

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
21 August 2008 (21.08.2008)

PCT

(10) International Publication Number
WO 2008/100786 A1

(51) International Patent Classification:
C07C 2/64 (2006.01) *C07C 15/107* (2006.01)

(21) International Application Number:
PCT/US2008/053335

(22) International Filing Date: 7 February 2008 (07.02.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
11/673,908 12 February 2007 (12.02.2007) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

[Continued on next page]

(54) Title: ENERGY INTEGRATED PROCESSES FOR MAKING DETERGENT RANGE ALKYL BENZENES

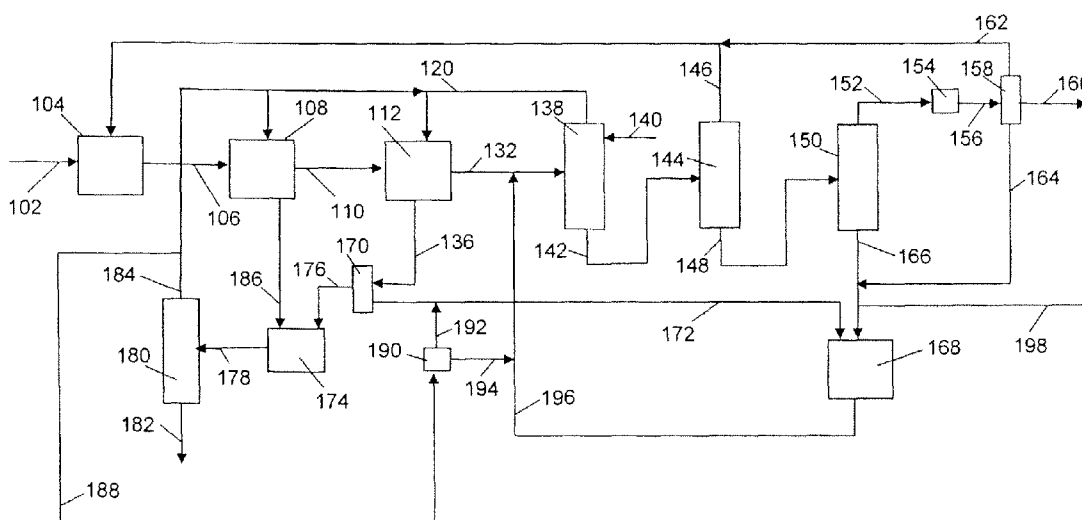


FIG. 1

(57) Abstract: Integrated, energy efficient process for making detergent range alkylbenzenes, heavies coproduced during the alkylation of benzene with olefin using a solid, acidic catalyst are transalkylated. Spent benzene (136) from regeneration of the solid, acidic catalyst used for alkylation (112) provides at least 50 percent of the benzene provided for the transalkylation (168). The integrated processes thus reduce the load on the benzene distillation assembly (138) used in the alkylbenzene refining system (138, 144, 150).

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- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

ENERGY INTEGRATED PROCESSES FOR
MAKING DETERGENT RANGE ALKYL BENZENES

BACKGROUND OF THE INVENTION

[0001] This invention pertains to energy integrated processes for making detergent
5 range alkylbenzenes, and particularly to such processes using a solid, acidic catalyst for
benzene alkylation. In the processes of this invention, benzene from the regeneration of the
solid, acidic catalyst for benzene alkylation is used as a feed to a transalkylation of heavies
co-produced during the benzene alkylation.

[0002] Alkylation of benzene with olefin of 8 to 16 carbon atoms produces
10 alkylbenzenes that may find various commercial uses, e.g., alkylbenzenes can be sulfonated
to produce detergents. As used herein, alkylbenzenes refers to phenylalkanes wherein the
alkane group has between 8 and 16 carbon atoms. Alkylbenzenes are produced as a
commodity product in large-scale facilities, e.g. often in amounts of 50,000 to 200,000 metric
tonnes per year per plant. In the alkylation process, benzene is reacted with an olefin the
15 desired length to produce the sought alkylbenzene. The alkylation conditions comprise the
presence of homogeneous or heterogeneous alkylation catalyst such as aluminum chloride,
hydrogen fluoride, silica alumina or zeolitic catalysts and elevated temperature.

[0003] The alkylbenzene must meet stringent product specifications to be
commercially acceptable. For instance, alkylbenzenes, to be desirable for making sulfonated
20 surfactants, must be capable of providing a sulfonated product of suitable clarity,
biodegradability and efficacy. The benzene content of the alkylbenzene product should be
relatively free from benzenes, e.g., less than 1 part per million by weight (ppmw), and often
less than 0.5 ppmw. Also, desirable alkylbenzene products are relatively free, e.g., less than
50, preferably less than 5, ppmw, from byproducts such as dialkylbenzenes, oligomers of
25 olefins, and the like (herein referred to as "heavies"). Additional considerations for
commercial alkylbenzene products include the 2-phenyl content and linearity of the alkyl
substituent. With respect to efficacy, alkylbenzenes having higher 2-phenyl contents are
desired as they tend, when sulfonated, to provide surfactants having better detergency but less
solubility if the 2-phenyl content becomes too high. Thus alkylbenzenes having a 2-phenyl
30 isomer content in the range from 25 to 40 percent are particularly desired.

[0004] The catalysts are not selective and other reactions of olefins can occur to produce heavies, i.e., dimers and dialkylaryl compounds. Also, skeletal isomerization of the olefin can occur, resulting in a loss of selectivity to the sought alkylbenzene. The formation of dialkylaryl compounds is particularly problematic as the reaction approaches complete conversion of the olefin and the concentration of the alkylbenzene has thus increased thereby increasing the likelihood that an olefin molecule will react with an alkylbenzene molecule rather than benzene. Accordingly, typical processes use a large excess of benzene to reduce the molar ratio of the sought alkylbenzene to the olefin in the reactor. For homogeneous hydrogen fluoride catalyzed processes, the benzene to olefin ratio is generally in the range of 6:1 to 8:1. Solid catalysts are prone to generate more heavies. Hence, for these solid catalysts the mole ratio of benzene to olefin is typically greater than 15:1. For making alkylbenzenes with reduced skeletal isomerization, the benzene to olefin ratio is often in excess of 20:1 and sometimes as much as 30:1.

[0005] As the ratio of benzene to olefin increases, additional process costs are also incurred in the recovery and recycling of the unreacted benzene in the alkylation product. The refining system for alkylbenzene production is summarized in Pujado, Linear Alkylbenzene (LAB) Manufacture, Handbook of Petroleum Refining Processes, Second Edition, pp 1.53 to 1.66 (1996), especially pages 1.56 to 1.60. Especially for large-scale, commercial alkylation processes such as are used for the production of linear alkylbenzenes, capital and operating costs can be very important, and the addition of additional distillation steps can thus be undesirable. Of the distillations effected in the alkylbenzene refining system, the benzene distillation requires the highest heat duty.

[0006] Transalkylation of heavies from the alkylation of benzenes using solid catalysts has been proposed. However, the transalkylation requires benzene and, for purposes of regeneration, benzene is the preferred regenerant. Typically better catalyst performance is obtained with higher ratios of benzene to dialkylbenzene in the heavies being transalkylated. Often the mole ratios of benzene to dialkylbenzene are greater than 20:1. Accordingly, a transalkylation unit operation will be a significant consumer of benzene. Hence, the benzene distillation would have to produce incremental benzene for the transalkylation. This incremental production requires both a distillation assembly of sufficient size and additional reboiler duty. Transalkylation is not practiced in commercial complexes to make detergent range alkylbenzenes. Transalkylation has found application in making other alkylaromatics

having low molecular weight substituents such as xylenes, ethylbenzene, and the like. But the refining systems and product quality issues differ from those in making alkylbenzenes.

[0007] In addition to being a reactant to make alkylbenzenes, benzene is also commonly used for other purposes in an alkylbenzene production complex. For instance, benzene is used for regeneration of solid, acidic alkylation catalysts. Where the olefin-containing feedstock is derived from the dehydrogenation of paraffins, it is often treated with a solid sorbent to remove impurities, especially aromatics, and benzene is used as a regenerant. Proposals have been made to use benzene from the regeneration of solid, acidic alkylation catalyst for regenerating solid sorbent.

[0008] A desire exists for an integrated alkylbenzene production facility that can employ a transalkylation unit operation in an economically viable manner to enhance production of alkylbenzenes.

SUMMARY OF BACKGROUND DISCLOSURES

[0009] The use of alkylation and transalkylation unit operations in the preparation of monoalkylated aromatics is well known. Often such processes have been particularly suggested for making ethylbenzene and cumene although broader disclosures have been made. See, for instance, US 4,870,222, column 1, lines 30 to 34.

[0010] Specific suggestions for transalkylating heavies made in the alkylation of benzenes for detergent range alkylbenzenes include Ganeshpure, et al., Transalkylation of Benzenes with Heavy Alkylbenzenes, Consisting of Dialkylbenzenes and Diphenylalkanes (C₁₀-C₁₄ alkyl chains) Catalysed by Nafion-H, Indian Journal of Technology, Vol. 31, July 1993, pp. 503-506. Radici, et al., in US 5,574,198 disclose a process for producing linear alkylbenzenes using an aluminum chloride catalyst. At column 3, lines 35 to 40, the patentees indicate that the heterogeneous catalytic phase makes possible a transalkylation of polyalkylated species.

[0011] Travers, et al., in US 2003/0040653 disclose the use of a heteropolyacid catalyst for alkylation. At paragraph 0023 the applicants provide for the recycle of at least a portion of a fourth fraction from the alkylation product, which fraction contains polyalkylbenzene, to the reaction zone so as to be at least partially transalkylated. They also

contemplate a separate transalkylation zone containing a different catalyst. See paragraph 0025.

[0012] Euzen, et al., in US 2005/0177017 disclose the use of a catalyst based on silicated alumina for alkylation. At paragraph 0219 the applicants provide for the recycle of at least a portion of a fourth fraction from the alkylation product, which fraction contains polyalkylbenzene, to the reaction zone so as to be at least partially transalkylated. They also contemplate a separate transalkylation zone containing a different catalyst. See paragraph 0225.

[0013] Euzen, et al., in US 2006/0224030 disclose the use of a catalyst based on silica-alumina for alkylation. At paragraph 0237 the applicants provide for the recycle of at least a portion of a fourth fraction from the alkylation product, which fraction contains polyalkylbenzene, to the reaction zone so as to be at least partially transalkylated. They also contemplate a separate transalkylation zone containing a different catalyst. See paragraph 0243.

