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Treball Final de Grau

Efficiency assessment of chemical processes: reactor and separation.
Evaluación de la eficiencia de procesos químicos: reactor y separación.

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Si buscas resultados diferentes, no hagas siempre lo mismo.

Albert Einstein

En primer lugar, agradecer a toda mi familia la confianza y el apoyo incondicional durante estos años de carrera. Por enseñarme a no rendirme y luchar por aquello que me propongo.

A mis tutores, Dr. Jordi Bonet y Dra. Alexandra Bonet, por la paciencia y dedicación mostrada durante estos meses de trabajo.

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Por último, dedicar este trabajo a esas personas que a día de hoy no están aquí presentes.

GRACIAS.

CONTENTS

SUMMARY

Chemical sector is one of the big sectors in the world. The shortage of raw materials, the importance in the sustainability, as the environmental requirements, and the increased of competition make the necessity of investigation and application of more efficient and cost-effective processes (Recker et al, 2015).

One tool in the search or optimization of process is the use of simulators, which allow us obtaining results quickly and easily in complex processes using simplified models, allowed us to do changes or variations in same process to compare with each other. However, rigorous simulations requires a great effort and therefore it is not suitable for process screening.

Due to the shortage of methods that study the efficiency of the process at early process design stages, in this work has been developed a short cut method that allows obtaining the efficiency of the alternative process schemes considering reactor and separation jointly. This method is based on application of DSE (Distillation Sequence Efficiency), to which is added a correction factor to take into consideration the reactor.

ETBE (Ethyl Tert-Butyl Ether) production process is used as case study. Analyzing the different alternatives of design of the chosen alternative, trough simulations in AspenPlus®, is determined the feasibility of each of the alternatives suggested.

The DSE with the correction factors for the calculation of the efficiency is implemented using FORTRAN® in AspenPlus®.

Keywords: Simulation, ETBE production process, Optimization, Reaction and Separation, Efficiency, AspenPlus®.

RESUMEN

El sector de la química es uno de los grandes sectores en el mundo. El aumento en la escasez de materias primas, la importancia en la sostenibilidad, así como las exigencias medioambientales, y el aumento de competitividad obliga de manera directa a la investigación y aplicación de procesos con mayor eficiencia y rentabilidad (Recker et al, 2015).

Una herramienta en la búsqueda u optimización de procesos es el uso de simuladores, los cuales nos permiten obtener resultados rápidos y de manera fácil en proceso complejos usando modelos simplificados. Además, las simulaciones rigurosas requieren un gran esfuerzo y por tanto, no es adecuado para el proceso de selección.

Debido a la escasez de métodos que estudian la eficiencia de un proceso en las primeras etapas de diseño, en este trabajo ha sido desarrollado un "short cut" método que permite obtener la eficiencia de los alternativos esquemas de procesos considerando reactor y separación de manera conjunta. Este método se basa en la aplicación del DSE (Distillation Sequence Efficiency) al cual se añade un factor de corrección que integra el reactor en el DSE.

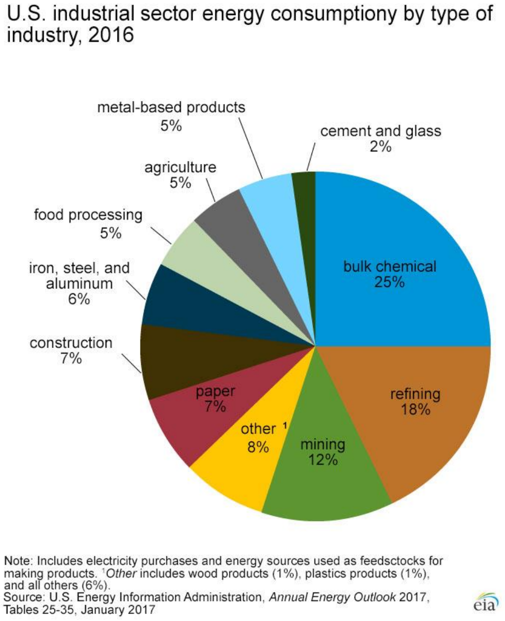
El proceso de producción de ETBE (Etil Tert-Butil Éter) es usado como caso de estudio en este proyecto. Analizando las diferentes alternativas de diseño del caso escogido, mediante simulaciones en AspenPlus®, es determinada la factibilidad de cada una de las alternativas propuestas.

El DSE junto a los factores de corrección para determinar el cálculo la eficiencia es implementado en AspenPlus® mediante programación en FORTRAN®.

Palabras clave: Simulación, Proceso de producción de ETBE, Optimización, Reacción y Separación, Eficiencia, AspenPlus®.

INTRODUCTION

Nowadays, the operation of the natural resources and the increase of the industrial demand cause in the chemical industry the desire of making processes more efficient and sustainable (Recker et al, 2015). In detail, the chemical industrial sector is the one with a higher energetic demand in the U.S. consuming it the 48% of the total energetic consume (Figure 1).



Note: Includes electricity purchases and energy sources used as feedsctocks for making products. ¹*Other* includes wood products (1%), plastics products (1%), and all others (6%).
Source: U.S. Energy Information Administration, *Annual Energy Outlook* 2017, Tables 25-35, January 2017

Figure 1. U.S Industrial sector energy consumption, 2016 (EIA, 2018)

The research or implementation of efficient processes is a task of great importance. Carrying out a study of the first stages of design, it is possible to prevent future possible mistakes and determines the potential of improvement of the process. The more advanced is the design of process, the more exponentially increases its costs of design. This is why the optimization of the design minimizes the costs, increases the efficiency and improves the planning capacity (Dowling and Biegler, 2015).

A nowadays approach is the onion diagram where first is optimized the reactor and in a second layer is optimized the separation process without taking into account that the reactor and separation scheme become linked by the recycle streams. Many of the nowadays methods proposed focus only in the separation process without taking into account the reactor.

Few are the methods based in the optimization of the processes that value systems of reaction separation jointly (Recker et al., 2015). This is because of the difficulty of the calculus that presents the simultaneous optimization of the flowsheet structure, the unit specifications and the operating points (Kallrath, 2000).

After a bibiographic research of many papers through the database Scopus (Scopus, 2018) it has been just found an paper that evaluates jointly the reaction and the separation in the early stages of design for process screening. The paper is called “A unifying framework for optimization-based design of integrated reaction-separation processes” of Recker, S.; Skiborowski, M.; Redepenning, C.; Marquardt, W published in 2015 (Recker et al, 2015).

This paper raises, among other things, various process diagrams for the production of ETBE.

The ETBE (Ethyl Tert-Butyl Ether) is an additive of gasoline that is formed by IB (Isobutylene) and EtOH (Ethanol), as is shown in the Figure 2. This reaction is produced with a strong acidic macroporous ion exchange resign in liquid phase at 10 bar (Thiel, Sundmacher and Hoffman, 1997).

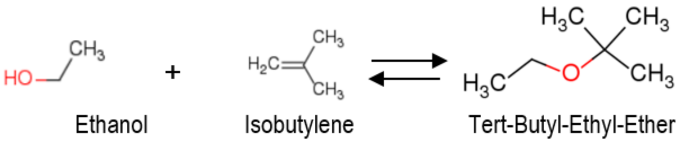


Figure 2. Reaction of the ETBE

Starting with a simple process are determined four processes more complex with two different focuses. The first group is focused on improving of the separation and the second is focused on improving of the reaction yield. The process diagrams are screen through the simulation of shortcut methods and the most promising diagrams are optimized rigorously to determine the best alternative.

The diagrams suggested to the production of ETBE consist of two entering streams. The first stream introduces the IB flow in the system. The IB is usually not pure since contains an n-Butane (nBa) fraction. The composition of this flow is 40% IB and 60% nBa. The second stream introduces the EtOH flow.

Hereafter, there are described in different subsections the different processes determined in the paper commented. The two last alternatives, Reactive distillation and BREF have been added by own choice.

1.1. **ALTERNATIVE 1.1**

This is the primitive alternative (Figure 3). It contains only a reactor and column to carry out the process. The two feed flow rates enter in the reactor and it is performed the reaction. The column separates the ETBE for the bottom due to its lower boiling point. For the top of the column it is separated an EtOH/IB/nBa mixture. An amount of distillate is recirculated with the raw material introduced in the system. Thanks to this recirculation is recovered an amount of the EtOH and IB unreacted. The total recirculation is not feasible and it is due the nBa inert that it has to be purged.

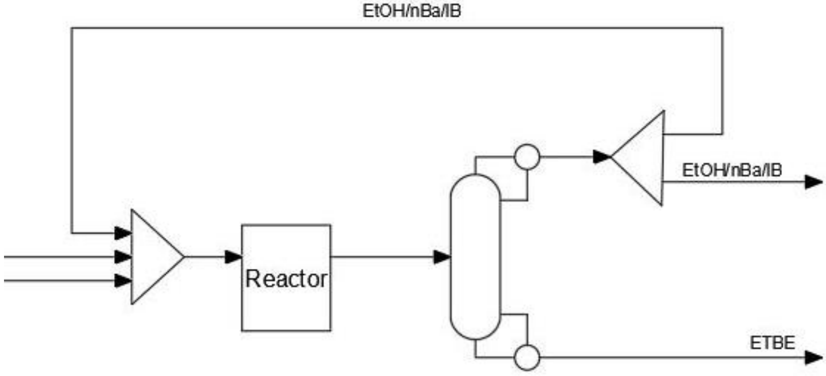


Figure 3. Process scheme of alternative 1.1

1.2. ALTERNATIVE 1.2

The alternative 1.2 proposes an improving separation varying the number of columns with regards of the alternative 1.1 (Figure 3). This alternative uses three distillations columns and only one reactor (Figure 4).

Due the use of three columns after the reactor, this first column separates in a different way to alternative 1.2 the outlet flow rate of the reactor. The first column separates a chemical mixture of EtOH/nBa/IB for the distillate. For the bottom separates a chemical mixture of EtOH/ETBE.

The distillate flow rate of the first column is sent to a second column that separates the IB for the distillate and an azeotropic mixture of EtOH/nBa by the bottom. The recovered IB for the distillate is recirculated to the entrance of the reactor. The azeotropic mixture of EtOH/nBa obtains for the bottom is withdraw of the system.

The flow rate of the bottom in first column is sent to third column that separates pure ETBE of the mixture. Due the EtOH/ETBE azeotrope is not possible a completely separation between EtOH and ETBE. For this reason, the azeotropic composition, which is obtained for the distillate is recirculated to reactor. With this recirculation is avoided the loss of product and it is reused of the reactant EtOH. The pure ETBE is obtained thus for the bottom of the second column.

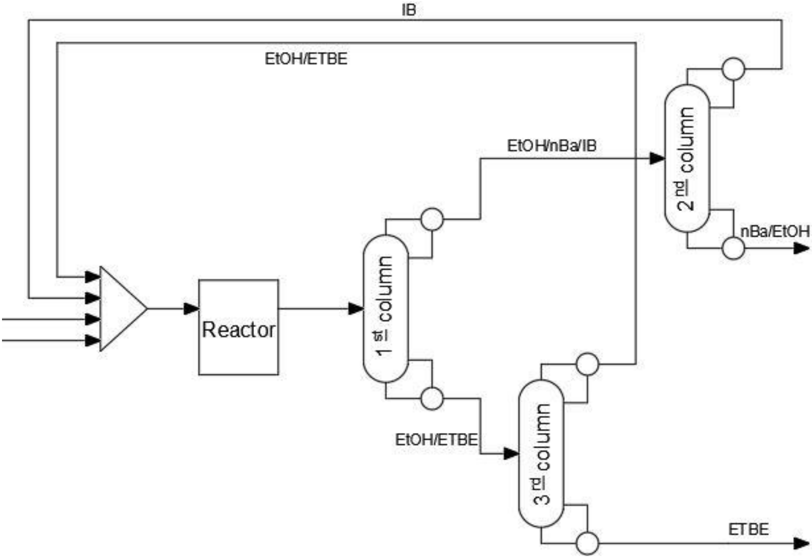


Figure 4. Process scheme of alternative 1.2

1.3. ALTERNATIVE 1.3

The alternative 1.3 (Figure 5) is an extension of the last commented alternative (Figure 4). This alternative is composed of one distillation column more than the alternative 1.2

The fourth distillation column is added after of the column responsible for separating the EtOH of the ETBE. Since between the EtOH and the ETBE exist an azeotrope, the strategy in this alternative is to work with this fourth column in a work pressure different from the system. Varying the work pressure of the fourth column, the azeotropic composition varies favoring the pure separation of a compound. In this case, decreasing the pressure of the fourth column, the azeotropic composition of the ETBE increases, favoring the separation of the reactant EtOH.

