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A new process for ternary separations: Semicontinuous distillation without a middle vessel

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Abstract

In this work, a novel semicontinuous process for the separation of ternary mixtures is presented. The new Semicontinuous without Middle Vessel (SwoMV) configuration is a process intensification technique that makes separation of three components to desired purities possible in a single distillation column without the necessity of the middle vessel as opposed to the conventional semicontinuous processes. The elimination of the middle vessel omits the charging and discharging modes of conventional semicontinuous processes, reduces the direct costs of plant and facilitates the retrofit of available distillation columns for purification of new products. Furthermore, SwoMV configuration improves the conventional semicontinuous system by reducing the energy consumption in most cases and expanding the range of system capacities at which it is economically optimal. The separation of benzene, toluene, and o-xylene is used as a case study to show the feasibility of the SwoMV configuration. An economic analysis is performed, and conventional continuous distillation, conventional semicontinuous, SwoMV and single side stream column configurations are compared by calculating the total annualized cost of these systems over a range of production rates. The results show the feasibility, applicability and profitability of the novel proposed configuration.

Keywords: Semicontinuous Separation; BTX; Semicontinuous Without Middle Vessel; Ternary Separation; Economic Evaluation

1. Introduction

Distillation is one of the most common unit operations for purification of mixtures into more valuable high-purity components. Since it is a mature and well-studied unit operation, most recent advances in distillation system design have come in the form of advanced process intensification strategies. The semicontinuous distillation configuration proposed by Phimister and Seider (2000a) was one such strategy. For the separation of ternary mixtures to any desired
purities using conventional continuous distillation configurations, two distillation columns are required. However, the novelty of the proposed configuration by Phimister and Seider was to eliminate one of the distillation columns and replace it with a simple storage tank (called a Middle Vessel, MV) and purify all three components to their desired specifications using an unsteady-state approach.

In the semicontinuous distillation configuration, the middle vessel is charged with fresh feed. It continuously feeds the column and a side draw is collected is recycled back to the tank. As the light and heavy components are removed from the system in a continuous fashion in the distillate and bottom streams, respectively, the intermediate-boiling component concentrates in the middle vessel. When its concentration reaches the desired specification, the middle vessel is discharged and the product is gathered. The middle vessel is then charged again with fresh feed for the next cycle.

Several studies have investigated the range of applicability of the semicontinuous separation for various systems. Phimister and Seider (2000b, 2000c) have showed application of the semicontinuous configuration for extractive and pressure-swing distillation. To model the system, they used the simplifying assumption of pseudo-steady-state energy balances in their simulations, and integrated the resulting dynamic MESH equations in FORTRAN 90. In 2004, Monroy-Loperena and Alvarez-Ramirez studied a semicontinuous separation process and compared it to continuous and batch process alternatives. They modeled the system under the assumptions of negligible vapour holdup, theoretical trays, and constant operating pressure.

Adams and Seider (2006, 2008 and 2009a) investigated the feasibility of integration of reaction and separation in a semicontinuous configuration where the reaction took place in the middle vessel. They concluded that when reactive distillation is infeasible the semicontinuous distillation with chemical reaction in a middle vessel process is an economical option for a wide range of production rates.

Adams and Seider in 2009b further developed the semicontinuous separation process by designing a packed distillation column which switches between reactive extraction and reactive distillation for separation of 1,3-propanediol from a dilute mixture with water obtained from an upstream biofermentation process.

In 2013, Pascall and Adams looked into the applicability of semicontinuous separations for biofuel production. They used Aspen Plus and Aspen Dynamics software for their studies. They concluded that by using semicontinuous technology, a remarkable reduction in the cost of producing bio-DME can be achieved for small-scale distributed networks.

In 2013 Niesbach et al. proposed the use of semicontinuous distillation for the separation of butyl acrylate from a mixture of several light and heavy boiling point impurities. When the bioresource feedstock used to produce butyl acrylate is changed (such as switching between different types of wood), different impurities might be produced in the product. They concluded that by using the semicontinuous system, high purities of product can be achieved without
changing the operating conditions of the column. Furthermore, they showed that this process is quite flexible with respect to variations in the impurities present in the feedstock.

To recap, the profitability of semicontinuous separation over conventional continuous and batch systems for low to intermediate production rates has been well-illustrated in the existing literature and it has been shown that where flexible separation in terms of purities is required, semicontinuous separation is a good choice. Therefore, this separation technique can effectively be used for the production of bio-fuels (such as biodiesel, where plant capacities are low (Wen et al., 2009)) and down-stream purifications are essential to achieve fuel-grade quality. Several studies have shown that constructing multiple, distributed, smaller bio-refineries instead of one large, centralized plant can reduce the transportation costs of biomass, which can reap significant benefits (Carolan et al., 2007). For example, Bowling et al. (2011) used a mathematical programming model to determine the optimal location and size of biorefineries. Using this systematic method they concluded that the smaller distributed configurations usually are better options over the large, centralized plants. Sultana and Kumar (2012) performed a similar study for Alberta and concluded that the distributed facilities were more preferable. Depending on the geographical distribution of biomass, both of these studies have showed that smaller distributed biofuel plants may be more economically favourable. As such, it is probable that semicontinuous processes would be more suitable for these smaller distributed plants, and possibly even shift the optimum sizes down even more.

