Air Stripping Designs and Reactive Water Purification Processes for the Lunar Surface

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Air stripping designs are considered to reduce the presence of volatile organic compounds in the purified water. Components of the wastewater streams are ranked by Henry’s Law Constant and the suitability of air stripping in the purification of wastewater in terms of component removal is evaluated. Distillation processes are modeled in tandem with air stripping to demonstrate the potential effectiveness and utility of these methods in recycling wastewater on the Moon. Scaling factors for distillation and air stripping columns are presented to account for the difference in the lunar gravitation environment. Commercially available distillation and air stripping units which are considered suitable for Exploration Life Support are presented. The advantages to the various designs are summarized with respect to water purity levels, power consumption, and processing rates.

An evaluation of reactive distillation and air stripping is presented with regards to the reduction of volatile organic compounds in the contaminated water and air. Among the methods presented, an architecture is presented for the evaluation of the simultaneous oxidation of organics in air and water. These and other designs are presented in light of potential improvements in power consumptions and air and water purities for architectures which include catalytic activity integrated into the water processor. In particular, catalytic oxidation of organics may be useful as a tool to remove contaminants that more traditional distillation and/or air stripping columns may not remove. A review of the current leading edge at the commercial level and at the research frontier in catalytically active materials is presented. Themes and directions from the engineering developments in catalyst design are presented conceptually in light of developments in the nanoscale chemistry of a variety of catalyst materials.

Nomenclature

°C = Degrees Celsius
cm = Centimeter
CO₂ = Carbon Dioxide
EPA = Environmental Protection Agency

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**I. Introduction**

Many designs for water purification feature disposable parts or processes that produce waste. For example, carbon dioxide (CO2) removal with lithium hydroxide is an effective, but not readily regenerable process [1]. The reaction product of CO2 and lithium hydroxide is lithium carbonate, which makes this process non-regenerable. Biocatalytic processes are also less than favorable due to their high maintenance requirements. Distillation and air stripping are physico-chemical processes, which are robust and well established. This report evaluates the power consumptions, component removal feasibility, and scaling factors for the purification of wastewater on the lunar surface through these processes.

**II. Air Stripping**

![Diagram of air stripping process]

- Water sprayed over packing material
- Air rises through packing material
- Water trickles to bottom
- Air blower
- Clean water
- Pump
- Polluted water
- Gas and air collect
- Air stripper

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Steam strippers [3] and air strippers [4] (Figure 1) are common designs for the treatment of wastewater produced by industries for the removal of pharmaceutical contaminants [5], oil-related contaminants [6], VOCs in contaminated soil [7], and urine wastewater [8]. Because catalytic oxidation [9] consumes relatively little power and can be effective in removing contaminants in the gas and liquid phases, air stripping and steam stripping can both be considered. This report takes into account air stripping. Tables M and N show the components of the combined wastewater streams and their Henry’s law constants when available.

### Table A: Mixture of Humidity Concentrate and Urine Wastewater

Note: A crew of four is anticipated to produce 6.0 kilograms (kg) of urine and 7.8 kg of humidity condensate per day. To this amount, 33.9 grams (g) of oxone and 14.7 g of sulfuric acid is added. It is estimated that the components with the light blue background may be removed with air stripping. The remaining components feature constants in accordance with Henry’s law, which are too high for consideration.

<table>
<thead>
<tr>
<th>Component (alcohols written in orange, organic acids written in pink)</th>
<th>$-\frac{d\ln K_H}{d(1/T)}$ [K]</th>
<th>Component Conc. HCA-Blue + Urine-Green [mg/L]</th>
<th>Urine+HC Total initial conc.</th>
<th>% Total Comp</th>
<th>Target Conc. [mg/L] EPA</th>
<th>MCL written in Violet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon disulfide</td>
<td>0.031</td>
<td>2800 [31]</td>
<td>0.785</td>
<td>3.936</td>
<td>21.1</td>
<td>0.044</td>
</tr>
<tr>
<td>Phenol</td>
<td>0.055</td>
<td>2900 [32]</td>
<td>2.92</td>
<td>126</td>
<td>23.5</td>
<td>0.017</td>
</tr>
<tr>
<td>Dibutyl amine</td>
<td>0.078</td>
<td>4800 [33]</td>
<td>0.566</td>
<td>0.317</td>
<td>0.032</td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>11</td>
<td>600 [34]</td>
<td>0.348</td>
<td>0.195</td>
<td>0.020</td>
<td></td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>19</td>
<td>600 [35]</td>
<td>18.04 + 468</td>
<td>211</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Ammonia</td>
<td>58</td>
<td>4100 [36]</td>
<td>0.937</td>
<td>15.9</td>
<td>20.7</td>
<td>0.049</td>
</tr>
<tr>
<td>1-butanol</td>
<td>$1.3 \times 10^9$</td>
<td>7200 [35]</td>
<td>46.3</td>
<td>25.9</td>
<td>0.046</td>
<td></td>
</tr>
<tr>
<td>2-propanol</td>
<td>$1.3 \times 10^9$</td>
<td>7500 [35]</td>
<td>8.18 + 1.5</td>
<td>5.58</td>
<td>6.4</td>
<td>0.0025</td>
</tr>
<tr>
<td>Ethanol</td>
<td>$1.9 \times 10^9$</td>
<td>6600 [35]</td>
<td>18.10 + 1.5</td>
<td>5.58</td>
<td>6.4</td>
<td>0.0025</td>
</tr>
<tr>
<td>Methanol</td>
<td>220</td>
<td>5200 [35]</td>
<td>3.737 + 5.133</td>
<td>4.45</td>
<td>0.63</td>
<td>0.0042</td>
</tr>
<tr>
<td>Isobutyric acid</td>
<td>1100</td>
<td>[37]</td>
<td>0.32</td>
<td>0.179</td>
<td>0.019</td>
<td>0.000009</td>
</tr>
<tr>
<td>Diethylphthalate</td>
<td>1200</td>
<td>5600 [38]</td>
<td>0.499</td>
<td>0.279</td>
<td>0.006</td>
<td></td>
</tr>
<tr>
<td>Pentanoic acid</td>
<td>2200</td>
<td>6900 [39]</td>
<td>0.441</td>
<td>0.247</td>
<td>0.026</td>
<td>0.00013</td>
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<tr>
<td>Acetic acid</td>
<td>4100</td>
<td>6300 [40]</td>
<td>14.61</td>
<td>8.18</td>
<td>0.66</td>
<td>0.0043</td>
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<tr>
<td>Butanoic acid</td>
<td>4700</td>
<td>[37]</td>
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<td>0.207</td>
<td>0.022</td>
<td>0.00011</td>
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<tr>
<td>Formaldehyde</td>
<td>$7.0 \times 10^9$</td>
<td>6400 [30]</td>
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<td>0.046</td>
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<tr>
<td>Formic acid</td>
<td>$8.9 \times 10^9$</td>
<td>6100 [38]</td>
<td>7.239 + 64</td>
<td>31.57</td>
<td>3.3</td>
<td>0.017</td>
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<tr>
<td>1,2-propanediol</td>
<td>$6.0 \times 10^9$</td>
<td>[41]</td>
<td>45.23</td>
<td>25.33</td>
<td>4.7</td>
<td>0.024</td>
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<tr>
<td>Ethylene glycol</td>
<td>$4.0 \times 10^9$</td>
<td>[42]</td>
<td>10.22</td>
<td>5.73</td>
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<td>Oxalic acid</td>
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<td>[41]</td>
<td>27</td>
<td>15.12</td>
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<tr>
<td>Citric acid</td>
<td>$3.0 \times 10^9$</td>
<td>[41]</td>
<td>793</td>
<td>1.341</td>
<td>0.036</td>
<td>0.00016</td>
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<tr>
<td>4-hydroxy-4-methyl-2-pentanone</td>
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<td>n/a</td>
<td>1.247</td>
<td>0.698</td>
<td>0.070</td>
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<tr>
<td>2-butoxyethoxyethanol</td>
<td>n/a</td>
<td>n/a</td>
<td>1.13</td>
<td>0.6328</td>
<td>0.12</td>
<td>0.00059</td>
</tr>
</tbody>
</table>
Note: A crew of four is anticipated to produce 6.0 kg of urine and 7.8 kg of humidity condensate per day. To this amount, 33.9 g of oxone and 14.7 g of sulfuric acid is added. The strippable components are highlighted in this table.

