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Ethylene oxide

HIGHLIGHTS

Processes and technology status – The basic materials for ethylene oxide (EO) production are high-purity grade oxygen and ethylene. The direct oxidation of ethylene, can be air-based or oxygen-based and the general process scheme is depicted in Figure 1^{-1} , ².

The conventional shell direct oxidation technology is composed of the different parts which are the reaction system, absorption system, CO_2 removal section, and EO purification system. The reaction system occurs in the shell-and-tube packed plug flow reactors, which contain silver/alumina catalyst. The catalyst eases the partial oxidation of ethylene to EO and the complete combustion of ethylene to carbon dioxide and water ³.



Figure 1. EO production flow sheet by direct oxidation route ⁴

Cost - The whole working value (uncooked supplies, utilities, fastened prices and depreciation prices) estimated to supply EO was about $\notin_{2015}577.2^{-1}$ per ton of EO within the fourth quarter of 2015. The evaluation was primarily based on a plant constructed within the U.S. with capability to supply 550,000 metric tons per 12 months of EO ¹.

Potential and barriers – The high ethylene costs and the low selectivity of the oxidation process exerts partial recycling of the reaction products. However, the side reactions lead to

¹ The values are converted from \$ to € based on $1 \in {}_{2015}=1,11$ \$ ${}_{2015}$ 22



the 20-25% of ethylene lost in general ⁵, ⁶. On the other hand, the emitted process base CO₂ has high purity which makes it a suitable candidate for implementation of carbon capture technology at first industrial approaches ⁴.

Ethylene oxide - Ethylene oxide (EO) is the only cyclic ether, extremely reactive and considered among the most versatile chemical intermediates. Therefore, EO is a chemical intermediate that cannot be directly used and is further reacted to produce a wide spectrum of products. Ethylene glycols (mono-, di-, triethylene glycol) constitute by far the single/largest outlet for ethylene oxide, accounting for about 73% of the EO market in 2018. Other dominant end uses include higher-value derivatives such as ethoxylates, ethanolamines, glycol ethers, polyethylene glycol, polyether polyols, surfactants and glycol ethers¹. EO is, also, used as a de-icing material ⁷, ⁸.

Production and consumption in Belgium – Ethylene oxide (EO) production lines in Belgium are BASF and Ineos plants located in Antwerp with capacity of 500,000 ton/year and 420,000 ton/year respectively at 2013 ⁹.

By 20th November 2019, BASF SE announced their plan on extending of EO production capacity at Antwerp, Belgium by about 400,000 tons/year. The start-up phase of the expansion is scheduled for 2022 ¹⁰, ¹¹. Moreover, on 14th September 2018, Ineos announced to invest at its Zwijndrecht site in Antwerp, Belgium to upgrade (EO) production which includes modernizing EO storage and distribution facilities beside debottlenecking and increasing EO production ¹². They declared that underground EO storage capacity of Ineos plant at Zwijndrecht will increase seven fold ¹³. Hence, EO production had an increasing trend in history and is under development toward increasing the quantity in the close future.



Process overview - Ethylene oxide (EO) manufacturing was primarily based on the chlorohydrin course in which ethylene reacts with hypochlorous acid. However, this process is no longer considered to be installed due to emerging of the direct oxidation pass which costs 3-4 times less than the chlorohydrin process and is more environmental friendly process ¹. The other disadvantage of the chlorohydrin process is the problem of treating the large waste stream containing calcium chloride and amounts of chlorinated hydrocarbons and glycols ⁶.

The selectivity of the EO formation through direct oxidation technology is around 81%, while the ethylene conversion to EO is around 10%. Since the reactions are exothermic, water is used as a cooling medium on the shell side of the reactor and is later used to produce large quantities of low-pressure steam ³.

Air-based vs. Oxygen-based Process - Different industries use either air or oxygen as feed streams to obtain an oxygen source to react ethylene with oxygen. The oxygen-based process is chosen due to its many advantages. For all plant capacities and a given type of catalyst, the oxygen-based reactor yields a higher selectivity and requires less catalyst. Although the air-based process may cost lower to run (for small to medium-sized plants), the initial building costs of the air-based plant is more than the oxygen-based plant. While the oxygen-based process requires a carbon dioxide removal section, more stainless steel, and some expensive instrumentation, the air-based process requires more catalyst, more reactors (to achieve a comparable selectivity), a multi-stage compressor, air purification units, a vent gas treating system, and two to three reactor train in series.

