Process Design Alternatives for Producing Ultra-high-purity Electronic-Grade Propylene Glycol Monomethyl Ether Acetate

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ABSTRACT: Ultra-high-purity propylene glycol monomethyl ether acetate (PGMEA) is required as a solvent to meet the stringent requirements of the electronic-grade semiconductor industry. Here, a comparative study of two process intensification configurations—a coupling reaction and separation in the transesterification route for PGMEA production—is presented. Reactive distillation (RD), despite being technically feasible for the transesterification reaction, poses severe challenges owing to its operational/design limitations. For instance, the homogeneous catalyst sodium methoxide is insoluble in the reaction mixture and deposited on the reactive packing surface of the RD column. An intensified configuration of the side-reactor column (SRC) configuration is analyzed as an alternative to mitigate the operational limitations of RD. An economic evaluation is conducted for both configurations, showing that the SRC configuration can match the performance of an RD column with only a 5% increase in total annual cost.

1. INTRODUCTION

Semiconductor and display manufacturing are among the largest industries in the world, and have undergone rapid growth and development in the past few decades.† The semiconductor industries extensively utilize solvents for substrate deposition/removal, drying of wafers, and equipment cleaning. A high-purity solvent with extremely low acidity is essential to address the needs of electronic-grade semiconductor processing. Propylene glycol methyl ether acetate (PGMEA) is one of the important solvents used for photoresist processing in the semiconductor industry.‡ Owing to its excellent properties, it is used as a multipurpose solvent for multiple industrial applications.§,∥ Conventional PGMEA is manufactured by the esterification of PGME with acetic acid (AA) by a process involving acid catalysis. In a traditional batch reactor, the esterification of PGME with AA is hindered by low PGME conversion due to chemical equilibrium limitations. Integrated process configurations, such as reactive distillation (RD) and reactive chromatography (RC), have been applied to enhance the conversion and intensify the conventional—reaction—separation PGMEA process.¶,† The synthesis of PGMEA through esterification in a RD column over a solid acid catalyst is an ideal configuration, because the reactants are midboiling components, AA (118 °C) and PGME (120 °C), allowing the products, water (100 °C), and PGMEA (145 °C), to be easily removed as the top and bottom products, respectively. Despite this esterification reaction being technically feasible in an RD column, it has some crucial drawbacks. The existence of a homogeneous azeotrope between PGME and water leads to a low conversion rate, which is usually compensated for by using an external solvent (entrainer) to improve the overall process.¶ In addition, because of the involvement of a heterogeneous acid catalyst in the RD operation, the resulting PGMEA is acidic, which can create difficulties in satisfying the stringent requirements for electronic-grade PGMEA. Alternatively, the acidic nature of the PGMEA product can be avoided through the transesterification route (Figure 1), which uses a base catalyst; both homogeneous and heterogeneous base catalysts are available and can enable the production of less-acidic electronic-grade PGMEA.

Homogeneous catalysts are preferable as they provide high activity and selectivity.¶,∥ Wang et al.§ conducted experiments on a homogeneous catalyst (sodium methoxide) to determine the kinetic parameters of this reaction. They also presented a feasibility study for the conceptual design of PGMEA production in an RD column via the transesterification route. However, no simulation studies were reported in their article.

RD (Figure 2a) is a wise choice to overcome thermodynamic limitations in equilibrium-limited reactions.†¶,†∥ Despite recent advances in the design and simulation of RD
columns for various industrial processes, their design complexity, operational difficulties, and expensive equipment requirements restrict the introduction of new production processes based on RD technology. For PGMEA synthesis, in particular, the transesterification route is also hindered by some important equipment and operational constraints. The major operational and maintenance difficulties are related to the use of a homogeneous sodium methoxide base catalyst. For instance, the very small particle diameter of sodium methoxide hinders its direct loading into a column compared with the case of an ion-exchange-resin catalyst. Furthermore, the sodium methoxide base catalyst is insoluble in the reaction mixture; hence, a mass of catalyst may collect at the structured/random packing surfaces if the column is continuously fed with reactants. In addition, removal of the deposited catalyst mass on the reactive trays requires plant shutdowns, which are inconvenient in a continuous process. This clustering of catalyst in the column results in deterioration of the vapor–liquid mass transfer. For homogeneous RD columns, in particular, an enhancement of the counter-current mass-transfer contact between the vapor and liquid flows can be achieved in a multitray column or in a structured- or random-packed column. Keeping in mind higher reactant conversion and product yields, bubble-cap-tray columns are more efficient as they provide maximum liquid holdup and residence time. However, in RD operations, larger liquid holdups result in severe equipment limitation problems, and the residence time distribution is of crucial importance for the RD tray design. Another issue is the existence of a  MeOH–MeOAc minimum boiling azeotrope; the transesterification reaction in an RD requires a high MeOAc:PGME molar feed ratio to achieve the complete conversion of PGME and to eliminate the azeotrope when the reaction occurs. It should be noted that the complete conversion of PGME is essential to simplify the subsequent separation process. The stringent requirements of electronic-grade PGMEA have thus forced academic and industrial researchers to identify alternative configurations with the ability to overcome the equipment and operational issues limiting existing production processes and meet the growing market demand for this important industrial solvent.