[0014] Bozzano, et al., in US 6,740,789 and US 6,979,394, disclose the use of benzene that is spent from the regeneration of alkylation catalyst for further use in an alkylbenzene complex, such as for regenerating selective sorbent used to treat the olefin-containing feed and recycle to the alkylation reactor.

SUMMARY OF THE INVENTION

[0015] By this invention, processes are provided for enhancing the production of alkylbenzene of detergent range having desirable product quality through the integrated use of a transalkylation unit operation while still achieving low energy consumption. In the processes of this invention spent benzene from regeneration of solid, acidic catalyst for the alkylation of benzene is used as at least 50 mass percent, and preferably between 80 and essentially all, of the benzene supplied to the transalkylation unit operation. Often, the amount of benzene used for regeneration of alkylation catalyst is between 20 and 25 percent of the total benzene from the benzene distillation. Accordingly, ample benzene from the regeneration of the catalyst is available to maintain a high ratio of benzene to dialkylbenzene in the transalkylation unit.

[0016] In accordance with the broad aspects, the continuous, integrated processes of this invention for preparing linear alkylbenzenes by the alkylation of benzene with olefin having between 8 and 16 carbon atoms, said olefin being contained in admixture with paraffin, in the presence of regenerable, solid, acid alkylation catalyst comprise:

- 5 a. continuously supplying benzene and a mixture of said olefin and paraffin to at least one alkylation zone of at least two alkylation zones, said alkylation zone being at alkylation conditions including the presence of a catalytically effective amount of said catalyst to provide an alkylation product containing alkylbenzene, dialkylbenzenes and unreacted benzene, wherein said alkylation deactivates said catalyst;
- 10 b. separating benzene from the alkylation product to provide a benzene-rich fraction, at least a portion of which is recycled to step (a) and a substantially benzene-free fraction, said fraction containing alkylbenzene, paraffin and dialkylbenzene;
- c. separating paraffin from said substantially benzene-free fraction to provide a paraffin-rich fraction and a substantially paraffin-free fraction containing
- 15 alkylbenzene and dialkylbenzenes;
- d. separating alkylbenzene from said paraffin-free fraction to provide an alkylbenzene fraction and a heavies fraction containing dialkylbenzenes;
- e. periodically regenerating said catalyst in at least one of said alkylation zones by continuously passing through said zone benzene under regeneration conditions to
- 20 provide a spent benzene-containing regeneration stream;
- f. subjecting at least a portion of the heavies fraction to transalkylation conditions comprising the presence of a catalytically effective amount of solid transalkylation catalyst and benzene, at least 50 mass percent, and preferably between 80 and essentially all, of which is derived from the spent benzene-containing stream,
- 25 to provide a transalkylation product containing alkylbenzene and unreacted benzene; and
- g. passing the transalkylation product to step (b).

[0017] In a preferred aspect of the processes of this invention, the mole ratio of benzene to olefin supplied to step (a) is sufficiently low that dialkylbenzene to total

30 alkylbenzene and dialkylbenzene in the alkylation product is greater than 5, and sometimes in the range of between 6 and 10, mass percent. Often the mole ratio of benzene to olefin supplied to step (a) is between 6:1 to 30:1, most preferably between 8:1 to 25:1, and

sometimes between 10:1 and 20:1. At the lower benzene to olefin mole ratios, further advantages exist even though more dialkylbenzene will be co-produced at lower ratios than at higher ratios. Not only will a portion of the dialkylbenzene be converted to alkylbenzene product to maintain desirable alkylbenzene production rates, but also the amount of benzene needed to be distilled in the refining system is reduced because of the lower ratio and because benzene for the transalkylation is derived from spent benzene from regenerating alkylation catalyst.

[0018] In preferred embodiments of the processes of this invention, the mole ratio of benzene to total alkylbenzene and dialkylbenzene (Bz:TAB) in the heavies fed to the transalkylation of step (f) is between 2:1 to 100:1 and preferably between 20:1 to 80:1. At the higher mole ratios, transalkylation catalyst stabilities tend to improve.

[0019] The processes of this invention may use all or a portion of the spent benzene-containing regeneration stream as feed for transalkylation. Where a portion of the spent benzene-containing stream is used, it may be an aliquot portion or may be taken from select stages of the regeneration process. In one preferred embodiment, the regeneration of step (e) produces a spent benzene-containing stream having a varying degree of impurities, and the portion of the benzene from the spent benzene-containing stream used for step (f) is that containing a lesser degree of impurities. The spent benzene-containing stream may also be subjected to purification conditions prior to being introduced into step (f) as a feed for transalkylation. For instance, if the spent benzene-containing stream contains olefin purged from the catalyst being regenerated, a clay treatment may be used.

[0020] While the processes of this invention are continuous, it is within the scope of this invention to operate the transalkylation of step (f) in a semicontinuous or continuous manner. For instance, the heavies fraction from step (d) may be allowed to accumulate and the transalkylation of step (f) conducted in a batch mode. In a semicontinuous mode, the transalkylation product may be passed immediately to step (b) or may be allowed to accumulate to provide a relatively constant flow of transalkylation product to step (b).

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] Figure 1 is a schematic representation of an alkylbenzene complex using the processes of this invention.

[0022] Figure 2 is a schematic representation of an alkylation reactor assembly suitable for use in the alkylbenzene complex of Figure 1.

[0023] Figure 3 is a schematic representation of a transalkylation assembly suitable for use in the alkylbenzene complex of Figure 1.

5 Parameters

Color

[0024] As used herein, color bodies are components of a mixture that impart color to the mixture, and Saybolt color refers to Saybolt color as determined by ASTM D-156-00, Standard Test Method for Saybolt Color of Petroleum Products (Saybolt Chronometer
10 Method), which is available from ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, Pa., USA.

Linearity

[0025] As used herein, linearity is the mass percent of normal alkylbenzenes to total alkylbenzenes.

15 Bromine Index

[0026] There are a number of methods for determining a bromine index of an alkylbenzene, but the methods often provide results that are not consistent with each other. Hence, for purposes herein, the bromine index is that measured by UOP Method 304-90, "Bromine Number and Bromine Index of Hydrocarbons by Potentiometric Titration", which
20 is in effect on July 31, 2004, available from ASTM International.

2-Phenyl Content

[0027] The 2-phenyl content of an alkylbenzene is the mass percent of the alkylbenzene that is a 2-phenylalkane.

DETAILED DISCUSSION

25 [0028] Various processes have been proposed for the alkylation of benzene. See, for instance, Pujado, Linear Alkylbenzene (LAB) Manufacture, Handbook of Petroleum Refining Processes, Second Edition, pp 1.53 to 1.66 (1996). One type of process uses a solid acidic catalyst involving contacting an olefin with a stoichiometric excess of benzene at elevated

temperature to produce alkylbenzene. The reaction product stream will contain, in addition to alkylbenzene, benzene, some unreacted olefin, and reaction byproducts such as dialkylbenzene and oligomers and polymers of the olefin. For commercial processes, the feedstocks may include other components as well. For instance, the olefin may be obtained
5 by the dehydrogenation of a paraffinic feedstock and thus contain significant amounts of paraffin.

The Olefin-containing Feedstock

[0029] Olefin-containing aliphatic compound and benzene are used for the alkylation process. The selection of the olefin is dependent upon the sought alkylation product. The
10 olefin-containing aliphatic compound is preferably has between 8 and 16, and for detergent applications 9 to 14, carbon atoms. The olefin-containing aliphatic compound is an acyclic, mono-olefinic compound. The positioning of the olefinic bond in the molecule is not critical as most alkylation catalysts have been found to promote migration of the olefinic bond. However, the branching of the hydrocarbon backbone is often more of a concern as the
15 structural configuration of the alkyl group on the alkylbenzene product can affect performance especially in surfactant applications and for biodegradation properties. For instance, where alkylbenzenes are sulfonated to produce surfactants, undue branching can adversely affect the biodegradability of the surfactant. On the other hand, some branching may be desired such as the lightly branched modified alkylbenzenes such as described in
20 US 6,187,981. The olefin may be unbranched or lightly branched, which as used herein, refers to an olefin having three or four primary carbon atoms and for which none of the remaining carbon atoms are quaternary carbon atoms. A primary carbon atom is a carbon atom which, although perhaps bonded also to other atoms besides carbon, is bonded to only one carbon atom. A quaternary carbon atom is a carbon atom that is bonded to four other
25 carbon atoms. Although branched, these alkylbenzenes have been characterized by their 2-phenyl content, see for instance, US 6,589,927.

[0030] The olefin-containing aliphatic compound is usually a mixture of two or more olefins. For commercial processes, the feedstocks may include other components as well such as aromatics, lighter mono-olefins, diolefins, paraffins, halogenated hydrocarbons, and
30 oxygenated hydrocarbons such as aldehydes, ethers, esters and carboxylic acids. For instance, the olefin may be obtained by the dehydrogenation of a paraffinic feedstock and

thus contain paraffin. Of course, other olefin synthesis procedures such as dehydration of alcohols and dechlorination, can provide the olefin-containing feedstock. Feedstocks from such sources may have little, if any, paraffin.

[0031] The paraffin is inert in the alkylation reaction but it can serve an important function as a heat sink as the alkylation reaction is exothermic. Where lower benzene to olefin feed ratios are used, the importance of paraffins as heat sinks to adsorb the heat of the alkylation reaction, becomes more important. Nevertheless, in the broad aspects of the processes of this invention, the olefin may be in any concentration in the feedstock including substantially pure. Often, however, the feedstock comprises at least 5 or 10 mole percent olefin. Especially where the feedstock is from the catalytic dehydrogenation of paraffin, the olefin is usually in an amount of 5 to 30, and more frequently 9 to 20, mass-percent of the feedstock.

[0032] Where the olefin is obtained by the dehydrogenation of paraffin, the source of the paraffinic feedstock is not critical although certain sources of paraffinic feedstocks will likely result in the impurities being present. Conventionally, kerosene fractions produced in petroleum refineries either by crude oil fractionation or by conversion processes therefore form suitable feed mixture precursors. Fractions recovered from crude oil by fractionation will typically require hydrotreating for removal of sulfur and/or nitrogen prior to being fed to the subject process. The boiling point range of the kerosene fraction can be adjusted by fractionation to adjust the carbon number range of the paraffins. In an extreme case the boiling point range can be limited such that only paraffins of a single carbon number predominate. Kerosene fractions contain a very large number of different hydrocarbons and the feed mixture to the subject process can therefore contain 200 or more different compounds.

