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Validación Experimental de Modelo de Columna de Destilación
Reactiva con Pared Dividida

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**Experimental Model Validation of an Integrated Reaction and
Separation Process**

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CON PARED DIVIDIDA**

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Trabajo de Tesis, presentado en cumplimiento parcial de los requisitos para la obtención del título de Ingeniero Civil Químico y grado de Magíster en Ciencias de la Ingeniería Química de la Universidad Técnica Federico Santa María.

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I declare that I have developed and written the enclosed Master Thesis completely by myself, and have not used sources or means without declaration in the text. Any thoughts from others or literal quotations are clearly marked.

Valparaíso, May 11th, 2017

Nicolás Antonio Ramos Ojeda

Preface

First, I would like to thank to Mr. Prof. Fieg for giving me the opportunity to write my thesis at the Institute of Process-and Plant Design. Besides, I thank to Mr. Prof. Liese for the acceptance to co-examine this work.

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Resumen

La integración de procesos representa uno de los mayores atractivos dentro de la ingeniería química. Entre los beneficios de la integración de procesos se encuentran la reducción de equipos y tamaño de las plantas, cómo también mejoras en términos de eficiencia. Dentro de estos procesos de integración, se encuentra la integración de operaciones de reacción y destilación, siendo los principales aparatos la “Columna de Destilación Reactiva” y “Columna de Destilación Reactiva con Pared Dividida” (RDWC), los cuales integran reacción y destilación en una sola unidad. Sin embargo, parte de los desafíos a resolver que implican la integración de procesos es remover las incertidumbres en términos de modelación, operación, control y diseño.

En vista de lo anterior, la presente tesis busca reducir las interrogantes asociadas al modelamiento de la RDWC, particularmente en estado estacionario. La hipótesis a ser validada considera que un modelo basado en etapas de equilibrio es suficiente para predecir el comportamiento de la RDWC en estado estacionario. Para dar respuesta a la hipótesis planteada, resultados experimentales que puedan ser comparados con las predicciones del modelo son necesarios para confirmar si este es adecuado. Considerando lo anterior, distintos experimentos deben ser ejecutados para evaluar la calidad el modelo bajo distintas condiciones de operación, e.g. reacción, separación, distribución de los compuestos y composición de los productos.

El modelo de simulación empleado fue desarrollado en Aspen Custom Modeller® por el Instituto de Diseño de Procesos y Plantas de la Universidad Técnica de Hamburgo (TUHH). Un total de 8 experimentos fueron ejecutados en la planta piloto perteneciente a la misma Universidad, equivalentes a 80 horas de operación de la columna. La comparación de los resultados de la simulación con los resultados generados experimentalmente permitió dar respuesta a la hipótesis planteada.

En particular, los perfiles de temperatura, concentración y composiciones de los productos predichos por el modelo fueron comparados y analizados con los datos experimentales a fin de constatar las diferencias. Los resultados muestran una correcta predicción de los perfiles de temperatura y composición de los productos. En cada experimento, el error medio cuadrático para las diferencias de temperatura entre simulación y experimento fueron inferiores a los 2 °C. La máxima variación de los flujos molares ascendió a un 2.4 mol %. Por otro lado, las máximas diferencias en la composición de los productos alcanzaron valores de 1.6, 4 y 10 w % para el destilado, fondo y corriente lateral respectivamente. Considerando lo anterior, un modelo basado

en etapas de equilibrio es suficiente para predecir adecuadamente el comportamiento de una RDWC en estado estacionario. No obstante, también fue posible concluir que la discretización de la zona reactiva del modelo dista del óptimo, lo cual impide el correcto cálculo de la conversión de los reactantes especialmente bajo fuertes variaciones en el perfil de concentración. Además, las diferencias entre experimento y simulación son fuertemente afectadas por pequeños cambios en la energía administrada por el rehervidor, lo cual puede implicar una falta de ajuste en la distribución del vapor y el líquido a lo largo de los lados de la pared que divide la columna. Adicionalmente, el trabajo desarrollado permitió mejorar la determinación del coeficiente de transferencia de calor en el submodelo de pérdidas al medioambiente. Los resultados del análisis realizado confirmaron que un valor cercano a $1.5 \text{ W/m}^2/\text{K}$ puede ser adoptado.

Resumiendo, la siguiente tesis aporta significativamente en la interrogante referida al modelamiento de una RDWC. Gracias al trabajo desarrollado, se puede concluir que un modelo de etapas de equilibrio es suficiente para modelar una RDWC en estado estacionario. No obstante, si se busca mejorar la calidad del modelo las siguientes recomendaciones pueden ser seguidas: Primero, una mayor resolución en la discretización de la zona reactiva del modelo de la RDWC. Asimismo, se puede complementar la precisión en esta zona mediante la formulación de un modelo que considere la transferencia de materia entre la fase líquida y gaseosa. En términos experimentales, un mayor número de zonas de muestreo en la zona reactiva mejorarían el detalle de los análisis comparativos entre simulación y experimento. Adicionalmente, sistemas de reacción diferentes podrían ser probados para ampliar el espectro de validez del modelo empleado.

Objectives

General Objective

To validate a reactive dividing wall column model based on an equilibrium-stage model approach

Specific Objectives

- To evaluate the model under different operation conditions by means of planned experiments that affect relevant aspects of the reaction and separation modelling.
- To explain the agreements and disagreements between the simulation and experiments and identify the weaknesses and strengths of the model.
- To formulate alternatives to improve the current model.
- To provide understanding about RDWC Operation

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List of Symbols

Latin Characters

A	Heat transfer area	$[\text{m}^2]$
A	Reactant A	
B	Reactant B	
C	Product C	
D	Product D	
E	Impurity or by-product E	
E_A	Activation Energy	$[\text{kJ mol}^{-1}]$
F	F-Factor	$[\text{Pa}^{0.5}]$
k	Heat transfer coefficient	$[\text{Kw m}^{-2} \text{K}^{-1}]$
k_0	Reaction constant	$[\text{mol s}^{-1}]$
L	Liquid stream	
m	Mass	$[\text{kg}]$
N	Molar Flow	$[\text{mol h}^{-1}]$
n	Mol	$[\text{mol}]$
P	Heat power	$[\text{kW}]$
p	Pressure	$[\text{mbar}]$
Q	Heat	$[\text{kW}]$
R	Ideal gas constant	$[\text{J mol}^{-1} \text{K}^{-1}]$
r	Reaction rate	$[\text{mol s}^{-1}]$
S	Section (column)	
s	Side	
T	Temperature	$[\text{°C}]$
t	Time	$[\text{h}]$
u	Linear speed	$[\text{m s}^{-1}]$
V	Vapor stream	

w	Mass fraction	[kg kg ⁻¹]
x	Liquid molar fraction	[mol mol ⁻¹]
y	Gas molar fraction	[mol mol ⁻¹]
z	Height	[m]

Greek Characters

α	Activity coefficient	[mol mol ⁻¹]
μ	Chemical potential	[J mol ⁻¹]
ρ	Density	[kg/m ³]
χ	Reactant conversion	[mol/mol]

Subscript

cat	Catalyst
g	Gas phase
l	Liquid phase
sim	Simulation

Abbreviations

ACM	Aspen Custom Modeler®
Az	Azeotrope
BuAc	Butyl Acetate
BuOH	Butanol
BVM	Boundary Value Method
CD	Component Distributor
COM	Computer Object Model
DLL	Dynamic Library Link
DW	Dividing wall

DWC	Dividing Wall Column
eRDWC	Enzymatic catalyst Reactive Dividing Wall Column
FID	Flame Ionization Detector
GC	Gas Chromatograph
HeAc	Hexyl Acetate
HeOH	Hexanol
HU	Liquid Holdup
INSERT	Integrating Separation and Reaction Technologies
lo	low
LS	Liquid Split
MC	Main Column
mid	middle
MV	Manipulated Variable
P&ID	Process and Instrumentation Diagram
PAT	Process and Plant Design
PF	Prefractionator
PH	Pseudo Homogeneous
PI	Proportional Integrative (Control)
PV	Process Variable
RD	Reactive Distillation
RDC	Reactive Distillation Column
RDWC	Reactive Dividing Wall Column
TUHH	Hamburg University of Technology
UNIQUAC	Universal Quasi Chemical
VLE	Vapor Liquid Equilibrium

1 Introduction

Nowadays, the industrial sector has to face up with the high competition pressure and the environment care, which implies new challenges in the efficiency of the production processes. With this in mind, the application of sustainable processes technologies is an important target especially in industrially developed countries [1]. In this context, the new developments in the chemical industry aim the reduction of the energy consumption and number of equipment compared to established processes.

As part of the solutions, new alternatives focused on process integration have been developed, whose main purpose is to link different unit operations in one apparatus, taking advantage of the synergies of some operations [2]. In this way, considerably shrinking in size of the process plants and efficiency increase have been accomplished [3], which is traduced in great investment and operational cost reduction. Some well-known examples in this area are the reactive distillation (RD) that integrates reaction and separation in one apparatus, and the dividing wall column (DWC), which consists of a single distillation column able to separate mixtures of at least three components into high purity products. These processes have already been implemented in industrial scale showing positive results [1, 4]. The combination of both, the reactive dividing wall column (RDWC) promises further reductions in investment costs and space requirements. Additionally, new research applies enzyme catalyst in reactive distillation processes to achieve more selective reaction routes. However, so far, there are no industrial applications of the RDWC and scarce information about its operating. Within this framework, the Institute of Process and Plant Design (PAT) of the Hamburg University of Technology (TUHH) has carried out experimental research of enzymatic catalyst RDWC (eRDWC) to remove uncertainties concerning modelling and operation. Nevertheless, the successful model validations are within a delimited range. Therefore, the available investigations cannot guarantee to fit correctly to other operating conditions.

In view of the above, the present thesis work pursues to reduce the uncertainties related to the RDWC modelling, particularly in steady state. The hypothesis called into question is the suitability of a RDWC model based on equilibrium stages is a proper approach to predict the RDWC steady state behavior. In order to answer this question, a set of different experiments have been planned and performed to compare these results with the values predicted by the RDWC model and therefore to assess the quality of the employed model.

Based on the foregoing, the main goals are: first, to verify the suitability of a model based on an Equilibrium-Stage approach into a Reactive Dividing Wall Column, second, to evaluate the model under different operation conditions by means of planned experiments that affect relevant aspects of the reaction and separation modelling, third, to explain the agreements and disagreements between the simulation and experiments and identify the weaknesses and strengths of the model and finally, the last objective is to formulate alternatives to improve the current model.

The contents of this work are presented as follows: in chapter 2 the theoretical framework of the relevant integrated reaction and separation processes are introduced. In addition, the state of the art of the enzyme catalyzed reactive distillation and RDWC are presented to contextualize the investigative focus of this work. Chapter 3 describes the basics of the applied simulation model. Subsequently the methods related to the sampling process are explained. Finally, the last part of this section is dedicated to the general strategy utilized in the sensitive analyses. In Chapter 4, the RDWC pilot plant and experimental results employed for the model validation are presented. The following chapter shows a comprehensive study on the quality of the simulation model. Finally, the last chapter contains the conclusions and further research suggestions based on the findings of this work.

2 Theoretical Framework

In this chapter, the theoretical basics of the integrated reaction and separation processes relevant to this thesis are introduced. Thereby, the main principles of the reactive distillation, the dividing wall column and reactive dividing wall column are presented. Furthermore, the current works about enzyme catalyzed reactive distillation are briefly described. Moreover, in order to visualize the research challenges of the RDWC, the state of the art of the RDWC is exposed. In this subsection, a short summary of the available investigations with their results and conclusions is depicted.

2.1 Integrated Reaction and Separation Processes

The process integration links different unit operations in one apparatus, taking advantage of the synergy of some operations [2]. The pertinent examples for this work are the reactive distillation, the dividing wall column and the combination of both, the reactive dividing wall column. In this section, these processes and apparatus are described.

2.1.1 Reactive Distillation

The reactive distillation integrates in one single apparatus a reaction and a distillation process. Therefore, separation and reaction take place in the same shell. This can result in significant reductions in both energy and equipment costs in systems that have an adequate match of these processes [5].

The RD is of advantage only if the reactant and product have a favorable boiling point sequence. In cases, where the products are lighter and/or heavier than the reactants [5], the formed products are simultaneously separated from the non-converted reactants shifting the reaction equilibrium to the products. In this way, under ideal conditions there is no need of further apparatus to separate the reaction products. Moreover, in order to achieve feasible reaction rates in the RD, the most reactions are catalyzed. There are three different options thereof, homogeneous, heterogeneous, and auto catalysis [6]. KAIBEL describes the different catalyst

types [6]. The mostly applied is the heterogeneous catalyst, since it allows fixing of the reactive zone to a specific section of the reactive distillation column. Furthermore, the most investigated reaction type using reactive distillation in the literature is described by Eq. 2-1 [5]. Besides, the four components follow the next relative volatility sequence, C, A, B, D. This means, that the products are the lightest and heaviest boiling components, while the reactants are the intermediate ones.



Figure 2-1 depicts a reactive distillation column based on the reaction system from Eq. 2-1 catalyzed by a heterogeneous catalyst, which is fixed in the middle of the column [5]. The two feed inlet arrangement allows a longer contact time between the reactants, since the component A flows up and reacts with the flowing down component B. The reaction yields the components C and D. These components are removed from the reactive section (the light product C is quickly removed in the vapor phase from the reaction zone and subsequently flows up the column, while product D is quickly removed in the liquid phase and flows thereafter down the column). Component C is separated from the other components in the rectification zone, while component D is separated in the stripping section. Thereby the distillate contains mostly product C. Likewise, the bottom stream consists mainly of product D.

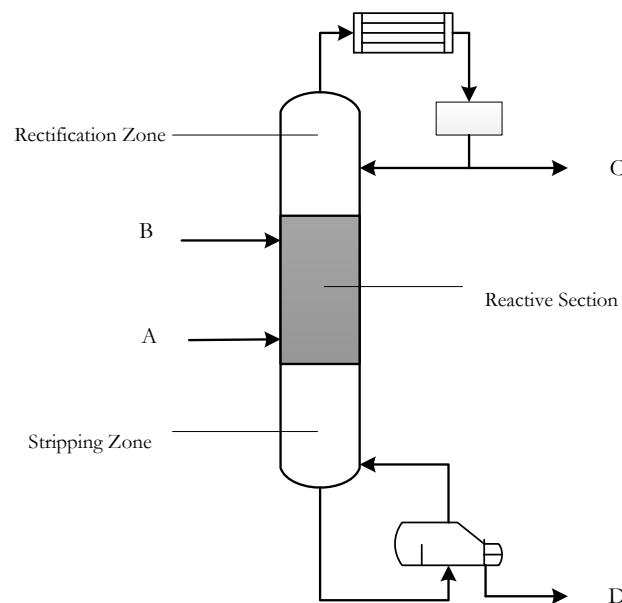


Figure 2-1 Reactive distillation column diagram

Taking into account the principle of LE CHATELIER, product removal from the reactive section shifts the reaction equilibrium and promotes the formation of products. TAYLOR AND KRISHNA

summarize the advantages and disadvantages of the reactive distillation: Among the most important benefits are the increasing of the reactant conversion and the significant capital savings against the conventional alternatives[4]. On the other hand, among the drawbacks of the RD are the process condition mismatch and the volatility constraints [4].

2.1.2 Dividing Wall Column

The dividing wall column (DWC) is a second example of process integration. In the most investigated cases, the DWC has a symmetric structure, which consists of a single shell column with a partition wall that physically divides the middle section of the column into a feed section, acting as a prefractionator, and a side draw section which allows concentration of the medium boiling component to a very high purity [1]. Figure 2-2 exhibits a symmetrical DWC which considers a three component mixture (A, B, C), where A is the lightest, C the heaviest and B the medium boiling component.

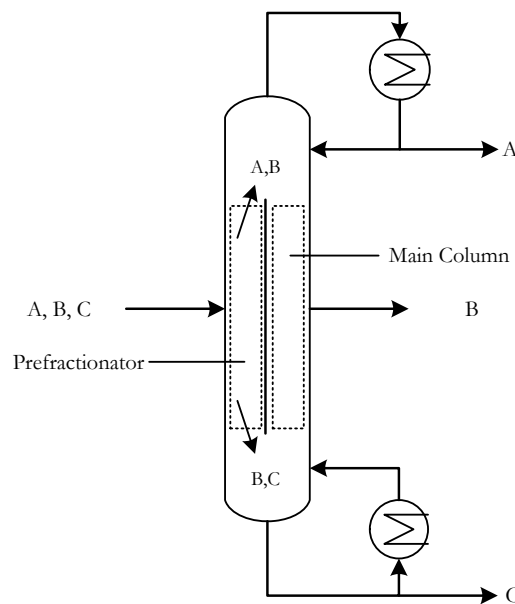


Figure 2-2 Dividing wall column diagram

As Figure 2-2 shows in an ideal case, the feed enters the column and the medium boiling component (B) leaves the feed section on both sides without heavy components at the upper end of the vertical partition and light components at the lower end. Additionally, in the side draw section or main column, the medium boiling component is separated from the light and heavy components. In this way, B can be obtained as a third pure stream in the side discharge. This characteristic highlights the DWC apart of the conventional distillation columns, since it reduces the number of required condenser, reboiler and also distillation columns shells. The DWC review

from DEJANOVIĆ ET AL [1] shows capital savings of up to 30 % compared to conventional distillation column arrangements. In terms of energy consumption, the DWC allows a reduction between 20 and 30 % of energy requirements [7]. The reason for this is the avoidance of remixing of internal streams, which in two columns in series arrangements exhibits concentration peaks of middle boiling components either above or below the feed. This mixing as well as remixing of streams with different compositions that occurs at feed point(s) and along column, which is inevitably accompanied by entropy of mixing formation, is an intrinsic source of thermodynamic inefficiency of the separation process occurring in a multicomponent distillation column[1].

2.1.3 Reactive Dividing Wall Column

A further process integration step is the reactive dividing wall column, which results out of the integration of the DWC and the RD column. As SCHRÖDER [8] explains[8], the extending of the CABD reaction system by a middle boiling component E is reasonable for the RDWC. In view of this the reaction system CAEBD is obtained. The example presented by SCHRÖDER shows clear the advantages of the RDWC over other process alternatives, this example is illustrated by Figure 2-3, which exhibits a RDWC with a vertical partition in the middle of the column and a fixed reactive section in the prefractionator.

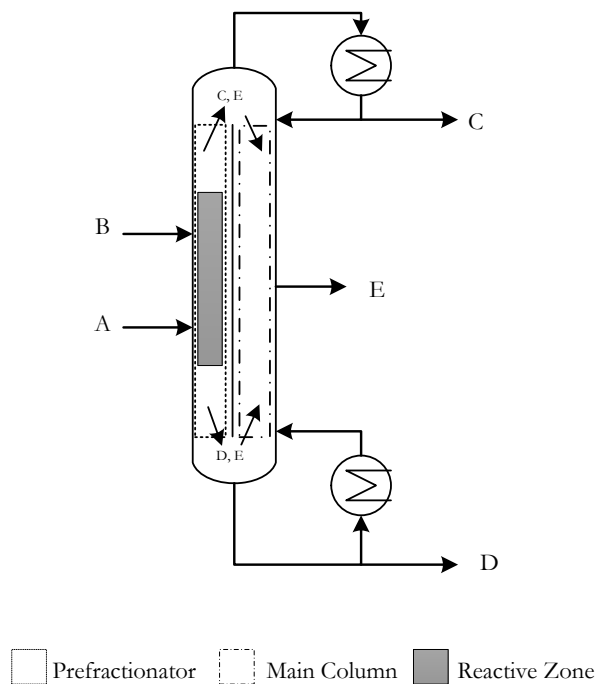


Figure 2-3 Reactive dividing wall diagram

Additionally, the reaction system features an optimal order of boiling components [8]. The products C and D remain the absolute light-and heavy-boiling components and can be withdrawn from the reactive zone without removing the reactants. Thereby, the conversion can be shifted again towards full conversion [8]. Moreover, as illustrated in Figure 2-3 the middle boiling component E can be split in the prefractionator and removed through the side stream. Component E can represent an inert in the feed, a product from a side reaction, or a product resulting from a feed stock mixture with reactants. As indicates SCHRÖDER [8], all of these cases describe typical reaction system in the process industry and are, therefore, relevant for industrial process. Figure 2-4 shows other possible scenarios available in the literature, in which the RDWC could be an advantageous alternative for such processes.

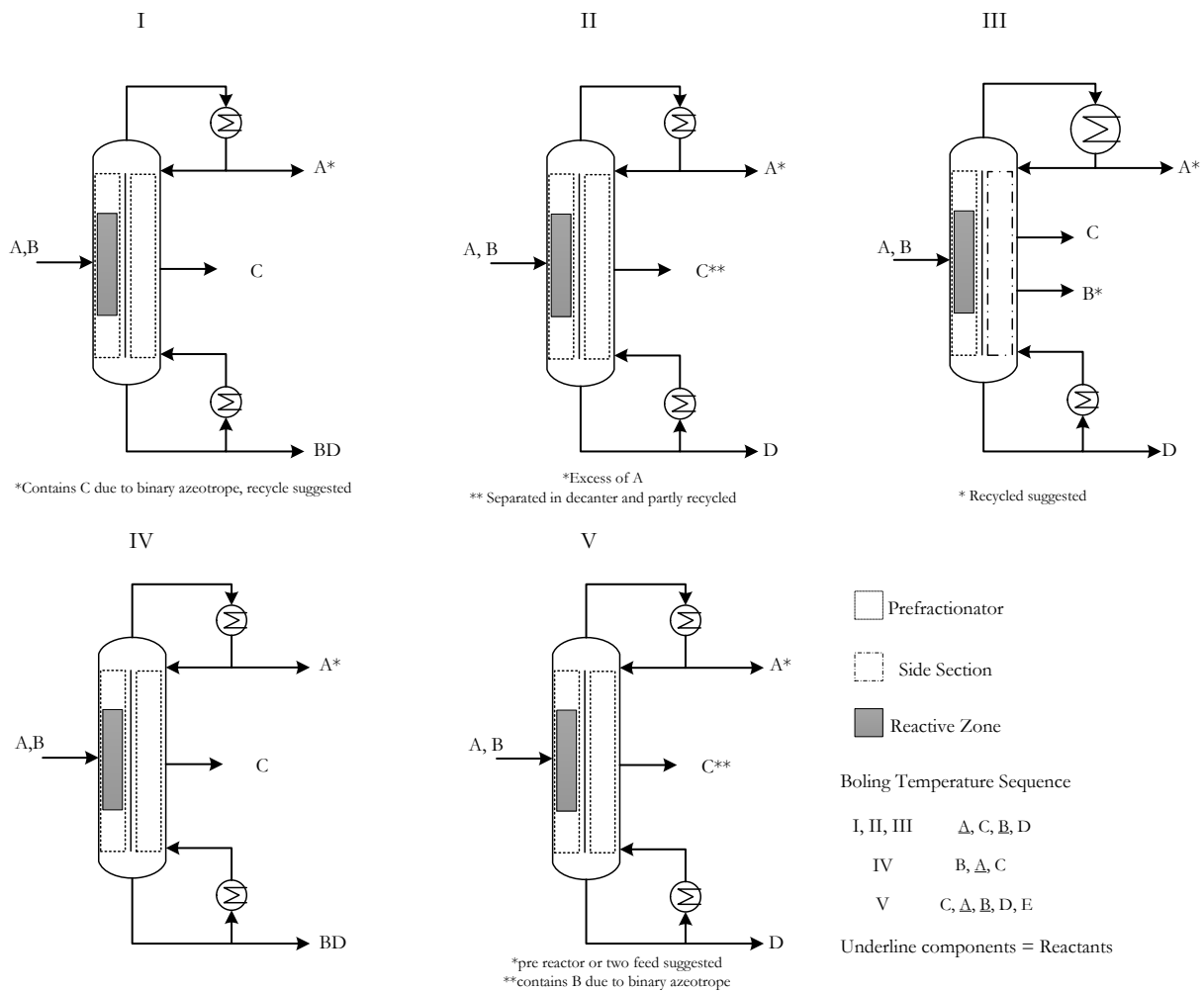


Figure 2-4 Interesting cases for the reactive dividing wall column, based on SCHRÖDER [8]

Considering this, the RDWC emerges as an option to reduce investment and operation costs, as well as space utilization, due to the less required apparatus. Nevertheless, the high degree of integration involves different challenges in the RDWC. First, the performance of the reaction and distillation in the same shell implies a coupling of the temperature and pressure operation. Consequently, these must be adequate to fulfill the requirements of both processes. This is the same constraint presented by the RD. Secondly; the extra complexity given by this integration is the correct distribution of the components along the two sides of column, prefractionator and main column.

2.2 Enzymatic Reactive Distillation

The combination of reactive distillation and enzymatic catalyzed reaction creates synergies enabling the efficient production of totally new products [9]. The employment of enzymes in reactive distillation columns enables new or more selective reaction routes. However, the RD catalyzed by enzymes must match the operation conditions for the reaction, separation and enzyme properties. This is especially important as the temperature operation affects the thermal stability with the consequently deactivation of the enzymes. This sub-chapter reviews the published researches about this topic.

The first works leading to enzymatic catalyzed RD consisted of a fixed bed reactor with immobilized lipase that was connected to the bottom of the distillation column. The conversion of esterification or transesterification reactions was enhanced by the product removal through azeotropic distillation [10].

The first full reactive distillation setup was carried out by PAIVA ET AL [11]. In the experimental work, they perform a batch operation of the alcoholysis between butanol and ethyl butanoate, catalyzed by an immobilized lipase in a liquid-vapor system, where chemical reaction and physical separation are simultaneously carried out. The results of this research show the conversion increase through the continual removal of the products and the effectiveness of the enzyme as a catalyst [11]. However, there is no comparison with a conventional batch reaction.

Further investigations in this topic were performed by HEILS ET AL [12]. Once again, a batch reaction process is studied, wherein the transesterification of the ethylbutyrate with butanol takes place. Nonetheless, the focus lays on an alternative method of enzyme immobilization. In their method, the enzymes are coated with a silica-gel matrix that was applied onto commercially available Montz A3-500 packings. Concerning to the results, the experimental setup allows a

stable process with a conversion of 98 %. Besides, the loss of silica coating was approximately 2 w % per run [12].

The first continuous reactive distillation column study was also carried out by HEILS ET AL [13]. In this research, a feasibility study for an enzymatic reaction in a continuously operated reactive distillation column is presented. The reaction system is the transesterification of ethyl butyrate with n-butanol in the presence of candida antarctica lipase B (CALB). The process was tested through a simulation model that showed feasible results, which were experimentally validated in the publication from WIERSCHEM [9].

Considering the enzymatic reactive dividing wall column, the works from HARDING and KEUSER are available [14, 15]. Those are framed in the current project of the PAT-Institute of the Hamburg University of Technology. In their work, different experimental runs in a pilot reactive dividing wall column plant with a heterogeneous catalyst enzyme (Novozym 435) were performed to validate a RDWC simulation model. A relevant result of these works is the avoidance of side product formation, due to the employment of the enzyme catalyst.

2.3 State of the Art of the RDWC

In the following section, the relevant state of the art for this work is presented. First, a general overview is depicted to visualize the pending challenges in the RDWC. Moreover, a summary of the literature related to experimental works about the RDWC is displayed.

2.3.1 General Overview

Although the first mentioning of the RDWC can be found in 1984 [16], so far no industrial applications have been reported [8, 16]. Until now, the majority of the investigations on the RDWC deal with simulation studies related with design methods, such as the works from DANIEL ET AL [17], SUN AND BI [18], NGUYEN [19], KANG AND LEE [20], MÜLLER [2, 21] and SCHRÖDER [8]. DANIEL ET AL [17] propose a shortcut design method for the RDWC based on the decomposition of the RDWC into several conventional columns combined with a graphically-based boundary value method (BVM). Likewise, SUN AND BI [18] propose an alternative shortcut method design, which extends the minimum vapor flow method from HALVORSEN [22] to the reactive dividing wall column, for the examples of methyl tert-butyl ether, ethyl tert-butyl ether, and dimethyl ether synthesis. Furthermore, MÜLLER [2, 21] decomposes the RDWC into several columns to apply a rigorous rate-based simulation model. NGUYEN [19]

bases on the work from MÜLLER to present a design method which decomposes the RDWC into a RD unit and two conventional distillation columns. KANG AND LEE [20] present a graphical approach limited to three components. Moreover, SCHRÖDER [8] published a semi-shortcut method to predict the minimum vapor demand of the RDWC and thereby its energy-saving potential. Additionally, other publications deal with the theoretical design and control of the RDWC. These are the works from WANG [23], AN ET AL [24] and DAI ET AL [25].

On the other hand, there are relatively few sources regarding experimental research works on the RDWC. The first forays in the experimental operation of the RDWC were performed in the framework of the INSERT (Integrating Separation and Reaction Technologies) project. The experimental part was performed in a mini plant laboratory at BASF in Ludwigshafen and in a pilot plant at Sulzer Chemtech Winterthur [26], the RDWC designs are presented in Figure 2-5. Moreover, other investigations have been carried out by the PAT-Institute of the TUHH, whose goals are to reduce the uncertainties concerning modelling and operating RDWCs.