A potential alternative is distillation with a reactive pump-around or column with a side-reactor (SRC) configuration. This is, in fact, an intensified form of the reactor and distillation column configuration, where reactive pump-arounds and/or a side-reactor are connected by an external loop to a non-RD column, as illustrated in Figure 2b. The SRC could be an excellent choice to overcome the design and operational limitations of the RD column, for example, unfavorable volatilities, slow reaction rates, and hydraulic problems. Figure 3 illustrates the quantitative framework for trade-off between operational and design performances, and the selection criteria for RD/SRC. Further quantification, however, relates to a pertinent process under consideration.

For homogeneous catalysts in particular, clustering of the catalyst can be easily avoided using an SRC, as it has no specially structured packings where catalyst deposition can
occur. Moreover, recent experimental studies have demonstrated that these technologies ensure the presence of catalyst within the reaction mixture and its effective separation from reactor products. Many other design and operation limitations, such as compensation for large liquid holdups or catalyst amount and catalyst replacement, loading, or deposition, can be easily overcome by the SRC design, which is seldom feasible in RD operation.

In the current study, the feasibility of an RD column to carry out the transesterification reaction as suggested by Wang et al., is demonstrated through a simulation in Aspen Plus V.9. RD can be conceptually designed using a shortcut method, based on initial information, before the detailed rigorous distillation simulation design is developed. Such shortcut methods are based on the assumptions of constant molar overflow, negligible heat of reaction compared with the enthalpy of the vapor phase, and a partial condenser. Owing to various design assumptions in the shortcut method, the final result may differ from a rigorous column simulation. The design and operational difficulties associated with RD columns are discussed in detail and, based on the results, an alternative configuration based on distillation with side-reactor is suggested. A detailed economic analysis of both configurations is then carried out. For the desired PGMEA yield of 99%, comparison of the results from both configurations reveals that the total annual cost (TAC) of the SRC-based design only needs to increase by 5% to match the performance of an RD column. However, more importantly, technical issues (such as expensive equipment design) and operational limitations (such as the clustering of catalyst mass at the packing surface) of the RD column can be easily overcome by the SRC configuration.

2. PROCESS DEVELOPMENT

All steady-state simulations were performed using an Aspen Plus V.9 software package. For the SRC, a rigorous continuous-stirred tank reactor (RCSTR) model was used. The RD and non-RD columns were simulated using rigorous RadFrac modules.

2.1. Thermodynamic Model. Appropriate physical property parameters are key to a successful and reliable simulation. In this work, the binary interaction parameters for PGME, MeOAc, PGMEA, and MeOH at atmospheric pressure were obtained from the literature, except those for MeOAc + MeOH, which were from the Aspen Plus databank. The adjustable parameters of the nonrandom two-liquid (NRTL) equation model in Aspen Plus are as follows:

\[
\ln \gamma_i = \frac{\sum_j S_{ij} G_{ji}}{\sum_i x_i G_{ji}} + \frac{\sum_j x_j G_{ij} \left( \tau_{ij} - \sum_m x_m x_m^m G_{mj} \right)}{\sum_i x_i G_{ij}}
\]

(1)

\[
G_{ij} = \exp(-\alpha_{ij} \tau_{ij})
\]

(2)

\[
\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} + c_{ij} \ln T + f_{ij} T
\]

(3)

\[
\alpha_{ij} = c_{ij} + d_{ij}(T - 273.15) K
\]

(4)

\[
\tau_{ii} = 0, \quad G_{ii} = 1, \quad \alpha_{ii} = \alpha_i
\]

