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CONVERSION OF ALKYLATED AROMATIC HYDROCARBONS

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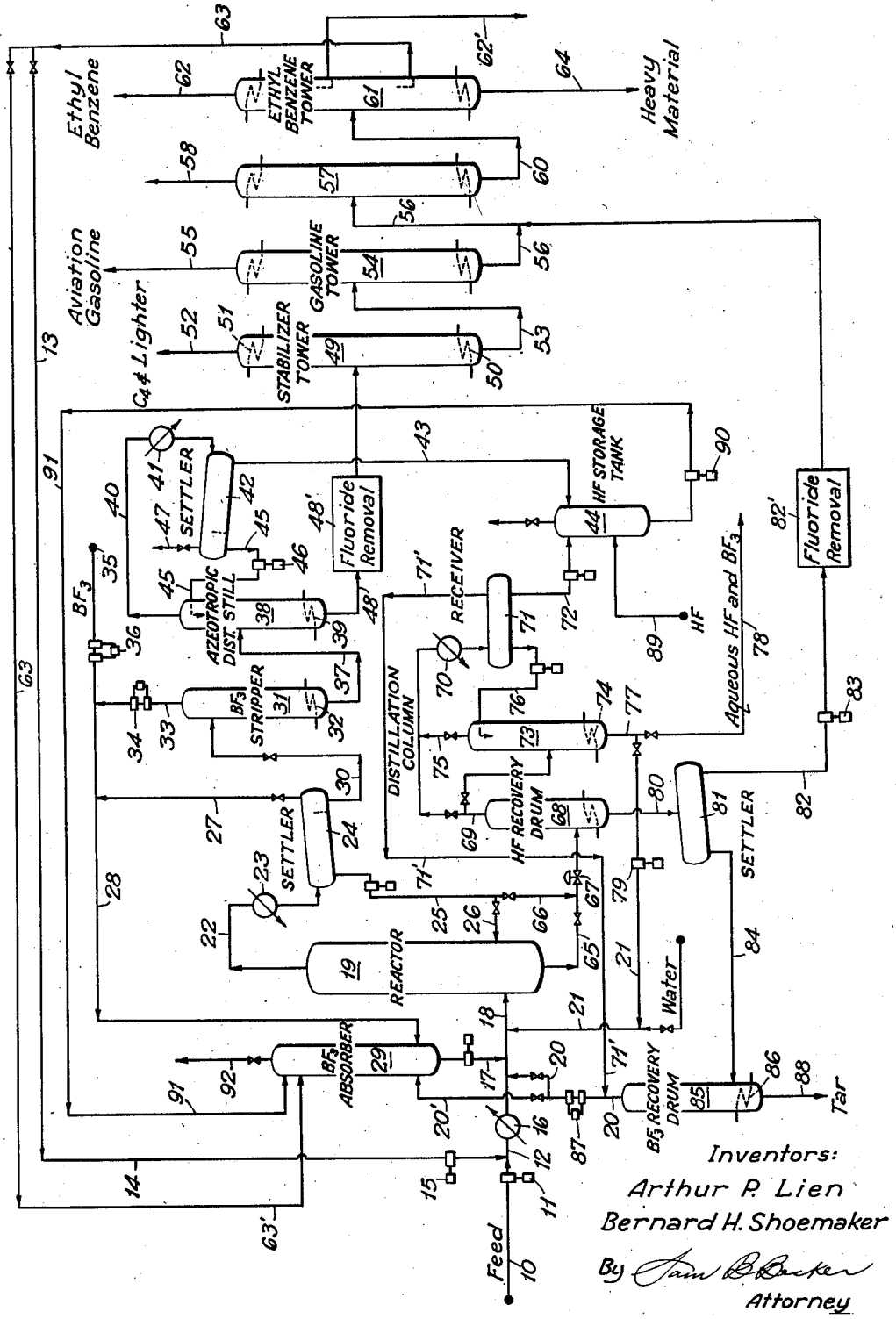

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CONVERSION OF ALKYLATED AROMATIC HYDROCARBONS

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This invention relates to a process for the conversion of alkyl aromatic hydrocarbons. More particularly, it relates to a process for the conversion of alkyl aromatic hydrocarbons containing at least three carbon atoms in the alkyl group to alkyl aromatic hydrocarbons containing less than three carbon atoms in the alkyl group, particularly ethylbenzene, by the use of a catalyst consisting essentially of hydrogen fluoride and boron fluoride.