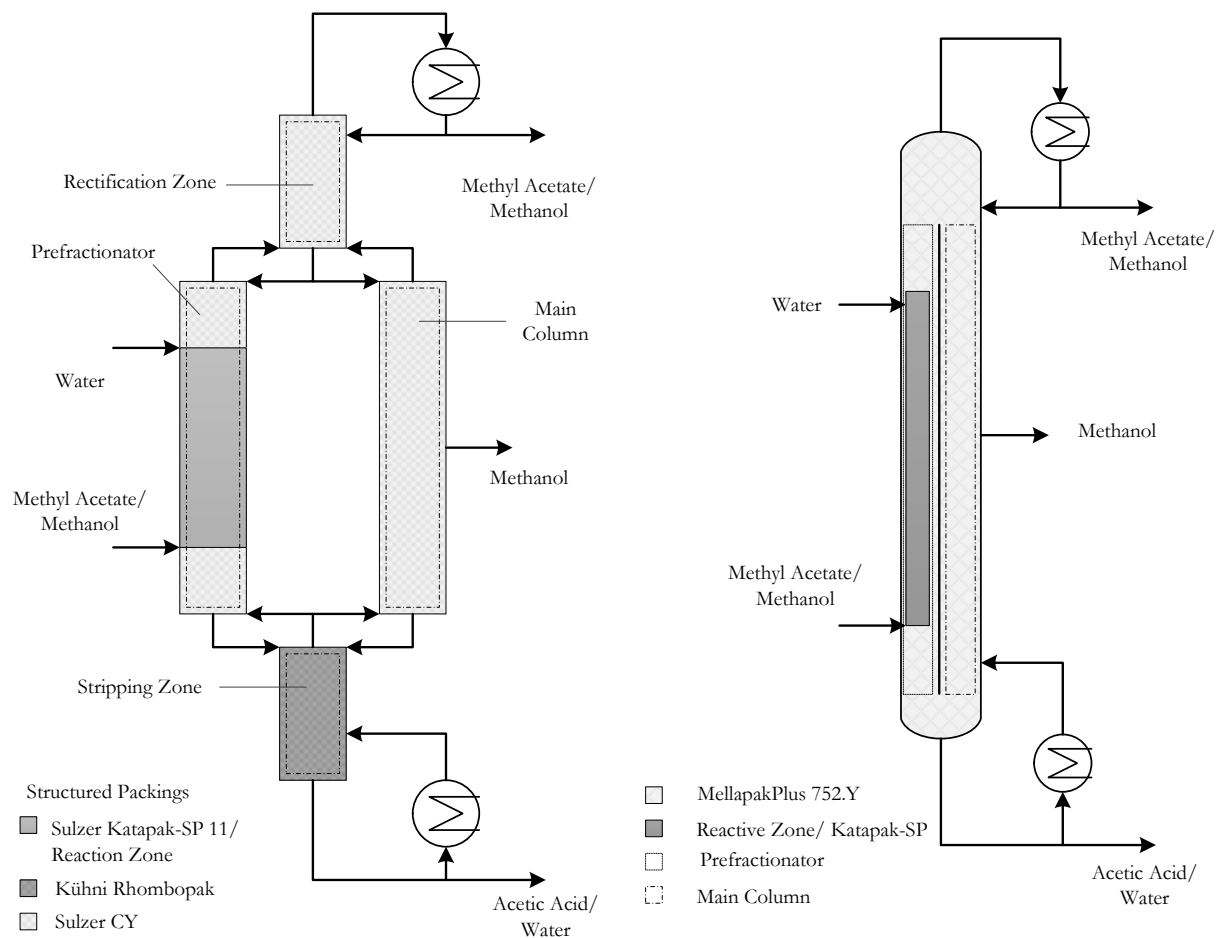


Figure 2-5 Sketch of the employed reactive dividing wall columns, lab-column design (left), industrial scale design (right) based on SANDER ET AL [26]

As can be noticed, the research about the RDWC has focused on simulation studies. Taking this into account, there is still a lack of knowledge about the experimental operation of the RDWC. Therefore, further investigations should aim to reduce the complexities and uncertainties about the RDWC operation. The following section summarizes the few sources regarding the experimental operation.

2.3.2 Experimental Researches

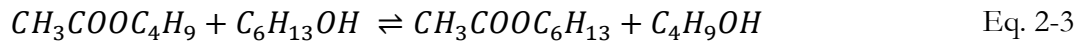
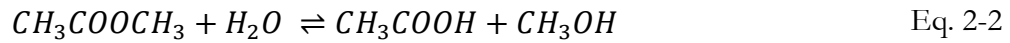
As was mentioned before, there are two relevant research groups, who have performed experiments with the RDWC. These are the INSERT project and the PAT-Institute of the TUHH. In order to visualize the progress of the experimental works of the RDWC, the available researches are summarized. In both investigations simulation models have been developed and validated through experimental operation. Nevertheless, the performed experiments and applied simulation models present some differences respect to the assumptions, reaction system and catalyst, simulation software and others. Table 2-1 shows the main characteristics of the researches, the performed experiments and the deviations between the simulation models and the experiments.

Table 2-1 Experimental RDWC researches summary

Property	INSERT PROJECT				PAT-Institute		Units
	Sander [26]	Ryll [27]	Müller [21]	Egger [28]	Harding [14]	Keuser [15]	
Column Height	6.5	14.3	6.5	4	4	4	m
Equilibrium Assumption	yes	yes	no	yes	yes	yes	-
Reaction System	Eq. 2-2	Eq. 2-2	Eq. 2-2	Eq. 2-3	Eq. 2-3	Eq. 2-3	
Reaction model	PH 2 nd order	PH 2 nd order	PH 2 nd order	PH 2 nd order	PH 2 nd order	PH 2 nd order	-
Catalyst	Amberlyst 48	Amberlyst 48	Amberlyst 48	Amberlyst 35	Novozym 435	Novozym 435	
Simulation Software	PRO/II	O.CH.	ACM	ACM	ACM	ACM	-
Successful experiments	1	8	2	3	4	3	-
Study cases	None	Product distribution	Feed flow	T-profile	T-profile	Pressure	-
				Product distribution	Liquid split	Liquid split	-
Max temperature deviations	*	*	*	*	4.5	3	°C
Max concentration deviations	*	2	*	9	4.5	11	w %
Max component mass flow deviations	*	5	*	2	1.5	3.75	%

* Only qualitative analysis

The works in frame of the INSERT project investigates the methyl acetate hydrolysis as reaction system (see Eq. 2-2), while the research from PAT-Institute employs the transesterification of butyl acetate (BuAc) with hexanol (HeOH) to butanol (BuOH) and hexyl acetate (HeAc) as Eq. 2-3 shows.



As Table 2-1 shows, the published experimental model validation from SANDER ET AL utilizes only qualitative analysis. The results exhibit a good correspondence of the temperature profile. Conversely, the concentration profile of the simulation does not adjust properly to the experimental data, especially in the reactive section [26]. The model validation from RYLL [27] offers more results compared to the work from SANDER ET AL[26]. RYLL analyzes the model adjustment considering different product distribution. The comparison between the simulation and the experimental data provides positive results to RYLL. The concentration difference for the product streams reaches only a maximum of 2 w %. In addition, the mass flow reaches a maximum difference of 5 %. MÜLLER presents another model, taking into account the mass transfer process. As MÜLLER indicates, each single stage is described via the film model first suggested by LEWIS AND WHITMAN [29]. Müller considers a dividing wall column equipped with trays, whereas each tray is related to one rate-based stage [30]. Nevertheless, the model validation considers only two experiments with only a qualitative analysis of the model adjustment.

The work from EGGER [28] validates an RTWK model utilizing the transesterification of hexanol with butyl acetate to butanol and hexyl acetate [28]. The model validation is presented through the comparison of three different experiments, which considers different temperature profiles. The results show high deviations in the product concentration due to the presence of side products, which affect the quality of the model. Therefore, the experiments performed by HARDING [14] and KEUSER [15] employs an enzyme catalyst. As HARDING and KEUSER present, the employment of the enzyme catalyst improves the reaction selectivity and inhibits the side reactions. Nevertheless, the simulation model still present differences compared to the experimental data, reaching up to 11 w % in the results presented by KEUSER.

In view of the results of the mentioned works, successful model validations are represented by a small sample. Thus, the simulation models cannot guarantee to fit correctly to other conditions. For example: high reboiler power, different liquid distribution, less reaction conversion.

Considering this, in order to provide a model, which ensures a safe design and operation conditions prediction, further experiments are required.

The present work aims to run different experiments with drastic changes in the operation parameters. In that way, the model fitness can be compared allowing identifying the weaknesses and strengths of the simulation model. The next chapter presents the methodology of this work with the characteristic of the model.

3 Methodology

The hypothesis of the present work considers that a RDWC in steady state can be properly modelled by applying the equilibrium stage approach. The employed model has been already developed in Aspen Custom Modeler (ACM) by the PAT-Institute of the Hamburg University of Technology. Therefore, the required work to answer the presented hypothesis is to plan and perform a set of experiments under conditions that challenges relevant aspects of the model, such like the reaction, the liquid and vapor distribution and the separation submodels. Subsequently, the model has to be validated with the experimental results. Hence, further work is needed to obtain information able to be compared with the simulation results. Particularly, the analysis of concentration samples, the reconciliation of the data and a sensitive analysis are part of this.

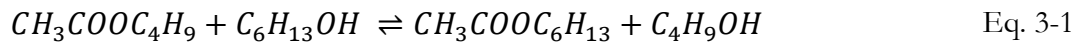
In this chapter, a complete description of the steps and main pieces that configures the mentioned methodology is described. First of all, the simulation model and materials employed during the performed experiments are presented. Second, the planned experiments and data processing are detailed. Finally, an overview of the method to assess the quality of the model is explained.

3.1 Reaction System

Previous, to initiate the modelling and model validation, a reaction system has to be selected. The selected reaction system has to fulfill several important requirements. First of all, the avoidance of side reactions is essential to decreases unwanted complexities. Therefore, an enzyme catalyst is employed, which ensures a high selectivity. Nevertheless, as most enzymes are deactivated at high temperatures the process temperature needs to be relatively low. Finally, the reactants must be safely manageable at the university laboratory and commercially available in quantities of 1 t per reactant. Therefore, the selected reference system is the transesterification of butyl acetate with hexanol to butanol and hexyl acetate (Eq. 3-1), which was already mentioned in chapter 2.3.

Furthermore, the reaction is catalyzed by an immobilized lipase enzyme Novozym 435 (Candida antarctica lipase B immobilized on acrylic resin) from the company Novozymes A/S Denmark.

In this section some important properties concerning the vapor liquid equilibrium (VLE) and the boiling temperature are presented. This information is crucial to modelling the reaction and separation processes of the RDWC.



For the performed experiments the chemicals presented in Table 3-1 were employed. On the table, the manufacturer, CAS-Number, the purity declared by the manufacturer and the measured by gas chromatograph (GC) analysis in the PAT-Institute laboratory are displayed.

Table 3-1 Properties of the applied compounds

Compound	Purity according to manufacturer w %	Measured purity (GC analysis) w %	Manufacturer	CAS-Nr.
1-hexanol	>99	99.0	Sasol	111-27-3
Hexyl acetate	>98	99.5	Roth	142-92-7
n-butyl acetate	>99	99.0	Oxea	71-36-3
1-butanol	>99	99.0	Roth	123-86-4

The VLE data from the reference system was investigated by FÖRSTER [31]. In this work, the operation pressure is within the range of 25-30 mbar. At this pressure, the reference system presents some particularities. First, BuAc and BuOH form a minimum azeotrope (Az). Conversely, HeOH and HeAc form another minimum azeotrope. The azeotrope concentrations reported by FÖRSTER [31] are presented in Table 3-2.

Table 3-2 Calculated azeotrope concentration of the mixtures by FÖRSTER [31]

Pressure mbar	Az. BuOH/BuAc		Az. HeOH/HeAc	
	BuOH	BuAc	HeOH	HeAc
	w %		w %	
25	19.5	80.5	37.5	62.5
30	21.5	78.5	40	60

In the work from FÖRSTER, the boiling sequence of the pure components is reported as well. Table 3-3 shows the values at 25 and 30 mbar. As Table 3-3 points out, the lightest boiling

component is butyl acetate, while hexanol is the heaviest boiling component. BuOH and HeAc are the middle boiling components.

Table 3-3 Boiling temperature of the pure components of the reaction system [31]

Pressure mbar	T _{BuAc}	T _{BuOH}	T _{HeAc}	T _{HeOH}
	°C			
25	33.8	39.3	69.9	71.0
30	37.1	42.1	73.6	74.0

Considering the presented data and the enzyme limitation temperature, e.g. operation pressure, the presence of azeotrope mixtures cannot be avoided during the experiments. This scenario does not sound interesting from an economical point of view, since mixed product streams will be generated and reaction rates below the 100 % are expected. Thus, the main advantages of the RDWC will not be visible under these conditions. Nevertheless, the scope of this thesis is not to show empirically the RDWC benefits, rather to answer if the steady state operation of a RDWC can be reliably predicted by the employed model approach. However, if the reader is interested, the paper from SCHRÖDER [8], quoted already in Chapter 2, shows a detailed study about the economic potential of a RDWC (e.g. its energy saving potential compared to other types of (reactive) distillation columns).

3.2 Simulation Model

The objective of the following section is to explain the fundamentals of the employed simulation model. For the RDWC, an equilibrium stage model is implemented in the Aspen Custom Modeler (ACM). The reactive dividing wall column model belongs to the PAT-Institute of the Hamburg University of Technology.

The simulation model bases on different structures, which represent the different packing sections of the column, such as the reactive, stripping and rectification zone. These sections are discretized by means of equilibrium stages. Moreover, there are distributor structures, which serve to allow the inlet and outlet of streams, such as the feed and side streams. Those structures do not represent an equilibrium stage. Figure 3-1 illustrates the simulation model structure. However, for the purposes of this work, not all of them are active, since they do not represent the real setup of the pilot plant. Table 3-4 shows this information.

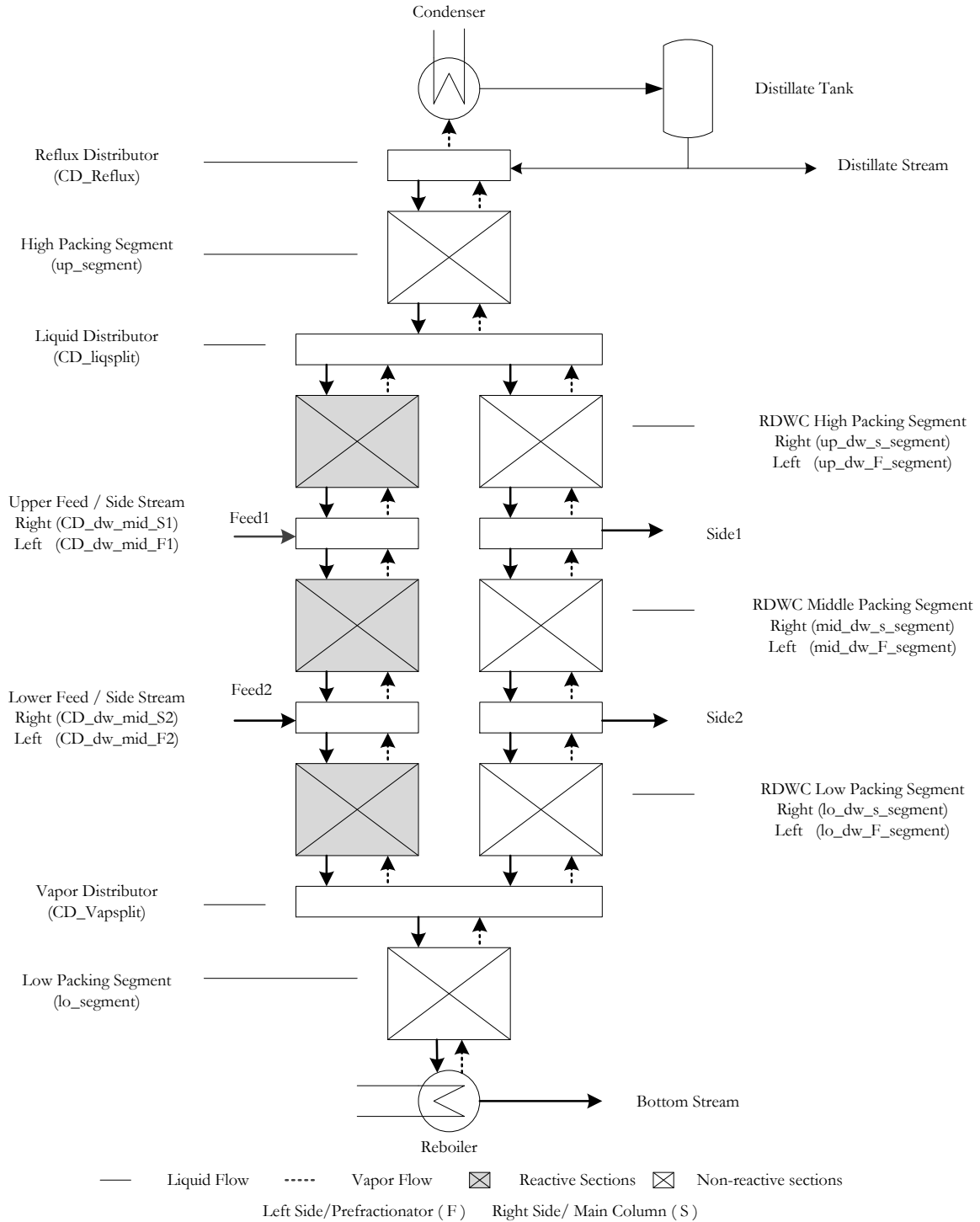


Figure 3-1 Simulation model structure

Table 3-4 Summary of the model structures

Model structure	Active	Number stages	Reaction present
reboiler	yes	1	-
lo	yes	6	-
CD_Vap_Split	yes	0	-
lo_dw_F	yes	2	yes
lo_dw_S	yes	6	-
CD_dw_mid_F2	-	0	-
CD_dw_mid_S2	-	0	-
mid_dw_F	yes	0	-
mid_dw_S	yes	0	-
CD_dw_mid_F1	yes	0	-
CD_dw_mid_S1	yes	0	-
up_dw_F	yes	2	yes
up_dw_S	yes	6	-
CD_Liq_Split	yes	0	-
up	yes	6	-
CD_Reflux	yes	0	-
distillate_Tank	yes	0	-

The number of stages per segment aligns with previous experiments concerning the separation performance of the RDWC. In total, six theoretical stages are considered for the non-reactive segments and two for each reactive section [14]. Besides, each of these segments has a length of 1 m.

A schematic equilibrium stage is represented by Figure 3-2. The description of the scheme, is as the following; the vapor stream V_{j+1} leaves the stage at the upper side and the liquid stream L_j goes out in direction to the stage below. On the other hand V_j enters from the stage below, while the stream L_{j+1} is coming from the stage above. Every stage is connected with the next one and is governed by the mass and energy balance equations. The fundamental assumptions of the equilibrium stage model are the following: each stage is in thermodynamic equilibrium. This is represented by equations Eq. 3-2 to Eq. 3-4.

$$T^g = T^l \quad \text{Eq. 3-2}$$

$$p^g = p^l \quad \text{Eq. 3-3}$$

$$\mu_j^g = \mu_j^l \quad \text{Eq. 3-4}$$

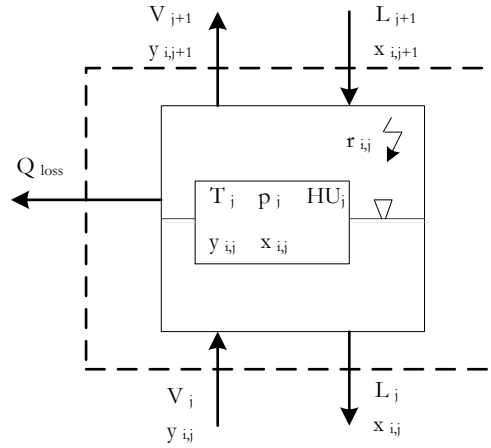


Figure 3-2 Equilibrium stage diagram

For the simulation model, the reaction kinetic bases on a second order pseudo homogeneous model. The reactive stages are perfectly mixed and the reaction rates are calculated by the product between the activity coefficients (Eq. 3-5 and Eq. 3-6) and the catalyst mass. The activity coefficients are calculated by means of the UNIQUAC model. The required UNIQUAC parameters were obtained experimentally by FÖRSTER [31].

$$r_j = m_{cat} \cdot k_0 \cdot e^{\left(\frac{-E_A}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right)} \cdot \prod \alpha_i \quad \text{Eq. 3-5}$$

$$r_i = m_{cat} \cdot k_0 \cdot e^{\left(\frac{-E_A}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right)} \cdot \prod \alpha_j \quad \text{Eq. 3-6}$$

j: 1 to every product $\in$ [BuOH, HeAc]

i: 1 to every reactant $\in$ [BuAc, HeOH]

As there are different packing types, the pressure drop is calculated for every section and every distributor segment via Eq. 3-7 and Eq. 3-8. The applied pressure drop parameters are exhibited in Table 3-5.

$$\frac{\Delta p}{\Delta z} = a \cdot F_v^b \cdot (1 + c \cdot u_l) \quad \text{Eq. 3-7}$$

$$F_v = u_g \cdot \sqrt{\rho_g} \quad \text{Eq. 3-8}$$

The modelling of the pressure drop has a fundamental importance, since the flow resistance on both sides the dividing wall determines how the vapor stream is split up at the lower end of the dividing wall between both sides. As SCHRÖDER ET AL published, the value of the vapor split can be of very high importance in order to reach energy efficient column operation. Nevertheless, in

real operations, the vapor split can hardly be measured directly. Taking this into account the availability of mathematical models being able to describe the resulting vapor split based on accurate pressure drop correlations is of very high importance.

Table 3-5 Pressure drop parameters

Packing Type	a	b	c
Montz B1 500	0.958	1.773	0.03
Sulzer Katapak SP	1.073	1.817	0.017
Distributors (CD_Segments)	0.15	2	0

Furthermore, the model distributes the vapor (Vapor Split) to ensure an identical pressure drop in the prefractionator and main column (Eq. 3-9).

$$\Delta p_{PF} = \Delta p_{MC} \quad \text{Eq. 3-9}$$

To estimate the heat loss to the surrounds the equation Eq. 3-10 is applied. Previous works conclude that the determination of the heat transfer coefficient value is difficult. In view of that, this value is adapted after every simulation run to calculate a proper reflux [14].

$$Q_{loss} = k \cdot A \cdot \Delta T \quad \text{Eq. 3-10}$$

3.3 Planned Experiments

Based on the model structure and phenomenology of the process, the main aspects of the model are the reaction, separation, pressure drop and distribution of the liquid and vapor flows along both sides of the wall. These are completely linked to the quality of the simulation prediction, which relies on the proper modelling of these processes. Therefore, operating variables that allow important changes in the involved processes must be selected and varied to assess and verify the model fitness under a broad spectrum of operating conditions.

The manipulated variables correspond to: the liquid split, which determines the reflux distribution along to both sides of the columns, the heat power, the feed composition and the feed flow. These variables can be easily changed in the different experiments and do not put in risk the operability of the pilot plant. Furthermore, each of these variables should strongly affect the process behavior.

First of all, the liquid split controls the amount of reflux allocated to the prefractionator and main column. Hence, by changing the value of this variable, the distribution of the liquid flow and the temperature profile will be affected. As show the Table 3-6, the liquid split is operated from 0.35 up to 0.50. This variable is formulated as the ratio of the reflux that goes to the prefractionator.

Thus, a value of 0.50 means an equal reflux distribution along both sides of the column. Different values were considered to visualize experimentally different temperature profiles and therefore to test the ability of the model to predict correctly the reaction kinetics and separation performance. The variation of the heat power increases the vapor boilup in the column, which impacts in the pressure drop, and vapor and liquid flow distribution along both sides of the column. With this in mind, low and high heating loads were considered for the planned experiments. The feed composition set the available moles of each reactant for the reaction; therefore: three different scenarios consider the values exhibited in the Table 3-6, excess of the reactant 1, equimolar feed and excess of the reactant 2. As can be expected, the excess of one reactant changes the reaction equilibrium and the reactant conversions, which is a relevant test for the ability of the model to predict properly the reaction process in the RDWC. Finally, the increase of the feed flow, aims to test the model fitness when less catalyst per kg of reactants is observed. Taking this into account, one of the experimental runs was carried out with a mass flow twice bigger than the other cases.

Table 3-6 Values of the Manipulated Variables during the Pilot Plant Experiments

Variable	Planned Values				
Liquid split	0.35	0.40	0.45	0.50	-
Heating power	850	1034	1204	1332	kW
Feed flow	1.80	3.70			kg/h
W _{Feed, BuAc}	43.3	52.9	69.0		kg/kg
W _{Feed, HeOH}	31.0	47.6	56.7		kg/kg

3.4 Model Validation Method

In order to validate the model, two set of data are required. These are the experimental values and the simulation runs to be contrasted with the experimental data. In this section, the procedure to obtain the data is explained. Moreover the criteria that are considered to determine if the model approach is appropriate is presented.

3.4.1 Experimental Data Acquisition

The reactive dividing wall column plant features an online measuring and control technique. The temperature, mass flows, pressure and tank levels values are measured every 0.1 s. The description of the instrumentation and control technique is described in the next Chapter. The obtained information is read through the software WinErs-Professional, which gives a user interface to supervise and control the RDWC during the operation. Nevertheless, this is not the case of the product compositions, which is measured offline. Therefore, in order to get the

composition of the streams, samples from the feed and product streams are collected. The method employed by the Gas Chromatograph is detailed hereafter.

The model validation of this thesis focuses on the RDWC steady state. Considering this, the temperature, pressure, mass flows and composition are evaluated during the operation in order to determine if the experiments performed fulfill this requirement. The strategy for confirming the steady state begins with the analysis of the product compositions, since it allows delimiting faster the time periods that could represent the stationary state. Subsequently a set of criteria are applied for the temperatures and mass flows. The complete method is described in the next Chapter, which is referred exclusively to the experimental work.

Gas Chromatograph

To analyze the samples a gas chromatograph type Clarus 500 from the company Perkin Elmer is employed. The applied capillary column is type Supelco SLB-5 with a length of 30 m, its internal diameter 0.32 mm and its film thickness 0.5 μm . The GC has an autosampler, which allows a maximum of 86 samples in one run. The syringe extracts a fraction of the sample. This is abruptly vaporized and transported by the carrier gas (mobile phase) towards the end of the capillary column.

In principle, the GC performs a separation of the compounds. To this end, the capillary column possesses a stationary phase, which is crossed by a mobile phase. The basic principle of the GC is the different retention time of every component, which depends on the interaction between the mobile phase and the stationary phase. The composition of the sample is estimated according to the different retention time that measures the GC. Moreover, in order to quantify the hydrocarbons, the GC has a flame ionization detector (FID). In this detector, electrodes are located adjacent to a flame fueled by hydrogen/air near to the exit of the column, and when carbon containing compounds exit the column they are pyrolyzed by the flame [32]. This detector works only for organic/hydrocarbon containing compounds due to the ability of the carbons to form cations and electrons upon pyrolysis, which generates a current between the electrodes (see Eq. 3-11). The electronic signal is translated as peaks over the time. This diagram is the well-known chromatogram (Figure 3-3).



The GC requires a method to apply the analysis. Table 3-7 summarizes the settings of the employed method from the PAT-Institute.

Table 3-7 GC analysis method

Setting	Value	Units
Temperature		
Furnace	140	°C
Flame	340	°C
Carrier gas		
Pressure	31	kPa
Flow	0.60	mL/min
Linear speed	15	cm/s
Split ratio	200:1	-
Gas flow		
H ₂	45	mL
Air	450	mL

The chromatogram is evaluated by the software TotalChrom Navigator. Figure 3-3 shows the gas chromatogram from the sample “Side_Std_NR_Level10”. As shows in the figure, the components appear at different times with different heights. The software also provides the absolute and the relative area under every peak.

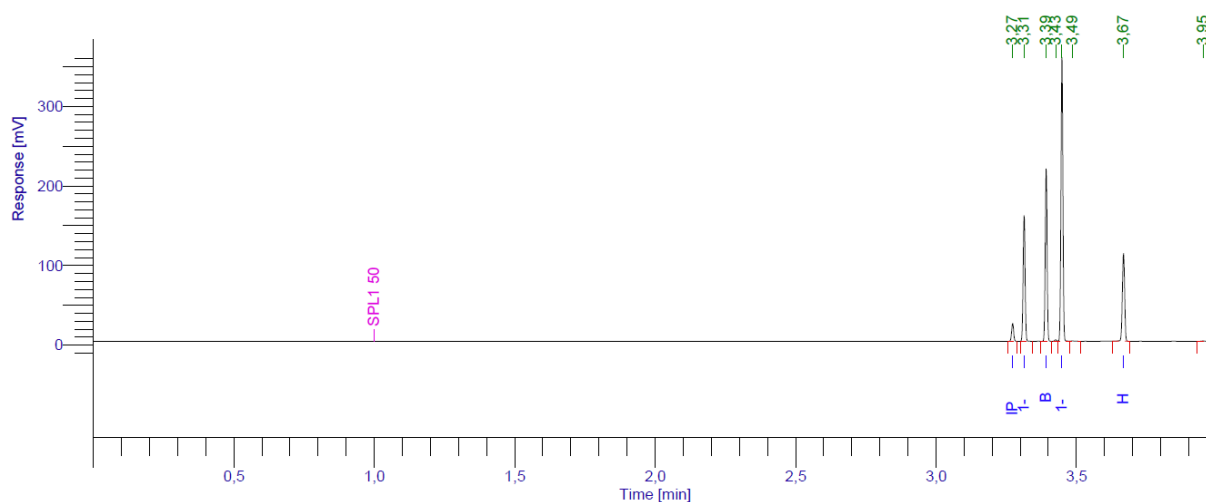


Figure 3-3 Gas chromatogram “Side_Std_NR_Level10”

The detected components for this sample are isopropanol, butanol, butyl acetate, hexanol, and hexyl acetate. The exact time interval of every component is presented in Table 3-8 . Furthermore, Table 3-8 exhibits the calculated data by the software, such as the area and the height of the peaks.

Table 3-8 GC analysis report “Side_Std_NR_Level10”

Component	Time Interval	Area [μ Vs]	Height [μ V]	Area [%]
propanol	3.27 – 3.30	11189	22370	2.61
butanol	3.31 – 3.35	77297	157881	18.04
butyl acetate	3.39 – 3.42	100173	215596	23.37
hexanol	3.44 – 3.48	175857	358126	41.03
hexyl acetate	3.66 – 3.72	62758	110057	14.64

It is clear that the results still do not represent the weight percentage of the samples. Therefore, standards with measured weight percentage were contrasted with the GC analysis to provide an appropriate regression between the peak area and weight percentage. The mentioned standards data are presented in appendix A.1.1.

