Constrained Purification of Dimethyl Ether

Purification of fuel grade Dimethyl Ether in a ready-to-assemble plant

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ABSTRACT

Due to the remote and dispersed nature of Alberta's oil wells, it is not economical for the energy industry to capture all of the solution gas produced and as a result, the gas is being flared and vented in significant amounts. The objective of this research is to aid in the conversion of solution gas into dimethyl ether (DME) in a remote location by designing a distillation column that purifies DME and its reaction by-products, carbon dioxide, methanol and water.

In order to develop an implementable solution, the distillation equipment must fit inside of a 40-foot shipping container to be transported to remote locations. Given the size constraint of the system, process intensification is the best strategy to efficiently separate the mixture. Several process intensification distillation techniques are explored, including semicontinuous distillation, the dividing wall column (DWC) and a novel semicontinuous dividing wall column (S-DWC).

The traditional semicontinuous distillation column purifies DME to fuel grade purity, however the other components are not separated to a high enough grade given the height constrain of the system. The DWC and S-DWC both purify DME to its desired purity along with producing high purity waste streams. The S-DWC purifies the reaction intermediate methanol to a grade slightly higher than the DWC and is pure enough to recycle back to the reactor.

An economic comparison is made between the three systems. While the DWC is a cheaper method of producing DME, the trade-off is the purity of the methanol produced.

Overall, this research shows that it is possible to purify DME and its reaction by-products in a 40-foot distillation column at a cost that is competitive with Diesel.

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LIST OF ABBREVIATIONS

ACCE	Aspen Capital Cost Estimator
CCA	Capital Cost Allowance
CO_2	Carbon Dioxide
DME	Dimethyl Ether
DWC	Dividing Wall Column
H_2O	Water
MeOH	Methanol
MV	Middle Vessel
PPDP	Product and Process Design Principles
S-DWC	Semicontinuous Dividing Wall Column
SwoMV	Semicontinuous without Middle Vessel

DECLARATION OF ACADEMIC ACHIEVEMENT

All research studies presented in the thesis was executed and written by Sarah Ballinger under the supervision of Dr. Thomas Adams. This thesis contains material that was submitted to the journal Computers and Chemical Engineering for peer-review, and is reproduced here according to Elsevier's policies.

CHAPTER 1 INTRODUCTION

1.1 Motivation

1.1.1 Flare gas

A major problem facing Alberta's energy industry is the flaring and venting of solution gas from crude oil and crude bitumen production operations. Solution gas is natural gas that is dissolved in crude oil before extraction, and is released at atmospheric pressure. Oil producers are making a great effort to capture these gasses and use them downstream, however due to the dispersed and remote nature of oil production in Alberta, it is not always economical to capture the solution gas; the uncaptured gas is flared or vented to the atmosphere. According to the Alberta Energy Regulator, the energy industry captured 95.6 per cent of solution gas produced in 2014, up from 95.3 per cent in 2013, however not as high has 96.3 per cent in 2005 [1]. Alberta's legislation on flaring, incineration and venting at upstream petroleum wells puts a daily limit on the amount of gas discharged at each extraction site. All solution gas flares and vents that exceed this limit must implement gas conservation technologies if the NPV of the effort is greater than negative $55,000 [2]. Low natural gas prices and high pipeline and compression costs challenge the economic viability of gas conservation [1]. Conversely, failing to generate useful energy from the flared gas relinquishes the opportunity to offset electricity production from Diesel generators at the high cost of \$0.40/kWh [3]. As such, the solution to the problem of flaring and venting unwanted gas at dispersed petroleum wells is to convert the energy into a useful form using economical and small-scale technology.

1.1.2 Dimethyl Ether

Dimethyl ether (DME) is the simplest aliphatic ether and is a non-toxic, non-corrosive, and non-carcinogenic odourless gas [4]. It can be produced from a variety of feedstocks including natural gas and organic material. DME has similar physical properties to liquefied petroleum gas, and as such, it can be transported using the existing infrastructure [5].

1.1.2.1 Dimethyl ether as a fuel alternative

Dimethyl ether is a new fuel that is becoming a popular alternative to traditional combustion fuels. DME has traditionally been used as a propellant and was first considered as a fuel alternative after oil prices increase in the 1970’s and 1980’s [5]. A study by the Volvo Group comparing seven renewable fuels found DME as the leading fuel alternative in terms of cost, energy efficiency, land use, environmental impact, fuel potential, vehicle adaptation, and fuel infrastructure [6].

A favourable property of DME is that it can be used in a Diesel engine. Only small adjustments need to be made to the engine: the fuel injection system and the lubricity of the fuel must be transformed [5]. In comparison to Diesel, DME burns significantly cleaner, creating no sulphur oxide or particulate emissions and producing minimal nitrous oxides and carbon monoxide [4]. One drawback of DME is that it has a density about 80% of diesel (at recommended storage conditions) and its specific energy content is about 70% of the energy content of Diesel; therefore, it is necessary to inject twice the fuel volume to yield the same power output as Diesel [5].

1.1.2.2 Dimethyl ether production routes

Dimethyl ether is commonly produced using one of two production pathways: a two-step and a one-step process. The two-step process first converts the syngas feedstock to methanol through the water-gas shift and methanol formation reactions. In the following step, cleaned methanol is dehydrated to form DME. The product out of the DME reactor is a mixture of DME, unreacted methanol and water. This process is particularly useful since the production of methanol from natural gas is a mature industry and DME production can be added to existing methanol plants. On the other hand, the one-step process combines these reactions in one reactor and produces DME directly from syngas, with methanol being a reaction intermediate. In the single reactor, the water produced in the dehydration step helps drive the water-gas shift reaction forward, resulting in a higher conversion rate than the two-step process. Since there is no intermediate clean-up of methanol, the product out of the one-step reactor is a mixture of four components: DME, methanol, water (H_2O) and carbon dioxide (CO_2) [5].

1.1.3 Commercial opportunities

Due to restrictions on solution gas flaring and venting, oil producers are interested in the development of technologies that convert raw natural gas into a useful product, such as dimethyl ether. Pioneer Energy and ChemBio Power are two companies developing technologies that will transform solution gas into dimethyl ether at petroleum wells [3, 7].

Pioneer Energy has “developed and tested a novel Mobile Methanol and Dimethyl Ether manufacturing system” [8]. The system converts flare gas into methanol and dimethyl ether using equipment sitting on the bed of a truck. The products are then used for energy on-site or shipped to external markets. The technologies have been patented and are ready for commercialization [3, 9]. The DME production technology first uses an absorption column to separate the CO_2 from the DME mixture, then uses a distillation column to purify the DME from the water and methanol [9].

Another company interested in harnessing the energy in flared and vented gas is ChemBioPower, a small company focused on developing the technology necessary for power and heating applications of DME. They are interested in producing a turn-key solution to transition all generators into using DME instead of Diesel [7]. ChemBioPower has expressed direct interest in developing a separation unit for a DME production process at petroleum wells. The inspiration for this project came from ChemBioPower; they provided the reactor product composition and the specific space restrictions in which the process equipment must fit (a shipping container) [10].

Additional possible applications of a small scale DME production facility include the transformation of other distributed methanol sources such as landfill gas or the decomposition of manure [5].

1.2 Background

1.2.1 Process intensification

As global efforts increase to improve the efficiency of all industrial processes, major chemical plant improvement is demonstrated with process intensification. Process intensification is defined as the drastic reduction in size, energy usage or waste production from a chemical plant [11]. These improvements are more easily developed because of recent advancements in computational speed making it faster to explore less common configurations of chemical processes [12]. Distillation, an energy intensive separation unit, has seen significant research in the area of process intensification. Examples of intensified distillation are semicontinuous distillation, semicontinuous without middle vessel distillation and diving wall distillation.

1.2.2 Traditional Semicontinuous Distillation

Traditionally, distillation columns have been used in batch and continuous operation, with both forms requiring one less column than the number of components in the mixture to be separated effectively. Semicontinuous distillation, on the other hand, uses a single column to separate any number of components, replacing the deleted columns with simple tanks. This type of process was first described by Phimister and Seider in 2000 and is depicted in Figure 1 [13].

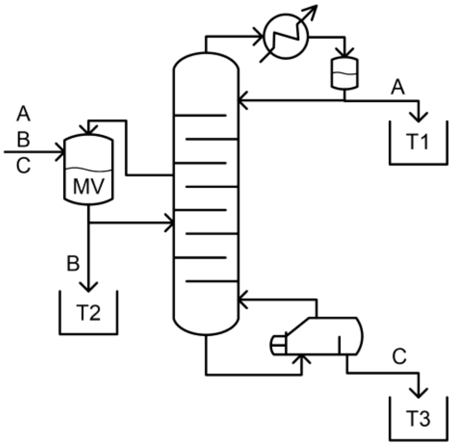

Figure 1: Schematic of a semicontinuous distillation column with a middle vessel. Adapted from [13].

The operation of a semicontinuous distillation column can be described by considering a ternary equimolar mixture of A, B and C. Semicontinuous distillation requires a single column with a large vessel (MV) connected between the rectifying and stripping sections. Tanks T1, T2 and T3 collect the high purity streams of A, B and C respectively. During operation, a liquid stream from the rectifying section is continuously sent to the middle vessel, and liquid from the vessel is sent back to the top of the stripping section of the column. As flow rates are adjusted throughout the column, components A, B and C are removed at high purities [13].

The column operates in three modes. During Mode 1, the middle vessel (MV) is quickly charged with the mixture of A, B and C. Once the vessel is full, Mode 2 begins. During Mode 2, the liquid from the MV is fed to the column. The lightest and heaviest components, A and C, separate from B at the top and the bottom of the column and are collected in tanks T1 and T3 respectively, in a continuous stream. As these components are removed from the system, the purity of B in the MV increases. As a result of the decrease in A and C in the MV, the amount of A and C in the stream entering the column also diminishes, this requires the flowrates of the distillate and bottoms to reduce to maintain their purities. Once the composition of MV achieves the desired purity, such as 98% B, the contents of MV are drained into T2; this is Mode 3. After MV is drained to a nominal level, Mode 1 begins again with the vessel being refilled with an equimolar mixture of A, B and C [13].

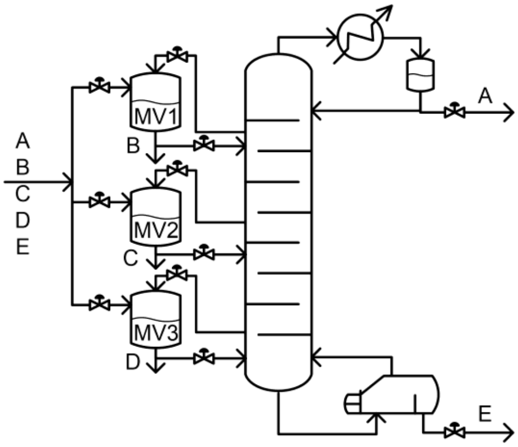

Figure 2: Semicontinuous distillation set up for the separation of a five component mixture. Adapted from [14].

Semicontinuous distillation columns are not limited to separating ternary mixtures. Wijesekera and Adams demonstrated distillation processes that purify four or five components with one column and two or three middle vessel tanks [15, 14]. The five-component configuration is shown in Figure 2. The most and least volatile components are drawn as the distillate and bottoms streams of the column, while the three middle components concentrate in the three middle vessels. This study used the results of the quintenary separation to generalize semicontinuous distillation to separate any number of components using one column and two less middle vessel tanks than components [14]. As a result, there are endless applications for semicontinuous distillation.

The major advantage to operating a distillation column in a semicontinuous manner is the economic benefit. The capital investment required is greatly reduced compared to continuous distillation [12] and the operating costs are significantly lower than batch distillation. As a result, semicontinuous distillation is cheaper than both batch and continuous distillation for intermediate production rates [16, 17]. Figure 3 shows the crossover points where each separation strategy becomes most economical. At very low throughputs, the capital cost of a batch distillation column is much smaller than the other two forms, while at very large throughputs, economies of scale take hold and continuous operation has the lowest operating cost. In the middle, semicontinuous distillation becomes most economical because it uses the best of both strategies.

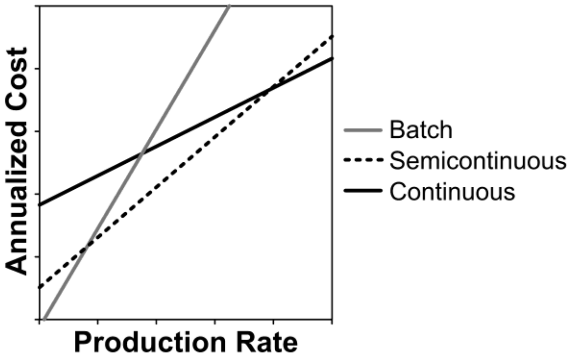

Figure 3: Generalized sketch of the total annualized cost of different separation strategies at a variety of production rates. Adapted from [16]

Due to its economical and compact advantages, semicontinuous distillation is a great candidate to use as a separation unit used in the production of DME at petroleum well sites. Pascall and Adams studied semicontinuous distillation for the production of DME and were able to perform a ternary separation with the DME reaction by-products. They were able to separate the two-step reaction by-products DME, methanol and water into three high purity streams [18]. In addition, they separated the one-step reaction by-products, CO_2, DME, methanol and water using a partial condenser, and combining the methanol and water at the bottom of the column [19]. To date, the separation of the four one-step reaction by-products has not been demonstrated with semicontinuous distillation in the open literature.