Ethylbenzene is of great commercial importance for the manufacture of synthetic rubber, plastics, and for many other purposes. Of the higher alkyl benzenes, cumene has found some application as a component of aviation gasoline blends but this application has been relatively limited. Alkyl aromatic hydrocarbons having more than three carbon atoms in the alkyl group have found no commercial application per se, although heavy oils such as lubricants are believed to contain such alkyl aromatic hydrocarbons.

Of the petroleum refinery olefins, ethylene and the butylenes have found extensive commercial applications. Propylene in particular, is available in relatively high purity at low cost as a by-product of various petroleum refinery conversions, e. g., the cracking of petroleum oils. By the invention hereinafter set forth, refinery propylene fractions and benzene can be converted to high yields of ethylbenzene, this product being heretofore made almost exclusively from benzene and ethylene.

An object of our invention is to provide a simple, efficient and relatively inexpensive process for producing ethylbenzene. A further object is to provide a process for the preparation of ethylbenzene from benzene and olefins of greater molecular weight than ethylene, particularly from benzene and propylene. An additional object of our invention is to provide a process for the simultaneous production of ethylbenzene and valuable by-products such as aviation gasoline blending stocks, toluene, ethyltoluene, diethylbenzenes, etc.

A further object of our invention is to produce ethylbenzene and other valuable products from aromatics and readily available cheap hydrocarbons which are not themselves valuable gasoline components or chemical synthesis materials and to convert such hydrocarbons into valuable components and chemical synthesis materials simultaneously with the production of ethylbenzene. A further object is to employ such charging stocks and operating conditions as will enable the production and recovery of desired reaction products in relatively pure state; in other words, to avoid the presence or production of undesirable hydrocarbons of approximately the same boiling range as that of the desired products.

A further object of our invention is to provide an improved method and means for effecting hydrocarbon conversion with hydrogen fluoride-boron fluoride catalysts whereby such catalysts can be used with maximum effectiveness and with minimum losses. A further object is to provide an improved method and means for recovering hydrogen fluoride, boron fluoride and valuable aromatic hydrocarbons from the relatively spent catalyst material or complex which is produced in the reaction.

Briefly, we have found that alkyl benzenes having at least three carbon atoms in the alkyl group can be converted to valuable lower and higher boiling products containing an unexpected product in large proportion, viz., ethylbenzene, by intimately contacting said alkyl benzenes with a catalyst consisting essentially of hydrogen fluoride and boron fluoride under conversion conditions of temperature, pressure and time. Suitable charging stocks for our process include n-propylbenzene, isopropylbenzene, ethyltoluene, diethylbenzenes, diisopropylbenzene, isobutylbenzene and amylbenzenes. These charging stocks can be prepared by alkylating benzene with the appropriate olefins in the presence of alkylation catalysts. Thus, benzene can be alkylated with an olefin such as propylene by the use of phosphoric acid supported on kieselguhr. The reaction is carried out at 400–500° F., in the presence of 0.1 to 10% of steam to inhibit dehydration of the catalyst. Although the ratio of propylene to benzene in the alkylation step will affect the ratio of mono- to polyalkylbenzenes, some polyalkylbenzenes will invariably be formed and can be utilized, along with the cumene, in the conversion process of this invention.

The conversion may be effected at a temperature within the approximate range of 150 to 400° F.; the higher temperatures being employed with relatively low boron fluoride concentrations and the lower temperatures being employed with relatively high boron fluoride concentrations. The pressure should be sufficient to maintain substantially liquid phase conversion conditions and may be within the approximate range of about 200 to 2000 pounds per square inch. Hydrogen up to 1500 p. s. i. can be used to inhibit undesirable side reactions such as ring fusion and to prolong catalyst life. The time of contact will be somewhat dependent upon catalyst composition and temperature employed and may range from about

a minute to several hours. The space velocity in a continuous reaction system may be within the approximate range of about 0.2 to 4 volumes of hydrocarbon charging stock per hour per volume of catalyst in the reaction zone.

