

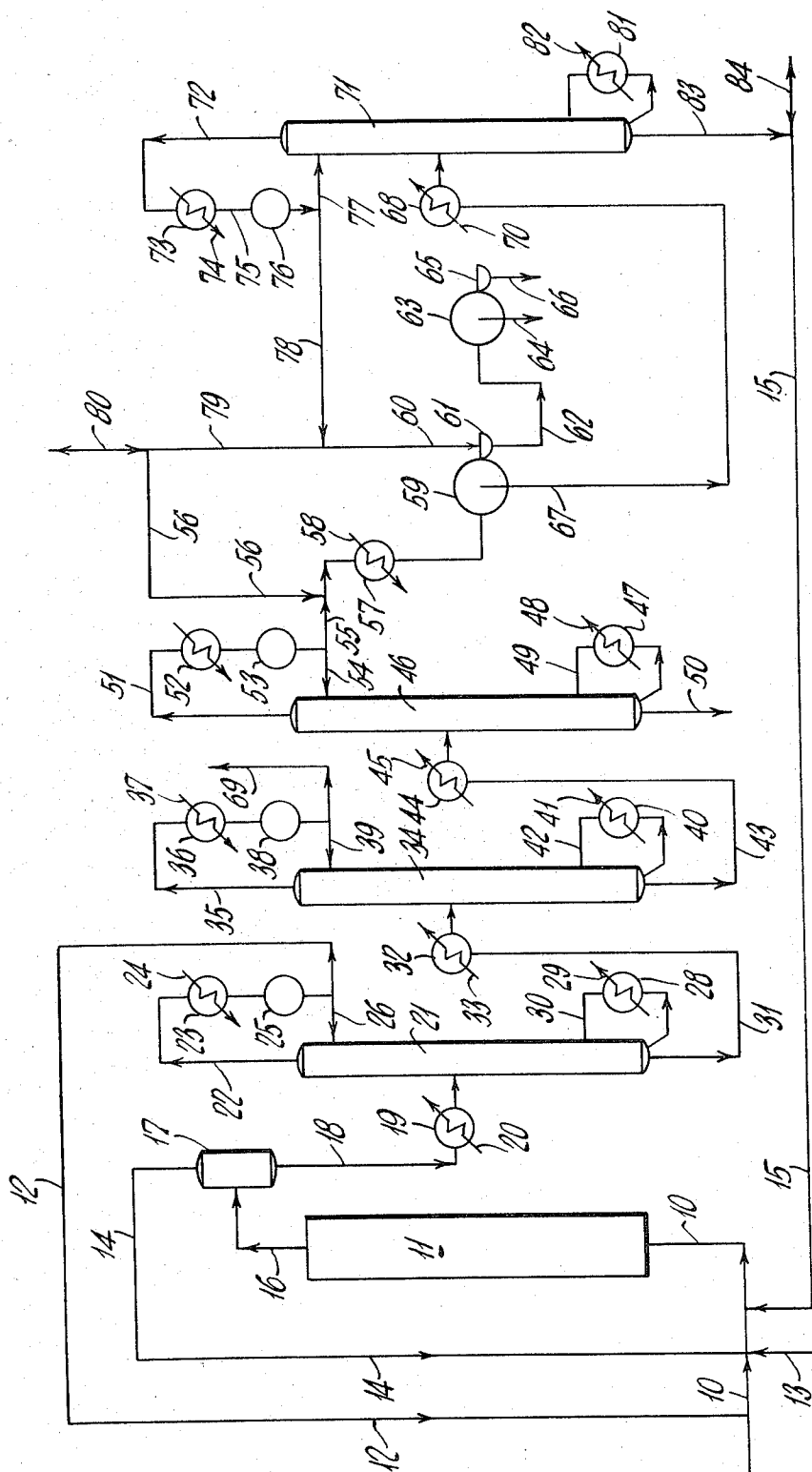
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METHOD OF SEPARATING DICYCLOHEXYL BENZENES

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METHOD OF SEPARATING DICYCLOHEXYL BENZENES

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20 Claims

ABSTRACT OF THE DISCLOSURE

Para-dicyclohexyl benzene may be separated from non-para-dicyclohexyl benzene by cooling a mixture preferably in the presence of lower alkanols, and separating crystals of para-isomer from the mixture.

FIELD OF THE INVENTION

This invention relates to the separation of para-dicyclohexyl benzene. More specifically it relates to the separation of para-dicyclohexyl benzene from mixtures of isomers of dicyclohexyl benzene.

BACKGROUND OF THE INVENTION

As is well known to those skilled in the art, it is possible to hydroalkylate aromatic, preferably mononuclear, hydrocarbons such as benzene by reaction with hydrogen in the presence of hydroalkylation catalyst under hydroalkylation conditions to yield product hydroalkylate. This product primarily contains desired cyclohexyl benzene together with by-product ortho-, meta-, and para-isomers of dicyclohexyl benzene.

