

Complex Systems of Distillation Columns Used in the Production of the Propylene Oxide

MARILENA NICOLAE*

Petroleum - Gas University of Ploiești, 39 Bucuresti Blvd., 100680, Ploiesti, Romania

Complex systems of distillation columns were intensively studied within last decades and continue to show interest for researchers and for industrial application. The first designed complex distillation column with heat integration was the Petlyuk column and the development of complex systems of columns continued up to dividing wall columns (DWC) which are increasingly being used in industry. DWC are usually used to separate three products, components or fractions, from a multicomponent mixture. This study attempts to find the best fitting of complex systems of columns in the process of propylene oxide (PO) obtaining using the method of propylene chlorination and presents a proposed variant of separation which can lead to a reduced energy consumption. The fabrication of PO through this method lead to a multicomponent mixture which is separated in two main products: propylene oxide (PO) and heavier components containing as valuable compound 1,2 dichloropropane (DCP). Both products, PO and DCP, have important uses in the chemical industry. The study of complex schemes of columns used for PO separation was assessed by simulation using a simplified method based on Fenske - Underwood - Gilliland correlation (F.U.G.) [1]. The systems studied in this work include the following configurations of columns: column with prefractionator; column with partially coupled prefractionator; the Petlyuk column, the dividing wall column, column with side stripper, column with side rectifier, the direct and the indirect sequence.

Keywords: complex systems of distillation columns, separation, propylene oxide

Propylene oxide (PO) is an intermediary chemical compound used in manufacturing of propylene glycols, ethers of propylene glycols, polyether polyols, synthetic lubricants and extinguishing agents.

Currently, in a petrochemical plant from Romania, PO is obtained by propylene chlorination method. This method suppose obtaining the PO in three steps: (1) propylene chlorination with an aqueous solution of chlorine; (2) saponification with calcium hydroxide in a reactive distillation column; (3) purification of raw propylene oxide in a distillation column. The initially process scheme of PO separation is given in figure 1. Column C1 from figure 1 is the saponification column, having as distillate product the raw propylene oxide. Column C2 from figure 1 represents the PO purification column. This column separates the commercial PO as distillate liquid product, volatile compounds (propylene) as vapor distillate product and 1,2-dichloro-propane and heavier compounds as bottom product. This original plant was modified beginning with 1999 due to severe quality conditions for PO. The new specifications reduced the volatiles (propylene) content

to 50 ppmw (old, more than 2500 - 3500 ppmw), water to 10 ppmw (old, more than 100 ppmw) and aldehyde to 20 ppmw (old more than 100 ppmw), and increased the purity of propylene oxide to 99.9% (old, 99.5%). The first proposed and applied revamp of the plant is subject of a Romanian patent [2]. The process flowsheet diagram of the process is given in figure 2. PO is obtained as side liquid product, as presented in figure 2, ensuring achievement of specified quality regarding the content of volatiles in the commercial product, since the PO product is not in equilibrium with vapor from top separator. The second revamping proposal [3] suggest that all the vapor from the top of saponification tower will directly feed the second column (fig.3). This action would eliminate disadvantages concerning the heat loss by total condensation of vapors from the top of saponification tower and concerning the heat supplied for raw PO vaporization in the purification column. But adopting this proposal implies using of a turbo blower which was considered inadequate because of its high price, taking into consideration corrosiveness and the temperature of the stream.

