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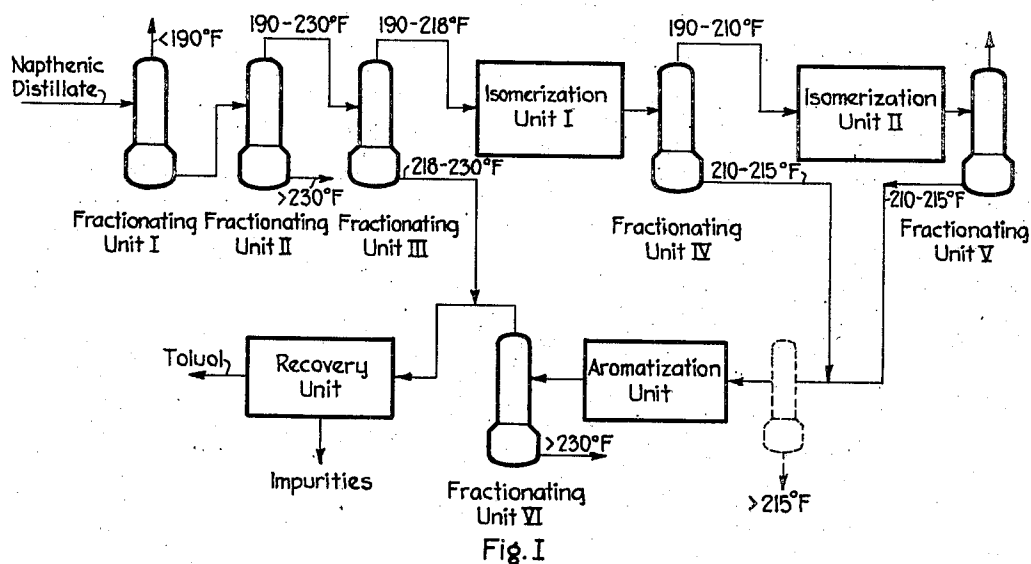
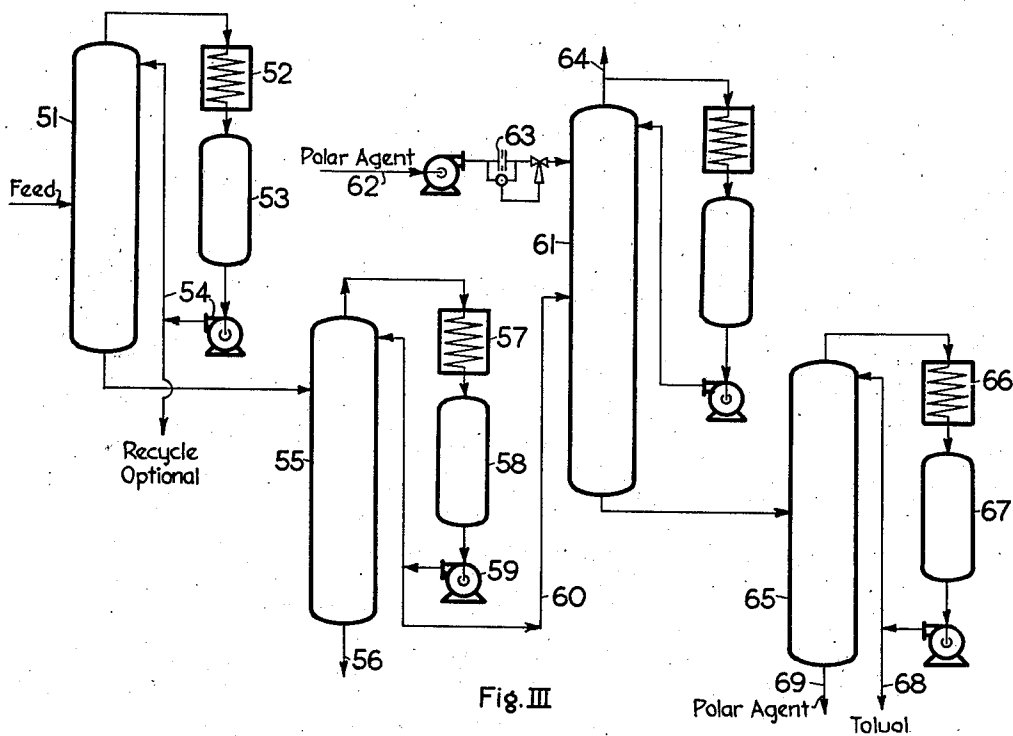
F. M. McMILLAN ET AL

