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Distillation of a Complex Mixture. Part II: Performance Analysis of a Distillation Column Using Exergy

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Abstract: To analyze the performance of the separation process, we have introduced the thermodynamic concept of exergy through the exergetic efficiency of the column. The simulation results show that the exergetic output is relatively low and that the produced irreversibility fluxes are distributed throughout the whole column in a non-uniform manner. They are particularly significant in the condenser, boiler and tray feed. The influence of the various operating parameters (temperature, concentration and irreversibility in both sections of the column) is also established. To emphasize the results, the relation in equation **17**, is presented graphically to evaluate the cumulative irreversibilities from the overhead to the bottom. This presentation is equivalent to the Grassmann diagram.

Keywords: High pressure distillation, complex mixture, exergetic efficiency, irreversibility, pinch temperature.

1. Introduction

Distillation is one of the processes of the chemical industry of separation that is most widely exploited in the petrochemical facilities with significant energy consumption. In the design and performance analysis of a distillation column, the principles of matter and energy conservation are often referred to. However, it is clear that the reversible model leads to a minimum of deterioration of the energy quality [9]. Calculations of the chemical processes of rectification of complex mixtures show that their efficiency is very low (30- 40%). Such results account for the high operating costs, resulting in an increasingly expensive product. Some studies aiming at reducing operating costs

propose technological diagrams which consist in integrating energy process savings while exploiting the (hot and cold) utilities existing on site. Such a design requires a thermodynamic analysis involving treatment of the properties of the fluid by means of a suitable function of state f(P, V, T) = 0, which characterizes the mixture to be rectified, on the one hand, and allows calculation of all essential thermodynamic functions (enthalpy, entropy, fugacity, etc.) and tray equilibrium , on the other hand. Thermodynamic analysis of the distillation column is important for the synthesis and design of the most effective process of the distillation from the energy point of view. Indeed, it leads to the localization and reduction of the losses of exergy arising from:

- Heat transfer due to a finite temperature difference δT
- Mass transfer due to the mixing liquid and vapour streams
- Heat losses through the column wall.

This analysis makes possible the identification of the irreversibility in each tray and the comparison with results obtained for an ideal model [10]. As a criterion of column performance, the exergetic efficiency can thus provide valuable information on the separation capacity of the column as well as the possibility for improvement. Thorough analysis of the various definitions of the exergetic efficiency shows that the concept of rational efficiency allows the analysis of the energy performance of the installations in a correct way [2] .Being based on a concept which would take into account of the objective for which the installation is designed, it gives sufficient information on the process.

$$\eta_{simple} = 0.463 \qquad \eta_{rational} = 0.271 \qquad \eta_{exerg.trans} = 0.369$$

The profiles of exergetic losses (Irreversibilities) give the distribution of the potential of transfer within the column which can be exploited to make some modifications referring to the conditions of its operation (Localization of the feed tray, relative position of the system condenser/reboiler). Indeed, Ratkje *et al*. [16], showed analytically that the entropy production flux (exergy losses) is minimum when the potential of separation (of transfer) is distributed uniformly along the column. For his part, Rivero [17] showed that the exergy loss profiles and the quantity of heat extracted along the column are symmetrical and that the minimum of exergy loss is obtained when the standard deviation of the losses is minimal. However, for a given number of trays, the distance between the equilibrium curve and the operating line corresponds to the optimal exergy and exergy loss could not be more reduced without modification of the size of the column (number of trays). In the distillation of complex mixtures, it is impossible to operate with reversible separation diagrams. This difficulty is overcome by resorting to the concept of pseudo-ternary mixture, based on the concept of light-and-heavy key components, while analyzing the process in a T-H diagram [1,7]. To locate the feed tray, Bandyopadhyay [1] introduced a pair of T-H curves related respectively to the rectifying and stripping sections, called the rectifying-stripping invariant (R.S.I.). By analyzing the flow of exergy destruction on a Φ-H diagram, Bandyopadhyay [2], notes the influence of the feed thermal conditions on the thermodynamic performances of the column. A single column could not meet the needs for separation of a complex mixture. Among the diagrams most recently suggested, there is in particular the thermally coupled diagrams of distillation for the energy gain and installation (Peltyuk *et al*. [15]).

