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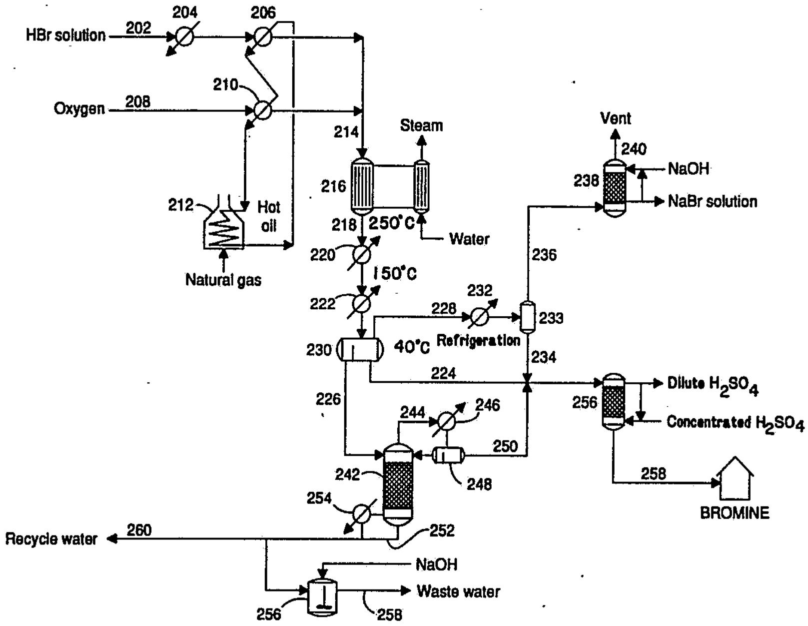
(54) Title: PROCESS AND CATALYST FOR PRODUCING BROMINE

(57) Abstract

This invention is a catalyst and a process using that catalyst for oxidizing hydrogen bromide to form elemental bromide. The inventive catalyst comprises a composition of promoted or stabilized copper bromide on a zirconium-containing support. In the figure, an HBr stream (202) is sent to an evaporator (204) and to a super heater (206). The O_2 feed stream (208) is warmed with heater (210). The O_2 and HBr mixed reactor feed stream (214) is introduced into reactor (216). The reactor stream (218) may be cooled in two stages (220) and (222) and also condensed. The device (230) separates condensed liquid into (224), (226) and (228) streams. The vapor stream (228) is chilled in refrigeration unit (232) to remove Br_2. A resulting Br_2 stream (234) is mixed with stream (224). A non-condensed O_2 vapor stream (236) is scrubbed in a gas treater (238). The treated O_2 is vented (240) or may be recycled to reactor (216). The aqueous stream (226) coming from the separator (230) is then stripped of Br_2 in a distillation column (242) and produces two streams (244) and (250), where (240) is condensed in condenser (246) and collected in drum (248). The stream (250) is mixed with other Br_2 streams (224) and (234) for further treatment in counter-current absorption tower (256) producing a Br_2 product stream (258).



PROCESS AND CATALYST FOR PRODUCING BROMINE

Field of the Invention

This invention is a catalyst and a process using that catalyst for oxidizing hydrogen bromide to form elemental bromine. The inventive catalyst comprises a composition of promoted or stabilized copper bromide on a zirconium-containing support.

Background of the Invention

This invention is both a catalyst and a process for producing elemental bromine from hydrogen bromide using that catalyst. Bromine is a chemical feedstock often used for the production of bromoalkanes or olefins from alkanes. Bromine is found in nature only in dilute sources such as seawater or as brine well deposits. The classic process for obtaining bromine from such sources involves a multistage process involving electrolyzing, chlorinating, or acidifying the seawater or brine to release elemental bromine or hydrogen bromide into a solution, aerating or steaming the resulting dilute solution, absorbing the bromine or hydrogen bromide from the aeration effluent, and distilling the resulting absorbate to recover the bromine.

It is, of course, desirable not to be placed in the position of requiring fresh bromine if another suitable bromine-containing source is available from which to produce elemental bromine. Hydrobromic acid or hydrogen bromide (HBr) is a byproduct of a wide variety of chemical processes. This invention is a process utilizing a hydrogen bromide feed in producing elemental bromine.

There are a number of processes described in the open literature which produce bromine according to the equation:

$$4\ HBr + O_2 \text{ ---> } 2\ Br_2 + 2\ H_2O.$$

One such process (British Patent 930,341) involves the conversion of hydrobromic acid solutions using dissolved metal ion catalysts. The soluble metal may be gold, cerium, chromium, nickel, platinum, thorium, titanium, or vanadium; but preferably is iron or copper. A gas containing oxygen is passed through the acidic solution containing HBr and the dissolved metal, all at a temperature below the boiling point of the acidic solution. The gaseous effluent is then separated via condensation and distillation into the product bromine, water, and HBr which is recycled to the oxidation step.

Similarly, U.S. Pat. No. 3,179,498, to Harding et al., discloses a process in which a nitrite catalyst is employed in an acidic, aqueous solution of HBr to effect the oxidation of the HBr to Br_2. The temperature of the liquid is maintained between 0° and 100°C. Although any inorganic or organic nitrite is said to be suitable, preferred catalysts are alkali metal or alkaline earth metal nitrites.

There are a number of processes which use heterogeneous catalysts to effect the conversion of HBr to Br_2.

U.S. Pat. No. 2,536,457, to Mugdan, teaches such a process. The conversion is carried out at a temperature between 800° and 1200°C (preferably between 800° and 1000°C) with an excess of oxygen. The catalyst is preferably cerium oxide and may be supported on pumice granules or other suitable refractory materials. If excessive water is included in the reactor, a combustible gas such as hydrogen is included to maintain the reaction temperature. Clearly the reaction temperature for this process is quite high.

U.S. Pat. No. 3,273,964, to De Rosset, shows a process in which the effluent from a dehydrobromination reaction is contacted with a catalyst-adsorbent composite. The effluent contains olefinic hydrocarbons and is produced by a series of steps in which an alkane is brominated to form a bromoalkane; the bromoalkane is then dehydrobrominated to form the effluent of olefinic hydrocarbons and HBr. The catalyst-adsorbent composite adsorbs the HBr in a first step and, during regeneration, catalyzes the oxidation of HBr to form the desired Br_2. The composite contains an adsorbent of a basic metal oxide such as magnesium, calcium, or zinc oxide, and a catalyst of a Group IV-B metal oxide such as titania, magnesia, or zirconia. The preferred composite contains magnesia and zirconia in a ratio from about 0.5:1 to about 5:1.

U.S. Pat. No. 3,260,568, to Bloch _et al_, teaches a process in which a stream containing substantially dry HBr is contacted with a solid adsorbent containing a metal "subchloride", which subchloride is the reaction product of a refractory metal oxide and a metal chloride. The contact takes place at conditions where the HBr replaces at least a portion of the chloride in the adsorbent. When the adsorbent has reached about six percent by weight, the adsorbent is regenerated by contacting it with a dry hydrogen chloride gas. The patent does not appear to suggest the conversion of the adsorbed HBr to Br_2. The adsorbent is suggested to be selected from metal chlorides such as aluminum, antimony, beryllium, iron, gallium, tin, titanium, and zinc chlorides.

U.S. Pat. No. 3,310,380, to Lester, discloses a process for the adsorption of combined bromine (e.g., HBr and alkyl bromides) on a catalytic-adsorbent composite, recovering unsaturated hydrocarbons, and when the adsorbent is filled, contacting the composite with an oxygen-containing gas at a temperature between 50° and 450°C to produce a Br_2 stream, also containing water and unreacted HBr. This stream (also in admixture with an oxygen-containing gas) is then contacted with a second stage reactor, also containing the composite, but at a temperature between 200° and 600°C. The composite in the first stage comprises, preferably, 0.5 to 10% by weight of copper or cerium oxide composited on magnesium oxide: the second stage composite comprises, preferably, 2.0 to about 50% by weight of copper or cerium oxide composited on an alumina or zirconia support.

Similarly, U.S. Pat. No. 3,346,340, to Louvar et al, suggests a process for the oxidation of HBr to Br_2 using a catalyst-inert support composite. The composite comprises a copper or cerium oxide on an inert support having a surface area between 5 and 100 square meters per gram and containing less than about 50 micromoles of hydroxyl per gram. The supports may be alpha- or theta-alumina or zirconia. The preferred temperature is between 300° and 600°C.

U.S. Pat. No. 3,353,916, to Lester, discloses a two stage process for oxidizing HBr to form Br_2 by the steps of mixing the HBr-containing gas with an oxygen-containing gas and passing the mixture at a temperature of at least 225°C over a catalyst selected from the oxides and salts of cerium, manganese, chromium, iron, nickel, and cobalt and converting a major portion of the HBr to Br_2. The partially converted gas, still containing excess oxygen, is then passed through a second stage catalyst comprising a copper oxide or salt at a temperature of at least about 225°C but not exceeding a "catalyst peak temperature" of 350°C to convert the remaining HBr. The preferred support appears to be zirconia.

This two-stage arrangement is carried out to prevent loss of the copper catalyst. Because the preferred copper oxide is converted to copper bromide during the course of the reaction, at reaction conditions, and copper bromide volatilizes at "temperatures in excess of about 350°C", the "copper bromide migrates through the catalyst mass in the direction of flow with eventual loss of copper bromide and premature deactivation." Use of a first catalyst stage which is tolerant of high temperatures, although apparently not as active a catalyst as is copper, allows a cooler second catalyst stage containing copper to complete "quantitative conversion of bromine from hydrogen bromide."

U.S. Pat. No. 3,379,506, to Massonne et al, teaches a process for the selective oxidation of hydrogen bromide to bromine in the presence of fluorocarbons by passing the mixture of gases over a Deacon catalyst at a temperature of 250° to 500°C, preferably between 300 and 400°C. The Deacon catalyst is said to be a "mostly porous carrier such as pumice, alumina, silica gel, clay, or bentonite, impregnated with a solution of bromides or chlorides of metals such as copper, iron, titanium, vanadium, chromium, manganese, cobalt, molybdenum, tungsten, or mixtures thereof." The preferred catalyst is said to be a chloride of copper. The patent notes that:

> "[a] very efficient and stable catalyst is an oxidation catalyst which is prepared by impregnating active alumina with chlorides of copper, rare earths and\or alkali metals, drying at about 120°C and subsequent activation at a temperature of 300° to 450°C."

