

**POLITECNICO DI MILANO**

School of Industrial and Information Engineering

Master of Science in Chemical Engineering

Department of Chemistry, Material and Chemical Engineering  
“Giulio Natta”



---

**Molecular Tracking: A Novel Approach for  
Multicomponent Distillation Column Design**

---

in collaboration with

Process and Systems Engineering Center (PROSYS), Department of Chemical  
and Biochemical Engineering, Technical University of Denmark



***Supervisors:***

*Professor, Flavio Manenti*

*Assistant Professor, Seyed Soheil Mansouri*

***Co-supervisors:***

*Associate Professor, Jens Abildskov*

*Postdoctoral Fellow, Isuru A. Udugama*

***Master's Thesis***

***Author:***

***Nima Nazemzadeh***

***ID: 10554143***

***Academic Year: 2018/2019***







---

## Abstract

The early stage design of side-draw distillation units has always been a challenging task both for academic and industrial practitioners due to a lack of simple and reliable methods to determine the side-draw location corresponding to the minimum energy demand of the system. Existing methods are based on trial and error or complex mathematical optimization, which mostly become sophisticated and tedious and often also require a validated simulation of the unit. In this work, a novel, simple framework, similar in concept to conventional methods is proposed to design side-draw distillation units with infinite dilution of impurities of middle boiling component using the concept of molecular tracking. This concept is based on a probability function highly correlated to thermodynamic properties of the system, which evaluates that how probable is for a single molecule of a component in the mixture moving upward/downward on each stage in the unit. A systematic framework is developed to find the corresponding location of side-draw on a column. First, a binary distillation is designed for the key components in the mixture using driving force-based method well-known as an energy efficient approach. Since driving force-based method forces the column to operate at maximum driving force, the “column only” requires the minimum energy exchange for operation. An in detail illustration of which is discussed in this study. Then, the impurity is introduced in the feed as the middle boiling component and the probability profile of such impurity is generated based on the thermodynamic properties of this component and molar flows of the column. Thereafter, the side-draw is located on a tray, in which the molecules of the impurity prefer to stay, instead of moving either upward or downward. The concept of molecular tracking and driving force are both followed by simple examples to represent their functionalities. Moreover, two side-draw distillation units are designed for the two case studies of ideal ternary mixtures with molecular tracking framework. In order to compare molecular tracking with other existing methods, the side-draw location of each case is also found by classical driving force-based method. The configurations of each method are compared to each other in terms of reboiler duties. The configuration designed by molecular tracking represents lower energy required for the reboiler of the column, which directly affects operating costs of the separation task. At the end of the work, an uncertainty analysis on relative volatility miscalculation and an economic evaluation of the possible design alternatives of side-draw distillation for the two case studies are carried out. The uncertainty analysis illustrates that the framework developed by the author is capable of proposing the same result even with an uncertainty in system’s thermodynamics in terms of relative volatility. Moreover, the side-draw distillation is economically more suitable for an ideal ternary mixture with trace amounts of middle boiling component.

## Preface

The dissertation “Molecular tracking; a novel approach for multicomponent distillation design” the basis of which is a presentation provided by Clifford Maat from TPC Group in AIChE 2017 Spring Meeting – Kister Distillation Symposium March 2017 in San Antonio Texas, has been written to fulfill the graduation requirements of the master degree program of Process Engineering at the Department of Chemistry, Material and Chemical Engineering of Politecnico di Milano. I was engaged in researching and writing this dissertation from March 2018 to March 2019.

The project was undertaken at the request of PROSYS (Process and Systems Engineering Research Centre) of Chemical and Biochemical Engineering Department of Technical University of Denmark (DTU) where I took a visiting scholar position. My research question was formulated together with my supervisors Seyed Soheil Mansouri, Flavio Manenti and my tutors Jens Ablidskov and Isuru A. Udugama. As the first researchers focusing on such a novel topic, I found the procedure so difficult, but carrying out an extensive investigation has allowed me to answer the question that we identified. Fortunately, my supervisors and my tutors were always available and willing to answer my queries.

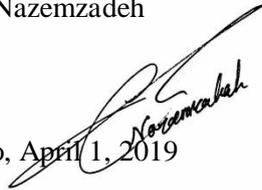
I would like to thank my supervisors and tutors for their excellent guidance and support during the process. I would also want to thank all respondents, without whose cooperation I have not been able to accomplish this study.

To my other colleagues at PROSYS: I would like to thank you for your cooperation as well. It was always helpful to bat ideas about my research around with you. I also benefitted from debating issues with my friends and family. If I ever lost interest, you kept me motivated. My parents deserve a particular note of thanks: your wise counsel and kind words have, as always, helped me well.

I hope you enjoy your reading.

Nima Nazemzadeh

Milano, April 1, 2019

A handwritten signature in black ink, appearing to read 'Nima Nazemzadeh', is written over the printed name and date.

# Table of Contents

<i>Abstract</i> .....	<i>i</i>
<i>Preface</i> .....	<i>ii</i>
<i>Table of Contents</i> .....	<i>iii</i>
<i>List of Figures</i> .....	<i>v</i>
<i>List of Tables</i> .....	<i>vii</i>
<i>Nomenclature</i> .....	<i>viii</i>
<i>List of Abbreviations</i> .....	<i>x</i>
<b>Chapter 1: Introduction</b> .....	<b>1</b>
1.1. <i>Background</i> .....	<i>1</i>
1.2. <i>Problem Statement</i> .....	<i>8</i>
1.3. <i>Hypothesis</i> .....	<i>8</i>
<b>Chapter 2: Concepts</b> .....	<b>11</b>
2.1. <i>Driving Force</i> .....	<i>11</i>
2.2. <i>Molecular Tracking</i> .....	<i>17</i>
2.2.1. <i>Rectifying Section</i> .....	<i>18</i>
2.2.2. <i>Stripping Section</i> .....	<i>19</i>
2.2.3. <i>Feed Tray</i> .....	<i>20</i>
2.2.4. <i>Condenser</i> .....	<i>20</i>
2.2.5. <i>Side-draw</i> .....	<i>20</i>
<b>Chapter 3: Methodology</b> .....	<b>23</b>
3.1. <i>Molecular Tracking</i> .....	<i>23</i>
3.1.1. <i>Design a binary distillation using driving force</i> .....	<i>23</i>
3.1.2. <i>Find side-draw location using molecular tracking</i> .....	<i>27</i>
3.2. <i>Driving force method for side-draw</i> .....	<i>30</i>
<b>Chapter 4: Case Studies and Results</b> .....	<b>33</b>
4.1. <i>Molecular tracking application</i> .....	<i>33</i>
4.1.1. <i>Benzene, p-xylene mixture with trace amounts of toluene</i> .....	<i>34</i>
4.1.2. <i>n-Pentane, n-heptane with trace amounts of n-hexane</i> .....	<i>37</i>
4.2. <i>Application of classical driving force method</i> .....	<i>41</i>
4.2.1. <i>Benzene, p-xylene mixture with trace amounts of toluene</i> .....	<i>41</i>
4.2.2. <i>n-Pentane, n-heptane mixture with trace amounts of n-hexane</i> .....	<i>42</i>
<b>Chapter 5: Concluding Remarks</b> .....	<b>45</b>
5.1. <i>Molecular tracking against driving force</i> .....	<i>46</i>
5.2. <i>Uncertainty analysis</i> .....	<i>49</i>
5.3. <i>Economic Evaluation</i> .....	<i>53</i>

---

5.3.1. Benzene, <i>p</i> -xylene with trace amounts of toluene .....	53
5.3.2. <i>n</i> -Pentane, <i>n</i> -heptane with trace amounts of <i>n</i> -hexane .....	56
References .....	59
Appendix A: Current design methods of side-draw distillation.....	61
A.1. McCabe-Thiele Extension .....	61
A.2. Geometric Method .....	64
A.3. Shortcut design method.....	65
Appendix B: MATLAB codes .....	66
B.1. Molecular tracking.....	66
B.2. T-XY data determination.....	73
B.3. Nonlinear regression for relative volatility determination.....	74
Appendix C: Datasheets .....	75
C.1. BTX Case Study.....	75
C.2. PHH Case Study.....	77

## List of Figures

<i>Fig 1-1. Schematic figures of intensified distillation unit application: side-stream distillation (a), heat integrated distillation column (b), cyclic distillation column (c), reactive distillation column (d) [2].....</i>	<i>2</i>
<i>Fig 1-2. Global primary energy mix in the new policies scenario (Mtoe) [1].....</i>	<i>5</i>
<i>Fig 1-3. Illustration of Side-stream distillation column as a process intensification unit.....</i>	<i>5</i>
<i>Fig 2-1. Schematic diagram of driving force with the important design parameters [2].....</i>	<i>12</i>
<i>Fig 2-2. A generic driving force diagram (a) and the corresponding McCabe-Thiele diagram (b).....</i>	<i>13</i>
<i>Fig 2-3. A driving-force diagram with the operating lines intersecting at <math>x = Dx</math>. The measurements a, b and c are indicated on the figure, for better understanding of the reasoning behind using driving force to obtain the lowest column energy transfer [2]......</i>	<i>14</i>
<i>Fig 2-4. Driving force diagram and Gibbs free energy of liquid and vapor phase for an ideal binary mixture of hypothetical components with <math>\alpha = 2</math>.....</i>	<i>17</i>
<i>Fig 2-5. Rectifying section of the column.....</i>	<i>19</i>
<i>Fig 2-6. Stripping section of the column.....</i>	<i>19</i>
<i>Fig 2-7. (a) Schematic of a side-draw distillation column with representative molecular pathways, (b) Number of hits of light key and heavy key components, (c) Number of hits of trace component versus stage number [21].....</i>	<i>22</i>
<i>Fig 3-1. General framework overview.....</i>	<i>23</i>
<i>Fig 3-2. XY diagram of benzene and p-xylene at 1 atm.....</i>	<i>25</i>
<i>Fig 3-3. Driving force diagram of benzene and p-xylene at 1 atm.....</i>	<i>26</i>
<i>Fig 3-4. McCabe-Thiele and T-XY diagrams of proposed distillation task.....</i>	<i>27</i>
<i>Fig 3-5. Probability profile of ethanol in the distillation task.....</i>	<i>29</i>
<i>Fig 4-1. XY diagram of benzene, p-xylene at 1 atm.....</i>	<i>34</i>
<i>Fig 4-2. Benzene, p-xylene driving force diagram at 1 atm.....</i>	<i>34</i>
<i>Fig 4-3. Reflux ratio and minimum reflux ratio on driving force diagram of benzene and p-xylene.....</i>	<i>35</i>
<i>Fig 4-4. McCabe-Thiele diagram for benzene, p-xylene at 1 atm, <math>RR=1.46</math>.....</i>	<i>35</i>
<i>Fig 4-5. T-XY diagram and temperature profile of the column for benzene and p-xylene.....</i>	<i>35</i>
<i>Fig 4-6. Schematic figure of the distillation unit for Ben and p-X.....</i>	<i>35</i>
<i>Fig 4-7. Probability profile of Tol inside the column.....</i>	<i>36</i>
<i>Fig 4-8. Trays in which Tol probability is 50%.....</i>	<i>36</i>
<i>Fig 4-9. Reboiler duty of the BTX column versus side-draw location.....</i>	<i>36</i>
<i>Fig 4-10. HYSYS flowsheet of BTX column.....</i>	<i>37</i>

---

<i>Fig 4-11. McCabe-Thiele diagram of n-Pen and n-Hep at 5 atm</i> .....	38
<i>Fig 4-12. Driving force diagram of n-Pen and n-Hep at 5 atm</i> .....	38
<i>Fig 4-13. Reflux ratio and minimum reflux ratio on driving force diagram of n-Pen and n-Hep</i> ...	38
<i>Fig 4-14. McCabe-Thiele diagram for n-Pen, n-Hep at 5 atm, RR=1.9</i> .....	39
<i>Fig 4-15. T-XY diagram and temperature profile of the column for n-Pen and n-Hep</i> .....	39
<i>Fig 4-16. Schematic figure of the distillation unit for n-Pen and n-Hep.</i> .....	39
<i>Fig 4-17. Probability profile of n-Hex inside the column</i> .....	39
<i>Fig 4-18. Trays in which n-Hex probability is 50%</i> .....	40
<i>Fig 4-19. Reboiler duty of the PHH column versus side-draw location</i> .....	40
<i>Fig 4-20. HYSYS flowsheet of PHH column</i> .....	40
<i>Fig 4-21. Binary driving force for BTX mixture at 1 atm</i> .....	41
<i>Fig 4-22. Minimum reflux ratio of distillation unit for BTX column</i> .....	41
<i>Fig 4-23. Joint driving force diagram of BTX column at 1 atm</i> .....	41
<i>Fig 4-24. Binary driving force for PHH mixture at 5 atm</i> .....	42
<i>Fig 4-25. Minimum reflux ratio of PHH distillation unit at 5 atm</i> .....	42
<i>Fig 4-26. Joint driving force diagram of PHH column at 5 atm</i> .....	43
<i>Fig 5-1. Driving force and Gibbs free energy diagram of benzene, p-xylene</i> .....	47
<i>Fig 5-2. Corresponding composition of feed and side-draw for BTX distillation column</i> .....	47
<i>Fig 5-3. Corresponding composition of feed and side-draw for PHH distillation column</i> .....	48
<i>Fig 5-4. Corresponding composition of feed and side-draw for PHH distillation column</i> .....	49
<i>Fig 5-5. Probability profiles of toluene in BTX column corresponding to a <math>\pm 5\%</math> perturbation on relative volatility of benzene and p-xylene</i> .....	51
<i>Fig 5-6. Probability profiles of toluene in BTX column corresponding to a <math>\pm 10\%</math> perturbation on relative volatility of benzene and p-xylene</i> .....	51
<i>Fig 5-7. Probability profiles of toluene in PHH column corresponding to a <math>\pm 5\%</math> perturbation on relative volatility of n-pentane and n-heptane</i> .....	52
<i>Fig 5-8. Probability profiles of toluene in PHH column corresponding to a <math>\pm 10\%</math> perturbation on relative volatility of n-pentane and n-heptane</i> .....	53
<i>Fig 5-9. HYSYS flowsheet of BTX sequential distillation units</i> .....	54
<i>Fig 5-10. Comparison of BTX alternatives in terms of costs</i> .....	56
<i>Fig 5-11. HYSYS flowsheet of PHH sequential distillation units</i> .....	57
<i>Fig 5-12. Comparison of BTX alternatives in terms of costs</i> .....	58

---

## List of Tables

<i>Table 1-1. General comparison of side-stream column design methods</i> .....	7
<i>Table 3-1. Feed composition of Example 3.1</i> .....	25
<i>Table 3-2. Feed composition of hypothetical binary mixture</i> .....	25
<i>Table 3-3. Process specifications</i> .....	26
<i>Table 3-4. Feed composition of Example 3.2</i> .....	28
<i>Table 4-1. Datasheet of BTX case study</i> .....	34
<i>Table 4-2. Datasheet of n-Pentane, n-Heptane and n-Hexane case study</i> .....	38
<i>Table 4-3. Datasheet of BTX case study designed by driving force</i> .....	41
<i>Table 4-4. Datasheet of PHH case study designed by driving force</i> .....	42
<i>Table 5-1. Parameters required for column design</i> .....	54
<i>Table 5-2. Parameters required for column sizing</i> .....	55
<i>Table 5-3. Costs of BTX alternatives</i> .....	55
<i>Table 5-4. Parameters required for column design</i> .....	57
<i>Table 5-5. Parameters required for column sizing</i> .....	57
<i>Table 5-6. Costs of PHH alternatives</i> .....	57

## Nomenclature

$CC$	Ratio of reflux ratio and minimum reflux ratio	[-]
$D_S$	Liquid composition corresponding to side-draw location	$\left[\frac{mol}{mol}\right]$
$D_x$	Liquid composition corresponding to feed location	$\left[\frac{mol}{mol}\right]$
$D_y$	Value of maximum driving force	$\left[\frac{mol}{mol}\right]$
$F$	Feed flowrate	$\left[\frac{kmol}{h}\right]$
$F_D$	Driving force value	$\left[\frac{mol}{mol}\right]$
$G$	Molar Gibbs free energy	$\left[\frac{J}{mol}\right]$
$\Delta G^{vap}$	Gibbs free energy of vaporization	$\left[\frac{J}{mol}\right]$
$\Delta G/RT$	Dimensionless Gibbs free energy	[-]
$\Delta H$	Molar enthalpy	$\left[\frac{J}{mol}\right]$
$K\text{-value}$	Ratio of binary relative volatilities	[-]
$L$	Liquid flowrate of rectifying section	$\left[\frac{kmol}{h}\right]$
$L'$	Liquid flowrate of stripping section	$\left[\frac{kmol}{h}\right]$
$L''$	Liquid flowrate of the section between side-draw and feed	$\left[\frac{kmol}{h}\right]$
$N_F$	Feed tray in distillation unit	[-]
$N_S$	Side-stream tray in distillation unit	[-]
$N_T$	Total number of theoretical trays	[-]
$P$	Pressure	[ <i>atm</i> ]
$p^{sat}$	Saturation pressure or vapor pressure	[ <i>atm</i> ]
$Q$	Heat flow	[ <i>MW</i> ]
$Q$	Feed extent of vaporization or feed vapor fraction	$\left[\frac{mol}{mol}\right]$
$R$	Gas constant	$\left[\frac{J}{mol.K}\right]$

---

$S$	Side-stream flowrate	$[\frac{kmol}{h}]$
$T$	Temperature	$[^{\circ}C]$
$V$	Vapor flowrate of rectifying section	$[\frac{kmol}{h}]$
$V'$	Vapor flowrate of stripping section	$[\frac{kmol}{h}]$
$V''$	Vapor flowrate of the section between side-draw and feed	$[\frac{kmol}{h}]$
$X$	Liquid composition of light key component	$[\frac{mol}{mol}]$
$x_B$	Light key composition of bottom product	$[\frac{mol}{mol}]$
$x_D$	Light key composition of distillate product	$[\frac{mol}{mol}]$
$x_S$	Light key composition of side-stream	$[\frac{mol}{mol}]$
$Y$	Vapor composition of light key component	$[\frac{mol}{mol}]$
$z_F$	Light key composition in feed stream	$[\frac{mol}{mol}]$
$\alpha$	Relative volatility of two components	$[-]$
$\beta$	Probability value	$[-]$
$\gamma^{\infty}$	Activity coefficient in infinite dilution	$[-]$
$\varphi^{\infty}$	Fugacity Coefficient in infinite dilution	$[-]$

## List of Abbreviations

<i>Abbreviation</i>	<i>Explanation</i>
<i>Ben</i>	<i>Benzene</i>
<i>BR</i>	<i>Boilup ratio</i>
<i>BR<sub>min</sub></i>	<i>Minimum boilup ratio</i>
<i>BTX</i>	<i>Mixture of benzene, toluene and p-xylene</i>
<i>DF</i>	<i>Driving force</i>
<i>Fig</i>	<i>Figure</i>
<i>MB</i>	<i>Middle boiling component in a ternary mixture</i>
<i>MT</i>	<i>Molecular tracking</i>
<i>Mtoe</i>	<i>Millions tonnes of oil equivalent for energy production</i>
<i>n-Hep</i>	<i>Normal heptane</i>
<i>n-Hex</i>	<i>Normal hexane</i>
<i>n-Pen</i>	<i>Normal pentane</i>
<i>OPEX</i>	<i>Operating expenditure</i>
<i>PFD</i>	<i>Process flow diagram</i>
<i>PHH</i>	<i>Mixture of n-pentane, n-hexane and n-heptane</i>
<i>p-X</i>	<i>para-Xylene</i>
<i>RR</i>	<i>Reflux ratio</i>
<i>RR<sub>min</sub></i>	<i>Minimum reflux ratio</i>
<i>Tol</i>	<i>Toluene</i>
<i>Vap</i>	<i>Vaporization</i>
<i>VLE</i>	<i>Vapor liquid equilibrium</i>





# Chapter 1: Introduction

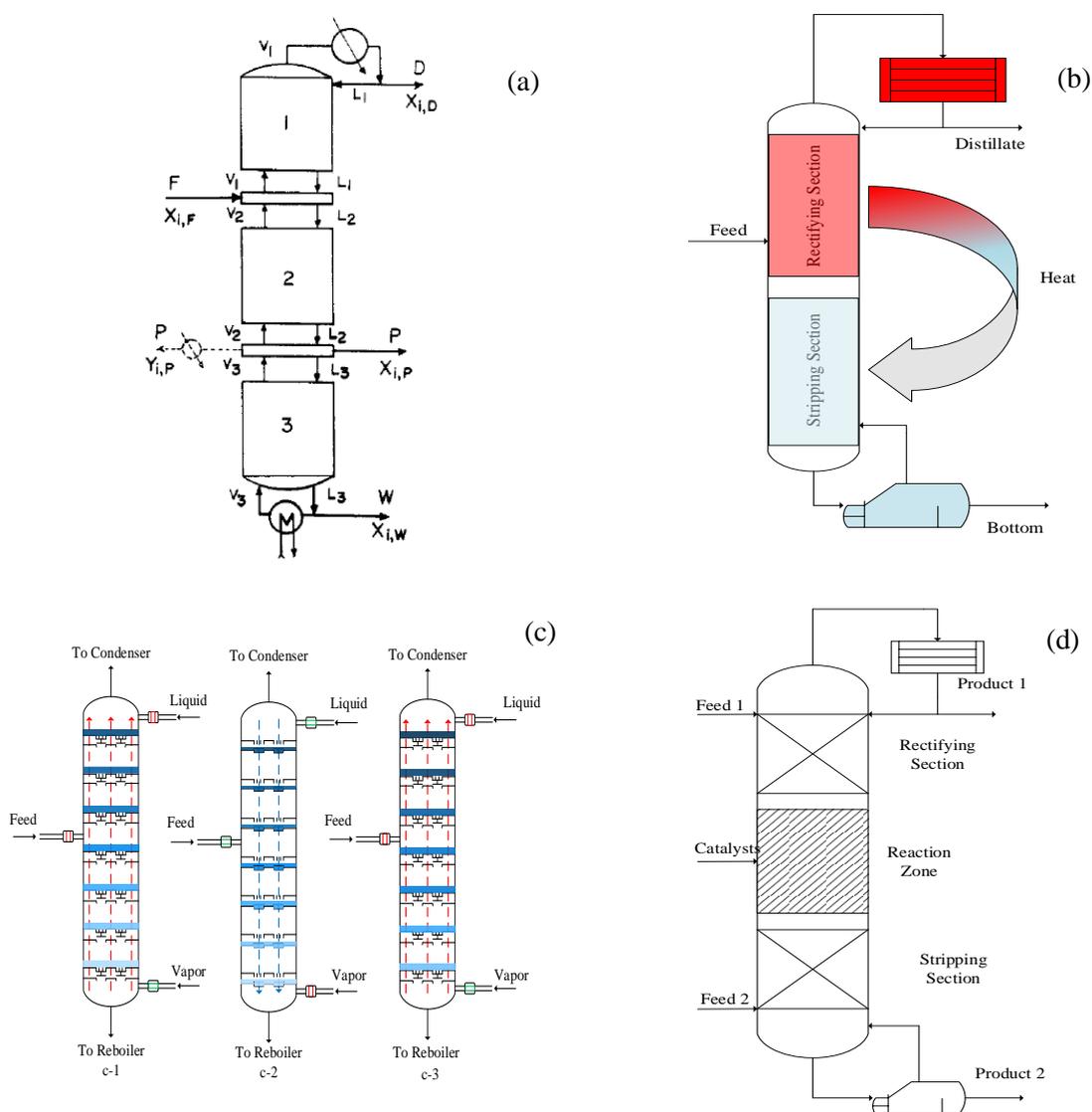
## 1.1. Background

The requisiteness of this study lies behind the importance of saving energy over chemical processes regarding the economical point of view as well as the consequent detriments that inattentive energy consumption may cause to the environment. Moreover, energy has recently come to be a global issue, due to the finite sources of energy and drastic increase of energy consumption across the globe. According to the International Energy Agency scenario, reported in 2016, the global energy demand will rise nearly 30% from 2014 to 2040 [1], which means on an average annual rate of 1.25%. In so doing, an effective strategy has to adopt to decelerate the energy consumption growth rate. The author strongly believes that chemical processes are one of the areas always highly prone to develop novel approaches to this end.

Distillation has for decades been the academic and industrial work horse for large volume fluid separation [2]. In distillation, the separation is achieved through vaporization of the liquid phase and generation of a vapor phase with a different composition due to difference in the volatility of the compounds being processed. Liquid and vapor is moving counter currently through the column by a number of trays or packing material designed to enhance phase contact and reduce back mixing for both the liquid and vapor flows. The vapor leaving the column in the top is rich in the most volatile components and this stream is condensed and used as liquid reflux back to the column as well as the distillate product. Likewise, the liquid leaving the column in the bottom stream is rich in the least volatile components. This liquid stream is partially vaporized and used as vapor reflux and the rest leaves the column as the bottom product. The feed mixture is introduced somewhere along the column. The column section above the feed is referred to as the rectification section and the part below the stripping section. With over 40,000 distillation units in operation nowadays, even slight developments will be able to reduce drastically both production and maintenance costs of distillation column [2,3].

One way to achieve such improvements can be utilizing the difference in boiling points between distillate and bottom products, energy required for vaporization at a higher temperature that can be recovered by the condensation of the overhead vapor [2]. Moreover, separation efficiencies in tray columns are not optimal in use due to liquid back mixing and a flow pattern, which is not the ideal counter current flow [2]. Additionally, process intensification can be used, where in distillation, different units are combined together to create an application of intensified and multi-fractional processes in chemical industry [4]. Several applications of intensified distillation column applications are proposed so far on an industrial scale including side-stream distillation, heat

integrated distillation, cyclic distillation and reactive distillations. The schematic figures of these units are represented in Fig 1-1.