2,392,398

PROCESS FOR THE PRODUCTION OF TOLUOL

Filed July 23, 1940

2 Sheets-Sheet 1



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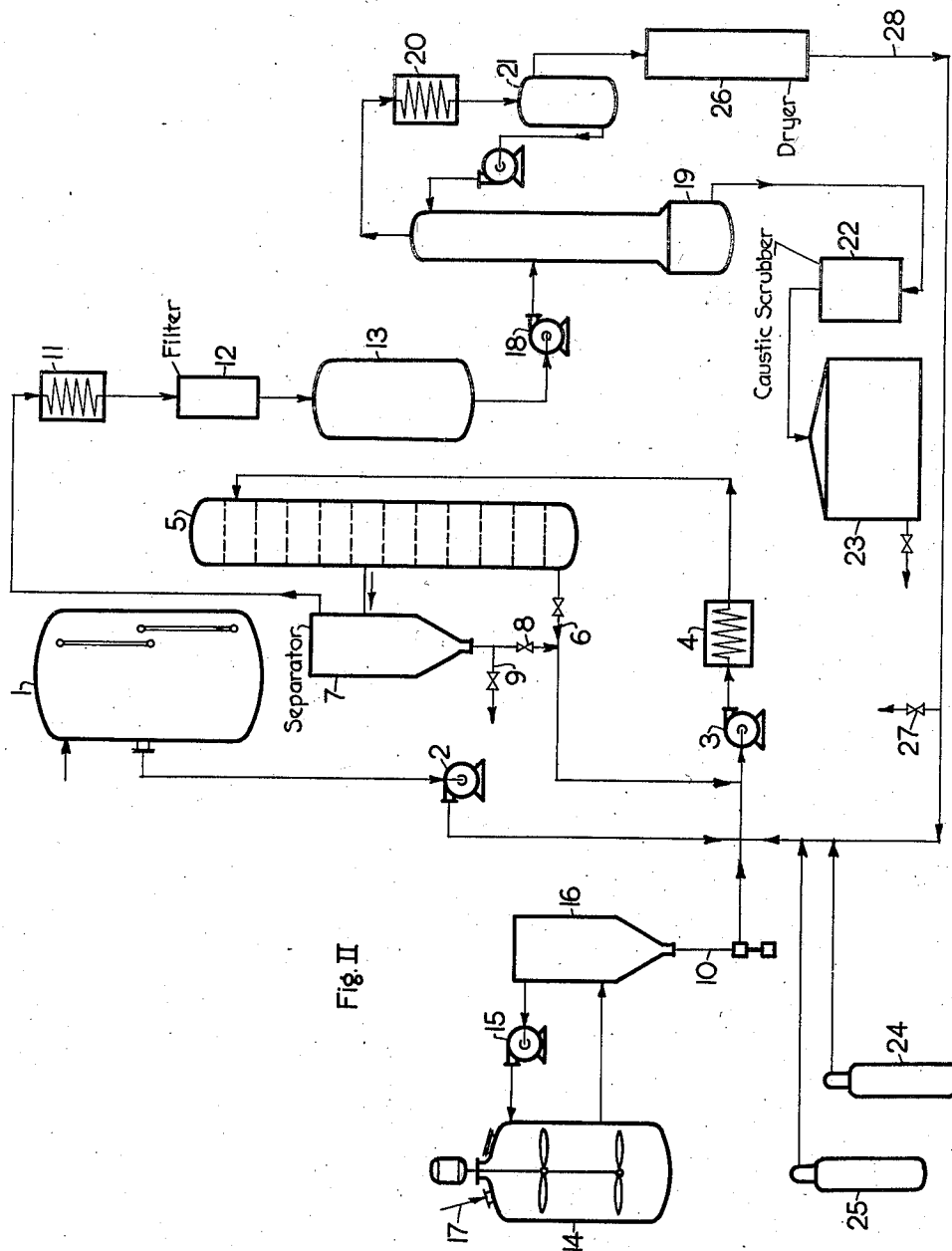
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UNITED STATES PATENT OFFICE

2,392,398

PROCESS FOR THE PRODUCTION OF
TOLUOL

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Application July 23, 1940, Serial No. 346,972

10 Claims. (Cl. 260-668)

The present invention relates to a process for the production of toluol from naphthenic distillates. An object of the invention is to provide a method whereby commercial grades of toluol suitable for nitration, solvent use, and the like may be produced in a most economical manner from available naphthenic hydrocarbon fractions of natural and/or synthetic origin.

Toluol is one of the primary compounds upon which aromatic chemistry is based. It is employed in large quantities as a starting material for the syntheses of a great variety of useful products such as dyestuffs. Explosives, drugs, flavors, perfumes, photographic developers, plastics, intermediate chemicals, and many others. Virtually the only source of toluol is, however, a by-product from the distillation of coal, being recovered in a yield of about 0.00125% based on the coal treated or about 0.25% based on the coal-tar obtained. Consequently, the supply of toluol is primarily dependent upon the condition of the steel and coal-tar industries and is in any case limited. Aside from the numerous uses where its application is more or less obligatory, toluol has a great many potential uses which have been curtailed by its limited supply and relatively high price. As a consequence considerable attention has been given to the possibility of producing toluol from other sources.

This problem has been considered from two angles. The first of these is to recover toluol from aromatic petroleum fractions, particularly cracked distillates. It is known that distillates from certain petroleum and most highly-cracked distillates contain appreciable quantities of aromatic hydrocarbons from which it is possible to recover highly aromatic distillates and even relatively pure aromatic hydrocarbons by a suitable combination of steps involving fractionation and extraction. The recovery of toluol from such distillates is, however, quite difficult and has not proven to be economical. In the first place, only a small proportion of the aromatic hydrocarbons in these distillates is toluol, and consequently, large quantities of material must be processed to recover relatively small yields. Furthermore, the toluol in these distillates, even after a preliminary close fractionation, is present in an extremely complicated mixture of hydrocarbons from which it is most difficult to separate a toluol of satisfactory purity. For some applications, such in particular as its use as a solvent, pure toluol is not necessary. For most of its applications, however, particularly where it is used as a starting material in various chemical syntheses, toluol of at least 98% purity is demanded. One of the major uses of toluol, for example, is in the production of T. N. T. Toluol for this purpose must be water-white, have a boiling range of not more than 1° C., and have a

specific gravity at 15.5/15.5° C. between 0.866 and 0.874. It must furthermore pass the standard sulphuric-acid wash test which means that it must be free of all but the minutest traces of olefine hydrocarbons and other impurities which are normally present in considerable quantities in the parent petroleum distillate. It is known that during the World War T. N. T. was produced from relatively impure toluol fractions obtained from petroleum distillates. This, however, necessitated executing the nitration step-wise with intermediate treatments for the removal of the impurities and was only resorted to due to the emergency at the time. While toluol of sufficient purity can be separated from cracked distillates if the separation and purification processes are carried far enough, the low yields obtained and the expense of the recovery generally make such processes impractical for commercial application.