The proportion of boron fluoride to hydrogen fluoride is important. The use of too much boron fluoride results in excessive amounts of aromatics dissolving in the complex or catalyst layer which in turn requires an unduly high recycle ratio of complex for product and catalyst recovery. The use of too small amounts of boron fluoride leaves the aromatics undissolved and outside the sphere of catalytic influence. While 2 to 20% of boron fluoride by weight, based on hydrogen fluoride, is the preferred range for maximum catalyst effectiveness it should be understood that beneficial results may be obtained with the presence of only about 1% by weight of boron fluoride or an even lesser amount thereof and in some instances beneficial results may be obtained with the presence of even more than 20% by weight of boron fluoride. The catalyst should be substantially but not absolutely anhydrous since a trace of water (0.01 to 1% by weight) may improve the catalyst activity and water contents of 2 or 3% may be used.

Since boron fluoride is an expensive reagent it is essential that its losses from the conversion system be minimized. When light hydrocarbon gases such as methane must be purged from the system the problem of avoiding boron fluoride losses is considerably augmented. In our invention we absorb the tail gases from the hot settler following the reactor and/or from the boron fluoride stripper in an absorber liquid which can be relatively cool incoming hydrogen fluoride maintained at sufficient pressure so that the boron fluoride is absorbed or bound while hydrocarbons are substantially unabsorbed so that they can be removed in the liquid or gaseous state. A particularly desirable absorber liquid is an intimate mixture of an aromatic hydrocarbon, such for example as diethylbenzene, with hydrogen fluoride because boron fluoride forms a complex with such intimate mixtures or solutions and hence may be readily separated from other gases at pressures as low as atmospheric pressure.

The relatively spent catalyst material (which is a liquid mass containing catalyst complex, tarry material, dissolved catalyst components, aromatics, etc.) is reduced to a relatively low pressure and heated to about 90 to 200° F., preferably 100 to 160° F., to drive off dissolved or loosely bound hydrogen fluoride and boron fluoride, thus liberating substantial amounts of aromatic hydrocarbons from combination with the boron fluoride - hydrogen fluoride - hydrocarbon complex. The heated material is then allowed to settle for the separation and recovery of aromatic hydrocarbons. The remaining material is then heated to a higher temperature of about 200 to 500° F. for decomposing any complex present and thus recovering residual boron fluoride and hydrogen fluoride. A preferred temperature range is 230 to 350° F. when the operation is carried out at substantially atmospheric pressure, higher temperatures being required when higher pressures are employed. The boron fluoride and hydrogen fluoride thus recovered can be returned to the reactor.

Hydrogen fluoride may be recovered from the product stream by azeotropic distillation. Since no olefins are employed in the charging stock the problem of removing alkyl fluorides is greatly minimized if not entirely eliminated. The product stream will consist of a relatively few hydrocarbons so that the desired products can be readily separated from each other by simple fractionation.

The invention will be more clearly understood from the following detailed description read in conjunction with the drawing which forms a part of this specification and which is a schematic flow diagram of our improved continuous conversion process.

An alkyl benzene containing at least three carbon atoms in the alkyl group, for example, cumene or a mixture of cumene and diisopropylbenzenes, is introduced from source 10 by pump 11 through line 12. This hydrocarbon charge, which may be blended with a diethylbenzene fraction from a source hereinafter described, passing through lines 13 and 14 and pump 15, is passed through heater 16, admixed with catalyst from line 17, and introduced through line 18 at a low point in reactor 19.

