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An analytic model for a ^{13}C isotope separation process by cryogenic distillation

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Abstract

In this paper we present a structured approach to the modeling of an isotope separation plant that makes use of distillation principles for ^{13}C isotope separation. In the first part of the paper, after a brief review of isotope separation processes with an accent on isotope separation by distillation, we define our initial-boundary-value problem, which is a partial differential equation. By applying the Laplace transform to the partial differential equation that governs the evolution of the desired isotope with respect to height and time, we obtain a linear homogeneous ordinary differential equation. After solving the obtained ordinary differential equation, we use Heaviside's expansion theorem to find the inverse Laplace transform, and thus, the analytic model of the isotope separation process follows. Using the analytic model it is possible to determine the concentration of the desired isotope at any height, at any moment of time, with respect to plant parameters and thus, expensive experiments can be avoided. In the second part of the paper we use the analytic model to simulate the isotope separation process, followed by the assessment of the results against experimental data.

Keywords: Mathematical modeling, Isotope separation, Cryogenic distillation, Analytic model, Simulation

1. Introduction

Isotope-based applications are met in a variety of fields such as chemistry, medicine, hydrology, and energy. The use of isotopic labeled compounds in order to explore different chemical, biological, or hydrological mechanisms is well known [1–4]. Likewise, the practical applications of radioisotopes in energy generation has been studied extensively, at this moment resulting in 436 working nuclear plants worldwide and another 63 plants under construction [5–8]. Moreover, there is an increasing interest in the use of isotopes in medical investigations [9, 10]. Particularly,

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the ^{13}C isotope plays an important role in oceanic and atmospheric studies, as well as in medical diagnosis based on breath CO_2 tests ($^{13}C/^{12}C$ ratio) used to avoid common invasive procedures [11, 12].

In order to increase the concentration of a certain isotope, one can adopt an isotope separation method. Isotope separation techniques depend on several factors, among which are the properties of the chemical compound involved, the various applications that require different concentrations, and the cost of the isotope separation process [13–17].

Urey [18] was among the first to show that the isotopic compounds do not only differ in thermodynamical properties but also in their physical and chemical properties. In [19] Bigeleisen and Mayer proposed a calculation method for the equilibrium constant of the isotopic exchange reactions. Bigeleisen continued his work on isotopes providing a comprehensive review in [13] and a survey with emphasis on isotope effects in [15]. A description of various isotope separation techniques can be found in [4, 20–22]. Cohen has developed the general theory of multistage isotope separation processes in [23], also treating briefly the behavior of liquid-gas countercurrent chemical exchange towers. In [24] London provides an insightful study on isotope separation. Referring to ^{13}C isotope separation processes, McInteer presents in [25] the design issues of a ^{13}C cryogenic rectification plant, while Andreev et al. [26] present the characteristics of different ^{13}C isotope separation plants. In [27], following first-principles knowledge, we have presented a structured modeling approach for a ^{13}C isotope separation process that uses distillation principles. We acknowledge the work of Zemansky [28] regarding thermal phenomena, while in the field of mass transfer and separation processes Cussler, King, and Benitez [29–31] are insightful references. Concerning the dynamics and control of distillation columns, Skogestad et al. [32–36] provide a detailed and comprehensible treatment. Regarding distributed parameter systems and partial differential equations we mention [37–41]. In the field of complex analysis and its applications we acknowledge the work of Townsend, LePage, Duffy, and Brown [42–45], while in the field of numerical analysis [46–48] represent standard works.

Isotope separation processes have, like most physical, chemical, or biological processes, a coupled time-space nature, and thus they belong to the class of distributed parameter systems [37, 38, 49, 50]. Modeling of a distributed parameter system, in general, and modeling of an isotope separation process in particular, is a time-consuming task and requires knowledge from different fields. Numerical methods are widely used in order to solve different mathematical models. However, closed-form solutions (i.e. analytical solutions) are preferred, since they are in general faster and allow a more meaningful analysis of the process and they ease the linking to

the physics of the process [40, 51–54].

The objective of this paper is to provide the analytic solution of the model of a ^{13}C isotope separation process followed by the simulation of the isotope separation plant and hence, to provide a basis for future studies in optimization and process control design. The main contribution of this study consists in the comprehensive determination of the analytic model of the ^{13}C isotope separation process by cryogenic distillation of carbon monoxide. This approach is applicable to other isotope separation processes as well. The assessment of the analytic model is made via simulation. Using the analytic model one can determine the concentration of desired isotope at any height and at any moment of time, with respect to plant parameters and thus, expensive experiments can be avoided. To the authors' best knowledge we are the first to treat these issues for a ^{13}C cryogenic distillation plant.

The paper is structured as follows. In Section 2 we give a brief account of isotope separation processes with emphasis on isotope separation by distillation, followed by a short review of the experimental pilot-scale plant developed at the National Institute for Research and Development of Isotopic and Molecular Technologies in Cluj-Napoca, Romania. In Section 3, based on the linear partial differential equation that governs the evolution of the desired isotope concentration with respect to space and time, we derive the analytic model of the isotope separation process. In Section 4 we use the obtained analytic model to determine the evolution of the concentration of the desired isotopic compound at both ends of the distillation column. The concentration evolution is compared with experimental data. Next, we simulate the isotope concentration distribution in the column followed by the assessment of the results. Section 5 concludes the paper.

The list of tables and figures present the tables and figures referred to within this paper. The most frequent notations used in this paper are listed in Table 1.

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2. Isotope separation process

Isotope separation techniques have their origins in the isotope effects of different isotopic compounds that arise from the differences in the nuclear properties of the isotopes. Some practical isotope separation methods are based on chemical exchange processes, gaseous diffusion, gas centrifuge, laser separation, electromagnetic isotope separation (which is a form of mass spectrometry), and distillation [21, 22].

2.1. Isotope separation by cryogenic distillation

In the case of light elements like boron, carbon, nitrogen, or oxygen, due to the large relative mass difference, distillation was successfully applied to the separation of isotopes [17, 24]. Separation processes by distillation are based on the notion of *relative volatility*, which is a comparative measure for the vapor pressure of the components within a mixture [30, 32].

Regarding the separation of carbon isotopes, it has been shown that the vapor pressure isotope effect is the highest in the case of carbon monoxide (CO) and methane (CH_4). Thus, these substances are preferred as raw material in ^{13}C isotope separation by distillation. Since both carbon monoxide and methane are gaseous in standard conditions, cryogenic distillation is applied [26, 55, 56].

Table 1: Nomenclature

	Latin symbols	
F	feed flow rate	mol/(m^{2}s)
H	hold-up per unit volume	mol/m^3
K	volumetric overall mass transfer coefficient	mol/(m^{3}s)
L	liquid molar flow rate per unit area	mol/(m^{2}s)
n	^{13}CO mole fraction in vapor phase	–
N	^{13}CO mole fraction in liquid phase	–
P	product flow rate	mol/(m^{2}s)
t	time	s
V	vapor molar flow rate per unit area	mol/(m^{2}s)
W	waste flow rate	mol/(m^{2}s)
z	height (position)	m
Z	total height	m
	Greek symbols	
α	relative volatility	–
ε	enrichment factor	–
τ	molar transfer rate per unit volume	mol/(m^{3}s)
	Superscript	
0	pure component	–
13	atomic number	–
	Subscript	
0	natural abundance	–
^{13}CO	isotopic species	–
c	column	–
F	is referring to feed flow rate	–
g	general	–
j	index	–
k	index	–
l	liquid	–
p	particular	–
P	is referring to product flow rate	–
r	rectifying	–
s	stripping	–
v	vapor	–
W	is referring to waste flow rate	–

Since this paper treats the modeling and simulation of a ^{13}C separation plant by cryogenic distillation of carbon monoxide, in the following we will refer to carbon monoxide. Due to the fact that carbon has two stable isotopes, ^{12}C and ^{13}C with a natural abundance of 98.89 % and 1.11 % respectively, and oxygen has three stable isotope, ^{16}O, ^{17}O, and ^{18}O with natural abundances of 99.76 %, 0.04 %, and 0.20 % respectively, in the process of cryogenic distillation of carbon monoxide, six molecular species are involved. However, considering the low natural abundances of ^{17}O and ^{18}O, it is reasonable to relate the carbon monoxide to a binary mixture form of $^{12}C^{16}O$ and $^{13}C^{16}O$ [25]. The separation factor, when the ^{13}CO (i.e. the less volatile component) is the product, is expressed by[1] [32]:

$$\alpha = \frac{p^0_{^{12}\mathrm{CO}}}{p^0_{^{13}\mathrm{CO}}} = \frac{N/(1-N)}{n/(1-n)} \tag{1}$$

where $p^0_{^{12}\mathrm{CO}}$ and $p^0_{^{13}\mathrm{CO}}$ are the vapor pressure of the pure components ^{12}CO and ^{13}CO, N and n refer to the ^{13}CO mole fraction in the liquid phase respectively vapor phase, while $1-N$ and $1-n$ are the ^{12}CO mole fraction in the liquid and vapor phase, respectively.

An accepted value for α, at the boiling point of CO in normal conditions (i.e. 81.6 K), is $\alpha = 1.0069$ [26, 57].

2.2. The pilot-scale experimental plant

At the National Institute for Research and Development of Isotopic and Molecular Technologies, Cluj-Napoca, Romania, an experimental ^{13}C isotope separation plant has been developed. The plant is shown in Fig. 1. The configuration consists of a single column of 7000 mm in height with an inner diameter of 16 mm, packed with Heli-Pak stainless steel wire of 1.8 mm×1.8 mm×0.2 mm.

The experiments used to validate the analytical solution were conducted in total-reflux regime at a pressure of approximately 0.8×10^5 Pa.

