

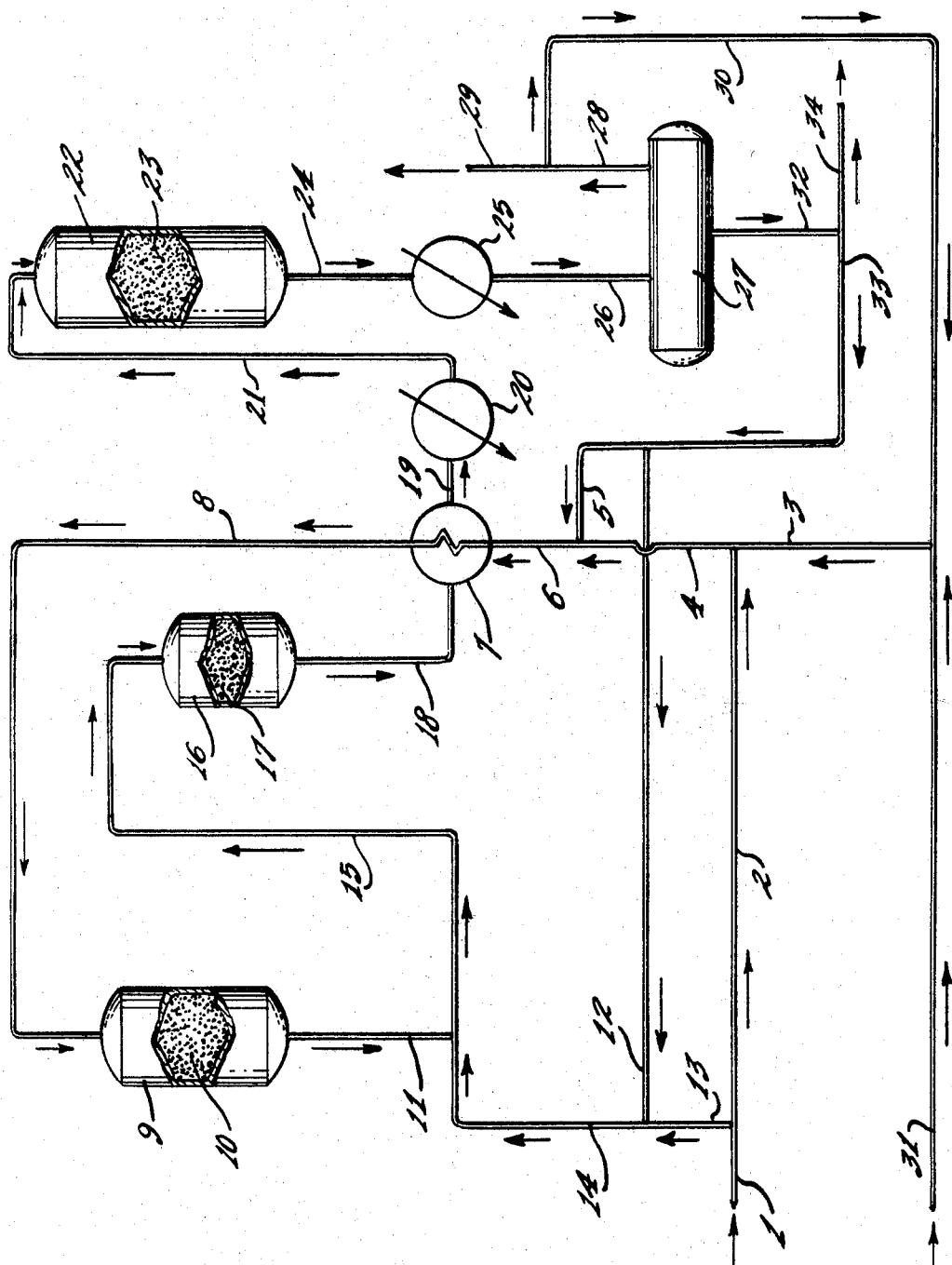
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CATALYTIC HYDROGENATION OF AROMATIC HYDROCARBONS

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1

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## CATALYTIC HYDROGENATION OF AROMATIC HYDROCARBONS

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This invention relates to an improved process for the catalytic hydrogenation of aromatic hydrocarbons to their corresponding cycloaliphatic hydrocarbons. More especially, the process for this invention is particularly applicable to the manufacture of high purity cyclohexane from benzene.