In spite of the extra equipment for the air-based process, the production level of EO for an airbased process is still less than the oxygen-based process. The average selectivity ranges from 65-75% compared to 70-80% for the oxygen-based process. Furthermore, the oxygen-based plants can have a yield of up to 0.1 kg EO per kg ethylene more than the air-based plants. Due to this reason, the oxygen-based process is a more attractive choice.

Since the silver catalyst is expensive, the length of catalyst life is an important consideration. For the oxygen oxidation, the catalyst lasts longer and less is required for the catalyst charge. The air-based oxidation generally needs 1.5 times the catalyst charge of the other process. The



required amount of catalyst and length of catalyst life also makes the oxygen-based process a more economically viable choice ³.

Production - A typical direct oxidation of EO in which pure oxygen is used as the oxidizing agent is shown in Figure 2. The EO direct oxidation process can be subdivided into three main sections/sub-processes: (1) oxidation; (2) reagents restoration; and (3) product separation ¹.



Figure 2. The diagram exhibits the manufacturing of ethylene oxide by way of direct oxidation of ethylene ¹

Oxidation - Initially, contemporary ethylene, methane make-up and oxygen are combined with recycle gasoline (recovered downstream). Methane is used as ballast gasoline to manage flammable limits. The combination is heated by warmth alternate with reactor effluent and fed to a multi-tubular catalytic reactor. There, EO is selectively produced over a silver catalyst supported on alumina. The warmth from this exothermic response generates steam on the reactor shell aspect, and is used for heating functions all through the method. Additionally, a part of the ethylene is combusted, producing carbon dioxide and water ¹.

Reagents restoration - The gaseous stream obtained from the reactor outlet is countercurrently contacted with chilly water in an absorber for the separation of sunshine gases



(primarily CO₂, unreacted ethylene, oxygen and methane). The majority of the gaseous overhead stream is straight cycled again to the EO response by a compressor. The rest of the gaseous overhead stream is handled for CO₂ elimination earlier than being dispatched again to the reactor. A liquid resolution of EO dissolved in water is withdrawn from the absorber as an aspect stream ¹.

Separation of final products - The EO/water stream from the absorber is fed to the highest of a stripper, the place EO is separated from water. The stripper bottoms — a water/ethylene glycol combination — is routed to a column for recovering antifreeze-grade monoethylene glycol (MEG), which is bought as a byproduct. The overhead gaseous stream, comparatively concentrated in EO, is condensed and dispatched to a light-ends elimination unit. Crude EO withdrawn from the underside of this unit is fed to a closing purification column for the elimination of water and heavy impurities. Excessive-purity EO (99.9 wt.%) is obtained from the column overhead and is condensed and dispatched to storage ¹.

Reaction and process main parameters

- $C_2 H_4 + 0.5 O_2 \rightarrow CH_2O.CH_2O$
- Ethylene to air ratio: 3 10 % (The molar ratio of oxygen to ethylene at the reactor ethylene should be 6:1 ¹⁴.)
- Side reaction products: CO₂, H₂O
- Catalyst: Silver oxide on alumina
- Operating temperature and pressure: 250 300°C and 120 300 psi
- Suppressing agent for side reactions: Ethylene dichloride
- Reaction is exothermic ⁶

The details of reaction and side reaction are depicted in figure 3.



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Figure 3. Simplified macroscopic reaction scheme ⁵.

Investment and production costs - Ethylene makes up for approximately 68% of the total cost of the EO process ⁵. Therefore, it is important to optimize the selectivity towards EO and thus reduce the consumption of ethylene ⁶.

A cost analysis at 2010 at a U.S. Gulf Coast location is carried out based upon a 320,000 t/yr plant and released the following estimated costs for EO production plant. The original reported costs were in $\$_{2010}$ and are converted into \pounds_{2010} based on the mean exchange rate².

