

Tutor/s

Dr. Jordi Bonet i Ruiz
Dra. Alexandra Bonet Ruiz
Departament d'Enginyeria Química i Química Analítica



Màster en Enginyeria Química

Treball Final de Màster

**Contribution to the Study of Methyl Acetate Transesterification by Reactive
Pressure-Swing Distillation**

**Contribución al Estudio de la Transesterificación del Acetato de Metilo mediante
Rectificación Reactiva con Cambio de Presión**

Alvaro Risco Morillo

February 2018



UNIVERSITAT DE
BARCELONA

Dos campus d'excel·lència internacional

B:KC Barcelona
Knowledge
Campus

HUB Health Universitat
de Barcelona
Campus

Aquesta obra esta subjecta a la llicència de
Reconeixement-NoComercial-SenseObraDerivada



<http://creativecommons.org/licenses/by-nc-nd/3.0/es/>

REPORT

CONTENTS

1. SUMMARY	1
2. INTRODUCTION.....	2
2.1. Separation Methods in the Chemical Industry.....	2
2.2. Separation by Phase Creation: Distillation	4
2.3. Enhanced Distillation: Pressure-Swing Distillation.....	7
2.4. Polyvinyl Alcohol Process: Methyl Acetate–Methanol Azeotrope Case Study....	9
2.5. Methyl Acetate Transesterification	11
2.5.1. Reaction Kinetics.....	12
2.6. Methyl Acetate–Methanol Azeotrope Case Study: Proposed Technologies	13
2.6.1. Reactive and extractive distillation.....	13
2.6.2. Reactive distillation with pervaporation	14
2.6.3. Reactive and pressure swing distillation.....	16
3. OBJECTIVES	18
4. METHODOLOGY.....	19
4.1. Reaction System and Thermodynamic Model.....	19
4.2. Simulation Environment	20
4.3. Process Optimization.....	21
4.4. Product Specifications	22
5. RESULTS AND DISCUSSION	23
5.1. Effect of Interval between Feed Stages	23
5.2. Effect of Feed Stage: Optimal Number of Stages in the Rectifying Section.....	25
5.3. Optimal Number of Stages in the Stripping Section	26
5.4. Optimal Number of Reactive Stages	27
5.5. Optimal Pressure Swing	30
5.6. LPC Optimization	35
5.7. Optimized Process.....	37
5.8. Effect of the Amount of Catalyst	40
5.9. Economic Aspects.....	42
6. CONCLUSIONS	48
7. NOTATION.....	51
8. REFERENCES AND NOTES	53

1. SUMMARY

Distillation is the most widespread operation used to separate homogeneous mixtures since it is a mature industrial technology and offers advantages over other separation methods. However, when thermodynamic conditions are unfavorable, i.e. close-boiling systems or azeotropes, other techniques that are ultimately also based on distillation are used: enhanced distillation operations. Pressure-swing distillation is the only enhanced distillation technique that solely depends on an energy-separating agent. Nevertheless, this process is only feasible when the composition of species to be separated is significantly sensitive to pressure variation.

Methyl acetate–methanol system is the case study used as an example of a mixture that forms an azeotrope with a pressure-sensitive composition. This mixture is collected in large amounts from a residual stream of polyvinyl alcohol production process. Accordingly, methods to separate and convert this components into more valuable chemicals are being studied. One of the most attractive possibilities is transforming methyl acetate into isobutyl acetate via transesterification with isobutanol, since methanol, which is a reactant for the polymer synthesis, is also generated as by-product.

Due to the nature of methyl acetate–methanol mixture, pressure-swing distillation can be used to separate both species. In addition, this technology can be performed jointly with reactive distillation, another enhanced distillation technique, to carry out separation and reaction operations simultaneously and, thus, reduce capital and energy costs. Therefore, in this report, transesterification of methyl acetate using the reactive and pressure-swing distillation process is developed.

Transesterification, catalyzed by the ion-exchange resin Amberlyst 15, is described using the pseudohomogeneous kinetic model. The process is simulated in Aspen Plus using a vapor–liquid equilibrium-stage approach and optimized to obtain products with commercial specifications. The design procedure involves finding the optimal number of stages for rectifying, stripping and reaction sections and the most appropriate operating pressure considering design factors such as heat duties, available pressure-levels of hot utilities and the recommended operating temperature for the catalyst.

2. INTRODUCTION

In this chapter, the different properties exploited in industrial operations to separate homogeneous mixtures are detailed. Distillation is the most widely used operation and, when the system is composed of close-boiling components or azeotropes, enhanced distillation techniques are usually preferred to perform the separation. Among the different enhanced distillation technologies, pressure-swing distillation can overcome azeotropes by using columns operating at different pressures. However, the azeotropic composition of the mixture desired to be separated must be sensitive to pressure to make this process viable, which is an instance that does not occur frequently.

Methyl acetate and methanol form an azeotrope that meets the pressure sensitiveness condition required in pressure-swing distillation. This mixture is obtained as a residual stream in the production of polyvinyl alcohol and, in recent years, processes to convert methyl acetate into a more valuable product and, thus, to increase the polymer synthesis profitability are being studied. Since n-butyl and isobutyl acetate are the chemicals that offer greater profits, the reaction involved in their production and the alternatives to perform this process proposed in the literature are described.

2.1. Separation Methods in the Chemical Industry

Mixtures are generally separated by creating two or more phases. Depending on the type of species to be separated, these phases differ in physical conditions such as temperature, pressure, composition and/or phase state. When these spatial locations are generated, each component behaves in a different way depending on the specific conditions of the section the compound is in and, consequently, is distributed in each zone with different concentrations. In other words, species are shifted towards the new state of equilibrium, which acts as driving force for the separation. Therefore, separation operations are based on the exploitation of differences in molecular, thermodynamic and transport properties of species (Table 1) when they are subjected to a change in the state of equilibrium.

The most common techniques to separate mixtures in the chemical industry involve a new immiscible phase, generated using energy (*energy-separating agent*, ESA), adding

a new substance (*mass-separating agent*, MSA), or by the presence of a solid barrier or solid agents (Table 2).

Table 1. List of molecular, thermodynamic and transport properties.

Molecular properties		
Molecular weight	Acentric factor	Dielectric constant
van der Waals volume	Dipole moment	Electric charge
van der Waals area	Polarizability	Radius of gyration
Thermodynamic and transport properties		
Vapor pressure	Adsorptivity	Diffusivity
Solubility		

Methods based on energy-separating agents use heat transfer or pressure reduction to create the new phase. Common operations that use an ESA are flash vaporization or distillation, in which species are separated between vapor and liquid phases exploiting their difference in volatility. On the other hand, an example of operations using a MSA is liquid–liquid extraction, where species desired to be separated have greater affinity for the added phase.

Table 2. Common separation operations.

Separation operations based on an energy-separating agent		
Partial condensation	Partial vaporization	Distillation
Drying	Evaporation	Crystallization
Lyophilization		
Separation operations based on a mass-separating agent		
Liquid-liquid extraction	Supercritical-fluid extraction	Extractive distillation
Absorption	Stripping	
Separation operations based on a barrier		
Osmosis	Reverse osmosis	Dialysis
Microfiltration	Ultrafiltration	Pervaporation
Separation operations based on a solid agent		
Adsorption	Chromatography	Ion-exchange

Other techniques, whose relevance in the industry has increased significantly in recent years, are based on the usage of a barrier, generally a polymer membrane, exploiting differences of species permeability through this material; or are based on contacting the fluid feed with a solid agent that selectively adsorbs certain species.

Among the common separation operations, techniques that require a MSA have some disadvantages in comparison to technologies that use an ESA. In most instances, the separation of a binary mixture requires at least one unit and, accordingly, more complex mixtures, that is, systems containing more than two components, involve using more separation units progressively. Thus, in processes based on the usage of a MSA, since a new substance is added to the system, a *recovering unit* for this agent is required.

In addition, because attaining perfect separation, i.e. obtaining pure components, is unpractical, even highly purified product streams contain small amounts of other species that constitute the mixture. Therefore, even though the mass-separating agent is recovered in its corresponding unit, a *make-up* for the MSA is still required since, as the operation is continuously performed, its amount within the separation system is gradually reduced.

Furthermore, this type of operations involves using more complex design procedures and selecting the most befitting agent to maximize the extent of the separation or avoid product contamination. Hence, when taking these factors into consideration, operations that depend on an *energy-separating agent*, e.g. distillation, are usually preferred, since they also are technologically mature processes (Seader, Henley & Roper, 2011).

2.2. Separation by Phase Creation: Distillation

Commonly, a mixture whose components have a significant difference in volatility, a property expressed in vapor–liquid equilibrium ratios or K-values (Eq. 1), operations such as *partial condensation* or *partial vaporization* (Figure 1) are sufficient to achieve the desired products.

$$K_i = \frac{x_i}{y_i} = \frac{\gamma_{iL}\phi_{iL}}{\phi_{iV}} \quad (1)$$

where K_i is the vapor–liquid equilibrium ratio of the component i , x_i is the mole fraction of i in the liquid phase, y_i is the mole fraction of i in the vapor phase, γ_{iL} is the activity coefficient of the liquid phase, ϕ_{iL} and ϕ_{iV} are the pure component fugacities of liquid and vapor phases respectively.

As explained previously, the second phase can be created by adding or removing heat from the mixture and/or changing its pressure. Partial condensation is usually performed by removing heat from the vapor feed mixture, which results in the formation of a liquid phase, enriched with the heavier components, and its separation by gravity from the vapor phase, enriched with the more-volatile species.

Alternatively, partial vaporization is generally carried out by abruptly reducing the feed pressure (*flash vaporization*), using a valve or a turbine, and separating likewise the resulting phases.

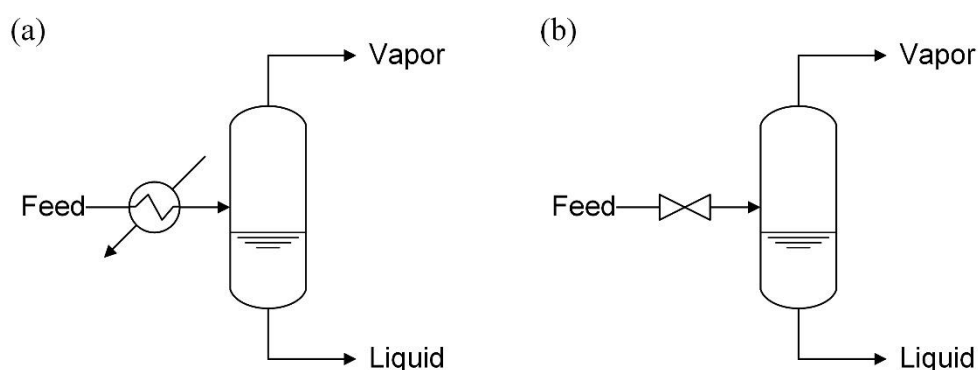


Figure 1. Schematic diagrams of (a) partial condensation and (b) flash vaporization.

Nevertheless, volatility differences among species are typically not sufficiently large to attain the desired purities of products with a single contact between vapor and liquid phases. In these situations, *distillation* is the most widely used separation operation.

Distillation entails multiple contacts between vapor and liquid phases within the unit. Contacts, which are also commonly referred to as *stages*, involve mixing both phases to approach the new state of equilibrium and separate species by mass transfer. Stages are the result of the flow of streams of these phases through devices, such as *packings* or *trays*, stacked and enclosed along a cylindrical shell to form a *column* (Figure 2).

The mixture to be separated is typically fed at one point along the column, which results in the division of the unit in two zones, an upper section, often referred to as *rectifying section*, and a lower section, often called the *stripping section*.

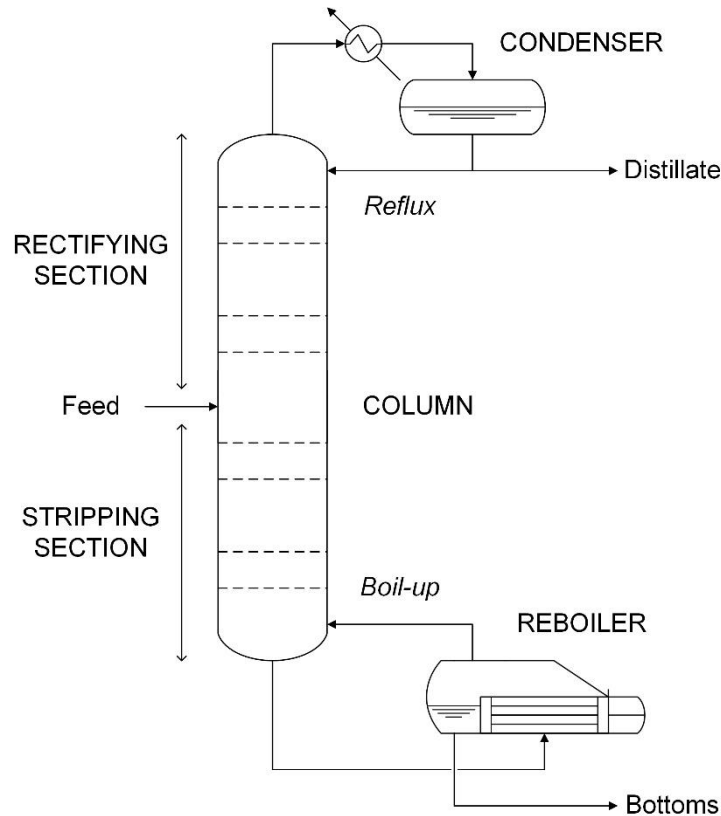


Figure 2. Schematic distillation column.

Unlike operations described above, in distillation, liquid flows down the column through a series of trays, or a packing bed, until reaching the unit bottom, where it is partially vaporized in the *reboiler* to generate a vapor stream (*boil-up*), which flows up the column. The remaining liquid is simultaneously removed from the unit as a stream called *bottoms*.

Vapor reaching the top of the unit is either totally or partially condensed in the overhead *condenser*. Part of the condensed liquid (*reflux*) is returned to the top of the column, where starts to flow down. The liquid remaining in the condenser, or vapor when condensation is partial, is withdrawn as *distillate*, which is the overhead product. This countercurrent flow pattern between reflux and boil-up streams along the unit is what generates the multiple contacts between phases that enhances the separation.

Because of the mechanism of this process, the lighter species, that is, components with a lower boiling point, concentrate in the vapor phase, while the heavier species are accumulated in the liquid phase. Consequently, vapor phase, which is ultimately

collected as distillate, becomes increasingly enriched in the more-volatile components, and liquid phase, which is finally withdrawn as bottoms, is progressively enriched with the less-volatile species. The separation achieved between product streams depends on the relative volatilities of the species, the number and efficiency of contacting trays and the liquid phase flow rate to the vapor flow rate ratio (L/V).

2.3. Enhanced Distillation: Pressure-Swing Distillation

Although many compounds are separated by distillation, there are several instances in which the composition variation in vapor and liquid phases from one tray to another becomes almost negligible, which complicates achieving the desired products purities. When this happens, stages are said to be under *pinch conditions*.

These situations occur when relative volatilities, expressed as ratios of species K -values (Eq. 2), are lower than 1.10 (*close-boiling mixtures*), or when vapor and liquid phases have identical compositions because of the formation of an *azeotrope* (Figure 3).

$$\alpha_{ij} = \frac{K_i}{K_j} \quad (2)$$

where α_{ij} is the relative volatility of components i and j , and K is the vapor–liquid equilibrium ratio.