**Fig 1-1.** Schematic figures of intensified distillation unit application: side-stream distillation (a), heat integrated distillation column (b), cyclic distillation column (c), reactive distillation column (d) [2]

Throughout the twentieth century, distillation column was classified as the most used unit operation for vapor liquid mixture separation in chemical processes. This unit operation is woefully considered as a highly intensive technique that consumes nearly 40% of total required energy of a chemical plant [2]. Distillation energy contribution was reported nearly 3% of the total U.S national energy consumption in 1976 [5]. Approximately, two-thirds of that energy is consumed in petroleum refining, where distillation is used to separate crude oil into petroleum fractions, light hydrocarbons and aromatic compounds [5]. As, both industrial and academic practitioners have declared a profound intention and put considerable efforts to diminish the required energy for this unit operation.

The synthesis of separation configurations and sequences is a key area of the overall process synthesis as separation is one of the most important elements in any chemical process. As such, a large effort has been placed on determining ways of finding the best separation configurations, especially concerning distillation columns. Categories of the methods for synthesis of separations are methods based on heuristics, algorithmic methods and graphical methods [2].

*Heuristic methods:* Sometimes these methods are referred to as rule-based methods, which are the oldest methods in the field of process synthesis [2]. Review of such methods are thoroughly represented in a prior publication [6]. Despite the ease of application of these methods and their quick natures, there exist some drawbacks to this type of method; occasionally the rules of the method are conflicting or contradictory in nature that must be reconciled based on the personal judgement [7,8]. Heuristic methods still have their functionality in process design and synthesis, specifically in preliminary screening methods, to reduce the complexity of the problem and simultaneously maintaining the consistency of the results. Many heuristic methods has been developed and still are being implemented or are the foundation for more recent heuristic developments [9–12].

*Algorithmic methods:* The purpose of developing such methods is to synthesize the optimal separation configuration or sequence by using optimization methods and tools [2]. The general feature of these methods is they are rigorous, therefore, computational cost is required [2]. Algorithmic methods can be divided into three different subcategories: parametric methods based on thermodynamic insights and methods including mathematical programming [2]. Parametric methods try to identify the impact of different parameters on the process scheme and configuration. In separation processes, there are a lot of parameters affecting the system configuration. Hence, the application of this study will be limited [2]. Thermodynamic-based methods employ the relationships between physiochemical and separation principles. Mathematical programming methods however are to synthesize the optimum configuration of the process by using optimization techniques. They are mostly preferred due to their rigor that they only can guarantee an optimal solution [2]. Despite the optimal solution these methods may propose, their application can be only easily seen in simplified problems and the requisiteness of complex mathematical formulation and extensive computational costs are inevitable in more complicated problems.

After the review paper of Nishida *et al.* (1981), the developments on algorithmic and heuristic methods are highlighted to determine the better systems of non-heat integrated distillation columns in [13]. Malone *et al.* [14] conflicts and inaccuracies of heuristic-based methods to the selection of distillation sequences and how they can be covered by developing an analytical criteria. Their works illustrates that analytical approach gives better predictions than the heuristic-based

approaches. Moreover, they have represented that some of qualitative approaches employed in heuristic methods are incorrect.

Graphical tools have always been an option to design simple distillation units. These tools can intuitively provide the information for a first stage design of distillation columns. The combination of these information with the essential balances (material and energy balances) over the unit can also facilitate to optimize the design configuration of this unit [2]. However, by introducing intensified distillation units, the use of these methods has become more complicated and some special adjustment shall be applied on the existing tools to fit with the unit that the study is carried out on. A graphical tool uses ternary information, which is discussed in [15] in order to design distillation units for zeotropic and azeotropic mixtures. The authors of that study represents that using the graphical tool can eliminate the infeasible specifications on top and bottom product composition in a ternary distillation. The simple and well-known graphical tools employed for the design of distillation units are McCabe-Thiele and Ponchon-Savarit that have been used to design binary distillation columns. Moreover, one of the recent published methods, which is well-known as driving force also takes the advantage of using these tools in order to reduce the complexity of the mathematical formulation of distillation column. Driving force uses the difference of the chemical physical properties of the liquid and vapor phases in the system. It uses the maximum driving force between the liquid and vapor phase and makes the column to operate at that point. This is fully described in the next chapter of this dissertation by presenting a complete mathematical proof that the configuration proposed by this method would be a local optimum or near optimum solution in terms of the column duty.

Distillation columns are thoroughly categorized into two types of simple and complex units. The first group is well-known with simple binary distillation columns that only has two product streams (distillate and bottom), which for optimal/near optimal design approaches are provided such as driving force approach [16]. However, complex distillation columns are intensified process unit operations such as divided wall and side-draw units. Design procedure of these units are challenging and requires rigorous mathematical formulation or trial/error design approaches, which are inherently sophisticating. This work proposes a simple novel approach to design some specific complex distillation units that are currently in use in chemical industry.

During the past decades, profound efforts have been dedicated to develop novel and efficient frameworks for designing the side-stream distillation columns. This type of distillation is well-known as a process intensification at unit operation level, which is illustrated in Fig 1-3. Separation process of a ternary mixture can be operated as a sequential distillation column. The logic behind sequential distillation is simple. In first column, separation occurs between the two

components. Hence, one of the streams is purified by one component and the other outlet stream is a mixture of the other two compounds. The latter stream is fed to the second column and it separates the other remaining two components.

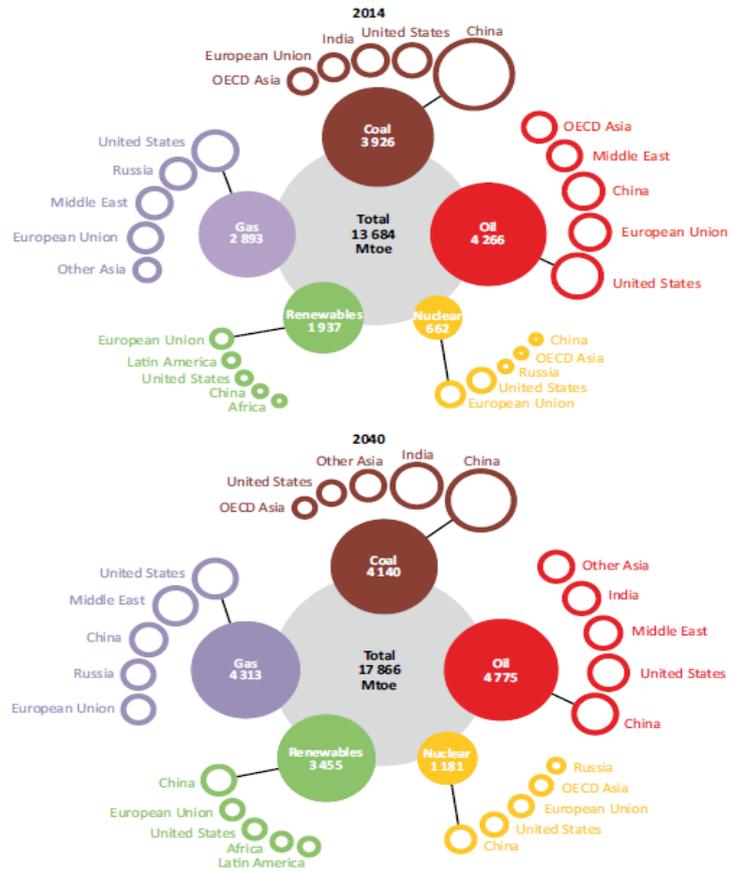


Fig.1-2. Global primary energy mix in the new policies scenario (Mtoe) [1]

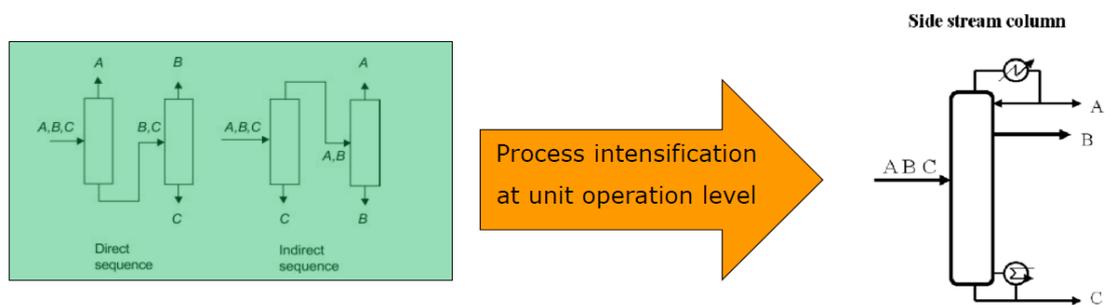


Fig 1-3. Illustration of Side-stream distillation column as a process intensification unit

A few of design methods of side-stream distillation columns are briefly introduced in the following. The design algorithms of McCabe-Thiele extension, geometric method and shortcut design are provided in Appendix. The design algorithm of driving force-based method for side-stream is fully

represented in Chapter 3. A general comparison of the aforementioned methods are represented in Table 1-1.

*McCabe-Thiele Extension:* The first method of designing a side-stream column has been introduced as an extension of McCabe-Thiele method. In order to design the column using this method, the composition of the light key component in the side-stream must be specified. Hence, the tray in which the side-stream should be located is implicitly determined by that defined composition. This may lead a deviation from optimality of operation. In other words, the reboiler should provide more energy to the mixture to make the separation scheme feasible. The design algorithm will slightly change by locating the side-draw in rectifying section or stripping section.

*Geometric Method:* Geometric method is also an intuitive method that has been used to design side-stream columns [17]. The method is based on the residue curve maps of the mixture on that separation task is carried out. The assumption of constant molar flow in the system can be relaxed. In this method, either reflux ratio or the side-stream flowrate should be specified and then the location of side-stream (tray) should be specified. Therefore, likewise McCabe-Thiele extension this method is not able to consider optimality and it only provides a feasible configuration of the column.

*Shortcut Design:* The shortcut design introduced in [18] is a mathematical approach to design side-stream columns. This method is more time consuming compared to the first two methods. In shortcut design method, a feasibility of the side-stream composition is taken into account. Like the other two methods introduced before, this method also requires the side-stream composition to be specified and there is not guarantee to optimal solution. The method has been highly evaluated for an ideal mixture in sharp separations in terms of accuracy.

*Driving Force-Based Method:* This method has a different approach to design side-stream columns. It is based on the optimal/ near optimal solution strategy. In driving force, the location of feed and side-stream is determined to have a minimum reboiler duty for the separation task. The specifications required for this algorithm is the top and bottom product purity and the number of stages. The concept of driving force will be fully discussed in the next chapter.

Table 1-1. General comparison of side-stream column design methods

Method	Pros	Cons
<b>McCabe-Thiele Extension</b>	<ul style="list-style-type: none"> <li>• Intuitive</li> <li>• Balance equations are solve graphically</li> <li>• Computationally inexpensive</li> </ul>	<ul style="list-style-type: none"> <li>• The solution is not necessarily optimum</li> <li>• Complex for multicomponent mixtures</li> </ul>
<b>Geometric</b>	<ul style="list-style-type: none"> <li>• Intuitive</li> <li>• Assumption of constant molar flow can be relaxed</li> <li>• Feasibility analysis can be carried out</li> </ul>	<ul style="list-style-type: none"> <li>• Complex graphs</li> <li>• Not necessarily optimum</li> </ul>
<b>Shortcut</b>	<ul style="list-style-type: none"> <li>• Accurate</li> <li>• Feasibility analysis can be carried out</li> </ul>	<ul style="list-style-type: none"> <li>• Not optimal</li> <li>• Mathematically complex</li> <li>• Time consuming</li> </ul>
<b>Driving Force</b>	<ul style="list-style-type: none"> <li>• Optimal/near optimal solution proposed</li> <li>• Intuitive</li> <li>• Computationally inexpensive</li> </ul>	<ul style="list-style-type: none"> <li>• Not appropriate for trace level of concentrations</li> <li>• The number of trays shall be known</li> </ul>
<b>Optimization Based [2]</b>	<ul style="list-style-type: none"> <li>• Accurate</li> <li>• Flexible for economic evaluation</li> <li>• Model parameter uncertainty issues can be taken into account</li> </ul>	<ul style="list-style-type: none"> <li>• Computationally expensive</li> <li>• Completely mathematical</li> <li>• Requires sophisticated solution strategies depending on the model complexity</li> </ul>

## 1.2. Problem Statement

The parametric study in industrial distillation carried out by Tedder *et al.* [19], asserts that for all ternary mixtures that a low middle product purity is acceptable, a side-draw distillation should be taken into account as one of the possible configurations. Hence, side-draw distillation is one of the approaches that can be adopted for separation of ternary mixtures with trace concentration level of middle boiling component, because the purity of the middle product (side-draw) is not as predominant as the purity of middle volatile component in distillate and bottom products. Often, the early stage design of distillation columns with side-draw has always been a challenging task due to lack of a reliable simple method to quickly, and efficiently obtain the optimal/near optimal feed and side draw locations. As previously mentioned, to design side-draw distillation, applying a trial/error or rigorous mathematical formulation, which often also requires a validated process simulation of the process is virtually inevitable. Obviously, these approaches turn into highly time consuming approaches as the system become more complicated.

This study intends to develop an innovative simple approach, similar in concept to conventional distillation design for such applications that quickly and efficiently finds an optimal/near optimal feed and side-draw location, such that the time required for design along with OPEX of the system can lessen.

## 1.3. Hypothesis

The aim of this work is to develop a new efficient design approach for side-draw distillation column of a ternary mixture at trace concentration level of middle boiling component as such that intuitively suggests an optimal/near optimal design configuration regarding the OPEX of the system and reduce the time required for design as well. To this end, Clifford M. from TPC group proposed a new simple concept of molecular tracking in AIChE Spring Meeting – Kister Distillation Symposium March 2017. Molecular tracking is a method that helps to deepen the understanding of a single molecule behavior inside the column. This method analyzes the probability of transference of a single molecule on each stage to the upper/lower stage in vapor or liquid phase.

Presumably, in a binary distillation column of a ternary mixture, the most volatile compound easily flows towards the top of the column and the least volatile component will be directed to the bottom product stream. However, the middle boiling component spends most of its time at somewhere between the two main product streams. The tray that this molecule spends most of its time or in other words, the tray with largest residence time, is the most probable location of side-draw. Removing the middle product in that location, facilitates the separation task. In so doing, the total energy of the system should be the minimum amongst the all alternative locations of the side stream. In fact, in this approach an early distillation design for key components separation is

required, which task can be easily fulfilled by one of the existing conventional design approaches such as McCabe-Thiele, Ponchon-Savarit, driving force based approach and etc. Afterwards, in order to find the location of side-draw, molecular tracking applies. In this work, the early design for a binary distillation is followed by driving force approach that is fully discussed by [16]. The accomplishment of this study depends on the fulfilment of the following objectives:

1. Define the key concepts of molecular tracking.
2. Develop/use the methodology required for the target.
3. Integrate the developed methodology to establish a systematic framework of design approach.
4. Apply the framework on defined case studies.
5. Carry out economic evaluation and uncertainty analysis on the framework.







## Chapter 2: Concepts

### 2.1. Driving Force

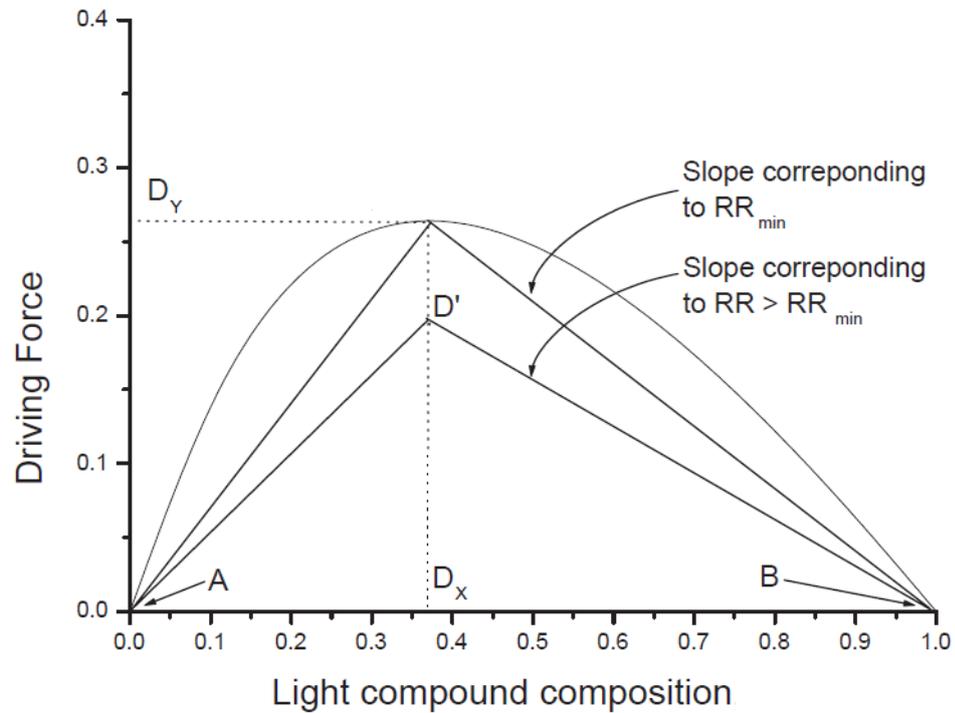
According to [16], it is advantageous to carry out an early stage driving force analysis in separation processes, because most of such processes somehow uses this concept to achieve the desired separation specifications. In these processes, driving force is referred to the difference between chemical/physical properties of the two co-existing phases. In distillation, the difference between the compositions of two co-existing phases are known as the driving force, which is caused by the difference between the volatility of component  $i$  in the system and all other components. As the driving force of component  $i$  in the system approaches to zero, separation of that component becomes more difficult, while driving force approaches a maximum, the separation of the corresponding component in the system becomes easier, since driving force is inversely proportional to the energy required to maintain the two phases (vapor-liquid) in the system. Therefore, as the feed is introduced to the column in the maximum driving force point, the energy required for the column (reboiler and condenser duties) will be minimized with respect to the other possible feed locations. Considering that the relative volatility between two components  $i$  and  $j$  is constant in the system operating conditions, the vapor composition in equilibrium with the liquid phase is calculated due to (2-1). As such, driving force between the two components can be easily calculated by (2-2) [16].

$$y_i = \frac{\alpha_{i,j} x_i}{1 + (\alpha_{i,j} - 1)x_i} \quad (2-1)$$

$$DF_{i,j} = y_i - x_i = \frac{\alpha_{i,j} x_i}{1 + (\alpha_{i,j} - 1)x_i} - x_i \quad (2-2)$$

Where  $x$  and  $y$  represent the liquid and vapor fractions respectively. Indices  $i$  and  $j$  are representative of the two key components of the mixture in a multicomponent solution and obviously  $\alpha_{i,j}$  is the relative volatility between component  $i$  and  $j$ . The schematic figure of the driving force is illustrated in Fig 2-1, which clearly shows a maximum point. Due to the maximum driving force, the feed operating line should intersect the corresponding vertical line of  $x = D_x$ . Given the feed conditions (composition, temperature, pressure and vapor fraction), the degree of freedom in order to make the column to operate at maximum driving force is its vapor composition. The required vapor fraction can be provided by using a pre-heater before the column in order to bring the feed to the desired condition. Regarding (2-1) and (2-2), it can be easily conceived that the driving force is vapor-liquid equilibrium diagram rotated  $\pi/4$  clockwise. Like, McCabe-Thiele

method [20], this method is a graphical tool for design the distillation units. Although driving force requires much more complex calculations rather than the other method, the outcome design configuration is optimal/near optimal without relying on a mathematical optimization.



*Fig 2-1. Schematic diagram of driving force with the important design parameters [2]*

In the following, an elaborate discussion of driving force-based method with corresponding mathematical formulation is provided. In order to have a proper understanding of driving force, an analogy between this method and McCabe-Thiele is used. To this end, a McCabe-Thiele diagram and its corresponding driving force diagram is illustrated in Fig 2-2.

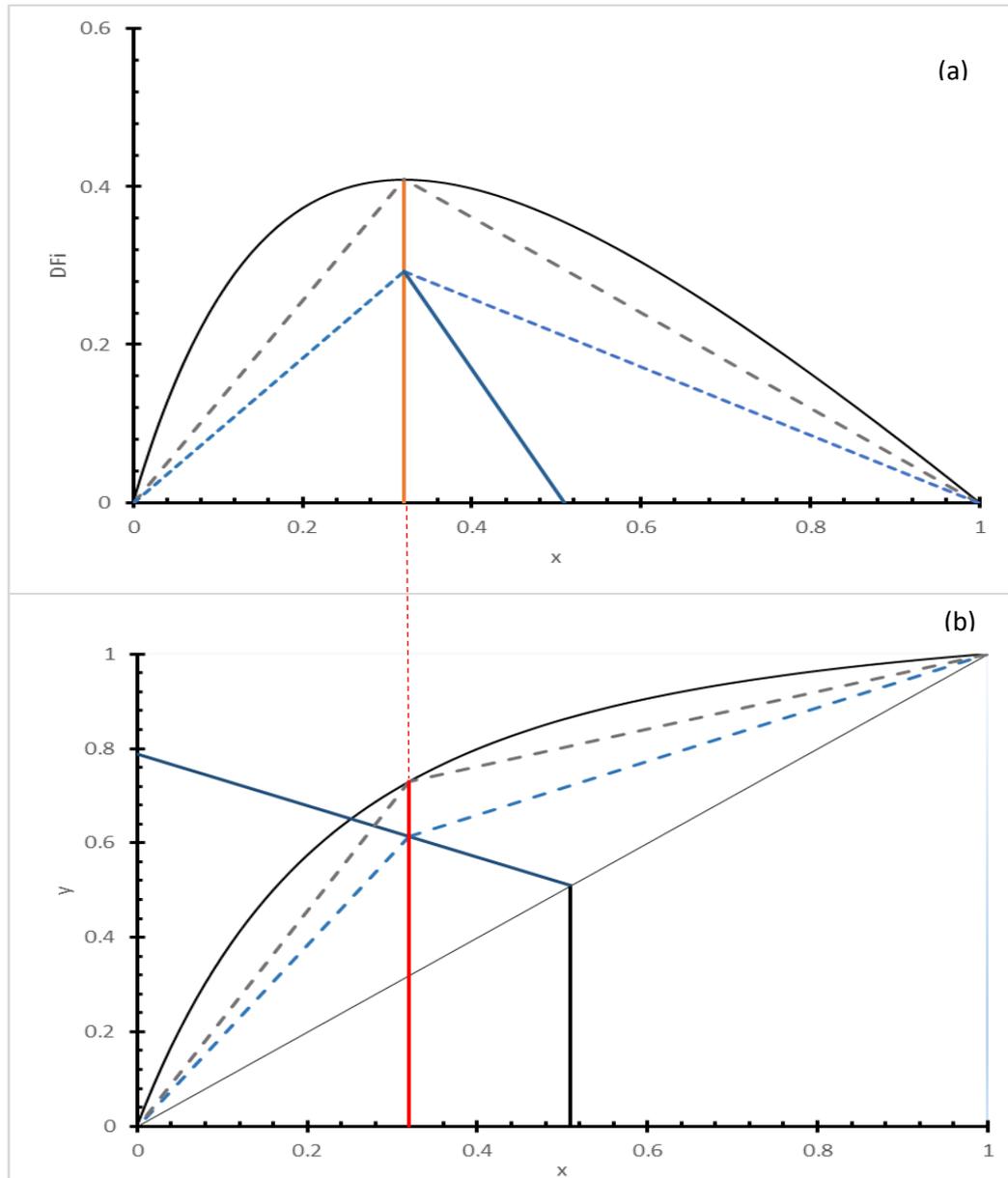


Fig 2-2. A generic driving force diagram (a) and the corresponding McCabe-Thiele diagram (b)

McCabe-Thiele method represents that the operating lines of the column is as the equations provided in (2-3) and (2-4) for rectifying and stripping section respectively.

$$y_i = \frac{RR}{1+RR} x_i + \frac{x_D}{1+RR} \quad (2-3)$$

$$y_i = \frac{1+BR}{BR} x_i - \frac{x_B}{BR} \quad (2-4)$$

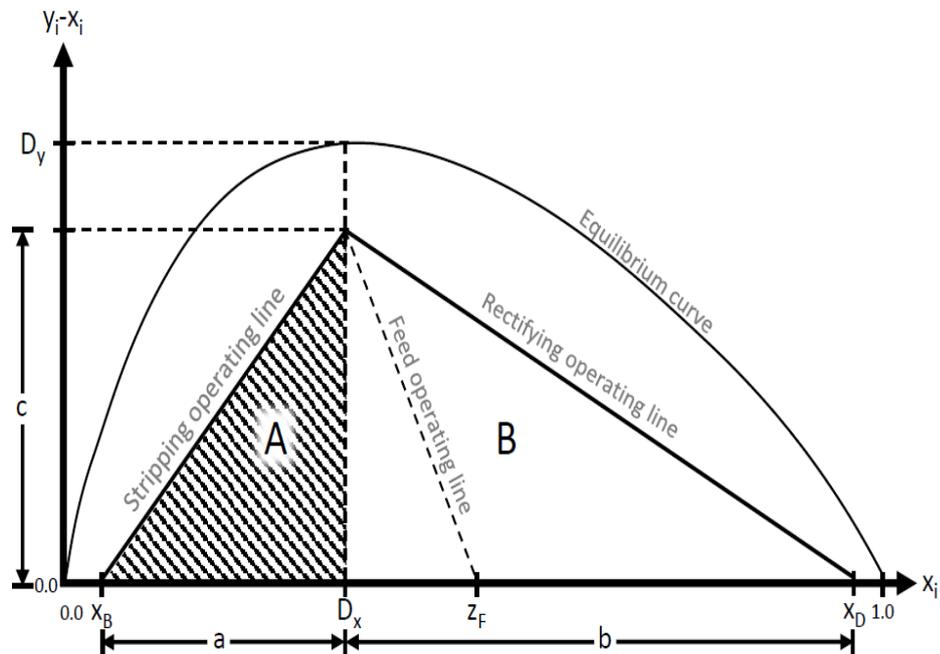
Where  $RR$  and  $BR$  are reflux ratio and boilup ratio,  $x_i, y_i$  are the liquid and vapor compositions of component  $i$  on stage  $n$  and  $x_D, x_B$  are purity required in the distillate and bottom streams. The

operating line equations in driving force diagram can be easily derived by adding  $-x_i$  to both (2-3) and (2-4). The rectifier and stripper operating lines are illustrated in (2-5) and (2-6) respectively.

$$DF_i = y_i - x_i = -\frac{1}{1+RR}x_i + \frac{x_D}{1+RR} \quad (2-5)$$

$$DF_i = y_i - x_i = \frac{1}{BR}x_i - \frac{x_B}{BR} \quad (2-6)$$

As previously discussed, driving force makes the column to operate at the maximum driving force. To this end, the operating lines must intersect at a composition, in which the system has maximum driving force. The only degree of freedom to meet this condition is the state of the feed (vapor fraction). A follow up discussion comes up to justify that the corresponding outcome configuration has the minimum energy of the system (column only).



