MASS INTEGRATION
AND POLLUTION PREVENTION

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MOTIVATING EXAMPLE
ACRYLONITRILE PROCESS
Target for water usage and discharge?
Minimum cost strategies to attain target?

And the optimum solution is …
OBSERVATIONS

- Numerous alternatives
- Intuitively non-obvious solutions
- Focus on root causes not symptoms, must go to heart of process
- Need a systematic methodology to extract optimum solution
- Process must be treated as an integrated system
Conventional Engineering Approaches

• Brainstorming among experienced engineers

• Evolutionary techniques: copy (or adapt) the last design we or someone else did

• Heuristics based on experience-based rules
State of the art:
Systematic, fundamental, and generally applicable techniques can be learned and applied to synthesize optimal designs for improving process performance.

This is possible via *Process Synthesis and Integration + Optimization*:

You will learn the fundamentals and applications of process synthesis, integration, and optimization
Process Design = 

\[ \text{Process Synthesis} + \text{Process Analysis} \]
A holistic approach to process design and operation that emphasizes the unity of the process and optimizes its design and operation
Mass-Energy Matrix of a Process
**PROCESS INTEGRATION = MASS INTEGRATION + ENERGY INTEGRATION**

**Mass Integration**
A systematic methodology that provides fundamental understanding of the global flow of mass within a process and employs this understanding in identifying performance targets and optimizing the generation and routing of species throughout the process.
Overall Philosophy

**BIG**
**PICTURE FIRST,**
**DETAILS LATER**

**FIRST,** understand
the global picture
of the process and
develop system insights

**LATER,** think equipment,
detailed simulation, and
process details.
TARGETING APPROACH OF PROCESS INTEGRATION

Identification of performance targets for the whole process AHEAD of detailed design!!

Specific Performance Objectives

• Profitability improvement
• Yield enhancement
• Resource (mass and energy) conservation
• Pollution prevention/waste minimization
• Safety improvement

How?
ELEMENTS OF PROCESS INTEGRATION

• **Task Identification**: Explicitly express the goal as an *actionable* task
  Examples: - Pollution prevention = decrease flowrate of wastewater, pollutant loading, etc.
  - Debottlenecking = reduction in wastewater flowrate

• **Targeting**: Benchmark performance ahead of detailed design

• **Generation and selection of alternatives (synthesis)**

• **Evaluation of selected alternatives (analysis)**
LECTURE OUTLINE

• Overall mass targeting
• Stream rerouting and direct recycle opportunities
• Incorporation of separation
• General strategies for mass integration

Will focus on graphical techniques
We will learn:

⇒ How to identify best achievable pollution-prevention targets for a process WITHOUT detailed calculations.
⇒ How to systematically reach the target at minimum cost?
⇒ How to determine optimal stream rerouting?
⇒ How to place additional units and determine their performance?
⇒ How to understand the BIG picture of a process and use it to reduce waste from any plant?
OVERALL MASS TARGETING

WHAT IS TARGET FOR MINIMUM AA FRESH PURCHASE?

VAM PROCESS
Current Purchase of AA = 15,100 kg/hr
How to benchmark performance for mass objectives of the whole process ahead of detailed design?

- Minimization of waste discharge/losses
- Minimization of purchase of fresh resources (raw materials, material utilities)
- Maximization of desired products/byproducts

Need a holistic and generally applicable procedure
Example 1: Reduction of Terminal Losses or Discharge of Waste

- Terminal Load (out) = Fresh Load (in) + Net Generation

Overall Mass Balance Before Mass Integration (BMI)

\[ T^{BMI} = F^{BMI} + Net\_G^{BMI} \]

For fixed generation:

Minimum terminal (out) corresponds to minimum fresh (in)

To minimize fresh:

1. Adjust design and operating variables
2. Maximize recycle to replace fresh usage
1. Adjust Design and Operating Variables to Reduce Fresh

- What are the design and operating variables in the process that influence fresh consumption?
- Which ones are allowed to be changed (manipulated variables)?
- How is fresh usage related to these design and operating variables?
  Fresh Usage = f (manipulated design variables, manipulated operating variables)

\[ F_{AFR} = \text{minimize } f \text{ (manipulated design variables, manipulated operating variables)} \]

Overall Mass Balance after Fresh Reduction

\[ T_{AFR} = F_{AFR} + Net_G^{BMI} \]
2. Maximize Recycle to Reduce Fresh Usage

Overall Mass Balance after Fresh Reduction

\[ \text{T}_{\text{AFR}} = \text{F}_{\text{AFR}} + \text{Net}_{\text{G}^{\text{BMI}}} \]

Need to replace maximum load of fresh load with recycled terminal load

What is maximum recyclable load?
Recycle Rules to Reduce Terminal Load (continued):

- Recovery devices can recover (almost) all terminal load and render acceptable quality to replace fresh feed. During targeting, cost and details of recovery are not relevant (yet).
- Maximize recycle from outlet path to fresh inlets (can recycle the smaller of the two loads: total recovered terminal vs. total needed fresh). $R_{\text{max}} = \arg\min \{F_{\text{AFR}}, T_{\text{AFR}}\}$

