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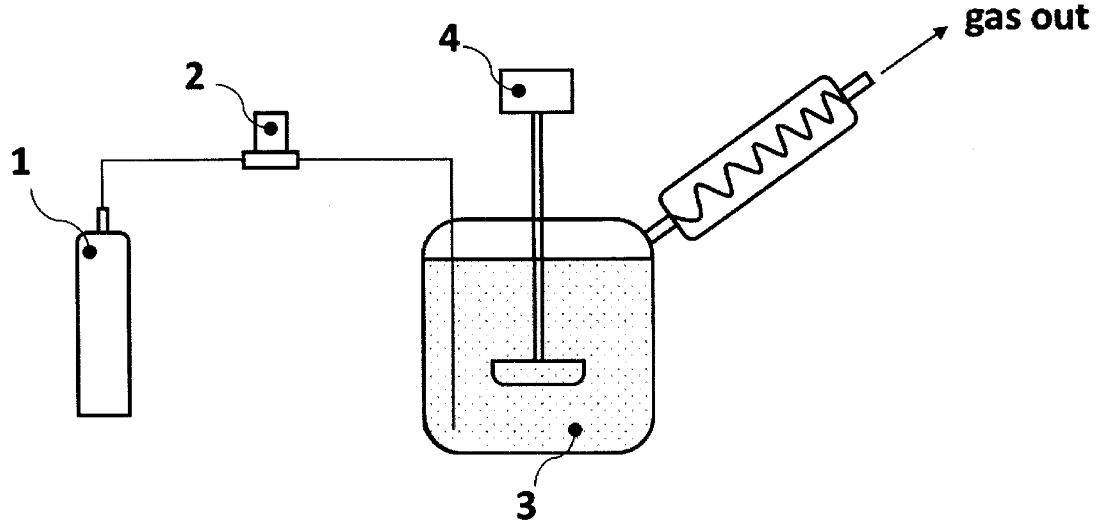

Figure 1

(57) **Abstract:** The invention relates to methods of hydrogen production by electrolysis, methods of hydrogen purification, separation, concentration and recovery; the present invention relates also to methods of purifying flows from sulfur-containing and nitrogen-containing substances, and the concomitant production of sulfur or sulfuric acid.

WO 2021/177931 A1

METHOD OF HYDROGEN PRODUCTION

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The invention relates to methods of hydrogen production by electrolysis of an aqueous solution of hydrobromic acid; as well as methods of hydrogen purification, separation, concentration and recovery of hydrogen, as well as methods of purifying flows from sulfur-containing and nitrogen-containing compounds.

BACKGROUND OF THE INVENTION

Method of Hydrogen Production

Hydrogen can be obtained from several sources, such as fossil fuels, biomass, water and even from H_2S, or extracted from natural gas (natural hydrogen). Recent scientific and technical papers have highlighted the possibility that commercially valuable low-cost natural hydrogen may exist in many places of the world. The demand for hydrogen is expected to increase significantly in the upcoming decades. According to the Hydrogen Council (http://hydrogencouncil.com/wp-content/uploads/2017/11/Hydrogen-scaling-up-Hydrogen-Council.pdf), considering hydrogen as one of the central pillars for the deep decarbonization of the transport, industry and energy sectors could potentially generate a tenfold increase in the demand for hydrogen, increasing from 8 EJ (2015) to almost 80 EJ by mid-century. Today, steam methane reforming (SMR) holds the largest share (48 %) for hydrogen production, followed by the catalytic reforming of liquid hydrocarbons (30 %) and coal gasification (18 %). Currently, conversion of fossil fuels into hydrogen yields significant amounts of CO_2 as by-product. Generally, the global production of hydrogen at current levels results on the emission of approximately 500 Mt CO_2 per year (IEA, Technology Roadmap: Hydrogen and Fuel Cells, 2015). The global production of hydrogen from electrolysis of water is gaining momentum and could increase significantly on the long-term as abundant electricity from renewable sources becomes more widely available. However, the present technology consumes a huge amount of electricity per mol of hydrogen, requires significant water resources, does not use co-produced oxygen, and requires high capital investments (uses noble metal like iridium). However, in all mentioned technologies of hydrogen production the separation, purification, and compression of hydrogen is required.

Possible methods of hydrogen separation and recovery are as follows:

(1) pressure swing adsorption (PSA): the present technology bases on differences in the adsorption properties of gases to separate them under pressure, and represents a method of pure hydrogen production;

(2) hydrogen-permeable membranes: they fall generally into three classes: polymeric membranes, inorganic (non-metal porous or nonporous) membranes, and dense (nonporous) metal membranes;

(3) chemical looping and improved adsorption systems with hydride types of materials;

(4) cryogenic or low temperature technologies for gas separation based on their difference in boiling points: the application of this technology for H_2 separation requires the cooling of the gas to cryogenic temperatures of – 200°C.

Choosing of the most appropriate hydrogen production technology depends on the quality of the available feedstock, required hydrogen purity and production capacity. In many cases, the further hydrogen application requires high pressure flow, which could be only realized with gas compressors. A proven method of compress hydrogen is to apply reciprocating piston compressors. Widely used in refineries, they are the backbone of refining crude oil. Reciprocating piston compressors are commonly available as either oil-lubricated or non-lubricated; for high pressure (350-700 bar) non-lubricated compressors are preferred to avoid oil contamination of hydrogen.

If there are known solutions to this technical problem, how or in what respect the earlier solutions are lacking?

In PSA, the impurities (CH_4, CO_2, CO, H_2O, etc.) in the gas flow are removed in adsorbent beds. The adsorbents are normally made of molecular sieves, activated alumina or silica gel, depending on the nature of the impurities. The impurities are adsorbed at higher partial pressure and desorbed at lower pressure. H_2 adsorption relative to other gases and light hydrocarbons is not very significant; therefore, it is obtained as highly purified. The adsorbent bed or beds are regenerated by reducing the pressure from feed to tail gas pressure and subsequently purging with a portion of the product H_2. The adsorption method due to above reason is industrially known as Pressure Swing

Adsorption (PSA). The technique is more suitable for the hydrogen flow of high concentration. Typically, depending on tail gases, about 60-85 of H_2 is obtained if high purity 99,9% is required. The hydrogen recovery decreases the amount of heavy hydrocarbons (C_3+) and should be applied as a method to avoid condensation occurrence. Main limitation of PSA approach is the ratio between the hydrogen recovery and hydrogen purity; non-recovered hydrogen should either be returned or lost.

