AMERICAN JOURNAL OF INNOVATION IN SCIENCE AND ENGINEERING (AJISE)

ISSN: 2158-7205 (ONLINE)

VOLUME 3 ISSUE 3 (2024)

PUBLISHED BY
E-PALLI PUBLISHERS, DELAWARE, USA

American Journal of Innovation in Science and Engineering (AJISE)

Volume 3 Issue 3, Year 2024
ISSN: 2158-7205 (Online)
DOI: https://doi.org/10.54536/ajise.v3i3.3419
https://journals.e-palli.com/home/index.php/ajise

Plant Design for the Production of Propylene Oxide by Isopropylbenzene 2-phenylpropane, or (1-Methylethyl) Benzene (Cumene)

Daniel Asiedu[1*], Clara Afia Amoah Dankwa[2]

Article Information

Received: August 06, 2024
Accepted: September 10, 2024
Published: September 14, 2024

Keywords

Conversion/Selectivity Attitude, Chemical Process Simulation, Continuous Stirred-Tank Reactor (CSTR) Cascade, Total Annual Cost (TAC), Cumene To Cumene Hydroperoxide (CHP), Total Annual Cost (TAC)

ABSTRACT

Cumene is a colorless, volatile liquid with a gasoline-like odor. It's also known as isopropylbenzene, 2-phenylpropane, or (1-methylethyl) benzene. It's a natural component of coal tar and crude oil, and it can also be employed in gasoline as a blending component. Cumene hydroperoxide is produced by oxidizing cumene with benzene and propylene in the presence of air. As a result, the cumene hydroperoxide is changed to cumyl alcohol, which is then transformed to propylene without the use of oxygen. Propylene oxide is an organic compound produced through various methods such as the cumene process and the hydroperoxide process. The cumene method is preferred due to its low by-product production and high market value of co-products. The reactive distillation process is a feasible method for producing propylene oxide with high purity and reduced costs. Future work includes optimizing processes, developing new catalysts, and improving efficiency. Propylene oxide has practical applications in the production of polyurethane foams, coatings, adhesives, polyether polyols, and propylene glycols.

INTRODUCTION

PO, or propylene oxide, is an organic substance. It has an ethereal odor and is a colorless, volatile liquid. A few well-known techniques for producing PO are the hydroperoxide and chlorohydrin procedures. Certain restrictions of these procedures determine the price of the PO in the economy. Among the restrictions are the significant releases of dangerous chemicals and the production of a lot of coproducts with little market value. In a report on the market value of PO published by MarketsandMarkets on August 18, 2017, it was projected that by 2022, the global PO market would reach 17.53 billion USD. There arose the need to find a PO-only production process that produces a significantly less amount of by-product thus increasing the market value of the PO; this brought about the discovery of PO production by cumene by Sumitomo Chemical Limited in 2006. It is the most recent PO-only production process implemented. Propylene oxide is used in the production of polyethers which is the primary component of polyurethane foams. It is also used in the production of propylene glycol which is used by the chemical, food, and pharmaceutical industries. Propylene oxide also acts as mild depressant in the central nervous system.

This project focuses on the production of PO by the cumene method. Some notable unit processes that occur in this method include oxidation, epoxidation, hydrogenation and purification.

LITERATURE REVIEW

Propylene oxide (PO) is a colorless, organic liquid that has a low boiling point, an odor reminiscent of ether, and is highly volatile. Propene oxide, sometimes referred to as 1,2-epoxypropane, methyloxirane, or propylene oxide, is a crucial raw material used in the chemical industry. More than 10% of the propene produced is used in the synthesis of propene oxide. Oser, a chemist, made the initial discovery of it in 1861. Levene and Walti reported on the first attempt to polymerize PO in 1927. Since PO has been more and more in demand worldwide over time, the industry produces it as a high production volume (HPV) chemical. Propylene is used as an ingredient in many different products, including propylene glycols, propylene glycol ethers, and polyether polyols. The hydroperoxide and chlorohydrin processes are the ones used in the industry right now to produce PO. As of now, this method has proven to be straightforward, economical, highly selective, yield-maximizing, and environmentally benign because it solely generates water as a byproduct.

Propene oxide's primary use is in the 65% synthesis of polyether polyols, which are primarily utilized to make (polyurethane) foams. The manufacturing of propene glycol (30%) and propene glycol ethers (4%), respectively, accounts for the second and third major applications. While propene glycol ethers are largely utilized as solvents, propene glycols are mostly used in the manufacture of polyesters. Currently, the hydroperoxide process and the

[1] State Key Laboratory of Materials Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing, 211816, China
[2] School of Environmental And Chemical Engineering, Jiangsu University of Science And Technology, Zhenjiang, 212000, China
[*] Corresponding author's e-mail: asiedudaniel170@gmail.com

chlorohydrin process are the two different commercial methods used to manufacture propene oxide. To produce propene oxide, a significant amount of research has gone into creating substitute direct epoxidation methods. The goal has been to create a method for direct gas-phase oxidation that is comparable to ethene's direct epoxidation. Unfortunately, the selectivity of the catalysts discovered thus far for the direct epoxidation with air or oxygen is simply too low to provide a practical process (often less than 30%, with the remaining propene being transformed to carbon dioxide). Hydrogen peroxide and organic peroxides are better options for other epoxides used in fine chemistry since their costs are significantly lower than those of the final product. Another method being developed to produce propene oxide is propene epoxidation, which involves utilizing a gold-titanium catalyst with a combination of hydrogen and oxygen. Numerous research organizations worked on this catalyst after Haruta and associates identified it nearly ten years ago. Propene oxide selectivity is very high, however there is still room for improvement in terms of low conversion and hydrogen efficiency. Furthermore, it's yet unknown how the catalyst works.

MATERIALS AND METHODS

The need for propene oxide (PO), an essential building element in industry, is constantly rising. The two main technologies for producing PO, the hydroperoxide and chlorohydrin processes, have various drawbacks, such as the manufacture of a co-product whose market dictates the process's economy or the discharge of significant quantities of toxic chemicals. These profitable technologies continue to occupy the largest market share of PO manufacturing, notwithstanding their drawbacks. Nevertheless, finding a more effective PO-only substitute is preferred. In the most recent PO synthesistechnique, propane is oxidizing using aqueous hydrogen peroxide (HPPO), which just yields water as a byproduct. The synthesis of propylene glycols (mono-, di-, tri-, and higher), which are basic ingredients for the creation of unsaturated polyester resins used in the building and textile industries, is the second major use of PO. Ultimately, ethylene glycol ethers are gradually being replaced by propylene glycol ethers as the solvent for paints, coatings, inks, and other applications, thanks to a developing market for PO (Perez Ferrandez, 2015). (PO production techniques)

The Chlorohydrin Process

The chlorohydrin methods have historically been used to manufacture propylene oxide (PO). The original purpose of this technology was to produce ethylene oxide. This process produces propylene chlorohydrin and a tiny quantity of chlorinated organic coproducts, primarily 1,2-dichloropropane, by mixing propylene and chlorine gases in roughly equimolar proportions with an excess of water. The process of epoxidation, also known as dehydrochlorination, involves treating the chlorohydrin solution with either milk of lime (aqueous calcium hydroxide) or caustic soda. The resulting sodium chloride or calcium chloride brine is steam-treated to remove propylene oxide and other organic materials. Before being released, the brine is treated—typically through biological oxidation—to lower its organic content. Through distillation, the lighter and heavier components are eliminated from the propylene oxide until it meets sales requirements. As a by-product, two tons of sodium or calcium chloride are produced for every ton of PO. As a result, the procedure generates a significant amount of waste water that contains the alkali salt and has a

