

SEPARATION OF LIGHT GASES FROM HALOGENS

FIELD OF THE INVENTION

[0001] This invention generally relates to processes for separating inert gases and other compounds from halogens.

BACKGROUND OF THE INVENTION

[0002] The choice between air and oxygen as a medium for oxidation has been explored for many industrial processes. For processes where air can be used for oxidation without adversely affecting the reaction chemistry, air is preferred over a pure oxygen feed for reduced capital and operating cost. The higher cost of oxygen results from the expense of separating oxygen from nitrogen, conventionally accomplished using either membranes or distillation. One example where the use of pure oxygen is preferred over air is in syngas production, which is the first step in the production of liquid hydrocarbons from natural gas using Fischer Tropsch synthesis. In addition to affecting the reaction chemistry, the use of air in the syngas generation requires nitrogen to be separated from unconverted natural gas. The separation of nitrogen from natural gas is cost-intensive, and is conventionally carried out using membranes or pressure swing adsorption.

[0003] A conventional method of capturing trace bromine in inert gas streams is to use an alkaline scrubber, for example, an aqueous NaOH solution. It is not easy to recover the captured bromine from the conventional scrubbing method. Other conventional methods include the use of sodium sulfite, sodium bisulfite, or an aqueous solution of calcium hydroxide, etc., each of which suffers from the same drawback that the captured bromine is difficult to recover.

[0004] Technology developed by GRT, Inc., of Santa Barbara, CA, allows higher hydrocarbons to be synthesized from methane or natural gas by mixing the hydrocarbon(s) and halogen in a reactor to form alkyl halides and hydrogen halide, HX. The alkyl halides and HX are directed into contact with a metal oxide or similar material to form higher hydrocarbons and a metal halide. The metal halide is oxidized to metal oxide and halogen, both of which are recycled. When air is used for oxidation, the halogen that is generated contains inert gases such as nitrogen and carbon dioxide which, if not removed, would pass through the halogenation section and the coupling section where higher hydrocarbons are produced. In other technology developed by GRT, Inc., hydrocarbons are formed by reacting alkyl halides with halogen in the presence of a catalyst, HX is formed as a byproduct. To regenerate halogen for use in a subsequent cycle of the overall process, HX is oxidized with air or oxygen in the presence of a catalyst. For both types of technologies, it is desirable to separate the regenerated halogen from N₂, CO₂, and other light gases (such as unreacted light hydrocarbons), and water before the halogen is used in the next process cycle. For a cyclic or

1 continuous process, such gases, particularly nitrogen, would rapidly accumulate if not
separated. A clear need exists for an efficient, cost-effective process of separating inert gases
and other compounds from halogens.

5 SUMMARY OF THE INVENTION

[0005] According to the invention, a process is provided for separating one or more light
gases from bromine or chlorine using one or more physical separations and contact with a
chemical scrubber to recover additional halogen. According to one aspect of the invention,
the process comprises (a) providing a feed of halogen containing one or more light gases to a
10 distillation column or flash vaporizer; (b) operating the distillation column or flash vaporizer
to separate the feed into (i) a first liquid containing a major amount of halogen and no more
than a minor amount of light gas(es), and (ii) a first vapor containing a major amount of light
gas(es) and no more than a minor amount of halogen; and (c) providing the vapor to a
chemical scrubber to recover halogen from the vapor.

15 [0006] In a second aspect of the invention, two or more physical separations are used,
with each separation leading to successively greater enrichment of, respectively, the halogen
in the liquid phase and the light gas(es) in the vapor phase. For example, the vapor from a
distillation column (enriched in light gas(es)) can be fed to a second distillation column,
which further separates the material into a new vapor and a new liquid, the new vapor being
20 more enriched in light gas(es), and the new liquid being more enriched in halogen.

[0007] The chemical scrubber utilized in the invention contains one or more halogen
scavengers, materials which are capable of chemically sorbing halogen, in some
embodiments through a redox reaction with the halogen. A preferred material is copper (I)
bromide (CuBr, "cuprous bromide"), which can adsorb bromine by conversion into copper
25 (II) bromide (CuBr₂, "cupric bromide").