(5)
where $\gamma_i$ is the activity coefficient of component $i$; $x$ is the mole fraction; $\tau_{ij}$ ($\neq \tau_{ji}$) is the interaction parameter; $\alpha_{ij}$ is the nonrandomness constant for binary interactions; and $a_{ij}$, $b_{ij}$, $c_{ij}$, $d_{ij}$, $e_{ij}$, and $f_{ij}$ are binary parameters between the pair of components $i$ and $j$. The binary parameters data for PGME, MeOAc, PGMEA, and MeOH were in the original form of the equations as derived by Renon and Prausnitz; the quantity $\tau_{ij}$ is related to the difference in the intermolecular Gibbs free energies of interaction, $\Delta g_{ij}$, by the expression:

$$
\tau_{ij} = \frac{\Delta g_{ij}}{RT}
$$

(6)

To make the Renon NRTL original form equivalent to the expression used in Aspen Plus NRTL, the parameters $a_{ij}$, $d_{ij}$, $e_{ij}$, and $f_{ij}$ were set to 0. Thus,

$$
b_{ij} = \frac{\Delta g_{ij}}{R}, \quad \alpha_{ij} = \epsilon_{ij}
$$

(7)

The binary interaction parameters (Table A1) used in Aspen plus and the calculated VLE results validated by experimental data (Figure A1, A2, A3, and A4) are provided in Appendix A of the Supporting Information.

### 2.2. Reaction Chemistry

The equilibrium-limited reaction between propylene glycol methyl ether and methyl-acetate to produce propylene glycol monomethyl ether acetate ($C_8H_{12}O_3$) and methanol can be expressed as

$$
C_8H_{10}O_2 + C_2H_6O_2 \leftrightarrow C_8H_{12}O_3 + CH_3OH
$$

(8)

The reaction kinetic parameters for the transesterification reaction of PGME with MeOAc in an RD, catalyzed by homogeneous sodium methoxide catalyst, were taken from Wang et al. and are summarized in Appendix B of the Supporting Information.

### 3. BASIS FOR ECONOMICS AND EQUIPMENT SIZING

For both process alternatives, an economic analysis was carried out that considered both the purchased capital investment (reactor, heat exchangers, and distillation column) and the operating costs (steam for the reboiler and cooling utilities for the condenser). The economics and detailed equipment sizing were based on textbooks by Douglas and Turton and are summarized in Appendix C of the Supporting Information. The TAC as an objective function was evaluated using eq 9 assuming a payback period of three years.

$$
TAC \text{ ($/year$)} = \text{operating cost ($/year$)} + \frac{\text{capital cost ($)}}{\text{payback period (year)}}
$$

(9)

### 4. SIMULATION OF PROPOSED CONFIGURATIONS

#### 4.1. RD Configuration

The optimal design configuration (developed in subsequent sections) of the RD column for the PGMEA process is shown in Figure 4. It includes a total of 26 stages with a total condenser and a partial reboiler. The stages are numbered from top to bottom, with the condenser being the first stage. The low boiling reactant, methyl acetate
(MeOAc), was fed at stage 16, while the PGME was fed at stage 7. The lighter reactant, MeOAc, went up to the column, while the heavy reactant, PGME, went down between the reactive trays (7−16) where the reaction took place. For simplicity, we assumed that the catalyst was loaded continuously with the feed. However, to control the reaction on the tray, the feed tray position for low and high boiling points was adjusted so the reaction would occur only on the reactive trays. With these assumptions, the reaction only took place between two feed locations. The calculated liquid holdup of 0.008 m³ per stage was set to produce 99.99 mol % PGMEA at the bottom of the RD column. The distillate contained the excess methyl acetate together with methanol produced by the transesterification reaction.

4.1.1. Optimal Design of the RD Configuration. A common approach to design an optimal distillation column is to estimate the values of the design variables that minimize an objective function, usually the TAC.33 Other operating parameters that need to be optimized for an RD column include the PGME/MeOAc feed ratio, stage holdups, reactive trays, and feed locations. Note that, to achieve these design objectives, a complete conversion of PGME is essential. By ensuring that the product specifications (PGMEA at 99.9% yield and 99.99% mole purity) were continuously satisfied, the final values of the design parameters were obtained using the sensitivity analysis-based procedure shown in Figure 5. The

initial design specifications for these variables were set mainly based on guess values, and the final design parameters are obtained through sensitivity analysis. During the analysis of each variable, other parameters remained fixed at the values listed in Table 1.

