



US 20110068046A1

(19) **United States**

(12) **Patent Application Publication**
Tullos et al.

(10) **Pub. No.: US 2011/0068046 A1**

(43) **Pub. Date: Mar. 24, 2011**

(54) **MERCURY REMOVAL FROM WATER**

Publication Classification

(75) Inventors: **Erin E. Tullos**, Bartlesville, OK (US); **Joseph B. Cross**, Bartlesville, OK (US); **Sally A. Thomas**, Bartlesville, OK (US)

(51) **Int. Cl.**
C10G 33/00 (2006.01)

(52) **U.S. Cl.** **208/187**

(73) Assignee: **ConocoPhillips Company**, Houston, TX (US)

(57) **ABSTRACT**

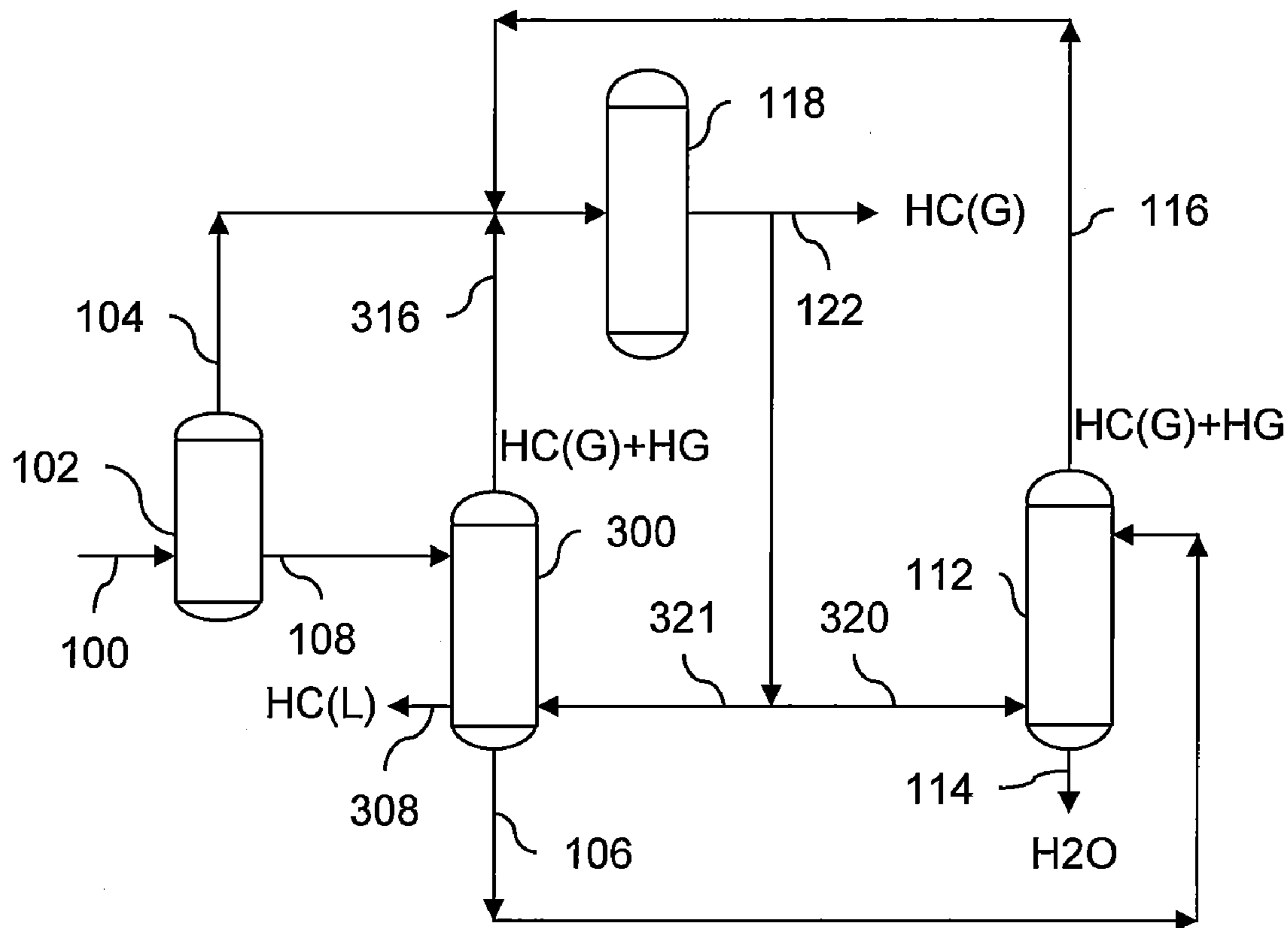
(21) Appl. No.: **12/879,724**

Methods and apparatus relate to removal of mercury from water. The removal relies on transferring mercury from an aqueous stream to a natural gas stream upon contacting the aqueous stream with the natural gas stream. Processing of the natural gas stream after used to strip the mercury from the aqueous stream removes the mercury from the natural gas stream.