The distillation column is fed with highly purified carbon monoxide in liquid state. From the top of the column the waste gas (^{12}CO enriched) is withdrawn, while from the bottom of the column the product (^{13}CO enriched) is taken out. A variable heating resistance (up to 150 W) ensures the vapor stream, while the total condenser provides the reflux. The total condenser uses liquid nitrogen as cooling agent (N_2 has a boiling point in normal conditions of 77.3 K [57]).

[1] For brevity, in the following, the atomic number of the oxygen is omitted, i.e. we use ^{13}CO as a short notation for $^{13}C^{16}O$. Similarly, $^{12}C^{16}O$ is indicated as ^{12}CO.

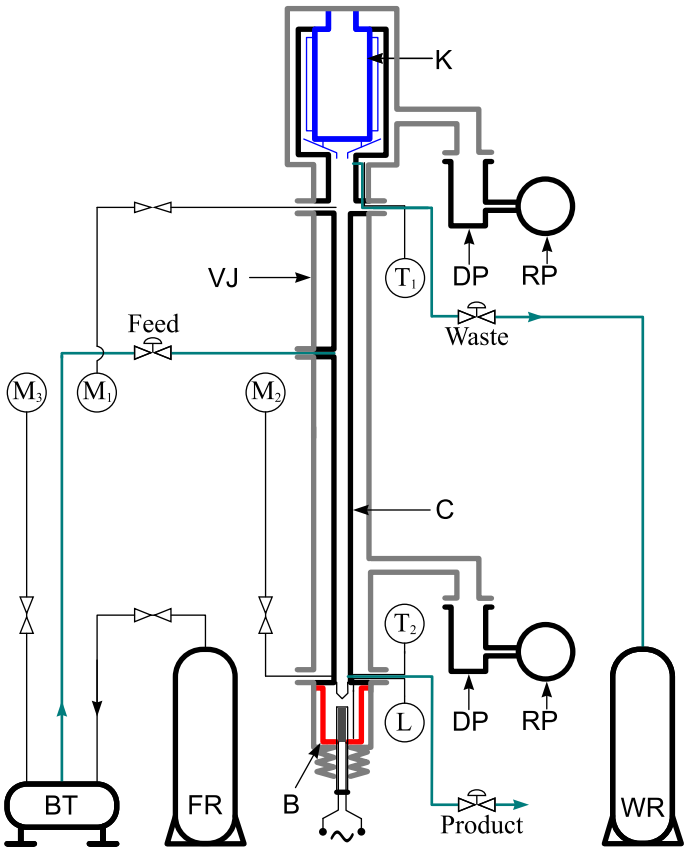


Figure 1: Experimental pilot-scale cryogenic distillation plant with condenser K, distillation column C, reboiler B, vacuum jacket VJ, rough pump RP, diffusion pump DP, temperature sensors T_1-T_2, manometers M_1-M_3, level sensor L, feed reservoir FR, buffer tank BT, and waste reservoir WR.

A multilayered vacuum jacket provides the thermal insulation. The pressure within the jacket was 1.07×10^{-2} Pa [27].

2.3. Isotope separation PDE model

In a previous paper [27], we have derived, using first-principles knowledge, a full nonlinear model for the isotope separation by cryogenic distillation. Due to the complexity of the full nonlinear model we have considered two alternative modeling approaches. Two simplified models followed, a quasi-linear model and, when the isotope concentration achieved by the separation plant was low, a linear model. Subsequently, we have shown that the linear model is a valid modeling approach for ^{13}C isotope separation by cryogenic distillation.

The linear model for the isotope separation process in a rectifying column is described by the

following partial differential equation (PDE):

$$(H_{\mathrm{l}} + H_{\mathrm{v}})\frac{\partial N}{\partial t} = \left(\frac{LV}{K}\right)\frac{\partial^2 N}{\partial z^2} - \left[P + L(\alpha - 1)\right]\frac{\partial N}{\partial z} \tag{2}$$

where $H_{\mathrm{l}} + H_{\mathrm{v}}$ is the total hold-up per unit volume of the raw material in the column, both in liquid and vapor phase, L and V stand for the liquid and vapor molar flow rates per unit area, K is the volumetric overall mass transfer coefficient, while P is the product flow rate given by[2] $P = L - V$. The initial condition is represented by the natural abundance of ^{13}C, while the boundary conditions are determined by the concentration achieved at the top of the column ($z = 0$) respectively at the bottom of the column ($z = Z_{\mathrm{c}}$) [27]. In the following, based on the above isotope separation PDE model, we will determine the analytical solution of the isotope separation process.

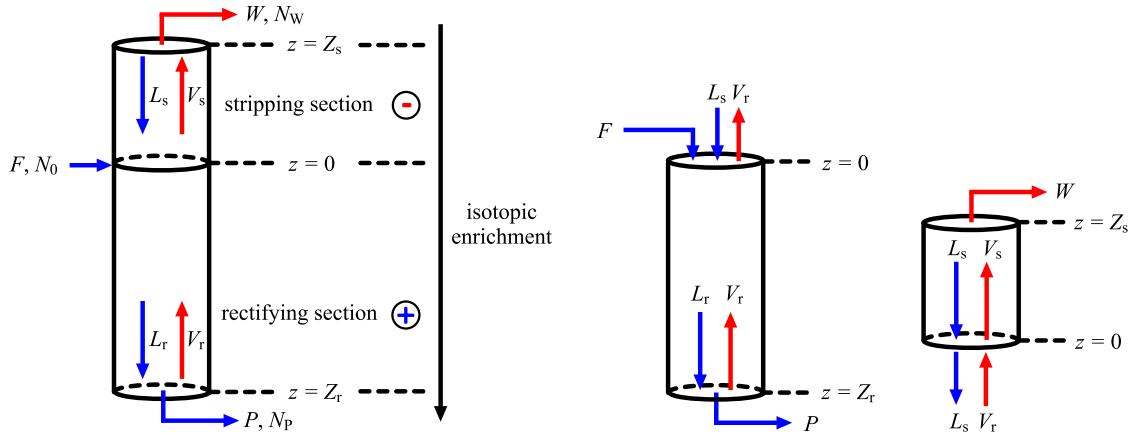
3. Analytical solution of the model of the isotope separation process

It is well known that the Laplace transform is a powerful tool for transforming initial-value problems involving ordinary differential equations (ODE) into algebraic equations [58, 59]. The Laplace transform can be also applied for transforming a PDE into another PDE with one independent variable less, or, if the original PDE had two independent variables, into an ODE [60, 61]. In this section, based on the PDE model that governs the evolution of the desired isotope during the isotope separation process, we will define our initial-boundary-value problem. Using the Laplace transform we will obtain a linear homogeneous ODE. After solving the obtained ODE, by applying the inverse Laplace transform we will obtain the analytical solution of the model of the isotope separation process.

Fig. 2(a) shows the schematic representation of the ^{13}C cryogenic distillation plant. The plant operates in extraction regime. We have denoted by F the feed flow rate, by P the product flow rate, and by W the waste flow rate. The feed point divides the column in two sections, the rectifying section and the stripping section. When the product is represented by the less volatile component, the rectifying section starts from the feeding point and ends at the bottom of the column, while the stripping section starts from the feeding point and ends at the top of the column[3]. In steady state, from the end of the rectifying section of the column, the product is

[2] When the product is represented by the less volatile component.

[3] When the product is represented by the more volatile component, the rectifying section starts from the feeding point and ends at the top of the column, while the stripping section starts from the feeding point and ends at the bottom of the column.



(a) Cryogenic distillation column. (b) Rectifying section. (c) Stripping section.

Figure 2: Schematic representation of the ^{13}C cryogenic distillation and of the column's rectifying and stripping section.

taken out with a constant flow rate P and a ^{13}C concentration equal to N_{P}. From the end of the stripping section of the column, the waste is taken out with a constant flow rate W and a ^{13}C concentration equal to N_{W}. Highly purified carbon monoxide is fed the column with a constant flow rate F and a ^{13}C concentration equal to the ^{13}C natural abundance, N_0. The internal liquid and vapor molar flow rates per unit area in the rectifying section are denoted by L_{r} and V_{r} and by L_{s} and V_{s} in the stripping section.

In the rectifying section, the gradient of the height is positive by convention, while in the stripping section it is negative [13, 15, 23, 24]. The feeding point corresponds to height $z = 0$. The bottom of the column corresponds to the height $z = Z_{\mathrm{r}}$ ($Z_{\mathrm{r}} > 0$) and the top of the column to the height $z = Z_{\mathrm{s}}$ ($Z_{\mathrm{s}} < 0$).

In the following we will derive the analytical solution of the isotope separation process in the rectifying section of the ^{13}C cryogenic distillation column. The obtained model is applicable to the stripping section too; however, in that case, the height gradient will be negative.

3.1. Defining the initial-boundary-value problem

The linear partial differential equation that governs, with respect to both time and space, the evolution of ^{13}C isotope in the liquid phase (i.e. enriched phase) in the rectifying section (see Fig. 2(b)) is given by [23, 27]:

$$(H_{\mathrm{l}} + H_{\mathrm{v}})\frac{\partial N}{\partial t} = \left(\frac{L_{\mathrm{r}} V_{\mathrm{r}}}{K_{\mathrm{r}}}\right)\frac{\partial^2 N}{\partial z^2} - \left[L_{\mathrm{r}}(\alpha - 1) + P\right]\frac{\partial N}{\partial z} \tag{3}$$

where $H_\mathrm{l} + H_\mathrm{v}$ is the total carbon monoxide hold-up per unit volume in the rectifying section[4], while K_r stands for the volumetric overall mass transfer coefficient in the rectifying section.

In the case of the stripping section (see Fig. 2(c)), the partial differential equation that governs the ^{13}C evolution in the liquid phase is given by :

$$(H_\mathrm{l} + H_\mathrm{v})\frac{\partial N}{\partial t} = \left(\frac{L_\mathrm{s}V_\mathrm{s}}{K_\mathrm{s}}\right)\frac{\partial^2 N}{\partial z^2} - \big[L_\mathrm{s}(\alpha - 1) - W\big]\frac{\partial N}{\partial z} \tag{4}$$

where K_s is the volumetric overall mass transfer coefficient in the stripping section.