[0033] The paraffinic feedstock may be at least in part derived from oligomerization or alkylation reactions. Such feed mixture preparation methods are inherently imprecise and produce a mixture of compounds. The feed mixtures to the process may contain quantities of paraffins having multiple branches and paraffins having multiple carbon atoms in the branches, cycloparaffins, branched cycloparaffins, or other compounds having boiling points relatively close to the desired compound isomer. The feed mixtures to the process of this invention can also contain aromatic hydrocarbons.

[0034] Another source of paraffins is in condensate from gas wells. Usually insufficient quantities of such condensate are available to be the exclusive source of paraffinic feedstock. However, its use to supplement other paraffinic feedstocks can be desirable. Typically these condensates contain sulfur compounds, which have restricted their use in the past. As this invention enables the use of sulfur-containing feeds, these condensates can be used to supply paraffins for alkylation.

[0035] Paraffins may also be produced from synthesis gas (Syngas), hydrogen and carbon monoxide. This process is generally referred to as the Fischer-Tropsch process. Syngas may be made from various raw materials including natural gas and coal, thus making it an attractive source of paraffinic feedstock where petroleum distillates are not available. The Fischer-Tropsch process is a catalytic process conducted under elevated temperature and pressure. The reaction is temperature sensitive, and temperature control is essential to achieve a desired hydrocarbon product. The products from the Fischer-Tropsch process include not only paraffins but also monoolefins, diolefins, aromatics and oxygenates such as alcohols, ethers, aldehydes and ketones, and thus are normally treated to eliminate oxygenates.

[0036] The olefin-containing feedstock should be sufficiently free of impurities that can unduly adversely affect the life of the alkylation catalyst and that can adversely affect the quality of the alkylbenzene product. The dehydrogenation of paraffins will result in a product containing aromatics, herein referred to as aromatic by-products. The aromatic by-products can comprise substituted phenyl compounds such as toluene, xylenes, and higher methylated benzenes; ethylbenzene, diethylbenzene, and triethylbenzenes; isopropylbenzene (cumene), n-propylbenzene, and higher propylbenzenes; butylbenzenes; and pentylbenzenes and the like; biphenyl compounds and substituted biphenyl compounds; and fused ring compounds and substituted fused ring compounds such as naphthalenes, indanes, tetralins, and the like. Where the feedstocks are used to make alkylbenzenes and a paraffin-containing stream is generated during the purification of the alkylbenzenes and is recycled to the dehydrogenation, the feedstocks may also contain alkylbenzenes. In many instances, the aromatic by-products have the same carbon number as the mono-olefins. The concentration of the aromatic by-products can vary widely, e.g., from 0.3 to 10 mass-percent based upon the mass of the feedstock.

[0037] Advantageously at least a portion of the aromatic by-products in the mono-olefin-containing feedstock is removed using at least one aromatics removal zone. An aromatics removal zone may be placed in one or more locations. For instance, where the feedstock is obtained from a catalytic dehydrogenation including a selective diolefin hydrogenation zone, the aromatic by-products may be selectively removed before or after the selective hydrogenation.

[0038] Suitable aromatics removal zones for this embodiment of the invention include sorptive separation zones. Sorptive separation zones include fixed bed or moving or fluidized sorbent bed systems, but the fixed bed system is preferred. The sorbent may be installed in one or more vessels and in either series or parallel flow. The flow of the feedstock containing the aromatic by-products through the sorptive separation zones is preferably performed in a parallel manner so that one or more sorption beds can be undergoing regeneration while one or more beds are removing aromatic by-products.

[0039] Suitable sorbents may be selected from materials which exhibit the primary requirement of selectivity for the aromatic by-products and which are otherwise convenient to use. Suitable sorbents include, for example, molecular sieves, silica, activated carbon activated charcoal, activated alumina, silica-alumina, clay, cellulose acetate, synthetic magnesium silicate, macroporous magnesium silicate, and/or macroporous polystyrene gel. It should be understood that the above-mentioned sorbents are not necessarily equivalent in their effectiveness. The choice of sorbent will depend on several considerations including the capacity of the sorbent to retain aromatic by-products, the selectivity of the sorbent to retain the aromatic by-products which are more detrimental to solid alkylation catalysts, and the cost of the sorbent. The preferred sorbent is a molecular sieve, and the preferred molecular sieve is 13 X zeolite (sodium zeolite X).

[0040] Those skilled in the art are able to select the appropriate conditions for operation of the sorbent without undue experimentation. For example, a fixed bed sorptive separation zone containing 13 X zeolite may be maintained at a temperature generally from 20°C to 300°C, and preferably from 100°C to 200°C, a pressure effective to maintain the stream containing the aromatic by-products in a liquid phase at the chosen temperature, and a liquid hourly space velocity from 1 hr⁻¹ to 10 hr⁻¹ and preferably from 1 hr⁻¹ to 3 hr⁻¹. The flow of the feedstock through a fixed or moving sorption bed may be conducted in an upflow, downflow or radial-flow manner.

[0041] Although both liquid and vapor phase operations can be used in many sorptive separation processes, liquid phase operation is preferred for the sorptive separation zone because of the lower temperature requirements and because of the higher sorption yields of the aromatic by-products that can be obtained with liquid phase operation over those obtained with vapor phase operation. Therefore, the temperature and pressure of the sorptive separation are preferably selected to maintain the feedstock in a liquid phase. The resulting unsorbed stream having a reduced concentration of aromatic by-products is a desorption effluent. However, the operating conditions of a sorptive separation zone can be optimized by those skilled in the art to operate over wide ranges which are expected to include the conditions in the reaction zones of the invention and its variants. Therefore, a sorptive separation zone may be contained in a common reaction vessel with the dehydrogenation zone, the selective diolefin hydrogenation zone, or the selective alkylation zone.

[0042] A sorbent bed is periodically subjected to regeneration conditions. A benzene-containing stream is used for the regeneration. Generally it is preferred that the benzene be highly pure to avoid undue sorption of any impurities on the sorbent during regeneration. Nevertheless, the regenerant may contain components that do not materially interfere with the regeneration and are acceptable in the sorption effluent. For integrated processes where the sorption effluent is used as a feed to a benzene alkylation reactor and benzene from the refining system is used as regenerant, to prevent undue buildup of paraffins in the regeneration effluent distillation system, the regenerant should contain less than 0.1 mass-percent paraffins, more preferably less than 100 mppm (mass part per million) paraffins. Typically the regenerant contains at least 50, preferably at least 90 or 99, more preferably to at least 99.5, to essentially 100, mass-percent benzene. A purge may be intermittently or continuously withdrawn from at least one point in the recycle loop consisting of the sorber assembly and the regeneration effluent distillation system in order to avoid excessive concentrations of paraffins. Where the sorption effluent is used as a feed to an alkylation reactor to make alkylbenzene, the regenerant is conveniently a pure benzene stream from the refining of the alkylbenzene-containing reaction effluent. Any suitable regeneration method may be used, including altering the temperature and pressure of the sorbent and treating with liquid or vaporous or mixed phase regenerant to displace or desorb aromatic by-products.

[0043] The spent benzene from the regeneration of the sorbent may be recycled to the alkylbenzene refining system or may be treated as disclosed in copending US 11/313071, filed December 20, 2005, herein incorporated by reference in its entirety.

The Alkylation

5 [0044] In the alkylation step, benzene and olefin feedstock are reacted under alkylation conditions to provide an alkylbenzene product. Alkylation conditions include the presence of a solid, acidic catalyst. The alkylation conditions selected will affect the nature of the alkylbenzene product as well as the conversion and selectivity to alkylbenzenes. For instance, higher alkylation temperatures can reduce the linearity of the alkylbenzene product and the type of catalyst can affect the 2-phenyl content of the alkylbenzene product. The
10 benzene to olefin mole ratio is a major determinant of the extent of heavies generated during the alkylation.

[0045] Alkylation conditions generally include a temperature in the range between 80°C and 200°C, most usually at a temperature not exceeding 175°C. Since the alkylation is typically conducted in at least partial liquid phase, and preferably in either an all-liquid phase
15 or at supercritical conditions, pressures must be sufficient to maintain benzene as a liquid. The requisite pressure necessarily depends upon the temperature, but normally is in the range of 1300 to 7000 kPa(g), and most usually between 2000 and 3500 kPa(g). Preferably the alkylation conditions do not result in substantial skeletal isomerization of the olefin. For instance, less than 15 mole percent, and preferably less than 10 mole percent, of the olefin,
20 the aliphatic alkyl chain, and any reaction intermediate undergoes skeletal isomerization.

[0046] Any suitable alkylation catalyst may be used in the present invention, provided that the requirements for conversion, selectivity, and activity are met. Alkylation catalysts comprise zeolites having a zeolite structure type selected from the group consisting of FAU, BEA, MOR, MTW, and NES. Such zeolites include mordenite, ZSM-4, ZSM-12, ZSM-20, ZSM-38, MCM-22, MCM-36, MCM-49, UZM-8, offretite, gmelinite, zeolite Y, NU-87, and gottardite. Another class of acidic, solid catalyst components are acidified refractory oxides such as chlorided, fluorided, or sulfated alumina, gallia, boria, molybdia, ytterbia, titania, chromia, silica, zirconia, and the like and combinations thereof. Clays and amorphous
25 catalysts may also find utility. Further discussion of alkylation catalysts can be found in US 5,196,574; US 6,315,964 and US 6,617,481.
30

[0047] The catalyst may contain suitable binder or matrix material such as inorganic oxides and other suitable materials. The relative proportion of molecular sieve or other catalytically active component in the catalyst may range from 10 to 99 mass-percent, with 20 to 90 mass-percent being preferred. A refractory binder or matrix can be used to facilitate fabrication of the catalyst, provide strength and reduce fabrication costs. The binder should be uniform in composition and relatively refractory to the conditions used in the process. Suitable binders include inorganic oxides such as one or more of alumina, magnesia, zirconia, chromia, titania, boria and silica. The catalyst also may contain, without so limiting the composite, one or more of (1) other inorganic oxides including, but not limited to, beryllia, germania, vanadia, tin oxide, zinc oxide, iron oxide and cobalt oxide; (2) non-zeolitic molecular sieves, such as the aluminophosphates of US 4,310,440, the silicoaluminophosphates of US 4,440,871 and ELAPSOs of US 4,793,984; and (3) spinels such as MgAl_2O_4 , FeAl_2O_4 , ZnAl_2O_4 , CaAl_2O_4 , and other like compounds having the formula $\text{MO—Al}_2\text{O}_3$ where M is a metal having a valence of 2; which components can be added to the composite at any suitable point.

