

Article

Pressure Swing-Based Reactive Distillation and Dividing Wall Column for Improving Manufacture of Propylene Glycol Monomethyl Ether Acetate

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Abstract: Propylene glycol monomethyl ether acetate (PGMEA) is a commonly used solvent in the rapidly developing semiconductor industry. Ultra-high purity PGMEA is required for this ultra-precision industry and to satisfy the current strict waste management regulations. The traditional PGMEA production process consumes considerable energy and has a high production cost. In this study, a novel heat integrated and intensified design, which applies a dividing wall column, reactive distillation, and pressure swing techniques, was proposed for improving the energy efficiency and reducing the cost of PGMEA production. Heat integration was applied to maximize the heat recovery of the process. All processes were simulated using the commercial simulator Aspen Plus V11. The economic and environmental parameters of the process alternative were assessed for a fair comparison with the conventional process. The results showed that heat integration of the optimal pressure swing-based reactive distillation and dividing wall column processes could reduce the energy requirement and TAC by 29.5%, and 20.8%, respectively, compared to that of the optimal conventional process. The improved design provides a strong basis for achieving more sustainable PGMEA production.

Keywords: dividing-wall column; process intensification; pressure swing; reactive distillation; propylene glycol monomethyl ether acetate; optimization



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1. Introduction

Propylene glycol monomethyl ether acetate (PGMEA) is a substantial and multipurpose solvent with a wide range of industrial applications. As one of the largest industries in the world undergoing rapid development, the semiconductor and display-material manufacturing industry requires ultra-high purity PGMEA with ultra-low acidity to satisfy the extremely tight specifications of semiconductor processing [1]. PGMEA is a crucial solvent for photoresist processing [2,3] owing to its excellent physical and chemical properties [4]. PGMEA is traditionally produced by the esterification of propylene glycol monomethyl ether (PGME) with acetic acid (AA) using a batch reactor [5]. This process affords low PGME conversion owing to chemical equilibrium limitations. To solve this problem, several studies have employed reactive distillation (RD) to improve the conversion and reduce production costs. However, the acidic catalyst route of PGMEA synthesis in RD column has two major drawbacks. First, an additional entrainer is required to accomplish a higher rate of reactant conversion by overcoming the homogenous azeotrope between PGME and

water [6]. Second, the reaction catalyzed by acidic catalyst might unavoidably result in the production of undesirable acidic PGMEA, which is challenging to qualify the tight condition of electronic-grade PGMEA for semiconductor process [1]. It is thus necessary to tackle the issues of product quality and reduce the capital, energy, and environmental costs associated with the manufacture of electronic-grade PGMEA. Consequently, a continuous process of PGMEA production associated with sustainability elements, which can be achieved by process intensification (PI), is necessary to qualify the stringent specifications for electronic-grade semiconductor solvents.

Recently, an attempt toward a sustainable process of continuous PGMEA production was reported [7]. First, a base-catalyzed reaction between propylene oxide (PO) and methanol (MeOH) was used to synthesize PGME. The excess methanol was then removed by distillation to purify PGME. After that, high purity PGME directly proceeded into PGMEA synthesis section in a high pressure RD column. The reaction in the RD between PGME and methyl acetate (MeAc) is also catalyzed by a basic catalyst to synthesize PGMEA and MeOH. The target product, ultra-high purity PGMEA, goes to a bottom stream of RD. At the top RD product, the more volatile mixture, MeAc and MeOH, as a binary azeotrope, was introduced into the low pressure distillation column section. Figure 1 presents a schematic diagram of the novel PGMEA production process [7]. That study showed that intensified RD and pressure swing distillation (PSD) techniques could increase the PGMEA conversion; thus, the energy requirement was significantly decreased compared to that of the traditional process [7]. However, that study focused only on enhancing the performance of the RD and PSD, whereas the energy-intensive distillation unit was not considered. In fact, C1 and C2 (Figure 1) consumed 71.1% of the total energy required for the PGMEA process [7].

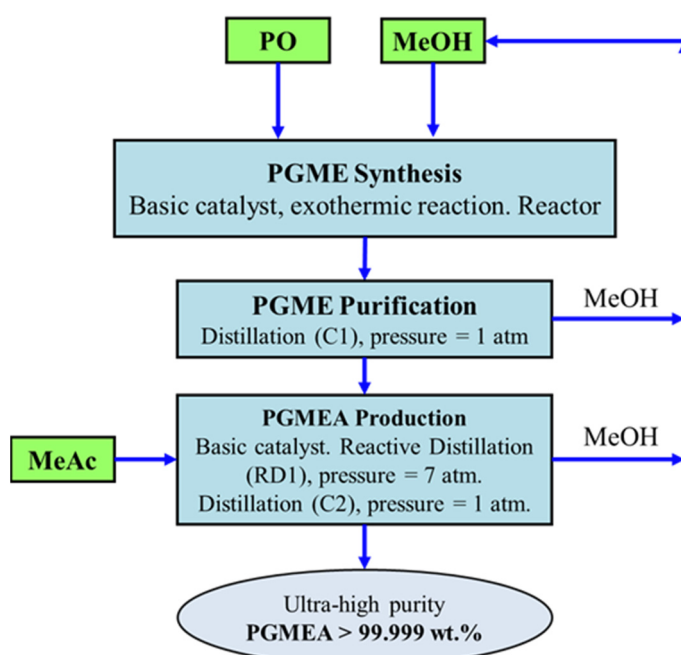


Figure 1. Schematic base case diagram of the intensified PGMEA production process.

Among various methods that have been developed for improving distillation column performance, PI and heat integration (HI) are considered as proven methods in academia and the industrial sector [8–12]. Interestingly, PI has been extensively used to improve the energy efficiency and cost reduction of chemical and distillation processes [2,4,13–17] and can achieve a sustainable chemical process of the reactive-pressure swing with inherent advantages of safety, environment, and economics [18]. A dividing wall column (DWC) [19,20], which allows compacting two-column and avoiding unnecessary energy waste due to remixing in the split, is one of the best examples of PI.