$F_{\text{AMI}} = F_{\text{AFR}} - R_{\text{MAX}}$

$T_{\text{AMI}} = T_{\text{AFR}} - R_{\text{MAX}}$

Target After Mass Integration (AMI)
Example 2: Reduction of Terminal Losses or Discharge of Waste for Variable Generation

- **Terminal Load (out) = Fresh Load (in) + Net Generation**

\[ T_{BMI} = F_{BMI} + Net_{G_{BMI}} \]

- **Overall Mass Balance Before Mass Integration (BMI)**

- **Minimize generation of waste (or targeted species)**

- **Minimize fresh:**
  1. Adjust design and operating variables
  2. Maximize recycle to replace fresh usage

Minimizing Generation of Waste

Minimize generation (or maximize depletion) of targeted species (e.g., Describe generation quantitatively then identify values of design and operating conditions of reactors to minimize generation)

Terminal Load (out) = Fresh Load (in) + Generation (- Depletion)

Overall Mass Balance after Minimization of Generation

\[
T_{AGMIN} = F_{BMI} + Net_{G^{MIN}}
\]
Adjust Design and Operating Variables to Reduce Fresh

Terminal Load (out) = Fresh Load (in) + Generation (- Depletion)

Total Fresh Load (In) \( F_{AFR} \)

WHOLE PLANT

Net Generation \( Net_G^{MIN} \)

Overall Mass Balance after Fresh Reduction and Minimization of Generation

\[ TAGMIN, AFR = F_{AFR} + Net_G^{MIN} \]
Recycle Rules to Reduce Terminal Load (continued):

- Recovery devices can recover (almost) all terminal load and render acceptable quality to replace fresh feed. During targeting, cost and details of recovery are not relevant (yet)
- Maximize recycle from outlet path to fresh inlets (can recycle the smaller of the two loads: total recovered terminal vs. total needed fresh). \( R^{\text{max}} = \arg\min \{ F^{\text{AFR}}, T^{\text{AGMIN}}, AFR \} \)

\[
F^{\text{AMI}} = F^{\text{AFR}} - R^{\text{MAX}}
\]

Target After Mass Integration (AMI)
TARGETING PROCEDURE TO MINIMIZE TERMINAL LOSS OR WASTE DISCHARGE

Generation/Depletion Model/Data
(e.g., chemical reaction, fugitive emissions, etc.)

Stream Data
(fresh and terminal loads of targeted species)

Minimize generation of targeted species

Adjust design and operating variables to minimize fresh load, then carry out overall material balance on targeted species

Minimum generation

Revised data for fresh and terminal loads of targeted species

Maximize recycle (to minimize fresh load)
Maximum recycle = \arg\min \{\text{fresh load, recoverable terminal load}\}

Maximum total recycle

Revise overall material balance on targeted species

Target of minimum terminal load
CASE STUDY I: MINIMIZE AA FRESH PURCHASE IN VAM PROCESS
**Overall AA Balance Before Mass Integration**

- To Acid Tower: 10,000 kg/hr
- To First Absorber: 5,100 kg/hr
- Absorber II Bottoms: 1,200 kg/hr
- Primary Tower Bottoms: 6,800 kg/hr
- Loss in Product: 100 kg/hr
- AA Consumption: 7,000 kg/hr

**Targeting for Minimum Purchase of Fresh AA**

- Fresh AA: 7,100 kg/hr
- 10,000 kg/hr
- 5,100 kg/hr
- AA Consumption: 7,000 kg/hr
- Recovery: 8,000 kg/hr
- 1,200 kg/hr
- 6,800 kg/hr
- AA Losses: 100 kg/hr
EXAMPLE II: MINIMIZE WATER DISCHARGE IN TIRE-TO-FUEL PROCESS

\[ G_1 + G_2 + W_{rxn} = W_1 + W_2 + W_3 \]

\[ W_{rxn} = 0.152 + (5.37 - 7.84 \times 10^{-3} T_{rxn}) e^{(27.4 - 0.04T_{rxn})} \]

\[ 690 \leq T_{rxn} (K) \leq 740 \]

\[ G_1 = 0.47 e^{-0.009 P_{comp}} \quad 70 \leq P_{comp} (atm) \leq 90 \]

\[ G_2 = 0.15 \quad W_2 = G_2 \quad W_3 = 0.4 G_1 \]
OVERALL WATER BALANCE BEFORE MASS INTEGRATION

Water-jet Makeup
$G_1 = 0.25 \text{ kg/s}$

Seal-Pot Feed Water
$G_2 = 0.15 \text{ kg/s}$

Tire-to-Fuel Plant

$\text{Net}_\text{process}_{\text{water}} = -0.12 \text{ kg/s}$

Decanter Wastewater
$W_1 = 0.27 \text{ kg/s}$

Seal Pot Wastewater
$W_2 = 0.15 \text{ kg/s}$

Water with the Wet Cake
$W_3 = 0.10 \text{ kg/s}$
Minimize generation of targeted species

\[ W_{\text{rxn}} = 0.152 + (5.37 - 7.84 \times 10^{-3} \ T_{\text{rxn}}) \ e^{(27.4 - 0.04 \ T_{\text{rxn}})} \]
Adjust design and operating variables to minimize fresh load, then carry out overall material balance on targeted species

\[ G_1 = 0.47 e^{-0.009P_{comp}} \]

\[ 70 \leq P_{comp} \text{ (atm)} \leq 90 \]

