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## PRODUCTION OF ETHYLENE OXIDE IN THE PRESENCE OF SELECTIVE CATALYSTS

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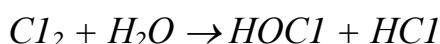
**Tashkent Institute of Chemical Technology  
Karakalpak State University named after Berdakh**

Ethylene oxide is widely used to produce ethylene glycols, glycol ethers, fibers, antifreezes, ethanalamines, brake fluids, and a number of other products.

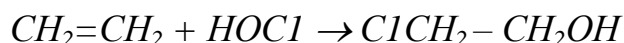
World production exceeds 18 million tons per year, and continues to grow dynamically by 4-5% per year. There is no production of ethylene in our republic.

Industrial production of ethylene oxide began only in the 1920s, almost 100 years after its discovery by Wurtz [1, 2]. At the first industrial plant of the Union Carbide Company (USA), a multi-stage process for producing ethylene oxide by the chlorohydrin method was used.

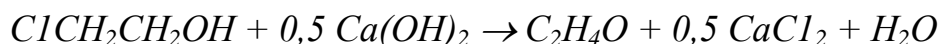
In the first stage, hypochlorous acid is formed from chlorine in the aquatic environment.



The resulting hypochlorous acid reacts with ethylene dissolved in water to form ethylene chlorohydrin.



In the second stage, an aqueous solution of ethylene chlorohydrin is saponified with calcium or sodium hydroxide to form ethylene oxide.

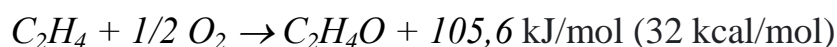


The chlorohydrin process had a simple instrumentation, low consumption of ethylene and energy resources, but this did not compensate for a number of serious shortcomings, especially the formation of a large amount of wastewater containing by-products of organochlorine products and a dilute solution of calcium chloride.

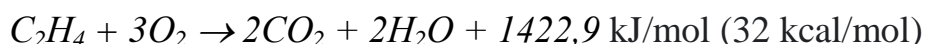
Therefore, after Lefort discovered the method of direct oxidation of ethylene on silver catalysts [3], he began to displace the chlorohydrin method for producing ethylene oxide.

The first industrial plant for the production of ethylene oxide by direct oxidation of ethylene with air was installed by the same company Carbide and Carbon with a capacity of 7000 tons per year in 1937.

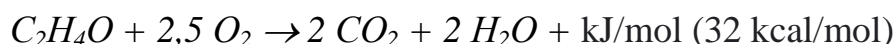
The industrial technology for producing ethylene oxide is based on the reaction of partial oxidation of ethylene-to-ethylene oxide



accompanied by the complete oxidation of ethylene



At elevated temperatures, further oxidation of ethylene oxide is possible



At the same time, under the conditions of obtaining ethylene oxide, reactions of the formation of impurities - aldehydes (formaldehyde, acetaldehyde) proceed at a low rate, including due to the isomerization of ethylene oxide.

Sometimes technical solutions concern only individual nodes of the technological scheme. Thus, in the US patent [4], in addition to the above-described technological scheme, it is proposed to pass the gas mixture after the separation of ethylene oxide and carbon dioxide through a semi-permeable membrane made of polysulfone or polymethyl silicone to remove part of the argon contained in the gas mixture.

In the Shell patents [5, 6], it is proposed to gradually increase the ethylene concentration during operation with the adjustment of the oxygen content in the initial mixture, provided that the gas mixture is explosion-proof.

In a number of Shell patents, it is proposed to improve the ethylene oxidation process by using more advanced carriers for catalyst preparation [7–9].

Recently, the industry has mainly used the "oxygen" version of the ethylene oxidation process. With a production capacity of more than 20 - 30 thousand tons per year, the efficiency of the "oxygen" process in comparison with the "air" process exceeds the costs of an air separation unit and some additional equipment.

The reaction rate and catalyst productivity when using the oxygen process is almost 2 times higher than for the air process, and, accordingly, the catalyst load at the same power is also almost 2 times less. Ethylene consumption per 1 ton of ethylene oxide is also noticeably lower, and the selectivity is somewhat higher than for the air process [10–12].