The membrane flows can be used to recover hydrogen from highly concentrated flows with purity of more than 80%. The technology is very sensitive to contaminants, especially to the presence of H_2S, H_2O, C_3+ hydrocarbons. About 95% of H_2 is typically recovered with purity of above 90%. Membrane separation lacks efficiency and is not suitable for production of pure hydrogen. The presence of contaminants limits the lifetime thereof.

In case of metal hydrides, the main problem is the limited weight adsorption capacity, which would require a huge amount of material for separation, and high sensitivity to contaminants. The best achievable adsorption limit is about 0.07 kg of H_2 per kg of material.

The cryogenic method is a low-temperature separation method, which uses the difference in the boiling temperatures (relative volatilities) of feed components to carry out the separation. H_2 has a very high relative volatility compared to hydrocarbons. Therefore, cryogenic method has been used to recover H_2 from the refinery and petrochemical off gas for many years.

For H_2 production from the feed flows containing low boiling impurities such as CO and N_2, the CH_4 wash column is used, which washes the impurities from the H_2 flow. CO_2 and water content should be reduced to less than 1 permille by passing the feed flow through a gas dehydration system. CO_2 is removed to 100 permille level in an amine treatment column. The cryogenic method is thermodynamically more efficient than the other H_2 upgrading methods. High recovery rate in the range of between 92 and 98% is easily achieved at 95%+ purity and the losses in recovery in case of increased hydrogen purity is less than for membrane systems.

The main disadvantage of all the discussed methods is high cost, high energy requirement, moderate hydrogen recovery rate, and necessity to design for highly concentrated H_2 flows.

Higher H_2 content of the feed promotes the PSA and membrane methods, and lower H_2 content promotes the cryogenic separation. Flows with 75-90 vol.% of H_2 are most economically purified by PSA or membrane methods with the selection being based on flow, pressure, and pretreatment requirements. Cryogenic separation technology is applicable to large flows with 30-75 vol.% of H_2. The larger the CH_4 content of a flow, the more Joule-Thomson refrigeration is available to the cryogenic method.

If the H_2 is produced from steam reforming of CH_4 (natural gas) or crude oil, no heavier hydrocarbons are present in the reformer product gas. The reformer gas mainly consists of H_2, CO, CO_2 and N_2. The H_2 flow can be purified using a PSA system only, since it is the only method that can remove the above components easily and completely.

If the H_2 flow is a refinery off gas, then the content of heavier hydrocarbons (C_5+) is an important factor in the development of all three methods. Membrane systems will remove these components, but higher concentrations increase the condensation temperature of the retentate, which makes the reliability of the system more dependent on proper operation of the pretreatment system. PSA systems will remove heavier hydrocarbons, but increased concentrations result in larger systems with lower recovery due to difficulty in stripping of the mentioned impurities from the adsorbents. Heavier hydrocarbons concentrations in the feed for a cryogenic system must be limited in order to avoid freezing in the method, which makes this system also more dependent on the operation of the pretreatment systems. Benzene is of particular concern in the membrane and cryogenic methods due to its high boiling point.

If a gas flow contains H_2S and NO_x that must be removed, then the membrane method is not suitable, as H_2S has a relatively high permeation rate, and will leave with the H_2 product. If H_2S is present in concentrations exceeding a few hundred permille, then PSA method is advantageous, since the cryogenic method will require a separate H_2S removal system.

Changes in the Feed Concentration

If there is a gradual change in the feed quality, this will impact the performance of all the separation technologies. Thus, the operating flexibility of the purification system should be sufficient to respond to feed quality changes with a reaction time that does not result method upsets. The PSA method is the most flexible method of the three methods under consideration in its ability to maintain H_2 purity and recovery under changing conditions. As the concentration of a feed impurity increases in the feed (at constant feed pressure), the partial pressure of the impurity also increases. An increase in the impurity partial pressure normally results in an increase in the amount of the impurity that would be adsorbed. Thus, the method is self-compensating to a large extent and even relatively large changes in feed impurity concentrations have little impact on hydrogen purity but would reduce the recovery rate.

In membrane methods, an increase in the concentration of a feed impurity tends to cause an increase in the concentration of that particular impurity in the product. Product purity can be maintained for small feed composition changes by adjusting the feed-to-permeate pressure ratio. However, the relatively strong impact of the product purity on recovery for these systems means that H_2 recovery can be significantly affected. The reaction time of membrane systems is essentially instantaneous, and corrective action has immediate results, but operators have less time to react.

The cryogenic method is less flexible than the other two methods. Particular attention must be given to high freezing point constituents, which are removed in the pretreatment system, since failure to remove those contaminants can result in plugging of the heat exchangers. Changes in the concentration of the lower-boiling components of feed affect the product purity directly. Recovery is not strongly affected.

None of those techniques are economically advantageous for the hydrogen recovery from waste diluted flows.

Method of Purification of Sulfur-Containing Flows

To use the electrolysis of hydrobromic acid as a method of hydrogen production, it is necessary to provide a reducing agent to re-obtain hydrobromic acid from bromine. One of the practically available reducing agents may be sulfur or sulfur-containing substances, hydrogen sulfide and sulfur-containing organics. The source of sulfur-containing reducing agents is, in particular, natural gas; biogas; exhaust gases from refineries, combustion plants, coal-fired power plants, metallurgical plants; flue gases, exhaust gases, etc.

