Energy-economic analysis of the applicability of supercritical fluid extraction of ethylene oxide

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Abstract. A new scheme has been developed for the separation of ethylene oxide from its aqueous solution using supercritical carbon dioxide and further concentration of the product. An energy and economic comparative analysis of new methods of the separation of ethylene oxide from an aqueous solution and its further concentration with the traditional scheme has been carried out. This analysis showed that a scheme with supercritical fluid extraction with carbon dioxide and the addition of propane into the scheme is energetically and economically advantageous.

1. Introduction
Current trends in the application of supercritical technologies are based on the development of energy-saving and environmentally friendly industries. For the Republic of Tatarstan, where the chemical industry is sufficiently developed, this issue is particularly relevant. The reduction of energy consumption in large-capacity production of ethylene oxide is one of the most interesting tasks assigned to developers today.

Ethylene oxide is produced industrially by the reaction of ethylene and oxygen in the presence of a silver catalyst. In addition to the main reaction, side reactions also occur in the reactor, such as the decomposition of ethylene oxide, its isomerization, and the formation of glycols and acetic acid. Next, the resulting product with a mixture of unreacted components and side reaction products is absorbed by water to separate ethylene oxide from the mixture of reaction gases. Subsequent dehydration and concentration of ethylene oxide are associated with high energy consumption. The dehydration of ethylene oxide is traditionally carried out by evaporation of the product from its aqueous solution. To carry out the evaporation process, large expenditures of thermal energy are required, and the process is limited in maintaining the maximum permissible temperature (not higher than 373 K). P.V. Zimakov et al. [1] note that when this temperature is exceeded, the likelihood of monoethylene glycol formation as a result of the reaction between ethylene oxide and water increases sharply. Therefore, the traditional process of separating ethylene oxide from its aqueous solution is not only energy consuming, but also associated with undesirable product losses. To solve the problem of reducing energy costs, the authors of [2] proposed using the supercritical extraction process.

2. Research methods
In this work, we simulated several variants of technological schemes for the separation of ethylene oxide from its aqueous solution and subsequent purification of the product to the required concentrations using supercritical fluid technology and a technical and economic comparison of the developed schemes with
traditional technology. The simulation was carried out in the environment of the universal modeling program Hysys, which has proven itself in solving separation problems that occur at high pressures, including in the supercritical region. The extraction column was simulated using the Iside-Out algorithm. The calculations of the thermodynamic equilibrium state, as well as the calculation of the enthalpies of coexisting phases, are based on the Peng-Robinson equation of state, for the developed schemes, and the NRTL method, for the traditional scheme.

3. Results

Figure 1 shows one of the developed schemes for a supercritical extraction process in which carbon dioxide in the supercritical state with the addition of propane is used as an extractant. The consumption of raw materials entering the separation is 1254659 kg/h (production data) with an ethylene oxide content of 1.8 mass%. Raw materials enter the upper part of the T1 extraction column (column operating mode: T = 323 K; P = 11.5 MPa). In the extraction column, due to the contact of the feedstock with supercritical carbon dioxide moving in countercurrent, ethylene oxide passes into the fluid phase. The depleted solution is returned to the absorber, and the mixture of carbon dioxide, propane and ethylene oxide, passing through the control valve V1, enters the rectification column T2 (operating mode: P = 6 MPa, top temperature 308 K, bottom 323 K). The distillate (a mixture of carbon dioxide and propane) is recycled.

![Diagram of the separation process](image)

Figure 1. Technological scheme of the separation of ethylene oxide from its aqueous solution (Extractant is a mixture of supercritical carbon dioxide and propane): H1, H2, H3 - pumps; K1 - an extraction column; M1, M2, M3 - mixers; K2, K3, K4 - distillation columns; TO1 - heat exchanger; TO2 - condenser; B1, B2, B3 - control valves; KM – compressor.