The limited commercial utility of the crude mixture or of the ortho- and the meta-isomers requires that para-dicyclohexyl benzene be separated and recovered.

It is an object of this invention to provide a process for the recovery of para-dicyclohexyl benzene. It is another object of this invention to provide a process for the separation of para-dicyclohexyl benzene from a mixture thereof with non-para-dicyclohexyl benzenes. Other objects will be apparent to those skilled in the art.

STATEMENT OF THE INVENTION

In accordance with certain of its aspects, the novel process of this invention for separating para-dicyclohexyl benzene from a dicyclohexyl benzene charge containing para-dicyclohexyl benzene and at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene may comprise:

Cooling said dicyclohexyl benzene charge to a temperature below its incipient crystallization temperature and within the para-dicyclohexyl benzene crystallization range thereby forming a solid phase containing para-dicyclohexyl benzene in a liquid phase containing at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene;

Separating said solid phase containing para-dicyclohexyl benzene from said liquid phase containing at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene; and

Maintaining said solid phase containing para-dicyclohexyl benzene and said liquid phase containing at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene at temperature within the para-dicyclohexyl benzene crystallization range during said separating.

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DESCRIPTION OF THE INVENTION

The dicyclohexyl benzene charge which may be treated by the process of this invention may be a charge mixture which commonly contains para-dicyclohexyl benzene together with at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene. Typically the process of this invention may be used to treat a dicyclohexyl benzene containing 0.5–15 parts, say 2.6 parts of para-dicyclohexyl benzene, 0.2–15 parts, say 5.4 parts of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene.

Commonly mixtures of dicyclohexyl benzenes may be recovered as by-products from the hydroalkylation of benzene. In a typical hydroalkylation such a stream may be obtained by separating lighter fractions including hydrogen, benzene, methyl cyclopentane, and desired cyclohexyl benzene, etc. as well as heavier fractions including tricyclohexyl benzenes. Commonly the charge mixture of dicyclohexyl benzenes which may be treated by the process of this invention may be the dicyclohexyl benzene stream (containing ortho-, meta-, and para-isomers) recovered during the workup of the effluent from the hydroalkylation of a benzene.

The benzenes which may be hydroalkylated may be mixed with with hydroalkylating quantity of hydrogen and passed to a hydroalkylation operation. The charge to hydroalkylation also preferably includes at least one dicyclohexyl benzene. Preferably the dicyclohexyl benzene admitted with the charge benzene may be a meta-isomer, or an ortho-isomer, typically a mixture thereof, and most commonly a mixture of dicyclohexyl benzene isomers from which the para-isomer has been removed. It may alternatively be a dicyclohexyl benzene stream which has been recovered from a hydroalkylation operation and which contains ortho-, meta-, and para-dicyclohexyl benzenes.

The hydroalkylation charge may include, in addition to fresh charge benzene, other components including cyclohexyl benzene, para-dicyclohexyl benzene, tricyclohexylbenzenes, etc. The composition of the total charge entering the reactor may include:

TABLE

Component	Parts	Typical
Benzene	40–99.5	92.6
Cyclohexyl benzene	0–5	0.6
Ortho-dicyclohexyl benzene	0.5–15	5.2
Meta-dicyclohexyl benzene		
Para-dicyclohexyl benzene	0–15	1.6
Methyl cyclopentane	0–5	0
Cyclohexane	0–5	0

Other components which may be present may include methyl cyclopentyl benzenes, bicyclohexyl, and tricyclohexyl benzenes.

Preferably 100 parts of charge benzene and a hydroalkylating quantity, preferably 0.3–3 parts, say 1.8 parts of hydrogen may be admitted to the hydroalkylation operation. Reaction may be carried out at an inlet temperature of 25° C.–300° C., preferably 100° C.–200° C., say 130° C. at 100–1500 p.s.i.g., preferably 100–500 p.s.i.g., say 500 p.s.i.g. The pressure is normally sufficient to maintain the reactants substantially in liquid phase (except for the hydrogen which is in gas phase).

Hydroalkylation may be effected in the presence of a hydroalkylation catalyst and a hydroalkylating quantity of hydrogen. The hydrogen need not be pure; but preferably hydrogen of 80%–95% may be used. The hydrogen should preferably be free of any impurities which may poison the catalyst. Hydrogen recovered from a reforming operation may be suitable. The catalyst may contain a Group VIII transition metal component, e.g. cobalt,

nickel, ruthenium, rhodium, palladium, iridium, and platinum. The preferred type of catalyst may include a Group VIII metal, typically nickel, or cobalt, and preferably 0–30%, typically 10%–20%, say 19% of a Group VI metal, typically tungsten, on a silica-alumina, zeolite, or alumina catalyst support. When the Group VIII metal is Co or Ni, it will preferably be present in amount of 2%–30%, typically 4.0%–25%, say 22%. When the Group VIII metal is a noble metal, i.e. other than Co or Ni, it may be present in amount of 0.2%–5%, say 1%. Such a catalyst may be prepared for example by impregnating a commercial NH_4 exchanged Y zeolite catalyst with e.g. nickel nitrate (or cobalt nitrate) and thereafter with ammonium metatungstate solution and then drying the catalyst in air at say 100° C. The so-dried catalyst may be further dried at 150° C. and then calcined to a maximum temperature of 800° C.

