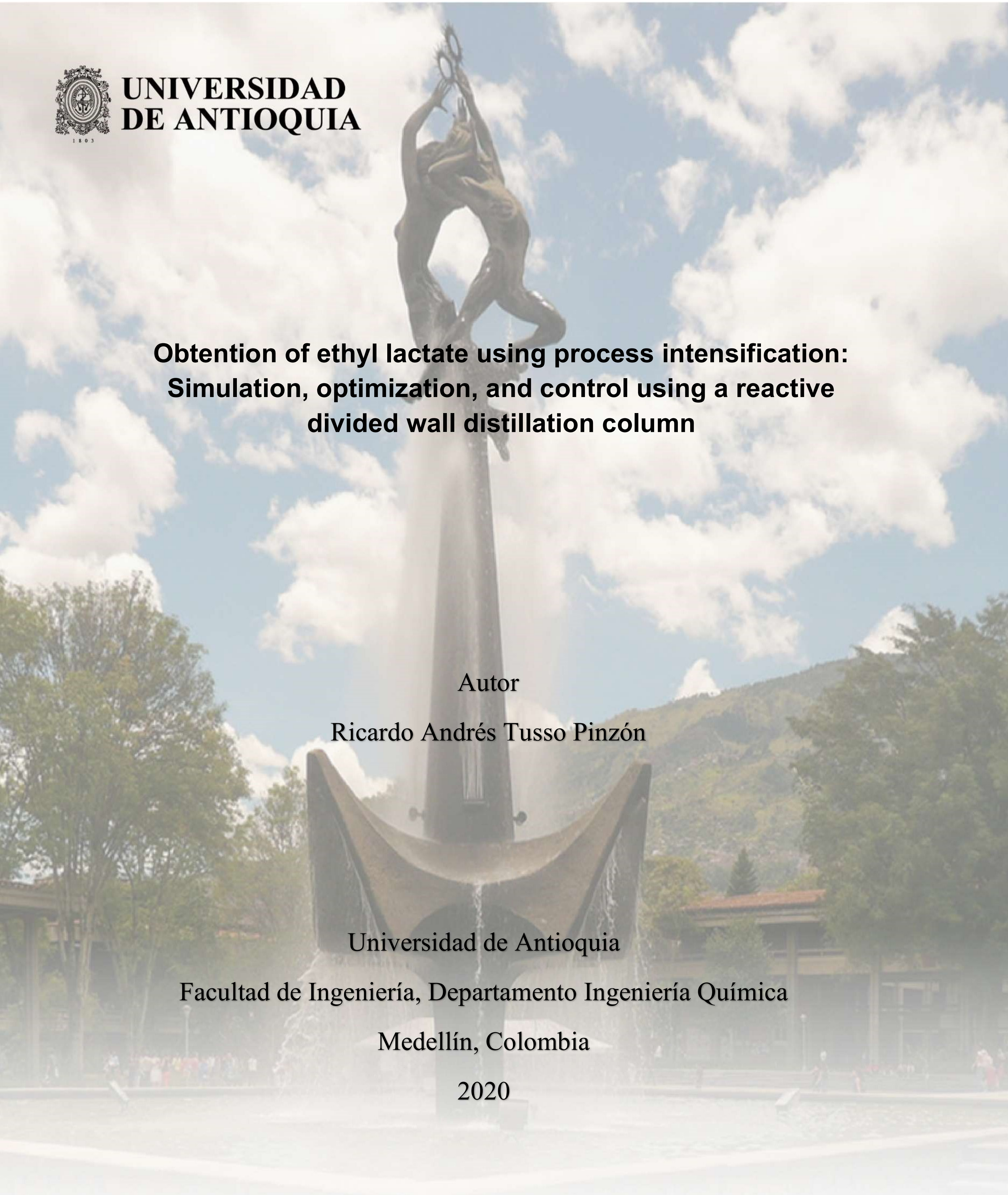

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ABSTRACT

The implementation of a chemical process must enforce the development of solvents that are environmentally liable, considering the economic and safety factors. In that way, process intensification extends the possibility to adapt conventional processes to reroute a feasible production of these solvents. The sustainability development in separation-reaction processes associates higher energy efficiency and pollutant reduction. This work proposes to minimize the number of units required in a conventional process, including separation and reactions, initially through a shortcut method of the analysis of the statics, to generate a feasible reactive distillation flowsheet. Then, rigorous simulations state the condition of the process, including the kinetic subroutine and the phase equilibria information, resulting in the generation of more sustainable designs, through the identification of the phenomena tasks in each unit, leads to the gradual intensification and bringing the final flowsheet alternatives. It shows the feasibility to intensify gradually a base case into an intensified process, keeping the production requirements with the improvement of economic and sustainability factors. Finally, two control structures schemes, composition, and temperature, will present the transient behavior in a reactive divided wall distillation column to synthesize ethyl lactate. All control structures include PI control loops to manipulate three variables, reflux flow, liquid split ratio and the heat duty in the reboiler. To handle these variables is necessary to locate the controllers, two in the main column and the third in the prefractionator, showing that a temperature control structure has a better performance under flow and compositions perturbations.

Keywords: Design, Simulation, Control, Reactive distillation, reactive divided wall column, Process intensification.

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1. INTRODUCTION

Nowadays, the approach in chemical engineering is the development of process intensification, that has innovations that generate new applications and products in an efficient way to establish a competitive chemical product. All of these go together with the technology of the equipment, the synthesis of the product, and the performance of the process.

According to Stankiewicz and Moulijn, (2000), process intensification is a strategy for making dramatic reductions in the size of a chemical plant to reach a given production objective, transforming a process into a smaller, more sustainable, safer and with less energy consumption. In that sense, process intensification relates the productivity in terms of producing of a good, and the inputs required to achieve a task in all the stages of the development of the process, design, and implementation (Becht, *et al.*, 2009).

For that reason, process intensification involves the intensification of equipment, which includes the heat and mass transfer phenomena inside of equipment, and the intensification of methods, such as separation and reaction merging in a single unit and its operation in transient or steady-state. All of these determines the degree of innovation in terms of the identification of these tasks.

Reactive distillation and reactive divided wall columns belong to the process intensification technology, offering several improvements over sequential reactor-separator, in terms of the reduction of bottlenecks or recycles streams to improve the conversion of reactants to products. The achievements of the adoption of these technologies are subject to the identification of opportunities to produce greener products, in comparison with a conventional process, and the analysis of the resulting possible alternatives.

As a result, the design of reactive distillation units presents more complexities and the most important issues, related to the catalyst election, the internal structure of internal devices, and the location of the reactive zone to reach the product requirements. Also, several methods have contributed to implement the integration and the intensification of reactive distillation, from the mathematical perspective, heuristics or combined criteria, through the help of computer-aided tools that performs process intensification, predicting the interaction of the inherent properties of the system, and the reliability of the process project (Babi, *et al.*, 2014).

1.1. Aim and motivation of the work

In separation-reaction processes, it is important to point out that this industry requires an environmentally friendly and sustainable development, highlighted by using higher energy efficiency and reduction of some pollutants, as greenhouse gases on air; and others in soil and water, under local legislations requirements.

On the other hand, economic pressures are always present in worldwide markets, reflected by considerable cost reduction inside the operations. At this point, it is valuable a competitive industry in terms of adaptation and flexible processes, under some oscillations and variations in raw material availability, prices, etc., that could be covered by dynamic processes.

A new paradigm is present in a separation process, and it could be possible to overcome these new challenges through process intensification, specifically in reactive distillation. These expectations are raising many scientific and technical issues for modern process technologies and their control.

As a result, the research question would be: How much the energetic requirements will be reduced, when a divided reactive distillation wall column is employed, in comparison with the conventional system, reactor-separator, and reactive distillation column for the production of ethyl lactate?

The main objective of this work is to establish a design, simulation, optimization, and control structure for reactive divided wall column (DWRDC), through the following strategy:

- To propose an algorithm for modeling and simulating a (DWRDC) for the obtention of Ethyl Lactate from Lactic Acid.
- To apply non-linear dynamics techniques through mathematical programming applied to the project problem.
- To analyze energetically the minimum demands on each arrangement.
- To propose a control scheme for the DWRC, through simulation validation.

1.2. Outline of the thesis

This work is composed of 6 chapters, chapter 1 presents the introduction, the motivation and the objectives of the work. In chapter 2 a state of the art of the green solvent ethyl lactate covers the synthesis, the main uses and recent findings. Then, a summary of the main advances in the intensification of conventional reaction and separation interaction represented in the reactive distillation and reactive wall distillation column.

Chapter 3 presents the graphical analysis of the statics approach, to generate a feasible flow sheet, using the physicochemical information of the system, and the stoichiometry of the reaction. This results in a feasible intensified scheme flowsheet of a reactive distillation column (RD).

Chapter 4 establishes the degrees of freedom of a reactive distillation column and the reactive wall distillation column, with the specification of the operating variables. Also, the specification of MESH equations, that configures the model of esterification of lactic acid with ethanol, considering the RD and RDWC. Finally, a validation of the model of reactive distillation with the experimental data available, and an energetic study that will compare the performance between the RDWC and a conventional direct sequence, an RD followed by a conventional distillation column.

In chapter 5, the objective is the minimization of the number of equipment of process, and evaluate the effect on the reduction of economic and environmental metrics. Also, the degree of intensification alternatives is based on the phenomena building blocks, which will develop the degree of intensification without a formal optimization problem.

In chapter 6 will present two different PI control structures in a proposed RDWC, investigating the transient behavior in a reactive divided wall distillation column. Both control structures include the different control loops, to manipulate key variable to maintain a minimum energy consumption. Finally, the main results and the comparisons of these schemes will show the key findings of these schemes, in the face of some disturbances.

1.1. List of publications

Currently, 3 publications are under submission, as follows:

- Ricardo A. Tusso-Pinzón, Luis G. Matallana-Pérez. PRODUCTION OF ETHYL LACTATE THROUGH PROCESS INTENSIFICATION.
- Ricardo A. Tusso-Pinzón, Luis G. Matallana-Pérez. CONTROL OF A REACTIVE DIVIDED WALL DISTILLATION COLUMN FOR THE SYNTHESIS OF ETHYL LACTATE.
- Ricardo A. Tusso-Pinzón, Arick Castillo-Lander, Luis G. Matallana-Pérez, Arturo Jiménez-Gutiérrez. INTENSIFIED SYNTHESIS FOR ETHYL LACTATE PRODUCTION INCLUDING ECONOMIC, SUSTAINABILITY AND INHERENT SAFETY CRITERIA

2. STATE OF THE ART

2.1. Introduction

The chemical solvents market is on the order of 20 million metric tons, as raw material (Clark, *et al*, 2015). Nowadays, most of them become from traditional petrochemical sources, as volatile compounds that have demonstrated widely the enormous impacts and risks in the environment and health. In almost all industries, and manufacturing depends on the use of solvents, Figure 2-1.

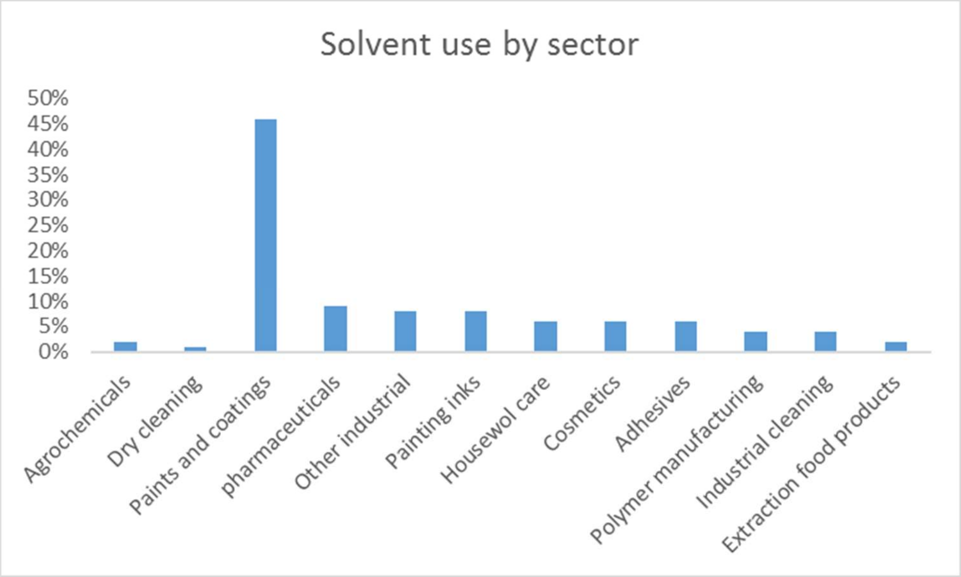


Figure 2-1 Solvent demand by market segment

The demand for solvents is forecast to rise 1.1 percent per year through 2020, in the case of the USA, reflecting continued economic growth and, in particular, ongoing healthy increases in construction activity. Strength in both nonresidential and residential building construction will stimulate demand for construction-related materials, such as paint and coatings and adhesives and sealants (Global Markets insight, 2018).

In the case of ethyl lactate, China and North America are the main product and consume the market. China consumption 7251 tons in 2017, while North America consumption is 9375 tons accounting for 35.82 percent of the global consumption.

Corbion and Galactic are the world leaders, for the time being, taking 18.41% and 13.55% of the global ethyl lactate production respectively. The worldwide market for Ethyl Lactate is expected to grow at a CAGR of roughly 3.4% over the next five years, will reach 92 million US$ in 2024, from 76 million US$ in 2019. In 2017, 46.13% ethyl lactate was used in the industrial application industry and 30.13% was used in Food and Beverage. (Markets and Reseach, 2019).

As can be seen, ethyl lactate as a green chemical is a new great competitor compared with traditional industries, this is a new challenge in terms of increasing the performance of emerging processes. In that sense, it has a repercussion from the economic and social point of view, fitting this new paradigm into the regulation of the nations.

For that reason, many efforts recall the chemical engineering to deal and to adapt the conception of green chemistry to most of the processes. In those efforts, green chemistry structured as a new branch with big objectives, establishing some principles that classify a process or a product as greener.

The green chemistry principles enumerate the practices that assess the degree of a greener process or products (Anastas and Zimmerman, 2003). The formalization of green chemistry comes together with the evaluation of the harmless as compared with a conventional solvent, considering the toxicity, the biodegradability, emissions, greenhouse effect, its safety, in terms of risk of explosion, and logically, the costs, and the availability (Häckl and Kunz, 2018).

Another concept that is linked to green chemistry is the life cycle analysis, which considers all the stages in the useful life of a solvent, from the beginning as a raw material until the final disposal, passing through intermediate steps. The life cycle not only considers the disposal of a solvent but also recognizes the impact in terms of energy consumption under certain conditions (Carvalho, 2016).

In the same manner, a green solvent is also a safe solvent that regards to sustainability that is implicit in the emissions into the environment. Given the condition of the process, the sustainability factors consider the carbon footprint, the human toxicity by ingestion and exposure, the global warming potential, and the carcinogenic impacts (Kalakul, *et al*., 2014).

On the other hand, the possibility of generating a greener process consists in the identification of certain phenomena involved that could improve the final flowsheet. The representation of these phenomena involves the tasks that represent the interaction between energy, momentum and transfer phenomena (Lutze, *et al*., 2013).

As a result, the process intensification is an alternative to consider in the generation of greener process that produces greener solvents, improving those metrics. Specifically, reactive distillation and reactive wall distillation columns have spread the scope in process intensification, giving the possibility to integrate the separation phenomena with reaction phenomena.

The study of this kind of equipment covering the design, optimization, and control, with different methods, shortcut methods or rigorous at steady state. The main findings in its feasible application and adaptations relate to the reduction of utility and energy demands in terms of cost savings and the improvement in the relation of conventional processes (Yildirim, *et al*., 2011).

In this work, a state of the art of the green solvent ethyl lactate covers the synthesis, some studies that consider the inclusion of oligomers in a phenomenological model, represented with the experimental data. Also, the main uses and recent findings in how this solvent eventually replaced other solvents from petrochemical sources, and the origin of the raw material lactic acid and ethanol.

Finally, a summary of the main advances in the intensification of conventional reaction and separation interaction, represented in the reactive distillation and reactive wall distillation column, from the design point of view, then showing some works where have been adapted successfully. In the end, the implementation and control of these kinds of devices in the recent decade.

2.2. State of the art on ethyl lactate

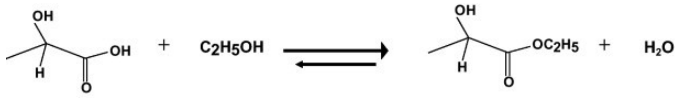
2.2.1. Synthesis of Ethyl Lactate

Today, Ethyl lactate is being projected as a bio-based benign solvent to the environment for chemical transformations, with important advantages over solvents of petrochemical source, such as low toxicity, high biodegradability, good solvation capacity, no flammability, and easy recycling (Dandia, *et al*., 2013).

Additionally, the use and production of ethyl lactate as a green solvent in organic reactions and pharmaceuticals or food additives, and its industrial production is emerging as relevant to the domestic chemical industry. Ethyl lactate is produced by the reaction between an aqueous solution of lactic acid and ethanol, through the following steps: esterification of lactic acid, lactic acid oligomerization, esterification of the oligomers and ultimately the transesterification of the ester oligomers directly to ethyl lactate (Komesu *et al*., 2015). Also, can be produced separated efficiently, obtaining high yields of product, esterification of lactic acid with an excess of ethanol, using a single operating step through a reactive distillation process.

On the other hand, Ethyl lactate can be either in the Levo (S) or Dextro (R) forms, and it is industrially produced as a racemic mixture through a reversible reaction between ethanol and lactic acid, wherein water is a by-product. The natural product is exempt from many restrictions placed upon the use and disposal of solvents. Because both enantiomers are found in nature, and ethyl lactate is easily biodegradable, it is considered as a green solvent (Pereira, *et al*., 2010).

In another case, the influence of different kinetic and pervaporation parameters such as initial reactant molar ratio, amount of catalyst, temperature and the ratio of membrane area/initial volume of reaction was analyzed in terms of ethyl lactate yield. For dilute lactic acid aqueous solutions, the effect of catalyst loading has been found not to have a great influence, unlike the other parameters. Additionally, the effect of the initial concentration of the lactic acid aqueous solution was evaluated by performing experiments with different lactic acid aqueous solutions concentrations. In this case, for dilute lactic acid aqueous solutions, only the monomer has to be considered, therefore the only reaction is the esterification of monomeric lactic acid with ethanol as follows: (Delgado, *et al.*, 2007a).



2.2.2. Oligomers formation

Lactic Acid presents intermolecular esterification in aqueous concentrated solutions, forming oligomers as di-lactic acid, tri-lactic acid, and other higher polymers chains. The esterification phenomenon rises with the Lactic Acid concentration, generating a complex use as a reagent, because in the esterification with Ethanol, its oligomers react for forming Ethyl Lactate polymers.

$$2L_1 \underset{K_1}{\leftrightarrow} L_2 + H_2O$$

$$L_2 + L_1 \underset{K_2}{\leftrightarrow} L_3 + H_2O$$

$$L_1 + EtOH \underset{K_3}{\leftrightarrow} L_1E + H_2O$$

$$L_2 + EtOH \underset{K_4}{\leftrightarrow} L_2 + H_2O$$

$$L_3 + EtOH \underset{K_5}{\leftrightarrow} L_3E + H_2O$$

In that sense, the monomeric Ethyl Lactate, the desired product, could be separated from the oligomers mixture in further processes. However, the reaction selectivity decreases due to their presence, although these oligomers could be used as plasticizers, do not have a specific market yet (Asthana, *et al.*, 2005).

2.2.3. Simplification of the kinetic model of oligomers

The oligomers and polymers formation of Ethyl Lactate in the synthesis reaction is present due to the Lactic Acid nature. Unfortunately, all these mathematical models developed in these works presented high deviations concerning the experimental data, in concentrated solutions of Lactic Acid, predicting higher values of oligomers of Lactic Acid and the polymers of Ethyl Lactate in equilibrium. These deviations are caused by the lack of activity coefficients reported in the literature and thermodynamic data of the oligomers of Lactic Acid, and the Ethyl Lactate of the esters polymers, as well as the correlation with the use of heterogeneous catalysts (Asthana *et al*., 2005), and (Tanaka, *et al*., 2002).

Nevertheless, it is possible to predict the activity coefficients of the oligomers with different methods, like UNIFAC through the functional group contributions, but this causes uncertainty related to the high concentrations of the oligomers. As an example, Vu, *et al*., (2006) simulated an esterification reaction taking into account the activity of the oligomers, determined by UNIFAC. The results presented high deviations with the experimental data and compared with a model with ideal conditions.

Despite this, monomeric Ethyl Lactate raises, giving diverse reversible reactions taking place and displaces the equilibrium to the formation of monomeric Lactic Acid and then to the monomeric Ethyl Lactate. In this transition stage, the concentration of Lactic Acid reduces, meanwhile the concentration of Ethyl Lactate rises (Pereira, *et al*., 2008a).

In Table 2-1 enumerates the publications that considerate the presence of oligomers in the diverse kinetic models for the synthesis of Ethyl Lactate, showing the reaction and the concentration of polymers and oligomers after reaching the chemical equilibrium (Manic *et al*., 2012), and (Pereira, *et al*., 2011).

Table 2-1. Consideration of oligomers presence on the literature

Authors	**Catalyst employed**	**Lactic Acid solution (%)**	**Oligomers presence**	**Oligomers in equilibrium**
(Tanaka *et al*., 2002)	Amberlyst 15	91	Yes	2,4 (RetOH/AL=1)
(Benedict, *et al*., 2003), (Engin, *et al*., 2003)	Amberlyst XN1010	88	No	
(Petlyuk, 2004)	Hetero polyacid Lewait-5100	88	No	

(Zhang, Ma, and Yang, 2004)	*002	92	No	
	NKC	20	No	
(Asthana *et al.*, 2005).	Amberlyst 15	20-88	Yes	0,4 (RetOH/AL=3)
(Delgado, *et al.*, 2007b)	Amberlyst 15	20	No	
	Without catalyst	20	No	
(Pereira *et al.*, 2008)	Amberlyst 15	88	No	
(Bamoharram, Heravi, *et al.*, 2010)	Preyssler acid	20	No	

2.2.4. Ethyl lactate uses

Recently, many studies analyzed the process in the food industry, aiming to reduce environmental impacts in comparison to conventional and harmful solvents. and costs (Findrik, *et al.*, 2012), (Gao, *et al.*, 2007), (Pereira, *et al.*, 2008b), (Pereira, *et al.*, 2010), and (Moore, 1999). In that sense, ethyl lactate replaced some toxic solvents, such as acetone and methylene chloride solvents.

Pereira, *et al.*, (2010) reported the use of ethyl lactate in the polystyrene, wood, and metal branches, as a coating solvent. In the same way, ethyl lactate can dissolve pesticides and herbicides, also available in anthelmintic formulations, and in the cosmetic and pharmaceutical industry to improve the solubility of other agents (Smith and Wiley, 1994), and (Kay and Chen, 2005).

At the same time, in the food industry, ethyl lactate applications are growing up to date, mainly as extraction solvent. For example, Ishida and Chapman, (2009) used ethyl lactate to extract B-Carotene, lycopene, and lutein from carrots, tomato, and corn. The effectivity of ethyl lactate, in terms of solubility, was much higher than using ethyl acetate, as reported by Strati and Oreopoulou, (2011).

Moreover, Vicente, *et al.*, (2011) found the use of ethyl lactate as a solvent to recover tocophenol and squalene from olive oil, deodorizer distillates (Hernández *et al.*, 2011). In that sense, Villanueva Bermejo *et al.*, (2015) discussed the possibility of extracting thymol, using ethanol, limonene and ethyl lactate, through the pressurized liquid extraction, replacing hexane as a non-green solvent, and the discussion of the use of conventional distillation and soxhlet extraction.

Additionally, some studies, the analysis of the selectivity of ethyl lactate in green coffee beans and green tea leaves and the possibility of production of decaffeinated products was carried out by Bermejo, *et al*., (2015), and Villanueva Bermejo *et al*., (2015).

Finally, Villanueva Bermejo, *et al*., (2017) enumerates the different upgrading in the use of ethyl lactate in the extraction of caffeine. The most relevant is the work of Manic *et al*., (2012), that studies the solubility of ethyl lactate in caffeine at ambient pressure and a range of temperatures, compared with other possible solvents, such as ethyl acetate, acetone, and methanol.

2.2.5. Ethanol as raw material

Ethanol is one of the largest raw materials from biomass source, that had replaced petroleum fuels source gradually, mainly for the generation of greenhouse gases, and the costs and the dependencies of this energy source.

In the mid-20th century, the first generation of ethanol production is produced mainly from sugar cane and starch, in Brazil and the US. According to Mohanty and Swain, (2019), the production achieved in these countries about 27 billion litters in Brazil, from sugarcane sources, and 57 billion in the US, from corn source.

Meanwhile, the second generation reaches a great expansion from the source of the raw material, aiming to find new sources instead of sugar or corn, as lignocellulose biomass, keeping the ethanol demands. For that reason, this development stage focuses on the hydrolysis of polysaccharides, to release glucose and then to produce ethanol.

In that sense, to keep a high production of ethanol is a challenge in terms of technologies that could optimize each cluster of the process, technologies of pretreatments of lignocellulose, cellulose, hydrolysis of the cellulose, fermentation of hexose and pentose to produce other products. Until now, those technological aspects improved the performance of the process, although the cellulosic ethanol is still not economically competitive in comparison with sugar cane or starch-based. Under this scenario, the continuous operation of the biorefineries will depend on the improvement of critical stages in the process, such as hydrolysis of biomass, and to overcome the poor performance in the lignocellulose fractionation (Liu *et al*., 2019).

Finally, the third generation in the production of ethanol focuses on the production of ethanol using microalgae as a main source, through the algae cultivation. Additionally, the biomass from microalgae can be converted into energy sources that could be bioethanol or biodiesel (Alam, *et al*., 2015).

As a conclusion, the production of bioethanol is a complex task, in terms of competitiveness, from an economic and technical point of view. Conversely, the countries emphasize the importance of ethanol, not only as a source of energy but also in different uses in the green industry without leaving the food safety at risk.

2.2.6. Lactic Acid as raw material

In general, Lactic Acid origins from some sources. coming from the fermentation of agricultural waste, using bacteria and fungi. Lactic Acid production links some operations, hydrolysis, fermentation, separation and the treatment of waste streams (Djukić-Vuković, *et al*., 2019).

Initially, the fermentation stage consists of the production of fermentable sugars, in the saccharification process. According to Panesar and Kaur, (2015) gelatinization, liquefaction and saccharification processes improve the starch feedstock. Lignocellulose is a good alternative in the source of raw material, in terms of costs and the availability, but has a difficulty in the hydrolysis and fermentation of Lactic acid.

Abdel-Rahman, *et al*., (2013) and Abdel-Rahman, *et al*., (2011) emphasized the importance of the treatment and the hydrolysis procedure, in terms of toxicity and emissions, when acid solvents are applied. In that sense, these reports focus mainly on the treatment and the enhancement of this stage of the process, achieving efficient fermentable sugars requirements, reducing the costs in terms of product purification and further treatment.

On the other hand, the esterification process is commonly used for commercial production of methyl lactate, ethyl lactate, and n-butyl lactate. Methyl lactate and acetate are water-soluble and not very easy to remove water from the reaction mixture (Dandia *et al*., 2013), (Harmsen, 2007), and (Tanaka *et al*., 2002). Besides this, the reactive distillation column performed a more effective lactic acid recovery from the aqueous solution (Kumar and Daoutidis, 1999). The method involves the esterification of lactic acid followed by distillation and hydrolysis, where lactic acid is purified through methyl ester (Tanaka *et al*., 2002).

The vapor stream from the CSTR, containing methyl acetate, water and methanol are fed into the reactive distillation column where the methyl acetate reacts with water to produce lactic acid. In this part, it is possible to adapt two reactive distillation columns, to improve the process, and combine those two towers, reactive distillation tower or reactive divided wall column, reducing the number of units to obtain pure lactic acid (Tanaka *et al*., 2002).

2.3. State of the art of process intensification in reactive and separation process

2.3.1. Divided wall columns (DWC)

The first known system referred to energy integration explicitly proposed by Wright in 1949, now known as distillation with divided walls, and its theoretical foundations laid by Petlyuk, Platonov, Slavinskii in 1965 (Petlyuk, 2004). During the last two decades, new concepts developed the operation and control of these columns and the ability to develop more complex models separation.

2.3.1.1. Divided wall columns configurations

The divided wall distillation column is a device with a vertical partition with a flat slab, it uses only one condenser and one reboiler. In comparison with conventional sequential configurations, the objective of DWC is to reduce the operational and capital cost, associated with the reduction of vessels and the energy demands.

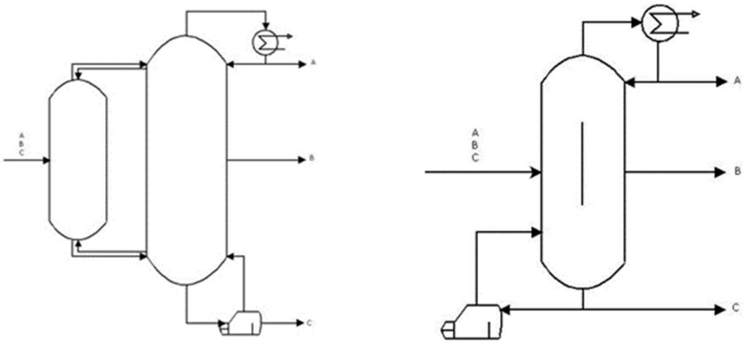
In some cases, when the market requires high-quality product specifications, the equipment isolates thermally. Usually, the colocation of the wall is in the middle of the column, although it could locate in some region of the column when the concentration of the intermediate product could have a lower concentration (Asprion and Kaibel, 2010).

This configuration provides an advantage over the conventional system whose inefficiency produced by the thermodynamic irreversibility during mixing of power flow with going inside the equipment, top, and bottom is reduced in this integrated equipment (Seader and Henley, 1999).

The Petlyuk configuration in Figure 2-2 A, represents an arrangement that can separate three or more components using a single reboiler and a single condenser. The vessel where the feed stream, is called the fractionator, while the section where the condenser and the reboiler are located, is called the main column.

The exchange of vapor and liquid between the columns in the Petlyuk configuration poses strict pressure and operability constraints. Figure 2-2 B represents the dividing wall column configuration which is the most compact and allows for both considerable energy and capital saving.

There is a partition between the feed and side draw sections of the column which provides greater capacity and increased separation efficiency yet still externally resembles a normal side-draw column. The Petlyuk configuration is thermodynamically equivalent to the DWC. The flows inside the two columns of the Petlyuk configuration can be calculated from the liquid and vapor splits above and below the dividing wall (Mueller, *et al*., 2007).



A. Petlyuk column B. Divided wall column

Figure 2-2 Thermally coupled distillation columns

2.3.1.2. Divided wall columns design methods

Most of the shortcut methods evaluate the feasible separation in a column, assuming that constant molar flux, and volatilities constants, occurs in the equipment. These methods are adaptations from the conventional distillation column, fixing the operation subject to the purity of products, and feed conditions.

In one of these methods, 3 conventional columns linked the main column, which is divided into two sections, the rectifying and the stripping section. This strategy consists in achieve de bottom composition in the rectifying section equals the top composition in the stripping section Figure 2-2.

As a result, mass and energy balances establishes the nonlinear restrictions, using nonlinear programming, and specifying the conditions of feed streams, such as composition and thermal condition, product requirements, or recovery fractions (Amminudin, *et al*., 2001).

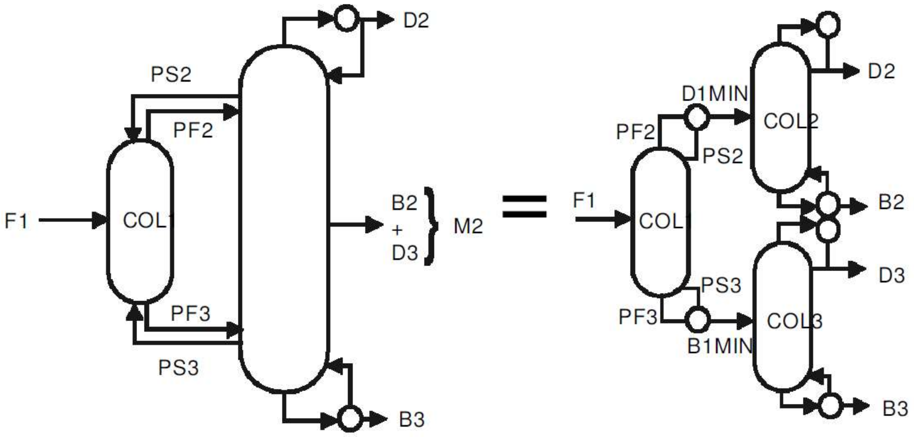


Figure 2-3 Three column configuration

Another alternative, proposed by Cerda and Westerberg, (1981), finds an approximate value for the different variables of operation at the limit reflux condition. The columns could be considered as a set of interlinked separators, having the set of reflux ratios during the separations task, depicted in Figure 2-3.

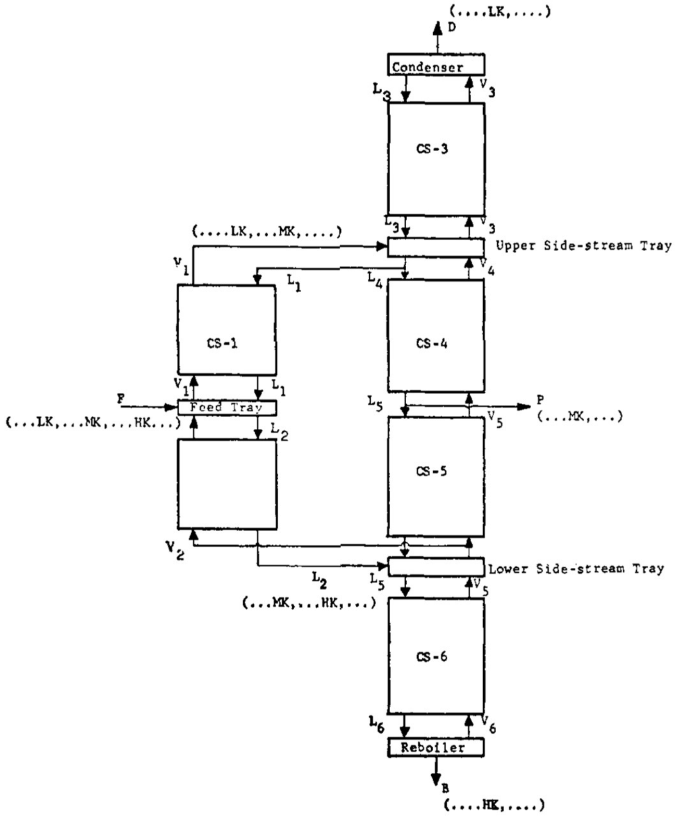


Figure 2-4 Configuration of DWC as a set of fractionators

In the DWC configuration, the number of independent variables equals to the number or fractionators that compounds the system. These variables relate the degree of separation between de components, the internal liquid and vapor flows, in Table 2-2

Table 2-2. List of variables in the design of DWC with one feed as a set of fractionators

Variable	Relation
Reflux ration in the main column	$R = \frac{L_3}{D}$
Liquid fraction that returns to the prefractionator	$x_L = \frac{L_1}{L_3}$
Vapor fraction that returns to the prefractionator	$x_V = \frac{V_2}{V_6}$
Reboiler ratio in the main columns	$S = \frac{V_6}{B}$

Feed thermal condition	$S = (r+1)\left(\frac{D}{B}\right)(1+q)\left(\frac{F}{B}\right)$
The ratio between vapor and liquid fluxes around the prefractionator	$X_{V,m}$
Pinch point relation	$(r'\,X_V)_m = (r'\,X_L)_m\left(\frac{D}{B}\right) + q\left(\frac{F}{B}\right)\frac{(L_2 - V_2)_m}{B}$

On the other hand, another alternative in the design stage is the conventional shortcut methods, given by Frenske, Underwood, and Gilliland (Seader and Henley, 1999). The most representative work that relates these heuristics is Halvorsen, *et al*., (2013) with a graphical method that represents the minimum energy demands through the generation of vapor flows.

Given the Underwood equations, and some assumptions, such as an infinite number of stages and molar constant flow, the vapor distribution is given by the condition of the feed. The diagram shows a distribution of the vapor flow through the column with the flow of products according to the recoveries and compositions.

Also, it represents the minimum vapor flow to achieve a degree of separation. In the V_{min} diagram, the highest peak represents the most difficult binary separation, and the calculation of the number of stages is given by the Frenske equation.

2.3.2. The reactive divided wall distillation column (RDWC)

In the lasts decades, the process has focused on how is possible to achieve operational and control objectives with a minimum number of devices. The divided wall distillation column as the first step of this integration, then the patent of the reactive distillation operation, to produce methyl acetate developed by Eastman Kodak (Agreda and Partin, 1982).

Reactive distillation represents probably the most important example of such integration. The advantages of reactive distillation include the raising of yield, overcoming thermodynamics equilibrium limitations, the increase of the selectivity, suppressing undesired reactions, the reduction of energy demands, the capacity of separating close boiling components (Mueller and Kenig, 2007).

In that sense, the integration of a DWC and RD, have concerned the academy and the industrial field, overcoming some complexities. These relate the design and simulation tools that need to be developed that include reactions, residence time distribution, mass transfer, heat transfer, and impulse transfer. The same approach can be applied to process intensification in general.

As a consequence of this, the dynamics of the column determines the start-up procedure, the ranges of the stable work, the possibility of optimal steady-state achievement and a control system. Taking into account the chemical reaction course, usually with strong nonlinear kinetics, introduces new phenomena and significantly increases difficulties of numerical nature.

Besides, this highly integrated unit enables more efficient separation of products and no converted reactants, resulting in a reduction in the number of units of separation. Moreover, both reactive distillation columns and dividing wall columns are further developments of a conventional distillation unit.

On the other hand, they represent two different ways of integration, combining reactive distillation and dividing wall column principles. The resulting integrated unit is called the reactive dividing wall distillation column, which combines both integration types Figure 2-4.

While in the conventional distillation column each has a range of pressures that can work, the divided wall columns can only work with a single operating pressure. As a consequence, it results in larger temperature differences between the reboiler and condenser as mentioned by Mueller and Kenig, (2007).

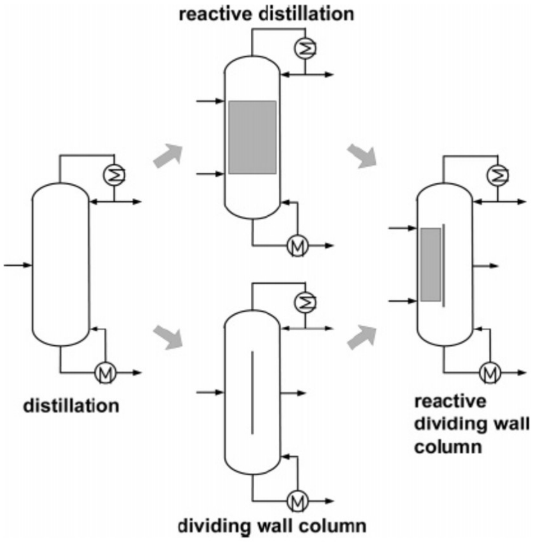


Figure 2-5 Reactive divided wall distillation column (RDWC)

2.3.3. Rigorous simulation

There are essentially two main modeling techniques in use for reactive distillation simulation, the equilibrium stage model, and the rate-based mass transfer model. Chemical reaction models can incorporate chemical equilibrium models or kinetic expression models. Some cases have been successfully applied using rigorous equilibrium model of a reactive distillation column for ETBE, and then extended to the dynamic case, producing accurate estimates of operating conditions and product compositions synthesis (Sneesby, *et al*., 1998), and (Sneesby, *et al*., 1999).

2.3.3.1. Equilibrium model

The equilibrium stage model uses the MESH equations and can readily be extended to reactive distillation with the inclusion of appropriate equations to model the relevant chemical reactions. An equilibrium stage dynamic model for the synthesis of tertamyl methyl ether of the RD has been formulated and solved by writing dynamic continuity equations of mass and energy balance. In developing the equilibrium stage model for a reactive distillation column, the kinetics terms representing the rate of reactions are added to the material balance equations (Baur, *et al*, 2000).

Similarly, Sharma and Singh, (2012) modified the energy balance equations by the inclusion of heat of reaction terms, including column holdup, rigorous phase equilibria, and chemical reaction on the plates and in reboiler. The high conversion steady state is the desirable state and the normal operating condition.

On the other hand, low conversion steady-state is associated with higher temperatures throughout the column. The medium conversion steady-state operating conditions are all between the high conversion and low conversion solutions, variating the costs associated with shutting down a unit to replace spent catalyst.

2.3.3.2. Non-equilibrium simulations (NEQ)

The NEQ stage may represent a tray or a cross-section of a packed column, the stage equations are the traditional equations for mass and energy balances for individual phase, in which mass and heat transfer rates are also included. Bulk variables, compositions, flow rates, molar fluxes, energy fluxes, and temperatures, are different from the interface variables.

Equilibrium is assumed to be only at the interface and temperatures of vapor and liquid streams are not identical, condenser and reboiler are treated as equilibrium stages. Moreover, for the NEQ model, the liquid and vapor flow rates in the packed sections are not responsible for the higher index as algebraic equations for these variables in terms of pressure drop and holdup correlations are incorporated in the model, but the liquid and vapor flows associated with the condenser and the reboiler can pose high-index problems as those are modeled using equilibrium assumptions (Katariya, *et al*., 2008).

On the other hand, two different approaches for the mass-transfer rates are used: namely, a rigorous description using the Maxwell-Stefan equations and an approach using Fick’s law with effective diffusivities. For the Maxwell-Stefan approach, the rate-based method is used to relate the multicomponent mass transfer rates to binary mass-transfer coefficients (Baur, *et al*., 2000), and (Mueller and Kenig, 2007).

The phenomenon of the heat transfers in the column, including both the transfer within the stage and the heat conduction through the dividing wall, represents a peculiar feature of this column configuration, influencing the separation efficiency. Under these circumstances, the prefractionator and the main column are linked by the heat-transfer flux between them, considering a complete cross-section of the dividing wall column (Ehlers, *et al*., 2018).

Alternatively, the RDWC was modeled considering equilibrium and non-equilibrium models in four zones: the prefractionator, hosting reactive packing, modeled with backflow cell model (BCM) with forward flow of liquid and backflow of vapor, upper separation zone in prefractionator, modeled as absorber standard unit, below the reaction zone, modeled also as absorber standard unit and finally upper, right side and lower DWC separation zone, modeled together as standard distillation column (Bumbac, *et al*., 2007).

2.3.4. Implementation of RDWC

Cossio-Vargas, *et al*., (2012) evaluated the conventional reactive distillation sequence and partially heat integration configurations, in terms of the performance in the esterification reactions of fatty organic acids and a mixture of fatty organic acids with the RDWC column. Mainly, they demonstrated the reduction of the number of units and produce esters using the principles of process intensification.

As a result, the energy reduction reaches about 30% less than in conventional reactive distillation configuration, achieving high purity products under an acid catalyst system.

Cossio-Vargas, *et al*., (2011) configured a reactive distillation to produce biodiesel, proposing side strippers and side rectifiers, also a completely intensified process, RDWC. Initially, they show the aspects of the thermodynamic behavior of the system of the esterification of fatty acids, Linoleic acid, Oleic Acid, and N-dodecanoic acid, where each of them was simulated using MESH equations. The results showed that is feasible to implement the heat integrated system in terms of purity compositions and energy consumption. The column can produce biodiesel with complete separation.

Kiss, *et al*., (2012) proposed a process fatty acid with an excess of 15% of methanol to produces biodiesel, acid methyl esters (FAME), whose source are vegetable oils, animal fat or waste cooking oils. The problem associates the economic and environmental impact generated in the application of homogeneous catalyst, in a conventional reaction and separation scheme.

On the other hand, an optimization problem states the continuous and discrete variables, for minimizing the reboiler heat duty as a function of those variables, through simulated annealing optimization strategy. In the optimal project design, the total annual cost calculated as a reduction of 25% in utility demand, in comparison with a conventional reactive distillation configuration, improving the use of raw materials, and the reduction of the capital investment in additional equipment.

Barroso-Muñoz, (2007) presented the reaction of acetic acid with ethanol to produce ethyl acetate and water, using four different schemes. A conventional reactive distillation column followed by a conventional distillation column, a partially integrated scheme with side stripper and side rectifier, and an RDWC configurations scheme.

The performance of conversion evaluates the behavior of the system in each scenario, generating a high incidence in the reduction in energy costs, associated with the amount of water produced is a critical factor that could improve the process. This shows that the conversion for TCDS with the rectifier was 68%, while conversions for TCDS arranged with the stripper and the RDWC column were 80%, concluding that the in an intensified process, the conversion increases about 50%.

Santaella, *et al*., (2015) analyzed the production of ethyl acetate, the thermodynamic information, and kinetics. A base case of conventional reaction and separation, then a reactive distillation with pressure swing and finally an RDWC comparing the performance of these configurations, given an optimization problem.

The minimization of economic objective function included conversion, productivity, mass intensity, mass productivity, and also sustainability factors such as E-Factor, EW-Factor, and energy intensity. The RDWC configuration presented the best performance, under these metrics, the remaining schemes presented a bad performance in other metrics despite having a favorable cost.

Kiss and Suszwalak, (2012) discussed the possibility to produce dimethyl ether (DME) synthesized by methanol dehydration, given the drawback of having increased the number of equipment that increases the operational cost and requires a large footprint. To solve the problem an (RDWC) is proposed as an alternative to improvement.

Then an optimization problem found the minimum energy requirements in a reactive distillation column, restricted to the DME purity, 99% wt. The base case consisted of a reactor and separator system, reaching a conversion of methanol up to 92%, the RDWC reduced considerably the energy demands, but with 50% of conversion of methanol and 30% fewer emissions. The RD configuration reached energy savings of 11%.

In the same manner, Kaur and Sangal, (2017) studied the production of ethyl tertiary butyl ether (ETBE) using a reactive distillation column and RDWC. The analysis carried out by comparing the energy demands, the costs associated with the process and the CO_2 emissions, resulting in a considerable reduction in all the metrics, up to 74% in an RDWC, the energy requirements reduced about 68%.

Kiss, *et al*., (2007) proposed a new intensified process with complex equilibrium reactions of ten species with a homogeneous catalyst, then separated in a set of a sequence of distillation columns, with some streams recycled to the reactor. The results pointed out that the intensification of the process improves by 35% in capital costs 15% of energy costs.

Cho, *et al*., (2008) created a conventional flowsheet to recovery Lactic Acid, analyzing the hydrolysis and the esterification reactions consist of two-phase CSTR, an evaporator, and a reactive distillation column. The process intensification carried out to get an RDWC device, through an optimization problem, setting up the yield, the recovery and the energy consumption in the RDWC, finding a reduction of 22% in energy demands, compared to the case base.

Qian, *et al*., (2015) proposed the hydrogenation of ethylene comparing the RDWC performance to a base case. It shows that both configurations achieve a high degree of purity, above 99%, with savings of 27,88% in the total annual cost.

Wang, *et al*., (2017) performed the alternative to produce dichlorohydrin with a RDWC, an intermediate for synthesizing epichlorohydrin, used to produce epoxy resins. The kinetic model suited to the RDWC performance and compared with three schemes, two tank reactors, and a reactive distillation column, showing savings about 43%

2.3.5. Control of RDWC

Some of the rigorous steady-state simulations extended their findings in dynamic simulations and control structures. One case was the implementation of a quaternary ideal separation in an RDWC, controlling the ratio at the feed streams, through a composition with PID control structure and then with a temperature PID control structure.

From the feed streams, an internal temperature control presented a better performance than a composition control, whose measurements presented some bias (Wang, *et al*., 2011). The control structure involved the interaction of the reflux ratio the reboiler duty, and the liquid split flow rate. The disturbances 20% in the feed flow of the system, maintaining the operation parameters values.

S. Hernández *et al*., (2009) tested the setpoint changes through aspen dynamics simulations, to produce ethyl acetate in an RDWC, installing Temperature PI controllers. The performance fitted adequately to disturbances, minimizing the integral of absolute error.

Wu, *et al*., (2012) developed a project to synthesize n-hexyl acetate, through the esterification of n-hexanol and n-amyl alcohol with acetic acid. The system has two feeds in the side rectifier connected to the main column, using Amberlysts-15 heterogeneous catalysts.

The control system holds 3 pressure controllers and 6 level controllers, remaining the reflux flow rate, the feed ratio, the reboiler duty, as manipulated variables. The disturbances applied to the process include 10% changes in the compositions of alcohol and acetic acid, also a disturbance of 10% of the vapor ratio. As a result, the configuration could keep the product purity under considerable disturbances.

Similarly, the production of n-propyl propionate from propanoic acid and n-propanol performed dynamic simulations, suited in aspen environment. The installation of PID temperature controllers, using a sensitivity criterion along the stages of the column carries out.

In that sense, the disturbances evaluated in this project, the feed flow in 20%, the temperature in the feed stream of 10%, and the ratio in the feed about 2%. The results showed that a presence of large deviations, although the control structure improved by the variation of pressure and linking the reboiler duty to the feed, reducing considerably these deviations and achieving the quality demands of products. (Dai, *et al*., 2015).

Qian, *et al*., (2016) studied the hydrogenation and separation of C3. Four PI control structures proposed to control this unit, two temperature schemes, and two compositions schemes. In the face of disturbances, the feed flow rate presented

20% disturbances and the compositions. All the proposed schemes presented adequate behavior in terms of stability, reaching the desired products.