One example shows the production and use of a catalyst of alumina, potassium, copper, and an amount of "rare earths of the cerite group as chlorides".

Another patent which notes the problem with the volatilization of copper bromide in the oxidation of hydrogen bromide to bromine is U.S. Pat. No. 3,437,445, to Hay et al. The solution is to eliminate the copper in favor of a noble metal, such as platinum and palladium. The reaction is carried out at a temperature between about 175° and about 700°C, with a contact time of at least about 0.1 sec, "but for best operation a contact time of about five and 25 seconds is preferred." The yield of bromine is only between 28 and 78 molar percentage.

U.S. Pat. No. 4,131,626, to Sharma et al, suggests a process in which bromide salts are heated in the presence of an oxygen-containing gas, silicon dioxide, and an oxidation catalyst at a temperature of about 500° to 1000°C. The bromine is produced in conjunction with sodium silicate.

None of these documents suggest a catalytic HBr oxidation process in which the catalyst comprises a stabilized or promoted copper bromide on a zirconia support. Furthermore, none of those disclosures show a process in which the copper bromide is as stable nor produces Br_2 in as efficient a yield as is done by our process.

Summary of the Invention

This invention is a catalyst and a process for oxidizing hydrogen bromide to form elemental bromine using that catalyst. The catalyst composition comprises copper bromide stabilized or promoted by one or more of calcium-, yttrium-, and/or rare earth-containing materials or metals having an ionic radius between 0.9 and 1.4 Å. The composition utilizes a zirconium-containing support.

In the inventive process, hydrogen bromide is vaporized and mixed with an oxygen-containing gas and heated to a temperature between 125° and 475°C or more. The heated gas mixture is passed over the catalyst at conditions suitable for the formation of bromine. The bromine may then be separated from the co-produced water.

Brief Description of the Drawings

Figure 1 shows a block diagram of a generic embodiment of the inventive process.

Figures 2 and 3 depict a schematic diagrams of the preferred process embodiments of this invention.

Figure 4 is a graph depicting the reaction rate for a set of $CuBr_2$ catalyst compositions as a function of the ionic radius of the catalyst promoters.

Figure 5 shows the reaction rate for a desired catalyst as a function of temperature.

Figure 6 is a graph showing the effect of organic bromide impurities on the rate of HBr conversion to Br_2.

Figure 7 is a graph showing the effect of organic bromide impurities on the reaction temperature.

Description of the Invention

As noted above, this invention is a catalyst composition and a process for oxidizing hydrogen bromide with an oxygen-containing gas to form elemental bromine using that catalyst composition according to the equation:

$$4\ HBr + O_2 \text{ ---> } 2\ Br_2 + 2\ H_2O.$$

The catalyst comprises copper bromide stabilized and promoted by one or more promoters, and utilizes a zirconium-containing support.

The Catalyst

The catalyst of this invention is exceptionally stable at the temperatures of operation. Unlike the catalysts of the prior art, the copper bromide does not substantially migrate from the catalyst composition nor among different regions of the catalyst and is very active. The exceptionally high activity of the catalyst composition permits the use of comparatively lower temperatures thereby enhancing, even more, the catalyst's stability.

Unlike other catalysts in this art, the inventive catalyst is produced by placing copper bromide directly onto the support, and is not made by converting another copper-bearing material into copper bromide on the support. Although we believe that the direct addition of the copper bromide to the support is critical to the stability and activity of the catalyst, we do not wish to be bound to that theory. Additionally, the addition of certain promoters to the supported copper bromide catalyst appears to add substantial stability to the catalyst. Finally, although the support most desirably comprises a zirconium-containing material such as zirconia, other supports are suitable although overall catalyst operation has not been seen to be as good.

Specifically the catalyst is a composite comprising or desirably consisting essentially of copper bromide; promoter/stabilizer selected from materials containing one or more salts, oxides, or complexes of metals selected from Ca, Y, Nd, or La or of metals having an ionic radius between about 0.9 and 1.4 Å; and an oxidic zirconium-containing catalyst support. The preferred promoters are Nd and La. Most preferred is La.

The copper bromide should be present in an least a catalytic amount, that is to say, an amount sufficient at least to catalyze the reaction of HBr and oxygen to produce Br_2. We have found that copper bromide in the amount of 0.1 % to 20 % (by weight) of the overall composition is desirable; 1.0 % to 10 % (by weight) of copper bromide is more desirable and 3.0 % to 6.0 % (by weight) of copper bromide is most desirable.

The presence of other bromide salts, e.g., cerium series metal salts and in particular cerium bromide, in the catalyst composition in amounts suitable to promote or to otherwise enhance the catalytic activity of the catalyst composition is desirable.

We have found that the introduction of the copper catalyst onto the zirconium-containing catalyst support in the form of copper bromide results in a catalyst composition that is both more stable and more active than compositions in which the catalyst is introduced in another form, such as by the oxide. We have additionally found that the x-ray diffraction spectrum (Cu_α) of the catalyst composition does not show the presence of crystalline $CuBr_2$. Specifically, the x-ray diffraction spectrum of crystalline $CuBr_2$ contains the following lines:

2θ (°)	I/I_0
14.485	1.0
29.063	1.0
36.041	0.85

The absence of the most distinctive line ($2\theta = 14.485°$) demonstrates the substantial absence of copper bromide crystallinity. Catalyst compositions prepared using CuO, which converts to copper bromide in the HBr oxidation process, show the presence of that distinctive line ($2\theta = 14.485°$). We believe this to indicate that the copper bromide introduced to the zirconium-containing support, in contrast to copper bromide produced on the support from another material, is essentially amorphous.

We have not, however, found the source of the promoters/stabilizers to be of significant importance. Any salt or complex of the noted metals, whether oil or water soluble, which can be impregnated onto the zirconium-containing support or mixed with the zirconium support, e.g., as by ball milling with the zirconium support precursor, is suitable. The bromide salts are especially suitable, but other halides (iodide or chloride), oxyhalides, oxides, phosphates, sulfides, sulfates, complexes such as acetylacetonates, and the like are also suitable. Lanthanum bromide, oxybromide, oxide, and mixtures are useful and conveniently available. The promoter/stabilizer metal-bearing material should be present in an amount such that the overall content (in whatever form) is desirably between

0.1 % and 20 % (by weight) of the overall composition; 1.0 % to 6.0 % (by weight) is more desirable; 1.0 % to 4.0 % (by weight) is most desirable.

The zirconium-containing support typically should contain more than about 50% (wt) of zirconia. A minor amount of other metal oxides, e.g., alumina, titania, hafnia, yttria, silica, etc., may be included as a binder or extrusion aid or to increase surface area if so desired. We have found that it is very desirable to use a zirconia support which has significant porosity in the range between 30 and 100Å, e.g., > 0.01 cc/gm pore volume in the range of 30 and 100Å pore diameter. The zirconium-containing material may be utilized in any physical form convenient to the process in which it is utilized. Such forms may include tablets, extrudates, raschig or Pall rings, or the like. The reaction is very exothermic and consequently the relative external surface area may be an important consideration in some reactor/process configurations.

The catalyst desirably is prepared by dissolving the appropriate copper and the promoter/stabilizer metal compounds or complexes independently in aqueous HBr solutions and impregnating them into the zirconium-containing catalyst supports. The zirconium-containing catalyst supports should be dried at, e.g., 110° to 135°C in air, before impregnation to allow accurate measurement of the metal content added to the support. The method and sequence of impregnating the support has not been found to be critical. If the various compounds are compatible, e.g., they don't react together and don't precipitate from solution, a single solution containing the metals may be used as the impregnating solution. Depending upon the impregnating procedure chosen, the solutions may be saturated or not. If an incipient wetness method is selected, the amount of solution will match the pore volume of the support requiring that the composition of the solution be adjusted to assure that the amount of metal added to the support is appropriate. If other procedures are elected, saturated solutions may be used and a particular amount of the solutions chosen.

The impregnated support is then dried and ready for use.

Process

The process involves the step of producing Br_2 by oxidizing a vaporous or gaseous HBr stream using an oxygen-containing gas in the presence of the catalyst composition discussed just above. Desirably, although optionally, the process may also comprise HBr feed preparation steps and Br_2 product separation steps.

Figure 1 shows a schematic diagram of a generic embodiment of the process including the optional feed treatment and product Br_2 separation steps. In this process, HBr may be acquired from a variety of sources, such as a byproduct from the bromination of synthetic rubber or hydrocarbons or from other bromide salts or directly from natural sources such as seawater or salt or saltwater deposits. The feed pretreatment steps may include any steps necessary or desirable in performing such functions as concentrating or diluting HBr to an economically appropriate level to send to the oxidizing step, cleansing the feed of hydrocarbons or impurity metals, removal of or conversion of bromide salts to HBr, and the like.

The oxidation step involves the simple expedient of mixing the gaseous or vaporous HBr from the feed preparation step with a suitable amount of an oxygen-containing gas, such as air, oxygen-enhanced air, or oxygen and passing the mixture to the catalyst. The O_2 is desirably added in an amount producing an $HBr:O_2$ molar ratio of between about 3.00 and 4.25. The O_2 may be present in excess not only to assist in the HBr oxidation but also to oxidize any hydrocarbonaceous materials present in the feedstream. Nevertheless an HBr:O_2 molar ratio of between above 3.9 and up to 4.1 is preferred.