(22) Filed: **Sep. 10, 2010**

Related U.S. Application Data

(60) Provisional application No. 61/243,879, filed on Sep. 18, 2009.



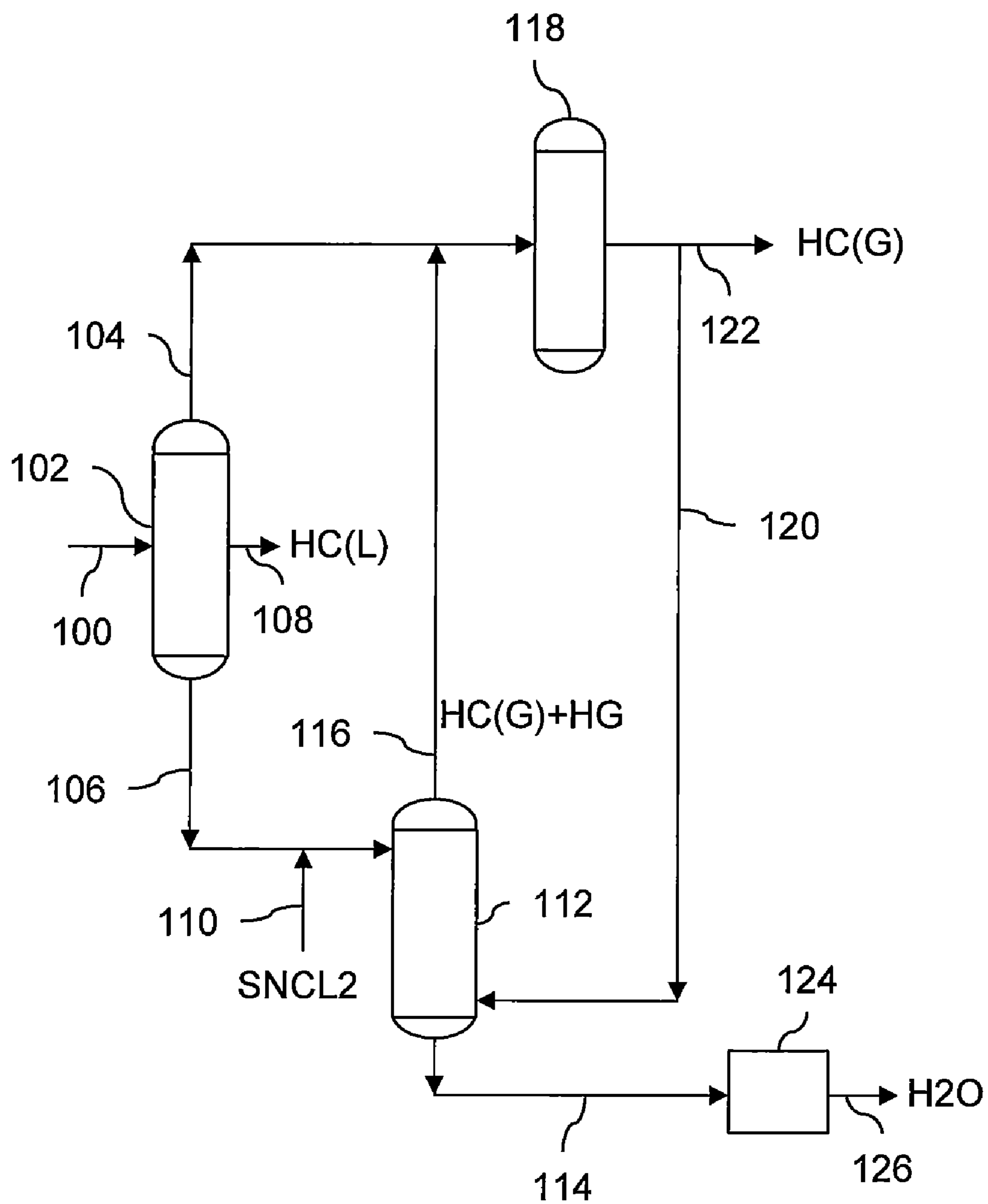


FIG. 1

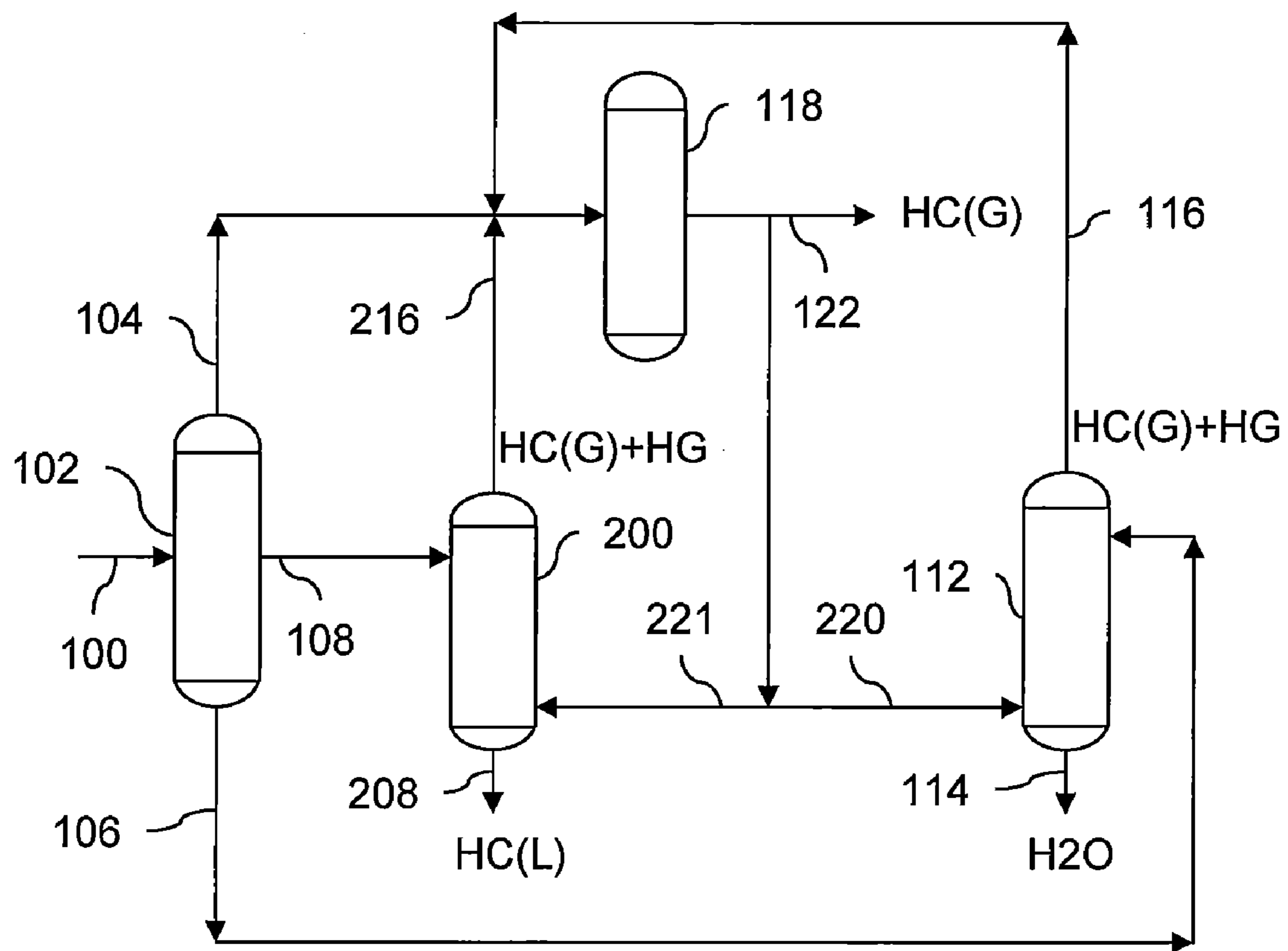


FIG. 2

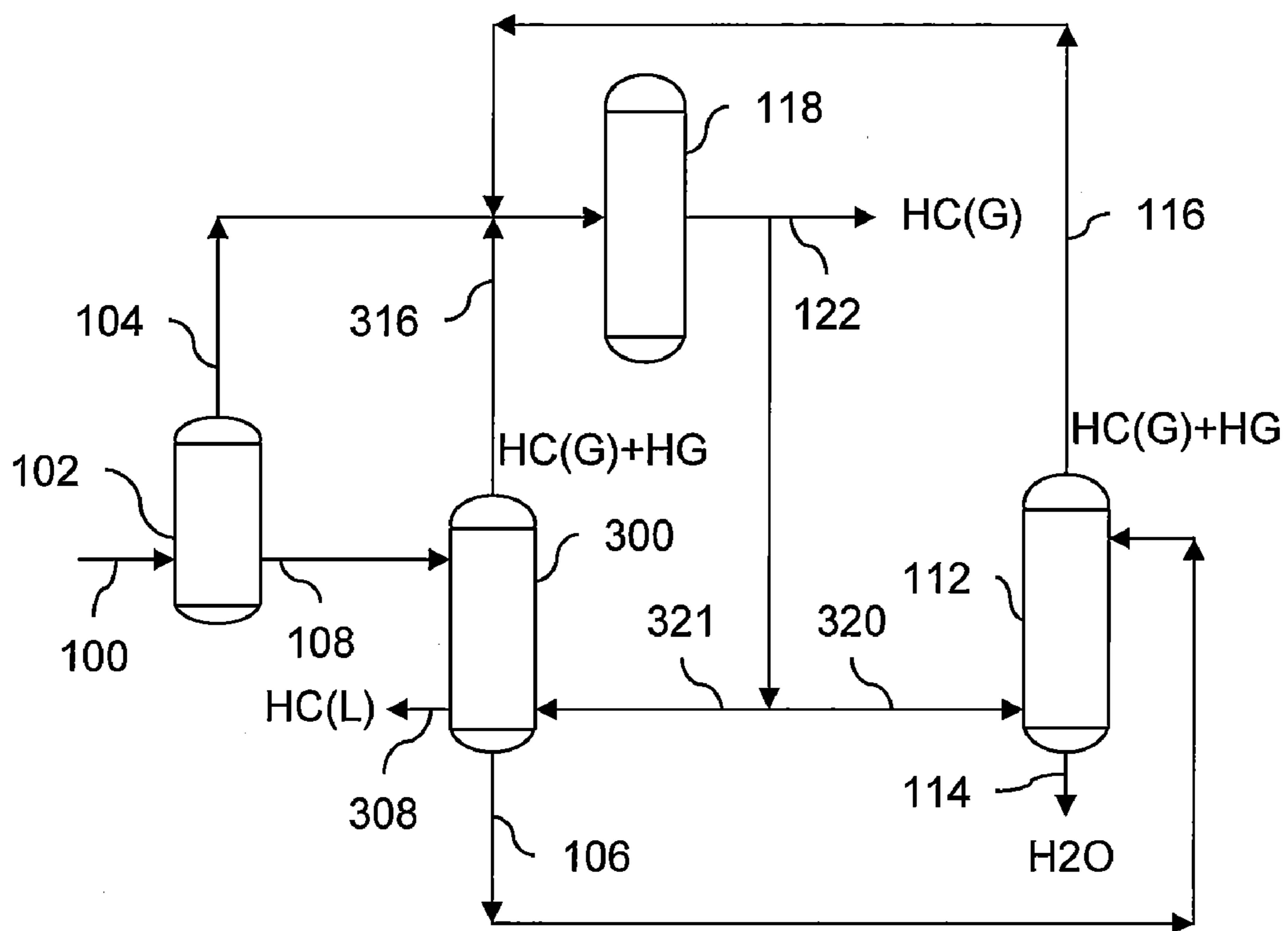


FIG. 3

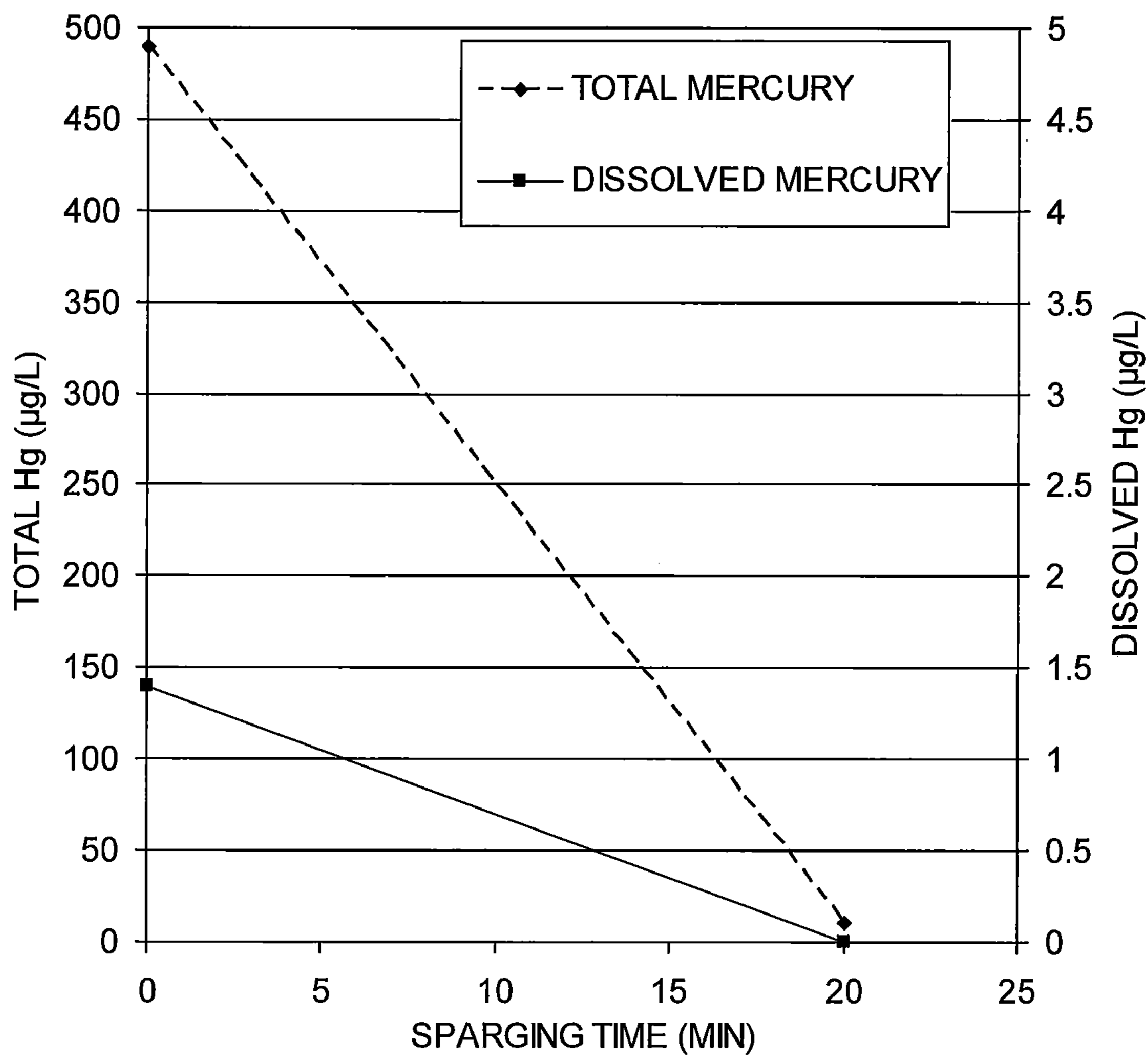


FIG. 4

MERCURY REMOVAL FROM WATER**CROSS-REFERENCE TO RELATED APPLICATIONS**

[0001] This application is a non-provisional application which claims benefit under 35 USC §119(e) to U.S. Provisional Application Ser. No. 61/243,879 filed Sep. 18, 2009, entitled "MERCURY REMOVAL FROM WATER," which is incorporated herein in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] None

FIELD OF THE INVENTION

[0003] Embodiments of the invention relate to methods and systems for removing mercury from water.

BACKGROUND OF THE INVENTION

[0004] Recovered fluids from wells drilled into hydrocarbon reservoirs often include water. Separators remove the water from oil and gas products also produced. However, the water from some reservoirs contains mercury. The mercury in the water presents environmental and safety concerns and may prevent ability to discharge the water without first being treated.