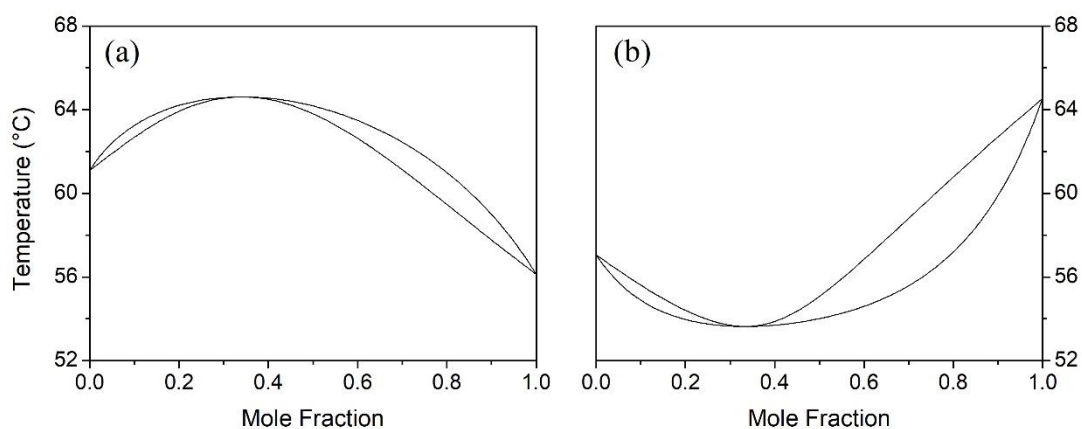


Figure 3. Isobaric-phase diagrams for binary (a) homogeneous maximum-boiling and (b) homogeneous minimum-boiling azeotropes.

When mixtures consist of close-boiling species, a large number of trays and huge reflux ratios are required to achieve the desired product specifications. Consequently, energy consumption and column height increase considerably, making this separation operation economically and/or technologically unfeasible. When a mixture of azeotropic composition is formed, separation by distillation is thermodynamically unpracticable.

For close-boiling systems and mixtures containing azeotropes, alternative operations that are fundamentally based on mechanisms to modify even further the vapor–liquid behavior of components have been developed. These technologies, which are often referred to as *enhanced distillation*, can be classified in the following categories.

1. *Azeotropic distillation* and *pressure-swing distillation*. Techniques that rely on the behavior of certain azeotropes when system conditions are subjected to a change, altering the vapor–liquid equilibrium and separability of the mixture.
2. *Extractive distillation* and *salt distillation*. Procedures which exploit the effect of the addition of an agent on the liquid-phase behavior, making relative volatilities of key components more favorable for its separation.
3. *Reactive distillation*. Technology in which a chemical added to the system selectively and reversibly reacts with at least one of the components constituting the mixture, modifying the system composition to promote the operation purpose. Afterwards, the inverse reaction can be carried out to recover the initial reactants.

Most of the enhanced distillation technologies involve adding a new chemical to the system, whose presence results in the formation of a new environment that favors the separation. Hence, these techniques share, to some extent, the drawbacks of operations based on the usage of MSA.

Nonetheless, pressure is a variable that alters the vapor–liquid behavior without the need to rely on additional compounds. The composition of azeotropes changes with the system pressure and, seldom, the azeotrope itself can disappear. This phenomenon can be exploited to separate azeotropic mixtures by pressure-swing distillation.

Pressure-swing distillation is an operation in which an azeotrope is separated using two columns operating at different pressures –a high-pressure column (HPC) and a low-pressure column (LPC)– and exploiting the variation of its composition (Figure 4).

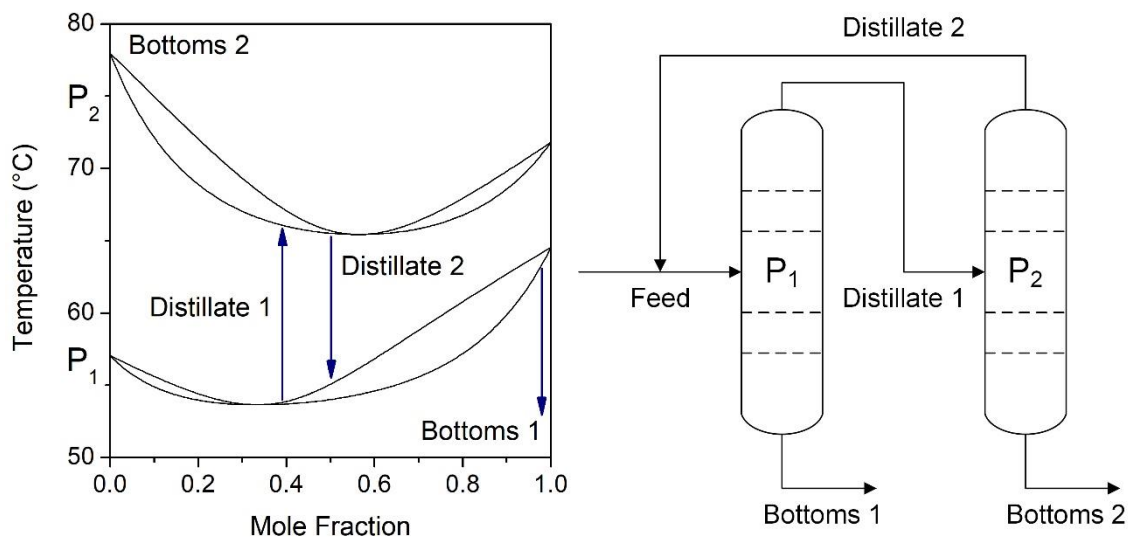


Figure 4. Schematic separation sequence for a minimum-boiling azeotrope using pressure-swing distillation.

Nevertheless, this technology is only viable when the azeotropic composition undergoes a significant shift with the change of pressure, which does not occur for most mixtures. It must vary at least 5 percent –preferably more than 10 percent– over a pressure swing not higher than 10 atmospheres (Perry, Green & Maloney, 1999).

2.4. Polyvinyl Alcohol Process: Methyl Acetate–Methanol Azeotrope Case Study

Polyvinyl alcohol (PVA) is the most produced synthetic and water-soluble polymer worldwide. PVA has outstanding chemical and physical properties and, consequently, has a large diversity of applications, such as textile and paper sizing, adhesives, protective colloids for polymerization, or fibers. It is non-flammable, non-toxic and biodegradable by adapted microorganisms (Kirk-Othmer, 2001).

Unlike other polymers, polyvinyl alcohol is not obtained from its monomer, because vinyl alcohol takes the form of acetaldehyde spontaneously, which is the result of the tautomeric equilibrium. Accordingly, PVA is produced via alternative routes, such as the hydrolysis or transesterification of polyvinyl esters. The process commercially used

is *polyvinyl acetate transesterification*, since the reaction can be controlled easily and no undesired products are generated through side reactions.

Polyvinyl acetate produced to subsequently manufacture PVA is obtained via polymerization in methanol, where the molecular mass of polyvinyl acetate, the polymerization temperature and vinyl acetate–methanol ratio are accurately controlled to attain the optimal properties. Afterwards, PVA is preferably produced by polyvinyl acetate transesterification with methanol and a small quantity of base, such as sodium or potassium methoxide, to promote the ester exchange. The resulting mixture, which contains the reaction products, i.e. *polyvinyl alcohol and methyl acetate*, is subsequently separated using filters, screw pressers or centrifuges and driers (Hallensleben, 2011).

Therefore, methyl acetate (MEAC) is generated as by-product in a large amount in PVA synthesis. This ester is collected as a *minimum-boiling azeotropic mixture* which also contains methanol (MEOH), which acts as solvent and reactant in this process: 1.68 tons of azeotrope are obtained per ton of PVA produced.

MEAC–MEOH mixture can be separated by enhanced distillation, e.g. extractive distillation. Nonetheless, reactive distillation is the technology used to overcome the thermodynamic limitation. MEAC reacts with water to produce acetic acid and methanol, a mixture easier to separate. Although reaction products can be converted back to obtain MEAC, acetic acid is preferably commercialized in this form. However, the generated amount of acetic acid is so high that PVA price is dictated by acetic acid market value.

In recent years, alternative procedures to separate this mixture and convert MEAC into a product more valuable than acetic acid –such as n-butyl or isobutyl acetate– have been proposed in the literature. On one hand, n-butyl acetate (BUAC) is an important solvent used in the paint and coating manufacture; on the other hand, isobutyl acetate (IBAC) is used as solvent in the production of nitrocellulose, pesticides and lacquer or as an additive in the food and pharmaceutical industries (Suo et al., 2017). The most attractive reaction to obtain either of these esters from MEAC is *transesterification*, since MEOH is also generated as by-product, thus, it can be separated and recycled for its reutilization in the polymer synthesis process.

2.5. Methyl Acetate Transesterification

Transesterification, or alcoholysis, is the reaction where the organic group (R_1) of an ester is substituted for the organic group (R_2) of an alcohol (Figure 5) (Meher, Vidya Sagar & Naik, 2006).

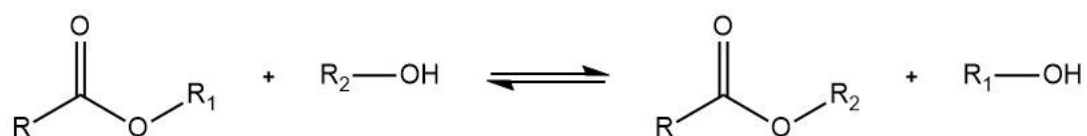


Figure 5. General transesterification reaction.

Transesterification is a *reversible reaction* that occurs spontaneously by the contact between reactants. However, catalysts are used to accelerate the process, since it is known to have low reaction rates. It can be catalyzed by Bronsted acids, preferably sulfonic or sulfuric acids, strong bases or enzymes, and the usage of either compound depends on the species the system is composed of. In addition, this reaction has an equilibrium constant close to the unity, thus, reactive distillation can be used to enhance the reaction conversion (Steinigeweg & Gmehling, 2004).

The alcoholysis of methyl acetate to obtain more valuable products from the PVA process residual stream has been thoroughly studied when it is catalyzed by acids. Among the different possibilities, heterogenous catalysts are preferred to homogeneous catalysts, e.g. sulfuric acid, because they offer more advantages regarding downstream separation operations. One of the most studied heterogeneous catalysts for MEAC transesterification is the *strongly acidic ion-exchange resin* Amberlyst™ 15, since it is a catalyst commercially used to accelerate other organic equilibrium-controlled reactions such as esterification or etherification (*Amberlyst™ Polymeric Catalysts*, 2011).

Ion-exchange resins, however, are characterized for having a low thermal stability (Jiménez et al., 2002), which becomes an important obstacle in processes performed at high temperatures. Therefore, processes using resins as catalysts must operate at conditions such that temperatures do not exceed the maximum operating temperatures recommended by manufacturers.

2.5.1. Reaction Kinetics

Transesterification, which is known to be a second-order reaction, can be described using the pseudohomogeneous model (PH, Equation 3) and the adsorption-based Langmuir-Hinshelwood (LH, Equation 4) model (Bozek-Winkler & Gmehling, 2006). The PH model is applicable because the reaction takes place in the liquid phase and mass-transfer resistance is negligible. No significant difference can be found between PH and LH models and, since the former requires less parameters, its usage to adjust experimental data is preferred (Jiménez et al., 2002; Bozek-Winkler et al., 2006).

$$r = k_+x_Ax_B - k_-x_Cx_D \quad (3)$$

$$r = \frac{k_+x_Ax_B - k_-x_Cx_D}{(1 + \sum K_{a,i}x_i)^2} \quad (4)$$

where r is the reaction rate, k_+ and k_- are the forward and backward rate constants, x_i is the mole fraction, and $K_{a,i}$ is the adsorption constant for the corresponding species.

Cui et al. (2011) compared the catalytic activity of ionic liquids with sulfuric acid in methyl acetate transesterification with n-butanol (Figure 6). Reported results –obtained when using both catalysts in the same molar concentrations– show that the ionic liquid had similar activity to sulfuric acid despite being molecules with different natures. Therefore, the catalytic activity can be attributed to sulfonic group of these compounds.

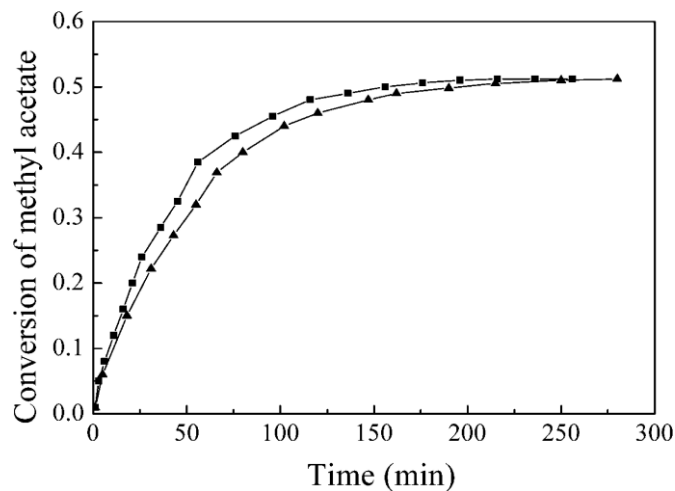


Figure 6. Methyl acetate transesterification with n-butanol using ionic liquid (—■—) and sulfuric acid (—▲—) as catalyst (Cui et al., 2011).

2.6. Methyl Acetate–Methanol Azeotrope Case Study: Proposed Technologies

Methods suggested in the literature to separate MEAC–MEOH azeotrope and convert MEAC into BUAC or IBAC are ultimately based on three processes: extractive distillation, pervaporation or pressure-swing distillation, and their combination with *reactive distillation*.

Reactive distillation is a technology that combines reaction and distillation operations in a single unit. This process has been exhaustively researched in the past two decades since it reduces both equipment and energy costs and enhances conversions of equilibrium reactions considerably by performing the reaction and removing products simultaneously.

2.6.1. Reactive and extractive distillation

Reactive and extractive distillation combines reactive distillation and extractive distillation in an operation where a solvent is used to break the azeotrope and improve the contact between reactants. One of the advantages of this process is its ability to adjust reactants and products relative volatilities with the entrainer. The most fitting entrainers for the MEAC–MEOH mixture are alkylbenzenes and alkanes and, after taking into consideration diverse factors such as safety, cost or physical properties, o-xylene has been proved to be the best entrainer (España, F., 1996; Jiménez et al., 2002).

In the last few years, the usage of ionic liquids (IL) as entrainers has also been thoroughly researched. The most relevant property of these compounds is having a negligible vapor pressure. Therefore, they can be separated from volatile chemicals by distillation and, thus, reduce energy consumption. Another significant property is their Bronsted and Lewis acidity, which also makes the usage of IL as catalysts possible (Cai, Cui & Yang, 2011). Accordingly, specific ionic liquids can be used as both entrainers and catalysts in this process (Figure 7).

Nonetheless, these processes have the drawbacks characteristic of operations based on the usage of MSA discussed in Section 2.1.

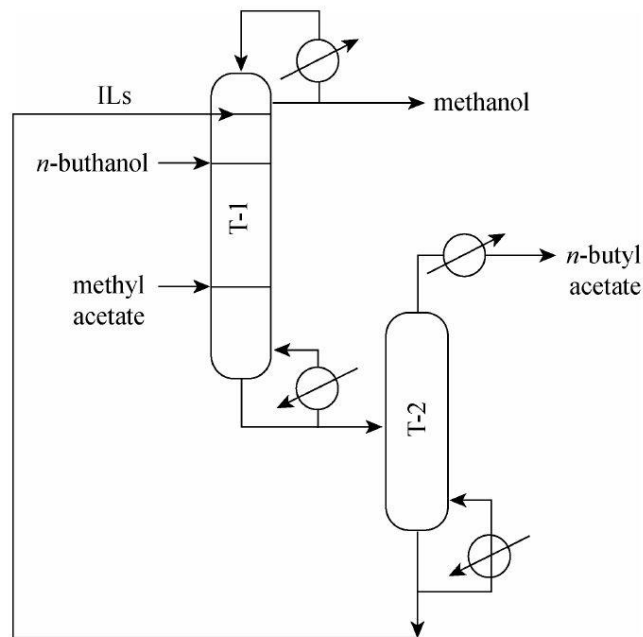


Figure 7. Methyl acetate transesterification via reactive and extractive distillation using an ionic liquid (Cai et al., 2011).

2.6.2. Reactive distillation with pervaporation

Pervaporation, also known as vapor permeation, is a technology based on the usage of a barrier which allows overcoming certain thermodynamic limitations physically. Species with higher permeability are continuously withdrawn in vapor state as permeate from the mixture, which is at a pressure high enough to maintain itself in the liquid phase, through a membrane. Meanwhile, components with lower permeability remain in the initial liquid phase and are collected as retentate.

Low-selectivity membranes are usually only one-component selective. Hence, in the MEAC–MEOH azeotrope case, the permeate stream is mainly constituted of MEOH. However, large membrane areas are required to attain a highly concentrated retentate, since the concentration gradient is the driving force for this process. Additionally, a distillation column is needed to separate MEOH from MEAC further.

