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(54) Title: PRODUCTION OF SODIUM BICARBONATE FROM A BASIC PROCESS STREAM

(57) Abstract: The present invention is in the area of the treatment of a gas flow containing carbon dioxide obtained from burning at least one organic waste or feed stream, on the one hand to produce sodium bicarbonate and optionally remove and/or recover molybdenum compounds and/or other impurities from the said waste streams for further use and on the other hand to produce an effluent that is sufficiently clean to be discharged into surface water.
Title: Production of sodium bicarbonate from a basic process stream.

The present invention is in the area of the treatment of a gas flow containing carbon dioxide obtained from burning at least one organic waste or feed stream, on the one hand to produce sodium bicarbonate and optionally remove and/or recover molybdenum compounds and/or other impurities from the said waste streams for further use and on the other hand to produce an effluent that is sufficiently clean to be discharged into surface water.

Sodium bicarbonate has a rather low solubility in water and has many applications in different fields including the chemical, pharmaceutical and food industry. Industrial production of sodium bicarbonate is typically by precipitation in a bubble column.

In a number of processes, effluent or waste streams are produced which contain both organic and inorganic components, such as molybdenum salts. Examples are the molybdenum catalysed oxidation processes. One such example is the styrene monomer/propylene-oxide production.

When the usually caustic effluent or waste stream contains both organic and inorganic components, a suitable solution is to burn the waste stream. The flue gases are washed with water resulting in an aqueous solution containing dissolved sodium carbonate and/or sodium bicarbonate and dissolved molybdenum salts and/or other impurities. In order to recover the molybdenum compounds, which are valuable components for amongst others the metal (steel) industry, presently the solution is first acidified with an acid, e.g. sulphuric acid. Following which molybdenum compounds are recovered by ion exchange and the resulting sulphate solution is discharged into the environment. Disadvantages of this process are the high costs, due to the combined acidification and the ion exchange of the total flow. Further, the discharge of the final salt solution into the surface water is not always possible. In addition, it might be economically advantageous if the sodium bicarbonate could be recovered too.
Another aspect of the present invention is in the recovery of carbon dioxide from flue gases from the burning of hydrocarbon feed streams, such as natural gas. In view of the increasing efforts to reduce global warming by capturing carbon dioxide at the origin, there is a need for an easy and economic process for capturing carbon dioxide and recovering this in a suitable way for further use.


AU-A 2004320909 discloses a method for producing alkali metal hydrogen carbonate. The method comprises reacting an aqueous solution containing alkali metal ions with carbon dioxide in a prescribed crystallizer. Further the prescribed crystallizer further comprises a crystallizer and dissolution apparatus.

WO-A 01/14254 discloses a process for producing alkali metal hydrogen carbonate. The process comprises crystallizing crystals from the reaction of an aqueous solution containing alkaline metal ions and carbon dioxide, wherein an operation is intermittently repeated in which the concentration of the alkali metal hydrogen carbonate dissolved in the crystallization solution in the crystallizer is regulated to below the saturation concentration to dissolve away fine particles of the alkali metal hydrogen carbonate.

FR-A 2108958 discloses the process for production of alkali carbonates and bicarbonates following the Solvay process by adsorption of carbon dioxide from synthesis gases in alkali hydrate solutions.

Gornev, S.U., Trudy Vsesoyuzn. Inst. Sodovi Prom, 9, 36-44, 1956, discloses a process for the production of soda and potash by carbonization of weakly basic solutions from Al₂O₃ production comprising sodium and potassium carbonates and sulfates.
It is an object of the invention to provide an improved process, wherein on the one hand sodium bicarbonate is produced and on the other hand molybdenum compounds and/or other impurities are removed and/or recovered as an aqueous solution having an increased concentration, thereby enabling a much easier and more economical recovery thereof.

One of the problems of separating the various components of the waste stream resides in the crystallisation behaviour of the salts. A substantial fraction of sodium molybdate would be expected to be included in sodium bicarbonate when a combined solution thereof is subjected to crystallisation (co-crystallization). This would rule out any crystallisation method, as the presence of molybdenum in sodium carbonate and/or sodium bicarbonate would make it impossible for further use or sale. Surprisingly, it has now been found that pure sodium bicarbonate can be produced from a caustic effluent or waste stream by treating said caustic effluent or waste stream with carbon dioxide. The sodium bicarbonate has a lower solubility than that of the starting materials and will crystallize from the solution. The resulting sodium bicarbonate crystals are removed and recovered by filtration and the mother liquor can be recycled into the process. The sodium bicarbonate crystals can be further purified by washing with water. In the case wherein the effluent or waste stream additionally contains further impurities, such as molybdenum compounds, only part of the mother liquor is recycled and another part is removed from the process to remove and/or recover said impurities.

