Revista de Chimie
https://revistadechimie.ro
https://doi.org/10.37358/Rev. Chim.1949

Computational Design Applied to Equilibrium-Staged and Rate-Based Absorption Processes

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Abstract: *Simulators are of great interest in Chemical Engineering because they facilitate process optimization and help evaluate different solutions through the so-called "what-if" approach. They include the most advanced thermodynamical models and complete libraries for the calculation of physicochemical properties and estimation of phase equilibria data which are successfully integrated in the process design. Moreover, simulators allow addressing both stationary and batch operations. For this reason, their use in the design of Industrial Chemistry processes has gained much acceptance in the last decades. Even so, simulations should be accompanied by another computational tool which allows the professionals to implement specific algorithms which relate inputs and outputs, so as to get the most out of the computing power. We herein exemplify how Aspen Plus and Mathcad Prime software packages were successfully integrated in a case study on the removal of carbon disulphide by contact with a paraffinic oil in an absorption tower. This absorption operation was studied in both trayed and packed columns. Regarding the first contact type, i.e. trays, Mathcad's powerful programming tool and graphical interface enabled to corroborate and to better understand the effect of temperature on the number of theoretical stages previously observed with Aspen Plus.*

Keywords*: chemical engineering, absorption, simulations, design, computing*

1. Introduction

Absorption, which involves the transfer of one (or several) solute(s) from a gas phase into a liquid phase, is one of the most extensive practices in the chemical industry. Absorption is used to separate gas mixtures, remove impurities, or recover valuable chemicals [1]. Professionals working in the chemical processes industry all over the world, hence, need to address the design and optimization of this unit operation. According to the contact method, the operation can be categorized into equilibrium-staged and continuous contact. Equilibrium-staged absorption requires to determine the number of theoretical plates, whilst for a continuous contact absorption process the packing height has to be calculated. In both cases, professionals demand computational strategies which are flexible enough so as to analyze the effect of the different variables involved in a fast and effective way. Under such circumstances, the incorporation of process simulators can have many benefits, as they provide great flexibility for examining "what-if" scenarios and for developing process optimization [2-4]. After distillation, absorption is probably the second most reported application of process simulators, with Aspen Plus and Aspen Hysys being the most used software packages. This is the case, for example, of a book edited by the American Institute of Chemical Engineering (AIChE) on general process design, which presents a case study dealing with the removal of HCl from air in a Pall rings column [5]. Al-Malah published a book reporting the use of Aspen Plus in Chemical Engineering applications, which includes a case study of CO_2 removal from gas natural in a trayed scrubber [6].

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Despite the above reported list of proved advantages, Chemical Engineering professionals need complementary computational tools with which they can implement their own algorithms targeted to achieving a more efficient control on the way simulators handle the key process variables. In the present research, we report the parallel use of Aspen Plus simulations and Mathcad Prime calculations in order to create the most skilled modelling environment. Mathcad Prime is a powerful math software for engineering calculations with an easy-to-use interface, natural mathematical notation, units intelligence, and which integrates calculations, graphs, text and images. The software has been utilized, for example, in the optimization of wastewater treatment [7] and for reaction engineering design [8]. By using Mathcad, the algorithms involved in the design of equilibrium-staged and rate-based absorption columns were readily implemented, and the results obtained were compared with the simulations.

With this contribution we demonstrate that, if successfully integrated, Aspen Plus and Mathcad may catalyze a more efficient design of chemical processes, in this particular case involving mass transfer between phases, and a better understanding on the effect of the key variables.

2. Materials and methods

Detailed information is herein presented on the removal of a pollutant (carbon disulfide) from a nitrogen gas stream, by counter-current contact with a light paraffin (n-tridecane) in: a) a trayed column; b) a random packing (Raschig rings) tower. The examples will, hopefully, provide professionals with some key guidelines on how to address process design in such a way that enables to get the most out of the latest computational tools available in the market. With that purpose, the process simulator Aspen Plus v.9 (from the AspenTech company, USA) and the Engineering maths software Mathcad Prime v.4 (from the PTC company, USA) were used. First, the design was carried out by using the simulator. The process was fast and simple. Even though, some outcomes still remained unclear in terms of the core reason behind. So, the approach consisted in utilizing the Mathcad functions to build process models that shed light on the issue. Mathcad and Aspen Plus (used as reference) results were then contrasted and compared.