In the same way that in the alternative 1.2, the first column separates a EtOH/nBa/IB mixture for the distillate and a EtOH/ETBE mixture by the bottom. The distillate is sent to second column that separates the IB for the distillate, which is recirculated. The azeotrope nBa/EtOH is purged by the bottom.

The mixture obtained for the first column bottom is separated in the third column in EtOH/ETBE for the distillate and the pure ETBE by the bottom. The EtOH/ETBE azeotrope of the distillate is separated in the fourth column. This fourth column in different of last column separates the pure reactant EtOH (majority compound) of the azeotrope EtOH/ETBE. The pure reactant EtOH is obtained for the bottom and it is recirculated to reactor. The flow rate obtained for the distillate, azeotropic mixture, is recirculated at the entrance of the previous column. Due to the majority composition of ETBE in the azeotropic mixture obtained is not recirculated at the entrance of the reactor as the alternative 1.2.

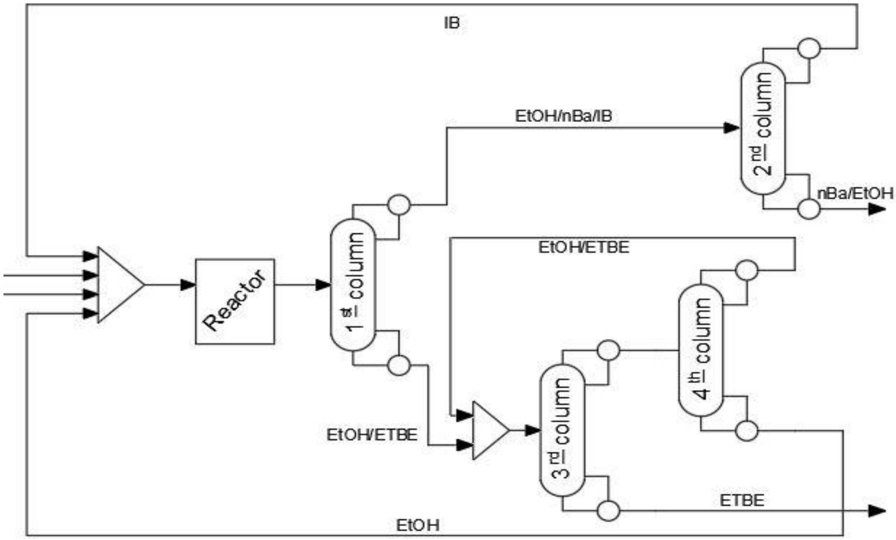


Figure 5. Process scheme of alternative 1.3

1.4. **ALTERNATIVE 2.1**

The alternative 2.1 is focused on improve the reaction yield. This alternative is based on 2 reactors and 2 distillation columns. It is similar to the alternative 1.1 adding a reactor for the distillate flow rate of the first column (Figure 6).

Once the raw material has reacted in the first reactor, it is sends to first distillation column. The first column separates the pure product ETBE by the bottom. The EtOH/IB/nBa mixture is obtained for the distillate flow rate. Because the distillate mixture is free of product and it contains both reactants, it is introduced in the second reactor. The reactants introduce in the second reactor generate new product ETBE. This flow rate obtained of the second reactor is introduced in the next column. This column separates for the distillate an IB/nBa/EtOH mixture being the ethanol amount the corresponding to azeotropic fraction of EtOH in the azeotrope nBa/EtOH. For the bottom of the column is obtained an ETBE/EtOH mixture, which is sent to the reactor inlet.

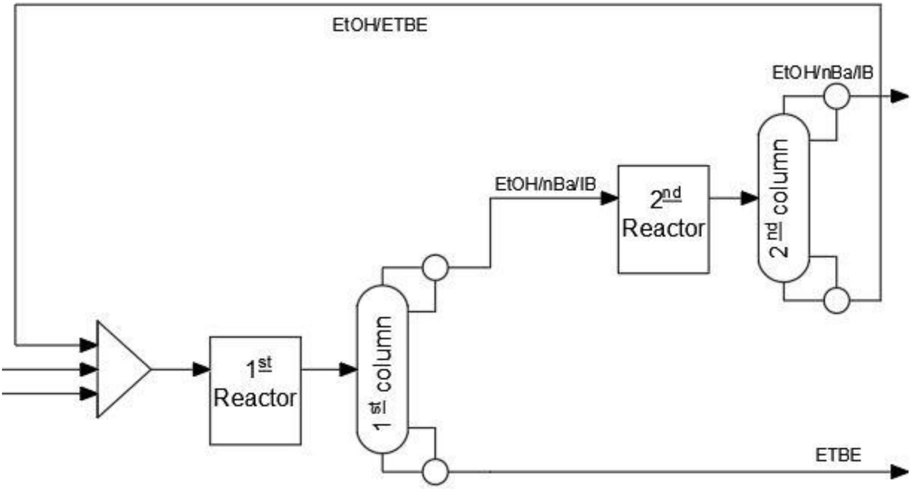


Figure 6. Process scheme of alternative 2.1

1.5. ALTERNATIVE 2.2

This alternative (Figure 7) is an extension of the last commented (Figure 6). As with the alternative 2.1, the design is focused to improve the reaction yield. Adding a third distillation column in the process that allows the increase of the main EtOH stream differs from last alternative.

Once they react the reactants in the first reactor, it is sent to first distillation column. The first column separates the three compounds (EtOH/IB/nBa) for the distillate flow rate. This flow rate is introduced to second reactor that sends its outlet flow rate at a second column. This column separates the compounds IB/nBa/EtOH for the distillate and an EtOH/ETBE mixture by the bottom. This flow rate obtained in the bottom is recirculated at the reactor inlet.

The flow rate obtained for the bottom in the first column consist of EtOH/ETBE mixture. Due to use of a third column, a greater flow of EtOH in the principal inlet is can use in respect of alternative 2.1. This third column separates the ETBE as pure product for the bottom and the azeotrope EtOH/ETBE by the distillate flow rate. This flow rate is forwarded to the reactor inlet since it is contains reactant and product.

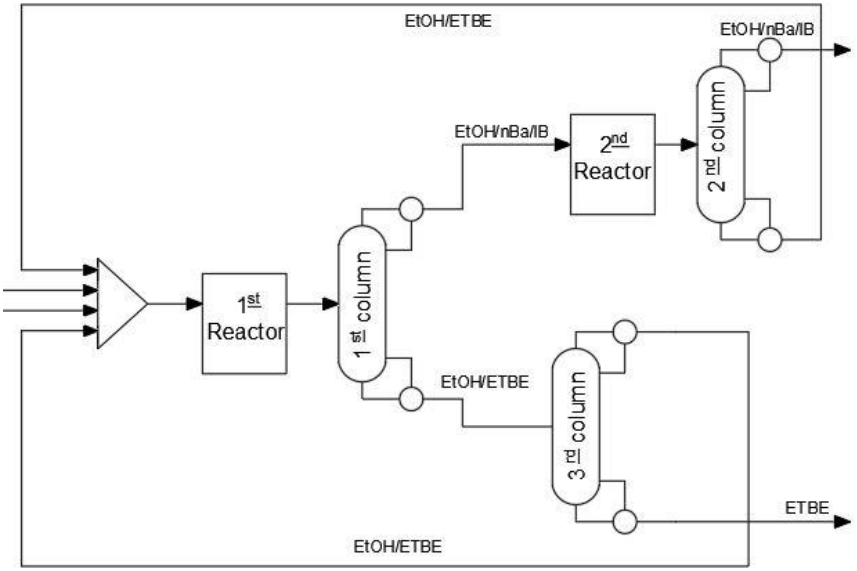


Figure 7. Process scheme of alternative 2.2

1.6. REACTIVE DISTILLATION

This alternative consist of an intensification process called reactive distillation (Figure 8). Reactive distillation is a process that combines reaction and separation in the same vessel (Luyben & Yu, 2008; Stankiewicz, 2003). Reactive distillation has been successfully applied to the production of gasoline oxygenated-additives, such as methyltert-butyl ether (MTBE) and more recently both ethyl tert-butylether (ETBE) and tert-amyl methyl ether (TAME) (Luyben & Yu, 2008).

They exist studied cases where reactive distillation was applied to the production of methyl acetate, reducing the consumed energy in the conventional process by a factor of 5 (Agreda et al, 1990 ; Siirola, 1996).

Therefore, this alternative has been selected to take into account in this project. The raw material is introduced in the reactive column. The EtOH and IB is reacted inside of column. At the same time that is formed the ETBE, it is acquired by the bottom. The inert nBa is distilled through the azeotrope nBa/EtOH, which has the lowest boiling point. A total conversion of IB is achieved in a single unit (Domingues et al, 2014).

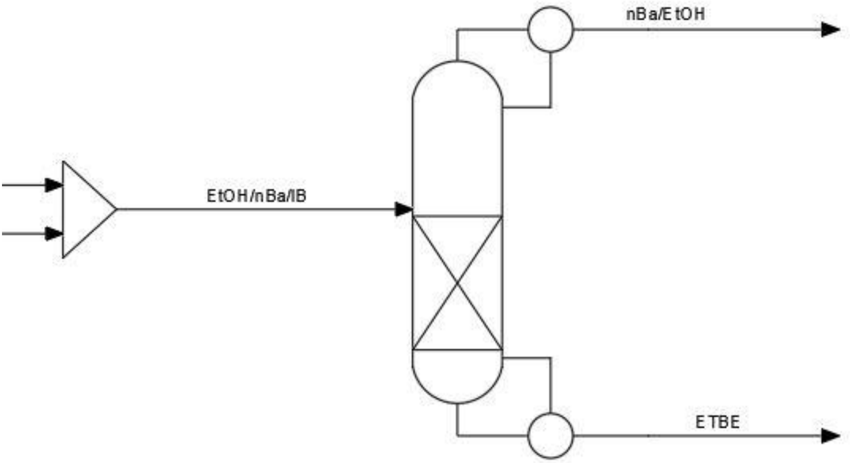


Figure 8. Process Scheme of Reactive distillation

1.7. ALTERNATIVE OF THE BREF

This alternative has been extracted from BREF document (European Commission, Joint Research Centre, 2018). The document BREF is developed under the IPPC Directive and the IED and it is proposed by the European Commission.

The process scheme of the figure 9 is based on the official document. This process represents the best available process for the ETBE production proposed by the UE. Any novel process should be equal or better than this.

The proposed alternative for the BREF consist of one reactor, two distillation columns and one extraction column L-L. The pressure in all the system is 14 bar.

The raw materials are introduced the reactor. The outlet flow rate of reactor is sent to first distillation column. This column separates the pure product (ETBE) by the bottom. For the distillate is obtained an EtOH/IB/nBa mixture.

The distillate is sent to extraction column L-L. In the extraction column separates the IB and nBa of the EtOH through a water flow rate by countercurrent. The EtOH is dissolved in the water flow rate and the water-EtOH mixture is sent to second distillation column. The IB and nBa extracted from extraction column L-L are withdrawn of the system.

In this column is separate the azeotrope EtOH/Water for the distillate. The distilled water due to the azeotrope is purged and the reactant EtOH recirculates the reactor. The pure water obtained for the bottom of the column is recirculated to the extraction column L-L to be reused.

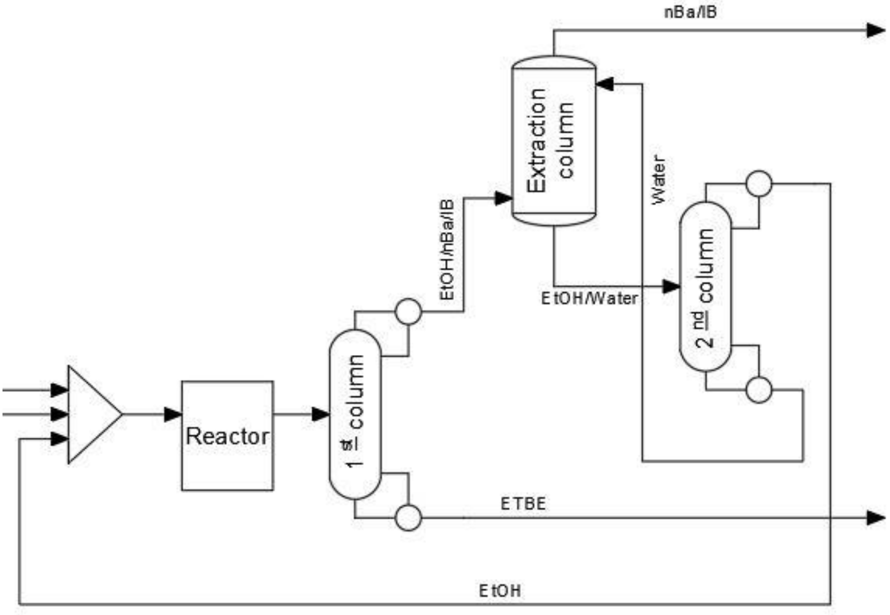


Figure 9. Process scheme of alternative of the BREF

2. OBJECTIVES

To make this project it is necessary to accomplish these objectives:

- Determine and explain a simple and reliable method that allows evaluating the efficiency of any chemical process trough general simplifications, considering reaction and separation jointly during the calculation.
- Evaluate the ETBE production process, applying the assimilated knowledge in AspenPlus v10 to perform the appropriate simulations and to get a coherent result.
- Compare the data obtained of the evaluation of the ETBE production process done with the results extracted of the found papers in the bibliographic search for the first stages design. Being able to establish a comparative of both results.
- Determine the screen process more efficient in the chosen example of ETBE production process.