Although the columns of Peltyuk are adapted to the treatment of complex mixtures $[C \geq 3]$, their configurations with a condenser and a reboiler are characterized by a significant number of sections of columns with rather complex ramifications. Nakaiwa *et al*. [14] studied the exergetic losses in a distillation column with integrated energy source. The conditions of separation and the effects of the feed composition were estimated by the simplified model simulation while supposing that the tray is described by the theoretical tray model. They supposed that for heat exchange to occur, the difference in temperature necessary between the available utilities and the ends of the column respectively is δT=10 K. Ultimately, they showed that the column with integrated energy source is as good as the conventional column and that functioning with vapour compression at the condenser. Indeed, the adiabatic arrangement of Peltyuk by a total thermal coupling, by integrating the heat source, contributes to a significant reduction of the energy expenditure [8]. The rational efficiency of the distillation column of raw oil varies between 0.270 and 0.373 according to the column operating conditions (raw distillation, flash distillation), whereas the total rational efficiency of all the distillation installation including heating and heat exchangers is very low, and equal to 0.0518 [5]. In order to optimize the heat source integration system in the raw oil [13] had exploited the temperature and distillation unit by reducing the exergy losses, Lee *et al*. [13] had exploited the temperature and composition pinch analysis. For this reason, Bouchekima *et al*. [4] analyzed the performance of the distillation column by using solar energy in hot areas. In this article and taking into account of the strong consumption of process energy, all the operating parameters related to the operation of the distillation column of a light hydrocarbons mixture were exploited and calculated by simulation to determine the local irreversibilities at each tray and to improve performance on the energy level. Moreover, the total performance of the column is approached by using the rational efficiency.

2. Theoretical Considerations

The method for the calculations of columns is based on mass and enthalpy balance. Taking into account the limitations of the method and in order to locate the imperfections due to the irreversible characters of the operation, the concept of maximum useful work introduced by Keenan [11] is used. For a system (mass stream) undergoing a reversible transformation with the surrounding medium characterized by the variables of state (T_0, P_0), its expression is written:

$$W = Ex - Ex_{\min} , \tag{1}$$

where Ex is the stream exergy under the conditions of temperature and of pressure (T,P) and $Ex_{\min}$ is the exergy of the same stream when it is in equilibrium with the ambient conditions (T_0, P_0) defined as being the dead state. By definition, the exergy function has as an expression:

$$Ex = H - T_o S \tag{2}$$

where H and S are respectively the entropy and enthalpy calculated under the conditions of the system at the pressure P and the temperature T with a chosen state of reference (T_{ref}, P_{ref}).. As the mathematical expression allowing the calculation of the enthalpy was presented in part I, the expression of the entropy is presented in appendix ADI. In addition, for a real system, site of an irreversible transformation, effective work (useful) is lower than that calculated for a reversible process. Thus, the variation of available work for a system working in steady state is a measurement of

the net degradation of exergy irreversibility which accompanies the real transformation. Technical thermodynamics shows that mechanical work is a very noble form of energy and of higher quality compared to heat. The conversion factor connecting them is the factor of Carnot [22]:

$$\Phi = 1 - \frac{T_0}{T} \tag{3}$$
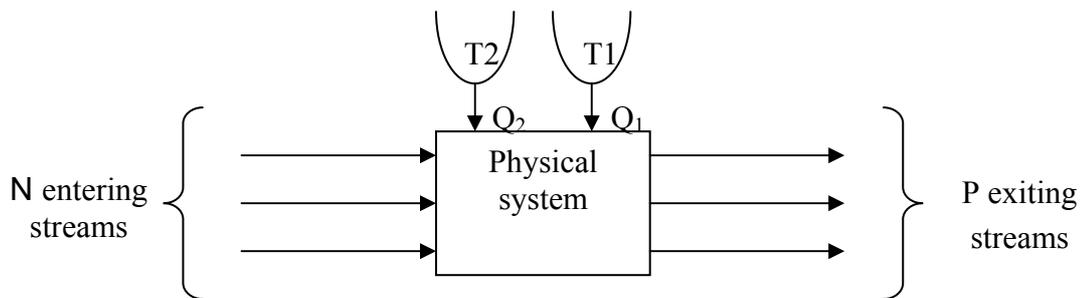
Figure 1. Model of the interacting system with its surrounding medium.

In steady state, if enthalpy calculation is checked by using the first principle of thermodynamics, the entropic assessment on the system represented in Figure 1, delimited by a hypothetical control volume, makes it possible to show easily that the sum of input exergies is always higher than that of output exergies. However, there is no difference for a reversible process. The difference between these two entities constitutes the flow of production of irreversibility. Analytically, this assertion is expressed by:

$$\dot{I} = \sum_{i=1}^{n} (m_i * Ex_i) - \sum_{i=1}^{p} (m_i * Ex_i) + \sum_{i=1}^{q} Ex_{Q_i} \quad , \tag{4}$$

with n and p being the numbers of entering and exiting external streams in interaction with the system and *m i* and *E x i* the molar flow and the molar exergy of stream i respectively. It should be noted that for the physical processes of separation, not accompanied by chemical reaction, the total exergetic balance does not require chemical exergy involvement. Indeed, this remark takes into account the fact that for a well-defined control volume the contribution of this component is cancelled out between the entering and exiting streams in a steady state. It will be supposed that the host element for exergetic analysis is the column tray, independently of its position. The exergetic balance applied to the tray, represented in Figure 2, takes into account of the various streams interacting with it (matter and heat). It is possible to locate and quantify the flow of the irreversibilities. It is written:

$$\dot{I}_j = L_{j-1} * Ex_{j-1}^L + V_{j+1} * Ex_{j+1}^V F_j * Ex_j^F + Ex_{Qj} - (L_j + M_j) * Ex_j^L - (V_j + U_j) * Ex_j^V \quad , \tag{5}$$

with Ex_{Qj} being the thermal exergy exchanged with the tray J, given by following equation:

$$Ex_{Qj} = Q\left(1 - \frac{T_0}{T}\right) \tag{6}$$
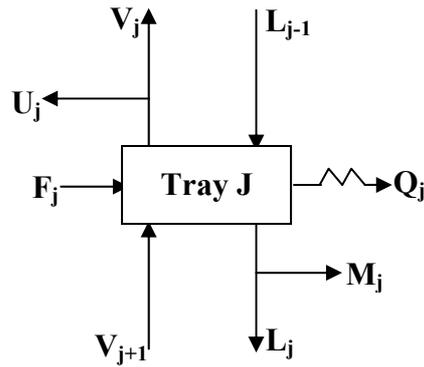
Figure 2. Theoretical tray with side streams (heat and mass).

Its sign would depend on the thermodynamic direction of transfer of heat. While supposing that the column functions with a mode of total condensation, the exergetic balance at the condenser is written:

$$V_1 = 0, L_0 = 0 \tag{7}$$

$$\dot{I}_1 = V_2 * Ex_2^V + Ex_{Qc} - (L_1 + D) * Ex_1^L , \tag{8}$$

with

$$Ex_{Qc} = Q_C * \left(1 - \frac{T_0}{T_1}\right) . \tag{9}$$

In an identical way and taking into account of the reboiler operation, the exergetic balance is written as:

$$V_{N+1} = 0, F_N = 0 \tag{10}$$

$$\dot{I}_N = -V_N * Ex_N^V + Ex_{Qr} - L_N * Ex_N^L + L_{N-1} * Ex_{N-1}^L \tag{11}$$

If a pinch temperature δT is chosen between the source and the reboiler temperature, the expression of the thermal exergy takes the form:

$$Ex_{Qr} = Q_r * \left(1 - \frac{T_0}{(T_N + \delta T)}\right) \tag{12}$$

To characterize the exergetic performance of the distillation column of the complex mixture, many researchers, and particularly Kotas, Szartgut *et al.*, [6,12,20] have proposed the following definition of the mixture separation efficiency:

$$Exergy\ efficency = \frac{useful\ exergy\ variation}{consumed\ energy\ tranformation.}$$

For an adiabatic distillation column except at the ends, the variation of exergy associated with the separation of the components of the mixture constitutes the minimal work of separation defined by:

$$\ddot{W}_{\min} = \sum_1^N M_j * Ex_j^L + \sum_1^N U_j * Ex_j^V - \sum_1^N F_j * Ex_j^F \tag{13}$$

Taking into account the fact that heat exchange between the column and the surrounding medium takes place only at the two ends (condenser and reboiler), the paid exergy can be expressed as:

$$Ex_{paid} = Ex_{Qr} - Ex_{Qc} \tag{14}$$

It should be noted that the mechanical work associated with fluid circulation is negligible with respect to the heat amount exchanged between the column and the external medium. Consequently, the exergetic efficiency for a real column is written:

$$\eta_{ex} = \frac{L_N * Ex_N^L + D * Ex_1^D - F * Ex^F}{Ex_{Qr} - Ex_{Qc}} \tag{15}$$

3. Simulation of the Column

Taking into account of the complexity of the interactions between the various streams at each tray and the redundancy of parameters due to the successive trays relationships, the determination of externally controllable variables imposes the application of the method of calculation of the system degrees of freedom. For recall, the calculation of the operational parameters (T_j, X_j, Y_j, L_j, V_j, H_j), was obtained by resorting to the rigorous method based on the determination of bubble point. To simplify our analysis, we put forth the following assumptions:

- Negligible pressure losses.
- Adiabatic column except at the ends.
- The tray obeys the model of continuously stirred reactor.