⇒ Set \( P_{comp} = 90 \text{ atm} \) \[ G_1 = 0.47 e^{-0.009 \times 90} = 0.2 \]

⇒ Minimum water for shredding \( G_1 = 0.2 \text{ kg/s} \)

\[ W_3 = 0.4 \ G_1 = 0.08 \text{ kg/s} \]
OVERALL WATER BALANCE
AFTER MASS INTEGRATION

Tire-to-Fuel Plant

Water-jet Makeup
$G_1 = 0.20 \text{ kg/s}$

Seal-Pot Feed Water
$G_2 = 0.15 \text{ kg/s}$

Net process water
$-0.08 \text{ kg/s}$

Decanter Wastewater
$W_1 = 0.20 \text{ kg/s}$

Seal Pot Wastewater
$W_2 = 0.15 \text{ kg/s}$

Water with the Wet Cake
$W_3 = 0.08 \text{ kg/s}$

WATER TARGETING

Tire-to-Fuel Plant

No Fresh Water

Water-Jet Makeup

Seal Pot Feed Water

Net process water
$-0.08 \text{ kg/s}$

Decanter Terminal Wastewater
$W_1^T = 0.00 \text{ kg/s}$

Seal Pot Terminal Wastewater
$0.00 \text{ kg/s}$

Water with the Wet Cake
$W_3^T = 0.08 \text{ kg/s}$
ACHIEVING THE TARGET
Mass Integration Strategies

No Cost/Low Cost Strategies
- Modest Sink/Generator Manipulation (e.g., Moderate Changes in Operating Conditions)
- Minor Structural Modifications (Segregation, Mixing, Recycle, etc.)

Moderate-Cost Modifications
- Equipment Addition/Replacement (Interception/Separation devices, etc.)
- Material Substitution (Solvent, Catalyst, etc.)

New Technologies
- Technology Changes (New Chemistry, New Processing Technology, etc.)
Consider the VAM process described earlier. A new reaction pathway has been developed and will to be used for the production of VAM. This new reaction does not involve acetic acid. The rest of the process remains virtually unchanged and the AA losses with the product are 100 kh/hr. What are the targets for minimum fresh usage and discharge/losses of AA?
DIRECT RECYCLE STRATEGIES

Objective: to develop a graphical procedure that determines the target and implementation for minimum usage of the fresh resource, maximum material reuse, and minimum discharge to waste as a result of direct recycle.

Direct Recycle: rerouting of streams without the addition of new units. It involves segregation, mixing, and allocation.
DIRECT RECYCLE REPRESENTATION

**Sources**

**Segregated Sources**

**Sinks**
Constraints on feed flowrate and composition

**Source**: A stream which contains the targeted species

**Sink**: An existing process unit/equipment that can accept a source
PROBLEM STATEMENT

Consider a process with a number of process sources (e.g., process streams, wastes) that can be considered for possible recycle and replacement of the fresh material and/or reduction of waste discharge. Each source, i, has a given flow rate, \( W_i \), and a given composition of a targeted species, \( y_i \). Available for service is a fresh (external) resource that can be purchased to supplement the use of process sources in sinks. The sinks are process units such as reactors, separators, etc. Each sink, j, requires a feed whose flow rate, \( G_j \), and an inlet composition of a targeted species, \( z_j \), must satisfy certain bounds on their values.
DESIGN CHALLENGES

- Should a stream (source) be segregated and split? To how many fractions? What should be the flowrate of each split?

- Should streams or splits of streams be mixed? To what extent?

- What should be the optimum feed entering each sink? What should be its composition?

- What is the minimum amount of fresh resource to be used?

- What is the minimum discharge of unused process sources?
SOURCE-SINK MAPPING DIAGRAM

- Flowrate
- Sink: ○
- Source: •

Composition

- a
- b
- c
How to Identify Bounds on Sinks?
1. From physical limitations (e.g., flooding flowrate, weeping flowrate, channeling flowrate, saturation composition)
2. From manufacturer's design data
3. From technical constraints (e.g., to avoid scaling, corrosion, explosion, buildup, etc.)
4. From historical data
5. By constraint propagation

How to identify bounds on sinks? (continued)

**Unknown Constraints**

\[ z_j^{\text{min}} \leq z_j^{\text{in}} \leq z_j^{\text{max}} \]

\[ z_j^{\text{in}} \rightarrow \text{Unit } j \]

