MINIMUM NUMBER OF TRANSFER UNITS AND REBOILER DUTY FOR 
MULTICOMPONENT DISTILLATION COLUMNS

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Abstract

Some guidelines to evaluate distillation columns, considering only basic thermodynamic data and principles, are provided in this paper. The method allows a first insight to the problem by simple calculations, without requiring column variables to ensure rational use of energy and low environmental impact. The separation system is approached by two complementary ways: minimum and infinite reflux flow rate. The minimum reflux provides the minimum energy requirements, and the infinite reflux provides the feasibility conditions. The difficulty of separation can be expressed in terms of number of transfer units (NTU). The applicability of the method is not mathematically limited by the number of components in the mixture. Several mixtures are rigorously simulated as illustrative examples, to verify the applicability of the approach. The separation of the mixtures, performed by distillation columns, is feasible if a minimum NTU can be calculated between the distillate and bottom compositions. Once verified the feasibility of the separation, the maximum thermal efficiency depends
only on boiling point of bottom and distillate streams. The minimum energy requirements corresponding to the reboiler can be calculated from the maximum thermal efficiency, and the variation of entropy and enthalpy of mixing the distillate and bottom streams.

**Keywords:** distillation column, thermal efficiency, minimum number of transfer units, residue curve map, feasibility, minimum reboiler duty, infinite/infinite analysis.

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**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$</td>
<td>distillate flowrate (kmol/h)</td>
</tr>
<tr>
<td>$L$</td>
<td>reflux flowrate (kmol/h)</td>
</tr>
<tr>
<td>$M$</td>
<td>number of chemical reactions</td>
</tr>
<tr>
<td>$NC$</td>
<td>number of components in the system</td>
</tr>
<tr>
<td>$Q$</td>
<td>overall thermodynamically calculated distillation column duty (kW)</td>
</tr>
<tr>
<td>$Q'$</td>
<td>distillation column duty required for mixture separation (kW)</td>
</tr>
<tr>
<td>$Q''$</td>
<td>enthalpy of vaporization flow for the distillate stream (kW)</td>
</tr>
<tr>
<td>$Q_{\text{min}}$</td>
<td>minimum distillation column duty, estimated by simulation (kW)</td>
</tr>
<tr>
<td>$R$</td>
<td>ideal gas constant, 8.314 kJ/(kmol·K)</td>
</tr>
<tr>
<td>$r$</td>
<td>reflux ratio (kmol/kmol distillate)</td>
</tr>
<tr>
<td>$r_j$</td>
<td>reaction rate of the reaction j (kmol/(kmol·h))</td>
</tr>
<tr>
<td>$r_{\text{min}}$</td>
<td>minimum reflux ratio (kmol/kmol distillate)</td>
</tr>
<tr>
<td>$S$</td>
<td>entropy (kJ/(kmol·K))</td>
</tr>
</tbody>
</table>
\begin{itemize}
  \item \( T \) \hspace{1cm} \text{temperature (K)}
  \item \( T \Delta S_{\text{sep}} \) \hspace{1cm} \text{entropic contribution to energy of mixing (kW)}
  \item \( x_i \) \hspace{1cm} \text{mOLE fraction of component } i \text{ in liquid phase}
  \item \( \mathbf{y} \) \hspace{1cm} \text{vector of vapour mole fraction in direct contact with the liquid}
  \item \( y_i \) \hspace{1cm} \text{mOLE fraction of component } i \text{ in vapour phase}
  \item \( \Delta H_{\text{mixing}} \) \hspace{1cm} \text{enthalpic contribution to the energy of mixing (kW)}
  \item \( \Delta S_{\text{sep}} \) \hspace{1cm} \text{entropy of mixing/separation (kW/K)}
  \item \( \xi \) \hspace{1cm} \text{dimensionless space coordinate}
  \item \( \nu_{r,j} \) \hspace{1cm} \text{net generation of moles from the reaction } j
  \item \( \nu_{i,j} \) \hspace{1cm} \text{stoichiometric coefficients for component } i \text{ in chemical reaction } j
  \item \( \eta \) \hspace{1cm} \text{thermal efficiency of a Carnot cycle}
  \item \( \Lambda \) \hspace{1cm} \text{liquid hold-up in the rectifying section, m}^3
  \item \( \lambda \) \hspace{1cm} \text{molar enthalpy of vaporisation (kJ/kmol)}
  \item \( \tau \) \hspace{1cm} \text{retention time, h}
\end{itemize}

\begin{itemize}
  \item \textbf{Subscripts and superscripts}
  \item \( c \) \hspace{1cm} \text{condenser}
  \item \( \text{dist} \) \hspace{1cm} \text{distillate stream}
  \item \( \text{feed} \) \hspace{1cm} \text{feed stream}
  \item \( i \) \hspace{1cm} \text{component } i
  \item \( j \) \hspace{1cm} \text{chemical reaction } j
  \item \( \text{min} \) \hspace{1cm} \text{minimum}
  \item \( r \) \hspace{1cm} \text{reboiler}
\end{itemize}
1. Introduction

At early stages of process strategy for a new design, i.e. conceptual design step, it is important to gather the required information to decide when it is worth to proceed to further detailed studies, avoiding the possibility to obtain novel design with low improvement potential. This first decision should be taken based on thermodynamic data, before details about the process are available. This lack of data is compensated by the fact that in early design stages, process operating parameters exact values are not expected. Therefore, instead of fixing an arbitrary reflux to the column, it would be preferable to fix it to infinite, or to its minimum value. Although it is not industrially realistic, these assumptions provide the potential for the proposed process, and the alternative processes to be compared easily, based on fast calculations.

One of the methods simplifying the distillation column model is the infinite/infinite analysis. The Mass Equilibrium Summation Enthalpy (MESH) rigorous model used by most of commercial process simulators usually has five degrees of freedom which basically are covered by the following parameters: distillate flow rate, reflux ratio, number of stages, feed stage and pressure, at a specified feed stream. Assuming an
infinite reflux flow rate, then the feed stream has no influence on the set of feasible column profiles, only the pressure influences them. Once fixed the feed stream and the distillate flow rate, the compositions of bottom and distillate streams are defined by mass balance, that fulfils the condition of feasibility (existence of a column profile between the distillate and bottoms compositions) and that the column profile contains a singular point (pure component or azeotrope) according to the infinite/infinite hypothesis [1]. The infinite/infinite analysis can provide easily interesting insights of complicated processes that would be difficult to obtain by rigorous simulations, e.g. [2]. The uncertainty between unfeasibility and mathematical convergence difficulties is avoided. This analysis has been recently extended to study kinetically controlled reactive distillation columns by Plesu et al [3], where the importance of energy savings is underlined for any small improvement of the distillation process. The above mentioned advantages of the infinite/infinite analysis allow to be used and computer implemented by important chemical companies [4].

However, the assumption that some parameters are infinite, does not imply that all the others must be also infinite, all the intensive variables, such as concentrations, degrees of recovery, and temperatures, remain finite. In the same time, an infinite reflux flow rate inside the distillation column, does not exclude finite input and output flow rates. No output streams are obtained at total reflux (D=0), however these can be considered, when the reflux flow rate is infinite (L → infinite). Similarly, an infinite reflux ratio can be obtained when L → infinite, or D is zero (r=L/D), and the infinite/infinite analysis assumes L infinite. At infinite reflux, a certain separation in two output compositions is achieved by a minimum number of transfer units, who in turn can be infinite. The infinite number of transfer units is generated by the presence of a singular point, and their location is around this point, and not all along the column height.
Usually, the feasibility of a certain separation is checked by the so-called residue curve maps, which are assumed to represent graphically a set of composition column profiles of a packed column, operated at infinite reflux flow rate [5]. The determination of the number of transfer units (NTU) for these profiles provides a quantification of the difficulty of the separation, which is not provided directly by the residue curves alone [6, 7]. The agreement between residue curves and packed column profiles at infinite reflux has been corroborated by some authors [8, 9] but for reactive distillation it is not always true [10].

