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Ethyl acetate manufacturing process: Intensification and Simulation

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DEDICATION

First and the foremost,

In the name of Allah, the most Gracious, the most Merciful All praise is for ALLAH,

we praise Him, we seek His aid, and we ask for His forgiveness.

My highest gratitude to **ALLAH** for all the blessings I had that led me to fulfill this work.

This dissertation`s work is dedicated to

My mother, whose words of encouragement ring in my ears.

and all those who are dear to me…

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To mom and Dad

Who always picked me up on time

And encouraged me to go on every adventure

Especially this one

To my brothers and those who shared with me all the moments of emotion during the realization of this work they warmly supported and encouraged me throughout my journey

To all my friends who have always encouraged me and to whom I wish more success

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الملخص

خلات الإيثيل (EA) هي أحد الأمثلة الرئيسية لمذيبات الأسترة المستخدمة في الصناعات المختلفة. ومع ذلك، فإن الإنتاج التقليدي لهذا المذيب يخضع لقيود مهمة. للإجابة على هذا السؤال، يقدم تكثيف العملية (PI) حلاً جديدًا لهذه المشكلة؛ تم ذكر أربع دراسات، تم تصميم اثنتين منها ومقارنتهما) تم تصميم العملية التقليدية كدراسة أساسية؛ التقطير التفاعلي بوحدة فصل مشتق من العملية التقليدية، وعمود التقطير التفاعلي مع متجرد (RDS) وعمود التقطير التفاعلي مع تفاعل كيميائي مساعد (ترطيب أكسيد الإيثيلين).بناء على نتائج المحاكاة ، وجد أن RDS يمكن أن يمنع إزالة الماء الذي يأتي من الأسترة وفصل الخليط الأزيوتروبي ويضمن التحويل الكلي لحمض الأسيتيك في عمود RD مقارنة بالقاعدة الأولى. تم تقييم الطاقة والاقتصاد والسلامة في العملية. نظرًا لأن النتائج قريبة جدًا من البيانات التجريبية في التراث العلمي المنشور، تم التحقق من صحة الدراسة من خلال محاكاة ناجحة باستخدام البرنامج الشهير Aspen Plus لمحاكاة العمليات.

الكلمات المفتاحية: خلات الايثيل، محاكاة، تكثيف العملية، التقطير التفاعلي.

Résumé

L'acétate d'éthyle (EA) est l'un des principaux exemples de solvants d'estérification utilisés dans diverses industries. Cependant, la production conventionnelle de ce solvant est soumise à d'importantes restrictions. Pour répondre à cette question, l'intensification des procédés (IP) offre une nouvelle solution à ce problème ; quatre études ont été mentionnées, dont deux ont été conçues et comparées (le procédé conventionnel est conçu comme une étude de base ; la distillation réactive avec une unité de séparation est dérivée du procédé conventionnel, la colonne de distillation réactive avec un stripper (RDS) et la colonne de distillation réactive avec une réaction chimique auxiliaire (hydratation de l'oxyde d'éthylène)). Les résultats de la simulation montrent que le RDS peut empêcher l'élimination de l'eau provenant de l'estérification et la séparation des azéotropes du mélange et garantir la conversion totale de l'acide acétique dans la colonne RD par rapport à la colonne de base. L'énergie, l'économie et la sécurité du processus ont été évaluées. Comme les résultats sont assez proches des données expérimentales de la littérature, l'étude est validée par une simulation réussie à l'aide d'Aspen Plus.

Mots-clés : L'acétate d'éthyle, Simulation, L`intensification Des Procédés, Distillation Réactive.

ABSTRACT

Ethyl Acetate (EA) is one of the major examples of esterification solvents which are employed in various industries. However, there are significant restrictions on the conventional production of this solvent. To answer this question, process intensification (PI) offers a novel solution to this problem; there were four studies mentioned, including two that were designed and compared (conventional process set-up is designed as a base case study; reactive distillation with a separation unit is derived from the conventional process set-up, reactive distillation column with a stripper (RDS) and reactive distillation column with an auxiliary chemical reaction (ethylene oxide hydration). Based on the simulation results, it has been found that RDS can prevent the removal of water which comes from esterification and the separation of the azeotropes of the mixture and ensure total conversion of acetic acid in the RD column compared with the base one. The energy, economy, and safety of the process were evaluated. Since the results are quite close to the experimental data in the literature, the study is validated by a successful simulation using Aspen Plus.

Key words: Ethyl Acetate, Simulation, Process Intensification, Reactive Distillation.

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LIST OF ABBREVIATIONS

AA	Acetic acid
AP	Aspen plus
BOPP	Biaxially Oriented Polypropylene
CSTR	Continuous stirred tank reactor
EA, EtAc	Ethyl acetate
ED	Extractive distillation
EO	Ethylene oxide
EPIC	European process intensification conferences
EQ	Equilibrium stage
EtOH	Ethanol
EUROPIC	European process intensification center
H_2O	Water
HOC	Hayden–O'Connell equation of state
HEX	Heat exchanger
MEG	Monoethylene glycol
NEQ	Non-equilibrium stage
NRTL	Non-random two liquids
OEC	Overall energy consumption
PI	Process intensification
PSD	Pressure-swing distillation
RD	Reactive distillation
RDAR	Reactive distillation with auxiliary reaction
RDS	Reactive distillation with stripper
RAPID	Rapid Advancement in Process Intensification Deployment
IPIC	International process intensification conferences
TPC	Total production cost \$ t^{-1}
VLE	Vapor–liquid phase equilibria
VOC	Volatile organic compound

NOMENCLATURE AND SYMBOLS

N	Number of theoretical stages, total condenser, and reboiler are included	_
N_R	Reactive section stages	_
F	Feed stage position	_
R	Reflux ratio	_
D	Column internal diameter	**[m]**
H	Packed section height	**[m]**
T	Temperature	**[°C]**
V	Volume flow	**[$m^3 h^{-1}$]**
P	Pressure	**[bar]**
Q_w	Reboiler duty	**[Kw]**
Q_c	Condenser duty	**[Kw]**
C_{AC}	Acetic acid concentration	**[$mol.m^{-3}$]**
C_{ETOH}	Ethanol concentration	**[$mol.m^{-3}$]**
C_{ETAC}	Ethyl acetate concentration	**[$mol.m^{-3}$]**
C_{H2O}	Water concentration	**[$mol.m^{-3}$]**
r	reaction rate	**[Kmol. m^{-3}. s^{-1}]**
Ea	Activation energy	**[KJ. $Kmol^{-1}$]**

GENERAL INTRODUCTION

GENERAL INTRODUCTION

Ethyl Acetate is a moderately polar solvent with volatile, non-toxic and non-hygroscopic properties that make it a desirable product. It is commonly used as a solvent or a diluting agent, and can be found in several consumer products (**Heuser et al., 2019)**, including food and beverage, pharmaceutical, cosmetics, textiles paints and coatings, adhesives and sealants, and others **(Patil & Gnanasundaram, 2020).** Ethyl acetate sales currently top $4 billion annually and are expanding more quickly than the global GDP. In 2016, there was a 3.7 MMT global demand for this product. The ethyl acetate market has some excess capacity, which is mostly present in the Asia-Pacific region **(Heuser et al., 2019).**

The industrial production of ethyl acetate- among other processes- is generally based on a classical Fischer esterification process **(Toth, 2019).** A typical Fisher esterification reaction involves heating a mixture of carboxylic acids and an excess amount of corresponding alcohols in the presence acetate/ethanol/water mixture forms multi-azeotropes, which are difficult to separate by conventional distillation **(Meng et al., 2020)**. For separating such mixtures with azeotropes or low relative volatility, unconventional distillation technologies, e.g., azeotropic distillation, pressure-swing distillation (PSD), and extractive distillation (ED), have been extensively applied **(Feng et al., 2020)**. A significant energy cost and a large number of devices should be anticipated even though azeotropic mixtures can be separated **(Branislav et al., 2020).**

The major challenge in developing sustainable technology is achieving cost effectiveness and efficient downstream processing in a green environment. Thus, the concept pf process intensification steps in that it promises minimum consumption of material and energy while offering higher engineering flexibility as well as higher purity of the products **(Pal & Nayak, 2016)**.

Reactive distillation (RD) is one of the best success stories of process intensification (PI) technology **(Kiss et al., 2018),** and it can assist in lowering operational costs, capital expenditures, and environmental effects. RD, an innovative hybrid process combining chemical reaction with distillation, has the function of reaction and distillation

in a single unit where both the reaction and the distillation process are intensified by each other. However, problems that exist in the RD system for ester production are still hard to solve. The removal of the water which comes from the esterification, and the separation of the azeotropes of ester-alcohol (-water) are two main problems**(Li et al., 2018).**

To solve the problems above and taking RD to the next level of process intensification requires more advanced RD configuration allowing an additional range of operating conditions (not available in classic RD setups) **(Branislav et al., 2020),** we will use a RD column with a stripper and an auxiliary chemical reaction in the RD system will use as the chemical path of intensification. One by-product of the main reaction will be consumed by the auxiliary reaction; another valuable product can be obtained. As a simulation tool, ASPEN PLUS was chosen.

The specific objectives are summarized as:

i. To review the state of the art relating to the intensification of processes
ii. To carry out a case study of the intensification of the manufacturing process of ethyl acetate and steady-state simulation using the Aspen Plus process simulator

The presentation of this work is structured around three chapters:

1. The first chapter provides an overview of process intensification and production of ethyl acetate.
2. The second chapter presents a review of the literature on simulation and the ASPEN plus and HYSYS simulator.
3. The simulation part of Aspen Plus is presented in the third chapter, which begins with a purely literary account of the idea of reactive distillation as a major branch of process intensification, and ends with the representation of the results obtained then their discussion.

Finally, the work finished with a general conclusion and some perspectives of future studies.

CHAPTER I
LITERATURE REVIEW

CHAPTER I LITERATURE REVIEW

I.1 INTRODUCTION

This chapter aims to illustrate the basic tools of process intensification (PI), including historical development, definitions and an explanation of the fundamentals, in the first section. An overview of ethyl acetate (EA) will be exposed in the second section by indicating how EA is manufactured in process industries and it`s relevance and range of industrial applications. The chapter will end with a conclusion.

I.2 PROCESS INTENSIFICATION

I.2.1 Brief history of process intensification

The first appearance of process intensification was East European publications on metallurgy already in the mid-1960s and early 1970s, it was meant simply as equivalent to ‘‘process improvement’’.

In chemical engineering, process intensification, as it is known today, was first introduced by Colin Ramshaw from the ICI`s new science group in his paper on the application of centrifugal fields (so-called ‘‘HiGee”) in distillation processes published in 1983. The ICI project had been triggered by one of the NASA research projects to produce high transfer rates by using centrifugal fields in a zero-gravity environment.

In the first years after its birth process intensification (PI) was controlled by the rotating equipment, which still presents an important area of PI. Gradually, new technologies such as heat exchanger (HEX) reactors, intensive mixing devices, or micro-channel reactors emerged within the PI domain.

Until the early 1990s, PI was almost exclusively a British discipline. It was also the British BHR group that organized the first international conference on PI in 1995.The real acceleration came in the last years of the second and, in particular, the first years of the third millennium, when a fast growth of PI-related activities in industry and in academia was observed. National academic–industrial PI networks have been established, first in the United Kingdom, later in the Netherlands, and in Germany.

PI has found its way into the university curricula. In 2007, Primary books on PI were published, and the first PI-dedicated journal Chemical Engineering and Processing: Process Intensification was launched. In 2005, the European Federation of Chemical Engineering acknowledged the importance of PI by establishing the Working Party on Process Intensification. Ever since, the Working Party organized five European Process Intensification Conferences (EPIC) and two International Process Intensification Conferences (IPIC) held in Barcelona 2017 and in Leuven in 2019.

The European Roadmap for PI, published in 2008 which is based on the contributions of experts from 16 countries, laid down a foundation for short- and mid-term research programs in the field. In 2009–2011, the roadmap got a purse informed of the Delft Skyline Debates project, during which a multidisciplinary team of 75 leading academics and industrialists from different countries created a scientific vision of long-term developments in the field of PI that would reach beyond the horizon of 2050. The vision was published as a series of position papers and also delivered a long-term research agenda for PI. Note that the above research agenda has gone beyond the traditional application area of PI, i.e., the chemical process industries, and has also addressed other areas including energy, water, and health.

In 2009, the European Process Intensification Centre (EUROPIC) was established. The center presents an industry-driven platform for knowledge transfer in PI and comprises chemical and pharmaceutical manufacturers, technology providers, equipment vendors, and engineering companies.

Moreover, the recently established Rapid Advancement in Process Intensification Deployment (RAPID) Institute, with private and governmental (US Department of Energy) funding exceeding 140 million dollars, presents a major development in this field in the United States and a proof of the importance of PI for the American economy. It is interesting to note that after almost 40 years of development, PI has been brought again in connection with the space programs. Micro-channel reactors for CO Methanation are considered a promising technology for the in-situ resources utilization (ISRU) on Mars or on the Moon. It appears that process intensification may one day revisit its birthplace – the Space**(Stankiewicz, Andrzej., Van Gerven, Tom., Stefanidis, 2019).**

I.2.2 Definitions

Process intensification is considered one of the most promising progress paths for development of more sustainable chemical processes. The following are commonly known definitions of process intensification (PI) available in the literature**(Cremaschi, 2014):**

Ramshaw and Arklev (1983):

‘’Is the devising exceedingly compact plant which reduces both the main ‘main plant item’ and the installations costs’’**(Tonkovich & Daymo, 2018)**

The European roadmap on process intensification (PI) describes PI as providing:

‘‘A set of innovative principles applied in process and equipment design, which can bring significant benefits in terms of process and chain efficiency, lower capital and operating expenses, higher quality of products, less wastes and improved process safety’’**(Dimian et al., 2014)**.

Baldea (2015):

‘’ Any chemical engineering development that leads to substantially smaller, cleaner, safer and more energy efficient technology or that combine[s] multiple operations into fewer devices (or a single apparatus)’’ **(Baldea, 2015)**.

I.2.3 Fundamentals of process intensification

I.2.3.1 The principles

- Maximize the effectiveness of intra- and inter-molecular events:

This principle is mostly about changing the kinetics of a process, which is the root of low conversions and selectivity, unwanted side-products and other issues.

- Give each molecule the same processing experience:

When all molecules go through the same history, the process delivers ideally uniform products with minimum waste. The meso- and micro-mixing temperature gradients, macroscopic residence time distribution, dead zones or bypassing play a significant role.

- Optimize the driving forces at every scale and maximize the specific surface area to which these forces apply:

This principle is about the transport rates across interfaces. The resulting effect of the driving forces (e.g., concentration difference) needs to be maximized, and this is done by maximizing the interfacial area, to which that driving force applies. Increased transfer

areas (or surface-to-volume ratios) can be obtained by moving from mm-to-mm scales of channel diameters.

- Maximize the synergistic effects from partial processes:

Synergistic effects should be required and used, whenever it is possible and at all possible scales. Such application occurs in the form of multi-functionality on the macro-scale, as, for example, in reactive separation units, where the reaction equilibrium is shifted by removing the products in situ, from the reaction environment.**(Dimian et al., 2014)**

I.2.3.2 Approaches

A completely intensified process is successful in realizing all these PI principles (see figure I.1), by making use one or more fundamental approaches in four domains **(Dimian et al., 2014)**:

- Structure: spatial domain

Structure in molecular events,

Structure in catalysts,

Structure in phase contracting,

Structure in transport phenomena.

- Energy: thermodynamic domain

Bringing energy to molecules (what form and how),

Bringing energy to catalysts,

Energy transfer in hydrodynamics, mixing and transport processes,

Energy management in reactors and separation systems,

- Synergy: Functional domain

Synergy on molecular scale,

Synergy in transport processes,

Synergy in processing units-multifunctional reactors and separators.

- Time: Temporal domain

Timing of events,

Applying dynamics,

Special process control.**(Tonkovich & Daymo, 2018)**

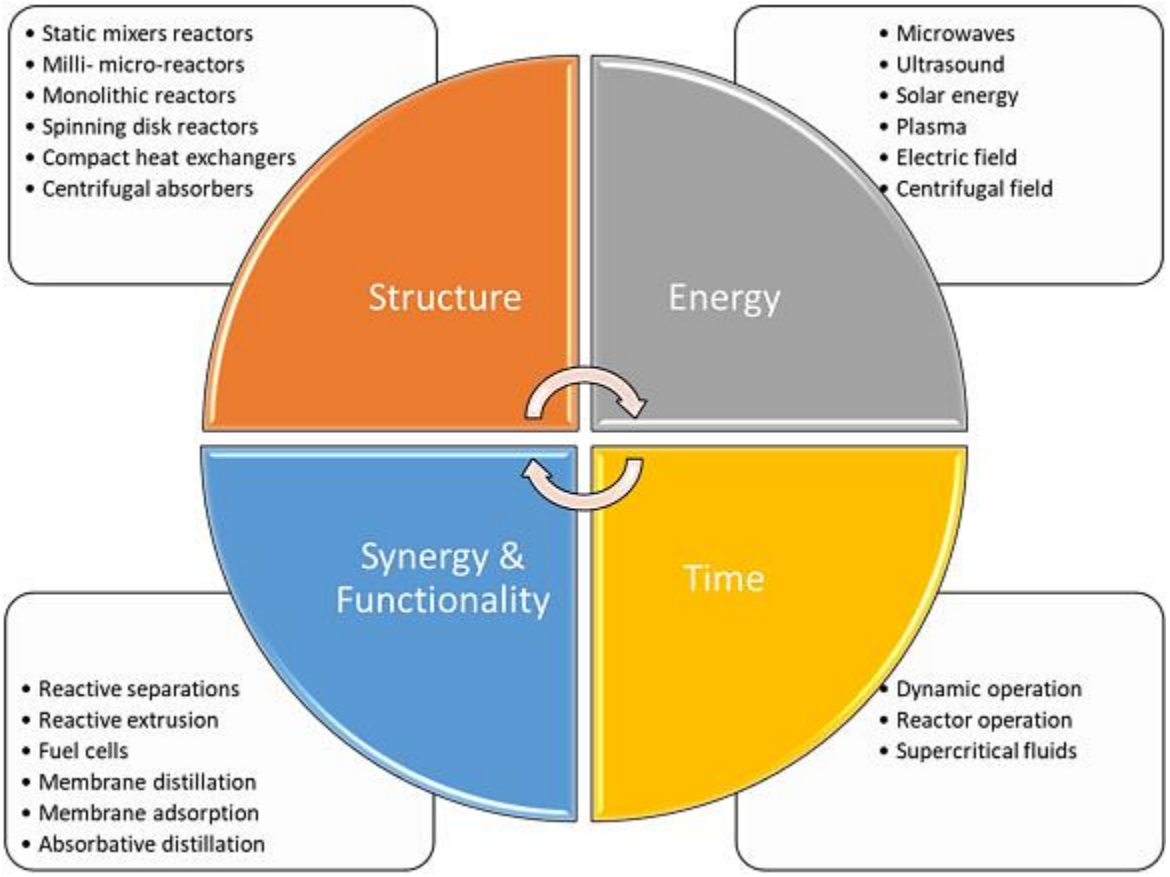


Figure I.1 Principles of Process Intensification: definition of the main concepts of PI with application examples**(Haase et al., 2022)**

I.2.4 Why intensify?

In a highly competitive industrial context, where societal and environmental expectations are increasingly present, intensification can be an effective tool to improve the performance of chemical processes while being part of a sustainable development approach. This intensification approach includes different economic, environmental and societal issues.

I.2.4.1 Economics issues

The main purpose of PI is to reduce capital costs by decreasing the size of the equipment and the space captured by the production facilities. Other expected improvements are the reduction of production costs, obtained by increasing productivity and energy efficiency. The intensified process will be more sober in consumption of raw materials and energy and will limit the amount of waste to be treated.

In a global market, technological advances can bring a remarkable competitive advantage. The use of intensified equipment offers the opportunity of better control of the reaction conditions which allows for improving either the quality of the products or the operating conditions of the synthesis when these are challenging to achieve in conventional equipment. The quality of the final product can be improved by increasing the selectivity of the process. The intensified process can also lead to new product qualities.

Furthermore, it allows the acceleration of the development phase of a new process. The size of the intensified reactors at the pilot scale is very close to the production size; so, the hydrodynamics and the surface-to-volume ratios are maintained during the scale-up phase. The scale-up of the process to industrial production; and the time to market of a new product is reduced which is mostly important for the pharmaceutical industry

I.2.4.2 Environmental issues

From an environmental point of view, intensification allows the development of more environmentally friendly processes. They can be more energy and raw material efficient (Table I.4.1) because they are smaller; and more efficient in terms of heat and mass exchange. The precise control of the reaction conditions can limit the formation of impurities and thus reduce the separation/purification steps.

Table I.1 Evaluation of the potential energy gain through an intensification approach for the UK.

Chemicals Sector	Potential Energy Savings
Compact heat exchangers	16
Separators	6.5
Reactors	11
Overall plant intensification	40
Effluent treatment	1

I.2.4.3 Societal issues

From a societal point of view, intensification can enhance the acceptability of chemical industries. In fact, they are recognized as one of the most dangerous industries and serious accidents have left their mark, such as Bholpal in 1994 and Toulouse in 2001. On the one hand, intensified processes are inherently safer because they are smaller. Even in the case of a serious accident, the size of the reactor and therefore the quantity of reagents involved is limited, and the potential damage to both plant workers and the surrounding population is significantly reduced.

Also, by shrinking the size of the equipment, it is feasible to reduce the space that the workshops take up and more easily integrate the plant into its surroundings (Figure I.2). So, it is easier to tolerate the existence of chemical industries(CHEVREL, 2014)

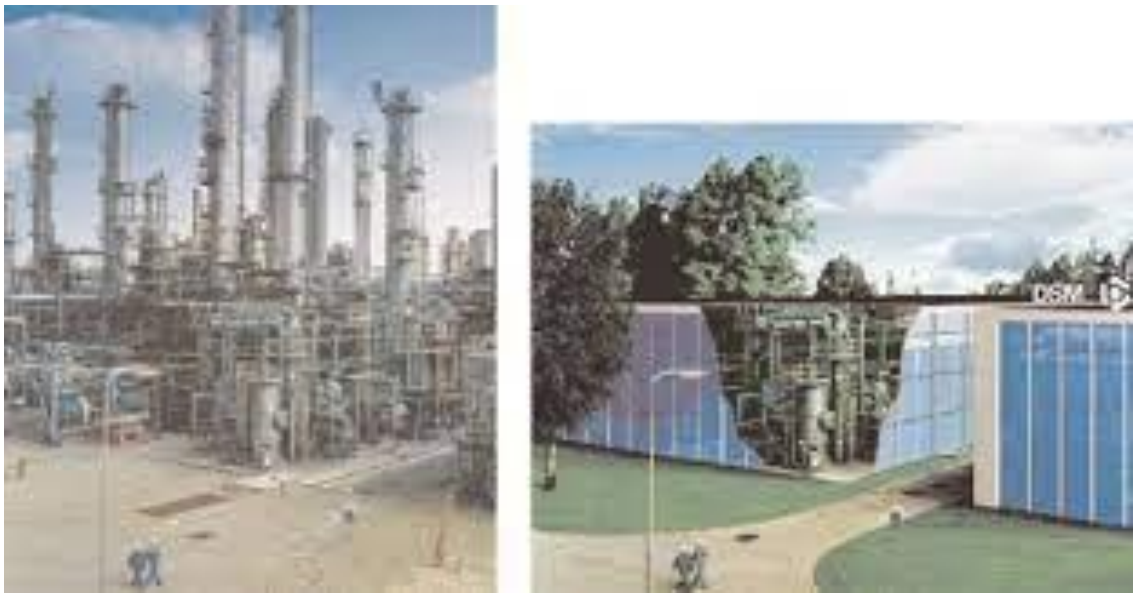


Figure I.2 Artist's view of the future factory after DMS.**(Stankiewicz & Jacob A. Moulijn, 2000)**

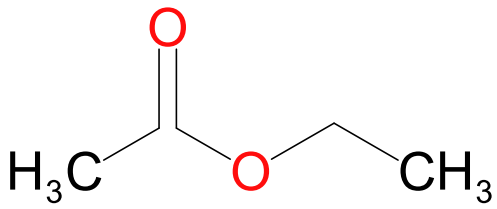
I.3 ETHYL ACETATE

I.3.1 Background Information

Ethyl acetate (EA) is an organic compound (an oxygenated solvent) with the formula $CH_3COOC_2H_5$ and has a molecular weight of 88.10 g/mole. This colorless liquid has a characteristic, pungent smell like certain glues or nail polish removers, in which it is used.