### HCA + Urine Wastewater Model Components (Cont.)

<table>
<thead>
<tr>
<th>Component (alcohols written in orange, organic acids written in pink)</th>
<th>Error! Bookmark not defined.Henry's Law Constants Ref</th>
<th>Component Conc. (HCA-Blue + Urine-Green) [mg/L]</th>
<th>Urine+HC Total initial conc.</th>
<th>% Total Comp.</th>
<th>Component Target Conc. [mg/L]</th>
<th>EPA MCL written in Violet</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-acetyl morpholine</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>1.092</td>
<td>0.612</td>
<td>0.061</td>
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<tr>
<td>Caprolactam</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>11.83</td>
<td>6.62</td>
<td>0.066</td>
</tr>
<tr>
<td>2-butoxyethanol</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>0.803</td>
<td>0.450</td>
<td>0.084</td>
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<tr>
<td>Glycolic acid</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>10.19</td>
<td>5.71</td>
<td>0.60</td>
</tr>
<tr>
<td>N,N-dimethylformamide</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>0.606</td>
<td>0.340</td>
<td>0.034</td>
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<tr>
<td>Propanoic acid</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>3.916</td>
<td>2.19</td>
<td>0.23</td>
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<tr>
<td>Morpholine</td>
<td>n/a</td>
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<td>n/a</td>
<td>0.384</td>
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<td>0.022</td>
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<tr>
<td>2-ethoxyethanol</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>0.504</td>
<td>0.282</td>
<td>0.053</td>
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<tr>
<td>Lactic acid</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>369 + 0.32</td>
<td>159</td>
<td>16.7</td>
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<tr>
<td>2-ethyl Hexanoic Acid</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>0.37</td>
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<td>0.021</td>
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<tr>
<td>2-2-ethoxyethoxyethanol</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>0.354</td>
<td>0.198</td>
<td>0.037</td>
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<tr>
<td>Hexanoic Acid</td>
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<td>n/a</td>
<td>n/a</td>
<td>0.582</td>
<td>0.326</td>
<td>0.034</td>
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<td>1-methyl-2-pyrrolidinone</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>0.339</td>
<td>0.190</td>
<td>0.019</td>
</tr>
<tr>
<td>Nonanoic acid</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>0.335</td>
<td>0.188</td>
<td>0.019</td>
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<td>Taurine</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>523</td>
<td>225</td>
<td>23.6</td>
</tr>
<tr>
<td>Histidine</td>
<td>n/a</td>
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<td>n/a</td>
<td>116.9</td>
<td>50.3</td>
<td>5.3</td>
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<tr>
<td>L-glutamic acid</td>
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<td>n/a</td>
<td>n/a</td>
<td>412</td>
<td>177</td>
<td>18.6</td>
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<tr>
<td>Hippuric acid</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>171.1</td>
<td>73.6</td>
<td>7.7</td>
</tr>
<tr>
<td>α-D-glucose</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>793</td>
<td>341</td>
<td>64</td>
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<tr>
<td>Creatinine</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>1787</td>
<td>768</td>
<td>76</td>
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<tr>
<td>4-ethyl morpholine</td>
<td>n/a</td>
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<td>n/a</td>
<td>2.516</td>
<td>1.41</td>
<td>0.14</td>
</tr>
<tr>
<td>Urea</td>
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<td>n/a</td>
<td>n/a</td>
<td>13400 +</td>
<td>5760</td>
<td>576</td>
</tr>
<tr>
<td>Uric acid</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>471</td>
<td>203</td>
<td>21</td>
</tr>
</tbody>
</table>

1.1 Design of an Ammonia Stripper – 99.8 Percent Removal of Ammonia

1.1.1 Flow Rates and Column Diameter

The modeling of the distillation of urine and humidity condensate was studied at a flow rate of 20 liters per hour (L/hour). For this reason, the wastewater flow rate through a stripper will be studied at the same flow rate. The temperature of the wastewater is estimated as 40 °C. The first of the stripper designs examined was an ammonia stripper. Stripping has previously been used for the recovery of ammonia from urine [10]. Generally, an alkaline pH is preferred for ammonia stripping [11]. While the pH of the pretreated urine and humidity condensates is particularly acidic prior to distillation, the pH could be increased in the distillate by systematic addition of lime. At pH 10 and at 40 °C, 95 percent of ammonia is present as the gas. These conditions allow for successful removal of ammonia from water with efficiency.

In summary, a column design is specified with the dimensions of 1.2 meters (m) in height and 1.7 cm in diameter. The gas pressure drop is 1630 pascals per meter (Pa/m). The gas flow rate is 0.508 kilograms per square meter (kg/m²). The liquid flow rate is 20 L/day. The stripping factor is 2. The packing is 6.35-mm diameter Raschig rings.

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The packing factor for 6.35-mm ceramic Raschig rings is 1600 [12]. The dimensionless Henry’s law constant for ammonia at 40 °C, \( H \), is 0.001436 [46]. The minimum air-to-water ratio corresponds to the condition when the effluent gas from the stripper is in equilibrium with the incoming water. It is represented as follows:

\[
\left( \frac{Q_a}{Q} \right)_{\text{min}} = \frac{C_0 - C_e}{H C_0}
\]

The influent concentration of a mixed stream of urine and humidity condensate, as described in Appendix A, is 211 mg/L. The target concentration is 0.5 mg/L. In the equation above, the influent concentration is \( C_0 \) and the effluent (or target concentration is \( C_e \)). The minimum air-to-water ratio under these conditions is calculated to be 695.

In the next part of the design study, the cross-sectional area for the packed tower is determined. In order to calculate this value, the actual air-to-water ratio (taking into account the stripping factor), the air pressure drop at half the value for flooding, the gas loading rate, and the liquid loading rate are required.

The air-to-water ratio was calculated with the following equation:

\[
\left( \frac{Q_a}{Q} \right)_{\text{min}} = \frac{S}{H_{\text{ammonia}}}
\]

Where \( S \) is the stripping factor (in this case, 2) and \( H_{\text{ammonia}} \) is the dimensionless Henry’s law constant for ammonia at 40 °C. The air-to-water ratio is calculated to be 1390.

Raschig rings with a diameter of 6.35 mm are reported to have a pressure drop of 4 inches of water per foot at flooding [13a]. The pressure drop used will be half of that value (1630 Pa/m²/m). See Figure 29.
In order to determine the gas loading rate, the x-value for the Eckert gas pressure drop (Figure 2) is calculated.

\[ \frac{G_m}{L_m} = \left( \frac{Q_s}{Q} \right) \left( \frac{\rho_s}{\rho_l} \right) = (1390) \left( \frac{1.13 \text{ kg (air (40°C))}}{m^3} \right) \left( \frac{992.2 \text{ kg (water (40°C))}}{m^3} \right) = 1.59 \frac{\text{kg (air)}}{\text{kg (water)}} \]

Equation (3)

\[ \rho_s = 1.13 \frac{\text{kg (air (40°C))}}{m^3} \] (Density of air at 40°C)

\[ \rho_l = 992.2 \frac{\text{kg (water (40°C))}}{m^3} \] (Density of water at 40°C)

\[ x = \frac{L_m}{G_m} \left( \frac{\rho_s}{\rho_l - \rho_s} \right)^{0.5} \]

Equation (4)
\[
    x = \frac{1}{1.59} \frac{\text{kg(water)}}{\text{kg(air)}} \left( \frac{1.13 \cdot \text{kg(air(40\degree C))}}{m^3} - \frac{992.2 \cdot \text{kg(water(40\degree C))}}{m^3} - \frac{1.13 \cdot \text{kg(air(40\degree C))}}{m^3} \right)^{0.5}
\]

Error! Bookmark not defined. \( x = 0.0212 \)

It is estimated that the corresponding y-value to this x in Figure 29 is about 0.15 for a 2-in. water pressure drop. With this value in hand, the gas loading rate, \( G_m \), is calculated.

\[
    G_m = \left( \frac{y \rho_g (\rho_l - \rho_g)}{C_f \mu_l} \right)^{0.5}
\]

Equation (5)

\( C_f = 1600 \) (Packing Factor)

\( \mu_l = 0.653 \times 10^{-3} \frac{\text{kg}}{m \cdot s} \) (viscosity of water at 40\degree C)

\( G_m = 0.468 \frac{\text{kg}}{m^2 \cdot s} \)

The water loading rate, \( L_m \), is now calculated from the relation:

\[
    L_m = \frac{G_m}{Q (\rho_g / \rho_l)}
\]

Equation (6)

\( L_m = 0.296 \frac{\text{kg}}{m^2} \)

With the values for the liquid flow rate and the liquid loading rate, the column area is now determined as:

\[
    A = \frac{Q \rho_l}{L_m}
\]

Equation (8)

\( A = 9.1 \times 10^{-4} m^2 \)

The diameter of the column is therefore 3.4 cm.

