Exploitation of distillation for energy-efficient and cost-effective environmentally benign process of waste solvents recovery from semiconductor industry

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HIGHLIGHTS

• Distillation configurations are exploited to reclaim valuable components from waste solvent
• Green solvent as entrainer for extractive distillation
• Economic and environmental analysis to achieve energy-efficient and cost-effective environmentally benign process
• Significant reduction of CO2 emissions released into the atmosphere

GRAPHICAL ABSTRACT

Synopsis
Integrating renewable energy into waste solvent recovery process to increase cost saving and achieve lower environmental impact.

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ABSTRACT

The waste solvent is unavoidably generated from the high solvent dependable processes. One of them is the semiconductor industry. The waste solvent is frequently incinerated to eliminate hazardous waste and this practice raises the issue of environmental and treatment costs. Thus, recovery of waste solvent is a substantial environmental mitigation option. This study explores the recovery of multicomponent waste solvents from the semiconductor industry. To achieve a greener and energy-efficient process, the recovery process is proposed through investigation of mixture thermodynamic behavior, process design, optimization, economics, and integration of renewable energy for environmental advantages. Herein, Distillation, a practical technology option for solvent recovery, with green solvent for extractive distillation and a new approach using renewable energy in waste solvent recovery are explored. As the result, waste solvent recovery by distillation with conventional energy exhibits bold advantages to cost and lower carbon process compared to waste disposal. The integration of renewable energy with about 37 % share of conventional energy as the backup indicates the highest annual cost-saving and reduces about 89.4 % of annual carbon emission compared to carbon emission from waste disposal.

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1. Introduction

The growth rate of economic development and industrial acceleration exerts the need for the sustainable process associated with energy demand, production costs, and stricter environmental regulations (Chaniago et al., 2016a, 2019; Chaniago and Lee, 2018; Duflo et al., 2012; Voorad et al., 2018). The synchronous both advancing fabrication output and reducing production footprint associated with energy expense and environmental pollution are the challenges for various industries (Saw et al., 2019). For hundreds of years, solvents have already been vital component of various industries (Cseri et al., 2018). After being used, the waste solvent is considered hazardous waste. However, the solvents are frequently disposed of due to purity concerns after one process cycle which is unfavorable in sustainability practice (Raymond et al., 2010). The industry of fine chemicals, pharmaceuticals, and semiconductors are identified as significant sources of chemical waste (Abou-Shehada et al., 2016; Chaniago et al., 2015; Sheldon, 2017). Thus, many industry activities are expected to address the issue of sustainability and safety related to solvent consumption. In the pharmaceuticals and semiconductor industry, the considerable capacity of waste solvents is generated after a large number of various solvents are utilized in processing (Chaniago et al., 2015; Raymond et al., 2010). An issue in waste treatment rises to the surface because various waste solvents discharged is incinerated at high temperature (Slater et al., 2010). Incineration can release acidic gases and other atmosphere hazardous pollutants into the atmosphere, resulting in a negative impact on human health and environmental contaminants (Abagay et al., 2021; Sharma et al., 2013). Another concern is the economic consideration associated with solvent purchasing cost because incineration commonly disposes of valuable solvents. With solvent recovery, the cost associated with material purchase can be avoided (Cseri et al., 2018). Thus, solvent recovery presents a better mitigation option than any disposal method.

2. Waste reduction and solvent recovery

The general aim of green chemistry and engineering is to minimize material usage, waste, and energy consumption as well as increase renewable sources and process efficiency, all without the loss of economic viability (Anastas and Zimmerman, 2003; Chen et al., 2020; Clarke et al., 2018). The most effective methods are to reduce waste output in chemical reaction output and perform neat separation (no solvent involved). However, among major industries in the world, the semiconductor industry heavily relies on solvents or fine chemicals for photoresist cleaning and makes the generation of waste solvents unavoidable (Chaniago and Lee, 2018). In this industry, the semiconductor processing applies huge amounts of various chemicals which inevitably discharge huge valuable chemicals as waste solvents. Recently, an industrially popular method of waste treatment is to incinerate waste solvents at high temperatures (Chaniago et al., 2016b). Under cost-competitive burden and environmental issues, recovering valuable chemicals from semiconductor industrial waste solvents for reuse purposes is an attractive approach. Implementing waste solvent recovery reflects the focus of sustainability practice to boost the circular economy (Abagay et al., 2021). Solvent recovery from various industries can be retrieved by recovery methods, among those are membranes, adsorption, liquid-liquid extraction (LLE), crystallization, and distillation (Chaniago and Lee, 2022). Pervaporation (PV) membrane demonstrates its capability for the recovery of tetrahydrofuran (Slater et al., 2012). However, the core issue of any membrane's method is membrane material properties itself rather than the process (Othman et al., 2022; Qyrum et al., 2020). This issue hinders one material that can be used for any membrane process. Adsorption is capable to recover isopropyl alcohol (IPA) from waste solvent (Lin and Wang, 2004). Similar to the membrane method, the adsorption method relies on its material. LLE method offers an attractive way to recover methanol using water as a solvent (Yi et al., 2018). This method is based on mixture relative solubilities in two different immiscible liquids (Berk, 2018). Thus, when the mixtures don't exhibit liquid-liquid partition, the method is not applicable. Distillation demonstrates a practicable option for solvent recovery. Bayer Corporation report total cost savings in their solvent recycling facility reached $7 million per year related to purchasing cost-saving (Cseri et al., 2018). Pfizer was capable to save $65 million as well as reducing its carbon emission by 677,000 kg per year (Cseri et al., 2018).