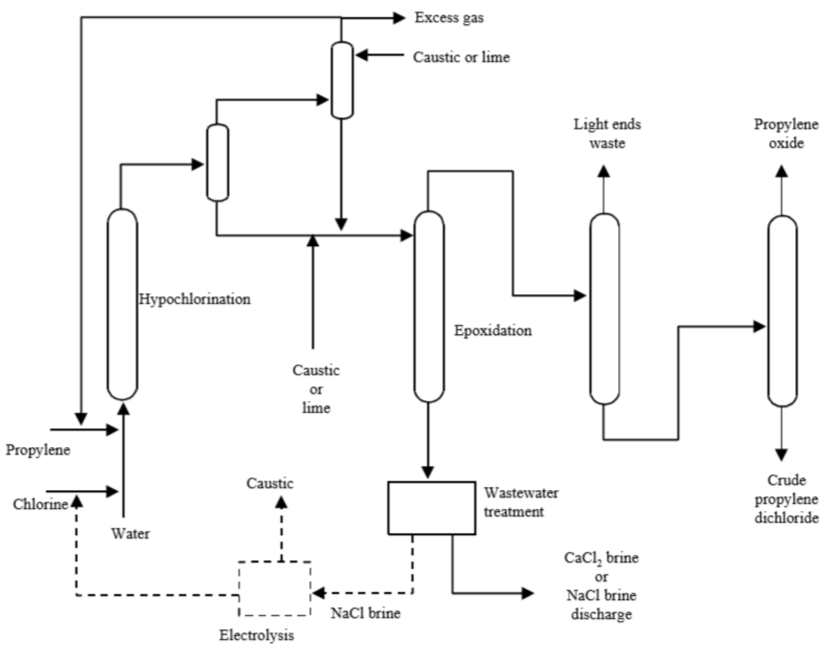


Figure 1: The chlorohydrin process (K. H. Simmrock, Hydrocarbon process)

very high waste water load (Sumitomo, 2006).A major challenge for appropriate disposal or reuse is the volume of water effluent, which is around 40 times more than the volume of propylene oxide produced during the chlorohydrin process. Depending on the alkali employed, there are many ways to handle the water effluent from the epoxidation process. When lime is used in epoxidation, a calcium chloride brine (4-6 weight percent) is produced that is discharged because it has no market value. When caustic soda is used in epoxidation, a sodium chloride brine is produced. This brine can be recycled or released into a chloroalkali electrolysis unit, which produces caustic and chlorine. Before being discharged or recycled, the effluent undergoes biological treatment to lower the organic content. (Simmrock, 78).

The Perioxide Method

The peroxide method, which employs either ethylbenzene or isobutane, is an additional production technique.Using tertbutyl hydroperoxide or ethylbenzene hydroperoxide as the organic peroxide, propene is indirectly oxidized to produce propylene oxide. Procedure for Tert-Butyl Hydroperoxide: The process begins with the liquid-phase air oxidation of isobutane to tert-butyl hydroperoxide (TBHP) with 10–30 weight percent of tert-butyl alcohol (TBA) present.

With a temperature range of 95-150 °C and a pressure range of 2075-5535 kPa (300-800 psi), 20-30% of the isobutane is converted, and there is a 60-80% selectivity for TBHP and 20-40% for TBA. Temperature and reaction time increases can be used to boost conversion at the expense of TBHP selectivity. Recycled back into the hydroperoxide-forming reactor are the unreacted isobutane and a part of the TBA that were isolated from the result. Equation 1 Oxidation of isobutane to tert-butyl hydroperoxide

$$\mathrm{CH_3\overset{\overset{CH_3}{|}}{C}HCH_3 \; + \; O_2 \longrightarrow CH_3C(CH_3)_2OOH}$$

In order to react with propylene, the tert-butyl hydroperoxide is then combined with a catalyst solution. During this stage of the process, some TBHP will break down into TBA. Usually, an organometal that dissolves in the reaction mixture serves as the catalyst. The best combination of selectivity and reactivity can be found in molybdenum complexes with napthenates or carboxylates. The metal can be tungsten, vanadium, or molybdenum. Usually, 200–500 ppm of catalyst is added to a 55% TBHP and 45% TBA solution. There is less than 0.5% water content.

In order to recycle or dispose of the homogenous metal catalyst, it must be taken out of the solution. There is some metal elution from the support surface, especially molybdenum, even with the use of heterogeneous catalysts.

To optimize hydroperoxide conversion and selectivity to propylene oxide, an excess of 2–10 mol propylene is utilized in place of hydroperoxide. The hydroperoxide will convert more than 95% at this temperature and pressure range of 1480-3550 kPa (215-515 psi) and for a considerable amount of time (2 hours). One possible solvent to use is an organic one, like t-butanol, chlorobenzene, or benzene.

Based on TBHP and propylene, the selectivity to propylene oxide is 95–98% and 97-98%, respectively. Propylene glycol, methyl formate, and a propylene dimer are the main byproducts. It can be challenging to eliminate some of these byproducts from the propylene oxide product. Reduced product selectivity occurs when acids, such as carboxylic acids, are present. Following the epoxidation process, a distillation is carried out in order to extract the propylene, along with some of the TBHP and TBA above. The catalyst residue, TBA, TBHPA, and a few contaminants including acetic and formic acid are all found in the distillation bottoms.

Evaporating the majority of the TBA and other organics, adding other chemicals to produce a metal precipitate

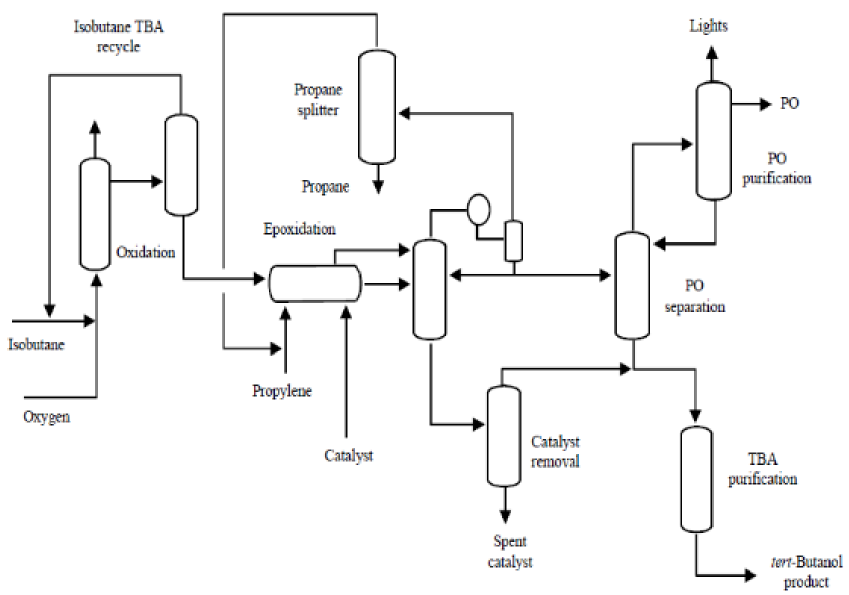


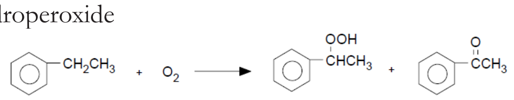
Figure 2: The tert-butyl hydroperoxide process to propylene oxide (PO) and tert-butanol (TBA)
(Source: U.S. Pat. 4,128,587)

that is filtered from the organics, or liquid extraction with water are the methods used to concentrate this catalyst residue for recycling or disposal. Adsorption on solid magnesium silicate can be used to remove low (<500ppm) concentrations of soluble catalyst. Propylene oxide is finally purified through a sequence of extractive and ordinary distillations. Water, methyl formate, acetone, methanol, formaldehyde, acetaldehyde, propionaldehyde, and a few heavier hydrocarbons are among the impurities found in the crude product.In order to utilize it as a gasoline additive going forward, the tert-butanol (TBA) co-product is refined.

Ethylbenzene Hydroperoxide Process

Ethylbenzene is oxidized in liquid phase with oxygen or air at 206-275 kPa (30-40 psia) and 140-150 °C. It takes 2-2.5 hours for 10-15% of the ethylbenzene to convert to hydroperoxide. Temperature regulation in reactors is achieved through the recycling of inert gases, like nitrogen. Water and other impurities in the ethylbenzene are managed to reduce the hydroperoxide product's breakdown and occasionally added to promote product production. Selectivity to by-products includes less than 1% organic acids, 5-7% 1-phenyl ethanol, and 8–10% acetophenone. By distillation, EBHP is concentrated to a 30–35% level. The oxidation reactor receives the recycled overhead ethyl benzene. It is necessary to neutralize the organic by-product acids with an alkali hydroxide or carbonate wash because they break down EBHP and reduce the activity of the epoxidation catalyst.

