(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
4 December 2014 (04.12.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/193563 A1

(51) International Patent Classification:
C07C 2/66 (2006.01) *B01J 29/40* (2006.01)
C07C 7/20 (2006.01)

(21) International Application Number:
PCT/US2014/035027

(22) International Filing Date:
22 April 2014 (22.04.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/829,360 31 May 2013 (31.05.2013) US

(71) Applicant: **EXXONMOBIL CHEMICAL PATENTS INC.** [US/US]; 5200 Bayway Drive, Baytown, TX 77520-5200 (US).

(72) Inventors: **BENDER, Timothy P.**; 15718 Starcreek Lane, Houston, TX 77044 (US). **ZHENG, Xiaobo**; 17102 Loblolly Bay Ct., Houston, TX 77059 (US). **TINGER, Robert G.**; 903 Murphy Lane, Friendswood, TX 77546 (US). **DETJEN, Todd E.**; 11815 Mighty Redwood Drive, Houston, TX 77059 (US).

(74) Agents: **BELL, Catherine L.** et al.; ExxonMobil Chemical Company, Law Department, P.O. Box 2149, Baytown, TX 77522-2149 (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).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

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

WO 2014/193563 A1

(54) Title: TRANSALKYLATION SYSTEM

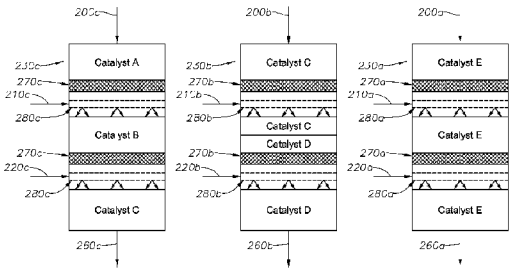


FIG. 2A FIG. 2B FIG. 2C

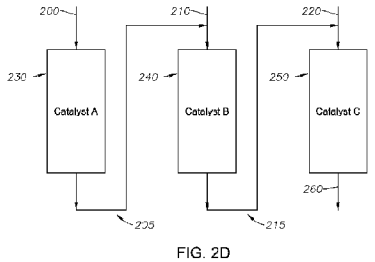


FIG. 2D

(57) Abstract: The invention relates to a transalkylation system to convert feedstreams containing benzene and/or toluene (C7- aromatic hydrocarbons) and feedstreams containing C9+ aromatic hydrocarbons into a product stream comprising xylenes.

TRANSALKYLATION SYSTEM

FIELD OF THE INVENTION

[0001] The invention relates to a transalkylation system to convert feedstreams containing benzene and/or toluene (C7- aromatic hydrocarbons) and feedstreams containing C9+ aromatic hydrocarbons into a product stream comprising xylenes.

BACKGROUND OF THE INVENTION

[0002] The manufacture of xylene using transalkylation processes utilize one or more catalysts to convert feed streams containing benzene and/or toluene (collectively, C7- aromatic hydrocarbons) and feed streams containing heavy aromatics, i.e., C9+ aromatic hydrocarbons, into a xylene-containing product stream. The demand for xylenes, particularly paraxylene, has increased in proportion to the increase in demand for polyester fibers and film. Supplying the ever-increasing demand has required solving many problems in the production of paraxylene by transalkylation, such as discussed in U.S. Patent Nos. 5,030,787; 5,763,720; 5,942,651; 6,893,624; 7,148,391; 7,439,204; 7,553,791; 7,663,010; 8,071,828; 8,163,966; 8,183,424; U.S. Patent Publication Nos. 2010-0298117 and 2012-0024755; U.S. Patent Application Serial No. 13/811403; and U.S. Provisional Patent Application Nos. 61/418,212 and 61/496,262. The value of the product is so great that these processes still merit improvement and there is constant research in this area.

[0003] A transalkylation system utilizing a single catalyst for transalkylation is illustrated schematically in Figure 1C, wherein catalyst **F** is contacted in reactor **120** with feedstream **100** comprising the C7- aromatic hydrocarbons and C9+ aromatic hydrocarbons to produce product **110** comprising xylenes. In a specific example, the catalyst **F** is ZSM-12 comprising a hydrogenation component and a support, such as Al_2O_3. The hydrogenation component may be at least one metal or compound thereof, from Groups 6-12 of the Periodic Table.

[0004] A dual catalyst system for transalkylation is illustrated schematically in Figure 1B. In Figure 1B a feedstream **101** comprising C7- aromatic hydrocarbon and C9+ aromatic hydrocarbon first contacts catalyst **D** in reactor **121** and then the product of the contact with catalyst **D** contacts catalyst **E**, providing product **111** comprising xylenes. One example of a two-catalyst system **D** followed by **E**, respectively, is ZSM-12 comprising a hydrogenation component and a support, followed by a catalyst comprising ZSM-5 without a hydrogenation component. In this case the presence of the second catalyst is found to improve purity by cracking certain undesired co-boilers that make separation of the desired product(s) more difficult. A second example of a two-catalyst system **D** followed by **E**, respectively, is ZSM-

5 comprising a hydrogenation component followed by ZSM-12 comprising a hydrogenation component. In this case the ZSM-5 and hydrogenation component facilitates de-alkylation of C10+ aromatic hydrocarbons to enhance recovery of desired products and/or reduce aging of the downstream ZSM-12 component.

[0005] A three-catalyst system for transalkylation is illustrated schematically in Figure 1A. In Figure 1A a feedstream **102** comprising C7- aromatic hydrocarbons and C9+ aromatic hydrocarbons contacts catalysts **A**, then catalyst **B**, then catalyst **C**, to produce product **112** comprising xylenes. One example of such a three-catalyst system is ZSM-5 with a hydrogenation component, followed by ZSM-12 comprising a hydrogenation component, and then ZSM-5 without a hydrogenation component, where again the ZSM-5 as the third component cracks certain undesired co-boilers to enhance purity of the final product.

[0006] A typical feed to such process can be any conventional C_8+ aromatic hydrocarbon feed available in a petroleum or petrochemical refinery, such as a catalytic reformate, FCC or TCC naphtha, or a xylene isomerizate from which heptanes and lighter components have been removed. The feed is initially passed through a xylenes fractionation column or columns to remove the C_8 aromatic components from the feed and leave a C_9+ aromatic hydrocarbon-rich fraction which can then be fed to a transalkylation reactor for reaction with benzene or toluene in the presence of a transalkylation catalyst system, such as described above, to produce lighter aromatic products, primarily benzene, toluene, and xylenes (collectively, "BTX"). These components can then be separated by methods well-known in the art, and all or a portion of the benzene and toluene can be recycled through the transalkylation system.

