

## Energy efficiency improvement of dimethyl ether purification process by utilizing dividing wall columns

Le Quang Minh, Nguyen Van Duc Long, and Moonyong Lee<sup>†</sup>

School of Chemical Engineering, Yeungnam University, Gyeongsan 712-749, Korea  
(Received 6 December 2011 • accepted 5 April 2012)

**Abstract**—The alternative fuel, dimethyl ether (DME), which can be synthesized from natural gas, coal or biomass syngas, has been traditionally used as a diesel substitute or additive. DME purification processes with a conventional distillation sequence consume a large amount of energy. We used dividing wall columns (DWCs) to improve the energy efficiency and reduce the capital cost of the DME purification process. Various possible DWC arrangements were explored to find the potential benefits derived from thermally coupled distillations. The results show that utilizing DWCs can significantly reduce both the energy consumption and investment cost of the DME purification process. The lower energy consumption also results in the reduction of the CO<sub>2</sub> emission.

Key words: Distillation, Dimethyl Ether, DME, Dividing Wall Column, DWC, Thermally Coupled Distillation Column

### INTRODUCTION

To reduce the environmental problems caused by the direct combustion of fossil fuels and the diminishing energy supply, there is an urgent need to investigate alternative fuels and energy systems [1]. Dimethyl ether (DME), which can be synthesized from natural gas, coal or biomass syngas, has been traditionally used as a diesel substitute or additive [2,3]. It does not attack the stratospheric ozone and allows for the better emission control of NO<sub>x</sub>, CO, SO<sub>x</sub>, non-methane hydrocarbons and particulates such as soot [4]. DME represents a potential alternative to liquefied petroleum gas, liquefied natural gas and diesel. DME can also be an ideal fuel in the form of a hydrogen carrier, due to its high H/C ratio, high energy density, ease of storage, and ease of transportation [5].

Traditionally, DME has been produced in a two-step process (the conventional route) where syngas (typically generated from the steam reforming of methane) is first converted to methanol, followed by its dehydration to DME [6]. Natural gas is not the only resource that can be used to generate syngas; coal and biomass can also be used. Hence, DME production is not limited to one feedstock. Also, new processes are being commercialized to produce DME in a single step via auto-thermal reactors and slurry phase reactors. In comparison with the two-step method, the single-step procedure is attracting more attention because of its economic value and theoretical significance. The research at present into the single-step procedure for producing DME from syngas is focused on the best catalyst to use, as well as the process conditions and synergy effect of the reactions.

In the single-step procedure, the effluent stream from the reactors contains DME, methanol, water, carbon dioxide and other gases [7-9], and a separation unit to purify DME is necessary and crucial to the overall economics of the production process. The contributions made so far focusing on the separation of the mixture are still

limited, particularly in terms of the distillation technology. Moreover, the huge energy consumption required for the purification of DME from the effluent mixture needs to be reduced. Therefore, the main target for process engineers has been to develop a new process utilizing the energy sources efficiently and improving the energy efficiency significantly in every particular unit of the DME purification processes.

Distillation, as a workhorse of chemical process industries, is an energy-intensive process and, therefore, it is the first to be addressed to improve the energy efficiency over the short- and long-term. Furthermore, since the huge amount of energy consumed in the distillation process has a big impact on greenhouse gas emissions, saving energy in this area has become an important issue from an environmental standpoint [10,11]. To reduce the total annualized cost (TAC), which includes the operating and capital costs, the use of complex distillation arrangements should be considered, such as heat

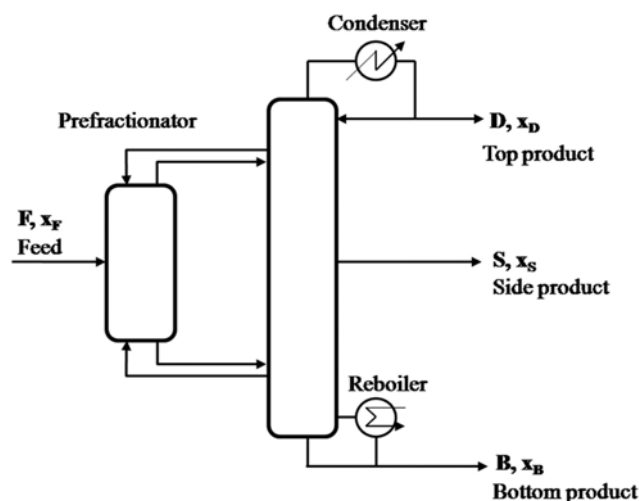


Fig. 1. Schematic diagram of fully thermally coupled distillation configuration.

<sup>†</sup>To whom correspondence should be addressed.  
E-mail: mynlee@yu.ac.kr

integration, thermal coupling, and heat pumping [12]. Some studies have proven that a fully thermally coupled configuration (Fig. 1) requires the lowest amount of energy among all of the systems of columns used for the separation of ideal ternary mixtures into pure product streams [13-18]. Instead of having an external one, a pre-fractionator can be incorporated into a single shell arrangement by installing an internal wall. This vertical wall divides a column into a pre-fractionator and a main column. This arrangement, called a dividing wall column (DWC), is thermodynamically equivalent to the Petlyuk column, providing there is no heat transfer across the dividing wall [19]. In addition, its single shell feature including only one condenser and reboiler, compared to the conventional sequences with two condensers and reboilers, offers additional benefits in terms of reducing the capital cost and spatial area. Thus, there are better prospects for DWCs as a standard distillation configuration in the next 50 years [20]. The increasing energy cost and concerns about global warming in recent times have rendered DWC technology an attractive alternative for reducing the energy consumption in distillation processes.