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] The features and advantages of the invention will become better understood when
considered in light of the following detailed description, and by making reference to the
30 following drawings, wherein:

[0009] Figure 1 is a schematic diagram of a process for separating light gases from
bromine according to one aspect of the invention;

[0010] Figure 2 is a schematic diagram of the process shown in Figure 1, with the
additional elements of bromine formation ("bromine regeneration") and water adsorption;

35 [0011] Figure 3 is a schematic diagram of a process for separating light gas(es) from
bromine, utilizing three flash vaporizers run in series, according to another aspect of the
invention;

1 [0012] Figure 4 is a schematic diagram of a continuous process for converting natural gas into higher hydrocarbons and including a subprocess for separating bromine formed during the process from light gases, according to one aspect of the invention;

5 [0013] Figure 5 is a schematic illustration of an experimental method of determining halogen breakthrough in a halogen scavenger used in one embodiment of the invention;

[0014] Figure 6 is a photograph of a tube of CuBr that has been exposed to a bromine/nitrogen stream, according to one aspect of the invention.

DETAILED DESCRIPTION OF THE INVENTION

10 [0015] In the novel process of this invention, one or more light gases are separated from bromine or chlorine by physically separating a feed of the halogen containing one or more light gases into a liquid and a vapor, the liquid containing a major amount of halogen and no more than a minor amount of light gas(es), and the vapor containing a major amount of light gas(es) and no more than a minor amount of halogen. Additional halogen is removed from the vapor by passing it through a chemical scrubber containing a halogen scavenger. As used
15 herein, a "light gas" is one having a lower boiling point than the halogen with which it is mixed. The boiling points of bromine and chlorine at atmospheric pressure approximately 59 °C and -34 °C, respectively. Included in the definition are such gases as nitrogen (N₂), carbon dioxide (CO₂), and "light hydrocarbons" -- C₁ - C₄ hydrocarbons, with the caveat that
20 C₄ hydrocarbons (butanes and butenes) are not considered "light gases" if chlorine is the halogen of interest, as the boiling point of chlorine is less than that of C₄ hydrocarbons. The terms "major amount" and "minor amount" are relative; a liquid (or vapor) containing a major amount of a first component and a minor amount of a second component contains more of the first component than of the second component. In general, in most of the embodiments of the
25 invention, a given liquid (or vapor) phase will consist *predominately* of one component (halogen or light gas(es), with very little of the other component.

[0016] One embodiment of the present invention is illustrated in Figure 1, which depicts a system 10 for separating light gases (in this case, nitrogen and carbon dioxide) from bromine. A feed 12 of bromine containing N₂ and CO₂ is provided to a distillation column 14
30 having a top 16 and a bottom 18. Heat exchangers 20 and 22 act as partial condenser and total reflux, respectively, allowing a liquid "bottoms" enriched in bromine (and containing no more than a minor amount of light gases -- typically, no more than the solubility limit of the two gases in bromine) to be withdrawn from the distillation column, with additional lowering of temperature achieved by heat exchanger 24.

35 [0017] At the top of the column, total reflux of the liquid from the reflux drum is facilitated by heat exchanger 22, yielding a vapor enriched in light gases (and containing no more than a minor amount of bromine), which is routed to a chemical scrubber 26, where the

1 minor amount of bromine is removed, yielding a light gas (nitrogen and carbon dioxide output). As described below, bromine can be recovered from the scrubber by heating it.

[0018] In another embodiment of the invention (not shown) two or more distillation columns are connected in series, with the head (vapor) of each column being routed as a feed
5 into the next column, for continual light gas-enrichment of the vapor and bromine-enrichment of the "bottoms" stream from each column.

[0019] For a distillation set-up, typical pressures range from 0.1 bar to 50 bar, more preferably 5 to 20 bar, with a temperature dependent on the distillation system pressure, keeping in mind that the normal boiling point of bromine is approximately 59°C. The
10 number of stages can range from 2 to 200, more preferably 5 to 30.