[0007] In the case of the use of multiple catalysts, the first, second and optional third catalyst beds may be located in separate reactors, such as illustrated schematically in Figure 1D. Figure 1D illustrates an alternative to Figure 1A. In Figure 1D, feedstream **103** contacts catalyst A in first reactor **123**, then catalyst B in second reactor **124**, and finally catalyst C in third reactor **125**, providing product **112** comprising xylenes.

[0008] In the case of multiple catalysts in a single reactor, the catalysts will typically be separated from each other by spacers or by inert materials, such as, alumina balls or sand. Alternatively, the first and second catalyst beds could be located in one reactor and the third catalyst bed (when present) is located in a different reactor. As a further alternative, the first catalyst bed could be located in one reactor and the second and third catalyst beds (when present) are located in a different reactor. In all situations illustrated, the separate catalysts such as **A**, **B**, and **C** in both Figure 1A and Figure 1D are not mixed and the hydrocarbon

feedstocks and hydrogen are arranged to contact the first catalyst bed prior to contacting the second catalyst bed. Similarly, if the third catalyst bed is present, the hydrocarbon feedstocks and hydrogen are arranged to contact the second catalyst bed prior to contacting the third catalyst bed. However, numerous systems are known wherein at least two different catalysts are mixed together in a single bed. Likewise, while the Figures 1A-1D show axial flow reactors, it will be appreciated by one of skill in the art that radial flow reactors could also be used, alone or in combination with axial flow reactors.

[0009] U.S. Patent No. 7,629,499 describes a process for transalkylation comprising: (a) introduction of alkyl-aromatic feedstock at the inlet of a first reaction zone to contact a first zeolite catalyst to obtain an effluent; (b) introduction of at least a portion of the effluent from the first reaction zone and a feedstock that contains benzene and toluene to the inlet of a second reaction zone that contains a second zeolite catalyst to obtain a second effluent; and (c) separation of at least a portion of the second effluent. An improvement in xylene yield is said to be achieved by this method. Hydrogen is introduced at each inlet.

[0010] Catalyst life and extent of aromatic ring loss reactions across the reactor are two important performance characteristics for transalkylation catalysts and catalyst systems. Typically it is ideal to maximize catalyst life, while at the same time reducing the extent of aromatic ring loss reactions (which reduces yield), and generally increasing the desired products (paraxylene in particular) and decreased the undesired products (such as benzene co-boilers).

[0011] The present invention uses two or more separate staged feed locations to the transalkylation reactor system in order to improve yields (including reduced ring loss reaction) and to increase catalyst life and attenuates the introduction of hydrogen through the two or more separate staged feed locations to effect improved results.

SUMMARY OF THE INVENTION

[0012] The invention is directed to a process for transalkylation of C7- and C9+ aromatic hydrocarbons by contact with a catalyst or catalyst system to produce a product stream comprising xylenes, wherein two or more separate staged feed locations are provided to at least one transalkylation reactor. Hydrogen gas is selectively introduced through one or more of the staged feed locations. In embodiments improvements include at least one of improved yields and increased catalyst life.

[0013] As used herein the term "catalyst system" means at least two different catalysts, which may be mixed together or separated, and may be in single or multiple reactors in series or in parallel, or any combination thereof.

[0014] In a preferred embodiment of this invention, a first feedstream comprising C9+ aromatic hydrocarbon stream, preferably heavy-aromatics-rich stream, e.g., 50+ wt%, more preferably 80+ wt% C9+ aromatic hydrocarbons, is fed to the top bed of the reactor, which is preferably a fixed bed reactor comprising a catalyst or catalyst system optimized for dealkylation and/or heavy aromatic hydrocarbon conversion, and a second feedstream comprising benzene and/or toluene, preferably benzene and/or toluene-rich feed, e.g., 50+ wt%, more preferably 70+ wt% C7- aromatic hydrocarbons, is fed directly into the second bed of the reactor, which is preferably a fixed bed reactor comprising a catalyst or catalyst system optimized for benzene and/or toluene conversion and more preferably also an additional conversion of C9+ aromatic hydrocarbon, such as up to 30 wt% conversion. The first and second beds may be in separate reactors or they may be in the same reactor but are not mixed. In preferred embodiments, the amount of hydrogen present, if any, is in amounts sufficient to saturate at least a portion of the olefins formed in the top bed of the reactor while minimizing saturation of the aromatic species.

[0015] Surprisingly, advantages realized by the present invention include, in embodiments, as least one or more of reduced top bed ring loss reactions, increased xylene yields via disproportionation mechanism versus dealkylation mechanism, increased benzene byproduct purity, and increased reactor top bed cycle length.

[0016] These and other objects, features, and advantages will become apparent as reference is made to the following detailed description, preferred embodiments, examples, and appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] In the accompanying drawings, like reference numerals are used to denote like parts throughout the several views.

[0018] Figures 1A-1D illustrate schematically reactor systems for transalkylation according to the prior art.

[0019] Figures 2A-2D illustrate schematically embodiments of the reactor systems for transalkylation according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0020] According to the invention, a C9+ aromatic hydrocarbon feed stream is provided to the inlet of a reactor system comprising a first catalyst for dealkylation of said C9+ aromatic hydrocarbons, preferably C10+ aromatic hydrocarbons, more preferably C10+ aromatic hydrocarbons having C2+ alkyl groups, such as C2-C4 alkyl groups, to make aromatic hydrocarbons having less side groups, such as C9- aromatic hydrocarbons, with co-

production of olefins, such as C2-C4 olefins, and, in the presence of hydrogen gas in an amount sufficient to hydrogenate said olefins and minimize saturation of aromatic rings, convert at least a portion of said olefins to alkanes, such as C2-C4 alkanes. The product of this reaction, comprising C9 aromatic hydrocarbons and a reduced amount of C10+ aromatic hydrocarbons, preferably a reduced amount of C10+ aromatic hydrocarbons having C2+ side chains when compared with said C9+ aromatic hydrocarbon feed stream, is then introduced, along with a C7- aromatic feed stream (benzene and/or toluene), to a second catalyst for transalkylation of benzene and/or toluene with C9+ to produce an effluent comprising xylenes. The C7- feed stream is introduced to the second catalyst through a second inlet downstream of said first inlet, preferably to minimize contact with said first catalyst system in the presence of hydrogen. Hydrogen gas may be provided through said second inlet with said C7- aromatic feed stream, and/or separately through an inlet downstream of said first inlet. The xylene effluent may then contact yet a third catalyst, such as a catalyst suitable to crack non-aromatic species, such as cyclohexane.

