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(54) **Title:** SEPARATION MEMBRANE

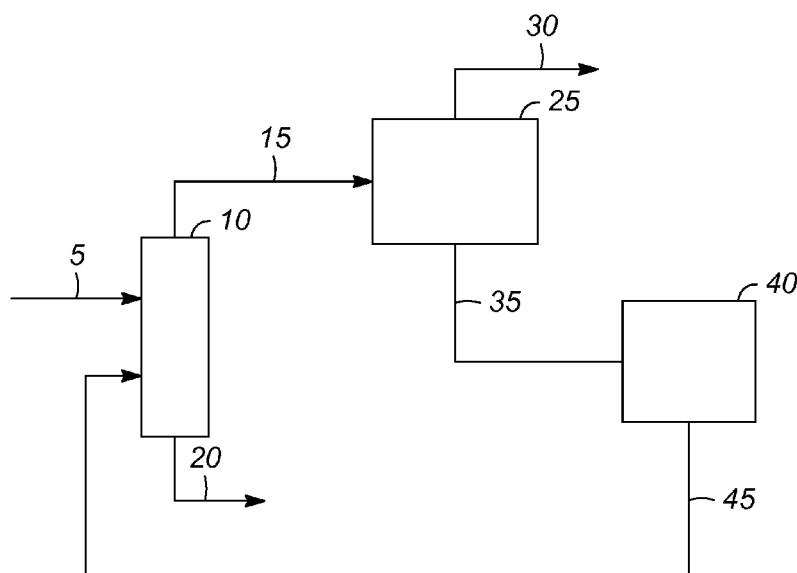


FIG. 1

(57) **Abstract:** A separation membrane is described. The separation membrane comprises a porous inorganic membrane, the pores of the inorganic membrane being coated with a polybenzoxazole polymer coating. Methods of making the separation membrane and methods of separating xylenes using the separation membrane are also described.

SEPARATION MEMBRANE

STATEMENT OF PRIORITY

This application claims priority to U.S. Application No. 13/645,782 which was
5 filed on October 5, 2012.

FIELD OF THE INVENTION

The present invention relates generally to separation membranes and more
particularly to high temperature stable membranes, methods of making high temperature
10 stable membranes, and methods of using high temperature stable membranes.

BACKGROUND OF THE INVENTION

When xylenes are subjected to isomerization, they form mixtures of para-
xylene, ortho-xylene and meta-xylene. At the temperatures at which xylene isomerization is
15 typically conducted, para-xylene forms 24% of the equilibrium mixture, ortho-xylene 23%,
and meta-xylene 53%. The C8 aromatic ethylbenzene is usually also present in a mixture of
xylenes. Although each of these products has commercial value, the highest demand is for
the para-xylene isomer.

Commercial processes for recovering para-xylene involve the selective
20 removal of para-xylene by selective crystallization or sorption. One embodiment of a
combined xylene separation process is illustrated in Fig. 1. The feed 5, having previously
been stripped of all materials lighter than C8 aromatics, enters the C8 distillation column 10
and is separated into a stream 15 of C8 hydrocarbons and a stream 20 of C9+ hydrocarbons.
The stream 15 of C8 hydrocarbons is sent to a sorption or crystallization zone 25 where it is
25 separated into a stream 30 of highly pure para-xylene and a stream 35 containing ortho-
xylene, meta-xylene, and ethyl benzene. Stream 35 is sent to an isomerization zone 40 where
the xylenes are isomerized to an equilibrium xylene mixture, and some portion of any
ethylbenzene present is either dealkylated (to benzene and ethylene) or converted to a xylene.
Stream 45 which is a mixture of equilibrium xylenes and unconverted ethylbenzene is then
30 recycled to the C8 distillation column 10.

The recycle loop typically contains separation operations (not shown)
downstream of the isomerization zone, including, but not limited to, one or more of a toluene
splitter to remove toluene and lighter hydrocarbons from the xylenes, and a xylene splitter to
remove a portion of the o-xylene and heavier hydrocarbons from the C8 hydrocarbons as a

separate product. In most commercial processes, other components are present in the recycle loop, such as saturates that boil in the C8 aromatic range or other components formed in the isomerization zone, such as hydrocarbons lighter than C8, hydrocarbons heavier than C8, and naphthenes.

