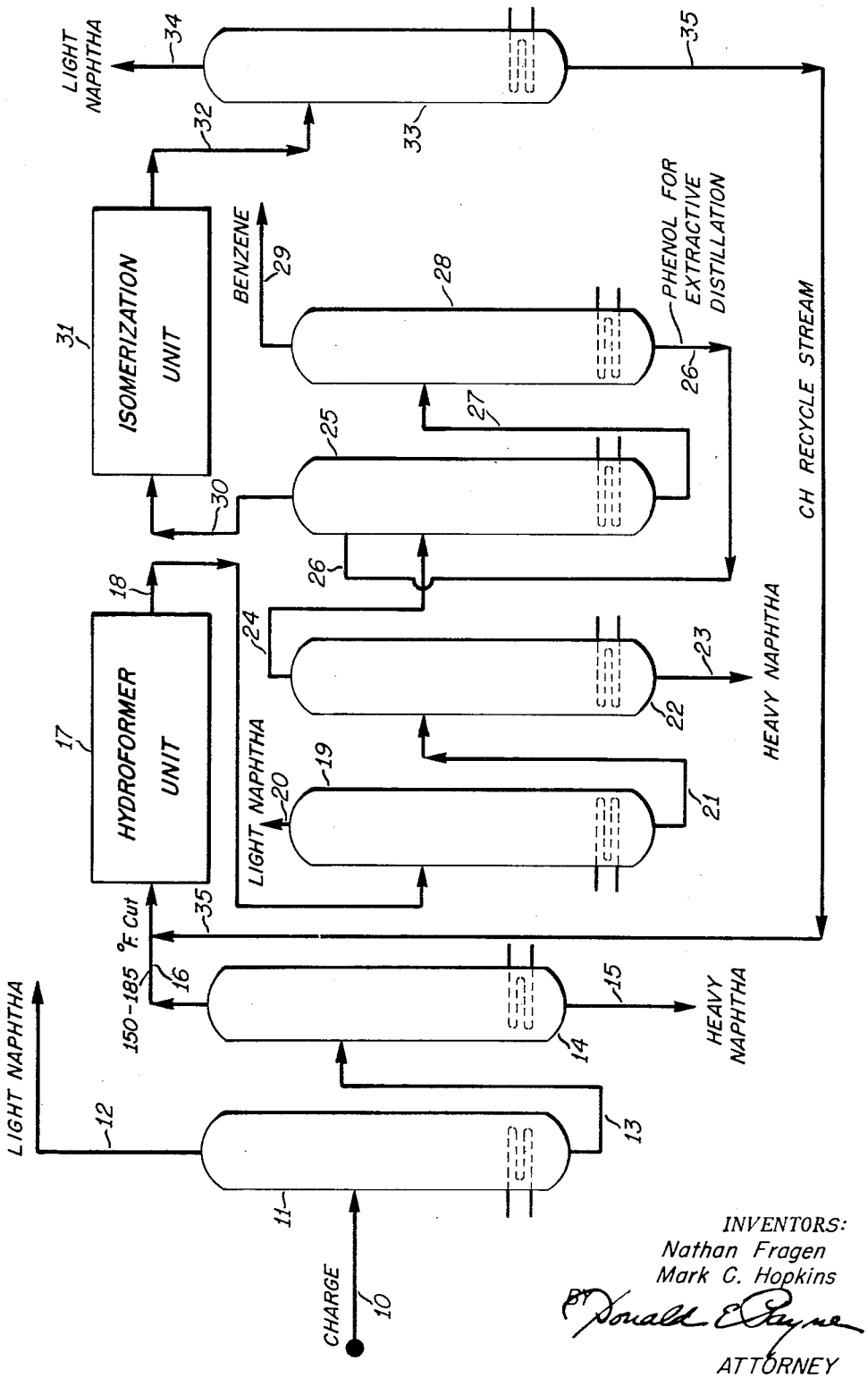
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PRODUCTION OF AROMATIC HYDROCARBONS FROM VIRGIN NAPHTHA

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PRODUCTION OF AROMATIC HYDROCARBONS FROM VIRGIN NAPHTHA

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This invention relates to the production of an aromatic hydrocarbon from virgin naphtha and it pertains more particularly to an improved method for increasing the amount of benzene obtainable from a given naphtha charge by a new combination of fractionation, dehydrogenation, isomerization and recycling steps.