**Known Constraints**

\[ z_{j+1}^{\text{min}} \leq z_{j+1}^{\text{in}} \leq z_{j+1}^{\text{max}} \]

\[ z_{j+1}^{\text{in}} \rightarrow \text{Unit } j+1 \]

From process model:

\[ z_{j+1}^{\text{in}} = 2 z_j^{\text{in}} \]

\[ 0.03 \leq z_j^{\text{in}} \leq 0.04 \]

\[ 0.06 \leq z_{j+1}^{\text{in}} \leq 0.08 \]
How to identify bounds on sinks? (continued)

6. Tolerate a certain deviation from nominal case (e.g., allow +/- certain %ages from nominal flowrate and compositions)
LEVER-ARM RULES

Flowrate

\[ W_a + W_b \]

Composition

\[ y_s (W_a + W_b) = y_a W_a + y_b W_b \]

\[ \frac{W_a}{W_b} = \frac{y_b - y_s}{y_s - y_a} \]
LEVER-ARM RULES

Flowrate

\[ W_a + W_b \]

Resulting Mixture

\[ \text{Resulting Mixture} \]

Source

Source

Source

Resulting Mixture

Resulting Mixture

Resulting Mixture

Resulting Mixture

Composition

\[ Y_a \]

\[ Y_s \]

\[ Y_b \]

\[ W_b \]

Arm for b

Arm for a

Total arm

\[ \frac{W_a}{W_b} = \frac{\text{Arm for } a}{\text{Arm for } b} \]

\[ \frac{W_a}{W_a + W_b} = \frac{\text{Arm for } a}{\text{Total Arm}} \]
LEVER-ARM RULES FOR FRESH USAGE

Flowrate

Source a

Fresh

Feed to Sink j

Fresh arm

Total arm

\[ y_F = \frac{\text{Fresh flowrate used in sink}}{\text{Total flowrate fed to sink}} \]

\[ z \quad \text{Feed to sink} \]

\[ y_a \quad \text{Composition} \]

\[ \frac{y_a - z \text{Feed to sink}}{y_a - y_F} \]
SINK COMPOSITION RULE

Flowrate

Sink j

Fresh

Source a

$Z_{j}^{\text{min}}$, $Z_{j}^{\text{avg}}$, $Z_{j}^{\text{max}}$, $Y_{a}$

What should be feed composition to sink to minimize fresh usage?
What should be feed composition to sink to minimize fresh usage?

**Sink Composition Rule:** When a fresh resource is mixed with process source(s), the composition of the mixture entering the sink should be set to a value that minimizes the fresh arm. For instance, when the pure fresh, the composition of the mixture should be set to the maximum admissible value.
Which source (a or b) should be used to minimize fresh usage?

**Source Prioritization Rule:** To minimize the usage of the fresh resource, recycle of the process sources should be prioritized in order of their fresh arms starting with the source having the shortest fresh arm.
Targeting Rules

Recycle Strategies

Fresh_Load_{k,1} → Terminal_Load_{k,1}
Fresh_Load_{k,2} → Terminal_Load_{k,2}
Fresh_Load_{k,3} → Terminal_Load_{k,3}

Process Before Recycle

Recycle Alternatives to Reduce Terminal Load

Fresh_Load_{k,1} → Terminal_Load_{k,1} \( - R_{k,1} + R_{k,2} \)
Fresh_Load_{k,2} → Terminal_Load_{k,2} \( - R_{k,2} \)
Fresh_Load_{k,3} → Terminal_Load_{k,3} \( + R_{k,3} \)

Poor Recycle

Net terminal load unchanged
Effective Recycle From Terminal

\[ \text{Fresh\_Load}_{k,1} - R_{k,2} \]
\[ \text{Fresh\_Load}_{k,2} - R_{k,1} \]
\[ \text{Fresh\_Load}_{k,3} \]
\[ \text{Terminal\_Load}_{k,1} - R_{k,1} \]
\[ \text{Terminal\_Load}_{k,2} - R_{k,2} \]
\[ \text{Terminal\_Load}_{k,3} \]
\[ \text{Terminal\_Load}_{k,4} \]

Effective Recycle From Terminal and Intermediate

\[ \text{Fresh\_Load}_{k,1} - R_{k,2} \]
\[ \text{Fresh\_Load}_{k,2} - R_{k,1} \]
\[ \text{Fresh\_Load}_{k,3} \]
\[ \text{Terminal\_Load}_{k,1} - R_{k,1} \]
\[ \text{Terminal\_Load}_{k,2} - R_{k,2} \]
\[ \text{Terminal\_Load}_{k,3} \]
\[ \text{Terminal\_Load}_{k,4} \]
Example: Minimization of AA Usage in VAM Process by Direct Recycle

Acid Tower (Evaporator)

Reactor (7,000 kg/hr Acetic Acid Reacted)