3. METHODOLOGY

In this section is commented in a detailed way all the information to understand and reproduce the results obtained in this project.

Along all the project is applied the ∞/∞ analysis (Petlyuk and Avet'yan, 1971, 1972). This analysis, among other things, assumes infinite stage and reflux flow rate in a packed distillation columns, doing easier and faster the simulations. The behavior of the distillation process can be determined using residue curve maps in the ∞/∞ analysis. (Bonet, 2006). Therefore, the analysis has been used to carry out all the simulations studied in this project instead of using a rigorous simulation.

3.1. RESIDUE CURVE

The residue curves are obtained from the study of simple distillation process in the time (open evaporation) (Ung and Doherty, 1995). An example of simple distillation process is the Rayleigh distillation, scheme shown in figure 10.

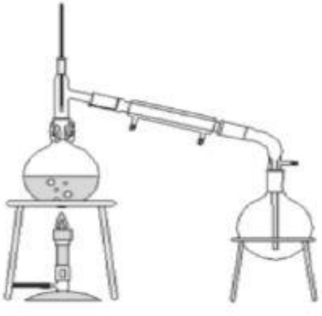


Figure 10. Rayleigh Distillation

The residue curve maps (Figure 11) are shown at fixed pressure. In each corner, the pure component at a given boiling temperature is located. The residue curve maps give an easy visualization of chemical equilibrium and combined phase. It is possible to determine the existence of reactive azeotropes or nonreactive azeotropes in them (Ung and Doherty, 1995).

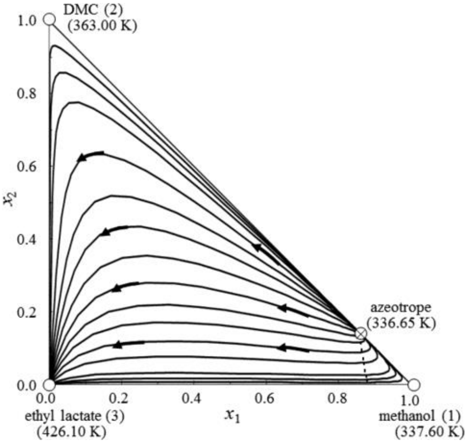


Figure 11. . Example of residue curve map (Matsuda et al, 2017)

The use of the ∞/∞ analysis allows to check the feasibility of the process based on the residue curve map.

In order to check the feasibility of a process, through the use of the, it has to be considered the feasibility of all the individual distillations that were produced. A separation is feasible if in the residue curves maps are met three conditions. First of all, it is must fulfil the mass balances. If the composition of the bottom, distilled and feed can be joined by a straight line then, it meets the mass balances. Another condition that has to be fulfill is that is has to be a residue curve that conduces from the composition of the distilled up to the bottom. The last condition is that the residue curve must contain a singular point.

The simulator AspenPlus, among other simulators, contains an option to generate residue curve maps between different desired compounds. The option used for this project is “Use distillation synthesis ternary maps”, since this option allows choosing the residue curve that is wanted to show, indicating the exact composition.

This option also has been used to locate the azeotropes. It allows to shown a table with the azeotropes searched and the different presents compounds in the mixture in the form of a report. In this report are indicated the concentrations azeotropes in mole and mass basis and the boiling temperature of the compounds and azeotropes by the imposed specifications.

All the residue curves maps obtained in this project have been performed with the same specifications (Table 1) through AspenPlus®.

Table 1. Conditions used for generated the residue curves maps

Pressure	8 bar
Property Model	
VLE Model	UNIFAC
LLE Model	UNIFAC
Phase	VAP-LIQ-LIQ

3.2. SIMULATION OF ALTERNATIVES

As it has been said before, to do all the simulations of this project, it has been used the software of simulation, AspenPlus® version 10.

Several factors are considered while it has been performing the different simulations, for example the thermodynamic model selected. In this case, it has been selected the model UNIFAC. The predictive thermodynamic UNIFAC is useful for preliminary design calculations.

Another factor to consider is the type of block used for each unit operation:

For the rectification columns, “Block CX”, it has been used a separator. This is due to the use of the ∞/∞ analysis for carrying out the process. In the “Separators” tab has been selected the block Sep2 (Figure 12). This block allows separating compounds into two outlet streams based on split fraction or mole fraction.

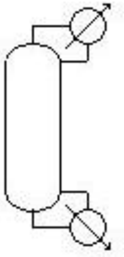


Figure 12. Column Sep2 in AspenPlus®

For the reactor, it has been used two different reactors. Both of them are found in the tab Reactor.

For the “Block RX” of the Figure 13 it has been used a reactor RGibbs. This reactor determines the reaction and it is equilibrium in base on Gibbs free energy minimization. It has been selected in based on the calculate of the DSE. The reactors does not consume so much energy as distillations, thus, it is not necessary bear the reactor in mind for the calculus of the DSE.

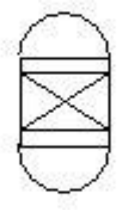


Figure 13. Reactor RGibbs in AspenPlus®

For the “Block RR” (Figure 14) it has been used a reactor RStoic. This reactor is based on the stoichiometry, and the molar extend or conversion is known for each reaction and it is useful when the reaction kinetics is unknown.

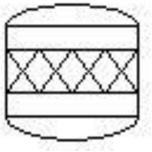


Figure 14. Reactor RStoic in AspenPlus®

In the case of the heat exchangers, “Block BX”, it has been used the block “Heater”, which stays in the “Exchangers” (Figure 15). This block allows to do phase changes and temperatures in a simple way. The Heat exchangers have been used for determining the temperatures in all the streams of the system for obtaining the DSE.

Figure 15. Exchanger Heater in AspenPlus®

The blocks used to join or separate streams are the blocks Mixer and FSplit respectively (Figure 16 and Figure 17). These are in the “Mixers/Splitters” tab.

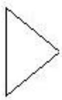


Figure 16. Mixer in AspenPlus®

Figure 17. FSplit in AspenPlus®

Finally, for the extraction column L-L, Block EX (Figure 18), it has been used the block “Extract”, which is in the “Columns” tab. This block performs a rigorous simulation in countercurrent for the extraction of a liquid with a solvent through models liquid-liquid extractors.

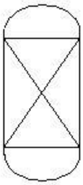


Figure 18. Block Extract in AspenPlus®

Even though some alternatives between them seem very similar, many simulations contain different settings for them. Thus, the different blocks used for all the simulations carried out together with the used design specifications and impost conditions, have been grouped into different subsections. Below it is going to be explained how it has been configured each block to accomplish with the demanded specifications and in the last point is described how to perform an analysis of sensitivity.

3.2.1. Block C1 and C2

The block C1 is used in the alternative 1.1, 2.1 and BREF meanwhile the block C2 is used in alternatives 1.2, 1.3 and 2.2.

The blocks C1 and C2 are the blocks most complex to configure. These blocks separate the four compounds that leave the reactor. On the one hand, he block C1 separates the four compounds that come from the reactor, withdrawing the pure ETBE by the bottom. On the other hand, the block C2 withdraws by the bottom a mixture of EtOH/ETBE. For a determined composition in the input of the reactor, the composition in the distillate varies. The configuration applied in these blocks consist of variating the mole composition of EtOH linearly, in function of the molar composition of entrance of IB in the in the column. The methodology used to implement these restrictions consists in the process commented below:

In the section of Specifications inside of the block, C1 or C2, are determined the compounds that must be withdrawn by the distillate in the way shown in the table 2.

Table 2. Specifications of Blocks C1 and C2

Component ID	1st Spec	
ETBE	Split fraction	0
IB	Split fraction	1
nBa	Split fraction	1
EtOH	Split fraction	1

Hereafter it has been created a specification of design in the section Flowsheeting Option where it is introduced the specification that must fulfill.

Then, are defined two variables of Mole-Frac type called XDET and XDIB. These variables represent the mole fractions of EtOH and IB respectively in the stream of distillate of the column.

The equation that has to fulfill the column to assure the existence of a residue curve between bottom and distillate is programmed in the section FORTRAN®. This equation determines the mole fraction of EtOH in the distillate through the mole fraction of IB in the entry of the column. To program in FORTRAN® is necessary to take into account a series of requirements (Paniagua and Solé, 2007)

As specification is introduced the condition that the distillate composition fulfilling the mas balance must be the same that the distillate composition which fulfills the condition of the existence of residue curve between bottoms and distillate (Table 3).

Table 3. Design Specification Expressions

Spec	XDET/XDETC
Target	1
Tolerance	0.0001

(a) XDETC is the theoretical value obtained in the equation of line in the "Fortran" tab.

The condition used is based on the division of the outlet of real EtOH mole fraction between the outlet of theoretical EtOH mole fraction. Once XDET and XDETC are equal with a less tolerance at 0.0001 the process converges to the solution.

As it was reported at the begging of the section 3.2.1, C1 does not contain EtOH in the flow rate of the bottom, and C2 does contain EtOH there. Thus, the manipulated variable for the block C1 and the block C2 are not same.

Block C1

For this column the molar composition of EtOH in the entrance of the column has to be equal to the molar composition of EtOH in the distillate, reaching this way withdrawing the pure ETBE by the bottom. Thus, the entrance flow of EtOH to the system is manipulated until making coinciding with the molar composition in the distillate (determined by the equation programmed by FORTRAN®). This variable is defined in AspenPlus in the Table 4. To ensure the convergence in the system is used a wide range of possible values of EtOH flow.

Table 4. Summary of the block C1 for the tab "Vary"

Manipulated variable	
Type	Stream-Var
Variable	MOLE-FLOW
Units	mol/sec
Manipulated variable limits	
Lower	1
Upper	100

<u>Block C2</u>:

In the case of this column, it has to be variated the split fraction value of EtOH achieving to obtain the composition of EtOH in the distillate determined by the programmed equation in FORTRAN®. In order to manipulate the value of the split fraction in AspenPlus it has to be used a variable of Block-Var type with variable FLOW/FRAC. The “Manipulated variable limits” are 0 for “Lower” and 1 for “Upper”. These values correspond to maximum and minimum value permissible for the split fraction.

Table 5. Summary of the block C2 for the tab “Vary”

Manipulated variable	
Type	Block-Var
Block	C2
Variable	FLOW/FRAC
ID3	EtOH
Manipulated variable limits	
Lower	0
Upper	1

3.2.2. Block CX (Except 1 and 2)

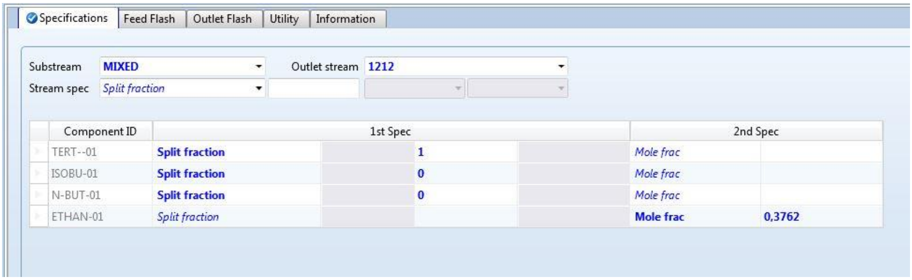
The block C3 is used in the alternative 1.2 and 1.3. The block C4 is used in the alternative 1.2, 1.3 and 2.2. The block C5 is used in the alternative 1.3. The block CR is used in alternative Reactive Distillation and finally, the block CB is used in the alternative of the BREF

The simulation of these blocks is done by a simpler way:

These blocks are configured for separate an inlet stream in 2 outlet streams. The first stream contains a determined composition (the azeotropic composition). The other stream is dependent on the last stream.