The conversion may be effected in any suitable type of reactor on a batchwise, multiple batch, semi-continuous or continuous basis but we prefer to employ a continuous process with a tower-type reactor and to effect the conversion by passing the charging stock upwardly through the column of catalyst maintained in the liquid phase either with or without mechanical agitation. The reactor may be of the type generally used for effecting alkylation of olefins with isoparaffins as exemplified by U. S. 2,238,802 or it may be of the type described in U. S. 2,349,821 for effecting isomerization of paraffins. It may be about 5 to 50 feet in height and should be designed to withstand a maximum operating pressure which with the high temperatures may be as high as 2000 pounds per square inch. Before the reaction is initiated the reactor may be filled about half to three-fourths full of catalyst and heated by any conventional means to reaction temperature.

The catalyst in the reactor in this specific example is hydrogen fluoride containing 10 weight per cent (based on hydrogen fluoride) or boron fluoride. For each volume of hydrocarbon introduced into the reactor we may introduce between about 0.05 and 0.5, e. g., about 0.1, volume of the catalyst mixture, the bulk of this mixture being introduced through line 17 but a portion of it being introduced through line 20. With a substantially anhydrous charging stock a trace of water may be added and/or a small amount of aqueous hydrogen fluoride through line 21 so that the catalyst in the reactor will contain about 0.01 to 1% but not substantially more than 2 or 3% of water.

The reactor in this case can be operated at a temperature of about 300 to 330° F. and a pressure of the order of 1000 pounds per square inch. The charging stock passes upwardly through the liquid column of catalyst in the reactor and the bulk of the catalyst separates from the effluent product stream in the upper part of the reactor although some catalyst material is carried with the effluent product stream through line 22 and cooler 23 to separator 24. Catalyst material which settles out in this settler may be returned by lines 25 and 26 to the reactor. In this particular case the space velocity in the reactor can be about 1 volume of hydrocarbon charging stock per hour per volume of catalyst in the reactor.

The settler 24 may be operated at substantially reactor pressure and at sufficient elevation so that the liquid catalyst may flow by gravity back to the reactor. Alternatively we may employ

a pressure reducing valve in line 22 and operate the settler at a much lower pressure, for example of the order of about 200 to 400 pounds per square inch in which case a pump will be employed in line 25. When operating at such pressure that there is gas separation the gases are withdrawn through lines 27 and 28 to absorber 29. The overhead product stream passes through line 30 to boron fluoride stripper 31 which is provided with a suitable reheating means or reboiler 32 at its base. Line 30 may be provided with a suitable pressure reducing valve or pump depending upon the relative pressures in settler 24 and stripper 31 respectively. The stripper may operate at a pressure of about 200 to 300 pounds, for example about 250 pounds per square inch, and sufficient heat is supplied to insure the removal of substantially all of the boron fluoride which passes by line 33, compressor 34, and line 28 to the base of absorber 29. We prefer to operate the stripper and absorber at such temperatures and pressures that the use of compressor 34 may be eliminated. Make-up boron fluoride may be supplied from source 35 and introduced into the system by compressor 36 to line 28.

After removal of boron fluoride the product stream passes by line 37 to azeotropic distillation still 38 which is provided with a suitable heating means or reboiler 39 at its base and which may likewise be provided with reflux means at its top. A butane-hydrogen fluoride azeotrope passes overhead through line 40, through condenser 41 to settler 42 which is operated at as low a temperature as can be obtained with available cooling water, preferably well below 100° F. The condensed azeotrope separates into a heavier hydrogen fluoride layer which is withdrawn by line 43 to hydrogen fluoride storage tank 44. The upper butane layer is returned as reflux by line 45 and pump 46 to still 38 and eventually passes downwardly with the product stream. Any propane or lighter gases may be vented through line 47; such gases should contain no boron fluoride but if they do they may be compressed if necessary and introduced through line 28 to absorber 29.

If the product stream withdrawn from the base of azeotropic still 38 through line 48 is substantially free from alkyl fluorides and hydrogen fluoride it may require no special treatment for fluoride removal. A conventional bauxite or equivalent treating system 48' is, however, preferably employed at this point to insure the removal of any traces of alkyl fluorides and hydrogen fluoride which may be present.