[0005] Techniques utilizing solid absorbents for mercury removal from the produced water tend to result in fouling of mercury removal beds. Other factors limiting applicability of prior approaches to remove mercury include expense and size requirements given limited space available when used at platforms. Due to mercury solubility in the water, effectiveness problems arise with some of the prior approaches since the mercury contaminating the water tends to be part of inorganic compounds or a mixture of the inorganic compounds and elemental mercury.

[0006] Therefore, a need exists for improved methods and systems for removing mercury from water.

SUMMARY OF THE INVENTION

[0007] In one embodiment, a process of removing mercury from water includes separating crude production into a gaseous hydrocarbon stream, a liquid hydrocarbon stream and an aqueous stream. Water forms a majority of the aqueous stream. Removing mercury from a contaminated gas stream including the gaseous hydrocarbon stream provides a treated gas stream. Further, contacting the treated gas stream with the aqueous stream transfers mercury from the aqueous stream to the treated gas stream such that mercury removal from the aqueous stream is independent from the liquid hydrocarbon stream.

[0008] According to one embodiment, a method of removing mercury from water includes adding a reducing agent to an aqueous stream such that mercury-containing compounds in the aqueous stream are converted to form elemental mercury. The method further includes transferring the elemental mercury from the aqueous stream to a methane-containing gas stream. The transferring occurs upon contacting the gas stream with the aqueous stream combined with the reducing agent. In addition, the method includes removing the elemental mercury from the gas stream.

[0009] For one embodiment, a process of removing mercury from water includes separating crude production into a gaseous hydrocarbon stream, a liquid hydrocarbon stream and an aqueous stream. Water forms a majority of the aqueous stream. Transferring mercury from the liquid hydrocarbon stream to a first portion of a treated gas stream occurs by contacting the first portion of the treated gas stream with the liquid hydrocarbon stream. Furthermore, transferring mercury from the aqueous stream to a second portion of the treated gas stream by contacting the second portion of the treated gas stream with the aqueous stream is independent of the first portion of the treated gas stream being contacted with the liquid hydrocarbon stream. The treated gas stream forms by removing mercury from the gaseous hydrocarbon stream mixed with the first and second portions of the treated gas stream recycled after the contacting with the liquid hydrocarbon and aqueous streams.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] The invention, together with further advantages thereof, may best be understood by reference to the following description taken in conjunction with the accompanying drawings.

[0011] FIG. 1 is a schematic of a production system for mercury removal from water, according to one embodiment of the invention.

[0012] FIG. 2 is a schematic of a production system having elements shown in FIG. 1 with a subunit for removing mercury from a hydrocarbon liquid stream, according to one embodiment of the invention.

[0013] FIG. 3 is a schematic of a production system having elements shown in FIG. 1 with a subunit for initial removal of mercury from a hydrocarbon and water mixture, according to one embodiment of the invention.

[0014] FIG. 4 is a graph showing mercury concentration in water before and after being contacted with a stream of hydrocarbon gas, according to one embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0015] Embodiments of the invention relate to removal of mercury from water. The removal relies on transferring mercury from an aqueous stream to a natural gas stream upon contacting the aqueous stream with the natural gas stream. Processing of the natural gas stream after used to strip the mercury from the aqueous stream removes the mercury from the natural gas stream.