However, the temperature schemes delay in reaching the operation conditions, but under disturbances presented smaller deviations than the compositions schemes. Due to the high incidence found in the behavior of the column, in terms of the hydraulics, and energy demands, the authors suggested that the liquid split ratio could not be a manipulated variable with the consideration of the use or temperature control schemes.

Qian, *et al*., (2016) studied the model predictive control (MPC) in this kind of configuration, together with the optimization of the liquid split. Then, using a Pareto diagram of a set of optimum solutions performed a search in the tuning parameters. Some disturbances tested the stability of the model, changing 20% the flow rate and the compositions at the feed stream, achieving a considerable reduction of the amplitude of oscillations.

Cabrera-Ruiz, *et al*., (2017) studied the hydrolysis of methyl acetate, using an MPC in a RDWC, in SIMULINK as a linearized space model and validated in Aspen dynamics. The disturbances of 5% in the feed flow rate were applied, reaching stability to the operating conditions without difficulty.

Zheng, *et al*., (2017), applies the SVD criterion to establish a PI temperature control structure in the synthesis of diethyl carbonate, considering that the wall was located at the bottom of the column. Another characteristic is the reboiler duty/feed flow rate ratio installed in the configuration. Besides that, the feed-forward controller scheme faced disturbances in 20% in the flow rate and the composition in the feed stream. Finally, the control structure returned close to the specification values in a short time.

2.4. Conclusions

Ethyl lactate is being projected as a bio-based raw material for diverse chemical transformations, pharmaceuticals or food additives, and as a solvent. It is present either in the Levo (S) or Dextro (R) forms, and it is industrially produced as a racemic mixture through a reversible reaction between ethanol and lactic acid, wherein water is a by-product.

The esterification phenomenon rises with the Lactic Acid concentration, generating a complex use as a reagent, because in the esterification with Ethanol, its oligomers react for forming Ethyl Lactate polymers. Despite that, all the mathematical models developed in these works presented high deviations about the experimental data, caused by the lack of thermodynamic information. To overcome this, a recompilation of research showed that is possible to model this reaction without considering the formation of the oligomers.

On the other hand, the production of bioethanol is a complex task, in terms of competitiveness, from an economic and technical point of view. Conversely, the countries emphasize the importance of ethanol, not only as a source of energy but also in different uses in the green industry without leaving the food safety at risk.

Lactic Acid production links some operations, hydrolysis, fermentation, separation and the treatment of waste streams. Initially, the fermentation stage consists in the production of fermentable sugars, in the saccharification process, but has a difficulty in the hydrolysis and fermentation of Lactic acid, which is a drawback in terms of costs and sustainability.

From the process point of view, the process intensification in separation and reaction operations is a promising alternative that satisfies the demands of products, reducing the energy demands, and improving the conversion, the selectivity, and the yield. The main findings in this work are associated with the development of models that would contribute to the innovation of conventional processes.

Nowadays, many methods have proposed to design this kind of device, shortcut methods, optimization routines of feasible operations. It is encouraging to address these findings with experimental work, that could fill the gaps in this area.

Most of the works reported a reduction of energy demands in comparison to conventional base case design. Whereas, a reduced number of works considered other metrics such as environmental factors or security factors, detailing that could be an opportunity to explore the behavior that these variables in a project.

3. PRELIMINARY DESIGN OF REACTIVE DISTILLATION COLUMNS USING THE ANALYSIS OF THE STATICS

3.1. Introduction

The separation-reaction processes require an environmentally friendly and sustainable development, highlighted by using energy efficiency and the reduction of pollutants. In that way, process intensification reduces considerably these challenges, expecting the raising of many scientific and technical developments from design, optimization, control, and implementation.

Additionally, process intensification becomes an attractive topic, its scope achieves in the reduction of costs, the environmental impact, and also the size of a plant. Whereas, process synthesis enforces to generate alternatives of separations that translate in a feasible, efficient, and performed process (Stankiewicz and Moulijn, 2000).

From the phenomenological point of view, an intensified process provides an advantage over the conventional system, whose inefficiency produced by the thermodynamic irreversibility during mixing of power flow with going inside the equipment, is reduced in these integrated settings (Seader and Henley, 1999).

In that sense, reactive separation, or reactive divided wall distillation columns, present higher reliability of the intensified system (Mueller and Kenig, 2007a), (Harmsen, 2007). For instance, integrated separation and reaction phenomena, have been widely adopted in some processes, such as esterification, hydrolysis (Pöpken, *et al*., 2001), etherification (Aiouache and Goto, 2003), and alkylation reactions (Albright, *et al*., 1988).

On the other hand, the feasibility of this equipment is given by the possibility to configure a process under specification of the composition of the products, translating in a feasible profile. Additionally, the possibility of satisfying all the balances involved in the column, to achieve the specification of products and an effective consecution of the product objectives.

The conceptual design of reactive distillation units, presents more complexities and the most important issues, related to the catalyst election, the internal structure of internal devices, and the location of the reactive zone to reach the product requirements.

From the design point of view, some approaches that analyze the feasibility of reactive distillation columns. For example, Ung and Doherty, (1995) generated a computation of reactive residue curve, considering vapor-liquid chemical equilibrium, (Barbosa and Doherty, 1988), including single and double feed in the device, with equilibrium kinetics and kinetically controlled kinetics. Finally, Ciric and Gu, (1994) proposed the MINLP optimization routine as a design strategy, adapted to multiple reactions and numerically robust programming.

Alternatively, the analysis of the statics method lies in a progressive introduction of the process complexity on the steady-state condition (Thery, *et al*., 2005). This method can develop a feasible operation with minimal information, the reaction stoichiometry, and the thermodynamic interactions of the species, with the chemical equilibrium interaction (Pisarenko, *et al*., 2001).

The final procedure obtained from this analysis will give a group of complete steady states with their operation conditions, establishing the separation-reaction scheme, location of the reactive zone, through the description of all steady states feasibility.

This chapter considers the graphical analysis of the statics approach to generate a feasible flow sheet, under the steady state condition, determining all the different steady states that could lead with a potential configuration of the reactive distillation scheme. This includes the reactive zone location, under the consideration of a large number of stages and reflux ratio, to produce ethyl lactate through the esterification reaction of lactic acid with ethanol.

Finally, the generation of a coupled scheme that represents the RDWC will be the first stage, as a set of three columns, that corresponds to the RD obtained with the analysis of the statics, that represents the prefractionator, and two conventional columns representing the main column.

3.2. Analysis of the structure for reaction and separation scheme

3.2.1. The chemical equilibrium surface

The residue curve maps (RCM) shows the presence of nonreactive azeotropes that occurs in the reactions, also the presence of distillation boundaries for continuous distillation, giving the initial liquid compositions (Ung and Doherty, 1995). Also, such RCM is a useful way to represent liquid-vapor equilibria and relates the intrinsic thermodynamic performance of the mixture and the nature of the separation in both batch columns and continuous processes (Song, et. al., 1998). Consequently, that set or RCM finds the chemical equilibrium surface.

Meanwhile, the calculation of surfaces for mixtures with a single reaction has been developed by Barbosa and Doherty, (1988), who derived the set of autonomous ordinary differential equations, equation 3-1, describing the dynamics of homogeneous reactive simple distillation using a set of transformed composition variables, as shown in equations 3-2 and 3-3.

$$\frac{dX_i}{d\tau} = Y_i - X_i \tag{3-1}$$

$$X_i = \frac{x_i - v_i^T \left(v_{ref}\right)^{-1} x_{ref}}{1 - v_{total}^T \left(v_{ref}\right)^{-1} x_{ref}} \tag{3-2}$$

$$Y_i = \frac{y_i - v_i^T \left(v_{ref}\right)^{-1} y_{ref}}{1 - v_{total}^T \left(v_{ref}\right)^{-1} y_{ref}} \tag{3-3}$$

Where:

x_i	Liquid molar fraction of component i.
X_i	Transformed liquid composition of component i.
y_i	Vapor molar fraction of component i.
Y_i	Transformed vapor composition of component i.
υ_i	Stoichiometric coefficient of component i in a reaction.
υ_{ref}	Stoichiometric coefficient of component or reference in a reaction.
υ_{total}	Stoichiometric coefficient a reaction.

In the presence of multiple singular points, could lead to the division of the diagram into separate distillation regions, following different trajectories on the surface with different unstable and stable node depending on the starting composition of the liquid residue. After defining these different regions or separatrices, which connect two or more singular point in the composition space, each distillation region has one unstable and one stable node between which the residue curves locate (Giessler *et al.*, 2001)

In that sense, the plane divides de composition simplex into two regions. One of them represents a sector in the direct reaction that takes place, and the second one represents the inverse reaction. The dimension of this space is subjected to the Gibbs phase rule. Whether multiple reactions are taking place, the intersection between these planes will determine the chemical equilibrium through the simplex.

At the same time, is necessary to solve simultaneously the chemical equilibrium with the phase equilibria in the liquid phase present in the system, represented by the equations 3-4 and 3-5. Additionally, the expression for the reaction equilibrium constant was obtained from previous by using kinetic and phase equilibrium data work (Pereira, et. al., 2008), equation 3-6, and the NRTL parameters corresponds to the ASPEN plus properties database.

$$K_{eq,k} = \prod_{i=1}^{n} (\gamma_i x_i)^{v_i} \qquad k \in (1, n_{rx}) \qquad 3\text{-}4$$

$$y_i = f(P, T, x_i, x_{i+1}, x_{n-1}) \qquad i \in (1, n) \tag{3-5}$$

$$\sum_{i=1}^{n} X_i = \sum_{i=1}^{n} Y_i = 1 \tag{3-6}$$

$$ln(K_{eq,k}) = 2{,}9625 - \frac{515{,}13}{T} \tag{3-7}$$

Where

K_{eq}	Chemical equilibrium constant.
P	Pressure (atm)
T	Temperature (°K)
γ_i	Activity coefficient of component i.

The inputs for solving the simultaneous equilibrium are the pressure of the system, initial liquid compositions, which subsequently will relate the thermodynamics properties such as temperature, vapor phase composition. In Figure 3-1, the algorithm to calculate the chemical equilibrium surface, or residue curve maps in a reactive or non-reactive distillation system, in a steady state condition.

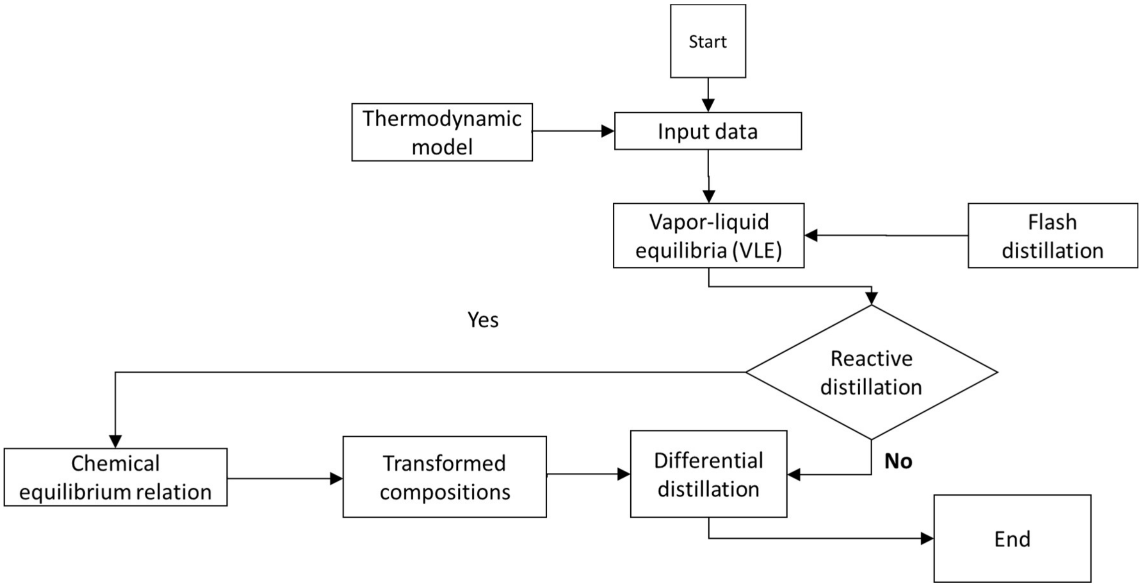


Figure 3-1. Strategy to solve residue curve maps in a reactive and non-reactive system

3.2.2. The chemical interaction manifold (CIM)

The dimension of the CIM is equal to the number of linearly independent chemical reactions, called the pseudo initial composition at total reflux and an infinite number of stages, ∞/∞. The initial mixture compositions and the reaction stoichiometry configure the concentration simplex, these lines represent the moles formed resulting from the chemical conversion (Pisarenko *et al.*, 2001).

On the other hand, the reaction pole (Π) denotes an initial coordinate of the extent of reaction in the concentration simplex as a vector, shown in equation 3-8. It identifies the direction and progression of the reaction. Once this point is set, the definition of the lines of advance configures the highest conversion in the reaction plane.

$$L_1 = L_2 - \frac{N_P}{N_P - N_R} \tag{3-8}$$

Where:

L_1: Is the necessary distance for finding the pole Π.

L_2: Distance from the point of stoichiometric feed to the point of the product formation.

N_P: Amount of moles of products.

N_R: Amount of moles of reactants.

3.2.3. The search for limiting steady states with P/W=f(x') coordinate

The P/W=f(x) trajectory splits as tranches that correspond to the compositions of the products in a determined location of the simplex, resulting in a direct or indirect scheme of separation. It subjects to the trajectories that pass from one subregion to another, through the balance line P/W

These compositions correspond to the bottoms and distillate compositions, X_W and X_D, that leaves the region located at the border of the distillation zone, known as a formulated distillate P or formulated bottom W. As a result, with each P/W generated in the pseudo initial composition X^* for each steady-state in each branch.

The maximum conversion characterizes each steady-state in the subregions of distillation, which is called the limiting steady states. The P/W ratio is shown in equation 3-9.

$$\frac{P}{W} = \frac{\overline{X_W X^*}}{\overline{X_D X^*}} \tag{3-9}$$

3.2.4. Feasibility of the predicted steady-state

Finally, the separation is feasible, if the following conditions are satisfied (Pisarenko, et. al., 2001):

1. A trial trajectory pinching the material-balance line, whose location is governed by the compositions of the predicted product flows, belongs to the direct reaction zone.
2. The trial trajectory must be developed through the concentration simplex, that is, for each component of the mixture, there must exist a section of the trial trajectory where the concentration of this component is nonzero.

The analysis focuses to verify the probability of its required productivity, in terms of conversion of products and the trajectory of the P/W line in the diagram. The product flows to be withdrawn specifies the rate and compositions, that results in a tentative location of the reaction zone for selected steady states.

Given the chemical equilibrium surface, and the identification of the unstable, stable and saddle points, Figure 3-2 depicts the procedure of the analysis of the statics for identifying the limiting steady states for the system and the respective reactive distillation configuration.

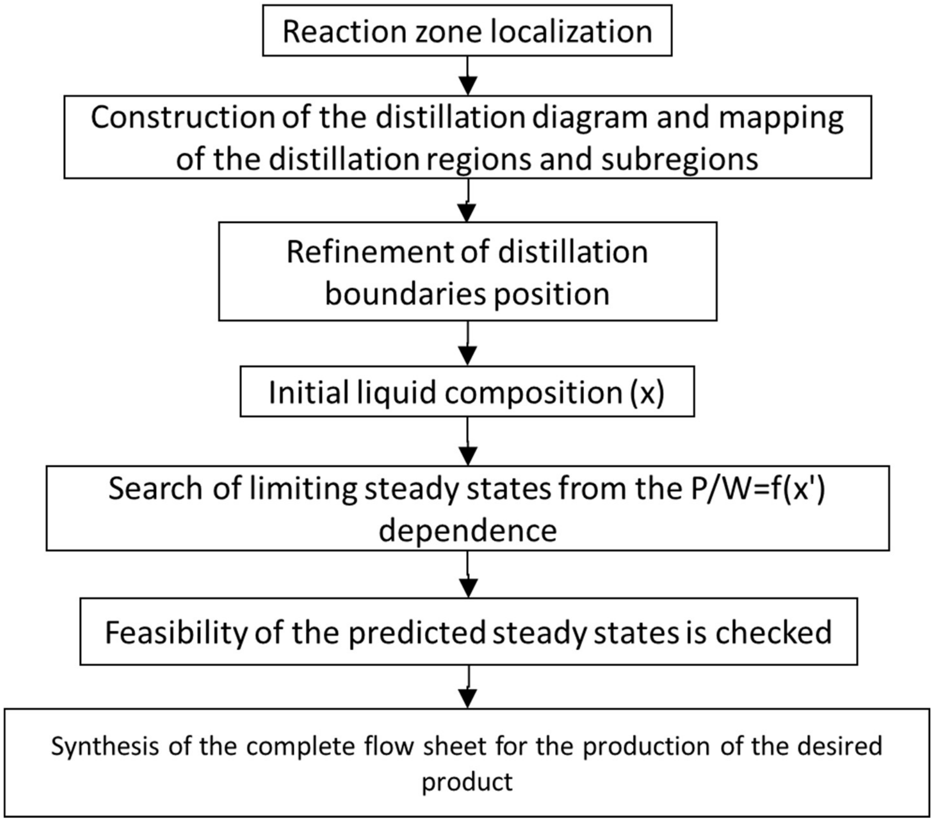
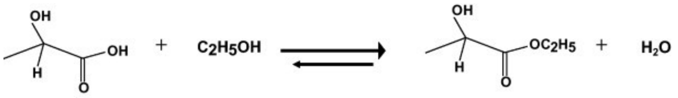


Figure 3-2. Main stages for analysis of statics

3.3. Results

Ethyl lactate is produced by the reaction between an aqueous solution of lactic acid and ethanol, through the esterification of lactic acid with an excess of ethanol, as shown in equation 3-10. Ethyl lactate can be produced separated efficiently, obtaining high yields of product, through the reactive distillation process. (Komesu *et al*., 2015). This process aims to purify ethyl lactate, as a main product.



3-10

3.3.1. Location of the reactive zone

Following the algorithm in Figure 3-1 In the residue curves trajectories Figure 3-3.A, begin from the unstable point (water-ethanol azeotrope), and end in a stable point, in the Lactic Acid vertex. Table 3-1 describes the distillation region. Furthermore, Table 3-2 shows the sub-regions of the system, in the direct separations three sub-regions exist, while the indirect sequence, two.

Table 3-1. Distillation sub-regions for direct and indirect separation

Point	Classification	Molar fraction	Temperature (°K)
Azeotrope Water-Ethanol	Unstable node	Water 0.1048 Ethanol 0.8952	351.3
Azeotrope Water-Ethyl lactate	Saddle point	Water 0.9697 Ethanol 0.0303	373.0
Pure Water	Saddle point		373.15
Pure Ethyl Lactate	Saddle point		427.64
Pure lactic acid	Stable point		489.78
Pure Ethanol	Saddle point		351.46

In that sense, the residue curves depart from the unstable node, the azeotrope Water-Ethanol to the stable point of Lactic Acid vertex.

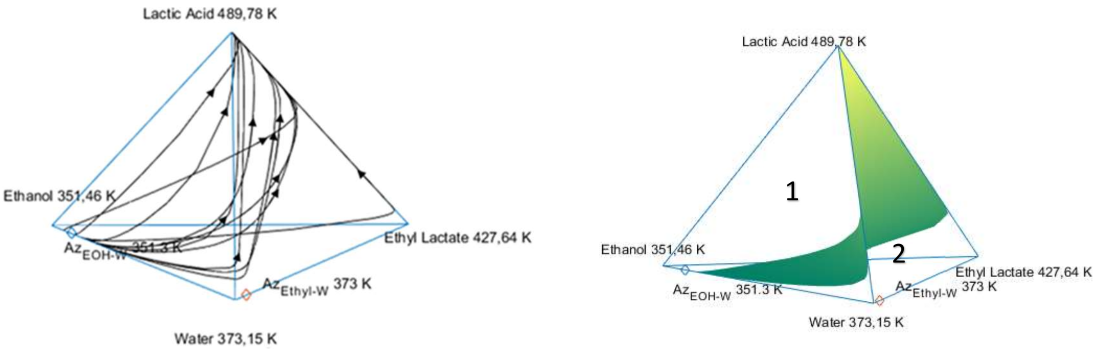
Table 3-2. Subregions for indirect and direct separation scheme

Direct configuration	Indirect configuration
Az_{EL-EOH} – Az_{ET-W} – W	EOH – EL – LA
Az_{EL-EOH} – Az_{ET-W} – EOH – W	Az_{EL-W} – W – LA
	Az_{EL-W} – EL - LA

In the indirect configuration, the distillate stream is the azeotrope water-ethanol, and the bottom stream is a ternary mixture of Ethanol (EOH)- Lactic acid (LA) –Ethyl lactate (EL), in one subregion. For the remaining distillation zones, a ternary system constituted by Ethyl lactate (EL) – Water (W) - Lactic Acid (LA). In direct separation, a mixture of LA and EL results as a bottom flow, while in the distillate flow, a mixture of EOH, W and the binary azeotrope.

Meanwhile, in indirect separation, a mixture of LA and EL are obtained as a bottom flow, while in the distillate flow, a mixture of EOH, W and the binary azeotropes (water-ethanol and ethanol ethyl lactate).

In Figure 3-3.B, two sections are identified, the forward and backward reaction direction. In this case, the forward reaction zone is numbered as 1 (favorable to the ethyl lactate formation), and the backward reaction zone as 2.



A. Phase Diagram

B. Chemical Equilibrium Surface

Figure 3-3. Non-reactive residue curve maps (A) and Chemical equilibrium surface (B)

3.3.2. Determination of the P/W dependence, given the pseudoinitial compositions X_i^*

Given the stoichiometry of the reaction, Equation 3-8 shows that the direction of the extent of the reaction line tends to the pole π=∞, representing a set of parallel vectors to the equimolar feed vector, as shown in Figure 3-4.

$$L_1 = L_2 \frac{2}{2-2}$$

$$L_1 = L_2 * \infty$$

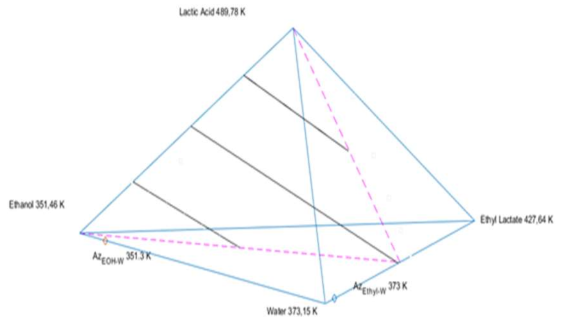
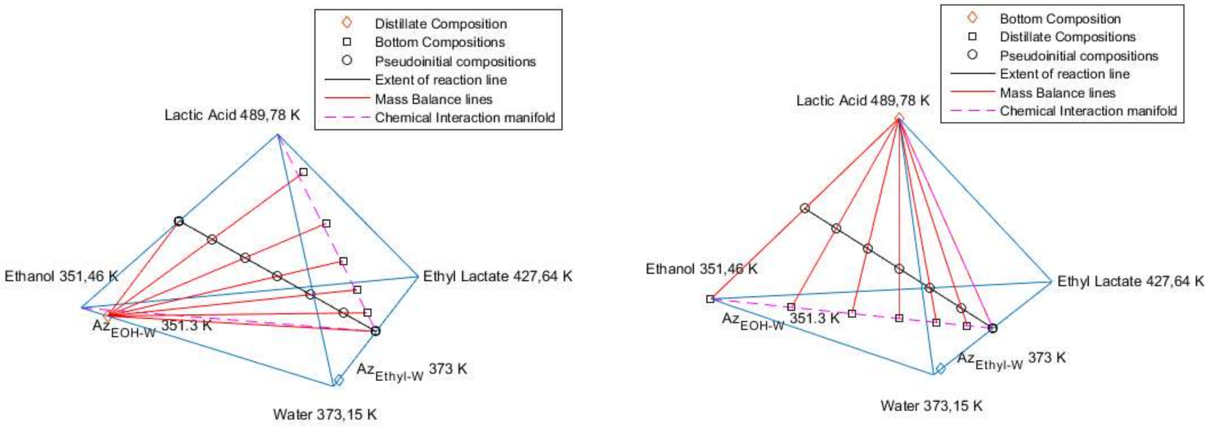


Figure 3-4. Extent of the reaction line for equimolar and excess composition at the feed

The extent of the reaction vector traces a set of initial compositions and the reaction stoichiometry, generating and locating different pseudo initial compositions X_i^*. Then, the balances line map of direct and indirect separations, and finally equation 3-9, evaluates the different P/W ratios, choosing the maximum steady-state, for direct and indirect sequences, as shown in Figure 3-5.

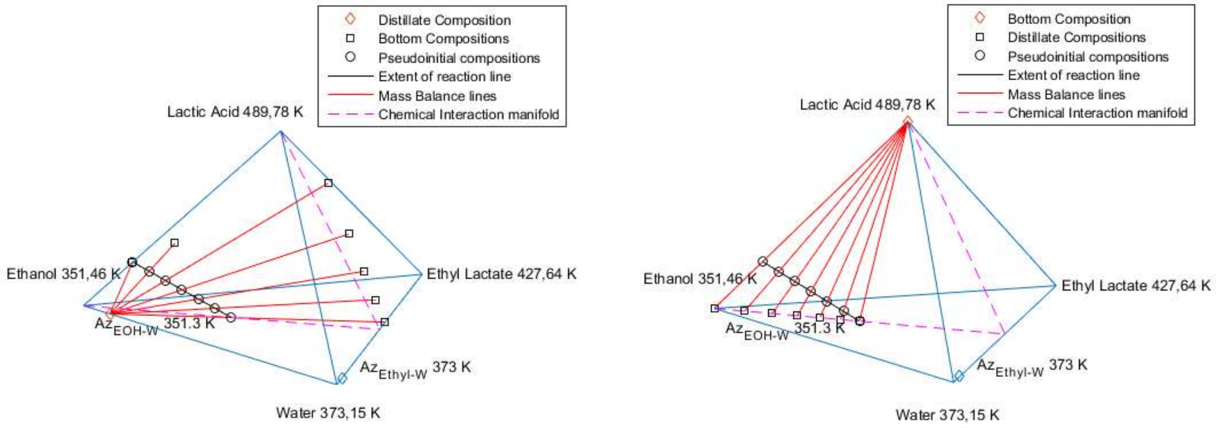
In that sense, the maximum conversion is subject under three possible scenarios, the first scenario with an equimolar feed of lactic acid and ethanol, the second with an excess of ethanol, and finally, an excess of lactic acid. The extent of the reaction line location visualizes these conditions, all the limit steady states.


Equimolar feed (Direct)

Equimolar feed (Indirect)

Excess of Ethanol (Direct)

Excess of Ethanol (Indirect)



Excess of Lactic acid (Direct)

Excess of Lactic acid (Indirect)

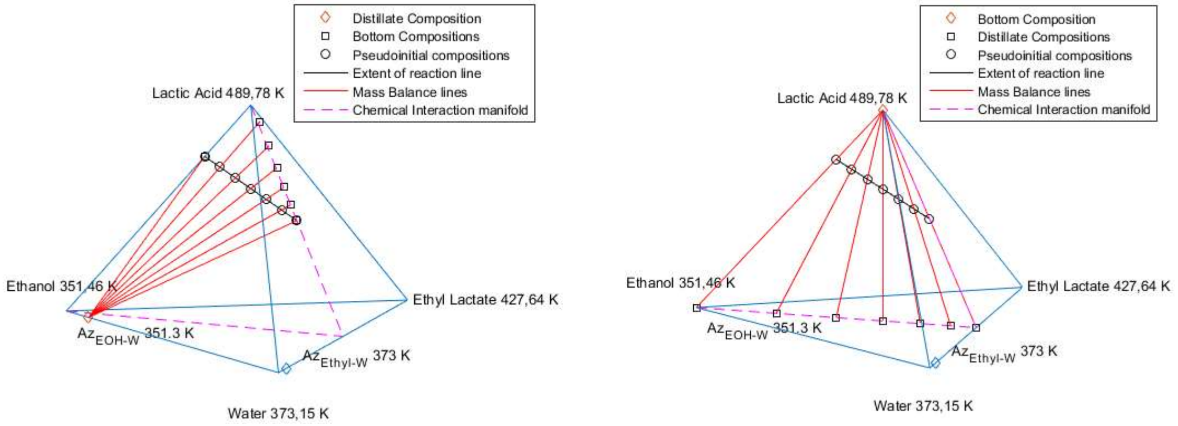


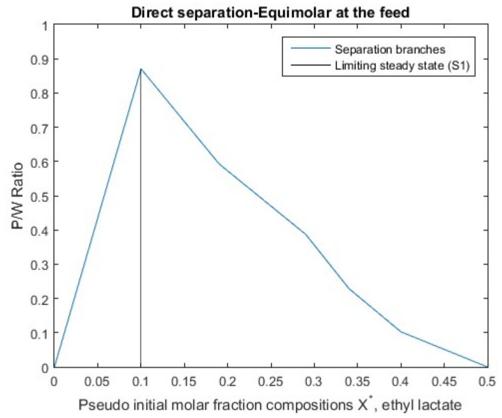
Figure 3-5. Calculation of P/W ratio for direct and indirect separation schemes

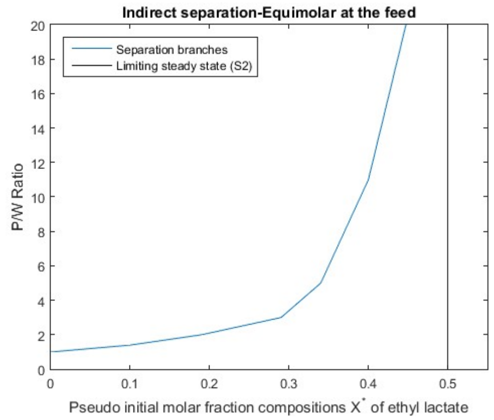
With these values and the resulting P/W ratios in each X_i^*, the limiting steady states are chosen, for direct and indirect sequences, SI and SII as minimum or maximum points. The whole of the calculated limit steady states is summarized in Table 3-3 and represented in the simplex in Figure 3-6.

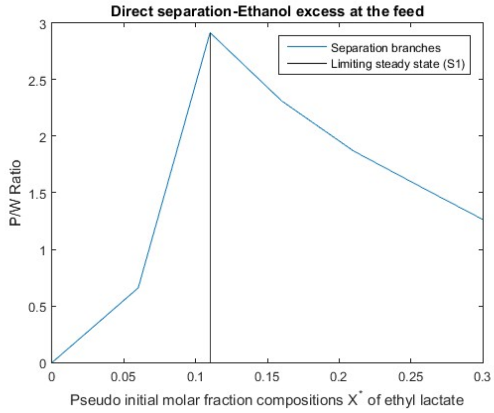
Table 3-3. Pseudo initial compositions and P/W ratio in all generated steady states

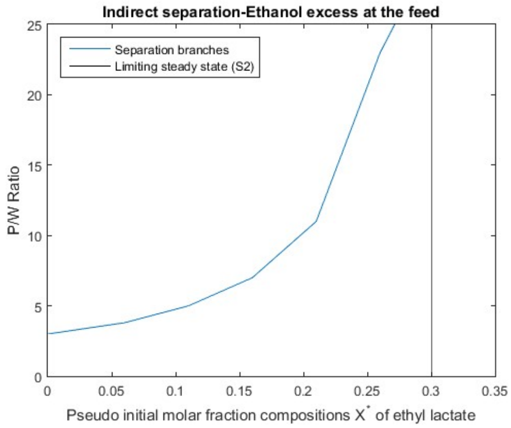
Compositions at the feed			**Pseudo initial compositions X_i^***				**Conversion %**		**P/W Ratio**	
Ethanol	**Lactic Acid**	**Ethyl lactate**	**Ethanol**	**Lactic Acid**	**Ethyl lactate**	**Water**	**Lactic acid**	**Ethanol**	**Direct separation**	**Indirect Separation**
0.5	0.5	0	0.50	0.50	0.00	0	0.00	0.00	0.0000	1.0000
			0.40	0.40	0.10	0.1	20.00	20.00	0.8707	1.4000
			0.31	0.31	0.19	0.19	38.00	38.00	0.5933	2.0000

			0.21	0.21	0.29	0.29	58.00	58.00	0.3875	3.0000
			0.16	0.16	0.34	0.34	68.00	68.00	0.2288	5.0000
			0.10	0.10	0.40	0.4	80.00	80.00	0.1026	11.0000
			0.00	0.00	0.50	0.5	100.00	100.00	0.0000	inf
0.7	0.3	0	0.70	0.30	0.00	0	0.00	0.00	0.0000	3.0000
			0.64	0.24	0.06	0.06	20.00	8.57	0.6600	3.8000
			0.59	0.19	0.11	0.11	36.67	15.71	2.9172	5.0000
			0.54	0.14	0.16	0.16	53.33	22.86	2.3131	7.0000
			0.49	0.09	0.21	0.21	70.00	30.00	1.8705	11.0000
			0.44	0.04	0.26	0.26	86.67	37.14	1.5322	23.0000
			0.40	0.00	0.30	0.3	100.00	42.86	1.2652	inf
0.3	0.7	0	0.30	0.70	0.00	0	0.00	0.00	0.0000	0.3333
			0.24	0.64	0.06	0.06	8.57	20.00	0.3033	0.4118
			0.20	0.60	0.10	0.1	14.29	33.33	0.2288	0.5000
			0.16	0.54	0.15	0.15	22.86	46.67	0.1623	0.6000
			0.11	0.51	0.19	0.19	27.14	63.33	0.1026	0.7143
			0.08	0.46	0.23	0.23	34.29	73.33	0.0488	0.8462
			0.00	0.38	0.31	0.31	45.71	100.00	0.0000	1.0000









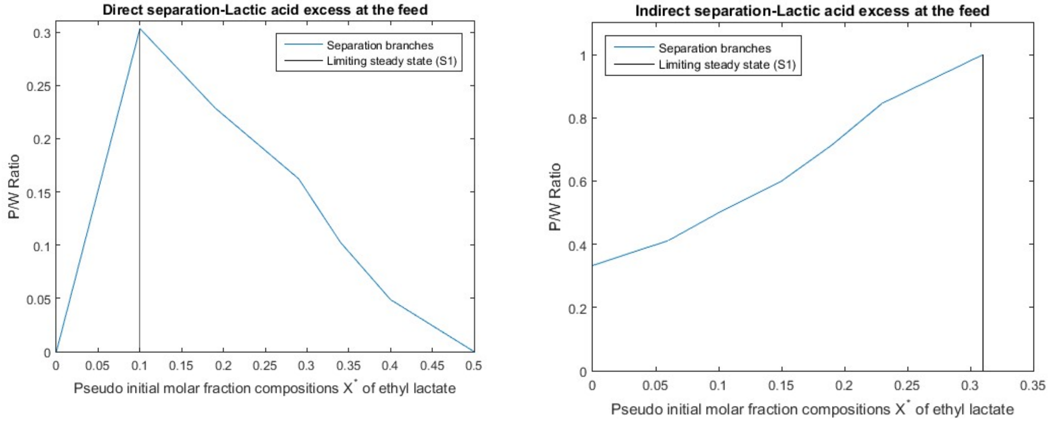


Figure 3-6. P/W ratio values as a function of Xi*

3.3.3. Estimation of the practical feasibility for limiting steady states

Table 3-4 shows a set of limiting steady states resulting from the evaluation of the trajectories traced, whether a reaction and separation phenomena occur. According to the interaction of the P/W line and the chemical reaction surface, this information guarantees those steady states.

Table 3-4. Limiting steady states of the system

Sequence	Compositions at feed X^F		Pseudo initial compositions X_i^*				P/W Ratio at limit states	Scheme
	EOH	LA	EOH	LA	EL	WATER		
Direct	0.5	0.5	0.40	0.40	0.10	0.10	0.8707	A
Direct			0.00	0.00	0.50	0.50	0.0000	B
Direct	0.7	0.3	0.59	0.19	0.11	0.11	2.9172	C
Direct			0.40	0.00	0.30	0.30	1.2652	D
Direct	0.3	0.7	0.24	0.64	0.06	0.06	0.3033	E
Direct			0.00	0.38	0.31	0.31	0.0000	F
Indirect	0.5	0.5	0.00	0.00	0.50	0.50	inf	G
Indirect	0.7	0.3	0.40	0.00	0.30	0.30	inf	H
Indirect	0.3	0.7	0.00	0.38	0.31	0.31	1.000	I

3.3.4. Attempt trajectories at limit steady states direct sequence

Scheme A, Figure 3-7, is located in the forward reaction region, moreover, it is developed in full concentration simplex and reaches the chemical equilibrium surface, it means that this steady state is feasible.

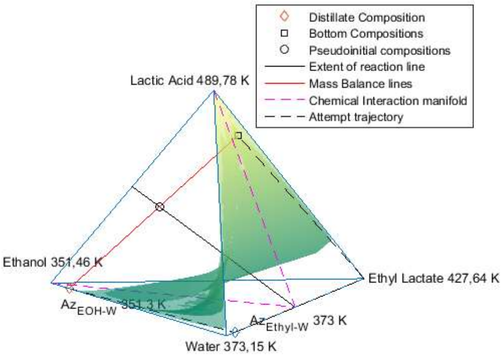


Figure 3-7. Attempt path with equimolar feed. Direct separation

Scheme B in Figure 3-8, is located within a small part of the forward reaction zone, relating direct separations. Nevertheless, is not developed in full concentration simplex, this limiting steady state is not feasible.

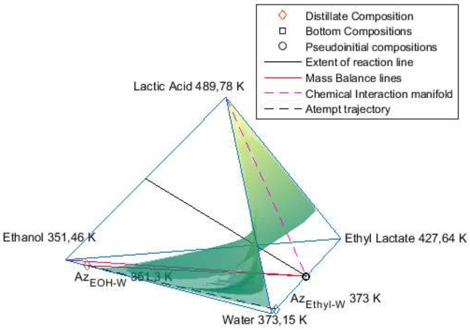


Figure 3-8. Attempt path with equimolar feed. Direct separation

The scheme C, Figure 3-9, is located in the forward reaction region, it is developed in full concentration simplex and reaches the chemical equilibrium surface, it means that this steady state is feasible, with similar behavior of scheme A.

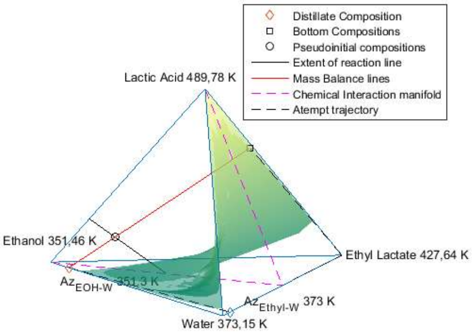


Figure 3-9. Attempt path with an excess of ethanol at the feed. Direct separation

The limiting steady-state, scheme D in Figure 3-10, is located within a small part of the forward reaction zone. However, it does not attain all the full concentration simplex and is classified as not feasible.

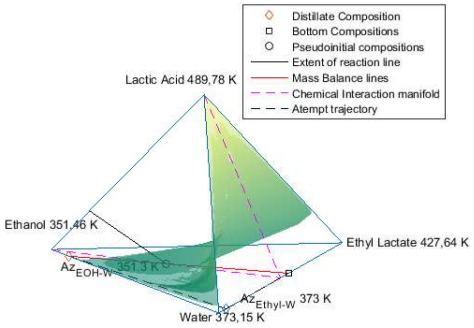


Figure 3-10. Attempt path with an excess of ethanol at the feed. Direct separation

In the same way, the scheme E, Figure 3-11, is located in the forward reaction region, developing in full concentration simplex and attaining the chemical equilibrium surface, obtaining a possible feasible steady-state.

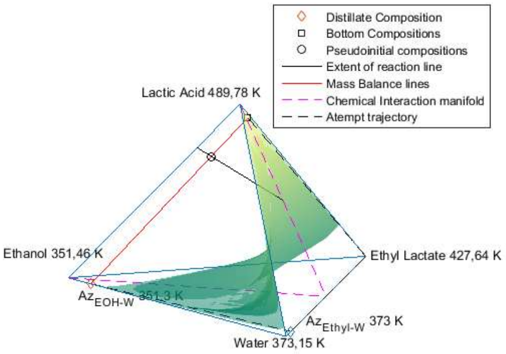


Figure 3-11. Attempt path with an excess of Lactic acid at the feed. Direct separation

For scheme F in Figure 3-12 the attempt trajectory does not reach the forward reaction region, resulting in an impractical operation under that limiting steady state, although the balance line goes through the concentration simplex.

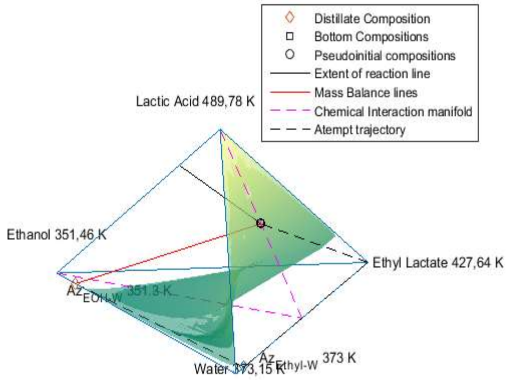


Figure 3-12. Attempt path with an excess of Lactic acid at the feed. Direct separation

3.3.5. Attempt trajectories at limit steady states indirect sequence

The scheme G in Figure 3-13. The attempt trajectory does not reach the forward reaction region completely, but it reaches the equilibrium surface, resulting in insufficient coverage of the simplex. This situation turns this steady-state impractical and not feasible. Similarly, the scheme H and scheme I, represented in Figure 3-14 and Figure 3-15, respectively, show a similar situation, which means that an infinite volume reaches a feasible steady-state.

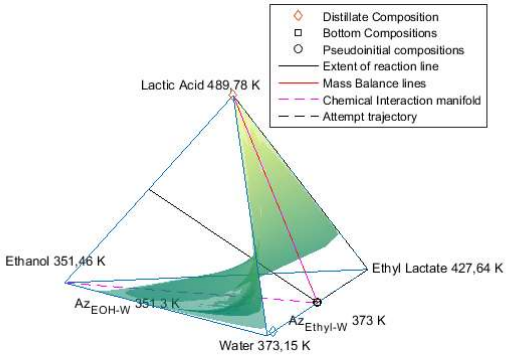


Figure 3-13. Attempt path with an excess of Lactic Acid at the feed. Indirect separation

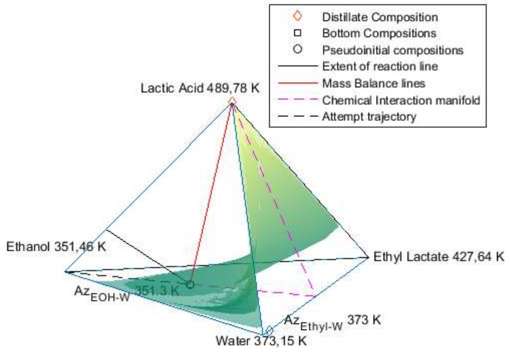


Figure 3-14. Attempt path with an excess of ethanol at the feed. Indirect separation

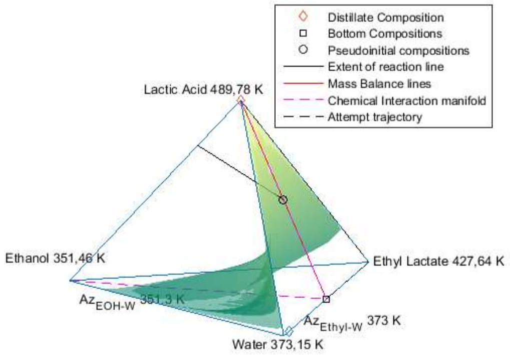


Figure 3-15. Attempt path with Lactic Acid excess at the feed, indirect separation

3.3.6. Location of the conventional reactive zone in the distillation column configuration

After evaluating all the possible separation diagrams of each limiting steady state, the configuration of the flowsheet of the process corresponds to the practical steady-state that is given under the performance of the conversion as well. Based on the attempt trajectories and the tendency of the p/w vector, the trajectory of the optional path for the column that shares the zone of backward and forward reaction represents the middle of the column, as shown in Figure 3-16.

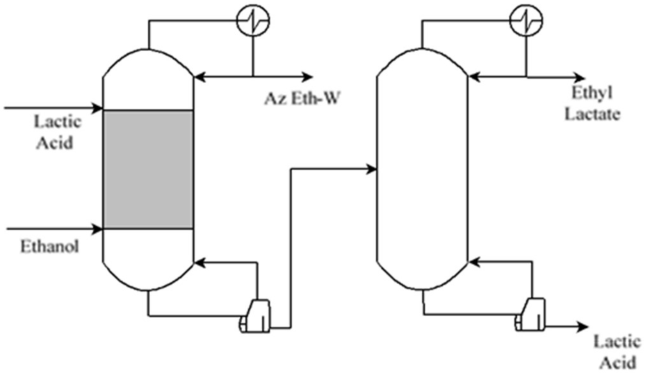


Figure 3-16. Reactive distillation scheme for ethyl lactate obtention

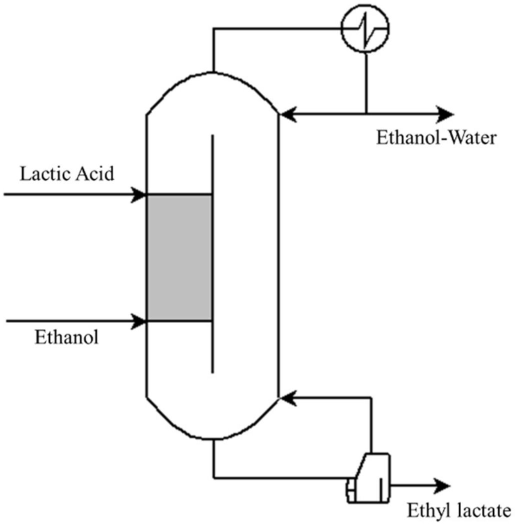
As a result, scheme C is chosen because it attains the conditions of limit steady state, its path considers the forward and backward reaction, also because it has a reasonable degree of conversion, even in the case of excess of ethanol, as presented in Table 3-3. In that way, the bottoms product is a Lactic acid – Ethyl lactate mixture. It is necessary to separate this binary mixture in another conventional distillation column to recover the product of ethyl lactate with the desired purity specifications.

Finally, the distillate stream is the Water – Ethanol azeotrope, which must be subsequently fed to another column to separate the Ethanol from Water, where the ethanol is dehydrated.

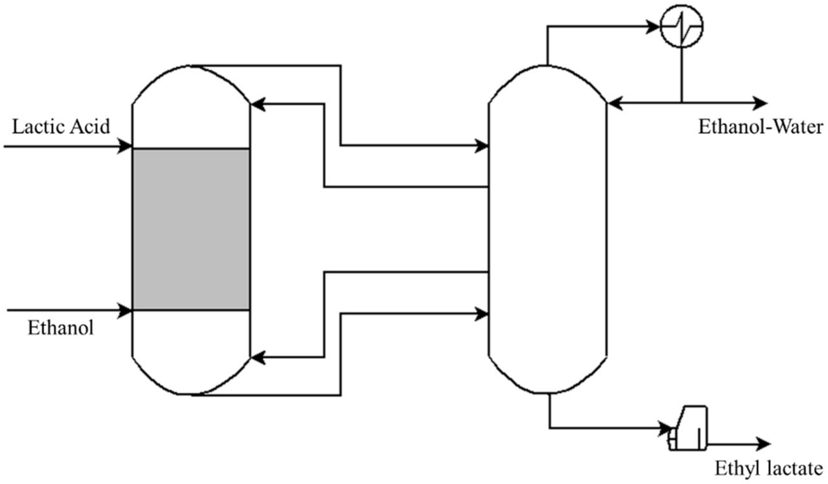
3.3.7. Implementation of the analysis of the statics in an RDWC

The results given of the location of the reactive zone for a conventional reactive distillation, using the analysis of the statics procedure, are adapted to configure RDWC. This heat integrated unit has a prefractionator, where the reactive zone is located, and the main column, where the separation of the components occurs.

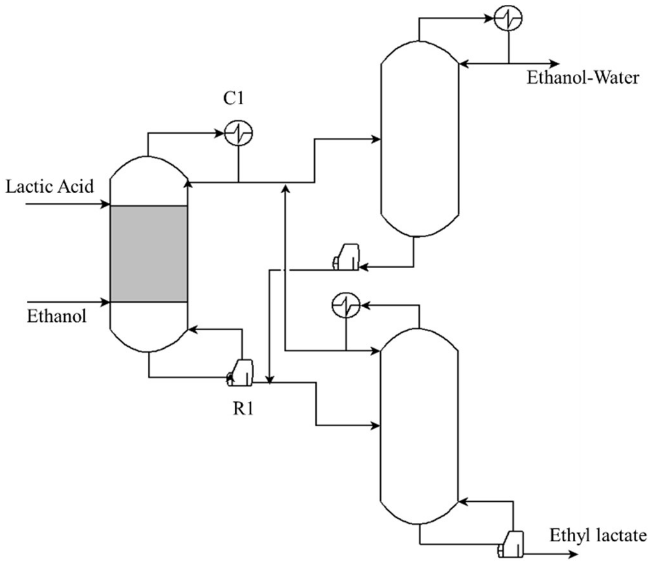
According to that, the scheme of the RDWC can be decomposed as a set of two columns, a RD representing the prefractionator, and a conventional column representing the main column. At the same time, two columns decompose the main column, generating a thermally coupled distillation column, as shown in Figure 3-17.