The product stream is then introduced by line 48 into stabilizer or debutanizer tower 49 which is provided with a suitable heater or reboiler 50 at its base and suitable reflux means 51 at its top. In this and other fractionating towers any conventional heating and cooling means may be employed and in practice the reflux is usually obtained by condensing the overhead and returning at least a part of the resulting condensate to the top of the tower. A butane stream is withdrawn overhead through line 52 and it will consist chiefly of isobutane, which is valuable for producing isooctane by alkylation with butenes and for other purposes.

The stabilized or debutanized product stream then passes by line 53 to fractionating tower 54 which is likewise provided with a reboiler at its base and reflux means at its top and which is operated to take overhead a fraction boiling from about 70 to 140° F., i. e., to take overhead through line 55 pentanes (which consist chiefly of isopentane), neohexane and diisopropyl. The overhead stream is thus an exceptionally high quality aviation gasoline blending stock since it consists chiefly of isopentane and neohexane. The overhead may, however, contain at least a part of the methyl pentanes although we prefer to include the methyl pentanes as well as the normal hexane in the stream which is withdrawn from the base of tower 54 through line 56 to fractionating tower 57 which is provided with suitable reboiler and reflux means. Tower 57 is operated under such conditions as to take overhead through line 58 all hydrocarbons boiling between about 140 and about 260° F., namely methyl pentane, normal hexane, heptanes, benzene and toluene. It will be understood of course that if and when toluene is a desired product it may be separately fractionated and recovered, preferably by the use of a separate fractionating column.

The bottoms from tower 57 pass through line 60 to the ethylbenzene fractionating tower 61 which is provided with suitable reboiler and reflux means and from the top of which the ethylbenzene stream is recovered through line 62. A feature of our invention is the production of ethylbenzene rather than xylenes. Any minor amount of xylenes that may be produced may be separated from the ethylbenzene stream by super-fractionation, azeotropic distillation or any other means. An ethyltoluene fraction boiling chiefly in the range between about 320 and 335° F. may be withdrawn as a side stream through line 62' from tower 61 for dehydrogenation to produce methylstyrene or may be recycled to reactor 19. A diethylbenzene fraction may be recycled by line 63 via lines 13 and 14 through pump 15 and thence through lines 12 and 18 back to the reactor 19 or introduced by line 63' to absorption tower 29. Heavier material is preferably withdrawn from the system through line 64.

Relatively spent catalyst material may be withdrawn from the reactor through line 65 or from settler 24 through lines 25 and 66 and thence passed through pressure reducing valve 67 to recovery drum 68 which is preferably operated near atmospheric pressure, for example at about 5 pounds gauge pressure and at a temperature of the order of 100 to 160° F. Under these conditions, hydrogen fluoride and dissolved or loosely bound boron fluoride are liberated, passing overhead through line 69. This mixed effluent may pass directly through condenser 70 to receiver 71 where hydrogen fluoride is collected as a liquid and from which boron fluoride may be flashed overhead through line 71' to line 20. Liquid hydrogen fluoride may be pumped from receiver 71 via line 72 to hydrogen fluoride storage tank 44. If there is a tendency for moisture to accumulate in the system we may introduce the effluent from line 69 into distillation column 73 which is provided with heating means 74 and we may take substantially anhydrous hydrogen fluoride and boron fluoride overhead through line 75 and condenser 70 to receiver 71 returning a portion of condensate through line 76 to serve as reflux. Aqueous hydrogen fluoride-boron fluoride may be withdrawn from the base of column 73 through line 77 and withdrawn from the system through line 78 although a small part of the aqueous acid mixture may be returned through line 21 by pump 79 in order to supply the desired trace of water in the reactor.

