



## Invention Article

## A safe production process of alkylene oxide from alkylene carbonates

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## ARTICLE INFO

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## ABSTRACT

Alkylene oxides of low molecular weight, ethylene, and propylene oxides, have a widespread use in industry. They are used to produce other chemicals and products such as solvents, surfactants, antifreeze, adhesives, polyurethane foams, and pharmaceuticals. They are also used as fumigants in agricultural products and as sterilant for medical equipment and supplies. Unfortunately, it is worth noting that alkylene oxides also possess several physical and health hazards that merit special attention. They are flammable, explosive and their storage and transportation warrant stringent safety rules. The obvious solution to reduce the risk is to generate them from intermediate safety materials only when and only where they are necessary. The literature suggests that correspondent carbonates are very stable precursors. The scope of our study is that of identifying the optimal conditions to generate ethylene and propylene oxide in the moment just before their reaction and uses. The patent deals with some equipment and process conditions that guarantee a fast and reliable dissociation of carbonates in their correspondent oxides. The natural output of the patent is a unit able to provide the dangerous material *in situ*, under controlled conditions. As a results, all the risks related to transportation and storage are eliminated.

## Specifications Table

Subject code	1500 General Chemical Engineering
Specific subject area	The present invention is a process to produce alkylene oxides from carbonates.
Industry code	C07D 303/04 (Compounds containing oxirene rings and containing only hydrogen and carbon atoms in addition to the ring oxygen atom).
Details of inventors	Davide Moscatelli (davide.moscatelli@polimi.it; Politecnico di Milano) Mattia Sponchioni (mattia.sponchioni@polimi.it; Politecnico di Milano) Alberto Cesana (alberto.cesana@polimi.it; Politecnico di Milano) Gianmarco Polotti (gianmrco.polotti@polimi.it; Politecnico di Milano) Loic Ronin (loic.ronin@polimi.it; Politecnico di Milano)
Dates of invention	The invention was conceived in 2019 (proof of concept) and publicly disclosed in 2020 (after the filing of the priority patent application).
Patent details (Only if patented)	The priority patent application was filed on September 24th, 2020 (application number (continued on next column)

(continued)

Intended use	102,020,000,022,624); an international patent application was filed on September 13th, 2021 (application number: PCT/IB2021/ and published on March 31st, 2022 (publication number: WO 2022/064,320 A1); a European patent application was filed on August 2 <sup>nd</sup> 2023 (application number 21782818.5; publication number EP4217351) Patent owner: Politecnico di Milano Patent attorney or agent: Perani & Partners (Raffaella Asensio) Contact for service: Massimo Barbieri (Politecnico di Milano, Technology Transfer Office) Link to the international patent application: <a href="https://worldwide.espacenet.com/patent/search/family/073793619/publication/WO2022064320A1?q=WO2022064320A1">https://worldwide.espacenet.com/patent/search/family/073793619/publication/WO2022064320A1?q=WO2022064320A1</a>
Related research article	The invention is available for licensing to a company interested in developing an industrial plant. N/A (continued on next page)

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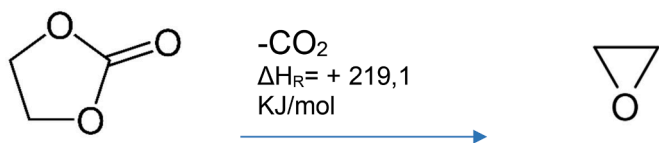


Fig. 1. Decomposition reaction of carbonate to form ethylene oxide.

(continued)

Related other sources: (datasets, software, diagrams, plans, etc.)	N/A
Funding/sponsor acknowledgement	This invention did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

### 1. Value of the invention

- The patented process allows to produce ethylene and propylene oxides in the needed quantity, *in situ*, and exactly before their use or consumption.
- Instead of dangerous alkylene oxides, safe and stable carbonates are transported and stored.
- The production is continuous, fast, extra pure, and easily controllable. The process can be carried out both on a small scale and in large quantities. The derived products are ready to be used in further reactions.