3.4.2 Data Reconciliation

Evidently the GC analysis and the measured mass flows provide important information for the model validation. Nevertheless, the experimental errors are inherent to every value. Thus the information could be faintly inconsistent. For the purpose of solving this problem, the PAT-Institute has developed an adjusted mass balance model, which bases on the well-known method of Lagrange multipliers. The raw data of the product composition and mass flows is set into the adjusted mass balance model to obtain consistency values. Moreover, the error tolerance bases on the maximum error allowed from the employed instruments. Table 3-9 shows these values.

Table 3-9 Mass balance model error tolerance

Parameter	Interval	Error
Mass flow	every case	$0.05 + 0.01 \cdot \text{Mass Flow}$
Mass fraction	$>5\%$	$0.01 + 0.01 \cdot \text{Mass Fraction}$
Mass fraction	$<5\%$	$0.01 \cdot \text{Mass Fraction}$

In order to confirm the error tolerance of the mass fraction, 12 samples with different compositions were measured separately by means of an analytical weight. Table 3-10 exhibits the difference between the GC standards and the data measured through the analytical weight. As can be noticed from Table 3-10, the results are below the error tolerance reported by Table 3-9. The measured values are presented in appendix A.1.1.

Table 3-10 Mass fraction difference between analytical weight and GC-Standards

Standard Name	ΔBuAc kg/kg	ΔBuOH kg/kg	ΔHeAc kg/kg	ΔHeOH kg/kg
Level-0	0.0037	0.0006	-	-
Level-1	0.0020	0.0020	-	-
Level-2	0.0026	0.0022	0.0002	-
Level-3	-	-	0.0071	0.0036
Level-4	-	-	0.0066	0.0043
Level-5	-	-	0.0069	0.0051
Level-6	0.0059	0.0079	0.0024	-
Level-7	0.0002	0.0024	0.0048	0.0012
Level-8	0.0002	-	-	0.0002
Level-9	0.0003	-	-	0.0003
Level-10	0.0008	-	-	0.0008
Level-12	0.0034	0.0014	0.0001	0.0019

3.4.3 Simulation Runs

For a detailed model validation, simulations corresponding to each experiment in steady state are carried out with experimental inputs. To obtain plausible input values, the data from the experiments during the steady state is averaged. Moreover the mass flows and product composition are input in the adjusted mass balance model to ensure the consistency of the mass balance.

The selected inputs allow changing in the operating conditions and observe how the RDWC model responds to these variations. In this way, the most important outputs of the RDWC, such as product composition, reactant conversion, temperature profile are free and can be compared with the experimental results.

3.4.4 Sensitive Analysis

In order to test the robustness of the model a sensitive analysis is considered. The main objective is to vary slightly the values of some inputs to visualize if the simulation outputs still results in plausible values. For this task, a routine in MATLAB has been created to automatize this procedure. The communication between MATLAB and ACM is by means of a COM-Server and COM-interfaces, which enable the communication between MATLAB and ACM. The COM-Server and interface have been created by the PAT-Institute.

The COM-Server achieves the communication through a dynamic link library (DLL). The DLL is programmed in Visual Basic.NET and saves the most important methods used in ACM, such as the reading and overwriting of variables and the initialization of the simulation run. Figure 3-4 shows the communication process between MATLAB and ACM.

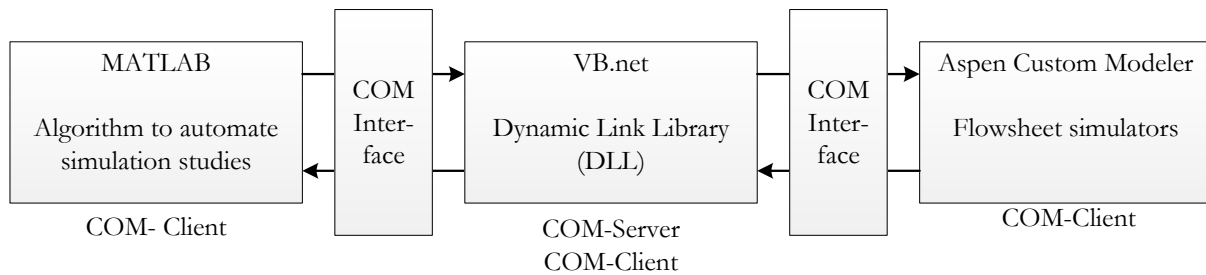


Figure 3-4 Communication process between MATLAB and ACM

With this feature the free displacement of the information between ACM and MATLAB is possible. Additionally, MATLAB can be used to program an automated sensitive analysis. Figure 3-5 illustrates the employed algorithm to perform the sensitive analysis of this work.

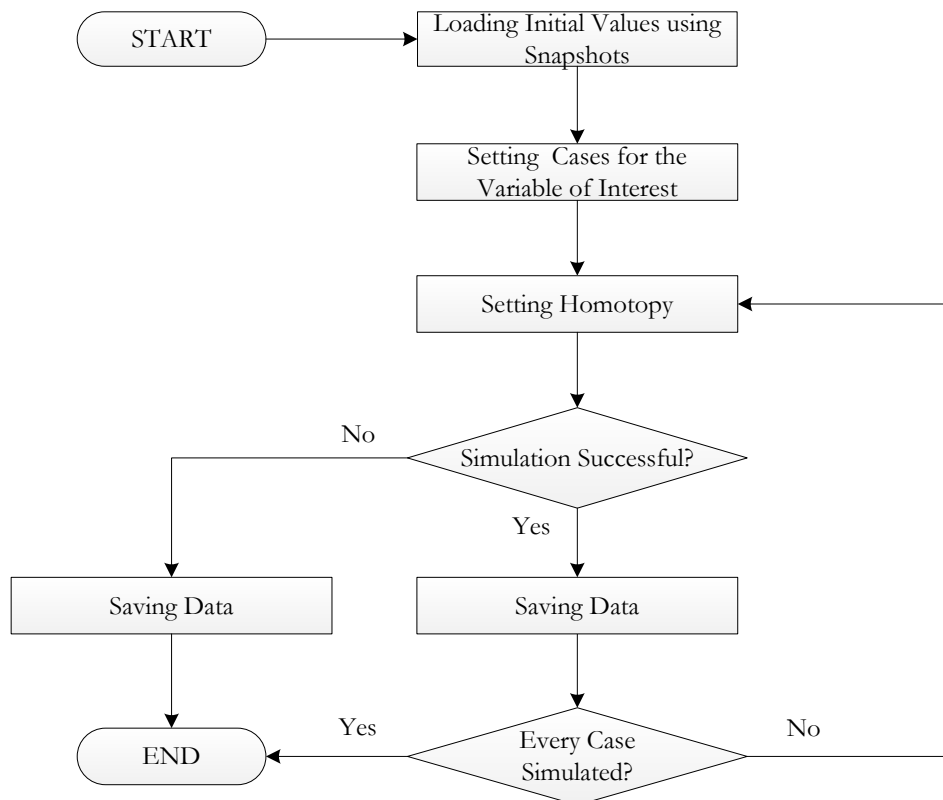


Figure 3-5 Sensitive analysis algorithm

As Figure 3-5 shows, the first step is the loading of initial values by means of snapshots. ACM has among its tools the creation of snapshots; these are a saved set of values and specifications,

for all variables in a simulation. With this feature a set of interest values can be loaded before to starting a new simulation. Afterwards, the algorithm sets the cases that must be simulated. The variable of interest is changed using the homotopy technique to facilitate the convergence of the solution. The simulation will succeed if the change of the variable value is feasible with the process, in case that the simulation is successful the generated data is saved and the next case is initiated. On the other hand, the simulation will finish when all the cases are simulated or if the simulation is unsuccessful.

3.4.5 Model Validation Criteria

Once the experimental and simulation results are able to be contrasted, a method to assess the quality of the model is required. Therefore, in order to validate the simulation model, the experimental results are compared with their respective simulation runs. The quality of the model is assessed through the comparisons of the variables that allow to determine how well the reaction and separation modelling is. Therefore, the differences between the simulation and the experiment results from the temperature profiles, the concentration profiles and the component mass flows are calculated. The detailed criteria, agreements and disagreements are presented in Chapter 5, which deals exclusively with the model validation results.

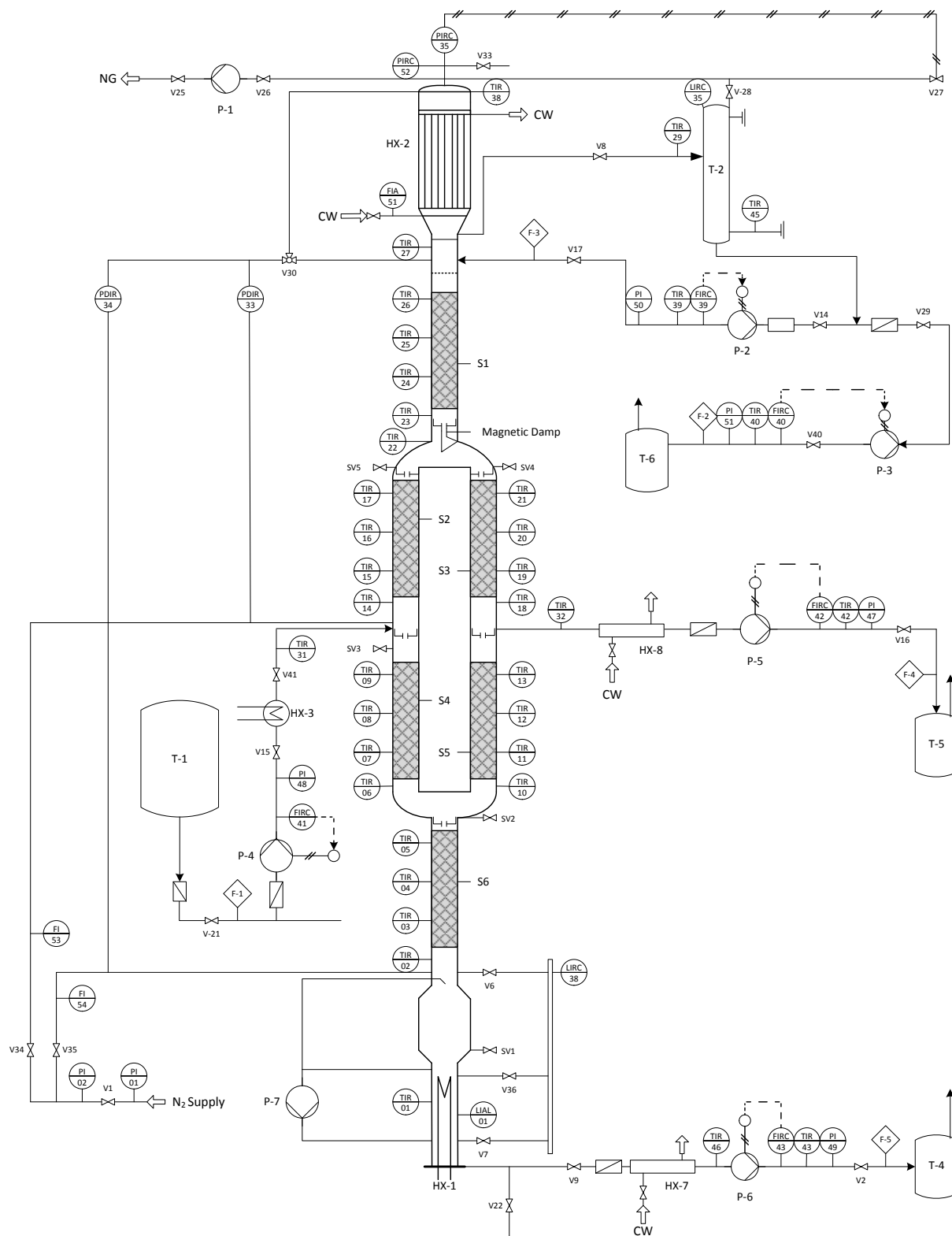
4 Experimental Operation

As was mentioned before, the simulation model has to be evaluated under different operation conditions by means of planned experiments that affect relevant aspects of the reaction and separation modelling. Considering this, this section pursues to show the experimental setup and results to confirm that the manipulation of the selected operation variables really modifies the RDWC process behavior. In total, eight experiments were carried out at the pilot RDWC plant of the Hamburg University of Technology.

In this Chapter, first, the pilot plant and its instrumentation and control technique are presented. The second part of this chapter deals with the operation of the RDWC, which includes the experiment preparation, the startup strategy and the applied control system. Furthermore, section 4.3 presents the measured values of the dynamic behavior and the steady state in order to give relevant information concerning the understanding of the process. In section 4.4 the experimental results are evaluated. First, the steady state tests are outlined. Second, the effects of the variation of the heat power, liquid split, feed flow and composition on the RDWC operation are explained. Finally, an overview of the results of the chapter is presented.

4.1 Reactive Dividing Wall Column Plant

In the following section, the reactive dividing wall column plant is described. The process and instrumentation diagram (P&ID) of the reactive dividing wall column pilot plant is illustrated by Figure 4-1. In section 4.1.1 the main elements of the plant are introduced, while section 4.1.2 deals with the instrumentation and control technique.



HX-1	HX-2	HX-3	HX-7	HX-8	P-1	P-2	P-3	P-4	P-5	P-6	P-8
Reboiler	Condenser	Micro heat exchanger	Plate heat exchanger	Double pipe heat exchanger	Vacuum Pump	Reflux Pump	Feed Pump	Distillate product pump	Side product pump	Bottom product pump	Recirculated bottom pump
T-1	T-2	T-4	T-5	T-6	F-1	F-2	F-3	F-4	F-5	CW	NG
Feed container	Distillate container	Bottom product container	Side product container	Distillate product container	Feed stream	Distillate stream	Reflux	Side stream	Bottom	Cooling water	Non-condenser gases

Figure 4-1 P&ID reactive dividing wall column pilot plant

4.1.1 RDWC Plant Description

The column structure is based on a petlyuk shell design. The prefractionator and the main column are connected at the top of S6 and below S1. As can be inferred from Figure 4-1, the design of the column avoids the direct contact of the walls from the prefractionator and main column and therefore the heat transfer between the two sides of the column can be excluded.

The condenser (HX-2) and reboiler (HX-1) are located above and below the column respectively. The reboiler heating power can achieve a maximal value of 1850 W. The employed condenser has a heat transfer surface of 1 m². The service stream is a water-glycol mixture at 5 °C, which is supplied by a cooling unit.

The prefractionator comprises the packing sections S2 and S4. Both have an inner diameter of DIN 50 and are filled with Katapak-SP11 reactive packing along its 2 m. The total number of reactive packing elements is 20 containing 281 g of CALB enzyme catalyst (Novozym 435). Conversely, the main column comprises four sections, they are filled with Montz-Pak-B1-500 structured packing covering a length of 4 m.. From top to bottom, S1 is located on the top of the column shell, above the liquid split, S4 and S5, at the right side of the RDWC shell and S6 is below the separated columns, but above the reboiler. The inner diameter of sections S1 and S6 is DIN 65, while, the inner diameters of the other sections are DIN50. The liquid distribution along the column packing sections is achieved by means of collector and distributor elements. The controlled distribution of the reflux is realized through a magnetic damper, which allows passing liquid to the prefractionator and the main column based on a time ratio.

The top of the column is connected to a vacuum pump (P-1), whose minimum operation pressure is 5 mbar. The non-condensed gases are conducted out of the pilot plant, as Figure 4-1 indicates. Furthermore, the pilot plant possesses five gear pumps. They transport the feed (P-3), side (P-5), distillate (P-3), reflux (P-2) and bottom flows (P-6). Moreover, there are six small containers available, T-1 for the feed with a volume capacity of 60 L. On the other hand, the containers T-4, T-5 and T-6 receive the product outflows and have a capacity of 30 L. Besides, the distillate accumulation tank (T-2) can store up to 5 L. As Figure 4-1 shows, there are three heat exchangers in operation. HX-3 preheats the feed, while HX-7 and HX-8 cool down the bottom and the side streams.

4.1.2 Instrumentation and Control Technique

The reactive dividing wall column plant features an online measuring and control technique. The data is measured every 0.1 s. The obtained information is read through the software WinErs-Professional, which gives a user interface to supervise and control the RDWC during the operation. Table 4-1 summarizes the error related to each measuring instrument.

Table 4-1 Error tolerance of the measuring instruments

Measuring instrument	Variable	Error	Units
PT-100	T	$\pm (0.15+0.002 \cdot T)$	°C
Coriolis Mass Flow Meter	M	$\pm (0.05+0.01 \cdot M)$	kg/h
Pressure drop	Δp	$\pm 1\% \cdot \Delta p$	mbar
Vega Flex 65	Height level	± 10	mm
Capacitive pressure sensor	p	$\pm 1\% \cdot p$	mbar

Temperature

As Figure 4-1 shows, the column and streams are connected to temperature sensors. In every packing, four temperature sensors are implemented. They are type PT100 resistive thermometers. In the reactive zone (S2 and S3), the sensors are located exactly between the packing elements in order to avoid possible damages to the enzyme packings. In the sections S4 and S5, the PT100 are located directly on the middle of the packing elements. However, TIR18 and TIR10 are at the lowest position of the section S4 and S5 respectively.

Mass Flow

The mass flows of the feed (F-1), distillate (F-2), reflux (F-3), side (F-4) and bottom (F-5), are measured via Coriolis mass flow meters. Furthermore, the distillate, side and bottom mass flow are measured manually in order to compare the results and confirm the proper calibration of the instruments.

Pressure

The pressure in the column is measured by means of three capacitive pressure sensors. PIRC 52 quantifies the absolute pressure of the column. PDIR 34 measures the pressure drop between the top and bottom, while the pressure drop between the top and the feed inlet can be read from PDIR33. As Figure 4-1 shows, the pressure drop sensors are connected to the nitrogen supply line. The nitrogen flows along the column wall preventing the presence of liquid in the sensors.

Level

In order to measure the height of the liquid phase in the distillate tank and reboiler, two level sensors are available: LIRC 37 and LIRC 38. Both are type Vega Flex 65. The measuring principle of these sensors utilizes a high frequency microwave signal, which is sent to the liquid interface. The time between the sending and the returning of the reflected microwave allows the calculation of the height level.

Product Mass Fraction

As was mentioned in Chapter 3.3, the mass fractions of the product flows are measured offline. The samples of every stream are collected and analyzed after the experiment by means of GC-analysis. The sampling time depends on the operation state. If the temperature and stream are stable, it is 10 minutes. Otherwise it is 20 minutes. Moreover, five sample valves are along the RDWC to analyze the concentration profile (SV-1, SV-2, SV-3, SV-4 and SV-5).

4.2 Reactive Dividing Wall Column Operation

This section presents the applied procedure for operating the reactive dividing wall column. First, the experiment preparation is depicted. Subsequently, the startup and implemented control system are explained. Finally, a summary of the performed experiments is exhibited.

4.2.1 Experiment Preparation

The cooling unit for the condenser service stream is turned on 30 minutes before the start. Afterwards, the supply valves of cold water for the side and bottom streams are opened. Subsequently, the process control system WinErs Professional is started.

To ensure that the column is tight and there is no leak alongside, a tightness test must be performed. The reason for this test is avoiding the inflow of oxygen, which can form a flammable atmosphere within the column. The inertisation of the column is achieved with nitrogen to reduce oxygen presence therein. Thereby, a dilution factor of 1:225 is achieved. Additionally, the nitrogen valves (V-34, V-35) are opened to wash out the sensors. Finally, the vacuum pump is set at the operation pressure and the heat power is turned on.

4.2.2 Startup

The previous works of HARDING [14] and KEUSER [15] have established a safe startup strategy for the enzyme catalyzed reactive dividing wall column. The most important criteria for the

startup strategy are the temperature limit in the reactive zone and the fast achievement of the temperature profile and product mass flows predicted by the simulation model. Based on the investigation from MAHMUD ET AL [33] the temperature of the reactive zone must not exceed 60 °C in order to avoid enzyme destruction.

The first step is starting the reboiler heat power, if the required liquid mixture level is proper. The reboiler mixture composes mostly hexanol and hexyl acetate (≈ 95 w %), and the condensed gases of the light components from previous experiment (≈ 5 w %). In this way, the steady state concentration of the heavy components in the bottom is achieved faster.

The feed is started once the temperature of TIR06 rises. With the addition of the feed mixture, the reaction can start. Likewise the distillate and reflux pump are started after the temperature of TIR23 increases. The distillate and the reflux are set at high and small mass flows respectively. In this way, the concentration of light components is reduced and the temperature continues ascending. Afterwards, the reboiler level control system is activated. Once the temperatures and the mass flows stabilize, the control systems for the prefractionator column and the distillate level are activated. Approximately, after 1 – 1.5 h the mass flows and the temperature are relatively stable. At that moment, the side outflow is started. Initially, the side mass flow is set at the predicted value of the simulation. Subsequently, the control system for regulating the main column temperature is activated.

4.2.3 Control System

As was mentioned in 4.1.2, the software WinErs Professional provides a user interface to supervise and control the RDWC during the operation. In this section, the applied control systems are explained.

The control loop for the reboiler level (LIRC38) is by means of a proportional control system (P-control), whose manipulated process variable (MV) is the bottom outflow (FIRC43). Likewise, the distillate level has also a P-control with the distillate outflow (FIRC40) as MV. Moreover, the temperature profiles of the prefractionator and the main column are also regulated by a control system. For the prefractionator, the process variable (PV) is the temperature TIR14 and the manipulated variable is the reflux (FIRC39). Similarly, TIR10 (or TIR11, TIR12) is the process variable in the main column, which is controlled by the side outflow (FIRC42). Both control systems are proportional and integrative controls (PI-control). Table 4-2 shows the applied parameters.

Table 4-2 Settings of the applied control systems

Property	Bottom level	Distillate level	Main column temperature	Prefractionator temperature	Units
Process variable	LIRC37	LIRC35	TIR10	TIR14	-
Manipulated variable	FIRC43	FIRC40	FIRC42	FIRC39	-
Control system	P	P	PI	PI	-
Proportional constant	0.03 - 0.1	0.03 - 0.1	0.1	0.5	-
Integrative time	-	-	100 - 400	600 - 745	s

4.2.4 Performed Experiments

As it has been emphasized in the previous chapters, the validation of the reactive dividing wall column model requires successful experiments with different operating conditions. Considering this and the previous works on this topic, a set of parameter were selected in this thesis to be varied: the liquid split (LS), the heat power, the feed composition and the feed flow. In this way, the column operating is carried out under different temperature and concentration profiles, reactant conversions, product distributions and pressure drops. The selection and reasons of the variables and values to be tested were already depicted in section 3.3. A summary of the experiments is presented in Table 4-3.

Table 4-3 Performed experiments

Variable	TWK99	TWK100	TWK101	TWK102	TWK103	TWK104	TWK105	TWK106	Units
Liquid split	0.35	0.35	0.35	0.40	0.45	0.35	0.40	0.50	-
Heating power	863	1204	852	851	850	860	1034	1332	kW
Feed flow	1.89	1.84	1.79	1.94	1.68	1.85	3.69	1.80	kg/h
W _{Feed, BuAc}	52.9	52.8	69.0	69.4	43.3	(Error)	51.8	52.9	kg/kg
W _{Feed, HeOH}	47.1	47.2	31.0	30.6	56.7	(Error)	48.2	47.1	kg/kg
Pressure	25	25	25	25	25	25	25	25	mbar
Setpoint TIR14	38.8	41.5	38.2	37.3	38.0	38.3	39.4	41.0	°C
Setpoint TIR11	-	-	-	-	66.6	62*	61.5**	70.5**	°C
Distillate	0.68	0.59	0.76	0.57	0.49	0.58	1.05	0.64	kg/h
Reflux	4.99	7.52	4.62	4.97	5.11	4.89	5.67	8.23	kg/h
Bottom	1.00	0.97	0.68	0.73	0.80	0.91	1.90	0.75	kg/h
Side	0.22	0.28	0.35	0.64	0.39	0.32	0.74	0.41	kg/h
Reflux Ratio	7.37	12.84	6.10	8.65	10.41	7.60	5.38	12.91	-
Steady State	yes	yes	no	yes	yes	no	yes	yes	-

* T12 instead of T11 **T13 instead of T11

4.3 Measured Values

At the end of each experiment, the historical data is exported to be analyzed and evaluated. This includes the information delivered by the sensors mentioned in section 4.1.2 (temperature, mass flow, pressure and level). Furthermore, as outlined previously, the mass compositions of the product streams are obtained through GC analysis, which is complemented by the adjusted mass balance model. In this section, the measured values are presented to give the bases for the subsequently experiment evaluation and model validation. First, the dynamic behavior is depicted. Additionally, those experiments that achieved the steady state are presented in terms of the temperature profiles, mass flows and product compositions.

4.3.1 Dynamic Behavior

In order to visualize the different stages during the RDWC operating, such as the startup and start of the steady state, the dynamic behavior of the experiment TWK99 is described. The key features of this experiment are representative for all the performed experiments. Figure 4-2 exhibits the course of the mass flows during the experiment. As Figure 4-2 shows, the feed enters into the column after 1 h. Then, the start of the distillate and reflux takes place. Few moments later, the bottom stream is initiated. Finally, the side stream starts after 3.5 h.

As can be noticed, the feed starts with a high mass flow to fill the pipes and fittings. Afterwards, the feed is set at the operation value which remains constant during the operation. For the case of the distillate, reflux and bottom streams, two unstable periods can be observed. The first lapse comprises the second hour after start. In this phase the temperature profile is still ascending and the level control systems are trying to reach the setpoint. Thereafter, the column stabilizes and an early steady state is achieved. This status is steady until the start of the side stream, which generates a new source of instability. As Figure 4-2 illustrates, the mass flow distribution changes according to the expected constraints of the mass balance. Hence, the distillate flow descends. When observing the course of the mass flows, the steady state is achieved at the seventh hour. Evidently, the changes along the process cannot be explained with the mass flow distribution only. For this reason, the temperature profile and concentration of the products during the process are displayed on Figure 4-3 and Figure 4-4.

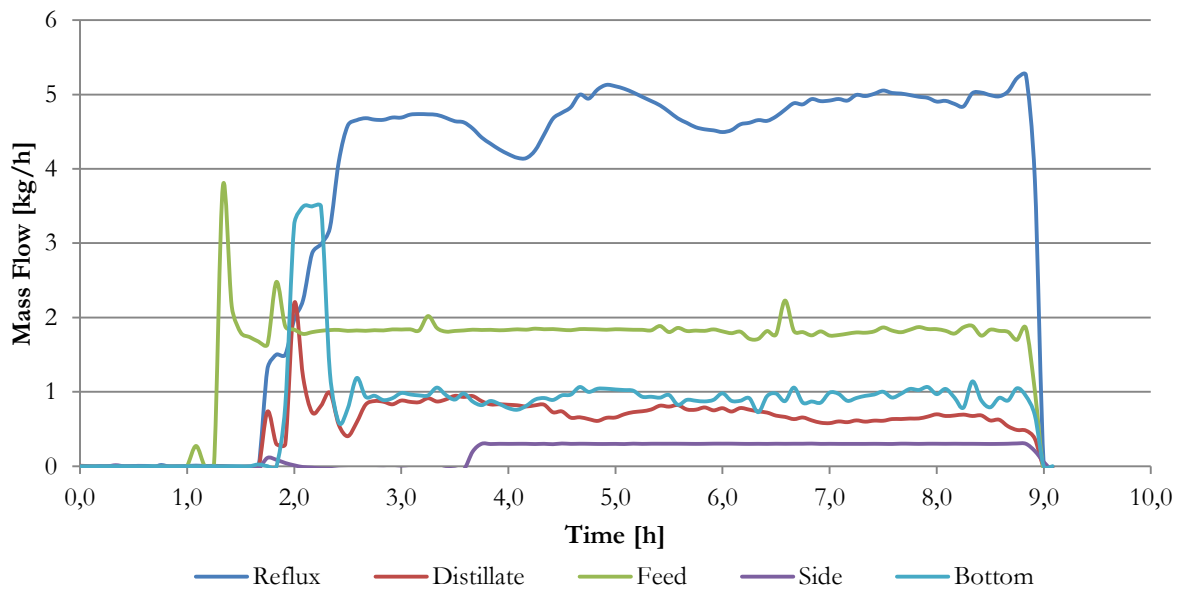


Figure 4-2 Course of the mass flows of the experiment TWK99

The reactive dividing wall column possesses 24 sensors distributed in the packings. Considering this, representative sensors are selected to show a clearer trend of the temperature in every section. As it can be seen from Figure 4-1, TIR02 is located in the first packing (bottom), TIR07 in the reactive packing below the feed, TIR10 at the beginning of the main column, TIR14 above the feed, TIR19 above the side stream, and TIR24 at the top of column. The measurements from TIR01, TIR14, TIR19 and TIR24 are relative stable and after 2 h reach a constant value.

