



(51) International Patent Classification:

C07C 2/64 (2006.01) *C07B 63/00* (2006.01)
C07C 7/10 (2006.01)

(21) International Application Number:

PCT/US2014/040852

(22) International Filing Date:

4 June 2014 (04.06.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

13/923,125 20 June 2013 (20.06.2013) US

(71) Applicant: UOP LLC [US/US]; 25 East Algonquin Road,
P. O. Box 5017, Des Plaines, Illinois 60017-5017 (US).

(72) Inventor: MAJUMDER, Debarshi; UOP LLC, 25 East
Algonquin Road, P. O. Box 5017, Des Plaines, Illinois
60017-5017 (US).

(74) Agent: GOODING, Arthur E.; UOP LLC, 25 East Al-
gonquin Road, P. O. Box 5017, Des Plaines, Illinois
60017-5017 (US).

(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, BN, BR, BW, BY, BZ, CA, CH, CL, 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, IR, IS, JP, KE, KG, 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, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, 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, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: RECYCLE OF REACTOR EFFLUENT IN AN ALKYLAROMATIC PROCESS

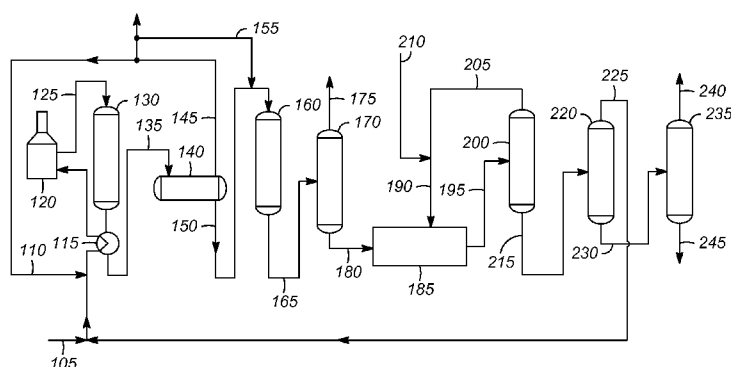


FIG. 1

(57) Abstract: A process for preparing linear alkylaromatics is described. The process involves contacting the aromatic compound and a feed comprising a mixture of 12 to 30% olefins and 70 to 88% other components under alkylation conditions including a catalytically effective amount of a catalyst to provide an alkylation product. The alkylation product is divided into a first portion which is recycled to the alkylation zone and a second portion which is separated into an aromatic-rich fraction containing the unreacted aromatic compound and a substantially aromatic compound-free fraction containing alkylaromatics, unreacted other components, and dialkylaromatics. The substantially aromatic compound-free fraction is separated into a fraction containing the unreacted other components and a fraction containing the alkylaromatics, and dialkylaromatics. The fraction containing the alkylaromatics, and dialkylaromatics is separated into a fraction containing the linear alkylaromatics and a fraction containing the dialkylaromatics.

RECYCLE OF REACTOR EFFLUENT IN AN ALKYLAROMATIC PROCESS

STATEMENT OF PRIORITY

This application claims priority to U.S. Application No. 13/923,125 which was filed June 20, 2013, the contents of which are hereby incorporated by reference in its entirety.

5

BACKGROUND OF THE INVENTION

Linear alkylbenzenes (LAB) are compounds that have significant commercial importance. Linear alkylbenzene sulfonate (LAS) compounds made by sulfonation of linear alkylbenzene are used in the manufacture of detergents and other products. Because linear alkylbenzenes are more easily biodegradable than branched alkylbenzenes, linear
10 alkylbenzenes have essentially replaced branched alkylbenzenes in detergents and other products. In particular, linear alkylbenzenes with long alkyl chains, such as chains having 10 to 14 carbons, are commonly used. However, linear alkylbenzenes with longer chains and with shorter chains also are commercially important.

Linear alkylbenzenes often are made by alkylation of benzene with olefins. Positional
15 isomers, such as 2-phenyl, 3-phenyl, 4-phenyl, 5-phenyl, and the like, result from this alkylation of benzene with long chain olefins. The distribution of the phenyl along the alkyl chain produces different products.

Historically, linear alkylbenzenes have been manufactured commercially using Friedel-Crafts condensation employing catalysts such as aluminum chloride, or by using
20 strong acid catalysts such as hydrogen fluoride, for example, to alkylate benzene with olefins. In 1995, a solid bed alkylation process, the Detal™ process, using a solid non-corrosive acid catalyst was introduced.

Linear alkylbenzenes with a high percentage of the 2-phenyl isomer are highly desired because, when sulfonated, such compounds have long tails that provide enhanced solubility
25 and detergent properties.

The 2-phenyl isomer content of the product is process dependent. Solid alkylation catalysts, such as those used in the Detal™ process, produce products with 2-phenyl isomer

content between 25 and 35 percent. HF-catalyzed processes typically yield a 2-phenyl isomer content less than 20 percent, and AlCl_3 typically yield between 30 and 33 percent. The properties of linear alkylbenzenes and linear alkylbenzene sulfonate produced from these three processes have been disclosed by Berna and coworkers in the following publications.

5 Journal of Surfactants and Detergents, Vol. 3, No. 2 (July 2000) pages 353 through 359, JAOCS, Vol. 72, No. 1 (1995) pages 115 through 122, and Tenside Surfactants Detergents 25 (1988) 4, pages 216 through 221.

Current LAB manufacturing processes employing solid alkylation catalysts use kerosene-based C_9 to C_{16} material from a PacolTM dehydrogenation process, which is

10 typically a mixture of 9-15% olefins in paraffin.

Gas-to-liquid (GTL) technologies for the generation of C_9 to C_{16} range of hydrocarbons have raised interest in the possibility of producing LAB using a GTL-based feed source. The ability to use a GTL feedstock would reduce dependence on crude-based feedstocks.

15 Thus, there exists a need for additional methods for making linear alkylaromatics by alkylating aromatic compounds with olefins.

SUMMARY OF THE INVENTION

One aspect of the invention is a process for preparing linear alkylaromatics by the alkylation of an aromatic compound with olefins having between 8 and 20 carbon atoms. In

20 one embodiment, the process involves contacting the aromatic compound and a feed comprising a mixture of 12 to 30% olefins and 70 to 88% other components in an alkylation zone under alkylation conditions including a catalytically effective amount of a catalyst to provide an alkylation product containing alkylaromatics, dialkylaromatics, unreacted aromatic compound, and unreacted other components. The alkylation product is divided into

25 a first portion and a second portion. The first portion of the alkylation product is recycled to the alkylation zone. The second portion of the alkylation product is separated into an aromatic-rich fraction containing the unreacted aromatic compound and a substantially aromatic compound-free fraction containing alkylaromatics, unreacted other components, and dialkylaromatics. The substantially aromatic compound-free fraction is separated into an

other component-rich fraction containing the unreacted other components and a substantially other component-free fraction containing the alkylaromatics, and dialkylaromatics. The substantially other component-free fraction is separated into an alkylaromatic fraction containing the linear alkylaromatics and a heavies fraction containing the dialkylaromatics.