On the other hand, nowadays, the main drawback at the initial stage of process design is the lack of a commonly used, non-iterative and fast method to estimate the energy requirements of a distillation column [11], and usually these are determined later by rigorous simulation (MESH model) [12]. A simultaneous approach is required to link the models of the distillation columns with those of process heat exchange network [13]. Estimation of distillation columns minimum energy requirements would be very useful, as input for pinch analysis, which could provide an early value for the minimum energy requirement of the global process. The environmental and economic aspects can be assessed only after the energy requirements are determined. Energy efficiency improvement for existing processes contributes to CO$_2$ emissions reduction [14]. Resource (energy) efficiency is a very important future trend in Process Systems Engineering [15]. An exact cost value is very difficult to calculate, but a value proportional to the cost can be provided for a distillation column, based on the minimum number of transfer units (NUT$_{\text{min}}$) required and the minimum reboiler duty [16].

Hence, this paper focuses on the determination of minimum heat duty requirements of an adiabatic distillation column, considering only thermodynamic data and principles,
as a basic method towards understanding and application to some more special schemes, such as vapour recompression (e.g. [17], [18]), heterogeneous azeotropic distillation [19], diabatic columns, divided wall column. Therefore, a divided wall column can be modelled as combination of adiabatic distillation columns [20] or as a column globally adiabatic [21] because the heat exchange takes place just internally. The lower energy consumption of the divided wall columns can be related to higher second law efficiency [22].

2. Method development

2.1 Brief state of the art of methods to calculate distillation column parameters

The available methods to calculate distillation columns parameters are classified in three main groups [24]: rigorous simulation models, stage by stage calculations and analysis fixing parameters at limit conditions. The rigorous simulation models require have as input data the reflux, number of stages (discrete variable) and feed plate among the variables provided, e.g. MESH model [25] and the product purities are output data. The resolution of these models requires a high computation effort as the model is made of a large number of equations that are solved together until convergence is achieved. Moreover, it is the key product purity that is usually known and not the column parameters required by the model.

The second group, the stage by stage calculation models, deals with the sequential resolution of the model as a consequence of using a product composition as input parameter. This simpler resolution of the model is based on the fact that the data flow
can be inverted as long as the number of degrees of freedom of the distillation unit is the
same (Figure >>>>>>). The key-component composition in an output stream calculated
from the rigorous models is used now as input stream while the number of stages
becomes a calculated output. For binary mixtures, McCabe-Thiele method assumes
mass balances and constant molar overflow while Ponchon Savarit method takes into
account the energy balances e.g. [26]. The input data are the product key component
purity and an optimal feed plate condition that minimizes the required number of stages,
while the number of stages and optimal feed plate becomes output data. The reflux is
usually fixed according to a rule of thumb that calculates its optimum value starting
from its minimum value (in the interval of 1.2 to 1.5 times the minimum). The stage by
stage method can be extended to ternary mixtures, but in this case two degrees of
freedom are required to define the output stream, e.g. Boundary Value Method [27]
[28]. A further increase in the number of components cannot be easily handled due to
the limitation of the five degrees of freedom available in the distillation column. Three
degrees of freedom are fulfilled when specifying the pressure (affects thermodynamics),
reflux (direct influence on operation costs) and number of stages (direct influence on
capital costs), i.e. the reflux and number of stages are required to optimize the column.
These drawbacks appearing for multicomponent mixtures can be solved searching the
distillate composition that requires the shortest line from distillate to bottoms
composition becoming an optimization problem [29] [30]. This criteria of the shortest
line is an approximation of the lower number of stages criteria used by McCabe Thiele.
The above mentioned methods can be used to calculate the minimum reflux by
decreasing the reflux value until the number of stages becomes infinite. However, the
methods are simplifying from the beginning the model, assuming infinite number of
stages and require less computational effort to calculate the minimum reflux.
The third group of methods simplifies the model by fixing the number of transfer units and/or reflux at boundary conditions, i.e. minimum or infinite values. Infinite reflux means that for non-reactive packed column, its column composition profile matches a section of a residue curve. Infinite NTUs means that the column composition profile will reach a pinch point (non-evolution of the concentration). Infinite NTUs and infinite reflux means that the pinch points reached are singular points. The Static Analysis [32] assumes infinite reflux flow rate and minimum NTU. The Static Analysis is used to provide a feasible value for distillate and bottoms streams compositions to be used in the stage by stage calculation models, whose results are then employed as initialization values of rigorous models [24]. The assumption of finite reflux and infinite NTU is used by the pinch-based methods to calculate the minimum reflux under the Zero Volume Criterion [32], Minimum Angle Criterion [33] or Eigenvalue Criterion [34]. All these criteria suffer the drawback that the selection of the relevant pinch points can be rather complicated, particularly for mixtures with more than three components. The Rectification Body Method [34] [35] calculates all the pinch points for the rectifying and stripping sections and defines a polyhedron body for each section where the pinches are the vertex. The minimum reflux corresponds to the point where both bodies intersect each other. When a column profile composition is known, this point can be used as initial value for a stage by stage calculation model. This occurs in a distillation column operated at minimum reflux characterized by a feed pinch. The feed pinch composition can be calculated by the Rectification Body Method and then Feed Pinch Method [37] is applied to perform the stage by stage calculation from feed pinch composition to both column ends. The idea of using infinite NTU to calculate the minimum reflux was also developed in the USSR literature [38]. The Feed Angle Method [39] is combining elements of the above mentioned methods and an additional vertex is added to the
linearized rectification bodies to take into account the curvature providing very accurate results for the minimum energy demand or reflux. Therefore, the nowadays available methods to determine the minimum energy demand are based on a trial and error method to find the minimum reflux that assures a feasible column profile from distillate to bottoms composition under the infinite number of stages or transfer units assumption. In a similar way as the infinite number of stages assumption at finite reflux, the assumption of infinite reflux flow rate and infinite number of transfer units was developed in USSR in 1971 [1], rediscovered in 1993 [40] achieving nowadays a high grade of maturity [3]. A new method in mid-way of the rigorous and shortcut models has recently been proposed [31]. The mass/energy balance calculation for an overall distillation column as well as certain key stages are incorporated into the short-cut model and solved iteratively. It has solved successfully complex distillation systems. In the present manuscript, an original non iterative method based on thermodynamic efficiency is proposed. Composition profiles are determined for reactive packed distillation columns operated at infinite reflux. The calculation of the minimum reflux or energy demand of a distillation column is performed based on thermodynamic efficiency, assuming a thermodynamic cycle. The number of stages and the reflux are related by their minimum values [41] and therefore provides a base for more rigorous computations. The aim of the proposed methodology is to provide additional fast and easy to use tools for the conceptual design and not to substitute any of the existing methods. It is recommended to explore an initial great number of alternatives, proceed then with methods of increasing accuracy and then apply rigorous enough simulation models. On the way, the alternatives with lower performance are disregarded and in the end, the few most promising alternatives are subjected to a detailed evaluation. The
simplest existing methods to calculate the minimum number of stages and reflux are useful for ideal mixtures, e.g. [42] [43], and the proposed method is able to solve any multicomponent distillation process in a simplified way.