However, while promising, semicontinuous separations have limitations such as the smaller scales at which they are economically optimal and generally higher operating costs than conventional continuous systems. This study tries to tackle these issues by proposing a novel configuration called Semicontinuous without Middle Vessel (SwoMV). This configuration is a process intensification technique that makes the separation of three components to desired purities possible in a single distillation column without the necessity of the middle vessel as opposed to the “conventional” semicontinuous process used in all prior semicontinuous studies. The elimination of the middle vessel omits the charging and discharging modes of the conventional semicontinuous process, reduces the direct costs of the plant, and depending on the initial composition of the feed, reduces the operating costs, thereby increasing the economical range of production. Furthermore, the new process facilitates the retrofit of existing distillation columns for purification of new products or elimination of introduced impurities in the process without installing any new vessels or columns.

In the SwoMV configuration the side stream is recycled back, mixed with the fresh feed and re-fed to the column. The required product purities are achieved by adjusting the total feed flow rate to the column in two modes of operation. It is worth mentioning that a distillation column with several side streams (without recycling) is a popular configuration for fractional distillation. Fractional distillation is commonly used in petroleum refineries to separate a multicomponent feedstock into multiple fractions via each side stream of the column. Each fraction consists of a group of components with similar boiling points. To further purify each fraction to pure
components, subsequent distillation columns are required. However, if the feed consists of only three components, any desired product purities may be obtained by using a single column with a side stream and no recycling. However, a column utilizing a side stream has been shown in prior work to only be economical compared to the conventional continuous system (two consecutive distillation columns) when the mole percent of the intermediate component in the feed is above 80% (Doukas and Luyben, 1978). For other feed compositions, the side stream column has been shown to be uneconomical since it requires generally higher operating costs and column diameters (therefore capital costs), leading to higher total annualized costs (Alatiqi and Luyben, 1985). An economic analysis is performed in this study to compare the SwoMV and the single side stream configuration.

To study the feasibility of the SwoMV configuration, the separation of benzene, toluene, and o-xylene (BTX) to high purities is chosen as a case study. BTX separation is an important part of petrochemical refineries in which BTX is produced in a naphtha reforming process and are then separated for sale or other use (Chauvel and Lefebvre, 1989). In conventional refineries, the products are separated to high-purity benzene, toluene, xylene and heavy components successively in three consecutive columns with binary distillation. The first two columns of the fractionation process in the naphtha reforming unit are replaced with one distillation column working in a semicontinuous mode in this study.

BTX separation is also a good choice for a case study in demonstrating the new SwoMV concept because of the relative volatilities (7.1, 2.2 and 1) and normal boiling points (80-144°C) of the species are in easily manageable ranges. Furthermore, BTX separation may be necessary in biorefineries which produce transportation fuels via Fischer-Tropsch synthesis (Demirbas, 2009), and such refineries are likely to be optimal at lower production rates where semicontinuous systems are likely to be optimal. However, it is important to note that the proposed SwoMV system can be applicable to a wide variety of other chemical mixtures.

After designing the SwoMV configuration and its appropriate control structure, simulations are performed in Aspen Dynamics and economic analyses are performed to compare the profitability of conventional continuous, conventional semicontinuous, single side stream, and SwoMV, systems.

2. Process Modeling

2.1. Conventional Continuous Process

Figure 1 shows the optimum configuration of the conventional continuous system for the separation of an equimolar feed of BTX with high purities of 99 mol%, according to the work of Ling and Luyben (2009). The equimolar BTX mixture at 358 K and 0.5 bar is fed to the first column just above stage 14. The first column is modeled with 30 equilibrium stages and the
reflux drum operates at vacuum pressure (0.37 bar) such that cooling water can be used as a cooling medium. Benzene is recovered in the distillate stream and the mixture of toluene and o-xylene recovered in the bottoms is fed to the second column on tray 14. This column has 28 stages and the reflux drum operates at 0.13 bar. A pressure drop of 0.0068 bar per tray and Murphree efficiency of 0.75 is used for both columns. Simulations are performed using Aspen Plus V8 with the RadFrac equilibrium-based model for distillation columns. The vapour-liquid equilibria (VLE) are modelled using the NRTL model with ideal gas and Henry's law (Kiss and Rewagad, 2011). These specifications were chosen to be consistent with the aforementioned work.

In this study, the optimum configuration of the conventional continuous system for two other cases with different feed compositions is also determined. For both the toluene-rich feed composition case (10, 80 and 10 mol% of BTX, respectively) and toluene-lean feed composition case (45, 10 and 45 mol% of BTX), all design parameters are the same as the equimolar feed case, except that the feed enters at stages 15 and 17 in the first and second columns, respectively.

2.2. Conventional Semicontinuous Process

In the conventional semicontinuous (CSC) ternary distillation configuration, which is shown in Figure 2, one distillation column is replaced with a middle vessel which is integrated tightly with the distillation column in the system. The process operates in a stable limit cycle consisting of three operational modes.