In this study, based on a novel process reported in a previous work [7], a novel heat integrated and intensified process is developed to enhance the process efficiency for PGMEA production. The DWC is designed and optimized to replace the two distillation columns. All configurations are rigorously simulated using the commercial simulator Aspen Plus. A promising intensified process of PGMEA production is proposed by considering the evaluation of economic and environmental impacts.

2. Methods

2.1. Design and Simulation

This study evaluates a PGMEA production process. The design of the base process was taken from a previously published study, as shown in Figure 1 [7]. First, PO was reacted with MeOH in a continuous stirred tank reactor (CSTR) under heterogeneous base catalysis to produce PGME. The product stream was introduced into a distillation column to separate PGME and unreacted MeOH before feeding the PGME stream to the RD. MeAc was then fed into the RD for esterification with PGME to synthesize PGMEA. The pure PGMEA was collected at the RD bottom stream, whereas the mixture of MeAc and MeOH was delivered to another distillation column to separate MeAc and MeOH for reuse in the process.

Aspen plus V11 is used to rigorously simulate all processes with the non-random two-liquid (NRTL) fluid package to predict the liquid activity coefficients. The binary interaction parameters for PGME, MeOAc, PGMEA, and MeOH at atmospheric pressure were obtained from the literature [1,21], except those for MeOAc + MeOH, which were from the Aspen Plus databank. The binary interactions used in Aspen Plus are shown in Table 1. The Aspen Plus calculated VLE result was validated by experimental data as shown in Figure 2.

Table 1. Binary system and NRTL binary parameters ($R = 8.314 \text{ J/mol}\cdot\text{K}$).

Binary System		NRTL Parameters		
<i>i</i>	<i>j</i>	<i>b_{ij}</i>	<i>b_{ji}</i>	<i>c_{ij} = α_{ij}</i>
PGME	PGMEA	329.49	−225.96	0.3
MeAc	PGME	541.23	−276.32	0.3
MeOH	PGMEA	422.49	−134.10	0.3
MeAc	PGMEA	604.55	−399.10	0.3
MeAc	MeOH	234.87	130.51	0.3
MeOH	PGME	114.10	72.10	0.3

2.2. Optimization Scheme

A common approach for obtaining the best specification variable in a distillation column is to minimize the objective function of the design variables. The classical issue of distillation design is the trade-off between the number of trays/stages and energy consumption. With the same target specification, more trays increase the capital costs but result in lower reflux ratios and reboiler duties, which reduces the energy cost [22]. The total annual cost (TAC), which balances the capital and energy costs, is used as the objective function. Some methods employ manual iterative and automatic optimization. However, these methods require long iteration steps and complex simulations, leading to a complex process that increases the complexity of the optimization procedure and simulation. Alternatively, a semi-iterative method that combines manual and automatic optimization can be used. The semi-iterative method finds the minimal value one variable that affects the operation cost between a lower bound (lb) and upper bound (ub) while iterating other variables that affect the capital cost, in order to find the optimum total annual cost (TAC) [3,5]. The reflux ratio (RR) is employed in the Aspen Plus design specification, which automatically finds the minimal solution of RR between the lb and ub while continually satisfying the PGMEA yield. This semi-iterative optimization is a hybrid manual iterative method and simulator optimization.

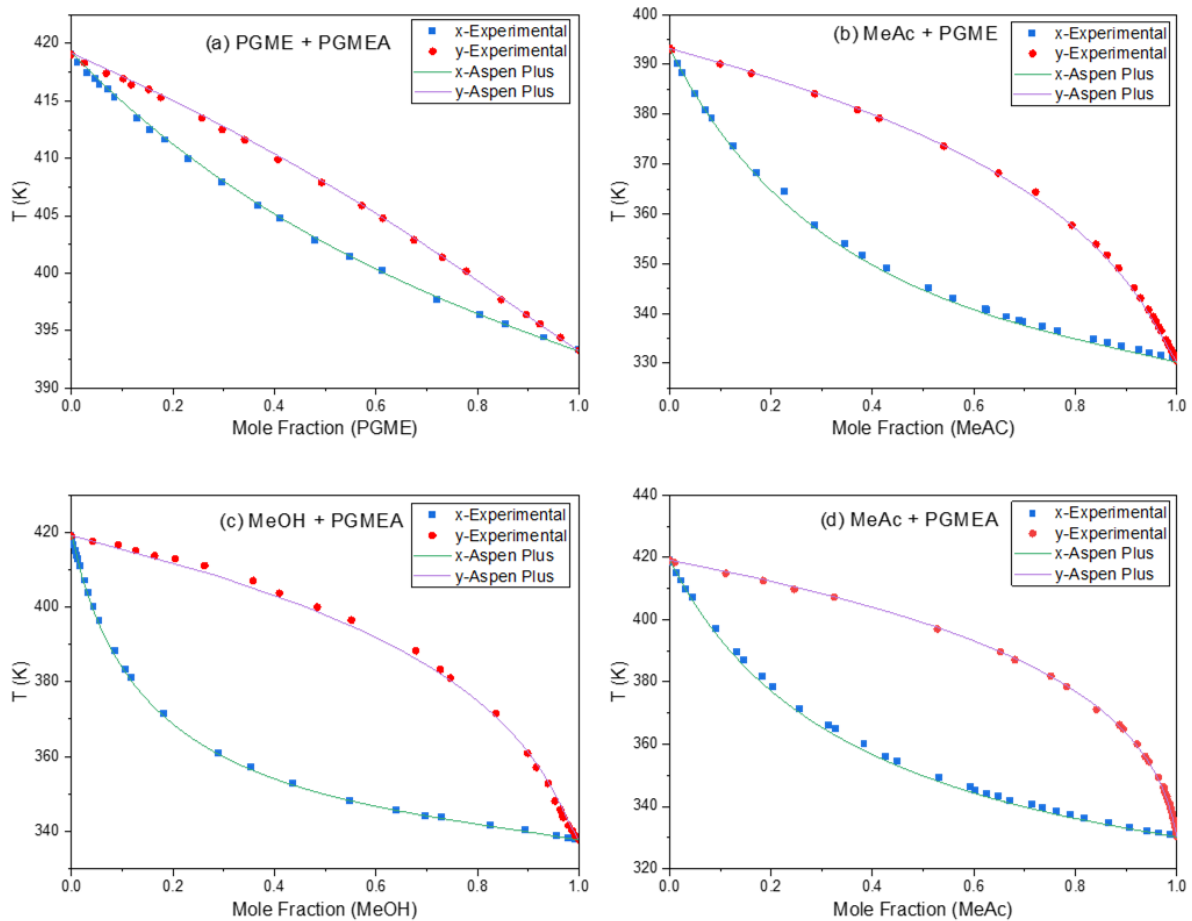


Figure 2. Comparison: T-xy binary diagram between Aspen Plus calculated VLE and experimental data: (a) PGME + PGMEA; (b) MeAc + PGME; (c) MeOH + PGMEA; (d) MeAc + PGMEA.