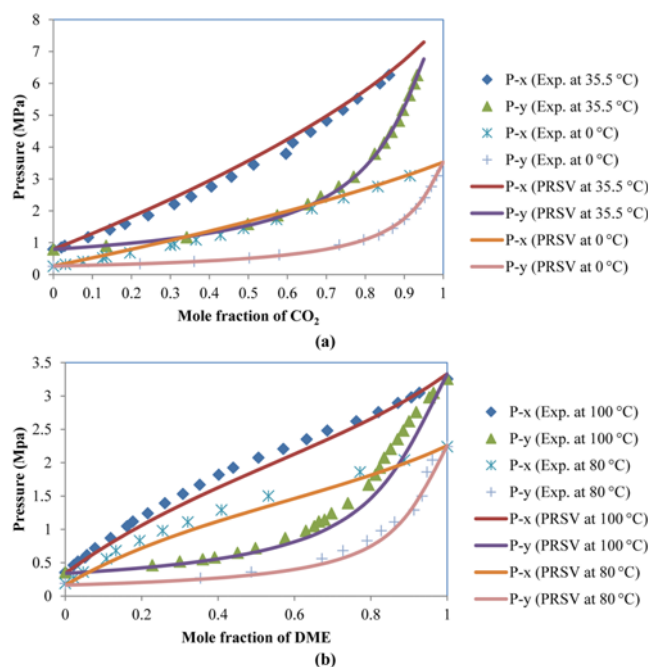
Our aim was to find a configuration suitable for improving the energy efficiency and reducing the capital cost of the DME purification process mainly via the utilization of DWCs. Various arrangements were studied by replacing several conventional distillation columns with DWCs. The results show that this novel application of DWCs can significantly reduce the investment and operating costs in the DME purification process and, accordingly, the CO<sub>2</sub> emission levels.

### CONVENTIONAL DISTILLATION COLUMN SEQUENCE FOR DME PURIFICATION

In this work, DME is the main product of the conversion process of natural gas. The effluent from the reactors is sent to the separation unit consisting of five distillation columns to purify DME from the feed mixture [21]. A process capacity of 3000 metric tons per day was chosen and the desired purity of the DME product was 99 wt%. Simulations were performed using Aspen HYSYS V7.1. Several previous works [22-24] applied the Peng-Robinson (PR) equation for the CO<sub>2</sub>-DME system and the Soave-Redlich-Kwong (SRK) model for the DME-CH<sub>3</sub>OH, and concluded that the conventional PR and SRK equations still can be reasonably used for the DME system. On the other hand, another report [21] recommended Peng-Robinson-Stryjek-Vera (PRSV) for a DME system. The PRSV equation is a two-fold modification of the PR equation that extends the application of the original PR method to highly non-ideal (non-electrolytic) systems [21]. In this study, therefore, the PRSV equation of state was chosen to predict the vapor-liquid equilibrium more accurately. To confirm its validity, the predictions of PRSV equation were compared with the experimental data for CO<sub>2</sub>/DME mixture and DME/Methanol mixture, respectively [23,24]. As shown in Fig. 2, the PRSV equation of state predicts phase compositions in good agreement with experimental data for design purposes.

Due to the low boiling point of the components, the operating pressure in the process is set to 30 bars to maintain the liquid phase on each tray. The conditions of the feed mixture are listed in Table 1.

Fig. 3 illustrates the conventional distillation column sequence and its current operating conditions. In the conventional distillation



**Fig. 2. Comparison of experimental data with the predictions of the PRSV equation of state: (a) Isothermal pressure-composition data for CO<sub>2</sub>/DME; (b) Isothermal pressure-composition data for DME/Methanol.**

**Table 1. Conditions of the feed mixture**

Feed conditions		
Component	Mass flow (kg/hr)	Mole fraction (%)
Methanol	2252.0	1.64
H <sub>2</sub> O	880.1	1.14
DME	120033.0	60.81
Methane	295.6	0.43
Hydrogen	37.2	0.43
CO	24.0	0.02
CO <sub>2</sub>	67008.7	35.53
Temperature (°C)		3.2
Pressure (bar)		30.0
Mass flow (kg/hr)		190530.0

configuration, the final products including DME are separated with the desired purity through five distillation columns (T100, T101, T102, T103 and T104). The feed stream consisting of DME, carbon dioxide (CO<sub>2</sub>), methanol (MeOH), water (H<sub>2</sub>O) and other gases is fed to the pre-fractionation column (T100) where the light and heavy key components (CO<sub>2</sub> and MeOH) are separated. The bottom stream from T100 contains DME and the heavy components and is sent to the heavy-cut column (T103) to separate DME from MeOH and water. The overhead stream of T100 is subsequently sent to the light-cut pre-column (T101) and the CO<sub>2</sub> removal column (T102) to remove the CO<sub>2</sub> completely. The compositions of CO<sub>2</sub> in the top product of T101 and T102 are enriched to 95 and 97 mol%, respectively. The distillate stream of T103 with 99 wt% DME is mixed with the bottom streams from T101 and T102 to form the final DME prod-

