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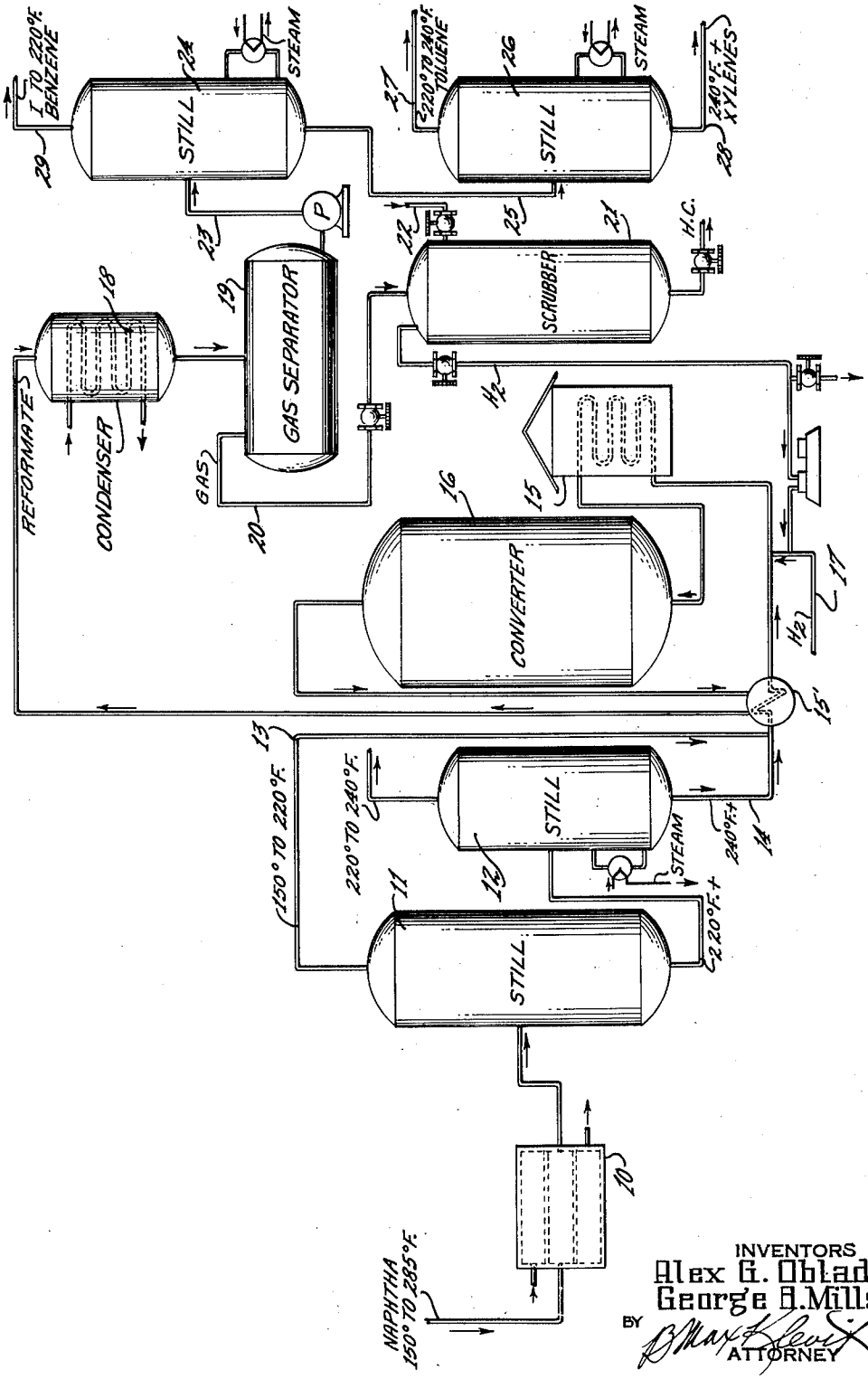

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PRODUCTION OF AROMATIC HYDROCARBONS

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The present invention relates to the production and recovery of aromatic hydrocarbons from a naphtha charge and is particularly concerned with improvements in operation of the process whereby the reaction products obtained include desired yields of aromatics, such as, benzene, toluene and xylenes, the reaction products being in a form such that they are readily separable by distillation to recover toluene of relatively high purity.

