

HYDRO- AND THERMODYNAMIC PROCESSES IN ^{13}C CRYOGENIC SEPARATION COLUMN

Clement Festila¹, Eva-Henrietta Dulf¹, Tudor Buzdugan¹, Mihaela-Ligia Unguresan²

Technical University of Cluj-Napoca
¹*Department of Automatic Control*
26-28 Gh. Baritiu Sr., 400027 Cluj-Napoca, Romania
<http://aut.utcluj.ro>
e-mail: Clement.Festila@aut.utcluj.ro
²*Department of Chemistry*

Abstract: The ^{13}C cryogenic separation process, which proceeds in dedicated column, is strongly influenced by more “auxiliary” processes. They create the conditions for efficient column operation. The most important are the hydrodynamic processes, related to the flow rate balance and pressure distribution and the thermodynamic processes, which operate with thermal input and output energy, temperature distribution, etc. The paper models the hydrodynamic processes in column, based on the fundamental laws of physics. In order to obtain a simplified linear model, some initial assumptions are introduced. Using the law of thermodynamics, the energy balance and the input and output energy levels are modeled. The simplified hydrodynamic model is validated using some experimental data. Using the SIMULINK software, the hydrodynamic behavior is simulated.

Copyright

!

Keywords: cryogenic isotope separation column, modeling, hydrodynamic process, thermodynamic process

1. INTRODUCTION

In the case of carbon, there are two stable isotopes: base component (^{12}C) with the natural abundance of 98.89 at.% and the „heavier” stable isotope (^{13}C), with 1.11 at.% concentration (Cohen, 1951; London, 1962; Axente, 1994). Using dedicated equipment, the detection of any substance with a higher concentration of (^{13}C) proves its „synthetic” origin. Based on this feature, the (^{13}C) isotope may be used as marker in scientific research, medicine, environmental protection, etc. There are known more methods able to rise the concentration of the (^{13}C) isotope in some substances (Cohen, 1951; London, 1962; Axente, 1994). One of them is the “cryogenic distillation” having some common characteristics

with the industrial cryogenic air distillation, for instance.

For pure carbon-monoxide, by vaporization temperature of nitrogen (about -190°C), the liquid and gaseous phase co-exist (Axente, 1994; Festila, 2006; Radoi, 1999). Because the maximum vapor pressure by (^{12}CO) is higher than the pressure of (^{13}CO), the theory demonstrates and the practice proves the accumulation of the (^{13}C) in liquid phase, where it may be collected and extracted as final product. In the static contact of both phases, the concentration increasing is very small, given by the “elementary separation factor” (α), $\alpha \approx 1.011$ (Axente, 1994; Cohen, 1951; London, 1962).

A continuous counter current of an ascendant gaseous stream and a descendent liquid stream of carbon-monoxide increase the (¹³C) concentration in liquid and decrease in gas, evacuated as “waste”.

The equipment dedicated to this process and concentrations in (¹³C) up to (8-10) at.% is the separation column (Radoi, 1999; Axente, 1994), with the simplified representation in figure 1.

The *counter-current* is created using the *hydro- and thermodynamic processes*. In the column base, a boiler (B), electrically heated, evaporates the liquid carbon-monoxide and creates the ascendant upstream. In the column top side, a condenser (K), cooled with liquid nitrogen by atmospheric pressure, produces the condensation of (CO) in small drops, as a descendent stream. During the time, the (¹³C) concentration rises up to an equilibrium condition..