Distillation is a separation method based on phase behavior and relative volatility (the difference that is relatively simple and widely adopted in the industry. Distillation account for the major portion of all liquid separation in the chemical process industries (CPI). The outstanding role of distillation in the reality is proved that it is the only separation unit competent with high capacity and high purities for multiple target constituents. Although there is a misconception about process efficiency and technology maturity (Agrawal and Tumbalam Gooty, 2020), distillation has been the main choice among all available unit operations. While distillation is a well-established technology for solvent recovery, this technology remains much room for improvement and can be used as the benchmark for other technologies. In the practical issue, multicomponent waste solvent occasionally exists. Recently, several studies reported multicomponent waste solvent recovery from the semiconductor industry by distillation (Chaniago et al., 2015, 2016a, 2016b) without considering renewable power source implications to economic and environmental impacts. Since progressive policy recommendations for faster adoption of renewable energy to the various sector in the national energy mix to attain a low-carbon grid (Gatto and Drago, 2021), herein, we rectify the new approach by implementing renewable energy in the waste solvent recovery. Commonly, the integration of renewable energy into the electricity grid is independent of each other. In this study, natural gas (NG) based power from conventional utility steam and renewable energy is utilized. Steam is used for distillation reboiler and is conventionally generated by utilizing NG combustion. To accommodate renewable energy for steam requirements, the steam is generated by electric boiler (Zantye et al., 2021) and powered by renewable energy, solar photovoltaic (PV), and wind turbine. The purpose of the research is to present the evaluation accounting economic and environmental implications by considering renewable energy in the efficient recovery process design of solvent recovery from the waste solvent of the semiconductor industry as shown in Fig. 1.

The designed process performance associated with cost and emission are compared to the disposal process without recovery. To clearly show the effectiveness of the efficient design and the use of renewable energy. The multiple solvent components that increase the complexity of thermodynamic behavior in designing are studied. The real industrial waste solvents that typically exist in the semiconductor industry consist of water (H2O), N, N-dimethylacetamide (DMA), diethylene glycol monomethyl ether (DGMME), N-methyl-2-pyrrolidone (NMP), 1-piperazineethanol (HEP) are used as studied components. The mixture exhibits zeotropic and azeotropic behavior that represent two main problems in the vapor-liquid separation. Thus, this design method can be used to design waste solvent recovery from semiconductor activities when vapor-liquid separation is available for any different mixtures in the liquid form.

3. Greener pathway for recovery of waste solvent

The solvent recovery process for the reduction of solvent wastes, typically by the distillation process, comprises part of several strategies (Welton, 2015). Process synthesis and design of the recovery process for the distillation sequence selection procedure must conform to the thermodynamic method, feasible separation, and constraints (Chaniago et al., 2016b; Chaniago and Lee, 2018). To identify a preferable distillation sequence using sharp split separation, a superstructure distillation design (Andrecovich and Westerberg, 1985) is conducted while considering the design procedure. In particular constraints, the H2O impurity is normally controlled to <2–3 wt% and the operating temperature condition is <200 °C to prevent thermal decomposition of HEP deformation, resulting in a color shift to yellow (Chaniago et al., 2016b). To secure high purity of solvent for selling or recycling to industrial process, the constrains design is solvent recovery minimum purity at electronic grade or 99.9 wt%.
3.1. Thermodynamic and vapor-liquid behavior

The mixture can be specified as ideal or non-ideal by mixture vapor-liquid equilibrium (VLE) in the equilibrium system in two ways, by VLE data or relative volatility. The standard of nonideality is expressed by deviation from unity of the activity coefficient of the liquid phase, \( \gamma_i \), and fugacity of vapor phase, \( \varphi_i^V \), for low pressure \( \varphi_i^V = 1 \) (Widagdo and Seider, 1996). VLE is defined by Eq. (1), where \( \gamma_i \) and \( x_i \) are the mole fractions of component i in the vapor and liquid phase, respectively. \( P_{i,SAT}^V \) is vapor pressure of component i at temperature \( T \) and \( P \) is total pressure. \( K_i \) is K-value that relates the vapor and liquid mole fraction.