The other approach to the problem is the synthesis of toluol from non-aromatic hydrocarbons. It has long been known that hydroaromatic hydrocarbons may be catalytically dehydrogenated to aromatic hydrocarbons. Thus, it has been shown in the laboratory that toluol may be easily produced from methylcyclohexane by catalytic dehydrogenation. While this has long been known it has not led to the commercial production of toluol due primarily to the lack of a suitable source of methylcyclohexane. It is known that certain naphthenic distillates contain appreciable quantities of methylcyclohexane. Here again, however, the small yields and difficulty of separation of a commercial grade of toluol detract from the practicability of the process.

Quite recently it was discovered by Moldavskii and co-workers that cyclic hydrocarbons can be produced catalytically from open-chain hydrocarbons by a new reaction now known as cyclization. Thus, it has been shown by laboratory experiments that fair yields of toluol may be produced from normal heptane, 2-methylhexane, 3-methylhexane and the corresponding olefines. The preparation of toluol from these open-chain hydrocarbons may be effected catalytically by passing vapors of the hydrocarbon over a cyclization catalyst under appropriate conditions whereby a simultaneous dehydrogenation and ring-closure takes place. It is thus seen that, starting from petroleum, toluol may be potentially produced from three sources: (a) recovery of naturally-occurring toluol, (b) formation of toluol from methylcyclohexane, and (c) formation of toluol from paraffinic hydrocarbons (n-heptane, 2-methylhexane, and 3-methylhexane) by cyclization-dehydrogenation.

According to the process of the invention, we produce toluol from naphthenic distillates. By naphthenic distillates we mean hydrocarbon distillates of natural or synthetic origin, containing

an appreciable quantity of naphthenic and paraffinic hydrocarbons having seven carbon atoms in the molecule. Suitable naphthenic distillates are obtained from a large number of crude petroleum. A few typical crudes from which suitable naphthenic distillates may be obtained are, for example, Los Angeles Basin crude, Huntington Beach crude, Dominguez Hill crude, Ventura crude and El Capitan crude. The naphthenic distillate is preferably fractionated to separate a narrow cut containing the larger part of the hydrocarbons having seven carbon atoms in the molecule. Such a fraction may, for example, boil between about 190° F. to 230° F. The boiling points of these convertible paraffin hydrocarbons are:

Normal heptane	209.2° F.
2-methylhexane	194° F.
3-methylhexane	197.3° F.

This fraction, if from a naphthenic distillate, also contains substantially all of the methylcyclohexane (boiling point 213° F.) present. These naphthenic distillates also usually contain a small but significant amount of toluol. Any toluol naturally present in the distillate is also included in such fractions.

A suitable method for the separation of such a fraction is illustrated in the attached Figure I. Referring to Figure I, it is seen that the naphthenic oil is fed to a still wherein all material boiling below the initial boiling point of the desired fraction is removed overhead. The bottoms from this still pass to a second still wherein the desired fraction is taken off overhead. The quantity of this fraction will vary according to the character of the distillate, but in most cases will be a sizable fraction. Typical analyses of these fractions from such crudes are, for example:

Aromatic hydrocarbons	1-10 by weight
Naphthenic hydrocarbons	15-75 by weight
Paraffin hydrocarbons	25-85 by weight

It is not practical, however, to produce toluol directly from such naphthenic fractions. This is due primarily to the fact that when subjecting such commercial fractions to a catalytic dehydrogenation-cyclization treatment the active life of the catalyst is very short. This requires frequent stopping of the reaction and reactivation of the catalyst. The reactivation treatment, which is effected by carefully burning deposited carbonaceous material from the catalyst under controlled conditions, greatly decreases the economy of the process since it is time-consuming, causes loss of material, causes a gradual permanent loss of the catalyst activity, and requires the handling of large quantities of reactivating and flushing gases. The results obtained upon subjecting such fractions to a conventional dehydrogenation treatment are illustrated by the following example:

Example

A straight run naphthenic gasoline was fractionated to prepare a 190-230° F. heart cut. A detailed investigation of its composition showed that it contained C₇ components in the following volume ratios:

Dimethyl cyclopentanes	1.1
Methyl hexanes	0.6
Methylcyclohexane	1.0
n-Heptane	0.5
Toluol	0.3

This material was subjected to a catalytic dehydrogenation-cyclization treatment under the following conditions:

- 5 Catalyst=Chromium oxide supported upon activated alumina (11% Cr.)
- Temperature=975° F.
- Time=6 hours
- Space velocity=0.73 vol. liquid/vol. catalyst/hour
- 10 Pressure=15 lbs./sq. in. exit pressure

Pure n-heptane, or pure methylcyclohexane, or a synthetic mixture of pure n-heptane and pure methylcyclohexane, when treated under these conditions, give excellent yields of toluol with little formation of carbon and gas. The above fraction, however, afforded a conversion to toluol of only about 7% to 10% (i. e. 15% to 17% toluol in the product). Moreover, the carbonaceous material deposited on the catalyst amounted to 4.6% by weight of the feed treated, and approximately 13% by weight of the feed was converted to gases. Under optimum conditions it required about 4 hours to regenerate the catalyst.

25 According to the process of the present invention, not only are the yields of toluol obtained from any given naphthenic distillate much greater, but the decline in the catalytic activity of the catalyst is much slower and less time is required for regeneration, and a crude toluol is produced from which commercial grades of toluol may be recovered more economically.

