



(51) International Patent Classification:

C07C 15/08 (2006.01) CIOG 25/00 (2006.01)
C07C 5/22 (2006.01) BOLD 15/00 (2006.01)
C07C 7/12 (2006.01) BOLD 3/00 (2006.01)
C07C 7/08 (2006.01) BOW 11/04 (2006.01)
C07C 7/04 (2006.01)

(21) International Application Number:

PCT/US20 12/056027

(22) International Filing Date:

19 September 2012 (19.09.2012)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

13/326,824 15 December 2011 (15.12.2011) US

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

(72) Inventor: CORRADI, Jason T.; Uop LLC, 25 East Algonquin Road ,
P. O. Box 5017, Des Plaines, Illinois 60017-5017 (US).

(74) Agent: WILLIS, Mark R.; Uop LLC, 25 East Algonquin Road ,
P. O. Box 5017, Des Plaines, Illinois 60017-5017 (US).

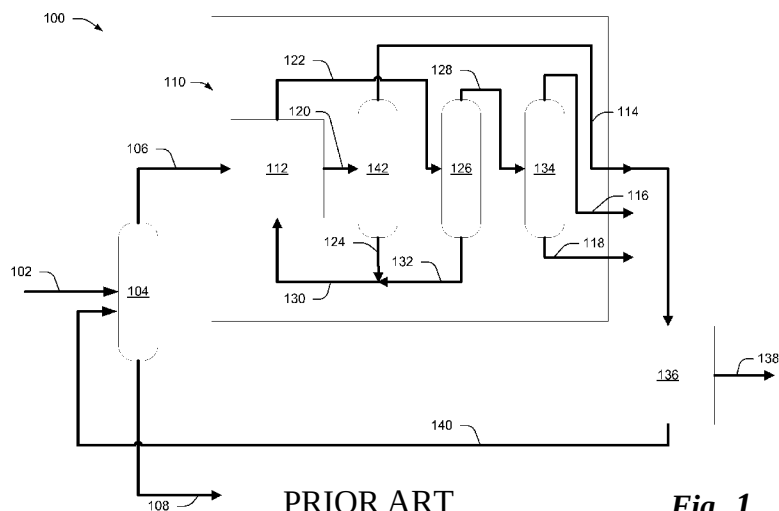
(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, 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, ML, MR, NE, SN, TD, TG).

Published:

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

(54) Title: PROCESS AND APPARATUS FOR PARA-XYLENE PRODUCTION USING MULTIPLE ADSORPTIVE SEPARATION UNITS WITH SHARED RAFFINATE PROCESSING



(57) Abstract: A process for separating para-xylene from a plurality of aromatic compounds, wherein the process introduces a first mixed xylene stream comprising a plurality of xylene isomers into a first adsorptive separation unit to produce a first para-xylene enriched stream and a first raffinate stream. The process further introduces a second mixed xylene stream comprising a plurality of xylene isomers into a second adsorptive separation unit to produce a second para-xylene enriched stream and a second raffinate stream. The process further feeds both the first raffinate stream and the second raffinate stream into a shared raffinate column.

PROCESS AND APPARATUS FOR *para*-XYLENE PRODUCTION USING MULTIPLE
ADSORPTIVE SEPARATION UNITS WITH SHARED RAFFINATE PROCESSING

STATEMENT OF PRIORITY

[0001] This application claims priority to U.S. Application No. 13/326,824 which was
5 filed on December 15, 2011.

FIELD OF THE INVENTION

[0002] The disclosure relates to a process for the formation and adsorptive separation of a
select xylene isomer, preferably **para**-xylene, from a feed stream containing a mix of
aromatic and non-aromatic hydrocarbons. More specifically, the disclosure relates to
10 increasing the efficiency of **para**-xylene production by eliminating the need to vaporize the
product stream from the isomerization process. Most specifically, the disclosure relates to a
para-xylene process comprising multiple adsorptive separation units, each using a different
desorbent, to eliminate fractional distillation of the isomerized product stream, and a raffinate
column shared between the adsorptive separation units.

15

BACKGROUND OF THE INVENTION

[0003] **Para**-xylene, an aromatic hydrocarbon, is an important intermediate which finds
wide and varied application in chemical syntheses. Upon oxidation, *para*-xylene yields
terephthalic acid. Polyester fabrics and resins are produced from a polymer of ethylene
20 glycol and terephthalic acid. These polyester materials are used extensively in a number of
industries and are used to manufacture such items as, for example, clothing, beverage
containers, electronic components, and insulating materials.

[0004] The production of *para*-xylene is practiced commercially in large-scale facilities
and is highly competitive. Concerns exist not only about the effective conversion of
25 feedstock through one or more of isomerization, transalkylation and disproportionation to
produce **para**-xylene and effective separation of **para**-xylene from the resultant mixture of C8
aromatic isomers, but also with the energy costs and capital costs associated with such
processes.

[0005] In prior art processes, C9 aromatics are separated from the C8 aromatics, i.e.
30 xylene isomers, by fractional distillation. This requires heating of the admixture to vaporize
the C8 and lighter aromatics. A large portion of the isomerization stream must be vaporized

to accomplish the C9 separation because the stream is generally composed primarily of C8 and lighter aromatics. This separation requires a substantial amount of energy and associated cost. After the C9 aromatic removal, the C8-containing stream is then recycled into the adsorptive separation unit.

5 [0006] Accordingly, it would be an advance in the state of the art to provide a process for the production of para-xylene, including separation and isomeric formation from an admixture of C8 aromatic isomers, that removes the need to vaporize the isomerized stream for removal of C9 aromatics, thereby lowering operational expenses, in the form of energy consumption, and capital expenditures, in the form of required processing equipment and the
10 size of such processing equipment.

SUMMARY

[0007] A process for separating para-xylene from a plurality of aromatic compounds is presented. The process introduces a first mixed xylene stream comprising a plurality of
15 xylene isomers into a first adsorptive separation unit to produce a first para-xylene enriched stream and a first raffinate stream. The process further introduces a second mixed xylene stream comprising a plurality of xylene isomers into a second adsorptive separation unit to produce a second para-xylene enriched stream and a second raffinate stream. The process further feeds both the first raffinate stream and the second raffinate stream into a shared
20 raffinate column.

[0008] An apparatus for separating para-xylene from a plurality of aromatic compounds is presented. The apparatus comprises a first adsorptive separation unit, a second adsorptive separation unit, and a raffinate column in fluid communication with both the first adsorptive separation unit and the second adsorptive separation unit.
25

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] FIG. 1 is a diagram of a prior art process;

[00010] FIG. 2 is a diagram of one embodiment of the disclosed process where light impurities are removed early in the process and a drag stream is fed into the xylene
30 fractionation column;

[00011] FIG. 3 is a diagram of one embodiment of the disclosed process where light impurities are removed early in the process and a drag stream is fed into an aromatic conversion unit; and

[00012] FIG. 4 is a diagram of one embodiment of the disclosed process where light impurities are removed late in the process and a drag stream is fed into an aromatic conversion unit.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[00013] *Para*-xylene is typically recovered from a mixed aromatic hydrocarbon fraction derived from various sources such as catalytic reforming by liquid-liquid extraction and/or fractional distillation. The *para*-xyhns is commercially separated from a feed stream that typically contains all three xylene isomers, namely ortho-xylene, meta-xylene, and *para*-xylene. The *para*-xylene, or other desired isomer, is separated by either fractional crystallization or adsorptive separation or a combination of these two techniques. Adsorptive separation is generally preferred as it has a significantly higher single pass recovery (-97%) relative to crystallization separation (-65%).