2.2 A method to estimate the minimum Number of Transfer Units (NTU)

Very often packed columns are modelled considering the concept of Number of Transfer Units (NTU), according to a dimensionless expression [23]. The NTU necessary for a given separation depends only on the composition column profile, and it does not depend on the characteristics and performance of the packing. The NTU was defined by [44] as:

\[
NTU_i = \frac{\int y_i \, dy}{\int \Delta y} = \frac{\int \frac{dy_i}{y_i (y_i - y)}}{\int \frac{dy}{y (y - y)}}
\]  

where \( y \) is the vapour concentration in equilibrium with the liquid, and \( \bar{y} \) is the vapour concentration in direct contact with the liquid. The difference \( \bar{y}_i - y_i \) is the driving force for the component i transfer from the liquid phase to the vapour phase. This expression is used when the total number of transfer units along the overall height of the column is fixed. Applying differentiation, it becomes:

\[
dNTU = \frac{d\bar{y}_i}{\left( y_i - y_i \right)}
\]

In this way, the dependence of the composition versus NTU is:

\[
\frac{d\bar{y}_i}{dNTU} = y_i - y_i
\]

For a non-reactive distillation column, the mass balance on the rectifying section is:
\[ V \cdot y_i = L \cdot x_i + D \cdot x_i^0 \]  \hspace{1cm} (4)

Where, \( V \) is the vapour molar flow rate, \( L \) is the liquid molar flow rate, and \( D \) is the distillate flow rate. Assuming infinite reflux flow rate then \( L \) and \( V \) are infinite, whereas \( D \) is a finite number and applying the l'Hôpital rule,

\[ y_i = x_i \]  \hspace{1cm} (5)

and, the NTU expression becomes, in the case of infinite reflux, the following equation:

\[ \frac{dx_i}{dNTU} = x_i - y_i \]  \hspace{1cm} (6)

The similitude of this equation with the residue curve expression, without chemical reaction, is obvious. The dimensionless time of the residue curve can be directly related to the number of transfer units (NTU).

\[ d\xi = dNTU \]  \hspace{1cm} (7)

The coincidence of the residue curve profile with the profile of a packed column operating at infinite reflux, makes the residue curves useful to check the feasibility of distillation systems, without chemical reaction. In this paper, the dimensionless time of the residue curves has been equalised to NTU. This is one of the main contributions of the present paper, as this fact has important implications. The agreement between residue curves and packed column profiles at infinite reflux for non-reactive systems has been corroborated by some authors [8, 9] but it was not previously identified in literature that the dimensionless time of the residue curves matches the minimum NTU. The residue curve maps are just used to check the feasibility of separation systems, but as it is related to the NTU, it means that it is also possible to quantify how difficult is the separation.
\[
\frac{d\text{NTU}}{dx_i} = \frac{1}{x_i - y_i}
\]
(8)

The value of NTU necessary to change the concentration of a component between \(x_i^0\) and \(x_i\) is:

\[
\text{NTU} = \int_{x_i^0}^{x_i} \frac{dx_i}{x_i - y_i}
\]
(9)

A similar equation for NTU dependence of composition can be also determined for reactive systems. The molar balance for the rectifying section of a reactive distillation column is:

\[
V \cdot \bar{y}_i = D \cdot x_i^D + L \cdot x_i + \Lambda \cdot \sum_{j=1}^{M} v_{i,j} \cdot r_j
\]
(10)

where, \(\Lambda\) is the liquid hold-up in the rectifying section and \(r_j\) is the reaction rate in rectifying section. The overall molar balance is:

\[
V = D + L + \Lambda \cdot \sum_{j=1}^{M} v_{T,j} \cdot r_j \text{ where } v_{T,j} = \sum_{i=1}^{N} v_{i,j}
\]
(11)

From the last two equations:

\[
\left( D + L + \Lambda \cdot \sum_{j=1}^{M} v_{T,j} \cdot r_j \right) \cdot \bar{y}_i = D \cdot x_i^D + L \cdot x_i + \Lambda \cdot \sum_{j=1}^{M} v_{i,j} \cdot r_j
\]
(12)

From these equations, one obtains:

\[
\bar{y}_i = \frac{D \cdot x_i^D + x_i + \frac{\Lambda}{L} \cdot \sum_{j=1}^{M} v_{i,j} \cdot r_j}{D \cdot \frac{1}{L} + 1 + \frac{\Lambda}{L} \cdot \sum_{j=1}^{M} v_{T,j} \cdot r_j}
\]
(13)

As \(L\) is infinite and \(D\) is a finite number, then \(D/L \rightarrow 0\) and \(\Lambda/L\) corresponds to the residence time \((\tau)\) on the column section:
\[
\bar{y}_j = \frac{x_i + \tau \cdot \sum_{j=1}^{M} D_{i,j} \cdot r_j}{1 + \tau \cdot \sum_{j=1}^{M} D_{T,j} \cdot r_j}
\]  

(14)

1. Notice that the overall molar balance in the rectifying section becomes independent of distillate composition withdrawal. Assuming that the distillate composition is close to \(x_i\) composition, then \(r_j\) can be calculated for composition \(x_i\). Otherwise, an average reaction rate for the overall section should be considered, and the method could lose its simple form. The retention time is linked to the height of the column for which \(r_j\) is calculated.

2. Therefore, assuming an average reaction rate, the retention time is changing along the column profile, depending on initialization point.

3. \[
\frac{d\bar{y}_i}{dNTU} = \frac{d\bar{y}_i}{dx_i} \cdot \frac{dx_i}{dNTU}
\]

(15)

4. From Eqs. (3) and (14) results in:

5. \[
\frac{dx_i}{dNTU} = \left( y_i - \frac{x_i + \tau \cdot \sum_{j=1}^{M} D_{i,j} \cdot r_j}{1 + \tau \cdot \sum_{j=1}^{M} D_{T,j} \cdot r_j} \right) \cdot \left( \frac{d\bar{y}_i}{dx_i} \right)^{-1}
\]

(16)

6. For the case of simple distillation and for first order reactions, without variation of number of moles, \(\frac{d\bar{y}_i}{dx_i} = ct = 1\) the Eq. (16) can be written as:

7. \[
\frac{dx_i}{dNTU} = y_i - x_i
\]

(17)
For systems of reactive distillation, the expression $\frac{dy_i}{dx_i} \neq ct$ and is more complex. The present study is focused on the simplified case when $\frac{dy_i}{dx_i} = ct = 1$. In this case, Eq. (16) becomes:

$$\frac{dx_j}{dNTU} = y_j - \frac{x_i + \tau \cdot \sum_{j=1}^{M} \nu_{i,j} \cdot r_j}{1 + \tau \cdot \sum_{j=1}^{M} \nu_{r,j} \cdot r_j}$$

Eq. (18)

Therefore, in this paper, some new points of view related to residue curve maps are introduced, such as the use of integration results in a NTU map, in addition to the differential results in a residue curve map. This provides additional information about the difficulty of the separation.

2.3 A method to determine the minimum reboiler duty and reflux

For a distillation column, a first approach to determine the minimum energy consumption is assuming it proportional to the distillate flow rate [45], without taking into account the reflux. This is in agreement with heuristic, that a direct separation sequence is preferable to other topologies.

