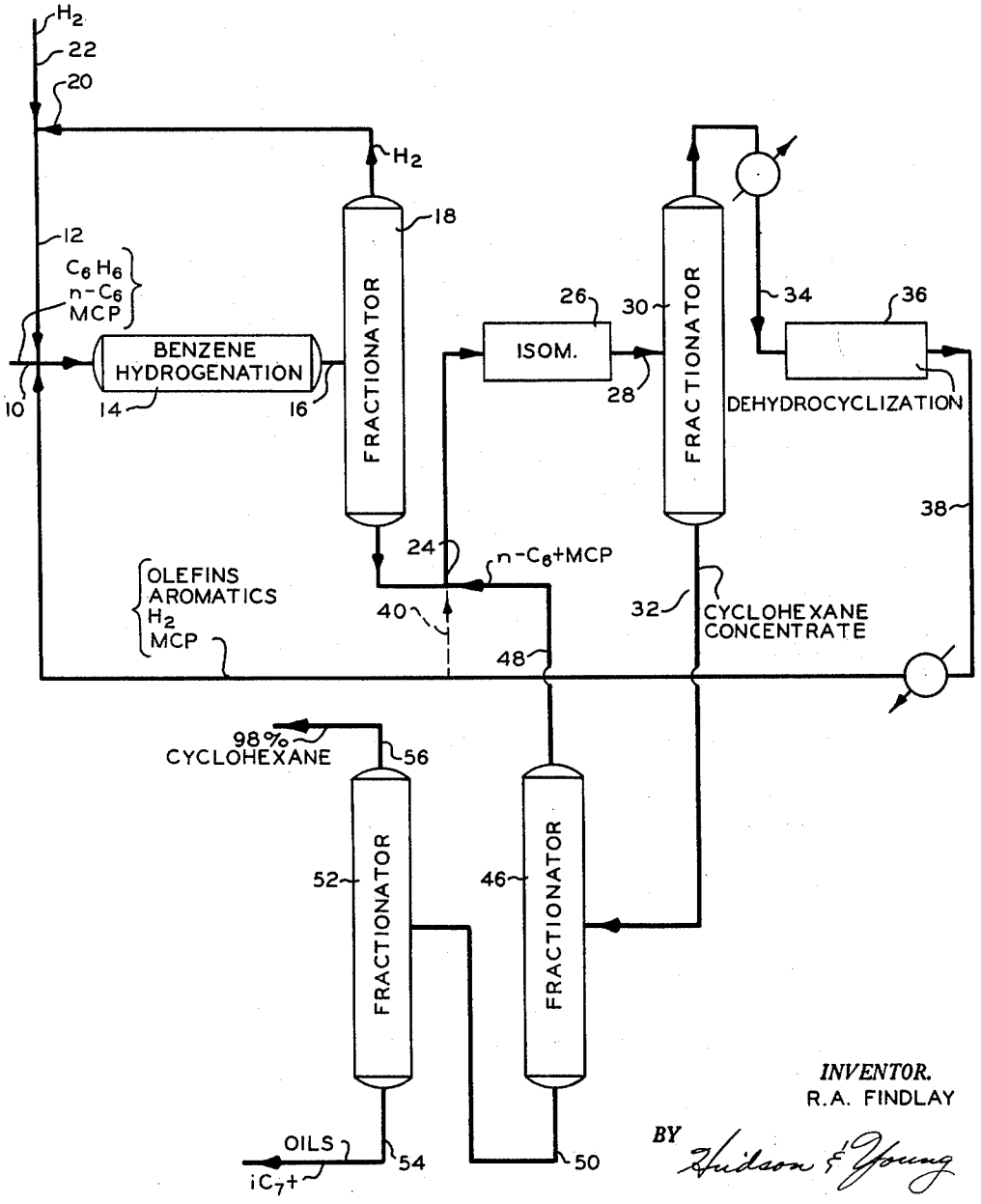
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PROCESS FOR PRODUCING CYCLOHEXANE

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PROCESS FOR PRODUCING CYCLOHEXANE

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This invention relates to an improved process for producing cyclohexane by isomerizing a hydrocarbon fraction comprising methylcyclopentane and normal hexane.