In known procedures for the production of desired aromatic hydrocarbons of substantial purity from petroleum, it has been the practice to treat only a very narrow fraction of the naphtha, rich in the component or components capable of being converted to the desired aromatic hydrocarbon. Thus, for the production of toluene, a naphtha cut of 200–250° F. boiling range and rich in methyl cyclohexane is charged to dehydrogenation. Often to obtain desired yields the hydrocarbon material charged is specially prepared; for instance, one or more dimethyl cyclopentane fractions are isomerized to produce methyl cyclohexane which is added to the methyl cyclohexane cut from the original naphtha to provide the charge for dehydrogenation. If other aromatic hydrocarbons are also to be produced by such separately blocked out operations, the process becomes cumbersome and expensive from the standpoint of additional equipment requirements.

By the present invention a novel method is provided whereby a selected naphtha fraction is reformed to convert C_7 naphthenes therein to toluene, while other components of the charge are simultaneously converted to aromatic hydrocarbons such as benzene and xylene, and the toluene cut distilled from the reformate is composed of toluene of relatively high purity; that is, in a form substantially uncontaminated by other hydrocarbons of approximately the same boiling point as toluene. This desirable result is achieved in accordance with the invention by distilling a naphtha fraction having a boiling range to include components from methyl cyclopentane through dimethylcyclohexane, to remove a heart cut of materials boiling within about 10° (F.) above and below toluene and comprising paraffins which would pass through the reforming process largely in unconverted form, or at least in noncyclicized form. The remaining naphtha, free of the heart cut, is then subjected to a step of dehydrogenation and reforming, the products of which step are distilled and a middle fraction boiling approximately in the range of 220–240° F. recovered, which cut will contain

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toluene in a state of fairly high purity. In the products boiling above and below this range a xylenes fraction and a benzene fraction, respectively, are separated.

The details of the process will be understood from the description which follows read in connection with the accompanying drawing illustrating the same by a schematic flow diagram.

A light naphtha charge, for example, a fraction boiling in the range of 150–285° F. and preferably of high naphthene content, is heated to required distillation temperature by being passed through a heating means such as a furnace or heat exchanger 10, and the heated charge is sent to a series of fractionating stills 11 and 12 to remove a heart cut in the toluene boiling range, for instance, that cut boiling in the range of 220–240° F. For example, in the still 11 the naphtha is separated into a light fraction boiling up to about 220° F. and a heavy fraction boiling above about 220° F., the latter being sent to still 12 to separate out therefrom lower-boiling material as an overhead fraction boiling for instance up to 240° F. The light fraction from still 11 is taken off overhead through line 13 and together with the higher boiling materials removed from still 12 by line 14 is heated to required temperature by being passed through heater 15 and sent to the reforming step carried out in a suitable pressurized converter 16, to which hydrogen or a hydrogen-rich gas is also admitted, supplied by line 17. The effluent from the reforming step is suitably cooled (18) and sent to a gas separator 19 wherein the condensed liquid components of the charge are separated from the fixed lower boiling point gases. The latter are withdrawn by a line 20 and the hydrogen-rich gas stream recycled to the reforming step carried out in converter 16. Preferably the gas and vapors in line 20 are further purified by being passed through a scrubber 21 to remove the major portion of the light hydrocarbon gases, in known manner, as by use of a suitable scrubbing liquid supplied through line 22.

The condensed liquid from the gas separator is sent by a line 23 to still 24 for separation into an overhead benzene cut boiling up to about 220° F. and a cut boiling above 220° F. withdrawn through line 25. The higher boiling cut is sent to a still 26 wherein it is separated into a toluene fraction containing the materials boiling over the range of 220–240° F. and a xylene fraction comprising the materials boiling above 240° F. The overhead from still 26 withdrawn through line 27 may have an average toluene concentration of