\[
\gamma_i = \frac{y_i P_{i,SAT}^V}{x_i P}
\] (1)

\[
K_i = \frac{y_i}{x_i} = \frac{y_i P_{i,SAT}^V}{P}
\] (2)

when \( \gamma_i = 1 \), the behavior is ideal. A maximum-boiling azeotrope occurs for \( \gamma_i < 1 \). For minimum-boiling point azeotropic, \( \gamma_i > 1 \). The ratio of equilibrium K-values for two components measures their relative volatility (\( \alpha \)). Relative volatility is separation key in distillation system. The unity deviation of vapor-liquid component composition ratio \( \alpha > 1 \). The number of separations can be straightforwardly arranged in exactly N−1 column using superstructure to generate feasible separation and without considering intensification and integration (Caballero et al., 2021). To achieve a minimum solvent purity of 99.9 wt% due to azeotropic compositions, recovery of NMP, DGMME, and HEP recovery must be maximized. For this matter, each solvent is recovered at a water content of less than constraints of target purity at 1 atm, however, the azeotrope of NMP and HEP is disappeared at 0.2 atm. Thus, there is no obstruction for separation at 0.2 atm. Since the temperature of mixture separation consisting HEP must be below 200 °C, adjusting pressure to 0.2 atm satisfy operation constraints and eliminate the azeotrope of NMP and HEP.

3.2. Non-azeotropic sequence using superstructure design

The number of separations can be straightforwardly arranged in exactly N−1 column using superstructure to generate feasible separation and without considering intensification and integration (Caballero and Grossmann, 2006). In the case of four components, the number separation task in all cases is definitely three columns (Caballero et al., 2021). To achieve a minimum solvent purity of 99.9 wt% due to azeotropic compositions, recovery of NMP, DGMME, and HEP recovery must be maximized. For this matter, each solvent is recovered at a water content of <0.005%. There are several routes for recovery by conventional distillation. All available sequences are projected until each solvent and binary azeotropic component are obtained. The azeotropic mixture will be treated by advanced distillation. In the concept, DGMME and NMP are considered as 1 stream. The sequence number for the component are:

- Water = 1, DMA = 2, DGMME = 3, NMP = 3, HEP = 4. All available splits are 1. Direct sequence (DS): 1/234 → 2/34 → 3/4. 2. Indirect sequence: 123/4 → 12/3+1/2. 3. Modified DS: 1/234→23/4 → 2/3. 4. Middle Split: 12/34→1/2 + 3/4. In the simulation, no column pressure drop is assumed. The complete possible superstructure is shown in Fig. 2.
All sequences are possible to recover DGMME and NMP at a composition ratio is about DGMME = 63 % and NMP = 37 % with total mass flow of about 270 kg h.

### 3.3. Azeotropic separation sequence using additional green solvent as entrainer

Pressure sensitivity of azeotropic mixture must be checked before considering another method. Avoiding the use of additional solvent is necessary because current system is solvent recovery. When additional solvent is required in the system, the additional solvent must address its green characteristics (Clark et al., 2013; Dutta et al., 2020) to conform greener process. The greenest process is without the use of solvent or neat process, followed by water, renewable solvent, and petroleum-based solvents as the last option in the hierarchy of green processes (Isoni et al., 2016). However, the first option using pressure sensitivity is less preferable in this system. Conceptually, the pressure swing distillation method without using the solvent shows the different azeotrope composition is only 5.5 % which is close to the minimum 5 % (Chaniago and Lee, 2018) for pressure alteration range between 1 and 10 atm. Detailed VLE of DGMME and NMP is shown in Fig. 3.a. Further, the highest-pressure condition overlaps the high bound of high-pressure steam at temperature 330 °C, another more expensive heating medium is required, and it is not preferable. Although the pressure can be reduced more from 1 to 0.1 atm to accommodate the range of high-pressure steam, the pressure alteration exhibits undesirable azeotropic composition differences because the difference is <5 % as shown in Fig. 3.b.

On the other hand, azeotrope issue can be overcome by altering relative volatility (α) of mixture. Extractive distillation (ED) utilizes additional solvent or entrainer to alter α to recover the target constituent. This later distillation option can be applied using water or additional renewable solvent as entrainer to conform green process. To be viable as green process in the case of ED for waste solvent recovery, the solvent selection must conform to

#### Table 1

Waste solvent component properties.