**Fig 2-3.** A driving-force diagram with the operating lines intersecting at  $x = D_x$ . The measurements  $a$ ,  $b$  and  $c$  are indicated on the figure, for better understanding of the reasoning behind using driving force to obtain the lowest column energy transfer [2].

To obtain the minimum energy required for distillation, summation of reboiler and condenser duties have to be minimized. To this end, the energy of condenser and reboiler are reformulated with design parameters of the system i.e. RR and BR. It is assumed that the vapor is at dew point in condenser and liquid is at boiling point in reboiler. In addition, a total condenser is assumed for analysis. The following equations are the general formula to obtain the condenser and reboiler duties.

$$|Q_{reboiler}| = \overline{\Delta H}_{vap, reboiler} \cdot V_s \quad (2-7)$$

$$|Q_{condenser}| = \overline{\Delta H}_{vap, condenser} \cdot V_r \quad (2-8)$$

While  $V_r$  represents the vapor molar flow in rectifying section and  $V_s$  is the vapor molar flow in stripping section. Therefore, the summation of RR and BR can be written as follows.

$$RB + RR = \frac{V_r}{D} + \frac{V_s}{B} - 1 \quad (2-9)$$

$$RR + BR = \frac{|Q_{condenser}|}{D \times \Delta H_{evap, cond}} + \frac{|Q_{reboiler}|}{B \times \Delta H_{evap, reb}} \quad (2-10)$$

In addition to (2-9) and (2-10), summation of reflux ratio and boilup ratio can be derived from the parameters shown in Fig 2-2 as derived in (2-11).

$$RR + BR = \frac{x_D - x_B}{c} - 1 \quad (2-11)$$

Keeping the number of stages constant, column duty will be minimum, when parameter  $c$  become maximum. This situation occurs only at maximum driving force. Therefore, the advantage of driving force method over McCabe-Thiele is that the constraint of operating at maximum driving force, causes the energy required for the system to become minimum.

This method has been used in several design and synthesis of industrial applications since it has been published. Besides the success in design, synthesis and control applications, there has often been a misunderstanding of this strong method that leads many academic and industrial practitioners to criticize the method. However a thermodynamic analysis can be employed as a support to clarify the issue. The analysis is based on Gibbs free energy of the liquid and vapor mixture present in the column. The study illustrates that the Gibbs free energy of liquid and vapor intersect at the location of maximum driving force. In other words, the Gibbs free energy of either vaporization or condensation is equal to zero at the maximum driving force.

In the following, an in detail analysis is carried out for an ideal binary mixture to support the driving force concept. A generic ideal binary mixture is considered for separation task at constant pressure. Hence, assumption of constant relative volatility for the mixture is reasonable. Vapor liquid equilibrium data can be predicted by using (2-1) as illustrated before.

By assuming that the relative volatility in the system is constant, the vapor composition is only a function of liquid composition. Hence, the total derivative of the driving force with respect to liquid composition would become as the equation illustrated in the following.

$$\frac{dF_D}{dx_i} = \frac{1 - 2x_i - (\alpha - 1)x_i^2}{(1 + (\alpha - 1)x_i)^2} \quad (2-12)$$

The maximum driving force occurs at the liquid composition in which the derivative of the driving force is equal to zero. Therefore, by assigning zero to the (2-12), the liquid composition at

$$\text{maximum driving force would be } x_{i,\max} = \frac{\sqrt{\alpha} - 1}{\alpha - 1} \text{ and } x_{j,\max} = \frac{\alpha - \sqrt{\alpha}}{\alpha - 1}.$$

The Gibbs free energy of the ideal mixture can be calculated as the two following equations for vapor phase and liquid phase respectively.

$$G^V/RT = \sum_{i=1}^2 y_i \ln y_i \quad (2-13)$$

$$G^L/RT = \sum_{i=1}^2 x_i \ln x_i \quad (2-14)$$

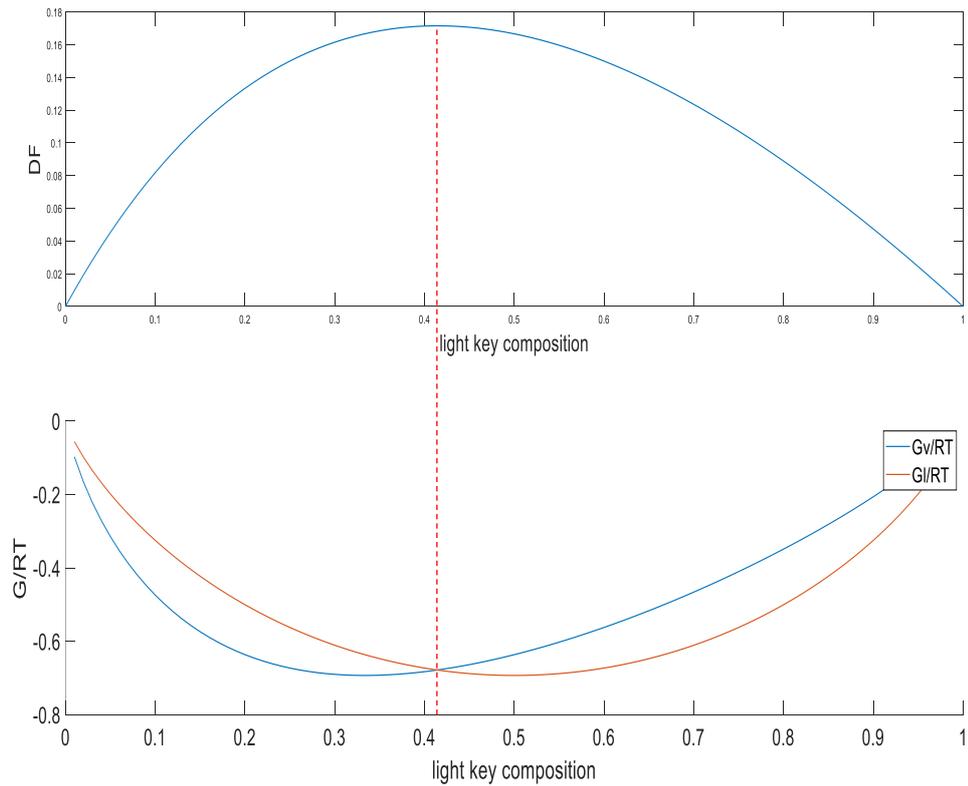
Hence, the energy change of vaporization can be calculated as the difference between vapor phase and liquid phase Gibbs free energy. The following equation is representing the Gibbs free energy of vaporization for the case of ideal binary mixture.

$$\Delta G^{\text{vap}}/RT = y_1 \ln y_1 + y_2 \ln y_2 - x_1 \ln x_1 - x_2 \ln x_2 \quad (2-15)$$

Substituting liquid compositions corresponding to maximum driving force into (2-1) results to determine the vapor compositions of that location. The vapor compositions would be as

$$y_{i,\max} = \frac{\alpha - \sqrt{\alpha}}{\alpha - 1} \text{ and } y_{j,\max} = \frac{\sqrt{\alpha} - 1}{\alpha - 1}. \text{ It can be clearly seen that by substituting these compositions into}$$

(2-15) will nullify the Gibbs free energy of vaporization. Fig 2-4 illustrates the consistency of the mathematical formulation discussed for a generic binary and ideal mixture. An ideal binary mixture of hypothetical components is analyzed with a constant relative volatility of  $\alpha = 2$ . Based on the mathematical formulation of maximum driving force, maximum driving force occurs at  $x_{D,\max} = 0.41$ . Fig 2-4 shows that Gibbs free energy of vapor phase and liquid phase also intersect at the liquid composition corresponding to the maximum driving force.



**Fig 2-4.** Driving force diagram and Gibbs free energy of liquid and vapor phase for an ideal binary mixture of hypothetical components with  $\alpha = 2$

## 2.2. Molecular Tracking

Molecular tracking (MT) is a computer aided intuitive method that helps to enrich the understanding the thermo-physical behavior of the system and statistically can predict the molecular pathways inside the column. This pathway is a rough estimation of the real pathway that each molecule goes through to be removed from the column. Regarding the thermo-physical data of the system, a probability function is introduced such that declares the possibility of a single molecule to go to the vapor phase and upper trays or vice versa, which has to be defined over each tray. The probability is defined as the ratio between the existing vapor flowrate of a molecule over the total flowrate of the same molecules on each stage. In the following, a general mathematical expression of the function is provided in (2-16). When a molecule is introduced to the column through feed stream, a frequent random generator must be used to follow the molecule to the point it removes from the column. This value has to be compared with the corresponding probability value. If the random number is smaller than the probability value, the molecule will be transferred to the upper tray in vapor phase and if not, it will move to the lower tray in liquid phase. This operation is held until the molecule leaves the column either from distillate or bottom stream.

$$\beta_i^n = \frac{V_n y_i^n}{V_n y_i^n + L_n x_i^n} \quad (2-16)$$

Where  $n$  is an indicator for the stage number in the column.  $V$  and  $L$  are representative of vapor and liquid molar flows in the system.

For the further analysis, the expression of (2-16) will be modified into a more comprehensible form regarding the design parameters of the column. It is more convenient to substitute the compositions with a well-known parameter  $K$ -value. By conducting a simple algebraic reformulation, (2-16) turns into (2-17). In this study, all the calculations are based on the following equation.

$$\beta_i^n = \frac{V_n K_i^n}{V_n K_i^n + L_n} \quad \text{Where: } K_i^n = \left(\frac{y_i}{x_i}\right)_n \quad (2-17)$$

An in detail analysis is inevitable for understanding the behavior of the aforementioned function. To this end, it is suggested to refer to McCabe-Thiele method for column design. Hence, there are some assumptions that should be applied for this analysis.

1. Since the study is based on molecules, it is preferred to use molar dimensions instead of mass.
2. Vapor and liquid molar flowrates are constant above the feed.
3. Vapor and liquid molar flowrates are constant below the feed.

Regarding the McCabe-Thiele method, the molar vapor and liquid flowrates are constant in rectifying and stripping sections. Hence, there has to be at least two different expression for two separate sections of the column. However, the feed location is not considered neither in top and bottom sections, it has its own expression; because, vapor flowrate of this stage is in top and corresponding liquid flowrate is in the bottom section. The analysis is followed by three different sections: Above the feed, below the feed and feed location, which are fully discussed in the following. Moreover, due to assumption of total condenser, the behavior of function around it should be analyzed separately. A further analysis also should be carried out for the side-draw in order to understand the function behavior.

### 2.2.1. Rectifying Section

Vapor and liquid molar flows in rectifying section can be substituted with reflux ratio of the column. Therefore, there will be only one parameter in the equation and the mathematical behavior of the function will be more clear for further analysis. The expression of the function regarding the

reflux ratio is written in (2-18). Moving from feed stage to the condenser causes a decrease in K-values, which shows that moving to the edge of separation, makes this process much more difficult.

$$\beta_i^n = \frac{K_i^n}{K_i^n + L/V}$$

$$V = L + D \Rightarrow V/L = 1 + D/L = (1 + RR)/RR$$

$$\beta_i^n = \frac{K_i^n}{K_i^n + RR/(1 + RR)}$$

(2-18)

### 2.2.2. Stripping Section

Considering  $V'$  and  $L'$  as vapor and liquid flowrates in stripper respectively, will lead the expression of the function as is followed in (2-19). In order to derive the expression with respect to design parameters, knowing the feed vapor fraction is necessary. If the feed is introduced to the column with  $q$  as vapor fraction, the following calculation can lead to the final expression of bottom function.

$$\beta_i^n = \frac{K_i^n}{K_i^n + L'/V'}$$

$$L' = V' + B \Rightarrow L'/V' = (1 + BR)/BR$$

$$\beta_i^n = \frac{K_i^n}{K_i^n + BR/(1 + BR)}$$

(2-19)

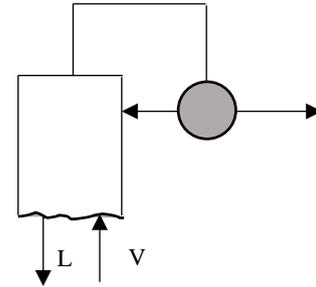


Fig 2-5. Rectifying section of the column

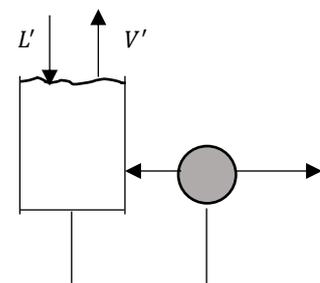


Fig 2-6. Stripping section of the column

### 2.2.3. Feed Tray

Feed stage has to be considered with different behavior, because the vapor flow belongs to rectifying section and the liquid flow to stripping section. Therefore, (2-17) turns into (2-20) with a very simple reformulation.

$$\beta_i^F = \frac{VK_i^F}{VK_i^F + L + (1-q)F} \quad (2-20)$$

Where  $q$  is the extent of vaporization of feed.

### 2.2.4. Condenser

The probability value for condenser has to be formulated with respect to its type. In the following, there are two different approaches of probability calculation for partial condenser and total condenser. Partial condenser can be considered as an equilibrium stage like reboiler. In so doing, the function will remain the same as a tray in rectifying section. However, a total condenser is totally different. Total condenser contains only liquid and it can be assumed as a splitter. Therefore, the probability will be the ratio between the distillate molar flow and the total outlet flow of condenser. Probability value for this type of condenser has to be determined from (2-21) for all of the components.

$$\beta_i^C = \frac{D}{D+L} = \frac{1}{1+RR} \quad (2-21)$$

### 2.2.5. Side-draw

In multicomponent distillation columns, the middle boiling components behave differently from light key and heavy key components. They have a higher residence time somewhere between the top and bottom streams. The stage in which they are accumulated will be the right choice for putting the side-draw to remove these molecules from the column. MT can be applied to this units by finding the highest residence time. Since the design method is for a steady state operation of column, the residence can be considered as the number of times that a single molecule can pass on each stage. Middle boiling components moves alternately up and down on some stages. These stages are the probable choices for side-draw. MT can record the number of passes of each molecule on every stage and select the maximum value and its corresponding stage number as the optimum location of side-draw. Therefore, the equations derived for MT will remain the same, but observing the number of passes over each stage will be required.

Moving alternately up and down on a stage means that the molecule has the same probability to go to vapor phase and upper tray or the liquid phase and lower tray. Hence, probability value of the side-draw location approximately equals to 50%. At this point, the molecules have nearly an equal tendency to go into vapor phase or liquid phase. In other words, the separation is not effective in that location. Therefore, that stage is the most probable location of side-draw to remove middle product. Fig 2-7 illustrates the concept of molecular tracking applied to the heavy key, light key as well as the middle boiling components. As shown in the figure, the light key component has a tendency to move directly towards the top of the column while the heavy key component has a tendency to move directly towards the bottom of the column. However, the middle boiling trace component tends to spend several steps in the middle of the column before eventually exiting the column. In order to have a better understanding of the concept of alternate movement of a molecule a MATLAB code has been provided, which follows a single molecule inside the system. The code is based on a random generator function. This function generates a random number for each molecule at each stage. The generated number will be compared to the probability value of that molecule on its current stage. If the random number is larger than the probability value of that molecule on that stage, the molecule will move to the lower stage in liquid phase. Else, the molecule will move to the upper stage in vapor phase. This procedure is continued to the point that molecule move out the system either from the distillate or the bottom product stream. In case of side-stream column, the side-stream should not be defined on the column. In other words, the middle boiling component has also to be removed from one of the top or bottom streams. The code is written to calculate the number of times that each components passes through each stage. The complete code is enclosed in the Appendix B.

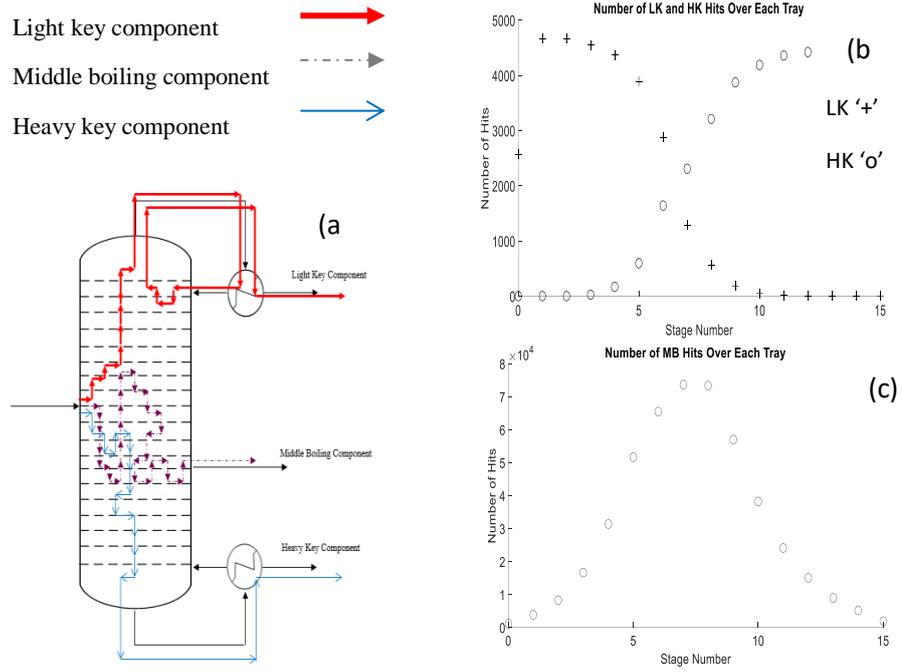


Fig 2-7. (a) Schematic of a side-draw distillation column with representative molecular pathways, (b) Number of hits of light key and heavy key components, (c) Number of hits of trace component versus stage number [21]

## Chapter 3: Methodology

### 3.1. Molecular Tracking

The author has established a systematic framework to design a side-draw distillation column at infinite dilution of middle boiling component for an ideal ternary mixture. The framework is a combination of existing method driving force [16] and new concept of molecular tracking developed by the author. Fig 3-1 represents a general overview of the framework. The framework is divided into two steps for ease of following the procedure. Moreover, Information required and generated outputs of each step is listed in the same figure. The overall methodology is also split into two parts and each one is followed by a very simple example.

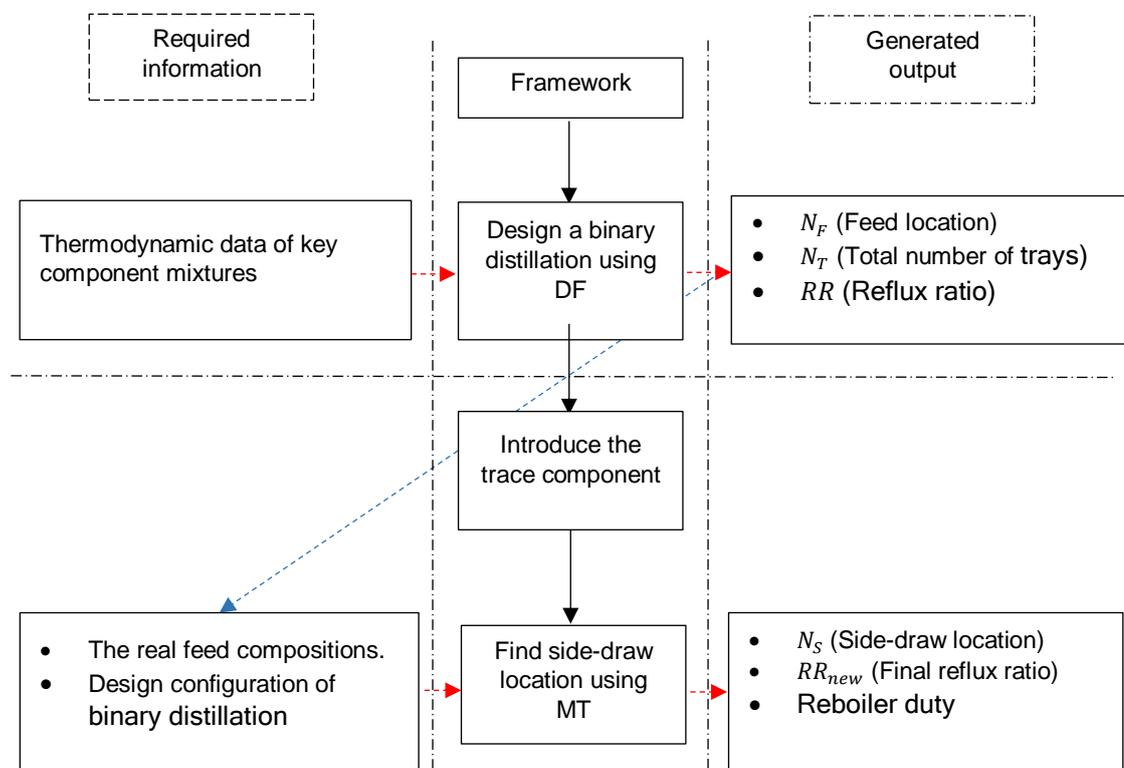


Fig 3-1. General framework overview

#### 3.1.1. Design a binary distillation using driving force

First part of the framework stipulates the design algorithm to design a binary distillation for the key components inside the ternary mixture. As mentioned above, the middle boiling component in the distilling mixture is present at trace level of concentrations. Hence, the light and heavy components are considered as the key components in the system. Accordingly, the design algorithm of this part of framework is provided based on Bek Pedersen and Gani (2003) [16] for these components in the

system. Algorithm D1 of that study is employed to determine a feasible distillation configuration for this hypothetical binary mixture. A step by step algorithm is provided in the following.

### Design Algorithm

**Step 1.** Generate or retrieve VLE data for the key components in the mixture.

**Step 2.** Calculate the driving force of key components and plot the driving force diagram as a function of liquid light key composition.

**Step 3.** Locate the maximum driving force and its corresponding composition.

**Step 4.** Specify the product specifications.

**Step 5.** Calculate the minimum required reflux ratio for this separation task based on the following equation.

$$-\frac{1}{1 + RR_{\min}} = \frac{D_y}{D_x - x_D} \quad (3-1)$$

**Step 6.** Consider a value based on process requirements for ratio of actual reflux ratio and minimum reflux ratio. Calculate the actual reflux ratio based on that value and the minimum reflux ratio calculated in step 5.

$$CC = \frac{RR}{RR_{\min}} \quad (3-2)$$

**Step 7.** Determine the feed quality required for the reflux ratio acquired in Step. 6 based on the following equation.

$$q = \frac{Z_F - D_x}{D'_y} \quad (3-3)$$

**Step 8.** Draw feed, rectifying and stripping operating lines in VLE diagram and based on McCabe-Thiele method find the total number of stages and feed location.

**Step 9.** Determine temperature and composition profile in this distillation process regarding T-XY and McCabe-Thiele diagram.

**Step 10.** Based on McCabe-Thiele assumption of constant vapor and liquid internal flows, calculate these variable based on a simple material balance over rectifying and stripping sections.

$$V = (1 + RR) \times D \quad (3-4)$$

$$L = V - D \quad (3-5)$$

$$V' = V - qF \quad (3-6)$$

$$L' = L + (1 - q)F \quad (3-7)$$

In the following, a very simple example is analyzed to have a better understanding of the proposed algorithm.

**Example 3.1) Consider a mixture of benzene and p-xylene and trace amounts of toluene with following compositions.**

*Table 3-1. Feed composition of Example 3.1*

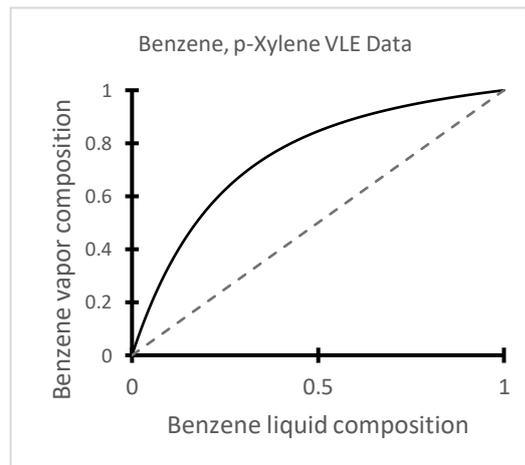
Composition	Composition (molar fractions)
Benzene	58%
Toluene	1%
p-Xylene	41%

Data preprocessing: The key components in this mixture are benzene and p-xylene. Hence, the compositions shall be adjusted for these components.