In order to solve (3) and (4) it is necessary to define the initial condition and the boundary conditions [37, 38]. The time-space domain of (3) and (4) is determined by the duration of the isotope separation process and by the length of the column.

The initial condition in both cases is represented by the desired isotope concentration at the moment of time $t = 0$ and it is given by the natural abundance of ^{13}C:

$$N(z, t = 0) = N_0 \tag{5}$$

The boundary conditions are given by the desired isotope evolution at height $z = 0$ (feeding point) and at the ends of the column, i.e. the bottom of the column in the case of the rectifying section ($z = Z_\mathrm{r}$) and the top of the column in the case of the stripping section ($z = Z_\mathrm{s}$).

Since during the extraction regime, the feeding is continuous and the raw material is represented by carbon monoxide with a natural abundance of ^{13}C, the boundary condition at height $z = 0$ is given by:

$$N(z = 0, t) = N_0 \tag{6}$$

By integrating (3) with respect to height, we obtain:

$$\int (H_\mathrm{l} + H_\mathrm{v})\frac{\partial N}{\partial t}dz + \mathcal{C}_\mathrm{i} = \left(\frac{L_\mathrm{r}V_\mathrm{r}}{K_\mathrm{r}}\right)\frac{\partial N}{\partial z} - \big[L_\mathrm{r}(\alpha - 1) + P\big]N \tag{7}$$

where $\mathcal{C}_\mathrm{i}$ is an integration constant. The general form of (7) is referred to in [23, 24] as the *transport equation* and it relates the amount of the desired isotope carried along a column to the gradient of the mole fraction [24, 62]:

$$\mathcal{T} = \big[L_\mathrm{r}(\alpha - 1) + P\big]N - \left(\frac{L_\mathrm{r}V_\mathrm{r}}{K_\mathrm{r}}\right)\frac{\partial N}{\partial z} \tag{8}$$

[4]Since the hold-up is distributed homogeneously in the distillation column, the total carbon monoxide hold-up per unit volume in the rectifying section is equal to the total carbon monoxide hold-up per unit volume in the stripping section and is equal to the total carbon monoxide hold-up per unit volume in the column.

where $\mathcal{T}$ stands for the desired isotope flow rate. At the end of the isotope separation column, we have [23, 24, 63]:

$$\mathcal{T} = NP \tag{9}$$

From (8) and (9) we obtain the boundary condition at the end of the rectifying section:

$$N(z = Z_{\mathrm{r}}, t) = \frac{V_{\mathrm{r}}}{K_{\mathrm{r}}(\alpha - 1)} \frac{\partial N}{\partial z} \tag{10}$$

Analogously, the boundary condition at the end of the stripping section is given by:

$$N(z = Z_{\mathrm{s}}, t) = \frac{V_{\mathrm{s}}}{K_{\mathrm{s}}(\alpha - 1)} \frac{\partial N}{\partial z} \tag{11}$$

Below we will use the following notations:

$$\eta_{\mathrm{r}} \equiv \frac{(H_{\mathrm{l}} + H_{\mathrm{v}})K_{\mathrm{r}}}{L_{\mathrm{r}}V_{\mathrm{r}}} \tag{12}$$

$$\theta_{\mathrm{r}} \equiv \frac{K_{\mathrm{r}}(\alpha - 1)}{2V_{\mathrm{r}}} \tag{13}$$

$$\psi_{\mathrm{r}} \equiv \frac{P}{L_{\mathrm{r}}(\alpha - 1)} \tag{14}$$

Using (12), (13), and (14), (3) can be written as:

$$\eta_{\mathrm{r}} \frac{\partial N}{\partial t} = \frac{\partial^2 N}{\partial z^2} - 2\theta_{\mathrm{r}}(1 + \psi_{\mathrm{r}}) \frac{\partial N}{\partial z} \tag{15}$$

and the boundary condition (10) becomes:

$$N(z = Z_{\mathrm{r}}, t) = \frac{1}{2\theta_{\mathrm{r}}} \frac{\partial N}{\partial z} \tag{16}$$

For the stripping section, the analogous notations are:

$$\eta_{\mathrm{s}} \equiv \frac{(H_{\mathrm{l}} + H_{\mathrm{v}})K_{\mathrm{s}}}{L_{\mathrm{s}}V_{\mathrm{s}}} \tag{17}$$

$$\theta_{\mathrm{s}} \equiv \frac{K_{\mathrm{s}}(\alpha - 1)}{2V_{\mathrm{s}}} \tag{18}$$

$$\psi_{\mathrm{s}} \equiv \frac{-W}{L_{\mathrm{s}}(\alpha - 1)} \tag{19}$$

and (4) can be written as:

$$\eta_{\mathrm{s}} \frac{\partial N}{\partial t} = \frac{\partial^2 N}{\partial z^2} - 2\theta_{\mathrm{s}}(1 + \psi_{\mathrm{s}}) \frac{\partial N}{\partial z} \tag{20}$$

while the boundary condition (11) becomes:

$$N(z = Z_{\mathrm{s}}, t) = \frac{1}{2\theta_{\mathrm{s}}} \frac{\partial N}{\partial z} \tag{21}$$

It can be seen that the relations for the stripping section are similar to the relations for the rectifying section.

3.2. Laplace transform

By applying the Laplace transform, the partial differential equation (15) turns into:

$$\eta_{\mathrm{r}}\big[sG(z,s) - N_0\big] = \frac{d^2}{dz^2}G(z,s) - 2\theta_{\mathrm{r}}(1+\psi_{\mathrm{r}})\frac{d}{dz}G(z,s) \tag{22}$$

while the boundary conditions (6) and (16) become:

$$G(0,s) = \frac{N_0}{s} \tag{23}$$

$$G(Z_{\mathrm{r}},s) = \frac{1}{2\theta_{\mathrm{r}}}\frac{d}{dz}G(Z_{\mathrm{r}},s) \tag{24}$$

where:

$$G(z,s) = \mathcal{L}\{N(z,t)\} = \int_0^\infty N(z,t)e^{-st}dt \tag{25}$$

Since the independent variable of (22) is the height z, while s is a parameter [60, 64], in the following we will use the simpler notation $G(z)$ instead of $G(z,s)$. The relation (22) can then be written as:

$$\frac{d^2}{dz^2}G(z) - 2\theta_{\mathrm{r}}(1+\psi_{\mathrm{r}})\frac{d}{dz}G(z) - \eta_{\mathrm{r}}sG(z) = -\eta_{\mathrm{r}}N_0 \tag{26}$$

It can be seen that (26) is an homogeneous linear ODE of the second order [65, 66].

The complementary equation of (26) is:

$$\frac{d^2}{dz^2}G(z) - 2\theta_{\mathrm{r}}(1+\psi_{\mathrm{r}})\frac{d}{dz}G(z) - \eta_{\mathrm{r}}sG(z) = 0 \tag{27}$$

So the solution of (26) has the following form:

$$G(z) = G_{\mathrm{p}}(z) + G_{\mathrm{g}}(z) \tag{28}$$

where G_{p} is the particular solution of (26) and G_{g} is the general solution of (27).

In order to find the particular solution of (26) we will choose the *method of undetermined coefficients*. Therefore, the particular solution, which is a polynomial of the same degree as the non homogeneous term, will verify (26). It can be easily found that the particular solution G_{p} is given by:

$$G_{\mathrm{p}} = \frac{N_0}{s} \tag{29}$$

The *auxiliary equation* of (27) is [65]:

$$r^2 - 2\theta_{\mathrm{r}}(1+\psi_{\mathrm{r}})r - \eta_{\mathrm{r}}s = 0 \tag{30}$$

with roots:

$$r_1 = \frac{2\theta_{\mathrm{r}}(1+\psi_{\mathrm{r}}) + \sqrt{4\theta_{\mathrm{r}}^2(1+\psi_{\mathrm{r}})^2 + 4\eta_{\mathrm{r}}s}}{2} \tag{31}$$

$$r_2 = \frac{2\theta_{\mathrm{r}}(1+\psi_{\mathrm{r}}) - \sqrt{4\theta_{\mathrm{r}}^2(1+\psi_{\mathrm{r}})^2 + 4\eta_{\mathrm{r}}s}}{2} \tag{32}$$

Hence, the general solution of (27) is given by [66, 67]:

$$G_{\mathrm{g}}(z) = C_1 e^{r_1 z} + C_2 e^{r_2 z} \tag{33}$$

where C_1 and C_2 are constants. The solution of (26) follows:

$$G(z) = G_{\mathrm{p}}(z) + G_{\mathrm{g}}(z) = \frac{N_0}{s} + C_1 e^{r_1 z} + C_2 e^{r_2 z} \tag{34}$$

The constants C_1 and C_2 can be found by replacing (34) in (23) and (24).