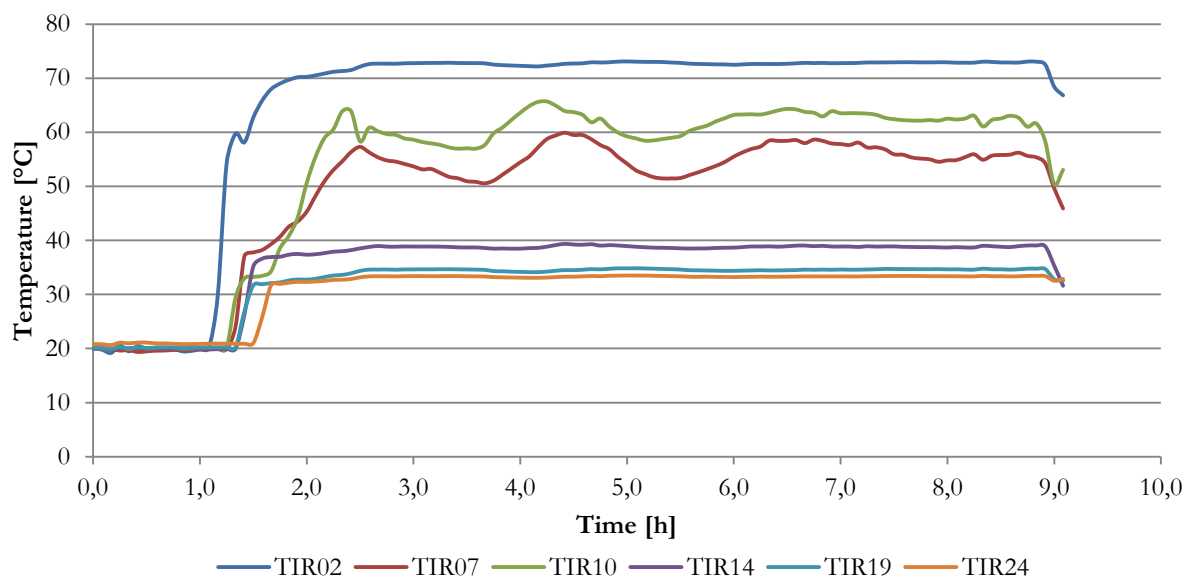


Figure 4-3 Course of the temperature sensors TIR01, TIR07, TIR10, TIR14, TIR19 and TIR24 of the experiment TWK99

Conversely, the temperatures of TIR10 and TIR07 change continuously during the experiment. The temperature in these sections is more sensitive to the redistribution of the mass flows, but reacts with some delay. Moreover, Figure 4-4 depicts the evolution of the product mass composition. The composition of the distillate is constant since the first moment, which explains the stable temperature of TIR24 at the top of the column. As was mentioned in section 3.1, the light components (BuOH and BuAc) form an azeotrope at a pressure of 25 mbar. Regarding to the bottom product, Figure 4-4 shows that the composition reaches a steady value after 5.5 h with oscillations smaller than 1 w %. When observing the behavior of the side composition, at the beginning the presence of heavy components is detected. Nevertheless, over the course of the experiment, the side composition shows merely light components. A constant side composition is observed from the sixth hour until the end of the column operation.

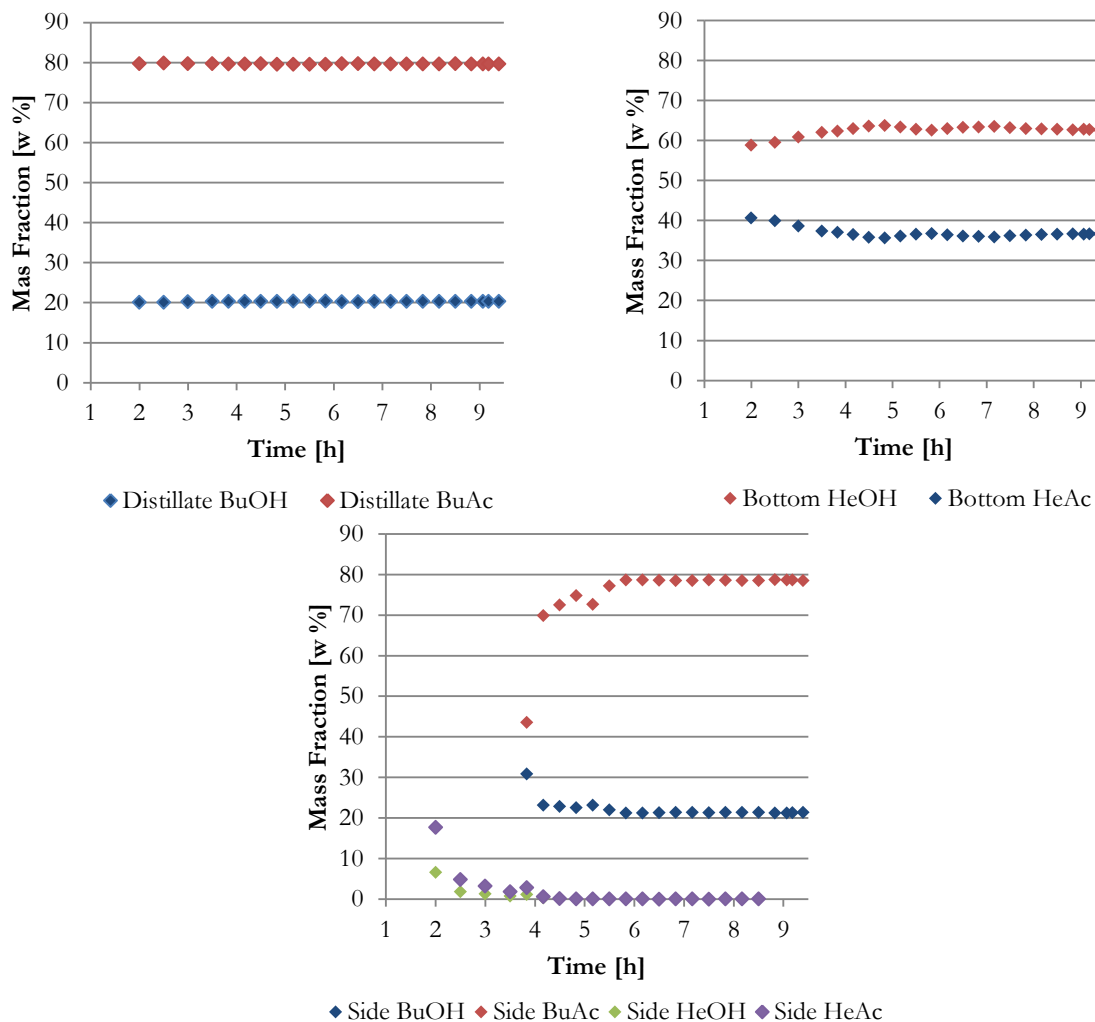


Figure 4-4 Course of the mass compositions of the product streams of the experiment TWK 99, distillate (left above), bottom (right above), side (below)

4.3.2 Steady State Data

In this section the measured values of the stationary period of the experiments are presented. For a structured interpretation and fast comparison of the experiments, the temperature profile (T-profile), the product mass flow and the composition are presented. The experiment TWK101 does not accomplish the stationary state during the operation and TWK104 is inconsistent with the mass balance results, therefore they are not included in this part.

Temperature Profile

Figure 4-5 exhibits the temperature profile of the main column and the prefractionator. The experimental values delivered by the temperature sensors are displayed together by means of a linear interpolation. The temperature profile in the prefractionator shows a maximum difference of 10 °C among all the experiments. The T-profiles of TWK100 and TWK106 are clearly shifted to highest temperatures.

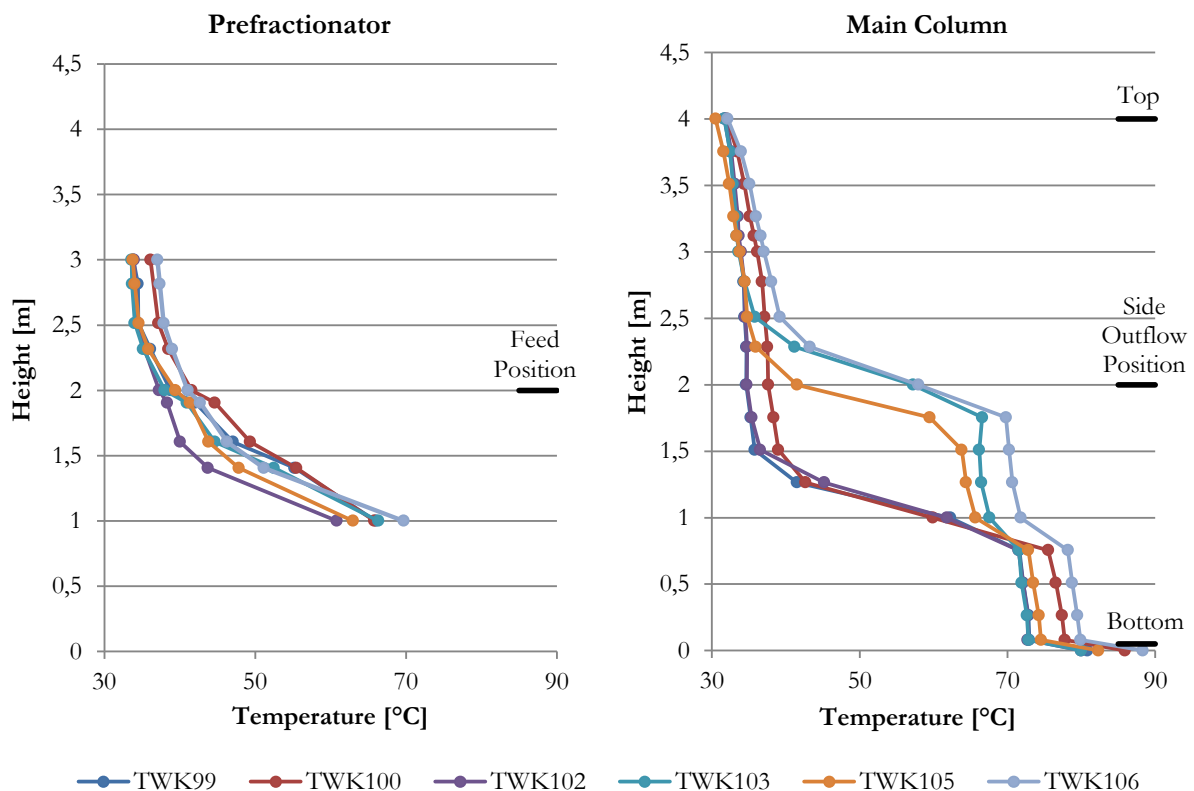


Figure 4-5 Temperature profile of the experiments TWK 99, TWK100, TWK102, TWK103, TWK105 and TWK106 in stationary state, prefractionator (left), main column (right)

Observing the main column, the greater differences among the experiments occur within the range of 1 up to 3 m (S4 and S5), being evidently strong below the side outflow (maximum

difference of 35 °C). Focusing on this zone it is possible to see that the temperature profile obeys qualitatively the same pattern in all the experiments, but the T-profiles of TWK103, TWK105 and TWK106 are displaced upwards. This implies that the separation of the light and heavy components succeeds at different heights along the RDWC. The temperature at the top of the column changes slightly among the experiments. Conversely, the temperature profiles at the bottom show differences up to 10 °C in the experiments TWK100 and TWK106.

Mass Flows

In the following section, the mass flows and the component mass flows of each experiment are presented. As Table 4-3 exhibits, TWK105 is the only experiment with high feed flow (3.7 kg/h). The other experiments have a feed flow of 1.8 kg/h.

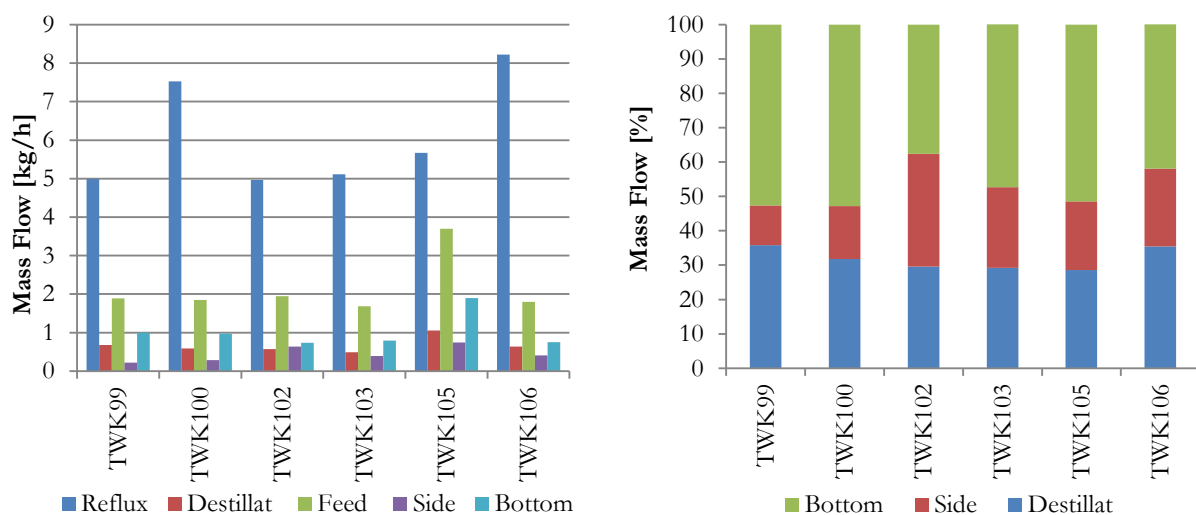


Figure 4-6 Mass flow of the experiments TWK 99, TWK100, TWK102, TWK103, TWK104 and TWK106 in stationary state, absolute values (left), relative values (right)

The left diagram of Figure 4-6 shows that the experiments with less heat power (TWK 99, TWK102 and TWK103) have a reflux around 5 kg/h. On the other hand, the reflux from TWK100 and TWK106 is over 7 kg/h. The distribution of the products streams differs within the experiments. Based on the right diagram of Figure 4-6, the distillate represents one third of the total product flow (distillate, side and bottom together), while the side stream covers a range of 12 up to 33 % of the total mass flow. Likewise, for the bottom stream the minimum percentage is 38 % and its maximum is 53 %.

Figure 4-7 exhibits the mass flow per components (BuOH, BuAc, HeOH, and HeAc). A general overview of the Figure 4-7 shows that the mass flow of the reactants changes stronger than the mass flow of the products of the reaction.

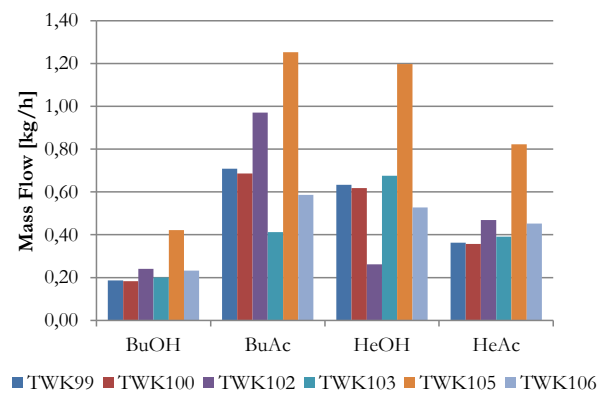


Figure 4-7 Component mass flow of the experiments TWK 99, TWK100, TWK102, TWK103, TWK104 and TWK106 in stationary state

Product Composition

Figure 4-8 illustrates the composition of the products streams. One important observation is the constant composition of the distillate, approximately 20 w % BuOH, 80 w % BuAc. The same does not occur with the bottom, which is strongly affected by the feed composition.

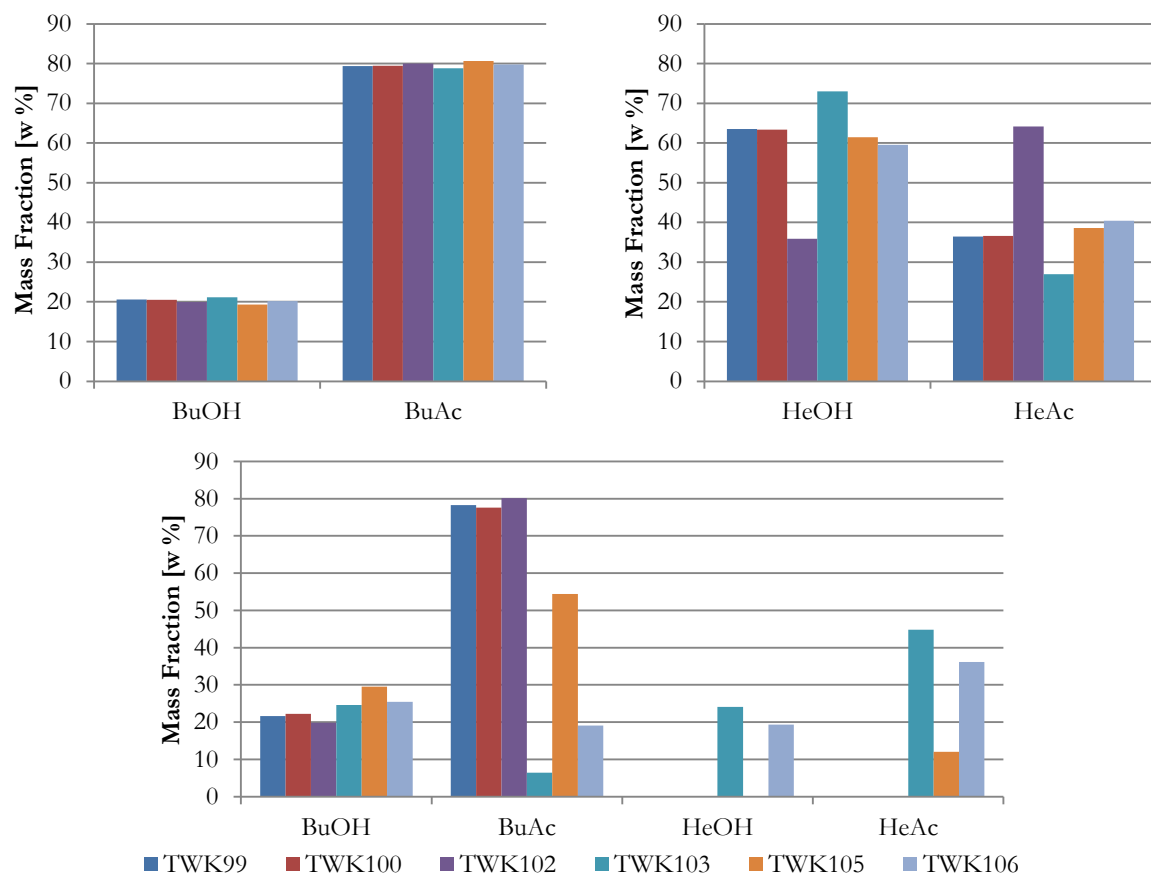


Figure 4-8 Product mass composition of the experiments TWK 99, TWK100, TWK102, TWK103, TWK105 and TWK106 in stationary state, distillate (left above), bottom (right above), side (below)

The highest deviations are exhibited by TWK102 and TWK103, which are the experiments with no equimolar feed. Regarding the composition of the side, two groups appear, one without heavy components (TWK99, TWK100 and TWK102) and one with the presence of them (TWK103, TWK105 and TWK106).

Concentration Profile

Table 4-4 presents the concentration profile of the experiments TWK99, TWK100, TWK103, TWK105 and TWK106. The sampling positions are described in section 4.1. These correspond to the first packing section (S1), the vapor distributor, the feed position and the liquid distributor at both sides of the column. As can be seen in Table 4-4, the compositions in S1 are relatively similar. TWK103 is the only experiment that exhibits different values compared to the others cases. The composition of the vapor split varies clearly throughout the experiments. In the most of the experiments, the fraction of heavy components is higher than the fraction of light components. Nevertheless, TWK106 exhibits a composition richer in light components. Furthermore, the feed position is similarly varying in respect to the composition. The mass fractions variations of BuAc, BuOH and HeOH are 7, 9 and 13.4 w % respectively.

Table 4-4 Concentration profile of the experiments TWK99, TWK100, TWK103, TWK105 and TWK106

Position	Experiment	BuAc	BuOH	HeAc	HeOH	Units
S1	TWK99	-	-	36.5	62.9	w %
	TWK100	-	-	36.8	62.7	w %
	TWK103	-	-	25.9	73.26	w %
	TWK105	-	-	38.1	61.1	w %
	TWK106	-	-	40.3	59.7	w %
Vapor Split	TWK99	11.6	5.8	44.1	38.5	w %
	TWK100	23.8	10.5	35.4	30.3	w %
	TWK103	5.3	4.6	44.2	45.2	w %
	TWK105	16.8	8.1	38.2	36	w %
	TWK106	38.2	44.6	11.4	5.4	w %
Feed	TWK99	63.1	9.2	3.1	24.2	w %
	TWK100	65.4	12.5	2.1	19.8	w %
	TWK103	62.9	12.9	1.6	22.4	w %
	TWK105	64.7	4.8	1.4	28.7	w %
	TWK106	70.1	13.8	0.7	15.3	w %
Liquid Split (Main Column Side)	TWK99	79.8	20.1	-	-	w %
	TWK100	78.3	21.6	-	-	w %
	TWK103	77.6	22.4	-	-	w %
	TWK105	81.1	18.9	-	-	w %
	TWK106	76.4	23.6	-	-	w %
Liquid Split (Prefractionator Side)	TWK99	79.6	20.3	-	-	w %
	TWK100	78.3	21.6	-	-	w %
	TWK103	77.3	22.7	-	-	w %
	TWK105	80.6	19.4	-	-	w %
	TWK106	76	24	-	-	w %

On the other hand, the composition of the samples from the liquid split are approximately constant, there is no significant difference of the composition in respect to the place where the sample is taken (prefractionator or main column). Besides the liquid split composition is approximately the same as the distillate.

4.4 Experiment Evaluation

As chapter 4.3 shows, the experiments performed differ clearer from one another. Taking this into account, the measured values are evaluated to provide a better understanding of the process and each experiment. In this section, the criteria to determine the steady state of every experiment are introduced at the beginning. In the next step, a structured comparison of the steady state experiments is realized.

4.4.1 Steady State Tests

A certain process can be considered stationary if there is no change of the state variables with the time. Considering this, the temperature, pressure, mass flows and composition are evaluated during the operation in order to determine if the experiments performed fulfill this requirement.

The column pressure is controlled by the vacuum pump and stays constant during the course of every experiment. The temperature and mass flows are measured by WinErs Professional every 0.1 s. Hence, the saved data is available to visualize the variation of these variables. Finally, the GC analysis provides the data about the distillate, bottom and side composition during the operation. The strategy for confirming the steady state begins with the analysis of the product compositions, since it allows delimiting faster the time periods that could represent the stationary state. The criterion for asserting that the composition is in steady state is based on the variation of the composition with the time, described by Eq. 4-1.

$$\frac{\Delta w_{i,j} \%}{\Delta t} \quad \text{Eq. 4-1}$$

$$i=\text{stream}, j \in [\text{BuOH}, \text{BuAc}, \text{HeOH}, \text{HeAc}]$$

As soon as the product composition stabilizes, the variation decreases approximately to zero. In that case, it is possible to say that the variables are constant. Figure 4-9 shows the variation of the mass fractions from each product stream of the experiment TWK99. In Annex A.2, selected measured values of the mass fractions of every stream and component are presented. The displayed variations are comprised from the moment the first side product sample is taken. As it was mentioned in the previous section of this chapter, the distillate composition is relatively

constant during the course of each experiment and even among them. This statement is once more confirmed by the calculus of the variation shown in Figure 4-9. On the other hand, the bottom and side mass fractions show a different behavior. Both start with high variations (the side stream stronger), but with the progress of the operation trend to zero. In this way, the promising steady state period is visually delimited and confirmed by the results of the temperature and mass flows.

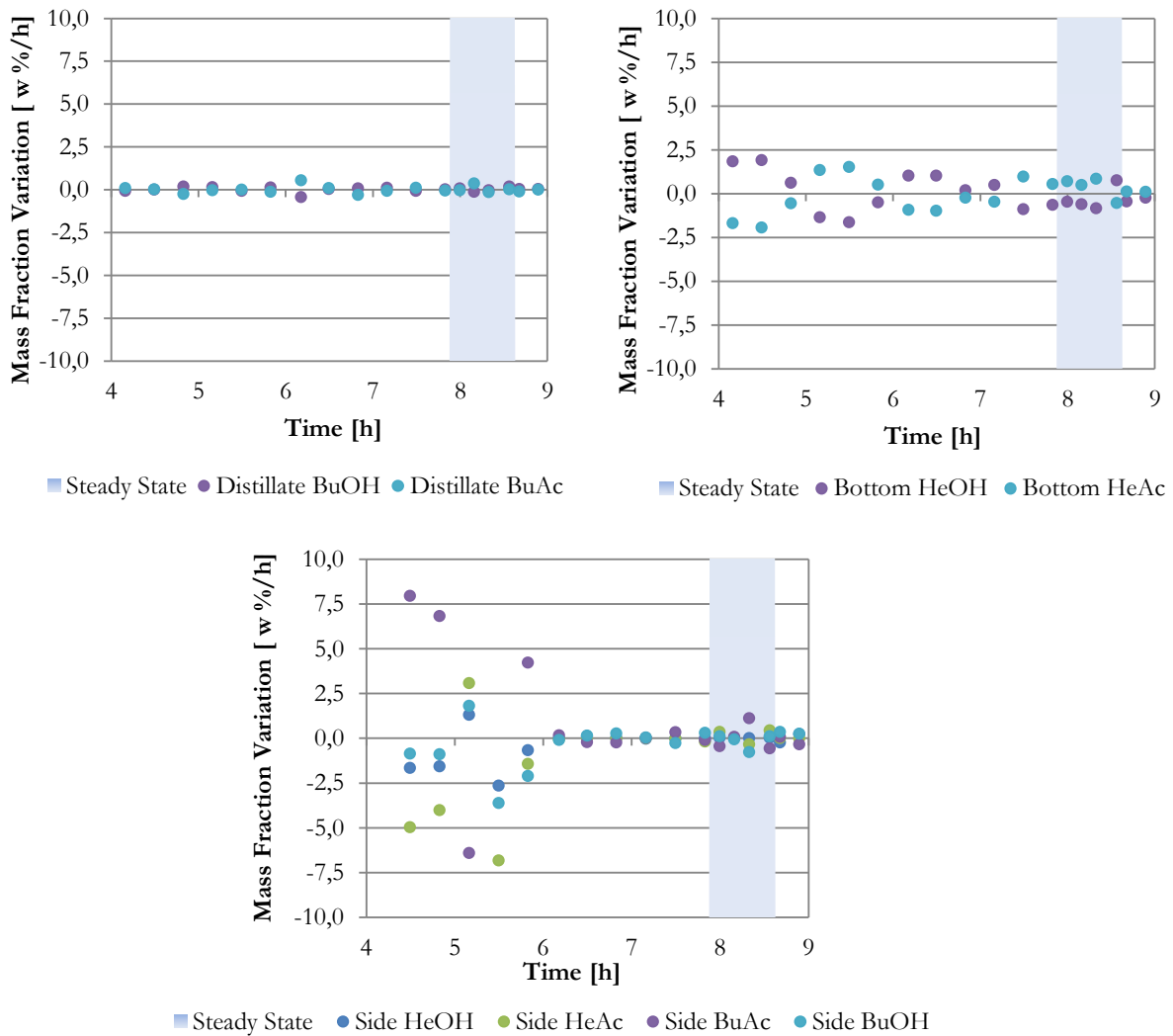


Figure 4-9 Product composition variation of the experiment TWK 99, distillate (left above), bottom (right above), side (below)

Figure 4-10 results from the application of the same criterion to the mass flows. As shown in Figure 4-10, there is no pattern in the variation of the distillate, reflux and bottom flows. The sources of these oscillations can be attributed to the instrumentation and the process itself. Taking this into account, a second criterion is applied: the sum of the variation must be

approximately zero. This means that the positive and negative variations are equally distributed and therefore the process is in steady state.

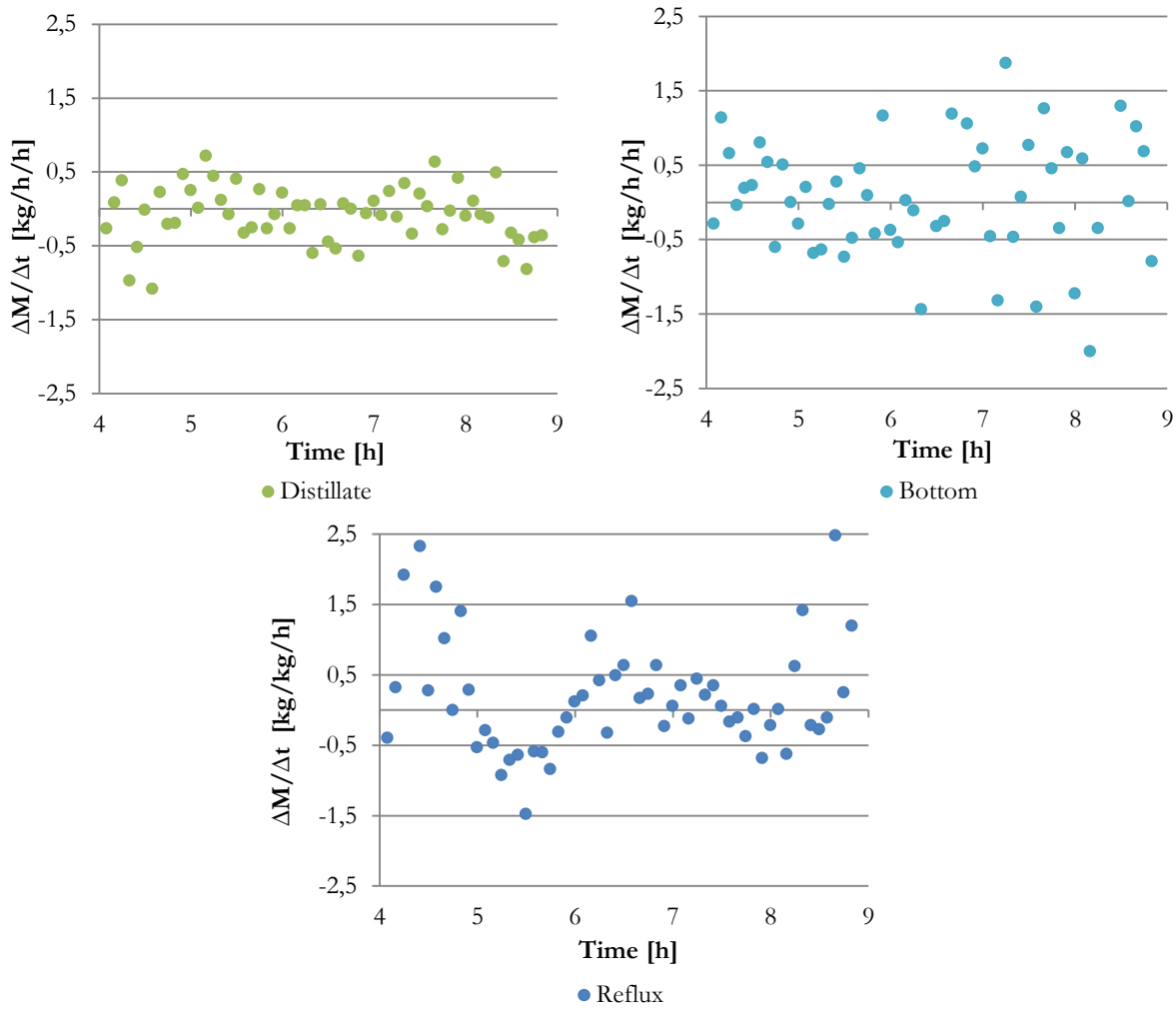


Figure 4-10 Mass flow variation of the experiment TWK 99, distillate (left above), bottom (right above), reflux (below)

In order to calculate the variations faster, the values are averaged every 5 minutes and subtracted from the corresponding previous value, (see Eq. 4-2 until Eq. 4-4). This criterion is also applied for the temperature. Once, the possible steady state period is identified, the subtraction between the start and end point is calculated.

$$\frac{\Delta M}{\Delta t} = \frac{M_i - M_{i-1}}{t_i - t_{i-1}} \quad \text{Eq. 4-2}$$

$$t_i - t_{i-1} = \frac{5}{60} [h] \quad \text{Eq. 4-3}$$

$$\sum_i^I \frac{\Delta M_i}{\Delta t} \approx 0 \quad \text{Eq. 4-4}$$

Next, the results are exhibited to show the experiments that have achieved the steady state. In the case of the temperature, one temperature sensor from every section is considered. Table 4-5 shows each experiment with its preliminary steady state period and the results of the previously explained criterial for the temperature.