30 It is found that the above-described fractions from naphthenic distillates invariably contain considerable quantities of alkylated cyclopentanes, such in particular as:

	Boiling point, °F.
1,1-dimethylcyclopentane	189.5
1,3-dimethylcyclopentane	195.3
1,2-trans-dimethylcyclopentane	197.2
1,2-cis-dimethylcyclopentane	210.6

Other hydrocarbons which are usually found to be present to various extents include:

	Boiling point, °F.
3,3-dimethylpentane	186.8
2,3-dimethylpentane	193.5
3-ethylpentane	199.9
Propylcyclobutane	210.2-212
2,2,4-trimethylpentane	210.7

50 These latter hydrocarbons when present act primarily as inert diluents and are only detrimental insofar as they make the recovery of the toluol more difficult. The above-mentioned alkylcyclopentanes, on the other hand, are found to be very detrimental. When present, even in quite small quantities in the hydrocarbon fraction to be treated, they cause a rapid deterioration of the activity of the catalyst. It is found that if these detrimental alkylcyclopentanes are removed, the active life of the dehydrogenation-cyclization catalyst is greatly improved, much less frequent reactivation of the catalyst is required, and the process is made much more economical.

65 According to the process of the present invention, these detrimental-acting dimethylcyclopentanes are not only removed from the hydrocarbon fractions to be treated, but they are converted into toluol, thus materially increasing the yield. The removal of these poisoning dimethylcyclopentanes is effected by subjecting them to a suitable isomerization treatment whereby they are converted to a large extent to methylcyclohexane.

75 If such a hydrocarbon fraction from a naph-

thenic distillate, boiling for example between 190° and 230° F., is subjected to an appropriate isomerization treatment, it is found that a material improvement in the yield of toluol and economy of the process results. We found, however, that a much greater improvement is obtained if the naphthenic distillate is first separated into two fractions, one containing the major part of the normal heptane and methylcyclohexane (for instance, boiling above 200° F.), and the other containing the larger part of the dimethylcyclopentanes and methyl hexanes (for instance, boiling below 200° F.), and only the latter is subjected to the isomerization treatment. This improved method for producing toluol from such naphthenic distillates is more fully described and claimed in our copending application Serial No. 339,732, filed June 10, 1940.

We have now found that the method of our above-mentioned copending application does not afford the optimum yields and economy and that still further material improvement in the process may be realized by operating in a modified manner. According to the process of the present invention, the naphthenic distillate, consisting largely of hydrocarbons having seven carbon atoms in the molecule, is separated into two fractions. The separation of the two fractions in the present method, however, differs fundamentally from that of the method of the above-mentioned copending application. In the present method the naphthenic fraction is separated into a lower-boiling fraction (boiling, for example, up to about 218° F.) containing the major portion of the dimethylcyclopentanes and the methylcyclohexane and a higher-boiling fraction (boiling, for example, above about 218° F.) containing the major portion of any toluol present along with various higher-boiling impurities. These fractions are then treated as shown in the flow diagram, Figure I. Referring to Figure I, it is seen that the lower-boiling of the two above-described fractions taken overhead in the third fractionating column is subjected to an isomerization treatment. The isomerate passes to a fractionating column wherein it is separated into two fractions boiling below and above about 210° F. The lower-boiling fraction from the isomerate which contains considerable unconverted dimethylcyclopentane is subjected to a second isomerization treatment in a second isomerization unit and then to another fractionation. The lower-boiling fraction from the isomerate from the second isomerization unit contains any unconverted dimethylcyclopentanes and is removed from the system. The higher-boiling fractions from the fractionation of the isomerates are subjected to a catalytic aromatization treatment. The product from the aromatization treatment is fractionated to remove higher-boiling materials and the overhead fraction, together with the toluol fraction from the original naphthenic distillate, is passed to a recovery unit wherein toluol of the desired purity is recovered.

In the above description of the process the various fractions have been designated and described by their primary constituents. The preferred boiling ranges of the various fractions are shown in Figure I. It will be apparent, however, that certain deviations from the preferred boiling ranges shown are possible without departing from the spirit of the invention. Thus, for example, the fractionation in the third fractionating unit is designed to separate the distillate into a lower-boiling fraction containing the dimethyl-

cyclopentanes and methylcyclohexane and a higher-boiling fraction containing as much of any toluol present as may be conveniently separated without excessive loss of valuable methylcyclohexane from the lower-boiling fraction. When using conventional fractionating equipment the separation between these two fractions is preferably made at about 218° F. A certain amount of deviation is, however, permissible and may even be advisable in certain cases. The initial boiling point of the lower-boiling fraction may vary considerably, for example, from about 170° F. up to about 195° F. If the initial boiling point is chosen much below 190° F. more non-convertible hydrocarbons are included. On the other hand, if the initial boiling point is chosen much above 190° F. a loss in toluol yield may result. In general, the initial boiling point of the lower-boiling fraction is chosen at about 190° F., for example, 180° F. to 195° F. The final boiling point of the higher-boiling or toluol fraction is preferably chosen somewhat above 220° F., for example, 225° F. to 240° F. Although higher-boiling material may be included in the fraction, its presence is in general undesirable since it makes the recovery of pure toluol more difficult.