Treatment of H_2S containing flows or flows containing other sulfur-containing compounds is currently carried out basically following two main approaches:

(1) amine washing followed by Claus method. This method includes three steps: first, H_2S present in the flows is being adsorbed in an amine or amine mixture and

purified ("sweet") gas flow is recovered from the unit; then, obtained saturated amine solution is directed to the desorption step, wherein H_2S rich gaseous flow is obtained and unsaturated amine is returned to the first step; finally, H_2S is reacted with air in Claus furnaces to obtain sulfur and water vapor;

(2) adsorption of contaminants on filters comprising activated carbon as a main component: this commercial solution demands disposal of H_2S-saturated filters after use;

(3) Halogen cycles (WO1994001205A1 – utilizing catalytic oxidation of HBr to Br_2, US20090028767A1- oxidation of carbon-containing and sulfur-containing materials with halogens, US5433828A – oxidation of H_2S and CS_2 in flue gases with bromine followed by electrolysis of HBr)

How or in what respect the earlier solutions are lacking?

The amine washing/Claus method consumes a lot of energy, requires high capital investments and is economically advantageous only at high scale. The amine is an expensive consumable of the method, which needs to be gradually replaced due to thermal degradation. In addition, the presence of S-organic compounds reduces efficiency and increases purification costs. Resulting elemental sulfur is of low quality, which prevents sales opportunities thereof. It is worth mentioning that this solution is not economically justified for treatment of biogas, as the scale of biogas production is too small and its delivery to the treatment units demands either costly transportation or investments into entire pipeline network, which will significantly hinder opportunities for remote small-scale biogas producers. The adsorption by carbon filters will demand further infrastructure for treatment of waste filter material.

The disadvantage of halogen cycles is multiphase reaction system. Br_2 is poorly soluble in water and directing the two-phase system in electrolytic cell will destabilize the system. Moreover, the two-phase system will form the emulsion and significantly reduce the efficiency of the oxidation method. For instance, reaction with water and bromine in US5433828A will be extremely hindered due to phase separation of CS_2, aqueous solution of H_2S and water, and bromine. It should be mentioned that the method consumes a huge amount of water and water needs to be continuously added. It is not just sufficient to recirculate the reaction medium.

SUMMARY OF THE INVENTION

Technical Problem

The present invention is aimed at solving several problems, the main of which is the optimization of the electrolysis method of a solution of hydrobromic acid in water in the presence of bromine to produce hydrogen. Solving this problem leads to the development of an optimal method of hydrogen production by electrolysis of a solution of hydrobromic acid in water and the solution of related problems - providing optimal methods of concomitant disposal of more reducing agents, which in turn solves the problem of purification of various flows from the mentioned reducing agents and production of related products by oxidizing the mentioned reducing agents.

Solution of the Technical Problem

The problem is solved by taking into account the unique discovery of the inventors, which became the basis of the present invention, in the electrolysis conditions. Namely, the discovery that the electrolysis of hydrobromic acid in the water/hydrobromic acid/bromine system is most effective in maintaining the single-phase nature of the system, i.e. that the resulting bromine does not form a separate fluid phase separated from water. The inventors have found that bromine is soluble in an aqueous solution of hydrobromic acid, without forming a separate fluid phase, in a molar ratio to hydrobromic acid not exceeding 1 (bromine : hydrobromic acid $\leq$1). Carrying out electrolysis in the disclosed conditions, it is possible to use most easily more economically advantageous conditions of obtaining hydrogen, which is provided by the electrolysis of aqueous solution of hydrobromic acid in comparison with the electrolysis of water.

Useful Results of the Invention

The main technical result of the present invention is to provide a novel method of hydrogen production by the electrolysis of an aqueous solution of hydrobromic acid in a single-phase system. An additional useful result is the concomitant disposal of reducing agents required for the reduction of bromine and the formation of hydrobromic acid to close the reaction cycle on which the said method is based. The derived technical result from the disposal of reducing agents is the concomitant purification of flows (in particular, flows of saturated hydrocarbons and CO_2). Also, one of the additional technical results of the present invention is the recovery of hydrogen from flows wherein hydrogen is present in small concentrations. Finally, one of the additional technical results is obtaining some oxidation products, which are themselves useful, in particular, sulfuric acid or sulfur (or its condensed forms).

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a reactor which including a pyrex glass vessel equipped with a temperature regulator, a heating element, a Liebig refrigerator, and a mechanical stirrer coated with a layer of polytetrafluoroethylene (PTFE).

POSSIBILITY OF IMPLEMENTING THE INVENTION

Detailed Description of the Invention

In this section, the proposed invention will be described through its best, preferred and most preferred embodiments.

In the most preferred embodiment, the technical solution of the present invention is a method of hydrogen production which includes:

(a) providing the flow A, containing at least one reducing agent, and the single-phase fluid flow B, containing water, bromine and hydrobromic acid;

(b) contacting of the said flows under conditions sufficient for the reaction of the components of the flow A with bromine from the flow B with obtaining hydrobromic acid from bromine;

(c) separating a side flow containing at least one non-oxidizable by bromine compound;

(d) obtaining the fluid flow from step (b), wherein the said fluid flow contains essentially water, hydrobromic acid and residual bromine, and which is single-phase;

(e) directing the said fluid flow from step (d) to an electrolyser to convert at least a portion of the hydrobromic acid to bromine and hydrogen; and

(f) obtaining the fluid flow from step (e) and redirecting thereof to step (a).

The substance not oxidized by bromine, in step (c), is meant to be either the non-oxidizable component of the flow A, or the oxidation product of reducing agent from the flow A by bromine, which is incapable of further oxidation by bromine under the conditions of the method according to the invention, or both.

In preferred embodiments of the method according to the invention, the separation of the side flow in step (c) can occur, in particular, by decantation (when the fluid flows are not mixed), or the side flow is gaseous and thus facilitates its separation; also the side flow may be aqueous and require, in particular, the distillation for its separation.

In some embodiments, the side flow in step (c) is further washed and dried, and optionally at least one oxidation product of the reducing agent is separated from the flow A.

In part of the preferred embodiments, the said flow A in the method according to the invention contains hydrogen as a reducing agent in the amount of at least 500 ppm. In other embodiments, hydrogen in the flow A may be present in the amounts from 100 ppm up to 90% by weight.

In other embodiments of the invention, the said flow A may contain ammonia, nitrogen-containing organic compounds, amines and/or amides in the amount of at least 500 ppm as a reducing agent. Accordingly, the said side flow in step (c) may contain nitrogen. In a separate embodiment of the present invention, the above flow A contains carbon monoxide in the amount of at least 10 ppm as a reducing agent.