In mode 1, the middle vessel is charged with fresh feed. After the tank is charged valve V1 is closed and mode 2 begins. During this mode, the middle vessel feeds the column and the light and the heavy boiling point components (benzene and o-xylene, respectively) are withdrawn from the system at the desired purity of 99 mol% in the distillate and bottom streams,
respectively. The side stream (rich in the intermediate component, toluene) is recycled back to the middle vessel. As the middle vessel is gradually depleted of benzene and o-xylene, the concentration of toluene increases in the vessel. When the desired concentration of toluene is achieved (99 mol% in this study) mode 3 starts by opening valve V2 and discharging the toluene product. Subsequently, valve V2 closes when the level of the middle vessel reaches a specified small value and the system cycles back to mode 1.

Figure 2- Schematic of the conventional semicontinuous configuration applied to a BTX system.

During all modes, the middle vessel continuously feeds the column, and the distillate and bottom products are withdrawn such that the column is always in operation without any shut-downs or start-ups. However, there are no steady-states during any part of the cycle since the composition and flow rate of the feed to the column changes over time.

Before dynamic simulations can commence, key design information must be determined, such as the number of stages, feed and side stream locations, column diameter, reflux drum size, and sump height. In addition, an initial state of the column is needed. To do this, an analogous flow sheet at steady-state is first simulated in Aspen Plus V8. Although the semicontinuous process is never at steady-state, the Aspen Plus model is a very good guess at a snapshot of the dynamic system at the beginning of mode 2. The column is modeled using the equilibrium-based RadFrac model in Aspen Plus, which is then exported to Aspen Dynamics, where additional modifications are necessary to complete the model. Our methodology is described next.

The pressure condition for the conventional semicontinuous column is considered to be the same as the first column in the conventional continuous configuration (reflux drum pressure of 0.37 bar). The number of column stages, as well as the feed and side draw locations, are determined as is explained later. Note that the side stream leaving the column is not connected to the middle vessel in the Aspen Plus model in order to enable convergence to a steady-state solution. Next, the design heuristics of Luyben (2006) is implemented to size the reflux drum and sump to allow
for 5 min of liquid holdup when the vessel is 50% full, based on the total liquid entering or leaving these vessels. The middle vessel was sized such that it initially holds 100 kmol of fresh feed and the valves are sized to handle 3 bar pressure drop. These values are reasonable choices for a base case study based on a comparison with similar systems (Pascall and Adams, 2013).

At present, the distillation column model in Aspen Dynamics uses an equilibrium-based model and does not have a dynamic rate-based model available. Therefore, in order to incorporate the effect of sub-equilibrium behaviour (tray efficiencies of less than 100%) in the dynamic simulations, steady-state rate-based simulations were performed in Aspen Plus for a range of feed flow rates and compositions that might be encountered at different times during the semicontinuous cycle starting with an equimolar feed composition. The rigorous rate-based RadFrac model in Aspen Plus is then used to estimate tray efficiencies. As an example, the tray efficiencies calculated based on the rate-based model for the 50 stage design are shown in Figure 3. The tray efficiencies are fairly constant throughout the cycle and depend very little on feed flow rate and composition. Therefore, a tray efficiency of 0.75 was adopted for all stages of the column (a conservative estimate) for the equilibrium-based model.

![Figure 3- Calculation of tray efficiencies using rate-based simulations in Aspen Plus for different scenarios.](image)

Once all of this was completed, the simulation was exported to Aspen Dynamics as a pressure-driven simulation. After an initialization run is completed in Aspen Dynamics, a control system was added and the side stream was connected to the middle vessel. Because the system operates in a limit cycle, a well-designed control structure is needed to drive the cycle and achieve the desired performance. Pascall and Adams (2013) have looked into this issue and compared the performance of eight different control structures. Based on their work, the control structure
shown in Figure 2 was implemented for the simulation, which was identified to be the best in terms of controller performance, cycle stability, and robustness in the face of disturbances.

In this control structure, the reflux drum and sump levels are controlled by manipulating the feed flow rate to the column and the reboiler heat duty, respectively. The column pressure is controlled by manipulating the condenser heat duty. The purities of the distillate and bottom streams are controlled by manipulating the flow rate of these streams. The ideal side-draw recovery arrangement is implemented to control the side stream (Adams and Seider, 2008). A dead time of 3 min is assumed for composition analysers in the simulation. Proportional-integral (PI) control is used for composition and pressure loops while proportional-only (P) control is implemented for level and side stream flow. Controllers are tuned for each case of different initial feed compositions by hand such that the integral squared error (ISE) of benzene composition in the distillate and o-xylene in the bottoms are minimized. The event-driven task feature is used within Aspen Dynamics to handle the switching of the control system to different operational modes.