*Table 3-2. Feed composition of hypothetical binary mixture*

Composition	Composition (molar fractions)
Benzene	58.58%
p-Xylene	41.41%

Step 1. VLE data of benzene and p-xylene.



*Fig 3-2. XY diagram of benzene and p-xylene at 1 atm*

Step 2, 3. Driving force diagram of key components and the corresponding maximum driving force.

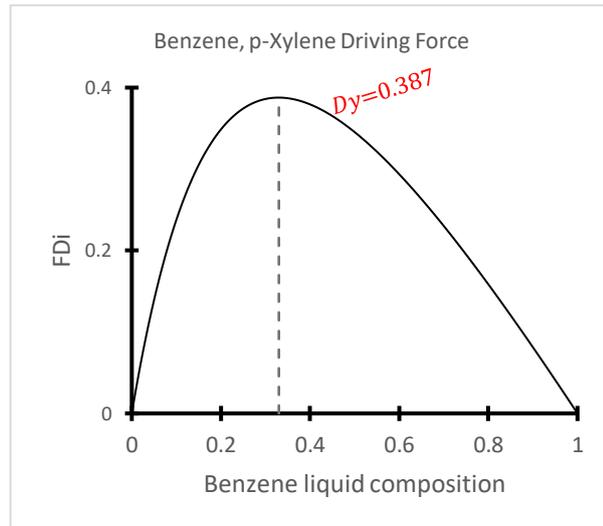


Fig 3-3. Driving force diagram of benzene and p-xylene at 1 atm

Step 4, 5. Product specifications and minimum reflux ratio.

Table 3-3. Process specifications

Stream	Specification
Distillate	99.95% benzene
Bottom	0.05% benzene

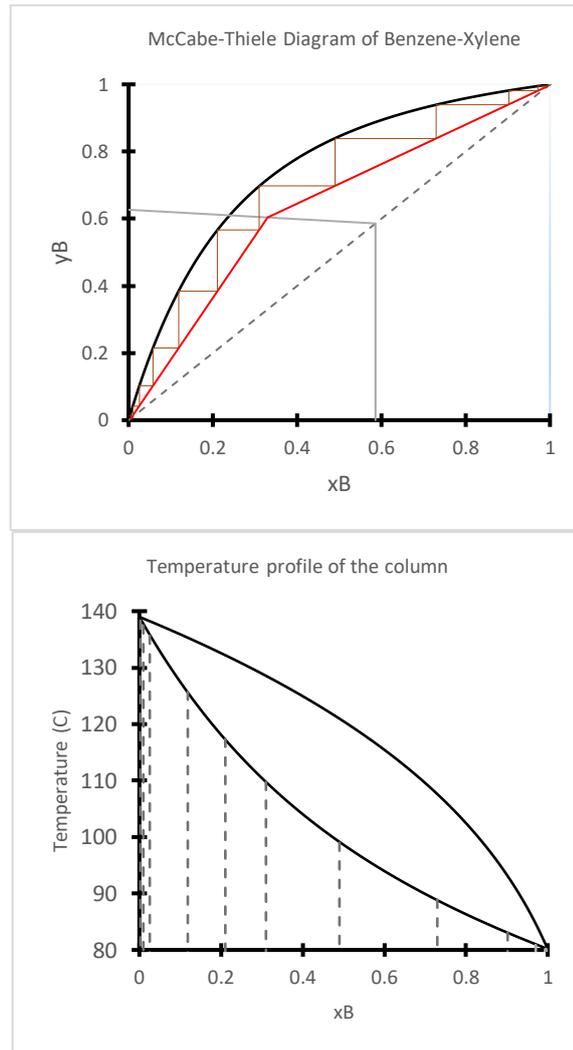
$$-\frac{1}{1 + RR_{\min}} = \frac{0.387}{0.33 - 0.995} \Rightarrow RR_{\min} = 0.72$$

Step 6. Considering  $CC = 2$ , reflux ratio shall be 1.44.

Step 7. Regarding Eq.(3-3), the required extent of vaporization of the feed is as follows.

$$q = 0.93$$

Step 8, 9. McCabe-Thiele and T-XY diagrams.



**Fig 3-4.** McCabe-Thiele and T-XY diagrams of proposed distillation task

Total number of trays are 10, while a partial reboiler and a total condenser is to be considered for this separation task. Feed tray has to be at tray 5.

### 3.1.2. Find side-draw location using molecular tracking

The aim of this part is to locate the side-draw at a tray in which molecules are to be accumulated in the system, given the design configuration generated at section 3.1. The idea is to consider the non-key component in the mixture flowing through the column in feed stream. The side stream to remove this component from the system should be located based on the following algorithm. An illustrative example is provided after the algorithm.

**Design Algorithm**

**Step 1.** Determine the vapor pressure of middle boiling component (using Antoine equation or any other reliable correlation).

**Step 2.** Calculate K-value for this component based on (3-4).

$$K_{MB} = \frac{y_{MB}}{x_{MB}} = \frac{P_{MB}^{sat} \gamma_{MB}^{\infty}}{P \phi_{MB}^{\infty}} \quad (3-8)$$

**Step 3.** Calculate the probability profile for middle component based on the following equation.

$$\beta_{MB} = \frac{K_{MB} V}{K_{MB} V + L} \quad (3-9)$$

**Step 4.** Find the trays where probability value calculated in Step 4. is 50%.

**Step 5.** If only one tray is found in Step 5, the side-draw must be located on that tray. Else, go to step 6.

**Step 6.** Simulate the column in a simulation software and locate the side-draw with fixed molar flowrate on the trays found in Step 5 and choose the one proposes minimum reboiler duty as side-draw tray.

The algorithm is followed by a very simple example. A validated process simulation of a high purity distillation column for methanol is available [22]. The number of trays, feed location has been determined in that study. Hence, the author has applied molecular tracking concept to locate the side-draw. An in detail analysis of molecular tracking algorithm is represented in the following.

**Example 3.2) A saturated liquid mixture of methanol, water with trace concentration of ethanol is the feed of distillation with compositions provided in Table 3.3. The column has 88 trays with a partial reboiler and total condenser. The product streams must contain less than 10 ppm impurity.**

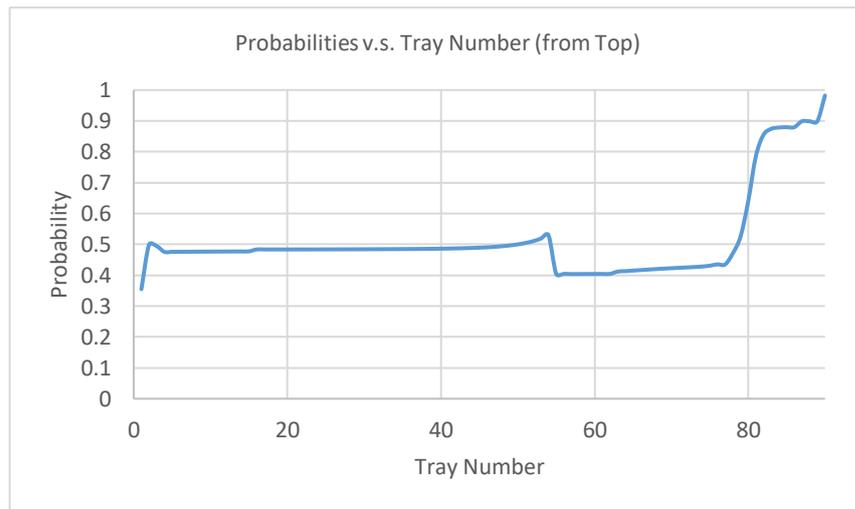
*Table 3-4. Feed composition of Example 3.2*

Composition	Composition (molar fractions)
Methanol	67.58%
Ethanol	0.04%
Water	32.37%

**Step 1.** Use the temperature profile shown in simulation case and Antoine equation to determine the vapor pressure profile of ethanol in the column.

**Step 2.** K-values of ethanol in the system is calculated based on the left part of (3-8), since the simulation represents the liquid and vapor compositions of this component in the column.

**Step 3.** The probability profile is simply determined based on (3-9). In the following figure the probability profile of ethanol in the system is illustrated



*Fig 3-5. Probability profile of ethanol in the distillation task*

**Step 4.** Trays 49, 55 and 79 are the trays with probability 50%.

**Step 5.** The algorithm and the following HYSYS simulation suggest that the optimum location of side-draw is tray, however the tray correspondent to the minimum reboiler duty is reported tray 79 in [22].

### 3.2. Driving force method for side-draw

A driving force method for designing a side-draw distillation unit is proposed by [16]. In this method the concept of driving force is used to find the optimum/near optimum locations of feed and side-draw simultaneously. The developed methodology is represented in the following toolbox.

**Step 1.** List the compounds with respect to their boiling points.

**Step 2.** Consider a binary mixture between light and middle boiling component and a binary between middle boiling and heavy component.

**Step 3.** Extract VLE data for these two binary mixtures introduced in 2 (XY data).

**Step 4.** Plot driving forces of these mixtures versus the liquid compositions of light component.

**Step 5.** Determine which of the plots has the maximum driving force.

**Step 5.1.** If the maximum occurs in the mixture of light compound and the middle, the side-draw will be between feed and bottom stream.

**Step 5.2.** If the maximum occurs in the mixture of middle and heavy component, the side-draw will be located between feed and distillate.

**Step 6.** Find  $D_x$  on the x-axis as the light compound composition corresponding to the maximum driving force.

**Step 7.** Specify the product specifications.

**Step 8.** Given the number of trays, calculate the minimum reflux ratio of the column.

**Step 9.** Plot the joint driving force diagram. Two driving force data sets have to be plotted versus a rescaled x-axis.

**Step 9.1.** Assume a value (c) in the range (0, 1).

**Step 9.2.** Replace c with 0 in liquid composition of light and middle component and reproduce the relative compositions for this mixture in the range (c, 1).

**Step 9.3.** Plot DF for the mixture versus (c, 1).

**Step 9.4.** Replace 1-c with 1 in liquid composition of middle and heavy component and reproduce the relative compositions for this mixture in the range (0, 1-c).

**Step 9.5.** Plot DF for the mixture.

**Step 9.6.** The two exhibited plots must intersect on the maximum point of the lower diagram in 4. If this is so, go to 8, if not go to 7.1.

**Step 10.** Locate  $D_s$  as the relative composition from the intersection of joint driving force diagram..

**Step 11.** Calculate the side-draw location using  $N_s = N(1 - D_s)$ , N is the number of trays counted from top.

**Step 12.** From the binary driving force diagram, calculate the feed location.

**Step 12.1.** If the feed is between side-draw and distillate, the feed location has to be calculated using  $N_F = N_S(1 - D_x)$ .

**Step 12.2.** If the feed is introduced between side-draw and bottom, locate the feed using  $N_F = N_S + (N - N_S)(1 - D_x)$ .

**Step 13.** Simulate the column with HYSYS and record the reboiler duty and reflux ratio for each design to find the optimum operation.







## Chapter 4: Case Studies and Results

The application of the developed methodology is highlighted through two different separation tasks. The first distillation column is designed for a benzene p-xylene mixture with toluene as impurity (infinite dilution), while the second case study is dedicated to a separation of n-pentane and n-hexane with trace amounts of n-hexane. In both case studies, non-ideality is neglected due to the thermodynamic properties of the molecules present in the mixture. In order to predict the thermodynamic properties, a proper VLE equation of state, has been selected. In this work, Peng-Robinson has been evaluated as an appropriate property package, since the molecules of each case are highly similar to each other and this package is able to roughly estimate the properties of these mixtures. Regarding the methodology developed in chapter 3, first the number of trays and feed location is determined for each case study by employing a driving force based method and then, the most probable side-draw locations are highlighted for each case using the molecular tracking based approach. Molecular tracking narrows down the most possible locations of the side-draw, which allows to purely removing the products and with the process simulation narrow it down to the location with the most efficient energy of the column. A comparison is carried out between the outcome configuration of the methodology developed in this study and corresponding configuration from classical driving force based method fully described in [16]. The number of theoretical trays for each separation in classical driving force based method has been considered the same as one determined at first part of the methodology described in chapter 3. Hence, only feed and side-draw locations are to be determined and eventually, the reboiler duty of each methodology outcome is compared to each other.

Accordingly, the rest of this chapter is dedicated to the two aforementioned case studies and the comparison with results of classical driving force.

### 4.1. Molecular tracking application

In this section, the application of methodology developed in chapter 3 is presented on two case studies. First a side-draw distillation unit is designed for a mixture of benzene, p-xylene mixture with trace level of concentration of toluene using the methodology of chapter 3 and afterwards another side-draw distillation column is designed for a mixture of n-pentane, n-heptane with trace amounts of n-hexane.

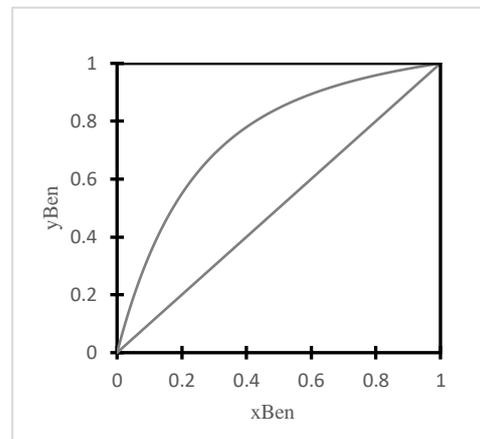
#### 4.1.1. Benzene, p-xylene mixture with trace amounts of toluene

Benzene, toluene and p-xylene are considered as major upstream components in petrochemical processes. The production of the most chemical products, intermediate substrates and final products initiate based on these three components. Hence, there is a large production rate of these components in chemical industries and as such, the energy consumption of the corresponding processes are extremely large like in crude oil distillation. Employing a more efficient methodology for separation of these components are always appreciated. Moreover, the mixture compounded with these components is an ideal mixture. Therefore, the thermodynamic properties estimation will be more easily handled and the concept of molecular tracking can be evaluated individually.

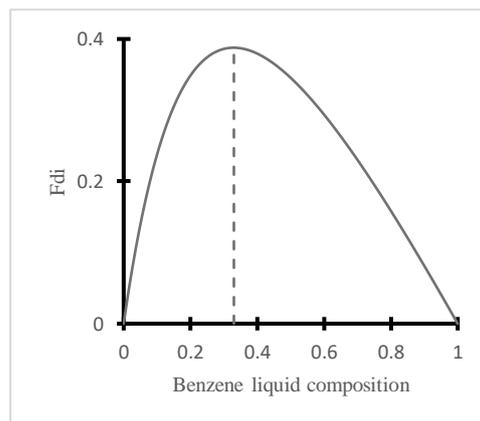
*Table 4-1. Datasheet of BTX case study*

Action	Feed: (Ben 58 %, Tol 1,000 ppm p-X 41.9 %)
Design a binary distillation using driving force	

- Steps  
1-3
1. Generate the VLE data for benzene and p-xylene
  2. Calculate and plot driving force versus liquid composition of benzene
  3.  $D_x = 0.33$  and  
 $D_y = 0.387$



*Fig 4-1. XY diagram of benzene, p-xylene at 1 atm*



*Fig 4-2. Benzene, p-xylene driving force diagram at 1 atm*

- Steps  
4-7
4.  $x_{D,benzene} = 99.95\%$   
 $x_{B,p-xylene} = 99.95\%$
  5.  $RR_{min} = 0.73$
  6.  $CC = 2$  and  
 $RR = 1.46$
  7.  $q = 0.93$

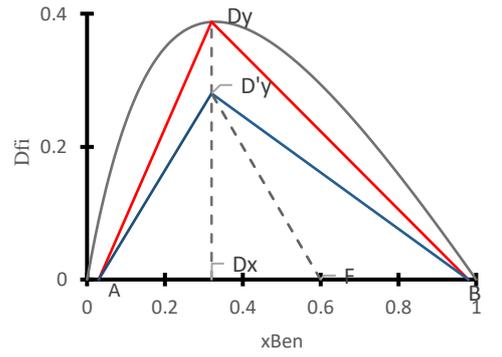


Fig 4-3. Reflux ratio and minimum reflux ratio on driving force diagram of benzene and p-xylene

- Steps  
8,9
8. Draw McCabe-Thiele diagram and find the number of stages and feed location  
 $N_T = 14, N_F = 6$
  9. T-XY diagram

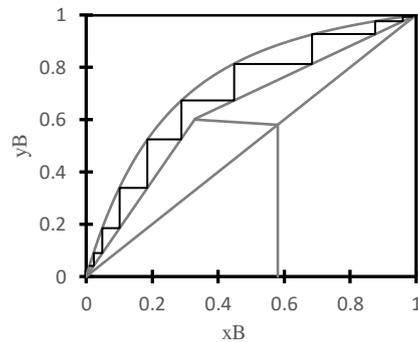


Fig 4-4. McCabe-Thiele diagram for benzene, p-xylene at 1 atm,  $RR=1.46$

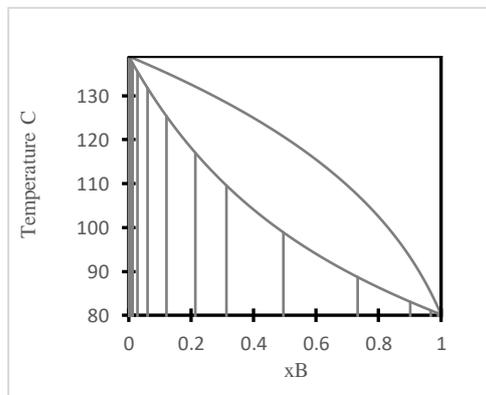


Fig 4-5. T-XY diagram and temperature profile of the column for benzene and p-xylene

- Step  
10
- $$L = 420.98 \text{ kmol/h}$$
- $$V = 711.31 \text{ kmol/h}$$
- $$L' = 461.98 \text{ kmol/h}$$
- $$V' = 252.31 \text{ kmol/h}$$

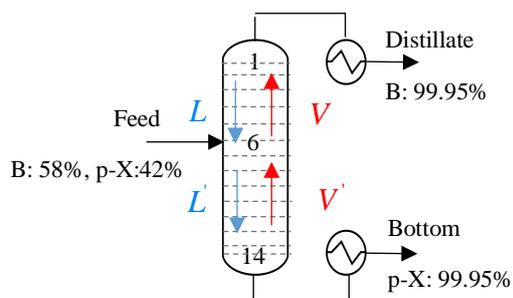


Fig 4-6. Schematic figure of the distillation unit for Ben and p-X

## Find side-draw location using molecular tracking

- Steps 1-3
1. Use Antoine equation and determine vapor pressure profile of toluene in the column
  2. Calculate K-value profile for toluene.
  3. Calculate probability profile and draw the probability diagram

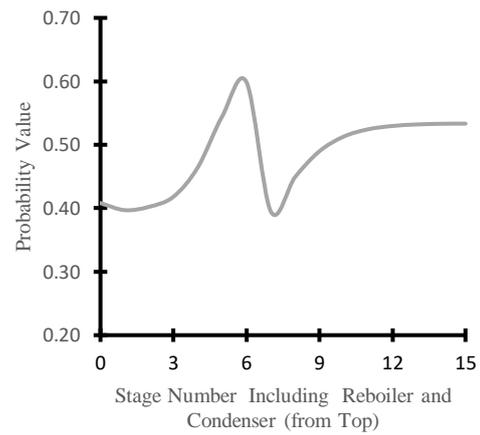


Fig 4-7. Probability profile of Tol inside the column

- Steps 4-6
4. Trays with 50% probability are 5, 7 and 10.
  5. The number of possible side-draw locations are more than one tray

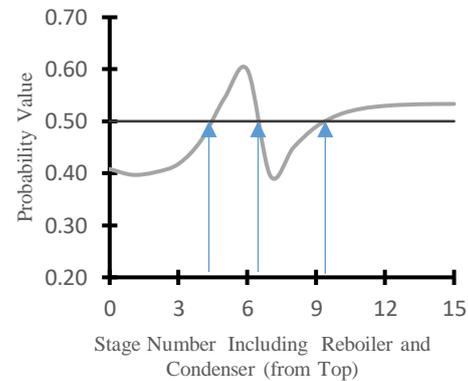


Fig 4-8. Trays in which Tol probability is 50%

- Step 6
- Simulate the column and choose the tray with minimum reboiler duty as the side-draw location.

$$N_s = 7$$

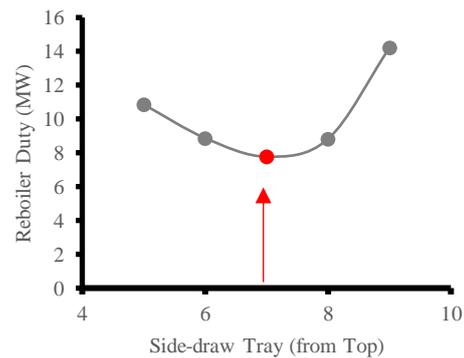


Fig 4-9. Reboiler duty of the BTX column versus side-draw location

The final configuration of the column proposed by methodology is illustrated in Fig 4-10 with tables concerning feed and stream products as well as reboiler duty.

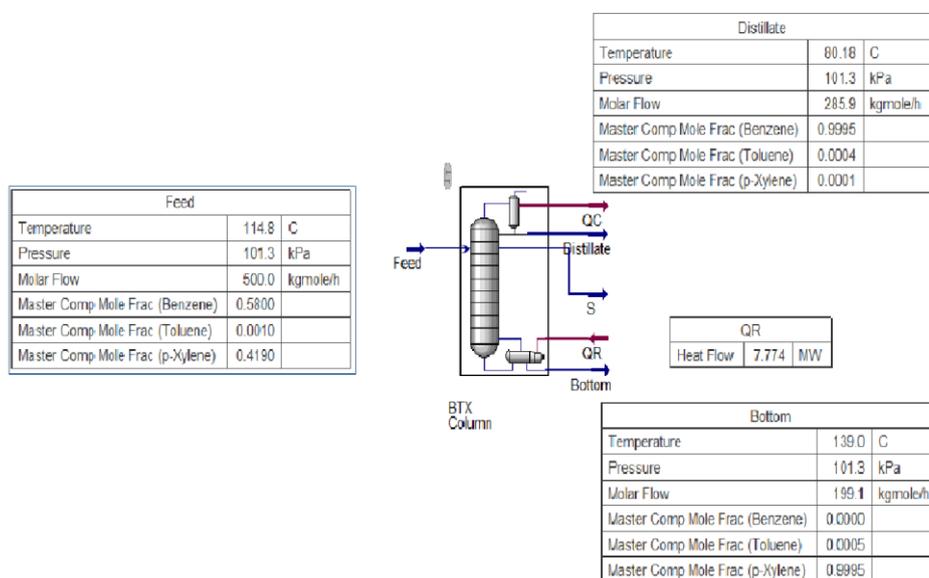


Fig 4-10. HYSYS flowsheet of BTX column

#### 4.1.2. n-Pentane, n-heptane with trace amounts of n-hexane

Bek Pedersen and Gani (2003) have designed a distillation unit for a mixture of n-pentane, n-heptane and n-hexane by using driving force based method. Since, the mixture deviation from thermodynamic ideal behavior is infinitesimal, it can be a perfect case study in this work. The author has presumed a mixture of n-pentane and n-heptane with n-hexane as an impurity in trace levels of concentration. Peng Robinson equation of state is used to predict the thermodynamic properties of such system. According to the design algorithm, the following table is representing an step by step results of this case study. The operating pressure is considered to be 5 atm.

