US 20110068046A1

(19) United States

(12) Patent Application Publication

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

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

Tullos et al.

(54) **MERCURY REMOVAL FROM WATER**

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

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

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

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

Related U.S. Application Data

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

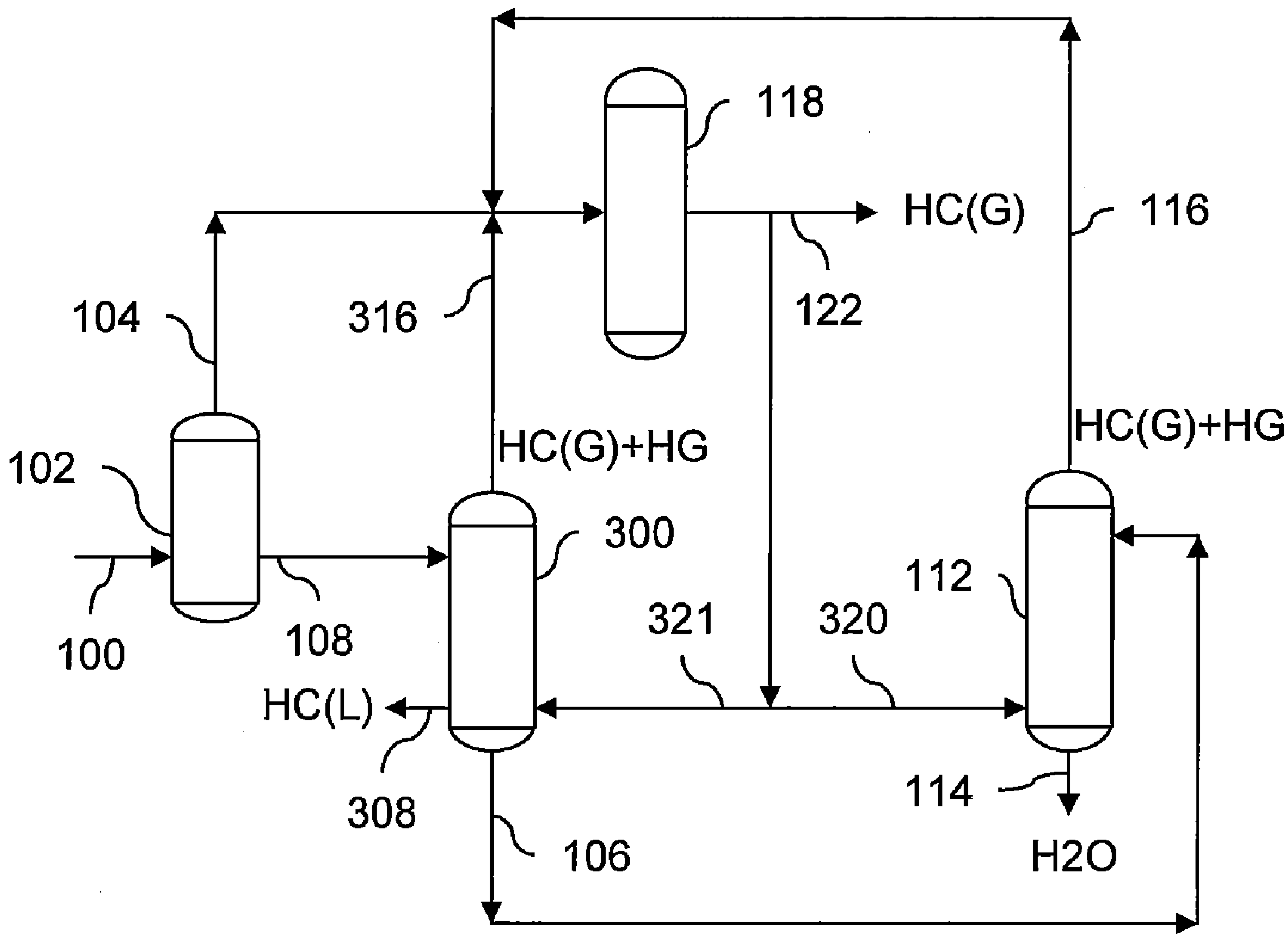
Publication Classification

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

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

(57) **ABSTRACT**

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.