Heating of the product in drum 68 results in

decomposition of the loosely bound boron fluoride-hydrogen fluoride complex and by removal of the fluoride components and of excess hydrogen fluoride solvent the aromatic hydrocarbons are thrown out of solution. The residue in drum 68, consisting of aromatic hydrocarbons and more-firmly-bound fluoride complex, is withdrawn through line 80 to settler 81 wherein an upper aromatic layer may be recovered from the lower complex layer and passed by line 82, pump 83 and a bauxite system 82' for fluoride removal to line 56. By removing boron fluoride and hydrogen fluoride from the spent catalyst material and employing the settling or separation step a considerable amount of aromatic hydrocarbons is recovered which would otherwise be lost. The larger the ratio of boron fluoride to hydrogen fluoride which is employed in the reactor the larger will be the amount of aromatics recovered in settler 81.

The complex and tarry material which settles out in settler 81 is withdrawn through line 84 to drum 85 which is provided with heating means 86. This drum is operated at about atmospheric pressure and at a temperature of the order of 230° to 350° F. or more under which conditions the complex is decomposed and boron fluoride and hydrogen fluoride are liberated. The liberated boron fluoride and hydrogen fluoride may be compressed by compressor 87 and returned by lines 20 and 18 to reactor 19, but is preferably introduced through line 20' to the base of absorber 29, the latter arrangement offering the advantage of providing better control on the amount and composition of catalyst entering the reactor. A tarry residue is withdrawn from the system through line 88.

Make-up hydrogen fluoride may be added to the system from source 89 to storage tank 44. Hydrogen fluoride is pumped from this storage tank by pump 90 and passed by line 91 to the upper part of absorber 29 which may operate at a pressure which may be as high as 1000 pounds per square inch and in this particular example may operate at about 240 pounds per square inch. At such pressures and at the relatively low temperature of the order of about 100° F. or lower the boron fluoride is absorbed in or chemically bound to the hydrogen fluoride but the hydrocarbon gases are unabsorbed therein and may be vented from the top of the absorber through line 92. By this means, losses of boron fluoride are substantially prevented while the system is being purged from methane and any other light gases which may tend to accumulate therein. It should be understood that make-up hydrogen fluoride may be introduced directly into the top of the absorber and that line 43 and/or 72 may likewise lead to the absorber rather than to a hydrogen fluoride storage tank.

Our invention is not limited to the use of hydrogen fluoride as the absorption medium, but it is important to note that absorption systems of the type used for hydrogen chloride in isomerization plants are not suitable for boron fluoride recovery, particularly since it is desirable to vent any propane through line 92 rather than from line 47. We have discovered that a most effective absorbent for boron fluoride is an intimate mixture or solution of an aromatic hydrocarbon such as toluene, ethyl-toluene, diethylbenzene, or the like with hydrogen fluoride. It appears that boron fluoride chemically reacts with such mixture to form a complex which is soluble in liquid hydrogen fluoride. By utilizing such complex formation to remove boron fluoride, it may be separated from extraneous gases at atmospheric pressure, so that compressor 87 may be eliminated as well as compressor 34.

An effective method of operation is to introduce enough diethylbenzene from line 63' to the upper part of absorber 29 to maintain a liquid hydrocarbon layer above the acid level in the absorber. Intimate mixing can be obtained by spraying hydrofluoric acid laterally or downwardly into this diethylbenzene layer (or by any other means) so that any boron fluoride not absorbed in the lower part of tower 29 will react with the intimate mixture in the top thereof to form complex and be positively prevented from leaving the absorber with extraneous gases. The resulting complex is scrubbed out of the mixture by incoming hydrogen fluoride and carried as a solution therein with the catalyst leaving the absorber through line 17.

Results obtainable by our invention are shown by a batch run wherein 3.1 mols each of benzene and cumene, 331 grams of hydrogen fluoride and 33 grams of boron trifluoride were introduced into a bomb provided with stirring mechanism and reacted at a temperature of 334° F. for 50 minutes under a pressure which rose to about 860 p. s. i. during the reaction period. Practically no hydrocarbon gases lighter than propane were produced and the amount of complex formed was estimated to be about 6.5 grams per mol of cumene charged. In a similar run employing aluminum chloride-hydrogen chloride, the "red oil" complex amounted to 28.3 grams per mol of cumene charged or more than 4 times the amount of complex that was produced in our hydrogen fluoride-boron fluoride run. This is an extremely important advantage of our invention because it effects enormous savings in charging stock and catalyst requirements, moreover, our catalyst may be always quantitatively recovered while the aluminum chloride complex can not be recovered by any practical method. In our process, the recovered hydrocarbons consisted of 14.5 weight per cent condensible normally gaseous hydrocarbons and 85.5 weight per cent of normally liquid hydrocarbons.