1.2.3 Semicontinuous Distillation without Middle Vessels

In order to improve upon the limited flow rate of semicontinuous distillation, semicontinuous distillation without a middle vessel (SwoMV) was developed to increase the throughput of the process and decrease the overall cost. The SwoMV configuration is shown in Figure 4 using the ternary mixture of A, B and C. There are a few defining differences between the SwoMV and conventional semicontinuous distillation processes. The column is fed with fresh feed continuously in the SwoMV configuration (although at variable flow rates), and the destination of the side stream changes throughout each cycle. During the non-producing mode, the side draw is recycled and mixed with the feed stream to enter the column again. The purity of the side draw increases over the period of this mode. Once the purity of component B in the side draw meets an upper bound, the side draw is diverted from being recycled and is collected as product. During this mode, the purity of the side draw decreases until it meets the lower bound. At this point in time, the product stops being collected and the side draw returns to being recycled. The end result of the SwoMV configuration is a column that produces components A and C continuously but at a variable continuous flow rates, and B intermittently [20].

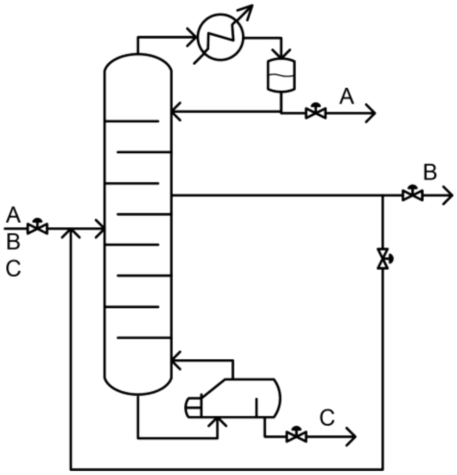

Figure 4: Schematic of the Semicontinuous without Middle Vessel System. Adapted from [20].

An advantage of the SwoMV configuration is the increased economical range of production rates due to the reduced capital cost and operating cost compared to conventional semicontinuous distillation. Also, this configuration allows existing distillation columns to be retrofitted to be able to remove a third component [20]. Some disadvantages of the SwoMV configuration are a result of the process being in a single unit; the column is limited to one operating pressure and has larger temperature differences [21]. Also, the unit is restricted to a small range of economical throughputs. The SwoMV configuration has been demonstrated for the purification of a benzene, toluene and o-xylene mixture [20], however no one has used it to separate DME from its reaction by-products or for four-component mixtures.

1.2.4 Dividing Wall Distillation

The dividing wall column (DWC) is another process intensification separation technology that operates more economically and energy favourably than continuous distillation systems. The DWC configuration is shown in Figure 5, and the column is run continuously to separate a three-component mixture in a single shell with a sheet partitioning the middle section of trays. The intermediate component B accumulates on the right side of the wall and is directly withdrawn in a side draw stream. The most and least volatile components, A and C, are withdrawn as the distillate and bottoms streams. Since there is only one column and two heat exchangers to separate three components, this configuration not only has a lower capital cost, but also is more energetically favourable than continuous distillation [22]. However, with only one column, the process is limited to one operating pressure and a higher temperature difference between the distillate and bottoms [21]. For certain situations, continuous DWC are cheaper than conventional continuous distillation [22].

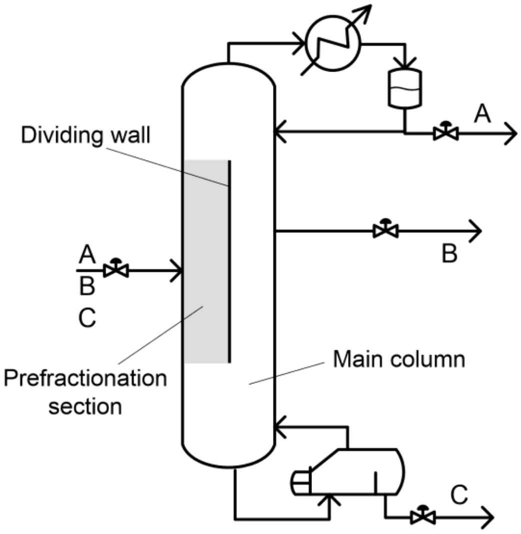

Figure 5: Schematic of a Dividing Wall Column. Adapted from [22].

The use of a dividing wall column for the purification of dimethyl ether has been studied and found to be more economical than the conventional DME production route. Kiss and Ignat modeled the production of ultra-high purity DME, methanol and water using only one column by using a dividing wall column and by considering several different configurations [23]. Kiss and Suskwalak combined reactive distillation with a divided wall column to dehydrate methanol to produce DME, methanol and water [24]. Minh, et al. separated the four one-step reaction by-products using only two dividing wall columns with significant energy savings compared to continuous distillation [25]. Even though recent process intensification studies have made large advances in the efficiency of DME production, purifying DME from its one-step reaction by-products in a single column (a four species mixture) has not been shown yet.

1.3 Objectives

The objective of this research is to design and analyze a portable system that can help produce DME from raw natural gas in a remote location. An intensified process is likely the most economical option since the dispersed nature of the DME plants necessitates low production rates. The goal of this thesis is to develop a separation unit using the process intensification techniques mentioned above that can be used to purify DME from its reaction by-products at a petroleum well with equipment that is small enough to transport using standard shipping systems. The cost of the DME produced should be competitive with Diesel delivered to the petroleum wells. The reaction pathway chosen is the one-step reaction pathway because it is requires a less complex system and is more efficient than the two-step pathway. As such, the inlet feed to the separation process is a mixture of CO_2, DME, methanol and water.

The following work explains a solution to the problems described above. First, the conventional semicontinuous distillation is able to purify the by-products in a compact column. Secondly, the dividing wall column will be used to determine if it can produce high purity DME. Lastly the dividing wall column and SwoMV operation will be combined to purify DME in a manner that is competitive with the diesel market.

CHAPTER 2 METHODOLOGY

2.1 Design specification

The inspiration for this project and the main design constraints were provided by ChemBioPower. ChemBioPower is developing technology to transform raw natural gas into dimethyl ether using the single-step syngas to DME reaction pathway. They require a separation unit to purify the DME to fuel grade purity. The goal of this project is to design a system to meet their requirements.

The product constraints of the separation unit, provided by ChemBioPower, are outlined in Table 1. The input to the separation unit is a mixture of carbon dioxide (CO_2), DME, methanol and water. The actual reactor output has trace amounts of carbon monoxide, hydrogen, methane and oxygen; however these components are ignored in this project. The required purities of the components depend on their end uses; DME and methanol are fuel alternatives while carbon dioxide and water are considered waste streams. Methanol is also a reaction intermediate in the syngas to DME one-step pathway. If it is not possible to obtain methanol at fuel grade purity (99.85%), concentrated methanol can be recycled to the reaction unit to be used to push the reaction forward. The actual feed conditions used in this work were chosen from the range shown in Table 1, but are redacted for industrial confidentiality.

Table 1: Inputs and desired outputs of the separation unit

Component	Feed purity (mol%)	Final desired purity (mol%)
Carbon Dioxide (CO_2)	18-24%	99.5%
Dimethyl Ether (DME)	25-32%	98.5% (fuel grade)
Methanol	6-12%	99.0% (recycle grade)
Water	38-45%	99.5%
Feed Temperature	190-210°C	
Feed Flow Rate	4-6 tonne/hr	

In order to provide a turnkey solution to multiple remote petroleum wells, the cost of shipping the equipment must be kept low. As a result, ChemBioPower is only interested in a separation unit that is small enough to fit inside of a 40-foot shipping container in order to use the global shipping network for delivery [10]. The exterior and interior dimensions of a standard shipping container are listed in Table 2, as well as the maximum weight restriction. Industrial scale distillation columns are typically much taller than 40 feet, therefore it will be a challenge to fit the separation unit inside this dimension.

Table 2: ISO 1AA 40' Shipping container dimensions [26].

	Height	Width	Length	Rating
Exterior Dimensions	2,591mm (8ft 6in)	2,438mm (8ft)	12,192mm (40ft)	30,480 kg
Interior Dimensions	2,350mm (7ft 9in)	2,330mm (7ft 8in)	11,998mm (39ft 4in)	

The final constraint imposed by ChemBioPower is the total cost of the project. Dimethyl ether can economically replace Diesel at $0.54 per litre of DME when the price of diesel is \$1.01 per litre [7]. Since separation costs generally make up over half of the cost of a pure substance [27], a conservative design criteria used in this study is to keep the cost of separation for DME to under \$0.25 per litre.

Overall, the goal of this project is to separate DME to fuel grade purity from its reaction by-products in a 40’ foot distillation column at a cost of \$0.25 per litre.

2.2 Process Modelling

The separation unit was modeled using Aspen Plus V8.8 including both the steady state (Aspen Plus) and dynamic simulators (Aspen Dynamics). The vapour-liquid equilibrium properties were modeled using the Peng-Robinson equation of state, the Wong Sandler mixing rule and the UNIFAC model for calculating the excess Helmholtz energy. This property method (PRWS-UNIFAC) was selected because it has been proven experimentally to predict efficiently the vapour-liquid behaviour of the quaternary, ternary and binary systems [28]. The distillation units were modeled using the `Rad-Frac` model, which performs rigorous equilibrium-stage calculations. The column uses sieve trays with an assumed pressure drop of 0.1psi (0.0068atm) per stage and a Murphree efficiency of 85% for all stages. In dynamic simulations, PI controllers were used because they are easy to implement and require no knowledge of the highly non-linear underlying system.

Previous work has been done to optimize semicontinuous distillation and streamline the modeling, using gPROMS [17]. It was not possible to use this method because the property packages are limited in gPROMS and do not include dimethyl ether in its database.

CHAPTER 3 PROCESS DESIGN AND RESULTS

3.1 Case 1: Quaternary Semicontinuous Distillation

3.1.1 Process Description

The first process studied as a solution to separate DME in a 40-foot column is quaternary semicontinuous distillation. The proposed process has a similar configuration to the general form of the quaternary process described by Wijesekera and Adams [15]. A schematic diagram of the process is shown in Figure 6. The distillation column purifies the reactor product using a partial-condenser, a kettle reboiler and a 25 tray column with 18-inch spacing. The tray sizing calculations done by Aspen Plus show that the required diameter of the column is 3 feet. Liquid is fed to the column from two middle vessels that are filled with fresh feed each cycle. The column operates and produces a vapour distillate containing concentrated carbon dioxide and a bottoms stream with nearly pure water. The two side streams collect liquid rich in DME and methanol and recycle them to the two middle vessels. As the cycle progresses, DME and methanol concentrate in the middle vessels (DME in MV1, methanol in MV2), until their desired purities are met. The quaternary separation was modelled using one `RadFrac` distillation column, two flash drums as middle vessels and two pumps to withdraw the side draw liquids.

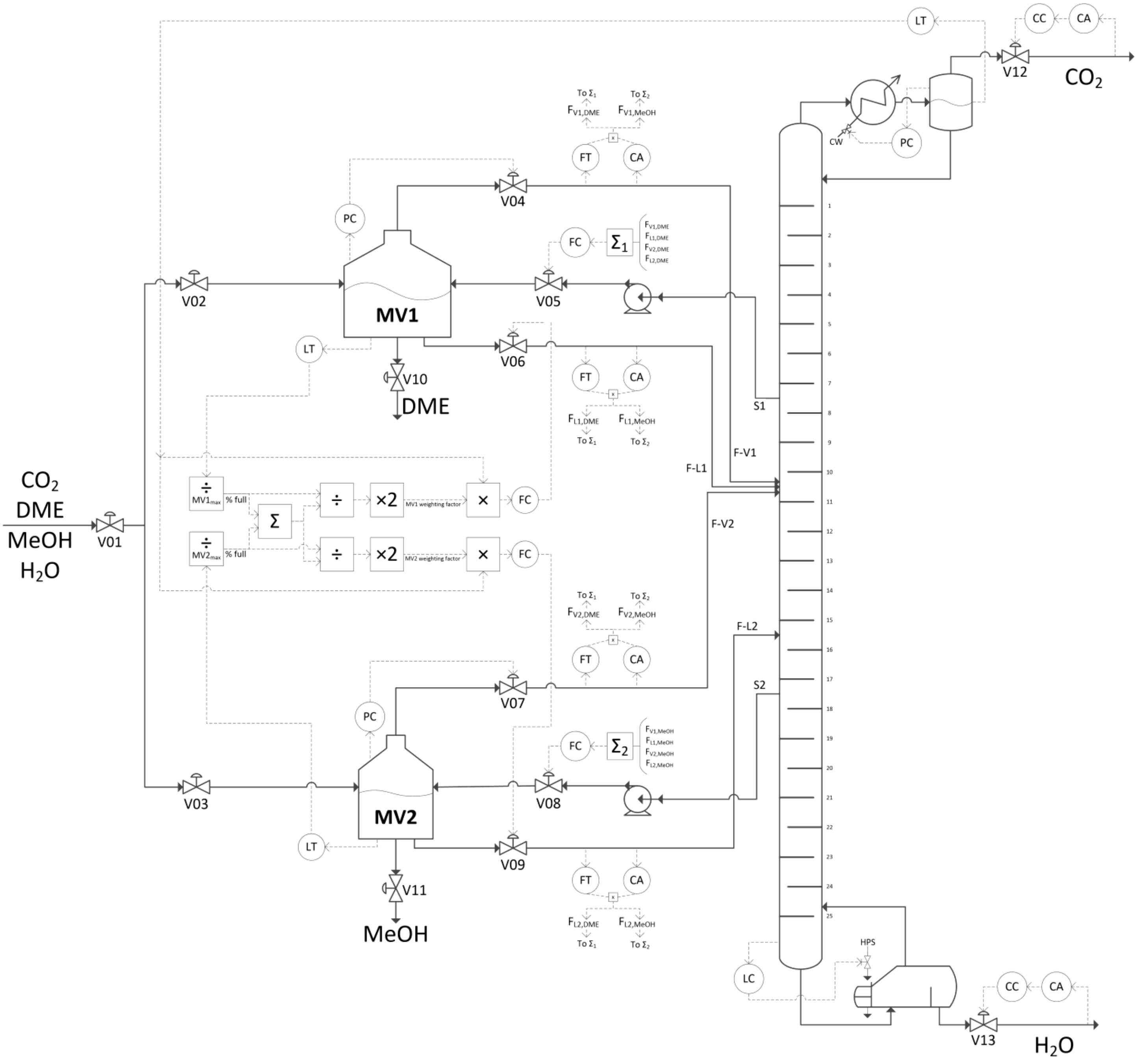

Figure 6: Schematic diagram of the quaternary distillation column that purifies DME from its reaction by-products. The control scheme is also illustrated.