2.3. Economic Evaluation

The capital cost, total operating cost (TOC), and TAC of all processes were calculated for economic evaluation. The detailed method was described in our previous work [14]. The equipment costs were calculated using correlations from the Turton and Biegler textbooks [23,24]. Tray spacing, column heights, and diameters were designed based on maximum column flooding velocity. The TIC was updated to the level of 2020 with a chemical engineering index of 596.2. The heat exchangers, compressors, condensers, reboilers, tray stacks, column vessels, and blowers were considered in the TIC. A cooling water price of 11 \$/kW year, low-pressure (LP) steam price of 245 \$/kW year, and high-pressure (HP) steam price of 311 \$/kW year were used for the TOC calculations [24]. A plant lifetime was assumed to be 10 years, while a fixed interest rate of 8% was applied to the TAC estimates.

2.4. Environmental Assessment

The total annual carbon dioxide CO₂ emissions (TCE) of all processes were evaluated for environmental assessment. Gadalla's method was used to calculate the CO₂ emissions from the steam reboilers and compressors [25]:

$$[CO_2]_{emiss} = \left(\frac{Q_{fuel}}{NHV} \right) \left(\frac{C\%}{100} \right) \alpha, \quad (1)$$

where NHV is the net heating value of the fuel, and $C\%$ is the carbon content. The molar mass ratio of CO_2 to carbon was $\alpha = 3.67$. Q_{fuel} , which denotes the amount of fuel used, was calculated as follows:

$$Q_{fuel} = \left(\frac{Q_{proc}}{\lambda_{proc}} \right) (h_{proc} - 419) \left(\frac{T_{FTB} - T_0}{T_{FTB} - T_{stack}} \right) \quad (2)$$

where Q_{proc} is the required heat duty of the system, λ_{proc} (kJ/kg) is the latent heat, and h_{proc} (kJ/kg) is the enthalpy of steam. The flame temperature (T_{FTB}) was 1800 °C, the stack temperature (T_{stack}) was 160 °C, and the ambient temperature (T_0) was 25 °C.

3. Results and Discussion

This study used previous intensified configuration [7] that is shown in Figure 1 as the base case with unoptimized C1 is further optimized. The C1 objective function is reboiler duty with reflux ratio and the number of trays as decision variables. First, MeOH and PO streams with a mass ratio of 10:1 were input into the PGME continuous stirred tank reactor (CSTR) for PGME synthesis. In the presence of a basic heterogeneous catalyst, MeOH reacts with PO in the liquid phase to produce PGME:



$$k_1 = 2 \times 10^7 \exp\left[\left(\frac{3000}{R}\right)\left(\frac{1}{1000} - \frac{1}{T}\right)\right] \quad (4)$$

where R is the ideal gas constant; T and T_0 (Kelvin) are absolute temperatures.

The reaction is exothermic, and the reactor was modeled as a conversion reactor under the assumption that 100% PO is converted to PGME. Subsequently, the PGME and unreacted MeOH mixture were introduced into the distillation column C1 to separate MeOH at the top and PGME at the bottom. MeOH was recycled back to R1 for use as a reactant. The PGME product stream and MeAc were then input to RD1 at stages 15 and 21, respectively, for PGMEA production:



$$k_2 = 2.8 \times 10^9 \exp\left(\frac{-13,304}{RT}\right) \quad (6)$$

$$k_3 = 8972 \exp\left(\frac{-3449}{RT}\right) \quad (7)$$

Reaction (5) is reversible and endothermic. Solid sodium methoxide, which is insoluble in the reaction mixture, was used as a basic homogeneous catalyst. A mass ratio of PGME/MeAc of 1:3 and liquid holdup of 0.008 m³ per tray were implemented to achieve the production requirements. RD1 produced 99.999 wt% of PGMEA as the bottom product, whereas the azeotropic mixture of MeAc and MeOH was delivered at the top stream. Because the azeotropic composition of MeAc and MeOH shifts as the operating pressure changes, this azeotrope (63.8 wt% MeAc and 36.2 wt% MeOH at 7 atm) was sent to a low-pressure distillation column C2 (1 atm) to separate MeOH at the bottom and the azeotrope (81 wt% MeAc and 29 wt% MeOH at 1 atm) at the top. In this PSD configuration, the RD acted as the high-pressure column (HPC), while C2 acted as the low-pressure column (LPC). The MeOH stream was recycled to R1 for reuse as the reactant, whereas the azeotropic mixture of MeAc and MeOH returned to RD1. Table 2 lists the key parameters for all distillation columns, including the column diameters, energy requirements of the reboilers, condensers, TIC, TOC, and TAC.

Table 2. Basis and details of equipment sizing for the base case process.