The catalyst may be calcined—during which the nitrates are decomposed and the catalyst is dehydrated. The catalyst may (after loading into the hydroalkylation unit) be reduced in the presence of hydrogen for a minimum of 1 hour and typically at least 4–8 hours at a temperature preferably above about 300° C. and typically 300° C.–700° C., say 500° C.

The so-prepared typical catalyst may contain, on a dry basis, 6% nickel, 19% tungsten, and 22% hydrogen-Y zeolite, the remainder being amorphous silica-alumina support.

Hydroalkylation may be effected by using this catalyst at an LHSV of 0.5–15, typically 2–6, say 2.

As will be apparent to those skilled in the art, the composition of the hydroalkylate product will be a function of the charge to the hydroalkylating operation. In a preferred embodiment, wherein the charge benzene is benzene *se* plus recycle orthodicyclohexyl benzene, metadicyclohexyl benzene, and para-dicyclohexyl benzene, the product may typically contain the following:

TABLE

Component:	Preferred parts
Benzene	58.9
Cyclohexyl benzene	28.0
Ortho-dicyclohexyl benzene	5.4
Meta-dicyclohexyl benzene	
Para-dicyclohexyl benzene	2.6
Methylcyclopentane	0.8
Cyclohexane	3.8
Dicyclohexyl and others	0.9

The hydroalkylate product in amount of 100 parts may be passed, in liquid phase to a separation operation wherein any hydrogen present, usually less than 1.5 parts, may be flashed off. Hydrogen, if present e.g. because of low catalyst activity, may be recycled to the hydroalkylation operation.

The flashed product liquid may be preferably heated and passed to a benzene recovery tower. Typically 58.9 parts of benzene may be recovered as overhead and condensed against water.

A portion of the condensate is returned as pumped reflux to the benzene recovery tower; and the remainder of the recovered benzene may be recycled to the hydroalkylation operation preferably after purification to remove e.g. C_6 naphthenes.

41.1 parts of bottoms may be heated and passed, in the preferred embodiment, to cyclohexyl benzene recovery tower. Overhead cyclohexyl benzene may be condensed against water and a portion thereof may be returned as pumped reflux to the cyclohexyl benzene recovery tower.

Bottoms from the cyclohexyl benzene recovery tower, in amount of 8 parts may be heated and passed in the preferred embodiment to the dicyclohexyl benzene recovery tower. Bottoms from the dicyclohexyl benzene recovery tower may typically include tricyclohexyl (and higher boiling) benzenes.

The overhead from the dicyclohexyl benzene distillation operation may include dicyclohexyl benzene; and typically this stream may include less than 10% of other components. It may be found that the dicyclohexyl benzene fraction recovered as overhead from the dicyclohexyl benzene distillation tower may contain 0.5–15 parts, say 2.6 parts of para-isomer and 0.2–15 parts, say 5.4 parts of the mixed ortho- and meta- isomers.

In practice of the novel process of this invention the dicyclohexyl benzene charge fraction so recovered may typically be in liquid phase at temperature above its incipient crystallization temperature. It will be apparent to those skilled in the art that the incipient crystallization temperature (i.e. the temperature at which para-dicyclohexyl benzene begins to precipitate from a liquid mixture containing non-para dicyclohexyl benzenes) may vary somewhat depending upon the composition of the dicyclohexyl benzene and particularly the amount of the various components contained therein e.g., the para-isomer, the non-para-isomers, solvents, diluents, impurities, etc.

Commonly however it may be found that the incipient crystallization temperature may be below about 49° C. (120° F.). When the dicyclohexyl benzene is substantially pure (i.e. substantially free of non-dicyclohexyl benzenes), the incipient crystallization temperature may be 27° C.–32° C. (80° F.–90° F.). When the dicyclohexyl benzene is dissolved in a lower alkanol, for example, the incipient crystallization temperature at which the para-dicyclohexyl benzene begins to precipitate may, depending on the concentration of the para-isomer and the species of alcohol, typically be below about 49° C. (120° F.) more commonly at 27° C.–49° C. (80° F.–120° F.), preferably about 38° C.–49° C. (100° F.–120° F.).

