STUDIA UNIVERSITATIS BABEȘ-BOLYAI, CHEMIA, XLVII, 1-2, 2002

Dedicated to Professor Ionel Haiduc
on the occasion of his 65th birthday

MODELING AND SIMULATION OF 3-AMINOPROPIONITRILE SYNTHESIS USING DEDICATED SOFTWARE PACKAGES

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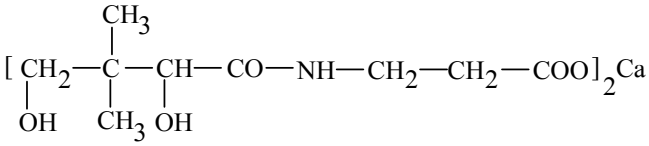
ABSTRACT. Calcium pantothenate is one of the most used pro-vitamins in the therapy for human beings and for veterinary use. In the synthesis of D,L calcium panthotenate, pantolactone and β-alanine are used as starting materials. β-Alanine is obtained from alkaline hydrolysis of 3-aminopropionitrile. The synthesis of 3-aminopropionitrile involves the addition of ammonia at acrylonitrile at high temperature and pressure.

In this paper the continuous synthesis of 3-aminopropionitrile is described. The synthesis takes place at temperature (100 – 120°C) and pressure (15 – 20 atm). Secondary products can be formed; to avoid this fact a high molar ratio between reactants (ammonia / acrylonitrile = 10 / 1) is used. The synthesis process was modeled and simulated using HYSYS Plant, PRO/II and ChemCAD software packages to demonstrate the reliability of the packages and their performances. From simulation results very valuable information can be obtained regarding real plant operation.

1. INTRODUCTION

Calcium pantothenate is one of the most used pro-vitamins in the therapy for the human beings and for the veterinary use. Pantothenic acid is a vitamin from the complex of vitamins B; it plays an important role in the metabolism [1] (its biological active form is Coenzyme A). The chemical formula of calcium pantothenate is presented below:

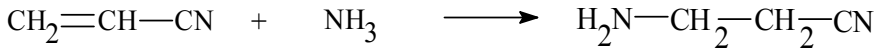


The synthesis of D,L calcium pantothenate is a complex process. The synthesis involves three major steps [2]: the first step is the manufacture of pantolactone (α-hydroxy-β,β-dimethyl-γ-butyrolactone), the second step consists of the manufacture of sodium β-alaninate and in the final step of the synthesis these intermediates are coupled resulting the target product.

One of the intermediates, sodium β-alaninate, is obtained from alkaline hydrolysis of 3-aminopropionitrile. 3-Aminopropionitrile can be obtained from addition reaction of acrylonitrile and ammonia at high temperature (100 – 120°C) and pressure (15 – 20 atm) using high molar ratio between reactants (acrylonitrile / ammonia = 1 / 10) [3, 4, 5].

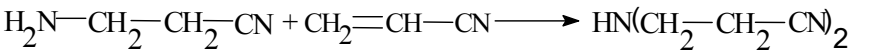
In this paper, the continuous synthesis of 3-aminopropionitrile is described. The chemical reactions are presented below:

(i) Main reaction:

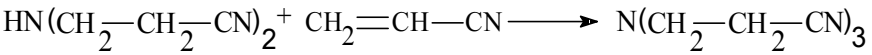


Acrylonitrile — Ammonia — 3-Aminopropionitrile (beta-Aminopropionitrile)

(ii) Secondary reactions:



3-Aminopropionitrile (beta-Aminopropionitrile) — Acrylonitrile — 3,3'-Iminodipropionitrile (bis-(beta-cyanoethyl)-amine)



3,3'-Iminodipropionitrile (bis-(beta-cyanoethyl)-amine) — Acrylonitrile — 3,3',3"-Nitrilotripropionitrile (tris-(beta-cyanoethyl)-amine)