In virgin naphtha, such as straight run and natural gasolines, the amount of benzene is usually quite small but there are considerably larger amounts of cyclohexane and methylcyclopentane. These three components of the virgin naphtha may be concentrated by fractionation into a heart cut boiling in the range of about 150° F. to 185° F. The cyclohexane component of the heart cut may be directly dehydrogenated to produce additional benzene, but the methylcyclopentane component must be isomerized to cyclohexane before it can be converted to benzene. It has been proposed to first treat a naphtha heart cut containing both cyclohexane and methylcyclopentane with an isomerization catalyst to convert a substantial amount of the methylcyclopentane to cyclohexane and then subject the resulting hydrocarbon mixture to dehydrogenation (U. S. 2,288,866), such procedure having been alleged to improve the effectiveness of the dehydrogenation catalyst by diminishing requirements of catalyst regeneration and replacement. It has now been found that the isomerization of such a heart cut prior to dehydrogenation presents serious operating difficulties, particularly when the virgin naphtha contains appreciable amounts of benzene. An object of this invention is to provide a distinctively different method of operation which will avoid the operating difficulties and disadvantages of said prior process. A further object is to provide a method of operation whereby the size and cost of the isomerization equipment will be greatly reduced, the effectiveness of the isomerization step will be remarkably increased, and the effectiveness of the dehydrogenation catalyst will likewise be enhanced with the overall result of obtaining a phenomenal increase in total benzene yield at lower operating costs than was heretofore believed possible.

A more specific object of the invention is to provide a process wherein a minimum amount of benzene is present in the charge to the isomerization step whereby the isomerization of methylcyclopentane to cyclohexane may be effected more rapidly and to a greater extent with minimum side reactions, such as alkylation. A further object is to provide a process which will enable charging to the dehydrogenation step a total hydrocarbon mixture which contains a higher percentage of naphthenes (both methylcyclopentane and cyclohexane) than was present in the initial heart cut. Still another object is to provide an improved method and means for eliminating paraffinic hydrocarbons from a recycle system in order to effect ultimate conversion of substantially all of the methylcyclopentane as well as the cyclohexane into benzene. Other objects of the invention will be apparent as the detailed description of the invention proceeds.

In practicing the invention, the heart cut (about 150° F. to about 185° F.) of virgin naphtha is supplemented and enriched with a recycle stream which is rich in both cyclohexane and methylcyclopentane, which is substantially free from benzene and from which hydrocarbons boiling below about 157° F. have been eliminated. This enriching step may actually increase the percentage of methylcyclopentane in the total dehydrogenation charge stream and it always increases the per cent of cyclohexane. It will thus be seen that there is no elimination of methylcyclopentane from the original heart cut component of the dehydrogenation charge; the dehydrogenation charge desirably contains considerable amounts of methylcyclopentane particularly when the dehydrogenation is effected in the so-called hydroforming operation by contact with an alumina molybdena catalyst (or other known dehydrogenation catalyst having isomerization properties) since some isomerization of methylcyclopentane to cyclohexane is effected in such hydroforming step itself which minimizes the amount of isomerization which must be effected in the separate isomerization step. The term molybdena as employed herein has the meaning commonly ascribed to it in the hydroforming catalyst art, i. e. it means molybdenum oxide just as chromia means chromium oxide, alumina means aluminum oxide etc.

The effluent stream from the dehydrogenation (hydroforming) step is again fractionated to obtain a heart cut having a true boiling point range from about 150° F. to 185° F. and this second heart cut is extractively distilled with a selective solvent, such as phenol, to remove substantially pure benzene and give an overhead or raffinate stream which consists chiefly of methylcyclopentane but which contains less than 5% and preferably less than 3% of benzene and which is much smaller in volume than the original heart cut. The isomerization of this fraction may be effected under known conditions with known catalysts, a preferred catalyst being an aluminum chloride-hydrocarbon complex which is too low in catalyst activity to effect extensive conversion of the paraffinic hydrocarbons which are present. The isomerization unit may be relatively small because the charge thereto is only about one-half to one-third the volume of the initial heart cut and the isomerization is effected more rapidly and with greater ultimate yields and with less by-product formation (by alkylation, etc.) because of the absence of benzene which was removed by the extractive distillation step.

The product stream from the isomerization unit is then fractionated by simple distillation or stripping to remove normal hexane and lighter hydrocarbons (some of which are methyl pentanes resulting from a small amount of isomerization of n-hexane) from a recycle stream which consists chiefly of cyclohexane and methylcyclopentane. The very small amount of benzene in this distillation or stripping step enables a more effective separation than would be obtained in the presence of larger amounts of benzene. The recycle stream is employed as a supplement for enriching the initial heart cut and providing an improved total charge for the dehydrogenation step.

