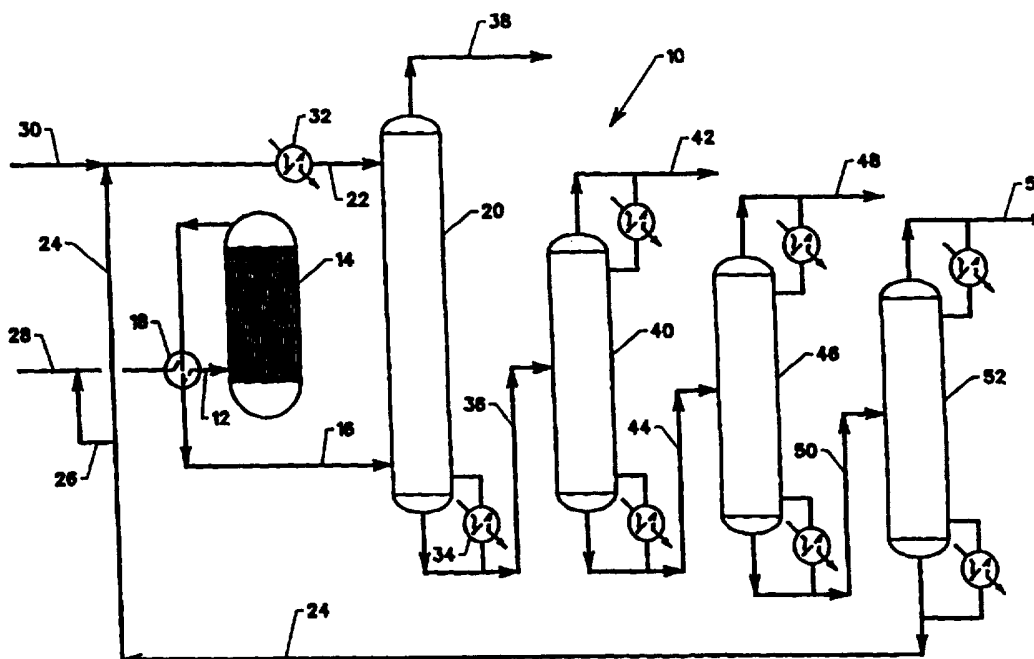




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(54) Title: PROCESS FOR EXTRACTION AND RECOVERY OF ANHYDROUS HYDROGEN CHLORIDE FROM MIXTURES WITH NON-CONDENSABLE GASES



(57) Abstract

A process is described for the recovery of hydrogen chloride in anhydrous form (42) from a dry mixture of one or more non-condensable gases, hydrogen chloride and heavier components which may be present (16), which process comprises using a halogenated hydrocarbon solvent (22), and especially a chlorinated hydrocarbon solvent, to preferentially absorb hydrogen chloride and heavier materials from the dry mixture, with the non-condensable gases contained in the mixture being carried through as a gas stream (38) and the rich solvent stream (36) being processed to separate out and recover the hydrogen chloride therein in anhydrous form.

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PROCESS FOR EXTRACTION AND RECOVERY OF ANHYDROUS HYDROGEN CHLORIDE FROM MIXTURES WITH NON-CONDENSABLE GASES

The present invention relates to processes for separating out and recovering
5 hydrogen chloride from mixtures including non-condensable gases such as hydrogen. More particularly, the present invention relates to processes which are able to recover hydrogen chloride from such mixtures in a desirable anhydrous form.

A number of processes are described in the art for converting a chlorinated hydrocarbon feedstock to a less-chlorinated hydrocarbon and hydrogen chloride, by reaction
10 of the chlorinated hydrocarbon feedstock with hydrogen over a selected catalyst.

Exemplary of these processes are those described in EP 015665 (converting 1,1,2-trichloroethane to ethylene or vinyl chloride), GB 1 400 529 (converting "hydrocarbon chlorides" to "chlorine-free hydrocarbons"), DD 235 630 A1 (converting 1,2-dichloropropane to propylene), United States Patents No. 4,899,001 and 4,929,781 (the hydrogenation of
15 halogenated hydrocarbons), CA 1 119 203 (converting perchloroethylene to trichloroethylene), DE 3 804 265 A1 (same) and United States Patent No. 5,091,603 (same).

