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Title: Space-Constrained Purification of Dimethyl Ether through Process Intensification using Semicontinuous Dividing Wall Columns

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Key words: dimethyl ether, process intensification, dividing wall column, semicontinuous distillation, plant-on-a-truck, mobile plant, computer simulation, Aspen Plus Dynamics

Abbreviations: ACCE, Aspen Capital Cost Estimator; CCA, Capital Cost Allowance; CO2, Carbon Dioxide; DME, Dimethyl Ether; DWC, Dividing Wall Column; H2O, Water; MeOH, Methanol; MV, Middle Vessel; PPDP, Product and Process Design Principles; S-DWC, Semicontinuous Dividing Wall Column; SwoMV, Semicontinuous without Middle Vessel;

ABSTRACT

In this work, a distillation system that purifies dimethyl ether (DME) from its reaction by-products is designed to aid in the conversion of natural gas, flare gas, or solution gas into a useful energy product in remote locations. The distillation equipment must fit inside of a 40-foot shipping container to be easily transported. 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 the dividing wall column (DWC) and a novel semicontinuous dividing wall column (S-DWC). The traditional DWC and the S-DWC both purify DME to fuel grade purity along with producing high purity waste streams. The S-DWC purifies the reaction intermediate methanol to a higher grade 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.

1. INTRODUCTION

1.1 Motivation

A major problem facing the energy industry of Alberta, Canada is the flaring and venting of solution gas from crude oil and crude bitumen production operations. Oil producers are making a great effort to capture these gasses and use them downstream, however it is not always economical to capture the solution gas and it is flared or vented to the atmosphere. According to the Alberta Energy Regulator, the energy industry captured 95.6% of solution gas produced in 2014, up from 95.3% in 2013 (Alberta Energy Regulator, 2016). 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 and requires the implementation of gas conversion technologies if this limit is exceeded (Ellis, 2011). Low natural gas prices and high pipeline and compression costs challenge the economic viability of gas conservation (Alberta Energy Regulator, 2016). However, failing to generate useful energy from the flared gas misses the opportunity to offset electricity production from Diesel generators at the high cost of $0.40/kWh (Zubrin et al., 2016) . As such, the solution is to convert the energy in the gas into a useful form using economical and small-scale technology. Due to recent tightening in Alberta's legislation (Ellis, 2011), there is a strong business case for the development of technologies that convert raw natural gas into a useful product, such as dimethyl ether.

Dimethyl ether (DME) is a new fuel that is becoming a popular alternative to traditional combustion fuels. DME is a non-toxic, non-corrosive, and non-carcinogenic odourless gas (Muller and Hubsch, 2000) and can be produced from a variety of feedstocks including natural gas and organic material. DME can be transported using the existing liquefied petroleum gas infrastructure and it can be used to power a Diesel engine with small modifications(California Environmental Protection Agency, 2015). 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 (AB Volvo, 2007). In comparison to Diesel, DME burns significantly cleaner, creating no sulphur oxide or particulate emissions and producing minimal nitrous oxides and carbon monoxide (Muller and Hubsch, 2000). 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 (California Environmental Protection Agency, 2015).

Dimethyl ether is commonly produced using one of two reaction 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 a separate reactor, 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 and carbon dioxide (California Environmental Protection Agency, 2015).

1.2 Background

Process intensification is the drastic reduction in size, energy usage or waste production from a chemical plant and is used to improve the overall efficiency of industrial processes (Stankiewicz and Moulijn, 2000). Lately, these improvements are more easily developed because of recent advancements in computational speed making it faster to explore less common configurations of chemical processes (Phimister and Seider, 2000a). Distillation, an energy intensive separation unit, has seen significant research in the area of process intensification in recent years. The intensified distillation technologies explored in this work are semicontinuous distillation, semicontinuous without middle vessel distillation and diving wall distillation.

Conventionally, distillation columns are used in batch and continuous operation, with each column separating a mixture into two different chemical streams. 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, demonstrating a ternary separation (Phimister and Seider, 2000b). Wijesekera and Adams demonstrated distillation processes that purify four or five components with one column and two or three middle vessel tanks (Wijesekera and Adams, 2015a). In the five-component configuration, the most and least volatile components are drawn as the distillate and bottoms streams of the column, while the three middle components concentrate in 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 (Wijesekera and Adams, 2015b). 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 (Phimister and Seider, 2000a) 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 (Adams and Seider, 2006).

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. In two different simulations, they were able to separate DME, methanol and water into three high purity streams (Pascall and Adams, 2013) and CO_2, DME, methanol and water into high purity CO_2 and DME while combining the methanol and water at the bottom of the column(Pascall and Adams, 2014). To date, the separation of CO_2, DME, methanol and water into four high purity streams has not been demonstrated with semicontinuous distillation in the open literature.

Semicontinuous distillation without a middle vessel (SwoMV) was developed to increase the throughput of the process and decrease the overall cost of traditional semicontinuous distillation. 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 the intermediate component 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 purifies the lightest and heaviest components at a variable continuous flow rates, and the intermediate component intermittently (Meidanshahi and Adams, 2015b). The SwoMV configuration has been demonstrated for the purification of a benzene, toluene and o-xylene mixture (Meidanshahi and Adams, 2015b), however no one has used it to separate DME from its reaction by-products or any four-component mixtures.

The dividing wall column (DWC) is another process intensification separation technology that operates more economically and energy favourably than continuous distillation systems. The DWC 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 accumulates on the right side of the wall and is directly withdrawn in a side draw stream. The most and least volatile components, 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 (Yildirim et al., 2011). For certain situations, continuous DWC are cheaper than conventional continuous distillation (Yildirim et al., 2011).

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 separation 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 (Kiss and Ignat, 2013). Kiss and Suskwalak combined reactive distillation with a divided wall column to dehydrate methanol to produce DME, methanol and water (Kiss and Suszwalak, 2012). 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 (Minh et al., 2012). 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 separation unit that can help produce DME from raw natural gas in a remote location by purifying it from its one-step reaction by-products. 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 work is to develop a separation unit using the process intensification techniques mentioned above 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 since the product is expected to be used as a Diesel substitute for wellhead machinery.