To carry out the simulation is determined the stream that contains the azeotrope in function of the boiling points. For this reason, in the section of Specifications, inside of the block, is selected the determined stream in the outlet stream tab. In the specification "mole frac" is written the azeotropic mole fraction of one of them. For the components that must leave by determined outlet stream are indicated values of 1 in the specification "split fraction" or a value of 0 in opposite case.

An example is shown below:



Substream MIXED

Outlet stream 1212

Stream spec *Split fraction*

Component ID	1st Spec		2nd Spec	
TERT--01	**Split fraction**	**1**	*Mole frac*	
ISOBU-01	**Split fraction**	**0**	*Mole frac*	
N-BUT-01	**Split fraction**	**0**	*Mole frac*	
ETHAN-01	*Split fraction*		**Mole frac**	**0,3762**

Figure 19. Example of column configuration

3.2.3. Block RX

This block is used in all the performed alternatives, except in the alternative Reactive distillation.

The reactor works at isothermal mode and at the pressure of the system.

In the section of Specifications, inside of the block, is used the calculation option "Calculate phase equilibrium and chemical equilibrium". The operating conditions are set at a pressure of 8 bar and a temperature of 90ºC. This temperature is determined in function of the used catalyst.

In the section "phase" is unselect the checkbox "Include vapor phase". This condition caused incorrect values in the results of temperature.

In the alternative of the BREF must be defined the products of reaction. This is performed in the Product tab, changing the option "RGibbs considers all components as products" by the option “Indentify possible products”. In the table have to be added all the compounds except to water. The valid phases selected is “Mixed”.

As in this alternative is used water, if it is not applied this modification, the reactor tries to converge taking into account the water in the reaction. This causes a convergence error in the simulator due to the “non-entry” of water in the reactor.

3.2.4. Block RR

This block is used in the alternative Reactive distillation.

The section of Specifications is configured of the same way that the block RX. In the section reactions requires at least one reaction inserted for this block. The reaction introduced is EtOH + IB → ETBE. The IB and the EtOH are reactants with coefficients -1 and the ETBE is the product with coefficient 1. The nBa is not introduced because it does not intervene in the reaction. In the zone of Products generation is selected the option Fractional conversion. The value of fractional conversion is 1 for the component IB.

3.2.5. Block BX

These blocks are present in all the outlet stream of the columns.

The exchangers are used to determine the temperature in the different streams in liquid phase. In the section of Specifications is used as flash type two variables, pressure and vapor fraction. The value of the pressure is the pressure of the system (8 bar) and the value of the vapor fraction is 0.

3.2.6. Block EX

The block EX is used only in the alternative of the BREF (E1). This block performs a rigorous simulation, therefore, its configuration is more complex.

As specification has been fixed a number of stages of 100. Since is applied the ∞/∞ analysis there must be a high number of stages. In the thermal options has been selected the Specify temperature profile indicated a 60ºC of temperature for each stage.

The key components selects for 1st liquid phase is Water and EtOH. For the 2nd liquid phase are selected the other compounds, ETBE/IB/nBa.

The feed streams has been determined at the ends of the column. Thus, the entrance of the stream to separate is in the stage 100 and the water inlet is in the stage 1. The outputs of product streams are in the stage 1 and 100 for the streams with 2nd liquid and 1st liquid respectively. Finally, the pressure set in the different stages is 8 bar.

3.2.7. Analysis of sensitivity

The analysis of sensitivity is an integrated tool in the AspenPlus®. This tool allows to perform different consecutively simulations manipulating a variable by automatically way. Hereunder are represented the results in the table together with the other defined variables for each manipulated value. In addition, it is shown a column, which indicates if the obtained results are correct or wrong (no converged).

First of all, it is necessary to indicate the variable to manipulate in the analysis. This variable, must be defined between two values to analyze with a determined increase, or indicating determined desire values. After that, are defined the variables that are wanted to see in the results table, or used to do the programming in FORTRAN. Finally, in the “Tabulate” tab have to be declared all the variables previously defined, that are wanted to be seen at the end of the analysis.

It is recommended to indicate in the “Options” tab the options of “Reinitialize all blocks” and “Reinitialize all streams”. They carry out after each execution, a reset in the system for avoiding false convergences.

3.3. EFFICIENCY OF THE SYSTEM

The study of the efficiency of this project has been determined with the DSE method. The DSE method just contemplates the efficiency in the distillation columns of the process. In order to be able to evaluate the reactor, have been added two factors that allow correcting the efficiency obtained with the DSE. These factors are combined in the DSE, multiplying them.

Both correction factors ($F_{Reactor}$ and F_{Cata}) are personal contribution to this project. Since in the paper of Marquardt commented in the section Introduction, the evaluation is made depending on the economic costs.

Finally, the equation determined for the efficiency is the equation 1.

$$Efficiency = DSE \cdot F_{Reactor} \cdot F_{Cata} \tag{1}$$

The DSE and the two correction factors are commented in different subsections below. Furthermore, it is described the procedure carried out in AspenPlus® to be able to implement the calculation of the efficiency through the analysis of sensitivity.

3.3.1. DSE (Distillation Sequence Efficiency)

In most processes, the dominate factor in the total cost of a chemical process is associated with the separation steps. It is important that the distillation sequence is efficient to obtain an efficient process (Marquardt, 2008)

The DSE is a method that determines the most efficient column sequence. This method is based on heuristics and assumes that a distillation is a heat engine working between a hot source (reboiler) and a cold source (condenser) producing a change of entropy instead of work. Applying the ∞/∞ analysis is only necessary to know the stream flows, compositions and temperatures in the system.

The equation of DSE (Equation 2) relates the flow rate of stream (W_i) with crude feed flow rate (Fc). This relation is multiplied by the efficiency of each column. The efficiency of the column is calculated through the Carnot Efficiency. If it is a stream of distillate, then it is multiplied by efficiency of the column. If it is a stream of bottom then it is multiplied by 1. In the case that there is a recirculation stream it is necessary subtract 1 from the efficiency. Thus, the recirculation streams decrease the value of the DSE (Bonet, 2015).

$$DSE = \sum^{i} \frac{W_i}{F_c} \cdot \prod_{C} \eta_{iC} \tag{2}$$

In the example of the figure 20, it is show the application of the DSE in a system of three distillation columns with a recirculation between two of them.

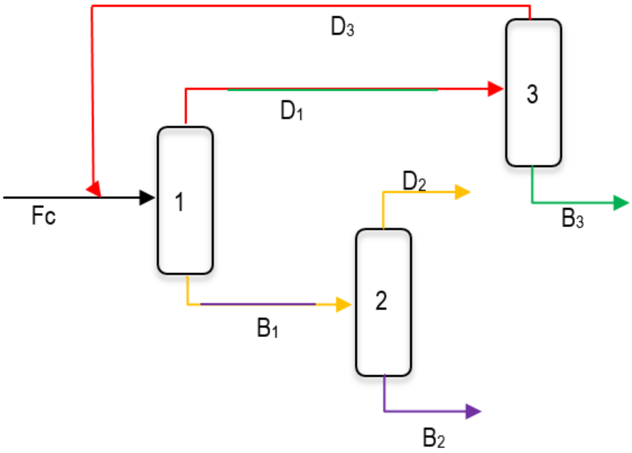


Figure 20. Example of process scheme for the application of the DSE method

$$DSE = \frac{B_2}{F_C} + \frac{D_2}{F_C} \cdot \eta_2 + \frac{B_3}{F_C} \cdot \eta_1 + \frac{D_3}{F_C} \cdot (\eta_1 \cdot \eta_3 - 1) \tag{3}$$

Where,

$$\eta_1 = 1 - (T_{D1}/T_{B1}) \tag{4}$$

$$\eta_2 = 1 - (T_{D21}/T_{B2}) \tag{5}$$

$$\eta_3 = 1 - (T_{D3}/T_{B3}) \tag{6}$$

3.3.2. 1st Correction Factor ($F_{Reactor}$)

This Factor relates the product quantity generated in function of the reactant introduced in the system. With this factor is obtained information of the overall performance of the process with regard to generated product. For a set feed flow rate in the system, the increase of generation of product in the outlet stream of the process produces a greater value of $F_{Reactor}$ and therefore a more efficiency process.

To define this factor is used the equation 7.

$$F_{Reactor} = \frac{W_{Product}}{W_{Reactant}} \cdot \frac{\sum_{i=1}^{N} n_{Ri}}{\sum_{i=1}^{N} n_{Pi}} \tag{7}$$

Where n_{Ri} and n_{Pi} are the stoichiometric coefficients for the reactants and the products respectively.

3.3.3. 2nd Correction Factor (F_{Cata})

This correction factor is useful in a process that uses a catalyst in the reactor, as is this case. The factor relates the introduced raw materials in the system with the total stream of feed in the reactor. Thanks to this factor, it is possible to consider the wear of catalyst for a process in comparison to the rest. For a fixed feed, for a higher inlet stream in the reactor, higher is the wear of the catalyst and therefore, the value of F_{Cata} is lower. Therefore, this factor is influences the use of recirculation streams to the reactor in a process.

To define this factor is used the equation 8.

$$F_{cata} = \frac{W_{Feed}}{W_{Reactor}} \tag{8}$$

This factor ranges from the value of 0 to 1. Being the value of 1 as greater efficiency and the value of 0 as lower efficiency.

For the alternatives, 2.1 and 2.2 are used two reactors. In each reactor has been used a different F_{cata}. For these cases it has been determined a factor F_{Cata} through the arithmetic mean between F_{cata1} and F_{cata2}.

$$F_{cata} = \frac{F_{Cata1} + F_{Cata2}}{2} \tag{9}$$

Being for the alternatives 2.1 and 2.2,

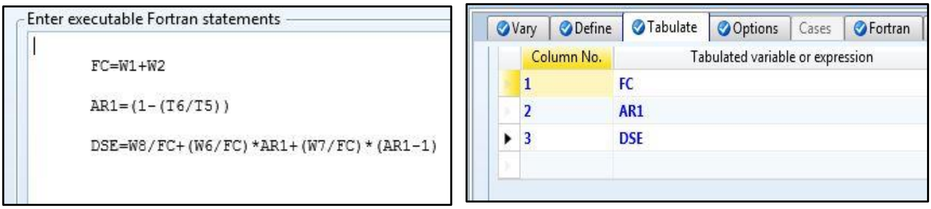
$$F_{Cata1} = \frac{W_1 + W_2}{W_3} \tag{10}$$

$$F_{Cata2} = \frac{W_{A1}}{W_6} \tag{11}$$

3.3.4. Implementation of the calculating in AspenPlus®

The implementation in AspenPlus® of the calculation of the efficiency has been performed through the Analysis of sensitivity. The procedure to follow consists in the commented subsection 3.2.6 with a few variations.

As variable to manipulate is fixed any variable but setting the desire value in the option “List of values”. They must be to define the entire used variable for the different equations. The equation system, like DSE and the correction factors are programmed in FORTRAN®. This equations are entered with the same name that the previously defined variables. Finally, in the “Tabulate” tab must be introduced manually the names of the written equations in FORTRAN®. In the figure 21 has been shown an example of an equations system in FORTRAN® together with its visualization.



Enter executable Fortran statements

```
FC=W1+W2

AR1=(1-(T6/T5))

DSE=W8/FC+(W6/FC)*AR1+(W7/FC)*(AR1-1)
```

Column No.	Tabulated variable or expression
1	FC
2	AR1
3	DSE

Figure 21. Example of integration of the DSE in AspenPlus®

In the next section, all the methodology implemented in this section is carry out to perform all the calculations pertinent to this project. The subsections 3.2.1 and 3.2.7 provides the main basis for section 4 of the results.

4. RESULTS

In order to carry out the simulations of this process, first has been checked the feasibility of the process. Using AspenPlus have been generated the maps of residue curves of the present compounds mixture in the system, setting the pressure at 8 bar. Due to our system contains 4 different compounds, have been generated 4 different maps of residue curves to fulfill all the possible combinations. These maps of reside curves jointly form a tridimensional structure (3D) building a tetrahedron.