On pure silver, the selectivity of ethylene oxidation to ethylene oxide does not exceed 40–50% [13, 14]. The first industrial catalysts had a selectivity of about 60 - 65%. To do this, promoters were introduced into silver - electronegative additives, for example, chlorides [15]. During operation, a partial loss of promoting additives occurred, especially in the first catalyst layers along the gas flow. To compensate for the loss of the promoter, organochlorine compounds, such as dichloroethane, ethyl chloride, and others, must be introduced into the gas mixture before the reactor [16]. The mechanism of action of promoters is considered, for example, in [17, 18]. As a result of comprehensive research and experimental, pilot work, over the past 40 years, the selectivity of catalysts for the oxidation of ethylene-to-ethylene oxide has increased significantly.

Of great importance is the composition and optimal porous structure of the support, as well as the geometry of the support granules (sphere, rings). Without analyzing in detail, the composition and formulation of the catalyst, methods of its preparation, we note only a number of published works, mainly patents.

Shell is constantly researching to improve the formulation of the catalyst and the method of its preparation. Moreover, to increase the selectivity of the process, new promoting additives based on cesium and rhenium compounds with small additions of co-promoters are used.

In a number of Shell patents, it is proposed to use a silver catalyst promoted with additives of an alkali metal, rhenium, and a co-promoter - boron, phosphorus, or mixtures thereof on a support with a specific surface area of 0.05–10 m<sup>2</sup>/g [19]; a catalyst containing a promoting additive of rhenium, sulfur compounds, boron and phosphorus; a catalyst containing a promoting additive of rhenium, and boron and phosphorus compounds. The SRI International patent provides for the oxidation of ethylene with oxygen on a silver catalyst on a ring support containing promoter additives of halogen, rare earth elements, rhenium, and sodium. The combination of a highly selective catalyst and carefully selected technological parameters provide a high economic efficiency of the process [20]. A silver catalyst promoted with halogen, rare earth elements, and lanthanides has been patented [21].

From the analysis of the literature, it follows that in all industrial production of ethylene oxide, the process of ethylene oxidation with oxygen or air is carried out in tubular reactors in a fixed bed of selective and active catalysts "silver with additives" on an inert corundum carrier. The process is carried out at a pressure of about 20 atm. and temperature 220 - 260 °C. Modern high-capacity production facilities use the process of ethylene oxidation with pure oxygen in the presence of inert additives (nitrogen or methane) in the initial gas mixture. Optimum technological parameters should ensure trouble-free operation of production.

The problem of ensuring the stable safe operation of reactors is one of the most important. Therefore, the purpose of our work is to analyze industrial reactors of existing production facilities for the oxidation of ethylene-to-ethylene oxide and cases of emergency shutdowns and thermal disruptions.

**Experimental part.** The catalyst for the oxidation of ethylene was prepared in the following sequence: 60 ml of 5% acetic acid and 50 ml of 3.0 - 5.9% hydrochloric acid was added to 100 g of purified and activated bentonite. 10 - 25 g of silver nitrate and 10 - 25 g of brown coal were added to the resulting suspension with stirring. The catalyst mass was molded in the form of a "cylinder" by passing through a filter with a diameter of 3 mm. The molded catalyst mass was withered at room temperature (20 - 30 °C) for 12 - 16 hours and dried at 100 ± 5 °C for 3 hours. Then the temperature was gradually raised by 30 - 50° per hour to 400 - 450 °C for 5 hours. Then it was cut into cylinders 4-5 mm long, sieved from dust.

Dalle, to determine the inertness of methane and ethane added to an ethylene-containing mixture, under the conditions of the reaction of ethylene oxidation with oxygen on modern industrial catalysts, a flow-through laboratory installation made of stainless steel was mounted, the scheme of which is shown in Fig.1.

A flow reactor (5) was used, which is a U-shaped stainless-steel tube with an inner diameter of 20 mm and a wall thickness of 1.8 mm with a catalyst bed length of up to 1000 mm. To prepare the initial gas mixture, bottled purified ethylene, pure

gaseous oxygen and nitrogen, methane and ethane of high purity (produced by the Shurtan Gas Chemical Plant (SGChP)) were used.

