QUATERNARY AND QUINTENARY SEMICONTINUOUS DISTILLATION

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LAY ABSTRACT

Traditionally, several large distillation columns (that can be hundreds of feet tall) are required to split a mixture of liquid chemicals into its individual components. Distillation is the separation of mixtures due to differences in boiling points. When the mixture is heated, the vapour phase will contain the components with lower boiling points, which can be separated once the vapour phase is cooled and condensed. The main goal of this research is to create a new system that can carry out the same separation, but using complex techniques that require only one column and a few extra storage tanks that are much cheaper and smaller than a distillation column. Different liquid mixtures were used to show how well the new process is able to separate the liquid into its individual components, while remaining in safe operating limits.

ABSTRACT

The separation of four or more components traditionally requires the use of three or more distillation columns. Due to the associated high costs, process intensification techniques have been studied. Semicontinuous separation is one method that allows multiple separations using one column integrated with middle vessels.

This thesis aims to develop a new semicontinuous separation process that can separate a mixture with four or more components into high purity products with one column and two or more middle vessels. It is an extension of the conventional ternary semicontinuous process, which has been repeatedly shown to be profitable at intermediate throughputs when compared to continuous systems. The semicontinuous process operates in a forced cycle, with three operating modes that ensure separation objectives are met.

The performance of the proposed quaternary semicontinuous separation is analyzed through rigorous dynamic simulations over a range of production capacities. To determine the feasibility, operability, and applicability to non-ideal mixtures, three case studies were considered:

1. Equimolar mixture of alkanes (*n*-hexane; *n*-heptane; *n*-octane; *n*-nonane).
2. Equimolar mixture of aromatics (benzene; toluene; ethyl-benzene; and *o*-xylene).
3. Non-ideal mixture of mixed-alcohols (methanol, ethanol, and water; propanol; isobutanol; pentanol and hexanol)

The extendibility of the quaternary semicontinuous separation process, referred to as quintenary semicontinuous separation, is then evaluated on a five-component alkane mixture (*n*-hexane; *n*-heptane; *n*-octane; *n*-nonane; *n*-decane), via three case studies:

1. Equimolar mixture
2. Non-equimolar mixture, rich in light and heavy components.
3. Non-equimolar mixture, rich in intermediate components.

The results for both the quaternary and quintenary semicontinuous processes indicate that this new technique is successful at achieving separation objectives while staying within safe operating limits. Comparison of both equimolar mixtures of alkanes for quaternary and quintenary semicontinuous processes with continuous systems indicates that the proposed system is profitable for intermediate flow rates.

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I would like to start by thanking my advisor, Dr. Adams, for the immeasurable amount of support, guidance, and valuable ideas provided throughout my entire study. This thesis would not have been possible without his assistance, and for that I owe him my deepest gratitude.

I would like to thank the entire Adams' group for always showing your support, providing constructive feedback, and overall just making research fun! I am grateful and honoured to be a part of such a talented group. I would especially like to thank Vida and Chinedu for their invaluable guidance throughout my research. And a big thanks goes out to my penthouse friends and colleagues who helped make this an enjoyable journey. Also, I would like to acknowledge financial support from the Ontario Research Fund – Research Excellence Grant (ORF RE-05-072).

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LIST OF ABBREVIATIONS AND SYMBOLS

d_H	Tray hole diameter (m)
F_1	Molar flow rate of the 1st feed stream from the MV to the column (kmol/hr)
F_2	Molar flow rate of the 2nd feed stream from the MV to the column (kmol/hr)
F_3	Molar flow rate of the 3rd feed stream from the MV to the column (kmol/hr)
$\mathrm{F}_{\mathrm{min}}$	Minimum gas load ($\mathrm{Pa}^{0.5}$)
g	Acceleration due to gravity ($\mathrm{m/s}^2$)
$\mathrm{K_c}$	Proportional gain (%/%)
LC_{output}	Reflux drum controller output (valve % opening)
$MV_{1,Level}(t)$	Middle vessel 1 liquid level (m)
$MV_{2,level}(t)$	Middle vessel 2 liquid level (m)
$MV_{3,level}(t)$	Middle vessel 3 liquid level (m)
N	Number of components
$S_1(t)$	Molar flow rate of the 1st side draw (kmol/hr)
$S_2(t)$	Molar flow rate of the 2nd side draw (kmol/hr)
$S_3(t)$	Molar flow rate of the 3rd side draw (kmol/hr)
TAC	Total annualized costs ($/yr)
$\mathrm{u}_{\mathrm{min}}$	Minimum vapour velocity (m/s)

$V6_{\%\ opening}\ (t)$	Valve manipulating F_1 for quaternary semicontinuous process
$V7_{\%\ opening}\ (t)$	Valve manipulating F_2 for quaternary semicontinuous process
$V11_{\%\ opening}\ (t)$	Valve manipulating F_1 for quinternary semicontinuous process
$V12_{\%\ opening}\ (t)$	Valve manipulating F_2 for quinternary semicontinuous process
$V13_{\%\ opening}\ (t)$	Valve manipulating F_3 for quinternary semicontinuous process
$x_{f,Heavy,1}$	Mole fraction of the heavy intermediate species in F_1
$x_{f,Heavy,2}$	Mole fraction of the heavy intermediate species in F_2
$x_{f,Heavy,3}$	Mole fraction of the heavy intermediate species in F_3
$x_{f,Light,1}$	Mole fraction of the lighter intermediate species in F_1
$x_{f,Light,2}$	Mole fraction of the lighter intermediate species in F_2
$x_{f,Light,3}$	Mole fraction of the lighter intermediate species in F_3
$x_{f,Middle,1}$	Mole fraction of the middle intermediate species in F_1
$x_{f,Middle,2}$	Mole fraction of the middle intermediate species in F_2
$x_{f,Middle,3}$	Mole fraction of the middle intermediate species in F_3

Greek Letters

φ	Relative free area
ρ_L	Liquid density (kg/m^3)
ρ_V	Vapour density (kg/m^3)
τ_i	Integral time (min)

Abbreviations

BTEX	Benzene, toluene, ethyl benzene, *o*-xylene
DME	Dimethyl ether
DOF	Degrees of freedom
ISE	Integral squared error
MAS	Mixed alcohol synthesis catalyst
MV	Middle vessel
NRTL	Non-Random-Two-Liquid
NRTL-RK	Non-Random-Two-Liquid Redlich-Kwong
P	Proportional control
PI	Proportional integral control
PSO	Particle swarm optimization
UNIQUAC-RK	Universal Quasichemical Redlich-Kwong
VOC	Volatile organic compounds
VLE	Vapour-liquid equilibrium

DECLARATION OF ACADEMIC ACHIEVEMENT

This thesis contains material (in Chapters 2 and 3) that has been accepted to a peer-reviewed journal. The feed conditions for case study 2 in Chapter 3 was generously obtained from a study carried out by my colleague, Chinedu Okoli. All other research studies presented in this thesis were executed and written by the author, Kushlani Wijesekera, and the entire thesis was completed under the supervision of Dr. Thomas Adams.

Chapter 1

INTRODUCTION

Excerpts from this chapter have been accepted for publication in the following journal:

Wijesekera, K. N., and Adams, T. A. (2015). Semicontinuous distillation of quaternary mixtures using one distillation column and two integrated middle vessels. *Industrial & Engineering Chemistry Research*. doi: 10.1021/ie504584y

1.1 Motivation

Among the numerous possible chemical separation technologies available, distillation is one of the most commonly used techniques. The separation occurs due to differences in relative volatilities of the main components in the feed mixture. Most distillation processes have high capital and energy requirements, thereby forming a large portion of the overall costs. As such, even small improvements in distillation technology can have large impacts. Because distillation is a mature subject, several approaches have been introduced as improvements for conventional distillation processes. One such approach is process intensification, which aims to reduce the number or size of equipment through innovative ideas (Ramshaw, 1983; Errico, Rong, Tola, & Turunen, 2009). Semicontinuous separation is a process intensification strategy whereby multiple separations can occur in a single separation column (Phimister & Seider, 2000a). This separation technique uses one column integrated with one or more middle vessels (MVs) to achieve separation objectives while operating in a forced cyclic campaign. Capital costs are greatly reduced because the separation occurs in just one column. While it has been well illustrated that semicontinuous separation is more profitable at intermediate production rates for a variety of applications, the focus has been on ternary separation (Phimister & Seider, 2000b; Adams & Seider, 2006, 2008a, 2009b; Monroy-Loperena & Alvarez-Ramirez, 2004; Pascall & Adams, 2013, 2014; Meidanshahi & Adams, 2014). This forms the basis for motivation of applying this process intensification technique to a four or more component separation process in order to improve its profitability. Therefore, in this study we extend the applicability of conventional ternary semicontinuous separation to the semicontinuous separation of four or more products.

1.2 Background

Ternary semicontinuous separation for non-azeotropic mixtures was first proposed by Phimister and Seider (2000a). Using a nearly ideal equimolar mixture of alkanes (*n*-hexane, *n*-heptane, and *n*-octane) they developed a system that separated the components into high purity products using one separating column and one integrated MV. The separation occurs in a forced cyclic campaign involving three operating modes. The MV is charged with the alkane mixture that needs to be separated into three parts. This MV continuously feeds the column while receiving a side draw from the column. The intermediate-boiling component concentrates in the MV while the light and heavy components are removed in the distillate and bottom streams, respectively. Once the intermediate product purity is reached, the liquid in the MV is drained and collected, and the cycle is repeated, thus achieving the same separation as if two continuous distillation columns were used.

Over the past fifteen years several studies have shown the range of applicability of the proposed ternary semicontinuous system. In 2000, Phimister and Seider (2000b) proposed a semicontinuous alternative to extractive and pressure-swing distillation. In 2004, Monroy-Loperena and Alvarez-Ramirez validated the initial work of Phimister and Seider (2000a) by investigating the effect of different feed compositions in the MV and successfully separating the constituent components into their specified product purities. Adams and Seider (2006, 2008, 2009a) further developed the semicontinuous separation process for distillations with chemical reactions. They determined that when intermediate flow rates are required and conventional reactive distillation is infeasible, their proposed semicontinuous process becomes a viable strategy. In 2009, Adams and Seider (2009b) further developed a semicontinuous process for reactive extraction and reactive distillation where the forced cycle alternates between the two kinds in a packed separation column. Adams and Pascall (2012) provide a thorough review on ternary semicontinuous separation methods, detailing various applications and methods used in this separation technique.

More recently, significant advancements have been made to expand the applicability of semicontinuous systems. In 2013, Pascall and Adams presented a methodology for a semicontinuous approach to biomass-to-dimethyl ether (DME) production. They showed that significant reductions in cost are achieved by using semicontinuous separation for intermediate flow rates. In 2014, Meidanshahi and Adams proposed a new semicontinuous configuration without the use of MVs. They showed that semicontinuous systems without MVs outperformed both conventional semicontinuous systems and conventional continuous systems for some cases. Later in 2014, Tabari and Ahmad proposed a semicontinuous approach for azeotropic distillation. They economically compared the semicontinuous to a dividing wall column and a continuous process and determined the semicontinuous process was more favourable.

These ternary semicontinuous systems have shown the possibility of reducing costs for processes that operate at intermediate capacities. Intermediate capacity plants requiring the separation of four or more components in a compact space may be able to benefit from using a semicontinuous quaternary separation because of its ability to achieve specified purity objectives using just one column and two MVs. These processes include growing industries such as specialty chemicals and biorefineries (Pascall & Adams, 2014; Wen, Jiang, & Zhang, 2009). In contrast to the bulk chemicals industry, these areas are better suited for intermediate capacities because of the flexibility required by supply and demand uncertainty (Roberge, Ducry, Bieler, Cretton, & Zimmermann, 2005; Wright &

Brown, 2007; Wen et al., 2009; Sultana & Kumar, 2011; Bruins & Sanders, 2012). For example, some pharmaceutical chemicals are produced at low volumes because of the short lifetime of final products (Roberge et al., 2005). Some specialty chemical companies are also interested in installing facilities operating between pilot and full-scale throughput in order to increase business in high-value, low-volume chemicals (Mullin, 2013). Similarly, plant capacities of biorefineries are sensitive to several factors such as biomass feedstock supply and spatial distribution, and are generally operated at intermediate flow rates (Gan & Smith, 2011). Studies have shown that the use of multiple smaller, distributed biorefineries, instead of one large centralized plant can show significant cost savings due to lower transportation costs (Carolan, Joshi, & Dale, 2007). Bowling, Ponce-Ortega, & El-Halwagi (2011) presented a systematic approach for optimal placement of distributed biorefineries, and concluded that distributed configurations with smaller individual plants were more profitable than centralized solutions. Later, Sultana and Kumar (2012) carried out a similar study and determined that multiple distributed facilities would be economically favourable. More recently, Daoutidis, Marvin, Rangarajan, & Torres (2013) provided a perspective on biomass conversion processes and found that there is a movement towards local biomass-to-biofuel processing facilities with small-scale design units. Then in 2014, Santibañez-Aguilar, González-Campos, Ponce-Ortega, Serna-González, & El-Halwagi proposed an optimization model to design and plan distributed biorefineries, and established that optimal configurations required distributed biomass processing units situated near local harvesting sites. Following these results, it seems that semicontinuous separation would be an ideal candidate for smaller, distributed biorefineries.

1.3 Objectives

It has been well illustrated that ternary semicontinuous separation processes are more profitable than continuous cases for low to intermediate production rates. However the extension of this ternary semicontinuous process has yet to be studied. Therefore it is the purpose of this research to develop and analyze a quaternary and quintenary semicontinuous separation system that may be used in industries with low to intermediate production rates. The proposed system will encompass the characteristics of semicontinuous separation (i.e. the integration of one column with MVs) while achieving the specified separation objectives. The system will be analyzed using the proposed model to examine feasibility, operability, applicability, and extendibility.

1.4 Main Contributions

- **Development of a semicontinuous separation system for a mixture of four or more components** – The ternary semicontinuous separation process has been extended, for the first time, to mixtures with four or more components. The proposed design and control configuration was used to analyze the feasibility, operability, applicability, and extendibility of separating a mixture of four or more components. Dynamic simulation results show the expected successful performance of the different mixtures studied.

- **Application of the proposed system to a real industrial example (mixture of alcohols)** – The proposed quaternary semicontinuous separation system was successfully used on an industrially relevant example of separating and obtaining fuel-grade quality isobutanol from a thermochemical process. The non-ideal nature of the mixture comes from the fact that it is close to being azeotropic. These preliminary results will be extended in future work to include the entire alcohol separation section from the process.

1.5 Thesis Outline

The following summarizes the remaining thesis chapters:

- **Chapter 2**: This chapter focuses on determining the feasibility and operability of a four-component mixture of alkanes (*n*-hexane, *n*-heptane, *n*-octane, and *n*-nonane).
- **Chapter 3**: The applicability of the proposed quaternary semicontinuous process to non-ideal mixtures is determined in this chapter by examining two industrially relevant examples. The first example examines a mixture of benzene, toluene, ethyl-benzene, and *o*-xylene, and the second example examines a mixture of six alcohols and water.
- **Chapter 4**: This chapter examines the extendibility of the proposed quaternary semicontinuous process by extending it to a five-component mixture of alkanes (*n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane). In this case the proposed quintenary semicontinuous process involves one column and three integrated MVs.

- **Chapter 5**: This chapter summarizes the findings from the previous chapters and outlines recommendations for future work.

Chapter 2

QUATERNARY SEMICONTINUOUS DISTILLATION OF AN ALKANE MIXTURE

The text in this chapter has been accepted for publication in the following journal:

Wijesekera, K. N., and Adams, T. A. (2015). Semicontinuous distillation of quaternary mixtures using one distillation column and two integrated middle vessels. *Industrial & Engineering Chemistry Research*. doi: 10.1021/ie504584y

2.1 Introduction

Intermediate capacity plants requiring the separation of four or more components in a compact space may be able to benefit from using a semicontinuous quaternary separation because of its ability to achieve specified purity objectives using just one column and two MVs. The proposed quaternary semicontinuous design would require much less capital than a traditional continuous distillation configuration, which would require three columns to separate four components. The feasibility and operability of an equimolar mixture of alkanes (*n*-hexane, *n*-heptane, *n*-octane, and *n*-nonane) is determined in this chapter using rigorous dynamic simulations.

Figure 2.1 shows a comparison between a conventional ternary and the proposed quaternary semicontinuous systems. Figure 2.1 A shows a ternary semicontinuous separation method for the separation of A, B, and C, where the components are ordered in decreasing volatility. The intermediate component, B, accumulates in the MV, as seen in the mole fraction trajectory in Figure 2.1 B. This configuration has been used for many applications for more than a decade. Figure 2.1 C shows the proposed quaternary semicontinuous system for a mixture of A, B, C, and D, ordered in decreasing relative volatilities. This configuration separates a quaternary mixture into nearly pure components by using a single distillation column and two highly integrated MVs. The two intermediate components, B and C, accumulate in their respective MV, as seen in Figure 2.1 D. The quaternary semicontinuous separation process is described in detail in section 2.2.2.

The lower capital cost of this system (compared to the three-column continuous alternative) is attractive to companies who desire rapid development and quick turnarounds, which is important when considering market uncertainty and investment risk, especially for smaller systems. This system is also flexible, which means that variations in feed mixture composition can be effectively handled.

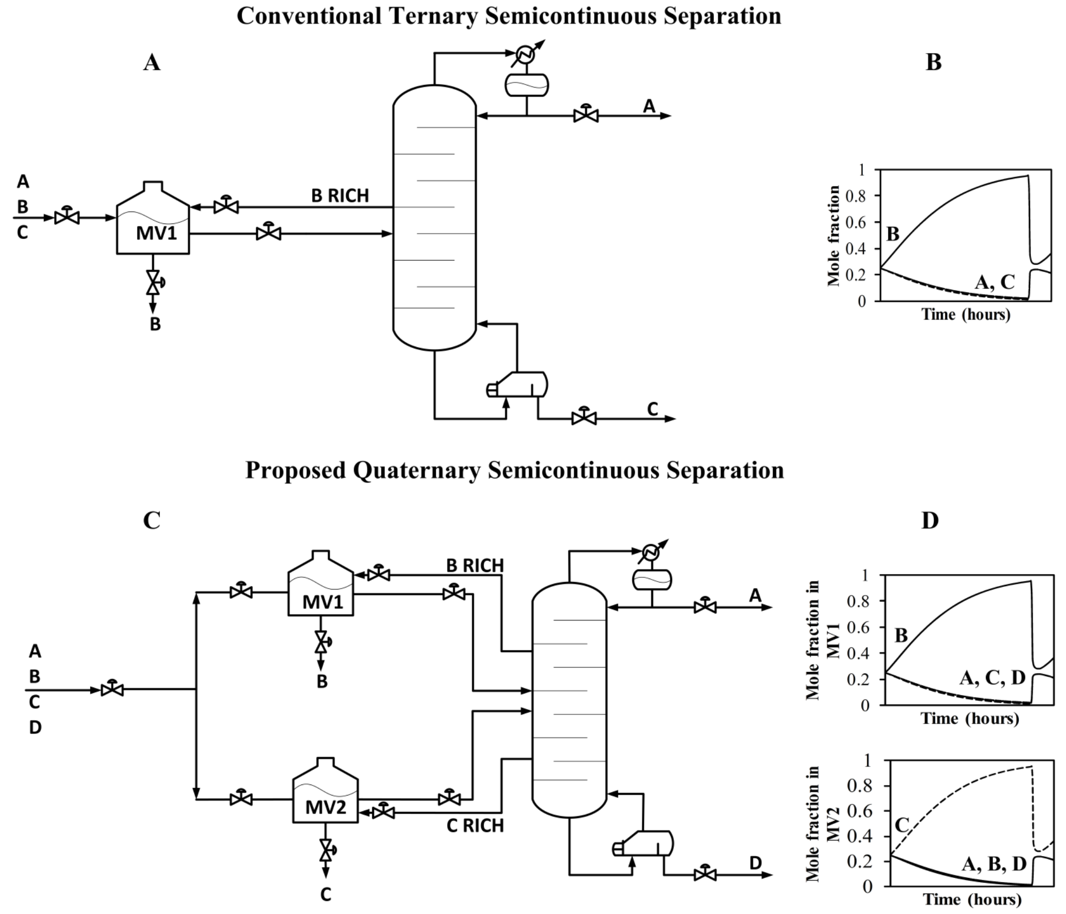

Figure 2.1. Schematic of ternary (A) and quaternary (C) semicontinuous separation processes, with middle vessel mole fraction trajectories (B) and (D).

