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(54) Title: COMPOSITION COMPRISING CYCLOHEXYLBENZENE AND 1 - PHENYL - 1 -METHYLCYCLOPENTANE AND USE THEREOF IN OXIDATION PROCESSES

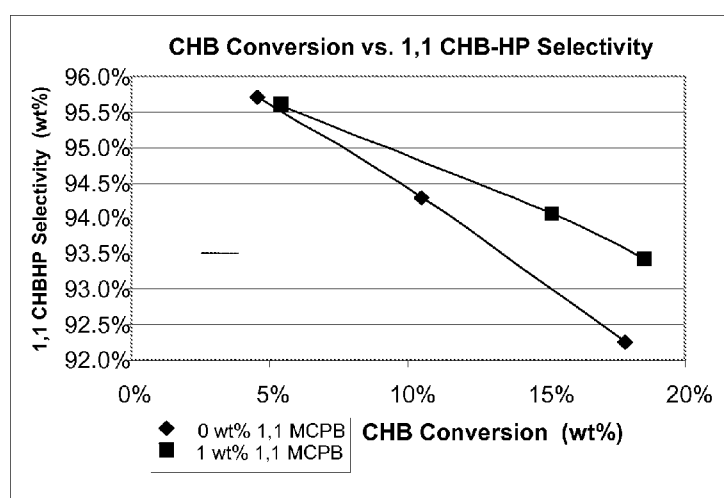


Figure 1

(57) Abstract: Disclosed herein is an oxidation having: (i) greater than 0.2 wt% by weight of 1- phenyl- 1-methylcyclopentane; and (ii) greater than 50 wt% by weight of a second alkylaromatic compound. The composition may be oxidized to convert a portion of the 1- phenyl- 1-methylcyclopentane and/or the second alkylaromatic compound to an alkylaromatic oxygenate.



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**OMPRISING CYCLOHEXYLBENZENE AND 1 - PHENYL - 1 -
METHYLCYCLOPENTANE AND USE THEREOF IN OXIDATION PROCESSES**

PRIORITY CLAIM

[0001] This application claims priority to U.S. Application Serial No. 61/424,229 (Atty. Docket No. 2010EM325), filed December 17, 2010; and European Patent Application 11151462.6 filed January 19, 2011; and U.S. Application Serial No. 61/424,236 (Atty. Docket No. 2010EM367), filed December 17, 2010, all of which are incorporated herein by reference in their entirety.

CROSS REFERENCE TO RELATED APPLICATIONS

[0002] This application is related to U.S. Publication No. US2010/0234589, published September 16, 2010; U.S. Publication No. US2010/0222609, published September 2, 2010; U.S. Publication No. 2010/0228047, published September 9, 2010; International Patent Cooperation Treaty Publication No. WO2010/042273, published April 15, 2010; International Patent Cooperation Treaty Application No. PCT/US2010/041801, filed July 13, 2010; International Patent Cooperation Treaty Application No. PCT/US2010/050970, filed September 30, 2010.

FIELD

[0003] The present invention relates to compositions and processes.

BACKGROUND

[0004] Phenol is an important product in the chemical industry and is useful in, for example, the production of phenolic resins, bisphenol A, ϵ -caprolactam, adipic acid, and plasticizers.

[0005] Currently, the most common route for the production of phenol is the Hock process. This is a three-step process which involves alkylation of benzene with propylene to produce cumene, oxidation of the cumene to the corresponding hydroperoxide and cleavage of the hydroperoxide to produce equimolar amounts of phenol and acetone.

[0006] Another process for producing phenol involves oxidizing cyclohexylbenzene (CHB) to the corresponding hydroperoxide and then cleaving the hydroperoxide using an acidic catalyst to form phenol and cyclohexanone.

[0007] Certain catalysts are useful in the oxidation reactions discussed above. For example, U.S. Patent No. 7,326,815 describes methods for oxidizing alkylaromatic compounds in the presence of a cyclic imide catalyst (e.g., an N-hydroxy substituted cyclic imide) to achieve high selectivity to the desired alkylaromatic hydroperoxide.

[0008] Although such cyclic imides can be useful oxidation catalysts, further improvements to enhance product selectivity in oxidation reactions are desirable. That said, it has now been discovered that oxidizing alkylaromatic compounds in the presence of methylcyclopentylbenzene (MCPB), particularly when a cyclic imide is used to catalyze the reaction, further improves selectivity to the desired alkylaromatic hydroperoxide. Without wishing to be bound to any particular theory, it is believed that the cyclic imide catalyst selectively abstracts hydrogen from the tertiary benzylic C-H bond. MCPB does not have a tertiary benzylic C-H bond, and its oxidation is only catalyzed by non-selective radicals. The non-selective radicals can also catalyze oxidation of the alkylaromatic compound to unfavorable byproducts, but in the presence of MCPB, fewer non-selective radicals are involved in the oxidation. This improves the selectivity to the prime alkylaromatic hydroperoxide.

[0009] It is known that MCPB can be formed during the production of CHB. For example, U.S. Patent Pub No. 2010/0179351 entitled "Process for Producing Cyclohexylbenzene" filed on December 7, 2009 discloses that reacting benzene and hydrogen in the presence of a bifunctional catalyst comprising at least one hydrogenation metal and a molecular sieve of the MCM-22 family forms CHB with MCPB as a by-product. This publication further discloses that the formation of MCPB is particularly undesirable because it has a boiling point that is very close to CHB and is therefore very difficult to separate. As such, MCPB can build up in the system and interfere with later stages of the phenol production process. PCT Pub. Nos. WO/2009/128984 and WO/2010/138248 also disclose that MCPB may be formed during the production of CHB.

[0010] In view of the above-noted disadvantages associated with the formation of MCPB, various processes have been proposed for removing MCPB from phenol production systems. For example, PCT Pub. No. WO/2010/098916 entitled "Process for Producing Phenol" published February 9, 2010 discloses removing certain isomers of MCPB (namely, 1,2-MCPB and 1,3-MCPB), through oxidation of 0 to 50 wt% of these isomers to the corresponding hydroperoxide, followed by cleavage of the hydroperoxide to phenol and 2- and 3-methylcyclopentanone.

[0011] Moreover, although not prior art, U.S. Prov. No. 60/424,236 (Atty. Docket No. 2010EM367) entitled "Process for Producing Cycloalkylaromatic Compounds," and filed concurrently with the present application, discloses removing MCPB isomers through treatment with an acid catalyst, such as faujasite.

[0012] However, it has now been discovered that having greater than about 0.2 wt% of 1,1 MCPB in the stream during oxidation of alkylaromatic compounds improves selectivity to the desired hydroperoxide. Such a discovery is an improvement upon existing processes.

SUMMARY

5 [0013] In one aspect, the invention relates to a composition that has (i) greater than 0.2 wt% of 1-phenyl-1-methylcyclopentane; and (ii) greater than 50 wt% of a second alkylaromatic compound, and the wt% based upon total weight of the composition.

[0014] In another aspect, the invention relates to oxidizing a composition containing greater than about 0.2 wt% by weight of 1-phenyl-1-methylcyclopentane (1,1 MCPB) and a second
10 alkylaromatic compound in an oxidation reaction zone to convert at least some MCPB or the second alkylaromatic compound to an alkylaromatic oxygenate. Conveniently, the second alkylaromatic compound cumene, sec-butylbenzene or cyclohexylbenzene.