The product recovered by the bottom stream of the distillation column has been heated, but the entire product collected by the distillate stream has been previously evaporated, consuming more energy. The extractive agents used to enhance some distillation processes usually have high flowrates, their boiling point is relatively high and they are not evaporated, being recovered by the bottom stream. The refluxed flowrate which
represents a material stream making a closed cycle inside the column is not taken into account (Figure 1).

The heat distribution taking place in the distillation column is schematically represented in Figure 1. On one side there is the closed thermodynamic cycle in which the separation takes place (black area). On the other side there is the energy required to collect the distillate flowrate at the top of the column (grey area). According to this distribution, the overall reboiler duty is calculated as a sum between the energy required to perform the separation and the energy required to produce the distillate stream. The thermodynamic cycle as represented is a simplification which allows us to estimate the energy consumption induced by the reflux rate. In a real distillation column, there is the mixing between liquid and vapour streams. The mixing between the descending liquid and the ascending vapour generates irreversibility, which cannot be avoided, no matter the number of stages or transfer units employed. Although the distillation column can be considered having a great number of stages or transfer units, the change of composition takes places only in a few stages and most of the column profile presents wide sections where the compositions do not change. In order to avoid column profiles calculations, as a first approximation, a reversible cycle can be assumed with no internal mixing, where the feed stream does not produce a change of entropy in the feed plate.

The ideal (Carnot) efficiency is widely used for heat engines, e.g. [46], but it has never been applied before to a distillation column, even though Carnot [47] already claimed that any system consuming heat at a certain temperature and delivering it at a lower temperature can be studied as a thermal cycle. In literature, the thermodynamic aspects of distillation columns are studied from exergy point of view, e.g. [48], which provides a performance value that cannot be related to the reflux and does not provide any information about the minimum heat requirements of the column. In a similar way, as in
the case of a thermal engine, the minimum heat consumption can be determined in relation with the hot and cold temperatures to produce a certain work, for a distillation column the minimum heat consumption can be calculated to achieve a certain separation. In this section, the thermal cycle for a distillation column is presented, and the minimum heat calculated.

For this purpose, a delimited number of moles circulating inside a distillation column is considered to perform a thermodynamic cycle, as shown in the T-S diagram (Figure 2). Due to the mass transfer, the composition of the delimited number of moles is changing while ascending or descending along the column. This change of composition by itself does not affect the performance of the cycle because the performance is independent of the working fluid composition. A reversible process is assumed; therefore the heat is provided at a small finite temperature difference above the reboiler temperature ($T_r$) and eliminated at a small finite temperature difference below the condenser temperature ($T_c$). There is an isothermal phase change in the reboiler and condenser (liquid/vapour) (segments 1-2 and 3-4-5-6). The vapour decreases its temperature while ascending (segment 2-3) by exchanging heat with the descending liquid (segment 6-1) whose temperature increases. At any point inside the distillation column, the liquid and vapour in contact are in equilibrium and therefore have the same temperature. Assuming that the column is adiabatic, the heat eliminated by the ascending vapour must be equal to the heat received by the descending liquid. Therefore, at any column height, the sum of the entropy of the liquid and the vapour must be constant along the column. The change of certain amount of entropy in the liquid is compensated by the same amount of entropy in the vapour. According to this, the grey area under the segment 6-1 (area 6-1-5-8-7-6) should be equal to the grey area under the segment 2-3 (area 2-3-10-9-4-2). In the same time, the process reversibility should be assured. The input and output streams
should be at the same specific entropy that the point to or from they are feed or
extracted. Hence, the optimal feed stage is the stage with the same specific entropy, as
the feed stream.

The overall heat provided to the cycle would be the area under 6-1-2-3 (area 6-1-2-3-10-
9-8-7-6), but as there is a heat exchange between both grey areas (6-1 and 2-3), then the
heat duty provided is the area under the isotherm 1-2 (area 1-2-4-9-8-5-1). The overall
heat to be removed from the cycle is the area under the isotherm 3-6 (area 3-4-5-6-7-8-
9-10) which should be considered entirely, as there is no regeneration section as for the
heat duty. The result is that the area under the isotherm 1-2 (area 1-2-4-9-8-5-1) is equal
to the area under the isotherm 3-6 (area 3-4-5-6-7-8-9-10), this implies that the heat
provided to the cycle is equal to the heat eliminated from the cycle. Hence, a distillation
column has not a net consume of energy, but it creates a decrease of energy quality. The
same heat provided to the reboiler is collected in the condenser, but at a lower
temperature (usually there is a small difference between these values, equal to the
enthalpy variation between input and output streams). Therefore:

\[ Q_r = Q_s = Q \]  

(19)

According to the heat distribution illustrated in Figure 1, the distillation column heat
duty can be divided into the duty required to produce the distillate stream, and the duty
required to perform the separation.

\[ Q'_r + Q'^* = Q'_s + Q'^* \]  

(20)

The heat eliminated to produce the distillate \( (Q'^*_c) \) requires that the same amount that it
was provided to the reboiler \( (Q'^*_r) \).

\[ Q'^*_r = Q'^*_s = Q'^* = \lambda \cdot D \]  

(21)
As it is the same amount, the energy required by the vapour, which is collected as distillate, to reach the top of the column is not considered in the following relations, which take into account only the energy of separation.

\[ Q_r = Q'_r = Q' \]  \hspace{1cm} (22)

\[ T_r \cdot (S_2 - S_1) = T_c \cdot (S_4 - S_5) + T_c \cdot (S_3 - S_4) + T_c \cdot (S_5 - S_6) \]  \hspace{1cm} (23)

As \( S_2 - S_1 = S_4 - S_5 \) and \( S_3 - S_4 = S_5 - S_6 \)

\[ \frac{T_r - T_c}{T_r \cdot T_c} = 2 \cdot \frac{S_5 - S_6}{T_c \cdot (S_2 - S_1)} \]  \hspace{1cm} (24)

As \( T_r \cdot (S_2 - S_1) = Q'_r \), then:

\[ T_c \cdot 2 \cdot \frac{S_5 - S_6}{Q'_r} = \frac{T_r - T_c}{T_r} \]  \hspace{1cm} (25)

The thermal efficiency of Carnot cycle is:

\[ \eta = \frac{T_r - T_c}{T_r} \]  \hspace{1cm} (26)

\[ T_c \cdot 2 \cdot (S_5 - S_6) = Q'_r \cdot \eta \]  \hspace{1cm} (27)

The distillation column uses the provided heat with the same thermal efficiency defined by a thermal engine. However, instead of using it to produce work, the distillation column uses it to produce a change of entropy, in other words, to produce the separation. The degradation of thermal energy between reboiler and condenser makes possible to lower the entropy of the material, which is the separation of a liquid mixture [49]. Then the term \( T_c \cdot 2 \cdot (S_5 - S_6) \) should be equal to the difference of entropy between the output streams and the input streams feed to the column at constant temperature \( T_c \). Therefore, the minimum heat required for a certain separation depends on the increment of entropy of mixing the product streams to obtain the original feed.
streams (change of entropy required by the separation) divided by the thermal efficiency of Carnot.

\[
Q'_r = \frac{T_c \cdot \Delta S_{sep}}{\eta} \quad (28)
\]

