

SPECIFICATION

PROCESS FOR PRODUCING ALKYLENE CARBONATE

FIELD OF ART

The present invention relates to a process for producing alkylene carbonate. More particularly, it relates to a process for producing high-quality alkylene carbonate by using as a starting material carbon dioxide gas in the oxidation reaction gas formed by gas-phase oxidation of ethylene.

BACKGROUND ART

Alkylene carbonate is a compound useful as an organic solvent or a reaction reagent. Especially, it is used as a solvent for secondary lithium batteries and a material for forming alkylcarbonate.

For the production of alkylene carbonate, it is a conventional process in the art to react alkylene oxide with carbon dioxide gas, and many reports have been made on the catalysts and processes for such a reaction.

The carbon dioxide gas generally used industrially as a starting material for the production of alkylene carbonate is provided from by-product carbon dioxide gas produced in a hydrogen forming process for the production of ammonia or

from carbon dioxide gas produced in a fermentation process, and such carbon dioxide gas usually has a purity of not less than 99.5 vol% as it is passed through the steps of recovery and refining. Also, carbon dioxide gas further enhanced in purity as required is commercially available.

Carbon dioxide gas is also produced as a by-product in an ethylene oxide production process. For the production of ethylene oxide, usually there is used such a method that ethylene is partially oxidized by using a silver catalyst, and in this process a complete oxidation reaction of ethylene takes place as a side reaction to produce carbon dioxide gas. Carbon dioxide gas is generally eliminated as it is harmful to the partial oxidation reaction of ethylene, and the eliminated carbon dioxide gas is usually released into the atmosphere.

If such released by-product carbon dioxide gas can be utilized as a starting material for the production of ethylene carbonate, it would be not only of great advantage economically but would also be beneficial in environmental terms as this carbon dioxide gas, which is an earth-warming gas, can be fixed and won't be released into the atmosphere. Especially in case where the objective product is ethylene carbonate, as both starting materials can be obtained from a same plant, it becomes possible to greatly simplify the facilities for the storage and transport of the materials.

Therefore, this is of great economical benefit.

Use of carbon dioxide gas produced as a by-product in the ethylene oxide production process as a starting material for the production of alkylene carbonate is per se disclosed in, for instance, Japanese Patent Application Laid-Open (KOKAI) No. 9-67365.

Also, the method of separating and recovering carbon dioxide gas produced as a by-product in the ethylene oxide production process is disclosed in, for instance, Japanese Patent Application Laid-Open (KOKAI) No. 50-40508.

Thus, utilization of carbon dioxide gas produced as a by-product and recovered in the ethylene oxide production process for the production of alkylene carbonate has many advantages. However, this recovered carbon dioxide gas is usually notably low in purity as compared to the said industrially used carbon dioxide gas and generally contains a large amount, usually not less than 1 vol%, of hydrocarbons. In an alkylene carbonate production process, the starting carbon dioxide gas is supplied in an excess amount to a reactor and the unreacted carbon dioxide gas is used cyclically, so that use of the said low-purity carbon dioxide gas tends to cause accumulation of hydrocarbons in the reaction system in the said carbon dioxide gas circulation process, inducing a reduction of the partial pressure of carbon dioxide gas in the reactor. This does

harm to the alkylene carbonate forming reaction and promotes the undesirable side reactions to affect the quality of the product ethylene carbonate.

For avoiding such a problem, it usually needs to purge a greater amount of carbon dioxide gas containing the starting alkylene oxide, but this leads to a loss of the starting carbon dioxide gas as well as a loss of the starting alkylene oxide and also necessitates enlargement of the purged gas disposing equipment to provide economical disadvantages.

As means for purifying carbon dioxide gas to a high degree, there is known, for instance, a method called cryogenic distillation method, but this method requires a great deal of energy and can hardly be an appropriate method for obtaining a large amount of carbon dioxide gas to be used industrially as a starting material.