[0021] Pilot plant data on two-bed systems wherein the feeds (aromatic hydrocarbons and hydrogen gas) are treated by conventional reactor systems wherein the entire feed (C7- and C9+ aromatic hydrocarbons) is provided only to the top catalyst bed demonstrates that 40-80% of undesired ring loss reactions across the reactor occur in the top bed of the reactor. Secondly, pilot plant data demonstrates that toluene and benzene are net created (not converted) across the top bed. Therefore, benzene and toluene in the feed to the top bed provide a net negative yield impact to the top bed because they dilute the partial pressure of the reactive C9+ aromatic hydrocarbons. By removing/minimizing benzene and/or toluene and/or hydrogen feed to the top bed or by staging the benzene and/or toluene and/or hydrogen feed to further down the top bed, the C9+ dealkylation kinetics will be increased resulting in the ability to achieve higher conversion at constant temperature and weight hourly space velocity (feed rate/catalyst weight). This reduces the amount of catalyst needed to perform the top bed dealkylation reactions. Pilot plant data also demonstrates that at constant conversion ring loss reactions are reduced with increased WHSV. In addition, reduced toluene and benzene composition in the top bed will drive higher net benzene and toluene production across the top bed which will increase the second bed benzene/toluene to C9+ aromatic ratio, which in turn will drive higher xylene yields via disproportionation across the second bed of the reactor.

[0022] Moreover, ring loss reaction kinetics are favored at lower temperatures, whereas dealkylation reactions are favored at relatively higher temperatures. By introducing the

benzene/toluene rich stream downstream of the top bed or staged lower into the top bed, flexibility is gained to operate the top bed at higher than typical starting temperatures (740-800°F versus 730-740°F typical; about 393-427°C versus 388-393°C) and cool the second bed temperature to normal operating temperatures (750-770°F; about 399-410°C) by introducing the benzene/toluene feed stream at lower than target second bed reactor temperature (700-740°F; about 371-427°C) to cool the top bed effluent.

[0023] Furthermore, a portion of the total hydrogen feed to the reactor can also be staged with or without the benzene/toluene rich stream lower into the top bed and/or below the top bed of the reactor. Hydrogen serves two main functions in the reactor. First hydrogen is needed to saturate olefinic gas created in the dealkylation reactions (predominantly occurring in top reactor bed). Saturating the olefinic gas prevents these molecules from undergoing undesired reactions with aromatic compounds. Secondly, hydrogen is fed to the reactor to reduce coke production rates and extend the catalyst life. However, as the partial pressure of hydrogen to the reactor increases, undesired ring loss reaction yields increase. Staging a portion of the hydrogen lower into the top bed and/or below the top bed of catalyst will result in reduced hydrogen partial pressure at the reactor inlet, and more uniform hydrogen partial pressure through-out the reactor. The lower hydrogen partial pressure at the reactor inlet will reduce ring loss reactions which are kinetically more favored at the entry to the top reactor bed because it operates at lower temperatures than the rest of the reactor (dealkylation is exothermic, resulting in net temperature increase across the reactor). In addition, staged hydrogen injection lower into the top bed and/or below the top bed can be managed to elevate hydrogen partial pressure in the lower sections of the reactor to control/reduce aging of the catalyst relative to traditional methods of injecting all hydrogen at the inlet to the top reactor bed or even in a system where hydrogen is injected at two points in the system but not controlled or attenuated.

[0024] In addition, experimental data shows that benzene byproduct purity increases as the hydrogen to hydrocarbon ratio is reduced to the reactor. Benzene byproduct purity can be monitored downstream of the catalyst system for transalkylation, which would be recognized by one of skill in the art in possession of the present disclosure. Staged hydrogen injection reduces the localized hydrogen to hydrocarbon ratio in the top bed and potentially a portion of the bottom bed of the reactor, thus reducing the benzene co-boiler byproduct yields that result in reduced benzene byproduct purity. By operating the reactor with staged feed as discussed above, with higher operating top bed temperature (740-800°F; about 393-427°C) and typical second bed temperatures (730-750°F; 388-393°C), undesired ring loss reaction

yields across the reactor are reduced, xylene yields are increased, benzene byproduct purity is increased, and top bed catalyst life can be extended due to improved reaction kinetics.

[0025] In the transalkylation reaction, temperatures exceeding 450°C lead to higher catalyst deactivation rates due to increased paring reaction rates and coke condensation. By quenching the effluent from the first reaction with toluene and/or hydrogen, the temperature of the transalkylation reaction can be controlled below this critical 450°C, should the top bed require higher operating temperature than the transalkylation reactor. Alternatively, a heat exchanger can be placed between the top bed and the transalkylation reactor to further adjust the operating temperature of the transalkylation reactor.

[0026] One specific example of a transalkylation system that can benefit from the present invention has been described in PCT/US2012/039136, wherein the combined C7- and C9+ aromatic hydrocarbon feed contacts a catalyst bed comprising a molecular sieve having a Constraint Index in the range of about 3 to about 12, such as ZSM-5, and at least one hydrogenation component, which is at least one metal or compound thereof of Groups 6 to 12 of the Periodic Table of the Elements, such as platinum, palladium, iridium, rhenium, and mixtures thereof, generally present in an amount from about 0.01 to about 10 wt. % of the catalyst composition, the first catalyst bed maintained under conditions effective to dealkylate aromatic hydrocarbons containing C_2+ alkyl groups in the heavy aromatic feedstock and to saturate the resulting C_2+ olefins. Suitable conditions for operation of the first catalyst bed comprise a temperature in the range of about 100 to about 800°C, preferably about 300 to about 500°C, a pressure in the range of about 790 to about 7000 kPa-a, preferably about 2170 to 3000 kPa-a, a H_2:HC molar ratio in the range of about 0.01 to about 20, preferably about 1 to about 10, and a WHSV in the range of about 0.01 to about 100 hr^{-1}, preferably about 2 to about 20 hr^{-1}. Modifying this catalyst system with the findings of the present invention, the first bed should operate no higher than 450C and have a much lower H2:HC molar ratio, e.g., below 1.5:1.