For liquid ideal solutions, where the enthalpy of mixing is close to zero, the excess entropy is negligible. The entropy of mixing of ideal liquids can be approximated to the mixing entropy of gases [50], according to the following equation:

\[
\Delta S_{sep} = R \left[ (D + B) \left( \sum x_i^{\text{feed}} \cdot \ln x_i^{\text{feed}} \right) - D \left( \sum x_i^{\text{distil}} \cdot \ln x_i^{\text{distil}} \right) - B \left( \sum x_i^{\text{reboiler}} \cdot \ln x_i^{\text{reboiler}} \right) \right] \quad (29)
\]

Notice that \( Q'_r \) represents only the energy to perform the separation. Therefore, the heat required by the distillate to reach the top of the column should be added to obtain the overall minimum reboiler requirements. When two streams of different compositions are mixed, there is entropy of mixing, but sometimes the enthalpy of mixing can be significant enough to be taken into consideration. Therefore the energy provided to the column corresponds to the reboiler duty, adding the enthalpy of mixing as a factor of correction.

\[
Q'_r + \Delta H_{mixing} = \frac{T_c \cdot \Delta S_{sep}}{\eta} + \lambda \cdot D \quad (30)
\]

The reboiler duty of a distillation column should be higher than the previously calculated value, due to the irreversibility produced when mixing the column internal flows, and also when mixing the feed streams with the internal flows. The irreversibility produced by the feed streams is obvious in multicomponent systems by the deviation of the column profile around this point.

Another assumption in addition to the reversibility of the process is to consider a constant molar overflow along the column. According to this, an estimate of the minimum reflux ratio can be calculated as follows:
\[ r = \frac{L \cdot \dot{\lambda}}{D \cdot \dot{\lambda} + \Delta H_{\text{mixing}}} \]  

(31)

where

\[ L \cdot \dot{\lambda} = \frac{T_c \cdot \Delta S_{\text{sep}}}{\eta} \]  

(32)

dtherefore:

\[ r = \frac{T_c \cdot \Delta S_{\text{sep}}}{\eta \cdot (D \cdot \dot{\lambda} + \Delta H_{\text{mixing}})} \]  

(33)

In this case, the reflux represents the ratio between the energy to perform the separation including the efficiency of Carnot and the energy required to collect the distillate stream at the top of the column.

3. Validation of the method by rigorous simulation

3.1 Validation of the minimum Number of Transfer Units

There are no real stages or integral steps in a packed distillation column, and therefore the NTU are different from the number of theoretical stages proposed by Daniels and Alberty (1975) \[51\] and calculated discrete liquid vapour equilibrium changes at each stage (it is not a continuous variation). These are only equal when the equilibrium curve is parallel to the operation line, a condition rarely occurring. If the driving force values increase \((y_i-x_i)\) in Eq. 3), fewer transfer units than theoretical plates are required; if values of driving force decrease, the reverse is true. Therefore, a condition of equimolar flow rate distribution between distillate and bottom is considered in the illustrative examples used to check the NTU. The number of theoretical stages provided by
rigorous simulation is used together with the infinite reflux condition to cancel the
above mentioned deviations. Therefore, the equilibrium and operating line diverge over
part of the distillation range and converge over another part providing a total number of
transfer units practically equal to the total number of theoretical plates [44].

Rigorous simulation using a great reflux ratio is used to validate Eq. 18. A reflux ratio
of 1000 considered, for approaching to the assumption of infinite reflux flow rate, and
therefore, to obtain the minimum number of stages. The mixtures evaluated (expressed
in molar fractions) are shown in Table 1, the calculation basis implemented for all of
them is of 100 kmol/h. Feed mixtures considered, allow equimolar sharp split between
distillate and bottom and therefore the distillate flow rate is set to 50 kmol/h.

The results of rigorous simulation are presented graphically in Figures 3 - 5 illustrating
the distillation column composition profiles. The x-axis represents the number of stages
required resulted from simulation, while the calculated NTUs with the proposed method
are presented on the secondary y-axis. The slope of NTU points with values around 1
confirms the equivalence between NTU and minimum number of stages as expected for
the proposed conditions.

The NTU calculated are around 11% more than the number of stages resulted from
rigorous simulation for both binary mixtures studied (case A is shown in Figure 3 and
case C is shown in Figure 4). Since the simulations are performed at infinite reflux,
cases B and D are included as a part of the previous figures. In this case, the purity of
the distillate and bottom streams was not set as a design specification. Counting the
number of stages between any two composition values provides the required minimum
number of stages necessary for the separation.
For the binary cases, as the number of stages increases, the purity of the products in
distillate and bottoms increases as well. An increase of the number of stages graphically
results in a larger flat zone near pure products compositions at both profile ends. For the
multicomponent mixture, the simulation results are represented as a residue curve
following binary mixtures, where the singular points of the column profile are pure o-
cresol and pure p-cresol. An increase of the number of stages graphically results in a
larger flat zone near these two pure products in the middle of the profile (Figure 5). The
ratio between number of stages resulted from simulation and the NTU calculated with
the proposed method changes according to the binary mixture present. At the bottoms of
the column, the NTUs are 21% more than the number of stages and at the top of the
column are 7% less, while in the centre, where the equilibrium curve becomes parallel
to the diagonal, are almost identical. Therefore, the number of stages obtained from
rigorous simulation and calculated NUTs are in agreement along most of the distillation
column profile.

3.2 Validation of the minimum reboiler duty and reflux

The proposed method (point 2.2) calculates the minimum reflux and the minimum
energy requirements using only the thermodynamic information from the input and
output streams of the distillation column at the condenser temperature. Therefore, these
can be calculated considering a process scheme design opposite to distillation: feed the
distillate and bottoms streams to a mixer to obtain as output the column feed
composition. For validation of the proposed method, the results obtained by rigorous
simulation of a distillation column are compared with the values calculated from the
entropy and enthalpy of mixing (Figure 6). These properties of mixing are calculated at
a constant temperature corresponding to the condenser temperature. The enthalpy of mixing is calculated according to the cooling required to bring the resulting mixed stream back to condenser temperature.

The mass and energy balances inside the column, taking into account the irreversibility, are calculated by distillation column rigorous simulation with AspenPlus®, considering UNIFAC thermodynamic model. The ascending vapour is mixed with the descending liquid and the entrance of feed streams produces irreversibility. To validate the data collected by the simple mixer, a rigorous simulation of a distillation column at 1 bar with a big number of stages (200 stages) with the feed stage in the middle is used. A design specification changes the reflux ratio at the total condenser, for getting the desired purity in the output streams. As the number of stages is big enough, the reflux and reboiler duty should be close to their minimum values. The mixtures evaluated (expressed in molar fractions) and design specifications are shown in Table 1, the calculation basis implemented for all of them is of 100 kmol/h. Feed mixtures considered, allow equimolar sharp split between distillate and bottom, and therefore the distillate flow rate is set to 50 kmol/h.

The specific entropy for the input and output streams in the mixing process (Figure 6b) and the heat duty to the cooler for each case (enthalpy of mixing) are presented in Table 2. The boiling points of the distillate and residue streams correspond to the temperatures in the reboiler and in the column condenser, being presented in Table 3, together with minimum reboiler duty and minimum reflux, estimated by rigorous simulation. The column efficiency can be calculated using the condenser and reboiler temperatures in the same way as for a thermal engine (Eq. 26); the results are presented in Table 4. The energy loss due to mixing the streams (Figure 6b) is calculated between input and output streams, as product of the specific entropy and flow rates for each stream.
multiplied by the condenser temperature (see column T·ΔS_{sep} in Table 4). The reboiler duty required to separate again the mixture (Q’) is calculated according to (Eq. 28). Moreover, an additional reboiler duty Q” related to the distillate should be taken into account (Eq. 20), according to the scheme in Figure 1, allowing to obtain the overall reboiler duty Q (Table 4). The results of the minimum reboiler duty and minimum reflux estimated by rigorous simulation are compared to their equivalent values calculated by the proposed method (Table 5). The discussion of the results is provided in the following paragraphs.