3.1.2 Liquid Phase Mass Transfer Coefficients of the Ammonia Stripper

In order to determine the length of the column, the mass transfer coefficients must be determined.

The liquid phase mass transfer coefficient is calculated from the wetted surface area of the column:
\[ a_w = a_1 \left( 1 - e^{-1.45 \left( \frac{\sigma_c}{\sigma} \right)^{0.75} \left( \frac{Re}{Fr} \right)^{0.3} \left( \frac{We}{Pr} \right)^{0.1}} \right) \]  
Equation (9)

\[ \text{Re} = \frac{L_m}{\alpha_1 \mu_l} \quad \text{Reynolds number} \quad \text{Equation (10)} \]

\[ Fr = \frac{(L_m)^2 a_1}{(\rho_l)^2 g} \quad \text{Froude number} \quad \text{Equation (11)} \]

\[ We = \frac{(L_m)^2}{\rho_l a_1 \sigma} \quad \text{Weber number} \quad \text{Equation (11)} \]

\[ a_w = 106 \frac{m^2}{m^3} \quad \text{The wetted surface area for this column design} \]

Liquid-phase mass transfer coefficient:

\[ k_l = 0.0051 \left( \frac{L_m}{a_w \mu_l} \right)^{2/3} \left( \frac{\mu_l}{\rho_l D_l} \right)^{-0.5} \left( a_1 d_p \right)^{0.4} \left( \frac{\rho_l}{\mu_l g} \right)^{-1/3} \]  
Equation (12)

\[ D_l = \frac{13.26 \times 10^{-5}}{\left( \frac{\mu_w}{\rho_l} \right)^{0.14} \left( \frac{V_b}{\mu_l} \right)^{0.589}} \]  
Equation (13)

\[ V_b \] is the molar volume of ammonia at the boiling point. This is determined through the LeBas method to be 26.7 cubic centimeters (cm³)/mole.

The viscosity of water at 40 °C, \( \mu_w \), is 0.563 cP.

\[ D_l = 3.11 \times 10^{-5} \frac{cm^2}{s} \]

The liquid phase mass transfer coefficient, \( k_l \), is calculated as \( 8.4 \times 10^{-5} \) meters per second (m/s).

### 3.1.3 Gas Phase Mass Transfer Coefficients for the Ammonia Stripper

In order to calculate the gas phase mass transfer coefficients, the gas phase diffusion coefficient for ammonia must be determined at 40 °C. The Wilke-Lee modification of the Hirsch-Felder-Bird-Spottz correlation is used for this:


\[
D_g = \left( \frac{1.084 - 0.249}{M_{\text{ammonia}}} + \frac{1}{M_{\text{air}}} \right)^{T^{1.5}} \left( \frac{1}{M_{\text{A}}} - \frac{1}{M_{\text{air}}} \right)
\]

Equation (14)

Molecular separation at collision for ammonia:

\[
\frac{1}{2} \left( \frac{L}{mol} \right)^{1/3} = 0.353 \cdot \text{nm}
\]

Equation (15)

Molecular separation at collision for air:

\[
r_{\text{air}} = 0.3711 \cdot \text{nm}
\]

Molecular separation at collision for ammonia and air:

\[
r_{\text{ammonia-air}} = \frac{1}{2} \left( r_{\text{ammonia}} + r_{\text{air}} \right)
\]

Equation (16)

\[
r_{\text{ammonia-air}} = 0.362 \cdot \text{nm}
\]

Energy of molecular attraction for ammonia:

\[
\frac{\varepsilon_{\text{ammonia}}}{k} = 1.21 \cdot T_{\text{boiling, ammonia}}
\]

Equation (17)

\[
k = 1.3804 \times 10^{-16} \frac{\text{g} \cdot \text{cm}^2}{\text{s}^2 \cdot \text{K}}
\]

Boltzmann’s constant

\[
T_{\text{boiling, ammonia}} = 239.8 \cdot \text{K}
\]

\[
\frac{\varepsilon_{\text{ammonia}}}{k} = 290
\]

Energy of molecular attraction for air:

\[
\frac{\varepsilon_{\text{air}}}{k} = 78.6
\]

\[
\frac{\varepsilon_{\text{air-ammonia}}}{k} = \sqrt{(290)(78.6)} = 151
\]

Collision function:
\[
\frac{kT}{e_{\text{air-ammonia}}} = \frac{T}{e_{\text{air-ammonia}}} = \frac{313}{151} = 2.07 \quad \text{Equation (18)}
\]

\[
ee = \log_{10}\left(\frac{kT}{e_{\text{air-ammonia}}}\right) = 0.316 \quad \text{Equation (19)}
\]

\[
\xi = \left(\frac{0.14329 - 0.48343(ee) + 0.1939(ee)^2 + 0.13612ee^3 - 0.20578ee^4 + 0.083899ee^5 - 0.011491ee^6}{0.14329 - 0.48343(ee) + 0.1939(ee)^2 + 0.13612ee^3 - 0.20578ee^4 + 0.083899ee^5 - 0.011491ee^6}\right) \quad \text{Equation (20)}
\]

\[
\xi = -0.274
\]

\[
f\left(\frac{kT}{e_{\text{air-ammonia}}}\right) = 10^\xi = 0.532 \quad \text{Equation (21)}
\]

\[
D_g = \left(\frac{1.084 - 0.249}{M_{\text{ammonia}}} + \frac{1}{M_{\text{air}}}\right)^{T^{1.5}} \left(\frac{1}{M_{\text{ammonia}}} - \frac{1}{M_{\text{air}}}\right)
\]

\[
P_r \left(r_{\text{ammonia-air}}\right)^2 f\left(\frac{kT}{e_{\text{ammonia-air}}}\right) \quad \text{Equation (22)}
\]

\[
D_g = 2.41 \cdot \frac{cm^2}{s} \text{ at 0.1 bar}
\]

### 3.1.4 Gas Phase Mass Transfer Coefficient

\[
k_g = 5.23(a_tD_g)^{0.7}\left(\frac{G_m}{a_t\mu_g}\right)^{(1/3)} \quad \text{Equation (23)}
\]

\[
k_g = 0.22 \frac{m}{s}
\]

### 3.1.5 Overall Mass Transfer Rate Constant for the Ammonia Stripper

\[
\frac{1}{K_{La}} = \frac{1}{k_g a} \frac{1}{k_g a_n H} = \frac{1}{(8.4 \times 10^{-5})(108)} + \frac{1}{(0.22)(108)(0.001436)} = 137 \cdot s \quad \text{Equation (24)}
\]

\[
K_{La} = 0.00730 \cdot s^{-1}
\]

### 3.1.6 Length of the Ammonia Stripper Column

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\[ L = \frac{Q}{AK_La} \left( \frac{S}{S-1} \right) \ln \left( 1 + \frac{C_0}{C_{ro}} \left( \frac{S-1}{S} \right) \right) \] 
Equation (25)

\[ L = 2 \times \frac{2.3 \times 10^{-7} \cdot m}{9.1 \times 10^{-4} \times 0.00730} \ln \left( \frac{1 + 0.5}{2} \right) = 0.37 \cdot m \]

It has been demonstrated that removal of ammonia may be achieved at the target levels described in the beginning of this report for a column, which is about 1 ft in height and 0.7 in. in diameter. This design is compatible with and requires basic wastewater. One architecture, which may be worth considering, is to have an ammonia stripper upstream from a distillation column. In this way, ammonia can be removed along with other VOCs initially and then organic acids (such as acetic acid) may be removed with the brine water at the distillation column.

3.2 Design of a Methanol Stripper - 99.9 Percent Removal of Methanol

The Henry’s law constant for methanol in 0.97 mole per kilogram (mol/kg) [58 grams per liter (g/L)] of sodium chloride (NaCl) has been determined experimentally to be 0.29 \pm 0.04. The amount of salt in the mixed humidity condensate is about 11 g/L. In the absence of a closer Henry’s coefficient for the salinity of the solution, this value is used as an approximation for the actual conditions.