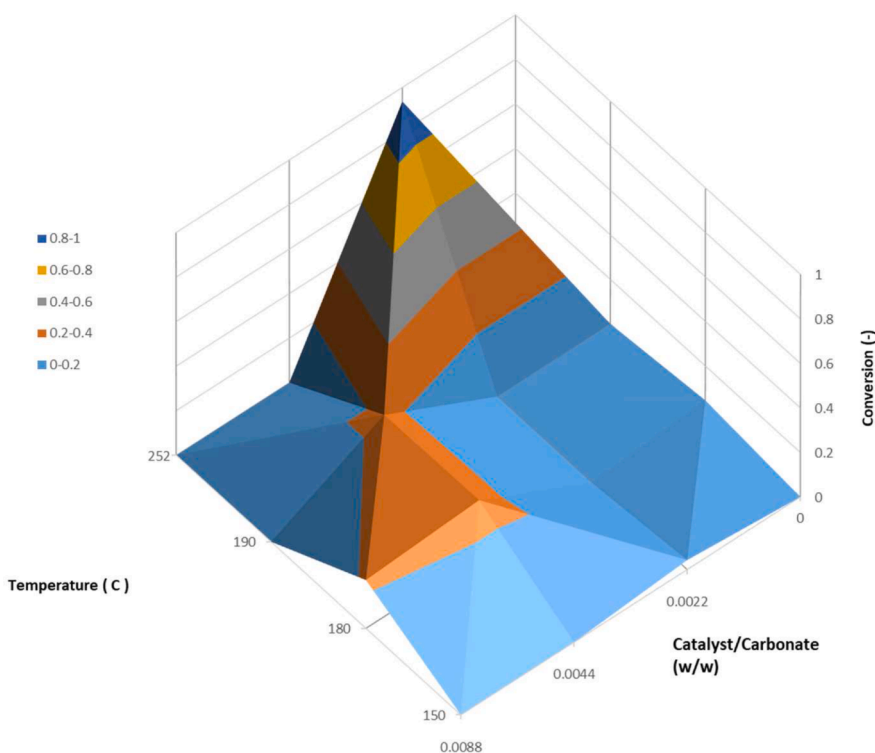


Fig. 2. Conversion vs reactor temperature and catalyst amount.

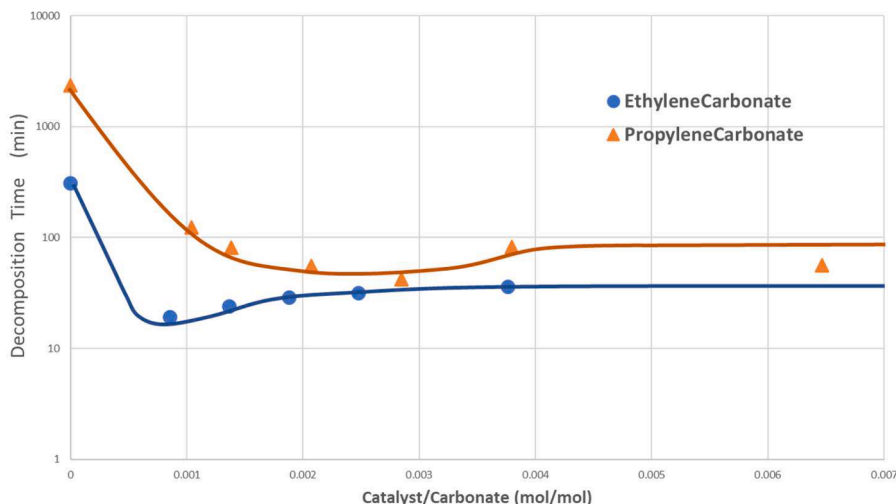


Fig. 3. Minima of decomposition time for carbonates.

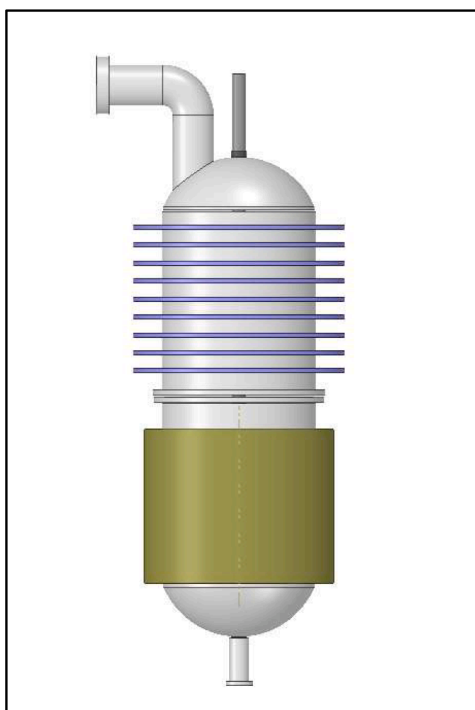


Fig. 4. A possible configuration of the generation unit.