In many preferred embodiments of the present invention, the said flow A contains sulfur-containing compounds or sulfur in the concentration of not less than 1 ppm as a reducing agent. The sulfur-containing compound according to this embodiment may be CS_2, H_2S, SO_2, COS, dimethyl sulfide, dimethyl disulfide, methyl mercaptan and/or ethyl mercaptan.

In the most preferred embodiments of the method according to the present invention, at least one oxidation product of the reducing agent is separated from the fluid flow in step (d) from the flow A. The said separation from the fluid flow in step (d) can be carried out by distillation or extraction.

In preferred embodiments of the previous embodiment of the invention, the above said oxidation product of the reducing agent is sulfur and/or forms of condensed sulfur. In other embodiments of the disclosed embodiment of the present invention, the said oxidation product is sulfuric acid. In the preferred embodiment of the disclosed embodiment of the method according to the invention in step (a) the flow C containing water is additionally provided.

In some preferred embodiments of the invention, the flow A is gaseous. In these embodiments, the gaseous flow A can be provided at a pressure from 0.5 to 60 atmospheres. In one or other acceptable embodiments of the invention, the gaseous flow after extraction in step (c) is additionally washed and dried by molecular sieve or distillation. In another preferred embodiment of the present invention, the said gaseous flow contains essentially CO_2. In other preferred embodiments, this gaseous flow contains essentially methane and/or other saturated hydrocarbons. In a separate embodiment of the invention, the gaseous flow may contain nitrogen.

In many preferred embodiments of the method according to the present invention the water is additionally added in step (d).

In all preferred embodiments of the method according to the invention, the weight percent of hydrobromic acid in the flow B does not exceed 62% w/w. In more preferred embodiments of the present invention, the weight percent of hydrobromic acid in the flow B does not exceed 48% w/w.

In the most preferred embodiments of the method according to the present invention, the molar ratio of bromine to hydrobromic acid in the flow B is less than or equal to 1.

Also, in the most preferred embodiments of the present invention, the potential in the electrolyser does not exceed 1.23 V relative to the standard hydrogen electrode.

In some embodiments of the present invention, it is possible to additionally conduct a recuperation of the thermal energy released in the reaction of the reducing agent with bromine.

In other embodiments of the present invention, it is possible to additionally conduct a recuperation of the electrical energy in the same or another electrolytic cell (electrolyser).

In certain embodiments of the present invention, in addition to the flow B, a water-miscible organic solvent and water-miscible compounds are added. Such water-miscible organic solvents or compounds may be, in particular, methanol, acetone, acetic acid, nitromethane, sulfolene (butadiene sulfone), dimethyl sulfoxide, dimethyl formamide, acetonitrile, propionitrile, and/or ionic fluids, in particular, the imidazolium, pyrrolidinium, pyridinium salts, as, for example, bromides or sulfates.

In most preferred embodiments of the present invention, the concentration of unsaturated hydrocarbons in the flow A is lower than 100 ppm. In some embodiments of the method according to the present invention, after the contacting of the flow A with bromine and hydrobromic acid but before the electrolysis, a step of removing bromides and dibromides formed from olefins in such a reaction is performed. In particular, the disclosed removal is carried out by distillation and subsequent decomposition, in particular, thermal.

Also, in most preferred embodiments of the method according to the present invention, the temperature at each step, in which bromine is present, is maintained below 80 °C.

In some individual embodiments of the method according to the present invention, the flow A is additionally concentrated before step (a). In other individual embodiments of the method according to the invention, the said fluid flow from step (c) is concentrated, in particular by extractive distillation with, in particular, concentrated solutions of alkaline earth metal bromides or sulfuric acid, before being loaded to the electrolyser.

Industrial Applicability

This section is devoted to examples of use of various embodiments of the present invention.

General conditions for carrying out the method according to the invention

The present invention is based on the features of the electrolysis of hydrogen bromide in aqueous solution, which were discovered by the inventors:

$2HBr = H_2 + Br_2$ (potential in the electrolyser does not exceed 1.23 V relative to the standard hydrogen electrode)

This method, as discovered by the inventors, is effective only when there is a single fluid phase. As researched by the inventors, a solution of bromine in aqueous hydrobromic acid exists without the formation of the second fluid phase only under certain conditions: the ratio of bromine to hydrobromic acid is less than or equal to one.

The inventors of the present invention also found that there are some other limitations of single-phase nature and method efficiency: the weight percent of hydrobromic acid in water cannot exceed 62% (and the amount of bromine relative to water has no significance as it binds to hydrobromic acid). The most optimal value for the concentration of hydrobromic acid in water is 48 % w/w, which coincides with the concentration of azeotropic solution of hydrobromic acid.

Another important parameter is the temperature: although bromine begins to enter the gas phase at 60 °C, it is at a temperature of 80 °C, as found by the inventors, that a flow stratification and the bromine transition into the gas phase occur; starting from this temperature it is very difficult to control the method from a technical point of view.

Among other important conditions for the effective implementation of the method according to the invention, it should be noted that the concentration of unsaturated hydrocarbons in the flow A, which is reacted with bromine dissolved in aqueous hydrobromic acid, must be lower than 100 ppm. Unsaturated hydrocarbons (olefins) in contact with bromine and hydrobromic acid form bromide and dibromide derivatives, which accumulate in the system and create problems with electrolysis, reducing its efficiency. If necessary, the removal of bromides and dibromides formed from olefins in this reaction should be carried out. In particular, the disclosed removal can be performed before the electrolysis step; to remove these substances, in particular, distillation and subsequent decomposition, e.g. thermal, can be used.

To maintain the single-phase nature of the reaction fluid in the method of the present invention, it is also possible to add to the flow B some organic solvents or fluids that are miscible with water, in particular methanol, acetone, acetic acid, nitromethane, sulfolene (butadiene sulfone), dimethyl sulfoxide, dimethyl formamide, acetonitrile, propionitrile, and/or ionic fluids, in particular, the imidazolium, pyrrolidinium, pyridinium salts, as, for example, bromides or sulfates. Person skilled in the art, if desired or necessary, will be able to perform simple experiments and optimize the composition of the flow B by modifying it with the content of water-miscible organic solvents or water-miscible fluids.