For $z = 0$, from (34) and (23) we obtain:

$$G(0) = \frac{N_0}{s} = \frac{N_0}{s} + C_1 e^0 + C_2 e^0 \tag{35}$$

whence:

$$C_1 = -C_2 \equiv C \tag{36}$$

For $z = Z_{\mathrm{r}}$, from (34) and (24) we obtain:

$$2\theta_{\mathrm{r}} G(Z_{\mathrm{r}}) - \frac{d}{dz} G(Z_{\mathrm{r}}) = 0 \tag{37}$$

whence, referring to (34) and (36):

$$G(Z_{\mathrm{r}}) = \frac{N_0}{s} + C e^{r_1 Z_{\mathrm{r}}} - C e^{r_2 Z_{\mathrm{r}}} \tag{38}$$

The term $\frac{d}{dz} G(Z_{\mathrm{r}})$ is given by:

$$\frac{d}{dz} G(Z_{\mathrm{r}}) = r_1 C e^{r_1 Z_{\mathrm{r}}} - r_2 C e^{r_2 Z_{\mathrm{r}}} \tag{39}$$

From (37), (38), and (39) we obtain:

$$C\Big(r_1 e^{r_1 Z_{\mathrm{r}}} - r_2 e^{r_2 Z_{\mathrm{r}}}\Big) - 2\theta_{\mathrm{r}} C\Big(e^{r_1 Z_{\mathrm{r}}} - e^{r_2 Z_{\mathrm{r}}}\Big) = 2\theta_{\mathrm{r}} \frac{N_0}{s} \tag{40}$$

In the following we will define the term $\beta(s)$ as:

$$\beta(s) \equiv \sqrt{\theta_{\mathrm{r}}^2(1+\psi_{\mathrm{r}})^2 + \eta_{\mathrm{r}} s} \tag{41}$$

The roots of the auxiliary equation can then be written as:

$$r_1 = \theta_{\mathrm{r}}(1+\psi_{\mathrm{r}}) + \beta(s) \tag{42}$$

$$r_2 = \theta_{\mathrm{r}}(1+\psi_{\mathrm{r}}) - \beta(s) \tag{43}$$

Using (42) and (43), (40) becomes:

$$Ce^{\theta_{\mathrm{r}}(1+\psi_{\mathrm{r}})Z_{\mathrm{r}}}\Big\{\big[\theta_{\mathrm{r}}(1+\psi_{\mathrm{r}})+\beta(s)\big]e^{\beta(s)Z_{\mathrm{r}}}-\big[\theta_{\mathrm{r}}(1+\psi_{\mathrm{r}})-\beta(s)\big]e^{-\beta(s)Z_{\mathrm{r}}}-2\theta_{\mathrm{r}}\Big(e^{\beta(s)Z_{\mathrm{r}}}-e^{-\beta(s)Z_{\mathrm{r}}}\Big)\Big\} = 2\theta_{\mathrm{r}}\frac{N_0}{s} \tag{44}$$

whence the constant C follows:

$$C = 2\theta_{\mathrm{r}}\frac{N_0}{s}e^{-\theta_{\mathrm{r}}(1+\psi_{\mathrm{r}})Z_{\mathrm{r}}}\frac{1}{\beta(s)\big(e^{\beta(s)Z_{\mathrm{r}}}+e^{-\beta(s)Z_{\mathrm{r}}}\big)-\theta_{\mathrm{r}}(1+\psi_{\mathrm{r}})\big(e^{\beta(s)Z_{\mathrm{r}}}-e^{-\beta(s)Z_{\mathrm{r}}}\big)} \tag{45}$$

Using Euler's formula [43]:

$$e^{ix} = \cos(x) + i\sin(x) \tag{46}$$

whence:

$$\cos(x) = \frac{1}{2}\big(e^{ix}+e^{-ix}\big) \tag{47}$$

$$\sin(x) = \frac{1}{2i}\big(e^{ix}-e^{-ix}\big) \tag{48}$$

we can write:

$$\Big(e^{\beta(s)Z_{\mathrm{r}}}+e^{-\beta(s)Z_{\mathrm{r}}}\Big) = 2\cos\big(i\beta(s)Z_{\mathrm{r}}\big) \tag{49}$$

$$\Big(e^{\beta(s)Z_{\mathrm{r}}}-e^{-\beta(s)Z_{\mathrm{r}}}\Big) = (-2i)\sin\big(i\beta(s)Z_{\mathrm{r}}\big) \tag{50}$$

Referring to (49) and (50), (45) turns into:

$$C = C_1 = -C_2 = 2\theta_{\mathrm{r}}\frac{N_0}{s}e^{-\theta_{\mathrm{r}}(1+\psi_{\mathrm{r}})Z_{\mathrm{r}}}\frac{1}{2\big[\beta(s)\cos\big(i\beta(s)Z_{\mathrm{r}}\big)-\theta_{\mathrm{r}}(1-\psi_{\mathrm{r}})(-i)\sin\big(i\beta(s)Z_{\mathrm{r}}\big)\big]} \tag{51}$$

The solution of (26) follows:

$$G(z) = \frac{N_0}{s} + Ce^{\theta_{\mathrm{r}}(1+\psi_{\mathrm{r}})z}(-2i)\sin\big(i\beta(s)z\big) \tag{52}$$

By defining:

$$\gamma(s) \equiv i\beta(s) \tag{53}$$

we can write (52) as:

$$G(z,s) = \frac{N_0}{s} + 2\theta_{\mathrm{r}}\frac{N_0}{s}e^{\theta_{\mathrm{r}}(1+\psi_{\mathrm{r}})(z-Z_{\mathrm{r}})}\frac{\sin\big(\gamma(s)z\big)}{\gamma(s)\cos\big(\gamma(s)Z_{\mathrm{r}}\big)-\theta_{\mathrm{r}}(1-\psi_{\mathrm{r}})\sin\big(\gamma(s)Z_{\mathrm{r}}\big)} \tag{54}$$

Analogously, in the case of the striping section we obtain:

$$G(z,\tilde{s}) = \frac{N_0}{\tilde{s}} + 2\theta_{\mathrm{s}}\frac{N_0}{\tilde{s}}e^{\theta_{\mathrm{s}}(1+\psi_{\mathrm{s}})(z-Z_{\mathrm{s}})}\frac{\sin\left(\gamma(\tilde{s})z\right)}{\gamma(\tilde{s})\cos\left(\gamma(\tilde{s})Z_{\mathrm{s}}\right) - \theta_{\mathrm{s}}(1-\psi_{\mathrm{s}})\sin\left(\gamma(\tilde{s})Z_{\mathrm{s}}\right)} \tag{55}$$

where

$$\gamma(\tilde{s}) \equiv i\sqrt{\theta_{\mathrm{s}}^2(1+\psi_{\mathrm{s}})^2 + \eta_{\mathrm{s}}\tilde{s}} \tag{56}$$

By applying the inverse Laplace transform to (54) and (55) we obtain the analytical solution of the isotope separation process.

3.3. Inverse Laplace transform and the analytical solution of the isotope separation process

In order to find the inverse of the Laplace transform of a function, one can use the contour integration, the convolution theorem, tables of integral transforms, or Heaviside's expansion theorem [41, 44, 45, 68–71].

Given the complexity of (54) and (55) it is convenient to use the generalized Heaviside's expansion theorem [68, 72, 73] for finding the inverse Laplace transform.

In order to apply the Heaviside's expansion theorem we will rewrite (54) as:

$$G(z,s) = \frac{N_0}{s} + \frac{2\theta_{\mathrm{r}}N_0 e^{\theta_{\mathrm{r}}(1+\psi_{\mathrm{r}})(z-Z_{\mathrm{r}})}\frac{\sin\left(\gamma(s)z\right)}{\sin\left(\gamma(s)Z_{\mathrm{r}}\right)}}{s\left[\gamma(s)\frac{1}{\tan\left(\gamma(s)Z_{\mathrm{r}}\right)} - \theta_{\mathrm{r}}(1-\psi_{\mathrm{r}})\right]} \tag{57}$$

By defining

$$g(s) \equiv \gamma(s)\frac{1}{\tan\left(\gamma(s)Z_{\mathrm{r}}\right)} - \theta_{\mathrm{r}}(1-\psi_{\mathrm{r}}) \tag{58}$$

the relation (57) becomes:

$$G(z,s) = \frac{N_0\left[g(s) + 2\theta_{\mathrm{r}}e^{\theta_{\mathrm{r}}(1+\psi_{\mathrm{r}})(z-Z_{\mathrm{r}})}\frac{\sin\left(\gamma(s)z\right)}{\sin\left(\gamma(s)Z_{\mathrm{r}}\right)}\right]}{sg(s)} \equiv \frac{q(s)}{p(s)} \tag{59}$$

where

$$q(s) \equiv N_0\left[g(s) + 2\theta_{\mathrm{r}}e^{\theta_{\mathrm{r}}(1+\psi_{\mathrm{r}})(z-Z_{\mathrm{r}})}\frac{\sin\left(\gamma(s)z\right)}{\sin\left(\gamma(s)Z_{\mathrm{r}}\right)}\right] \tag{60}$$

and

$$p(s) \equiv sg(s) \tag{61}$$

The zeros of $p(s)$ are $s_1 = 0$ and the solutions of:

$$g(s) = 0 \tag{62}$$

or

$$\tan\left(\gamma(s)Z_{\mathrm{r}}\right) = \frac{\gamma(s)}{\theta_{\mathrm{r}}(1-\psi_{\mathrm{r}})} \tag{63}$$

The relation (63) is a *transcendental equation* and its solution will be discussed in Section 3.4.

In the case of the stripping section, the analogous transcendental equation is:

$$\tan\left(\gamma(\tilde{s})Z_{\mathrm{s}}\right) = \frac{\gamma(\tilde{s})}{\theta_{\mathrm{s}}(1-\psi_{\mathrm{s}})} \tag{64}$$

For finding the function that describes the evolution of the concentration of the desired isotope in the rectifying section, we will apply the Heaviside's expansion theorem to (59). Thus, the function N will have the form [41, 60, 72]:

$$N(z,t) = \sum_{k=1}^{n} \mathrm{a}_k e^{s_k t} \tag{65}$$

where

$$\mathrm{a}_1 = \lim_{s\to s_1} sG(z,s) \tag{66}$$

while

$$\mathrm{a}_j = \frac{q(s_j)}{p'(s_j)} \tag{67}$$

where s_j, for $j = 2, 3, \ldots, n$, are the solutions of (63).