In any event, the HBr-O_2 mixture is then passed through one or more beds of the catalysts described above. As noted elsewhere, this reaction is highly exothermic. The temperature in the reactor may be controlled in a variety of ways. For instance, if an adiabatic reactor is desired, the feed HBr likely will need be diluted with steam, nitrogen, air, product stream recycle, or the like to prevent excessive temperature rise in the reactor. Specifically, the HBr feedstream may have an HBr content of between 25% and 99.5% (wt) but desirably has an HBr content between 35% and 55% (wt) but most preferably between 45% and 55% (wt). Use of anhydrous (or highly concentrated) HBr and pure O_2 as the oxidant is difficult in that the temperature rise in an adiabatic reactor is nearly 2000°C; even the use of air and anhydrous HBr results in an adiabatic temperature rise of 1000°C -- a possible but unlikely candidate for ease of operation. Consequently, the use of air and an HBr feed of between 45% and 55% (wt) is very desirable and readily operable.

In other reactor configurations, some provision may be made for removing or controlling the heat of reaction, e.g., by inclusion of the bed or beds in an appropriately cooled heat exchanger (such as by tubes of catalyst in a steam generator), by adding the oxygen-containing gas in a series of steps with cooling steps amongst sequential catalyst beds, etc. The catalyst bed or beds may be fluidized or ebullated if so desired. Fluidization allows superior control of the bed temperature and prevents the occurrence of "hot-spots" in the catalyst.

The materials of construction for the reactor should be selected using normal materials criteria but bearing in mind that the system is fairly corrosive. For instance, if the reactor is operated at the lower end of the reaction range noted above and the reactor is a nickel alloy, the reactor should be maintained above the temperature of condensation lest liquid phase corrosion occur. Similarly, the upper range of temperature should be controlled to prevent vapor phase corrosion. If a ceramic system is chosen, similar criteria are applicable to prevent dissolution of the ceramic or to prevent creep of the polymeric seals used at joints and flanges.

The product separations stage may include the generic steps of quenching the reactor product, recovering and concentrating the Br_2, and recovering materials such as HBr for recycle.

Figures 2 and 3 show desirable integrated processes for the oxidation of HBr to Br_2 using the catalyst described above. Figure 2 shows a process using reasonably pure O_2 as the process feed; Figure 3 shows a process in which air is the process feed. The inventive process may be designed to handle intermittent or variably flowing HBr feedstreams as might be encountered if the process were used as a method of regenerating an HBr stream emanating from a batch process. The aqueous HBr streams used in the process integrate nicely between the recycle steps found in the product recovery section and the absorption steps of the feed preparation stage.

Oxygen Process

In this embodiment of the inventive process, shown in Figure 2, an HBr stream (202) is introduced from outside the battery limits. Depending upon the source and quality of the feedstream, it may be desirable to submit the feed to preliminary treatment. For instance, if the feed contains HCl, it may be treated in the feed pretreatment section to remove the HCl or the HCl may pass through the remainder of the operational steps and be removed in the bromine recovery section. If the stream is not pure or if the selected process design so requires, the feedstream may be treated using known techniques to raise or to lower the HBr concentration or to remove various inorganic and organic impurities.

In any event, the HBr feedstream (preferably of about 48% HBr in water) is sent to an evaporator (204) and to a superheater (206). The resulting HBr vapor should be at a temperature of about 230-250°C. The oxygen feedstream (208) is similarly warmed to about 230-250°C with superheater (210). The heat for superheaters (206) and (210) may, for instance, be supplied by a circulating hot oil system including hot oil heater (212).

The heated HBr feedstream and the heated oxygen feedstream are then mixed to form a reactor feedstream (214) which is then introduced into reactor (216). The reactor (216) is desirably of a multi-tube design containing the catalyst described above or may be of a multi-bed design. Since the reaction is quite exothermic, reactor designs which are capable of removing the heat of reaction from the catalyst mass are obviously very desirable. The reactor design shown is also used as a steam generator.

The reaction product stream (218) may then be cooled in two stages. The first stage of cooling (220) shown is a desuperheater and merely lowers the temperature of the stream down to the neighborhood of the stream's dew point, e.g., about 150°C. This stream is then condensed and cooled to a temperature of about 40°C in condenser (222).

The condensate is then separated into a liquid Br_2 stream (224) saturated with water, a water stream (226) saturated with Br_2, and a vaporous vent stream (228) containing unreacted oxygen, bromine, water, and a small amount of inerts. The device used for that separation (230) may be a simple phase separation device such as a decanter. Other density separation devices are just as suitable.

The vapor stream (228) is then chilled in refrigeration unit (232) to a temperature sufficient to remove most of the Br_2 found in the vent stream. The condensed Br_2 stream is separated in drum (232) and the resulting Br_2 stream (234) is mixed with Br_2 stream (224) for further processing. The resulting non-condensed oxygen vapor stream (236) is scrubbed in a gas treater (238) using, for instance, sodium hydroxide to remove any remaining Br_2 before the treated oxygen is vented (240) into the atmosphere. The vent gas treatment step may be omitted and the oxygen may be recycled into the reactor (216) if the oxygen is of sufficient purity.

The aqueous stream (226) coming from the separator (230) is then stripped of its Br_2 content in a distillation column (242). Distillation column (242) produces two streams. The overhead vapor stream (244) is condensed in overhead condenser (246) and collected in reflux drum (248). The reflux drum (248) is a decanter design. The lighter phase is largely water and is recycled to the distillation tower (242) as reflux. The heavier phase is Br_2 and the stream (250) is mixed with other Br_2 streams, (224) and (234), for further treatment such as by drying with strong H_2SO_4 in a countercurrent absorption tower (256). The tower produces a weaker H_2SO_4 stream and the desired Br_2 product stream (258).

The bottom stream (252) from distillation tower (242) is partially reboiled in reboiler (254). The remainder of the stream is mostly water containing unconverted HBr feed and the water of reaction formed in the reactor (216). All or a portion of this stream may be treated by neutralization with, e.g., caustic soda, to produce a waste water stream (258). If the inventive process is used as an integrated portion of a process which is capable of using a dilute HBr, the dilute HBr stream may be so recycled.

There are other ways of eliminating the water produced in the reactor. For instance, by operating separator (232) at different conditions, e.g., at a temperature above 40°C, the overhead stream (236) will contain the water of reaction.

Air Process

The process is preferably operated using a less concentrated oxygen feedstream, e.g., air or oxygen-enriched air. This variation is shown in Figure 3.

In a general sense, the process scheme is similar to that used in the oxygen process described above. The reactor and condensation sections are identical.

As above, an HBr feedstream is sent to an evaporator (304) and to a superheater (306). The air feedstream (308) is compressed in compressor (309) and heated in superheater (310). The heat for superheaters (306) and (310) may, for instance, be supplied by a circulating hot oil system including hot oil heater (312).

The heated HBr feedstream and the heated oxygen feedstream are then mixed to form a reactor feedstream (314) which is then introduced into reactor (316). The reactor (316) is desirably of a design similar to that described above although because of the additional diluent in the feedstream is a little less sensitive to reactor design, but those which are capable of removing the heat of reaction from the catalyst mass are obviously very desirable.

The reaction product stream (318) may then be cooled in two stages. The first stage of cooling (320) shown is a desuperheater and lowers the temperature of the stream down to the neighborhood of the stream's dew point, e.g., about 150°C. This stream is then condensed and cooled to a temperature of about 40°C in condenser (322). The condensed reactor product stream (324) is fed to a phase separator (326) where it is separated into an aqueous stream (328) saturated in Br_2 and containing any unconverted HBr and an overhead vapor stream (330) containing all of the Br_2.

The aqueous stream (328) may be treated in a manner similar to that discussed above. The aqueous stream (328) coming from the separator (326) is stripped of its Br_2 content in a distillation column (330). Distillation column (330) produces an overhead vapor stream (332) which is condensed in overhead condenser (334) and collected in reflux drum (336). Water from the drum is recycled to the distillation tower (330) as reflux. The Br_2 stream (338) is mixed with other Br_2 streams for further treatment such as drying.

The bottom stream (340) from distillation tower (330) is reboiled. The stream is mostly water and contains unconverted HBr feed and the water of reaction formed in the reactor (316). All or a portion of this stream (342) may be neutralized to produce a waste water stream (346) or maybe recycled via line (348).

Returning to the phase separator (326), the overhead vapor stream (N_2, Br_2, and H_2O) may be introduced into the bottom of an absorption column (350) where cold (-15°C) lean NaBr brine (352) is fed into the top to act as absorption media for Br_2. The overhead stream (354) is substantially free of Br_2.

The bottom stream (356) is heated [preferably in feed-effluent heat exchanger (358) with the heat from the bottom of stripper column (360)] and introduced into stripper column (360). In that column, Br_2 is stripped from the NaBr brine into an overhead stream (362). That steam is condensed in exchanger (364) and collected in reflux vessel (366). The water stream is decanted in reflux vessel (366) and is both used as reflux in stripper tower (360) and in the feed to distillation tower (330).

The vapor line (368) from the reflux drum (366) may be mixed with the overhead vapor stream (354) from absorber (350) and treated by neutralization in absorber (370) to remove any remaining HBr before disposing of the N_2 via vent (372).

The decanted Br_2 (374) from reflux vessel (366) may be mixed with the Br_2 stream (338) from reflux vessel (336) and treated with concentrated H_2SO_4 in absorber (376) to remove water and produce the dry product Br_2.

This process is a desirable embodiment of the overall concept of the invention. There are others which are suitable for synthesizing the desired Br_2 product from a bromine-containing feed.

The invention has been disclosed by direct description. Below may be found a number of examples showing various aspects of the invention. The examples are only examples of the invention and are not to be used to limit the scope of the invention in any way.

EXAMPLES

Example 1

This example compares the reaction rates of three different HBr oxidation catalysts made using two different copper compounds -- CuO and $CuBr_2$ -- on a ZrO_2 support. This example shows that the $CuBr_2$ catalyst is more productive on a ZrO_2 support than is a catalyst which is initially in the form of CuO, whether the CuO is supported on a ZrO_2 or coprecipitated with ZrO_2. This is true even though the CuO is believed largely to become $CuBr_2$ in situ during the term of the reaction.