The following work explains a solution to the problems described above. Initially, the conventional semicontinuous distillation was explored. However, it was found that the space constraints imposed resulted in a system that had far fewer trays than would normally be optimal for such a system, thus requiring far higher reflux and reboil ratios (and thus higher energy costs per unit separated) to compensate. The result was too expensive for this application and therefore has been omitted for brevity. Instead, this work focuses on the two more successful options: the dividing wall column system and the novel semicontinuous dividing wall column system, which combines concepts from DWC and SwoMV systems. Both are able to purify DME in a manner that is competitive with the diesel market, with different strengths and weaknesses.

2. MATERIALS AND METHODS

2.1 Design specification

The feed conditions and some of the product purity goals were provided by ChemBioPower. This company 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 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 and would normally leave with the CO_2 product. 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%	98.9% (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, the separation unit must be small enough to fit inside of a 40-foot shipping container. 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 is a challenge to fit the separation unit inside this dimension.

Table 2: ISO 1AA 40' Shipping container dimensions (*ISO 669: International Standard: Series 1 Freight Containers - Classification, Dimensions and Ratings*, 1995).

	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 is the total cost of the project. Based on energy content, dimethyl ether can economically replace Diesel at $0.54 per litre of DME, which is equivalent to a sale price of $1.01 per litre of Diesel (ChemBioPower, 2016). Since separation costs generally make up over half of the cost of a pure substance (Kin, 1980), 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 units were modeled using Aspen Plus V8.8 including either the steady state (Aspen Plus) and dynamic simulators (Aspen Plus Dynamics) as needed. 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 previously shown to predict accurately the vapour-liquid behaviour of the relevant quaternary, ternary and binary systems(Ye et al., 2011) . 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.

The dividing wall columns are modelled using a combination of two column models since Aspen Plus does not have a built in dividing wall column unit. The prefractionation section is modelled using a `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 main column several trays below the top and several trays above the bottom of the main section, respectively. Also, a portion of the liquid and vapour flows from these connection trays 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 (Okoli and Adams, 2015).

2.3 Economic Analysis

2.3.1 Capital Costs

The cost to manufacture each piece of equipment was estimated using two methods, the Aspen Capital Cost Estimator (ACCE) V8.8 (Aspen Technology Inc, 2014) and the capital cost correlations described in *Product and Process Design Principles* (PPDP) (Seider et al., 2009). ACCE is a rigorous costing program that uses a knowledge base of designs, methods and models to develop detailed engineering procurement construction estimates (Aspen Technology Inc, 2012). 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 (Okoli and Adams, 2015). 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 (Seider et al., 2009). In all cases, the columns operate around 13 atm, however every column was designed to withstand pressures up to 16 atm for safety purposes (Seider et al., 2009). 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.

2.3.2 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) (Seider et al., 2009). 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) (Seider et al., 2009). The most costly source of electricity in a remote location would be a Diesel generator (40¢/kWh) (Zubrin et al., 2016) whereas a cheaper option would be to use electricity from the grid (example: 8.02¢/kWh - 2013 Alberta average (Alberta Electric System Operator, 2014)) although this may not be available in remote locations. Another refrigeration option is an absorption chiller which is ideal for locations with high electricity costs and low fuel costs (Chicco and Mancarella, 2009). 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 (Chicco and Mancarella, 2009) 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 the most conservative estimate. Note that in practice, a portion of the DME produced would be used instead of Diesel, which using either the proposed systems would have approximately the same cost.

The reboilers are fired heaters are powered by natural gas since it is readily 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) (EIA - Official Energy Statistics from the US Government, 2016)and using a factor of 0.85 to account for heater inefficiencies (Towler, 2008).

2.3.3 Total Cost per unit

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 3 are used to calculate the production rate in different units.

Table 3: Physical properties used in the economic analysis.

Molecular weight of DME (98.5%)	45.87122	gm/mol	(Aspen Technology Inc, 2014)
Lower heating value (DME)	28.882	MJ/kg	(Boundy, B., Diegel, S. W., Wright, L., & Davis, 2011)
Lower heating value (Low Sulfur Diesel)	42.612	MJ/kg	(Boundy, B., Diegel, S. W., Wright, L., & Davis, 2011)
Density of DME	665	gm/L	(Boundy, B., Diegel, S. W., Wright, L., & Davis, 2011)
Density of Diesel	847	gm/L	(Boundy, B., Diegel, S. W., Wright, L., & Davis, 2011)
Energy density of DME	1,325	MJ/kmol	Calculated
Energy in 1L of diesel	36.09	MJ/L	Calculated

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 (Peters and Timmerhaus, 2003). 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 calculated.

2.3.4 Business Case Analysis

A business model analysis to determine the price a customer is willing to pay for a distillation unit that purifies fuel grade DME. The assumptions made about the customers and their environment are listed in Table 4. 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 over 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 to separate DME is \$0.25/L of DME. 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-site fuel generation, as opposed to trucking in fuel to remote locations. Estimating 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%. Also, the customers will be large corporations in Alberta and subject to the corporate tax rate of 27% (Sherman, 2015), and use the capital cost investment against their income taxes owed through the capital cost allowance of manufacturing equipment (Class 43) (Sherman, 2015). 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 4.

$$Present\ Value = \frac{CdT}{d+r}\left(\frac{1+0.5r}{1+r}\right) - \frac{SdT}{d+r}\left(\frac{1}{(1+r)^n}\right)$$ (Horngren et al., 2016)

Table 4: Rates used to conduct a business model analysis.

Max price of DME customer will pay for the purification step	$0.25 / L DME
Discount rate (Required rate of return, high risk investment) *(r)*	30%
Corporate tax rate (Alberta) (Sherman, 2015)*(T)*	27%
CCA rate: Class 43: Manufacturing equipment (Sherman, 2015) *(d)*	30%
Salvage value (conservative) *(S)*	$0
Project lifetime *(n)*	3 years

3. RESULTS AND DISCUSSION

3.1 Case 1: Continuous Dividing Wall Distillation

3.1.1 Process Description

The first potential solution to separate DME in a 40-foot column is the dividing wall distillation column. Two different dividing wall distillation columns of different heights were analyzed in this section. The column of the first design is under 40-feet whereas the second column is designed to meet all other constraints other than the height requirement in order to understand how the height limit affects performance. In the first design, the column shown in Figure 1, 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 2, the column has 38 trays, all of which are spaced 18 inches apart. The smaller tray spacing at the bottom of the column in the first design 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 (Fair, J., Steinmeyer, D., Penney, W., & Crocker, 1997).

