by fractional distillation, fractionally distilling the resulting product to separate therefrom substantially pure aromatic compound.

7. Process as defined in claim 6, in which said first mentioned metal oxide is a chromium oxide and said second mentioned metal oxide is a molybdenum oxide.

8. Process as defined in claim 6, in which said first mentioned metal oxide is a vanadium oxide.

9. Process as defined in claim 6, in which said first mentioned metal oxide is a molybdenum oxide.

10. Process for the production of hydrocarbon distillate fractions rich in aromatic compounds which comprises subjecting a selected paraffinic petroleum fraction to the action of a metal oxide aromatizing catalyst containing as the active component an oxide of a metal selected from the group consisting of the metals in the left-hand columns of groups IV, V and VI of the periodic system at a temperature of 800° to 1050° F. in the presence of added hydrogen and at a pressure of about atmospheric to about 50 pounds per square inch, fractionally distilling the product to separate a cut boiling in approximately the same range as the original charge and containing the desired aromatic, subjecting the so separated cut to a second catalytic treatment with a catalyst containing as the active component an oxide of a metal selected from the groups consisting of the metals of the left hand columns of groups IV, V, and VI of the periodic system at a higher pressure than employed in the first stage to render the aromatic compound in said cut separable therefrom by fractional distillation and fractionating the resulting product to separate in substantially pure form the aromatic rich liquid produced.

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