[0048] Alkylation of benzene by the olefins is conducted in a continuous manner, i.e., both the benzene and the olefin-containing feedstock are continuously introduced into the alkylation zone containing the catalyst bed. For purposes herein, a catalyst bed is termed a reactor whether in the same or a separate vessel from another bed. The catalyst may be used as a packed bed or a fluidized bed. The feed to the reaction zone may be passed either upflow or downflow, or even horizontally as in a radial bed reactor. In one desirable variant, olefin-containing feedstock may be fed into several discrete points within the reaction zone.

[0049] One or more alkylation zones can be used. The alkylation zones may be configured in parallel with the same or different catalyst in each. Alkylation zones may also be configured in series, especially with a portion of the olefin-containing feedstock being fed to two or more alkylation zones. The benzene may be fed to the first reaction zone thereby providing a high benzene to olefin ratio in that zone, and the alkylation product is then fed, with additional olefin-containing feedstock to a subsequent reaction zone. Often 3 reactors are used to achieve an advantageous combination of performance and capital expense avoidance with one alkylation reaction zone being off-line for regeneration.

[0050] Where a low benzene to olefin ratio is used, there is less benzene to adsorb the heat of the alkylation reaction. As higher alkylation temperatures can result in loss of

linearity of the alkylbenzene product can occur. It may be desired to use a plurality of alkylation zones with cooling there between. For instance, benzene and a portion of the olefin feedstock at a first blend temperature can be passed to a first zone where the mass ratio of benzene to olefin feedstock is sufficient that the temperature of the first zone effluent is less than 15°C, preferably less than 12°C, and most preferably less than 10°C, above the blend temperature; the first zone effluent is cooled and combined with another portion of the aliphatic feedstock at a second blend temperature. This mixture is passed to a second reaction zone to produce a second zone effluent comprising alkylbenzene and the mass ratio of benzene to olefin feedstock is sufficient that the temperature of the second zone effluent is less than 15°C, preferably less than 12°C, and most preferably less than 10°C, above the blend temperature. This technique can be repeated a sufficient number of times to use the olefin feedstock.

[0051] The cooling of each zone effluent may be by direct or indirect heat exchange, and is preferably at least partially effected by direct heat exchange with the portion of the olefin feedstock being passed to the zone, the olefin feedstock being provided at a cooler temperature than the preceding zone effluent. The cooling is often sufficient to reduce the temperature increased experienced in the previous reaction zone by at least 60 percent, and preferably the temperature reduction is at least to that of the blend temperature of the previous reaction zone.

[0052] A trim reaction zone containing solid alkylation catalyst can be used in any alkylation reaction scheme. The trim reaction zone does not receive any portion of the aliphatic feedstock but rather is maintained under liquid phase alkylation conditions sufficient to consume substantially all olefin contained in the zone effluent from the last of the zones.

[0053] Another technique is to remove at least a portion of the alkylbenzene between alkylation zones to reduce the production of dialkylbenzenes. The separation may be by any convenient means including membrane separation, selective sorption and distillation. In one technique a lights distillation is used to recover a portion of the unreacted benzene contained in the effluent from an alkylation reaction zone. The benzene is recycled to the alkylation zone, and the remaining portion of the unreacted aromatic compound is recovered in a subsequent distillation. The column size and energy requirements for the subsequent distillation are thus reduced. Because the lights distillation need not provide a relatively pure aromatic stream, the energy requirements and size of the lights distillation can be

commercially viable. Often, the lights distillation is effected using less than 5 theoretical distillation trays, especially a flash distillation. Thus, the overhead can contain appreciable amounts of alkylbenzene product as well as paraffins, if paraffins are present in the alkylation reactor effluent. Although arylalkane can be reacted to produce heavies under alkylation conditions, the processes of this invention can still provide an alkylation reaction effluent without an undue amount of heavies. Advantageously, the distillation is conducted at a lower pressure than the alkylation zone, and is often at between 80 and 250 kPa absolute such that a significant portion of the aromatic compound in the at least a portion of the effluent fed to the first distillation zone, is vaporized.

10 Catalyst regenerations

[0054] During use, the catalyst becomes deactivated. This deactivation is substantially reversible and thus the catalyst can be regenerated. Without intending to be limited to theory, it is believed that a significant portion of the deactivation occurs through the deposit of deactivating components on the catalyst and in its pore structure. Hence, when using two or more selective alkylation reactors, at least one is on-stream where alkylation occurs and at least one off-stream where catalyst regeneration takes place. Regeneration is effected by contacting the catalyst in the off-stream reactor with a stream comprising benzene.

[0055] After a reactor has been taken off-stream but before catalyst regeneration begins, the catalyst is typically purged, or flushed, to remove at least some of the unreacted monoolefins, paraffins, and alkylbenzene from the void volume of the now off-stream reactor. The purging conditions are not critical and may be any conditions that are effective for at least partially purging the void volume of the alkylation catalyst. Preferably the off-stream reactor purging conditions comprise at least a partial liquid phase.

[0056] The contacting conditions for purging the catalyst in the off-stream reactor can be the same throughout the off-stream reactor purging, although some changes could be made. The purging can be started by simply stopping the flow of the olefinic feed stream to the on-stream reactor, thereby taking the on-stream reactor off-stream. The contacting temperature is preferably low enough that the deactivating components on the catalyst are not removed. The temperature is usually between 120°C and 170°C. The duration of the purge step can vary widely. The purging need not be complete prior to entering the subsequent step

of ramping the temperature up to a suitable regeneration temperature. Often, the duration of the purge step will be determined by the use of the benzene from the purge step and by the cycle time for regeneration that is available. See, for instance, US 6,740,789, herein incorporated by reference in its entirety.

5 [0057] After purging, catalyst regeneration can begin. The catalyst regeneration conditions are not critical to the success of this invention. The regeneration conditions can be any conditions that are effective for at least partially reactivating the alkylation catalyst. Although olefins may contact the catalyst bed during regeneration, preferably no olefins contact or pass to the catalyst during regeneration. Preferably the regeneration conditions
10 comprise at least a partial liquid phase.

[0058] The contacting conditions can be the same throughout the regeneration, but typically some changes in conditions are made. Commonly, the contacting temperature is changed during regeneration.

[0059] Typically a heating stage is used to increase the temperature to that suitable
15 for regeneration. Generally, the temperature is raised by from 50°C to 200°C above the temperature of the purging. Typically the regeneration is conducted at a temperature between 200°C and the critical temperature of benzene, and preferably between 220°C and 270°C. The temperature may be ramped up steadily or can be increased step-wise with temperature holds. Any suitable method may be used to raise the temperature. One method is heating the
20 benzene by indirect heat exchange and then passing it into the reactor.

[0060] As the temperature increases, the benzene-containing stream begins to remove
deactivating components that accumulated on the surface of the catalyst and block reaction sites. Since some of the components are gum-like materials that have some color (i.e., are color bodies), the presence of these materials in the regeneration effluent may begin to lower
25 its Saybolt color.

[0061] Once the desired temperature for regeneration is reached, usually a hold period follows. The period of time for the regeneration depends on the nature of the catalyst and the extent and nature of the catalyst deactivation, typically from 2 to 20 hours. As the catalyst becomes depleted in the deactivating components, the amount and concentration of these
30 materials in the spent benzene regenerating stream will decline. The regeneration is typically deemed complete when the content of the deactivating components in the spent benzene regeneration stream drops to a relatively low level.

[0062] Finally the reactor is cooled down. The inlet regeneration temperature is reduced from the temperature at the end of the second step to the alkylation temperature. The manner and rate of temperature decrease is not critical to the success of this invention. The temperature may be ramped down steadily or dropped step-wise with temperature holds.

5 Refining

[0063] The alkylbenzene effluent from an alkylation reactor generally has the components and concentrations as set forth in Table 1.

TABLE 1

Component	Concentration (mass)	Typical Concentration (mass)
Alkylbenzene	0.05 to 30 %	2 to 25 %
Benzene	33 to 99 %	40 to 75 %
Total olefin	0.00001 to 2 %	0.0001 to 1 %
Total paraffin	0 to 66 %	1 to 50 %
Heavies	0.001 to 10 %	0.5 to 2 %

[0064] Typically refining of the alkylbenzene product involves the use of a benzene distillation, a paraffin distillation and a heavy alkylate distillation, the benzene distillation is generally conducted with a bottoms temperature of less than 300°C, preferably less than 275°C, usually between 230° and 270°C, and at a pressure at which the overhead is provided of between 5 and 300, preferably between 35 and 70, kPa gauge. The overhead generally contains less than 2, preferably less than 1.5, weight percent paraffins. The benzene distillation assembly may comprise one or more distillation columns. More than one overhead may be obtained from the benzene distillation assembly. For instance, a highly pure stream may be obtained for process needs such as regenerating catalysts or sorbents, e.g., having a paraffin concentration less than 1, preferably less than 0.1, weight percent. A lesser purity overhead may be obtained from the benzene distillation assembly, e.g., as a side draw, for use as a recycle to the alkylation reaction.

[0065] Each column may contain any convenient packing or distillation trays, but most often trays such as sieve and bubble trays, are used. Often the assembly provides at least 5, say 6 to 70, and preferably 20 to 50, theoretical plates. The reflux ratio (herein

defined as the distillate to reflux weight ratio) is often in the range of 2:1 to 1:10, preferably 1.5:1 to 1:5. The bottoms stream from the benzene distillation generally contains less than 1000 ppmw, preferably less than 50 ppmw, and sometimes less than 5 ppmw, benzene. The benzene distillation may occur in a single column or two or more distinct columns may be used. For instance, a stripping column may be used to remove a portion, e.g., 20 to 50 percent, of the benzene and then the bottoms from the stripping column would be subjected to rectification in a subsequent column to obtain the desired separation.

[0066] The paraffin distillation is generally conducted with a bottoms temperature of less than 300°C, preferably less than 275°C, usually between 250°C and 275°C, and at a pressure at which overhead is provided of between 5 and 110, preferably between 10 and 50, kPa absolute. The column may contain any convenient packing or distillation trays, but most often sieve trays are used. Often the paraffins distillation assembly provides at least 5, say 7 to 20, theoretical plates. The reflux ratio is often in the range of 3:1 to 1:10, preferably 1:1 to 1:3. The bottoms stream from the paraffins distillation generally contains less than 10, preferably less than 5, weight percent paraffins and preferably less than 10, often less than 1, ppmw benzene. Preferably, the bottoms stream contains between 0.5 and 5, say 1 to 5, weight percent paraffins. The paraffins distillation may occur in a single column or two or more distinct columns may be used.