According to the present process, the lower-boiling of these two fractions is subjected to an isomerization treatment. This may be effected by contacting the fraction in the liquid or vapor phase, preferably in the liquid phase, under suitable conditions with an isomerization catalyst, a hydrogen halide promoter, and, if desired, hydrogen. Preferable isomerization catalysts are those comprising anhydrous aluminum chloride and/or aluminum bromide. Of these, aluminum chloride is preferred since it is less expensive, easier to employ and has much less tendency than aluminum bromide to cause degradation of the naphthenic hydrocarbons. Other acid-acting catalysts of the Friedel-Crafts type such as the halides of Zr, Zn, Sn, Be, Nb, Ta, Sb, B, Cu and Cd may also be employed if desired in conjunction with the aluminum chloride. The catalyst may, if desired, be employed as a solid, either in suspension in the liquid reaction mixture or as a fixed bed. In the latter case it is preferably employed as lumps, granules or pellets of suitable size, preferably deposited upon or mixed with a suitable solid support. Particularly effective catalysts are produced when aluminum chloride is supported upon or intimately mixed with one of the various preferably adsorptive siliceous and/or aluminous materials of natural or synthetic origin which contain an appreciable amount of firmly-bound water. Suitable materials of this category are, for example, the naturally-occurring minerals and clays such as pipe clay, bauxite, fuller's earth, bentonite, Florida earth, meerschau, kaoline, infusorial earth, kieselguhr, diatomaceous earth and the like; the various treated clays and clay-like materials such as "Tonsil," "Celite," "Sil-O-Cel," "Terrana" and the like; and artificially prepared materials such as "Activated-Alumina," silica gel, the artificial permutites and the like. These materials are preferably heated in a dry atmosphere at a moderately elevated temperature, such, for instance, as about 200° to 400° C., until they substantially cease to give off water. Although these materials produce preferred catalysts when combined with aluminum chloride, other supporting materials such as activated carbon, coke, crushed brick, pumice and the like may also be used.

While solid catalysts may be suitably employed, we have developed an improved and advantageous method whereby the isomerization treatment may be effected in a continuous manner using liquid catalysts. Particularly suitable liquid catalysts are those of the Gustavson (C. 1903 II, 1113) and Ansolvo (German Patent No. 535,473) acid types wherein aluminum chloride is in combination with various organic compounds such as organic acids, ethers, esters, hydrocarbons, etc. and those of the metal double-salt type in which the aluminum chloride is in loose combination with similar metal halides such, for instance, as the halides of Sb, Sn, Zr, Cu, Ti, Na, K, Li and the like. By employing aluminum chloride in combination with certain of these metal halides, excellent isomerization catalysts may be prepared which melt to free-flowing liquids at very moderate temperatures and may be pumped through the reaction system with or counter-current to the hydrocarbon fraction to be isomerized. The use of liquid catalysts in the isomerization has definite advantages. The naphthenic distillates to be treated often contain small amounts of aromatic and/or olefinic hydrocarbons. These hydrocarbon types, if present, are generally quite detrimental when employing fixed beds of catalysts. When employing fluid catalysts, hydrocarbon fractions containing small amounts of olefines and/or aromatic hydrocarbons may be treated without difficulty. These liquid catalysts, moreover, have a considerably milder action and in general are much less prone to cause degradation of the naphthenic hydrocarbons. Also, they allow the isomerization to be effected in simple apparatus in a continuous and most practical manner. A flow diagram of a suitable isomerization unit employing this principle is illustrated in the attached Figure II. Referring to Figure II, the hydrocarbon to be treated is fed from a storage tank 1 via pump 2 to a circulating pump 3 wherein it is mixed with a liquid catalyst and promoter and circulated through a heater 4 and time tank 5, and back to the circulating pump 3 via a valved line 6. The time tank 5 is preferably equipped with perforated baffles or other means to insure thorough contact with the hydrocarbon and liquid catalyst. All or a portion of the material passing through time tank 5 is withdrawn to a separating device 7 wherein the liquid catalyst is separated from the bulk of the hydrocarbon. The liquid catalyst from separator 7 is recycled to the circulating pump 3 via valve 8 and line 9. A portion of the partially-spent liquid catalyst may be continuously or intermittently removed if desired via valved outlet 9 and an equivalent amount of fresh catalyst may be added via pipe 10. The hydrocarbon from separator 7 is passed through a cooler 11 and filter 12 to remove any globules of suspended catalysts and is then passed to tank 13.

The assembly of apparatus illustrated diagrammatically in Figure II is adapted for the use of liquid catalysts of the above-mentioned Gustavson or Ansolvo acid types. The catalyst may be prepared in any conventional manner and supplied to the system, for instance, via line 10. For the sake of completeness provision is also made for the preparation of the catalyst in the flow diagram of Figure II. This apparatus, which may be considerably modified if desired, comprises a mixing vessel 14 interconnected in a circulatory system via circulating pump 15 to a small chamber 16. Aluminum chloride or other catalyst is charged to the mixing vessel 14 and a quantity of

the organic material to be reacted therewith to form the complex catalyst is introduced via line 17. This may be any one or a mixture of a great number of organic compounds. In case the complex catalyst is one of the Gustavson type (C. 1903 II, 1113) the liquid added may be an aromatic hydrocarbon or a hydrocarbon mixture rich in aromatic hydrocarbons. Aromatic hydrocarbons, as a class, are generally suitable. Thus, for example, benzol and the various alkyl derivatives thereof may be used. Particularly suitable catalysts of this type may be prepared from the so-called bright-stocks or Edeleanu extracts obtained by the extraction of aromatic-containing distillates with sulphur dioxide. These catalysts are found to contain approximately twice as much aluminum chloride, for example, as catalysts of the same general type prepared from benzol or toluol. They therefore have a much longer life. Catalysts of this type are described in United States Patents Nos. 1,671,517, 1,586,357, 1,999,345 and British Patent No. 7,112 (1914). Aromatic extracts obtained by extraction with other selective solvents may, of course, likewise be employed.