For the conventional semicontinuous process, the number of stages, column diameter, feed location, and side draw location are key design parameters which significantly affect the performance of the cycle and the total annualized cost (TAC). Furthermore, for each combination of those four key design parameters, there is some optimum set of control parameters (such as the controller gains and integral time constants) required to achieve a stable, functioning limit cycle with the minimum cost. There are many constraints which must be satisfied, such as ensuring that flooding and weeping never occur in the column at any point in the cycle (see section 3.2).

Therefore, it can be quite challenging to find the parameters which yield the optimum design (the lowest TAC). The equation-based dynamic optimization tools provided with Aspen Dynamics are not suitable for semicontinuous systems because they do not work for systems with discrete events (such as mode switching) for which the exact times of their occurrences are not known a priori. Previous attempts to optimize semicontinuous systems in Aspen Dynamics using black-box techniques such as particle swarm optimization have been successful, but required very long run times due to both the length of time required to perform each dynamic simulation (about 4 minutes) and the high degree of dimensionality (Pascall and Adams, 2013). To make matters worse, this must be repeated for each individual production rate studied, since the column and corresponding control system must be re-designed to handle different flow rates, resulting in approximately 1 cpu-year of computation time required for formal optimization.

Consequently, we have adapted a shortcut procedure to achieve very good (but probably suboptimum) results in a much more reasonable amount of time. A series of steady-state simulations were performed in Aspen Plus to mimic the conditions of what the column would be at the beginning of mode 2. A range of number of stages was considered. For each number of stages considered, the feed tray location and side draw location was determined such that the operating cost of utilities are minimized and design specification of 99 mol% purities of the
distillate and bottoms products are achieved by using the NQ curves tool in Aspen Plus. The NQ Curves tool optimizes the number of trays and feed locations in a RadFrac column by plotting the heat load versus the number of stages. The NQ curves analysis performs an intelligent search, varying the number of stages in a column, optimizing the location of one feed stream at each step, and adjusting the locations of other feed and side-draw streams according to rules the user specifies. Subsequently, the column diameter necessary to prevent flooding was calculated using the results of the analysis, which is then used to compute the total direct costs of the column using the Aspen In-Plant Cost Estimator V8 software tool available from within Aspen Plus V8. The total direct costs include the equipment, piping, civil, instrumentation, electrical, paint, installation, and other details.

The operating costs were calculated considering only the utility costs of steam and cooling water. The cost of steam for the reboiler was estimated using the method of Towler and Sinnott (2012) which estimates the cost using the price of natural gas ($2.51/MMBtu (EIA, 2012)) and the electricity price ($0.0491/kWh (IESO, 2012)). According to a similar methodology (Towler and Sinnott, 2012), the cooling water cost was estimated based on the electricity price ($0.0491/kWh (IESO, 2012)) and the water make-up and chemical treatment price ($0.02/1000 US gal (Towler and Sinnott, 2012)). Electricity is typically used to recirculate water and its cost is usually between 1-2 kWh/1000 US gal of circulating water (Towler and Sinnott, 2012). The electricity cost constitutes a significant portion of the cooling water cost and its variation has a significant effect of the price of cooling water. The resulting cost of steam at 147.75°C is $0.5655 per GJ of heating load and the cost of cooling water at 24°C is $0.3164 per GJ of cooling load. Therefore, the steam price is about 1.78 times the cooling water cost. For equimolar feed composition, the condenser and the reboiler heat duties are approximately in the same order therefore the cooling water cost represents approximately about 35% of the total operating cost.

Together, the energy costs and capital costs are combined to compute the TAC (assuming a three-year plant lifetime and 8400 hours per year of operation) according to Eq. 1 (Luyben, 2010).

\[
TAC = \frac{\text{Total Direct Cost}}{\text{Payback Period}} + \text{Annual Operating Cost} 
\]

When completed, a few cases with the lowest TAC are selected for further consideration. These analyses were based on the steady-state results which mimic the conditions of what the column would be at the beginning of mode 2, and not the entire cycle. Therefore, these candidate cases are then explored further in Aspen Dynamics considering the entire mode of operation.

For each of these candidate cases (i.e, columns with different numbers of stages with corresponding feed and side draw locations), dynamic simulations are performed over a range of production rates. The control system for each case was designed and tuned manually in order to complete the design objectives, minimize the energy costs, and ensure that flooding and weeping are prevented throughout the cycle. Some of the cases were found to not satisfy the purity constraints when considering the entire cycle and all ranges of production rates and were
discarded. The TAC is then calculated for each remaining case. Subsequently, the case with the lowest TAC which satisfies the purity constraints of all three streams over the entire cycle was then selected as the best configuration.

This procedure is repeated for three cases of feed compositions and the results are listed in Table 1. This methodology reduces the number of simulations significantly to find a good configuration in a reasonable amount of time. Although the result is sub-optimal, it is still very good. In this case, 40 stages was always the most economic choice; anything larger had higher TAC and anything lower had purity constraint violations at some point during the cycle. However, a detailed dynamic optimization is required to find the optimum configuration which possibly could improve the performance of the system even more. This is outside the scope of this work.