EA is the ester from ethanol and acetic acid; it is manufactured on a large scale for use as a solvent. EA is a moderately polar solvent that has the advantages of being volatile, relatively non-toxic, and non-hygroscopic. It is a weak hydrogen bond acceptor; and is not a donor due to the lack of an acidic proton. EA can dissolve up to 3% water and has a solubility of 8% in water at room temperature. It is unstable in the presence of strong aqueous bases and acids. It is soluble in most organic solvents, such as alcohol, acetone, ether and chloroform. It has been also used as a solvent in many chemical processes for

replacing aromatic compounds which generate serious damage to the environment and human beings**(Pattanaik & Mandalia, 2011).**



Molecular structure of Ethyl acetate

I.3.2 Properties of ethyl acetate

I.3.2.1 Physical properties of ethyl acetate

Table I.2 Physical properties of Ethyl Acetate**(Toxicologiques, 2022)**

Details	
Formula	$C_4H_8O_2$
N° CAS	141-78-6
Physical state	Liquid
Odor - Olfactory limit	3.9 ppm
Solubility	85g/l at 20 °C 64 g/L at 25 °C
Molar mass	88.12
Melting point	-83°C
Boiling point	77°C
Density	0.90
Gas/vapor density	3.04
Vapor pressure	9.3 to 11.3 kPa at 20 °C
Evaporation index	2.9
Flash point	- 4 °C (in closed cup)
Auto-ignition temperature	426 -460°C
Explosive or flammable limits Flammability limits (by volume% in air)	Lower limit: 2%. upper limit: 12.8%
Partition coefficient n-octanol / water (log pow).	0.66 -0.73

I.3.3 Chemical properties

Under normal conditions, EA is a stable product. However; it hydrolyzes relatively easily in contact with water, such as moisture in the air, forming acetic acid and ethanol. This reaction is faster in the presence of catalysts, especially acids and bases.

EA reacts vigorously with strong oxidizers, and the reaction can be violent with the possibility of fire and explosion. It decomposes (hydrolysis) with strong acids and bases: the reaction is exothermic and can be violent.

It is not corrosive for usual metals: iron, aluminum, steel, copper, nickel and their alloys. Still, acetic acid is released in case of hydrolysis of EA can cause corrosion of some metals, particularly copper. EA degrades some rubbers and plastics**(Toxicologiques, 2022).**

I.3.4 Synthesis of ethyl acetate

Ethyl Acetate can be produced industrially in three ways:

a) Tishchenko reaction

(Eq. (I.1)) between two similar aldehydes (acetaldehyde) gives an ester (ethyl acetate) by adding an alkoxide catalyst to acetaldehyde.

$$2CH_3CHO \rightarrow CH_3COOC_2H_5 \quad \textbf{(I.1)}$$

b) The addition of acetic acid to ethylene

(Eq. (I.2)) is newly commercialized. It uses clay and heteropoly acids (HPA) as catalysts.

$$CH_2 = CH_2 + CH_3COOH \rightarrow CH_3COOHC_2H_5 \quad \textbf{(I.2)}$$

However, due to the relatively high price of raw materials and the possibility of undesired by-products forming by these pathways of alternative synthesis, the classic Fischer esterification is found to be the most commonly used reaction for the EA synthesis.

c) Fischer esterification

(Eq. (I.3)) is a classic process in which ethyl acetate is formed by the reaction of ethanol and acetic acid using acidic catalysts such as sulfuric acid and para-toluene sulfonic acid (PTSA).

$$C_2H_5OH + CH_3COOH \leftrightarrow CH_3COOC_2H_5 + H_2O \quad \textbf{(I.3)}$$

This reaction converts EA in about 65% yield at ambient temperature. In the United States, this technique is used commercially to produce more than 100 million pounds of

ethyl acetate annually, mostly used as a solvent in the paint industry, but also as a solvent for nail polish and various types of glues.**(Ahmad, 2015)**

The system is strongly non-ideal due to the presence of ethanol (EtOH), acetic acid and water. The separation of pure components is very difficult due to the existence of five normal azeotropes, namely ethanol-water; water-acetic acid; ethyl acetate-ethanol; ethyl acetate-water and ethanol-ethyl acetate-water.

The normal boiling point of ethyl acetate, ethanol, water and acetic acid is 77.1, 78.4, 100 and 118.1 in °C respectively.

The order of volatility is ethyl acetate, ethanol, water and acetic acid. EtOH and water do not differ greatly in volatility, making it difficult to move ethanol up the column. The minimum-boiling binary homogeneous azeotropes are formed by ethanol–water at 78.2°C With 10.57mol% water and by ethyl acetate–ethanol at 71.8°C with 46 mol% ethanol. A minimum-boiling binary heterogeneous azeotrope is formed by ethyl acetate–water at 70.4°C with 24mol% water, and a ternary, minimum-boiling azeotrope is formed by ethanol–ethyl acetate–water at 70.3°C with 12.4mol% ethanol and 60.1 mol% ethyl acetate **(Kumar, 2010)**.

I.3.5 Reaction kinetics and parameters

Out of these three processes, we will focus on Fischer esterification as the process to be simulated. The reversible esterification reaction is shown as below:

$$C_2H_5OH + CH_3COOH \leftrightarrow CH_3COOC_2H_5 \quad \textbf{(I.4)}$$

The rate model is:

$$r = K_1 C_{HAC} C_{EtOH} - K_2 C_{EtAc} C_{H_2O} \quad \textbf{(I.5)}$$

Where K_1 and K_2 are forward and backward rate constants.

The rate constants K_1 and K_2 can be presented by Arrhenius equation:

$$K_1 = A \exp\left(\frac{-Ea}{RT}\right) \qquad , K_2 = A` \exp\left(\frac{-Ea`}{RT}\right) \quad \textbf{(I.6)}$$

Where **A** is a pre-exponential factor and the Ea is activation energy. Several authors have calculated the kinetic parameters by conducting the experiment such as CALVAR and ERO.

Calvar et al., studied the homogeneous reaction (esterification of hydrolysis) catalyzed by acetic acid by taking into account the activity coefficient. The kinetic parameters were calculated using ASOG and UNIFAC methods.

Erol carried out an experiment of esterification with an acidic polymer catalyst and observed that a heterogeneous catalyst is very effective from the point of view of activity, selectivity, reuse and non-corrosiveness compared to homogeneous catalyst**(Ahmad, 2015)**.

I.3.6 Applications of ethyl acetate

Ethyl Acetate has a wide range of applications across many industries, including:

- Surface coating and thinners

Ethyl acetate is one of the most popular solvents and finds wide use in the manufacture of nitrocellulose lacquers, varnishes and thinners, to dissolve the pigments for nail varnishes. It exhibits high dilution ratios with both aromatic and aliphatic diluents and is the least toxic of industrial organic solvents.

- Pharmaceuticals

EA is an important component in extractants for the concentration and purification of antibiotics. It is also used as an intermediate in the manufacture of various drugs.

- Flavors and essences

Ethyl acetate finds extensive use in the preparation of synthetic fruit essences, flavors and perfumes

- Flexible packaging

Substantial quantities of ethyl acetate are used in the manufacture of flexible packaging and in the manufacture of polyester films and BOPP films. It is also used in the treatment of aluminum foils.

- Occurrence in wines

Ethyl acetate is the most common ester found in wine, being the production of the most common volatile organic acid-acetic acid and the ethanol alcohol created during the fermentation of wine. The aroma of ethyl acetate is most vivid in younger wines and contributes to the general perception of "fruitiness" in the wine. Sensitivity varies with most people having a perception threshold around 120 mg/lit. An excessive amount of ethyl acetate is considered a wine fault. Exposure to oxygen can exacerbate the fault due to the oxidation of ethanol creating acetaldehyde. This can leave the wine with sharp a vinegar-like taste.

- Electronics

Small quantities of ethyl acetate are also used in the manufacture of video/audio tapes. Magnetic media of tapes are purified with ethyl acetate. It is also used for head cleaning. In fact, ethyl acetate of 99.7% quality is the best solvent for cleaning, etc.

- Miscellaneous

Ethyl acetate is used in the manufacture of adhesives, cleaning fluids, nail polish removers and silk, coated papers, textiles, explosives, artificial leather etc. In the field of entomology, ethyl acetate is an effective poison for use in insect collecting and study. In a killing jar charged with ethyl acetate, the vapors will kill the collected (usually adult) insect quickly without destroying it. Because it is not hygroscopic, ethyl acetate also keeps the insect soft enough to allow proper mounting suitable for a collection.

High purity product (ethyl acetate) can be used as a viscosity reducer for resins used in photo resist formulations in the electronics industry.

Ethyl acetate is also used as a solvent in a variety of coating formulations including epoxies, urethanes, cellulosics, acrylics and vinyls. These coatings are used for wood furniture and fixtures, agricultural, construction and mining equipment, containers and closures, auto refinishing, and maintenance and marine applications. Over the past twenty years, ethyl acetate coatings have been losing share to waterborne and high solids coatings, powder and two-component coatings systems, due to environmental constraints on volatile organic compound (VOC) emissions. Ethyl acetate is used as a solvent in inks for flexographic and rotogravure printing, where it ‘s main function is to dissolve the resin, control the viscosity and modify the drying rate. As with industrial coatings, the decline in the use of acetate because of environmental constraints has largely been completed.

(Pattanaik & Mandalia, 2011)

I.4 CONCLUSION

Ethyl acetate also known as ethyl ethanoate is an organic compound known to be one of the most commonly used solvents as an intermediary in a variety of chemical reactions. This solvent has various properties and many important industrial applications. Until now, the production and the intensification of EA has shown to be the focus of an important number of research groups. A process simulation is usually performed first before the application in the real world. For this we proposed the use of Aspen plus software which will be presented in the next chapter.

CHAPTER II

SIMULATIONAND SOFTWARE

CHAPTER II SIMULATION AND SOFTWARE

II.1 INTRODUCTION

Process simulation are basic tools of technicians and process engineers; they make it possible to establish easily and rigorously the material and energy balances on the processes**(Badra, 2022)** Aspen-one is one of the most common simulation processes in the field of chemical engineering. This simulator package consists of Aspen plus (for process and chemical industry) and Aspen HYSYS (for oil and gas industry), flare net (for flare analyses), batch process model, GC model, distillation model, heat exchanger model and many more. This chapter will introduce Aspen plus and Aspen HYSYS.

II.2 DEFINITION OF SIMULATION

Computer simulation, or numerical simulation, is a series of calculations carried out on a computer and reproducing a physical or chemical phenomenon. It leads to the description of the result of this phenomenon as if it had really taken place. This representation can be a series of data, an image, or even a video film. Process simulation is the virtual design or realization based on real and concrete results**(Badra, 2022)**

Simulation stands in contrast to analytical approaches to the solution of models. In an analytical approach, the model is expressed as a set of equations that describe how the system state changes over time. We solve these equations using standard mathematical methods algebra and calculus to determine the distribution of the state at any particular time. The result is a general, closed-form solution, which gives the state at any time as a function of the initial state, the input, and the model parameters. When models can be solved analytically, this is always the preferred approach. However, for complex systems this is almost never the case.

Simulations also may be categorized according to their implementation strategy. Continuous system simulation, Monte Carlo simulation, discrete-event simulation, hybrid simulation, and agent-based simulation all have particular implementation strategies.**(White & Ingalls, 2009).**

II.3 OBJECTIVES OF THE SIMULATORS

The main objectives of process simulators are as follows:

- Solve the material and energy balance equations for all the process devices.
- Calculate the characteristics (flow rate, composition, temperature, pressure, physical properties) of all the fluids that circulate between the devices.
- Provide the elements necessary for the sizing of the equipment, such as the quantities of heat exchanged or the internal flow rates of a column.
- The estimation of investment and operating costs and, in the context of sustainable development, the impact on the environment and safety.
- The optimization of the operating conditions of the process.
- The analysis of the operation of an existing unit or the study of the modifications to be made to adapt the unit to a new industrial context.

Simulators make it possible to establish, in an efficient and rigorous manner, material and energy balances on chemical processes. The fundamental aspect for the simulation of the processes is the identification of the elementary components whose assembly makes it possible to build the model of the process**(Badra, 2022)**

II.4 ASPEN PLUS SOFTWARE

In the 1970s the researchers at MIT's Energy Laboratory developed a prototype for process simulation. They called it Advanced System for Process Engineering (ASPEN). This software has been commercialized in the 1980's by the foundation of a company named AspenTech. ASPEN PLUS offers a complete integrated solution to chemical process industries. This sophisticated software package can be used in almost every aspect of process engineering from design stage to cost and profitability analysis. It has a built- in model library for distillation columns, separators, heat exchangers, reactors, etc. Custom or proprietary models can extend its model library. These user models are created with FORTRAN subroutines or Excel worksheets and added to its model library. Using Visual Basic to add input forms for the user models makes them indistinguishable from the built-in ones. It has a built- in property database for thermodynamic and physical parameters. During the calculation of the flow sheet any missing parameter can be estimated automatically by various group contribution methods**(Kumar, 2010)**

Aspen Plus (AP for short) is the leading Chemical Process Simulator in the market (or at least in the Chemical Engineering World). AP (Figure II.1) is a software that will allow the user to build a process model and then simulate it using complex calculations (models, equations, math calculations, regressions,) There are many perks in AP, from designing new processes to improving existing ones. That is so, that even AP ensures so its website: (it will) Maximize profits using a plant-wide simulation solution that combines unparalleled accuracy and engineering collaboration with time saving workflows**(Emmanuel, 2023)**

II.5 ASPEN PLUS BUILT-IN HELP

Help topics are under three categories:

- Contents

Used to browse through the documentation. The "User Guides" and "Reference Manuals" are all included in the help.

- Index

Used to search for help on a topic using the index entries.

- Search

Used to search for help on a topic that includes any word or phrase (Al-malah, 2017)

The following Table II.1 Shows a comparison between Aspen Plus with other software **(Eden & II, 2017)**

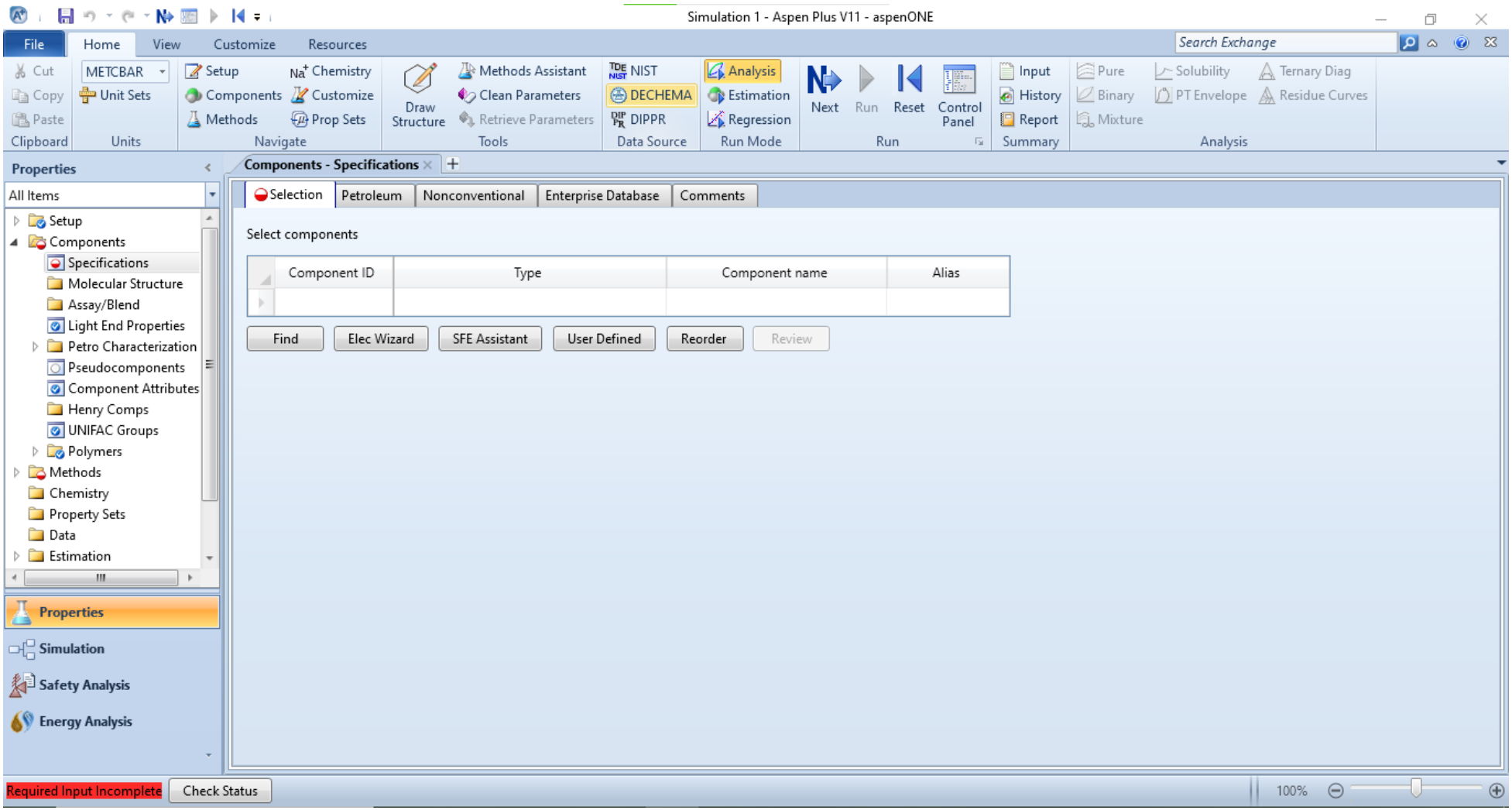


Figure II.1 Aspen plus window

Table II. 1: Aspen Plus vs. Other Competing Software

Our ratings, as appropriate for an undergraduate course setting	Aspen plus	Aspen Hysys	Pro II	Pro Max	gProms	COCO
Cost of academic licenses	Free*	Free*	Free*	Free*	Low	Free*
Installation on student computers	No	No	No	?	?	Yes
Extensive property/ chemicals database	Best	Best	Good	OK	OK	Poor
Extensive unit operation models	Best	Best	Good	OK	Good	Poor
Commercially relevant	Yes	Yes	Yes	Yes	Yes	Limited
Ease of use, Ease of Teaching	Not easy	Not easy	easier	easier	Hard	Ok
Connectivity with Microsoft Excel	Yes	Yes	Yes	Yes	Yes	Yes
Capital cost estimation	Yes	yes	No	No	No	No
Heat exchanger network optimization	Yes	yes	No	no	no	No
Extendible to dynamic simulation	Good	best	Good	no	best	no
Market Share / Popularity	most	good	good	some	good	Little

II.6 ASPEN HYSYS

Aspen HYSYS is a process simulation environment designed to serve many processing industries. It is an interactive, intuitive, open and extensible program. It also has many add on options to extend its capabilities into specific industries. With this program, rigorous steady state and dynamic models for plant design can be created. Apart from this, monitoring, troubleshooting, operational improvement, business planning and asset management can be performed with the HYSYS simulator. Through the completely interactive HYSYS interface, process variables and unit operation topology can be easily manipulated **(RAMDANI & MAHDI, 2020)**

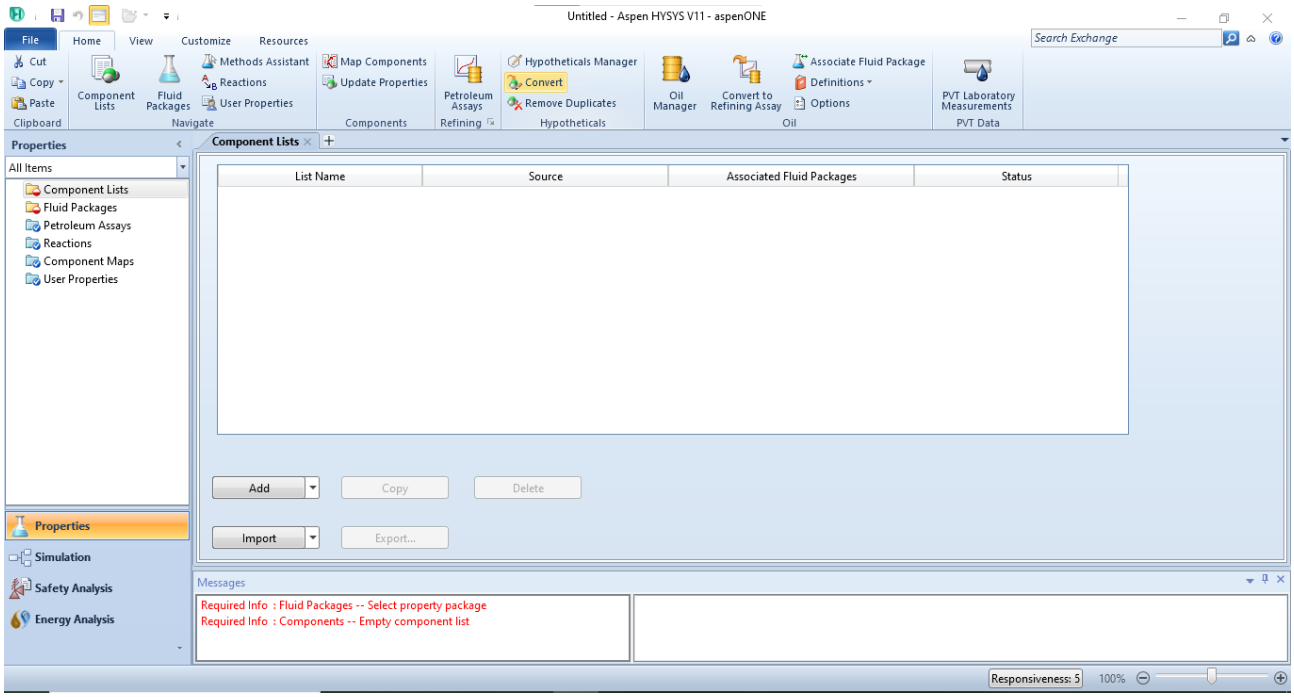


Figure II.2 Aspen HYSYS window

So far there is a large among of publication related the simulation with both aspen plus and aspen HYSYS (Table II.2) summaries some of the most interesting contribution in the chemical engineering field.**(Patil & Gnanasundaram, 2020)**

Table II.2 Summary of Reactive Distillation Simulation and Other Process Parameters for EA Production.