[0027] The product of the first catalyst bed is then contacted with a second catalyst bed comprising a molecular sieve having a constraint index less than 3, such as ZSM-12, and at least one hydrogenation component, which is at least one metal or compound thereof of Groups 6 to 12 of the Periodic Table of the Elements, such as platinum, palladium, iridium, rhenium, and mixtures thereof, generally present in an amount from about 0.01 to about 10 wt. % of the catalyst composition, the second catalyst bed maintained under conditions effective to transalkylate C_9+ aromatic hydrocarbons with the C7- aromatic hydrocarbons. Suitable conditions for operation of the second catalyst bed comprise a temperature in the

range of about 100 to about 800°C, preferably about 300 to about 500°C, a pressure in the range of about 790 to about 7000 kPa-a, preferably about 2170 to 3000 kPa-a, a H_2:HC molar ratio in the range of about 0.01 to about 20, preferably about 1 to about 10, and a WHSV in the range of about 0.01 to about 100 hr^{-1}, preferably about 1 to about 10 hr^{-1}. Again, modifying this second bed with the finding of the present invention, the temperature should be no higher than 450°C.

[0028] Where present, the third catalyst bed is maintained under conditions effective to crack non-aromatic cyclic hydrocarbons in the effluent from the second catalyst bed comprising a third molecular sieve having a Constraint Index from about 1 to 12, such as ZSM-5. No hydrogenation component is present in this optional third catalyst bed. Suitable conditions for operation of the third catalyst bed comprise a temperature in the range of about 100 to about 800°C, preferably about 300 to about 500°C, a pressure in the range of about 790 to about 7000 kPa-a, preferably about 2170 to 3000 kPa-a, a H_2:HC molar ratio in the range of about 0.01 to about 20, preferably about 1 to about 10, and a WHSV in the range of about 0.01 to about 100 hr^{-1}, preferably about 1 to about 50 hr^{-1}.

[0029] The invention may be better understood by reference to the following detailed examples, illustrated schematically in Figures 2A-2D.

[0030] Figure 2A shows reactor **230c** from the perspective of a side view, with conduit **200c** at the top of the structure providing a feed to the reactor **230c** so as to flow, such as by gravity, down the reactor **230c** and out conduit **260c** at the bottom, as reactor effluent, and containing a catalyst system comprising catalyst A, catalyst B, and catalyst C. Plural grid structures **270c**, which may be of the type conventional in the art, and which may be the same or different throughout the reactor, are provided to support the solid catalysts A and B, and also allow liquid and gas flowing down the reactor **230c** to pass through and contact catalyst B. One or more of the grid structures **270c** may be used to introduce hydrogen gas to increase the amount of staging of hydrogen into the system. Conduit **210c** is provided to allow introduction of a second feed into the reactor; conduit **210c** is shown with perforations **280c** and also spargers (as an example of a distributor), indicated by arrows, with one or both present to distribute the second feed material so as to mix with the fluid (liquids and gases) flowing down from catalyst A. The combined fluids from conduit **210c** and from the contact with catalyst A then contact catalyst B. Conduit **220c**, which may be of the same or different design and material as conduit **210c**, is provided to distribute a third feed material so as to mix with the fluids flowing down from catalyst B. As with conduit **210c**, conduit **220c** also is provided with perforations, as shown, and/or spargers, shown by arrows, as an example of

a distributor), so as to facilitate mixing of the liquids and gases. The combined liquids flowing down the reactor **230c** from catalyst B and from conduit **220c** then contact catalyst C. The resultant effluent from contact of the fluids across catalyst C then leaves the reactor **230c** via conduit **260c**.

[0031] In an embodiment of the system illustrated by Figure 2A, Catalyst A comprises a catalyst optimized for dealkylation of C10+ aromatic hydrocarbons, Catalyst B comprises a catalyst optimized for transalkylation of C7- and C9+ aromatic hydrocarbons, and Catalyst C comprises a catalyst optimized for cracking non-aromatic species. The feed introduced via **200c** comprises C9+ aromatic hydrocarbons (such as a molar ratio of [benzene+toluene]/C9+ of about 10:90) with no more hydrogen gas than is sufficient to hydrogenate olefins produced in the dealkylation process to make light alkanes, such as an H_2:HC ratio of 1.5:1 or less, including as an option no hydrogen gas. The feed introduced into **210c** comprises C7- (such as with a molar ratio of [benzene+toluene]/C9+ intermediate between the feed into **200c** and **220c** and a H_2:HC ratio also between the feed **200c** and **220c**. The feed introduced into **220c** comprises C7- (such as with a molar ratio of [benzene+toluene]/C9+ at about 90:10) and an H_2:HC molar ratio of 0.5:1.0.

[0032] Figure 2B shows reactor **230b** from the same perspective as Figure 2A, with conduit **200b** at the top of the structure providing a feed to the reactor **230b** so as to flow, such as by gravity, down the reactor **230b** and out conduit **260b** at the bottom, as reactor effluent, and containing a catalyst system comprising catalyst C, packed into two different beds, and catalyst D, also packed into two different beds. Such an arrangement allows increased staging of plural reactant feeds. Plural grid structures **270b**, which may be of the type conventional in the art, and which may be the same or different throughout the reactor, are provided to support the solid catalysts, and also allow liquid and gas flowing down the reactor **230b** to pass through and contact catalyst C and D, each in stages. One or more of the grid structures **270b** may be used to introduce hydrogen gas to increase the amount of staging of hydrogen into the system. Conduit **210b** is provided to allow introduction of a second feed (which may be liquid or gas or both) into the reactor; conduit **210b** is shown with perforations **280b** and also spargers (as an example of a distributor), indicated by arrows, with one or both present to distribute the second feed material so as to mix with the fluid (liquids and gases) flowing downstream from inlet **200b** to outlet **260b**. The combined fluids from conduit **210b** and from the contact with the uppermost bed comprising catalyst C then contact the next bed of catalyst C and then the first bed of catalyst D. Conduit **220b**, which may be of the same or different design and material as conduit **210b**, is provided to distribute

a third feed material, a fluid, liquid or gaseous or both, which may be the same or different from the first and/or second feed, so as to mix with the fluids flowing down from contact with catalyst D. As with conduit **210b**, conduit **220b** also is provided with perforations **280b**, as shown, and/or spargers, shown by arrows, as an example of a distributor), so as to facilitate mixing of the liquids and gases. The combined liquids flowing down the reactor **230b** from catalyst D and from conduit **220b** then contact the second bed of catalyst D. The resultant effluent from contact of the fluids across the successive catalyst beds then leaves the reactor **230b** via conduit **260b**.