The equimolar mixture of alkanes is used as a proof-of-concept because the relative volatilities and boiling point temperatures are in easily manageable ranges. A parametric analysis, a disturbance rejection analysis, and an economic comparison to a conventional continuous process are conducted on this alkane mixture. For all examples, the proposed system is simulated in Aspen Dynamics V8.0 with appropriate control configurations that have been studied in depth previously for ternary systems (Pascall & Adams, 2013).

2.2- Process Description

2.2.1 Conventional Continuous System

Traditionally, N-1 distillation columns are required to separate an N-component non-azeotropic mixture using continuous separation (Agrawal, 1996). The columns can be arranged in a variety of different configurations, known as distillation column sequences, and the number of possible configurations increases combinatorially as N increases (Agrawal, 1996; Shah & Agrawal, 2010). For example, a 4-component feed has 18 possible configurations, while a 7-component feed has 185,421 possible configurations (Shah & Agrawal, 2010). Figure 2.2 shows the continuous separation configuration chosen for this study where the two lightest components are separated in the second column and the heavier components are separated in the third column.

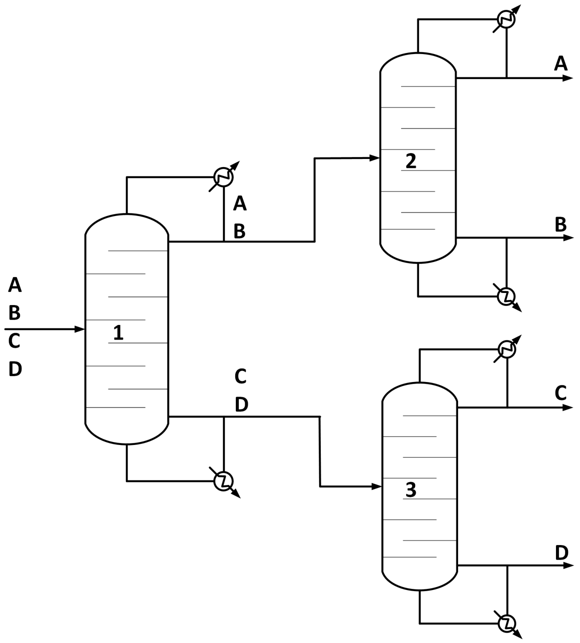

Figure 2.2. Conventional continuous separation process.

2.2.2 Semicontinuous System

The semicontinuous quaternary separation design, depicted in Figure 2.1 C, uses a single distillation column with two tightly integrated MVs. This separation system can be described by three operating modes that are used in a cyclic campaign:

i. Mode 1 - The mixture to be separated is charged to the MVs, divided evenly between them. During this mode, each MV both feeds to and receives a side draw from the distillation column which continues to operate. Distillate and bottoms are collected as well. However, mode 1 is relatively short, and the flow rates of the feeds, side draws, distillate, and bottoms are all rather small. Once the MV liquid levels have both reached their specified values, charging is complete and mode 2 begins.
ii. Mode 2 - The feed to the MVs is stopped, and the distillate (A) and bottoms (D) are removed in much larger but gradually diminishing flow rates, at the specified product purity. As the distillate and bottoms products are removed, the side stream components (rich in B, and C) are recycled back to the MVs. During this mode, the one MV begins to concentrate in B, and the other MV begins to concentrate in C. Once the MVs have reached the desired purity of either B or C, mode 3 begins.
iii. Mode 3 - During this brief mode, the MVs are emptied of their contents. The distillation column continues to function with feeds, side draw, distillate, and bottoms streams all still active, although at low flow rates.

The system cycles back to mode 1 once both MVs are nearly empty (a complete drain is avoided to ensure that the column feed is never interrupted). The process does not have start-up or shutdown phases between cycles, and it exhibits unsteady-state behaviour throughout each cycle. This semicontinuous quaternary separation is simulated according to the procedure described in Section 2.3.2.

2.3 – Process Simulation

2.3.1 Continuous Process

The continuous distillation process for case study 1 was modeled in Aspen Plus (V8.0 was used in this study) using the equilibrium-based RadFrac model. The vapour-liquid equilibrium (VLE) is modeled using the UNIQUAC activity coefficient model with the Redlich-Kwong equation of state for the vapour phase (UNIQUAC-RK). The default binary parameters contained in the Aspen databank were used. The first column was modeled with 35 stages, with the feed entering stage 15 at 100°C and 1.14 atm (1.16 bar). The second and third columns were modelled with 20 and 25 stages, respectively. A pressure drop of 0.0068 bar per tray and Murphree efficiency of 85% were used for all three columns.

2.3.2 Semicontinuous Process

Before simulating the dynamic semicontinuous system, a steady state simulation was modeled in Aspen Plus. The design spec/vary function within the RadFrac unit in Aspen Plus was used to achieve the desired distillate and bottoms purities, by varying the reflux and boilup ratios. The locations of the feed and side draws were manually adjusted to ensure that these constrained purities are met. In this simulation, the side draws from the column are not recycled back into the MVs in order to ensure convergence to a steady state solution. Although the semicontinuous process never reaches a steady state, the Aspen Plus steady state simulation provides a good approximation of the state of the column at the beginning of mode 2, which is used as a starting point for dynamic simulation. Once the simulation is exported to Aspen Dynamics as a pressure-driven simulation and initialized, then a control structure is added, the side streams are connected to the MVs, and dynamic simulation can begin.

In Aspen Dynamics, several cycles are executed, and the system reaches a stable limit cycle within one or two cycles. Those early cycles are merely a result of the strategy used to find a stable limit cycle and have little real-world meaning, so throughout this work, the trajectories shown define time zero as the beginning of mode 2 of the first stable limit cycle.

In case study 1, the distillation column is simulated using an equilibrium-based RadFrac model with 50 stages. The VLE is modeled using the UNIQUAC-RK property method, and the feed enters the column at 100°C and 1.14 atm (1.16 bar). For each case, the physical property methods were chosen because they were shown to match experimental phase equilibrium data very well when used with the default parameters found in the Aspen Properties database (Lee, Chen, Ko, Lee, & Chang, 2009). It is assumed that the columns have a constant Murphree efficiency of 85% for all trays, and use atmospheric pressure as the set point in the reflux drum. The MVs are sized to each hold roughly 25 kmol of fresh feed (this is varied later as a parameter, see section 2.4.2.2) and a pressure set point large enough to meet the column pressure after accounting for losses. Design heuristics, as defined by Luyben, are used to size the reflux drum and sump to allow for 10 minutes of liquid holdup (Luyben, 2006). These values are reasonable choices for this case study as they have been used in similar systems (Pascall & Adams, 2013; Meidanshahi & Adams, 2014; Pascall & Adams, 2014).

Since getting a suitable initial state in Aspen Plus is not trivial, it is useful to note that the columns in Aspen Plus were set to have a pressure drop of 0.0068 bar per tray for case study 1.

2.3.3 Control

The forced cyclic design of this model means that the control schemes, which drive process dynamics, are paramount to the success of the process. This process has seven degrees of freedom (DOF): the condenser heat duty; the reboiler heat duty; feed to the column; distillate rate; bottoms rate; and side draws. The corresponding manipulated variables are: condenser pressure; reflux and sump levels; distillate and bottoms compositions; and side draw flow rates. Based on previously developed heuristics that have been repeatedly shown to be quite successful in ternary semicontinuous systems at obtaining stable dynamic performance, the distillate and bottoms (‘DB’) dual composition control structure is chosen for this simulation (Pascall & Adams, 2013; Meidanshahi &

Adams, 2014; Pascall & Adams, 2014; Phimister & Seider, 2000a). 'DB' control has been shown to provide good dynamic performance for semicontinuous systems because of the lack of mass balance constraints between the distillate and bottoms flow rates (Phimister & Seider, 2000a).

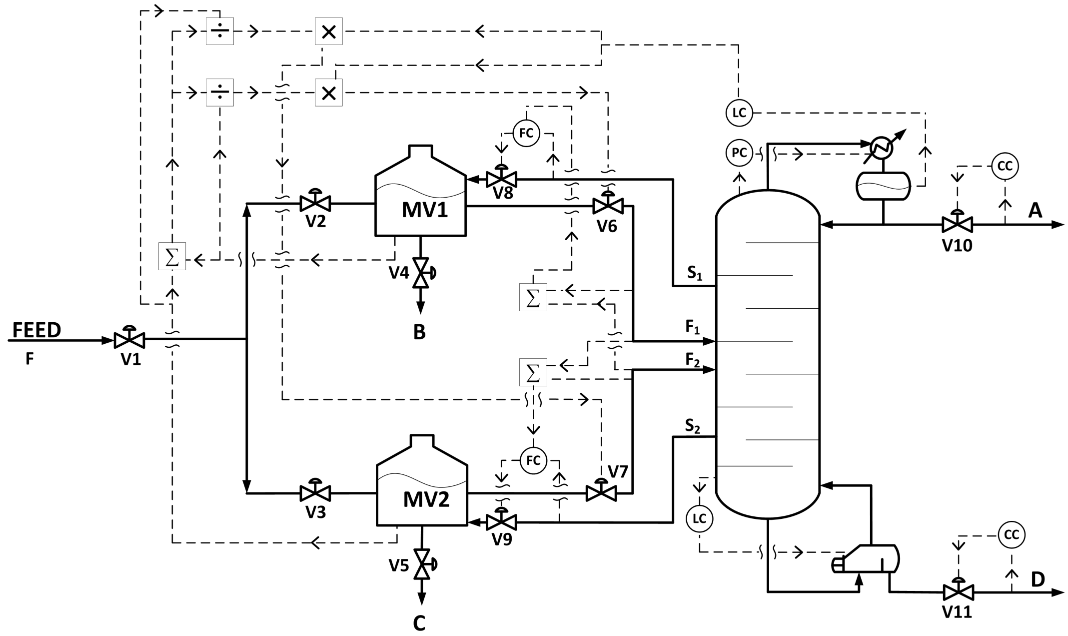

Figure 2.3. Dynamic quaternary semicontinuous separation system

Figure 2.3 depicts the control strategy used for the quaternary semicontinuous process. The condenser pressure is controlled by manipulating the condenser heat duty, and the sump level is controlled by manipulating the reboiler heat duty. In this case, the distillate and bottoms molar flow rates are used to control the distillate and bottoms compositions, respectively. These composition controllers are modeled with a dead time of 3 minutes, which is based on previously used heuristics (a composition controller with a higher dead time of 10 minutes was also tested, and the resulting system was found to have essentially the same performance as one with a 3 minute dead time) (Pascall & Adams, 2013; Meidanshahi & Adams, 2014; Pascall & Adams, 2014; Luyben, 2006). It should be noted that it has previously been shown that that temperature-inferential could be used instead of composition control with a 3 minute dead time with approximately the same performance (Pascall & Adams, 2013).

The flow rate of the side draw is controlled using the ideal side-draw recovery strategy to reduce loss of intermediate species and ensure high purity side streams. In ternary semicontinuous systems, this side stream flow rate is controlled by (Adams & Seider, 2008; Pascall & Adams, 2013):

$$S(t) = F(t)x_{f,Species}(t) \tag{2.1}$$

where $S(t)$ is the molar flow rate of the side draw, $F(t)$ is the molar flow rate of the feed stream from the MV to the column, and $x_{f,Species}(t)$ is the mole fraction of the intermediate species in the feed stream to the column. In the case of quaternary semicontinuous separation, equation (2.1) has to be extended to deal with two intermediate species. In this case, the side stream flow rates are controlled by:

$$S_1(t) = F_1(t)x_{f,Light,1}(t) + F_2(t)x_{f,Light,2}(t) \tag{2.2}$$

$$S_2(t) = F_1(t)x_{f,Heavy,1}(t) + F_2(t)x_{f,Heavy,2}(t) \tag{2.3}$$

where $S_1(t)$ and $S_2(t)$ are the molar flow rates of each side draw, $F_1(t)$ and $F_2(t)$ are the molar flow rates of the feeds to the column, $x_{f,Light,1}(t)$ and $x_{f,Light,2}(t)$ are the mole fractions of the lighter intermediate species (i.e. *n*-heptane in case study 1) in feed streams 1 and 2 to the column, and $x_{f,Heavy,1}(t)$ and $x_{f,Heavy,2}(t)$ are the mole fractions of the heavier intermediate species (i.e. *n*-octane in case study 1) in feed streams 1 and 2 to the column.

In most control structures used in ternary semicontinuous systems, the reflux drum level is controlled by manipulating the feed flow rate to the column. However, because the quaternary semicontinuous systems use two feed flows to the column, the drum level is controlled by manipulating the sum of F_1 and F_2. F_1 and F_2 are individually manipulated by adjusting valves V6 and V7 to ensure that the desired sum was obtained while keeping the ratio of the valve openings of V6 and V7 to be the same as the ratio of the molar holdup of each MV to the average holdup of both MVs:

$$V6_{\%\,opening}\,(t) = \left[2\left(\frac{MV_{1,level}(t)}{MV_{1,Level}(t)+MV_{2,Level}(t)}\right)\times LC_{output}(t)\right] \tag{2.4}$$

$$V7_{\%\,opening}(t) = \left[2\left(\frac{MV_{2,level}(t)}{MV_{1,Level}(t)+MV_{2,Level}(t)}\right)\times LC_{output}(t)\right] \tag{2.5}$$

where $V6_{\%\,opening}\,(t)$ and $V7_{\%\,opening}\,(t)$ are the valves manipulating F_1 and F_2, $MV_{1,Level}(t)$ and $MV_{2,level}(t)$ are the middle vessel liquid levels, and $LC_{output}(t)$ is the reflux drum controller output. In all three cases, this strategy was shown to be successful at maintaining appropriate reflux drum levels while ensuring that both MVs reach their purity goals at approximately the same time each cycle.

Composition and pressure loops use proportional-integral (PI) control while level and side draw controllers use proportional-only (P) control because they do not require stringent control. The controllers are manually tuned to attempt to minimize the integral squared error (ISE) of the distillate and bottoms compositions. Changes between operational modes are handled using the event-driven task feature in Aspen Dynamics, which controls the opening and closing of valves as appropriate. In mode 1, valves V2 and V3 are fully opened until the specified MV liquid level is reached. Valves V4 and V5 are closed during this time to prevent intermediate product leakage. Mode 2 begins when both MVs have completed charging. In this mode, valves V2 and V3 are closed to allow the concentration of the side draw products. After the desired product purities in both MVs are attained, mode 3 begins with the opening of valves V4 and V5, enabling the discharge of the intermediate products. This continues until a specified liquid level is reached. Once both MVs have been almost completely drained (a small amount of liquid is left in the MV to ensure that the column feed is never interrupted), the cycle repeats and goes back to mode 1. It should be noted here that the MVs do not have any pressure controllers as the model used in the simulation only considers the liquid phase at a fixed pressure.

2.4 - Results and Discussion

2.4.1 Case Study 1

The performance of the quaternary semicontinuous distillation system is illustrated using an equimolar feed of alkanes (25 mol% each of *n*-hexane, *n*-heptane, *n*-octane, and *n*-nonane). The column diameter chosen for this example is 7 feet. Figure 2.4 A depicts the MV liquid levels during the cyclic campaign, while Figures 2.4 B and C show the MV mole fraction trajectories. Note that time zero begins at mode 2 (with full MVs).

For case study 1, 95 mol% purity was desired for all four components. As the distillate (*n*-hexane) and bottoms (*n*-nonane) streams are continuously removed in mode 2, the liquid level in each MV drops over time. After 4 hours, the desired purity in each MV (*n*-heptane, *n*-octane) has been reached, and mode 3 begins. This is visible as the sharp drop in liquid level. Mode 1 is visible as the recharging of the liquid level, which continues until the specified liquid level in each MV has been reached. Figures 2.4 B and 2.4 C depict how the mole fractions in the MVs change over several cycles. During mode 2, the composition of the undesired species in each MV decreases steadily over time. As each intermediate component concentrates in its corresponding MV, the composition of each increases steadily over time. As expected, the system reaches a stable cycle throughout its campaign.

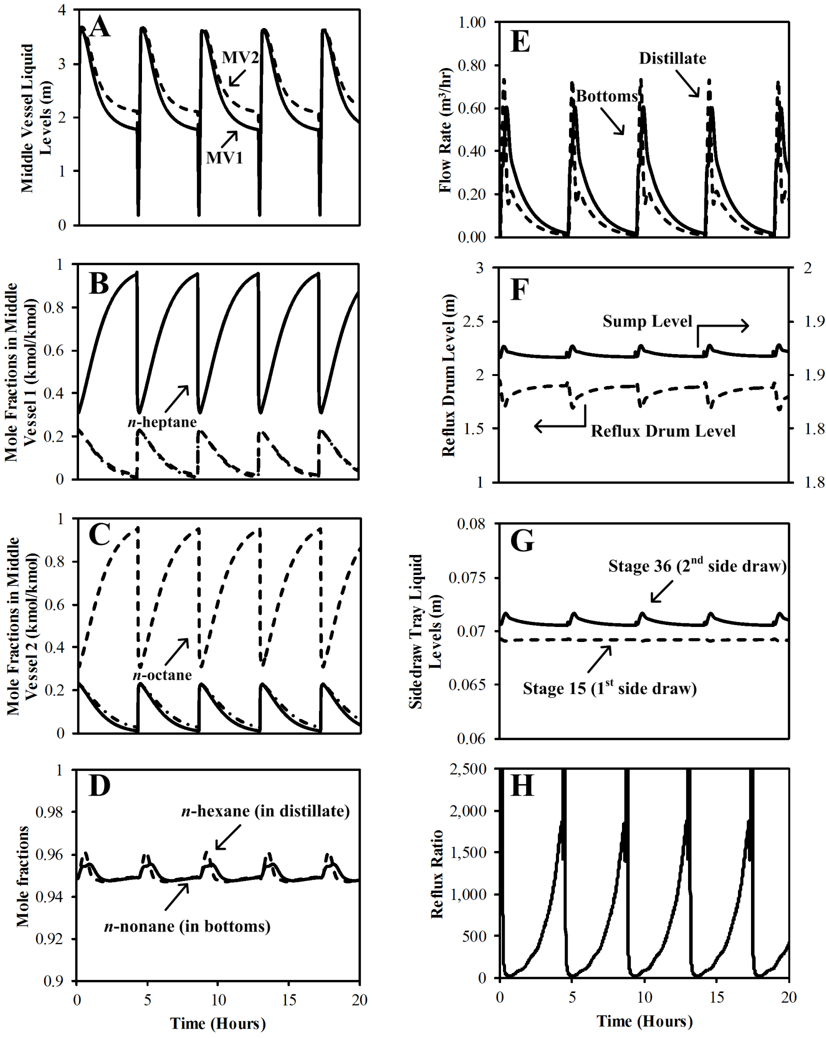

Figure 2.4. Middle vessel liquid levels (A), mole fraction trajectories in middle vessel 1 (B) and 2 (C), distillate and bottoms compositions (D) and flows (E), reflux and sump levels (F), side draw tray liquid levels (G), and reflux ratio (H).