S. No.	Type of Study	Catalyst	Thermodynamic Model	Process ParametersStudied	Ref
1.	Simulation (Aspen Hysys)	Sulfuric acid	NRTL	Effect of ethanol low rate, Ethylene oxide flow rate and Reflux ratio on temperature and component compositions in RD column.	Y. Tavan (2013)
2.	Simulation (Aspen Plus 11.1)	Amberlyst 36	RADFRAC (For VLE data) NRTL (For nbutyl acetate) UNIQUAC (For ethyl acetate)	Effect of feed molar ratio of ethanol to n-butanol on product purities and energy consumption	H. Tian (2012)
3.	Experimental and Simulation (Aspen Plus V 8.4)	1-Sulfobutyl-3-methylimidazolium hydrogen sulfate	RADFRAC	1. Comparison ofKinetic models andcatalysts. 2. Effect of reaction temperature, catalystconcentration, initialreactant molar ratio,Feed tray location ofethanol, theoretical plate number ofrectifying and trayholdup on product purity.	R. He (2018)
4.	Experimental and Simulation (Aspen Plus 11.1)	Amberlyst 36	RADFRAC (For VLE data) NRTL (For nbutyl acetate) UNIQUAC (For ethyl acetate)	Effect of ethanol feed location, acetic acid feed location, feed stage of the reaction mixture of acetic acid and n-butanol, reflux ratio of ethyl acetate reactive distillation column, and distillate to feed ratio of n-butyl acetate column, on the ethanol/n-butanol conversions, ethyl acetate/n-butyl acetate purity, and energy consumption.	I. K. Lai (2008)

5.	Experimental and Simulation	Acidic ion-exchange resin	NRTL	1. Steady stateconditions for a feedconfiguration withexcess ethanol 2. Stoichiometric feed configuration effecton catalyst activity 3. Effect of feed flow rates, reflux flow rate and heat duty	M. F. Fernande z (2019)
6.	Simulation (Aspen Plus)	Para-toluenesulfonic Acid	NRTL	1. Comparison of EQ and rate-based models in Aspen Plus 2. Effect of number of stages on productpurity 3. Effect of feed stage location on ethanolconversion 4. The combined effect of feed location and the addition of fresh ethanol on heatduty	D. Singh (2019)
7.	Experimental and Simulation (Aspen Plus)	Amberlyst 35	-	1. Experimentalruns for Type II RD Process 2. Study theinitial charges to the column holdups and astart-up procedure forcontinuous production	H. Y. Lee (2006)
8.	Simulation (Aspen Plus)	Sulfuric Acid Purolite CT179	RADFRAC NRTL	Comparison of catalyst cost, capital investment cost and energy cost,reaction rate, number oftrays for homogeneousandheterog eneouscatalytic processes.	H. Y. Lee (2007)
9.	Simulation (Aspen Plus)	NA	UNIQUAC	Comparison of conventional and RDprocesses based on product purity, totalannual cost, operatingcost, equipment and utility cost and installed cost.	A. Giwa (2013)

10.	Simulation (ChemCad)	Potassium butanolate	NRTL	1. RD column top mixture (Ethanol +Ethyl acetate) separation by Extractive Distillation, Pressure SwingDistillationand Convectional distillation and to calculate annual cost for each method. 2. Study of Heat integration andthermal couplingbetween two columns.	S. J. Wang (2010)
11.	Simulation (Aspen Plus)	Sulfuric acid	NRTL	Comparison of two basic control schemes anddevelopment of a new control scheme	Y. T. Tang (2003)
12.	Simulation (Aspen Plus)	Sulfuric acid	NRTL	Design of an ethyl acetate system to find optimum operating conditions to minimize the totaloperating cost.	C. Chilev (2017)
13.	Simulation (Aspen Plus)	Purolite CT179 (For EA) Amberlyst 15 (For IPAc)	NRTL	Effects of reactant purity on the design and control of reactive distillation	I. K. Lai (2007)
14.	Experimental and Simulation	Amberlyst 15	UNIQUAC	Effect of feed composition and reflux ratio	N. Calvar (2007)
15.	Simulation (Aspen Plus)	NA	14 Different models	Comparison of 14 property models for highest EA and NBA production	S. O. Giwa (2013)
16.	Simulation (Aspen Plus)	Sulfuric Acid Purolite CT179	RADFRAC	Comparison of threeprocess flowsheets tooptimize the quantitativedesign based on Totalannual cost	Y. T. Tang (2005)
17.	Experimental and	Amberlyst-15	NRTL	Experimental study for a fixed number of catalyst	J. Park

	Simulation			packed trays on ethyl acetate concentration	(2006)
18.	Simulation (Chemcad)	Sulfuric acid	NRTL	Effect of reflux ratio, distillate rate, feed tray location and activity model on ethyl acetate composition	A.N. Amenaghawon (2012)

II.7 CONCLUSION

Commercial simulation programs Aspen HYSYS and Aspen PLUS have been defined in this chapter. Aspen Plus is the Leading Process Simulation Software in the Chemical Industry, while Aspen Hysys is the industry's different from Aspen One process simulation Software. Both of them claim to be applicable for bulk chemicals, downstream, Engineering, procurement construction, midstream LNG, and upstream. Although Aspen Plus and Aspen Hysys can be used for the same application in many industries, when you start a new simulation you can identify that Aspen Plus fits better for fine chemistry, or all other nonpetro processes, such as acids, and pharma, while Aspen Hysys has more features related to for petrochemical/petroleum/downstream operations such as natural gas, liquified gases, fractionation of crude oil, characterization of petroleum. In our study, we will use Aspen Plus for simulating the production of ethyl acetate which will be furthermore explained in the next chapter.

CHAPTER III

SIMULATION OF ETHYL ACETATE REACTIVE DISTILLATION USING ASPEN PLUS

CHAPTER III Simulation of Ethyl acetate reactive distillation using Aspen plus

III.1 INTRODUCTION

Process intensification entails building more compact and cost-effective processes with production capacities many times larger than those of conventional processes through the development of relevant methodologies, techniques, and equipment.
This chapter will discuss the outcomes produced by the employed program, Aspen Plus.

III.2 PROCESS MODELING

III.2.1 fluid package

In the Ethyl Acetate production process, the system involves ethyl acetate (EtAc), ethanol (EOH), water (H_2O), acetic acid (AA); Ethylene oxide (EO) and monoethylene glycol (MEG) are used to expand two case studies **(Branislav et al., 2020).** This quaternary reactive system under study (AA–EtOH–EtAc– H2O) exhibits non-ideal behavior with the formation of **(Santaella et al., 2015):**

- Three homogeneous azeotropes:
  (EtOH–H2O), (EtOH–EtAc) and (EtAc–EtOH–H2O).
- One heterogeneous azeotrope:
  (EtAc–H2O).**(Branislav et al., 2020)**

Acetic acid is well recognized for its strong association in the vapor phase and the formation of diners, even though it does not form an azeotropic mixture with the other participating molecules; When combined with the other components mentioned, monoethylene glycol does not generate an azeotropic combination. Ethylene oxide is a gas at normal temperature, unlike other components.**(Branislav et al., 2020).** The simulation works presented in this chapter were conducted on the Aspen Plus V11.1 package, with the NTRL-HOC (Figure III.1) model being employed for the column, since this has proved successful with this system. NRTL is used to calculate liquid activity coefficients, while the Hayden-O'Connell equation of state, which predicts dimerization in the vapor phase, is used to calculate thermodynamic properties for the vapor phase. **(Filipe et al., 2005)**

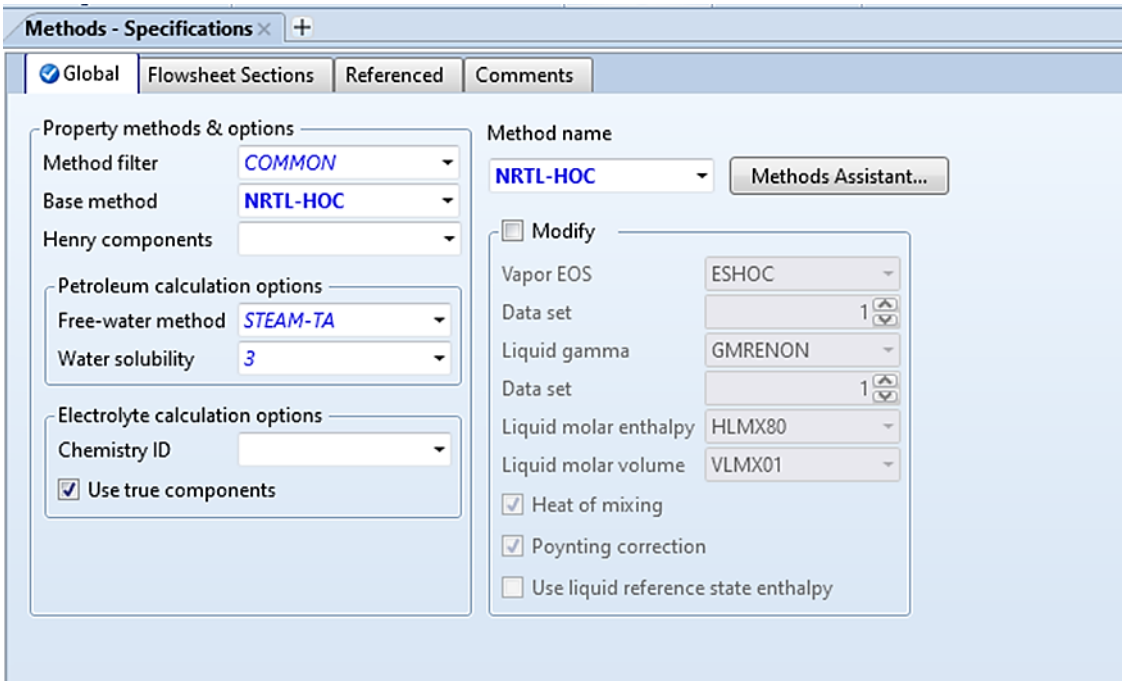


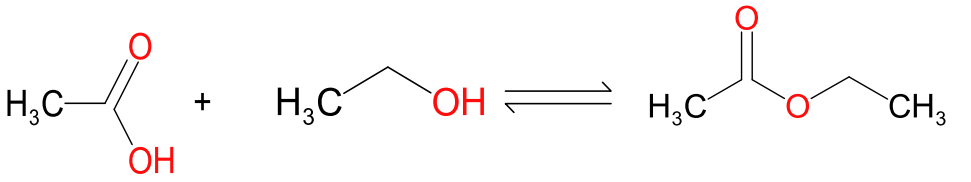
Figure III.1 NRTL-HOC method input window.

III.2.2 Kinetic model

Many kinetic investigations utilizing acid catalysts on fischer esterification to EtAc have been published **(Mazoti et al.1997, Ismail et al.2001, Calvar el al.2007)**. Because it`s more active than the majority of commercial homogeneous (such as p-toluene sulfonic acid and methane sulfonic acid) and heterogenous (such as ion exchange resins) catalysts, H_2SO_4 has historically been used extensively as a catalyst.

Commercial applications typically use H_2SO_4 loadings between 0.2 and 1% Wt. of the reactive mixture **(Santaella et al., 2015):**

Based on the research that is presented in the article **(Branislav et al., 2020),** homogeneous catalysis using sulfuric acid was assumed, Equation (III.1):



(III.1)

Acetic Acid Ethanol Ethyl Acetate Water

Equation (III.2), which has been employed in publications, expresses the reaction rate (r [kmole $m^{-3}s^{-1}$])

$$r = K_1 C_{AA} C_{EtOH} - K_2 C_{H2O} C_{EtAc} \qquad \textbf{(III.2)}$$

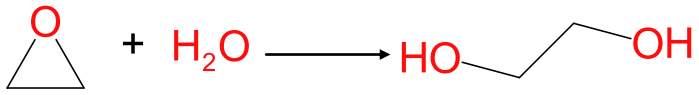
Where:

i. $K_1 = 2.8 \times 10^4 \exp\left(-\frac{41.868}{RT}\right)$

ii. $K_2 = 7.1 \times 10^3 \, exp\left(-\frac{41.868}{RT}\right)$

The reaction occurs in the liquid phase; liquid phase molar concentrations (C [kmole. m^{-3}]) are used. The concentration of sulfuric acid catalyst was low, so its presence in the phase equilibrium calculation was neglected.

As it was mentioned, an auxiliary chemical reaction was included to enhance the reactive distillation process in the last case study. This auxiliary reaction was chosen to ensure the removal of the main esterification reaction by-product—water. Ethylene oxide (EO) hydration was used, Equation (III.3):



Ethylene oxide water Monoethylene glycol **(III.3)**

Monoethylene glycol (MEG) is produced as the main product of the auxiliary reaction. Further reactions towards higher glycols (diethylene glycol, Tri ethylene glycol) were omitted because of the lower reaction rate and negligible change in the composition of product streams.

The auxiliary reaction rate is expressed by Equation (III.4)

$$r_2 = 3.15 \times 10^{12} \exp\left(-\frac{79{,}374}{RT}\right) C_{EO} C_{H2O} \qquad \textbf{(III.4)}$$

III.2.3 Equipment model

Aspen plus software, version of 11.1, is a process modeling software suitable for a variety of steady-state modeling applications. The Aspen system is based on blocks corresponding to unit operations as well as chemical reactors, through which most of the industrial operations can be simulated. By interconnecting the blocks using material, work, and heat streams, a complete process flow sheet can be constructed. **(Sarkar & Bhattacharyya, 2012)**

Three principal equipment model types were utilized in this study:

- **Continuous stirred tank reactor (CSTR)**

It is possible to simulate a chemical reactor using a continuous stirred tank reactor (CSTR) model, which assumes ideal mixing and rate-controlled chemical reactions based on established kinetics. Both isothermal and adiabatic operation of the reactor are options. The residence time parameter was used to convert the desired way. In the case of esterification (1), the chemical reaction rate is represented by equation III.6 and only takes place in the liquid phase. The acceptable chemical reaction (liquid, vapor-liquid) was specified.

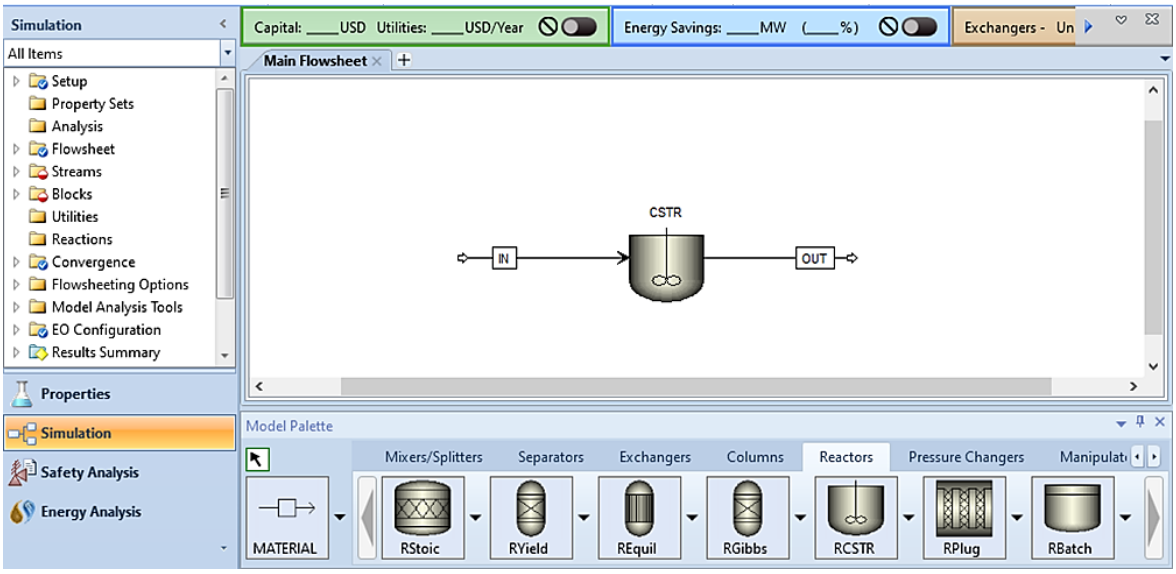


Figure III.2 CSTR model window

- **Heat exchangers**

Heat exchangers were simulated by the Heater and HeatX models, respectively. A shortcut set-up was applied to reach the desired stream temperature. Heat integration was applied to improve the optimal process design. The minimum stream temperature difference was set to 10°C.

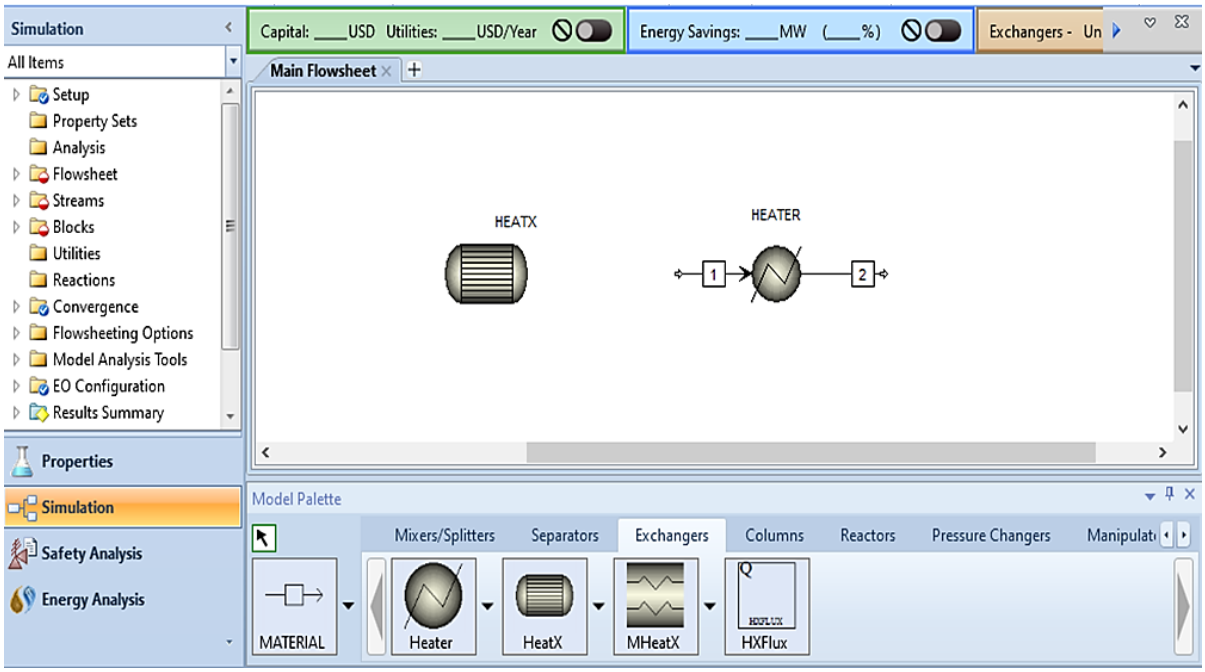


Figure III.3 Heat exchangers model window

- **RadFrac column**

Both for conventional distillation and RD modeling, a rigorous RadFrac column model was employed (see Figure III.4).

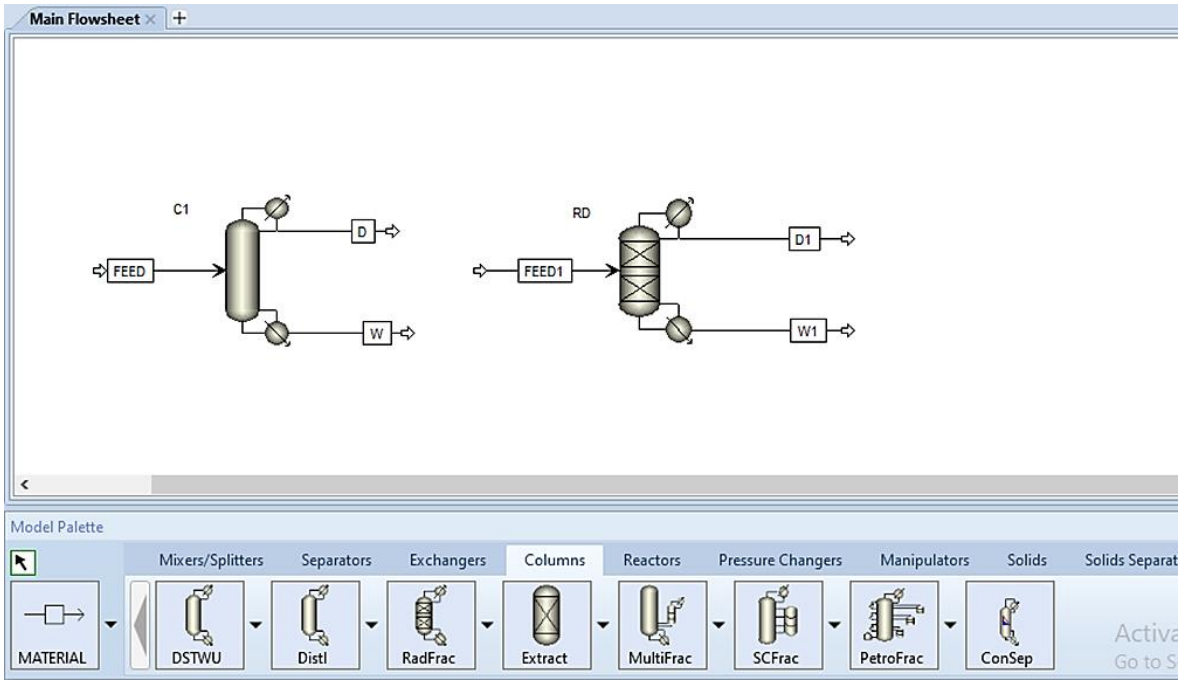


Figure III.4 RadFrac column model window

This model allows both EQ and NEQ approaches. Building an NEQ model of reactive separation or separation is not as straightforward as it is in the EQ model. The NEQ model requires much more reliable parameters compared to the EQ model. Consequently, the NEQ model is more difficult to calculate, and convergence problems often occur. To improve NEQ model convergence, a good initial guess of stage temperature, liquid phase composition, and vapor phase composition must be used. For this purpose, the EQ model of each column was made in the first step of the simulation using initial column parameters such as the number of theoretical stages (N), reactive zone (NR), feed stage position (f), and reflux ratio (R). These parameters can be found in the literature. The results of the EQ model simulation provide a very good starting point for building the NEQ model. Another advantage of first building the EQ model is the possibility of faster testing of individual case studies. When the suitable case study concept is selected, the NEQ model is built based on the EQ model results.

Rate-based set-up must be enabled in the Aspen Plus in the NEQ model. Therefore, a detailed column internal configuration is required next. A packed column is selected similarly to simulation-experimental works. Mass and heat transfer correlation methods were selected according to the recommendation for the packing type (Rashing Ralu-Ring). Column hydraulics was simulated by Aspen Plus built-in hydraulic function assuming correlation for Rashing Ralu-Ring packing type. Column internal configuration (internal diameter (d), packing height (H), packing dimensions) were set during the calculation procedure regarding reasonable column hydraulics, pressure drop, and approach to flood.