Theorem 1. ***Final value theorem*** [59]**.** *If F is the Laplace transform of the function f, then:*

$$\lim_{s\to 0} sF(s) = \lim_{t\to\infty} f(t) \tag{68}$$

It can be seen that the value of the coefficient a_1 is the final value of the function N:

$$\mathrm{a}_1 = \lim_{s\to 0} sG(z,s) = \lim_{t\to\infty} N(z,t) \tag{69}$$

By solving (66), using (68), we obtain the stationary value of the concentration of the desired isotope at an arbitrary height z in the rectifying section:

$$\lim_{t\to\infty} N(z,t) = N_0 \frac{e^{2\theta_{\mathrm{r}}(1+\psi_{\mathrm{r}})z} + \psi_{\mathrm{r}} e^{2\theta_{\mathrm{r}}(1+\psi_{\mathrm{r}})Z_{\mathrm{r}}}}{1 + \psi_{\mathrm{r}} e^{2\theta_{\mathrm{r}}(1+\psi_{\mathrm{r}})Z_{\mathrm{r}}}} \tag{70}$$

Analogously, the stationary value of the concentration of the desired isotope at an arbitrary height z in the stripping section is given by:

$$\lim_{t\to\infty} N(z,t) = N_0 \frac{e^{2\theta_{\mathrm{s}}(1+\psi_{\mathrm{s}})z} + \psi_{\mathrm{s}} e^{2\theta_{\mathrm{s}}(1+\psi_{\mathrm{s}})Z_{\mathrm{s}}}}{1 + \psi_{\mathrm{s}} e^{2\theta_{\mathrm{s}}(1+\psi_{\mathrm{s}})Z_{\mathrm{s}}}} \tag{71}$$

Since s_j are the solution of $g(s) = 0$, (60) yields:

$$q(s_j) = N_0 \left[2\theta_{\mathrm{r}} e^{\theta_{\mathrm{r}}(1+\psi_{\mathrm{r}})(z-Z_{\mathrm{r}})} \frac{\sin\big(\gamma(s_j)z\big)}{\sin\big(\gamma(s_j)Z_{\mathrm{r}}\big)} \right] \tag{72}$$

and

$$p'(s_j) = s_j g'(s_j) \tag{73}$$

By derivation with respect to s, (58) becomes:

$$g'(s_j) = \frac{\eta_{\mathrm{r}} Z_{\mathrm{r}}}{2} - \frac{\eta_{\mathrm{r}}}{2\big(\gamma(s_j)\big)^2} \theta_{\mathrm{r}}(1-\psi_{\mathrm{r}})\big[1 - Z_{\mathrm{r}}\theta_{\mathrm{r}}(1-\psi_{\mathrm{r}})\big] \tag{74}$$

From (72) and (74) we obtain the value of the coefficient a_j:

$$\mathrm{a}_j = \frac{N_0 \left[2\theta_{\mathrm{r}} e^{\theta_{\mathrm{r}}(1+\psi_{\mathrm{r}})(z-Z_{\mathrm{r}})} \frac{\sin\big(\gamma(s_j)z\big)}{\sin\big(\gamma(s_j)Z_{\mathrm{r}}\big)} \right]}{s_j \left\{ \frac{\eta_{\mathrm{r}} Z_{\mathrm{r}}}{2} - \frac{\eta_{\mathrm{r}}}{2(\gamma(s_j))^2} \theta_{\mathrm{r}}(1-\psi_{\mathrm{r}})\big[1 - Z_{\mathrm{r}}\theta_{\mathrm{r}}(1-\psi_{\mathrm{r}})\big] \right\}} \tag{75}$$

The analytical solution of the isotope separation process, in the rectifying section, follows:

$$N(z,t) = N_0 \frac{e^{2\theta_{\mathrm{r}}(1+\psi_{\mathrm{r}})z} + \psi_{\mathrm{r}} e^{2\theta_{\mathrm{r}}(1+\psi_{\mathrm{r}})Z_{\mathrm{r}}}}{1 + \psi_{\mathrm{r}} e^{2\theta_{\mathrm{r}}(1+\psi_{\mathrm{r}})Z_{\mathrm{r}}}} + \sum_{j=2}^{n} \frac{N_0 \left[2\theta_{\mathrm{r}} e^{\theta_{\mathrm{r}}(1+\psi_{\mathrm{r}})(z-Z_{\mathrm{r}})} \frac{\sin\big(\gamma(s_j)z\big)}{\sin\big(\gamma(s_j)Z_{\mathrm{r}}\big)} \right]}{s_j \left\{ \frac{\eta_{\mathrm{r}} Z_{\mathrm{r}}}{2} - \frac{\eta_{\mathrm{r}}}{2(\gamma(s_j))^2} \theta_{\mathrm{r}}(1-\psi_{\mathrm{r}})\big[1 - Z_{\mathrm{r}}\theta_{\mathrm{r}}(1-\psi_{\mathrm{r}})\big] \right\}} e^{s_j t} \tag{76}$$

where θ_{r}, ψ_{r}, and $\gamma(s_j)$ are the parameters of the isotope separation process in the rectifying section (see (12), (13), (14), and (53)), while s_j, for $j = 2, 3, \ldots, n$, are the solutions of the transcendental equation (63).

Analogously, in the case of the stripping section, the analytical solution is given by the similar relation:

$$N(z,t) = N_0 \frac{e^{2\theta_{\mathrm{s}}(1+\psi_{\mathrm{s}})z} + \psi_{\mathrm{s}} e^{2\theta_{\mathrm{s}}(1+\psi_{\mathrm{s}})Z_{\mathrm{s}}}}{1 + \psi_{\mathrm{s}} e^{2\theta_{\mathrm{s}}(1+\psi_{\mathrm{s}})Z_{\mathrm{s}}}} + \sum_{j=2}^{\tilde{n}} \frac{N_0 \left[2\theta_{\mathrm{s}} e^{\theta_{\mathrm{s}}(1+\psi_{\mathrm{s}})(z-Z_{\mathrm{s}})} \frac{\sin\big(\gamma(\tilde{s}_j)z\big)}{\sin\big(\gamma(\tilde{s}_j)Z_{\mathrm{s}}\big)} \right]}{\tilde{s}_j \left\{ \frac{\eta_{\mathrm{s}} Z_{\mathrm{s}}}{2} - \frac{\eta_{\mathrm{s}}}{2(\gamma(\tilde{s}_j))^2} \theta_{\mathrm{s}}(1-\psi_{\mathrm{s}})\big[1 - Z_{\mathrm{s}}\theta_{\mathrm{s}}(1-\psi_{\mathrm{s}})\big] \right\}} e^{\tilde{s}_j t} \tag{77}$$

In this case, θ_{s}, ψ_{s}, and $\gamma(\tilde{s}_j)$ are the parameters of the isotope separation process in the stripping section (see (17), (18), (19), and (53)), while $\tilde{s}_j$, for $j = 2, 3, \ldots, \tilde{n}$, are the solutions of the transcendental equation (64).

Using (76) and (77) one can determine the concentration of the desired isotope at any height z and at any moment of time t, with respect to plant parameters like the hold-up, liquid and vapor molar flow rate, separation factor, and the height of the distillation column.

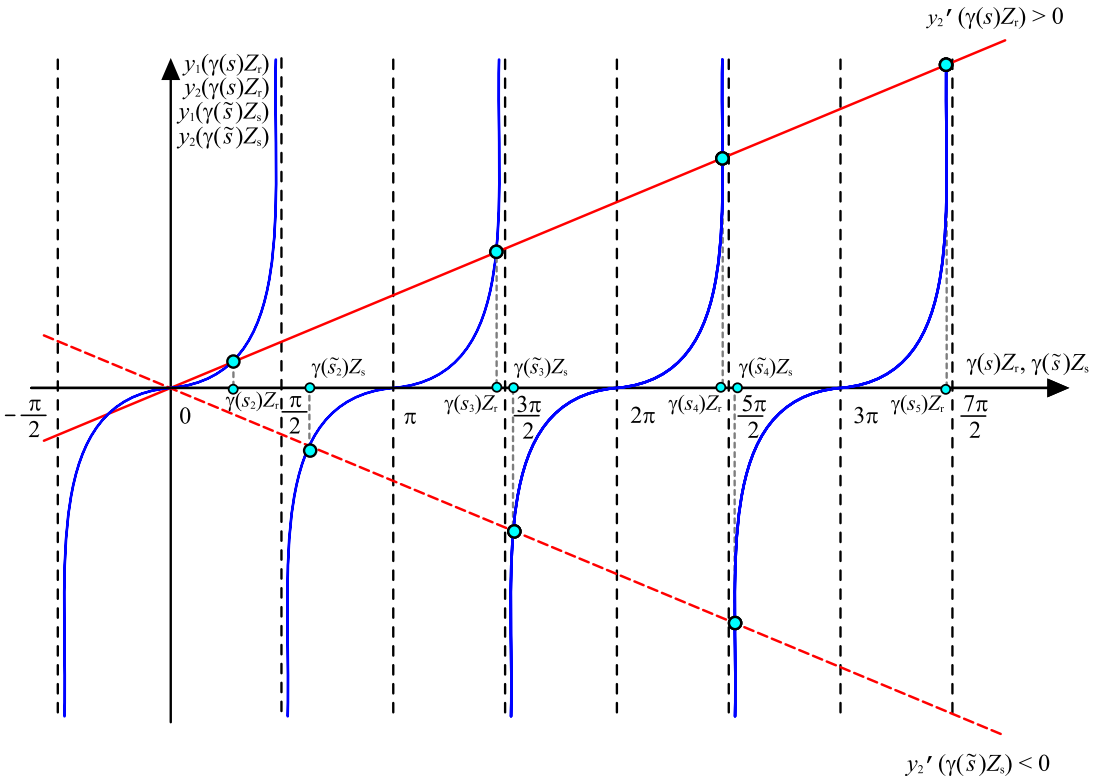


Figure 3: Graphical representation of the functions $y_1\big(\gamma(s)Z_\mathrm{r}\big)$, $y_1\big(\gamma(\tilde{s})Z_\mathrm{s}\big)$ and $y_2\big(\gamma(s)Z_\mathrm{r}\big)$, $y_2\big(\gamma(\tilde{s})Z_\mathrm{s}\big)$.