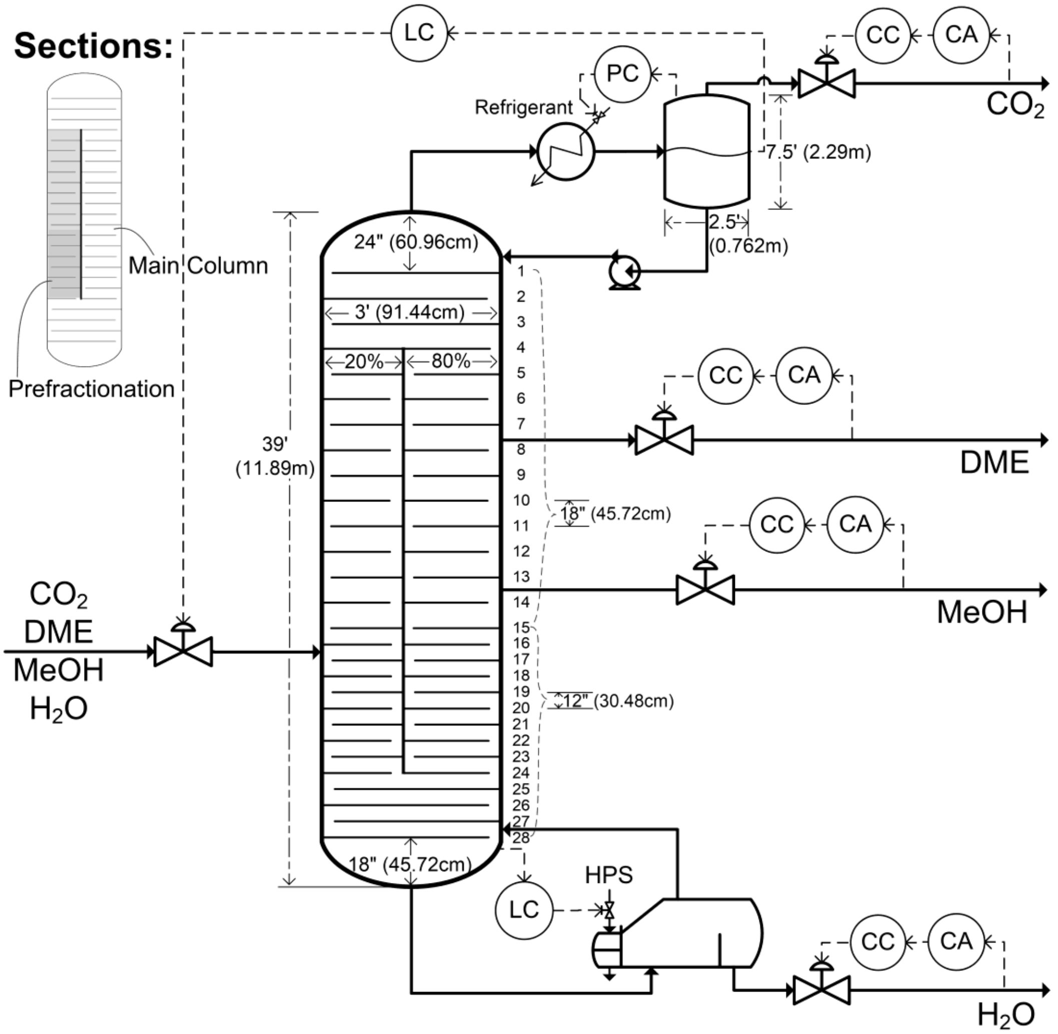

Figure 1: A schematic of the DWC with 28 trays and a 40 foot height restriction.