Accordingly, the object of present invention is to provide a process for producing high-quality alkylene carbonate by using as a starting material carbon dioxide gas which is produced as a by-product in the production of ethylene oxide by an oxidation reaction of ethylene.

DISCLOSURE OF THE INVENTION

As a result of earnest studies for solving the above problems, the present inventor has found that it was

possible to produce ethylene carbonate efficiently with avoiding the said problems by limiting the impurity concentration in the carbon dioxide gas recovered from the ethylene oxide production process to a certain level or below.

Thus, in an aspect of the present invention, there is provided a process for producing alkylene carbonate by reacting alkylene oxide and carbon dioxide gas, said process comprising using as starting carbon dioxide gas, the carbon dioxide gas which has been recovered from at least a part of the oxidation reaction waste gas left after recovery of ethylene oxide from the oxidation reaction gas in gas phase oxidation of ethylene and which has a purity of not less than 99.5 vol%.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a flow chart illustrating an example of operation procedure of the production apparatus used in the process of the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention is explained in detail below with reference to the embodiments thereof.

[Production of ethylene oxide]

Ethylene oxide is usually produced by catalytic gas-

phase oxidation of ethylene using a silver catalyst. In this method, as described in Ullmanns Encyclopedia of Industrial Chemistry, 5th Ed., Vol. A10, p. 117 ff., starting gas mainly comprising ethylene, oxygen and methane as a diluent gas, are passed through a multiple tube reactor packed with a silver catalyst to carry out their reaction. Selectivity of ethylene into ethylene oxide is approximately 80%, with remaining approximately 20% of ethylene being made into carbon dioxide gas and water by the complete oxidation reaction. The oxidation reaction gas discharged from the reactor comprises produced ethylene oxide, unreacted ethylene, carbon dioxide gas, oxygen, diluent gas, etc. Produced ethylene oxide is absorbed into the liquid phase in an absorber using water as absorbing solution. Ethylene oxide absorbed into the absorbing solution is stripped in an ethylene oxide stripper, then recovered from the column overhead as a high-concentration aqueous solution, and further subjected to dehydration refining in a distillation tower to become a product. The product ethylene oxide can be used as a starting material for the production of ethylene carbonate according to the process of the present invention.

[Recovery of carbon dioxide gas]

The oxidation reaction waste gas produced after absorption of ethylene oxide is sent in its entirety or

partly to a carbon dioxide gas removal system (carbon dioxide gas recovery equipment).

According to Ullmanns Encyclopedia of Industrial Chemistry, 5th Ed., Vol. A10, p. 124 ff., the oxidation reaction waste gas comprises about 15 to 40 vol% of ethylene, 1 to 60 vol% of methane and 5 to 15 vol% of carbon dioxide gas although the gas composition is somewhat variable depending on the plant operating conditions.

The carbon dioxide gas removal system (carbon dioxide gas recovery equipment) comprises a carbon dioxide gas absorber, a preliminary stripping apparatus and a carbon dioxide gas stripper.

The oxidation reaction waste gas sent to the carbon dioxide gas removal system is first introduced to the bottom of the carbon dioxide gas absorber and cleaned by a carbon dioxide gas absorbing solution comprising an aqueous solution containing a carbon dioxide gas absorbent, whereby the most part of carbon dioxide gas in the waste gas is removed. As the carbon dioxide gas absorbent, for instance, alkaline metal carbonates such as potassium carbonate, alkanolamines such as diisopropanolamine, and alkaline metal salts of amino acids can be mentioned, of which potassium carbonate is especially preferable. In the above cleaning treatment, ethylene used as a starting material and methane used as a diluent gas are also dissolved in slight amount,

in the absorbing solution along with carbon dioxide gas. The oxidation reaction waste gas reduced in content of carbon dioxide gas is discharged from the column overhead and joined with the portion of oxidation reaction waste gas which was not sent to the carbon dioxide gas removal system, and after supplied with the consumed amounts of oxygen and ethylene, it is again sent to the oxidation reactor as a starting oxidation reaction material.