The simulation flow chart of the high pressure column (20 bar) is reported in Figure 3. Some points deserve to be clarified: The rate of reflux flow expressing the rate of recycling at the condenser is:

$$R = \frac{L_1}{U_1} = 2.4 \tag{16}$$

1. The compositions, the temperatures and the stream flow rates at each tray are determined by the iterative methods of nonlinear algebraic Thomas equations. In order to initialize calculations, it is supposed that the temperature profile is linear along the column with the temperatures at the ends (condenser and reboiler) determined by the method of bubble.
2. The balance calculation is completed when convergence criteria are met.
3. At this step, the program will calculate the exergy of the various streams after having considered the ambient conditions as the dead state whose temperature is T0 = 298.15 K.
4. The last step of the execution consists in calculating the exergetic efficiency by using Equation (15).

Initial guess

Enter: *N, C, R, F_j, Z_{i,j}, Pf_j, Tf_j, P_j, U_j*

$L(0)=0$, $V(N+1)=0$, $W(1)=0$, $U(N)=0$

Total condensation

Yes → $V(1) \neq 0$, $U(1)=0$

No → $V(1)=0$, $U(1) \neq 0$

$K=1$

Initialise variables
$T^{(0)}_j$, $V^{(0)}_j$

Calculation of Xi,j by Thomas' method

$K=K+1$

$T_j^{(0)} = T_j^{(k)}$
$V_j^{(0)} = V_j^{(k)}$

Normalise Xi,j

Calculate modified $T_j^{(k)}$

Calculate modified $V_i^{(k)}$

$|critT+critV| \leq \varepsilon$

No →

Yes → Exergetic calculation

Printing of results

End
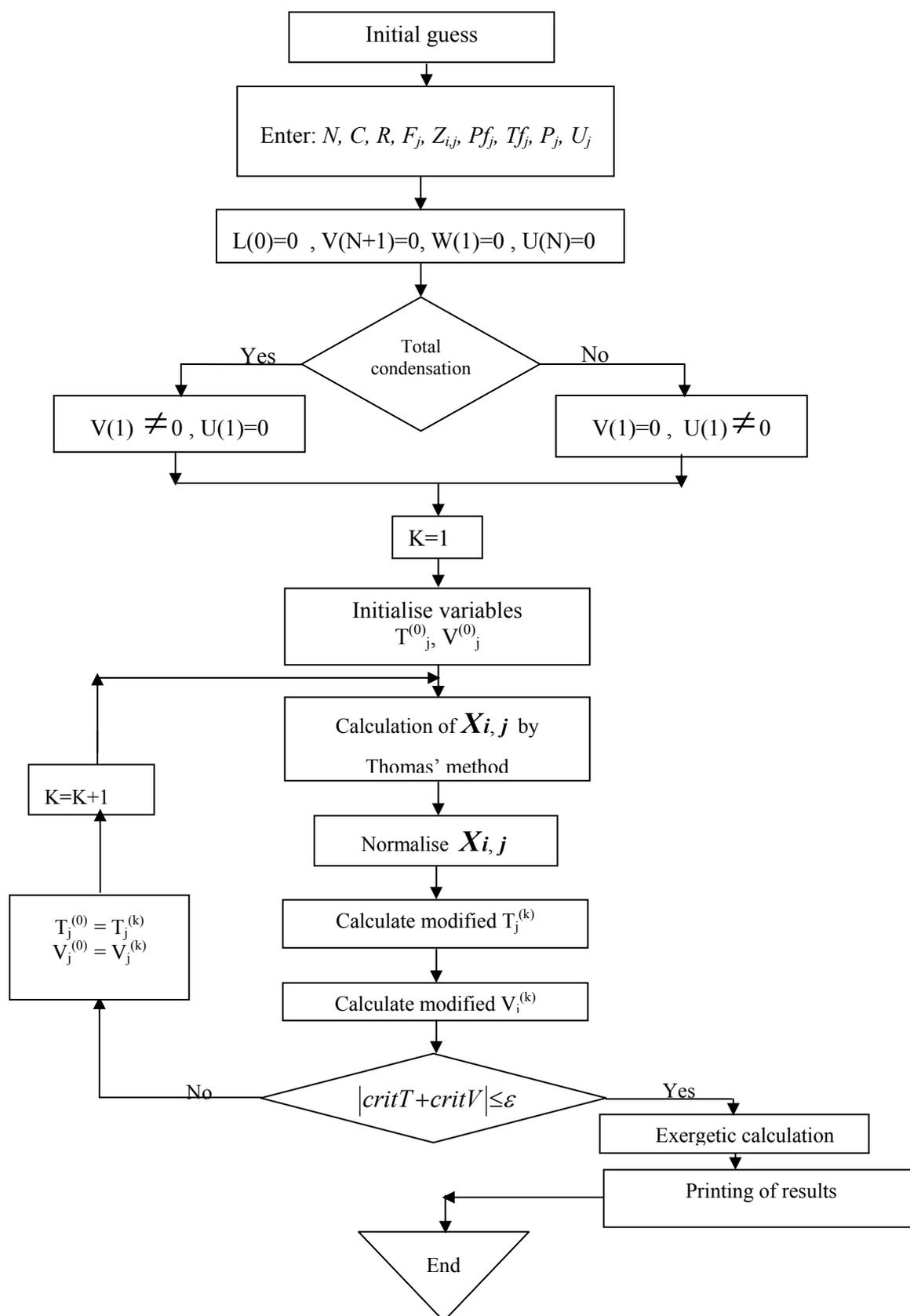
Figure 3. Flow chart of simulation and exergetic calculations
for the distillation column of complex mixtures.