Parameters	C1	RD1	C2
Diameter (mm)	964	550	465
Theoretical stages	54	26	30
Reflux ratio	0.38	0.55	0.995
Reboiler duty (kW)	1260	526	618
Condenser duty (kW)	1216	339	711
Reboiler temperature (°C)	120	230	65
Condenser temperature (°C)	65	117	54
Total investment cost (m\$)	1.01	0.37	0.38
Total operating cost (m\$/y)	0.41	0.19	0.14
TAC (m\$/y)	0.57	0.24	0.20

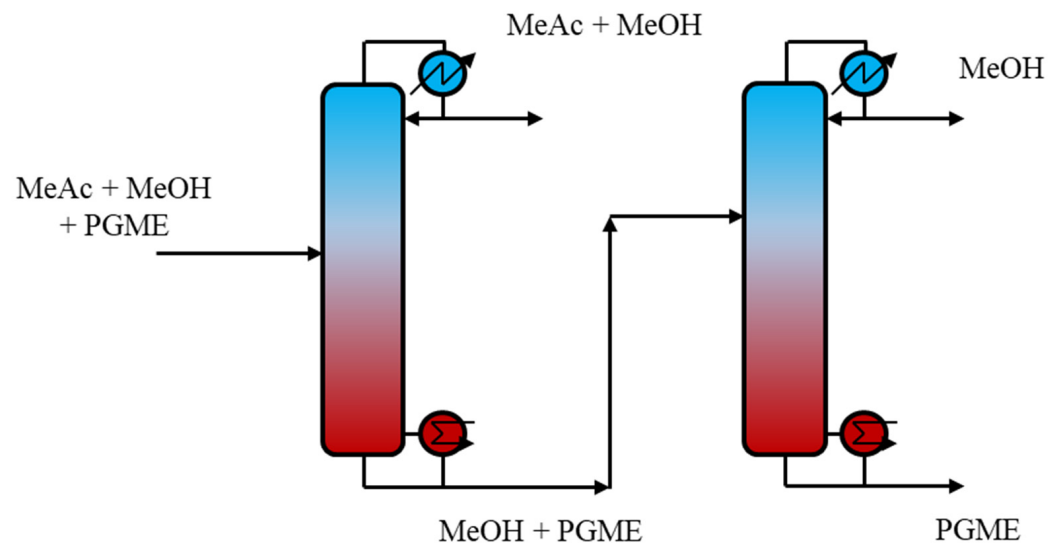
The results show that C1 consumed the most energy (1260 kW), while RD1 and C2 required 526 kW and 618 kW, respectively, in their reboilers. Medium-pressure steam was used for RD1, whereas low-pressure steam was used for C1 and C2.

3.1. Process Intensification for PGMEA Production

3.1.1. Feasibility of Applying DWC

The reboiler energy requirements of C1 and C2 accounted for 78.1% of the total reboiler energy requirement in the entire PGMEA process. A high reboiler duty was required for MeOH and PGME separation in C1 because of the high fraction of the low boiling point component at the top. Therefore, improving the energy efficiency of these distillation columns should inevitably bring great benefits to the entire process. Note that the C1 top temperature of 55 °C is significantly different from the C1 bottom temperature of 120 °C; thus, it is not economically feasible to apply the heat pump here. The PGMEA process is based on PS distillation technology, in which C1 and C2 operate at 1 atm, whereas the RD operates at 7 atm. The PSD configuration makes the application of intensified techniques much more challenging.

In this situation, the C1 and C2 columns have the same pressure of 1 atm if this process is assumed to become a separation train with two columns. The light boiling point (BP) fraction is the azeotrope of MeAc and MeOH, while the medium BP fraction is MeOH, and the heavy BP fraction is PGME. The sequence of this concept is illustrated in Figure 3.

**Figure 3.** Concept sequence where MeOH as the middle BP fraction is the major component.

When a high-purity middle component (MeOH) is desired, C1 and C2 may be replaced with a DWC. The feed to C1 comprises ~76.2 wt% MeOH (as the middle product), which conforms to the typical rule of thumb wherein the DWC is the most advantageous [26]. When MeOH comprises a significant portion of the feed, a DWC can be advantageous as long as the split between MeAc (light product) and MeOH (middle product) is at least as difficult as that between MeOH and PGME. When both MeAc/MeOH and MeOH/PGME splits are fairly easy, the superiority of the DWC may not be sufficient to warrant its selection over a conventional direct sequence [26]. Figure 4 shows the relative volatilities of MeAc/MeOH and MeOH/PGME. The relative volatility (α) values are less than unity or not large for MeAc and MeOH only; thus, the DWC may not be significantly advantageous in terms of energy improvement. However, the PI configuration may improve the column cost owing to the column compactness.