5

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is an illustration of one embodiment of an integrated process of making LAB.

Fig. 2 is an illustration of one embodiment of a process of making LAB according to the present invention.

Fig. 3 is an illustration of one embodiment of a reactor zone in the process shown in

10 Fig. 2.

DETAILED DESCRIPTION OF THE INVENTION

Alkylbenzenes, also known as phenyl alkanes, are important for many different products. When the alkyl group has 8 to 20 carbon atoms, among the common usages is in the formation of detergents. Alkylbenzenes are an intermediate product used to form
15 alkylbenzene sulfonates, which are surfactants that form the basis of many detergents. The alkylbenzene sulfonates are known to exhibit different physical properties based upon the position of the aromatic group on the alkyl chain. In the production of alkylbenzene sulfonates, the intermediate product alkylbenzenes with 2-phenyl isomer content in the range from 30 to 40 percent are particularly desired.

20

Integrated processes for producing LABs using solid alkylation catalysts have been developed. One example of an integrated process is shown in Fig.1 which includes a dehydrogenation process, followed by a selective catalytic hydrogenation process, and an alkylation process. A paraffin feed 105 is mixed with hydrogen 110 and sent through heat exchanger 115 and charge heater 120. The heated stream 125 is sent to dehydrogenation zone
25 130. The dehydrogenation effluent 135 exchanges heat with the feed 105 and hydrogen 110 in heat exchanger 115. The dehydrogenation effluent 135 is then sent to a separator 140 and separated into a hydrogen gas stream 145 and liquid stream 150. The liquid stream 150 is mixed with hydrogen 155 sent to a selective hydrogenation zone 160 where any diolefins are

hydrogenated to monoolefins. The effluent 165 from the selective hydrogenation reactor 160 is sent to a stripper 170 where light ends 175 are removed. The bottoms stream 180 from the stripper 170 is sent to the alkylation zone 185 where it is mixed with a benzene stream 190. The effluent 195 from the alkylation zone 185 is sent to a benzene distillation column 200. The benzene overhead stream 205 can be mixed with fresh benzene 210 to form the benzene stream 190. The bottoms stream 215 from the benzene column 200 is sent to a paraffin distillation column 220. The paraffin overhead stream 225 is mixed with paraffin feed 105 and sent to the dehydrogenation zone 130. The bottoms stream 230 from the paraffin column 220 is sent to a linear alkylbenzene distillation column 235 where it is separated into an overhead stream 240 containing the linear alkybenzene and a bottoms stream 245 containing heavy alkylates. The overhead stream 240 can be further processed, for example, in a finishing column (not shown), if desired. The bottoms stream of heavy alkylates can be further processed, for example, in a transalkylation unit (not shown), to further enhance the yield of linear alkylbenzene, if desired.

The linear alkylbenzene product stream can be rated by its 2-phenyl content, and alkylbenzene sulfonates having a higher 2-phenyl content have higher solubility and viscosity in an aqueous media. The 2-phenyl content depends on the molar ratio of benzene:olefin in the reactor and requires precise control to maintain optimum product quality. A level higher or lower than the optimum range can make the LAB quality unacceptable.

Linearity is another significant property in the LAB product. Linearity is responsible for the biodegradability of the surfactant, and should be maintained as high as possible, desirably above 90%. The linearity of LAB is highly dependent on the effluent temperature of the alkylation reaction zone. A higher temperature is detrimental to the linearity and can render the LAB unacceptable for commercial applications.

The use of feeds other than crude-based feedstocks in the alkylation process can present problems. For example, the product of the GTL process has a higher percentage of olefins (e.g., 25% olefins and 75% paraffins) in the mixture than a feed from the Pacol™ dehydrogenation process (9-15% olefins). The alkylation of olefins and benzene is an exothermic process, and higher concentrations of olefins in the feed result in a higher exotherm which must be considered in controlling the process.

In order to address these problems, alkylation processes utilizing recycle streams have been developed.

The aromatic compound used in the alkylation process can be any suitable aromatic compound, including, but not limited to, benzene, toluene, ethylbenzene, xylenes, or combinations thereof. Benzene is the most commonly used aromatic compound. Consequently, benzene will be used for ease of discussion.

The feed will typically have a concentration of olefins between 12 wt% and 30 wt% and of paraffins between 70 wt% to 88 wt%. Within the range of 20 wt to 30 wt%, there is a clear optima for each olefin content, as well as sufficient energy savings to make the process economically justifiable and more attractive compared to other alternative solutions. When the concentration of olefins is below 20%, the flow rate of the recycle stream is low, and the design loses its attractiveness as a superior configuration because it does not lead to substantial energy savings, although it is effective. Under such conditions, other exotherm control designs, such as using an additional amount of recycle benzene, or a paraffin slip-stream to act as the heat-sink may be equally applicable, depending on the specific concentration of olefins. When the concentration is above 30%, the amount of benzene in the recycle stream relative to the recycle benzene from the benzene column is increased, making the benzene to olefin ratio in the different beds significantly different. This leads to a lack of control in the 2-phenyl content when linearity is maintained, and vice versa.

The aliphatic feedstock used in the alkylation processes of this invention contains aliphatic mono-olefin of 8 to 20, or 8 to 18, or 8 to 17 carbon atoms per molecule. The aliphatic olefin is usually a mixture of olefins having different molecular weights. The olefin may be an alpha-olefin or comprise a mixture of olefin isomers. In most instances, the positioning of the olefinic bond in the molecule is not critical as most solid alkylation catalysts have been found to promote migration of the olefinic bond.

For commercial processes, other components may be present in the aliphatic feedstock with the olefin-containing aliphatic compound. These other components may comprise paraffins of 8 to 20, or 8 to 18, or 8 to 17 carbon atoms per molecule. However, such amounts of paraffin are not critical to the processes of this invention, and aliphatic feedstocks having an essential absence of paraffins can be used. If paraffins are not present,

then another component that can act a heat sink and remains unreacted under the process conditions will need to be present to maintain the LAB linearity and 2-phenyl content.