As with the ammonia stripper previously described, the liquid flow rate is defined as 20 L/hour. The temperature of the wastewater is estimated as 40 °C. The pH is not as great a concern for the removal of methanol so it can be either acidic or basic. As will be discussed later, this flexibility enables the removal of methanol or a volatile organic (non-organic acid) of greater or equal Henry’s law constant to be removed before or after distillation depending on the chosen water purification architecture.

The initial concentration of methanol in the wastewater is 4.45 mg/L. The target concentration is 0.0042 mg/L.

The minimum air-to-water ratio is therefore:

\[ \left( \frac{Q_a}{Q} \right)_{\min} = \frac{C_0 - C_e}{HC_e} = 5950 \]

With a stripping factor, S, of 2. The air-to-water ratio is:

\[ \left( \frac{Q_a}{Q} \right) = \frac{S}{H_{\text{methanol}}} = 11900 \]
As with the methanol stripper, Raschig rings with a diameter of 6.35 mm are chosen for the methanol stripper. The same gas pressure drop is used (1630 Pa/m.m).

In order to determine the gas loading rate, the x-value for the Eckert gas pressure drop is calculated.

\[
G_m = \left( \frac{Q_g}{Q} \right) \left( \frac{\rho_g}{\rho_l} \right) = (11900) \left( \frac{1.13 \frac{kg(air)(40\degree C)}{m^3}}{992.2 \frac{kg(water)(40\degree C)}{m^3}} \right) = 13.6 \frac{kg(air)}{kg(water)}
\]

\[
\rho_g = 1.13 \frac{kg(air)(40\degree C)}{m^3} \quad \text{(Density of air at 40\degree C)}
\]

\[
\rho_l = 992.2 \frac{kg(water)(40\degree C)}{m^3} \quad \text{(Density of water at 40\degree C)}
\]

\[
x = \frac{L_m}{G_m} \left( \frac{\rho_g}{\rho_l - \rho_g} \right)^{0.5} = 1 \frac{kg(water)}{13.6 \frac{kg(air)}{m^3}} \left( \frac{1.13 \frac{kg(air)(40\degree C)}{m^3}}{992.2 \frac{kg(water)(40\degree C)}{m^3}} - 1.13 \frac{kg(air)(40\degree C)}{m^3} \right)^{0.5}
\]

Error! Bookmark not defined. \( x = 0.00248 \)

It is estimated that the corresponding y-value to this x in Figure 29 would be about 0.17 for a 2-in. water pressure drop. With this value in hand, the gas loading rate, \( G_m \), is calculated.

\[
G_m = \left( \frac{y \rho_g (\rho_l - \rho_g)}{C_f \mu_l} \right)^{0.5} = \left( \frac{0.17 \cdot 1.13(992.2 - 1.13)}{1600 \cdot (0.653 \times 10^{-3})^{0.1}} \right)^{0.5} = 0.498
\]

\( C_f = 1600 \) (packing factor)

\( \mu_l = 0.653 \times 10^{-3} \frac{kg}{m \cdot s} \quad \text{(viscosity of water at 40\degree C)} \)

\( G_m = 0.498 \frac{kg}{m^2 \cdot s} \)

The water loading rate, \( L_m \), is now calculated from the relation:

\[
L_m = \left( \frac{Q_g}{Q} \right) \left( \frac{\rho_g}{\rho_l} \right) = 0.0367
\]
With the values for the liquid flow rate and the liquid loading rate, the column area is now determined as:

\[ A = \frac{Q \rho_L}{L_m} \]

\[ A = 5.4 \times 10^{-4} \, m^2 \]

The diameter of the column is therefore 2.6 cm.

### 3.2.1 Liquid Phase Mass Transfer Coefficients of the Methanol Stripper

In order to determine the length of the column, the mass transfer coefficients must be determined.

The liquid phase mass transfer coefficient is calculated from the wetted surface area of the column and the liquid diffusivity, \( D_L \):

\[ a_w = a_l \left( 1 - e^{-\frac{-1.45 (\frac{\rho_L}{\sigma})^{0.75} (Re)^{0.1} (F^2)^{0.05} (We)^{0.1}}{1}} \right) \]

\[ \text{Re} = \frac{L_m}{a_l \mu_l} \quad \text{Reynolds number} \]

\[ Fr = \frac{(L_m)^2 a_l}{(\rho_l)^2 g} \quad \text{Froude number} \]

\[ We = \frac{(L_m)^2}{\rho_l a_l \sigma} \quad \text{Weber number} \]

\[ a_w = 90.0 \, m^2 \quad \text{The wetted surface area for this column design} \]

\[ k_l = 0.0051 \left( \frac{L_m}{a_w \mu_l} \right)^{2/3} \left( \frac{\mu_l}{\rho_l D_l} \right)^{-0.5} \left( a_w \rho \right)^{0.4} \left( \frac{\rho_l}{\mu_l g} \right)^{-1/3} \quad \text{Liquid-phase mass transfer coefficient} \]

\( D_l \) can be calculated through the Hayduk-Laurie correlation:

\[ D_l = 13.26 \times 10^{-5} \left( \frac{\mu_w}{(L_m)^{14} (V_b)^{0.589}} \right) \]

\( V_b \) is the molar volume of ammonia at the boiling point. This is determined through the LeBas method to be 39.5 cm³/mole.

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The viscosity of water at 40°C, \( \mu_l \), is 0.563 cP.

\[
D_l = 2.93 \times 10^{-5} \frac{\text{cm}^2}{\text{s}}
\]

\[
k_l = 0.0051 \left( \frac{L_m}{a_w \mu_l} \right)^{2/3} \left( \frac{\mu_l}{\rho_l D_l} \right)^{0.5} \left( a_c d_p \right)^{0.4} \left( \frac{\rho_l}{\mu_l g} \right)^{-1/3}
\]

The liquid phase mass transfer coefficient, \( k_l \), is calculated as \( 8.47 \times 10^{-6} \) m/s.

### 3.2.2 Gas-Phase Mass Transfer Coefficients for the Methanol Stripper

In order to calculate the gas-phase mass transfer coefficients, the gas-phase diffusion coefficient for ammonia must be determined at 40°C. The Wilke-Lee modification of the Hirsch-Felder-Bird-Spottz correlation is used for this:

\[
D_g = \left( \frac{1.084 - 0.249}{1} \right) \left( \frac{1}{M_{\text{methanol}}} + \frac{1}{M_{\text{air}}} \right)^{0.5} \left( \frac{1}{M_{\text{methanol}}} - \frac{1}{M_{\text{air}}} \right) \left( \frac{P_T}{r_{\text{methanol-air}}^2 f} \right) \left( \frac{kT}{e_{\text{methanol-air}}} \right)
\]

Molecular separation at collision for methanol:

\[
r_{\text{methanol}} = 1.18 \left( \frac{V_{b,a}}{} \right)^{1/3} = 1.18 \left( 0.0395 \frac{L}{\text{mol}} \right)^{1/3} = 0.402 \cdot \text{nm}
\]

Molecular separation at collision for air:

\[
r_{\text{air}} = 0.3711 \cdot \text{nm}
\]

Molecular separation at collision for ammonia and air:

\[
r_{\text{methanol-air}} = \frac{1}{2} \left( r_{\text{methanol}} + r_{\text{air}} \right)
\]

\[
r_{\text{methanol-air}} = 0.387 \cdot \text{nm}
\]

Energy of molecular attraction for methanol:

\[
\frac{e_{\text{methanol}}}{k} = 1.21 \cdot T_{\text{boiling methanol}}
\]
\[ k = 1.3804 \times 10^{-16} \text{ g} \cdot \text{cm}^2 \text{ s}^{-2} \cdot \text{K} \]  

Boltzmann’s constant

\[ T_{\text{boiling, methanol}} = 337.8 \cdot \text{K} \]

\[ \frac{\varepsilon_{\text{methanol}}}{k} = 409 \]

Energy of molecular attraction for air:

\[ \frac{\varepsilon_{\text{air}}}{k} = 78.6 \]

\[ \frac{\varepsilon_{\text{air-methanol}}}{k} = \sqrt{\frac{\varepsilon_{\text{methanol}}}{k} \times \frac{\varepsilon_{\text{air}}}{k}} = \sqrt{(409)(78.6)} = 179 \]