4.1.2. MeOAc−PGME Molar Feed Ratio for RD. The molar feed ratio of MeOAc to PGME is a crucial parameter to achieve a complete conversion of PGME. Wang et al.9 suggested a MeOAc−PGME molar feed ratio greater than 2.882 to eliminate the azeotrope from the reaction mixture and achieve the complete conversion of PGME. Here, the MeOAc−PGME molar feed ratio was varied to achieve complete conversion of the PGME reactant. As illustrated in Figure 6, this process showed that complete conversion of PGME in an RD column is possible. The PGME conversion increased from 64.87 to 99.88% when the MeOAc−PGME molar feed ratio was set to 3:1.

4.1.3. Effect of RD Pressure. For a kinetically controlled reaction, the operating pressure has a significant effect on the net production rate.34,35 For an endothermic reversible reaction, equilibrium conversion, and net production rate increase with increasing operating pressure owing to the temperature rise in the reactive trays. The operating pressure of the RD column was varied in order to observe its effects on the net reaction rate profile. Initially, an operating pressure of 1 atm was chosen and the reflux ratio was varied to satisfy the PGMEA yield requirement. Figure 7 shows the net reaction rate profile for a range of operating pressures.

To meet the design specifications, a lower operating pressure requires a larger reflux ratio and liquid holdups on the reactive trays. To assess the overall economic impact of the operating pressure, a number of RD column case studies were run with varying pressures. A detailed economic analysis for different operating pressures is illustrated in Table 2, where it can be seen that the low operating pressure required large liquid holdups on the reactive trays to meet the design specification.
The column diameter and the condenser cost increased as pressure decreased, which had a direct impact on the plant capital investment. At an operating pressure of 2.0 atm, the TAC increased owing to the requirement for high-pressure steam (474 K) in the reboiler. At 1.0 atm operating pressure, the overall TAC was lowest compared with those of the other pressure levels. At an operating pressure of 2.0 atm, the pressure decreased, which had a direct impact on the plant capital investment. Therefore, an operating pressure of 1 atm was chosen, which required a molar reflux ratio of 0.957 to maintain the desired PGMEA production rate.

4.1.4. Effect of Liquid Holdups. An adequate liquid holdup on the reactive trays is essential to realize the complete conversion of reactants. Larger holdups resulted in higher reactant conversions; however, excessive liquid heights can result in severe hydraulic limitations. The optimal column pressure of 1 atm resulted in a column diameter of 0.674 m. For holdup calculations, the following assumptions were made: (1) a reasonable weir height ($h_{weir}$) of 0.0508 m (2 in.); (2) the base catalyst occupied half of a reactive tray; and (3) the downcomer ($R_{DC}$) occupied 10% of the tray area. With these assumptions, the holdup volume was evaluated using eq 10.

$$V_e = \frac{\pi D^2}{4} \frac{h_{weir}}{2} (1 - R_{DC})$$

The liquid holdup was estimated at 0.008 m$^3$ for each tray. The desired PGMEA conversion could also be achieved at lower holdups, but at the cost of higher reflux ratios and column reboiler duties. Figure 8 illustrates the effects of reactive holdup on the required reflux ratio and corresponding heat duty for the desired conversion of PGME. As holdup was increased, reflux and duty steadily decreased. There was little change for holdups greater than 0.008 m$^3$ estimated based on column diameter. Therefore, a liquid holdup of 0.008 m$^3$ on each reactive tray was finally selected.

4.1.5. Effect of Number of Reactive Trays. In this section, the effects of changing the number of reactive trays are discussed. In conventional columns, more trays are better. However, this is not the case with a RD column involving two reactants and two products. Table 3 lists the effects on the TAC of changing the number of reactive trays. The optimal number of reactive trays was estimated to be 10. If more reactive trays were added, the total capital cost increased owing to the requirement for greater catalyst weights on the reactive trays.

4.1.6. Effect of Total Number of Trays. Adding more trays resulted in reduced energy demand at the column base. However, the addition of more trays requires more capital investment. Similarly, adding more trays resulted in a reduced column diameter. All these competing effects were quantitatively analyzed by optimizing the total number of trays for an RD column. Table 4 illustrates the TAC optimization of the number of trays. The optimum number of trays for an RD column was 26, where the overall objective function (TAC) was at a minimum.