The coprecipitated CuO/ZrO_2 catalyst (catalyst A) was prepared generally using the co-precipitation procedure found in U.S. Pat. No. 3,346,340, specifically as follows. An amount of $ZrOCl_2 \bullet 8H_2O$ (126.07 gm) was dissolved in 140 ml of distilled water. Additionally, 4.58 gm of $Cu(NO_3)_2 \bullet 2.5H_2O$ was dissolved in 7 ml of distilled water and combined with the first solution. A caustic solution of 121.23 gm of 50% NaOH was diluted to about 500 ml and magnetically stirred. The Cu/Zr solution was slowly added to the caustic solution. The solid which formed was powder blue. The solids were separated by centrifugation and washed several times using a mild caustic solution (7.2 gm of 50% NaOH diluted to about 1 liter) using a process of reslurrying, centrifuging, and discarding the liquid. The solids were dried in a 130°C oven for about 14 hours, in air and then pressed in to a cake using 24 klb/in^2 of pressure. The wafers were crushed and sieved to 10-20 mesh and calcined at 600°C for about 2.5 hours. The color of the catalyst was gray.

Catalyst B was prepared by first crushing zirconia extrudates containing 2% alumina (from Alfa) and screening the crushed extrudates to 10-20 mesh. A solution of 2.71 g of $Cu(NO_3) \bullet 2.5\ H_2O$ dissolved in 2.62 g of H_2O was added to a 30.8332 g sample of the crushed zirconia particles. Additional water was added slowly until all of the particles were just wetted. The sample was placed in a beaker and placed in an oven at 130°C for about 14 hours. The dried sample was removed from the oven and calcined at 600°C for 2 hours. The finished catalyst nominally contained 3% CuO.

Catalyst C was prepared by the same process as catalyst B, except that $CuBr_2$ was used in place of $Cu(NO_3)\cdot 2.5\ H_2O$. The $CuBr_2$ was added in sufficient quantity to give the same molar ratio of Cu to zirconia on the finished catalyst as for Catalyst B.

The catalysts were then tested for activity using the following procedure:

A 1 cm OD by 45 cm long glass reactor tube was filled to about its length-wise center with glass beads. A glass wool plug was then inserted. About 1 cc of catalyst was placed on the glass wool. Another glass wool plug was placed over the catalyst bed. The remainder of the glass tube was packed with glass beads. The glass reactor was then placed in a tube furnace with an aluminum sleeve between the outer reactor wall and the inner wall of the furnace to aid in heat distribution. A thermocouple was included at the center of the catalyst bed. A 48% HBr solution was delivered to the reactor at a rate of 5 cc/hr using a syringe pump. Oxygen was fed to the reactor using a mass flow controller. The feeds were added such that a molar ratio of about $1.2:4::O_2:HBr$ was produced. The reaction products and unreacted feed materials were condensed in traps containing KI. In the traps, the product Br_2 formed reacts there with the KI to form I_3^-. The I_3^- was then titrated with $Na_2S_2O_3$. The amount of bromine formed in the reactor was calculated from the titration results. The reactor effluent was collected in the traps, measured at various intervals, and the reaction rates calculated for each of the three samples. The calculated reaction rate for the samples is shown in Table I.

Table I	
Catalyst Reaction Rates at 300°C	
Catalyst	Reaction Rate (μmol-cc^{-1}-sec^{-1})
Catalyst A - (co-ppt. CuO/ZrO_2)	1.0
Catalyst B - (CuO/ZrO_2)	2.0
Catalyst C - ($CuBr_2/ZrO_2$)	6.2

Catalyst C shows a superior reaction rate although when the reactors were disassembled, the copper in each of the catalysts demonstrated some tendency to migrate and consequently additional work was considered necessary to lessen or eliminate that tendency of the copper to migrate.

Example 2

This Example shows the relationship between the presence of various promoter/stabilizers (and the ionic radius of their respective metals) in a $CuBr_2/ZrO_2$ catalyst with their reaction rate in producing Br_2 from HBr. These data are presented in Figure 4.

The catalysts were made using zirconia extrudates containing 2% alumina as the support. Impregnation solutions were prepared by dissolving copper bromide and the co-promoter salt (bromide or chloride) in sufficient water to impregnate the support to incipient wetness with 0.2 mmoles $CuBr_2$ and 0.6 mmoles of the co-promoter per cc of catalyst. The samples were dried at 130°C overnight and then calcined for two hours at 600°C. The catalytic performance of the samples was tested in the same manner as those in Example 1. The average reaction rate data for a 2 hour test, shown in Table II for 300°C bed temperature, show that the lanthanum bromide co-promoter gave a catalyst with the highest activity. Substantial activity enhancement was also observed with neodymium bromide and calcium bromide, and some improvement with yttrium bromide. The salts of cesium, scandium, lutetium, and magnesium showed poorer performance than the case of no promoter. The ionic radius of the metal bromide co-promoter suggests there is an optimum size for the metal co-promoter ion.

Table II

Catalyst	MBr_x Co-Promoter	Co-Promoter Metal Ionic Radius (Å)	Rate (μmol-cc^{-1}-sec^{-1})
D	none	-	1.38
E	$LaBr_3$	1.06	3.84
F	$NdBr_3$	0.995	3.10
G	$CaBr_2$	0.990	2.87
H	YBr_3	0.930	1.91
I	$LuBr_3$	0.850	1.11
J	$ScCl_3$	0.81	1.00
K	CsBr	1.69	0.66
L	$MgBr_2$	0.660	0.10

There was no visual evidence of migration of the catalyst from any of the catalysts.

Example 3

This example shows the effect of pore size distribution of the zirconia support on the performance of the finished catalyst.

Four different pure zirconia supports with different pore size distributions were used to prepare highly desirable $CuBr_2/LaBr_3/ZrO_2$ catalysts. Supports N, O, and P were tabletted zirconia supports which were ground to give 20-30 mesh particles. These were impregnated with solutions of $CuBr_2$ and $LaBr_3$ to give 0.2 mmoles/cc of $CuBr_2$ and 0.6 mmoles/cc of $LaBr_3$. Support M is a powdered zirconia support. It was impregnated with solutions of $CuBr_2$ and $LaBr_3$ and pressed in a die using a Carver press. This pressing was then ground and sieved to give a 20-30 mesh fraction. The finished catalyst M also had 0.2 mmoles/cc of $CuBr_2$ and 0.6 mmoles/cc of $LaBr_3$. The pore size distributions were determined using a Micromeritics Autopore II 9220 mercury porosimeter. The reactor studies were performed as in Example 1, except the rate of 48% HBr feed was 6 cc/hr, and the rate of O_2 feed was 6 cc/min. The reactor bed temperature was 300°C. The catalytic results in Table III are the average rate measured for a 2 hour test. They show that although all of the $CuBr_2/LaBr_3/ZrO_2$ catalysts gave better performance than Catalyst A, the best performance was obtained with supports having significant porosity in the 30-100 Å range.

Table III			
Sample	Pore Volume (cc/g) 600-1000Å	Pore Volume (cc/g) 30-100Å	Rate (μmol-cc^{-1}-sec^{-1})
Catalyst A	0.081	0.009	1.5
Support M	0.098	0.093	-
Catalyst M	0.085	0.050	4.4
Support N	0.192	0.002	-
Catalyst N	0.131	0.001	2.9
Support O	0.146	0.076	-
Catalyst O	0.144	0.015	5.3
Support P	0.008	0.039	-
Catalyst P	0.008	0.006	5.8

Example 4

This example shows the use of the preferred $CuBr_2/LaBr_3/ZrO_2$ (Catalyst M) catalyst in the temperature range between 150°C and 350°C.

Catalyst M and Catalyst A (a comparative coprecipitated ZrO_2/CuO catalyst) were tested as in Example 1, except the rate of 48% HBr feed was 6 cc/hr, and the rate of O_2 feed was 6 cc/min. The temperature was varied to produce bed temperatures ranging from 150° to about 350°C. Figure 5 shows the average reaction rates for the catalysts as a function of temperature for a 2 hour test.

Example 5

This example shows a long term test of the a highly desired inventive $CuBr_2/LaBr_3/ZrO_2$ catalyst (Catalyst M).

Catalyst M was tested as in Example 1, except the rate of 48% HBr feed was 6 cc/hr, and the rate of O_2 feed was 6 cc/min. The bed temperature was approximately 275°C throughout the 100 hour test. During the test, the syringe pump had to be refilled about every 20 hours. During the refilling period, nitrogen was passed through the reactor. Upon readmittance of HBr to the reactor, an initially lower reaction rate was observed in the first 20 minutes of testing. However, the rate then returned to the rate prior to the refilling of the syringe. The measured rate at intervals over the 100 hours is shown in Table IV. The data show no decrease in activity over the 100 hour run, and perhaps show some increase in activity during that period. This indicates good long term life for the $CuBr_2/LaBr_3/ZrO_2$ Catalyst M.

Table IV

Time on Stream (hrs)	Rate (μmol-cc^{-1}-sec^{-1})
2	2.7
20	3.2
50	2.9
80	3.7
100	4.1

Example 6

This Example gives the comparative x-ray results of several catalysts. Catalysts A, B, and C from Example 1 (after testing) and preferred catalyst M from Example 3 (after 2 hours running time) and from Example 5 (after 5 hours running time) were examined by x-ray diffraction using a Scintag Inc. XDS 2000 x-ray diffractometer. Catalysts A and B showed distinct peaks at $2\theta = 14.485°$ but Catalysts C and M did not exhibit such peaks.

This Example demonstrates that catalysts formulated using CuO converted to $CuBr_2$ of sufficient crystallinity and amount to be detected by x-ray diffraction analysis. When the copper was added initially as copper bromide, it remained amorphous.

Example 7

This Example shows the substantial lack of any effect of iron contaminants on the preferred $CuBr_2/LaBr_3/ZrO_2$ catalyst (Catalyst M).

The catalyst was tested by impregnating samples of the $CuBr_2/LaBr_3/ZrO_2$ (Catalyst M) with aqueous solutions of $FeBr_3$. The sample was dried at 130°C for 2 hours prior to use. The reactor studies were performed as in Example 1, except the rate of 48% HBr feed was 6 cc/hr, and the rate of O_2 feed was 6 cc/min. The reactor bed temperature was 315°C. The data presented in Table V show that the iron impurity had little effect on the catalyst's activity.

