



NASS INTEGRATION ND POLLUTION PREVENTION

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Ref. El-Halwagi, M. M., "Pollution Prevention through Process Integration: Systematic Design Tools", Academic Press (1997)



OBSERVATIONS

- > <u>Numerous</u> alternatives
- > Intuitively <u>non-obvious</u> solutions
- Focus on <u>root causes</u> not symptoms, must go to heart of process
- Need a systematic methodology to extract optimum solution
- Process must be treated as an <u>integrated</u> 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 <u>Process Synthesis and</u> <u>Integration + Optimization</u>:

You will learn the fundamentals and applications of process synthesis, integration, and optimization⁶

Process Design = <u>Process Synthesis + Process Analysis</u>



PROCESS INTEGRATION

A holistic approach to process design and operation that emphasizes the <u>unity</u> of the process and optimizes its design and operation



Mass-Energy Matrix of a Process

PROCESS INTEGRATION = Energy MASS INTEGRATION + ENERGY INTEGRATION Process

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 throughout₀ 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 <u>AHEAD</u> 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)



We will learn:

- \Rightarrow How to identify best achievable pollutionprevention targets for a process <u>WITHOUT</u> detailed calculations.
- ⇒How to <u>systematically</u> reach the target at minimum cost?
- \Rightarrow How to determine optimal stream rerouting?
- ⇒ How to place additional units and determine their performance?
- \Rightarrow How to understand the BIG picture of a process and use it to reduce waste from <u>any</u> plant?

OVERALL MASS TARGETING WHAT IS TARGET FOR MINIMUM AA FRESH PURCHASE?



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OVERALL MASS TARGETING



How to benchmark performance for mass objectives of the whole process <u>ahead of detailed design?</u>

- 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:

Adjust design and operating variables
 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}= minimize f (manipulated design variables, manipulated operating variables)



Overall Mass Balance after Fresh Reduction

$$T^{AFR} = F^{AFR} + Net_G^{BMI}$$
¹⁹

2. Maximize Recycle to Reduce Fresh Usage



Overall Mass Balance after Fresh Reduction

 $T^{AFR} = F^{AFR} + Net_G^{BMI}$

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

What is maximum recyclable load?

Example 1: Reduction of Terminal Losses or Discharge of Waste 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^{max} = argmin {F^{AFR}, T^{AFR}}



Target After Mass Integration (AMI)

Example 2: Reduction of Terminal Losses or Discharge of Waste for <u>Variable Generation</u>

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



When generation and fresh cannot be decoupled, see Noureldin, M. B. and M. M. El-Halwagi, 1999, "Interval-Based Targeting for Pollution Prevention via Mass Integration", Comp. Chem. Eng., 23, 1527-1543. **Example 2: Reduction of Terminal Losses or Discharge of Waste** with Variable Generation

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 $T^{AGMIN} = F^{BMI} + Net G^{MIN}$ **Example 2: Reduction of Terminal Losses or Discharge of Waste** with Variable Generation

Adjust Design and Operating Variables to Reduce Fresh

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



Overall Mass Balance after Fresh Reduction and Minimization of Generation

$$T^{AGMIN, AFR} = F^{AFR} + Net G^{MIN}$$

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^{max} = argmin {F^{AFR}, T^{AGMIN, AFR}}



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.)



CASE STUDY I: MINIMIZE AA FRESH PURCHASE IN VAM PROCESS



Overall AA Balance Before Mass Integration



Targeting for Minimum Purchase of Fresh AA



EXAMPLE II: MINIMIZE WATER DISCHARGE IN TIRE-TO-FUEL PROCESS



OVERALL WATER BALANCE BEFORE MASS INTEGRATION



Minimize generation of targeted species

 $W_{rxn} = 0.152 + (5.37 - 7.84x10^{-3} T_{rxn}) e^{(27.4 - 0.04Trxn)}$



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

$$G_1 = 0.47 e^{-0.009Pcomp}$$

$$70 \le P_{comp}(atm) \le 90$$

Set
$$P_{comp} = 90$$
 atm $G_1 = 0.47 e^{-0.009*90} = 0.2$

• Minimum water for shredding $G_1 = 0.2 \text{ kg/s}$

 $W_3 = 0.4 G_1 = 0.08 kg/s$



OVERALL WATER BALANCE AFTER MASS INTEGRATION



WATER TARGETING



ACHIEVING THE TARGET Mass Integration Strategies



PRACTICE EXERCISE

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



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_i, and an inlet composition of a targeted species, z_i, 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



Composition

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

Known Constraints



From process model:

$$z_{j+1}^{in} = 2 z_j^{in}$$

$$0.03 \le z_j^{in} \le 0.04$$
 $0.06 \le z_{j+1}^{in} \le 0.08$

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

LEVER-ARM RULES



LEVER-ARM RULES



LEVER-ARM RULES FOR FRESH USAGE



SINK COMPOSITION RULE



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

SINK COMPOSITION RULE



What should be feed composition to sink to minimize fresh usage? <u>Sink Composition Rule:</u> 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.