3.1.2 Control System

The quaternary semicontinuous distillation column uses the control configuration that has been found to provide the best control for semicontinuous distillation by Pascall and Adams [18]. The control scheme is shown in Figure 6 and uses exclusively PI controllers. The distillate and bottoms flows are drawn continuously and their purities are controlled by their respective flow rates. The condenser and reboiler duties control the pressure inside the condenser and the liquid level in the sump, respectively. The liquid level in the condenser drum is controlled by the total flow rate into the column. Since there are two liquid streams entering the column, the controller-determined change in total inlet flow rate is distributed to each stream proportionately to the level of liquid inside its middle vessel. This division of flow rate change is clearly depicted in Figure 6. The pressure of each middle vessel is controlled by the vapour flow rate from the middle vessels to the column. All of the aforementioned flows and control loops operate continuously throughout the cycle's modes.

The column operates by cycling through three modes. At the beginning of the cycle, Mode 1, the middle vessels are charged with fresh feed. Each middle vessel is charged with a volume proportionate to the amount of that species in the feed, following the heuristic suggested by Wjesekera and Adams [15]. MV1 is fed with 4.2 times the volume of MV2 since the feed is 25% DME and 6% methanol. Once the vessels are filled to the desired amount, the feed valve is shut off and Mode 2 begins. The liquid and vapour streams from the middle vessels are continuously fed to the column and the DME and methanol rich side streams are returned to their respective middle vessels. Once the purity of the MV1 reaches 98.5% DME, Mode 3 occurs by draining both vessels. Mode 1 begins again by refilling the middle vessels with fresh feed.

3.1.3 Column Performance

The quaternary semicontinuous distillation column is able to meet some but not all of the design specifications. This result is the best output possible after much manipulation of parameters by hand; the results may be improved with a more systematic method of parameter optimization.

DME and water are purified to their desired purities; however, the purities of methanol and CO_2 are not at their desired targets. The average purities throughout are calculated by weighting the purity with the flow rate of the stream at each time step. All averaged variables are calculated using Simpson's 3/8 rule [29].

Figure 7 shows the chemical composition of the liquid phase in MV1 throughout time. The desired saw-tooth shape is seen as DME reaches 98.5 per cent purity at the end of every cycle before it is drained and refilled with fresh feed. This figure shows all cycles from the beginning of the simulation until an apparent steady cycle is repeated. The simulation was run for over 60 hours, and the cycle times increased over this time, however the purity of DME was reached every time. The call-out of three cycles shows the same data in more detail and represents the three cycles that will be shown in subsequent figures.

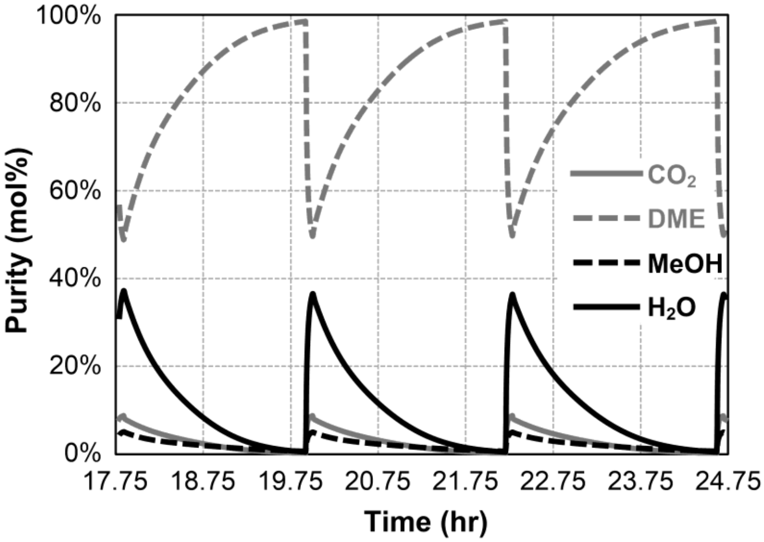

Figure 7: The composition of the liquid phase in MV-1 throughout 16 cycles, starting from steady state. The callout shows the three cycles that will be focused on for the analysis.

The chemical composition of MV2 is shown in Figure 8. The purity of the methanol reaches only 94 per cent before the purity of MV1 triggers both middle vessels to be drained. The main impurity in MV2 at the end of the cycle is water. It is more difficult to separate methanol and water than the other two components in the system because they have a low relative volatility.

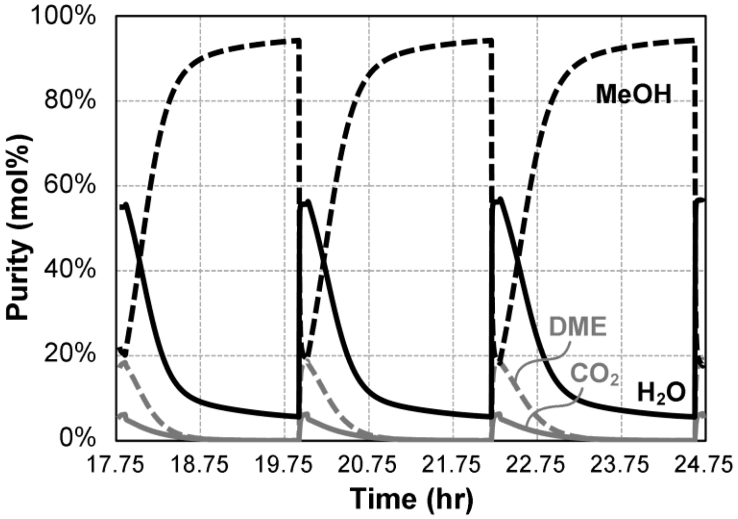

Figure 8: The composition of the liquid phase in MV-2.

The liquid level in each middle vessel can be seen in Figure 9. The level decreases as the impurities are removed during each cycle, and then the vessels are drained and refilled, shown by the abrupt changes. The amount of DME and methanol collected is calculated based on the change in volume of liquid inside each middle vessel.

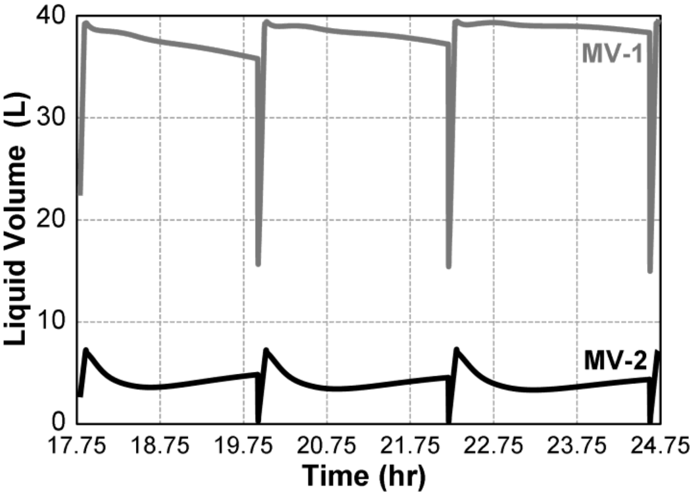

Figure 9: The liquid volume inside the middle vessels during three cycles.

The purities and flow rates of the distillate and bottoms streams can be seen in Figure 10 and Figure 11. The average purity of the bottoms stream is 99.55 per cent water, while the average purity of the distillate stream is 92.86 per cent carbon dioxide. The flow rate of the bottoms stream fluctuates smoothly to maintain its purity, whereas the flow rate of the distillate is zero for most of the cycle since the purity is far below the set point of 99.5 per cent.

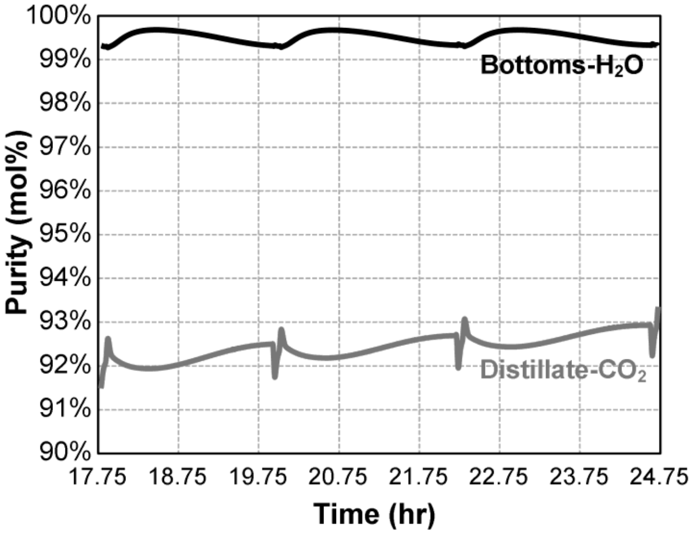

Figure 10: The purity of the distillate and bottoms streams over three cycles.

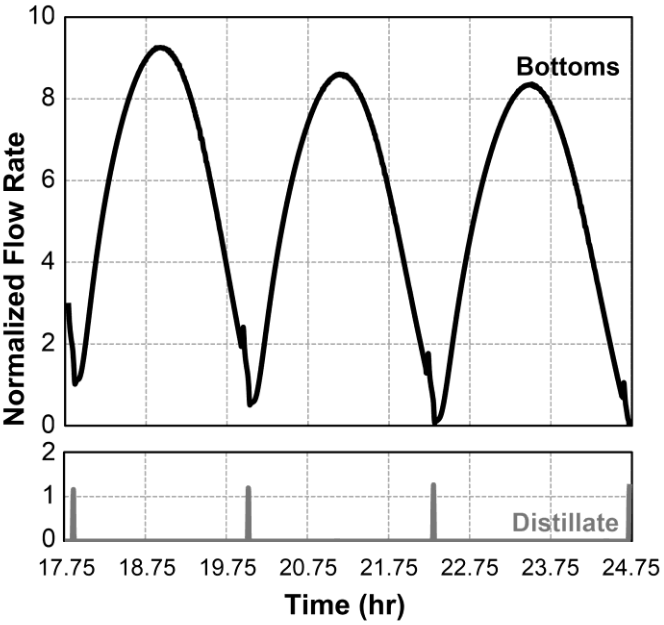

Figure 11: The outlet flow rates of the distillate and bottoms streams.

The power required to reboil and condense the fluid inside the distillation column is shown in Figure 12. The two duties track each other well within each cycles, with abrupt changes occurring when the mode of the cycle changes. The average of the duties are calculated in Table 3.

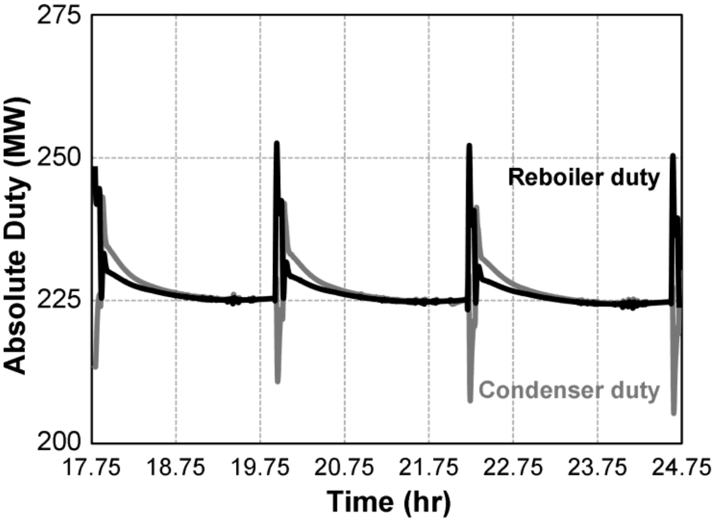

Figure 12: The absolute duty of the condenser and reboiler over three cycles.