[0033] Figure 2C illustrates yet another embodiment of the invention, wherein a first feed comprising most C9+ aromatic hydrocarbon is provided through inlet **200a** to reactor **230a** which comprises successive beds of catalyst E separated by plural grids **270a**, and provided with conduits **210a** and **220a**, each with plural perforations **280a** and/or spargers, shown by unnumbered plural arrows, to provide effluent **260a**. This illustrates plainly the staged injection to a single catalyst system, which may be a single reactor out of several in series, such as illustrated in the next figure, Figure 2D. Note that in one embodiment of the invention the transalkylation reaction envisioned may be one primarily concerned with converting benzene to toluene by reaction with C9+ aromatic hydrocarbons, which by way of illustration using Figure 2C, would comprise the feeding of a feed comprising C9+ aromatic hydrocarbons and benzene (with perhaps only inevitable impurities of toluene) via conduit **200a** into reactor **230a** to contact successive beds of a transalkylation catalyst E, optimized for transalkylation of benzene and C9+ species to toluene. The inlets at **210a** and **220a** could then provide feeds with successively attenuated ratios of benzene:C9+ aromatic hydrocarbons and/or successively attenuated concentrations of hydrogen, to yield an effluent out of bottoms conduit **260a**, rich in toluene. Such an arrangement, for instance, would be advantageously provided upstream of a reactor system for the conversion of toluene and methanol to xylenes, such as taught in U.S. Application Serial Nos. 13/875,373 and 13/875,402.

[0034] Figure 2D illustrates a further embodiment of the inventions wherein successive catalysts A, B, and C, are provided in beds situated in separate reactors **230**, **240**, **250**, respectively, in series. A first feed stream, such as one primarily comprising C9+ aromatic hydrocarbons, is provided to Catalyst A, preferably a catalyst for dealkylation of C10+ aromatic hydrocarbons, via conduit or inlet **200**, and the effluent from the reactor, comprising an aromatic hydrocarbon stream having a decreased amount of C10+ aromatic hydrocarbon, is provided via conduit **205** to contact catalyst B in the presence of benzene and/or toluene provided via inlet or conduit **210**. The effluent from reactor **240**, preferably rich in xylenes

(or rich in toluene, in the case where the preferred transalkylation product is toluene, such as just discussed in a previous example) is passed via conduit **215** to reactor **250** comprising catalyst C, which might be, for example, a catalyst for cracking of small alkanes and/or cyclic non-aromatic hydrocarbons. The species introduced via conduit **220** may be a diluent, with or without hydrogen, or it may be nothing at all.

[0035] One of skill in the art in possession of the present disclosure will recognize many additional advantages can be achieved. For instance, the hydrogen introduced into the reactor(s) can be staged based on the level of dealkylation achieved and the amount of alkyl aromatics in the feed stock. By reducing hydrogen partial pressures to the optimum, one can reduce ring loss and improve benzene purity.

[0036] By way of example, when the reactor feed to the first catalyst bed comprising a dealkylation catalyst is 80% C9+ aromatic hydrocarbon and 20% toluene and the targeted conversion are 90+% de-propylation and ~60% de-ethylation, it has been found that optimum hydrogen ratios are preferred to be based on the amount of alkyl groups that will be formed during the reaction rather than the total hydrocarbon, the latter being the conventional understanding. With the conventional approach there will be a wide variation in performance – catalyst life, ring loss, and benzene purity - as it is very likely excess hydrogen will be provided and optimum hydrogen is not achieved for both beds for changes in feed composition and severity. The present inventors have recognized that hydrogen be controlled based upon the amount of alkyl groups that are removed in the reaction. Furthermore, in order for the catalyst to saturate the ethylene and propylene formed in the dealkylation reactions a directionally higher metal function is preferred for long catalyst life and high conversions. By establishing the proper level of hydrogen undesired reactions may be minimized. It may be advantageous to operate the second and third beds after additional hydrogen injection to maximize life. In these beds the undesired side reaction are potentially less prevalent.

[0037] The invention has been described above with reference to numerous embodiments and specific examples. Many variations will suggest themselves to those skilled in this art in light of the above detailed description. All such obvious variations are within the full intended scope of the appended claims. Trade names used herein are indicated by a ™ symbol or ® symbol, indicating that the names may be protected by certain trademark rights, e.g., they may be registered trademarks in various jurisdictions. All patents and patent applications, test procedures (such as ASTM methods, UL methods, and the like), and other documents cited herein are fully incorporated by reference to the extent such disclosure is not

inconsistent with this invention and for all jurisdictions in which such incorporation is permitted. When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated.

CLAIMS:

What is claimed is:

1. A process for producing xylenes by transalkylation comprising:

(a) providing a reactor system comprising at least two catalysts, a first catalyst and a second catalyst, wherein said first catalyst is contained in a first bed and the second catalyst is contained in a second bed, said reactor system characterized by plural inlets for providing fluids to said reactor system;

(b) introducing a first fluid comprising C9+ aromatic hydrocarbons at the location of said first catalyst, said first catalyst characterized as suitable for dealkylating at least a portion of said C9+ aromatic hydrocarbon, to provide a first product comprising (i) olefins; (ii) alkanes resulting from the saturation of said olefins; (iii) cycloalkanes; and (iv) a decreased amount of C10+ aromatic hydrocarbons having C2+ side chains, when compared with said first fluid; and

(c) introducing a second fluid comprising benzene and/or toluene at the location of said second catalyst, in the presence of said first product, said second catalyst characterized as suitable for transalkylation of benzene and/or toluene and C9+ aromatic hydrocarbons to produce a second product;

the improvement comprising the staged injection of hydrogen at plural inlets to said reactor system, whereby the amount of hydrogen present in step (b) is sufficient to increase (ii) and decrease (iii) in said first product.

2. The process of Claim 1, wherein said second fluid comprises $\geq$90 mol% benzene, based on the amount of benzene and toluene in said second fluid.

3. The process of any one of Claims 1 and 2, wherein said second product is provided to an alkylation reactor for the conversion of aromatic hydrocarbons and methanol and/or dimethylether to xylenes.