The linearity parameter is feed dependent. The drop in linearity occurs due to isomerization of olefins in the presence of the acid sites of the alkylation catalyst. As the isomerized branched olefins react with the benzene in alkylation, they make non-linear mono-alkylbenzene. As discussed more fully below, the higher the exotherm (ΔT) across the catalyst bed, the higher the drop in linearity. By restricting the ΔT across the catalyst bed by supplying a heat sink through the use of the recycle stream, the linearity drop can be minimized. If the feed is x% linear (i.e., x% linear olefins and 100-x % branched olefins), the drop in linearity between the olefin feed and product mono-alkylbenzene is desirably no more than 10%.

In some embodiments, a multi-bed alkylation reaction zone and a split feedstream for controlling the 2-phenyl content in an alkylbenzene product stream are employed. This arrangement is described in US Patent No. 8,389,787, which is incorporated herein. The split-bed design of US Patent No. 8,389,787 is optimized for feedstock utilization and energy consumption. A recycle stream is added to manage the exotherm by increasing the heat sink in the reactor, while still maintaining the desired local benzene:olefin ratio in the alkylation reaction zone for optimal catalyst performance and product quality.

The local benzene to olefin molar feed ratio should be between 1 and 30, or between 10 and 25, or between 15 and 25. By local benzene to olefin molar feed ratio we mean the actual benzene to olefin molar feed ratio that is established at the reactor-bed in the presence of the catalyst. The desired local ratio is catalyst dependent. Zeolitic catalysts will have a lower requirement compared to amorphous catalysts.

The global benzene to olefin molar feed ratio should be between 2 and 20, or between 2 and 12, or between 2 and 10. By global benzene to olefin molar feed ratio we mean the molar ratio of the actual flowrate of benzene brought in the recycle benzene stream to the total olefins feed to the alkylation zone. In other words, the global ratio is a measure of the fractionation load on the benzene column. The global ratio is dependent on the process design parameters such as number of beds in a multi-bed alkylation reaction zone, and actual flow configuration.

The actual amount of benzene brought to the reactor is substantially lower compared with the existing process. However, splitting the olefin stream into multiple streams artificially increases the local benzene to olefin ratio. Therefore, lower global aromatic compound to aliphatic feedstock ratios (benzene to olefin ratios in the case of alkylbenzene) can be used, while providing an alkylated product of the desired quality. This results in savings in recovery and recycling of the aromatic compound.

The ratio of olefins to other components in the incoming feed is 0.12 to 0.3 (12-30 wt%), or 0.2 to 0.3 (20-30 wt%), as discussed above. After the recycle has been mixed with the incoming feed, the ratio typically drops below 0.2.

The aromatic compound and the olefin are reacted under alkylation conditions in the presence of a solid alkylation catalyst. These alkylation conditions generally include a temperature in the range between 80°C and 200°C, most usually at a temperature not exceeding 175°C, e.g., 100°C to 160°C. Typically, as the catalyst ages, the temperature of the alkylation is increased to maintain desired activity. The alkylation is an exothermic reaction, and thus in a substantially adiabatic reactor, the effluent is at a higher temperature than that of the feed (Reaction Zone Delta T). A substantially adiabatic reactor is one where the increase in temperature of the effluent over that of the feed accounts for at least 75 percent of heat generated by the reactions in the reaction zone.

Typically, the temperature within a reaction zone has been maintained within a suitable range by providing a large excess of aromatic compound to the reaction zone to absorb heat. Where the aliphatic feedstock contains paraffins, the paraffins also serve to absorb heat from the exothermic reactions. High exothermic temperatures during the alkylation can result in negative effects not only in terms of catalyst deactivation, but also in terms of product quality degradation, especially skeletal isomerization, and, in particular, skeletal isomerization of the olefin.

The ratio of aromatic compound (or preceding reaction zone effluent with respect to the subsequent reaction zones in the series) to aliphatic feedstock fed to each reaction zone in accordance with the processes of this invention is selected such that the Reaction Zone Delta T is less than 15°C, or less than 12°C, or less than 10°C, or between 2°C to 10°C. Desirably, the amount of aliphatic feedstock to each reaction zone is such that no reaction zone has a

Reaction Zone Delta T greater than 5°C than any other reaction zone. Desirably, the difference in the Reaction Zone Delta T among the reaction zones is less than 5°C.

Since the alkylation is typically conducted in the presence of a liquid phase, and preferably in either an all-liquid phase or at supercritical conditions, pressures must be sufficient to maintain reactants in the liquid phase. The requisite pressure necessarily depends upon the olefin and temperature, but normally is in the range of 1300 to 7000 kPa(g), and most usually between 2000 and 3500 kPa(g).

In some embodiments, alkylation of benzene by the olefins is conducted in a continuous manner using three or more catalyst beds in flow series. For purposes herein, a catalyst bed is termed a reaction zone whether in the same or a separate vessel from another bed. Each reaction zone has an inlet region and an outlet region. The reactants may be in admixture prior to entering the inlet region of the reaction zone, or they may be individually introduced and mixed in the reaction zone.

The catalyst may be used as a packed bed, a moving bed, or a slurry bed. The feed to the reaction zone may be passed either upflow or downflow, or even horizontally as in a radial bed reactor; however, the flows of the aromatic compound and olefin are co-current. In one desirable variant, olefin may be fed into several discrete points within the reaction zone. The feed mixture, that is, aromatic compound and aliphatic feedstock to a reaction zone, is often provided at an overall liquid hourly space velocity (overall LHSV) between 0.3 and 6 or 10 hr⁻¹, and most frequently between 0.4 and 6 hr⁻¹ depending upon, e.g., alkylation temperature and the activity of the catalyst. The overall LHSV is determined from the LHSV's of each of the beds. The reciprocal of the overall LHSV is the sum of the reciprocals of the LHSV of each of the beds in series.

It is usually desired that sufficient residence time in the reaction zone be used such that at least 90, or at least 95, or at least 98, and often at least 99.5, mass percent of the olefin fed to a reaction zone is reacted in that reaction zone.

Any suitable solid alkylation catalyst may be used in the present invention, provided that the requirements for conversion, selectivity, and activity are met. Typically, the catalysts are acidic. Preferred alkylation catalysts comprise zeolites having a zeolite framework type

selected from the groups consisting of beta, MOR, MWW, FAU and NES. Suitable zeolites include mordenite, ZSM-4, ZSM-12, ZSM-20, offretite, gmelinite, beta, NU-87, UZM-8, MCM-22, MCM-36, MCM-49, zeolite Y, zeolite X, and gottardite. The MOR, MWW, FAU, NES, and other zeolite framework types are described in Ch. Baerlocher, W. M. Meier and D. H. Olson, "Atlas of Zeolite Framework Types," 5th Ed., Elsevier: Amsterdam, 2001, herein incorporated by reference. The FAU and UZM-8 molecular sieves may have any convenient particle size. Often the particle sizes of the molecular sieves range upwards of 5 microns or more in major dimension, for example, 50 to 5000 nanometers in major dimension. Particle sizes in the lower portion of the range are sometimes preferred as the coproduction of heavies may be reduced. Major particle dimensions of less than 500, e.g., from 50 to 300, nanometers are often desirable. Another class of acidic, solid catalysts 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 catalysts may also find utility. Further discussion of alkylation catalysts can be found in U.S. Pat. Nos. 5,196,574; 6,315,964B1 and 6,617,481B1.