5 It would be desirable to improve the separation of xylene isomers.

SUMMARY OF THE INVENTION

One aspect of the invention is a separation membrane. In one embodiment, the separation membrane comprises a porous inorganic membrane, the pores of the inorganic
10 membrane being coated with a polybenzoxazole polymer coating.

Another aspect of the invention is a method of making a separation membrane. In one embodiment, the method comprises dissolving a polybenzoxazole precursor in a solvent to form a solution. A porous inorganic membrane is coated with the solution. The coated porous membrane is heated to form a polybenzoxazole polymer coated porous
15 membrane.

Another aspect of the invention is a method of separating xylenes. In one embodiment, the method comprises contacting a vapor or liquid stream comprising para-xylene, and at least one of ortho-xylene, meta-xylene, and ethylbenzene with a porous inorganic membrane, the pores of the inorganic membrane being coated with a
20 polybenzoxazole polymer coating, forming a membrane permeate stream enriched in para-xylene, ethylbenzene, or both, and a membrane retentate stream enriched in ortho-xylene, meta-xylene, or both.

BRIEF DESCRIPTION OF THE DRAWINGS

25 Fig. 1 is an illustration of a separation process including a crystallization or sorption zone and an isomerization zone.

Fig. 2 is an illustration of one embodiment of a process using the porous inorganic membrane modified with a polybenzoxazole polymer.

Fig. 3 is an illustration of another embodiment of a process using the porous
30 inorganic membrane modified with a polybenzoxazole polymer.

Fig. 4 is an illustration of still another embodiment of a process using the porous inorganic membrane modified with a polybenzoxazole polymer.

DETAILED DESCRIPTION OF THE INVENTION

The high temperature stable membranes can be used for xylene separation in xylene isomerization processes, and combined isomerization and crystallization or adsorptive separation processes. The high temperature stable membrane may be used in processing effluents from processes producing C8 aromatics including toluene disproportionation units, reforming units, C6 to C9 transalkylation units, and steam cracking units. The membranes are stable up to an operating temperature of 500°C, are insoluble in organic solvents, and have a high flux (or permeance) for xylene separation.

The high temperature stable membrane is a porous inorganic membrane modified with a polybenzoxazole (PBO) polymer. The porous inorganic membrane incorporates a layer of PBO polymer on the inside wall of the pores of the separation surface. The PBO polymer enhances the membrane's selectivity compared to the unmodified porous inorganic membrane.

The inorganic membrane can be made of any suitable porous inorganic material, including, but not limited to, silica, metals such as stainless steel, alumina (including α -alumina, γ -alumina, and transition alumina), ceramics, molecular sieves, or combinations thereof. The selection of the material will depend on the conditions of the separation as well as the type of porous structure formed. The porous inorganic membranes can have different geometries, including, but not limited to, disks, tubes, hollow fiber, and the like.

The pore size is generally less than 1000 nm, or less than 500 nm, or less than 400 nm, or less than 300 nm, or less than 200 nm, or less than 100 nm, or less than 50 nm, or in a range of 0.5 nm to 50 nm.

The PBO polymer can be derived from PBO precursors including, but not limited to, poly(hydroxyl imide), poly(hydroxyl amic acid), poly(hydroxyl amide), or mixtures thereof. The PBO precursors are soluble in solvents. Suitable solvents include, but are not limited to, organic solvents. Suitable organic solvents include, but are not limited to, 1-methyl-2-pyrrolidone, *N,N*-dimethylacetamide, *N,N*-dimethylformamide, 1,3-dioxolane, dichloromethane, or combinations thereof.

The porous inorganic membrane modified with a polybenzoxazole (PBO) polymer can be made using the following process. The porous inorganic membrane is cleaned and dried. One surface of the porous inorganic membrane is immersed in a PBO precursor solution for 30 seconds to 5 minutes. The excess solution on the surface of the porous inorganic membrane can be removed, and the surface carefully cleaned. The porous

inorganic membrane with the PBO precursor can be dried at room temperature under vacuum, followed by drying at 100-300°C under vacuum. The porous inorganic membrane can then be heated to 350°C to 500°C, or 400°C to 450°C for 5 minutes to 2 hours to convert the PBO precursor polymer inside the pores of the porous inorganic membrane to form the high temperature stable PBO polymer.