[0067] The heavy alkylate distillation is generally conducted with a bottoms temperature of less than 300°C, preferably less than 275°C, usually between 250°C and 275°C, and at a pressure of between 0.5 and 30, preferably between 1 and 5, kPa absolute. The column may contain any convenient packing or distillation trays, but most often structured packing is used. Often the heavy alkylate distillation assembly provides at least 5, say 10 to 30, and preferably 10 to 20, theoretical plates. The reflux ratio is often in the range of 2:1 to 1:5, preferably 0.2:1 to 1:1. The overhead from the heavy alkylate distillation generally contains less than 2 weight percent, preferably less than 1 weight percent, and sometimes less than 0.1 weight percent, total heavies. The benzene content of the overhead stream is generally less than 5, preferably less than 1, ppmw and the paraffins content is often less than 10 weight percent.

[0068] In some instances a finishing distillation may be used where a lights-containing overhead stream is provided, it is not essential that the paraffin distillation substantially remove all the paraffin from the alkylbenzene stream. Hence opportunities exist

for energy savings. For instance, the amount of reboiler heat can be reduced as the internal reflux in the distillation column need not be as great as when the bottoms stream has a lesser concentration of paraffins. Also, for a given column, the capacity of the column can be increased, e.g., to debottleneck an existing refining system.

5 **[0069]** With respect to the heavy alkylate distillation column, the finishing column can remove, as a bottoms stream, heavies. Therefore the heavy alkylate column can be operated to permit significant amounts of heavies to be in the overhead. As with the paraffins distillation, the flexibility provided by these processes enables a reduction in reboiler duty for the heavy alkylate distillation. This reduction, in turn, reduces the reflux in the column
10 thereby allowing more heavies to pass into the overhead stream. In addition to the reduction in reboiler heat duty that could be achieved, the capacity of a given distillation column can be increased.

[0070] The finishing distillation is generally conducted with a bottoms temperature of less than 300°C, preferably less than 275°C, usually between 250°C and 275°C, and at a
15 pressure of between 5 and 110, preferably between 10 and 50, kPa absolute. The assembly may contain any convenient packing or distillation trays, but most often structured packing is used. Often the assembly provides at least 2, say 5 to 20, theoretical plates. The mid-cut is generally taken from a point where at least 2, often at least 3, theoretical plates exist above and at least 2, often at least 3, theoretical plates exist below. Preferably the distillation
20 assembly is a divided wall column or has an internal column with a dedicated reboiler. The finishing distillation assembly may also be two separate columns.

[0071] In some instances it may be desired to subject an alkylbenzene stream that contains olefinic components to a catalytic operation to improve bromine index, the alkylbenzene stream is passed to a catalytic conversion zone containing an acidic catalyst
25 under olefin reduction conditions. The particular unit operation is not critical to the broad aspects of the invention and any suitable operation may be used.

[0072] A number of processes for improving the quality of alkylbenzenes and reducing olefin content have been proposed. The catalysts may be clay or molecular sieve (natural or synthetic). Included in the clays are smectites, laponite, saponite, and pillared
30 clays. Filtrol F-24 (Engelhard Corporation, Iselin, New Jersey) is a preferred clay. Molecular sieves include zeolites A, beta, L, S, T, X and Y and omega, mordenite, erionite, chabazite, boggsite, cloverite, gmelinite, offretite, pentasil molecular sieves having silica to

alumina ratios greater than 10, and SAPO (such as SAPO 5 and 41). Engelhard Corporation represents that Filtrol F-24 has a pH of 3.5.

[0073] The bromine index reduction is typically conducted at temperatures between 25°C and 250°C, and most often between 70°C and 150°C, under a pressure sufficient to maintain the stream under liquid conditions, e.g., within the range of 0.1 to 150 kPa absolute. The contact time with the catalyst is sufficient to provide the desired reduction in bromine index. For a fixed bed system, the weight hourly space velocity is typically in the range of 0.1 to 20 hr⁻¹. The bromine index of the treated alkylbenzene stream is preferably below 10. The bromine index reduction conditions also cause byproducts such as the formation of dialkylbenzene and benzene from alkylbenzene and form oligomers and polymers from olefinic components.

[0074] The effluent from the bromine index reduction is subjected to the fourth distillation to remove as an overhead, benzene, and heavies such as the dialkylbenzene and the oligomers and polymers from olefinic components.

Transalkylation

[0075] The bottoms from the heavy alkylate column can be recovered and used as a heavy alkylate product, or can be subjected to a further separation, e.g., by distillation to recover alkylbenzene contained therein, or can be subjected to a transalkylation in the presence of benzene to convert, e.g., dialkylbenzenes to monoalkylbenzene.

[0076] The transalkylation can be continuous or batch (semicontinuous). The transalkylation conditions including catalyst can vary widely. Typical catalysts include those having acidic functionality. Acidic catalysts comprise zeolites having a zeolite structure type selected from the group consisting of FAU, BEA, MOR, MTW, and NES. Such zeolites include mordenite, ZSM-4, ZSM-12, ZSM-20, ZSM-38, MCM-22, MCM-36, MCM-49, UZM-8, offretite, gmelinite, zeolite Y, NU-87, and gottardite. Another class of acidic, solid catalyst components are acidified refractory oxides such as chlorided, fluorided, or sulfated alumina, gallia, boria, molybdia, ytterbia, titania, chromia, silica, zirconia, and the like and combinations thereof. Clays such as beidellite clays, hectorite clays, laponite clays, montmorillonite clays, nontonite clays, saponite clays, bentonite clays and mixtures thereof and amorphous catalysts may also find utility.

[0077] If desired, the transalkylation catalyst may be metal stabilized. The metal component typically is a noble metal or base metal. The noble metal is a platinum-group

metal is selected from platinum, palladium, rhodium, ruthenium, osmium, and iridium. The base metal is selected from the group consisting of rhenium, tin, germanium, lead, cobalt, nickel, indium, gallium, zinc, uranium, dysprosium, thallium, and mixtures thereof. The base metal may be combined with another base metal, or with a noble metal. Preferably the metal component comprises rhenium. Suitable metal amounts in the transalkylation catalyst range from 0.01 to 10 mass-percent, with the range from 0.1 to 3 mass-percent being preferred, and the range from 0.1 to 1 mass-percent being highly preferred. In some instances, it may be desirable to modify the catalyst such as by sulfiding either in-situ or ex-situ.

[0078] The catalyst may contain suitable binder or matrix material such as inorganic oxides and other suitable materials. The relative proportion of molecular sieve or other catalytically active component in the catalyst may range from 10 to 99 mass-percent, with 20 to 90 mass-percent being preferred. A refractory binder or matrix can be used to facilitate fabrication of the catalyst, provide strength and reduce fabrication costs. The binder should be uniform in composition and relatively refractory to the conditions used in the process. Suitable binders include inorganic oxides such as one or more of alumina, magnesia, zirconia, chromia, titania, boria and silica. The catalyst also may contain, without so limiting the composite, one or more of (1) other inorganic oxides including, but not limited to, beryllia, germania, vanadia, tin oxide, zinc oxide, iron oxide and cobalt oxide; (2) non-zeolitic molecular sieves, such as the aluminophosphates of US 4,310,440, the silicoaluminophosphates of US 4,440,871 and ELAPSOs of US 4,793,984; and (3) spinels such as MgAl_2O_4 , FeAl_2O_4 , ZnAl_2O_4 , CaAl_2O_4 , and other like compounds having the formula $\text{MO—Al}_2\text{O}_3$ where M is a metal having a valence of 2; which components can be added to the composite at any suitable point.

[0079] The transalkylation is conducted in the liquid phase with a benzene to total alkyl substituted benzenes ratio (Bz:TAB) of at least 1:1. Often this ratio is between 2:1 to 100:1. In general, higher Bz:TAB is preferred as the liquid flow assists in removing coke precursors from the catalyst, thereby enhancing time on stream prior to regeneration or replacement. Preferred Bz:TAB will depend upon the severity of the transalkylation conditions, the superficial liquid velocity in the catalyst bed and the conversion per pass. Typically, the Bz:TAB is within the range of 20:1 to 80:1, say, 30:1 to 60:1. The spent benzene-containing regeneration stream may be used directly or may be subjected to a purification to remove undesirable components such as gums and coke precursors. The

purification may be a selective sorption, membrane separation or, preferably, a distillation. Advantageously, adequate purification via a distillation may be obtained by a flash distillation or one containing up to 2 theoretical distillation plates and low reflux to feed ratios. The spent benzene-containing stream provides at least 50 mass percent

5 [0080] As stated above, the processes of this invention may use all or a portion of the spent benzene-containing regeneration stream as feed for transalkylation. Where a portion of the spent benzene-containing stream is used, it may be an aliquot portion or may be taken from select stages of the regeneration process. The regeneration of the alkylation catalyst proceeds in generally four stages, purge, heating stage, hold period and cool down period.

10 The composition of the spent benzene-containing stream will vary by each stage. As the spent benzene stream from the purge stage contains paraffins, alkylbenzene, and heavies from the interstices of the catalyst bed, it can readily be used as a benzene source for the transalkylation. When the regeneration of the alkylation catalyst proceeds to stages where deactivating components are being removed, often the spent benzene can be used without

15 intervening treatment such as a flash distillation, without undue adverse effects on the transalkylation catalyst stability or alkylbenzene product quality.

[0081] Conditions employed for transalkylation normally include a temperature of from 130°C to 270°C, preferably from 180°C to 240°C. At higher temperatures, a greater amount of cracking occurs with increased co-production of lights, i.e., aliphatic hydrocarbons

20 having 9 and fewer carbon atoms. Also, the higher temperatures tend to result in loss of linearity of the alkylbenzene which is not desirable for alkylbenzenes to be used for sulfonation to detergents. Hence, the more preferred transalkylation temperatures are from 190°C to 220°C. Moderately elevated pressures broadly ranging from 100 kPa to 10 MPa absolute are also used for transalkylation such that the reactants remain in the liquid state.

25 [0082] The transalkylation reaction can be effected over a wide range of space velocities, with higher space velocities enhancing the stability of the catalyst but at the expense of conversion of dialkylbenzenes to monoalkylbenzene. Often, the conversion of dialkylbenzenes in the feed to a transalkylation zone is less than 60 mass percent, say, between 20 and 50 mass percent. Weight hourly space velocity generally is in the range of

30 from 0.1 to 30, and frequently between 0.5 and 4, hr⁻¹. In general, lower space velocities are preferred with lower Bz:TAB's from the standpoint of catalyst stability. The adding of hydrogen is optional. If present, free hydrogen is associated with the feedstock and recycled

hydrocarbons in an amount of 0.1 moles per mole of TAB up to 10 moles per mole of TAB. As the temperature for transalkylation is typically more severe than that used for the alkylation of benzene, isomerization of the alkyl groups is more prevalent. Since the ratio of dialkylbenzene to total alkylbenzenes from the alkylation reaction is typically low, the linearity of the combined alkylbenzenes, that from the alkylation and that from the transalkylation, is often at least 85, preferably at least 88, mass percent.