Newer alkylation catalysts can also be used in this process. For example, one such catalyst comprises a mixture of two types of zeolitic materials, where the zeolites are mixed and produced to have two zeolites within a single catalyst pellet. With the new catalysts, the first zeolite is also characterized by its acidity, wherein the acidity is characterized by having less than 70% of NH_3 desorption off the zeolite at temperatures greater than 400°C . The NH_3 -TPD experimental procedure comprises: calibration of the NH_3 -TPD system with 5 injections of 0.2 cc pulses of NH_3 at 2 minute intervals into a flow of UHP grade helium at 40 cc/minute. The data collected from the Thermal Conductivity Detector is integrated and used to calibrate the detector response to a known quantity of NH_3 . An equilibrated sample, for moisture content is weighed at F250 mg and placed in the reactor. The sample is pretreated in a flow of 20% O_2/He UHP grade at a rate of 100 cc/minute and with a temperature ramp of $10^\circ\text{C}/\text{minute}$ up to a maximum temperature of 650°C . The sample is held at this temperature for one hour, then purged with UHP grade helium for 15 minutes and cooled to the saturation temperature. The pretreatment is for removal of water and residual contaminants. The sample is saturated with anhydrous NH_3 at 150°C using multiple pulses of NH_3 injected into He flowing at 40 cc/min. The minimum quantity of NH_3 used to saturate the sample is 50 cc. The

excess ammonia is purged from the sample in flowing (40 cc/min) UHP grade helium for 8 hours. The NH₃ is desorbed from the sample in a flow (40 cc/min) of UHP grade helium with a temperature ramp of 10°C/minute to a final temperature of 605°C. All gases have been purified using appropriate gas purifiers. The NH₃ desorbed is detected with a Thermal Conductivity Detector. The detector response is converted to moles of NH₃ using the detector response obtained at the beginning of the experiment. The integrated results are reported by integration of the temperature range of interest and reported as mmoles NH₃/g sample. An example of the first zeolite is UZM-8.

The second zeolite having a silica to alumina molar ratio less than 8, and includes a rare earth element incorporated into the zeolitic framework in an amount greater than 16.5 wt %. The first zeolite component is in an amount between 10 and 90% by weight of the catalyst, and the second zeolite component is in an amount between 10 and 90% by weight. The zeolites are intermingled into single catalyst particles. An example of the second zeolite is a rare earth substituted X zeolite, Y zeolite, or a zeolite having an EMT/FAU intergrowth. The incorporation of rare earth exchanged ions in a low ratio zeolite reduces the acidity due to an increase in the number of framework alumina at low ratios, and also reduces geometric space in the supercage. The reduced acidity and reduced space significantly suppresses the isomerization and cracking pathways, while the leaving the primary alkylation reaction unaffected. This decreases the undesired side reactions that reduce the amount and quality of the LAB product. This is contrary to what one would expect, as it has been found that incorporating or leaving some alkali or alkaline earth cations in the catalyst significantly improves the catalyst performance. This is especially true with respect to the performance around the linearity of the alkylbenzene, and the retention of linearity as the operating temperatures are increased. Normally, the alkali or alkaline earth cations are removed because without the rare earth exchange, the alkali or alkaline earth cations are detrimental to the catalyst life and regenerability.

The same or different catalyst may be in each reaction zone of the alkylation reactor assembly.

The alkylation reaction zone may contain at least 2, or at least 3, and most frequently between 3 and 10, reaction zones in series to which a portion of the aliphatic feedstock is fed.

Often a trim alkylation reaction zone follows the series to react residual olefin in the effluent from the last reaction zone in series. The reaction zones may be in a common vessel or in separate vessels. The reaction zones may be the same or different sizes. Additional reaction zones may be used in parallel.

5 The number of reaction zones in series will be related to the overall aromatic compound to aliphatic feed ratio desired and to the desired Reaction Zone Delta T. For example, for a given ratio, more reaction zones will be required to achieve a given Reaction Zone Delta T than for a higher Reaction Zone Delta T.

10 A heat exchanger may be provided between each of the reaction zones in the series. If desired, a heat exchanger can be provided immediately upstream of any trim reaction zone, but the use of such a heat exchanger is not required. As used herein, a heat exchanger is a unit operation which provides controlled cooling of the effluent from the preceding reaction zone by direct, indirect, or a combination thereof heat exchange and does not refer to ambient heat loss. The amount of cooling to be effected between each reaction zone can be varied widely.

15 Generally, the cooling is at least sufficient to remove at least 75 percent of the heat generated in the preceding reaction zone. The cooled effluent is often at a temperature at least 5°C, and sometimes between 5°C and 20°C, lower than the temperature of the effluent fed to the heat exchanger. Often the cooling is sufficient to provide the effluent at substantially the same temperature as the feed to the preceding reaction zone. In one embodiment, the cooling of the

20 effluent is sufficient to reduce the temperature of the effluent by at least an amount of 60 percent of the Reaction Zone Delta T of the reaction zone producing the effluent. Thus, the cooling counters the Reaction Zone Delta T of the preceding reaction zone.

25 A portion of the aliphatic feed is fed to each of the reaction zones in the series. Advantageously, this feed can be cooler than the preceding reaction zone effluent and serves to provide direct heat exchange. Alternatively or in addition, indirect heat exchange can be used to reduce the temperature of the effluent. The cooling medium for the indirect heat exchange may be water or any conveniently available, cooler process fluid.

30 The optional trim reaction zone typically assures that at least 99, preferably at least 99.5, mole percent of the olefin is reacted. In one preferred embodiment, substantially all of the olefin contained in the zone effluent that is passed to the trim reaction zone is consumed.

The effluent from the last reaction zone (or trim reaction zone if used) is directly passed to the refining system. The alkylbenzene refining system serves to remove aromatic compound, olefins, heavies, and, if present, paraffins, from the alkylated product.