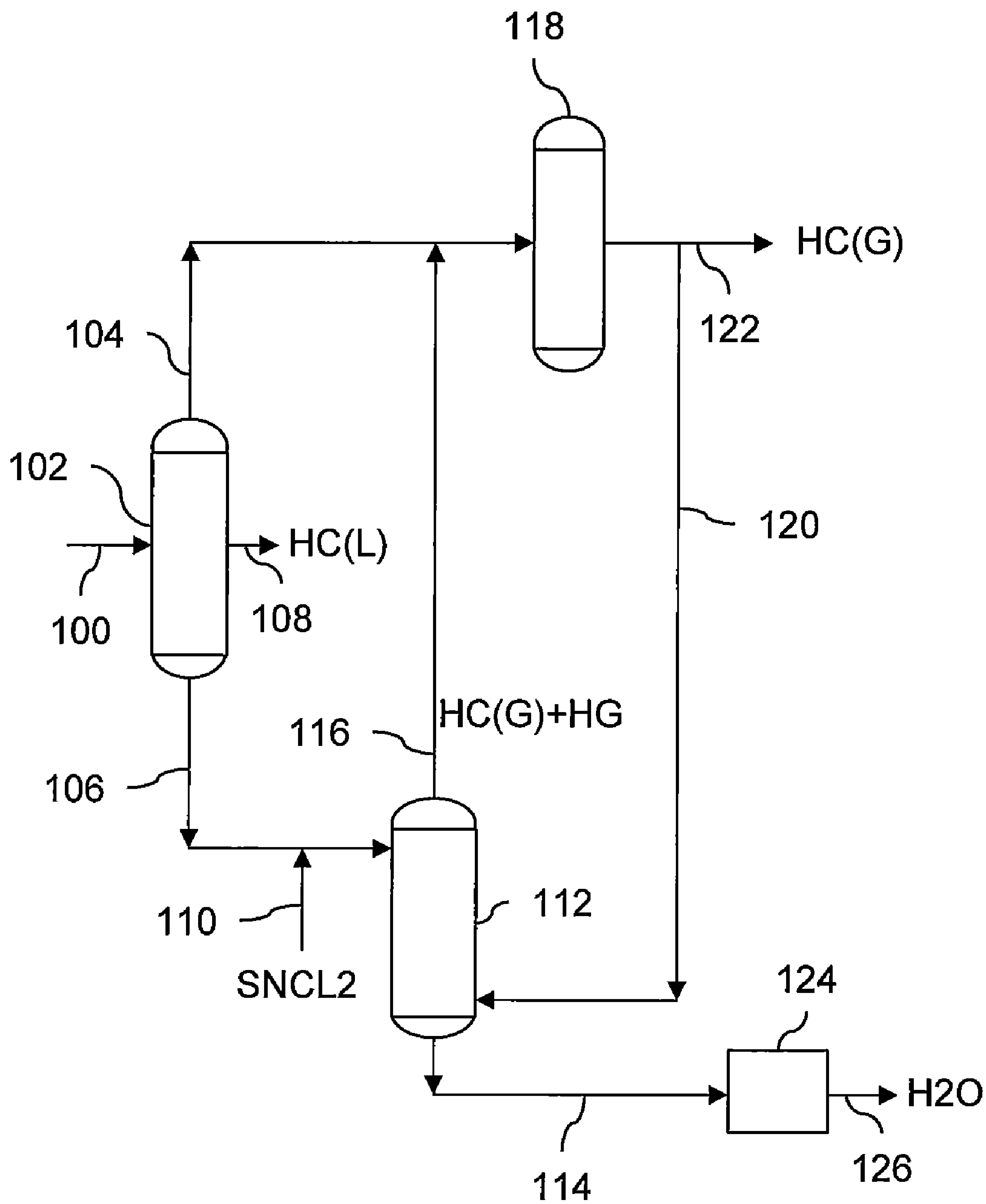

118
HC(G)
104
122
102
120
HC(L)
108
100
HC(G)+HG
116
106
112
110
SNCL2
124
H2O
126
114

FIG. 1

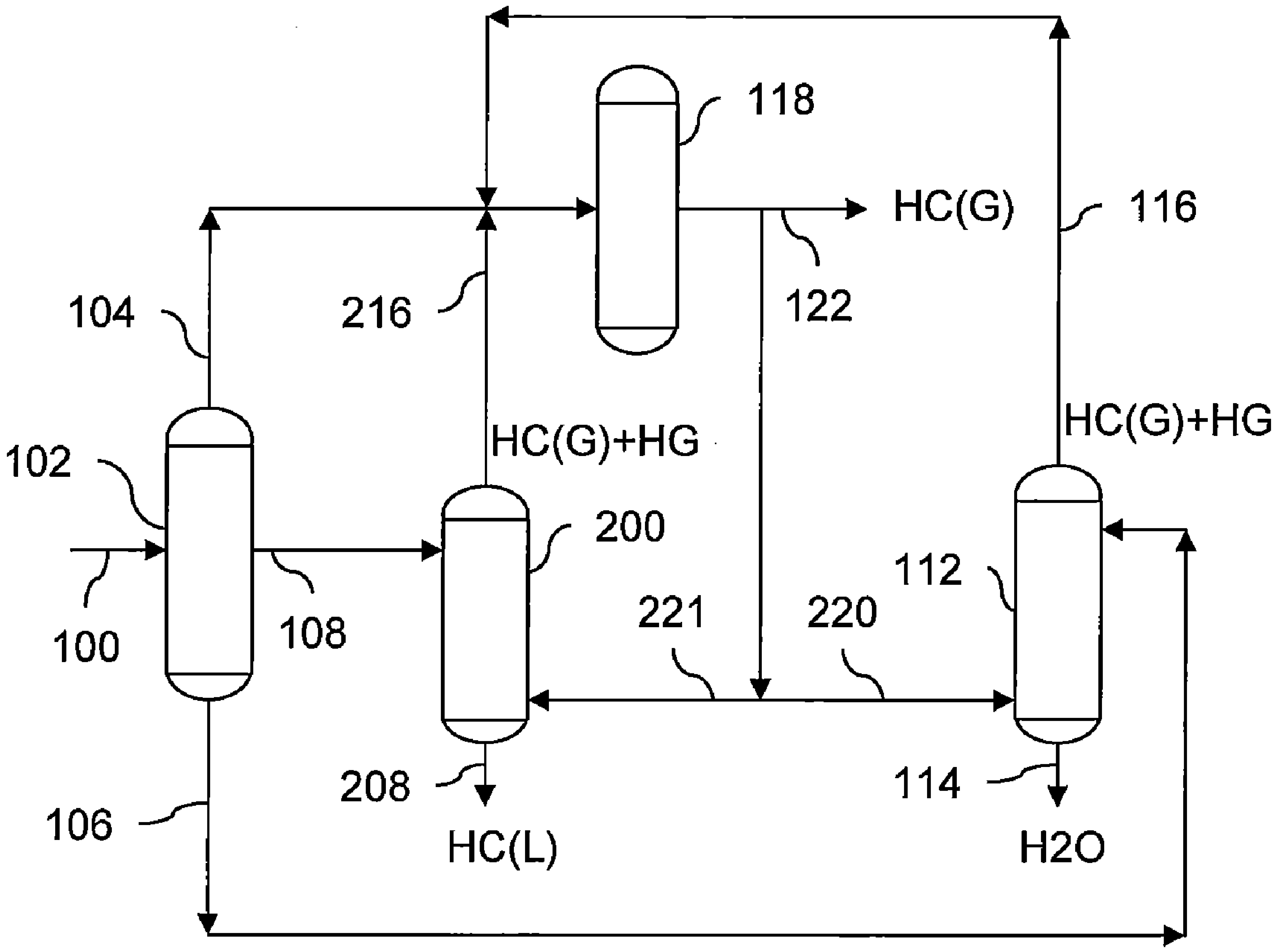

118
HC(G)
116
104
216
122
HC(G)+HG
HC(G)+HG
102
200
112
221
220
100
108
208
114
106
HC(L)