The porous inorganic membrane modified with PBO can be used to enrich at least a portion of the recycle stream from an isomerization zone. The enriched stream, when combined with the remaining feed to a sorption or crystallization zone, will improve the efficiency of the selective sorption or crystallization zone because the feed will contain a higher concentration of para-xylene. Advantageously, the porous inorganic membrane modified with PBO can separate para-xylene and ethyl benzene from ortho-xylene and meta-xylene. The membrane permeate is enriched in para-xylene and ethyl benzene, and the residue or retentate is enriched in ortho-xylene and meta-xylene. By “enriched in para-xylene” it is meant that greater than 50 wt%, or greater than 60 wt%, or greater than 70 wt%, or greater than 80 wt%, or greater than 90 wt%, or greater than 95 wt% of the para-xylene present in the stream entering the porous inorganic membrane modified with PBO is recovered in the permeate stream. By “enriched in ortho-xylene and meta-xylene,” it is meant that greater than 50 wt%, or greater than 60 wt%, or greater than 70 wt%, or greater than 80 wt%, or greater than 90 wt%, or greater than 95 wt% of the ortho-xylene and meta-xylene present in the stream entering the porous inorganic membrane modified with PBO is recovered in the retentate stream.

The membrane has high permeate flux. The selectivity for para-xylene and ethyl benzene over ortho-xylene and meta-xylene can be relatively low, while still providing a substantial process benefit because any material which can be sent back to the isomerization zone without going through the fractionation and separations zones reduces the capital and energy costs.

Although the entire xylene recycle stream can be subjected to the membrane separation, only a portion of the stream can be sent, if desired. In some embodiments, only 10 to 50 percent by volume of the stream (preferably an aliquot portion) is sent to the membrane, with the remainder going to a xylene column for recycle to the selective para-xylene removal unit operation. The membrane separation is operated to recover at least 50 wt%, at least 60 wt%, at least 70 wt%, or at least 75 wt%, or at least 80 wt%, or at least 85 wt%, or at least 90 wt%, or at least 95 wt% of the para-xylene in the slip stream. Thus, the increase in the feed to the isomerization zone, as well as the downstream unit operations

such as strippers and deheptanizers, as a result of the retentate being combined with the effluent from the para-xylene recovery unit operation is minimized.

In one embodiment, the porous inorganic membrane modified with PBO can be used in a combined isomerization and sorption or crystallization process, as illustrated in Fig. 2. A feed stream 105 enters the C8 distillation column 110 where it is separated into a stream 115 of C8 hydrocarbons and a stream 120 of C9+ hydrocarbons. Stream 120 can be further processed, if desired. The stream 115 of C8 hydrocarbons is sent to the membrane separation zone 130. In the membrane separation zone 130, stream 115 is separated by the porous inorganic membrane modified with PBO into permeate stream 135 enriched in para-xylene and ethyl benzene, and retentate stream 140 enriched in ortho-xylene and meta-xylene. .

In a typical process, the permeate stream 135 contains 97 wt% of the para-xylene (97 wt% recovery) from stream 115, and 95 wt% of the ethyl benzene (95 wt% recovery) from stream 115. Retentate stream 140 contains 94 wt% of the ortho-xylene and 94 wt% of the meta-xylene from stream 115.

Para-xylene enriched stream 135 can then be sent to a sorption or crystallization zone 145 where it is separated into stream 150, which is highly pure para-xylene (e.g., 99.7%), and stream 155, which contains ethyl benzene and some ortho- and meta-xylene.

Stream 155 is sent to isomerization zone 160 where it is isomerized to produce an equilibrium mixture of xylene isomers. Some conversion of ethylbenzene either to benzene and ethylene or to xylene is also accomplished in the isomerization zone. Retentate stream 140 can also be sent to the isomerization zone, if desired. Stream 165, which is an equilibrium mixture of xylene isomers and unconverted ethylbenzene, can be recycled back to the C8 distillation column 110.

Because of the separation that takes place in the membrane separation zone 130, the sorption or crystallization zone 145 can be smaller than the sorption or crystallization zone 25 in the process shown in Fig. 1.