In the first case (A), a binary mixture of methanol and ethanol is evaluated (case A Table 1). This is discussed in more detail, according to the proposed method. A stream with 95% methanol and 5% ethanol at 1 bar, at its boiling point is mixed with another stream containing 5% methanol and 95% ethanol at 1 bar and same temperature. Both streams have same flowrate i.e. 50 kmol/h, (Figure 6b). In this way, both streams are at the same temperature as the column distillate temperature (T_c = 337.8 K) (Figure 6a). Due to the enthalpy of mixing, the temperature of the mixed stream increases slightly (T=343.1 K). Therefore the heat exchanger B3 is used to cool this stream back to the temperature of the feed streams. The heat consumed by this cooler corresponds to the enthalpy of mixing (ΔH_{mixing} = 4.57 kW).

Once mixed, a higher amount of energy is required to separate it again. This energy must come from a distillation column that can be considered as a thermal machine working between a hot and cold source, the reboiler being the hot source and the condenser the cold source. As demonstrated previously, efficiency of Carnot is also applicable to the distillation columns and therefore the required heat for the separation (Q’ = -942.32 kW) represents the energy due to the entropy of mixing (TΔS_{sep} = -33.52
kW) divided by the efficiency of the Carnot cycle ($\eta = 0.0356$) (Eq. 28). The entropy of mixing and the efficiency are calculated as follows.

The entropy of each stream is calculated as product of its flow rate and specific entropy (Table 2). The difference of entropy between the input and the output streams at temperature $T_c$ provides the entropy of mixing ($-355.3 \text{ kJ} \cdot \text{h}^{-1} \cdot \text{K}^{-1}$). The product between the entropy of mixing and the temperature $T_c$ provides the energy loss by the entropy generated: 33.52 kW (Table 4). The temperature in the reboiler ($T_r$) is 350.26 K which represents the boiling point of 95% ethanol stream. The temperature in the condenser ($T_c$) is of 337.8 K (Table 3), representing the boiling point of 95% methanol stream. Therefore, the efficiency calculated from the previous temperature values (Eq. 26) is of 3.56% (Table 4).

The reboiler duty ($Q = -1,435.15$ kW) is the sum of the energy required by the distillate stream ($Q'' = -492.83$ kW) and the energy required to separate the mixture ($Q' = -942.32$ kW) (Table 4). The enthalpy of mixing is added to the minimum reboiler duty simulated ($Q_{min}$), but in this case its influence is negligible. By rigorous simulation of a distillation column, the condenser duty resulted is of 1,640.40 kW, only 14% higher than the one calculated thermodynamically. Using these results and the Eq. (33) to determine the reflux, a calculated reflux of 1.9 is obtained versus a value of 2.3 estimated by rigorous simulation (Table 5). Therefore, the values thermodynamically calculated are in very good agreement with the values estimated by rigorous simulation.

In case B, the same separation is considered as in case A (methanol and ethanol), but they are separated to a higher purity of 99% (Table 1). The efficiency obtained is similar to that obtained for case A (3.85%), but the enthalpy of mixing is not any more negligible ($-495.24$ kW) (Table 2). The minimum thermodynamic reboiler duty is
greater than in case A, as expected ($Q = -1,594.08 \text{ kW}$), but the simulated condenser
duty ($Q_{\text{min}} = -1,779.50 \text{ kW}$) is 61.9% higher than the one thermodynamically calculated
(Table 4). When the enthalpy of mixing is added to the simulated minimum reboiler
duty, the difference between them is about 43%. These results show that when the
enthalpy of mixing is not negligible, the irreversibility inside the column is higher.

In case C separation of binary mixture benzene and toluene is considered to obtain
purity of 95% (Table 1). The enthalpic and entropic contribution to the mixing is similar
to the previous B case (Table 2 and 4), e.g. $\Delta S_{\text{sep}} (C: 455.62 \text{ kJ·h}^{-1}·\text{K}^{-1} \text{ and B:451.44 kJ·h}^{-1}·\text{K}^{-1})$ are almost the same. The higher difference between the condenser and
reboiler temperature (for case C: 353.8 – 381.1 K and for case B: 337.4–351.0 K)
produces a higher efficiency (7.15%) and the resulting $Q'$ required for the separation
becomes considerable smaller (-622.78 kW) (Table 4). When $Q'$ is compared to the
condenser duty value obtained by rigorous simulation of the distillation column ($Q_{\text{min}} =
-932.17 \text{ kW}$), the difference is of 48.6%. When the enthalpy of mixing is taken into
account this difference becomes 29%. Also the reflux for case C is smaller than for case
B. The thermodynamically calculated reflux is of 1.08 and the estimated reflux value
obtained by rigorous simulation is of 1.16, which is in good agreement. Therefore,
higher is the difference between the distillate and bottoms temperatures, the process is
more efficient and a lower reflux is required.

In case D same binary system as in case C is considered, but at a higher purity of 99%
for the output streams (Table 1) is imposed. The enthalpy of mixing and energy required
for the distillate stream are almost similar to case C. But as the purities are higher, the
temperatures of distillate and bottom streams differ more, while the efficiency also
increases (7.8%). Nevertheless, the entropic contribution to the energy of mixing
increases at a higher extent resulting in a higher thermodynamic condenser duty (Q’) of
-726.35 kW (Table 4), although the efficiency is higher. The condenser duty estimated
by simulation is of -242.75 kW, the difference to the one calculated thermodynamically
being around 38.7% (Table 3). When corrected using the enthalpy of mixing, the
difference is of 25%. The calculated reflux is of 1.19 and the value estimated by
rigorous simulation is of 1.37, with only 15% of difference. Therefore, the higher
condenser duty and the reflux required to obtain a higher purity is mainly consequence
of the higher entropy of mixing. Notice that the minimum condenser duty to separate a
binary mixture in pure components is a finite value, and it can be used to calculate the
energy requirements of a process under the infinite/infinite assumption.

Once verified the obtained results with the estimated values by rigorous simulations for
binary mixtures, in case E (Table 1) the results obtained for an equimolar
multicomponent mixture of 100 kmol/h composed of phenol, o-cresol, m-cresol and
3,5-xylenol are presented. Phenol and o-cresol are separated in distillate stream with an
overall purity of 95% whereas m-cresol and 3,5-xylenol are separated in bottoms
stream, using a distillate flow rate of 50 kmol/h. The enthalpy of vaporization for the
distillate stream (Q’’) is -655.70 kW, the enthalpy of mixing is -2.63 kW and the energy
required for separation (Q’) is of -1,071.75 kW (efficiency of 5.14%) resulting in
condenser duty of -1,727.45 kW. The difference between calculated value and the value
resulted from rigorous simulation for the condenser duty (-2,599.91 kW) is of 51%.
This difference is quite high compared to the equivalent case A, with a negligible heat
of mixing. The irreversibility is caused by the perturbation produced by the feed stream.
This is illustrated by column composition profile. The feed position can be easily
identified in Figure 7 due to the deviations and break of the composition column profiles near the feed point.