From the above description, it will be seen that the process of this invention improves the effectiveness and the efficiency of both the hydroformer unit and the isomerization unit, but the most remarkable advantage of this process is that from a given amount of an initial heart cut it results in the obtaining of about 40% more benzene than could be obtained by the prior process of isomerizing initial heart cut to convert methylcyclopentane to cyclohexane prior to subjecting the initial heart cut to dehydrogenation.

The invention will be more clearly understood from the following detailed description of a specific example read in conjunction with the accompanying drawings which form a part of this specification and which illustrate a

schematic flow diagram of a plant for processing 17,130 barrels per day of straight run and natural gasolines.

The virgin naphtha in this example is a mixture of straight run and natural gasolines containing 1.2% benzene (all percentages are by volume), 3.9% methylcyclopentane, 2.8% cyclohexane and 92.1% of paraffinic hydrocarbons which may be considered as inerts in this process. This virgin naphtha is charged by line **10** to fractionator **11** for the removal of hydrocarbons boiling below about 150° F. (all boiling points recited are true boiling points at atmospheric pressure). Fractionator **11** may be a conventional tower containing about 65 trays and provided with the required reboiler and reflux means (not shown) and in this example about 5,629 barrels per day of light naphtha is taken overhead through line **12**.

The bottoms from tower **11** are introduced by line **13** to fractionator **14** which also has 65 trays. This fractionator like all other fractionators hereinafter described is provided with conventional heating means at its base and reflux means at its top. Tower **14** is operated to take overhead the first heart cut boiling from about 150° F. to about 185° F. and to remove as bottoms through line **15** about 8,449 barrels per day of heavy naphtha. The heart cut which is taken overhead through line **16** in amounts of about 3,052 barrels per day contains 6.2% benzene, 19.6% methylcyclopentane, 14.2% cyclohexane and 60.0% paraffinic or inert hydrocarbons.

Instead of subjecting this heart cut to isomerization for converting methylcyclopentane to cyclohexane, the heart cut is supplemented or enriched by a recycle stream in amounts of about 1021 barrels per day to give a total dehydrogenation charging stock of 4,073 barrels per day containing 5.0% benzene, 20.4% methylcyclopentane, 25.2% cyclohexane and 49.4% paraffinic hydrocarbons. It will thus be observed that in this example the charge to the dehydrogenation unit contained a higher percentage of methylcyclopentane, a higher percentage of cyclohexane, a lower percentage of benzene and a lower percentage of paraffinic hydrocarbons than were contained in the initial heart cut.

The dehydrogenation may be effected by the use of any known dehydrogenation catalysts under known conditions for said catalysts, but it is preferred to effect the dehydrogenation in a so-called hydroformer unit **17**. The hydroformer may be of the fixed bed, moving bed or fluid type and the catalyst employed therein is preferably molybdena on alumina, although other known hydroforming catalysts, such as chromia or other group VI oxides on alumina, cobalt molybdate, nickel tungstate, etc., may be employed. The hydroforming is usually effected with molybdena alumina catalyst at a temperature in the range of about 850 to 1050° F., under a pressure in the range of about 100 to 500 p. s. i., with a hydrogen recirculation rate of 1000 to 10,000 cubic feet per barrel and a space velocity of 0.2 to 2 volumes of charging stock per hour per volume of catalyst. Other known dehydrogenation processes may be employed, such as hydrofining, autofining, platforming (U. S. 2,479,109–10), etc., the specific operating conditions being chosen in any instance to correspond with the catalyst employed. Since no invention is claimed in the dehydrogenation step per se, this step does not require description in any further detail. However, the invention is particularly applicable to the use of hydroforming catalyst and operating conditions for effecting the dehydrogenation because of the improvement in the quality of other products produced and the conversion to benzene of certain components of the feed other than hydro-aromatics.