<table>
<thead>
<tr>
<th>Component</th>
<th>Composition (Wt%)</th>
<th>Normal boiling point (NBP) (°C)</th>
<th>Boiling point at 0.2 atm (°C)</th>
<th>Azeotrope composition (Mass basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>28</td>
<td>100.0</td>
<td>60.3</td>
<td>DGMME + NMP at 1 atm; 212.66 °C</td>
</tr>
<tr>
<td>DMA</td>
<td>14</td>
<td>166.1</td>
<td>114.0</td>
<td>NMP + HEP at 1 atm; 245.94 °C</td>
</tr>
<tr>
<td>DGMME</td>
<td>17</td>
<td>193.6</td>
<td>141.8</td>
<td>DGMME + NMP at 0.2 atm; 155.99 °C</td>
</tr>
<tr>
<td>NMP</td>
<td>10</td>
<td>204.3</td>
<td>147.3</td>
<td>NMP + HEP at 0.2 atm</td>
</tr>
<tr>
<td>HEP</td>
<td>31</td>
<td>245.9</td>
<td>188.5</td>
<td>No Azeotrope</td>
</tr>
</tbody>
</table>

![Fig. 2. All possible configuration for solvent recovery process.](image-url)
the metrics of industry green solvent (Soh and Eckelman, 2016), solvent or entrainer capability to increase $\alpha$ (Chaniago and Lee, 2018; Sprakel et al., 2019), and availability that represent cheap and available on large scale (Gu and Jérôme, 2010).

A selection guide that covers safety, health and environment criteria (Prat et al., 2016; Soh and Eckelman, 2016) is used to conform green metric of additional solvent or entrainer for this study. The guide classifies green rank of solvents into recommended, problematic, hazardous and highly hazardous. Table 2 shows the selected list of recommended solvent with the price. Fig. 4 shows alteration of $\alpha$ mixture for each recommended additional solvent at entrainer mass fraction 0.1 and 0.3 correspond to without entrainer.

Water is first choice in the green hierarchy when process with no additional solvent is not available. However, water failed to confirm its capability to increase $\alpha$ of DGMME + NMP as shown in Fig. 4.

Glycerol, valuable green solvent from the waste of the biodiesel industry (Gu and Jérôme, 2010), is abundantly available, cheap, and has excellent properties to increase the $\alpha$ of DGMME and NMP as shown in Fig. 4. For separation of an azeotropic mixture by the ED, glycerol is frequently used.

![Fig. 3. Vapor-liquid equilibrium for DGMEE and NMP. (a) at 1 atm and 10 atm. (b) at 0.1 atm and 1 atm.](image)

![Fig. 4. Detail $\alpha$ mixture alteration by different additional entrainer (a) Entrainer fraction = 0.1; (b) Entrainer fraction = 0.3.](image)

**Table 2**

<table>
<thead>
<tr>
<th>Solvent (Pure)</th>
<th>Molecular class</th>
<th>NBP (°C)</th>
<th>Price/$kg$</th>
<th>Price (References)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol</td>
<td>Alcohol</td>
<td>287.85</td>
<td>0.595–0.904</td>
<td>(Abdul Raman et al., 2019)</td>
</tr>
<tr>
<td>Methanol</td>
<td>Alcohol</td>
<td>64.7</td>
<td>0.463</td>
<td>(Hanik et al., 2018)</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Alcohol</td>
<td>78.29</td>
<td>0.735–1.034</td>
<td>(&quot;Ethanol Market and Pricing Data – January 5, 2022 - U.S. GRAINS COUNCIL,” n.d.; González-Peñas et al., 2020; Moraes et al., 2019)</td>
</tr>
<tr>
<td>Acetone</td>
<td>Keton</td>
<td>56.13</td>
<td>0.763</td>
<td>(González-Peñas et al., 2020)</td>
</tr>
</tbody>
</table>
as the effective heavy solvent (García-Herreros et al., 2011; Gil et al., 2012). However, these benefit green solvent, glycerol is much viscous at a temperature below 60 °C and may affect the mass transfer of the process. Therefore, any separation involving glycerol as solvent must advance at a temperature above 60 °C.

3.4. Renewable energy integration

Electric boiler has many convenient factors, such as convenient use and maintenance, high efficiency, and low emission release to the environment (Du et al., 2022). An electric boiler uses electricity to generate steam with an efficiency reaching 95–99.9 % with no NOx released into the atmosphere. In this study, we assume the efficiency of the boiler is 99 %. The integration of renewable energy into the solvent recovery process is evaluated using 100 % renewable energy and combination between conventional energy and renewable energy.

3.5. Total annual cost estimation

Total annual cost (TAC) for the column is determined by distillation optimization. One approach to obtaining optimal cost is to specify TAC as the objective function. A semi-automatic or hybrid optimization method is used. This method exploits automatic searching optimum value by design specification and manual adjusting of other decision variables in the Aspen Plus V11 (Chaniago et al., 2021; Hussain et al., 2019). Detail optimization flowchart with the constraints is presented in Fig. 5 and Table 3, respectively. The variables are optimized while maintaining target solvent purity at 99.9 wt%. The optimization flowchart is described for direct sequence design and can be repeated for 3 remaining designs. The steam used in the process is the high-pressure steam (HPS) and medium-pressure steam (MPS).