[0020] Figure 2 illustrates a variation on the embodiment shown in Figure 2, with the halogen feed (e.g., Br₂) coming from a halogen regeneration unit 28. In this embodiment, the halogen feed from 28 contains water, which is removed in a water adsorption unit (containing a desiccant). Alternatively, the feed is first distilled to remove the bromine from the water, up
15 to the limits of the bromine-water azeotrope that forms, with residual water being removed in a water-sorbing column of desiccant.

[0021] In an alternate embodiment of the invention, one or more vapor-liquid flash separation units ("flash vaporizers") are used to separate the feed of halogen and light gases, followed by additional separation in the chemical scrubber. Figure 3 illustrates one such a
20 system 50, in which a feed of bromine, containing nitrogen and carbon dioxide, is provided to a first flash vaporizer 52. The contents of the vaporizer are flashed, yielding a first liquid enriched in bromine (e.g., 97% Br₂ recovery), and a first light gas-enriched vapor (N₂, CO₂) containing only a minor amount of bromine. The first vapor is fed to a second flash vaporizer and the contents are flashed, yielding a second bromine-enriched liquid (where, e.g., an
25 additional 1.5% Br₂ is recovered) and a second light-gas enriched vapor, which passes through a second heat exchanger 58 and then fed to a third flash vaporizer 60. The contents of the third flash vaporizer are then flashed, yielding, e.g., an additional 0.5% Br₂ (liquid) and a vapor very highly enriched in light gases. The trace amount of bromine in this third stream of vapor is removed in a bromine scrubber 62.

[0022] If desired, additional flash vaporizers can be utilized. As a practical matter, however, there is a point of diminishing returns (in terms of the amount of additional bromine recovered) beyond which increased capital requirements and operating expenses will likely
30 not be justified.

[0023] Mixed systems, employing both distillation column(s) and flash vaporizer(s), can
35 be used.

[0024] In general, for the separation of light gases from bromine, each flash vaporizer is operated at a temperature of from -60°C to 40°C, more preferably -20°C to 10°C and a pressure of 0.1 to 50 bar, more preferably 5 to 20 bar, keeping in mind the differences in

1 boiling points between the halogen and the contained light gas(es). One to three flashes are
preferred. The pressure can be varied in the flashes; however, to reduce costs, it is desirable
to operate the flashes at the system pressure to avoid compression, which is expensive. The
temperature for operating the flashes is dependent on the pressure. For example, a high-
5 pressure operation can allow good bromine separation even at modestly high temperatures.
For lower pressures, however, a refrigerant may be needed for cooling the flash units. The
series of vapor-liquid flashes can consist of one or more flashes.

[0025] An important aspect of this invention is the method of chemically scrubbing
bromine or chlorine) from a very dilute gas stream consisting mostly of light gases. The
10 method uses a halogen scavenger capable of sorbing halogen. Preferably, the scavenger
absorbs bromine vapors from the diluted gas stream and then can reversibly release it back as
free bromine, quantitatively. Adsorption of bromine can occur at room or elevated
temperature.

[0026] In general, any material capable of reacting with bromine and releasing it upon
15 heating can be used as bromine scavenger. Nonlimiting examples of materials considered to
be suitable for use as halogen scavengers include CuBr, CuCl, FeBr₂, FeCl₂, AuCl, AuBr,
InBr, InCl, FeO, Cu₂O, Hg₂Br₂, Cu, Ag, Au, Hg, Pt, Pd, Ru, Rh, Fe, Os, and Ir, used alone or
in combination. At present, CuBr is preferred. If copper bromide with high surface area (on
a support) is used, much higher activity is observed even though the total amount of copper
20 bromide is much smaller. It has also been found that CuBr made by a precipitation process is
better than stock CuBr.

[0027] Copper (I) bromide reacts with bromine to form copper (II) bromide according to
the following reaction: $2\text{CuBr} + \text{Br}_2 \rightarrow 2\text{CuBr}_2$. The reaction is quick and complete and,
advantageously, occurs at low temperatures. The reaction appears to be surface-bound.