Table V

Catalyst	$FeBr_3$ (wt%)	Fe (wt%)	Rate (μmol-cc^{-1}-sec^{-1})
Q	0.3	0.06	6.4
R	0.7	0.13	5.6

Example 8

This example shows the resistance of the preferred $CuBr_2/LaBr_3/ZrO_2$ catalyst (Catalyst M) to deactivation from hydrocarbons which might be present in an industrial HBr stream.

A series of test reactions were conducted in which 6 cc/hr of HBr and a brominated organic were fed over Catalyst M in the presence of 20% excess oxygen. The amount of excess oxygen was based on the amount needed for converting the HBr to Br_2 and for complete combustion of the organic. The brominated organics tested were 1-bromobutane, bromobenzene, and bromoacetic acid. The 1-bromobutane and bromobenzene were fed to the reactor by a different syringe pump than the one used for the 48% HBr feed because those hydrocarbons are not soluble in the aqueous HBr solution. The bromoacetic acid was added to the 48% HBr solution to give a solution containing 2.4 wt% bromoacetic acid. The conditions for the reaction are shown in Table VI. The initial reactor setpoint temperature was 315°C. Operating to achieve partial HBr conversion was needed to determine whether there was any catalytic activity loss with time. Figures 6 and 7 show the results of the organic contaminant experiments. There was no activity loss with any of the hydrocarbons fed. From the increase in bed temperature observed for 1-bromobenzene, it is evident that a substantial amount of the hydrocarbon was combusted. The lesser increase in temperature for the bromoacetic acid suggests that some, but not all of this hydrocarbon was combusted. The lack of a significant increase in bed temperature for the bromobenzene suggested that little if any bromobenzene was combusted. In spite of the different relative amounts of hydrocarbon combustion over the catalyst, no activity loss could be observed over the course of the eight hour tests. This indicates that catalyst M is resistant to deactivation by brominated hydrocarbons.

Table VI		
Brominated Hydrocarbon	Hydrocarbon Feed Rate (cc/hr)	Oxygen Feed Rate (cc/min)
1-bromobenzene	0.1688	16.5
bromobenzene	0.1449	16.5
bromoacetic acid	-	12.5

It should be clear that one having ordinary skill in this art would envision equivalents to the catalysts and processes found in the claims that follow and that those equivalents would be within the scope and spirit of the claimed invention.

WE CLAIM AS OUR INVENTION:

1. An HBr oxidation catalyst composition comprising:
   - a. copper bromide,
   - b. a promoter/stabilizer, and
   - c. an oxidic zirconium-containing catalyst support.

2. The catalyst composition of claim 1 in which the overall copper bromide content of the composition is within the range of about 0.1% to 20% by weight.

3. The catalyst composition of claim 2 in which the overall copper bromide content of the composition is within the range of about 1.0% to 10% by weight.

4. The catalyst composition of claim 3 in which the overall copper bromide content of the composition is within the range of about 3.0% to 6.0% by weight.

5. The catalyst composition of claim 1 in which the promoter/stabilizer comprises a salt, oxide, or complex of one or more metals selected from Ca, Y, Nd, or La or metals having an ionic radius between about 0.9 and 1.4Å.

6. The catalyst composition of claim 5 in which the promoter/stabilizer comprises a salt, oxide, or complex of one or more metals selected from Nd or La.

7. The catalyst composition of claim 2 in which the promoter/stabilizer comprises lanthanum oxide, lanthanum bromide, lanthanum oxybromides, or a mixtures thereof.

8. The catalyst composition of claim 3 in which the promoter/stabilizer comprises lanthanum bromide.

9. The catalyst composition of claim 1 where the zirconium-containing catalyst support comprises zirconia.

10. The catalyst composition of claim 4 where the zirconium-containing catalyst support comprises zirconia.

11. The catalyst composition of claim 5 where the zirconium-containing catalyst support comprises zirconia.

12. The catalyst composition of claim 8 where the zirconium-containing catalyst support comprises zirconia.

13. The catalyst composition of claim 8 having an x-ray diffraction graph with substantially no peak at $2\theta = 14.485°$.

14. The catalyst composition of claim 9 where the porosity of the zirconia is greater than 0.01 cc/gm for pores with diameters between 30 and 100Å.

15. The catalyst composition of claim 11 where the porosity of the zirconia is greater than 0.01 cc/gm for pores with diameters between 30 and 100Å.

16. An HBr oxidation catalyst composition comprising:

a. copper bromide in an amount such that the overall copper bromide content of the composition is within the range of about 0.1% to 20% by weight,

b. a promoter/stabilizer of La or Nd-containing compound selected from oxides, bromides, oxybromides, or mixtures thereof, and

c. a zirconia catalyst support.

17. The catalyst composition of claim 16 in which the overall copper bromide content of the composition is within the range of about 1.0% to 10% by weight.

18. The catalyst composition of claim 17 in which the overall copper bromide content of the composition is within the range of about 3.0% to 6.0% by weight.

19. The catalyst composition of claim 16 where the promoter/stabilizer is a lanthanum-containing compound comprising lanthanum bromide, lanthanum oxybromides, or mixtures thereof.

20. The catalyst composition of claim 16 where its x-ray diffraction graph shows substantially no peak at $2\theta = 14.485°$.

21. The catalyst composition of claim 16 where the porosity of the zirconia is greater than 0.01 cc/gm for pores with diameters between 30 and 100Å.

22. A process for catalytically converting HBr to Br_2 comprising the steps of:

a. contacting a vaporous or gaseous HBr feed and an O_2-containing gas with a catalyst composition comprising copper bromide, a promoter/stabilizer, and an oxidic zirconium-containing catalyst support under conditions sufficient to convert at least a portion of the HBr to Br_2 and produce a reaction effluent stream, and

b. recovering the Br_2 product.

23. The process of claim 22 where the overall copper bromide content of the composition is within the range of about 0.1% to 20% by weight.

24. The process of claim 23 where the overall copper bromide content of the composition is within the range of about 1.0% to 10% by weight.

25. The process of claim 24 where the overall copper bromide content of the composition is within the range of about 3.0% to 6.0% by weight.

26. The process of claim 22 in which the promoter/stabilizer comprises a salt, oxide, or complex of one or more metals selected from Ca, Y, Nd, or La or metals having an ionic radius between about 0.9 and 1.4Å.

27. The process of claim 26 in which the promoter/stabilizer comprises a salt, oxide, or complex of one or more metals selected from Nd or La.

28. The process of claim 27 in which the promoter/stabilizer comprises lanthanum oxide, lanthanum bromide, lanthanum oxybromides, or a mixtures thereof.

29. The process of claim 28 in which the promoter/stabilizer comprises lanthanum bromide.

30. The process of claim 22 where the zirconium-containing catalyst support comprises zirconia.

31. The process of claim 24 where the zirconium-containing catalyst support comprises zirconia.

32. The process of claim 25 where the zirconium-containing catalyst support comprises zirconia.

33. The process of claim 29 where the zirconium-containing catalyst support comprises zirconia.

34. The process of claim 33 having an x-ray diffraction graph with substantially no peak at $2\theta = 14.485°$.

35. The process of claim 30 where the porosity of the zirconia is greater than 0.01 cc/gm for pores with diameters between 30 and 100Å.

36. The process of claim 33 where the porosity of the zirconia is greater than 0.01 cc/gm for pores with diameters between 30 and 100Å.

37. The process of claim 22 in which the molar ratio of $HBr:O_2$ is between about 3.25 and 4.25.

38. The process of claim 37 in which the molar ratio of $HBr:O_2$ is between about 3.9 and 4.1.

39. The process of claim 22 additionally comprising the step of producing HBr feed by acidifying a stream of a bromide salt.

40. The process of claim 22 additionally comprising the steps of absorbing HBr from an HBr stream in an aqueous stream containing HBr to produce an HBr absorbate stream and desorbing HBr from that absorbate stream as needed to produce the HBr feed.

41. The process of claim 22 in which the Br_2 product is effected by quenching the reaction effluent in a quench stream containing HBr and removing unreacted HBr, absorbing Br_2 from the quenched reaction effluent in a stream containing NaBr to form a Br_2 absorbate stream, desorbing Br_2 from the Br_2 absorbate stream, decanting Br_2 from a water phase to produce a Br_2 product stream.

42. The process of claim 30 additionally comprising the step of drying the Br_2 product stream by contacting it with strong H_2SO_4.

43. A process for catalytically converting HBr to Br_2 comprising the steps of:

a. contacting a vaporous or gaseous HBr feed and an O_2-containing gas in a molar ratio of $HBr:O_2$ between about 3.25 and 4.25 with a catalyst composition comprising copper bromide in an amount such that the overall copper bromide content of the composition is within the range of about 0.1% to 20% by weight, a lanthanum-containing compound selected from the group of lanthanum oxide, lanthanum bromide, lanthanum oxybromides, or mixtures thereof, and a zirconia catalyst support, under conditions sufficient to convert at least a portion of the HBr to Br_2 and produce a reaction effluent stream, and

b. quenching the reaction effluent in a quench stream containing HBr and removing unreacted HBr,

c. absorbing Br_2 from the quenched reaction effluent in a stream containing NaBr to form a Br_2 absorbate stream,

d. desorbing Br_2 from the Br_2 absorbate stream,

e. decanting Br_2 from a water phase to produce a Br_2 product stream.

44. The process of claim 43 additionally comprising the step of drying the Br_2 product stream by contacting it with strong H_2SO_4.

45. The process of claim 43 additionally comprising the step of producing HBr feed by acidifying a stream of a bromide salt.