Cycloaliphatic hydrocarbons, such as cyclohexane, having a purity of at least 99.5% and often 99.9%, are presently required for many industrial uses. Due to the similarity in boiling points of hydrocarbons found in petroleum fractions as well as the tendency of cyclic hydrocarbons to form azeotropes, high purity cyclohexane cannot be obtained from petroleum fractions by distillation. Accordingly, various processes have been proposed for obtaining cyclohexane of the desired purity by the catalytic hydrogenation of substantially pure benzene. Known continuous catalytic processes, however, suffer from various disadvantages, including: a minimum number of at least four reactors in some suggested systems, low conversion at high space rates and difficult temperature control due to the exothermic nature of the hydrogenation reaction.

It has now been discovered that cycloaliphatic hydrocarbons, such as cyclohexane, may be obtained at a purity of approximately 99.9% at substantially 100% conversion of the feed material in operations conducted at space velocities of approximately two. Moreover, as more fully described below, the unique process design of the present invention avoids the necessity for complex and expensive internal or external reactor zone cooling means.

While the process of this invention is of interest in the conversion of benzene to cyclohexane, toluene to methyl cyclohexane, xylenes to dimethyl cyclohexane and naphthalene to tetra- or decahydronaphthalene, for simplicity the invention will be particularly described in terms of the conversion of benzene to cyclohexane.

In accordance with the present invention, a mixture of 20 to 35 weight percent and preferably 25 to 30 weight percent of the benzene feed stock, recycle cyclohexane and excess hydrogen, sufficient to provide a minimum hydrogen to hydrocarbon ratio of 2, at a temperature of 275 to 375° F. and a pressure of 350 to 550 p.s.i., is introduced to the first of three reaction zones and contacted with hydrogenation catalyst. In this reaction zone substantially complete hydrogenation occurs. The effluent, at a temperature within the range of 425 to 485° F., is blended with a mixture of recycle cyclohexane and the remainder of the benzene feed stock, having a temperature of about 100° F.

The blended mixture, at a temperature of 275 to 375° F., is then contacted with hydrogenation catalyst in a second reaction bed which is approximately a quarter to a third the volume of the first reaction zone. Conversion in the second reaction zone is maintained substantially within the range of 35 to 60 percent and preferably 40 to 50 percent by control of the amount and type of hydrogenation catalyst employed.

Reactants withdrawn from the second reaction zone, at a temperature of about 425 to about 485° F., are cooled by indirect heat exchange with the benzene feed stock supplied to the first reaction zone and then passed to the third and last reaction zone wherein substantially complete hydrogenation occurs. The third reaction bed is

2

about one and a quarter to about two times the volume of the first reaction bed.

The effluent stream from the last reaction zone is withdrawn, cooled to a temperature which is usually between 75 to 150° F. and passed through a flash drum for separation into a gaseous phase and a liquid phase. All or a portion of the gaseous phase, which comprises substantially pure hydrogen, is combined with make-up hydrogen and recycled to the first reaction zone. A portion of the liquid phase, which comprises substantially pure cyclohexane, is recycled back to the first and second reaction zones. The ratio of the cyclohexane recycle to total benzene feed stock is maintained between 0.5 to 3 and preferably is about 2. The remaining portion of cyclohexane is recovered as final product, which may be subjected to such additional treatment, if any, as desired.