The calculation of TAC during optimization of distillation is sum of total annualized investment cost (CAPEX) and total annualized operating expense (OPEX) which are influenced by variables optimization. Capital recovery factor (CRF), which is the ratio to a constant investment cost that incurs for a given length of time to determine present value, can be obtained by the following equation.

\[ CRF = \left( \frac{1 + \Delta t}{\Delta t} \right)^n - 1 \]  

where \( \Delta t \) is an interest rate and \( n \) is a project period or total lifespan of equipment. The equipment cost ($) of the distillation column designed in process simulation was calculated by dividing it into five parts—the distillation tray columns, the vessel of reboiler and condenser, reboiler, and condenser (Seider et al., 2016). To reflect the capital cost fluctuated with the passage of time, the chemical engineering plant cost index (CEPCI) was adopted.

\[ C_2 = C_1 \left( \frac{I_{2021}}{I_{2016}} \right) \]  

where \( C_2 \) is a cost of equipment and \( I_i \) is a CEPCI. One characteristic of wind and solar energy is that they have intermittency because the possible production is temporarily variable by surroundings (Asiaban et al., 2021; Cai and Bréon, 2021). To reflect this characteristic, the scale of the wind turbine and solar PV was determined higher than the requirement of total heat duty as 0.5, 1.0, and 1.5 MW, the real requirement of heat duty were 0.0–0.3, 0.3–0.7, and 0.7–1.2 MW, respectively. In the case electric boiler utilization, the produced electricity is used for generating HPS and MPS through the electric boiler which has 99 % of efficiency. In addition, the land cost of the wind turbine and solar PV was considered especially because they take up a lot of space compared with the recovery process. The detailed costs and information on the economic assumptions for calculating capital expenditures are shown in Table 4. CAPEX ($ y⁻¹) was determined by ratio estimation, based on the CRF of each of the equipment, as shown in Eq. (7).

\[ \text{CAPEX} = \sum_{i=1}^{n} CRF_i \times C_i \]  

where \( i \) is an equipment in the process simulation, \( CRF_i \) is a capital recovery factor, and \( C_i \) is an equipment cost reflected CEPCI.

The OPEX is the sum of the utility cost which is used at the condenser and reboiler of the distillation columns, and cooler of the ED cycle. The cost of glycerol is 0.750 $ kg⁻¹ (Abdul Raman et al., 2019) for solvent in the ED. Cooling water of 0.025074 $ ton⁻¹ was used at the reboiler and cooler for cooling down the temperature (Turi et al., 2017). The required amount of cooling water was calculated by a function of the Aspen Plus V11. NG and electricity produced by the wind turbine and solar PV were respectively used in NG combustion and electric boiler, and HPS and MPS were used to supply the necessary amount of heat. HPS of 250 °C and 572 psia and MPS of 175 °C and 127 psia were needed for 1204.7 BTU lb⁻¹ and 1191.4 BTU lb⁻¹ of the heat. In the case of the NG combustion efficiency of 85.7 % and NG price of 3.843 $ MMBTU⁻¹ (Price at the beginning of the year 2022), the cost of the HPS and MPS were estimated as 11.91 and 11.78 $ ton⁻¹, respectively.

The annualized cost of the fuel consumption ($ y⁻¹), which accounts for the largest portion of utility cost was considered to estimate the OPEX of the waste disposal plant. Each solvent component per unit mass can be calculated by the following equation (Aboagye et al., 2021)

\[ C_{WW} = P_f \times \Delta H_C \]  

where \( C_{WW} \) is a waste disposal cost ($) g⁻¹, \( P_f \) is a price of fuel ($ kJ⁻¹), and \( \Delta H_C \) is a heat of combustion (kJ g⁻¹).

The waste disposal cost of NMP, DMA, HEP, and DGMME was assumed as 0.000110, 0.000108, 0.000116, and 0.000095 $ g⁻¹, respectively. Before the waste disposal process, purchasing solvent components is required in industrial operation. Therefore, the price of each component of the waste solvent was considered as 4.3 $ kg⁻¹ for NMP (Tozzi et al., 2018). DMA, HEP, and DGMME equation prices are from open literature and expressed in Eqs. (9), (10), and (11).

\[ C_{DMA} = f_{DMA} \times 46.74 \times 8,000 \quad \text{h} \]  

\[ C_{HEP} = f_{HEP} \times 259.9 \times 8,000 \quad \text{h} \]  

\[ C_{DGMME} = f_{DGMME} \times 53.54 \times 8,000 \quad \text{h} \]  

where \( C_i \) is the cost of each component \( x \) ($) and \( f_i \) is the mass flow rate of the component \( x \) (kg h⁻¹).