25 When using bulk CuBr, approximately 1% of the solid is used before breakthrough occurs.
(The density of CuBr and CuBr₂ is very similar and the surface does not refresh well; 4.6
versus 4.0 g/cm³). Because the reaction of CuBr with Br₂ vapor is a reaction of a gas with a
solid, the reaction rate is limited by the solid-gas interface and, correspondingly, the higher
the surface area, the higher the reactivity. Indeed, large crystals of neat CuBr are the least
30 effective adsorbent. When breakthrough occurs (Br₂ is no longer retained by the solid), the
amount of spent CuBr is approximately 0.2% of the total solid capacity, which means that
only the surface of the solid participates in the reaction. The low reaction temperature
dismisses the possibility of ion migration and use of the remaining present bulk CuBr.

[0028] The ability of CuBr to sorb Br₂ at low temperatures is advantageous in part
35 because the inert gas stream (containing a trace amount of bromine) that comes out of the
bromine separation is at a low or ambient temperature; therefore, operating the scrubber at or
near ambient temperatures requires no additional energy input.

[0029] The scrubbed bromine is recovered by regenerating the solid (in this case copper (II) bromide) by heating it to above 250 °C, typically from 250°C to 275°C. The regeneration reaction is: $2\text{CuBr}_2 \xrightarrow{\text{heat}} 2\text{CuBr} + \text{Br}_2$. Where copper bromide is the scavenger, the regeneration is thermally activated and does not require oxygen.

[0030] The halogen scavenger can be used as a bulk powder or deposited on a support. Nonlimiting examples include silica, alumina, zirconia, titania, WO_3 , CaO , MgO , Cr_2O_3 , and various carbides, nitrides, and similar materials. The primary requirement is that the support have a surface area of from 5 to 1500 M^2/g . In our experiments we have used solid Cu(I)Br or Cu(I)Br deposited on Davicat SiZr4700 or Davicat Si1151A (Davidson Corporation), silicas with high surface area (approximately 300 m^2/g . Si4700B contains ~3wt.% ZrO_2 . Other supports should be equally effective in carrying out the scrubbing reaction over copper bromide.

[0031] The halogen scavenger, or scavenger plus support, can be utilized in a packed column reactor configuration or other configurations, such as a shell and tube reactor. Standard heat transfer mediums can be used to deliver the required heat to bring the active ingredients of the scrubber to the regeneration temperature. The process scheme can include two reactors, in which one undergoes scrubbing, while the other one undergoes regeneration.

[0032] The solid scrubbing agent is capable of completely retaining all bromine content from the inert gas flow (bromine loss from the scrubber was estimated to be less than 1 ppb). Supported copper (I) bromide shows reproducible results after multiple cycles of exhaustion and regeneration.

[0033] When a support (such as silica) is used, the inhomogeneous surface generates nucleation sites which cause the formation of smaller crystallites, with appreciably larger surface area. Even where the supported material contains only 15wt.% CuBr , its higher CuBr surface area renders it a better material for bromine vapor retention.

[0034] To explore the effectiveness of copper (I) bromide as a halogen scavenger, a series of experiments were conducted, using commercially available CuBr , supported CuBr , and CuBr formed by precipitation. The original scavenger (CuBr) was regenerated by heating the CuBr_2 . Results are presented in Table 1.

TABLE 1 - RESULTS OF Br_2 SCAVENGING

<u>Scavenger/Support</u>	<u>Time Exposed to Br_2 Vapor</u>			
	<u>10 min.</u>	<u>20 min.</u>	<u>40 min.</u>	<u>80 min.</u>
CuBr (commercial)	100%	70-75%	not tested	not tested
CuBr/Si4700B	not tested	100%	~100%*	not tested
CuBr/Si1151A	to be tested	to be tested	to be tested	to be tested

1 CuBr, precipitated** 100% 100% 100% 100%

Notes:

The % is the amount of total Br retained by the scavenger.

5 Regeneration is complete at 275°C within 10-15 min.

Several cycles were tested without diminishing in activity for CuBr/4700B.

* - trace of AgBr formed, but the weight measured is $<10^{-4}$ g.