3.4. Solving the transcendental equations (63) *and* (64)

In our case, (63) can be written as:

$$\tan\big(\gamma(s)Z_\mathrm{r}\big) = \frac{\big(\gamma(s)Z_\mathrm{r}\big)}{\theta_\mathrm{r}Z_\mathrm{r}(1-\psi_\mathrm{r})} \tag{78}$$

Both sides of (78) can be expressed as two functions of the same argument:

$$y_1\big(\gamma(s)Z_\mathrm{r}\big) = \tan\big(\gamma(s)Z_\mathrm{r}\big) \tag{79}$$

$$y_2\big(\gamma(s)Z_\mathrm{r}\big) = \frac{\big(\gamma(s)Z_\mathrm{r}\big)}{Z_\mathrm{r}\theta_\mathrm{r}(1-\psi_\mathrm{r})} \tag{80}$$

Fig. 3 shows the graphical representation of the functions $y_1\big(\gamma(s)Z_\mathrm{r}\big)$, $y_1\big(\gamma(\tilde{s})Z_\mathrm{s}\big)$ and $y_2\big(\gamma(s)Z_\mathrm{r}\big)$, $y_2\big(\gamma(\tilde{s})Z_\mathrm{s}\big)$. Since the height gradient is positive in the rectifying section and negative in the stripping section, $y_2'\big(\gamma(s)Z_\mathrm{r}\big) > 0$, while $y_2'\big(\gamma(\tilde{s})Z_\mathrm{s}\big) < 0$.

The solutions of (78) are given by the points for which the following is true:

$$y_1\big(\gamma(s_j)Z_\mathrm{r}\big) = y_2\big(\gamma(s_j)Z_\mathrm{r}\big) \tag{81}$$

or, in other words, in the intersection points of the two functions.

By knowing the value of $\big(\gamma(s_j)Z_{\rm r}\big)$, where $j = 2, 3, \ldots, n$, one can find the solutions of (62), and the analytic solution of the isotope separation process in the rectifying section becomes completely determined. Knowing that (see (53)):

$$\big(\gamma(s_j)Z_{\rm r}\big) = i\left(\sqrt{\theta_{\rm r}^2(1+\psi_{\rm r})^2 + \eta_{\rm r}s_j}\right)Z_{\rm r} \tag{82}$$

we obtain the solutions of (62):

$$s_j = -\left[\frac{\big(\gamma(s_j)Z_{\rm r}\big)^2 + {Z_{\rm r}}^2\theta_{\rm r}^2(1+\psi_{\rm r})^2}{\eta_{\rm r}{Z_{\rm r}}^2}\right] \tag{83}$$

Since $\eta_{\rm r}$ is a positive quantity (see (12)) one can see from (83) that $s_j < 0$. Thus, the terms in the infinite series (see (76)) are transient and the series converges.

Analogously, in the case of the stripping section we obtain:

$$\tilde{s}_j = -\left[\frac{\big(\gamma(\tilde{s}_j)Z_{\rm s}\big)^2 + {Z_{\rm s}}^2\theta_{\rm s}^2(1+\psi_{\rm s})^2}{\eta_{\rm s}{Z_{\rm s}}^2}\right] \tag{84}$$

For determining the intersection points $\big(\gamma(s_j)Z_{\rm r}\big)$ and $\big(\gamma(\tilde{s}_j)Z_{\rm s}\big)$ as plotted in Fig. 3 we have used the MATLAB function *fzero*. The function *fzero* find the roots of a continuous function of one variable around an arbitrary point [74, 75].

4. Validation of the analytical solution of the isotope separation process

Usually, the only points where the isotopic concentration is measurable are at the bottom and at the top of the column. In order to validate the analytical solution, we will use (76) and (77) written for the boundary conditions $z = Z_{\rm r}$ (the end of the rectifying section, i.e. the bottom of the column) and $z = Z_{\rm s}$ (the end of the stripping section, i.e. the top of the column).

In the following we will refer to three isotope separation experiments carried using the experimental pilot-scale plant developed at the National Institute for Research and Development of Isotopic and Molecular Technologies in Cluj-Napoca, Romania. The three experiments were conducted in total-reflux regime for different electrical powers that supplied the heating resistance, i.e. 24 W, 27 W, and 29 W.

The analytical solution (76) written for $z = Z_{\rm r}$ is given by:

$$N(z = Z_{\rm r}, t) = N_0\frac{(1+\psi_{\rm r})e^{2\theta_{\rm r}(1+\psi_{\rm r})Z_{\rm r}}}{1+\psi_{\rm r}e^{2\theta_{\rm r}(1+\psi_{\rm r})Z_{\rm r}}} + \sum_{j=2}^{n}\frac{N_0 2\theta_{\rm r}}{s_j\left\{\frac{\eta_{\rm r}Z_{\rm r}}{2} - \frac{\eta_{\rm r}}{2(\gamma(s_j))^2}\theta_{\rm r}(1-\psi_{\rm r})\big[1 - Z_{\rm r}\theta_{\rm r}(1-\psi_{\rm r})\big]\right\}}e^{s_j t} \tag{85}$$

Since the experiments were conducted in total-reflux regime, no withdrawal was performed and therefore:

$$F = P = W = 0 \tag{86}$$

whence (see (14)) $\psi_{\mathrm{r}} = 0$. Thus, (85) becomes:

$$N(z = Z_{\mathrm{r}}, t) = N_0 e^{2\theta_{\mathrm{r}} Z_{\mathrm{r}}} + \sum_{j=2}^{n} \frac{N_0 2\theta_{\mathrm{r}}}{s_j \left[\frac{\eta_{\mathrm{r}} Z_{\mathrm{r}}}{2} - \frac{\eta_{\mathrm{r}} \theta_{\mathrm{r}}}{2(\gamma(s_j))^2} (1 - Z_{\mathrm{r}} \theta_{\mathrm{r}}) \right]} e^{s_j t} \tag{87}$$

Analogously, the analytical solution written for the boundary condition $z = Z_{\mathrm{s}}$ and the total-reflux condition $\psi_{\mathrm{s}} = 0$ is given by:

$$N(z = Z_{\mathrm{s}}, t) = N_0 e^{2\theta_{\mathrm{s}} Z_{\mathrm{s}}} + \sum_{j=2}^{\tilde{n}} \frac{N_0 2\theta_{\mathrm{s}}}{\tilde{s}_j \left[\frac{\eta_{\mathrm{s}} Z_{\mathrm{s}}}{2} - \frac{\eta_{\mathrm{s}} \theta_{\mathrm{s}}}{2(\gamma(\tilde{s}_j))^2} (1 - Z_{\mathrm{s}} \theta_{\mathrm{s}}) \right]} e^{\tilde{s}_j t} \tag{88}$$

The relations (87) and (88) describe the evolution of the mole fraction of the desired isotopic compound at the bottom and at the top of the column with respect to process parameters like hold-up, internal molar flow rates, height of the column, and the separation factor.

4.1. Parameters of the analytical solution of the isotope separation process

Since the plant's configuration consists of one distillation column with a single reboiler, the vapor molar flow rate in the rectifying section is equal to the vapor molar flow rate in the stripping section ($V_{\mathrm{r}} = V_{\mathrm{s}}$). The vapor internal stream is determined by the electrical power that supplied the heating resistance and the heat transfer through the multilayered vacuum jacket [76–78]. The liquid molar flow rate is determined by the total-reflux condition. The total hold-up in the column $H_{\mathrm{l}} + H_{\mathrm{v}}$ is determined by measuring the quantity of raw material fed to the column during the operations prior to the beginning of each experiment.

Naturally, during the total-reflux experiment, the raw material will have, at a certain height z, in steady state, the natural isotopic abundance (N_0). When the product is represented by the less volatile component, under the height corresponding to the natural isotopic abundance (toward to the bottom of the column) the concentration of the desired isotope will be higher than its natural abundance, while above this height, the isotope concentration will be lower than its natural abundance. Therefore, the total-reflux regime can be analyzed as a particular case of the extraction regime, when no withdrawal is performed and thus, the feed flow rate F, the product flow rate P, and the waste flow rate W are zero, and the feed point will correspond to the height for which the raw material isotopic concentration corresponds to the natural abundance (see Fig. 2(a), Fig. 2(b), and Fig. 2(c)).

The rate of transfer of the heavy isotopic compound (the product) to the liquid phase across the interface per unit volume, in the rectifying section, is given by [23, 27]:

$$\tau_{\mathrm{r}} = -K_{\mathrm{r}}\big[(N-n) - n(\alpha-1)(1-N)\big] \tag{89}$$

where the separation factor α is:

$$\alpha = \frac{\frac{N}{1-N}}{\frac{n}{1-n}} \tag{90}$$

Analogously, the rate of transfer of the light isotopic compound to the vapor phase in the stripping section is given by:

$$\tau'_{\mathrm{s}} = -K_{\mathrm{s}}\big[(n'-N') - N'(\alpha'-1)(1-n')\big] \tag{91}$$

where n' and N' correspond to the mole fraction of the light isotopic compound in the vapor phase, while α' is:

$$\alpha' = \frac{\frac{n'}{1-n'}}{\frac{N'}{1-N'}} > 1 \tag{92}$$

Since during the total-reflux regime no products are withdrawn and the feed flow rate is zero, the rate of transfer of the heavy isotopic compound to the liquid phase in the stripping section will be equal but in opposite sign to the rate of transfer of the heavy isotopic compound to the liquid phase in the rectifying section:

$$\tau_{\mathrm{s}} = \tau'_{\mathrm{s}} = -\tau_{\mathrm{r}} \tag{93}$$

In our case, the raw material corresponds to a binary mixture, and thus [27, 32]:

$$n' = 1 - n \tag{94}$$

$$N' = 1 - N \tag{95}$$

$$\alpha' = \alpha \tag{96}$$

The description of τ_{s} follows:

$$\tau_{\mathrm{s}} = -K_{\mathrm{s}}\big[(N-n) - n(\alpha-1)(1-N)\big] \tag{97}$$