Collision function:

\[ \frac{kT_{\text{air-methanol}}}{\varepsilon_{\text{air-methanol}}} = \frac{T}{\varepsilon_{\text{air-methanol}}} = \frac{313}{179} = 1.75 \]

\[ \epsilon_{\text{e}} = \log_{10}\left( \frac{kT}{\varepsilon_{\text{air-methanol}}} \right) = 0.243 \]

\[ \xi = (-0.14329 - 0.48343(\epsilon_{\text{e}}) + 0.1939(\epsilon_{\text{e}})^2 + 0.13612\epsilon_{\text{e}}^3 - 0.20578\epsilon_{\text{e}}^4 + 0.083899\epsilon_{\text{e}}^5 - 0.011491\epsilon_{\text{e}}^6) \]

\[ \xi = -0.274 - 0.117 + 0.0145 + 0.001953 - 0.0007172 + 0.000071086 - 0.000002365 = -0.378 \]

\[ f\left( \frac{kT}{\varepsilon_{\text{air-methanol}}} \right) = 10^{\xi} = 0.419 \]

\[ D_g = \left( 1.084 - 0.249 \sqrt{\frac{1}{M_{\text{methanol}}} + \frac{1}{M_{\text{air}}}} \right) (T^{1.5}) \sqrt{\frac{1}{M_{\text{methanol}}} - \frac{1}{M_{\text{air}}}} \]

\[ P_{\text{r}} (r_{\text{methanol-air}})^2 f\left( \frac{kT}{\varepsilon_{\text{methanol-air}}} \right) \]

\[ D_g = \frac{(1.084 - 0.249 \sqrt{0.0657}) (5538) \sqrt{0.0657}}{(10132.5)(0.387)^2(0.419)} = 2.3 \cdot \frac{\text{cm}^2}{\text{s}} \text{ at 0.1 bar} \]
3.2.3 Gas-Phase Mass Transfer Coefficient

\[ k_G = 5.23 \left( \frac{a_i D_g}{a_i \mu_g} \right)^{0.7} \left( \frac{\mu_g}{\rho_g D_g} \right)^{1/3} \left( a_i d_p \right)^{-2} \]

\( \mu_g \) is the air viscosity

\[ k_G = 5.23 \left( \frac{710 \cdot 2.3}{710 \cdot 1.75 \times 10^{-5}} \right)^{0.7} \left( \frac{1.75 \times 10^{-5}}{1.13 \cdot 2.3 \times 10^{-4}} \right)^{1/3} (710 \cdot 0.00635)^{-2} \frac{m}{s} \]

\[ k_G = (5.23)(1633)(13.25)(0.407)(0.0492) = 2270 \frac{m}{s} \]

3.2.4 Overall Mass Transfer Rate Constant for the Methanol Stripper

\[ \frac{1}{K_L a} = \frac{1}{k_i a} + \frac{1}{k_g a_{wH}} = 1310 \cdot s \]

\[ K_L a = 0.00076 \cdot s^{-1} \]

3.2.5 Length of the Methanol Stripper Column

\[ L = \frac{Q}{AK_i a} \left( \frac{S}{S-1} \right) \ln \left( 1 + \frac{C_0}{C_T} \right) \frac{(S-1)}{S} \]

\[ L = 2 \times \frac{2.3 \times 10^{-7} \cdot m}{5.4 \times 10^{-4}} \left( 0.00076 \right) \ln \left( \frac{1 + \frac{4.45}{0.0042}}{2} \right) = 7.0 \cdot m \]

3.3 An Adapted Commercial Air Stripper

All of the companies that were contacted about air stripping of wastewater deal with much larger throughput volumes than are required for purification of wastewater for a four- to seven-person crew. QED Environmental Systems, one of the companies contacted, develops air strippers and is interested in developing an air stripper for these purposes. The vendor for this company has made some calculations for the power requirements for the removal of ethanol and ammonia from wastewater. These are shown in Figure 3. One of the features of this air stripper is that it is easy to clean. One problem with air stripping wastewater is the fouling of the equipment. QED Environmental Systems uses a sliding tray technology, so that the trays in the unit can be removed periodically for cleaning. While a packed column is generally preferable for smaller-scale processing, this feature indicates easy maintenance, which may make a tray column preferable.
1. Water Results

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Influent (ppb)</th>
<th>Target (ppb)</th>
<th>4-Tray Results (ppb)</th>
<th>4-Tray %Removal</th>
<th>6-Tray Results (ppb)</th>
<th>6-Tray %Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>ammonia</td>
<td>18000</td>
<td>0</td>
<td>6.1</td>
<td>99.966</td>
<td>&lt; 1</td>
<td>100.000</td>
</tr>
<tr>
<td>ethyl alcohol</td>
<td>8000</td>
<td>0</td>
<td>4.1</td>
<td>99.949</td>
<td>&lt; 1</td>
<td>100.000</td>
</tr>
</tbody>
</table>

Air Temp: 40 °C  
Flow: 0.4 lpm

Water Temp: 40 °C

Stripper: EZ-Stacker 2.xp - Click for details

Stripper Air Flow: 3.96 m3/min

Figure 3: Ammonia Readily Removed by the Air Stripper Design by QED Environmental Systems can custom design an air stripper based on their plastic E-Z Stacker 2.XP model stripper. This custom design would process 5.4 liters of wastewater per hour. The blower required for operation consumes an average of 500 W. The temperature for operation is 40 °C. The calculations were determined for 1 atmosphere of pressure. With an influent concentration of 10 parts per million (ppm) ethanol, the system can get the concentration of ethanol below parts per billion (ppb) levels. A picture of the basic unit produced by QED Environmental Systems is provided in Figure 4. In Figure 5 is the overall design of the EZ Stacker. The dimensions of the custom unit are shown in Figure 6. These dimensions are for operation on the Earth surface.

Figure 4. The QED Environmental Systems, Inc. EZ Stacker 2.XP.
Figure 5. QED Environmental Systems EZ Stacker basic design.

Note: The dimensions in Figure 5 do not apply to the custom design. Figure 5 presents the basic design of the unit which can be customized.
Figure 6. Dimensions of the custom design of the QED Environmental EZ Stacker provided by Dave Fischer, Vice President of Technology at QED Environmental Systems, Inc. This stainless steel, four tray EZ stacker design has an estimated dry weight of 200 kg.
4.0 Distillation and Air Stripping in Tandem

Figure 7: Outline for the Model of a Gravity-Based Purification System

Note: The feed stream is used as cooling water for the condenser of the still. The heated feed is sent to distill. The distillate is then passed through an air stripper to remove light key organic compounds from the water and transfer them into air. The air feed would then be passed through a catalytic oxidizer to mineralize the VOCs.

In Figure 7 is the distiller-air stripper design modeled in Aspen. The same air flow rate was chosen for this stripper as was calculated in the ammonia stripper discussed earlier. The 6-mm packing was selected. The suggested diameter for the column was suggested by Aspen to be 5.3 cm.

The components used in this model were decided to be ethanol, acetic acid, sodium chloride, ammonia, and water. All of these components were added in the concentrations present in the humidity condensate wastewater. A simulation was run with these components in basic pH (when sodium hydroxide was added to the feed) and compared with a simulation run under acidic conditions (when sulfuric acid was added to the feed). The results of these simulation experiments are shown in Table O and Table P.
Table C: Distiller Concentrations from an Air Stripper and Distiller Operating in Series from an Initially Alkaline Wastewater Solution

<table>
<thead>
<tr>
<th>Component</th>
<th>Feed</th>
<th>Distillate</th>
<th>Brine Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>$9.98 \times 10^{-1}$</td>
<td>1.00</td>
<td>$9.89 \times 10^{-1}$</td>
</tr>
<tr>
<td>Ethanol</td>
<td>$5.58 \times 10^{-6}$</td>
<td>$6.55 \times 10^{-6}$</td>
<td>$1.03 \times 10^{-7}$</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>$1.92 \times 10^{-13}$</td>
<td>$3.33 \times 10^{-30}$</td>
<td>$7.76 \times 10^{-13}$</td>
</tr>
<tr>
<td>$H_2O^+$</td>
<td>$1.13 \times 10^{-14}$</td>
<td>$1.54 \times 10^{-32}$</td>
<td>$1.19 \times 10^{-44}$</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>$8.23 \times 10^{-4}$</td>
<td>$1.28 \times 10^{-30}$</td>
<td>$5.48 \times 10^{-9}$</td>
</tr>
<tr>
<td>$OH^-$</td>
<td>$4.23 \times 10^{-4}$</td>
<td>$8.93 \times 10^{-6}$</td>
<td>$2.82 \times 10^{-3}$</td>
</tr>
<tr>
<td>$CH_3CO_2^-$</td>
<td>$8.04 \times 10^{-6}$</td>
<td>$2.62 \times 10^{-29}$</td>
<td>$5.36 \times 10^{-5}$</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>$3.82 \times 10^{-4}$</td>
<td>$1.97 \times 10^{-30}$</td>
<td>$2.55 \times 10^{-3}$</td>
</tr>
<tr>
<td>Ammonia</td>
<td>$2.11 \times 10^{-4}$</td>
<td>$2.39 \times 10^{-4}$</td>
<td>$1.23 \times 10^{-7}$</td>
</tr>
<tr>
<td>Ammonium</td>
<td>$2.38 \times 10^{-7}$</td>
<td>$9.47 \times 10^{-6}$</td>
<td>$4.04 \times 10^{-11}$</td>
</tr>
</tbody>
</table>