In practice the incipient crystallization temperature of a mixture of dicyclohexyl benzenes containing para-dicyclohexyl benzene may be determined by heating a mixture until it is a homogenous liquid and thereafter slowly cooling. The temperature at which the first precipitate of the crystalline flat plates of the para-dicyclohexyl benzene is noted as the incipient crystallization temperature of para-dicyclohexyl benzene for the particular system.

In practice of one preferred embodiment of the process of this invention, there may be added to the dicyclohexyl benzene charge mixture (containing 0.5–15 parts, say 2.6 parts of para-isomer and 0.2–15 parts, say 5.4 parts of mixed ortho- and meta-isomers)—before it is cooled to below its incipient crystallization temperature—1.6–4 parts of a diluent, typically a lower alkanol.

Cooling the dicyclohexyl benzene charge to a temperature below its incipient crystallization temperature may be effected by passage through appropriate heat exchangers which typically cool the charge to a temperature within the para-dicyclohexyl benzene crystallization range. The upper limit of the para-dicyclohexyl benzene crystallization range may normally coincide with the incipient crystallization temperature of para-dicyclohexyl benzene.

The lower limit of the para-dicyclohexyl benzene crystallization range may be the point at which the para-crystals being formed contain undesirably large quantities of non-para-isomers. Commonly as the temperature is lowered, the amount of para-isomer which crystallizes increases as does the amount of non-para isomer. Thus the purity of para isomers (in terms of increasing content of non-para-isomers) may decrease as the temperature of crystallization or precipitation is lowered. As a practical matter, it may be found that little or no substantial additional amount of para-isomer appears to precipitate below about minus 10° C. (15° F.) from a mixture containing substantially only dicyclohexyl benzenes. When solvent is present, typically alcohol, the temperature below which little or no substantial additional amounts of para-isomer precipitate may be minus 20° C. (minus 4° F.).

Thus the para-dicyclohexyl benzene crystallization range may typically be from about 27° C. (80° F.) down to minus 10° C. (15° F.) or more preferably to

minus 7° C. (20° F.) when no solvent is present. The preferred range may be 27° C. down to minus 29° C., more preferably down to about minus 20° C. (−4° F.) when solvent is present.

Para-dicyclohexyl benzene may be recovered in practice of the process of this invention from the charge dicyclohexyl benzene. Although the charge dicyclohexyl benzene need not be above the incipient crystallization temperature of para-dicyclohexyl benzene, it will most preferably be above that temperature. If the charge be below this temperature, it will in the preferred embodiment be heated to a temperature 10° C. to 20° C. above this temperature and maintained at that point for time sufficient to establish equilibrium i.e. usually until a homogeneous liquid is obtained—and this homogeneous liquid may then be cooled.

In practice of the process of this invention, the charge dicyclohexyl benzene is cooled to a temperature which is below the incipient crystallization temperature and within the para-dicyclohexyl benzene crystallization range. In a preferred embodiment, there may be added to the 8.0 parts of dicyclohexyl benzene charge, 1.6–4 parts, say 2 parts of a diluent typically a lower alkanol. The preferred lower alkanols may include C₁ to C₄ lower alkanols such as methanol, ethanol, n-propanol, i-propanol, n-butanol, i-butanol, and t-butanol. The preferred lower alkanols may include methanol and isopropanol.

In one embodiment, it may be desirable to add to the dicyclohexyl benzene mixture, to which the alcohol is added, water in amount of 5%–10% of the quantity of the alcohol i.e., 0.08–4.0 parts, say 1.4 parts.

During cooling into the para-dicyclohexyl benzene crystallization range, the para-isomer may crystallize—the ortho- and meta-isomers remaining in liquid phase i.e. either neat or in diluent solution. The cooled mixture, a slurry of solid phase para-isomer in liquid phase containing the ortho- and meta-isomer and typically diluent, may be passed to a separation operation, typically a filtration operation.

In practice of the process of this invention, it will be apparent that the charge dicyclohexyl benzene may be treated according to various specific embodiments depending upon the particular makeup of the composition. In one embodiment, the charge may be cooled, in the absence of diluent, to a temperature within the crystallization range of minus 10° C. to plus 27° C., say 20° C. and filtered to remove para-isomer, the filtrate being further processed as desired.

In an alternative embodiment, the charge may be cooled in two steps within the para-dicyclohexyl benzene crystallization range—firstly to 16° C. to 27° C., say 20° C., precipitated para-isomer being filtered, and thence to minus 7° C. to plus 16° C., after which a second crop of crystals of para-isomer may be filtered.

In still another embodiment, the charge may be diluted with diluent and cooled to minus 20° C. to 27° C., in one step or in two steps: firstly to 0° C.–27° C. and thence to minus 20° C. to 0° C.—with crystals of para-isomer being recovered after each cooling step.