III.2.4 Intensification of Ethyl acetate production

III.2.4.1 Conventional Process Set-Up

Most ethyl acetate production plants apply the process defined by Riemenschneider (2008) which consists of a continuous stirred tank reactor (CSTR) and several separation columns. Even though the capacity of large plants can be up to about 100,000 tons of EtAc per year, this process is problematic and inefficient for several reasons, separation of the reaction mixture from the CSTR reactor can be seen as the main problem. As it has been mentioned in Section III.2.1, the azeotropic mixture is formed during the separation. Moreover, the separation of unreacted acetic acid is an energy-intensive process, even in large distillation columns. Overcoming the distillation boundary to produce pure EtAc was

reported as the next issue. A decanter is most often used for this purpose, adding a certain amount of pure water to obtain an organic (EtAc rich) and an aqueous phase. Losses of ethyl acetate in the aqueous phase and the regeneration of used water have also to be solved. Thus, high recycle flows and large energy consumption of this process are inevitable.

- Flowsheet Design (Figure III.5)

The conventional set-up consists of four key equipment units. The esterification reaction proceeds in a CSTR reactor, which is followed by an azeotropic distillation column and two conventional columns. A Detailed flowsheet with streams attachment is depicted in Figure III.5.

Raw material streams (AA0 and ETOH0) are mixed with recycled streams and lead to the adiabatic CSTR reactor (R1). As the esterification reaction conversion is slightly over 60%, the reaction mixture contains four compounds (acetic acid, ethanol, water, and ethyl acetate). Reactor products stream (P1) is then preheated in the heat exchanger EX1.

This mixture is separated into azeotropic distillation column C1 (Figure III.5) which has two feed streams: reaction mixture from the CSTR (P2) and pure ethyl acetate (AZ) used as azeotropic distillation entrainer. The bottom product (W11) contains unreacted acetic acid and water, and it was recycled back to the CSTR. The water-ethanol-ethyl acetate azeotropic mixture was gained as a distillate (D11).

Pure water was added to overcome the distillation boundary and the mixture (D12) was cooled down in the heat exchanger EX2. The water phase (H2OL) and organic phase (ORG) were separated into decanter DEC (Figure III.5). The organic phase contains mainly ethyl acetate.

Pure ethyl acetate was separated in distillation column C2 as a bottom product (W21). A part of pure ethyl acetate flow was recirculated as the azeotropic entrainer (AZ) back to column C1. The final product (W22) was cooled down in the heat exchanger EX7. The C2 column distillate (D21) contains a ternary mixture of water, ethanol, and ethyl acetate; it was then cooled down in C2 preheater EX3 and recirculated back to the decanter.

The water phase (H2OL) was rich in unreacted ethanol; thus, it was regenerated in distillation column C3 (Figure III.5). The C3 column feed (F31) was preheated in two heat exchangers: EX4 and EX5. Pure water (W31) was obtained as the C3 column bottom product and the concentrated ethanol-water mixture was separated in distillate (D31) which

was cooled down in EX4 and recirculated back to the CSTR. The bottom product (W31) was cooled down in EX5 and then divided into the water final product stream (H2OP1) and water for recirculation back to the decanter (H2OREC).(**Branislav et al., 2020)**

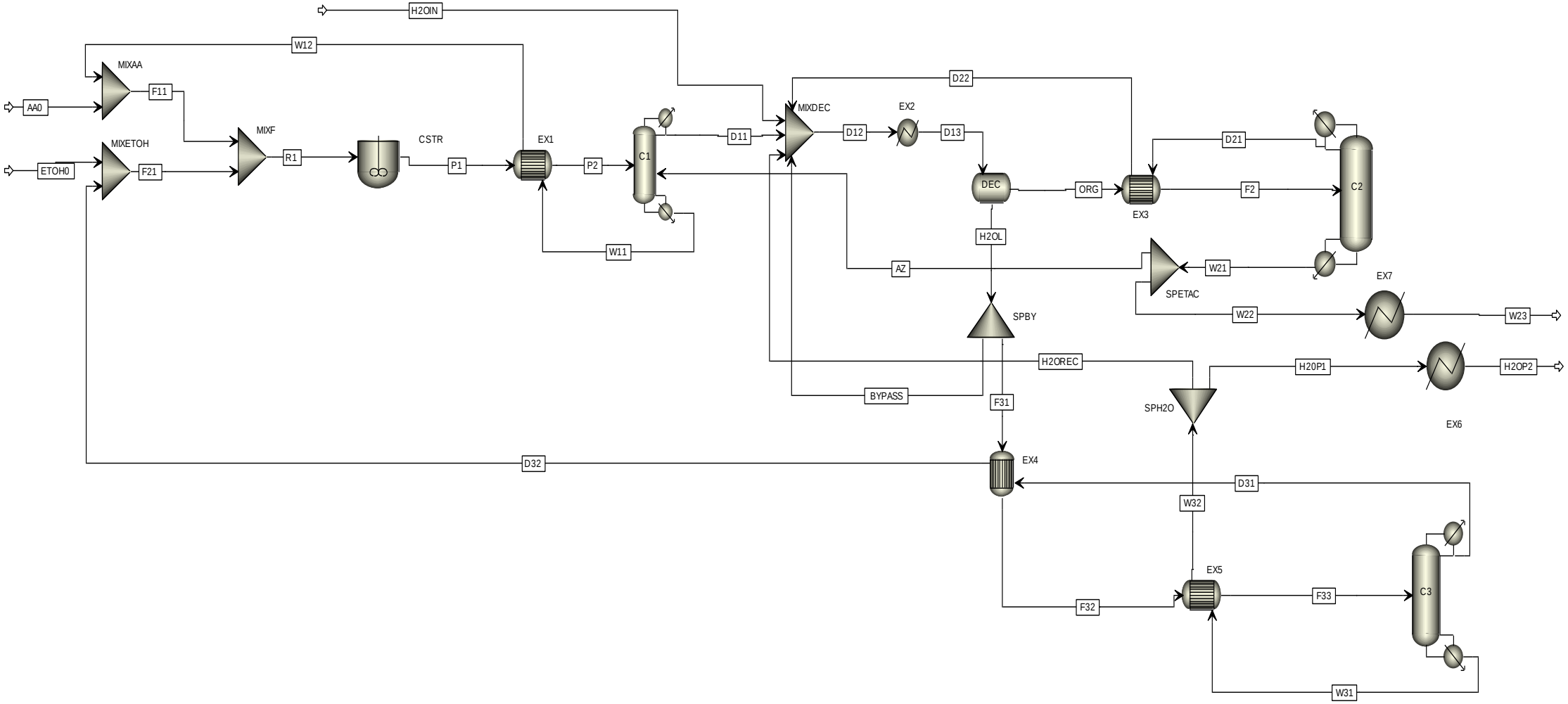


Figure III.5 Ethyl acetate production via conventional process set-up.

III.2.4.2 Reactive Distillation Column with a Separation Unit

Integration and intensification of the convention process set-up can be achieved by combining reaction and separation together via the reactive distillation process. Several RD plants for ethyl acetate production are operated worldwide with the reported individual plant annual production capacity of around 20,000 tons of EtAc.

As RD is a multifunctional reactor concept combining the mechanism of reaction and separation in one single unit, benefits such as the reduction of equipment and plant size, improvement of process efficiency, and, consequently, better process economy are expected.

In this case study, the main benefit expected is the reduction of the number of equipment units and overcoming the distillation boundary which limits the conventional set-up. CSTR, EX1, and C1 columns are put together into an RD column.

As a result, one main equipment unit (CSTR) and two heat exchangers are removed from the process compared to the conventional set-up (Figure III.6).

- Flowsheet Design (Figure III.6)

The reactive distillation set-up is derived from the conventional one (Figure III.6). A detailed process scheme is depicted in Figure III.6.

The reactive distillation column has two feed streams: acetic acid feed (AA0) and mixed ethanol feed (ETOH). Raw ethanol is added to the process in the (ETOH0) stream. All acetic acid is consumed in the RD. Therefore, RD distillate (D11) contains a nearly azeotropic mixture of EtAc-EtOH-water, while the bottom product (W11) contains a water-ethanol mixture (Figure III.6). The distillate composition was from a different distillation region than that of distillate in the conventional process set-up (D11 in Figure III.5). Therefore, stream (D11 in Figure III.6) can be separated directly. Distillation column C1 is deployed to separate the final pure EtAc (Figure III.6). The C1 column bottom product (W21) contains pure EtAc which is cooled down in heat exchanger EX5.

The EtAc-EtOH-water ternary azeotrope is present in the C1 column distillate (D21 in Figure III.6) Thus, columns C1 column (Figure III.6) and C2 in conventional process set-up (Figure III.5) are operated in the same way. The distillate (D21) is cooled down in heat exchangers EX1 and EX2 and fed into decanter DEC to extract EtAc (Figure III.6).

Pure water is fed to DEC; organic phase (ORG1) and aqueous phase (H2OL) are separated. The organic phase (ORG1) is preheated in EX1 and mixed with (D11). The aqueous phase (H2OL) contains some amount of EtOH and EtAc and therefore it has to be regenerated. The (H2OL) stream is mixed with the RD column bottom product (W11) and preheated in heat exchanger EX3 (Figure III.6).

For water regeneration, distillation column C2 is used (Figure III.6). All EtOH and EtAc are obtained in the C2 distillate (D31) which is recirculated back to the RD column. Pure water is separated in the C2 bottom product (W31) and it is cooled down in EX3 and EX4 (Figure III.6). An equimolar ratio of water to EtAc product (W22) is separated (H2OP) as a final by-product and the rest of the water is recirculated back to the decanter (H2OREC).**(Branislav et al., 2020)**

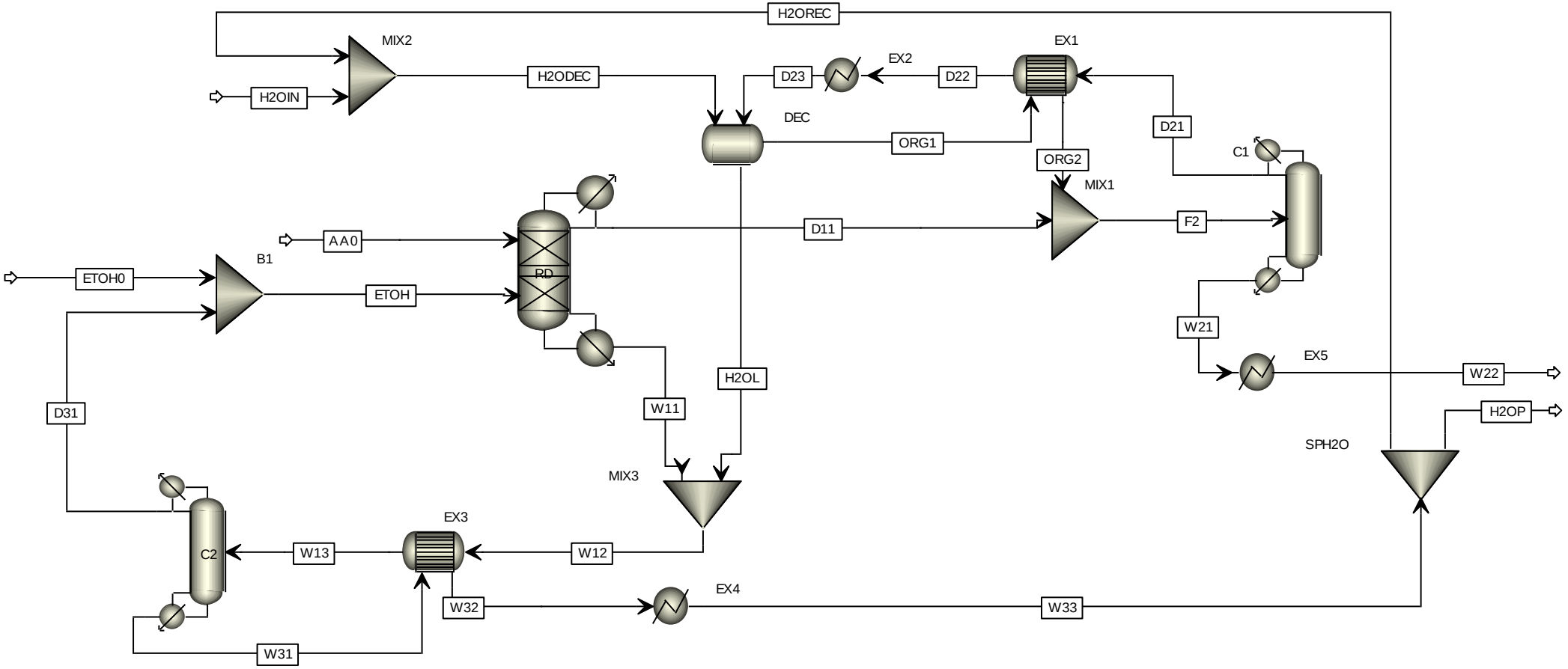


Figure III.6 Ethyl acetate production via reactive distillation column with a separation unit

III.2.4.3 Reactive Distillation Column with a Stripper

Even though the RD column with a separation unit (Figure III.6) represents process integration and intensification compared to the conventional set-up (Figure III.5), there is still a place for improvement such as the reduction of the large flow of recycled stream to the decanter or reduction of equipment number.

As the reaction in the RD process has overcome the distillation boundary, it is possible to remove the decanter and to solve the azeotropic mixture regeneration via distillation. Also, the ethanol-water mixture from the RD column (W11 in Figure III.6) can be easily separated into pure water (high boiling point) and ethanol-water mixture at high ethanol concentrations. Therefore, the flowsheet of the RD column with a separation unit (Figure III.6) was modified as follows:

- C2 column has been integrated into the bottom part of the RD column;
- decanter and heat exchangers EX1 and EX2 were removed;
- C1 column condenser was removed and overheated vapors from C1 were recirculated back to the RD column (Figure III.7).

Thus, the process scheme in Figure III.7 contains two columns and two heat exchangers less than the process scheme shown in Figure III.6. The main idea behind such integration is based on thermal coupling. Two columns are thermally coupled if a vapor (liquid) stream is sent from the first column to the second column, and then a return liquid (vapor) stream is set between the same columns. These streams, when introduced at the top or bottom of a column, provide (at least partial) reflux or boil-up to this column. This approach is commonly used in the petrochemical industry.

- Flowsheet Design (Figure III.7)

This process set-up is composed of two columns: reactive distillation column RD and stripper column C1 (Figure III.7). The reactive distillation column has three feed streams: (AA0) consists of pure acetic acid and was led to the upper section of the RD column; (ETOH0) contains pure ethanol and was attached to the bottom section of the RD column; and overheated vapors (AZ1) from stripper C1 fed in the middle of the RD column (Figure III.7). The RD column has two product streams: liquid distillate (D1) brought to the head of stripper C1; liquid bottom product (W11) which has been cooled down in the heat exchanger EX1. The stripper column has only one product stream (W21), which was cooled down in the heat exchanger EX2.**(Branislav et al., 2020)**

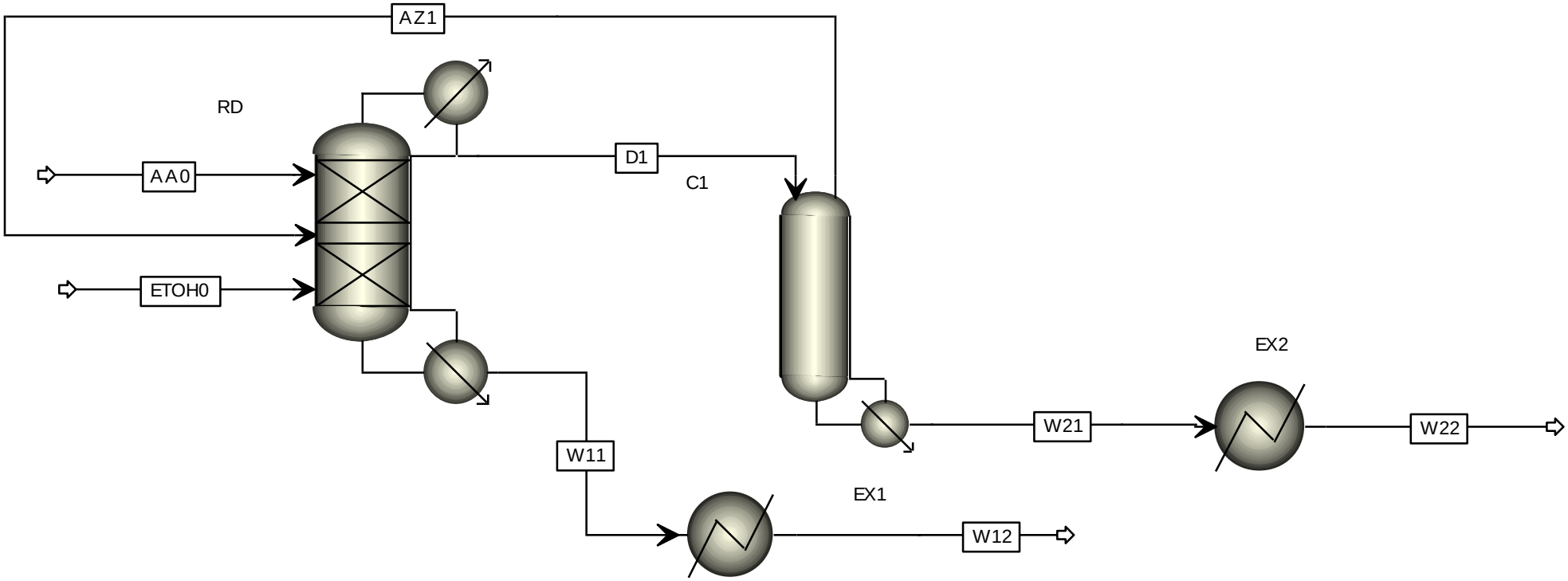


Figure III.7 Ethyl acetate production via reactive distillation column with a stripper.

III.2.4.4 Reactive Distillation Column with an Auxiliary Reaction

The RD column with a stripper set-up (Figure III.7) has reduced the number of equipment units significantly compared to the conventional process set-up (Figure III.5) and the RD column with a separation unit (Figure III.6).

Further process integration and intensification are limited by the presence of water. As the ternary azeotrope EtAc-EtOH-water is formed, at least two columns (RDS) are needed for its separation. Moreover, equilibrium esterification reaction (1) conversion is suppressed by the increasing concentration of products. Therefore, the removal of water as a by-product is attempted to intensify the process and reduce the number of equipment units. Water can be consumed by an auxiliary chemical reaction. If Ethylene oxide (EO) hydration is applied as the auxiliary chemical reaction; the ternary azeotrope is removed and another valuable product, monoethylene glycol (MEG), is obtained. The idea is derived from industrial glycol production.

An RD column with total reflux and selective ethylene oxide hydration is used to obtain the desired glycol in the RD column bottom product. Such an innovative approach was first tested by Tavan, who used the simulation environment of Aspen HYSYS. However, inaccurate results can be obtained because of the presence of acetic acid. The Aspen Plus software is more suitable for the simulation of processes with organic acids as its built-in thermodynamic model NRTL-HOC, omitted in HYSYS, can be used. In this chapter, a rigorous NEQ model of the RD column has been built and the RD column internals has been shown in more details which provides more accurate simulation results compared to the EQ model used by Tavan.

- Flowsheet Design (Figure III.8)

  The last flowsheet contains only one column (Figure III.8) with three feed streams:

  1. raw acetic acid (AA0) was fed to the top section;
  2. raw ethanol (ETOH0) was fed to the middle section and
  3. pure ethylene oxide (EO) was fed to the lower part of the RD column.

As this set-up is fully integrated and intensified, there are two product streams only:

a. Distillate (D1) contains pure EtAc ;
b. Bottom product (W1) contains monoethylene glycol.

Both product streams were cooled down in heat exchangers EX1 and EX2, respectively (FigureIII.8).**(Branislav et al., 2020)**

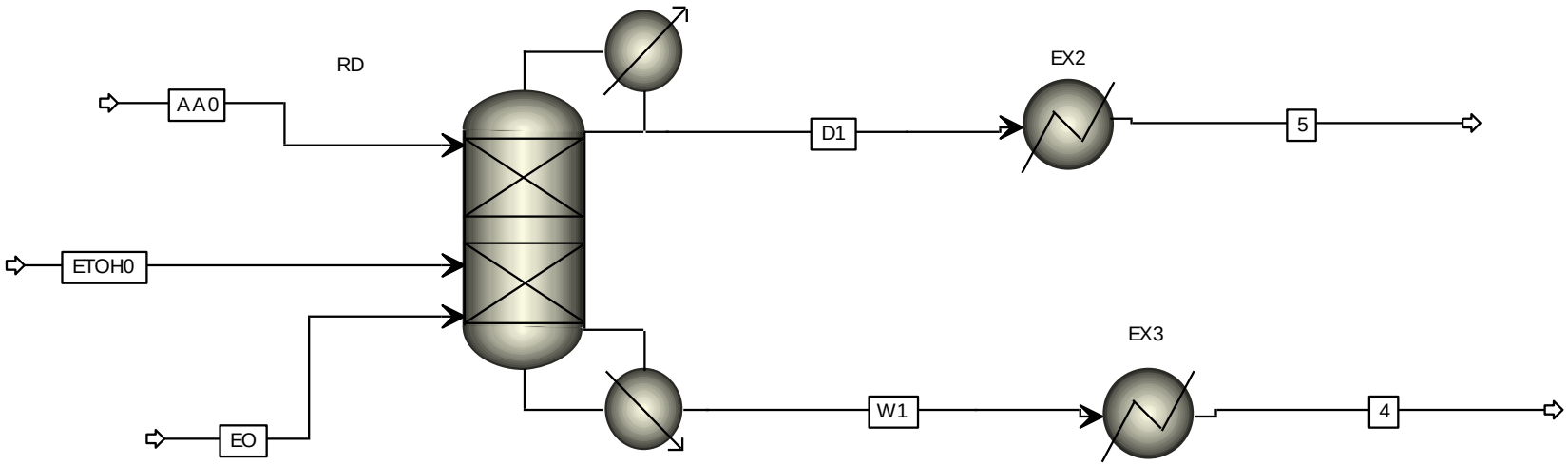


Figure III.8 Ethyl acetate production via reactive distillation column with an auxiliary reaction.

III.3 SIMULATION RESULTS

This section describes the conventional process in detail and its condition, besides the steps of the simulation using Aspen Plus V11 Simulation Software, and then we will present the results obtained from the simulation and compare them with the intensified case.

III.3.1 Simulation setup

For each case study, the initial input specifications listed below were entered:

- Equimolar raw material input (10 kmol $h^{-1}$for both ethanol and acetic acid)
- Process inlet and outlet streams temperature of 25 °C
- atmospheric pressure

After having successfully introduced all the necessary inputs (The components: AA, EtOH, EtAC, H2O) and fluid package (NRTL-HOC), we will enter the simulation environment in terms of flow and design of all models.