4.1.7. Effect of Reactive Zone/Feed Tray Location. After finding the number of reactive trays and total trays of an RD column, we analyzed the effects of changing the reactive tray location. Initially, it was observed that after changing the reactive tray location, the TAC remained constant. Table 5 illustrates the effects of changing the feed tray location. After finding the number of reactive trays and total trays of an RD column, we analyzed the effects of changing the reactive tray location. Initially, it was observed that after changing the reactive tray location, the TAC remained constant.
The side-reactor configuration (developed in subsequent sections) of a non-RD column with a side-reactor for the PGMEA process is shown in Figure 9. The distillation column had a total of 30 stages including the condenser and the reboiler. The column was operated at 0.7 atm. The isothermal continuous stirred tank (CSTR) reactor was operated at 405 K and 25 atm, and was connected in an external loop. A liquid feed stream of 24 kmol/h at 349.6 K was withdrawn from stage 8 of the nonreactive zone (RZ) was manually changed in a gradual manner with a step size of one tray starting from tray number four. In addition, the feed location (FL) was also changed to study their compound effect on reboiler duty. Figure 9 demonstrates the effect of changing the location of the reactive trays and corresponding feed locations on the column reboiler duty. As can be seen, the minimum reboiler duty was obtained when the feed tray locations were (MeOAc/PGME = 16/7) associated with the reactive zone between trays 7 and 16.

### 4.2. Distillation with SRC Configuration

An optimal design configuration (developed in subsequent sections) of a non-RD column with a side-reactor for the PGMEA process is shown in Figure 10. The distillation column had a total of 30 stages including the condenser and the reboiler. The column was operated at 0.7 atm. The isothermal continuous stirred tank (CSTR) reactor was operated at 405 K and 25 atm, and was connected in an external loop. A liquid feed stream of 24 kmol/h at 349.6 K was withdrawn from stage 8 of the nonreactive zone and fed into the external reactor. The fresh MeOAc feed of 30 kmol/h was directly introduced into the CSTR. The homogeneous catalyst was continuously loaded into the reactor feed location, reactor-effluent return tray, and the number of side-reactors. The initial design specification for these variables were set mainly based on guess values, and final design parameters were obtained through sensitivity analysis. For analysis of each variable, the other parameters remained fixed at the values listed in Table 5.

For an economic analysis and fair comparison, the MeOAc-PGME molar feed ratio was chosen to be the same as that used for the RD process. For a given feed condition and required PGMEA purity, the optimum values of all these parameters were estimated using a sequential optimization procedure, as shown in Figure 11.

#### 4.2.1. Optimal Design of the SRC Configuration

The optimal structural and operational parameters in an SRC design include the column pressure, total number of trays, side-reactor feed location, reactor-effluent return tray, and the number of side-reactors. The initial design specification for these variables were set mainly based on guess values, and final design parameters were obtained through sensitivity analysis. For analysis of each variable, the other parameters remained fixed at the values listed in Table 5.

For an economic analysis and fair comparison, the MeOAc-PGME molar feed ratio was chosen to be the same as that used for the RD process. For a given feed condition and required PGMEA purity, the optimum values of all these parameters were estimated using a sequential optimization procedure, as shown in Figure 11.

#### 4.2.2. Effect of the Operating Pressure of the SRC Configuration

Similar to the RD case, the pressure of the non-RD column connected to the external reactor was optimized for minimum TAC. Since there was no reaction taking place in the distillation column, the pressure optimization was fairly straightforward, as in the case of a conventional distillation operation. An increase in column pressure usually increases the required reboiler heat load, but the column diameter and the condenser area can then be reduced. Operation under vacuum conditions might result in an economical design, since the boiling points of the components involved are considerably higher than the water-cooled condenser temperature (32 °C). To study these competing effects, the pressure was varied in the nonreactive column. Table 6 shows the detailed optimization results used to select the appropriate pressure for the distillation column.

The minimum practical operating pressure of 0.4 atm was chosen because pressures lower than this did not permit the use of cooling water as a heat removal medium. Analysis of the results from the pressure optimization revealed that column operation between 0.4 and 0.6 atm was not economically attractive. This was because of the very small differential temperature between the condenser and heat removal medium, which resulted in a larger heat exchanger area. The pressure optimization revealed that the minimum TAC was associated with an operating pressure of 0.7 atm. Further increases in pressure resulted in higher energy demands at the column base, leading to higher TACs.