- The catalyst is optimized to the minimum level, does not decompose, and does not need to be supported or mixed with any reactants. It is subsequently quickly removed from the products via moderate cooling.

## 2. Invention description

The invention relates to a catalytic process for producing alkylene epoxides (ethylene and propylene) starting from the corresponding alkylene carbonates by means of a decomposition reaction, using sodium bromide as catalysts, according to the scheme shown in Fig. 1.

The reaction temperatures range between 207 and 245 °C, while the catalyst is added in amounts comprised between  $5 \times 10^{-4}$  and  $8 \times 10^{-3}$  mol per mole of alkylene carbonate.

Sodium bromide turned out to be the most efficient catalyst in term of product conversion, which is almost complete.

A strong correlation between the amount of catalyst used and the reaction temperature was demonstrated for ethylene carbonate, as shown in Fig. 2.

Moreover, it was established that an excessive amount of catalyst does not further the decomposition, but rather increases the secondary by-products, thereby reducing the conversion.

Based on the previous observations, it was possible to define that for ethylene and propylene oxide certain ranges of temperature and catalyst amount optimized the conversion, while keeping almost complete the selectivity. The optimal ranges are evident for both species in Fig. 3, where the decomposition time is minimal in comparison with the optimal value of the catalyst.

The alkylene oxides are generated as a result of the catalyst (in the form of microcrystals) being suspended in the liquid carbonate and cannot evaporate. The carbonate decomposes producing only gaseous species (oxide and carbon dioxide) with the only need of abundant heating but without the need for agitation.

The heat flow rate is directly correlated with the alkylene oxide generation, and it can be used to modulate its production. The ceasing of heat flow causes the immediate interruption of the decomposition.

Another advantage of the in-situ generation of alkylene oxide from carbonates is the constant presence of inert gas thereby avoiding excessive concentration of vapours, normally given by the addition of additional inert gasses such as nitrogen.

Fig. 4 shows a possible configuration of the generation unit. From the bottom, the liquid carbonate enters the reactor which is kept at a constant temperature (between 210 and 250 °C). The external mantle provides the necessary heat flow using steam and electrical power. The catalysis occurs as the small crystal salts fluctuate inside the liquid in the reactor, without the need for agitation. Agitation is guaranteed by the intense formation of bubbles of the incoming products. Oxide and carbon dioxide exit from the top after a natural cooling in the upper part of the reactor occurs, condensating the carbonate vapor.

The generation unit runs for a long time since the catalysis is not easily affected by the reduction activity and the number of impurities is limited.

The generation unit represents a continuous step for the alkylene oxide generation which can easily be associated with continuous or batch processes that already exist without the need for a general plant redesign. It may be possible, depending on the process conditions, that