One of the main examples of use of the proposed invention is the method of recovering and separating hydrogen from gas flows.

The method of the invention is a low-cost and low-carbon method of reduction and production of high purity hydrogen from flows, which may contain complex mixtures of hydrogen, CO, CO_2, H_2S, CS_2, alkanes, nitrogen, nitrogen oxides, ammonia and noble gases, wherein hydrogen in the disclosed flows may be contained in amounts from 100 ppm up to 90% by weight.

As it is known, hydrogen easily reacts with bromine at room temperature:

$H_2 + Br_2 = 2HBr$

with the formation of hydrogen bromide, which is then reduced again to bromine by electrolysis with hydrogen obtaining captured from the flow of low concentration.

Thus, hydrogen in this method is both a reducing agent and the product to the recovery of which this method is directed.

The method according to the invention can also be used to purify flows of CO_2 for their subsequent transportation, as in many cases the amount of H_2 is a very critical parameter.

Hydrogen reduction in this solution is close to 100%. The mentioned solution is not sensitive to changes in gas concentration and composition. This methodology is suitable even for the recovery of traces of hydrogen.

This method can be used for:

(a) small-scale, mobile units for bio-refineries;

(b) small-scale units for removal H_2 from CO_2 flow;

(c) large-scale stationary units for additional recovery of H_2 from flows after PSA, membrane, and cryogenic separation units;

(d) large-scale stationary units for treatment of natural gas coming from reservoirs located in big hubs or in a proximity to natural gas reservoirs;

(e) large-scale stationary units for treatment of off-gases from refineries, incinerators, coal power plants, metallurgical factories, flue gases and exhaust gases.

Method of treating sulfur-containing flow to produce hydrogen from water with co-oxidation of sulfur-containing compounds to sulfuric acid and the method of purifying sulfur-containing flows

In this family of methods, the reducing agent used to regenerate the hydrobromic acid spent on electrolysis is sulfur or sulfur-containing compounds, such as CS_2, H_2S, SO_2, COS, dimethyl sulfide, dimethyl disulfide, methyl mercaptan and/or ethyl mercaptan. The sulfur source flow in step (1) may be a gaseous flow or a fluid flow containing at least one S-containing compound.

Depending on the amount and nature of the available reducing agent (sulfur or sulfur-containing compounds), conditions (in particular, temperature) of excess water and the ratio between the reducing agent and bromine, different chemical reactions can occur and different products are formed, for example:

$H_2S + Br_2 = 2HBr + S$ (carried out at low temperature)

$H_2S + 4Br_2 + 4H_2O = 8HBr + H_2SO_4$ (excess bromine is required, water is consumed; this reaction is carried out at 80 °C)

$S + 3Br_2 + 4H_2O = H_2SO_4 + 6HBr$ (excess bromine is required)

$SO_2 + Br_2 + 2H_2O = H_2SO_4 + 2HBr$

$CS_2 + 2Br_2 + 2H_2O = CO_2 + 4HBr + 2S$

$CS_2 + 8Br_2 + 10H_2O = CO_2 + 16HBr + 2H_2SO_4$ (excess bromine is required, water is consumed)

Accordingly, depending on the need for specific products, the concentration of reducing agent, possibility of supply of bromine and water, this method can be used for producing hydrogen, splitting water to produce hydrogen, the conversion of sulfur-containing waste into sulfur or sulfuric acid, for desulfurization of gas flows (removal of CS_2, H_2S, SO_2, COS) of different nature (natural gas; biogas; waste gases from refineries, combustion plants, coal power plants, metallurgical plants; flue gases, exhaust gases) on different scales. These can be:

(a) large-scale stationary plants for the production of hydrogen from water using sulfur-containing compatible raw materials from natural gas tanks, biogas plants, waste gases from oil refineries, sulfur waste, combustion plants, coal power plants, metallurgical plants, flue gases and exhaust gases;

(b) large-scale stationary plants for waste gas treatment from refineries, combustion plants, coal power plants, metallurgical plants, flue and exhaust gases;

(c) large-scale stationary plants for purification of natural gas coming from tanks located in large hubs or in the immediate proximity of natural gas tanks;

(d) large-scale stationary biogas treatment plants located in large centers;

(e) conversion of sulfur-containing waste at oil refineries and gas plants into sulfuric acid and hydrogen, which are easier to transport;

(f) small-scale mobile devices for biogas purification on site, for remote biogas producers;

(g) small-scale devices for private composting;

The method according to the invention is a simple and low-carbon method of purification of sulfur-containing flows (wherein sulfur is present in the form of H_2S, CS_2, COS, sulfur or S-organic) including in remote places with the joint production of high value products: hydrogen, sulfuric acid or sulfur; the invention provides a technology that can be easily presented on an enlarged or reduced scale, depending on specific requirements, and can be adjusted to produce sulfur or sulfuric acid when water is added.

In addition to purification from sulfur and sulfur-containing compounds, the methods of the present invention can be used to purify flows from carbon monoxide and ammonia and certain nitrogenous substances.

When using carbon monoxide (at a minimum concentration of 10 ppm) as a reducing agent for the reduction of bromine, the carbon dioxide is obtained, which can also be collected as a useful product, according to methods known to a person skilled in the art.

According to the present invention, it is possible to use the following substances as ammonia, nitrogen-containing organic compounds, amines and/or amides in the amount of at least 500 ppm as nitrogen-containing compounds as reducing agents in the flow A. Molecular nitrogen is formed as a product in reactions with the following reducing agents:

$2NH_3 + 3Br_2 = 6HBr + N_2$

which can also be collected as a useful product, by methods known to a person skilled in the art.

Since the essence of the present invention is to dramatically improve the efficiency of electrolysis of hydrobromic acid in water due to the unexpected discovery of the inventors of the present invention, the description of the invention focuses on the disclosure on which the present invention is based. The direct detailed implementation of the above disclosed methods on a domestic, small or large industrial scale, materials, equipment, conditions of reactions and actions that are not related to the disclosure of the present invention and have long been well known to a person skilled in the art was not included in this disclosure as it is not the essence of the present invention. Person skilled in the art after reading the disclosure of the present invention, will be able to use his knowledge and the information available in the prior art to apply the methods of the present invention on any scale without the involvement of additional inventions.