In common commercial configurations for alkylbenzene, the refining assembly comprises a distillation assembly that recovers essentially all the benzene from the alkylation effluent and provides a relatively pure benzene stream as the overhead. The bottoms stream from this distillation assembly would then be passed to a distillation assembly to separate as the overhead, paraffins and unreacted olefins, and the bottoms from this second distillation assembly would be fed to a heavies distillation assembly where the alkylbenzene product is contained in the overhead. If desired, a finishing column may be used to further purify the alkylbenzene, especially after a clay treatment to remove color formers.

In further detail for purposes of illustration, the benzene distillation is generally conducted with a bottoms temperature of less than 300°C, preferably less than 275°C, usually between 230°C 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.

Each column used for benzene distillation 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 theoretical plates, for example, 6 to 70, or 20 to 50. The reflux ratio is often in the range of 2:1 to 1:10, or 1.5:1 to 1:5. The bottoms stream from the benzene distillation generally contains less than 1000 ppmw, or 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.

The paraffin distillation is generally conducted with a bottoms temperature of less than 300°C, or 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 kPa absolute, or 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 theoretical plates, or 7 to 20. The reflux ratio is often in the range of 3:1 to 1:10, or 1:1 to 1:3. The bottoms stream from the paraffins distillation generally contains less than 5000, or less than 500, parts by million by weight (ppmw) paraffins and less than 10, often less than 1, ppmw benzene. The paraffins distillation may occur in a single column, or two or more distinct columns may be used.

The heavy alkylate distillation is generally conducted with a bottoms temperature of less than 300°C, or less than 275°C, usually between 250°C and 275°C, and at a pressure of between 0.5 and 30 kPa absolute, or 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 theoretical plates, for example 10 to 30, or 10 to 20. The reflux ratio is often in the range of 2:1 to 1:5, or 0.2:1 to 1:1. The overhead from the heavy alkylate distillation generally contains less than 1000, or less than 100 ppmw, and sometimes less than 50 ppmw, total heavies.

The refining system may contain additional distillation zones, e.g., to recover additional alkylbenzene from heavies.

In one separation step, an aromatic-rich fraction is separated from a substantially aromatic compound-free fraction. By aromatic-rich fraction, we mean that there is at least 95 wt% aromatic compounds, or at least 97 wt%, or at least 99 wt%, or at least 99.9 wt%. By substantially aromatic compound-free fraction, we mean there is less than 5 wt% aromatic compounds, or less than 3 wt%, or less than 1 wt%, or less than 0.1 wt%.

In another separation step, the substantially aromatic-free fraction is separated into another component-rich fraction containing the unreacted other components and a

substantially other component-free fraction containing the alkylaromatics, and dialkylaromatics. By other component-rich fraction, we mean that there is at least 95 wt% unreacted other components, or at least 97 wt%, or at least 99 wt%, or at least 99.9 wt%. By substantially other component-free fraction, we mean there is less than 5 wt% unreacted other components, or less than 3 wt%, or less than 1 wt%, or less than 0.1 wt%.

In another separation step, the substantially other component-free fraction is separated into a monoalkylaromatic fraction containing the linear monoalkylaromatics and a heavies fraction containing the dialkylaromatics. The monoalkylaromatic fraction contains at least 95 wt% monoalkylaromatics, or at least 97 wt%, or at least 99 wt%, or at least 99.9 wt%. The heavies fraction contains less than 15 wt% monoalkylaromatics, or less than 10 wt%, or less than 5 wt%, or at least 1 wt%.

One embodiment of the process is shown in Fig. 2. The GTL feed 305 is sent to alkylation reaction zone 315 along with a benzene stream 310. The alkylation effluent 320 is split into a product portion 325 and a recycle portion 330. Recycle portion 330 is mixed with the GTL feed 305 and sent to the alkylation zone along with benzene stream 310. The product portion 325 is sent to benzene distillation column 335 to be separated into benzene overhead stream 340 and the bottoms stream 345. The benzene overhead stream 340 can be combined with a fresh benzene stream 350 to form benzene stream 310. The bottoms stream 345 is sent to the paraffin distillation column 355 where it is separated into the paraffin overhead stream 360 and the bottoms stream 365. The bottoms stream 365 is sent to the linear alkylbenzene distillation column (not shown).

Recycling a portion of the reaction zone effluent to back into the reaction zone lowers the exotherm. If only benzene were recycled without any effluent recycle, the amount of 2-phenyl in the product would be significantly less than the commercial solid-bed alkylation product. If only paraffin were recycled without any effluent recycle, the LAB product would be obtained, but the cost would be significantly higher because of the added fractionation cost in the benzene and paraffin columns. Recycling a portion of the reactor effluent containing both benzene and paraffins substantially reduces the amount of recycle benzene needed to maintain the benzene:olefin ratio for optimum product quality because the benzene in the effluent supplements the recycled benzene. The paraffin in the effluent provides an

unreactive heat-sink without incurring the added fractionation cost in the benzene and paraffin columns. The effluent recycle process significantly reduces the fractionation load needed to maintain LAB product quality.

Fig. 3 shows one embodiment of a split bed alkylation reaction zone 315 that can be used in the process. The GTL feed 305 is mixed with recycle portion 330 and split into three feed portions 410, 415, 420. The 3 portions of GTL feed 410, 415, 420 are sent to three alkylation reactors 425, 430, 435. The benzene stream 310 is sent to the first alkylation reactor 425 to be reacted with the first feed portion 410. The effluent 445 from the first alkylation reactor 425 is sent to the second alkylation reactor 430 to be reacted with the second feed portion 415. The effluent 450 from the second alkylation reactor 430 is sent to the third alkylation reactor 435 to be reacted with the third feed portion 420. The effluent 320 from the third alkylation reactor 435 is split into the product portion 325 which is sent to the benzene column (not shown) and a recycle portion 330 which is recycled and added to the GTL feed stream 305.

Example:

The GTL feed 305 contains 100 paraffins and 32 olefins by weight. The system uses a three-bed reactor system with solid bed zeolitic Detal catalyst. As the olefin content of this feed is 25%, additional heat sink is required to maintain the linearity of the linear alkylbenzene product. If additional benzene is used to provide heat-sink, the 2-phenyl content in the product is significantly lower. If a portion of the paraffin is recycled to provide the heat sink, additional fractionation and circulation costs are required. By recycling a portion of the reactor effluent, a significantly lower global benzene to olefin molar ratio of 4.25 provides appropriate benzene to olefin ratio in all three reactors. The benzene stream 310 contains 64.87 benzene. The recycle portion 330 contains 122.3 paraffins and 61.6 benzene. After the GTL feed 305 and recycle portion 330 are mixed, the feed contains 222.3 paraffins, 32 olefins, and 61.6 benzene. The molar benzene to olefin ratio of the mixed feed is 4.04. The local benzene to olefin ratio in the first alkylation reactor 425 is 17, in the second alkylation reactor 430 is 20, and in the third alkylation reactor 435 is 23.