The continuous synthesis of 3-aminopropionitrile involves the following steps. The raw materials, acrylonitrile and a solution of ammonia are introduced in the process using two dispensing pumps (output pressure 15 atm). Ammonia solution stream is heated at about 105 - 110°C and mixed with acrylonitrile stream. The mixture of the reactants is introduced in a Plug Flow Reactor (PFR) where the chemical reactions take place. Because of the secondary reactions, a high molar ammonia excess is used (acrylonitrile / ammonia = 1 / 10). The synthesis process is exothermic. The reaction heats are the following: the first reaction ΔH_{r1} = -45.76 kJ/mole, the second reaction ΔH_{r2} = -60.815 kJ/mole and the third reaction ΔH_{r3} = -79.871 kJ/mole. Temperature of the outlet stream is about 100 – 120°C. Because of high ammonia excess the product stream must be processed in order to recycle ammonia. The reactor outlet stream is depressurised at 2 atm and the gaseous phase resulted is separated from liquid phase using a flash unit. The liquid phase, containing 3-aminopropionitrile, is fed to a desorbtion column when the rest of ammonia from the product stream is removed. The gaseous phases, containing ammonia, resulted from flash unit and from desorption column are mixed and cooled. The resulted stream is fed to a flash unit where a phase separation takes place. The liquid phase (containing a small quantity of 3-aminopropionitrile) is recycled to desorption

column. The gaseous phase, containing ammonia, is sent to an absorption column where gaseous ammonia is absorbed in water. Ammonia solution resulted from absorption column is recycled in the process. 3-Aminopropionitrile stream resulted at the bottom of desorption column is sent to alkaline hydrolysis in order to obtain sodium β-alaninate.

2. MODELING AND SIMULATION OF THE SYNTHESIS

The continuous synthesis of 3-aminopropionitrile can be modeled and simulated using a CAD software package for chemical processes. In this case HYSYS Plant, PRO/II and ChemCAD were used. These software packages use flowsheet modeling environment techniques. One of the purposes of the work was to establish how reliable the simulation software packages are and if the results are comparable.

The parameters of the model are presented below:

- Dispensing pumps (for ammonium solution and acrylonitrile streams)
  - Output pressure: 15 atm
- Heat exchanger for ammonia solution
  - Output temperature: 105 - 110°C
- Synthesis reactor (Plug Flow Reactor)
  - Length of tube: 140 m
  - Diameter of tube: 0.04 m
  - Number of tube: 1
  - Reaction temperature: 100 – 120°C
  - Pressure: 15 atm
  - Molar ratio between reactants: acrylonitrile / ammonia = 1 / 10
  - Heat of reactions: Reaction 1: ΔH_{r1} = -45.76 kJ/mole
    Reaction 2: ΔH_{r2} = -60.815 kJ/mole
    Reaction 3: ΔH_{r3} = -79.871 kJ/mole
  - Kinetic data: Reaction 1: Rate = $k_1 C_{NH3} C_{Acryilonitrile}$
    Reaction 2: Rate = $k_2 C_{3\text{-}Aminopropionitrile} C_{Acryilonitrile}$
    Reaction 3: Rate = $k_3 C_{3,3'\text{-}Iminodipropionitrile} C_{Acryilonitrile}$
  - Contact time: 2 – 5 min
- Lamination (depressurise) valve
  - Output pressure: 2 atm
- Flash units
  - Use inlet temperature and pressure
- Desorbtion column
  - Number of trays: 6
  - Top pressure: 1.6 atm
  - Bottom pressure: 2 atm
  - Recovery of 3-aminopropionitrile (bottom): 99 %
- Heat exchanger for gaseous phase
  - Output temperature: 25°C
- Absorption column
  - Number of trays: 6
  - Top pressure: 2 atm

Bottom pressure: 2.5 atm
Side cooler: tray 3
Heat duty for side cooler: -200 MJ/h
Recovery of ammonia (bottom): 99.9 %

For 3-aminopropionitrile synthesis the flowsheet is presented below (using ChemCAD and HYSYS Plant software packages).