The isomerization treatment is preferably executed in the presence of a hydrogen halide promoter such, for example, as hydrogen chloride. The amount of promoter preferably employed depends upon the activity of the catalyst and the prevailing temperature, and may vary from a small amount such as about 0.05% up to several percent. In one preferred method of operation, wherein the hydrocarbon fraction is treated in a continuous manner in the liquid phase, a considerable excess of hydrogen chloride (for example, a partial pressure of hydrogen chloride vapor of at least 1 to 3 atmospheres) is employed and the hydrogen chloride is recycled through the reaction zone. Thus, in Figure II the product from tank 13 is forced via pump 18 to a stripping column 19 wherein the HCl promoter and any other lower-boiling material is taken off overhead. The overhead fraction is passed through a cooler 20 into a vessel 21. Condensed liquid in vessel 21 is pumped back to the stripping tower to serve as reflux. The bottom product from tower 19 is passed through a caustic scrubber 22 to remove any last traces of promoter and is then stored in tank 23. The hydrogen chloride promoter separated from the product in the stripping column is recycled back to the isomerization system via line 24. The hydrogen halide (and hydrogen, if this is used) recycled to the system is preferably passed through a drier 26 containing a suitable drying agent such as CaCl_2 , P_2O_5 , activated alumina, or the like. Small amounts of excess gas may be vented from time to time by valved outlet 27. Make-up hydrogen chloride is supplied to the system from any convenient source such as a high-pressure cylinder 24. As pointed out above, however, when using liquid catalysts the isomerization process may be executed with only very small amounts of hydrogen chloride promoter, for instance, less than 1%. In such cases, it may be more economical not to attempt to recover and recycle the promoter. In this case the product from tank 13 may be simply caustic-washed and sent to storage. Instead of feeding in hydrogen halide per se, the hydrogen chloride or other hydrogen halide promoter may be carried to the reaction zone, dissolved in one of the reactants, or may be generated in the reaction zone from added materials which under the reaction conditions react or decompose to liberate hydrogen halide.

Suitable materials which may be added for this purpose are, for example, organic halides such as organic alkyl halides, organic hydroxy compounds such as the various phenols and alcohols, inorganic salts containing molecularly-bound hydrogen halide such as $\text{PbSO}_4 \cdot 2\text{HCl}$, $\text{CuSO}_4 \cdot 2\text{HCl}$ and the like.

The isomerization may be effected over a wide range of temperatures depending upon the space velocity, concentration of promoter employed and upon the activity of the catalyst. Although temperatures ranging from about room temperature up to about 400° F. may be employed, the isomerization may be effected economically at quite moderate temperatures such, for example, as from about 100° F. to 200° F. In some cases, especially when the catalyst is particularly active or the temperature is somewhat high, it may be found that the isomerization is accompanied by appreciable amounts of side reactions. This may be easily remedied if it occurs by slightly decreasing the temperature or concentration of promoter, or if desired, by effecting the isomerization treatment in the presence of hydrogen. Hydrogen, if employed, may be conveniently recycled with the hydrogen halide promoter. Although the use of hydrogen is not generally necessary, provision for its use is shown in Figure II. Thus, if hydrogen is recycled along with the promoter, make-up hydrogen may be added from cylinder 25.

The isomerate from the first isomerization treatment is, according to the present process, subjected to a suitable fractionation designed to separate methylcyclohexane originally present and formed in the isomerization from unisomerized dimethylcyclopentanes and other lower-boiling non-aromatizable constituents. As shown in Figure I, the fractions may, for example, be cut at about 210° F. The lower-boiling dimethylcyclopentane fraction from the isomerate is subjected to a second isomerization treatment, as described, and refractionated. In this way a maximum yield of aromatizable hydrocarbons is separated with a minimum of detrimental dimethylcyclopentanes.

The higher-boiling fractions from the isomerates (boiling, for example, between about 210° and 215° F.) are subjected to a catalytic aromatization treatment in the usual manner. This may be most practically effected in one apparatus employing the recombined fractions, but it may also be effected separately with each fraction if, for any reason, this is desired. The dehydrogenation treatment may be effected by any of the conventional methods, using any of the conventional dehydrogenation and/or cyclization catalysts. In general, however, the dehydrogenation-cyclization treatment is effected by passing the vapors of the hydrocarbon through a reaction zone containing a bed of catalyst and maintained under suitable reaction conditions. The optimum reaction conditions depend upon the catalyst employed and may vary considerably. In some cases, for example, such as when employing a catalyst composed of nickel and tungsten sulfides, the reaction is preferably executed under a considerable hydrogen pressure, for example, from 20 to 100 atmospheres. In other cases, for example, when employing a catalyst comprising an oxide of a metal of the 4th, 5th or 6th group of the periodic system, the process is preferably executed under about atmospheric pressure, for example, from 1 to 4 atmospheres, with a mol ratio of hydrogen ranging from 0 up to about 8, de-

pending upon the temperature activity of the catalyst, space velocity, etc. Likewise, the temperature may vary considerably. Temperatures in the order of 900° to 1100° F. are, however, generally most suitable.

While the above-described process illustrated in Figure I of the drawings is entirely practical and suitable for general application with most naphthenic distillates, in certain cases it may be desirable to modify the treatment somewhat. Most naphthenic distillates contain small amounts of toluol. This toluol, although usually too small in amount to be of practical value per se, is recovered in the above-described process and increases the toluol yield. In certain cases, however, it may be found that the amount of toluol naturally present in the naphthenic distillate is too small to warrant its recovery. In such cases the third fractionating column may be eliminated and the overhead fraction from the second fractionating column, which is then preferably cut at about 190° to 218° F., may be passed directly to the first isomerization unit. Also, it may be advantageous to subject the isomerate to a second fractionation to remove small amounts of higher boiling products which may be formed under certain conditions prior to subjecting it to the catalytic aromatization treatment. A fractionating apparatus for this purpose is shown in Figure I in broken lines. Also, the fractionating column between the aromatization unit and the recovery unit (Fractionating unit VI in Figure I) may be eliminated, if desired, by returning the product from the aromatization unit directly to the naphthenic feed (for instance, to the feed to Fractionating units I or II). In general, however, the product from the aromatization unit consists almost entirely of toluol and is preferably fractionated in a separate unit (Fractionating unit VI).