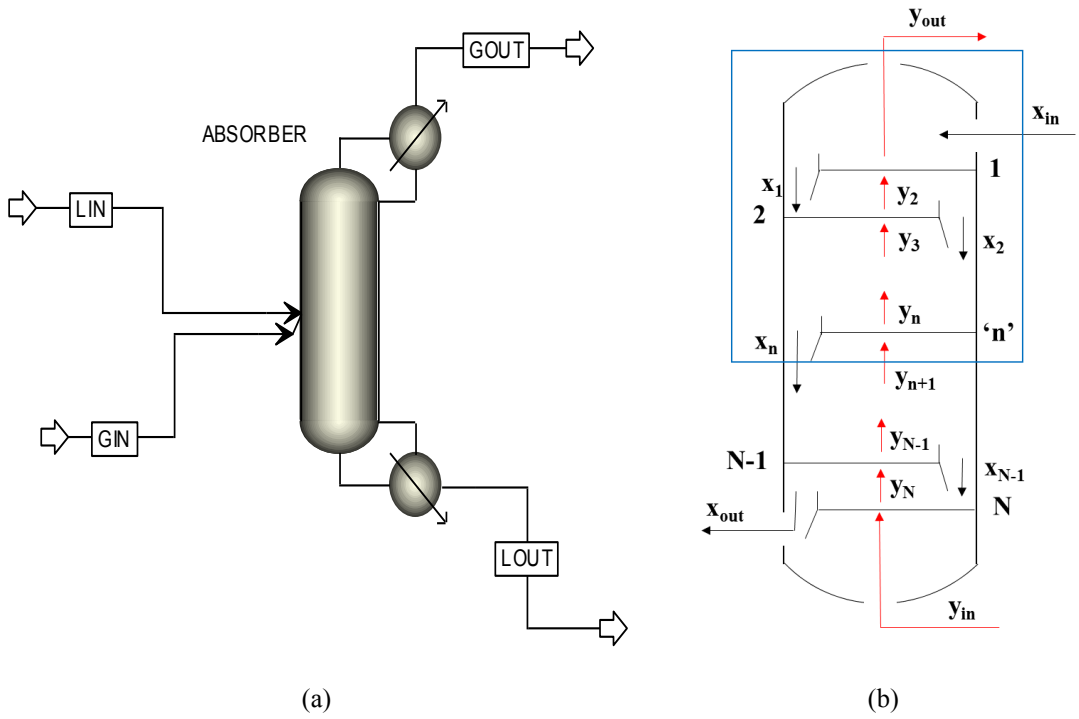
3. Results and discussions

Case study 1a: Design of a trayed column

A mixture of CS_2-N_2 (ideal behavior) is to be washed with n-tridecane (n-C_{13}) in a sieve plates column. The feed enters the column at a rate of 0.370 m^3/s, at 20 ºC and 1 atm. The solute molar fraction is to be reduced from 6.58 to 0.6 %. The n-tridecane mass flow rate, at 20 ºC, is 5900 kg/h.

The problem was firstly approached with Aspen Plus. Under the "Properties" environment, the components (carbon disulfide, nitrogen and n-tridecane) are chosen, and the IDEAL property method is specified. Subsequently, under the "Simulation" environment, a RadFrac type column is selected from the "Columns" tab within the Model Palette. The column is renamed as ABSORBER. Four material streams are connected to the column: two inlets, L_{IN} and G_{IN}, and two outlets, L_{OUT} and G_{OUT} (Figure 1a).

