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MODELING AND SIMULATION OF SODIUM BETA-ALANINATE SYNTHESIS

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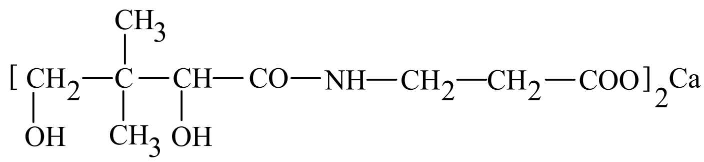
ABSTRACT

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 sodium beta-alaninate has been described. The synthesis takes place at temperature (100 – 120°C) and pressure (15 – 20 atm). Secondary products can be formed, to avoid that a high molar ratio between reactants (ammonia / acrylonitrile = 10 / 1) is used. The synthesis process was modelled and simulated using HYSYS Plant, PRO/II and ChemCAD software packages. From simulation results very valuable information can be obtained regarding real plant operation.

KEY WORDS: Modeling, simulation, sodium beta-alaninate

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 intermediaries are coupled resulting the final product.

One of the intermediaries, 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 sodium beta-alaninate has been described. The chemical reactions are presented below [3]:

- Main reactions:

$$\underset{\text{Acrylonitrile}}{CH_2{=}CH{-}CN} + \underset{\text{Ammonia}}{NH_3} \longrightarrow \underset{\text{3-Aminopropionitrile}}{H_2N{-}CH_2{-}CH_2{-}CN} \tag{1}$$

$$\underset{\text{3-Aminopropionitrile}}{H_2N{-}CH_2{-}CH_2{-}CN} + NaOH \xrightarrow{+\,H_2O} \underset{\text{Sodium beta-alaninate}}{H_2N{-}CH_2{-}CH_2{-}COONa} + NH_3 \tag{2}$$

- Secondary reactions:

$$H_2N{-}CH_2{-}CH_2{-}CN + CH_2{=}CH{-}CN \longrightarrow HN(CH_2{-}CH_2{-}CN)_2 \tag{3}$$

$$HN(CH_2{-}CH_2{-}CN)_2 + CH_2{=}CH{-}CN \longrightarrow N(CH_2{-}CH_2{-}CN)_3 \tag{4}$$

$$HN(CH_2{-}CH_2{-}CN)_2 + 2NaOH \xrightarrow{+\,2H_2O} HN(CH_2{-}CH_2{-}COONa)_2 + 2NH_3 \tag{5}$$

$$N(CH_2{-}CH_2{-}CN)_3 + 3NaOH \xrightarrow{+\,3H_2O} N(CH_2{-}CH_2{-}COONa)_3 + 3NH_3 \tag{6}$$

The continuous synthesis of sodium beta-alaninate involves the following steps. The raw materials, acrylonitrile and a solution of ammonia are introduced in the process using two dosing 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 (1), (3) and (4) 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 following, the first reaction ΔH_r= -45.76 kJ/mole, the third reaction ΔH_r= -60.815 kJ/mole and the fourth reaction ΔH_r= -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 recycled ammonia. The reactor outlet stream is depressurised at 2 atm and an aqueous solution of sodium hydroxide is added in order to hydrolyse 3-aminopropionitrile. Gaseous phase resulted is separated from liquid phase using a flash unit. The liquid phase is fed to a desorbtion column where the hydrolyse reactions (2), (5) and (6) take places and where the excess of ammonia from the stream is removed. The hydrolyse process of 3-aminopropionitrile is exothermic. The reaction heats are following, the second reaction ΔH_r= -66.13 kJ/mole, the fifth reaction ΔH_r= +258.74 kJ/mole and the sixth reaction ΔH_r= +397.6 kJ/mole. 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 and sodium beta-alaninate) 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. Sodium beta-alaninate stream, resulted at the bottom of desorption column, is sent to a CSTR (continuous stirred tank reactor) in order to accomplish the alkaline hydrolysis. The sodium beta-alaninate solution is sent, first to a concentration process and then to the condensation process with pantolactone.

2. MODELING AND SIMULATION OF THE SYNTHESIS

The continuous synthesis of sodium beta-alaninate can be modelled and simulated using CAD software packages for chemical processes. In this case HYSYS Plant, PRO/II and ChemCAD were used. These software packages use flowsheet modelling environment techniques.