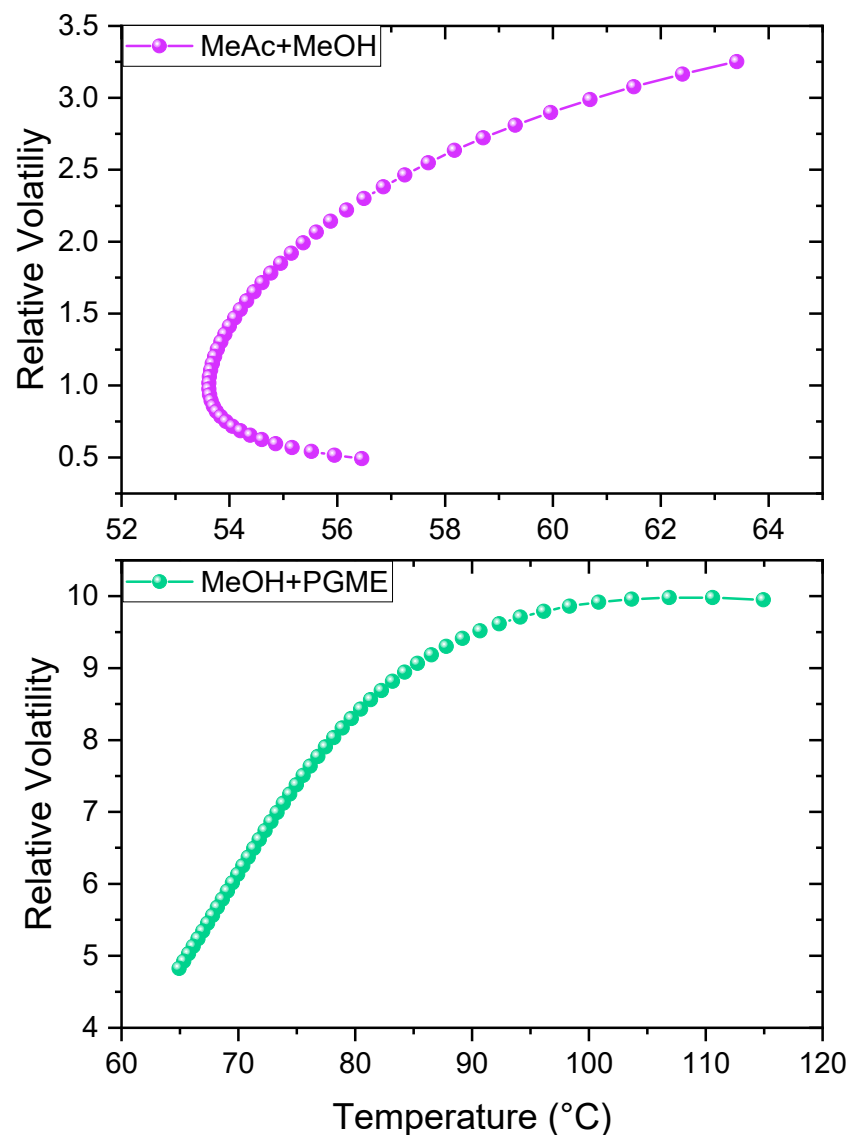


Figure 4. Relative volatility of MeAc and MeOH and MeOH and PGME within temperature interval.

To conceptually design the DWC, the column requires a prefractionator to split the middle BP into the top and bottom streams. This column conforms to the preferred separation [27] in which the column operates at double pinch or the lowest energy required to eliminate the remixing effect [28]. The preferred separation lever rule line is almost perpendicular to the medium BP and inside the feasible region in total [27]. To identify

the feasible separation region, all product lines must lie on a straight line through the feed location point. To further clarify the feasible separation region, the residue curve must pass through the feed composition point along the product line [3]. For ternary MeAc + MeOH + PGME, the top and bottom product compositions were estimated based on the lever rule position for preferred separation [27] as shown in Figure 5.

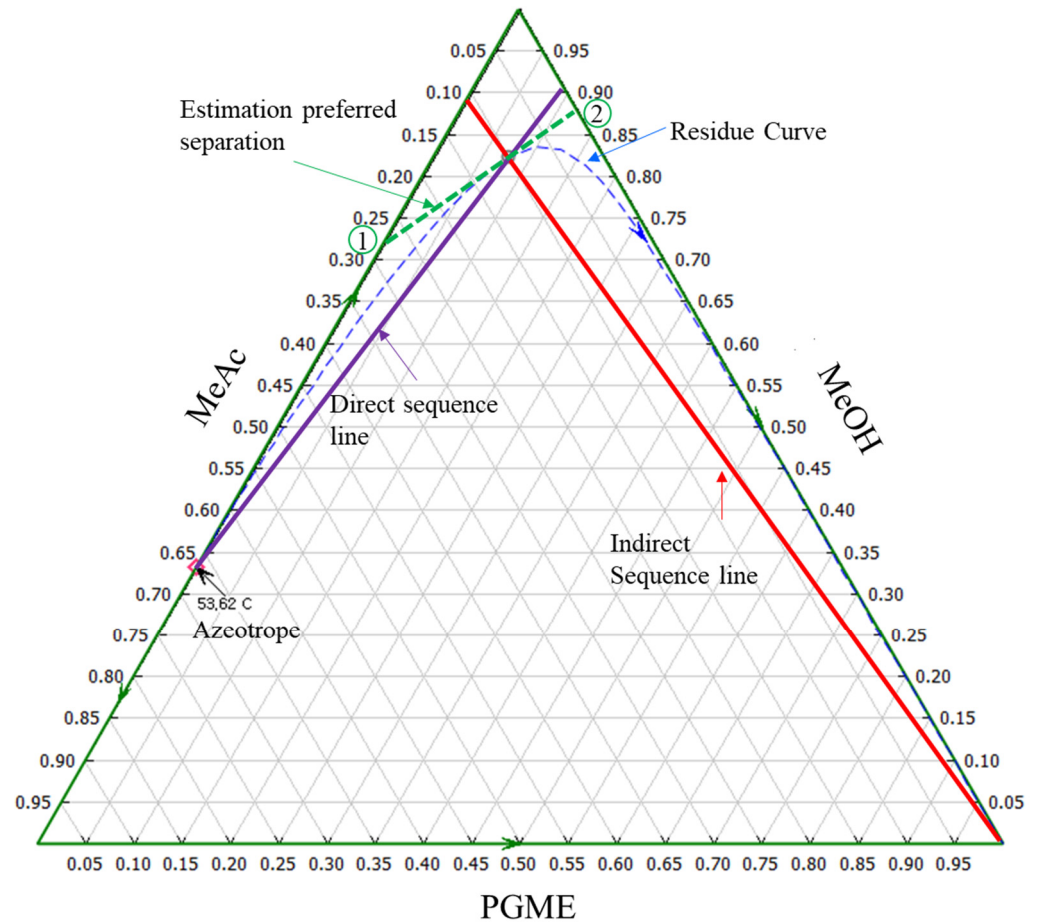


Figure 5. Estimation of lever rule inside feasible separation region for designing prefractionator. The estimation value is Point 1. MeAc = 0.28 and MeOH = 0.72. Point 2. MeOH = 0.85 and PGME = 0.15.

3.1.2. Semi-Iterative Optimization of DWC Structure

In this study, the semi-iterative optimization utilizes several decision variables to determine the optimum conditions for the DWC. The flowchart for the optimization process, and the decision variables are presented in Figures 6 and 7, and Table 3, respectively.

Table 3. Optimization variables and result.