- Capital investment of about €2010433.85 million
- The product value: about \in_{2010} 0.945/kg
- Production cost: \in_{2010} 0.75/kg ¹⁵

As another case, EO plant economy on 1999 was reported for the 150,000 t/yr considering mainly the reactor section of the process 3 :

- Capital cost involved: €20106.99 million
- Yearly operating cost: €201069.17 million

 $^{^2}$ The values are converted from \$ to € based on 1 €_{2010} = 1.33 \$_{2010} ^{22}



Energy requirements - The warmth from the exothermic reaction during partial oxidation of ethylene, generates steam on the reactor shell, and is used for heating functions all through the method. Therefore, except the possible start-up requirements, no fuel burning is required.

Carbon capture and storage (CCS) in EO production - Overall, processes with high purity CO₂ emissions are interesting as first sources for CO₂ capture. High purity CO₂ emission chemical processes mainly includes ethylene oxide and ammonia production, natural gas processing and steam-methane reforming for hydrogen production which all have purities over 95% ¹⁶. The CCS for the EO plant should be implemented in the reaction subsection as shown in Figure 4.

In the Dutch industry, CO₂ concentration in flue gas is predicted to be 100% for EO plant in 2025 and 2040. The estimated electricity requirements (incl. compression) is 0.4 GJe/tCO₂captured for the same years with the estimated specific capital costs³ equal to 20 - 40 (\notin_{2008} /t CO₂ captured/yr) for year 2025 and 20-25 (\notin_{2008} /t CO₂ captured/yr) for year 2040 ¹⁷.

CCS offers viable opportunities in the two EO plants in the Dutch industry abating ~0.1 Mt CO_2 ¹⁷.

The stoichiometry of the process suggests it is produced at a ratio of 6/2 EO to CO₂, which would mean that CO₂ generation is about a third of total ethylene oxide production ⁴.

 $^{^{3}}$ - The specific capital costs refer to the equipment and installation costs. Ranges indicate the lowest and highest values used for that sector.



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Figure 4. Block flow diagram of a conventional oxidation process for the EO production. Dashed line units present in the oxygen based process ²

Typical properties of gas streams that are subject to CO₂ separation/capture is shown in table 1.

Table 1. Typical properties of gas stream from EO plant which is subjected to CO₂ separation/capture ⁴.

Activity	Source	CO ₂ conc	Pressure	Partial pressure (MPa;	CO ₂ conc
	stream	(%; inlet)	(MPa)	CO ₂)	(%; outlet)
Ethylene oxide	Reactor	8	2.5	0.2	30-100

Many of the processes use similar technologies to separate the CO₂ from the gas mixtures, including ⁴:

- Membrane separation;
- Chemical solvents, including amine-based solutions (e.g. MEA and MDEA) and hot potassium carbonate based processes (e.g. the Benfield[™] process);
- Physical sorbent based process to remove CO₂ from gas mixtures (e.g. SelexolTM, Rectisol);
- Pressure swing adsorption (PSA); and,
- Cryogenic separation processes.



Selection of the appropriate process is dependent on a number of factors including end use specification, gas inlet pressure, cost, size, weight and maintenance needs.

There are no known plans to undertake capture and storage from EO production at present. As CO_2 emissions from most existing plants are typically small (around 150-250 ktCO₂ per year) it is likely that economies of scale would preclude cost-effective capture unless emissions could be captured as part of an integrated multi-source CCS network. Early opportunities may exist for integrated chemical complexes and larger facilities combined with ethylene and/or ethylene glycol production ⁴.

Yearly estimated total direct CO_2 emissions related to Belgian EO production volume - Due to heat recovery at reaction sub-plant and its utilization for heat requirements there is considerable fuel related CO_2 emission.

As for the process related CO₂ emission, emission factors of ethylene oxide production $(t_{CO2.eq}/t_{EO})^{18}$ are:

- Electricity use = 0.16
- Thermal production = 0.17
- Direct Process = 0.55
- Total $= 0.88^{-18}$

Total GWP (according to IPCC 2007) = 1.6 tons CO₂-equivalet per 1 ton of Ethylene
Oxide 100% active substance ¹⁹.