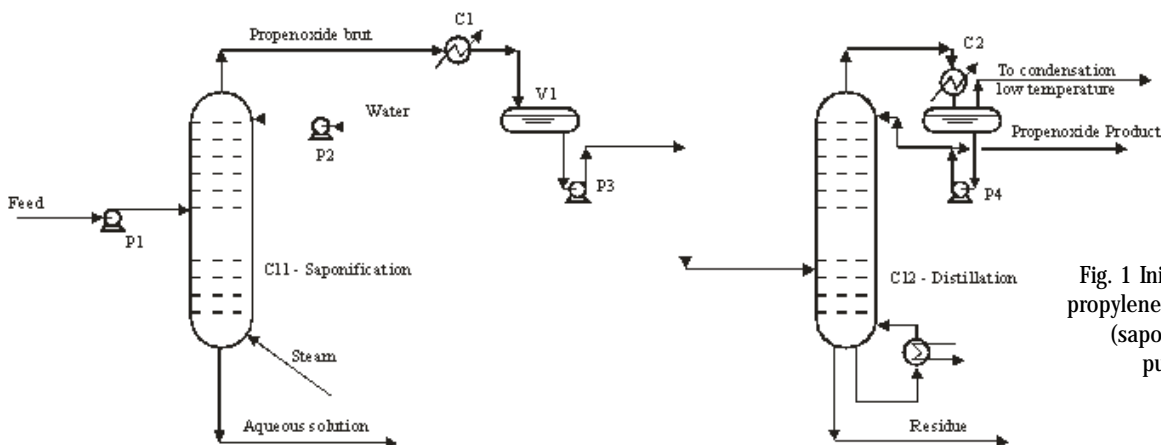


Fig. 1 Initially process for propylene oxide production (saponification and purification)

* email: nicolae_marilena@yahoo.com Tel. : +40-244-576 211/161

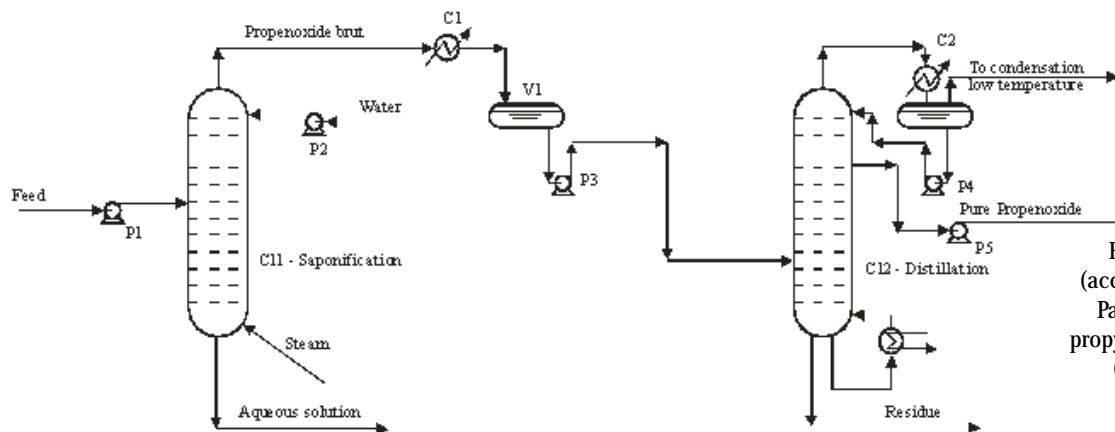


Fig. 2. New process (according with Romanian Patent 116277/2000) for propylene oxide production (saponification and purification)

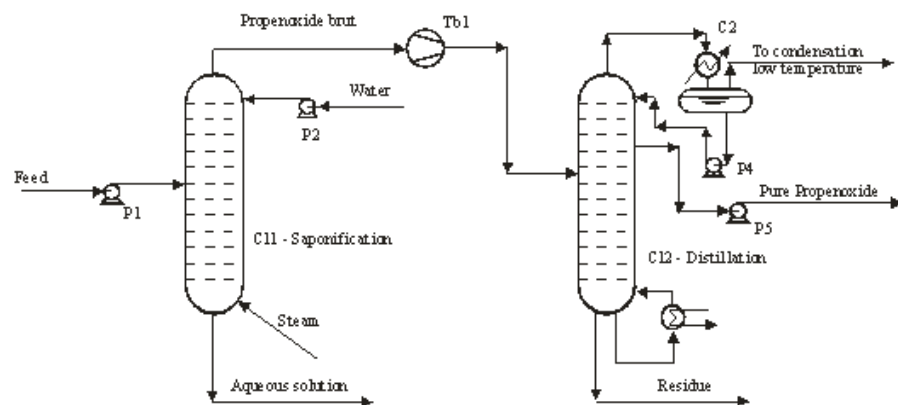


Fig. 3. Flow sheet for Romanian Patent 119883/2005

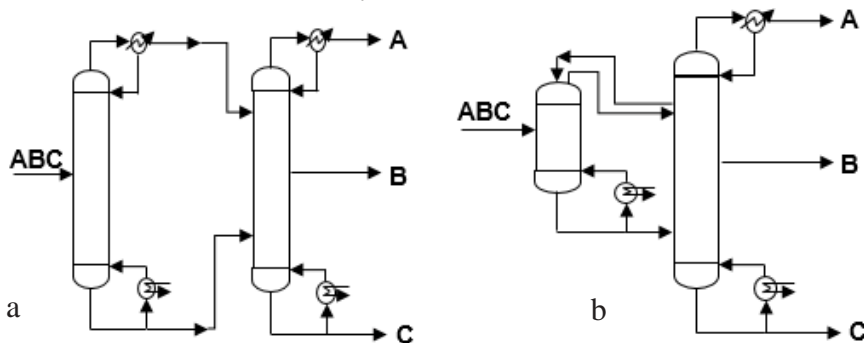


Fig. 4. Column with prefractionator (a) and column with partially coupled prefractionator (b)

Taking into account the considerations on energy savings, our study intends to evaluate the development of PO separation process (the integration of the saponification column with the purification column) using complex systems of distillation columns, with heat integration, aiming to identify the best solution in terms of energy consumption.

Complex systems of distillation columns with heat integration are alternatives to classical schemes of distillation, as direct sequence or indirect sequence. The main schemes are: column with prefractionator, column with partially coupled prefractionator, the Petlyuk column, the dividing wall column (DWC), the column with side stripper, the column with side rectifier. Usually, these

complex heat integrated columns have the advantage of a reduced energy consumption. An early approach to reducing energy is the Brugma distillation concept [4], which achieves the minimization of energy consumption by using reboiled towers in series (the column with prefractionator, fig. 4a). The design uses the multi-component or boiling fraction composition profile developed in the upstream tower, making a rough separation. A Brugma system may be viewed as an early form of distributed distillation. The idea of Brugma was reintroduced by Petlyuk [5] in 1965 and the coupled arrangement of columns became known as Petlyuk column (fig. 5a). Considering for distillation a

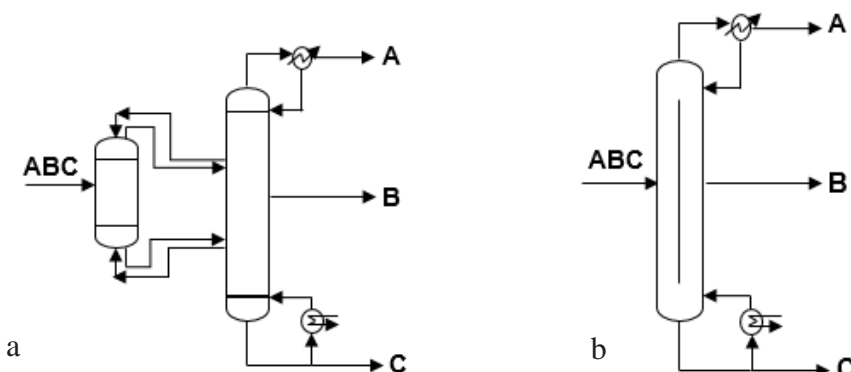


Fig. 5. Petlyuk column (a) and dividing wall column (b)

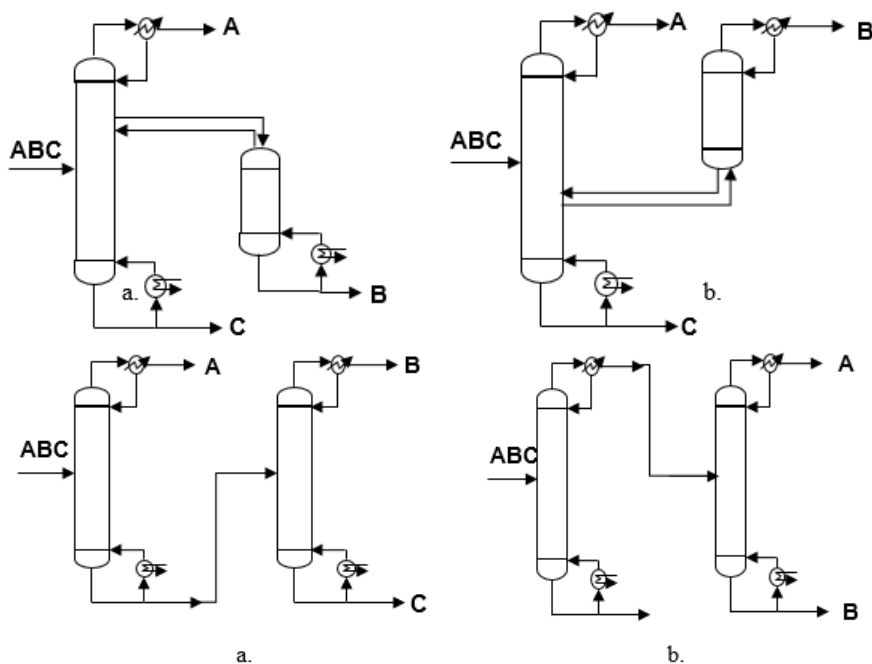


Fig. 6 Column with side stripper (a) and column with side rectifier (b)

Fig. 7. Direct separation sequence (a) and indirect separation sequence (b)

multicomponent mixture which will be separated in three components A, B and C (volatility order is: $A > B > C$), a Petlyuk configuration will separate in the first tower streams rich in A/B and B/C. In the second column the component B is obtained as side product. The specificity of Petlyuk design consists in elimination of the condenser and reboiler associated with the first tower in the Brugga style system, all reboil heat input being supplied at the higher temperature required for boiling component C, and heat is rejected at the condensing temperature of component A [4]. An important issue in applying this concept is the control of vapor and liquid flows between the towers (the stripping and reflux rates control), which needs an external source of energy if the columns operate at close pressures. In order to obtain that effect there could be used an ejector, a single stage compressor or a single impeller compressor. Otherwise, the vapor circulation is achieved only by pressure drop between the columns. The optimization of Petlyuk column was studied by many researchers. Z. Fidkowski, analyzed the operation degrees of freedom of the Petlyuk column and searched the values for boil up minimization [6]. They calculated the minimum vapor flow in the column sections using the Underwood classic method [7].

The dividing wall column (DWC) which is presented in figure 5b is considered thermodynamically equivalent to the Petlyuk column when they separate three products, even if they have a different external aspect. The DWC is built in a single shell and has a vertical wall that divides its core in two parts: one operates as prefractionator and the other works as the main column from Petlyuk configuration. Both configurations, Petlyuk and DWC, offer the advantage of no remixing the flows in the column during feeding. In this way the feed mismatch is reduced and implicitly a thermal benefit is recorded. It was estimated that the energy savings are up to 30% beside the conventional configurations [7].

Another interesting options for separation of ternary mixtures (or three products) are the columns with side stripper (fig. 6a) and columns with side rectifier (fig. 6b). These are simple columns with a side stream connected to a side section. When the added section is a rectifier we talk about simple column with side rectifier, and when the added section is a stripper a simple column with side stripper is obtained. Columns with side stripper and side rectifier present thermal coupling at the connection

between the main columns and the added section. Thermal coupling consists in the heat and mass transfer through the contact of material streams between the main column and added section. Thermally coupled distillation systems are arrangements where different columns are connected by liquid and vapor countercurrent streams. Condensers or reboilers are eliminated at some ends of upstream distillation columns and the liquid or vapor flows needed as refluxes are side streams of downstream columns of the distillation arrangement. The columns with side rectifier of side stripper only have one thermal coupling connection. Due to their partial heat integration, the simple column with side stripper and the simple column with side rectifier have lower minimum energy consumption than the direct and indirect sequences [8].

Problem statement

Propylene oxide separation from a resulting reaction mixture by chlorination of propylene is simulated using the simplified method of F.U.G. [9]. The simulation of PO separation is performed in schemes of complex columns, and aims to identify the best operation schemes in terms of energy consumption, respectively reboiler and condenser duties.

Normally, the simulation of the separation of propylene oxide obtained by propylene chlorination should be performed in reactive distillation columns. The reaction system is very complex leading to many secondary components. Because there are not enough data in literature in order to allow kinetic modelling and its simulation, modelling of the saponification column was realized by adapting to the existing column and defining the theoretical trays number in such a manner that allows the model to provide the same parameters (flows, composition, temperature and pressure) of resulting products as the industrial column. By using this approach, the simulation in any other conditions will provide similar results to the ones obtained in the industry.

Starting from the known composition of the products (volatile, PO and residue) of the existent saponification column from a Romanian petrochemical plant, was established the composition of the feed. The feed flowrate corresponding to the capacity specified is 1520 kmol/h and its composition is given in table 1. The feed stream is introduced in the column at its boiling temperature (104°C)

	Feed	Product A	Product B	Product C
Flowrate, kmol/h	1520	0.4734	38.89	1481
Component	Mass fraction	Mol fraction	Mol fraction	Mol fraction
Propylene	0.0004	0.5851	0.0025	0
Propylene oxide	0.0775	0.4149	0.995	0.0001
Propionaldehyde	0.0004	0	0.0025	0.0001
Acetone	0.0004	0	0	0.0001
1-Dichloro propane	0.0136	0	0	0.0024
Water	0.9031	0	0	0.9966
alpha-Epichlorohydrin	0.0008	0	0	0.0002
Dichloro diisopropylether	0.0038	0	0	0.0004

Table 1
FEED AND PRODUCTS
COMPOSITION

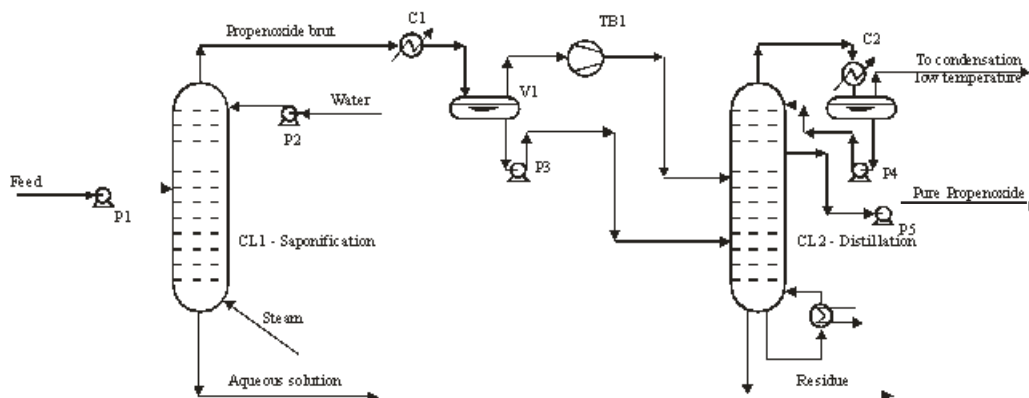


Fig. 8. Flow sheet for
Romanian Patent 127017 A2/
2012

corresponding to a pressure of 137.3 kPa. Water is used as a cooling agent as the first condensation, that is followed by a final condensation using a cooling agent with lower temperature. The recovery grade of propylene oxide was established to 99% and the recovery grades of the other components, especially of adjacent ones, were established in order to maintain the prescribed PO purity. The feed and products composition from table 1 correspond to all simulation variants that will be discussed in this paper, this fact allowing us to compare their specific energy consumptions.

In all simulated variants of systems of complex columns the first split of the mixture was made between propylene and propylene oxide (product A is propylene), and the second split was made between propylene oxide and Propionaldehyde (product B is propylene oxide, while product C is constituted from components heavier than propylene oxide - table 1). Columns operate at ratio R/R_{min} equal to 1.1. Table 1 gives the composition of the feed and obtained products.

Starting from the idea of energy consumption reduction by heat integration, namely from the concept of avoiding the remixing effect in the PO purification column, was proposed to use a partial condensation of the top vapor (vapor with 30-40% propylene oxide, 90-100°C and 1.0 – 1.3 bars) of the saponification column (fig. 8) up to 55 – 70°C (most likely 60°C). The resulted streams by partial condensation will feed the purification column on optimal feed trays: the vapor stream feeds the second column (using a turbo blower) on a tray somewhere at the top of the rectification section, while the liquid stream (using a pump) feeds the second column on a tray somewhere at the bottom of the rectification section [10]. This proposal is energy efficient because using partial condensation, a part of the heat of the vapor stream is recovered, steam consumption of the second column reboiler being reduced with more than 30% and cooling water consumption for saponification column is reduced with 60%. This proposal could lead to the reduction of energy consumption and

implicitly to the minimization of operation cost. The simulation of this operation proposal was rigorously achieved in PRO II simulation software.

For each separation variant discussed in this work were displayed the thermal duties of the heat exchangers (condenser and reboiler) of the columns, and based on this values and the actual price for steam (45\$/Gcal) and water (0.025\$/ton), were calculated the operating costs for each separation variant. The prices of the utilities were estimated at the level of year 2015.

Results and discussions

The conventional variants of direct and indirect separation sequences were simulated beside the schemes of complex columns with heat integration (column with prefractionator, column with partially coupled prefractionator, column with side stripper, column with side rectifier, Petlyuk column and dividing wall column). The results of all the simulations are presented below.

Column with prefractionator and column with partially coupled prefractionator

The prefractionator arrangement is similar to the Petlyuk Column, but with simple connections (instead of thermal coupling connections) between the prefractionator and the main column. It requires two more exchangers, one at each prefractionator extreme, this meaning that more energy is required. In the prefractionator a rough separation AB/BC is performed, and PO is obtained as side product in the main column. The arrangement of the partially coupled prefractionator is very similar to the prefractionator arrangement, with the characteristic of the thermal coupling at the distillate stage with the main column.

Petlyuk column and dividing wall column

Thermal coupling is the characteristic feature of the Petlyuk Column. In the case of the Petlyuk Column, thermal coupling is present at both ends of the prefractionator (Fully Thermally Coupled Distillation Column) (fig. 5a). The main advantage of thermal coupling is to avoid heat exchangers.

Table 2
OPERATING PARAMETERS FOR THE COLUMN WITH PREFRACTIONATOR AND THE COLUMN WITH PARTIALLY COUPLED PREFRACTIONATOR

Scheme type	Column with prefractionator		Column with partially coupled prefractionator	
	Prefractionator	Main column	Prefractionator	Main column
Number of trays	11	100	11	72
Condenser duty, MW	0.3580	4.740	-	6.523
Reboiler duty, MW	0.5883	7.249	0.5883	9.446

Table 3
OPERATING PARAMETERS FOR THE PETLYUK COLUMN AND DIVIDING WALL COLUMN

Scheme type	Petlyuk column						Dividing wall column					
	Sect.1	Sect.2	Sect.3	Sect.4	Sect.5	Sect.6	Sect.1	Sect.2	Sect.3	Sect.4	Sect.5	Sect.6
Number of trays	5	6	1	4	55	40	5	6	1	4	55	40
Condenser duty, MW	-	-	4.751	-	-	-	-	-	4.751	-	-	-
Reboiler duty, MW	-	-	-	-	-	7.317	-	-	-	-	-	7.317

Scheme type	Column with side stripper		Column with side rectifier	
	Main column	Side stripper	Main column	Side rectifier
Number of trays	92	11	56	46
Condenser duty, MW	3.663	-	0.3150	4.435
Reboiler duty, MW	5.104	0.3465	7.358	-

Table 4
OPERATING PARAMETERS FOR THE COLUMN WITH SIDE STRIPPER AND COLUMN WITH SIDE RECTIFIER

Also, thermal coupling permits a reversible mixing of streams at the end of the column that has lost the heat exchanger [5]. In the studied case of the separation the DWC column is equivalent to the Petlyuk column, but it has the advantage of reduced capital costs due to the fact that all six sections are included in a single shell. Both Petlyuk and DWC separate propylene as distillate, PO as side product and heavier components as bottom product.

Column with side stripper and column with side rectifier

Propylene and PO-heavier separation is performed in the sections adjacent to the feed of the column with side stripper. In the upper section of the first column, propylene is removed. The stripper purifies PO. In the column with side rectifier, propylene - PO and heavier separation is performed in the sections adjacent to the feed. In the lower section of the first column, PO is removed from heavier components fraction. The rectifier purifies product PO. Therefore, any specified recoveries or purities in the three products can be attained in both, a column with side rectifier and a column with side stripper. Columns with side stripper and side rectifier present thermal coupling at the connection between the main columns and the added section.

Direct separation sequence and indirect separation sequence

Direct separation sequence and indirect separation sequence are considered to be the conventional arrangements for ternary distillations and are able to separate the ternary mixtures into products of any desired purity. In these arrangements each simple column has two sections, this meaning that totally there are four sections in the sequence. In the direct column sequence the propylene (A product) is separated, as distillate, from PO (B product) and heavier components in the mixture (C product). This column is connected at the bottom stage to the second column which carries out the PO -heavier components separation (B-C separation). The indirect

separation sequence performs first the AB-C separation (propylene and PO from heavier) in a simple column, which is connected to another simple column at the distillate stage. The second column carries out the propylene - PO separation.

Table 5 displays the energy consumption for the direct and the indirect separation sequences. It can be observed that between all the complex schemes described until now in this article, in case of the indirect separation sequence the heat exchangers duties (reboiler and condenser) are the smallest. Because the separation of propylene oxide from reaction mixture is an energy consuming process due to the great quantity of water in the mixture, and in case of indirect separation sequence the whole quantity of water from feed is removed at the bottom of the first column, this leads to a considerable reduction of the condenser and reboiler duties in the second column.

The proposed separation scheme (fig. 8) combines the advantages of the indirect separation sequences and Brugma distillation tower. This proposed scheme is the subject of a Romanian Patent [10]. In the proposed separation scheme, the combination of advantages of the indirect separation sequence (minimized energy consumption in the first tower, through water elimination as base product) with the benefits of Brugma Tower concept (avoiding the *remixing* effect in the feed zone of the column through the splitting of the feed stream into a vapor stream and a liquid stream, and placing these two streams into the column in the area where the vapor and liquid concentrations on the tray correspond to the concentrations of the liquid and vapor stream introduced in the column) applied in the second column of the proposed scheme, leads to more energy savings in terms of steam consumption. This proposed scheme was simulated rigorously (see the simulation scheme in fig. 9). The input data (composition and flowrate of the feed stream) are identical to those utilized for the eight complex schemes discussed above. At the top of the first column (saponification column) the vapors are partially condensed

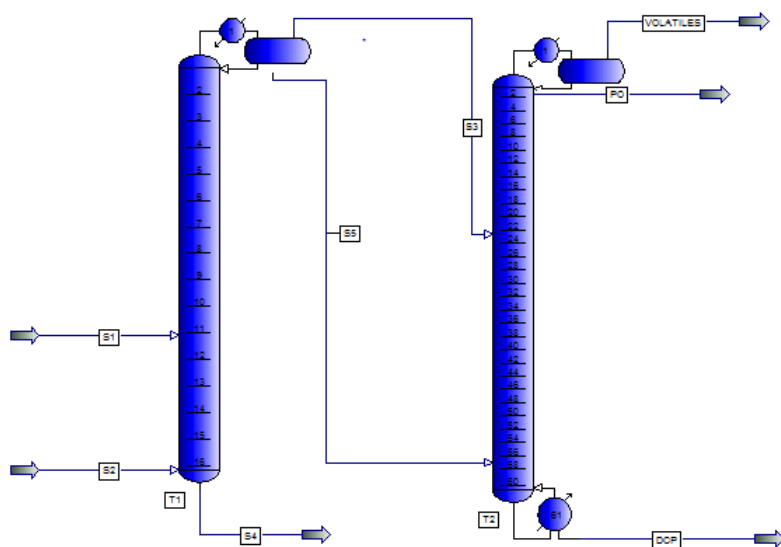


Fig. 9. Simulation scheme of the proposed separation installation for PO obtaining

Scheme type	Direct separation sequence		Indirect separation sequence	
	First column	Second Column	First column	Second Column
Parameter				
Number of trays	12	50	51	14
Condenser duty, MW	0.3150	3.237	2.431	0.02738
Reboiler duty, MW	0.4744	4.751	3.546	0.02722

Table 5
OPERATING PARAMETERS FOR
THE DIRECT SEPARATION
SEQUENCE AND INDIRECT
SEPARATION SEQUENCE

Stream	Product A	Product B	Product C
Composition (mass fraction)			
Propylene	0	$7.4124 \cdot 10^{-4}$	$7.0727 \cdot 10^{-8}$
Propylene oxide	0	0.9905	0.0213
Propionaldehyde	0	0	0
Acetone	0	0	0
1-Dichloro propane	0	$5.5046 \cdot 10^{-8}$	0.1252
Water	1	$8.8017 \cdot 10^{-3}$	0.8481
alpha-Epichlorohydrin	0	0	0
Dichloro diisopropylether	0	$1.4442 \cdot 10^{-15}$	$5.3663 \cdot 10^{-3}$
Number of trays	First column: 16 Second column: 61		
Condenser duty, MW	First column: 11.51 Second column: 2.11		
Reboiler duty, MW	First column: Steam injection: 8.2 t/h steam of low pressure Second column: 1.368		

Table 6
SIMULATION
RESULTS OF THE
PROPOSED SCHEME

Table 7
OPERATING COSTS FOR PO SEPARATION IN SYSTEMS OF COMPLEX DISTILLATION COLUMNS AND PROPOSED SEPARATION SCHEME

Scheme type	Indirect separation sequence	Direct separation sequence	Column with side stripper	Column with side rectifier	Dividing wall column	Petlyuk column	Column with prefractionator	Column with partially coupled prefractionator	Proposed Separation scheme
Expenditure									
Operating Cost, \$/year	$1.5 \cdot 10^6$	$2.25 \cdot 10^6$	$2.96 \cdot 10^6$	$4.03 \cdot 10^6$	$4.04 \cdot 10^6$	$4.04 \cdot 10^6$	$4.32 \cdot 10^6$	$5.54 \cdot 10^6$	$0.761 \cdot 10^6$

with air (the temperature in condenser is about 93°C). The resulted liquid feeds the second column (PO purification column) on tray 59, while the uncondensed vapor from the first tower are feeding the PO purification column on tray 23. The results of the simulation are displayed in table 6. It can be observed that while the specifications of the main product are preserved, this is achieved with less energy

consumption in the proposed scheme, if we take into account the reboiler and condenser duties resulted from the simulation of the proposed scheme, compared with all other separation sequences discussed previously. Table 7 displays the operating costs for all variants discussed above, calculated with the utilities prices estimated at the level of year 2015. The values of the operating costs reflect

that the proposed separation variant is far the best and cheap separation variant, leading to savings up to three quarters million US \$ per year, comparatively with the next cheaper separation variant (the indirect separation sequence).

Conclusions

The analysis of complex systems of columns for propylene oxide separation was accomplished and was compared with a proposed separation variant. The analysis of eight complex separation systems show that between all studied variants, the most convenient is the indirect separation variant, which for the thermal duties of condensers and reboilers of the two columns in the sequence are the smallest, but significantly greater than the thermal duties of the condenser and reboiler in case of the proposed variant. The costs analysis show that for the proposed variant, the operating cost is the smallest, this due, on the one hand to utilization of the air for the condensation of the vapor in the saponification unit, and, on the other hand, due to the utilization of a significant reduced quantity of steam in the bottom of the purification column.

References

1. GILLILAND, E. R, *Ind. Eng. Chem.*, **32**, 1940, p. 1220.
2. STRĂTULĂ, C., OPREA, F., ROIBU, C., PREOTEASA, V., BEJENARU, I., BALINT, GH., MOLDOVAN, N., Romania, Patent 116277B1, 2000, OSIM BOPI 12/2000.
3. STRĂTULĂ, C., ROIBU, C., PREOTEASA, V., ATANASOAI EI, I., BEJENARU, I., OPREA, F., MOLDOVAN, N., Romania, Patent 119883 B1, 2005, OSIM BOPI 5/2005.
4. REID, J. A., *PTQ*, **Q4**, 2000, pp. 85.
5. PETLYUK, F.B., PLATONOV, V.M., SLAVINSKII, D.M, *Int. Chem. Eng.*, **5**, no.3, 1965, p. 555.
6. FIDKOWSKI, Z., KROLIKOWSKI, L., *AIChE J.*, **32**, 4, 1986, p. 537.
7. FIDKOWSKI, Z., KROLIKOWSKI, L., *AIChE J.*, **33**, 4, 1987, p. 643.
8. SERRA I PRAT, M., Phd Thesys, Universitat Politecnica de Catalunya, Barcelona, 2000.
9. UNDERWOOD, A.J.V, *Chem Eng Progress*, **44**, 1948, p. 603.
10. OPREA, F FENDU E.M., NICOLAE, M., ROIBU, C., MOLDOVAN, N., ANDREI, L., ZARNOIANU, D., Romania, Patent 127017 A2, 2012, OSIM BOPI 1/2012.

Manuscript received: 24.06.2015