Commonly-assigned United States Patent Application Ser. No. 08/112,042, now substantially published as WO 94/07828, is also relevant in describing a process for converting 1,2-dichloropropane (a significant co-product of the chlorohydrin process for making
20 propylene oxide from propylene) to propylene and hydrogen chloride.

Each of these processes produces a product stream from the reactor section thereof which contains the desired less-chlorinated hydrocarbon product(s), hydrogen chloride and unreacted hydrogen in some amount, generally along with some unconverted chlorinated hydrocarbon feedstock and some less-chlorinated hydrocarbonaceous byproducts.

25 Certain processes have been made known for separating the hydrogen chloride and heavier materials from the non-condensable unreacted hydrogen and other non-condensable gases which may conceivably be present in smaller amounts in the product streams from these processes, for example, methane, carbon monoxide and nitrogen.

For example, United States Patents No. 5,314,614 and 5,316,663 describe related
30 processes wherein the effluent from a hydrogenation reaction zone is introduced into a "vapor-liquid separator" at essentially the same pressure as employed in the hydrogenation reaction zone (that is, atmospheric to 2000 psig (13.8 MPa, gauge), and especially 100 psig (0.7 MPa, gauge) to 1800 psig (12.4 MPa, gauge)) and at temperatures ranging from -57 degrees Celsius to 16 degrees Celsius in the case of the '614 patent (as compared to reaction
35 temperatures of from 10 degrees Celsius to 450 degrees Celsius), or from -57 degrees Celsius to 4.4 degrees Celsius in the '663 patent (reaction temperatures of 50 degrees Celsius to 454 degrees Celsius).

In the '614 patent, a hydrogen-rich gaseous recycle stream is produced for recycle to the hydrogenation reaction zone which also contains hydrogen halide, the amount of hydrogen halide being controlled by a selection of pressure and temperature in the vapor-liquid separator to minimize the decomposition or undesirable polymerization of thermally unstable compounds in the feedstock to the hydrogenation reaction zone. In the '663 patent, the feedstock is not expressly described as necessarily containing the thermally unstable compounds of the '614 patent, and the vapor-liquid separator is said simply to produce a hydrogen-rich gaseous recycle stream.

In both patents, the liquid hydrocarbonaceous stream from the vapor-liquid separator is then described as being separated, for example by stripping, flashing or fractionating, to produce an anhydrous hydrogen halide stream and a liquid hydrocarbonaceous stream, the liquid hydrocarbonaceous stream then being separated to produce a hydrogenated hydrocarbonaceous product stream containing a reduced level of halogen and a stream primarily comprised of halogenated organic compounds for possible recycle to the hydrogenation reaction zone.

The only example provided to demonstrate the separation capabilities of the described processes under the prescribed conditions of pressure and temperature in the vapor-liquid separator is found in the Example in the '663 patent, wherein the effluent from a hydrogenation reaction zone operating at 80 degrees Celsius and a pressure of 5171 kPa gauge (or 750 psig) was cooled to a temperature of about -15 degrees Celsius and introduced into the vapor-liquid separator. The hydrogen-rich gaseous recycle stream from the separator was comprised of about 2000 mols/hr of hydrogen, 850 mols/hr of hydrogen chloride and 70 mols/hr of chlorinated hydrocarbons, whereas the liquid hydrocarbonaceous stream (from which anhydrous hydrogen chloride was subsequently recovered as a product stream) contained a total of 140 mols/hr of non-chlorinated hydrocarbon (in this case propane, at 50 mols/hr), hydrogen chloride (60 mols/hr) and chlorinated hydrocarbons (25 mols/hr). Consequently, more than 93 percent of the hydrogen chloride in the effluent was not recovered in the vapor-liquid separator as anhydrous hydrogen chloride.