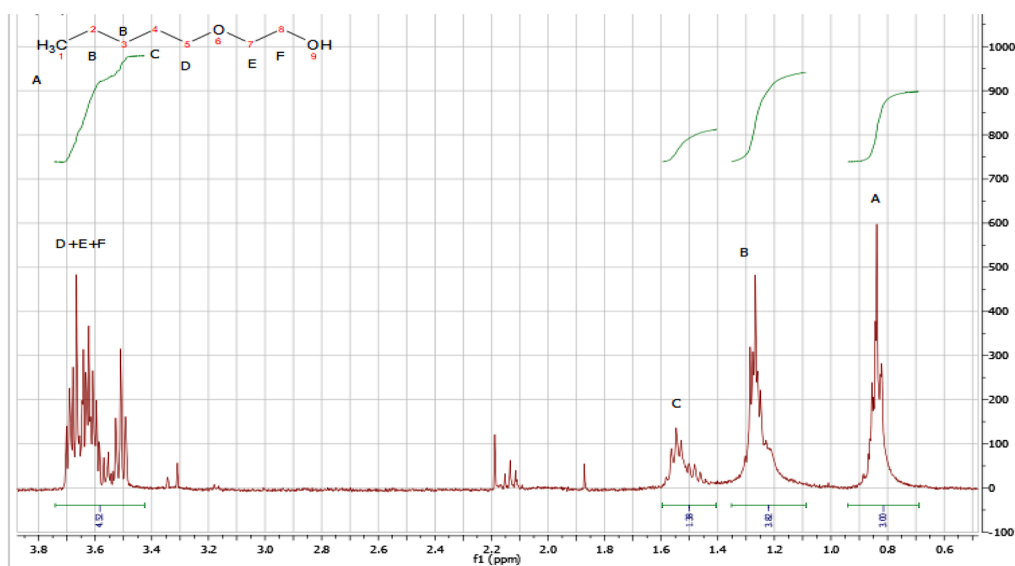


Fig. 5. NMR analysis of polyglycols.

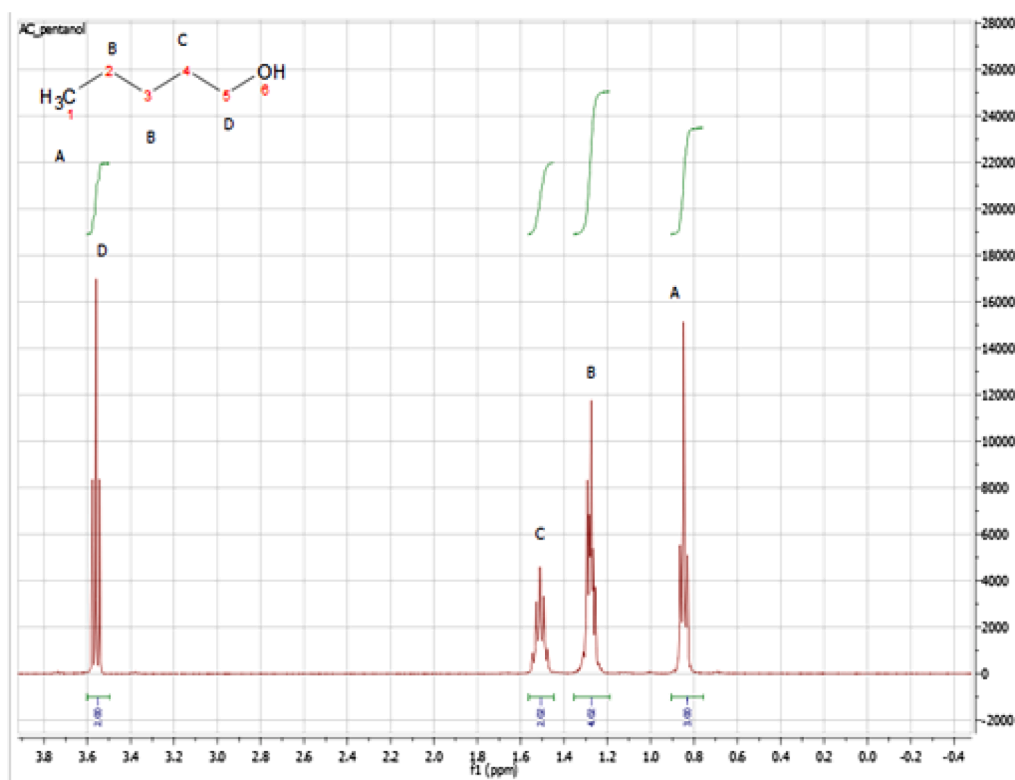


Fig. 6. NMR analysis of ethoxylated alcohols.

the gas mixture at the exit needs to be compressed at high pressure since our tests show that the decomposition runs up to 2 bars only.

To show that the alkylene oxides generated are exactly equal to the standard raw materials, we synthesized a polyglycol (Fig. 5) and we ethoxylated a fatty alcohol (Fig. 6) using the standard procedures highlighted in the literature, as proved by the NMR spectra.