Fig. 3 illustrates another embodiment of a process incorporating the porous inorganic membrane modified with PBO. The feed 205 enters C8 distillation column 210 where it is separated into a stream 215 of C8 hydrocarbons and a stream 220 of C9+ hydrocarbons. The stream 215 of C8 hydrocarbons is sent to the sorption or crystallization zone 225 where it is separated into a highly pure para-xylene product stream 230 and stream 235 containing ortho-xylene, meta-xylene, and ethyl benzene. Stream 235 is sent to an

isomerization zone 240 where it is isomerized to produce a stream 245 of a mixture of xylenes. Stream 245 is sent to the membrane separation zone 250. In the membrane separation zone 250, stream 245 is separated by the porous inorganic membrane modified with PBO into permeate stream 260 and retentate stream 255. Retentate stream 255, which is enriched in m-xylene and o-xylene, is recycled to the isomerization zone 240. Permeate stream 260, which is enriched in p-xylene and ethylbenzene, is recycled to the C8 distillation column 210. In some embodiments, stream 260 may be sent directly to sorption or crystallization zone 225. In some embodiments, a slip stream from stream 255 may be sent to C8 distillation column 210 to prevent the build up of heavy components in the isomerization zone. Stream 255 returns m-xylene and o-xylene directly back to the isomerization zone without needing to pass through the C8 distillation column or the selective p-xylene extraction zone. As a result, these units can be smaller than the sorption or crystallization zone 25 in the process shown in Fig. 1.

In the embodiment illustrated in Fig. 4, the feed 305 is sent to C8 distillation column 310 where it is separated into C8 stream 315 and C9+ stream 320. Stream 315 is sent to the sorption or crystallization zone 325 and separated into the highly pure para-xylene stream 330 and stream 335 containing ortho-xylene, meta-xylene, and ethyl benzene. Stream 335 is sent to a membrane reactor 340 in which the porous inorganic membrane coated with PBO forms a shell around the catalyst performing the isomerization. The PBO coated membrane is preferentially permeable to para-xylene and ethylbenzene. As the para-xylene and ethylbenzene are preferentially removed from the active area of the catalyst, the meta-xylene and ortho-xylene concentrations rise, allowing continued conversion of the meta-xylene and ortho-xylene to para-xylene. This higher conversion per pass of meta-xylene and ortho-xylene to para-xylene in the equilibrium limited xylene isomerization reaction reduces the recycle stream, allowing the C8 fractionation column 310 and sorption or crystallization zone 325 to be smaller than the analogous units in Fig. 1. Permeate stream 345 from the membrane reactor 340 is recycled to the C8 distillation column 310. In some embodiments, permeate stream 345 may be sent directly to sorption or crystallization zone 325. In some embodiments, a slip stream from the membrane reactor 340 may be sent to C8 distillation column 310 to prevent the build up of heavy components in the membrane reactor.

Example:

A porous ceramic membrane disk having a diameter of 39.0 mm, a thickness of 2.0 mm, and 180 nm pores (available from ECO Ceramics BV) was used.

The porous ceramic membrane disk was cleaned by rinsing with 2-propanol and water to remove surface impurities and dried at 110°C for 24 hours in a vacuum oven. One surface of the porous ceramic membrane was immersed in a PBO precursor solution for 30 seconds. One PBO precursor solution was a solution of poly(hydroxyl imide) in 1-methyl-2-pyrrolidone, and another was poly(hydroxyl amic acid) in 1-methyl-2-pyrrolidone,. The excess solution on the surface of the ceramic membrane was removed, and the surface was carefully cleaned. The ceramic membrane with the PBO precursor was dried at room temperature under vacuum, followed by drying at 200°C under vacuum. The membrane was then heated to 400°C for 30 minutes to convert the PBO precursor polymer inside the pores of the ceramic membrane to form the high temperature stable PBO polymer.

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

WHAT IS CLAIMED:

1. A separation membrane comprising:
a porous inorganic membrane, the pores of the inorganic membrane being coated with a polybenzoxazole polymer coating.

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2. A method of making a separation membrane comprising:
dissolving a polybenzoxazole precursor in a solvent to form a solution;
coating a porous inorganic membrane with the solution; and
heating the coated porous membrane to form a polybenzoxazole polymer coated
porous inorganic membrane.