The process of the present invention provides a means whereby toluol of almost any desired degree of purity may be obtained in high and practical yields from naphthenic distillates. Due to the substantially complete removal of detrimental dimethylcyclopentanes from the feed to be aromatized, the catalytic aromatization in the present process is much more efficient. The aromatization in the present process may, in general, be effected with exceptionally long and high conversions. Also, the feed to the aromatization step, which is the most costly phase, is reduced to a minimum without impairing the toluol yield. The products obtained from the dehydrogenation-cyclization treatment, according to the present process, are generally much higher in toluol and much lower in undesirable hydrocarbon impurities than those obtained from other methods. In many cases it is of sufficient purity to be used without further purification as a solvent and the like where a toluol of high purity is not required. An advantage of the present process is that the toluol may be recovered from the product in almost any desired degree of purity by relatively simple methods and with greater efficiency and economy. This is due largely to the fact that a considerable proportion of the contaminating impurities have been converted into toluol. Thus, it is generally possible to produce almost a complete yield of toluol meeting the stringent requirements for nitration by a simple extractive distillation. In some cases a wash with dilute sulphuric acid may be required.

The recovery of toluol of the desired purity may be effected by any one or combination of

conventional methods such as fractional distillation, azeotropic distillation, solvent extraction, extractive distillation, crystallization, or the like. Extractive distillation, being both highly effective and economical, is a preferred method. A suitable recovery unit employing extractive distillation is illustrated in the flow diagram of Figure III. Referring to Figure III, the toluol-containing material from the dehydrogenation unit is fed to a fractionating column 51, provided with condenser 52, collector 53, and means 54 for returning a part of the overhead material to establish reflux. Fractionating column 51 is adjusted to remove the greater part of the non-converted and lighter-boiling hydrocarbons. This lighter overhead fraction may be disposed of for other purposes such as motor fuel or may, depending upon its composition, be recycled. If it consists largely of open-chain paraffins including normal heptane, it may be recycled through the dehydrogenation-cyclization unit. If, as is sometimes the case, it also contains any appreciable quantities of alkyl cyclopentanes, it is preferably recycled through the isomerization treatment. The bottom product from fractionating column 51 may be subjected directly to the extractive distillation treatment. However, it is often advisable to first remove a relatively pure toluol fraction in a second fractionating column 55. The bottom product from column 55 consists of small amounts of higher-boiling impurities. This is withdrawn via line 56. The toluol fraction from column 55, after passing through the cooler 57 and collector 58, is pumped via pump 59 and line 60 to a column 61 adapted for extractive distillation. A suitable polar agent is fed at a suitable point near the top of the column in regulated quantity via pipe 62 and automatic control means 63. The polar agent employed in the extractive distillation may be any one of the many polar solvents having a preferential solubility for toluol and preferably having a boiling point of at least 220° F. Particularly suitable polar agents for this purpose are cresylic acid and other higher-boiling alkyl phenols, anilin, furfural, carbital, antimony trichloride, and the like. Hydrocarbon impurities are removed overhead from column 61 via pipe 64. The bottom product from column 61 containing the toluol and the polar agent is then fed to a fractionating or stripping column 65 wherein the toluol is separated from the polar agent. Substantially pure toluol is removed overhead via cooler 66, collector 67, and is led to storage or to a dilute acid treatment via pipe 68. The polar agent is recovered as a bottom product via pipe 69. It may be sent to storage and re-used in column 61. Further details regarding extractive distillation may be found in French Patent No. 815,302.

In the foregoing we have explained our invention in considerable detail indicating various preferred embodiments as well as certain modifications thereof. Numerous other suitable modifications, many of which may afford slightly more economical operation under certain circumstances, will at once be apparent to those skilled in the art. It is therefore to be understood that the invention is not limited to the exact form or forms described and that all such modifications as fall within the spirit of the invention are intended to be embraced in the language of the accompanying claims.

We claim as our invention:

1. In a process for the production of toluol from naphthenic straight run gasolines via catalytic

dehydrogenation, the method of producing increased yields of substantially pure toluol while realizing maximum catalytic efficiency which comprises separating from a naphthenic straight run gasoline stock by fractional distillation a fraction boiling between about 190° F. and about 218° F., treating said fraction with an aluminum chloride isomerization catalyst under isomerization conditions, separating the isomerizate by fractional distillation into a lower boiling fraction boiling between about 190° F. and about 210° F. and a higher boiling fraction, treating said lower boiling fraction of said isomerizate with an aluminum chloride isomerization catalyst under isomerization conditions, separating the isomerizate by fractional distillation into a lower boiling fraction boiling between about 190° F. and about 210° F. and a higher boiling fraction, subjecting said higher boiling fractions from the isomerizates to catalytic dehydrogenation with a dehydrogenation catalyst under dehydrogenation conditions, and recovering substantially pure toluol from the dehydrogenated product.

2. In a process for the production of toluol from naphthenic straight run gasolines via catalytic dehydrogenation, the method of producing increased yields of substantially pure toluol while realizing maximum catalytic efficiency which comprises separating from a naphthenic straight run gasoline stock by fractional distillation a fraction boiling between about 190° F. and about 218° F., treating said fraction with an aluminum chloride isomerization catalyst under isomerization conditions, separating the isomerizate by fractional distillation into a lower boiling fraction boiling between about 190° F. and about 210° F. and a higher boiling fraction, treating said lower boiling fraction of said isomerizate with an aluminum chloride isomerization catalyst under isomerization conditions, separating the isomerizate by fractional distillation into a lower boiling fraction boiling between about 190° F. and about 210° F. and a higher boiling fraction, separating the higher boiling fractions of said isomerizates by fractional distillation into a higher boiling fraction boiling above about 215° F. and a lower boiling fraction boiling between about 210° F. and about 215° F., subjecting said last-mentioned fraction to catalytic dehydrogenation with a dehydrogenation catalyst under dehydrogenation conditions, and recovering substantially pure toluol from the dehydrogenated product.