Equation 2 Oxidation of ethylbenzene to ethylbenzene hydroperoxide



Propylene is added to each compartment of a horizontally compartmentalized reactor that receives EBHP combined with a catalyst solution. For 1-2 hours, the reactor runs at 95-130 °C and 2500-4000 kPa (360-580 psi). It uses 5-7 mol propylene/1 mol EBHP to convert EBHP 95-99% of the time and has a 92-96% selectivity toward propylene oxide. An organic acid, such as acetate, napthenate, stearate, etc., plus molybdenum, tungsten, or titanium are combined to create the homogenous catalyst. The components of heterogeneous catalysts are titanium oxides on silica supports. Propylene oxide, surplus propylene, and propane are distilled overhead following epoxidation. Propylene is returned to the epoxidation reactor while propane is eliminated from the process. To counteract the acids, a basic, like sodium hydroxide, is added to the bottoms liquid. The 1-phenyl ethanol is dehydrated to styrene by the acids in this stream. In these conditions, styrene polymerizes easily. Phase separation is made possible by neutralization and water washing, allowing the molybdenum catalyst and salts to stay in the aqueous phase. Following its separation from the epoxidation reactor effluent, crude propylene oxide is further refined by a sequence of traditional and extractive distillations, which lowers the concentration of acetone, water, ethylbenzene, and aldehydes. Together with acetophenone from the hydroperoxide reactor and the co-product 1-phenyl ethanol from the epoxidation reactor, these two products are dehydrated to styrene in a vapour-phase reaction over a catalyst made of titanium dioxide or silica gel at 250–280 °C and atmospheric pressure. Then, in order to recover purified styrene and separate water and high-boiling organics for disposal, this product is distilled.

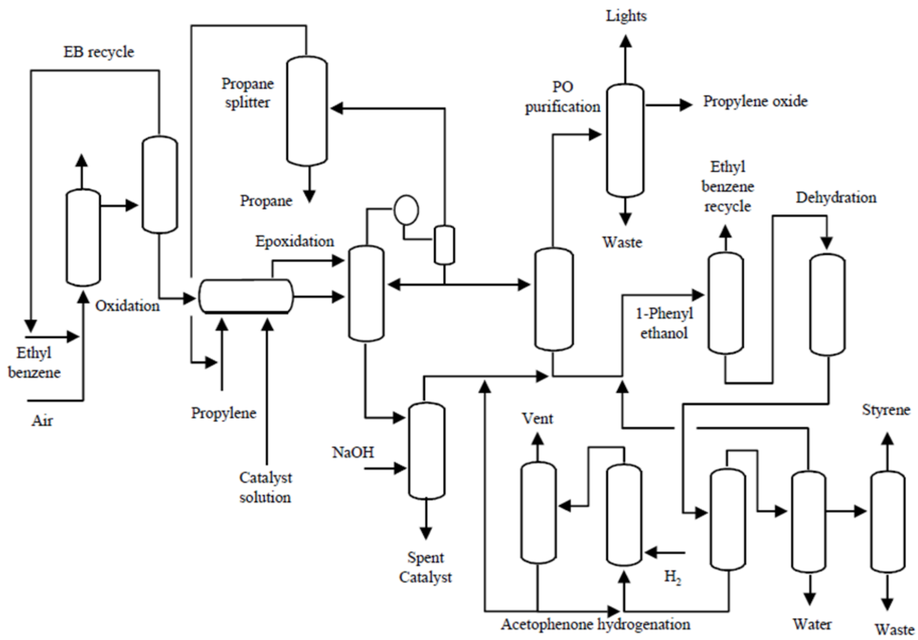


Figure 3: Propylene oxide (PO) and styrene are produced via the ethylbenzene (EB) hydroperoxide method *(Source: U.S. Pat. 3, 351, 635)*

The Hydroperioxide Method

Over time, more experimental methods for producing PO have been devised. One of them employed methyltrioxorhenium (MTO), a powerful organometallic catalyst, in media to extract water from aqueous hydrogen peroxide solutions.Low temperatures, as low as -10°C, were used in this procedure to reduce the amount of propylene glycol that was produced by hydrolyzing the PO product.The industrial functioning of extremely exothermic reactions is hindered by these temperatures.

H_2O_2 is needed for the oxidation in these reactions. Water is the primary byproduct of this reaction, making it potentially a green process. Nevertheless, this procedure is dependent on the Anthraquinone-auto Oxidation (AO) process, which is known to be a difficult and incompletely green method of producing H_2O_2 (Chen, 2008).Numerous characteristics, including the explosive nature of the reactants, the low solubility of hydrogen, the low selectivity, and the instability of H_2O_2, are known to contribute to the complexity of this reaction (Samanta, 2008). Methods of productions in the chemical engineering industries are mostly considered feasible to industrialized base on the following factors;

1. Cost of plant design (Economics).
2. Operation conditions.
3. Percentage yield.
4. Availability of raw materials.
5. Safety of the process and designed.
6. Effect of the process on the environment etc.

The main factors/parameters considered for the choice of method or process are the quantity of by-products produced, market value of co-products and cost of production. A summary is given in the table below;

Table 1: Comparision of the po methods

Factors/Parameters	Chlorohydrin Method	Organic Peroxide methods	Hydroperoxide route
By products	The main by product for the methods are alkali salts and water. From the chemical reaction, every mole of PO produce generates a mole of water and half a mole of salt. As a result, a remarkably high amount of waste water containing alkali salt is generated. This raises serious questions about reuse or disposal.	Propylene glycol, methyl formate, and a difficult-to-remove propylene dimer are the main byproducts. This methods produces less waste compare to the chlorohydrin process	The only by product for this process is water, making it a clean technology
Co Products	This process has no co-product	For this method styrene is produced as the co-product when ethylbenzene is used and isobutylene when isobutene is used. 2.5 tons of styrene are created for methylbenzene and 2.1 tons of isobutylene are produced for isobutene for every one ton of PO produced. It is challenging to determine whether this approach is the best one because the co-products are significantly impacted by market conditions	No co-products
Cost of Production	High cost in the treatment of the huge amount of waste produced.	Fluctuations in the market value of the co-product makes it the process economically unstable.	High price of commercially available hydrogen peroxide as the main raw material, makes the process economically unfavourable to produce PO.

From the above table, the drawbacks of the various PO productions method have made the production PO by the cumene the most suitable method. In this report, the production of PO by the cumene is selected.

Process Selection And Description

Process Selection Basis

Propylene production methods that have been industrialized are the chlorohydrin method of PO production and the organic peroxide method of PO production. Direct oxidation of the propylene form PO and the use of Hydrogen peroxide to oxidize propene to produce PO are only methods perform in the laboratory which are yet to be industrialized. Only one company in Japan (Sumitomo Company) have been able to industrialize the production of PO by the cumene method.

Justification of Selected Process

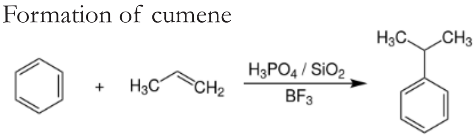
The main by product for the production of PO by the cumene in significant amount is the cumyl alcohol. This alcohol is hydrogenated to regenerate cumene which is recycle back to the oxidation section. The other byproduct produce by side reaction are phenols, acetophenone, dicumyl peroxide and the decomposition of the hydroxide to form acids. These products are readily remove from the main stream as it applies to the other organic peroxide methods. The quantities of by-products produce are negligible compare to the products of the chlorohydrin process as such this method is referred to as the PO only method. The method by cumene does not produce any co-product hence, the market value of co-product does not affect the gross income of the process. The main raw materials needed for the process are cumene and propylene. In Ghana propane is produce in sufficient quantities, which is used to produce propylene for the process as well as for sale to generate income. Propylene has a low price in the chemical market industrially due to its low demand compared to ethyl benzene.

Production of PO Using Cumene

This method of producing PO is fundamentally similar to the organic peroxide methods but the distinguishing feature with this is using cumene as the reaction medium in the epoxidation catalyst. Also in the traditional organic peroxide methods, co-products are produced and undesirably, their demands on the market influences the PO production process. Using cumene as a reaction medium allows for a PO only process where a Ti based epoxidation catalyst is used to catalyze the epoxidation step. The production method consists of three fundamental stages which leads to the final product, propylene oxide and the regeneration of cumene. The stages of production are discussed in the sections below.