One way to be able to work with the maps of residue curves (tetrahedron) is drawing an open figure (Figure 22). If this figure is observed, are found two different azeotropes, one between EtOH/ETBE and another between nBa/EtOH. These azeotropes have a determined composition and boiling point, which are listed in the table below next to pure compound. (Table 6)

Table 6. Report of the Azeotropes and pure compound

Pure compound and Azeotropes	*Boiling Point*	*Type*	*ETBE*	*IB*	*nBa*	*EtOH*
IB	61.44	Homogeneous	0	1	0	0
nBa	69.45	Homogeneous	0	0	1	0
EtOH	142.23	Homogeneous	0	0	0	1
ETBE	156.96	Homogeneous	1	0	0	0
EtOH/nBa	68.86	Homogeneous	0	0	0.9603	0.0397
EtOH/ETBE	133.42	Homogeneous	0.4252	0	0	0.5748

(a) Values extracted of AspenPlus®

(b) Pressure set at 8 bar

(c) Composition in mole base

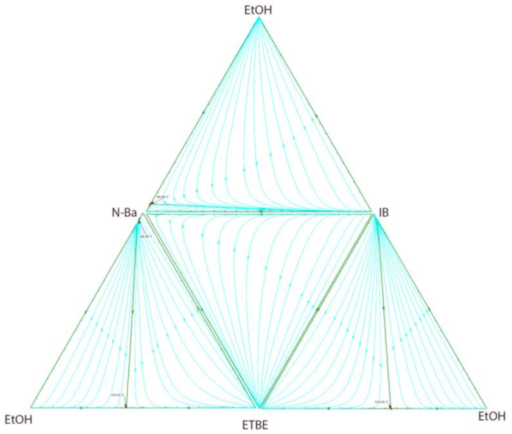


Figure 22. Open tetrahedron (Picture extracted of AspenPlus®)

Analyzing the first distillation (Figure 23) it has been found just a residue curve that conduces from the bottom composition up to the distilled composition, passing through the singular point, if it stays above the red line indicated.

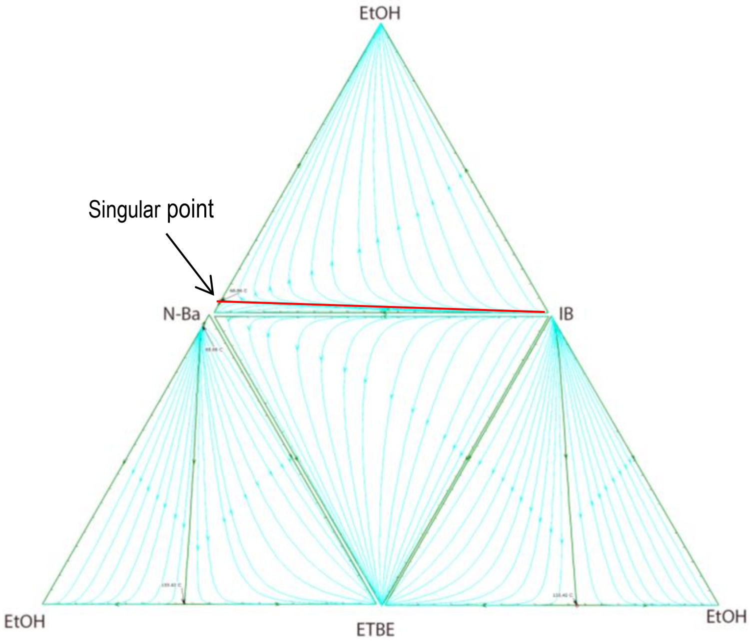

Singular point

Figure 23. Analysis of the first column (Picture extract from AspenPlus®)

The tetrahedron in 3D has been designed through AutoCAD®, and represented the azeotropic planes, to gain a better understanding (Figure 24).

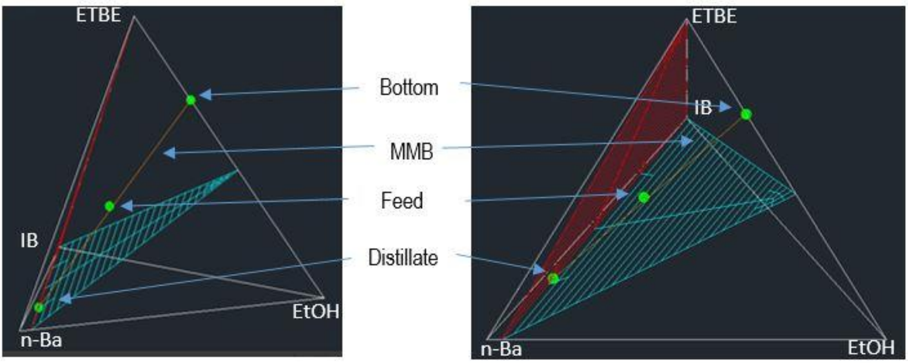


Figure 24. Tetrahedron in 3D designed through AutoCAD®

In the figure, can be observed that there is one straight line that joins the composition in the distilled with the composition in the bottom, passing through the feed point and fulfilling the third condition to be feasible. Once the first distillation has been realized, the other distillations contain a maximum of three chemical compounds.

It is necessary to extract from the map of residue corves of the compound EtOH, nBa and IB the equation of line to be able to do the design specifications in the first column of the simulation with AspenPlus®. In order to obtain this equation of line, it has been used the calculation program Microsoft Excel®, creating a table with the initial and end point of the line.

Table 7. Value and equation of line

Compound	Initial Point	End Point	Equation of line
EtOH	0.0397	0	$X_{EtOH} = -0.0397\ X_{IB} + 0.0397$
IB	0	1	

Plotting the values and adding a trend line between the values of the graphic, is determined the regression line. This line gives the composition of each compound in the distillate of the first column.

In the next point, are shown the results obtained for difference alternatives. All of them are simulated on basis of 100 mol/s for feed alimentation of nBa/IB in the system.

4.1. ALTERNATIVE 1.1

In this alternative is observed that there is a degree of freedom in the system. The fraction of recirculation can assume any value except 1. If the recirculation was 1, it would collapse for excess of inert.

In order to assign a value of recirculation it has been applied an analysis of sensitivity through AspenPlus®. The analysis consists of calculating the value of the DSE and the correction factors for different values of recirculation.

Once it has been done the analysis of sensitivity, the values contained in the table have been plotted in the figure 25. The plot is made of two vertical axis and one horizontal axis. The main axis represents the values obtained of the DSE/$F_{reactor}$/F_{cata} vs recirculation values. The secondary axis represents the value of the efficiency vs recirculation values.

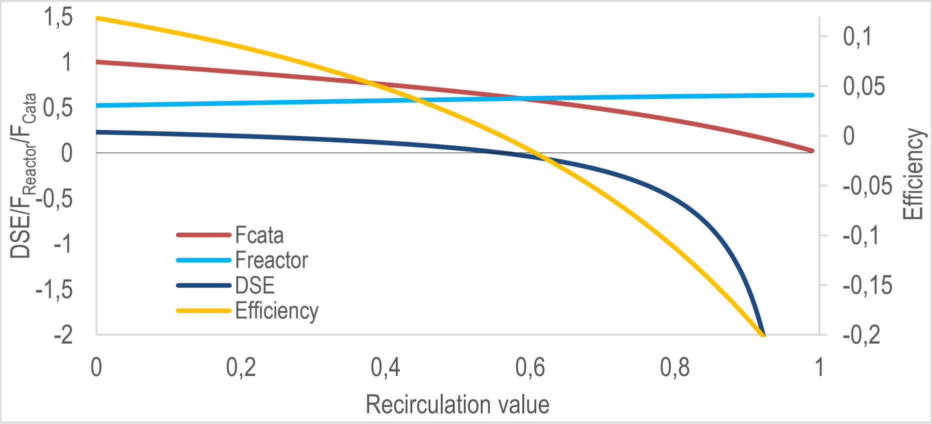


Figure 25. Graph of DSE/$F_{reactor}$/F_{cata} vs Recirculation values vs Efficiency

A negative tendency is observed while recirculation values are increased up to approximately the value of 1. Thus, the increase in recirculation value causes a decrease in the DSE and F_{Cata} as it was comment in the sections 3.3.1 and 3.3.3. Finally, although ETBE production increases in the system with the recirculation value, the system is less efficiency. Therefore, it is considered unnecessary a recirculation in "∞/∞ conditions".

Making the simulation with AspenPlus of the first alternative (Figure 26). The results can be seen in the table 8, contemplating that the value of recirculation is 0.

Table 8. Results of Alternative 1.1

Stream	1	2	3	4	5	6	7	8
Temperature [ºC]	65.1	142.7	67.3	90.0	159.0	67.6	-	67.6
Total Flow [mol/s]	100	32.63	132.63	102.45	30.18	72.28	0	72.28
Mole Fraction								
ETBE	0	0	0	0.2945	1	0	0	0
IB	0.4	0	0.3016	0.0959	0	0.1359	0	0.1359
nBa	0.6	0	0.4524	0.5856	0	0.8301	0	0.8301
EtOH	0	1	0.2460	0.0240	0	0.0340	0	0.0340

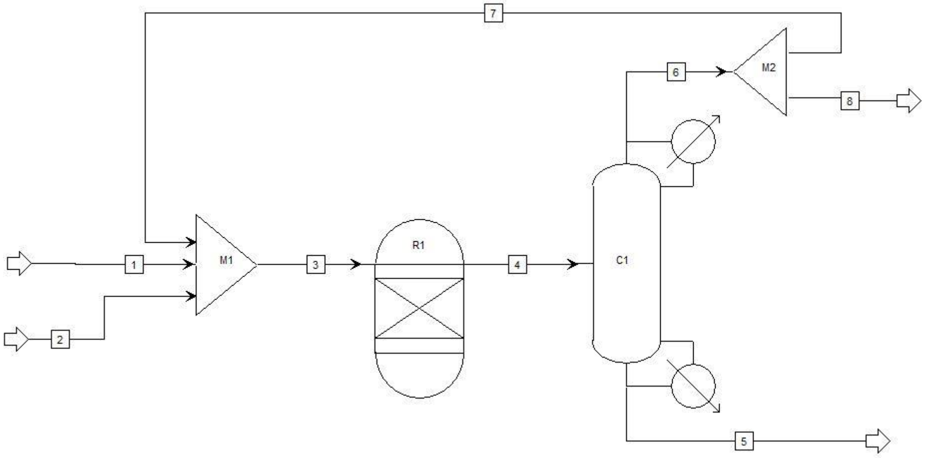


Figure 26. Process Scheme of the alternative 1.1

The efficiency obtained in the alternative 1.1 through DSE (equation 20) and correction factors are illustrated in the table 9.

Table 9. Values of efficiency

DSE	$F_{Reactor}$	F_{Cata}	Efficiency
0.2275	0.8310	1	0.1891

4.2. ALTERNATIVE 1.2

This alternative is different from the alternative 1.1, since it does not have degrees of freedom. From the database in the system the table 10 is performed the mass balance in all the system and they are obtained the results shown in the table 11 (Appendix 1).

Table 10. Set values in system

Set values in system

W_1 [mol/s]	$X_{1\ nBa}$	$X_{1\ IB}$	$X_{7\ EtOH}$	$X_{7\ nBa}$
100	0.6	0.4	0.0397	0.9603

Table 11. Values obtained in balance of material

Values obtained in balance of material

W_2 [mol/s]	W_7 [mol/s]	R [mol/s]	W_{10} [mol/s]
42.48	62.48	40	40

Introducing the values obtained through the mass balances in the simulator AspenPlus®. The results acquired are collected in the table 12.