In the following section, the possibility of embodiment of the methods of the present invention was tested and proven in experimental laboratory examples.

Experimental Examples

The bromine-containing mixtures for Examples 1-3 were prepared using an azeotrope HBr (48 % w/w), fluid Br_2 and distilled water.

Example 1.

The gas mixture (1) containing 97 vol.% of CH_4 and 3 vol.% of H_2S was used as a raw material for the reaction, and a single-phase solution containing water, HBr and Br_2 (52% w/w, 43 % w/w and 5% w/w, respectively) was used for the oxidation reaction of H_2S to H_2SO_4. The applied reactor was a plant including a pyrex glass vessel (3) equipped with a temperature regulator, a heating element, a Liebig refrigerator, and a mechanical stirrer (4) coated with a layer of polytetrafluoroethylene (PTFE). The feed gas was fed through a PTFE tube connected to a Bronckhorst mass flow regulator (2), which was calibrated for the said gas mixture using an external flow meter.

The reaction was carried out at the temperature of 55-60°C, the reactor was loaded with 1000 g of the single-phase solution, and the mechanical stirrer was maintained at 400 rpm throughout the experiment. The feed gas mixture flow was maintained for 10 hours at a flow rate of 2 l/h, and the Liebig refrigerator was constantly washed with water to avoid undesired loss of fluid products due to evaporation.

The gas samples collected at the refrigerator outlet down into the reactor were collected with a gas-tight syringe every 2 hours of the experiment and analyzed using gas chromatography. Only traces of H_2S were detected in all collected initial samples, which confirmed that the oxidation of H_2S with Br_2 occurred.

$Br_2 + H_2S + 4H_2O \rightarrow H_2SO_4 + 8HBr$

The fluid in the reactor was cooled and analyzed by available analytical methods after completion of the reaction. According to the gravimetric analysis results, the total amount of H_2SO_4 was 2.55 g, which indicated an almost complete conversion of H_2S to H_2SO_4.

Example 2.

The gas mixture containing 97 vol.% of CH_4 and 3 vol.% of H_2S was used as a raw material for the reaction, and a single-phase solution containing water, HBr and Br_2 (53% w/w, 27% w/w and 20% w/w, respectively) was used for the oxidation reaction of H_2S to H_2SO_4. The applied reactor was a plant including a pyrex glass vessel equipped with a temperature regulator, a heating element, a Liebig refrigerator, and a mechanical stirrer coated with a layer of PTFE. The feed gas was fed through a PTFE tube connected to a Bronckhorst mass flow regulator calibrated for the said gas mixture using an external flow meter.

The reaction was carried out at the temperature of 55-60°C, the reactor was loaded with 1000 g of the single-phase solution, and the mechanical stirrer was maintained at 400 rpm throughout the experiment. The feed gas mixture flow was maintained for 10 hours at a flow rate of 10 l/h, and the Liebig refrigerator was constantly washed with water to avoid undesired loss of fluid products due to evaporation.

The gas samples collected at the refrigerator outlet down into the reactor were collected with a gas-tight syringe every 2 hours of the experiment and analyzed using gas chromatography. Only traces of H_2S were detected in all collected initial samples, which confirmed that the oxidation of H_2S with Br_2 occurred.

The fluid in the reactor was cooled and analyzed by available analytical methods after completion of the reaction. According to the gravimetric analysis results, the total amount of H_2SO_4 was 12.97 g, which indicated an almost complete conversion of H_2S to H_2SO_4.

Example 3.

The gas mixture containing 97 vol.% of CH_4 and 3 vol.% of H_2S was used as a raw material for the reaction, and a single-phase solution containing water, HBr and Br_2 (52% w/w, 43 % w/w and 5 % w/w, respectively) was used for the oxidation reaction of H_2S to H_2SO_4. The applied reactor was a plant including a pyrex glass vessel equipped with a temperature regulator, a heating element, a Liebig refrigerator, and a mechanical stirrer coated with a layer of PTFE. The feed gas was fed through a PTFE tube connected to a Bronckhorst mass flow regulator calibrated for the said gas mixture using an external flow meter.

The reaction was carried out at the temperature of 55-60°C, the reactor was loaded with 1000 g of the single-phase solution, and the mechanical stirrer was maintained at 400 rpm throughout the experiment. The feed gas mixture flow was maintained for 10 hours at a flow rate of 6 l/h, and the Liebig refrigerator was constantly washed with water to avoid undesired loss of fluid products due to evaporation.

The gas samples collected at the refrigerator outlet down into the reactor were collected with a gas-tight syringe every 30 minutes of the experiment and analyzed using gas chromatography. At the initial stage of the experiment, only traces of H_2S were detected in the initial samples, while after 8 h the intensity of the H_2S peak in GC increased. At this point, the color of the fluid in the reactor gradually changed from orange-red to yellow, indicating that Br_2 was almost completely spent.

Example 4.

The fluid product obtained in Example 3 was placed in a distillation unit with a round bottom flask, reflux condenser and refrigerator. The fluid was diluted with 100 ml of distilled water, as some of the water was consumed during the reaction with H_2S and distilled at 124-127 °C for 6 hours in a well-ventilated exhaust hood. The total amount of almost colorless fluid collected in the receiver flask was 1072 g, and the amount of fluid residue with a higher boiling point in the round bottom flask was 33 g. This residue was analyzed for sulfuric acid content using gravimetric analysis. It was found that the total amount of H_2SO_4 was 7.63 g, which indicated an almost complete conversion of H_2S to H_2SO_4 during Example 3. The analysis of this distillate showed that it was an 8.2 M HBr solution close to an azeotrope (8.89 M).

Example 5.