#### 4.2.3. Effect of the SRC Column Total Trays

After selecting the column operating pressure, the next step was to find the optimum number of trays to minimize the objective function. Owing to the inverse relationship between the column trays and the reflux ratio, adding more trays could result in a less-expensive energy demand in the reboiler. Lower energy input in the reboiler further reduces the vessel diameter and reboiler/condenser heat-exchanger area. However, adding more trays results in higher capital investment owing to an increase in the height of the distillation column. These trade-offs were quantitatively analyzed by varying the number of trays of the distillation column. A detailed economic evaluation for the total number of trays is given in Table 7. The optimization of the total number of trays confirmed that of 44.7 mol % MeOAc, 21.7 mol % MeOH, 9.3 mol % PGME, and 24.2 mol % PGMEA, was fed back to stage 10 of the non-RD column. The bottom of the distillation column produced 9.99 kmol/h at 99.99 mol % of PGMEA, while the distillate contained the excess methyl acetate together with methanol and trace amounts of unreacted PGME.

Table 4. Effect of Total Number of Trays on TAC

<table>
<thead>
<tr>
<th>design parameters</th>
<th>total trays ((N_t)) of RD column</th>
</tr>
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<tbody>
<tr>
<td></td>
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<tr>
<td>ID (m)</td>
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<tr>
<td>molar reflux ratio (mol/mol)</td>
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<td>catalyst cost ((10^6 \text{ S}))</td>
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<td>total operating cost ((10^8 \text{ S/yr}))</td>
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<td>total capital cost ((10^8 \text{ S}))</td>
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</tr>
<tr>
<td>TAC ((10^6 \text{ S/yr}))</td>
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</table>

Figure 9. Effect of reactive zone/feed tray location on reboiler duty.
column diameter and heat exchanger cost were significantly reduced by adding more trays. Similarly, the reboiler duty also decreased as the number of trays increased. The optimum number of total trays was 30, giving the minimum TAC.

4.2.4. Optimal Reactor Side-Draw/Effluent Return Tray. In the next step, the optimal locations of the side-draw and reactor effluent return tray were determined. Usually, the feed to the side-reactor is withdrawn from a location where the reactants are abundant. In the PGMEA SRC design, fresh MeOAc was directly introduced into the side-reactor. However, the fresh PGME feed was fed at stage 7 of the nonreactive distillation column. The optimal location based on minimum energy in the reboiler was found to be stage 8, as shown in Figure 12a. Similarly, the optimization of the reactor—effluent return tray was analogous to finding the optimum feed tray location that minimized the reboiler duty.10 The precise location of the reactor product-return tray was optimized by minimizing the reboiler heat duty. Figure 12b shows the optimization of the reactor—effluent feed-tray location. The optimum tray location for the reactor—product stream was found to be stage 10. After finding the optimal side draw and reactor effluent return tray locations, an economic analysis in terms of plant capital, operating costs, and TAC was carried out. The total capital cost was estimated at 0.254 × 10^6$, while the plant operating costs were estimated at 0.112 × 10^6$/year. The corresponding TAC was calculated to be 0.196 × 10^6$/year.

4.2.5. Optimal Number of Side-Reactors. An important aspect of side-reactor distillation is finding the optimal number of side-reactors. Usually, the desired number of side-reactors should be between 3 and 6 for practical implementation of the SRC configuration.14 Krishna11 used the concept of reflux ratio vs reactant conversion by varying the number of side-reactors to match the performance of an RD column for MeOAc production. Intuition suggests that adding more side-reactors would have a direct impact on plant capital investment. The optimal results obtained with a single side-reactor required a 0.740 molar reflux ratio to maintain a 0.0001 mole fraction of PGME in the bottom of the nonreactive distillation column. We chose this as the design specification to study the economic effects of adding more side-reactors. For this purpose, the Aspen Plus built-in sensitivity analysis tool was utilized to vary the column reflux ratio to achieve the required 0.0001 mole fraction of PGME in the bottom stream. The specification of PGME impurity in the bottom stream of the nonreactive distillation column was essential to achieve the desired 99.99 mol % PGMEA product. The following assumptions were made in finding the optimal number of side-reactors: (i) the reactors are of equal sizes; (ii) fresh

<table>
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<th>design variables</th>
<th>base case</th>
<th>final design</th>
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<tr>
<td>column pressure (atm)</td>
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<td>total number of stages (a)</td>
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<td>feed location fresh PGME</td>
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<td>reflux ratio</td>
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<td>side-reactor feed location</td>
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<td>reactor effluent return tray</td>
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</tr>
<tr>
<td>no. of side-reactors</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

\(a\) Including the condenser and reboiler.

