Exergy Analysis of a Reactive Distillation MTBE Unit[*]

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Abstract

In this paper application of exergy analysis to the reactive distillation system of a Methyl TerButyl Ether (MTBE) production unit of a crude oil refinery is presented. In a refinery, the MTBE is obtained from methanol, and butanes (isobutylenes) produced in the fluidized catalytic cracking (FCC) unit. The reactives (isobutylenes) after purification are introduced to the main reaction system, the products of which are sent to the reactive distillation system to complete the reaction. A top rectification section, a bottom stripping section and a medium reaction section, compose the reactive column. The results of the exergy analysis of the unit indicate that the main exergy losses (about 63%) of the MTBE plant occur in the reactive distillation system, particularly in the distillation column itself and in its associated condenser. A detailed exergy analysis of the system, is presented in this paper.

Key words: exergy analysis, reactive distillation, MTBE, improvement potential

1. Introduction

The objective of the work presented in this paper is to establish the optimal operating conditions of the reactive distillation column of a Methyl TerButyl Ether (MTBE) production unit, and to evaluate its main exergy performance parameters in order to determine the operating conditions minimizing exergy losses in the reactive distillation system.

Gasoline mixtures have been reformulated incorporating ethers such as MTBE, which increases the octane number, and reduces pollutant gases emissions. The MTBE production process is a relatively new process, which uses reactive distillation columns. Distillation and chemical reaction occur simultaneously in a packed and tray column. This combination shows important advantages over the packed-bed reactor and over the distillation system, including the use of the heat of reaction for the separation of products, a relatively easy control of the temperature profile in the catalytic section, low operation costs due to high reaction yields, and low capital costs due to reduced equipment items.

Process simulation studies help in determining the influence of operating parameters such as the column feed location, methanol flowrate, and the reboiler and condenser heat duties.

With the exergy analysis of the simulated process it is possible (1) to establish the optimal operating conditions producing a higher amount of high quality products, (2) to establish the critical equipment items with the highest exergy losses, and (3) to evaluate the improvement potential of the reactive distillation system.

2. Process Description

In the refinery scheme the MTBE unit is located after the Fluid Catalytic Cracking (FCC) unit, the obtained products are the MTBE which is sent to the gasoline pool and the raffinate which is sent to the alkylation unit.