4. Results and Discussion

In the first part, simulation results show that the model gives results in perfect adequacy with the experimental data. At this stage, they can be exploited to consider the energetic performance of the column. Theoretically, the distillation column, containing 33 theoretical trays, is fed from a mixture of light hydrocarbons whose composition is given in the table 1 and which supposed to obey the equation of state of Starling [19].

Table 1. Average LPG composition.

Component	C_1	C_2	C_3	Iso-C_4	n-C_4	Iso-C_5	n-C_5	C_6^+
Composition (% mol.).	1.00	3.00	55.00	10.50	25.00	5.00	0.50	Traces

The simulation results analysis proves extremely delicate because of the interactions between the various parameters to the extent that when a parameter is modified, all the others are affected. By taking into account of this remark, it seemed more instructive for us to restrict the operation column analysis to various feed rates. If the feed is supplied at the saturated liquid state and under a pressure of 20 bar, its temperature would be about 71°C. The analysis of column operation and the determination of the parameters were acquired by the rigorous method using the algorithm presented in Part I. The method being completely numerical does not put forth any distinctive preliminary assumption between the species present in the mixture [3, 10, 19].

4.1. Profile of key component composition versus tray position

For a feed of fixed composition, due to the interactions between the various components of the mixture, the molar composition in C3 in the distillate is slightly affected by the increase in the feed rate. This variation starts decreasing after having reached a flow rate neighbouring 150 kmol/hr. Indeed, the temperature at the two ends of the column appreciably affects the composition of the products of the column. In steady state, the molar fraction in C3 in the distillate varies between 88.32 and 82.78 % in the flow rate variation range. As to the profile along the column, the decrease continues until the last tray corresponding to the reboiler. To improve the purity of the products, it would be more adequate to vary the reflux flow rate or the number of trays, in the extreme case. From the calculations point of view, this improvement results in a longer computing time taking into account the nonlinear character of the simulation model. As to the feed tray, the curves C3, nC4 = f(N_{trays}) presented in Figure 4 are not derivable and that for component C3, the trays higher than 24 are almost inactive. Such a result is confirmed by the local exergetic analysis. However, due to the complexity of the interactions in the mixture to be distilled, the profile of component C4 composition continues its progression according to a profile identical to that of the temperature up to the reboiler where the temperature is equal to that of bubble point of the residue. Indeed, this complexity in the distillation of the mixtures requires systematic methods for column sequence determinations. The problem would more become complicated for highly non ideal systems or with chemical reaction (reactive distillation) where the resolution of the equations of the model leads to

multiple solutions. In such cases, the geometrical methods are particularly effective in the localization of the solutions

Mole fraction.
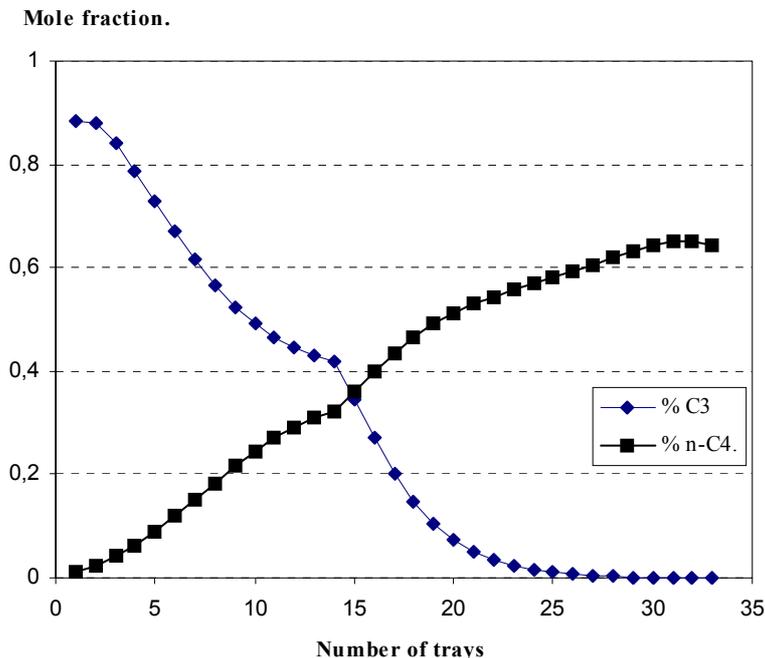
Figure 4. Key components composition profiles in the column.
Feed tray = 14. Saturated liquid flow rate = 100 kmol/hr.