The product stream from the dehydrogenation step, i. e. from hydroformer unit **17**, is passed by line **18** to fractionating column **19**, which in this example is provided with 55 trays with conventional reflux and reboiler. In this example, 3,185 barrels per day of hydroformer effluent is thus fractionated, the total hydroformer effluent containing about 30.3% benzene, 23.6% methylcyclopentane, 6.4% cyclohexane, and 39.7% paraffinic or inert hydrocarbons. In this example, 287 barrels per day of light naphtha boiling below about 150° F. is taken overhead from tower **19** through line **20**. The bottoms from tower **19** are passed by line **21** to tower **22** which is provided with 65 trays and is operated to take overhead a second heart cut boiling in the range of about 150° F. to 185° F., in amounts of about 2,298 barrels per day. Thus, about 600 barrels per day of heavy naphtha is withdrawn from the base of tower **22** by line **23**.

The second heart cut is passed by line **24** to about the 20th or 25th tray of extractive distillation column **25** into which an extractive distillation solvent, such as phenol is introduced through line **26** at about the 40th or 50th plate in a 65 plate column. The extractive distillation column is operated with a phenol to charge ratio of about 2:1 to 10:1, e. g. about 8:1, so that substantially all of the benzene is carried with the phenol to the bottom of the tower which is provided with a suitable reboiler whereby substantially all hydrocarbons, other than benzene, are vaporized and discharged from the top of the column. The phenol-benzene solution is withdrawn from the base of the extractive distillation column through line **27** to stripper **28** from which about 965 barrels per day of benzene is recovered through line **29**. The lean phenol is recycled from the bottom of the stripper to the upper part of the extractive distillation column by line **26**. For simplicity, reflux means, reboilers, heat exchangers, etc. have been omitted from the drawings and more detailed description of the extractive distillation system is not required because such systems are well known to those skilled in the art.

The overhead from extractive distillation column **25** amounts to about 1,333 barrels per day and contains about 1.5% benzene, about 56.4% methylcyclopentane, 15.3% cyclohexane and 26.8% paraffinic or inert hydrocarbons. It will be observed that this overhead stream is much smaller in volume than the initial heart cut so that a relatively small isomerization unit may be employed. It contains only a small amount of benzene (preferably not more than about 3% benzene) and a relatively small amount of paraffinic hydrocarbons, but it is very rich in methylcyclopentane.

This stream is introduced by line **30** to isomerization unit **31** which is preferably a unit employing an aluminum chloride-hydrocarbon complex catalyst. Such catalysts are well known in the art (note U. S. 2,250,118). In this example, the catalyst is an aluminum chloride-aromatic hydrocarbon complex, although aluminum chloride complexes may be prepared from paraffinic, olefinic, and/or naphthenic hydrocarbons. The hydrocarbon content of the complex may be in the range of 30 to 40% or more by weight, for example about 35% by weight. The aluminum chloride-hydrocarbon complex is preferably milder in activity than the conventional aluminum chloride-hydrocarbon complex catalyst used for effecting disproportionation and/or isomerization of paraffinic hydrocarbons. The temperature employed for effecting the isomerization of methylcyclopentane to cyclohexane is lower than that employed for isomerizing or disproportioning paraffin hydrocarbons and is preferably in the range of about 160° to 220° F. Lower temperatures favor the desired equilibrium for obtaining maximum conversion of methylcyclopentane to cyclohexane, but lower temperatures likewise result in lower reaction rates. Higher temperatures improve reaction rates but lead to unfavorable equilibrium conditions (less methylcyclopentane conversion) and unduly high temperatures may lead to a substantial amount of paraffin conversion which in turn requires more make-up aluminum chloride for maintaining the desired catalyst activity. Because of the mild reaction conditions, no hydrogen is required for suppressing side reactions. A small amount of HCl promoter may be employed but is

not always necessary. No invention is claimed in the isomerization step per se and it should be understood that any known isomerization catalysts may be employed under their known operating conditions. The invention is particularly applicable to the use of catalysts such as aluminum halide-hydrocarbon complexes because with such catalysts the presence of excessive amounts of aromatics in the charging stocks inhibits the isomerization; the extractive distillation step for removing benzene immediately precedes the isomerization step and thus provides an ideal charge for this type of isomerization catalyst.

The isomerization effluent product stream is introduced by line **32** to fractionating or stripping column **33** which may be provided with about 65 trays and with the usual reboiler at its base. The stream introduced into tower **33** may contain about 1.5% benzene, about 23.4% methylcyclopentane, 47.7% cyclohexane and 27.4% paraffn hydrocarbons. The normal hexane and lighter hydrocarbons are removed overhead from column **33** through line **34** at the rate of about 285 barrels per day. The bottoms from column **33** are recycled through line **35** to supply the diluent for the first heart cut in line **16**. This recycle stream contains about 1.4% benzene, 22.5% methylcyclopentane, 57.9% cyclohexane and 18.2% paraffinic hydrocarbons. It will be noted that this recycle stream is actually richer in methylcyclopentane than the initial heart cut itself but it contains less benzene and inert paraffin hydrocarbons and consists chiefly of cyclohexane.