Table D: Air Stripping Concentrations from an Air Stripper and Distiller Operating in Series from an Initially Alkaline Wastewater Solution

<table>
<thead>
<tr>
<th>Component</th>
<th>Distillate Feed</th>
<th>Pure Water</th>
<th>Dirty Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1.00</td>
<td>1.00</td>
<td>$7.25 \times 10^{2}$</td>
</tr>
<tr>
<td>Ethanol</td>
<td>$6.55 \times 10^{-6}$</td>
<td>$1.12 \times 10^{-6}$</td>
<td>$3.12 \times 10^{-6}$</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>$3.33 \times 10^{-30}$</td>
<td>0.00</td>
<td>$1.09 \times 10^{-31}$</td>
</tr>
<tr>
<td>$O_2$</td>
<td>0.00</td>
<td>$5.15 \times 10^{-6}$</td>
<td>$7.42 \times 10^{-1}$</td>
</tr>
<tr>
<td>$N_2$</td>
<td>0.00</td>
<td>$6.25 \times 10^{-7}$</td>
<td>$1.85 \times 10^{-3}$</td>
</tr>
<tr>
<td>$H_2O^+$</td>
<td>$1.54 \times 10^{-12}$</td>
<td>$1.37 \times 10^{-10}$</td>
<td>0.00</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>$1.28 \times 10^{-30}$</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>$OH^-$</td>
<td>$8.93 \times 10^{-6}$</td>
<td>$2.58 \times 10^{-9}$</td>
<td>0.00</td>
</tr>
<tr>
<td>Ammonia</td>
<td>$2.39 \times 10^{-4}$</td>
<td>$2.69 \times 10^{-11}$</td>
<td>$1.39 \times 10^{-4}$</td>
</tr>
<tr>
<td>Ammonium</td>
<td>$9.47 \times 10^{-6}$</td>
<td>$2.61 \times 10^{-9}$</td>
<td>0.00</td>
</tr>
</tbody>
</table>

It can be seen that at these flow rates ethanol is not readily removed from the distillate water by air stripping. The ammonia is removed below the target concentration. Ammonia removal is a pH-dependent process. Air stripping of ammonia is only effective at high pH. On the other hand, separation of ammonia from water by distillation is only effective at low pH.

Since the removal of ethanol is not effective at this incoming air flow rate, the air flow rate is adjusted in Aspen as per the calculations for the methanol air stripper to be 13.6 times the mass flow rate of the incoming water stream.

The next calculation was done with 0.1-percent sulfuric acid to make the initial wastewater stream acidic (See Table Q). The result is that all ammonia is separated from the distillate water in the first distillation step. In the next step, it is observed that air stripping for the removal of ethanol is more than effective at this higher air flow rate. Acetic acid, on the other hand, is not effectively removed in this process. Air stripping of acetic acid is known to be difficult and requires huge excesses of air-to-water to achieve separation (See Table R). With this design of an air stripper distillation column, acetic acid can be removed only if the pH is alkaline. If the pH cannot be made alkaline at any stage in the process, then an additional unit will need to be added to remove the acetic (and formic) acid.
Table E: Distillation Concentrations from an Air Stripper and Distiller Operating in Series from an Initially Acidic Wastewater Solution

<table>
<thead>
<tr>
<th>Component</th>
<th>Distillate</th>
<th>Brine Water</th>
<th>Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1.00</td>
<td>9.87 x 10^{-1}</td>
<td>9.98 x 10^{-1}</td>
</tr>
<tr>
<td>Ethanol</td>
<td>6.55 x 10^{-6}</td>
<td>1.06 x 10^{-7}</td>
<td>5.58 x 10^{-6}</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>5.11 x 10^{-7}</td>
<td>4.74 x 10^{-5}</td>
<td>8.14 x 10^{-6}</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>2.31 x 10^{-7}</td>
<td>4.03 x 10^{-5}</td>
<td>1.08 x 10^{-4}</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>1.28 x 10^{-30}</td>
<td>1.65 x 10^{-3}</td>
<td>2.48 x 10^{-4}</td>
</tr>
<tr>
<td>HCl</td>
<td>2.02 x 10^{-30}</td>
<td>1.27 x 10^{-9}</td>
<td>1.22 x 10^{-11}</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>5.88 x 10^{-11}</td>
<td>7.49 x 10^{-14}</td>
<td>4.39 x 10^{-14}</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CO}_2^-$</td>
<td>7.16 x 10^{-7}</td>
<td>8.93 x 10^{-8}</td>
<td>3.57 x 10^{-8}</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>1.97 x 10^{-30}</td>
<td>2.55 x 10^{-3}</td>
<td>3.82 x 10^{-4}</td>
</tr>
<tr>
<td>$\text{H}_2\text{SO}_4$</td>
<td>5.44 x 10^{-30}</td>
<td>2.57 x 10^{-13}</td>
<td>1.21 x 10^{-15}</td>
</tr>
<tr>
<td>HSO$_4^-$</td>
<td>5.39 x 10^{-30}</td>
<td>3.12 x 10^{-3}</td>
<td>2.24 x 10^{-4}</td>
</tr>
<tr>
<td>$\text{SO}_4^{2-}$</td>
<td>5.33 x 10^{-30}</td>
<td>3.44 x 10^{-3}</td>
<td>7.57 x 10^{-4}</td>
</tr>
<tr>
<td>Ammonia</td>
<td>6.38 x 10^{-29}</td>
<td>1.47 x 10^{-10}</td>
<td>2.10 x 10^{-11}</td>
</tr>
<tr>
<td>Ammonium</td>
<td>8.29 x 10^{-27}</td>
<td>1.49 x 10^{-3}</td>
<td>2.23 x 10^{-4}</td>
</tr>
</tbody>
</table>

Table F: Air Stripper Concentrations from an Air Stripper and Distiller Operating in Series from an Initially Acidic Wastewater Solution

Note: The pH of the starting feed is dropped to 1 through the addition of sulfuric acid. The air flow rate is adjusted to be 13.6 times (by mass) the water flow rate in the stripper.

<table>
<thead>
<tr>
<th>Component</th>
<th>Distillate</th>
<th>Pure Water</th>
<th>Dirty Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1.00</td>
<td>1.00</td>
<td>3.88 x 10^{2}</td>
</tr>
<tr>
<td>Ethanol</td>
<td>6.55 x 10^{-6}</td>
<td>0.00</td>
<td>3.93 x 10^{7}</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>5.11 x 10^{-7}</td>
<td>1.73 x 10^{-6}</td>
<td>9.37 x 10^{9}</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>2.31 x 10^{-7}</td>
<td>4.25 x 10^{-7}</td>
<td>0.00</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>1.28 x 10^{-30}</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>5.88 x 10^{-11}</td>
<td>8.39 x 10^{-13}</td>
<td>0.00</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CO}_2^-$</td>
<td>7.16 x 10^{-7}</td>
<td>1.32 x 10^{-6}</td>
<td>0.00</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>1.97 x 10^{-30}</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>$\text{H}_2\text{SO}_4$</td>
<td>5.44 x 10^{-30}</td>
<td>0.00</td>
<td>8.27 x 10^{38}</td>
</tr>
<tr>
<td>HSO$_4^-$</td>
<td>5.39 x 10^{-30}</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>$\text{SO}_4^{2-}$</td>
<td>5.33 x 10^{-30}</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Ammonia</td>
<td>6.38 x 10^{-29}</td>
<td>0.00</td>
<td>5.04 x 10^{25}</td>
</tr>
<tr>
<td>Ammonium</td>
<td>8.29 x 10^{-27}</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Beyond these basic components, there are 12 compounds for which the Henry’s law constants are not available. The compounds, which are not adequately removed in a single pass by a combination of distillation through a ten-stage column and air stripping are shown in Table G.