The carbon dioxide gas absorber is operated under a high pressure of usually 1.0 to 2.5 MPa, preferably 1.5 to 2.2 MPa and at a temperature of usually 30 to 150°C, preferably 60 to 120°C. The type of the carbon dioxide gas absorber used in the present invention is not specifically restricted; it is possible to use either a tray column or a packed column. The carbon dioxide gas concentration in the carbon dioxide gas absorbing solution obtained from the bottom of the carbon dioxide gas absorber cannot be specified unequivocally as it depends on the type of the absorbing solution and the operating temperature of the absorber, but usually it is 3 to 20 wt%.

The carbon dioxide gas absorbing solution which has absorbed carbon dioxide gas is sent to a preliminary stripping apparatus. The absorbing solution contains trace amounts of ethylene and methane as mentioned above, so that if the solution is subjected directly to a carbon dioxide

gas stripping treatment, ethylene and methane may be mixed in the recovered carbon dioxide gas to reduce its purity. In the preliminary stripping apparatus, a part of the gases absorbed in the carbon dioxide gas absorbing solution is stripped before stripping of the whole amount of the gases to thereby reduce the concentration of the low-boiling point impurity gases such as hydrocarbons staying dissolved in the carbon dioxide gas absorbing solution. As for the structure of the preliminary stripping apparatus, although it is possible to use a packed column or a tray column, there is no need of installing a specific distillation column, and it is usually sufficient for the purpose to use a simple vacuum flash vessel, since solubility of methane and ethylene is far lower than that of carbon dioxide gas. A reboiler may be provided for promoting stripping. As the gas stripped by preliminary stripping contains ethylene and methane, it is preferably recycled to the ethylene oxide recovery system (absorber) or to the step for gas phase oxidation of ethylene.

The preliminary stripping apparatus is operated at a temperature of usually 50 to 150°C, preferably 95 to 120°C, under a pressure of usually 0.1 to 1.0 MPa, preferably 0.1 to 0.5 MPa. If, in this operation, the amount of gas stripped is insufficient, removal of hydrocarbons is not effected sufficiently, with the result that the purity of

carbon dioxide gas recovered from the carbon dioxide gas stripper becomes insufficient for the production of alkylene carbonate. Simple increase of the stripping rate is also unfavorable as it leads to low efficiency of the process.

In the present invention, it is necessary that the purity of carbon dioxide gas finally recovered from the carbon dioxide gas stripper be not less than 99.5 vol%, preferably not less than 99.6 vol%, more preferably not less than 99.7 vol%, but the said purity is practically decided by the degree of removal of hydrocarbons by the stripping treatment in the preliminary stripping apparatus. Usually a good result can be obtained when the stripping operation is controlled so that the ratio of the amount of stripping (A) in the preliminary stripping apparatus to the sum (B) of the said amount of stripping in the preliminary stripping apparatus and the amount of carbon dioxide gas recovered from the top of the carbon dioxide gas stripper (the sum (B) being substantially equal to the amount of gas absorbed in the carbon dioxide gas absorber) (the ratio, B/A , being hereinafter referred to as stripping rate in the preliminary stripping apparatus) will become usually not less than 2%, preferably not less than 2.5%, more preferably not less than 3%. However, if the stripping rate is increased excessively, although purity of carbon dioxide gas is enhanced, efficiency of the carbon dioxide gas recovery process lowers

as a whole. Therefore, the upper limit of the stripping rate is usually set at 10%.

The carbon dioxide gas absorbing solution discharged from the preliminary stripping apparatus is sent to the carbon dioxide gas stripper. This carbon dioxide gas stripper is schemed for stripping substantially the whole amount of carbon dioxide gas staying dissolved in the carbon dioxide gas absorbing solution. The structural type of the carbon dioxide gas stripper used in the present invention is preferably a packed column or a tray column in view of stripping efficiency. Stripping is preferably of a system in which a reboiler is provided at the bottom of the carbon dioxide gas stripper or steam is blown into the tower, or both of these systems are combined to conduct heat stripping.