For a 3-split-bed reactor without the present invention, the local benzene to olefin ratio is maintained at 20 and the global ratio is 7. An additional paraffin slip-stream from

stream 360 will also be needed to control the exotherm. For the same reactor using the present invention, the local ratio will be 20, but the global ratio is 4.25, which is a one third reduction in the benzene column fractionation load. Also, no paraffin slip-stream is needed, leading to 50% reduction in paraffin column fractionation load.

5

SPECIFIC EMBODIMENTS

While the following is described in conjunction with specific embodiments, it will be understood that this description is intended to illustrate and not limit the scope of the preceding description and the appended claims.

10 A first embodiment of the invention is a process for preparing linear alkylaromatics by the alkylation of an aromatic compound with olefins having between 8 and 20 carbon atoms comprising contacting the aromatic compound and a feed comprising a mixture of 12 to 30 wt% olefins and 70 to 88 wt% other components in an alkylation zone under alkylation conditions including a catalytically effective amount of a catalyst to provide an alkylation product containing monoalkylaromatics, dialkylaromatics, unreacted aromatic compound,
15 and unreacted other components; dividing the alkylation product into a first portion and a second portion; recycling the first portion of the alkylation product to the alkylation zone; separating the second portion of the alkylation product into an aromatic-rich fraction containing the unreacted aromatic compound and a substantially aromatic compound-free fraction containing alkylaromatics, unreacted other components, and dialkylaromatics;
20 separating the substantially aromatic-free fraction into another component-rich fraction containing the unreacted other components and a substantially other component-free fraction containing the monoalkylaromatics, and dialkylaromatics; and separating the substantially other component-free fraction into a monoalkylaromatic fraction containing the linear monoalkylaromatics and a heavies fraction containing the dialkylaromatics. An embodiment of
25 the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising subjecting at least a portion of the heavies fraction to transalkylation conditions including a catalytically effective amount of transalkylation catalyst and the aromatic compound to provide a transalkylation product containing monoalkylaromatics, unreacted dialkylaromatics, and unreacted aromatic
30 compound. An embodiment of the invention is one, any or all of prior embodiments in this paragraph

up through the first embodiment in this paragraph wherein the feed comprises an effluent from a gas-to-liquid process. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein a linearity of the linear monoalkylaromatics is not more than 10% less than a linearity of the olefins. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein a mole ratio of the olefins to the other components supplied to the alkylation zone including the recycled first portion is in a range of 0 to 0.2. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising recycling at least a portion of the aromatics-rich fraction to the alkylation zone. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein a global mole ratio of aromatic compound to olefin supplied to the alkylation zone is in a range of 2 to 20. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein a temperature of the alkylation product exiting the alkylation zone is in a range of 100°C to 160°C. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the aromatic compound is benzene, toluene, ethylbenzene, xylenes, or combinations thereof. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the alkylation zone comprises at least two alkylation zones and further comprising periodically regenerating the catalyst in at least one of the alkylation zones by continuously passing benzene through the at least one alkylation zone under regeneration conditions to provide a spent benzene stream containing deactivating components. The process of claim 1 wherein the catalyst comprises a first zeolite comprising UZM-8 and a second zeolite comprising a rare-earth substituted X or Y zeolite intermingled into single catalyst particles. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising controlling a ratio of the first portion of the alkylation product to the second portion of the alkylation product to obtain a specified 2-phenyl content of the linear monoalkylbenzene product. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the ratio of the first portion of the alkylation product to the second portion of the alkylation product is between 0.5 and 2.5. An embodiment of the invention is one, any or all of prior embodiments in this

paragraph up through the first embodiment in this paragraph wherein the aromatic compound is benzene, and the other components are paraffins having between 8 and 20 carbon atoms.

A second embodiment of the invention is a process for preparing linear alkylbenzenes by the alkylation of benzene with olefins having between 8 and 20 carbon atoms comprising
5 contacting benzene and an effluent from a gas-to-liquid process comprising a mixture of 12 to 30 wt% olefins and 70 to 88 wt% paraffins in an alkylation zone under alkylation conditions including a catalytically effective amount of a catalyst to provide an alkylation product containing monoalkylbenzenes, dialkylbenzenes, unreacted benzene, and unreacted paraffins; dividing the alkylation product into a first portion and a second portion; recycling the first
10 portion of the alkylation product to the alkylation zone; separating the second portion of the alkylation product into a benzene-rich fraction containing the unreacted benzene and a substantially benzene-free fraction containing alkylbenzenes, unreacted paraffins, and dialkylbenzenes; separating the substantially benzene-free fraction into a paraffin-rich fraction containing the unreacted paraffins and a substantially paraffin-free fraction
15 containing the monoalkylbenzenes, and dialkylbenzenes; separating the substantially paraffin-free fraction into an monoalkylbenzene fraction containing the linear monoalkylbenzenes and a heavies fraction containing the dialkylbenzenes; and controlling a ratio of the first portion of the alkylation product to the second portion of the alkylation product to obtain a specified 2-phenyl content of the linear monoalkylbenzene product. An
20 embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein a linearity of the linear alkylbenzenes is not more than 10% less than a linearity of the olefins. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein a mole ratio of the olefins to the paraffins supplied to the alkylation zone including the recycled
25 first portion is in a range of 0 to 0.2 and wherein a global mole ratio of benzene to olefin supplied to the alkylation zone is in a range of 2 to 20. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph further comprising recycling at least a portion of the benzene-rich fraction to the alkylation zone. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up
30 through the second embodiment in this paragraph wherein the alkylation zone comprises at least two alkylation zones and further comprising periodically regenerating the catalyst in at least

one of alkylation zones by continuously passing benzene through the at least one alkylation zone under regeneration conditions to provide a spent benzene stream containing deactivating components. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the ratio of the first
5 portion of the alkylation product to the second portion of the alkylation product is between 0.5 and 2.5.

While at least one exemplary embodiment has been presented in the foregoing detailed description of the invention, it should be appreciated that a vast number of variations exist. It should also be appreciated that the exemplary embodiment or exemplary
10 embodiments are only examples, and are not intended to limit the scope, applicability, or configuration of the invention in any way. Rather, the foregoing detailed description will provide those skilled in the art with a convenient road map for implementing an exemplary embodiment of the invention. It being understood that various changes may be made in the function and arrangement of elements described in an exemplary embodiment without
15 departing from the scope of the invention as set forth in the appended claims.