A conventional operation sequence for reactive distillation with pervaporation (Figure 8) consists of a reactive distillation column (RDC), a pervaporation unit (PV) and a methanol column (MC). Using this configuration, it is possible to avoid the

azeotropic composition and obtain highly purified products of the methyl acetate transesterification using a reasonable membrane area.

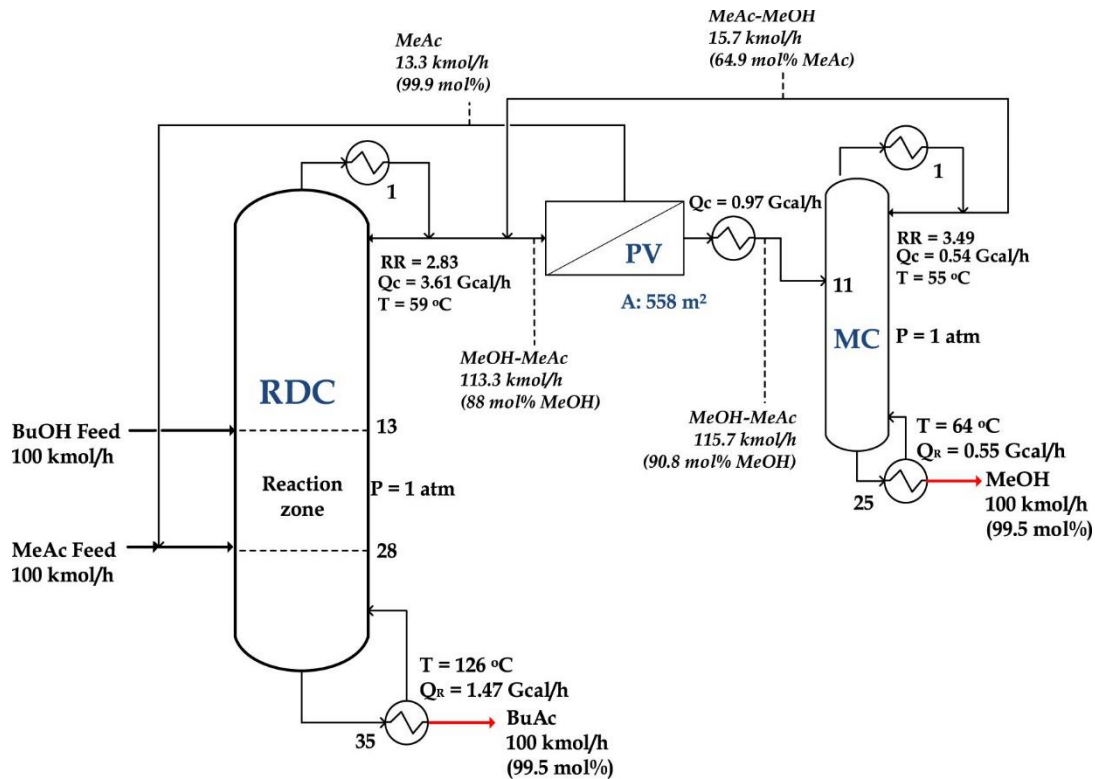


Figure 8. Reactive distillation with low selectivity pervaporation (Harvianto et al., 2017).

High concentrations of components in both sides of the pervaporation membrane are also achievable by implementing a high selectivity membrane. Reactive distillation with high selectivity pervaporation enables achieving high purities of the desired ester and methanol without needing a column for the alcohol (MC). This configuration reduces significantly energy and equipment costs in comparison with reactive distillation with low selectivity pervaporation (Harvianto et al., 2017).

Although MEAC–MEOH azeotrope can be overcome using pervaporation, the usage of membranes in the industry implies drawbacks associated to membranes nature, and, thus, ultimately bound to their lifetime, which directly affect operational costs. Some of these disadvantages are the need of long-life membranes, modules of high surface areas and/or clean-up operations to prevent membrane deterioration and degradation due to caking, plugging and fouling (Seader et al., 2011).

2.6.3. Reactive and pressure swing distillation

According to the thermodynamic data (Figure 9), the composition of MEAC–MEOH azeotrope varies about 14 percentage points in a mole basis when pressure is shifted from 1 to 5 bar. Thus, overcoming the azeotropic composition to attain highly purified products via pressure-swing distillation is practical according to conditions stated in Section 2.3.

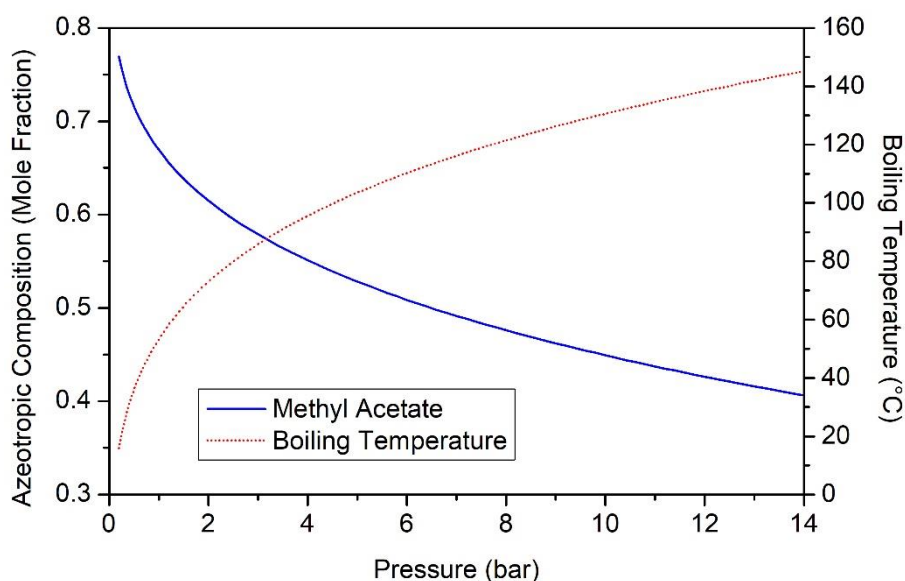


Figure 9. Effect of pressure on methyl acetate–methanol azeotropic composition and boiling temperature.

As stated previously, this enhanced distillation technique can be combined with reactive distillation to generate a more valuable chemical from MEAC such as n-butyl or isobutyl acetate. The alcohol which acts as reactant in the transesterification reaction, like MEOH, forms an azeotrope with the ester generated in the process, i.e. butanol and isobutanol form azeotropes with n-butyl and isobutyl acetate respectively (Table 3). Nevertheless, these azeotropic mixtures are also broken with pressure-swing distillation.

Table 3. Impact of pressure on alcohol–ester azeotropic composition.

Pressure	Alcohol Mole Fraction	
	1 bar	3 bar
n-Butanol–Butyl Acetate	0.776	0.998
Isobutanol–Isobutyl Acetate	0.866	0.992

Therefore, taking the described factors into account, reactive pressure-swing distillation is an attractive technology to separate MEAC–MEOH azeotrope and transform MEAC into a solvent with higher value via transesterification. This novel configuration for MEAC revalorization was previously proposed by Bonet et al. (2005) and Suo et al. (2016). However, despite being an innovative separation sequence, related literature is limited and, thus, further research is required.

This Introduction Chapter has provided a general insight into the state-of-the-art technologies proposed to overcome azeotropes. The separation processes, which are classified according to the agents used to perform the separation of homogeneous mixtures, were detailed. The most used methods are based on the usage of energy-separating agents (ESA), such as distillation, since these technologies are considerably more mature in the chemical industry. In addition, these operations do not have the drawbacks that entails adding new substances, which are typical of operations that depend on the use of mass-separating agents (MSA). Consequently, pressure-swing distillation is an attractive enhanced distillation technology to separate close-boiling systems or azeotropes, because no additional chemicals are needed. Mixtures to be separated, however, must be pressure-sensitive to make the process viable, which is the case of the azeotropic mixture composed of methyl acetate and methanol.

This mixture is obtained in large amounts in the polyvinyl alcohol process, which results in a dependence of the polymer price on the income obtained from these by-products. Accordingly, processes that combine the reaction operation –to convert this residual stream into more valuable substances– with separation technologies have been thoroughly researched and reported in the literature. Reactive pressure-swing distillation is an innovative alternative to achieve this objective. Nevertheless, papers regarding this technology are limited and available information does not offer an insight into the all the variables involved in its optimization. Therefore, reactive pressure-swing distillation applied to the methyl acetate–methanol azeotrope case study will be studied and optimized to explain the factors that have an important effect on this process.

3. OBJECTIVES

The purpose of this report is modeling and studying a separation system integrating pressure-swing and reactive distillation to produce a valuable compound from methyl acetate, which is generated as by-product in the polyvinyl alcohol synthesis process as part of a minimum-boiling azeotrope with methanol, via transesterification. Units involved in the process are optimized to obtain products fulfilling the commercial specifications by selecting the appropriate design factors to reduce costs.

The schematic separation sequence is represented in Figure 10. Transesterification takes place in the column that operates at a high pressure (HPC). In this unit, the surplus of methyl acetate to the azeotropic composition reacts with isobutanol to produce methanol, which takes part in the azeotropic composition at high pressure, and isobutyl acetate, which is withdrawn as bottoms. The high-pressure azeotrope leaves the column as distillate and is introduced into the column that operates at a lower pressure (LPC), where methanol excess with respect to the azeotrope at low pressure is removed as bottoms and the low-pressure azeotropic mixture, which is collected as distillate, is recycled to the reactive column.

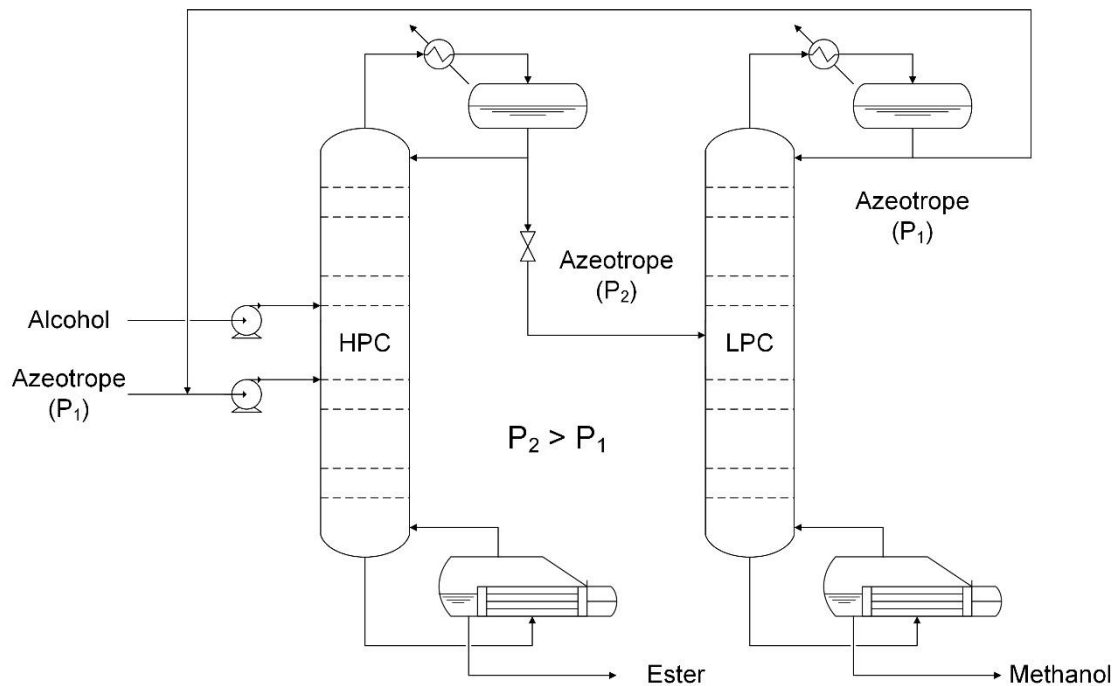


Figure 10. Schematic operation sequence.

4. METHODOLOGY

In this chapter, the thermodynamic model applied to the reactive pressure-swing distillation process and the chemical compounds used in this system were specified. In addition, the procedure followed to generate the process configuration in the simulation environment and the different tools used to perform the optimization analysis are also described.

4.1. Reaction System and Thermodynamic Model

The separation sequence (Figure 10) is modeled using Aspen Plus. To simplify calculations, only the components involved in the reaction (Figure 11) are considered to perform this simulation, namely, methyl acetate (MEAC), methanol (MEOH), isobutyl acetate (IBAC) and isobutanol (IBOH), thus, feedstock is assumed to be pure.

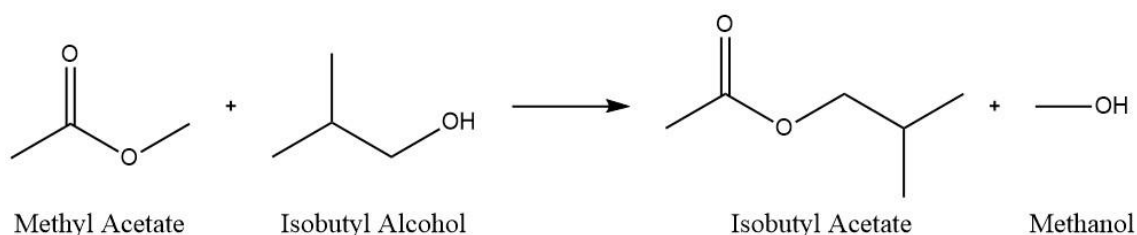


Figure 11. Methyl acetate transesterification with isobutanol.

The kinetic data of the transesterification reaction catalyzed by the ion-exchange resin Amberlyst 15 (Table 4) was reported by Suo et al. (2017). The authors used the PH model to determine the parameters, assuming the temperature dependence described by Arrhenius equation for pre-exponential factors.

Table 4. Kinetic parameters for the pseudohomogeneous model.

Kinetic Parameter	Pre-exponential factor, A	Activation energy, E_A
Units	$\text{kmol s}^{-1} \text{m}^{-3}$	kJ mol^{-1}
Forward Reaction	$8.96 \cdot 10^{10}$	86.56
Backward Reaction	$2.58 \cdot 10^9$	75.96

Nonidealities in the liquid phase are taken into consideration by using activity coefficients γ_i , which are determined using the built-in NRTL equation. Since some

binary interaction parameters are missing from Aspen Plus database, the NRTL (B_{ij}) and non-randomness (C_{ij}) parameters collected by Jie et al. (2016) are used (Table 5).

Table 5. NRTL binary interaction parameters (Jie et al., 2016).

Component i	Component j	B_{ij}	B_{ji}	C_{ij}
Methyl Acetate	Isobutanol	505.09	-227.25	0.2
Methyl Acetate	Isobutyl Acetate	187.6801	-137.569	0.3
Methyl Acetate	Methanol	146.111	223.376	0.296
Isobutanol	Isobutyl Acetate	210.636	-59.6116	0.3053
Isobutanol	Methanol	70.9559	8.96165	0.3018
Isobutyl Acetate	Methanol	-463.77	366.8	0.399

4.2. Simulation Environment

Columns are modeled with *RadFrac* modules, using the *Equilibrium* calculation type, which is based on the vapor–liquid equilibrium-stage concept. Total condensers are used in HPC and LPC. The selected convergence method is *Strongly non-ideal liquid* due to the presence of azeotropes (Section 2.6.3). Specified pressures are assumed to remain constant along columns.

Feedstock is fed to the reactive distillation column (RDC) using the *Above-Stage* convention and through independent streams to ease the analysis of the effect of feed stage location. The pressure of RDC feed streams are raised to the value specified in the HPC using pumps and their temperatures are then increased to boiling point before introducing them into the corresponding column. IBOH is fed in equimolar proportion to the excess of MEAC with respect to the high-pressure azeotrope, i.e. the difference between MEAC azeotropic composition at P_2 and P_1 .

Kinetic model parameters of transesterification are specified in *Reactions* section of the simulation environment. Stoichiometry of forward and backward reactions are input after selecting *REAC-DIST* as reaction type. In the *Kinetic* tab, the kinetic data is introduced using the built-in *Power Law* expression. Since the reaction takes place in the liquid phase and the PH model parameters were calculated according to reactants activities (Suo et al., 2017), reacting phase and [Ci] basis are changed to *Liquid* and *Mole gamma* respectively.