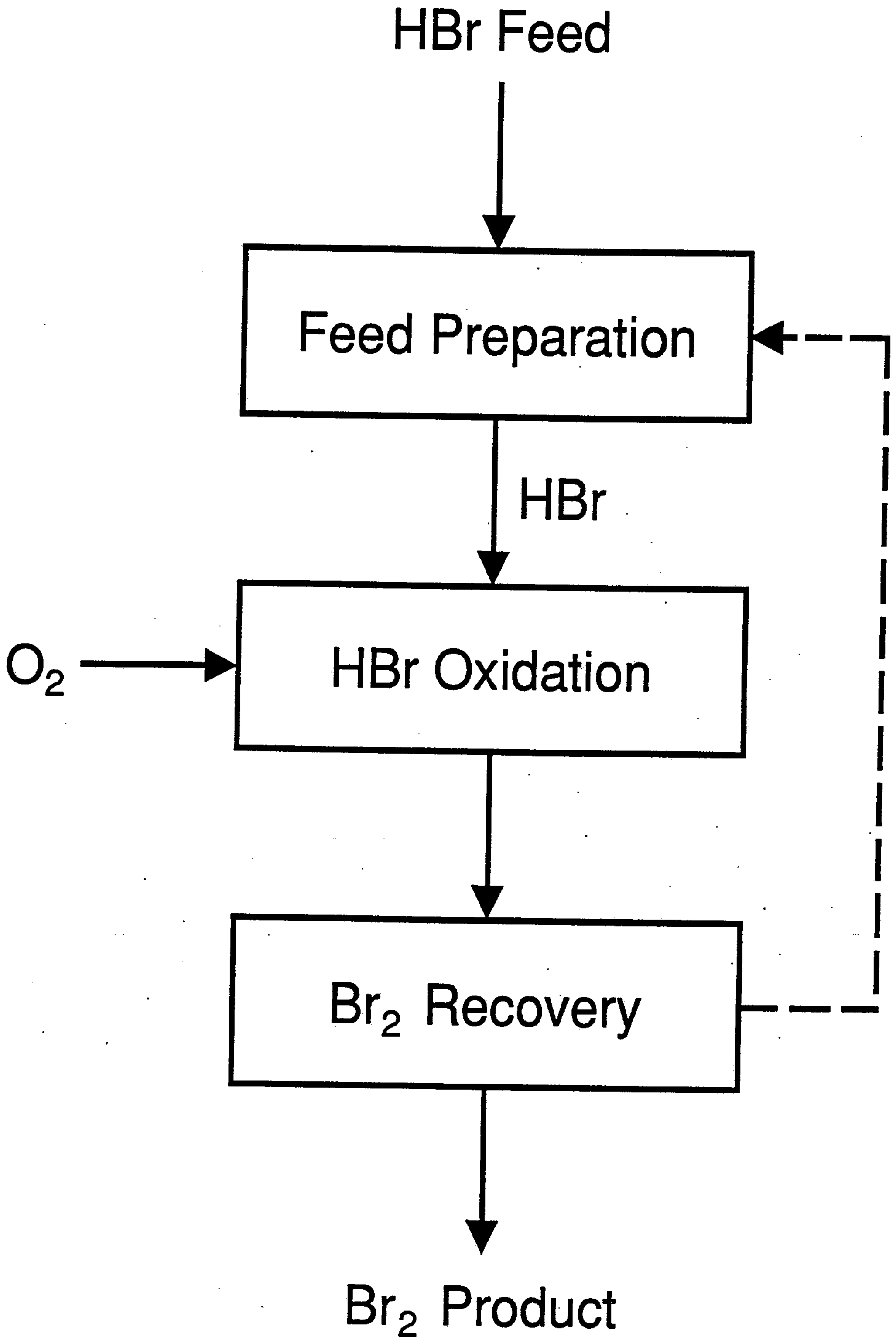

HBr Feed
Feed Preparation
HBr
O_2
HBr Oxidation
Br_2 Recovery
Br_2 Product

Fig. 1

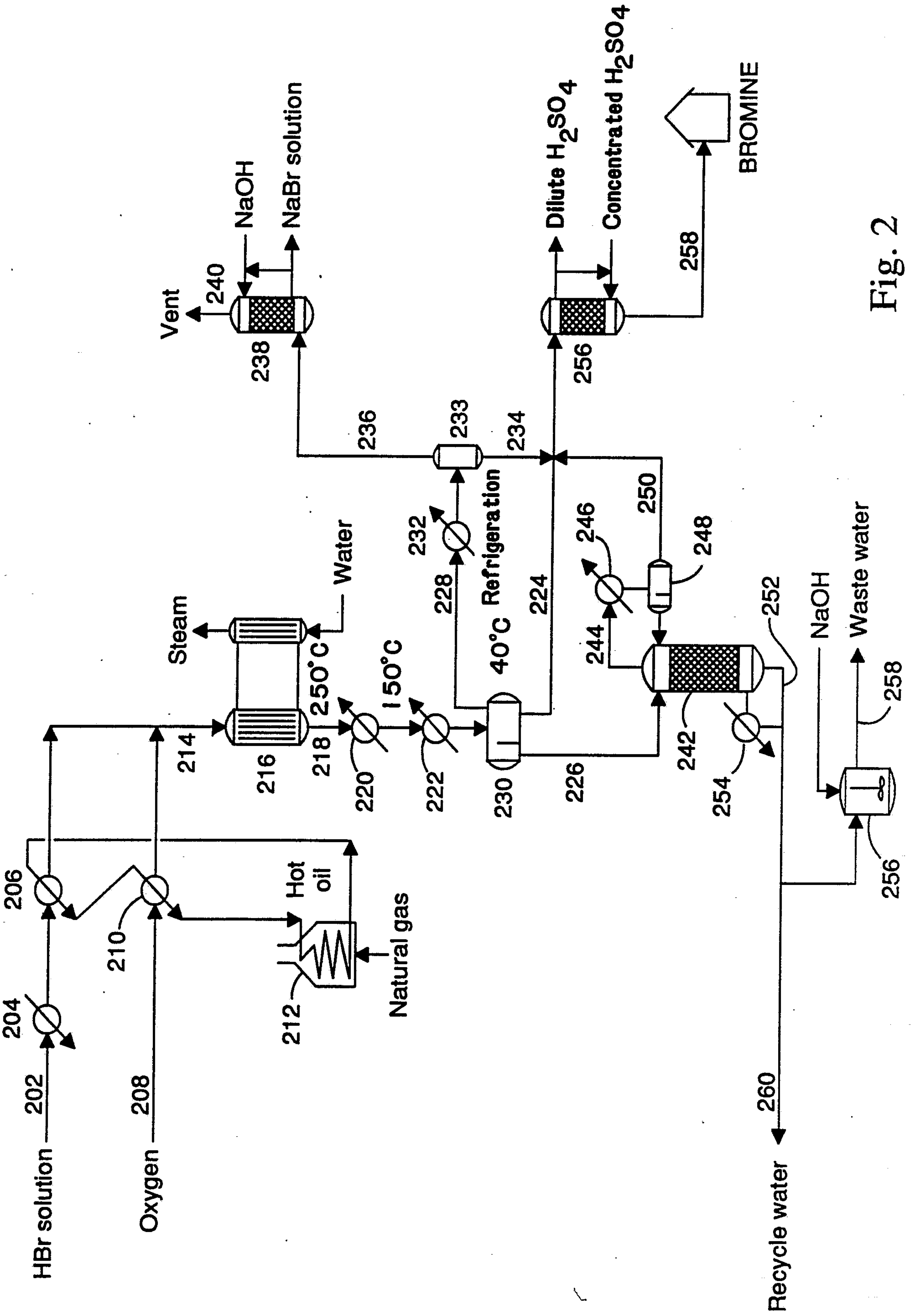

HBr solution
202
204
206
Oxygen
208
210
212
Hot oil
Natural gas
214
216
Steam
Water
218
250°C
220
150°C
222
230
40°C
224
226
228
Refrigeration
232
233
234
236
238
Vent
240
NaOH
NaBr solution
Dilute H_2SO_4
Concentrated H_2SO_4
256
258
BROMINE
242
244
246
248
250
252
254
NaOH
Waste water
258
256
260
Recycle water