In still another preferred embodiment, the charge dicyclohexyl benzene may be cooled, without solvent addition, to 16° C. to 27° C., say 20° C. The resultant crystals of para-isomer may be filtered and solvent added to the liquid which may then be cooled to minus 29° C. to plus 16° C., say 0° C. to precipitate a second crop of crystals which may be filtered.

In the embodiment wherein 1.6–4 parts, say 2 parts of diluent may be added to 8 parts of dicyclohexyl benzene charge, the cooled mixture at e.g. minus 20° C. to plus 27° C., say minus 10° C., may be filtered to yield 0.2–10 parts say 1 part of crystals of para-dicyclohexyl benzene (containing typically 0.1–1 part, say 0.2 part of mixed ortho- and meta-isomers). These crystals are separated as filter cake from filtrate which contains 0.5–15 parts, say 5.2 parts of ortho- and meta-isomers (and 0.1–4 parts, say 1.6 parts of para-dicyclohexyl benzene).

The filter cake may be washed, as by slurrying with diluent, typically a lower alkanol such as isopropanol, and recovered therefrom as by further filtration. Further yield of para-dicyclohexyl benzene filter cake may be 0.2–10 parts, say 1 part.

It is a feature of this invention that it may readily be possible to recover para-dicyclohexyl benzene from mixtures thereof with ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene—in high yields and of high purity. Specifically it may be possible to obtain recrystallized para-isomer in yields of 80% or greater in purity approaching 98%–100%.

DESCRIPTION OF A PREFERRED EMBODIMENT

Practice of the process of this invention may be apparent to those skilled in the art from inspection of the following wherein, as elsewhere in this specification, all parts are parts by weight unless otherwise stated. The process of this invention may be carried out in accordance with the process flow sheet set forth in the accompanying schematic drawing.

Charge to hydroalkylation operation 11 includes fresh benzene admitted through line 10, recycle benzene admitted through line 12, fresh charge hydrogen admitted through line 13, recycle hydrogen admitted through line 14.

There is also admitted through line 15 a recycle stream containing ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene.

The charge entering operation 11 contains:

Component:	Parts
Hydrogen -----	1.8
Benzene -----	92.6
Cyclohexyl benzene -----	0.6
Ortho- and meta-dicyclohexyl benzene -----	5.2
Para-dicyclohexyl benzene -----	1.6

Charge in line 10 to hydroalkylation operation 11 is in liquid phase at 130° C. and 500 p.s.i.g. In hydroalkylation operation 11, is a bed of nickel-tungsten on a support, prepared by impregnating with a solution of nickel nitrate and ammonium metatungstate an amorphous silica-alumina matrix that contains 22 weight percent of a hydrogen form of Y zeolite that had been calcined at 800° C. The product catalyst contains 6% nickel and 19% tungsten.

The charge passes through the hydroalkylation operation at 2 LHSV. Hydroalkylation product, withdrawn through line 16 contains the following components:

Component:	Parts
Hydrogen -----	0.7
Benzene -----	59.6
Ortho- and meta-dicyclohexyl benzene -----	5.4
Para-dicyclohexyl benzene -----	2.6
Cyclohexyl benzene -----	28
Methyl cyclopentane -----	0.8
Cyclohexane -----	3.8
Dicyclohexyl and others -----	0.9

Hydroalkylation product in line 16 is passed to separation operation 17 wherein 0.7 part of hydrogen are separated. The separated hydrogen is withdrawn through line 14.

Flashed product liquid is passed through line 18 to heat exchanger 19 heated by steam in line 20 wherein it is heated before being passed to benzene recovery operation 21. Overhead in amount of 59.6 parts of benzene and 0.8 part of methylcyclopentane and 3.8 parts of cyclohexane is withdrawn through line 22, condensed in heat exchanger 23 (cooled by water in line 24), and collected in condensate drum 25. A portion of the benzene condensate is returned as pumped reflux through line 26; and the remainder is passed through line 12 to be recycled to operation 11.

Bottoms in tower 21 are boiled in heat exchanger 28 by steam in line 29 and returned to tower 21 through line 30. Net bottoms, in amount of 36.9 parts, contain cyclohexyl benzenes, ortho-dicyclohexyl benzene, meta-dicyclohexyl benzene, and para-dicyclohexyl benzene, as well as dicyclohexyl and other cyclohexyl benzene impurities such as methylcyclopentyl benzenes.

Net bottoms in line 31 are passed to heat exchanger 32 heated by steam in line 33 wherein they are heated and then passed to cyclohexyl benzene recovery operation 34. Cyclohexyl benzene, along with dicyclohexyl and the methylpentyl benzenes, is withdrawn through line 35, condensed in heat exchanger 36 against water in line 37, and collected in collection vessel 38. A portion of the condensate is passed as pumped reflux to tower 34 through line 39. Cyclohexyl benzene is withdrawn through line 69.