From (89), (93), and (97) we obtain:

$$K_{\mathrm{r}} = K_{\mathrm{s}} \tag{98}$$

Previously we have determined the stationary value of the concentration of the desired isotope at an arbitrary height z in the separation column (see (70) and (71)). Usually, the only points

were the isotopic concentration is measurable are at the top of the column and at the bottom of the column. By referring to (70) and (71) and knowing that the experiments were conducted in total-reflux regime and therefore $\psi_{\mathrm{r}} = \psi_{\mathrm{s}} = 0$ (see (14) and (19)) we obtain the stationary value of the concentration at the end of the rectifying section $z = Z_{\mathrm{r}}$ (bottom of the column) and at the end of the stripping section $z = Z_{\mathrm{s}}$ (top of the column):

$$\lim_{t\to\infty} N(Z_{\mathrm{r}}, t) = N_0 e^{2\theta_{\mathrm{r}} Z_{\mathrm{r}}} \tag{99}$$

$$\lim_{t\to\infty} N(Z_{\mathrm{s}}, t) = N_0 e^{2\theta_{\mathrm{s}} Z_{\mathrm{s}}} \tag{100}$$

Since the stationary values of the desired isotope concentration are determined experimentally, by referring to (13) and (18), the description of K_{r} and K_{s} follows:

$$K_{\mathrm{r}} = \frac{V_{\mathrm{r}}}{(\alpha-1)Z_{\mathrm{r}}} \ln\left(\frac{\lim\limits_{t\to\infty} N(Z_{\mathrm{r}}, t)}{N_0}\right) \tag{101}$$

$$K_{\mathrm{s}} = \frac{V_{\mathrm{s}}}{(\alpha-1)Z_{\mathrm{s}}} \ln\left(\frac{\lim\limits_{t\to\infty} N(Z_{\mathrm{s}}, t)}{N_0}\right) \tag{102}$$

From (98), (101), and (102), and knowing that $Z_{\mathrm{c}} = Z_{\mathrm{r}} - Z_{\mathrm{s}}$ is possible to determine the height of the rectifying and stripping section of a distillation column that operates in total-reflux regime:

$$Z_{\mathrm{r}} = Z_{\mathrm{c}} \frac{\ln\left(\frac{\lim\limits_{t\to\infty} N(Z_{\mathrm{r}}, t)}{N_0}\right)}{\ln\left(\frac{\lim\limits_{t\to\infty} N(Z_{\mathrm{r}}, t)}{\lim\limits_{t\to\infty} N(Z_{\mathrm{s}}, t)}\right)} \tag{103}$$

$$Z_{\mathrm{s}} = Z_{\mathrm{c}} \frac{\ln\left(\frac{\lim\limits_{t\to\infty} N(Z_{\mathrm{s}}, t)}{N_0}\right)}{\ln\left(\frac{\lim\limits_{t\to\infty} N(Z_{\mathrm{r}}, t)}{\lim\limits_{t\to\infty} N(Z_{\mathrm{s}}, t)}\right)} \tag{104}$$

Since the heights of the rectifying and stripping section (Z_{r} and Z_{s}) depend on measurable parameters like the total height of the column Z_{c}, the stationary values of the concentration at the ends of the column, and on the natural abundance of $^{13}\mathrm{C}$, one can determine the constant concentration point Z_0 as being at height Z_{s} from the top of the column or Z_{r} from the bottom of the column (see Figure 2(a)).

Knowing the vapor and liquid molar flow rates, the total hold-up in the column ($H_{\mathrm{l}} + H_{\mathrm{v}}$), the heights of the rectifying and stripping section (Z_{r} and Z_{s}), and the separation factor (α), it is possible to determine the parameters of the analytical solution and, thus, to obtain the isotope distribution with respect to both time and height by computing (76) and (77).

Table 2: Parameters of the analytical solution and the heights of the rectifying and stripping section in the case of all three isotope separation experiments.

$P_{\text{electrical}}$ (W)	$\eta_{\text{r}} = \eta_{\text{s}}$ $\left(\frac{\text{s}}{\text{m}^2}\right)$	$\theta_{\text{r}} = \theta_{\text{s}}$ $\left(\frac{1}{\text{m}}\right)$	$\psi_{\text{r}} = \psi_{\text{s}}$ (-)	Z_{r} (m)	Z_{s} (m)
24	12198.062	0.168	0	2.390	-4.610
27	9664.195	0.143	0	2.956	-4.044
29	9798.104	0.152	0	2.884	-4.116

Table 3: The values of $\left(\gamma(s_j)Z_{\text{r}}\right)$ and $\left(\gamma(\tilde{s}_j)Z_{\text{s}}\right)$ when j = 2, 3, 4, 5, and 6 in the case of all three isotope separation experiments.

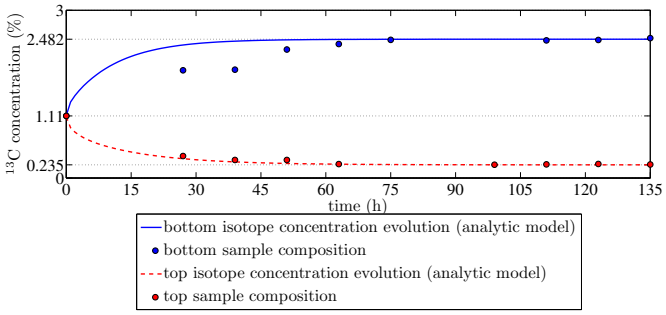
$P_{\text{electrical}}$ (W)	$\left(\gamma(s_2)Z_{\text{r}}\right)$ $(-)$	$\left(\gamma(s_3)Z_{\text{r}}\right)$ $(-)$	$\left(\gamma(s_4)Z_{\text{r}}\right)$ $(-)$	$\left(\gamma(s_5)Z_{\text{r}}\right)$ $(-)$	$\left(\gamma(s_6)Z_{\text{r}}\right)$ $(-)$
24	1.262	4.625	7.802	10.958	14.108
27	1.242	4.621	7.799	10.956	14.107
29	1.226	4.617	7.797	10.955	14.105
$P_{\text{electrical}}$ (W)	$\left(\gamma(\tilde{s}_2)Z_{\text{s}}\right)$ $(-)$	$\left(\gamma(\tilde{s}_3)Z_{\text{s}}\right)$ $(-)$	$\left(\gamma(\tilde{s}_4)Z_{\text{s}}\right)$ $(-)$	$\left(\gamma(\tilde{s}_5)Z_{\text{s}}\right)$ $(-)$	$\left(\gamma(\tilde{s}_6)Z_{\text{s}}\right)$ $(-)$
24	1.949	4.870	7.951	11.065	14.191
27	1.870	4.831	7.926	11.047	14.177
29	1.891	4.841	7.933	11.052	14.181

Table 2 summarizes the parameters of the analytical solution, as well as the heights of the rectifying section and stripping section in the case of the three isotope separation experiments. The first five values[5] of $(\gamma(s_j)Z_{\text{r}})$ and $(\gamma(\tilde{s}_j)Z_{\text{s}})$ are listed in Table 3.

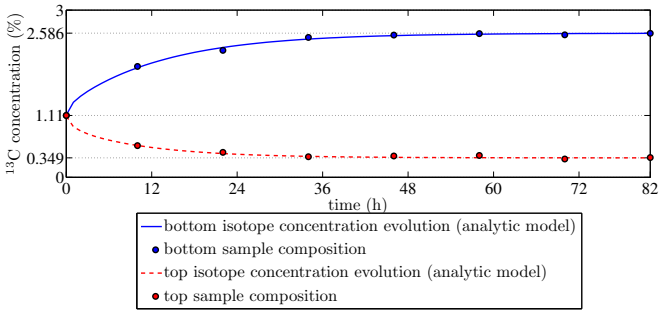
4.2. Assessment of the analytical solution of the isotope separation process

Fig. 4(a), 4(b), and 4(c) show the ^{13}CO mole fraction evolution at both ends of the distillation column in the case of the three isotope separation experiments. The results were obtained by computing the analytical solution described by (87) and (88). In addition, the measured values are also plotted.

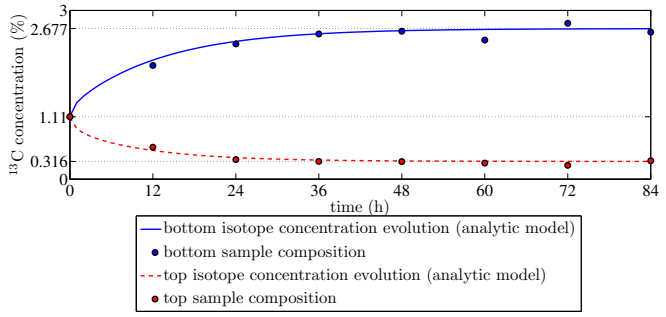
[5]For brevity, we remind that the first solution of the transcendental equations is indicated by the index $j = 2$.



(a) 24 W case.



(b) 27 W case.

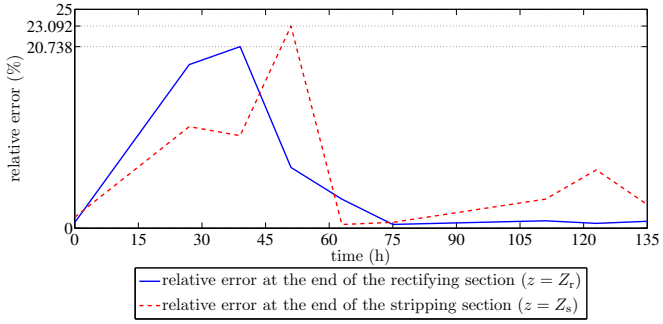


(c) 29 W case.