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3. The method of claim 2, wherein the polybenzoxazole precursor comprises poly(hydroxyl imide), poly(hydroxyl amic acid), poly(hydroxyl amide), or mixtures thereof.

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4. The method of any of claims 2-3, wherein the solvent is an organic solvent.

5. The method of claims 2-4, wherein the solvent is 1-methyl-2-pyrrolidone, *N,N*-dimethylacetamide, *N,N*-dimethylformamide, 1,3-dioxolane, dichloromethane, or combinations thereof.

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6. The method of any of claims 2-5, wherein the coated porous membrane is heated to a temperature in a range of 350°C to 500°C.

7. A method of separating xylenes comprising:
contacting a vapor or liquid stream comprising para-xylene, and at least one of ortho-xylene, meta-xylene, and ethyl benzene 115 with a porous inorganic membrane, the pores of the inorganic membrane being coated with a polybenzoxazole polymer coating, forming a membrane permeate stream 135 enriched in para-xylene, ethylbenzene, or both and a membrane retentate stream 140 enriched in ortho-xylene, meta-xylene, or both.

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8. The method of claim 7, wherein the stream comprising para-xylene and at least one of ortho-xylene, meta-xylene, and ethyl benzene 115 is an overhead stream from a C8 distillation column 110, and wherein the permeate stream 135 is introduced into a xylene adsorptive separation zone 145.

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9. The method of claim 7, wherein the stream comprising para-xylene and at least one of ortho-xylene, meta-xylene, and ethylbenzene 245 is an effluent stream from an isomerization zone and wherein the permeate stream 260 is introduced into a C8 distillation zone.

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10. The method of claim 7, wherein the stream comprising para-xylene and at least one of ortho-xylene, meta-xylene, and ethylbenzene 115 is an overhead stream from a C8 distillation column 110, and wherein the permeate stream 135 is introduced into a para-xylene selective crystallization separation zone 145.

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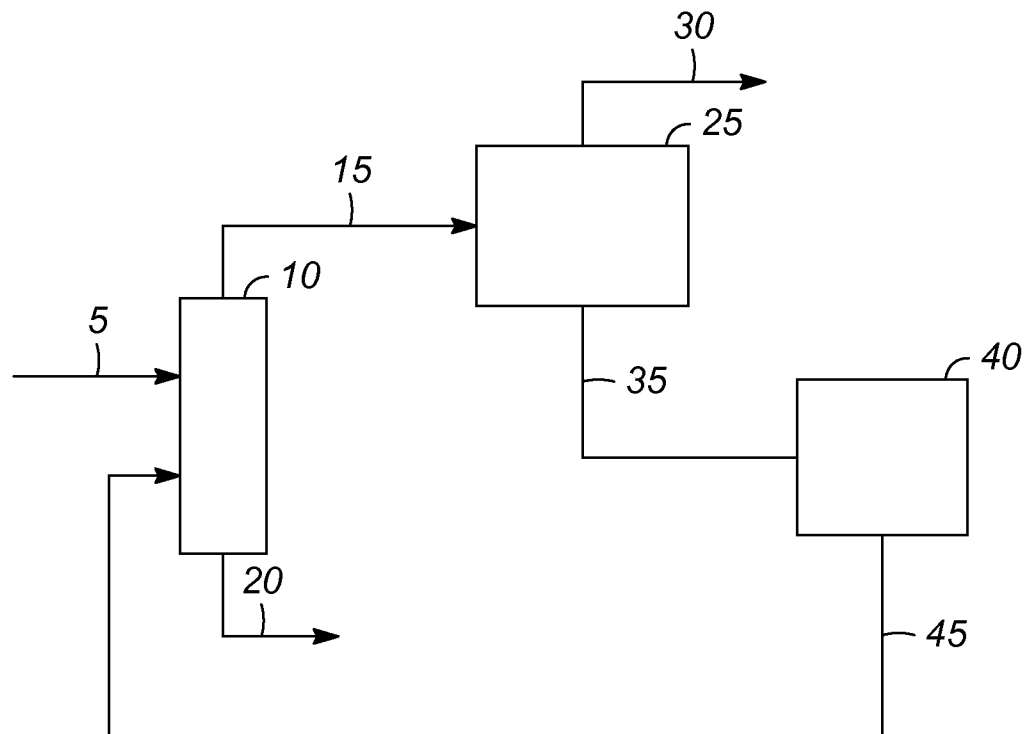