[0016] In some embodiments, the water comes from crude production and is thus recovered from reservoirs along with hydrocarbons that may be liquid and gaseous. Mercury concentrations in the water that is produced often prevent outputting the water as waste due to environmental issues and regulations. The removal of the mercury from the water thereby enables discharge of the water separated from the hydrocarbons. As used herein, "mercury" refers to mercury within or from compounds, such as mercuric chloride, mercury oxide and combinations thereof, containing mercury and at least one other element and/or elemental mercury. Location for removing the mercury depends on application and can be performed onsite at offshore platforms with limited space and facilities.

[0017] FIG. 1 illustrates a system in which crude production removed from a well defines an input stream **100** introduced into a separator **102** for separation into a hydrocarbon

gas stream 104, a hydrocarbon liquid “HC(L)” stream 108, and an aqueous stream 106 that are each individually removed from the separator 102. Water forms a majority of the aqueous stream 106. Mercury-containing gas, including in part at least a portion of the hydrocarbon gas stream 104, feeds into a mercury removal unit (MRU) 118 for removal of mercury from the mercury-containing gas, thereby forming a treated gas stream 122 output from the MRU 118. The treated gas stream 122 includes hydrocarbon gas “HC(G),” such as methane, and may provide a supply for natural gas usable in part for sales or as fuel.

[0018] Part of the treated gas stream 122 forms a recycle gas stream 120, which is introduced into a water-gas contactor 112 for contact with at least a portion of the aqueous stream 106 that also enters the water-gas contactor 112. Through such contacting, at least a portion of the mercury contained in the aqueous stream 106 transfers to the recycle gas stream 120, thereby forming a water-passed gas stream 116 output from the water-gas contactor 112 and a treated water “H₂O” stream 114 output from the water-gas contactor 112. The water-passed gas stream 116 hence includes hydrocarbon gas and mercury “HC(G)+HG.” For some embodiments, the water-passed gas stream 116 mixes with the hydrocarbon gas stream 104 and provides a portion of the mercury-containing gas that feeds into the MRU 118.

[0019] In some embodiments, an optional chemical additive stream 110 mixes with the aqueous stream 106 to introduce a reducing agent into the aqueous stream 106 upstream from passing of the recycle gas stream 120 in contact with the aqueous stream 106. The reducing agent breaks molecular bonds between mercury atoms and other elements in mercury-containing compounds. As used herein, the reducing agent may be provided as a liquid and includes any substance that forms a compound with such released non-mercury elements to prevent recombination with elemental mercury. Examples of the reducing agent include stannous chloride (SnCl₂; “SNCL2”), sodium borohydride, and hydrazine. Amount of the reducing agent introduced via the additive stream depends on concentration of mercury in the aqueous stream 106 and may be sufficient to establish an excess mole ratio of the reducing agent relative to the mercury.

[0020] The reducing agent supplied through the additive stream 110 may facilitate effectiveness of sparging within the water-gas contactor 112 since mercury removal ability via the sparging is higher for elemental mercury relative to when not in elemental form. Reducing inorganic compounds, such as mercury oxide or mercuric chloride, in the aqueous stream 106 tends to promote the mercury removal. Even though the mercury in the aqueous stream 106 can tend to remain in elemental form while at elevated formation temperatures, the elemental mercury may convert into mixed element compounds due to cooling of the aqueous stream 106 and temperature influence on solubility of the elemental mercury. In operation, the aqueous stream 106 may cool upon coming out of the well making introduction of the additive stream 110 desirable to reduce the inorganic compounds to the elemental mercury.

[0021] For some embodiments, the treated water stream 114 passes through an optional filtration system 124 to remove suspended particulates from the treated water stream 114. The filtration system 124 operates based on size exclusion to trap or retain particles above a certain size, such as about 0.2 micron or about 0.4 micron. The cooling that is inevitable after the input stream 100 comes out of the well

promotes adherence of the mercury to the particulates. Generation of a filtered water stream 126 flowing out of the filtration system 124 thus results in further mercury removal .since residual mercury still within the treated water stream 114 is associated with the particulates.

[0022] In some embodiments, the water-gas contactor 112 includes multiple (e.g., 2, 4, 6 or more) theoretical stages of separation between vapor and liquid phases. Either trays or packing material of the water-gas contactor 112 may form the theoretical stages by being in a flow path of fluids described herein passing through the water-gas contactor 112. For example, the packing material making up an internal part of the water-gas contactor 112 may include random oriented objects or a shaped structure and may be made of metallic, ceramic, plastic or other solid material. For some embodiments, amount of the packing material utilized depends on a desired number of the stages provided by the packing material.