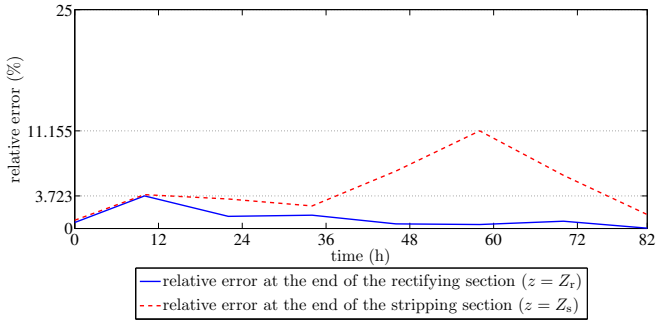
Figure 4: ^{13}C concentration evolution according to the analytical solution and ^{13}C concentrations achieved by the pilot-scale experimental plant.

Fig. 5(a), 5(b), and 5(c) show the relative error of the analytical solution at both ends of the separation column. Explicitly, in all three cases, the relative error was calculated using:

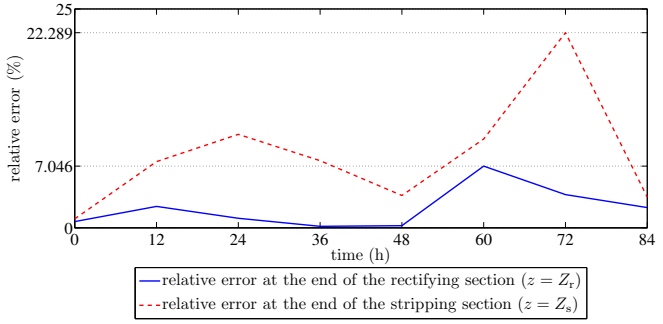
$$\zeta(z = Z_{\mathrm{r}}, t) = \left| \frac{N_{\mathrm{analytic}}(z = Z_{\mathrm{r}}, t) - N_{\mathrm{experimental}}(z = Z_{\mathrm{r}}, t)}{N_{\mathrm{analytic}}(z = Z_{\mathrm{r}}, t)} \right| \tag{105}$$



(a) 24 W case.



(b) 27 W case.



(c) 29 W case.

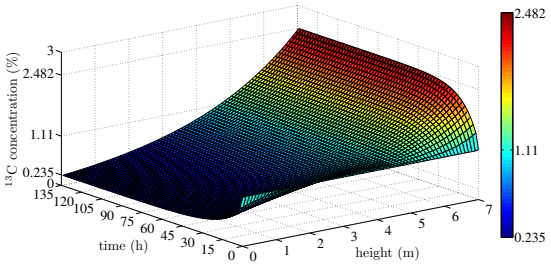
Figure 5: Relative errors between simulated and measured data at the end of the rectifying section (bottom of the column) and at the end of the stripping section (top of the column).

411 for the rectifying section. For the stripping section the relative error was calculated similarly.

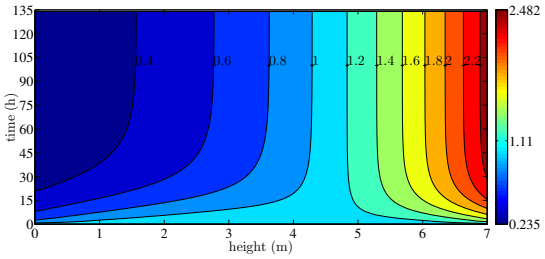
412 Fig. 6(a), 6(b), 6(c), 6(d), 6(e), and 6(f) show the ^{13}CO mole fraction distribution in the

413 column with respect to both height and time. The isotope distribution was obtained by com-

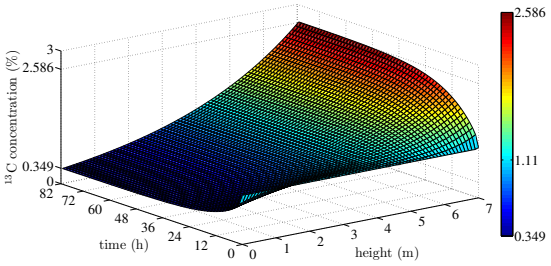
414 puting the analytical solution described by (76) and (77). The simulation results were obtained



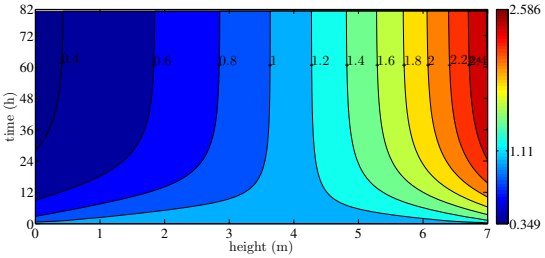
(a) ^{13}C isotope concentration distribution. The electrical power applied to the heater was 24 W.



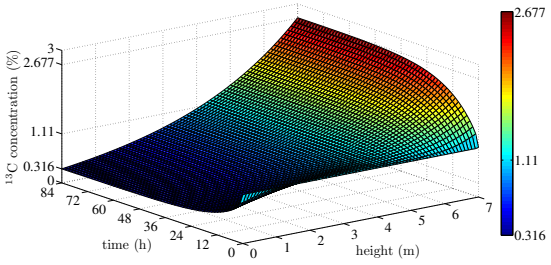
(b) ^{13}C isotope concentration distribution (contour view). The electrical power applied to the heater was 24 W.



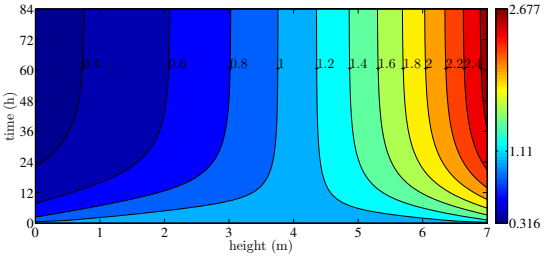
(c) ^{13}C isotope concentration distribution. The electrical power applied to the heater was 27 W.



(d) ^{13}C isotope concentration distribution (contour view). The electrical power applied to the heater was 27 W.



(e) ^{13}C isotope concentration distribution. The electrical power applied to the heater was 29 W.



(f) ^{13}C isotope concentration distribution (contour view). The electrical power applied to the heater was 29 W.

Figure 6: ^{13}C isotope concentration distribution with respect to time and height.

for a 70 discretization divisions applied to the space domain (i.e. a height step of 0.1 m) and a time step of 1800 s emphasizing that the isotopic concentration can be simulated at any moment of time and at any height. The simulation time was approximately 1.5 s in the case of all three experiments.

In Table 4 we have listed the values of the maximum and average relative error at the ends of the separation column, in the case of all three experiments.

Table 4: The values of the maximum and average relative error between simulated and measured data at the ends of the separation column.

$P_{\text{electrical}}$ (W)	$\max\left(\zeta(z=Z_{\text{r}},t)\right)$ (%)	$\max\left(\zeta(z=Z_{\text{s}},t)\right)$ (%)	$\overline{\zeta(z=Z_{\text{r}},t)}$ (%)	$\overline{\zeta(z=Z_{\text{s}},t)}$ (%)
24	20.738	23.092	5.880	6.696
27	3.723	11.155	1.144	4.516
29	7.046	22.289	2.225	8.318

When the electrical power applied to the heater was 24 W, the average relative error at the bottom of the column was 5.8 %, while at the top of the column it was 6.6 %. When the electrical power was 27 W, the average relative error was 1.1 % at the bottom of the column and 4.5 % at the top of the column. In the case of 29 W, the average relative error was 2.2 % at the bottom and 8.3 % at the top of the column.

The volumetric overall mass transfer coefficient is determined by plant parameters such as the internal vapor molar flow rate V, the separation factor α, the heights of the rectifying and stripping sections of the distillation column (Z_{r} and Z_{s}), and to the steady-state values of the concentration achieved at the ends of the separation column. Using the results of Section 4, one can use interpolation to determine the volumetric overall mass transfer coefficient with respect to the above parameters, and thus, expensive experiments could be avoided.

5. Conclusions

Isotope separation processes have a coupled time-space nature and their inputs, outputs, and parameters can vary both in time and space. Modeling of such complex processes requires time and knowledge from a variety of fields. However, finding an appropriate analytic model eases the linking to the physics of the process and brings considerable advantages in understanding the subprocesses and the associated interactions. In this paper we have presented a modeling approach in order to find the analytic expression of a ^{13}C isotope separation process by cryogenic distillation of carbon monoxide. Firstly, after a short review of isotope separation processes, based on the partial differential equation that governs the isotope separation process, we have defined the initial-boundary-value problem. Using the Laplace transform, we have transformed the PDE into a linear homogeneous ODE. Next, we have determined the solution of the ODE and, by using Heaviside's expansion theorem, we have found the inverse Laplace transform. The analytic model

of the isotope separation process followed. The only points where the isotopic concentration is measurable in practice are at the ends of the distillation column. In order to validate the analytic model, we have simulated the evolution of the desired isotope in total-reflux regime, at both the bottom and the top of the column, and compared it with experimental data gathered from an experimental ^{13}C isotope separation plant. The three experiments were conducted in total-reflux regime for different electrical powers that supplied the heating resistance, i.e. 24 W, 27 W, and 29 W. When the electrical power was 24 W, the average relative error at the bottom of the column was 5.8 %, while at the top of the column it was 6.6 %. In the case of 27 W, the average relative errors were 1.1 % at the bottom of the column and 4.5 % at the top of the column. When the electrical power was 29 W, the average relative error at the bottom of the column was 2.2 % and 8.3 % at the top of the column, showing that the analytic model is a valid modeling approach.

Future studies will involve withdrawal-regime isotope separation experiments, in order to further analyze the analytic model and the volumetric overall mass transfer coefficient. Also, the effects of the packing over the hold-up and response time, internal flow rates, and production will be treated in order to optimize the isotope separation process. Using the obtained analytic model, the effects of the hydrodynamical variables fluctuations over the separation process will be studied from the control point of view.

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