Table 3: The average duty used by the semicontinuous distillation column.

	Condenser	**Reboiler**
Average Energy Use	226.6 kW	226.9 kW

Table 4 summarizes the average purities and flow rate of the semicontinuous system. The purity of the CO_2–rich stream is far from its setpoint with its main impurity being DME, meaning the DME in this stream is wasted. Also, the distillate has a very low average flow rate, much lower than the CO_2 entering the system. This suggests that the CO_2 is accumulating within the system and a stable limit cycle has not been reached. It is also apparent that CO_2 is accumulating in the system by looking at the increasing cycle times of each cycle in Figure 7 since it is becoming more and more difficult to remove CO_2 from MV1. Additionally, the methanol purity achieved in the middle vessel is not high enough to be effectively recycled back to the reactor.

Table 4: The average purity and DME flow rate of the three cycles studied. The other flow rates are redacted for industrial confidentiality.

	Average Purity (mol%)	**Average Flow rate (mol/hr)**
CO_2	92.86%	
DME	98.51%	120.6 mol/hr
Methanol	94.19%	
H_2O	99.55%	

Overall, this process does not fulfill all of the requirements proposed by ChemBioPower. The main two requirements of the column being under 40’ and the purification of fuel grade DME are achieved. Additionally, the water is purified to its high purity set point. On the other hand, the purities of the CO_2 and methanol streams are not as high as desired. By following traditional semicontinuous design method of manipulation the system’s variables by hand [14, 15, 18, 19], it is not possible to design a 40-foot column that separates DME from its reaction by-products. It appears as though the fundamental problem with the purification of DME is the column’s height restriction. A systematic approach to parameter modification would be required to determine if this hypothesis is indeed true.

The design method developed by Meidanshahi and Adams would be a candidate for systematically designing a semicontinuous distillation column. Their method uses gPROMS to choose both the design and control parameters through outer approximation optimization using built-in models for the controllers and the equipment [17]. However, this method cannot be used because DME is a not in the main chemical database of gPROMS and technical limitations of the optimization software built into gPROMS prevent the use of external databases such as MultiFlash for chemical properties. With the current semicontinuous distillation design methods, the quaternary semicontinuous distillation column fails to meet all of the design criteria of this project.

3.2 Case 2: Continuous Dividing Wall Distillation

3.2.1 Process Description

The second process intensification technique studied is the dividing wall distillation column. Two different dividing wall distillation column designs were analyzed in this section. The column of the first design is under 40-foot tall whereas the second column is designed to meet all other constraints other than the height requirement. Both DWC were modelled in Aspen Plus V8.8, using the steady state simulator. In the first design, the column shown in Figure 13, has 28 trays, 15 of which are spaced at 18 inches and 13 are spaced at 12 inches. In the second design, the column shown in Figure 14, the column has 38 trays, all of which are spaced 18 inches apart. The smaller tray spacing at the bottom of the first column is possible because the bottom half of trays has lower vapour flow rates than the top half. This means that trays at the bottom can be stacked more closely without risking flooding. Fair flooding calculations were performed to verify this allowing more trays to be packed into the column with the restricted height [30]. The shorter DWC has a dividing wall that starts below the fourth tray from the top and ends above the fourth tray from the bottom. The dividing wall in the taller column starts below the fifth tray from the top and ends above the fifth tray from the bottom.

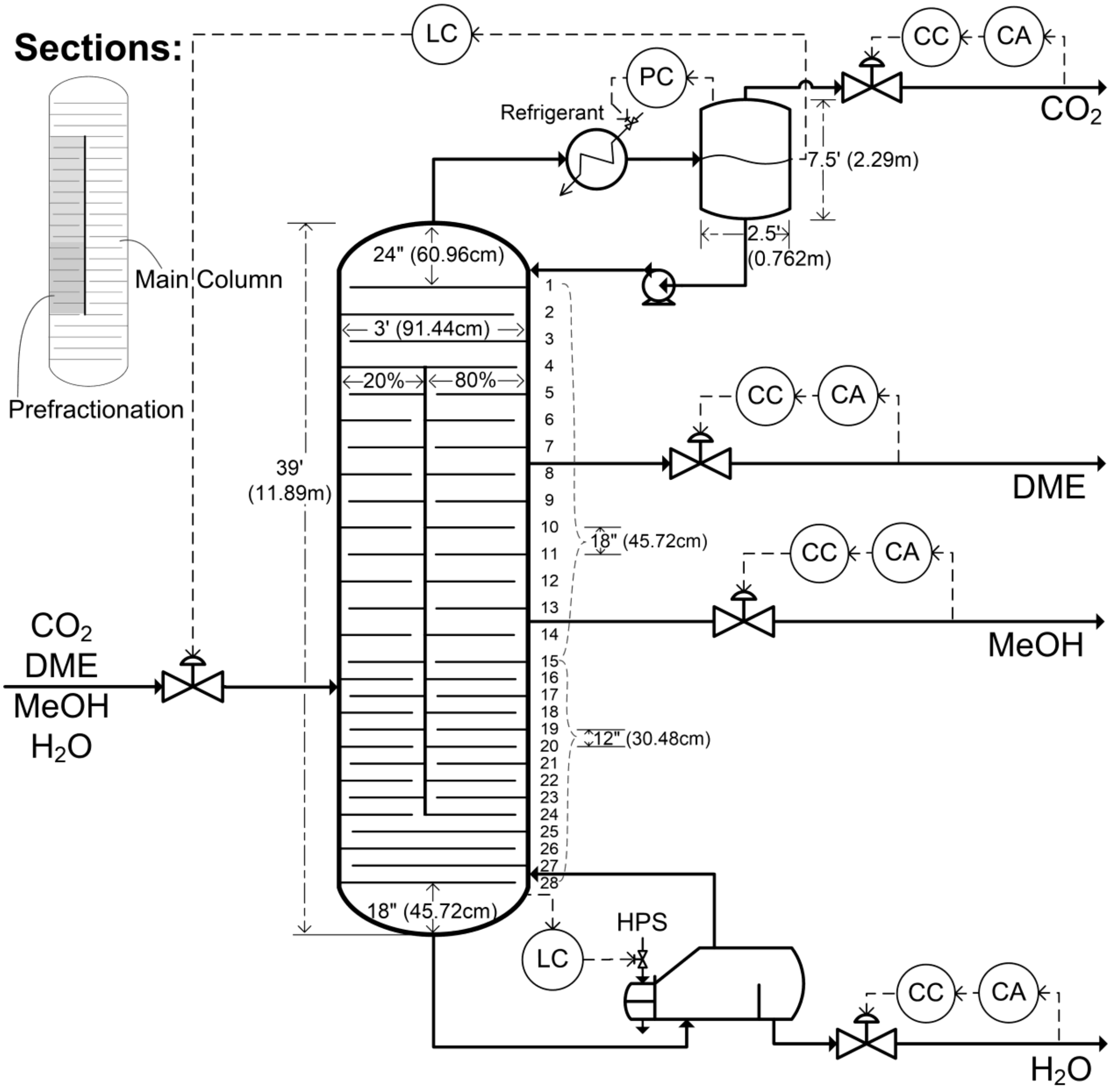

Figure 13: A schematic of the DWC with 28 trays.

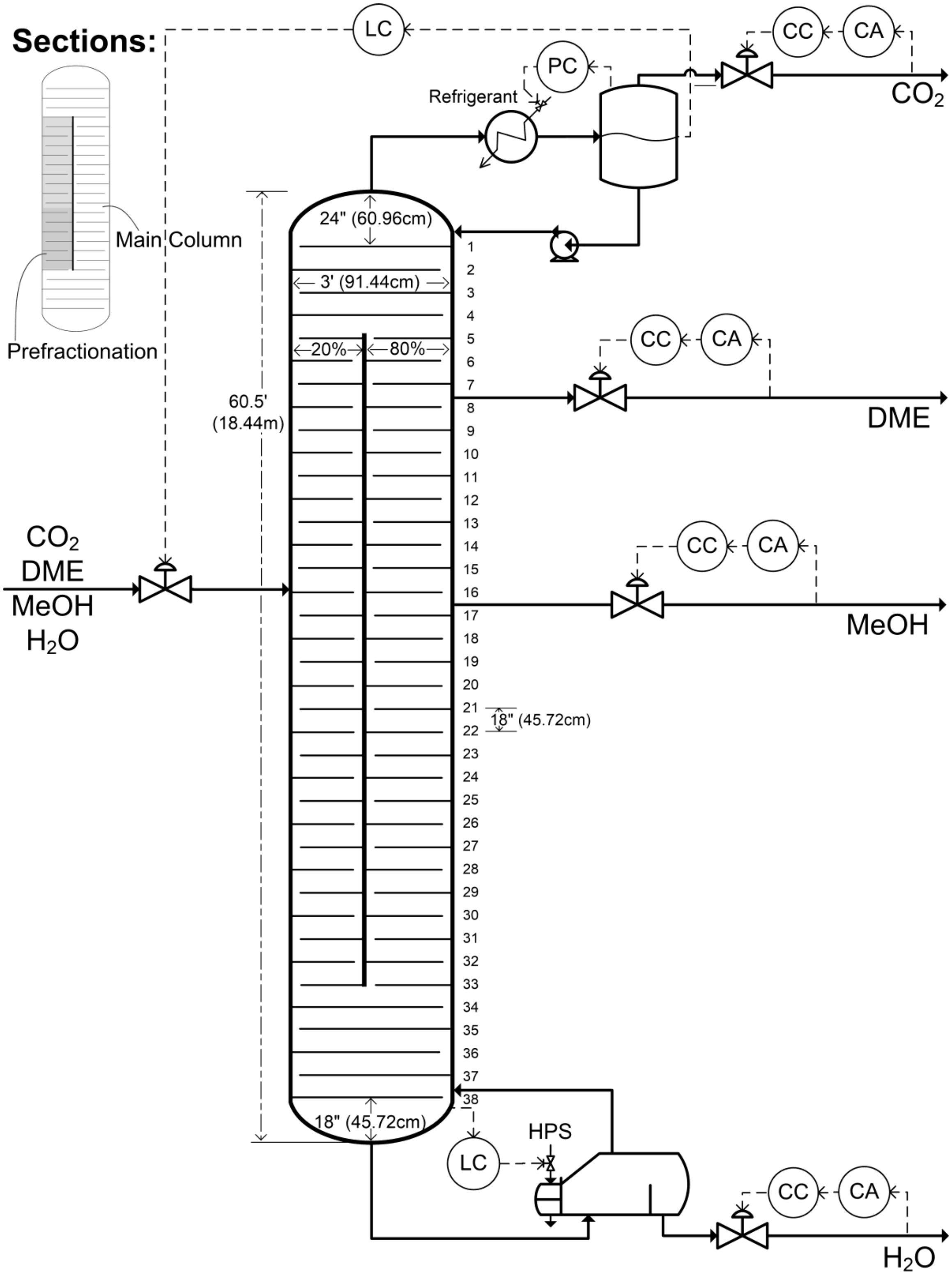

Figure 14: A schematic of the DWC with 38 trays.

For both columns, the feed enters the column and separates partially in the prefractionation section. The vapour and liquid products from the prefractionation section enter the main section over the top and bottom of the dividing wall, respectively. In the main section, CO_2 and water are drawn from the distillate and bottoms, respectively. The DME and methanol concentrate on the right side of the wall and are drawn continuously at high purities at two different side draw locations.

The dividing wall column is modelled using a combination of two columns since Aspen Plus does not have a built in dividing wall column unit. The prefractionation section is modelled using a separate `RadFrac` column without a reboiler or condenser, while the main section of the column is modelled using a second `RadFrac` column with different specified diameters for each section to account for the fact that the active tray areas above, beside and below the dividing wall will be different. The vapour and liquid outflows from the prefractionation section are connected to the trays 4 below the top and 4 above the bottom of the main section, respectively. Also, a portion of the liquid flow from the 4th from the top tray and the vapour flow from the 4th from the bottom tray are diverted to the top and bottom of the prefractionation section, respectively. These internal recycled flow rates were determined by the minimum energy mountain diagram method described by Okoli and Adams [31].