Table 4-5 Temperature variation of the experiments during the preliminary steady state

Experiments	Time	T04	T09	$T_{\text{end}} - T_{\text{start}} [^{\circ}\text{C}]$				T23	T04	T09	$\sum(\Delta T_i / \Delta t_i) [^{\circ}\text{C}/\text{h}]$			
				T12	T14	T19	T23				T12	T14	T19	T23
TWK99	16:01-16:56	0,16	0,16	-0,13	0,02	-0,06	-0,05	-1,26	-0,44	-0,49	-0,44	-0,67	-0,56	
TWK100	12:40-13:20	0,24	-0,97	0,21	-0,24	0,26	0,23	3,36	-9,67	2,46	-1,99	3,10	2,94	
TWK101	12:50-13:20	0,05	-0,40	-4,65	0,96	0,05	-0,14	-0,71	4,07	61,96	-1,51	-0,52	-0,32	
TWK102	12:20-13:20	-0,06	-0,08	-0,09	-0,01	-0,09	-0,03	-0,76	-0,97	-1,13	-0,13	-1,07	-0,31	
TWK103	12:25-12:55	0,19	0,21	0,30	0,16	0,39	0,04	2,06	2,88	3,36	1,44	3,31	0,49	
TWK105	15:40-16:10	0,07	0,02	-0,61	0,04	-0,19	0,01	-0,12	0,12	-6,50	0,24	-2,41	0,24	
TWK106	14:00-14:40	0,02	-0,12	0,70	-0,18	0,49	-0,04	1,76	1,18	3,36	0,67	3,71	1,24	

As it can be noticed in the experiment TWK101, T12 exhibits a variation of 4.65 °C and an accumulative value of 62 °C/h during the selected period. This implies that there is a sustained raise of the temperature in this section, as Figure 4-11 confirms. In view of that, the experiment TWK101 does not fulfill the requirements of the stationary state. The other experiments show good temperature stability during the preselected periods; the differences between start and end are less than 1 °C. Additionally, the most of the variation sums are within the range of 1 up to 3 °C.

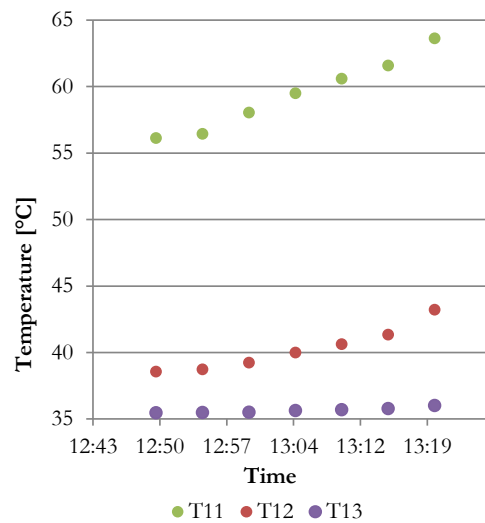


Figure 4-11 Measured temperature of the section 5 during the preliminary steady state of the experiment TWK101

Moreover, Table 4-6 shows the variation of the mass flows. From all the experiments, the 77 % of the differences between the initial and final value are within the range of 0.01 – 0.06 kg/h, which is close to the instrumentation error. Furthermore, in relative terms, the cumulative mass flow variation is high at least in one stream in every experiment. Nevertheless, this could be explained by the pumps performance, since they present constantly offset. By analyzing the course of the mass flow of each experiment it is possible to observe permanent oscillations around a constant value. Therefore, for confirming the steady state it is enough that the differences between initial and final point are close to the instrumentation tolerance.

Table 4-6 Mass flow variation of the experiments during the preliminary steady state

Experiments	Time	$M_{end}-M_{start}$ [kg/h]					$\sum(\Delta M_i/\Delta t_i)$ [kg/h/h]				
		Reflux	Distillate	Feed	Side	Bottom	Reflux	Distillate	Feed	Side	Bottom
TWK99	16:01-16:56	-0,03	0,03	-0,06	0,01	-0,03	-0,32	0,26	-0,74	0,17	-2,18
TWK100	12:40-13:20	0,23	-0,10	-0,07	0,00	0,02	1,61	-1,67	-0,10	0,00	0,64
TWK101	12:50-13:20	0,04	-0,02	0,00	0,00	-0,01	-0,01	0,78	-0,13	0,04	0,44
TWK102	12:20-13:20	-0,16	0,04	0,01	0,00	0,00	-1,97	0,43	0,07	0,02	0,02
TWK103	12:25-12:55	0,13	0,00	0,02	-0,09	-0,01	1,26	0,02	-0,06	-1,06	0,12
TWK105	15:40-16:10	0,05	-0,01	0,04	0,00	0,09	0,49	-0,24	1,06	0,06	0,36
TWK106	14:00-14:40	0,02	-0,02	-0,11	-0,01	-0,13	0,23	-0,17	0,48	0,00	0,55

Finally, Table 4-7 presents the absolute change of the mass flow composition during the preselected time. The results indicate that the differences are below 0.13 % for the distillate and about 1 % for the bottom and side streams.

Table 4-7 Mass composition variation of the experiments during the preliminary steady state

Experiments	Time	$w_{end} \% - w_{start} \%$ [kg/kg]							
		Distillate		Bottom			Side		
		BuAc	BuOH	HeAc	HeOH	HeOH	HeAc	BuAc	BuOH
TWK99	16:01-16:56	0,01	-0,01	0,51	-0,54	0	-0,06	0,09	-0,03
TWK100	12:40-13:20	-0,01	-0,03	0,33	-0,34	0	0	-0,38	0,45
TWK101	12:50-13:20	0,02	-0,02	0,29	-0,26	0	0	-0,1	0,1
TWK102	12:20-13:20	0,02	-0,02	0,06	-0,09	0	0	-0,1	0,2
TWK103	12:25-12:55	0,13	-0,13	-1,42	1,39	-1,33	0,23	0,74	-1,33
TWK105	15:40-16:10	-0,03	0,03	0,09	-0,31	-0,71	-1,6	2,12	0,18
TWK106	14:00-14:40	0,02	-0,03	0,14	-0,18	0,94	0,9	0,2	-2

In view of the presented results, the following experiments are valid results as steady state operation: TWK99, TWK100, TWK102, TWK103, TWK104, TWK105, and TWK106. TWK101 is the only experiment that does not reach the stationary state, due to the unstable temperature behavior. However, the high successful rate confirms that the startup strategy is valid to operate the RDWC.

4.4.2 Experiment Comparisons

The variation of the liquid split, heating power, feed composition and feed flows had as goal to create a set of different process behaviors that can challenge the quality of the model to predict correctly the reaction, separation, pressure drop and liquid and vapor flow traffic. However, all the expected variations and outputs cannot be foreseen. Taking this into account, for the purpose of understanding the process behavior of the RDWC, the experiments are compared by forming groups of experiments. In each comparison, the expected behaviors are contrasted with the experimental results

TWK99/TWK100

The most important variations among these experiments are the heat power and the reflux ratio. The heat power of TWK100 is 40 % higher than the one applied to TWK99. Likewise, the reflux ratios are 7.37 and 12.84 for the experiments TWK99 and TWK100 respectively. As Table 4-3 shows, the experiments TWK99 and TWK100 have a similar feed flow with an equimolar composition. The distribution of the reflux along the sides of the column (liquid split) is the same for both of them, 35 % of the reflux goes to the prefractionator and 65 % goes to the main column. The distribution of the product streams is approximately equal in both cases with a slight difference in the side and distillate streams. The percentages are presented in Table 4-8.

Table 4-8 Product stream distribution of the experiments TWK99 and TWK100

Experiment	Distillate	Side	Bottom	Units
TWK99	36	12	53	%
TWK100	32	15	53	%

Considering the operating parameters, increased heat power should increase the pressure drop and the temperature along the column. In view of this, the reaction process can be affected by the change in the reaction kinetics and concentration profile. Furthermore, the increase of the reflux ratio in TWK100 should improve the separation process.

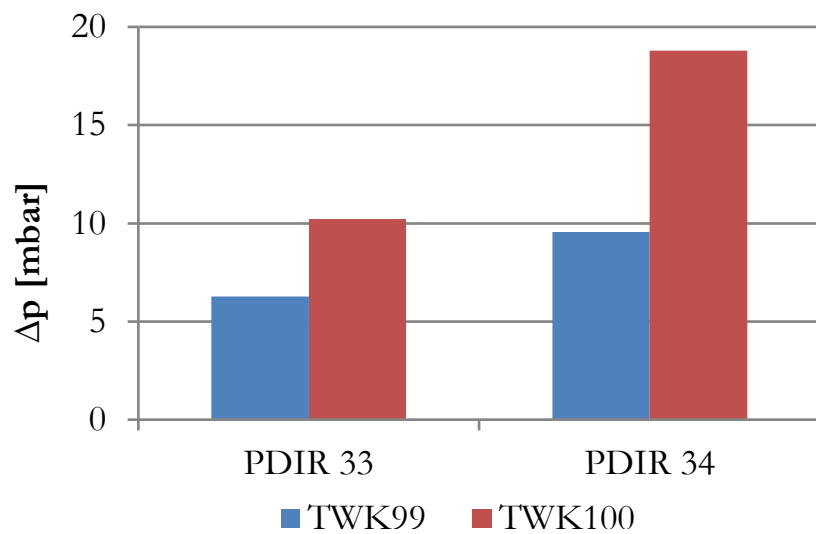


Figure 4-12 Pressure drop of the experiments TWK99 and TWK100

As is expected, the pressure drop is clearly bigger in TWK100. The value given by the sensor PDIR 34 (between top and bottom) shows that the pressure drop is up to two times bigger in TWK100 compared to TWK99, while the pressure drop between top and feed (PDIR 33) is 66 % higher in TWK100 compared to TWK99. The results are exhibited on Figure 4-12.

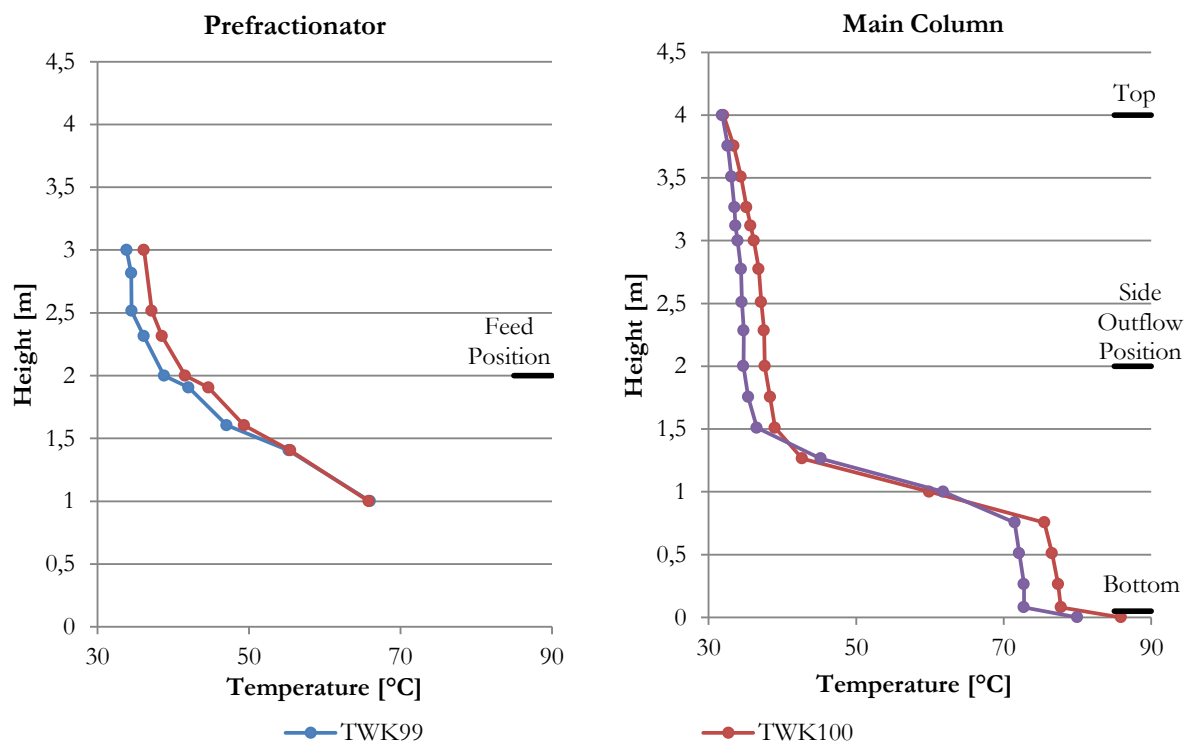


Figure 4-13 Temperature profiles of the experiments TWK99 and TWK100, prefractionator (left), main column (right)

Figure 4-13 illustrates the temperature profile of both experiments. The results agree with the expected increase of the temperature in TWK100. In the prefractionator, the temperatures from TWK100 are up to 3 °C higher, while in the main column the differences reach up to 4 °C. Nevertheless, the temperatures at the height of 1 – 1.5 m are similar in the prefractionator and the main column, which cannot be elucidated with the effect of the heat power only.

The reaction differences are analyzed by means of the reactant conversion, which is calculated for both reactants via Eq. 4-5. Besides, an overall conversion is calculated by taking the total moles that react divided by the sum of the reactant moles which enter to the column (see Eq. 4-6).

$$\chi_i = \frac{n_{i,in} - n_{i,out}}{n_{i,in}} * 100 \quad \text{Eq. 4-5}$$

$$\chi_{overall} = \frac{\sum_i^N (n_{i,in} - n_{i,out})}{\sum_i^N n_{i,in}} * 100 \quad \text{Eq. 4-6}$$

Contrary to the expectations, the reactant conversions do not show significant differences. As Table 4-9 shows, the reactant conversion for both reactants is approximately 29 mol %.

Table 4-9 Reactant conversions of the experiments TWK99 and TWK100

Experiment	χ_{BuAc}	χ_{HeOH}	$\chi_{overall}$	Units
TWK99	29.2	28.9	29.1	mol %
TWK100	29.0	29.5	29.3	mol %

Figure 4-14 exhibits the concentration profile of both experiments. The measured values are connected to visualize better the course of the components along the column. First, the compositions at the top, bottom and side outflow are the same. Observing the main column, the separation of the light components from the heavy ones occurs almost at the same height (1 m). In the prefractionator the reactants are more concentrated where the feed enters, which is appropriate to promote the product formation. However, with the figure, is not possible to see at which exact position the reactants are pulled away from the reactive zone. Moreover, the curves of the product are according to the theory; the heavy product (HeAc) becomes richer in the lower section of the reactive zone, while the light product (BuOH) increases its mass fraction in the upper section. Nevertheless, considering the azeotrope formation, a further concentration increase of these components in the top and bottom is limited.

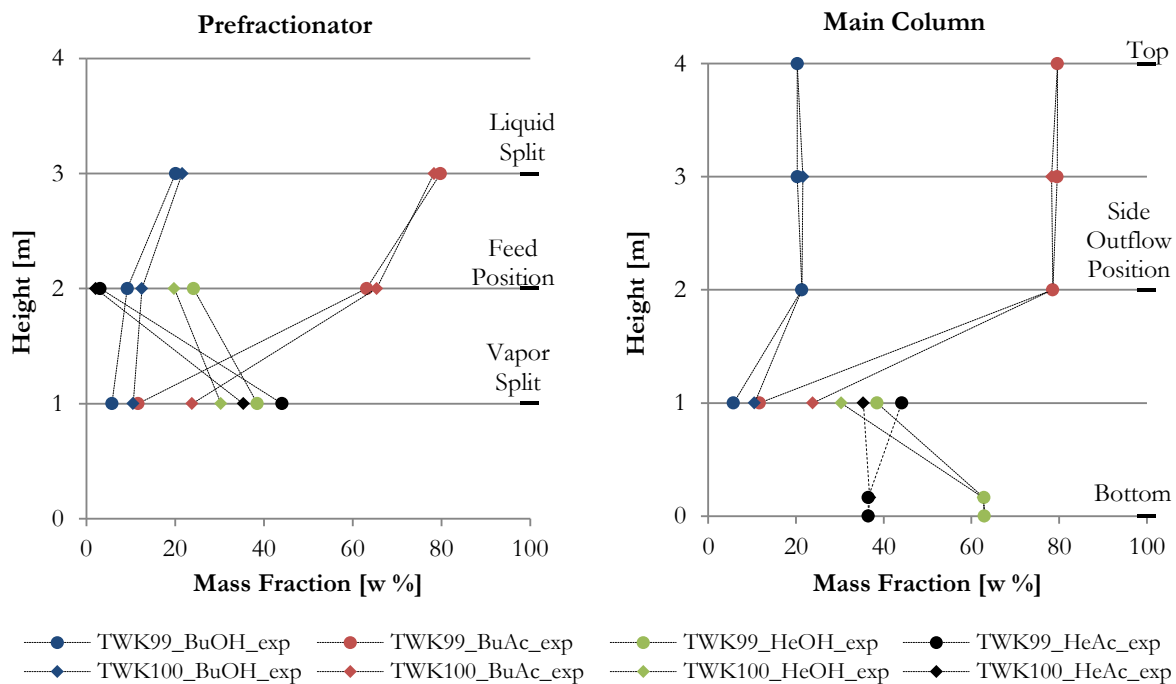


Figure 4-14 Concentration profiles of the experiments TWK99 and TWK100, prefractionator (left), main column (right)

Although the concentration profiles show some differences, the little information along the column does not allow asserting how well or bad are the reaction and separation processes in each experiment, but these help to visualize empirically the basics of the RDWC.

Summarizing, both the reaction and separation process do not agree with all the expected results. In fact, these two experiments provide information about, how different behavior along the RDWC can render similar outputs, such as reactant conversion and product compositions.

TWK99/TWK102/TWK103

The experiments TWK99, TWK102 and TWK103 are grouped to analyze mainly the effect of the feed composition in the reaction process. TWK 99 has an equimolar feed composition (54 w % BuAc, 46 w % HeOH). On the other hand, the feed of TWK102 is rich in butyl acetate (70 w % BuAc), while TWK103 contains more hexanol (57 w %). Besides, other operating conditions are also different in these experiments. The liquid split is 0.35, 0.40 and 0.45 for TWK99, TWK102 and TWK103 respectively. The product mass flow distribution is also different (see Table 4-10). The feed flow and heat power are similar, as Table 4-3 shows.

Table 4-10 Product stream distribution of the experiments TWK99, TWK102 and TWK103

Variable	Distillate	Side	Bottom	Units
TWK99	36	12	53	%
TWK102	30	33	38	%
TWK103	29	23	47	%

Taking into account the excess of reactants in the experiments TWK102 and TWK103, an increase in the limiting reactant conversion is expected. Besides, considering the feed composition, the component mass flows of the light components should be greater in TWK102, while in TWK103, the greatest share should represent the heavy components. Finally, the effect of the liquid split can be confused with the other variations. These effects should be clearly reflected in the temperature and concentration profiles.

Once again, the reaction is analyzed by means of the reactant conversion. The results are presented in Table 4-11. As it was mentioned above, the expected effect in the reaction is observable in the experimental results. The reactant conversion of the educts with lower molar fraction increases as is expected, but it is interesting that the conversion of the second reactant remains constant. Summarizing, due to the excess of reactants in the feed of TWK102 and TWK103, the reaction shifts to the products and the overall reactant conversion increases in both experiments. This effect is stronger in TWK102, since the BuAc reactant is twice as much the other reactant, while the ratio HeOH/BuAc is 1.5 in TWK103. The increase in the overall conversion is 8 mol % in TWK102 and 6 mol % in TWK103 respect to TWK99.

Table 4-11 Reactant conversions of the experiments TWK99, TWK102 and TWK103

Experiment	χ_{BuAc}	χ_{HeOH}	χ_{overall}	Units
TWK99	29.2	28.9	29.1	mol %
TWK102	28.0	55.9	37.3	mol %
TWK103	43.3	29.5	34.8	mol %

Table 4-12 shows the distribution of the light and heavy components product mass flows. As expected, the results indicate that the column possesses more BuAc and BuOH in TWK102 and more HeAc and HeOH in TWK103.

Table 4-12 Distribution of the light and heavy components of the experiments TWK99, TWK102, TWK103

Experiment	BuAc + BuOH	HeAc + HeOH	Units
TWK99	47	53	w %
TWK102	62	38	w %
TWK103	36	64	w %

Figure 4-15 illustrates the temperature profile of these three experiments. In the prefractionator, the greater differences are in the zone of 1 up to 2 m. TWK102 presents a lower temperature profile compared to TWK99 and TWK103, which have temperatures profiles with slight differences. The distinct T-profiles can confirm the reactant conversion differences. Nevertheless, it is not possible to assert which is the cause and consequence for these behaviors, since the reaction is affected by the temperature, but at the same time the reaction process affects the concentration profile and therefore the temperature profile as well. Furthermore, in this zone there are no sampling points in between. Thus, it is not possible to display a more detailed concentration profile of the prefractionator for observing these differences. In relation to the main column, the T-profiles are very similar for TWK99 and TWK102 and clearly cooler compared to TWK103. The greater differences exhibited by TWK103 are where the side outflow takes place, as Table 4-13 shows, the side composition of TWK103 is rich in heavy components, which shows the known dependency between concentration and temperature.

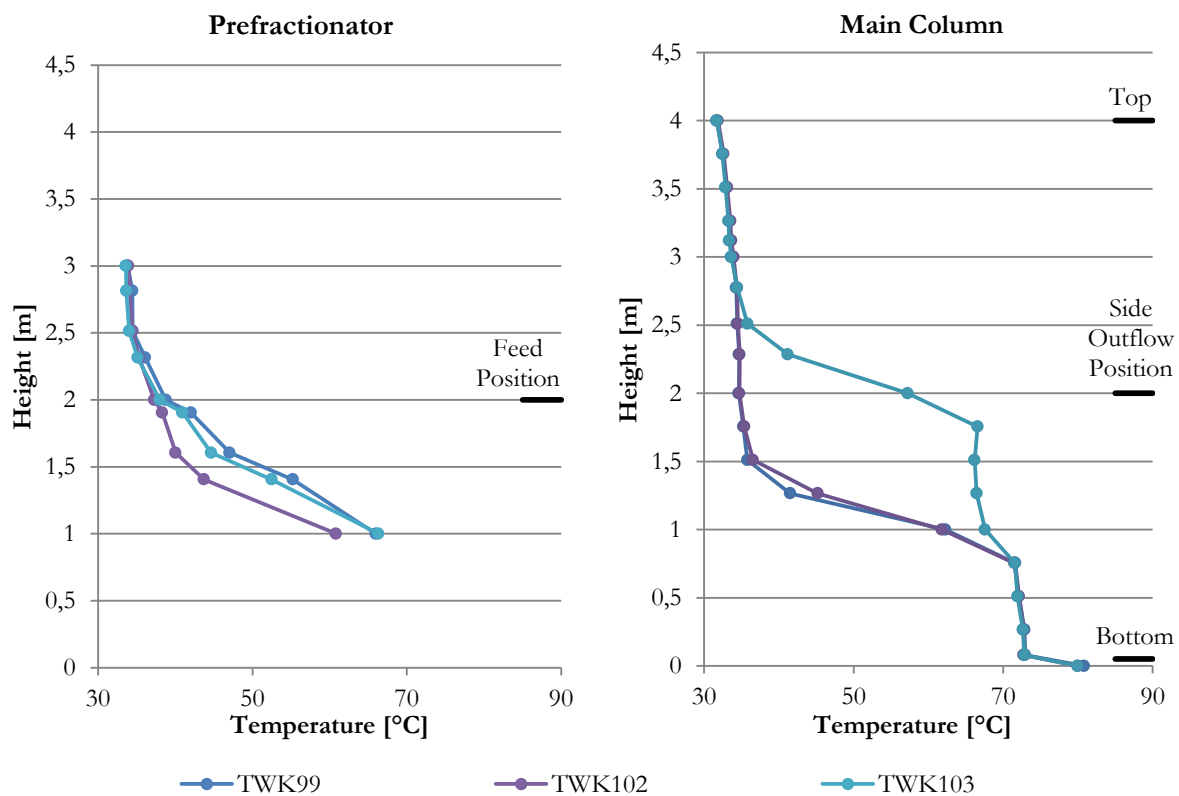


Figure 4-15 Temperature profiles of the experiments TWK99, TWK102 and TWK103 prefractionator (left), main column (right)

In conclusion, the results agree with the expected change in the reactant conversion and temperature profile. Nevertheless, the exact behavior and variable dependencies along the

reactive zone cannot be fully explained. However, the further model validation can help to understanding the process.

Table 4-13 Side stream composition of the experiments TWK99, TWK102 and TWK103

Experiment	BuAc	BuOH	HeAc	HeOH	Units
TWK99	78.24	21.61	0.07	0.00	w %
TWK102	80.14	19.82	0.00	0.04	w %
TWK103	6.45	24.64	44.79	24.12	w %

TWK100/TWK105

The experiments TWK100 and TWK105 are compared to analyze the drastic change of the different ratio between the catalyst mass and the feed, since the feed is twice as high in TWK105 compared to TWK100. Moreover, both experiments have the same feed composition and a similar heat power. On the other hand, the liquid split is 0.35 in TWK100 and 0.40 in TWK105. As Table 4-10 shows the product mass flow distribution is moderately different.

Table 4-14 Product stream distribution of the experiments TWK100 and TWK105

Variable	Distillate	Side	Bottom	Units
TWK100	32	15	53	%
TWK105	29	20	51	%

Considering the operating condition, the reactant conversion should decrease in TWK105, because of the smaller amount of catalyst mass per reactant mol. The effect of the liquid split cannot be completely explained with this comparison, due to the probable changes in the reaction process.

Table 4-15 Reactant conversions of the experiments TWK100 and TWK105

Experiment	χ_{BuAc}	χ_{HeOH}	χ_{overall}	Units
TWK100	29.0	29.5	29.3	mol%
TWK105	34.6	32.7	33.6	mol%

Contrary to the expectations, the results of Table 4-15 show that the overall conversion increases 5 mol % in TWK105. Figure 4-16 shows the prefractionator temperature profiles of both experiments in order to provide more information about this result. As Figure 4-16 shows, TWK105 presents lower temperatures compared to TWK100. Considering this, the conversion increase can be related to a lower temperature profile. Nevertheless, it cannot be stated that lower temperatures improve the reactant conversion. For example the comparison between TWK99 and TWK100 shows that a different temperature profile in the prefractionator does not significantly affect the reactant conversion.

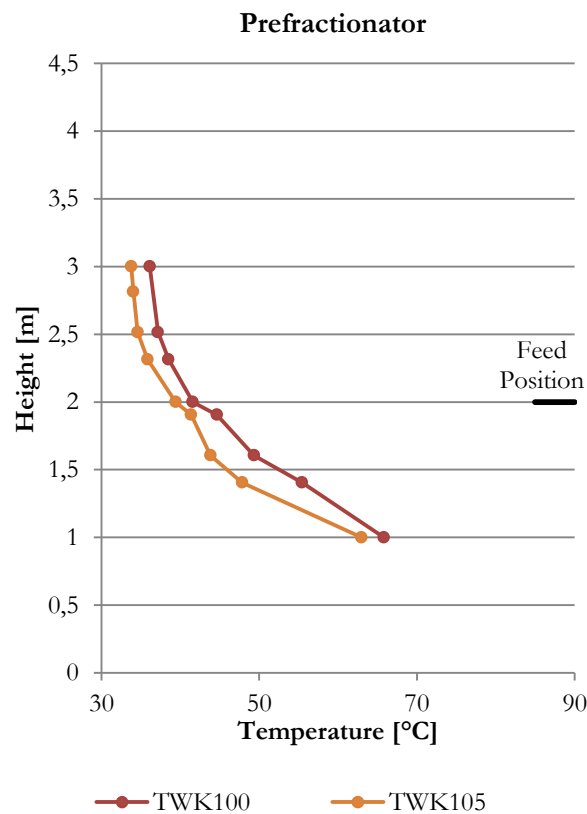


Figure 4-16 Prefractionator temperature profile of the experiments TWK100 and TWK105

In conclusion, the increase of the feed flow does not worsen the reactant conversion under these conditions. In view of this, it is possible to assume that the catalyst is not utilized at maximum efficiency in the experiments and therefore the reaction is not necessarily worse. However, this does not explain the increase of the reactant conversion. One possible explanation can be attributed to the liquid volume increase in the reactive zone, due to the feed raise, which facilitates the contact of the reactants and therefore improves the reaction, but this statement should also take into consideration the increase of the liquid split in TWK105.