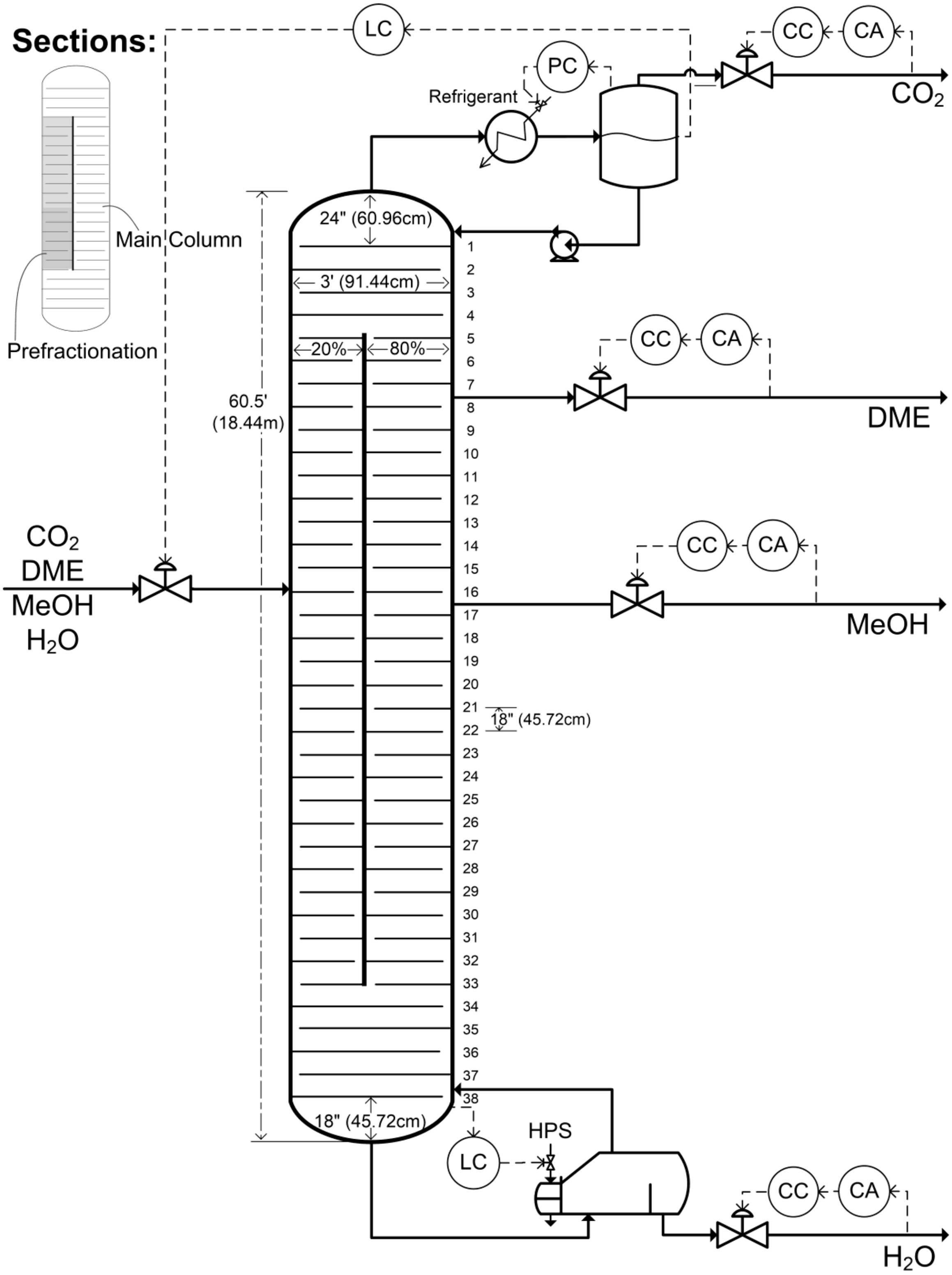

Figure 2: A schematic of the DWC with 38 trays and no height restriction.

For both columns, the feed enters the column and separates partially in the prefractionation section. 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.

3.1.2 Column Performance

Both of the dividing wall column designs 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. Both columns produce CO_2, DME and water at the same purities and flow rates. The 28-tray DWC produces 98.57% methanol (not quite recycle grade) whereas the 38-tray column produces 98.92% pure methanol (recycle grade). Also, the taller column has drastically lower reflux and boilup ratios, along with approximately half of the condenser and reboiler duty; 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 and 38-tray divided wall columns.

	28-tray DWC	**38-tray DWC**
Purity (mol%)		
CO_2	99.50%	99.50%
DME	98.50%	98.50%
Methanol	98.57%	98.92%
Water	99.50%	99.50%
DME Flowrate	25.23 kmol/hr	25.21 kmol/hr
Condenser duty	1.0173 MW	0.5378 MW
Reboiler duty	1.1425 MW	0.6632 MW
Condenser Temperature	242.6 K	242.6 K
Reboiler Temperature	465.4 K	465.6 K

3.2 Case 2: Semicontinuous without Middle Vessel, Dividing Wall Distillation

3.2.1 Process Description

The distillation configuration proposed as Case 2 is a dividing wall column operated similarly to the Semicontinuous without Middle Vessel (SwoMV) set up developed by Meidanshahi and Adams (Meidanshahi and Adams, 2015b). In the previous sections, it was found that the continuous divided wall column is an inadequate process intensification techniques to meet all of the desired product purities with the height restriction. The proposed method is a combination the two and will be referred to as the semicontinuous dividing wall column (S-DWC).

A schematic diagram of the S-DWC process is shown in Figure 3. The column is three feet in diameter 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 3. 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 control scheme is shown in Figure 3. 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 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. The methanol is collected intermittently, as its purity bounces between two bounds.

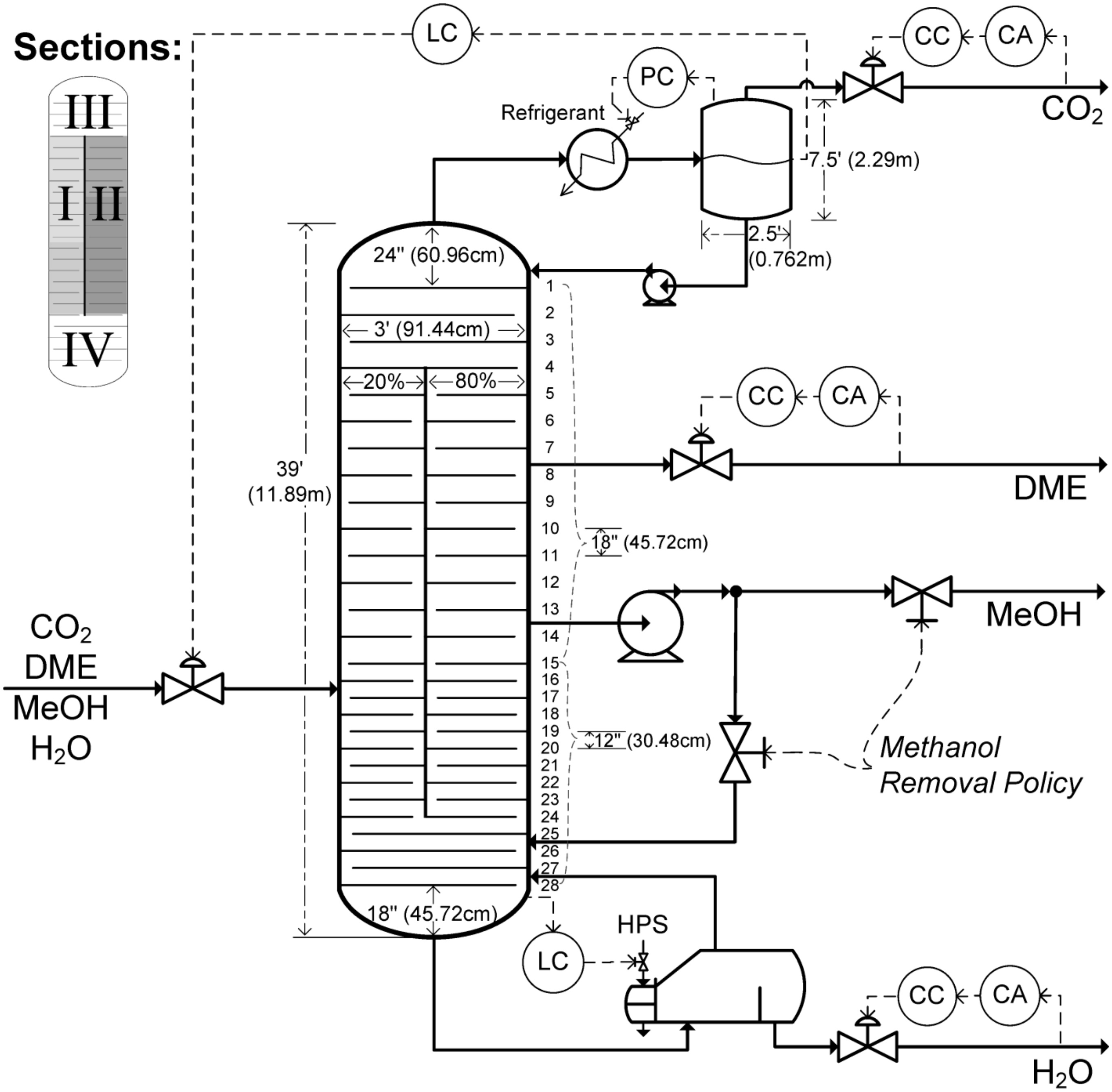

Figure 3: Design structure and control scheme for the S-DWC configuration.