Table 4-2. Datasheet of n-Pentane, n-Heptane and n-Hexane case study

Actions	Feed: (n-Pen 38 %, n-Hex 1,000 ppm n-Hep 61.9 %)
Design a binary distillation using driving force	

- Steps  
1-3
1. Generate the VLE data for Pentane and Heptane
  2. Calculate and plot driving force versus liquid composition of n-Pentane
  3.  $D_x = 0.38$  and  $D_y = 0.317$

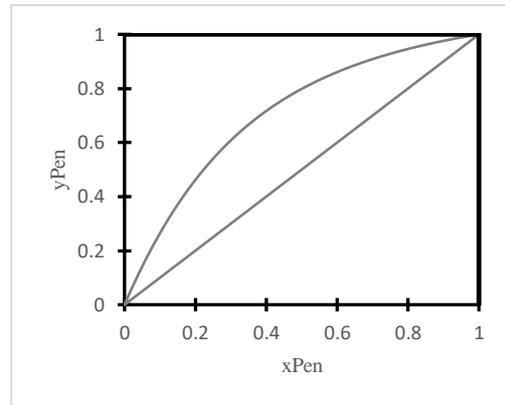


Fig 4-11. McCabe-Thiele diagram of n-Pen and n-Hep at 5 atm

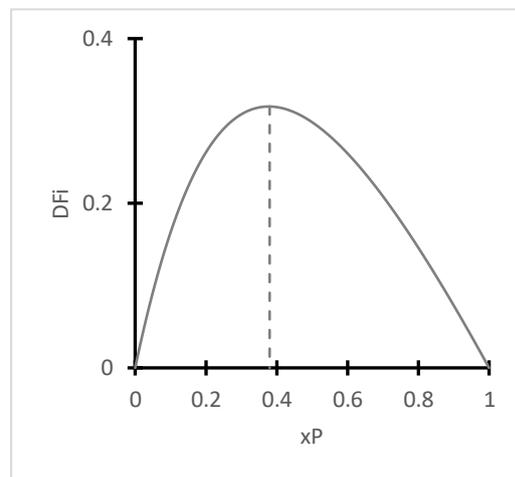


Fig 4-12. Driving force diagram of n-Pen and n-Hep at 5 atm

- Steps  
4-7
4.  $x_{D,n-Pen} = 99.95\%$   
 $x_{B,n-Hep} = 99.95\%$
  5.  $RR_{min} = 0.95$
  6.  $CC = 2$  and  $RR = 1.90$
  7.  $q = 0$

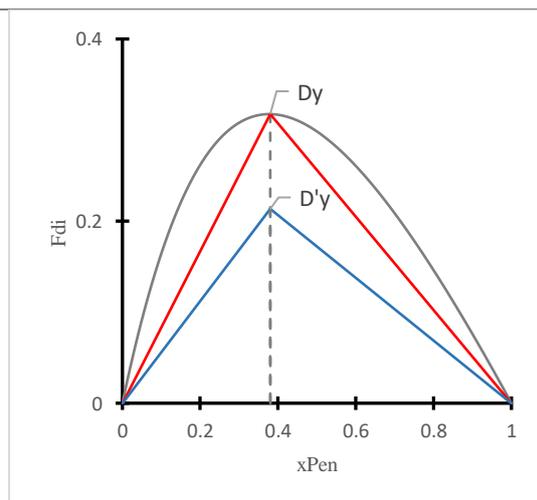


Fig 4-13. Reflux ratio and minimum reflux ratio on driving force diagram of n-Pen and n-Hep

Steps  
8,9

8. Draw McCabe-Thiele diagram and find the number of stages and feed location

$$N_T = 18, N_F = 7$$

9. T-XY diagram

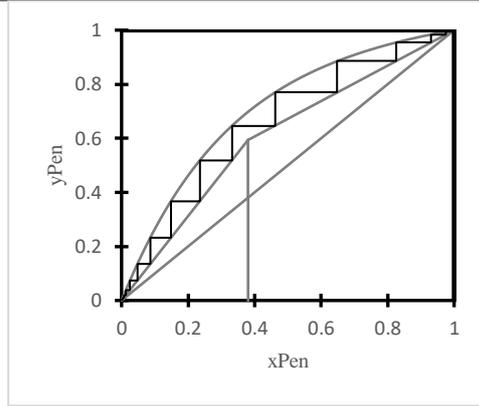


Fig 4-14. McCabe-Thiele diagram for n-Pen, n-Hep at 5 atm, RR=1.9

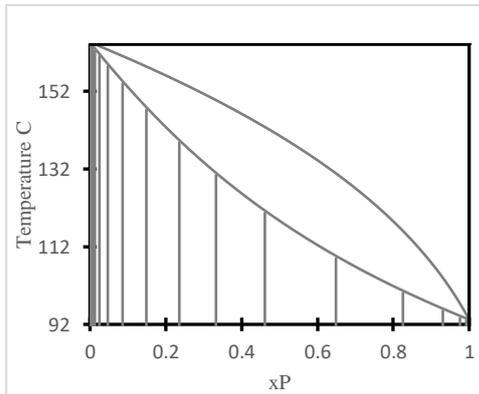


Fig 4-15. T-XY diagram and temperature profile of the column for n-Pen and n-Hep

Step  
10

$$L = 361.25 \text{ kmol/h}$$

$$V = 551.38 \text{ kmol/h}$$

$$L' = 861.25 \text{ kmol/h}$$

$$V' = 551.38 \text{ kmol/h}$$

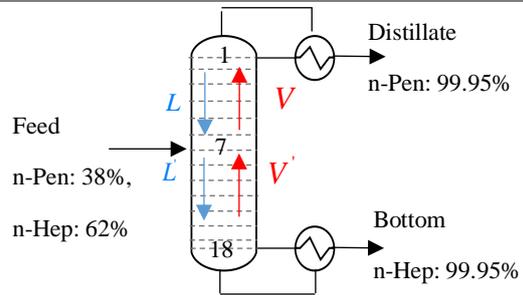


Fig 4-16. Schematic figure of the distillation unit for n-Pen and n-Hep.

**Find side-draw location using molecular tracking**

Steps  
1-3

6. Use Antoine equation and determine vapor pressure profile of n-Hex in the column
7. Calculate K-value profile for n-Hex.
8. Calculate probability profile and draw the probability diagram

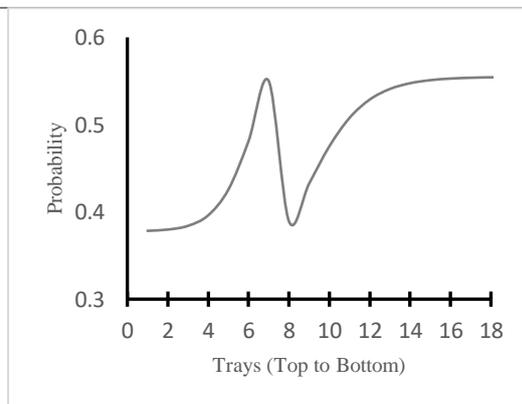


Fig 4-17. Probability profile of n-Hex inside the column

- Steps 4-6
- 9. Trays with 50% probability are 6, 7, 8, 10 and 11.
  - 10. The number of possible side-draw locations are more than one tray

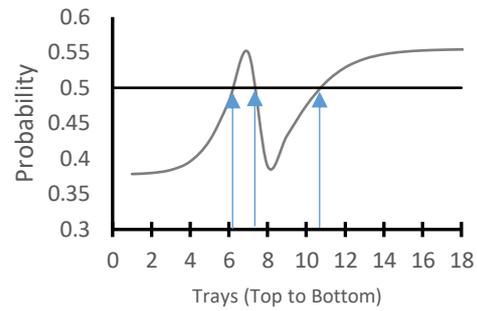


Fig 4-18. Trays in which n-Hex probability is 50%

- Step 6
- Simulate the column and choose the tray with minimum reboiler duty as the side-draw location.

$$N_s = 8$$

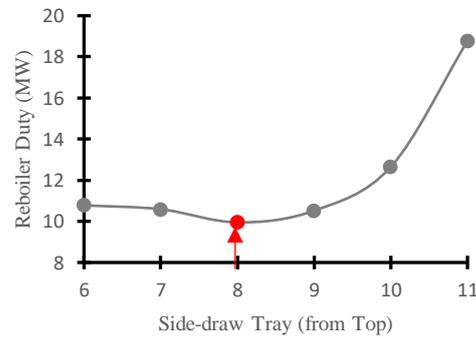


Fig 4-19. Reboiler duty of the PHH column versus side-draw location

The configuration of this column is represented in the following figure.

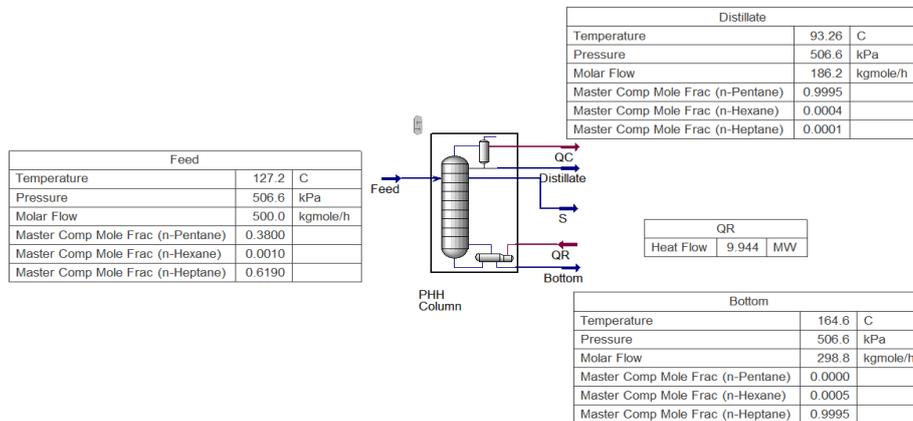


Fig 4-20. HYSYS flowsheet of PHH column

## 4.2. Application of classical driving force method

In this section, the same case studies are analyzed by using a driving force based method developed by Bek Pedersen and Gani (2003). In that paper, the framework is provided for the case that total number of trays be given. Hence, the number of trays are considered to be the same as what found in previous sections. Therefore, the feed and side-draw streams of the unit will be located based on this method.

### 4.2.1. Benzene, p-xylene mixture with trace amounts of toluene

Table 4-3. Datasheet of BTX case study designed by driving force

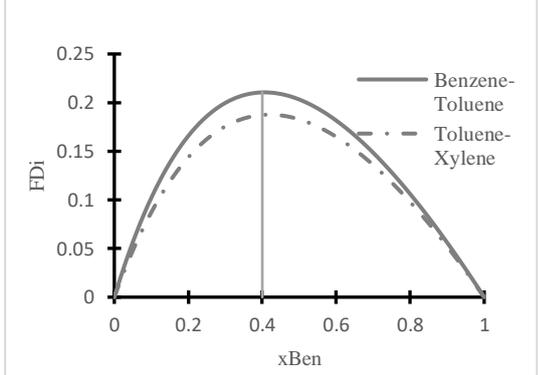
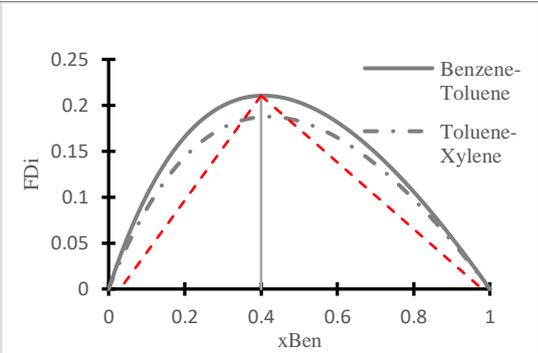
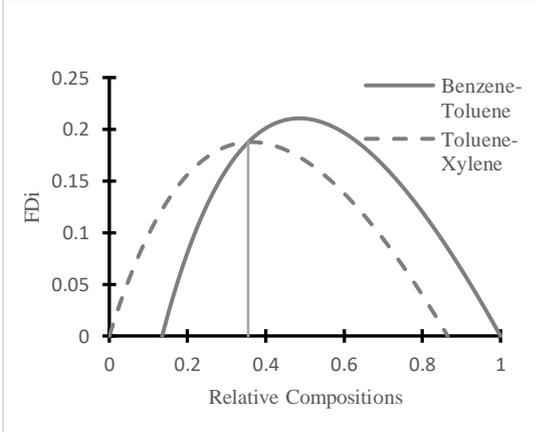
Actions		Feed (Benzene: 58%, Toluene: 1000 ppm p-Xylene: 41.9%)
Steps 1-6	$D_x = 0.4$	
Steps 7, 8	Given number of trays equal to 14 $RR_{\min} = 0.35$	
Steps 9-11	$D_s = 0.36$ $N_s = 14 \times (1 - 0.36) = 9.38$ $N_s = 9$ or $10$	

Fig 4-21. Binary driving force for BTX mixture at 1 atm

Fig 4-22. Minimum reflux ratio of distillation unit for BTX column

Fig 4-23. Joint driving force diagram of BTX column at 1 atm

Step 12	$N_F = 9 \times (1 - 0.4) = 5.4 \cong 5 \text{ or } 6$ $N_F = 10 \times (1 - 0.4) = 6$
Step 13	$N_F = 5, N_S = 9 : Q_R = 14.95 \text{ MW}, RR = 6.82$ $N_F = 6, N_S = 9 : Q_R = 14.21 \text{ MW}, RR = 6.52$ <b>Optimal Configuration</b> $N_F = 6, N_S = 10 : Q_R = 10.14 \text{ MW}, RR = 3.72$

The reboiler duty of the configuration proposed by molecular tracking 8.97 MW and the duty corresponding to driving force is 14.21 MW. Molecular tracking configuration saves the energy required for the reboiler of the column by 37%. Hence, the operating cost of the distillation unit will be lower. The framework developed in chapter 3, successfully found the location of side-draw, which operates with lower reboiler duty by a very simple calculation of corresponding probability profile of the middle boiling component.

#### 4.2.2. n-Pentane, n-heptane mixture with trace amounts of n-hexane

Table 4-4. Datasheet of PHH case study designed by driving force

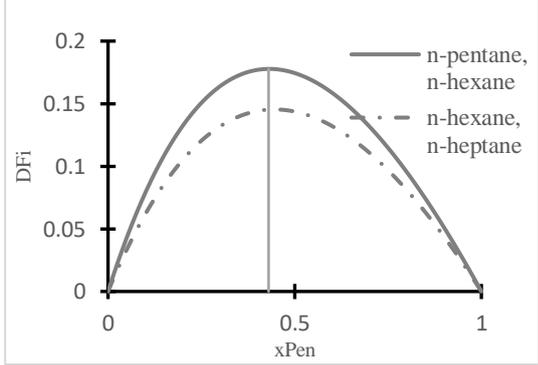
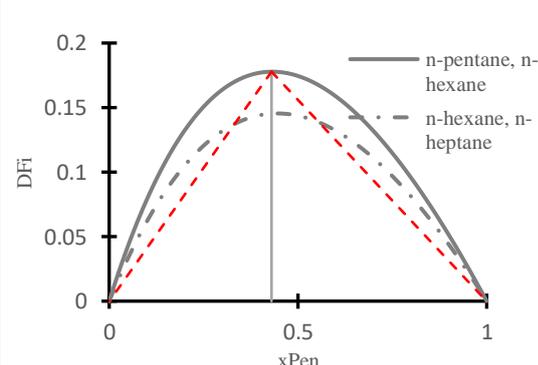
Actions		Feed (Benzene: 58%, Toluene: 1000 ppm p-Xylene: 41.9%)
Steps 1-6	$D_x = 0.43$	
Steps 7, 8	Given number of trays equal to 18 $RR_{\min} = 0.31$	

Fig 4-24. Binary driving force for PHH mixture at 5 atm

Fig 4-25. Minimum reflux ratio of PHH distillation unit at 5 atm

Steps  
9-11

$$D_S = 0.37$$

$$N_S = 18 \times (1 - 0.37) = 11.64$$

$$N_S = 11 \text{ or } 12$$

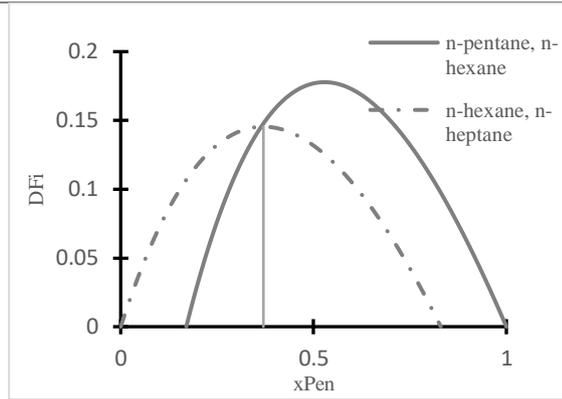


Fig 4-26. Joint driving force diagram of PHH column at 5 atm

Step  
12

$$N_F = 11 \times (1 - 0.43) = 6.27 \cong 6 \text{ or } 7$$

$$N_F = 12 \times (1 - 0.43) = 6.84 \cong 6 \text{ or } 7$$

Step  
13

$N_F = 6, N_S = 11 : Q_R = 19.18 \text{ MW},$	$RR = 14.90$
$N_F = 6, N_S = 12 : Q_R = 57.17 \text{ MW},$	$RR = 47.24$
$N_F = 7, N_S = 11 : Q_R = 18.77 \text{ MW},$	$RR = 14.55$ <b>Optimal Configuration</b>
$N_F = 7, N_S = 12 : Q_R = 56.22 \text{ MW},$	$RR = 46.23$

The reboiler duty of optimal solution proposed by driving force is 18.77 MW, while the reboiler duty of the configuration proposed by molecular tracking is 9.95 MW. An energy saving equivalent to 46% is concluded by using molecular tracking to design side-draw columns for such mixtures.







## Chapter 5: Concluding Remarks

This study has focused on the problem of energy consumption in distillation columns. As distillation column has always been known the most energy demanding unit operation in chemical plants, any slight improvement on energy consumption of such units would be appreciated. Optimization of energy consumption for distillation columns can be performed in design, control or operation phase of these units likewise the other units. However, an optimal/near optimal solution in design phase can be useful to reduce the efforts in next phases drastically in order to implement more simple tools in control and operation steps. The main focus of this study was to develop a novel framework to design side-draw distillation column, which is an intensified unit of operation. The main application of such intensified unit is when an impurity is present in the feed stream of the column. Several methods exist to design a side-draw distillation unit. McCabe-Thiele extension, shortcut methods, driving force-based method and geometric methods are the most popular methods for designing the side-draw distillation columns, but it is required to specify the side-draw composition in terms of the light key component. Therefore, the location of side-draw is implicitly determined by that composition. Among these methods, driving force-based method uses the difference between vapor and liquid composition of the light key component to determine the optimal/ near optimal location of feed and side-draw simultaneously. Although this method is able to predict the location of side-draw, the total number of stages of the column has to be known and there is no framework to design the column from scratch. Moreover, optimization-based methods are the ones able to design the column and find the side-draw and feed locations due to the mathematical formulation of the column, but they are mathematically too complex and may become time consuming. In order to reduce the time required for these methods, a reasonable initial configuration of the column is also necessary. Molecular tracking can provide this initial configuration and let the optimization methods to find the optimum solution more quickly.

To this end, a new concept of molecular tracking is introduced. Molecular tracking has been implemented to follow the molecules inside the column. The concept was based on a probability function, which evaluates the probability of a single molecule to move to either upper stage or lower stage based on the thermodynamic properties of the system, vapor liquid flows inside the column and the composition profile of that molecule. However, this probability function is not able to fully design a column from scratch; it can be combined with another method to design such unit. In this work, driving force-based method is used to design a column for the binary mixtures of key components in the system. Then, the impurity component is introduced in the feed. Since the impurity is in trace level of concentration, presence of this component will not change the temperature profile of the column significantly. Hence, K-values of this component can be roughly

estimated using the vapor liquid equilibrium. By calculating the probability profile of the impurity in the column, the tray with 50% of probability shall be selected as the possible location of side-draw. The full methodology also described in chapter 3. The tray with 50% of probability represents that the molecules are indifferent to move to the upper stage of the lower one, so they will be trapped and accumulated on that stage. Hence, the separation can operate with lower energy by putting side-draw on the stage, in which the molecules of middle boiling component are trapped. Therefore, the overall operating cost of the separation task will reduce. In so doing, molecular tracking framework proposes a configuration of side-draw distillation column that has a lower operating cost compared to the corresponding configurations resulted by employing the other existing methods.

### **5.1. Molecular tracking against driving force**

As case studies, two ideal ternary mixtures with trace level of concentration of middle boiling components have been selected. For each case, a side-draw distillation unit has been designed using molecular tracking methodology to find the column configurations required for the corresponding separation tasks. While the methodology of classical driving force [16] is also used to design the side-draw column and compare the two configurations proposed by each framework.

First case study was a ternary mixture of benzene, p-xylene with infinite dilution of toluene. A simple distillation column is designed using driving force approach to separate benzene and p-xylene. In this phase the number of theoretical trays, reflux ratio is determined by using the first part of the methodology developed in chapter 3 (design a binary distillation using DF). The feed is located at maximum driving force. The composition of driving force is at  $x_D = 0.33$  and the composition corresponding to zero Gibbs free energy of vaporization is at  $x_D = 0.32$ . The deviation may derives because the mixture is not completely ideal. However, the deviation is infinitesimal, so the assumption of ideal mixture is not far from reality.

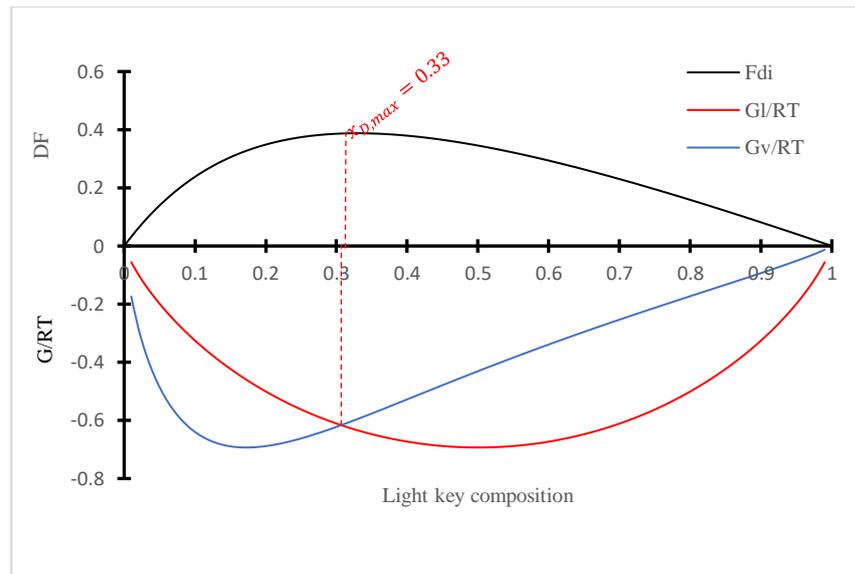


Fig 5-1. Driving force and Gibbs free energy diagram of benzene, p-xylene

Then, toluene was introduced in the system and then by following the methodology of finding side-draw location, followed by a simulation of the column, the optimum location of side-draw is found. The corresponding side-draw composition and feed composition are represented in the similar figure of driving force and Gibbs free energy of the mixture. The feed is deviated from the maximum driving force. Since, the column is at first designed for a hypothetical binary mixture of key components and then the column is to operate for the ternary mixture. The side-draw composition is located on the left of maximum driving force composition.

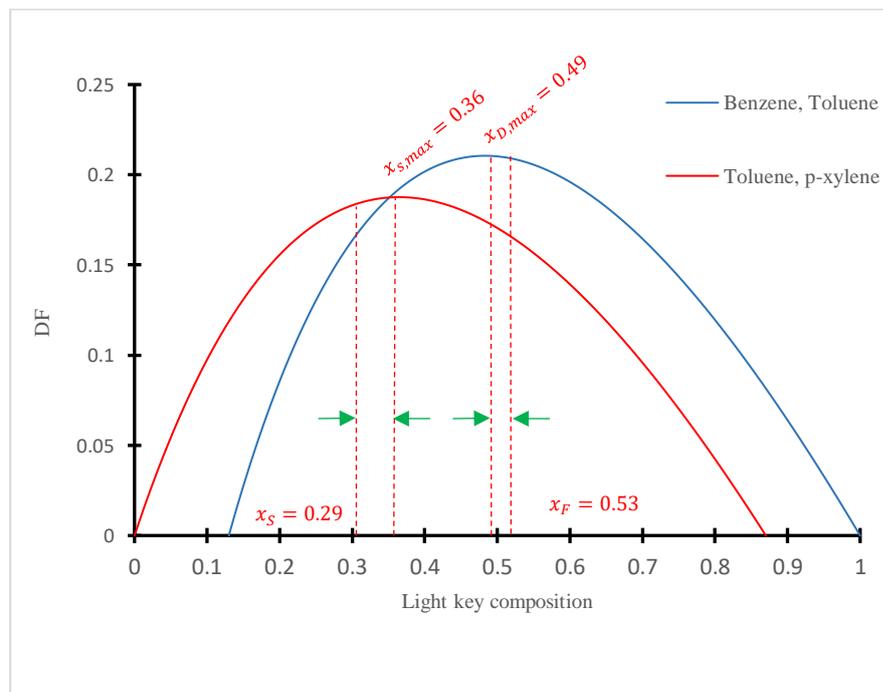
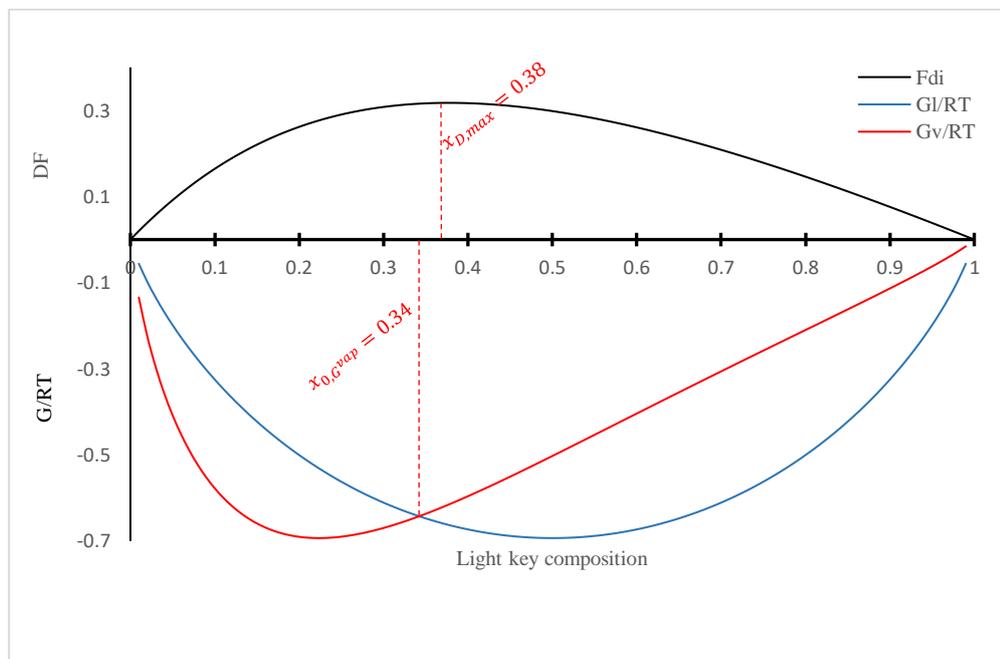


Fig 5-2. Corresponding composition of feed and side-draw for BTX distillation column

Although the feed and side-draw composition is deviated from the one proposed by Bek Pedersen and Gani (2003) [16], the final configuration proposed by molecular tracking showed that the reboiler duty is less than the configuration proposed by driving force. The established driving force methodology for side-draw distillation column is not able to handle the mixtures with infinite dilution of impurities. On the other hand, molecular tracking methodology can find the optimum location of side-draw.