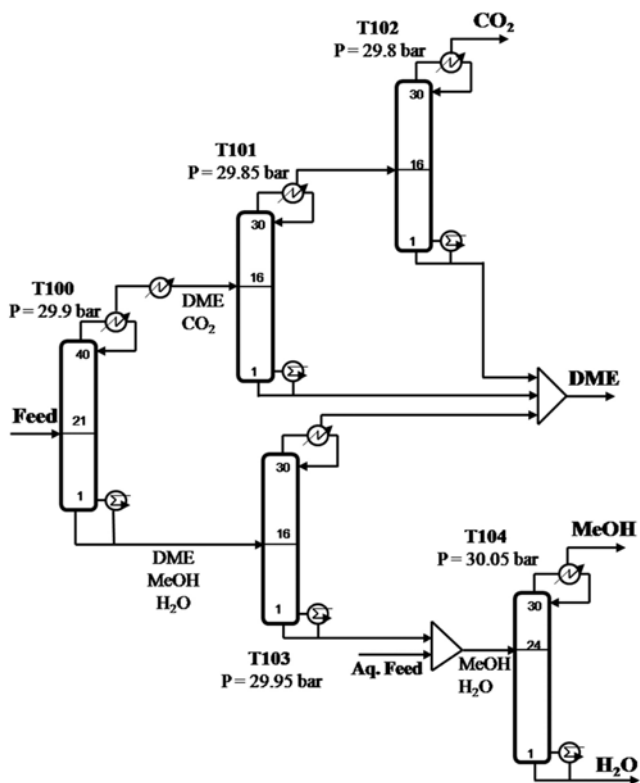


Fig. 3. Simplified flow sheet illustrating DME purification process.

uct. The bottom stream from T103 is mixed with the aqueous feed stream, which contains MeOH and water, from the upstream separator and then fed to the MeOH recovery column (T104) to remove the water. The purified MeOH from the top of T104 is recycled to

Table 2. Column hydraulics, energy performance of the conventional column sequence

	T100	T101	T102	T103	T104
Number of trays	40	30	30	30	30
Tray type	Sieve	Sieve	Sieve	Sieve	Sieve
Column diameter (m)	3.8	2.5	1.2	2.6	2.7
Number of flow paths	1	1	1	1	1
Tray spacing (mm)	609.6	609.6	609.6	609.6	609.6
Max flooding (%)	79.22	80.41	84.62	81.15	79.17
Reboiler duty (MW)	16.170	7.239	0.804	8.762	51.33
Condenser duty (MW)	0.436	0.941	0.977	1.904	24.73

the reactors for producing DME continuously.

Based on the feed composition and product specifications of the conventional distillation sequence, a simulation was performed to quantify the energy consumption as well as the total annualized cost (TAC). Table 2 includes the reboiler and condenser duties for each column. To minimize the refrigeration costs, all of the columns were designed to operate at relatively high pressures of approximately 30 bars. The column hydraulics and flooding conditions were considered to estimate the capital cost. To determine its maximum flooding level, the rating mode was simulated based on the internal specifications of the column such as the type of trays, column diameter, tray spacing, and number of passes. The hydraulic parameters used in this study are also listed in Table 2. All of the columns were designed with a load of near 80% to prevent their flooding [25]. Guthrie's modular method [26] was applied to estimate the capital cost. The capital cost for conventional distillation is the total cost of the column and auxiliary equipment, such as the reboiler and condenser,

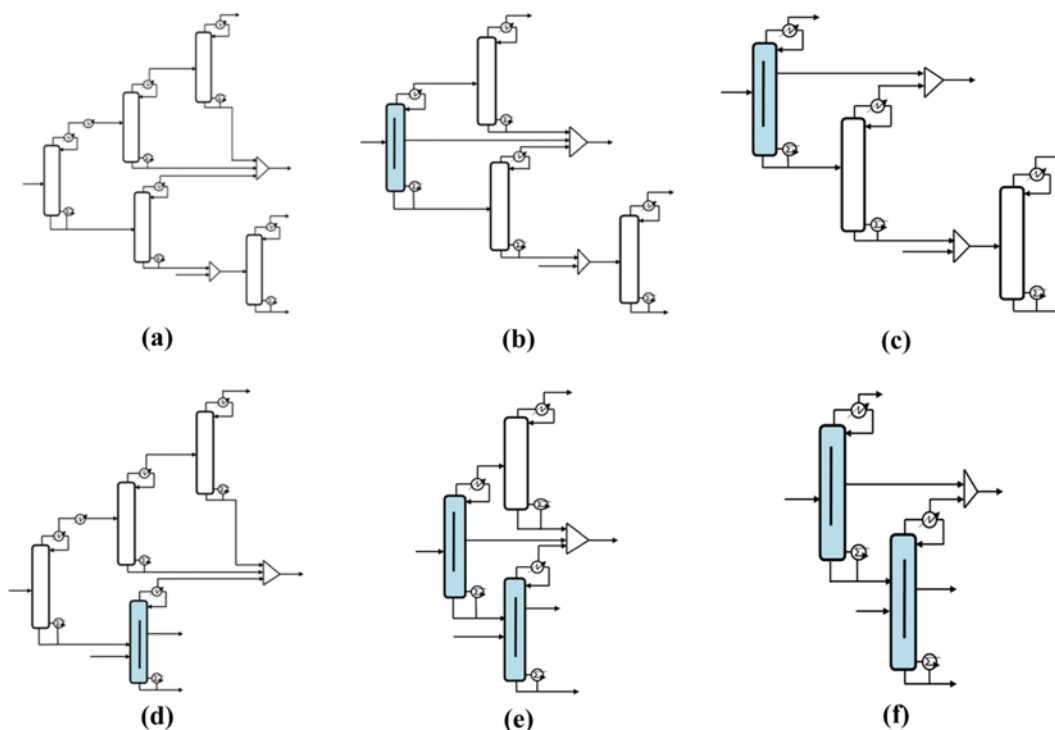


Fig. 4. Various configurations of complex column network used to purify DME. All of the gray columns are newly replaced DWCs.

while for the DWC it entails the additional cost of the dividing wall. For cost updating, a Chemical Engineering Plant Cost Index of 575.4 was used [27,28].

### PROPOSED ARRANGEMENTS USING DWCs

Various distillation configurations utilizing DWCs were explored to enhance the energy efficiency in the DME purification process. Fig. 4 shows both the conventional and nonconventional column arrangements employed for the DME purification process. Configuration (a) is the conventional sequence consisting of five conventional distillation columns. In configurations (b), (c) and (d), some of the columns are replaced with one new DWC, while configurations (e) and (f) use two new DWCs.