Absorber I

Absorber II

Primary Tower

Gas Purification

Ethylene Oxygen

10,000 AA 200 H₂O

5,100 AA

1,200 AA + Ethylene, O₂ and CO₂

10,000 VAM 6,900 AA 2,300 H₂O

6,800 AA 2,300 H₂O (75% AA)

10,000 VAM 100 AA 200 H₂O

To Neutralization and Biotreatment

Ethylene Oxygen

CO₂

H₂O 200

10,000 AA 200 H₂O (86% AA)
Source-Sink Mapping Diagram for AA Example

Flowrate, kg/hr

Water content, wt.%

S1
Acid Tower

S2
Abs. I

R1
Bottoms of Absorber II

R2
Bottoms of Primary Tower

S1

S2

53
For $S_1$, $R_1$ has shortest AA arm

\[
\text{Fresh AA used in } S_1 = \frac{10,200}{0.14 - 0.10} = \frac{0.14 - 0.00}{2,914 \text{ kg/hr}} \quad \text{Fresh AA in } S_1 = 2,914 \text{ kg/hr}
\]

\[
W_{R_1 \rightarrow S_1} = 10,200 - 2,914 = 7,286 \text{ kg/s}
\]

⇒ Use all of $R_1$ (1,400 kg/s)
Acid Tower Continued

Flowrate, kg/hr

Bottoms of Primary Tower R₂

Bottoms of Absorber II R₁

Water content, wt.%

Acid Tower

Abs. I

S₁

S₂

1,400*0.14+W_{R₂→S₁}*0.25 + Fresh AA in S₁*0.0
= 10,200*0.10

\[ W_{R₂→S₁} = 3,296 \text{ kg/hr} \]

Fresh AA in S₁ = 10,200 – 1,400 – 3,296 = 5,504 kg/hr
Absorber I Calculations

Water content, wt.%

Flowrate, kg/hr

Fresh AA used in \( S_2 \) = \( \frac{5,100}{0.25 - 0.05} \times R_2 \rightarrow S_2 = 5,100 - 1,020 = 4,080 \text{ kg/hr} \)

Bottoms of Absorber II

Bottoms of Primary Tower

Abs. I

Acid Tower

[Diagram with various flowrates and calculations]
SOLUTION TO AA MINIMIZATION PROBLEM

R₁
1,400 kg/hr

R₂
3,296 kg/hr
9,100 kg/hr
1,020 kg/hr

S₁
Acid Tower
5,504 kg/hr

S₂
Abs. I
4,080 kg/hr

Fresh AA
9,584 kg/hr

Waste
4,784 kg/hr
ALTERNATE SOLUTION TO AA MINIMIZATION PROBLEM

Start with $S_2$ and use $R_1$ for shortest arm.

$R_1$
- 1,400 kg/hr

$R_2$
- 9,100 kg/hr

Fresh AA
- 9,584 kg/hr

$S_1$
- Acid Tower
- 4,080 kg/hr
- 6,120 kg/hr

$S_2$
- Abs. I
- 3,464 kg/hr

Waste
- 4,784 kg/hr
ALTERNATE SOLUTION TO AA MINIMIZATION PROBLEM

Split $R_1$ between two sinks.

$R_1$
- 1,400 kg/hr
- 700 kg/hr

$R_2$
- 9,100 kg/hr
- 628 kg/hr

Fresh AA
- 9,584 kg/hr

S1
- Acid Tower
- 700 kg/hr
- 5,812 kg/hr

S2
- Abs. I
- 3,688 kg/hr
- 3,772 kg/hr
- 628 kg/hr

Waste
- 4,784 kg/hr

Same target, infinite implementations.
Need a targeting procedure before detailed implementation.
MATERIAL RECYCLE PINCH DIAGRAM
Sink Composite Diagram

Rank in ascending order of composition

\[ 0 \leq z_j^{\text{in}} \leq z_j^{\max} \]

\[ M_j^{\text{Sink, max}} = G_j z_j^{\max} \]
Source Composite Diagram

\[ M_i^{\text{Source}} = W_i y_i \]

Load

\[ M_3^{\text{Source}} \]

\[ M_2^{\text{Source}} \]

\[ M_1^{\text{Source}} \]

Flowrate

\[ W_1 \]

\[ W_2 \]

\[ W_3 \]

Rank in ascending order of composition

Source Composite Curve
Sink Composite Must Lie Above Source Composite
Integrating Source and Sink Composites

Load

Flowrate

Source Composite Curve

Sink Composite Curve

Material Recycle Pinch Point
Rigorous targets ahead of detailed design

Material Recycle Pinch Diagram

Load

Sink Composite Curve

Material Recycle Pinch Point

Source Composite Curve

Minimum Fresh (pure fresh)

Maximum Recycle

Flowrate

Minimum Waste

Passing Flow through the Pinch
(not enough integration)

Load

Flowrate

Sink Composite Curve

Source Composite Curve

Fresh

Recycle

Waste

Minimum Fresh

Minimum Waste

α

α

α
Infeasible Recycle (too much integration)
Material Recycle Pinch Diagram for Impure Fresh