CCS characteristics as innovative technology¹⁸

- Process CO₂ reduction ⁴
- Year of availability $= 2030^5$
- Reference capacity (kt/y) = 260
- Cost (ϵ_{2013}/t_{CO2}) = 39
- Investment cost (\in_{2013}) = 500000

The investment costs for the application have been calculated as follow:

Investment cost = GHG Reduction \times Process emission factor \times CCS cost \times Reference capacity

As far as the ethylene oxide production is concerned, CCS is a possible technology for this subsector and is installed in facilities after 2030. By 2050 70% of the facilities practice CCS, which leads to emission savings as illustrated in Figure 5.



Figure 5. Trends of total GHG emissions in ethylene oxide production, according to the baseline scenario

⁴ Due to lack of data, a conservative value of 50% has been assumed (in reference 18) 18

⁵ Lack of information. (According to (Carbon Counts, 2010) this industry shows low interest to implement

CCS.). Hence 2030 can be acceptable



The specific energy consumptions for ethylene oxide is 25.3 TJ/kt_{EO} in 2050.

Improving efficiency and reducing emission in EO production Innovations

A novel route employing supersonic separator (SS) to prevent EO losses using liquid-water injection as depicted in Figure 6. SS route reduces oxide losses by 83.33 kg/h, representing +0.9% greater EO production, 95% less EO losses, entailing 2.5% higher net value for 20 operation years despite 0.11% higher investment, and consequently exhibiting the best environmental, technical, health and safety and economic performances 20 .



Figure 6. EO Conventional-Route and EO SS-Route (SS-EO-Recovery and CCS unit highlighted)²⁰

Moreover, due to the high ethylene costs, the selectivity is the main factor for the economics of the process. A membrane reactor with an advanced cooling strategy is proposed as best technical reactor. With this reactor design it is possible to increase the selectivity of the ethylene epoxidation by approximately 3% compared to an optimized reference case ⁵.

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The first option (purge treatment) gives the opportunity to reduce hydrocarbons losses (e.g., C_2H_4 , CH_4) with a resulting lower make-up into the reactor. As a consequence of increasing ethylene price and more stringent environmental restrictions, significant cost savings can be achieved, particularly in large size plants, as showed in table 2 ²¹.

Table 2. Economy of the ethylene and methane recovered in EO manufacture process ²¹.

		2005	2010
Ethylene recovery (75%)	130 kg/h	620,000 \$/y	1.05 million \$/y
Methane recovery	70 kg/h	215,000 \$/y	121,500 \$/y

Membrane gas separation is an efficient system to recovery unconverted ethylene, methane and also argon from the purge stream reducing hydrocarbon losses with benefits in terms of environment protection and cost saving. CO_2 removal from the oxygen-based cycle can be performed by membrane contactors or gas separation membranes as alternative to a conventional hot K₂CO₃-based absorption process ²¹.



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Table3. Summary Table: Key EO Data and Figures

Technical Performance	Oxidation	Reagents restoration	Separation of		
			final products		
Energy input	Utilization of	-	Chilly water for		
	recovered heat		separation section		
	(steam)				
Output	-	Steam (The warmth of	-		
		exothermic reaction			
		generates steam on the			
		reactor shell.)			
EO production in Belgium	2013		2022*		
Overall production rate (t/yr)	920,000	≥ 1,320,000			
Costs					
The whole working value ^{**} $(\notin_{2015}/\text{ton of ethylene oxide})^{1}$	577.2				
Plant size of 320,000 t/yr ¹⁵	Capital investment	Product value (€ ₂₀₁₀ /kg)	Production cost		
	(m€ ₂₀₁₀)		(€ ₂₀₁₀ /kg)		
	288.98	1.11	0.88		
Materials (For air based production) ⁶	(t/t EO)				
Ethylene	0.92				
Oxygen	0.9				
Steam	0.1				
Water	180				
Methane	Inert gas to provide stability and manage flammable limits				

* Ineos will invest at its Zwijndrecht site in Antwerp, Belgium to upgrade (EO) production which includes modernizing EO storage and distribution facilities beside debottlenecking and increasing EO production. This can increase the amount of production reported for 2022.

** The whole working value includes uncooked supplies, utilities, fastened prices and depreciation prices.



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