Reactive divided wall distillation column



Petlyuk configuration



Three column decomposition

Figure 3-17. Decomposition of a RDWC as a set of RD column linked with two conventional distillation columns

This decomposition carries out with the assumption adiabatic stages and not heat transfer across the wall, the assumption of a partial condenser in C1 and partial reboiler R1 in the RD that is the prefractionator. The difference between this configuration proposed with other configurations that are available in the literature, such as Amminudin, *et al*., (2001) and Mueller and Kenig, (2007), is the existence of the side stream for a middle point component.

However, according to the volatility order, ethyl lactate will out on the bottom stream. For that reason, the distillate stream of the stripping column links to the feed of the rectifying column, and in the same manner, the bottom stream of the rectifying section links to the feed of the stripping section, giving the first approximation to the configuration of a RDWC.

Finally, this heat integration does not consider the energy requirements, only the flowsheet that configures the integrated flowsheet considering the interaction of the reactive zone determined using the analysis of the statics procedure.

As seen, the analysis of the statics procedure offered a qualitative analysis in a reaction-separation system, also it provides an indication concerning to the configuration of the process. However, it is recognizable that the procedure has very restrictive assumptions and its graphical analysis could turn into a complex analysis. (Doherty, 1988; Giessler et al., 2001).

Consequently, the analysis of statics field covers to a feasibility analysis, and helped with the residue curve maps for multicomponent systems, couple the L-V equilibrium chemical equilibrium phenomena. The feasibility analysis relies in assumptions that requires a complementary with a rigorous model.

3.4. Conclusions

A shortcut method, the analysis of the static, was implemented in a project design offering some advantages with little information in the design step. It was possible to develop the esterification of lactic acid with ethanol to produce ethyl lactate using reactive distillation.

With minimum information, the introduction into the complexity of the process included the equilibrium reaction and the physicochemical data concerning to the components. The results lied in a feasible steady-state that allowed to present a scheme under some characteristics, such as the feed condition, according to the production requirements.

Additionally, the results obtained in the implementation of the analysis of statics procedure, the decomposition of a RDWC into a RD with two interlinked conventional distillation columns allowed to configure reach the configuration of a feasible operation.

Finally, the procedure presented an adequate approximation of the feasibility of a heat integrated columns, and extend the applicability to design unconventional processes, such as partially thermal coupling reactive distillation columns with the adiabatic condition among the reaction and separation stages.

4. CONVENTIONAL REACTIVE DISTILLATION COLUMN AND REACTIVE DIVIDED WALL DISTILLATION COLUMN MODELING

4.1. Introduction

Reactive distillation (RD) is the improvement of a classical sequential reaction and separation, that generates interactions in terms of the phenomenon and mathematical, that could increase the difficulty of its operation. Meanwhile, the reduction of the expenditure of energy and costs could benefit the process with a favorable environmental impact or sustainability factors.

Additionally, the integration of reaction and separation has experienced fast progress, providing a convenient way of alleviating kinetic and thermodynamic constraints usually present in the more traditional sequential configuration (Paiva and Malcata, 2000).

In this case, the esterification of lactic acid with ethanol to produce ethyl lactate consists conventionally in a reactor and a train of distillation columns that recycles the excess of lactic acid that did not react and the remaining amount of ethanol. As a consequence, this situation creates hot spots that could reduce the remixing involved in the recycles, and lower conversion.

The mathematical models used for chemical process simulation and design are increasingly large due to the inclusion of many equipment details and realistic descriptions of the behavior of chemical and physical properties of raw materials and products (Alfradique and Castier, 2005). All of these lead to complex interactions between equilibrium, mass transfer in vapor and liquid phase, and chemical kinetics.

Additionally, the strong non-linearity introduced by the coupling between diffusion and chemical kinetics in counter-current contacting, have been shown to satisfy the steady-state condition and complex dynamics behavior, (Sharma and Singh, 2012). For that reason, many contributions in this area focused on the equilibrium methods for solving reactive distillation models, addressing to the steady-state condition. Computer-aided tools have an approximation to the experimental data, dealing with the non-linearity and the condition of the complexity of the kinetic model, all the strategies point to the reduction of the computer time (Taylor and Krishna, 2000).

Whereas, this progress leads to model more integrated systems, such as DWC and RDWC, identifying the main variables that rationalize the degrees of freedom that derive in the adequate operation of these configurations. As a result, the specification and the assumption of a pressure drop across the column will determine the behavior of the vapor and liquid flow rates profile (Sangal, *et al*., 2012).

In this work, the analysis of degrees of freedom of a reactive distillation column and the reactive wall distillation column will specify the operation variables, that will affect the performance of the configurations. Then the specification of MESH equations, including the kinetic model that configures the esterification of lactic acid with ethanol, considering the RD and RDWC.

Then, with the experimental data available in the literature, a validation of these assumptions will show how RD achieves the requirements of the output, in terms of the characteristics of the feed stream, the purity of ethyl lactate, up to 99.99% mole fraction. the conversion of reactants. Finally, an energetic study for the production of ethyl lactate in a RDWC is presented by adapting the equilibrium stage model, and compared with conventional direct sequence, a RD followed by a conventional distillation column.

4.2. Specification of variables in RD and RDWC

4.2.1. Degrees of freedom analysis of RD

A continuous reactive distillation column consists of N-stage arranged in countercurrent cascade Separating C components. A schematic representation of Reactive Distillation, where stage 1 is a total condenser that produces a saturated liquid and stage N is a partial reboiler. This reactive distillation system includes each equipment of the separation unit, splitter, feed stages, stripping section, rectifying section, and reactive section, as shown in Figure 4-1.

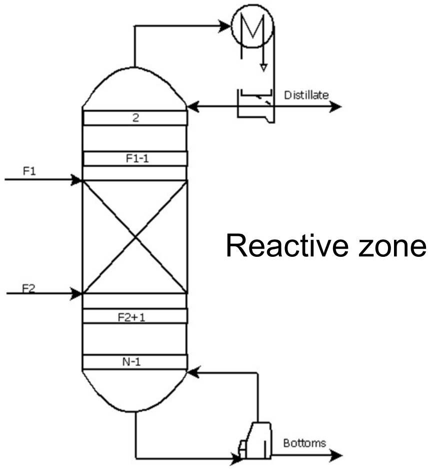


Figure 4-1. Main sections of a conventional reactive distillation column

In Table 4-1, the number of variables declares the problem of reaction and separation in the same device. Moreover, the number of reactions, the location of the reactive zone as a discrete variable, and the number of catalysts increase the number of variables to consider in the analysis of degrees of freedom. In Table 4-2 depicts the variable inputs consider in a conventional column, that links the attributes of the conventional column in the same way as in the reactive distillation column.

Table 4-1. Variables specification for a conventional RD with two feeds streams

Equipment	Degrees of freedom
Total condenser	C+4
Splitter	C+5
Internal stages above feed 1	$2M_1+2C+5$
Feed stages	2(3C+8)
Internal stages under feed 1.	$2M_2+2C+5$
Internal stages under feed 2.	$2M_3+2C+5$
Partial reboiler	C+4
$M_T=M_1+M_{2+} M_3$	$2(M_1+M_2+ M_2)+15C+38$
Redundant streams	13(C+2)-13
Number of reactions	j
Total	$\Sigma(Nv)= 2M_T+2C+12+j$

Table 4-2 Variables for a single RD column with two feeds streams

Variable	Degrees of freedom
Pressure drop across the column	M_T
Adiabatic stages, except heat exchangers	M_T -2
Feed streams	2(C+2)

Splitter pressure	1
Adiabatic splitter	1
Number of reactions	j
Total	$2M_T +2C+4+j$

The final input variables for solving this system relates the manipulated variables in the design step, classified in continuous and discrete variables. According to this, rigorous simulation requires completing all the specifications, shown in Table 4-3.

Table 4-3. Variables specification in a conventional RD column

Project variable	Number of specified variables
Number of non-reactive stages	1
Number of reactive stages	1
Distillate flow	1
Reflux ratio	1
Feed stages	2
Catalyst holdup	1
Condensate condition	1
Total	**8**

4.2.2. Degrees of freedom analysis of RDWC

A RDWC simulation is not a straightforward task, in the case of the conventional distillation columns and conventional reactive distillation columns, the number of the specified variable are higher before a simulation performs. Specifically, the analysis of degrees of freedom for this arrangement refers to the rigorous simulation.

In Table 4-4, the main column analysis degrees of freedom are performed, as well as the prefractionator in Table 4-5 (Seader and Henley, 1999). This includes all sections of the column, splitter, condenser, internal stages, reboiler, and the reactive zone.

Table 4-4 Degrees of freedom for the main column

Main column	Degrees of freedom
Total condenser	C+4
Splitter	C+5
Internal stages M1	$2M_1+2C+5$
Connect. stream (liquid) S1	3C+9
Internal stages M2	$2M_2+2C+5$
Side draw stream S2	2C+7
Internal stages M3	$2M_3+2C+5$
Connect. Stream (Vapor) S3	3C+9

Internal stages M4	$2M_4$+2C+5
Partial reboiler	C+4
$M_T=M_1+M_2+M_3+M_4+5$	$2(M_T-5)+19C+58$
Redundant streams	17(C+2)
Total	$2M_T+2C+19$

Table 4-5 Degrees of freedom for the prefractionator section

Prefrac. component	Degrees of freedom
Internal stages with two feeds	2(2N1+3C+8)
Redundant streams	4(C+2)
Total	$2N_1+2C+8$

In this analysis, after eliminating the redundant streams, which is shown in Table 4-6, the specification of the system is summarized in Table 4-7, given 12 degrees of freedom

Table 4-6 Degrees of freedom for a RDWC

Device	Degrees of freedom
Main Column	$2M_T+2C+19$
Prefract.	$2N_T+2C+8$
Redundant streams	4(C+2)
Total	**$2M_T+2N_T+18$**

Table 4-7 Assumptions of the model

Device	Degrees fo freedom
Main Column Pressure	MT
Prefrac. Pressure	NT
Adiabatic internal stages	MT+NT+NR-2
Feed	2(C+2)
Splitter pressure	1
Adiabatic splitter	1
Catalyst loading/holdup	1
Degrees of freedom	**12**

Finally, in Table 4-8, the project variable specifies the decision variables in the problem of achieving the minimum heat duty in the production of ethyl lactate. As shown, the decision variables characterized by discrete and continuous variables. Inside the continuous variables, are mainly the flows, reflux ratio, and the discrete variables, the number of stages, reactive and non-reactive, the stages location of the vapor and liquid flows between the main column and the prefractionator.

Table 4-8 Variables specification for a RDWC project

Project variable	Degrees of freedom
Distillate rate	1
Reflux rate	1
Side draw flow	1
Connections flow	2
Feeds stages location	2
Connections	2
Stages main column	
Non-reactive number of stages	2
Reactive number of stages	1

4.3. Rigorous simulation of RD and RDWC

To this project, the implementation of the model concerns the following stages:

1. Setting up the variables mentioned in section 4.4.2. The production goals consist in the production of ethyl lactate with a composition of 99% mol.
2. Configuring the main balances in the columns internals, section 4.3.1. in the case of a RD, and section 4.3.2. for a RDWC.
3. The phase-equilibria model, applied in the previous analysis of the static model.
4. The kinetic model investigation, that leads the chemical reaction inside the column.

4.3.1. Rigorous simulation of RD

The equilibrium stage consists of the interaction of vapor from the stage below and liquid from the stage above in the stage with fresh feed, the vapor, and the liquid leaves the stage, being in equilibrium with each other. All of these phenomena are represented through the material balance, the energy balance, the phase equilibrium balances, and the composition.

The representation of a reactive stage is given in Figure 4-2. The material balance, equation 4-1 corresponds to the stage j, referred to the component i in the reaction l:

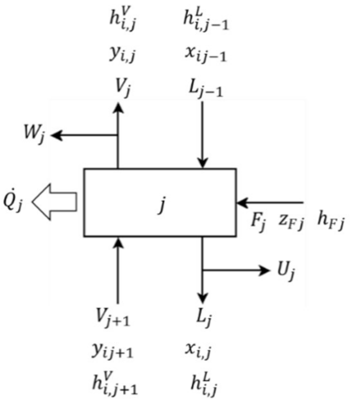


Figure 4-2. Equilibrium stage and reactive distillation column with multiple stages

$$\frac{dM_j}{dt} = F_j + L_{j-1} + V_{j+1} - \left(L_j + U_j\right) - \left(V_j + W_j\right) + \sum_{l=1}^{NR} \vartheta_{i,l} r_{j,l} \qquad 4\text{-}1$$

$2 \leq j \leq NS - 1$

Where

M_j	Holdup in the stage j $(mole)$
V_{j+1}	Vapor stream that comes from the stage $j+1 (kmol\, h^{-1})$
L_{j-1}	Liquid stream that comes from the stage $j-1$ $(kmol\, h^{-1})$
L_j	Liquid stream that leaves the stage j $(kmol\, h^{-1})$
U_j	Liquid side stream of stage j $(kmol\, h^{-1})$
V_j	Vapor stream that leaves the stage j $(kmol\, h^{-1})$
W_j	Vapor side stream of stage j $(kmol\, h^{-1})$
F_j	Feed stream in the stage j $(kmol\, h^{-1})$
$r_{j,l}$	Reaction rate of reaction l in stage j
$\vartheta_{i,l}$	Stoichiometric coefficient of component i in reaction l
NR	Number of chemical reactions
NS	Number of stages

In the same way, the component material balance is given by, equation 4-2

$$\frac{dM_j x_{ij}}{dt} = F_j z_{F,j} + L_{j-1} x_{i,j-1} + V_{j+1} y_{i,j+1} - \left(L_j + U_j\right) x_{i,j} - \left(V_j + W_j\right) y_{i,j} + \sum_{l=1}^{NR} \vartheta_{i,l} r_{j,l} \qquad 4\text{-}2$$

$2 \leq j \leq NS - 1$

Where

$x_{i,j}$ Mole fraction of liquid of component i in stage j

$y_{i,j}$ Mole fraction of vapor of component i in stage j

z_{Fj} Mole fraction at feed stream in stage j

The energy balances, given in equation 4-3 :

$$\frac{dM_j h_{i,j}^L}{dt} = F_j h_{F,j} + L_{j-1} h_{i,j-1}^L + V_{j+1} h_{i,j+1}^V - (L_j + U_j) h_{i,j}^L - (V_j + W_j) h_{i,j}^V - \dot{Q}_J \qquad 4\text{-}3$$

$2 \leq j \leq NS - 1$

Where

$h_{i,j}^L$ Enthalpy of liquid of component i in stage j $(KJ\ kmol^{-1})$

$y_{i,j}$ Enthalpy of vapor of component i that leaves the stage j $(KJ\ kmol^{-1})$

h_{Fj} Enthalpy fraction at feed stream in the stage j $(KJ\ kmol^{-1})$

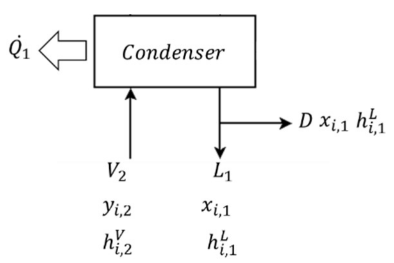
$\dot{Q}_J$ Heat duty in stage j $(KJ\ h^{-1})$

Molar fraction restrictions, equations 4-4 and 4-5.

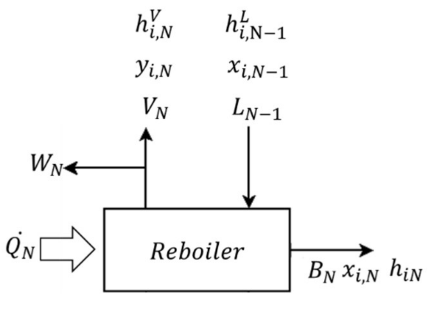
$$\sum_{i=1}^{j} y_{ij} = 1 \qquad 4\text{-}4$$

$$\sum_{i=1}^{j} x_{ij} = 1 \qquad 4\text{-}5$$

Similarly, the main balances in the condenser, stage 1, are shown in equations 4-6, 4-7, and 4-8. Meanwhile, the balances in the reboiler are shown in equations 4-9, 4-10, and 4-11. Both schemes are shown in Figure 4-3.



Representation of total condenser



Representation of partial condenser

Figure 4-3. Condenser and reboiler as equilibrium stages

$$\frac{dM_j}{dt} = L_{j-1} + V_{j+1} - \left(L_j + D\right) \tag{4-6}$$

$$\frac{dM_j x_{ij}}{dt} = L_{j-1} x_{ij-1} + V_{j+1} y_{ij+1} - \left(L_j + D\right) x_{i,j} \tag{4-7}$$

$$\frac{dM_j h_{i,j}^{L}}{dt} = L_{j-1} h_{i,j-1}^{L} + V_{j+1} h_{i,j+1}^{V} - \left(L_j + U_j\right) h_{i,j}^{L} - \left(V_j + W_j\right) h_{i,j}^{V} - \dot{Q}_J \tag{4-8}$$

$$j = 1$$

$$\frac{dM_j}{dt} = L_{j-1} - B_j - \left(V_j + W_j\right) \tag{4-9}$$

$$\frac{dM_j x_{ij}}{dt} = L_{j-1} x_{i,j-1} - B_j x_{i,j} - \left(V_j + W_j\right) y_{i,j} \tag{4-10}$$

$$\frac{dM_j h_{i,j}^{L}}{dt} = L_{j-1} h_{i,j-1}^{L} - B_j h_{i,j}^{L} - \left(V_j + W_j\right) h_{i,j}^{V} + \dot{Q}_J \tag{4-11}$$

$$j = N$$

Where

D	Distillate stream flow rate $(kmol\, h^{-1})$
B_j	Bottom stream flow rate $\left(kmol\, h^{-1}\right)$

4.3.2. Rigorous simulation of reactive divided wall distillation column (RDWC)

In the project development in a reactive divided wall distillation column (RDWC), and conventional reactive distillation column, the different balances, MESH equations, sets the behavior of the integrated device. These equations refer to the prefractionator and the main column.

The difference between the conventional reactive distillation column and the RDWC, that is portioned in four sections, as shown in Figure 4-4. The reactive zone is located in the prefractionator section, and is represented as an absorber. At the same time, the main column is represented by three sections, a rectifier at the top, hosting the condenser, an absorber at the middle, reflecting the wall, and finally a stripper, where the reboiler is present. (Ling and Luyben, 2009).

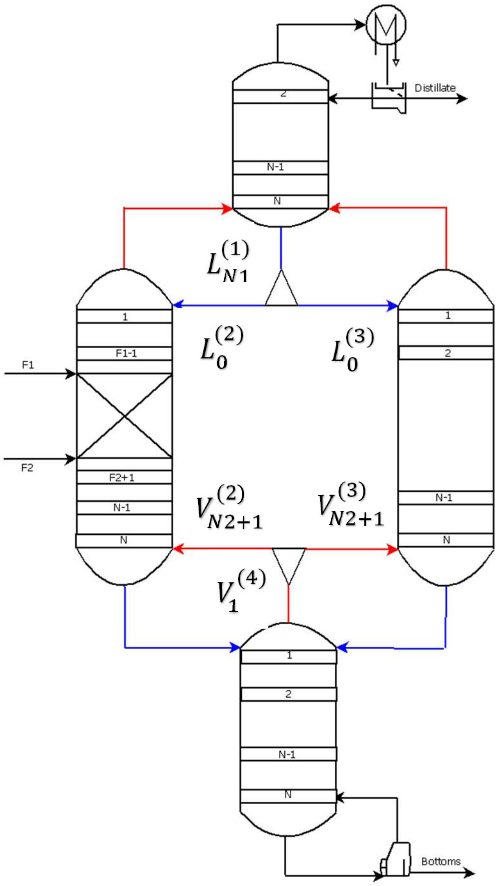


Figure 4-4. Reactive distillation column scheme

Recalling the main balances in the conventional reactive distillation column, equations 4-1 to 4-11 and applied in the RDWC, all of them apply in all sections of the device. Other additional information that requires in the modeling of this column, includes the intersection of the rectifying section with the prefractionator and the main column, which is represented by equation 4-12.

$$L_0^{(2)} = \alpha\, L_{N1}^{(1)} \qquad \text{4-12}$$

$$L_0^{(3)} = (1-\alpha) L_{N1}^{(1)}$$

In this case, the liquid molar fraction is represented:

$$x_{0,i}^{(2)} = x_{N1,i}^{(1)}$$

$$x_{0,i}^{(3)} = x_{0,i}^{(1)}$$

At the same way, the vapor splitting that connects the stripping section with the prefractionator and the main column given by equation 4-13

$$\begin{aligned} V_{N2+1}^{(2)} &= \beta\, V_1^{(4)} \\ V_{N2+1}^{(3)} &= (1-\beta) V_1^{(1)} \end{aligned} \tag{4-13}$$

Where

α	Liquid split fraction
β	Vapor split fraction
$L_0^{(2)}$	Liquid stream that goes form the main column to the top of prefractionator
$L_{N1}^{(1)}$	Liquid stream that leaves the stage upper of the wall
$L_0^{(3)}$	Liquid stream that enters the first stage at the right of the wall
$V_1^{(4)}$	Vapor stream that leaves the stage lower of the wall
$V_{N2+1}^{(2)}$	Vapor stream that goes form the main column to the bottom of prefractionator
$V_{N2+1}^{(3)}$	Vapor stream that enters the last stage at the right of the wall

4.3.3. Hydraulics

The Francis weir equation, equation 4-14, calculates the hydraulics for a single pass, relating the amount of liquid on the tray to the liquid flow rate in a tray. The height of the liquid crest is the difference between the height of liquid on the tray and the weir height. The high of the liquid is the ratio of the volume of liquid to the active area of the tray (Grassi, 1992).

$$Q_L = K_{weir} L_{weir} h_{crest}^{1.5} \tag{4-14}$$

Where

Q_L	Volumetric liquid flow rate from the stage
K_{weir}	Weir constant
L_{weir}	Total weir length
h_{crest}	Height of the liquid crest over the weir

The active area of the tray is specified as a percentage of the tray area with a default value is 90%. To simulate a single pass tray, the default ratio of weir length to column diameter is 0,7267. Moreover, the pressure drop shown in equation 4-15, relates the flooding of the stage along the column, increases from the top to the bottom of the column.

$$P_j = P_{j-1} + \Delta P_j \qquad 4\text{-}15$$

4.3.4. Phase equilibria model

The selection of the thermodynamic model is not a trivial task. According to Carlson, (1996), this election must include criteria related to the nature of the property of interest, the composition of the mixture, the conditions of pressure and temperature operation, and the availability of parameters.

In that sense, all of these items have an incidence in the behavior of the components during the calculation, in terms of their intermolecular interactions and the proximity between them. These phenomena have a relevant incidence in the liquid phase, while in the vapor phase other factors, such as the complexity of the structure or the association of hydrogen bonds of the components are crucial.

In the case of the mixture ethanol, ethyl lactate, lactic acid, and water, the NRTL model determines the activity coefficient, through binary interactions. As a first instance, the availability of parameters, and the different experimental data to this system have been developed by Delgado *et al*., (2007a), Vu *et al*., (2006) the system ethanol-ethyl lactate by Peña-Tejedor, *et al*., (2005).

Additionally, the nature of the mixture the evidence of polar compounds, such as ethanol, water and in a less degree ethyl lactate and lactic acid. Moreover, the pressure of the process is lower than 10 atm, so the vapor phase does not account for the deviation of the vapor phase., following the decision tree proposed by Carlson, (1996).

The NRTL model calculates the activity coefficient in the liquid phase, given in equation 4-16 and the parameters are shown in equations 4-17 and 4-18. The NRTL parameters corresponds to the ASPEN plus properties database.

$$ln\,\gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_j x_j \tau_{ji} G_{ji}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{ki}} \left(\tau_{ji} \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{kj}} \right) \qquad 4\text{-}16$$

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} \qquad 4\text{-}17$$

$$\alpha_{ij} = c_{ij} \qquad 4\text{-}18$$

Then, γ_i inputs into the vapor-liquid equilibrium, equation 4-19.

$$y_i = \frac{P_i^{sat} \gamma_i x_i}{P} \qquad 4\text{-}19$$

With

$$log\, P_i^{sat} = A - \frac{B}{T + C - 273.15} \qquad 4\text{-}20$$

4.3.5. The reaction kinetic model

The reaction kinetic may describe in terms of the concentration of the reactants, having in mind the reaction reversibility. The kinetic model that describes the synthesis of Ethyl lactate in Equation 4-18 (Benedict, *et al.*, 2003).

$$-r_{a=} k_a \left(C_A\, C_B - \frac{C_B\, C_B}{K_{eq}} \right) \qquad 4\text{-}21$$

However, the behavior of the quaternary mixture is considerable away from the ideal mixture. Additionally, whether the model expresses the reaction rate in terms of concentrations, it carries great deviations based on the experimental data. For those reasons, the kinetic model could represent the reaction rate in activity terms, as shown in Equation 4-22 (Delgado, *et al.*, 2007b), and (Mitkowski, 2011).

$$-r_{a=} k_a \left(a_A\, a_B - \frac{a_B\, a_B}{K_{eq}} \right) \qquad 4\text{-}22$$

Different reaction models represent the esterification reactions with heterogeneous catalysts. The Langmuir-Hinshelwood kinetic model is the most appropriated for predicting the reaction between Lactic Acid and Ethanol. It includes the adsorption and desorption term between reactants and products on the catalyst (Zhang *et al.*, 2004).

Moreover, it assumes that the reactions that occur on the catalyst control the reaction. For the synthesis of Lactic Acid, reported the following kinetic model, Equation 4-23, for obtaining the reaction rate. (Zhang *et al.*, 2004), and (Delgado *et al.*, 2007b), (Pereira *et al.*, 2008)

$$-r_{a=}K_A \frac{\left(a_{Et}\, a_{LA} - \frac{a_{EL}\, a_W}{K_{eq}}\right)}{(1 + K_{Et}a_{Et} + K_W a_W)^2}$$

4-23

On the other hand, the reaction rate constant is subject through the Arrhenius equation, letting predict the behavior of the kinetics as a function of the medium temperature, equation 4-24. The activation energy values for this reaction, E_a, the pre-exponential term, k_0, using the Amberlyst 15® (Pereira *et al.*, 2008).

$$K_A = k_0 e^{\frac{E_a}{RT}}$$

4-24

$$k_0 = 2.7 * 10^7 \frac{mol}{g\ min}$$

$$E_A = -44980 \frac{J}{mol}$$

According to that, the kinetic model includes the adsorption parameters for Ethanol (Et), Water (W), Ethyl Lactate (EL), and Lactic Acid (LA) from the Langmuir-Hinshelwood thermodynamic model (K_{ET},K_W, respectively). Lactic Acid and Ethyl Lactate are not reported because of their low effect on the reaction as shown in equations 4-25 and 4-26. In equation 3-7, the equilibrium constant will be part of the driving force contribution for obtaining the reaction rate (Delgado *et al.*, 2007b).

$$K_{Et} = 1.22\, e^{\frac{359.63}{T(K)}}$$

4-25

$$K_W = 15.19\, e^{\frac{12.01}{T(K)}}$$

4-26

Finally, the relations of the reaction rate constant and the equilibrium constant as a function of temperature are determined to perform kinetic batch simulations for this reaction, shown in equation 4-26 (Fogler, 2005), and (Pereira *et al.*, 2008).

$$\frac{dX}{dt} = |\nu_i| \frac{1}{n_{l,o}} W_{Cat} r_a \tag{4-27}$$

Where $n_{l,o}$ and ν_i are the initial number of moles and the stoichiometric coefficient of the limiting reactant, Lactic Acid. Additionally, the initial condition is given by $t = 0;\ X = 0$, in the differential equation 4-27, combined with the rate expression given in equation 4-23, solves numerically as shown in equation 3-1 and 4-28.

$$\frac{dX}{dt} = |\nu_i| \frac{1}{n_{l,o}} W_{Cat}\ K_A \frac{\left(a_{Et}\ a_{LA} - \frac{a_{EL}\ a_W}{K_{eq}}\right)}{(1 + K_{Et} a_{Et} + K_W a_W)^2} \tag{4-28}$$

4.4. Equilibrium stage model implementation

The algorithm RADFRAC, that is part of the commercial software Aspen Plus, models the RD and RDWC columns and RDWC. This algorithm is able both equilibrium reactions and kinetic limited reactions as well, and in equilibrium or rate based mode. To this project, the inside-out algorithm to calculate both columns structures.

The configuration of the RADFRAC model relates the use of the inside-out algorithm, with two nested itraration loops. Firstly, configuring the initial values, which means the temperature, composition and internal flows profile. Then, after configuring all the inputs, such as inlet variables, thermodynamics, and reaction rate parameters, the Broyden method achieves with enough reliability to these systems. These calculations incorporate the thermodynamic model, into the interactive loops, and integrating them into the loops. (Seader & Henley, 1999).

4.5. Results

4.4.1. Validation of the kinetic model

In the work reported by Pereira *et al.*, (2008) the effect of various conditions, such as catalyst loading, the initial molar ratio between ethanol and lactic acid, and reaction temperature, on lactic acid conversion as a function of time is studied, varying the condition under evaluation and keeping constant the remaining conditions.

Besides, the simplified L-H model, equation 4-23, uses to describe the kinetic behavior of the esterification of lactic acid with ethanol with Amberlyst 15-wet as a catalyst. To validate the model, at least two different experiments, different initial molar ratios were performed for each temperature, which varied from 323.15 to 363.15 K, as shown in Table 4-9.

Table 4-9. Experimental and Calculated Equilibrium Compositions

	Equilibrium composition							
	Experimental mole fraction				**Calculated mole fraction (NRTL)**			
T (°K)	**Ethanol**	**Ethyl Lactate**	**Water**	**Lactic Acid**	**Ethanol**	**Ethyl Lactate**	**Water**	**Lactic Acid**
323.15	0.3598	0.1776	0.3732	0.0894	0.3562	0.1812	0.3768	0.0858
323.15	0.3336	0.1773	0.3840	0.1051	0.3256	0.1853	0.3920	0.0971
323.15	0.1812	0.1854	0.4527	0.1808	0.1778	0.1875	0.4553	0.1794
333.15	0.3561	0.1813	0.3769	0.0857	0.3540	0.1834	0.3790	0.0836
333.15	0.3307	0.1802	0.3869	0.1021	0.3233	0.1876	0.3943	0.0948
333.15	0.1794	0.1871	0.4544	0.1790	0.1752	0.1901	0.4579	0.1768
343.15	0.3527	0.1847	0.3803	0.0823	0.3520	0.1854	0.3810	0.0816
343.15	0.3297	0.1812	0.3879	0.1012	0.3211	0.1897	0.3965	0.0926
343.15	0.1799	0.1866	0.4539	0.1796	0.1727	0.1926	0.4604	0.1743
343.41	0.4510	0.1682	0.3295	0.0512	0.4544	0.1649	0.3261	0.0546
343.41	0.4495	0.1698	0.3311	0.0497	0.4544	0.1649	0.3261	0.0546
353.4	0.1983	0.1975	0.4525	0.1517	0.1989	0.1969	0.4519	0.1523
362.87	0.4474	0.1719	0.3331	0.0476	0.4503	0.1690	0.3303	0.0504
362.87	0.4459	0.1734	0.3347	0.0461	0.4503	0.1690	0.3303	0.0504

Similarly, Pereira *et al*., (2008) varied the catalyst loading from 1.2 to 3.9 wt %, as shown in Figure 4-5. Here, the effect of the catalyst loading evaluates the incidence of the Lactic Acid conversion, with a ratio of ethanol to lactic acid of 1.82 and 353.49 K. It shows how the proposed model can response under some catalyst loading variation.

On the other hand, other validation criteria are the initial molar ratio of the reactants incidence on the conversion of lactic acid. The initial number of moles ratio varies from 1.1 to 2.8 as shown in Figure 4-6. In this case, this effect on the conversion of Lactic Acid as a function of time was performed at 353.40 K and a catalyst load of 2.4 wt %.

As a result, the equilibrium conversion increases with the increase of the initial molar ratio of ethanol to lactic acid and that the equilibrium is achieved faster for upper initial molar ratio values (Pereira *et al*., 2008).

According to Delgado *et al*., (2007b), after higher values of a ratio of 3:1 of ethanol, a minimal increasing or low incidence on the conversion of lactic acid for producing Ethyl Lactate.

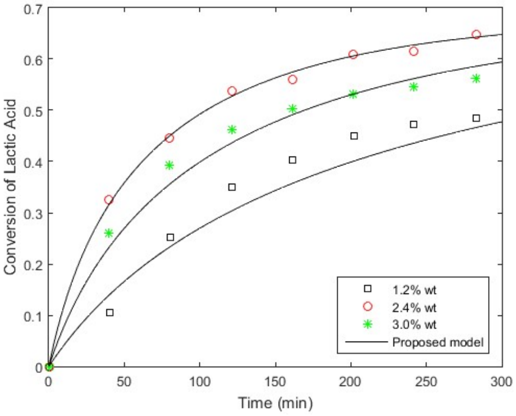


Figure 4-5. Effect of catalyst loading on the conversion of lactic acid

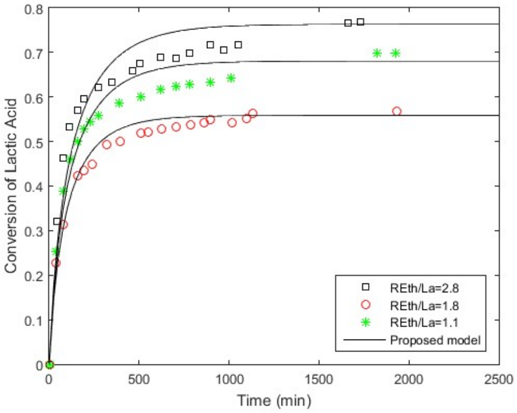


Figure 4-6. Effect of the initial molar ratio of ethanol to lactic acid on the conversion of lactic acid

Delgado *et al*., (2007b) showed that the reaction rate increases with increasing reaction temperature. However, the equilibrium conversion was nearly equal in the range of temperatures considered in this work. In general, in most esterification reactions, the equilibrium constant is a weak function of the temperature because of the small value of the heat of reaction, and Zhang *et al*., (2004) also found the L-H model to be suitable for predicting lactic acid esterification with ethanol. The effect of the reaction temperature is shown in Figure 4-7.

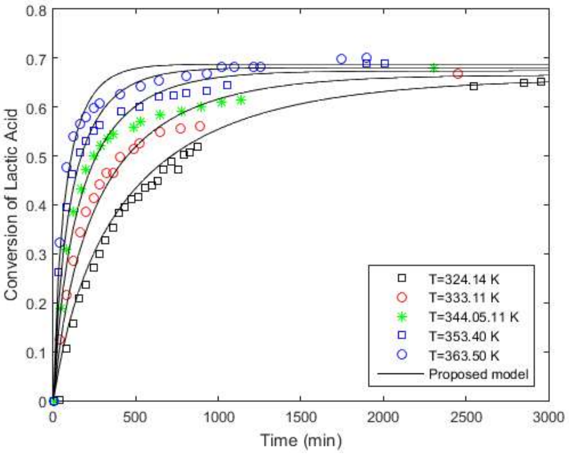


Figure 4-7. Effect of reaction temperature on the conversion of lactic acid

4.4.2. Steady-state validation of RD

For validating this model, the experimental data gave by Gao, *et al.*, (2007) were used. The characteristics of the column are:

- The height of the reaction catalytic zone is 700 mm.
- The feed points determine the height of the reaction zone, the distance of each feed is 100 mm respectively. Reaction kinetics is implemented as a subroutine in ASPEN PLUS®.
- The value of HETP is 50 mm heights.

As a result, the simulated top and bottom stream compositions compared with the experimental data, shown in Table 4-9. The comparison of the simulation results and the experimental axial temperature profile along the column is evaluated with the proposed kinetic model in a conventional reactive distillation column modeled in Aspen Plus®, presented in Figure 4-3. This data corresponds to the simulation of a conventional column with an excess or ethanol of 4:1.

Table 4-10. Mass fraction composition in the bottom and distillate streams obtained in the simulation model and experimental data brought by (Gao, *et. al*., 2007).

	Distillate stream		**Bottom Stream**	
Component mass fraction	**Simulation**	**Experimental**	**Simulation**	**Experimental**

Ethanol	0.9366	0.9278	0.0867	0.1742
Lactic Acid	2.2015E-07	0	0.3277	0.2610
Ethyl Lactate	8.2012E-06	0	0.5823507	0.5285
Water	0.0634	0.0722	0.003217	0.0363

Finally, according to these results, it is possible to produce ethyl lactate via reactive distillation, where ethyl lactate is obtained from the bottom of the column and, the heterogeneous azeotrope ethanol-water is obtained at the top of the column.

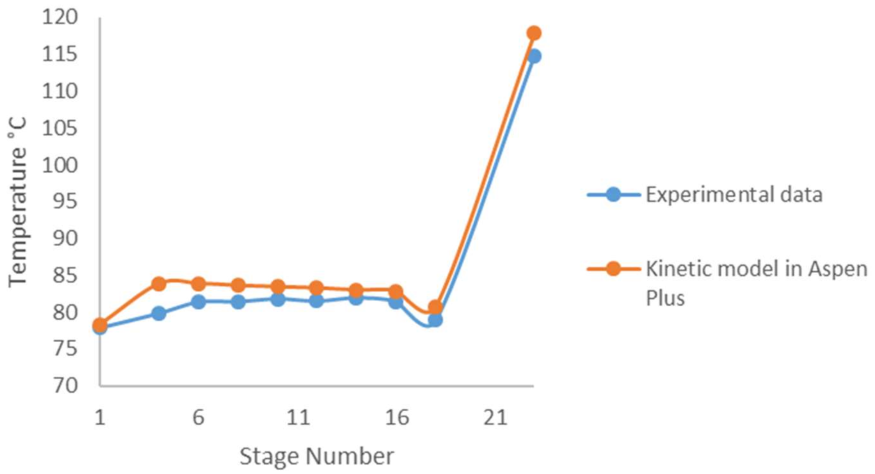


Figure 4-8. Temperature profiles in a conventional reactive distillation column

On the other hand, Figure 4-9 shows the conventional RD followed by a conventional distillation column. The raw material enters the reactive zone of RD, the non-reactant lactic acid and the produced ethyl lactate goes to the conventional distillation column, where finally, ethyl lactate is obtained at the top of the distillation column, and lactic acid exits and bottom stream.

In Figure 4-11, the main parameters of the direct sequence show the configuration of the conditions that lead to a feasible reaction and separation of the esterification of lactic acid with ethanol to produce ethyl lactate.

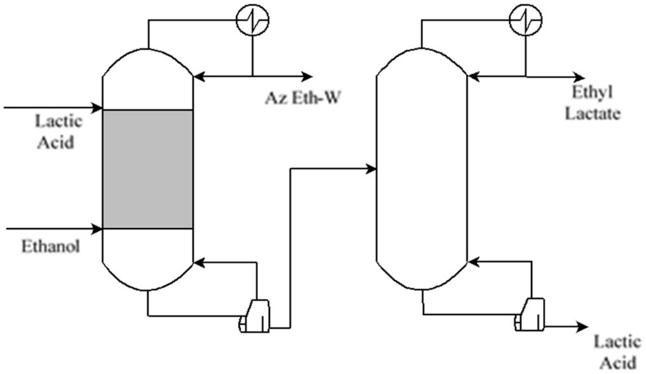


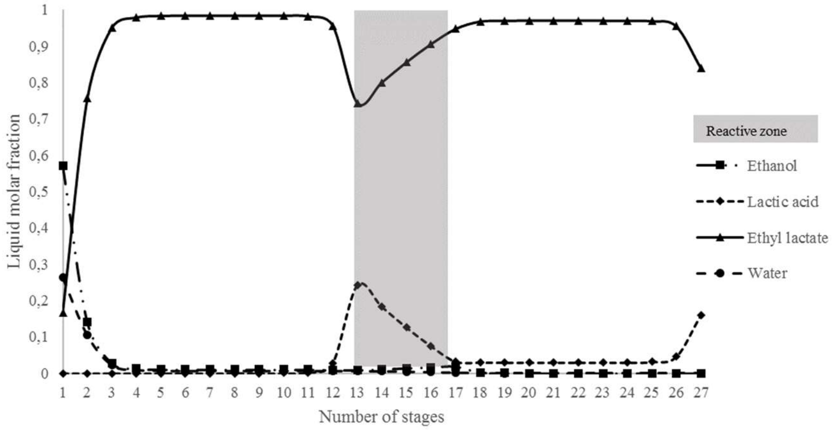
Figure 4-9. Scheme for ethyl lactate production with a direct sequence

Table 4-11. Direct sequence parameters for rigorous simulation

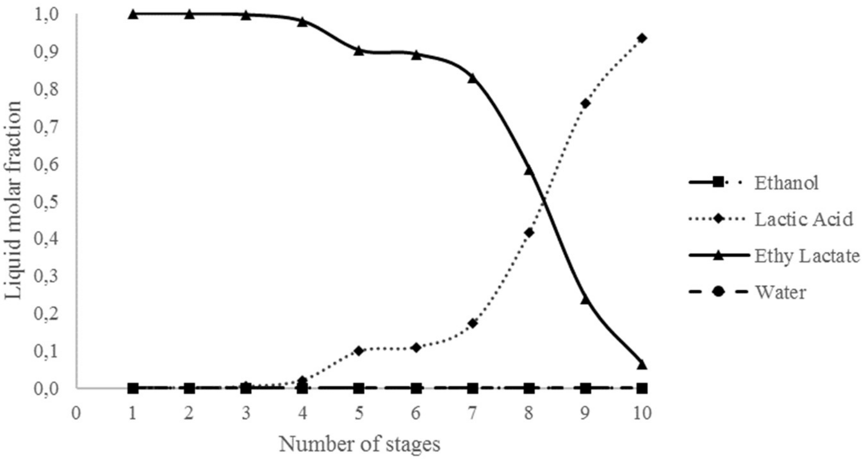
Reactive distillation column configuration	
Total Number of stages	27
Reactive number of stages	5
Ethanol feed stream location	17
Lactic acid feed stream location	13
Reflux ratio	1.6743
Reboiler duty (kj/h)	1182825.6228
Condenser duty (kj/h)	1108218.8150
Net duty (kj/h)	2299491
Catalyst weight kg	272.5
Distillate flow kmol/h	9.5240
Bottom flow kmol/h	6.2260
Ethyl lactate composition in bottom stream	0.8398

Conventional distillation column configuration	
Total Number of stages	10
Feed stream location	5
Reflux ratio	2.8355
Reboiler duty (kj/h)	414827.478
Condenser duty (kj/h)	415481.8644
Net duty (kj/h)	830309.342
Distillate flow kmol/h	4.562
Bottom flow kmol/h	1.2159
Ethyl lactate composition in distillate stream	0.95

In Figure 4-10, the internal profiles along the reactive distillation column present the analysis of the statics results, showing clearly the feasible separation between ethanol-water azeotrope, and ethyl lactate and the lactic acid at the bottom of the column. Additionally, the direct sequence achieves a high composition of ethyl lactate in the second column, about 99%.



Reactive distillation column



Conventional distillation column

Figure 4-10. Direct sequence liquid composition internals

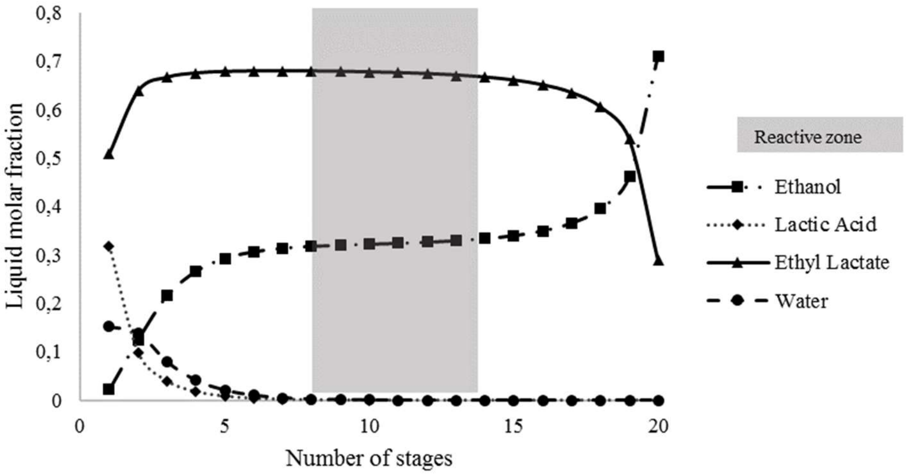
4.4.3. RDWC results

The RDWC configuration has two feed streams and the reactive zone in the prefractionator, in the main column the separation of the products occurs. Table 4-12 sets the main parameters of the reactive distillation column and the conventional distillation column configuration and Table presents the operational conditions established for the RDWC configuration.

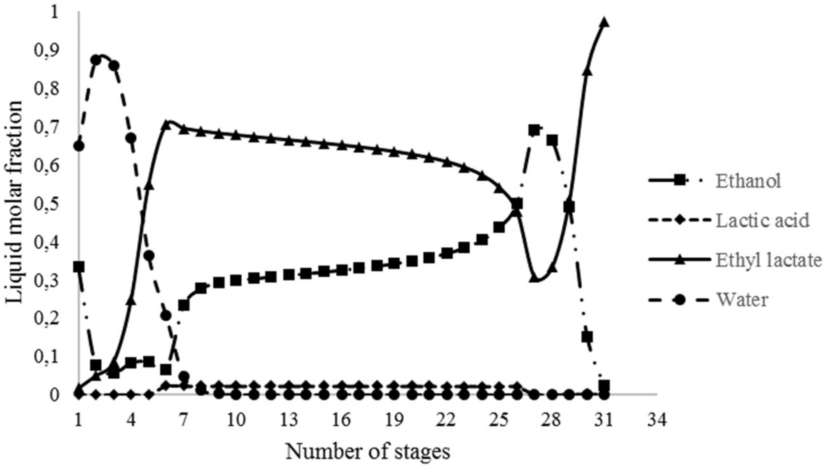
Table 4-12. Parameters of the reactive divided wall column RDWC for rigorous simulation

RDWC configuration	
Total Number of stages main column	28
Total Number of stages prefractionator column	20
Reactive number of stages	4
Ethanol feed stream location	7
Lactic acid feed stream location	4
Reflux ratio	0.5
Reboiler duty (kj/h)	664463.0556
Condenser duty (kj/h)	594275.1912
Net duty (kj/h)	1188550.3824
Catalyst weight kg	272.5000
Distillate flow kmol/h	9.4000
Bottom flow kmol/h	6.195
Ethyl lactate composition in bottom stream	0.991
Liquid connection ratio from main column to prefractionator.	0.6
Vapor connection ratio from main column to prefractionator.	0.82

In Figure 4-11, the liquid composition along the RDWC presents the behavior in the prefractionator reactive section and the main column. The results show in the same manner, that a purity of 99% of ethyl lactate is achievable.



Prefractionator section



Main Column section

Figure 4-11. RDWC liquid composition internals

Table 4-13 shows the result of conversion given the rigorous simulations of the direct sequence, and the RDWC configuration. In contrast, the increase in the conversion in a RDWC scheme is related to the implicit recycle of the non-reactant lactic acid through the column. In sequential schemes, is necessary to create recycle streams that could improve the conversion of the limited reactants. As a consequence, these recycle create hot spots and the increasing of the costs in a conventional process (Babi *et al.*, 2015).

Table 4-13. Conversion results

Configuration	**Conversion**
Rigorous simulation conventional RD	69.11%
Rigorous simulation RDWC	83.41%

On the other hand, Table 4-14 shows the reduction of the energy demands in a conventional sequence and the RDWC. Although both configurations achieve a high composition of ethyl lactate, the reduction of heat exchangers saves a net duty of 38%. Kiss and Suszwalak, (2012), evaluated the influence of the feed characteristics through the evaluation of the volatilities between each component and found the high impact of the composition at the feed stream, which could affect considerably the energy demands.

Table 4-14. Parameters of the reactive divided wall column RDWC for rigorous simulation

	Direct sequence	**RDWC**	**Energy Reduction %**
Net reboiler duty (kj/h)	1597653.1224	664463.0556	
Net Condenser duty (kj/h)	1523700.6835	594275.1912	
Net duty (kj/h)	3129800.1287	1188550.3824	38.53
Ethyl lactate molar fraction in the product stream	0.99	0.99	
Ethyl lactate stream flow flow (kmol/h)	4.56	6.19	

4.5. Conclusions

An analysis of degrees of freedom considered the definition of variables that allows finding the performance of a RDWC and a RD. According to this, in the case of the RDWC, a set of variables that relates the liquid and vapor split on the zone of the wall must be specified.

In that sense, the pressure drop, and the hydraulics account not only the steady-state condition, but also in the dynamic condition, stably keeping the operation, and under the feasible condition of operability. The designation of these variables will configure the control structure in the case of a RDWC.

Similarly, the MESH equation considered the kinetic model, the vapor-liquid equilibrium, the hydraulics. The consideration of neglecting oligomers allows identifying the model implementation in the case or the RD, though the validation with the experimental data.

Finally, the procedure was applied into a RDWC, showing an improvement in the conversion and the energy demands, as a consequence of the reduction in the number of heat transfers operations, compared with a conventional scheme. Additionally, the performance in terms of the purity of products was guaranteed during the project design.

