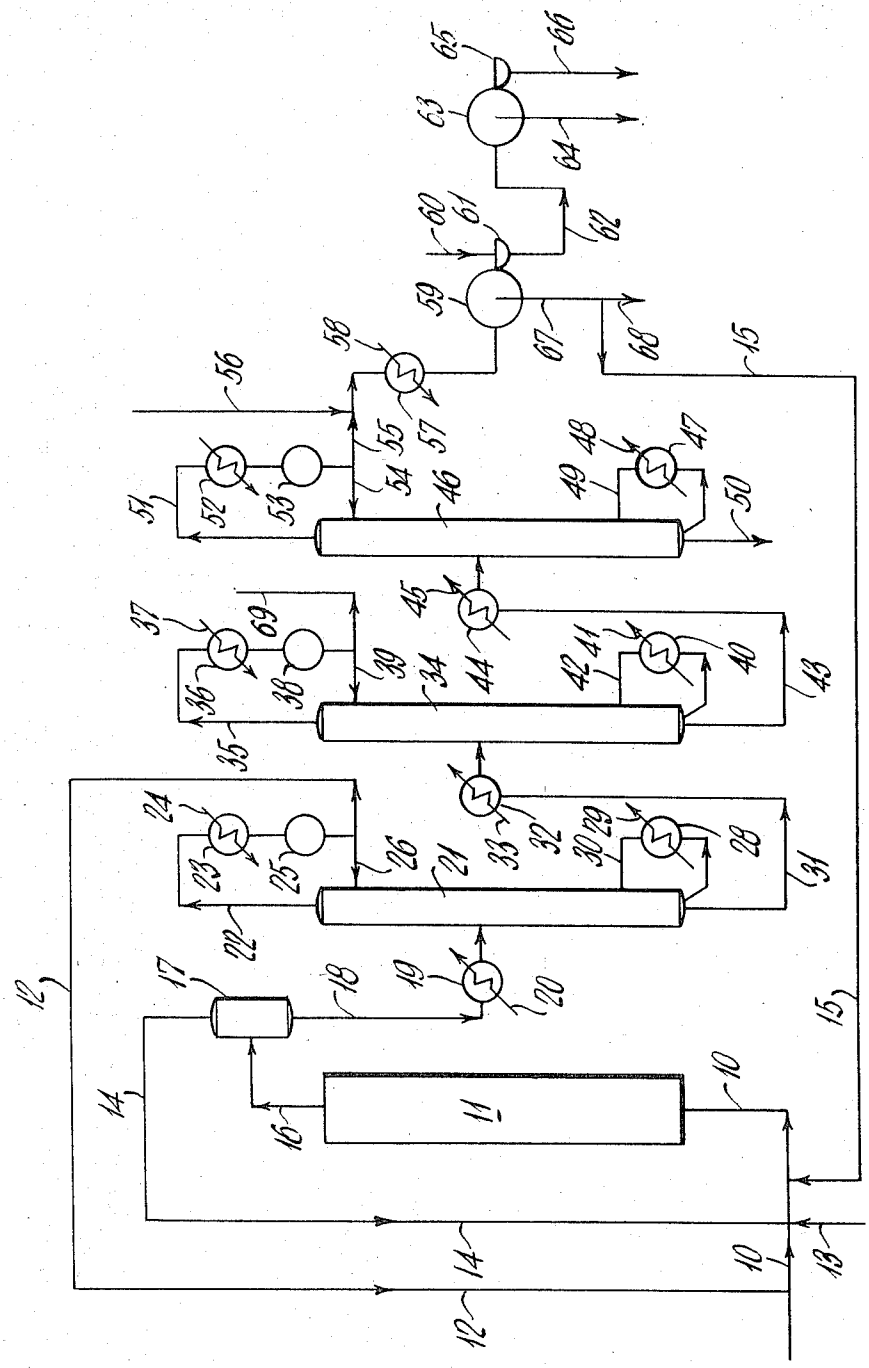
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HYDROALKYLATION PROCESS

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HYDROALKYLATION PROCESS

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ABSTRACT OF THE DISCLOSURE

Increased yield of cyclohexyl benzene may be achieved by hydroalkylating benzene in the presence of dicyclohexyl benzene.