Although not shown in the figures, simulations were run to 10 cycles or more to ensure that, indeed, the limit cycle was stable. Table 2.1 summarizes the tuning parameters and the feed and side draw locations for case study 1.

Table 2.1. Tuning parameters for case study 1.

Controller	Proportional Gain, K_c (%/%)	Integral Time, τ_i (min)
Condenser pressure	20	12
Reflux drum level	10	-
Sump level	10	-
Distillate composition	50	75
Bottoms composition	75	75
1st Side draw flow	1	-
2nd Side draw flow	1	-
1st Feed stage	20	
2nd Feed stage	25	
1st Side draw stage	15	
2nd Side draw stage	36	

Figure 2.4 D shows the effectiveness of the composition controllers in maintaining a 95 mol% purity of the distillate and bottoms streams. Despite the significantly changing flow rates during each mode (shown in Figure 2.4 E) and the transitions between cycles, the composition controllers are able to provide a fairly stable control. Similarly, the sump and reflux drum holdups are maintained to satisfaction as shown in Figure 2.4 F. Also, Figure 2.4 G shows how the liquid levels on the side draw trays are maintained throughout the cyclic campaign, and Figure 2.4 H depicts how the reflux ratio varies through mode 2. Note the reflux ratio reaches infinity as the modes transition and the valve closes.

One of the indirect benefits to this particular control configuration is that the liquid and vapour flow rates inside the column remain sufficiently balanced throughout the cycle such that flooding and weeping do not occur. Flooding and weeping calculations are computed throughout the cycle to ensure that these situations are avoided. The flooding approach is calculated using the Fair correlation (Fair, Steinmeyer, Penney, & Crocker, 1997). Flooding occurs due to excessive vapour flow, which causes entrainment of liquid leaving the downcomers. This phenomenon is considered to be an upper limit of tray operation (Perry & Green, 1997). Figure 2.5 shows the flooding profile for each stage over four cycles. The flooding approach limit (80%) is never exceeded ensuring the column operates within safe operating limits.

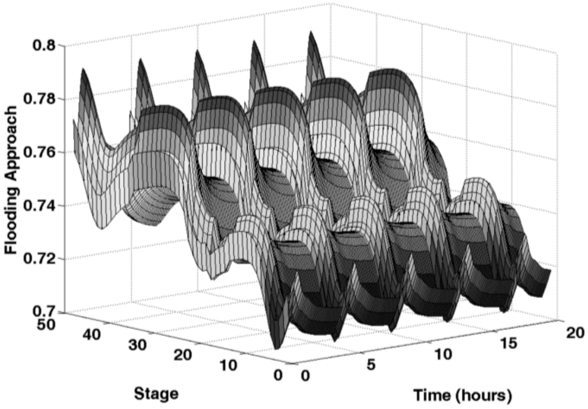

Figure 2.5. Flooding approach profile for case study 1.

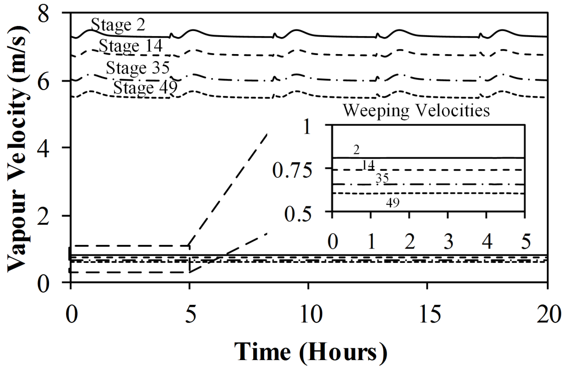

Figure 2.6. Vapour and weeping velocities for case study 1.

Weeping is a result of excessive flow of liquid through sieve tray perforations and is considered to be the lower limit of tray operation (Perry & Green, 1997). During weeping, the vapour flow is insufficient to hold up the liquid on the trays and liquid leaks through the perforations. Weeping velocities in the top, bottom and middle sections are calculated using the equations shown by Mersmann, Kind, & Stichlmair (2011) (equations 2.6, 2.7).

$$\mathrm{F_{min}} = \varphi\sqrt{0.37 d_H g \frac{(\rho_L-\rho_V)^{1.25}}{\rho_V^{0.25}}} \tag{2.6}$$

$$\mathrm{u_{min}} = \frac{F_{\min}}{\sqrt{\rho_V}} \tag{2.7}$$

where $\mathrm{F_{min}}$ is the minimum gas load, φ is the relative free area, d_H is the tray hole diameter, g is the acceleration due to gravity, ρ_L and ρ_V are the liquid and vapour densities, and $\mathrm{u_{min}}$ is the minimum vapour velocity. Weeping profiles for this system over four cycles is shown in Figure 2.6. The actual vapour velocities were calculated in Aspen Dynamics at each time step, and it is clear that the vapour velocities are always above the weeping velocity, thereby avoiding weeping.

2.4.2 Sensitivity Analysis

Systems with different column diameters or batch charges tend to operate similarly to each other as long as they use the same tuning parameters for the control system. For example, for the same control system tuning, systems with larger column diameters have larger product flow rates, larger side draw rates, and larger column feed flow rates in approximately the same proportion, and the shapes of the trajectories will be similar.

These larger flow rates in turn lead to shorter cycle times. Conversely, systems with larger MVs (i.e. larger batch charges), have longer cycle times, although more will be processed per cycle. However, in both cases, there are trade-offs in terms of the total annualized costs (TAC), and so the effect of changes in these parameters is explored in this section. The TAC is calculated using equations (2.8-3.0), assuming a 3-year plant lifetime (payback period) and 8400 hours per year of operation, which is based on values used in similar studies (Pascall & Adams, 2013; Meidanshahi & Adams, 2014; Pascall & Adams, 2014).

$$TAC\ \left(\frac{\$}{yr}\right) = \frac{Total\ Direct\ Cost\ (\$)}{Payback\ Period\ (yr)} + Annual\ Operating\ Cost \left(\frac{\$}{yr}\right) \tag{2.8}$$

$$Total\ Direct\ Costs\ (\$) = \textstyle\sum_i Equipment\ Cost + \sum_i Installation\ Cost \tag{2.9}$$

where i represents the column tower, reboiler, reflux drums, condensers, pumps, and MVs.

$$Total\ Operating\ Costs\ \left(\frac{\$}{yr}\right) = \frac{Utility\ Cost\ (\$)}{\#\ cycles \times total\ cycle\ time\ (hr)} \times 8400\ \left(\frac{hr}{yr}\right) \tag{3.0}$$

The total direct costs were computed using equation (2.9) and values obtained from Aspen Process Economic Analyzer V8.0. The direct cost includes equipment, electrical, piping, instrumentation, civil, paint, and insulation. The operating costs were calculated using equation (3.0) by considering only the utility costs of steam and cooling water. The cost of steam was estimated using the price of natural gas, \$2.51/MMBtu (U.S Energy Information Administration (EIA – Official Energy Statistics from the US Government), 2012) and electricity, \$0.0491/kWh (Independent Electricity System Operator (IESO), 2012), as outlined in the method of Towler and Sinnot (2012). Similarly, the cost of cooling water was estimated using the same price of electricity, and the price of water make-up and chemical treatment, ($0.02/1000 US gal (Towler & Sinnot, 2012)). From this, the cost of steam at 160°C was estimated as $8.49 per GJ of heating load, and the cost of cooling water at 24°C was estimated as $0.69 per GJ of cooling load. Using the total direct and operating costs, the TAC was calculated for the following scenarios. The TAC used for the following scenarios are based on per volume of mixture separated, and is therefore shown in units of ($/m^3). These TAC values provide a good metric for the economies of scale of this proposed quaternary semicontinuous system.

2.4.2.1 Effect of column diameter

To determine the effect of column diameter, the column diameter was changed in six-inch increments (in keeping with standard sizes) while keeping the MV size constant. The control structure automatically modifies the flow rates of all product and feed streams from or to the column. The flow rates of the feed to the MV in mode 1 are increased or decreased proportionally, such that the mode is faster or slower with the same relative proportions between the internal flows. Figure 2.7 depicts the direct (A), operating (B), TAC per volume of mixture separated (C), and total mixture separated per year (D), for this case. All operating costs were computed using the average of at least 5 limit cycles (since there were minor variations between each cycle).

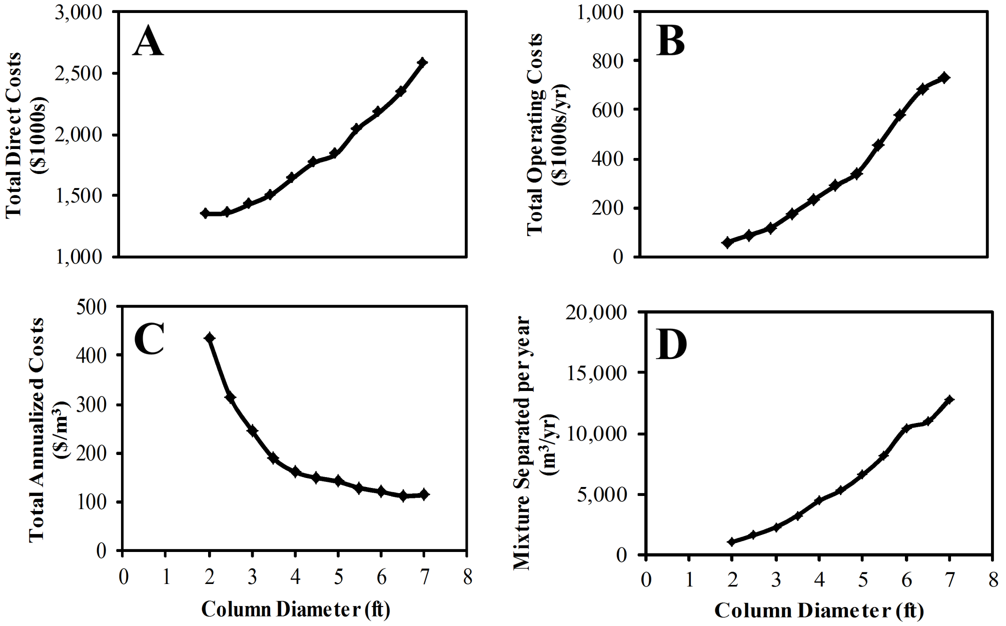

Figure 2.7. Effect of changing column diameter on direct costs (A), operating costs (B), TAC (C), and total mixture separated per year (D).

As expected, the direct costs, operating costs, and production rate all increase with increasing column diameter. Operating costs and the production rate both grow at approximately the same rate as column diameter increases, but the direct costs grow much more slowly due to economies of scale. As a result, as shown in Figure 2.7 C, the TAC *per volume of mixture separated* decreases. This is expected and is a normal result of economies of scale. The net effect is that systems with low throughputs (those separating about 1,000 m^3/year using a column 2.0 ft. in diameter) cost about four times as much as those with large throughputs (separating 13,000 m^3/year with a column 7 ft. in diameter), and the benefits from economies of scale become insignificant for systems with columns larger than 7 ft.

2.4.2.2 Effect of middle vessel size

To determine the effect of MV size, the sizes of both MVs were changed while keeping the length to diameter (L/D) ratio and the column diameter fixed. Two column diameters at 4 ft. and 7ft. were used for the analysis. Figure 2.8 shows the direct costs (A), operating costs (B), TAC per volume of feed separated (C), and the total mixture separated per year (D).

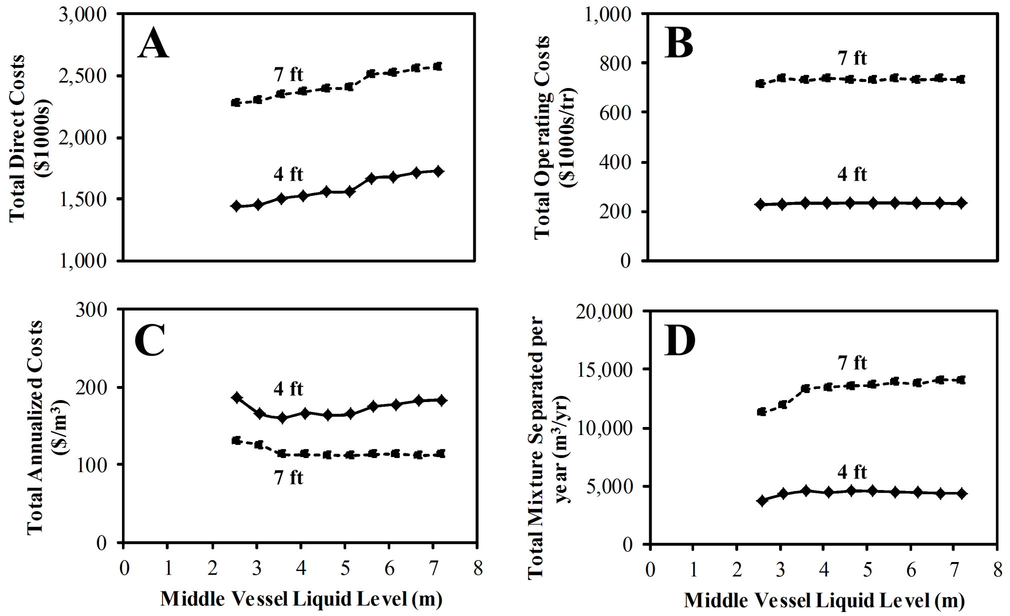

Figure 2.8. Effect of changing the middle vessel size on direct costs (A), operating costs (B), TAC (C), and total mixture separated per year (D).

Though different in absolute amounts, the trends for the two column diameters are similar, indicating that column diameter does not impact the general trends. The staircase-like shape of the direct cost curves corresponds to the discrete way the MVs are actually purchased. This shape also directly impacts the TAC contributing to the non-smooth curve in Figure 2.8 C. The key result is that smaller MVs are more economical up to a certain point, at which the molar holdups in the MVs become insufficient to drive mode 2 to completion and the cost of separation actually increases slightly. The idea is that smaller MVs result in less mixture separated per cycle, but more cycles can be completed in a given time, and in this case, the total production rate per year was a little bit higher for larger MVs. This is a similar result to prior work for ternary semicontinuous systems and so it makes sense to use smaller vessels (Adams & Seider, 2008, 2009). In fact, for ternary semicontinuous systems, it has been shown that an alternative configuration with no MV at all can have an even lower TAC than traditional semicontinuous configurations with a MV (Meidanshahi & Adams, 2015). However, it is not immediately obvious if that MV-free configuration is feasible or desirable for quaternary separations, and is an area of future research.

2.4.3 Disturbance Rejection

In practice, disturbances can enter the system and disrupt the operation of the process. In order to determine whether the proposed system can maintain normal operation under disturbances, a batch-to-batch disturbance was chosen as an illustrative example. A step change in fresh feed composition was introduced during the charging mode (mode 1) of the first stable limit cycle. Figures 2.9 and 2.10 show the response of the MV mole fractions and the distillate and bottoms compositions to a ±40% change in *n*-heptane in the fresh feed. The other components were varied proportionally to give a fresh feed composition of 20% *n*-hexane, 35% *n*-heptane, 25% *n*-octane, and 20% *n*-nonane for a +40% change.

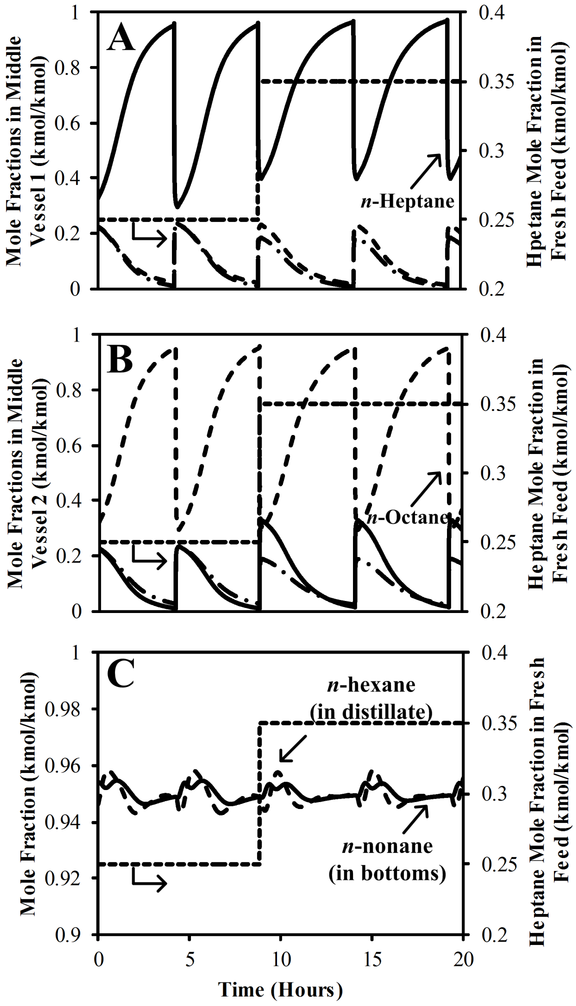

Figure 2.9. Mole fraction trajectories (A) and (B), and distillate and bottoms compositions (C) for a +40% step change in *n*-heptane in the fresh feed.

For a -40% change, a composition of 30% *n*-hexane, 15% *n*-heptane, 25% *n*-octane, and 30% *n*-nonane was used. As seen in Figures 2.9 and 2.10, the control system can effectively reject the disturbance with minimal to no change in the shape of the trajectories.