5. FLOWSHEET SYNTHESIS FOR ETHYL LACTATE PRODUCTION APPLYING PROCESS INTENSIFICATION AND SUSTAINABILITY CRITERIA

5.1. Introduction

Process synthesis consists of the selection of unit operations, their interconnections, and operational conditions to generate a flowsheet alternative, given some goals and constraints. These goals relate the identification of tasks to be accomplished, together with the chemical and physical phenomena, where finally the available raw materials convert into products.

However, other decision factors have changed the paradigm of process engineering design, taking advantage of computers and new process technologies. These paradigms have a relation with the importance of the development of other factors such as sustainability and economy.

For that reason, process synthesis intensification establishes a strategy for achieving reductions in the size of a chemical plant at a given production volume, as mentioned by Rong, *et al*., (2008)(Rong et al., 2008)(Rong et al., 2008)(Rong et al., 2008)(Rong et al., 2008)(Rong et al., 2008)(Rong et al., 2008)(Rong et al., 2008)(Rong et al., 2008)(Rong et al., 2008). Consequently, process intensification seeks multifunctional devices, which are implemented in traditional operations. For example, Mueller and Kenig, (2007), showed the integration of processes that combine reaction and separation procedures into a single unit. In that sense, the process intensification offers some advantages, such as a lower capital expenditure due to decrease of recycling streams and heat removal, lower feedstock cost due to the higher product selectivity, and a longer catalyst life due to washing with cleans refluxes, reduced oligomer formation, as mentioned by Harmsen (2007).

From the environmental point of view, Zhang, *et al*., (2004) reported a reduction in emissions above 20% in process intensification, involving the intensification of a reactor-separator system. Whereas, Caballero and Grossmann, (2004) and Agrawal, (1996), proposed an MINLP strategy for configuring a thermally coupled distillation system, where heat is supplied to the system by a single reboiler, and heat removed through a simple single condenser.

At the same time, the integration of reaction and separation has experienced fast progress in this decade because it provides a convenient way of alleviating kinetic and/or thermodynamic constraints usually present in the more traditional sequential configurations. In this situation, Paiva and Malcata, (2000) compared quantitatively the fractional recovery of the desired product in an integrated processing unit and a sequential one. The objective function was set as the local temperature, which maximizes the recovery of the product in the vapor phase leaving the integrated unit.

However, despite these efforts to define an economical and sustainable process, recent concepts that generate a methodology to develop intensified projects involving an efficient implementation of such metrics are present. Those concepts relating to the task scale (Siirola, 1996), (Agreda *et al*., 1990) and the phenomena scale (Lutze *et al*., 2013). Through these approaches, the life cycle analysis and the sustainable and economic metrics are possible to generate better performance in terms of maximization or minimization of utility consumption and inventory of feedstock.

As a result, the analysis and identification of hot-spots are targets that describe the limitations and bottlenecks associated with the tasks, overcoming regularly, and giving better performance and efficient design the degree of intensification and generation of the possible alternatives. The tendency on these works is the implementation of the phenomena building blocks, which prove an effective alternative to accomplish an intensification operation.

In this section, the objective established was the minimization of the number of process equipment, and evaluate the effect on the reduction of economic and environmental metrics. Also, the degree of intensification alternatives is based on the phenomena building blocks, which is developed without a formal optimization problem.

The remaining is organized as follows. Section 5.2. introduces a description of the tools of process intensification, phenomena building blocks and the simultaneous building blocks concepts are presented. In section 5.3, the algorithm for generating the process intensification flowsheet is described. In section 5.4., two cases of study describe the esterification reaction of lactic acid with ethanol to produce ethyl lactate, a green solvent employed in pharmaceuticals and food additives, and the dehydration of sub-product ethanol-water azeotrope. Finally, the main results of the work are presented. Finally, a conclusion section encloses the chapter.

5.2. Tools for process intensification

5.2.1. Phenomena Building Blocks (PBB) and Simultaneous Phenomena Building Blocks (SPB)

The phenomena-based synthesis procedure is used to identify the main tasks in a unit operation and generate alternative flowsheet. Babi *et al*. (2015) described a phenomena building block (PBB) as the smallest unit that performs a task in one piece of equipment.

Basically, these tasks represent the different interactions between mass, energy and momentum transfer phenomena. The combination of one or more PBBs results into simultaneous phenomena building blocks (SPBs), which serve as a basis to form structures that carry out a set of tasks, for instance those observed in unit operations.

For example, Figure 5-1 describes the SPBs associated with one reactive distillation column, with a total condenser, a partial reboiler and a finite number of stages; some stages serve to carry out the reaction task, while others perform the purification of the products. The reaction and separation phenomena involves two phases, vapor and liquid (VL). The representation of PBBs in a RD consist of mixing (M), two-phase mixing (2phM), cooling (C), heating (H), phase separation (PS), phase contact (PC), phase transition (PT) and chemical reaction (R), provide the generation of SPBs in the unit.

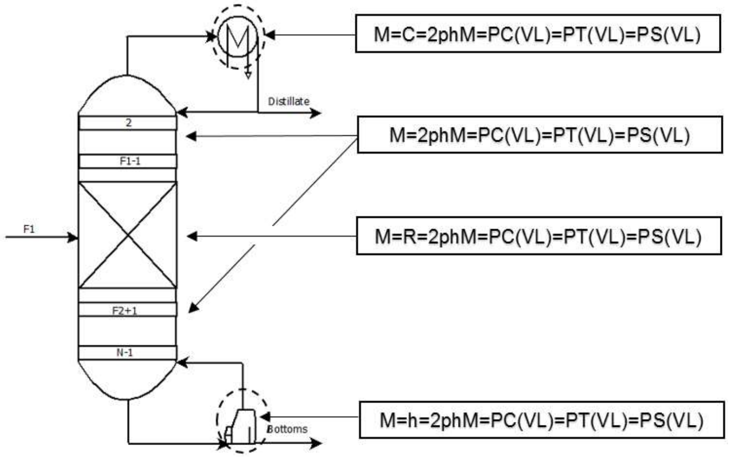


Figure 5-1 Representation of a unit operation. A single feed RD column. (Mixing (M), two-phase mixing (2phM), cooling (C), heating (H), phase separation (PS), phase contact (PC), phase transition (PT) and chemical reaction (R)).

5.2.2. Economical and sustainability metrics

For the comparison the alternatives generated in this work, suitable economic, sustainability. The economic factors include utility costs, purchase costs, and profits. Sustainability factors include carbon footprint, human toxicity potential by ingestion (HTPI), human toxicity potential by exposure (HTPE), global warming potential (GWP), human toxicity, and carcinogenic impacts (HTC) (Kalakul *et al*., 2014)

5.3. Methodology

The methodology used in this work for process intensification takes as a basis the work by Babi *et al*., (2015). It consists of the analysis of the task-phenomena-based synthesis as follows:

1. Identification of the main tasks of the process.
2. Identification of the PBBs, in each equipment involved in the process.
3. Generation of feasible flowsheets, based on the task of each piece of equipment.

4. Comparison and selection of the flowsheet alternatives, based on the performance of each equipment unit.

As mentioned by Castillo-Landero, *et al*., (2018), Figure 5-2 shows the algorithm applying three main stages. The first stage establishes the problem definition and the objectives of the process. The second stage implements computational work based on simulation and additional software tools of the base case, bringing information of several economical and sustainability metrics, and finally, the third stage designs the PBBs and develop their combinations into SPBs, providing the basis for the generation of new process alternatives that gradually minimize the number of pieces of equipment. Each stage has 15 steps as is following explained.

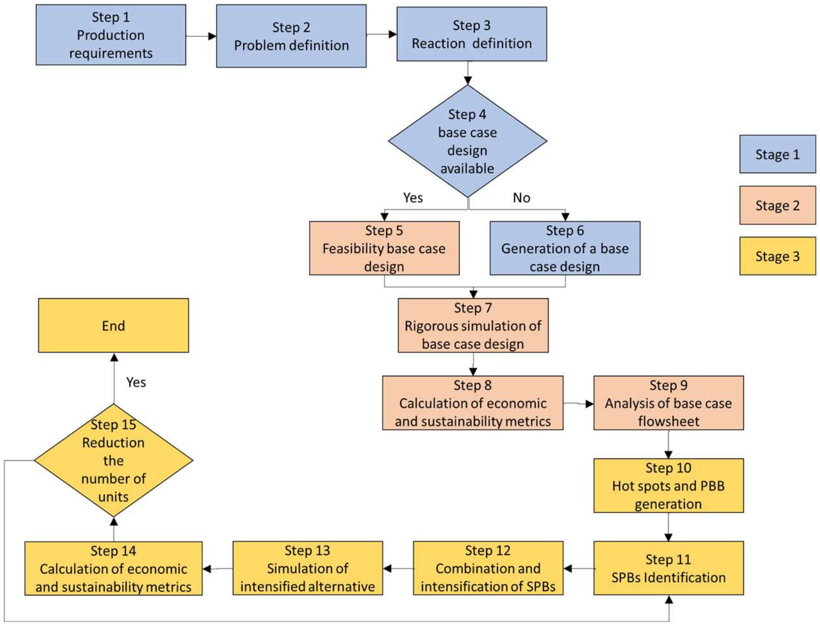


Figure 5-2. Diagram for process intensification

Step 1. Inputs information. To obtain raw material and product costs, availability of flowsheets in literature survey and annual production estimation.

Step 2. Problem Definition. To describe the problem definition, involving the transformation of a set of raw materials into specified chemical products, given the purity of products, to use a minimum number of pieces of equipment.

Step 3. Reaction Definition. Reaction features such as raw material and product phase, reaction kinetics, and type of catalyst are to be identified.

Step 4. Availability of the base case design. If the base case is provided, continue; otherwise, go to step 6.

Step 5. Feasibility of the base case. In case of the availability of the base case design, a characterization of the base case, collecting the necessary items for the process analysis and simulation. This information relates input/output flows, physical and chemical properties, prices for reactants and products, recycles in the flowsheet, type of process (continuous or batch), size and operating conditions for each piece of equipment, the performance of reactor (including reaction temperature, the heat of reaction, equilibrium constants, and/or kinetic parameters) and separation systems (including heat duties of reboilers and condensers for distillation, solvent consumption for solvent-based separation systems.

Step 6. Base case design generation. In the absence of a base case design, a processing route must be identified, given thermodynamics insights, where interaction between pure compounds and mixtures involved in the process, bringing feasible tasks (Jaksland, *et al*., 1995).

Step 7. Base case design rigorous simulation. A rigorous simulation is carried out, from which the major characteristics of the process are obtained.

Step 8. Economic and Sustainability Factors. After the rigorous simulation, the process is analyzed to determine process bottlenecks, or hot spots identified and improved from the base case.

Step 9. Analysis of the Base Case Design. A transformation and implementation of the flowsheet into a block flow diagram following phenomena building block (PBB).

Step 10. Generation of Hot Spots and PBBs. Part of the diagnostic of the base design includes the identification of hot spots that have the potential to improve the process, under the following guideless:

- Check if there is a problem with the equilibrium of the reaction in case of many nonreaction components.
- Check if there is a high exothermic or endothermic reaction, given the high demand for utilities.
- Check if there is an explosive mixture or if there is a degradation of the product by temperature.
- Check any separation difficulty, including the identification of possible azeotropes.

Step 11. Generation of SPBs. Identify which SPBs have the potential to improve the process tasks and design new alternatives.

Step 12. Combination of SPBs. SPBs from different units merging into a new piece of equipment to develop an intensified alternative.

Step 13. Rigorous Simulations of New Alternatives. Perform the simulation of the new alternatives, given the product specifications.

Step 14. Calculate the Economic and Sustainability factors of the new design.

Step 15. Check if the Minimum Number of Units has been achieved. If further reduction in the number of units is possible, satisfying the performance criteria, such as improvements in sustainability and economical metrics, in comparison with the base case design.

5.4. Process intensification case study

5.4.1. Base case design

For developing the proposed intensification methodology, the case study is the production of ethyl lactate through the esterification of lactic acid with ethanol. The basic design for the conventional distillation units were taken from Adams and Seider, (2008). considered the treatment of that mixture by pervaporation. In this work, extractive distillation is selected as the separation method.

In the work by Gil et al. [46] a mixture of these entrainers was considered to take advantage of the low-cost glycerol coming as a by-product from biodiesel production, and the lower viscosity of ethylene glycol that helps the performance of the separation system. As for the blend, the work by Gil *et al.*, (2014) suggested the use of an ethylene glycol/glycerol mixture of 60/40 for implementation. We selected this mixture as the first entrainer to be tested., and the second the use of acetol as a solvent, obtained from on the ICAS® thermodynamic analysis and selection, the operation conditions were obtained after a feasibility analysis.

Two conventional columns are part of the base flowsheet. For the one that splits the reactor exit in the middle, 97% of the ethyl lactate fed to the column was specified to go to the bottoms stream. For the second column, which purifies the process product, ethyl lactate, a purity of 99.99% was specified. The flowsheet is completed with the extractive distillation section; the conceptual structure is the same regardless of the entrainer used. The description of the implementation and results of the two entrainers selected for analysis is given in the remainder of this work.

Table 5-1 shows the operation condition of the base case when ethylene-glycol and glycerol employ as a solvent, and Table 5-2 presents the operation conditions when acetol is used.

In both cases, ethanol is fed in stream S12, and Lactic acid in S2 at a mole ratio of 4:1, of ethanol to the esterification PFR reactor. The reactor outlet consists of a multi-component mixture of ethyl lactate, ethanol and water, and a non-reacted lactic acid. The minimum boiling azeotrope exists between ethanol and water, followed by four distillation columns. In the first column, C-01, the mixture of Ethyl lactate and the non-reacted Lactic acid feed to the column C-02, stream S11, where ethyl lactate is present. Finally, the recovered lactic acid recycles to the reactor. The base case flowsheet is presented in Figure 5-3.

Meanwhile, at the top of C-01, a Water-Ethanol azeotrope is fed to the extractive section, stream S3. At the same time, the solvent is fed through the stream S13. In column C-03. The stream S16, a mixture of solvent and water feeds column C-04, where the water separated from it. The remaining solvent returns to the extractive distillation (ED) column, stream S7.

Table 5-1. Parameters for base flowsheet simulation for case 1

Parameter	Reactor	Column 1	Column 2	Extractive column	Column 3
Pressure (atm)	1	1	1	1	0.2
Theoretical stages	-	13	13	20	8
Feed stage	-	5	5	12	8
Solvent stream Feed stage	-	-	-	4	-
Reflux Ratio	-	10	2.5	3.5	2.5
Distillate rate case (kmol/h)	-	9.89	6	5	4.6
Condenser temperature (ºC)	-	82.63	154.49	78.31	59.36
Reboiler temperature (ºC)	-	159.87	216.54	189.73	201.91

Table 5-2. Parameters for base flowsheet simulation for case 2

Parameter	Reactor	Column 1	Column 2	Extractive column	Column 3
Pressure (atm)	1	1	1	1	0.2
Theoretical stages	-	13	13	20	8
Feed stage	-	5	5	12	4
Solvent stream Feed stage	-	-	-	4	-
Reflux Ratio	-	10	2.5	6.5	15
Distillate rate case (kmol/h)	-	9.92	6	3.2	7
Condenser temperature (ºC)	-	82.73	154.49	78.34	60.87
Reboiler temperature (ºC)	-	159.99	216.56	129.28	99.13

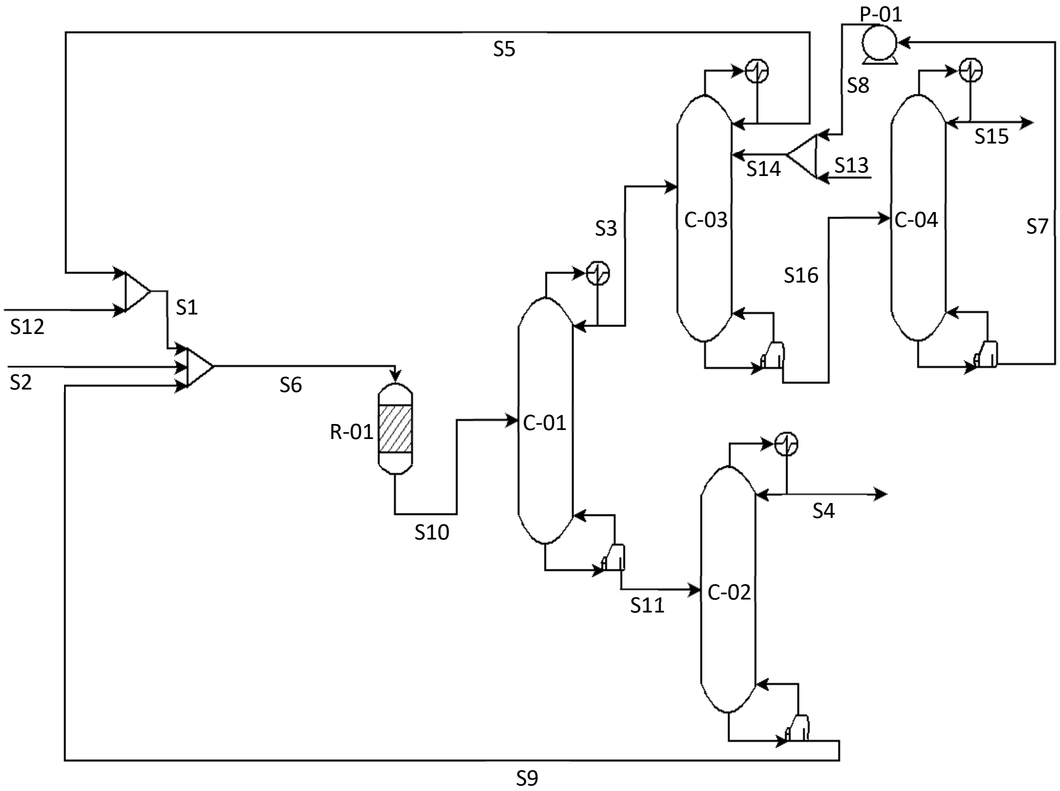


Figure 5-3. Base case diagram

5.4.1. Reaction definition

The conversion of lactic acid is 83%, and the heat of reaction is 0.02344 GJ/h. According to this, the base case design is available and the methodology applied by Castillo-Landero *et al*., (2018), allows developing the process intensification, given all the possible flowsheets. In this case, the kinetic data are available in Pereira, *et al*., (2008b). The major inefficiency or hot spots provide the information for generating the intensified cases. The NRTL model was used as a thermodynamic model simulated in Aspen Plus V8.8 ®. In Figure 5-4, the operations tasks describe the flowsheet, while in Figure 5-5 shows the block phenomena flow diagrams for the base case design

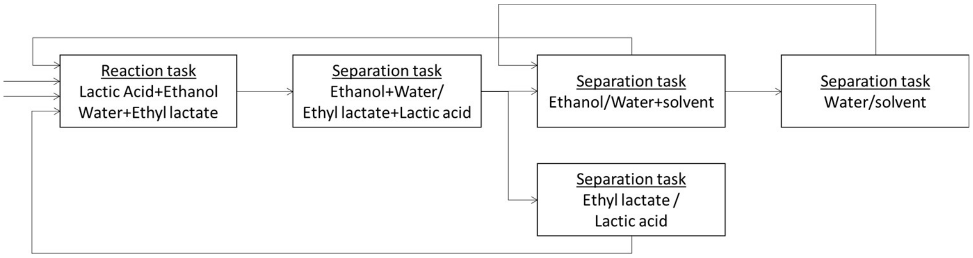


Figure 5-4. Block flow diagram for base case design

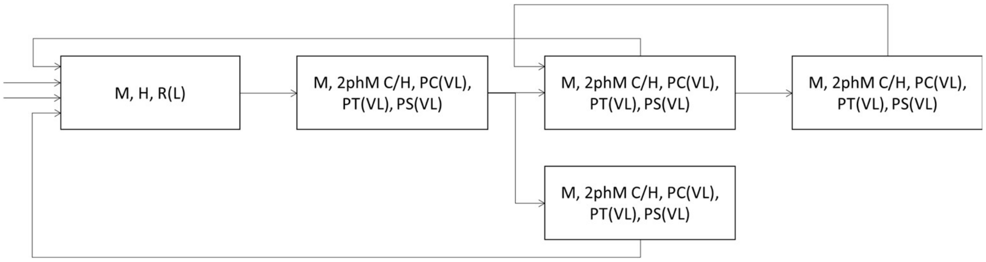


Figure 5-5. Phenomena flow diagram *for* base case design

5.4.2. Economic sustainability analysis

To detect process inefficiencies of the base case flowsheet, we identify the hot spots, which show opportunity areas for process improvement. The procedure involves the identification of open and closed paths, obtained through the flowsheet decomposition and the generation of new feasible alternatives, as described by Carvalho *et al*. (2008). The search was aided with the LCSoft® software (Kalakul *et al.*, 2014).

The open route, which serves to quantify losses of reactants in the output streams from the process, shown in Table 5-3 contains a flow of 2 kg/h of an excess of ethanol, giving a loss of 1.81 $/h. this effect could be improved through process intensification, particularly by making the reaction more efficient. On the other hand, the analysis of closed paths, which serves to identify loses due to products that are not part of the exit streams, shows loses of 1.31 $/h because of 0.8 kg/h of ethyl lactate that are being recycled to the reactor..

Table 5-3. Identification of paths with the highest potential for improvement for case 1

Path	Component	Path flow (Kg/h)	Streams							MVA ($/h)	EWC ($/h)
C10	Glycerol	0.7845	S12	S1	S6	S1	S3	S16	S15		1.31
OP2	Ethanol	2	S16	S7	S8	S14				-86.9379	1.8091

MVA: Mass value-added EWC: Energy and waste cost

This expense relates to the high flow of ethanol, resulting in high energy consumption and the use of utilities. Figure 5-6 presents carbon footprints generated by the units of the base case. According to this, the targets to be achieved are the reduction of energy consumption, reduce the utility cost, reduction in the number of units, to maintain the production target, reduction of operational costs, and reduction of wastes (Babi *et al*., 2015).

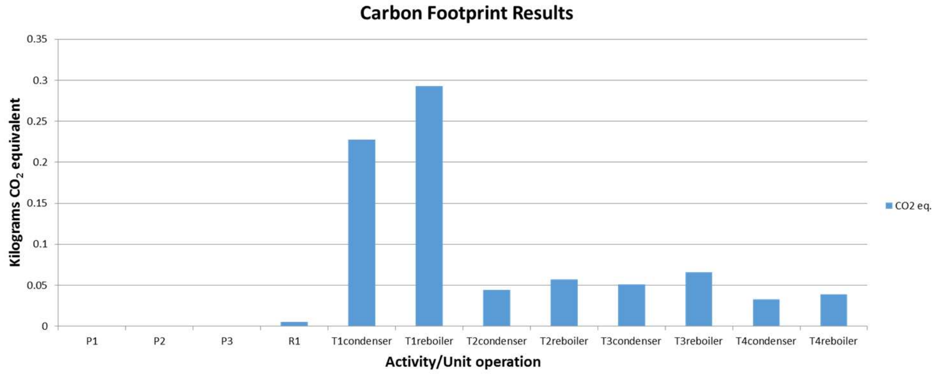


Figure 5-6. Sustainability factor results in the base case, with ethylene-glycol and glycerol as extraction solvents

On the other hand, in the second case, the open route is shown in Table 5-4 a flow of 5.2 kg/h of an excess of acetol, giving a loss of 4.2 $/h. For that reason, this route could consider a possible intensification, improving the extractive zone. Meanwhile, the closed path, produces an expense of 58.5 $/h of energy waste cost, due to the accumulation of acetol in this flowsheet.

Table 5-4. Identification of paths with the highest potential of improvement for case 2

Path	**Component**	**Path flow (Kg/h)**	**Streams**							**MVA ($/h)**	**EWC ($/h)**
C10	Acetol	1.25E-06	S12	S1	S6	S10	S3	S16	S15		10.4929302
OP5	Acetol	50	S13	S14	S16	S15				-105.8841	13.3549209

MVA: Mass value-added EWC: Energy waste cost AF: Accumulation factor

In the same way, shown in Figure 5-7, the carbon footprints in the second case show a considerable generation of CO_2 per ethyl lactate produced. Given the base flowsheet, the objective is to intensify the production process of ethyl lactate, reducing the number of units. Some interactions among the equipment could help to identify the type of intensification carried out.

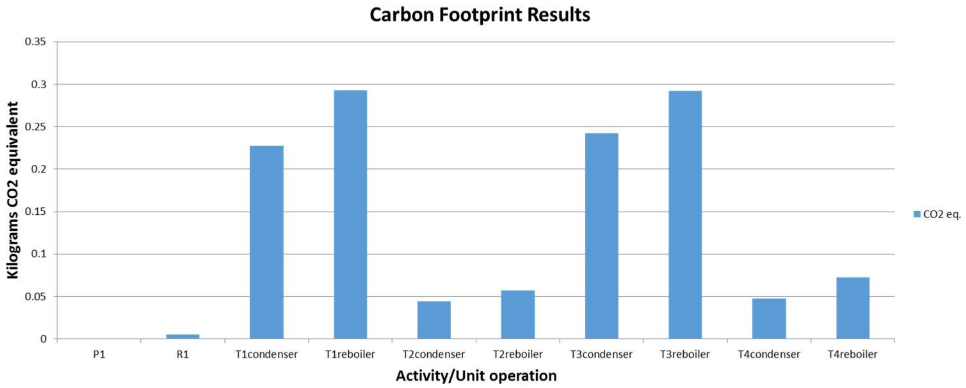


Figure 5-7. Sustainability factor results in the base case, with acetol as an extraction solvent

As seen in the base case in Figure 5-3, the stream S6 and S10 correspond to the open path and is considered feasible to intensify R-01 Task-1 with the first distillation column C-01 Task-2, creating a RD column with the PBB (M=R=2phM=PC(VL)=PT(VL)=PS(VL). Consequently, it is found feasible because SPBs that performs simultaneous reaction and separation constraint the system characteristics, such as the presence of an azeotrope, and the reaction in the liquid phase. Table 4-5 presents the SPB´s in each alternative.

As a result, the first alternative consists of the new Task 1, where reactants ethanol and lactic acid are fed, the outputs are ethyl lactate and no- reactant lactic acid at the stripping zone, then is fed to the separation column C-02. Meanwhile, the azeotrope ethanol-water goes from the rectifying section of the RD column to the extractive zone, columns C-03 and C04, as shown in Figure 5-8.

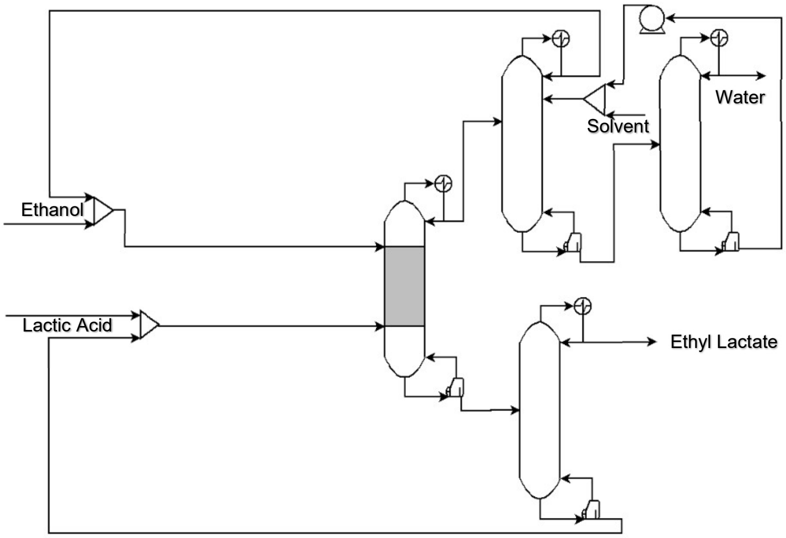


Figure 5-8. Flowsheet of alternative 1

The second alternative, the train of distillation columns C-03 and C-04 in the extraction section perform similar tasks, such as separation phases, and heat transfer. Given the feasibility of merging the flowsheets S3, S17 and S7, located inside the close paths analysis, creating an extractive divided wall distillation column (EDWC)

In that sense, the EDWC contains two condensers and one reboiler. At the top, the dehydrated ethanol returns to the RD column. On the other side of the wall, water leaves de process at the top, and the solvent outs from the bottom and returns to the EDWC. Figure 5-9 shows the flowsheet of alternative 2.

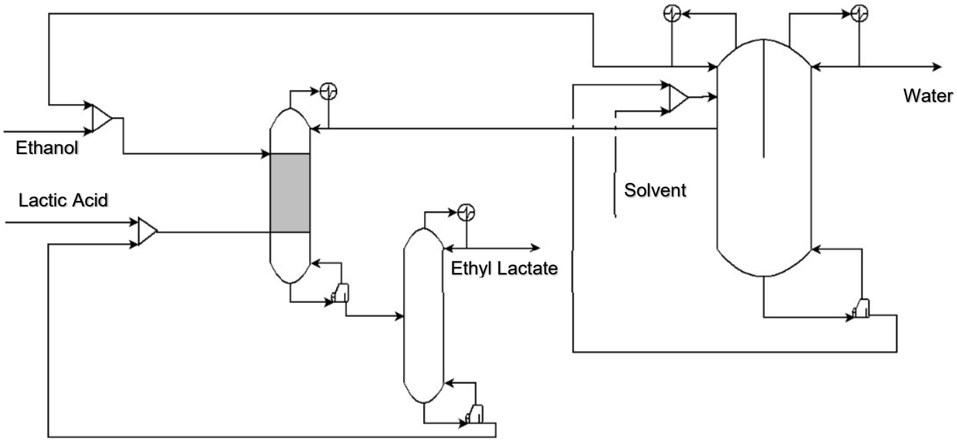


Figure 5-9. Flowsheet of Alternative 2

The third alternative, in general, the interaction of PBBs are mainly the interaction between phases between task 1 and task 2 in alternative 2. For that reason, both tasks can be integrated into one unit, configuration a reactive divided wall distillation column (RDWC). Finally, this alternative has two tasks, the merged task of reaction and separation, and the second task related to the extractive zone as presented in Figure 5-10.

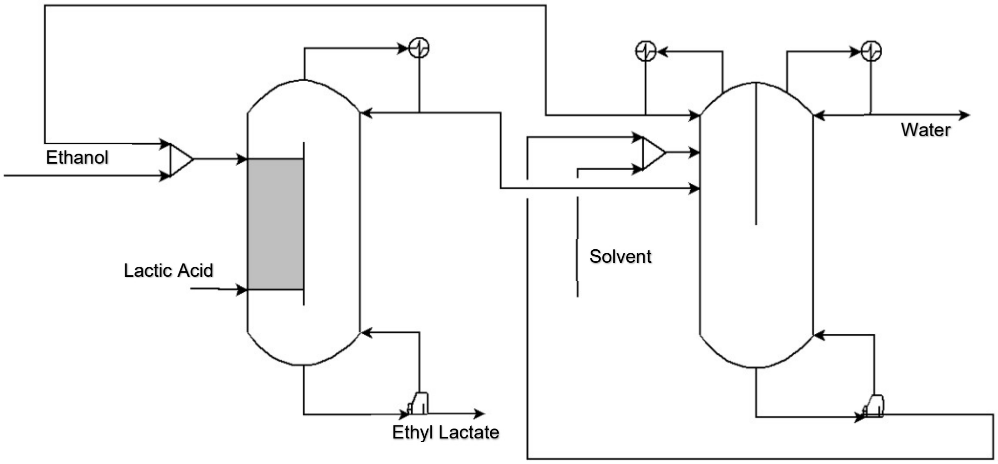
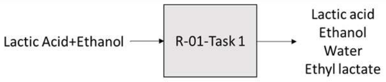
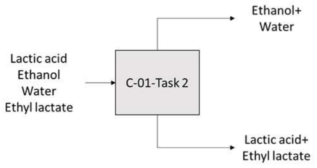
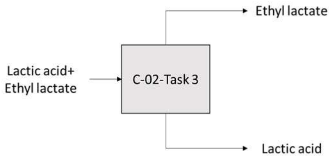
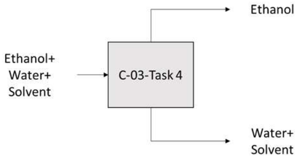
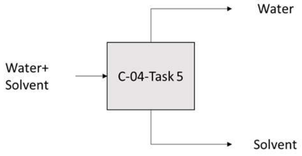
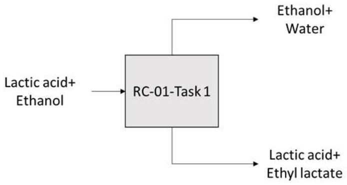


Figure 5-10. Flowsheet of Alternative 3

In general, following the combination of SPBs given the reaction and separation tasks intensifies the process is gradual, evaluating the economic and sustainability metrics and the effects on each structure. Given five equipment in the original structure, a different merging of SPBs allows us to asses three alternatives with different degrees of intensification. In Figure 5-11 describes the selected blocks with reaction and separation tasks.

Table 5-5. SPBs Identification in each alternative

SPBs	**Task**
Base case	
M(L)= R(L)=H	
M=C=2phM=PC(VL)=PT(VL)=PS(VL) M=2phM=PC(VL)=PT(VL)=PS(VL) … M= 2phM=PC(VL)=PT(VL)=PS(VL) M=H=2phM=PC(VL)=PT(VL)=PS(VL)	
M=C=2phM=PC(VL)=PT(VL)=PS(VL) M=2phM=PC(VL)=PT(VL)=PS(VL) … M= 2phM=PC(VL)=PT(VL)=PS(VL) M=H=2phM=PC(VL)=PT(VL)=PS(VL)	
M=C=2phM=PC(VL)=PT(VL)=PS(VL) M=2phM=PC(VL)=PT(VL)=PS(VL) … M= 2phM=PC(VL)=PT(VL)=PS(VL) M=H=2phM=PC(VL)=PT(VL)=PS(VL)	
M=C=2phM=PC(VL)=PT(VL)=PS(VL) M=2phM=PC(VL)=PT(VL)=PS(VL) … M= 2phM=PC(VL)=PT(VL)=PS(VL) M=H=2phM=PC(VL)=PT(VL)=PS(VL)	
Alternative 1	
M=C=2phM=PC(VL)=PT(VL)=PS(VL) M=2phM=PC(VL)=PT(VL)=PS(VL) … M=R=2phM=PC(VL)=PT(VL)=PS(VL) … M= 2phM=PC(VL)=PT(VL)=PS(VL) M=H=2phM=PC(VL)=PT(VL)=PS(VL)	

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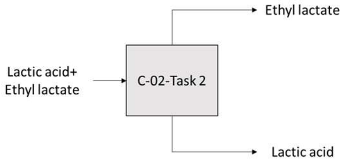
M=H=2phM=PC(VL)=PT(VL)=PS(VL)</td><td>
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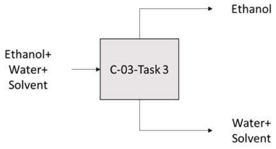
M=H=2phM=PC(VL)=PT(VL)=PS(VL)</td><td>
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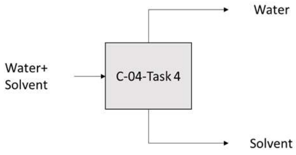
M=H=2phM=PC(VL)=PT(VL)=PS(VL)</td><td>
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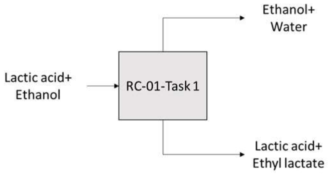
M=H=2phM=PC(VL)=PT(VL)=PS(VL)</td><td>
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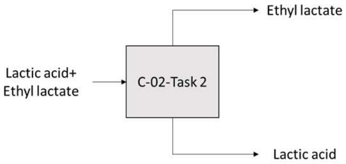
M=H=2phM=PC(VL)=PT(VL)=PS(VL)</td><td>
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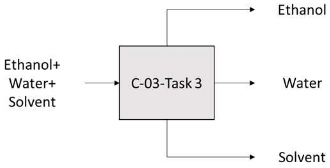
M=H=2phM=PC(VL)=PT(VL)=PS(VL)</td><td>
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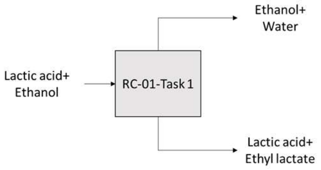
M=H=2phM=PC(VL)=PT(VL)=PS(VL)</td><td>
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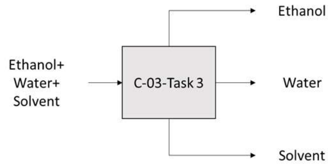
M=C=2phM=PC(VL)=PT(VL)=PS(VL) M=C=2phM=PC(VL)=PT(VL)=PS(VL) M=2phM=PC(VL)=PT(VL)=PS(VL) … M= 2phM=PC(VL)=PT(VL)=PS(VL) M=H=2phM=PC(VL)=PT(VL)=PS(VL)	

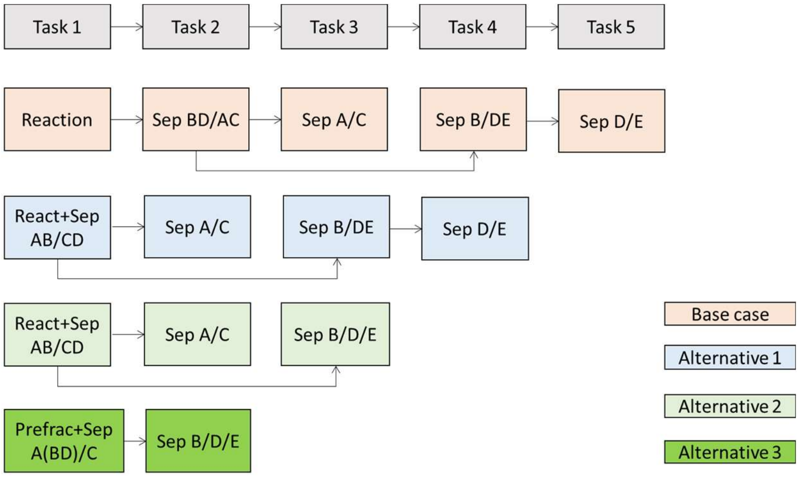


Figure 5-11. Degree of intensification in each alternative using SPBs

The use of simulation software such as Aspen Plus together with tools as ECON, to evaluate the economic metrics, and Sustain Pro, to perform the environmental metrics.

In this context, Table 5-6 relates the different parameters of production, economic and sustainability factors, given for the case base and the different alternatives of intensification, using ethylene glycol and glycerol as a solvent for ethanol dehydration. In alternatives one and two, the utility cost decreases by about 30% to the case base.

Although alternative 1 and alternative 2 could consider economically and environmentally feasible, alternative 3 contributes significantly to the reduction of energy demands and emissions of CO_2. Also, the production of ethyl lactate increases in the RDWC, and energy reduction is mainly significant in the intensification of this zone.

As a result, the evaluated parameters obtained from the schemes respect with the base case show a reduction of 70% utilities, 80% in the carbon footprint, and 96% in the global warming metrics, which translates into 80% of profits increasing.

This behavior reflects the impact of intensification in the RDWC, increasing the conversion from reactant to products, also the capacity of the utility reduction in this section of the process rather than in the extractive section. For that reason, alternative 1 and alternative 2 show a slice reduction in the parameters.

In this case, the evidence of a decrease in energy demands, represented in the utility costs the carbon footprints index. According to the hot spots identification methodology, the mass balance path showed the streams in the case base presents several losses from the energy and economical items.

Consequently, the process intensification reaches an effective improvement, from the environmental and economical point of view. Figure 5-12 shows the ratio among the evaluated parameters in the process intensification, for each alternative with the base case flowsheet and the improvement through each evaluated parameter.

Table 5-6. Economic and sustainability results for 4 flowsheets alternatives of intensification for case 1.

Parameter	**Base case**	**Alternative 1**	**Alternative 2**	**Alternative 3**
Ethyl Lactate Production (kg/h)	565.9413	588.6565	604.4878	708.7066
Days of labor	330	330	330	330
Ethyl lactate purity	0.999	0.999	0.999	0.999
Utilities (GJ/h)	14.250	8.813	8.810	3.288
Economic factors				
Utility cost ($/year)	471670	320009	311821	116165
Raw Material Costs (M$/year)	39.24884	39.24884	39.24884	39.24884
Profit (M$/year)	316.44	321.70	331.55	395.54
Sustainability factors				
Carbon footprint	8.1545E-01	5.8830E-01	5.7287E-01	1.8281E-01
HTPI (1/LD 50)	5.1708E-02	9.0510E-04	6.9710E-05	2.7601E-05

HTPE (1/TWA)	1.7521E+01	2.8823E-01	2.3511E-02	9.3188E-03
GWP (CO_2 eq.)	8.1516E-01	5.8827E-01	5.7287E-01	1.8281E-01
HTC (kg benzene eq.)	3.5100E-02	5.2145E-03	3.7828E-04	1.3306E-04

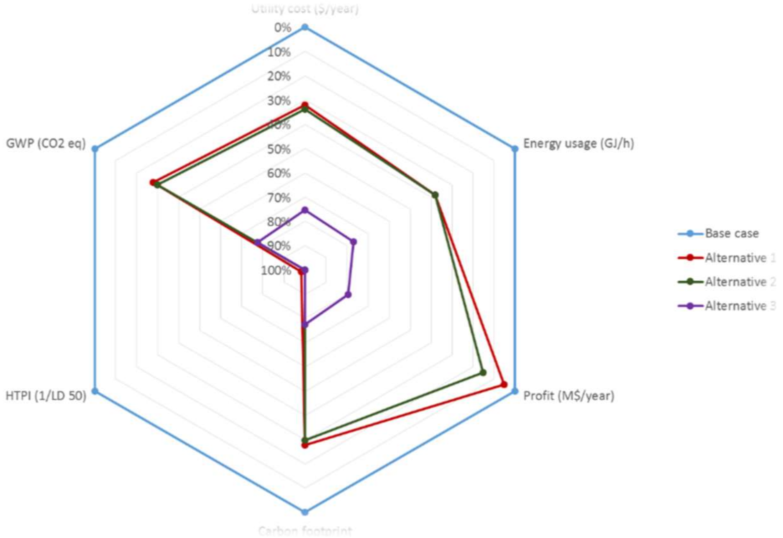


Figure 5-12. Economic and sustainability metrics in the intensified alternatives for case 1.

At the same time, in Table 5-7, the parameters of production of ethyl lactate, using acetol as a solvent for dehydrating ethanol, such as economic and sustainability factors, for each case of intensification. In alternatives one and two, the utility cost decreases by about 15% to the case base.

In this case, the intensification alternatives follow the same pattern as in the first case. The evidence of diminution of energy demands, represented in the utility costs the carbon footprints index. According to the hot spots identification methodology, the mass balance path showed the streams in the case base presented several losses from the energy and economical items.

As a result, the evaluated parameters obtained from the schemes respect with the base case shows a reduction of 42% of utilities, 45% in the carbon footprint, 30% in utilities demands, and 40% in the global warming metrics, which translates into 60% of profits rising, as observed in Figure 5-13.

A comparison of the intensification effects of using the glycols mixture and acetol as entrainer shows relevant differences. The use of the ethylene glycol/glycerol mixture provided a more energy-efficient option, with savings reaching 50% for the second intensified option, and almost 80% for the final flowsheet with two units with respect to the acetol option; this is translated into lower carbon footprint metrics. On the other hand, all the sustainability factors evaluated here, HTPI, HTPE, GWP and HTC, are benefited from the use of acetol as entrainer for the extractive distillation of the ethanol-water mixture..

Table 5-7. Economic and sustainability results for four flowsheets alternatives of intensification for case 2.

Parameter	**Base case**	**Alternative 1**	**Alternative 2**	**Alternative 3**
Ethyl Lactate Production (kg/h)	571.8427	587.8043	690.7862	722.9791
Days of labor	330	330	330	330
Ethyl lactate purity	0.999	0.999	0.999	0.999
Utilities (GJ/h)	22.4628	19.609	16.2613	15.857
		Economic factors		
Utility cost ($/year)	695.585	593.016	512.732	465.509
Raw Material Costs (M$/year)	20.5627	18.761755	18.4168	25.4319
Profit (M$/year)	334.51	341.33	404.95	417.74
		Sustainability factors		
Carbon footprint	1.2808E+00	1.1128E+00	1.0839E+00	8.4020E-01
HTPI (1/LD 50)	6.8679E-07	6.1620E-07	5.8380E-07	4.4939E-07
HTPE (1/TWA)	3.5823E-06	3.2141E-06	3.0451E-06	2.3440E-06
GWP (CO_2 eq)	1.2809E+00	1.1128E+00	1.0838E+00	8.4016E-01
HTC (kg benzene eq)	3.8658E-04	3.4685E-04	3.2860E-04	2.5295E-04

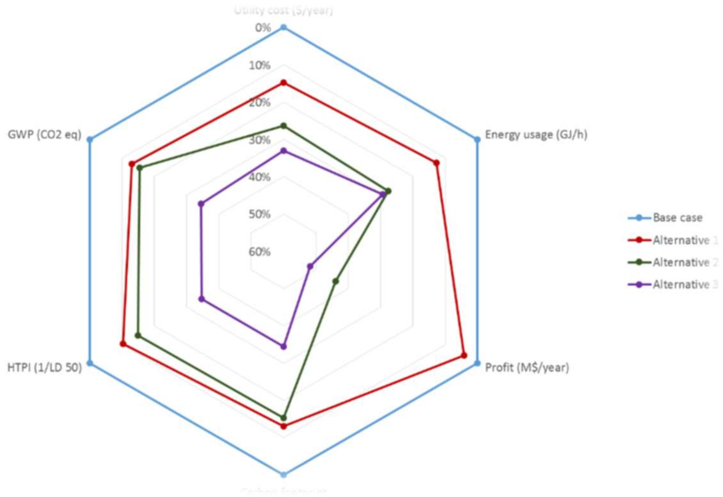


Figure 5-13. Economic and sustainability metrics in the intensified alternatives for case 2.

5.5. Conclusions

Process intensification for minimizing the number of equipment for producing ethyl lactate using two different cases has been presented. In the first situation, an ED, for dehydrating the ethanol-water mixture, using a mixture of glycerol and ethyl lactate was carried out. The second case was using acetol as a solvent.

In this process, the flowsheet of the base case flowsheet reported by Adams and Seider (2008), and Gil, *et al*., (2014), in the first case. Meanwhile, in the second case, a feasible design was carried out from step 1.

The identification, analysis, and decomposition of the different flowsheets determined the hot spots through the base flowsheets, resulting in the open and closed paths, which guide the generation of new alternatives of intensification.

During the intensification of the base case process, the degree of interaction in the process was analyzed from two different scales. The first scale corresponds to the phenomena building blocks (PBB), the second scale corresponds to the simultaneous building blocks (SPB), and finally the definition of a task in a process unit.

According to that, the generation of the intensified alternatives follows a sequential step that targets improvements in terms of economic factors, and sustainability metrics during each alternative synthesis, with the use of computer-aided tools.

The interaction of PBBs to generate SPBs, and then the formation of unit operations, which comply with the task of reaction, reaction-separation and a set of separations, generated three feasible alternative flowsheets. Among the alternatives generated, the most prominent alternative was the RDWC with an EDWC.

As a result, the reduction in energy consumption in the first case varies between 40% and 70%, and a reduction in the sustainability factors from 40% to 80%. At the same manner, the second case showed that the profits achieved varies between 5% and 60%, and a reduction from 12% to 45% in the utility costs and the sustainability factors.

Finally, some prospect works involving this methodology could include more metrics as controllability and safety indexes, represented in a multiobjective optimization problem as developed by Sánchez-Ramírez, *et al*., (2017). Moreover, as a complement of the phenomena building blocks and giving a trade-off between all metrics, and checking if an intensified process offers better controllability and security indexes as a part of the design processes stage. (Roy *et al*., 2016).

6. CONTROL OF A REACTIVE DIVIDED WALL DISTILLATION COLUMN FOR THE SYNTHESIS OF ETHYL LACTATE

6.1. Introduction

The reactive divided wall distillation column (RDWC) is characterized by the integration of two-column sections sharing a single condenser and a single reboiler with a reactive zone. This equipment is sought to decrease the total cost of the reaction-separation process for multicomponent mixtures.

If it can successfully operate in practice and controlled under some disturbances, then an RDWC is feasible. Due to their nonlinear balances, it is more difficult to control, likewise other integrated columns, such as Reactive Distillation or Divided Wall Distillation columns.

Several simulations have been performed. For instance, Wang and Wong, (2007) studied the effects of liquid split and vapor split ratios between the energy efficiency and controllability of a divided wall column system for separating ethanol, n-propanol, and n-butanol. The main findings are related to the deviations of the nominal operating conditions in terms of stability and the achievement of low energy consumption.

Dai *et al*., (2015) analyzed control of an RDWC for the reaction of propanoic acid and n-propyl alcohol to synthesize n-propyl propionate and water with a heterogeneous catalyst of Amberlyst 46. To select the temperature control trays, the sensitivity criterion was used to detect temperature profiles changes with a slight variance in reboiler duty. Then, the PI control strategy was tuned and implemented under some disturbances of feed flow rate by 20%, temperature by 10°C, and feed ratio by percent.

The result had large transient deviations and settling times in some cases. The basic control structure was improved by varying the pressure control and cascading the reboiler to the feed flow controller, giving lower deviations in the configuration.

Qian, *et al*., (2016) studied a steady-state RDWC for the selective hydrogenation and separation of a C3 stream. The steady-state model for the system, which consists of a feed into a side stripper thermally connected with a conventional distillation column.

Four different PI control schemes were proposed, two that use composition control, and two that use temperature control. The control structures were all tested with 20% disturbances in fresh feed flow rate and fresh feed composition by changing the compositions of each feed component by 20%.