** - after regeneration its effectiveness diminishes to that of the commercial material.

10 [0035] Figure 6 is a photograph of a tube of precipitated CuBr exposed to a bromine/nitrogen stream for thirty minutes at room temperature. The dark material is CuBr₂. Upon heating, the color reverses back to the pale green of CuBr, releasing bromine.

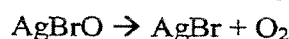
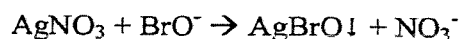
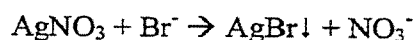
15 [0036] **Experimental Protocol:** 30 sccm/min. N₂ mixed with 1.5 sccm N₂ going through Br₂ bubbler cooled to 0°C. The solid adsorbent bed was contained in a cylindrical glass tube with a diameter of 1 cm. The duration of the exposure to such created diluted bromine in nitrogen was 40 minutes at room temperature. The scrubber treated gas was bubbled through a trap containing 1 M NaOH.

20 [0037] **Preparation of the supported CuBr materials:** The support was dispersed in a ~20 wt.% CuBr₂ solution in water and bubbled with SO₂ until the color of the solution became almost colorless. The suspension was filtered and dried at 115°C overnight.

[0038] **Regeneration:** The regeneration of the retained bromine was conducted by heating the reactor with the solid scrubbing agent after exhaustion at 275°C for 20 minutes. The released bromine was collected and quantified by capturing the released bromine in a 1M NaOH trap solution. Near complete recovery of the captured bromine is possible.

25 [0039] **Quantification:** The amount of bromine not retained by the scrubbing agent or regenerated from the exhausted scrubbing agent was quantified by absorption in a NaOH trap, which at the end was acidified with HNO₃ until the pH dropped to 5 or below followed by precipitation of AgBr using excess 0.5 M AgNO₃ (added until no further precipitation occurred) . The amount of the bromine present was calculated from the mass gain of a glass fritted filter used to filter and dry the precipitate of AgBr until its weight does not change.

30 [0040] Bromine breakthrough is determined by using a precipitation of the Br and BrO⁻ with Ag⁺, wherein, the NaOH trap is acidified with HNO₃ until acidic; AgNO₃ is added until no more precipitation form; the suspension is allowed to age for 40 minutes then filtered on a dry, pre-weighted glass-fritted funnel, dried until constant weight and the mass difference is AgBr.



1 [0041] The solubility constant K_{sp} for AgBr is $5 \times 10^{-13} \text{ mol}^2 \text{ l}^{-2}$. The AgNO_3 solution is
0.5M -3ml (or more) added to a total of ~20-25 ml acidified NaOH trap. The final Ag^+
concentration is ~0.06M. The lowest detectable concentration of Br- is $\sim 8 \times 10^{-12} \text{ M}$ which
5 corresponds to ~0.6 ppb. Even if a non-ideal case is assumed (high ionic, strength, ion
activity different than 1) still the sensitivity is in the ppb range.

Example:

10 [0042] An inert gas stream of nitrogen at a flow rate of 40 sccm (standard cubic cm per
minute) containing approximately 25% bromine by volume was treated according to the
method described in the current embodiment. The stream was cooled to a temperature of 25
°C, which industrially can be accomplished by using an air-cooled heat exchanger. The
stream, which is at a pressure of 25 bar, is then flashed in a single vapor liquid flash unit
operating at a temperature of 5 °C. The liquid outlet from the flash contains more than 98%
of the bromine in the original feed along with some inert gas that is dissolved in the bromine
stream. The vapor stream containing the inert gas and trace bromine was then passed over a
15 bed of supported copper (I) bromide at room temperature. The bromine capture from the
inert gas stream was complete, and the scrubbing bed performed complete bromine capture
for a period of 40 min. The exhausted scrubbing bed containing copper (II) bromide and
copper (I) bromide was heated to 275 °C, and a near complete bromine recovery was
observed in a time period of 15 min.