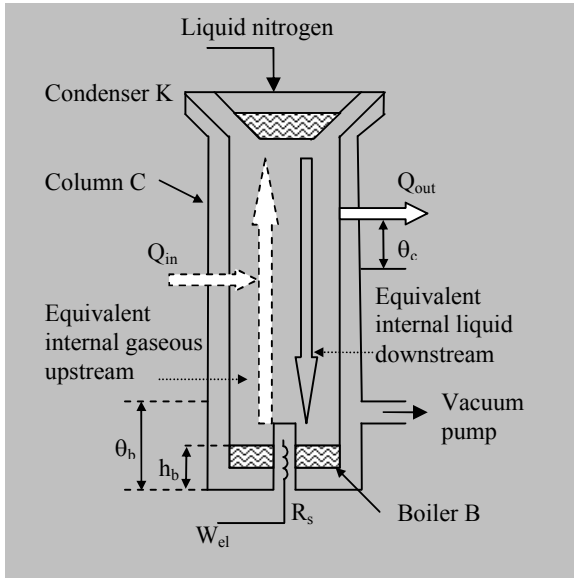


Figure 1. Column simplified scheme

2. MATHEMATICAL MODEL OF THE HYDRODYNAMIC PROCESS

Although the internal evaporation gas-flow (q_{ev}) generated by the boiler and the liquid flow (q_l) given by the condenser are essential in the column operation, any kind of direct measurement is impossible (Axente, 1994; Radoi, 1999; Gligan, 1997). The level of liquid carbon monoxide (h_b) in the boiler, which can be measured, is an important information about the flow rates balance; so that (Fishbane, 2005):

$$\frac{dh_b}{dt} \cong q_c(t) - q_{ev}(t) \quad (1)$$

Based on the typified equation of evaporation (condensation) (Fishbane, 2005):

$$q = k \cdot \frac{p_m - p_1}{p^*} \quad [\text{Mole/sec}] \quad (2)$$

it is possible to model the evolution of the flow-rates process (“hydrodynamic” process), where:

- p_m is the maximum (saturation) vapor pressure;
- p_1 is the actual vapor pressure;
- p^* is the “environmental” pressure;
- k is a proper constant.

In order to conceive a simplified model (Dorf, 2006), some assumptions are made:

- I: the average pressure (p^*) is constant
- II: the model is assumed with “lumped parameter” as an approximation for the real “distributed parameter” process
- III: the maxim vapor pressure is linearly dependent on the local temperature in the condenser region, different from the column average temperature (θ_{av}) and the new variable is:

$$T_c = (\theta_c - \theta_{av}) < 0 \quad (3)$$

IV: for the boiler:

$$T_b = (\theta_b - \theta_{av}) > 0 \quad (4)$$

V: the maximum saturation vapor pressure depends linearly on the generated heat in boiler:

$$\Delta p_{mb} = \alpha_1 \cdot W_{el} \quad (5)$$

by evaporation and on the sink heat in the condenser:

$$\Delta p_{mc} = W_s \quad (6)$$

where (W_s) is the sink heat by condensation, which depends also linearly on the liquid nitrogen level (h_c) in condenser, so that:

$$\Delta p_{mc} = -\alpha_2 \cdot h_c \quad (6^*)$$

Now, equation (1) may be approximated by (Festila, 2006):

$$\begin{aligned} \frac{dh_b}{dt} &= \frac{K}{p^*} [(p_1 - \Delta p_{mc}) - (\Delta p_{mb} - p_1)] = \\ &= \frac{K}{p^*} [2p_1 + \alpha_2 \cdot h_c - \alpha_1 \cdot W_{el}] \end{aligned} \quad (1^*)$$

The previous equation is valid if the feeding carbon monoxide inflow (Q_{in}) is equal to the evacuated out-flow (Q_{out}):

$$Q_{in} = Q_{out} \quad (7)$$

During the separation process, the changes in the in-flow (Q_{in}) are expected so that, the column internal pressure changes (Fishbane, 2005; Radoi, 1999):

$$\Delta p(t) = k \cdot \int [Q_{in}(t) - Q_{out}(t)] dt \quad (8)$$

or

$$\begin{aligned} \overline{\Delta p} &= \int \left[\frac{Q_{in}(t)}{k} - \frac{Q_{out}(t)}{k} \right] dt = \\ &= \int [Q_{in}^*(t) - Q_{out}(t)] dt \end{aligned} \quad (8^*)$$

It is known that under higher pressure, the condensation process is augmented in detriment of the evaporation (Fishbane, 2005), so that the previous equation may be completed to:

$$\frac{dh_b}{dt} = \frac{K}{p^*} [2p_1 + \overline{\Delta p}(t) + \alpha_2 h_c(t) - \alpha_2 W_{el}(t)] \quad (9)$$

with $\overline{\Delta p} \ll p^*$.