[0083] For purposes herein, a catalyst bed is termed a reactor whether in the same or a separate vessel from another bed. The catalyst may be used as a packed bed or a fluidized bed. The feed to the reaction zone may be passed either upflow or downflow, or even horizontally as in a radial bed reactor. In one desirable variant, olefin-containing feedstock may be fed into several discrete points within the reaction zone.

[0084] One or more transalkylation zones can be used. The transalkylation zones may be configured in parallel with the same or different catalyst in each. A preferred transalkylation process effectively uses the benzene by separating at least a portion of the benzene from at least one transalkylation zone and passing that benzene to one or more transalkylation zones as all or a part of the benzene. The separation, if by distillation, will result in some of the lights also being recycled and a continuous or intermittent purge may be required to maintain the lights at a suitable concentration, e.g., less than 20, preferably less than 10, volume percent of the separated benzene. Preferably the fraction containing the alkylbenzene will also contain benzene to assist in maintaining a steady state operation. One advantage with this preferred process using a separation unit operation associated with the transalkylation zone is that the amount of fresh benzene required is reduced while still being able to provide a high Bz:TAB.

[0085] With respect to the associated separation being a distillation (transalkylation distillation), the amount of effluent from one or more transalkylation zones that is directed to the transalkylation distillation may be as little as 20 weight percent of the total effluent or may comprise the entire effluent stream. Often at least 50, and sometimes at least 80, weight percent of the effluent is subjected to the transalkylation distillation. Where more than one transalkylation zone is used, the effluent from one or more of the zones can be fed to the transalkylation distillation.

[0086] In any event, sufficient fluid must be removed from the transalkylation zone and the transalkylation distillation loop to prevent an undue build-up of inerts or other

impurities in the loop. Typically the concentration of lights in the alkylation zone is less than 20 weight percent, and preferably less than 10, weight percent. Only a portion of the benzene contained in the feed to the transalkylation distillation zone is intended to be recovered in the overhead. The amount of the aromatic compound recovered in the overhead is often between 20 and 98, say, 50 to 70 or 90, weight percent of that in the distillation feed. The overhead may also contain lights.

[0087] Advantageously, the distillation equipment need not be extensive to achieve such recovery, e.g., the distillation may be accomplished with less than 5 theoretical plates. Moreover, the lights distillation is preferably conducted without significant reboiler heat.

Preferably the sought recovery of benzene is accomplished by a flash distillation due to temperature of the effluent from the transalkylation zone without the need for a heat source. Where heat is supplied to the transalkylation distillation, e.g., to provide for internal reflux in a fractionation column, it preferably is less than 40, more preferably less than 30, kilocalories per kilogram of the feed to the transalkylation distillation. Where a reflux is used, the rate of external reflux (distillation feed to reflux, F/R) is preferably between 0.1:1 to 2:1, more preferably between 0.4:1 and 0.8:1, kilogram per kilogram of effluent fed to the transalkylation distillation zone.

[0088] The transalkylation distillation may be effected in an open vessel for a flash distillation or may contain suitable trays or packing for a fractionation. A flash distillation may contain a demister to prevent liquid carryover in the overhead. Heat to the lights distillation zone may be provided by indirect heat exchange at the bottom of the zone, or by withdrawing, heating and recycling to the base of the column a portion of the liquid contained at the bottom of the lights distillation zone. The transalkylation distillation will provide a higher boiling fraction containing alkylbenzene, heavies and benzene.

[0089] All or a portion of the transalkylation product (obtained either or both from the transalkylation zone or the separation) is passed to the benzene column of the refining section. Unreacted heavies, of course, will be recovered in the refining section and can be thus recycled to the transalkylation unit operation. Where the transalkylation is operated to achieve a low conversion per pass, say, 20 to 40 weight percent conversion of the dialkylbenzenes, a portion of the transalkylation product (obtained either or both from the transalkylation zone or the separation) can be passed to a transalkylation zone for further

conversion. Since low conversion is acceptable, lower temperatures can be used to enhance the linearity of the alkylbenzene produced by the transalkylation.

[0090] In some instances it may be desired to regenerate the transalkylation catalyst. Any suitable regeneration conditions may be used. Conveniently, the regeneration is effected by passing through the catalyst bed benzene at elevated temperature. The benzene may be from any suitable source, especially a portion of the spent benzene-containing stream from the regeneration of the alkylation catalyst. The temperature for the regeneration should not be so high as to adversely affect the transalkylation catalyst. Usually the temperature is in the range of 170°C to 300°C, say, 190°C to 220°C or 250°C. The duration of the regeneration may vary depending upon the extent of regeneration sought and the other conditions for the regeneration. Typically, the regeneration proceeds for at least 1 hour, e.g., from 4 to 50 hours. The spent regenerant can be disposed of in any suitable manner. The spent benzene-containing regenerant may be subjected to a flash distillation to remove high boiling impurities such as carbonaceous deposits and precursors, and then passed to the benzene distillation in the alkylbenzene refining system.

THE DRAWINGS

[0091] The drawings are provided in illustration of an embodiment of the invention and are not in limitation thereof.

[0092] Figure 1 schematically depicts an alkylbenzene complex 100 including the dehydrogenation of paraffin feedstock to make the olefin-containing feedstock for the alkylation. As shown, paraffin feedstock is supplied via line 102 to olefin production unit 104. Olefin production unit dehydrogenates paraffin and yields an olefin-containing feedstock which is withdrawn via line 106. Within olefin production unit 104 is not only a dehydrogenation reactor but also a distillation refining system and a selective hydrogenation unit operation to eliminate diolefins. The olefin-containing feedstock in line 106 contains predominantly paraffins, 10 to 15 volume percent olefins and other co-boiling hydrocarbons including aromatics. Thus the feedstock is passed to selective sorption unit 108 for removal of aromatic impurities. The selective sorption unit 108 may be of any suitable design such as disclosed above. The selective sorption unit uses solid sorbent which can be regenerated with a benzene stream as will be discussed later.

[0093] The treated olefin-containing feedstock is then passed via line 110 to alkylation reaction assembly 112. Alkylation reaction assembly is discussed in connection with Figure 2. In Figure 2, the olefin-containing feedstock in line 110 is passed to olefin header 114 and then to control valve assemblies 116a, 116b and 116c associated with reactors 118a, 118b and 118c. Control valve assemblies may be one or more valves to control flows into and out of each reactor.

[0094] Benzene is supplied via line 120 to benzene header 122 which is in flow communication with each of control valve assemblies 116a, 116b and 116c. Each of control valve assemblies 116a, 116b and 116c are in fluid communication with reactors 118a, 118b and 118c, respectively via lines 124a, 124b and 124c. Reactors 118a, 118b and 118c are in fluid communication with the next sequential control valve assembly 116b, 116c and 116d, respectively via lines 126a, 126b and 126c. Each of control valve assemblies 116a, 116b, 116c and 116d are in fluid communication with internal flow header 128. Internal flow header 128 allows for the passage of a reactor effluent from one reactor to the inlet for another reactor. Each of control valve assemblies 116b, 116c and 116d are in fluid communication with alkylation effluent header 130 which in turn is in communication with line 132 for withdrawing alkylation effluent from alkylation reaction assembly 112. Each of control valve assemblies 116b, 116c and 116d are also in fluid communication with spent benzene header 134 which in turn is in communication with line 136 for withdrawing spent benzene from alkylation reaction assembly 112.

[0095] In operation, alkylation reactor assembly permits two reactors to be sequentially on stream while one reactor is undergoing regeneration and permits any of the reactors to be the first reactor in the series on stream. By way of illustration, olefin-containing feedstock in header 114 is partitioned by valve assemblies 116a, 116 b and 116c to provide a portion of the feedstock only to reactors 118a and 118b. With reactor 118a being the first in the series, the control valve assemblies provide for benzene for the alkylation reactor to be all introduced into reactor 118a. Thus control valve assembly 118b permits no benzene from benzene header 122 from entering into reactor 118b. However, control valve assembly 116c permits benzene at a rate suitable for regeneration to be introduced into reactor 118c. The effluent from reactor 118a passes via line 126a to control valve assembly 116b. As reactor 118b is the next reactor in series, the effluent is directed via line 124b to reactor 118b. Control valve assembly directs the effluent from reactor 118b which is

conveyed by line 126b to alkylation effluent header 130 to be withdrawn from reactor assembly 112 via line 132. Reactor 118c is undergoing regeneration and the spent benzene regenerant is passed via line 126c from reactor 118c to control valve assembly 116d which directs it to benzene purge header 134 and withdrawal from alkylation reactor 112 via line 136.

[0096] Upon completion of the regeneration of the catalyst in reactor 118c, it is placed back on-line and one of the other reactors is taken out of service for catalyst regeneration. Typically, the second reactor in the series on line is transitioned to regeneration. In such event, reactor 118c becomes the first reactor in the series and reactor 118a becomes the second in series. The control valve assembly appropriately changes the flows of the various streams. Thus, the benzene for the alkylation reaction is passed through valve assembly 116c and line 124c to reactor 118c while no benzene passes through valve assembly 116a. Benzene for regeneration is passed through valve assembly 116b and line 124b to reactor 118b. Olefin-containing feedstock is partitioned between valve assemblies 116a and 116c. The effluent from reactor 118c is passed via line 126c to valve assembly 116d to internal flow header which directs the effluent to valve assembly 116a to be passed to reactor 118a. Valve assembly 116b directs the effluent from reactor 118a to alkylation effluent header 130. The effluent from reactor 118b, which is being regenerated, is directed by valve assembly 116c to benzene purge header 134.

[0097] As can be seen from the above, each of the reactors can be cycled to different positions while on stream and taken off-stream for regeneration.

[0098] Returning to Figure 1, alkylation effluent from reactor assembly 112 is passed via line 132 to benzene column 138 to provide a benzene-containing fraction which is recycled via line 120 to reactor assembly 112. Fresh benzene is provided via line 140 to benzene column 138. Not shown, but optional uses for the benzene-containing fraction from benzene column 138 is as a feed to the transalkylation reaction system and as a regenerant for the solid sorbent in selective sorption unit 108.