Cumene

Cumene is an organic molecule based on an aromatic hydrocarbon with an aliphatic substitution. It is often referred to as isopropylbenzene, 2-phenylpropane, or (1-methylethyl) benzene, and its preferred IUPAC name is Propan-2-yl) benzene. It has the chemical formula C_9H_{12}, a molar mass of 120.195 g•mol−1 and a density of 0.862 g cm−3. It is a component of both crude oil and refined fuels. It's a colorless, combustible liquid with a smell similar to gasoline, boiling at 152°C, melting at -96°C, and having a vapour pressure of 8 mm (20°C). The majority of cumene generated on an industrial scale as a pure compound is transformed into cumene hydro peroxide, which is used as an intermediary in the synthesis of several significant chemicals for industry, mainly phenol, acetone, and methyl styrene. In turn, these compounds have a wide range of chemical and industrial applications. The manufacturing of polymers, including polystyrene, phenol-formaldehyde resins, and polycarbonates, is among its most significant applications. With a viscosity of 0.777 cP (21 °C), cumene is miscible with most organic solvents, ethyl alcohol, benzene, ether, and acetone, but it is insoluble in water. Cumene irritates the respiratory system, skin, and eyes. It can induce headaches, sore throats, headaches, coughing, and loss of muscle coordination if breathed. When used in excessive quantities, it has a narcotic effect that can cause unconsciousness as well as drowsiness and insensitivity to pain and other stimuli. Cumene is present in emissions from petroleum products, including vehicle exhaust from the burning of some motor fuels, gasoline station evaporation, and oil spills, due to its volatility and natural occurrence as a component of crude oil. About 20% of the world's benzene demand is met by producers of cumene (Ceresana, 2011).The initial method of producing cumene involved alkylating benzene in the liquid phase with sulfuric acid acting as a catalyst. However, this process has been completely supplanted due to the complex neutralization and recycling procedures needed, as well as corrosion issues. An alternate catalyst was solid phosphoric acid (SPA) supported on alumina. Equation 3 - Formation of cumene



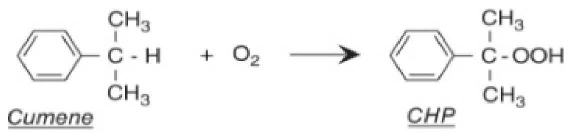
Commercial production has been using zeolite-based catalysts since the mid-1990s. The manufacture of cumene in this process typically has an efficiency of 70–75%. Polyisopropyl benzenes make up the majority of the remaining ingredients. An enhanced cumene method employing aluminum chloride as a catalyst was created in 1976. For this procedure, the cumene conversion rate can reach 90% overall. Di-isopropylbenzene is produced by adding two propylene equivalents (DIPB). DIPB is comproportionated with benzene by means of trans-alkylation (Vora Kocal *et al.*, 2003).

Cumene Oxidation Process

In the cumene oxidation process, cumene is oxidized to cumene hydroperoxide (CHP). The cumene oxidation process takes advantage of the selective oxidation of the tertiary C atom at the propyl group of the cumene molecule. Hydroperoxide compounds are relatively stable, especially in the starting hydrocarbon solutions. In the case where hydroperoxides are made in high concentrations (80-90 percent), special safety measures are necessary for handing them, such

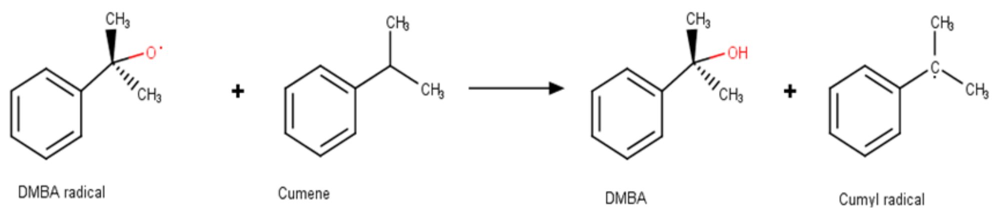
- Temperature control to prevent overheating
- Absence of decomposition catalyst- metals of variable valency and their salts, acids etc.

The selectivity with respect to the hydroperoxide is increased mainly by a decrease in temperature and degree of conversion. It is useful to slower the temperature as the hydroperoxide is formed in order to slow down its decomposition. For instance, In the oxidation of cumene, the successive conversion of the cumene hydroperoxide can be prevented by limiting the degree of conversion to the range of 30%. Also, the production of cumene hydroperoxide can be strongly retarded by inhibitors such as phenols, olefins and sulphuric compounds leading to the appearance of an induction period, which is why the starting hydrocarbons must be thoroughly purified from undesirable impurities. For this reason, cumene produced by the alkylation in the presence of solid phosphoric acid catalyst is not suitable for oxidation. The elimination of the induction period and the acceleration of the reaction at its initial stage are favored by addition of the hydroperoxide or the reaction mass containing the hydroperoxide to the feedstock. Alkyl aromatic hydroperoxides are mainly produced by using reactors of the tray-column type with the counter flow of the liquid and the gas and the heat being removed by means of internal coils placed on the tray columns. The resultant solution of the hydroperoxide and the by-products in the hydrocarbon feedstock is usually strengthened or concentrated by the distillation of the hydrocarbon. For this purpose, a sufficiently deep vacuum is used in the production of alkyl aromatic hydroperoxides. In order to reduce the residence time of the hydroperoxide at elevated temperatures and lower the degree of its decomposition, it is suggested that the hydrocarbon be distilled off in film apparatus. In industrial processes, oxygen from air is used in large bubble columns. Oxygen dissolves in the cumene/CHP liquid and reacts according to the equation below:

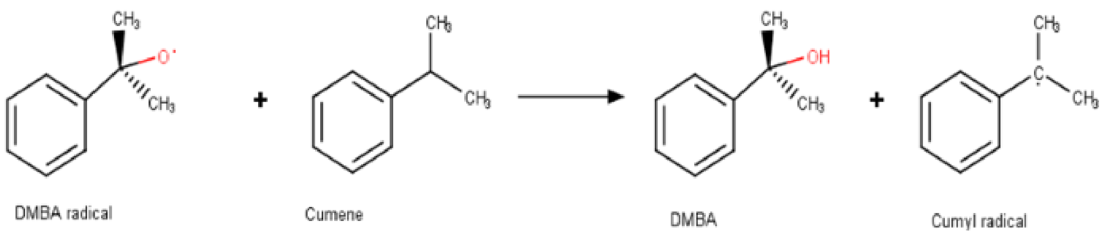


Equation 4.1, Cumene oxidation. The radicals from CHP's thermal breakdown serve as the catalysts for the free-radical chain reaction that creates CHP in industrial cumene oxidation processes. According to Shannon (2016), thermal breakdown releases 270 kJ/mol of heat. As a result, auto-oxidation refers to the response of the cumene oxidation process to CHP. The following steps are involved in the oxidation of liquid phase by oxygen: initiation, propagation, and termination. Where RH is cumene, CHP is ROOH and R • is the cumyl radical.