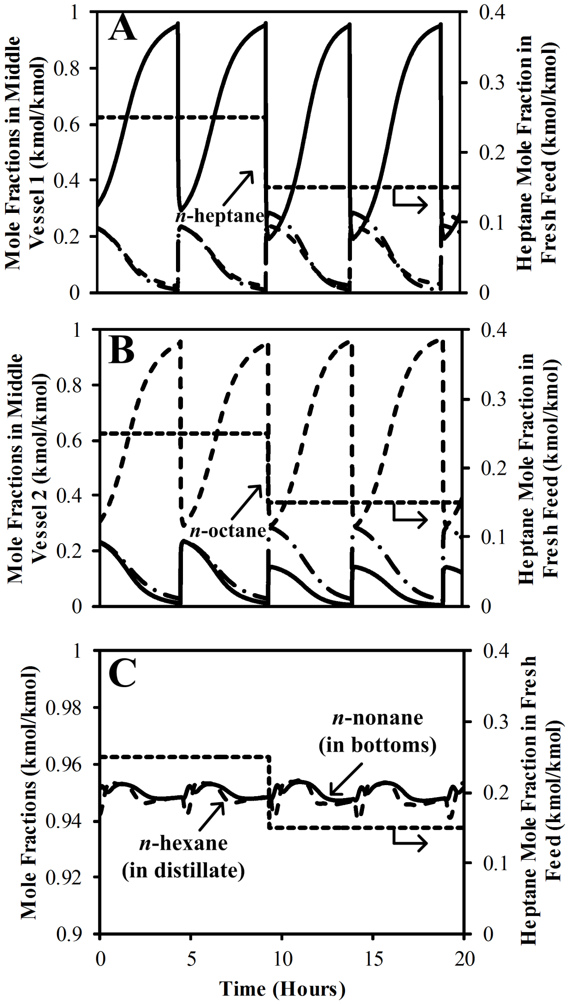

Figure 2.10. Mole fraction trajectories (A) and (B), and distillate and bottoms compositions (C) for a –40% step change in *n*-heptane in the fresh feed.

Although there are many kinds of disturbances that the system could potentially experience, a robust study of possible disturbances is outside the scope of this study and is a subject for future work. These include other kinds of disturbances such as changes in flows and temperatures of the feed and utilities, or equipment fault-related disturbances such as valve stiction or sensor failure.

2.4.4 Comparison between Continuous and Semicontinuous Processes

The economics of a conventional continuous process was compared to that of the proposed quaternary semicontinuous design over a range of production rates. The continuous distillation columns were first optimized using the NQ curves tool in Aspen Plus. The optimization tool systematically varies the feed stage location and the number of stages, and determines the optimal number of stages, feed tray location, reflux and boilup ratios that minimizes the objective function (total heat duty as a function of the number of stages), while meeting the product specifications. The three continuous columns are constrained by the design spec/vary function in order to obtain the desired 95 mol% product purities for all four components. The resulting column diameters that is necessary to prevent flooding (and are at least at a minimum standard diameter of 1.5 ft.) (Aspen Technology Inc, 2011) are used in the direct cost estimation via Aspen Process Economic Analyzer V8.0. The operating costs are calculated using the utility costs of steam and cooling water, as mentioned previously in section 2.4.2.

Figure 2.11[1] A and B shows the direct and operating costs for the continuous and semicontinuous systems. The total direct cost for the semicontinuous system is considerably cheaper than the continuous system below a production rate of 8,300 m^3/yr. At higher production rates, a larger column diameter is required to achieve the desired separation, and this significantly increases capital cost. At smaller production rates, the semicontinuous system is more profitable as the process only requires one column. The

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[1] Figure 2.11 is different from the figure that was submitted in the manuscript because a more optimal continuous separation case was found.

total operating cost for the semicontinuous process increases rapidly as the production rate increases because of the high reflux and boilup ratios necessary to maintain product purities. Figure 2.11 C shows the TAC ($/yr) for the two systems and it is seen that the semicontinuous system has a lower TAC then the continuous system for production rates below 3,400 m^3/yr. These results are promising, as the continuous design has been optimized, while the semicontinuous system is sub-optimal with room for improvement. These results are expected as previous studies have shown that semicontinuous systems are more profitable compared to continuous systems at low to intermediate capacities. A formal global optimization strategy is in development and will be used to determine the optimal quaternary semicontinuous system in a future work.

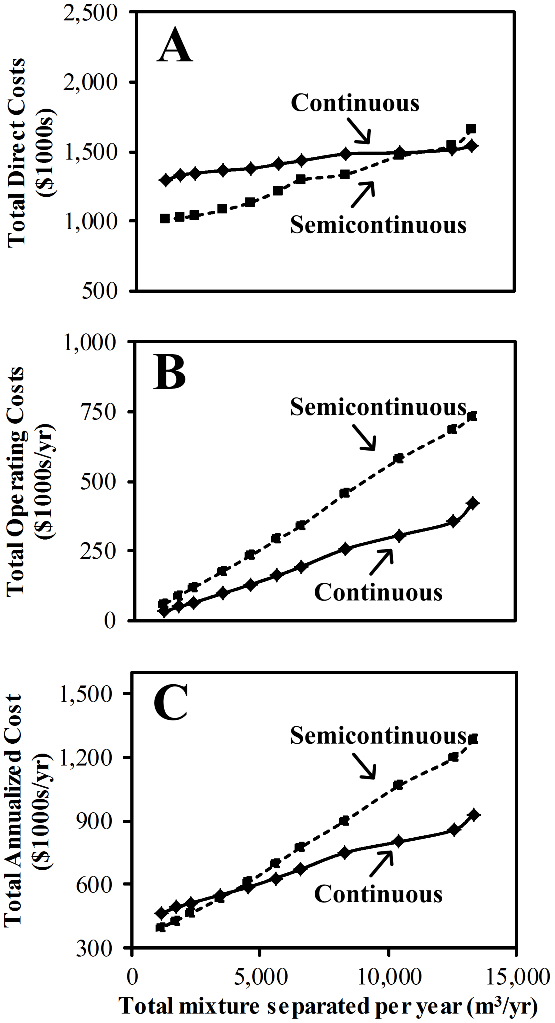

Figure 2.11. Total direct costs (A), operating costs (B) and total annualized costs (C) for continuous and semicontinuous systems for various production rates.

2.5 Conclusion

A quaternary semicontinuous separation process has been developed and analyzed via rigorous dynamic simulation for the first time for a four-component separation using just one distillation column. This separation method is based on a cyclic design in which the distillate and bottoms products are continuously removed in a distillation column, while the intermediate products are concentrated in two MVs. The use of the MVs eliminates the need for additional columns, thereby greatly reducing both the capital cost and the complexity of the system.

Using an ideal alkane mixture, our analysis showed that the proposed system was effective at reaching MV purity objectives while meeting distillate and bottoms purity objectives. Despite the changing flow rates experienced from cycle to cycle, the control structure is able to prevent flooding and weeping in the column. A stable limit cycle was attained indicating the efficiency of the control structure. The results from the parametric analysis indicates that smaller MVs are more optimal up to a certain point, at which point smaller molar holdups become insufficient to drive mode 2. The throughput is determined by varying the column diameter. Large column diameters have a higher throughput and were shown to have a lower TAC per volume of mixture separated due to the benefits of economies of scale. Previous work has shown that ternary semicontinuous is cheaper than continuous for low to intermediate capacities, and this has been confirmed for quaternary semicontinuous processes. Results show that the sub-optimal quaternary semicontinuous process has a lower TAC at production rates of 3,400 m^3/yr and lower, when compared to an optimal continuous process. Also, the proposed control structure can effectively reject disturbances of ±40% of n-heptane in the fresh feed.

Chapter 3

APPLICABILITY OF QUATERNARY SEMICONTINUOUS DISTILLATION TO TWO INDUSTRIALLY RELEVANT EXAMPLES

The results in this chapter have been accepted for publication in the following journal:

Wijesekera, K. N., and Adams, T. A. (2015). Semicontinuous distillation of quaternary mixtures using one distillation column and two integrated middle vessels. *Industrial & Engineering Chemistry Research*. doi: 10.1021/ie504584y

3.1 Introduction

The previous chapter examined the feasibility and operability of a quaternary semicontinuous separation process to an ideal mixture of alkanes. This chapter extends the proposed system to two industrially relevant examples:

1. Separation of an equimolar mixture of petrochemical derivatives.
2. Separation of a non-ideal mixture of mixed-alcohols to obtain fuel-grade quality biofuels.

The first example examines the separation of benzene, toluene, ethyl benzene and *o*-xylene (BTEX). Removing BTEX compounds from industrial waste is important as they are volatile organic compounds (VOCs) that can be harmful to the environment. The BTEX compounds are commonly formed during petroleum refining processes and if not eliminated properly, these contaminated waste streams can impact ozone formation and enhance the green house effect (Rahul & Balomajumder, 2013). These compounds have also been shown to have carcinogenic properties, impacting human health (Rahul & Balomajumder, 2013). Remediation of BTEX from waste streams is generally achieved through physical or biological treatment where adsorption or biodegradations are the key removal methods. Some physical methods, such as adsorption onto activated carbon granules, have been shown to be effective; however the subsequent elimination of the contaminated granules may cause environmental damage because of the buildup of toxic residues (Mazzeo, Levy, de Angelis, & Marin-Morales, 2010). Some biological methods show uncertainty in the removal of BTEX due to dependence on microbial distribution and growth conditions, and may take a long time to degrade (Lin, Chen, & Lai, 2010). As BTEX compounds are used in several manufacturing industries such as paint chemicals, and printing and laminating (Lin et.al, 2010), semicontinuous separation of BTEX may be a cost-effective process of producing high purity BTEX compounds without eliminating them completely.

The second example examines the separation of a reaction mixture produced by a mixed alcohol synthesis (MAS) catalyst to obtain a fuel grade quality isobutanol stream.

Considerable interest in this biofuel has been driven by the need for sustainable and renewable fuels. Biomass-derived isobutanol (an isomer of butanol) has a high-energy content, low affinity to water and higher compatibility with existing internal combustion engines (Kumar & Gayen, 2011; Okoli and Adams, 2014). This makes it an attractive candidate as a biofuel. Typically, biochemical and thermochemical methods are used for butanol production. The most common biochemical route is acetone-butanol-ethanol (ABE) fermentation (Ranjan & Moholkar, 2012). However low yields and toxicity to participating microorganisms are challenges that have to be overcome using this method (Abdehagh, Tezel, & Thibault, 2014). Thermochemical routes involve the gasification of biomass and the subsequent conversion of syngas over a MAS catalyst. Okoli and Adams (2014) developed a thermochemical process of producing butanol using a MAS catalyst and they determined that their design was economically competitive with traditional biochemical routes. From their design, three distillation columns are used in series to obtain their desired butanol specification. These columns may be able to benefit from the proposed quaternary semicontinuous process intensification technique, and therefore the second example in this chapter examines the intensification of the second and third columns by using one column and two MVs.

3.2 Process Simulation

The two examples are designed and controlled in a similar method to that described in Chapter 2 sections 2.3.2 and 2.3.3. In case study 1, the column is simulated with 100 stages and the feed enters the column at 85°C and 1.14 atm. Phase equilibria are modeled using the Non-Random-Two-Liquid activity coefficient model (NRTL) and ideal gas in the vapour phase. In case study 2, the column is simulated with 60 stages, the feed enters the process at 94°C and 1.32 atm (1.34 bar), and the VLE is modeled using the Non-Random-Two-Liquid activity coefficient model with the Redlich-Kwong equation of state (NRTL-RK). The physical property methods were chosen because they were shown to match experimental phase equilibrium data very well when used with the default parameters found in the Aspen Properties database (Kiss & Rewagad, 2011; Okoli & Adams, 2014). Both examples were modeled with 85% Murphree efficiency constant for all trays and a flooding factor of 80%. A pressure drop of 0.0141 bar was used for case study 1 and a pressure drop of 0.0172 bar was used for case study 2.

3.3 Results and Discussion

3.3.1 Case Study 1 (Separation of BTEX)

The feasibility of the proposed quaternary semicontinuous separation system was examined by separating an equimolar mixture (25 mol % each) of benzene, toluene, ethyl benzene, and *o*-xylene. Figure 3.1 depicts the MV liquid levels (A) and the MV mole fraction trajectories (C, D), for a simulation using a column diameter of 7.5 feet and a MV charge size of 32 kmol each. Other configurations were simulated successfully with similar results.

For the purposes of this case study, it was required to obtain 95 mol% product purities for all four components. As expected, the MV liquid level decreases during mode 2, sharply drops during mode 3, and then sharply increases during the re-charge phase of mode 1. Figures 3.1 C and D clearly shows the intermediate components (toluene and ethyl benzene) concentrating in the MVs and then being discharged once the desired purities (95 mol%) have been attained. As shown in Figure 3.1 B, the distillate and bottoms purities were satisfactorily close to 95% purity throughout each cycle, and Figures 3.2 and 3.3 confirm that flooding and weeping constraints were never violated. Table 3.1 shows the tuning parameters and the feed and side draw locations used for this case study.

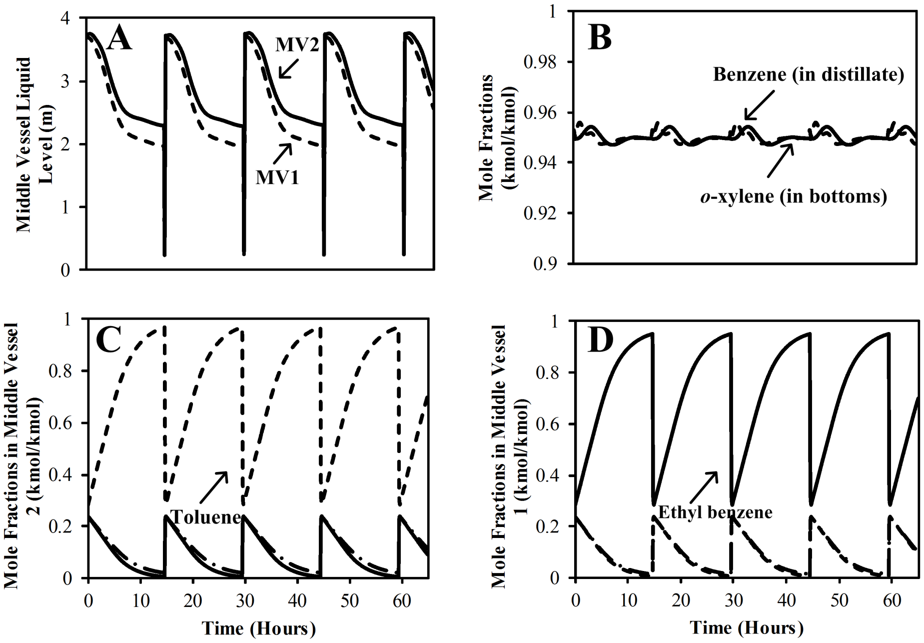

Figure 3.1. Middle vessel liquid levels (A), distillate and bottoms compositions (B), and mole fraction trajectories in middle vessels 1 (C) and 2 (D), for case study 1.

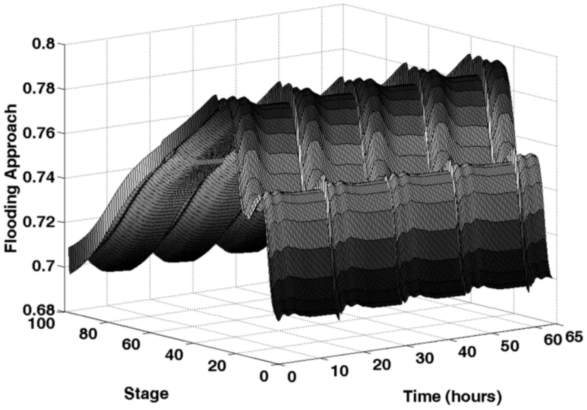

Figure 3.2. Flooding approach profile for case study 1.

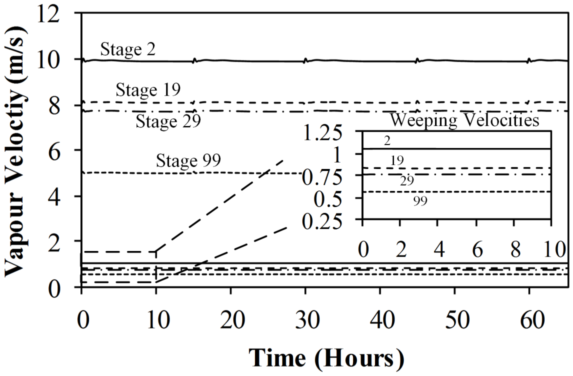

Figure 3.3. Vapour and weeping velocities for case study 1.

In this example, the number of stages is too high to likely be attractive in practice. The number of stages can potentially be reduced through different designs found through formal optimization techniques, which is an area of future research. If it cannot be reduced, it may be simply that the semicontinuous approach is not suitable for this particular system of chemicals, and that a traditional method is favourable.

Table 3.1. Tuning parameters for case study 1.

<table>
<tr><th>Controller</th><th>Proportional Gain, Kc (%/%)</th><th>Integral Time, τi (min)</th></tr>
<tr><td>Condenser pressure</td><td>20</td><td>12</td></tr>
<tr><td>Reflux drum level</td><td>5</td><td>-</td></tr>
<tr><td>Sump level</td><td>20</td><td>-</td></tr>
<tr><td>Distillate composition</td><td>50</td><td>70</td></tr>
<tr><td>Bottoms composition</td><td>50</td><td>50</td></tr>
<tr><td>1st Side stream flow</td><td>5</td><td>-</td></tr>
<tr><td>2nd Side stream flow</td><td>5</td><td>-</td></tr>
<tr><td>1st Feed stage</td><td colspan="2">20</td></tr>
<tr><td>2nd Feed stage</td><td colspan="2">30</td></tr>
<tr><td>1st Side draw stage</td><td colspan="2">10</td></tr>
<tr><td>2nd Side draw stage</td><td colspan="2">55</td></tr>
</table>

3.3.2 Case Study 2 (Separation of mixed alcohols)

The mixture to be separated consists of methanol (2.1 mol%), ethanol (5.6 mol%), water (5.5%), propanol (27.6%), isobutanol (52.7 mol%), pentanol (3.6 mol%), and hexanol (2.9 mol%), which is the product of that thermochemical biomass-to-butanol process after the first column in the alcohol separation step. Although water can form a heterogeneous azeotrope with the higher alcohols, there is not enough water in this mixture to form an azeotrope as a result of the upstream separation steps.

The separation objectives were to achieve a mixture of methanol, ethanol, and water in the distillate with less than 1 mol% isobutanol impurity, 91 vol% pure propanol (cosmetic grade) (Logsdon & Loke) in the first MV, 96 vol% isobutanol (fuel grade) (ASTM D7862-13 Standard Specification for Butanol for Blending with Gasoline for Use as

Automotive Spark-Ignition Engine fuel, 2013) in the second MV, and a mixture of pentanol and hexanol with no more than 5 mol% isobutanol impurity in the bottoms.

Although many configurations were used with similar results, the examples shown in Figure 3.4 are for a column diameter of 13.5 feet and an initial molar holdup of 42 kmol. The initial holdup is slightly larger than the previous case studies in order to account for non-idealities in the feed mixture. Figure 3.4 shows the MV liquid levels (A) and the MV mole fraction trajectories (B, C) for this example.

