LIST OF MAIN WORKS – PATENTS, PUBLISHED AND CONFERENCE PAPERS

DIPLOMA WORK – LINEAR PROGRAMMING IN 0 AND 1 FOR SYTHESIS OF HEAT EXCHANGE NETWORKS - JULY 1980

DOCTORATE THESIS – SEPARATION OF AZEOTROPIC MIXTURE – FEBRUARY 1999

Proposal for a new azeotropic distillation process for separation of the azeotrope cumene - phenol using a common entrainer. The entrainer forms two new azeotropes (water – cumene and water-phenol) but more easier to separate than initial one. In the thesis were done:

- experimentals concerning liquid-vapor equilibrium;
- modeling, simulation and optimisation of the new process;
- experimentals on an lab column Sulzer packing (continuous operation) concerning separation cumene–phenol using azeotropic distillation with water, comparison with simulation;

The new process is object of a Romanian Patent *Process for phenol separation from mixture with cumene and alpha methyl styrene* (120067 B1/2000), already applied in industry.

THE MOST IMPORTANT PATENTS, PAPERS AND INDUSTRIAL REVAMPING (with short presentations)

PATENTS and INDUSTRIAL PLANT REVAMP

I am couathor of 19 Romanian Patents, 12 of them already applied, another 6 patent demand are in examination process. The most important are:

1. *Volatile Removal from Propenoxide,* Romanian Patent 116277 B1/1999 and revamp

Awarded with Gold medal – International Invention Fair in Middle East, Kuwait City, November 2011.

Propenoxide plant has three parts:

- 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.

Beginning with 1999 the propenoxide product 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 incresed the purity of propenoxide to 99.9% (old, 99.5%).

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. In the new configuration the propenoxide product is not obtained as top product of the column, but as side product from the tray number 4 at the top, and, 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 vapor 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 with the same heat consumption (steam) at the bottom of the column;
- also, the condenser duty remain almost the same.

As result of all of these improvements, the profit of the propenoxide plant increased with about 1 million euro/year.

2. ***New Process for Propenoxide Separation*****, Romanian Patent 127017/2010 and revamp**

Awarded with Gold medal – International Invention Fair in Middle East, Kuwait City, November 2011

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

- the vapor 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.

The advantages of this solution are:

- using partial condensation, a part of the heat of the vapor 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; the cost of the turboblower will be retrived in about half year from the obtained profit;
- existing equipments (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.

Reduction of operation cost is about 1.5 million euros/year for actual capacity and about 2.18 million euro/year for the new incresed capacity of the propenoxide plant.

3. ***Process and Installation for the treatment and removal of used alkaline solutions from Merox and Exomer Unit*****,**

- patent demand OSIM A/00358/2010 and revamp

Awarded with Gold medal – International Invention Fair in Middle East, Kuwait City, November 2011

- already industrial applied in one Romanian refinery.

The new process proposes integrated treatment and removal of both used alkaline solutions (from Merox unit and from Exomer unit). After neutralization, dillution and oxidation the solutions are removed at waste water treatment plant without any influence.

The advantages of this process are:

- the proposed technology was proved at laboratory scale;
- all effluents were analyzed according maximum allowable levels;
- the values of the concentration of contaminants in resulted streams are below the limits allowed by maximum allowable levels at the entrance in wastewater treatment unit;
- in the process doesn't result any gaseous or solid streams with pollution potential;
- the technology ensure that the contaminants remain in the aqueous phase under maximum allowable levels to entry in the water treatment station;
- from this technology does not result new or unknown compounds who can charge water treatment station;

- the technology do not appeal to processes that take place at high temperatures and pressures, does not consume energy in pumping out power to the determination of dilution and neutralization
- the technology does not require use of a highly qualified personnel;
- the technology is simple, safe, easy to control, operating costs are reduced;
- the technology is safe in operation, any trouble shootings can not cause pollution of the environment;
- the technology ensure both current and accumulated alkaline solutions discharge;
- from this technology does not result any hazardous wastes;
- the technology provides the reuse of the acid solution from the EXOMER unit to neutralize soda from Merox unit.