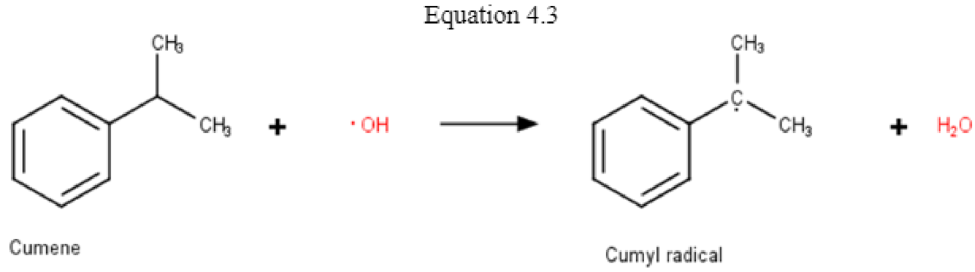
Initiation



Equation 4.2

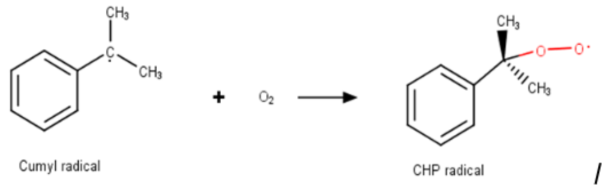


Equation 4.3

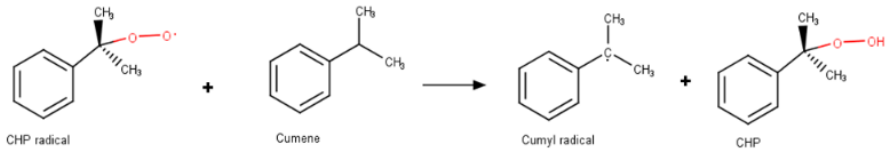


Equation 4.4

Propagation

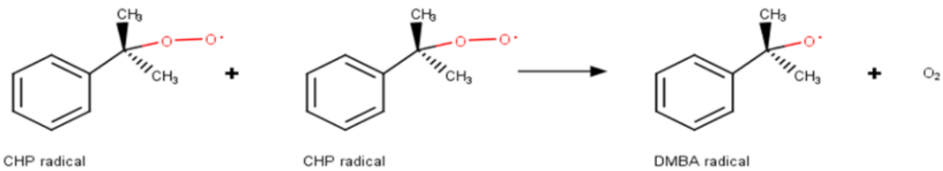


Equation 4.4

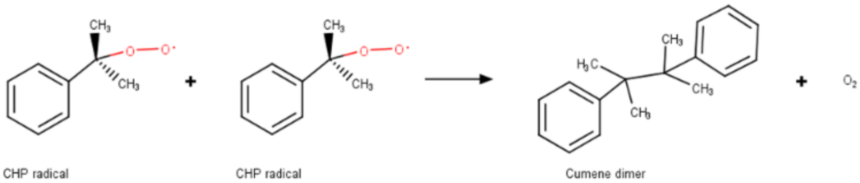


Equation 4.5

Termination (Examples)



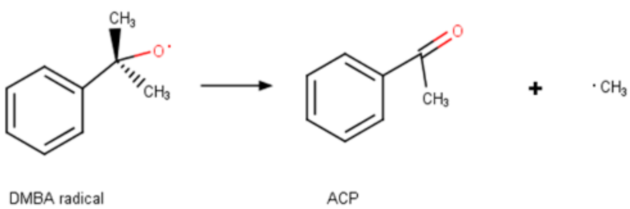
Equation 4.6



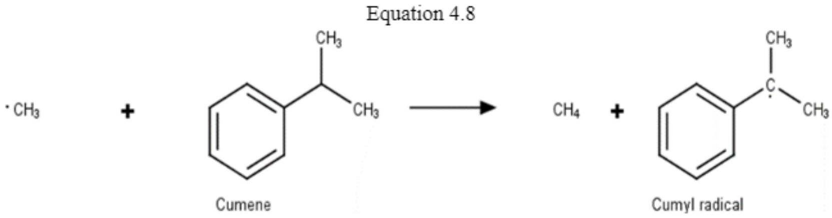
Equation 4.7

Equation 4.4 and Equation 4.5 are the chain reactions which leads to the formation of CHP. A cumyl radical R • reacts quickly with dissolved oxygen to form a peroxide radical ROO •. The peroxide radical and cumene (RH) combine in the second phase to create CHP (ROOH). The chain reaction is determined by this slower reaction. The newly generated cumyl radical R • returns to start the reaction in Equation 4.4. The mechanism becomes more selective the more times this cycle repeats. The average number of cycles from a single commencement is the chain length. The chain length in industrial oxidation processes is typically 10. The chain is broken by the aforementioned termination reactions and needs to be restarted by the thermal breakdown of CHP.

Dimethylbenzyl alcohol, or DMBA, is the main by-product formed during the oxidation of cumene and is created when CHP breaks down. Equation 4.2, the reaction chain's initiation step, where DMBA is ROH, represents this reaction. When RO • breaks down, acetophenone (ACP) and a methyl radical—which mostly turns into methane—are produced. This is another competing process. These responses are displayed in Equation 4.8 and Equation 4.9 below.



Equation 4.8

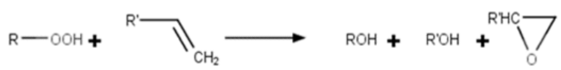


Equation 4.9

From the reactions in Equation 4.2 and Equation 4.3, it can be seen that they occur when there is an excess of cumene. This does not mean cumene should be reduced as these two reactions lead to the production of R • which goes into the propagation step where CHP is formed. A decrease in cumene feed leads to the decomposition of RO • as stated in Equation 4.8 and Equation 4.9. Generally speaking, as an oxidation product, the molar ratio of DMBA to ACP from moderate heat breakdown is roughly 10:1. On the other hand, this ratio falls as more ACP is generated if the decomposition is hastened due to adiabatic conditions and a complete breakdown of CHP eventually occurs at high temperatures (runaway). Dicumylperoxide, commonly known as ROOR, is a compound that occurs in trace amounts during the chain reaction's termination step. Cumene oxidation results in the creation of numerous micro-impurities in addition to the primary and minor by-products already described. The methyl radical CH_3 • from the thermal breakdown of CHP is important. Formaldehyde and methyl hydroperoxide (MHP) are produced when oxygen is present. After further oxidation, formaldehyde becomes formic acid, which can catalyze the acidic breakdown of CHP into phenol and acetone. Since phenol is a potent inhibitor of the radical chain reaction, it is necessary to control these side reactions in order to maintain the concentration of phenol below a few weight parts per million. According to Shannon (2016), it is crucial to bring the phenol and organic acid concentrations in the cumene feed down to "zero." An alkali reagent is added by adding additives like ammonia, $(NH_4)_2CO_3$, an alkali metal ammonium carbonate, or the like, or alkali metal compounds like NaOH or KOH, or alkali metal carbonates like Na_2CO_3 or $NaHCO_3$.

Cumene Epoxidation Process

For a considerable amount of time, the synthesis of α-oxides using organic hydroperoxides did not yield excellent results. It was not until the early 1960s that the use of metal complex catalysts in the liquid phase for epoxidation produced satisfactory results. The equation below (Equation 5) shows the general epoxidation reaction with organic hydroperoxides and olefins.



Equation 5

The nature of the metal in the catalyst strongly determines the rate and selectivity of the reaction as well as the form in which the catalyst is used. The nature of the hydroperoxide has a substantial effect on the selectivity and conversion parameters. For example, the following conversions were achieved using a molybdenum naphthenate catalyst at 100° in 15 minutes.

Table 2: Variations in conversion of different hydroperoxides

Organic Hydroperoxide	Conversion
Ethyl benzene hydroperoxide	92%
Propyl benzene hydroperoxide	79%
Isopentane hydroperoxide	29%

Mechanism

In the study of the epoxidation of olefins by hydroperoxides, the reaction kinetics has shown the existence of an induction period, during which an active catalyst is formed. It has been observed that the reaction is retarded by a number of compounds including the α-oxides formed, showing the characteristics of metal-complex catalysis.

Let metal catalyst = Cat.

Hydroperoxide = ROOH

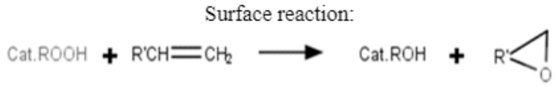
The formation of the active metal catalyst corresponds to the following scheme of process:

Adsorption

$$\text{Cat.} + \text{ROOH} \rightleftharpoons \text{Cat.ROOH}$$

Equation 6.1

Surface reaction:



Equation 6.2

Desorption:

$$\text{Cat.ROH} \rightleftharpoons \text{Cat.} + \text{R—OH}$$

Equation 6.3

It is presumed that the role of the catalyst is to activate the hydroperoxide metals which coordinates by its oxygen atom with the central metal ion which is in one of the higher valence states (Ti3+). The main side reaction to this reaction is the decomposition of the hydroperoxide which can also occur in the surface of the catalyst as shown in Equation 6.4 below

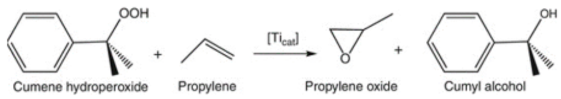
$$\text{ROOH} \longrightarrow \text{ROH} + 0.5O_2$$