4. The process of any one of the preceding claims, and wherein the first bed is maintained at a temperature greater than said second bed.

5. The process of any one of the preceding claims, wherein step (c) occurs in a reactor maintained at a temperature not exceeding 450°C.

6. The process of any one of the preceding claims, wherein said second fluid in step (c) is introduced at a temperature lower than the temperature of said first product in step (b).

7. The process of any one of the preceding claims, further comprising reducing H_2:HC ratio in the first bed in response to benzene purity monitored downstream of said catalyst system for transalkylation.

8. The process of any one of the preceding claims, wherein said first bed is maintained at a temperature of about 393-427°C and said second bed is maintained at a temperature of about 388-393°C.

9. The process of any one of the preceding claims, wherein the H_2:HC ratio is attenuated in response to a change in the amount of alkyl aromatics introduced in step (b).

10. The process of any one of the preceding claims, wherein:
(i) said first catalyst comprises a molecular sieve having a Constraint Index in the range of about 3 to about 12, preferably ZSM-5, and at least one hydrogenation component selected from Groups 6 to 12 of the Periodic Table of the Elements, preferably platinum, palladium, iridium, rhenium, and mixtures thereof, preferably present in an amount from about 0.01 to about 10 wt. % of the catalyst composition, and
(ii) said second catalyst comprises a molecular sieve having a constraint index less than 3, preferably ZSM-12, and at least one hydrogenation component selected from Groups 6 to 12 of the Periodic Table of the Elements, preferably platinum, palladium, iridium, rhenium, and mixtures thereof, preferably present in an amount from about 0.01 to about 10 wt. % of the catalyst composition.

11. The process of Claim 10, further comprising a third catalyst bed, maintained under conditions effective to crack non-aromatic cyclic hydrocarbons in the effluent from the second catalyst bed, preferably in the absence of all but inevitable amounts of hydrogen, said third catalyst bed comprising a molecular sieve having a Constraint Index from about 1 to 12, preferably ZSM-5.

12. A catalyst system for transalkylation of benzene and/or toluene with C9+ aromatic hydrocarbons comprising at least two separate catalyst beds, wherein the first catalyst bed is separated from the second catalyst bed by a plural grid structure to allow liquids and gases produced from a first feed material to flow through the plural grid structure from the first catalyst bed to the second catalyst bed and a conduit having perforations or a distributor to distribute a second feed material to the second catalyst bed, the first catalyst bed comprising a molecular sieve having a Constraint Index in the range of about 3 to about 12, preferably ZSM-5, and at least one hydrogenation component selected from Groups 6 to 12 of the Periodic Table of the Elements, and the second catalyst bed comprising a molecular sieve having a constraint index less than 3, preferably ZSM-12, and at least one hydrogenation component selected from Groups 6 to 12 of the Periodic Table of the Elements.

13. The catalyst system according to Claim 12, further comprising a third catalyst bed, wherein the second catalyst bed is separated from the third catalyst bed by a plural grid structure to allow liquids and gases to flow through the plural grid structure from the second catalyst bed to the third catalyst bed and a conduit having perforations or a distributor to distribute a third feed material to the third catalyst bed, wherein the third catalyst bed is maintained under conditions effective to crack non-aromatic cyclic hydrocarbons in the effluent from the second catalyst bed, preferably in the absence of all but inevitable amounts of hydrogen, said third catalyst bed comprising a molecular sieve having a Constraint Index from about 1 to 12, preferably ZSM-5.

14. The catalyst system according to Claim 12 wherein the at least one hydrogenation component selected from Groups 6 to 12 of the Periodic Table of the Elements comprises platinum, palladium, iridium, rhenium, and mixtures thereof.

15. The catalyst system according to Claim 14 wherein the at least one hydrogenation component is present in an amount from about 0.01 to about 10 wt. % of the catalyst composition.

16. The catalyst system according to Claim 12, further integrated with a system for alkylation of C7- aromatic hydrocarbons with methanol to produce xylenes, a system for toluene disproportionation, or a combination thereof.

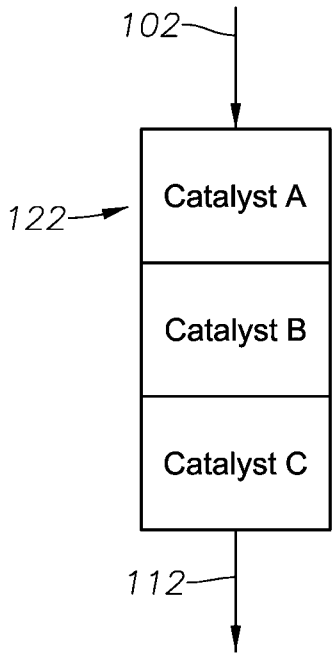


FIG. 1A
(Prior Art)

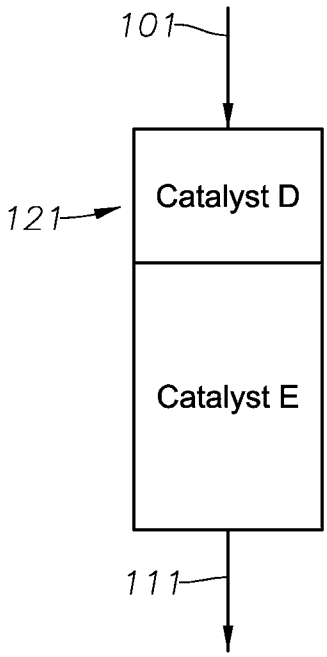


FIG. 1B
(Prior Art)

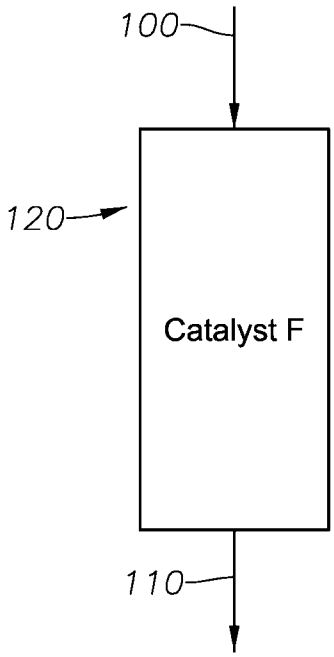


FIG. 1C
(Prior Art)