Bottoms in tower 34 are reboiled in heat exchanger 40 heated by steam in line 41 and returned to tower 34 through line 42. Net bottoms in line 43 in amount of 8+ parts may contain principally ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene (in total amount of 5.4 parts), and 2.6 parts of para-dicyclohexyl benzene. Small amounts of other components may be present including higher boiling components typically tricyclohexyl benzenes.

In this embodiment, net bottoms in line 43 are passed through heat exchanger 44 heated by steam in line 45 and passed to dicyclohexyl benzene recovery operation 46. Bottoms are reboiled in heat exchanger 47 heated by steam in line 48 and returned to dicyclohexyl benzene recovery tower 46 through line 49. Net bottoms in line 50 may be essentially tricyclohexyl benzenes.

Overhead from tower 46 is withdrawn through line 51, condensed in heat exchanger 52 against water, and collected in collection vessel 53. The dicyclohexyl benzenes passed to vessel 53 may contain 32.5 wt. percent of para-dicyclohexyl benzene and 67.5 wt. percent of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene.

Pumped reflux is returned through line 54 to tower 46; and 8 parts are withdrawn through line 55.

It is a feature of the process of this invention that it is readily possible to separate the para-isomers from the ortho- and meta-isomers which are present in the dicyclohexyl benzene present in line 55. In this embodiment of the invention, 2.4 parts of diluent isopropyl alcohol are admitted through line 56 and the mixture is cooled to minus 10° C. in heat exchanger 57 by refrigerant in line 58. At this point, the mixture is below the incipient crystallization temperature and within the para-dicyclohexyl benzene crystallization range.

The cooled mixture of dicyclohexyl benzenes, now primarily a slurry of solid phase containing para-isomer in a liquid phase containing isopropyl alcohol and the ortho-isomer and the meta-isomer, is passed to separation operation 59. Filtration at minus 10° C. permits recovery of 1 part of para-dicyclohexyl benzene filter cake (containing 0.2 part of mixed ortho- and meta-isomers). Isopropanol is admitted through line 60 to slurry the filter cake; and the slurry is withdrawn from collector 61 passed through line 62 at minus 10° C. to filter 63.

Filtrate from filter 63, containing principally isopropanol, is withdrawn through line 64; and filter cake in amount of 1.2 parts is withdrawn from collector 65 through line 66. Para-dicyclohexyl benzene in line 66 in amount of 1.2 parts may be recovered.

Filtrate from filtration operation 59 is withdrawn at minus 10° C. through line 67. This filtrate contains principally meta-dicyclohexyl benzene, ortho-dicyclohexyl benzene, and isopropanol.

In practice of this embodiment of this invention, filtrate in line 67 at minus 10° C. is passed to heat exchanger 68 heated by steam in line 70 and passed to stripping operation 71 wherein isopropanol is separated from the mixture of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene. Overhead recovered in line 72, isopropanol, is

condensed in heat exchanger 73 cooled by water in line 74 and passed through line 75 to collection drum 76. A portion of the condensate may be passed as pumped reflux through line 77 to stripping tower 71.

The net overhead from tower 71 is passed through line 78 to isopropanol feed line 60; a second portion of isopropanol is passed from line 78 through line 79 to isopropanol feed line 56. Isopropanol may be removed from or added to line 79 through line 80.

Dicyclohexyl benzene, principally the ortho- and meta-isomers, is reboiled in heat exchanger 81 heated by steam in line 82. Net ortho- and meta- bottoms are removed through line 83 and passed through line 15 to hydroalkylation operation 11. Dicyclohexyl benzene may be added to or withdrawn from the system through line 84.

It will be observed in particular that the 8.0 parts of total dicyclohexyl benzenes in line 55 (containing 2.6 parts, 32.5%, of para- and 5.4 parts of ortho- and meta-isomers) may be treated in this embodiment to yield:

- (a) 2.2 parts (85% yield) of para-dicyclohexyl benzene containing 0.44 part of ortho- and meta-isomers (para-purity of 83.3% which may be increased by recrystallization); and
- (b) 5 parts of ortho- and meta-dicyclohexyl benzene containing 0.4 part of para-isomer (ortho- and meta-purity of 93% which may be increased by recrystallization).

It will be apparent to those skilled in the art that the use of this novel process unexpectedly permits ready separation of para-dicyclohexyl benzene from ortho-dicyclohexyl benzene and para-dicyclohexyl benzene.

This novel process may be particularly useful in connection with the hydroalkylation of benzene.

The use of this novel process, in this illustrative embodiment, yields hydroalkylation reaction effluent in line 16 which desirably contains substantially decreased proportions of undesirable cyclohexyl benzene impurities (dicyclohexyl and methylcyclopentyl benzenes).