[0099] The bottoms fraction from benzene column, which contains alkylbenzene, heavies and paraffin is passed via line 142 to paraffins column 144. A lower boiling fraction rich in paraffins is passed via line 146 to olefin production unit 104. The bottoms fraction of paraffins column 144, which contains alkylbenzene and heavies is passed via line 148 to heavy alkylate column 150. Heavy alkylate column 150 provides a lower boiling fraction

rich in alkylbenzene that is withdrawn via line 152. This fraction may also contain some benzene and paraffins as well as some olefinic components and thus a clay treater and finishing column are used. As shown, the lower boiling fraction in line 152 is passed to clay treater 154 and then via line 156 to finishing column 158. A side draw from finishing column 158 is taken via line 160 which is the alkylbenzene product. An overhead fraction containing paraffin and benzene is passed via line 162 to line 146 for ultimate recycling to olefins production unit 104. The bottoms fraction from finishing column 158 contains dialkylbenzene and is passed via line 164 for combination with the bottoms fraction from heavy alkylate column 150 which is withdrawn via line 166. The bottoms fraction from the heavy alkylate column contains heavies, i.e., dialkylbenzene, other heavier aromatics and olefin oligomers, and some alkylbenzene. The combined stream passes to transalkylation assembly 168. A stream may be split off via line 198 either as a purge to prevent undue build-up of heavy hydrocarbons or for further refining to provide a dialkylbenzene-containing product.

[00100] Returning to alkylation reactor assembly 112, spent benzene regenerant, which contains benzene as well as deactivating components removed from the catalyst, is passed via line 136 to distributor assembly 170. While not essential, distributor assembly directs the spent benzene regenerant that contains little color formers and gums directly to transalkylation assembly 168 via line 172. This spent benzene is from a purge of the reactor undergoing regeneration and thus contains alkylbenzenes, paraffin, and dialkylbenzene from the interstitial regions and from the catalyst surface and possibly some of the regenerant as the reactor cools down to temperatures suitable for alkylation. As the color formers and gums start to be removed from the regenerating catalyst, distributor 170 directs the spent benzene regenerant to hold tank 174 via line 176. Hold tank 174 serves as a reservoir for the spent benzene regenerant from which a constant flow of benzene can be withdrawn via line 178 for distillation in column 180.

[00101] A bottoms fraction containing higher molecular weight color formers and deactivating components is withdrawn via line 182 from column 180. A benzene fraction is withdrawn via line 184. As shown, a portion of the benzene fraction in line 184 is directed to selective sorption unit 108 as regenerant. The spent regenerant from selective sorption unit 108 is passed via line 186 to hold tank 174.

[00102] A portion of the benzene fraction in line 184 is passed via line 188 to valve assembly 190 which can direct all or part of the stream via line 192 to line 172 for the transalkylation assembly 168 and all or part of the stream via line 194 to line 196 which is in communication with benzene column.

5 [00103] Transalkylation assembly 168 is described further with reference to Figure 3. The combined bottoms fraction from heavy alkylate column 150 and from finishing column 158 is passed to transalkylation assembly 168 via line 166, and a portion of the stream is directed to each of reactors 200 and 202 via lines 204 and 206, respectively. The make-up benzene is supplied by line 172 to line 204 and is passed to transalkylation reactor 200. The
10 transalkylation effluent is withdrawn from reactor 200 via line 208 and supplied to stripping column 210 which serves to provide a benzene-containing fraction in line 212. A purge of the benzene-containing fraction can be effected via line 214. This purge can be passed to the benzene column, used for fuel value or exhausted from the complex. As shown, a portion of the benzene-containing fraction can be recycled, if desired, to reactor 200. The balance of
15 this fraction is passed via line 218 to serve as the benzene for the transalkylation in reactor 202. Alternatively, part of the make-up benzene in line 172 can be passed to reactor 202. The effluent from reactor 202 is passed via line 220 to stripping column 210.

[00104] The bottoms fraction from stripping column 210 contains alkylbenzene produced by the transalkylation, unreacted dialkylbenzene, other heavies and a portion of the
20 benzene. The bottoms fraction is withdrawn via line 196 and passed to benzene column 138 where benzene is recovered. The remaining unit operations in the refining section recover alkylbenzene, paraffin and return dialkylbenzene to the transalkylation assembly. If desired, a stream can be removed from line 196 and recycled to reactors 200 and 202 via lines 222 and 224, respectively for further conversion of unreacted dialkylbenzene.

CLAIMS:

1. A continuous, integrated process for preparing linear alkylbenzenes by the alkylation of benzene with olefin having between 8 and 16 carbon atoms, said olefin being contained in admixture with paraffin, in the presence of regenerable, solid, acid alkylation catalyst

5 comprising:

a. continuously supplying benzene and a mixture of said olefin and paraffin to at least one alkylation zone (118) of at least two alkylation zones (118a,b), said alkylation zone (118) being at alkylation conditions including the presence of a catalytically effective amount of said catalyst to provide an alkylation product containing alkylbenzene, dialkylbenzenes and unreacted benzene, wherein said alkylation deactivates said catalyst;

b. separating benzene from the alkylation product to provide a benzene-rich fraction, at least a portion of which is recycled to step (a) and a substantially benzene-free fraction, said fraction containing alkylbenzene, paraffin and dialkylbenzene;

15 c. separating paraffin from said substantially benzene-free fraction to provide a paraffin-rich fraction and a substantially paraffin-free fraction containing alkylbenzene and dialkylbenzenes;

d. separating alkylbenzene from said paraffin-free fraction to provide an alkylbenzene fraction and a heavies fraction containing dialkylbenzenes;

20 e. periodically regenerating said catalyst in at least one of said alkylation zones (118) by continuously passing through said zone benzene under regeneration conditions to provide a spent benzene-containing regeneration stream;

f. subjecting at least a portion of the heavies fraction to transalkylation conditions comprising the presence of a catalytically effective amount of solid transalkylation catalyst and benzene, at least 50 mass percent of which is derived from the spent benzene-containing stream, to provide a transalkylation product containing alkylbenzene and unreacted benzene; and

25 g. passing the transalkylation product to step (b).

2. The process of claim 1 wherein the mole ratio of benzene to olefin supplied to step (a) is sufficiently low that dialkylbenzene to total alkylbenzene and dialkylbenzene in the alkylation product is greater than 5.

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3. The process of claim 2 wherein the mole ratio of benzene to olefin supplied to step (a) is between 10:1 and 20:1.
4. The process of claim 1 wherein the mole ratio of benzene to total alkylbenzene and dialkylbenzene in the heavies fed to the transalkylation of step (f) is between 20:1 to 80:1.
- 5 5. The process of claim 1 wherein the regeneration of step (e) produces a spent benzene-containing stream having a varying degree of impurities, and the portion of the benzene from the spent benzene-containing stream used for step (f) is that containing a lesser degree of impurities.
6. The process of claim 1 wherein at least two alkylation zones (118a,b) are used and at
10 any given time during the process, one (118c) of which is being regenerated in step (e).
7. The process of claim 1 wherein between 70 mass percent and essentially all of the benzene for step (f) is spent benzene-containing stream of step (e).
8. The process of claim 7 wherein substantially all of the benzene for step (f) is from the spent benzene-containing stream.
- 15 9. The process of claim 1 wherein the spent benzene-containing stream to be used in step (f) is subjected to purification conditions prior to being introduced into step (f).
10. The process of claim 1 wherein step (f) is continuous.