The RDC (HPC) is defined by applying the REAC-DIST reaction and specifying the same liquid holdup to all the stages. In Aspen Plus, heterogeneous reactions are treated as pseudohomogeneous and thus the holdup basis determines the units for the kinetic model. Pre-exponential factor units are $\text{kmol s}^{-1} \text{ holdup-unit}^{-1}$, where holdup-unit is kg, kmol or m^3 depending on the holdup basis specified in the RDC (*Aspen Plus Reference Manual*, 2017). Hence, holdup basis is changed to *Volume*, in accordance with the units indicated in Table 4.

HPC distillate pressure is adiabatically reduced to the value specified in the LPC using a valve and is then introduced into the column. The overhead product collected in the LPC is recirculated and mixed with the fresh feed stream that contains the azeotropic mixture.

4.3. Process Optimization

The separation sequence is optimized by minimizing variables that have a significant impact on energy and equipment costs. The optimization procedure is performed using the built-in *Sensitivity* tool. Each factor is analyzed independently maintaining other factors that might interfere in the analysis unchanged.

A flow rate of 100 kmol/h for the HPC azeotrope feed stream is set as basis of calculation to prevent convergence problems during iterations of sensitivity analysis. The basis is kept invariable by recalculating the necessary amount of fresh azeotropic mixture considering the flow rate of azeotrope recycled from the LPC. This adjustment is implemented by specifying the corresponding mass balance equations in the *Design Specs* tool assuming that the LPC overhead product has the same composition as fresh azeotrope. The flow rate of alcohol introduced into the system is likewise adjusted.

The effect of pressure on the azeotropic composition is also taken into account in these adjustments by using a column of reference. This column, which is also modeled using a RadFrac module, has a number of stages and a reflux ratio sufficiently high to achieve the azeotropic composition of MEAC and MEOH in the distillate. The pressure of the column of reference is set to change along with the HPC pressure to determine the azeotropic composition at the different pressures the simulated process is analyzed.

The data collected in this unit (azeotropic composition) is subsequently used in the Design Specs tool to readjust flowrates of feedstock as described above.

4.4. Product Specifications

The process studied in this document is optimized to achieve the specifications shown in Table 6, which were obtained from chemical manufacturers.

Table 6. Isobutyl acetate and methanol specifications.

	Units	Isobutyl Acetate	Methanol
Purity on dry basis	% w/w Min	99.00	99.85
Water	% w/w Max	0.05	0.10
Acetone	mg/kg Max	N/A	30
Ethanol	mg/kg Max	N/A	50
Isobutanol	% w/w Max	0.50	N/A
Acidity as acetic acid	mg/kg Max	100	30
Specific gravity 20/20°C		0.871-0.875	0.791-0.793

Although the American Standard Test Method (ASTM) organization has developed a standard specification for isobutyl acetate (ASTM D1718, 95% Grade), manufacturers like EASTMAN (*Eastman™ Isobutyl Acetate*, 2009) commercializes this chemical with higher purities, thus, these product specifications are used to design the process. Specifications for methanol were obtained from the International Methanol Producers and Consumers Association (*IMPCA Methanol Reference Specifications*, 2015).

In the Methodology Chapter, the procedures followed to model and optimize the studied process in Aspen Plus simulation environment were explained. Nonidealities in the liquid phase are considered using the NRTL model and only species involved in the transesterification reaction are included in the simulation. The reaction is described by using the pseudohomogeneous kinetic model, which is subsequently used to define the reactive column. The reactive pressure-swing distillation process is enhanced to obtain products with commercial specification using sensitivity analysis, which is performed along with different tools implemented in the program.

5. RESULTS AND DISCUSSION

The main source of energy consumption in a separation sequence comprised of distillation columns are heat exchangers. Heat duties depend on the flow rate of the stream desired to be cooled or heated, and, from an economic perspective, exchangers using hot utilities, i.e. reboilers, are more relevant, because the involved costs are considerably higher.

Heat duties of condenser (Q_C) and reboiler (Q_R) are closely related variables. Using these variables as design factors, however, may lead to unrealizable operating conditions in an optimization process. Hence, in the design of distillation columns, the design factor used to optimize energy consumption is reflux ratio (R), since heat duties depend, to a great extent, on this variable. Consequently, to reduce Q_C and Q_R , and, ultimately, energy costs, R must be minimized. A decrease of R results in a reduction of column diameter and utilities requirements, but, at the same time, entails an increase of the number of stages required to achieve product specifications. Therefore, when this design factor is optimized, both equipment and energy costs must be taken into account.

The optimal reflux ratio is estimated from the analysis of the total annualized cost (TAC), which results from the annualized fixed investment costs and energy-related annualized costs. The optimal minimum reflux ratio R/R_{min} accepted in the industry ranges from 1.05 to 1.50, although columns are frequently designed with higher reflux ratios for flexibility (Seader, 2011). The process studied in this document is more complex than a regular distillation sequence, however, it is essentially based on this technology and thus it is modeled and optimized considering this heuristic.

5.1. Effect of Interval between Feed Stages

One of the design factors that influences reflux ratio is the feed stage. In the process studied in this report, however, two feed lines are connected to the HPC, one for the mixture of MEAC–MEOH and another for IBOH reacting with MEAC. Accordingly, the appropriate feed stages must be determined considering the effect of the location of the other stream along the column. This factor is analyzed by performing simulations using different combinations of feed stages. The number of stages and the catalyst

amount of the RDC are sufficiently large not to influence the required R is used to evaluate this variable. IBOH is heavier than MEAC (Table 7), thus, its corresponding feed stream could be expected to be introduced into a tray placed above the azeotrope feed stream to obtain a countercurrent flow of reactants.

Table 7. Effect of pressure on species boiling point.

Species	Boiling Temperature (°C)		
	1 bar	5 bar	10 bar
Azeotrope*	53.3	103.4	130.4
Methyl Acetate	56.7	111.9	143.0
Methanol	64.2	111.5	136.8
Isobutanol	107.3	159.9	189.8
Isobutyl Acetate	116.0	179.0	215.4

* Azeotropic composition varies with pressure.

After performing several simulations, it was observed that the factor influencing reflux ratio was the gap between azeotrope and alcohol feed stages, namely, the number of trays separating these two feed streams. According to these results, reflux ratios obtained when this gap is kept unchanged are the same despite the actual position of these streams along the column. For instance, when alcohol and azeotrope are fed in stages 20 and 25 or 35 and 40 respectively, Aspen Plus returns identical reflux ratio values. Therefore, the effect of the stages gap between feed streams on the reboiler heat duty, minimizing the required reflux ratio, is analyzed (Figure 12).

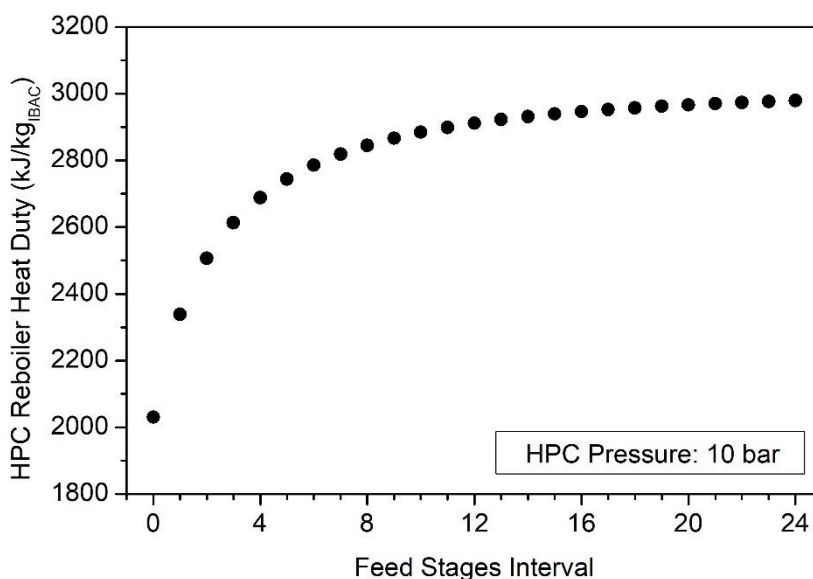


Figure 12. Effect of interval between feed stages on reboiler heat duty.

Figure 12 shows that both azeotrope and alcohol must be fed in the same stage to achieve the lowest energy consumption. Reflux ratio and, thus, HPC reboiler heat duty increases with the interval between azeotrope and alcohol feed stages by closely following the tendency of a logarithmic function, where the minimum value is obtained when there is no gap between feed stages.

5.2. Effect of Feed Stage: Optimal Number of Stages in the Rectifying Section

The influence of feed stages of these streams along the column on the required energy consumption was studied to determine the optimal stages in the rectifying section (Figure 13). As stated previously, other factors were such to ensure that their effect on the analyzed variable can be neglected.

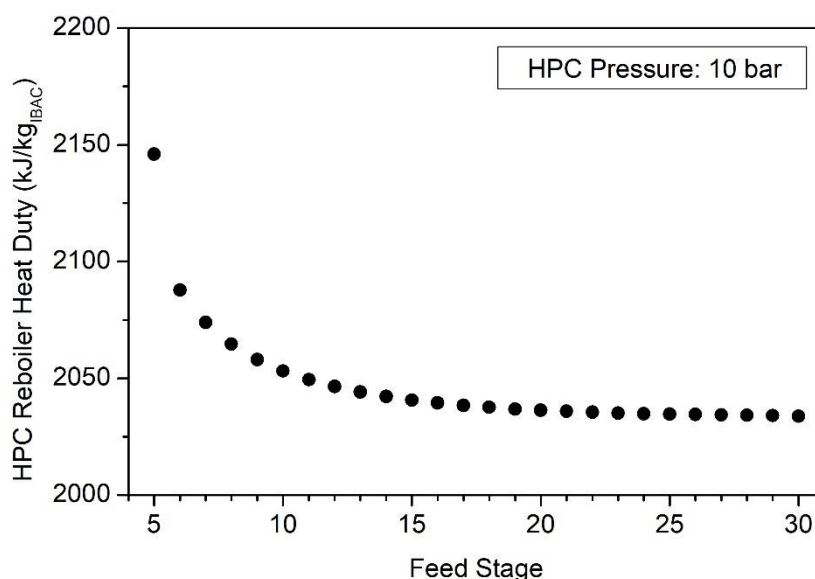


Figure 13. Effect of feed stage on reboiler heat duty.

The evolution of reboiler heat duty –required to achieve the IBAC purity specified in Table 6– with the feed stage of both azeotrope and alcohol is represented in Figure 13. Heat duty escalates considerably when feed streams are placed near the unit ends –top or bottom of the column– since the available number of stages is insufficient to attain the desired specifications. If this effect on the bottom end (stripping section) is ignored, the trendline of this variable resembles an asymptotic function. Consequently, there is a zone in which a significant shift of the studied factor, i.e. feed stage, only results in a small variation of the function value.

According to this information, the substantial variation of Q_R^{HPC} occurs when feed streams are introduced within the first 10 stages from the top. Therefore, stages ranging from 10 to 20 can be considered the suitable to feed azeotrope and alcohol streams, since lowering their position along the column further involves only a slight decrease of energy cost that might be offset by the raise of the column cost resulting from its height increase.

5.3. Optimal Number of Stages in the Stripping Section

The optimal number of stages in the column is also determined by evaluating its influence on the HPC reboiler heat duty. Figure 14 shows the impact of this variable at different feed stages.

Like the previous analyzed factors, the evolution of heat duty for a specific feed stage at different stages in the stripping section also tracks asymptotic function. When total number of stages in the column is sufficiently large not to affect the required R , values of Q_R^{HPC} are the same as the ones shown in Figure 13. However, as the number of stages in the stripping zone decreases, energy requirements in the column begins to increase progressively.

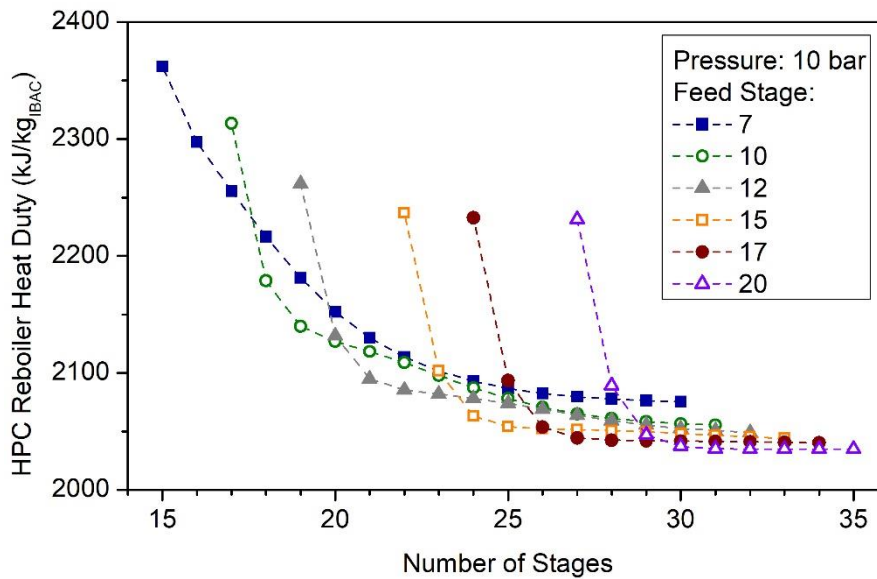


Figure 14. Effect of total number of stages at different feed stages on reboiler heat duty.

Despite the distinct variation of the required thermal power for the different feed stages analyzed, there is a number of stages that does not involve a significant increase of the reflux ratio for each case (Table 8). These optimum number of stages is dictated by the optimal number of stripping section stages, which according to this data, is 10.

Table 8. Optimal number of stages for different feed stages.

Stages			R	Δ	Q_R^{HPC}	Δ
M	N	Total	mol/mol		GJ/mt _{IBAC}	
40	10	50	0.207		2.03	
20	10	30	0.211	2.0%	2.04	0.3%
17	10	27	0.215	4.1%	2.04	0.7%
15	10	25	0.221	7.1%	2.05	1.2%
12	10	22	0.241	16.3%	2.09	2.7%
10	10	20	0.266	28.6%	2.13	4.7%

The minimum reflux ratio ($R_{min} = 0.207$), is achieved when the feed stage is 40 and $M + N$ is 50, where M and N are the number of stages in the rectifying and the stripping section respectively. Taking the R/R_{min} heuristic into account, a column with 25 stages can be considered appropriate, since a further rise of the feed stage position does not result in a significant decrease of the total number of contacting trays.

5.4. Optimal Number of Reactive Stages

The number of reactive stages is also an important design factor because it affects the investments on catalyst, an element whose relevance primarily depends on catalyst cost and lifetime.

As described in Section 4.2, all stages in the HPC were initially set up as reactive. Taking into consideration that, on one hand, the lower stages of the column are more concentrated with IBAC and, on the other hand, when a reversible reaction system is highly concentrated with products, the equilibrium is shifted towards the formation of reactants, catalyst is expected to promote the backward reaction in the stripping section. This effect is represented in the reaction profile of the RDC (Figure 15).

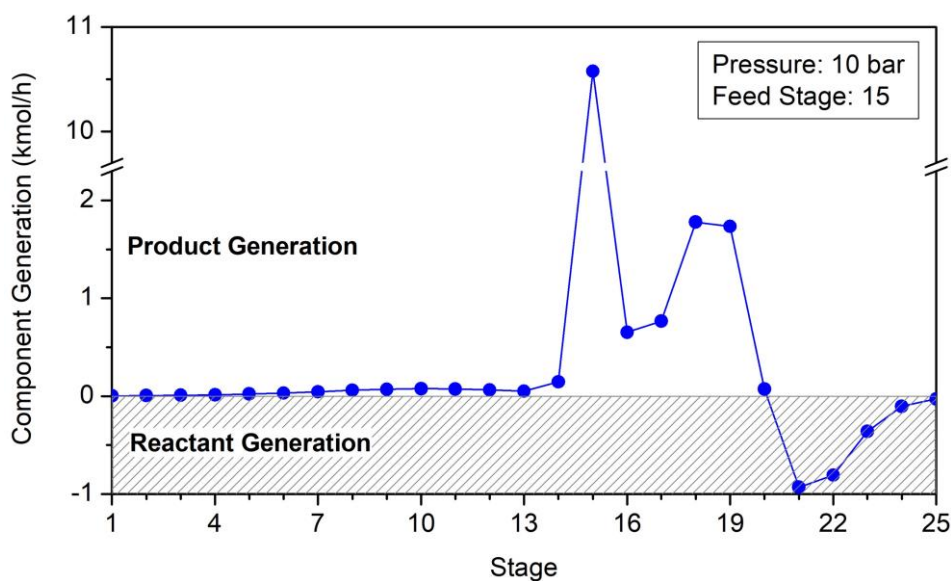


Figure 15. High-pressure column reaction profile.