[00014] A typical adsorptive separation process first involves the separation of C8 aromatic hydrocarbons, including ortho-xylene, meta-xylene, *para*-xylsns, and ethylbenzene, from heavier aromatic hydrocarbons (i.e., C9+) and non-aromatic hydrocarbons through fractional distillation.

[00015] Those skilled in the art will appreciate that the designator "CX" refers to a compound comprising X carbon atoms, "CX+" refers to a compound comprising X or greater carbon atoms, and "CX-" refers to a compound comprising X or fewer carbon atoms.

[00016] The *para*-xylsns isomers are then separated from the C8 isomer admixture using a simulated countercurrent moving-bed (SMB) adsorptive separation unit. This simulation is performed using established commercial technology wherein an adsorbent, commonly a solid zeolitic material, is held in place in one or more cylindrical adsorbent chambers. The positions at which the streams involved in the process enter and leave the chamber(s) are slowly shifted along the height of the chamber(s). Normally there are at least four streams (feed, desorbent, extract and raffinate) employed in this procedure and the location at which the feed and desorbent streams enter the chamber and the extract and raffinate streams leave the chamber are simultaneously shifted in the same direction at set intervals in a step-wise

manner. Each shift in location of these transfer points delivers or removes liquid from a different bed within the chamber.

[00017] A typical chamber has a single line for each bed. The flow into or out of a particular line, as the case may be, is controlled by a rotary valve. The shifting of streams
5 along the bed simulates movement of the adsorbent in a direction opposite the flow of liquid, even though the adsorbent is fixed in place within the chamber. SMB chambers are also well suited for high volume production because the input and output streams have nearly constant compositions throughout simulated motion of the adsorbent material in the bed.

[00018] A typical SMB unit recycles a heavy desorbent, such as para-diethylbenzene, to
10 separate high purity *para*-xylene from the other C8 isomers. Para-diethylbenzene is a CIO aromatic that is separated from *para*-xylene by fractional distillation.

[00019] The admixture of non-*para*-xylene isomers from the adsorptive separation unit is subjected to catalytic isomerization to reestablish an equilibrium amount of *para*-xylsns isomers in the admixture. In addition to *para*-xylene and other C8 isomers, the isomerized
15 stream typically contains an amount of C9+ aromatics, which will accumulate in the desorbent and, therefore, must be removed.

[00020] Processes for isolating a desired isomer of xylene without the vaporization of the full isomerized product stream are presented. The process comprises two adsorptive separation units. The first unit utilizes a heavy desorbent and the second unit utilizes a light
20 desorbent. Those skilled in the art will appreciate that a desorbent used in combination with a simulated moving bed adsorbent system facilitates removal of an adsorbed material from the adsorbent bed. This being the case, a useful desorbent will have an affinity for the desired material, i.e. *para*-xylene, that is substantially the same as the affinity of the adsorbent bed for that desired material.

[00021] As used herein, the terms heavy and light are generally in reference to the boiling point of the desorbent relative to the C8 aromatics, namely, *ortho*-, *meta*-, *para*-xylene and ethylbenzene.

[00022] In certain embodiments, the heavy desorbent is selected from the group consisting of para-diethylbenzene, para-diisopropylbenzene, tetralin, and the like, and combinations
30 thereof. In certain embodiments, toluene and the like can be used as the light desorbent. The *para*-diethylbenzene has a higher boiling point than the C8 aromatic isomers and, as such, the *para*-diethylbenzene is the bottoms (i.e., heavy) product when separated from the C8 isomers

in a fractional distillation column. Similarly, toluene has a lower boiling point than the C8 aromatic isomers and, as such, the toluene is the overhead (i.e., light) product when separated from the C8 isomers in a fractional distillation column.

[00023] Unlike prior art processes, Applicant's process comprises feeding a stream of material containing a desired xylene isomer formed in an isomerization unit into a second adsorptive separation unit, as opposed to being fed back into a fractional distillation column. An extract stream from the second adsorptive separation unit, rich in the desired xylene isomer, is fed back into a first adsorptive separation unit for isolation of the desired xylene isomer. The process is presented in greater detail below.

[00024] Referring to FIG. 1, a diagram 100 of a prior art process for the production of *para*-xylene is depicted. A feed stream 102 enters a xylene fractionation unit 104. The feed stream typically contains *ortho*-, *meta*-, and *para*-xylene isomers and may also contain quantities of ethylbenzene, toluene, C8 cycloalkanes, alkanes, and hydrocarbons having more than eight carbon atoms per molecule.

[00025] The xylene fractionation unit 104 is a fractional distillation column. The xylene fractionation unit 104 divides the incoming stream into an overhead stream 106 comprising the C8 and lighter aromatics, including the xylene isomers, ethylbenzene, and toluene, and a bottoms 108 and one or more side cut streams (not shown) comprising C9+ aromatics.

[00026] Table 1 recites an example composition for feed stream 102.

TABLE 1

<u>Component</u>	<u>Amount</u>
<i>para</i> -xylene	10-20 wt %
Total C8 Aromatics	60 wt %
ethylbenzene	10-20 wt %
toluene	0.5-2.0 wt %
C9+	25-30 wt %
Nonaromatic hydrocarbons	< 0.5 wt %
Nitrogen	1.0 mg/kg
Sulfur	1.0 mg/kg

[00027] The overhead stream 106 enters the separation assembly 110, where the input stream 106 is separated into a raffinate stream 114, a toluene stream 116, and a *para*-xylene stream 118. The raffinate stream 114 has been substantially depleted of *para*-xylene but contains other C8 aromatics, including *ortho*-xylene, meto-xylene and ethylbenzene.

5 [00028] Within the separation assembly 110, the stream 106 enters an adsorptive separation unit 112. The adsorptive separation unit 112 separates the incoming stream 106 into a raffinate stream 120 and an extract stream 122. The adsorptive unit 112 typically comprises two SMB chambers and a rotary valve. Each individual chamber typically has 12 beds. A bedline connects each bed to the rotary valve. The rotary valve controls the flow of
10 material into or out of each SMB chamber in a step-wise manner to create a simulated moving bed.

[00029] A heavy desorbent, typically para-diethylbenzene, is used to facilitate the separation of the raffinate stream 120 and extract stream 122. The raffinate stream 120 comprises ethylbenzene, meto-xylene, and *ortho*-xylene diluted with desorbent and any
15 heavies. Heavies are hydrocarbons with a boiling point greater than that of the C8 aromatic isomers and include C9+ aromatics. The extract stream 122 comprises *para*-xylene diluted with desorbent and light ends. Light ends are hydrocarbons with a boiling point below that of the C8 aromatic isomers and include toluene and other C7- aromatics.