The advantages of the present invention are that the new process produces a new product in the form of sodium bicarbonate, no acid is required, no ion exchange column is required to recover sodium molybdate, achieves a higher production of distilled water, no waste stream into the environment and less carbon dioxide emission since the process consumes carbon dioxide.
Accordingly the present invention is directed to a process for treating a gas flow containing carbon dioxide obtained from burning at least one organic waste or feed stream, comprising the steps of:

i) quenching the gas flow using an alkaline aqueous liquid;

ii) crystallizing sodium bicarbonate from the product flow of step i) by treatment with carbon dioxide, wherein said crystallizing may occur simultaneously with, or subsequent to the quenching.

iii) removing the resulting sodium bicarbonate crystals from the liquid; and

iv) recycling the resulting mother liquor from step iii) into the process as alkaline aqueous liquid in step i).

In a preferred embodiment according to the invention, the solution of step i) is quenched at a temperature of > 40 °C, preferably at a temperature of > 50°C. Alternatively, the solution of step i) is quenched at a temperature of > 90 °C. The pH of the said aqueous alkaline liquid of step (i) is at least 8, preferably between 9 and 12.

Accordingly the present invention is further directed to a process for treating a gas flow containing carbon dioxide obtained from burning at least one organic waste or feed stream, which is incinerated, resulting in the gas flow containing carbon dioxide, which additionally contains further impurities, such as molybdenum compounds, and wherein only part of the mother liquor from step iii) is recycled and another part is removed from the process to remove and/or recover said impurities.

The molybdenum compounds are recovered from the part of the mother liquor that is not recycled by eutectic freeze crystallization. The aqueous liquid, comprising sodium bicarbonate and one or more molybdenum compounds, is treated according a process comprising freeze crystallising the solution at the eutectic freezing point thereof and recovering substantially pure ice crystals, substantially pure sodium bicarbonate and an aqueous product solution containing dissolved molybdenum compounds.

In freeze crystallisation at a eutectic freezing point (Eutectic freeze crystallisation; EFC) on the one hand crystalline material is obtained, and on the other hand ice crystals. It has surprisingly been found that in this process, sodium bicarbonate crystallises, whereas the molybdenum compounds will remain in the liquor and will build up in a recycle stream, from which a bleed is used as molybdenum product stream.

In the context of the present invention pure sodium bicarbonate crystals are recovered. In this respect pure or substantially pure refers to amounts of molybdenum and other contaminants, that are below 200 ppm (mg/kg), preferably less than 20 ppm and most preferred less than 2 ppm.

The sodium bicarbonate produced by the process of the present invention can be used for various purposes. In the first place it can be used as such in application where presently the conventionally produced sodium bicarbonate is used. It is also possible to use it as a temporary storage of carbon dioxide, for example when the process of the invention is used in conjunction with a cogeneration system for green houses. Quite often carbon dioxide is recovered from the flue gas as a carbon supply to the green house. However, the production of carbon dioxide and the amounts needed are often not in balance. The present invention allows capturing excess carbon dioxide and converting this into sodium bicarbonate. The sodium bicarbonate can be stored and, when needed be decomposed into carbon dioxide and sodium carbonate. The latter can then be reused for the quenching at a later stage.

As indicated above, an important application of this process is in the treatment of waste streams originating from burning of waste streams originating from oxidation processes. An example is the styrene monomer/propylene oxide production using a molybdenum based catalyst. In
such a process the amount of molybdenum compounds (calculated as molybdenum) in the said aqueous solution comprising sodium bicarbonate and molybdenum compounds is between 2 and 20,000 ppm and in the said aqueous product solution containing dissolved molybdenum compounds between 4 and 50,000 ppm. It is preferred that in the said aqueous product solution comprising sodium bicarbonate and molybdenum compounds, the molybdenum content is at least twice as high as in the original solution.

In general, caustic waste streams contain between 1 and 15 wt.%, more in particular between 2 and 10, more in particular between 2 and 2.5 wt.%, of sodium (as ion).

In another embodiment of the invention, the organic feed stream is a fuel fed into a gas motor to produce heat and power ( cogeneration), the exhaust gases from the motor being quenched with additional supply of sodium hydroxide or sodium carbonate.

In figures 1 and 2, flow sheets are given of two embodiments of the process of the invention. Figure 3 shows an EM photograph of the product obtained by the process of figure 2.