No.	Variables	Lower Bound	Upper Bound	Optimal
1	RHPC-TOP stage location at main DWC (NRHPC) at B2	3	10	6
2	R-EEF stage location at DWC pre-fractionator (NREF) at B1	20	45	35
3	MEOH side stream location at DWC (NMEOH) at B2	25	32	30
4	Prefractionator location in DWC (NPREF-LOC) at B1	8–43	10–49	10–45
5	Prefractionator number of trays (NPREF-NT) at B1	33	36	35
6	DWC main column trays (NMC-NT) at B2	49	55	51
7	LIQ1 flow (FLIQ1)	14.3	20	15
8	VAP1 flow (FVAP1)	53	56	55

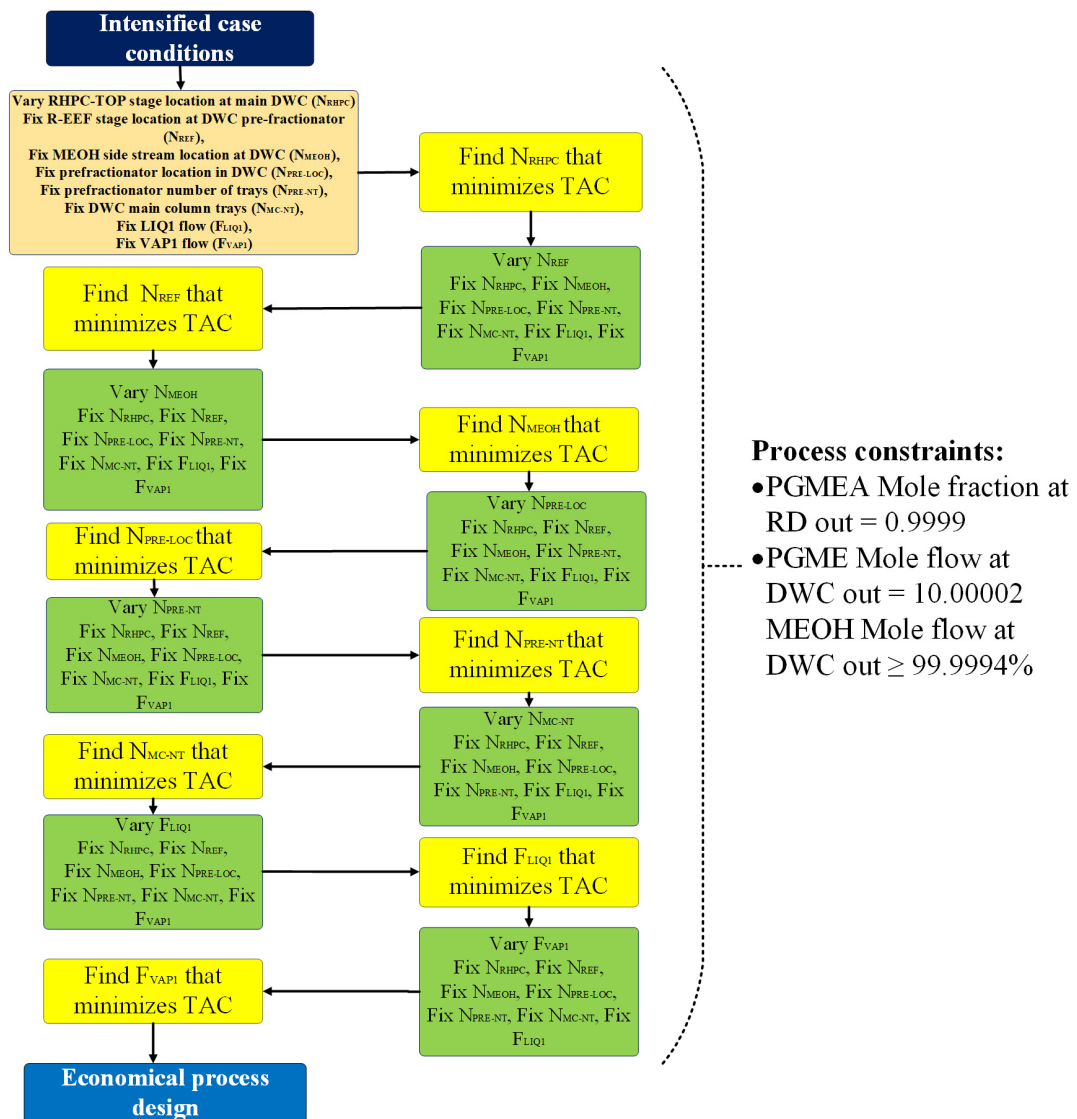


Figure 6. Flowchart for semi-iterative optimization of DWC structure.

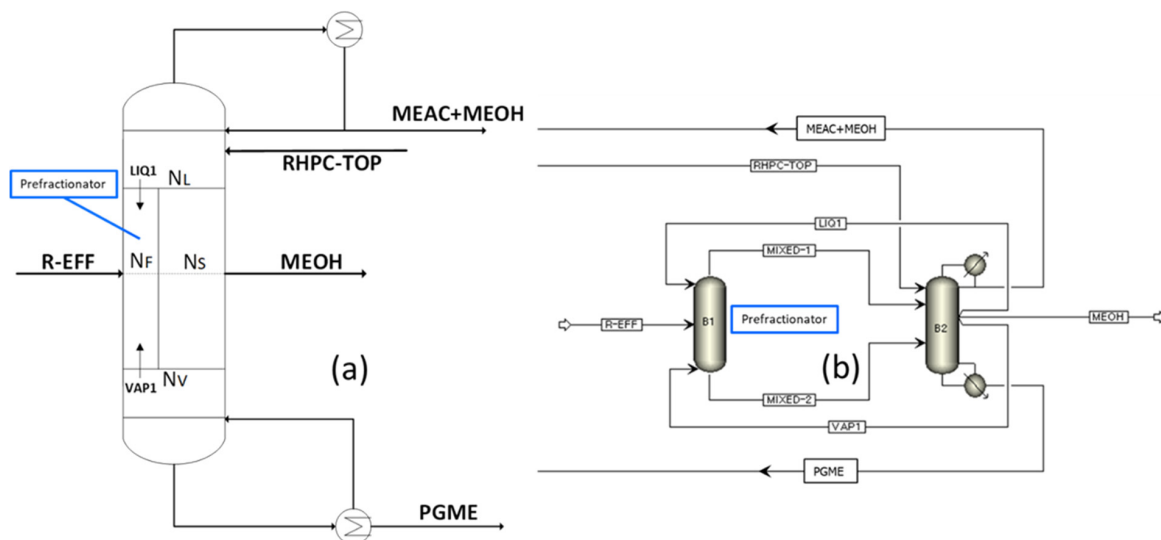


Figure 7. Optimization of DWC structure. (a) DWC is noted as D2 column; (b) fully-thermally coupled column equivalent to DWC in Aspen Plus Simulation. Column D2 has two columns B1 (prefractionator) and B2 (main column).