In case F, similar multicomponent separation problem to case E is proposed, but the purity of product streams is imposed to 99% (Table 1). The entropic contribution to the energy of mixing in this case increases, as expected, to a higher value (-67.40 kW), but the main difference is that the enthalpy of mixing is not any more negligible (-656.27 kW). The calculated condenser duty (Q) is -1,907.66 kW and the estimated one by rigorous simulation (Q_min) is -2,942.79 kW which becomes -3,599.40 kW (Table 5) when taking into account the enthalpy of mixing. In this case, the difference is 89% compared to the thermodynamically calculated one. The reason for the higher discrepancy for multicomponent mixtures can be explained by the composition profiles which present a remarkable break of the tendency for some of the components at the feed plate. This leads to a high degree of irreversibility. Furthermore, the irreversibility produced by the enthalpy of mixing is sharpened by the irreversibility produced at the feed plate. A continuous computation of the packed columns would provide values closer to the calculated ones, assuming a reversible separation instead of the rigorous model implemented in the simulator which takes into account discrete stages.

4. TAME synthesis as illustrative example for the proposed method

The previously presented problems are easily studied directly by rigorous simulation, but there are more complex processes not so easy to analyse. For instance, the synthesis of TAME (tert-amyl-methyl-ether), an important gasoline additive, can be performed using the technology of catalytic distillation (from methanol and isoamylenes) in a
hybrid reactive distillation column with the non-reactive section in the bottom. The feasibility and the influence of several design parameters on the number of stages and energy consumption of such a complex process is not an easy task to be analysed by rigorous simulation. The convergence of the simulation environment requires a long time of trials and the difficulty to reach a converged flowsheet is not always a sign of non-feasibility of the configuration considered. To determine all the feasible combinations of parameters influencing the system is not always straightforward. Therefore, the proposed method simplifies the model at the extreme conditions to avoid the convergence problems and provide a fast insight of the problem behaviour.

This behaviour is reflected in two kinds of complementary maps: a map illustrating feasibility and minimum number of stages and a map showing the distillation column thermal efficiency. The first map is based on the assumption of infinite reflux flow rate and the difficulty of the separation is reflected in the NTUs required according to the Eq. (18). The second map is based on the thermal efficiency that defines the minimum energy requirements of the distillation column and the minimum reflux. The thermal efficiency of the distillation column depends only on the temperatures of distillate and bottom streams. The aspect of both graphics is similar to a topographic map. The main coincidence between them is that the maximum and minimum temperatures coincide also with singular points (pure components or azeotropes) at which the difficulty of separation is maximum as well. As differences, the temperature map topology does not depend on the retention time inside the reactive distillation column, while the NTUs map topology strongly depends on the retention time. Pressure influences both types of map topology, but at different extent. These maps are discussed for this illustrative example in more detail in the following paragraphs.
Figure 8 illustrates the maps at 4 bar. The NUTs map is composed of a set of curves obtained when applying Eq. (18). Any feasible separation composition can be placed on a common residue curve and the section of curve between them corresponds to the distillation column composition profiles assuming a packed column operated at infinite reflux flow rate. The minimum NTUs for the required separation are mathematically obtained integrating Eq. (18). Graphically, the minimum NTUs can be directly obtained when counting the number of circles in the section of curve corresponding to the column profile. The NUTs map for TAME synthesis is divided in two distillation regions with a common unstable node (isoamylens/methanol azeotrope). Most of the feasible column profiles depart from this azeotrope and converge to pure TAME vertex, while some other column profiles converge to pure methanol. The optimum profile corresponds to minimum NTUs required for a separation, fulfilling certain restrictions to bottoms and distillate compositions. It is obtained when the profile crosses regions where the separation is fastest (maximum difference between the $y_i$ term and the rest in Eq. 18) and the way is shortest (the overall NTUs resulted from integration).

Comparing both maps (Figure 8), the maximum temperatures correspond to stable nodes, e.g. pure TAME, and the minimum temperature corresponds to the unstable node, i.e. methanol/isoamyleneazeotrope. The column efficiency can be determined easily from Eq. (26) as it only depends on temperature. Therefore, when the distillation column is operated in the distillation region corresponding to methanol stable node, the NTUs are small but the thermal efficiency is low. On the other hand, the operation in the distillation region corresponding to TAME stable node requires more NTUs, but the thermal efficiency is higher. The presence of the reaction term does not change the column efficiency as the boiling points at each composition are the same. The enthalpy of the reaction must be taken into account when the minimum reboiler duty is
calculated. However, the presence of reaction influences the topology of the NTUs map, changing the position of the nodes and saddles and affecting the difficulty of separation (Figure 9).

The temperatures map and the representation of NTUs on residue curve maps provide an useful tool and a valuable additional information to propose more energy efficient process schemes and designs.

5. Summary of the proposed method

The feasibility of a distillation process requires the fulfilment of the mass balances and the existence of a column profile between the distillate and bottoms composition. The existence of the column profile can be checked at infinite reflux using the following expression (Eq. 16) for packed columns:

\[
\frac{dx_i}{dNTU} = \left( x_i + \frac{\tau \cdot \sum_{j=1}^{M} v_{i,j} \cdot r_j}{1 + \tau \cdot \sum_{j=1}^{M} \theta_{r,j} \cdot r_j} \right) \cdot \left( \frac{dy_i}{dx_i} \right)^{-1}
\]

(16)

This expression is implemented in most of the commercial simulators but only for non-reactive mixtures and does not indicate the NTU. The NTU is an important parameter as it provides an insight of the capital costs associated to the separation. In a more approximated manner, the capital costs associated can be considered related to the residue curve or profile length. Eq. (16) is a general expression taking into account the reaction kinetics, but it can be simplified for non-reactive systems to Eq. (6):

\[
\frac{dx_i}{dNTU} = x_i - y_i
\]

(6)
The last expressions are the basis for the infinite reflux assumption analysis models, e.g. infinite/infinite analysis, and therefore the output streams compositions and flow rate can be determined. A separation is feasible only if the reflux is higher than its minimum value, therefore the minimum reflux is valuable information that in turn is related to the operational costs. The optimum reflux is usually calculated with rules of thumb that relate it with its minimum value. The present paper presents an original way to calculate it from thermodynamic assumptions (Eq. 33):

\[ r = \frac{T_c \cdot \Delta S_{sep}}{\eta \cdot (D \cdot \lambda + \Delta H_{mixing})} \]  

where

\[ \eta = \frac{T_r - T_c}{T_r} \]  

\[ \Delta S_{sep} = R \left( (D + B) \left( \sum x_i^{feed} \cdot \ln x_i^{feed} \right) - B \left( \sum x_i^{distil} \cdot \ln x_i^{distil} \right) - \sum x_i^{reboil} \cdot \ln x_i^{reboil} \right) \]  

The results of this method (minimum NTU and reflux) can be used as initialization values for iterative more rigorous methods.