III.3.1.1. Flowsheet 1 (Figure III. 5)

Feed flow

Specify the feed streams. Click Streams | **AA0**| **ETOH0**|**H2OINInput**. Under Composition select temperature| pressure| Mole-Flow and mole-fraction then enter a value for each specification as shown in the **figures III.9**, **III.10** and **III.11**, respectively**.**

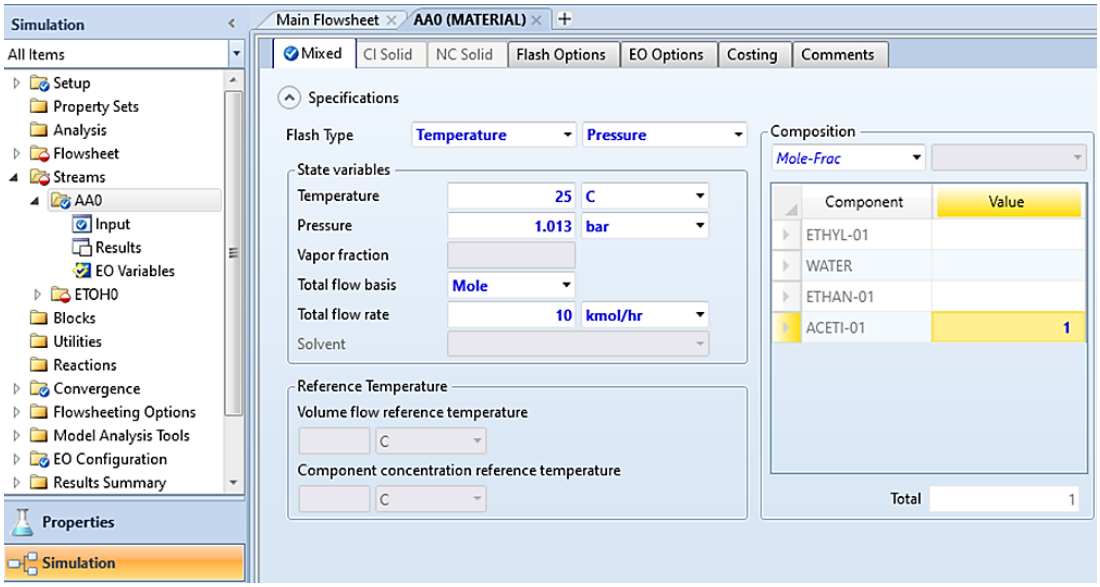


Figure III.9 AA0 feed window

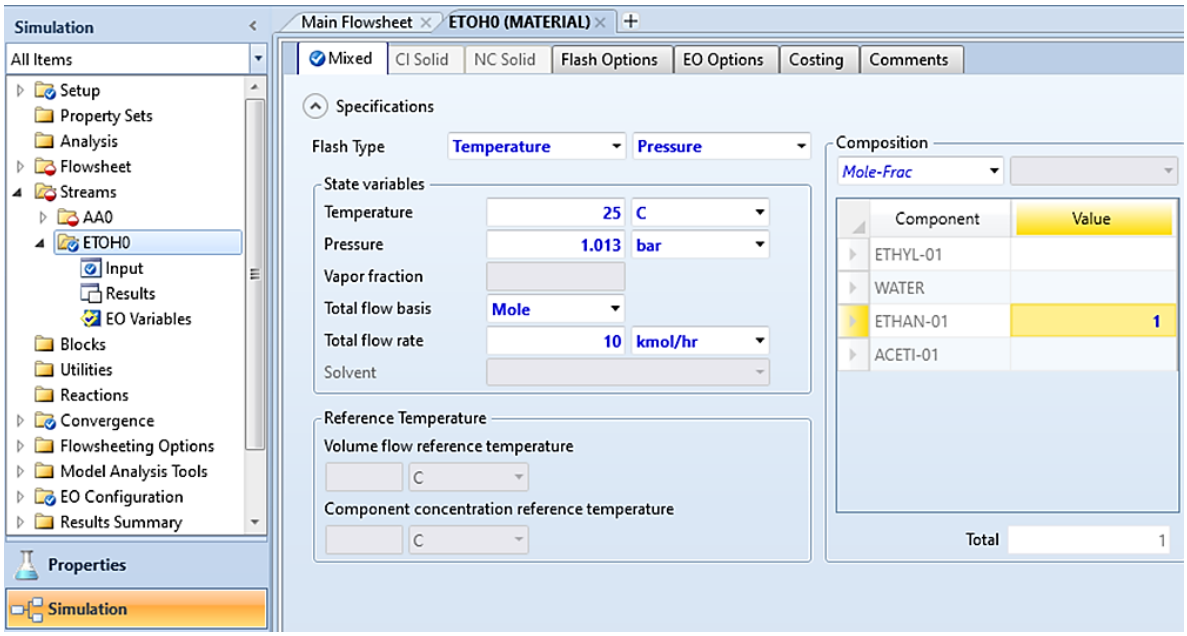


Figure III.10ETOH0 feed window

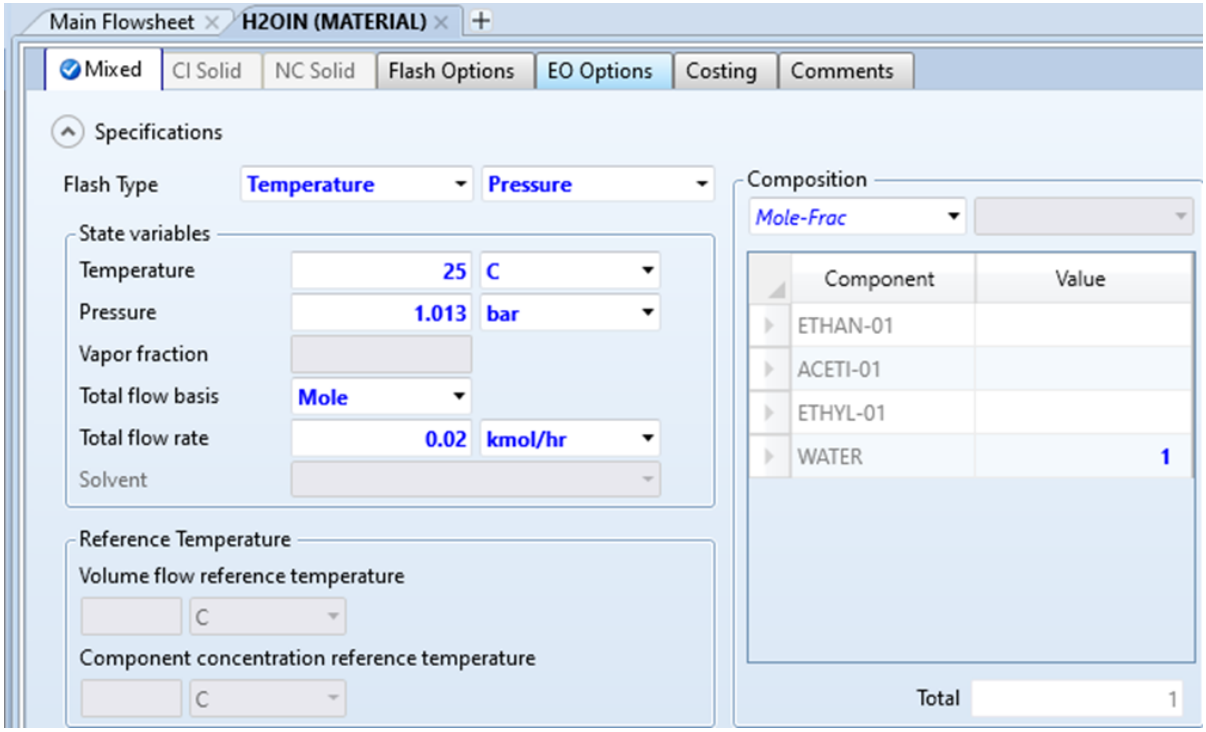


Figure III.11 H2OIN feed window

The CSTR reactor

Specify the CSTR operating conditions (figure III.12) by clicking **Blocks| CSTR | Setup**. Enter **P = 1.013 bar** and **T = 25°C**. Select **Liquid-Only** for Valid phases, and volume for Specification type. Enter **V=8.9 m^3**. (**Branislav et al., 2020)**

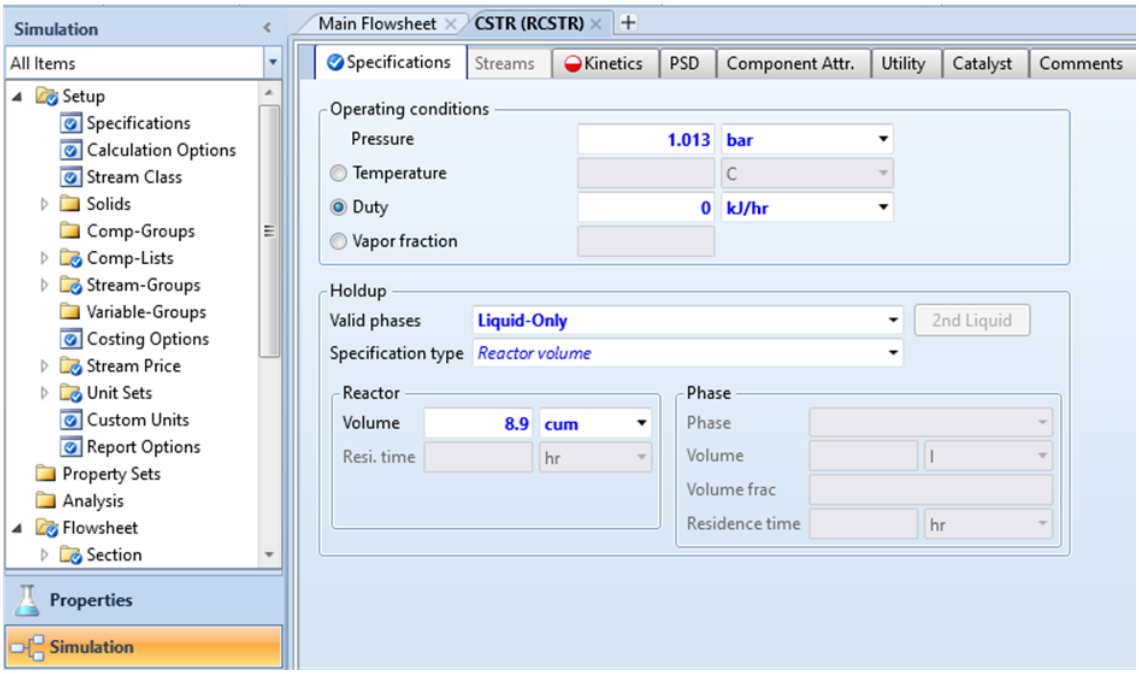


Figure III.12specification of CSTR

Click on the **Kinetics** tab| **New** to create reaction set ID| **R-1**click **OK**| select **POWER LAW** for reaction type| (Figure III.13)

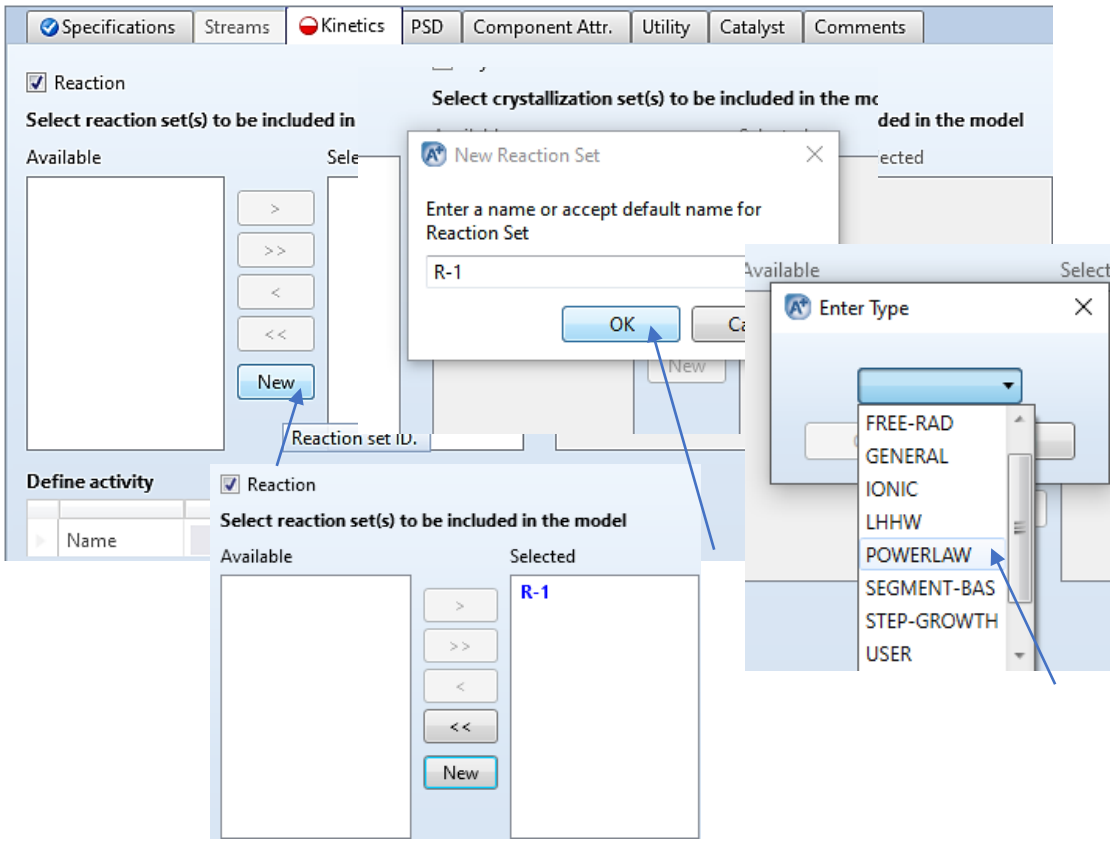


Figure III.13 specify the type of new reaction

Now, go to the **Reactions** folder in the navigation pane |In **R-1**, click **New** which will open a stoichiometry window. Give the reaction a name, select the reactants and products for this reaction and specify the stoichiometric coefficients as shown in the figures III.14 and III.15

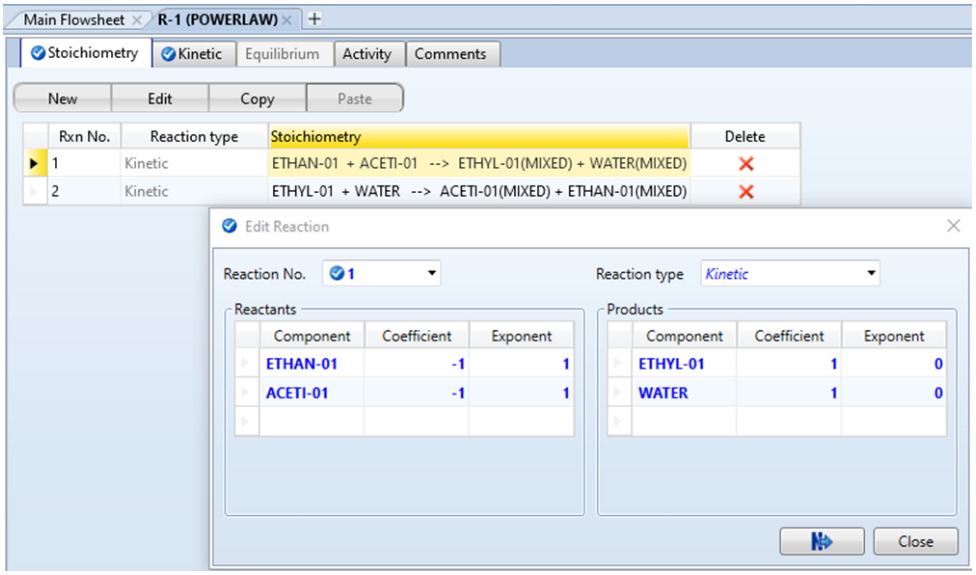


Figure III.14 Stoichiometry specification No.1

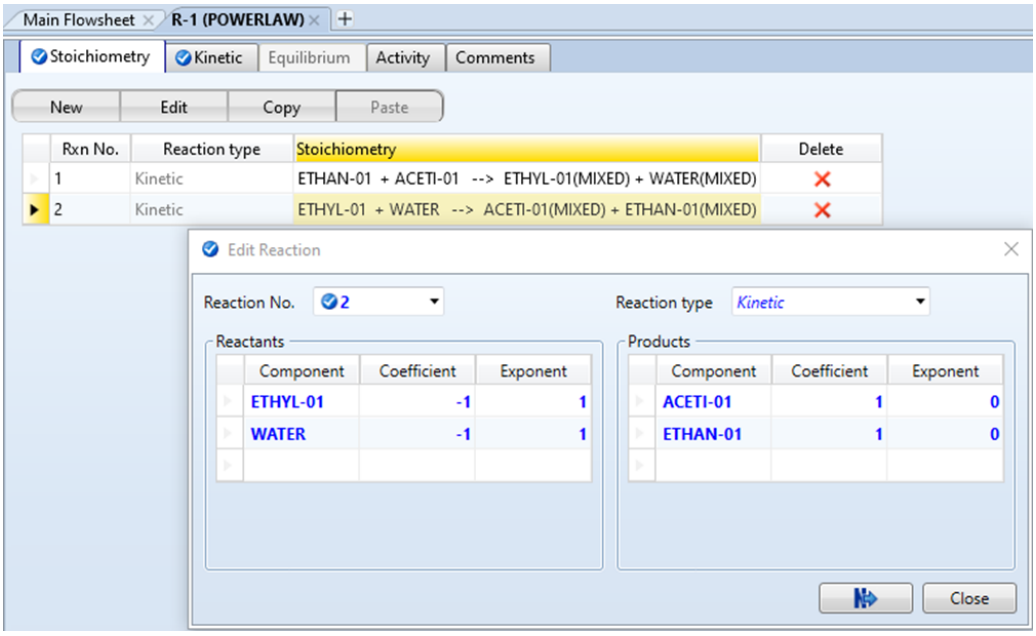


Figure III.15 Stoichiometry specification No.2

Click the **Kinetic** tab, The drop-down arrow on the first line allows you to select one of the two reactions. The kinetic parameters of reaction "1"and "2" are shown in figures III.16 and III.17.

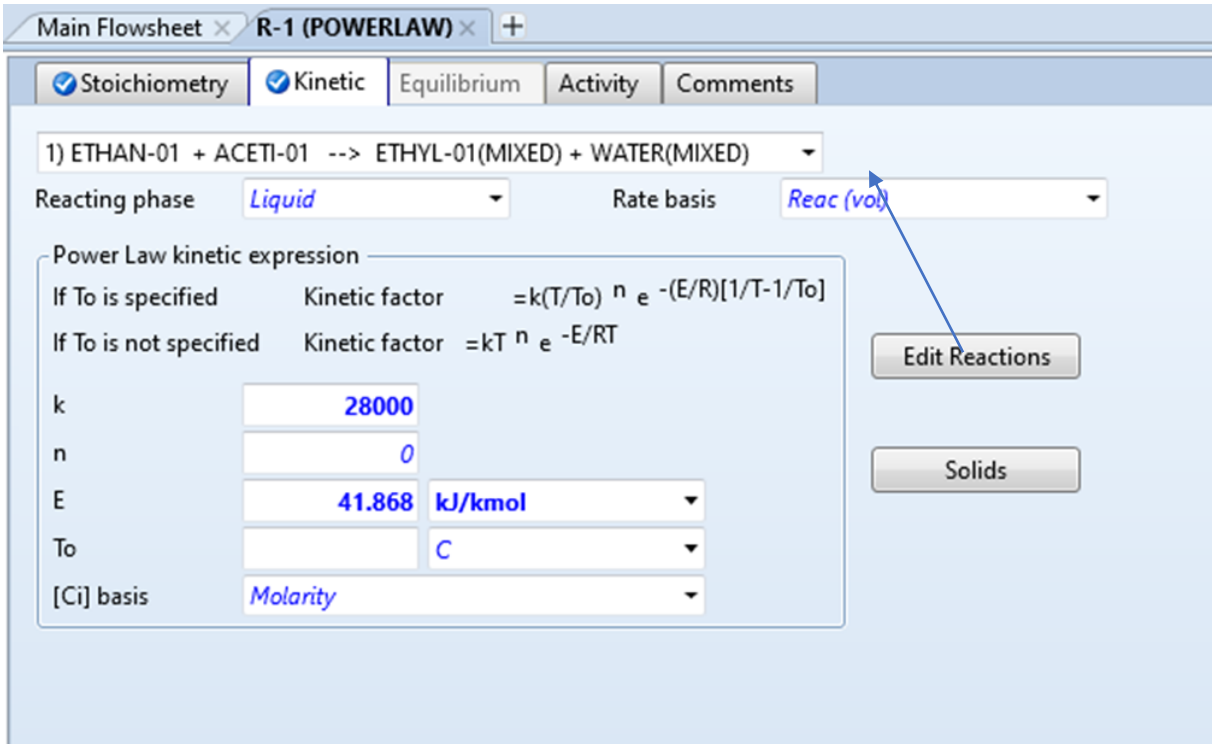


Figure III.16 Kinetic specification No.1

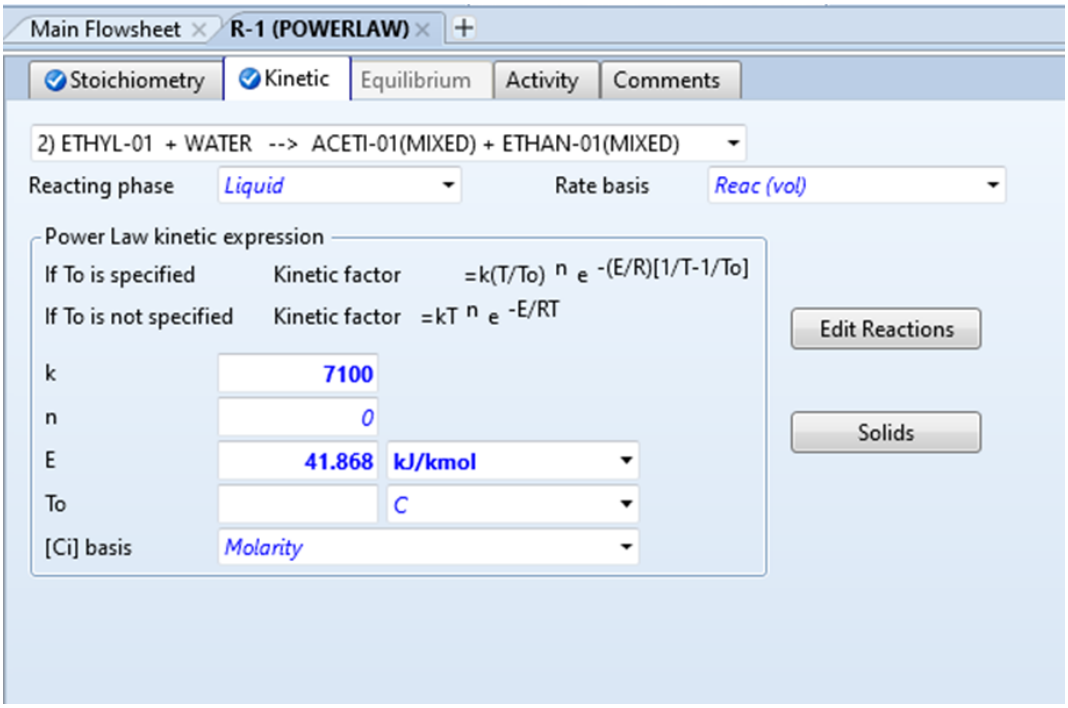


Figure III.17 Kinetic specification No.2

Heater (HeatX)

The input sheet for the Heater block will appear next. Click on the **shortcut** method then **Tube** for hot fluid. The next step is to define the "**Exchanger specification**." If you click on the down arrow a list of choices will appear. Enter in **Hot stream outlet temperature=49 °C** as shown in the following figure III.18

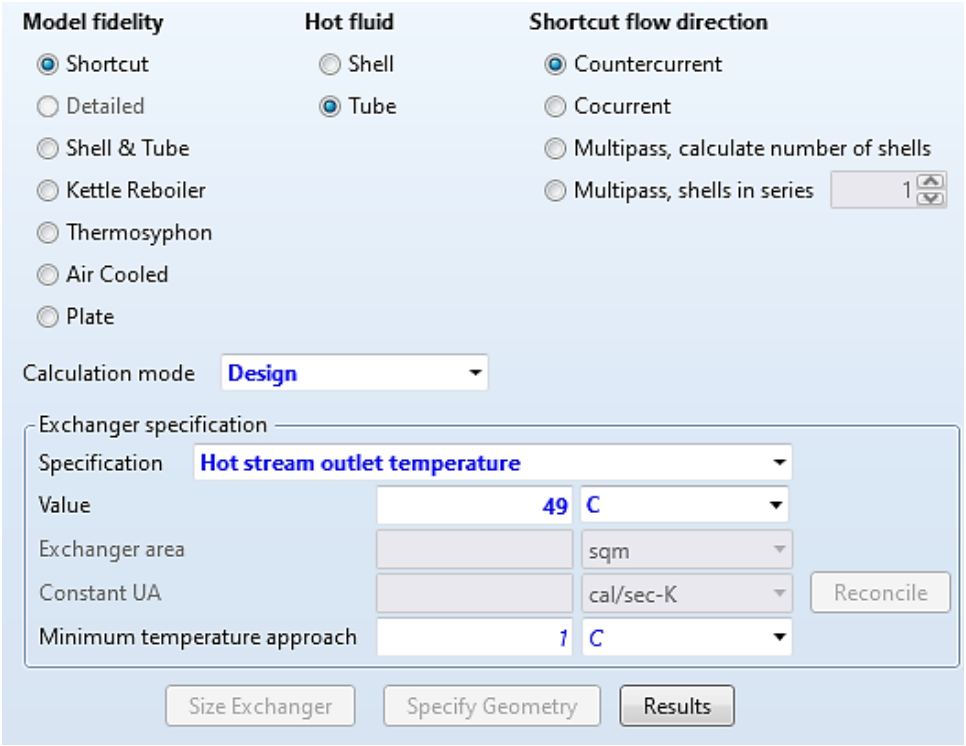


Figure III.18 EX1 block specification by temperature

Column C1 (Rad Frac)

Define the azeotropic distillation column C1(Figure III.5) (design parameters for C1, C2 and C3 mentioned in table III.2); in the **Configuration** tab under Setup, define the **calculation type**, **number of stages**, **condenser** and **reboiler type**, **valid phases**, and **convergence method**; as valid phases select **Vapor-Liquid**. use the **Azeotropic method** for Convergence. Move to **Operating specifications** and enter the values of the **bottoms rate** and the **reflux ratio** (Figure III.19).