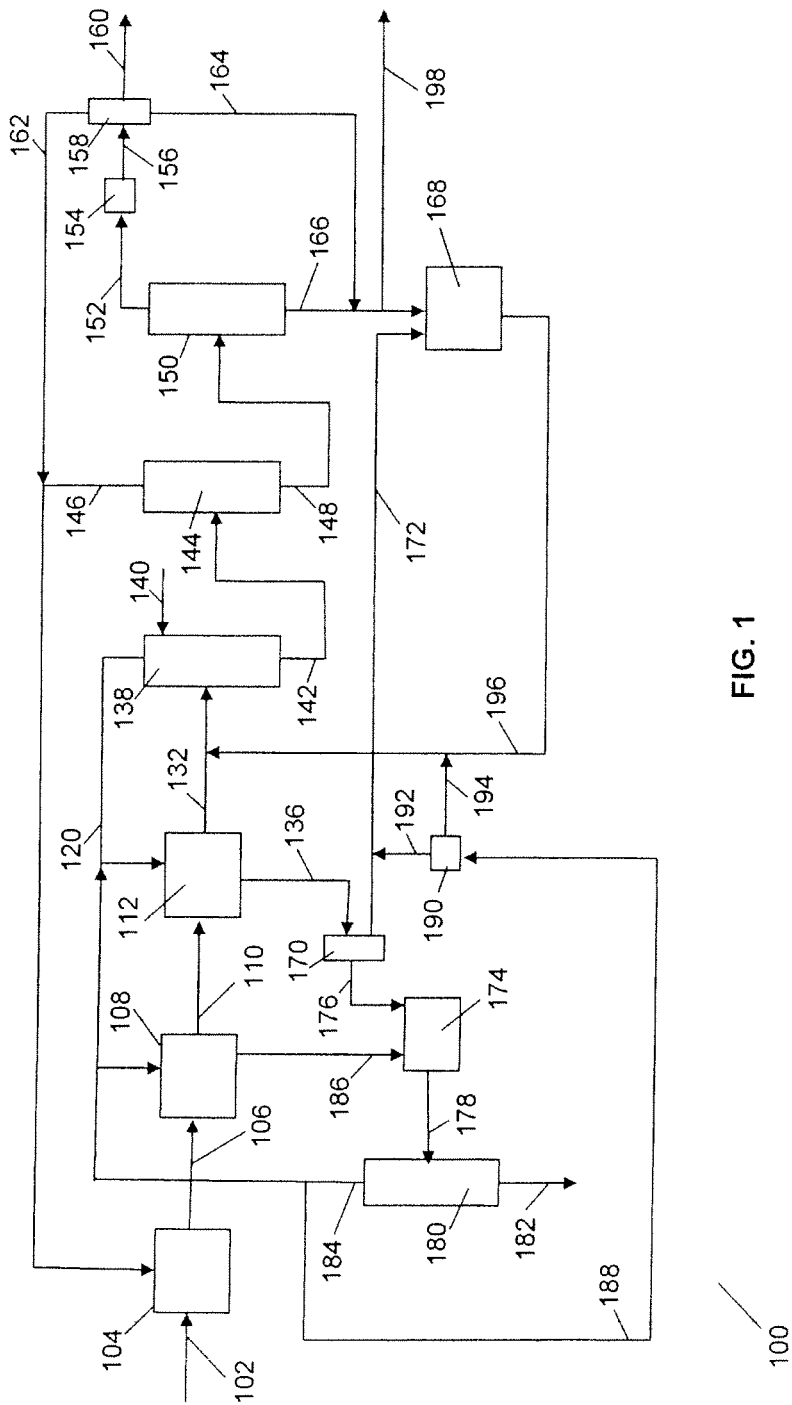


FIG. 1

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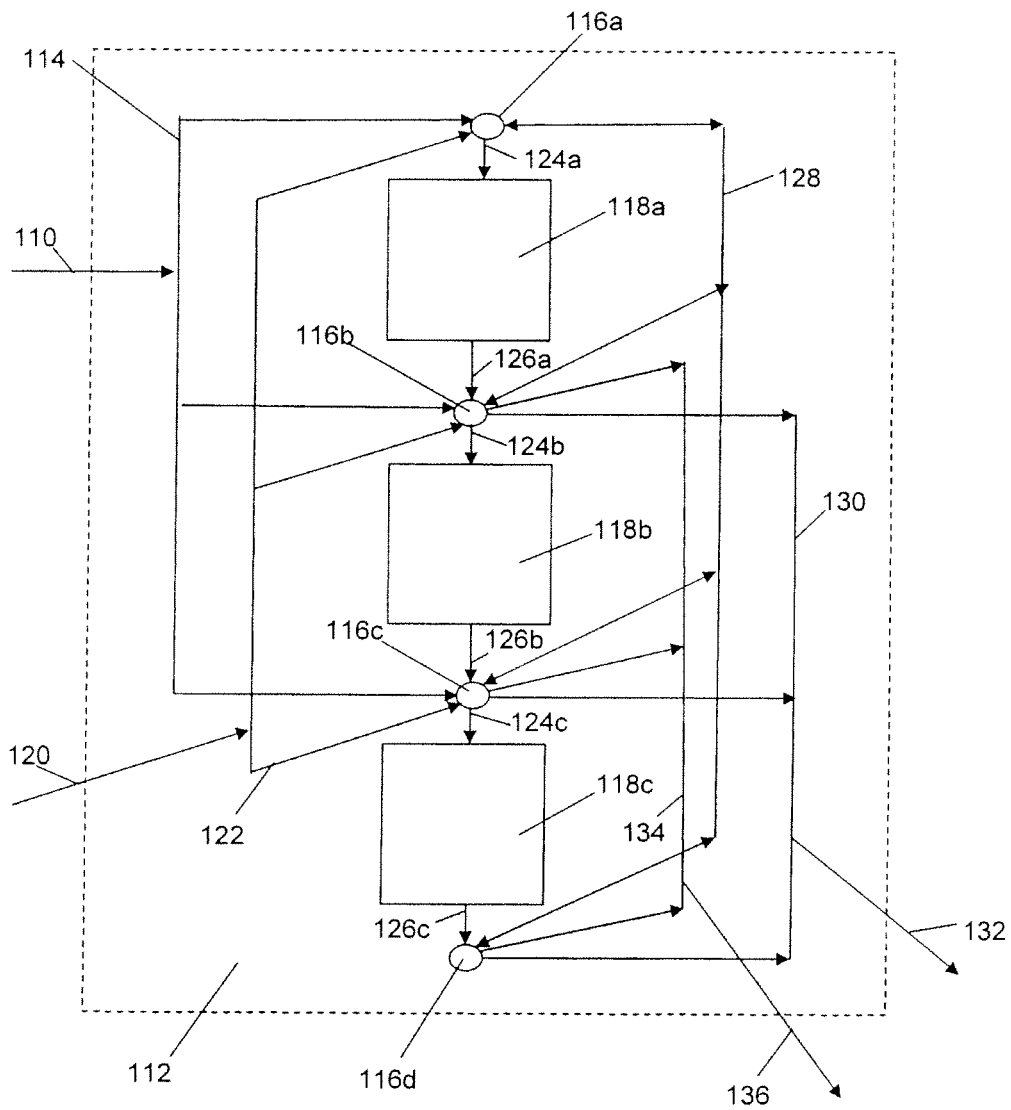


FIG. 2

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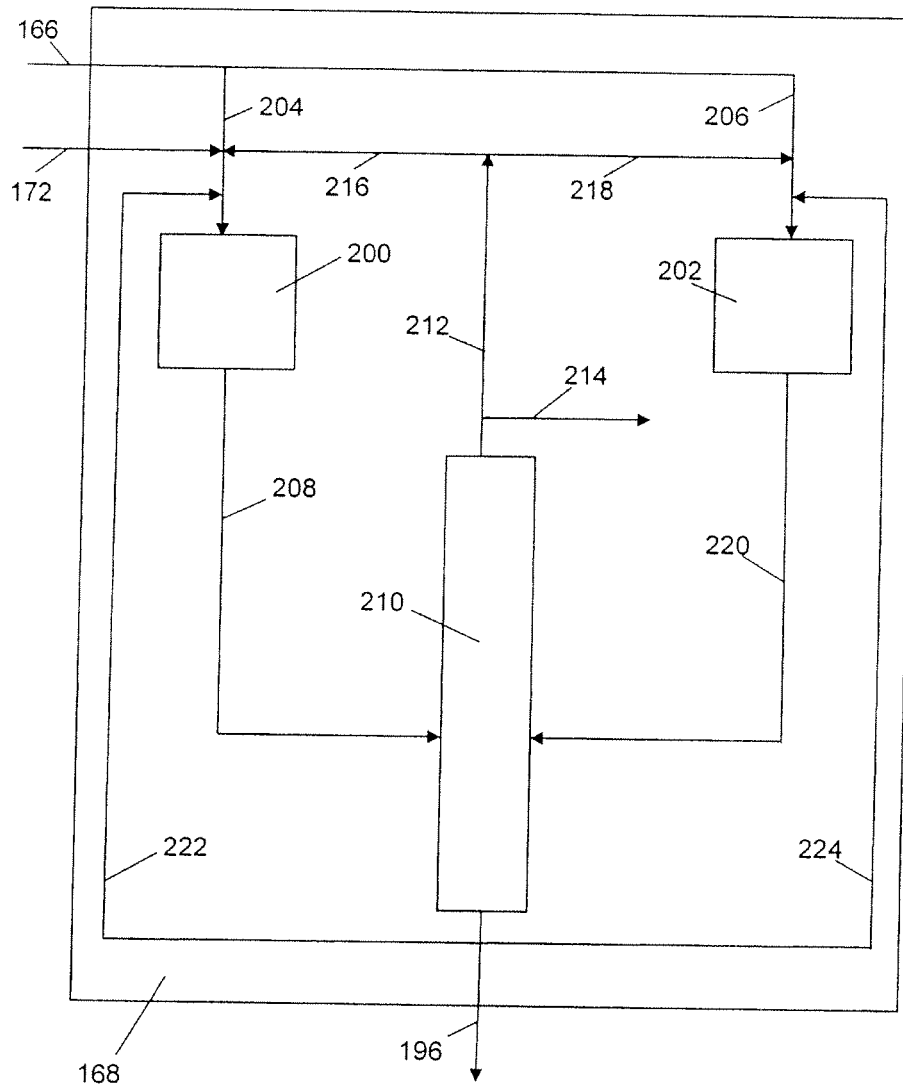


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2008/053335**A. CLASSIFICATION OF SUBJECT MATTER***C07C 2/64(2006.01)i, C07C 15/107(2006.01)i*

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)

IPC 8 C07C 2/64, 15/00

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 practicable, search terms used)

e-KIPASS, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6,740,789 B1 (Andrea G. Bozzano, et al.) 25 May 2004 See claims 1-11 and Figure.	1-10
A	US 2006/0224030 A1 (Patrick Euzen, et al.) 05 October 2006 See claims 1-25.	1-10
A	US 6,225,516 B1 (Pierino Radici, et al.) 01 May 2001 See claim 17.	1-10
A	US 5,574,198 A (Pierino Radici, et al.) 12 November 1996 See claim 10.	1-10
A	US 5,003,119 A (Helion H. Sardina, et al.) 26 March 1991 See claims 9-19 and Figures 1 & 6.	1-10
A	US 5,185,485 A (David R. Dyroff, et al.) 09 February 1993 See claims 1-29. -----End of documents-----	1-10

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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"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 JUNE 2008 (24.06.2008)

Date of mailing of the international search report

24 JUNE 2008 (24.06.2008)

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2008/053335

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6740789 B1	25.05.2004	US 2004-267065 A1 US 2005-003949 A1 US 6979394 BB	30.12.2004 06.01.2005 27.12.2005
US 2006-224030 A1	05.10.2006	US 7297828 BB	20.11.2007
US 6225516 B1	01.05.2001	CN 1167653 C CN 1249292 A ES 2162735 BA MI 981631 A0 MI 981631 A1 RU 2169134 C2	22.09.2004 05.04.2000 01.04.2003 16.07.1998 17.01.2000 20.06.2001
US 5574198 A	12.11.1996	AT 160560 E BG 61806 B1 BG 98121 A CA 2106621 AA CA 2106621 C DE 69315403 T2 DK 589511 T3 EP 0589511 A1 EP 0589511 B1 ES 2109424 T3 GR 3025535 T3 IT 1255512 A IT 92502177 A0 PL 174412 B1 PL 300466 A1 RO 111360 B1 RO 111455 B1	15.12.1997 30.06.1998 15.11.1994 25.03.1994 17.02.2004 09.04.1998 04.05.1998 30.03.1994 26.11.1997 16.01.1998 27.02.1998 09.11.1995 24.09.1992 31.07.1998 18.04.1994 30.09.1996 31.10.1996
US 5003119 A	26.03.1991	None	
----- Continued in the next page.			

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2008/053335

US 5185485 A	09.02.1993	AT 144761 E	15.11.1996
		BR 9202474 A	09.02.1993
		CA 2072487 AA	29.12.1992
		CA 2072487 C	21.01.2003
		CN 1034658 C	23.04.1997
		CN 1068100 A	20.01.1993
		DE 69214884 C0	05.12.1996
		DE 69214884 T2	12.06.1997
		EP 0520975 A2	30.12.1992
		EP 0520975 B1	30.10.1996
		EP 0520975 A3	25.05.1994
		ES 2053422 T1	01.08.1994
		ES 2053422 T3	16.01.1997
		JP 2642281 B2	20.08.1997
		JP 5271115 A2	19.10.1993
		KR 10-1993-0000444	15.01.1993
		KR 95-0012994 B1	24.10.1995
		MX 9203445 A1	28.01.1993