A similar approach is carried out for the second case study. The binary driving force diagram of n-pentane and n-heptane is represented in Fig 5-3 against Gibbs free energy of the mixture of these two components. The composition corresponding to the maximum driving force is  $x_D = 0.38$ , while the composition corresponding to zero Gibbs free energy of vaporization is  $x_{0,G^{vap}} = 0.34$ . This deviation also comes from the fact that this mixture is not completely ideal like the first case study. However the deviation is not significant and the assumption of ideal mixture is still valid.



**Fig 5-3.** Corresponding composition of feed and side-draw for PHH distillation column

Likewise, the first case study, has feed been located at the maximum driving force and by following the first part of methodology the number of trays and the feed tray have been found. By knowing the configuration of the unit for a binary mixture, the impurity, n-hexane in this case, has been introduced in the feed and the molecules of n-hexane have been followed by molecular tracking methodology to find the tray in which it has the maximum accumulation or in other words the corresponding probability is 50%. Then, the column is simulated in HYSYS to find the best option for side-draw location. The configuration, which has the minimum reboiler duty is the optimum solution in the defined design space.

In order to have a comparison between the design configurations proposed by driving force and molecular tracking methodology, the column with the same number of stages is designed with the classical deriving force provided by Bek-Pedersen and Gani (2003) [16]. The configuration proposed by molecular tracking methodology represented a lower energy demand in the system. By taking the compositions of feed and side-draw streams of molecular tracking design from HYSYS, it can be clearly seen in Fig 5-4 that the column is not operating at the two maximum driving forces represented by Joint driving force diagram of this mixture.

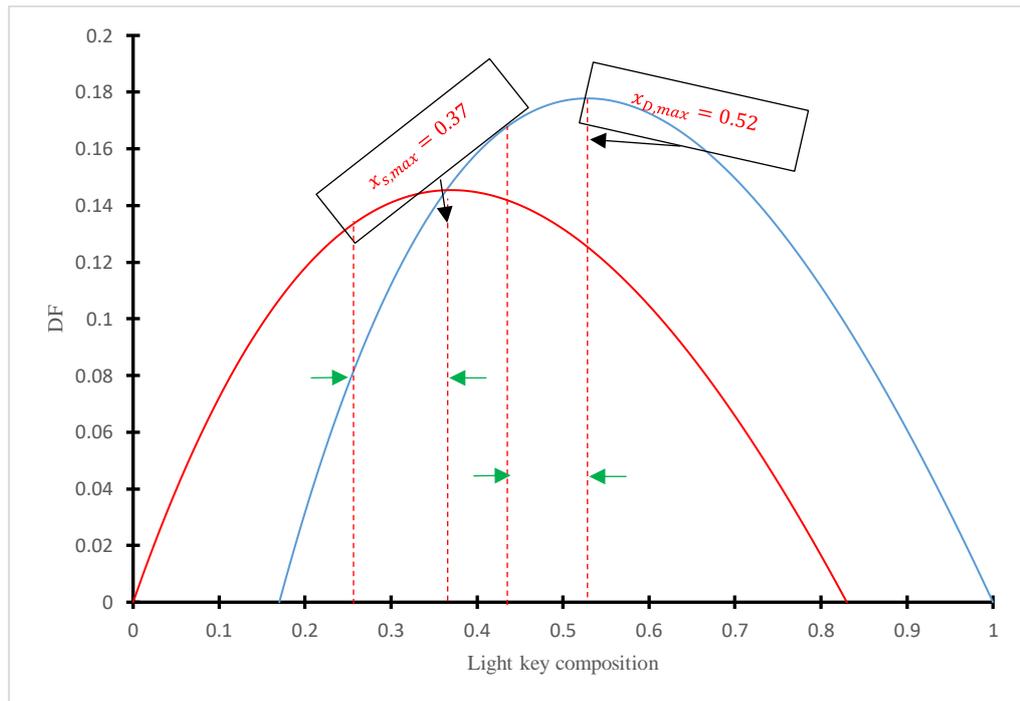


Fig 5-4. Corresponding composition of feed and side-draw for PHH distillation column

## 5.2. Uncertainty analysis

It has recently been realized that computer aided design methods are highly dependent upon thermodynamic and transport properties [23]. Therefore, these two sources have to be considered as the main causes of uncertainty on the design procedure of the chemical processes. Distillation column operation is mainly based on vapor-liquid equilibrium. Hence, often all the design methods proposed for this unit of operation work on the basis of thermodynamic equilibrium of the mixture between vapor and liquid phases, which makes it to have more significant role in uncertainty analysis compared to transport properties. Although several methods proposed to carry out an uncertainty analysis, it is considered a simple approach for industrial practitioners due to the lack of educational backgrounds and the complexity of those proposed methods [23]. Due to the necessity of uncertainty analysis, five of the most important journals in the field of thermodynamics (*Journal of Chemical Thermodynamics*, *Journal of Chemical and Engineering Data*, *Termochimica*

*Acta, Fluid Phase Equilibria and International Journal of Thermophysics*) have obliged reporting the experimental data with an uncertainty analysis together [24].

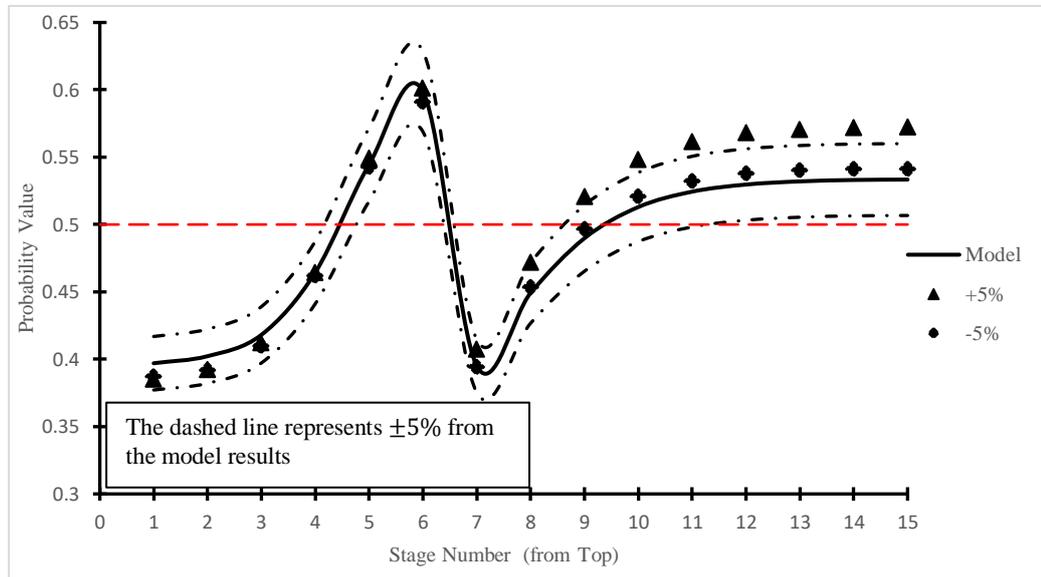
An uncertainty analysis has been carried out on the design methodology developed by the author of this work to evaluate its robustness. The author has assumed a perturbation on the relative volatility of the key components (light key and heavy components) and observed its impact on the probability function of molecular tracking. As discussed previously, a binary distillation unit was designed for the key components in the mixture using the VLE data of that binary mixture. Since the data is represented numerically, the relative volatility has to be determined by a nonlinear regression based on the (2-1) to find the most proper  $\alpha_{i,j}$  that can predict the VLE with minimum sum of squared errors (SSE). To this end, a MATLAB code has been developed to look for that  $\alpha_{i,j}$ . The MATLAB code is represented in Appendix B.3. Then, the relative volatility is changed by 5% and 10%, which are average values to have a perturbation on this parameter. The vapor composition predicted by new relative volatility is generated. However the concentration profile of the column is assumed to be the same as the one determined in chapter 4. Therefore, only the temperature profile of the column will be modified based on (5-1). For the vapor pressure correlation the Antoine equation proposed by HYSYS has been used. Given the column operating pressure and the XY data, the new boiling temperature (TX) is calculated by employing the code represented in Appendix B.2. Hence, by knowing the boiling temperature and the liquid composition profile of light key component, the temperature profile of the column is determined. Now, the probability profile of the impurity in the column can be determined by using (3-8). The new probability profiles are plotted against the ones represented in chapter 4.

$$y_i P = x_i p_i^{sat} \quad (5-1)$$

In the following, the analysis discussed so far, is conducted for the two case studies shown in chapter 4 of this work and it is illustrated that the methodology developed by the author is robust in case of such perturbation.

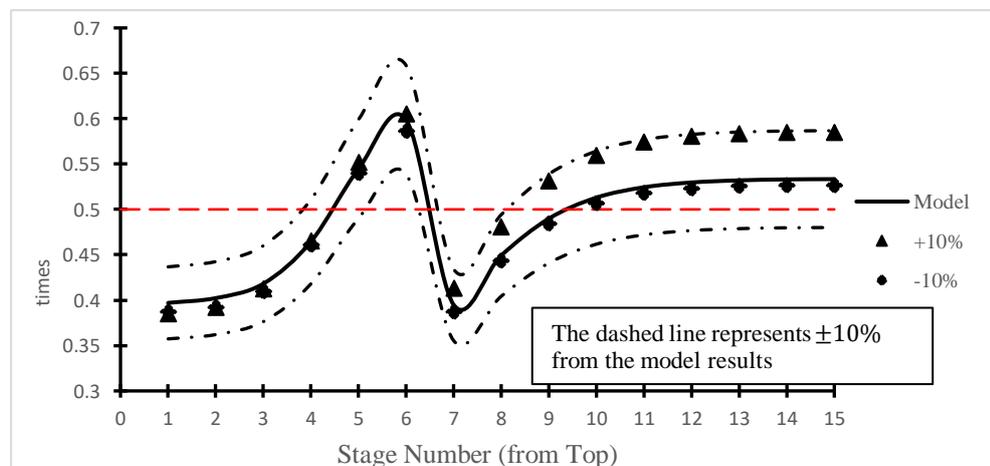
Investigating the VLE data of the first case study of BTX separation task by following the nonlinear regression MATLAB code, concluded that the XY data of benzene and p-xylene mixture could be predicted by assuming a constant relative volatility of  $\alpha_{b,p-x} = 5.0004$ . By changing the relative volatility by  $\pm 5\%$  and  $\pm 10\%$  the new probability profiles of toluene (impurity) can be generated. Fig 5-5 represents the probability profile of this component. It can be observed that in an area between trays 6 and 7 the probability function will not change significantly. This area is the area that the simulation of the column confirms that is the optimum side-draw location in that design

space. A perturbation of  $\pm 5\%$  and  $\pm 10\%$  on relative volatility of benzene and p-xylene will not relocate the side-stream.



**Fig 5-5.** Probability profiles of toluene in BTX column corresponding to a  $\pm 5\%$  perturbation on relative volatility of benzene and p-xylene

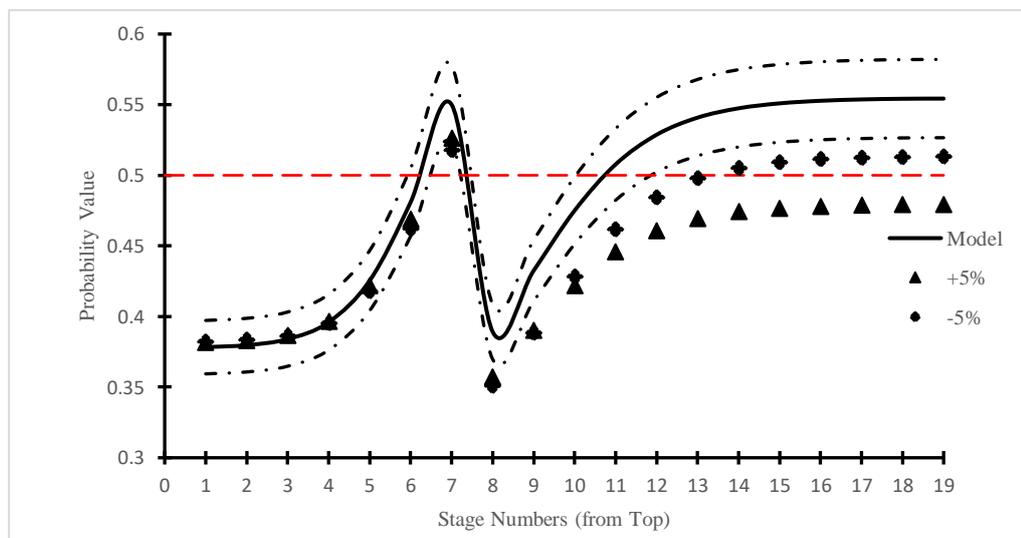
The areas in which the probability value is equal to 50% have slightly been relocated. The first area is the same as the corresponding area determined from model (tray 4 or 5). The second area is also the same as the model prediction (tray 6 or 7). The only area has one tray shifted is the third area. While the third area that model proposed is between trays 9 and 10, the  $\pm 5\%$  perturbation on relative volatility shows that the corresponding area is shifted one tray above i.e. between trays 8 and 9. The same procedure is followed for a perturbation of  $\pm 10\%$  and the probability profile is represented in the following figure.



**Fig 5-6.** Probability profiles of toluene in BTX column corresponding to a  $\pm 10\%$  perturbation on relative volatility of benzene and p-xylene

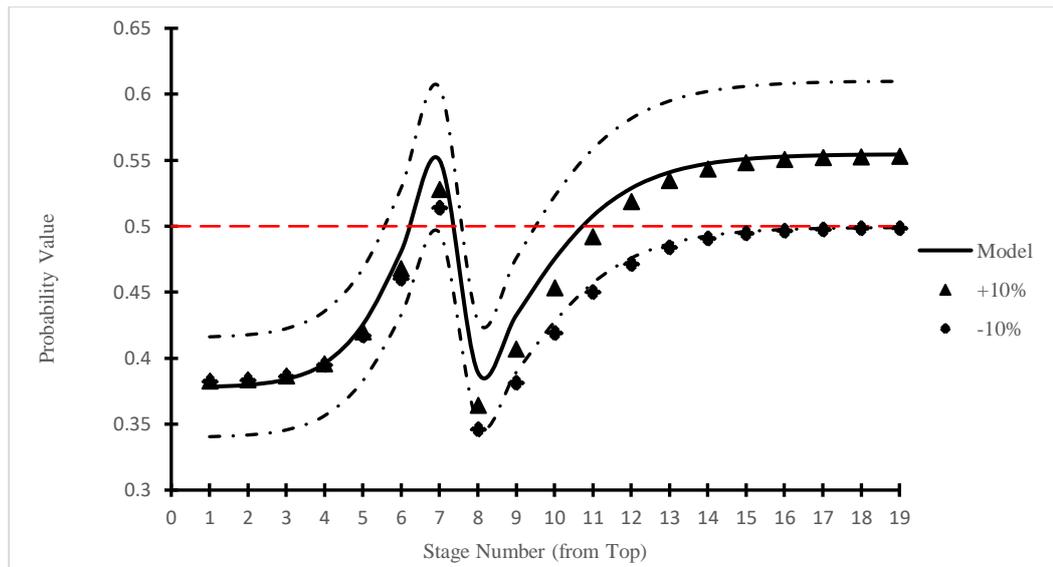
The same analysis is conducted on the second case study of chapter 3 i.e. the mixture of n-pentane and n-heptane with trace amounts of n-hexane. To this end, relative volatility of the key components (pentane and heptane) is determined employing the same MATLAB code as  $\alpha_{Pen,Hep} = 3.629$ . Perturbations of  $\pm 5\%$  and  $\pm 10\%$  are applied to relative volatility to calculate the new T-XY diagram of the binary mixture of key components; assuming that the composition profile of the column is the same as calculated in chapter 4. Hence, regarding the new temperature profile, n-hexane K-value profile can be determined. Using this K-value profile and vapor liquid molar flows, the probability profile of n-hexane can easily be determined. The results of this analysis are provided in Fig 5-7 for  $\pm 5\%$  and in Fig 5-8 for  $\pm 10\%$ .

In case of  $-5\%$  perturbation, the side-draw locations will not change significantly except the one between trays 10 and 11, which the tray in that area will be shifted two trays below the one proposed by the model i.e. between trays 12 and 13, while it can be clearly observed that in  $+5\%$  only two areas are found for locating the side-draw and the third corresponding area of 50% probability is eliminated, since the probability value is below 50% between stages 8 and 15 (reboiler).



**Fig 5-7.** Probability profiles of toluene in PHH column corresponding to a  $\pm 5\%$  perturbation on relative volatility of n-pentane and n-heptane

In case of  $\pm 10\%$  analysis, a similar behavior can be seen in Fig 5-8. The side-draw locations are shifted very slightly and also negative perturbation causes the elimination of one of the options for side-draw (the one close to the bottom of the system). The only difference is that for positive perturbation, none of the side-draw locations that the model proposed will be shifted (not even the option at the bottom of the column).



**Fig 5-8.** Probability profiles of toluene in PHH column corresponding to a  $\pm 10\%$  perturbation on relative volatility of *n*-pentane and *n*-heptane

The analysis carried out in this section shows that even with an uncertainty on thermodynamics of the systems, the result of the developed framework will be the same, however the proposed trays with 50% probability change slightly, the final side-draw tray corresponding to the minimum reboiler duty is the same as the ones reported in chapter 4. Therefore, the framework is able to find the optimum location of side-draw for the two case studies regardless of miscalculation of system's thermodynamics.

### 5.3. Economic Evaluation

This section is intended to provide an economic landscape for the alternative design configurations of the two aforementioned case studies of this dissertation. As such, for both case studies, a sequential distillation consists of two columns in series are designed to accomplish the separation tasks required for the process. A brief analysis is carried out to compare CAPEX, OPEX and TAC of the alternatives for each case study.

#### 5.3.1. Benzene, *p*-xylene with trace amounts of toluene

In this case, benzene is the most abundant component in the system. Hence, the separation sequence will be more efficient separating benzene as the first component, but due to the simulation case provided in HYSYS, the reflux ratio required for the second column will be infeasible. Therefore, in first column *p*-xylene is completely separated and then in the second column (shorter unit) benzene is separated from toluene. In order to have a reasonable comparison between the two alternatives, the recovery rates of the main products are considered the same as the column with side-draw. Moreover, the first column is operating at maximum driving force. Distillate of the first column is fed to the second column but it cannot operate at maximum driving force because the

state of the feed will exceed the critical temperature of the components present in the mixture. Hence, the feed of the second column is saturated liquid. The number of trays required for both of the columns are simply determined according to McCabe-Thiele method. The flowsheet of the simulation case is represented in the following figure. The figure is followed by the tables corresponding to the data required for the design of the columns.

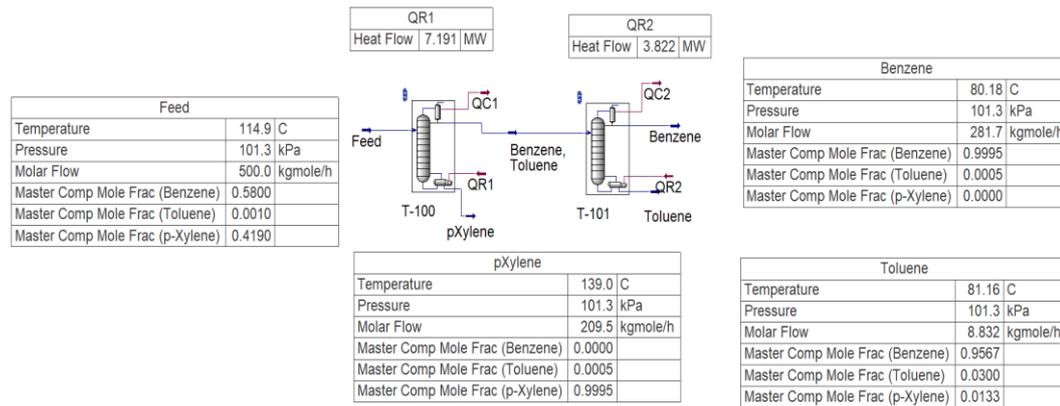


Fig 5-9. HYSYS flowsheet of BTX sequential distillation units

Table 5-1. Parameters required for column design

Parameter	T-100	T-101
$N_T$	13	5
$N_F$	6	2
$RR$	3.6	0.6

In order to determine CAPEX and OPEX of each alternative it is necessary to size the columns. As such, an industrial rule of thumb is taken into account, which claims that by considering that the maximum vapor loading in the column is  $0.3 \text{ ft/s}$ , the column diameter can be directly calculated without relying on a trial and error approach. Moreover, in all columns tray spacing is considered 24 in or equivalently  $0.6096 \text{ m}$ . Accordingly, by only considering flooding, the other negative phenomena such as entrainment, weeping are prevented. Column diameters are calculated with respect to the following equations. The actual vapor velocity is considered 85% of the flooding velocity. It is also considered that the active area of tray is 80% of the active area ( $A_N$ ).

$$V_f = C_{BS} \left( \frac{\rho_L - \rho_V}{\rho_V} \right)^{0.5} \quad (5-1)$$

$$A_N = \frac{V_{max}}{V_{act}} \quad (5-2)$$

Where,  $C_{BS}$  is the maximum vapor loading and  $V_{max}$  is the maximum vapor flowrate inside the column. According to the equations above, the column diameters and heights of alternative design configurations for BTX case study are provided in the following table.

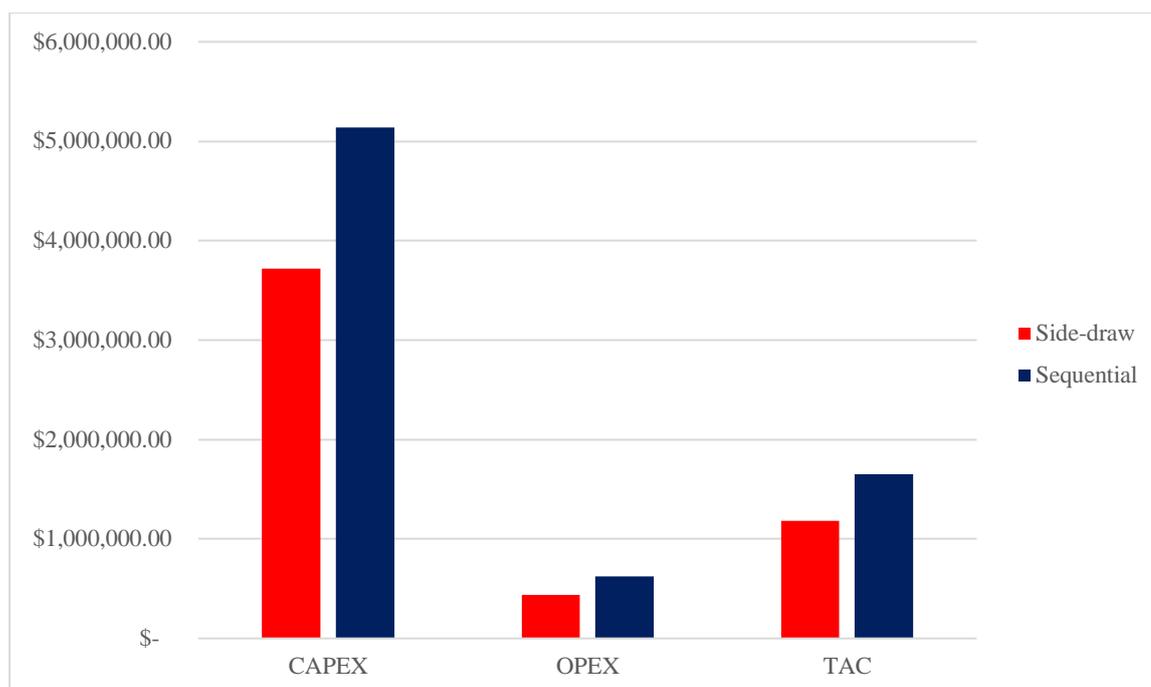
*Table 5-2. Parameters required for column sizing*

Parameter	Side-draw	Sequential Distillation	
		T-100	T-101
$D_T(m)$	3.65	3.65	2
$H_{TOT}(m)$	13	12	7

The CAPEX of each column is determined by using economic evaluation tool of Aspen HYSYS. However, for the OPEX of the columns only the duty of the reboilers are taken into account and LP steam as the proper utility. The cost of LP steam is considered as 4 \$/tonne. The CAPEX of the columns are spread equally within 5 years of operation, which is a reasonable assumption for distillation units. Therefore, the corresponding CAPEX, OPEX of each configuration is provided in the following table. It has to be mentioned that CAPEX values are only to determine a range of capital expenditure and they do not match exactly with the real industrial data. This is due to the lack of data required for CAPEX evaluation. However, for the operation of sequential distillation units it is required to implement two pressure vessels, while side-draw distillation units are only one unit of operation. Hence, the CAPEX of side-draw units are to be lower than sequential distillation columns.