The process of this invention is explained in more detail with reference to the accompanying drawing showing schematically a preferred embodiment of the present invention. While three distinct reactors are shown in the drawing, it should be understood that these reactors or additional reactors could be incorporated in a common housing or that one vessel having separate reaction zones could be employed. Valves, pumps, heaters, condensers, compressors, etc., have been omitted from the drawing for the sake of simplicity.

Hourly, 363 mols of benzene at 100° F. and 530 p.s.i.g. is passed along line 1. 91 mols of this benzene proceeds through line 2 and is added to a 100° F. mixture of 3263 mols of hydrogen and 1003 mols of methane from line 3. 308 mols of cyclohexane at 100° F. from line 5 is then added to the admixture in line 4 and the resulting mixture is passed through line 6 to heat exchanger 7 where it is heated to about 300° F. The heated mixture is next transmitted by line 8 to the first reaction zone 9 wherein substantially complete hydrogenation is effected in the presence of catalyst bed 10.

The effluent from the first reaction zone, at a temperature of 450° F., passes through line 11 and is combined with a 100° F. mixture (from line 14) of 453 mols of cyclohexane (line 12) and 272 mols of benzene (line 13). The combined materials in line 15, at a temperature of 300° F., are then passed to the second reaction zone 16 where 40 to 50 percent conversion is effected in the presence of catalyst bed 17.

The effluent from the second reaction zone, at a temperature of 470° F. in line 18, is subjected to indirect heat exchange with the line 6 material in heat exchanger 7. The cooled effluent is then transmitted through line 19 and further cooled by injection of recycle cyclohexane in means not shown or by cooler 20 to provide a material having a temperature of 300° F. in line 21 which is introduced into the third and final reaction zone 22. Complete hydrogenation is effected in this last reaction zone in the presence of catalyst bed 23.

The effluent from the third reaction zone (line 24), at a temperature of about 445° F. is condensed by cooler 25 and passed through line 26 into a high pressure flash drum 27. Liquid and vapor phases are separated in flash drum 27. The vapor phase (line 28) consists substantially of hydrogen. A portion of this vapor phase is vented in line 29, while the remainder is recycled in line 30 and combined with a make-up gas mixture of 1200 mols of hydrogen and 62 mols of methane from line 31. Similarly, a portion of the liquid phase (in line 32), at 100° F. and 530 p.s.i., is recycled through line 33 to lines 5 and 12 while the remainder is recovered in line 34 as final product having a composition of 362 mols of cyclohexane and 3 mols of methane.

The catalyst employed is conventional hydrogenation catalyst and may be the same or different in each reaction zone. Such catalysts include nickel, cobalt, platinum,

palladium, rhodium, iron or ruthenium preferably supported on a material such as alumina, silica, pumice stone, asbestos, kieselguhr, diatomaceous earth, etc. These catalysts may be used in the form of a stationary, moving or fluid bed. However, the stationary or fixed bed is preferred.

In the present process, hydrogen may be used either in pure form or in admixture with diluent gases such as nitrogen or methane. If desired, a portion of the recycled gases may be liquefied to separate one or more of the inert or diluent gases from the hydrogen.

From the foregoing description, it may be seen that the process of this invention provides a means of obtaining substantially pure cycloaliphatic hydrocarbons in a continuous process that is well adapted to large scale commercial operation. It is also seen that the exothermic hydrogenation reaction is completely and effectively controlled—thereby avoiding local over-heating of the catalyst and destructive temperatures within the reaction zones which could result in degradation reactions causing product contamination. This temperature control is accomplished by the present invention without the necessity for either internal or external reaction zone cooling means.