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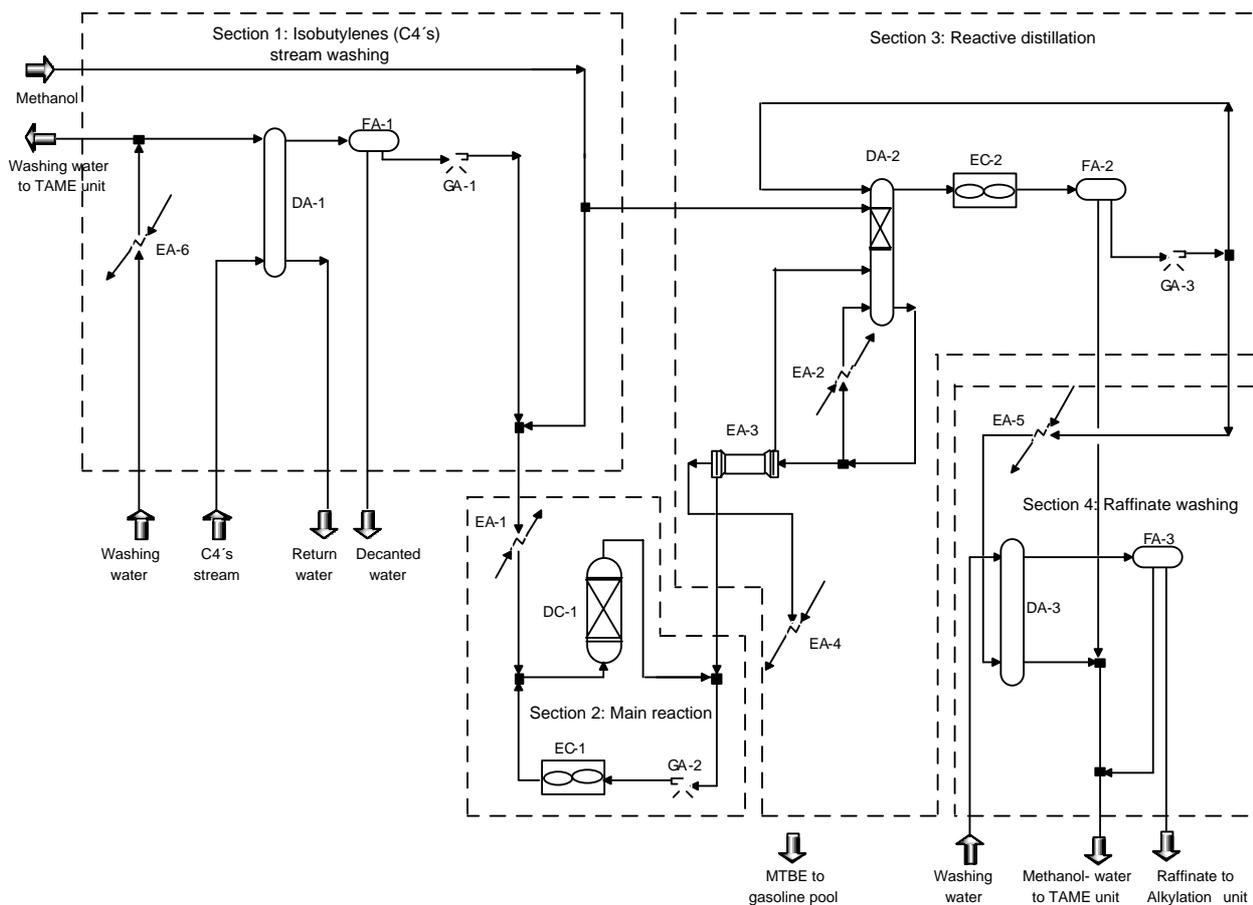
Figure 1. Process flowsheet of the MTBE unit.
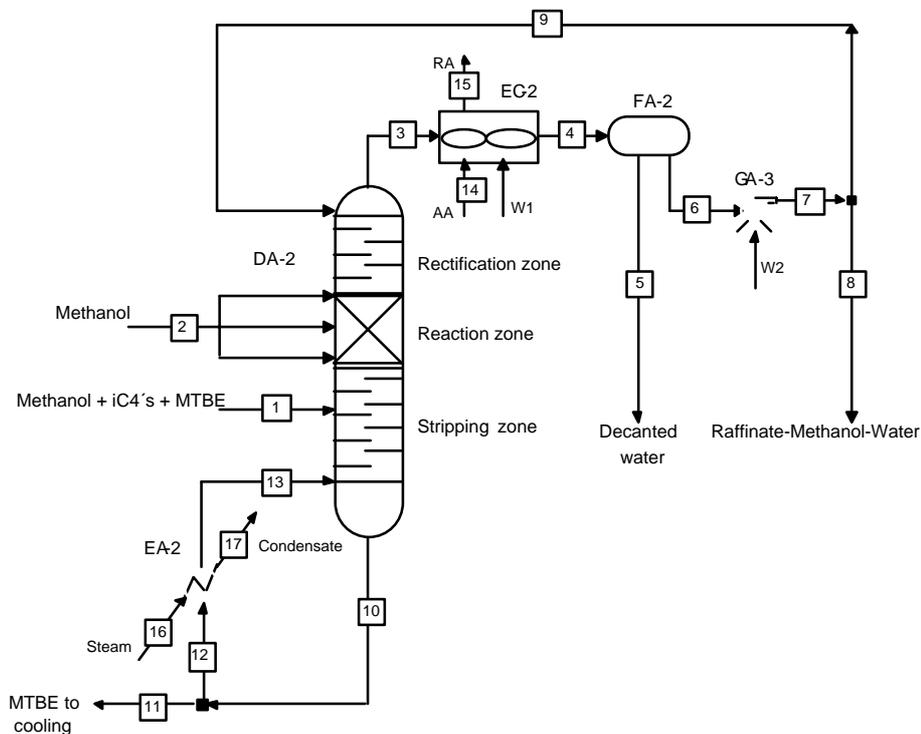
Figure 2. Reactive distillation scheme