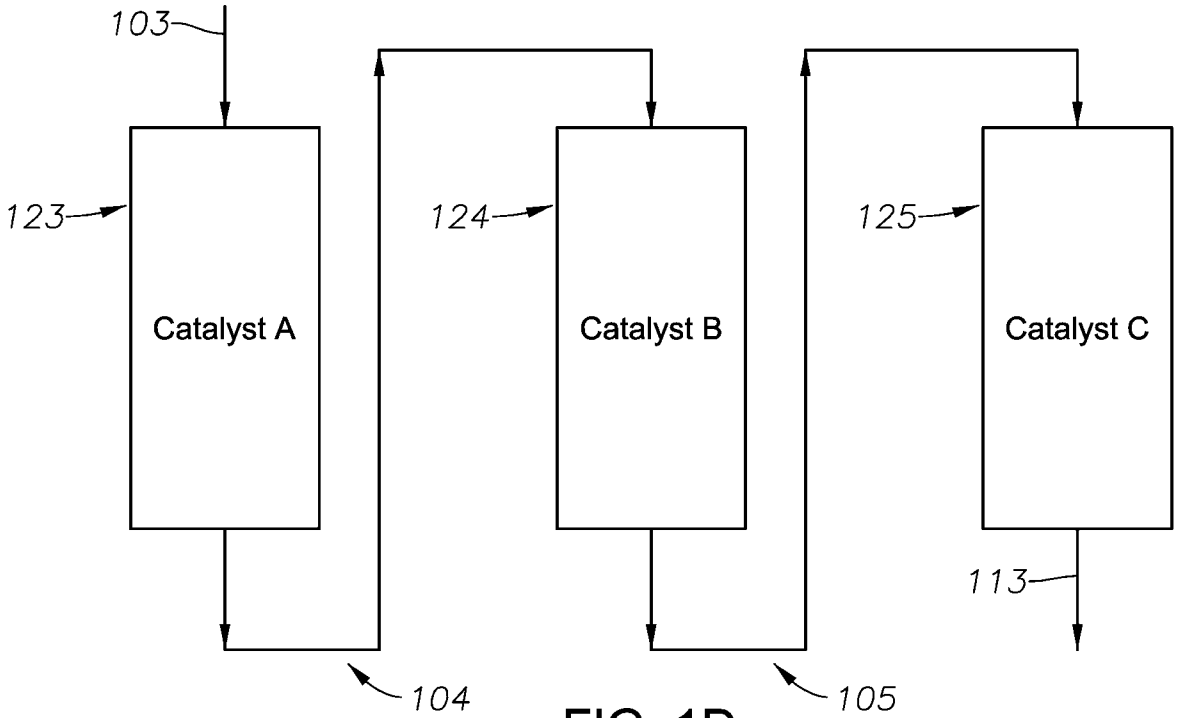


FIG. 1D
(Prior Art)