Then, the entering streams L_{IN} and G_{IN} are specified in terms of flow rate, composition, temperature and pressure according to the problem statement. The following step is to establish conveniently the setup options corresponding to the absorption column. Hence, "Equilibrium" is used as the calculation type for an equilibrium-staged column with no condenser and no reboiler (this is only for distillation purposes). Valid phases (vapour-liquid) and convergence method (wide-boiling) are also specified, and a first trial of 4 theoretical stages (N) is used. The column pressure is set to 1 atm, and the material streams location is properly assigned. Upon running the simulation, convergence is attained very fast and the results are available from the folders "Results" and "Stream Results" within Blocks>ABSORBER.



(a) (b)

Figure 1. (a) Aspen plus flowsheet for the absorption column in case study 1a; (b) Schematic diagram of the absorption plate column internals

The results allow concluding that: a) the outlet gas stream does not meet the specification (y_{out}=0.0068>0.006), so the number of stages has to be increased; b) the process is not isothermal (due to the heat of absorption, the liquid and vapour temperatures inside the column can achieve up to nearly 29 ºC); c) the transfer of nitrogen and n-tridecane are negligible, so they can be considered simply as "carriers", and the problem can be tackled as single solute absorption. When the number of equilibrium stages is raised to N=5, the column is under specifications, with y_{out}=0.0046 (<0.006). This means that the number of equilibrium stages is in fact a fractional between 4 and 5.

The Mathcad software facilitates the visualization of the solving procedure. We will assume that the Raoult's law applies to the absorption equilibrium studied, so that vapour and liquid compositions can be related by:

$$y_n = m(T) \cdot x_n \tag{1}$$

$$m(T) = \frac{10^{A-B/(T+C)}}{P} \tag{2}$$

where: y_n and x_n are the solute molar fractions of gas and liquid phases, respectively, leaving the same stage (in equilibrium); A, B, C are the Antoine's equation constants [9] for the solute, CS_2; T and P are the column temperature and pressure, respectively. As for the operating line, a straight line is obtained if the mass balance (over the tower section delimited by the blue line in Figure 1b) is written in terms of "solute-free" compositions for gas and liquid, Y and X, respectively:

$$\frac{L_S}{G_S} = \frac{Y_{n+1} - Y_{out}}{X_n - X_{in}} \tag{3}$$

where: G_S and L_S are the flow rates of N_2 and n-tridecane, respectively.

Some programming is required in order to solve this problem with Mathcad. We need to develop a logic algorithm which steps off the stages, with alternate use of the operating and equilibrium lines, until a specified condition is met. Figure 2 shows the Mathcad code which enables the visualization of