[0015] The invention also relates to an oxidation process in which: (a) benzene and hydrogen are reacted to form cyclohexylbenzene (CHB) and 1-phenyl-1-methylcyclopentane;
15 and (b) a composition comprising at least a portion of the CHB and 1-phenyl-1-methylcyclopentane (1,1 MCPB) from step a (a) is oxidized in the presence of an oxidation catalyst to produce a composition comprising cyclohexylbenzene hydroperoxide. The 1,1 MCPB content is adjusted upstream of the oxidation reaction zone to be present in an amount of about 0.2 to about 10 wt% upstream, based upon total weight of the composition.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] Figure 1 shows CHB Conversion vs. Selectivity to cyclohexyl-1-phenyl-1-hydroperoxide (1, 1 CHBHP) during oxidation of compositions containing 0 wt% and 1 wt% of 1-phenyl-1-methylcyclopentane (1,1 MCPB).

[0017] Figure 2 shows CHB Conversion vs. Selectivity to 1,1 CHBHP during oxidation of
25 compositions containing 0 wt% and 10 wt% of 1,1 MCPB.

[0018] Figure 3 shows CHB Conversion vs. Selectivity to 1,1 CHBHP during oxidation of compositions containing 0 wt% and 1.5 wt% of 1,1 MCPB.

[0019] Figure 4 shows CHB Conversion vs. Selectivity to 1-phenylcyclohexanol (PhCHOH-1) during oxidation of compositions containing 0 wt% and 1.5 wt% of 1,1 MCPB.

30 [0020] Figure 5 shows CHB Conversion vs. Selectivity to 2-phenylcyclohexanol during oxidation of compositions containing 0 wt% and 1.5 wt% of 1,1 MCPB.

[0021] Figure 6 shows CHB Conversion vs. Selectivity to secondary cyclohexylbenzene hydroperoxide (CHB-HP-2) during oxidation of compositions containing 0 wt% and 1.5 wt% of 1,1 MCPB.

[0022] Figure 7 shows CHB Conversion vs. Selectivity to 6-hydroperoxy hexaphenone (6-HP-HexPhone) during oxidation of compositions containing 0 wt% and 1.5 wt% of 1,1 MCPB.

[0023] Figure 8 shows CHB Conversion vs. Selectivity to 2-phenylcyclohexanone (PhCHone) during oxidation of compositions containing 0 wt% and 1.5 wt% of 1,1 MCPB.

5 DETAILED DESCRIPTION OF THE EMBODIMENTS

[0024] Various specific embodiments, versions and examples of the invention will now be described, including preferred embodiments and definitions that are adopted herein for purposes of understanding the claimed invention. While the following detailed description gives specific preferred embodiments, those skilled in the art will appreciate that these
10 embodiments are exemplary only, and that the invention can be practiced in other ways. For purposes of determining infringement, the scope of the invention will refer to any one or more of the appended claims, including their equivalents, and elements or limitations that are equivalent to those that are recited. Any reference to the “invention” may refer to one or more, but not necessarily all, of the inventions defined by the claims.

15 [0025] That said, this disclosure relates to a composition that has (i) greater than 0.2 wt% of 1-phenyl-1-methylcyclopentane (1,1 MCPB); and (ii) greater than 50 wt% of a second alkylaromatic compound, and the wt% based upon total weight of the composition.

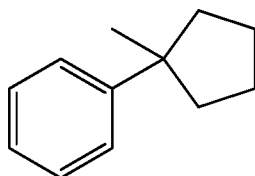
[0026] The composition may be oxidized to form one or more alkylaromatic oxygenates. The amount of MCPB may be adjusted upstream of the oxidation reaction to be present in a
20 targeted amount.

Production of Alkylaromatics

[0027] As discussed above, disclosed herein is a composition (also referred to as a composition) containing MCPB and a second alkylaromatic compound and process for oxidizing the composition to form one or more alkylaromatic oxygenates.

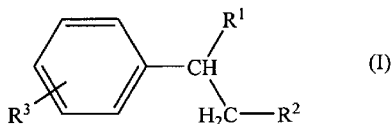
25 [0028] As used herein, methylcyclopentylbenzene (MCPB) is also referred to as phenyl-methylcyclopentane. These terms are used interchangeably.

[0029] The MCPB may be any isomer: 1-phenyl-1-methylcyclopentane (1,1 MCPB), 1-phenyl-2-methylcyclopentane (1,2 MCPB), and 1-phenyl-3-methylcyclopentane (1,3 MCPB). Preferably, it is 1,1 MCPB:



1-phenyl-1-methyl cyclopentane .

[0030] The second alkylaromatic compound (referred to as "second" because MCPB is also an alkylaromatic compound) may be of the general formula (I):



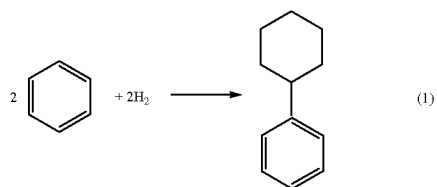
in which R^1 and R^2 each independently represents hydrogen or an alkyl group having from 1 to 4 carbon atoms, provided that R^1 and R^2 may be joined to form a cyclic group having from 4 to 10 carbon atoms, said cyclic group being optionally substituted, and R^3 represents hydrogen, one or more alkyl groups having from 1 to 4 carbon atoms or a cyclohexyl group. The phrase "provided that R^1 and R^2 may be joined" and so on is used herein to mean that, as an alternative to each of R^1 and R^2 being a ("monovalent") alkyl group, the two "alkyl" entities designated " R^1 " and " R^2 " are joined into a ("divalent") hydrocarbyl chain (having 2 to 8 carbons in that chain), with respective ends of that "divalent" chain begin linked to the C atoms specifically shown in formula (I) to form a ring. Thus, in an embodiment, R^1 and R^2 together constitute a hydrocarbyl moiety that connects to the carbon atoms of formula (I) form a cyclic group having from 4 to 10 carbon atoms, conveniently a cyclohexyl group, which may be substituted with one or more alkyl groups having from 1 to 4 carbon atoms or with one or more phenyl groups.

[0031] Examples of suitable second alkylaromatic compounds are ethylbenzene, isopropylbenzene (cumene), sec-butylbenzene (SBB), sec-pentylbenzene, sec-hexylbenzene and p-methyl-sec-butylbenzene, as well as cycloalkylaromatic compounds such as 1,4-diphenylcyclohexane, cyclopentylbenzene, cyclohexylbenzene (CHB) and cyclooctylbenzene, with SBB and CHB being preferred.

[0032] The MCPB and second alkylaromatic compound may be produced using any known or hereinafter devised technique.

[0033] In various embodiments, the second alkylaromatic compound is CHB and is produced during an alkylation process (i.e., contacting benzene with cyclohexene in the presence of an acid catalyst, such as zeolite beta or an MCM-22 family molecular sieve, or by oxidative coupling of benzene to make biphenyl followed by hydrogenation of the biphenyl).

[0034] Alternatively, CHB can be produced by hydroalkylation (i.e., contacting the benzene with hydrogen under hydroalkylation conditions in the presence of a hydroalkylation catalyst whereby the benzene undergoes the following reaction (1) to produce CHB):



[0035] For an example of hydroalkylation of benzene in the presence of hydrogen for the production of CHB, see U.S. Pat. Nos. 6,730,625 and 7,579,511 which are incorporated by reference for this purpose. Also, see International Applications WO2009131769 or
 5 WO2009128984 directed to catalytic hydroalkylation of benzene in the presence of hydrogen for the production of CHB.

[0036] The hydroalkylation reaction can be conducted in a wide range of reactor configurations including fixed bed, slurry reactors, and/or catalytic distillation towers. In addition, the hydroalkylation reaction can be conducted in a single reaction zone or in a plurality
 10 of reaction zones, in which at least the hydrogen is introduced to the reaction in stages. Suitable reaction temperatures are between about 100°C and about 400°C, such as between about 125°C and about 200°C, or about 125°C and about 160°C, or about 125°C and about 150°C, or about 125°C and about 140°C while suitable reaction pressures are between about 100 and about 7,000
 15 kPa, such as between about 500 and about 5,000 kPa. Suitable values for the molar ratio of hydrogen to benzene are between about 0.15:1 and about 15:1, such as between about 0.4:1 and about 4:1 for example between about 0.4 and about 0.9:1.