The stripping treatment in the carbon dioxide gas stripper is usually carried out under a pressure equal to or lower than that used for the preliminary stripping, preferably not more than 0.3 MPa, and at a temperature of usually 50 to 150°C, preferably 80 to 120°C. The carbon dioxide gas absorbing solution is introduced into the carbon dioxide gas stripper from its top and desorbs the absorbed carbon dioxide gas as the bottom portion of the column is heated by a heat exchanger or other means. If necessary, steam may be blown through the solution to conduct stripping so as to promote stripping.

The carbon dioxide gas absorbing solution is subjected to the stripping treatment in the carbon dioxide gas stripper, and the absorbed carbon dioxide gas is released in the column, whereby the solution is regenerated and returned to the carbon dioxide gas absorber as a carbon dioxide gas absorbing solution.

The high-purity carbon dioxide gas recovered from the ethylene oxide production process in the manner described above has a sufficient purity for use as a starting material for the production of alkylene carbonate and can be applied favorably to the intended use.

[Production of alkylene carbonate]

The carbon dioxide gas recovered from the ethylene oxide production process in the manner described above is reacted with alkylene oxide to produce alkylene carbonate.

As the catalyst for the alkylene carbonate forming reaction, it is possible to use the known catalysts, for example, bromides or iodides of alkaline metals (Japanese Patent Publication (KOKOKU) No. 38-23175), halides of alkaline earth metals (U.S. Patent No. 2,667,497), alkylamines, quaternary ammonium salt (U.S. Patent No. 2,773,070), organotin, organogermanium or tellurium compounds (Japanese Patent Application Laid-Open (KOKAI) No. 57-183784), and halogenated organophosphonium salts

(Japanese Patent Application Laid-Open (KOKAI) No. 58-126884). Among these compounds, halides of alkaline metals such as potassium bromide and potassium iodide, and halogenated organophosphonium salts are preferred in view of activity and selectivity.

As the reactor for the production of alkylene carbonate, there have been proposed a series-arranged combination of plural tubular reactors and condensers (Springmann: Fette Seifen Anstrichemittl, Vol. 73, pp. 396-399, 1971), a loop type reactor (Peppel: Industrial and Engineering, Vol. 50, pp. 767-770, 1958), and a bubble column reactor (Japanese Patent Application Laid-Open (KOKAI) No. 6-345699). Any of the said means can be used, but a bubble column reactor with an external circulation is particularly preferable because it excels in diffusion supply of carbon dioxide gas to the liquid phase and in prevention of runaway reactions by cooling.

Since the above reaction is exothermic, the reaction temperature is controlled by the heat removal. The reaction temperature, although variable depending on the catalyst used, is usually 80 to 200°C, preferably 100 to 180°C.

The alkylene carbonate forming reaction rate is controlled by the partial pressure of carbon dioxide gas used as a starting material, so that the pressure under which the reaction is to be carried out is preferably as

high as it can be. Rise of reaction pressure, however, entails a corresponding enhancement of the required pressure resistance of the reactor and associated equipment, which leads to an increase of equipment cost. The preferred range of reaction pressure is usually 1 to 10 MPa, preferably 1 to 5 MPa.

Carbon dioxide gas is supplied to the reactor in an amount usually 1 to 20 times by mole the amount of ethylene oxide supplied to the reactor. Carbon dioxide gas does not merely serve as a starting material but it also functions to prevent the side reactions from taking place due to distribution of the composition and distribution of heat by stirring the solution in the reactor, so that carbon dioxide gas is supplied in excess of the amount necessary for the reaction. The unreacted and surplus portions of carbon dioxide gas are partly purged for preventing accumulation of the by-product low-boiling substances and impurities in the starting carbon dioxide gas and circulated back to the reactor for reuse. Purging is controlled while monitoring the amount of accumulation of impurities. The amount of gas purged is usually 0.1 to 8%, preferably 0.2 to 5%, based on the flow rate of the recycled carbon dioxide gas.