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 in pressure-driven mode, there must be a pressure drop between all units. For the purpose of modelling, valve models (VALVE-LO, VALVE-HI, LO-R-VAL and HI-R-VAL) are placed on the internal flow stream in between the prefractionation and main column section to account for the pressure losses associated with pipe flows, even though there is no actual valve in practice. Additionally, compressors and pump models are installed before the valve models to negate the pressure drop over the valves so that there is no pressure drop along internal flows within the DWC, and again, the pumps (PUMP-LO and PUMP-HI) and compressors (COMP-HI and COMP-LO) are not present in practice. A screen capture of the units in Aspen Plus, before being exported to Aspen Plus Dynamics is shown in Figure 4.

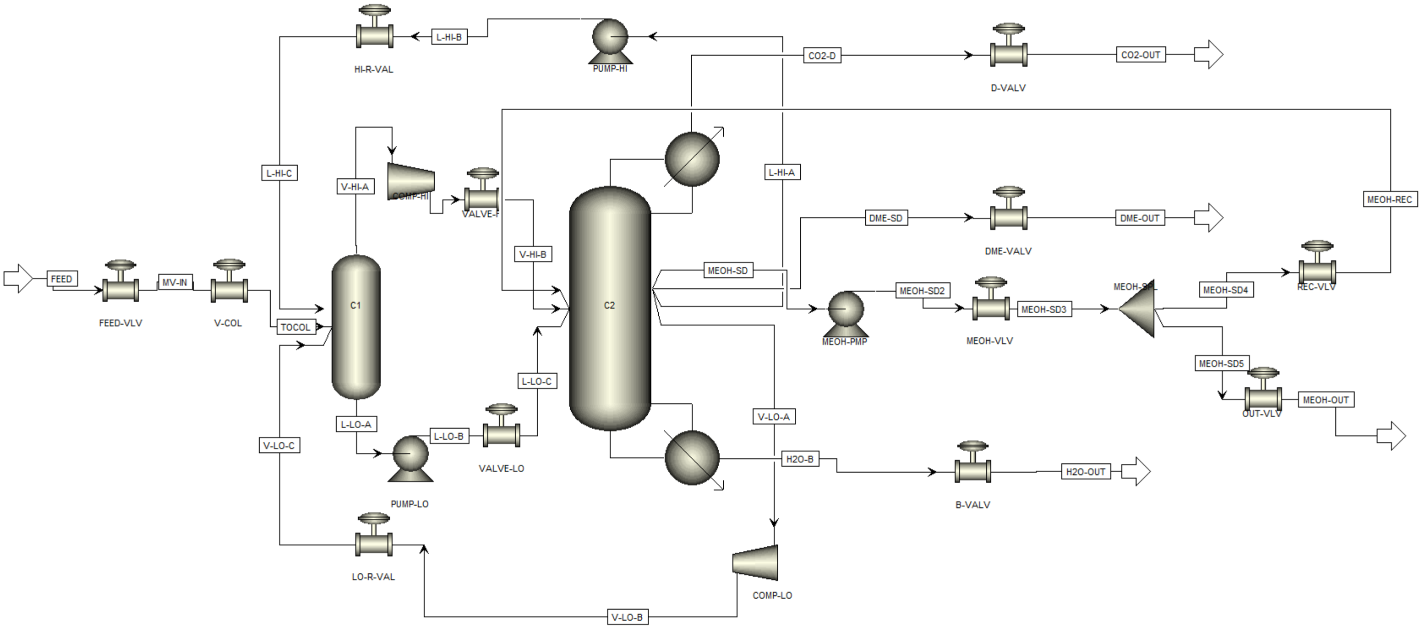

Figure 4: A screen capture of the S-DWC modelled in Aspen Plus.

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 6. The equivalent diameters are the diameters used to model each section of the column.

Table 6: 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 5, 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 (Wankat, 1988). 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 (Wankat, 1988). These areas are summarized in Figure

5 (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 7. Note that Sections III and IV each have 90% active area, the same as the actual divided trays.

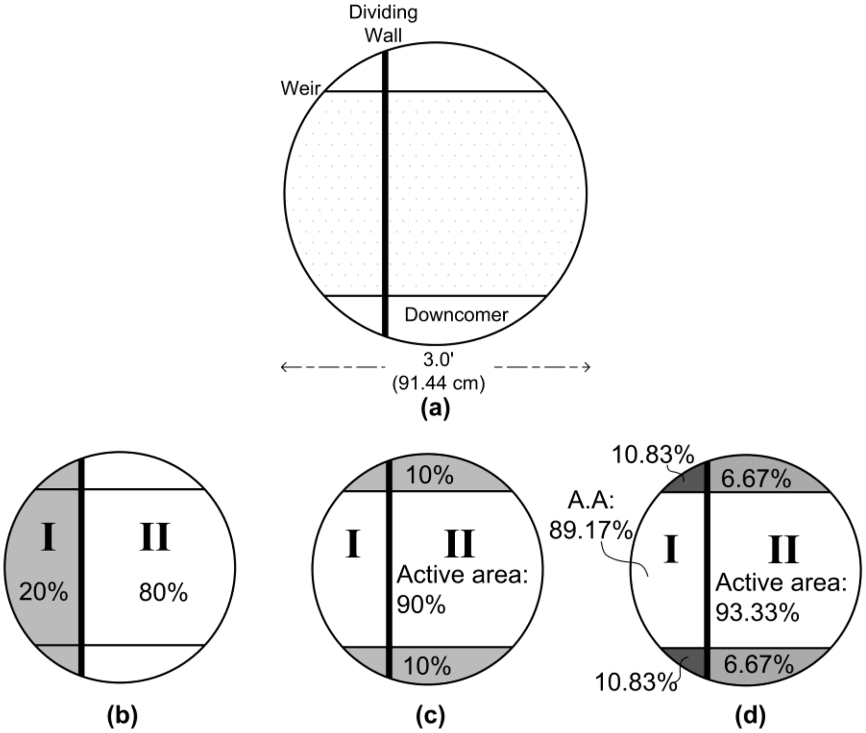

Figure 5: Divided tray geometry. (a) Geometry of the downcomer, weir and dividing wall locations. (b) Illustration of the proportionate area on either side of the dividing wall. (c) Illustration of the downcomer area. (d) Illustration of the active and inactive areas on each side of the dividing wall.