The results demonstrate that for feed flow disturbances, settling time is longer for temperature control than composition control. Although the temperature control schemes have a smaller deviation than the composition control schemes for feed composition disturbances.

On the other hand, Ethyl lactate is obtained by the synthesis of esterification of lactic acid and ethanol reaction. Those raw materials may be obtained by low-cost biomass fermentation Pereira, *et al*., (2008). Whereas, ethyl lactate can easily replace halogenated solvents and also be applied in the industrial field. The purpose of this chapter is to combine the benefit of reactive distillation with DWC to produce Ethyl Lactate, focusing on the performance evaluation of temperature and composition control structures in the RDWC configuration.

The first part of this work will present the case study, the esterification of lactic acid with ethanol to produce ethyl lactate, in a proposed RDWC. Then, the composition and temperature control schemes will show the behavior in the control of key variables, such as the reflux flow rate, the liquid split, and the reboiler duty. Finally, the main results and the comparisons of these schemes will show the key findings of these schemes, in the face of some disturbances

6.2. Process description

The column operates at certain reflux ratio and energy demands, leading to the internal recycling of lactic acid, affected by the split vapor and liquid ratios in the crosssectional area of the wall that passes by the prefractionator side. The flowsheet to produce Ethyl Lactate in a RDWC is shown in Figure 6-1.

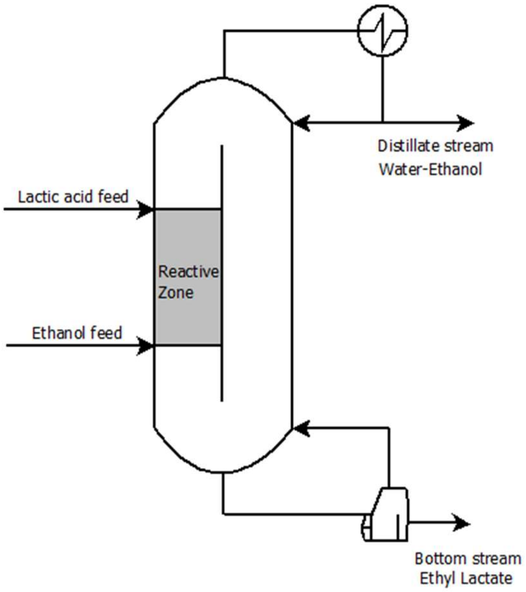


Figure 6-1. RDWC flowsheet to produce Ethyl Lactate

The control objectives relate a stable operation to minimize energy consumption, in the face of disturbances in feed streams such as composition and flowrates. The use of ethanol impurity instead of ethyl lactate purity at the bottom stream is a standard process control principle because one wants to control a variable that is sensitive to the manipulated variable, Ling and Luyben, (2009). According to that, the column operation specifications, given the steady-state condition, are shown in Table 6-1.

Table 6-1. RDWC specification of variables

Parameter	Value
Main column number of stages	28
Prefractionator number of stages	20
Reactive number of stages	4
Ethanol feed stream location	7
Lactic acid feed stream location	4
Reflux ratio	0.5
Bottom flow (kmol/h)	6.195
Liquid split ratio	0.6
Vapor split ratio	0.82
Temperature of ethanol feed stream (°C)	88.98
Pressure of ethanol stream (atm)	1.5
Temperature of lactic acid feed stream (°C)	227.39
Pressure of acid lactic stream atm	1.2

6.3. Control schemes configuration

Four vessels can represent the RDWC flowsheet, two absorbers, one stripper, and a rectifier. This representation is also called the Petlyuk column, which is a practical way to implement RDWC.

On the other hand, the vapor split is fixed as a design default value, meanwhile, the liquid split ratio can be manipulated to achieve the control objective.

The steady-state model in Aspen Plus ® considers a pressure drop of 0.0068 atm with the respective hydraulic configuration. After these specifications, the file was exported to Aspen Dynamics®.

6.3.1. Composition Control Structure

In RDWC configuration, three manipulated variables are available: reflux ratio, liquid split, and reboiler heat duty. Figure 6-2 shows the proposed composition control structure.

The reflux rate affects the composition of the outputs streams, but it affects directly the composition in the distillation stream. In the composition control loop CC 101, we control the ethyl lactate molar fraction at the top of the main column. Meanwhile, the reboiler duty can control the bottoms composition efficiently. At the bottom stream, the most volatile component, ethanol impurity, is controlled in CC 102. The third control loop, CC 103 in the control structure, relates the behavior of LA vapor phase composition at the top of the fractionator.

The main function of the prefractionator is to guarantee that all the lactic acid feeds into the column react in this zone of the RDWC, which increases the conversion through the internal recycle created around the wall.

According to this, the lactic acid that is present in the vapor stream at the top of the prefractionator must be controlled employing the liquid split ratio flowing down into the sidestream of the wall. The concentration of lactic acid in the liquid phase must be higher, avoiding an increase of the concentration in the vapor phase and forcing to leave to the stripping section of the main column.

Wolff and Skogestad, (1995) Discussed the importance of the manipulation of the liquid split in terms of energy consumption at steady-state conditions. Also, they demonstrated that holding the heaviest composition at the top, achieved a minimization of the energy consumption given a change in the feed composition.

6.3.2. Temperature Control Structure

As in the composition control structure, three temperature control loops configure the temperature control structure. In that sense the criteria for selecting the trays that hold the temperature controllers through the selection of the sensitivity analysis and the singular valor decomposition (SVD), Ling and Luyben, (2009). The SVD decomposition represents the most sensitive combination of the tray temperatures in the column.

The SVD numerical algorithm criteria require a change of about 0.1% in each manipulated variable keeping the remaining constant. In the case of the RDWC, the manipulated variables are the reflux ratio (R), the liquid split ratio (S_L), and the reboiler duty (Q_B). Each change in the manipulated variable a new temperature determines the new profile across the column obtaining a new steady state. Figure 6-3 shows the temperature control structure proposed for the RDWC configuration.

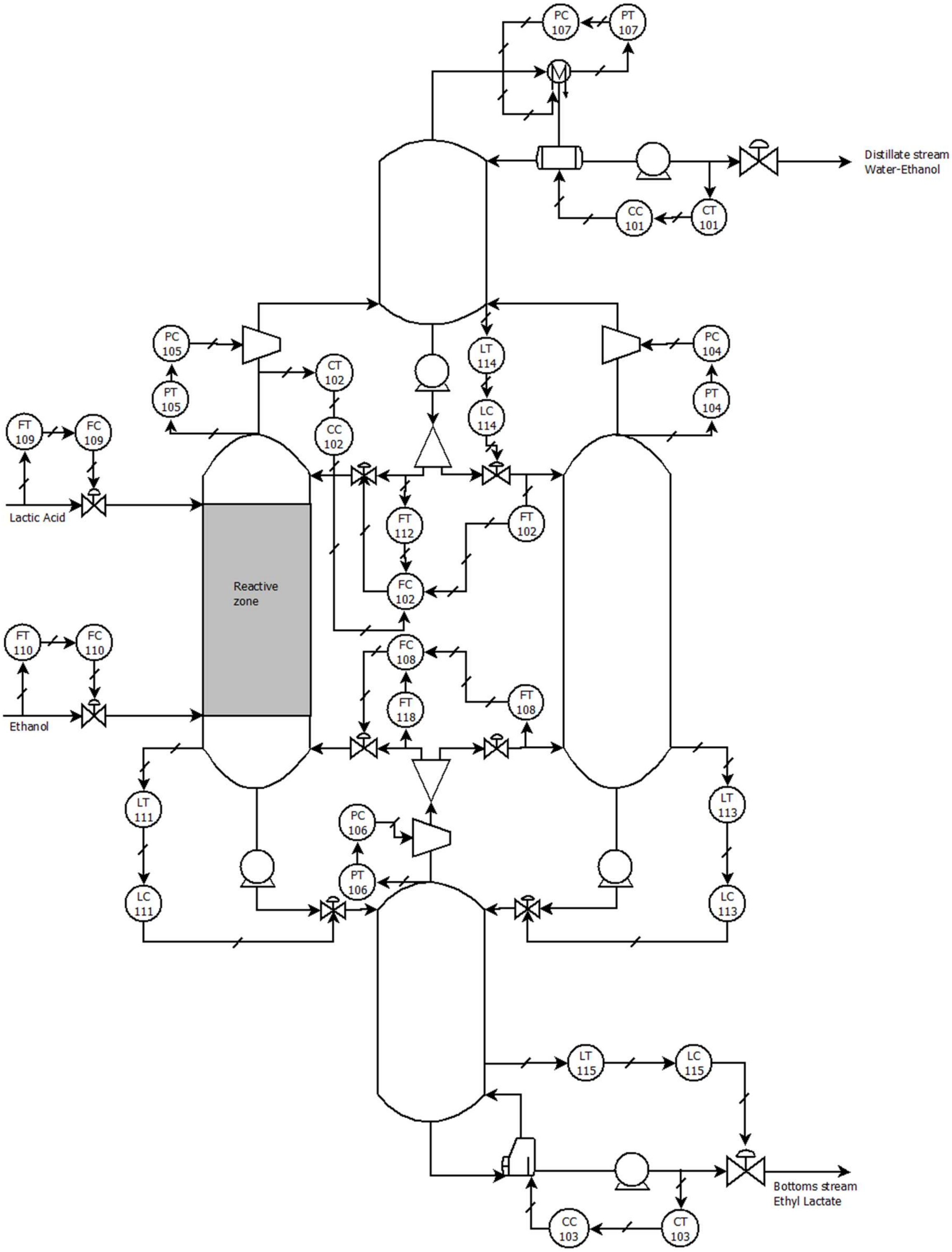


Figure 6-2. RDWC Composition control structure

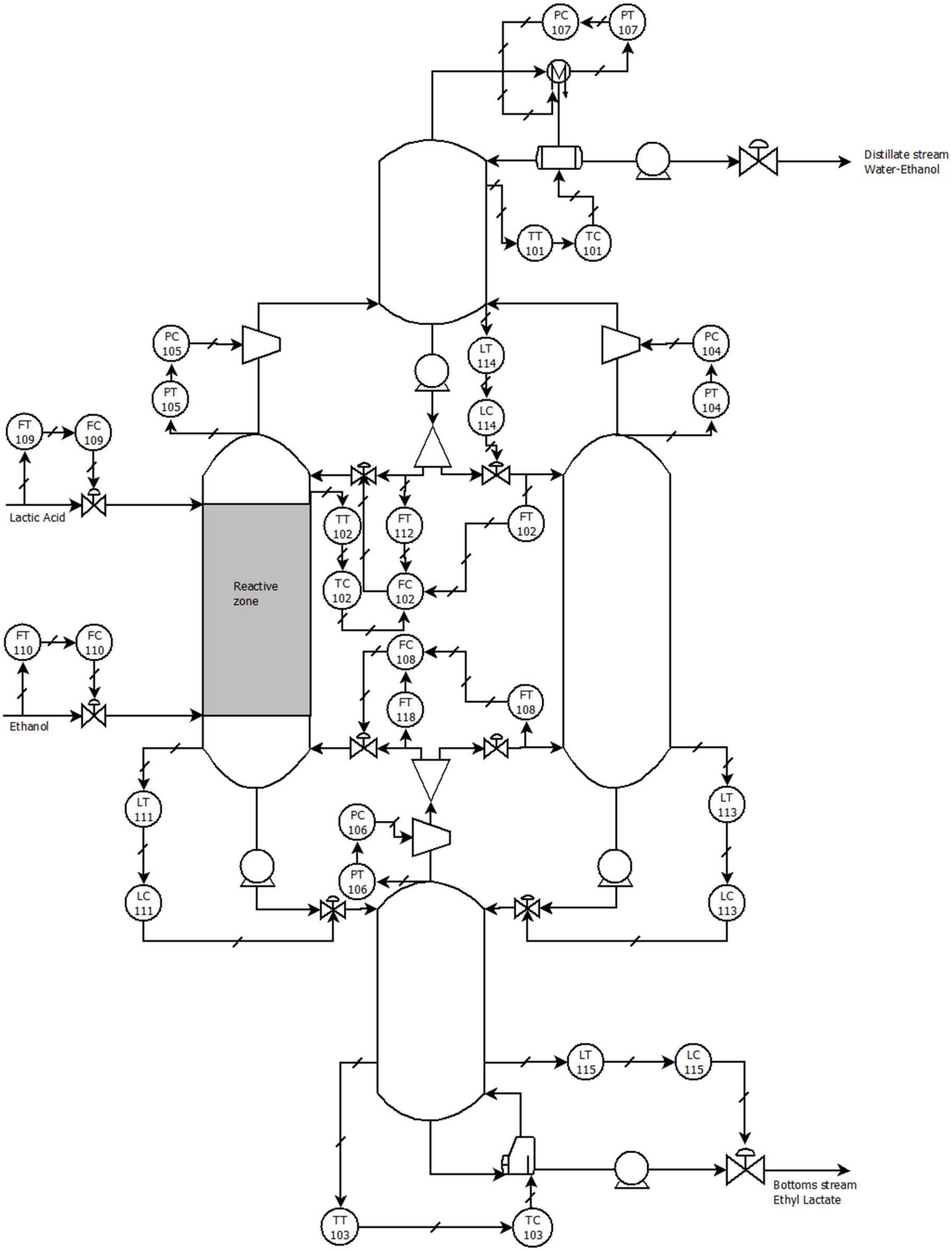


Figure 6-3. RDWC Temperature control structure

6.4. Results and discussion

The three compositions control loops have 5 min dead time each. Tyreus-Luyben tuning rules were used, tuning in the first place the $Q_B, x_{B\ ET}$, then the loop $R, x_{D\ EL}$ and finally the loop $S_L, x_{B\ ET}$. Additionally, positive and negative changes, 5% in magnitude inflow, and negative composition of the feed were implemented after 2 h of operation. Similarly, the three temperature control loops have 1 min dead time each.

Authors like Chien *et al*., (2003) propose a tuning method called BMI (Internal Model Control) that seeks to approach the tuning of parameters of a PID control for processes where its transfer function is of the form of a pure integrator with dead time. Tyreus and Luyben, (1992) point out that the IMC method can lead to poor control and from this they propose a method Alternative using classic frequency response methods. Chidambaram *et al*., (2003) also proposes a method to obtain the tuning of the parameters for a PID controller especially for integrator processes with deadtime. Then, L. Wang and Cluett, (1997) derive from the previous methods rules of explicit tuning for integrator processes with dead time.

The methods mentioned before, are applicable only to processes with dead time, except for the IMC method. The method proposed by Tyreus and Luyben also has a uniqueness and that is that it can be used for processes integrators without deadtime (Kaya, 2003).

6.3.3. Composition Control Structure

Based on this structure, the disturbances in the feed flow rate, and feed composition were fixed to evaluate its dynamic behavior. Figure 6-4 depicts the results of the dynamic response when the feed flow rate of LA was subjected to ±5% disturbances after 2 h and evaluated after 20 h of operation. Table 6-2, presents composition control parameters results for all three PI loops.

Table 6-2. Composition controller parameters

Controller	Controlled Variable	Manipulated Variable	Controller Gain k_c	Controller Integral Time (min)
CC 101	$x_{D\ EL}$	R	0.81754	55.4400
CC 102	$y_{prefrac\ LA}$	S_L	0.71869	40.9200
CC 103	$x_{B\ ET}$	Q_B	0.04020	33.0000

The controlled composition, CC 103 at the B stream returned to the steady-state after 13 h, and the value of the EL composition reaches about 99.1% mol. Although, the production requirements decrease by about 8%, and reach a lower energy demand when the LA has a 5% lower flowrate.

Additionally, the disturbances either in a higher or lower LA flowrate, all the compositions controllers present high disturbances between 2h and 13h, reaching a not regular steady-state, until 20 h.

In that sense, the manipulated variables, such as the reflux rate, and the liquid split ratio, shows a high incidence in the performance of the column, affecting the production requirements of EL. On the contrary, the performance at -5% flow rate of LA presents the same behavior, in general exhibits shorter transient deviation, as shown in Figure 6-4.

For ET flowrate disturbances, it shows the same proportional amount deviations as high as LA disturbances, offering a regular performance, such as the R and the S_L, about 15% of deviation, having a clear incidence in the final production, as mentioned by Wolff and Skogestad, (1995). The utility in the reboiler reaches as much as 5% of deviation from the nominal value but reaching in a great manner the EL purity requirements.

Figure 6-5 presents the behavior of three composition controllers to the set point in each of them, during 20 h of operation. It reflects that under disturbances of the ET flow rate, the control configuration reaches a stable state after 14 hours, finding that the control composition is very sensitive to disturbances of LA.

Figure 6-6 presents the behavior of three composition controllers when the compositions of ET and LA in the feed streams are disturbed, during 20 h of operation as well. It reflects that under disturbances of ET composition, the control configuration presents a difficult stabilization in terms of reaching the nominal value and represented in a real steady state.

Mainly, S_L, which shows that is necessary to flow all the liquid from the rectifying section, but in less degree in the case of the reflux rate. In the case of the production requirements, only when ET is fed with 5% less composition, the EL molar composition remains slightly above the nominal value, increasing the heat duty, and rising the bottoms rate.

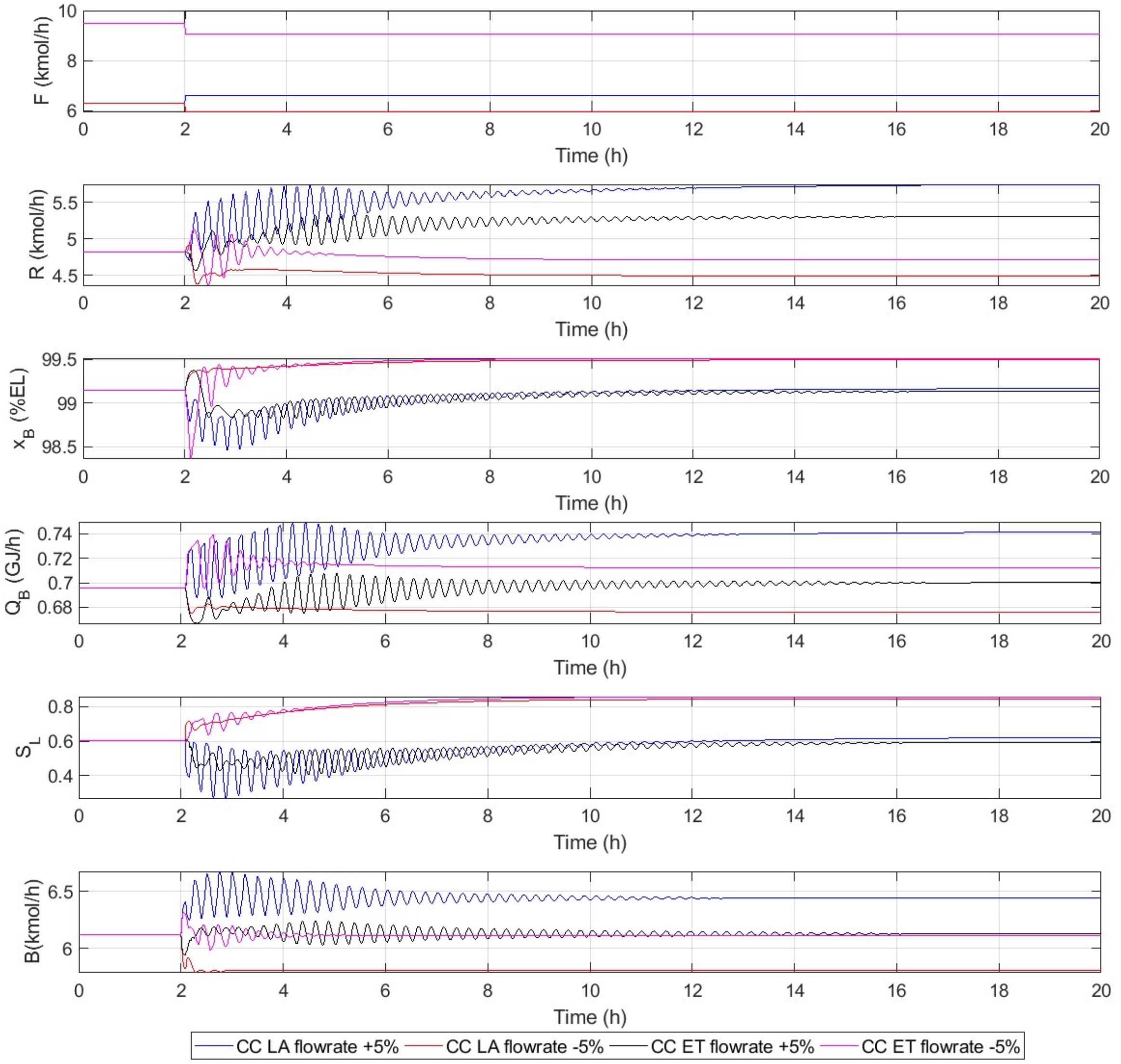


Figure 6-4. Performance of control composition structures in the RDWC after 5% LA and ET flowrate disturbances

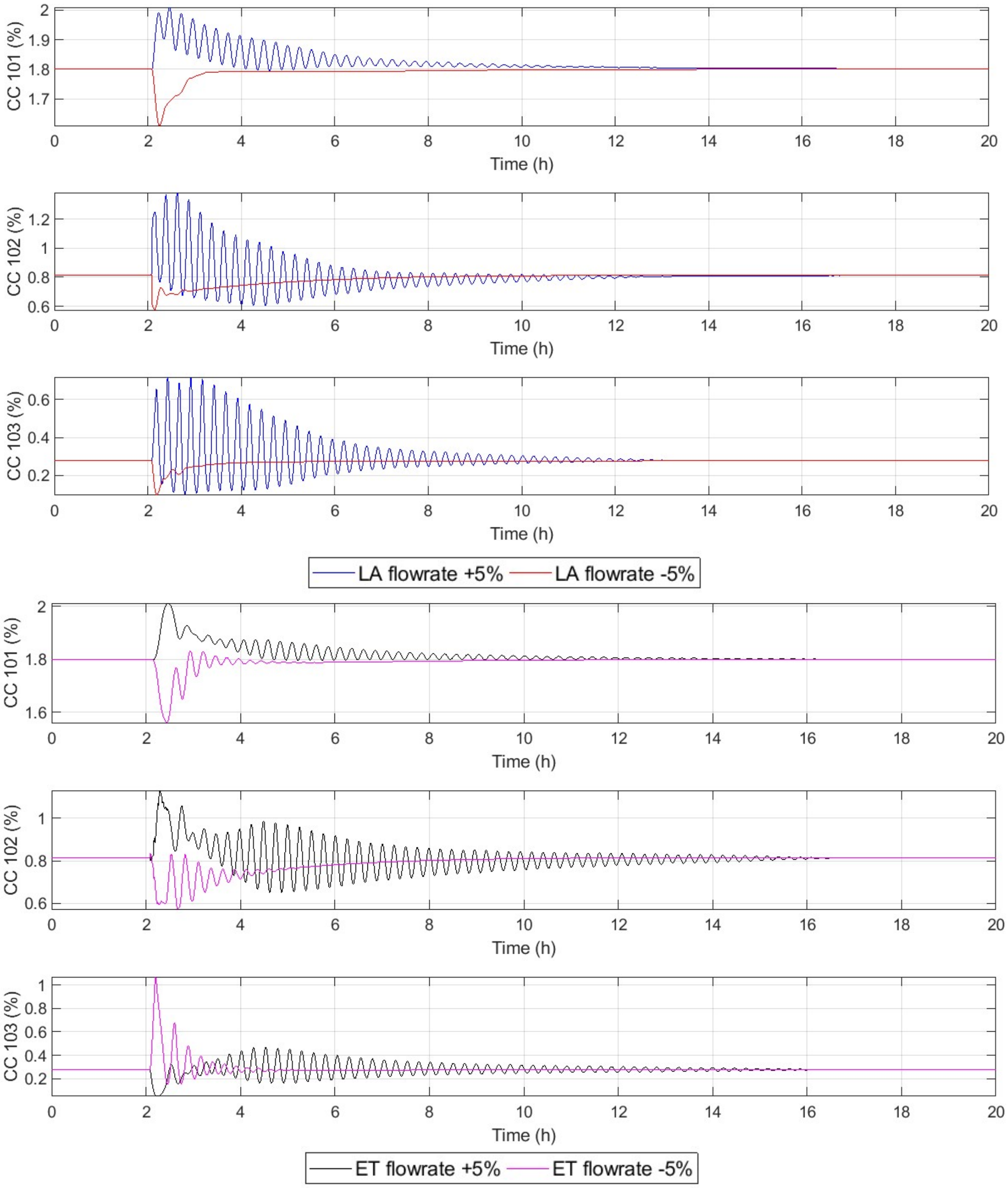


Figure 6-5. Performance of process variables of control structure in the RDWC after flowrates disturbances

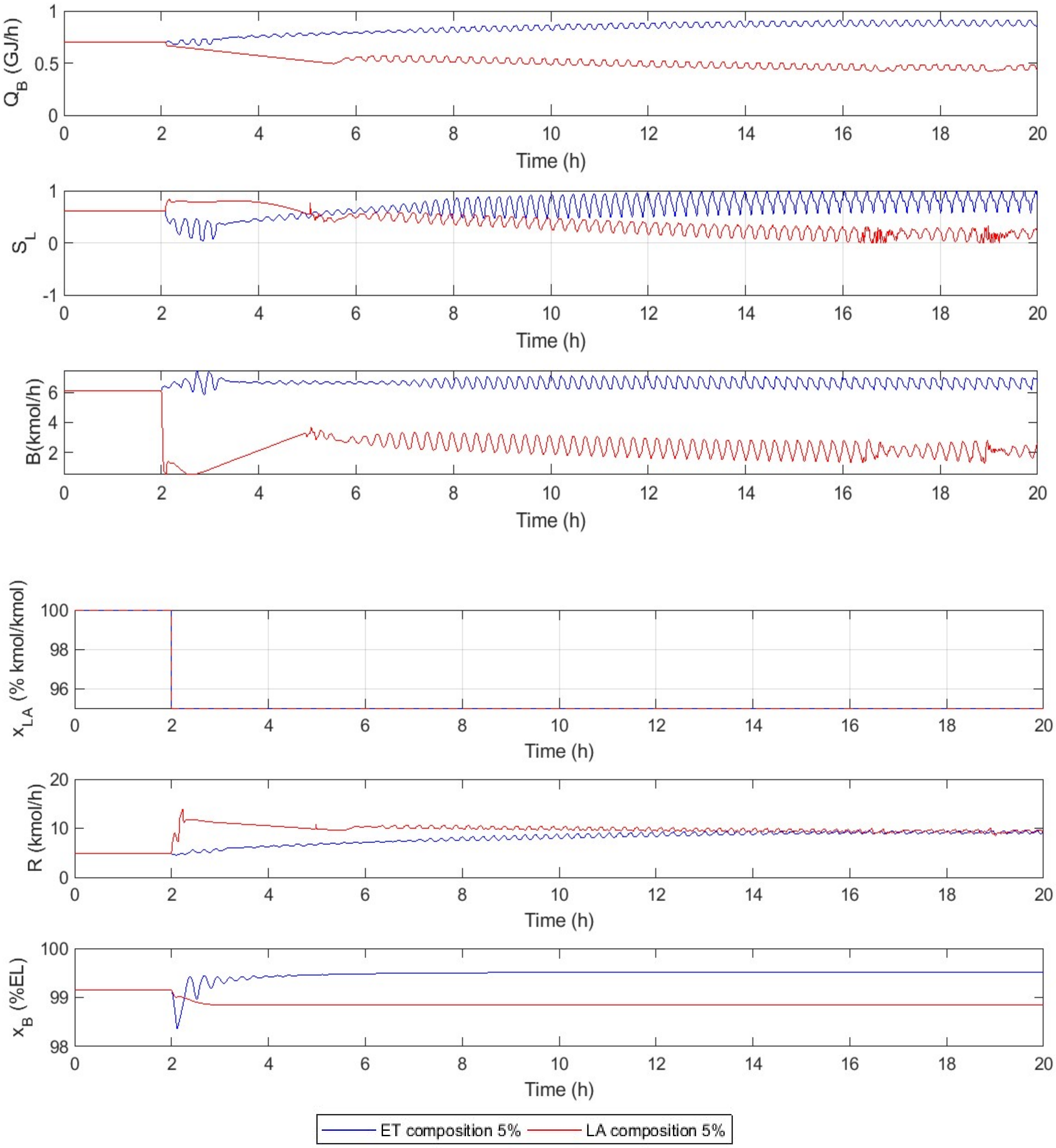


Figure 6-6. Performance of composition control structures in the RDWC after composition disturbances

6.3.4. Temperature Control Structure

Figure 6-8 gives the results of the singular value decomposition (SVD) for the main column and the prefractionator. Firstly, the steady-state gains, showing that in general, there are peaks at stages 5 and 31, in the main column and at stage 2, in the prefracionator section. Additionally, The U vectors that indicate the sensitive trays in the column. The sensitive locations are stages 5 and 31 of the main column section and stage 2 in the prefractionator section. From these results and the consideration of the dynamic relationships between the location of the temperatures and the manipulated variables, the control structure TC 101 selected controls stage 5 temperature with R, and, TC 103 controls stage 31 temperature with reboiler duty Q_B, and TC 102, the stage 2 of the prefactionator with S_L.

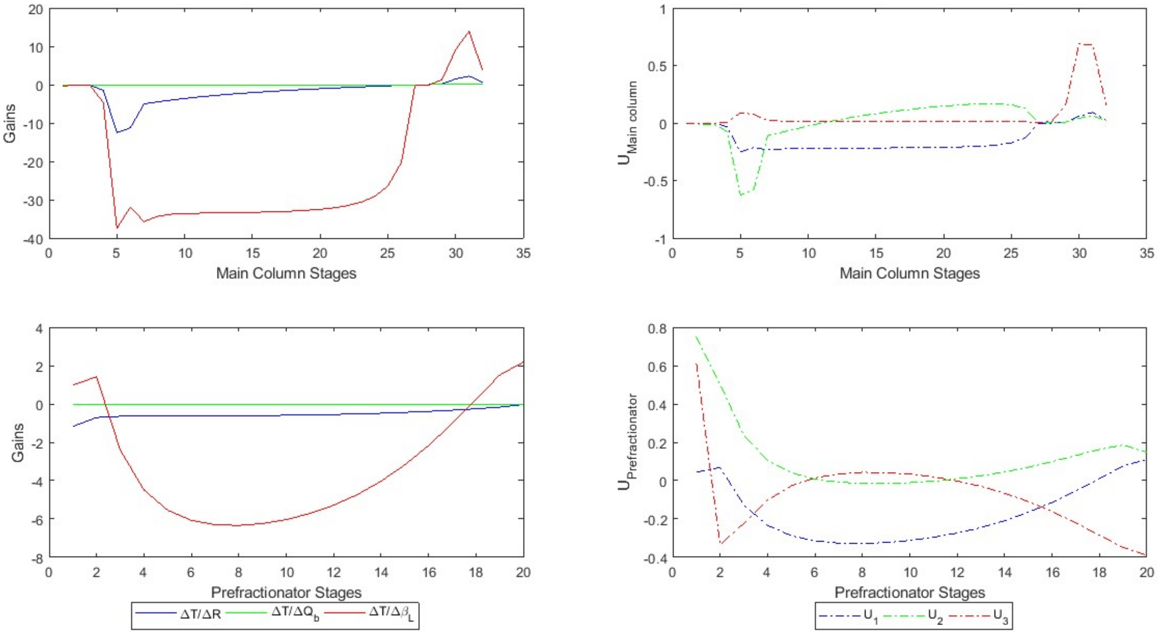


Figure 6-7. Singular value decomposition analysis (SVD) for the main column and prefractionator section

Table 6-3 summarizes the controlling tuning parameters for all the temperature control loops.

Table 6-3. Temperature Controller Tuning Parameters

Controller	**Controlled Variable**	**Manipulated Variable**	**Controller Gain k$_c$**	**Controller Integral Time (min)**
TC 101	$x_{D\ EL}$	R	7.3580	6.6000
TC 102	$y_{prefrac\ LA}$	S_L	14.1413	6.6000
TC 103	$x_{B\ ET}$	Q_B	0.9992	9.2400

Figure 6-9 shows the responses of RDWC in 5% in feed flowrates disturbances. A stable process is achieved with product purities returning closely to their specifications in about 4 h. This stabilization is much faster than the behavior observed in the composition control structure. The composition control structure could not be a feasible alternative in terms of stability and the implementation of this reactive distillation configuration, also the time of response implemented in each structure.

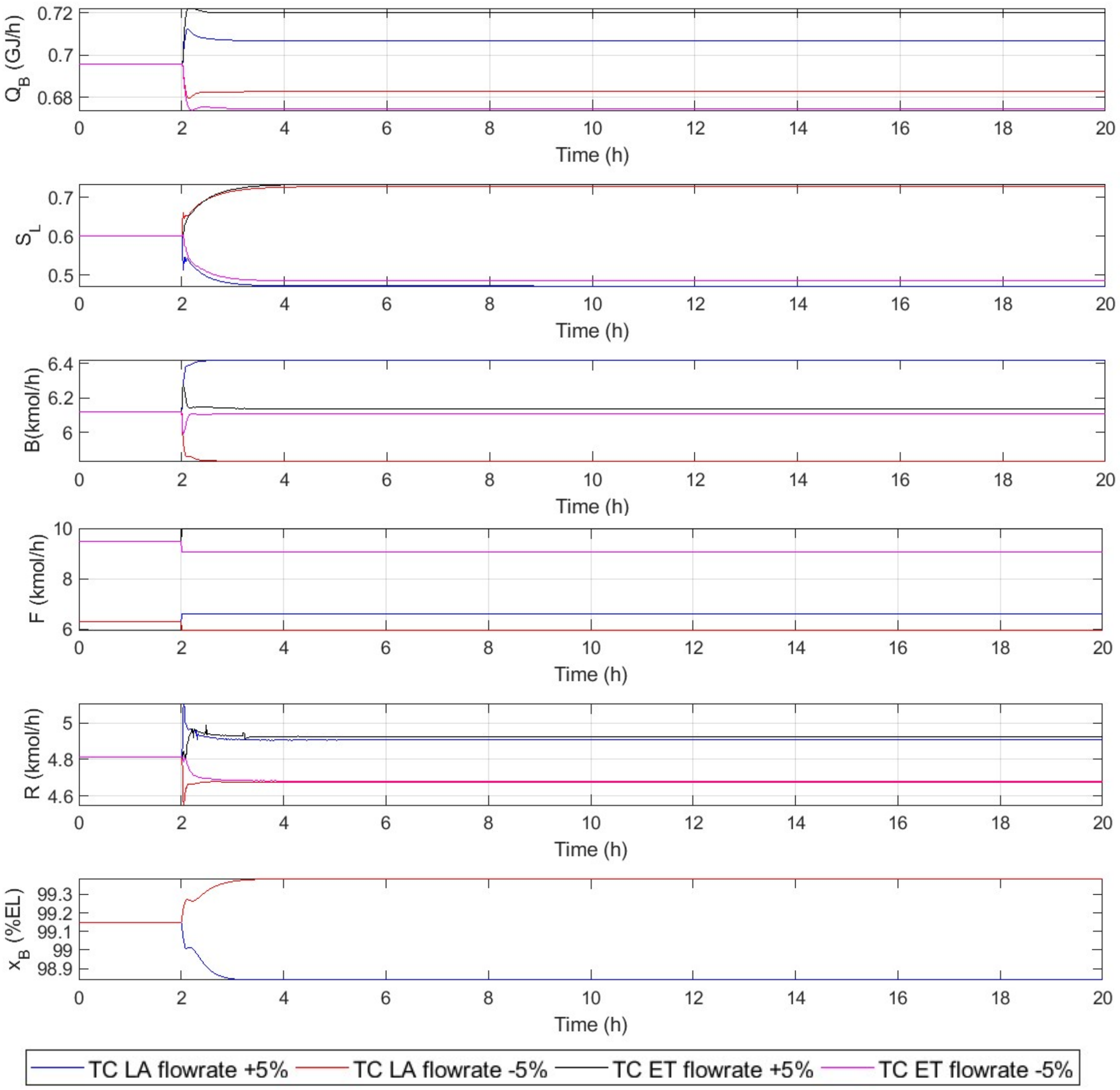


Figure 6-8. Performance of manipulated variables in the temperature control structure in the RDWC after 5% LA and ET flowrate disturbances

As a result of these disturbances, Figure 6-10 shows the performance of the controllers in each control loop. In the case of both flowrates disturbances at the feed streams, the stability reaches the set point adequately, but in the case of the temperature controller TC 102, it reaches the steady-state 1 h later that controllers TC 101 and TC 103, affecting the liquid split ratio relatively, in about 10%.

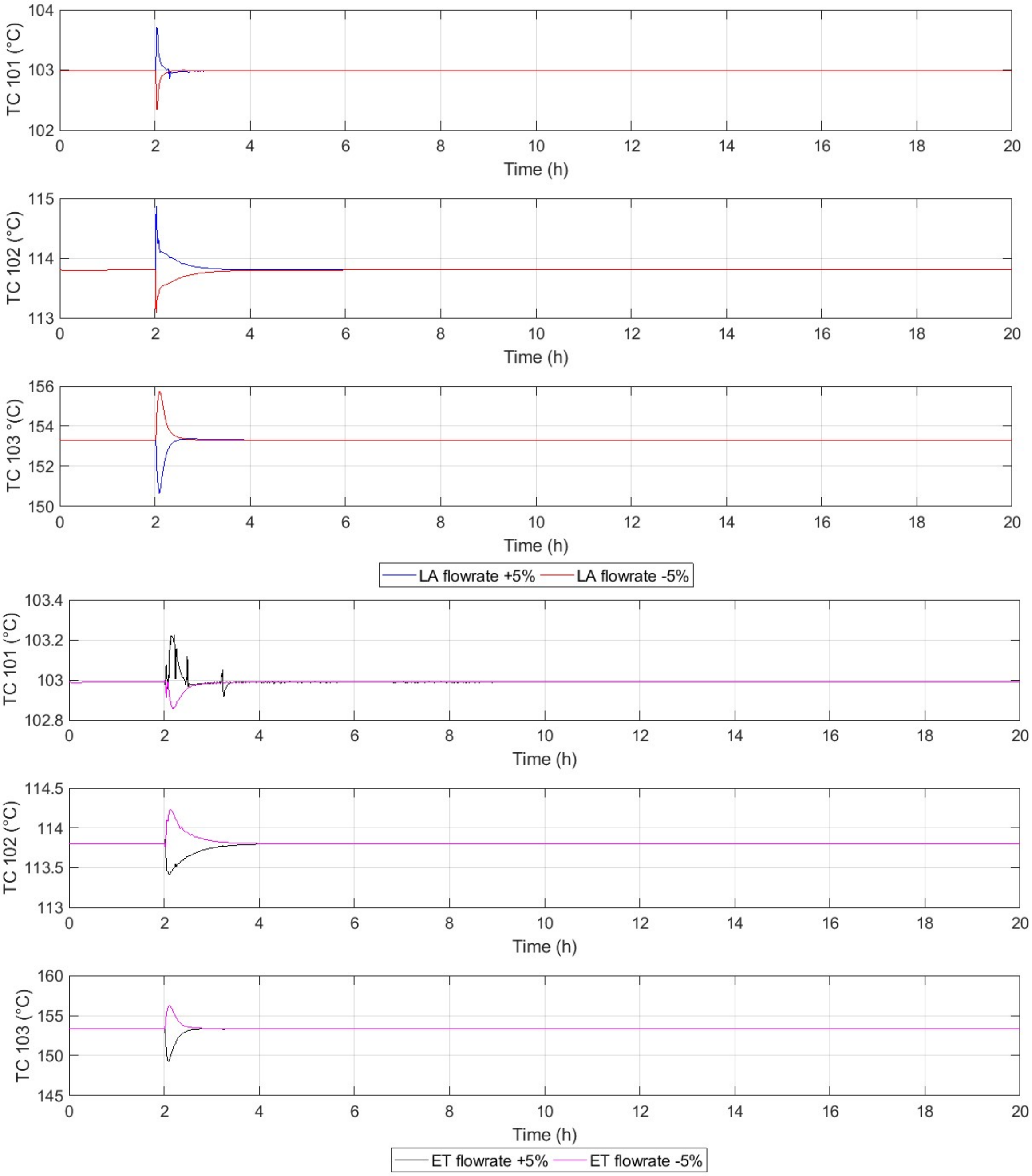
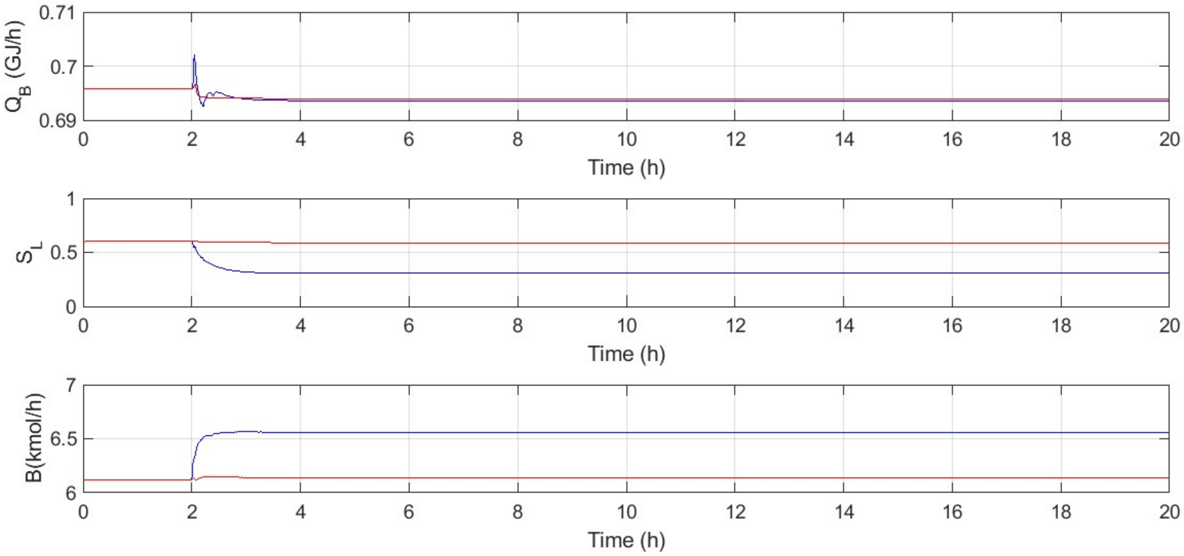


Figure 6-9. Performance of controlled variables in the temperature control structure in the RDWC after flowrates disturbances

The manipulated variables reach the new steady-state levels that are 5% higher or lower than the original. Thus, these variables ratio up and down directly with the feed flow rate. Then the conventional temperature control structure handles throughput changes well.

On the other hand, Figure 6-11 depicts the results for 5% changes in feed composition for both components. In the case of ET, the change goes to 95% mol composition, while LA remains constant. As a result, Figure 6-12 shows the temperature control structure reaching the nominal values, given the high disturbances in the moment of the composition change.



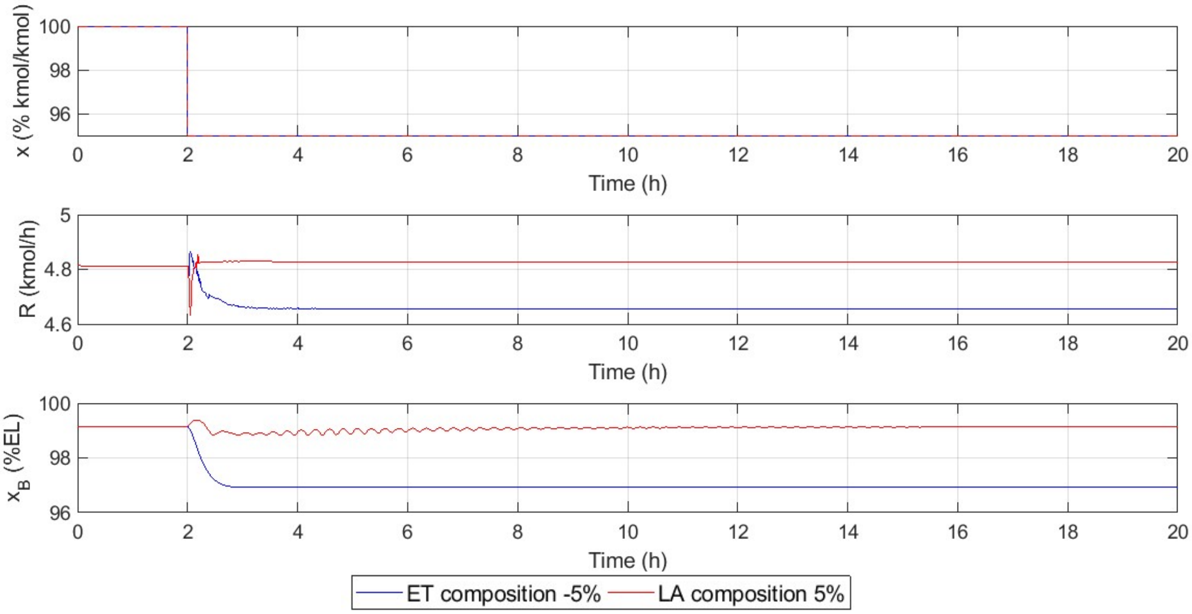


Figure 6-10. Performance of manipulated variables in the temperature control structure in the RDWC after ET and AL composition disturbances at feed streams

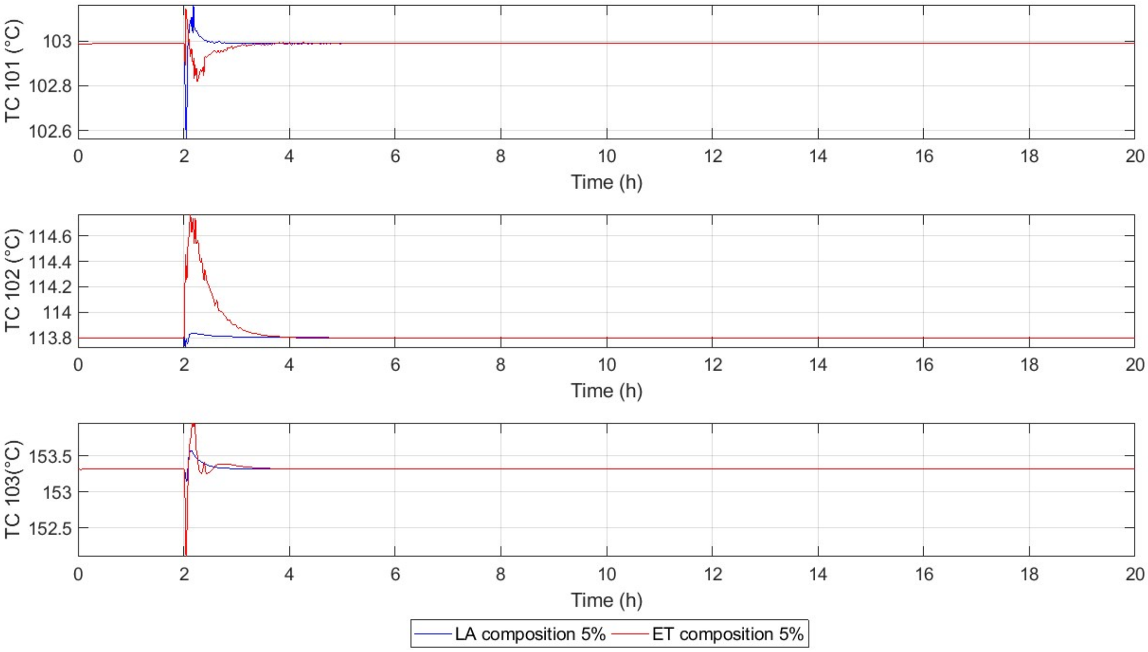


Figure 6-11. Performance of controlled variables in the temperature structure in the RDWC after composition disturbances at feed streams

In the case of LA disturbances, it faces a very low deviation to fit the steady-state, keeping the EL under the production and quality requirements. Also, the remaining manipulated variables change in less than 10%, remarking a diminution in the utility demands and insignificant change in the liquid split ratio. The response of the reflux flow rate does not affect the operation completely, and finally reaches the steady-state immediately, and despite a change of 0.5% in the instant of the disturbance occurs.

On the other hand, when the LA disturbance occurs, it presents higher deviations in terms of the quality requirements, in 2% less than in the initial value. Also, the effect in the reflux rate affects the liquid split ratio is more evident, as well as the liquid split ratio that reduces the liquid flow by 50% to the fractionator. This behavior avoids the deviation of the energy demands, that keeps quite similar to the nominal demand. It indicates that the product purity deviations are all small and acceptable for 5% disturbances in ET better than LA. Product purity returns to 99%.

In industrial applications temperature controllers are preferred to concentration control as they are less expensive and provide faster dynamics, due to lack of dead times. However, the temperature only represents the composition in the column indirectly. (Egger and Fieg, 2019).

The highly complex interactions of reaction and separation in the RDWC might lead to ambiguous representation of the concentrations by the temperature (von Harbou, *et al.*, 2017). The allocation of control and manipulated variables in this study was decided according to the proximity of both variables. Depending on the algorithm selecting the control variables different control structures might arise. Furthermore, it might be also possible, analogue to considerations of Ling and Luyben, (2009), to control the light boiling reactant on the lowest stage of the prefractionator.

6.5. Conclusions

This work proposed a temperature and composition control structures to evaluate the behavior of a RDWC to produce ethyl lactate in transient mode. The main disturbances were the composition and the flowrates of raw materials.