<table>
<thead>
<tr>
<th>Feed mol% of B/T/X</th>
<th>Number of stages</th>
<th>Feed stage</th>
<th>Side draw stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>45 / 10 / 45</td>
<td>40</td>
<td>35</td>
<td>15</td>
</tr>
<tr>
<td>33 / 33 / 34</td>
<td>40</td>
<td>24</td>
<td>14</td>
</tr>
<tr>
<td>10 / 80 / 10</td>
<td>40</td>
<td>25</td>
<td>20</td>
</tr>
</tbody>
</table>

2.3. Semicontinuous without Middle Vessel (SwoMV)

The new configuration proposed in this work aims to exploit the semicontinuous technique for ternary separation and modify it so that the middle vessel is eliminated from the system to further reduce the direct and operating costs of the process, and also to eliminate the charging and discharging modes of the conventional semicontinuous system. We call the new configuration semicontinuous without middle vessel (SwoMV).

The SwoMV configuration is shown in Figure 4. The distillation column for the SwoMV design has the same structural and design parameters as the column in the conventional semicontinuous design. In this configuration, the bottoms and distillate streams are always collected (albeit at varying flow rates) in the same manner as in the conventional semicontinuous design. However, the fresh BTX feed from upstream is continuously fed to the system (though at variable rates), and the intermediate component (toluene) is now collected directly via the side draw, with a variable purity over the course of the cycle.

The system has two modes: the non-producing mode and the producing mode. Toluene is collected according to the following policy. First, an upper and lower bound for purity of the intermediate component is defined, and should be chosen such that the average purity that is in
between the bounds would be the desired purity. In this example, we have chosen an upper bound of 99.5 mol% and a lower bound of 98.5 mol% to achieve an approximate average purity of 99 mol%.

![Figure 4- Schematic of the novel SwoMV system.](image)

The side stream splits into two streams (see Figure 4). The cycle starts with the non-producing mode during which the purity of the toluene in the side stream is below the upper bound. During this mode valve $V1$ is closed, valve $V2$ is fully open, and the side stream is recycled back (mixed with the fresh feed and fed to the column). During this mode, the purity of the side draw gradually increases. Once the purity of the side stream reaches the desired upper bound, the producing mode starts, valve $V1$ is fully opened, and toluene product is withdrawn. The rate at which toluene is collected is a degree of freedom and is discussed in section 3.3. Note that because stream flow is simulated using a pressure-driven model, valve $V2$ must be partially closed in order to achieve the desired recycle ratio during the producing mode. The open fraction of $V2$ was pre-determined manually using off-line tests. The purity of the side draw now gradually decreases. As soon as the purity of this stream falls below the lower bound, $V1$ closes and $V2$ opens completely, and a new cycle begins. The opening and closing functions of valves $V1$ and $V2$ during producing and non-producing modes are determined by using Aspen Dynamics event-driven task.

The rest of the control structure is essentially the same as in the conventional semicontinuous system and the controllers are tuned in the same way. Note that the fresh BTX feed from upstream is now manipulated in order to manage the reflux drum level, instead of the feed to the column (after mixing with the side draw). As a result, the flow rates of all of the streams vary throughout each cycle.
2.4. Side Stream Column

For the purpose of economic comparison, a single distillation column with a side stream is also simulated (Figure 5). The column is designed to have the same structural and design parameters as the column in the conventional semicontinuous and SwoMV designs. The distillate flow rate, the side draw rate and the reflux ratio of the column are adjusted such that the required purities of all three products are obtained.

![Figure 5: Schematic of the side stream column for BTX separation.](image)

3. Results and Discussion

3.1. Performance of the Conventional Semicontinuous Process

The performance of the conventional semicontinuous system is illustrated in this section for the example using a feed composition of 45, 10 and 45 mol% of BTX. As shown in Figure 6a, the middle vessel is initially charged with fresh feed. The liquid level in the MV drops as it feeds the column, and the benzene and o-xylene are withdrawn from the system. After about 32 hours, the desired purity of 99 mol% for toluene is attained in the middle vessel as shown in Figure 6b, and the toluene product is discharged (seen in Figure 6a as a sharp drop in the MV level). To avoid any shut-downs and start-ups, the MV does not discharge completely, which is why the initial concentration of toluene is higher than the fresh feed of 10 mol% in Figure 6b. The middle vessel is subsequently charged with fresh feed at time 35 hr and the second cycle starts.
As the cycle proceeds, the mole fraction of benzene and o-xylene in the middle vessel and the feed stream decreases as they are removed, thus making it more difficult to maintain the purity of the distillate and bottom stream. As a result, the control system gradually increases the reflux and boilup ratios as can be seen in Figure 7. Simultaneously, the control system also decreases the feed flow rate to the column (see Figure 8a) in order to maintain a constant reflux drum level. Ultimately, this serves to keep the internal liquid and vapour flow rates in the column balanced such that flooding and weeping do not occur. As the feed flow rate is reduced, the distillate and
bottoms flow rates are reduced as well (Figure 8b). Overall, the control system successfully maintains the desired 99 mol% purity of the distillate and bottom streams as shown in Figure 8c.