*Table 5-3. Costs of BTX alternatives*

Cost	Side-draw	Sequential Distillation
CAPEX (\$)	3,720,020.00	5,138,890.00
OPEX (\$/y)	440,351.00	623,980.00
TAC (\$/y)	1,184,355.00	1,651,760.00



*Fig 5-10. Comparison of BTX alternatives in terms of costs*

As it is clearly seen, all the cost categories have decreased by using side-draw configuration. Capital expenditure of the system is 27% lower than sequential configurations, while operating cost and total annualized cost of the column are 29% and 28% lower respectively by using the intensified unit operation.

### **5.3.2. n-Pentane, n-heptane with trace amounts of n-hexane**

The procedure to determine CAPEX, OPEX and TAC of this case study is similar to that described in the first case study. In this case, n-heptane is the most abundant component in the system. Hence, the first component to be separated from the mixture is n-heptane and then in the shorter unit n-pentane is separated from n-hexane. First column operates at maximum driving force. The distillate of the first unit is fed to the second column to separate n-pentane and n-hexane. Despite the first column, feed of the second unit is only a saturated liquid, since, in order to operate the second column at maximum driving force it is required to exceed the critical temperature of the components. The rest of the procedure is carried out similarly to the first case study. The HYSYS flowsheet of the sequential distillation is illustrated in the following figure.

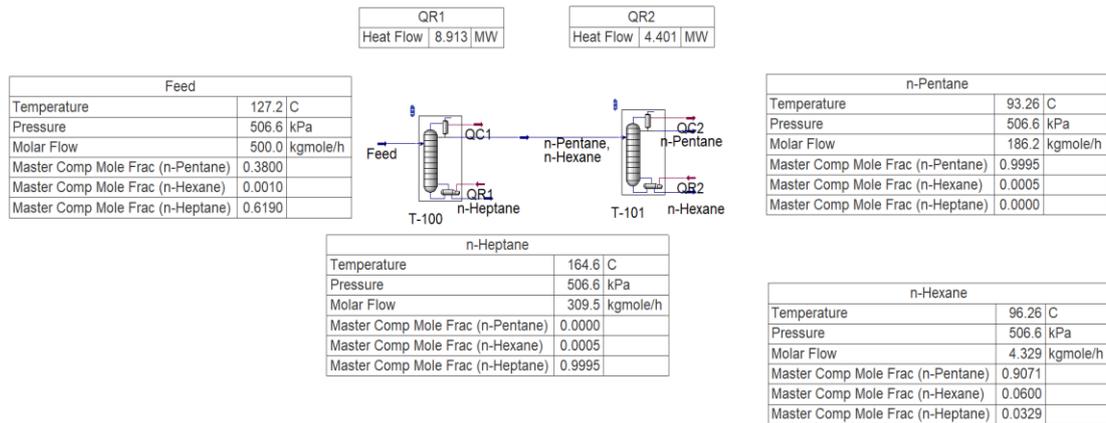


Fig 5-11. HYSYS flowsheet of PHH sequential distillation units

Table 5-4. Parameters required for column design

Parameter	T-100	T-101
$N_T$	17	6
$N_F$	7	2
$RR$	6.1	2.8

Columns are sized with a similar approach implemented in the first case study. Therefore the results of sizing are provided for the two alternatives in the following table.

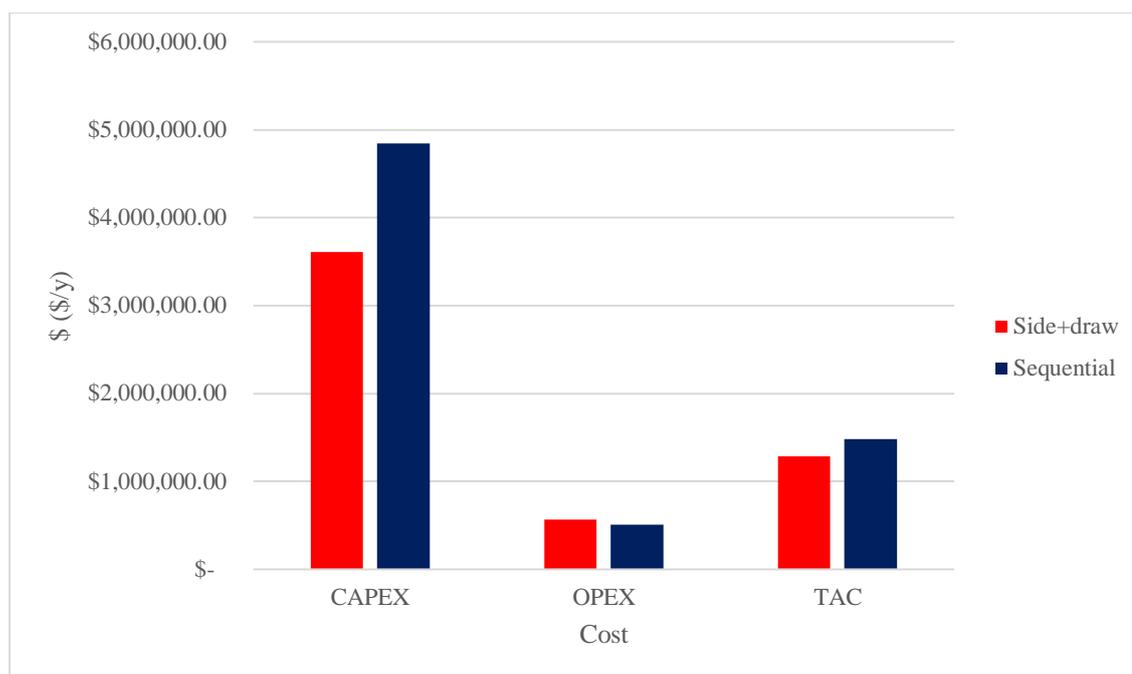
Table 5-5. Parameters required for column sizing

Parameter	Side-draw	Sequential Distillation	
		T-100	T-101
$D_T(m)$	2.9	2.72	1.94
$H_{TOT}(m)$	15.4	14.75	8

In order to calculate the CAPEX of the configurations, the economic evaluation of HYSYS has been used and for OPEX the same LP steam is used as the utility. The table below represents the costs of each alternative for this separation task, which is followed by the corresponding diagram to visualize the comparison of the two approaches more easily.

Table 5-6. Costs of PHH alternatives

Cost	Side-draw	Sequential Distillation
CAPEX (\$)	3,605,950.00	4,842,100.00
OPEX (\$/y)	563,328.00	512,136.00
TAC (\$/y)	1,284,518.00	1,480,556.00



**Fig 5-12.** Comparison of BTX alternatives in terms of costs

CAPEX of the intensified unit operation is 25% lower than the sequential configuration, while its operating cost is 9% higher. Total annualized cost of the intensified unit however is 13% lower than the corresponding sequential distillation configuration.

## References

- [1] WEO/IEA, World Energy Outlook, (2016). [www.iea.org/t&c](http://www.iea.org/t&c).
- [2] N. Nazemzadeh, I.A. Udugama, F. Nielsen, Rasmus, K. Meyer, E.S. Perez-Cisneros, M. Sales-Cruz, J.K. Huusom, J. Abildskov, S.S. Mansouri, Graphical Tools for Designing Intensified Distillation Processes: Methods and Applications, in: F.I. Gómez-Castro, J.G. Segovia-Hernández (Eds.), *Process Intensif. Des. Methodol.*, 2019.
- [3] A.A. Kiss, Distillation technology - still young and full of breakthrough opportunities, *J. Chem. Technol. Biotechnol.* 89 (2014) 479–498. doi:10.1002/jctb.4262.
- [4] N.M. Nikačević, A.E.M. Huesman, P.M.J. Van den Hof, A.I. Stankiewicz, Opportunities and challenges for process control in process intensification, *Chem. Eng. Process. Process Intensif.* 52 (2012) 1–15. doi:10.1016/j.cep.2011.11.006.
- [5] D. Seader, E.J. Henley, D.K. Roper, Separation process principles, *Choice Rev. Online.* 36 (1999) 36-5112-36–5112. doi:10.5860/CHOICE.36-5112.
- [6] N. Nilshda, A Review of Process Synthesis, 27 (1981).
- [7] J.J. Siirola, *Synthesis of System Designs* :, 17 (n.d.) 677–682.
- [8] R. Nath, R.L. Motard, Evolutionary synthesis of separation processes, *AIChE J.* 27 (1981) 578–587. doi:10.1002/aic.690270407.
- [9] M.D. Lu, R.L. Motard, Computer-aided total flowsheet synthesis, *Comput. Chem. Eng.* 9 (1985) 431–445. doi:10.1016/0098-1354(85)80021-1.
- [10] V.M. Nadgir, Y.A. Liu, *Studies in Chemical Process Design and Synthesis : Part V: A Simple Heuristic Method for Systematic Synthesis of Initial Sequences for Multicomponent Separations*, *AIChE J.* 29 (1983) 926–934. doi:10.1002/aic.690290609.
- [11] S.H. Cheng, Y.A. Liu, *Studies in Chemical Process Design and Synthesis. 8. A Simple Heuristic Method for the Synthesis of Initial Sequences for Sloppy Multicomponent Separations*, *Ind. Eng. Chem. Res.* 27 (1988) 2304–2322. doi:10.1021/ie00084a016.
- [12] Y.A. Liu, T.E. Quantrille, S.H. Cheng, *Studies in Chemical Process Design and Synthesis. 9. A Unifying Method for the Synthesis of Multicomponent Separation Sequences with Sloppy Product Streams*, *Ind. Eng. Chem. Res.* 29 (1990) 2227–2241. doi:10.1021/ie00107a007.
- [13] A.W. Westerberg, O. Wahnschafft, *Synthesis of Distillation-Based Separation Systems*, *Adv. Chem. Eng.* 23 (1996) 63–170. doi:10.1016/S0065-2377(08)60202-1.
- [14] M.F. Malone, K. Glinos, F.E. Marquez, J.M. Douglas, Simple, analytical criteria for the sequencing of distillation columns, *AIChE J.* 31 (1985) 683–689. doi:10.1002/aic.690310419.
- [15] J.G. Stichlmair, J. -R Herguajuela, Separation regions and processes of zeotropic and azeotropic ternary distillation, *AIChE J.* 38 (1992) 1523–1535. doi:10.1002/aic.690381005.
- [16] E. Bek-Pedersen, R. Gani, Design and synthesis of distillation systems using a driving-force- based approach, *Chem. Eng. Process. Process Intensif.* 43 (2004) 251–262. doi:10.1016/S0255-2701(03)00120-X.
- [17] R.E. Rooks, M.F. Malone, M.F. Doherty, A Geometric Design Method for Side-Stream Distillation Columns<sup>†</sup>, *Ind. Eng. Chem. Res.* 35 (1996) 3653–3664. doi:10.1021/ie960036t.

- 
- [18] K. Gillnos, M. Malone, Design of Sidestream Distillation Columns, *Ind. Eng. Chem. Process Des. Dev.* 24 (1985) 822–828. doi:10.1021/i200030a050.
- [19] D.W. Tedder, D.F. Rudd, Parametric studies in industrial distillation: Part I. Design comparisons, *AIChE J.* 24 (1978) 303–315. doi:10.1002/aic.690240220.
- [20] W.L. McCabe, E.W. Thiele, Graphical Design of Fractionating Columns, *Ind. Eng. Chem.* 17 (1925) 605–611. doi:10.1021/ie50186a023.
- [21] N. Nazemzadeh, I.A. Udugama, M.A. Taube, J. Abildskov, S.S. Mansouri, Molecular Tracking: A Novel Approach for Multicomponent Distillation Column Design, in: *Eur. Symposium Comput. Aided Process Eng.*, Eindhoven, 2019.
- [22] M.A. Kraller, I.A. Udugama, R. Kirkpatrick, W. Yu, B.R. Young, Side draw optimisation of a high-purity, multi-component distillation column, *ASIA-PACIFIC J. Chem. Eng.* 11 (2016) 958–972. doi:10.1002/apj.2030.
- [23] P.M. Mathias, Effect of VLE uncertainties on the design of separation sequences by distillation - Study of the benzene-chloroform-acetone system, *Fluid Phase Equilib.* 408 (2016) 265–272. doi:10.1016/j.fluid.2015.09.004.
- [24] P.M. Mathias, Sensitivity of process design to phase equilibrium-A new perturbation method based upon the Margules equation, *J. Chem. Eng. Data.* 59 (2014) 1006–1015. doi:10.1021/je400748p.
- [25] T. Bisgaard, M. Mauricio-iglesias, J.K. Huusom, K. V Gernaey, J. Dohrup, M.A. Petersen, J. Abildskov, Adding Value to Bioethanol through a Purification Process Revamp, (2017) 488–490. doi:10.1021/acs.iecr.7b00442.

## Appendix A: Current design methods of side-draw distillation

This section is dedicated to an in detail description of McCabe-Thiele extension, geometric and shortcut design algorithms for side-draw distillation units. More information can be also retrieved by referring to the corresponding references [17,18].

### A.1. McCabe-Thiele Extension

The design algorithm of McCabe-Thiele for side-draw is only discussed for a non-azeotropic binary mixture. In order to design the column with this method, four variables shall be specified; reflux ratio, distillate composition in terms of light component, bottom composition of light component, the composition of light key in side-stream and eventually the side-draw flowrate. Afterwards, the column can be designed by following the algorithm provided in the toolbox below.

#### McCabe-Thiele extension for side-stream in rectifying section

**Step 1.** Generate the VLE data of the binary mixture and plot XY diagram in terms of light key liquid composition.

**Step 2.** Specify the product specifications (light key compositions in distillate, bottom and side-stream).

**Step 3.** Draw a vertical line from the feed composition on x-axis to intersect the diagonal line.

**Step 4.** Consider  $q$  as the vapor feed fraction. Continue the feed line from the intersection point shown in step 3 with the slope provided in the following equation. Continue the line to intersect the equilibrium curve.

$$\text{Slope} = -\frac{1-q}{q} \quad (\text{A-1})$$

**Step 5.** Considering the purity needed in distillate and bottom for the light key component ( $x^D, x^B$ ), determine the location of distillate and bottom specifications on the XY diagram regarding the coordinates ( $x^D, x^D$ ) and ( $x^B, x^B$ ) respectively.

**Step 6.** If the reflux ratio is specified go to step 8, considering the given reflux ratio, else draw a line from  $(x^D, x^D)$  to the intersection between feed line and the point derived in step 4 and continue the line to cross the vertical axis. Regarding the expression provided below, find the minimum reflux ratio of the column.

$$\text{Slope} = \frac{RR_{\min}}{1 + RR_{\min}} \quad (\text{A-2})$$

**Step 7.** Considering the side-stream specification, draw a vertical line from the corresponding composition to intersect the equilibrium curve.

**Step 8.** Relying on the equation provided below, find the operating reflux ratio of the column and calculate the slope of the operating line of rectifier.

$$RR = CC \times RR_{\min} \quad \text{Where } CC = [1.2, 1.8] \quad (\text{A-3})$$

**Step 9.** If the side-stream is in stripping section, draw the rectifier operating line and continue it to intersect the feed operating line. The slope of the operating line is provided in the following equation.

$$\text{Slope} = \frac{RR}{1 + RR} \quad (\text{A-4})$$

**Step 10.** Based on the overall and componential material balance of rectifying section determine the liquid and vapor flowrates of this section.

$$\frac{RR}{1 + RR} = \frac{L}{V} \quad (\text{A-5})$$

$$V = L + D \quad (\text{A-6})$$

$$F = D + B + S \quad (\text{A-7})$$

$$Fz = Dx_D + Bx_B + Sx_S \quad (\text{A-8})$$

**Step 11.** Based on side-stream flowrate, calculate the vapor and liquid molar flow of the middle section; calculate the slope of the middle operating line. The slope can be determined as provided in the following equation.

$$Slope = \frac{L''}{V''} \tag{A-9}$$

**Step 12.** Draw the middle operating line from the point reached in step 9 to intersect the side-stream operating line.

**Step 13.** Draw the stripping operating line from the final point reached in step 12 to the point  $(x_B, x_B)$ .

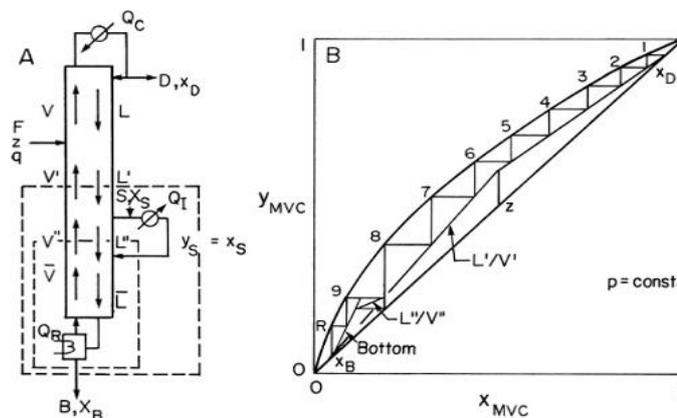
**Step 14.** From  $(x^D, x^D)$  draw a horizontal line to intersect the equilibrium curve of rectifying pressure and from that point draw a vertical line to intersect the corresponding operating line. Continue the same procedure until either the last horizontal or vertical line passes  $(x_B, x_B)$ .

**Step 15.** Count the number of horizontal lines. That would be the number of theoretical stages required for that separation task.

**Step 16.** Find the tray that crosses the feed operating line as the feed tray.

**Step 17.** Find the tray that crosses the side-stream operating line as the side-stream tray.

Fig A.1 illustrates the McCabe-Thiele diagram of a side-stream column, which side-draw is located in the rectifying section



**Fig A.1.** McCabe-Thiele diagram and column configuration of a side-draw column (side-draw located in rectifying section)

## A.2. Geometric Method

The geometric method implements the concept of residue curve maps to determine the feasible area of operation. The algorithm of designing the side-draw columns in which the side-draw is located in rectifying section is represented in the following toolbox. The mathematic formulation required for this method is provided in...

### **Geometric algorithm of side-stream in rectifying section [17]**

**Step 1.** Specify the column pressure, feed rate, feed composition and liquid feed fraction.

**Step 2.** Specify the column specifications in distillate and bottom.

**Step 3.** Select a reflux ratio.

**Step 4.** Determine the composition profile in the rectifying section.

**Step 5.** Based on the material balance in the system determine the distillate, bottom and side-stream flowrates.

**Step 6.** Determine the composition profile in the middle section.

**Step 7.** Determine the composition profile of the stripping section.

**Step 8.** If the intersection of middle and stripping profiles occurs, stop. Else, go to step 9.

**Step 9.** Adjust reflux ratio or another specifications and repeat the procedure from step 2.

The following figure represents the final triangular diagram of side-stream column designed by geometric method.

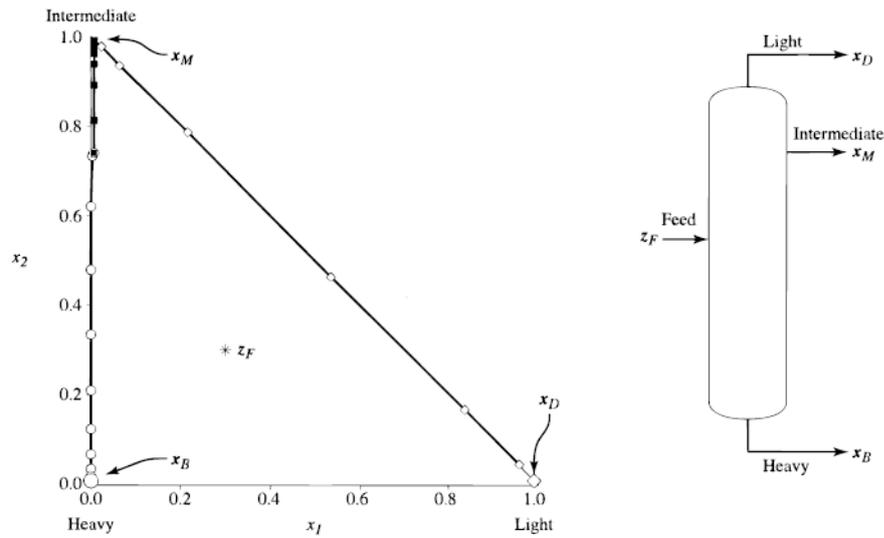


Fig A. 2. Triangular diagram and column configuration of a side-draw column designed by geometric method (side-draw located in rectifying section)

### A.3. Shortcut design method

The shortcut design method uses a more complex mathematical formulation of the side-stream column compared to the first two methods described above. The complete formulation is provided in [18].

#### Geometric algorithm of side-stream in rectifying section [18]

**Step 1.** Specify the specifications of the primary separation by setting the recoveries, molar fractions or flows. Do not specify the side-stream composition or the recoveries.

**Step 2.** Based on the specifications in step 1, calculate minimum reflux ratio or the minimum vapor flowrate of rectifying section (Use Eq.1 or 6 or analogous equation provided in appendix of [17]).

**Step 3.** Calculate the limiting side-stream composition with Eq. 16 or A-5 and 19 in [17].

**Step 4.** Select the operating reflux ratio  $RR = RR_{\min} \times 1.2$  and the side-stream composition 5% to 10% above the minimum (or below the maximum).

**Step 5.** Complete the mass balance over the column.

**Step 6.** Determine the number of theoretical trays with Eq. 9, 10 and 12 or A-2 from the Appendix of [17].

## Appendix B: MATLAB codes

### B.1. Molecular tracking

```
clc
close all

%Define the number of molecules for the analysis and an
initial value of 0
%for the molecules go to distillate
k = 0;
N_Molec =500;

%Define the number of stages for the column including
condenser and reboiler
Stages = (1:16);

%Define intial matrix for the pathways of the molecule
Path = zeros(N_Molec,1000);
Time = zeros(1,N_Molec);

% Set the figure axes, title and initiatives
figure('units','normalized','outerposition',[0 0 1 1])
figure(1);
title('Toluene Pathways','fontsize',32);
xlabel('Steps','fontsize',32);
ylabel('Stages','fontsize',32);
set(gca,'fontsize',32);

hold on
for i = 1 : N_Molec

    tic
    FeedStage = 7;
    Stage = FeedStage;
    NStages = 16;
    j = 1;
    Path(i,j) = FeedStage;
    Path(i,j) = Stage;
    %Define the condition of which next molecule should be
analyzed
    while Stage <= NStages && Stage >= 1

        %Generate the random function
        j = j + 1;
        Rand_Num = rand;
        %Insert the probability of the molecule from the
excel file and
        %rename the variable as you prefer
        P =Benzene(Stage);

        %Compare the probability with the random number and
determine the
        %pathway
```

```
        if Rand_Num < P
            Stage = Stage - 1;
            Path(i,j) = Stage;
        else
            Stage = Stage + 1;
            Path(i,j) = Stage;
        end

        if Stage == 0
            k = k + 1;
            break
        end

        end
        %Online plot of the molecule's pathway
        plot(Path(i,:));
        pause(0.1);

        Time(i)=toc;
    end
    hold off
    %Count the number of molecules that go to distillate (to
    check the
    %distillate compositions
    Count = k;

    Steps = length(Path(i,:));
    Hits = zeros(1,NStages);

    %Based on the pathway matrix, calculate the number of passes
    of that
    %component on each tray
    for i = 1 : N_Molec

        for L = 1 : Steps

            S = Path(i,L);
            if S ~=0 && S ~= NStages + 1
                Hits(1,S) = Hits(1,S) + 1;
            end
        end
    end

    end

    %Plot the number of passes of each component versus the stage
    number
    Stage_Real=(0:NStages-1);
    figure('units','normalized','outerposition',[0 0 1 1])
    figure(2);
    scatter(Stage_Real,Hits,400,'o','k');
    title('Number of MB Hits Over Each Tray','fontsize',32);
```



**Table B.1.** Stream summary of Inbicon demonstration plant [25]

Stream ID		1	2	3	4	5	6	7	8	9	10
Phase	-	Liquid	Liquid	Liquid	Vapor	Vapor	Liquid	Liquid	Liquid	Liquid	Vapour
Flow rate	kg·h <sup>-1</sup>	7867	1275	1260	272.7	254.6	6592	15.27	970.7	16.39	18.06
	m <sup>3</sup> ·h <sup>-1</sup>	7.997	1.374	1.381	70.91	170.1	6.707	0.02036	1.009	0.0201	30.8
Pressure	kPa	24.18	24.18	104.3	291.7	105	29.81	102.5	309.7	302.5	105
Temperature	K	304.8	325.5	359	380.6	388.2	342.1	351.2	407.8	386.6	388.2
Molecular weight	g·mol <sup>-1</sup>	18.41	20.76	20.64	41.72	46.01	18.02	41.95	18.02	26.07	18.02
Density	kg·m <sup>-3</sup>	983.8	927.6	912.3	3.845	1.497	982.9	749.8	961.8	815.5	0.5862
Composition											
Water	wt-%	96.48	78.29	79.15	6.623	0.0007092	100	7.015	100	51.02	100
Ethanol	wt-%	3.485	21.5	20.68	93.09	99.69	0	89.79	0	40.51	0
Acetaldehyde	mg·kg <sup>-1</sup>	6.1	38	0	0.0037	0.0039	0	3200	0	0	0
1-Propanal	mg·kg <sup>-1</sup>	12	76	0.0063	0.029	0.031	0	6300	0	0	0
1-Butanal	mg·kg <sup>-1</sup>	0.097	0.6	0	0.0028	0.003	0	50	0	0	0
Crotonaldehyde	mg·kg <sup>-1</sup>	0.035	0.22	0.16	0.73	0.78	0	4.7	0	0.33	0
Benzaldehyde	mg·kg <sup>-1</sup>	0.024	0.15	0.15	0	0	0	0	0	11	0
Ethyl acetate	mg·kg <sup>-1</sup>	42	260	0.0015	0.007	0.0075	0	21000	0	0	0
Methanol	mg·kg <sup>-1</sup>	100	630	630	2700	2900	0.13	930	0.0012	2700	0
1-Propanol	mg·kg <sup>-1</sup>	63	390	390	140	150	0	42	0	28000	0
1-Butanol	mg·kg <sup>-1</sup>	0.3	1.9	1.9	0.0022	0.0023	0	0.0045	0	140	0
2-Butanol	mg·kg <sup>-1</sup>	0.68	4.2	4.2	2.5	2.7	0	1.4	0	280	0
2-Methyl-1-propanol	mg·kg <sup>-1</sup>	71	440	440	14	15	0	13	0	34000	0
2-Methyl-1-butanol	mg·kg <sup>-1</sup>	16	97	98	0.022	0.024	0	0.09	0	7600	0
3-Methyl-1-butanol	mg·kg <sup>-1</sup>	26	160	160	0.02	0.021	0	0.084	0	12000	0

The first column is a beer stripper containing 18 trays  $N_T = 18$ . Tray numbering is from bottom top. The feed (stream 1) is set to enter the column at tray 18 ( $N_F = 18$ ). The aim of this unit is to strip off the ethanol from the fermentation broth by using steam. The column is operating at sub-atmospheric pressure such that the temperature is low to avoid degradation of enzymes. The concentration of ethanol will be roughly 20% [25]. The second column is an aldehyde column consisting of 30 trays with feed entering the column at tray 22. Pressure of the corresponding distillate is 102.4 kPa. The impurities compound mainly of smaller oxidized organic components are removed from the top product stream as distillate [25]. The impurities also include aldehydes. The third column referred to as a rectification column is a side-draw distillation unit. A validated simulation of the column demonstrates that the column has 40 trays, while feed has to be located at tray 11 and the side-stream should be located at tray 16. The bottom product removes water from the column, while fuel oil referred to as heavy alcohols is removed in the side-stream. Azeotropic alcohol is produced at the top of the column as the distillate product. Afterwards, molecular sieve units are implemented to remove water in order to have anhydrous ethanol as the final product. Since the operation is continuous, two molecular sieves are in use in a dehydration/regeneration cycle.