WHAT IS CLAIMED IS:

1. A process for preparing linear alkylaromatics by the alkylation of an aromatic compound with olefins having between 8 and 20 carbon atoms comprising:

5 contacting the aromatic compound (310) and a feed (305) comprising a mixture of 12 to 30 wt% olefins and 70 to 88 wt% other components in an alkylation zone (315) under alkylation conditions including a catalytically effective amount of a catalyst to provide an alkylation product (320) containing monoalkylaromatics, dialkylaromatics, unreacted aromatic compound, and unreacted other components;

10 dividing the alkylation product (320) into a first portion (330) and a second portion (325);
 recycling the first portion (330) of the alkylation product (320) to the alkylation zone (315);

 separating the second portion (325) of the alkylation product (320) into an aromatic-rich fraction (240) containing the unreacted aromatic compound and a substantially aromatic
15 compound-free fraction (345) containing alkylaromatics, unreacted other components, and dialkylaromatics;

 separating the substantially aromatic-free fraction (345) into an other component-rich fraction (360) containing the unreacted other components and a substantially other
 component-free fraction (365) containing the monoalkylaromatics, and dialkylaromatics; and

20 separating the substantially other component-free fraction into a monoalkylaromatic fraction containing the linear monoalkylaromatics and a heavies fraction containing the dialkylaromatics.

 2. The process of claim 1 further comprising subjecting at least a portion of the heavies
 fraction to transalkylation conditions including a catalytically effective amount of
25 transalkylation catalyst and the aromatic compound to provide a transalkylation product
 containing monoalkylaromatics, unreacted dialkylaromatics, and unreacted aromatic
 compound.

3. The process of any of claims 1-2 wherein the feed comprises an effluent from a gas-to-liquid process.

4. The process of any of claims 1-2 wherein a linearity of the linear monoalkylaromatics is not more than 10% less than a linearity of the olefins.

5. The process of any of claims 1-2 wherein a mole ratio of the olefins to the other components supplied to the alkylation zone including the recycled first portion is in a range of 0 to 0.2.

6. The process of any of claims 1-2 further comprising recycling at least a portion of the aromatics-rich fraction to the alkylation zone.

7. The process of any of claims 1-2 wherein a global mole ratio of aromatic compound to olefin supplied to the alkylation zone is in a range of 2 to 20.

8. The process of any of claims 1-2 wherein the aromatic compound is benzene, toluene, ethylbenzene, xylenes, or combinations thereof.

9. The process of any of claims 1-2 further comprising controlling a ratio of the first portion of the alkylation product to the second portion of the alkylation product to obtain a specified 2-phenyl content of the linear monoalkylbenzene product.

10 The process of claim 9 wherein the ratio of the first portion of the alkylation product to the second portion of the alkylation product is between 0.5 and 2.5.