With respect to the hydroperoxide the differential selectivity of the reaction can be approximated to equation 6.5 below

$$r = \frac{1}{1 + \frac{r_2}{r_1}} = \frac{1}{1 + \frac{k_2}{k_1(olefin)}}$$

Equation 6.5

To increase the selectivity of the ROOH and RCH=1CH_2, the ratio k_2/k_1 would need to be reduced to the minimum. This can be achieved by increasing the concentration of the unsaturated propylene (which requires a high pressure for gaseous olefins) and also using a moderate temperature since the activation energy of the decomposition of the hydroperoxide is higher than the activation energy of the epoxidation reaction. Due to the above conditions, the reaction is dictated to be carried out in the liquid phase, and for this reaction, it would be carried out in the solution of the hydrocarbon (hydroperoxide solution), at 90 – 110^o and about 2 – 5-fold excess of the propene. Propylene oxide and cumyl alcohol are produced during the epoxidation step. Propylene and cumene hydroperoxide, which was produced during the oxidation process, react to accomplish this. In order to achieve high yield and high selectivity, the epoxidation step is best carried out in the presence of an epoxidation catalyst, more specifically, a catalyst comprising silicon oxide that contains titanium. The reaction for this step is shown in Equation 6.6 below:

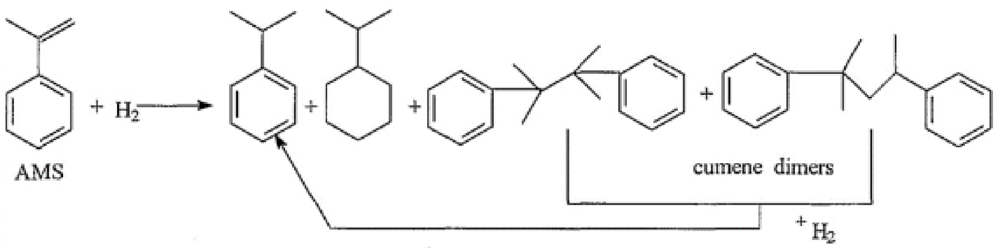


Equation 6.6

Sumitomo Chemical claims that because of the extraordinarily high reaction rates attained and the good stability of the cumene hydroperoxide and the highly active Ti epoxidation catalyst, the reaction may be carried out at a relatively mild temperature. Propylene must be brought into liquid phase with cumene hydroperoxide using a solvent to initiate the epoxidation process. At the reaction's operational temperature and pressure, this solvent ought to be liquid. This solvent could be a compound that was initially discovered to be present in the hydroperoxide solution, such as cumene, which is the raw material used to make CHP. Generally speaking, the epoxidation temperature ranges from 0 to 200°C, with 25 to 200°C being the ideal range (EP1681288A1, 2004). A level of pressure that is adequate to maintain the reaction mixture's liquid state should be maintained. The pressure range that is typically employed is 100–10,000 kPa (EP1681288A1, 2004). Ti-silica catalysts, which have titanium chemically linked to silicon oxide, are the best option for the catalyst. These could include zeolite compounds containing titanium, catalysts made by supporting titanium compounds on silica carriers, and catalysts made by mixing titanium compounds with silicon oxide using the sol gel or co-precipitation methods. Because the epoxidation reaction mentioned above is exothermic, the extra heat causes the breakdown of CHP, which in turn causes a surge in side reactions. This necessitates the use of heat exchangers for adequate cooling. Propylene oxide needs to be extracted by distillation from the reaction solution following the epoxidation reaction. Crude petroleum oil (Crude PO) is the light stream obtained during distillation, whereas cumyl alcohol (CMA) and cumene—the solvent used for the epoxidation—make up the heavy stream.

Cumen hydrogenation process

This is the stage where cumyl alcohol is recycled back into cumene so as to be fed back to the oxidation stage described in earlier sections. There are two methods through which this conversion can be done. One is the dehydration-hydrogenation process, which involves first dehydrating cumyl alcohol to produce α-methylstyrene (AMS) and then hydrogenating AMS to get cumene. Another technique is to directly convert cumyl alcohol into cumene by hydrogenolysis. First, the dehydration-hydrogenation process would be explained. This process involves separating the PO that is produced during epoxidation from the cumyl alcohol solution prior to dehydration. Acids like sulfuric acid, phosphoric acid, and p-toluene sulfonic acid, as well as metal oxides like titania, zirconia, silica-alumina, and zeolites, are utilized as catalysts in the dehydration process. Activated alumina is the preferred catalyst in terms of selectivity, life, and separation from the reaction mixture (EP1681288A1, 2004). Because cumene and alpha-methyl styrene stay on the hydrogenation bed after being created, significant amounts of i-propylcyclohexane and cumene dimer are produced as unwanted by-products during the hydrogenation stage (WO2005005402A2, 2004). The hydrogenation reaction is shown below:



Equation 7

Oil-water separation or a similar method can be used to separate the produced water. One reactor or more reactors may be used for the hydrogenation and dehydration processes. Because the reaction is endothermic (as opposed to exothermic due to Equation 7's hydrogenation), the temperature decreases as the process proceeds. The temperature and pressure of the reaction are chosen to prevent condensation of the water present in the α-methylstyrene solution following dehydration. Water may condense at the dehydration catalyst's outflow when the temperature is too low or the pressure is too high, which would impair the catalyst's effectiveness. Furthermore, an excessively high pressure is detrimental to the dehydration reaction equilibrium.

It may become detrimental when the temperature or pressure are too high or too low because excessive gas phase component production might create wailing or other similar effects that decrease the catalyst's life.
The amount of dehydration catalyst employed might be sufficient to convert cumyl alcohol, and a conversion rate of 90% or more is preferred. The quantity of hydrogenation catalyst utilized can be sufficient to change α-methylstyrene into cumene, with a minimum conversion rate of 98%. Regarding the second method of hydrogenolysis-based cumyl alcohol regeneration. Hydrogen and cumyl alcohol are combined with a catalyst to initiate the hydrogenolysis process. Any catalyst with the ability to hydrogenate can be employed, regardless of the type of catalyst. Copper-based catalysts are preferred from the perspective of suppressing by-products, even though examples of catalysts include metal-based catalysts of metals of Groups 8 to 10 such as cobalt, nickel, and palladium metal and metal-based catalysts of metals of Groups 11 and 12 such as copper and zinc (EP1681288A1, 2004). Either a gas phase or a liquid phase with a solvent can be used to carry out the reaction. Reactants and products should be largely inert to the solvent. The material present in a cumyl may serve as the solvent.

Purification of Unit PO
Some by-products of epoxidation processes may be readily separable by distillation. Taking epoxidation with an organic hydroperoxide (cumene hydroperoxide) as an example, the organic hydroperoxide is predominantly reduced to the corresponding alcohol (cumyl alcohol), which tends to be easy to separate. Also produced, are small amounts of acetophenone, dicumyl peroxide and cumene. It is known to employ fractional distillation techniques to help separate impurities from propylene oxide.

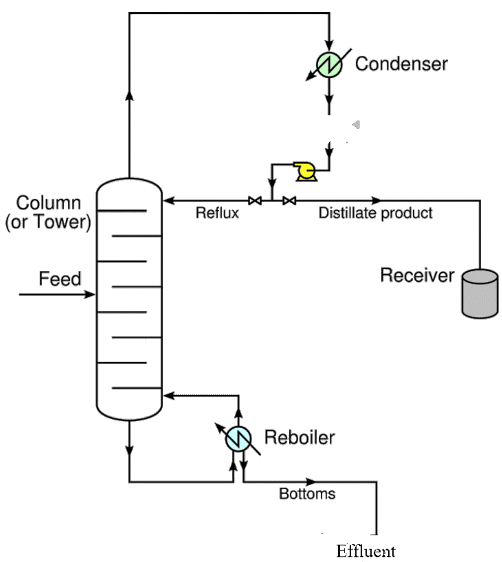


Figure 4: Tray Simple Distillation Column

Process
Prior to purification, the propylene oxide typically contains 95-99 wt% of propylene oxide and 1-5 wt% impurities. The propylene oxide to be purified is fed into the distillation column at the centre, the Propylene oxide vaporises out through the overhead and pumped to the storage tanks. The bottom stream consists of the impurities contained in the PO feed stream. The distillation takes place at atmospheric pressure, a rectification temperature of 50°-70° and stripping pressure of 90°-120°. The impurities namely cumyl alcohol, acetophenone, dicumyl peroxide and cumene have boiling points of 202°, 202°,130° and 152.4° respectively, and thus the need to keep the rectification temperature below these boiling points so as to keep the impurities in liquid state and prevent them from joining the pure propylene oxide stream at the overhead. Part of the overhead is recycled as well as the bottom stream to maintain the temperature in the column.