The content of the main substance in methane and ethane is 99.9%, impurities of nitrogen and oxygen up to 0.04%, ethane (methane) and propane 0.03%, water vapor up to 0.002%, respectively. Components of the initial gas mixture from cylinders through a system of valves and gas flow regulators (2) at a pressure of 10-11 atm. They entered the activated carbon columns (3) and, after mixing, were fed into the reactor (5) placed in a bath (6) with a high-temperature polymethyl siloxane coolant of the brand PMS-200. The required temperature in the reactor was provided by electric heating of the bath, controlled by a laboratory autotransformer (8). The temperature was measured by thermocouples (7). The pressure in the system was determined by manometers (4). The total flow of the gas mixture at the outlet of the system was controlled after reduction by a rotameter.

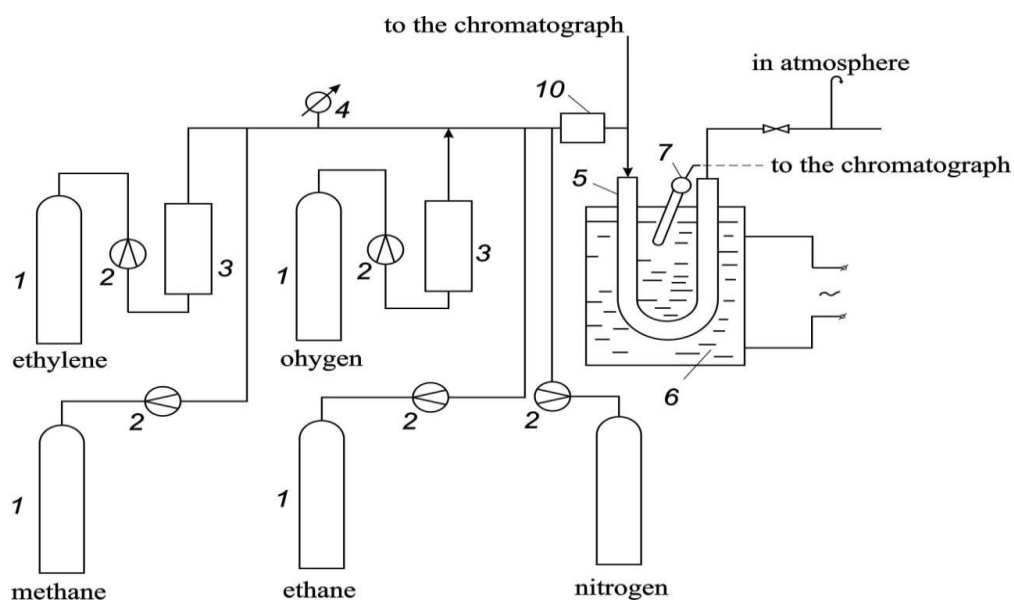


Fig.1. Scheme of a laboratory installation for the oxidation of ethylene with oxygen in the presence of saturated hydrocarbons: cylinders with ethylene, methane (ethane), oxygen and nitrogen; gas flow regulator; gas purification system in columns with activated carbon; manometer; figurative reactor; bath with silicone oil and electric heating; thermocouple; laboratory autotransformer for reactor temperature control; rotometer; mixer. The analysis of the content of the components of the initial and obtained in gas mixtures was carried out chromatographically (under the conditions of ShGChP). In the study of the process of ethylene oxidation with oxygen in the presence of methane and ethane, a catalyst prepared according to the above method was used, with a silver content in the catalyst from 10 to 25%.

In table. Figures 1, 2, and 3 show the results of experiments with additions of nitrogen, methane, and ethane. The values given in the tables are the average of 4-5 determinations with stable operation of the catalyst.

The experiments were carried out at possibly close oxygen concentrations in the initial mixture in order to eliminate the effect of oxygen on the reaction rate with an excess of ethylene against the stoichiometric one.