Although the amount of reactant generated in the stripping zone is not significant compared to the overall amount of product obtained –due to the low concentration of MEOH in the lower section of the unit–, this fact increases the required reflux ratio and thus energy consumption. Therefore, the location of the reaction section, is another factor that must be considered, since, when a reversible reaction takes place in the system, catalysts might accelerate the inverse reaction if they are not placed in the suitable stages. In addition, the stages catalysts are placed along the column is a decisive factor for the optimization of other variables that are influenced by the recommended operating conditions of the catalyst –this effect is thoroughly studied in Section 5.5.

The impact of the number of reactive stages on HPC reboiler heat duty was analyzed by changing the starting reaction stage, keeping constant the ending stage of the reaction zone, and vice versa (Figures 16 and 17). With this procedure, the effect of the presence of catalyst on rectifying and stripping sections can be evaluated independently.

The HPC is modeled to obtain IBAC with high purity as bottoms, thus, the rest of the components are expected to be more concentrated in upper trays. Since some of these species are reactants of transesterification, the impact of removing reactive stages (catalyst) from the rectifying zone on Q_R is more significant than the effect on the stripping zone. Figure 16 shows that when the starting reactive stage is lowered, R and, consequently, heat duties increase. This effect is progressively enlarged when the

reaction section begins from lower stages because the concentration of reactants, i.e. free MEAC and IBOH, in these trays is gradually higher.

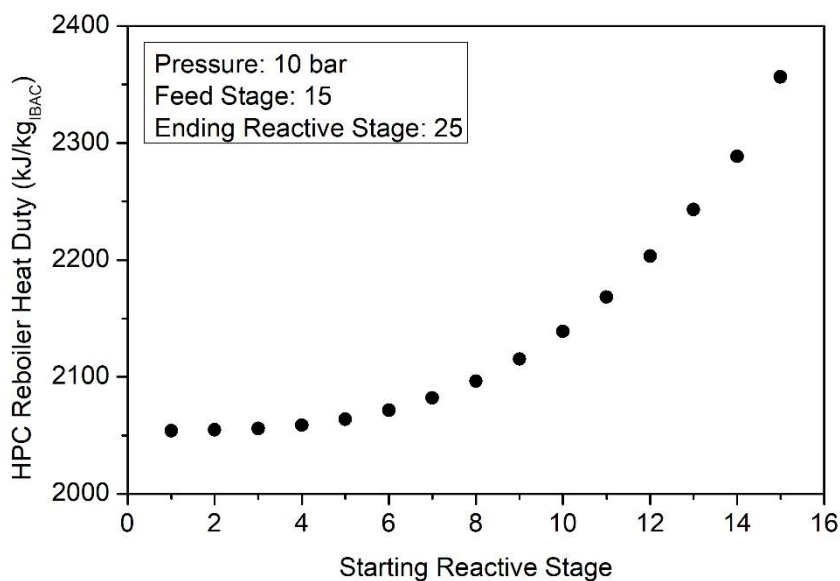


Figure 16. Impact of starting stage of reaction section on heat duty.

The evolution of heat duty represented in Figure 17 does not track the usual asymptotic function due to the reversible nature of transesterification reaction. Energy consumption decreases as the ending reactive stage is shifted towards upper trays until reaching a minimum value, which corresponds to the stage where concentration of species is such that the backward reaction no longer occurs.

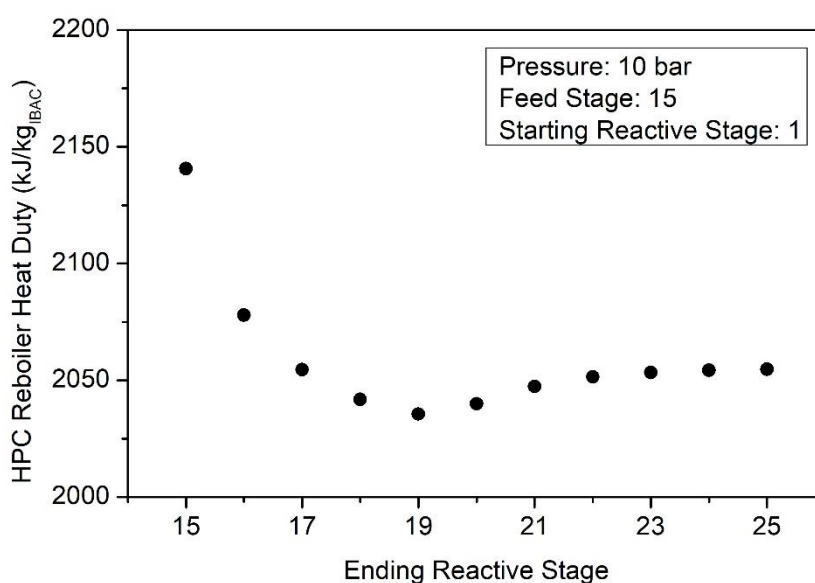


Figure 17. Impact of ending stage of reaction section on heat duty.

Analyzing the described factors, a reaction section with a starting stage ranging from 2 to 5 and an ending stage of 16–19 seem to be appropriate.

5.5. Optimal Pressure Swing

MEAC surplus to azeotropic composition, consequently, MEAC reacting to produce IBAC, increases as the pressure difference between columns broadens. Accordingly, HPC and LPC pressures should theoretically be shifted towards the maximum and minimum limits, respectively, to enhance the process yield.

Nevertheless, although the biggest change in the azeotropic composition takes place at high-vacuum conditions (Figure 9), operating under these circumstances entails using columns with tough materials, sophisticated structures and vacuum pressure changers, which ultimately escalates capital investment and operation costs. Therefore, operating at atmospheric pressure is preferred, unless system species or equipment integrities are at stake due to decomposition, polymerization or corrosion (Seader, 2011).

Furthermore, on one hand, pressure increases boiling points significantly (Table 7) and, thus, raises the column temperature profile along with distillate and bottoms temperatures. This instance involves (1) a conditioning of required hot utilities and (2) a restriction of catalysts that can be used in the process –resulting from their thermal stability– or a limitation of the HPC operating pressure, which corresponds to the one that raises the temperature of the lowest stage that contains catalyst (ending reactive stage) to the maximum operating temperature recommended for the catalyst.

On the other hand, an increase of pressure difference between HPC and LPC also results in a greater pump energy consumption. However, even though electricity is considerably more expensive than thermal power, pumps work (W_P) is insignificant in comparison with HPC reboiler heat duty (Table 8).

Table 8. Comparison of thermal and electric power consumptions.

Pressure	2 bar	5 bar	10 bar
Q_R^{HPC} (kJ/kg _{IBAC})	8380	3190	2040
W_P (kJ/kg _{IBAC})	4.7	8.1	12.6

In industrial processes, steam is the preferred hot utility because it offers diverse advantages (Towler & Sinnott, 2012):

- High heat of condensation per unit mass of steam at constant temperature.
- Steam temperature can be controlled with pressure.
- High heat-transfer coefficients.
- Nontoxicity and nonflammability.

Steam pressure typically ranges from 3 to 50 bar to raise its temperature up to 265°C. However, although a wide range of temperatures can be achieved by changing steam pressure, it is conventionally generated and classified in three different pressure levels (Turton et al., 2012), which usually differ from site to site. Steam pressure levels used in Aspen Plus Economics, for instance, are the ones listed in Table 9.

Table 9. Process steam pressure levels.

Steam	Pressure		Temperature	Cost
	psi	bar	°C	USD/GJ*
Low pressure steam (lps)	100	6.9	164	9.66
Medium pressure steam (mps)	165	11.4	186	12.01
High pressure steam (hps)	400	27.6	229	15.82

* Latent heat only.

Hence, the maximum achievable temperature in the HPC reboiler and, consequently, operation temperatures are restricted by the available steam pressure-levels. As stated above, as pressure increases, the azeotropic composition is shifted further and more product is obtained. Therefore, for a better analysis of the studied variables, the effect of pressure on heat duties of reboiler and preheaters –used to raise feedstock temperatures– are expressed per unit mass of product generated (Figure 18).

The energy consumption of heat exchangers per unit mass of product is largely reduced when the HPC operates at high pressures. According to this information, and considering the steam temperature limitation (265°C), to perform the reactive distillation process using steam as hot utility, the maximum achievable pressure, which corresponds to the global minimum of the function, is approximately 19 bar, assuming a minimum temperature approach of $\Delta T = 10^\circ\text{C}$.

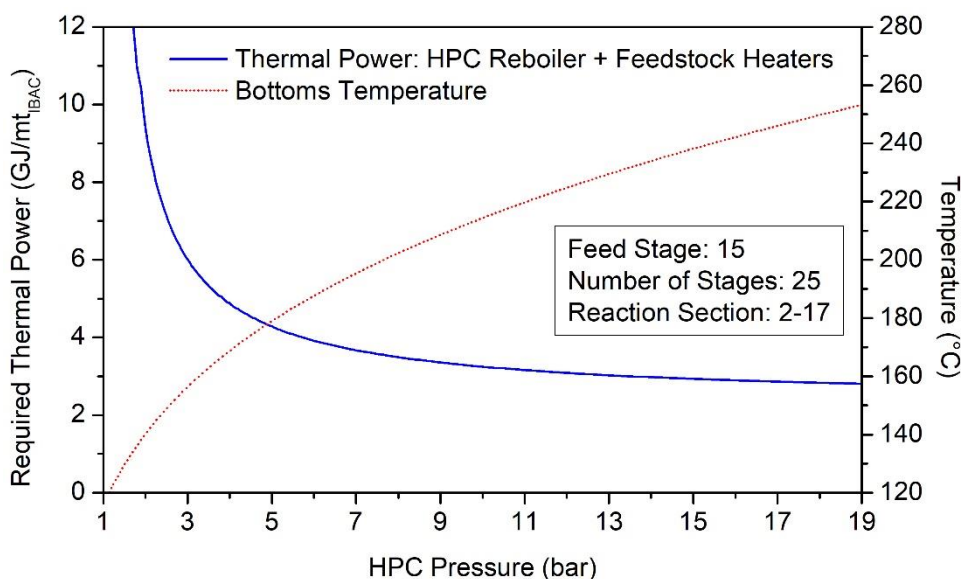


Figure 18. Effect of pressure on energy consumption of heat exchangers per metric ton of isobutyl acetate produced and bottoms temperature.

Nonetheless, as stated previously, optimal operating pressure, which defines column temperature profile, is also conditioned by the maximum operating temperature of the catalyst. Consequently, this factor also affects the selection of the most suitable ending reactive stage and thus the optimal feed stage, since, as shown in Figure 17, the suitable tray for the ending reactive stage is located 1–4 trays below the feed stage for this system. Hence, moving the feed stage to upper positions along the column, even though results in an increase of R and heat duties, allows operating at higher pressures and produce more IBAC.

This effect is evaluated by representing the evolution of temperature in the ending reactive stage (stage 17) with pressure. In addition, the impact of pressure on energy was once more analyzed assuming that the available heat source is comprised of steam pressure levels listed in Table 9. The results of the analysis are represented in Figure 19.

The variation of steam cost with pressure has two significant local minimums, which correspond to pressures where a change of the steam pressure level is required in the reboiler, namely, a change from lps to mps at 2.90 bar, and a replacement of mps with hps at 4.65 bar. The global minimum (10.9 bar) corresponds to the maximum operating pressure achievable with the specified hps. There are other minor local minimums (at 4.3 and 7.3 bar) that result from the change of the type of steam in the heat exchangers

used to raise feed streams temperatures to boiling point. Nevertheless, since the energy consumption of these units is lower than the required in the HPC reboiler, the effect is not relevant. The presence of local minimums in utility costs must be considered when processes are optimized using algorithms that rely on finding a function minimum—such as the TAC—, like the Simulated Annealing Algorithm used by Wang et al. (2016).

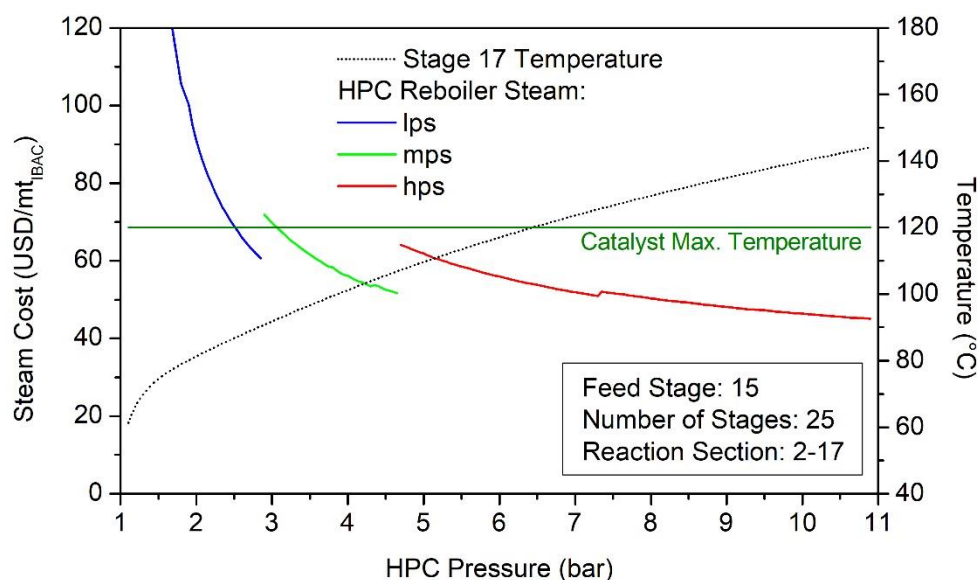


Figure 19. Impact of pressure on the steam cost of HPC reboiler and preheaters and temperature of the ending reactive stage.

The maximum operating temperature recommended for Amberlyst 15, according to its manufacturer, is 120°C (*Amberlyst™ Polymeric Catalysts*, 2011). Hence, if this restriction is added to the optimization procedure, the optimal pressure for the reactive column is 4.65 bar, which corresponds to the local minimum indicated previously. The recommended temperature for the catalyst is reached in the ending stage of the reaction section at 6.4 bar (Figure 19), however, the energy cost per unit mass of product at this pressure is higher than the steam cost that entails operating at 4.65 bar.

Therefore, the most important restriction in this process is the maximum operating temperature recommended for the catalyst. As shown in Section 5.4, on one hand, energy cost might be reduced by setting up the stage 19 as the end of the reaction zone (Figure 17). On the other hand, the increase of Q_R^{HPC} resulting from locating the ending reactive stage in tray 16 might be compensated by the higher amount of IBAC generated by this configuration, since, the higher the ending reactive stage is placed, the lower the

temperature of this tray is and, consequently, it can operate at higher pressures without putting the catalyst at risk. These configurations were compared assuming different operating temperatures for the catalyst (Figure 20).