about 85%. Toluene of higher purity can be obtained in the effluent from still 26 by operating that still on separate batches of the 220° F.+ material from still 24 and separately collecting that portion of the overhead from still 26 constituting approximately the middle portion of the 220–240° F. boiling range material, for example that boiling at between 230–235° F. Or, if desired, the entire 220–240° F. fraction from still 26 may be redistilled and the toluene collected in a state of higher purity. The higher boiling materials from still 26, constituting the xylene fraction, are withdrawn through line 28 may be further separated and/or purified in known or desired manner, or may be employed as such in the blending of gasoline or the preparation of industrial products. Likewise, the benzene-containing cut from still 24 is withdrawn through line 29 and may be further fractionated and/or treated to recover benzene of desired purity. For instance, the benzene-containing cut or any desired distillate thereof may be subjected to selective extraction of the aromatics, for instance by chromatographic adsorption on silica gel. The invention is not limited to any particular method of treating or purifying the benzene fraction or the xylene fraction, details of one suitable method of operation employing an adsorption-desorption technique for recovery of aromatics are described in Olsen, U. S. 2,564,717, issued August 21, 1951.

The 220–240° F. cut taken out in still 12 constitutes but a minor part of the initial naphtha charge (150–285° F.), ordinarily less than about 10–15% thereof, and may contain a small amount of toluene. While the exclusion of the 220–240° F. materials separated in still 12 from the hydrocarbons charged to converter 16 may appear to represent some slight loss in possible toluene recovery, such exclusion is more than compensated by the improved purity of the obtained toluene fraction recoverable without substantial loss in yield by simple distillation of the reformate. It will be understood, of course, that the toluene content of the 220–240° F. fraction separated in still 12 may be separately recovered, if desired.

The various cuts from distillation which are not directly employed in the recovery of the desired benzene, toluene and xylene fractions are suitable for use as gasoline blending products or in other industrial applications requiring hydrocarbons. This applies, for instance, to the 220–240° F. cut from still 12 as well as to distillates that may be obtained by redistillation of the benzene cut in line 29.

The reforming step in converter 16 is preferably operated under conditions favoring the dehydrogenation of C_6 ring naphthenes accompanied by the dehydro-isomerization of alkyl cyclopentanes. The reforming operation is carried out at temperatures in the order of 850–1050° F. and pressures of from about 10–40 atmospheres, hydrogen being added to the charge in a quantity providing 1–10 mols per mol of hydrocarbon; space rates of from about 1 to 10 volumes of hydrocarbon per hour per volume of catalyst may be employed.

It has also been found that in the conversion of cyclohexane and/or methylcyclopentane to benzene over noble metal catalyst the pressure employed in the operation has a pronounced effect on the aromatics yield whereas in the case of forming toluene from methylcyclohexane or dimethylcyclopentane the effect of pressure while in the same direction is considerably less important. Accordingly, in the preferred operation of the reforming step employed in the present process when charging a naphtha distillate containing both benzene-forming and toluene-forming naphthenes, the pressure conditions are selected to favor good benzene yields. While progressive decrease in total pressure from about 800 to about 100 or 150 pounds per square inch results in increased benzene production, such pressure reduction also favors side reactions leading to coke build up, so that for a continuous non-regenerative process the selection of operating pressure should be accordingly limited. At an operating pressure of from about 250 to 400 pounds per square inch (gauge) good yields of both benzene and toluene are obtained without significant coke formation.

The preferred catalysts for the process are of the noble metal type, particularly supported platinum, the supporting carrier being one which has a high surface area and preferably little or no catalytic activity as such, for promoting carbon-carbon scission or polymerization. Suitable supports include activated alumina which has been leached with a mild acid, such as acetic acid; alumina which has been pre-treated with alkali earth metal oxide, for instance, that incorporating 0.5 to 5% MgO; and magnesia itself as a support. Only a relatively small amount of platinum is incorporated in the carrier as from about 0.05 to 2% by weight thereof, preferably less than 1%.

The lighter portion of the materials charged to reforming, the overhead fraction from still 11, which typically would comprise about 50% or more of the original naphtha charged to the still, contains principally paraffins and naphthenes in varying amounts depending upon the source of the naphtha, and perhaps a small amount of aromatics in the order of about 5% of the cut. The C_6 ring naphthenes, including cyclohexane and methylcyclohexane, are substantially completely dehydrogenated to benzene and toluene respectively, while the C_5 ring naphthenes, including methylcyclopentane and dimethylcyclopentane, are also largely converted to corresponding aromatic through dehydro-isomerization. Paraffins in the cut pass through largely unchanged.