3.2. Performance of SwoMV Process

In order to illustrate the performance of SwoMV, the separation of a BTX mixture with 45, 10 and 45 mol% is studied. The column has the same design parameters as the conventional semicontinuous system (Table 1). The SwoMV cycle starts with the non-producing mode during which the side product valve (VI) is closed and all of the side stream flow is recycled back to the column, shown for example in Figure 9a. During this mode, the recycle flow rate increases (Figure 9b) and the flow rate of the fresh feed decreases since this stream is being manipulated to control the reflux drum level. On the other hand, the feed to the column (which is the combination of the fresh feed and the recycled side stream) increases at first due to increases in the recycled stream flow rate, but then eventually decreases as the fresh feed flow rate declines. The distillate and bottom flows follow the same trend as the feed to the column (Figure 9a) as a result of the control system acting to maintain purities as the fresh feed flow rate decreases and the amounts of light and heavy components in the system are reduced (Figure 9c).
Figure 8- Flow rates of (a) feed, (b) product streams and (c) mole fractions during three conventional semicontinuous cycles for feed composition of 45, 10 and 45 mol% of BTX.

At about time 2 hr, the concentration of the side stream reaches the upper defined value of 99.5 mol% percent as shown in Figure 9c, valve V1 opens, and part of side stream is withdrawn as the product (Figure 9a). During this producing mode, the flow rate of fresh feed, distillate, and bottoms increases, which results in a reduction of side stream purity. When the side-stream
purity reaches the defined lower bound of 98.5 mol%, VI closes and the system goes back to the non-producing mode and a new cycle begins.

Figure 9- Cyclic behaviour of SwoMV for separation of BTX with feed composition of 45/10/45 mol%.
During the SwoMV cycles, the purity of the distillate and bottom streams has a minor fluctuation around the desired purity of 99 mol% (Figure 9c) and the purity of the side product fluctuates between the lower and upper bounds. However, with proper controller tuning parameters, the 99 mol% time integral average purity for all three streams is achieved.

For both the conventional semicontinuous and the SwoMV system, weeping and flooding calculations are performed throughout each cycle to ensure that weeping and flooding do not occur at any point during the operation of the column. The Fair correlation is used to calculate the flooding approach (Fair et al, 1997) for this purpose. Typically, columns are designed such that the flooding approach is about 0.75-0.85 (meaning that the flow rates are about 75-85% of the flooding limit), providing enough “wiggle room” to ensure that the approach to the flooding limit never reaches 1.0 (Seider et al., 2008). For example, the flooding profile for each stage in the SwoMV example over the course of four cycles never goes above 0.8, as shown in Figure 10, and therefore remains within safe operating limits.

To calculate the weeping velocities Eqs. (2) and (3) are used (Mersmann et al., 2011):

\[
\begin{align*}
    f_{\text{min}} &= \varphi \sqrt{0.37 d_H g (\rho_L - \rho_V)^{1.25}} \\
    u_{\text{min}} &= \frac{f_{\text{min}}}{\sqrt{\rho_V}}
\end{align*}
\]

where, \( F_{\text{min}} \) is the minimum gas load, \( \varphi \) is the relative free area, \( d_H \) is the tray hole diameter, \( g \) is the acceleration due to gravity, \( \rho_L \) and \( \rho_V \) are the liquid and vapour densities, and \( u_{\text{min}} \) is the minimum vapour velocity required to prevent weeping. The vapour velocities for the top, middle
and bottom stages are calculated for the SwoMV example for the duration of three cycles, and they are well above the minimum velocity, as shown in Figure 11, and thus there is little danger of weeping.

![Figure 11- Vapour and weeping velocities for SwoMV configuration.](image)

### 3.3. Effect of Operational Parameters on SwoMV Configuration

During the producing mode, valve V1 opens, V2 closes partially, and the side product is withdrawn. However, the rate at which the intermediate product is collected is a degree of freedom subject to optimization and has a significant effect on the performance of the SwoMV system. For the example shown in Figure 12, if the side product collection rate is about 1.1 kmol/hr, the collection mode takes about 42 min. Alternatively, if the collection rate is higher (for example, initially about 5.2 kmol/hr), the collection time is much shorter (only about 15 min). Note that the flow rates are not constant because the flow rate for this fully-open value is purely pressure-driven and a function of the composition of the stream, which changes during the collection mode. Therefore, for a given design, the size of V1 (and therefore the approximate flow rate at which it is withdrawn) is the key parameter of interest.

A range of valve sizes (expressed as the valve coefficient $C_v$) is considered for V1 as shown for the 45/10/45 example in Figure 13. Increasing $C_v$ results in a decrease of operating cost per benzene produced and an increase in the benzene production rate up to a $C_v$ of $424 \frac{cm^{1.5} g^{0.5}}{atm^{0.5} s}$. This is because with larger product collection rates, there is less mixing of the purified side draw product with the fresh feed. Consequently, this value is chosen as the optimum valve coefficient for V1 for the 45/10/45 case. Valves larger than that are only marginally better in terms of
operating costs and product flow rates, but would have much higher capital costs, and so are overall less optimal.

Figure 12- Effect of side product removal rate on the performance of SwoMV for the case of feed composition of 45/10/45 mol%.