[0037] The catalyst employed in the hydroalkylation reaction may be a bifunctional catalyst comprising a molecular sieve of the MCM-22 family and a hydrogenation metal. The term “MCM-22 family material” (or “material of the MCM-22 family” or “molecular sieve of the
 20 MCM-22 family”), as used herein, includes molecular sieves having the MWW framework topology. (Such crystal structures are discussed in the "Atlas of Zeolite Framework Types", Fifth edition, 2001, the entire content of which is incorporated as reference.)

[0038] Molecular sieves of MCM-22 family include MCM-22 (described in U.S. Patent No. 4,954,325), PSH-3 (described in U.S. Patent No. 4,439,409), SSZ-25 (described in U.S. Patent
 25 No. 4,826,667), ERB-1 (described in European Patent No. 0293032), ITQ-1 (described in U.S. Patent No. 6,077,498), ITQ-2 (described in International Patent Publication No. WO97/17290), MCM-36 (described in U.S. Patent No. 5,250,277), MCM-49 (described in U.S. Patent No. 5,236,575), MCM-56 (described in U.S. Patent No. 5,362,697), UZM-8 (described in U.S. Patent No. 6,756,030), and mixtures thereof. Preferably, the molecular sieve is selected from
 30 (a) MCM-49; (b) MCM-56; and (c) isotypes of MCM-49 and MCM-56, such as ITQ-2.

[0039] Any known hydrogenation metal can be employed in the hydroalkylation catalyst, although suitable metals include palladium, ruthenium, nickel, zinc, tin, and cobalt, with palladium being particularly advantageous. Generally, the amount of hydrogenation metal present in the catalyst is between about 0.05 and about 10 wt%, such as between about 0.1 and about 5 wt%, of the catalyst.

[0040] Suitable binder materials include synthetic or naturally occurring substances as well as inorganic materials such as clay, silica, and/or metal oxides. Suitable metal oxide binders include silica, alumina, zirconia, titania, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, as well as ternary compositions, such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia, and silica-magnesia-zirconia.

[0041] Although the hydroalkylation reaction is highly selective towards CHB, the effluent from the hydroalkylation reaction will normally contain some dialkylated products, as well as unreacted benzene and the desired monoalkylated species. The unreacted benzene is normally recovered by distillation and recycled to the alkylation reactor. The bottoms from the benzene distillation are further distilled to separate the monocyclohexylbenzene product from any dicyclohexylbenzene and other heavies. Depending on the amount of dicyclohexylbenzene present in the reaction effluent, it may be desirable to either (a) transalkylate the dicyclohexylbenzene with additional benzene or (b) dealkylate the dicyclohexylbenzene to maximize the production of the desired monoalkylated species.

[0042] Transalkylation with additional benzene is typically effected in a transalkylation reactor, separate from the hydroalkylation reactor, over a suitable transalkylation catalyst, such as a molecular sieve of the MCM-22 family, zeolite beta, MCM-68 (see U.S. Patent No. 6,014,018), zeolite Y, zeolite USY, and mordenite. The transalkylation reaction is typically conducted under at least partial liquid phase conditions, which suitably include a temperature of about 100 to about 300°C, a pressure of about 800 to about 3500 kPa, a weight hourly space velocity of about 1 to about 10 hr⁻¹ on total feed, and a benzene/dicyclohexylbenzene weight ratio about of 1:1 to about 5:1.

[0043] In various embodiments, the MCPB is produced as a byproduct of a reaction to make CHB (e.g., by one of the above-described alkylation or hydroalkylation processes). Additionally or alternatively, the MCPB may be provided from a fresh source or recycled from a process to produce phenol.

Alkylaromatic Oxidation

[0044] As discussed above, the invention relates to a composition having: (i) greater than 0.2 wt% of 1-phenyl-1-methylcyclopentane; and (ii) greater than 50 wt% of a second alkylaromatic compound, and the wt% based upon total weight of the composition.

5 [0045] In various embodiments, the composition may comprise greater than about 0.2 of the 1-phenyl-1-methylcyclopentane, or greater than about 0.25 wt%, or greater than about 0.3 wt%, or greater than about 0.35 wt%, or greater than about 0.4 wt%, or greater than about 0.45 wt%, or greater than about 0.5 wt%, or greater than about 0.7 wt%, or greater than about 1 wt% of 1,1 MCPB, or greater than about 5 wt% of 1,1 MCPB, or greater than about 10 wt% of
10 1,1 MCPB, the wt%s based upon total weight of the composition. In other embodiments, the lower limit may be about 0.2 wt%, about 0.25 wt%, about 0.3 wt%, about 0.35 wt%, about 0.4 wt%, about 0.45 wt%, about 0.5 wt%, about 1 wt%, about 1.5 wt%, about 2 wt%, about 2.5 wt%, about 3 wt%, about 3.5 wt%, about 4 wt% and about 5 wt%; and/or the upper limit may be about 20 wt%, about 10 wt%, about 8 wt%, about 7 wt%, about 5 wt%, about 4 wt%, about
15 3 wt%, about 2 wt%, about 1 wt%, and about 0.5 wt% with ranges from any lower limit to any upper limit being contemplated.

[0046] In various embodiments, the composition comprises greater than 50 wt% of a second alkylaromatic compound, or greater than 60 wt%, or greater than 70 wt%, or greater than 80 wt%, or greater than 90 wt%, or greater than 95 wt% of the second alkylaromatic compound,
20 based upon total weight of the composition. For purposes of calculating the wt% of the second alkylaromatic compound in the composition, all isomers of the second alkylaromatic compound are included.

[0047] In various embodiments, the composition comprises an amount of 1,1 MCPB that is sufficient to increase selectivity to the desired alkylaromatic oxygenate at a given conversion
25 of the second alkylaromatic compound. In various embodiments, the presence of the 1,1 MCPB increases selectivity to the desired alkylaromatic oxygenate to greater than 94 % for a cyclohexylbenzene conversion of 15%. Moreover, the composition may comprise an amount of 1,1 MCPB that is sufficient to decrease selectivity to undesirable impurities, such as 1-phenylcyclohexanol, secondary cyclohexylbenzene hydroperoxide, 6-hydroperoxy
30 hexaphenone, and/or 2-phenylcyclohexanone.

[0048] In various embodiments, the composition is contacted with oxygen under oxidation conditions to convert a portion of at least one of the MCPB and the second alkylaromatic compound to an alkylaromatic oxygenate.

[0049] Suitable oxidation conditions include a temperature between about 70°C and about 200°C, such as about 90°C to about 150°C, or about 90°C to about 130°C and a pressure of about 50 to 10,000 kPa, such as about 50 to 500 kPa. A basic buffering agent may be added to react with acidic by-products that may form during the oxidation. In addition, an aqueous phase may be introduced. The reaction can take place in a batch or continuous flow fashion.

[0050] In various embodiments, the oxidation reaction zone comprises a reactor or plurality of reactors. The reactor(s) may be any type of reactor that allows for introduction of oxygen to alkylaromatic compound (e.g., CHB), and may further efficaciously provide contacting of oxygen and alkylaromatic compound to effect the oxidation reaction. For example, the oxidation reactor may comprise a simple, largely open vessel with a distributor inlet for the oxygen-containing stream. In various embodiments, the oxidation reactor may have means to withdraw and pump a portion of its contents through a suitable cooling device and return the cooled portion to the reactor, thereby managing the exothermicity of the oxidation reaction. Alternatively, cooling coils providing indirect cooling, say by cooling water, may be operated within the oxidation reactor to remove the generated heat. In other embodiments, the oxidation reactor may comprise a plurality of reactors in series, each conducting a portion of the oxidation reaction, optionally operating at different conditions selected to enhance the oxidation reaction at the pertinent conversion range of CHB or oxygen, or both, in each. The oxidation reactor may be operated in a batch, semi-batch, or continuous flow manner.