Table G: Remaining Compounds not adequately Removed by a Combination of Air Stripping and Distillation

<table>
<thead>
<tr>
<th>Organic Acids</th>
<th>Acetic Acid</th>
<th>Formic Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Removable with catalytic oxidation or distillation from alkaline solutions</td>
<td></td>
</tr>
</tbody>
</table>

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Further investigation into air stripping may demonstrate how multiple pass processes will be useful. Multiple passes in air stripping could remove some organic acids. It may be useful to use a group contribution method to calculate the Henry’s constant for these compounds.

### III. Effects of Different Gravitational Environments on Column Size

#### 1.1 Tray Columns [14]

Since both the vapor and liquid velocities change, as will be demonstrated later, there is a risk of both flooding and weeping when the gravitation field is changed for a given column of set dimensions. The distance between trays, the diameter of the perforations in the trays, heights of the weirs, and cross sectional area of the column are all variables, which may be taken into account when adapting the optimal conditions to the column for different gravitational environments.

When considering the effect of gravity on the dynamics of a gravity-based distillation column, it is useful to think of the combination of the velocity of gas bubbles percolating upward through the plates and the down-coming liquid flowing in the opposite direction. These velocities change when the acceleration, due to gravity, changes. To begin with, the gas velocity, $V_F$, is defined as $Q_G/A_n$. The formula for $V_F$ is given below:

$$V_F = \frac{Q_G}{A_n} = C_F \sqrt{\frac{\rho_L - \rho_G}{\rho_G}}$$  \hspace{1cm} \text{Equation (26)}

$\rho_L$ and $\rho_G$ are the liquid and gas phase densities and $C_F$ is the flooding coefficient. This gas velocity is directly related to the bubble velocity. The bubble velocity can be calculated by setting the drag forces and buoyancy forces equal to each other. The following equation is the equation for the drag force:

$$F_d = \frac{\pi \rho_L V^2_{gb} d^2 \theta}{8}$$  \hspace{1cm} \text{Equation (27)}

This equation is for the buoyant force:
\[ F_b = \frac{(\rho_L - \rho_g)g\pi d^3}{6} \]  
Equation (28)

After setting Equations 6 and 7 equal to each other and solving for \( V_B \), the following equation is obtained:

\[ V_B = \sqrt{\frac{4d^3 g (\rho_L - \rho_g)}{3\theta (\rho_L)}} \]  
Equation (29)

From Equation 8 it follows that

\[ V_B \propto \sqrt{g} \]  
Equation (30)

Since from Equation 5 \( A_n = A_g/N_F \), and since \( V_B \) is proportional to \( V_F \), the following equation must hold true:

\[ A_n \propto \frac{Q_g}{g} \]  
Equation (31)

If the column pressure, feed, and reflux ratio are kept constant, then \( Q_g \) will be the same between Earth, Mars, and the Moon. From here one can obtain a generalized ratio for how the area scales from one lunar or planetary body (1) to the next (2):

\[ \frac{A_{n,1}}{A_{n,2}} = \sqrt{\frac{g_2}{g_1}} \]  
Equation (32)

Scaling the area of the downer is now of interest. In order to do this one must consider the liquid flow rate, \( Q_L \). The equation for the rate of laminar flow due to gravity in a vertical pipe is as follows:

\[ Q_L = \frac{(A_d)^2 \rho_L g}{\pi 8 \mu_L} \]  
Equation (33)

From this equation one sees the same relation as inverse proportionality between area, \( A \), and the square root of acceleration due to gravity, \( g \), as in Equation 10. See the following equation:

\[ A_d \propto \frac{1}{\sqrt{g}} \]  
Equation (34)

Similarly to Equation 11, the scaling ratio is:

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Taking Equation 9, one can determine the ratio of bubble velocities to be as follows:

\[
\frac{V_B|_1}{V_B|_2} = \sqrt{\frac{g_1}{g_2}} \left( \frac{d_1}{d_2} \right) \tag{36}
\]

Equation (36)

Thus, Equations 12, 15, 16 provide the scaling ratios for the plate area, downer area, and bubble velocity for a gravity-based column on one heavenly body to another.

In designing a column, one can determine the size of the perforations in each plate and optimize them for the gravitational force experienced by the different droplets. For this reason the following relation is also of importance:

\[
\frac{Mg}{\sigma D|_1} = \frac{Mg}{\sigma D|_2} \tag{37}
\]

Equation (37)

Taking into account the diameter of the perforations, we are interested in calculating how column efficiencies may be affected by changes in gravitational field. Equation 5 is a useful proportionality in this regard. From this proportionality, the ratio of the \(\ln(E)\) on celestial body 1 to celestial body 2 can be determined to be:

\[
\ln(1-E)|_1 = \left( \frac{a_1}{a_2} \right) \left( \frac{h_1}{h_2} \right) \left( \frac{k_L|_1}{k_L|_2} \right) \left( \frac{V_B|_2}{V_B|_1} \right) \tag{38}
\]

Equation (38)

To get to the perforation diameter, one needs to consider them to have a direct influence on the bubble diameter. Then the bubble mass transfer coefficient can be reviewed to get a relation for how the mass transfer relates to changes in bubble contact time in the liquid, which is related to the bubble diameter.

\[
K_L = \left( \frac{D_{ab}}{\pi t} \right)^{1/2} \tag{39}
\]

Equation (39)

\(t\) is the bubble contact time in Equation 19. The contact time for the bubble in the liquid is going to be proportional to the size of the bubble divided by its velocity.

\[
K_L \propto \left( \frac{V_B}{d} \right)^{1/2} \tag{40}
\]

Equation (40)

Taking the ratio of \(K_L\) between two bodies, 1 and 2, and substituting into Equation 18 gives Equation 21.

\[
\ln(1-E)|_1 = \left( \frac{a_1}{a_2} \right) \left( \frac{h_1}{h_2} \right) \left( \frac{d_2}{d_1} \right)^{1/2} \left( \frac{V_B|_2}{V_B|_1} \right) \tag{41}
\]

Equation (41)

1.2 Randomly-Packed Columns [15]
Thus far, only the general case for distillation with plates has been discussed. If distillation is looked at on a small-scale basis, the best option is to use a fractional column with some kind of packing.

The way Pettit (1986) determined the scaling factors in the case of random packing was to consider the liquid flow as laminar flow and the sum of a group of "filmlets." Between all these filmlets is gas flowing in the opposite direction. From this, the volumetric flow of a given individual filmlet is:

\[ Q_f \propto \delta^3 W_f \cos \beta \]  
Equation (42)

From this equation \( \delta \) is the total film thickness, \( W_f \) is the filmlet width, and \( \beta \) is the filmlet angle to the direction of gravitational pull. Summing the filmlets according the cross-sectional area will help achieve a cross-sectional packing area. To sum up the filmlets, the total width of all the filmlets must be \( l A_c \), where \( l \) is the length of wetted packing surface per unit of cross sectional area and \( A_c \) is the cross sectional area of the column. \( l \) and \( \beta \) are independent of gravity -- their values depend on the packing material. Hence, the proportionality of concern for this study is:

\[ Q_L = \delta^3 A_c g \]  
Equation (43)

If one makes the assumption that the filmlet thicknesses do not change when changing the acceleration due to gravity and if \( Q_L \) is constant, the scaling ratio for change in liquid area is:

\[ \frac{A_c}{A_c} = \frac{g_2}{g_1} \]  
Equation (44)

It is now important to scale in relation to the gas flow. In order to determine these relations, Pettit (1986) equated the drag force and the gravitational force as he did previously with the bubble columns. Pettit found that the interface for turbulent gas flow is proportional to \( a_f V^2 \), where \( V \) is the gas velocity and \( a_f \) is the liquid area parallel to the gas flow (see Darcy friction factor). The gravitational force from the liquid is proportional to \( ga_f \delta \) where \( a_f \delta \) is the column of liquid contained in the packed bed. Equating the drag force and gravity forces one gets this equation:

\[ \frac{A_c}{A_c} = \left( \frac{g_2}{g_1} \right)^{1/2} \]  
Equation (45)

With this scaling factor for gas one gets that the lunar column area will increase by a factor of 2.45. If the scaling factor for liquid is used, the factor for scaling to the Moon will increase the column diameter by 6.