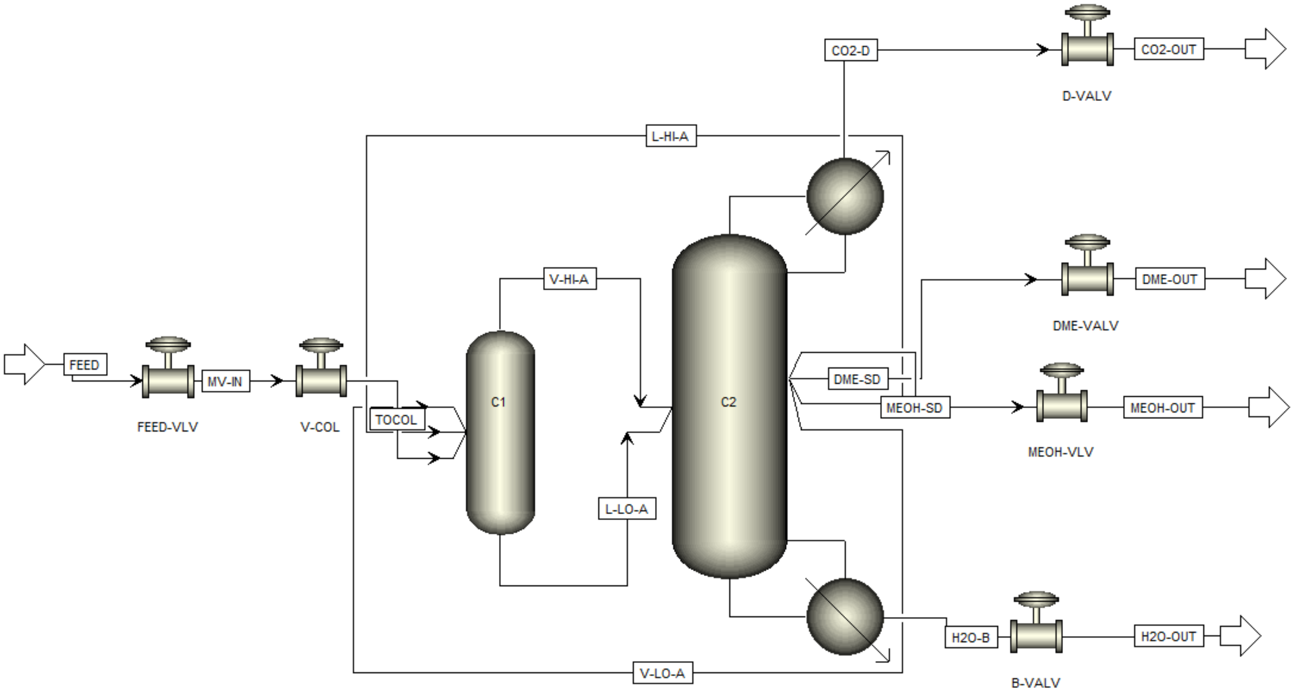

Figure 15: The screen capture of the DWC modeled using two `RadFrac` columns.

The purities of each stream were obtained using the `DESIGN SPEC` feature in Aspen Plus. The purity of the distillate was set by varying the reflux ratio while the purity of the bottoms determined the boilup ratio. The DME side draw flow rate was altered until its purity constraint was met. The purity of methanol was increased by decreasing the flow rate of its side draw stream until the `DESIGN SPEC` would no longer converge noting that a suitable side draw flow rate that achieved the desired purity could not be found either manually or by using the `DESIGN SPEC` feature. This indicates that it is not possible to achieve the desired purities of all streams given the restrictions imposed on the number of trays due to the height restriction. The second DWC was designed by simply adding trays to the first column until the desired methanol purity was obtained and all design specifications converged. The purpose of the second column is to prove that without the height constraint, it is possible to use a DWC to purify DME.

3.2.2 Column Performance

The dividing wall columns are able to purify the DME reaction mixture very well. A summary of the purity and flow rates of the streams are shown in Table 5 and Table 6. Both columns produce CO_2, DME and water at the same purities and flow rates. The 28-tray DWC produces 98.57% methanol whereas the 38-tray column produces 98.92% pure methanol. Also, the taller column has drastically lower reflux and boilup ratios, along with lower duties of the condenser and reboiler; this shows that it requires much less energy to purify the components with more trays available.

Table 5: Stream and unit results from the 28-tray divided wall column.

28-tray DWC	**Purity (mol%)**	**Flow rate (kmol/hr)**
CO_2	99.50%	
DME	98.50%	25.23
Methanol	98.57%	
Water	99.50%	
	Condenser	**Reboiler**
Ratios	10.228	2.516
Energy use	1.0173 MW	1.1425 MW
Temperature	242.6 K	465.4K

Table 6: Stream and unit results from the 38-tray divided wall column.

38-tray DWC	**Purity (mol%)**	**Flow rate (kmol/hr)**
CO_2	99.50%	
DME	98.50%	25.21
Methanol	98.92%	
Water	99.50%	
	Condenser	**Reboiler**
Ratios	5.404	1.460
Energy use	0.5378 MW	0.6632 MW
Temperature	242.6 K	465.6K

3.3 Case 3: Semicontinuous without Middle Vessel, Dividing Wall Distillation

3.3.1 Process Description

The distillation configuration proposed as Case 3 is a dividing wall column operated similarly to the Semicontinuous without Middle Vessel (SwoMV) set up developed by Meidanshahi and Adams [20]. In the previous sections, it was found that both the semicontinuous single column and the continuous divided wall column were inadequate process intensification techniques. The proposed method is a combination the two and will be referred to as semicontinuous dividing wall column (S-DWC).

A schematic diagram of the S-DWC process is shown in Figure 16. The column is three feet wide and has 28 trays, 15 of which are spaced at 18 inches and 13 are spaced at 12 inches. The column also has a dividing wall separating the middle 20 trays vertically, partitioning the area by a 20:80 split (20% of the surface area is on the prefractionation side of the wall). There are four trays above and four trays below the wall. The column can be divided into four sections for identification purposes. The area to the left of the divided wall is the prefractionation section and is labeled Section I, in Figure 16. Section II is the region to the right of the divided wall, where DME and methanol are purified. The four trays above the dividing wall is the rectifying section and is termed Section III, while the four trays below the dividing wall, where water is stripped from its impurities, is called Section IV.

The column operates with fresh feed being continuously fed to Tray 17 of Section I. Carbon dioxide and water are drawn continuously from the distillate and bottoms streams, respectively. DME is drawn at a high purity from Tray 8 in Section II and methanol is withdrawn from Tray 14 of Section II. The purity of methanol is initially not high enough and is recycled back to the 26th tray in Section IV until it is pure enough to be drawn from the system.

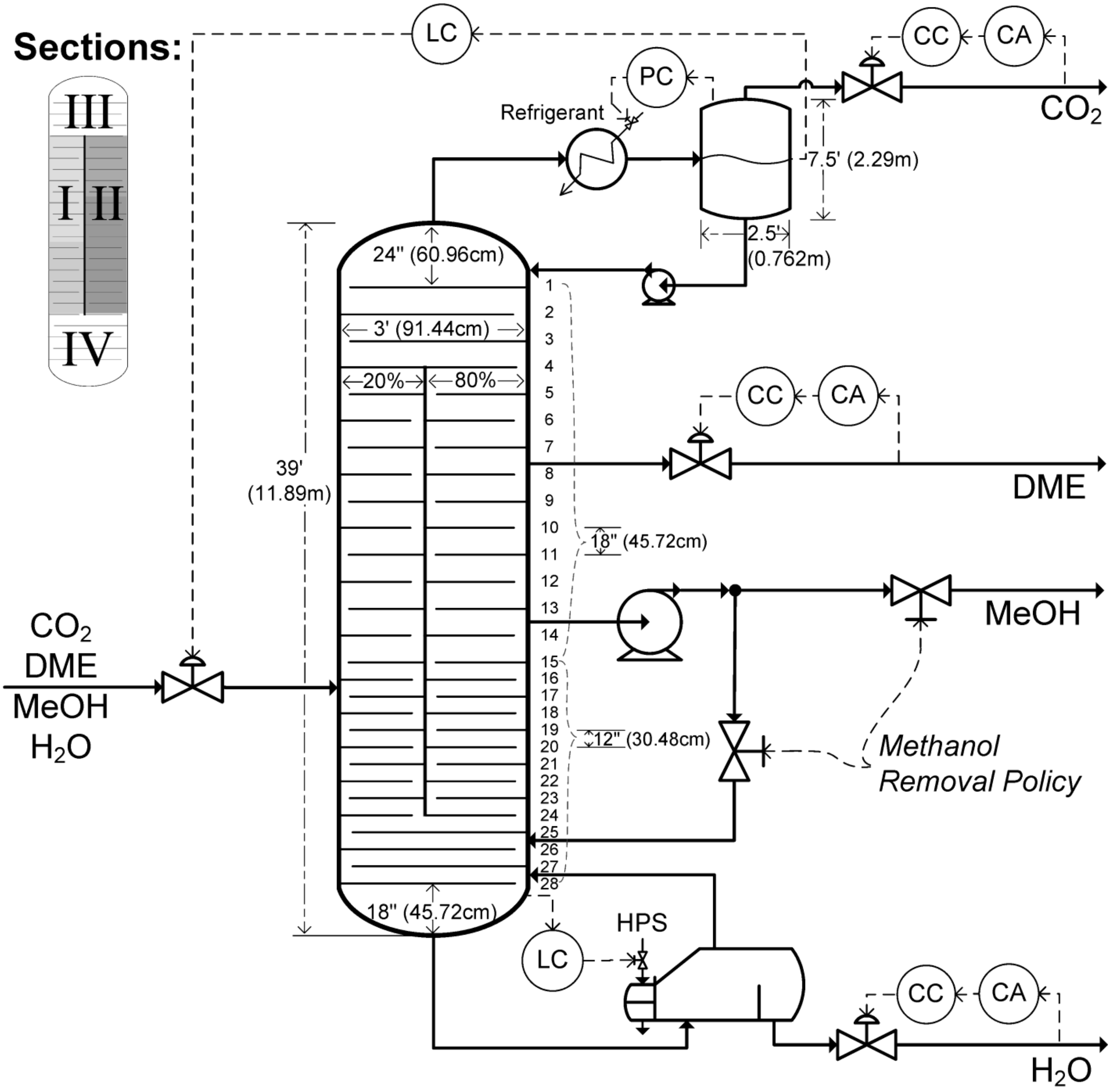

Figure 16: Design structure and control scheme for the S-DWC configuration.

The semicontinuous dividing wall column is modelled similarly to the continuous dividing wall column, except the model is implemented in Aspen Plus

Dynamics instead of Aspen Plus. In order for the model to be used in the dynamic simulator, there must be a pressure drop between all units. For the purpose of modelling, valves are placed on the internal flow stream in between the prefractionation and main column section to overcome this requirement. Additionally, compressors and pumps are installed before the valves to negate the pressure drop over the valves so that there is no pressure drop along internal flows within the DWC. In the actual system, none of these units exist. A screen capture of the units in Aspen Plus, before being exported to Aspen Plus Dynamics is shown in Figure 17.

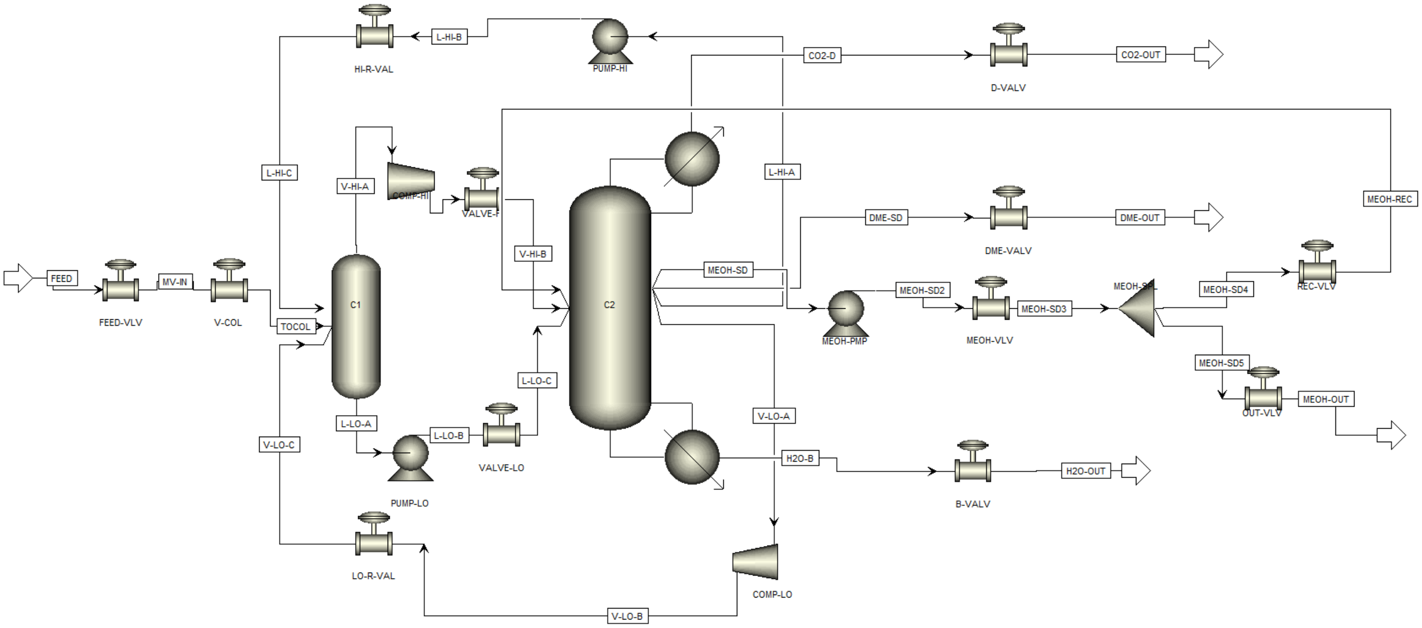

Figure 17: A screen capture of the S-DWC modelled in Aspen Plus.

The actual dividing wall column has a diameter of three feet, based on the desired total production rate. The dividing wall splits the tray area by a 20:80 ratio between Sections I and II. In order to model the area of each section, an equivalent diameter is calculated for each section of the column. A summary of the model equivalent diameters is below in Table 7. The equivalent diameters are the diameters used to model each section of the column.

Table 7: Equivalent model diameters for the different sections of the dividing wall column.