SOURCE PRIORITIZATION RULE



<u>Source Prioritization Rule:</u> 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



Process Before Recycle

Recycle Alternatives to Reduce Terminal Load





Effective Recycle From Terminal



Effective Recycle From Terminal and Intermediate

Example: Minimization of AA Usage in VAM Process by Direct Recycle



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Source-Sink Mapping Diagram for AA Example



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For S₁, R₁ has shortest AA arm



Acid Tower Continued



Absorber I Calculations



SOLUTION TO AA MINIMIZATION PROBLEM



ALTERNATE SOLUTION TO AA MINIMIZATION PROBLEM

Start with S_2 and use R_1 for shortest arm. \mathbf{R}_1 1,400 kg/hr S_1 4,080 kg/hr **Acid Tower** 6,120 kg/hr \mathbf{R}_2 9,100 kg/hr S_2 236 kg/hr Abs. I /3,464 kg/hr **Fresh AA** 9,584 kg/hr Waste 4,784 kg/hr

ALTERNATE SOLUTION TO AA MINIMIZATION PROBLEM

Split R_1 between two sinks.



Same target, infinite implementations. Need a targeting procedure before detailed implementation

MATERIAL RECYCLE PINCH DIAGRAM

Sink Composite Diagram



Source Composite Diagram



Sink Composite Must Lie Above Source Composite



Integrating Source and Sink Composites



Flowrate

Material Recycle Pinch Diagram



1*Ref.:* El-Halwagi, M. M., F. Gabriel, and D. Harell, "Rigorous Graphical Targeting for Resource Conservation via Material Recycle/Reuse Networks", Ind. Eng. Chem. Res., 42, 4319-4328 (2003)



Infeasible Recycle (too much integration)



Flowrate

Material Recycle Pinch Diagram for Impure Fresh





Effect of Interception



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Effect of Interception



Flowrate

Example Revisited: Minimization of AA Usage in VAM Process



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PRACTICE EXERCISE II: FOOD PROCESSING FACILITY



Two source (Condensate I and II), Two Sinks (Washer and Scrubber)

Sink Data for the Food Processing Example

Sink	Flowrate kg/hr	Maximum Inlet Mass Fraction	Maximum Inlet Load, kg/hr
Washer	8,000	0.03	240
Scrubber	10,000	0.05	500

Source Data for the Food Processing Example

Source	Flowrate kg/hr	Maximum Inlet Mass Fraction	Maximum Inlet Load, kg/hr
Condensate I	10,000	0.02	200
Condensate II	9,000	0.09	810



Critique project proposed by engineer: Recycle Condensate I to Scrubber → Reduce fresh water to 8,000 kg/hr (down from 18,000 kg/hr)



GRAPHICAL TECHNIQUES FOR MASS INTEGRATION 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

Ref. El-Halwagi, M. M., "Pollution Prevention through Process Integration: Systematic Design Tools", Academic Press (1997)

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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:

Mass integration

- Determine performance <u>targets</u> 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



(a) Overall Water Balance Before Mass Integration

ACRYLONITRILE PLANT



Target for minimum wastewater discharge = 12.0 - 7.2 = 4.8 kg/sTarget for minimum water usage = 0.0 kg/s ⁸³



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 86

Mass Integration Strategies



Source-Sink Mapping Diagram for Direct Recycle



Composition of Targeted Species

Integrating Source and Sink Composites



Flowrate

Effect of Interception



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Interception



Flowrate

DETAILING MASS INTEGRATION STRATEGIES



Ref. El-Halwagi, M. M., "Pollution Prevention through Process Integration: Systematic Design Tools". Academic Press (1997

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



(a) Overall Water Balance Before Mass Integration

ACRYLONITRILE PLANT



Target for minimum wastewater discharge = 12.0 - 7.2 = 4.8 kg/sTarget for minimum water usage = 0.0 kg/s ⁹⁵



Constraints and Data

Scrubber:

- 5.8 < Feed flowrate of scrubbing agent (kg/s) < 6.2
- 0.0 < 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



Source-Interception-Sink Representation



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

Direct-Recycle Alternatives



Note: No recycle to boiler because of 0.0 ppm constraints



Sink Composite Diagram for the AN Example



Source Composite Diagram for the AN Example



Material Recycle Pinch Diagram for the AN Example



Material Recycle Pinch Diagram for the AN Example

Source-Sink Mapping Diagram



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 $(5.0 \text{ kg} / \text{ s}).14 \text{ ppm} \text{ NH}_3 + 0 = 12 \text{ ppm} \text{ NH}_3$

which lies outside the zone of permissible recycle to the scrubber!!!! Can't recycle all off-gas condensate.



 \rightarrow 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?

$$\frac{(5.0 \text{ kg / s}). \text{ y}^{\text{t}} \text{ ppm } \text{ NH}_{3} + 0}{5.8 \text{ kg / s}} = 10 \text{ ppm } \text{ NH}_{3}$$

i.e. $y^t = 12 ppm$.

→ need to intercept off-gas condensate to reduce ammonia content from $y^s=14$ ppm to $y^t=12$ ppm



. Interception and Recycle Opportunities for the AN Case Study

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) 113

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** \rightarrow 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



Impact diagrams (Pareto charts) for the reduction in wastewater and the associated TAC



Impact

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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!