[0023] The MRU 118 defines a fixed bed including any mercury sorbent material capable of removing mercury from gases. In some embodiments, the treated gas stream 122 includes less than about 20 weight percent (wt. %) of the mercury within the mercury-containing gas, less than about 10 wt. % of the mercury within the mercury-containing gas, or less than about 1 wt. % of the mercury within the mercury-containing gas. The treated water stream 114 or the filtered water stream 126 may contain less than about 50 wt. %, 10 wt. %, or 1 wt. % of the mercury contained in the aqueous stream 106. The aqueous stream 106 for some embodiments contains at least about 5 parts-per-billion (ppb), 100 ppb or 500 ppb mercury.

[0024] For some embodiments, the recycle gas stream 120 contacts the aqueous stream 106 at ambient temperature, such as about 21° C., or from about 0° C. to about 300° C.; a pressure in the range of from about 0.1 Bars to about 15 Bars, from about 0.5 Bars to about 10 Bars, or from about 1 Bar to about 5 Bars; and a gas to liquid ratio in the range of from about 50 to about 300 standard cubic feet of gas/barrel of liquid (SCF/bbl) or from about 100 to about 200 SCF/bbl.

[0025] FIG. 2 illustrates a schematic of a production system that includes a subunit for removing mercury from the hydrocarbon liquid stream 108. The system incorporates an oil-gas contactor 200 of the subunit with elements already described herein with respect to FIG. 1 and identified by common reference numbers. A first portion 220 of the treated gas stream 122 enters the water-gas contactor 112 to generate the treated water stream 114. A second portion 221 of the treated gas stream 122 flows into the oil-gas contactor 200 and is introduced into the hydrocarbon liquid stream 108 also input into the oil-gas contactor 200. Such contacting transfers mercury from the hydrocarbon liquid stream 108 to the second portion 221 of the treated gas stream 122 and occurs subsequent to separation of the hydrocarbon liquid stream 108 from the aqueous stream 106. Resulting effluent from the oil-gas contactor 200 includes hydrocarbon liquids forming a treated oil stream 208 and hydrocarbon gases contaminated with mercury forming an oil-passed gas stream 216. The oil-passed gas stream 216 also passes through the mercury removal unit 118 and is thereby regenerated to make up part of the treated gas stream 122.

[0026] FIG. 3 shows a schematic of a production system with an exemplary alternative configuration such that a subunit provides initial removal of mercury from a hydrocarbon and water liquid mixture. U.S. patent application Ser. No.

12/538,606, which is herein incorporated by reference in its entirety, further describes such exemplary techniques depicted by the subunits in FIGS. 2 and 3 for liquid hydrocarbon processing to remove mercury. Similar to other embodiments, the water-gas contactor 112 generates the treated water stream 114 utilizing a first portion 320 of the treated gas stream 122. In addition to elements already described herein having like reference numbers, the system further incorporates an emulsion-gas contactor 300 of the subunit. The separator 102 may only provide separation for two phases leaving water in the hydrocarbon liquid stream 108 that feeds into the emulsion-gas contactor 300. A second portion 321 of the treated gas stream 122 flows into the emulsion-gas contactor 300 where introduced into the hydrocarbon liquid stream 108. Such contacting transfers mercury from the hydrocarbon liquid stream 108 to the second portion 321 of the treated gas stream 122 and occurs prior to separation of the aqueous stream 106 out of the hydrocarbon liquid stream 108. Three individual resulting effluents from the oil-gas contactor 200 include hydrocarbon liquids forming a treated oil stream 308, hydrocarbon gases contaminated with mercury forming an emulsion-passed gas stream 316, and the aqueous stream 106, which then feeds to the water-gas contactor 112 for further water treatment as set forth herein. The emulsion-passed gas stream 316 passes through the mercury removal unit 118 and is thereby regenerated to make up part of the treated gas stream 122.

[0027] Independence with respect to removing mercury from the aqueous stream enables mercury to be removed from the water alone or tailoring amount of mercury to be removed from each of the water and the hydrocarbon liquids as desired. Referring to FIGS. 2 and 3, the oil-gas contactor 200 and the emulsion-gas contactor 300 enable reducing mercury concentration in the hydrocarbon liquid stream 108 independent of utilizing the water-gas contactor 112 to remove the mercury from the aqueous stream 106. Thresholds for mercury concentrations in the hydrocarbon liquids depend on economics and marketability to refineries. However, mercury concentration in the water may need to meet separate set requirements necessitating individual treatment of the aqueous stream 106. Furthermore, independent processing of the aqueous stream 106 to remove mercury makes possible optional addition of the reducing agent, optional use of the filtration system 124, and conducting treatment without having to ensure certain temperatures of the aqueous stream 106 during the contacting to remove the mercury.

[0028] FIG. 4 depicts a graph showing mercury concentration in water before and after being contacted with a stream of hydrocarbon gas. Prior to being sparged with the gas, the water contained 489 micrograms per liter ($\mu\text{g}/\text{l}$) of total mercury and 1.4 $\mu\text{g}/\text{l}$ of dissolved mercury. The water after being sparged with the gas for 20 minutes contained no dissolved mercury and had only 10 $\mu\text{g}/\text{l}$ of the total mercury remaining. Since the 10 $\mu\text{g}/\text{l}$ of the total mercury remaining was associated with suspended particles greater than 0.45 microns in size, filtering provided an option for removing residual mercury from the water following the sparging. Results thus demonstrated effectiveness of such techniques for removing mercury from actual produced water.