The MV level and mole fraction trajectories in this example differ from the results obtained in 1 because the feed is not equimolar. As mode 2 progresses until the product purity is reached, the liquid level of MV2 (Figure 3.4 A) increases and plateaus out because the final amount of isobutanol collected in MV2 is actually more than the total amount (in moles) of any chemical charged to it initially. This is due to the policy of charging both MVs equally in mode 1, and because one of the intermediate products (isobutanol) consists of more than half of the mixture to be separated. Despite the non-ideal nature of the mixture, flooding and weeping were never violated (Figures 3.5, 3.6). The tuning parameters and the locations of the feed and side draw are shown in Table 3.2.

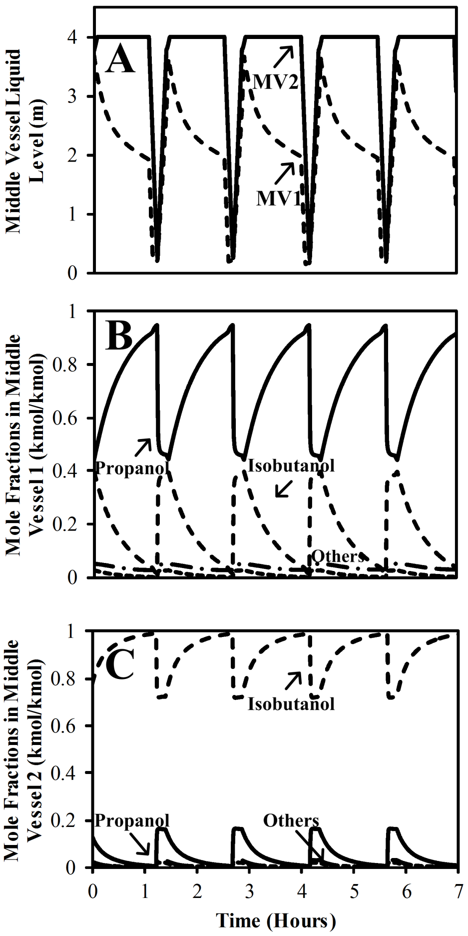

Figure 3.4. Middle vessel liquid levels (A), and mole fraction trajectories in middle vessels 1 (B) and 2 (C), for case study 2.

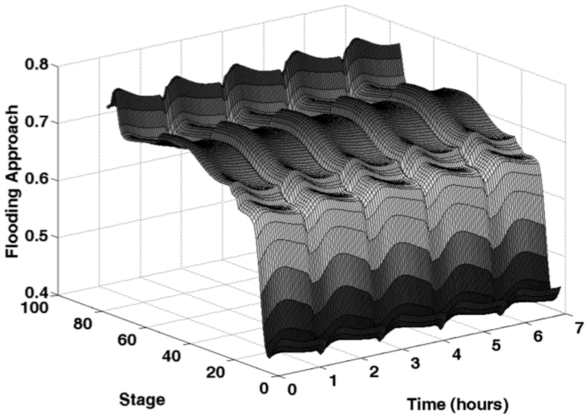

Figure 3.5. Flooding approach profile for case study 2.

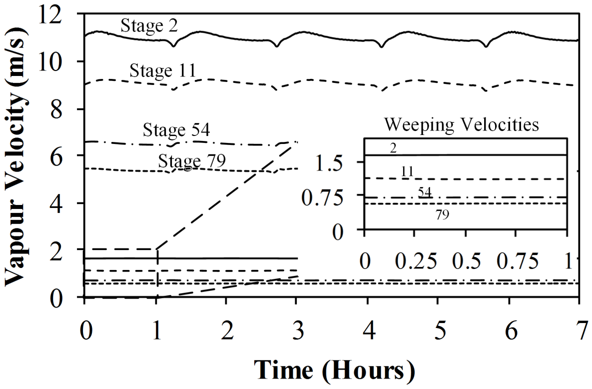

Figure 3.6. Vapour and weeping velocities for case study 2.

Table 3.2. Tuning parameters for case study 2.

<table>
<tr><th>Controller</th><th>Proportional Gain, K_c (%/%)</th><th>Integral Time, τ_i (min)</th></tr>
<tr><td>Condenser pressure</td><td>20</td><td>12</td></tr>
<tr><td>Reflux drum level</td><td>5</td><td>-</td></tr>
<tr><td>Sump level</td><td>10</td><td>-</td></tr>
<tr><td>Distillate composition</td><td>5</td><td>100</td></tr>
<tr><td>Bottoms composition</td><td>10</td><td>100</td></tr>
<tr><td>1st Side stream flow</td><td>10</td><td>-</td></tr>
<tr><td>2nd Side stream flow</td><td>10</td><td>-</td></tr>
<tr><td>1st Feed stage</td><td colspan="2">20</td></tr>
<tr><td>2nd Feed stage</td><td colspan="2">23</td></tr>
<tr><td>1st Side draw stage</td><td colspan="2">12</td></tr>
<tr><td>2nd Side draw stage</td><td colspan="2">55</td></tr>
</table>

In the example shown, both MV1 and MV2 are drained at the same rate, but since MV1 contains much less than MV2 at the beginning of mode 3, it finishes draining before MV2 has finished draining. As a result, the liquid level of MV1 can be seen increasing slightly during the end of Mode 3 because the drain valve V4 (Figure 2.4) has closed but the mode has not completed. While MV2 is finishing its drain, MV1 continues to receive a side draw from the column as well as feed to it for a few hours until MV2 is finished draining. This could be prevented by simply draining MV1 more slowly such that both MV1 and MV2 would end at approximately the same time. However, for this example the timing was intentionally offset to demonstrate that even when the draining of the MVs are not synchronized, stable behaviour can still be achieved.

To determine the impact of changing the amounts that each MV is charged, Figure 3.7 shows the results for charging the MVs in proportion to their final expected makeup instead of charging both evenly. In this example, MV2 was charged in each mode 1 to have 1.9 times more holdup than MV1 since the mole fraction of isobutanol is 1.9 times more than the mole fraction of propanol in the feed mixture.

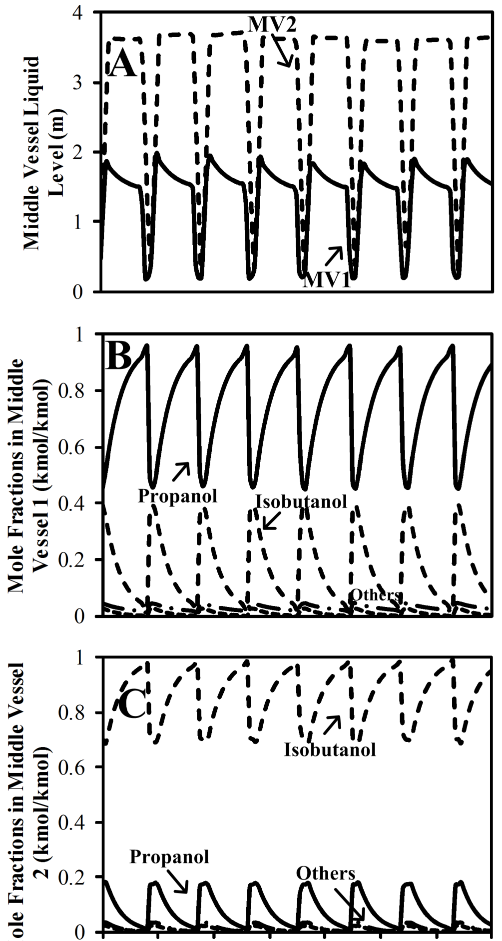

Figure 3.7. Middle vessel liquid levels (A), and mole fraction trajectories in middle vessel 1 (B) and 2 (C), for case study 2 – proportional MV charging.

It is clearly seen in Figure 3.7 that by changing the distribution of the MV charges in proportion to its final products, a higher productivity can be achieved with no difference in capital costs. By changing the MV charging distribution, the total amount of mixture separated per year increases by 5.5% and the reboiler heat duty per cycle decreases by 17%. These results indicate that charging the MVs equally is not an optimal policy, and the distribution of MV charges has a considerable impact on the performance of the separation. This is therefore a subject of future research.

3.4 Conclusion

This chapter illustrated the performance of the proposed quaternary semicontinuous process when applied to industrially relevant, non-ideal behaving mixtures. The different case studies showed that this proposed separation method is successful at achieving product purities, in the distillate and bottoms and the MVs, despite the changing modes and flow rates in the column. Stable limit cycles were attained for the two examples indicating cycle stability can be achieved even for non-ideal mixtures containing four or more components. This is the first time such applications have been intensified to a semicontinuous process (to the best of the authors knowledge). Flooding and weeping plots also show that the process is able to operate within safe operational limits.

Chapter 4

QUINTENARY SEMICONTINUOUS DISTILLATION

4.1 – Introduction

Previous chapters examined the feasibility, operability, and applicability of quaternary semicontinuous systems. The results show that the sub-optimal semicontinuous process is profitable for low to intermediate production rates when compared to conventional continuous systems. This is mostly due to the fact that quaternary semicontinuous designs only require one distillation column, whereas a conventional continuous design requires three. To further develop the theory on semicontinuous separation, this chapter examines the feasibility of the separation of a five-component mixture using a semicontinuous process. Traditional continuous separation of a five-component mixture would have 203 possible configurations and would require four distillation columns (Shah & Agrawal, 2010). The proposed five-component separation, which will be referred to as quintenary semicontinuous separation, only has one possible configuration and requires just a single distillation column and three integrated MVs. A quintenary semicontinuous separation process for the separation of *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane, was developed and the feasibility and profitability compared to a conventional continuous process was determined.

4.2 – Process Description

4.2.1 Conventional Continuous System

The conventional continuous separation process used for this study is shown in Figure 4.1. This candidate design is based on sequencing separation points that favour near equilibrium amounts of distillate and bottoms (Seider, Seader, & Lewin, 2004). The lighter components A, B and C are separated in column 2, where C is removed as the bottoms product. Components A and B are then separated in column four and the heaviest components, D and E are removed in column three.

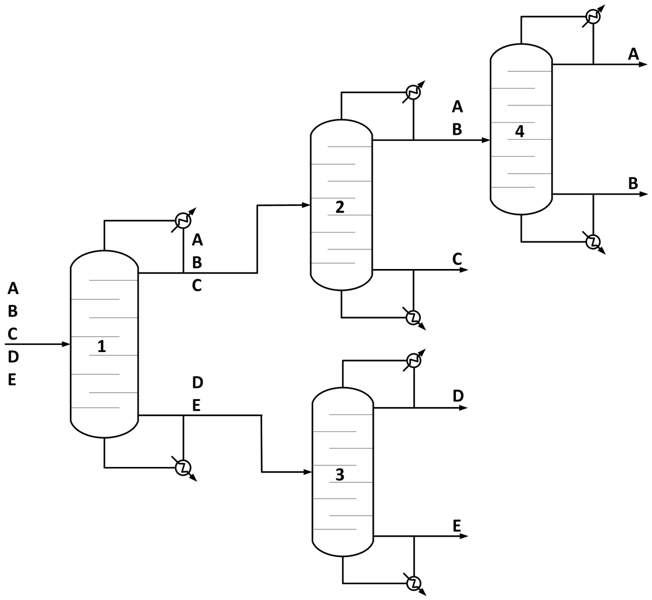

Figure 4.1. Conventional continuous design for the separation of a five-component mixture.

A formal optimization approach to find the best design out of the possible 203 options is too computationally intensive to solve in a reasonable amount of time, and as such this heuristic-based design was chosen. It is reasonable to assume that this design should be very close to the true optimal design.

4.2.2 Semicontinuous System

Figure 4.2 A depicts the quaternary semicontinuous process that was developed in previous chapters. Figure 4.2 B depicts the proposed quintenary semicontinuous design, which is an extension of the quaternary semicontinuous design. The quintenary semicontinuous process has just one column with three highly integrated MVs. The distillate and bottoms are removed as A and E, respectively. The three intermediate components, B, C, and D, are removed from their respective MVs.

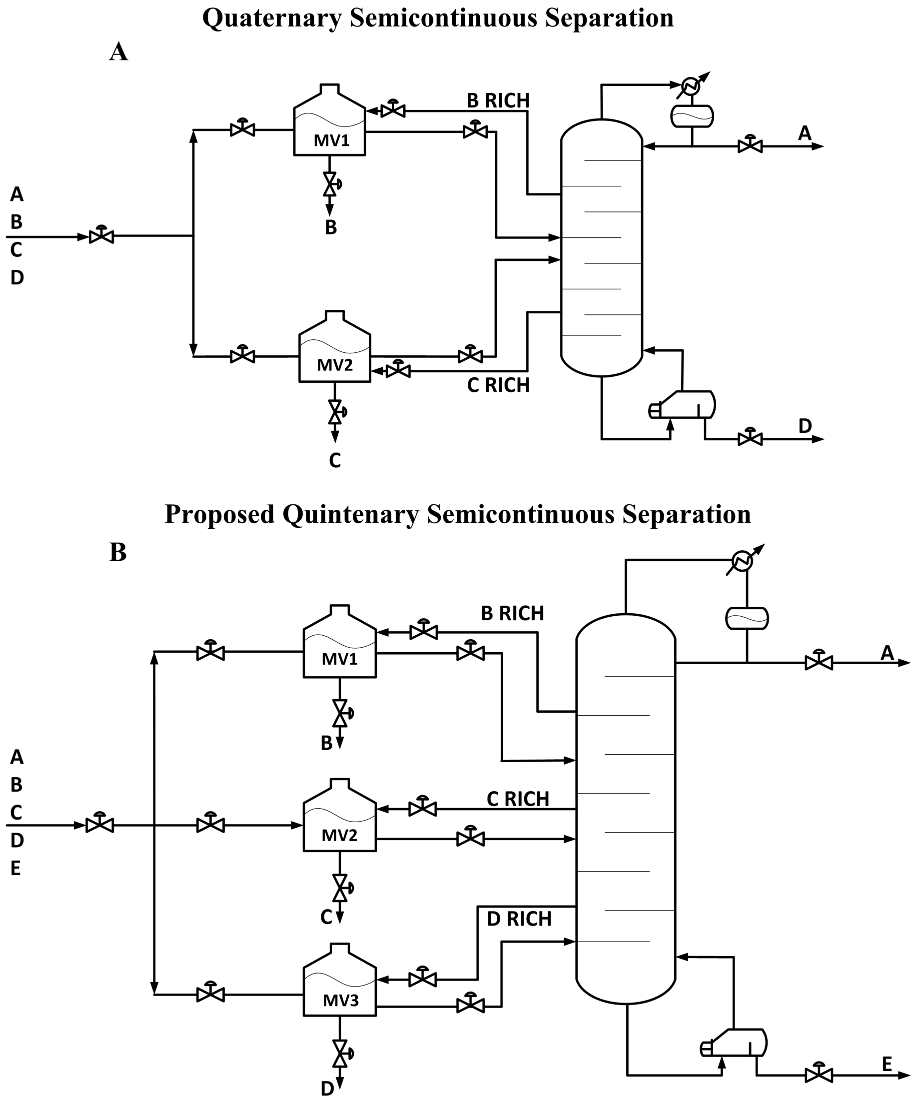

Figure 4.2. Schematic of quaternary (A) and quintenary (B) semicontinuous separation processes.

The three operating modes of the general semicontinuous process remain unchanged for the quintenary semicontinuous design. During mode 1, the mixture to be separated is evenly distributed to the three MVs, which are continuously feeding and receiving a side draw from the column. The distillate and bottoms streams continue to be collected. Once the MVs have reached a user-specified liquid level, the feed to the MV stops and mode 2 begins. In this mode, the distillate and bottoms are continuously removed at the required purity, although at diminishing flow rates. While the distillate and bottoms are removed, the intermediate components are recycled back through the side draws into the MVs. Once the desired purity of the intermediate components in their respective MVs has been attained, the cycle transitions to mode 3. During mode 3 the MVs are drained and the intermediate components are collected. During this cyclic campaign, the feed to the column, side draws, distillate and bottoms streams all remain active. Once the MVs have been drained to a specified level (never drained completely to ensure column feed is never interrupted), the cycle transitions to mode 1 and the campaign starts again. It should be noted that as in the developed quaternary semicontinuous process, there is no start-up or shutdown phase between the modes.

4.3 – Process Simulation

4.3.1 Conventional Continuous Process

The continuous separation process was designed in Aspen Plus (V8.0 was used in this study). The first column was modelled with 30 stages, with the feed entering the column at 100°C and 3.85 atm (3.90 bar). The second, third and fourth columns were modeled with 35, 30, and 24 stages, respectively. All columns were modeled using the equilibrium-based RadFrac block with a pressure drop of 0.0068 bar and a Murphree efficiency of 85%. The vapour-liquid equilibrium (VLE) is modeled using the UNIQUAC activity coefficient model with the Redlich-Kwong equation of state for the vapour phase (UNIQUAC-RK). This physical property method was chosen because it was shown to accurately predict the VLE when used with the default parameters found in the Aspen Properties database (Lee et al., 2009).

4.3.2 Semicontinuous Process

To begin, the quintenary separation system is simulated in Aspen Plus in order to obtain a good approximation of the process during mode 2. This approximation is then used as a starting point for dynamic simulations in Aspen Dynamics. The column is modeled as an equilibrium-based RadFrac model with 70 stages, with the feed entering the column at 100°C and 1.16 atm (1.18 bar). The VLE is modeled using UNIQUAC-RK. This physical property method was chosen because it matched experimental phase equilibrium data very well when used with the default binary parameters in the Aspen databank (Lee et al., 2009). It is assumed that all trays have a Murphree efficiency of 85% and a pressure drop of 0.0068 bar. The MVs are sized to hold about 30 kmol of fresh feed at a fixed pressure (at a pressure high enough to meet column pressure after accounting for losses), and previously used design heuristics are used to size the reflux drum and sump (Luyben, 2006). As the quintenary semicontinuous separation process is an extension of the quaternary semicontinuous system, the general simulation steps are the same. The readers are referred to Chapter 2 Section 2.3.2 for a more detailed simulation procedure.

The control structure used in this process is also an extension of that used in quaternary semicontinuous separation, and is depicted in Figure 4.3.