### 3. Background

Interest in using a precursor of alkylene oxides which is not dangerous and can hence be easily moved and stored is not novel in literature, with many articles being dated as far back as the 1980s. From the very beginning, the carbonates were identified as the best candidates to recover the corresponding oxide through homolytic dissociation.

Decomposition requires high temperatures, above 210 °C, and a catalyst. The catalysts have different structures: polyhalogenated hydrocarbons [1], arsonium salts [2], and alkali bromides [3]. Shapiro et al. [4] disclose a process for the decomposition of ethylene carbonate in the presence of sodium bromide (NaBr) at different temperature ranges and catalysts amount.

The patentability search reports (relating to the Italian and the International patent applications) cited four documents as background art:

- D1: EP 0,047,473 A1 [3]
- D2: EP 0,047,474 A1 [5]
- D3: US 4192,810 A [6]
- D4: "Decomposition of ethylcarbonate in the presence of alkali metal halides" [4]

The search was carried out using the subclass C07D (Heterocyclic compounds).

In the first Office Action of the Italian patent application, the examiner recognized the novelty requirement of claims 1 – 16, but not the inventive step.

Considering that claim 1 of the invention as a selection out of the

Table 1

List of the classification codes used in the state-of-the-art patent search.

Classification symbol	Definition
C07D303/04	Compounds containing three-membered rings having one oxygen atom as the only ring hetero atom • Compounds containing oxirane rings •• containing only hydrogen and carbon atoms in addition to the ring oxygen atoms
C07D301/02 B01J23/00	Preparation of oxiranes • Synthesis of the oxirane ring Catalysts comprising metals or metal oxides or hydroxides, not provided for in group B01J21/00
C07B61/00	Other general methods

process disclosed in D1 (the closest prior art document), and the technical problem to be solved can be seen as the provision of a more efficient method for the preparation of ethylene or propylene carbonate.

In this way, the technical effect achieved is a considerable increase in the reaction rate concerning the D1 process (about 8 times higher). It is obtained with a specific amount of catalyst and with the temperature ranges claimed. Were one to start with the technical teaching of D1, not even a skilled person would have reached the claimed invention. D2 is similar to D1. D3 does not mention the specific use of NaBr as a catalyst, while D4 discloses a decomposition reaction of ethylene carbonate in different temperatures and catalyst ranges. So, even by combining the technical teaching of these documents with D1, a skilled person would not have been able to solve the same objective technical problem.

In the Written Opinion of the PCT application, the examiner recognized all the claims as novel and inventive.

To confirm the invention's freedom of operation, a supplementary state-of-the-art patent search can be carried out on Espacenet (a free online patent database provided by the EPO) using the following queries:

(cl any "C07D303/04" OR cl any "C07D301/02" OR cl any "B01J23/00" OR cl any "C07B61/00") AND claims any "carbonate?" AND claims any "epoxide?" AND ctx any "alkylene" where cl stands for IPC or CPC

**Table 2**

List of queries used in FamPat database search.

No.	Results	Query
1	62	((CARBONATE? AND EPOXIDE?)/CLMS/ICLM AND (ALKYLENE?)/TI/AB/CLMS/ICLM) AND (C07D-303/04 OR C07D-301/02 OR B01J-023/00 OR C07B-061/00)/IPC/CPC

(International or Cooperative Patent Classification) and cctx stands for “Title, Abstract and Claims”. The definition of the classification symbols used is reported in Table 1.

A more precise and complete search can be performed on [Orbit Intelligence](#) (a fee-based platform provided by Questel), using FamPat as the reference database and the same keywords and classification codes.

The search queries and results are reported in Table 2.

62 patent families were retrieved (32 are alive), of which 27 are granted patents (see Fig. 7)

The filing trend of patent applications over the last twenty years is reported in Fig. 8.

#### 4. Application potential

Ethylene and propylene oxide derivatives are used as ingredients in industrial cleaners, heat transfer liquids, polyurethanes, and plasticizers. Despite their broad use, their toxicological profile is quite severe. Acute exposure to these gasses may result in respiratory irritation and lung injury, headache, nausea, vomiting, diarrhoea, shortness of breath, and cyanosis. Chronic exposure has been associated with the occurrence of cancer, negative effects on the reproductive system, mutagenic changes, neurotoxicity, and sensitization.