FIG. 1

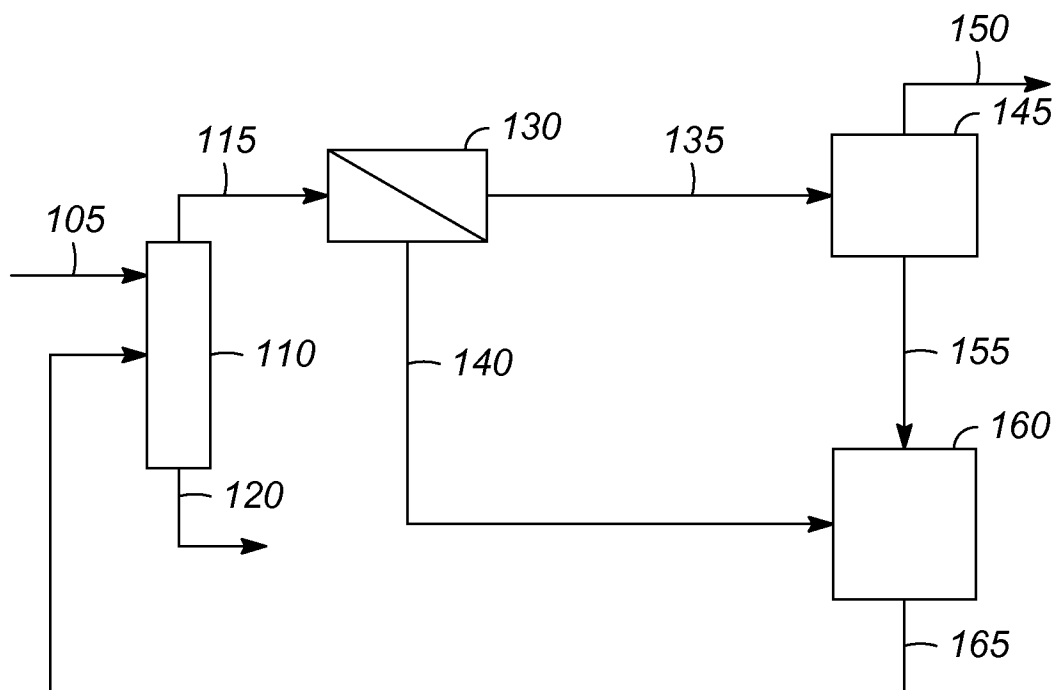


FIG. 2

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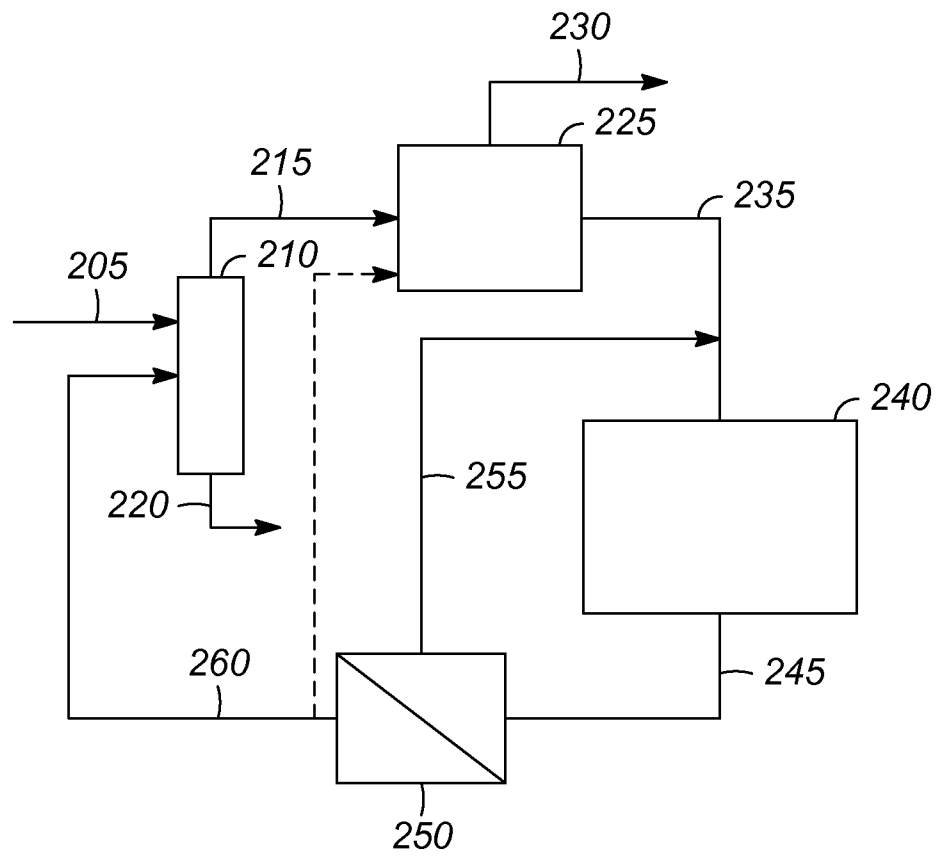