Another parameter that has been studied is the purity of the side stream. In the SwoMV configuration the purity of the intermediate component in the side product fluctuates between the defined upper and lower bounds, and the final product quality would have approximately the average value of those. Figure 14a shows the mole fraction of toluene in the side stream for three different target product purities, and Figure 14b illustrates how the side product flow rate changes to meet these specifications. In other words, to yield higher purities, higher recycling rates and subsequently longer non-producing modes are required with diminishing returns.

Figure 13- Effect of valve \( V / I \) coefficient on operating cost and benzene production rate for feed composition of 45/10/45 mol%.
Finally, in Figure 15 it is shown that increasing the side stream purity reduces the benzene production rate and increases operating cost per benzene produced as the separation becomes more difficult.
3.4. Effect of feed composition on the profitability of the SwoMV

To investigate the feasibility and the profitability of the novel proposed SwoMV configuration, three cases with different feed compositions have been studied. The economics of the conventional continuous, conventional semicontinuous, SwoMV and side stream configurations are compared over a production range for a wide feed composition range.

The first case is fresh feed with a composition of 45, 10 and 45 mol% of benzene, toluene and o-xylene, respectively. The economic analysis for this case is performed and the results are presented in Figure 16. The total direct costs of these configurations are shown in Figure 16a. As expected, the conventional continuous system has higher costs relative to the conventional semicontinuous and the SwoMV due to the presence of two distillation columns. The conventional semicontinuous system has a lower total direct cost with only one column and a middle vessel. However, for higher production rates, the conventional semicontinuous requires the column to have larger diameters relative to the conventional continuous system and also requires larger middle vessels. This ultimately results in higher total direct cost than the conventional continuous system for high overall production rates (above 30 Mmol/yr of benzene). The SwoMV has even lower capital costs than the conventional semicontinuous system since it requires only one column and no middle vessels. However, the total direct cost increases sharply with the production rate since the diameter requirements increase even faster with production rate. The same trend is observed for the side stream column, but in this case even larger column diameters are required for the separation which results in a sharper slope of this curve.

The corresponding operating costs are presented in Figure 16b. The conventional semicontinuous, SwoMV and side stream systems have higher operating costs than the conventional continuous system due to higher reflux and boil up ratios necessary to achieve the desired purities. However, the TAC for the SwoMV system is lower than the conventional continuous, conventional semicontinuous and side stream systems as shown in Figure 16c for production rates below about 20 Mmol/year of benzene. Overall, for low to intermediate production rates, SwoMV is the most economical configuration, and the conventional continuous system is the most economical for high flow rates. For low flow rates in particular, the TAC savings of the SwoMV system over the conventional continuous one is significant (up to 30%).

The second case study uses an equimolar feed composition with 33, 33 and 34 mol% of BTX, respectively. The economic evaluation is shown in Figure 17. Again, the same basic trends are observed, except that the total direct cost of SwoMV is lower than the other systems over a wider range of benzene production. This is because less recycle is required to bring the MV from 33% to 99 mol% than from 10% to 99 mol%. Therefore, the distillation column in the SwoMV designs do not have to be quite as large, which results in relatively lower direct costs.
Figure 16- Economic evaluations for feed composition of 45/10/45 mol% of BTX. On each subplot, the bottom x-axis corresponds to the benzene production rate, and the top x-axis corresponds to the toluene production rate.
The operating cost of SwoMV in this case (Figure 17b) is approximately the same as the conventional semicontinuous and higher than the conventional continuous system where the side stream column has remarkably higher operating costs than the other configurations. The TAC in Figure 17c shows that SwoMV is always more profitable than the conventional semicontinuous and side stream systems for purification of this feed composition, and more profitable than the conventional continuous system for flow rates below 60 Mmol/yr of benzene.

A third case study is for an intermediate-rich feed composition of 10, 80, and 10 mol% BTX, respectively. The total direct costs of the SwoMV for this case (Figure 18a) is even lower than the conventional semicontinuous as explained before [less recycling is required]. As discussed earlier, the single side stream column configuration is only suitable for intermediate-rich feed compositions since lower vapour boilups are required to obtain the product purities. Therefore, for this case the side stream column has slightly lower direct cost than the conventional semicontinuous system but still has higher cost than the SwoMV configuration. More importantly, the operating cost of SwoMV for this case is lower than the conventional semicontinuous and side stream systems (Figure 18b). The reason for this is that in the conventional semicontinuous system a large portion of the feed (80 mol%) needs to be recycled which adds to the operating costs of the system. Finally, for this case SwoMV is a better choice than the other systems and has a lower TAC over an even wider range of production rates (below 70 Mmol/yr of benzene or equivalently 560 Mmol/yr of toluene, see Figure 18c).