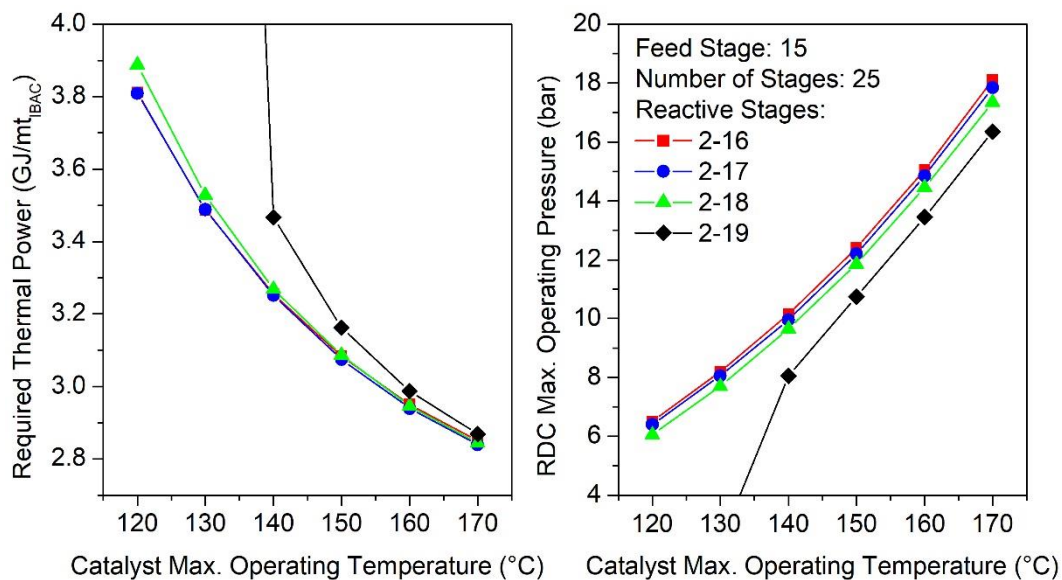


Figure 20. Effect of reaction section location on thermal power and operating pressure.

According to the information represented in Figure 20, assuming that the kinetic data used to model the process is the same for catalysts with different maximum operating temperatures, a RDC whose reaction section has its ending stage located in stage 17 is the best alternative for catalysts with relatively low thermal stability. A reaction zone ranging from stages 2 to 18, seem to be a better option for catalysts with a maximum operating temperature of 150–170°C.

The energy of hot utilities required for all the different alternatives seem to converge when the catalyst maximum operating temperature is higher than 170°C. Therefore, if a catalyst with high thermal stability was to be used in this process, a reaction section whose ending stage is located in stage 19 could be the best configuration, since it requires the same required thermal power, but operating at lower pressures.

Nonetheless, if steam costs (Table 9) restriction is taken into account along with the maximum recommended for Amberlyst 15, the selection of the most suitable location for the reaction zone differs from the abovementioned results, since, as previously stated, the HPC operating pressure (4.65 bar) is lower than the maximum operating pressure

resulting from the catalyst limitation (Table 10). Consequently, a reaction zone ranging from stage 2 to 18 is considered the best alternative.

Table 10. Impact of location of reaction section on steam costs.

Reaction Section		Max. Operating P	Optimal Op. P	Steam Cost
Starting Stage	Ending Stage	bar	bar	USD/mt _I BAC
2	16	6.50	4.65	52.18
2	17	6.40	4.65	51.67
2	18	6.05	4.65	51.43
2	19	1.50	1.50	159.17

5.6. LPC Optimization

The LPC was optimized to obtain methanol with commercial specifications from the HPC distillate generated at 4.65 bar. As explained in Section 4.2, LPC distillate rate was assumed to have the azeotropic composition of MEAC and MEOH to calculate the fresh azeotrope flow rate. Attaining this composition and highly purified MEOH jointly in distillate and bottoms respectively, however, involves using large number of stages and high reflux ratios (Figure 21).

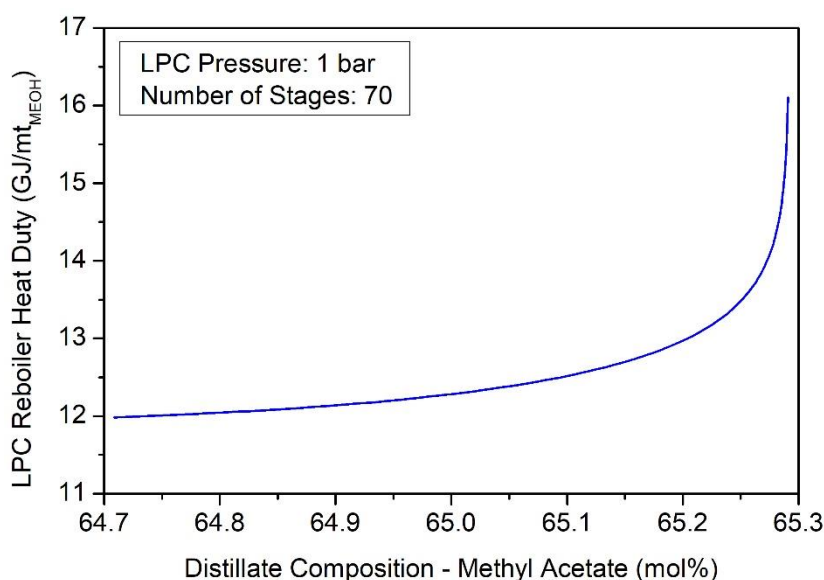


Figure 21. Effect of MEAC mole fraction on energy consumption.

LPC distillate composition can be modified by changing the amount of azeotropic mixture fed into the system. A reduction of the azeotrope flow rate involves a decrease of both MEAC composition in LPC distillate and the required thermal power. However,

bottoms flow rate (purified MEOH) also decreases in equal proportion to the reduction of the fresh azeotrope amount. In other words, decreasing feed flow rate results in a reduction of LPC energy costs and the income from MEOH.

Nevertheless, the variation of these two variables is not the same. While the decrease of MEOH income (Table 12) is proportional to the amount of feedstock reduced, the reduction of steam cost tracks the function represented in Figure 21. Therefore, the optimal flow rate of fresh azeotrope can be determined by taking these factors into account (Figure 22).

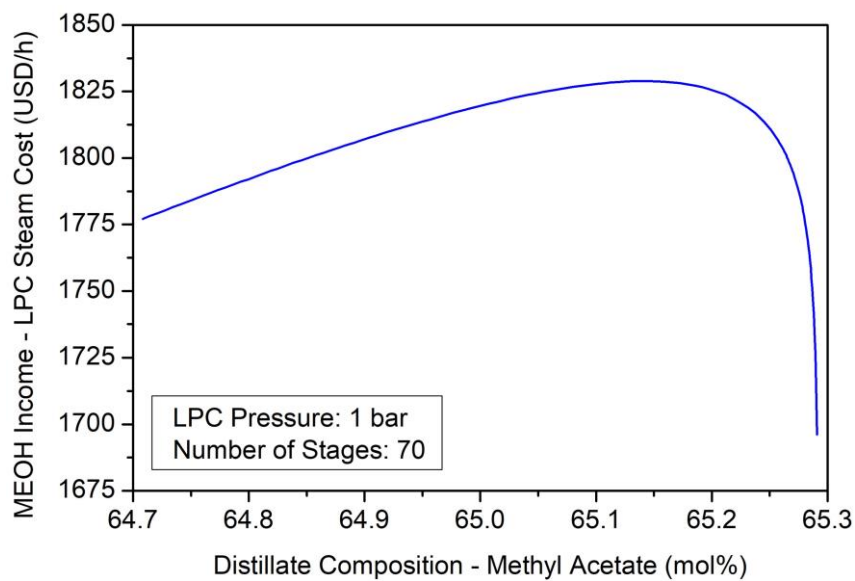


Figure 22. Influence of fresh azeotrope flow rate on MEOH income and costs.

When the azeotrope flow rate is relatively low, the impact of MEOH price is more relevant to the unit profitability, since the required energy per unit mass of MEOH remains constant. Hence, the increase of the difference between income from MEOH and steam cost is proportional to the feed flow rate until reaching a global maximum, which corresponds to the amount of azeotrope such that MEAC composition in the LPC distillate is approximately 65.15 mol%. From this point onwards, the required R to attain MEOH specifications and, thus, steam cost escalates considerably, making the income–cost difference tend to minus infinity ($-\infty$) at the flow rate corresponding to the azeotropic composition (66.29 mol%).

Although the optimal flow rate of fresh azeotrope is the one corresponding to the abovementioned function maximum, a *disturbance* of this design factor might result in a significant reduction of MEOH purity, assuming a constant R . Therefore, operating with a flow rate lower than 150.9 kmol/100 kmol_{IBOH} is recommended.

Rectifying and stripping sections stages were optimized according to the procedures described in Sections 5.2 and 5.3. LPC consists of 25 and 10 stages in rectifying and stripping zones respectively, which results in a $R/R_{min} = 1.17$.

5.7. Optimized Process

The proposed reactive pressure-swing distillation process is represented in Figure 23. The HPC design factors are selected in accordance with the results of analysis carried out in previous sections. This configuration involves a $R/R_{min} = 1.10$.

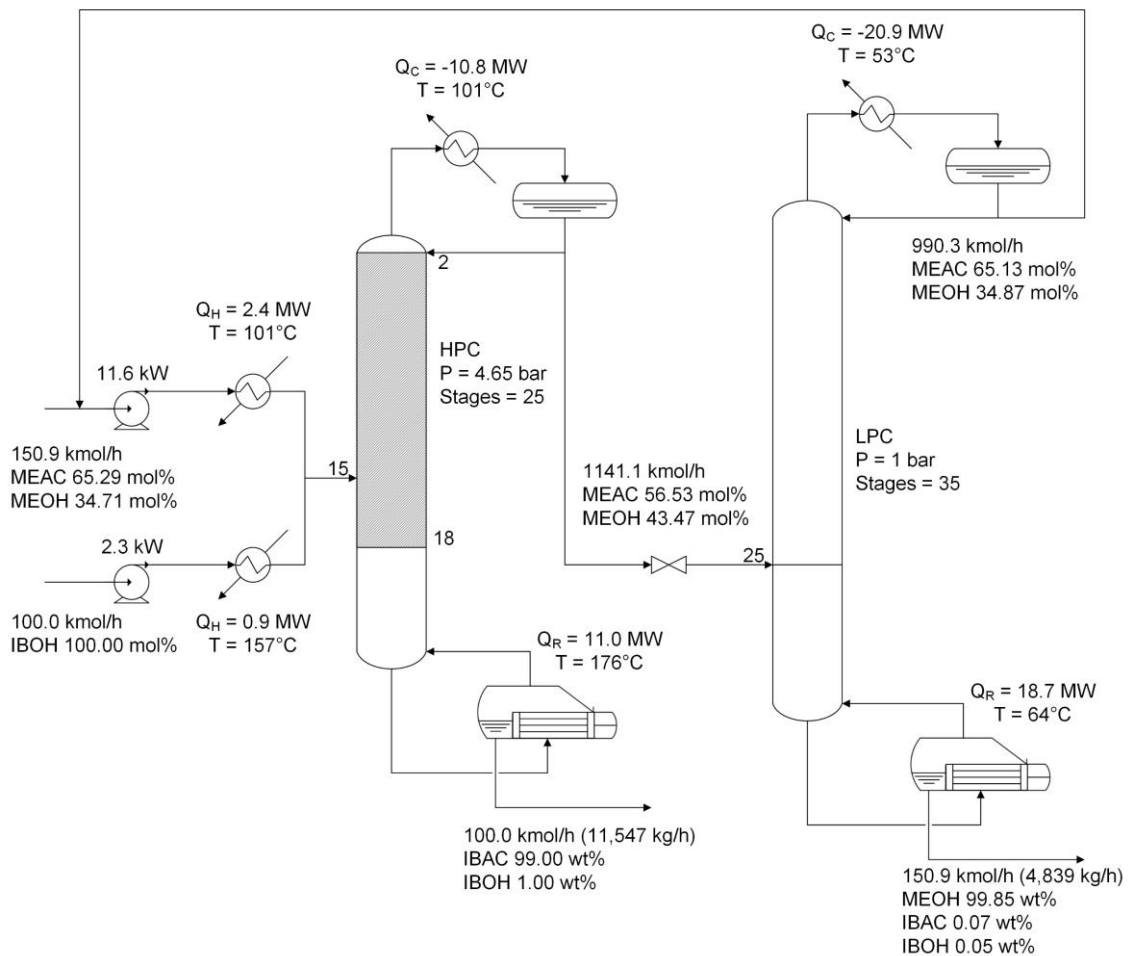


Figure 23. Reactive pressure-swing distillation.

The feedstock for the reactive pressure-swing distillation process are the azeotropic mixture of methyl acetate and methanol (MEAC 66.3 mol%, MEOH 34.7 mol%), which is obtained from PVA synthesis, and pure isobutanol. The fresh azeotrope is mixed with a stream containing a liquid with similar composition recycled from the LPC. Pressures of feed streams are raised to 4.65 bar and subsequently heated to boiling point using heat exchangers –azeotrope and alcohol temperatures are increased to 101°C and 157°C respectively. Both streams are then introduced into the stage 15 of the HPC.

The RDC is composed of 15 rectifying stages and 10 stripping trays. The reaction zone, in which the transesterification of MEAC with IBOH takes place in the presence of Amberlyst 15, ranges from stages 2 to 18. IBOH, fed in equimolar proportion to the MEAC in excess with respect to the azeotropic composition at the RDC operating pressure (4.65 bar), is converted into isobutyl acetate by 98.4% in a mole basis.

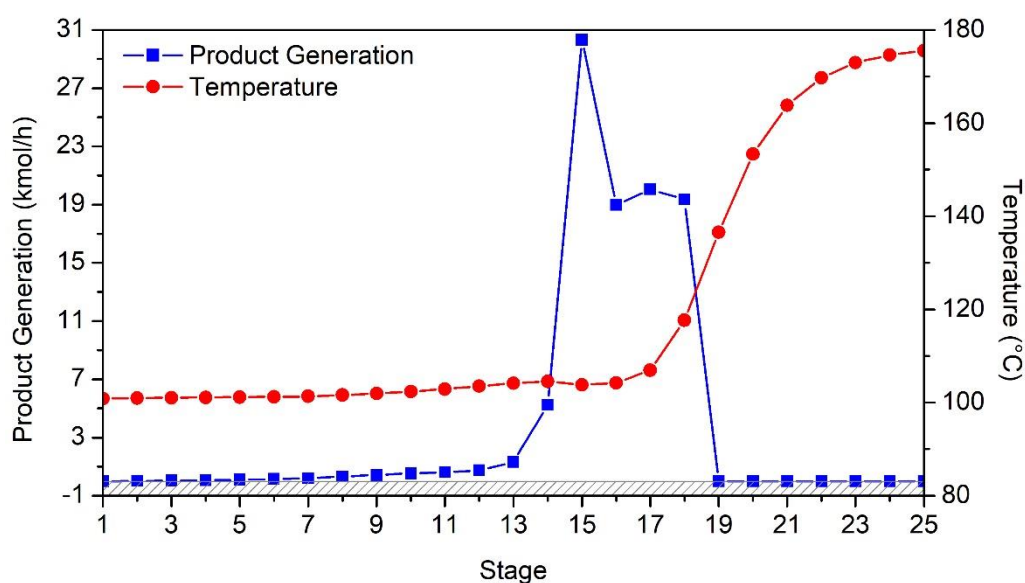


Figure 24. RDC component generation and temperature profiles.

Unlike results shown in Figure 15, no reactants are generated from products in any tray (Figure 24) due to the position of the reaction section along the column. Isobutyl acetate and methanol are mainly generated in stages 15–18, since the concentration of reactants in this region is higher (Figure 24). The ending reactive stage and thus the last stage containing catalyst (stage 18), operates at 118°C, i.e. 2 degrees Celsius below the maximum operating temperature for Amberlyst 15.

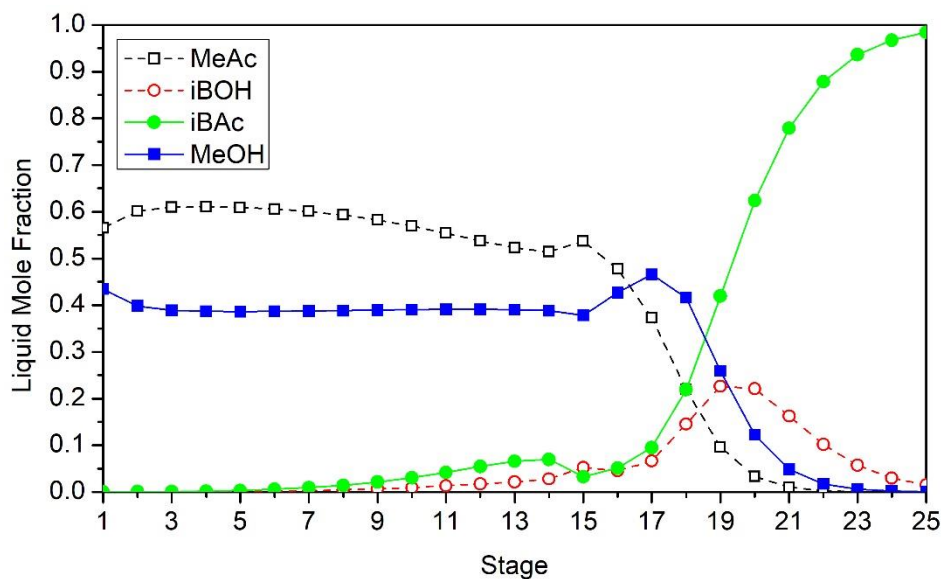


Figure 25. High-pressure column composition profile.