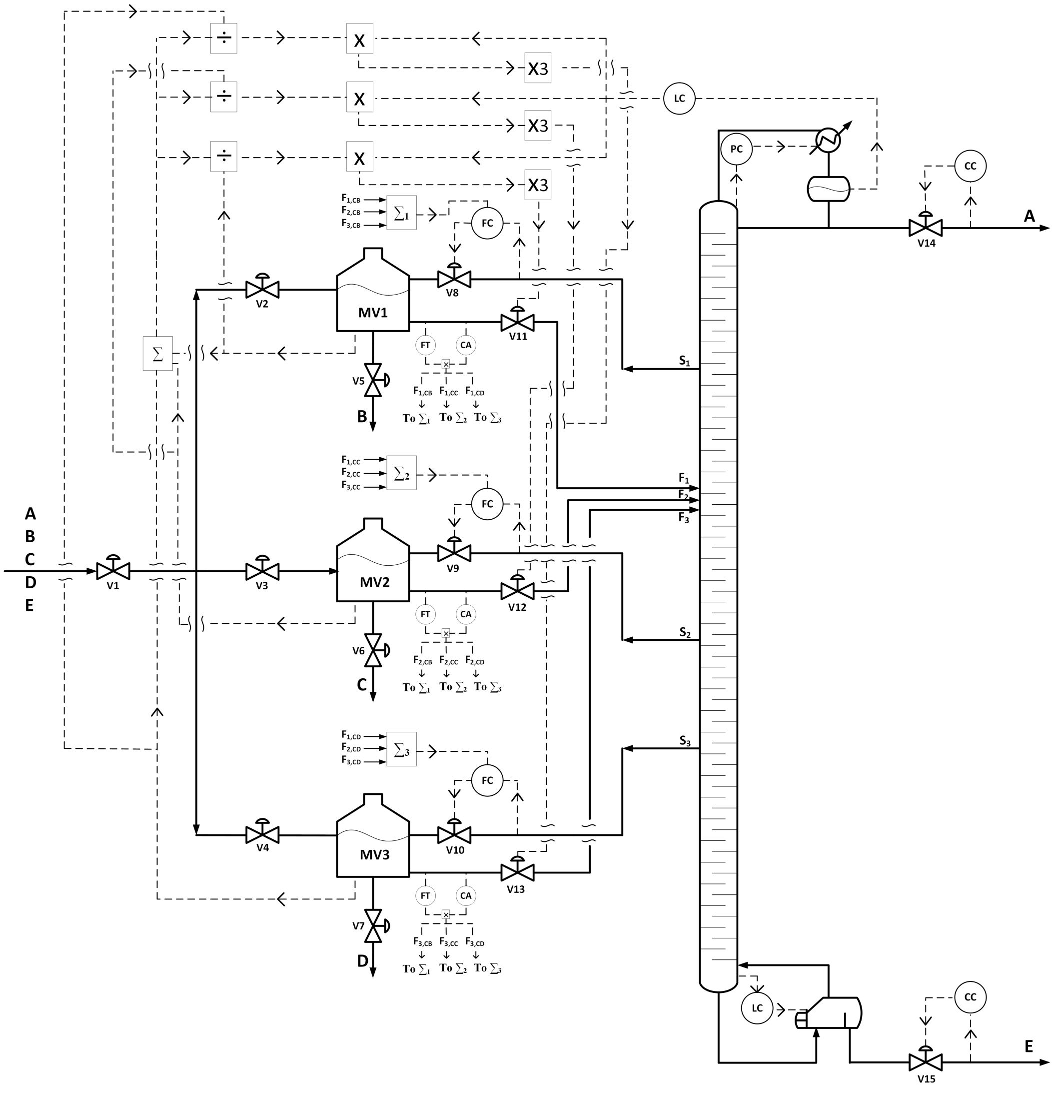

Figure 4.3. Dynamic quintenary semicontinuous separation system

This quintenary semicontinuous system has eight DOFs: condenser heat duty; reboiler heat duty; feed to the column; distillate rate; bottoms rate; and three side draws. The corresponding manipulated variables are: condenser pressure; reflux and sump levels; distillate and bottoms compositions; and the three side draw flow rates. The distillate and bottoms, 'DB' dual composition control structure is chosen based on its previous success at obtaining stable dynamic performance for semicontinuous separation (Pascall & Adams, 2013; Meidanshahi & Adams, 2014; Pascall & Adams, 2014; Phimister & Seider, 2000a). The distillate and bottoms compositions are controlled by manipulating the distillate and bottoms molar flow rates, respectively. The condenser pressure and sump level are controlled by manipulating the condenser heat duty and the reboiler heat duty, respectively.

The side draw flow rates and the reflux drum level is controlled in a similar manner as that used in quaternary semicontinuous separation (see Chapter 2 Section 2.3.3). The ideal side draw recovery strategy for quintenary semicontinuous separation is based on the following equations:

$$S_1(t) = F_1(t)x_{f,Light,1}(t) + F_2(t)x_{f,Light,2}(t) + F_3(t)x_{f,Light,3}(t) \tag{4.1}$$

$$S_2(t) = F_1(t)x_{f,Middle,1}(t) + F_2(t)x_{f,Middle,2}(t) + F_3(t)x_{f,Middle,3}(t) \tag{4.2}$$

$$S_3(t) = F_1(t)x_{f,Heavy,1}(t) + F_2(t)x_{f,Heavy,2}(t) + F_3(t)x_{f,Heavy,3}(t) \tag{4.3}$$

where $S_1(t)$, $S_2(t)$ and $S_3(t)$ are the molar flow rates of each side draw, $F_1(t)$, $F_2(t)$ and $F_3(t)$ are the molar flow rates of the feeds to the column, $x_{f,Light,1}(t)$, $x_{f,Light,2}(t)$ and $x_{f,Light,3}(t)$ are the mole fractions of the lighter intermediate species (i.e., *n*-heptane) in feed streams 1, 2 and 3 to the column, $x_{f,Middle,1}(t)$, $x_{f,Middle,2}(t)$ and $x_{f,Middle,3}(t)$ are the mole fractions of the middle intermediate species (i.e., *n*-octane) in feed streams 1, 2 and 3 to the column, and $x_{f,Heavy,1}(t)$, $x_{f,Heavy,2}(t)$ and $x_{f,Heavy,3}(t)$ are the mole fractions of the heavier intermediate species (i.e. *n*-nonane) in feed streams 1, 2 and 3 to the column.

The reflux drum level is controlled by manipulating the sum of the feeds to the column ($F_1(t)$, $F_2(t)$ and $F_3(t)$). The feeds to the column are changed by varying the valve % openings of valves V11, 12, and 13. As the molar holdups in each MV are different, the feed to the column has to be normalized by the relative amounts of molar holdup. Equations (4.4 – 4.6) depict how the output of the reflux drum controller is multiplied by the ratio of the MV level to the average MV level in all three tanks.

$$V11_{\%\,opening}\,(t) = \left(\frac{MV_{1,level}(t)}{Average\ MV_{Level}(t)}\right) \times LC_{output}(t) \tag{4.4}$$

$$V12_{\%\,opening}\,(t) = \left(\frac{MV_{2,level}(t)}{Average\ MV_{Level}(t)}\right) \times LC_{output}(t) \tag{4.5}$$

$$V13_{\%\,opening}\,(t) = \left(\frac{MV_{3,level}(t)}{Average\ MV_{Level}(t)}\right) \times LC_{output}(t) \tag{4.6}$$

where $V11_{\%\,opening}\,(t)$, $V12_{\%\,opening}\,(t)$ and $V13_{\%\,opening}\,(t)$ are the valves manipulating F_1 , F_2 and F_3, $MV_{1,Level}(t), MV_{2,level}(t)$ and $MV_{3,level}(t)$ are the middle vessel liquid levels, and $LC_{output}(t)$ is the reflux drum controller output. In practice however, the above control scheme is carried out using equations (4.7 – 4.9).

$$V11_{\%\,opening}(t) = \left[3\left(\frac{MV_{2,level}(t)}{MV_{1,Level}(t)+MV_{2,Level}(t)+MV_{2,Level}(t)}\right)\times LC_{output}(t)\right] \quad (4.7)$$

$$V12_{\%\,opening}(t) = \left[3\left(\frac{MV_{2,level}(t)}{MV_{1,Level}(t)+MV_{2,Level}(t)+MV_{2,Level}(t)}\right)\times LC_{output}(t)\right] \quad (4.8)$$

$$V13_{\%\,opening}(t) = \left[3\left(\frac{MV_{3,level}(t)}{MV_{1,Level}(t)+MV_{2,Level}(t)+MV_{2,Level}(t)}\right)\times LC_{output}(t)\right] \quad (4.9)$$

This strategy has been shown to be successful at maintaining appropriate reflux drum levels while ensuring that both MVs reach their purity goals at approximately the same time each cycle. The level and side draw controllers use proportional-only control because they do not require rigorous control and the composition and pressure controllers use proportional-integral control.

4.4- Results and Discussion

4.4.1 Case study 1

Quintenary semicontinuous separation is illustrated using an equimolar mixture of alkanes (25 mol% each of *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane and *n*-decane). A 7.0 ft. column and product purities of 95 mol% were chosen for this example. Figure 4.4

demonstrates the performance of this proposed separation process. Time zero begins at the beginning of mode 2 with full MVs.

The cyclic nature of this process is clearly seen throughout the entire separation campaign and the presence of stable limit cycles verify the efficiency of the control scheme mentioned in section 2.2. During mode 2, the liquid level in each MV gradually drops as the cycle removes distillate and bottoms and recycles enriched intermediate components into their respective tanks. Once the intermediate components in the MVs have reached the specified 95 mol% purity, the cycle transitions into mode 3. This discharging mode is clearly seen as the sharp drop in MV liquid levels in Figure 4.4 A. Figures 4.4 B, C, and D show the mole fraction trajectories in each MV. As the cycle progresses, the desired intermediate component concentrates in their MV while the compositions of the other components steadily decrease. Despite the diminishing feed to the column and the distillate and bottoms flow rates (Figure 4.4 F), the system is able to maintain the desired distillate and bottoms purities (Figure 4.4 E). Likewise Figure 4.4 G and H show that the reflux drum and sump levels, and the side draw tray liquid levels are maintained satisfactorily throughout the cycles. Although not shown, the simulations were run for at least 10 cycles to ensure that the system attains a stable limit cycle. Table 4.1 summarizes the tuning parameters and the feed and side draw locations for this example.

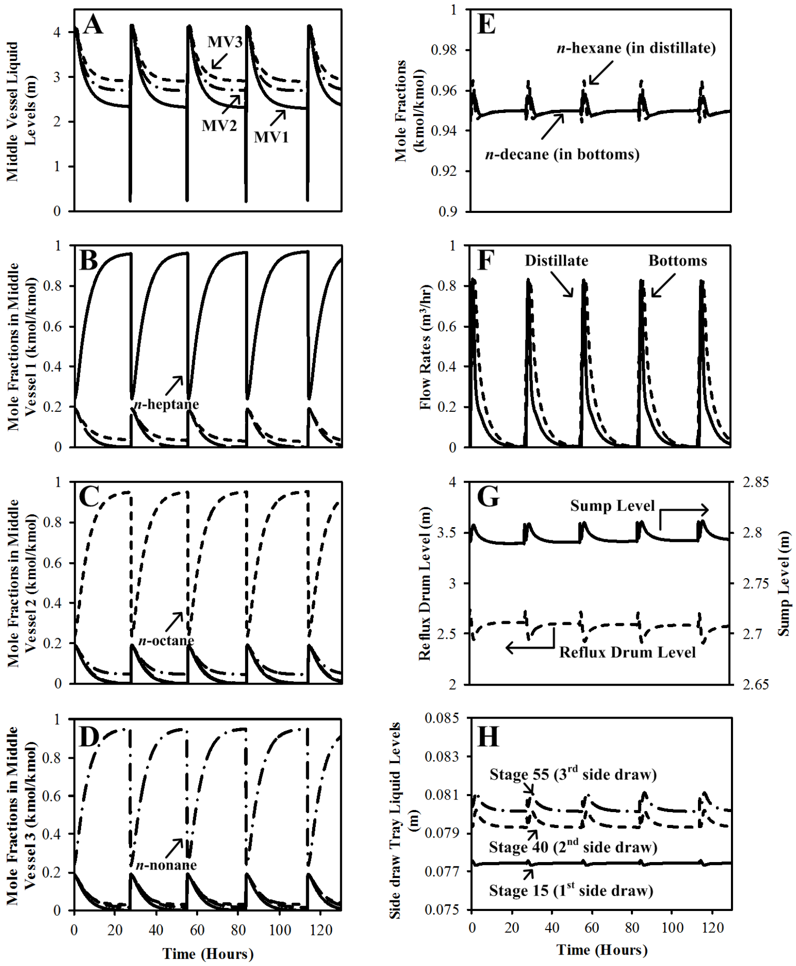

Figure 4.4. Middle vessel liquid levels (A), mole fraction trajectories in middle vessel 1 (B), 2 (C) and 3 (D), distillate and bottoms compositions (E) and flows (F), reflux and sump levels (G), and side draw tray liquid levels (H).

Previous studies have shown that this control configuration is successful at balancing vapour and liquid flow rates inside the column for ternary and quaternary semicontinuous systems. This is important to ensure that flooding and weeping do not occur, and so calculations were made to confirm that these phenomena were avoided in the quintenary system as well. The flooding approach is calculated using the Fair correlation (Fair et al., 1997), and weeping velocities were calculated using the equations (2.6 and 2.7). Figure 4.5 shows the flooding approach profile for 130 hours and it is clearly seen that the flooding approach factor (80% was used in this study) is never exceeded ensuring the column operates within safe operating limits. For safe operation, the weeping velocities must always be below the vapour velocities (which were calculated at each time step in Aspen Dynamics), and this is seen in Figure 4.6.

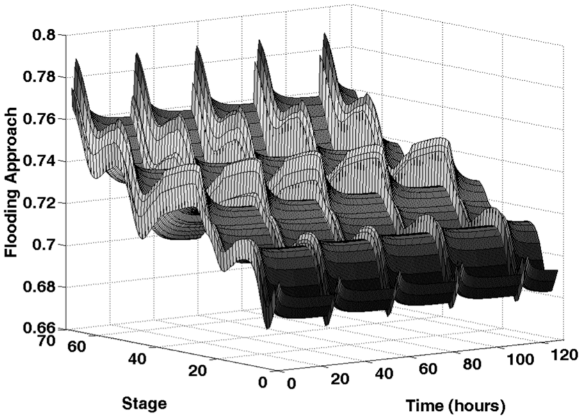

Figure 4.5. Flooding approach profile for case study 1.

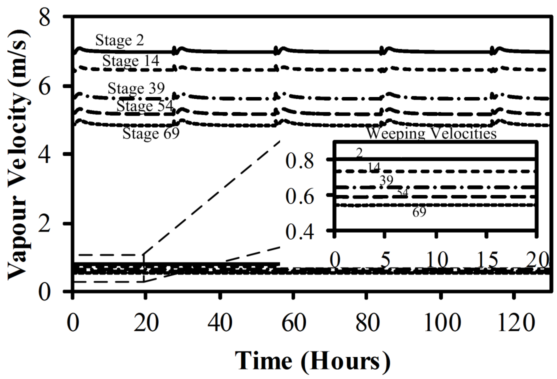

Figure 4.6. Vapour and weeping velocities for case study 1.

Table 4.1.Tuning parameters for case study 1.

Controller	**Proportional Gain, K_c (%/%)**	**Integral Time, τ_i (min)**
Condenser pressure	20	12
Reflux drum level	10	-
Sump level	10	-
Distillate composition	50	100
Bottoms composition	50	100
1st Side draw flow	5	-
2nd Side draw flow	5	-
3rd Side draw flow	5	-
1st Feed stage	26	
2nd Feed stage	27	
3rd Feed stage	28	
1st Side draw stage	15	
2nd Side draw stage	40	
3rd Side draw stage	55	

4.4.2 Case study 2

The feasibility of the proposed quintenary semicontinuous process was evaluated by examining two different non-equimolar mixtures. The first mixture (2a) is rich in distillate and bottoms, and the second mixture (2b) is rich in intermediate components. It was assumed that both examples required product purities of 95 mol% and had MVs holding about 32 kmol of fresh feed.

4.4.2.1 Non-equimolar Mixture rich in Light and Heavy Species (2a)

The feed mixture for this example consists of 32 mol% of *n*-hexane and *n*-decane, 12 mol% of *n*-heptane, 11 mol% of *n*-octane, and 13 mol% of *n*-nonane. Figure 4.7 shows the performance of the system with this mixture. The column diameter was chosen as 7.0 ft.

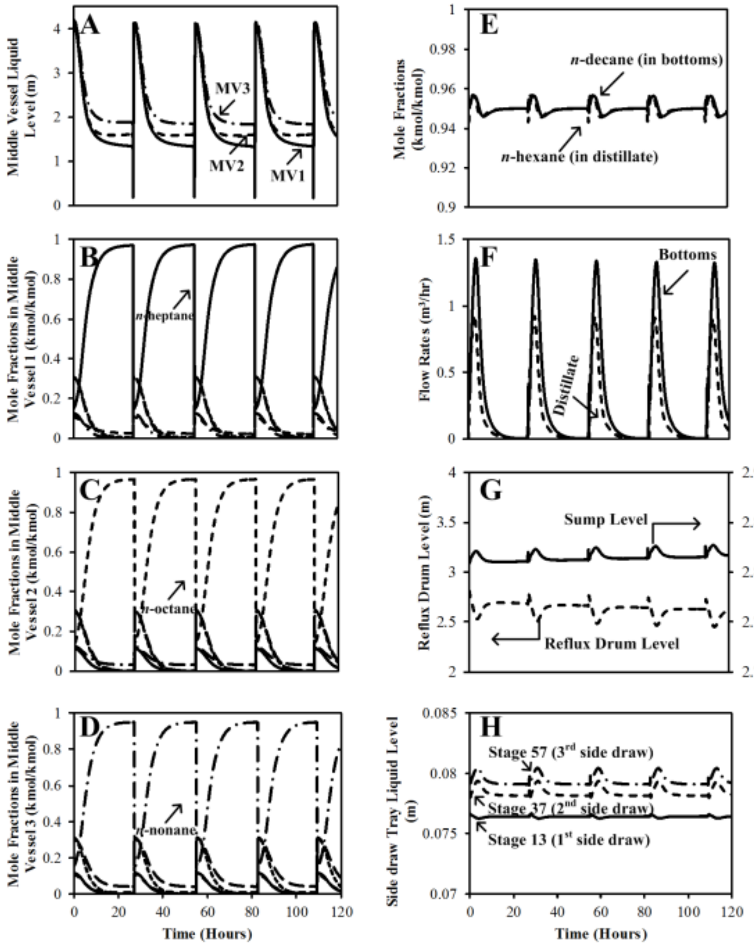

Figure 4.7. Middle vessel liquid levels (A), mole fraction trajectories in middle vessel 1 (B), 2 (C) and 3 (D), distillate and bottoms compositions (E) and flows (F), reflux and sump levels (G), and side draw tray liquid levels (H) for case study 2a.

As expected, the MV liquid levels gradually drop during mode 1, suddenly drop during mode 3 and then sharply increase during mode 1 (the re-charging mode). The mole fractions trajectories of the three intermediate species show the process attains a stable limit cycle. Figure 4.7 E show that the distillate and bottoms compositions are maintained satisfactorily throughout the cyclic campaign. Figures 4.8 and 4.9 show that flooding and weeping constraints are never violated, thereby ensuring safe column operation. Table 4.2 shows the tuning parameters and the feed and side draw locations for this example.

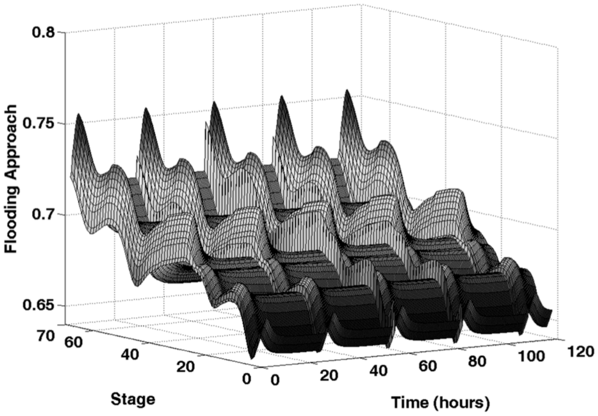

Figure 4.8. Flooding approach profile for case study 2a.