20 [0043] The invention should find utility in a large number of industrial processes that use
halogens as a feedstock or intermediates for chemicals production, where the halogen
recovery or purification is improved by the removal of inerts or light gases, resulting in
significantly reduced capital and operating costs. Among these are the processes for making
alcohols, ethers, olefins, and alkoxylates described in U.S. Patent Nos. 6,486,368, 6,472,572,
25 6,472,572, 6,465,696, 6,462,243, 6,403,840, and processes for making higher hydrocarbons,
as described in U.S. Patent Application entitled "Continuous Process for Converting
Hydrocarbon Feedstocks into Higher Hydrocarbons and Olefins" (Attorney Docket No.
56987/G506) filed on even date herewith, the entire contents of which are incorporated herein
by this reference. For example, in the process to make gasoline-range hydrocarbons from
30 natural gas, when air is used for regeneration, the nitrogen and carbon dioxide carry forward
into the bromination and the metathesis section. To recycle the unconverted methane,
separation of nitrogen from methane is required, which is cost-intensive. Also, the carbon
dioxide generated during regeneration must be separated from the unconverted methane
either using pressure swing adsorption or by using an amine-based system, both of which are
35 cost intensive. The separation of light gases from bromine not only reduces the reactor size
but also simplifies the separation of light gases from the products and unconverted reactants.
The separation process described herein offers a cost-effective way to separate light gases
(including nitrogen and carbon dioxide) from halogens such as bromine.

1 **[0044]** The invention has been described with various embodiments and examples, but is
not limited thereto. Other modifications, as well as equivalents of the appended claims, are
within the scope of the invention.

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1 CLAIMS

1. A process for separating light gas(es) from bromine or chlorine, comprising:
(a) providing a feed of halogen containing one or more light gases to a
distillation column or flash vaporizer;
5 (b) operating the distillation column or flash vaporizer to separate the feed into
(i) a first liquid containing a major amount of halogen and no more than a minor amount of
light gas(es), and (ii) a first vapor containing a major amount of light gas(es) and no more
than a minor amount of halogen; and
(c) providing the vapor to a chemical scrubber to recover halogen from the
10 vapor.

2. A process as recited in claim 1, further comprising providing the first liquid to
a distillation column or flash vaporizer to separate the first liquid into (i) a second liquid
containing a major amount of halogen and no more than a minor amount of light gas(es), and
15 (ii) a second vapor containing a major amount of light gas(es) and no more than a minor
amount of halogen; and
(c) providing the second vapor to a chemical scrubber to recover halogen from
the vapor.

20 3. A process as recited in claim 1, wherein the halogen is bromine.

4. A process as recited in claim 1, wherein the halogen is chlorine.

25 5. A process as recited in claim 1, wherein the light gas(es) comprise nitrogen.

6. A process as recited in claim 1, wherein the light gas(es) comprise nitrogen
and one or more of additional gases selected from the group consisting of carbon dioxide and
C₁ - C₄ hydrocarbons.

30 7. A process as recited in claim 1, wherein the chemical scrubber comprises a
bed of a supported or unsupported chemical scavenger.

8. A process as recited in claim 1, wherein the halogen scavenger comprises a
material selected from the group consisting of CuBr, CuCl, FeBr₂, FeCl₂, AuCl, AuBr, InBr,
35 InCl, FeO, Cu₂O, Hg₂Br₂, Cu, Ag, Au, Hg, Pt, Pd, Ru, Rh, Fe, Os, Ir and mixtures thereof.

9. A process as recited in claim 1, wherein the halogen scavenger comprises
CuBr.

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10. A process as recited in claim 1, wherein the halogen scavenger is supported on a material selected from the group consisting of metal oxides, metal carbides, metal nitrides, carbon, clay, and mixtures thereof.

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11. A process as recited in claim 1, wherein the halogen scavenger is supported on a material selected from the group consisting of Al_2O_3 , SiO_2 , ZrO_2 , TiO_2 , WO_3 , CaO , MgO , Cr_2O_3 , SiC , Mo_4C , TiN , W_2N , carbon, zeolite, vermiculite, and mixtures thereof.

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12. A process as recited in claim 1, further comprising heating the chemical scrubber to release halogen therefrom.

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