A specially designed electrolysis unit was used to decompose HBr into H_2 and Br_2. 600 ml of a solution containing 48% w/w of HBr in water was passed through an electrolysis unit using a peristaltic pump with a PTFE surface. The fluid yield from the electrolysis unit was collected in a glass vessel; the gaseous yield was released into the exhaust hood. The total duration of electrolysis was ~ 7 minutes, the average voltage during the run ~ 1.02 V, the average current ~ 82 A. The voltage during the experiment was stable. Liquid products were analyzed for Br_2 and HBr by titration and gravimetric analysis. The analysis showed a final content of HBr and Br_2 44% w/w and 4% w/w, respectively.

Example 6.

An individually designed electrolysis unit containing a nafion membrane was used as the reactor. The gas mixture (CH_4/H_2 95/5 vol.) and a single-phase solution comprising water, HBr and Br_2 (52% w/w, 43 % w/w and 5 % w/w, respectively) were used as raw material. The feed gas was fed through a PTFE tube connected to a Bronckhorst mass flow regulator calibrated for the said gas mixture using an external flow meter. The supply of the fluid phase was carried out by a syringe pump. The flow of this gas mixture was set at 5 l/h, the experiment was performed for 2 hours. The average cell voltage was 0.96 V, and the average current was 0.6 A.

Example 7 - comparative.

A specially designed electrolysis unit was used to decompose the model mixture, including water, HBr and Br_2 (35% w/w, 28% w/w and 36% w/w, respectively). 100 g of this solution was combined in a closed circuit with an electrolysis cell and recycled through the mentioned cell with an average flow rate of 15 ml/min. The average voltage during the run was approx. 1.03 V, the average current was approx. 39 A. After approximately 5 minutes of the experiment, a clear formation of a second layer at the flask bottom was observed, corresponding to a conversion of approximately 35 mol. % of HBr, i.e. the molar ratio of HBr/Br_2 is less than 1. At this point of the experiment, the voltage began to rise and reached a value of 1.34V at the point of 6.5 min; after all, the 1.34 V cell potential was accompanied by the formation of bubbles at the anode, which, as expected, were oxygen, formed due to the water decomposition.

Analytics.

Exhaust Gases Analysis

Agilent GC with TCD and FID detectors and SilicaPLOT columns was used to analyze the waste gases.

The total sulfate content was analyzed using gravimetric analysis. A solution containing H_2SO_4 was reacted with excess barium chloride. The reaction was carried out at 90 °C to complete the sedimentation, which was formed by barium sulfate. The sediment was filtered off and calcinated at the temperature of 600 °C for 12 h before measuring the mass.

$H_2SO_4 + BaCl_2 \rightarrow BaSO_4\downarrow + 2HCl$

The total bromine content was analyzed using gravimetric analysis.

This method is based on the HBr neutralization by adding excess sodium carbonate followed by the addition of silver nitrate and the sedimentation of AgBr. All manipulations were performed at the temperature of 40 °C and with vigorous stirring to ensure the completion of the reaction. Then the solid sediment of AgBr was filtered off, dried in air and calcinated at the temperature of 400 °C for 6 hours for providing the purity of the sample.

$2HBr + Na_2CO_3 \rightarrow 2NaBr + H2O + CO_2$

$2HBr + NaOH \rightarrow NaBr + H2O$

$NaBr + AgNO_3 \rightarrow NaNO_3 + AgBr\downarrow$

In the presence of polybromides $[Br_{2n+1}]^-$ the method was modified so that the initial step included the reduction of Br_2 to Br^- ions using a solution of sodium thiosulfate.

The molecular bromine content, which may be present in the form of polybromides, $[Br_{2n+1}]^-$, was analyzed using iodometric titration. In the first step, the polybromides were reacted with an excess solution of potassium iodide with obtaining molecular iodine. Then the formed iodine was titrated with a solution of sodium thiosulfate with colloidal starch as an indicator.

$[Br_{2n+1}]^- + 2nKI \rightarrow 2nKBr + Br^- + nI_2$

$I_2 + I^- \rightarrow I_3^-$

$I_3^- + 2S_2O_3^{2-} \rightarrow 3I^- + S_4O_6^{2-}$

The above examples shall not limit the present invention and are given solely to illustrate the possibility of its implementation. The scope of protection of the present invention is set forth in the following section - in the claims.

CLAIMS

1. The method of hydrogen production:

(a) providing the flow A, containing at least one reducing agent, wherein the concentration of unsaturated hydrocarbons in the flow A is lower than 100 ppm, and the single-phase fluid flow B, containing water, bromine and hydrobromic acid, wherein the weight percent of hydrobromic acid in the flow B does not exceed 62% w/w;

(b) contacting of the said flows with obtaining a hydrobromic acid from bromine;

(c) separating a side flow containing at least one non-oxidizable by bromine compound;

(d) obtaining the fluid flow from step (b), wherein the said fluid flow contains water, hydrobromic acid and residual bromine and is single-phase, wherein the molar ratio of bromine to hydrobromic acid is less than or equal to 1;

(e) directing the said fluid flow from step (d) to an electrolyser to convert at least a portion of the hydrobromic acid to bromine and hydrogen, provided that the potential in the electrolyser does not exceed 1.23 V relative to the standard hydrogen electrode; and

(f) obtaining the fluid flow from step (e) and redirecting thereof to step (a), provided that the temperature at each step, in which bromine is present, is maintained below 80 °C.

2. The method according to claim 1, wherein the said flow A contains hydrogen as a reducing agent in amount of at least 500 ppm.

3. The method according to claim 1, wherein the said flow A contains ammonia, nitrogen-containing organic compounds, amines and/or amides as a reducing agent in amount of at least 500 ppm.

4. The method according to claim 1, wherein the said flow A contains carbon monoxide as a reducing agent in amount of at least 10 ppm.

5. The method according to claim 1, wherein the said flow A contains sulfur-containing compounds or sulfur as a reducing agent in concentration of not less than 1 ppm.

6. The method according to claim 5, wherein the sulfur-containing compound is CS_2, H_2S, SO_2, COS, dimethyl sulfide, dimethyl disulfide, methyl mercaptan and/or ethyl mercaptan.

7. The method according to claim 1, wherein the flow A is gaseous.

8. The method according to claim 1, wherein at least one oxidation product of the reducing agent is further separated from the fluid flow in step (d) from the flow A.