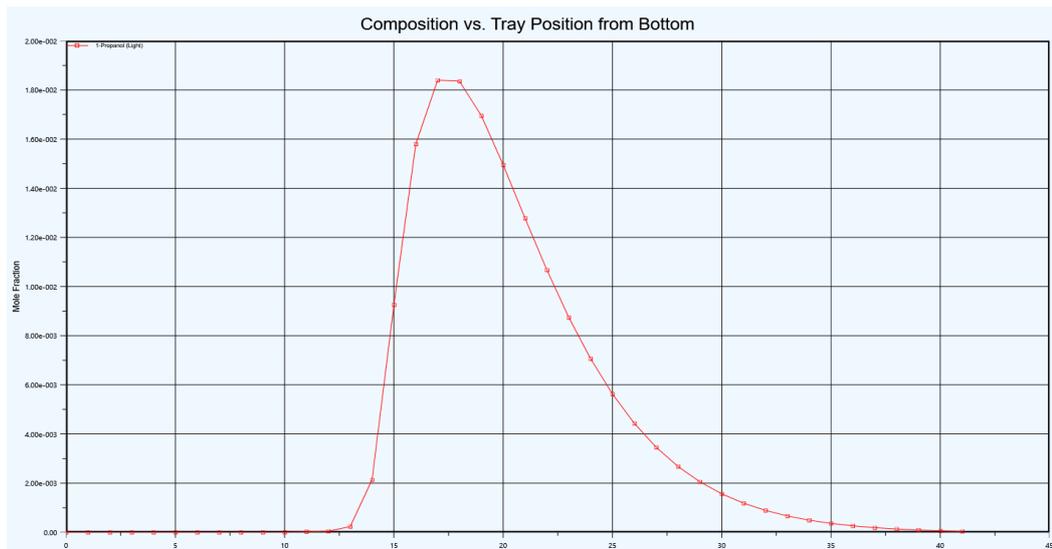
The author has examined the molecular tracking MATLAB code on the side-draw distillation unit of this plant in order to predict the location of side-draw on rectification column. To this end, a similar simulation of the rectification column with corresponding specifications has been provided

in HYSYS. The stream summary of the simulation case of rectification column in HYSYS is represented in Table B.2.

**Table B.2.** Stream summary of Inbicon demonstration plant simulation in HYSYS

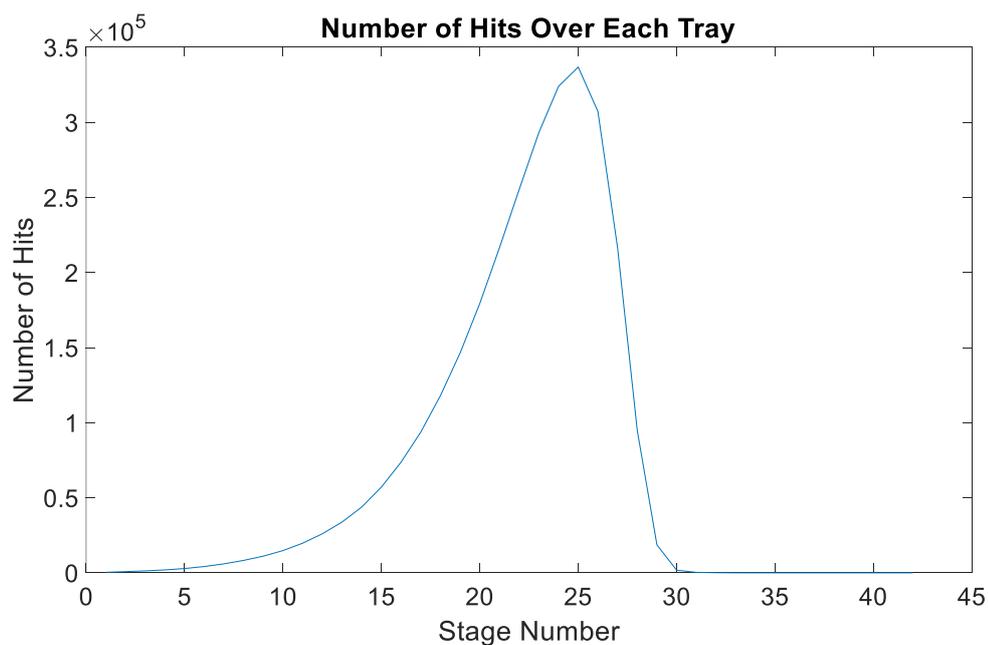
Stream ID		3	4	8	9
Phase	-	Liquid	Vapor	Liquid	Liquid
Flowrate	$kg.h^{-1}$	1260	266.6	977.1	16.39
Pressure	$kPa$	103.4	291.7	309.7	302.8
Temperature	$K$	359	380.55	407.75	384.65
Molecular Weight	$g.mol^{-1}$	20.64	42.18	18.02	32.23
Density	$kg.m^{-3}$	928.8	3.889	917.8	792.1
<b>Composition</b>					
Water	$wt\%$	79.15	5.834	100	52.21
Ethanol	$wt\%$	20.68	93.87	0	44.14
Acetaldehyde	$mg.kg^{-1}$	0	0	0	0
1-propanal	$mg.kg^{-1}$	0.0063	0.0298	0	0.0461
1-Butanal	$mg.kg^{-1}$	0	0	0	0
Crotonaldehyde	$mg.kg^{-1}$	0.16	0.0000291	0	12.29
Benzaldehyde	$mg.kg^{-1}$	0.15	0	0.19	0
Ethyl acetate	$mg.kg^{-1}$	0.0015	0.00704	0	0
Methanol	$mg.kg^{-1}$	630	2900	0.0234	1300
1-Propanol	$mg.kg^{-1}$	390	30.88	0	29500
1-Butanol	$mg.kg^{-1}$	1.9	0	0	146
2-Butanol	$mg.kg^{-1}$	4.2	0.00643	0	322
2-Methyl-1-propanol	$mg.kg^{-1}$	440	0.977	0	33800
2-Methyl-1-butanol	$mg.kg^{-1}$	98	0	126	0.0617
3-Methyl-1-butanol	$mg.kg^{-1}$	160	0	0	12229

As it is clearly seen, the compositions of each stream is regenerated due to the conditions specified in the paper. However, some deviations from the data reported in the original study exists. As far as the main concern of the study is to remove more than 90% of 1-propanol from the mixture in the side-draw the other corresponding compositions are not as important as 1-propanol in side-stream. The specifications of the column are as follows. The heat duty of reboiler, reflux ratio of the column and the side-draw flowrate. The composition profile of 1-propanol is provided in Fig B.2. It can be clearly seen that the maximum concentration of 1-propanol is at tray 17. The deviation with the reported tray i.e. tray 16 in the paper may arises because the simulation of the case study with the specifications in the paper was not possible in HYSYS.



**Fig B.2.** 1-propanol composition profile in rectification column

The data of the liquid and vapor flows inside the column in addition to 1-propanol composition profile in the column. By calculating the probability function due to the retrieved data, the MATLAB code of molecular tracking can be employed to find the tray with maximum number of passes of 1-propanol molecules over each stage in the column. The tray with maximum number of hits of 1-propanol molecules is tray 16. That is the same tray reported in [25] as the best location of side-draw. A representation of 100 molecules of 1-propanol and the number of hits of this molecule over each stage is provided in Fig B.3. The trays are numbered from the top to bottom in the molecular tracking MATLAB code. A similar behavior of the composition profile and the number of passes can be seen regarding the two Fig B.2 and Fig B.3.



**Fig B.3.** Number of hits of 1-propanol molecules on each tray in rectification column of Inbicon demonstration plant

Regarding the figure provided above, side-draw shall be located on tray 25 from top or equivalently 16 from the bottom to remove 1-propanol from the column to match the specifications. Thereby, following the middle boiling component in this column confirms the location of side-draw reported in the original study of [25].

*Table B.3. 1-Propanol probability profile of the column with data required to generate the probabilities*

Stage	Flowrate		Composition		K-Value	$\beta$
	Liquid	Vapor	Liquid	Vapor		
<b>Condenser</b>	22.12	6.32	0.00	0.00	0.57	0.250
<b>40</b>	22.10	28.44	0.00	0.00	0.57	0.422
<b>39</b>	22.08	28.42	0.00	0.00	0.57	0.423
<b>38</b>	22.07	28.40	0.00	0.00	0.57	0.424
<b>37</b>	22.05	28.39	0.00	0.00	0.57	0.424
<b>36</b>	22.04	28.37	0.00	0.00	0.58	0.425
<b>35</b>	22.03	28.36	0.00	0.00	0.58	0.426
<b>34</b>	22.01	28.34	0.00	0.00	0.58	0.427
<b>33</b>	22.00	28.33	0.00	0.00	0.58	0.4286
<b>32</b>	21.98	28.32	0.00	0.00	0.59	0.429
<b>31</b>	21.96	28.30	0.00	0.00	0.59	0.430
<b>30</b>	21.95	28.28	0.00	0.00	0.59	0.432
<b>29</b>	21.93	28.26	0.00	0.00	0.59	0.433
<b>28</b>	21.90	28.24	0.00	0.00	0.60	0.435
<b>27</b>	21.88	28.22	0.00	0.00	0.60	0.437
<b>26</b>	21.85	28.20	0.00	0.00	0.61	0.439
<b>25</b>	21.82	28.17	0.01	0.00	0.61	0.441
<b>24</b>	21.78	28.14	0.01	0.00	0.62	0.444
<b>23</b>	21.73	28.10	0.01	0.01	0.63	0.447
<b>22</b>	21.68	28.05	0.01	0.01	0.64	0.451
<b>21</b>	21.62	28.00	0.01	0.01	0.65	0.455
<b>20</b>	21.55	27.94	0.01	0.01	0.66	0.461
<b>19</b>	21.46	27.87	0.02	0.01	0.68	0.469
<b>18</b>	21.35	27.78	0.02	0.01	0.71	0.481
<b>17</b>	21.21	27.67	0.02	0.01	0.77	0.501
<b>16</b>	20.49	27.53	0.02	0.01	0.90	0.546
<b>15</b>	20.17	27.31	0.01	0.01	1.31	0.639
<b>14</b>	19.83	26.99	0.00	0.01	3.38	0.821
<b>13</b>	19.80	26.66	0.00	0.00	8.18	0.916
<b>12</b>	19.84	26.63	0.00	0.00	10.77	0.935
<b>11</b>	85.64	26.67	0.00	0.00	11.37	0.779
<b>10</b>	86.17	31.41	0.00	0.00	16.64	0.858
<b>9</b>	86.44	31.94	0.00	0.00	19.27	0.876
<b>8</b>	86.53	32.21	0.00	0.00	20.16	0.882
<b>7</b>	86.57	32.30	0.00	0.00	20.42	0.884
<b>6</b>	86.58	32.34	0.00	0.00	20.49	0.884
<b>5</b>	86.59	32.35	0.00	0.00	20.51	0.884
<b>4</b>	86.60	32.36	0.00	0.00	20.51	0.884
<b>3</b>	86.61	32.37	0.00	0.00	20.50	0.884
<b>2</b>	86.62	32.38	0.00	0.00	20.50	0.884
<b>1</b>	86.63	32.39	0.00	0.00	20.49	0.884
<b>Reboiler</b>	54.23	32.40	0.00	0.00	20.49	0.924

## B.2. T-XY data determination

```
clc
close all

global x y

%xx and yy are the XY data that should be imported from an
external file or
%inserted here
for i=1:length(xx)

    x=xx(i);
    y=yy(i);

    %initial guess to start fsolve
    T0=400;
    %The solution is in Kelvin
    TK(i)=fsolve(@myfun,T0);

end
%solution in C
T=TK-273.15;

%The function for fsolve based on yP=xp(sat)
function F=myfun(X)

global x y

T=X;

%Antoine coefficients of light key component to determine the
boiling
%T-X diagram
A=63.3315;
B=-5117.78;
C=0;
D=-7.48305;
E=7.77e-6;
F=2;

%Operating pressure
P=5;

%Vapor pressure of light key component
Psat=exp(A+B/(T+C)+D*log(T)+E*T^F)/101.32;

%function value
F=(y/x-Psat/5)*1000;
end
```

### B.3. Nonlinear regression for relative volatility determination

```
clc
close all

%import XY data of the key components of the mixture as x and y
%initial guess of relative volatility
alpha0=5;
alpha=nlinfit(x,y,@(alpha,x) (alpha*x./(1+(alpha-1)*x)),alpha0);
```

## Appendix C: Datasheets

In this section, the datasheets of each case study represented in chapter 4 is provided; including XY, T-XY data and the generated results of each case study in terms of K-value and probability profiles.

### C.1. BTX Case Study

*Table C 1. VLE data of benzene, p-xylene at 1 atm,  $\alpha \cong 5.0004$*

$x_{Ben}$	$y_{Ben}$	$T_{bub} (^{\circ}C)$	$T_{dev} (^{\circ}C)$
0	0	138.99	139.00
0.02	0.081	136.49	138.39
0.04	0.155	134.09	137.78
0.06	0.222	131.79	137.17
0.08	0.283	129.59	136.54
0.1	0.338	127.48	135.90
0.12	0.388	125.45	135.26
0.14	0.434	123.51	134.60
0.16	0.475	121.64	133.93
0.18	0.514	119.85	133.25
0.2	0.549	118.13	132.57
0.22	0.581	116.47	131.87
0.24	0.610	114.88	131.15
0.26	0.638	113.35	130.43
0.28	0.663	111.87	129.69
0.3	0.686	110.45	128.94
0.32	0.708	109.08	128.17
0.34	0.728	107.76	127.39
0.36	0.746	106.48	126.59
0.38	0.763	105.24	125.78
0.4	0.779	104.05	124.95
0.42	0.794	102.90	124.10
0.44	0.808	101.78	123.23
0.46	0.822	100.70	122.34
0.48	0.834	99.65	121.43
0.5	0.845	98.63	120.50
0.52	0.856	97.65	119.54
0.54	0.866	96.69	118.56
0.56	0.876	95.76	117.55
0.58	0.885	94.85	116.52
0.6	0.894	93.98	115.45
0.62	0.902	93.12	114.35
0.64	0.909	92.29	113.21
0.66	0.917	91.48	112.04
0.68	0.924	90.69	110.83
0.7	0.930	89.92	109.57
0.72	0.936	89.16	108.26
0.74	0.942	88.43	106.90
0.76	0.948	87.71	105.48
0.78	0.953	87.01	104.00
0.8	0.959	86.33	102.45
0.82	0.963	85.66	100.82
0.84	0.968	85.00	99.11
0.86	0.973	84.36	97.29
0.88	0.977	83.73	95.37
0.9	0.981	83.11	93.31
0.92	0.985	82.50	91.10
0.94	0.989	81.90	88.72
0.96	0.993	81.32	86.13
0.98	0.997	80.74	83.29
1	1	80.17	80.17

Table C 2. Datasheet of BTX distillation column

Stages	Temp (°C)	Temp (K)	Vapor Pressure (atm)				Press (atm)	Ben	p-X	Tol	LF (kmol/h)	VF (kmol/h)	Ben	p-X	Tol
			Ben	p-X	Tol	Press									
Condenser	80.23734	353.387	1.0473	0.1572	0.3863	1	1.0473	0.1572	0.3863	420.980	0.000	0.4082	0.4082	0.4082	
1	80.4905	353.640	1.0554	0.1587	0.3897	1	1.0554	0.1587	0.3897	420.980	711.311	0.6407	0.2115	0.3970	
2	81.12763	354.278	1.0761	0.1626	0.3983	1	1.0761	0.1626	0.3983	420.980	711.311	0.6452	0.2155	0.4023	
3	83.04976	356.200	1.1405	0.1748	0.4252	1	1.1405	0.1748	0.4252	420.980	711.311	0.6584	0.2280	0.4181	
4	88.69917	361.849	1.3463	0.2152	0.5130	1	1.3463	0.2152	0.5130	420.980	711.311	0.6946	0.2666	0.4643	
5	98.881	372.031	1.7849	0.3068	0.7074	1	1.7849	0.3068	0.7074	420.980	711.311	0.7510	0.3414	0.5445	
6	109.5472	382.697	2.3489	0.4341	0.9695	1	2.3489	0.4341	0.9695	461.980	711.311	0.7834	0.4006	0.5988	
7	117.0361	390.186	2.8160	0.5465	1.1951	1	2.8160	0.5465	1.1951	461.980	252.311	0.6060	0.2299	0.3949	
8	125.3942	398.544	3.4137	0.6981	1.4934	1	3.4137	0.6981	1.4934	461.980	252.311	0.6509	0.2760	0.4492	
9	131.7825	404.932	3.9294	0.8349	1.7580	1	3.9294	0.8349	1.7580	461.980	252.311	0.6821	0.3132	0.4898	
10	135.5164	408.666	4.2560	0.9242	1.9286	1	4.2560	0.9242	1.9286	461.980	252.311	0.6992	0.3354	0.5130	
11	137.3903	410.540	4.4272	0.9717	2.0189	1	4.4272	0.9717	2.0189	461.980	252.311	0.7074	0.3467	0.5244	
12	138.2622	411.412	4.5086	0.9944	2.0620	1	4.5086	0.9944	2.0620	461.980	252.311	0.7112	0.3520	0.5297	
13	138.6539	411.804	4.5455	1.0048	2.0816	1	4.5455	1.0048	2.0816	461.980	252.311	0.7129	0.3543	0.5320	
14	138.827	411.977	4.5619	1.0094	2.0903	1	4.5619	1.0094	2.0903	461.980	252.311	0.7136	0.3554	0.5331	
Reboiler	138.8769	412.027	4.5666	1.0107	2.0928	1	4.5666	1.0107	2.0928	461.980	252.311	0.7138	0.3557	0.5334	

$$K = \frac{y}{x} = \frac{P^{sat}}{P}$$

$$\beta = \frac{K.VF}{K.VF + LF}$$

## C.2. PHH Case Study

**Table C 3.** VLE data of *n*-pentane, *n*-heptane at 5 atm,  $\alpha \cong 3.269$

$x_{n-Pen}$	$y_{n-Pen}$	$T_{bub} (^{\circ}C)$	$T_{dew} (^{\circ}C)$
0	0	164.58	164.58
0.02	0.059	116.07	138.10
0.04	0.115	114.82	136.84
0.06	0.168	113.60	135.55
0.08	0.217	112.41	134.23
0.1	0.264	111.25	132.87
0.12	0.309	110.11	131.47
0.14	0.350	109.00	130.03
0.16	0.390	107.91	128.55
0.18	0.427	106.85	127.02
0.2	0.462	105.80	125.44
0.22	0.495	117.34	139.33
0.24	0.526	104.79	123.80
0.26	0.555	102.82	120.34
0.28	0.582	101.86	118.50
0.3	0.608	100.92	116.58
0.32	0.632	100.00	114.58
0.34	0.655	99.10	112.47
0.36	0.677	98.22	110.24
0.38	0.697	97.35	107.89
0.4	0.717	96.50	105.38
0.42	0.735	95.66	102.71
0.44	0.752	94.84	99.82
0.46	0.768	103.79	122.10
0.48	0.784	94.03	96.69
0.5	0.798	118.65	140.54
0.52	0.812	121.37	142.86
0.54	0.825	162.17	163.77
0.56	0.838	159.81	162.96
0.58	0.849	157.51	162.13
0.6	0.861	155.25	161.30
0.62	0.871	153.04	160.45
0.64	0.881	150.89	159.59
0.66	0.891	148.78	158.72
0.68	0.900	146.73	157.84
0.7	0.908	144.72	156.95
0.72	0.917	142.76	156.05
0.74	0.925	119.99	141.71
0.76	0.932	140.86	155.13
0.78	0.939	137.18	153.25
0.8	0.946	135.41	152.29
0.82	0.953	133.69	151.32
0.84	0.959	132.01	150.33
0.86	0.965	130.37	149.32
0.88	0.970	128.77	148.29
0.9	0.976	127.22	147.25
0.92	0.981	125.70	146.18
0.94	0.986	124.22	145.10
0.96	0.991	122.77	143.99
0.98	0.996	138.99	154.20
1	1.000	93.24	93.24

Table C.4. Datasheet of PHH distillation column

Stages	Temp ©	Temp (K)	Vapor Pressure (atm)			Press (atm)	$K = \frac{y}{x} = \frac{P^{sat}}{P}$			LF (kmol/h)	VF (kmol/h)	$\beta = \frac{K \cdot VF}{K \cdot VF + LF}$		
			n-Pen	n-Hex	n-Hep		n-Pen	n-Hex	n-Hep			n-Pen	n-Hex	n-Hep
Condenser	92.649	365.799	4.93	1.99	0.83	5	0.987	0.398	0.167	361.247	0	0.345	0.345	0.345
1	92.723	365.873	4.94	1.99	0.84	5	0.989	0.399	0.167	361.247	551.377	0.601	0.378	0.203
2	92.947	366.097	4.97	2.01	0.84	5	0.994	0.401	0.168	361.247	551.377	0.603	0.380	0.204
3	93.613	366.763	5.05	2.04	0.86	5	1.009	0.408	0.172	361.247	551.377	0.606	0.384	0.208
4	95.487	368.637	5.27	2.15	0.91	5	1.054	0.430	0.182	361.247	551.377	0.617	0.396	0.217
5	100.110	373.260	5.86	2.43	1.04	5	1.171	0.485	0.209	361.247	551.377	0.641	0.425	0.242
6	108.999	382.149	7.12	3.04	1.35	5	1.424	0.607	0.269	361.247	551.377	0.685	0.481	0.291
7	120.632	393.782	9.06	4.00	1.84	5	1.812	0.801	0.368	361.247	551.377	0.734	0.550	0.360
8	130.361	403.511	10.97	4.98	2.35	5	2.194	0.995	0.470	361.247	551.377	0.584	0.389	0.231
9	138.756	411.906	12.84	5.95	2.87	5	2.568	1.190	0.574	361.247	551.377	0.622	0.432	0.269
10	147.216	420.366	14.96	7.07	3.48	5	2.991	1.414	0.697	361.247	551.377	0.657	0.475	0.308
11	153.900	427.050	16.80	8.06	4.03	5	3.361	1.611	0.806	361.247	551.377	0.683	0.508	0.340
12	158.315	431.465	18.11	8.76	4.43	5	3.623	1.752	0.886	361.247	551.377	0.699	0.529	0.362
13	160.920	434.070	18.92	9.20	4.68	5	3.784	1.840	0.935	361.247	551.377	0.708	0.541	0.374
14	162.358	435.508	19.38	9.45	4.82	5	3.876	1.889	0.963	361.247	551.377	0.713	0.547	0.381
15	163.125	436.275	19.63	9.58	4.89	5	3.925	1.916	0.979	361.247	551.377	0.715	0.551	0.385
16	163.526	436.676	19.76	9.65	4.93	5	3.952	1.930	0.987	361.247	551.377	0.717	0.553	0.387
17	163.733	436.883	19.83	9.69	4.95	5	3.965	1.938	0.991	361.247	551.377	0.717	0.554	0.388
18	163.840	436.990	19.86	9.71	4.97	5	3.972	1.942	0.993	361.247	551.377	0.718	0.554	0.389
Reboiler	163.869	437.019	19.87	9.71	4.97	5	3.974	1.943	0.994	361.247	551.377	0.718	0.554	0.389