Table 7: 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

3.2.2 Control System

The unique feature of this dividing wall column is its semicontinuous operation. The control scheme of the S-DWC is similar to that described by Meidanshahi and Adams (Meidanshahi and Adams, 2015b) and is shown in Figure 3. 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 desired methanol purity somewhere in between. In this case, the lower bound is 98.7 mol% while the upper bound is 99.2 mol%, which were selected manually through trial-and-error. 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.

3.2.3 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 6. 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 7; both of these graphs are used to analyse the performance of the column. The average purities and DME flow rate are shown in Table 8.

From Figure 6 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. 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. The resulting average purity of methanol meets recycle grade requirements at 98.93 mol%.

The temperatures of the condenser and reboiler are listed in Table 8. The temperatures of the column vary insignificantly compared to the other variables within the column.

Table 8: Stream and unit results of the semicontinuous dividing wall column. The average results are calculated using the model data collected every 0.01 hours and estimated using Simpson's 3/8 rule (Isaacson and Keller, 1966).

	S-DWC
Average Purity (mol%)	
CO_2	99.53%
DME	98.50%
Methanol	98.93%
Water	99.51%
Average DME Flowrate	21.99 kmol/hr
Average Condenser duty	1.020 MW
Average Reboiler duty	1.128 MW
Average Condenser Temperature	242.6 K
Average Reboiler Temperature	465.4 K

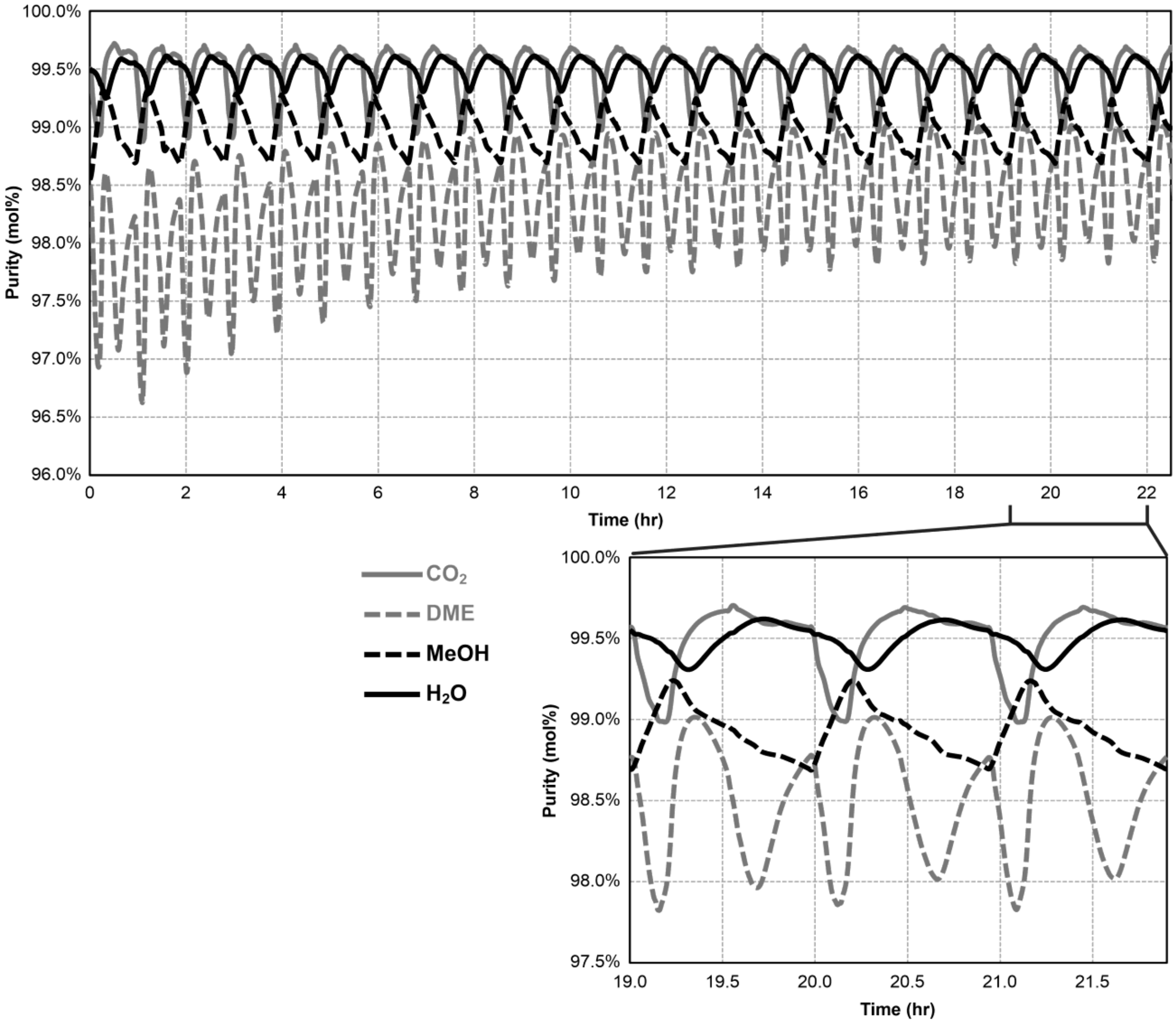

Figure 6: Purities of the outlet streams from the SwoMV-DWC showing the first 23 cycles of the 50 cycle run. The call-out shows three chosen cycles in more detail.