Total annualized cost (TAC) ($ y⁻¹) is the sum of the CAPEX and OPEX. And in this study, The TAC of the completed process can be considered as the total recovery cost which is the cost to recycle components of waste solvent. As the result, the total saving cost of recycling the waste solvent can be calculated by subtracting the total recovery cost from the total disposal cost.

3.6. Carbon dioxide emissions

Consuming the NG and generating electricity to supply heat duty for generating steam and operating waste solvent disposal process emits CO₂. In the case of using NG combustion which has 85.7 % of efficiency for generating HPS and MPS, annualized CO₂ emissions could be calculated by following Eqs. (12) and (13) (Andika et al., 2014; Gadalla et al., 2005).

\[ Q_{\text{fuel}} = \frac{Q_{\text{boiler}}}{\lambda_{\text{proc}}} \times (h_{\text{proc}} - 419) \times \left( \frac{T_{\text{FTB}} - T_0}{T_{\text{FTB}} - T_{\text{max}}} \right) \]  

where \( Q_{\text{fuel}} \) is the amount of fuel burnt (kW), \( Q_{\text{boiler}} \) is the reheating duty (heat duty required by the process) (kW), \( \lambda_{\text{proc}} \) is the latent heat of steam (kJ kg⁻¹), \( h_{\text{proc}} \) is the enthalpy of steam (kJ kg⁻¹), \( T_{\text{FTB}} \) is the flame
Intensified case conditions

Vary number of stages in Col-1, Design-1
Fix feed stage number in Col-1, Design-1
Fix number of stages in Col-2, Design-1
Fix feed stage number in Col-2, Design-1
Fix number of stages in Col-3, Design-1
Fix feed stage number in Col-3, Design-1

Find number of stages that minimizes TAC

Find feed stage number that minimizes TAC

Vary number of stages in Col-2, Design-1
Fix feed stage number in Col-2, Design-1
Fix number of stages in Col-1, Design-1
Fix feed stage number in Col-1, Design-1
Fix number of stages in Col-3, Design-1
Fix feed stage number in Col-3, Design-1

Find number of stages that minimizes TAC

Find feed stage number that minimizes TAC

Vary number of stages in Col-3, Design-1
Fix feed stage number in Col-3, Design-1
Fix number of stages in Col-1, Design-1
Fix feed stage number in Col-1, Design-1
Fix number of stages in Col-2, Design-1
Fix feed stage number in Col-2, Design-1

Find number of stages that minimizes TAC

Find feed stage number that minimizes TAC

Repeat same procedure for Design-2, 3, 4 and ED

Economical process design

Vary feed stage number in Col-1, Design-1
Fix number of stages in Col-1, Design-1
Fix feed stage number in Col-1, Design-1
Fix number of stages in Col-2, Design-1
Fix feed stage number in Col-2, Design-1
Fix number of stages in Col-3, Design-1
Fix feed stage number in Col-3, Design-1

Find number of stages that minimizes TAC

Vary feed stage number in Col-2, Design-1
Fix number of stages in Col-2, Design-1
Fix feed stage number in Col-2, Design-1
Fix number of stages in Col-1, Design-1
Fix feed stage number in Col-1, Design-1
Fix number of stages in Col-3, Design-1
Fix feed stage number in Col-3, Design-1

Find number of stages that minimizes TAC

Vary feed stage number in Col-3, Design-1
Fix number of stages in Col-3, Design-1
Fix feed stage number in Col-3, Design-1
Fix number of stages in Col-1, Design-1
Fix feed stage number in Col-1, Design-1
Fix number of stages in Col-2, Design-1
Fix feed stage number in Col-2, Design-1

Find number of stages that minimizes TAC

Repeat same procedure for Design-2, 3, 4 and ED

Fig. 5. Flow chart of economical process design. Col = column.

Table 3
Overall optimization constraints of conventional distillation.

<table>
<thead>
<tr>
<th></th>
<th>Column-1 (Col-1)</th>
<th>Column-2 (Col-2)</th>
<th>Column-3 (Col-3)</th>
<th>Column-4 (Col-4)</th>
<th>Column-5 (Col-5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O flow on the top</td>
<td>279.99 kg h</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass fraction of HEP</td>
<td>&gt;99.9 wt%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bottom temperature</td>
<td>&lt; 188.9 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass fraction of DMA</td>
<td>&gt;99.9 wt%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bottom temperature</td>
<td></td>
<td>&lt; MPS temperature</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass fraction of DGMME</td>
<td>&gt;99.9 wt%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bottom temperature</td>
<td></td>
<td>&lt; HPS temperature</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass fraction of NMP</td>
<td>&gt;99.9 wt%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bottom temperature</td>
<td></td>
<td>&lt; HPS temperature</td>
<td></td>
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The case of the waste solvent disposal plant, CO2 emissions were calculated based on the amount of the NG consumption according to the heat of combustion (kJ mol$^{-1}$) of the wind turbine and solar PV, respectively (Nugent and Sovacool, 2014). In conclusion, the waste solvent disposal process without recovery costs 195,234,573 $y^{-1}$. Total annual energy consumption and CO2 emissions for combusting waste solvent using NG as a fuel are shown in Table 6. The most energy consumption for this waste solvent disposal is to dispose of 1,949,407 kg y$^{-1}$ of HEP that emit the most CO2 as 4626 tCO2 y$^{-1}$. As the result, total CO2 emissions of the waste solvent disposal plant plunge to 10,087 tCO2 y$^{-1}$.