Figure 8 shows a schematic of the optimized pressure swing-based RD and DWC for the PGMEA production process with the key design parameters. In this process, DWC D2 was designed to replace C1 and C2 in the conventional process. In particular, PGME and unreacted MeOH from the output of R2 and the high-pressure azeotrope mixture (MeAc and MeOH) from the top of RD2 were introduced into D2 at the 6th and 35th stages, respectively. The function of D2 is to separate the low-pressure azeotrope of MeAc and MeOH at the top stream, and MeOH at the middle stream, whereas most of the PGME product is collected at the bottom stream. D2, which has a vertical wall in the middle and operates at 1 atm, plays the role of the LPC in the entire PS configuration. The unreacted MeOH from the D2 side stream was recycled back to R2 for reuse as a reactant. The PGME stream was mixed with the low-pressure azeotrope of MeAc and MeOH before being pressurized up to 7 atm and input into the reactive distillation RD2 at the 15th stage. In addition, MeAc was introduced into RD2 at the 21st stage for PGMEA synthesis. PGME reacts with MeAc to produce PGMEA in the liquid phase in the presence of a solid sodium methoxide catalyst. A PGME/MeAc mass ratio of 1:3 and liquid holdup of 0.008 m³ per stage were designed to achieve a target purity of 99.999 wt% PGMEA at the bottom stream.

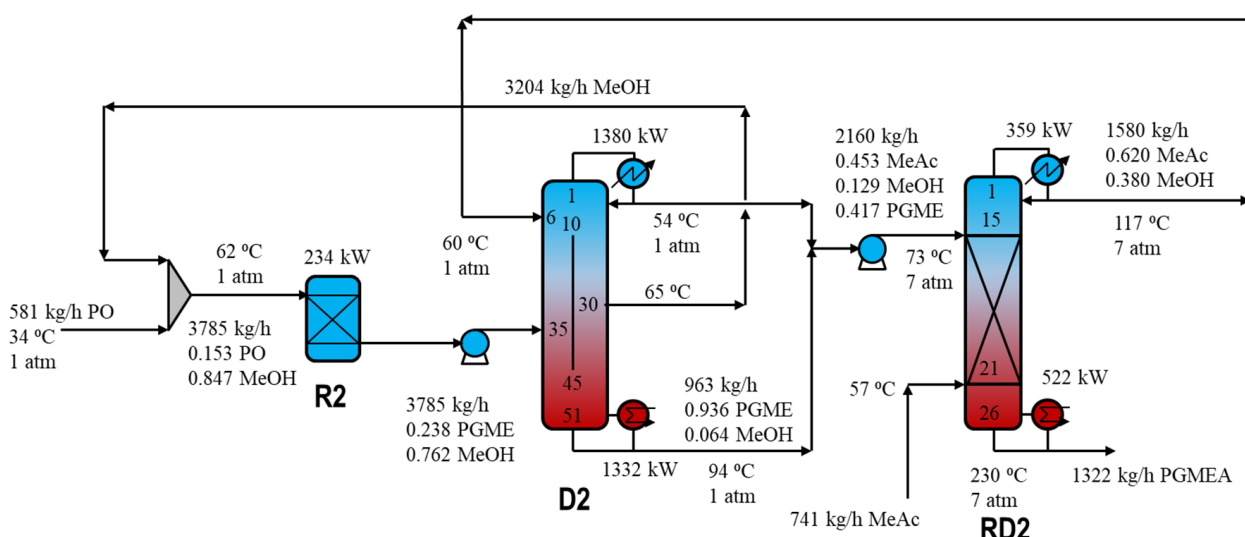


Figure 8. Pressure swing-based RD and DWC for the PGMEA production process.

The high-pressure azeotrope comprising 62 wt% MeAc and 38 wt% MeOH, which was delivered at the RD2 top stream, was returned to D2 at the 6th stage. Table 4 lists the diameter, energy requirements, and production costs for all columns in the optimized PS-based RD and DWC processes. High-pressure steam was used for the RD2 reboiler, whereas low-pressure steam was used for D2. The results show that the intensified process with RD and DWC configurations can reduce the energy requirement of the reboilers by 22.9% compared to the conventional process. Regarding the cost, the intensified process can save 24.4%, 17.6%, and 20.8% of TIC, TOC, and TAC, respectively.

3.2. Heat Integration of the Intensified PGMEA Process

In general, heat integration can be explored for all non-integrated distillation columns. The appropriate heat integration configurations can maximize the heat recovery over the entire process. Tables 5 and 6 list all hot and cold stream data for the conventional and intensified processes for PGMEA production, respectively.

Table 4. Basis and details of equipment sizing for optimized pressure swing-based RD and DWC.

Parameters	RD2	D2
Diameter (mm)	555	932
Theoretical stages	26	51
Reflux ratio	0.42	6.78
Reboiler duty (kW)	522	1332
Condenser duty (kW)	359	1380
Reboiler temperature (°C)	230	94
Condenser temperature (°C)	117	56
Total capital cost (m\$)	0.14	1.19
Total operating cost (m\$/y)	0.16	0.45
TAC (m\$/y)	0.18	0.62

Table 5. Hot and cold stream data for the conventional process for PGMEA production.

Equipment	Power/Duty (kW)	Inlet Temp. (°C)	Outlet Temp. (°C)	CO ₂ Emissions (kg)
Condenser @ C1	(1217)	64.5	64.5	
Condenser @ RD1	(339)	116.9	116.8	
Condenser @ C2	(711)	53.6	53.6	
Reboiler @ C1	1260	120.1	120.1	5,577,084
Reboiler @ RD1	526	229.9	230.0	2,275,621
Reboiler @ C2	618	64.5	64.5	1,243,896
				9,096,601

Table 6. Hot and cold stream data for the optimized intensified process for PGMEA production.