In the case of the composition structures, large transient deviations when the flowrates occurred, but reaching the steady-state. However, with compositions disturbances, besides the evidence of those deviations, the steady-state condition was not possible.

On the other hand, with the temperature control structure, offering a good alternative in terms of the stability of the system, and some cases, reaching the operation conditions with certain manipulation of the variables. In the case of the reflux rate and liquid split ratio, determines the energy demands.

7. CONCLUSIONS AND FURTHER WORK

7.1. Main conclusions and contributions

In the first place, a state of the art covered the synthesis, the main uses, and recent findings of the green solvent ethyl lactate. Also, it presented the main advances in the intensification of conventional reaction and separation interaction, represented in the reactive distillation and reactive wall distillation column. The challenge of the alternative of designing and implementing this kind of devices, through shortcut methods, or optimization routines could result in feasible operations.

Then, the analysis of the static method was implemented in project design, offering some advantages with little information in the design step. The inputs into the complexity of the process included the equilibrium reaction and the physicochemical data concerning to the components. The results lied in a feasible steady-state that allowed presenting a scheme under some characteristics, such as the feed condition, according to the production requirements.

Besides of this, the analysis of degrees of freedom of a reactive distillation column and the reactive wall distillation, the operation variables were specified. According to this, in the case of the RDWC, a set of variables that relates the liquid and vapor split on the zone of the wall are a key variable in the implementation of a RDWC.

Additionally, the pressure drop and the hydraulics determine not only the steady-state condition, but also the transient condition, stably keeping the operation, and feasible operability. Whereas, MESH equations described the model of both RD and RDWC, to perform an energetic study. This procedure showed an improvement in the conversion and the energy demands in the RDWC configuration, as a consequence of the reduction in the number of heat transfers, in comparison with a conventional scheme of a reactive distillation column followed by a conventional distillation column.

On the other hand, the feasible operation was evaluated in terms of the effect on the reduction of economic and environmental metrics, based on the phenomena building blocks, which was developed without a formal optimization problem. The intensification tended to minimize the number of equipment in ethyl lactate synthesis, using two different approaches. In the first situation, an extractive distillation column, for dehydrating the ethanol-water mixture, using a mixture of glycerol and ethyl lactate was carried out. The second case was using acetol as a solvent.

The identification, analysis, and decomposition of the different flowsheets determined the hot spots through the base flowsheets, resulting in the open and closed paths, which guide the generation of new alternatives of intensification. The degree of interaction in the process was analyzed from two different scales. The first scale corresponds to the phenomena building blocks (PBB), the second scale corresponds to the simultaneous building blocks (SPB), that defined a task in a processing unit.

As a consequence of this, the generation of the intensified alternatives follows a sequential step that targets improvements in terms of economic factors, and sustainability metrics during each alternative synthesis, with the use of computer-aided tools. The interaction of PBBs to generate SPBs, and then the formation of unit operations, which comply with the task of reaction, reaction-separation and a set of separations, generated three feasible alternative flowsheets. Among the alternatives generated, the most prominent alternative was the RDWC with an EDWC.

Finally, two different PI control structures implemented in a proposed RDWC. Investigating the transient behavior in a reactive divided wall distillation column. Both control structures include the different control loops to manipulate key variable to maintain a minimum energy consumption.

In the case of the composition structures, large transient deviations when the flowrates occurred, but reaching the steady-state. However, with compositions disturbances, besides the evidence of those deviations, the steady-state condition was not reachable in the middle term. Conversely, the temperature control structure offered a good alternative in terms of the stability of the system and reached the operation conditions with certain manipulation of the variables. In the case of the reflux rate and liquid split ratio, it had a high impact on energy demands.

7.2. Further work

Most of the works reported a reduction of energy demands in comparison to conventional base case design. Whereas, a reduced number of works considered other metrics such as environmental factors or security factors, detailing that could be an opportunity to explore the behavior that these variables in a project.

In the same way, more research encourages to address adequate new findings with experimental work, not only in the performance of the columns but also in the control field that could fill some gaps in this area.

It could be interesting the implementation of a double divided wall in the case of a higher degree of intensification, with a system of reaction zone with optional incorporation of extractive or azeotropic distillation with a solvent. Alternatively, the intensification could explore a viable implementation of permeation technologies that interact actively with the separation and reaction system.

On the other hand, a great interest in the inherent safety would evaluate the feasible process not only on energy demands but also in terms of controllability and safety, linking these items as an objective function of a multivariable optimization problem. In that sense, the design of the process does not involve the device as an isolated part of the process, it is important how the intensified process has a degree of impact on the environment.

Finally, another field that the process intensification could contribute to the current knowledge of these systems, is the relation of effective control systems or strategies that eventually would become a challenging task, in other words, the generation of a great numerical problem.

APPENDIX

APPENDIX A: THERMODYNAMIC AND PHYSICAL PROPERTIES

Pure components properties

Component	Ethanol	Lactic Acid	Ethyl Lactate	Water
Molecular formula	C_2H_5OH	$C_3H_6O_3$	$C_5H_{10}O_3$	H_2O
Molecular weight	46,069	90,079	118	18,015
Boiling temperature (K)	351,45	395,15	427,15	373,15
Critical temperature (K)	516,25	616	588	647,13
Critical pressure (bar)	63,84	59,65	36,6	221,2

Antoine equation coefficients

Component	A	B	C
Ethanol	7.1688	1552.6	222.42
Lactic Acid	7.2471	1968.21	158.94
Ethyl Lactate	7.8269	2489.7	273.15
Water	7.0436	1636.91	224.92

NRTL binary interaction parameters

Comp. i Comp. j	Ethanol Water	Lactic Acid Ethanol	Lactic Acid Water	Lactic Acid Ethyl	Ethanol Ethyl	Water Ethyl
a_{ij}	-0,8009	0	0	0	0	0
a_{ji}	3,4578	0	0	0	0	0
b_{ij}	246,18	13,3045	-363,3481	382,5054	343,3896	1179,0479
b_{ji}	-586,0809	30,4186	823,7980	-287,1459	-233,0714	-260,9502
c_{ij}	0,3	0,3	0,3	0,3	0,3	0,3

APPENDIX B: MATLAB CODES

Validation of the activity coefficients

```
clc
clear all
close all

T=[323.15
    323.15
    323.15
    333.15
    333.15
    343.15
    343.15
    343.15
    343.41
    343.41
    353.40
    362.87
    362.87];
Ea= 49.98; %Activation energy (Kj/mol)
k0_c= 2.70e7; %preexponential constant (mol/g*min)
K0_w=15.19; %Constant
K0_Eth=1.22; %Constant
[m,n]=size(T); %m=rows; n=columns
% pause
KW=zeros(m,n);
% pause
KEth=zeros(m,n);
kc=zeros(m,n);
Keq=zeros(m,n);
% pause
for i=1:m
    for j=1:n
KW(i,j)=K0_w*exp(12.01/T(i,j))
% pause
KEth(i,j)=K0_Eth*exp(359.63/T(i,j));
kc(i,j)=k0_c*exp(-Ea/(8.314*T(i,j)));
Keq(i,j)=exp(2.9625-(515.13/T(i,j)));
    end

end
```

Construction of the analysis of the statics procedure

```
clear all
close all
clc
```

```
% Returns the differential equation of the forward path of the RCM. It
% describes the change of the liquid composition in time.
% feed conditions

%Ethanol (1)
%Lactic Acid (2)
%Ethyl Lactate (3)
%Water (4)

% %% Properties of the system
```

Kinetic parameters

```
nu = [-1 -1 1 1];
ref = 1;
Comp = [2 3 4];
% System Pressure
P=101.325;
```

Initial liquid compositions reactive

```
Data_react = [0.5 0
0.05 0.05
0.10 0.10
0.20 0.20
0.20 0.79
0.30 0.69
0.40 0.59
0.50 0.49
0.60 0.39
0.65 0.34
0.70 0.29
0.75 0.24
0.80 0.19
0.90 0.09
0.99 0.01];


[XXfr,YYfr,ZZfr,XXbr,YYbr,ZZbr,XTf1,XTf2,XTf3,XTb1,XTb2,XTb3] =
react_alg(Data_react,P,nu,ref,Comp);

%%Plots
figure(1)
[AA,BB,CC,DD]=tetra_plot();
hold on
azeotrope_2= [0.9697 0.0303*sqrt(3) 0];
Az2=plot3(azeotrope_2(:,1),azeotrope_2(:,2),azeotrope_2(:,3),'d');
hold on
```

```
% pause
azeotrope=[0.1048 0 0]; %azeotrope (ethanol-water)
h=azeotrope;
Aze=plot3(h(1),h(2),h(3),'d');
text(h(1)-0.09,h(2)+0.03,h(3)-0.09, 'Az_E_O_H_-_W 351.3 K','FontName','Times New Roman');
text(azeotrope_2(1)+0.04,azeotrope_2(2)+0.03,azeotrope_2(3)+0.045, 'Az_E_t_h_y_l_-_W 373 K','FontName','Times New Roman');
% break
% Location of points
[Ad1,Ad2,II,Ex_OH,Ex_Lac]=Feed_lines(AA,BB,CC,DD); %Advance lines
Advance1=Ad1;       %upper Reaction advance surface limit
Advance2=Ad2;       %lower Reaction advance surface limit
Est=II; %Advance Stoichiometric line
hh=[0:1/6:1];
% Equation of planes
[A1,planefunction1]=plane_equation(AA,BB,CC);   %Equation of the polyhedron plane
[A2,planefunction2]=plane_equation(AA,BB,DD);   %Equation of the polyhedron plane
[A3,planefunction3]=plane_equation(AA,CC,DD);   %Equation of the polyhedron plane
[A4,planefunction4]=plane_equation(BB,CC,DD);   %Equation of the polyhedron plane
```

First case: ethanol and lactic (equimolar feed) direct sequence

```
[pseudo1,PP1]=P_WCalc(Est,h,planefunction3,A3,hh(1));    %Relation pw
[pseudo,PP2]=P_WCalc(Est,h,planefunction4,A4,hh(2:end));    %Relation pw
Pseudo=[pseudo1;pseudo];
PP=[PP1;PP2];
P0=PP1-pseudo1;
P_=PP2-pseudo;
P1=[P0;P_];
for i=1:length(PP)
    W1(i,:)=Pseudo(i,:)-h;
    pw1(i,:)=P1(i,:)/W1(i,:);
    point1(:,:)=[h;PP(i,:)];
    AAs=plot3(PP(:,1),PP(:,2),PP(:,3),'sk');
    As=plot3(point1(:,1),point1(:,2),point1(:,3),'-r');
    Us=plot3(Pseudo(:,1),Pseudo(:,2),Pseudo(:,3),'ko');
end
hold on
Es=plot3(Est(:,1),Est(:,2),Est(:,3),'-k');
hold on
Is=plot3(Advance2(:,1),Advance2(:,2),Advance2(:,3),'--m');
hold on
Os=plot3(Advance1(:,1),Advance1(:,2),Advance1(:,3),'--m');
hold off
axis off
legend([Aze,AAs,Us,Es,As,Is],'Distillate Composition','Bottom Compositions','Pseudoinitial compositions','Extent of reaction line','Mass Balance lines','Chemical Interaction manifold');
set(legend,'FontName','Times New Roman');
```

Second case: ethanol and lactic (equimolar feed) indirect sequence

```
figure(2)
[AA,BB,CC,DD]=tetra_plot();
hold on
azeotrope_2= [0.9697 0.0303*sqrt(3) 0];
Az2=plot3(azeotrope_2(:,1),azeotrope_2(:,2),azeotrope_2(:,3),'d');
text(azeotrope_2(1)+0.04,azeotrope_2(2)+0.03,azeotrope_2(3)+0.045, 'Az_E_t_h_y_l_-_W 373
K','FontName','Times New Roman');
hold on
Est=II;     %Stoichiometric line
h=DD;
[pseudo,PP]=P_WCalc(Est,h,planefunction1,A1,hh);    %Relation pw
Pseudo=pseudo;
W2=Pseudo-PP;
for i=1:length(PP)
    P2(i,:)=h-Pseudo(i,:);
    pw2(i,:)=(P2(i,:)/W2(i,:));
    point2(:,:)=[h;PP(i,:)];
    AAs=plot3(PP(:,1),PP(:,2),PP(:,3),'sk');
    As=plot3(point2(:,1),point2(:,2),point2(:,3),'-r');
    Us=plot3(Pseudo(:,1),Pseudo(:,2),Pseudo(:,3),'ko');
end
azeotrope=[0.1048 0 0]; %azeotrope (ethanol-water)
Aze=plot3(h(1),h(2),h(3),'d');
text(azeotrope(1)-0.09,azeotrope(2)+0.03,azeotrope(3)-0.09, 'Az_E_O_H_-_W 351.3
K','FontName','Times New Roman');
hold on
Es=plot3(Est(:,1),Est(:,2),Est(:,3),'-k');
hold on
Is=plot3(Advance2(:,1),Advance2(:,2),Advance2(:,3),'--m');
hold on
Os=plot3(Advance1(:,1),Advance1(:,2),Advance1(:,3),'--m');
hold off
axis off
legend([Aze,AAs,Us,Es,As,Is],'Bottom Composition','Distillate Compositions','Pseudoinitial
compositions','Extent of reaction line','Mass Balance lines','Chemical Interaction
manifold')
set(legend,'FontName','Times New Roman')
```

Third case: excess of ethanol (direct)

```
figure (3)
[AA,BB,CC,DD]=tetra_plot();
hold on
azeotrope_2= [0.9697 0.0303*sqrt(3) 0];
Az2=plot3(azeotrope_2(:,1),azeotrope_2(:,2),azeotrope_2(:,3),'d');
text(azeotrope_2(1)+0.04,azeotrope_2(2)+0.03,azeotrope_2(3)+0.045, 'Az_E_t_h_y_l_-_W 373
K','FontName','Times New Roman');
```

```
hold on
Est=Ex_OH;
h=azeotrope;
[pseudo1,PP1]=P_WCalc(Est,h,planefunction3,A3,hh(1:2));    %Relation pw
[pseudo,PP2]=P_WCalc(Est,h,planefunction4,A4,hh(3:end));    %Relation pw
Pseudo=[pseudo1;pseudo];
PP=[PP1;PP2];
P0=PP1-pseudo1;
P_=PP2-pseudo;
P3=[P0;P_];
for i=1:length(PP)
    W3(i,:)=Pseudo(i,:)-h;
    pw3(i,:)=P3(i,:)/W3(i,:);
    point3(:,:)=[h;PP(i,:)];
    AAs=plot3(PP(:,1),PP(:,2),PP(:,3),'sk');
    As=plot3(point3(:,1),point3(:,2),point3(:,3),'-r');
    Us=plot3(Pseudo(:,1),Pseudo(:,2),Pseudo(:,3),'ko');
end
Aze=plot3(h(1),h(2),h(3),'d');
text(h(1)-0.09,h(2)+0.03,h(3)-0.09, 'Az_E_O_H_-_W 351.3 K','FontName','Times New Roman');
hold on
Es=plot3(Est(:,1),Est(:,2),Est(:,3),'-k');
hold on
Is=plot3(Advance2(:,1),Advance2(:,2),Advance2(:,3),'--m');
hold on
Os=plot3(Advance1(:,1),Advance1(:,2),Advance1(:,3),'--m');
hold off
axis off
legend([Aze,AAs,Us,Es,As,Is],'Distillate Composition','Bottom Compositions','Pseudoinitial
compositions','Extent of reaction line','Mass Balance lines','Chemical Interaction
manifold')
set(legend,'FontName','Times New Roman')
```

Fourth case: excess of ethanol (indirect)

```
figure (4)
[AA,BB,CC,DD]=tetra_plot();
hold on
azeotrope_2= [0.9697 0.0303*sqrt(3) 0];
Az2=plot3(azeotrope_2(:,1),azeotrope_2(:,2),azeotrope_2(:,3),'d');
text(azeotrope_2(1)+0.04,azeotrope_2(2)+0.03,azeotrope_2(3)+0.045, 'Az_E_t_h_y_l_-_W 373
K','FontName','Times New Roman');

hold on
Est=Ex_OH;
h=DD;
[pseudo,PP]=P_WCalc(Est,h,planefunction1,A1,hh);   %Relation pw
Pseudo=pseudo;
W4=PP-Pseudo;
for i=1:length(PP)
```

```
    P4(i,:)=Pseudo(i,:)-h;
    pw4(i,:)=P4(i,:)/W4(i,:);
    point4(:,:)=[h;PP(i,:)];
    AAs=plot3(PP(:,1),PP(:,2),PP(:,3),'sk');
    As=plot3(point4(:,1),point4(:,2),point4(:,3),'-r');
    Us=plot3(Pseudo(:,1),Pseudo(:,2),Pseudo(:,3),'ko');
end
azeotrope=[0.1048 0 0]; %azeotrope (ethanol-water)
Aze=plot3(h(1),h(2),h(3),'d');
text(azeotrope(1)-0.09,azeotrope(2)+0.03,azeotrope(3)-0.09, 'Az_E_O_H_-_W 351.3
K','FontName','Times New Roman');
hold on
Es=plot3(Est(:,1),Est(:,2),Est(:,3),'-k');
hold on
Is=plot3(Advance2(:,1),Advance2(:,2),Advance2(:,3),'--m');
hold on
Os=plot3(Advance1(:,1),Advance1(:,2),Advance1(:,3),'--m');
hold off
axis off
legend([Aze,AAs,Us,Es,As,Is],'Bottom Composition','Distillate Compositions','Pseudoinitial
compositions','Extent of reaction line','Mass Balance lines','Chemical Interaction
manifold')
set(legend,'FontName','Times New Roman')
```

Fifth case Excess of lactic acid (direct)

```
figure (5)
[AA,BB,CC,DD]=tetra_plot();
hold on
azeotrope_2= [0.9697 0.0303*sqrt(3) 0];
Az2=plot3(azeotrope_2(:,1),azeotrope_2(:,2),azeotrope_2(:,3),'d');
text(azeotrope_2(1)+0.04,azeotrope_2(2)+0.03,azeotrope_2(3)+0.045, 'Az_E_t_h_y_l_-_W 373
K','FontName','Times New Roman');

hold on
Est=Ex_Lac;
h=azeotrope;
[pseudo1,PP1]=P_WCalc(Est,h,planefunction3,A3,hh(1));    %Relation pw
[pseudo,PP2]=P_WCalc(Est,h,planefunction4,A4,hh(2:end));    %Relation pw
PP=[PP1;PP2];
P0=PP1-pseudo1;
P_=PP2-pseudo;
P5=[P0;P_];
Pseudo=[pseudo1;pseudo];
% P5=PP-Pseudo;
for i=1:length(PP)
    W5(i,:)=Pseudo(i,:)-h;
    pw5(i,:)=P5(i,:)/W5(i,:);
    point5(:,:)=[h;PP(i,:)];
    AAs=plot3(PP(:,1),PP(:,2),PP(:,3),'sk');
```

```
    As=plot3(point5(:,1),point5(:,2),point5(:,3),'-r');
    Us=plot3(Pseudo(:,1),Pseudo(:,2),Pseudo(:,3),'ko');
end
Aze=plot3(h(1),h(2),h(3),'d');
text(h(1)-0.09,h(2)+0.03,h(3)-0.09, 'Az_E_O_H_-_W 351.3 K','FontName','Times New Roman');
hold on
Es=plot3(Est(:,1),Est(:,2),Est(:,3),'-k');
hold on
Is=plot3(Advance2(:,1),Advance2(:,2),Advance2(:,3),'--m');
hold on
Os=plot3(Advance1(:,1),Advance1(:,2),Advance1(:,3),'--m');
hold off
axis off
legend([Aze,AAs,Us,Es,As,Is],'Distillate Composition','Bottom Compositions','Pseudoinitial
compositions','Extent of reaction line','Mass Balance lines','Chemical Interaction
manifold')
set(legend,'FontName','Times New Roman')
```

Sixth case Excess of lactic acid (indirect)

```
figure (6)
[AA,BB,CC,DD]=tetra_plot();
hold on
azeotrope_2= [0.9697 0.0303*sqrt(3) 0];
Az2=plot3(azeotrope_2(:,1),azeotrope_2(:,2),azeotrope_2(:,3),'d');
text(azeotrope_2(1)+0.04,azeotrope_2(2)+0.03,azeotrope_2(3)+0.045, 'Az_E_t_h_y_l_-_W 373
K','FontName','Times New Roman');

hold on
Est=Ex_Lac;
h=DD;
[pseudo,PP]=P_WCalc(Est,h,planefunction1,A1,hh);    %Relation pw
Pseudo=pseudo;
W6=PP-Pseudo;
for i=1:length(PP)
    P6(i,:)=Pseudo(i,:)-h;
    pw6(i,:)=P6(i,:)/W6(i,:);
    point6(:,:)=[h;PP(i,:)];
    AAs=plot3(PP(:,1),PP(:,2),PP(:,3),'sk');
    As=plot3(point6(:,1),point6(:,2),point6(:,3),'-r');
    Us=plot3(Pseudo(:,1),Pseudo(:,2),Pseudo(:,3),'ko');
end
azeotrope=[0.1048 0 0]; %azeotrope (ethanol-water)
Aze=plot3(h(1),h(2),h(3),'d');
text(azeotrope(1)-0.09,azeotrope(2)+0.03,azeotrope(3)-0.09, 'Az_E_O_H_-_W 351.3
K','FontName','Times New Roman');
hold on
Es=plot3(Est(:,1),Est(:,2),Est(:,3),'-k');
hold on
Is=plot3(Advance2(:,1),Advance2(:,2),Advance2(:,3),'--m');
```

```
hold on
Os=plot3(Advance1(:,1),Advance1(:,2),Advance1(:,3),'--m');
hold off
axis off
legend([Aze,AAs,Us,Es,As,Is],'Bottom Composition','Distillate Compositions','Pseudoinitial
compositions','Extent of reaction line','Mass Balance lines','Chemical Interaction
manifold')
set(legend,'FontName','Times New Roman')
```

P/W plots

```
figure (7)
X_axe_direct=[0 0.1 0.19 0.29 0.34 0.4 0.5];
plot(X_axe_direct,pw1);
Point1=[0.1 0.1];
Point2=[0 max(pw1)];
hold on
ylim([0 1]);
plot(Point1,Point2,'-k')
legend('Separation branches','Limiting steady state (S1)')
set(legend,'FontName','Times New Roman')
ylabel('P/W Ratio','FontName','Times New Roman')
xlabel('Pseudo initial molar fraction compositions X^*, ethyl lactate','FontName','Times
New Roman')
title('Direct separation-Equimolar at the feed','FontName','Times New Roman')

figure (8)
pw2(end,1)=30;
X_axe_direct=[0 0.1 0.19 0.29 0.34 0.4 0.5];
plot(X_axe_direct,pw2);
Point1=[0.5 0.5];
Point2=[0 30];
hold on
ylim([0 20]);
xlim([0 0.55]);
plot(Point1,Point2,'-k')
legend('Separation branches','Limiting steady state
(S2)','Location','northwest','FontName','Times New Roman')
ylabel('P/W Ratio','FontName','Times New Roman')
xlabel('Pseudo initial molar fraction compositions X^* of ethyl lactate','FontName','Times
New Roman')
title('Indirect separation-Equimolar at the feed','FontName','Times New Roman')
% pause
figure (9)
X_axe_direct=[0 0.06 0.11 0.16 0.21 0.26 0.3];
plot(X_axe_direct,pw3);
Point1=[0.11 0.11];
Point2=[0 max(pw3)];
hold on
ylim([0 3]);
```

```
plot(Point1,Point2,'-k')
legend('Separation branches','Limiting steady state (S1)')
set(legend,'FontName','Times New Roman')
ylabel('P/W Ratio','FontName','Times New Roman')
xlabel('Pseudo initial molar fraction compositions X^* of ethyl lactate','FontName','Times
New Roman')
title('Direct separation-Ethanol excess at the feed','FontName','Times New Roman')

figure (10)
pw4(end,1)=30;
X_axe_direct=[0 0.06 0.11 0.16 0.21 0.26 0.3];
plot(X_axe_direct,pw4);
Point1=[0.3 0.3];
Point2=[0 30];
hold on
ylim([0 25]);
xlim([0 0.35]);
plot(Point1,Point2,'-k')
legend('Separation branches','Limiting steady state (S2)','Location','northwest')
set(legend,'FontName','Times New Roman')
ylabel('P/W Ratio','FontName','Times New Roman')
xlabel('Pseudo initial molar fraction compositions X^* of ethyl lactate','FontName','Times
New Roman')
title('Indirect separation-Ethanol excess at the feed','FontName','Times New Roman')

figure (11)
X_axe_direct=[0 0.1 0.19 0.29 0.34 0.4 0.5];
plot(X_axe_direct,pw5);
Point1=[0.1 0.1];
Point2=[0 max(pw5)];
hold on
ylim([0 0.31]);
plot(Point1,Point2,'-k')
legend('Separation branches','Limiting steady state (S1)')
set(legend,'FontName','Times New Roman')
ylabel('P/W Ratio','FontName','Times New Roman')
xlabel('Pseudo initial molar fraction compositions X^* of ethyl lactate','FontName','Times
New Roman')
title('Direct separation-Lactic acid excess at the feed','FontName','Times New Roman')

figure (12)
X_axe_direct=[0 0.06 0.10 0.15 0.19 0.23 0.31];
plot(X_axe_direct,pw6);
Point1=[0.31 0.31];
Point2=[0 max(pw6)];
hold on
ylim([0 1.1]);
plot(Point1,Point2,'-k')
legend('Separation branches','Limiting steady state
(S1)','Location','northwest','FontName','Times New Roman')
ylabel('P/W Ratio')
```

```
xlabel('Pseudo initial molar fraction compositions X^* of ethyl lactate','FontName','Times New Roman')
title('Indirect separation-Lactic acid excess at the feed','FontName','Times New Roman')

%%Limiting steady states
```

First case: ethanol and lactic (equimolar feed) direct sequence

```
figure(13)
[AA,BB,CC,DD]=tetra_plot();
hold on
azeotrope_2= [0.9697 0.0303*sqrt(3) 0];
Az2=plot3(azeotrope_2(:,1),azeotrope_2(:,2),azeotrope_2(:,3),'d');
hold on
% pause
azeotrope=[0.1048 0 0]; %azeotrope (ethanol-water)
h=azeotrope;
Aze=plot3(h(1),h(2),h(3),'d');
text(h(1)-0.09,h(2)+0.03,h(3)-0.09, 'Az_E_O_H_-_W 351.3 K'),'FontName','Times New Roman';
text(azeotrope_2(1)+0.04,azeotrope_2(2)+0.03,azeotrope_2(3)+0.045, 'Az_E_t_h_y_l_-_W 373 K','FontName','Times New Roman');
% break
% Location of points
[Ad1,Ad2,II,Ex_OH,Ex_Lac]=Feed_lines(AA,BB,CC,DD); %Advance lines
Advance1=Ad1;       %upper Reaction advance surface limit
Advance2=Ad2;       %lower Reaction advance surface limit
Est=II; %Advance Stoichiometric line
hh=[0:1/6:1];
% Equation of planes
[A1,planefunction1]=plane_equation(AA,BB,CC);   %Equation of the polyhedron plane
[A2,planefunction2]=plane_equation(AA,BB,DD);   %Equation of the polyhedron plane
[A3,planefunction3]=plane_equation(AA,CC,DD);   %Equation of the polyhedron plane
[A4,planefunction4]=plane_equation(BB,CC,DD);   %Equation of the polyhedron plane
```

Second case: ethanol and lactic (equimolar feed) indirect sequence

```
[pseudo1,PP1]=P_WCalc(Est,h,planefunction3,A3,hh(1));    %Relation pw
[pseudo,PP2]=P_WCalc(Est,h,planefunction4,A4,hh(2:end));    %Relation pw
Pseudo=[pseudo1;pseudo];
PP=[PP1;PP2];
P0=PP1-pseudo1;
P_=PP2-pseudo;
P1=[P0;P_];
% for i=1:length(PP)
    W1(2,:)=Pseudo(2,:)-h;
    pw1(2,:)=P1(2,:)/W1(2,:);
%     point1(:,:)=[h;PP(i,:)];
```

```
    point1(2,:)=PP(2,:);
    AAs=plot3(PP(2,1),PP(2,2),PP(2,3),'sk');
    As=plot3(point1(:,1),point1(:,2),point1(:,3),'-r');
    Us=plot3(Pseudo(2,1),Pseudo(2,2),Pseudo(2,3),'ko');
% end
hold on
Es=plot3(Est(:,1),Est(:,2),Est(:,3),'-k');
hold on
Is=plot3(Advance2(:,1),Advance2(:,2),Advance2(:,3),'--m');
hold on
Os=plot3(Advance1(:,1),Advance1(:,2),Advance1(:,3),'--m');
hold on

Trayectory1=[h;AA];
Trayectory2=[AA;CC];
Trayectory3=[CC;PP(2,:)];
T1=plot3(Trayectory1(:,1),Trayectory1(:,2),Trayectory1(:,3),'--k');
T2=plot3(Trayectory2(:,1),Trayectory2(:,2),Trayectory2(:,3),'--k');
T3=plot3(Trayectory3(:,1),Trayectory3(:,2),Trayectory3(:,3),'--k');

hold on
colormap hsv
A=surface(XXfr,YYfr,ZZfr);
B=surface(XXbr,YYbr,ZZbr);
colormap summer
shading interp
alpha 0.5;
axis off
hold off
axis off
% legend([Aze,AAs,Us,Es,As,Is,T3],'Distillate Composition','Bottom
Compositions','Pseudoinitial compositions','Extent of reaction line','Mass Balance
lines','Chemical Interaction manifold','Attempt trajectory','FontName','Times New Roman');
% break
```

Third case Indirect sequence equimolar feed

```
figure(14)
[AA,BB,CC,DD]=tetra_plot();
hold on
azeotrope_2= [0.9697 0.0303*sqrt(3) 0];
Az2=plot3(azeotrope_2(:,1),azeotrope_2(:,2),azeotrope_2(:,3),'d');
text(azeotrope_2(1)+0.04,azeotrope_2(2)+0.03,azeotrope_2(3)+0.045, 'Az_E_t_h_y_l_-_W 373
K','FontName','Times New Roman');
hold on
Est=II;     %Stoichiometric line
h=DD;
[pseudo,PP]=P_WCalc(Est,h,planefunction1,A1,hh);    %Relation pw
Pseudo=pseudo;
W2=Pseudo-PP;
```

```
% for i=1:length(PP)
    P2(end,:)=h-Pseudo(end,:);
    pw2(end,:)=(P2(end,:)/W2(end,:));
%     point2(end,:)=[h;PP(end,:)];
    AAs=plot3(PP(end,1),PP(end,2),PP(end,3),'sk');
    As=plot3(point2(:,1),point2(:,2),point2(:,3),'-r');
    Us=plot3(Pseudo(end,1),Pseudo(end,2),Pseudo(end,3),'ko');
% end
azeotrope=[0.1048 0 0]; %azeotrope (ethanol-water)
Aze=plot3(h(1),h(2),h(3),'d');
text(azeotrope(1)-0.09,azeotrope(2)+0.03,azeotrope(3)-0.09, 'Az_E_O_H_-_W 351.3
K','FontName','Times New Roman');
hold on
Es=plot3(Est(:,1),Est(:,2),Est(:,3),'-k');
hold on
Is=plot3(Advance2(:,1),Advance2(:,2),Advance2(:,3),'--m');
hold on
Os=plot3(Advance1(:,1),Advance1(:,2),Advance1(:,3),'--m');
hold on
Trayectory1=[h;CC];
% Trayectory2=[CC;CC];
Trayectory3=[CC;PP(end,:)];
T1=plot3(Trayectory1(:,1),Trayectory1(:,2),Trayectory1(:,3),'--k');
% T2=plot3(Trayectory2(:,1),Trayectory2(:,2),Trayectory2(:,3),'--k');
T3=plot3(Trayectory3(:,1),Trayectory3(:,2),Trayectory3(:,3),'--k');

colormap hsv
A=surface(XXfr,YYfr,ZZfr);
B=surface(XXbr,YYbr,ZZbr);
alpha 0.5
colormap summer
shading interp
C=[A;B];
hold off
axis off
```

```
figure (15)
[AA,BB,CC,DD]=tetra_plot();
hold on
azeotrope_2= [0.9697 0.0303*sqrt(3) 0];
Az2=plot3(azeotrope_2(:,1),azeotrope_2(:,2),azeotrope_2(:,3),'d');
text(azeotrope_2(1)+0.04,azeotrope_2(2)+0.03,azeotrope_2(3)+0.045, 'Az_E_t_h_y_l_-_W 373
K','FontName','Times New Roman');
hold on
Est=Ex_OH;
h=azeotrope;
[pseudo1,PP1]=P_WCalc(Est,h,planefunction3,A3,hh(1:2));    %Relation pw
[pseudo,PP2]=P_WCalc(Est,h,planefunction4,A4,hh(3:end));    %Relation pw
```

```
Pseudo=[pseudo1;pseudo];
PP=[PP1;PP2];
P0=PP1-pseudo1;
P_=PP2-pseudo;
P3=[P0;P_];
for i=1:length(PP)
    W3(i,:)=Pseudo(i,:)-h;
    pw3(i,:)=P3(i,:)/W3(i,:);
    if i==3
    point3(:,:)=[h;PP(i,:)];
    AAs=plot3(PP(i,1),PP(i,2),PP(i,3),'sk');
    As=plot3(point3(:,1),point3(:,2),point3(:,3),'-r');
    Us=plot3(Pseudo(i,1),Pseudo(i,2),Pseudo(i,3),'ko');
    end
end
Aze=plot3(h(1),h(2),h(3),'d');
text(h(1)-0.09,h(2)+0.03,h(3)-0.09, 'Az_E_O_H_-_W 351.3 K','FontName','Times New Roman');
hold on
Es=plot3(Est(:,1),Est(:,2),Est(:,3),'-k');
hold on
Is=plot3(Advance2(:,1),Advance2(:,2),Advance2(:,3),'--m');
hold on
Os=plot3(Advance1(:,1),Advance1(:,2),Advance1(:,3),'--m');
hold on
Trayectory1=[h;AA];
Trayectory2=[AA;CC];
Trayectory3=[CC;PP(3,:)];
T1=plot3(Trayectory1(:,1),Trayectory1(:,2),Trayectory1(:,3),'--k');
T2=plot3(Trayectory2(:,1),Trayectory2(:,2),Trayectory2(:,3),'--k');
T3=plot3(Trayectory3(:,1),Trayectory3(:,2),Trayectory3(:,3),'--k');

colormap hsv
A=surface(XXfr,YYfr,ZZfr);
B=surface(XXbr,YYbr,ZZbr);
alpha 0.5
colormap summer
shading interp
C=[A;B];
axis off
hold off
```

Fourth case: excess of ethanol (indirect)

```
figure (16)
[AA,BB,CC,DD]=tetra_plot();
hold on
azeotrope_2= [0.9697 0.0303*sqrt(3) 0];
Az2=plot3(azeotrope_2(:,1),azeotrope_2(:,2),azeotrope_2(:,3),'d');
text(azeotrope_2(1)+0.04,azeotrope_2(2)+0.03,azeotrope_2(3)+0.045, 'Az_E_t_h_y_l_-_W 373
```

```
K','FontName','Times New Roman');

hold on
Est=Ex_OH;
h=DD;
[pseudo,PP]=P_WCalc(Est,h,planefunction1,A1,hh);   %Relation pw
Pseudo=pseudo;
W4=PP-Pseudo;
for i=1:length(PP)
    P4(i,:)=Pseudo(i,:)-h;
    pw4(i,:)=P4(i,:)/W4(i,:);
    if i==length(PP)
    point4(:,:)=[h;PP(i,:)];
    AAs=plot3(PP(i,1),PP(i,2),PP(i,3),'sk');
    As=plot3(point4(:,1),point4(:,2),point4(:,3),'-r');
    Us=plot3(Pseudo(i,1),Pseudo(i,2),Pseudo(i,3),'ko');
    end
end
azeotrope=[0.1048 0 0]; %azeotrope (ethanol-water)
Aze=plot3(h(1),h(2),h(3),'d');
text(azeotrope(1)-0.09,azeotrope(2)+0.03,azeotrope(3)-0.09, 'Az_E_O_H_-_W 351.3
K','FontName','Times New Roman');
hold on
Es=plot3(Est(:,1),Est(:,2),Est(:,3),'-k');
hold on
Is=plot3(Advance2(:,1),Advance2(:,2),Advance2(:,3),'--m');
hold on
Os=plot3(Advance1(:,1),Advance1(:,2),Advance1(:,3),'--m');
hold on
Trayectory1=[h;CC];
Trayectory2=[CC;AA];
Trayectory3=[AA;PP(end,:)];
T1=plot3(Trayectory1(:,1),Trayectory1(:,2),Trayectory1(:,3),'--k');
T2=plot3(Trayectory2(:,1),Trayectory2(:,2),Trayectory2(:,3),'--k');
T3=plot3(Trayectory3(:,1),Trayectory3(:,2),Trayectory3(:,3),'--k');

colormap hsv
A=surface(XXfr,YYfr,ZZfr);
B=surface(XXbr,YYbr,ZZbr);
alpha 0.5
colormap summer
shading interp
C=[A;B];
hold off
axis off
```

Fifth case Excess of lactic acid (direct)

```
figure (17)
[AA,BB,CC,DD]=tetra_plot();
hold on
azeotrope_2= [0.9697 0.0303*sqrt(3) 0];
Az2=plot3(azeotrope_2(:,1),azeotrope_2(:,2),azeotrope_2(:,3),'d');
text(azeotrope_2(1)+0.04,azeotrope_2(2)+0.03,azeotrope_2(3)+0.045, 'Az_E_t_h_y_l_-_W 373
K','FontName','Times New Roman');

hold on
Est=Ex_Lac;
h=azeotrope;
[pseudo1,PP1]=P_WCalc(Est,h,planefunction3,A3,hh(1));    %Relation pw
[pseudo,PP2]=P_WCalc(Est,h,planefunction4,A4,hh(2:end));    %Relation pw
PP=[PP1;PP2];
P0=PP1-pseudo1;
P_=PP2-pseudo;
P5=[P0;P_];
Pseudo=[pseudo1;pseudo];
% P5=PP-Pseudo;
for i=1:length(PP)
    W5(i,:)=Pseudo(i,:)-h;
    pw5(i,:)=P5(i,:)/W5(i,:);
    if i==2
    point5(:,:)=[h;PP(i,:)];
    AAs=plot3(PP(i,1),PP(i,2),PP(i,3),'sk');
    As=plot3(point5(:,1),point5(:,2),point5(:,3),'-r');
    Us=plot3(Pseudo(i,1),Pseudo(i,2),Pseudo(i,3),'ko');
    end
end
Aze=plot3(h(1),h(2),h(3),'d');
text(h(1)-0.09,h(2)+0.03,h(3)-0.09, 'Az_E_O_H_-_W 351.3 K','FontName','Times New Roman');
hold on
Es=plot3(Est(:,1),Est(:,2),Est(:,3),'-k');
hold on
Is=plot3(Advance2(:,1),Advance2(:,2),Advance2(:,3),'--m');
hold on
Os=plot3(Advance1(:,1),Advance1(:,2),Advance1(:,3),'--m');
hold on

Trayectory1=[h;AA];
Trayectory2=[AA;CC];
Trayectory3=[CC;PP(2,:)];
T1=plot3(Trayectory1(:,1),Trayectory1(:,2),Trayectory1(:,3),'--k');
T2=plot3(Trayectory2(:,1),Trayectory2(:,2),Trayectory2(:,3),'--k');
T3=plot3(Trayectory3(:,1),Trayectory3(:,2),Trayectory3(:,3),'--k');

colormap hsv
A=surface(XXfr,YYfr,ZZfr);
B=surface(XXbr,YYbr,ZZbr);
alpha 0.5
```

```
colormap summer
shading interp
C=[A;B];
hold off
axis off
```

Sixth case Excess of lactic acid (indirect)

```
figure (18)
[AA,BB,CC,DD]=tetra_plot();
hold on
azeotrope_2= [0.9697 0.0303*sqrt(3) 0];
Az2=plot3(azeotrope_2(:,1),azeotrope_2(:,2),azeotrope_2(:,3),'d');
text(azeotrope_2(1)+0.04,azeotrope_2(2)+0.03,azeotrope_2(3)+0.045, 'Az_E_t_h_y_l_-_W 373 K','FontName','Times New Roman');

hold on
Est=Ex_Lac;
h=DD;
[pseudo,PP]=P_WCalc(Est,h,planefunction1,A1,hh);    %Relation pw
Pseudo=pseudo;
W6=PP-Pseudo;
for i=1:length(PP)
    P6(i,:)=Pseudo(i,:)-h;
    pw6(i,:)=P6(i,:)/W6(i,:);
    if i==length(PP)
    point6(:,:)=[h;PP(i,:)];
    AAs=plot3(PP(i,1),PP(i,2),PP(i,3),'sk');
    As=plot3(point6(:,1),point6(:,2),point6(:,3),'-r');
    Us=plot3(Pseudo(i,1),Pseudo(i,2),Pseudo(i,3),'ko');
    end
end
azeotrope=[0.1048 0 0]; %azeotrope (ethanol-water)
Aze=plot3(h(1),h(2),h(3),'d');
text(azeotrope(1)-0.09,azeotrope(2)+0.03,azeotrope(3)-0.09, 'Az_E_O_H_-_W 351.3 K','FontName','Times New Roman');
hold on
Es=plot3(Est(:,1),Est(:,2),Est(:,3),'-k');
hold on
Is=plot3(Advance2(:,1),Advance2(:,2),Advance2(:,3),'--m');
hold on
Os=plot3(Advance1(:,1),Advance1(:,2),Advance1(:,3),'--m');
hold on
Trayectory1=[h;CC];
Trayectory3=[CC;PP(end,:)];
T1=plot3(Trayectory1(:,1),Trayectory1(:,2),Trayectory1(:,3),'--k');
T3=plot3(Trayectory3(:,1),Trayectory3(:,2),Trayectory3(:,3),'--k');

colormap hsv
A=surface(XXfr,YYfr,ZZfr);
```

```
B=surface(XXbr,YYbr,ZZbr);
alpha 0.5
colormap summer
shading interp
C=[A;B];
hold off
axis off
```

Seventh case: ethanol and lactic (equimolar feed) direct sequence

```
figure(19)
[AA,BB,CC,DD]=tetra_plot();
azeotrope_2= [0.9697 0.0303*sqrt(3) 0];
Az2=plot3(azeotrope_2(:,1),azeotrope_2(:,2),azeotrope_2(:,3),'d');
hold on
% pause
azeotrope=[0.1048 0 0]; %azeotrope (ethanol-water)
h=azeotrope;
Aze=plot3(h(1),h(2),h(3),'d');
text(h(1)-0.09,h(2)+0.03,h(3)-0.09, 'Az_E_O_H_-_W 351.3 K','FontName','Times New Roman');
text(azeotrope_2(1)+0.04,azeotrope_2(2)+0.03,azeotrope_2(3)+0.045, 'Az_E_t_h_y_l_-_W 373
K','FontName','Times New Roman');
% break
% Location of points
[Ad1,Ad2,II,Ex_OH,Ex_Lac]=Feed_lines(AA,BB,CC,DD); %Advance lines
Advance1=Ad1;       %upper Reaction advance surface limit
Advance2=Ad2;       %lower Reaction advance surface limit
Est=II; %Advance Stoichiometric line
hh=[0:1/6:1];
% Equation of planes
[A1,planefunction1]=plane_equation(AA,BB,CC);   %Equation of the polyhedron plane
[A2,planefunction2]=plane_equation(AA,BB,DD);   %Equation of the polyhedron plane
[A3,planefunction3]=plane_equation(AA,CC,DD);   %Equation of the polyhedron plane
[A4,planefunction4]=plane_equation(BB,CC,DD);   %Equation of the polyhedron plane

[pseudo1,PP1]=P_WCalc(Est,h,planefunction3,A3,hh(1));    %Relation pw
[pseudo,PP2]=P_WCalc(Est,h,planefunction4,A4,hh(2:end));    %Relation pw
Pseudo=[pseudo1;pseudo];
PP=[PP1;PP2];
P0=PP1-pseudo1;
P_=PP2-pseudo;
P1=[P0;P_];
for i=1:length(PP)
    W1(2,:)=Pseudo(2,:)-h;
    pw1(2,:)=P1(2,:)/W1(2,:);
    if i==length(PP)
        point1(:,:)=[h;PP(i,:)];
        point1(i,:)=PP(i,:);
        AAs=plot3(PP(i,1),PP(i,2),PP(i,3),'sk');
        As=plot3(point1(:,1),point1(:,2),point1(:,3),'-r');
```

```
        Us=plot3(Pseudo(i,1),Pseudo(i,2),Pseudo(i,3),'ko');
    end
end
hold on
Es=plot3(Est(:,1),Est(:,2),Est(:,3),'-k');
hold on
Is=plot3(Advance2(:,1),Advance2(:,2),Advance2(:,3),'--m');
hold on
Os=plot3(Advance1(:,1),Advance1(:,2),Advance1(:,3),'--m');
hold on

Trayectory1=[h;azeotrope_2];
Trayectory3=[azeotrope_2;PP(end,:)];
T1=plot3(Trayectory1(:,1),Trayectory1(:,2),Trayectory1(:,3),'--k');
T3=plot3(Trayectory3(:,1),Trayectory3(:,2),Trayectory3(:,3),'--k');

colormap hsv
A=surface(XXfr,YYfr,ZZfr);
B=surface(XXbr,YYbr,ZZbr);
alpha 0.5
colormap summer
shading interp
C=[A;B];

axis off
hold off
axis off
```

Eight case excess of ethanol last state limit direct

```
figure (20)
[AA,BB,CC,DD]=tetra_plot();
hold on
azeotrope_2= [0.9697 0.0303*sqrt(3) 0];
Az2=plot3(azeotrope_2(:,1),azeotrope_2(:,2),azeotrope_2(:,3),'d');
text(azeotrope_2(1)+0.04,azeotrope_2(2)+0.03,azeotrope_2(3)+0.045, 'Az_E_t_h_y_l_-_W 373
K','FontName','Times New Roman');
hold on
Est=Ex_OH;
h=azeotrope;
[pseudo1,PP1]=P_WCalc(Est,h,planefunction3,A3,hh(1:2));    %Relation pw
[pseudo,PP2]=P_WCalc(Est,h,planefunction4,A4,hh(3:end));    %Relation pw
Pseudo=[pseudo1;pseudo];
PP=[PP1;PP2];
P0=PP1-pseudo1;
P_=PP2-pseudo;
P3=[P0;P_];
for i=1:length(PP)
    W3(i,:)=Pseudo(i,:)-h;
    pw3(i,:)=P3(i,:)/W3(i,:);
```

```
    if i==length(PP)
    point3(:,:)=[h;PP(i,:)];
    AAs=plot3(PP(i,1),PP(i,2),PP(i,3),'sk');
    As=plot3(point3(:,1),point3(:,2),point3(:,3),'-r');
    Us=plot3(Pseudo(i,1),Pseudo(i,2),Pseudo(i,3),'ko');
    end
end
Aze=plot3(h(1),h(2),h(3),'d');
text(h(1)-0.09,h(2)+0.03,h(3)-0.09, 'Az_E_O_H_-_W 351.3 K','FontName','Times New Roman');
hold on
Es=plot3(Est(:,1),Est(:,2),Est(:,3),'-k');
hold on
Is=plot3(Advance2(:,1),Advance2(:,2),Advance2(:,3),'--m');
hold on
Os=plot3(Advance1(:,1),Advance1(:,2),Advance1(:,3),'--m');
hold on
Trayectory1=[h;azeotrope_2];
Trayectory3=[azeotrope_2;PP(end,:)];
T1=plot3(Trayectory1(:,1),Trayectory1(:,2),Trayectory1(:,3),'--k');
T3=plot3(Trayectory3(:,1),Trayectory3(:,2),Trayectory3(:,3),'--k');

colormap hsv
A=surface(XXfr,YYfr,ZZfr);
B=surface(XXbr,YYbr,ZZbr);
alpha 0.5;
colormap summer
shading interp
C=[A;B];
axis off
hold off
```

Ninth case Excess of lactic acid (direct) last steady state

```
figure (21)
[AA,BB,CC,DD]=tetra_plot();

hold on
azeotrope_2= [0.9697 0.0303*sqrt(3) 0];
Az2=plot3(azeotrope_2(:,1),azeotrope_2(:,2),azeotrope_2(:,3),'d');
text(azeotrope_2(1)+0.04,azeotrope_2(2)+0.03,azeotrope_2(3)+0.045, 'Az_E_t_h_y_l_-_W 373 K','FontName','Times New Roman');

hold on
Est=Ex_Lac;
h=azeotrope;
[pseudo1,PP1]=P_WCalc(Est,h,planefunction3,A3,hh(1));    %Relation pw
[pseudo,PP2]=P_WCalc(Est,h,planefunction4,A4,hh(2:end));    %Relation pw
PP=[PP1;PP2];
PO=PP1-pseudo1;
P_=PP2-pseudo;
```

```
P5=[P0;P_];
Pseudo=[pseudo1;pseudo];

for i=1:length(PP)
    W5(i,:)=Pseudo(i,:)-h;
    pw5(i,:)=P5(i,:)/W5(i,:);
    if i==length(PP)
    point5(:,:)=[h;PP(i,:)];
    AAs=plot3(PP(i,1),PP(i,2),PP(i,3),'sk');
    As=plot3(point5(:,1),point5(:,2),point5(:,3),'-r');
    Us=plot3(Pseudo(i,1),Pseudo(i,2),Pseudo(i,3),'ko');
    end
end
Aze=plot3(h(1),h(2),h(3),'d');
text(h(1)-0.09,h(2)+0.03,h(3)-0.09, 'Az_E_O_H_-_W 351.3 K','FontName','Times New Roman');
hold on
Es=plot3(Est(:,1),Est(:,2),Est(:,3),'-k');
hold on
Is=plot3(Advance2(:,1),Advance2(:,2),Advance2(:,3),'--m');
hold on
Os=plot3(Advance1(:,1),Advance1(:,2),Advance1(:,3),'--m');
hold on
Trayectory1=[h;AA];
Trayectory2=[AA;CC];
Trayectory3=[CC;PP(end,:)];
T1=plot3(Trayectory1(:,1),Trayectory1(:,2),Trayectory1(:,3),'--k');
T2=plot3(Trayectory2(:,1),Trayectory2(:,2),Trayectory2(:,3),'--k');
T3=plot3(Trayectory3(:,1),Trayectory3(:,2),Trayectory3(:,3),'--k');

colormap hsv
A=surface(XXfr,YYfr,ZZfr);
B=surface(XXbr,YYbr,ZZbr);
colormap summer
shading interp
alpha 0.5;
C=[A;B];
hold off
axis off
```