IBAC is the less-volatile component in the system, hence its higher concentration in the lower stages of the HPC (Figure 25). Liquid mole fraction of IBOH along the column varies tracking a bell curve that reaches its maximum at stage 19. Since this alcohol is also considerably heavier than the lightest species, it is primarily collected in the bottoms product. Its concentration in the lowest stage, however, is such that the purity of IBAC meets the commercial specifications (Table 6). MEAC and MEOH mole fractions in the liquid phase gradually increase in the rectifying zone, approaching the azeotropic composition.

Bottoms consists of IBAC (99.00 wt%), IBOH (0.98 wt%), MEOH (0.02 wt%) and less than 30 wt ppm of MEOH and MEAC. The distillate stream transports the MEAC–MEOH mixture, whose proportions (MEAC 56.5 mol%, MEOH 43.5 mol%) are similar to the azeotropic composition at 4.65 bar, and has concentrations of IBOH and IBAC lower than 50 ppm on a mass basis. The overhead product undergoes an adiabatic flash through a valve, reducing its pressure to 1 bar, and is then introduced into the stage 25 of the LPC.

The LPC is comprised of 25 rectifying trays and 10 stripping stages. Due to the operating conditions of this unit, MEOH surplus to the azeotropic composition at 1 bar is gradually collected in the lower section of the column (Figure 26), attaining the desired purity in the last stage (MEOH 99.85 wt%). The heavier species are also

withdrawn as part of the bottoms product (IBOH 0.05 wt%, IBAC 0.07 wt%). In the rectifying section, concentrations of MEAC and MEOH approach the low-pressure azeotropic composition and the distillate (MEAC 65.1 mol%, MEOH 34.9 mol%) is recycled to the RDC as indicated above.

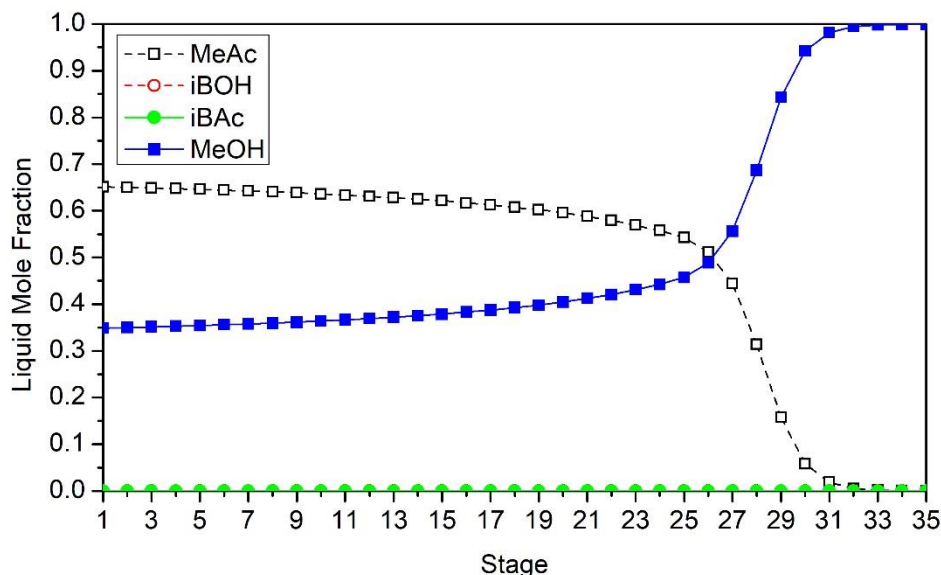


Figure 26. Low-pressure column composition profile.

5.8. Effect of the Amount of Catalyst

The RDC was modeled assuming a large amount of catalyst or a huge liquid holdup in each reactive stage. Consequently, MEAC conversion achieved in each tray is close to the one attained in the equilibrium. However, a column with such implementations is either economically or technologically unfeasible due to the significant cost of catalyst or the disproportionate dimensions they involve respectively. Hence, these factors must be necessarily reduced.

The influence of the catalyst amount on the reflux ratio required to obtain IBAC with the specified purity in the RDC is shown in Figure 27. Pre-exponential factor units were adjusted according to the information described by Suo et al. (2017).

Like other variables described in previous analysis, when the amount of catalyst used in each stage is reduced, the required reflux ratio and thus the energy consumed to attain product specifications increase progressively. When the catalyst weight is higher than

100 kg, its effect on the energy consumption can be neglected since a decrease of the amount of Amberlyst 15 from 200 kg to 100 kg only involves an energy consumption increase of 3.3% per unit mass of IBAC (Table 11). Nevertheless, factors such as the *catalyst price* and its *lifetime* under the conditions indicated in this document, including its impact on the required reflux ratio, have to be considered to rigorously evaluate and determine the optimum catalyst amount for this unit.

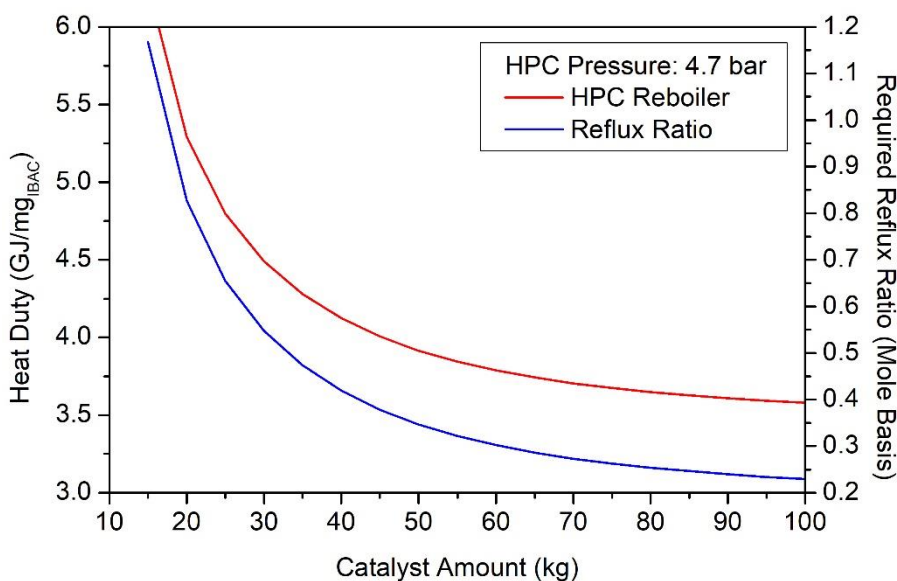


Figure 27. Influence of the catalyst amount on required reflux ratio.

Additionally, as represented in Figure 24, when a large amount of catalyst is used in each tray, products are mainly generated in the feed stage, the tray below it and, to a lesser degree, in stages located above. As the catalyst amount in each tray is changed, however, the amount of product generated in each stage varies (Figure 28).

Table 11. Impact of catalyst amount on energy consumption.

Catalyst	R	Δ	Q_R^{HPC}	Δ
kg/stage	mol/mol		GJ/mt _{IBAC}	
200	0.19		3.46	
100	0.23	21%	3.58	3.3%
50	0.35	83%	3.92	13.0%
30	0.55	189%	4.49	29.7%
20	0.83	338%	5.29	52.8%

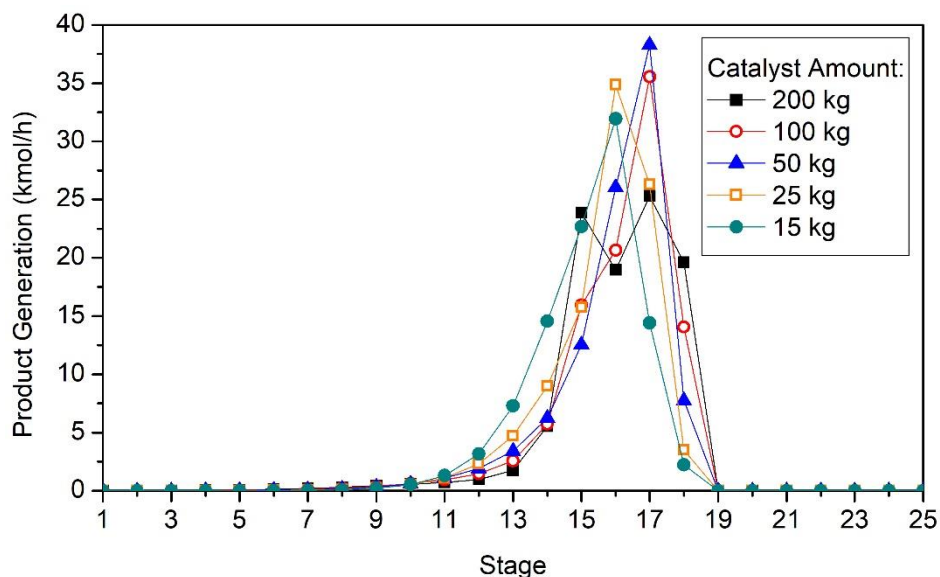


Figure 28. Product generation in RDC stages for different amounts of catalyst.

The generated amount of product within the RDC must remain the same to yield the desired purities. Accordingly, when the amount of catalyst used to perform the reaction is reduced, the maximum achievable conversion in stages is lowered, which mainly affects the stage where the largest volume of reactants is transformed, i.e. the feed stage. Therefore, the production in trays surrounding the feed stage must increase to maintain the overall formation of IBAC and MEOH in the unit. This new distribution of product generation in the HPC stages, however, is achieved at the expense of rising the required thermal power (Figure 27).

Since the importance of the higher stages is significantly lower than the contacting trays located around the feed stages, the total amount of catalyst required in the HPC could be reduced by distributing the weight of the catalyst along the reaction section according to the different productions attained in each stage.

5.9. Economic Aspects

According to the values listed in Table 12, using n-butanol or isobutanol as reactants does not involve a significant change of the process profitability. Considering that both alcohols and esters are isomers, thus, have identical molecular weights, the difference in price between an alcohol and the corresponding ester obtained via transesterification is essentially the same.

Table 12. Price of chemicals used in the reactive distillation process.

Product	Purity w/w %	Price USD/mt	Source
n-Butanol	99.5	970	ICIS
n-Butyl Acetate	99.5	1,060	ICIS
Isobutanol	99.0	1,000	Alibaba
Isobutyl Acetate	99.0	1,100	Alibaba
Methanol	99.85	500	Methanex

The production of IBAC and MEOH for the configuration represented in Figure 23 is 1.56 kg/kg_{IBOH} and 0.65 kg/kg_{IBOH} respectively. Consequently, assuming that the feed stream containing MEAC–MEOH azeotrope is a residual stream without cost, the difference between revenue and feedstock costs is approximately 1,040 USD/mt_{IBOH}. Therefore, the price of the system products is twice the cost of the feedstock.

Nevertheless, as stated in previous sections, distillation is known to be an energy intensive technology, hence the costs involved in the synthesis of IBAC (Figure 19). Assuming that prices of steams are the values displayed in Table 9, the cost of hot utilities involved in the production of IBAC and MEOH for the modeled configuration is approximately 53.7 USD/mt_{IBAC} (HPC + Heaters) and 134.6 USD/mt_{MEOH} (LPC) respectively. Thus, the energy cost involved in the recovery of MEOH from the high-pressure azeotropic mixture is more than twice the cost of producing IBAC from IBOH in the RDC per unit mass of product obtained in each unit. The effect of the catalyst load on the energy consumption was not considered in these estimations (Table 13).

Table 13. Estimated revenue and feedstock and thermal power costs.

	USD/mt _{IBOH}
REVENUE	2,041
Isobutyl Acetate	1,714
Methanol	326
COST	1,171
Feedstock (Isobutanol)	1,000
Heat Exchangers Steam	19
High-Pressure Column Steam	64
Low-Pressure Column Steam	88

The cost of thermal power in the LPC can be reduced by energetically integrating the HPC condenser and LPC reboiler as proposed by Wang et al. (2011). Assuming that no heat loss occurs, the required energy consumption can be reduced from 13.9 GJ/mt_{MEOH} to 5.9 GJ/mt_{MEOH}, which results in a 58% decrease of steam costs in this unit. This energy-efficient configuration also provides a decrease of cold utilities costs. Integrating columns heat exchangers, however, involves a considerable complication of the control system.

Several authors cited in this report (Section 2.6) have studied alternative separation technologies for similar chemical systems, i.e. processes containing MEAC, MEOH, BUOH/IBOH and BUAC/IBAC. Nonetheless, most of them assumed that the residual stream used as feedstock was only composed of pure MEAC and, thus, the proposed techniques were modeled to obtain the abovementioned products under these conditions. Consequently, comparing this data with the results obtained in this document may lead to inaccurate interpretation. The information collected from non-energetically-integrated techniques proposed by different authors, which comprises number of stages of column, reaction section trays, normalized energy consumptions, product purities and membrane areas if applicable, is listed in Table 14.

Table 14. Optimized technologies proposed by several authors
assuming pure MEAC feedstock.

		Wang et al. (2011)	Suo et al. (2016)	Harvianto et al. (2017)	Harvianto et al. (2017)
Technology		RD + PSD	RD + PSD	RD + LS-PV	RD + HS-PV
Alcohol		n-Butanol	Isopropanol	n-Butanol	n-Butanol
Purity					
Ester	wt%	99.7%	99.7%	99.7%	99.7%
Methanol	wt%	98.8%	99.2%	98.8%	98.8%
RDC					
Stages		35	67	35	37
Reactive		16	45	16	16
Pressure	atm	3	3	1	1
Reboiler Duty	GJ/mt _{MEAC}	1.77	4.03	0.83	0.58
MC					
Stages		25	40	25	N/A
Pressure	atm	1	1	1	N/A
Reboiler Duty	GJ/mt _{MEAC}	0.67	0.56	0.31	N/A
Membrane Area	m ²	N/A	N/A	558	269

Product specifications used to model processes shown in Table 14 can be considered the same and, thus, its effect on columns design factors, i.e. number of stages and reflux ratios (energy consumption), can be ignored.

Wang et al. (2011) and Suo et al. (2016) used reactive and pressure-swing distillation (RD + PSD) to overcome the azeotrope. However, the proposed configurations differ considerably in number of stages. Although Suo et al. (2016) use a different catalyst, its impact on the required thermal power and number of stages should not be significant, assuming that catalyst amounts are sufficiently high to attain high conversions.

Selected RDC pressures were such that minimum temperature approach between HPC condenser and LPC reboiler is higher than 15°C, in order to energetically integrate these heat exchangers. Nevertheless, the authors did not take into account the effect of rising the operating pressure further on the amount of product generated, as explained in the Section 5.5 of this document. According to the information provided by these authors, the energy consumed in the RDC is much higher than the required in the MC.

Harvianto et al. (2017) studied the transesterification of MEAC with BUOH by jointly using reactive distillation with low-selectivity pervaporation (LS-PV) and high-selectivity pervaporation (HS-PV). Authors based their research on the results obtained by Wang et al. (2011), hence the similar column design factors.

On one hand, the separation sequence with low-selectivity pervaporation reduces total thermal power requirement by 53% in comparison with the RD + PSD. On the other hand, the energy consumption of the process based on high-selectivity pervaporation is half the required in the RD + LS-PV system. Additionally, a RD + HS-PV process entails not using a MC, which results in an important reduction of capital investment, and half the membrane area in relation to a low-selectivity pervaporation. Nonetheless, polymers price, lifetime and clean-up operations costs (Section 2.6.2) must also be considered to evaluate this technology.

The optimized process proposed in this report was compared with the results of the reactive and extractive distillation technique obtained by Jiménez et al. (2002), since a similar feedstock is used (Table 15).