[0051] In various embodiments, the oxidation reaction is conducted in the presence of a catalyst. Suitable oxidation catalysts include N-hydroxy substituted cyclic imides described in U.S. Patent No. 6,720,462, which is incorporated herein by reference for this purpose. For example, N-hydroxyphthalimide (NHPI), 4-amino-N-hydroxyphthalimide, 3-amino-N-hydroxyphthalimide, tetrabromo-N-hydroxyphthalimide, tetrachloro-N-hydroxyphthalimide, N-hydroxyhetimide, N-hydroxyhimimide, N-hydroxytrimellitide, N-hydroxybenzene-1,2,4-tricarboximide, N,N'-dihydroxy(pyromellitic diimide), N,N'-dihydroxy(benzophenone-3,3',4,4'-tetracarboxylic diimide), N-hydroxymaleimide, pyridine-2,3-dicarboximide, N-hydroxysuccinimide, N-hydroxy(tartaric imide), N-hydroxy-5-norbornene-2,3-dicarboximide, exo-N-hydroxy-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide, N-hydroxy-cis-cyclohexane-1,2-dicarboximide, N-hydroxy-cis-4-cyclohexene-1,2 dicarboximide, N-hydroxynaphthalimide sodium salt or N-hydroxy-o-benzenedisulphonimide may be used. Preferably, the catalyst is N-hydroxyphthalimide. Another suitable catalyst is N,N',N''-thihydroxyisocyanuric acid.

[0052] These oxidation catalysts can be used either alone or in conjunction with a free radical initiator, and further can be used as liquid-phase, homogeneous catalysts or can be supported on a solid carrier to provide a heterogeneous catalyst. Typically, the N-hydroxy substituted cyclic imide or the N,N',N"-trihydroxyisocyanuric acid is employed in an amount
5 between 0.0001 wt% to 15 wt%, or about 0.005 to 5 wt%, or about 0.005 to about 1 wt% of the composition.

[0053] As used herein, an "alkylaromatic oxygenate" may be any alkylaromatic compound that includes oxygen as part of its chemical structure. Alkylaromatic oxygenates include alkylaromatic hydroperoxides such as cumene hydroperoxide, methycyclopentylbenzene
10 hydroperoxide, sec-butylbenzene hydroperoxide and cyclohexylbenzene hydroperoxide.

[0054] In one embodiment, the second alkylaromatic compound is CHB and the alkylaromatic oxygenate is a cyclohexylbenzene hydroperoxide (CHBHP) (e.g., cyclohexyl-1-phenyl-1-hydroperoxide (1,1 CHBHP)). This can be accomplished by contacting the CHB with an oxygen-containing gas, such as air and various derivatives of air. For example, it is possible
15 to use air that has been compressed and filtered to removed particulates, air that has been compressed and cooled to condense and remove water, or air that has been enriched in oxygen above the natural approximately 21 mol% in air through membrane enrichment of air, cryogenic separation of air or other conventional means.

[0055] Typically, the product of the CHB oxidation reaction contains at least 5 wt%, such as
20 at least 10 wt%, for example at least 15 wt%, or at least 20 wt% cyclohexyl-1-phenyl-1-hydroperoxide (1,1 CHBHP) based upon the total weight of the oxidation reaction effluent. Generally, the oxidation reaction effluent contains no greater than 80 wt%, or no greater than 60 wt%, or no greater than 40 wt%, or no greater than 30 wt%, or no greater than 25 wt% of 1,1 CHBHP based upon the total weight of the oxidation reaction effluent. The oxidation reaction
25 effluent may further comprise imide catalyst and unreacted CHB. For example, the oxidation reaction effluent may include unreacted CHB in an amount of at least 50 wt%, or at least 60 wt%, or at least 65 wt%, or at least 70 wt%, or at least 80 wt%, or at least 90 wt%, based upon total weight of the oxidation reaction effluent.

[0056] As previously mentioned, one disadvantage of conventional processes is that MCPB
30 is difficult to separate and can build up in the system and interfere with later stages of phenol production. As such, in various embodiments, the process comprises adjusting the amount of MCPB level in the composition. As used herein, "adjusting" means adding or removing MCPB from the composition. For example, MCPB can be removed by distillation. Additionally or alternatively, MCPB can be removed through treatment with a catalyst, especially an acid

catalyst such as faujisite (e.g., zeolite Y) alone or in the presence of benzene at a temperature of, for example, about 100°C to about 350°C. This method is disclosed in U.S. Prov. App. 60/424,236 (Atty. Docket No. 2010EM367) entitled "Process for Producing Cycloalkylaromatic Compounds" filed on December 17, 2010 and is incorporated by reference
5 for this purpose.

[0057] The MCPB content can be adjusted at any location upstream of the oxidation reaction zone. In one embodiment, the MCPB content is adjusted to be within the targeted range at entry to the oxidation reaction zone.

[0058] At least a portion of the composition may be subjected to a cleavage reaction, with or
10 without undergoing any prior separation or treatment.

[0059] In one embodiment, the oxidation reaction produces a composition comprising one or more of CHB oxygenates (e.g., CHBHP), MCPB oxygenates (e.g., methylcyclopentylbenzene hydroperoxide) and unreacted MCPB. The composition may be separated into a first composition rich in CHB oxygenates and a second composition rich in at
15 least one of MCPB oxygenates oxygenate and/or unreacted MCPB. As used herein, when a composition is described as being "rich in" or "enriched" in a specified species, it is meant that the wt% of the specified species in that stream is enriched relative to the feed stream prior to separation.

[0060] In one embodiment, all or a fraction of the oxidation reaction effluent may be
20 subjected to high vacuum distillation to generate a product enriched in unreacted CHB and leave a residue which is concentrated in the desired 1,1 CHBHP and which is subjected to the cleavage reaction. In general, however, such concentration of the 1,1 CHBHP is neither necessary nor preferred. Additionally or alternatively, all or a fraction of the composition, or all or a fraction of the vacuum distillation residue may be cooled to cause crystallization of the unreacted imide
25 oxidation catalyst, which can then be separated either by filtration or by scraping from a heat exchanger surface used to effect the crystallization. At least a portion of the resultant composition reduced or free from imide oxidation catalyst may be subjected to the cleavage reaction.

[0061] As another example, all or a fraction of the composition may be subjected to water
30 washing and then passage through an adsorbent, such as a 3A molecular sieve, to separate water and other adsorbable compounds, and provide a composition with reduced water or imide content that may be subjected to the cleavage reaction. Similarly, all or a fraction of the composition may undergo a chemically or physically based adsorption, such as passage over a bed of sodium carbonate to remove the imide oxidation catalyst (e.g., NHPI) or other adsorbable

components, and provide a composition reduced in oxidation catalyst or other adsorbable component content that may be subjected to the cleavage reaction. Another possible separation involves contacting all or a fraction of the composition with a liquid containing a base, such as an aqueous solution of an alkali metal carbonate or hydrogen carbonate, to form an aqueous phase comprising a salt of the imide oxidation catalyst, and an organic phase reduced in imide oxidation catalyst. An example of separation by basic material treatment is disclosed in International Application No. WO 2009/025939.

Alkylaromatic Hydroperoxide Cleavage

[0062] In various exemplary embodiments, one or more alkylaromatic hydroperoxides formed during oxidation is cleaved to form phenol and a ketone. For example, cyclohexylbenzene hydroperoxide (CHBHP) (e.g., 1,1 CHBHP) may be cleaved using an acid catalyst to produce phenol and cyclohexanone.