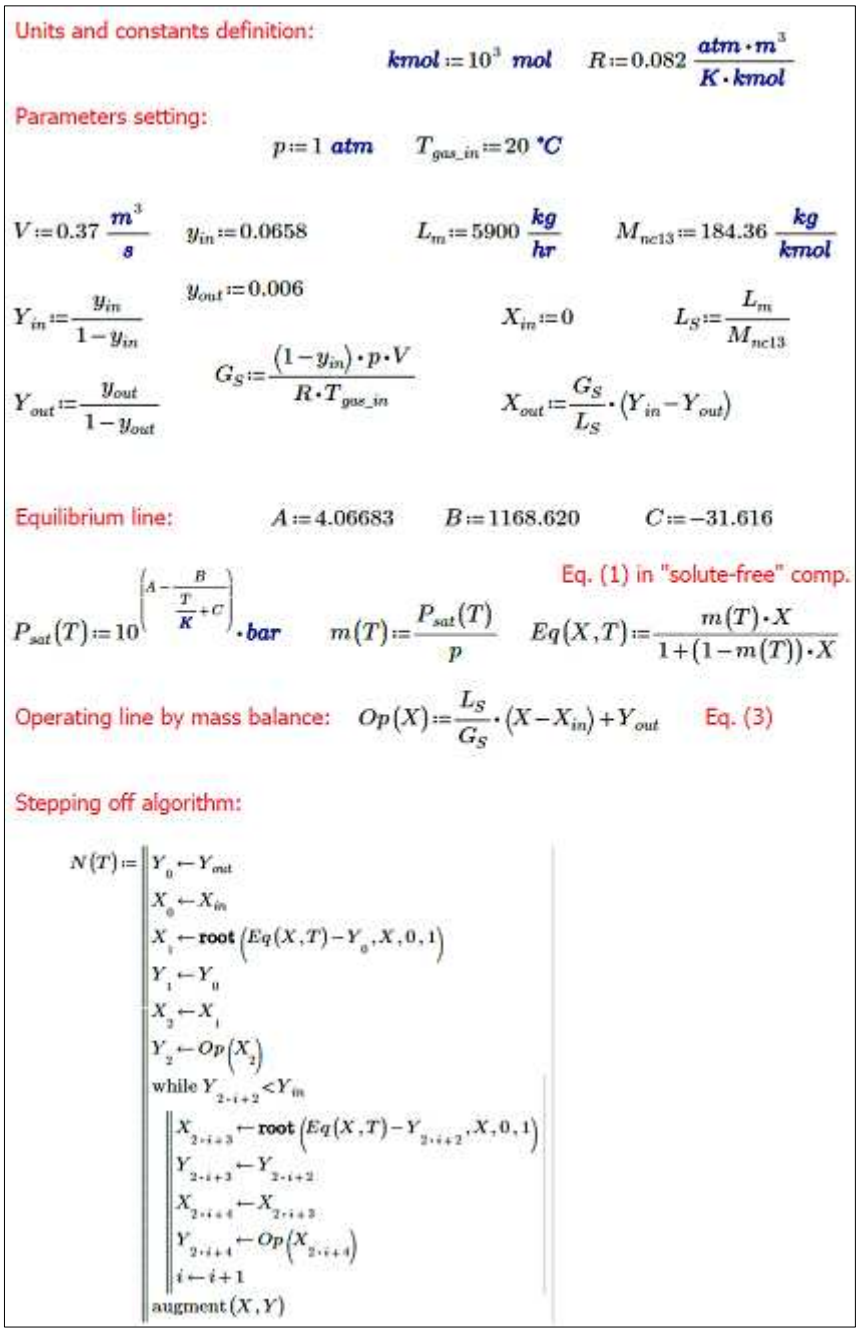


Figure 2. Mathcad worksheet for the calculation of the number of theoretical contacts in an absorption plate column.

the graphical solutions displayed in Figure 3. Starting from the point (X_{in},Y_{out}), which represents the column top concentrations, the program steps off the stages until the $Y \geq Y_{in}$. Please, note that the solution is the same no matter if the stages are stepped off from the top down (Figure 3) or, alternatively, bottom up.

For the sake of facilitating the calculations, the operation will be assumed isothermal. However, if temperature is set to 20ºC, the number of equilibrium stages results between 3 and 4 (Figure 3a), which does not match the above result provided by the Aspen Plus simulation. Instead, for an average column temperature of 25ºC, the number of theoretical plates required is between 4 and 5. The code is flexible enough so as to analyze the effect of temperature, because both N(T) and Eq(X,T) are expressed as a function of T. In consequence, Figures 3a and 3b provide clear evidence of the importance of

considering the heat of absorption, which increases the streams temperatures, yielding less favourable equilibrium conditions.