APPENDIX C: ASPEN PLUS SCRIPTS

Base case script

```
;
;Input Summary created by Aspen Plus Rel. 34.0 at 12:46:26 Mon May 27,
2019
;Directory D:\Documents\Dropbox\Doctorado\Thesis simmulations\Matlab-
Aspen\Aspen\Mexico  Filename
C:\Users\HP\AppData\Local\Temp\~ap2171.txt
;
DYNAMICS
   DYNAMICS RESULTS=ON
IN-UNITS SI FLOW='kg/hr' MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
      VOLUME-FLOW='cum/hr' PRESSURE=atm PDROP=atm  &
      INVERSE-PRES='1/atm'
DEF-STREAMS CONVEN ALL
MODEL-OPTION
DATABANKS 'APV88 PURE32' / 'APV88 AQUEOUS' / 'APV88 SOLIDS' /  &
      'APV88 INORGANIC' / 'APEOSV88 AP-EOS' / NOASPENPCD
PROP-SOURCES 'APV88 PURE32' / 'APV88 AQUEOUS' / 'APV88
SOLIDS' &
       / 'APV88 INORGANIC' / 'APEOSV88 AP-EOS'
COMPONENTS
   LACTI-01 C3H6O3-D1 /
   ETHAN-01 C2H6O-2 /
   WATER H2O /
   ETHYL-01 C5H10O3-D2
SOLVE
   RUN-MODE MODE=SIM
FLOWSHEET
   BLOCK DIST2 IN=S7 OUT=ETHYLPR DUMLAC
   BLOCK DISTI1 IN=OUTPLUG OUT=ETH-WATE ETLALA
   BLOCK RPLUG IN=FPLUG OUT=OUTPLUG
   BLOCK B7 IN=ETLALA OUT=S6
   BLOCK B8 IN=S6 OUT=S7
   BLOCK B9 IN=DATAFLAC DATAFEED DUMLAC OUT=FPLUG
   BLOCK MIETOH IN=SETHFEED ETHAZREC OUT=DATAFEED
   BLOCK DISTI3 IN=ETH-WATE OUT=ETHAZREC WATER
PROPERTIES NRTL
ESTIMATE ALL
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C
PDROP=bar  &
      INVERSE-PRES='1/bar'
PROP-DATA NRTL-1
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C
PDROP=bar  &
      INVERSE-PRES='1/bar'
   PROP-LIST NRTL
   BPVAL ETHAN-01 WATER -.8009000000 246.1800000 .3000000000  &
      0.0 0.0 0.0 24.99000000 100.0000000
   BPVAL WATER ETHAN-01 3.457800000 -586.0809000 .3000000000  &
      0.0 0.0 0.0 24.99000000 100.0000000
   BPVAL LACTI-01 ETHAN-01 0.0 13.30446790 .3000000000 0.0  &
      0.0 0.0 25.00000000 25.00000000
   BPVAL ETHAN-01 LACTI-01 0.0 30.41865980 .3000000000 0.0  &
      0.0 0.0 25.00000000 25.00000000
   BPVAL LACTI-01 WATER 0.0 -363.3480970 .3000000000 0.0 0.0  &
      0.0 25.00000000 25.00000000
   BPVAL WATER LACTI-01 0.0 823.7979690 .3000000000 0.0 0.0  &
      0.0 25.00000000 25.00000000
   BPVAL LACTI-01 ETHYL-01 0.0 382.5054530 .3000000000 0.0  &
      0.0 0.0 25.00000000 25.00000000
   BPVAL ETHYL-01 LACTI-01 0.0 -287.1459390 .3000000000 0.0  &
      0.0 0.0 25.00000000 25.00000000
   BPVAL ETHAN-01 ETHYL-01 0.0 343.3895750 .3000000000 0.0  &
      0.0 0.0 25.00000000 25.00000000
   BPVAL ETHYL-01 ETHAN-01 0.0 -233.0714010 .3000000000 0.0  &
      0.0 0.0 25.00000000 25.00000000
   BPVAL WATER ETHYL-01 0.0 1179.047910 .3000000000 0.0 0.0  &
      0.0 25.00000000 25.00000000
   BPVAL ETHYL-01 WATER 0.0 -260.9501820 .3000000000 0.0 0.0  &
      0.0 25.00000000 25.00000000
STREAM DATAFEED
   SUBSTREAM MIXED PRES=1. VFRAC=0. MOLE-FLOW=9.47
   MOLE-FRAC ETHAN-01 1.

STREAM DATAFLAC
   SUBSTREAM MIXED PRES=1. VFRAC=0. MOLE-FLOW=6.27
   MOLE-FRAC LACTI-01 1.
STREAM DUMLAC
   SUBSTREAM MIXED PRES=1. VFRAC=0. MOLE-FLOW=1E-010
   MOLE-FRAC LACTI-01 0.999
STREAM ETHAZREC
   SUBSTREAM MIXED PRES=1. VFRAC=0. MOLE-FLOW=1E-005
   MOLE-FRAC ETHAN-01 0.847 / WATER 0.153 / ETHYL-01 0.01
STREAM SETHFEED
   SUBSTREAM MIXED PRES=1. VFRAC=0. MOLE-FLOW=1E-005
   MOLE-FRAC ETHAN-01 1.
BLOCK B9 MIXER
   PARAM
BLOCK MIETOH MIXER
   PARAM
BLOCK DIST2 RADFRAC
   PARAM NSTAGE=13 ALGORITHM=NEWTON INIT-
OPTION=AZEOTROPIC  &
      MAXOL=200 DAMPING=SEVERE
   COL-CONFIG CONDENSER=TOTAL
   FEEDS S7 5
   PRODUCTS ETHYLPR 1 L / DUMLAC 13 L
   P-SPEC 1 1.
   COL-SPECS DP-STAGE=0. MOLE-D=6. MOLE-RR=10.
   T-EST 1 427.9 / 2 430.7 / 3 444.7 / 4 468.3 / 5  &
      481.1 / 6 487.9 / 7 489.4 / 8 489.7 / 9 489.8 /  &
      10 489.8 / 11 489.8 / 12 489.8 / 13 489.8
   L-EST 1 54.24 / 2 49.17 / 3 40.83 / 4 37.66 / 5  &
      42.77 / 6 42.92 / 7 42.97 / 8 42.99 / 9 42.99 /  &
      10 42.99 / 11 42.99 / 12 42.99 / 13 0.751
   V-EST 1 0. / 2 59.66 / 3 54.59 / 4 46.25 / 5 43.08 / &
      6 42.02 / 7 42.17 / 8 42.22 / 9 42.23 / 10  &
      42.24 / 11 42.24 / 12 42.24 / 13 42.24
   X-EST 1 ETHAN-01 4.704E-010 / 1 WATER 5.606E-008 / 1  &
      ETHYL-01 0.99 / 1 LACTI-01 0.01 / 2 ETHAN-01  &
      3.69E-011 / 2 WATER 5.547E-009 / 2 ETHYL-01 0.9061 /  &
      2 LACTI-01 0.09393 / 3 ETHAN-01 4.5E-012 / 3 WATER  &
      8.166E-010 / 3 ETHYL-01 0.564 / 3 LACTI-01 0.436 /  &
      4 ETHAN-01 2.034E-012 / 4 WATER 3.74E-010 / 4  &
      ETHYL-01 0.2016 / 4 LACTI-01 0.7984 / 5 ETHAN-01  &
      1.62E-012 / 5 WATER 3.01E-010 / 5 ETHYL-01 0.07139 /  &
      5 LACTI-01 0.9286 / 6 ETHAN-01 3.907E-014 / 6 WATER  &
      1.123E-011 / 6 ETHYL-01 0.01461 / 6 LACTI-01 0.9854 /  &
      7 ETHAN-01 9.17E-016 / 7 WATER 4.087E-013 / 7  &
      ETHYL-01 0.002885 / 7 LACTI-01 0.9971 / 8 ETHAN-01  &
      2.14E-017 / 8 WATER 1.48E-014 / 8 ETHYL-01 0.0005653 / &
      8 LACTI-01 0.9994 / 9 ETHAN-01 4.99E-019 / 9 WATER  &
      5.351E-016 / 9 ETHYL-01 0.0001106 / 9 LACTI-01  &
      0.9999 / 10 ETHAN-01 1.163E-020 / 10 WATER  &
      1.935E-017 / 10 ETHYL-01 2.164E-005 / 10 LACTI-01 1. / &
      11 ETHAN-01 2.711E-022 / 11 WATER 6.994E-019 / 11  &
      ETHYL-01 4.233E-006 / 11 LACTI-01 1. / 12 ETHAN-01  &
      6.319E-024 / 12 WATER 2.529E-020 / 12 ETHYL-01  &
      8.275E-007 / 12 LACTI-01 1. / 13 ETHAN-01 1.472E-025 / &
      13 WATER 9.137E-022 / 13 ETHYL-01 1.613E-007 / 13  &
      LACTI-01 1.
   Y-EST 1 ETHAN-01 5.585E-009 / 1 WATER 5.399E-007 / 1  &
      ETHYL-01 0.9991 / 1 LACTI-01 0.0009359 / 2 ETHAN-01  &
      4.704E-010 / 2 WATER 5.606E-008 / 2 ETHYL-01 0.99 /  &
      2 LACTI-01 0.01 / 3 ETHAN-01 7.997E-011 / 3 WATER  &
      1.056E-008 / 3 ETHYL-01 0.9144 / 3 LACTI-01 0.08559 /  &
      4 ETHAN-01 5.913E-011 / 4 WATER 7.295E-009 / 4  &
      ETHYL-01 0.614 / 4 LACTI-01 0.386 / 5 ETHAN-01  &
      6.028E-011 / 5 WATER 7.317E-009 / 5 ETHYL-01 0.3008 /  &
      5 LACTI-01 0.6992 / 6 ETHAN-01 1.649E-012 / 6 WATER  &
      3.064E-010 / 6 ETHYL-01 0.07266 / 6 LACTI-01 0.9273 /  &
      7 ETHAN-01 3.977E-014 / 7 WATER 1.143E-011 / 7  &
      ETHYL-01 0.01487 / 7 LACTI-01 0.9851 / 8 ETHAN-01  &
      9.333E-016 / 8 WATER 4.16E-013 / 8 ETHYL-01 0.002936 / &
      8 LACTI-01 0.9971 / 9 ETHAN-01 2.178E-017 / 9 WATER  &
      1.506E-014 / 9 ETHYL-01 0.0005753 / 9 LACTI-01  &
      0.9994 / 10 ETHAN-01 5.079E-019 / 10 WATER  &
      5.446E-016 / 10 ETHYL-01 0.0001126 / 10 LACTI-01  &
      0.9999 / 11 ETHAN-01 1.184E-020 / 11 WATER  &
      1.969E-017 / 11 ETHYL-01 2.202E-005 / 11 LACTI-01 1. / &
      12 ETHAN-01 2.759E-022 / 12 WATER 7.119E-019 / 12  &
      ETHYL-01 4.305E-006 / 12 LACTI-01 1. / 13 ETHAN-01  &
      6.429E-024 / 13 WATER 2.572E-020 / 13 ETHYL-01  &
      8.393E-007 / 13 LACTI-01 1.
   SPEC 1 MOLE-RECOV 0.9999 COMPS=ETHYL-01
STREAMS=ETHYLPR  &
```

```
      BASE-STREAMS=S7 SPEC-ACTIVE=YES
   VARY 2 MOLE-D 0. 20. VARY-ACTIVE=YES
   CONVERGENCE STABLE-METH=DOGLEG
BLOCK DISTI1 RADFRAC
   PARAM NSTAGE=13 ALGORITHM=NEWTON INIT-
OPTION=AZEOTROPIC  &
      MAXOL=200 DAMPING=SEVERE
   COL-CONFIG CONDENSER=TOTAL
   FEEDS OUTPLUG 5
   PRODUCTS ETLALA 13 L / ETH-WATE 1 L
   P-SPEC 1 1.
   COL-SPECS DP-COL=0. MOLE-B=7. MOLE-RR=11.
   T-EST 1 353.8 / 2 360.7 / 3 368.4 / 4 370.5 / 5  &
      374.4 / 6 400.2 / 7 422.5 / 8 427.4 / 9 428.1 /  &
      10 428.1 / 11 428.2 / 12 428.5 / 13 431.9
   L-EST 1 38.19 / 2 37.61 / 3 38.03 / 4 37.82 / 5  &
      49.31 / 6 47.47 / 7 51.55 / 8 52.89 / 9 53.07 /  &
      10 53.09 / 11 52.99 / 12 52.06 / 13 6.174
   V-EST 1 0. / 2 47.76 / 3 47.18 / 4 47.6 / 5 47.06 /  &
      6 43.14 / 7 41.29 / 8 45.38 / 9 46.71 / 10 46.9 / &
      11 46.91 / 12 46.82 / 13 45.89
   X-EST 1 LACTI-01 6.903E-012 / 1 ETHAN-01 0.4187 / 1  &
      WATER 0.5713 / 1 ETHYL-01 0.01 / 2 LACTI-01  &
      3.018E-009 / 2 ETHAN-01 0.1118 / 2 WATER 0.8555 /  &
      2 ETHYL-01 0.03269 / 3 LACTI-01 4.933E-007 / 3  &
      ETHAN-01 0.02683 / 3 WATER 0.9244 / 3 ETHYL-01  &
      0.04882 / 4 LACTI-01 8.229E-005 / 4 ETHAN-01 0.01784 / &
      4 WATER 0.8938 / 4 ETHYL-01 0.08822 / 5 LACTI-01  &
      0.01667 / 5 ETHAN-01 0.02947 / 5 WATER 0.5429 / 5  &
      ETHYL-01 0.411 / 6 LACTI-01 0.01802 / 6 ETHAN-01  &
      0.005664 / 6 WATER 0.146 / 6 ETHYL-01 0.8303 / 7  &
      LACTI-01 0.01695 / 7 ETHAN-01 0.0006247 / 7 WATER  &
      0.02029 / 7 ETHYL-01 0.9621 / 8 LACTI-01 0.0166 /  &
      8 ETHAN-01 6.049E-005 / 8 WATER 0.002432 / 8  &
      ETHYL-01 0.9809 / 9 LACTI-01 0.01656 / 9 ETHAN-01  &
      5.748E-006 / 9 WATER 0.0002856 / 9 ETHYL-01 0.9832 /  &
      10 LACTI-01 0.01664 / 10 ETHAN-01 5.45E-007 / 10  &
      WATER 3.344E-005 / 10 ETHYL-01 0.9833 / 11 LACTI-01  &
      0.01761 / 11 ETHAN-01 5.161E-008 / 11 WATER  &
      3.912E-006 / 11 ETHYL-01 0.9824 / 12 LACTI-01  &
      0.02843 / 12 ETHAN-01 4.841E-009 / 12 WATER  &
      4.543E-007 / 12 ETHYL-01 0.9716 / 13 LACTI-01 0.1304 / &
      13 ETHAN-01 4.132E-010 / 13 WATER 4.924E-008 / 13  &
      ETHYL-01 0.8696
   Y-EST 1 LACTI-01 6.168E-015 / 1 ETHAN-01 0.6236 / 1  &
      WATER 0.3754 / 1 ETHYL-01 0.0009673 / 2 LACTI-01  &
      6.903E-012 / 2 ETHAN-01 0.4187 / 2 WATER 0.5713 /  &
      2 ETHYL-01 0.01 / 3 LACTI-01 2.407E-009 / 3  &
      ETHAN-01 0.174 / 3 WATER 0.7979 / 3 ETHYL-01  &
      0.02809 / 4 LACTI-01 3.942E-007 / 4 ETHAN-01 0.1056 /  &
      4 WATER 0.8534 / 4 ETHYL-01 0.04102 / 5 LACTI-01  &
      6.53E-005 / 5 ETHAN-01 0.09585 / 5 WATER 0.8314 /  &
      5 ETHYL-01 0.07266 / 6 LACTI-01 0.0003907 / 6  &
      ETHAN-01 0.03369 / 6 WATER 0.6206 / 6 ETHYL-01  &
      0.3453 / 7 LACTI-01 0.001218 / 7 ETHAN-01 0.00651 /  &
      7 WATER 0.1678 / 7 ETHYL-01 0.8245 / 8 LACTI-01  &
      0.001515 / 8 ETHAN-01 0.0007097 / 8 WATER 0.02305 /  &
      8 ETHYL-01 0.9747 / 9 LACTI-01 0.001558 / 9  &
      ETHAN-01 6.848E-005 / 9 WATER 0.002754 / 9 ETHYL-01  &
      0.9956 / 10 LACTI-01 0.001572 / 10 ETHAN-01  &
      6.505E-006 / 10 WATER 0.0003232 / 10 ETHYL-01 0.9981 / &
      11 LACTI-01 0.001667 / 11 ETHAN-01 6.167E-007 / 11  &
      WATER 3.783E-005 / 11 ETHYL-01 0.9983 / 12 LACTI-01  &
      0.002735 / 12 ETHAN-01 5.836E-008 / 12 WATER  &
      4.421E-006 / 12 ETHYL-01 0.9973 / 13 LACTI-01  &
      0.01471 / 13 ETHAN-01 5.437E-009 / 13 WATER  &
      5.089E-007 / 13 ETHYL-01 0.9853
BLOCK DISTI3 RADFRAC
   PARAM NSTAGE=15 ALGORITHM=NONIDEAL INIT-
OPTION=AZEOTROPIC  &
      MAXOL=200 NPHASE=2 DAMPING=SEVERE
   COL-CONFIG CONDENSER=TOTAL
   FEEDS ETH-WATE 7
   PRODUCTS WATER 15 L / ETHAZREC 1 L
   P-SPEC 1 1.
   COL-SPECS MOLE-B=6.10486398 MOLE-RR=18.7735924
   T-EST 1 351.3 / 2 351.3 / 3 351.3 / 4 351.4 / 5  &
      351.4 / 6 351.5 / 7 351.5 / 8 351.7 / 9 352. /  &
      10 353.1 / 11 357.1 / 12 368. / 13 372.6 / 14  &
      373.1 / 15 373.2
   L-EST 1 56.42 / 2 56.39 / 3 56.35 / 4 56.31 / 5  &
      56.25 / 6 56.18 / 7 60.69 / 8 60.53 / 9 60.22 /  &
      10 59.53 / 11 57.99 / 12 58.64 / 13 59.21 / 14  &
      59.29 / 15 0.842
   V-EST 1 0. / 2 60.18 / 3 60.15 / 4 60.12 / 5 60.07 / &
      6 60.01 / 7 59.94 / 8 59.85 / 9 59.68 / 10  &
      59.38 / 11 58.69 / 12 57.15 / 13 57.8 / 14 58.37 / &
      15 58.45
   X-EST 1 ETHAN-01 0.8508 / 1 WATER 0.1492 / 1 ETHYL-01  &
      1.174E-012 / 2 ETHAN-01 0.8422 / 2 WATER 0.1578 /  &
      2 ETHYL-01 1.811E-011 / 3 ETHAN-01 0.832 / 3 WATER  &
      0.168 / 3 ETHYL-01 2.628E-010 / 4 ETHAN-01 0.8195 /  &
      4 WATER 0.1805 / 4 ETHYL-01 3.797E-009 / 4 LACTI-01  &
      8.471E-024 / 5 ETHAN-01 0.8037 / 5 WATER 0.1963 /  &
      5 ETHYL-01 5.476E-008 / 5 LACTI-01 9.638E-021 / 6  &
      ETHAN-01 0.7828 / 6 WATER 0.2172 / 6 ETHYL-01  &
      7.867E-007 / 6 LACTI-01 1.111E-017 / 7 ETHAN-01  &
      0.754 / 7 WATER 0.246 / 7 ETHYL-01 1.121E-005 / 7  &
      LACTI-01 1.302E-014 / 8 ETHAN-01 0.7184 / 8 WATER  &
      0.2816 / 8 ETHYL-01 1.332E-005 / 8 LACTI-01  &
      1.305E-014 / 9 ETHAN-01 0.6539 / 9 WATER 0.346 / 9  &
      ETHYL-01 4.311E-005 / 9 LACTI-01 1.312E-014 / 10  &
      ETHAN-01 0.5094 / 10 WATER 0.4902 / 10 ETHYL-01  &
      0.000415 / 10 LACTI-01 1.328E-014 / 11 ETHAN-01  &
      0.1843 / 11 WATER 0.8137 / 11 ETHYL-01 0.002035 /  &
      11 LACTI-01 1.37E-014 / 12 ETHAN-01 0.02118 / 12  &
      WATER 0.9766 / 12 ETHYL-01 0.002184 / 12 LACTI-01  &
      1.36E-014 / 13 ETHAN-01 0.001785 / 13 WATER 0.9966 /  &
      13 ETHYL-01 0.00158 / 13 LACTI-01 1.357E-014 / 14  &
      ETHAN-01 0.0001452 / 14 WATER 0.9988 / 14 ETHYL-01  &
      0.001091 / 14 LACTI-01 2.314E-014 / 15 ETHAN-01  &
      1.173E-005 / 15 WATER 0.9992 / 15 ETHYL-01 0.0007444 / &
      15 LACTI-01 9.372E-013
   Y-EST 1 ETHAN-01 0.8576 / 1 WATER 0.1424 / 1 ETHYL-01  &
      7.62E-014 / 2 ETHAN-01 0.8508 / 2 WATER 0.1492 / 2  &
      ETHYL-01 1.174E-012 / 3 ETHAN-01 0.8428 / 3 WATER  &
      0.1572 / 3 ETHYL-01 1.705E-011 / 4 ETHAN-01 0.8332 /  &
      4 WATER 0.1668 / 4 ETHYL-01 2.465E-010 / 5 ETHAN-01  &
      0.8215 / 5 WATER 0.1785 / 5 ETHYL-01 3.56E-009 / 5  &
      LACTI-01 7.94E-024 / 6 ETHAN-01 0.8066 / 6 WATER  &
      0.1934 / 6 ETHYL-01 5.133E-008 / 6 LACTI-01  &
      9.034E-021 / 7 ETHAN-01 0.7871 / 7 WATER 0.2129 /  &
      7 ETHYL-01 7.373E-007 / 7 LACTI-01 1.042E-017 / 8  &
      ETHAN-01 0.7646 / 8 WATER 0.2354 / 8 ETHYL-01  &
      8.89E-007 / 8 LACTI-01 1.028E-017 / 9 ETHAN-01  &
      0.7285 / 9 WATER 0.2715 / 9 ETHYL-01 2.997E-006 /  &
      9 LACTI-01 1.023E-017 / 10 ETHAN-01 0.6632 / 10  &
      WATER 0.3367 / 10 ETHYL-01 3.316E-005 / 10 LACTI-01  &
      1.076E-017 / 11 ETHAN-01 0.5167 / 11 WATER 0.4829 /  &
      11 ETHYL-01 0.0004102 / 11 LACTI-01 1.938E-017 / 12  &
      ETHAN-01 0.187 / 12 WATER 0.811 / 12 ETHYL-01  &
      0.002054 / 12 LACTI-01 8.269E-017 / 13 ETHAN-01  &
      0.02149 / 13 WATER 0.9763 / 13 ETHYL-01 0.002205 /  &
      13 LACTI-01 1.35E-016 / 14 ETHAN-01 0.001811 / 14  &
      WATER 0.9966 / 14 ETHYL-01 0.001592 / 14 LACTI-01  &
      2.443E-016 / 15 ETHAN-01 0.0001471 / 15 WATER 0.9988 / &
      15 ETHYL-01 0.001096 / 15 LACTI-01 9.968E-015
   BLOCK-OPTION FREE-WATER=NO
   CONVERGENCE STABLE-METH=DOGLEG
BLOCK RPLUG RPLUG
   PARAM TYPE=ADIABATIC LENGTH=1.846961284 DIAM=1.
NPHASE=1  &
      PHASE=L CATWT=275. IGN-CAT-VOL=YES CAT-PRESENT=YES  &
      CAT-RHO=1700.000000 REACSYS=YES
   COOLANT MAXIT=200
   BLOCK-OPTION FREE-WATER=NO
   REACTIONS RXN-IDS=R-1
BLOCK B7 PUMP
   PARAM DELP=0.9
BLOCK B8 VALVE
   PARAM CALC-CV=YES P-DROP=0.001 NPHASE=1 PHASE=L
   VALVE-DEF VAL-TYPE="BUTTERFLY" MFGR="NELES-JAMESBURY"
&
      SERIES="ANSI_CLASS_300" SIZE="24-IN"
   VAL-PARAM VP-DAT=10 CV-DAT=616 XT-DAT=0.42 FL-DAT=0.76 /  &
      VP-DAT=20 CV-DAT=1290 XT-DAT=0.42 FL-DAT=0.79 /  &
      VP-DAT=30 CV-DAT=2130 XT-DAT=0.43 FL-DAT=0.82 /  &
      VP-DAT=40 CV-DAT=3160 XT-DAT=0.44 FL-DAT=0.83 /  &
      VP-DAT=50 CV-DAT=4500 XT-DAT=0.45 FL-DAT=0.83 /  &
      VP-DAT=60 CV-DAT=6250 XT-DAT=0.44 FL-DAT=0.82 /  &
      VP-DAT=70 CV-DAT=8530 XT-DAT=0.4 FL-DAT=0.8 / VP-DAT=80  &
      CV-DAT=11200 XT-DAT=0.34 FL-DAT=0.75 / VP-DAT=90  &
      CV-DAT=14300 XT-DAT=0.27 FL-DAT=0.7 / VP-DAT=100  &
      CV-DAT=15400 XT-DAT=0.24 FL-DAT=0.65
   BLOCK-OPTION FREE-WATER=NO
EO-CONV-OPTI
```

```
CONV-OPTIONS
    PARAM TEAR-METHOD=BROYDEN SPEC-METHOD=BROYDEN
    WEGSTEIN MAXIT=1000 WAIT=4
    BROYDEN MAXIT=1000 WAIT=4
CONVERGENCE CV-1 BROYDEN
    TEAR DUMLAC
CONVERGENCE CV-2 BROYDEN
    TEAR DATAFEED 0.01
CONV-ORDER CV-1 CV-2
STREAM-REPOR MOLEFLOW MOLEFRAC MASSFRAC
PROPERTY-REP PCES
REACTIONS R-1 LHHW
    REAC-DATA 1 CBASIS=MOLE-GAMMA RBASIS=REAC-VOL
    RATE-CON 1 PRE-EXP=450000. ACT-ENERGY=44980000.
    STOIC 1 MIXED LACTI-01 -1. / ETHAN-01 -1. / WATER 1. /  &
        ETHYL-01 1.
    DFORCE-EXP-1 1 MIXED LACTI-01 1. / MIXED ETHAN-01 1. /  &
        MIXED WATER 0. / MIXED ETHYL-01 0.
    DFORCE-EXP-2 1 MIXED LACTI-01 0. / MIXED ETHAN-01 0. /  &
        MIXED WATER 0. / MIXED ETHYL-01 0.
    DFORCE-EQ-1 REACNO=1 A=2.9625 B=-515.13
    DFORCE-EQ-2 REACNO=1 A=-1000000000.
    ADSORP-EXP REACNO=1 CID=LACTI-01 SSID=MIXED EXPONENT=0.
0.  &
        0. / REACNO=1 CID=ETHAN-01 SSID=MIXED EXPONENT=0. 1.  &
        0. / REACNO=1 CID=WATER SSID=MIXED EXPONENT=0. 0. 1. /  &
        REACNO=1 CID=ETHYL-01 SSID=MIXED EXPONENT=0. 0. 0.
    ADSORP-EQTER REACNO=1 TERM= 1 A=0. / REACNO=1 TERM= 2  &
        A=0.198851 B=359.63 / REACNO=1 TERM= 3 A=2.72064  &
        B=12.01
    ADSORP-POW REACNO=1 EXPONENT=2.
    PARAM NTERM-ADS=3
BALANCE B-1
    M-BAL 1 BLOCKS=MIETOH
    CALCULATE SETHFEED
;
;
;
;
;
```

Direct sequence with conventional extractive distillation

```
;
;Input Summary created by Aspen Plus Rel. 34.0 at 13:20:52 Mon May 27,
2019
;Directory   Filename C:\Users\HP\AppData\Local\Temp\~apa8ba.txt
;

DYNAMICS
    DYNAMICS RESULTS=ON
IN-UNITS SI MOLE-FLOW='kmol/hr' PRESSURE=atm PDROP='N/sqm'
DEF-STREAMS CONVEN ALL
DIAGNOSTICS
    TERMINAL SIM-LEVEL=0 CONV-LEVEL=0 COST-LEVEL=0 PROP-
LEVEL=0  &
        ECON-LEVEL=0 STREAM-LEVEL=0 SYS-LEVEL=0
SIM-OPTIONS MASS-BAL-CHE=YES ATM-PRES=1. <atm>
MODEL-OPTION
SYS-OPTIONS INTERPRET=NO BLOCK-CHECK=NO
DATABANKS 'APV88 PURE32' / 'APV88 AQUEOUS' / 'APV88 SOLIDS' /  &
        'APV88 INORGANIC' / 'APEOSV88 AP-EOS' / NOASPENPCD
PROP-SOURCES 'APV88 PURE32' / 'APV88 AQUEOUS' / 'APV88
SOLIDS' &
        / 'APV88 INORGANIC' / 'APEOSV88 AP-EOS'
COMPONENTS
    ETHAN-01 C2H6O-2 /
    LACTI-01 C3H6O3-D1 /
    ETHYL-01 C5H10O3-D2 /
    WATER H2O /
    ACETOL C3H6O2-D1
SOLVE
    RUN-MODE MODE=SIM
FLOWSHEET
    BLOCK DISTI1 IN=LACTIC ETHFEED OUT=ETHW S2
    BLOCK DISTI2 IN=S2 OUT=ETHYL LAC-REC
    BLOCK EXTRACOL IN=ETHW SOLVENT OUT=ETH-REC WENTR
    BLOCK DISTI3 IN=WENTR OUT=WATER GLY-OUT
    BLOCK B1 IN=GLY-OUT OUT=ACE-REC
    BLOCK LAC-MIX IN=LAC-REC S-LAC OUT=LACTIC
    BLOCK ETH-MIX IN=S-ETH ETH-REC OUT=ETHFEED
    BLOCK MIX-ACE IN=ACE-REC S-SOLV OUT=SOLVENT
PROPERTIES NRTL
ESTIMATE ALL
    IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C
PDROP=bar  &
        INVERSE-PRES='1/bar'
PROP-DATA NRTL-1
    IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C
PDROP=bar  &
        INVERSE-PRES='1/bar'
    PROP-LIST NRTL
    BPVAL ETHAN-01 WATER -.8009000000 246.1800000 .3000000000  &
        0.0 0.0 0.0 24.99000000 100.0000000
    BPVAL WATER ETHAN-01 3.457800000 -586.0809000 .3000000000  &
        0.0 0.0 0.0 24.99000000 100.0000000
    BPVAL LACTI-01 ETHAN-01 0.0 13.30446790 .3000000000 0.0  &
        0.0 0.0 25.00000000 25.00000000
    BPVAL ETHAN-01 LACTI-01 0.0 30.41865980 .3000000000 0.0  &
        0.0 0.0 25.00000000 25.00000000
    BPVAL LACTI-01 WATER 0.0 -363.3480970 .3000000000 0.0 0.0  &
        0.0 25.00000000 25.00000000
    BPVAL WATER LACTI-01 0.0 823.7979690 .3000000000 0.0 0.0  &
        0.0 25.00000000 25.00000000
    BPVAL LACTI-01 ETHYL-01 0.0 382.5054530 .3000000000 0.0  &
        0.0 0.0 25.00000000 25.00000000
    BPVAL ETHYL-01 LACTI-01 0.0 -287.1459390 .3000000000 0.0  &
        0.0 0.0 25.00000000 25.00000000
    BPVAL ETHAN-01 ETHYL-01 0.0 343.3895750 .3000000000 0.0  &
        0.0 0.0 25.00000000 25.00000000
    BPVAL ETHYL-01 ETHAN-01 0.0 -233.0714010 .3000000000 0.0  &
        0.0 0.0 25.00000000 25.00000000
    BPVAL WATER ETHYL-01 0.0 1179.047910 .3000000000 0.0 0.0  &
        0.0 25.00000000 25.00000000
    BPVAL ETHYL-01 WATER 0.0 -260.9501820 .3000000000 0.0 0.0  &
        0.0 25.00000000 25.00000000
    BPVAL ETHAN-01 ACETOL 0.0 321.8773140 .3000000000 0.0 0.0  &
        0.0 25.00000000 25.00000000
    BPVAL ACETOL ETHAN-01 0.0 -123.8863480 .3000000000 0.0 0.0  &
        0.0 25.00000000 25.00000000
    BPVAL LACTI-01 ACETOL 0.0 -36.29691440 .3000000000 0.0 0.0  &
        0.0 25.00000000 25.00000000
    BPVAL ACETOL LACTI-01 0.0 -70.97466980 .3000000000 0.0 0.0  &
        0.0 25.00000000 25.00000000
    BPVAL ETHYL-01 ACETOL 0.0 83.41174500 .3000000000 0.0 0.0  &
        0.0 25.00000000 25.00000000
    BPVAL ACETOL ETHYL-01 0.0 4.925117560 .3000000000 0.0 0.0  &
        0.0 25.00000000 25.00000000
    BPVAL WATER ACETOL 0.0 585.8054600 .3000000000 0.0 0.0  &
        0.0 25.00000000 25.00000000
    BPVAL ACETOL WATER 0.0 -267.2661830 .3000000000 0.0 0.0  &
        0.0 25.00000000 25.00000000
DEF-STREAMS LOAD
STREAM ETH-REC
    SUBSTREAM MIXED PRES=1. VFRAC=0. MOLE-FLOW=1E-005
    MOLE-FRAC ETHAN-01 0.9800001 / LACTI-01 1.2669E-026 /  &
        ETHYL-01 8.6068E-015 / WATER 0.0146589 / ACETOL  &
        0.0053409
STREAM ETHFEED
    SUBSTREAM MIXED PRES=1. VFRAC=0. MOLE-FLOW=9.47
    MOLE-FRAC ETHAN-01 1.
STREAM LAC-REC
    SUBSTREAM MIXED PRES=1. VFRAC=0. MOLE-FLOW=1E-005
    MOLE-FRAC ETHAN-01 2.2674E-018 / LACTI-01 0.9994674 /  &
        ETHYL-01 0.000410294 / WATER 1.7039E-017

STREAM LACTIC
    SUBSTREAM MIXED PRES=1. VFRAC=0. MOLE-FLOW=6.27
    MOLE-FRAC LACTI-01 1.
STREAM S-ETH
    SUBSTREAM MIXED PRES=1. VFRAC=0. MOLE-FLOW=1E-005
    MOLE-FRAC ETHAN-01 1.
STREAM S-LAC
    SUBSTREAM MIXED PRES=1. VFRAC=0. MOLE-FLOW=1E-005
    MOLE-FRAC LACTI-01 1.
STREAM S-SOLV
    SUBSTREAM MIXED PRES=1. VFRAC=0. MOLE-FLOW=1E-005
    MOLE-FRAC ACETOL 1.
STREAM SOLVENT
    SUBSTREAM MIXED PRES=1. VFRAC=0. MOLE-FLOW=40.
    MOLE-FRAC ACETOL 1.
BLOCK ETH-MIX MIXER
    PARAM
BLOCK LAC-MIX MIXER
```

```
   PARAM
BLOCK MIX-ACE MIXER
   PARAM
BLOCK DISTI1 RADFRAC
   PARAM NSTAGE=13 ALGORITHM=NONIDEAL MAXOL=200
DAMPING=NONE
   COL-CONFIG CONDENSER=TOTAL
   FEEDS LACTIC 6 ON-STAGE / ETHFEED 10 ON-STAGE
   PRODUCTS ETHW 1 L / S2 13 L
   P-SPEC 1 1.
   COL-SPECS MOLE-B=6.2 MOLE-RR=5.
   REAC-STAGES 6 10 SUBRTN
   HOLD-UP 6 10 MASS-LHLDP=100.
   USERK-VECS NINT=1
   USERK-REAL VALUE-LIST=10.
   UTILITIES COND-UTIL=U-1 REB-UTIL=U-2
BLOCK DISTI2 RADFRAC
   PARAM NSTAGE=13 ALGORITHM=NONIDEAL INIT-
OPTION=AZEOTROPIC  &
      MAXOL=200 DAMPING=SEVERE
   COL-CONFIG CONDENSER=TOTAL
   FEEDS S2 5
   PRODUCTS ETHYL 1 L / LAC-REC 13 L
   P-SPEC 1 1.
   COL-SPECS MOLE-D=6. MOLE-RR=2.5
   T-EST 1 392.8 / 2 420.2 / 3 425.4 / 4 428.3 / 5  &
      439.8 / 6 453.9 / 7 471.8 / 8 483.5 / 9 488. /  &
      10 489.3 / 11 489.6 / 12 489.7 / 13 489.8
   L-EST 1 8.082 / 2 8.765 / 3 8.828 / 4 8.064 / 5  &
      14.92 / 6 13.87 / 7 13.39 / 8 13.38 / 9 13.42 /  &
      10 13.43 / 11 13.43 / 12 13.43 / 13 3.767
   V-EST 1 0. / 2 11.31 / 3 12. / 4 12.06 / 5 11.3 /  &
      6 11.16 / 7 10.1 / 8 9.62 / 9 9.613 / 10 9.648 /  &
      11 9.662 / 12 9.666 / 13 9.667
   X-EST 1 ETHAN-01 0.0001651 / 1 LACTI-01 7.804E-005 / 1  &
      ETHYL-01 0.7741 / 1 WATER 0.2257 / 2 ETHAN-01  &
      1.678E-005 / 2 LACTI-01 0.00122 / 2 ETHYL-01 0.9698 /  &
      2 WATER 0.02899 / 3 ETHAN-01 5.078E-006 / 3  &
      LACTI-01 0.011 / 3 ETHYL-01 0.9799 / 3 WATER  &
      0.009126 / 4 ETHAN-01 3.986E-006 / 4 LACTI-01  &
      0.08496 / 4 ETHYL-01 0.908 / 4 WATER 0.007072 / 5  &
      ETHAN-01 3.144E-006 / 5 LACTI-01 0.3805 / 5 ETHYL-01  &
      0.6136 / 5 WATER 0.005971 / 6 ETHAN-01 1.94E-007 /  &
      6 LACTI-01 0.6053 / 6 ETHYL-01 0.3942 / 6 WATER  &
      0.0005267 / 7 ETHAN-01 8.555E-009 / 7 LACTI-01  &
      0.8375 / 7 ETHYL-01 0.1625 / 7 WATER 3.491E-005 /  &
      8 ETHAN-01 3.06E-010 / 8 LACTI-01 0.9494 / 8  &
      ETHYL-01 0.0506 / 8 WATER 1.919E-006 / 9 ETHAN-01  &
      1.008E-011 / 9 LACTI-01 0.9859 / 9 ETHYL-01 0.01414 /  &
      9 WATER 9.784E-008 / 10 ETHAN-01 3.24E-013 / 10  &
      LACTI-01 0.9962 / 10 ETHYL-01 0.003819 / 10 WATER  &
      4.873E-009 / 11 ETHAN-01 1.034E-014 / 11 LACTI-01  &
      0.999 / 11 ETHYL-01 0.001018 / 11 WATER 2.411E-010 /  &
      12 ETHAN-01 3.291E-016 / 12 LACTI-01 0.9997 / 12  &
      ETHYL-01 0.0002673 / 12 WATER 1.19E-011 / 13  &
      ETHAN-01 1.038E-017 / 13 LACTI-01 0.9999 / 13  &
      ETHYL-01 6.643E-005 / 13 WATER 5.797E-013
   Y-EST 1 ETHAN-01 0.0008139 / 1 LACTI-01 1.072E-006 / 1  &
      ETHYL-01 0.248 / 1 WATER 0.7512 / 2 ETHAN-01  &
      0.0001651 / 2 LACTI-01 7.804E-005 / 2 ETHYL-01  &
      0.7741 / 2 WATER 0.2257 / 3 ETHAN-01 5.676E-005 /  &
      3 LACTI-01 0.0009119 / 3 ETHYL-01 0.917 / 3 WATER  &
      0.08198 / 4 ETHAN-01 4.798E-005 / 4 LACTI-01  &
      0.008076 / 4 ETHYL-01 0.9247 / 4 WATER 0.06717 / 5  &
      ETHAN-01 5.01E-005 / 5 LACTI-01 0.06067 / 5 ETHYL-01  &
      0.8697 / 5 WATER 0.06962 / 6 ETHAN-01 4.205E-006 /  &
      6 LACTI-01 0.1712 / 6 ETHYL-01 0.8208 / 6 WATER  &
      0.007987 / 7 ETHAN-01 2.663E-007 / 7 LACTI-01 0.4581 / &
      7 ETHYL-01 0.5412 / 7 WATER 0.0007232 / 8 ETHAN-01  &
      1.19E-008 / 8 LACTI-01 0.7739 / 8 ETHYL-01 0.2261 /  &
      8 WATER 4.858E-005 / 9 ETHAN-01 4.259E-010 / 9  &
      LACTI-01 0.9296 / 9 ETHYL-01 0.0704 / 9 WATER  &
      2.671E-006 / 10 ETHAN-01 1.402E-011 / 10 LACTI-01  &
      0.9804 / 10 ETHYL-01 0.01963 / 10 WATER 1.36E-007 /  &
      11 ETHAN-01 4.503E-013 / 11 LACTI-01 0.9947 / 11  &
      ETHYL-01 0.005282 / 11 WATER 6.773E-009 / 12  &
      ETHAN-01 1.436E-014 / 12 LACTI-01 0.9986 / 12  &
      ETHYL-01 0.00139 / 12 WATER 3.349E-010 / 13 ETHAN-01  &
      4.534E-016 / 13 LACTI-01 0.9997 / 13 ETHYL-01  &
      0.0003456 / 13 WATER 1.632E-011
   SPEC 1 MOLE-RECOV 0.9999 COMPS=ETHYL-01 STREAMS=ETHYL
&
      BASE-STREAMS=S2
```

```
   VARY 1 MOLE-D 0. 20.
   CONVERGENCE STABLE-METH=DOGLEG
BLOCK DISTI3 RADFRAC
   PARAM NSTAGE=8 ALGORITHM=NONIDEAL INIT-
OPTION=AZEOTROPIC  &
      MAXOL=200 NPHASE=3 DAMPING=SEVERE
   COL-CONFIG CONDENSER=TOTAL
   FEEDS WENTR 4
   PRODUCTS GLY-OUT 8 L / WATER 1 L
   P-SPEC 1 0.2
   COL-SPECS MOLE-D=5.21 MOLE-RR=15.
   L2-COMPS WATER
   L2-STAGES 1 8
   BLOCK-OPTION FREE-WATER=NO
   CONVERGENCE STABLE-METH=DOGLEG
BLOCK EXTRACOL RADFRAC
   PARAM NSTAGE=20 ALGORITHM=NONIDEAL INIT-
OPTION=AZEOTROPIC  &
      MAXOL=200 NPHASE=3 DAMPING=SEVERE
   COL-CONFIG CONDENSER=TOTAL
   FEEDS ETHW 12 / SOLVENT 4
   PRODUCTS WENTR 20 L / ETH-REC 1 L
   P-SPEC 1 1.
   COL-SPECS MOLE-D=4.5 MOLE-RR=7.
   L2-COMPS WATER
   L2-STAGES 1 20
   BLOCK-OPTION FREE-WATER=NO
BLOCK B1 PUMP
   PARAM PRES=1.
UTILITY U-1 GENERAL
   DESCRIPTION "Cooling Water, Inlet Temp=20 C, Outlet Temp=25 C"
   COST ENERGY-PRICE=2.12E-007 <$/kJ>
   PARAM UTILITY-TYPE=WATER PRES=1. PRES-OUT=1. TIN=20. <C>
&
      TOUT=25. <C> CALOPT=FLASH MIN-TAPP=5. <C>  &
      HTC=0.0135 <GJ/hr-sqm-C>
UTILITY U-2 GENERAL
   DESCRIPTION  &
      "High Pressure Steam, Inlet Temp=250 C, Outlet Temp=249 C,
Pres=572 psia"
   COST ENERGY-PRICE=2.5E-006 <$/kJ>
   PARAM UTILITY-TYPE=STEAM TIN=250. <C> TOUT=249. <C>
VFRAC=1.  &
      VFR-OUT=0. CALOPT=FLASH MIN-TAPP=10. <C> CALCCO2=YES
&
      FACTORSOURCE="US-EPA-Rule-E9-5711"
FUELSOURCE="Natural_gas"  &
      CO2FACTOR=5.58900000E-8 EFFICIENCY=0.85  &
      HTC=0.0216 <GJ/hr-sqm-C>
EO-CONV-OPTI
CONV-OPTIONS
   PARAM TEAR-METHOD=WEGSTEIN TOL=0.01 SPEC-
METHOD=BROYDEN
   WEGSTEIN MAXIT=1000
   BROYDEN MAXIT=1000 WAIT=4 XTOL=0.001
CONVERGENCE CV-1 BROYDEN
   TEAR ETH-REC
CONVERGENCE CV-2 BROYDEN
   TEAR LACTIC
CONVERGENCE CV-3 BROYDEN
   TEAR SOLVENT
CONV-ORDER CV-2 CV-1 CV-3
REPORT REPORT
STREAM-REPOR MOLEFLOW MASSFLOW MOLEFRAC MASSFRAC
PROPERTY-REP PCES
REACTIONS R-1 REAC-DIST
   REAC-DATA 1
   K-STOIC 1 A=2.9625 B=-515.13
   STOIC 1 ETHAN-01 -1. / LACTI-01 -1. / ETHYL-01 1. /  &
      WATER 1.
REACTIONS SUBRTN REAC-DIST
   PARAM SUBROUTINE=ETHLACTA
   REAC-DATA 1 KINETIC
   STOIC 1 LACTI-01 -1. / ETHAN-01 -1. / WATER 1. /  &
      ETHYL-01 1.
BALANCE B-1
   M-BAL 1 BLOCKS=ETH-MIX
   CALCULATE S-ETH
BALANCE B-2
   M-BAL 1 BLOCKS=LAC-MIX
   CALCULATE S-LAC
BALANCE B-3
   M-BAL 1 BLOCKS=MIX-ACE
```

```
   CALCULATE S-SOLV
;
;
;
;
;
```