[0063] Generally, the acid catalyst used in the cleavage reaction is at least partially soluble in the cleavage reaction mixture, is stable at a temperature of at least 185°C and has a lower volatility (higher normal boiling point) than CHB. Typically, the acid catalyst is also at least partially soluble in the cleavage reaction product. Suitable acid catalysts include, but are not limited to, Brønsted acids, Lewis acids, sulfonic acids, perchloric acid, phosphoric acid, hydrochloric acid, p-toluene sulfonic acid, aluminum chloride, oleum, sulfur trioxide, ferric chloride, boron trifluoride, sulfur dioxide, and sulfur trioxide. Sulfuric acid is a preferred acid catalyst.

[0064] In various embodiments, the mixture containing the alkylaromatic hydroperoxide that is being subjected to the cleavage reaction (also referred to as the “cleavage reaction mixture”) contains at least 50 weight-parts-per-million (wppm) and no greater than 5000 wppm of the acid catalyst, or at least 100 wppm to and no greater than 3000 wppm, or at least 150 wppm to and no greater than 2000 wppm of the acid catalyst, or at least 300 wppm and no greater than 1500 wppm of the acid catalyst, based upon total weight of the cleavage reaction mixture.

[0065] In various embodiments, the cleavage reaction mixture includes CHB in an amount of at least 50 wt%, or at least 60 wt%, or at least 65 wt%, or at least 70 wt%, or at least 80 wt%, or at least 90 wt%, based upon total weight of the cleavage reaction mixture.

[0066] Suitable cleavage conditions include a temperature of greater than 50°C and no greater than 200°C, or at least 55°C and no greater than 120°C, and a pressure of at least 1 and no greater than 370 psig (at least 7 and no greater than 2,550 kPa, gauge), or at least 14.5 and

no greater than 145 psig (at least 100 and no greater than 1,000 kPa, gauge) such that the cleavage reaction mixture is completely or predominantly in the liquid phase during the cleavage reaction.

[0067] The reactor used to effect the cleavage reaction may be any type of reactor known to those skilled in the art. For example, the cleavage reactor may be a simple, largely open vessel operating in a near-continuous stirred tank reactor mode, or a simple, open length of pipe operating in a near-plug flow reactor mode. In other embodiments, the cleavage reactor comprises a plurality of reactors in series, each performing a portion of the conversion reaction, optionally operating in different modes and at different conditions selected to enhance the cleavage reaction at the pertinent conversion range. In one embodiment, the cleavage reactor is a catalytic distillation unit.

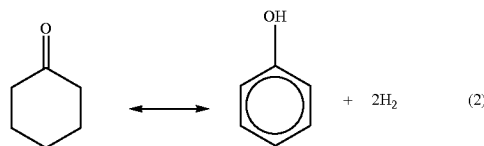
[0068] In various embodiments, the cleavage reactor is operable to transport a portion of the contents through a cooling device and return the cooled portion to the cleavage reactor, thereby managing the exothermicity of the cleavage reaction. Alternatively, the reactor may be operated adiabatically. In one embodiment, cooling coils operating within the cleavage reactor(s) remove any heat generated.

[0069] The major products of the cleavage reaction of cyclohexyl-1-phenyl-1-hydroperoxide are phenol and cyclohexanone, each of which generally comprise about 40 to about 60 wt%, or about 45 to about 55 wt% of the cleavage reaction product, such wt% based on the weight of the cleavage reaction product exclusive of unreacted CHB and acid catalyst.

[0070] The cleavage reaction product also typically contains unreacted acid catalyst and hence at least a portion of the cleavage reaction product is normally neutralized with a basic material to remove or reduce the level of acid in the product.

Cyclohexanone Dehydrogenation

[0071] In various embodiments, some or all of the cyclohexanone produced by the above-described process may be subjected to dehydrogenation to phenol according to the following reaction:



[0072] Various dehydrogenation processes are disclosed in U.S. PCT Application PCT/US2009/050497 entitled "Process for Producing Phenol," and filed on July 14, 2009 and

U.S. Prov. App. 61/301,780 entitled "Dehydrogenation Process" filed on February 5, 2010 and is incorporated by reference for this purpose.

[0073] The invention will now be more particularly described with reference to the following non-limiting Examples.

5 **Example 1: Oxidation of CHB and (0 wt% 1, 1 MCPB) with 0.1 wt% NHPI as the catalyst at 115 °C**

[0074] One hundred fifty (150) grams of cyclohexylbenzene (CHB) from TCI America and 0.16 g N-hydroxyphthalimide (NHPI) from TCI were weighed into a Parr reactor fitted with a stirrer, thermocouple, gas inlet, sampling port and a condenser containing a Dean-Stark trap for
10 water removal. The reactor contents were stirred at 1000 rpm and sparged with nitrogen at a flow rate of 250 cm³/minute for 5 minutes. The reactor, while maintained under a nitrogen sparge, was then heated to 115°C. When the reaction temperature was reached, the gas was switched from nitrogen to air and the reactor was sparged with air at cm³/minute for 4 hours. Samples were taken and analyzed by gas chromatography. After 4 hours, the gas was switched
15 back to nitrogen and the heat was turned off. The results are shown in Figure 1.

Example 2. Oxidation of CHB in the presence 1 wt% 1,1-MCPB with 0.1 wt% NHPI as the catalyst at 115°C

[0075] 148.5 g of CHB and 1.5 g of 1,1 MCPB and 0.16 g NHPI from TCI America were weighed into a Parr reactor fitted with a stirrer, thermocouple, gas inlet, sampling port and a
20 condenser containing a Dean-Stark trap for water removal. The reactor contents were stirred at 1000 rpm and sparged with nitrogen at a flow rate of 250 cm³/minute for 5 minutes. The reactor, while maintained under a nitrogen sparge and was then heated to 115°C. When the reaction temperature was reached, the gas was switched from nitrogen to air and the reactor was sparged with air at 250 cm³/minute for 4 hours. Samples were taken and analyzed by gas
25 chromatography. After 4 hours, the gas was switched back to nitrogen and the heat was turned off. The results are shown in Figure 1.

[0076] Comparing Examples 1 and 2 in Figure 1, selectivity to cyclohexy-1-phenyl-1-hydroperoxide (1, 1 CHBHP) was improved for a given CHB conversion for compositions containing 1 wt% vs. 0 wt% of 1, 1 MCPB.

30 **Example 3. Oxidation of CHB (and 0 wt% MCPB) using 0.1 wt% NHPI as the catalyst at 110°C**

[0077] 150 g of CHB from TCI America and 0.16 g NHPI from TCI were weighed into a Parr reactor fitted with a stirrer, thermocouple, gas inlet, sampling port and a condenser containing a Dean-Stark trap for water removal. The reactor contents were stirred at 1000 rpm

and sparged with nitrogen at a flow rate of 250 cm³/minute for 5 minutes. The reactor, while maintained under a nitrogen sparge and was then heated to 110°C. When the reaction temperature was reached, the gas was switched from nitrogen to air and the reactor was sparged with air at 250 cm³/minute for 4 hours. Samples were taken and analyzed by gas chromatography. After 4 hours, the gas was switched back to nitrogen and the heat was turned off. The results are shown in Figure 2.

Example 4. Oxidation of CHB and 10 wt% 1,1 MCPB with 0.1 wt% NHPI as the catalyst at 110°C

[0078] 135 g of CHB and 15 g of 1,1 MCPB from TCI America and 0.16 g NHPI from TCI were weighed into a Parr reactor fitted with a stirrer, thermocouple, gas inlet, sampling port and a condenser containing a Dean-Stark trap for water removal. The reactor contents were stirred at 1000 rpm and sparged with nitrogen at a flow rate of 250 cm³/minute for 5 minutes. The reactor, while maintained under a nitrogen sparge and was then heated to 110°C. When the reaction temperature was reached, the gas was switched from nitrogen to air and the reactor was sparged with air at 250 cm³/minute for 4 hours. Samples were taken and analyzed by gas chromatography. After 4 hours, the gas was switched back to nitrogen and the heat was turned off. The results are shown in Figure 2.