Load

Flowrate

Sink Composite Curve

Source Composite Curve

Material Recycle Pinch Point

Fresh Locus

Minimum Fresh

Maximum Recycle

Minimum Waste
Useful Design Rules For Material Recycle Pinch Diagram

- No flowrate should be passed through the pinch (i.e. the two composites must touch)
- No waste should be discharged from sources below the pinch
- No fresh should be used in any sink above the pinch
Effect of Interception

Load

Interceptor

Sink Composite Curve

Material Recycle Pinch Point

Source Composite Curve

Minimum Fresh

β

Flowrate

Minimum Waste

β
Effect of Interception

Load

Intercepted Load

Source Composite Curve

Interceptor

Sink Composite Curve

Flowrate
Example Revisited: Minimization of AA Usage in VAM Process
<table>
<thead>
<tr>
<th>Sink</th>
<th>Flowrate kg/hr</th>
<th>Maximum Inlet Mass Fraction</th>
<th>Maximum Inlet Load, kg/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorber I</td>
<td>5,100</td>
<td>0.05</td>
<td>255</td>
</tr>
<tr>
<td>Acid Tower</td>
<td>10,200</td>
<td>0.10</td>
<td>1,020</td>
</tr>
<tr>
<td>Source</td>
<td>Flowrate kg/hr</td>
<td>Maximum Inlet Mass Fraction</td>
<td>Maximum Inlet Load, kg/hr</td>
</tr>
<tr>
<td>-------------------------</td>
<td>----------------</td>
<td>-----------------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>Bottoms of Absorber II</td>
<td>1,400</td>
<td>0.14</td>
<td>196</td>
</tr>
<tr>
<td>Bottoms of Primary Tower</td>
<td>9,100</td>
<td>0.25</td>
<td>2,275</td>
</tr>
</tbody>
</table>
Material Reuse Pinch Point

Source Composite Curve

Sink Composite Curve

Fresh = 9.6

Waste = 4.8

Material Recycle Pinch Diagram For AA In the VAM Facility
PRACTICE EXERCISE II: FOOD PROCESSING FACILITY

Two source (Condensate I and II), Two Sinks (Washer and Scrubber)
### Sink Data for the Food Processing Example

<table>
<thead>
<tr>
<th>Sink</th>
<th>Flowrate kg/hr</th>
<th>Maximum Inlet Mass Fraction</th>
<th>Maximum Inlet Load, kg/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Washer</td>
<td>8,000</td>
<td>0.03</td>
<td>240</td>
</tr>
<tr>
<td>Scrubber</td>
<td>10,000</td>
<td>0.05</td>
<td>500</td>
</tr>
</tbody>
</table>

### Source Data for the Food Processing Example

<table>
<thead>
<tr>
<th>Source</th>
<th>Flowrate kg/hr</th>
<th>Maximum Inlet Mass Fraction</th>
<th>Maximum Inlet Load, kg/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condensate I</td>
<td>10,000</td>
<td>0.02</td>
<td>200</td>
</tr>
<tr>
<td>Condensate II</td>
<td>9,000</td>
<td>0.09</td>
<td>810</td>
</tr>
</tbody>
</table>
Critique project proposed by engineer:
Recycle Condensate I to Scrubber

⇒ Reduce fresh water to 8,000 kg/hr (down from 18,000 kg/hr)
CONCLUSIONS

• Source and sink optimization rules
• Stream rerouting and direct recycle opportunities using source-sink mapping
• Overall targeting for direct recycle using material recycle pinch diagram
• Big-picture insights unseen by detailed eng.
• Short-term projects must fit in integrated strategies
**Motivating Example: Debottleneck Acrylonitrile Process and Minimize Fresh Water Usage**

*Insights from flowsheet?*

*Target for water usage and discharge?*

*Minimum cost strategies to attain target*

Critical Need:

A systematic methodology that provides fundamental understanding of the global flow of mass within a process and employs this understanding in identifying performance targets and optimizing the generation and routing of species throughout the process.

To:

- Determine performance **targets** ahead of detailed design (e.g., minimum raw material consumption, maximum process yield, minimum waste discharge, maximum recovery, etc.)
- Identify optimum:
  1. Allocation (routing) of streams and species
  2. Changes in generation/depletion of species
  3. New units to be added to the process
  4. New materials/streams to be added to the process

Identify optimum revisions in flowsheet to reach target

*Big picture first, details later*
Design Tasks:

Can we determine:

⇒ Target for minimum wastewater discharge?
⇒ Recycle opportunities?
⇒ Separation needed?
⇒ Unit replacement?