#### 1. Replacing Two Columns (T100 and T101) with a Single DWC

From an energy efficiency point of view, integrated and coupled structures are usually better than non-integrated ones [29]. The integration of the pre-fractionation and light-cut columns using a DWC was studied. Fig. 5 shows the proposed arrangement, including the total number of trays, feed tray location and side tray location. The DWC structure was initially designed with a shortcut design procedure [30,31] based on the structural similarity between the conventional column configuration (Fig. 6(a)) and the DWC (Fig. 6(b)). In this sloppy configuration, the first column corresponds to the pre-fractionator section in the DWC. The rectifying section of the second column and the stripping section of the third column represent the top and bottom sections of the DWC, respectively. Both the stripping section of the second column and the rectifying section of the third column are equivalent to the dividing wall section of the DWC. Consequently, the structure of the DWC can be divided into four sections: the prefractionator section for the feed mixture; the top

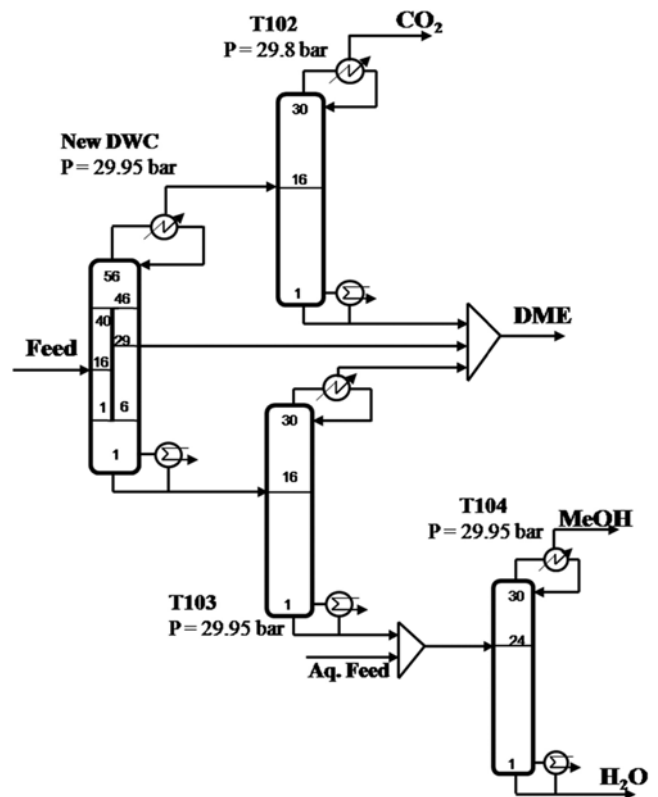


Fig. 5. Simplified flow sheet in which two columns (T100 and T101) are replaced with one DWC.

and bottom sections above and below the divided wall; and the dividing wall section [27]. The well-known Fenske-Underwood-Gilliland technique is normally sufficient to identify the proper sequence

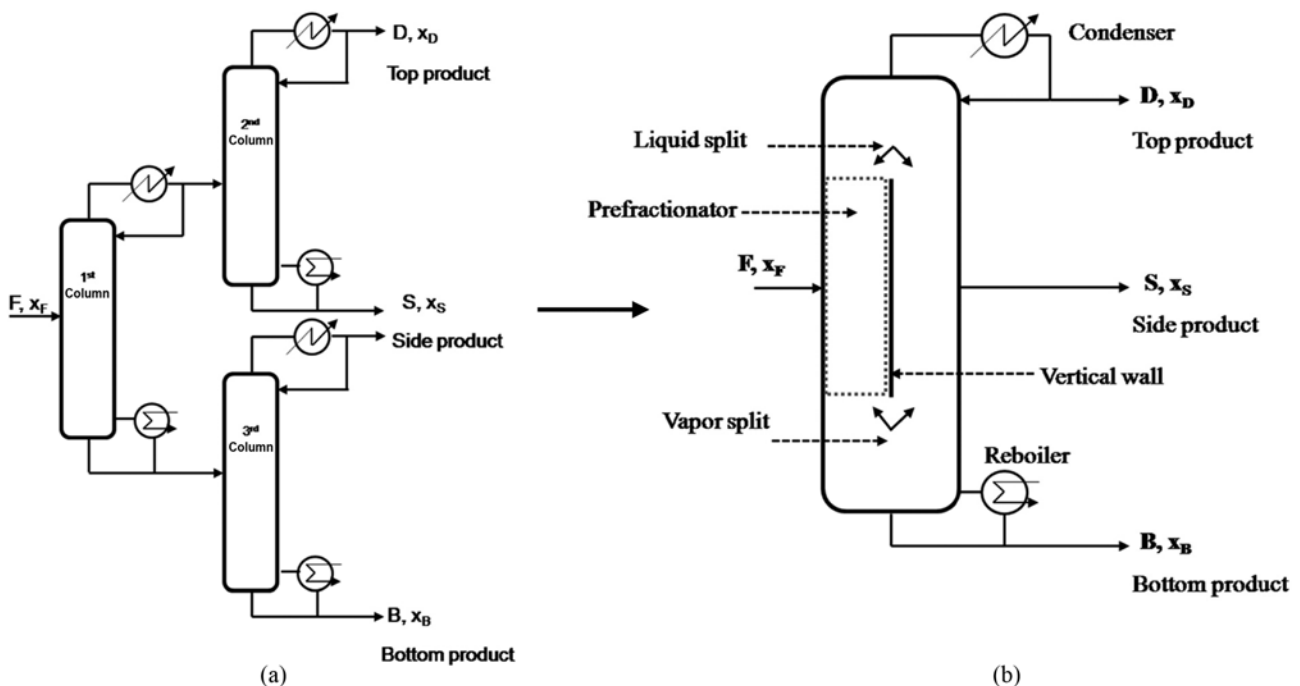


Fig. 6. Schematic diagram of: (a) the three-column sloppy configuration used for the initial design of the DWC structure; (b) a dividing wall column.

at the initial stage, but if necessary, the results can be used as a starting point for a rigorous simulation [32,33].