Table 12. Results of alternative 1.2

Stream	1	2	3	4	5	6	7
Temperature [ºC]	65.1	142.7	69.4	90.0	68.0	61.3	69.0
Total Flow [mol/sec]	100	42.48	160.82	120.82	69.46	6.99	62.48
Mole Fraction							
ETBE	0	0	0.0300	0.3710	0	0	0
IB	0.4	0	0	0	0	0.9401	0
nBa	0.6	0	0.3757	0.5000	0.8697	0.0599	0.9603
EtOH	0	1	0.3048	0.0746	0.0357	0	0.0397

Stream	*7*	*8*	*9*	*10*
Temperature [ºC]	69.0	142.9	134.3	159.0
Total Flow [mol/sec]	62.48	51.36	11.36	40.00
Mole Fraction				
ETBE	0	0.8728	0.4250	1
IB	0	0	0	0
nBa	0.9603	0	0	0
EtOH	0.0397	0.1272	0.5750	0

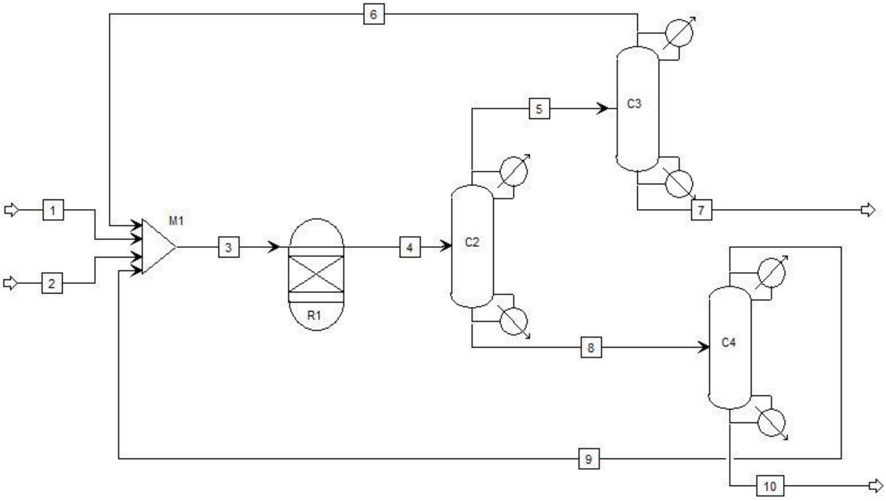


Figure 27. Flowsheet of alternative 1.2

The efficiency obtained in the alternative 1.2 through DSE (equation 21) and correction factors are illustrated in the table 13.

Table 13. Values of efficiency

DSE	$F_{Reactor}$	F_{Cata}	Efficiency
0.3970	0.9699	0.8859	0.3411

4.3. ALTERNATIVE 1.3

As it was commented in the section 1.3, this alternative is an extension of the alternative 1.2. It has only one more column for the stream of the bottom. Therefore, the results of mass balance for these alternatives are equals that is in the table 11.

Realizing the simulation with AspenPlus with the scheme of the Figure 28 are obtained the results of the table 14.

Table 14. Results of alternative 1.3

Stream	1	2	3	4	5	6	7
Temperature [ºC]	65.2	142.2	67.6	90.0	141.7	67.7	61.7
Total Flow [mol/sec]	100	42.48	156.85	116.85	45.64	71.21	8.73
Mole Fraction							
ETBE	0	0	0	0.3423	0.8765	0	0
IB	0.4	0	0.3074	0.0703	0	0.1154	0.9408
nBa	0.6	0	0.3858	0.5179	0	0.8498	0.0592
EtOH	0	1	0.3068	0.0695	0.1235	0.0348	0

Stream	8	9	10	11	12	13
Temperature [ºC]	68.9	139.0	156.9	133.4	134.4	142.2
Total Flow [mol/sec]	62.48	57.70	40.00	17.70	12.07	5.64
Mole Fraction						
ETBE	0	0.8237	1	0.4252	0.6238	0
IB	0	0	0	0	0	0
nBa	0.9603	0	0	0	0	0
EtOH	0.0397	0.1763	0	0.5748	0.3762	1

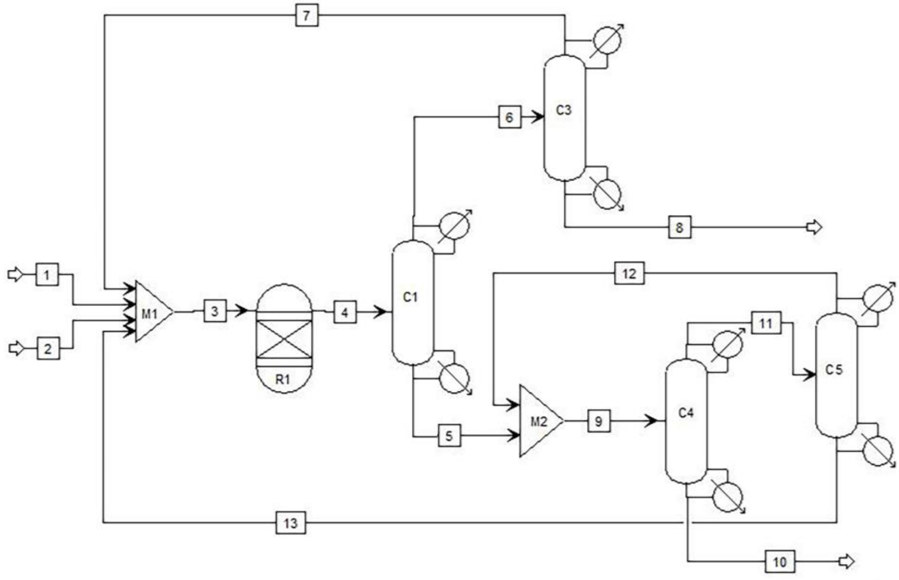


Figure 28. Flowsheet of alternative 1.3

The efficiency obtained in the alternative 1.3 through DSE (equation 22) and correction factors are illustrated in the table 15.

Table 15. Results of efficiency

DSE	$F_{Reactor}$	F_{Cata}	Efficiency
0.3341	0.9699	0.9084	0.2944

4.4. ALTERNATIVE 2.1

In this alternative is added one variable to the system. It does not appear in the design shown in the introduction (Section 1.4, Figure 6).This is due to the amount of EtOH in the distilled after the first column is too small. When the second reactor consumes almost all the present EtOH in the inlet flow rate, obstructs the necessary minimum relation between

EtOH/IB/nBa to fulfill the specification of design of the second column (Section 3.2.1). Thus, the variable that is added is an auxiliary flow rate of EtOH (stream A1) that is introduced before of the reactor 2.

Unlike the last two alternatives, in this one the IB does not react totally, therefore, the conversion is not complete. One variable that directly affects the conversion in the system is the auxiliary inlet of EtOH. Since the first column limits the principal inlet of EtOH in the first reactor (stream 2) the only variable to manipulate is stream A1.

In order to determine the value of this flow rate is done a sensitivity analysis varying the auxiliary flow rate of EtOH. This analysis has been performed in base on DSE, correction factors and efficiency of system.

In this alternative, the value of F_{Cata} is determined by arithmetical mean between Fcata1 and Fcata2 (Section 3.3.3, Equation (9)).

The values obtained correspond to the value of EtOH auxiliary flow, which have converged to the solution. The results obtained has been plotted (Figure 29) in a graph jointly DSE/$F_{Reactor}$/F_{Cata} vs EtOH Flow.

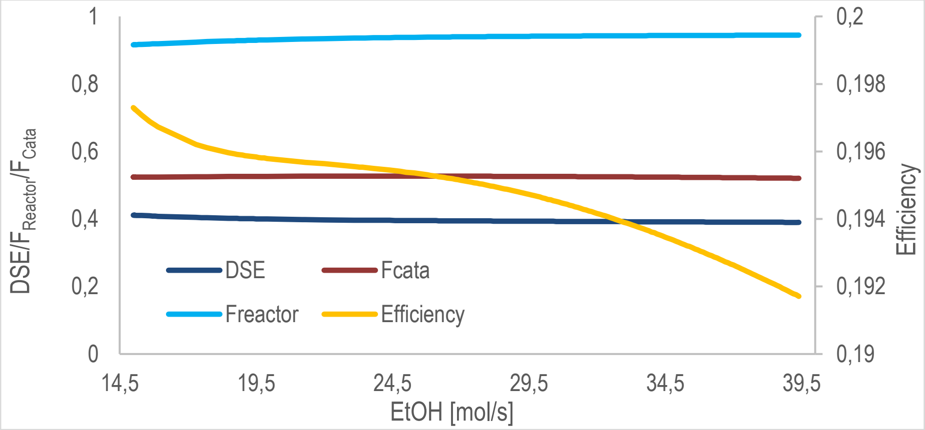


Figure 29. Graph of DSE/$F_{reactor}$/F_{cata} vs Recirculation values vs Efficiency

The increase of EtOH auxiliary flow in the second reactor cause a turning point in the intermediate values of EtOH flow for the efficiency. This situation is caused by the factor F_{Cata}.

The factor F_{Cata2} (equation 11) is directly affected by the increase in EtOH flow and it is grows faster than the factor F_{Cata1} (equation 10). This situation causes that the factor F_{Cata} to form a convex parabola.

The DSE, by contrast, decreases with the increase of the auxiliary flow rate of EtOH while the $F_{Reactor}$ increases indicating a greater ETBE production. Although the ETBE production is greater, the values of DSE and FCata influence the efficiency causing a negative trend.

Thus, the smaller value of auxiliary flow rate of EtOH is established to obtain a better value of efficiency.

Setting the value of the EtOH auxiliary flow rate in 15.06 mol/s is obtained through AspenPlus® the table 16, which collects the results obtained.

Table 16. Results of alternative 2.1

Stream	1	2	3	4	5
Temperature [ºC]	65.24	142.23	72.28	90.00	66.64
Total Flow [mol/sec]	100.00	23.31	138.33	117.11	81.21
Mole Fraction					
ETBE	0	0	0.1061	0.3065	0
IB	0.4	0	0.2892	0.1604	0.2313
nBa	0.6	0	0.4338	0.5123	0.7388
EtOH	0	1	0.1710	0.0208	0.0299

Stream	6	7	8	9	10	A1
Temperature [ºC]	67.84	90.00	68.24	152.46	156.93	142.23
Total Flow[mol/sec]	96.27	81.60	66.57	15.02	35.90	15.06
Mole Fraction						
ETBE	0	0.1799	0	0.9770	1	0
IB	0.1951	0.0503	0.0616	0	0	0
nBa	0.6232	0.7353	0.9013	0	0	0
EtOH	0.1817	0.0345	0.0371	0.0230	0	1

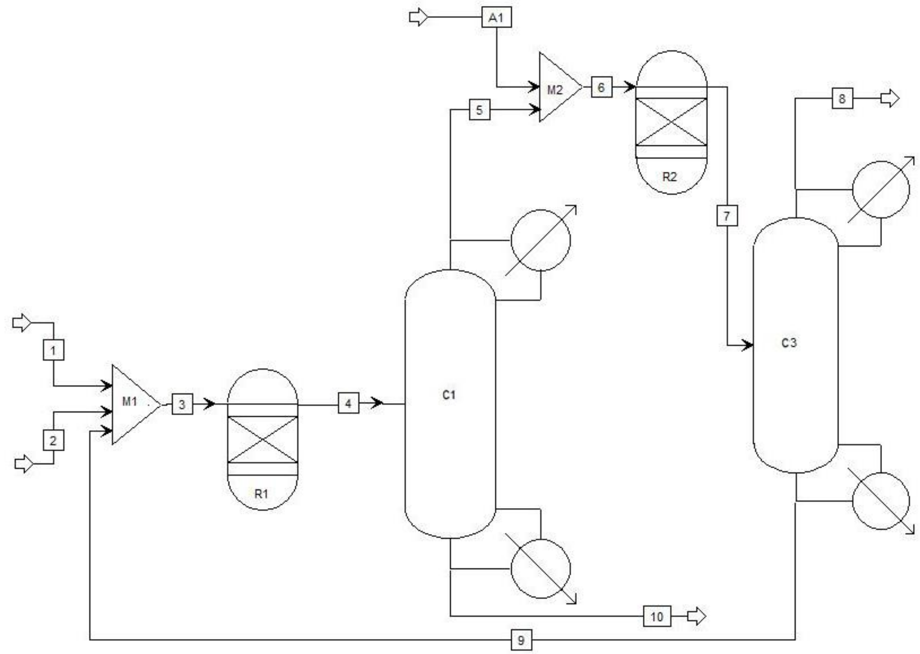


Figure 30. Flowsheet of alternative 2.1

The efficiency obtained in the alternative 2.1 through DSE (equation 23) and correction factors are illustrated in the table 17.

Table 17. Results of efficiency

DSE	$F_{Reactor}$	F_{Cata}		Efficiency
0.3662	0.9161	0.5239		0.1758
		F_{cata1}	F_{cata2}	
		0.8914	0.1564	

4.5. **ALTERNATIVE 2.2**

For this alternative is added one variable to the system for the same reason that the alternative 2.1. This variable does not appear in the design shown in the introduction 1.5 either (Figure 7).

In this alternative can be manipulated both flow rates of EtOH during the process simulation in contrast with of the alternative 2.1. This is due to the column C2 (Section 3.2.1) that is disposed in this alternative (Figure 31). This column allows to recirculate the EtOH that there is in excess, as it has been commented in the introduction (Section 1.5), allowing entering more EtOH in the first reactor and getting a more complete conversion.

To determine the value of EtOH of both flow rates, have been changed the values of EtOH in both flow rates of jointly way without having to connect the recirculation lines. Once found the minimum values possible of both, they have been subtracted from the main flow rate of EtOH (Stream 2) the values of the recirculate EtOH flow rates.