BACKGROUND OF THE INVENTION

This invention relates to hydroalkylation. More specifically it relates to the selective hydroalkylation of benzene to permit attainment of high yields of cyclohexyl benzene.

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

It is an object of this invention to provide a process for hydroalkylation. It is another object of this invention to provide a process for hydroalkylating a charge benzene to produce cyclohexyl benzene. Other objects will be apparent to those skilled in the art.

SUMMARY OF THE INVENTION

In accordance with certain of its aspects, the novel process of this invention for hydroalkylating a charge benzene with a hydroalkylating quantity of hydrogen may comprise:

Passing said charge benzene in the presence of hydrogen to a hydroalkylation operation thereby effecting hydroalkylation operation thereby effecting hydroalkylation to form a hydroalkylate product containing cyclohexyl benzene;

Passing to said hydroalkylation operation at least one dicyclohexyl benzene; and

Recovering cyclohexyl benzene from said hydroalkylation product.

DETAILED DESCRIPTION OF THE INVENTION

The charge benzenes which may be hydroalkylated by the process of this invention may be mixed with a hydroalklating quantity of hydrogen and passed to a hydroalkylation operation. In practice of the process of this invention, the charge to hydroalkylation also 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 charge which may be hydroalkylated by the process of this invention 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.ig 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 up to 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 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, meta-dicyclohexyl 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 Meta-dicyclohexyl benzene	5.4
Para-dicyclohexyl benzene	2.6
Methylcyclopentane	0.8
Cyclohexane	3.8
Dicyclohexyl and others	0.9

In the preferred embodiment, 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. Preferably 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 process of this invention, typically 8.0 parts of the dicyclohexyl benzene fraction may be cooled to minus 20° C. to plus 25° C., say minus 10° C. There may be preferably added to the fraction, prior to cooling, 1.6–4 parts, say 2.4 parts of a diluent, typically a lower alkanol such as isopropyl alcohol or methanol. During cooling, the para-isomer may crystallize and separate from the ortho- and meta-isomer which remain in the liquid phase. The cooled mixture, a slurry of the solid phase para-isomer in liquid phase containing the ortho- and meta-isomer and preferably diluent, may be passed to a separation operation, typically a filtration operation.

In the filtration operation, conducted at minus 20° C.–plus 25° C., say minus 10° C., 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-) are separated as filter cake from the filtrate which contains 0.5–15 parts, say 5.2 parts of ortho- and meta-dicyclohexyl benzenes (and 0.1–4 parts, say 1.6 parts of para-) and optionally say 0.6 part of cyclohexylbenzene.

The filter cake may be washed with lower alkanol, typically isopropanol and recovered therefrom as by further filtration. Yield of para-dicyclohexyl benzene (filter cake) may be 0.2–10 parts, say 1 part.

It is a particular feature of the novel process of this invention, in accordance with certain of its aspects that improved yields (per unit weight of benzene charged to the hydroalkylation operation and per unit volume of catalyst) of desired cyclohexyl benzene may be obtained by admitting to the hydroalkylation operation with the charge benzene, and dicyclohexyl benzene and preferably at least one dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene.

It may be possible to carry out the process of this invention by admitting to the hydroalkylation operation in the preferred embodiment 0.5–15 parts, say 5.2 parts of dicyclohexyl benzene, preferably non-para-dicyclohexyl benzenes. Preferably the dicyclohexyl benzene admitted to the hydroalkylation operation will contain less than 4 parts, typically 1.6 parts (more preferably it will contain as little as possible) of the para-isomer.

The stream of dicyclohexyl benzenes admitted with charge benzene to the hydroalkylation operation may be essentially meta-dicyclohexyl benzene (in amount of 0.5–15 parts, say 5.2 parts) or, less preferably, ortho-dicyclohexyl benzene (in amount of 0.5–15 parts, say 5.2 parts).