Since the design obtained by the shortcut method might not be the optimum, an optimizing step is essential. After the initial structure of the DWC was fixed by the shortcut method, the internal recycle flows to the prefractionator were optimized using a case study. Then, the total number of trays, feed tray location, side tray location, as well as the location of the dividing wall section, were also investigated to establish the optimal DWC structure. For each chosen structure, the internal vapor and liquid flow to the prefractionator were varied to minimize the energy consumption. To examine the effects of the feed tray on energy consumption, a number of simulation runs were carried out by varying the feed tray location to achieve the lowest reboiler duty and meet the required product specifications. Similarly, the side tray location and dividing section were also examined to find the optimal structure of the DWC. Consequently, the new DWC was designed with 56 trays. Its feed tray was the 16<sup>th</sup>. The dividing wall was located from the 6<sup>th</sup> to the 46<sup>th</sup> trays and the side stream was drawn from the 29<sup>th</sup> tray (Fig. 5). The power consumptions of the condenser and reboiler were 3.23 and 16.85 MW, respectively. This DWC can save up to 28.0% of the energy consumption based on those of T100 and T101, which corresponds to an energy saving of 7.8% for the whole process.

The cross sectional area of the middle section of this DWC is the sum of the pre-fractionator section area and the middle section area of the main fractionator. The diameter of the middle section can be calculated from its cross sectional area. On the basis of the results of the diameter of the top, middle and bottom sections of the DWC, the largest dimension of 4.2 m was chosen as the diameter of the DWC, which results in a significant reduction in the investment cost of 14.7% and 6.8% based on the two columns and the whole process, respectively.

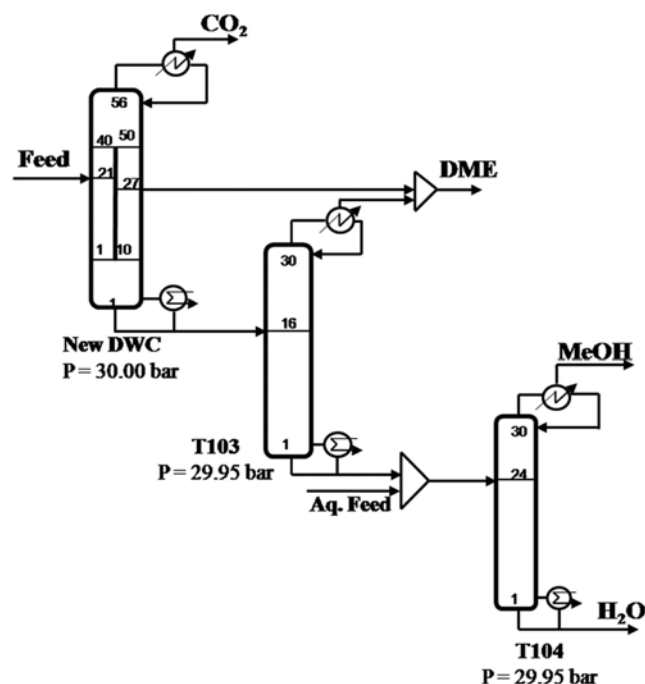


Fig. 7. Simplified flow sheet in which three columns (T100, T101 and T102) are replaced with one DWC.

## 2. Replacing Three Columns (T100, T101 and T102) with a Single DWC

Since the pre-fractionation (T100), light-cut (T101) and CO<sub>2</sub> removal (T102) columns are commonly involved in purifying CO<sub>2</sub> in a cascaded manner, the feasibility of replacing the three columns with one DWC was investigated to obtain an additional benefit from the previous arrangement of two column integration. Following the same steps used in the DWC design of the previous arrangement, a new DWC integrating the three conventional columns was designed and optimized. In the new DWC, the bottom streams from T101 and T102 could be integrated into one stream, because the compositions of the two bottom streams are almost the same. Fig. 7 shows the arrangement proposed to replace the three columns with a single DWC. The resulting condenser and reboiler duties of the new DWC are 3.51 and 16.97 MW, respectively. Thus, the new DWC results in a 29.9% reduction of the reboiler power compared with that of the three columns, which corresponds to an 8.6% improvement in the overall energy consumption in the whole process. Although this configuration improves the energy efficiency compared to the previous case in which T100 and T101 are integrated, the net additional benefit from the previous case seems to be relatively small. This is because little remixing occurs in the CO<sub>2</sub> removal column, which is used for trimming to get a higher recovery of DME. However, the replacement of the three columns with one DWC could give rise to a significant additional benefit in terms of the investment cost compared to the integration of two columns. This new configuration brought the savings up to 15.0% in terms of the investment cost, which is more than double that obtained by the previous configuration (b).