6. Conclusions

This paper proposes a new expression to model the compositions profile of a packed distillation column operated at infinite reflux flow rate. The results can be used to determine the minimum Number of Transfer Units for a given separation. NUT is useful to evaluate de difficulty of the separation, complementing the information from residue curve maps for the feasibility of the separation. An original treatment is proposed to evaluate feasibility/difficulty of separation for reactive distillation. On the other hand, it is proposed an original method to calculate the minimum reboiler duty, based on the thermodynamic efficiency of a distillation column, and the change of entropy between the input and output streams. Higher the difference between the distillate and bottoms compositions, more efficient is the distillation column. The separation leading to
streams of higher purity is associated to a higher efficiency. The entropic contribution to
the energy of mixing, increases the energy requirements at a higher extent than the
savings due to the increase of efficiency producing higher reboiler duty requirements.
The minimum reboiler duty to separate a binary mixture in pure components is a finite
value, but the number of transfer units to separate in pure components is considered
infinite. Therefore the method can be applied in combination with the infinite/infinite
analysis.
When the heat of mixing is negligible, the results are in very good agreement with the
values estimated by rigorous simulation. Otherwise, a higher difference is observed
between the minimum reboiler duty thermodynamically estimated, and the one
calculated by rigorous simulation. This is caused by irreversibility produced due to
mixing inside the distillation column between liquid and vapour flowing in opposite
directions. The irreversibility is sharpened in multicomponent mixtures due to the feed
stream that produces a clear perturbation of the composition profiles for several
compounds. Due to the irreversibility, the estimated minimum reboiler duty by rigorous
simulation can be several times bigger than the minimum thermodynamically calculated
value.

Acknowledgements The authors would like to thank the financial support of POSCCE
project ID 652 (Structural Funds for Development and Cohesion) and the project
CTQ2009-11465 (Ministry of Science and Innovation – Spanish Government) who
provided the opportunity to complete this research.

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<tr>
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<td>Methanol - Ethanol</td>
<td>0.5 – 0.5</td>
<td>0.95 methanol</td>
</tr>
<tr>
<td>B</td>
<td>Methanol - Ethanol</td>
<td>0.5 – 0.5</td>
<td>0.99 methanol</td>
</tr>
<tr>
<td>C</td>
<td>Benzene - Toluene</td>
<td>0.5 – 0.5</td>
<td>0.95 benzene</td>
</tr>
<tr>
<td>D</td>
<td>Benzene - Toluene</td>
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<td>Phenol</td>
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<td>0.95 phenol + o-cresol</td>
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<tr>
<td></td>
<td>o-cresol</td>
<td>0.25</td>
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<tr>
<td></td>
<td>m-cresol</td>
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<td>3,5-xylenol</td>
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<td>F</td>
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<td>0.25</td>
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### Table 2. Results of rigorous simulation for mixing (Figure 7b)

<table>
<thead>
<tr>
<th>Case</th>
<th>$S_{\text{feed}}$ (J/mol·K)</th>
<th>$S_{\text{dist}}$ (J/mol·K)</th>
<th>$S_{\text{residue}}$ (J/mol·K)</th>
<th>$\Delta H_{\text{mixing}}$ (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-273.58</td>
<td>-273.29</td>
<td>-322.82</td>
<td>-4.57</td>
</tr>
<tr>
<td>B</td>
<td>-273.75</td>
<td>-228.35</td>
<td>-328.17</td>
<td>-495.24</td>
</tr>
<tr>
<td>C</td>
<td>-264.05</td>
<td>-272.16</td>
<td>-306.81</td>
<td>-426.44</td>
</tr>
<tr>
<td>D</td>
<td>-264.47</td>
<td>-228.60</td>
<td>-311.87</td>
<td>-422.99</td>
</tr>
<tr>
<td>E</td>
<td>-337.45</td>
<td>-297.74</td>
<td>-385.52</td>
<td>-2.63</td>
</tr>
<tr>
<td>F</td>
<td>-337.74</td>
<td>-298.95</td>
<td>-387.19</td>
<td>-656.28</td>
</tr>
</tbody>
</table>
Table 3. Results of rigorous simulation for distillation (Figure 7a)

<table>
<thead>
<tr>
<th>Case</th>
<th>(T_r) (K)</th>
<th>(T_c) (K)</th>
<th>(Q_{\text{min}}) (kW)</th>
<th>(r_{\text{min}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>350.26</td>
<td>337.80</td>
<td>-1,635.82</td>
<td>2.32</td>
</tr>
<tr>
<td>B</td>
<td>350.95</td>
<td>337.44</td>
<td>-1,779.50</td>
<td>2.64</td>
</tr>
<tr>
<td>C</td>
<td>381.11</td>
<td>353.85</td>
<td>-932.17</td>
<td>1.16</td>
</tr>
<tr>
<td>D</td>
<td>382.91</td>
<td>353.05</td>
<td>-1,014.70</td>
<td>1.37</td>
</tr>
<tr>
<td>E</td>
<td>482.62</td>
<td>457.81</td>
<td>-2,597.27</td>
<td>2.96</td>
</tr>
<tr>
<td>F</td>
<td>483.23</td>
<td>457.26</td>
<td>-2,942.79</td>
<td>3.50</td>
</tr>
</tbody>
</table>
Table 4. Results for minimum heat duty calculated

<table>
<thead>
<tr>
<th>Case</th>
<th>$T \cdot \Delta S_{sep}$ (kW)</th>
<th>$\eta$ (%)</th>
<th>$Q'$ (kW)</th>
<th>$Q''$ (kW)</th>
<th>$Q$ (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-33.52</td>
<td>3.56</td>
<td>-942.32</td>
<td>-492.83</td>
<td>-1,435.15</td>
</tr>
<tr>
<td>B</td>
<td>-42.56</td>
<td>3.85</td>
<td>-1,105.25</td>
<td>488.83</td>
<td>-1,594.08</td>
</tr>
<tr>
<td>C</td>
<td>-44.54</td>
<td>7.15</td>
<td>-622.78</td>
<td>-430.94</td>
<td>-1,053.72</td>
</tr>
<tr>
<td>D</td>
<td>-56.64</td>
<td>7.80</td>
<td>-726.35</td>
<td>-428.16</td>
<td>-1,154.50</td>
</tr>
<tr>
<td>E</td>
<td>-55.09</td>
<td>5.14</td>
<td>-1,071.75</td>
<td>655.70</td>
<td>-1,727.46</td>
</tr>
<tr>
<td>F</td>
<td>-67.40</td>
<td>5.37</td>
<td>-1,254.42</td>
<td>653.24</td>
<td>-1,907.66</td>
</tr>
</tbody>
</table>
Table 5. Method validation results

<table>
<thead>
<tr>
<th>Case</th>
<th>Q (kW)</th>
<th>$Q_{\text{min}} + \Delta H_{\text{mixing}}$ (kW)</th>
<th>Difference (%)</th>
<th>$r_{\text{r}}$</th>
<th>$r_{\text{min}}$</th>
<th>Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-1,435.15</td>
<td>-1,640.40</td>
<td>14</td>
<td>1.89</td>
<td>2.32</td>
<td>22</td>
</tr>
<tr>
<td>B</td>
<td>-1,594.08</td>
<td>-2,274.73</td>
<td>43</td>
<td>1.81</td>
<td>2.64</td>
<td>45</td>
</tr>
<tr>
<td>C</td>
<td>-1,053.72</td>
<td>-1,358.60</td>
<td>29</td>
<td>1.08</td>
<td>1.16</td>
<td>7</td>
</tr>
<tr>
<td>D</td>
<td>-1,154.50</td>
<td>-1,437.69</td>
<td>25</td>
<td>1.19</td>
<td>1.37</td>
<td>15</td>
</tr>
<tr>
<td>E</td>
<td>-1,727.46</td>
<td>-2,599.91</td>
<td>51</td>
<td>2.87</td>
<td>2.96</td>
<td>3</td>
</tr>
<tr>
<td>F</td>
<td>-1,907.66</td>
<td>-3,599.07</td>
<td>89</td>
<td>2.25</td>
<td>3.50</td>
<td>56</td>
</tr>
</tbody>
</table>
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