In the preferred embodiment, the stream of dicyclohexyl benzenes admitted to the hydroalkylation operation may include 0.5–15 parts, say 5.2 parts of mixed ortho- and meta-isomers in amount substantially equal to the amount thereof formed during the hydroalkylation of benzene. In one embodiment, the dicyclohexyl benzene separated from the product hydroalkylate may, in whole or part, be recycled to the hydroalkylation reaction.

It is a particular feature of the process of this invention that of outstanding efficiencies may be obtained when the stream of non-para isomers is of similar composition to that obtained after recovery of the para-isomer from the separation or filtration operation in which solid para-isomer is recovered.

In the most preferred embodiment, the ortho- and meta-isomers passed to the hydroalkylation operation include at least one dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene.

The addition to the charge benzene of non-para-dicyclohexyl benzene (and preferably the stream of ortho- and meta-dicyclohexyl benzene recycle stream from which the para-isomer has been removed) permits attainment of outstanding results. This technique disposes of a less commercially desirable ortho- and meta-fraction and converts it to a more commercially desirable para- fraction. It permits hydroalkylation to be carried out with formation of higher concentration (per pass through the reaction zone) of the desired product cyclohexylbenzene as well as the preferred para-by-product. Typically the concentration of by-product para-isomer (which might be 0.5%–5%, say 1.7%), is increased to 1%–10%, say 2.6% (at the expense of non-para-isomers) by the addition of non-para-isomers.

It is also unexpectedly found that the use of the novel technique of this invention, typically including recycle, permits production of increased amounts of the desired cyclohexyl benzene with net formation of lesser quantities of the mixed dicyclohexyl benzene isomers. This higher concentration permits economies in work-up as well as permitting reaction in smaller volume reactors.

It is a further advantage of the process of this invention that the preferred recycle step (because inter alia of the decreased formation of dicyclohexyl benzene isomers) permits hydroalkylation with liberation of smaller amounts of heat. Alternatively expressed, this means in-

creased economies in the reactors; smaller reactors may be employed.

In comparative examples which illustrate the advantages which may be achieved by the process of this invention, wherein benzene was hydroalkylated to give about 27% yield of desired cyclohexyl benzene, it was found that the process of this invention yielded a hydroalkylation product containing only 0.9% cyclohexyl benzene impurities plus 4.3% naphthenes. In contrast, the process wherein no recycle of dicyclohexyl benzenes was employed yielded a hydroalkylation product containing 1.3% cyclohexyl benzene impurities plus 5.6% naphthenes. Thus practice of this process permits reduction of cyclohexyl benzene impurities by 32% from previous practice and also a substantial decrease in the naphthene content. Reduction in the cyclohexyl benzene impurities (including methyl cyclopentyl benzenes and bicyclohexyl) is highly significant because these impurities are difficultly separable by distillation from the desired cyclohexyl benzene.

It will be apparent that use of the novel process of this invention permits recovery of cyclohexyl benzene hydroalkylate product of higher purity than is produced by prior art processes.

It is also possible by practice of this invention to achieve comparable yields of hydroalkylate by the use of lower temperature. For example in one series of comparable runs, it was possible to obtain about 27% yield of cyclohexyl benzene at temperatures of e.g. 200° F.–300° F. by practice of the process of this invention; prior practice with no recycle of dicyclohexyl benzenes required temperatures of e.g. 300° F.–380° F. to effect comparable yield.

DESCRIPTION OF THE 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.

In practice of this embodiment of the process of this invention, 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** in this embodiment, a recycle stream containing orthodicyclohexyl benzene and meta-dicyclohexyl benzene.

The charge entering operation **11** contains:

Component:	Parts
Hydrogen	1.8
Benzene	96.6
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 which contains 22 weight percent of a hydrogen-form Y zeolite that had been calcined at 800° C. The catalyst is then dried in air at 150° C. and calcined to a maximum temperature of 800° C. to yield a product which contains 6% nickel and 19% tungsten. The catalyst is reduced, prior to use, by contact with hydrogen at 475° C.