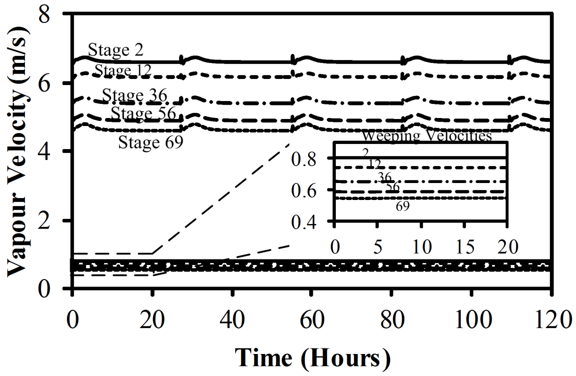

Figure 4.9. Vapour and weeping velocities for case study 2a.

Table 4.2. Tuning parameters for case study 2a.

Controller	**Proportional Gain, K_c (%/%)**	**Integral Time, τ_i (min)**
Condenser pressure	20	12
Reflux drum level	10	-
Sump level	10	-
Distillate composition	50	100
Bottoms composition	50	100
1st Side draw flow	15	-
2nd Side draw flow	4	-
3rd Side draw flow	11	-
1st Feed stage	26	
2nd Feed stage	27	
3rd Feed stage	28	
1st Side draw stage	13	
2nd Side draw stage	37	
3rd Side draw stage	57	

4.4.2.2 Non-equimolar Mixture rich in Intermediate Species (2b)

The feed mixture for this example consists of 13.5 mol% of *n*-hexane and *n*-decane, 24 mol% of *n*-heptane, 24 mol% of *n*-octane, and 25 mol% of *n*-nonane. For this example the column was modeled with 70 stages and a 7.0 ft. column diameter to be able to meet the specified product purities. Figure 4.10 shows the MV liquid levels, MV mole fraction trajectories, distillate and bottoms compositions and flows, reflux and sump levels, and side draw liquid levels for this example.

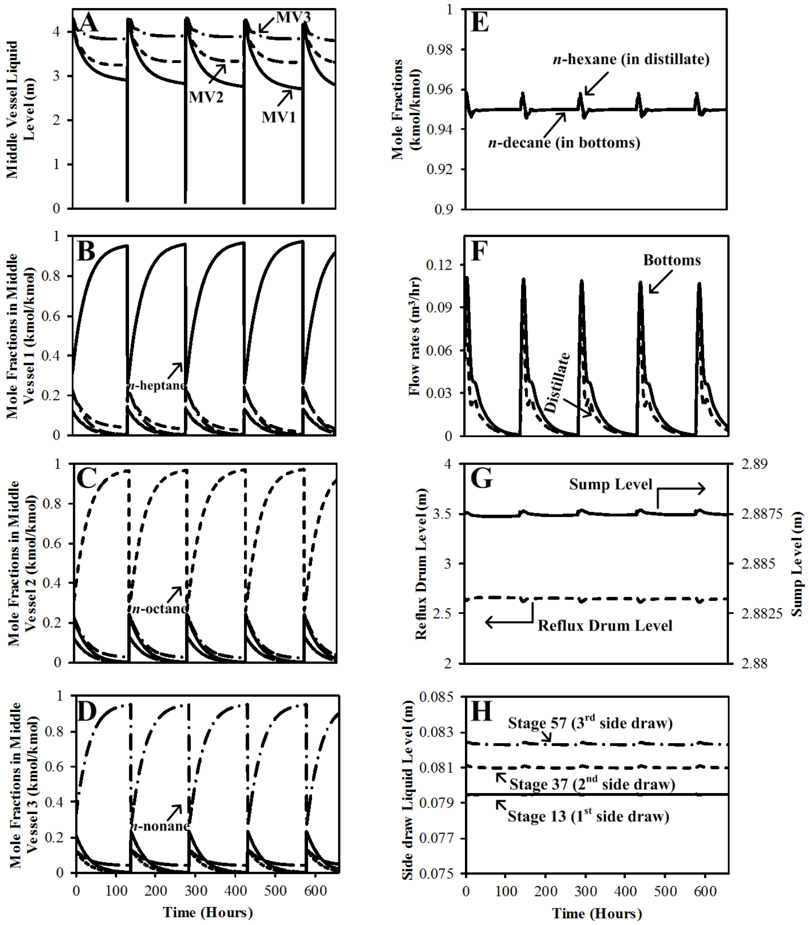

Figure 4.10. Middle vessel liquid levels (A), mole fraction trajectories in middle vessel 1 (B), 2 (C) and 3 (D), distillate and bottoms compositions (E) and flows (F), reflux and sump levels (G), and side draw tray liquid levels (H) for case study 2b.

The tuning parameters and feed and side draw locations used for case study 2b are summarized in Table 4.3. Figure 4.11 and 4.12 also show that flooding and weeping constraints are never violated.

Table 4.3. Tuning parameters for case study 2b.

Controller	**Proportional Gain, K_c (%/%)**	**Integral Time, τ_i (min)**
Condenser pressure	20	12
Reflux drum level	20	-
Sump level	10	-
Distillate composition	50	200
Bottoms composition	50	200
1st Side draw flow	5	-
2nd Side draw flow	1	-
3rd Side draw flow	1	-
1st Feed stage	26	
2nd Feed stage	27	
3rd Feed stage	28	
1st Side draw stage	13	
2nd Side draw stage	37	
3rd Side draw stage	57	

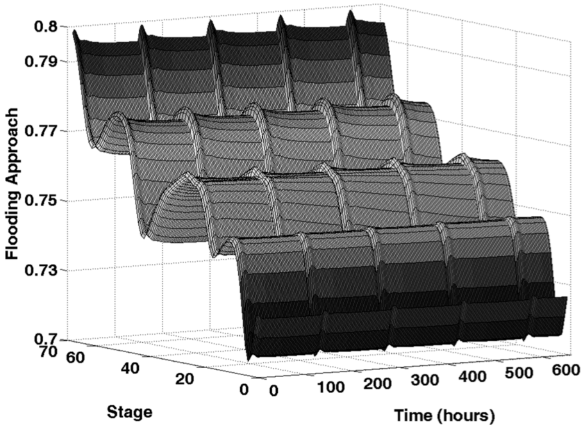

Figure 4.11. Flooding approach profile for case study 2b.

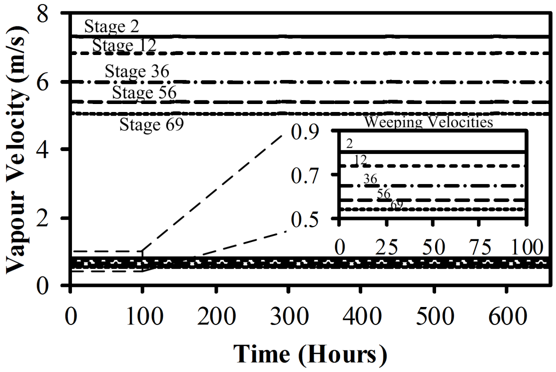

Figure 4.12. Vapour and weeping velocities for case study 2b.

Based on the above examples, and others that are not shown for brevity, it was found that the system better handles feed mixtures rich in distillate and bottoms (2a) than mixtures rich in intermediate components (2b). For systems rich in *n*-hexane and *n*-decane, the cycle times were comparable to the cycle times obtained from the equimolar mixture example (case study 1). However in case 2b, the cycle time greatly increases because the system has to work harder to maintain the distillate and bottoms compositions and purify the intermediate components. This may be due to the fact that the separation in case 2a is easier, however this is an area of future research.

By increasing the number of stages in case 2b to 80, the cycle time is greatly reduced and becomes comparable to case study 1. The MV liquid levels, mole fraction trajectories in the MV, the distillate and bottoms compositions and flows, sump and reflux drum levels, and side draw tray liquid levels are shown in Figure 4.13. As expected, the system forms a stable limit cycle and the distillate and bottoms compositions are maintained at the specified 95 mol%.

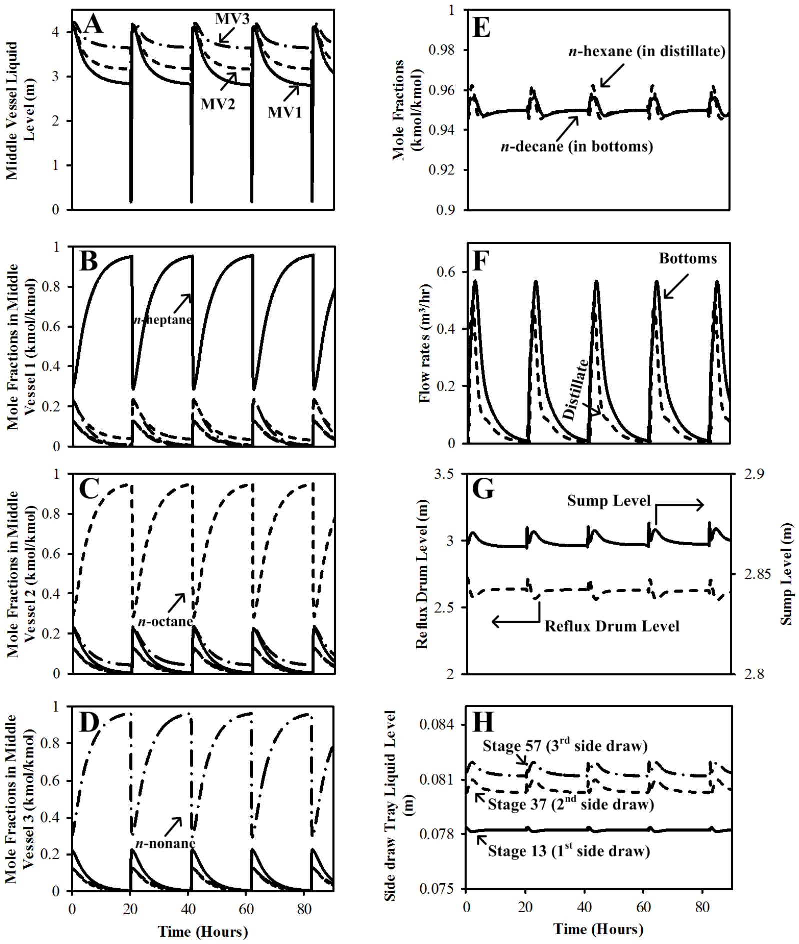

Figure 4.13. Middle vessel liquid levels (A), mole fraction trajectories in middle vessel 1 (B), 2 (C) and 3 (D), distillate and bottoms compositions (E) and flows (F), reflux and sump levels (G), and side draw tray liquid levels (H) for case study 2b.

4.4.3 Comparison Between Continuous And Semicontinuous Processes

The economics of the conventional continuous separation process and the proposed quintenary semicontinuous process were compared by evaluating the TAC for case study 1. The TAC was calculated using equations (4.10 - 4.12) assuming a 3-year plant lifetime and 8400 operational hours per year, which has been used in previous studies (Pascall & Adams, 2013; Meidanshahi & Adams, 2014; Pascall & Adams, 2014).

$$TAC\ \left(\frac{\$}{yr}\right) = \frac{Total\ Direct\ Cost\ (\$)}{Payback\ Period\ (yr)} + Annual\ Operating\ Cost\left(\frac{\$}{yr}\right) \tag{4.10}$$

$$Total\ Direct\ Costs\ (\$) = \sum_i Equipment\ Cost + \sum_i Installation\ Cost \tag{4.11}$$

where i represents the column tower, reboiler, reflux drums, condensers, pumps, and MVs.

$$Total\ Operating\ Costs\ \left(\frac{\$}{yr}\right) = \frac{Utility\ Cost\ (\$)}{\#\ cycles \times total\ cycle\ time\ (hr)} \times 8400\ \left(\frac{hr}{yr}\right) \tag{4.12}$$

The total direct costs (includes equipment, electrical, piping, instrumentation, civil, paint, and insulation) were computed using equation (4.11) and values obtained from Aspen Process Economic Analyzer V8.0. The operating costs were calculated using equation (4.12) by considering only the utility costs of steam and cooling water. The method of Towler and Sinnot (2012) was used to estimate the cost of steam using the price of natural gas, \$2.51/MMBtu (U.S Energy Information Administration (EIA – Official Energy Statistics from the US Government), 2012) and electricity, \$0.0491/kWh (Independent Electricity System Operator (IESO), 2012). The cost of cooling water was estimated using the same price of electricity, and the price of water make-up and chemical treatment, (\$0.02/1000 US gal (Towler & Sinnot, 2012)). From this, the cost of steam at 188°C was estimated as \$8.92 per GJ of heating load, and the cost of cooling water at 24°C was estimated as \$0.68 per GJ of cooling load.

The continuous separation process (as depicted in Figure 4.1) was first optimized using the NQ curves tool in Aspen Plus. This tool determines the optimal number of stages and the feed location by varying these variables in order to find a combination that minimizes the total heat load while meeting product purities. The design spec and vary function is used within each column to ensure that the final product purities are met at 95 mol%. The resulting column diameters, that prevent flooding but are at least at a minimum 1.5 ft., are then used in equation (4.11) to find the total direct costs. The operating costs are found in the method explained above.

Figure 4.14 shows the total direct, operating, and annualized costs for both the continuous and semicontinuous separation processes. Figure 4.14 A shows the direct costs for both processes. The semicontinuous system only requires one column and three MVs, compared to four columns for the continuous case. This means that the equipment and installation costs for three reboilers and condensers are eliminated for the semicontinuous case. Figure 4.14 B shows the operating cost curves. The operating cost for the semicontinuous process is higher because of the high reflux and boilup ratios necessary to maintain specifications. Based on previous semicontinuous work, it is expected that the TAC (Figure 4.14 C) for the semicontinuous process becomes cheaper than the continuous case for intermediate to low production rates. Larger production rates require a larger semicontinuous column to achieve the desired product purities. And so, at smaller production rates (less than 1,400 m^3/yr in this example), the TAC for the semicontinuous column becomes cheaper than the equivalent continuous process, resulting in the expected outcome. These curves have a lot of room for improvement as the continuous process has been optimized while the semicontinuous case is sub-optimal. Once a formal global optimization strategy has been implemented, the cost savings and the range of applicability of the quintenary semicontinuous process are expected to increase greatly.

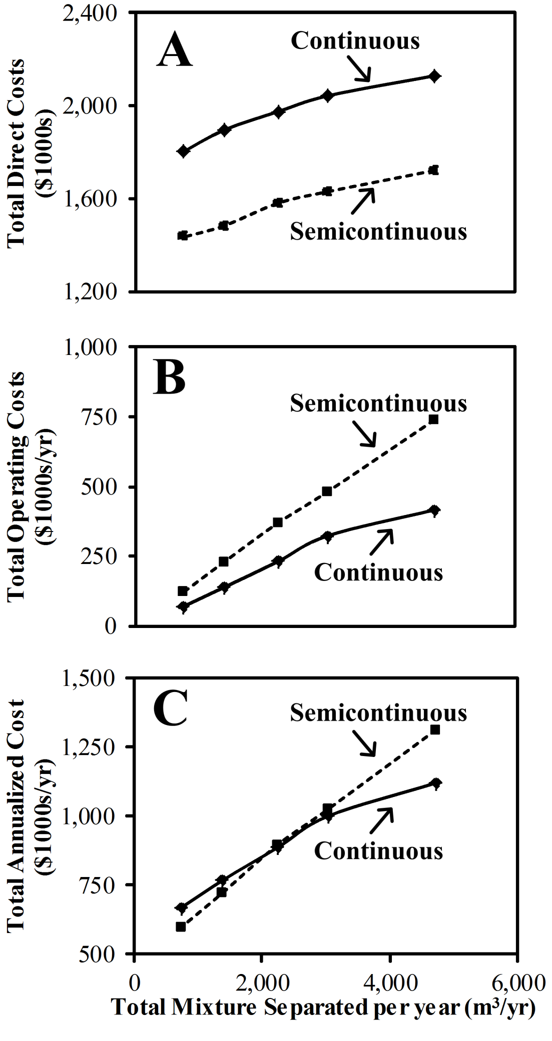

Figure 4.14. Total direct costs (A), operating costs (B) and total annualized costs (C) for continuous and semicontinuous systems for various production rates.

4.4.4 Disturbance rejection

As disturbances can enter the system and disturb normal operation, the proposed quintenary semicontinuous system was evaluated using batch-to-batch disturbances as an illustrative example. A step change in fresh feed composition was introduced during the charging mode (mode 1) of the fourth stable limit cycle. Figures 4.15 A, B, C, and D show the response of the mole fractions in MV1 to a step change of +10%, +15%, +20%, and +40% in *n*-heptane in the fresh feed, respectively. The mole fraction trajectories of MV2 and MV3 were very similar in shape and thus not shown for brevity.

For a step change of +10% of *n*-heptane, the components were varied proportionally to give a fresh feed composition of 19% *n*-hexane, 22% *n*-heptane, 20% *n*-octane, 20% *n*-nonane, and 19% *n*-decane. For a change of +15%, the fresh feed composition was 18.5% *n*-hexane, 23% *n*-heptane, 20% *n*-octane, 20% *n*-nonane, and 18.5% *n*-decane. For a of +20%, the fresh feed composition was 18% *n*-hexane, 24% *n*-heptane, 20% *n*-octane, 20% *n*-nonane, and 18% *n*-decane. Lastly, for a change of +40%, the fresh feed composition was 16% *n*-hexane, 28% *n*-heptane, 20% *n*-octane, 20% *n*-nonane, and 16% *n*-decane.

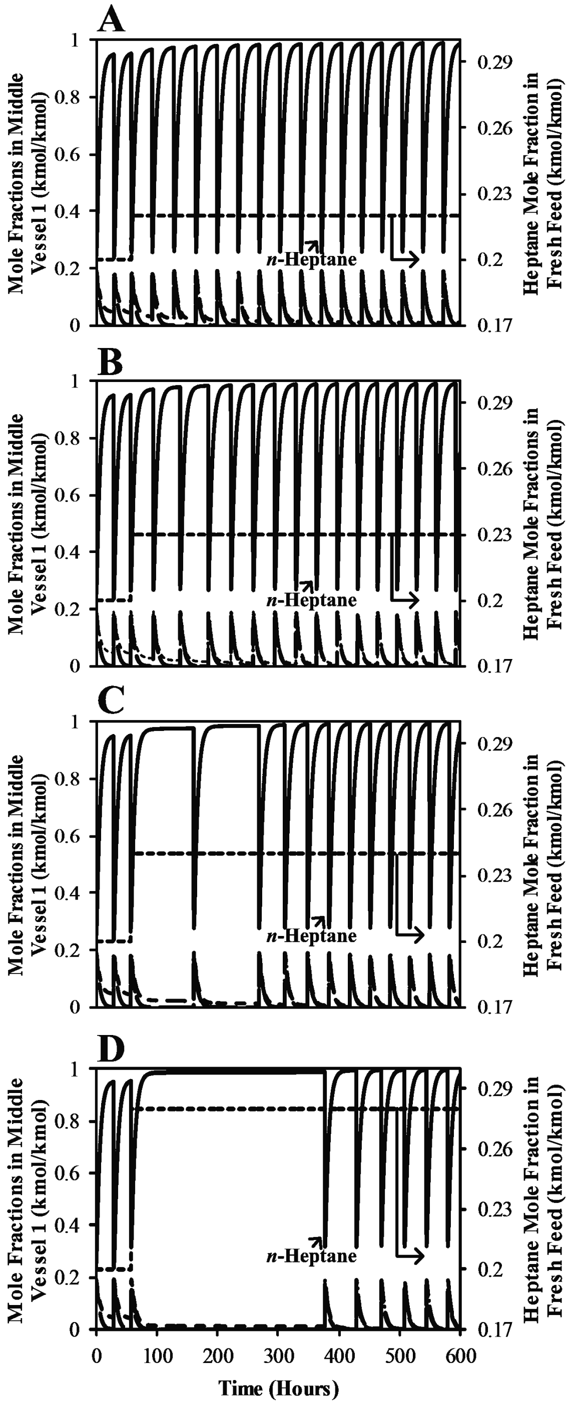

Figure 4.15. Mole fraction trajectories for middle vessel 1 for step changes of +10% (A), +15% (B), +20% (C), and +40% (D) in *n*-heptane in the fresh feed.