RESULTS AND DISCUSSION

More than 10% of the propene produced is used in the synthesis of propene oxide. Usually, the conversion of propylene is less than 2%. Propylene oxide selectivities are higher than 50% when propylene is oxidized gas-phase with oxygen in the presence of a molten nitrate salt (sodium, potassium, or lithium nitrate) and a co-catalyst (sodium hydroxide). The amount of dehydration catalyst employed might be sufficient to convert cumyl alcohol, and a conversion rate of 90% or more is preferred. The quantity of hydrogenation catalyst utilized can be sufficient to change α-methylstyrene into cumene, with a minimum conversion rate of 98%. The market for propylene oxide is anticipated to expand at a compound annual growth rate (CAGR) of roughly 5.9% from 2019 to 2024.Propylene oxide capacity has grown at an average annual rate of 3% since 2013, primarily due to recent advancements in Asia.In the meantime, the industry as a whole has seen an increase in average operating rates and a tightening of markets due to the faster-than-average growth in propane oxide consumption (4.2% annually).

Table 3: Components of output stream of oxidation reactor and their selectivity.

Compound	Selectivity
CHP	86.4
Dimethylbenzylalcohol	11.6
Acetophenone	1.8
Dicumylperoxide	0.2

Before being fed into the reactor, a propane feed with a purity of at least 99.5% is supplied into a charge heater where it is vaporized and heated to the reaction temperature.Cumene is oxidized to cumene hydroperoxide (CHP), which is then used to produce propylene oxide. Since this is a vapour-liquid reaction, the right reactor is required. Cumene and cleaned ambient air are used in enormous bubble columns for this reaction. The scheme of arrangement of feed and output streams are shown in the image below Since it is advisable to limit the conversion of cumene to cumene hydroperoxide to values lower than 40% so as to increase the selectivity of the reaction to the formation of CHP, oxidation is done using a series of bubble column reactors to meet the quantity requirements of CHP of the plant.

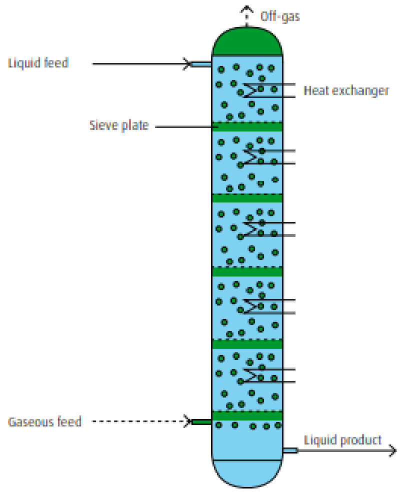


Figure 5: Bubble Column configuration for Cumene Oxidation (Adapted from Hans-Jürgen (2015)).

Air is pumped through the column filled with cumene liquid. The residence time for this reaction is about 10 hours. The conversion is to be maintained at 30%. The reaction mixture from the bottom of the bubble column reactors, which is comprised of about 30% CHP and 70% Cumene, is then sent to the concentration unit. The concentration unit comprises vacuum distillation columns which are used to separate cumene from CHP. Vacuum distillation is carried out at a temperature of about 80^o and a pressure of 10kPa to obtain a bottoms stream that comprises of 50% CHP. Figure 6 shows the vapour pressure curve simulated with Aspen Plus of Cumene.
The stream's cumene is removed via distillation, cleaned and then recycled back into oxidation reactor. To purify

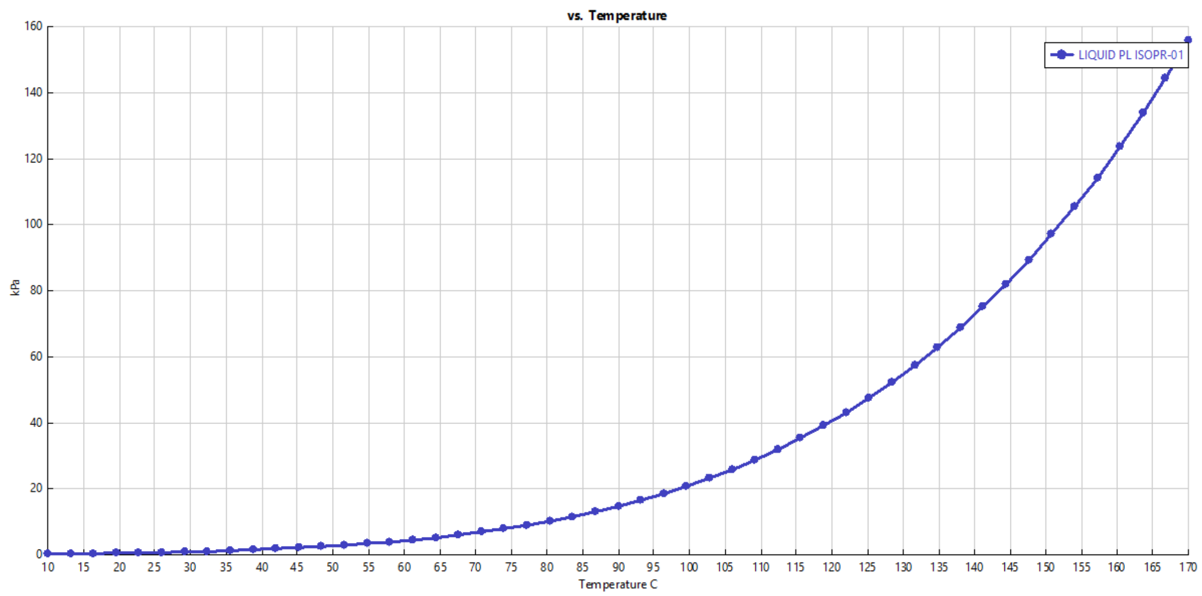


Figure 6: Vapour pressure curve of cumene.

the distilled cumene, water is added to the stream to dissolve trace amounts of phenol and acetone which are produced from the decomposition of the CHP as a result of acids such as formic acid. The presence of phenol in the cumene feed inhibits the formation of CHP hence this step is required. The cumene/water stream is then separated using liquid-liquid gravity separators. Since cumene is not soluble in water, it is assumed that no cumene is lost in the separation process. The purified cumene is added to the stream of fresh cumene and reheated to the oxidation temperature. The output stream from the vacuum distillation column at this point is made up of 50 vol% CHP and the rest is cumene. This solution is then stored and used as reactants in the epoxidation reactor.

Material Balances

Epoxidation

Table 4: (a) and (b) are material balances for input and output epoxidation while (c) and (d) are material balances for input and output oxidation respectively

a) Input stream

Components	Molar flow rates(km /h)	Mass flow rates(kg/h)	Mass Fractions
C_3H_6	307.52396	12940.5161	0.205073495
ROOH	170.60438	25964.3500	0.411467361
ROH	22.90521	3119.4846	0.049435711
ACP	3.5542580	427.03877	0.006767453
ROOR	0.19745	53.38616	0.000846032
CH_4	3.55425	57.01918	0.000903606
RH	170.89423	20540.05098	0.325506341
TOTAL		63101.84587	1.000000000

b) Output stream

Components	Molar flow rates(km/h)	Mass flow rates(kg/h)	Mass fractions
PO	153.76198	8930.35749	0.14152292
C_3H_6	153.76198	6470.25805	0.102536748
ROOH	11.43049	1739.611451	0.027568313
ROH	182.07911	24797.53641	0.392976403
ACP	3.5542580	427.03877	0.006767453
ROOR	0.19745	53.38616	0.000846032
CH_4	3.55425	57.01918	0.000903606
O2	31.9988	86.587351	0.001372184
RH	170.89423	20540.05098	0.325506341
TOTAL		63101.84587	1.000000000

Oxidation

c) Input stream

Components	Moler flow rates(km/h)	Mass flow rates(kg/h)	Mass fractions
RH	658.19594	79109.6232	0.724752
ROOH	27.58725	4173.79597	0.038237
ROH	3.68203	501.46036	0.004594
ACP	0.57135	68.6403	0.000628
ROOR	0.031741	8.58188	0.000078
CH_4	0.57135	9.16589	0.000083
C_2	184.03185	5888.78988	0.053949
N_2	692.30929	19393.9372	0.177675
TOTAL		109154.0014	1.000000

d) Output stream

Components	Molar flow rates(km/h)	Mass flow rates (kg/h)	Mass fractions
RH	460.73715	55376.73624	0.5073285
ROOH	198.02921	30138.146	0.2761076
ROH	26.5872	3620.94501	0.0331729
ACP	4.12560	495.68569	0.0045411
ROOR	0.22900	1.96804	0.0000180