The present invention is an improvement in the process of the application of Lloyd E. Dean et al., S. N. 698,607, filed November 25, 1957, now U.S. Patent No. 2,953,606, issued September 20, 1960, in which a hydrocarbon fraction comprising principally methylcyclopentane, n-hexane, and benzene is passed into a hydrogenation zone in admixture with H_2 to hydrogenate the benzene to cyclohexane in contact with a hydrogenation catalyst; a hydrocarbon fraction comprising methylcyclopentane, n-hexane, and cyclohexane is recovered from the effluent and contacted in an isomerization zone with an aluminum chloride-hydrocarbon complex catalyst promoted with HCl so as to form isohexanes and cyclohexane; the effluent from the isomerization zone is fractionated to separately recover isohexanes and cyclohexane; and the cyclohexane fraction is purified by deoiling to provide a cyclohexane concentrate of a purity upwards of 98%.

Since cyclohexane is a valuable hydrocarbon utilized in industry and, particularly, in the manufacture of nylon, it is desirable to convert as much of the feed to cyclohexane in the process of the above-identified application as possible.

Accordingly, it is an object of the present invention to provide an improved process for producing high yields of cyclohexane of high purity. Another object is to convert a maximum amount of a mixed stream of benzene, methylcyclopentane, and n-hexane to cyclohexane. A further object is to provide a process for converting methylcyclopentane and n-hexane to cyclohexane. It is also an object of the invention to provide an improved process for converting benzene, methylcyclopentane and n-hexane to cyclohexane in separate isomerization and dehydrocyclization steps with destruction of catalyst poisons formed in the process which tend to foul the isomerization and dehydrocyclization catalysts. Other objects of the invention will become apparent to one skilled in the art upon consideration of the accompanying disclosure.

One aspect of the improvement in the process of the invention comprises passing the isohexanes formed in the process of the above-identified application to a dehydrocyclization zone and there contacting same with a catalyst consisting essentially of platinum distended on a porous, inert support material, such as activated charcoal, silica, silica-alumina, etc., so as to convert the isohexanes to methylcyclopentane. Activated charcoal is the preferred support and this support is impregnated with a suitable platinum compound readily convertible to platinum in an amount which deposits or distends the Pt thereon in a concentration in the range of about 0.01 to 5.0 and preferably, 0.5 to 1.0 weight percent of the support. Chloroplatinic acid is a suitable impregnating compound and the impregnated support is heated in a hydrogen containing ambient at a temperature in the range of 400 to 700° F. to convert to Pt metal.

The temperature of the isohexane dehydrocyclization step is in the range of about 400 to 1025° F. and, preferably 575 to 650° F. High pressures in the dehydrocyclization zone require higher temperatures in order to effect the desired dehydrocyclization and it is therefore preferred to operate this zone at pressures below about 50 p.s.i.g. and more desirably at about atmospheric pressure. The space velocity may vary in the range of 0.05 to 10.0 liquid volumes of feed per volume of catalyst per hour. The catalyst is preferably in a fixed bed of suitable size particles to effect high contacting efficiency.

The effluent from the dehydrocyclization zone is passed to the benzene hydrogenation zone or to the isomerization zone, depending upon the amount of impurities in the effluent. In most instances, however, this effluent contains up to 2 mol percent olefins, up to 1.0 percent aromatics, and from 10 to 15 percent methylcyclopentane, together with hydrogen formed in the process. Since the olefins and aromatics are deleterious to the platinized charcoal, it is advantageous to pass the effluent from the dehydrocyclization zone into the benzene hydrogenation zone where they are destroyed and do not deactivate the catalyst, and where the hydrogen is used to advantage.

The platinum metals other than platinum itself do not have the effect of catalyzing the dehydrocyclization of isohexanes to methylcyclopentane. Other conventional dehydrocyclization catalysts are also ineffective in this reaction.

A more complete understanding of the invention may be had by reference to the accompanying schematic drawing which is a flow diagram of a preferred embodiment of the process of the invention.

Referring to the drawing, a feed comprising methylcyclopentane, n-hexane, and benzene is passed thru line **10** in admixture with hydrogen introduced thru line **12** to benzene hydrogenation zone **14**. The hydrogenation step effected in zone **14** is a conventional hydrogenation preferably utilizing a nickel catalyst deposited on a porous inert support such as silica gel, keiselguhr, or other highly siliceous material. The hydrogenated effluent from zone **14** is passed thru line **16** into fractionator **18** which effects separation of hydrogen from the effluent and returns same via line **20** to line **12** where it joins hydrogen introduced to the system thru line **22**. The hydrocarbon effluent from fractionator **18** is passed via line **24** to isomerization zone **26**. The catalyst utilized in zone **26** and the isomerization step effected therein are those employed in the process of the above-identified application. The preferred catalyst comprises $AlCl_3$-hydrocarbon complex, promoted with HCl.

The isomerizate from the first isomerization zone **26** is passed via line **28** to a suitable fractionator **30** which effects the desirable separation of cyclohexane, produced by hydrogenation of benzene in zone **14** and isomerization of methylcyclopentane in zone **26**, from the isohexanes formed in zone **26**. The cyclohexane concentrate recovered thru line **32** is passed to dehexanizer **46** from which the n-C_6 and MCP is recovered overhead and recycled to isomerizer **26** via lines **48** and **24**. The bottoms fraction containing cyclohexane and heavier oils is passed to fractionator **52** where the oils (iC_7 and heavier) are recovered thru line **54** and the cyclohexane of 98% purity is recovered thru line **56**.

The overhead fraction from fractionator **30**, containing the isohexanes, is passed via line **34** to a dehydrocyclization zone **36** where it is contacted with the platinum catalyst, under the conditions previously described, so as to convert the isohexanes to methylcyclopentane. The effluent from the dehydrocyclization zone **36** is passed thru line **38** to line **10** for recycling to the benzene dehydrogenation step. The olefins and aromatics in this stream are hydrogenated in zone **14** and the hydrogen in the recycle stream is used up therein. The methylcyclopentane passes thru the benzene dehydrogenation zone unchanged and is isomerized in the isomerization zone to cyclohexane.

In the event the recycle stream in line **38** is relatively free of olefins and aromatics, this stream may be passed

directly into line 24 thru line 40 for passage directly into the isomerization zone. It is also feasible to clean up the fraction in line 38, freeing it of deleterious materials in conventional manner and pass the concentrated isohexanes directly into zone 26.

The following example illustrates the invention and is not to be interpreted so as to unnecessarily limit the invention.

EXAMPLE

The data presented in the table represent those obtained when hydrogenating a typical refinery stream comprising principally isohexanes, n-hexane, and methylcyclopentane, isomerizing the resulting stream, fractionating the isomerizate to recover isohexanes overhead and a cyclohexane bottoms fraction, passing the isohexanes fraction to a dehydrocyclization zone to form methylcyclopentane, and passing the MCP to the hydrogenation step. The isohexane conversion step is effected at a temperature of 600° F. and at atmospheric pressure in contact with a catalyst consisting essentially of silica and 1 percent by weight of Pt reduced at 675° F. Isohexane space velocity in this step is 0.2 gal./gal./hr. The cyclohexane fraction is fractionated to remove overhead n-hexane and MCP which are recycled to the isomerization step. The bottoms fraction from this fractionation is again fractionated to recover an overhead cyclohexane stream of 98 percent purity and a bottoms fraction of iso–C_7 and heavier.