Figure 10. Proposed SRC configuration for the PGMEA process.

Table 5. Parameter Values for the Base Case and the Final Design of SRC
MeOAc feed is equally distributed into side-reactors; (iii) reactor temperature and pressure are kept constant.

The results of the sensitivity analysis for the addition of two side-reactors are illustrated in Figure 13. As can be seen, with the addition of one side-reactor, the molar reflux ratio to maintain the PGME mole fraction was estimated at 0.841. The extremely high temperature and pressure resulting from two side-reactor effluent streams might result in flashing and cause liquid to dry up on the trays, thus requiring slightly higher reflux to maintain the desired specification. Therefore, the final design included a single side-reactor for economic comparison with the RD configuration.

| Table 6. Effect of Column Operating Pressure on TAC |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| alternatives pressure of an SRC column for desired PGMEA yield | 0.4 atm | 0.5 atm | 0.6 atm | 0.7 atm | 0.8 atm | 0.9 atm |
| ID (m) | 0.600 | 0.584 | 0.574 | 0.567 | 0.561 | 0.560 |
| reboiler duty QR (MW) | 0.290 | 0.302 | 0.312 | 0.321 | 0.330 | 0.346 |
| condenser duty QC (MW) | 0.514 | 0.508 | 0.503 | 0.499 | 0.495 | 0.499 |
| reboiler temperature TR (K) | 390.0 | 396.4 | 402.3 | 407.2 | 411.6 | 415.5 |
| condenser temperature TC (K) | 304.2 | 309.4 | 313.7 | 317.5 | 320.9 | 324.0 |
| side-reactor energy (10^6 $/year) | 0.041 | 0.039 | 0.038 | 0.036 | 0.035 | 0.034 |
| total operating cost (10^6 $/year) | 0.118 | 0.120 | 0.120 | 0.125 | 0.129 |
| total capital cost (10^6 $) | 0.600 | 0.320 | 0.278 | 0.259 | 0.248 | 0.243 |
| TAC (10^6 $/year) | 0.318 | 0.226 | 0.212 | 0.207 | 0.208 | 0.210 |

| Table 7. Effect of SRC Column Operating Pressure on TAC |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| alternatives trays of an SRC column for desired PGMEA yield | 26 | 28 | 30 | 32 |
| ID (m) | 0.610 | 0.567 | 0.555 | 0.550 |
| feed tray (fresh PGME) | 6.000 | 6.000 | 7.000 | 8.000 |
| reboiler duty QR (MW) | 0.372 | 0.321 | 0.309 | 0.304 |
| condenser duty QC (MW) | 0.543 | 0.498 | 0.488 | 0.489 |
| side-reactor energy (106 $/year) | 0.0 | 0.0 | 0.0 | 0.0 |
| total operating cost (10^6 $/year) | 0.132 | 0.120 | 0.118 | 0.117 |
| total capital cost (10^6 $) | 0.270 | 0.259 | 0.261 | 0.266 |
| TAC (10^6 $/year) | 0.222 | 0.207 | 0.205 | 0.206 |

5. RESULTS AND DISCUSSION

5.1. Reactive Distillation Results. The distillate of the RD column had a total flow rate of 30.01 kmol/h with a composition of 66.68 mol % MeOAc, 33.29 mol % MeOH, and 0.03 mol % PGME. The condenser duty was 0.438 MW and the condenser temperature was 326.7 K. The required reboiler temperature was 419 K, using medium-pressure steam as a heat source. The required reboiler duty was 0.430 MW. The column diameter, as predicted by the Aspen tray-sizing option, was 0.617 m. Figure 14 shows the composition profile of the RD column.

5.2. Side-Reactor Distillation Results. The distillate from the SRC column had a total flow rate of 30.01 kmol/h with a composition of 66.68 mol % MeOAc, 33.29 mol % MeOH, and 0.03 mol % PGME. The condenser duty was 0.438 MW and the condenser temperature was 326.7 K. The bottom-product flow rate was 9.99 kmol/h, with 99.99 mol %
PGMEA and 0.01 mol % PGME. The column reflux ratio to obtain 99.99 mol % was estimated at 0.740. The reboiler temperature was 407.1 K, so it could use low-pressure steam. The required reboiler-heat duty was found to be 0.291 MW. The column diameter, as predicted by the Aspen tray-sizing option, was 0.539 m. Figure 15 shows the composition profile of the SRC column.