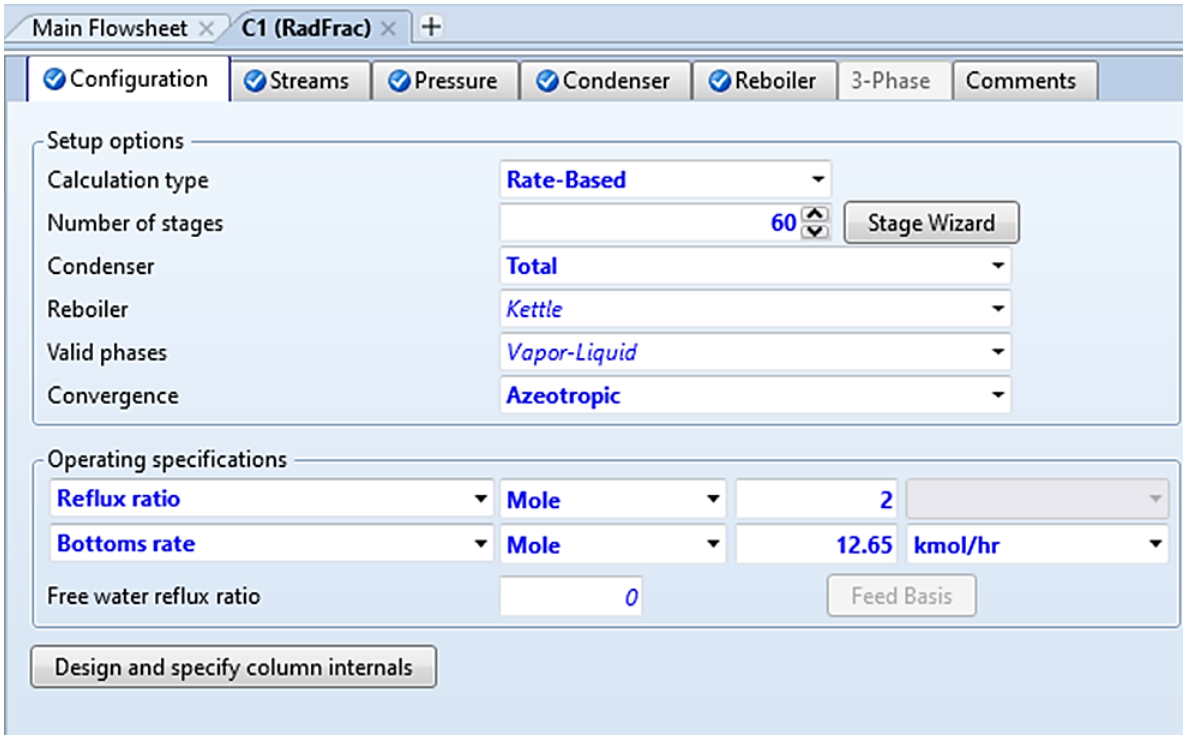


Figure III.19 Defining the column parameters 1.

On the Streams page, specify **feeding stages** for streams **P2** and **AZ** as shown in (Figure III.20) Use the default convention (**above stage**).

On the Pressure page, enter column pressure for **Top stage/Condenser Pressure**.

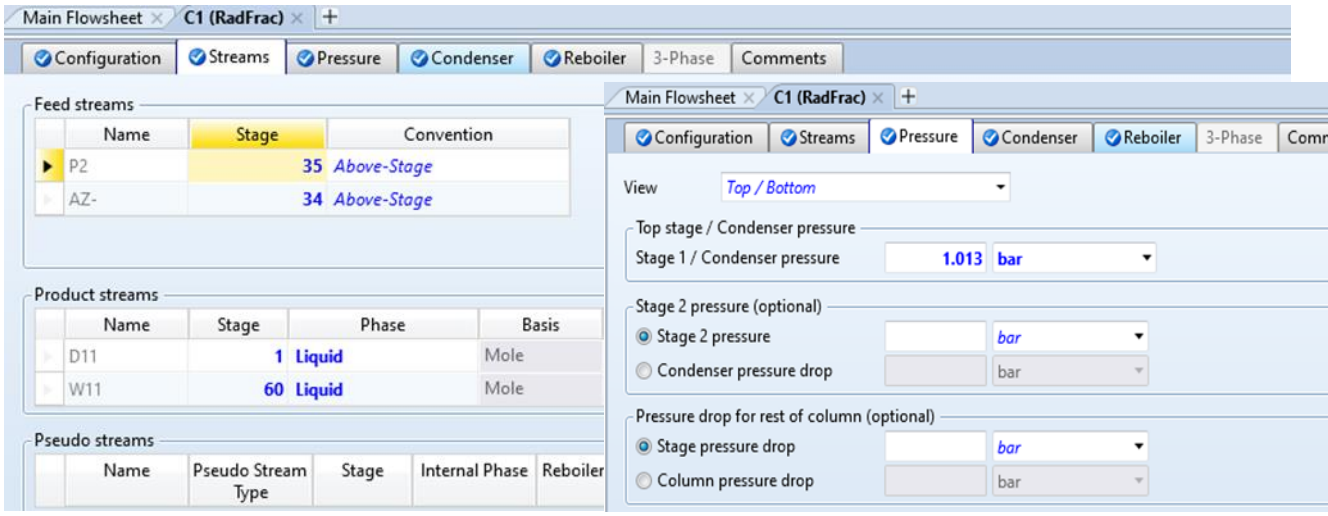


Figure III.20 Defining the column parameters 2 (Streams and pressure)

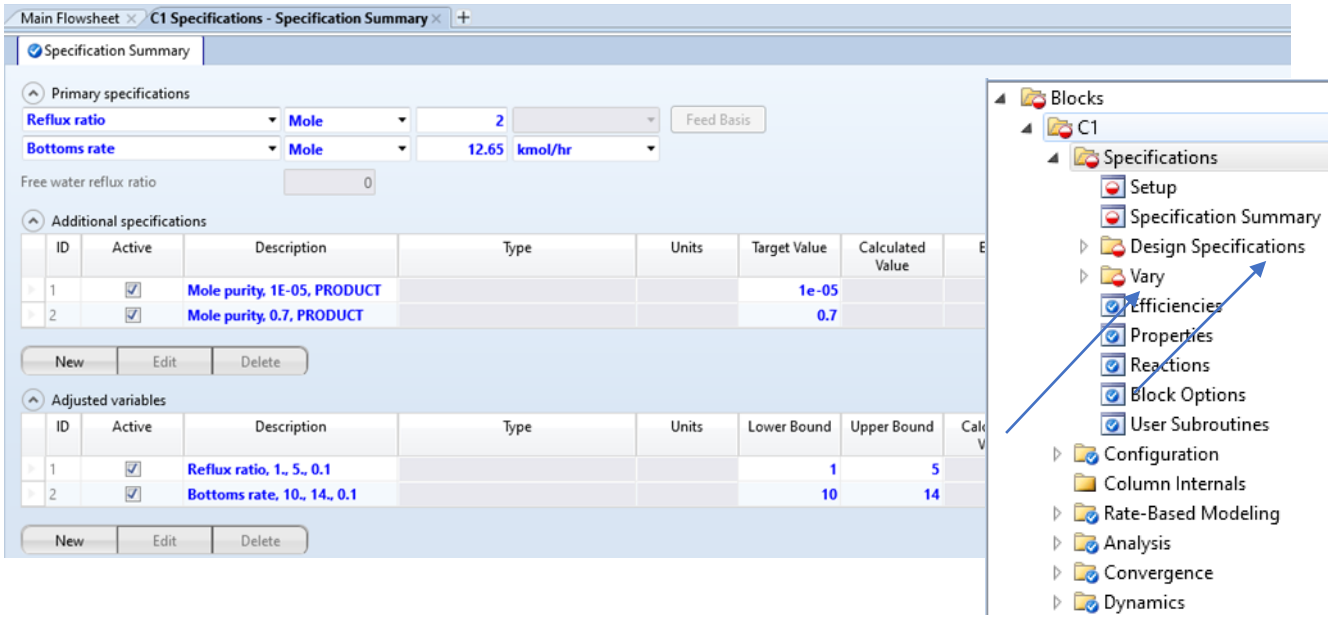


Figure III.21 Defining the column parameters 3 (purity and vary)

In the design specifications, add new |click the **type** field and select **mole purity** |**target value** for specifications |**selected components** then choose the **product stream**.

In the **Vary** tab (adjusted variables), specify the **reflux ratio** and **bottoms rate** as the manipulated Variable (figure III.21); only parameters specified on the Setup page can be defined as Vary.

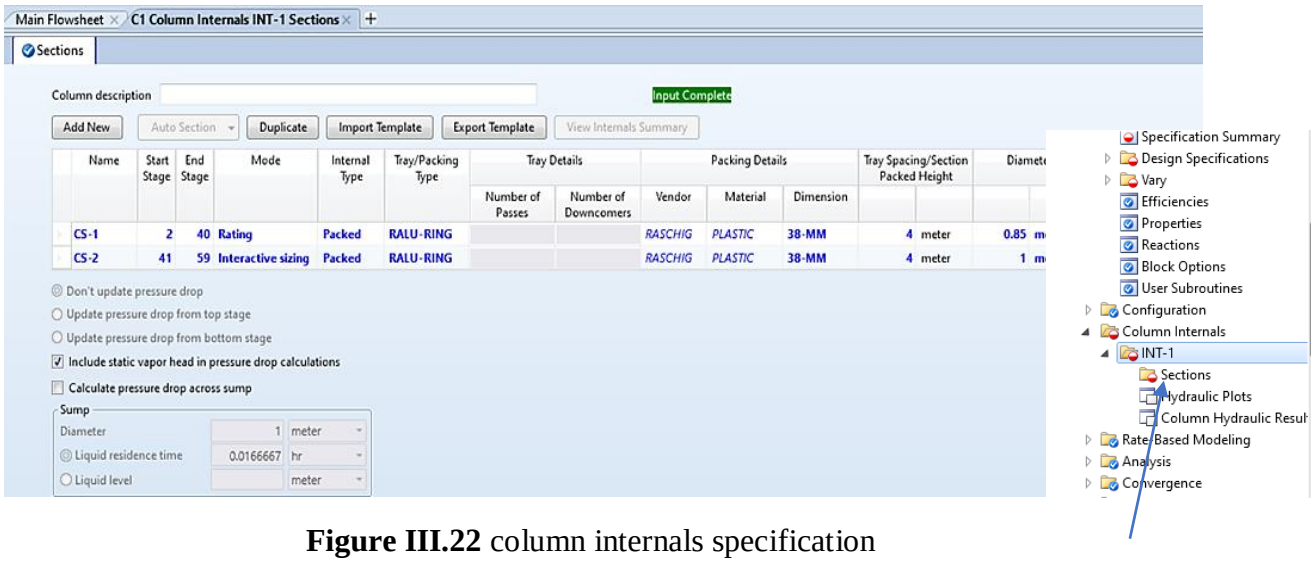


Figure III.22 column internals specification

In the **column internals**, add new **INT-1,** move than to **sections, create** now two sections **(CS-1** and **CS-2)** and we fill them as shown in the figure III.22

Heater (EX2)

In EX2block is used as cooler (Aspen Plus Heater is used when a stream is heated and Cooler when a stream is cooled). Specify the block by the pressure and the duty as shown in figure III.23

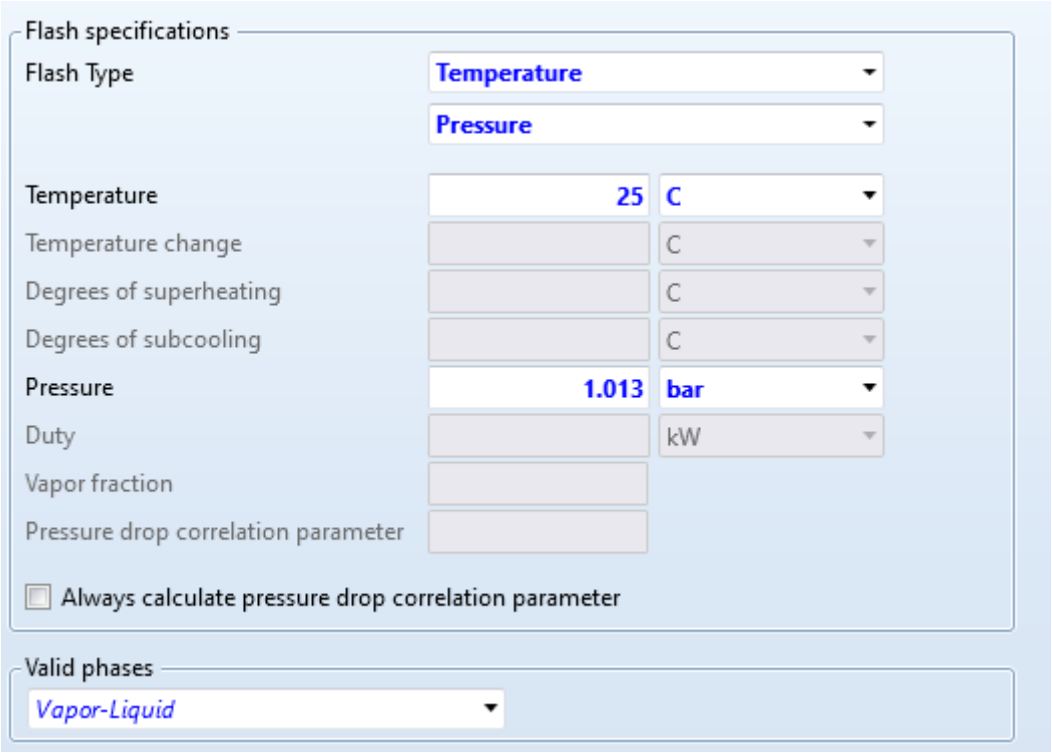


Figure III.23 Heater block specification by temperature and pressure

Decanter

Double-click on the DECANTER to specify the input. It operates at 0.85 KW and 1.013 bar. The Key component (in the second liquid phase) is WATER.

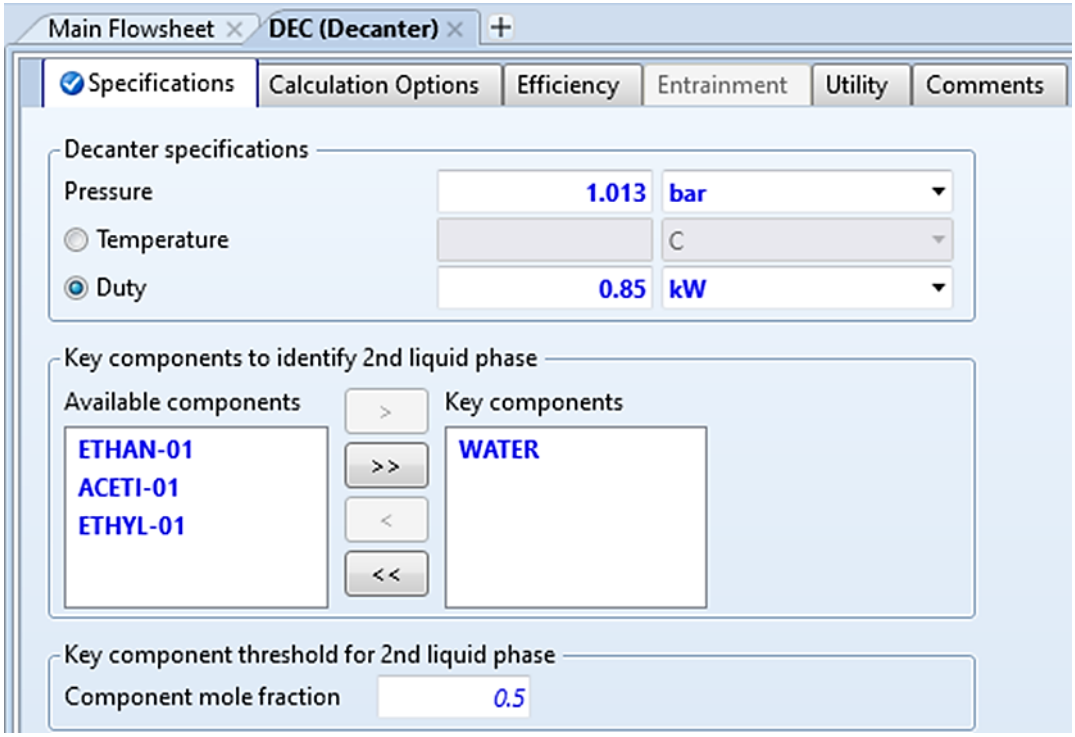


Figure III.24 decanter block specification

III.3.1.2 Flowsheet 2 (Figure III.7)

Reactive distillation column

The main aim in designing an RD column with a stripper (RDS in Figure III.7) is to ensure total conversion of acetic acid in the RD column.

- The RD column has three feeds **AA0**, **ETHO0** (the input shown in the table III.1) and one recycled stream **AZ**
- RD columns specifications are presented in (table III.4), Move to the **Reaction tab** under distillation column Specification and define **the reactive section** of the column and **liquid holdup** as shown in Figure III.25
- The chemical reaction taking place on the reactive stages is selected in step 3

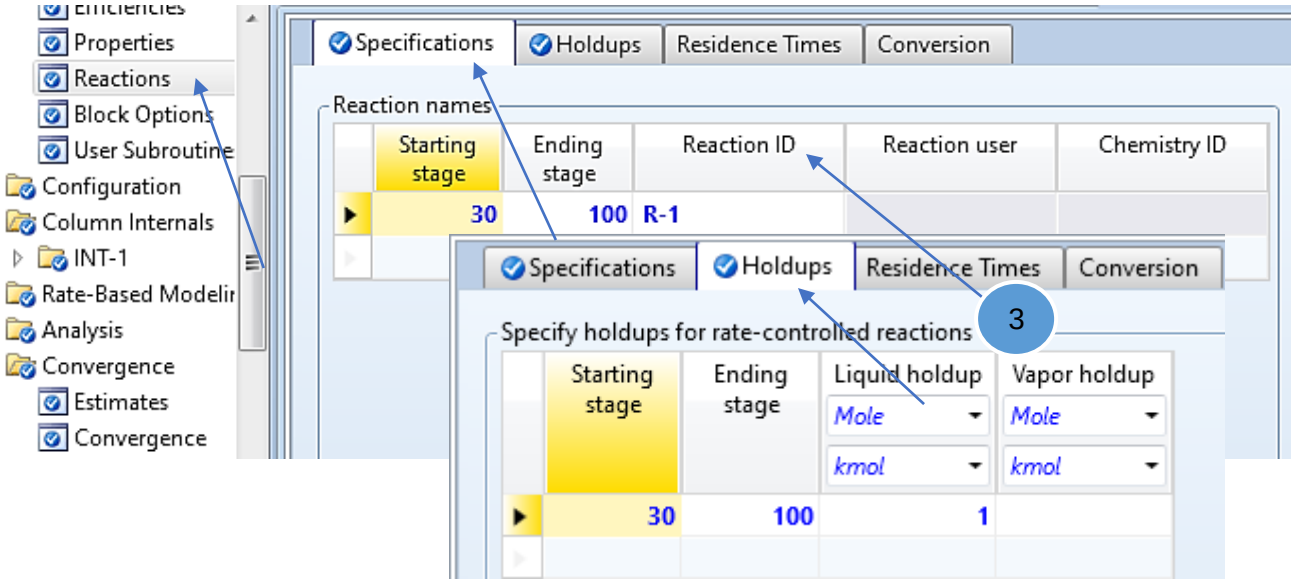


Figure III.25 Reactive stages and holdup specification

In the section **rate-based modelling**, **Sections**, specify the **liquid** and **vapor** phase (Figure III.26).

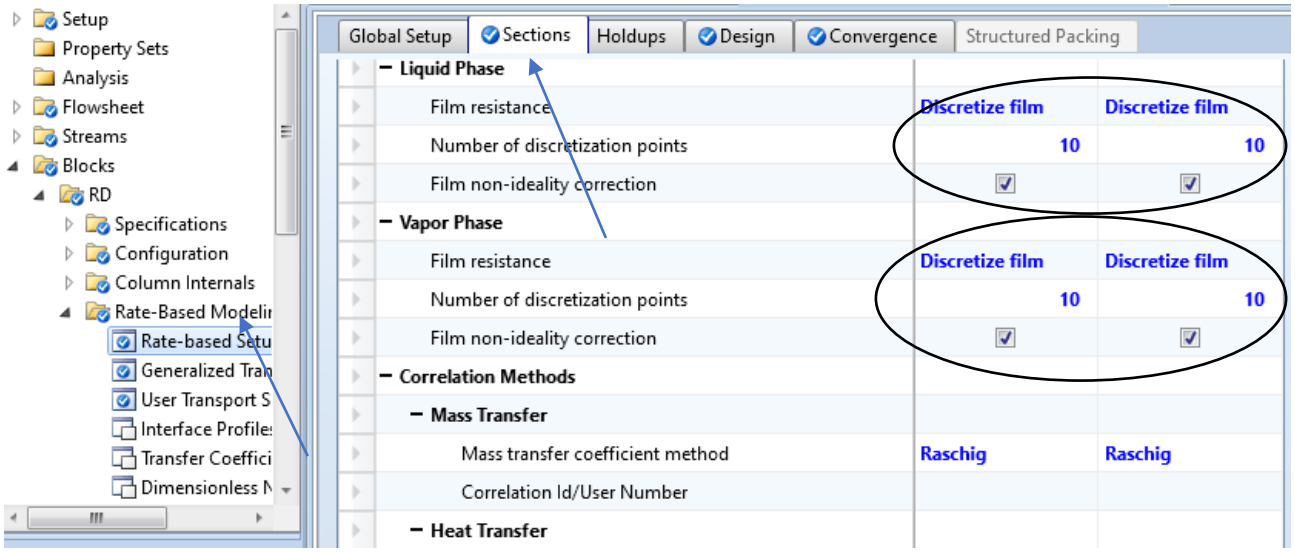


Figure III.26 Rate-based setup specification

Stripper (column 2)

Stripper column parameters are presented in the table III.3.