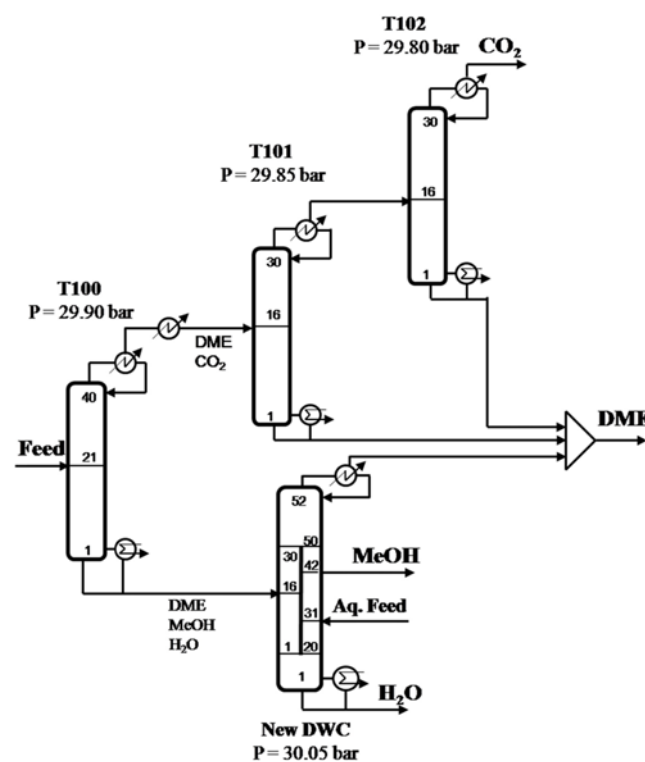


Fig. 8. Simplified flow sheet in which two columns (T103 and T104) are replaced with one DWC.

### 3. Replacing Two Columns (T103 and T104) with a Single DWC

The replacement of the heavy-cut column (T103) and the MeOH recovery column (T104) with a single DWC was considered. Fig. 8 illustrates the proposed arrangement. In the conventional sequence, the reboiler duty of T104 dominates over those of all of the other columns and seemingly has a significant impact on the energy efficiency. The energy consumption in the reboiler was decreased by up to 16.8% compared with the reboiler duties afforded by the two columns, and by 12.0% compared with the overall duties for the whole process. The investment cost was reduced by 7.4% compared with that of the two columns.

### 4. Replacing Four Columns with Two DWCs in Series

A possible configuration with further integration using DWCs is to use one DWC to replace T100 and T101 and another to replace T103 and T104, as shown in Fig. 9. The integrated process consists of two DWCs and one conventional column. It is apparent that the benefit from this arrangement is equal to the sum of those derived from configurations (b) and (d). Therefore, the energy consumption and investment cost for this case can be reduced by 19.8% and 10.1%, respectively, compared to that for the whole process.

### 5. Replacing Five Columns with Two DWCs in Series

Another option for further integration using a series of DWCs is the replacement of all five columns with two DWCs. Fig. 10 shows this fully integrated arrangement where the three columns, T100, T101 and T102, are integrated into one DWC and the two columns, T103 and T104, are replaced with another DWC. Since this configuration is equivalent to a combination of configurations (c)

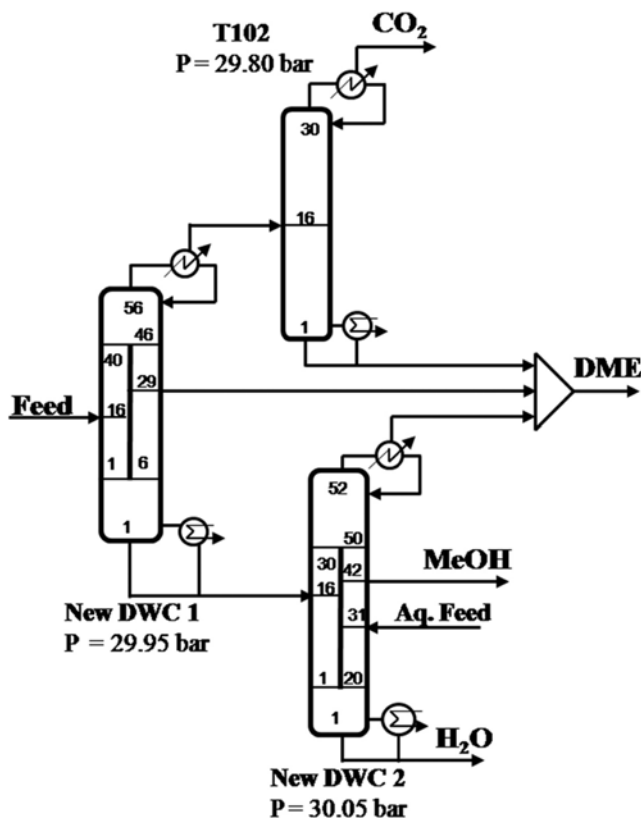


Fig. 9. Simplified flow sheet in which four columns (T100, T101, T103 and T104) are replaced with two DWCs.

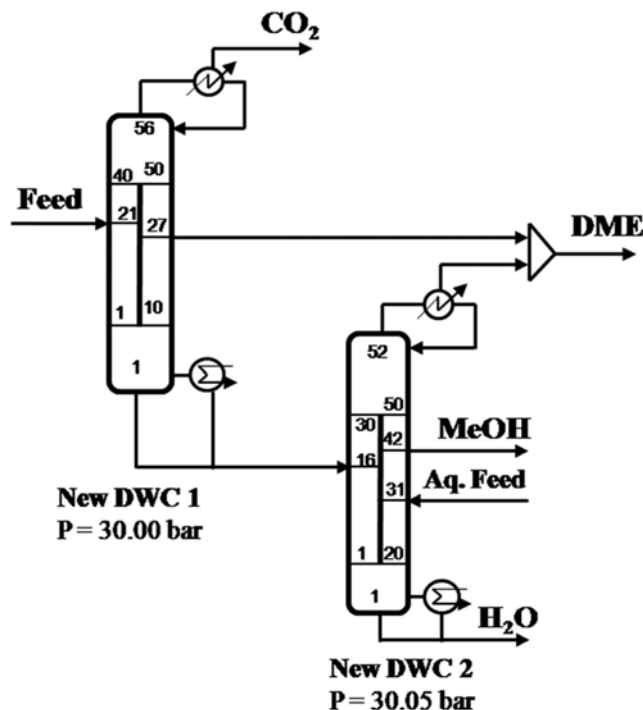


Fig. 10. Simplified flow sheet in which all five columns are replaced with two DWCs.

and (d), its benefit is the sum of those from these two configurations. The energy consumption and capital cost can be saved up to 20.6% and 18.3% in comparison with that of the whole conventional process, respectively.