We will learn how to do all of that systematically using mass integration techniques.
Targeting

- Water generation is fixed by AN production & stoichiometry (= 5.1 kg/s)
- Get overall data on fresh and terminal water from flowsheet

![ACRYLONITRILE PLANT Diagram](image)

(a) Overall Water Balance Before Mass Integration

(b) Overall Water Balance After Mass Integration

Target for minimum wastewater discharge = 12.0 – 7.2 = **4.8 kg/s**
Target for minimum water usage = 0.0 kg/s
Current Discharge

Current Fresh

Target Discharge

Target Fresh

12.0 kg/s

4.8 kg/s

7.2 kg/s

0.0 kg/s

How?
DEVELOPMENT OF MASS INTEGRATION STRATEGIES TO REACH THE TARGET
Process from a Species Perspective

**Source**: A stream which contains the targeted species

**Sink**: An existing process unit/equipment that can accept a source

**Interceptor**: A new unit/equipment that can process a source
Mass Integration Strategies

- **No Cost/Low Cost Strategies**
  - Modest Sink/Generator Manipulation (e.g., Moderate Changes in Operating Conditions)
  - Minor Structural Modifications (Segregation, Mixing, Recycle, etc.)

- **Moderate-Cost Modifications**
  - Technology Changes (New Chemistry, New Processing Technology, etc.)
  - Equipment Addition/Replacement (Interception/Separation devices, etc.)
  - Material Substitution (Solvent, Catalyst, etc.)

- **New Technologies**
  - Target

![Diagram showing the categorization of strategies based on cost, impact, and acceptability](Image)
Source-Sink Mapping Diagram for Direct Recycle

Flowrate (or Load of Targeted Species), kg/s

○ sink
● source

Composition of Targeted Species
Integrating Source and Sink Composites

Load

Flowrate

Sink Composite Curve

Material Recycle Pinch Point

Source Composite Curve
Effect of Interception

Load

Interceptor

Sink Composite Curve

Material Recycle Pinch Point

Source Composite Curve

Flowrate

Minimum Fresh

Minimum Waste

β

β
DETAILING

MASS INTEGRATION STRATEGIES
MOTIVATING EXAMPLE
ACRYLONITRILE PROCESS
Target for water usage and discharge?
Minimum cost strategies to attain target?

Motivating Example: Debottleneck an Acrylonitrile Process

- Sold-out product, need to expand. Biotreatment is bottleneck.
- Intuitive solution: install an additional biotreatment facility ($4 million in capital investment and $360,000/year in annual operating cost)! Should we??????
- Can we use mass integration techniques to devise cost-effective strategies to debottleneck the process?
Targeting

- Water generation is fixed by AN production & stoichiometry (= 5.1 kg/s)
- Get overall data on fresh and terminal water from flowsheet

Target for minimum wastewater discharge = 12.0 – 7.2 = 4.8 kg/s
Target for minimum water usage = 0.0 kg/s
Current Discharge

Target Discharge

12.0 kg/s

4.8 kg/s

Current Fresh

Target Fresh

7.2 kg/s

0.0 kg/s

How?
Constraints and Data

Scrubber:

- $5.8 < \text{Feed flowrate of scrubbing agent (kg/s)} < 6.2$
- $0.0 < \text{ammonia composition in scrubbing agent (ppm)} < 10$

Boiler Feed Water “BFW”:

- Flowrate of BFW = 1.2 kg/s
- Ammonia content in BFW (ppm) = 0.00
- AN content in BFW (ppm) = 0.00

For separation of ammonia, use adsorption.
Minor Process Modification:
Constraint on scrubber feed flowrate allows reduction of Fresh water from 6.0 kg/s to 5.8 kg/s
12.0 kg/s

11.8 kg/s

4.8 kg/s

Current Discharge

Minor process modification

Target Discharge

Current Fresh

7.2 kg/s

7.0 kg/s

0.0 kg/s

Target Fresh

Minor process modification

How?
Source-Interception-Sink Representation

Note: Recycle to sinks that employ a fresh resource (scrubber and boiler)
Direct-Recycle Alternatives

Off-Gas Condensate
Aqueous Layer
Distillation Bottoms
Ejector Condensate
Feed to Biotreatment
Fresh Water to Scrubber

Scruber

Aqueous Layer

Boiler/Ejector

Note: No recycle to boiler because of 0.0 ppm constraints
Sink Composite Diagram for the AN Example

Load
$10^{-6}$ kg NH$_3$/s

Flowrate, kg/s

Boiler
Scrubber
Material Recycle Pinch Diagram for the AN Example
$12 \times 10^{-6} = 5.0 \times (14.0 - \text{target composition})$

Target (intercepted) composition of ammonia in off-gas condensate = 11.6 ppm ~ 12 ppm

Material Recycle Pinch Diagram for the AN Example
To use minimum fresh water, start with sources closest to the sink. First distillation bottoms. Then off-gas condensate.
The flowrate resulting from combining these two sources (5.8 kg/s) is sufficient to run the scrubber. However, its ammonia composition as determined by the lever-arm principle \[
\frac{5.0 \text{ kg} \ / \ \text{s} \cdot 14 \ \text{ppm NH}_3 + 0}{5.8 \text{ kg} \ / \ \text{s}} = 12 \ \text{ppm NH}_3
\]
which lies outside the zone of permissible recycle to the scrubber!!!
Can’t recycle all off-gas condensate.
What is maximum recycle from off-gas condensate?