FIG. 3

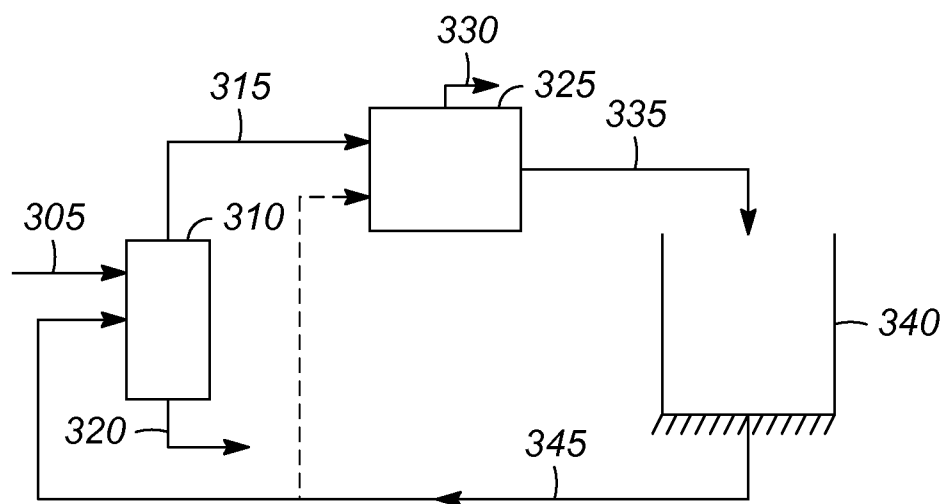


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2013/060509

A. CLASSIFICATION OF SUBJECT MATTER

B01D 53/14 (2006.01)**B01D 67/00** (2006.01)**B01D 71/56** (2006.01)

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)

B01D 53/00, 53/14, 53/52, 53/62, 53/74, 53/85, 63/00, 71/00, 71/06, 71/40, 71/56, 71/58, 71/60, 57/00

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

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

PatSearch (RUPTO internal), USPTO, PAJ, Esp@cenet, DWPI, EAPATIS, PATENTSCOPE, Information Retrieval System of FIPS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/0240763 A1 (UOP LLC) 27.09.2012, [0017], [0015], [0022]	1
Y		7-10
Y	US 2010/0311565 A1 (UOP LLC) 09.12.2010, [0013], claims	2
Y	WO 2011/163293 A2 (UOP LLC et al.) 29.12.2011, [0013], [0025], [0011]	2-4
Y	RU 2184106 C2 (EXXON CHEMICAL PATENTS, INC.) 27.06.2002, claim 1, p. 5, lines 43-53, p. 6, lines 1-2, 19-21, p. 8, lines 29-33, p. 20, lines 34-53, p. 21, lines 1-13, 30-51	7-10



Further documents are listed in the continuation of Box C.



See patent family annex.

*	Special categories of cited documents:	"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
"A"	document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier document but published on or after the international filing date	"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
"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)	"&"	document member of the same patent family
"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		

Date of the actual completion of the international search

10 December 2013 (10.12.2013)

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2013/060509

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.:
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:
(see extra sheet)
3. ☒ Claims Nos.: 5-6
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 additional 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 additional fees, this Authority did not invite payment of 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.