To summarize, the economic comparison of the SwoMV and a single distillation column with a side stream (without any recycling) shows that the SwoMV configuration can reduce the operating and the capital costs of the separation and is therefore a superior configuration. The novel SwoMV concept looks very promising from an economic perspective for a variety of potential applications. Overall, SwoMV tends to be better for applications with lower production rates. The SwoMV system is especially attractive for systems with higher concentrations of the intermediate component in the fresh feed, since it economical at even much larger scales. Interestingly, the conventional semicontinuous system is the opposite and is more attractive for systems with low concentrations of the intermediate component in the fresh feed. However, for our particular example, the conventional semicontinuous was rarely ever more economical than SwoMV.

One additional potential advantage to the SwoMV system over the conventional semicontinuous system is that it better integrates with systems where the feed is produced upstream in a continuous manner. In conventional semicontinuous systems, a second intermediate storage tank (not considered in this analysis) would be needed to link to an upstream process if that upstream process is continuous. For the SwoMV case, the flow rate variation of the feed is much smaller and so any upstream buffer tank required would also be much smaller. However, the difference may not be significant in many cases, as operation and safety requirements might require buffer tanks regardless.
Figure 17- Economic evaluations for feed composition of 33/33/34 mol% of BTX.
Figure 18- Economic evaluations for feed composition of 10/80/10 mol% of BTX.
4. Conclusion

Conventional semicontinuous separation is a relatively new configuration for performing ternary separation in one distillation column (where in conventional continuous systems two columns are typically required). Previous studies have shown the applicability of semicontinuous processes for separation of several chemical mixtures. This study extends the applicability and improves the performance of such systems by proposing a novel configuration called semicontinuous without middle vessel (SwoMV).

Unlike the conventional semicontinuous system, the SwoMV configuration does not use a middle vessel, nor does it require charging and discharging modes of operation, thus saving on capital and installment costs. Therefore, SwoMV not only reduces the total direct costs of the system but also facilitates the retrofit of available distillation columns for ternary purification. Furthermore, the new configuration improves the conventional semicontinuous system by reducing the operating costs for a range of feed compositions and extending the economically optimal range of production.

The separation of BTX is selected as a case study to investigate capabilities of the SwoMV configuration. However, it should be noted that the SwoMV concept should work for any non-azeotropic ternary mixture with sufficiently different relative volatilities. In this study, the column and the proper controller system are designed for the BTX separation application. The economics of SwoMV is compared to conventional continuous, conventional semicontinuous and single side stream column systems for three cases of feed compositions applied to a wide range of process scales. The results show that the total annualized cost of SwoMV is generally lower than the other configurations for the range of production rates studied. For example, for the purification of feeds with a higher proportion of intermediate components, SwoMV has lower TACs than the conventional semicontinuous system for a wider range of production rates, and also has lower operating costs. For instance, for production of 515 Mmol/yr of toluene, SwoMV has 42% less total direct cost, 45% less operating cost and 43% less total annualized cost relative to the conventional semicontinuous configuration and also has expanded the economical production range of conventional semicontinuous system by 44.5%. This result helps to extend the range of applicability for semicontinuous approaches. Furthermore, SwoMV also outperforms the single side stream column for all feed compositions and has a lower operating and direct costs.

Finally, the novel SwoMV configuration is a suitable ternary separation technique for processes such as pharmaceutical products, biofuels and specialty chemicals, where typically the production rate is low. Future studies should focus on application of SwoMV configuration to other processes to demonstrate its performance relative to conventional continuous and semicontinuous systems as well as determine the optimum column parameters via dynamic optimization to further improve the economics of this process. In addition, since the system is control driven, improvements in the control system would have a considerable effect on the performance of the system. To the best of our knowledge, only PI control has been used in all
proposed semicontinuous system processes. Therefore, the use of model predictive controllers in semicontinuous processes is an area of future research.

**Nomenclature**

\[
B \quad \text{Benzene} \\
C_v \quad \text{Valve coefficient } \left( \frac{cm^{1.5} gr^{0.5}}{atm^{0.5} s} \right) \\
d_H \quad \text{Tray hole diameter (m)} \\
f_{\text{min}} \quad \text{Minimum gas load (Pa}^{0.5}) \\
g \quad \text{Acceleration due to gravity (m/s}^2) \\
N \quad \text{Number of stages} \\
T \quad \text{Toluene} \\
\text{u}_{\text{min}} \quad \text{Minimum vapour velocity (m/s)} \\
V \quad \text{Valve} \\
X \quad \alpha\text{-xylene}
\]

**Greek Letters**

\[
\rho_L \quad \text{Liquid density (kg/m}^3) \\
\rho_V \quad \text{Gas density (kg/m}^3) \\
\varphi \quad \text{Relative free area}
\]

**Abbreviations**

\[
\text{BTX} \quad \text{Benzene, Toluene, } \alpha\text{-Xylene} \\
\text{CSC} \quad \text{Conventional semicontinuous} \\
\text{ISE} \quad \text{Integral squared error} \\
\text{MV} \quad \text{Middle vessel} \\
\text{NRTL} \quad \text{Non-random two-liquid} \\
\text{SwoMV} \quad \text{Semicontinuous without middle vessel} \\
\text{TAC} \quad \text{Total annualized cost ($/yr)} \\
\text{VLE} \quad \text{Vapour liquid equilibrium}
\]
References