Equipment	Power/Duty (kW)	Inlet Temp. (°C)	Outlet Temp. (°C)	CO ₂ Emissions (kg)
Condenser @ RD2	(359)	117.0	116.8	
Condenser @ B1	-	64.5	64.2	
Condenser @ D2	(1380)	53.6	53.6	
Reboiler @ RD2	522	230.0	230.0	2,309,978
Reboiler @ B1	-	66.4	66.4	-
Reboiler @ D2	1332	73.1	94.1	5,896,022
				8,214,473

The hot source can be utilized as a source for the cold stream, and vice versa. This energy transfer process has also been identified as a heat exchanger network (HEN) [7]. The HEN was constructed using Aspen Energy Analyzer V11 to investigate energy savings in the pressure-swing-based RD and DWC. The detailed HEN is shown in Figure 9. Table 6 lists all hot and cold stream data in the optimized intensified process for PGMEA production. One potential hot source is the top vapor flow of the high-pressure RD2. Some heat from RD2 is transferred to a lower temperature region in the reboiler of D2. With this approach, energy requirements from low pressure (LP) steam at reboiler D2 are reduced and the energy savings increased to 29.5%. The green circle represents the relationship between the hot stream (top RD2) and cold stream (Bottom D2). LP steam and high pressure (HP) steam are utilized as an energy source from utility. For additional cost saving, air can be used as cooling medium at D2 and RD2 condensers.

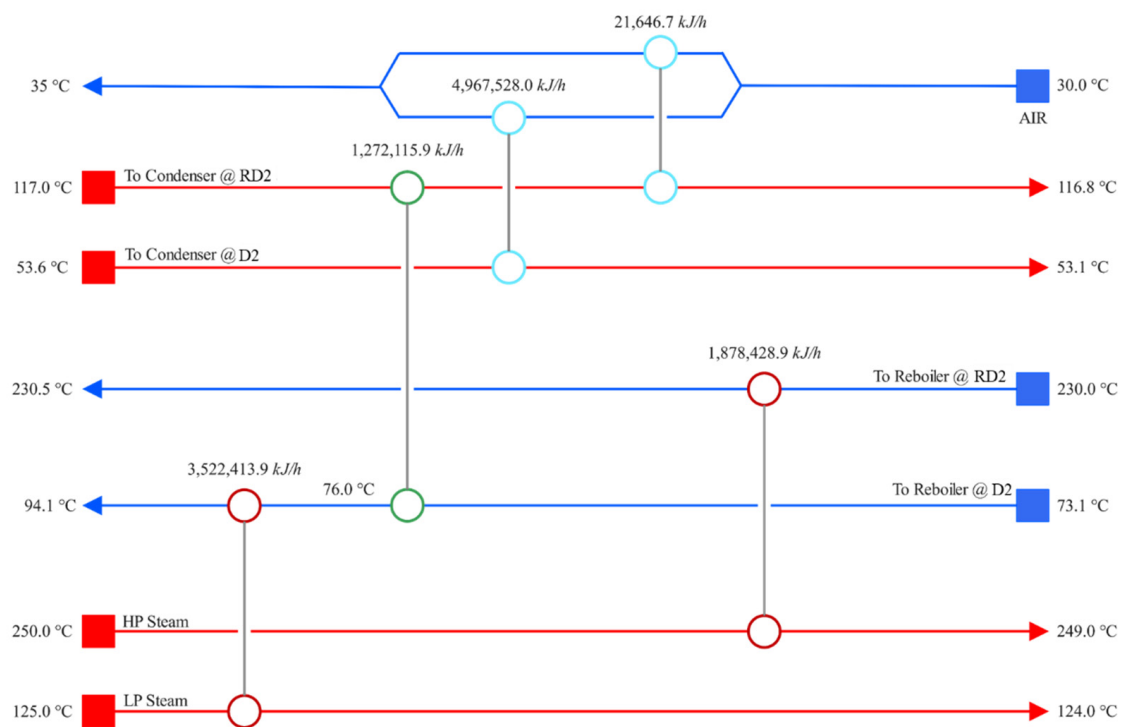


Figure 9. Detailed HEN between RD and DWC. Red lines are hot stream, blue lines are cold stream, and green circle is heat integration connection.

4. Conclusions

An advanced distillation process for the enhanced separation of PGMEA (the product) from PGME and PO was explored. The advanced intensified configuration of the DWC was designed and optimized to replace the two distillation columns in the conventional process. Unlike typical columns' intensification from direct or indirect sequences to DWC, this work approach intensified two energy-intensive columns (C1 and C2) from separated sequences using the concept of direct sequence intensification and pressure swing. This intensification presents novel configuration in the PGMEA production. The elaborately designed recycle structure with pressure swing-based RD and DWC configurations could successfully address the issues related to the azeotrope of MeAc and MeOH. A semi-iterative optimization method was employed to optimize the DWC structure. Heat integration has been suggested for improving the energy efficiency of intensified processes. The use of process intensified techniques such as RD, DWC, and heat integration is technically feasible and particularly promising for constructing a new plant for PGMEA production with lower energy requirements and environmental impact. The results show that heat integration of the optimal pressure swing-based RD and DWC processes could reduce the energy requirement and TAC by 29.5%, and 20.8%, respectively, compared to that of the optimal conventional process. The results provide a strong basis for the design and advancement of more sustainable PGMEA production technologies.

Author Contributions: Y.D.C. and L.C.N. contributed equally to this work by designing the study, performing the process simulations, and writing the article. A.N. and A.R. revised the manuscript. G.S.K. performed data curation. M.L. and H.L. conceived the core research concepts and provided academic advice. All authors have read and agreed to the published version of the manuscript.

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Abbreviations

AA	acetic acid
BP	boiling point
CO ₂	carbon dioxide
CSTR	continuous stirred tank reactor
DWC	dividing wall column
HEN	heat exchanger network
HI	heat integration
HPC	high-pressure column
lb	lower bound
LPC	low-pressure column
MeAc	methyl acetate
MeOH	methanol
NHV	net heating value
NRTL	non-random two-liquid
PI	process intensification
PGMEA	propylene glycol monomethyl ether acetate
PGME	propylene glycol monomethyl ether
PO	propylene oxide
PSD	pressure swing distillation
RD	reactive distillation
RR	reflux ratio
TAC	total annual cost
TCE	annual CO ₂ emissions
TIC	total investment cost
TOC	total operating cost
ub	upper bound

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