The process flowsheet of the MTBE unit is presented in *Figure 1*. This unit is composed by four sections: (1) The isobutylenes or 'reactives' (C4's) stream washing, in which catalyst contaminating impurities are eliminated in column DA-1; (2) the main reaction section in which most of the conversion of isobutylene to MTBE is achieved in reactor DC-1; (3) the reactive distillation section, in which the conversion to MTBE is completed and the MTBE is separated in column DA-2; and (4) the raffinate washing section in which unreacted isobutylenes are recovered and the methanol-water stream is separated in column DA-3 for sending it to the methanol recovery section of the TerAmyl Methyl Ether (TAME) unit.

Product MTBE is obtained in the reactive distillation section, cooled and sent to the gasoline pool. The reactive distillation system is presented in *Figure 2*.

3. Exergy Analysis

The main reaction of MTBE formation is (Yuxiang and Xien, 1992):

$$CH_3OH + CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_2}{\|}}{C}}-CH_3 \rightleftharpoons CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-CH_3$$

Methanol   Isobutylene   MTBE
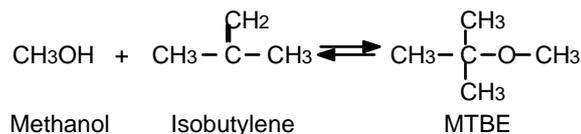
The formation rate is:

$$r_{MTBE} = k_+ C_{IB} - k_- C_{MTBE} \qquad (1)$$

where:

$$k_+ = 2.5152 * 10^7 \exp\left(-\frac{6844}{T}\right) \qquad (2)$$

$$k_- = 8.2680 * 10^{11} \exp\left(-\frac{11381}{T}\right) \qquad (3)$$

This equation considers that there is a methanol excess and the temperature range of the reaction is 60 - 80 °C.

The simulation of the plant has been conducted using the Aspen Plus simulation code and the exergy analysis subroutines developed by the IMP Exergy Group (Rivero, 2000a). The dead state conditions in all calculations are $T_0 = 25°C$ and $P_0 = 1$ atm and X_0 = Szargut model, (Szargut et al., 1988).

A complete exergy analysis of the naphtha reforming unit has been conducted in the frame of a research project (Rivero, 2000a) using the general methodology presented in previous papers (Rivero et al., 1989).

Figure 3 shows the block diagram of the reactive distillation system with all streams involved.

Irreversible Exergy Losses (exergy destruction) represent energy degradation in a quantitative manner; they are calculated simply as the difference between the total exergy input (Ex_{ti}) and the total exergy output (Ex_{to}) or as the difference between the net exergy supplied (Ex_{ns}) and the net exergy produced (Ex_{np}):

$$Irr = Ex_{ti} - Ex_{to} \qquad (4)$$

$$Irr = Ex_{ns} - Ex_{np} \qquad (5)$$

with:

$$Ex_{ti} = Ex_1 + Ex_2 + Ex_{14} + Ex_{16} + W_1 + W_2 \qquad (6)$$

$$Ex_{to} = Ex_5 + Ex_8 + Ex_{11} + Ex_{15} + Ex_{17} \qquad (7)$$

$$Ex_{ns} = (Ex_{16} - Ex_{17}) + W_1 + W_2 + \nabla Ex_{ph} \qquad (8)$$

$$Ex_{np} = (Ex_{15} - Ex_{14}) + \Delta Ex_{ch} \qquad (9)$$

It is important to mention that in this process there is an increase in the chemical exergy of the process streams which is a part of the net exergy produced and a decrease in the physical exergy of the process streams which is a part of the net exergy supplied:

$$\nabla Ex_{ph} = (Ex_{ph1} + Ex_{ph2}) - (Ex_{ph5} + Ex_{ph8} + Ex_{ph11}) \qquad (10)$$

$$\Delta Ex_{ch} = (Ex_{ch5} + Ex_{ch8} + Ex_{ch11}) - (Ex_{ch1} + Ex_{ch2}) \qquad (11)$$