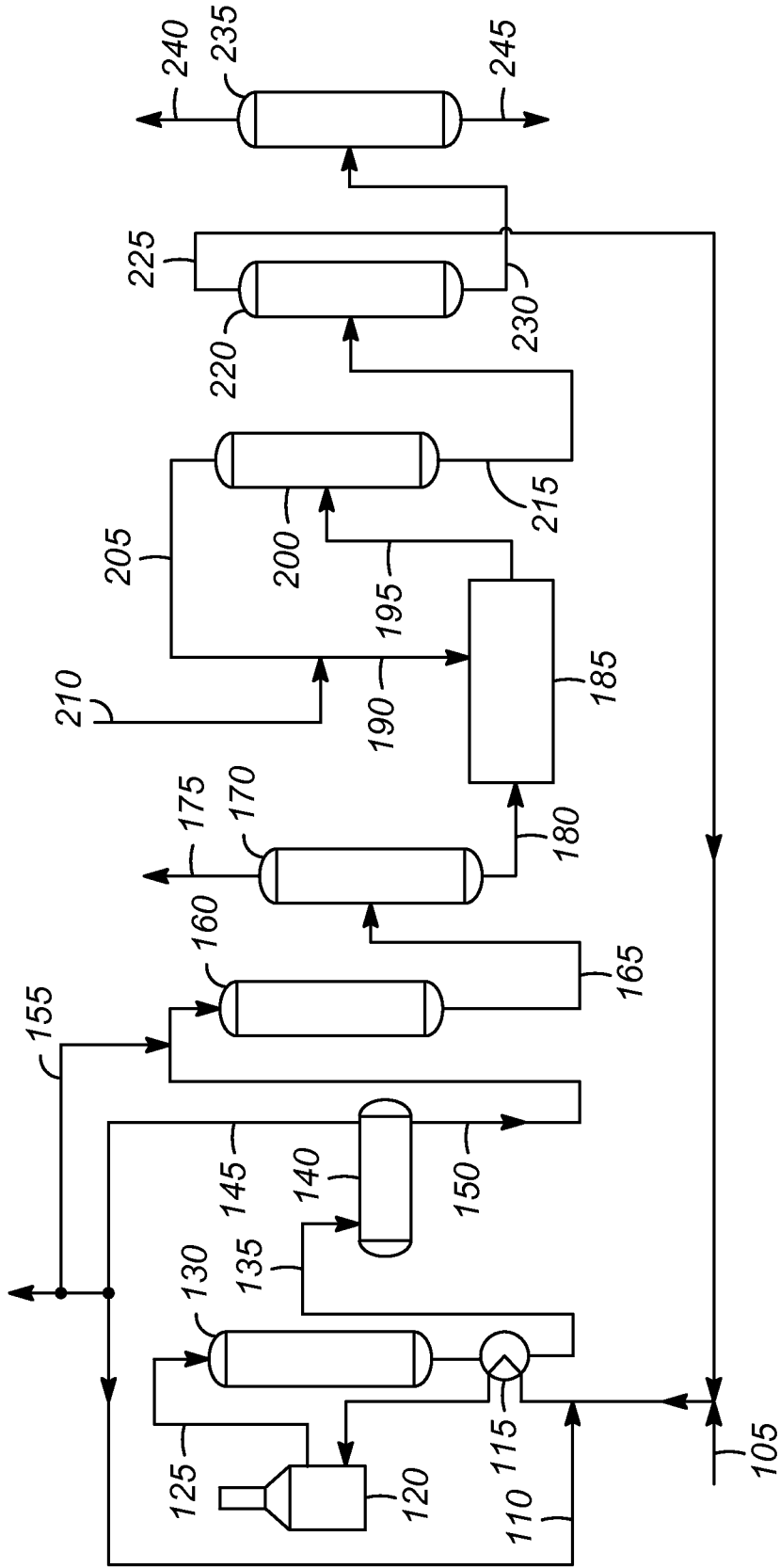


FIG. 1

2/2

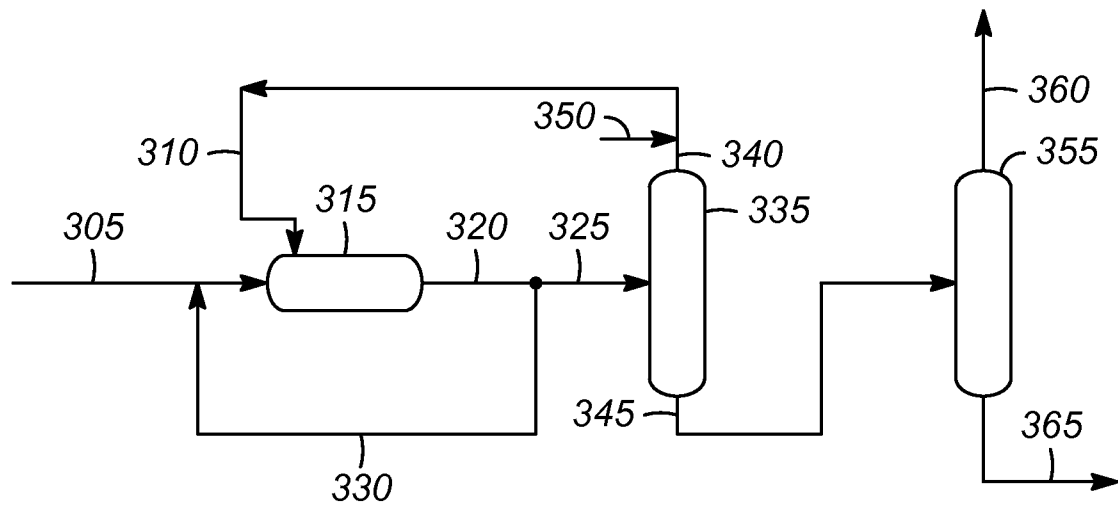


FIG. 2

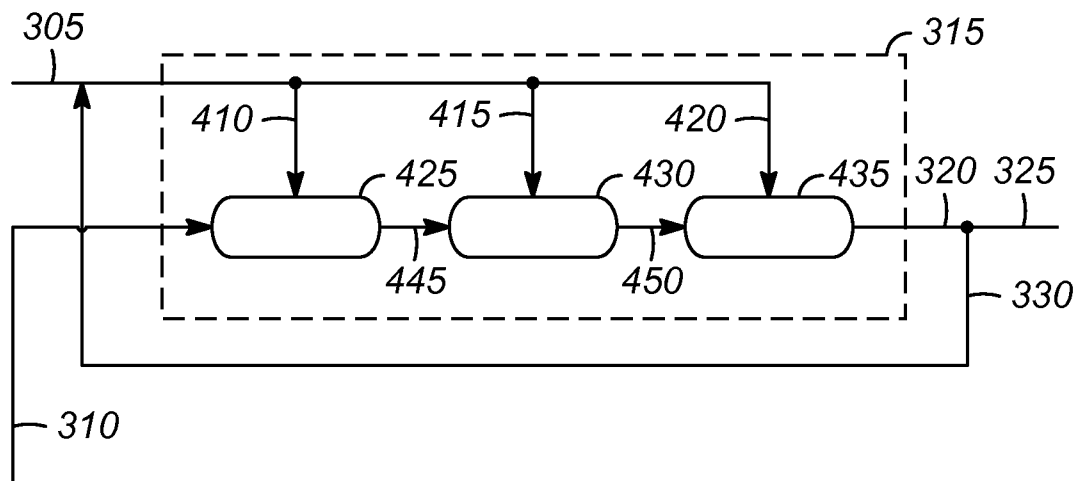


FIG. 3

A. CLASSIFICATION OF SUBJECT MATTER

C07C 2/64(2006.01)i, C07C 7/10(2006.01)i, C07B 63/00(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)
C07C 2/64; C07C 15/085; C07C 2/70; C07C 2/66; C07C 15/107; C07C 7/10; C07B 63/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: linear alkylaromatics , aromatic compound, olefins, alkylation

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 05254766 A (FUJITA, TERUNORI et al.) 19 October 1993 See claims 1-11.	1-10
A	JP 2007-077133 A (SUMITOMO CHEMICAL CO., LTD. et al.) 29 March 2007 See claims 1-4.	1-10
A	EP 1592648 B1 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 24 January 2007 See claims 1-36.	1-10
A	KR 10-0683509 B1 (UOP LLC) 16 February 2007 See claims 1-10.	1-10



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 application or patent 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

01 October 2014 (01.10.2014)

Date of mailing of the international search report

01 October 2014 (01.10.2014)

Name and mailing address of the ISA/KR



International Application Division
Korean Intellectual Property Office
189 Cheongsu-ro, Seo-gu, Daejeon Metropolitan City, 302-701,
Republic of Korea

Facsimile No. +82-42-472-7140

Authorized officer

Jung, Da Won

Telephone No. +82-42-481-8491



INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/US2014/040852

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 05254766 A	19/10/1993	CN 1029611 C	30/08/1995
		CN 1060833 A	06/05/1992
		CN 1060833 C0	11/06/1995
		EP 0481360 A2	22/04/1992
		EP 0481360 B1	15/01/1997
		JP 02-975702 B2	10/11/1999
		JP 04-154733 A	27/05/1992
		JP 04-288026 A	13/10/1992
		JP 04-352732 A	07/12/1992
		JP 05-024813 A	02/02/1993
		JP 05-025064 A	02/02/1993
		KR 10-1995-0001674 B1	28/02/1995
JP 2007-077133 A	29/03/2007	None	
EP 1592648 B1	24/01/2007	AT 352534 T	15/02/2007
		AU 2004-210850 A1	26/08/2004
		AU 2004-210850 B2	07/08/2008
		AU 2004-210850 B9	11/09/2008
		BR PI0407211 A	24/01/2006
		CN 1747912 A	15/03/2006
		DE 602004004507 D1	15/03/2007
		DE 602004004507 T2	08/11/2007
		EP 1592648 A1	09/11/2005
		ES 2279345 T3	16/08/2007
		JP 2006-517228 A	20/07/2006
		KR 20050094897 A	28/09/2005
		MX PA05008177 A	17/02/2006
		MY 135248 A	31/03/2008
		NZ 541354 A	26/09/2008
		RU 2005127623 A	20/01/2006
		WO 2004-071999 A1	26/08/2004
KR 10-0683509 B1	16/02/2007	KR 10-2001-0108537 A	08/12/2001