4. ***Production of Anhydrous Ethanol Using Azeotropic Distillation with Petroleum Cuts or Gasoline Pool*****, Romanian patent demand, 2013**

Also published in Revista de chimie, ISSN 0034-7752, pp 231-242, vol. 59, nr. 2, februarie 2008

The main goal of this study is to demonstrate that the leaving in bottom product of azeotropic distillation column, alcohol product, of certain amount of entrainer leads to lower heat consumptions. The increasing the entrainer content (in the bottom product of the column) decreases specific duties of reboiler (heat consumption reported to ethanol product flow rate). The difference between extreme cases (0.1 % and 5% weight entrainer in alcohol product) is important, from 5.43% for 2-methyl pentane to 12.71% for 3-methyl hexane. Almost the same ratio is for condenser duty too. This is a very important conclusion. So:

- leaving some entrainer in ethanol product decrease specific heat duty with important energy saving;

- the presence of entrainer do not affect the quality of ethanol that is used for adding in gasoline; contrary, the presence of certain quantities of some entrainers (like iso-paraffins and aromatics) bring an important contribution to octane number of gasoline. Any way, those entrainer are finally present in gasoline and does not matter if they are coming in gasoline with gasoline components or with ethanol;

- these entrainers are easy to find in refineries, especially iso-pentane and iso-hexane which are present in isomerizate (in some cases only iso-pentane, in the other cases both);

- this solution is easy to realize and does not bring important supplementary costs.

Finally, like entrainer could be used different petroleum cuts or gasoline pool that are presented in trade gasoline. For example, using the isomerizate (i-pentane and i-hexane) has proportional performances reported to both components. The availability of such entrainer in refineries is an clear advantage.

5. ***Recovery of octanols from residual octanols fraction obtained in plasticizers fabrication,***

- patent demand OSIM 2011-00081/2011 **and revamp**
- already industrial applied in a Romanian petrochemical plant.

The residual octanols fraction from platicizers fabrication are incinerated. The octanols from this fraction are recovered using some existing column in octanols plant. The results are:

- reducing of the specific consumption of octanol in platicizers fabrication;
- improvement of the operation of the excisting octanol plant;
- minimal investment cost.

6. ***Process for Propane Separation*****, Romanian patent 115531 B1/2000,**

- already industrial applied
- total plant products value - 20 millions euro/year

The new process proposed an injection of heavy fractions at the top of de-ethanizer column in order to increase the partial condensation temperature. In this way no refrigerant is used for condensation at the top of de-ethanizer column.

7. *1,2 dichloropropane recovery from propenoxide residue, Romanian patent 117252 B1/1999,*

Awarded 2003 Prize for Chemical Engineering from General Asociation of Romanian Engineers.

- already industrial applied in a Romanian petrochemical plant **(1.5 million euro/year profit);**

In the residue from propenoxide plant (this was incinerated before this patent) is present 1,2 dichloropropane.

The patent proposed a process for separation of 1,2 dichloropropane. The results were:

- reducing of the incinerated quantities with environmental impact;
- obtaining of a valuable product with low investment and operation cost the installation is very versatile and can be feeded with diferent raw material.

***8. Mechanical filter for oil/water mixtures,* Romanian patent 120400 B1/1998,**

- already industrial applied in a Romanian refinery (bitumen plant for wastewater separation and in a storage facilities for rain water)

The patent proposed a simple mechanical filter for separation of the mixtures water – oil products without energy consumption.

9. *Treatment and removal of residue gases from underground burning of liquids and solids,* Romanian patent 116348 B1/1994

The patent proposed a complex treatment of the residue gas from underground combustion of the oil. The experimental installation was used in a Romanian oil field.

10. *Process and installation for desulphurisation of liquid C_3-C_4 fraction from FCC plant,* Romanian patent 112636 B1/1997

The patent proposed a versatile process for desulphurisation of liquid C_3-C_4 fraction from FCC plant.

The process is already used in two Romanian refineries.

SELECTED PAPERS IN JOURNALS

19 – Fendu, E. M., F. Oprea, *Vapor–liquid equilibrium for propylene glycols binary systems: Experimental data and regression*, dx.doi.org/10.1016/j.fluid.2014.09.015, Fluid Phase Equilibria 382 (2014) 244–253

18 - Nicolae, M., F. Oprea, *Vapor–liquid equilibrium for the binary mixtures of dipropylene glycol with aromatic hydrocarbons: Experimental and regression*, dx.doi.org/10.1016/j.fluid.2014.03.003, Fluid Phase Equilibria 370 (2014) 34–42

17 – Fendu, E. M., F. Oprea, *Vapor−Liquid Equilibria for Water + Propylene Glycols Binary Systems: Experimental Data and Regression*, dx.doi.org/10.1021/je4009014, J. Chem. Eng. Data 2014, 59, 792−801

16 – Fendu, E. M., F. Oprea, *Vapor Pressure, Density, Viscosity, and Surface Tension of Tetrapropylene Glycol*, dx.doi.org/10.1021/je4004977, *J. Chem. Eng. Data*, 2013, *58* (11), pp 2898–2903