5.3. Side-Reactor. The isothermal CSTR connected to the non-RD column in an external loop received 24 kmol/h of feed from tray 8, at 349.6 K. Fresh MeOAc was directly fed to the CSTR at 30 kmol/h. The reactor products with a composition of 44.71 mol % MeOAc, 21.77 mol % MeOH, 9.30 mol % PGME, and 24.22 mol % PGMEA was fed back to tray 10 of a nonreactive distillation column. The reactor net heat duty for maintaining the reaction temperature (405 K) was estimated to be 0.149 MW.

6. ECONOMIC ANALYSIS OF BOTH CONFIGURATIONS

The frequently used economic indicator TAC was chosen to examine the competing effects on the plant capital and operating costs of the proposed configurations. The key economic indicators and their comparisons for the two proposed configurations are shown in Table 8. The results indicate that the SRC-based design can match the performance of RD with only a 5% increase in the TAC. The RD column process required lower capital investment than the SRC process, owing to the additional cost of the side-reactor vessel associated with the latter configuration. Similarly, the heat exchanger cost for the SRC design was 10.84% more expensive than for RD, owing to the small temperature difference between the reboil drum and the condenser heat removal medium. There was no substantial difference between the two configurations in terms of plant operating cost. Despite some small economic advantages of the RD configuration, the
proposed SRC design is a promising alternative to avoid the operational and hardware limitations of RD columns.

7. CONCLUSION

The transesterification route for ultrahigh purity PGMEA synthesis in an RD column is hindered by severe operational and hardware limitations. The homogeneous base catalyst used in an RD operation poses severe operational and equipment challenges, as it is insoluble in the reaction mixture. A distillation column with side-reactor configuration was proposed to overcome these operational limitations of the RD column. Catalyst accumulation on the surface of the reactive-tray packings could be avoided by using an external-reactor approach, which facilitates the perfect mixing of the homogeneous catalyst with the reaction mixture. Moreover, maintenance and catalyst replacement issues can be easily avoided. Comparison of the configurations in economic terms revealed that the SRC-based design was economically attractive, with only a 5% increase in TAC. Therefore, the design of an SRC-based configuration should be tested as a way of meeting the growing industrial demand for ultra-high-purity PGMEA.

Author Contributions
A.H. and Y.D.C. contributed equally.

Notes
The authors declare no competing financial interest.

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REFERENCES


Table 8. Comparison of Key Economic Indicators for the RD- and SRC-Based Designs

<table>
<thead>
<tr>
<th>design alternatives for PGMEA</th>
<th>reactive distillation (RD)</th>
<th>column with side-reactor (SRC)</th>
<th>economic comparison (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>side-reactor/catalyst cost (10^6 $)</td>
<td>0.001</td>
<td>0.032</td>
<td></td>
</tr>
<tr>
<td>Separation Column</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ID (m)</td>
<td>0.617</td>
<td>0.540</td>
<td></td>
</tr>
<tr>
<td>QR (MW)</td>
<td>0.430</td>
<td>0.291</td>
<td></td>
</tr>
<tr>
<td>QC (MW)</td>
<td>0.439</td>
<td>0.471</td>
<td></td>
</tr>
<tr>
<td>TR (K)</td>
<td>419.2</td>
<td>407.2</td>
<td></td>
</tr>
<tr>
<td>TC (K)</td>
<td>326.8</td>
<td>317.5</td>
<td></td>
</tr>
<tr>
<td>column capital cost (10^6 $)</td>
<td>0.105</td>
<td>0.103</td>
<td>1.98</td>
</tr>
<tr>
<td>heat exchanger costs (10^6 $)</td>
<td>0.108</td>
<td>0.120</td>
<td>-10.84</td>
</tr>
<tr>
<td>operating cost (10^6 $/y)</td>
<td>0.116</td>
<td>0.113</td>
<td>2.81</td>
</tr>
<tr>
<td>total capital cost (10^6 $)</td>
<td>0.214</td>
<td>0.254</td>
<td>-18.80</td>
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<tr>
<td>total operating cost (10^6 $/y)</td>
<td>0.116</td>
<td>0.113</td>
<td>2.59</td>
</tr>
<tr>
<td>TAC (10^6 $/y)</td>
<td>0.187</td>
<td>0.197</td>
<td>-5.20</td>
</tr>
</tbody>
</table>

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.8b04052.

Binary interaction parameters and VLE diagrams; kinetics of the transesterification reaction; detailed equipment sizing for both design alternatives (PDF)

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