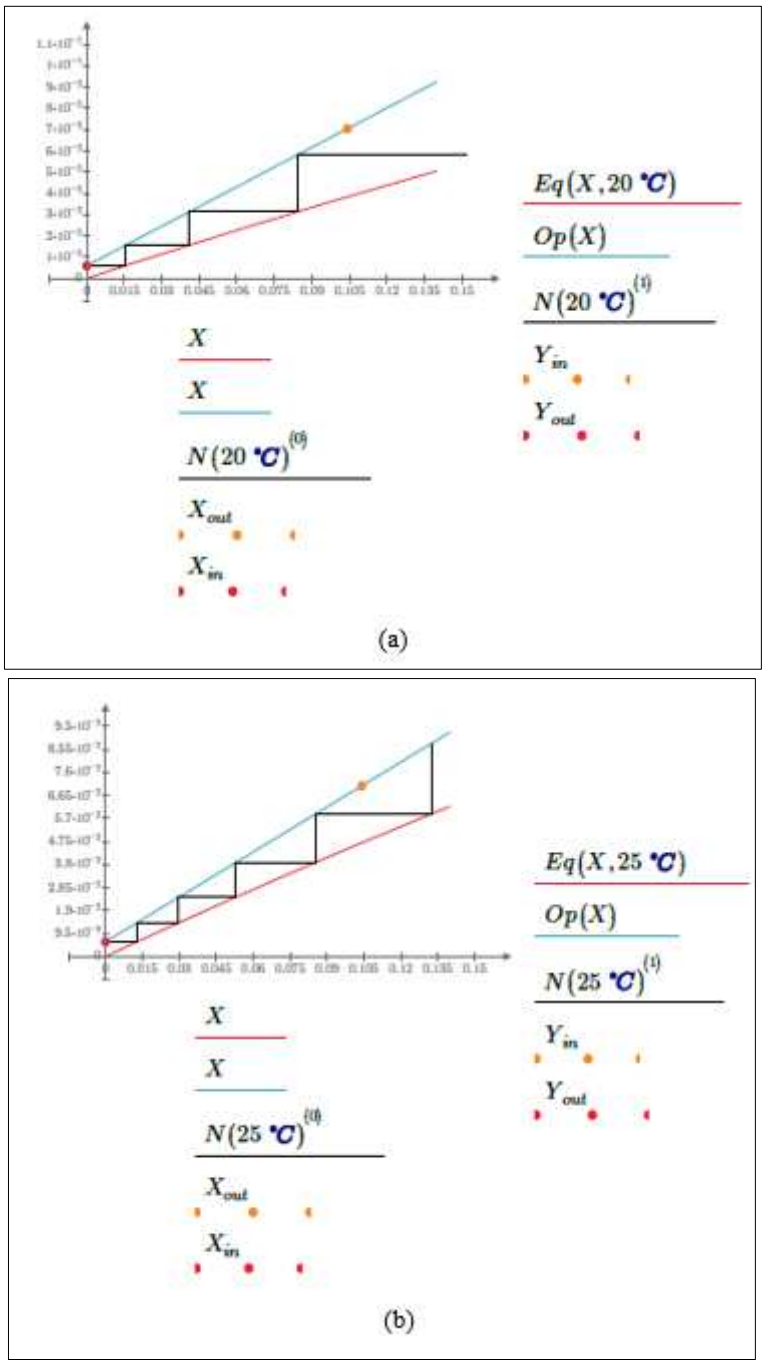


Figure 3. Graphical solutions of number of theoretical stages for case study 1a: a) 20 ºC; b) 25 ºC

Case study 1b: Design of a packed bed column

The separation described in case study 1a above will be carried out in a countercurrent packed bed column with 1-inch ceramic Raschig rings, working at a flooding percentage of 75 %.

The selection of components and method, and setting up and specifying the material streams entering the column is common to the above description in case study 1a. The main difference is the calculation type: "Rate-Based" is now chosen from the drop-down list because continuous contact

requires the use of mass transfer coefficients. As the packing is continuous, the number of stages does not refer to theoretical plates but to the number of sections that the software uses to plot the profiles (of temperature, flow rates, compositions, etc.). We enter, for example, N=6.

From Blocks>ABSORBER>column internals, a case is created so that the packing type (MTL ceramic 1-in Raschig rings) is selected for the whole column including the 6 sections. A first estimate of the column height has to be provided, so that the software provides the gas outlet concentration. For example, for a packing height of 3 m, y_{out} is 0.0081, which is higher than the required value (0.006). By using the option "interactive sizing", and entering a value of 75 for % approach to maximum capacity (L/V), i.e. flooding, the software returns a diameter of 0.828 m, as calculated for the "Eckert" pressure drop method. Other methods yield different results (Table 1).