In addition to the Irreversible Exergy Losses, there are Effluent Exergy Losses. This waste is simply the sum of all exergy streams rejected to the environment:

$$Efl = Ex_{15} \qquad (12)$$

Total Exergy Losses, Pex, represent total energy degradation both internally and externally:

$$Pex = Irr + Efl \qquad (13)$$

In order to determine how well is the desired effect of the system accomplished, the Effectiveness is calculated as the ratio of the net exergy produced to the net exergy supplied:

$$\varepsilon = \frac{Ex_{np}}{Ex_{ns}} \qquad (14)$$

Total Exergy Losses and Effectiveness are the quantitative and qualitative measures of energy degradation, and they can be combined to have a more complete parameter of the performance of the system. This parameter is called the Improvement Potential (Rivero et al., 1989) which provides a hierarchy of all systems or blocks composing a process for optimization purposes:

$$Pot = Irr(1 - \varepsilon) + Efl \qquad (15)$$
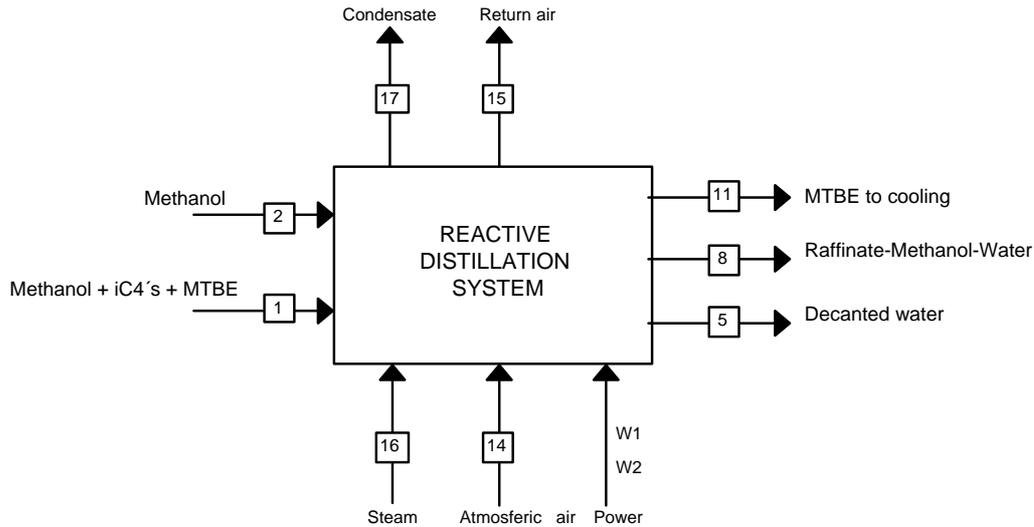
Figure 3. Block diagram of the reactive distillation system.

4. Results

Figure 4 shows the distribution of the total exergy losses of the different sections of the MTBE unit.
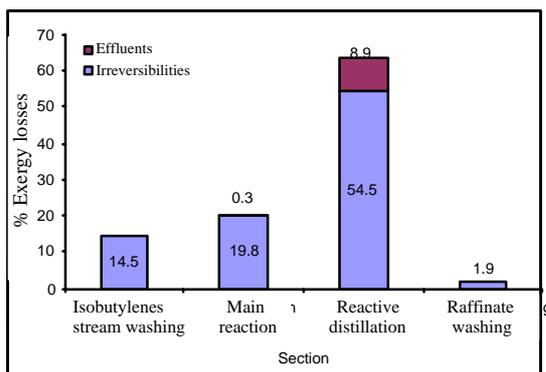
Figure 4. Exergy losses by sections

The main exergy losses of the MTBE unit (about 63% of the total) are located in the reactive distillation system, particularly in the distillation column itself (32%) and in its associated condenser (36%) (Rivero, 2000a).

The main reaction section is clearly not the most important one from the exergy losses viewpoint, even if this section has the lowest effectiveness as shown in *Figure 5*.

The reason why the main reaction section is not the most important from the exergy losses viewpoint steems from the fact that in the reactive distillation section a high energy degradation occurs between the reboiler and the condenser for separating the products.

By combining the imperfection aspects measured by both the exergy losses and the effectiveness one obtains the improvement potential.

Figure 6 gives the distribution of the improvement potential of the different sections of the MTBE unit..