[00030] The raffinate stream 120 is directed to a raffinate column 142. The raffinate
20 column 142 is a fractional distillation column that divides the incoming stream 120 into (i) an overhead raffinate stream 114 comprising ethylbenzene, meto-xylene, and *ortho*-xylene and (ii) a bottoms stream 124 comprising desorbent and any heavies. The bottoms stream 124 is recycled back to the adsorptive unit 112 through combined stream 130. The overhead raffinate stream 114 is directed to an isomerization unit 136.

25 [00031] The extract stream 122, comprising xylene isomers and ethylbenzene, enters extract column 126. Extract column 126 is a fractional distillation column that divides the incoming stream 122 into (i) an overhead stream 128 comprising *para*-xylene and toluene and (ii) a bottoms stream 132 comprising desorbent and heavies. The bottoms stream 132 containing desorbent is recycled back to the adsorptive unit 112 through combined stream
30 130. Heavies in the combined desorbent stream 130 may be removed by directing a slipstream of the desorbent into a small desorbent rerun column.

[00032] The overhead stream 128, comprising **para**-xylene and toluene, enters finishing column 134. Finishing column 134 is a fractional distillation column that divides the incoming stream 128 into (i) an overhead toluene stream 116 and (ii) a bottoms *para*-xylene stream 118. The bottoms *para*-xylene stream 118 contains the final desired product.

5 [00033] The raffinate stream 114 comprising ethylbenzene, *meta*-xylene, and *ortho*-xylene enters an isomerization unit 136. Catalysts in the isomerization unit 136 reestablish an equilibrium mixture of the *ortho*-, *meta*-, and **para**-xylene isomers and convert the ethylbenzene into xylenes and/or benzene.

10 [00034] Nonaromatic compounds in the raffinate stream 114 are cracked to light ends and removed in stream 138 along with any benzene. The isomerization process also creates quantities of C9 and heavier aromatics. The output stream 140 comprises an equilibrium mixture of xylene isomers as well as quantities of C9 aromatics and unreacted ethylbenzene. The output stream 140 is recycled back into the xylene fractionation unit 104.

15 [00035] The C9 aromatics produced during isomerization are separated from the C8 isomers in the xylene fractionation unit 104. While the C9 aromatics are only a very small portion of the stream, the entire C8 fraction must be vaporized to accomplish this separation.

20 [00036] Referring to FIG. 2, a diagram 200 of one embodiment of Applicant's process is depicted. A feed stream 202 enters a xylene fractionation unit 204. In one embodiment, the feed stream 202 contains *ortho*-, *meta*-, and **para**-xylene isomers. In one embodiment, the feed stream 202 contains quantities of ethylbenzene, toluene, C8 cycloalkanes, alkanes, and hydrocarbons having more than eight carbon atoms per molecule.

25 [00037] In one embodiment, the feed stream 202 is a result of hydrotreating naphtha to remove any sulfur and nitrogen contaminants and the subsequent catalytic reforming where paraffins and naphthenes in the decontaminated naphtha are converted to aromatics. The most light ends and C7- fractions are removed in a debutanizer and fractional distillation column, respectively. The feed stream 202, comprising a C8+ fraction, enters the xylene fractionation unit 204. In one embodiment, the feed stream 202 comprises 23 weight percent **para**-xylene.

30 [00038] The xylene fractionation unit 204 is a fractional distillation column. The xylene fractionation unit 204 divides the incoming stream into an overhead stream 206 comprising the C8- aromatics, including the xylene isomers, ethylbenzene, and toluene, and a bottoms stream 208 and one or more side cut streams (not shown) comprising C9+ aromatics.

[00039] The overhead stream 206 enters the extract column 210, where the stream 206 is separated into an overhead stream 212 and a bottoms stream 214. The overhead stream 212 comprises C7- aromatics and light impurities. The bottoms stream 214 comprises C8 aromatic isomers. In one embodiment, the bottom stream comprises a high concentration of *para-xylene*. Extract column 210 is a fractional distillation column that separates the heavier C8 aromatic isomer fraction from the light fraction comprising the desorbent toluene and other light C7- aromatic hydrocarbons.

[00040] The bottoms stream 214 enters adsorption separation unit 216. Adsorption separation unit 216 separates the incoming stream 214 into a raffinate stream 218 and an extract stream 220. In one embodiment, the heavy desorbent *para*-diethylbenzene is used to facilitate the separation of the raffinate stream 218 and extract stream 220. In certain embodiments, the heavy desorbent is selected from the group consisting of *para*-diethylbenzene, *para*-diisopropylbenzene, tetralin, and the like, and combinations thereof. The raffinate stream 218 comprises ethylbenzene, *meta*-xylene, and *ortho*-xylene diluted with desorbent. The extract stream 220 comprises *para-xylene* diluted with desorbent.

[00041] In one embodiment, adsorptive separation unit 216 comprises an SMB assembly and a rotary valve. In other embodiments, the adsorption separation unit 216 comprises an SMB assembly and one or more rotary valves, one or more computing device operated valves, or a combination thereof. In one embodiment, the SMB assembly comprises a single physical chamber. In one embodiment, the physical chamber includes 24 beds. In one embodiment, the physical chamber includes less than 24 beds. In one embodiment, the SMB assembly includes two physical chambers. In one embodiment, each physical chamber includes 12 beds. In one embodiment, each physical chamber includes less than 12 beds. In one embodiment, each physical chamber includes more than 12 beds. In one embodiment, the physical chambers have an unequal number of beds. A bed line connects each bed in the SMB assembly to the rotary valve. The rotary valve controls the flow of material into or out of the SMB assembly in a step-wise manner to create a simulated moving bed and to flush the bed lines between flows of differing material.

[00042] As a mixture of xylene isomers is fed into adsorptive separation unit 216, and flows downwardly, the mixture of xylene isomers contacts a solid adsorbent within the chamber. The zeolitic adsorbents disposed in adsorptive separation unit 216 have an affinity for *para-xylene*. As the mixture of xylene isomers flows over the solid adsorbent, the *para*-

xylene is selectively adsorbed into the adsorbent while the other isomers continue to travel downward in the chamber in the bulk liquid.

[00043] The raffinate stream 218 enters a raffinate column 222 at a first location 272.

[00044] The extract stream 220 enters the extract column 224. Extract column 224 is a fractional distillation column that separates the incoming stream 220 into (i) an overhead **para**-xylene product stream 226 comprising the light **para**-xylene fraction and (ii) a bottoms stream 228 comprising a heavy desorbent fraction, such as **para**-diethylbenzene, a CIO aromatic.