Other conventional approaches to separating hydrogen and other non-condensable gases from hydrogen chloride and heavier materials in the effluent from a catalytic process for the conversion of a chlorinated hydrocarbon feedstock to a desired less-chlorinated hydrocarbon and hydrogen chloride have included absorption in water or in an HCl-lean scrubbing solution, or neutralization of the hydrogen chloride followed by a vapor-liquid separation, see, for example, United States Patents No. 4,899,001 and 4,929,781. These approaches are limited at best to the production of concentrated hydrochloric acid, and consequently may implicate certain, expensive materials of construction as well as the other particular concerns and considerations associated with the manufacture of concentrated hydrochloric acid.

In the very broadest sense, the present invention concerns a process for the recovery of hydrogen chloride in anhydrous form from a dry (that is, containing 500 parts per million or less by weight of water) mixture of one or more non-condensable gases, hydrogen chloride and any heavier components (that is, heavier than hydrogen chloride) which may be present, which process comprises using a halogenated hydrocarbon solvent, and especially a chlorinated hydrocarbon solvent, to preferentially absorb hydrogen chloride and any heavier materials which may be present from the dry mixture, with the non-condensable gases contained in the mixture being carried through as a gas stream, such gas stream generally being vented or burned thereafter. The rich solvent stream from the absorber, containing the solvent, substantially all of the hydrogen chloride (that is, at least 95 percent by weight, and most preferably 99.9 percent or greater by weight) and the heavier materials from the dry mixture, is then conventionally distilled to recover at least anhydrous hydrogen chloride and halogenated hydrocarbon solvent for recycle to the absorber. Any desirable heavier materials are conventionally separated out as well, again for example by conventional distillation. The term "anhydrous", when used to denote the hydrogen chloride-containing product stream thus separated out and recovered, is to be understood as referring to a water content of 50 parts per million or less by weight.

In the context of a preferred application or use, hydrogen chloride in a product stream (dry, that is, containing less than 500 parts per million of water or water precursors, for example oxygenated compounds which when subjected to process conditions, may be converted in part to water in the presence of certain of the contemplated catalysts) from reacting a chlorinated hydrocarbon feedstock and hydrogen over a selected catalyst to produce a desired less-chlorinated hydrocarbon or hydrocarbons and said hydrogen chloride, may be separated from non-condensable gases in such product stream and recovered in anhydrous form but without the need for an expensive cryogenic (that is, at temperatures of from -150 degrees Celsius to -50 degrees Celsius) separation of the hydrogen chloride and the non-condensable gases.

Fundamentally, and in keeping with the above, more general summary of the present process, the preferred application involves using a chlorinated hydrocarbon solvent to preferentially absorb hydrogen chloride and heavier materials in the product stream (including the desired less-chlorinated hydrocarbon product(s), and typically including preferably lesser amounts of unconverted chlorinated hydrocarbon feedstock and some less-chlorinated byproducts), with the unreacted hydrogen and any other non-condensable gases contained in the product stream being carried through as a gas stream to be recycled, vented or burned. Subsequent to the absorption step, the hydrogen chloride is recovered in anhydrous form as the overhead stream from a conventional distillation of the rich solvent stream, and the desired less-chlorinated material is recovered in the desired purity as, for example, by a further

distillation. The unconverted chlorinated hydrocarbon feedstock resulting from this further distillation is generally conveniently recycled to the reactor(s) of the process.

Figure 1 illustrates one embodiment of an overall process employing the separation process of the present invention, in a particularly preferred context.

5 Figure 2 illustrates an alternate embodiment of the same overall process shown in Figure 1, again illustrating an application of the separation process of the present invention in a particularly preferred context.

 A particularly preferred use of the present invention is shown in Figures 1 and 2, in alternate embodiments of processes for reacting chlorinated hydrocarbon feedstocks with
10 hydrogen to produce less-chlorinated hydrocarbon materials and hydrogen chloride. For convenience and ease of understanding, conventional details and elements of the illustrated embodiments have largely been omitted, and for example, a single reactor is illustrated in both embodiments as being employed when more than one reactor may be employed in series or in parallel according to conventional practice in the processing of certain chlorinated
15 hydrocarbon-containing feedstocks, see, for example, United States Patent No. 4,895,995 to James Jr. et al. and the aforementioned United States Patent No. 4,899,001 to Kalnes et al.