The critical section of the plant indicated by the exergy losses is confirmed to be the reactive distillation section. It is then very important to further analize this section through a parametric study.
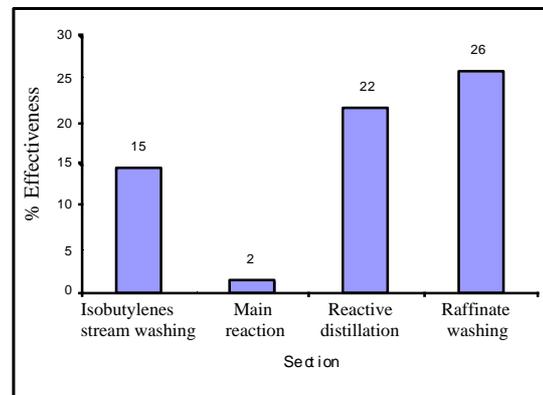
Figure 5. Effectiveness in the sections.
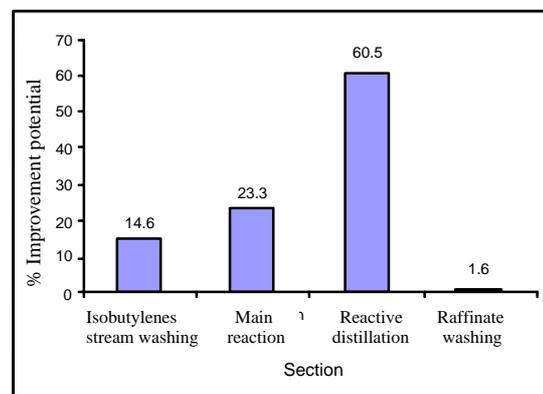
Figure 6. Improvement potential in the sections.

The reactive distillation column consists of 58 stages; the rectification zone is located from stages 2 to 14 (the condenser is stage 1), the catalytic zone is located between the 15th and 20th stages. It has been designed with three possible stages for methanol feed: stage 13 in the rectification zone and stages 15 and 17 in the catalytic zone.

The main operating conditions of the MTBE unit (base case) are shown in the TABLE I.

A parametric analysis of the effect of the methanol feed location, methanol flowrate, and reboiler heat duty, on the performance of the system has been conducted in order to find the optimal conditions both from the exergy parameters viewpoint (exergy losses, effectiveness and improvement potential) and from the MTBE production viewpoint.

TABLE I. MTBE UNIT OPERATING CONDITIONS (BASE CASE).

Parameter	Stream	(kg/kg of reactives)
Reactive column feed flow rate	1	1.1118
Methanol flow rate to the reactive distillation column	2	0.010
MTBE production	11	2.7125
Raffinate-Methanol-Water production	8	0.8506
Methanol feed location in the reactive distillation column		stage 14
Reboiler heat duty (kJ / kg of reactives)		440.09
Condenser heat duty (kJ / kg of reactives)		540.0
Reflux ratio	9/8	0.9312

4.1 Effect of the methanol feed location

The effect of the location of the methanol feed to the reactive column on the amount of MTBE produced is shown in *Figure 7*. When the feed is located below the catalytic zone, (stages 20 to 22) the amount of MTBE increases and then remains constant; this can be explained by a better contact between the reactives and the catalyst.

The increase in MTBE production is important from stages 10 to 20, so the exergy performance parameters were evaluated for this range of feed locations. *Figure 8* shows the Irreversible Exergy Losses for stages 10 to 19. Stage 20 is not included in the figure because the exergy losses increase dramatically (647 kJ/kg of reactives vs. 138 kJ/kg of reactives in average for all other feed locations).
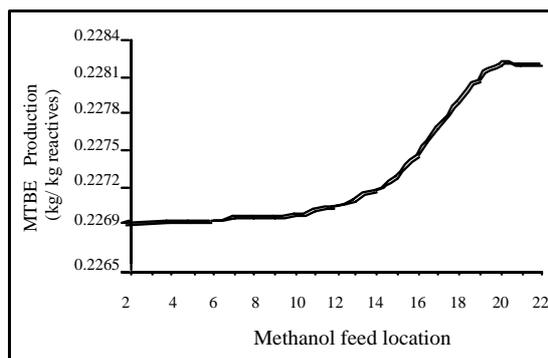
Figure 7. Effect of the methanol feed location.