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, containing 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 reboiled 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 benzene, ortho-dicyclohexyl benzene, meta-dicyclohexyl benzene, and para-dicyclohexyl benzene, as well as dicyclohexyl and other cyclohexyl benzene impurities such as methylcyclopentylbenzenes.

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 methylcyclopentylbenzenes are withdrawn as overhead 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 preferred 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 dicyclohexylbenzenes 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**.

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**.

The cooled mixture of dicyclohexyl benzenes, now primarily a slurry of solid para-isomer in a liquid con-

taining 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 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 minutes 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.

Prior to further handling, the filtrate in line **67** may preferably be passed to a stripping or fractionating operation (not shown) wherein the isopropanol may be removed from the mixture of dicyclohexyl benzenes by distillation. The isopropanol may be recycled to line **56**. The stripped dicyclohexyl benzene, now free of isopropanol, may be dried to remove water, and then passed through line **15** to line **10** where it joins with the charge to hydroalkylation operation **11**. A draw-off stream **68** may withdraw a bleed portion of the dicyclohexyl benzenes in line **67**.

It will be observed that the recycle of dicyclohexyl benzenes and, in the preferred embodiment, the separation of para-dicyclohexyl benzene and the recovery and recycle of the ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene, permits attainment of substantial advantages in the hydroalkylation of benzene to produce cyclohexyl 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 cyclohexylbenzene impurities (dicyclohexyl and methylcyclopentylbenzenes) and naphthenes.

Specifically by way of typical example, this novel process permits attainment of 27% yield of monocyclohexyl benzene (based upon benzene charged to hydroalkylation) containing 0.9% of undesirable dicyclohexyl and methylcyclopentylbenzenes and 4.3% naphthenes; without practice of the novel process of this invention, the product contains 1.3% of undesirable dicyclohexyl benzenes and 5.6% naphthenes—about one-third more than is obtained by this invention.

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 process for hydroalkylating a charge benzene with a hydroalkylating quantity of hydrogen which comprises

passing said charge benzene in the presence of hydrogen to a hydroalkylation operation thereby effecting hydroalkylation to form hydroalkylate product containing cyclohexyl benzene;

passing to said hydroalkylation operation at least one dicyclohexyl benzene; and

recovering cyclohexyl benzene from said hydroalkylation product.

2. The process for hydroalkylating a charge benzene with a hydroalkylating quantity of hydrogen as claimed in claim **1** wherein said dicyclohexyl benzene passed to said hydroalkylation operation includes at least one dicyclohexyl benzene selected from the group consisting of ortho-dicyclohexyl benzene, meta-dicyclohexyl benzene, and para-dicyclohexyl benzene.

3. The process for hydroalkylating a charge benzene with a hydroalkylating quantity of hydrogen as claimed in claim **1** wherein said dicyclohexyl benzene passed to said hydroalkylation operation consists essentially of non-para-isomers of dicyclohexyl benzene.

4. The process for hydroalkylating a charge benzene with a hydroalkylating quantity of hydrogen as claimed in claim **1** wherein said dicyclohexyl benzene passed to said hydroalkylation operation includes a mixture of isomers of dicyclohexyl benzene from which para-dicyclohexyl benzene has been removed.

5. The process for hydroalkylating a charge benzene with a hydroalkylating quantity of hydrogen as claimed in claim **1** wherein said dicyclohexyl benzene passed to said hydroalkylation operation contains ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene in amount substantially equal to the equilibrium amount thereof formed during the hydroalkylation of said benzene.

6. The process for hydroalkylating a charge benzene with a hydroalkylating quantity of hydrogen as claimed in claim **1** wherein said hydroalkylation operation is effected at 25° C.–300° C.