	Portion of total area	**Area**	**Equivalent diameter**
Section I	20%	0.131 m^2	40.89 cm
Section II	80%	0.525 m^2	81.79 cm
Section III	100%	0.675 m^2	91.44 cm
Section IV	100%	0.675 m^2	91.44 cm
Full column area and diameter:		*0.675 m^2*	*91.44 cm (3 feet)*

Along with an equivalent diameter, the area of the downcomers must be taken into consideration. To better illustrate the geometry of each tray, a diagram of a divided tray is shown in Figure 18, which assumed infinitely thin trays. The area occupied by the downcomer in the actual dividing wall column is 10 percent of the total tray area. This area is typical for sieve tray distillation columns [32]. Since the system is being modelled with two columns, the proportionate downcomer areas in each of the column sections need to be calculated. The active area is the area available for vapour flow, or the column's cross sectional area excluding one downcomer [32]. These areas are summarized in Figure 18 (d). By knowing the active area of each tray, the lengths of the model weirs can be calculated. The active areas and weir length-to-diameter ratios are inputted into the Aspen model and are summarized in Table 8. Note that Sections III and IV each have 90% active area, the same as the actual divided trays.

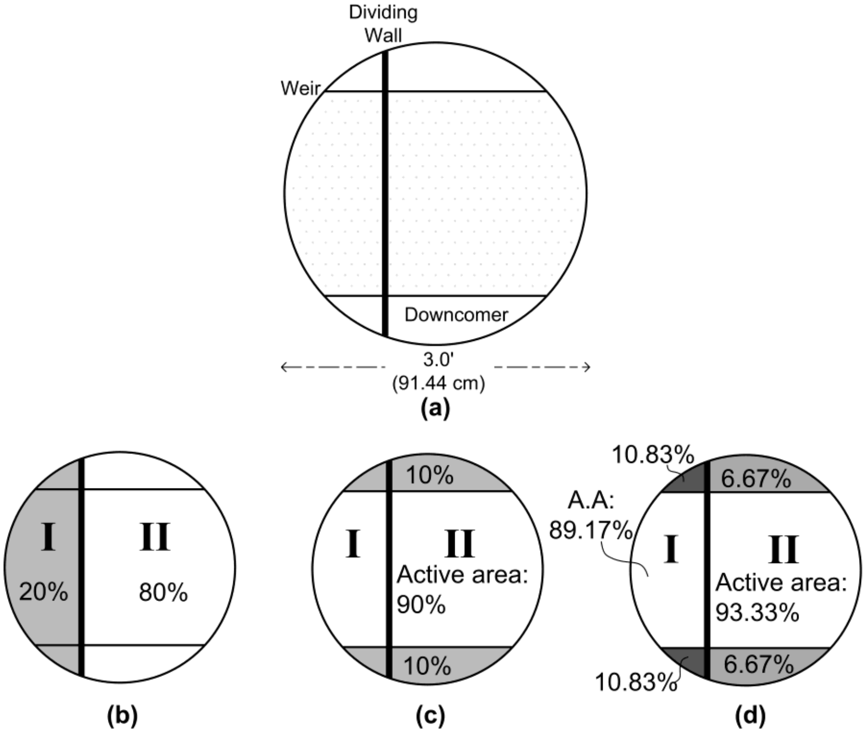

Figure 18: Divided tray geometry. (a) Geometry of the downcomer, weir and dividing wall locations. (b) Illustration of the proportionate area on either side of the dividing wall. (c) Illustration of the downcomer area. (d) Illustration of the active and inactive areas on each side of the dividing wall.

Table 8: Active area of trays in each section of the dividing wall column. The weir length-to-diameter ratio (L_w/D) is a function of the active area

	Active Area	**L_w/D**
Section I	93.33%	0.6464
Section II	89.17%	0.7430
Section III	90%	0.7266
Section IV	90%	0.7266

3.3.2 Control System

The unique feature of this dividing wall column is its semicontinuous operation. The control of the S-DWC is the same as described by Meidanshahi and Adams [20]. The control scheme is shown in Figure 16. The purities of the distillate, bottoms and dimethyl ether side draw are controlled by manipulating their individual flow rates. The pressure in the condenser drum and the sump level are controlled by the condenser and reboiler duties, respectively. The flow rate to the column is manipulated to control the level of the condenser drum.

The purity of the methanol side draw is controlled by a methanol removal policy. The purity of this stream is set by lower and upper bounds with the average of the two bounds being the desired methanol purity. In this case, the lower bound is 98.7 mol% while the upper bound is 99.2 mol%. Initially, the methanol side steam is recycled. While it is recycled, the purity of methanol in the side stream increases. Once the purity reaches the upper bound, the side draw valve opens and the recycle valve closes, and the high purity methanol is collected from the column. As the methanol is being removed from the column, its purity decreases. Once the purity reaches the lower bound, the side draw valve is closed, the recycle valve opens, and the methanol side draw is recycled again.

3.3.3 Column Performance

The process is simulated in Aspen Plus Dynamics from an initial state determined by an Aspen Plus steady-state simulation where the methanol side draw valve open and the methanol purity is lower than desired. After the process is simulated for several cycles it approaches a stable limit cycle. The purities of the outlet streams from 24 cycles are shown in Figure 19. The call-out shows three cycles in more detail and indicates the three cycles that will be shown for all other variables. The flow rates of each of the inlet and outlet streams are shown in Figure 20; both of these graphs are used to analyse the performance of the column. The average purities and DME flow rate are shown in Table 9.

From Figure 19 we can see the distillate and bottoms purities are bouncing around their set point of 99.5 mol% and their controllers are performing well to maintain the average purity at 99.53 mol%, and 99.51 mol%, respectively, as shown in Table 9. The purities of the two side draws vary from the set point as well, and their flow rates compensate for this action as well. The purity of the DME fluctuates the most, however due to its controller, its average purity ends up being right at the set point of 98.50 mol%. The purity of the methanol side draw rises and falls with the alternating between collecting and recycling modes. It is clearly seen that the change in purity switches direction when the methanol side draw valve either opens or closes at the upper and lower bounds. The resulting average purity of methanol is 98.93 mol%.

Table 9: The average purities and flow rates of the inlet and outlet streams of the semicontinuous dividing wall column. The average purities are calculated using the model data collected every 0.01 hours and estimated using Simpson's 3/8 rule [29].

	Feed	CO_2	DME	Methanol	H_2O
Average Purities (mol%)		99.53%	98.50%	98.93%	99.51%
Flow rate (kmol/hr)			21.99		

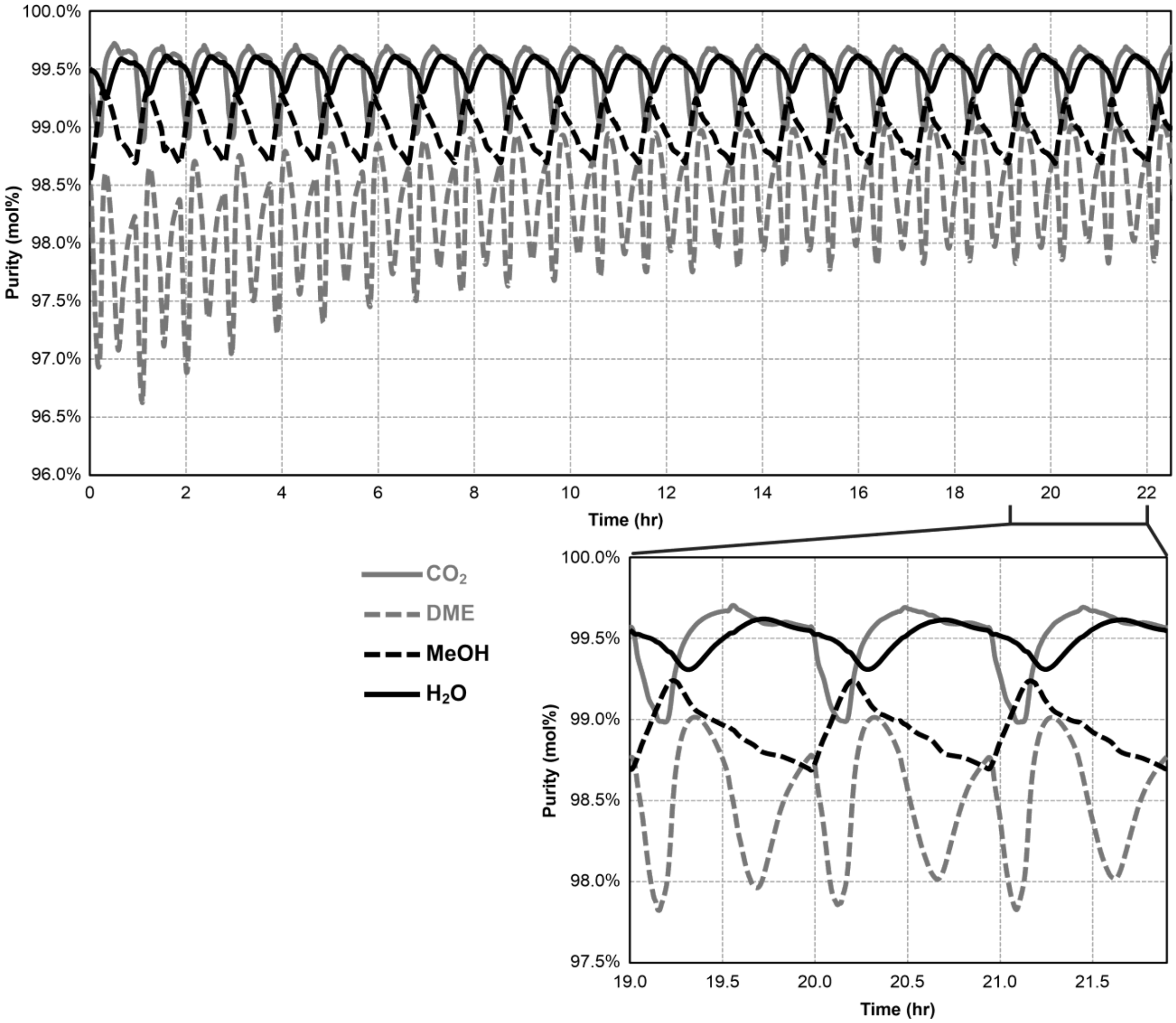

Figure 19: Purities of the outlet streams from the SwoMV-DWC showing the first 23 cycles of the 50 cycle run. The call-out shows three chosen cycles in more detail.

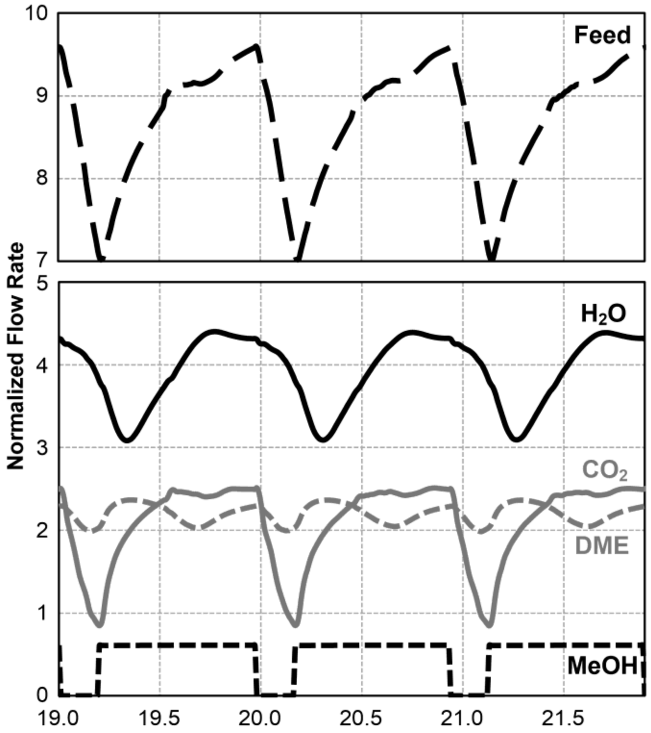

Figure 20: The flow rates of the outlet streams from the semicontinuous dividing wall column.

To demonstrate the operability of the column, the condenser drum and sump levels, condenser and reboiler energy usage and reflux and boilup ratios are shown in Figure 21, Figure 22 and Figure 23 respectively. The average utility usage is summarized in Table 10. The temperatures of the condenser and reboiler are listed in Table 11. The temperatures of the column vary insignificantly compared to the other variables within the column.

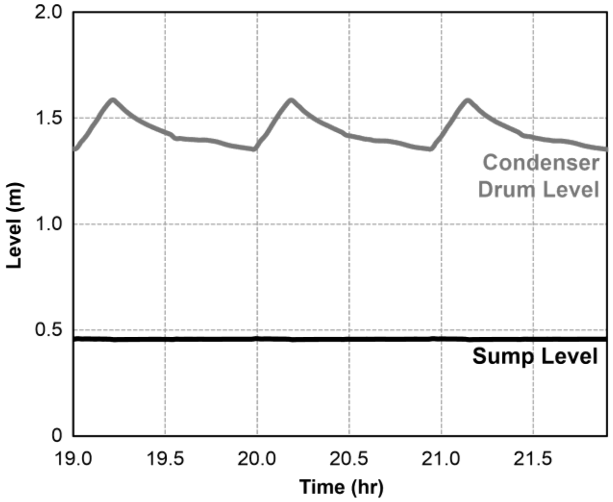

Figure 21: Condenser drum and sump level during each cycle, for three cycles.