The still residue of the T2 column, containing 4.65% ethylene oxide, enters the T3 distillation column (operating mode P = 2.6 MPa; top temperature T = 289.5, bottom T = 313 K), where the final separation of carbon dioxide occurs. The distillate of the T3 column (a mixture of carbon dioxide with a low propane content) is removed from the column in the vapor phase, compressed to some intermediate pressure, condensed in EX1 and returned to the extractor by pump P1. The still residue of the T3 column enters the distillation column T4, from which the residue of propane is removed as a distillate, and a commercial 99.99% ethylene oxide is obtained as the still residue (column operating mode: P = 1.5 MPa; top temperature 306 K, bottom T = 348 K).

The scheme of a supercritical extraction process using pure carbon dioxide as an extractant is modeled according to the same model at zero propane consumption. Naturally, there is no need to use
the T4 column. Moreover, in column T2 and condensers EX1, EX2, there is a need to maintain lower temperatures (T = 302 K), which requires the use of a refrigeration unit.

The traditional ethylene oxide production scheme includes an evaporation column (bottom temperature 393 K), a column for cleaning water (bottom temperature 373 K), a column for purifying the mixture from volatile gases (bottom temperature 328 K), a column for purifying from acetaldehydes (bottom temperature 348 K), a column of reabsorption of ethylene oxide from a mixture of light gases. This scheme is described in detail in [4].

As a result of the simulation of all three discussed schemes, the calculated thermal loads for all equipment positions were obtained, as well as the estimated power of the pump and compressor motors. These costs are shown in the graph in figure 2, and all costs are assigned to 1 kg / h of a commercial product. As can be seen from the data presented, the traditional method requires significantly greater energy costs for heating distillation columns, and most of the heat is spent on high-potential heat sources (heating to 373 K and above). The extraction schemes use low-grade heat, which allows the use of secondary energy resources.

Condensation and cooling processes in a traditional and developed scheme (with the addition of propane) are carried out using recycled water supply. In the traditional scheme, artificial cold (supported by the refrigeration unit) is used only when the finished product is condensed before being sent for storage and transportation. A scheme using supercritical carbon dioxide as an extractant without the addition of propane suggests a wider use of chilled water. The need to use a great-capacity refrigeration unit makes this scheme energetically unprofitable. Thus, the scheme characterized by the use of a mixture of carbon dioxide and propane in an approximately equal weight ratio as the extractant is characterized by the highest technical and economic indicators.

For completeness of the technical and economic comparison of the considered schemes, the calculations of the capital costs necessary for the implementation of the compared scheme solutions were also carried out. Distillation columns used in the proposed schemes were considered as non-standard equipment. Therefore, their cost was determined depending on their estimated weight. The approximate cost of heat exchange equipment, a compressor, and pumps was taken according to the
sites of Teploprofi, Soltec and VPK CONCORDIA, respectively. The cost of the finished product (ethylene oxide) is taken as the average from the official Sibur site.

The main technical and economic indicators are shown in figure 3. As it can be seen from this histogram, the lowest capital costs are required to implement the traditional scheme, since for this scheme the values of working and design pressures in distillation columns are an order of magnitude smaller than the corresponding indicators for schemes using supercritical extraction. The increase in working pressure leads to an increase in wall thickness, and hence the metal intensity of the columns. The cost of heat exchange, pumping and compressor equipment also increases with the increase of the main process pressure.

![Figure 3](image)

**Figure 3.** The main economic indicators of the schemes. 1 - capital costs, billion rubles; 2 - self cost, thousand rubles / t; 3 - profitability, %; 4 - extraction rate.

As we can see, the extraction scheme, using a mixture of ethylene oxide and propane as an extractant, is better than the compared schemes on almost all indicators. The advantage of this scheme with respect to increasing the degree of extraction of the target product to almost 1 is especially important. This means almost full use of the entire potential of the raw material resource and elimination of the negative impact of the enterprise on the environment (harmful emissions of organic products into the atmosphere and into water basins). The payback period for capital costs turned out to be relatively short (9 years) for facilities of such high complexity, especially when you consider that when comparing the schemes, the environmental protection advantages of extraction schemes are not taken into account. In the future they can become decisive.

**References**

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