As mentioned, this feed location corresponds also to the maximal MTBE production, but there are two interesting points in *Figure 8*. When the methanol feed is located in stage 13, a minimum of exergy losses is obtained but also a near-to-the-minimum MTBE production. However, when the feed is located in stage 19, a near-to-the-minimum exergy losses is obtained and a near-to-the-maximum MTBE production; stage 19 would be an adequate feed location from both points of view.

Figure 9 shows that all possible feed tray locations have improvement potentials of 127.1 kJ/kg of reactives with a very low fluctuation. When methanol is introduced at tray 20 exergy losses are greater than 647 kJ/kg of reactives with an improvement potential of 641.7 kJ/kg of reactives; it is at this possible feed location that irreversible exergy losses are the greatest of the process.
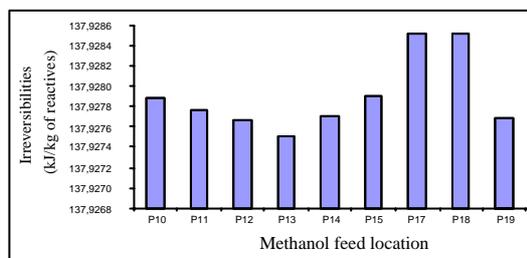
Figure 8. Irreversible exergy losses for different methanol feed locations.
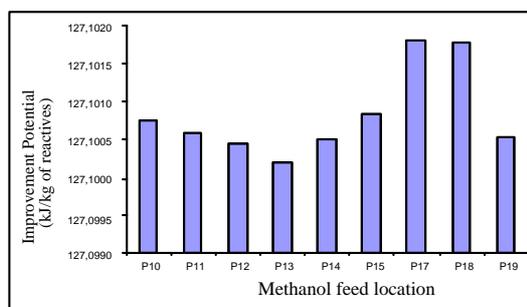
Figure 9. Improvement potential for different methanol feed locations.

In most of the possible feed locations the effectiveness is 25% as shown in *Figure 10*. At tray 20, not shown in the figure, the effectiveness falls to 3.15%.
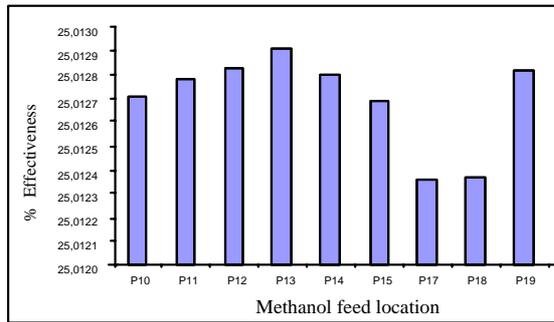
Figure10. Effectiveness for different methanol feed locations.

4.2 Effect of the methanol flow rate

The second variation was to change the methanol flow rate supplied to the column, keeping fixed all other design parameters and obtaining the following results. By varying the methanol flow rate to the reactive column (*Figure 11*) the flow rate to get the maximal MTBE yield is found; it is in the range of 0.011 to 0.013 kg/kg of reactives.
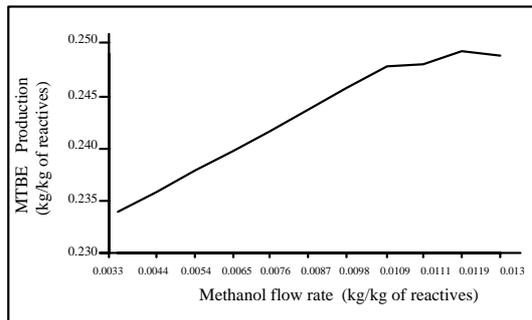
Figure 11. Change of the methanol flow rate.

As shown in *Figure 12*, system irreversibilities increase with the increase of the methanol flow rate because the MTBE production also increases.
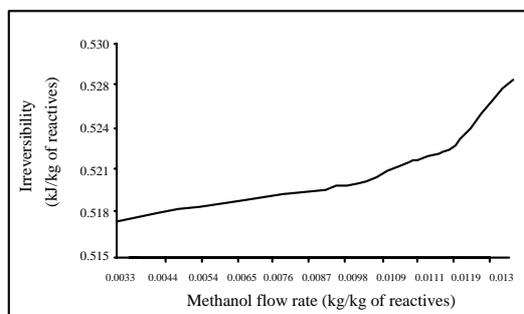
Figure 12. Irreversibility for different methanol flow rates.