 Those skilled in the art will additionally readily appreciate that numerous arrangements and variations of apparatus are conventionally possible for generating a dry product stream containing hydrogen chloride and one or more non-condensable gases from a
20 given chlorinated hydrocarbon-containing feedstock, from which anhydrous hydrogen chloride may be recovered in keeping with the process of the present invention. Illustrative of the arrangements and variations of apparatus which may conceivably be combined through the exercise of routine skill with the separation process of the present invention are those described in a number of United States Patents assigned to UOP Inc., for example, United States
25 Patents No. 4,747,937, 4,818,368, 4,840,721, 4,882,037, 4,895,995, 4,923,590, 4,927,520 and 5,013,424.

 Referring now to Figure 1, however, an overall process 10 is illustrated wherein a combined feed 12 comprising 1,2-dichloropropane (hereafter, PDC) and hydrogen is fed to a reactor 14 and in the presence of a catalyst is converted to reaction products including
30 propylene and hydrogen chloride, and most particularly is so reacted in the presence of a carbon-supported, platinum/copper catalyst according to a process described in greater detail in the aforementioned United States Patent Application Serial No. 08/112,042.

 A dry gaseous product stream 16 containing hydrogen, hydrogen chloride, propylene, unreacted PDC, less-chlorinated hydrocarbonaceous byproducts such as 2-
35 chloropropane and other inert, non-condensable gases like methane emerges from the reactor 14 and is preferably cross-exchanged with the combined feed 12 in an exchanger 18 to recover a portion of the heat in the product stream 16 to combined feed 12. The product stream 16 is then fed to the bottom of a packed absorption column 20, with a chlorinated hydrocarbon

solvent stream 22 being fed to the top of the column 20 to flow countercurrently with respect to the gaseous product stream 16. The chlorinated hydrocarbon solvent in solvent stream 22 can in principle be any mono-, di- or trichlorinated hydrocarbon (e.g., 1,2-dichloroethane or EDC) or can be a mixture of these, but in the context of the process of the '042 application is most conveniently simply PDC from a PDC recycle stream 24 (a separate portion 26 of which is recycled to form the combined feed 12 with a separate hydrogen/PDC source stream 28) supplemented as needed via a fresh PDC solvent stream 30 and cooled via exchanger 32. The absorption column 20 may operate with a reboiler 34 if desired to remove small amounts of non-condensables which would otherwise remain in the bottoms stream 36 carrying the hydrogen chloride and heavier materials like unreacted PDC and propylene.

The absorption column 20 will preferably be designed to effectuate as complete a separation as possible of the hydrogen chloride on the one hand and the hydrogen and other non-condensables in the product stream 16 on the other. Exemplary operating conditions will be such that PDC is fed to the column 20 in solvent stream 22 in a mass ratio of from 20 to 50 parts of PDC per part of hydrogen in the product stream 16 to the absorption column 20, the hydrogen to hydrogen chloride molar feed ratio in the product stream 16 from reactor 14 is from 0.5:1 to 10:1, the pressure in column 20 is from 1.0 to 1.3 MPa (absolute) and the PDC in solvent stream 22 is at a temperature of from -10 degrees Celsius to 20 degrees Celsius. Most preferably the column 20 will be operated at a PDC to hydrogen feed ratio of from 25:1 to 45:1, a hydrogen to hydrogen chloride molar feed ratio of from 0.5:1 to 5:1, a pressure of from 1.1 to 1.3 MPa (absolute) and a PDC temperature in stream 22 of from 10 to 20 degrees Celsius.