Furthermore, its storage must follow strict rules in terms of quantity, isolated areas, and a declaration must be made to the authorities in the case of accidental gas release. Transportation is even more restricted and although limited by ARD rules in Europe, it is at risk of a carpet ban.

Rules and advice on alkylene oxides storage and handling are listed

in the free publications of the producer’s association [7–8].

For all the industrial applications of alkylene oxides as raw materials, the invention allows for the generation of the oxides *in situ* in the same plant of use. Carbonates are liquid (or are easily melted) and can be fed units for a continuous generation of the correspondent oxide.

Alkylene oxides are used to produce fatty alcohols, acrylate compounds, diols, polysaccharides or the celluloses in flour or powder.

Ethylene oxide is also used to sanitize medical and pharmaceutical products that cannot support conventional, high-temperature steam sterilization procedures. Delicate, heat-sensitive medical devices that incorporate plastics and electronics could be warped or otherwise damaged by steam sterilization. Ethylene oxide gas will not damage low-temperature sterilizer medical devices. Ethylene oxide is also used to sterilize other healthcare products, such as bandages and ointments, reducing the potential damage on the product that may occur through other means of sterilization. Approximately 50 percent of medical supplies are sterilized with ethylene oxide, making it critical in particular for the U.S. healthcare industry [9].

For this application, the invention is also helpful because the ethylene oxide generation can be done in a small unit, which is easily integrable with common instruments used for disinfection as shown in Fig. 9.

In this case, the need to avoid the storage of the dangerous liquid ethylene oxide is even more critical. Now, the oxide is stored in small single-unit containers (no more than 200 cc) and kept in an armoured box inside sanitary site. A high risk of accidental mishandling of the chemical is possible and the cost of the technology is becoming excessive. The need for the correct quantity of ethylene oxide can be easily modulated through the electrical heating of the small-size generator. Finally, a ready mixture of ethylene oxide/carbon dioxide is delivered for disinfection.

#### Ethics statements

No specific ethic statements to declare.

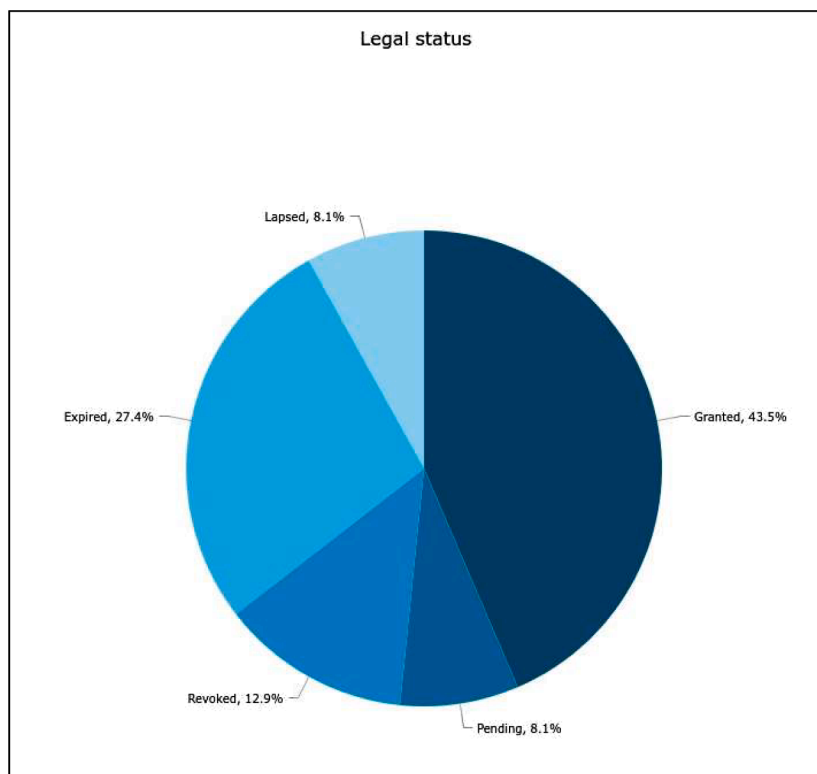


Fig. 7. Legal status of patent families (source: Orbit, accessed on 30 January 2023).