### 4.1. Waste solvent disposal process

Economic analysis of the waste solvent disposal process was calculated by total mass flow rate of waste solvent. CAPEX and OPEX of the waste solvent disposal process without recovery are shown in Table 5. CAPEX of the waste solvent disposal plant was calculated using the equation based on mass flow rate in Table 1. The CAPEX result is 689,960 $y^{-1}$. In the case of the without recovery process, 720 kg h$^{-1}$ of waste solvent should be treated, and lifespan of the plant was estimated as 30 y. OPEX was calculated into two different cases as the annualized disposal cost and annualized material purchase cost of each component—the results of the calculations were 729,920 and 193,814,694 $y^{-1}$, respectively. In conclusion, the waste solvent disposal process without recovery costs 195,234,573 $y^{-1}$.

Total annual energy consumption and CO2 emissions for combusting waste solvent using NG as a fuel are shown in Table 6. The most energy consumption for this waste solvent disposal is to dispose of 1,949,407 kg y$^{-1}$ of HEP that emit the most CO2 as 4626 tCO2 y$^{-1}$. As the result, total CO2 emissions of the waste solvent disposal plant plunge to 10,087 tCO2 y$^{-1}$.

### 4.2. Waste solvent recovery process

There are four different zeotropic distillation columns sequences to recover waste solvent as shown in Fig. 2 and the TAC of each sequence was calculated to figure out the most economical process. TACs were calculated as 631,516, 1,089,337, 563,749, and 565,131 $y^{-1}$ to operate four sequence types of distillation column sequences—direct, indirect, modified, and middle split-sequence. As the result, TAC applied modified sequence was required the lowest cost. The detailed information on each sequence of CAPEX and OPEX is shown in Table SI-1.

The complete design for recovery of waste solvent is illustrated in Fig. 6. There are modified DS of distillation columns for separating water, HEP, and DMA and ED columns (Col-4 and -5) for separating DGMME and NMP by using glycol as separation solvent.

The column performance and reboilers duty installed in two different ED columns are influenced by solvent temperature which can be adjusted.
by the Cooler in Fig. 6. To minimize the total heat duty of reboilers, sensitivity analysis was conducted at a Cooler temperature at 100–200 °C of the temperature range. The temperature of a Cooler in the complete process was determined by using the design specification of Aspen Plus V11, which automatically searches for the lowest energy possible for any independent variable of sensitivity. As the result of the sensitivity analysis, temperature of the Cooler was determined as 163 °C to obtain lowest total reboiler duty. Detail result is shown in Fig. 7.

The environmental impacts of the process configurations for waste solvent recovery were compared. The main CO2 generation equipment, i.e., steam reboilers, was selected, and then the annualized CO2 emissions of each piece of equipment were calculated using a mathematical model. The recovery process also shows lower CO2 emissions even though using NG as an energy source. When heat duty for the operating process was applied for 100 % NG, wind turbine, and solar PV, annualized CO2 emissions are shown in Table 7. The modified sequence process emitted the lowest CO2 as 1960 tCO2 y⁻¹ in the case of the total heat duty supplied by NG. Therefore, in sum of the results from economic and environmental analysis, the modified sequence was appropriate in this study.

TAC of heat duty from 100 % of NG, wind turbine, and solar PV was calculated to compare with economic feasibility, and results were assumed as 2,635,250, 1,301,953, and 2,696,017 $ y⁻¹, respectively. The completed recovery process shows bold benefit compared to the process without recovery due to the cost associated with disposal by incinerator and solvent purchasing. Waste management and material purchase cost saving are important output because solvent recovery reduce the purchase cost of important solvents. In addition, annualized CO2 emissions from heat duty for 100 % of NG, wind turbine, and solar PV were 2320, 409, and 599 tCO2 y⁻¹, respectively. However, among energy sources use for waste solvent recovery, the annual cost saving of 100 % solar PV based-power is the lowest.