Figure 4.15 clearly shows the proposed system is able to reject the disturbances without changing any controller tuning parameters. Figures 4.15 B, C and D show that the system may take one or two cycles after the disturbance has been introduced to reach a stable limit cycle, however the system eventually does perform as expected. The long cycle time after the introduction of the disturbance is due to the long processing time in the third MV to get to the desired purity of the heaviest intermediate component (i.e. *n*-nonane). These results indicate that when considering mixtures richer in the lightest intermediate component (*n*-heptane), the system has a harder time achieving specifications for the middle and heavy intermediate components. In practice, to reduce the wait times after the disturbance has been introduced, a slightly off-spec cut could be drained. Also, it would be interesting to see the impacts of including a fault detector that activates an alternative control strategy during the long processing times because some of the control valves are saturated in the current structure. Perhaps a different control approach will offset the large cycle times seen in Figures 4.15 C and D, and this is an area of future work.

4.5 – Conclusion

In this chapter, a novel quintenary semicontinuous separation process was developed and analyzed for a mixture of alkanes using just one column and three MVs. The reduction of three columns, when compared to a conventional continuous separation process, greatly reduces the capital cost, as only one third of reboilers, condensers, and installation is required.

The separation method uses a cyclic campaign to continuously remove distillate and bottoms from the column while concentrating the intermediate components in the three MVs via the three side draws. Different case studies showed that this proposed separation method is successful at achieving product purities, in the distillate and bottoms and the MVs, despite the changing modes and flow rates in the column. Flooding and weeping are never violated and the proposed control scheme is successful in achieving stable cyclic behaviour. An economic evaluation of the sub-optimal quintenary semicontinuous process and the continuous process showed that the semicontinuous process is more profitable at production rates of 1,400 m^3/yr or lower. Disturbance rejection examples demonstrate the system's ability to reject disruptions and eventually reach a stable limit cycle.

Chapter 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusions

The objective of this research was to develop and analyze an intensified semicontinuous separation process that can separate four or more component mixtures into high purity products. Different examples were used to show the effectiveness of the proposed semicontinuous separation process.

In Chapter 2, a quaternary semicontinuous separation process was developed and its performance was demonstrated via dynamic simulation for the first time for four-component mixtures using just one distillation column. The separation method achieves its separation objectives by following a forced cyclic campaign in which the distillate and bottoms products are continuously removed in a distillation column, while the intermediate products are concentrated in two MVs. The use of the MVs eliminates the need for additional columns, thereby greatly reducing both the capital cost and the complexity of the system.

The feasibility of the proposed quaternary semicontinuous process was illustrated by examining an ideal equimolar mixture of alkanes. The trajectories of mole fractions of the separated components and MV liquid levels show that a stable limit cycle was attained, indicating the effectiveness of the control configuration. The operability of the system was determined by the parametric analysis, in which the column diameter and the MV size were varied. Results from this analysis indicates that smaller MVs are more economical up to a certain point, and that larger column diameters have lower TAC per volume of mixture separated due to economies of scale. Economic comparisons of the sub-optimal semicontinuous process and an optimal continuous process show that the semicontinuous process is profitable for intermediate flow rates. This is expected as previous work has shown that ternary semicontinuous is cheaper than continuous for low to intermediate capacities.

Chapter 3 analyzed the applicability of the proposed system for two industrially relevant examples. The first example, an equimolar mixture of aromatic hydrocarbons (BTEX), showed that separations into high purity products are possible using this semicontinuous approach. However the number of stages may not be realistic, indicating that this intensification approach may not be economical for this mixture. The second example involved the separation of a fuel-grade quality isobutanol stream. Successful separation using the proposed semicontinuous was observed. This is the first time a semicontinuous separation approach has been conducted for a butanol separation process, with a non-ideal feed mixture. The proposed system was effective at reaching MV purity objectives while meeting distillate and bottoms purity objectives and preventing flooding and weeping in the column, despite the wide variety of flow rates experienced during the course of each cycle. Stable limit cycles were reached for both examples indicating that cycle stability can still be achieved for non-ideal mixtures.

In Chapter 4, the extendibility of the proposed system was analyzed for the separation of a five-component mixture. The performance of this quintenary semicontinuous separation process was determined by using a mixture of alkanes and an extended version of the control configuration proposed in Chapter 2. The control configuration was updated to include the extra MV and side draw flow rates, and was shown to be effective in maintaining product purities while avoiding flooding and weeping phenomena. Comparison with a conventional continuous process shows that the quintenary semicontinuous process is more cost-effective at intermediate production rates. Several disturbance tests show that the proposed system is effective at rejecting disruptions and attaining stable cyclic behaviour.

Overall, this research has shown that the conventional continuous separation system can be reduced to an equivalent semicontinuous separation setup with one column and two or more MVs (depending on how many products are required). Comparison with conventional continuous processes show that both quaternary and quintenary semicontinuous processes are more profitable over a range of production rates. This work has greatly expanded the range of applicability of semicontinuous separation, and has been generalized for N-component separation.

5.2 Recommendations for future work

Future work will use optimization algorithms currently in development to attempt to determine the optimal design and control parameters simultaneously. The key design variables are the total number of stages; the feed and side draw locations; column diameter; and the MV size and charge ratios. The key control decision variables subject to optimization are the set points and the controller tuning parameters. The set points are: condenser pressure; condenser drum level; sump level; distillate and bottoms compositions; and the side draw flow rates. The controller tuning parameters correspond to the controllers that manipulate the condenser duty, column feed flow rates, reboiler duty, distillate and bottoms flow rates, and the intermediate-species feed flow rates. The large number of DOFs add to the complexity of this system, and because of the tight integration of design and control decision variables on the behaviour and performance of each cycle, existing dynamic optimization methods (such as those included with Aspen Dynamics) have proven unsatisfactory, and thus the development of better methods is required. After developing a good optimization approach, a techno-economic analysis can be completed in order to understand the conditions when one system is better than the other, and relationships between key variables can be identified.

Advanced control methods, such as model-based fault detection control strategies should also be explored. All of the semicontinuous separation systems studied over the past fifteen years have used PID controllers, and although they are effective, there is reason to believe that model-based controllers may provide enhanced performance, and as such is an area of future work.

Another area of future work is to perform an economic comparison of this work versus other complex configurations such as dividing wall columns at a variety of desired production rates to determine the conditions when one configuration is more economical than the other.

LIST OF REFERENCES

Abdehagh, N., Tezel, F.H., & Thibault, J. (2014). Separation techniques in butanol production: Challenges and developments. *Biomass and Bioenergy. 60*, 222-246. doi:10.1016/j.biombioe.2013.10.003

Adams, T. A., & Pascall, A. (2012). Semicontinuous thermal separation systems. *Chemical Engineering & Technologyi*, *35*(7), 1153-1170. doi:10.1002/ceat.201200048

Adams, T.A., & Seider, W.D. (2006). Semicontinuous distillation with chemical reaction in a middle vessel. *Industrial & Engineering Chemistry Research, 45*(16), 5548-5560. doi: 10.1021/ie051139r

Adams, T. A., & Seider, W. D. (2008a). Semicontinuous distillation for ethyl lactate production. *AIChE Journal*, *54*(10), 2539–2552. doi:10.1002/aic.11585

Adams, T. A., & Seider, W. D. (2008b). Practical optimization of complex chemical processes with tight constraints. *Computers & Chemical Engineering*, *32*(9), 2099–2112. doi:10.1016/j.compchemeng.2008.02.007

Adams, T. A., & Seider, W. D. (2009a). Design heuristics for semicontinuous separation processes with chemical reactions. *Chemical Engineering Research and Design*, *87*(3), 263–270. doi:10.1016/j.cherd.2008.09.008

Adams, T. A., & Seider, W. D. (2009b). Semicontinuous reactive extraction and reactive distillation. *Chemical Engineering Research and Design*, *87*(3), 245– 262. doi:10.1016/j.cherd.2008.08.005

Agrawal, R. (1996). Synthesis of distillation column configurations for a Multicomponent separation. *Industrial & Engineering Chemistry Research. 35*(4), 1059-1071. doi: 10.1021/ie950323h

Aspen Technology Inc. (2011). Aspen Capital Cost Estimator V7 3.1: User Guide. Burlington, Massachusetts: Aspen Technology, Inc.

ASTM D7862-13. (2013). Standard specification for butanol for blending with gasoline for use as automotive spark-ignition engine fuel, ASTM International, West Conshohocken, PA, www.astm.org (accessed October 5, 2014)

Bowling, I. M., Ponce-Ortega, J. M., & El-Halwagi, M. M. (2011). Facility location and supply chain optimization for a biorefinery. *Industrial & Engineering Chemistry Research.50*(10), 6276-6286.
doi: 10.1021/ie101921y

Bruins, M.E., & Sanders, J.P.M. (2012). Small-scale processing of biomass for biorefinery. *Biofuels, Bioproducts and Biorefining. 6*(2), 135-145.
doi: 10.1002/bbb.1319

Carolan, J. E., Joshi, S. V., & Dale, B. E. (2007). Technical and financial feasibility analysis of distributed bioprocessing using regional biomass pre-processing centers. *Journal of Agricultural & Food Industrial Organization. 5*(10), 1-27. doi: 10.2202/1542-0485.1203,

Daoutidis, P., Marvin, W. A., Rangarajan, S., & Torres, A.I. (2013). Engineering biomass conversion processes: a systems perspective. *AIChE Journal*. *59*(1), 3-18.
doi: 10.1002/aic.13978

Errico, M., Rong, B., Tola, G., & Turunen, I. (2009). A method for systematic synthesis of multicomponent distillation systems with less than N-1 columns. *Chemical Engineering Processes: Process Intensification. 48*(4), 907-920. doi: 10.1016/j.cep.2008.12.005

Fair, J. R., Steinmeyer, D. E., Penney, W. R., & Crocker, B. B. (1997). Gas absorption and gas-liquid system design. In R. H. Perry & D. W. Green (Eds.), *Perry's Chemical Engineers' Handbook* (7th Ed.). McGraw-Hill

Gan, J., & Smith, C. T. (2011). Optimal plant size and feedstock supply radius: a modelling approach to minimize bioenergy production costs. *Biomass and Bioenergy. 35*(8), 3350-3359. doi:10.1016/j.biombioe.2010.08.062

Independent Electricity System Operator (IESO). (2012). Independent Electricity System Operator (IESO). *Hourly Ontario Energy Price*. Retrieved February 10, 2012, from http://www.ieso.ca/default.asp

Kiss, A. A., & Rewagad, R. R. (2011). Energy efficient control of a BTX dividing-wall column. *Computers & Chemical Engineering.35*(12), 2896-2904. doi: 10.1016/j.compchemeng.2011.03.024

Kumar, M., & Gayen, K. (2011). Developments in biobutanol production: new insights. *Applied Energy. 88*, 1999-2012. doi:10.1016/j.apenergy.2010.12.055

Lee, K., Chen, W., Ko, J., Lee, L., & Chang, C.J. (2009). Isothermal vapor-liquid equilibria for binary mixtures of hexane, heptane, octane, nonane and cyclohexane at 335.15 k, 343.15 k and 353.15 k. *Journal of the Taiwan Institute of Chemical Engineers. 40*(5), 573-579. doi: 10.1016/j.jtice.2009.03.002

Lin, C., Chen, L., I, Y., & Lai, C. (2010). Microbial communities and biodegradation in lab-scale BTEX-contaminated groundwater remediation using an oxygen-releasing reactive barrier. *Bioprocess Biosystems Engineering. 33*, 383-391. doi: 0.1007/s00449-009-0336-7

Logsdon, J. E., & Loke, R. A. Isopropyl Alcohol, *Kirk-Othmer Encyclopedia of Chemical Technology.*New York: John Wiley & Sons, Inc.

Luyben, W.L. (2006). *Distillation Design and Control Using Aspen Simulation*. Hoboken, N.J.: Wiley-Interscience.

Meidanshahi, V., & Adams, T. A. (2015). A new process for ternary separations: semicontinuous distillation without a middle vessel. *Chemical Engineering Research and Design. 93*, 100-112. doi:10.1016/j.cherd.2014.04.017

Mazzeo, D. E. C., Levy, C. E., de Angelis, D.F., & Marin-Morales, M. A. (2010). BTEX biodegradation by bacteria from effluents of petroleum refinery. *Science of the Total Environment. 408*, 4334 -4340. doi:10.1016/j.scitotenv.2010.07.004

Mersmann, A., Kind, M., & Stichlmair, J. (2011). *Thermal Separation Technology*: *Principles, Methods, Process Design* (1st ed., pp. 694). Heidelberg: Springer.

Monroy-Loperena, R., & Alvarez-Ramirez, J. (2004). Some aspects of the operation of semi-continuous, middle-vessel distillation columns. *Chemical Engineering Communications*, 191(11), 1437–1455. doi:10.1080/00986440490472607

Mullin, R. (2013). Fine chemicals: Optimism prevails over uncertainty. *Chemical & Engineering News*. *91*(2), p 14. Retrieved March 9, 2015 from http://cen.acs.org/articles/91/i2/Fine-Chemicals-Optimism-prevails-over.html

Okoli, C., & Adams, T. A. (2014). Design and economic analysis of a thermochemical lignocellulosic biomass-to-butanol process. *Industrial & Engineering Chemistry Research. 53*(28), 11427-11441. doi: 10.1021/ie501204r

Pascall, A., & Adams, T. A. (2013). Semicontinuous separation of dimethyl ether (DME) produced from biomass. *The Canadian Journal of Chemical Engineering*. 91(6), 1001-1021. doi:10.1002/cjce.21813

Pascall, A., & Adams, T. A. (2014) Semicontinuous separation of bio-dimethyl ether from a vapor-liquid mixture. *Industrial & Engineering Chemistry Research*. *53*(13), 5081-5102. doi: 10.1021/ie4012744

Phimister, J. R., & Seider, W. D. (2000a). Semicontinuous, middle-vessel distillation of ternary mixtures. *AIChE Journal*, *46*(8), 1508–1520. doi:10.1002/aic.690460804

Phimister, J. R., & Seider, W. D. (2000b). Semicontinuous, pressure-swing distillation. *Industrial & Engineering Chemistry Research*, *39*(1), 122–130. doi:10.1021/ie9904302

Phimister, J. R., & Seider, W. D. (2000c). Semicontinuous, middle-vessel, extractive distillation. *Computers & Chemical Engineering*, 24(2-7), 879–885. doi:10.1016/S0098-1354(00)00344-6

Rahul, Mathur, A.K., & Balomajumder, C. (2013). Biological treatment and modeling aspect of BTEX abatement process in a biofilter. *Bioresource Technology. 142*, 9-17. doi:10.1016/j.biortech.2013.05.005

Ramshaw, C. (1989). Higee distillation – An example of process intensification. *Chemical Engineering Research Design*, *389*, 13-14.

Ranjan, A., & Moholkar, V. S. (2012). Biobutanol: Science, engineering, and economics. *International Journal of Energy Research. 36*, 277-323. doi: 10.1002/er.1948

Roberge, D. M., Ducry, L., Bieler, N., Cretton, P., & Zimmermann, B. (2005). Microreactor technology: A revolution for the fine chemical and pharmaceutical industries?.*Chemical Engineering & Technology. 28*(3), 318-323. doi:10.1002/ceat.200407128

Santibañez-Aguilar, J. E., González-Campos, J.B., Ponce-Ortega, J.M., Serna-González, M., & El-Halwagi, M. M. (2014). Optimal planning and site selection for distributed multiproduct biorefineries involving economic, environmental and social objectives. *Journal of Cleaner Products.65*, 270-294. doi: 10.1016/j.jclepro.2013.08.004

Seider, W. D., Seader, J. D., & Lewin, D. R. (2004). *Product & Process Design Principles: Synthesis. Analysis, and Evaluation* (2nd ed., pp. 252). New York, NY: John Wiley & Sons, Inc.

Shah, V. H., & Agrawal, R. (2010). A matrix method for multicomponent distillation sequences. *AIChE Journal. 56*(7), 1759-1775. doi: 10.1002/aic.12118

Sultana, A., & Kumar, A. (2011). Optimal configuration and combination of multiple lignocellulosic biomass feedstocks delivery to a biorefinery. *Bioresource Technology.102*(21), 9947-9956. doi: 10.1016/j.biortech.2011.07.119

Sultana, A., & Kumar, A. (2012). Optimal siting and size of bioenergy facilities using geographic information system. *Applied Energy. 94*, 192-201. doi: 10.1016/j.apenergy.2012.01.052

Tabari, A., & Ahmad, A. (2015). A semicontinuous approach for heterogeneous azeotropic distillation processes. *Computers & Chemical Engineering. 73*, 183-190. doi: 10.1016/j.compchemeng.2014.12.005

Towler, G., & Sinnott, R. (2012). *Chemical Engineering Design: Principles, Practice and Economics of Plant and Process Design* (2nd ed., pp. 107–113). Massachusetts, USA: Butterworth-Heinemann.

U.S Energy Information Administration (EIA - Official Energy Statistics from the US Government). (2012). Henry Hub Gulf Coast Natural Gas Spot Price. Retrieved February 10, 2012, from http://www.eia.gov/dnav/ng/hist/rngwhhdW.htm

Wen, D., Jiang, H., & Zhang, K. (2009). Supercritical fluids technology for clean biofuel production. *Progress in Natural Science. 19*(3), 273-284. doi:10.1016/j.pnsc.2008.09.001

Wright, M., & Brown, R. C. (2007). Establishing the optimal sizes of different kinds of biorefineries. *Biofuels, Bioproducts and Biorefining. 1*(3), 191-200. doi: 10.1002/bbb.25

Yahaya, G. O. (2008). Separation of volatile organic compounds (BTEX) from aqueous solutions by a composite organophilic hollow fiber membrane-based pervaporation process. *Journal of Membrane Science. 319*(1-2), 82-90. doi: 10.1016/j.memsci.2008.03.024