Use of the novel process permits hydroalkylation to be carried out with liberation, during hydroalkylation, of much less heat per unit of cyclohexyl benzene formed than is obtained by prior art practice. This means that more throughput can be put through the reactor; or that the reactor can be made smaller; or that it can be operated at lower temperature to give the desired yield; or that it can be operated at the same temperature with higher effective yield.

In the prior art, a limiting determinant on the reaction has been the ability to control heat transfer in the hydroalkylation reactor to keep within desired temperature range and thus minimize formation of undesirable by-products.

The novel process is characterized by the ability to operate under conditions permitting attainment of high concentrations of cyclohexyl benzene (up to e.g. 30%) and to operate with decreased heat liberation due e.g. to decreased formation of exothermically produced dicyclohexyl benzenes.

It is also a feature of the process of this invention that it permits elimination of undesired ortho- and meta-dicyclohexyl benzene, their elimination being effected by isomerization, under hydroalkylating conditions, to the para-isomer.

Although this invention has been illustrated by reference to specific embodiments, it will be apparent to those skilled in the art that various changes and modifications may be made which clearly fall within the scope of this invention.

We claim:

1. The method of separating para-dicyclohexyl benzene from a dicyclohexyl benzene charge containing para-dicyclohexyl benzene and at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-di-

cyclohexyl benzene and meta-dicyclohexyl benzene which comprises

cooling said dicyclohexyl benzene charge to a temperature below its incipient crystallization temperature and within the para-dicyclohexyl benzene crystallization range thereby forming a solid phase containing para-dicyclohexyl benzene in a liquid phase containing at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene;

separating said solid phase containing para-dicyclohexyl benzene from said liquid phase containing at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene; and

maintaining said solid phase containing para-dicyclohexyl benzene and said liquid phase containing at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene at temperature within the para-dicyclohexyl benzene crystallization range during said separating.

2. The method of separating para-dicyclohexyl benzene from a dicyclohexyl benzene charge containing para-dicyclohexyl benzene and at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene as claimed in claim 1 wherein said para-dicyclohexyl benzene crystallization range is minus 20° C. to plus 27° C.

3. The method of separating para-dicyclohexyl benzene from a dicyclohexyl benzene charge containing para-dicyclohexyl benzene and at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene as claimed in claim 1 wherein said para-dicyclohexyl benzene crystallization range is minus 10° C. to plus 27° C.

4. The method of separating para-dicyclohexyl benzene from a dicyclohexyl benzene charge containing para-dicyclohexyl benzene and at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene as claimed in claim 1 which comprises

maintaining said dicyclohexyl benzene charge at temperature above its incipient crystallization temperature;

cooling said dicyclohexyl benzene charge to a temperature below its incipient crystallization temperature and within the range of 16° C. to 27° C. thereby forming a first solid phase containing para-dicyclohexyl benzene in a first liquid phase containing at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene;

further cooling said first liquid phase within the para-dicyclohexyl benzene crystallization range thereby forming a second solid phase containing para-dicyclohexyl benzene in a second liquid phase; and recovering para-dicyclohexyl benzene.

5. The method of separating para-dicyclohexyl benzene from a dicyclohexyl benzene charge containing para-dicyclohexyl benzene and at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene as claimed in claim 4 wherein said further cooling is to a temperature of minus 7° C. to plus 16° C.

6. The method of separating para-dicyclohexyl benzene from a dicyclohexyl benzene charge containing para-dicyclohexyl benzene and at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene as claimed in claim 4 wherein said first solid phase is separated prior to said further cooling.

7. The method of separating para-dicyclohexyl benzene from a dicyclohexyl benzene charge containing para-

dicyclohexyl benzene and at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene as claimed in claim 4 wherein said further cooling is carried out in the presence of a lower alkanol.

8. The method of separating para-dicyclohexyl benzene from a dicyclohexyl benzene charge containing para-dicyclohexyl benzene and at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene as claimed in claim 4 wherein said further cooling is carried out in the presence of a C₁ to C₄ lower alkanol.

9. The method of separating para-dicyclohexyl benzene from a dicyclohexyl benzene charge containing para-dicyclohexyl benzene and at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene as claimed in claim 4 wherein said further cooling is carried out in the presence of isopropanol.

10. The method of separating para-dicyclohexyl benzene from a dicyclohexyl benzene charge containing para-dicyclohexyl benzene and at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene which comprises

mixing said dicyclohexyl benzene charge with a lower alkanol; and

separating a solid phase of para-dicyclohexyl benzene from a liquid phase containing said lower alkanol and said non-para-dicyclohexyl benzene, at a temperature below the incipient crystallization temperature of para-dicyclohexyl benzene.

11. The method of separating para-dicyclohexyl benzene from a dicyclohexyl benzene charge containing para-dicyclohexyl benzene and at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene as claimed in claim 10 wherein said lower alkanol is a C₁-C₄ alkanol.