Table

[Values given are in pounds]

	Feed	Isohexane concentrate	Cat. chamber effluent	Dehexanizer product oils bottoms		
Lines in drawing	10	34	38	50	56	54
Isohexanes*	15.6	354.3	273.4			
n-Hexane	56.7	7.2	7.1			
Methylcyclopentane	21.0		70.4			
Benzene	1.6		2.5			
Isoheptanes and heavier	4.1			5.3	1.8	3.5
Cyclohexane	1.0			93.0	93.0	
Olefins			6.2			
Hydrogen			1.9			
	100.0	361.5	361.5	98.3	94.8	3.5

*The isohexanes consist mainly of 2-methylpentane and 3-methylpentane with only minor amounts of 2,2-dimethylbutane or 2,3-dimethylbutane.

Certain modifications of the invention will become apparent to those skilled in the art and the illustrative details disclosed are not to be construed as imposing unnecessary limitations on the invention.

I claim:

1. A process for producing cyclohexane comprising contacting n-hexane and methylcyclopentane in an isomerization zone with an aluminum chloride-hydrocarbon complex catalyst, promoted with HCl under isomerizing conditions so as to produce isohexanes and cyclohexane; separating an effluent from said isomerization zone into a cyclohexane fraction and an isohexane fraction; contacting said isohexane fraction in a dehydrocyclization zone with a catalyst consisting essentially of platinum distended on a porous inert support at a temperature in the range of about 400 to 1025° F. and at a pressure below about 50 p.s.i.g. to produce methylcyclopentane; passing resulting methylcyclopentane from said dehydrocyclization zone to said isomerizing zone; and recovering said cyclohexane as a product of the process.

2. The process of claim 1 wherein said support is activated charcoal and the amount of platinum is in the range of 0.01 to 5 weight percent of the charcoal.

3. The process of claim 2 wherein the temperature in said dehydrocyclization zone is in the range of about 575 to 650° F.

4. A process for producing cyclohexane comprising contacting a methylcyclopentane-n-hexane-benzene feed admixed with a hydrogenation catalyst in a hydrogenation zone so as to convert benzene to cyclohexane; contacting an effluent from said hydrogenation zone, principally methylcyclopentane, n-hexane, and cyclohexane, with an isomerization catalyst in an isomerization zone under isomerizing conditions so as to convert n-hexane to isohexanes and methylcyclopentane to cyclohexane; separating the effluent from said isomerization zone into an isohexane fraction and a cyclohexane fraction; contacting said isohexane fraction in a dehydrocyclization zone with a catalyst consisting essentially of platinum distended on a porous inert support at a temperature in the range of about 400 to 1025° F. and at a pressure below about 50 p.s.i.g. to convert isohexanes to methylcyclopentane; passing resulting effluent containing minor amounts of olefins, aromatics, and hydrogen from said dehydrocyclization zone to said hydrogenation zone to hydrogenate said olefins and aromatics thereby eliminating the poisonous effect of these constituents on the downstream catalyst; and recovering cyclohexane as a product of the process.

5. The process of claim 4 wherein said support is activated charcoal and said platinum is in the range of about 0.01 to 5 weight percent of the charcoal.

6. The process of claim 5 wherein said isomerization catalyst comprises an $AlCl_3$-hydrocarbon complex promoted with HCl.

7. The process of claim 5 including the steps of recovering H_2 from the effluent from said hydrogenation zone and recycling same to said hydrogenation zone.

8. The process of claim 4 including the steps of (*a*) passing said cyclohexane fraction to a first fractionation zone and recovering therefrom n-hexane and methylcyclopentane as an overhead fraction and cyclohexane and heavier hydrocarbons as a bottoms fraction; (*b*) passing said overhead fraction to said isomerization zone to form additional cyclohexane; and (*c*) passing said bottoms fraction to a second fractionation zone and recovering therefrom cyclohexane of high purity as said product and heavier hydrocarbons as a bottoms fraction.

References Cited in the file of this patent

UNITED STATES PATENTS

2,304,168	Heard	Dec. 8, 1942
2,918,511	Carter et al.	Dec. 22, 1959
2,953,606	Dean et al.	Sept. 20, 1960
3,009,002	Kron	Nov. 14, 1961