The improvement potential of the reactive column represents 78% of the system's total exergy losses. By changing the methanol flow rate to the reactive column, these losses could be reduced by a better choice of operating conditions as shown in *Figure 13*.
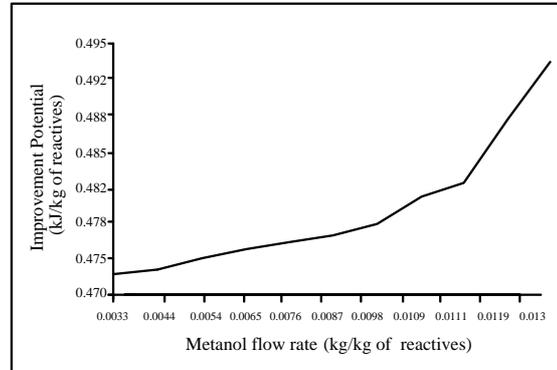
Figure 13. Improvement potential for different methanol flow rates.

Figure 14 shows that when methanol flow rate increases, the effectiveness is reduced from 25.6 to 23.8 %. Since this reduction is not very important the average effectiveness can be considered to be 25 %.
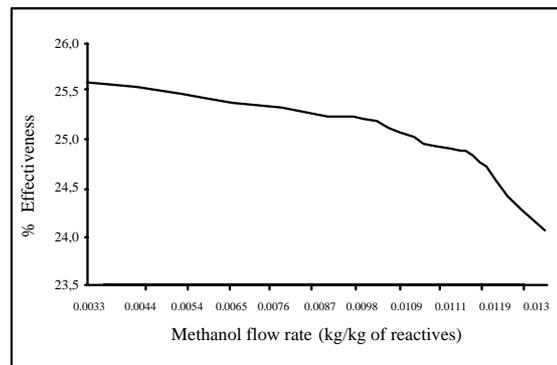
Figure 14. Effectiveness for different methanol flow rates.

4.3 Effect of the reboiler heat duty

It is important also to establish the maximal heat duty to be supplied to the distillation system at the reboiler EA-2. A parametric analysis of the reboiler heat duty gives the results shown in *Figure 15*.

The MTBE yield remains constant when the heat duty is greater than 422.3 kJ/kg of reactives so it is not necessary to increase the heating steam supply. This can also be observed from the irreversibility losses point of view (*Figure 16*).
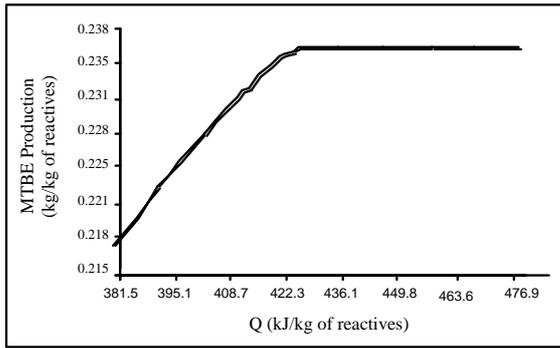
Figure 15. Parametric analysis of the reboiler heat duty.
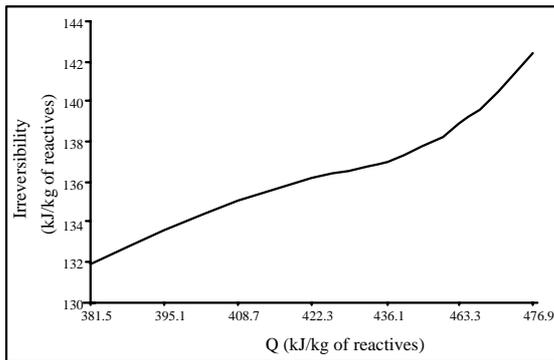
Figure 16. Irreversibility losses for different reboiler heat duties.

The improvement potential represents near 80% of the total irreversibility losses as shown in *Figure 17*.