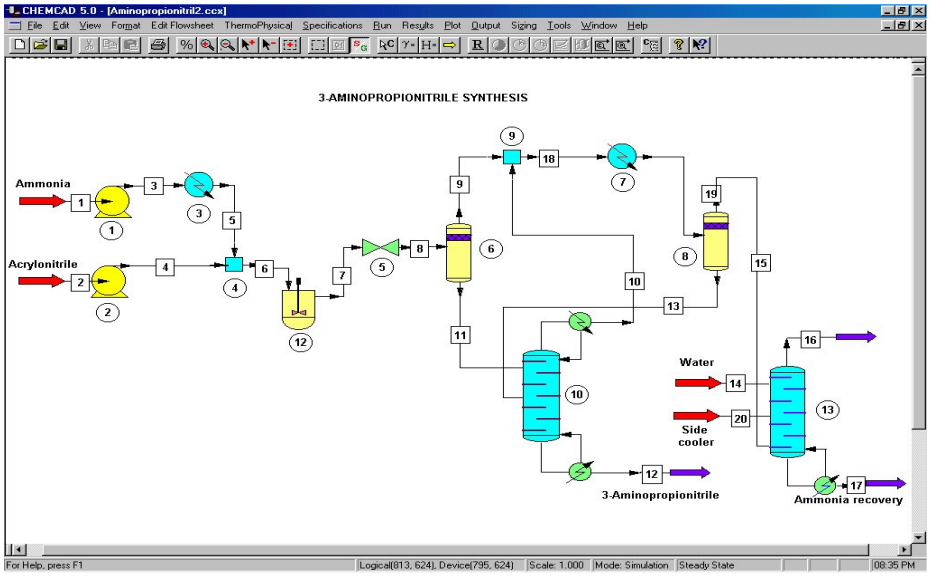


Figure 1. Simulation of 3-aminopropionitrile synthesis using ChemCAD

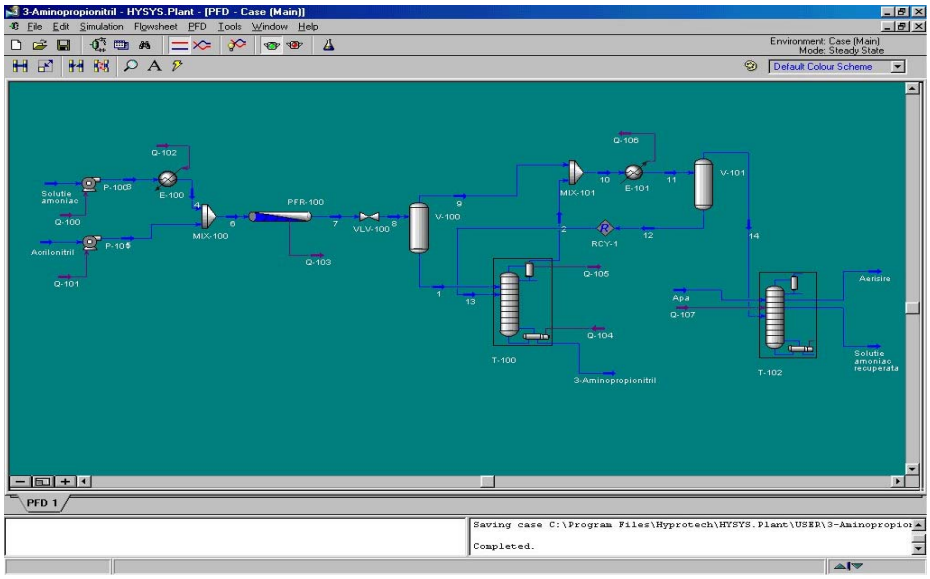


Figure 2. Simulation of 3-aminopropionitrile synthesis using HYSYS Plant

3. RESULTS AND DISCUSSIONS

The synthesis process of 3-aminopropionitrile was simulated using parameters described above. The process was simulated using PRO/II, ChemCAD and HYSYS Plant. The results obtained from simulation using these three simulation software packages are very similar.

For the synthesis reactor, the variation of the composition (molar fractions) for the reaction mass insight the Plug Flow Reactor (PFR) are presented below. Because of the high ammonia ratio the main reaction yield is about 75 – 80 %, the second reaction yield is about 20 - 25 % and the third reaction doesn't practically take place (yield small than 1 %).

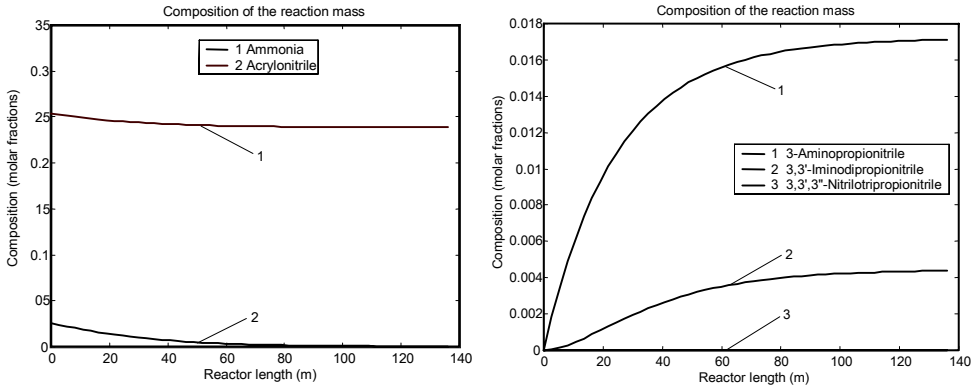


Figure 3. Composition (molar fractions) for reaction mass insight of PFR

For desorption and absorption columns below are represented temperature, liquid and vapour rates for each tray. These simulation results are similar using different software packages (PRO/II, ChemCAD and HYSYS Plant).