Figure 1 shows the recovery of bicarbonate from a caustic waste stream. Caustic, carbon dioxide, and trace impurities are introduced into quenching step 1. Mother liquor from filtration/washing step 3 is used as quenching liquor. Steam is generated in the quenching and removed from the step. The liquid is fed to carbonization step 2, wherein carbon dioxide is added. The crystal slurry from this step is filtered and washed in step 3, with addition of water. Bicarbonate crystals are obtained, as well as a mother liquor. The major part of the mother liquor is recycled as quenching liquid to step 1. A small amount is removed as bleed stream containing concentrated impurities.

In the flow sheet shown in figure 2 a carbon dioxide containing gas flow, for example from a gas motor, is fed to quenching step 1, where
the gas flow is quenched using fresh sodium carbonate and mother liquor from filtration step 2. In filtration step 2 the resulting slurry of sodium bicarbonate crystals is filtered and the mother liquor is recycled.

The invention is now elucidated on the basis of the following, non-limiting examples.

EXAMPLE

Example 1

Using the process of figure 1, 2 l of a representative industrial sample from a quench stream as described in relation to figure 1 above containing 679 ppm Mo in the form of sodium molybdate, 4.11 mass% sodium carbonate and 3.58 mass% sodium bicarbonate was saturated with an excess of carbon dioxide for 30 minutes at 40°C Celsius. After 10 minutes sodium bicarbonate crystals were formed. After 30 minutes reaction time the sodium bicarbonate crystals were filtered and washed with water. The sodium bicarbonate crystals contained 5 ppm Mo.

Example 2

200 l of a representative industrial sample from a quench stream as described in relation to figure 1 above containing 1390 ppm Mo in the form of sodium molybdate, 4.2 mass% sodium carbonate and 4.5 mass% sodium bicarbonate was saturated with an excess of carbon dioxide for 2 hours at 25°C Celsius. After 1 hour sodium bicarbonate crystals were formed. After 2 hours reaction time the slurry was cooled. At -2.3°C crystallisation of ice occurred and the temperature remained stable, indicating that the eutectic point was reached. Next, the sodium bicarbonate crystals were filtered and washed with
water. The sodium bicarbonate crystals contained 0.8 ppm Mo. An EM photograph of the crystals obtained in the example is given in figure 3.
Claims

1. Process for treating a gas flow containing carbon dioxide obtained from burning at least one organic waste or feed stream, comprising the steps of:
   i) quenching the gas flow using an alkaline aqueous liquid;
   ii) crystallizing sodium bicarbonate from the product flow of step i) by treatment with carbon dioxide, wherein said crystallizing may occur simultaneously with, or subsequent to the quenching,
   iii) removing the resulting sodium bicarbonate crystals from the liquid; and
   iv) recycling the resulting mother liquor from step iii) into the process as alkaline aqueous liquid in step i).

2. Process according to claim 1, wherein the solution of step i) is quenched at a temperature of > 40°C, preferably at a temperature of > 50°C.

3. Process according to claim 1, wherein the solution of step i) is quenched at a temperature of > 90°C.

4. Process according to claims 1-3, wherein at least one organic waste or feed stream is an organic waste stream containing organic acids, which is incinerated, resulting in the gas flow containing carbon dioxide, which additionally contains further impurities, such as molybdenum compounds, and wherein only part of the mother liquor from step iii) is recycled and another part is removed from the process to remove and/or recover said impurities.

5. Process according to claim 4, wherein the organic waste or feed stream is a waste stream from styrene-propylene oxide production.

6. Process according to claim 1-3, wherein the organic feed stream is a fuel fed into a gas motor to produce heat and power (cogeneration), the exhaust gases from the motor being quenched with additional supply of sodium hydroxide or sodium carbonate.
7. Process according to claim 6, wherein the sodium bicarbonate is stored and/or decomposed into carbon dioxide and sodium carbonate.

8. Process according to claim 4, wherein the further impurities, such as molybdenum compounds, are recovered from the part of the mother liquor that is not recycled by eutectic freeze crystallization.

9. Process according to any one of the claims 1-8, wherein the pH of the said aqueous alkaline liquid is at least 8, preferably between 9 and 12.

10. Process according to claim 1-9, wherein sodium concentration is between 1 and 15 weight%, preferably between 2 and 2.5 weight%
Figure 1:

Caustic, Carbon dioxide in fuel gas (in gas flow), Trace impurities

Quenching 1

Steam in fuel gas (in gas flow)

Carbon dioxide

motherliquor

Carbonation 2

Carbon dioxide

Filtration, washing 3

water

Bleedstream Containing Concentrated impurities

Bicarbonate crystals
Figure 2

Carbon dioxide in fuel gas (in gas flow)

Sodium carbonate

Quenching 1

Filtration 2

fuel gas (gas flow)

motherliquor

Sodium bicarbonate crystals

Fig 3: sodium bicarbonate crystals from example 2