4.3. Integrating renewable energy to waste solvent recovery system

Economic and environmental analyses of the process, supplying heat duty by the combination of natural gas and renewable energy, were conducted. As noted earlier, the installation location is limited, and renewable energy plants require a sufficient area of land to stably supply heat duty due to the intermittency characteristic. Further, the economic analysis indicates the utility cost of 100 % solar PV use is higher than conventional energy. Therefore, combining the NG and renewable energy to supply distillation reboiler duty can be expected to reduce CO2 emissions and stabilize the energy supply. The sensitivity analysis for the annualized cost-saving and CO2 emissions according to the ratio of the combination of NG are illustrated in Fig. 8. The sudden fluctuation of values due to the capacity of wind turbines and solar PV is a notable feature in the figure. As mentioned earlier, the larger capacity of the wind turbine and solar PV were determined due to the variability feature of renewable energy. Therefore, annual saving cost and CO2 emissions become suddenly changed as the proportion of each energy source changed.

In this study, excepting supplied heat duty by the NG, renewable energy supplied heat at the same rate for the heat duty through two methods which are the wind turbine and solar PV. As the result, using 100 % renewable energy (50 % wind turbine + 50 % solar PV) can be expected to have the 192,538,557 $ y⁻¹, respectively. The completed recovery process shows bold benefit compared to the process without recovery due to the cost associated with disposal by incinerator and solvent purchasing. Waste management and material purchase cost saving are important output because solvent recovery reduce the purchase cost of important solvents. In addition, annualized CO2 emissions from heat duty for 100 % of NG, wind turbine, and solar PV were 2320, 409, and 599 tCO2 y⁻¹, respectively.

Table 7

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Direct sequence</th>
<th>Indirect sequence</th>
<th>Modified sequence</th>
<th>Middle split</th>
<th>Extractive distillation</th>
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<tr>
<td>Total CAPEX</td>
<td>159,752</td>
<td>239,763</td>
<td>160,955</td>
<td>180,926</td>
<td>114,686</td>
</tr>
<tr>
<td>Total OPEX (steam from 100 % NG)</td>
<td>296,792</td>
<td>580,704</td>
<td>227,485</td>
<td>183,670</td>
<td>32,778</td>
</tr>
<tr>
<td>Total heat duty/kW</td>
<td>1271.4</td>
<td>5136.7</td>
<td>786.5</td>
<td>1061.3</td>
<td>114.5</td>
</tr>
<tr>
<td>Annualized CO2 emissions/CO2 y⁻¹</td>
<td>- NG 3168</td>
<td>12.798</td>
<td>1960</td>
<td>2644</td>
<td>360</td>
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<tr>
<td></td>
<td>- Wind turbine 546</td>
<td>1500</td>
<td>546</td>
<td>546</td>
<td>136</td>
</tr>
<tr>
<td></td>
<td>- Solar PV 798</td>
<td>2196</td>
<td>798</td>
<td>798</td>
<td>200</td>
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</table>

Fig. 6. Process flow diagram of the completed recovery process. T = temperature, P = Pressure.

Fig. 7. Sensitivity analysis result for the cooler temperature.
Fig. 8. Sensitivity result of annualized cost-saving and CO2 emissions for combination of NG-based power and renewable energy for utilities.

The lowest CO2 emissions with high-cost savings. The highest annualized cost saving with additional CO2 release was in the range of 37% NG share to renewable energy. At this share range, CO2 emission is about 1071.5 tCO2 yr⁻¹, or almost half the amount of 100% NG use or around 89.4% less amount compared to carbon emission by waste disposal. Considering renewable energy intermittent for the utility source, the maximum NG share to renewable energy for the utility is at 37% which still covers considerable CO2 reduction and the highest cost saving.

5. Conclusions

Waste solvent recovery by distillation demonstrates viable option and shows bold advantage compared to waste disposal. Without using renewable energy, the use of steam from NG-based power shows lower TAC and CO2 emissions compared to the waste disposal process. The main cost saving is from material reclamation which reduces solvent purchasing. The amount of CO2 emission is 2320 tCO2 yr⁻¹, which is far lower than the disposal process, 10,087 tCO2 yr⁻¹. When wind turbine and solar PV based-power is used to supply electricity for the electric boiler, the recovery process exhibits extremely low CO2 emissions by 409, and 599 tCO2 yr⁻¹, respectively. However, the economic advantage of 100% of renewable energy is not always the case. The favorable maximum combination for overall cost-saving and environmental benefit only can be achieved with the ratio of 50% wind turbine and solar PV at 37% NG use as the renewable energy back-up. At this share, the highest cost-saving, and 89.4% CO2 reduction compared to waste disposal emission were achieved. This study explicitly demonstrates the favorable share for conventional energy and renewable energy and presents the practical implication of renewable energy integration in the waste solvent recovery.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.sitotenv.2022.156743.

References