The internal streams from column need time to run between the column extremities. The middle ascendant and descendent speed is difficult to determine, so that the equivalent transport dead-time (τ_m) is known only by experiments.

If $p_1 = ct.$, using the Laplace transform, the equation (9) becomes (Dorf, 2006):

$$h_b(s) = \frac{K}{sp^*} [2p_1 + \overline{\Delta p}(s) + \alpha_2 h_c(s) - \alpha_2 W_{el}(s)] \quad (10)$$

If the experimental values of the dead times (Dorf, 2006) are introduced, the model diagram is given in figure 2, so that

$$\begin{aligned} h_b(s) &= \frac{Ke^{-s\tau_m}}{s^2 p^*} (Q_{in}^* - Q_{out}^*) + \frac{\alpha_2 K}{sp^*} e^{-s(\tau_{mc} + \tau_m)} \cdot h_c(s) - \\ &- \frac{\alpha_1 K}{sp^*} e^{-s\tau_m} \cdot W_{el}(s) + \frac{K e^{-s\tau_m}}{sp^*} \cdot 2p_1 \end{aligned} \quad (11)$$

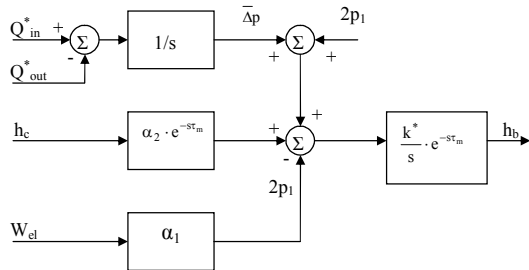


Figure 2. Linearized hydrodynamic model

3. THERMODYNAMIC PROCESS MODELING

If (η_c) is the efficiency coefficient of the boil in steady-state ($Q_{in} = Q_{out}$), the up-stream carbon monoxide flow rate (q_{up}) is given by the equation (Fishbane, 2005):

$$\eta_b \cdot W_{el} = \lambda_{CO} \cdot q_{up} \quad (12)$$

where (λ_{CO}) is the carbon monoxide latent heat of transformation coefficient [cal/mole]. This flow rate arrives to the “cold-wall” of the condenser and delivers the same thermal energy due to the very efficient thermal insulation of the column. The liquid nitrogen evaporation flow rate ($q_{n,out}$) is given by the equation (Fishbane, 2005):

$$\lambda_{CO} \cdot q_{up} = \frac{1}{\eta_c} \lambda_N q_{n,out} \quad (13)$$

where (λ_N) is the nitrogen latent heat of transformation coefficient [cal/mole] and (η_c) is the condenser efficiency coefficient ($\eta_c, \eta_b=80-85\%$). Because all coefficients in (13) are known, by measuring the ($q_{n,out}$), it is possible to estimate the internal flow rates in column, in order to avoid the internal and desired material mixing or even column “flooding”.

4. MODEL VALIDATION, SIMULATION RESULTS

In the actual paper, a simplified model is analyzed for $W_{el} = ct$ and $h_c = ct$ (hence, the variation are equal to zero) and for ($Q_{in}^* - Q_{out}^*$) is a symmetrical square wave with amplitude +/-1.3 and period 500[min].

The simulation scheme is given in figure 3. An additional measuring filter with

$$H_f = \frac{K_f}{T_f s + 1}; K_f = 145; T_f = 20[\text{min}] \quad (14)$$

was added.

In order to identify the values of the coefficients from the equation (11) (with $W_{el} = 0, h_c = 0, 2p_1 = 0$) a set of experimental data is presented in the Table 1 (Gligan, 1997; Radoi, 1999) and compared with the simulated values in figure 5. The continuous curve is a “segment” of the previous diagram for the time-interval 100-450[min]. The discrete points represent the experimental values. From the figure 5 results a good agreement between the mathematical model and the column behaviour.

5. CONCLUSIONS

The actual paper proves the possibility to operate the (^{13}C) isotope cryogenic separation column in a convenient mode, with a stable steady-state, using the out-flow (Q_{out}) as manipulated variable. The hydrodynamic control is the first step in control. Using the second manipulated variable – the electrical power dissipated in boiler – by changing the resistor voltage, the optimization of the column operation is possible.

!