[0029] The preferred embodiment of the present invention has been disclosed and illustrated. However, the invention is intended to be as broad as defined in the claims below. Those skilled in the art may be able to study the preferred embodiments and identify other ways to practice the invention that

are not exactly as described herein. It is the intent of the inventors that variations and equivalents of the invention are within the scope of the claims below and the description, abstract and drawings are not to be used to limit the scope of the invention.

1. A method, comprising:
 - separating crude production into a gaseous hydrocarbon stream, a liquid hydrocarbon stream and an aqueous stream, wherein water forms a majority of the aqueous stream;
 - removing mercury from a contaminated gas stream including the gaseous hydrocarbon stream to provide a treated gas stream; and
 - contacting the treated gas stream with the aqueous stream to transfer mercury from the aqueous stream to the treated gas stream such that mercury removal from the aqueous stream is independent from the liquid hydrocarbon stream.
2. The method according to claim 1, further comprising adding a reducing agent to the aqueous stream such that mercury-containing compounds in the aqueous stream are converted to form elemental mercury.
3. The method according to claim 1, further comprising adding stannous chloride to the aqueous stream.
4. The method according to claim 1, further comprising filtering the aqueous stream that has been contacted with the treated gas stream, wherein the filtering removes particles that include residual mercury.
5. The method according to claim 1, further comprising adding a reducing agent to the aqueous stream and filtering the aqueous stream that has been contacted with the treated gas stream.
6. The method according to claim 1, wherein the contaminated gas stream further includes a recycle stream formed of vapor effluent from the contacting of the treated gas stream with the aqueous stream.
7. The method according to claim 1, further comprising contacting the treated gas stream with the liquid hydrocarbon stream to transfer mercury from the liquid hydrocarbon stream to the treated gas stream.
8. The method according to claim 1, further comprising transferring mercury from a mixture of the liquid hydrocarbon stream and the aqueous stream to the treated gas stream, wherein the transferring is separate from and prior to the contacting of the treated gas stream with the aqueous stream.
9. The method according to claim 1, wherein removing mercury from the contaminated gas stream comprises introducing the contaminated gas stream into a mercury-sorbent based removal unit.
10. The method according to claim 1, further comprising removing mercury within vapor effluent from the contacting of the treated gas stream with the aqueous stream.
11. The method according to claim 1, wherein clean water discharge formed of liquid effluent from the contacting of the treated gas stream with the aqueous stream contains less than 10 weight percent of elemental mercury contained in the aqueous stream.
12. A method, comprising:
 - adding a reducing agent to an aqueous stream such that mercury-containing compounds in the aqueous stream are converted to form elemental mercury;
 - transferring the elemental mercury from the aqueous stream to a methane-containing gas stream, wherein the

transferring occurs upon contacting the gas stream with the aqueous stream combined with the reducing agent; and

removing the elemental mercury from the gas stream.

13. The method according to claim **12**, wherein the reducing agent is at least one of stannous chloride, sodium borohydride, and hydrazine.

14. The method according to claim **12**, wherein the reducing agent comprises stannous chloride.

15. The method according to claim **12**, further comprising separating crude production into the aqueous stream and vapors that form at least part of the gas stream upon being treated to remove mercury.

16. The method according to claim **12**, further comprising filtering the aqueous stream that has been contacted with the gas stream, wherein the filtering removes particles that include residual mercury.

17. A method, comprising:

separating crude production into a gaseous hydrocarbon stream, a liquid hydrocarbon stream and an aqueous stream, wherein water forms a majority of the aqueous stream;

transferring mercury from the liquid hydrocarbon stream to a first portion of a treated gas stream by contacting the first portion of the treated gas stream with the liquid hydrocarbon stream;

transferring mercury from the aqueous stream to a second portion of the treated gas stream by contacting the second portion of the treated gas stream with the aqueous stream independent of the first portion of the treated gas stream being contacted with the liquid hydrocarbon stream; and

forming the treated gas stream by removing mercury from the gaseous hydrocarbon stream mixed with the first and second portions of the treated gas stream recycled after the contacting with the liquid hydrocarbon and aqueous streams.

18. The method according to claim **17**, further comprising adding a reducing agent to the aqueous stream such that mercury-containing compounds in the aqueous stream are converted to form elemental mercury.

19. The method according to claim **17**, further comprising filtering the aqueous stream that has been contacted with the second portion of the treated gas stream, wherein the filtering removes particles that include residual mercury.

20. The method according to claim **17**, wherein the transferring mercury from the liquid hydrocarbon stream to the first portion of the treated gas stream occurs while the liquid hydrocarbon stream and the aqueous stream are mixed together.

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