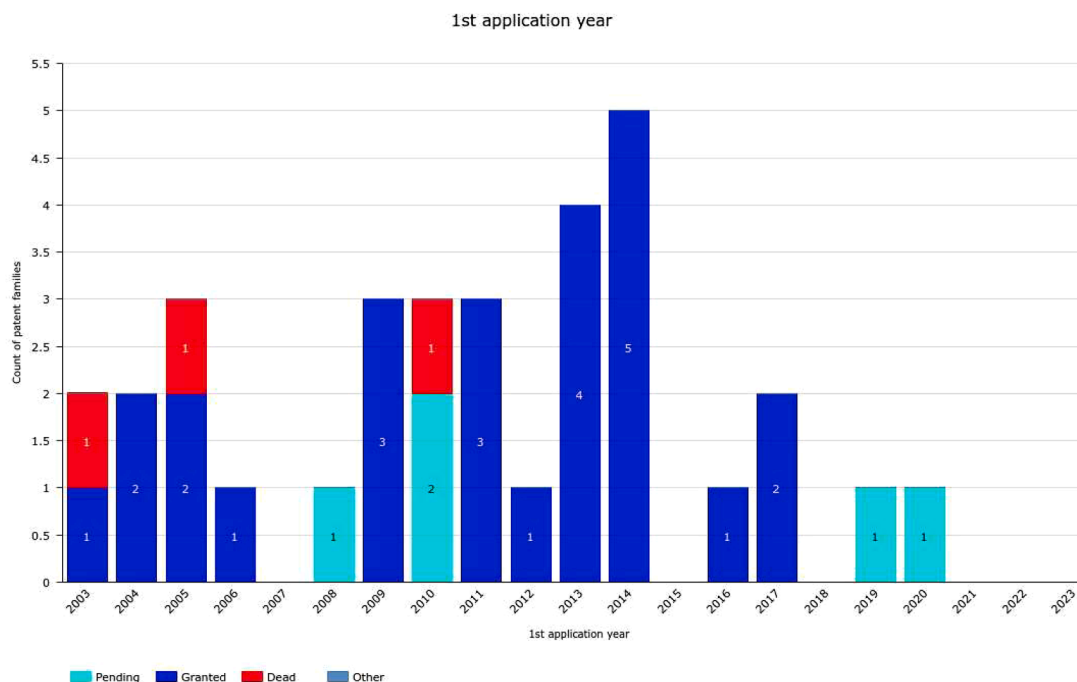


Fig. 8. Technology investment trend over the last 20 years (source: Orbit, accessed on 30 January 2023).

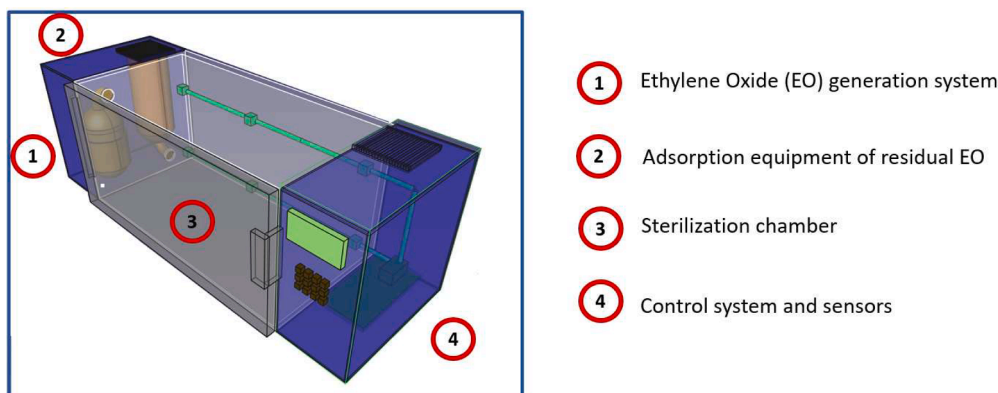


Fig. 9. Possible small disinfection apparatus using carbonates decomposition.

#### CRediT authorship contribution statement

**Gianmarco Polotti:** Data curation, Methodology, Writing – original draft. **Massimo Barbieri:** Writing – review & editing. **Davide Moscatelli:** Supervision, Conceptualization.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

The data that has been used is confidential.

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