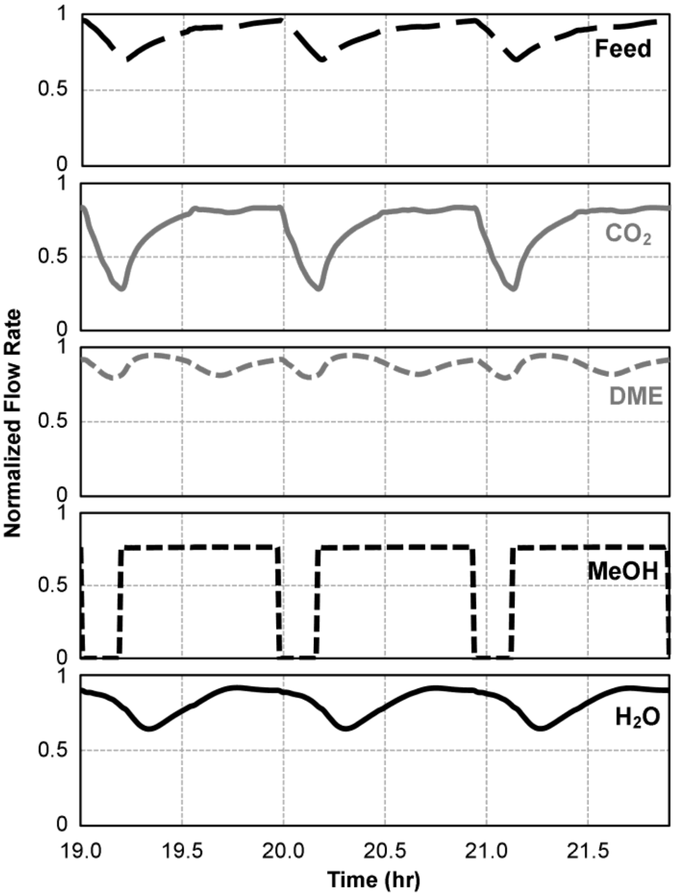

Figure 7: The flow rates of the outlet streams from the semicontinuous dividing wall column.

To demonstrate the operability of the column, the condenser drum and sump levels, condenser and reboiler energy usage, the vapour velocities and flooding approach fractions are shown in Figure 8. The average utility usage is summarized in Table 8**Error! Reference source not found.**. A select number of trays were tested for weeping using the Mersmann method (Mersmann et al., 2011). The four slowest vapour velocities are all larger than the highest weeping velocity, as shown in Figure 8 (C), proving there is a low risk of weeping. The Fair correlation (Fair, J., Steinmeyer, D., Penney, W., & Crocker, 1997) is used to calculate the flooding velocities. Figures (D) and (E) in Figure 8 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.

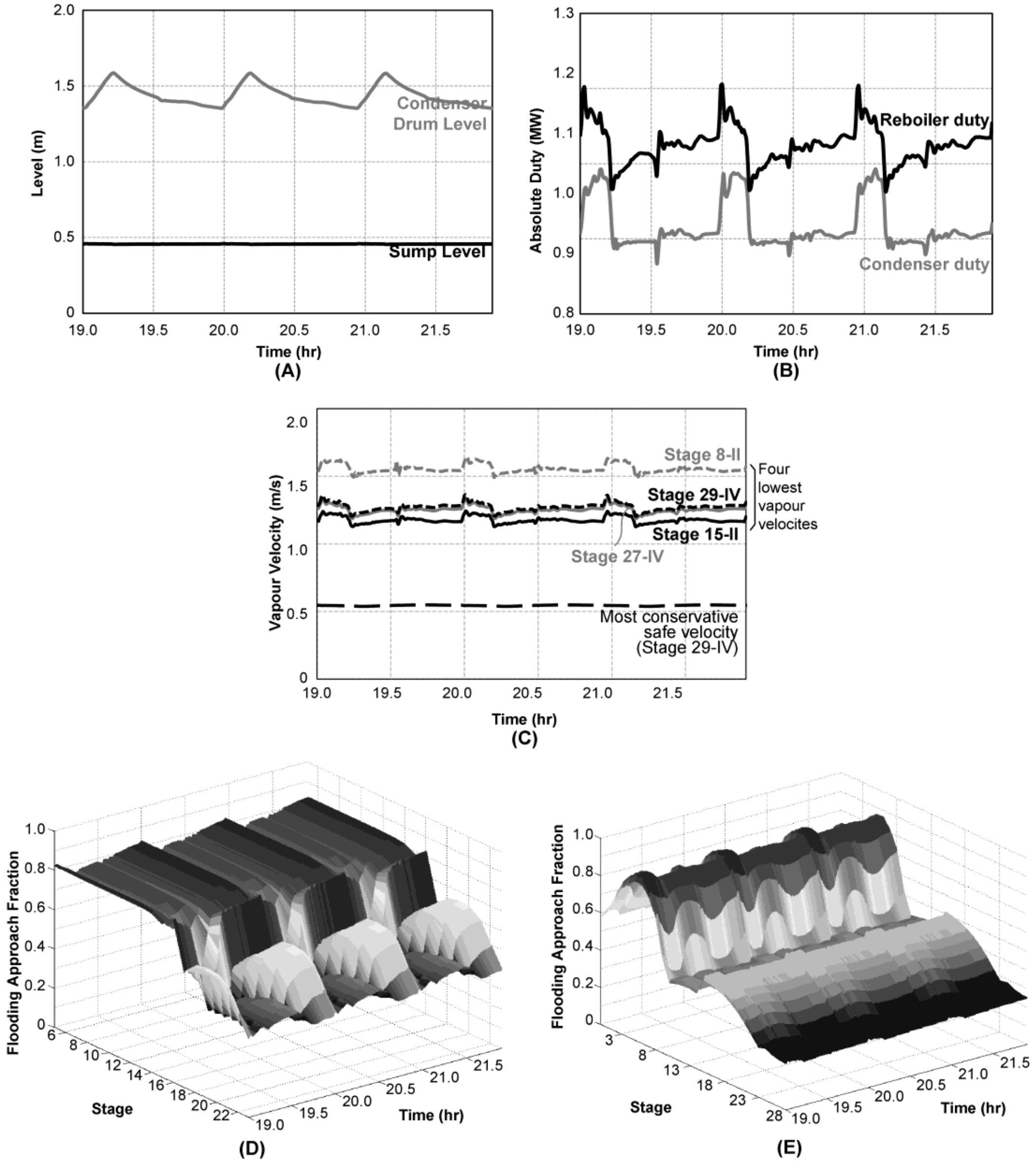

Figure 8: (A) Condenser drum and sump level during each cycle. (B) The absolute energy usage by the condenser and reboiler. (C) The vapour and weeping

velocities for the lowest vapour velocities and the most conservative minimum weeping velocity of the S-DWC. (D) The flooding approach profile for Section I of the S-DWC. (E) The flooding approach profile for Sections II, II and IV 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.