CH_4	4.12560	66.18507	0.0006063
O_2	0	0	
N_2	692.30929	19393.93732	0.1776756
TOTAL		109153.6033	1.0000000

CONCLUSION

The high purity evidence that propylene oxide can be produced in a reactive distillation (RD) column by epoxidizing propylene with an oxidant such peracetic acid (PAA) serves as part of the foundation for the current invention.Distillation and the epoxidation process occur simultaneously. Capital equipment costs are reduced when both reaction and distillation are done on the RD column. Moreover, the reboiler duty during the distillation process can be decreased due to the heat produced by the exothermic reaction.Modeling based on experimental kinetic data validated the correctness of the mechanism inferred from the experimental results. A portion of the invention focuses on a reactive distillation method that involves

(a) feeding propylene into a vertical column that has a feed zone, a top zone, and a bottom zone in order to continuously epoxidize it and produce propylene oxide.

(b) adding ethyl acetate, a solvent, and peracetic acid to the vertical column.

(c)reacting propylene and peracetic acid in a vertical column with a homogenous catalyst to produce propylene oxide, and then extracting the propylene oxide-containing mixture.

REFERENCES

Al-Zamil Company. (2001). Propylene sources sheet in propane-propylene based industries in Saudi Arabia (Propylene by propane dehydrogenation) - Feasibility study. *American Scientific Research Journal for Engineering, Technology, and Sciences (ASRJETS), 45*(1), 49-63.

Boccuti, M. R., Rao, K. M., Zecchina, A., Leofanti, G., & Petrini, G. (1989). Spectroscopic characterization of silicalite and titanium silicalite. In C. Morterra *et al.* (Eds.), *Stud. Surf. Sci. Catal.* (Vol. 48, p. 133). Elsevier.

Chen, Q., & Beckman, E. J. (2008). *Green Chemistry, 10*(9), 934.

Clerici, M. G., & Ingallina, P. (1993). Epoxidation of lower olefins with hydrogen peroxide and titanium silicalite. *J. Catal., 140*, 71.

Dhananjay, P. S., Sooryakant, G. H., & Dongare, M. K. (2000). Low-Cost Synthesis of Bimodal Mesoporous Silica-Based Materials by Pseudomorphic Transformation. *Journal of Materials Chemistry, 82*, 631. https://doi.org/10.1002/cplu.201402383.

EP1681288A1. (2004). Process for producing propylene oxide. Sumitomo Chemical Company, Limited, Tokyo, Japan.

Esposito, A., Neri, C., & Buonomo, F. (1984). Process for oxidizing alcohols to aldehydes and/or ketones. *US patent, 4*,480,135.

Glover, (2007). Light olefin technologies. In UOP LLC; *Journées Annuelles du Pétrole.*

GS Engineering/Construction (Ed.). (2008). *Propylene technology by PDH & metathesis.*

Huybrechts, D. R. C., Buskens, P. L., & Jacobs, P. A. (1992). P*hysicochemical and catalytic properties of titanium silicalites. J. Mol. Catal.,* 71, 129.

Huybrechts, D. R. C., De Bruycker, L., & Jacobs, P. A. (1990). Oxyfunctionalization of alkanes with hydrogen peroxide on titanium silicalite. *Nature, 345*, 240.

Huybrechts, D. R. C., Vaesen, I., Li, H. X., & Jacobs, P. A. (1991). Factors influencing the catalytic activity of titanium silicalites in selective oxidations. *Catal. Lett., 8,* 237.

"Cumene". (n.d.). Immediately Dangerous to Life and Health Concentrations (IDLH). National Institute for Occupational Safety and Health (NIOSH).

"NIOSH Pocket Guide to Chemical Hazards". (n.d.). "#0159". National Institute for Occupational Safety and Health (NIOSH).

Kraushaar, B., & van Hooff, J. H. C. (1988). A new method for the preparation of titanium-silicalite (TS-1). *Catal. Lett., 1*, 81.

Kraushaar, B., & van Hooff, J. H. C. (1989). A test reaction for titanium silicalite catalysts. *Catal. Lett., 2*, 43.

Lee, J. H., Jung, K. T., & Shul, Y. G. (1996). Synthesis of nanosized titanium silicalite-1. *HWAHAK KONGHAK, 34*(6), 765.

Market Study Benzene. (2011, July). Published by Ceresana.

Nomenclature of Organic Chemistry: IUPAC Recommendations and Preferred Names 2013 (Blue Book). (2014). Cambridge: The Royal Society of Chemistry.https://doi.org/10.1039/9781849733069-FP001

Notari, B. (1993). Titanium silicalites. Catal. Today, 18, 163.

Oyama, S. Ted. (2008). Mechanisms in homogeneous and heterogeneous epoxidation catalysis. Virginia, USA: Elsevier.

Padovan, M., Genoni, F., Leofanti, G., Petrini, G., Trezza, G., & Zecchina, A. (1991). Study on titanium silicate synthesis. In G. Poncelet, P. A. Jacobs, P. Grange, & B. Delmon (Eds.), *Stud. Surf. Sci. Catal.* (Vol. 63, p. 431). Elsevier.

Perez Ferrandez, D. M. (2015). Alternatives for the production of propene oxide. Eindhoven: Eindhoven University of Technology.

Samanta. (2008). *Applied Catalysis A: General, 350*(2), 133-149.

Shannon, S., Stahl, & Alsters, P. L. (2016). Liquid phase aerobic oxidation catalysis. Wiley-VCH. Weinheim, Germany.

Simmrock , K. H. (1978). *Hydrocarbon Process., 57*(11), 105-113.

Sumitomo Chemical. (2006). *Development of new propylene oxide process. Japan.*

Tatsumi, T., Nakamura, M., Negishi, S., & Tominaga, H. (1990). Shape selective oxidation of alkanes with H_2O_2 catalysed by titanosilicate. *J. Chem. Soc., Chem. Commun., 476*.

Trong On, D., Bonneviot, L., Bittar, A., Sayari, A., & Kaliaguine, S. (1992). Titanium sites in titanium silicalites: An XPS, XANES and EXAFS study. *J. Mol. Catal., 74*, 233.

Tuel, A., Diab, J., Gelin, P., Dufaux, M., Dutel, J.-F., & Taarit, Y. B. (1990). EPR evidence for the isomorphous substitution of titanium in silicalite structure. *J. Mol. Catal., 63*, 95.

U.S. Patent No. 3,351,635. (1967, November 7). J. Kollar (to Halcon International, Inc.).

U.S. Patent No. 4,128,587. (1978, December 5). J. C. Jubin (to Atlantic Richfield Co.).

van der Pol, A. J. H. P., & van Hooff, J. H. C. (1993) . Oxidation of linear alcohols with hydrogen peroxide over titanium silicalite 1. *Appl. Catal. A: General, 106*, 97.

van der Pol, A. J. H. P., Verduyn, A. J., & van Hooff, J. H. C. (1992). Oxidation of linear alcohols with hydrogen peroxide over titanium silicalite 1. *Appl. Catal., 92*, 113.

Won, W., Lee, K. S., Lee, S., & Jung, C. (2009). Repetitive control and online optimization of Catofin propane process. In *IFAC Proceedings* Volumes (IFAC-PapersOnline) (Vol. 7, No. PART 1, pp. 273–278).

WO2005005402A2. (2004). Process for producing alkylene oxide. Shell Internationale Research Maatschappij B.V.

Yong Sig Ko, & Wha Seung Ahn. (1998). *Korean Journal of Chemical Engineering, 15*(2), 182-191.

Zecchina, A., Spoto, G., Bordiga, S., Ferrero, A., Petrini, G., Leofanti, G., & Padovan, M. (1991). Framework and extraframework Ti in titanium-silicalite: Investigation by means of physical methods. In P. A. Jacobs, N. I. Jaeger, L. Kubelkova, & B. Wichterlova (Eds.), *Zeolite Chemistry and Catalysis* (p. 251). Elsevier.