Table 10: The average duty of the condenser and reboiler.

Condenser	Reboiler
1.020 MW	1.128 MW

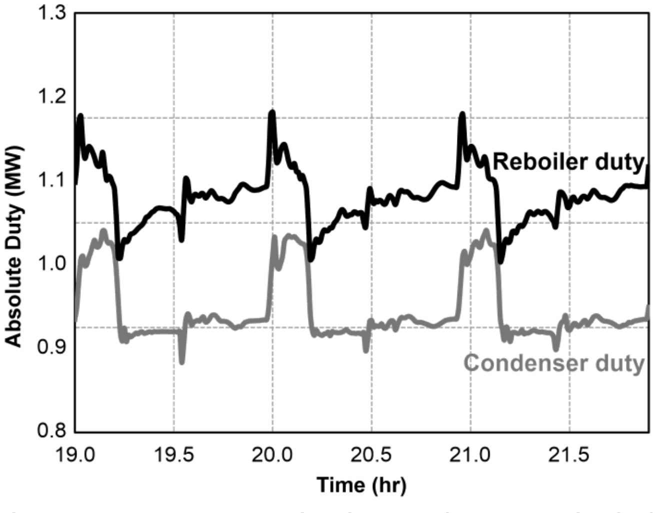

Figure 22: The absolute energy usage by the condenser and reboiler.

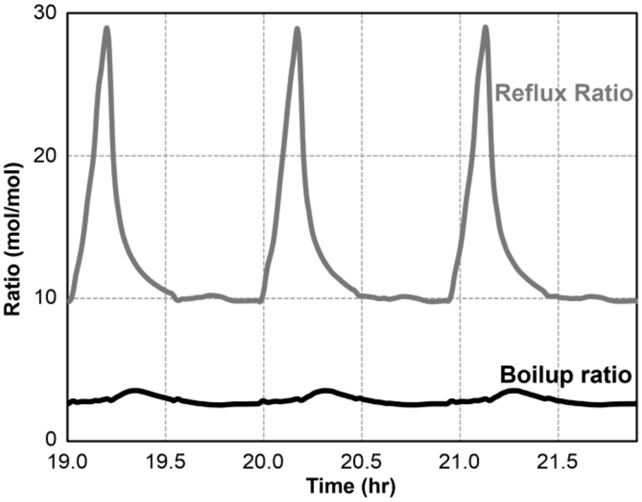

Figure 23: The reflux and boilup ratios of the semicontinuous dividing wall column.

Table 11: The average and extreme temperatures in the column.

	Average	Minimum	Maximum
Condenser	-30.6	-30.9	-29.7
Reboiler	192.2	191.9	192.4

To ensure that column does not violate flooding or weeping constraints, the vapour velocities are tracked throughout each cycle and compared to their bounds. The Fair correlation [30] is used to calculate the flooding velocities. Figure 24 and Figure 25 show that the vapour velocities never exceed 90% of the flooding velocities. Even with the narrow tray spacing in the bottom half of the column, the vapour velocities are low enough to not risk approaching the flooding constraints.

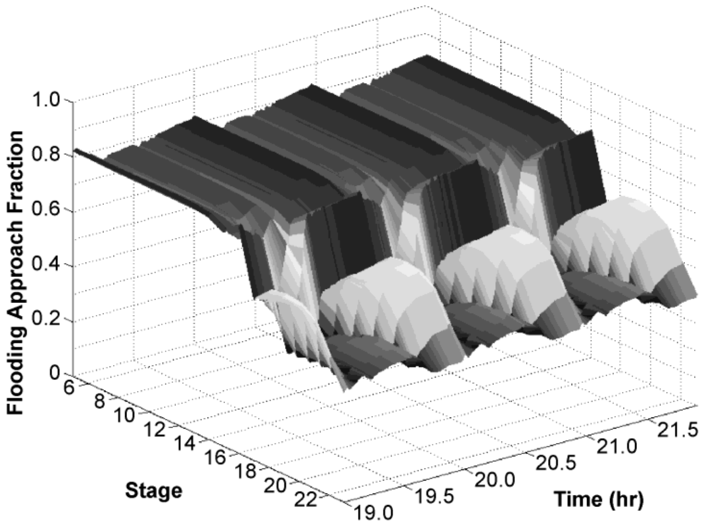

Figure 24: The flooding approach profile for Section I of the S-DWC.

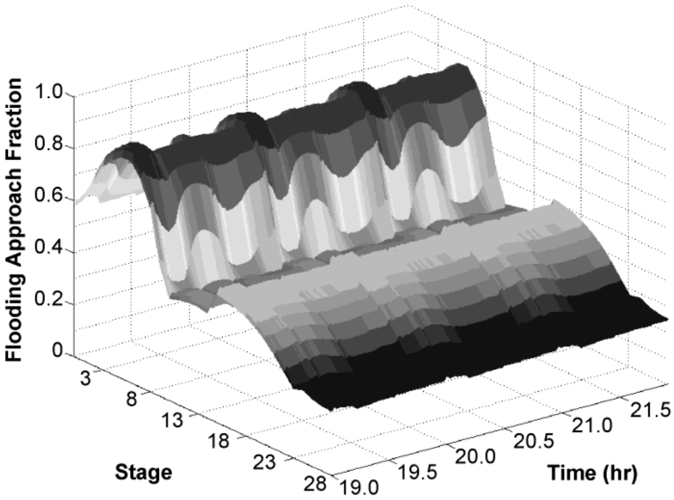

Figure 25: The flooding approach profile for Sections II, II and IV of the S-DWC.

Vapour velocities that are too low, risk causing weeping within the column. A select number of trays were tested for weeping using the Mersmann method [33]. The trays that are tested for weeping are the top and bottom trays along with all the trays that have either inlet or side draw streams. The four slowest vapour velocities are shown Figure 26. The highest weeping velocity is also shown, proving there is a low risk of weeping.

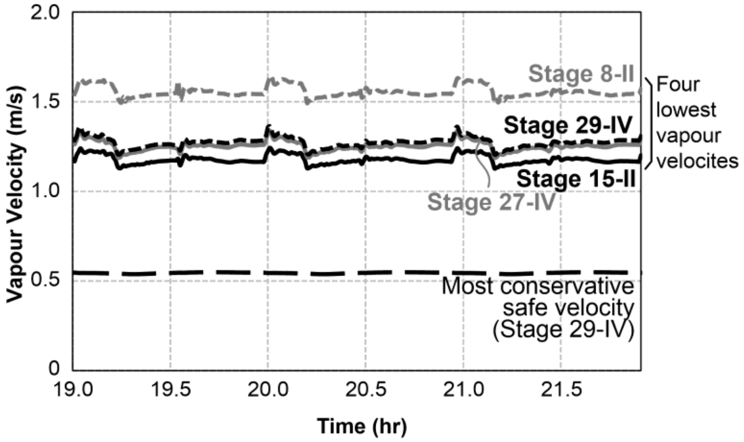

Figure 26: The vapour and weeping velocities for the lowest vapour velocities and the most conservative minimum weeping velocity of the S-DWC.

Overall, the semicontinuous dividing wall column performs extremely well meeting all of the specifications. As mentioned previously, the methanol stream can be recycled to the reactor in order to help the reaction conversion. Due to the successful modelling of this process, it is now possible to produce DME with a separation unit that fits inside of a shipping container.

CHAPTER 4 ECONOMICS

4.1 Capital Costs

Economics must be considered when evaluating the feasibility of each design. The cost to manufacture each piece of equipment was estimated using two methods, the Apsen Capital Cost Estimator (ACCE) V8.8 [34] and the capital cost correlations described in *Product and Process Design Principles* (PPDP) [35]. ACCE is a rigorous costing program that uses a knowledge base of designs, methods and models to develop detailed engineering procurement construction estimates [36]. This cost estimation tool was used to determine the price of most of the equipment. The capital cost equations from PPDP were used to predict the cost of the dividing wall columns and the fired heater reboilers since these units are not available in ACCE. The cost of the dividing wall column shell was estimated using the usual correlations for pressurized columns while the cost of the dividing wall trays was estimated by multiplying the cost of a typical sieve tray by 1.2 to account for the extra cost of the installation of the wall [31]. The material chosen for the construction of the equipment is 316 stainless steel because it is corrosion resistant to alcohols and ethers and can withstand temperatures up to 700°C [35]. In all cases, the columns operate around 13 atm, however every column was designed to withstand pressures up to 16 atm for safety purposes [35]. The weight of every piece of equipment is estimated using the Aspen Plus Capital Cost Estimator, which simultaneously estimates the mass of equipment as well as the cost. The mass of the columns and reboilers were calculated using Aspen Plus as if they were a regular column and a kettle reboiler respectively.

The following three tables outline the capital cost breakdown and the estimated weight of each piece of equipment required to operate the three design cases. The equipment cost is the estimated cost of manufacturing the units while the installed cost includes the cost of the controllers, piping, installation labour and other costs required to have the units operational.

Table 12: The capital cost breakdown for Case 1.

Case 1 – Semicontinuous Column	Equipment Cost	Installed Cost	Equipment Weight (kg)
DME recycle pump	$6,100	$32,300	95
MeOH recycle pump	$6,100	$33,500	91
Condenser Heat Exchanger	$36,500	$161,600	1,315
Condenser Drum	$67,200	$225,100	3,583
Reflux Pump	$14,400	$19,900	181
Reboiler	$12,000	$63,900	544
Tower	$91,400	$253,200	3,856
MV1-flash vessel	$46,700	$143,700	1,451
MV2-flash vessel	$46,700	$143,700	1,451
Total	$327,100	$1,076,900	12,569

Table 13: The capital cost breakdown for Case 2.

Case 2 – Continuous DWC	Equipment Cost	Installed Cost	Equipment Weight (kg)
Condenser Heat Exchanger	$83,700	$253,500	2,495
Condenser Drum	$27,000	$132,100	862
Reboiler	$194,663	$510,016	1,043
Reflux Pump	$6,700	$42,000	122
Tower	$147,416	$386,230	5,625
Total	$459,479	$1,323,846	10,147

Table 14: The capital cost breakdown for Case 3.

Case 3 – Semicontinuous DWC	Equipment Cost	Installed Cost	Equipment Weight (kg)
Condenser Heat Exchanger	$83,700	$253,500	2,495
Condenser Drum	$27,000	$132,100	862
Reboiler	$292,396	$766,078	1,043
Reflux Pump	$6,700	$42,000	122
Tower	$147,416	$386,230	5,625
Methanol Recycle Pump	$6,000	$33,600	95
Total	$563,212	$1,613,508	10,245

The three cases all have a total capital costs in the same order of magnitude because the size of the equipment used is similar. However, there are a few differences. The dividing wall columns are more expensive than the regular column because of the added wall material and installation. Case 1 has a lower throughput and smaller heating and cooling duties than the dividing wall cases, and as a result, the condenser and reboilers do not need to be as large. However, Case 1 has the two large middle vessel flash drums. The tables also show that each design case weighs much less than the 30,480 kg limit of the shipping container.

4.2 Operating Costs

The cost of operating the distillation columns is dependent on the duty of the condenser and reboiler. The refrigeration costs are estimated using the price listed in PPDP for refrigerating liquid to temperatures above -30°F (-34°C) (7.9¢/GJ) [35]. It is assumed that electricity is the energy source for refrigeration and the refrigeration price scales with the cost of electricity using the price of electricity listed in the same table (6¢/kWh) [35]. The most costly source of electricity in a remote location would be a Diesel generator (40¢/kWh) [3] whereas a cheaper option would be to use electricity from the grid (example: 8.02¢/kWh - 2013 Alberta average [37]). Another refrigeration option is an absorption chiller which is ideal for locations with high electricity costs and low fuel costs [38]. An indirect-fired absorption chiller would be a great option for this system since it can use the heat from the bottoms stream (190°C and 99.5% water) to power the chiller. Any extra energy required by the absorption chiller can be generated by burning natural gas [38] already available at the wellhead. The absorption chiller costs likely fall in between the cost of grid electricity and the Diesel generated electricity; therefore, in this economic analysis, the price of Diesel generated electricity (40¢/kWh) will be used as a conservative estimate.

The reboilers are fired heaters are powered by natural gas since it is ready available at the oil wellheads. High pressure steam could be used in kettle reboilers, however, the cost of having a separate steam generation plant on site is likely to be too high for a low throughput plant. The cost of the heating the reboiler is the revenue forgone by not selling solution gas as natural gas downstream. Therefore, the reboiler duty cost is estimated using the average Henry Hub spot price of natural gas for July 2016 ($2.51/MMBtu) [39] and using a factor of 0.85 to account for heater inefficiencies [40]. The duties of each distillation case are summarized in Table 15, as well as the estimated cost of each energy requirement.

Table 15: The cost of operating the columns for all three cases.

	Case 1: Semicontinuous Column	**Case 2: Continuous DWC**	**Case 3: Semicontinuous DWC**
Condenser duty (MW)	0.2266	1.017	1.020
Reboiler duty (MW)	0.2269	1.143	1.128
Annual Cost of Refrigeration	$360,892	$1,620,193	$1,624,493
Annual Cost of Heating	$21,576	$108,640	$107,261
Total Annual Operating Cost	$382,468	$1,728,833	$1,731,754

4.3 Total per unit cost

The total cost per unit of DME produced is calculated to compare the unit to its market price. The system is assumed to run for 8400 hours in a year and the physical properties listed in Table 16 are used to calculate the production rate in different units.