The overheads stream 38 containing principally hydrogen and generally minor amounts of other non-condensables is, as mentioned above, preferably vented, recycled to the reactor section of the process or burned, with recycling to hydrogen/PDC source stream 28 being most preferred for the process 10. The bottoms stream 36 from the absorption column 20, which will contain 95 percent by weight or greater of the hydrogen chloride in product stream 16 and most preferably will contain 99.9 percent by weight or greater of the hydrogen chloride in the stream 16, is preferably subsequently passed to a means for separating out and recovering the hydrogen chloride contained therein in anhydrous form, for example, a conventional distillation column 40 wherein the anhydrous hydrogen chloride is produced as overhead stream 42.

The bottoms stream 44 from this distillation column 40 is processed to separate out the desired propylene product from PDC and any unwanted chlorinated hydrocarbonaceous byproducts formed in the product stream 16 by a means for performing this separation, for example, a conventional distillation apparatus 46. Those skilled in the art will recognize that propylene recovered in overheads stream 48 from distillation apparatus 46 may be recycled to a PDC source chlorohydrin process for manufacturing propylene oxide, may

be further processed as necessary to be fed to an allyl chloride process, may be used in other processes or may be sold.

Bottoms stream 50 from the distillation apparatus 46 is then conveyed to a final conventional distillation apparatus 52, for recovering PDC recycle stream 24 to be used in part in the feed 12 to the reactor 14, and in part in the solvent stream 22 to absorption column 20. The less-chlorinated hydrocarbonaceous byproducts in product stream 16 are conveyed in overheads stream 54 from distillation apparatus 52 to be incinerated or otherwise disposed of.

An alternate process 56 is shown in Figure 2, and differs from the process 10 shown in Figure 1 in the handling of the bottoms stream 36 from the absorption column 20.

Bottoms stream 36 is conveyed as in Figure 1 to a conventional distillation apparatus 40 to produce an overheads stream 58 containing the hydrogen chloride and propylene components of the product stream 16 and a bottoms stream 60 containing the less-chlorinated byproducts and unreacted PDC. Overheads stream 58 is fed to a distillation apparatus 62 in an associated allyl chloride process, wherein anhydrous hydrogen chloride is produced in the overheads stream 64 and propylene is separated out and recovered in the bottoms stream 66. Bottoms stream 60 is conveyed to a conventional distillation apparatus 68, with the less-chlorinated C3 hydrocarbonaceous byproducts in product stream 16 again being separated out for disposal in overheads stream 70 and the unreacted PDC being recovered in PDC recycle stream 24.

While a specific application of the process of the present invention has been described and illustrated herein, namely to the recovery of propylene and anhydrous hydrogen chloride from a process as described in the '042 application, the process of the present invention may preferably be used in connection with the processing of product streams from the reaction of 1,2-dichloropropane or other significant chlorinated hydrocarbon waste products and co-products from commercial processes with hydrogen. A notable example would be in processing a product stream from the conversion of 1,1,2-trichloroethane and other chlorinated hydrocarbon waste products and co-products of an EDC (1,2-dichloroethane)/VCM (vinyl chloride) process to produce useful, less-chlorinated C2 hydrocarbons and hydrogen chloride, using preferably EDC as the chlorinated hydrocarbon solvent.