Table 15. Comparison between RD + PSD and RD + ED technologies.

Technology		RD + PSD	RD + ED
Alcohol		Isobutanol	n-Butanol
Purity			
Ester	wt%	99.00%	99.91%
Methanol	wt%	99.85%	99.82%
Reactive Distillation Column			
Stages		25	43
Reactive Stages		18	6
Pressure	atm	4.6	1.0
Reboiler Duty	GJ/mt _{BUOH}	3.43	4.90
Methanol Column			
Stages		35	30
Pressure	atm	1.0	1.0
Reboiler Duty	GJ/mt _{BUOH}	5.84	3.18
Entrainer Recovery Column			
Stages		N/A	30
Pressure	atm	N/A	1.0
Reboiler Duty	GJ/mt _{BUOH}	N/A	4.16
Overall Thermal Power	GJ/mt_{BUOH}	9.27	12.24

The feedstock used in the RD + ED process designed by Jiménez et al. (2002) is a non-azeotropic MEAC–MEOH mixture containing 30 wt% of MeAc. This stream is used to obtain highly concentrated MEOH and the abovementioned MEAC–MEOH azeotrope in the MC. Therefore, since the amount of MEOH recovered in the MC not only results from MEAC reaction, the energy requirement of the MC assigned to the MEOH obtained via transesterification is lower than the indicated in Table 15.

RDCs have energy consumptions with the same order of magnitude. The number of stages and the energy consumed in the RD + ED is higher because of the presence of the entrainer. Although the usage of a MSA reduces the required number of reactive stages, it involves using an additional unit to recover this solvent (Entrainer Recovery Column, ERC), as explained in Chapter 2, which ultimately escalates the TAC.

The purity of BUAC obtained with RD + ED is higher than the generated for IBAC in the RD + PSD process. Nevertheless, it must be kept in mind that the BUAC composition is obtained in an additional unit, namely, the BUAC Purification Column, which is not listed in Table 15, since no purification unit was used in the process studied

in this report. Consequently, energy consumptions of RDC and ERC can be considered comparable with the results obtained in the PD + PSD process despite the slight difference in product specifications.

In conclusion, the reactive pressure-swing distillation technology is more attractive than a reactive and extractive distillation process since it can provide the similar results with no need of an additional unit and reducing energy consumption by 24%.

6. CONCLUSIONS

In this report, the operation variables of a novel reactive pressure-swing distillation process using as case study the methyl acetate (MEAC) conversion to isobutyl acetate (IBAC) via transesterification using Amberlyst 15 as catalyst are investigated. This technology was modeled in Aspen Plus and optimized to obtain isobutyl acetate, an ester more valuable than methyl acetate, and methanol, feedstock for polyvinyl alcohol synthesis, with the purities specified by manufacturers. The optimization procedure was carried out considering heuristics used in the design of distillation columns, which are ultimately based on the analysis of total annualized costs (TAC) of fixed capital investment and energy consumption.

The design factors that have a significant effect on TAC and, consequently, the variables that must be evaluated in the optimization process are the interval or gap of trays between feed stages, the number of stages in the rectifying, stripping and reaction sections, the operating pressure of the reactive column and the maximum operating temperature recommended for the catalyst used in the RDC.

Transesterification or alcoholysis of MEAC is a reversible reaction. The reaction rate achieved when it is catalyzed by Amberlyst 15 and other catalysts of diverse nature is relatively high, thus, concentrations close to the equilibrium composition can be attained in all reactive stages. Accordingly, the reactants, i.e. the stream containing MEAC and the pipe transporting isobutanol (IBOH), must be fed in the same stage to obtain the desired products minimizing costs.

The lower zone of the reactive distillation column (RDC) is essentially a regular stripping section. Since IBAC is the heaviest component in the system, thus, withdrawn as bottoms, the rest of the species are substantially more concentrated in higher trays of the column. Hence, the ending reactive stage must be in a stage where the concentration of reactants is sufficiently high not to promote the inverse reaction of MEAC alcoholysis with IBOH. The optimal ending stage of the reaction zone is located 2–4 trays below the feed stage and, consequently, the number of stages in the stripping section (N) is fundamentally affected by the purity desired for the product obtained as

bottoms. A decrease of N results in a progressive increase of reflux ratio (R) and energy costs, since N becomes gradually insufficient to attain product specifications.

The location of the feed stage along the column also affects the energy consumption since it determines the number of rectifying section stages (M). Like the effect of N , as the feed stage is shifted upwards in the column, M decreases and energy requirements increase, since M becomes gradually insufficient to achieve the desired purity in the distillate.

The catalyst temperature restriction also influences the optimum position for the feed stage because of the optimal position of the ending stage of the reaction section –one tray below the feed stage. Therefore, for a given pressure, if the temperature in the ending reactive stage is above the maximum recommended temperature, the feed stage must be moved upwards to avoid a decomposition of catalyst materials and, thus, a significant reduction of its lifetime.

The position of the starting reactive stage has an effect similar to the ones described above. Reactants are more concentrated in trays closer to the feed stage, accordingly, shifting the starting stage of the reaction zone from the top of the RDC to lower trays progressively increases reflux ratio. If catalyst cost does not involve a significant capital investment in the project, selecting a starting reactive stage located in the higher stages of the column is recommended.

RDC operating pressure is the most relevant design factor in this process due to the pressure sensitiveness of MEAC–MEOH azeotropic composition. As the difference of pressure between high-pressure (HPC) and low-pressure (LPC) columns increases, the amount of MEAC that can react with IBOH and the volume of product generated become larger, thus, the energy consumed per unit mass of product decreases.

However, pressure also raises species boiling points in the RDC, i.e. entails an increase of temperature profile values, consequently, has an impact on the pressure-level of steams used as hot utilities and might significantly affect the catalyst lifetime depending on the temperatures reached on the reaction section as stated previously. Therefore, the optimal operating pressure for the HPC must be selected considering the

maximum operating temperature recommended for the catalyst and the cost of hot steam utilities.

Taking these elements into account, the optimal reactive pressure-swing distillation process modeled and analyzed in this document is comprised of:

1. A high-pressure column (HPC) or reactive distillation column (RDC) with the feed stage located in stage 15. Rectifying and stripping sections are composed of 15 and 10 stages respectively, which make the total number of stages in the column $M + N = 25$. The reaction section ranges from stage 2 to stage 18 and the optimal pressure for the reactive column is 4.65 bar, since the maximum operating temperature of Amberlyst 15 is 120°C. This configuration results in a $R/R_{min} = 1.10$.
2. A low-pressure column (LPC) with the feed stage located in stage 25. Rectifying and stripping zones are composed of 25 and 10 stages respectively, thus, the total number of stages in the column is $M + N = 30$. The configuration entails a $R/R_{min} = 1.17$ that complies with the heuristic used in the design of distillation columns in the chemical industry.

The amount catalyst per stage is also an important design factor since decreasing the load weight involves a reduction of the maximum conversion achieved in stages and, thus, an increase of thermal power required to attain product specifications. Catalyst price and lifetime and the effect of its amount on energy consumption must be evaluated jointly to determine the suitable catalyst load weight that minimizes the process TAC.

7. NOTATION

A	Pre-exponential factor, $\text{kmol m}^{-3} \text{s}^{-1}$
B_{ij}	NRTL binary interaction parameter
C_{ij}	Non-randomness parameter
E_A	Activation energy, kJ mol^{-1}
K	Vapor–liquid equilibrium ratio
K_a	Adsorption constant
k	Reaction rate constant, $\text{kmol m}^{-3} \text{s}^{-1}$
M	Rectifying section stages
N	Stripping section stages
P	Pressure, bar
Q_C	Condenser heat duty, kW
Q_H	Preheater heat duty, kW
Q_R	Reboiler heat duty, kW
R	Reflux ratio, mol/mol
r	Reaction rate, $\text{kmol m}^{-3} \text{s}^{-1}$
T	Temperature, $^{\circ}\text{C}$
W_P	Pump work, kW
x	Mole fraction in the liquid phase
y	Mole fraction in the vapor phase

Greek Letters

α	Relative volatility
Δ	Increment
ΔT	Minimum temperature approach, $^{\circ}\text{C}$
γ	Activity coefficient
ϕ	Pure component fugacity

Superscripts and Subscripts

+	Forward reaction
–	Backward reaction
i	Component

<i>j</i>	Component
<i>min</i>	Minimum
<i>L</i>	Liquid phase
<i>V</i>	Vapor phase

Abbreviations

BUAC	n-Butyl acetate
BUOH	n-Butanol
ED	Extractive distillation
ERC	Entrainer recovery column
ESA	Energy-separating agent
HPC	High pressure column
hps	High pressure steam
IBAC	Isobutyl acetate
IBOH	Isobutanol
IL	Ionic liquid
LH	Langmuir-Hinshelwood
LPC	Low pressure column
lps	Low pressure steam
MC	Methanol column
MEAC	Methyl acetate
MEOH	Methanol
mps	Medium pressure steam
MSA	Mass-separating agent
NRTL	Non-Random Two-Liquid model
PH	Pseudohomogeneous
PSD	Pressure-swing distillation
PVA	Polyvinyl alcohol
PV	Pervaporation
RD	Reactive distillation
RDC	Reactive distillation column
TAC	Total annualized cost, USD yr ⁻¹

8. REFERENCES AND NOTES

- Alibaba, **2018**.
www.alibaba.com (Accessed Feb 2, 2018).
- AspenTech. *Aspen Plus Reference Manual*, Bedford, MA, **2017**.
- Bonet, J. Contribution à l'étude de la transestérification de l'acétate de méthyle par distillation réactive (PhD. Dissertation), University of Barcelona & National Polytechnic Institute of Toulouse, **2002**.
- Bonet, J.; They, R.; Meyer, X.-M.; Meyer, M.; Reneaume, J.-M.; Galan, M.-I.; Costa, J. Infinite/infinite analysis as a tool for an early oriented synthesis of a reactive pressure swing process. *Comput-Aided Chem. Eng.* **2005**, 20(C), 97-102.
- Bozek-Winkler, E.; Gmehling, J. Transesterification of methyl acetate and n-butanol catalyzed by Amberlyst 15. *Ind. Eng. Chem. Res.* **2006**, 45(20), 6648-6654.
- Cai, J.; Cui, X.; Yang, Z. Simulation for transesterification of methyl acetate and n-butanol in a reactive and extractive distillation column using ionic liquids as entrainer and catalyst. *Chinese J. Chem. Eng.* **2011**, 19(5), 754-762.
- Cao, Y.; Li, M.; Wang, Y.; Zhao, T.; Li, X.; Zhu, Z.; Wang, Y. Effect of feed temperature on economics and controllability of pressure-swing distillation for separating binary azeotrope. *Chem. Eng. Process.* **2016**, 110, 160-171.
- Cui, X.; Cai, J.; Zhang, Y.; Li, R.; Feng, T. 2011. Kinetics of transesterification of methyl acetate and n-butanol catalyzed by ionic liquid. *Ind. Eng. Chem. Res.* **2011**, 50(20), 11521-11527.
- Eastman Chemical Company. Eastman Isobutyl Acetate: Sales Specifications, **2009**.
www.eastman.com/supplemental/Unrestricted/35/PM-000835.pdf
(Accessed Jan 22, 2018).
- España, F. J. Contribución al estudio de la transesterificación de acetato de metilo con etanol mediante rectificación extractiva reactiva catalítica heterogénea (PhD. Dissertation), University of Barcelona, **1996**.
- Hallensleben, M. L. Polyvinyl Compounds, Others. *Ullmann's Encyclopedia of Industrial Chemistry*, 7th ed; Wiley & Sons, **2011**.
- Harvianto, G. R.; Ahmad, F.; Lee, M. A hybrid reactive distillation process with high selectivity pervaporation for butyl acetate production via transesterification. *J. Membrane Sci.* **2017**, 543, 49-57.

- **ICIS, 2018.**
www.icis.com (Accessed Feb 2, 2018).
- International Methanol Producers and Consumers Association. IMPCA Methanol Reference Specifications, **2015.**
www.impca.eu/IMPCA/Technical/IMPCA-Documents (Accessed Jan 22, 2018).
- Jie, H.; Cui, X.; Zhang, Y.; Feng, T.; Li, X.; Lin, R.; Xu, L. Transesterification of Methyl Acetate with Isobutanol in a Reactive and Extractive Distillation Column with Ionic Liquid as Catalyst and Molecular Liquid as Entrainer. *Ind. Eng. Chem. Res.* **2016**, 55(2), 404-419.
- Jiménez, L. Simulación y diseño de un proceso de transesterificación de acetato de metilo con n-butanol mediante rectificación reactiva (Dissertation), University of Barcelona, **1997.**
- Jiménez, L.; Garvín, A.; Costa-López, J. The production of butyl acetate and methanol via reactive and extractive distillation. I. Chemical equilibrium, kinetics, and mass-transfer issues. *Ind. Eng. Chem. Res.* **2002**, 41(26), 6663-6669.
- Jiménez, L.; Costa-López, J. The Production of Butyl Acetate and Methanol via Reactive and Extractive Distillation. II. Process Modeling, Dynamic Simulation, and Control Strategy. *Ind. Eng. Chem. Res.* **2002**, 41(26), 6735-6744.
- Meher, L.C.; Vidya Sagar, D.; Naik, S.N. Technical aspects of biodiesel production by transesterification - A review. *Renew. Sust. Energ. Rev.* **2006**, 10(3), 248-268.
- Methanex. Methanol prices for North America, Europe and Asia, **2018.**
www.methanex.com/our-business/pricing (Accessed Feb 2, 2018).
- Perry, R. H.; Green, D. W.; Maloney, J. O. *Perry's Chemical Engineers' Handbook*, 7th ed; McGraw-Hill, **1999.**
- Seader, J. D.; Henley, E. J.; Roper, D. K. *Separation Process Principles*, 3rd ed; John Wiley & Sons, **2011.**
- Smith, R. *Chemical Process Design and Integration*, 2nd ed; John Wiley & Sons, **2016.**
- Steinigeweg, S.; Gmehling, J. Transesterification processes by combination of reactive distillation and pervaporation. *Chem. Eng. Process.* **2004**, 43(3), 447-456.
- Suo, X.; Ye, Q.; Li, R.; Dai, X.; Yu, H. The partial heat-integrated pressure-swing reactive distillation process for transesterification of methyl acetate with isopropanol. *Chem. Eng. Process.* **2016**, 107, 42-57.

- Suo, X.; Ye, Q.; Li, R.; Feng, S.; Xia, H. Investigation about Energy Saving for Synthesis of Isobutyl Acetate in the Reactive Dividing-Wall Column. *Ind. Eng. Chem. Res.* **2017**, 56(19), 5607-5617.
- The Dow Chemical Company. *Amberlyst™ Polymeric Catalysts*, **2011**.
msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_07c8/0901b803807c82cb.pdf (Accessed Jan 22, 2018).
- Turton, R.; Bailie, R. C.; Whiting, W. B.; Shaeiwitz, J. A.; Bhattacharyya, D. *Analysis, Synthesis and Design of Chemical Processes*, 4th ed; Prentice Hall, **2012**.
- Towler, G.; Sinnott, R. K. *Chemical Engineering Design: Principles, Practice and Economics of Plant and Process Design*, 2nd ed; Butterworth-Heinemann, **2012**.
- Vinyl Polymers: Vinyl Alcohol Polymers. *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed; Wiley & Sons, **2001**; Vol. 24, pp 475-494.
- Wang, S.-J.; Huang, H.-P.; Yu, C.-C. Design and Control of a Heat Integrated Reactive Distillation Process to Produce Methanol and n-Butyl Acetate. *Ind. Eng. Chem. Res.* **2011**, 50(3), 1321-1329.
- Wang, Y.; Bu, G.; Wang, Y.; Zhao, T.; Zhang, Z.; Zhu, Z. Application of a simulated annealing algorithm to design and optimize a pressure-swing distillation process. *Comput. Chem. Eng.* **2016**, 95, 97-107.
- Zheng, H.; Xie, L.; Cai, L.; Wu, D.; Zhao, S. Recovery of PVA by-product methyl acetate via reactive and extractive distillation. *Chem. Eng. Process.* **2015**, 95, 214-221.