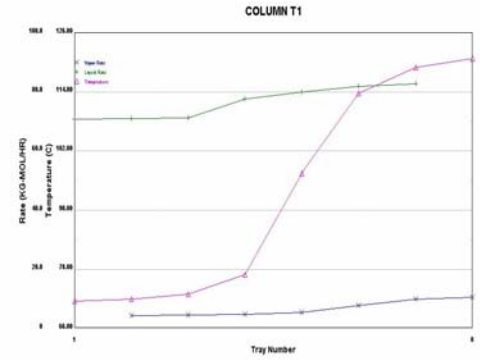


Figure 4. Desorption column

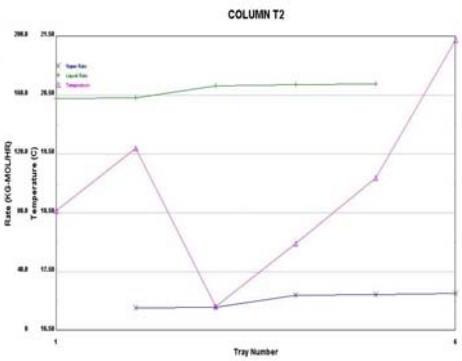


Figure 5. Absorption column

Calculated heat duties for different units of the plant are similar using PRO/II, ChemCAD and HYSYS Plant. For example, heat exchanger for heating ammonia solution has a duty about 600 MJ/h. For desorption column the reboiler duty is about 450 MJ/h. For absorption column heat duty for cooling ammonia solution is about –360 MJ/h and heat duty for side cooler is –200 MJ/h.

The model of the 3-aminopropionitrile synthesis can be used for sensitivity analysis. For example, the production of the plant (dependent variable) can be analyzed for different molar ratio between reactants (independent variable). A sensitivity study, realized using ChemCAD, is presented below (variation of the three products flows vs. ammonia solution flow).

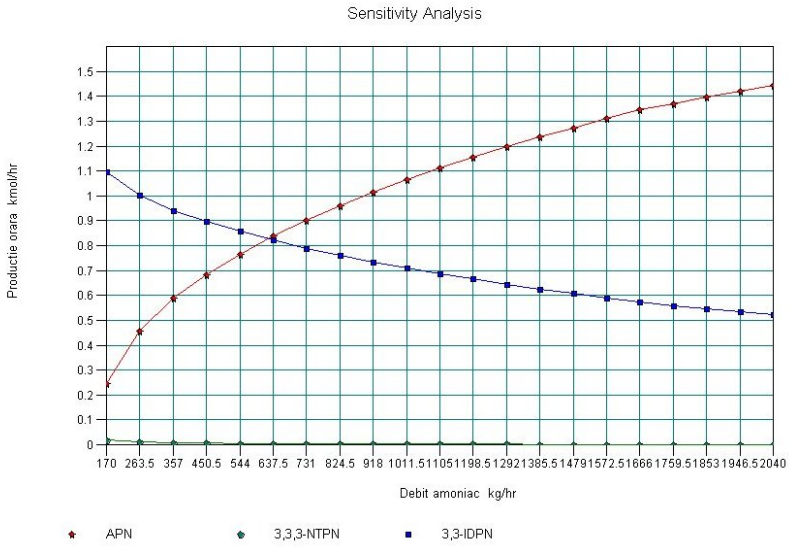


Figure 6. Variation of products flows vs. ammonia solution flow

4. CONCLUSIONS

In this paper the continuous synthesis of 3-aminopropionitrile has been described. The synthesis process was modeled and simulated using HYSYS Plant, PRO/II and ChemCAD software packages. The results obtained from simulation using these three simulation software packages are similar.

The model proved to be a reliable tool for analyzing this chemical process. Using the model of the synthesis process and the simulation results (for different conditions) very valuable information can be obtained for the real plant operation. Sensitivity studies can be made in order to analyze the influence of different factors (independent variables) on the process outputs (dependent variables).

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