4.2. Influence of the feed rate on the exergetic efficiency.

To visualize the impact of feed on the exergetic performances of the column, we present the results of simulation in Figure 5. It arises that the exergetic efficiency (η_{ex}) passes by a maximum value equal to 0.340 for a flow rate bordering 140 kmol/hr. In addition, we note a retained reflux rate of 2.4. This low efficiency could be improved.

η_{ex}
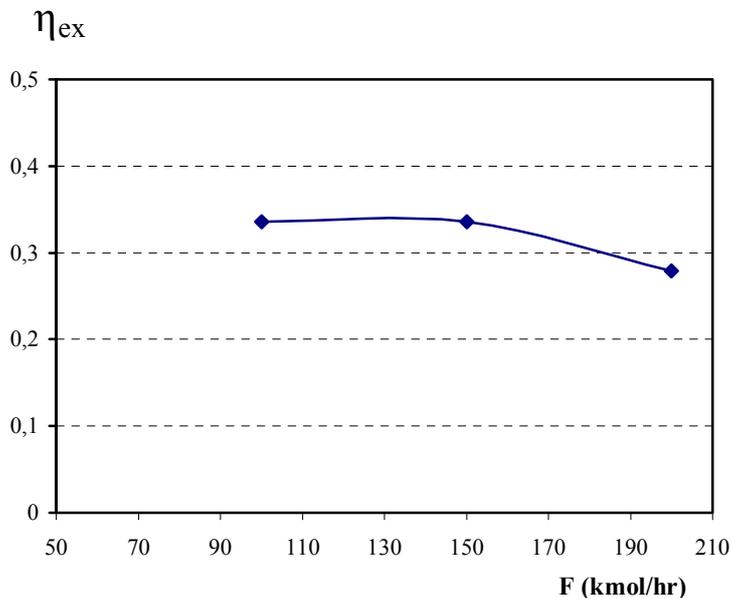
Figure 5. Influence of feed flow on the exergetic efficiency.