15 – Nicolae, M., F. Oprea, *Liquid−Liquid Equilibria for Dipropylene Glycol−Hydrocarbon Binary Systems: Experimental Data and Regression*, dx.doi.org/10.1021/je3009039, J. Chem. Eng. Data 2012, 57 (12), pp 3690−3695

14 – F. Oprea, ş.a., *New Process for Treatment and Removal of the Spent caustic Solutions from Refineries*, Revista de chimie, ISSN 0034-7752, vol. 61, nr. 6, iunie 2010

13 - F. Oprea, I. Stoica, *Production of Anhydrous Ethanol Using Azeotropic Distillation with Petroleum Cuts or Gasoline Pool*, Revista de chimie, ISSN 0034-7752, pp 231-242, vol. 59, nr. 2, februarie 2008

12 - C. Strătulă, F. Oprea, D. Mihăescu, *Anhidrizarea alcoolului etilic prin fracţionarea azeotropă utilizând un nou antrenant (Ethanol Anhydrization using Azeotrope Distillation with new Entrainer),* Revista de chimie, ISSN 0034-7752, pp 988-996, vol. 56, nr. 5, mai 2005

11 - C. Strătulă, F. Oprea, *Unele aspecte privind influenţa umidităţii gazelor naturale asupra preciziei măsurării comerciale a debitelor (The Influene of the Water Content of the Gas on Flowrate Measuring* , Revista de chimie, ISSN 0034-7752, pp 988-996, vol. 54, nr. 12, decembrie 2003

10 - C. Strătulă, Gh. Duca, F. Oprea, *Recuperarea solvenţilor în procesul de solventare a motorinei (Solvent recovery in Diesel Oil Solvent Extraction)*, Revista de chimie, ISSN 0034-7752, pp 632-637, vol. 54, nr. 7, iulie 2003 – **Awarded - Best Paper Published in Revista de chimie 2003.**

9 - Strătulă, C., Oprea, F., Mihaela Petre, *Diesel Oil Drying*, Revista de chimie, ISSN 0034-7752, English edition, nr. 1-2, vol 1, 2000.

8 - Strătulă, C., Oprea, F., Bejenariu, I., *Procedeu de recuperare a 1,2 diclorpropanului din reziduul de la fabricarea propenoxidului din propilenclorhidrină, Process for 1,2 dichloropropane recovery from propenoxide residues*, Revista de chimie, ISSN 0034-7752, nr.12, vol. 51, 2000.

7 - Strătulă C, Oprea, F., *Studiul eliminării mercaptanilor din fracţia lichidă de C_3-C_4, Mercaptans Removal from C_3-C_4 liquid fraction* , Revista de chimie, ISSN 0034-7752, vol. 51, nr. 5, 2000.

6 - Oprea, F., Strătulă, C., Petre, M., *Studiul uscării motorinelor prin vaporizare la echilibru în vacuum. III. Modelul matematic simplificat pentru calculul uscării motorinelor prin vaporizare la echilibru în vacuum*, Revista de chimie, ISSN 0034-7752, vol. 50 nr. 9 1999.

5 - Oprea, F., Strătulă, C., Petre, M., *Studiul uscării motorinelor prin vaporizare la echilibru în vacuum. II. Determinări experimentale necesare la calculul uscării motorinelo prin vaporizare la echilibru în vacuum*, Revista de chimie, ISSN 0034-7752, vol. 50, nr. 8, 1999.

4 - Strătulă, C., Oprea, F., Petre, M., *Studiul uscării motorinelor prin vaporizare la echilibru în vacuum. I. Unele consideraţii teoretice şi practice privind uscarea motorinelor*, Revista de chimie, ISSN 0034-7752, vol. 50, nr. 7, 1999.

3 - C. Strătulă, F. Oprea - *Consideraţii privind calculul gradului de umplere a recipientelor cu gaze lichefiate*, Revista de chimie, ISSN 0034-7752, vol. 48, nr. 5, 1997.

2 - C. Strătulă, I. Cheţa, T. Mihai, F. Oprea - *Studiul comparativ al purificării caprolactamei cu doi solvenţi. II. Studiul echilibrului lichid-vapori, Revista de chimie*, ISSN 0034-7752, 43, 9, septembrie 1992.

1 - C. Strătulă, I. Cheţa, T. Mihai, F. Oprea - *Studiul comparativ al purificării caprolactamei cu doi solvenţi. I. Studiul echilibrului lichid-lichid, Revista de chimie*, ISSN 0034-7752, 43, 7, iulie 1992.

Florin Oprea
January 2016