If the amount of impurities brought to the alkylene carbonate production process is large, such impurities are accumulated to cause troubles to the reaction. While the

influence of the accumulation of impurities itself to the reaction is unignorable, it is more serious that the partial pressure of carbon dioxide gas lowers relatively by the impurity accumulation to cause a drop of main reaction rate. This results in an elongation of the required time for reaction and a drop of productivity and product quality.

Regarding the drop of partial pressure of carbon dioxide gas, it is possible to maintain the partial pressure by increasing the said rate of purge, but this leads to a loss of carbon dioxide gas and alkylene oxide used as starting materials and also necessitates scale-up of the purged gas disposal equipment, etc., resulting in an economical disadvantage. The catalyst can be used in a proper concentration according to the activity of the catalyst used in consideration of the desired productivity within the allowable range of solubility. The catalyst is supplied together with a solvent to the reactor, separated from alkylene carbonate produced after the reaction, and after supplemented with a fresh supply for the deficiency as required, circulated back to the reactor for reuse. As the solvent, it is convenient and preferable to use the objective product alkylene carbonate.

The alkylene carbonate separated from the catalyst already has a sufficiently high purity, but if necessary it can be further refined to a higher purity by ordinary vacuum

distillation system, etc.

The modes of practice of the present invention will be described in further detail with reference to the examples thereof, but it should be understood that the following examples are merely intended to be illustrative and not to be construed as limiting the scope of the invention.

Example 1

The reaction was carried out using a producing apparatus having the operation procedure shown in FIG. 1.

(1) Recovery of CO_2 from ethylene oxide (EO) producing step:

In the following description, the flow rates of the materials are expressed in terms of parts by weight based on the weight velocity of the oxidation reaction waste gas introduced into the CO_2 absorber 1 as one part by weight.

One part by weight of the oxidation reaction waste gas (CO_2 concentration: 6 vol%, CH_4 concentration: 57 vol%, C_2H_4 concentration: 24 vol%) left after recovery of ethylene oxide from the oxidation reaction gas of ethylene obtained in the step of catalytic gas phase oxidation of ethylene using a silver catalyst was introduced through line L1 into the bottom of a carbon dioxide gas (CO_2) absorber 1 having a number of theoretical plates of 3 and operated at a

temperature of 110°C under a pressure of 1.7 MPa. From the top of the CO₂ absorber 1, 7 parts by weight of an aqueous solution of potassium carbonate (K₂CO₃) was introduced as an absorbing solution through line L4.

The absorbing solution which has absorbed CO₂ was introduced through line L3 into a preliminary stripping apparatus (flasher) 2 operated at 107°C under 0.15 MPa. After reduced in hydrocarbon concentration by the stripping treatment, the solution was supplied through line L7 into the top of a carbon dioxide gas (CO₂) stripper 3 having a number of theoretical plates of 5 and operated at 110°C under 0.1 MPa, and CO₂ was stripped and recovered. In this operation, the amount of gas released from flasher 2 through line L6 was equivalent to 5.0% (stripping rate: 5.0%) of the total of the amount of gas released from flasher 2 and the amount of CO₂ recovered from CO₂ stripper 3 through line L8.

Recovered CO₂ was compressed by a compressor (not shown) and supplied to carbonate forming reactor 4 through line L8.

Determining the concentrations of hydrocarbons contained in recovered CO₂, it was found that CH₄ was present in an amount of 0.03 vol% and C₂H₄ in an amount of 0.06 vol% (both being calculated by excluding water). From this result, CO₂ purity was determined to be 99.91 vol%.

(2) Ethylene carbonate (EC) forming reaction:

In the following description, the flow rates of the materials are expressed in terms of parts by weight based on weight velocity of ethylene oxide as one part by weight.