Table 1 shows the results of experiments on the oxidation of ethylene in the presence of nitrogen additives.

Table 1

**Oxidation of ethylene in the presence of a nitrogen additive.  
Catalyst loading 100 sm<sup>2</sup>, gas flow rate 4000 h<sup>-1</sup>**

Temperature, °C	Initial gas mixture, % vol.			Gas mixture after the reactor, % vol.		Selectivity, %	Catalyst capacity g/kg cat h
	C <sub>2</sub> H <sub>4</sub>	O <sub>2</sub>	N <sub>2</sub>	C <sub>2</sub> H <sub>4</sub> O	CO <sub>2</sub>		
224	40,0	6,9	53,0	1,35	0,92	74,3	106
228	39,8	7,1	53,1	1,36	0,96	73,9	106
232	40,1	7,0	52,9	1,34	0,94	74,1	105
236	41,2	6,8	52,0	1,46	1,03	74,0	114
240	39,1	6,9	53,9	1,47	1,05	73,6	115
244	40,7	7,2	52,1	1,51	1,09	73,5	118

Table 2 shows the results of experiments on the oxidation of ethylene in the presence of methane additives.

Table 2

**Ethylene oxidation in the presence of methane additive.  
Catalyst loading 100 sm<sup>3</sup>, gas flow rate 3950 h<sup>-1</sup>**

Temperature, °C	Initial gas mixture, % vol.				Gas mixture after the reactor, % vol.		Selectivity, %	Catalyst capacity g/kg cat h
	C <sub>2</sub> H <sub>4</sub>	O <sub>2</sub>	CH <sub>4</sub>	N <sub>2</sub>	C <sub>2</sub> H <sub>4</sub> O	CO <sub>2</sub>		
224	40,1	7,0	40,5	12,4	1,33	0,93	74,3	104
228	39,9	6,8	38,0	15,3	1,36	0,96	74,0	106
232	40,2	6,9	52,9	-	1,35	0,90	75,0	105
236	41,1	7,0	39,1	12,8	1,46	1,02	74,2	115
240	40,8	6,9	52,3	-	1,51	1,07	74,0	118
244	39,3	7,2	40,3	13,2	1,47	1,04	73,9	116

Table 3 shows the results of experiments on the oxidation of ethylene in the presence of an ethane additive.

Table-3

**Oxidation of ethylene in the presence of an ethane additive.  
Catalyst loading 100 sm<sup>3</sup>, gas flow rate 3950 h<sup>-1</sup>**

Temperature, °C	Initial gas mixture, % vol.				Gas mixture after the reactor, % vol.		Selectivity, %	Catalyst capacity g/kg cat h
	C <sub>2</sub> H <sub>4</sub>	O <sub>2</sub>	CH <sub>4</sub>	N <sub>2</sub>	C <sub>2</sub> H <sub>4</sub> O	CO <sub>2</sub>		
224	40,2	6,8	39,0	14,0	1,32	0,92	74,1	103

228	39,9	6,7	39,5	13, 9	1,35	0,96	73,7	105
232	41,0	7,0	52,0	-	1,33	0,93	74,0	104
236	40,3	6,9	39,9	12, 9	1,45	1,07	73,0	115
240	40,1	6,8	53,1	-	1,50	1,08	73,9	116
244	40,6	6,8	40,2	12, 4	1,46	1,06	73,5	112

As shown above, the presence of saturated hydrocarbons, in particular methane and ethane, makes it possible to increase the permissible explosion-proof oxygen content in the initial gas mixture. At a pressure of 20 atm., a temperature of 250 ° C and an ethylene concentration of 15-40% vol. the allowable oxygen content in the presence of nitrogen, methane or ethane will be 7, 8 or 9% vol., respectively.

However, the question of the advisability of using methane or ethane should be decided from a practical point of view by comparing the cost of these hydrocarbons, their purification from impurities, and their availability for use in a particular industrial production of ethylene oxide.

The data obtained indicate the inertness of methane and ethane additives in the process of ethylene oxidation to ethylene oxide on silver catalysts on a bentonite carrier, and the fundamental possibility of their use.

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