H2O

FIG. 2

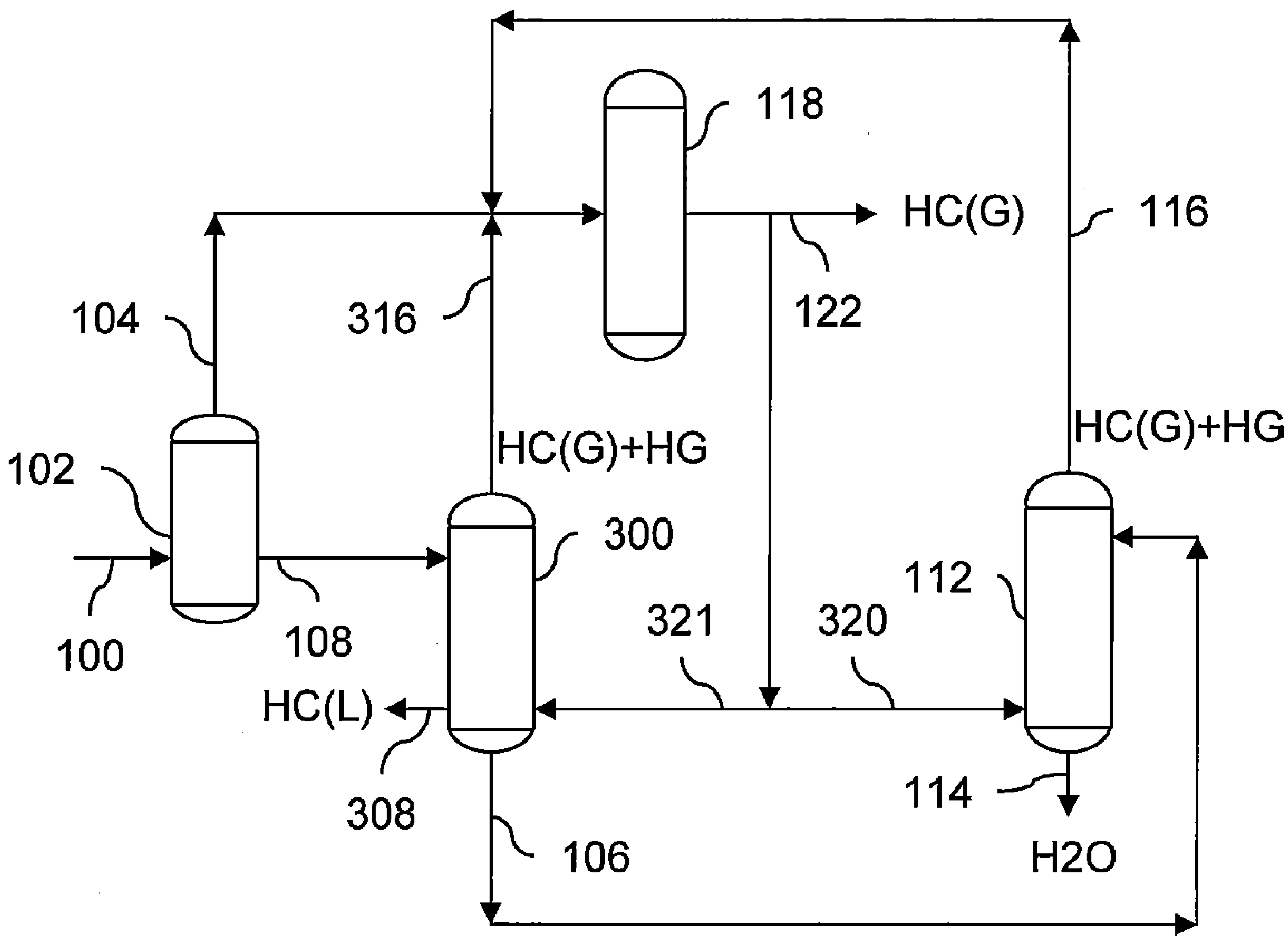

118
HC(G)
116
104
316
122
HC(G)+HG
HC(G)+HG
102
300
112
321
320
100
108
HC(L)
308
114
106
H2O

FIG. 3

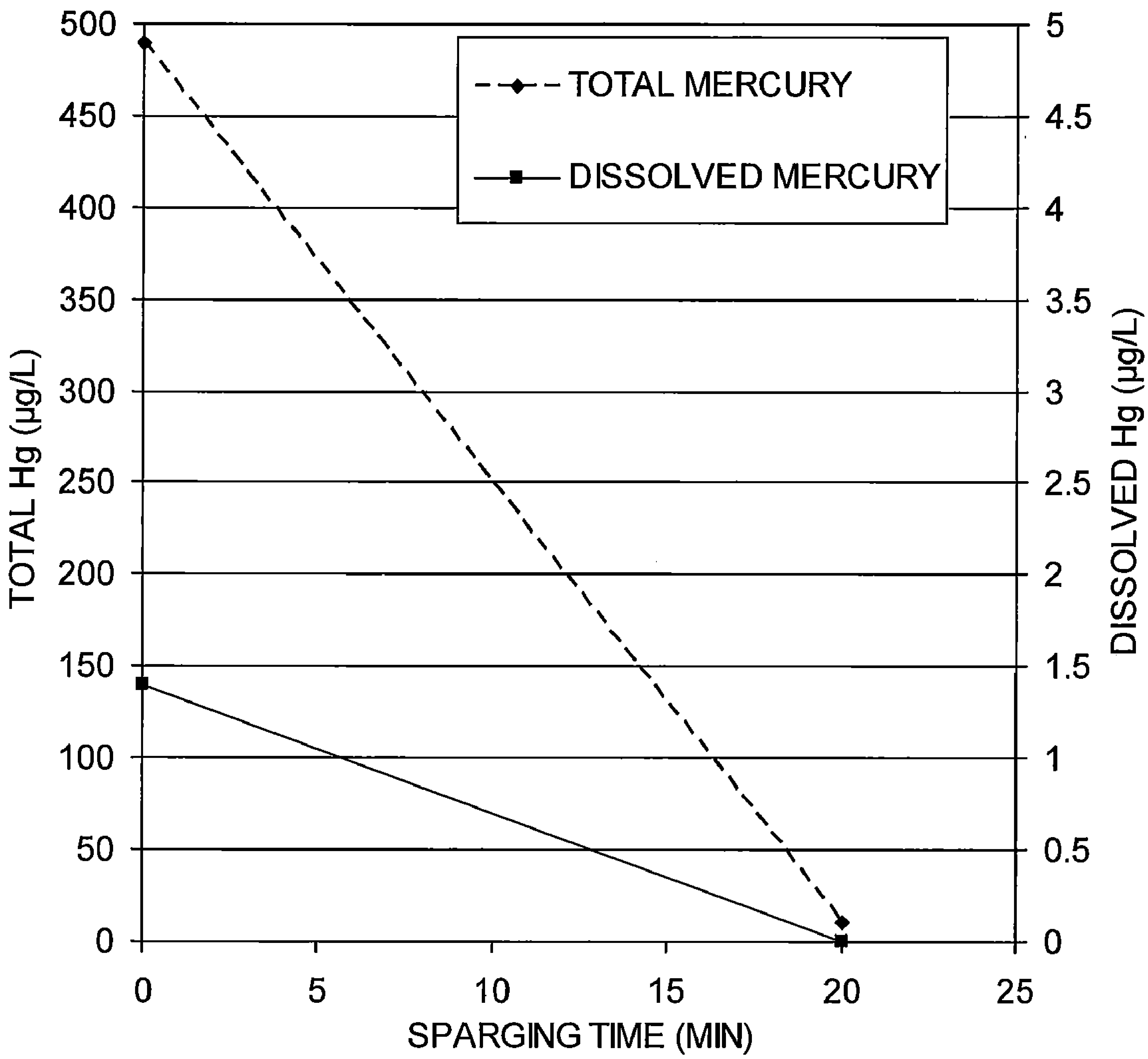

TOTAL MERCURY
DISSOLVED MERCURY
TOTAL Hg (µg/L)
DISSOLVED Hg (µg/L)
SPARGING TIME (MIN)
500
450
400
350
300
250
200
150
100
50
0
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
5
10
15
20
25

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 ($SnCl_2$; "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 (μg/l) of total mercury and 1.4 **82** g/l of dissolved mercury. The water after being sparged with the gas for 20 minutes contained no dissolved mercury and had only 10 μg/l of the total mercury remaining. Since the 10 μg/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.

* * * * *