TWK100/TWK106

The experiments TWK100 and TWK106 are compared to visualize how the component distribution along the column affects the process behavior. These experiments show variations related to the liquid split and product stream distribution. In TWK100 35 % of the reflux goes to the prefractionator, while in TWK106 the reflux is divided in equal fractions in the prefractionator and main column. Moreover, as Table 4-16 exhibits, the distribution of the side and bottom are very different in both experiments. As Table 4-3 shows, the heat power, feed flow and feed composition are similar for both experiments.

Table 4-16 Product stream distribution of the experiments TWK100 and TWK106

Experiment	Distillate	Side	Bottom	Units
TWK100	32	15	53	%
TWK106	35	23	42	%

Summarizing, in TWK106 the main column receives less reflux and the side flow increases at the expense of the bottom stream. In view of this, it can be expected that the temperature profile in the main column is hotter compared to TWK100. Moreover, the T-profile in the prefractionator of TWK106 should be cooler in comparison to TWK100. Figure 4-17 illustrates the temperature profiles of these experiments. The contrasts are notorious. The temperature difference reaches even a value of 30 °C in the main column at the height of 1.5 m. In TWK100, the greater reflux in the main column raises the concentration of light components (BuAc and BuOH) in this section, which reduces the temperature. On the other hand, the temperature in the prefractionator is cooler in TWK106. Nevertheless, this cannot be attributed to the reflux distribution (liquid split) only, since the reaction process takes greater relevance in this section.

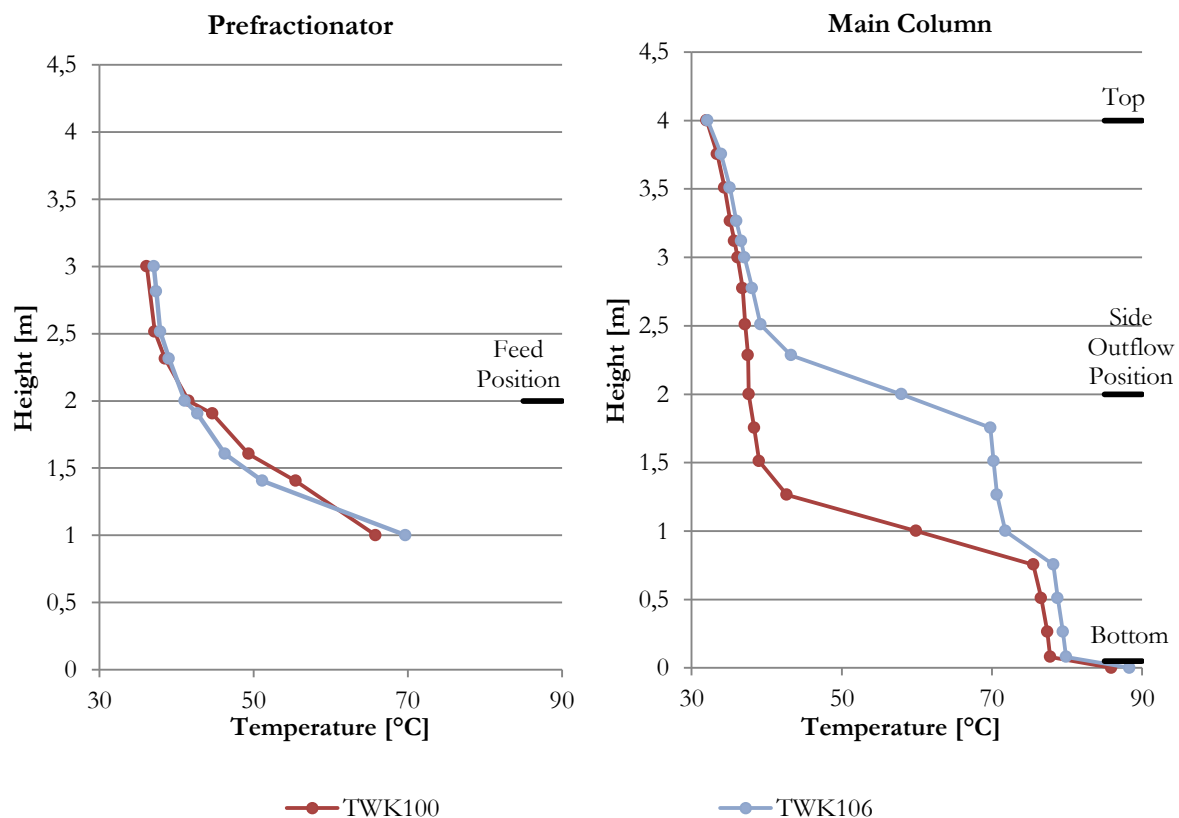


Figure 4-17 Temperature Profiles of the experiments TWK100 and TWK106, prefractionator (left), main column (right)

An analysis of the reactant conversion shows significant differences between these two experiments. As Table 4-17 presents, the overall conversion in TWK106 is 8.8 mol % higher than the one achieved in TWK100. Taking this into account, the differences in the prefractionator temperatures are also connected to this increase in the reactant conversion.

Table 4-17 Reactant conversions of the experiments TWK100 and TWK106

Experiment	χ_{BuAc}	χ_{HeOH}	χ_{overall}	Units
TWK100	29.0	29.5	29.3	mol %
TWK106	38.3	37.8	38.1	mol %

In view of the results, the liquid split has an unexpected effect in the reactant conversion. This can be elucidated with two considerations. In TWK100, the most of the reflux goes to the main column, while in TWK106 the reflux is equally distributed, and therefore there is more liquid volume in the prefractionator, which helps to the reactants contact. Besides, the composition in the liquid split is mainly BuAc (80 w %). Considering this, more reactants than product are returned to the reactive zone, which shifts the equilibrium to the product formation.

4.5 Summary

The collected data from the performed experiments allow a comprehensive analysis of the RDWC operating. The values measured during the whole experiment allow the description of the dynamic behavior and the steady state start evaluation. Particularly in this work, six successful steady state experiments are presented and analyzed. The experiments TWK99, TWK100, TWK101, TWK102, TWK105 and TWK106 fulfill the steady state condition. As section 4.3 shows, the analyzed experiment create a wide set of process behaviors. Taking this into account, such as was planned, the simulation model can be evaluated under different operation conditions by means of the generated experimental results. As can be read in section 4.3.2, the generated temperature profiles, product compositions, component mass flows, reactant conversion and pressure drop were successfully varied. Table 4-18 summarizes the temperature profile, mass flows, product composition, pressure drop and reactant conversion of the experiments that achieved the steady state.

Table 4-18 Experiment Results Summary

Variable	TWK99	TWK100	TWK102	TWK103	TWK105	TWK106	Units
Temperatures							
TIR01	80.8	85.9	80.0	80.0	82.3	88.3	°C
TIR07	55.2	55.4	43.7	52.5	47.8	51.1	°C
TIR13	35.2	38.3	35.4	66.6	59.4	69.8	°C
TIR14	38.8	41.6	37.3	38.0	39.4	41.1	°C
TIR19	34.7	37.5	34.8	41.2	35.9	43.2	°C
TIR24	33.4	35.1	33.5	33.2	32.9	36.0	°C
Mass Flows							
Distillate	0.68	0.59	0.57	0.49	1.05	0.64	kg/h
Reflux	4.99	7.52	4.97	5.11	5.67	8.23	kg/h
Bottom	1.00	0.97	0.73	0.80	1.90	0.75	kg/h
Side	0.22	0.28	0.64	0.39	0.74	0.41	kg/h
Product Composition							
W Distillate, BuAc	79.7	79.3	80.0	78.8	80.7	79.8	%
W Bottom, HeOH	63.0	63.4	35.9	73.0	61.9	59.5	%
W Side, BuOH	21.3	22.3	20.2	24.6	29.5	25.5	%
W Side BuAc	78.6	77.2	79.8	6.4	54.4	19.1	%
W Side, HeOH	-	-	-	24.1	4.0	19.3	%
W Side, HeAc	-	-	-	44.8	12.1	36.1	%
Pressure Drop							
PDIR33	6.1	10.3	6.1	5.7	8.6	12.6	mbar
PDIR34	9.2	18.4	9.5	8.7	14.4	23.7	mbar
Reactant Conversion							
χ_{BuAc}	29.2	29.5	28.0	43.3	34.6	38.3	mol%
χ_{HeOH}	28.9	29.0	55.9	29.0	32.7	37.8	mol%

Moreover, the particular experiment comparisons provide relevant information about the reaction and separation processes of the RDWC.

As section 4.4.2 presents, the different experiment comparisons help to visualize empirically the basics of the RDWC. The increase of the heat power in TWK100 is clearly reflected in an increase of the pressure drop and temperature. Nevertheless, compared to the experiment TWK99, which has less heat power, the reactant conversion and product compositions are very similar. Moreover, the excess of reactants in the experiments TWK102 and TWK103 causes an overall reactant conversion increase compared to the experiment TWK99, which has equimolar feed. A remarkable result is the increase of the reactant conversion in experiment TWK105, although the smaller amount of catalyst mass per reactant mol, which implies that the increase of the feed flow does not worsen the reactant conversion under the applied conditions. As section 0 indicates, a possible explanation can be attributed to the liquid volume increase in the reactive zone, due to the feed raise, which facilitates the contact of the reactants and therefore improves the reaction. Another important result is the conversion increase in TWK106, which can be attributed to the reactant contact improvement, due to the increase of liquid volume in the prefractionator by means of a liquid split change. Additionally, the composition in the liquid split

is mainly BuAc (80 w %). Considering this, more reactants than product are returned to the reactive zone, which shifts the reaction equilibrium to the product formation.

With the generated experimental data, the simulation model can be validated within a larger range of process behaviors. In view of the above, the performed experiments fulfill the goals of the present work. As can be inferred from the presented results, the exact behavior and variable dependencies along the column cannot be fully explained. Therefore, the further model validation can help to understanding the process.

5 Model Validation

In this chapter, a comprehensive study on the quality of the simulation model is presented. The major assessment criterion is the congruence to experimental data. Firstly, the method of performing the simulation and their results are depicted. The second section presents the quality of the model, which is evaluated by means of comparisons of the relevant variables of the reactive and separation process, such as component mass flows, stream compositions and temperature profile. In addition, the third subsection analyzes the disagreements between simulation/experiment identifying the probable causes. Through this analysis, the operating parameters with observable effect in the model quality are examined by a sensitive analysis. Finally, to verify the plausibility of relevant model assumptions, a simulation study of the heat loss sub model is carried out.

5.1 Simulations

For a detailed model validation, simulations corresponding to each experiment in steady state are carried out with experimental inputs; these are presented in Table 5-1. To obtain plausible input values, the data from the experiments during the steady state is averaged. Moreover the mass flows and product composition are simulated in the adjusted mass balance model to ensure the consistency of the mass balance.

5.1.1 Simulated Experiments

Simulations for six steady state experiments are performed. Table 5-1 shows the applied inputs values for the simulation runs. The selected inputs allow changing in the operating conditions and observe how the RDWC model responds to these variations. In this way, the most important outputs of the RDWC, such as product composition, reactant conversion, temperature profile are free and can be compared with the experimental results.

Table 5-1 Input variables for the simulation runs

Variable	TWK99 _{sim}	TWK100 _{sim}	TWK102 _{sim}	TWK103 _{sim}	TWK105 _{sim}	TWK106 _{sim}	Units
Liquid split	0.35	0.35	0.4	0.45	0.4	0.5	-
Heating power	863	1204	851	850	1034	1332	kW
Feed flow	1.89	1.84	1.94	1.68	3.69	1.80	kg/h
W _{Feed, BuAc}	52.9	52.8	69.4	43.3	51.8	52.9	%
W _{Feed, HeOH}	47.1	47.2	30.6	56.7	48.2	47.1	%
Pressure	25	25	25	25	25	25	mbar
T _{feed}	31.8	31.8	31.7	31.8	28.2	31.9	°C
T _{reflux}	22.1	23.2	22.2	22.3	22.5	23.8	°C
Distillate	0.68	0.59	0.57	0.49	1.05	0.64	kg/h
Bottom	1.00	0.97	0.73	0.80	1.90	0.75	kg/h
Side	0.22	0.28	0.64	0.39	0.74	0.41	kg/h
Reflux	4.99	7.52	4.97	5.11	5.67	8.23	kg/h

5.1.2 Results

The following section summarizes the simulation results. Figure 5-1 illustrates the temperature profiles of the main column and the prefractionator. The simulation considers one temperature value for each equilibrium stage. Taking this into account, the temperature values are assumed at the middle of the stage. Furthermore, the values are connected by means of a linear interpolation.

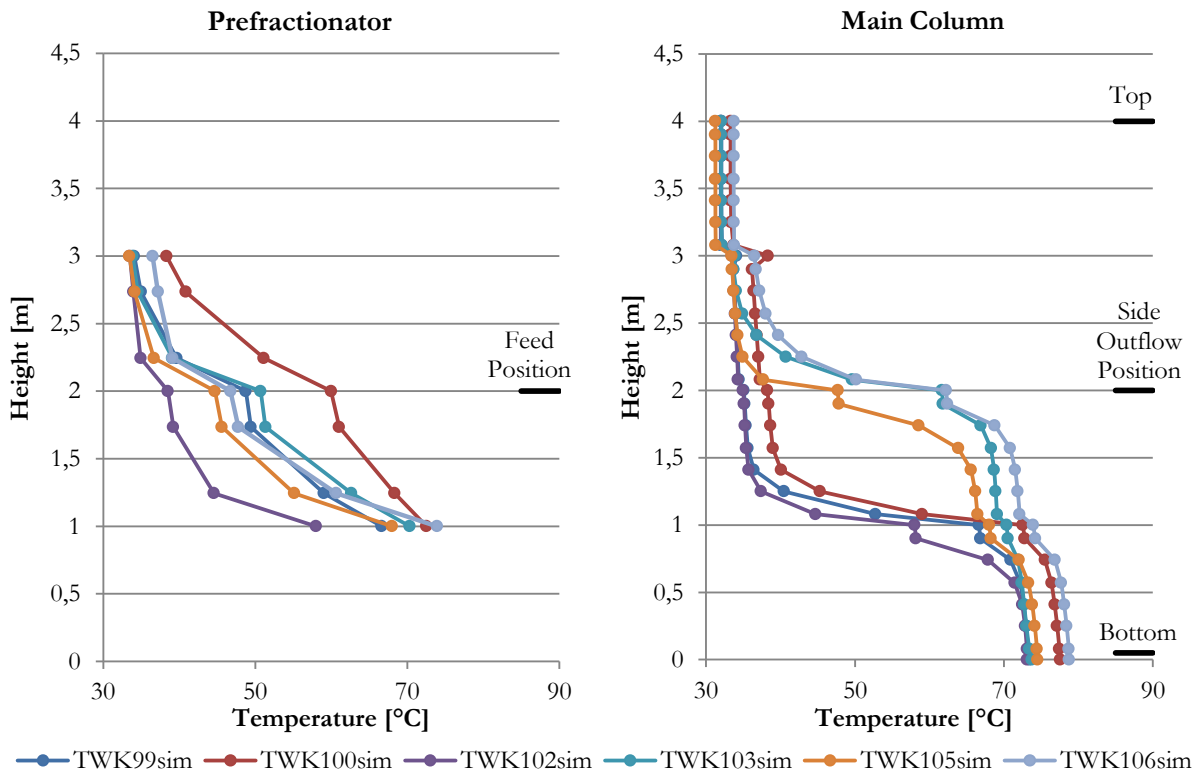


Figure 5-1 Temperature profiles of the simulation runs TWK99_{sim}, TWK100_{sim}, TWK102_{sim}, TWK103_{sim}, TWK105_{sim} and TWK106_{sim}, prefractionator (left), main column (right)

The most notorious differences among the experiments are located in the prefractionator and in the middle section of the main column. In the main column, the profiles of TWK103_{sim}, TWK105_{sim} and TWK106_{sim} present higher temperatures compared to the other simulations, which implies that the separation between the light and heavy components succeeds at different stages along the column. On the other hand, the top and the bottom of the column present variations smaller than 4 °C. In the case of the prefractionator, the temperature profiles are also very different. TWK102_{sim} and TWK100_{sim} represent the extreme cases. TWK100_{sim} show the highest temperatures, while TWK102_{sim} presents the lowest ones. The differences among the simulation runs TWK99_{sim}, TWK103_{sim}, TWK105_{sim} and TWK106_{sim} are delimited by a range of 3 – 6 °C.

Figure 5-2 illustrates the component mass flows of the simulation runs. Evidently, TWK105_{sim} shows the highest peaks, since the feed flow is twice as big compared to the other simulation runs. The product components (BuOH and HeAc) are relatively constant in the simulations TWK99_{sim}, TWK100_{sim} and TWK103_{sim}, while the results of TWK102 and TWK106 exhibit more formation of products, about 30 % more HeAc and 35 % more BuOH. Conversely, the reactants vary strongly along all the different experiments, because of the different feed compositions and reactant conversions.

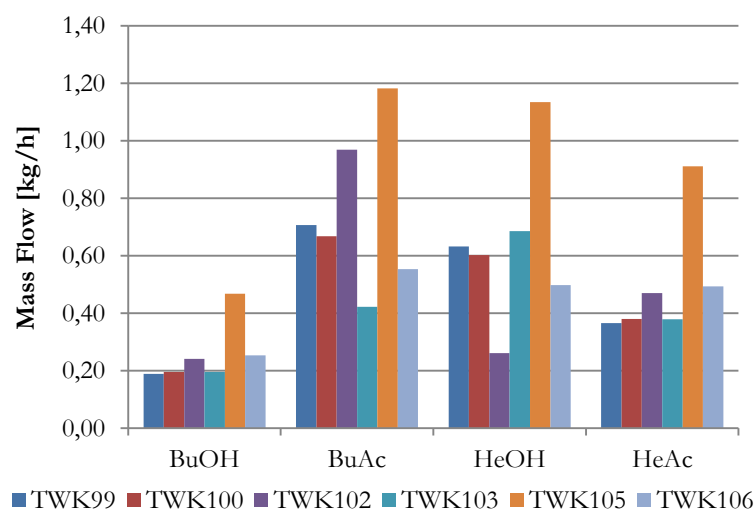


Figure 5-2 Component mass flow of the simulation runs TWK99_{sim}, TWK100_{sim}, TWK102_{sim}, TWK103_{sim}, TWK105_{sim} and TWK106_{sim}

Figure 5-3 exhibits the composition of the product streams. The distillate product presents a stable composition in all the simulation runs, approximately 20 w % BuOH and 80 w % BuAc. In the bottom, only the simulation run TWK103_{sim} presents a different behavior compared to the

other experiments, since the richest component is HeAc instead of HeOH. Finally, the side product composition is different in each experiment, showing cases with predominant presence of heavy components (TWK106_{sim}) and other simulation with a total absence of them (TWK99_{sim}).

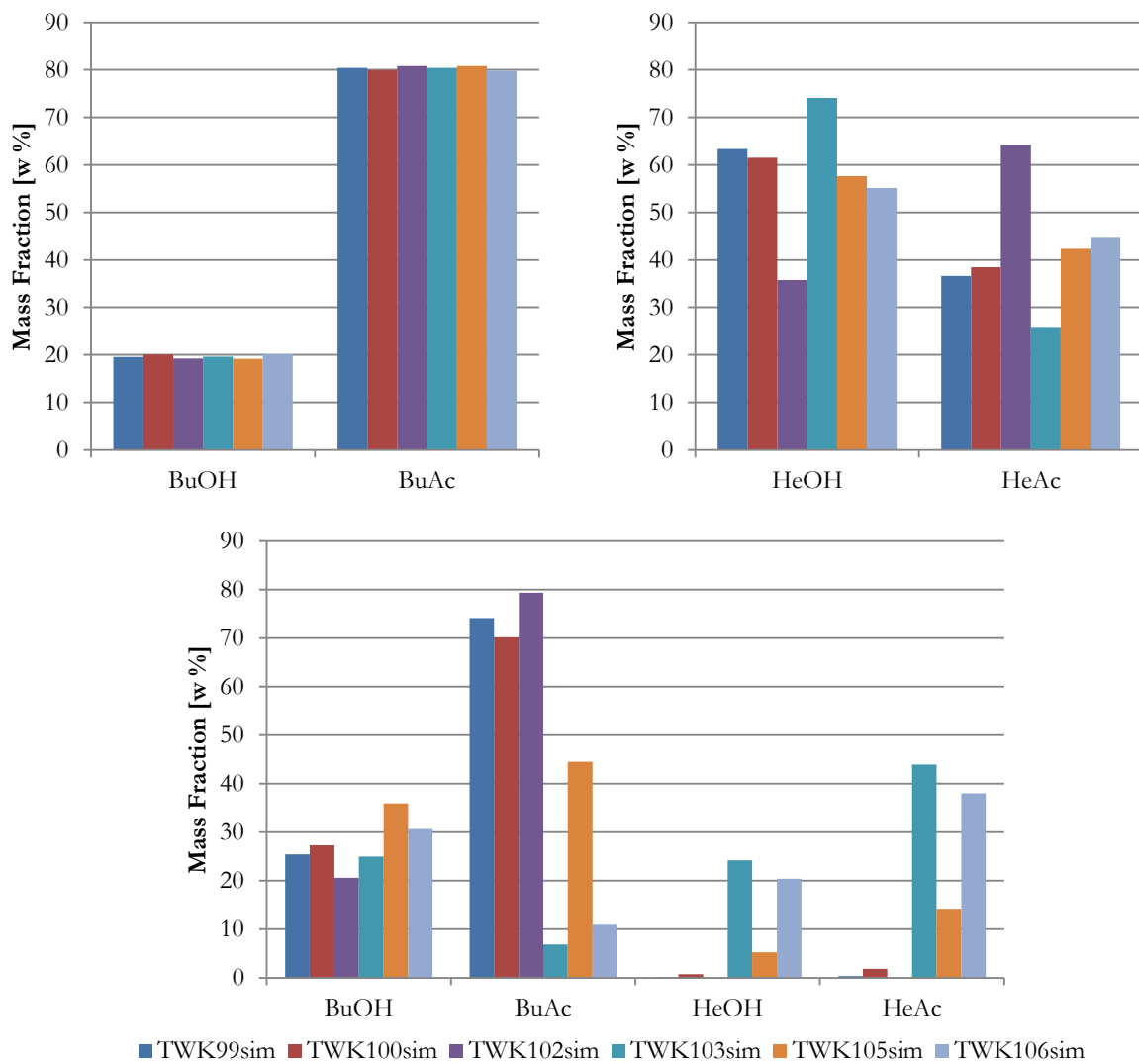


Figure 5-3 Product compositions of the simulation runs TWK99_{sim}, TWK100_{sim}, TWK102_{sim}, TWK103_{sim}, TWK105_{sim} and TWK106_{sim}, distillate (left above), bottom (right above), side (below)

5.2 Model Quality Results

In order to validate the simulation model, the experimental results are compared with their respective simulation runs. The quality of the model is assessed through the comparisons of the variables that allow to determine how well the reaction and separation modelling is. Therefore, the simulation and the experiment results from the temperature profiles, the concentration profiles and the component mass flows are compared. The results from this chapter are the basis for the further analysis of section 5.3.

5.2.1 Temperature Profile

To evaluate the temperature profile agreement, a graphic and a numerical analysis are carried out. First, the differences are depicted by means of a visual comparison of the experimental and simulative temperature profile. Subsequently, the deviations between experiment and simulation are calculated through the subtraction of the experimental values from their corresponding simulation pair (Eq. 5-1). For those cases where the corresponding height of the simulation value does not match exactly with the height from the temperature sensor, the simulative value is interpolated.

$$\Delta T_i = T_{exp} - T_{sim} \quad \text{Eq. 5-1}$$

Moreover, to give an analysis of the total deviation, the sum of the differences for the prefractionator and main column are calculated (Eq. 5-2). In this way, it is possible to assert if the model predicts a cooler or warmer temperature profile. In case that the sum is positive, the simulated T-profile is cooler than the experimental data. On the other hand, if the sum is negative, the predicted T-profile is warmer. This analysis is exhibited for the prefractionator and for the main column. In this way, in case of clear differences between the segments, these can be observed.

$$\Delta T_{sum} = \sum_i^N \Delta T_i \quad \text{Eq. 5-2}$$

Furthermore, to quantify the absolute mean variation of the model in respect to the experiment, the root mean square (RMS) of the differences is calculated.

$$\Delta T_{RMS} = \frac{\sqrt{\sum_i^N \Delta T_i^2}}{N} \quad \text{Eq. 5-3}$$

To facilitate the visual analysis of the temperature profiles, the simulation/experiment comparison is presented in two figures, Figure 5-4 and Figure 5-5. As it can be observed from Figure 5-4, the temperature profiles of the main column from TWK99_{sim}, TWK103_{sim} and TWK106_{sim} agree relatively exact with the experimental data. TWK99_{sim} predicts the values with a deviation of less than 1 °C. On the other hand, the prefractionator shows clear differences between simulation and experiment. The highest variation occurs close to the feed position, with differences about 10 °C.

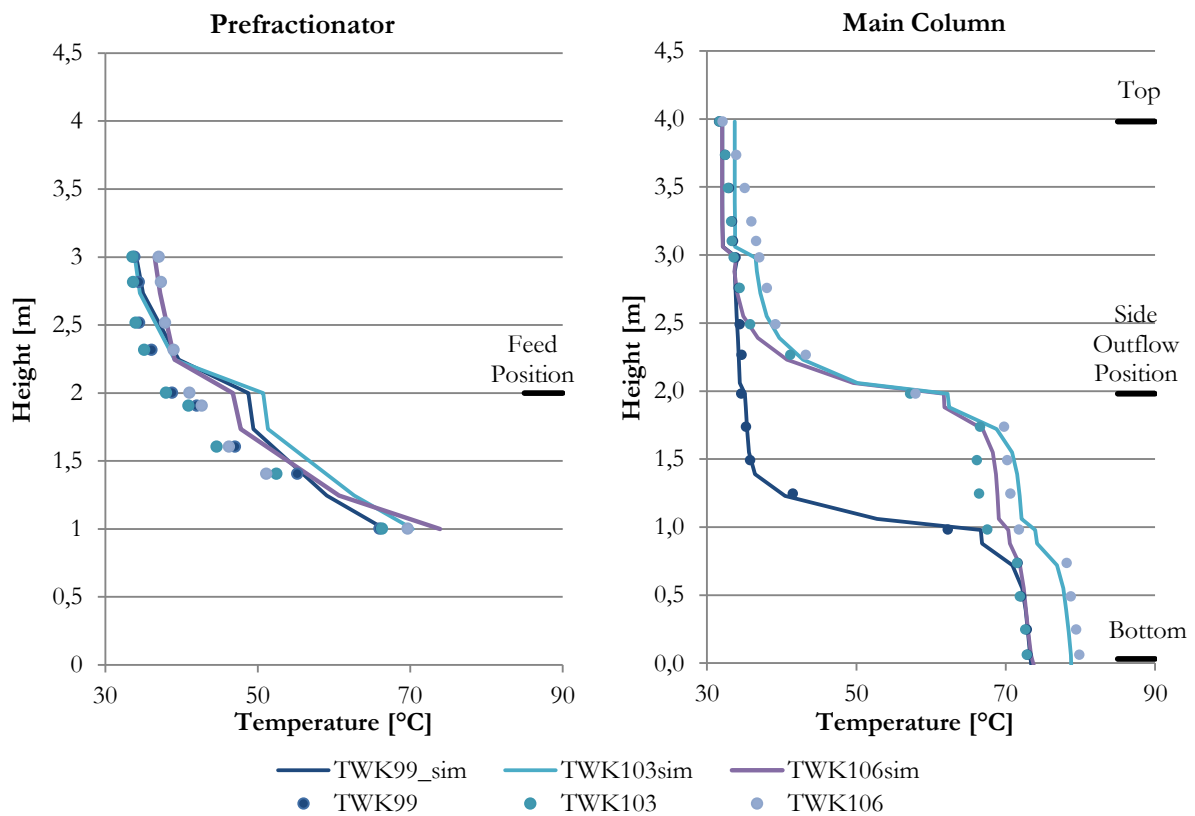


Figure 5-4 Simulation/Experiment temperature profile comparison of the experiments TWK 99, TWK103 and TWK106, prefractionator (left) main column (right)

Figure 5-5 shows a similar trend in respect to the accuracy of the simulation model. In the main column TWK100_{sim} and TWK105_{sim} exhibit differences below 3 °C, while TWK102_{sim} is slightly cooler than the real temperature profile. Furthermore, at the height of 0.75 to 1.26 m, the gap between simulation and experiment is about 6 °C. Observing the prefractionator, the differences show distinct magnitudes. First, TWK102_{sim} concurs relatively accurate to the experiment values. Likewise, the differences presented by TWK105_{sim} are within the range of the cases from Figure 5-4. TWK100_{sim} stands out as the case with the highest deviation between simulation and experiment, reaching a variation of 20 °C in the feed position.