[00045] In one embodiment, the overhead **para**-xylene stream 226 comprises 98.0 weight percent **para**-xylene. In one embodiment, the overhead **para**-xylene stream 226 comprises 99.2 weight percent **para**-xylene. In one embodiment, the overhead **para**-xylene stream 226 comprises 99.7 weight percent **para**-xylene. In one embodiment, the overhead **para**-xylene stream 226 comprises 99.9 weight percent **para**-xylene. In one embodiment, the overhead **para**-xylene stream 226 comprises greater than 99.9 weight percent **para**-xylene.

[00046] The bottoms stream 228 is recycled back to the adsorption separation unit 216 through combined stream 230.

[00047] In certain embodiments, **para**-ethyltoluene, structurally similar to **para**-xylene, may be introduced into the process by the isomerization unit 250. In some embodiments, the **para**-ethyltoluene is separated from the **para**-xylene in the adsorption separation unit 216 or in the extract column 224. In certain embodiments, the **para**-ethyltoluene is removed from the **para**-xylene product using any techniques known in the art.

[00048] Light desorbent stream 212 enters adsorption separation unit 234 by way of combined stream 232. Adsorption separation unit 234 separates the incoming stream 254 into a raffinate stream 236 and an extract stream 238. Stream 254 is an isomerized product stream from isomerization unit 250 comprising an equilibrium mixture of xylene isomers.

[00049] In one embodiment, the light desorbent toluene is used to facilitate the separation of the raffinate stream 236 and extract stream 238. In another embodiment, a light desorbent other than toluene is used to facilitate the separation of the raffinate stream 224 and extract stream 246. The raffinate stream 236 comprises ethylbenzene, meta-xylene, and *ortho*-xylene diluted with desorbent. The extract stream 238 comprises **para**-xylene diluted with desorbent.

[00050] In one embodiment, adsorptive separation unit 234 comprises an SMB assembly and a rotary valve. In other embodiments, the adsorption separation unit 234 comprises an SMB assembly and one or more rotary valves, one or more computing device operated valves, or a combination thereof. In one embodiment, the SMB assembly comprises a single physical chamber. In one embodiment, the physical chamber includes 24 beds. In one embodiment, the physical chamber includes less than 24 beds. In one embodiment, the SMB assembly includes two physical chambers. In one embodiment, each physical chamber includes 12 beds. In one embodiment, each physical chamber includes less than 12 beds. In one embodiment, each physical chamber includes more than 12 beds. In one embodiment, the physical chambers have an unequal number of beds. A bed line connects each bed in the SMB assembly to the rotary valve. The rotary valve controls the flow of material into or out of the SMB assembly in a step-wise manner to create a simulated moving bed and to flush the bed lines between flows of differing material.

[00051] As a mixture of xylene isomers is fed into adsorptive separation unit 234, and flows downwardly, the mixture of xylene isomers contacts a solid adsorbent within the chamber. The zeolitic adsorbents disposed in adsorptive separation unit 234 have an affinity for *para*-xylene. As the mixture of xylene isomers flows over the solid adsorbent, the *para*-xylene is selectively adsorbed into the adsorbent while the other isomers continue to travel downward in the chamber in the bulk liquid.

[00052] The raffinate stream 236 enters a raffinate column 222 at a third location 276.

[00053] The extract stream 238 is fed into the extract column 210. Extract column 210 separates the *para*-xylene product in the extract stream 238 from the light desorbent, such as toluene. The light desorbent is recycled in a light desorbent loop 212, 232, 238.

[00054] In one embodiment, a slipstream 242 is extracted from the overhead stream 212.

In one embodiment, slipstream 242 prevents the accumulation of any additional toluene introduced into the desorbent loop from the feed stream 202 and/or through the isomerization unit 250. In one embodiment, slipstream 242 prevents the accumulation as light impurities in the light desorbent loop. In one embodiment, slipstream 242 comprises high purity toluene. In one embodiment, slipstream 242 comprises toluene and light impurities from the feed stream 202.

[00055] Raffinate column 222 is a fractional distillation column that separates the raffinate streams 236 and 218, each comprising *para*-xylene depleted C8 aromatic isomers diluted

with light and heavy desorbent, respectively, into a C8 aromatic isomer stream 244, a light desorbent stream 246, and a heavy desorbent stream 248. The C8 aromatic isomer stream 244 exits the raffinate column 222 at a second location 274.

[00056] The light desorbent along with any light impurities have the lowest boiling point and are, as such, extracted as a net overhead stream 246. The heavy desorbent along with any heavies have the highest boiling point and are, as such, extracted as a net bottom stream 248. The *ortho*-xylene, meto-xylene, and ethylbenzene have an intermediate boiling point and are, as such, extracted at a sidecut tray. The heavy desorbent is recycled in a heavy desorbent loop 230, 220/218, 228/248.

[00057] In one embodiment, the C8 aromatic isomer stream 244 exits the raffinate column at a location below that of raffinate stream 236 and above that of raffinate stream 218. In one embodiment, the raffinate stream 236 enters raffinate column 222 at a location on the column where the composition within the column 222 is similar to the composition in stream 236. In one embodiment, the raffinate stream 218 enters raffinate column 222 at a location on the column where the composition within the column 222 is similar to the composition in stream 218. As used herein, with reference to fractional distillation columns, the term "above" refers to a location in or on the column such that liquid inserted at the location will flow down toward the reference point. Similarly, the term "below" refers to a location in or on the column such that liquid inserted at the location will flow down away from the reference point.

[00058] The C8 aromatic isomer stream 244 comprising meto-xylene, *ortho*-xylene, and ethylbenzene enters an isomerization unit 250. Catalysts in the isomerization unit 250 reestablish an equilibrium mixture of the *ortho*-, *meta*-, and *para*-xylens isomers. In one embodiment, the catalyst is an ethylbenzene dealkylation catalyst, which converts ethylbenzene to a benzene co-product. In one embodiment, the catalyst is an ethylbenzene isomerization catalyst, which converts the ethylbenzene into additional xylene isomers.

[00059] Nonaromatic compounds in the C8 aromatic isomers stream 244 are cracked to light ends and removed in stream 252 along with any benzene co-product created. The isomerization process may also create small quantities of C9 and heavier aromatics. In one embodiment, the output stream 254 comprises an equilibrium mixture of xylene isomers. In one embodiment, the output stream 254 comprises small quantities of C9+ aromatics. In one embodiment, the output stream 254 comprises unreacted ethylbenzene. In one embodiment,

the output stream 254 comprises 1.5 weight percent ethylbenzene or less. The isomerized output stream 254 enters adsorption separation unit 234.

[00060] In certain embodiments, certain C9+ aromatics and other heavies that may be introduced as a result of the isomerization of *ortho*-xylene, *meta*-xylene, and ethylbenzene at isomerization unit 250. Any C10+ heavies will accumulate in the heavy desorbent loop 230, 220/218, 228/248. In certain configurations of the raffinate column 222, any C9 aromatics will accumulate in the isomerization loop 254, 236, 244. In other configurations of the raffinate column 222, any C9 aromatics will accumulate in the heavy desorbent loop 230, 220/218, 228/248. In yet other configurations of the raffinate column 222, any C9 aromatics will accumulate in both the isomerization loop and the heavy desorbent loop.