By the improved combination of steps hereinabove described, it will be seen that substantially all of the methylcyclopentane and cyclohexane which was present in the initial virgin naphtha is ultimately converted into benzene so that in this particular example 965 barrels per day of benzene is obtained. With the same amount of the same charging stock employed in a system wherein isomerization of the methylcyclopentane in the initial heart cut is effected prior to the hydroforming or dehydrogenation step in a once through operation as heretofore practiced, only 685 barrels per day of benzene is produced. This remarkable increase in benzene recovery is obtained without any corresponding increase in operating cost or detriment to either the hydroforming or isomerization unit operation; on the contrary, the hydroformer catalyst retains peak activity because the charge enrichment step increases the relative amount of cyclohexane while decreasing the amount of paraffin hydrocarbons, the isomerization unit operates at peak effectiveness because of the absence of large amounts of benzene and the relatively small amount of paraffin hydrocarbons, and the removal of normal hexane and lighter hydrocarbons (in column **33**) can be effected without the loss of appreciable benzene because this separation step is effected at a portion of the system wherein benzene concentration is small.

While the invention is primarily directed to the production of benzene from a virgin naphtha heart cut boiling in the range of 150° to 185° F., the invention may also be applied to the production of toluene from a virgin naphtha fraction boiling in the range of about 200° F. to 240° F. and corresponding fractions for higher boiling aromatics. Other known means such as solvent extraction, silica gel adsorption, etc., may be used instead of extractive distillation for removing benzene from the second heart cut. Other modifications and alternatives will be apparent from the above description to those skilled in the art.

We claim:

1. The method of obtaining benzene from a virgin naphtha containing cyclohexane and methylcyclopentane, which method comprises fractionating said naphtha to obtain a first heart cut boiling in the range of 150° F. to 185° F., enriching said first heart cut with a recycle stream which is richer in cyclohexane than said first heart cut, contacting said diluted first heart cut with a hydroforming catalyst under conditions to convert most of the cyclohexane to benzene, fractionating the product from the hydroforming step to obtain a second heart cut boiling in the range of about 150° F. to 185° F., recovering benzene from said second heart cut, isomerizing that portion of the second heart cut from which benzene has been removed to convert at least a part of the methylcyclopentane contained therein to cyclohexane, removing components lower boiling than about 157° F. from isomerization products, and recycling components of the isomerization products boiling above 157° F. to serve as a supplement to the charge in the enriching step.

2. The method of claim 1 wherein the hydroforming catalyst is a group VI metal oxide supported on alumina and the hydroforming conditions include a temperature in the range of 850° F. to 1050° F., pressure in the range of 100 to 500 p. s. i. g. and a hydrogen recycle rate in the range of about 1000 to 5000 cubic feet per barrel.

3. The method of claim 1 wherein the isomerization is effected with an aluminum halide hydrocarbon complex at a temperature in the range of about 160° F. to about 220° F.

4. The method of claim 3 wherein the aluminum halide-hydrocarbon complex is a complex of aluminum chloride and an aromatic hydrocarbon.

5. The method of claim 3 wherein the benzene is recovered from the second heart cut by extractive distillation.

6. The method of obtaining benzene from a narrow cut naphthenic virgin naphtha in approximately the benzene boiling range with a hydrogenative reforming catalyst under conditions favoring dehydrogenation of hydroaromatic naphthene hydrocarbons to aromatics, thereby converting substantially all of the hydroaromatic naphthenes to aromatics, fractionating the dehydrogenation effluent to obtain a second narrow cut fraction of approximately the benzene boiling range, recovering benzene from said second fraction, isomerizing that portion of said second fraction from which benzene has been removed to convert at least a portion of the methylcyclopentane contained therein to cyclohexane, separating out a fraction rich in cyclohexane from the isomerization products, and recirculating said cyclohexane fraction to contact with the hydrogenative reforming catalyst in admixture with fresh naphtha feed.

7. The method of claim 6 in which the hydrogenative reforming catalyst is a group VI metal oxide supported on alumina.

8. The method of claim 7 wherein the hydrogenative reforming catalyst is a molybdena alumina catalyst.

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