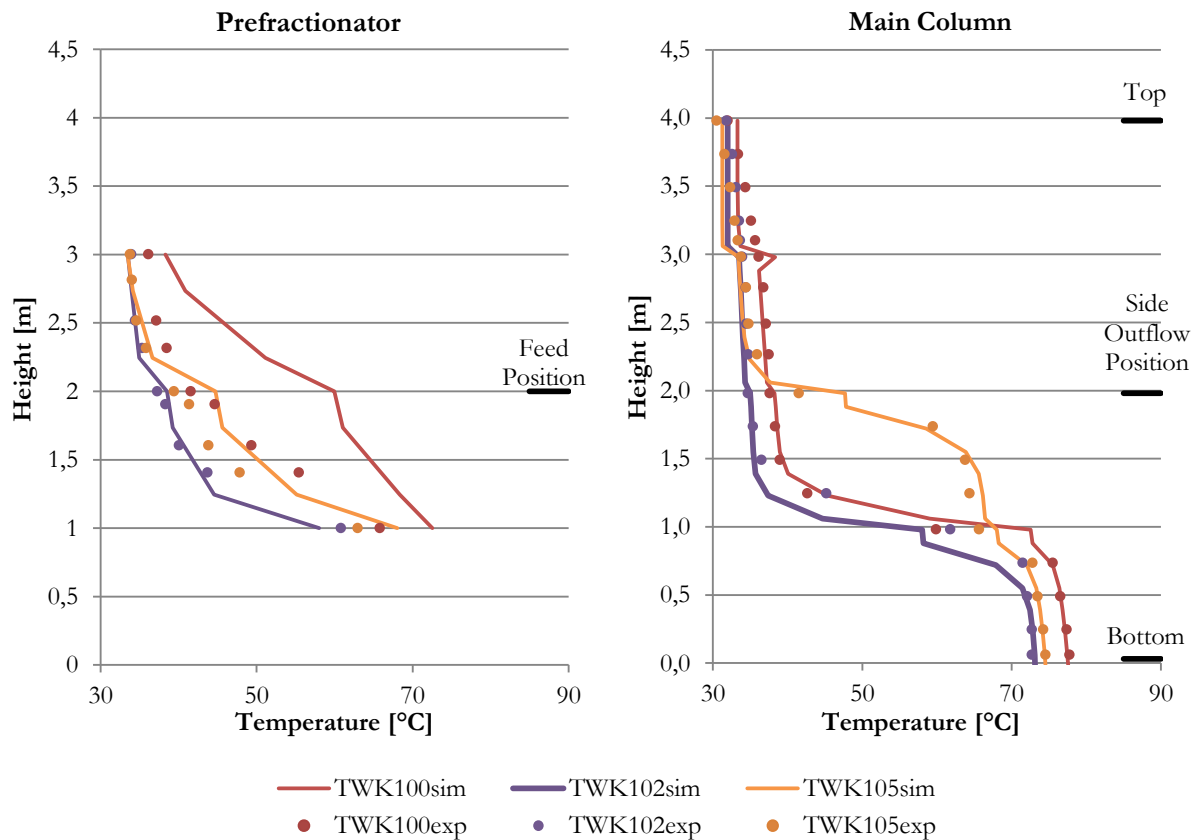


Figure 5-5 Simulation/Experiment temperature profile comparison of the experiments TWK100, TWK102 and TWK105, prefractionator (left), main column (right)

The temperature deviations between simulation and experiment are presented in Table 5-2. The results of the prefractionator and of the main column are exhibited separately, making it possible to identify clearly which section exposes the greatest differences with the experimental data. The results show that the variations in the main column are lower than 1 °C and the sums show maximal differences values in TWK100 and TWK102. On the other hand, the disagreements in the prefractionator are evidently higher compared to the main column. The maximum contrast is presented by TWK100 with 4.78 °C. Additionally, the overall root mean square deviation is lower than 1.5 °C for all the experiments.

Table 5-2 Deviations of the temperature profiles between experiment and simulation

Exp/Sim	Main column		Prefractionator		Overall	Units
	ΔT_{RMS}	ΔT_{sum}	ΔT_{RMS}	ΔT_{sum}		
TWK99	0.28	1.60	1.71	-28.90	0.54	°C
TWK100	0.71	-12.22	4.78	-84.45	1.50	°C
TWK102	0.55	24.08	0.48	2.05	0.42	°C
TWK103	0.35	-8.29	2.59	-48.75	0.81	°C
TWK105	0.59	7.67	1.27	-23.58	0.56	°C
TWK106	0.39	6.26	1.38	-24.57	0.49	°C

Figure 5-6 disaggregates the simulation/experiment differences from the prefractionator and main column into the model segments. The main column, as was mentioned before shows smaller differences compared to the prefractionator. The highest differences peaks are in the zone where the vapor split takes place. Nevertheless, the temperature of each segment concurs correctly to the experiments with differences below 2 °C. On the other hand, in the prefractionator, the model segment indicated as mid_dw_F presents the greatest temperature deviation between model and simulation, followed by the lo_dw_F segment. Summarizing, the lower middle section of the prefractionator and the vapor split distributor are the zones with greatest simulation/experiment deviations. Moreover, as it can be inferred from the sum of the variations, the temperature profile of the simulation is in each case hotter than the experimental one, except for TWK102, whose temperature profile is slightly cooler than predicted.

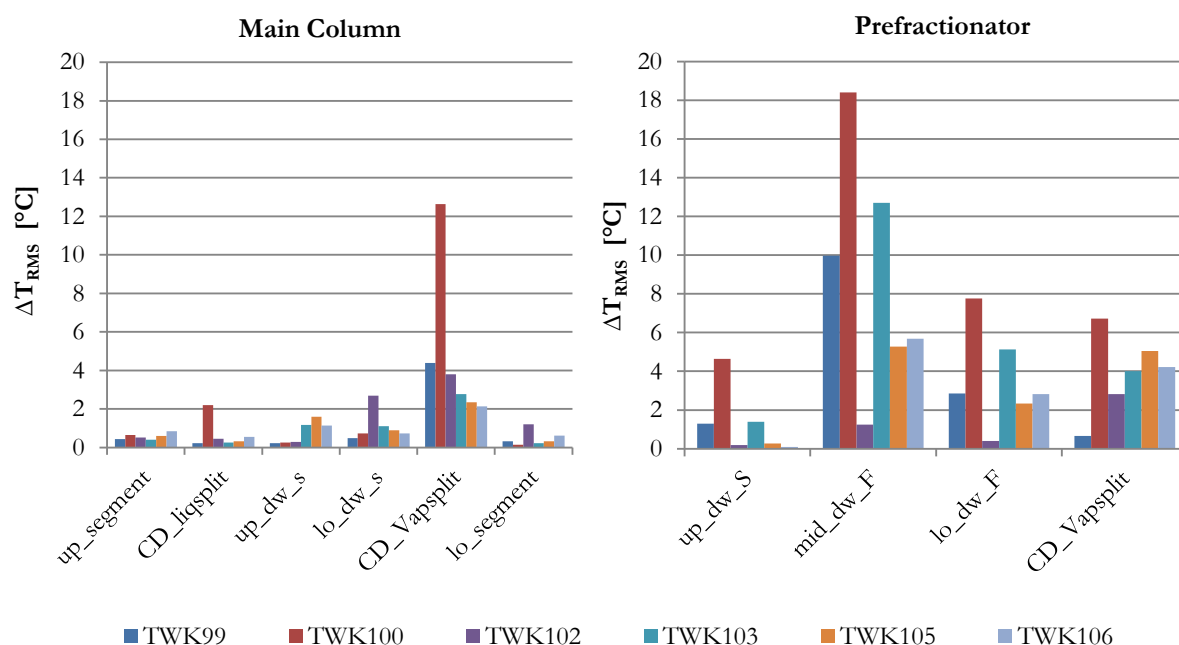


Figure 5-6 Temperature differences of the model segments

5.2.2 Component Molar Flow

For the purpose of assessing the quality of the reaction model, the differences from the cumulative amount of the different components inside the product streams are shown.

The absolute amount of products and remaining reactants can confirm if the reactant conversion corresponds to the real behavior. To quantify the difference, each experimental component molar flow is subtracted from the simulation value and subsequently divided by the molar feed

flow. Eq. 5-4 shows the applied equation. This criterion allows a fair comparison among the different components and experiments.

$$\Delta \dot{N}_i = \frac{\dot{N}_{exp} - \dot{N}_{sim}}{\dot{N}_{feed}} * 100 \quad \text{Eq. 5-4}$$

Figure 5-7 illustrates the differences of each component molar flows and every experiment. TWK99_{sim}, TWK102_{sim} are the simulation runs that correspond better to the experiment results, showing differences about 0.1 mol %, which is below the instrumentation error. Conversely, TWK105 and TWK106 display bigger deviations reaching even 1.8 mol % of molar flow differences. Moreover, from all the simulation/experiment comparisons, TWK103_{sim} is the only case that predicts less formation of products (BuOH and HeAc).

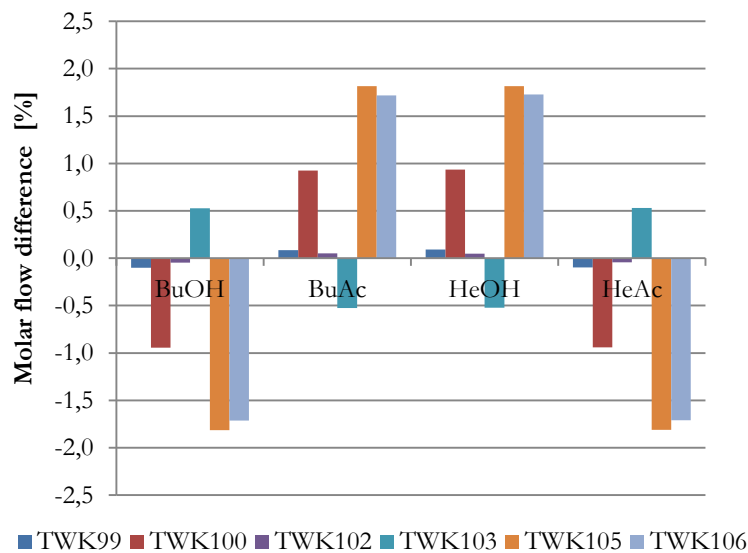


Figure 5-7 Component mass flow difference between experiment and simulation

To visualize in detail the agreement of the reactant conversion, the relative difference between the simulation and experiment is calculated (see Eq. 5-5).

$$\Delta \chi_i = \frac{\chi_{i,exp} - \chi_{i,sim}}{\chi_{i,exp}} * 100 \quad \text{Eq. 5-5}$$

The results are exhibited in Table 5-3. As is expected, the differences are greater for TWK105 and TWK106 with a value close to 10 mol %. On the other hand, TWK99_{sim} and TWK102_{sim} are more precise with the reactant conversion, showing an error lower than 1 mol %. Moreover, both reactant conversions present approximately the same differences.

Table 5-3 Total deviation of the reactant conversion

	TWK99	TWK100	TWK102	TWK103	TWK105	TWK106	Units
$\Delta\chi_{\text{BuAc}}$	-0.59	-6.32	-0.28	3.02	-10.79	-9.03	mol %
$\Delta\chi_{\text{HeOH}}$	-0.64	-6.39	-0.26	3.01	-10.81	-9.08	mol %

5.2.3 Concentration Profile

The accuracy of the concentration profiles allows observing the quality of the separation and reaction model. If they are described wrongly by the model, the differences must be visible in the concentration profile. The differences are calculated by the subtraction between experiment and simulation mass fractions via Eq. 5-6 and depicted by Figure 5-8.

$$\Delta w_i = w_{\text{exp}} - w_{\text{sim}} \quad \text{Eq. 5-6}$$

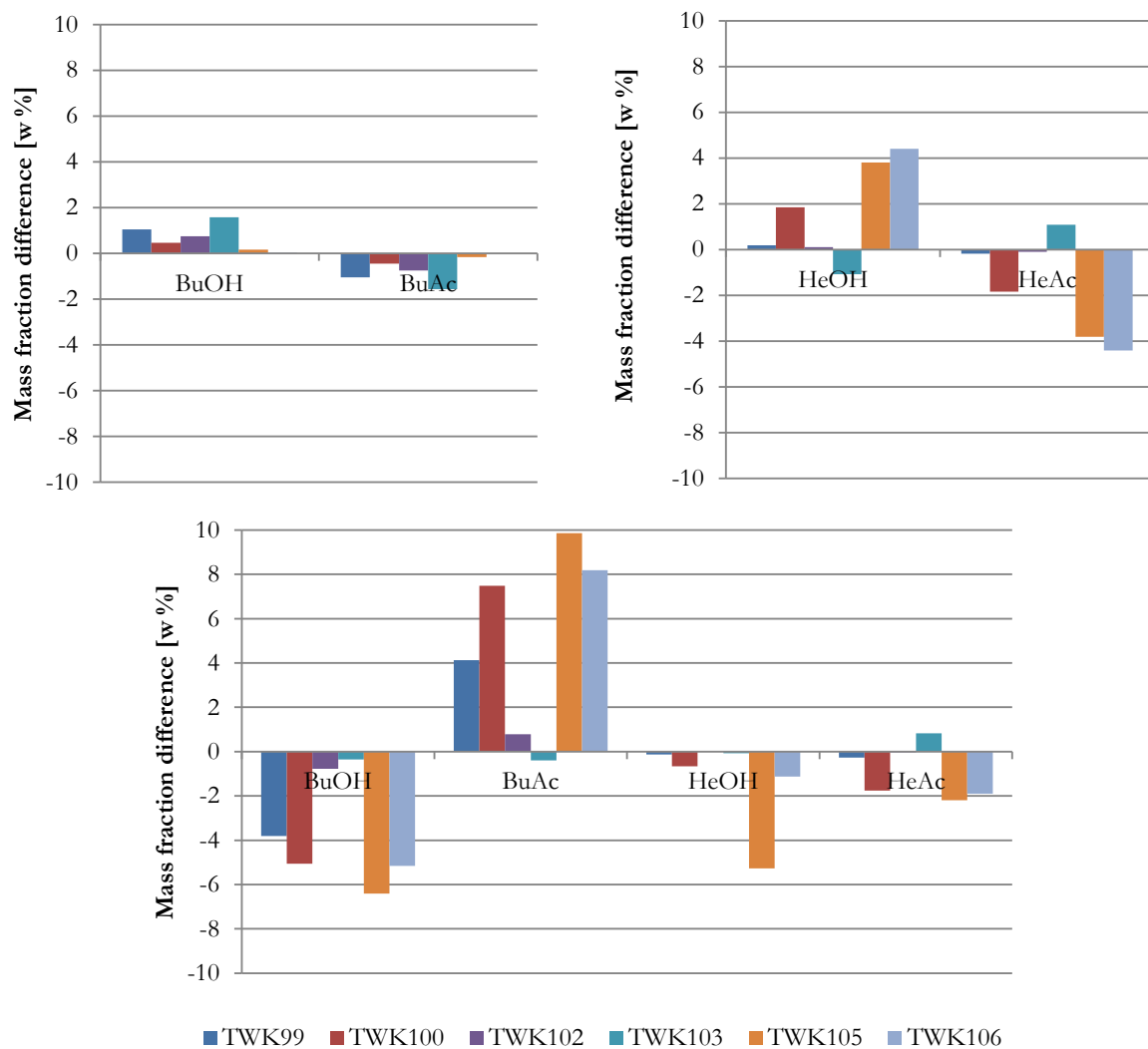


Figure 5-8 Mass fraction difference between experiment and simulation, distillate (left above), bottom (right above) side (below)

As can be noticed from Figure 5-8, the magnitudes of the differences vary according to the product streams. In the distillate, the maximum difference reaches 1.57 w %. For the case of the bottom, the deviations are unevenly distributed; in TWK99 and TWK102 they are lower than 0.2 w %. TWK105 and TWK106 have the highest peaks, with differences over 3.5 %. On the other hand, the composition of the side product is not well predicted by the model. Analyzing Figure 5-8, the model has greater problems with predicting the right mass fraction of the light components. These differences are notorious in TWK100, TWK105 and TWK106, which reach maximum peaks of 7.5, 9.86 and 8.19 w % respectively.

Besides, to quantify the total variation, the sums of the absolute differences are calculated via Eq. 5-7.

$$\Delta w_{sum} = \sum_i^I |\Delta w_i| \quad \text{Eq. 5-7}$$

The values for every stream are detailed in Table 5-2. In accordance with the results presented by Figure 5-8, the variations on the side stream show the biggest deviations. In view of the results, the experiments with better product composition prediction are TWK102 and TWK103. In these two experiments the error related to the side composition is smaller compared to the other four experiments.

Table 5-4 Total deviation of the product composition between experiment and simulation

	TWK99	TWK100	TWK102	TWK103	TWK105	TWK106	Units
Δw_{sum} Distillate	2.09	0.92	1.50	3.13	0.33	0.07	w %
Δw_{sum} Bottom	0.37	3.69	0.21	2.17	7.61	8.82	w %
Δw_{sum} Side	8.33	14.98	1.62	1.66	23.73	16.39	w %
Total	10.38	17.16	3.27	6.96	31.67	25.28	w %

Figure 5-9 illustrates the mass fraction differences in the first packing segment (S1), vapor split, feed position and liquid split. As it can be noticed in Figure 5-9, the model does not match properly the compositions along the column and the highest differences are in the vapor split and feed position. The liquid split shows the smallest simulation/experiment differences, followed by the first packing segment. Nevertheless, the deviation in these segments is over 5 w %. The vapor split and feed stage composition predicted by the model differs sharply from the real composition. The differences in the vapor distributor are almost 40 w % in TWK106, the other experiments present deviations below 20 w %. In the feed position, the greatest contrast is shown by TWK100, reaching up to 30 w %.

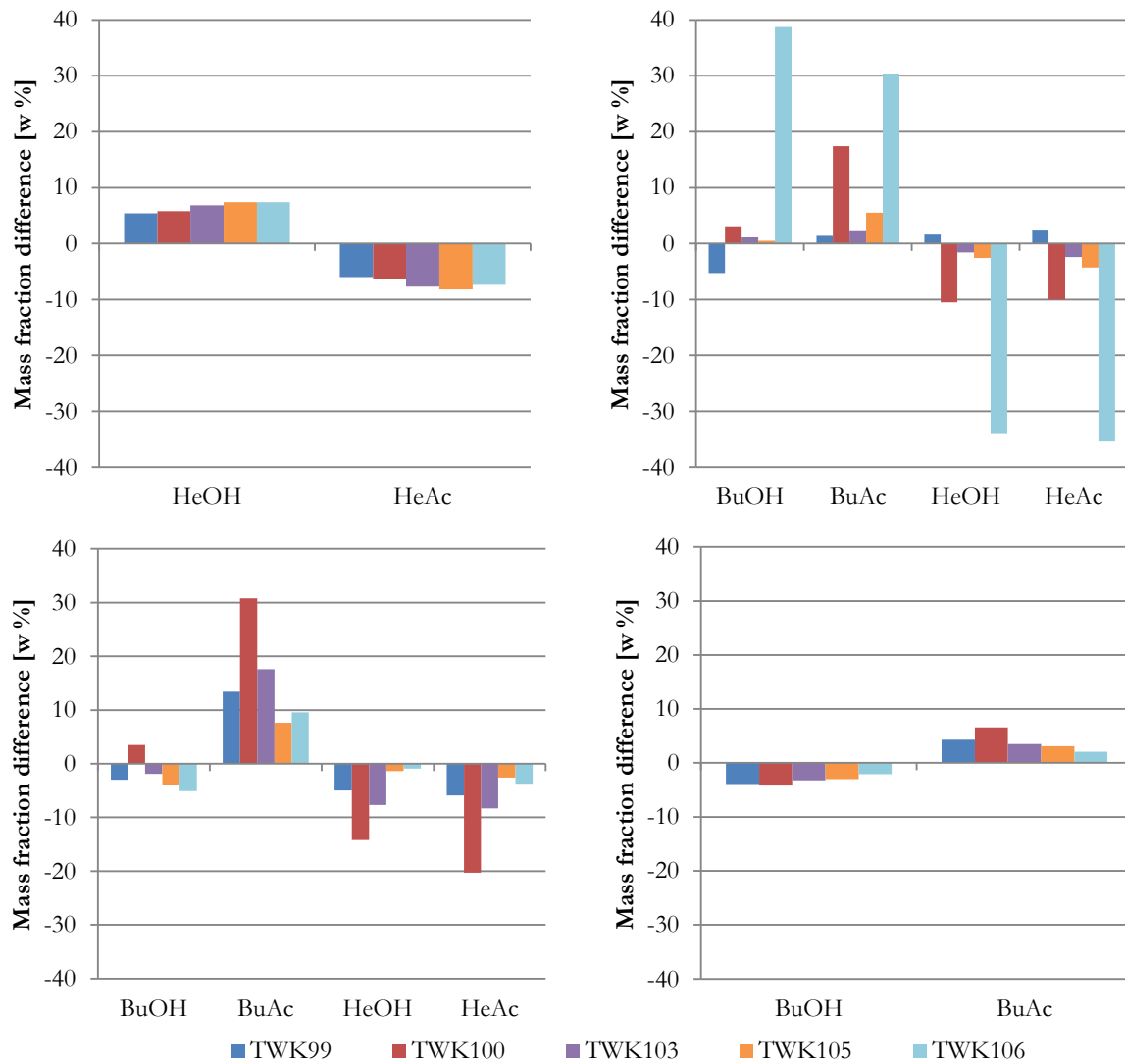


Figure 5-9 Mass fraction difference between experiment and simulation, S1 (left above) vapor split (right above) feed position (left below) liquid split (right below)

5.2.4 Overview

Overall, the quality of the model is appropriate. In relation to the temperature profile, the root mean square temperature difference is within the range of 0.28 up to 0.71 °C in the main column, while in the prefractionator is limited between 0.48 up to 4.78 °C. The maximal variation of the component molar flows displayed by this work is 2.4 %. Moreover, the product composition differences achieve 1.6, 4 and 10 w % as maximum values for the distillate, bottom and side respectively. However, more detailed results show that in some cases, the model does not predict well the temperature and composition of the prefractionator lower segment and the vapor split.

5.3 Model Quality Analysis

As presented in the previous section, the simulation model shows differences from the experimental data in all the cases. Nevertheless, the high degree of integration in the RDWC does not allow asserting that the reasons for the disagreements are originated by one single factor. With this in mind, the following section pursues to connect the differences presented in the reactant conversion, temperature and concentration profile in order to give a general picture of the model quality. Furthermore, as section 5.2 shows, the model quality differs from one experiment to another. For instance, the model shows better agreements with the experimental data from TWK99, TWK102 and TWK103 in comparison with the other experiments. In view of this, a second objective of this section is to correlate the model quality with the effects on the reaction and separation processes generated by the manipulation of the selected operating variables (heating power, feed composition, feed flow and liquid split).

5.3.1 General Evaluation

In general terms, the main simulation/experiment differences are observable in the feed position and vapor distributor, which is shown in Figure 5-6 and Figure 5-9. This is not surprising, since concentration and temperature have a known dependency. Moreover, further differences are visible in the reactant conversion and side stream composition. This result is also evident, a wrong concentration/temperature prediction must be also visible in the reaction process and therefore in the generated and distributed products towards the side stream. These four elements are completely connected. Now, how the model works and why it predicts wrongly must be analyzed.

The main analysis is focused on the reaction process, as it was mentioned in chapter 3.2. The reactive section is modelled through two reactive segments plus the feed inflow. The reactive segments represent two meters of reactive zone and are each discretized in two stages. Therefore four stages of 0.5 m are available in total. This implies that the reaction kinetics and subsequently concentration profile is calculated by means of four single points, which is questionable. Since, in case that the real reactant and product concentration varies stronger along the reactive zone, the model resolution will not be able to calculate a proper conversion of the reactants and therefore the concentration and temperature profiles will be wrongly predicted. Taking this into account, the inaccurate prediction of the temperature and concentration in the prefractionator can be related to the reactive zone discretization.

5.3.2 Model Quality according to Operating Changes

As it was mentioned above, the second objective of this chapter is to assess the model quality in terms of the changes of the process behavior due to the manipulation of the feed composition, feed flow, liquid split and heat power. As was mentioned in Chapter 3.3, the manipulation of these variables pursues to affect the reaction, pressure drop, e.g. vapor-liquid traffic, component distribution and product composition. Hence, the related sub-models can be assessed partially independently.

Feed Composition

In relation to the feed composition, the experiments TWK99, TWK102 and TWK103 have a different feed composition resulting in different reactant conversions and process behavior, as it was described in chapter 4. In this way, the simulation model has the challenge to predict the reaction behavior according to these changes. Successfully, the model quality of these cases shows a good agreement with the experimental data. As it was presented in section 5.2, the temperature deviation in the main column is below 1 °C in these cases. Besides, in the prefractionator they show also a good agreement, but some differences can be noticed. In descending order, the root mean square differences are 2.59, 1.71 and 0.48 °C for TWK103sim, TWK99sim and TWK102sim respectively. As it can be seen in Table 5-3, the reactant conversion difference follows the same order as the prefractionator temperature difference with values of 3.02, 0.59 and 0.28 mol %. Nevertheless, the differences are still lower. Taking this into account, the modifications in the feed composition with the subsequent effects in the process behavior are well predicted by the simulation model and particularly by the reaction submodel.

Feed Flow

TWK105 is the only experiment operated with a high feed flow. Taking into account the results from section 0, the model has to consider the reactant conversion increase caused by this change. As the results from section 5.2 show, TWK105 is the experiment with the highest deviations in respect to the values predicted by its simulation run. Observing the reactant conversion, the differences reach a value close to 11 mol %. Taking this into account, the model does not predict correctly the reaction. Moreover the heat power is also high in this experiment, thus the combining effect of a poor component distribution along both sides of the column and the already mentioned deficient discretization of the reactive zone could explain this high model/experiment disagreement.

Liquid Split

Among the different experiments, the liquid split was set at different values, (0.35, 0.4, 0.45 and 0.5). Considering this, the simulation model must predict the effects discussed in section 0. Observing the results, the simulation runs TWK102_{sim}, TWK99_{sim} and TWK103_{sim} show the smallest simulation/experiment differences. In order to clarify if the liquid split has an observable effect on the differences between simulation and experiment Figure 5-10 is elaborated.

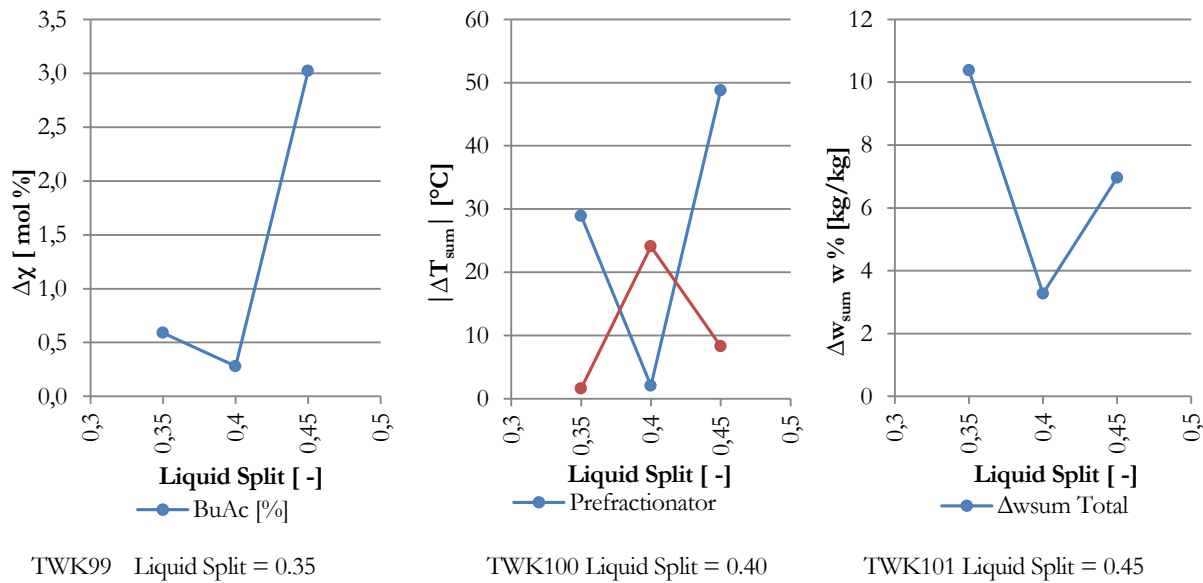


Figure 5-10 Deviations according to the liquid split, $\Delta\chi_{\text{BuAc}}$ (left), ΔT_{sum} (middle), Δw_{sum} (right)

On the left diagram it is possible to see that experiment with greater liquid split (TWK101) presents the biggest conversion difference. The middle diagram shows that the highest deviations of the prefractionator and main column T-profile do not have a pattern attributed to the liquid split. Finally the right diagram indicates that the total differences of the product compositions are higher in TWK99, which has 0.35 as liquid split. In view of these results, there is no evidence to affirm that the changes in the liquid split cause higher or lower simulation/experiment disagreements.

Heat Power

The experiments TWK100, TWK105 and TWK106 were operated with a high heating power, which considerably increases the pressure drop. As it can be observed in section 5.2, the predicted values of the simulation model related to the component mass flows, conversion and bottom and side compositions differ strongly from the experimental data. Moreover, the simulated prefractionator temperature profile from TWK100_{sim} exhibits the highest differences

in respect to the experimental results, with a root mean square difference of 4.76 °C. For this reason, it is possible to expect that the pressure drop and liquid vapor flow modeling is highly sensitive to heat power variations, which generate wrong model predictions. Taking this into account, a sensitive analysis of this parameter can provide more meaningful information.

5.4 Sensitive Analysis

In view of the previous results, only the heat power shows an observable effect on the model quality. Nevertheless, it is still not clear if this parameter is excessively sensitive to the variations causing model disagreements. Considering this, the following section shows the results from the heat power sensitive analysis in order to verify the possible effects on the reaction and separation processes prediction. The methodology by which to perform this sensitive analysis was presented in section 3.4.3.