3. In a process for the production of toluol from naphthenic straight run gasolines via catalytic dehydrogenation, the method of producing increased yields of substantially pure toluol while realizing maximum catalytic efficiency which comprises separating from a naphthenic straight run gasoline stock by fractional distillation a fraction boiling between about 190° F. and about 218° F., treating said fraction with an aluminum chloride isomerization catalyst under isomerization conditions, separating the isomerizate by fractional distillation into a lower boiling fraction boiling between about 190° F. and about 210° F. and a higher boiling fraction, treating said lower boiling fraction of said isomerizate with an aluminum chloride isomerization catalyst under isomerization conditions, separating the isomerizate by fractional distillation into a lower boiling fraction boiling between about 190° F. and about 210° F. and a higher boiling fraction, subjecting said higher boiling fractions from the isomerizates to catalytic dehydrogenation with a dehydrogenation catalyst under dehydrogenation conditions,

run gasoline stock by fractional distillation a fraction boiling between about 190° F. and about 230° F., separating said fraction by fractional distillation into a lower boiling fraction boiling between about 190° F. and about 218° F. and a higher boiling fraction boiling between about 218° F. and about 230° F., treating said lower boiling fraction with an aluminum chloride isomerization catalyst under isomerization conditions, separating the isomerizate by fractional distillation into a lower boiling fraction boiling between about 190° F. and about 210° F. and a higher boiling fraction, treating said lower boiling fraction of said isomerizate with an aluminum chloride isomerization catalyst under isomerization conditions, separating the isomerizate by fractional distillation into a lower boiling fraction boiling between about 190° F. and about 210° F. and a higher boiling fraction, separating the higher boiling fractions of said isomerizates by fractional distillation into a higher boiling fraction boiling above about 215° F. and a lower boiling fraction boiling between about 210° F. and about 215° F., subjecting said last-mentioned fraction to catalytic dehydrogenation with a dehydrogenation catalyst under dehydrogenation conditions, combining the dehydrogenated fraction with the above-said first higher boiling fraction boiling between about 218° F. and about 230° F., and extracting substantially pure toluol from said combined fractions.

7. In a process for the production of toluol from naphthenic straight run gasolines via catalytic dehydrogenation, the method of producing increased yields of substantially pure toluol while realizing maximum catalytic efficiency which comprises separating from a naphthenic straight run gasoline stock by fractional distillation a fraction boiling between about 190° F. and about 230° F., separating said fraction by fractional distillation into a lower boiling fraction boiling between about 190° F. and about 218° F. and a higher boiling fraction boiling between about 218° F. and about 230° F., treating said lower boiling fraction with an aluminum chloride isomerization catalyst under isomerization conditions, separating the isomerizate by fractional distillation into a lower boiling fraction boiling between about 190° F. and about 210° F. and a higher boiling fraction, treating said lower boiling fraction of said isomerizate with an aluminum chloride isomerization catalyst under isomerization conditions, separating the isomerizate by fractional distillation into a lower boiling fraction boiling between about 190° F. and about 210° F. and a higher boiling fraction, subjecting said higher boiling fractions from the isomerizates to catalytic dehydrogenation with a dehydrogenation catalyst under dehydrogenation conditions, removing from the product of said dehydrogenation treatment by fractional distillation material boiling above about 230° F., and combining the remaining fractions with the above-said first higher boiling fraction boiling between about 218° F. and about 230° F., and recovering substantially pure toluol from said combined fractions.

8. In a process for the production of toluol from naphthenic straight run gasolines via catalytic dehydrogenation, the method of producing increased yields of substantially pure toluol while realizing 'maximum' catalytic efficiency which comprises separating from a naphthenic straight run gasoline stock by fractional distillation a fraction boiling between about 190° F. and about 230° F., separating said fraction by fractional dis-

6. In a process for the production of toluol from naphthenic straight run gasolines via catalytic dehydrogenation, the method of producing increased yields of substantially pure toluol while realizing maximum catalytic efficiency which comprises separating from a naphthenic straight

tillation into a lower boiling fraction boiling between about 190° F. and about 218° F. and a higher boiling fraction boiling between about 218° F. and about 230° F., treating said lower boiling fraction with an aluminum chloride isomerization catalyst under isomerization conditions, separating the isomerizate by fractional distillation into a lower boiling fraction boiling between about 190° F. and about 210° F. and a higher boiling fraction, treating said lower boiling fraction of said isomerizate with an aluminum chloride isomerization catalyst under isomerization conditions, separating the isomerizate by fractional distillation into a lower boiling fraction boiling between about 190° F. and about 210° F. and a higher boiling fraction, separating the higher boiling fractions of said isomerizates by fractional distillation into a higher boiling fraction boiling above about 215° F. and a lower boiling fraction boiling between about 210° F. and about 215° F., subjecting said last-mentioned

fraction to catalytic dehydrogenation with a dehydrogenation catalyst under dehydrogenation conditions, removing from the product of said dehydrogenation treatment by fractional distillation material boiling above about 230° F. and combining the remaining fraction with the above-said first higher boiling fraction boiling between about 218° F. and about 230° F., and extracting substantially pure toluol from said combined fractions.

9. The method of claim 1 further characterized in that the dehydrogenation treatment is effected with a dehydrogenation catalyst comprising chromium oxide.

10. The method of claim 1 further characterized in that the recovery of toluol from the dehydrogenated product is effected by extractive distillation.

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