Table 16: Physical properties used in the economic analysis.

Molecular weight of DME (98.5%)	45.87122	gm/mol	[34]
Lower heating value (DME)	28.882	MJ/kg	[41]
Lower heating value (Low Sulfur Diesel)	42.612	MJ/kg	[41]
Density of DME	665	gm/L	[41]
Density of Diesel	847	gm/L	[41]
Energy density of DME	1,325	MJ/kmol	Calculated
Energy in 1L of diesel	36.09	MJ/L	Calculated

Table 17 shows the per-unit cost of DME for each distillation case. The total annualized cost of the projects are calculated by allocating the capital cost over a conservative lifetime (3 years) at a discounted rate of 20%, an appropriate minimum rate of return for new process in an existing market [42]. The annual utility cost is added to this number. The total cost is then divided by the DME production rate to obtain the per-unit cost for each unit of DME produced. Since the energy density of DME is much less than Diesel, the cost of the equivalent calorific content in one litre of diesel of DME is also listed in Table 17.

Table 17: Total annualized cost and cost per unit of DME.

	Case 1: Semicontinuous Column	**Case 2: Continuous DWC**	**Case 3: Semicontinuous DWC**
Capital Cost	*$1,076,900*	*$1,323,846*	*$1,613,508*
Annual allocation of capital cost (3 years, 20%)	$511,232	$631,351	$768,861
Cost of Production (Utilities)	$382,468	$1,728,833	$1,731,754
Total Annualized Cost	$893,700	$2,360,184	$2,500,615
DME production rate			
Molar rate (kmol/hr)	0.12	25.23	21.99
Volumetric rate (L/year)	69,859	14,614,839	12,738,022
Mass rate (tonnes/year)	46.5	9,722	8,473
Calorific rate (MJ/year)	1,342,129	280,778,656	244,721,468
Cost of DME			
$/L	$12.7929	$0.1615	$0.1963
$/energy in 1L Diesel equivalent	$24.0315	$0.3034	$0.3688

The per-litre cost of DME is less that the target $0.25/L for Case 2 and 3, while Case 1 does not meet this requirement by a long shot. This is mainly because the throughput of Case 1 is far less that the other cases, while its capital cost is relatively similar. In looking at the cost per energy equivalent litre of Diesel, and being aware that the price of diesel has approximately $1/L, the separation cost of DME for Case 2 and Case 3 are competitive since they are in line with the conventional wisdom that separation costs equate to 50% to the cost of a product.

The two top cases are compared in Table 18 to determine the best solution to remote DME purification. There is a clear trade-off between the two cases, the continuous DWC produces DME at a lower cost, but the purity of the methanol is not recycle purity. Whereas, the semicontinuous DWC produces DME at a higher price and meets all purity specification set out initially. Additionally, the continuous DWC has a higher throughput than the semicontinuous DWC case. There are other potential trade-offs which are not explored in this work, such as reliability, controllability, start-up costs and robustness in the face of disturbances or uncertainty. A more thorough comparison of the two options is an area of future work.

Table 18: A summary of the cost and production outputs of the two best cases.

	Case 2: Continuous DWC	Case 3: Semicontinuous DWC
Cost of DME ($/L)	$0.1615	$0.1963
Production average purities (mol%)		
DME average purity	98.5%	98.5%
Methanol average purity	98.5%	98.9%
DME Production Rate (tonnes/year)	9,722	8,473

4.4 Business Model for Case 3

A business model analysis was performed to determine the price a customer is willing to pay for a distillation unit that purifies fuel grade DME. Only Case 3 is considered for the business model analysis. The assumptions made about the customers and their environment are listed in Table 19. In this analysis, the suggested sale price (including sales tax) is computed by assuming the customer will be willing to pay the same amount of money after three years of use as they would have if they continued business-as-usual instead of making their own DME—namely simply buying an equivalent amount of Diesel at $1.01/L. Recall that this is equivalent to pricing the system such that after three years, the total cost to the customer is $0.25/L. The benefit to the company producing their own DME is avoiding CO_2 emissions (and associated carbon taxes and fines), as well as the value of on-side fuel generation, as opposed to trucking in fuel to remote locations. The value of these benefits is outside the scope of this work.

It is assumed that the customers require a conservative discounted value of money of 30%. At this discount rate, the total cost of purchasing Diesel over three years for Case 3 is $5,783,422. Also, the customers will be large corporations in Alberta and subject to the corporate tax rate of 27% [43], and use the capital cost investment against their income taxes owed through the capital cost allowance of manufacturing equipment (Class 43) [43]. The salvage value is assumed to be zero, a conservative estimate. Any capital expenditure warrants an annual capital cost allowance (CCA) against income taxes; this increases the benefit to the company. The present value of the total CCA tax shield is calculated using the following equation, where C is the sale price of the unit and the other parameters are indicated in Table 19.

$$Present\ Value = \frac{CdT}{d+r}\left(\frac{1+0.5r}{1+r}\right) - \frac{SdT}{d+r}\left(\frac{1}{(1+r)^n}\right) \quad [44]$$

A summary of the economic analysis is shown in Table 20.

Table 19: Rates used to conduct a business model analysis.

Cost to Customer, for the purification step	$0.25/L DME
Discount rate (high risk investment) *(r)*	30%
Corporate tax rate (Alberta) [43] *(T)*	27%
CCA rate: Class 43: Manufacturing equipment [43] *(d)*	30%
Salvage value (conservative) *(S)*	$0
Project lifetime *(n)*	3 years
Annual DME rate of production (L/year)	12,738,022

Table 20: The calculated sale price of an S-DWC unit for DME separation, compared to buying an equivalent amount of Diesel.

		S-DWC DME production	**Diesel**
Customer	**Sales Price, including tax (calculated)**	**$2,996,172**	$0
	Annual Operating Cost, discounted over 3 years	$3,145,061	$5,783,422
	CCA Tax Shield (Present Value) benefit	($357,812)	$0
	Salvage value	$0	$0
	Total Cost to company ($0.25/L DME x rate of production, discounted over 3 years)	$5,783,422	$5,783,422
Manufacturer	Sale Price including tax	$2,996,172	
	Sales tax (5% GST in Alberta) [43]	$275,401	
	Cost to manufacture equipment	($1,613,508)	
	Contribution Margin	$1,107,263	(39% of before tax sales price)

The price a company would be willing to pay for the DME separation step is approximately $3 million. If ChemBioPower were to produce these units at the estimated cost of $1,613,508, they could earn a contribution margin of $1.1 million per unit they produce. A respectable contribution margin is 45-55% of the sale price [44], and as such, the S-DWC system has a decent business case.

4.5 Sensitivity Analysis

The previous business analysis was done using the parameters listed in Table 19, however their values are likely to change given different conditions. The four variables that are believed to have the largest impact on the profitability of the project are the value of the DME to the customer, their required rate of return, the salvage value of the equipment and the annual utility expenses. The four variables were perturbed to determine the effect they have on the profitability of selling the semicontinuous DWC as a DME purification systems. The amounts by which each variable was changed are listed in Table 21. The salvage was varied to $800,000 which is half of the cost to manufacture the equipment and a likely upper bound to its true value. The sales tax was ignored in this analysis.

Table 21: The amount by which the variables were perturbed for the sensitivity analysis.

	Lower range		**Base Case**	**Upper range**	
Price of DME	$0.15/L	-40%	$0.25/L	$0.30/L	+20%
Rate of Return	20%	-33%	30%	50%	+67%
Annual Utility Expense	$865,877	-50%	$1,731,754	$2,597,631	+50%
Salvage Value	$0		$0	$800,000	

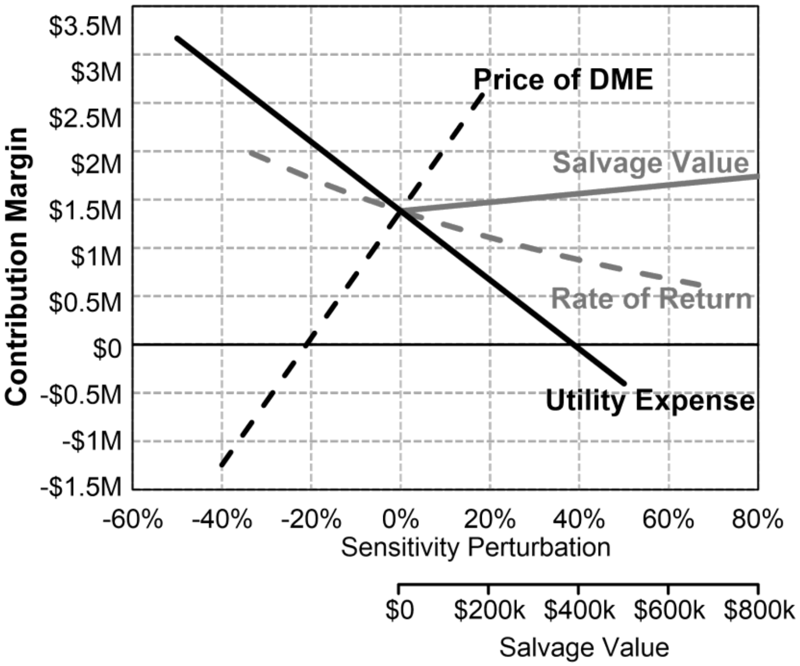

Figure 27: Sensitivity analysis of the effect of the chosen variables on the contribution margin for producing semicontinuous dividing wall columns.

Figure 27 shows the sensitivity of the contribution margin of the S-DWC when these four parameters are changed. The business model is affected the most by the price of the DME and the utility expense. The salvage value has little effect on the profitability of selling the system; this validates the conservative choice of its value being zero and any value at the end of the life of the system is just a bonus to the customer. The customer's desired rate of return has some effect on the profitability of the system, however, not as significant as the price of DME or the utility expense. In order to mitigate the risk imposed by the utility expense, further research must be done into the cost of different utility methods.

CHAPTER 5 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The objective of this research was to develop a distillation unit that separates the DME from its reaction by-products, using equipment that fits inside of a shipping container and for under $0.25 per litre.

In section 3.1, semicontinuous distillation was first looked at as a candidate for remote DME production. The system withdrew carbon dioxide and water from the distillate and bottoms, and concentrated DME and methanol in two middle vessels attached to different middle sections of the column with liquid feed and recycle streams. The system was able to purify DME and water to their desired purities, however, methanol and carbon dioxide were not purified to their standards. The height restriction on the column is the reason for the not being able to purify all the components to their individual targets.

In section 3.2, the well-studied dividing wall column was examined as a candidate for the purification of DME. It was shown to be able to purify carbon dioxide, water and DME to their desired purities with a column that is small enough to fit inside of a shipping container. The desired methanol purity was only achieved with a column that is too tall for a shipping container. The dividing wall column is a candidate for remote DME purification, only if the methanol purity constraints are relaxed.

In section 3.3, a novel distillation configuration was proposed. The semicontinuous mode of column operation was combined with the dividing wall column to produce a column that met all of the requirement for remote DME purification. The semicontinuous dividing wall column purifies carbon dioxide, DME and water to their purity specifications continuously while cyclically withdrawing and recycling the methanol rich phase to achieve a high methanol purity.

In Chapter 4, the economics for each of the cases was examined. All of the capital costs fell within the same range and the weight of the equipment in each case met the shipping container internal mass limitation. Case 2 and Case 3 were able to separate DME at a cost less than the required purification costs and Case 3 offers a compelling business case to market a remote DME purification system.

Overall, this research shows that it is possible to purify DME and reaction by-products in a remote location using a distillation column that has been enhanced through process intensification. Also, the DME produced is at a cost that is competitive with the price of diesel.

5.2 Recommendations for future work

After completing the research described, the following recommendations are proposed as future work.

1. **Semicontinuous DWC optimization**

The S-DWC proposed in this research was manipulated by hand to obtain a feasible design. It is recommended that an optimization strategy be developed to achieve a system that is more profitable that the one proposed. Variables that would likely have great effect on the economics of the system are the column diameter, the throughput flowrate, the methanol recovery scheme, and the method used to cool the condenser. The system could be optimized using the method described by Meidanshahi and Adams, using gPROMS, with a different quaternary mixture whose chemical properties are built into the main gPROMS database.

In addition, it is recommended that the same cyclical recovery scheme of recycle and withdrawal of the methanol be extended to the DME side draw stream. By doing this, it is expected that the column can achieve a higher throughput while maintaining outlet purities, or be more robust with varying feed compositions.

2. **Comprehensive comparison of the continuous DWC and the semicontinuous DWC**

After conducting the presented research, it is difficult to determine which of the two most promising technologies is better. After the semicontinuous DWC has been optimized, it should be compared to an optimized case of the continuous DWC. The columns' economics should be analyzed as well as the flexibility and operability of the two columns given variations in the feed composition and flow rate. In addition, an optimized DWC with only three outlet streams, having methanol and water be removed together in the bottoms stream, should also be compared to the two systems. Water-methanol separation is a mature process that might be more economical to perform after the DME and carbon dioxide are separated out. All three of these cases should be compared in a rigorous economic analysis.

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