The strategy to achieve the sensitivity analysis considers a constant heat transfer coefficient with the reflux and distillate flow free. Moreover to avoid drastic changes of these two variables the reflux ratio is fixed. In this way the variations of the reflux and distillate in respect to the original input values are lower than 5 %. Besides, the other inputs exhibited in Table 5-1 are not changed. However, with this procedure there are model constraints that are limiting the range of possible heat power changes. Therefore, the sensitive analysis of the heat power is reduced to the points presented in Table 5-5.

Table 5-5 Heat power sensitive analysis cases

Experiment	Cases							
TWK99	0.96 P	0.97 P	0.98 P	0.99 P	-	-	-	-
TWK100	0.96 P	0.97 P	0.98 P	0.99 P	-	-	-	-
TWK102	0.96 P	0.97 P	0.98 P	0.99 P	-	-	-	-
TWK103	0.96 P	0.97 P	0.98 P	0.99 P	1.01 P	1.02P	1.03 P	1.04 P
TWK105	0.96 P	0.97 P	0.98 P	0.99 P	1.01 P	1.02P	1.03 P	1.04 P
TWK106	0.96 P	0.97 P	0.98 P	0.99 P	1.01 P	-	-	-

Figure 5-11 illustrates the change in the calculated deviations according to the heat power value. The results reveal that even in this delimited sensitive analysis appear clear variations in the experiment/simulation differences. As Figure 5-11 shows, there is no pattern in the variations, less or more heat power does not necessarily worsen the model quality. Moreover, the clear changes are not exclusively related to the experiments that in the base case show great differences. The experiments TWK99, TWK102 and TWK103 show also big variations in this analysis. Summarizing, it is possible to affirm that the simulation prediction is highly affected by

the heat power. More accurate, the pressure drop and liquid vapor flow traffic along both sides of the column are predicted poorly causing wrong component distribution along the column and subsequent effects on the reaction and separation behavior.

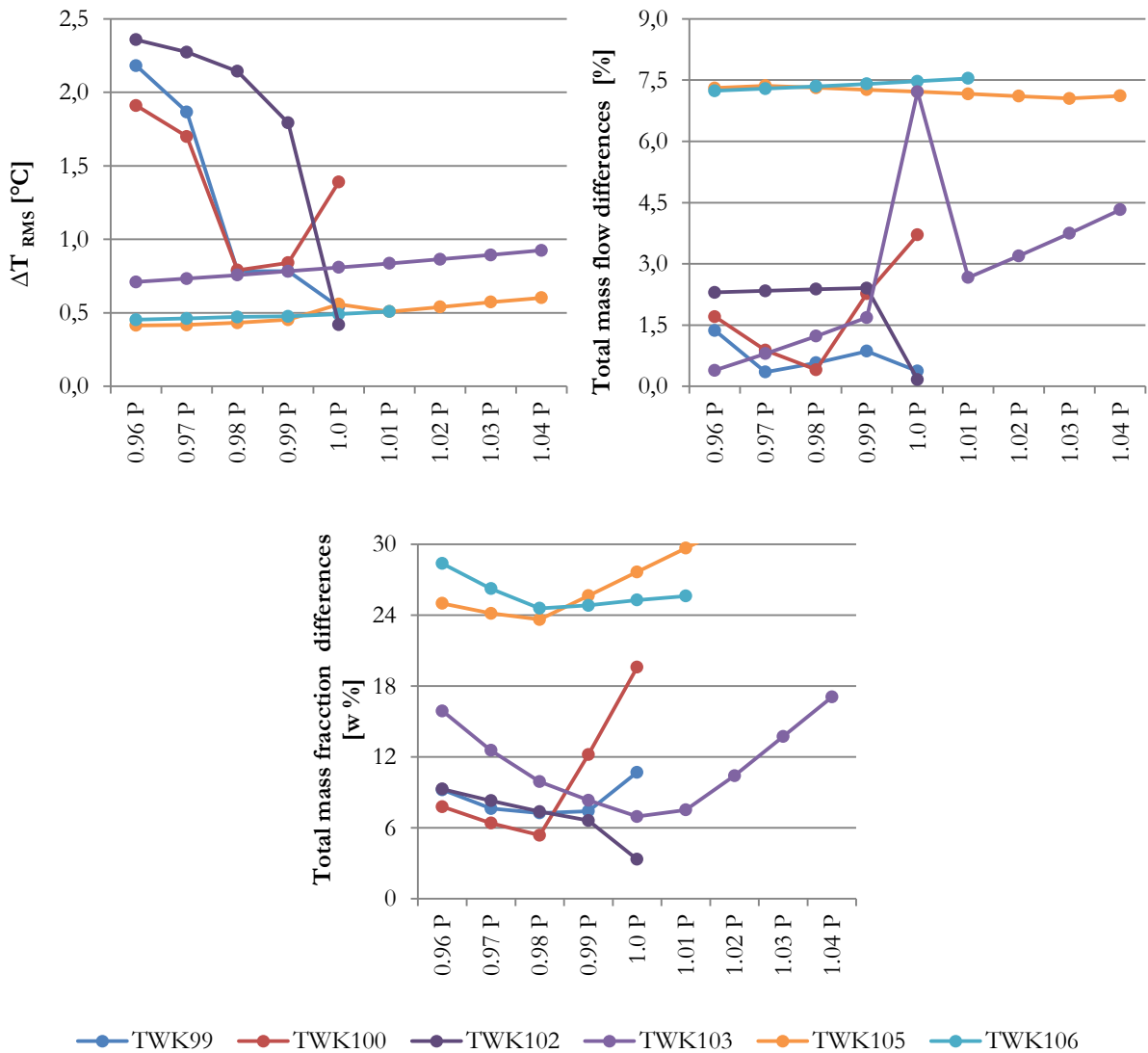


Figure 5-11 Heat power sensitivity analysis of the experiments TWK100, TWK105 and TWK106, temperature (left above), mass flow (right above) mass fraction (below)

5.5 Heat Loss Model Evaluation

The simulation model applied in this work assumes for the calculation of the heat loss a variable value of the heat transfer coefficient. As it was presented in section 3.2, the heat losses are calculated through the product among the heat transfer surface, temperature gradient and heat transfer coefficient (see Eq. 3-10). From these variables, the environment temperature is fixed at

20 °C and the heat transfer coefficient is set as a free variable and calculated in every simulation run. However, this assumption could imply that the heat transfer coefficient varies along a wide range, which does not allow determining a certain value of this variable. Taking this into account, a new strategy is employed to reduce this uncertainty. The k_{loss} values given by all the simulation experiments are enlisted to visualize the variation range. With these values, new simulations are carried out considering this variable as a constant and the environment temperature as a free parameter. In this way, if the different simulation shows that the environment temperature varies within an unfeasible range. Then, the range of the heat transfer coefficient is also unfeasible. On the other hand, if the environment temperature varies within a feasible range, then a determined heat transfer coefficient value can be selected within its range as a constant for further model validation research works.

The simulation results of the corresponding experiments show that the heat transfer coefficient is within the range 1.1 – 2.1 W/m²/K. With these results a sensitive analysis based on the method of section 3.4.3 is applied. The heat transfer value is varied along the already mentioned range by steps of 0.2 W/m²/K in order to visualize its effect in the environment temperature variation.

Table 5-6 Environment temperature sensitive analysis results

	Heat transfer coefficient						Units
	1.1	1.3	1.5	1.7	1.9	2.1	W/m ² /K
Experiment	Environment Temperature						
TWK99	17.1	20.6	23.1	25.0	26.5	27.7	°C
TWK100	13.3	17.8	21.2	23.7	25.7	27.4	°C
TWK102	10.8	15.0	18.0	20.3	22.2	23.7	°C
TWK103	19.9	23.3	25.8	27.7	29.2	30.4	°C
TWK105	20.4	23.5	25.7	27.4	28.7	29.8	°C
TWK106	-	12.3	16.5	19.7	22.3	24.3	°C

The results of this sensitive analysis are depicted in Table 5-6. As can be noticed, the temperature varies from 10.8 °C up to 30.4 °C, which represent a realistic range. Moreover, the most representative values of possible environment temperature are given by a heat transfer coefficient of 1.5 W/m²/K. Taking this into account, it is possible to assume preliminarily that the heat transfer coefficient oscillates around this value.

In conclusion, the present results allow affirming that the assumption of a variable heat transfer can be replaced by a variable environment temperature and constant heat transfer coefficient. This change has the advantage that is based on a more realistic assumption and can be therefore be measured. In view of the results of Table 5-6, a recommended value of k_{loss} can be around 1.5 W/m²/K.

5.6 Summary

The comparisons of the experimental and simulative results show that the RDWC model is able to predict properly the RDWC behavior in steady state under different temperature profiles and product distributions. Nevertheless, the simulation/experiment deviations differ from one experiment to another.

The results of the model validation are within the frame of the previous works of HARDING and KEUSER [14, 15]. First, the root mean square temperature difference is within the range of 0.28 up to 0.71 °C in the main column, while in the prefractionator it is limited between 0.48 up to 4.78 °C. In overall terms, the differences reach a maximum value of 1.50 °C. In the work of HARDING, the model/experiment temperature variations reach a minimum value of 2.9 °C and a maximum of 4.5 °C [14]. On the other hand, the results presented by KEUSER exhibit an average difference of about 3 °C [15]. Moreover, the product composition differences achieve 1.6, 4 and 10 w % as maximum values for the distillate, bottom and side respectively. Furthermore, the maximum differences reported by HARDING are 4.5 w % at the bottom and 4 w % in the side stream [14]. Likewise, KEUSER summarizes the model differences in 5.8 and 11.3 w % for the bottom and side respectively [15]. Additionally, the maximal variation of the component mass flows informed by this work is 2.4 %, while in the works by KEUSER and HARDING the deviations are 3.8 and 1.5 % respectively [14, 15]. Thus, the modeling based on equilibrium stages is suitable for the RDWC in steady state and no complex approaches are strictly required.

However, although the quality of the model prediction is reasonably good, some disagreements were found. The model evaluation concluded that the model resolution in the reactive zone is not able to calculate a proper conversion of the reactants under strong variations of the concentration profile in this segment. Taking this into account, the inaccurate prediction of the temperature and concentration in the prefractionator can be related to the reactive zone discretization. The sensitive analysis of the heat power allows to affirm that the simulation prediction is highly affected by the heat power. More accurate, the pressure drop and liquid vapor flow traffic along both sides of the column are predicted poorly causing wrong component distribution along the column and subsequent effects on the reaction and separation behavior.

Finally, the heat loss model evaluation allows to determine the heat transfer coefficient around 1.5 W/m²/K, which improves the theoretical model approach.

6 Conclusions and Outlook

Although, several theoretical studies about the RDWC have shown the economic potential of the RDWC, this technology is still not tested in industrial production processes. The scarce experimental research verifying the prediction performance of modelling approaches was mentioned as one of the reasons for that. Therefore, the present thesis work pursued to reduce the uncertainties related to the RDWC modelling particularly in steady state. The hypothesis called into question was the suitability of a RDWC model based on equilibrium stages to predict the RDWC steady state behavior. Thus, a set of different experiments were planned and performed to validate the model by means of the comparison between experimental and simulation results. The model validation had to be within a wide range of operating condition, which was achieved by carrying out six different successful experiments.

With the generated experimental data was possible to observe the following: The experimental/simulation differences are within the frame of the previous works by HARDING [14] and KEUSER [15]. The simulation model is able to correctly predict the temperature profiles and product distributions. In each experiment, the overall root mean square temperature differences are below 2 °C. The maximal variation of the component molar flows informed by this work is 2.4 mol %. On the other hand, the product composition differences achieved 1.6, 4 and 10 w % as maximum values for the distillate, bottom and side streams respectively. Thus, the modeling based on equilibrium stages is suitable for the RDWC in steady state and no complex approaches are strictly required.

However, although the quality of the model prediction is reasonably good, some disagreements were found. For instance, the model resolution in the reactive zone is not able to calculate a proper conversion of the reactants under strong variations of the concentration profile in this segment. Taking this into account, the reaction model can be well suited, but the discretization of the reactive section spoils the model accuracy.

Furthermore, the heat power sensitive analysis demonstrated that small changes on this variable strongly affect the simulation/experiment differences. Besides, these variations are not attributable to a high or low heat power. Therefore, the fundamental cause of these differences is the wrong component distribution prediction along the column, which is highly affected by small changes in the heat power. By reviewing the model, the reasons can be related to a wrong prediction of the vapor and liquid flow traffic along both sides of the column, which depends on the pressure drop model.

Additionally, to provide more understanding about the RDWC behavior was established as part of the objectives. With the generated experimental results and a comprehensive study of the experimental runs was possible to confirm some aspects of the theory behind the reactive dividing wall column. The analysis and comparisons of the experimental results proved the following: The increase of the reactant conversion, due to excess reactant, the pressure drop increase, because of the heat power raise, the dependency between the temperature and concentration profiles with the reactant conversions and component distribution. On the other hand, some experiments presented unexpected results. For instance, the reactant conversion in experiment TWK105 increased, although the amount of catalyst mass per reactant mol was less in comparison with the other experiments. This result was attributed to the liquid volume increase in the reactive zone, due to the feed raise, which facilitates the contact of the reactants and therefore improves the reaction. A second unanticipated result was the conversion increase in TWK106 as a consequence of greater reflux in the prefractionator compared to the other cases, which was related to the increase of returned reactant to the reactive zone, since the reflux composition is mainly BuAc (80 w %).

Finally, this work improves the theoretical model approach by determining the heat transfer coefficient of the heat loss model. The results of this analysis allow the affirmation that the assumption of a variable heat transfer can be replaced by a variable environment temperature and constant heat transfer coefficient around $1.5 \text{ W/m}^2/\text{K}$, which has the advantage that is based on a more realistic assumption and can be measured.

As an outlook, some recommendations for further research of the RDWC model validation are presented. First, the increase of the model discretization in the reactive zone is highly recommended. This can also be complemented with the application of a mass transfer model. In this way, a more accurate prediction can be achieved. Additionally, new sampling valves in the reactive zone would help to compare the simulation and experiment results in greater detail.

Second, experiment runs without reaction are also recommended to exclusively analyze the model separation prediction and vapor liquid traffic along the column. Finally, in order to extend the operating range of the simulation model, new experiments focused on an increase of the reactant conversion and separation performance can be carried out. Besides, the employment of a different reaction system without the generation of azeotropes mixtures or the replacement of the enzyme catalyst would also extend the possibilities of the RDWC model validation.

7 References

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Annexes

A.1 GC Analysis

A.1.1 GC Standards

Table A- 1 GC standards samples

Standard Name	BuAc	BuOH	HeOH	HeAc	BuAc	BuOH	HeOH	HeAc
	w %				Peak area [μ V]			
Distillate								
Level_0	100.00	0.00	-	-	376442.1	256.5	-	-
Level_1	79.55	20.45	-	-	293419.4	86575.8	-	-
Level_10	0.00	100.00	-	-	0.0	399903.8	-	-
Level_2	72.65	27.35	-	-	267430.8	114707.8	-	-
Level_3	64.57	35.43	-	-	236583.4	149397.8	-	-
Level_4	57.22	42.78	-	-	208839.9	179608.5	-	-
Level_5	50.38	49.62	-	-	182483.4	206818.7	-	-
Level_6	42.81	57.19	-	-	156289.7	237979.2	-	-
Level_7	35.36	64.64	-	-	126252.5	264125.0	-	-
Level_8	27.10	72.90	-	-	95530.1	296740.6	-	-
Level_9	22.10	77.90	-	-	77895.0	317831.5	-	-
Feed								
Level_0	0.00	-	100.00	-	319.6	-	436731.9	-
Level_1	21.66	-	78.34	-	75282.6	-	348692.6	-
Level_10	100.00	-	0.00	-	374290.4	-	259.4	-
Level_2	28.35	-	71.65	-	100102.4	-	320146.7	-
Level_3	36.02	-	63.98	-	128464.6	-	288949.4	-
Level_4	44.48	-	55.52	-	159504.4	-	252460.9	-
Level_5	52.12	-	47.88	-	190972.1	-	219589.3	-
Level_6	60.08	-	39.92	-	218251.0	-	182604.3	-
Level_7	67.57	-	32.43	-	245833.1	-	148171.1	-
Level_8	75.09	-	24.91	-	276073.2	-	114844.3	-
Level_9	82.12	-	17.88	-	305157.1	-	82575.8	-
Bottom								
Level_0	-	-	100.00	0.00	-	-	428055.9	948.4
Level_1	-	-	78.54	21.46	-	-	344476.1	85387.8
Level_10	-	-	0.00	100.00	-	-	878.2	424670.6
Level_2	-	-	72.65	27.35	-	-	324875.9	111556.3
Level_3	-	-	64.71	35.29	-	-	289743.2	143138.6
Level_4	-	-	56.73	43.27	-	-	254814.6	176458.3
Level_5	-	-	49.37	50.63	-	-	224930.5	208383.4
Level_6	-	-	41.87	58.13	-	-	188842.9	238336.2
Level_7	-	-	34.16	65.84	-	-	153794.4	270360.5
Level_8	-	-	26.50	73.50	-	-	120344.9	302894.8
Level_9	-	-	18.82	81.18	-	-	86663.7	340855.8
Side								
Level_10	25.02	24.03	38.25	12.70	88911.2	97928.3	171319.1	50686.2
Level_11	39.01	11.95	24.30	24.74	143319.3	47914.8	109740.6	103230.3
Level_13	55.94	14.46	14.43	15.17	204733.1	60446.6	65880.1	61908.5
Level_14	15.19	14.41	14.58	55.83	54764.9	59746.7	66865.6	230892.1
Level_15	15.13	55.21	14.52	15.14	52877.9	220300.3	64136.4	59875.8
Level_16	15.19	55.18	14.57	15.06	53167.0	224131.4	64044.3	59447.8
Level_2	35.75	14.31	35.10	14.84	129270.9	59022.8	159793.3	60116.6
Level_3	21.84	28.23	20.97	28.96	77225.3	115210.4	93636.9	115929.5
Level_4	26.92	17.96	26.19	28.93	97562.5	72514.9	118406.4	118247.5
Level_5	24.50	33.38	15.08	27.04	87984.6	135524.1	67435.3	109475.5
Level_7	28.89	21.31	28.11	21.69	103490.5	87268.6	126171.9	87303.1
Level_8	25.22	24.08	11.76	38.94	91070.1	99901.5	53202.5	159405.3
Level_9	12.89	38.24	24.07	24.79	45453.6	156627.5	107611.6	99467.8

Table A- 2 Mass fraction comparison between analytical weight and GC-Standards

Standard Name	BuAc	BuOH	HeAc	HeOH	BuAc	BuOH	HeAc	HeOH
	w %				w %			
Method	Analytical weight				GC-Standards			
Level-0	72.56	27.44	0.00	0.00	72.19	27.50	-	-
Level-1	71.41	28.59	0.00	0.00	71.21	28.79	-	-
Level-2	71.37	27.57	1.07	0.00	71.11	27.79	1.09	-
Level-3	0.00	0.00	34.57	65.43	-	-	33.86	65.79
Level-4	0.00	0.00	39.15	60.85	-	-	38.49	61.28
Level-5	0.00	0.00	63.47	36.53	-	-	62.78	37.04
Level-6	48.40	30.96	20.64	0.00	47.81	31.75	20.40	-
Level-7	22.23	25.03	31.16	21.58	22.25	25.27	30.68	21.70
Level-8	53.12	0.00	0.00	46.88	53.10	-	-	46.90
Level-9	62.83	0.00	0.00	37.17	62.80	-	-	37.20
Level-10	41.91	0.00	0.00	58.09	41.83	-	-	58.17
Level-12	70.29	27.44	1.18	1.09	69.95	27.58	1.19	1.28

A.2 Experimental Data

A.2.1 Mass Fractions

Table A- 3 Selected measured mass fraction values TWK99

Sample Name	Product Stream	Time	BuAc	BuOH	HeAc	HeOH
		[h]	w %			
TWK99_D06	Distillate	4.20	79.66	20.29		
TWK99_D09	Distillate	5.20	79.57	20.39		
TWK99_D12	Distillate	6.20	79.70	20.26		
TWK99_D15	Distillate	7.20	79.60	20.32		
TWK99_D18	Distillate	8.03	79.61	20.31		
TWK99_D19	Distillate	8.20	79.67	20.29		
TWK99_B06	Bottom	4.20			36.51	62.98
TWK99_B09	Bottom	5.20			36.12	63.36
TWK99_B12	Bottom	6.20			36.48	62.98
TWK99_B15	Bottom	7.20			35.90	63.54
TWK99_B18	Bottom	8.03			36.51	62.94
TWK99_B19	Bottom	8.20			36.59	62.84
TWK99_S02	Side	4.20	69.84	23.16	4.84	1.82
TWK99_S05	Side	5.20	72.62	23.16	2.87	1.17
TWK99_S08	Side	6.20	78.64	21.22	0.09	0.05
TWK99_S12	Side	7.20	78.48	21.36	0.07	0.08
TWK99_S14	Side	8.03	78.48	21.38	0.06	0.08
TWK99_S15	Side	8.20	78.50	21.37	0.06	0.08

Table A- 4 Selected measured mass fraction values TWK100

Sample Name	Product Stream	Time [h]	BuAc	BuOH w %	HeAc	HeOH
TWK100_D08	Distillate	4.28	79.31	20.63		
TWK100_D11	Distillate	5.28	79.36	20.61		
TWK100_D14	Distillate	6.28	79.36	20.61		
TWK100_D17	Distillate	7.28	79.38	20.58		
TWK100_D20	Distillate	7.78	79.33	20.60		
TWK100_D21	Distillate	7.95	79.32	20.60		
TWK100_B08	Bottom	4.28			36.18	63.38
TWK100_B11	Bottom	5.28			36.15	63.40
TWK100_B14	Bottom	6.28			37.22	62.32
TWK100_B17	Bottom	7.28			35.46	64.10
TWK100_B20	Bottom	7.78			36.04	63.54
TWK100_B21	Bottom	7.95			36.30	63.27
TWK100_S01	Side	4.28	78.37	21.40		
TWK100_S04	Side	5.28	77.16	22.77		
TWK100_S07	Side	6.28	77.18	22.76		
TWK100_S10	Side	7.28	77.13	22.80		
TWK100_S13	Side	7.78	77.21	22.73		
TWK100_S14	Side	7.95	77.14	22.80		

Table A- 5 Selected measured mass fraction values TWK101

Sample Name	Product Stream	Time [h]	BuAc	BuOH w %	HeAc	HeOH
TWK101_D07	Distillate	4.30	79.70	20.23		
TWK101_D10	Distillate	5.30	79.69	20.25		
TWK101_D13	Distillate	6.30	79.76	20.20		
TWK101_D17	Distillate	7.30	79.66	20.30		
TWK101_D20	Distillate	7.80	79.73	20.22		
TWK101_D21	Distillate	7.97	79.73	20.22		
TWK101_B07	Bottom	4.30			46.22	53.35
TWK101_B10	Bottom	5.30			53.10	46.56
TWK101_B13	Bottom	6.30			53.65	45.93
TWK101_B17	Bottom	7.30			58.19	41.46
TWK101_B20	Bottom	7.80			58.55	41.09
TWK101_B21	Bottom	7.97			58.19	41.39
TWK101_S02	Side	4.30	77.50	22.30	0.15	0.07
TWK101_S05	Side	5.30	81.90	16.10	0.89	0.33
TWK101_S08	Side	6.30	81.60	18.40		0.05
TWK101_S12	Side	7.30	83.30	16.40	0.12	0.08
TWK101_S15	Side	7.80	83.50	16.30	0.12	0.08
TWK101_S16	Side	7.97	83.10	16.70	0.09	0.07

Table A- 6 Selected measured mass fraction values TWK102

Sample Name	Product Stream	Time	BuAc	BuOH	HeAc	HeOH
		[h]	w %			
TWK102_D07	Distillate	3.75	79.89	20.07		
TWK102_D10	Distillate	4.75	79.77	20.18		
TWK102_D13	Distillate	5.75	79.67	20.28		
TWK102_D16	Distillate	6.75	79.69	20.26		
TWK102_D19	Distillate	7.75	79.70	20.24		
TWK102_D20	Distillate	8.08	79.68	20.26		
TWK102_B07	Bottom	3.75			62.76	36.80
TWK102_B10	Bottom	4.75			63.30	36.34
TWK102_B13	Bottom	5.75			63.61	36.02
TWK102_B16	Bottom	6.75			63.67	35.93
TWK102_B19	Bottom	7.75			63.86	35.78
TWK102_B20	Bottom	8.08			63.86	35.76
TWK102_S01	Side	3.75	81.40	18.50		
TWK102_S04	Side	4.75	77.60	18.90		
TWK102_S07	Side	5.75	79.90	20.00		
TWK102_S10	Side	6.75	79.80	20.20		
TWK102_S13	Side	7.75	79.10	20.40		
TWK102_S14	Side	8.08	79.00	20.20		

Table A- 7 Selected measured mass fraction values TWK103

Sample Name	Product Stream	Time [h]	BuAc	BuOH	HeAc	HeOH
				w %		
TWK103_D05	Distillate	3.75	79.43	20.52		
TWK103_D08	Distillate	4.75	79.34	20.62		
TWK103_D12	Distillate	5.75	79.26	20.69		
TWK103_D15	Distillate	6.25	79.28	20.67		
TWK103_D19	Distillate	6.92	79.35	20.61		
TWK103_D20	Distillate	7.08	79.34	20.62		
TWK103_B05	Bottom	3.75			39.01	60.44
TWK103_B08	Bottom	4.75			32.48	67.09
TWK103_B12	Bottom	5.75			28.52	71.08
TWK103_B15	Bottom	6.25			27.09	72.56
TWK103_B19	Bottom	6.92			25.65	74
TWK103_B20	Bottom	7.08			25.87	73.79
TWK103_S01	Side	3.75	79.0	20.8	0.15	20.81
TWK103_S04	Side	4.75	7.4	31.0	41.13	31.00
TWK103_S08	Side	5.75	5.3	21.9	47.37	21.95
TWK103_S11	Side	6.25	6.6	24.0	45.40	24.04
TWK103_S15	Side	6.92	6.7	22.4	46.18	22.38
TWK103_S16	Side	7.08	7.1	23.9	45.22	23.86

Table A- 8 Selected measured mass fraction values TWK104

Sample Name	Product Stream	Time [h]	BuAc	BuOH w %	HeAc	HeOH
TWK104_D07	Distillate	4.83	79.54	20.46		
TWK104_D10	Distillate	5.83	79.54	20.46		
TWK104_D13	Distillate	6.83	79.63	20.37		
TWK104_D18	Distillate	7.83	79.54	20.46		
TWK104_D20	Distillate	8.17	79.56	20.44		
TWK104_D21	Distillate	8.33	79.54	20.46		
TWK104_B07	Bottom	4.83			44.08	55.92
TWK104_B10	Bottom	5.83			46.99	53.01
TWK104_B13	Bottom	6.83			49.35	50.65
TWK104_B18	Bottom	7.83			50.87	49.13
TWK104_B20	Bottom	8.17			51.44	48.56
TWK104_B21	Bottom	8.33			51.69	48.31
TWK104_S01	Side	4.83	1.30	1.40	58.80	36.70
TWK104_S04	Side	5.83	76.80	21.40	1.15	0.63
TWK104_S07	Side	6.83	76.90	22.30		
TWK104_S12	Side	7.83	78.90	20.00		
TWK104_S14	Side	8.17	79.20	19.70		
TWK104_S15	Side	8.33	79.20	19.70		

Table A- 9 Selected measured mass fraction values TWK105

Sample Name	Product Stream	Time [h]	BuAc	BuOH	HeAc	HeOH
				w %		
TWK105_D08	Distillate	4.23	79.31	20.66		
TWK105_D11	Distillate	5.23	79.67	20.29		
TWK105_D14	Distillate	6.23	79.80	20.16		
TWK105_D20	Distillate	7.23	79.88	20.08		
TWK105_D23	Distillate	7.73	79.80	20.15		
TWK105_D24	Distillate	7.90	79.82	20.1		
TWK105_B08	Bottom	4.23			36.95	62.73
TWK105_B11	Bottom	5.23			36.88	62.84
TWK105_B14	Bottom	6.23			37.60	62.32
TWK105_B20	Bottom	7.23			38.03	61.97
TWK105_B23	Bottom	7.73			38.37	61.63
TWK105_B24	Bottom	7.90			38.5	61.47
TWK105_S01	Side	4.23	79.91	19.09	0.73	0.27
TWK105_S04	Side	5.23	39.09	39.19	16.26	5.45
TWK105_S07	Side	6.23	48.11	34.33	13.20	4.36
TWK105_S13	Side	7.23	53.58	30.46	11.88	4.08
TWK105_S16	Side	7.73	57.06	31.22	8.94	2.78
TWK105_S17	Side	7.90	58.92	31.27	7.57	2.24

Table A- 10 Selected measured mass fraction values TWK106

Sample Name	Product Stream	Time [h]	BuAc	BuOH	HeAc	HeOH
				w %		
TWK106_D05	Distillate	4.75	79.01	20.94		
TWK106_D08	Distillate	5.75	78.95	21.01		
TWK106_D11	Distillate	6.75	78.98	20.98		
TWK106_D16	Distillate	7.75	78.94	21.02		
TWK106_D19	Distillate	8.25	78.96	21.00		
TWK106_D20	Distillate	8.42	78.93	21.03		
TWK106_B05	Bottom	4.75			41.60	58.4
TWK106_B08	Bottom	5.75			40.12	59.81
TWK106_B11	Bottom	6.75			39.70	60.21
TWK106_B16	Bottom	7.75			39.87	60.03
TWK106_B19	Bottom	8.25			39.96	60.04
TWK106_B20	Bottom	8.42			40.09	59.91
TWK106_S01	Side	4.75	64.80	28.80	4.91	1.44
TWK106_S04	Side	5.75	10.80	22.70	42.47	24.07
TWK106_S07	Side	6.75	13.00	24.10	40.16	22.77
TWK106_S12	Side	7.75	18.20	25.60	36.16	20.03
TWK106_S15	Side	8.42	17.40	23.90	37.52	21.20