Fig. 2

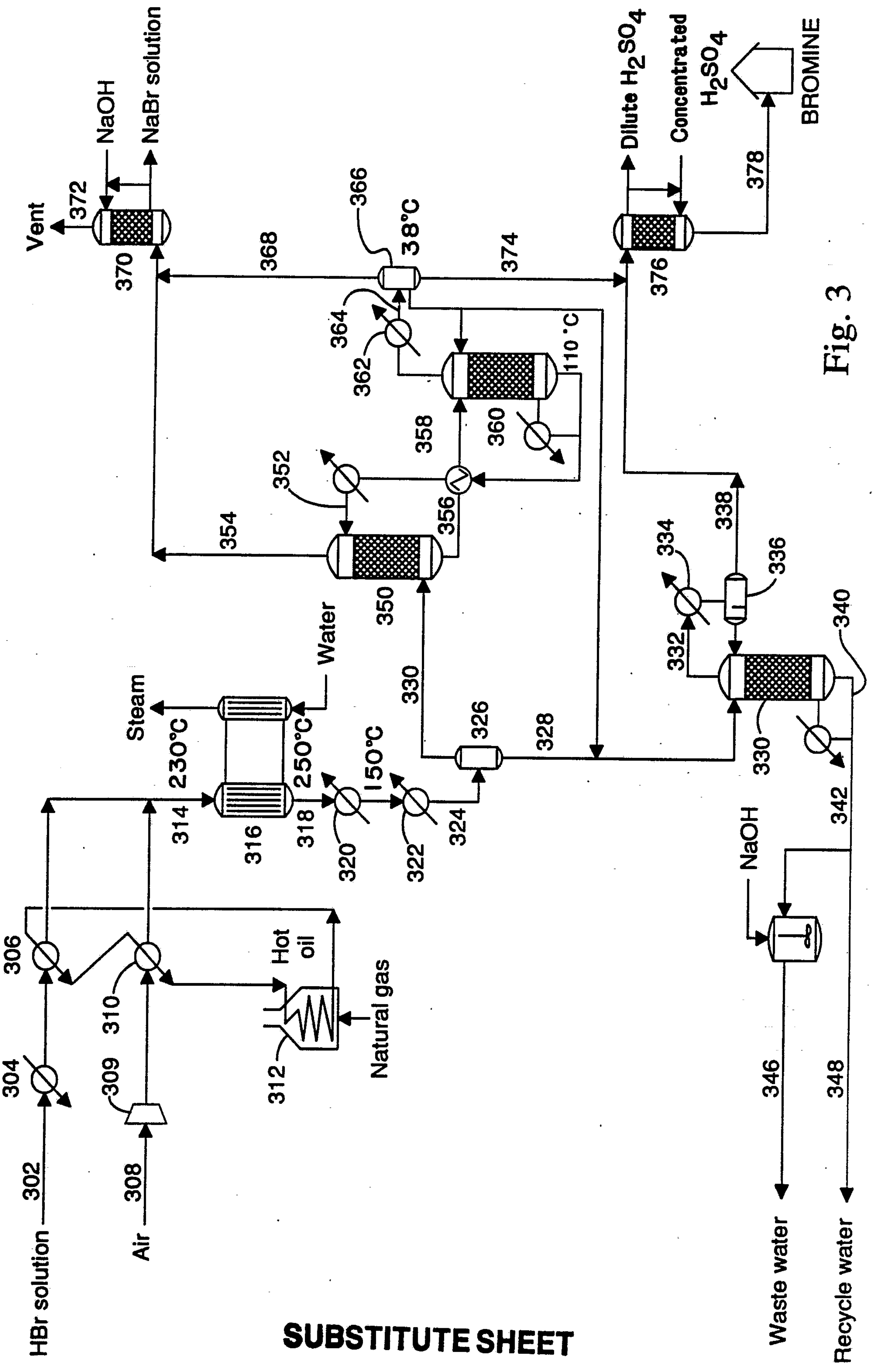

HBr solution
302
304
306
Air
308
309
310
Hot oil
312
Natural gas
314
230°C
316
Steam
Water
250°C
318
320
150°C
322
324
326
328
330
350
352
354
356
358
360
110 °C
362
364
366
38°C
368
370
Vent
372
NaOH
NaBr solution
374
376
Dilute H_2SO_4
Concentrated H_2SO_4
378
BROMINE
330
332
334
336
338
340
342
NaOH
346
348
Waste water
Recycle water

Fig. 3

Fig. 4

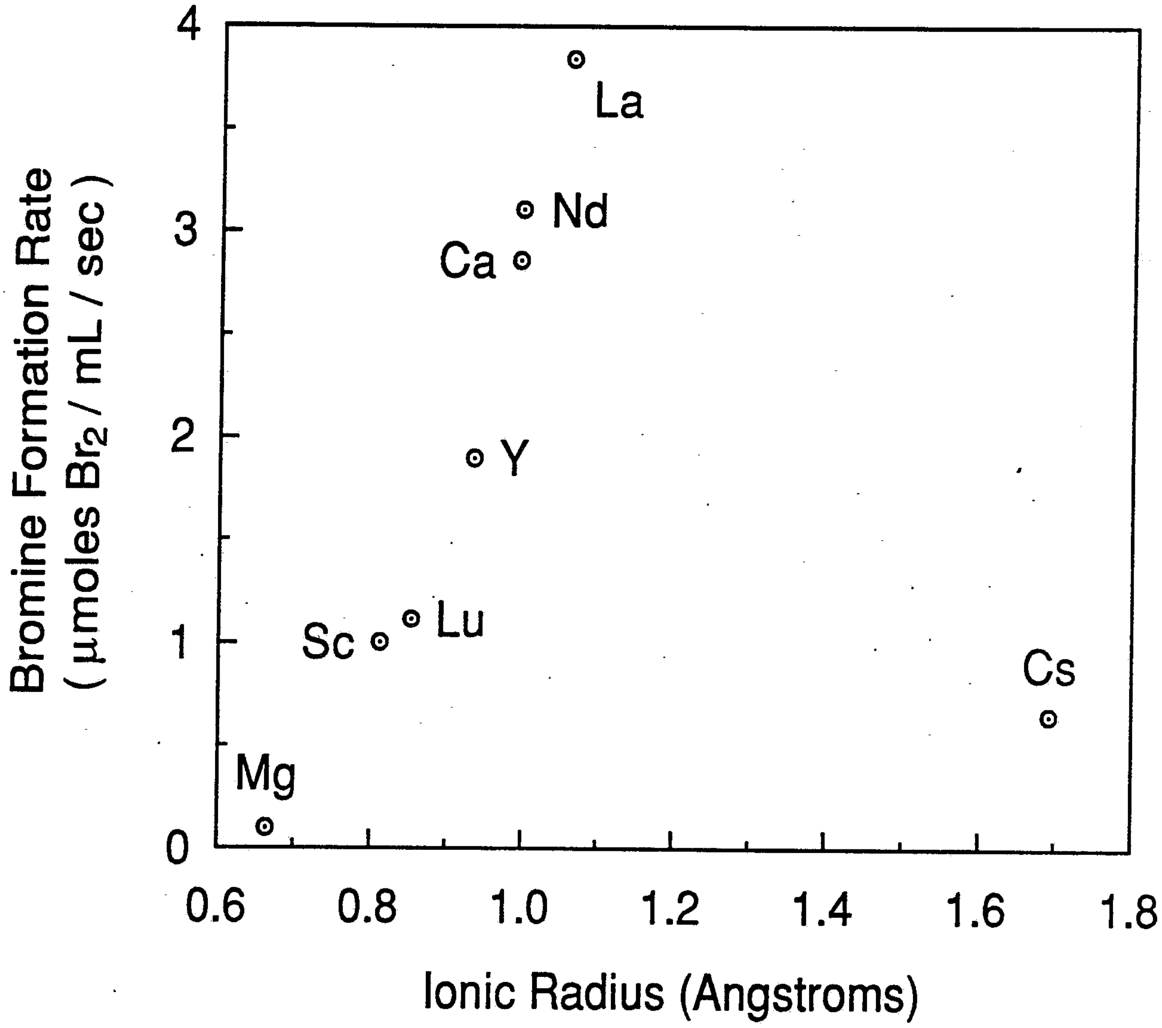

Bromine Formation Rate
(µmoles Br2 / mL / sec)
4
3
2
1
0
La
Nd
Ca
Y
Lu
Sc
Cs
Mg
0.6
0.8
1.0
1.2
1.4
1.6
1.8
Ionic Radius (Angstroms)

Fig. 5

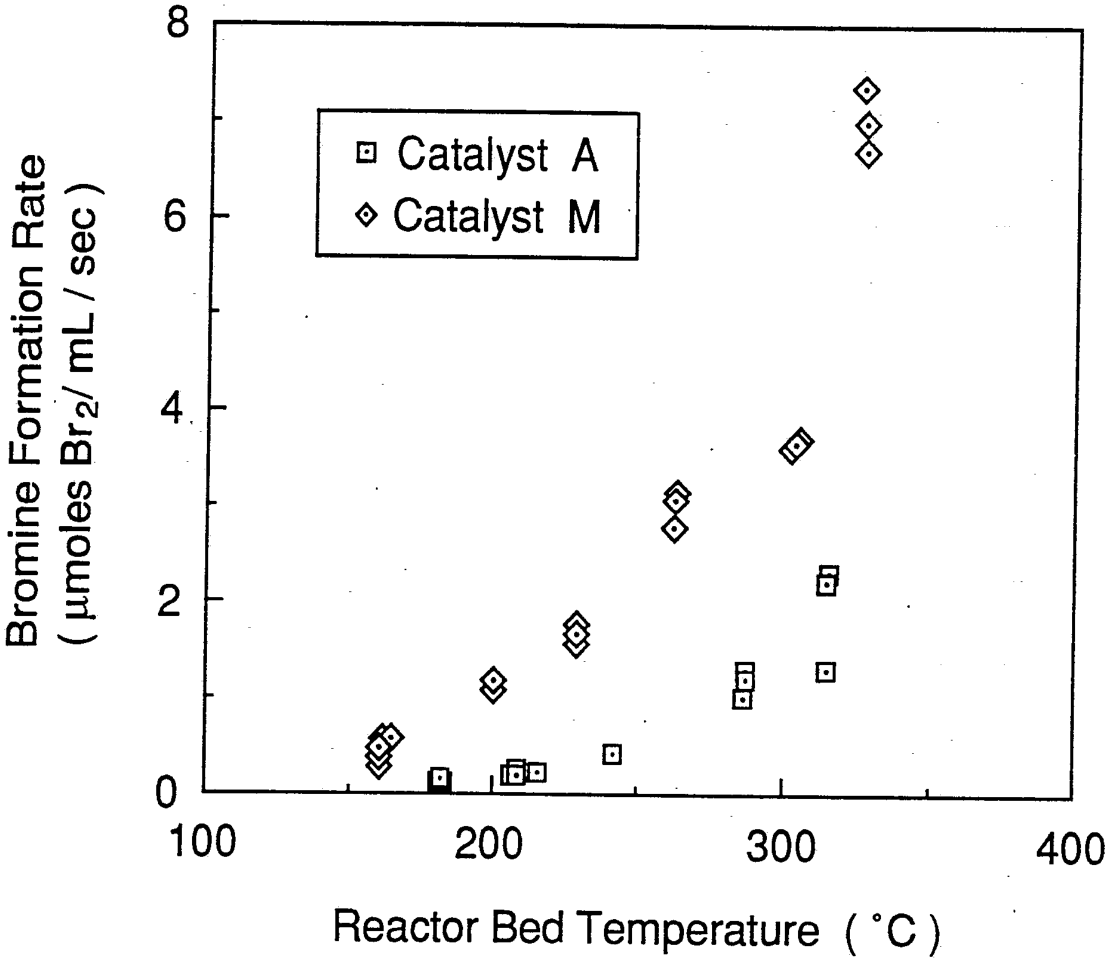

Catalyst A
Catalyst M
Bromine Formation Rate
(µmoles Br_2/ mL / sec)
0
2
4
6
8
100
200
300
400
Reactor Bed Temperature (°C)