[0079] Comparing Examples 3 and 4 in Figure 2, 1, 1 CHBHP selectivity was improved for a given CHB conversion for compositions containing 10 wt% vs. 0 wt% 1,1 MCPB.

[0080] Unexpectedly, Figures 1 and 2 illustrate that the presence of 1,1 MCPB improves the 1, 1 CHBHP selectivity.

Example 5. Oxidation of CHB in the presence of 0 wt% and 1.5 wt% 1,1-MCPB and 0.1 wt % NHPI as the catalyst at 110°C

[0081] Using the same techniques described above with reference to Examples 1 and 2, CHB was oxidized with 0 and 1.5 wt% 1,1-MCPB using 0.1 wt% NHPI as the catalyst at 110°C.

[0082] The results are shown in Figure 3-7. The presence of 1,1-MCPB alters the disposition of byproducts formed in CHB oxidation. Formation of alcohol byproducts (namely, 1-phenylcyclohexanol (PhCHOH-1) and 2-phenylcyclohexanol (PhCHOH-2)) is suppressed, as shown in Figures 4 & 5.

[0083] Similarly, lower levels of other major byproducts including secondary cyclohexylbenzene hydroperoxide (CHB-HP2) and 6-hydroperoxy hexaphenone (6-HP-HexPhone) are observed with the addition of low concentrations of 1,1-MCPB.

[0084] Slightly higher levels of the smallest byproduct 2-phenylcyclohexanone (PhCHone) were observed when 1,1 MCPB was added, but this increase is small compared to the decreases of the other byproducts.

5 [0085] While the present invention has been described and illustrated by reference to particular embodiments, those of ordinary skill in the art will appreciate that the invention lends itself to variations not necessarily illustrated herein. For this reason, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present invention.

PCT CLAIMS

1. A composition comprising:
 - (i) greater than 0.2 wt% of 1-phenyl-1-methylcyclopentane; and
 - (ii) greater than 50 wt% of a second alkylaromatic compound,5 wherein the wt%s are based upon total weight of the composition.
2. The composition of claim 1, wherein the second alkylaromatic compound is cyclohexylbenzene.
3. The composition of claim 1 or claim 2, wherein the composition comprises greater than 0.25 wt% of 1-phenyl-1-methylcyclopentane, the wt% based upon total weight of the
10 composition.
4. The composition of any one of the preceding claims, wherein the composition comprises greater than 70 wt% of the second alkylaromatic compound.
5. The composition of any one of the preceding claims, wherein at least some of the 1-phenyl-1-methylcyclopentane is formed by reacting benzene with hydrogen in the presence of
15 a bifunctional catalyst.
6. The composition of claim 5, wherein the reacting occurs at a temperature of about 125°C and about 200°C.
7. The composition of claim 5, wherein the bifunctional catalyst is a zeolite of the MCM-22 family containing at least one metal selected from palladium, ruthenium, nickel, zinc, tin, and
20 cobalt.
8. The composition of any one of the preceding claims, wherein the composition is oxidized to convert a portion of the second alkylaromatic compound to an alkylaromatic oxygenate.
9. The process of claim 8, wherein the composition is oxidized in the presence of N-hydroxyphthalimide.
- 25 10. The process of claim 8 or claim 9, wherein the second alkylaromatic compound is cyclohexylbenzene and the alkylaromatic oxygenate is cyclohexylbenzene hydroperoxide.
11. An oxidation process comprising:
 - contacting a composition comprising:
 - (i) greater than 0.2 wt% 1-phenyl-1-methylcyclopentane, the wt% based upon total
30 weight of the composition; and
 - (ii) a second alkylaromatic compound,

with oxygen under oxidation conditions in the presence of an oxidation catalyst to convert a portion of at least one of the 1-phenyl-1-methylcyclopentane and the second alkylaromatic compound to an alkylaromatic oxygenate.

12. The process of claim 11, wherein presence of 1-phenyl-1-methylcyclopentane increases the oxidation catalyst selectivity to 1,1 cyclohexylbenzene hydroperoxide relative to a process conducted in the presence of less than 0.2 wt% of 1-phenyl-1-methylcyclopentane.

13. The process of claim 11 or claim 12, wherein the amount of 1-phenyl-1-methylcyclopentane is an amount sufficient to decrease the oxidation catalyst selectivity to at least one of 1-phenylcyclohexanol, secondary cyclohexylbenzene hydroperoxide, 6-hydroperoxy hexaphenone, and 2-phenylcyclohexanone relative to a process conducted in the presence of less than 0.2 wt% of 1-phenyl-1-methylcyclopentane.

14. The process of any one of claims 11-13, wherein the oxidation catalyst is an N-hydroxy substituted cyclic imide.

15. The process of any one of claims 11-14, wherein the oxidation conditions include a temperature of about 70 to about 200°C and a pressure of about 50 to about 10,000 kPa.

16. The process of any one of claims 11-15, wherein the second alkylaromatic compound is cyclohexylbenzene.

17. The process of claim 11-16, wherein at least a portion of the 1-phenyl-1-methylcyclopentane is converted to one or more methylcyclopentylbenzene oxygenates and at least a portion of the cyclohexylbenzene is converted to cyclohexylbenzene hydroperoxide.

18. The process of claim 16-17, wherein at least one of the cyclohexylbenzene and the 1-phenyl-1-methylcyclopentane is produced by reacting benzene with hydrogen in the presence of a bifunctional catalyst.

19. The process of claim 17, further comprising cleaving at least a portion of the cyclohexylbenzene hydroperoxide to produce phenol and cyclohexanone.

20. An oxidation process comprising:

(a) reacting benzene and hydrogen to form cyclohexylbenzene and 1-phenyl-1-methylcyclopentane; and

(b) oxidizing a feed comprising at least a portion of the cyclohexylbenzene and the 1-phenyl-1-methylcyclopentane from step (a) in the presence of an oxidation catalyst in an oxidation reaction zone to produce a composition comprising cyclohexylbenzene hydroperoxide,

wherein the oxidation process further comprises adjusting the amount of 1-phenyl-1-methylcyclopentane in the feed upstream of the oxidation reaction zone to about 0.2 to about 10 wt%, based upon total weight of the composition.

21. The process of claim 20, wherein the adjusting step comprises adding or removing 1-phenyl-1-methylcyclopentane from the composition upstream of the oxidation reaction zone.
22. The process of claim 20 or claim 21, wherein the adjusting step comprises distilling at least some 1-phenyl-1-methylcyclopentane from the composition upstream of the oxidation reaction zone.
23. The process of claim 20 or claim 21, wherein the adjusting step comprises contacting at least a portion of the 1-phenyl-1-methylcyclopentane with an aluminosilicate zeolite under reaction conditions effective to convert at least a portion of the methylcyclopentylbenzene to a converted product.
24. The process of claim 23, wherein the aluminosilicate zeolite is zeolite Y.
25. The process of any one of claims 20-24, wherein the adjusting step is conducted in the presence of benzene.