Direct sequence with intensified EDWC

```
;
;Input Summary created by Aspen Plus Rel. 34.0 at 12:57:34 Mon May 27,
2019
;Directory   Filename C:\Users\HP\AppData\Local\Temp\~ap5291.txt
;
DYNAMICS
   DYNAMICS RESULTS=ON
IN-UNITS SI FLOW='kg/hr' MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
      PRESSURE=atm PDROP='N/sqm'
DEF-STREAMS CONVEN ALL
DIAGNOSTICS
   TERMINAL SIM-LEVEL=0 CONV-LEVEL=0 COST-LEVEL=0 PROP-
LEVEL=0  &
      ECON-LEVEL=0 STREAM-LEVEL=0 SYS-LEVEL=0
SIM-OPTIONS MASS-BAL-CHE=YES ATM-PRES=1.01325000E+5
MODEL-OPTION
SYS-OPTIONS INTERPRET=NO BLOCK-CHECK=NO
DATABANKS 'APV88 PURE32' / 'APV88 AQUEOUS' / 'APV88 SOLIDS' /  &
      'APV88 INORGANIC' / 'APEOSV88 AP-EOS' / NOASPENPCD
PROP-SOURCES 'APV88 PURE32' / 'APV88 AQUEOUS' / 'APV88
SOLIDS' &
       / 'APV88 INORGANIC' / 'APEOSV88 AP-EOS'
COMPONENTS
   ETHAN-01 C2H6O-2 /
   LACTI-01 C3H6O3-D1 /
   ETHYL-01 C5H10O3-D2 /
   WATER H2O /
   GLYCEROL C3H8O3 /
   ETHYLENE C2H6O2
SOLVE
   RUN-MODE MODE=SIM
FLOWSHEET
   BLOCK DISTI1 IN=LACTIC ETHFEED OUT=ETHW S2
   BLOCK DISTI2 IN=S2 OUT=ETHYL LAC-REC
   BLOCK ETH-MIX IN=MIX-REC S-ETH OUT=ETHFEED
   BLOCK LAC-MIX IN=LAC-REC S-LAC OUT=LACTIC
   BLOCK EXT1 IN=ETHW SOLVENT S9 OUT=S1 S4
   BLOCK EXT2 IN=S8 OUT=WATER S5
   BLOCK EXT3 IN=S6 OUT=S7 GLY
   BLOCK B4 IN=S4 S5 OUT=S6
   BLOCK B6 IN=S7 OUT=S8 S9
   BLOCK MIX-GLY IN=GLY S-MAKEUP OUT=SOLVENT
   BLOCK B2 IN=S1 OUT=MIX-REC
PROPERTIES NRTL
ESTIMATE ALL
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C
PDROP=bar  &
      INVERSE-PRES='1/bar'
PROP-DATA NRTL-1
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C
PDROP=bar  &
      INVERSE-PRES='1/bar'
   PROP-LIST NRTL
   BPVAL ETHAN-01 WATER -.8009000000 246.1800000 .3000000000  &
      0.0 0.0 0.0 24.99000000 100.0000000
   BPVAL WATER ETHAN-01 3.457800000 -586.0809000 .3000000000  &
      0.0 0.0 0.0 24.99000000 100.0000000
   BPVAL LACTI-01 ETHAN-01 0.0 13.30446790 .3000000000 0.0  &
      0.0 0.0 25.00000000 25.00000000
   BPVAL ETHAN-01 LACTI-01 0.0 30.41865980 .3000000000 0.0  &
      0.0 0.0 25.00000000 25.00000000
   BPVAL LACTI-01 WATER 0.0 -363.3480970 .3000000000 0.0 0.0  &
      0.0 25.00000000 25.00000000
   BPVAL WATER LACTI-01 0.0 823.7979690 .3000000000 0.0 0.0  &
      0.0 25.00000000 25.00000000
   BPVAL LACTI-01 ETHYL-01 0.0 382.5054530 .3000000000 0.0  &
      0.0 0.0 25.00000000 25.00000000
   BPVAL ETHYL-01 LACTI-01 0.0 -287.1459390 .3000000000 0.0  &
      0.0 0.0 25.00000000 25.00000000
   BPVAL ETHAN-01 ETHYL-01 0.0 343.3895750 .3000000000 0.0  &
      0.0 0.0 25.00000000 25.00000000
   BPVAL ETHYL-01 ETHAN-01 0.0 -233.0714010 .3000000000 0.0  &
      0.0 0.0 25.00000000 25.00000000
   BPVAL WATER ETHYL-01 0.0 1179.047910 .3000000000 0.0 0.0  &
      0.0 25.00000000 25.00000000
   BPVAL ETHYL-01 WATER 0.0 -260.9501820 .3000000000 0.0 0.0  &
      0.0 25.00000000 25.00000000
   BPVAL ETHAN-01 GLYCEROL 0.0 442.7130000 .3000000000 0.0  &
      0.0 0.0 50.00000000 75.00000000
   BPVAL GLYCEROL ETHAN-01 0.0 36.13900000 .3000000000 0.0  &
      0.0 0.0 50.00000000 75.00000000
   BPVAL WATER GLYCEROL -1.251500000 272.6075000 .3000000000  &
      0.0 0.0 0.0 25.00000000 290.0000000
   BPVAL GLYCEROL WATER -.7318000000 170.9167000 .3000000000  &
      0.0 0.0 0.0 25.00000000 290.0000000
   BPVAL ETHAN-01 ETHYLENE 14.84220000 -4664.405800 .4700000000
&
      0.0 0.0 0.0 50.00000000 190.0000000
   BPVAL ETHYLENE ETHAN-01 -.1115000000 157.5937000 .4700000000
&
      0.0 0.0 0.0 50.00000000 190.0000000
   BPVAL WATER ETHYLENE .3479000000 34.82340000 .3000000000  &
      0.0 0.0 0.0 30.40000000 196.7000000
   BPVAL ETHYLENE WATER -.0567000000 -147.1373000 .3000000000
&
      0.0 0.0 0.0 30.40000000 196.7000000
   BPVAL GLYCEROL ETHYLENE 0.0 -347.5824000 .3000000000 0.0  &
      0.0 0.0 96.50000000 152.8000000
   BPVAL ETHYLENE GLYCEROL 0.0 298.1435000 .3000000000 0.0  &
      0.0 0.0 96.50000000 152.8000000
   BPVAL LACTI-01 GLYCEROL 0.0 -181.9856110 .3000000000 0.0  &
      0.0 0.0 25.00000000 25.00000000
   BPVAL GLYCEROL LACTI-01 0.0 216.1906820 .3000000000 0.0  &
      0.0 0.0 25.00000000 25.00000000
   BPVAL LACTI-01 ETHYLENE 0.0 -181.9706390 .3000000000 0.0  &
      0.0 0.0 25.00000000 25.00000000
   BPVAL ETHYLENE LACTI-01 0.0 -85.59140790 .3000000000 0.0  &
      0.0 0.0 25.00000000 25.00000000
   BPVAL ETHYL-01 GLYCEROL 0.0 283.7726280 .3000000000 0.0  &
      0.0 0.0 25.00000000 25.00000000
   BPVAL GLYCEROL ETHYL-01 0.0 108.8768290 .3000000000 0.0  &
      0.0 0.0 25.00000000 25.00000000
   BPVAL ETHYL-01 ETHYLENE 0.0 1120.726700 .3000000000 0.0  &
      0.0 0.0 25.00000000 25.00000000
   BPVAL ETHYLENE ETHYL-01 0.0 -654.1763160 .3000000000 0.0  &
      0.0 0.0 25.00000000 25.00000000
DEF-STREAMS LOAD
STREAM ETHFEED
   SUBSTREAM MIXED PRES=1. VFRAC=0. MOLE-FLOW=9.47
   MOLE-FRAC ETHAN-01 1.
STREAM LAC-REC
   SUBSTREAM MIXED PRES=1. VFRAC=0. MOLE-FLOW=1E-005
   MOLE-FRAC ETHAN-01 2.2674E-018 / LACTI-01 0.9994674 /  &
      ETHYL-01 0.000410294 / WATER 1.7039E-017 / GLYCEROL  &
      2.4146E-011 / ETHYLENE 0.000122324
STREAM LACTIC
   SUBSTREAM MIXED PRES=1. VFRAC=0. MOLE-FLOW=6.27
   MOLE-FRAC LACTI-01 1.
STREAM MIX-REC
   SUBSTREAM MIXED PRES=1. VFRAC=0. MOLE-FLOW=1E-005
   MOLE-FRAC ETHAN-01 0.9999 / ETHYL-01 7.8305E-028 / WATER  &
      6.35494E-005 / GLYCEROL 6.2576E-012 / ETHYLENE  &
      3.64513E-005
STREAM S-ETH
   SUBSTREAM MIXED PRES=1. VFRAC=0. MOLE-FLOW=1E-005
   MOLE-FRAC ETHAN-01 1.
STREAM S-LAC
   SUBSTREAM MIXED PRES=1. VFRAC=0. MOLE-FLOW=1E-005
   MOLE-FRAC LACTI-01 1.
STREAM S-MAKEUP
   SUBSTREAM MIXED PRES=1. VFRAC=0. MOLE-FLOW=1E-005
   MOLE-FRAC GLYCEROL 0.4 / ETHYLENE 0.6
STREAM SOLVENT
   SUBSTREAM MIXED PRES=1. VFRAC=0. MOLE-FLOW=9.
   MOLE-FLOW GLYCEROL 0.4 / ETHYLENE 0.6
BLOCK B4 MIXER
   PARAM MAXIT=200 TOL=0.001
BLOCK ETH-MIX MIXER
   PARAM
BLOCK LAC-MIX MIXER
   PARAM
BLOCK MIX-GLY MIXER
   PARAM
BLOCK B6 FSPLIT
   FRAC S9 0.5
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BLOCK DISTI1 RADFRAC
   PARAM NSTAGE=13 ALGORITHM=NONIDEAL MAXOL=200
DAMPING=NONE
   COL-CONFIG CONDENSER=TOTAL
   FEEDS LACTIC 6 ON-STAGE / ETHFEED 10 ON-STAGE
   PRODUCTS ETHW 1 L / S2 13 L
   P-SPEC 1 1.
   COL-SPECS MOLE-B=6.2 MOLE-RR=5.
   REAC-STAGES 6 10 SUBRTN
   HOLD-UP 6 10 MASS-LHLDP=100.
   USERK-VECS NINT=1
   USERK-REAL VALUE-LIST=10.
   UTILITIES COND-UTIL=U-1 REB-UTIL=U-2
BLOCK DISTI2 RADFRAC
   PARAM NSTAGE=13 ALGORITHM=NONIDEAL INIT-
OPTION=AZEOTROPIC  &
      MAXOL=200 DAMPING=SEVERE
   COL-CONFIG CONDENSER=TOTAL
   FEEDS S2 5
   PRODUCTS ETHYL 1 L / LAC-REC 13 L
   P-SPEC 1 1.
   COL-SPECS MOLE-D=6. MOLE-RR=2.5
   T-EST 1 392.8 / 2 420.2 / 3 425.4 / 4 428.3 / 5  &
      439.8 / 6 453.9 / 7 471.8 / 8 483.5 / 9 488. /  &
      10 489.3 / 11 489.6 / 12 489.7 / 13 489.8
   L-EST 1 8.082 / 2 8.765 / 3 8.828 / 4 8.064 / 5  &
      14.92 / 6 13.87 / 7 13.39 / 8 13.38 / 9 13.42 /  &
      10 13.43 / 11 13.43 / 12 13.43 / 13 3.767
   V-EST 1 0. / 2 11.31 / 3 12. / 4 12.06 / 5 11.3 /  &
      6 11.16 / 7 10.1 / 8 9.62 / 9 9.613 / 10 9.648 /  &
      11 9.662 / 12 9.666 / 13 9.667
   X-EST 1 ETHAN-01 0.0001651 / 1 LACTI-01 7.804E-005 / 1  &
      ETHYL-01 0.7741 / 1 WATER 0.2257 / 2 ETHAN-01  &
      1.678E-005 / 2 LACTI-01 0.00122 / 2 ETHYL-01 0.9698 /  &
      2 WATER 0.02899 / 3 ETHAN-01 5.078E-006 / 3  &
      LACTI-01 0.011 / 3 ETHYL-01 0.9799 / 3 WATER  &
      0.009126 / 4 ETHAN-01 3.986E-006 / 4 LACTI-01  &
      0.08496 / 4 ETHYL-01 0.908 / 4 WATER 0.007072 / 5  &
      ETHAN-01 3.144E-006 / 5 LACTI-01 0.3805 / 5 ETHYL-01  &
      0.6136 / 5 WATER 0.005971 / 6 ETHAN-01 1.94E-007 /  &
      6 LACTI-01 0.6053 / 6 ETHYL-01 0.3942 / 6 WATER  &
      0.0005267 / 7 ETHAN-01 8.555E-009 / 7 LACTI-01  &
      0.8375 / 7 ETHYL-01 0.1625 / 7 WATER 3.491E-005 /  &
      8 ETHAN-01 3.06E-010 / 8 LACTI-01 0.9494 / 8  &
      ETHYL-01 0.0506 / 8 WATER 1.919E-006 / 9 ETHAN-01  &
      1.008E-011 / 9 LACTI-01 0.9859 / 9 ETHYL-01 0.01414 /  &
      9 WATER 9.784E-008 / 10 ETHAN-01 3.24E-013 / 10  &
      LACTI-01 0.9962 / 10 ETHYL-01 0.003819 / 10 WATER  &
      4.873E-009 / 11 ETHAN-01 1.034E-014 / 11 LACTI-01  &
      0.999 / 11 ETHYL-01 0.001018 / 11 WATER 2.411E-010 /  &
      12 ETHAN-01 3.291E-016 / 12 LACTI-01 0.9997 / 12  &
      ETHYL-01 0.0002673 / 12 WATER 1.19E-011 / 13  &
      ETHAN-01 1.038E-017 / 13 LACTI-01 0.9999 / 13  &
      ETHYL-01 6.643E-005 / 13 WATER 5.797E-013
   Y-EST 1 ETHAN-01 0.0008139 / 1 LACTI-01 1.072E-006 / 1  &
      ETHYL-01 0.248 / 1 WATER 0.7512 / 2 ETHAN-01  &
      0.0001651 / 2 LACTI-01 7.804E-005 / 2 ETHYL-01  &
      0.7741 / 2 WATER 0.2257 / 3 ETHAN-01 5.676E-005 /  &
      3 LACTI-01 0.0009119 / 3 ETHYL-01 0.917 / 3 WATER  &
      0.08198 / 4 ETHAN-01 4.798E-005 / 4 LACTI-01  &
      0.008076 / 4 ETHYL-01 0.9247 / 4 WATER 0.06717 / 5  &
      ETHAN-01 5.01E-005 / 5 LACTI-01 0.06067 / 5 ETHYL-01  &
      0.8697 / 5 WATER 0.06962 / 6 ETHAN-01 4.205E-006 /  &
      6 LACTI-01 0.1712 / 6 ETHYL-01 0.8208 / 6 WATER  &
      0.007987 / 7 ETHAN-01 2.663E-007 / 7 LACTI-01 0.4581 / &
      7 ETHYL-01 0.5412 / 7 WATER 0.0007232 / 8 ETHAN-01  &
      1.19E-008 / 8 LACTI-01 0.7739 / 8 ETHYL-01 0.2261 /  &
      8 WATER 4.858E-005 / 9 ETHAN-01 4.259E-010 / 9  &
      LACTI-01 0.9296 / 9 ETHYL-01 0.0704 / 9 WATER  &
      2.671E-006 / 10 ETHAN-01 1.402E-011 / 10 LACTI-01  &
      0.9804 / 10 ETHYL-01 0.01963 / 10 WATER 1.36E-007 /  &
      11 ETHAN-01 4.503E-013 / 11 LACTI-01 0.9947 / 11  &
      ETHYL-01 0.005282 / 11 WATER 6.773E-009 / 12  &
      ETHAN-01 1.436E-014 / 12 LACTI-01 0.9986 / 12  &
      ETHYL-01 0.00139 / 12 WATER 3.349E-010 / 13 ETHAN-01  &
      4.534E-016 / 13 LACTI-01 0.9997 / 13 ETHYL-01  &
      0.0003456 / 13 WATER 1.632E-011
   SPEC 1 MOLE-RECOV 0.9999 COMPS=ETHYL-01 STREAMS=ETHYL
&
      BASE-STREAMS=S2
   VARY 1 MOLE-D 0.0 20.00000000
   CONVERGENCE STABLE-METH=DOGLEG
BLOCK EXT1 RADFRAC
   PARAM NSTAGE=17 ALGORITHM=NONIDEAL INIT-
OPTION=AZEOTROPIC  &
      MAXOL=200 DAMPING=SEVERE
   COL-CONFIG CONDENSER=TOTAL REBOILER=NONE
   FEEDS ETHW 9 ON-STAGE / SOLVENT 4 ON-STAGE / S9 17  &
      ON-STAGE-VAP
   PRODUCTS S4 17 L / S1 1 L
   P-SPEC 1 1.
   COL-SPECS MOLE-D=4.2
BLOCK EXT2 RADFRAC
   PARAM NSTAGE=10 ALGORITHM=NONIDEAL INIT-
OPTION=AZEOTROPIC  &
      MAXOL=200 DAMPING=SEVERE
   COL-CONFIG CONDENSER=TOTAL REBOILER=NONE
   FEEDS S8 10 ON-STAGE-VAP
   PRODUCTS WATER 1 L / S5 10 L
   P-SPEC 1 1.
   COL-SPECS MOLE-RR=1.3
BLOCK EXT3 RADFRAC
   PARAM NSTAGE=3 ALGORITHM=NONIDEAL INIT-
OPTION=AZEOTROPIC  &
      MAXOL=200 DAMPING=SEVERE
   COL-CONFIG CONDENSER=NONE
   FEEDS S6 1 ON-STAGE
   PRODUCTS GLY 3 L / S7 1 V
   P-SPEC 1 1.
   COL-SPECS MOLE-B=9.
BLOCK B2 PUMP
   PARAM PRES=1.
UTILITY U-1 GENERAL
   DESCRIPTION "Cooling Water, Inlet Temp=20 C, Outlet Temp=25 C"
   COST ENERGY-PRICE=2.1200000E-10
   PARAM UTILITY-TYPE=WATER PRES=1. PRES-OUT=1.
TIN=293.1500000  &
      TOUT=298.1500000 CALOPT=FLASH MIN-TAPP=5.000000000  &
      HTC=3750.000000
UTILITY U-2 GENERAL
   DESCRIPTION  &
      "High Pressure Steam, Inlet Temp=250 C, Outlet Temp=249 C,
Pres=572 psia"
   COST ENERGY-PRICE=2.50000000E-9
   PARAM UTILITY-TYPE=STEAM TIN=523.1500000 TOUT=522.1500000
&
      VFRAC=1. VFR-OUT=0. CALOPT=FLASH MIN-TAPP=10.00000000
&
      CALCCO2=YES FACTORSOURCE="US-EPA-Rule-E9-5711"
FUELSOURCE= &
      "Natural_gas" CO2FACTOR=5.58900000E-8 EFFICIENCY=0.85  &
      HTC=6000.000000
EO-CONV-OPTI
CONV-OPTIONS
   PARAM TEAR-METHOD=BROYDEN SPEC-METHOD=BROYDEN
   WEGSTEIN MAXIT=1000
   BROYDEN MAXIT=1000 WAIT=4 XTOL=0.01
CONVERGENCE CV-1 BROYDEN
   TEAR ETHFEED
CONVERGENCE CV-2 BROYDEN
   TEAR LACTIC
CONVERGENCE CV-3 BROYDEN
   TEAR SOLVENT
CONV-ORDER CV-1 CV-2 CV-3
REPORT REPORT
STREAM-REPOR MOLEFLOW MASSFLOW MOLEFRAC MASSFRAC
PROPERTY-REP PCES
REACTIONS R-1 REAC-DIST
   REAC-DATA 1
   K-STOIC 1 A=2.9625 B=-515.13
   STOIC 1 ETHAN-01 -1. / LACTI-01 -1. / ETHYL-01 1. /  &
      WATER 1.
REACTIONS SUBRTN REAC-DIST
   PARAM SUBROUTINE=ETHLACTA
   REAC-DATA 1 KINETIC
   STOIC 1 LACTI-01 -1. / ETHAN-01 -1. / WATER 1. /  &
      ETHYL-01 1.
BALANCE B-1
   M-BAL 1 BLOCKS=ETH-MIX
   CALCULATE S-ETH
BALANCE B-2
   M-BAL 1 BLOCKS=LAC-MIX
   CALCULATE S-LAC

BALANCE B-3
   M-BAL 1 BLOCKS=MIX-GLY
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```
   CALCULATE S-MAKEUP
;
;
;
;
;
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RDWC + EDWC script

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;
;Input Summary created by Aspen Plus Rel. 34.0 at 13:12:35 Mon May 27,
2019
;Directory   Filename C:\Users\HP\AppData\Local\Temp\~ap1354.txt
;
DYNAMICS
   DYNAMICS RESULTS=ON
IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr' PRESSURE=atm
&
      PDROP='N/sqm'
DEF-STREAMS CONVEN ALL
DIAGNOSTICS
   TERMINAL SIM-LEVEL=0 CONV-LEVEL=0 COST-LEVEL=0 PROP-
LEVEL=0  &
      ECON-LEVEL=0 STREAM-LEVEL=0 SYS-LEVEL=0
SIM-OPTIONS MASS-BAL-CHE=YES RESTART=NO BYPASS-
PROP=YES  &
      ATM-PRES=1.01325000E+5
MODEL-OPTION
SYS-OPTIONS BLOCK-CHECK=NO
DATABANKS 'APV88 PURE32' / 'APV88 AQUEOUS' / 'APV88 SOLIDS' /  &
      'APV88 INORGANIC' / 'APEOSV88 AP-EOS' / NOASPENPCD
PROP-SOURCES 'APV88 PURE32' / 'APV88 AQUEOUS' / 'APV88
SOLIDS' &
       / 'APV88 INORGANIC' / 'APEOSV88 AP-EOS'
COMPONENTS
   ETHAN-01 C2H6O-2 /
   LACTI-01 C3H6O3-D1 /
   ETHYL-01 C5H10O3-D2 /
   WATER H2O /
   ACETOL C3H6O2-D1
SOLVE
   RUN-MODE MODE=SIM
FLOWSHEET
   BLOCK PREFRAC IN=LACTICAC ETHANOL LIQ1 VAP1
OUT=PRVAPDT  &
      PRLIQBT
   BLOCK MAIN2 IN=LIQ2 VAP2 OUT=M2VAP M2LIQ
   BLOCK MAIN1 IN=PRVAPDT M2VAP OUT=AZ-OHW S12
   BLOCK MAIN3 IN=M2LIQ PRLIQBT OUT=S6 BOTTOMS
   BLOCK DIVVAP IN=S6 OUT=VAP2 VAP1
   BLOCK DIVLIQ IN=S12 OUT=LIQ1 LIQ2
   BLOCK EXT3 IN=S11 OUT=S14 GLY-REC
   BLOCK EXT2 IN=S16 OUT=WATER S17
   BLOCK B7 IN=S14 OUT=S15 S16
   BLOCK EXT1 IN=S15 SOLVENT AZ-OHW OUT=S1 S18
   BLOCK B11 IN=S17 S18 OUT=S11
   BLOCK MIX-GLY IN=GLY-REC S-MAKEUP OUT=SOLVENT
   BLOCK MIX-ETH IN=ETOH S-ETHANO OUT=ETHANOL
   BLOCK B1 IN=S1 OUT=ETOH
PROPERTIES NRTL
ESTIMATE ALL
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C
PDROP=bar  &
      INVERSE-PRES='1/bar'
PROP-DATA NRTL-1
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C
PDROP=bar  &
      INVERSE-PRES='1/bar'
   PROP-LIST NRTL
   BPVAL ETHAN-01 WATER -.8009000000 246.1800000 .3000000000  &
      0.0 0.0 0.0 24.99000000 100.0000000
   BPVAL WATER ETHAN-01 3.457800000 -586.0809000 .3000000000  &
      0.0 0.0 0.0 24.99000000 100.0000000
   BPVAL LACTI-01 ETHAN-01 0.0 13.30446790 .3000000000 0.0  &
      0.0 0.0 25.00000000 25.00000000
   BPVAL ETHAN-01 LACTI-01 0.0 30.41865980 .3000000000 0.0  &
      0.0 0.0 25.00000000 25.00000000
   BPVAL LACTI-01 WATER 0.0 -363.3480970 .3000000000 0.0 0.0  &
      0.0 25.00000000 25.00000000
   BPVAL WATER LACTI-01 0.0 823.7979690 .3000000000 0.0 0.0  &
      0.0 25.00000000 25.00000000
   BPVAL LACTI-01 ETHYL-01 0.0 382.5054530 .3000000000 0.0  &
      0.0 0.0 25.00000000 25.00000000
   BPVAL ETHYL-01 LACTI-01 0.0 -287.1459390 .3000000000 0.0  &
      0.0 0.0 25.00000000 25.00000000
   BPVAL ETHAN-01 ETHYL-01 0.0 343.3895750 .3000000000 0.0  &
      0.0 0.0 25.00000000 25.00000000
   BPVAL ETHYL-01 ETHAN-01 0.0 -233.0714010 .3000000000 0.0  &
      0.0 0.0 25.00000000 25.00000000
   BPVAL WATER ETHYL-01 0.0 1179.047910 .3000000000 0.0 0.0  &
      0.0 25.00000000 25.00000000
   BPVAL ETHYL-01 WATER 0.0 -260.9501820 .3000000000 0.0 0.0  &
      0.0 25.00000000 25.00000000
   BPVAL ETHAN-01 ACETOL 0.0 321.8773140 .3000000000 0.0 0.0  &
      0.0 25.00000000 25.00000000
   BPVAL ACETOL ETHAN-01 0.0 -123.8863480 .3000000000 0.0 0.0  &
      0.0 25.00000000 25.00000000
   BPVAL LACTI-01 ACETOL 0.0 -36.29691440 .3000000000 0.0 0.0  &
      0.0 25.00000000 25.00000000
   BPVAL ACETOL LACTI-01 0.0 -70.97466980 .3000000000 0.0 0.0  &
      0.0 25.00000000 25.00000000
   BPVAL ETHYL-01 ACETOL 0.0 83.41174500 .3000000000 0.0 0.0  &
      0.0 25.00000000 25.00000000
   BPVAL ACETOL ETHYL-01 0.0 4.925117560 .3000000000 0.0 0.0  &
      0.0 25.00000000 25.00000000
   BPVAL WATER ACETOL 0.0 585.8054600 .3000000000 0.0 0.0  &
      0.0 25.00000000 25.00000000
   BPVAL ACETOL WATER 0.0 -267.2661830 .3000000000 0.0 0.0  &
      0.0 25.00000000 25.00000000
DEF-STREAMS LOAD
STREAM ETHANOL
   SUBSTREAM MIXED PRES=1. VFRAC=0. MOLE-FLOW=9.4736
   MOLE-FRAC ETHAN-01 1.
STREAM LACTICAC
   SUBSTREAM MIXED PRES=1. VFRAC=0.
   MOLE-FLOW LACTI-01 6.2764
STREAM S-ETHANO
   SUBSTREAM MIXED PRES=1. VFRAC=0. MOLE-FLOW=1E-005
   MOLE-FRAC ETHAN-01 1.
STREAM S-MAKEUP
   SUBSTREAM MIXED PRES=1. VFRAC=0. MOLE-FLOW=1E-005
   MOLE-FRAC ACETOL 1.
STREAM SOLVENT
   SUBSTREAM MIXED PRES=1. VFRAC=0. MOLE-FLOW=40.
   MOLE-FRAC ACETOL 1.

BLOCK B11 MIXER
   PARAM
BLOCK MIX-ETH MIXER
   PARAM
BLOCK MIX-GLY MIXER
   PARAM
BLOCK B7 FSPLIT
   FRAC S15 0.5
BLOCK DIVLIQ FSPLIT
   PARAM NPHASE=1 PHASE=L MAXIT=100 TOL=0.01
   FRAC LIQ1 0.2
   BLOCK-OPTION RESTART=YES FREE-WATER=NO ENERGY-
BAL=YES  &
      FLASH-METHOD=GIBBS
BLOCK DIVVAP FSPLIT
   PARAM NPHASE=1 PHASE=V MAXIT=100
   FRAC VAP1 0.92
   BLOCK-OPTION FREE-WATER=NO
BLOCK EXT1 RADFRAC
   PARAM NSTAGE=17 ALGORITHM=NONIDEAL INIT-
OPTION=AZEOTROPIC  &
      MAXOL=200 DAMPING=SEVERE
   COL-CONFIG CONDENSER=TOTAL REBOILER=NONE
   FEEDS S15 17 ON-STAGE-VAP / SOLVENT 4 ON-STAGE / AZ-OHW  &
      9 ON-STAGE
   PRODUCTS S18 17 L / S1 1 L
   P-SPEC 1 1.
   COL-SPECS MOLE-D=3.
BLOCK EXT2 RADFRAC
   PARAM NSTAGE=10 ALGORITHM=NONIDEAL INIT-
OPTION=AZEOTROPIC  &
      MAXOL=200 NPHASE=2 DAMPING=SEVERE
   COL-CONFIG CONDENSER=TOTAL REBOILER=NONE
   FEEDS S16 10 ON-STAGE
   PRODUCTS WATER 1 L / S17 10 L
   P-SPEC 1 1.
   COL-SPECS MOLE-RR=10.
   BLOCK-OPTION FREE-WATER=NO
BLOCK EXT3 RADFRAC
```

```
    PARAM NSTAGE=3 ALGORITHM=NONIDEAL INIT-
OPTION=AZEOTROPIC  &
        MAXOL=200 DAMPING=SEVERE
    COL-CONFIG CONDENSER=NONE REBOILER=KETTLE
    FEEDS S11 1 ON-STAGE
    PRODUCTS GLY-REC 3 L / S14 1 V
    P-SPEC 1 1.
    COL-SPECS MOLE-B=35.6
BLOCK MAIN1 RADFRAC
    PARAM NSTAGE=4 ALGORITHM=NEWTON INIT-
OPTION=AZEOTROPIC  &
        MAXOL=200 TOLOL=1E-005 NPHASE=2 DAMPING=SEVERE  &
        PHEQM-FORM=STANDARD
    COL-CONFIG CONDENSER=TOTAL REBOILER=NONE
    FEEDS PRVAPDT 4 ON-STAGE / M2VAP 4 ON-STAGE
    PRODUCTS AZ-OHW 1 L / S12 4 L
    P-SPEC 1 1. / 2 1.
    COL-SPECS MOLE-RR=1.
    T-EST 1 354.2 / 2 361.9 / 3 369.5 / 4 372.6
    L-EST 1 55.5 / 2 54.91 / 3 55.4 / 4 50.92
    V-EST 1 0. / 2 64.75 / 3 64.16 / 4 64.65
    X-EST 1 ETHAN-01 0.384 / 1 LACTI-01 1.073E-017 / 1  &
        ETHYL-01 0.01298 / 1 WATER 0.603 / 2 ETHAN-01  &
        0.09489 / 2 LACTI-01 4.199E-015 / 2 ETHYL-01 0.03912 / &
        2 WATER 0.866 / 3 ETHAN-01 0.02203 / 3 LACTI-01  &
        7.413E-013 / 3 ETHYL-01 0.06853 / 3 WATER 0.9094 /  &
        4 ETHAN-01 0.02126 / 4 LACTI-01 1.795E-010 / 4  &
        ETHYL-01 0.3151 / 4 WATER 0.6637
    Y-EST 1 ETHAN-01 0.6091 / 1 LACTI-01 1.007E-020 / 1  &
        ETHYL-01 0.001353 / 1 WATER 0.3895 / 2 ETHAN-01  &
        0.384 / 2 LACTI-01 1.073E-017 / 2 ETHYL-01 0.01298 /  &
        2 WATER 0.603 / 3 ETHAN-01 0.1366 / 3 LACTI-01  &
        3.595E-015 / 3 ETHYL-01 0.03535 / 3 WATER 0.8281 /  &
        4 ETHAN-01 0.07382 / 4 LACTI-01 6.353E-013 / 4  &
        ETHYL-01 0.06058 / 4 WATER 0.8656
    TRAY-SIZE 1 2 4 SIEVE
    BLOCK-OPTION FREE-WATER=NO
    CONVERGENCE STABLE-METH=DOGLEG
BLOCK MAIN2 RADFRAC
    PARAM NSTAGE=10 ALGORITHM=NEWTON INIT-
OPTION=AZEOTROPIC  &
        MAXOL=200 TOLOL=1E-005 DAMPING=SEVERE PHEQM-
FORM=STANDARD
    COL-CONFIG CONDENSER=NONE REBOILER=NONE
    FEEDS LIQ2 1 ON-STAGE / VAP2 10 ON-STAGE
    PRODUCTS M2VAP 1 V / M2LIQ 10 L
    P-SPEC 1 1. / 2 1.
    COL-SPECS
    T-EST 1 404.6 / 2 412.9 / 3 413.6 / 4 413.7 / 5  &
        413.7 / 6 413.7 / 7 413.7 / 8 413.7 / 9 413.8 /  &
        10 413.9
    L-EST 1 9.569 / 2 9.871 / 3 9.904 / 4 9.906 / 5  &
        3.906 / 6 3.905 / 7 3.903 / 8 3.898 / 9 3.885 /  &
        10 3.854
    V-EST 1 34.07 / 2 33.45 / 3 33.76 / 4 33.79 / 5  &
        33.79 / 6 33.79 / 7 33.79 / 8 33.79 / 9 33.78 /  &
        10 33.77
    X-EST 1 ETHAN-01 0.01098 / 1 LACTI-01 9.415E-009 / 1  &
        ETHYL-01 0.8878 / 1 WATER 0.1012 / 2 ETHAN-01  &
        0.008651 / 2 LACTI-01 6.606E-008 / 2 ETHYL-01 0.9384 / &
        2 WATER 0.05297 / 3 ETHAN-01 0.00834 / 3 LACTI-01  &
        4.263E-007 / 3 ETHYL-01 0.9424 / 3 WATER 0.04929 /  &
        4 ETHAN-01 0.008308 / 4 LACTI-01 2.723E-006 / 4  &
        ETHYL-01 0.9427 / 4 WATER 0.04899 / 5 ETHAN-01  &
        0.008305 / 5 LACTI-01 1.736E-005 / 5 ETHYL-01 0.9427 / &
        5 WATER 0.04896 / 6 ETHAN-01 0.008304 / 6 LACTI-01  &
        0.0001107 / 6 ETHYL-01 0.9426 / 6 WATER 0.04896 /  &
        7 ETHAN-01 0.008303 / 7 LACTI-01 0.0003451 / 7  &
        ETHYL-01 0.9424 / 7 WATER 0.04895 / 8 ETHAN-01  &
        0.008299 / 8 LACTI-01 0.0009326 / 8 ETHYL-01 0.9418 /  &
        8 WATER 0.04894 / 9 ETHAN-01 0.008291 / 9 LACTI-01  &
        0.002399 / 9 ETHYL-01 0.9404 / 9 WATER 0.04891 /  &
        10 ETHAN-01 0.008269 / 10 LACTI-01 0.006013 / 10  &
        ETHYL-01 0.9369 / 10 WATER 0.04884
    Y-EST 1 ETHAN-01 0.07266 / 1 LACTI-01 2.638E-010 / 1  &
        ETHYL-01 0.4286 / 1 WATER 0.4987 / 2 ETHAN-01  &
        0.07067 / 2 LACTI-01 2.907E-009 / 2 ETHYL-01 0.5946 /  &
        2 WATER 0.3348 / 3 ETHAN-01 0.06945 / 3 LACTI-01  &
        1.953E-008 / 3 ETHYL-01 0.612 / 3 WATER 0.3186 / 4  &
        ETHAN-01 0.0693 / 4 LACTI-01 1.252E-007 / 4 ETHYL-01  &
        0.6135 / 4 WATER 0.3172 / 5 ETHAN-01 0.06929 / 5  &
        LACTI-01 7.984E-007 / 5 ETHYL-01 0.6136 / 5 WATER  &
        0.3171 / 6 ETHAN-01 0.06929 / 6 LACTI-01 5.09E-006 /  &
        6 ETHYL-01 0.6136 / 6 WATER 0.3171 / 7 ETHAN-01  &
        0.06929 / 7 LACTI-01 1.588E-005 / 7 ETHYL-01 0.6136 /  &
        7 WATER 0.3171 / 8 ETHAN-01 0.06929 / 8 LACTI-01  &
        4.295E-005 / 8 ETHYL-01 0.6135 / 8 WATER 0.3172 /  &
        9 ETHAN-01 0.0693 / 9 LACTI-01 0.0001107 / 9  &
        ETHYL-01 0.6134 / 9 WATER 0.3172 / 10 ETHAN-01  &
        0.06932 / 10 LACTI-01 0.000279 / 10 ETHYL-01 0.6131 /  &
        10 WATER 0.3173
    TRAY-SIZE 1 1 5 SIEVE
    CONVERGENCE STABLE-METH=DOGLEG
BLOCK MAIN3 RADFRAC
    PARAM NSTAGE=4 ALGORITHM=NEWTON INIT-
OPTION=AZEOTROPIC  &
        MAXOL=200 TOLOL=1E-005 DAMPING=SEVERE PHEQM-
FORM=STANDARD
    COL-CONFIG CONDENSER=NONE
    FEEDS M2LIQ 1 ON-STAGE / PRLIQBT 1 ON-STAGE
    PRODUCTS S6 1 V / BOTTOMS 4 L
    P-SPEC 1 1. / 2 1.
    COL-SPECS MOLE-B=6.19
    T-EST 1 414.1 / 2 428.5 / 3 443.2 / 4 469.2
    L-EST 1 58.73 / 2 57.3 / 3 48.15 / 4 0.5
    V-EST 1 56.23 / 2 58.23 / 3 56.8 / 4 47.65
    X-EST 1 ETHAN-01 0.008217 / 1 LACTI-01 0.01468 / 1  &
        ETHYL-01 0.9285 / 1 WATER 0.04866 / 2 ETHAN-01  &
        0.0006856 / 2 LACTI-01 0.08179 / 2 ETHYL-01 0.9124 /  &
        2 WATER 0.005133 / 3 ETHAN-01 4.025E-005 / 3  &
        LACTI-01 0.4088 / 3 ETHYL-01 0.5907 / 3 WATER  &
        0.0004115 / 4 ETHAN-01 1.373E-006 / 4 LACTI-01  &
        0.8093 / 4 ETHYL-01 0.1907 / 4 WATER 2.097E-005
    Y-EST 1 ETHAN-01 0.06938 / 1 LACTI-01 0.0006899 / 1  &
        ETHYL-01 0.6124 / 1 WATER 0.3175 / 2 ETHAN-01  &
        0.008288 / 2 LACTI-01 0.007853 / 2 ETHYL-01 0.9348 /  &
        2 WATER 0.04907 / 3 ETHAN-01 0.0006916 / 3 LACTI-01  &
        0.07538 / 3 ETHYL-01 0.9187 / 3 WATER 0.005178 / 4  &
        ETHAN-01 4.066E-005 / 4 LACTI-01 0.4046 / 4 ETHYL-01  &
        0.5949 / 4 WATER 0.0004156
    TRAY-SIZE 1 1 2 CAPS
    CONVERGENCE STABLE-METH=DOGLEG
BLOCK PREFRAC RADFRAC
    PARAM NSTAGE=10 ALGORITHM=NEWTON MAXOL=200 TOLOL=1E-
005  &
        DAMPING=SEVERE PHEQM-FORM=STANDARD
    COL-CONFIG CONDENSER=NONE REBOILER=NONE
    FEEDS LACTICAC 3 / ETHANOL 10 / LIQ1 1 ON-STAGE /  &
        VAP1 10 ON-STAGE
    PRODUCTS PRVAPDT 1 V / PRLIQBT 10 L
    P-SPEC 1 1. / 2 1.
    COL-SPECS
    REAC-STAGES 3 10 SUBRTN
    HOLD-UP 4 7 MASS-LHLDP=100.
    T-EST 1 372.4 / 2 372.3 / 3 372.3 / 4 376. / 5  &
        373. / 6 369.4 / 7 364.1 / 8 365. / 9 367.4 /  &
        10 377.9
    L-EST 1 40.73 / 2 40.72 / 3 40.57 / 4 43.94 / 5  &
        45.32 / 6 46.51 / 7 56.04 / 8 55.98 / 9 55.58 /  &
        10 52.88
    V-EST 1 26.1 / 2 26.1 / 3 26.08 / 4 25.94 / 5  &
        23.03 / 6 24.41 / 7 25.6 / 8 25.65 / 9 25.6 /  &
        10 25.2
    X-EST 1 ETHAN-01 0.02411 / 1 LACTI-01 1.679E-009 / 1  &
        ETHYL-01 0.3149 / 1 WATER 0.661 / 2 ETHAN-01  &
        0.02556 / 2 LACTI-01 6.794E-007 / 2 ETHYL-01 0.3151 /  &
        2 WATER 0.6594 / 3 ETHAN-01 0.02642 / 3 LACTI-01  &
        0.0003076 / 3 ETHYL-01 0.3192 / 3 WATER 0.6541 / 4  &
        ETHAN-01 0.02582 / 4 LACTI-01 0.106 / 4 ETHYL-01  &
        0.3249 / 4 WATER 0.5432 / 5 ETHAN-01 0.05702 / 5  &
        LACTI-01 0.06095 / 5 ETHYL-01 0.3539 / 5 WATER  &
        0.5281 / 6 ETHAN-01 0.1184 / 6 LACTI-01 0.02549 /  &
        6 ETHYL-01 0.3708 / 6 WATER 0.4853 / 7 ETHAN-01  &
        0.2341 / 7 LACTI-01 0.00723 / 7 ETHYL-01 0.3229 /  &
        7 WATER 0.4358 / 8 ETHAN-01 0.1998 / 8 LACTI-01  &
        0.007238 / 8 ETHYL-01 0.3269 / 8 WATER 0.4661 / 9  &
        ETHAN-01 0.147 / 9 LACTI-01 0.007301 / 9 ETHYL-01  &
        0.3569 / 9 WATER 0.4888 / 10 ETHAN-01 0.07317 / 10  &
        LACTI-01 0.007948 / 10 ETHYL-01 0.5848 / 10 WATER  &
        0.3341
    Y-EST 1 ETHAN-01 0.08273 / 1 LACTI-01 5.847E-012 / 1  &
        ETHYL-01 0.05976 / 1 WATER 0.8575 / 2 ETHAN-01  &
        0.08718 / 2 LACTI-01 2.347E-009 / 2 ETHYL-01 0.05939 / &
        2 WATER 0.8534 / 3 ETHAN-01 0.08948 / 3 LACTI-01  &
        1.06E-006 / 3 ETHYL-01 0.05962 / 3 WATER 0.8509 /  &
        4 ETHAN-01 0.09118 / 4 LACTI-01 0.0004812 / 4  &
```

```
        ETHYL-01 0.06466 / 4 WATER 0.8437 / 5 ETHAN-01  &
        0.1759 / 5 LACTI-01 0.0002215 / 5 ETHYL-01 0.05999 /  &
        5 WATER 0.7639 / 6 ETHAN-01 0.3029 / 6 LACTI-01  &
        7.045E-005 / 6 ETHYL-01 0.05118 / 6 WATER 0.6459 /  &
        7 ETHAN-01 0.4645 / 7 LACTI-01 1.36E-005 / 7  &
        ETHYL-01 0.03448 / 7 WATER 0.501 / 8 ETHAN-01  &
        0.4213 / 8 LACTI-01 1.452E-005 / 8 ETHYL-01 0.03698 /  &
        8 WATER 0.5417 / 9 ETHAN-01 0.3468 / 9 LACTI-01  &
        1.731E-005 / 9 ETHYL-01 0.04508 / 9 WATER 0.6081 /  &
        10 ETHAN-01 0.2327 / 10 LACTI-01 4.113E-005 / 10  &
        ETHYL-01 0.1067 / 10 WATER 0.6606
    TRAY-SIZE 1 1 6 SIEVE
    USERK-VECS NINT=1
    USERK-REAL VALUE-LIST=1000.
    CONVERGENCE STABLE-METH=DOGLEG
BLOCK B1 PUMP
    PARAM PRES=1.
EO-CONV-OPTI
CONV-OPTIONS
    PARAM TEAR-METHOD=BROYDEN TOL=1E-005 SPEC-
METHOD=BROYDEN
    WEGSTEIN MAXIT=1000 WAIT=5
    BROYDEN MAXIT=1000 WAIT=4 XTOL=0.001
CONVERGENCE CV-1 BROYDEN
    TEAR SOLVENT 0.01
CONVERGENCE CV-2 BROYDEN
    TEAR ETHANOL 0.01
```

```
CONV-ORDER CV-1 CV-2
REPORT REPORT
STREAM-REPOR MOLEFLOW MASSFLOW STDVOLFLOW MOLEFRAC
MASSFRAC  &
        STDVOLFRAC
PROPERTY-REP PCES
REACTIONS R-1 REAC-DIST
    REAC-DATA 1
    K-STOIC 1 A=2.9625 B=-515.13
    STOIC 1 ETHAN-01 -1. / LACTI-01 -1. / ETHYL-01 1. /  &
        WATER 1.
REACTIONS SUBRTN REAC-DIST
    PARAM SUBROUTINE=ETHLACTA
    REAC-DATA 1 KINETIC
    STOIC 1 LACTI-01 -1. / ETHAN-01 -1. / WATER 1. /  &
        ETHYL-01 1.
BALANCE B-1
    M-BAL 1 BLOCKS=MIX-GLY
    CALCULATE S-MAKEUP
BALANCE B-2
    M-BAL 1 BLOCKS=MIX-ETH
    CALCULATE S-ETHANO
;
;
;
;
;
```

APPENDIX D: KINETIC SUBROUTINE

```
SUBROUTINE ETHLACTA (NSTAGE, NCOMP,   NR,     NRL,     NRV,
     2                   T,      TLIQ,    TVAP,   P,       VF,
     2                   F,      X,       Y,      IDX,     NBOPST,
     4                   KDIAG,  STOIC,   IHLBAS, HLDLIQ,  TIMLIQ,
     5                   IHVBAS, HLDVAP,  TIMVAP, NINT,    INT,
     6                   NREAL,  REAL,    RATES,  RATEL,   RATEV,
     7                   NINTB,  INTB,    NREALB, REALB,   NIWORK,
     8                   IWORK,  NWORK,   WORK)
      IMPLICIT NONE
C
C      DECLARE VARIABLES USED IN DIMENSIONING
C
      INTEGER NCOMP, NR,    NRL,   NRV,   NINT,
     +        NINTB, NREALB,NIWORK,NWORK, N_COMP
C
CC
CC   DECLARE PARAMETERS AND VARIABLES IN PARAMETERS
CC
        INTEGER K_ETOH, K_LACID, K_ETHLAC, K_WATER
        PARAMETER(K_ETOH=1)
        PARAMETER(K_LACID=2)
        PARAMETER(K_ETHLAC=3)
        PARAMETER(K_WATER=4)
        PARAMETER(N_COMP=4)
C
CC
CC DECLARE ARGUMENTS
CC
      INTEGER IDX(NCOMP),   NBOPST(6),    INT(NINT),
     +        INTB(NINTB),  IWORK(NIWORK),NSTAGE,
     +        KDIAG, IHLBAS,IHVBAS,NREAL, KPHI,
     +        KER,   L_GAMMA,      J
      REAL*8 X(NCOMP,3),   Y(NCOMP),
     +       STOIC(NCOMP,NR),     RATES(NCOMP),
     +       RATEL(NRL),   RATEV(NRV),
     +       REALB(NREALB),WORK(NWORK),  B(1),   T,
     +       TLIQ,  TVAP,  P,      VF,    F
      REAL*8 HLDLIQ,TIMLIQ,HLDVAP,TIMVAP,TZERO,
     +       FT
CC   DECLARE SYSTEM FUNCTIONS
      REAL*8 DLOG
CC   DECLARE LOCAL VARIABLES
      INTEGER IMISS, IDBG
      REAL*8 REAL(NREAL),  RMISS, C1,    C2,    C3,
     +       C4,    C5,    C6,    DKA,   DKR,
     +       Q,     RATE,  RATNET,  KEQ,    KETOH,
     +       KW,    KRATE
      REAL*8 PHI(N_COMP)
      REAL*8 DPHI(N_COMP)
      REAL*8 ACTIV(N_COMP)

#include "ppexec_user.cmn"
```

```
      EQUIVALENCE (RMISS, USER_RUMISS)
      EQUIVALENCE (IMISS, USER_IUMISS)
#include "dms_maxwrt.cmn"
#include "dms_ipoff3.cmn"
#include "dms_lclist.cmn"
      INTEGER FN
#include "dms_plex.cmn"
      EQUIVALENCE(B(1),IB(1))
C   DATA STATEMENTS
      DATA IDBG/0/
CC   Thermodynamic rate constant
CC   ===========================
 9010 FORMAT(1X,3(G13.6,1X))
 9000 FORMAT(' fugly failed at T=',G12.5,' P=',G12.5,' ker=',I4)
 9020 FORMAT(' compo ',I3,' mole-frac=',G12.5,' activity=',G12.5)
 9030 FORMAT(' stage=',I4,' spec-rate=',G12.5,' net-rate=',G12.5)
CC
CC   BEGIN EXECUTABLE CODE
CC   EQUILIBRIUM EQUATION
      KEQ=DEXP(2.9625-(515.13/T))
CC   %Adsorption parameters ethanol
      KETOH= (1.22*DEXP(359.63/T))
CC   %Adsorption parameters water
      KW=(15.19*DEXP(12.01/T))
CC   %Rate constant
      KRATE=2.7D+07*DEXP(-44980/8.314/T)
      IF (IDBG.GE.1)THEN
         WRITE(MAXWRT_MAXBUF(1),9010) FT,DKA,DKR
         CALL DMS_WRTTRM(1)
      ENDIF
      KPHI=1
CC   fugacity coefficient of components
      CALL PPMON_FUGLY(T,P,X(1,1)
     +   ,Y,NCOMP,IDX,NBOPST,KDIAG,KPHI,PHI,DPHI,KER)
      IF(KER.NE.0)THEN
         WRITE(MAXWRT_MAXBUF(1),9000) T,P,KER
         CALL DMS_WRTTRM(1)
      ENDIF
      L_GAMMA=IPOFF3_IPOFF3(24)
      DO J=1, NCOMP
         ACTIV(J)=DEXP(B(L_GAMMA+J))*X(J,1)
      END DO
      IF(IDBG.GE.1)THEN
      DO J=1,NCOMP
         WRITE(MAXWRT_MAXBUF(1),9020) J,X(J,1),ACTIV(J)
         CALL DMS_WRTTRM(1)
      END DO
      END IF
      REALB(1)=600.
      RATE=REALB(1)*KRATE*(ACTIV(K_ETOH)*ACTIV(K_LACID))
     &   -ACTIV(K_ETHLAC)*ACTIV(K_WATER)/KEQ
      RATE=(RATE/(1.D0+KETOH*ACTIV(K_ETOH)+KW*ACTIV(K_WATER))**2.d0)
     &   /1.d3
      RATES(K_ETOH)=-RATE
```

```
      RATES(K_LACID)=-RATE
      RATES(K_ETHLAC)=RATE
      RATES(K_WATER)=RATE
      IF(IDBG.GE.1)THEN
         WRITE(MAXWRT_MAXBUF(1),9030) NSTAGE,RATE,RATNET
         CALL DMS_WRTTRM(1)
      ENDIF
      RETURN
#undef P_MAX3
      END
```

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