9. The method according to claim 8, wherein the said separation is carried out by distillation or extraction.

10. The method according to claim 9, wherein the oxidation product is sulfur and/or forms of condensed sulfur.

11. The method according to claim 10, wherein the oxidation product is sulfuric acid.

12. The method according to claim 1, wherein the flow C containing water is additionally provided in step (a).

13. The method according to any one of the preceding claims, wherein the water is additionally added in the step (d).

14. The method according to any one of the preceding claims, wherein the weight percent of hydrobromic acid in the flow B does not exceed 48% w/w.

15. The method according to any one of the preceding claims, wherein the recuperation of thermal energy released in the reaction of the reducing agent with bromine is additionally conducted.

16. The method according to any one of the preceding claims, wherein the recuperation of electrical energy in the same or another electrolytic cell (electrolyser) is additionally conducted.

17. The method according to any one of the preceding claims, wherein the flow B additionally contains at least one water-miscible organic solvent and/or water-miscible compound, selected from the group containing methanol, acetone, acetic acid, nitromethane, sulfolene (butadiene sulfone), dimethyl sulfoxide, dimethyl formamide, acetonitrile, propionitrile, and/or ionic liquids, in particular imidazolium, pyrrolidinium and/or pyridinium salts.

18. The method according to claim 1 and claim 3, wherein the said side flow in step (c) additionally contains nitrogen.

19. The method according to claim 1, wherein the side flow is separated by distillation.

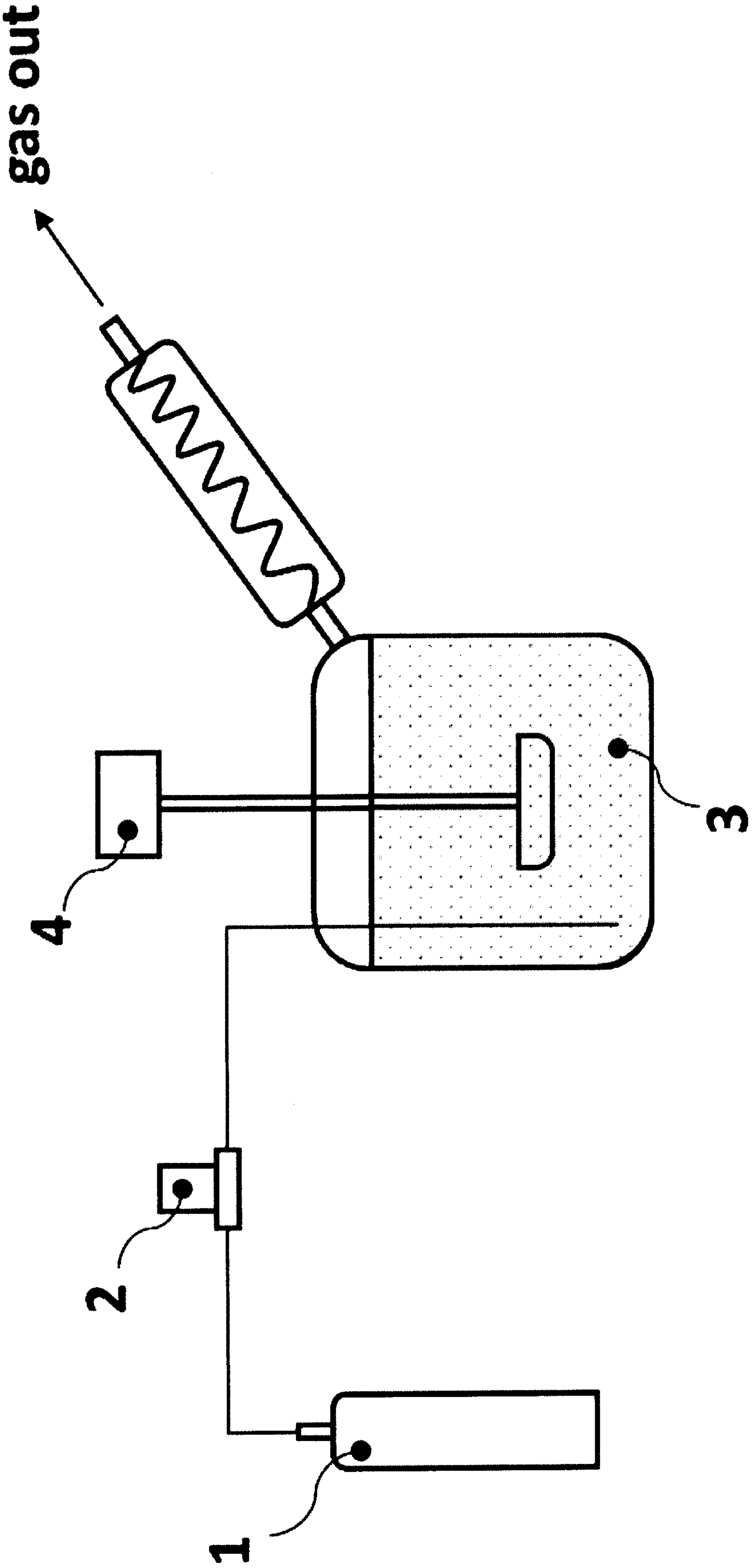

Figure 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/UA2021/000022

A. CLASSIFICATION OF SUBJECT MATTER
INV. C25B1/02 C01B17/74 C25B1/24 C25B15/08
ADD.

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)
C25B C01B

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	Parker Melahn Lyle: "METHOD FOR REMOVING HYDROGEN SULFIDE FROM SOUR GAS AND CONVERTING IT TO HYDROGEN AND SULFURIC ACID", Dissertation Doctor of Philosophy, 1 June 2010 (2010-06-01), pages 1-162, XP055816460, Retrieved from the Internet: URL:http://purl.stanford.edu/ww988vc1913 [retrieved on 2021-06-22] the whole document ----- -/--	1-19

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"P" document published prior to the international filing date but later than the priority date claimed

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"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search 22 June 2021	Date of mailing of the international search report 30/06/2021
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Ritter, Thomas

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INTERNATIONAL SEARCH REPORT

International application No
PCT/UA2021/000022

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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