Fig. 6

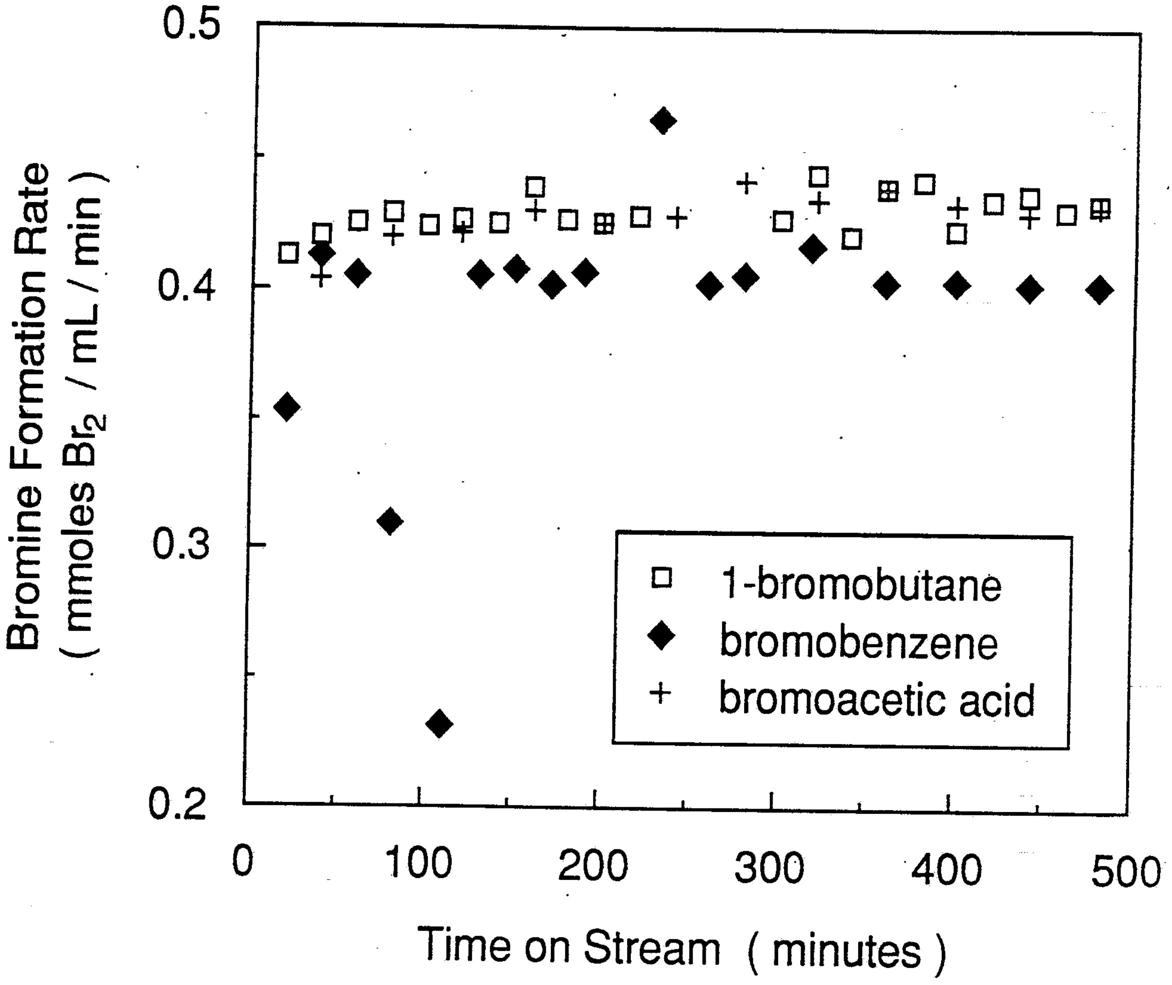
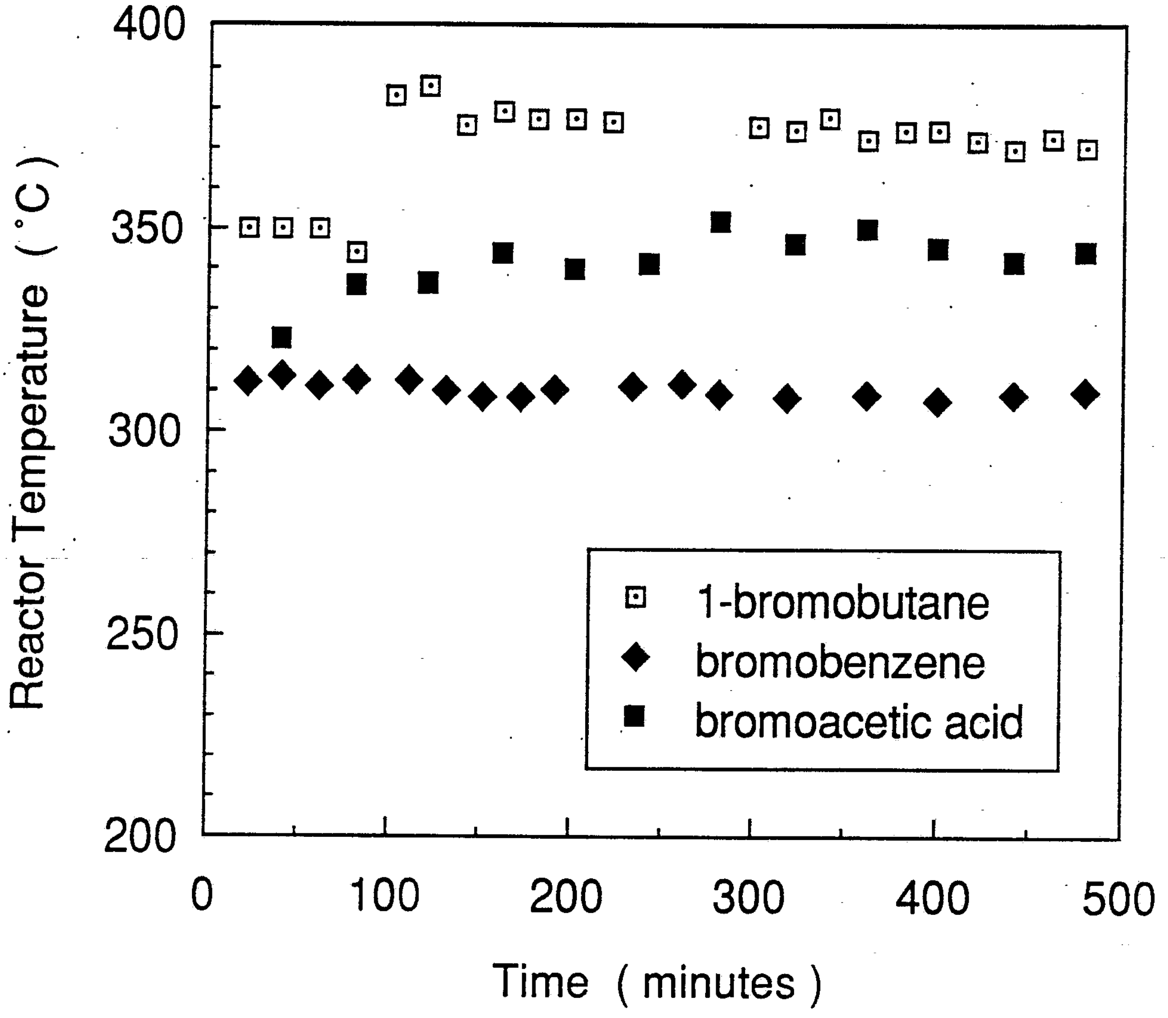

Bromine Formation Rate
(mmoles Br_2 / mL / min)
0.5
0.4
0.3
0.2
0
100
200
300
400
500
Time on Stream (minutes)
□ 1-bromobutane
◆ bromobenzene
+ bromoacetic acid

Fig. 7


400
350
300
250
200
0
100
200
300
400
500
Reactor Temperature (°C)
Time (minutes)
1-bromobutane
bromobenzene
bromoacetic acid

INTERNATIONAL SEARCH REPORT

PCT/US92/07816

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C01B 7/09,B01J 27/122,B01J 21/06
US CL :423/502, 502/225
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)

U.S. : 432/500,432/507,502/349

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A, 2,163,877 (HOOKER) 01 July 1937, see column 2 and column 3, lines 1-25.	1,16,22-45
Y	US,A, 1,379,731 (THEIMER) 31 May 1921 See column 2, lines 582-103.	39,45
Y	US,A, 2,536,457 (MUGDAN) 13 September 1945, see column 1, line 24; column 4 lines 30-65, and figure.	40,41,43
A	CA,A, 615,926 (DEAHL) 07 March 1961, see column 1, lines, 20-25 and column 2, lines 28-32.	1-45
Y	JP,A, 38-20358 (SHELL) 20 January 1960, See column 1 and column 2.	1-38,43
Y	US,A, 3.273,964 (DEROOSET) 20 September 1960 See column 2.	1-45

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be part of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search 05 NOVEMBER 1992	Date of mailing of the international search report 17 DEC 1992
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer Ngoc Ho Nguyen VALERIE ANN LUND NGUYEN NGOC-HO INTERNATIONAL DIVISION
Facsimile No. NOT APPLICABLE	Telephone No. (703) 308-1304

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/07816

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, 4,119,705 (RIEGEL, et al.) 10 October 1978, See abstract and column 2.	1-45
A	Chemical Enginering Science, Volume 23, 20 February 1968, RUTHVEN et al.,"The Kinetics of the Oxidation of Hydrogen Chloride over Molten Salt Catalysts", pages 981-988.	1-45
A	FR,A, 1,291,932 (CALIFORNIA RESEARCH) 19 March 1962 See abstract and column 2.	1-45
A	US,A, 3,816,599 (KAFES) 16 November 1971 See column 3, lines 1-40.	1-45
Y	US,A, 3,353,916 (LESTER) 21 November 1967 column 3, lines 5-20, column 4, lines 30-55.	1,8-11, 14-21,22-25 30-32