- **Simulation summary**

A list of the designed column parameters has been displayed as follows:

Table III.1 Input specifications of raw materials

Parameter		Value
AA0		
Molar flow (Kmol/h)		**10**
Molar fraction	Water	**–**
	Acid acetic	**1**
	Ethyl acetate	**–**
	Ethanol	**–**
Temperature (°C)		**25**
Pressure (bar)		**1.013**
ETOH0		
Molar flow (Kmol/h)		**10**
Molar fraction	Water	**–**
	Acid acetic	**–**
	Ethyl acetate	**–**
	Ethanol	**1**
Temperature (°C)		**25**
Pressure (bar)		**1.013**
H2OIN		
Molar flow (Kmol/h)		**0.02**
Molar fraction	Water	**1**
	Acid acetic	**–**
	Ethyl acetate	**–**
	Ethanol	**–**
Temperature (°C)		**25**
Pressure (bar)		**1.013**

Table III.2 Summary of varied parameters of designed columns C1, C2 and C3

Flowsheet 1		**C1**	**C2**	**C3**
number of theoretical stages, total condenser, and reboiler are included		60	60	30
Feed stage position	P_{12}	35	_	_
	AZ	34	_	_
	F_2	_	36	_
	F_{33}	_	_	18
Reflux ratio (R)		2	5	4
Pressure(bar)		1.013	1.013	1.013
condenser		Total	Total	Total
Reboiler		Kettle	Kettle	Kettle
Convergence		Azeotropic	Strongly non-ideal liquid	Strongly non-ideal liquid
Bottoms rate (Kmol/hr)		12.65	_	_
Distillate rate (Kmol/hr)		_	21.21	9.87
Design specification 1		$X_{D1}(AA) = 10^{-5}$	$X_{W21}(EtAc) = 0.999$	$X_{W31}(H2O) = 0.999$
Design specification 2		$X_{W11}(AA) = 0.70$	_	$X_{D31}(EtOH) = 0.56$
Column geometry				
Column section 1		2-40	2-59	2-29
Packing type		RALU-RING 38mm	RALU-RING 25mm	RALU-RING 38mm
Diameter d_1 (m)		0.85	1.20	0.60
Section packed height H_1 (m)		4	7	8
Column section 2		41-59	_	_
Packing type		RALU-RING 38mm	-	_
Diameter d_2 (m)		1	_	_
Section packed height H_2 (m)		4	_	_

Table III.3 Summary of parameters of designed columns RD and C1

Flowsheet 2		**RD**	**C1**
number of theoretical stages, total condenser, and reboiler are included		60	60
Feed stage position	AA0	30	_
	AZ	45	_
	ETOH0	60	_
	D1	_	1
Reaction stages			
Reflux ratio (R)		0.32	-
Pressure(bar)		1.013	1.013
condenser		Total	None
Reboiler		Kettle	Kettle
Convergence		Strongly non-ideal liquid	Strongly non-ideal liquid
Bottoms rate (Kmol/hr)		10	10
Design specification 1		$X_{D1}(AA) = 10^{-5}$	$X_{W21}(EtAc) = 0.999$
Design specification 2		$X_{W11}(H2O) = 0.999$	_
Column geometry			
RD			
section	**Stages**	Packing type	Diameter d_1 (m)	Section packed height H_1 (m)
CS_1	**2_15**	RALU-RING 25mm	1	3.4
CS_2	**16_30**			
CS-3	**31_44**			
CS-4	**45-60**	RALU-RING 15mm	0.75	4
CS-5	**61-85**			
CS-6	**86-99**		0.65	
C1				
CS-1	**1_59**	RALU-RING 25mm	1.3	3

III.3.2 Results

To view the results of the simulation, go to:

Results Summary | **Streams** | **Material sheet**. The result is displayed as follows:

III.3.2.1 flowsheet 1 results

Table III.4 Output streams results 1

Stream Name	Units	F11	F21	R1-1	P1	P2	W11	W12	D11	D12	D13
Temperature	C	39.409732	29.379072	36.8563	39.15336	54.440018	98.63292	48.758156	70.37831	49.310031	25.377083
Pressure	bar	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013
Mole Flows	kmol/hr	22.47472616	19.87	42.34472616	42.34472616	42.34472616	12.47472652	12.47472652	39.91999437	187.7305119	187.7305119
Mole Fractions											
ETHAN-01		1.05808E-05	0.783028888	0.367437063	0.131285439	0.131285439	1.90627E-05	1.90627E-05	0.139436513	0.053741744	0.053741744
ACETI-01		0.833483273	0	0.442376419	0.206224795	0.206224795	0.7	0.7	0.00001	5.66691E-06	5.66691E-06
ETHYL-01		0.166504096	0.130093256	0.149418535	0.38557016	0.38557016	0.299977244	0.299977244	0.566750347	0.186710442	0.186710442
WATER		2.05018E-06	0.086877856	0.040767983	0.276919607	0.276919607	3.69364E-06	3.69364E-06	0.29380314	0.759542147	0.759542147
Mass Flows	kg/hr	1454.640507	975.6280499	2430.268557	2430.268557	2430.268557	854.1149317	854.1149317	2461.129132	6121.874214	6121.874214
Volume Flow	l/min	23.74507514	19.76119386	43.88707377	44.1940417	45.17716305	15.5828945	14.47480795	48.49693512	112.175023	108.6053542

Stream Name	Units	ORG	F2	W21	AZ-	W22	W23	D21-1	D22-1	H2OL	BYPASS-1
Temperature	C	25.54225755	42.17935681	77.22727302	77.22727302	77.22727302	25.60157833	70.373992	35.84455022	25.54225755	25.54225755
Pressure	bar	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013
Mole Flows	kmol/hr	41.59195979	41.59195979	20.07761094	10.0499887	10.02762224	10.02762224	21.51434503	21.51434503	146.1385521	29.22771042
Mole Fractions											
ETHAN-01		0.072818274	0.072818274	0.00072609	0.00072609	0.00072609	0.00072609	0.140096124	0.140096124	0.048312443	0.048312443
ACETI-01		8.30028E-06	8.30028E-06	1.71874E-05	1.71874E-05	1.71874E-05	1.71874E-05	7.65105E-12	7.65105E-12	4.91744E-06	4.91744E-06
ETHYL-01		0.765588319	0.765588319	0.999	0.999	0.999	0.999	0.547763949	0.547763949	0.021958158	0.021958158
WATER		0.161585106	0.161585106	0.000256723	0.000256723	0.000256723	0.000256723	0.312139927	0.312139927	0.929724481	0.929724481
Mass Flows	kg/hr	3066.131692	3066.131692	1767.980632	884.975081	883.0055506	883.0055506	1298.150793	1298.150793	3055.742879	611.1485757
Volume Flow	l/min	56.61188687	57.96069293	35.51404787	17.77680526	17.73724261	16.42254324	25.55863595	24.24654104	52.92071668	10.58414334

Stream Name	Units	F31	F32	F33	D31-1	D32-1	W31-1	W32	H2OREC-1	H2OP1
Temperature	C	25.54225755	30.89758271	73.30378291	72.04555739	35.37887798	99.7015706	40.5152281	40.5152281	40.5152281
Pressure	bar	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013
Mole Flows	kmol/hr	116.9108417	116.9108417	116.9108417	9.896098565	9.896098565	107.0147434	107.0147434	97.04846038	9.966283057
Mole Fractions										
ETHAN-01		0.048312443	0.048312443	0.048312443	0.56	0.56	0.00099457	0.00099457	0.00099457	0.00099457
ACETI-01		4.91744E-06	4.91744E-06	4.91744E-06	2.41023E-10	2.41023E-10	5.36805E-06	5.36805E-06	5.36805E-06	5.36805E-06
ETHYL-01		0.021958158	0.021958158	0.021958158	0.259409301	0.259409301	6.21518E-08	6.21518E-08	6.21518E-08	6.21518E-08
WATER		0.929724481	0.929724481	0.929724481	0.180590699	0.180590699	0.999	0.999	0.999	0.999
Mass Flows	kg/hr	2444.594303	2444.594303	2444.594303	513.6832533	513.6832533	1930.911046	1930.911046	1751.0853	179.8257457
Volume Flow	l/min	42.33657334	42.58582401	997.0678103	10.74353881	10.14272558	35.05835181	32.89686073	29.83317609	3.06368464

✓ **Compositions profile**

Column C1

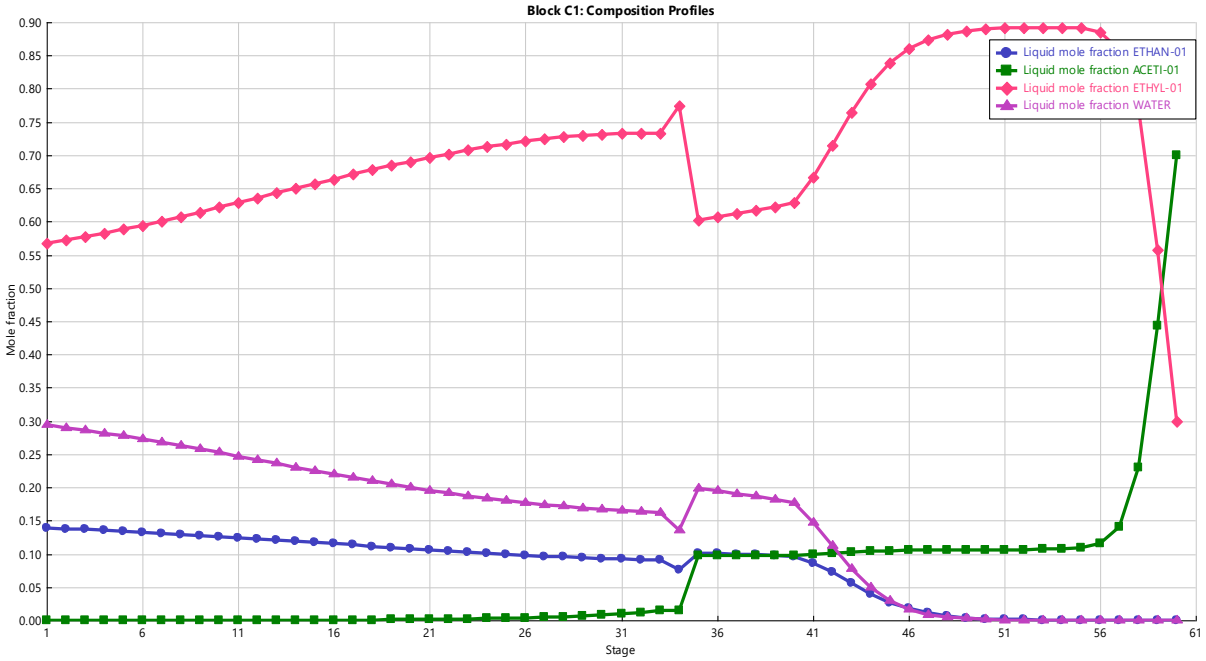


Figure III.27 Profile curve of the compositions of the compounds "AA, EtOH, EtAC, Water" in the liquid phase

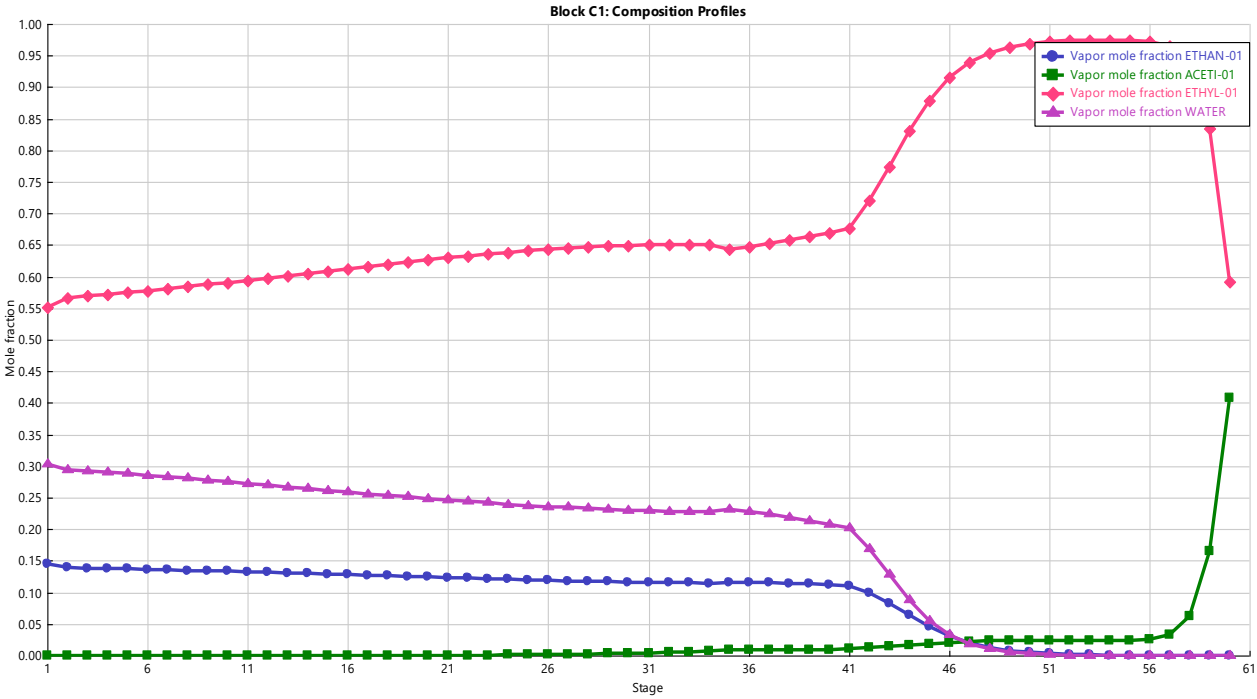


Figure III.28 Profile curve of the compositions of the compounds "AA, EtOH, EtAC, Water" in the vapor phase

Column C2

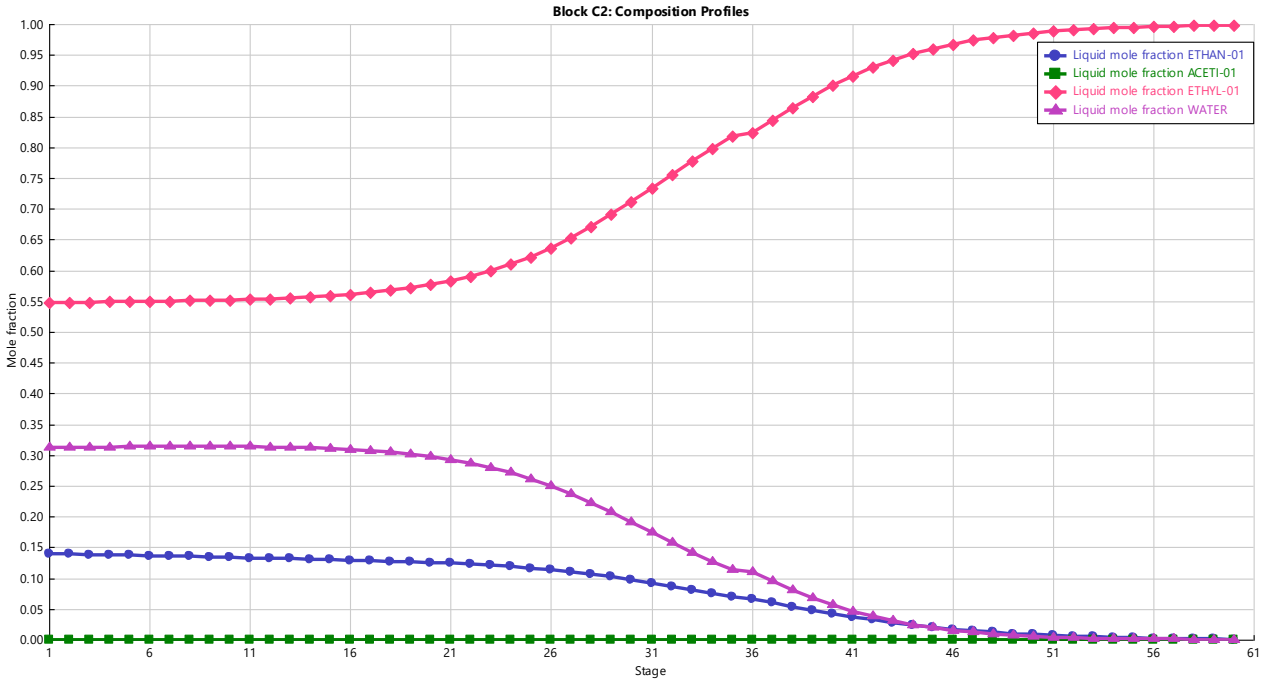


Figure III.29 Profile curve of the compositions of the compounds "AA, EtOH, EtAC, Water" in the liquid phase (C2)

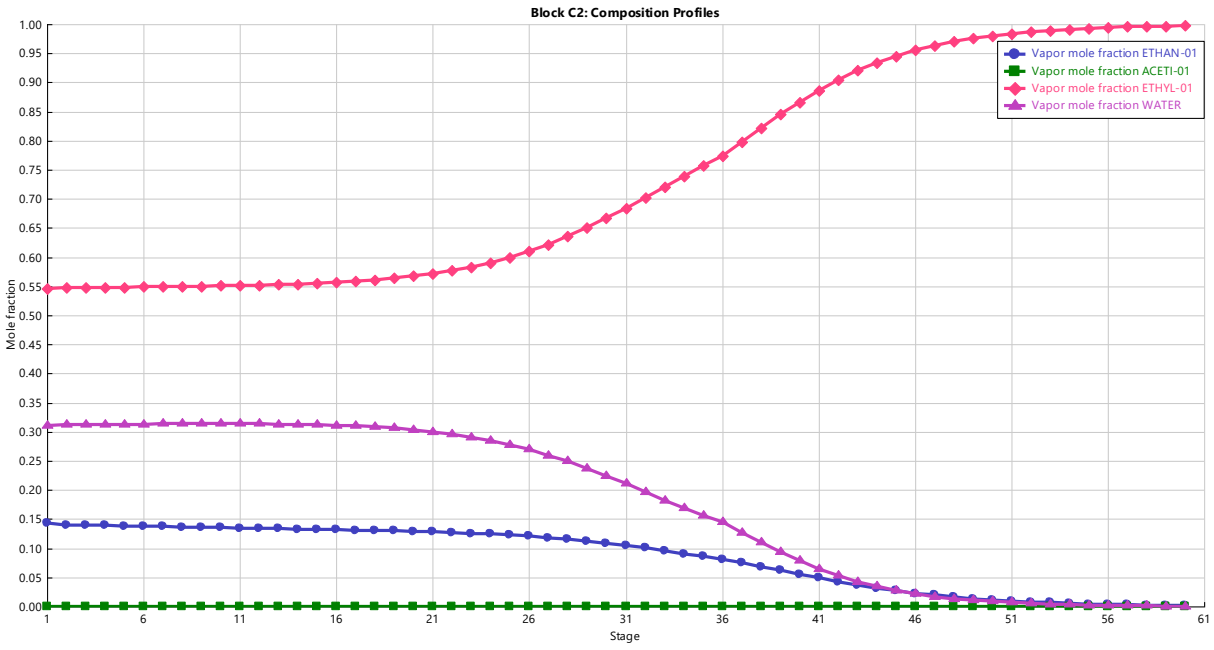


Figure III.30 Profile curve of the compositions of the compounds "AA, EtOH, EtAC, Water" in the vapor phase (C2)

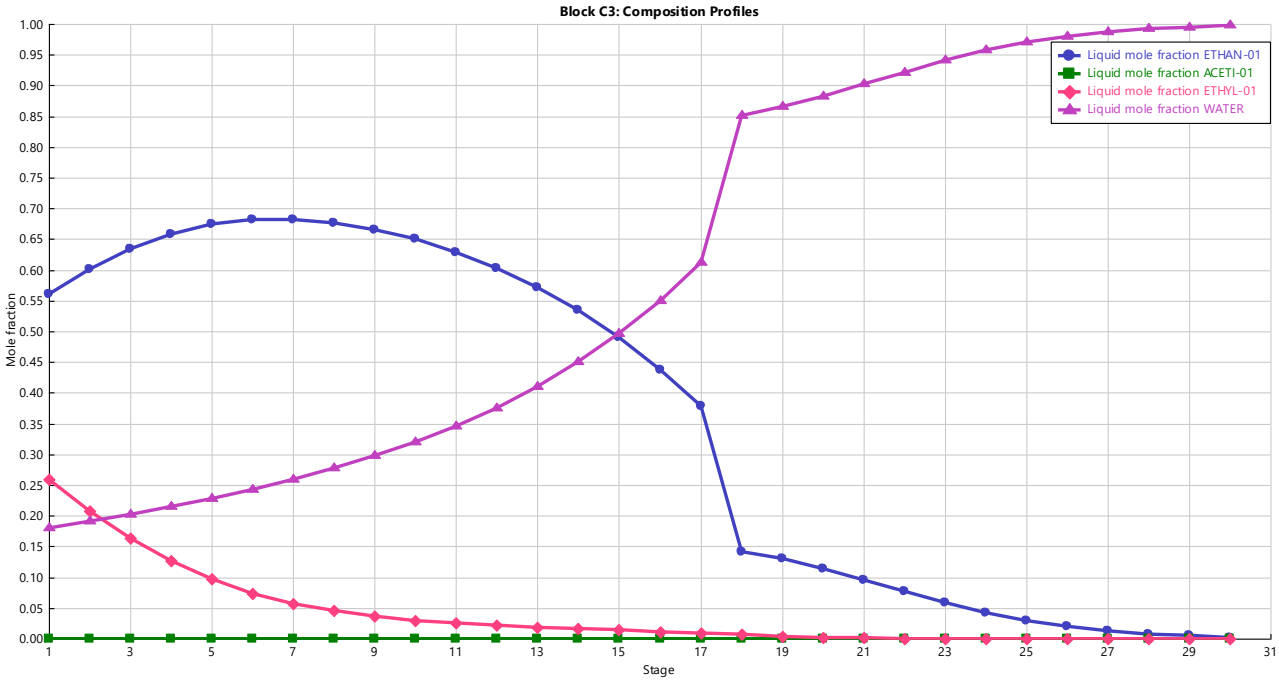


Figure III.31 Profile curve of the compositions of the compounds "AA, EtOH, EtAC, Water" in the liquid phase (C3)