The bottoms fraction (240–285° F.) charged to reforming likewise contains paraffins and naphthenes in proportions depending upon the source of the naphtha and generally a somewhat higher aromatics content than the lighter boiling cut. The paraffins which are mostly of the C_8 type pass through largely unchanged while the naphthenes are converted to xylenes. The 220–240° F. heart cut which is not charged to the reforming step contains paraffins boiling in the range of toluene and some naphthenes chiefly of the trimethylcyclopentane type.

Example

A straight run light naphtha boiling in the range of 150–270° F. was fractionated into (1) an overhead cut boiling up to 220° F. and comprising about 55 volume per cent of the naphtha, (2) a middle cut boiling in the range of 220–240° F. and comprising about 15 volume per cent, and (3) a bottoms cut of the remaining higher boiling materials constituting about 30 volume per cent. The middle cut being removed, the overhead and bottoms fractions were charged to reforming over a catalyst comprising 0.5% platinum on activated alumina which had been previously leached with acetic acid, operating at a pressure of 300 pounds per square inch at 950°

F., and at a space rate of 2 volumes of naphtha per hour per volume of catalyst; 3 mols of hydrogen being charged per mol of naphtha. Approximately 98% of the total naphthenes present were converted to aromatics but the paraffines remained substantially unchanged.

By distillation of the reformate and collecting the fraction boiling between about 220–240° F., toluene of about 85% purity is recovered, from which by redistillation toluene of 90–95% purity is obtained.

It will be understood of course, that the apparatus arrangement shown in the accompanying drawing is merely illustrative and that the operation of the process of the invention is not dependent thereon. For instance, the equipment requirements can be considerably simplified by resorting to batch or partial batch operation, and a single still can be used alternately for the various fractionating operations described, suitable provision being made for interim storage of collected products.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and therefore only such limitations should be imposed as are indicated in the appended claims.

What is claimed is:

1. The method of converting C_7 naphthenes in a naphtha charge to toluene with the simultaneous production of at least one aromatic hydrocarbon compound from the group consisting of benzene and xylenes, which method comprises: distilling a naphtha fraction of suitable boiling range to remove therefrom components boiling within 10° F. of toluene, reforming the remaining naphtha under dehydrogenating conditions effective at least to aromatize methyl cyclohexane, distilling the resulting reformate and recovering a toluene-containing distillate of narrow boiling range.

2. The method of producing toluene in a state of relatively high purity which comprises reforming in the presence of dehydrogenation catalyst a prepared naphthene-containing charge substantially devoid of hydrocarbon materials boiling in the range of about 220–240° F., and distilling the reformate to recover a reformed products fraction boiling within about 10° F. of toluene.

3. The method of reforming a naphtha charge for the recovery of a toluene distillate of enhanced purity from the reformate, which comprises distilling a naphtha fraction of suitable boiling range to separate out therefrom a middle cut boiling approximately over the range of 220–240° F., the remainder of the naphtha fraction including hydrocarbons boiling above and below the range of the middle cut and containing naphthenic C_7 hydrocarbons, subjecting to catalytic reforming at least a portion of said remainder substantially free from hydrocarbons boiling in the 220–240° F. range and containing said C_7 hydrocarbons, and distilling the resulting reformate to separate out a toluene-containing distillate, said distillate being of enhanced toluene purity.

4. The method as defined in claim 3 wherein said catalytic reforming is effected in the presence of a noble metal catalyst.

5. The method as defined in claim 3 wherein said original naphtha fraction of suitable boiling range is one of high naphthene content and comprises C_6 to C_8 hydrocarbon components.

6. The method according to claim 5 wherein said catalytic reforming is effected under pressure conditions favorable for the conversion of C_6 napthenes to benzene, without significant production of coke.

7. The method according to claim 5 wherein said catalytic reforming is effected in the presence of a noble metal catalyst and at a total operating pressure of from about 250–400 pounds per square inch gauge.

8. The method as defined in claim 5 wherein said catalytic reforming is effected in the presence of a catalyst comprising 0.05 to 2% Pt on an alumina support composed of activated alumina which has been leached with a mild acid.

9. The method as defined in claim 5 wherein said catalytic reforming is effected in the presence of a catalyst comprising 0.05 to 2% Pt on an alumina support composed of activated alumina which has been pretreated to incorporate 0.5 to 5% MgO therein.

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