Table 1. Tower diameter and height, as a function of the aspen plus method chosen

Pressure drop calculation method	Pressure drop calculation method
Eckert, D = 0.828 m	Bravo-Fair82, z = 3.81 m
Gpdc-85, D = 0.906 m	Onda-68, z = 3.40 m
Wallis, D = 0.753 m	

Subsequently, the mode is switched to "rating" so as to perform calculations on the column height. In Flowsheeting options>Design Specs, we set a new specification, by assigning the outlet gas mole fraction a value of 0.006, indicating the column height (variable: CA-PACK-HT) as manipulated variable. In this way, the software returns a value of 3.81 m for the column height if the method "Bravo-Fair82" is used for the calculation of mass transfer coefficients and interfacial areas. Other methods, which can be selected from Blocks>ABSORBER>Rate-based Modeling> Rate-based Setup, yield different results (Table 1), demonstrating how important this issue is for a correct interpretation of the results displayed by Aspen Plus. Another important issue is to indicate "countercurrent" as the Flow model.

With the aid of Mathcad, the packing size can be determined accurately. The required height for a packed bed absorption column can be assessed as follows:

$$z = HTU_G \cdot \int_{y_{out}}^{y_{in}} \frac{(1-y)_{\text{int}M}}{(1-y)\cdot(y-y_{\text{int}})} \cdot dy \tag{4}$$

$$(1-y)_{\text{int}M} = \frac{(1-y)-(1-y_{\text{int}})}{Ln\left(\frac{1-y}{1-y_{\text{int}}}\right)} \tag{5}$$

where: z is the column height; HTU¬G is the average height of a transfer unit for the gas; and the integral is the number of transfer units (NTU), with y and y_{int} being the bulk and interface gas mole fractions, respectively, as shown in Figure 4a.

Please, note that the correlation used below for HTU_G is valid for equimolar counter-difussion (distillation). Hence, for absorption the value has to be corrected by introducing the log mean concentration difference, $(1-y)_{intM}$ in Eq. (5). Moreover, $HTU_G=G/(k_G \cdot a \cdot S)$, with G being the gas molar flow rate, $k_G \cdot a$ the volumetric mass transfer coefficient and S the area of the column transversal section. According to the Whitman [10] two-film theory, the resistance to mass transfer (by molecular diffusion) is only localized in the gas and liquid stagnant films at both sides of the interface, with the interfacial concentrations being determined by the equilibrium relationship (Figure 4a).

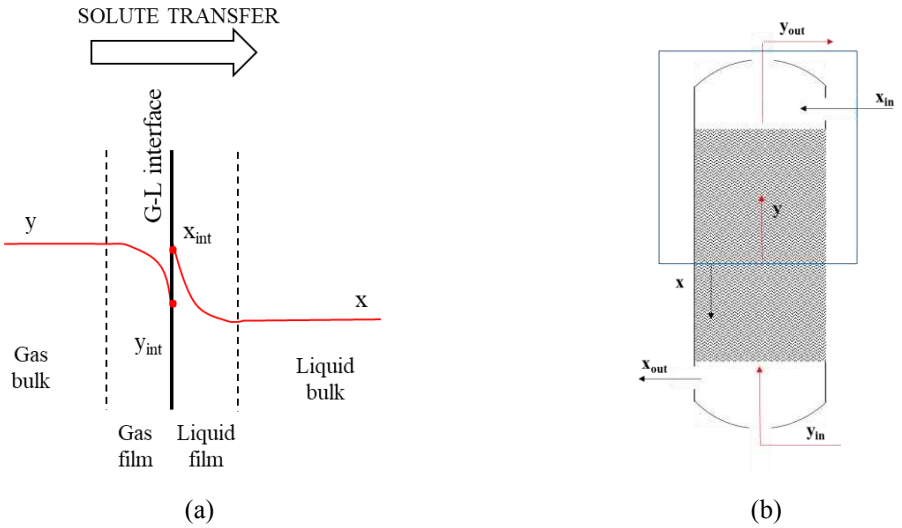


Figure 4. (a) Concentration profiles at both gas and liquid phases; (b) Schematic diagram of the absorption packed column