4.3. Distribution of the exergy losses in the column

The losses of exergy, expressed as a percentage along the rectifying section as a function of tray position, are presented in Figure 6. The exergy and other parameters are calculated on a tray by tray basis. Consequently, the functions represented in the graphs are discrete functions whose values depend on the conditions of the tray. It is noted that 60% of exergy losses are localised in the first five trays and that they remain constant starting from the seventh tray. This is explained by a significant composition gradient compared to equilibrium conditions and by a rather large separation in this section. Since the flow of production of entropy is a function of temperature and composition, it is obvious that the losses of exergy are maximal when these transfer potentials are so simultaneously. Moreover, it should be noted that the total loss of exergy in a column also depends on the feed conditions (composition, tray position, physical states) as well as on reflux flow rate. In addition, the losses of exergy, expressed as a percentage along the section of exhaustion versus tray position, are presented in Figure 7. They almost vanish starting from tray 23, and they reach significant values for the last plates close to the reboiler. It is clear that for a more uniform exergy loss distribution along the column, a quasi empirical approach is essential while proceeding by an increase in the proportion of the heat extracted from the tray where exergy loss is minimal and vice versa. Obviously, an uniform distribution of the heat exchanged with the column results from a uniform distribution of the potential of transfer [21] (Equipartition theorem).
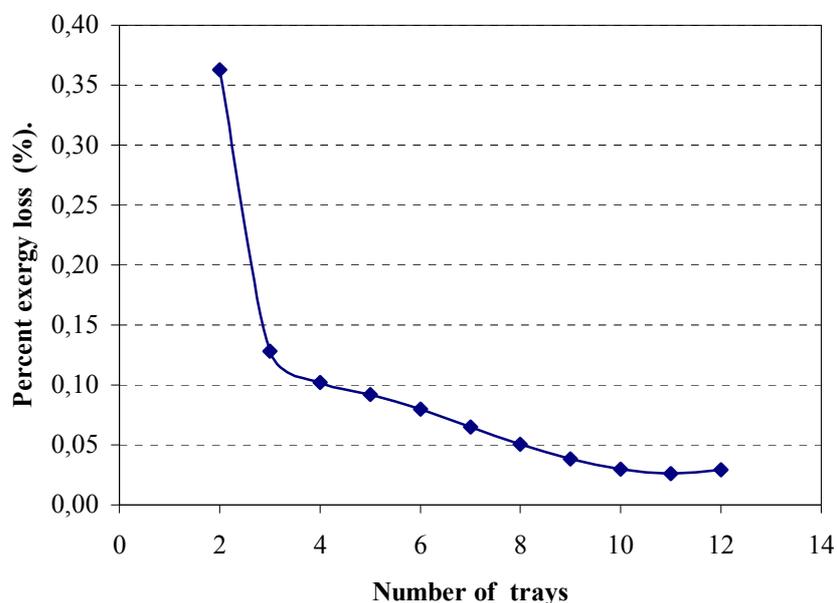
Figure 6. Exergy losses distribution in the rectifying section
(condenser and feed tray not included).
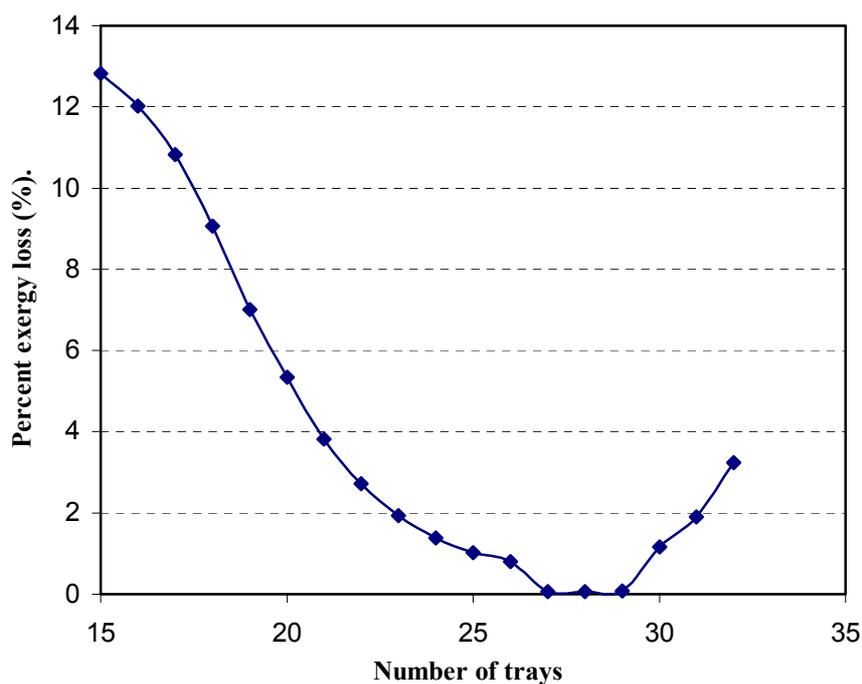
Figure 7. Distribution of exergy losses in the stripping section
(reboiler and feed tray not included).

4.4. Profile of the variation of the irreversibilities with tray position

To analyze the variation of the irreversibilities at the various trays as well as in the entire column, we introduced a cumulative function of the local irreversibilities. It is defined by:

$$\sum_{J=1}^{M} \dot{I}j = f(Tray) \qquad (M = 1, 2, ...N) \qquad (17)$$

This function presented in Figure 8 is particularly instructive owing to the fact that it simplifies graphic reading and quantification of the degraded powers from the top to the reboiler. This representation is equivalent to the diagram of Grassmann. Due to the discontinuity of contact between phases within the column, the graph is discontinuous (in staircase pattern) and each stage corresponds to one tray. One can note that the feed tray consists of a largely wide domain. Indeed, this observation shows that at this equilibrium level, the components undergo an effective separation.

The analysis of the variation of the composition on the adjacent trays confirms this result. Thus, for the various flows rates, the results of simulation are reported in Table 2. The distillate is mainly made up of C4 (90%) whereas C3 and C5 are in very small proportions (4 - 5%). This shows that for obtaining an increasingly pure distillate of more technical use, it would be necessary to consider an additional distillation column.
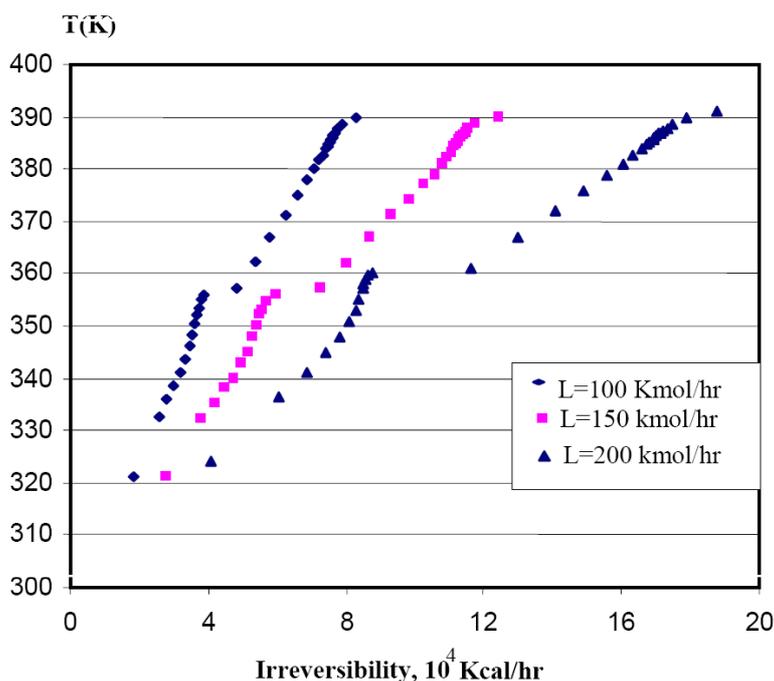
Figure 8. Cumulative irreversibility flux variation with tray position.