Constraint allows reduction of scrubber feed flowrate from 6.0 to 5.8 kg/s

Recycled flowrate of offgas condensate*14
+ 0.8*0.0 + Fresh*0.0 = 5.8*10

→ maximum flowrate of the off-gas condensate to be recycled to the scrubber is 4.1 kg/s

and the flowrate of fresh water is 0.9 kg/s (5.8 - 0.8 - 4.1).
Therefore, direct recycle can reduce the fresh water consumption (and consequently the influent to biotreamtment) by 5.8 – 0.9 = 4.9 kg/s.
The primary cost of direct recycling is pumping and piping. Assuming that the TAC for pumping and piping is $80/(m.yr) and assuming that the total length of piping is 600 m, the TAC for pumping and piping is $48,000/year.

After Direct Recycle:
Fresh water reduction = 6.0 - 0.9 = 5.1 kg/s
Still, 7.2 - 5.1 = 2.1 kg/s to go
Next, need to spend capital cost
Next, we include **interception**

In order to eliminate fresh water from the scrubber, what should be the composition of ammonia in the off-gas condensate?

\[
\frac{(5.0 \text{ kg/s}) \cdot y^t \text{ ppm NH}_3}{5.8 \text{ kg/s}} + 0 = 10 \text{ ppm NH}_3
\]

\[\text{i.e. } y^t = 12 \text{ ppm.}\]

⇒ need to intercept off-gas condensate to reduce ammonia content from \(y^s=14\) ppm to \(y^t=12\) ppm
Separation Unit:

TAC for the separation system is $119,000/yr.
As a result of minor process changes, segregation, interception and recycle, we have eliminated the use of fresh water in the scrubber leading to a reduction of fresh water consumption (and influent to biotreatment) by 6.0 kg/s.

We still have $7.2 - 6.0 = 1.2$ to go (related to steam jet ejector)
ALTERNATIVES TO STEAM JET EJECTOR

- Replacement of the steam-jet ejector with a vacuum pump. The operating cost of the ejector and the vacuum pump are comparable. Annualized fixed cost of the pump is $15,000/year.
- Operating the column under atmospheric pressure ➔ No steam. A simulation study is needed to examine the effect of pressure change.
- Relaxing the requirement on BFW quality to few ppm’s of ammonia and AN.
Optimum Solution

Reactor

- O₂
- NH₃
- C₃H₆

Distillation Column

- Tail Gases to Disposal
- Vacuum Pump

Scrubber

- Tail Gases to Disposal

Decanter

- Aqueous Layer

Adsorption Column

- Resin

Aqueous Layer

- Resin

Bottoms

- 0 ppm NH₃
- 0.1 kg AN/s
- 0.7 kg H₂O/s

Tail Gases to Disposal

- AN to Sales

Wastewater to Biotreatment

- 25 ppm NH₃
- 0.4 kg AN/s
- 4.8 kg H₂O/s
Impact diagrams (Pareto charts) for the reduction in wastewater and the associated TAC

Impact

Cost

Impact in Flowrate of Terminal Wastewater, kg/s

Total Annualized Cost, 1000$/yr

Segregation and Direct Recycle

Interception

Sink/Generator Manipulation

0.0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0

0.0 200 400 600 800

0.0 50 100 150 200
MERITS OF IDENTIFIED SOLUTION

- Acrylonitrile production has increased from 3.9 kg/s to 4.6 kg/s which corresponds to an **18% yield enhancement for the plant**. For a selling value of $0.6/kg of AN, the additional production of 0.7 kg AN/s can provide an annual revenue of **$13.3 million/yr**!

- **Fresh-water usage** and influent to biotreatment facility are decreased by 7.2 kg/s. The value of fresh water and the avoidance of treatment cost are additional benefits.

- **40% Debottlenecking**: Influent to biotreatment is reduced to 40% of current level. Therefore, the **plant production can be expanded 2.5 times** the current capacity before the biotreatment facility is debottlenecked again.

Superior solution to the installation of an additional biotreatment facility!
OBSERVATIONS

- **Target** for debottlenecking the biotreatment facility was determined *ahead* of design.
- Then, systematic tools were used to generate optimal solutions that realize the target.
- Next, an analysis study is needed to refine the results “big picture first, details later”.
- Unique and fundamentally different approach than using the designer’s subjective decisions to alter the process and check the consequences using detailed analysis.
- It is also different from using simple end-of-pipe treatment solutions. Instead, the various species are optimally allocated throughout the process.
- Objectives such as yield enhancement, pollution prevention and cost savings can be simultaneously addressed.

AND YOU CAN (AND SHOULD) TRY IT!
A process is an integrated system and must be treated as such.

Paradigm shift from end-of-pipe treatment to integrated process solutions.

Targeting for the whole system ahead of detailed design.

Systematic mass integration tools for recycle, reuse, separation, and modification.

Mass integration: Systematic, insightful, and cost effective.

CONCLUSIONS