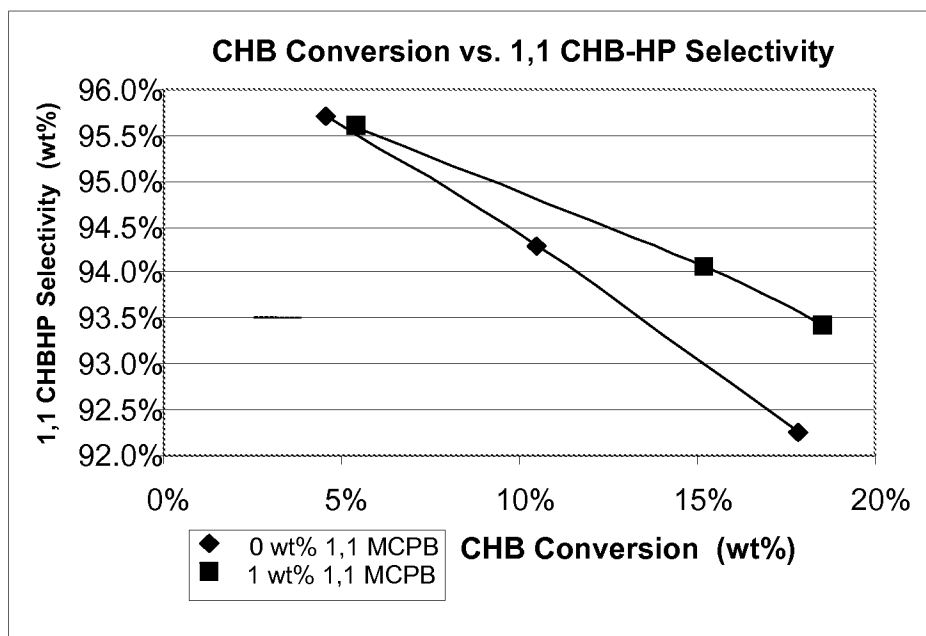
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Figure 1

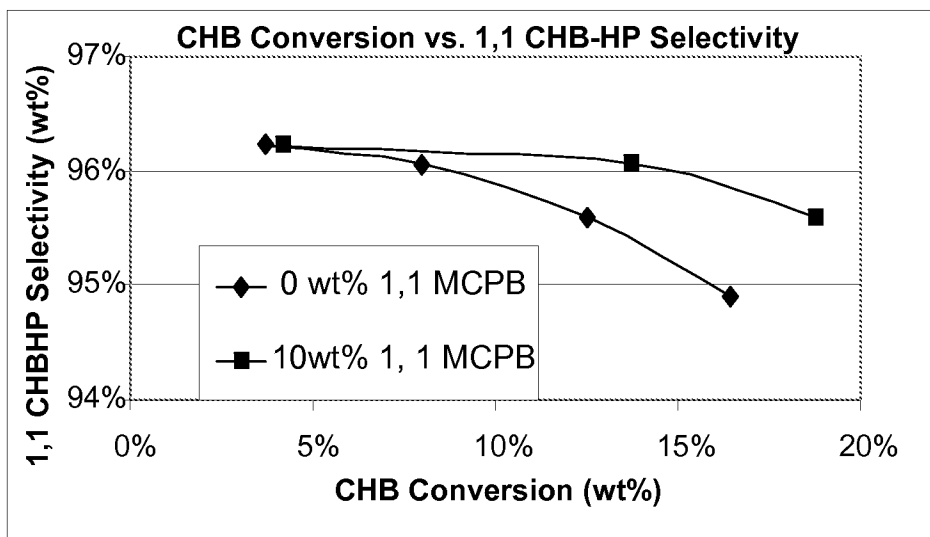


Figure 2

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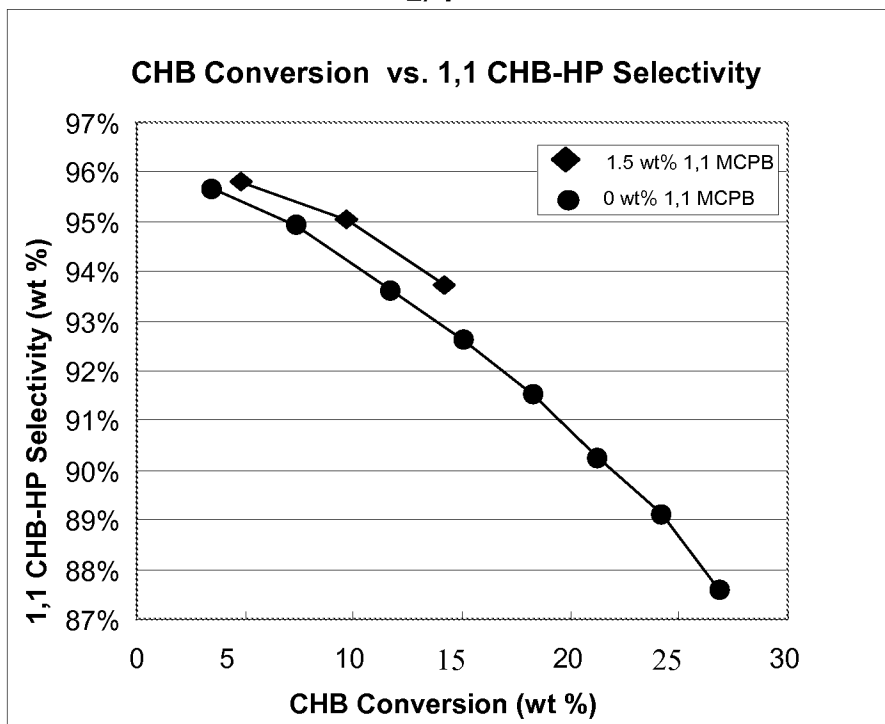


Figure 3

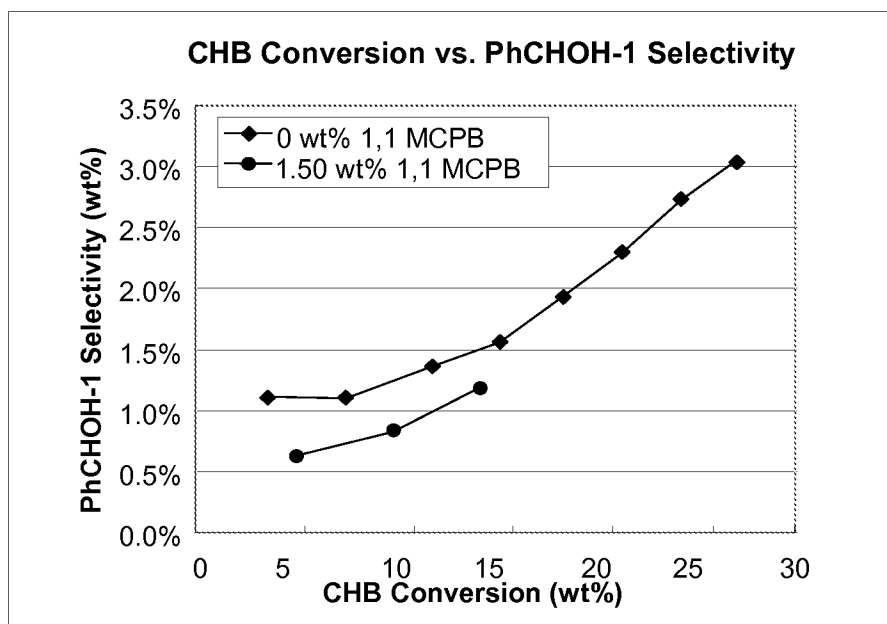


Figure 4

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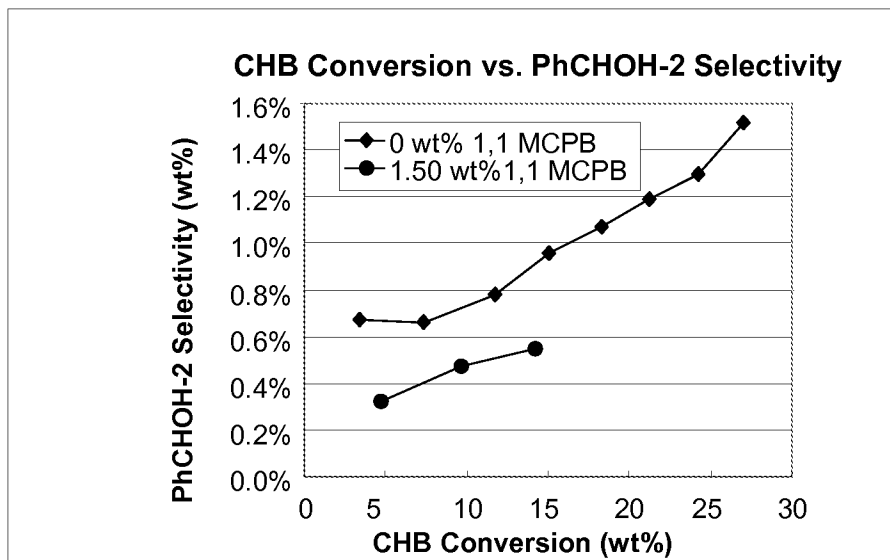