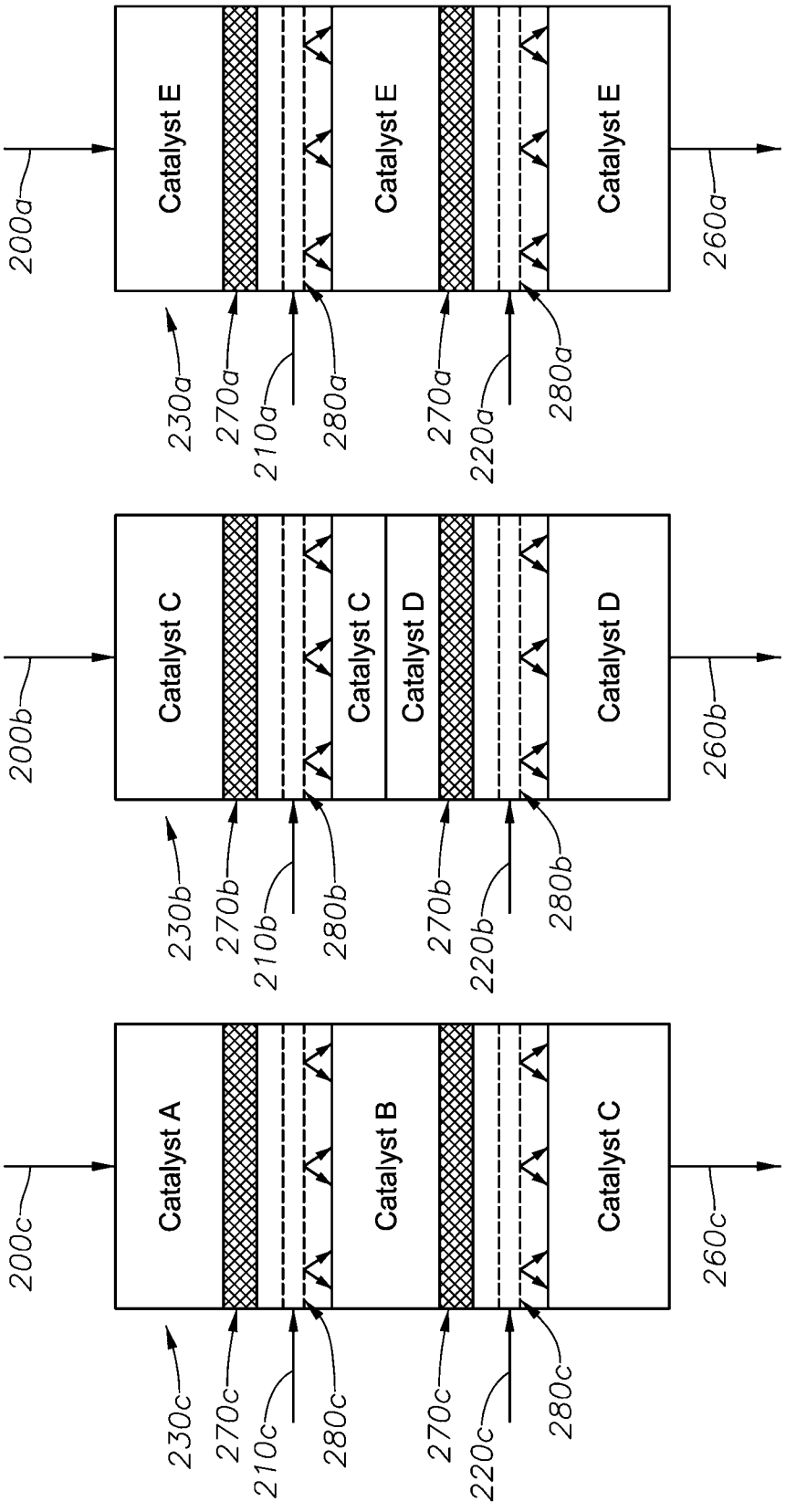


FIG. 2A

FIG. 2B

FIG. 2C

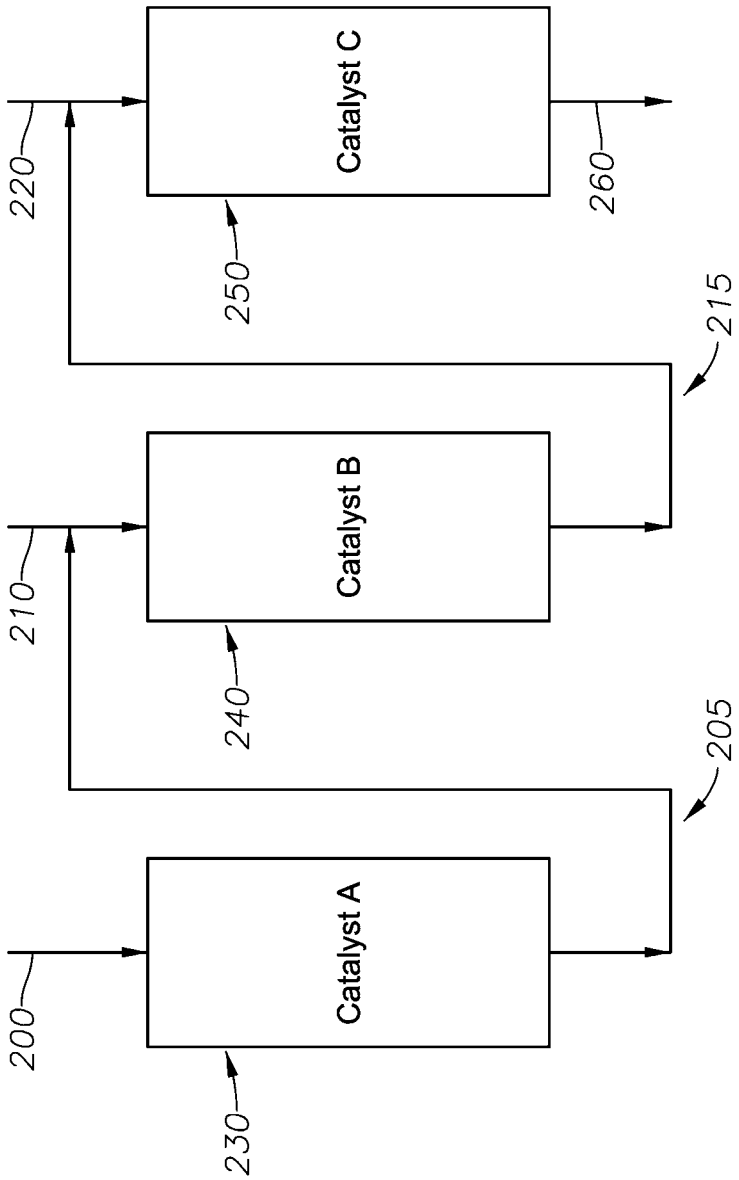

Catalyst C
Catalyst B
Catalyst A
200
210
220
230
240
250
260
205
215

FIG. 2D

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/035027

A. CLASSIFICATION OF SUBJECT MATTER

C07C 2/66(2006.01)i, C07C 7/20(2006.01)i, B01J 29/40(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 2/66; C07C 2/88; C07C 15/08; C07C 5/27; B01J 29/80; B01J 29/06; C07C 7/20; B01J 29/40

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: xylenes, transalkylation, catalyst, aromatic hydrocarbons, benzene, toluene, methanol, dimethylether, first catalyst, second catalyst, ZSM-5, ZSM-12

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2011-0201863 A1 (MATSUSHITA, KOICHI et al.) 18 August 2011 See abstract and claims 1-5	1-3,12-16
A	US 6867340 B2 (OH, SEUNG-HOON et al.) 15 March 2005 See abstract and claims 1-14	1-3,12-16
A	US 2011-0009682 A1 (MATSUSHITA, KOICHI et al.) 13 January 2011 See abstract and claims 1-5	1-3,12-16
A	US 2013-0072736 A1 (NAKAOKA, CHIKANORI et al.) 21 March 2013 See abstract and claims 1-7	1-3,12-16

☐ 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	Date of mailing of the international search report
28 August 2014 (28.08.2014)	**28 August 2014 (28.08.2014)**

Name and mailing address of the ISA/KR
International Application Division
Korean Intellectual Property Office
189 Cheongsa-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

International application No.
PCT/US2014/035027

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 11
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claim 11 is regarded to be unclear, since it refers to claim 10 which is not drafted in accordance with PCT Rule 6.4(a).

3. ☒ Claims Nos.: 4-10
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2014/035027

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011-0201863 A1	18/08/2011	JP 05-495531B2	21/05/2014
		JP 2010-089034 A	22/04/2010
		KR 20110066933 A	17/06/2011
		TW 201021914 A	16/06/2010
		US 8772564 B2	08/07/2014
		WO 2010-041573 A1	15/04/2010
US 6867340 B2	15/03/2005	CN 1122571 C	01/10/2003
		CN 1337890 A0	27/02/2002
		CN 1337890 C0	27/02/2002
		EP 1144113 A1	17/10/2001
		EP 1144113 B1	22/03/2006
		EP 1640066 A1	29/03/2006
		EP 1640066 B1	05/03/2008
		JP 04-351393 B2	28/10/2009
		JP 2002-533211 A	08/10/2002
		KR 10-0297586 B1	22/09/2001
		KR 10-0328677 B1	25/10/2002
		US 2003-0036670 A1	20/02/2003
		WO 00-38834 A1	06/07/2000
US 2011-0009682 A1	13/01/2011	CN 101980991 A	23/02/2011
		CN 101980991 B	01/01/2014
		JP 5520212 B2	11/06/2014
		KR 20100126443 A	01/12/2010
		TW 200946483 A	16/11/2009
		US 8609918 B2	17/12/2013
		WO 2009-119725 A1	01/10/2009
US 2013-0072736 A1	21/03/2013	JP 2011-206614 A	20/10/2011
		KR 20130062923 A	13/06/2013
		WO 2011-118668 A1	29/09/2011