The minimum values determined have been of 29.96 mol/s for the stream 2 and 9.30 mol/s for the auxiliary flow rate (Stream A1).

Establishing these values through AspenPlus® is obtained the table 18 with the results of the alternative 2.2.

Table 18. Results of alternative 2.2

Stream	1	2	3	4	5	6	7
Temperature [ºC]	65.2	142.2	68.9	90.7	68.8	68.8	68.9
Total Flow [mol/s]	100.00	29.96	142.82	115.30	74.93	84.23	74.61
Mole Fraction							
ETBE	0	0	0.0770	0.3340	0	0	0.1289
IB	0.4	0	0.2801	0.1082	0.1666	0.1482	0.0384
nBa	0.6	0	0.4201	0.5204	0.8008	0.7124	0.8042
EtOH	0	1	0.2228	0.0373	0.0327	0.1395	0.0286

Stream	8	9	10	11	12	A1
Temperature [ºC]	68.9	156.6	145.6	133.4	156.9	142.2
Total Flow [mol/s]	64.99	9.62	40.37	3.23	37.14	9.30
Mole Fraction						
ETBE	0	0.9991	0.9540	0.4252	1	0
IB	0.0441	0	0	0	0	0
nBa	0.9232	0	0	0	0	0
EtOH	0.0327	0.0009	0.0460	0.5748	0	1

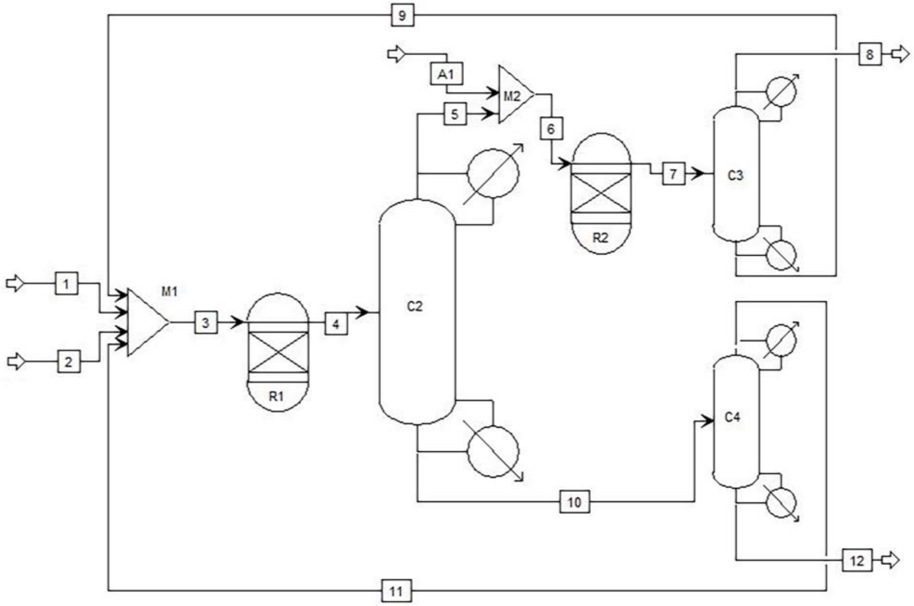


Figure 31. Flowsheet of alternative 2.2

The efficiency obtained in the alternative 2.2 through DSE (equation 24) and factor corrections are illustrated in the table 19.

Table 19. Results of efficiency of alternative 2.2

<table>
<tr><th>DSE</th><th>$F_{Reactor}$</th><th colspan="2">F_{Cata}</th><th>Efficiency</th></tr>
<tr><td rowspan="3">0.3522</td><td rowspan="3">0.9371</td><td colspan="2">0.5102</td><td rowspan="3">0.1684</td></tr>
<tr><td>F_{cata1}</td><td>F_{cata2}</td></tr>
<tr><td>0.9099</td><td>0.1104</td></tr>
</table>

4.6. REACTIVE DISTILLATION

In the global balance of material in the reactive distillation, is assumed total conversion of the reactant IB inside of column. Since in reactive distillation is purged the inert by the distillate and the product through the bottom, it is applied this condition respect of IB in the reactor used to simulate the reactive area of the column.

Due to boiling point, the composition in the distillate corresponds to the azeotrope EtOH/nBa, since the boiling point is the lowest, and the composition in the bottom corresponds to the pure ETBE product.

From the database in the system the table 20 is performed the mass balance in all the system and they are obtained the results shown in the table 21 (Appendix 1).

Table 20. Set values in system for BMM

Set values in system

W_1 [mol/s]	$X_{1\ nBa}$	$X_{1\ IB}$	$X_{D\ EtOH}$	$X_{D\ nBa}$
100	0.6	0.4	0.0397	0.9603

Table 21. Values obtained in balance of material

Values obtained in balance of material

W_2 [mol/s]	W_D [mol/s]	R [mol/s]	W_R [mol/s]
42.48	62.48	40	40

The simulation of the reactive distillation has been made through AspenPlus®. The results are shown in the table 22.

Table 22. Results of Reactive distillation

Stream	1	2	3	4	W_D	W_R
Temperature [ºC]	65.2	142.2	68.1	90.5	68.9	156.9
Total Flow [mol/s]	100.00	42.48	142.48	102.48	62.48	40.00
Mole Fraction						
ETBE	0	0	0	0.3903	0	1
IB	0.4	0	0.2807	0	0	0
nBa	0.6	0	0.4211	0.5855	0.9603	0
EtOH	0	1	0.2981	0.0242	0.0397	0

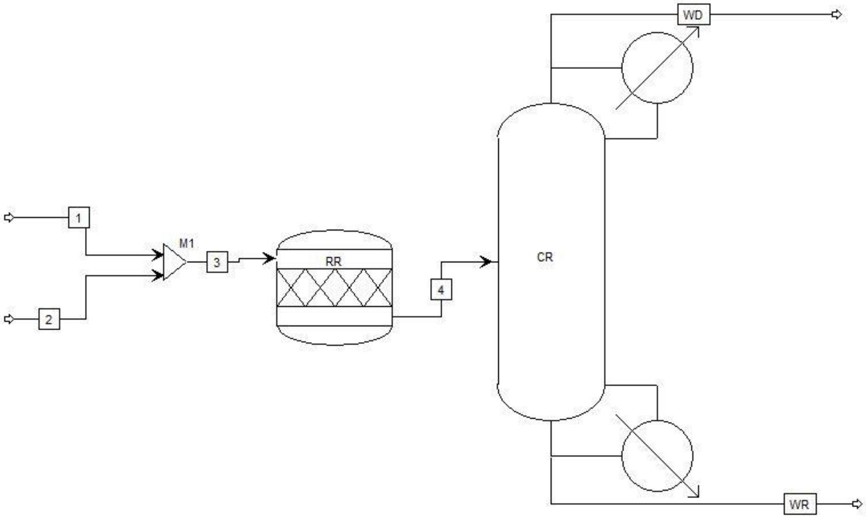


Figure 32. Flowsheet Reactive Distillation

The efficiency obtained in the alternative 1.3 through the DSE (equation 25) and correction factors are illustrated in the table 23.

Table 23. Values of efficiency

DSE	$F_{Reactor}$	F_{Cata}	Efficiency
0.5268	0.9699	1.000	0.5109

4.7. ALTERNATIVE OF THE BREF

The original alternative is carry out at work pressure of 14 bar as it is commented in the section 1.7. In this project has been carried out at work pressure of 8 bar like all the other alternatives to facilitate the comparison of results.

This alternative contain a quantity of water, which it does not react and it is does not expelled from the system. Since the AspenPlus® does not contain an option to configure it, it has been carried out through a continuous flow of water. This stream enters in the system and it leaves of the system constantly (Stream A1 and A2 in the Figure 34).

It is necessary to determine the value of the stream A1 of water that it is introduced in the block E1. The value of stream A1 must be large enough to absorb all the EtOH introduced in the block E1. In order to determine this value has been performed an analysis of sensitivity through AspenPlus®.

This analysis varies the quantity of water that is introduced in the block E1. It has been programmed in the analysis of sensitivity with FORTRAN® the calculation of the variation of EtOH between the EtOH flow in the stream 6 and the EtOH flow in the stream 8 (equation 12).

$$\Delta EtOH = W_{6EtOH} - W_{8EtOH} \qquad (12)$$

When the value of the equation 12 is 0, the quantity of water is the necessary to fulfill the system requirement.

The values obtained through the analysis of sensitivity are shown in the figure 33 in graphic form. This graphic represented the value of stream A1 vs ΔEtOH.

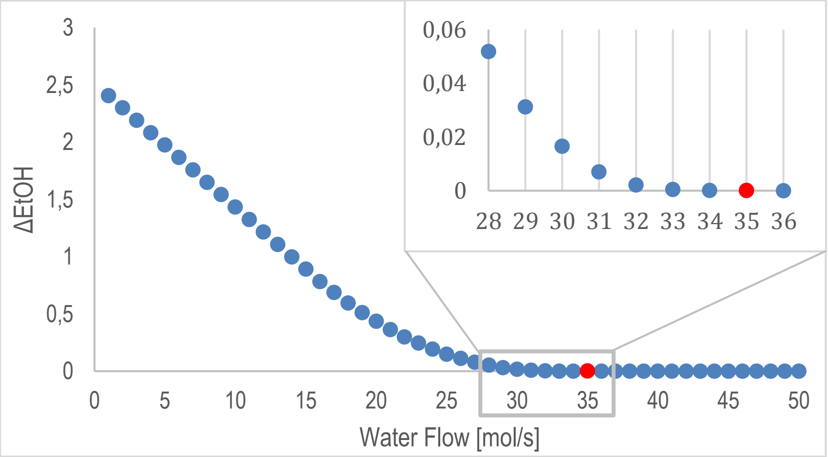


Figure 33. Results of analysis of sensitivity by the Alternative of the BREF

It is seen that for a value of 35 mol/s or higher the Water flow rate of Stream A1 is valid. The chosen value has been 35 mol/s because the higher the value of Water flow, the greater the energy consumption needed to recover the pure water.

From de value obtained from the stream A1 and taking into account the modification made in the reactor (Section 3.2.3), the simulation is carried out.

The results obtained for the alternative of the BREF are shown in the table 24 together with its process scheme in the Figure 34.

Table 24. Results of alternative of the BREF

Stream	1	2	3	4	5	6
Temperature [ºC]	65.1	142.7	67.3	90.0	159.0	67.6
Total Flow [mol/s]	100.00	30.21	132.84	102.63	30.21	72.42
Mole Fraction						
ETBE	0	0	0	0.2943	1	0
IB	0.4	0	0.3014	0.0957	0	0.1357
nBa	0.6	0	0.4527	0.5860	0	0.8304
EtOH	0	1	0.2459	0.0240	0	0.0340
Water	0	0	0	0	0	0

Stream	7	8	9	A1	A2
Temperature [ºC]	60.0	60.0	119.1	60.0	170.6
Total Flow [mol/s]	70.06	37.36	2.63	35.00	34.73
Mole Fraction					
ETBE	0	0	0	0	0
IB	0.1398	0.0009	0.0123	0	0
nBa	0.8564	0.0036	0.0517	0	0
EtOH	8.39E-08	0.0659	0.9361	0	0
Water	0.0039	0.9296	0	1	1

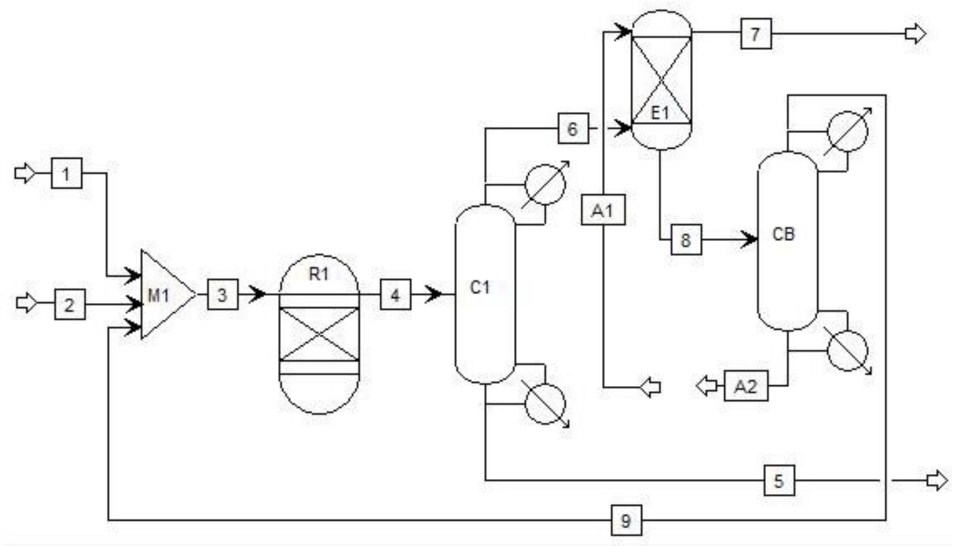


Figure 34. Flowsheet of Alternative of the BREF

The efficiency obtained in the alternative 1.3 through DSE (equation 26) and correction factors are illustrated in the table 25.