12. The method of separating para-dicyclohexyl benzene from a dicyclohexyl benzene charge containing para-dicyclohexyl benzene and at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene as claimed in claim 10 wherein said lower alkynol is a propanol.

13. The method of separating para-dicyclohexyl benzene from a dicyclohexyl benzene charge containing para-dicyclohexyl benzene and at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene as claimed in claim 10 wherein said lower alkanol is isopropanol.

14. The method of separating para-dicyclohexyl benzene from a dicyclohexyl benzene charge containing para-dicyclohexyl benzene and at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene as claimed in claim 10 wherein said lower alkanol is methanol.

15. The method of separating para-dicyclohexyl benzene from a dicyclohexyl benzene charge containing para-dicyclohexyl benzene and at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene as claimed in claim 10 wherein said separating is carried out in the presence of water.

16. The method of separating para-dicyclohexyl benzene from a dicyclohexyl benzene charge containing para-dicyclohexyl benzene and at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene as claimed in claim 10 wherein said separation is carried out in the presence of water in amount of 2%-15% of the lower alkanol.

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17. The method of separating para-dicyclohexyl benzene from a dicyclohexyl benzene charge containing para-dicyclohexyl benzene and at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene which comprises

mixing said dicyclohexyl benzene charge with a lower alkanol

heating said mixture to a temperature above the incipient crystallization temperature

cooling said mixture to a temperature below the incipient crystallization temperature thereby forming a slurry of (i) solid phase para-dicyclohexyl benzene crystals in (ii) liquid phase non-para-dicyclohexyl benzene; and

separating said solid phase para-dicyclohexyl benzene crystals from said liquid phase non-para-dicyclohexyl benzene

18. The method of separating para-dicyclohexyl benzene from a dicyclohexyl benzene charge containing para-dicyclohexyl benzene and at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene which comprises

cooling said dicyclohexyl benzene charge to 16°–27° C. thereby forming a solid phase containing para-dicyclohexyl benzene in a liquid phase containing at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene;

separating said solid phase containing para-dicyclohexyl benzene from said liquid phase containing at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene;

adding a lower alkanol to said liquid phase after said solid phase has been separated therefrom;

adding a lower alkanol to said liquid phase after said solid phase has been separated therefrom;

further cooling said liquid phase containing said non-para-dicyclohexyl benzene to minus 29° C. to plus 16° C. thereby forming a second solid phase containing para-dicyclohexyl benzene; and

separating said second solid phase.

19. The method of preparing para-dicyclohexyl benzene which comprises

hydroalkylating benzene in the presence of hydroalkylation catalyst and a hydroalkylating quantity of hydrogen;

maintaining said hydroalkylation at inlet temperature of 25° C.–300° C. and 100–1500 p.s.i.g. thereby pro-

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ducing product hydroalkylate containing dicyclohexyl benzene;

recovering a dicyclohexyl benzene fraction containing para-dicyclohexyl benzene and at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene; and

separating said para-dicyclohexyl benzene from said non-para-dicyclohexyl benzene.

20. The method of preparing para-dicyclohexyl benzene which comprises

hydroalkylating benzene in the presence of hydroalkylation catalyst and a hydroalkylating quantity of hydrogen;

maintaining said hydroalkylation at inlet temperature of 25° C.–300° C. and 100–1500 p.s.i.g. thereby producing product hydroalkylate containing dicyclohexyl benzene;

recovering a dicyclohexyl benzene fraction containing para-dicyclohexyl benzene and at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene;

maintaining said dicyclohexyl benzene at temperature above its incipient crystallization temperature;

cooling said dicyclohexyl benzene to a temperature below its incipient crystallization temperature and within the range of 16° C. to 27° C. thereby forming a first solid phase containing para-dicyclohexyl benzene in a first liquid phase containing at least one non-para-dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene;

further cooling said first liquid phase within the para-dicyclohexyl benzene crystallization range thereby forming a second solid phase containing para-dicyclohexyl benzene in a second liquid phase; and recovering para-dicyclohexyl benzene.

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CURTIS R. DAVIS, Primary Examiner

U.S. Cl. X.R.

260—667, 670, 674 R

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,784,619 Dated January 8, 1974

Inventor(s) J. M. CRONE, JR. and R. M. SUGGITT

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 2, line 65 "hdyroalkylating" should read

--hydroalkylating--

Col. 3, line 22 "east" should read --least--

Col. 5, line 71 "0.1-1 part, say 0.2 part" should read

--parts-- both instances

Col. 7, line 1 "boiled" should read --reboiled--

Col. 8, line 21 "0.44 part" should be --0.44 parts--

col. 8, line 26 "0.4 part" should be --0.4 parts--

Signed and sealed this 6th day of August 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents