

## PROPENOXIDE PLANT ENERGY INTEGRATION

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### ABSTRACT

Propenoxide plant based on chlorohydrination of propene has two distillation columns: one of them is saponification column (at top of the column results a mixture of volatiles, Propenoxide, water, dichloropropane and another components in small amount) and another is the purification column where, at the top is obtained propenoxide with small amounts of volatiles, and at the bottom a residue.

The changing of the propenoxide specifications imposed a modification in configuration of the purification column. We proposed a modification that has two results: improve the quality of the propenoxide and reduce energy consumption by reducing of the reflux ratio. This solution, applied in 110000 tonnes/year propenoxide plant, brings a reduction of the energy consumption of 1 million euros/year.

The second step was to reduce energy consumption by energy integration of the two columns. There were proposed two solutions. First, the vapour from top of saponification column are not condensed, the vapour being introduced directly in the purification column, and a small amount of water is used as reflux. The second solution used a partial condensation of the vapour from the top of saponification column, vapour and liquid phases

being introduced in different zones of the purification column. The difference between the two solutions is given by the different cost of the vapour phase compressor for the different temperatures.

The second solution, applied in the same plant, bring a reduction of the energy consumption of 1.5 million euros/year.

The content of this paper is subject of two Romanian Patents (116277/1999 and 119883/2003) and a Romanian Patent Demand OSIM 2010-00634/21.07.2010. Patent 116277/1999 and Patent demand OSIM 2010-00634/21.07.2010 received two gold metal at International Invention Fair in Middle East, Kuwait City, November 2011.

### THE FIRST REVAMP (1999)

Propenoxide plant has three parts (Măcriș, 1997; Velea, 1990):

- reaction of the propene with a aqueous solution of chlorine;
- saponification with calcium hydroxide in a reactive distillation column;
- purification of bulk propenoxide in a distillation column.

In the figure 1 is presented the old configuration of the both columns (saponification and purification).

Beginning with 1999 the propenoxide product (18000 tonnes/year) did not accomplished the specification for selling. 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 propenoxide to 99.9% (old, 99.5%).

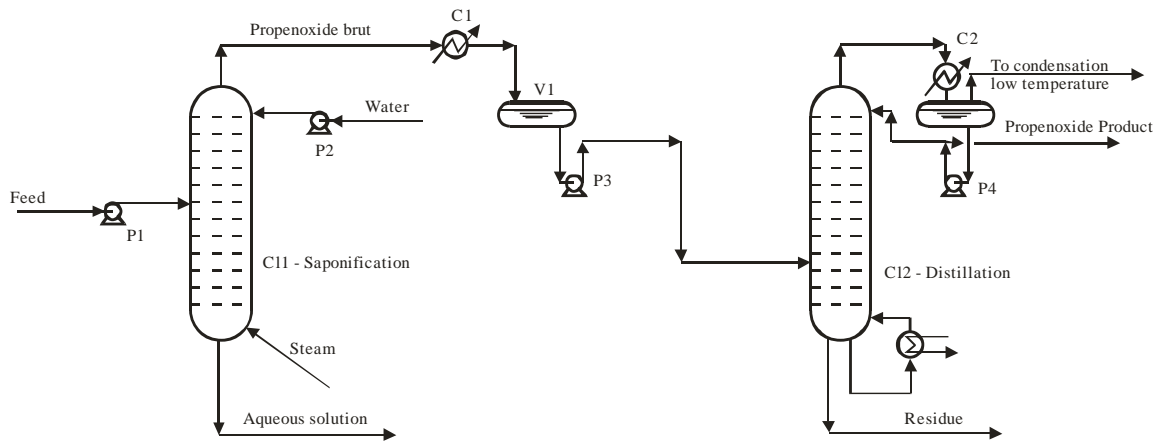


Fig. 1. Old process for propenoxide production (saponification and purification).

In order to maintain the plant on the market, the management decided to revamp the distillation/purification column. The adopted solution is the subject of Romanian Patent 116277/1999 (Strătuță, 1999). In the new configuration (see figure 2) the propenoxide product is not obtained as top product of the column, but as side product from the tray number 4 at the top. In this way the propenoxide product is not in equilibrium with vapour from top separator (volatile component as propylene), and the content of volatile components is reduced at the desired value.

The installation was simulated using PRO/II Simulator (Invensys Simulation Science, 1999) with respect of the next:

- the efficiency of the tray (valve tray) was obtained in the laboratory and has the value equal with 0.6;
- thermodynamic model was NRTL with completion of the lack binaries with UNIFAC;

- the influence of this is reduced because the lack binaries have small content in the streams;
- the model was verified and tuned for many cases from industrial operation considering: (1) profile of the flow rates, compositions of the streams, temperature and pressure; (2) flooding factor with respect of column configuration.

After the simulation of the column we decided also the modification of the feed tray (lower than initial situation, with influence on the reducing of water and aldehyde content in final propenoxide). The most important results of these modifications are:

- the content of volatiles is less than 30 ppmw;
- the water content is less than 10 ppmw;
- the aldehyde content is less than 20 ppmw;
- the purity of propenoxide product increased to 99.9%;

- the propenoxide loses in the vapour product from the top is reduced with more than 50%;
- the reflux ratio was reduced with 27% and this allowed the increasing of the capacity of the column to 23000 tonnes/year propenoxide production, with the same heat consumption (steam) at the bottom of the column;

- also, the condenser duty remain almost the same.

In the table 1 are presented the data about simulation of the distillation column in the two situations: (1) before and (2) after first revamp.

Table 1 Data about the simulation of the distillation column in the two situations: (1) before and (2) after first revamp

	Before first revamp (1999)	After first revamp (1999)
Number of theoretical trays	68+2	68+2
Number of the feed tray	34+1	45+1
Number of the side draw product	-	3+1
Flow rate of the feed, kg/h	3338	4265
Flow rate of the top (vapour), kg/h	100	30
Flow rate of the top (liquid) - PO, kg/h	2258	-
Flow rate of the side product - PO, kg/h	-	2875
Flow rate of the bottom product, kg/h	980	1360
Flow rate of the reflux, kg/h	15806	20030
Volatile content in PO product, ppm	2500 - 3500	<30
Water content in PO product, ppm	100	<50
Aldehyde content, ppm	100	20
PO product purity, % w	99.5	99.9
Condenser duty, MW	3.65	3.720
Reboiler duty, MW	3.87	3.910

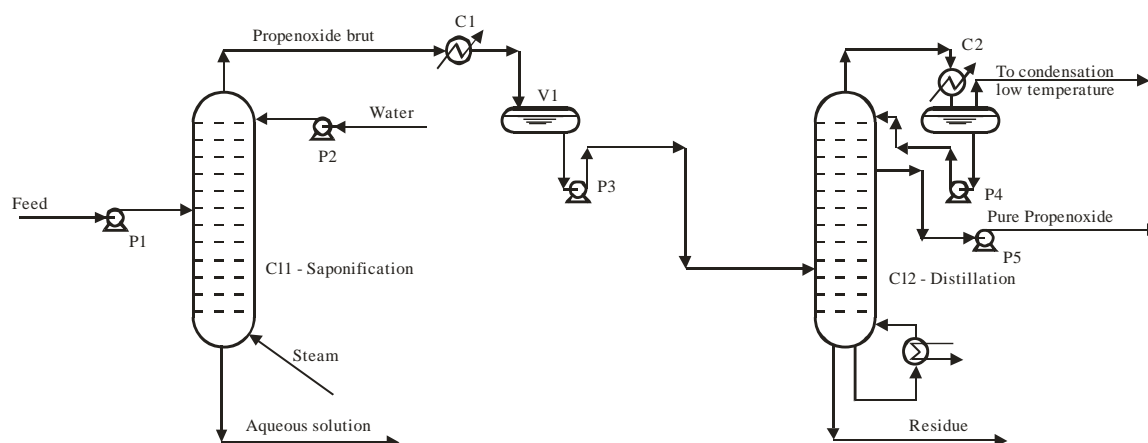


Fig. 2. New process (according with Romanian Patent 116277/1999 ) for propenoxide production (saponification and purification).

More, in the next years, the capacity of the plant increased to 110000 tonnes/year (adding new reactors, saponification and distillation columns). As result of all of these improvements the profit of the

plant increased with about 1 million euro/year. In the future the management of the plant decided to increase the capacity to 160000 tonnes/year.

## THE SECOND REVAMP (PROPOSAL 2003)

Concerning the operation of the saponification column there are some disadvantages:

- the top vapour are condensed, the heat is removed with cooling water at low level of temperature and lost;
- this heat must be supply in the second column for purification of bulk propenoxide;
- condensation need equipment (condenser, drum separator and pump) and water for cooling.

One of the proposed variants is those from Patent RO 115443/1998 (Ioniță, 1998). This solution is using a cooling with an interior bundle of tubes. This solution has important disadvantages:

- heat transfer area is low;
- the process can not properly controlled, also because reflux ratio is low;
- reflux ratio control is difficult.

Another Romanian Patent (119883/2003 – see figure 3) stipulate that all the vapour from the top of saponification tower will directly feed the second column. But this solution was not applied at industrial level, remaining only a proposal. The reasons to give up were:

- the pressure at the top of the saponification tower is low and the vapour have not enough pressure to feed the distillation/purification column;
- this enforced to build another columns in order to respect regulations for exploitation of vessels under pressure, with considerable increased of the investments costs;
- using of a turbo blower is inadequate because the price is high (considering corrosiveness and the temperature of the stream) and asked a partial condensation in order to reduce temperature, so that the temperature after compression does not increase too much.

Considering these reasons the management gave up this solution.

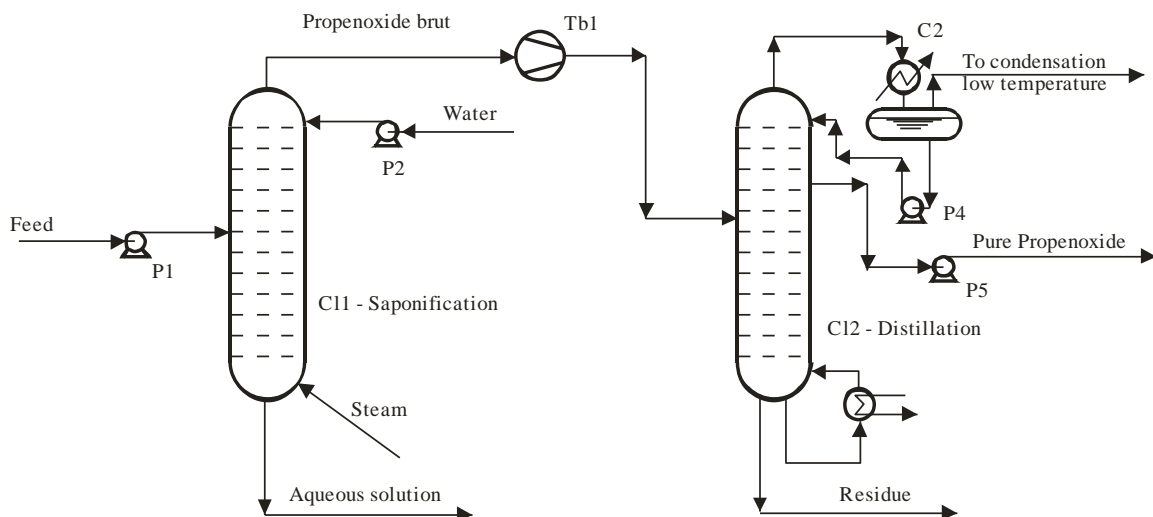


Fig. 3. Flow sheet for Romanian Patent 119883/2003.

## THE THIRD REVAMP (2011 PROPOSAL)

The ultimate solution (Oprea, 2010) is to use a partial condensation of the top vapour of the saponification column (vapour with 30-40% propenoxide, 90-100°C and 1.0 – 1.3 bars) at 55 – 70°C (most likely 60%). After separation of the mixed streams:

- the vapour stream feeds the second column (using a turbo blower) on a tray somewhere at the top of the rectification section;
- the liquid stream (using a pump) feed the second column on a tray somewhere at the bottom of the rectification section. For the saponification column the reflux is a small stream of water. This solution is presented in the figure 4.

The advantages of this solution are:

- using partial condensation, a part of the heat of the vapour stream is recovery, steam consumption of the second column reboiler is reduced with more than 0%;
- cooling water consumption for saponification column is reduced with 60%;
- investment cost is low; turbo blower price is 60% of the turbo blower used for the case of figure 3; the cost of the turbo blower will be retrieved in about half year from the obtained profit;
- existing equipment (condenser, separator, pumps) are used with nonessential modifications;
- the most important advantage is for the second column: every feed is introduced on optimal feed tray, in such way the reflux ratio is reduced with 10%; consequently;

- this reduction can have two results: (1) reducing the cooling water and steam consumptions for the same capacity; (2) increasing capacity for the same water and steam consumption;
- the operation of the columns is more resilient.

For 110 000 tonnes/year capacity the reduction of operation cost is about 1.5 million euros/year.

In the table 2 are presented the simulation data about distillation column after the third revamp.

For the next year the managements intend to increased capacity of the plant till 160 000 tonnes/year. In this way the profit will increased to 2.18 million euros/year.

## References

Invensys Simulation Science, Reference manual, 1999 and next;

Ioniță, C., e.a. , Romanian Patent 115443/1998.

Măcriș, V., Ingineria derivaților etilenei și propilenei. Derivații propilenei, vol.2, Editura tehnică, București, 1997.

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Strățulă, C., e.a., Romanian Patent 116277/1999.

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Velea, I., Ivănuș, Gh., Monomeri de sinteză, vol.2, Editura tehnică, București, 1990.

Table 2. The simulation data about distillation column after the third revamp.

	Before the third revamp (2010)	After the third revamp (2010)
Number of theoretical trays	68+2	36+2
Number of the feed tray (vapour)	-	29+1
Number of the feed tray (liquid)	45+1	45+1
Number of the side draw product tray	3+1	3+1
Flow rate of the vapour feed, kg/h	-	2406
Flow rate of the liquid feed, kg/h	4265	1859
Flow rate of the top (vapour), kg/h	30	20
Flow rate of the side product - PO, kg/h	2875	2880
Flow rate of the bottom product, kg/h	1360	1365
Flow rate of the reflux, kg/h	20030	19270
Volatile content in PO product, ppm	<30	<25
Water content in PO product, ppm	<50	<30
Aldehyde content, ppm	20	<15
PO product purity, % w	99.9	99.9
Condenser duty, MW	3.720	3.500
Reboiler duty, MW	3.910	2.650

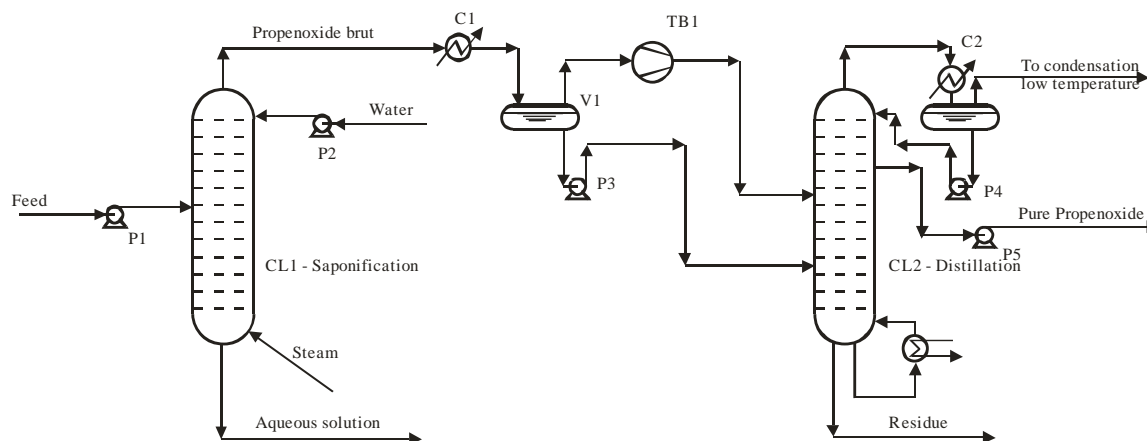


Fig. 4. Flow sheet for Romanian Patent Demand OSIM 2010-00634/21.07.2010.