[00061] In different embodiments, one or more drag streams are used to prevent the accumulation of C9 aromatics in the process. In one embodiment, if accumulation occurs in the heavy desorbent loop, a drag stream 264 is withdrawn from the desorbent loop by way of stream 230. Stream 230 comprises primarily heavy desorbent along with the C9 aromatic and heavy impurities. In certain embodiments, drag stream 264 is fed into a fractional distillation column 266, which separates the drag stream 264 into an overhead stream 268 and a bottoms stream 270. The bottoms stream 270 comprises high purity para-diethylbenzene, which is returned to the desorbent loop by way of stream 230. In one embodiment, the amount of material withdrawn in drag stream 264 is 1 to 20 volume percent of stream 230.

[00062] In another embodiment, if accumulation occurs in the isomerization loop (i.e., 254, 236, 244), a drag stream 262 is withdrawn from the isomerization loop by way of raffinate stream 244. Stream 244 comprises a mixture of *ortho*-xylene, *meta*-xylene, ethylbenzene along with the C9 aromatic and heavy impurities. The drag stream is fed into the xylene fractionation column 204 where substantially all C9+ aromatics are removed in bottoms 208 and the C8 aromatics are recycled back through the process. In one embodiment, the amount of material in the drag stream 262 is 1 to 20 volume percent of the raffinate stream 244.

[00063] In yet another embodiment, if the accumulation occurs in both the isomerization loop and the heavy desorbent loop, drag streams 262 and 264 are both used. In other embodiments, no drag streams are used. In other embodiments, the impurities are extracted by another process known in the art capable of separating C9 aromatics and heavies from para-diethylbenzene.

[00064] Referring to FIG. 3, diagram 300 illustrates one embodiment of Applicant's process including an aromatic conversion unit. To prevent accumulation of C9 aromatics in the isomerization loop (i.e., 254, 236, 244), a drag stream 302 is withdrawn from the isomerization loop by way of raffinate stream 244. The drag stream is fed into an aromatic conversion unit 306. All or a portion of the light desorbent slip stream 242, comprising toluene, is directed into the aromatic conversion unit 306 by way of stream 304.

[00065] The aromatic conversion unit 306 converts the incoming stream 304 comprising a mixture of toluene and C8+ aromatics into an output stream 308 comprising an equilibrium mixture of xylene isomers, ethylbenzene and benzene. The aromatic conversion unit 306 facilitates catalytic disproportionation reactions, which convert toluene into a mixture of benzene and xylene isomers. The aromatic unit 306 also facilitates catalytic transalkylation reactions, which convert a blend of toluene and C9 aromatic isomers to xylene isomers through the migration of methyl groups between methyl-substituted aromatics.

[00066] The aromatic conversion product stream 308 is introduced into the xylene fractionation unit 204. The C8 aromatics and toluene exit the xylene fractionation unit 204 by way of stream 206. The C9 aromatics and heavies exit the xylene fractionation unit by way of stream 208.

[00067] Referring to FIG. 4, diagram 400 illustrates another embodiment of Applicant's process including an aromatic conversion unit. The overhead stream 206 from the xylene fractionation unit 204 enters adsorption separation unit 216 by way of combined stream 206/214. Combined stream 206/214 comprises C8 aromatics as well as toluene and any other light impurities from the feed stream 202.

[00068] Combined stream 206/214, comprising a mixture of C7- aromatics, enters the adsorption separation unit 216. In certain embodiments, the selectivity of the adsorbent in the adsorption separation unit 216 for C7- aromatics and light ends is very close to that of *o*/*p*-xylene. As such, the C7- aromatics and light ends exit the adsorption separation unit 216 by way of extract stream 220. The C7- aromatics and light ends, being the lighter component in stream 220, exit the extract column 224 in the overhead stream 414.

[00069] Overhead stream 414 comprises a high *para*-xylene content as well as quantities of C7- aromatics and light ends. The finishing column 404 separates the overhead stream 414 into an overhead stream comprising C7- aromatics and light ends that entered the process by way of feed stream 202 and a bottoms stream 408 comprising high purity *para*-xylene.

[00070] In certain embodiments, **para**-ethyltoluene, structurally similar to **para**-xylene, may be introduced into the process by the isomerization unit 250. In some embodiments, the **para**-ethyltoluene is separated from the **para**-xylene in the adsorption separation unit 216 or in the extract column 224. In some embodiments, the **para**-ethyltoluene is removed from the **para**-xylene product using techniques known in the art.

[00071] In one embodiment, the bottoms **para**-xylene stream 408 comprises 99.2 weight percent **para**-xylene. In one embodiment, the bottoms **para**-xylene stream 408 comprises 99.7 weight percent **para**-xylene. In one embodiment, the bottoms **para**-xylene stream 408 comprises 99.9 weight percent **para**-xylene. In one embodiment, the bottoms **para**-xylene stream 408 comprises greater than 99.9 weight percent **para**-xylene.

[00072] Each of the disclosed processes avoid the vaporization of the isomerization product stream to extract C9 aromatic impurities. As such, the disclosed processes consume substantially less energy, resulting in lower operational expenditures, and require an overall reduction in equipment costs, resulting in lower capital expenditures, as compared to traditional xylene separation processes.

[00073] Referring to the foregoing paragraphs, this invention is described in preferred embodiments in the following description with reference to the Figures, in which like numerals represent the same or similar elements. Reference throughout this specification to "one embodiment," "an embodiment," or similar language means that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus, appearances of the phrases "in one embodiment," "in an embodiment," and similar language throughout this specification may, but do not necessarily, all refer to the same embodiment.

[00074] The described features, structures, or characteristics of the invention may be combined in any suitable manner in one or more embodiments. In the above description, numerous specific details are recited to provide a thorough understanding of embodiments of the invention. One skilled in the relevant art will recognize, however, that the invention may be practiced without one or more of the specific details, or with other methods, components, materials, and so forth. In other instances, well-known structures, materials, or operations are not shown or described in detail to avoid obscuring aspects of the invention.

[00075] While the invention is described through the above-described exemplary embodiments, it will be understood by those of ordinary skill in the art that modifications to,

and variations of, the illustrated embodiments may be made without departing from the inventive concepts disclosed herein. For example, although some aspects of separating *para*-xylene has been described, those skilled in the art should readily appreciate that functions, operations, decisions, etc., of all or a portion of each step, or a combination of steps, of the series of steps described may be combined, separated into separate operations or performed in other orders. Moreover, while the embodiments are described in connection with various illustrative processes, one skilled in the art will recognize that the methods and processes described herein can be embodied using a variety of techniques. Furthermore, disclosed aspects, or portions of these aspects, may be combined in ways not listed above.

Accordingly, the invention should not be viewed as being limited to the disclosed embodiment(s). The scope of the invention should be determined with reference to the pending claims along with their full scope or equivalents, and all changes which come within the meaning and range of equivalency of the claims are to be embraced within their full scope.