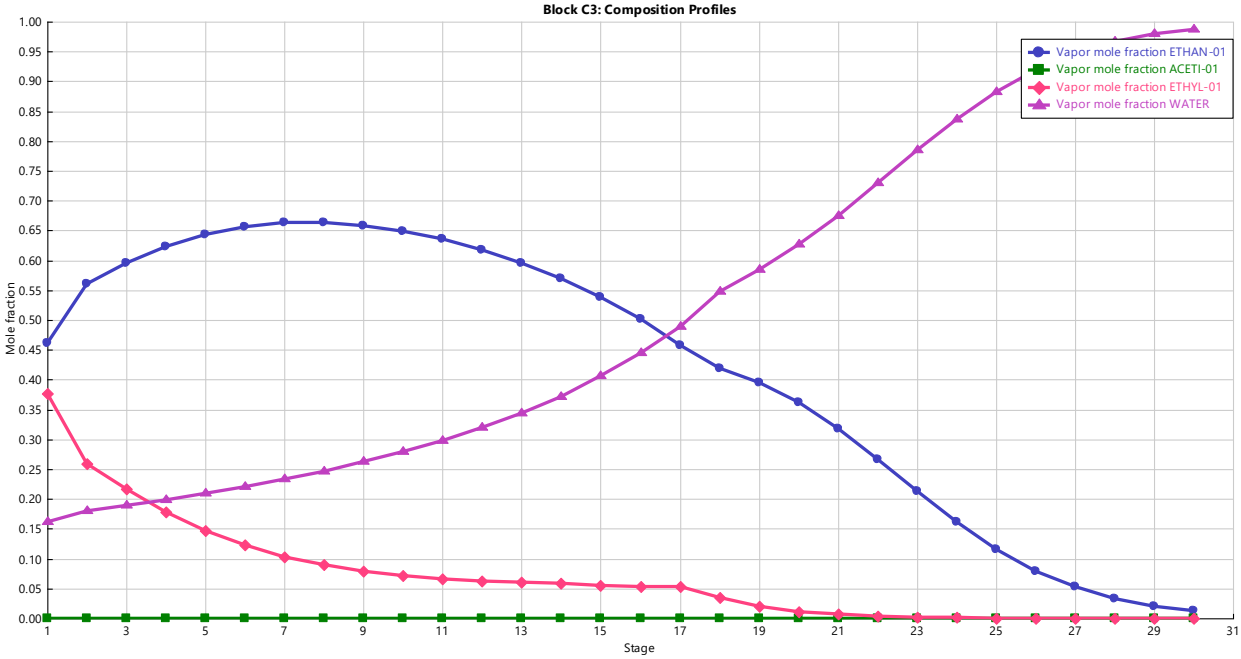


Figure III.32 Profile curve of the compositions of the compounds "AA, EtOH, EtAC, Water" in the vapor phase (C3)

III.3.2.2 flowsheet 2 results

Table III.5 Out-put streams results 2

Stream Name	Units	AZ1	D1	W11	W21	W12	W22
Temperature	C	70.40234188	70.40226636	99.7027779	77.2365258	25	25
Pressure	bar	1.013	1.013	1.013	1.013	1.013	1.013
Mole Flows	kmol/hr	150.9480392	160.8723656	10.0756736	10.1196896	10.0756736	10.1196896
Mole Fractions							
ETHAN-01		0.132447677	0.124224891	0.00099141	0.00064766	0.00099141	0.00064766
ACETI-01		4.69374E-07	0.00001	8.5568E-06	0.00015197	8.5568E-06	0.00015197
ETHYL-01		0.561471311	0.588984744	3.0819E-08	0.999	3.0819E-08	0.999
WATER		0.306080543	0.286780365	0.999	0.00020035	0.999	0.00020035
Mass Flows	kg/hr	9220.670514	10100.08655	181.799961	891.147839	181.799961	891.147839
Volume Flow	l/min	68599.11532	198.7988747	3.30082881	17.9006468	3.30082881	17.9006468

Reactive distillation

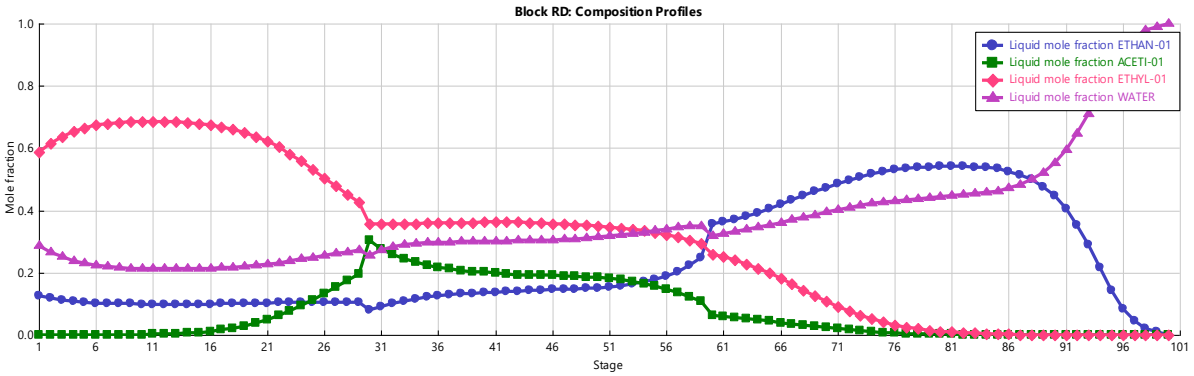


Figure III.33 Profile curve of the compositions of the compounds "AA, EtOH, EtAC, Water" in the liquid phase (RD)

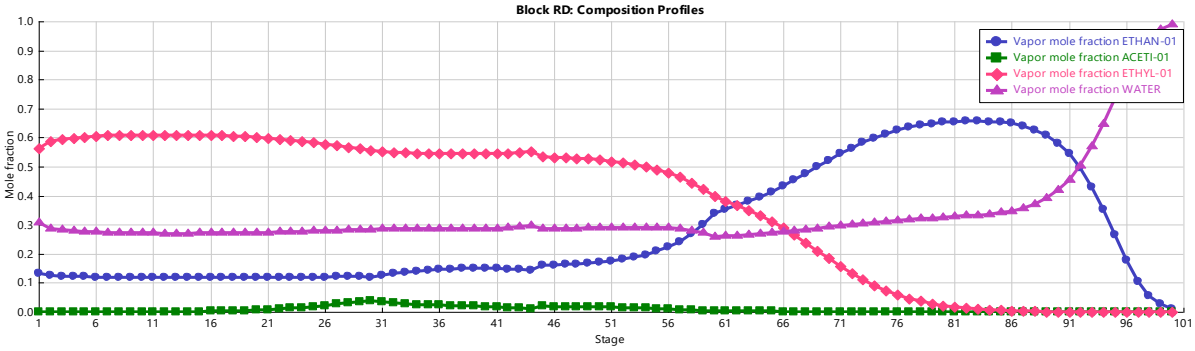


Figure III.34 Profile curve of the compositions of the compounds "AA, EtOH, EtAC, Water" in the vapor phase (RD)

Stripper

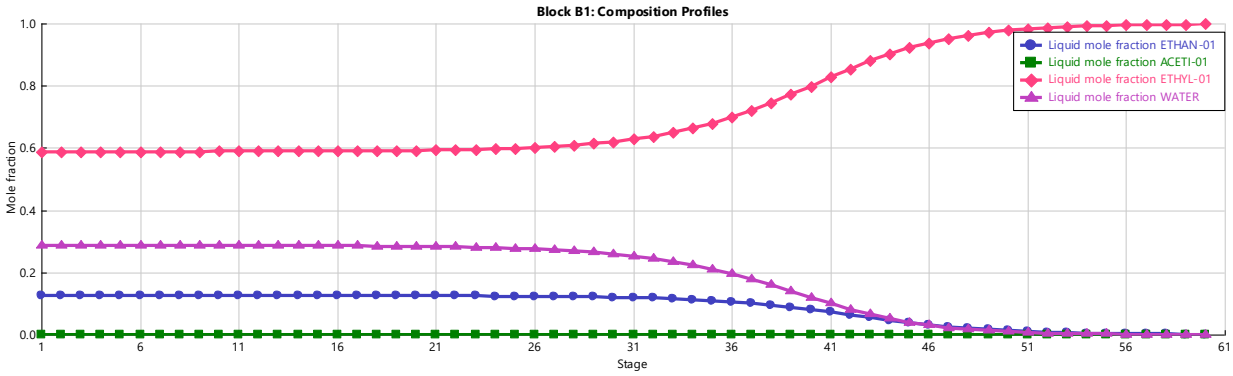


Figure III.35 Profile curve of the compositions of the compounds "AA, EtOH, EtAC, Water" in the liquid phase (stripper)

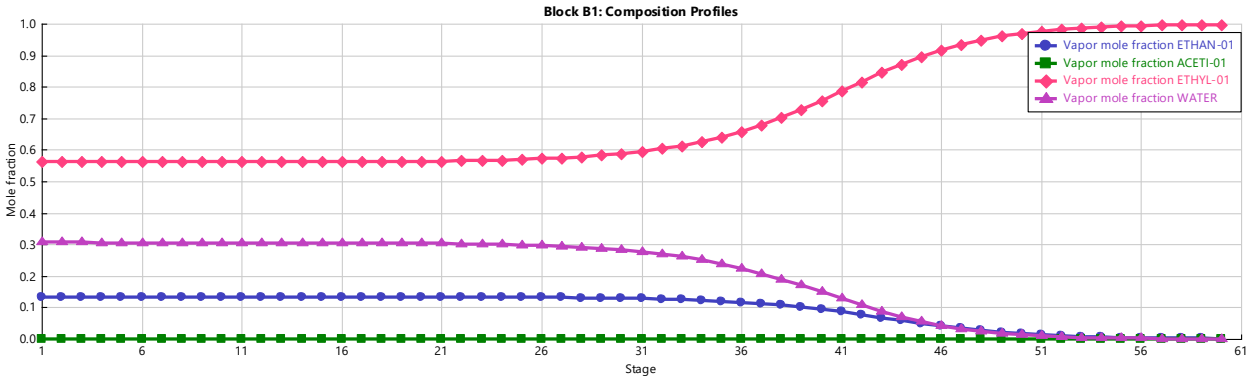


Figure III.36 Profile curve of the compositions of the compounds "AA, EtOH, EtAC, Water" in the vapor phase (stripper)

In summary, Table III.4 and III.5 shows a full results representation of the outputs given in terms of temperature, pressure, the molar fraction of the four compounds, molar flow rate, mass flow rate, and the volume flow rate for flowsheets 1 and 2, respectively. While Figures III.27 to III.32 and Figures III.33 to III.36 show the composition profile of the four compounds in the liquid and vapor phase of all models for flowsheets 1 and 2, respectively.

III.3.3 Discussion

III.3.3.1 Energy requirements

Energy consumption of individual equipment units was calculated based on the simulation results.

Reboiler duty (QW) and condenser duty (QC) of each column as well as the cooling duty of heat exchangers such as the heat integration were calculated and evaluated. Overall energy consumption (OEC) was calculated as a sum of required heating or cooling duties respectively; heat integration was excluded. To better compare individual case studies, OEC was normalized to the specific energy consumption (SEC, Equation (III.5)), which is related to the production of one ton of pure EtAc. Summary results of the energy requirements are listed in TableIII.6.

$$Specific\ energy\ consumption\ (SEC) = \frac{energy\ consumption\ (KW)}{mass\ of\ product\ (t)} \quad \textbf{III.5}$$

The conventional process set-up (Figure III.5) has three distillation columns in which both the reboiler and condenser are included. Thus, a highly energy-intensive process is expected. Distillation column for water regeneration C3 consumes almost 550 kW of heat, which represents 18.4% of the total heat duty required in whole the conventional path (FigureIII.5). However, the column for separation of unreacted acetic acid C1 and that for EtAc separation, C2 are even more energy-consuming (Figure III.5). Overall, 81.6% of the total required heat duty is consumed in these two columns. All three column condensers consume 2851 kW of cooling duty, which corresponds to 94.6% of the total cooling duty required. EX2, EX6, and EX7 heat exchangers consume less than 164 kW of cooling capacity to reach the required stream temperature. Therefore, from the energetic point of view, the C1 and C2 columns are the key equipment units, Table III.6. This is mainly due to large recycle flows (TableIII.4) and energy-intensive separation of the azeotropic mixture. The process is even more energy-intensive if the C1column (Figure III.5) is not operated as an azeotropic distillation column with an SEC of 3408 kW of heating duty and 3427 kW of cooling duty. Overall, five main equipment units along with seven heat exchangers are used (distillation columns, reboilers, and condensers are included as a part of the main column equipment), Table III. 6.

RD column with a stripper (FigureIII.7) shows significant process integration and intensification. The process philosophy has been enhanced as several pieces of equipment were removed or integrated into the main two columns (Figure III.7). The RD column reboiler duty (556 kW) is 2.31 times lower compared to that of the C1 stripper (Figure III.7, 1286 kW). Also, vapor flow in the stripper is almost three times higher than that in the second section of the RD column. Energy demands of both columns (Figure III.7) are quite high compared to the conventional path (FigureIII.5)**(Branislav et al., 2020)**

Table III.6. Energy requirements and the number of the equipment for designed ethyl acetate production pathways.

	Conventional Process set-up(Figure III.5)		**RD Column with a Stripper (RDS) (Figure III.7)**	
Equipment	**QC[KW]**	**QW[KW]**	**QC[KW]**	**QW[KW]**
CSTR a/RD	-	-	1816.43	556.42
C1	1135.23	1181.19	-	1286.57
C2	1212.97	1267.94	-	-
C3	502.97	549.35	-	-
DEC	0.85	-	-	-
EX1	25.01	-		-
EX2	133.75	-		-
EX3	31.04	-	-	-
EX4	13.73	-	-	-
EX5	131.31	-	-	-
EX6	3.10	-	-	-
EX7	25.85	-	-	-
OEC	3014.72	2998.48	1857.69	1842.99
SEC [kW t^{-1}EtAc]	3426.87	3408.41	2110.30	2093.59
Number of main equipment units	5		2	
Number of heat exchangers	7		2	

III.3.3.2 Economy Aspects

An economic evaluation of the presented case studies was preformed based on optimized simulations of the process models. Prices of commodities were selected according to market research Prices of both reactants and products and were chosen as a long-term average. Electricity, cooling water, and steam are considered to be energy utilities and their costs were obtained from the Aspen Plus database. These utility costs correspond with actual prices. Equipment cost was calculated using the Aspen Process Economic Analyzer Software Individual mapping and sizing of each equipment unit was applied, which is important as the case studies simulations were calculated using rate-based modeling with known equipment dimensions. Also, special RD column configuration has been introduced in the RDS and RDAR case studies (Figures III.7 andIII.8) multiple diameter columns, stripper column (without condenser, etc.).

To complete the economic analysis, total capital costs, total annual costs, total raw material cost, and product sales were calculated. A return rate of 20% per year and an annual work fund of 340 days were assumed. The capital costs are almost 10 mil. $ in the conventional path (FigureIII.5). Process integration and intensification can decrease total capital cost by 11% (RD column with a separation unit); 35% (RDS); or even 57% (RDAR). Total raw materials cost is similar (5.45 mil. $) except for RDAS (FigureIII.8) as the price of ethylene oxide has to be included. However, the highest product sales are in the RDAS set-up (16.4 mil. $ compared to 10.3 mil. $). Finally, a simple payback period was calculated: two years of project feasibility and preparation (projecting, building, licensing.) is included. The conventional process (FigureIII.5) has a payback period of over 10 years because of the highest capital and utilities cost. The RD column with a separation unit (FigureIII.6) becomes profitable 1.5 years earlier than the conventional process (FigureIII.5). The payback period is almost halved in the case of RDS (FigureIII.7), and only one-third in the case of RDAR (FigureIII.8) compared to the conventional process (FigureIII.5). Finally, total production cost (TPC) was evaluated, and the results are presented in Table III.7. From the TPC, it is clear that the most promising concepts are RDS (FigureIII.7) and RDAR (Figure III.8) from the economic point of view.(Branislav et al., 2020)

Table III.7. Total annual costs of individual case studies.

	Conventional Path (FigureIII.5)	**RD Column with A Separation Unit (FigureIII.6)**	**RDS (FigureIII.7**	**RDAR (Figure III.8)**
Total capital cost [mil. $]	9.91	8.84	6.43	4.24
Total installed cost [mil. $]	3.74	3.33	2.43	1.60
Total annual cost [mil. $ year^{-1}]	9.15	9.04	8.65	13.72
Total raw materials cost [mil. $ year^{-1}]	5.46	5.46	5.46	9.42
Total product sales [mil. $ year^{-1}]	10.27	10.27	10.27	16.40
Total utilities cost [mil. $ year^{-1}]	0.89	0.81	0.54	0.11
Pay-back period [year]	10.86	9.19	5.97	3.58
Total production cost [$ t^{-1}]	1273.91	1266.14	1231.32	1018.09

III.3.3.3 Safety Aspects

Individual risk is a risk assessment methodology that allows for numerical estimates of the level of risk associated with a certain activity or a series of activities to be estimated and then assessed.

To identify the list of incidents, a semi-automated approach was used. For each type of unit, a predefined set of representative incidents was prepared. The final choice of incidents is very difficult and requires judgment from an analyst; therefore, three main factors were taken into consideration: the size of the release, the state of releasing material (liquid, vapor), and whether the release is instantaneous or continuous. For distillation and reactive distillation columns, the incident list contained liquid leaks (full bore rupture and hole equivalent to 20% of diameter), vapor leaks, and complete rupture of the column.

- For heat exchangers, small leaks and full rupture were used.
- For all pipelines in the simulation, the only full rupture was considered.
- For the list of representative incidents, a number of different incident outcomes are possible.

To define the incident outcomes, three different generic event trees were used:

- continuous liquid release,
- continuous gaseous release,
- instantaneous release.

Probabilities were adjusted based on a recommendation from Consequence modeling that was performed using standard (and widely used) software system ALOHA (The Areal Location of Hazardous Atmospheres) provided by the US Environmental Protection Agency. Three representative weather conditions (wind speed 1, 2, and 4 m s^{-1} and atmospheric stability F, D, and C) were taken into account for all case studies. The wind was assumed to be uniformly distributed in all directions. Probabilities of individual representative weather conditions were adopted from information provided by the Slovak Hydrometeorological Institute. Results of individual risk estimation for the presented case studies are depicted. To compare all investigated case studies, individual risk is presented in the form of risk profiles as a function of distance. Based on the risk profiles, it is possible to conclude that, from the safety point of view, the conventional process set-up

(FigureIII.5) and reactive distillation column with a separation unit (FigureIII.6) were the worst alternatives. Both profiles are practically identical. Close to the center of the production unit, the conventional process set-up (Figure III.5) shows the highest individual risk from all presented case studies. If we focused only on the boundary of acceptable risk 10^{-5} year $^{-1}$for existing plants (TableIII.8), the least suitable set-up is the distillation column with a separation unit (FigureIII.6) due to the high number of equipment units but mainly due to the recirculation of large quantities of material and high flow rates through the columns. Based on the presented analysis, the best alternative, from the safety analysis point of view, is the reactive distillation column with an auxiliary reaction. This result can be a little bit surprising because in this case study, ethylene oxide (extremely flammable, explosive, and toxic gas) is added as a feedstock. On the other hand, the main advantage of this set-up (FigureIII.8) compared with the previous three, is the minimal number of operation units and no material recycles. Main reactions and separation are performed only in one unit (reactive distillation column and vapor and liquid flow through the column are lower than in all previous case studies. For this reason, the volume of hazardous materials in the column, reboiler, and other auxiliary equipment are also lower compared to the previous case studies. The concentration of the extremely flammable ethylene oxide is very low in the column and its mole fraction in the whole system is below 10%; except for 10 trays close to its feed location. From the comparison of individual risk of fatality estimation (Table III.8), it is clear that minimizing the number of equipment and internal recycles leads to a reduction of the level of risk. In the presented study, only the production and separation part of the case studies were evaluated. If required, the safety study can be extended to include storage facilities for each case study.(Branislav et al., 2020)

Table III.8 Distance from the center for individual case studies up to which individual risk of fatality is lower than 10^{-5} resp. 10^{-4} $year^{-1}$.

	Individual Risk 10^{-5}year	Individual Risk 10^{-4} $Year^{-1}$
	Distance from the Center [m]	Distance from the Center [m]
Conventional path (FigureIII.5)	122	95
RD column with separation unit (FigureIII.6)	166	59
RDS (Figure III.7)	122	43
RDAR (Figure III.8)	62	28

III.4 CONCLUSION

A simulation of ethyl acetate synthesis processes was carried out using the Aspen Plus V11 process simulator. We compared two cases: conventional process_ uses separate units for reaction and separation, such as a reactor and a distillation column_ With reactive distillation column with a stripper. In conclusion, the conversion was achieved, selectivity and purity of the products, also, energy consumption was reduced (by minimizing the number of equipment), and the total capital cost was reduced from 9.91 t [mil. $] to 6.43 [mil. $], as well as environmental impact.

GENERAL CONCLUSION

GENERAL CONCLUSION

A comprehensive study related to the intensification and simulation of the ethyl acetate manufacturing process has been highlighted in this thesis. A promising potential for process optimization and improvement available in the literature review has provided valuable perceptions into the importance of process intensification for enhancing productivity, energy efficiency, and environmental sustainability. For the process of ethyl acetate production, various intensification techniques, including reactive distillation hybrid separation processes and integrated reaction separation systems, can be identified as effective approaches for streamlining the production process. Furthermore, the examination of simulation software has demonstrated its pivotal role in optimizing the ethyl acetate manufacturing process.

Process simulation allows engineers and researchers to model and analyze the production process under different operating conditions, evaluate the impact of various parameters, and identify opportunities for improvement simulation, enables the exploration of alternative process configurations, catalysts, and operating conditions ultimately leading to a more efficient and sustainable ethyl acetate production process.

The combination of process intensification and simulation techniques not only enhances the overall efficiency of ethyl acetate production, but also contributes to reducing its environmental footprint by implementing intensified processes, and utilizing simulation software. The number of process steps and equipment can be minimized while maximizing yield and selectivity. This leads to Improved process economics, reduced energy consumption and minimized waste generation.

The study highlighted in this thesis shows that the integration and intensification of the convention process set-up was achieved by combining reaction and separation together via the reactive distillation process (CSTR, EX1, and C1 columns “flowsheet 1” are put together into an RD column “flowsheet 2”). Then, for better improvement, the large flow of the recycled stream to the decanter was also dealt with, which led to more reduction of equipment number. The use of those two ideas not only helps with reducing the number of equipment and plant size, but it also helps with the improvement of process efficiency,

and, consequently, a better process economy can be reached. Thus, the process scheme in Figure III.7 ends with 3 equipment and 5 heat exchangers less than the main process scheme of Figure III.5.and the total capital cost was reduced from 9.91 t [mil. $] to 6.43 [mil. $], as well as environmental impact.

In summary, this study emphasizes the significance of process intensification and simulation in the ethyl acetate manufacturing process it underscores the importance of conducting a thorough literature review to understand the current state of knowledge and highlights the value of simulation software in optimizing process parameters by harnessing these approaches the production of ethyl acetate can be made more efficient economically viable and environmentally sustainable fostering the development of a greener and more sustainable chemical industry.

To this end, as perspectives we propose Reactive Distillation Column with a Separation Unit figure III.6and Reactive Distillation Column with an Auxiliary Reaction figure III.8 as future work to be tested and evaluated.

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