A comparative summary of the key results is given in Fig. 11. Note that the conventional sequence results in both the highest annualized cost and the highest energy consumption among all those considered; therefore, it is considered as a basis for the other schemes. The relative savings of the other configurations are expressed with respect to this conventional sequence. The equivalent reductions of CO<sub>2</sub> emission are also calculated for all of the configurations and listed in Fig. 11. The results show that the DWC arrangement with full integration of the five conventional columns is the best option in terms of the energy saving, investment cost, and total annualized cost.

In addition, the replacement of the light-cut pre-column (T101) and the CO<sub>2</sub> removal column (T102) with a single DWC was examined. However, the saving of energy consumption in the reboiler was relatively small, only 4.1% from that afforded by the two columns. It is noted that the DWC application does not always take a benefit. Other possible configuration is to use one DWC to replace the pre-fractionation column (T100) and the heavy-cut column (T103). But, this configuration required more reboiling energy than that consumed in the two conventional columns. Another possible configuration for replacing T100 and T103 columns is the implementation of a top dividing wall column (TDWC) where the dividing wall is located on the top section for utilizing temperature difference of the top section between the two columns. The resulting TDWC reduced the energy consumption in the reboiler by 9.3% and reduced the investment cost by 13% compared with that for the two conventional columns.

Distillation Arrangement	(a)	(b)	(c)	(d)	(e)	(f)
Number of trays						
Col. 1	40	56	56	40	56	56
Col. 2	30	0	0	30	0	0
Col. 3	30	30	0	30	30	0
Col. 4	30	30	30	52	52	52
Col. 5	30	30	30	0	0	0
Reboiler duty [MW]						
Col. 1	16.170	16.846	16.963	16.170	16.846	16.963
Col. 2	7.239	0	0	7.239	0	0
Col. 3	0.804	0.804	0	0.804	0.804	0
Col. 4	8.762	8.762	8.762	50.000	50.000	50.000
Col. 5	51.330	51.330	51.330	0	0	0
$\Sigma$	84.305	77.742	77.055	74.213	67.650	66.963
Energy saving* [%]	0	7.8	8.6	12.0	19.8	20.6
Investment cost saving* [%]	0	6.8	15.0	3.3	10.1	18.3
TAC saving* [%]	0	3.0	4.3	11.7	14.6	16.0
CO <sub>2</sub> reduction* [%]	0	6.0	6.7	10.9	17.0	17.6

\* based on the whole process

Fig. 11. Comparison of different structural alternatives for the DME purification process.

## CONCLUSIONS

Various distillation arrangements using DWCs were studied to find the potential benefits afforded by thermally coupled distillations in DME purification processes. The results showed that utilizing DWCs can significantly reduce both the energy consumption and investment cost of the DME purification process. The integration of the pre-fractionation and light-cut columns using a DWC reduced the energy consumption by up to 28.0%. The DWC arrangement in which the pre-fractionation, light-cut and CO<sub>2</sub> removal columns are replaced with a single DWC attained a significant additional benefit in terms of the investment cost. This reduced the investment cost by up to 15.0%, which is more than twice that obtained by the integration of the two columns. The replacement of the heavy-cut and MeOH recovery columns, which dominate over all of the other columns in terms of their reboiler duty, by DWCs has great potential to improve the energy efficiency. The resulting DWC reduced the energy consumption in the reboiler by up to 16.8% and reduced the investment cost by 7.4% compared with that for the two conventional columns. Further integration using a series of DWCs provided for the further enhancement of the energy efficiency and reduced the capital cost, as well as the total annualized cost. The fully integrated DWC arrangement, in which all five conventional columns were replaced with two DWCs in series, maximized the energy efficiency and minimized the investment cost and TAC: the energy consumption, capital cost and TAC were reduced by up to 20.6%, 18.3% and 16.0%, respectively. Process compactness and reduced CO<sub>2</sub> emissions are an additional benefit from the DWC application.

## ACKNOWLEDGEMENT

This research was supported by a grant from the Fundamental R&D Program for Integrated Technology of Industrial Materials

funded by the Ministry of Knowledge Economy, Republic of Korea.