3.3 Economics

3.3.1 Capital Costs

Economics must be considered when evaluating each design. Table 9 outlines the capital cost breakdown and the estimated weight of each piece of equipment required to operate the two 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. Note that in Case 1, only the height-constrained column is considered.

Table 9: The capital cost breakdown for Case 1 and Case 2.

Case 1 – 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
Case 2 – 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

Both cases have a total capital costs in the same order of magnitude because the size of the equipment used is similar. Each design case weighs much less than the 30,480 kg limit of the shipping container.

3.3.2 Operating and Total Costs

The duties of each distillation case are summarized in Table 10, as well as the estimated cost of each energy requirement. In addition, the total cost per unit of DME produced is calculated to compare the unit to its market price. Table 10 shows the per-unit cost of DME for each distillation case.

Table 10: cost of operating the columns, the total annualized cost and cost per unit of DME for both cases.

	Case 1:	**Case 2:**

	Continuous DWC	**Semicontinuous DWC**
Condenser duty (MW)	1.017	1.020
Reboiler duty (MW)	1.143	1.128
Annual Cost of Refrigeration	$1,620,193	$1,624,493
Annual Cost of Heating	$108,640	$107,261
Total Annual Operating Cost	$1,728,833	$1,731,754
Capital Cost	*$1,323,846*	*$1,613,508*
Annual allocation of capital cost (3 years, 20%)	$631,351	$768,861
Cost of Production (Utilities)	$1,728,833	$1,731,754
Total Annualized Cost	$2,360,184	$2,500,615
DME production rate		
Molar rate (kmol/hr)	25.23	21.99
Volumetric rate (L/year)	14,614,839	12,738,022
Mass rate (tonnes/year)	9,722	8,473
Calorific rate (MJ/year)	280,778,656	244,721,468
Cost of DME Separation Step		
$/L	$0.1615	$0.1963
$/energy in 1L Diesel equivalent	$0.3034	$0.3688

The per-litre cost of DME is less that the target $0.25/L. In looking at the cost per energy equivalent litre of Diesel, and being aware that the price of diesel has approximately $1.01/L, the separation cost of DME for Case 1 and Case 2 are competitive since they are in line with the conventional wisdom that separation costs equate to 50% to the cost of a product.

The physical and economic characteristics of the two cases are compared in Table 11 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, which can have negative system level effects or require extra costs or modifications in the reactor that are not considered in this work. Alternatively, the semicontinuous DWC produces DME at a higher price but 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 11: A summary of the cost and production outputs.

	Case 1: Continuous DWC	Case 2: Semicontinuous DWC
Cost of DME Purification ($/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

3.3.3 Business Model Analysis

Only Case 2 is considered for the business model analysis, since it is the more expensive strategy and therefore a more conservative estimate. The price a customer is willing to pay for the S-DWC unit is calculated in Table 12.

Table 12: The calculated sale price of an S-DWC unit for DME separation, compared to the business-as-usual case of 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 customer ($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) (Sherman, 2015)	$275,401	
	Cost to manufacture equipment	($1,613,508)	
	Contribution Margin	$1,107,263	(39% of before tax sales price)

The price a customer would be willing to pay for the S-DWC separation system is approximately $3 million. If the manufacturer 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 (Horngren et al., 2016), and as such, the S-DWC system has a decent business case.

3.3.4 Sensitivity Analysis

The previous business analysis was done using the parameters listed in Table 4, 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 separation step 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 13. 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.

Table 13: The amount by which the variables were perturbed for the sensitivity analysis.

	Lower range		**Base Case**	**Upper range**	
Cost of DME Separation	$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	

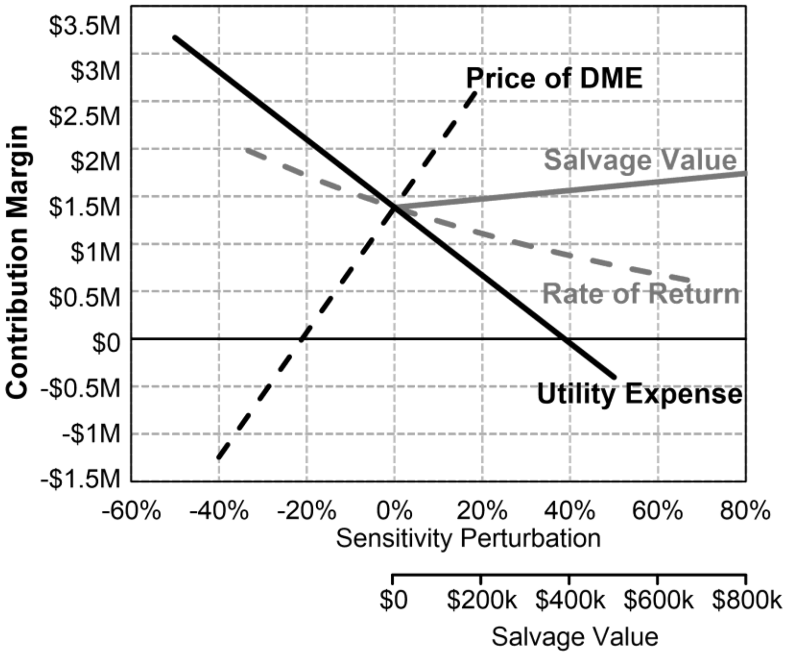

Figure 9: Sensitivity analysis of the effect of the chosen variables on the contribution margin for producing semicontinuous dividing wall columns.

Figure 9 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.

4. CONCLUSIONS

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.

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.

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.

The economics for each of the cases was examined and 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. Both cases were able to separate DME at a cost less than the required purification costs and Case 2 offers a compelling business case to market a remote DME purification system.

Overall, this research shows that it is possible to purify DME and three reaction by-products in a remote location using a single 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.

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