7. The process for hydroalkylating a charge benzene with a hydroalkylating quantity of hydrogen which comprises

passing said charge benzene in the presence of hydrogen to a hydroalkylation operation thereby effecting hydroalkylation to form hydroalkylate product containing cyclohexyl benzene and dicyclohexyl benzenes;

separating said cyclohexyl benzene from said dicyclohexyl benzene contained in said hydroalkylate product; and

recycling to said hydroalkylation operation at least a portion of said separated dicyclohexyl benzene.

8. The process for hydroalkylating a charge benzene with a hydroalkylating quantity of hydrogen as claimed in claim **7** wherein prior to recycling said dicyclohexyl benzene, para-dicyclohexyl benzene is separated therefrom.

9. The process for hydroalkylating a charge benzene with a hydroalkylating quantity of hydrogen which comprises

passing said charge benzene in the presence of hydrogen to a hydroalkylation operation thereby effecting hydroalkylation to form hydroalkylate product containing benzene, cyclohexyl benzene, and dicyclohexyl benzenes;

fractionating said hydroalkylate product to form (i) as

overhead benzene (ii) bottoms containing cyclohexyl benzene and dicyclohexyl benzenes;

fractionating said bottoms to form (i) as overhead product cyclohexyl benzene and (ii) as bottoms dicyclohexyl benzene; and

passing dicyclohexyl benzene to said hydroalkylation operation.

10. The process for hydroalkylating a charge benzene as claimed in claim **9** wherein at least a portion of the dicyclohexyl benzene passed to said hydroalkylation operation is that recovered as said dicyclohexyl benzene bottoms.

11. The process for hydroalkylating a charge benzene as claimed in claim **9** wherein said dicyclohexyl benzene bottoms is passed to said hydroalkylation operation.

12. The process for hydroalkylating a charge benzene as claimed in claim **9** wherein said dicyclohexyl benzene bottoms are further fractionated to recover as overhead dicyclohexyl benzene.

13. The process for hydroalkylating a charge benzene as claimed in claim **9** wherein the dicyclohexyl benzene passed to said hydroalkylation operation includes a mixture of dicyclohexyl benzenes from which para-dicyclohexyl benzene has been removed.

14. The process for hydroalkylating a charge benzene as claimed in claim **9** wherein the dicyclohexyl benzene passed to said hydroalkylation operation consists essentially of non-para-isomers of dicyclohexyl benzene.

15. The process for hydroalkylating a charge benzene as claimed in claim **9** wherein the dicyclohexyl benzene passed to said hydroalkylation operation contains ortho-dicyclohexyl benzene and meta-dicyclohexyl benzene in amount substantially equal to the equilibrium amount thereof formed during the hydrogenation of said benzene.

16. The process for hydroalkylating a charge benzene with a hydroalkylating quantity of hydrogen which comprises

passing to a hydroalkylation operation a charge mixture containing benzene, ortho-dicyclohexyl benzene,

meta-dicyclohexyl benzene, and a hydroalkylating quantity of hydrogen;

maintaining said hydroalkylation operation at 100–1500 p.s.i.g. and with an inlet temperature of 25° C.–300° C.;

hydroalkylating said charge mixture in the presence of a catalyst selected from the group consisting of (a) a Group VIII transition metal and (b) a Group VIII transition metal together with a Group VI metal;

withdrawing from said hydroalkylation operation a product hydroalkylate containing benzene, cyclohexyl benzene, and dicyclohexyl benzenes including ortho-dicyclohexyl benzene, meta-dicyclohexyl benzene, and para-dicyclohexyl benzene;

separating benzene from said product hydroalkylate;

returning said separated benzene to said hydroalkylation operation;

separating cyclohexyl benzene from said product hydroalkylate;

separating a dicyclohexyl benzene fraction from said product hydroalkylate; and

returning at least a portion of said separated dicyclohexyl benzene to said hydroalkylation.

17. The process for hydroalkylating a charge benzene with a hydroalkylating quantity of hydrogen as claimed in claim **16** wherein para-dicyclohexyl benzene is separated from said dicyclohexyl benzene before the latter is recycled to said hydroalkylation operation.

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