Table 25. Values of efficiency of Alternative of the BREF

DSE	$F_{Reactor}$	F_{Cata}	Efficiency
0.5246	0.8605	0.9802	0.4425

5. COMPARISON OF RESULTS

The efficiency values of the different alternatives are shown in the Figure 35. It can be seen a relevant difference between the reactive distillation and the other alternatives. As it has been said before, in the Section 1.6, the reactive distillation was selected because of its good values taken from the bibliographic research. The second best alternative chosen because of its efficiency is the alternative BREF (Section 1.7). It was chosen because it is the process proposed by the EU to ETBE production, allowing only using this process or another better than it.

Having into account the obtained alternatives in the paper "A unifying framework for optimization-based design of integrated reaction-separation processes", the best alternative to choose is the 1.2. (Figure 35).

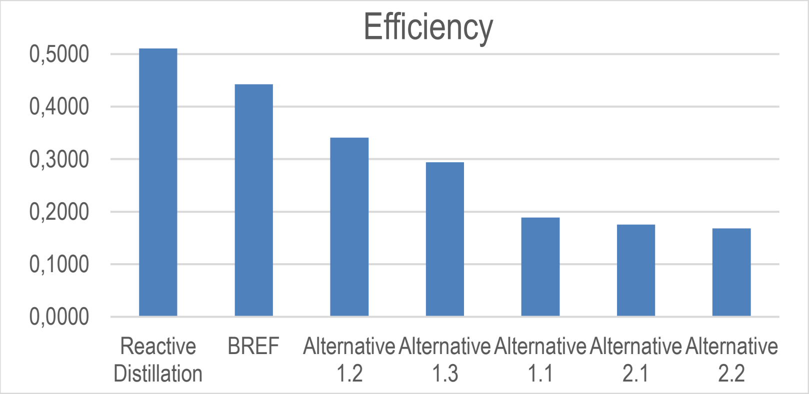


Figure 35. Comparison chart of all the efficiencies

Between the two best alternatives obtained (RD and BREF), the values obtained in the table 26 are equal between them except to the $F_{Reactor}$. This indicates a difference of less production of ETBE in based on the raw material introduced for the BREF alternative.

Between the alternatives that improve the separation (1.2 and 1.3), the alternative 1.3 takes a lower value in the DSE (Table 26). This is due to the use of other distillation column and a recirculation flow more. Comparing the four columns and three recirculation flows to the three columns and two recirculation of the alternative 1.2, it can be justified the decrease of the DSE value.

The factors $F_{Reactor}$ y F_{Cata} are practically identical in both alternatives. This is why, the fourth distillation column added in the alternative 1.2 affects negatively to the global efficiency of the process.

The alternatives 2.1 and 2.2 shown in the Table 26 contain values almost equal between them. The third column added in the alternative 2.2. does not improve the efficiency of the process. Therefore, between both alternatives is better to choose the alternative 2.1.

Between alternatives that improve the separation (1.2 and 1.3) are observed in the figure 35 better efficiencies respecting to the alternatives that improve the reaction yield (2.1 and 2.2). The use of two reactors in the process decreases drastically the F_{cata} factor (Table 26). This factor is the reason of the inequality between the efficiencies of the different alternatives.

Table 26. Comparison of alternatives

Alternative	DSE	$F_{Reactor}$	F_{Cata}	Efficiency
1.1	0.2275	0.8310	1	0.1891
1.2	0.3970	0.9699	0.8859	0.3411
1.3	0.3341	0.9699	0.9084	0.2944
2.1	0.3662	0.9161	0.5239	0.1758
2.2	0.3522	0.9371	0.5102	0.1684
RD	0.5268	0.9699	1	0.5109
BREF	0.5246	0.8605	0.9802	0.4425

In the paper “A unifying framework for optimization-based design of integrated reaction–separation processes” appears a table with the cost contributions for process alternatives extracted for this project (Table 27). Even if this table appears in costs, it is useful to compare from a global point of view the results obtained in this project (Figure 36).

Table 27. Results abstract from the paper "*A unifying framework for optimization-based design of integrated reaction–separation processes*" of Marquardt

Alternative	C_{Raw} (10^6 \$/annual)	C_{Cat} (10^6 \$/annual)	C_{Sep} (10^6 \$/annual)	C_{Op} (10^6 \$/annual)
1.1	54.1	2.2	2.2	58.5
1.2	49.2	0.1	1.9	51.2
1.3	49.2	0.1	1.9	51.2
2.1	49.3	2.1	1.5	52.9
2.2	49.3	2.1	1.5	52.9

The table 27 shows a high cost contributions for the process 1.1 respecting to the other alternatives, considering it the worst alternative. Even though, in the Table 26, the alternative 1.1 contains an efficiency similar to the ones of the alternatives 2.1 and 2.2 (Figure 36). This is due to the not-use of the recirculation along the simulation carried out in this project (Section 4.1, Figure 25).

It has to have taken into account that the alternatives 2.1 and 2.2 have been carried out in a different way (Section 4.4 and 4.5) from the ones of the paper in the Table 27.

The alternatives that improve the separation contain a low cost of C_{Cat}, what causes a higher value of F_{Cata} in the table 26. In the Table 27, the determining factor in the comparison between both groups of alternatives is the C_{Cat} factor.

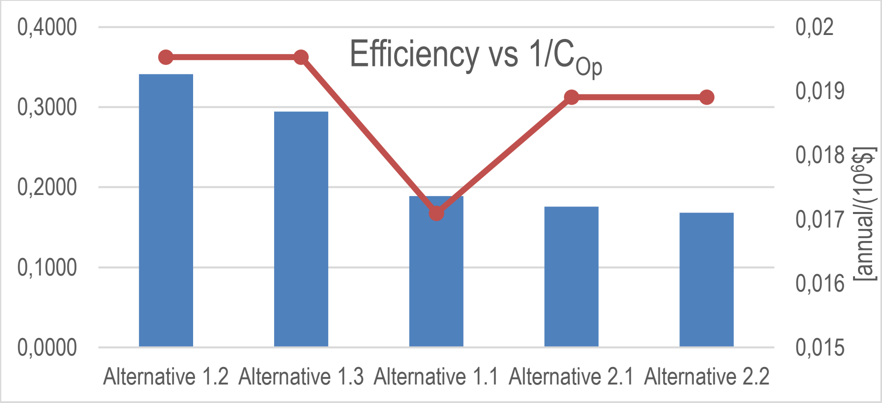


Figure 36. Comparison Project vs Paper

Through all the data obtained and the comparisons done, it is possible to reach many conclusions.

6. CONCLUSIONS

The proposed alternatives from the found paper in the bibliographic researched have allowed to carry out the study of this project. From the application of the ∞/∞ analysis, it has been made the previous study to a production process without the necessity of performing rigorous simulations in the design schemes.

The maps of the residue curves have been an useful and essential tool in this project to understand the scheme development, as well as the distillation in each column.

With the intention of analyzing the found paper in the initial research implementing the DSE method, the addition of the two correction factors along with the DSE method, have achieved to determine the evaluation of the reaction and separation systems jointly, under general simplifications.

From the comparison of the results done in the previous section from different approaches posed at the beginning of the project, have been determined the next points.

- Most of the results obtained from the evaluation of the method DSE “amplified” contrast with the results taken from the paper, proving the veracity of the applied method.
- The alternatives that improve the separation have results of higher efficiency comparing to the initial alternative and the alternatives that improve the reaction yield.
- The values of efficiency obtained in the two alternatives added from the bibliographic research of efficient production processes of ETBE, agree with the expected hypothesis.

Finally, the proposition of the reactive distillation as an intensification process has been selected as the best option followed by the proposed scheme in the BREF as systems with better efficiency respecting to the other proposed alternatives.

As general conclusion of the project, it can establish that the DSE method has been extended by the two proposed factors of correction. Furthermore, it has been possible to improved the DSE method by applying it for the first time in systems of reaction and separation jointly.

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ACRONYMS

3D	Three Dimensions
BREF	Best Available Techniques Reference
C_{Cat}	Cost of catalyst
C_{Sep}	Cost of separation
DSE	Distillation Sequence Efficiency
ETBE	Ethyl Tert-Butyl Ether or Tert-Butyl Ethyl Ether
EtOH	Ethanol
Fc	Crude feed Flow rate
F_{Cata}	Correction Factor of catalyst
$F_{Reactor}$	Correction Factor of Reactor
IB	IsoButylene
L-L	Liquid – Liquid
MMB	Macroscopic Mass Balance
nBa	n-Butane
n_{Pi}	Stoichiometric coefficient product i
n_{Ri}	Stoichiometric coefficient reactant i
ºC	Celsius Unit
RD	Reactive Distillation
T_{Bi}	Temperature Bottom of stream i
T_{Di}	Temperature distillate of stream i
UNIFAC	Universal Functional group Activity Coefficient
W_i	Mole flow rate of stream i
ΔEtOH	Variation of EtOH

η_{Ci}	Carnot efficiency of column c_i

APPENDICES

APPENDIX 1: EQUATIONS OF MMB AND DSE

The illustrated equations shown the overall Mass Balances performed for the Alternatives 1.2 and 1.3.

MMB nBa: : $X_{nBa,1} \cdot W_1 = X_{nBa,7} \cdot W_{10}$ (13)

MMB Isobuteno: $X_{IB,1} \cdot W_1 = R$ (14)

MMB Etanol: $W_2 = X_{EtOH,7} \cdot W_7 + R$ (15)

The illustrated equations shown the overall Mass Balances performed for the Reactive Distillation:

MMB global n-Butano: $X_{nBa,1} \cdot W_1 = X_{nBa,WD} \cdot W_D$ (16)

MMB global Isobuteno: $X_{IB,1}\ W_1 = R$ (17)

MMB global Etanol: $W_2 = X_{EtOH,WD} \cdot WD + R$ (18)

MMB global ETBE: $W_R = R$ (19)

The different DSE equations applied in all the alternatives are shown below.

$$DSE_{1.1} = \frac{W_5}{F_C} + \frac{W_6}{F_C} \cdot \eta_1 + \frac{W_7}{F_C} \cdot (\eta_{C1} - 1) \tag{20}$$

$$DSE_{1.2} = \frac{W_6}{F_C} \cdot (\eta_{C2} \cdot \eta_{C3} - 1) + \frac{W_7}{F_C} \cdot \eta_{C2} + \frac{W_9}{F_C} \cdot (\eta_{C4} - 1) + \frac{W_{10}}{F_C} \tag{21}$$

$$DSE_{1.3} = \frac{W_7}{F_C} \cdot (\eta_{C2} \cdot \eta_{C3} - 1) + \frac{W_8}{F_C} \cdot \eta_{C2} + \frac{W_{10}}{F_C} + \frac{W_{12}}{F_C} \cdot (\eta_{C4} \cdot \eta_{C5} - 1) + \frac{W_{13}}{F_C} \cdot (\eta_{C4} - 1) \tag{22}$$

$$DSE_{2.1} = \frac{W_8}{F_C} \cdot (\eta_{C1} \cdot \eta_{C3}) + \frac{W_9}{F_C} \cdot (\eta_{C1} - 1) + \frac{W_{10}}{F_C} \tag{23}$$

$$DSE_{2.2} = \frac{W_8}{F_C} \cdot (\eta_{C2} \cdot \eta_{C3}) + \frac{W_9}{F_C} \cdot (\eta_{C2} - 1) + \frac{W_{11}}{F_C} \cdot (\eta_{C4} - 1) + \frac{W_{12}}{F_C} \tag{24}$$

$$DSE_{RD} = \frac{W_D}{F_C} \cdot \eta_{CR} + \frac{W_R}{F_C} \tag{25}$$

$$DSE_{BREF} = \frac{W_5}{F_C} + \frac{W_7}{F_C} \cdot \eta_{C1} + \frac{W_9}{F_C} \cdot (\eta_{C1} \cdot \eta_{CB} - 1) \tag{26}$$