The analysis of products was as follows:

Condensibles

	Weight per cent
Propane	60.3
Isobutane	34.2
n-Butane	5.5

Liquids

	Volume per cent
Low boiling	1.4
Benzene	54.3
Toluene	10.7
Ethylbenzene	15.0
Ethyltoluene	5.7
Diethylbenzene and higher	12.9

Although benzene was added with the feed, it did not actually take part in the reaction. Therefore, based on the cumene charged, the following distribution of the liquid products is obtained:

	Volume per cent
Low boiling	2.3
Benzene	24.7
Toluene	17.6
Ethylbenzene	24.7
Ethyltoluene	9.4
Diethylbenzene and higher	21.3

An ultra-violet absorption spectrographic analysis of the ethylbenzene fraction yielded the following data:

	Per cent by volume
Ethylbenzene	94.8
m-Xylene	3.2
o-Xylene	None
p-Xylene	0.6

The relative freedom of the ethylbenzene fraction from xylenes is noteworthy.

It should be noted that under the reaction conditions as here used, there were indications of over-treatment, such as the appearance of a low boiling liquid fraction and the presence of n-butane in the condensibles fraction. Therefore, under milder conditions, a still more favorable distribution of products would be expected than that outlined above, especially as regards the production of condensibles and the ratio of isobutane to propane in the condensibles fraction. It will, of course, be appreciated that a considerably higher ultimate yield of ethylbenzene may be obtained by recycling ethyltoluene, diethylbenzene, and higher boiling fractions to the conversion process.

While we have described a preferred example of our invention in considerable detail it should be understood that our invention is not limited to the specific system or the particular conditions therein recited since many modifications and alternative conditions will be apparent from the above description to those skilled in the art. In some instances, for example, it may be desirable to hydrolyze the complex withdrawn from the bottom of settler 81 through line 84 instead of subjecting it to hydrogen fluoride-boron fluoride recovery. The complex withdrawn through line 84 is a mobile liquid, bright blue in color. It is insoluble in both hexane and benzene but after treatment with water, is soluble in these solvents. The hydrolyzed product has drying oil properties and may be utilized for the production of a drying oil or plastic materials instead of for the recovery of hydrogen fluoride and boron fluoride.

We claim:

1. A method for producing ethylbenzene which comprises intimately contacting an alkyl benzene containing at least three carbon atoms in the alkyl group with a catalyst consisting essentially of hydrogen fluoride and boron fluoride under elevated conversion conditions of temperature and pressure for a time sufficient to effect substantial conversion, and separating ethylbenzene from the conversion products.

2. The method of claim 1 wherein the alkyl benbene is isopropylbenzene.

3. The method of claim 1 wherein the alkyl benzene is diisopropylbenzene.

4. A hydrocarbon conversion process which comprises intimately contacting an alkyl benzene containing at least three carbon atoms in the alkyl group in a conversion zone with a catalyst consisting essentially of hydrogen fluoride promoted by about 2 to about 20% by weight of boron fluoride at a temperature in the range of about 150 to about 400° F. under sufficient pressure to maintain liquid phase conversion conditions for a period of time sufficient to effect substantial conversion.

5. The method of claim 4 wherein the alkyl benzene is isopropylbenzene.

6. A method for producing ethylbenzene which comprises intimately contacting isopropylbenzene in a conversion zone with a catalyst consisting essentially of hydrogen fluoride promoted by about 2 to about 20% by weight of boron fluoride at a temperature in the range of about 150 to about 400° F. under sufficient pressure to maintain liquid phase conversion conditions for a period of time sufficient to effect substantial conversion, removing conversion products from the conversion zone, separating ethylbenzene and higher boiling conversion products and recycling the last named products to the conversion zone.

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