An EC forming reaction was carried out using the said recovered CO₂. One part by weight of ethylene oxide (from line L9) obtained from the oxidation reaction of ethylene and 8.2 parts by weight of recovered CO₂ (from line L8) were introduced to the bottom of a bubble column carbonate-forming reactor 4. A solution of 0.01 part by weight of potassium iodide in 0.1 part by weight of ethylene carbonate was supplied (from line L10) as catalyst. The reaction solution was discharged along with the gas from the top of the bubble column reactor 4 and led into a gas-liquid separator 5 through line L11 for separation into gas and liquid. 0.5% of the whole of the separated gas was purged out of the system through line L13 while the remainder was passed through line L12, joined with the said stripped CO₂ (from line 8) via a compressor (not shown) and recycled to the EC forming reactor 4. Part of the separated liquid (line L15) was taken out as the product from line L14 and the remainder, after deprived of heat by a heat exchanger 6, was recycled to the bottom of the EC forming reactor 4. The reactor was controlled to a condition of 180°C and 2 MPa.

When the operation was carried out continuously under the above conditions, the hydrocarbon concentration in the

reactor 4 remained constant at about 4 vol% and a stable operation was possible. From the reaction solution recovered from line L14, ethylene carbonate was evaporated at 138°C under 4 kPa, thereby separating the catalyst to obtain ethylene carbonate.

Comparative Example 1

CO₂ having a purity of 98.9 vol% (containing 0.37 vol% of CH₄ and 0.74 vol% of C₂H₄ as impurities) was prepared as starting gas.

The EC forming reaction was carried out in the same way as in Example 1 except for use of the above prepared CO₂. As the continuous operation went on, the hydrocarbon concentration in the circulating gas arose, causing a relative drop of CO₂ concentration, with the hydrocarbon concentration finally reaching 24 vol%. Since a drop of EO conversion was observed, the material feed rate was controlled so that the conversion became constant. The ethylene carbonate obtained by separating the catalyst from the reaction solution had a tint which was considered attributable to the presence of the by-product aldehyde compound.

Comparative Example 2

The same procedure as defined in Comparative Example

1 was conducted except that the circulating gas purging rate was changed from 0.5% to 10% to maintain the partial pressure of CO₂ in the continuous operation. The CO₂ concentration was maintained at 96% and the product EC quality was substantially equal to that in Example 1, but the amount of EO purged increased approximately ten times.

INDUSTRIAL APPLICABILITY

According to the process of the present invention, there can be obtained the advantages in which it is possible to make effective use of carbon dioxide gas, to reduce discharge of carbon dioxide gas and alkylene oxide used as starting materials, and to produce high-quality alkylene carbonate.

What is claimed is

1. A process for producing alkylene carbonate by reacting alkylene oxide and carbon dioxide gas, said process comprising using as starting carbon dioxide gas, the carbon dioxide gas which has been recovered from at least a part of the oxidation reaction waste gas left after recovery of ethylene oxide from the oxidation reaction gas in gas phase oxidation of ethylene at the stripping rate of not more than 10% and which has a purity of not less than 99.5 vol%.

2. The process according to claim 1, wherein the recovery of carbon dioxide gas is carried out by introducing the reaction waste gas into a carbon dioxide gas recovering equipment comprising a carbon dioxide gas absorber, a preliminary stripping apparatus and a carbon dioxide gas stripper.

3. The process according to claim 2, wherein the carbon dioxide gas recovered from the carbon dioxide gas recovering equipment was obtained by such a manner that:

oxidation reaction waste gas is absorbed in a carbon dioxide gas absorbing solution in the carbon dioxide gas absorber,

the resulting absorbing solution is introduced into the preliminary stripping apparatus to strip part of the gas

absorbed in said absorbing solution, wherein the stripped gas is recycled to the ethylene oxide recovery system or to the step for gas phase oxidation of ethylene, and

the absorbing solution is introduced after the stripping treatment in the preliminary stripping apparatus to the carbon dioxide gas stripper for stripping carbon dioxide gas, wherein the stripping rate in the preliminary stripping apparatus is not less than 2%.