Table 2. Influence of feed rate on the irreversibilities at the rectifying and stripping sections.

Section	Operating parameters Exchanged heat and exergy	F=100 kmol/hr D= 0.72 m.	F=150 kmol/hr D=0.87 m.	F=200 kmol/hr D=1.05 m.
Rectifying section	Q_c (kcal/hr) exchanged heat at the condenser	$6.846 \ 10^5$	$1.0264 \ 10^6$	$1.4820 \ 10^6$
	IQ_c (kcal/hr): exergy exchanged at the condenser	$1.850 \ 10^4$	$2.7730 \ 10^4$	$4.1100 \ 10^4$
	I_{tot} (kcal/hr): Irreversibilities consumed at the section	$3.848 \ 10^4$	$5.7650 \ 10^4$	$8.7430 \ 10^4$
Stripping section	Q_r (kcal/hr): exchanged heat at the reboiler	$7.123 \ 10^5$	$1.0680 \ 10^6$	$1.5298 \ 10^6$
	IQ_r (kcal/hr): exergy exchanged at the reboiler	$4.456 \ 10^3$	$6.8160 \ 10^3$	$9.8040 \ 10^4$
	I_{tot} (kcal/hr): Irreversibilities consumed at the section	$3.485 \ 10^4$	$5.2280 \ 10^4$	$7.1530 \ 10^4$
Total exergy loss (kcal/hr)		$8.3288 \ 10^4$	$1.24811 \ 10^5$	$1.8790 \ 10^5$
Minimum separation work (kcal/hr)		$4.2069 \ 10^4$	$6.3163 \ 10^4$	$7.2796 \ 10^4$
Exergy consumed (kcal/hr)		$1.2536 \ 10^5$	$1.8790 \ 10^5$	$2,.070 \ 10^5$

5. Conclusions

It arises from this analysis that the process of mixture distillation is energetically extremely costly, on the one hand, and that the irreversibilities produced by exchange of matter and heat at the various trays cannot be easily reduced, on the other. Although the model of thermodynamic equilibrium at each tray is exploitable in order to determine all the column operating parameters, it would be more adequate to try to counter this considerable loss of energy. Analysis of the mathematical expression of the exergetic efficiency shows that the performance would be particularly sensitive to:

1. Temperature pinch $\delta T\ (= (T_N - T_1))$.
2. Thermal power exchanged at the condenser (Q_c) and the reboiler (Q_r).

Theoretically, to maximize the exergetic efficiency, it is imperative to minimize the temperature pinch where it is of interest to move along the column to work on closely neighbouring trays. The solution meeting this condition consists in inserting a heat pump functioning between two successive trays which play the role of condenser and reboiler. Indeed, the output would be optimal for a minimal pinch. Technically, the incorporation of a heat pump ($1.5 \leq COP \leq 4 \div 5$) functioning between the condenser and the reboiler leads to a considerable energy gain.

Nomenclature

COP	Coefficient of performance	
D	Distillate flow rate	(kmol/hr)
Ex	Stream exergy	(kcal/kmol)
F	Feed rate	(kmol/hr)
H	Stream enthalpy	(kcal/kmol)
I	Irreversibilities flux	(kcal/hr)
L	Liquid stream flow rate	(kmol/hr)
M	Liquid side stream	(kmol/hr)
m	Stream molar flow rate	(kmol/hr)
P_o	Ambient medium pressure	(1 atm.)
Q_c	Heat rate exchanged at the condenser	(kcal/hr)
Q_r	Heat rate exchanged at the reboiler	(kcal/hr)
S	Stream entropy	(kcal/kmol)
T_{ref}	Reference temperature	(K)
T_o	Ambient medium temperature	(273.15 K)
U	Vapor side stream	(298.15K)
V	Stream flow rate	(kmol/hr)
W	Applied mechanical work	(kcal/kmol)

Subscripts

i   Component i in the mixture
j   Tray number

Greek Symbols

Φ   Carnot's coefficient
η_{ex} Exergetic efficiency

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