Based on that, the interface concentrations can be obtained by solving simultaneously these two equations:

$$-\left(\frac{HTU_G}{HTU_L}\cdot\frac{(1-y)_{\text{int}M}}{(1-x)_{\text{int}M}}\cdot\frac{L}{G}\right)=\frac{y-y_{\text{int}}}{x-x_{\text{int}}} \tag{6}$$

$$y_{\text{int}}=m(T)\cdot x_{\text{int}} \tag{7}$$

where: HTU_G and HTU_L are the heights of a unit transfer for gas and liquid, respectively; G and L are the molar flow rate of gas and liquid (at the most unfavorable position, i.e. column bottoms), respectively. Equation (7) is computed at 25ºC, as in case study 1a. For the whole tower height, average values of HTU_G and HTU_L were calculated as described in [11] by means of the Bolles and Fair [12] correlations for random packing, including Raschig rings:

$$HTU_L=\phi C_{fl}\cdot Sc_L^{0.5}\cdot\left(\frac{z}{10}\right)^{0.15} \tag{8}$$

$$HTU_G=\frac{\psi\cdot Sc_G^{0.5}\cdot d_c^{\,1.24}\cdot\left(\frac{z}{10}\right)^{1/3}}{\left(W_L\cdot f_\mu\cdot f_\rho\cdot f_\sigma\right)^{0.6}} \tag{9}$$

where: Sc_G and Sc_L are the dimensionless Schmidt numbers for gas and liquid, respectively; ϕ and ψ are parameters related to the packing type and size; C_{fl} is a parameter related to flooding; z is the tower height; d_c is the tower diameter or 2 ft (which is lesser); W_L is the liquid mass velocity; and f_μ, f_ρ, f_σ are viscosity, density and surface tension correction factors. Average values of the physical properties were taken from Aspen Plus. The height provided by Aspen Plus was used as a first estimate of z. Upon calculation of z by Eq. (4), HTU_G and HTU_L were recalculated in successive iterative rounds until convergence was attained. The final values were 0.876 and 1.321 ft for HTU_G and HTU_L, respectively. The tower height was computed as 2.90 m, so being smaller than those in Table 1 for the two other methods. The use of the Mathcad FIND function facilitated the calculations, with no need of programming. Such a function enabled the simultaneous solution of Equations (5) and (6) to be determined accurately, and extended to a set of input (x, y) pairs corresponding to the operating line

"bulk" concentrations between (x_{out}, y_{in}) and (x_{in}, y_{out}), as shown in Figure 4b. Figure 5 displays the worksheet. The interface concentration profiles are visualized in the form of column vectors. The computing of Equation (4) is made by using the trapezoid rule, with the number of intervals, N, being tailored so as to improve the accuracy of the numerical integration result with no need for further effort. From the number of theoretical plates (NTP=4.5) and the packing height (z=2.90 m), the height equivalent to a theoretical plate, HETP=z/NTP is estimated to be about 0.65 m.