CLAIMS:

1. A process for separating **para**-xylene from a plurality of aromatic compounds, the process characterized by:
introducing a first mixed xylene stream 206 / 214 comprising a plurality of xylene isomers
5 into a first adsorptive separation unit 216 to produce a first *para*-xylene enriched stream 220 and a first raffinate stream 218;
introducing a second mixed xylene stream 254 comprising a plurality of xylene isomers into a second adsorptive separation unit 234 to produce a second *para*-xylene enriched stream 238 and a second raffinate stream 236; and
10 feeding both said first raffinate stream 218 and said second raffinate stream 236 into a raffinate column 222.
2. The process of claim 1, further characterized by:
producing by said raffinate column 222 a C8 raffinate stream 244; and
introducing the C8 raffinate stream 244 into an isomerization unit 250 to produce said second
15 mixed xylene stream 254.
3. The process of claim 1, further characterized by:
the first raffinate stream 218 enters the raffinate column 222 at a first location 272;
the C8 raffinate stream 244 exits the raffinate column 222 at a second location 274;
the second raffinate stream 236 enters the raffinate column 222 at a third location 276; and
20 wherein the second location 274 is disposed between the first location 272 and the third location 276.
4. The process of claim 2, further characterized by introducing said second enriched **para**-xylene stream 254 into a second extract column 210.
5. The process of claim 4, further characterized by introducing said first enriched *para*-
25 xylene stream 220 into a first extract column 224.
6. A apparatus for separating **para**-xylene from a plurality of aromatic compounds, characterized by:
a first adsorptive separation unit 216;
a second adsorptive separation unit 234; and

a raffinate column 222 in fluid communication with both said first adsorptive separation unit 216 and said second adsorptive separation unit 234.

7. The apparatus of claim 6, further characterized by:

an isomerization unit 250 in fluid communication with both said raffinate column 222 and
5 said second adsorptive separation unit 234.

8. The apparatus of claim 7, wherein:

said raffinate column 222 comprises a first input 272, a second input 276, and an output 274;
said first adsorptive separation unit 216 is in fluid communication with said first input 272;
and

10 said second adsorptive separation unit 234 is in fluid communication with said second input 276.

9. The apparatus of claim 8, further characterized by an isomerization unit 250 in fluid communication with said output 274.

10. The apparatus of claim 9, further characterized by:

15 a first extract column 224 in fluid communication with the first adsorptive separation unit 216; and
a second extract column 210 in fluid communication with the second adsorptive separation unit 234.