For a heat supply equal or lower than 422.3 kJ/kg of reactives the effectiveness of the system is 20% or lower which is lower than the 25% value of previous cases. However this lower effectiveness is still acceptable since the MTBE yield remains practically constant for any heat supply. On the other hand, if operation is fixed to have a 25% effectiveness, the total and irreversible exergy losses would be very high, as can be deduced by comparing *Figure 18* and *Figure 16*.
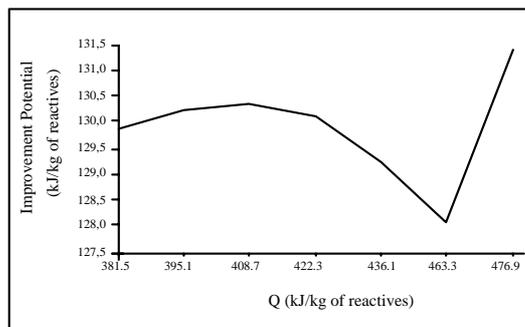
Figure 17. Improvement potential for different reboiler heat duties.
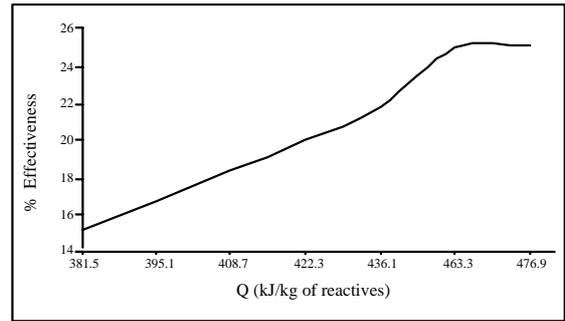
Figure 18. Effectiveness for different reboiler heat duties.

5. Conclusions

The parametric analysis of the system shows that the optimal methanol feed location from the posible locations available is stage 17. However if the column could be modified the optimal feed location would be stage 19.

The optimal heat duty of the reboiler is 422.3 kJ/kg of reactives and the optimal methanol flowrate is 0.0109 kg/kg of reactives.

The reactive distillation section of the MTBE unit is used to increase the conversión of the reaction from 95% in the reaction section to 99% after the reactive distillation. The exergy losses of the unit are almost doubled to obtain this additional 4% conversion. The convenience of finding an alternative to the use of reactive distillation in the plant is presently being studied (Rivero, 2000b).

Nomenclature

C	concentration
Efl	effluent exergy losses
Ex	exergy
Irr	irreversible exergy losses
k	rate constant of reaction, (m^3/kg catalyst h)
P	pressure
Pex	total exergy losses
Pot	improvement potential
Q	heat duty
r_{MTBE}	MTBE formation rate, (kmol/kg catalyst h)
T	absolute temperature, (K)
W	work
X	composition

Greek symbols

∇	decrease
Δ	increase
ε	effectiveness

Subscripts

0	dead state
+	forward reaction
-	reverse reaction

ch	chemical
np	net produced
ns	net supplied
ph	physical
ti	total input
to	total output

References

Rivero, R, 2000a, "Optimización Exérgica de un Esquema de Refinación", Proyectos E0A-7708, E0A-7709, E0A-7442, P.00257, F.00257, Grupo de Exergia - Instituto Mexicano del Petróleo.

Rivero, R, 2000b, "Investigación y Desarrollo Tecnológico de Proceso de Destilación Diabática" Grupo de Exergia - Instituto Mexicano del Petróleo.

Rivero R., González, G., García, V., Pulido, R., Escárcega, C., 1989, "Exergy Analysis of a Crude Oil Atmospheric Distillation Unit.", In: R.X. Cai & M.J. Moran, editors. International Academy Publishers - Pergamon Press. Beijing. pp. 506-511.

Szargut, J., Morris, D. R., Steward, F.R., 1988, "Exergy Analysis of Thermal, Chemical and Metallurgical Processes", New York: Hemisphere Publishing Corporation.

Yuxiang, Z., Xien, X., 1992, "Study on Catalytic Distillation Processes, Part II. Simulation of Catalytic Distillation Processes Quasi-Homogeneous and Rate-Based Model", Trans IchemE., 70(A): pp. 465-470.