The parameters of the model are presented below [6]:

- Dosing 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_1 = -45.76 kJ/mole
    Reaction 3: ΔH_3 = -60.815 kJ/mole
    Reaction 4: ΔH_4 = -79.871 kJ/mole
  - Kinetic data: Reaction 1: Rate = $k_1 C_{NH3} C_{Acryilonitrile}$
    Reaction 3: Rate = $k_3 C_{3\text{-Aminopropionitrile}} C_{Acryilonitrile}$
    Reaction 4: Rate = $k_4 C_{3,3'\text{-Iminodipropionitrile}} C_{Acryilonitrile}$
  - Contact time: 2 – 5 min
- Lamination (depressurise) valve
  - Output pressure: 2 atm
- Addition of sodium hydroxide solution
  - Pressure: 2 atm
- Flash units
  - Use inlet temperature and pressure
- Hydrolysis processes
  - Heat of reactions: Reaction 2: ΔH_2 = -66.13 kJ/mole
    Reaction 5: ΔH_5 = +258.74 kJ/mole
    Reaction 6: ΔH_6 = +397.6 kJ/mole
  - Kinetic data: Reaction 2: Rate = $k_2 C_{3\text{-Aminopropionitrile}} C_{NaOH}$
    Reaction 5: Rate = $k_5 C_{3,3'\text{-Iminodipropionitrile}} C_{NaOH}$
    Reaction 6: Rate = $k_6 C_{3,3',3''\text{-nitrilotripropionitrile}} C_{NaOH}$

- Desorbtion column
  - Number of trays: 6
  - Top pressure: 1.6 atm
  - Bottom pressure: 2 atm
- Heat exchanger for gaseous phase
  - Output temperature: 25^{o}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 %
- Synthesis reactor (Continuous Stirred Tank Reactor)
  - Volume: 6.3 m^3
  - Pressure: 1.5 atm

For continuous sodium beta-alaninate synthesis the flowsheet is presented below (using ChemCAD and HYSYS Plant software packages).

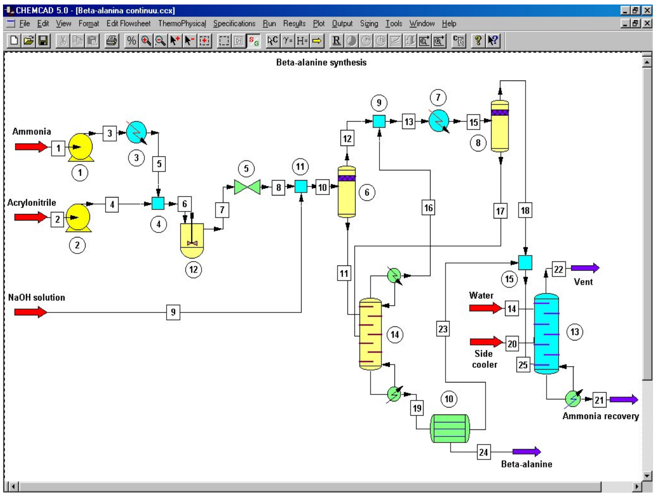


Figure 1. Simulation of sodium beta-alaninate synthesis using ChemCAD

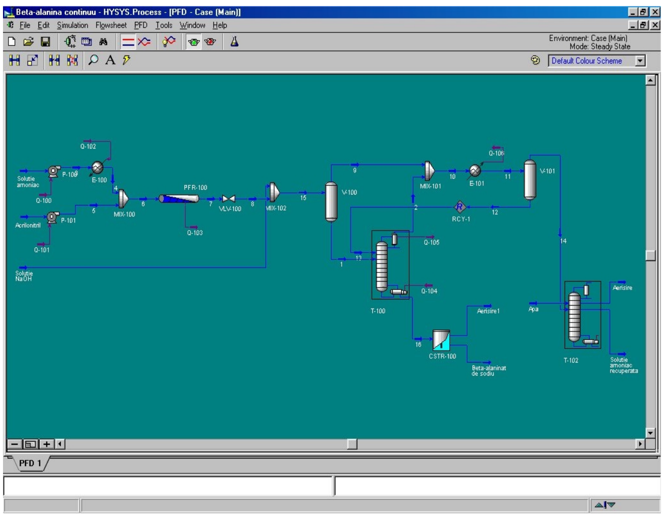


Figure 2. Simulation of sodium beta-alaninate synthesis using HYSYS Plant

3. RESULTS AND DISCUSSIONS

The synthesis process of sodium beta-alaninate 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 reaction (1) yield is about 75 – 80 %, the reaction (3) yield is about 20 - 25 % and the reaction (4) don't practically take place (yield small than 1 %).