### 1.3 Moon-Adapted Distillers and Air Strippers

From Section 5.2, scaling gravitational effects according to the gas flow rate and scaling according to the liquid flow rate in a packed column give two different results. It may be necessary to run computational fluid dynamics calculations to get a clearer picture of what the requirements would be for a packed column. The data presented below (see Table H) describing scaled distillation columns for use on the lunar surface shows a range. The low end of the range is from the scaling factor of 2.45 for the gas-flow scaled column and the high end of the range is the scaling factor, 6, as calculated for the liquid-scaled column. The liquid scaling factor provides a more conservative estimate for the column design so as to avoid flooding.
Table II: Scaling the Distillation Column and the Air Strippers Discussed in the Text for Operation on the Lunar Surface

<table>
<thead>
<tr>
<th></th>
<th>Diameter</th>
<th>Length</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Distillation Column</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Earth</td>
<td>6.4 cm</td>
<td>1.0 m</td>
</tr>
<tr>
<td>Moon</td>
<td>10.0 cm – 16.0 cm</td>
<td>1.0 m</td>
</tr>
<tr>
<td><strong>Ammonia Stripper</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Earth</td>
<td>3.4 cm</td>
<td>0.3 m</td>
</tr>
<tr>
<td>Moon</td>
<td>5.4 cm – 8.3 cm</td>
<td>0.3 m</td>
</tr>
<tr>
<td><strong>Methanol Stripper</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Earth</td>
<td>2.6 cm</td>
<td>7.0 m</td>
</tr>
<tr>
<td>Moon</td>
<td>4.2 cm – 3.9 cm</td>
<td>7.0 m</td>
</tr>
</tbody>
</table>

IV. Reactive Distillation and Reactive Air Stripping

1.1 Methods in Reactive Distillation (RD) Test and Used in Industry

A reactive distillation or air stripping design is considered to reduce the presence of volatile organic compounds in the purified water. Reactive purification, in this case, integrates a reactor with a distillation column. A review of the literature in this field has revealed a variety of functional reactive columns in industry. The design can be considered for homogeneous self-catalyzed reactions such as esterification and hydrolysis, in addition to heterogeneous catalysis [16]. A variety of RD reaction processes have been achieved. These include ester hydrolysis, transesterification, metathesis, esterification, nylon synthesis, isooctane synthesis, cumulene synthesis, and hydration of alkenes [17] and [18]. There have been some designs which have been used for the purification of wastewater. In particular, acetic acid has been removed from wastewater through esterification [19]. This process does require the addition of a primary alcohol to the water which ads a treatment step and is less desirable for purification of wastewater on the lunar surface. Process intensification through the addition of a catalyst to the distillation column would not only likely save power and volume costs in the overall equivalent system mass (ESM) of the unit but may also yield better purification of water. The reason for this is that in separation limited by azeotrope formation under non-reactive conditions, the addition of a reactive constantly changes the concentrations such that the separation can proceed beyond azeotrope formation. [Integrated Chemical Processes: synthesis, analysis, and control]

There have been concerns raised that when human urine is used as a fertilizer in agriculture certain pharmaceuticals are transferred to and pollute groundwater. In the interest of destroying these pharmaceuticals in urine ozonation has been sought as a pretreatment step to the use of urine as a fertilizer [20]. In particular, KMU Umweltschutz gmbh has developed an evaporator which includes ozonation for the purification of wastewater [21]. It has been demonstrated that this device will remove pharmaceutical compounds from wastewater.
A reactive distillation column has been designed by a group at the Slovak University of Technology (Figure 7). This group presented a theoretical model which it verified with a realized distillation reactor which was designed to remove organic chloroderivatives from wastewater [22].

1.2 Selection of the Catalyst for Reactive Distillation

There are three kinds of catalytic materials, which may be used for heterogeneous catalysis: monolithic catalysts, membrane catalysts, and arranged catalysts. Monolithic catalysts are often honeycomb-shaped and are of a continuous structure. The catalytically active particles are often deposited on or inside the walls of the passages of this structure. Membrane catalysts are different from monolithic catalysts in that they can demonstrate selectivity in mass transport rates for the various compounds that may try to pass through the permeable walls of the catalyst substrate. The kind of catalyst, which will be considered for distillation, is the arranged catalyst. Structural catalysts were used in this study for reactive distillation. These catalysts are a subset for arranged catalysts. They are usually made of superimposed sheets of a variety of geometric arrangements, which are coated with a catalytically active material.

In order to select a catalyst for reactive distillation one must be chosen from a large variety of tested compounds for gas-phase catalysis and wet-air oxidation catalysis since this is a two-phase system. Since in the column the material is vaporizing and recondensing, kinetic data available for a single-phase system may not be accurate in this multi-phase condition.

Platinum and palladium on gold have also demonstrated substantial promise in catalytic oxidation of polar organics under mild conditions [23]. Au/CeO2 catalysts have been reported to achieve 100-percent formaldehyde conversion at 75 °C [24]. An 18.2 percent Mn/Al2O3 catalyst with 0.1-percent palladium (Pd) has demonstrated to have complete combustion of methanol to carbon dioxide (CO2) at 90 °C [25].

One of the main drawbacks to wet-air oxidation (WAO) is the inability of catalysts to achieve complete mineralization of low molecular weight organics (such as acetic acid, propionic acid, methanol, ethanol, and acetaldehyde). The removal of acetic acid is usually negligible at temperatures lower than 573 Kelvin (K). A major benefit of WAO is that ammonia can be readily oxidized to nitrogen (N2) through this process [26]. It is necessary for further studies to be undertaken for the catalytic oxidation with a focus on reaction under ambient pressure. The reactions that have been reviewed up to this time require a positive pressure of oxygen (O2). This situation is not suitable for distillation where lower pressures are often sought to reduce the amount of heat transferred to the liquid in the reboiler.
New catalysts have been tested for the treatment of wastewater. One area of heterogeneous catalysis is dedicated to the destruction of halogenated organic compounds (HOCs). In this way, wastewater is detoxified by Pd on nanoscale supports, which catalyze the hydrodehalogenation of HOCs. Nanoscale supports previously used include gold, zero-valent iron, or magnetite [27] [28].

At this time the best catalyst for use in the reactive distillation column for wastewater purification may be the Au/CeO2 catalyst reported to achieve 100-percent formaldehyde conversion at 75 °C [29]. If this catalyst is incorporated into the distillation column, it needs to be tested for oxidation of a variety of other volatile organic compounds (VOCs). The durability, kinetics, and lifetime of the catalyst would also need to be determined. Along these lines, I contacted KMU Umweltschutz about the possibility of developing a packing material (e.g. Raschig rings) impregnated with a nanogold catalyst. They were interested in the concept and referred me to a colleague of theirs in Leipzig for further discussions.

Thermal catalytic oxidation is preferable to photocatalytic oxidation so long as the catalyst achieved complete oxidation of polar organics at 100 °C or below. Photocatalytic oxidation requires an additional power source to operate an external light source. The design of the column with regards to the placement of the bulbs and the integration of the cooling water would also be a concern for the photocatalytic system. Additionally, the cooling water would have an additional heat load from the ultraviolet (UV) light. Since catalysts have been reported to be active for methanol mineralization below 100 °C, the simplest solution is to use a thermally-activated catalyst.

IV. Conclusion

Air stripping is useful for the removal of ammonia and some of the volatile organics, which are not removed by the distillation process. This process requires relatively low power to remove components from water. A commercially-available unit was found, which would require 500 W to process 5.4 L of wastewater in one hour.

The scaling of these purification systems for the lunar gravitational environment is taken into account. Previous analysis of this particular problem reveals that scaling factors can be applied to the diameter of the columns to achieve the same purity levels that are achieved on earth. It will also be necessary to assess the role a low gravity environment would play in the physics of the water/air mixture (froth) and also containment and flow. Studies in computational fluid dynamics may shed additional light on this process for a more precise scaling factor for distillation columns and air strippers operating on the lunar surface.

The processing rate for the processes modeling in this report has been set to be 20 L/day. It may be of interest to determine the optimum processing time for a system architecture of an air stripper, fractional distillation column, catalytic oxidizer, and a CO2 removal bed. In this way, the total processing time can be optimized with respect to the required blower power, heating requirements, and cooling requirements. A study comparing the benefits of the complete water recovery system with air stripping as compared to steam stripping may also potentially be of interest.

References


[16] Tade, M.O.; Bisowarno, B.H.; Tian, Y.-C. “Modeling and Control of Reactive Distillation Systems.”