REFERENCES

- Axente, D., M. Abrudean, A. Baldea (1994). *Isotope Separation ^{15}N , ^{18}O , ^{10}B , ^{13}C by isotopic exchange* (in Romanian), Casa Cartii de Stiinta, Cluj-Napoca
- Cohen, K. (1951). *The Theory of isotope separation as applied to the large-scale production of U^{235}* , McGraw-Hill Book Company, Inc
- Dorf R.C. and Robert H. Bishop (2006). *Modern Control Systems, 10/e*, Pearson, Prentice Hall
- Festila, Cl., A. Baldea, M. Gligan, M. Abrudean (2006). About the Cryogenic Distillation Control for (^{13}C) Isotope Separation, *Proceedings of 2006 IEEE-TTC International Conference on Automation, Quality and Testing, Robotics*, IEEE Catalog Number: 06EX1370, ISBN: 1-4244-0360-X, Library of Congress: 2006924077, p. 285-288
- Fishbane, Paul M., S. G. Gasiorowicz, S. T. Thornton (2005). *Physics for Scientists and Engineers*, 3rd Ed., Prentice-Hall
- Gligan, M. et al. (1997). Experimental plant for the ^{18}O isotope separation using the low-temperature distillation of the nitrogen oxides (in Romanian), in *Revista de Chimie*, **48**, Nr.4.
- London, H., Dr. Phil, F.R.S.(1962). *Separation of Isotopes*, George Newnes Limited, Tower House, London
- Radoi, A. et al (1999). Experimental plant for the ^{13}C isotope enrichment based on carbon-monoxide distillation at low temperature”, in *Revista de Chimie*, **50**, Nr.3.

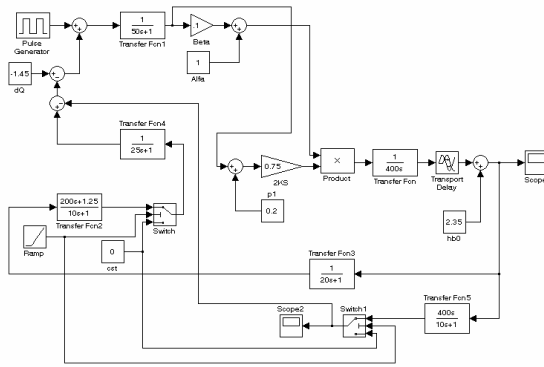


Figure 3. SIMULINK simulation scheme

One result of simulation is presented in figure 4.

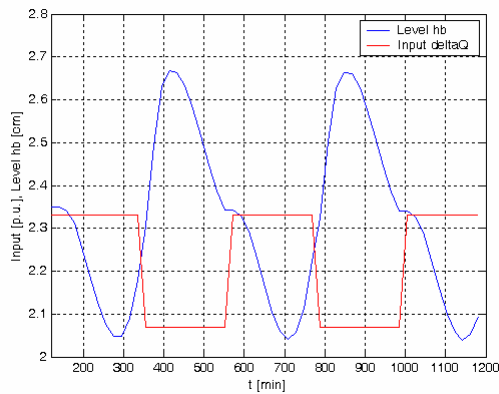


Figure 4. The evolution of the liquid carbon-monoxide level (h_b)

Table 1. A set of experimental data

Time θ [min]	0	30	60	90	120	150	180
h_b [p.u]	2.10	2.05	2.09	2.14	2.22	2.33	2.49

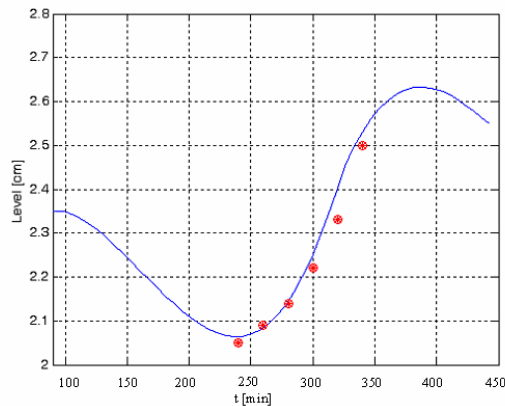


Figure 5. Simulated (—) and measured (\otimes) variables