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1. A process for the recovery of hydrogen chloride in anhydrous form from a dry mixture of one or more non-condensable gases with hydrogen chloride and which may further contain materials heavier than hydrogen chloride, comprising the steps of:
contacting the mixture with a halogenated hydrocarbon solvent to preferentially
5 absorb hydrogen chloride and any heavier materials present in the mixture into the solvent;
and
separating the hydrogen chloride in anhydrous form from heavier materials absorbed into the solvent and from the solvent.
2. A process as defined in Claim 1, wherein 95 percent by weight or greater of
10 the hydrogen chloride in the dry mixture is absorbed into the solvent.
3. A process as defined in Claim 1, wherein the hydrogen chloride is separated out and recovered in anhydrous form as an overheads stream from a distillation of the rich solvent stream from the absorption step.
4. A process as defined in any one of Claims 1-3, wherein the dry product
15 stream or mixture comprises hydrogen chloride, one or more non-condensable gases inclusive at least of hydrogen, propylene, 1,2-dichloropropane and less-chlorinated hydrocarbonaceous byproducts from the reaction of 1,2-dichloropropane with hydrogen in the presence of a catalyst to produce hydrogen chloride and propylene, and further wherein the chlorinated hydrocarbon solvent is 1,2-dichloropropane.
- 20 5. A process as defined in Claim 4, wherein the hydrogen chloride in the dry product stream or mixture is separated out and recovered in anhydrous form by a distillation of the rich 1,2-dichloropropane solvent stream from the absorption step to produce a bottoms stream comprised of the 1,2-dichloropropane and the less-chlorinated hydrocarbonaceous byproducts and an overheads stream comprised of the hydrogen chloride and propylene, and
25 then conducting distillations of the bottoms and overheads streams to produce separate streams of anhydrous hydrogen chloride, propylene, the less-chlorinated hydrocarbonaceous byproducts and unreacted 1,2-dichloropropane.
6. A process for making propylene and anhydrous hydrogen chloride from 1,2-dichloropropane, comprising the steps of:
30 reacting 1,2-dichloropropane and hydrogen in the presence of a catalyst and under conditions effective to produce propylene and hydrogen chloride in a dry product stream or mixture;
contacting the product stream or mixture with a chlorinated hydrocarbon solvent to preferentially absorb hydrogen chloride and any heavier materials present in the stream or
35 mixture into the chlorinated hydrocarbon solvent; and

separating the hydrogen chloride in anhydrous form from heavier materials absorbed into the chlorinated hydrocarbon solvent and from the chlorinated hydrocarbon solvent.

5 7. A process as defined in Claim 6, wherein 95 percent by weight or greater of the hydrogen chloride in the dry product stream or mixture is absorbed into the chlorinated hydrocarbon solvent.

8. A process as defined in Claim 6 or Claim 7, wherein the hydrogen chloride is separated out and recovered in anhydrous form as an overheads stream from a distillation of the rich solvent stream from the absorption step.

10 9. A process as defined in any one of Claims 6-8, wherein the chlorinated hydrocarbon solvent is 1,2-dichloropropane.

10. A process as defined in Claim 9, wherein the hydrogen chloride is separated out and recovered in anhydrous form as an overheads stream from a distillation of the rich 1,2-dichloropropane solvent stream from the absorption step.

15 11. A process as defined in Claim 9, wherein the hydrogen chloride is separated out and recovered in anhydrous form by a distillation of the rich 1,2-dichloropropane solvent stream from the absorption step to produce a bottoms stream comprised of the 1,2-dichloropropane and less-chlorinated hydrocarbonaceous byproducts and an overheads stream comprised of the hydrogen chloride and propylene, and then conducting distillations of the
20 bottoms and overheads streams to produce separate streams of anhydrous hydrogen chloride, propylene, the less-chlorinated hydrocarbonaceous byproducts and unreacted 1,2-dichloropropane.

12. A process as defined in Claim 11, wherein the unreacted 1,2-dichloropropane is recycled at least in part back to the process for converting such to propylene
25 by reaction with hydrogen in the presence of a catalyst, with any part not so recycled being recycled for use in the absorption step as the chlorinated hydrocarbon solvent.