## REFERENCES

- H. D. Ng, J. Chao, T. Yatsufusa and J. H. S. Lee, *Fuel*, **88**, 124 (2008).
- J. Hu, Y. Wang, C. Cao, D. C. Elliott, D. J. Stevens and J. F. White, *Ind. Eng. Chem. Res.*, **44**, 1722 (2005).
- E. D. Larson and H. Yang, *Energy Sustain Dev.*, **8**, 115 (2004).
- T. H. Fleisch, *Diesel Prog. Engines Drives*, **61**, 42 (1995).
- V. V. Galvita, G. L. Semin, T. M. Belyaev, T. M. Yurieva and V. A. Sobyenin, *Appl. Catal. A: Gen.*, **216**, 85 (2001).
- T. A. Semelsberger, R. L. Borup and H. L. Greene, *J. Power Sources*, **156**, 497 (2005).
- R. Vakili, E. Pourazadi, P. Setoodeh, R. Eslamloueyan and M. R. Rahimpour, *Appl. Energy*, **88**, 1211 (2011).
- M. Stiefel, R. Ahmad, U. Arnold and M. Döring, *Fuel Process. Technol.*, **92**, 1466 (2011).
- A. Hadipour and M. Sohrabi, *Chem. Eng. J.*, **137**, 294 (2008).
- M. A. Gadalla, Z. Olujić, P. J. Jansens, M. Jobson and R. Smith, *Environ. Sci. Technol.*, **39**, 6860 (2005).
- R. G. Guerra, J. G. S. Hernandez and S. Hernandez, *Chem. Eng. Res. Des.*, **87**, 145 (2009).
- R. Agrawal and Z. T. Fidkowski, *AIChE J.*, **44**, 2565 (1998).
- I. Dejanovic, Lj. Matijasevic and Z. Olujić, *Chem. Eng. Process.*, **49**, 559 (2010).
- M. Emtir, E. Rev, P. Mizsey and Z. Fonyo, *Comput. Chem. Eng.*, **23**, 799 (1999).
- Z. T. Fidkowski and L. Krolkowski, *AIChE J.*, **33**, 654 (1987).
- K. Muralikrishna, V. K. P. Madhavan and S. S. Shah, *Trans IChemE*, **80**, 155 (2002).
- R. C. van Dieggelen, A. A. Kiss and A. W. Heemink, *Ind. Eng. Chem. Res.*, **49**, 288 (2010).
- R. Agrawal and Z. T. Fidkowski, *Ind. Eng. Chem. Res.*, **37**, 3444

- (1998).
19. K. A. Ammidunin, R. Smith, D. Y.-C. Thong and G. P. Towler, *Trans IChemE*, **79**, 701 (2001).
  20. C. Bravo-Bravo, J. G. Segovia-Hernández, C. Gutiérrez-Antonio, A. L. Duran, A. Bonilla-Petriciolet and A. Briones-Ramírez, *Ind. Eng. Chem. Res.*, **49**, 3672 (2010).
  21. A. E. Karlsen, A. Esmalpour, K. Osmani, K. S. B. Plünnecke (cosupervisor: Mehdi Panahi) and Sigurd Skogestad, DME from natural gas (Autumn project) (2009), <http://www.nt.ntnu.no/users/skoge/diplom/prosjekt09/dme-project/>
  22. E. Chang, J. C. G. Calado and W. B. Streett, *J. Chem. Eng. Data*, **27**, 293 (1982).
  23. C. Y. Tsang and W. B. Streett, *J. Chem. Eng. Data*, **26**, 155 (1981).
  24. M. Teodorescu and P. Rasmussen, *J. Chem. Eng. Data*, **46**, 640 (2001).
  25. R. Premkumar and G. P. Rangaiah, *Chem. Eng. Res. Des.*, **87**, 47 (2009).
  26. L. T. Biegler, I. E. Grossmann and A. W. Westerberg, *Systematic methods of chemical process design*, Prentice Hall Inc.: Upper Saddle River, New Jersey, 110 (1997).
  27. N. V. D. Long, S. H. Lee and M. Y. Lee, *Chem. Eng. Proc.*, **49**, 825 (2010).
  28. N. V. D. Long and M. Y. Lee, *Asia-Pac. J. Chem. Eng.*, **6**, 338 (2011).
  29. M. Emtir, E. Rev and Z. Fonyo, *Appl. Therm. Eng.*, **21**, 1299 (2001).
  30. C. Triantafyllou and R. Smith, *Chem. Eng. Res. Des.*, **70**, 118 (1992).
  31. S. H. Lee, M. Shamsuzzoha, M. Han, Y. H. Kim and M. Y. Lee, *Korean J. Chem. Eng.*, **28**, 348 (2011).
  32. A. J. Finn, *Gas Sep. Purif.*, **10**, 169 (1996).
  33. N. V. D. Long and M. Y. Lee, *Comput. Chem. Eng.*, **37**, 119 (2012).

## APPENDIX: ESTIMATION OF CO<sub>2</sub> EMISSION REDUCTION [10]

In the combustion of fuels, air is assumed to be in excess to ensure complete combustion, so that no carbon monoxide is formed. The amount of CO<sub>2</sub> emitted, [CO<sub>2</sub>]<sub>Emiss</sub> (kg/s), is related to the amount of fuel burnt, Q<sub>Fuel</sub> (kW), in the heating device, as follows [10]:

$$[\text{CO}_2]_{\text{Emiss}} = \left( \frac{Q_{\text{Fuel}}}{\text{NHV}} \right) \left( \frac{\text{C}\%}{100} \right) \alpha$$

where  $\alpha$  (=3.67) is the ratio of the molar masses of CO<sub>2</sub> and C, while NHV, which is equal to 39,771 (kJ/kg), represents the net heating value of heavy fuel oil with a carbon content of 86.5%.

The flame temperature is lower in a boiler than in a furnace, because the heat of combustion is removed immediately to the steam. However, the same theoretical flame temperature of 1,800 °C may still be used. A stack temperature of 160 °C is also used in the calculations. The amount of fuel burnt can be calculated from [10]:

$$Q_{\text{Fuel}} = \frac{Q_{\text{Proc}}}{\lambda_{\text{Proc}}} (h_{\text{Proc}} - 419) \frac{T_{\text{FTB}} - T_o}{T_{\text{FTB}} - T_{\text{stack}}}$$

where  $\lambda_{\text{Proc}}$  (kJ/kg) and  $h_{\text{Proc}}$  (kJ/kg) are the latent heat and enthalpy of steam delivered to the process, respectively, while  $T_{\text{FTB}}$  (°C) is the flame temperature of the boiler flue gases. The above equation is obtained from the simple steam balance around the boiler required to relate the amount of fuel necessary in the boiler to provide a heat duty of Q<sub>Proc</sub>; the boiler feed water is assumed to be at 100 °C with an enthalpy of 419 kJ/kg.