1/4

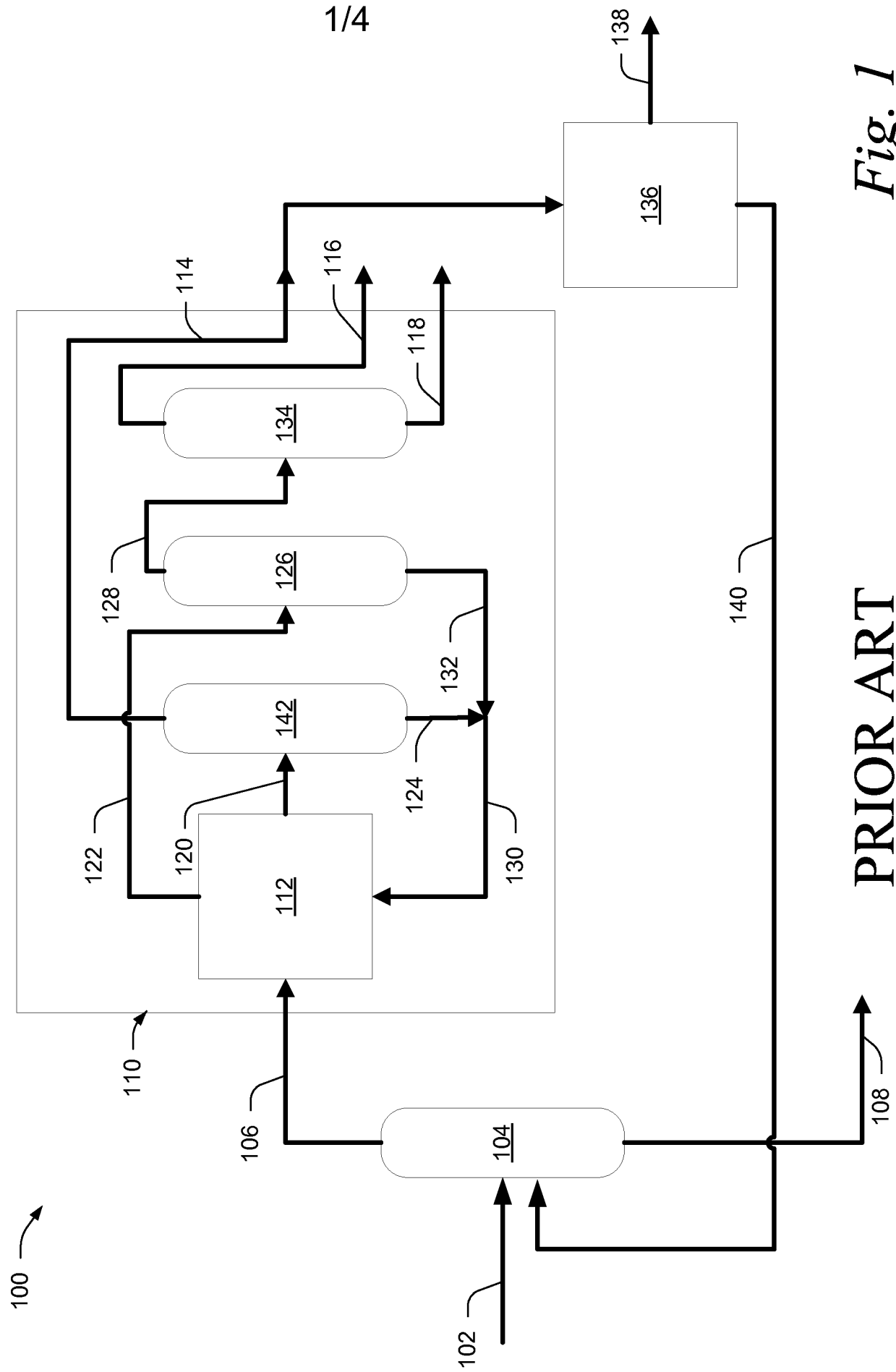


Fig. 1

PRIOR ART

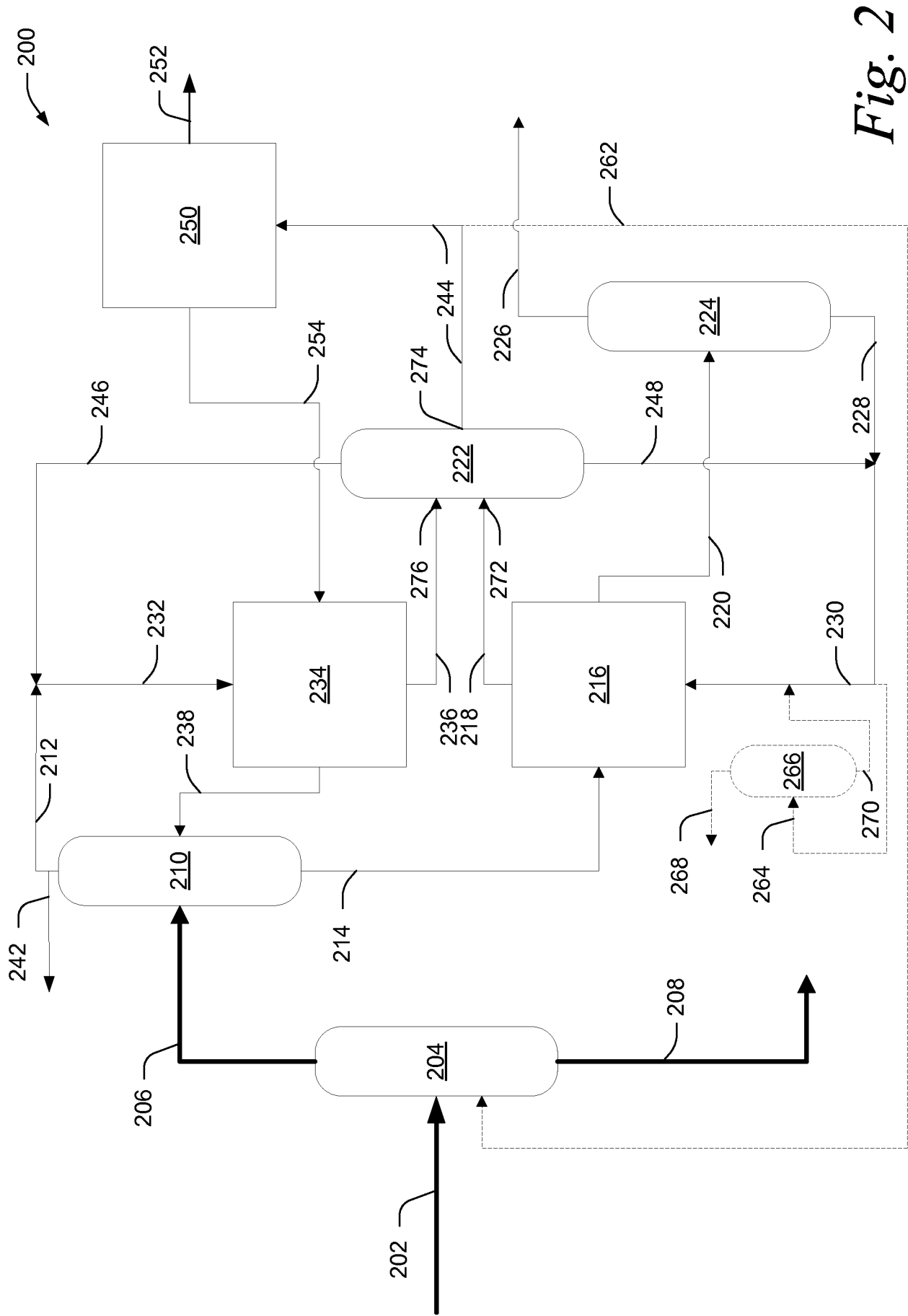


Fig. 2

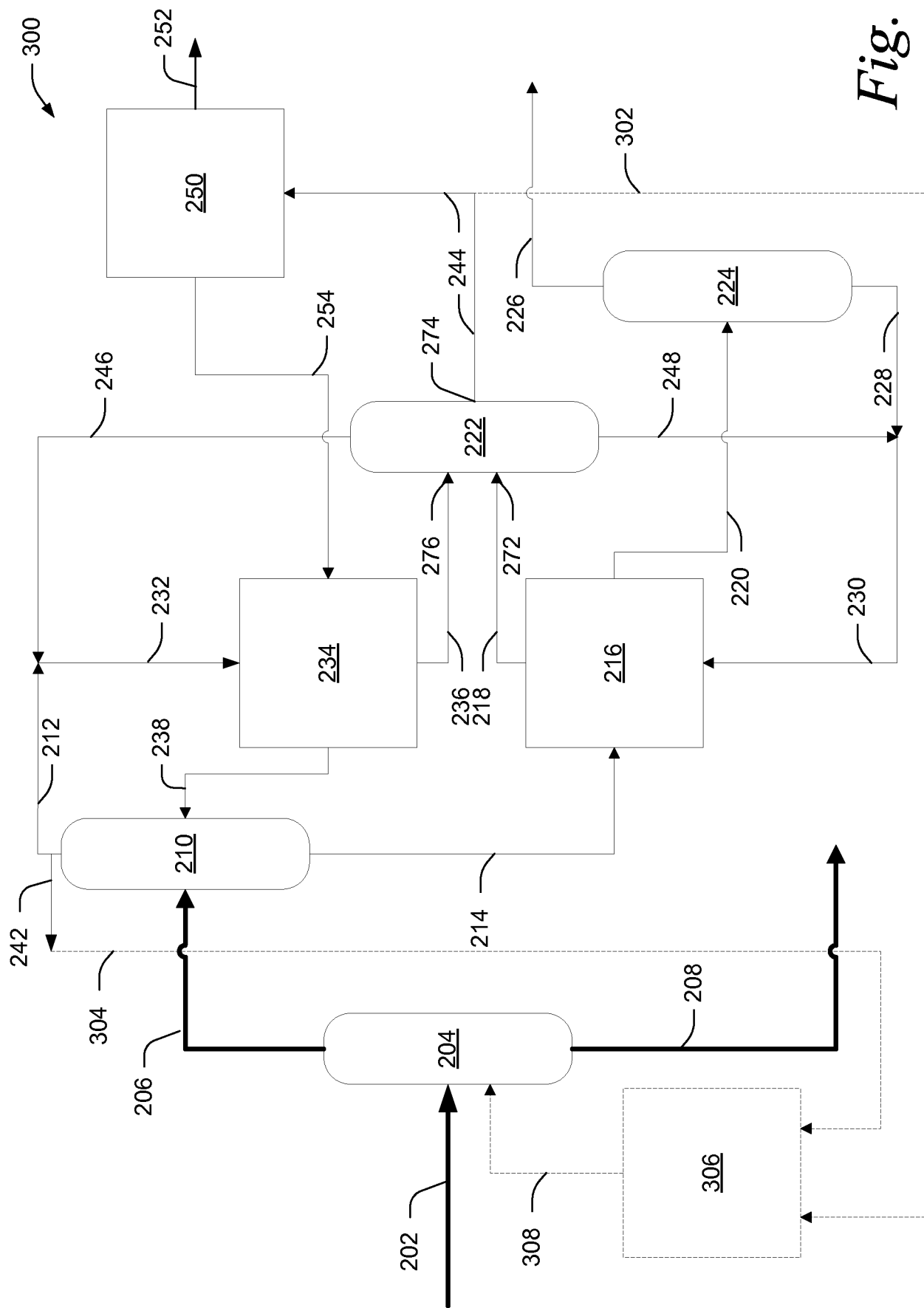


Fig. 3

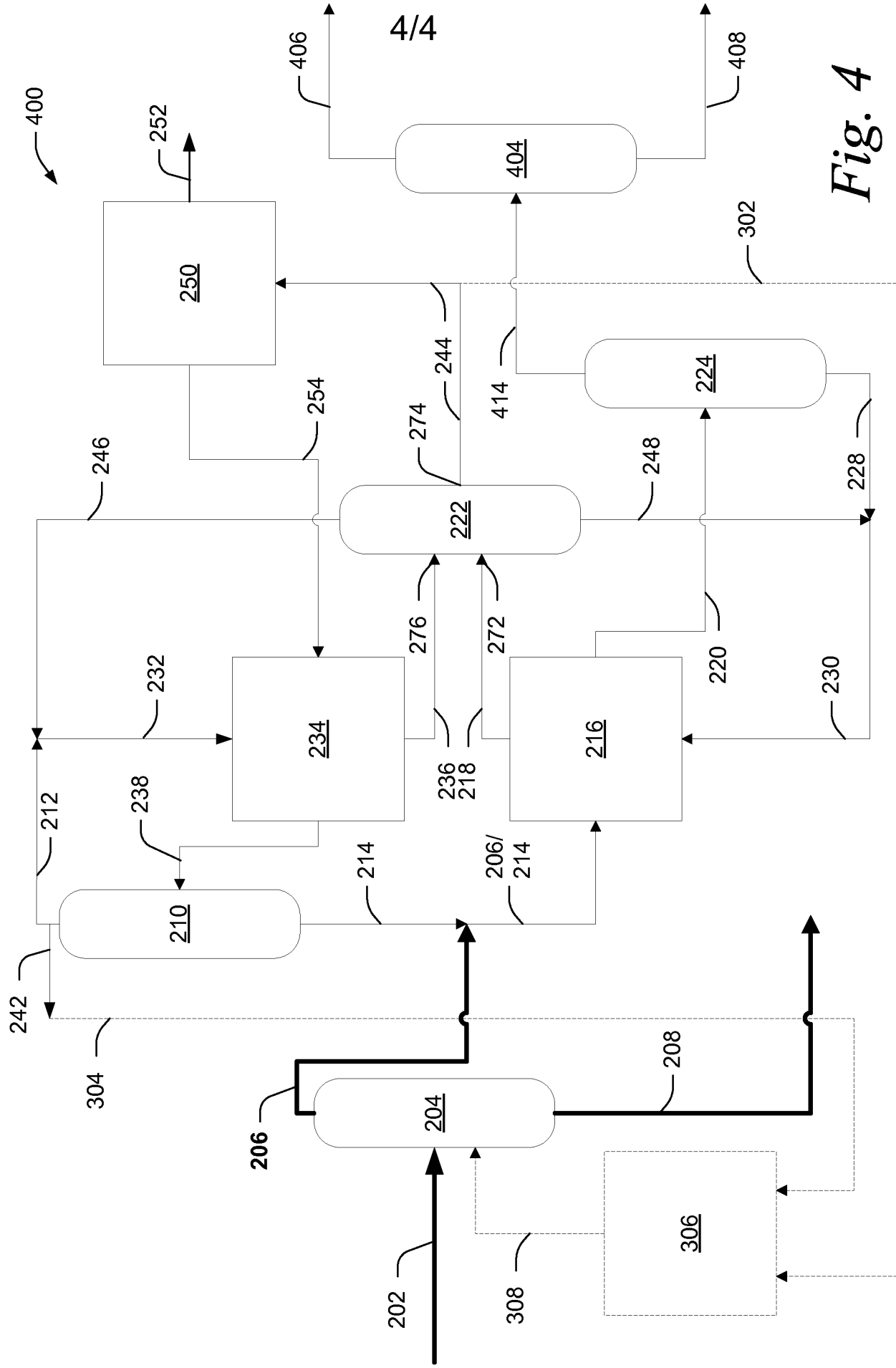


Fig. 4

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2012/056027

A. CLASSIFICATION OF SUBJECT MATTER		<i>C07C 15/08 (2006.01)</i> <i>C07C 5/22 (2006.01)</i> <i>C07C 7/12 (2006.01)</i> <i>C07C 7/08 (2006.01)</i> <i>C07C 7/04 (2006.01)</i> <i>CIOG 25/00 (2006.01)</i> <i>BOW 15/00 (2006.01)</i> <i>BOLD 3/00 (2006.01)</i> <i>B01D 11/04 (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 15/08, 5/22, 7/12, 7/08, 7/04, CIOG 25/00, B01D 15/00, 3/00, 11/04																						
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched																						
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)																						
USPTO, DEPATIS, RZH "KHIMIYA", EAPO, PatSearch																						
C. DOCUMENTS CONSIDERED TO BE RELEVANT																						
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.																				
X Y	US 5763714 A (CATALYTIC DISTILLATION TECHNOLOGIES) 09.06. 1998, fig. 1, col. 5, line 45 - col. 6, line 21	1, 6 3, 7-10																				
X Y	US 5 177295 A (UOP) 05.01 .1993, fig. 1, col. 5, line 7 - col. 6, line 67	1-4, 6 3, 5, 7-10																				
X Y	US 6369287 B1 (INSTITUT FRANCAIS DU PETROLE) 09.04.2002, fig. 1, col. 2, line 57 - col. 4 line 8 and col. 5, line 10 - col. 6, line 3	6 5, 10																				
☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.																						
* Special categories of cited documents: <table border="0"> <tr> <td>"A"</td> <td>document defining the general state of the art which is not considered to be of particular relevance</td> <td>"T"</td> <td>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</td> </tr> <tr> <td>"E"</td> <td>earlier document but published on or after the international filing date</td> <td>"X"</td> <td>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</td> </tr> <tr> <td>"L"</td> <td>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)</td> <td>"Y"</td> <td>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</td> </tr> <tr> <td>"O"</td> <td>document referring to an oral disclosure, use, exhibition or other means</td> <td>"&"</td> <td>document member of the same patent family</td> </tr> <tr> <td>"P"</td> <td>document published prior to the international filing date but later than the priority date claimed</td> <td></td> <td></td> </tr> </table>			"A"	document defining the general state of the art which is not considered to be of particular relevance	"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	"E"	earlier document but published on or after the international filing date	"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	"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)	"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	"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family	"P"	document published prior to the international filing date but later than the priority date claimed		
"A"	document defining the general state of the art which is not considered to be of particular relevance	"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																			
"E"	earlier document but published on or after the international filing date	"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																			
"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)	"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																			
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family																			
"P"	document published prior to the international filing date but later than the priority date claimed																					
Date of the actual completion of the international search		Date of mailing of the international search report																				
12 December 2012 (12. 12.20 12)		07 February 2013 (07.02.2013)																				
Name and mailing address of the ISA/ FPS Russia, 123995, Moscow, G-59, GSP-5, Berezhkovskaya nab., 30-1		Authorized officer I. Zaikina																				
Facsimile No. +7 (499) 243-33-37		Telephone No. (495)53 1-64-8 1																				