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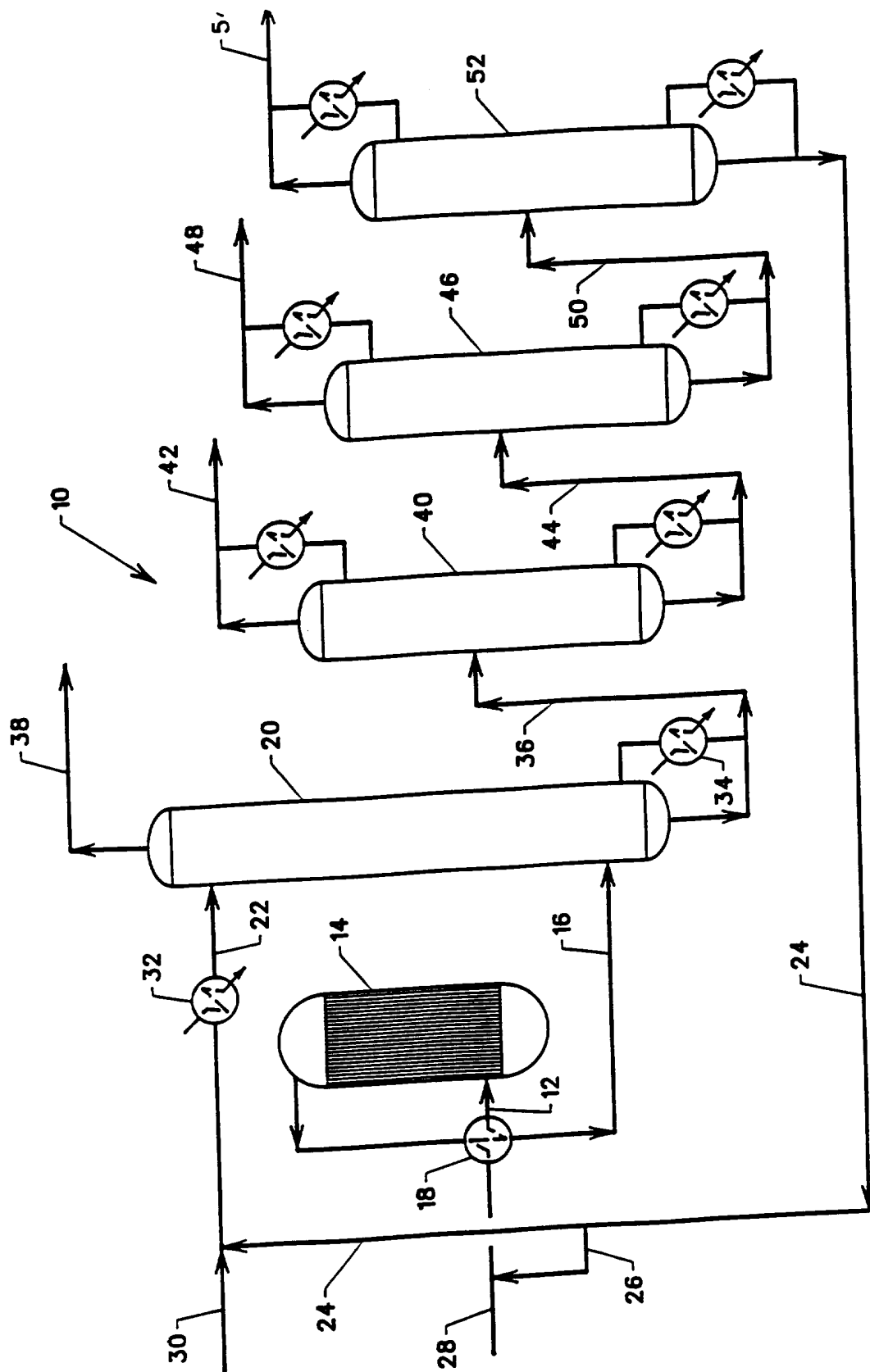
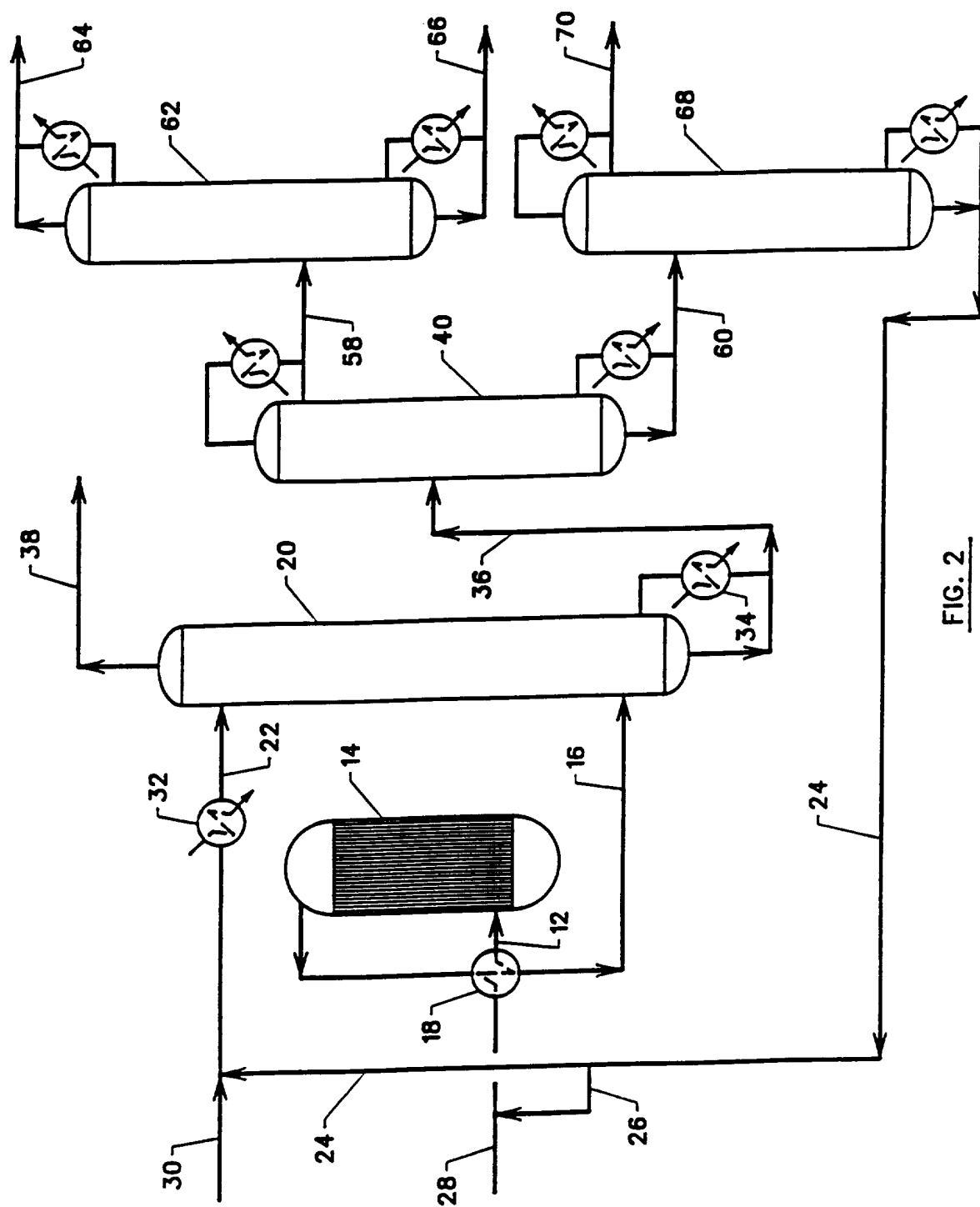


FIG. 1



INTERNATIONAL SEARCH REPORT

Int. Application No

PCT/US 95/13675

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C01B7/07 C07C17/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C01B C07C

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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Section Ch, Week 9027 Derwent Publications Ltd., London, GB; Class E36, AN 90-206166 & JP,A,02 137 704 (TOA GOSEI CHEM IND LTD) , 28 May 1990 see abstract</p> <p>---</p>	1,2
A	<p>US,A,5 314 614 (M. D. MOSER ET AL.) 24 May 1994 cited in the application see column 7, line 1 - line 29 see column 5, line 53 - column 6, line 51 see column 2, line 23 - line 48</p> <p>---</p> <p>-/--</p>	1-3

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,5 316 663 (R. B. JAMES, JR.) 31 May 1994 cited in the application see the whole document	1-3
A	<div style="text-align: center;">---</div> US,A,4 558 167 (H. RIEGEL ET AL.) 10 December 1985 see column 1, line 43 - column 2, line 58 see column 4, line 38 - column 5, line 47 <div style="text-align: center;">-----</div>	1-3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 95/13675

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-5314614	24-05-94	NONE	
US-A-5316663	31-05-94	NONE	
US-A-4558167	10-12-85	NONE	