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 process for the catalytic hydrogenation of an aromatic hydrocarbon to the corresponding cycloaliphatic hydrocarbon in three reaction zones which comprises: mixing 20 to 35 weight percent of the aromatic hydrocarbon feed stock with its corresponding cycloaliphatic hydrocarbon and hydrogen; contacting the resulting admixture with hydrogenation catalyst in the first reaction zone to effect substantially complete hydrogenation of said aromatic feed stock; cooling the effluent from the first reaction zone by admixture with the remaining total balance of 65 to 80 weight percent of the aromatic hydrocarbon feed stock and additional cycloaliphatic hydrocarbon corresponding to the aromatic hydrocarbon feed stock; contacting the resulting cooled effluent admixture with hydrogenation catalyst in a second reaction zone, which zone contains but from  $\frac{1}{4}$  to  $\frac{1}{3}$  the volume of catalyst in said first zone, to effect 35 to 60 percent hydrogenation of the aromatic hydrocarbon present; cooling the effluent from the second reaction zone; contacting the cooled effluent from the second reaction zone in a third combined polishing and reaction zone with hydrogenation catalyst to effect complete hydrogenation of the remaining aromatic hydrocarbons; separating the effluent from the third reaction zone into liquid and vapor phase materials; recycling a portion of the vapor phase material comprising hydrogen to the first reaction zone; recycling a portion of the liquid phase material comprising cycloaliphatic hydrocarbon to the first and second reaction zones; and recovering the remaining portion of the liquid phase material as cycloaliphatic hydrocarbon product material.

2. The method of claim 1 wherein the ratio of the recycled cycloaliphatic hydrocarbon material to the aromatic hydrocarbon feed stock is between 0.5 and 3.

3. The process for the catalytic hydrogenation of benzene to cyclohexane in three reaction zones which com-

prises: mixing 20 to 35 weight percent of the benzene feed stock with cyclohexane and hydrogen; contacting the resulting admixture with hydrogenation catalyst in the first reaction zone to effect substantially complete hydrogenation of said benzene feed stock; cooling the effluent from the first reaction zone by admixture with the remaining total balance of 65 to 80 weight percent of the benzene feed stock and additional cyclohexane; contacting the resulting cooled effluent admixture with hydrogenation catalyst in a second reaction zone, which zone contains but from  $\frac{1}{4}$  to  $\frac{1}{3}$  the volume of catalyst in said first zone, to effect 35 to 60 percent hydrogenation of the benzene present; cooling the effluent from the second reaction zone; contacting the cooled effluent from the second reaction zone in a third combined polishing and reaction zone with hydrogenation catalyst to effect complete hydrogenation of the remaining benzene; separating the effluent from the third reaction zone into a liquid phase and a vapor phase; recycling a portion of the vapor phase material to the first reaction zone; recycling a portion of the liquid phase material comprising cyclohexane to the first and second reaction zones; and recovering the remaining portion of the liquid phase material as product cyclohexane.

25 4. The method of claim 3 wherein the ratio of recycled cyclohexane to the benzene stock is between 0.5 to 3.

5. The method of claim 3 wherein the ratio of hydrogen to benzene and cyclohexane in the first reaction zone is at least 2.

6. The method of claim 3 wherein the operating conditions of pressure and temperature are substantially the same in each of the three reaction zones.

7. In a process for the catalytic hydrogenation of an aromatic hydrocarbon to its corresponding cycloaliphatic hydrocarbon in three catalytic reaction zones, through which hydrogen passes seriatim, and within each of which zones the outlet temperature is kept below 500° F., the improvement which comprises:

40 (a) feeding the first zone with 20 to 35 weight percent of the total aromatic hydrocarbon feed and effecting, solely within that zone, substantially total hydrogenation of said aromatic feed;

45 (b) providing in the second zone an amount of catalyst which is only  $\frac{1}{4}$  to  $\frac{1}{3}$  the amount in the first zone;

50 (c) feeding to the second zone the balance of the total aromatic hydrocarbon feed, not fed to the first zone, and effecting in said second zone from 35 to 60 percent hydrogenation of said fresh feed;

55 (d) feeding to said third zone the effluent from said second zone and effecting therein substantially complete hydrogenation and polishing of all aromatic material.

8. The process of claim 7 wherein said aromatic material comprises benzene and said corresponding cycloaliphatic product is cyclohexane.

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65 SAMUEL P. JONES, Primary Examiner.

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