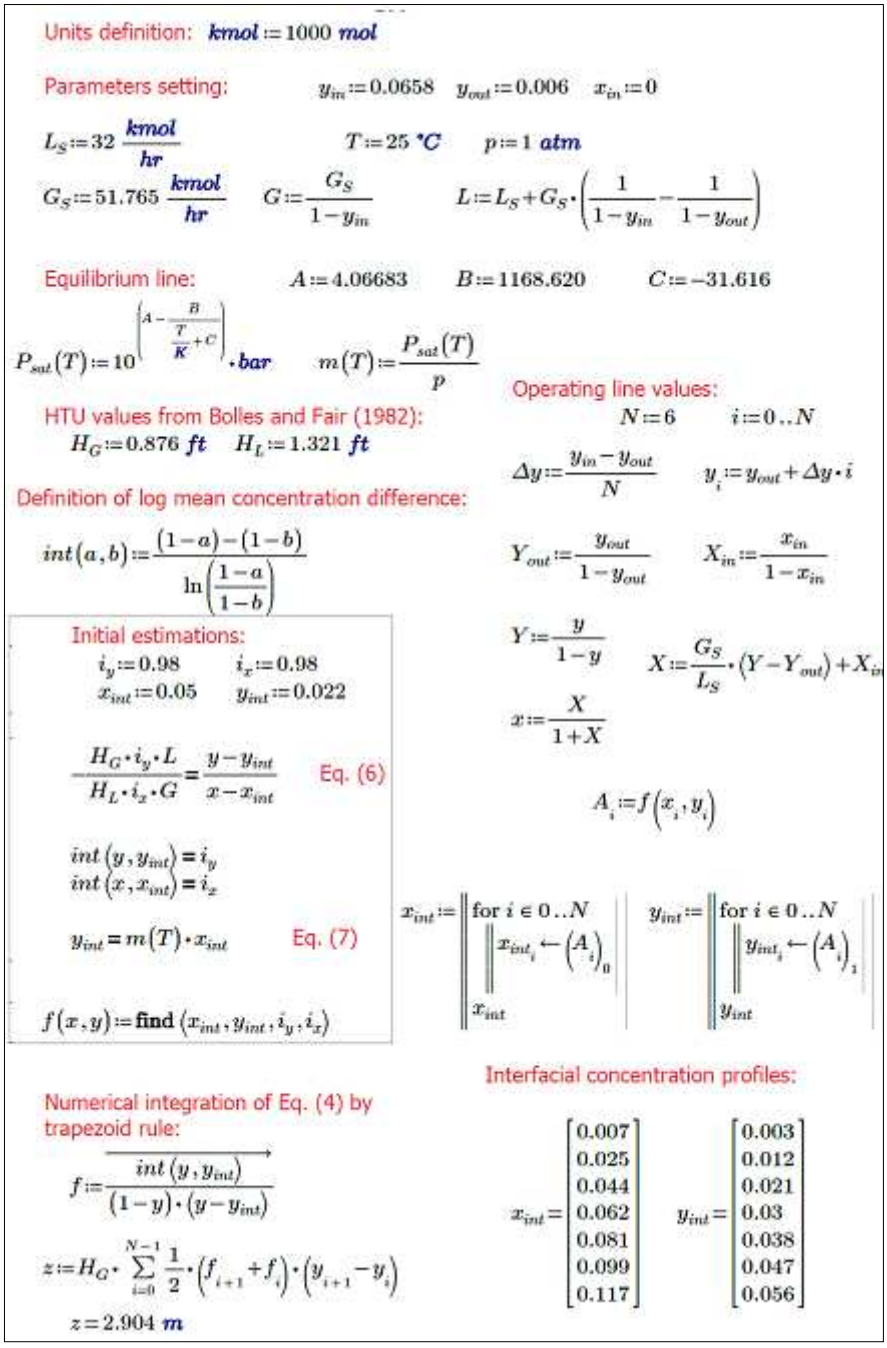


Figure 5. Mathcad worksheet for the calculation of the height of a packed absorption column

4. Conclusions

We herein presented a methodological approach based on computational tools for the study of absorption columns in Chemical Engineering. The proposal provided great flexibility for evaluating

the effect of different variables. From Aspen Plus, we observed that the heat of absorption caused a significant temperature increase, from 20 up to nearly 29ºC at certain column locations; N_2 and n-C_{13} can be considered as "carriers", so the problem can be treated as a single solute absorption; the method used for the flooding point determined the tower diameter, whilst the tower height depended on the equation for the mass transfer coefficients calculation. In this case, the Bravo-Fair82 resulted to be more conservative than the others, yielding much larger tower heights. By using Mathcad, we implemented a logic algorithm that enabled to visualize the calculation of the number of theoretical stages, and to study the effect of temperature. Temperature was seen to greatly affect the absorption equilibrium. An increase in temperature yielded an equilibrium curve with higher slope and thus a larger number of theoretical stages. Mathcad also enabled to find the interfacial concentrations profile all along the column height.

Acknowledgments: Authors acknowledge: Vicerrectorado de Innovación y Empleabilidad de la Universidad de Huelva for supporting the project entitled "La enseñanza de la Ingeniería Química en el Tercer Milenio: integración efectiva de herramientas computacionales" belonging to XXI Convocatoria de Proyectos de Innovación Docente; Cátedra CEPSA for funding the ASPEN ONE license; and Escuela Técnica Superior de Ingeniería (ETSI) for funding the PTC MATHCAD PRIME license.

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Manuscript received: 2.05.2020