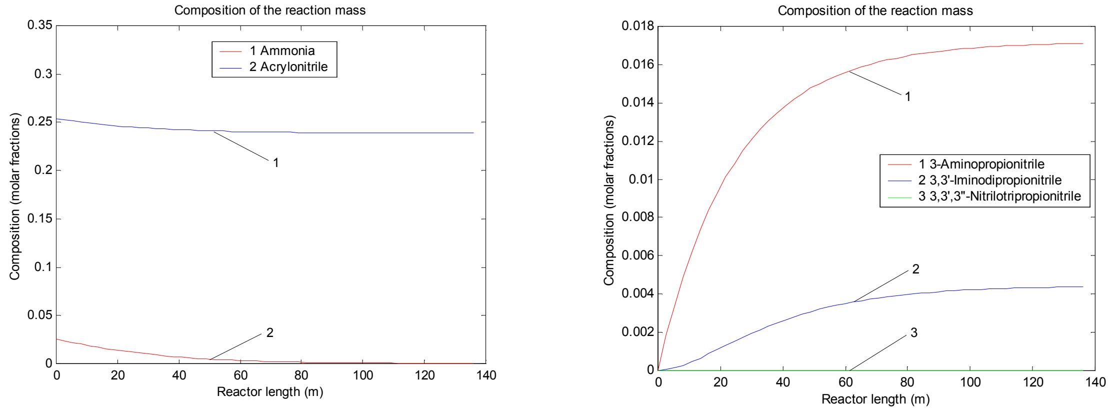


Figure 3. Composition (molar fractions) for reaction mass insight of PFR

For desorption and absorption columns below are represented temperature, liquid and vapour rates for each tray.

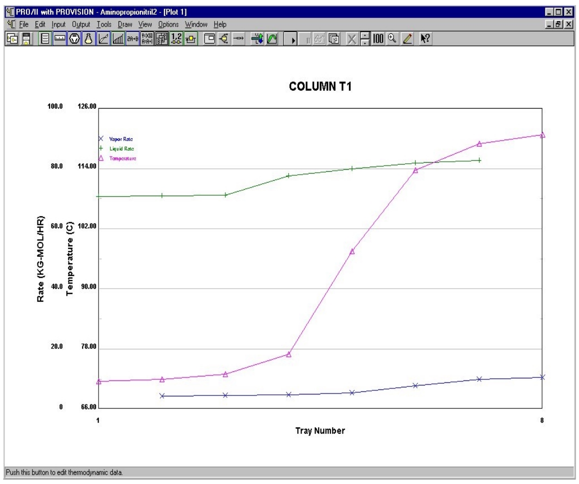


Figure 4. Desorption column

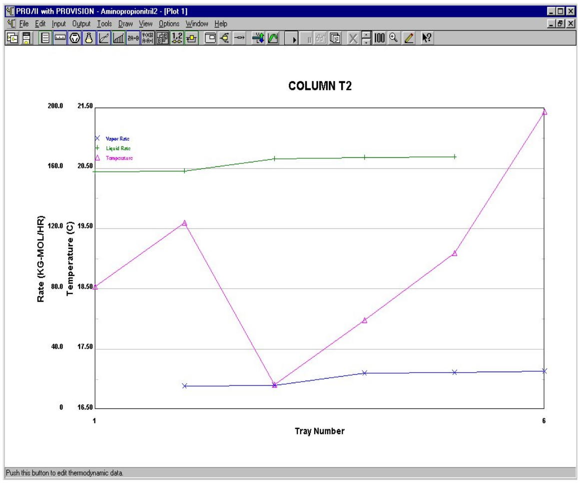


Figure 5. Absorption column

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 sodium beta-alaninate 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 is presented in the figure below (variation of the three products flows vs. ammonia solution flow).

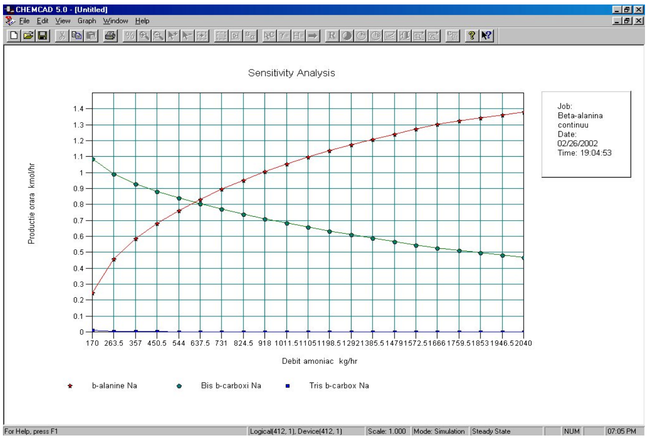


Figure 6. Variation of products flows vs. ammonia solution flow

In the figure above can be seen the variation of the synthesis products mole rate, sodium beta-alaninate (main product), sodium bis-(beta-carboxiethyl)-amine and sodium tris-(beta-carboxiethyl)-amine versus ammonia solution flow. When a molar ratio ammonia/acrylonitrile = 1 is used, the predominant product is sodium bis-(beta-carboxiethyl)-amine. When a higher molar ratio between the two reactants is used the preponderant product is sodium beta-alaninate (main product).

4. CONCLUSIONS

In this paper the continuous synthesis of sodium beta-alaninate 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 operational 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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