Figure 5

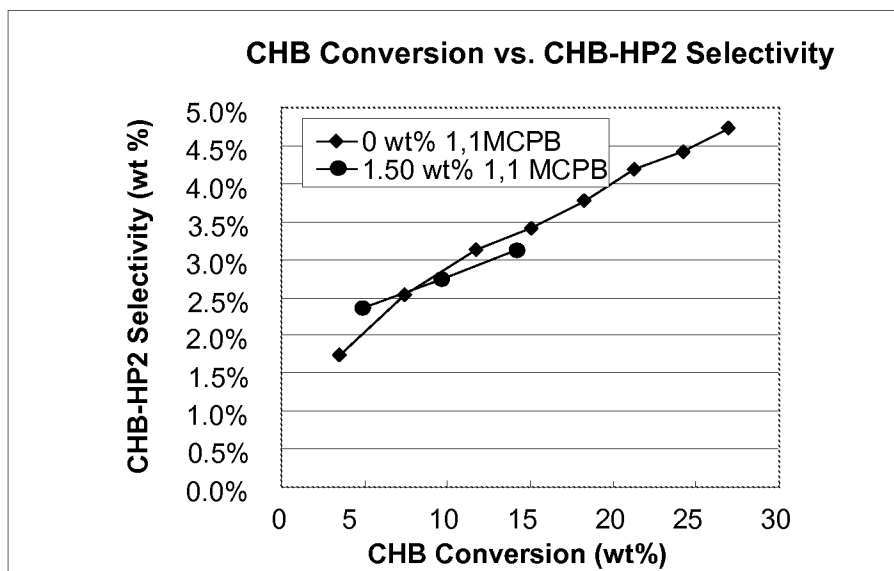


Figure 6

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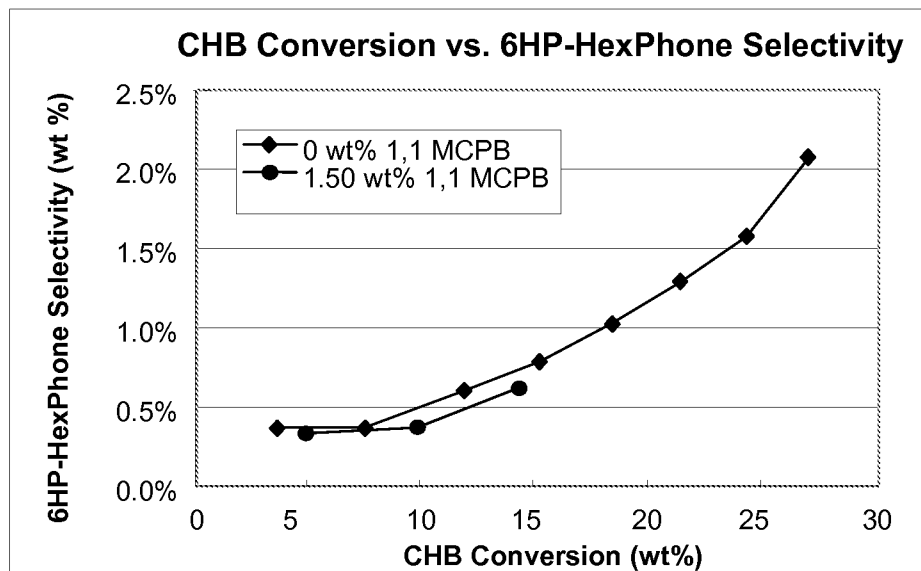


Figure 7

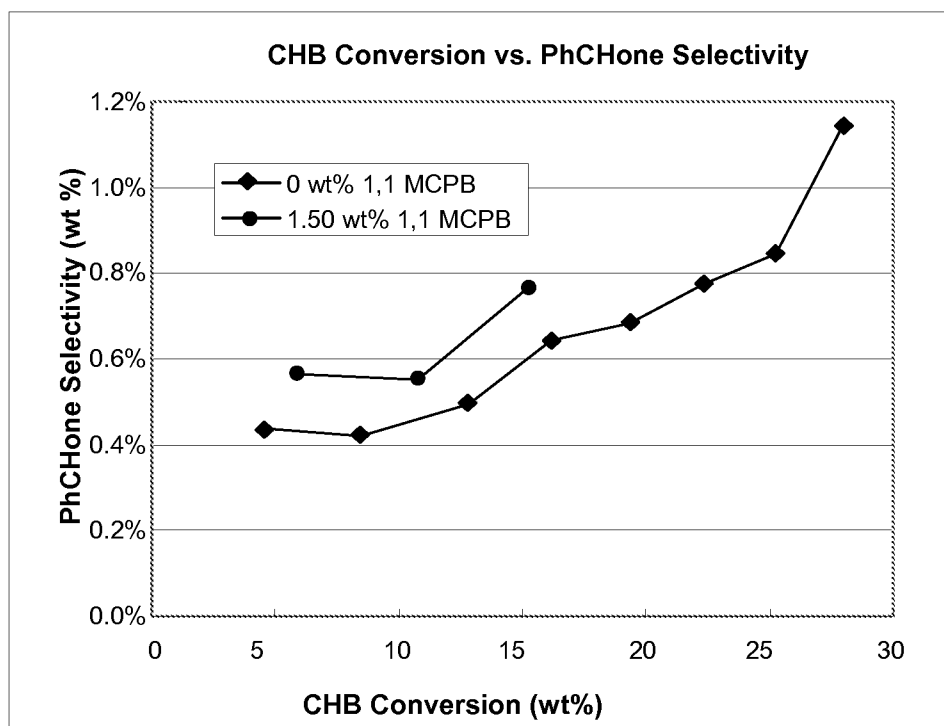


Figure 8

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/057330

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C2/74 C07C13/28 C07C409/14
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, INSPEC, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2010/138248 A2 (EXXONMOBIL CHEM PATENTS INC [US]; WANG KUN [US]; CHENG JANE C [US]; HE) 2 December 2010 (2010-12-02) cited in the application paragraphs [0001], [0012], [0020], [0021], [0028], [0031], [0044], [0046] - [0049], [0052]; claims 3-6; examples; table 1 -----	1-25
X	WO 2009/128984 A1 (EXXONMOBIL CHEM PATENTS INC [US]; CHENG JANE C [US]; CHEN TAN-JEN [US]) 22 October 2009 (2009-10-22) cited in the application paragraphs [0002], [0017], [0020], [0032], [0033], [0036], [0049]; claims 1,5-6,17-18; figure 2c; examples; tables 3-6 -----	1-25



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search

24 November 2011

Date of mailing of the international search report

06/12/2011

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Authorized officer

Seelmann, Marielle

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2011/057330

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2010138248 A2	02-12-2010	TW 201107283 A WO 2010138248 A2	01-03-2011 02-12-2010
WO 2009128984 A1	22-10-2009	CN 101998942 A EP 2297071 A1 TW 201000432 A US 2011015457 A1 WO 2009128984 A1	30-03-2011 23-03-2011 01-01-2010 20-01-2011 22-10-2009