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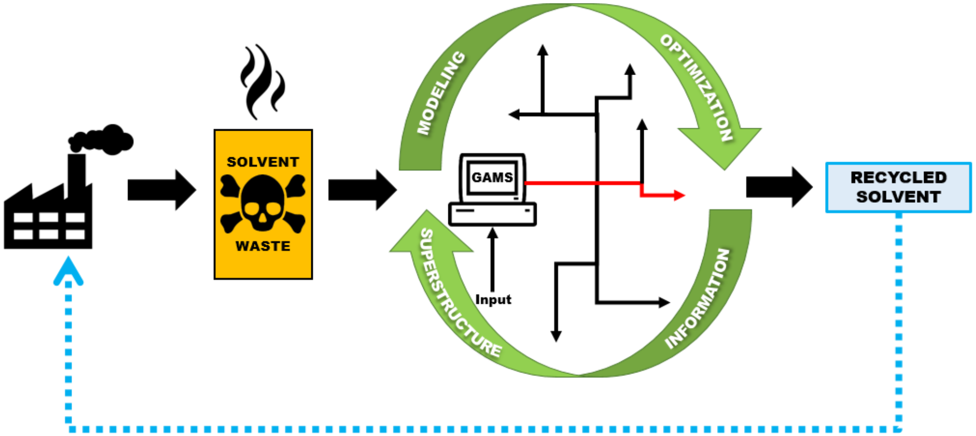

Synthesis and Systematic Evaluation of Solvent Recovery Pathways

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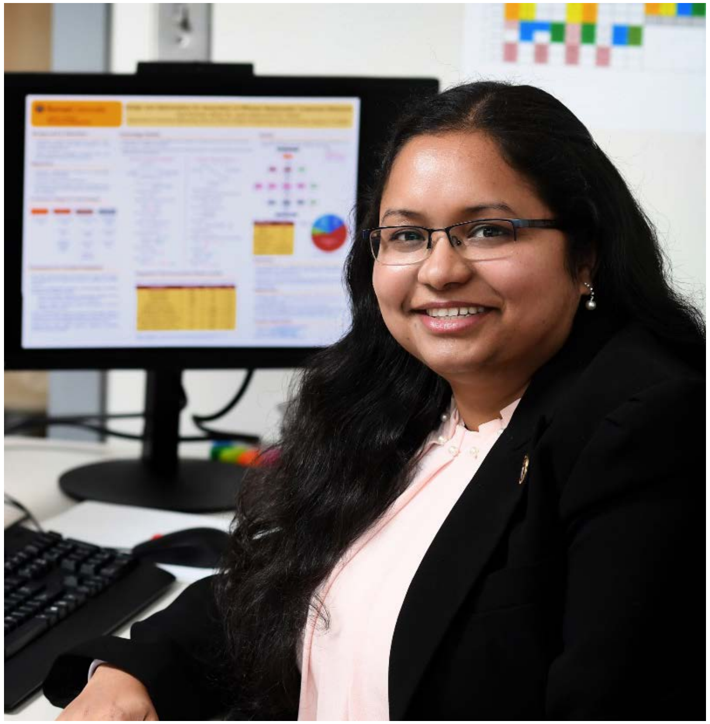
Speaker



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Education & Experience:

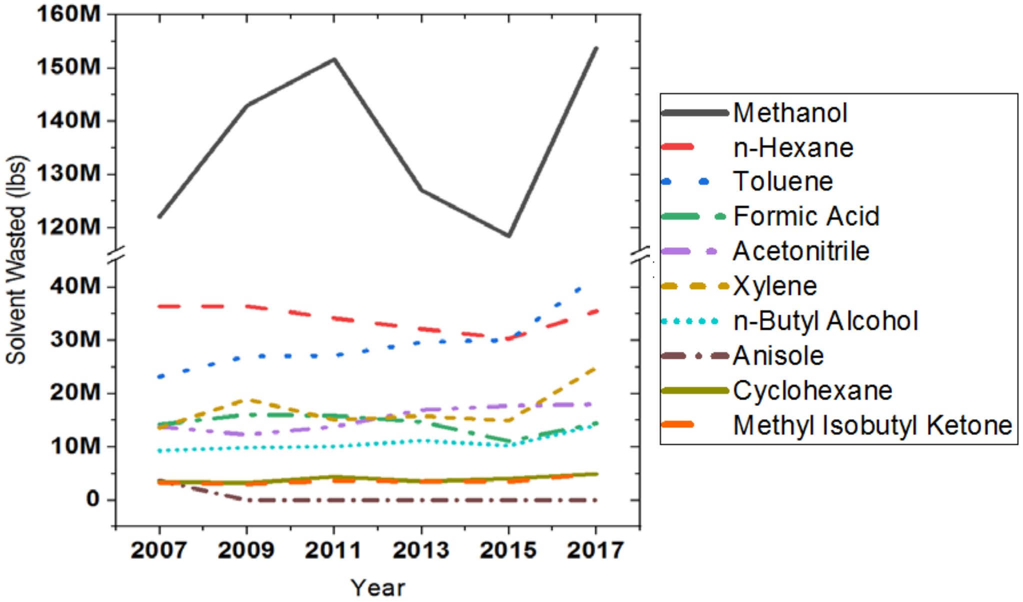
- Postdoc, University of Delaware (03/2017 to 08/2017)
- Postdoc, University of Wisconsin-Madison (01/2015-03/2017)
- Ph.D., University of Illinois at Chicago (UIC), USA, 2014
- M.Tech. Chemical Engineering., IIT Bombay, India, 2010
- B.Tech. Chemical Engineering, LIT, Nagpur, India, 2008

Dr. Yenkie's research focuses on leveraging Process Systems Engineering (PSE) principles in the areas of environmental sustainability and healthcare. She is a PI on the US EPA funded project on 'Roadmap for Solvent Recovery in Industrial Manufacturing' (2018-2020). This project aims to develop a universal framework for optimal solvent recovery and a computational tool that can be used by pharmaceutical and other manufacturing facilities.

At Rowan University, she teaches Process Dynamics and Control, Thermodynamics and Applied Optimization. Her teaching methodology to incorporate computational tools for explaining theoretical concepts led to her selection as one of the 20 Outstanding Young Chemical Engineering Educators by the CACHE (Computer Aids for Chemical Engineering) Committee (2019).

Expanding Chemical Market

- Global chemical industry is projected to double in production, capacity, and sales between 2017 – 2030[1]
- Harmful chemical emission from process inefficiencies
- Ineffective mitigation plan to reduce solvent waste



The Chemical Waste Trend for Top Ten Wasted Substances Between 2007 and 2017 from the US EPA's Toxic Release Inventory[1]

1. United Nations Environment Programme, "Global Chemicals Outlook II - From Legacies to Innovative Solutions - Synthesis Report (2019),"
2. O. US EPA, "TRI Data and Tools," US EPA, 03-Mar-2013.

Current State of Waste Handling

- Primary Methods[1]
  - On-site solvent disposal – Direct release into air, water, or injection well
  - Off-site solvent disposal – Third party, sold to other industries
  - Incineration – Decomposes organic materials with high efficiency

    - Cost up to 1/3 of original price of purchased solvent

    - Releases up to 6.7 kg CO_2 / kg organic compounds

Chemical Waste

https://www.hazardouswasteexperts.com/is-your-business-a-hazardous-waste-generator-epa-watching/

Incineration

https://www.torontoenvironment.org/tags/incineration

- Solvent recovery – improves greenness and sustainability of chemical processes[2]

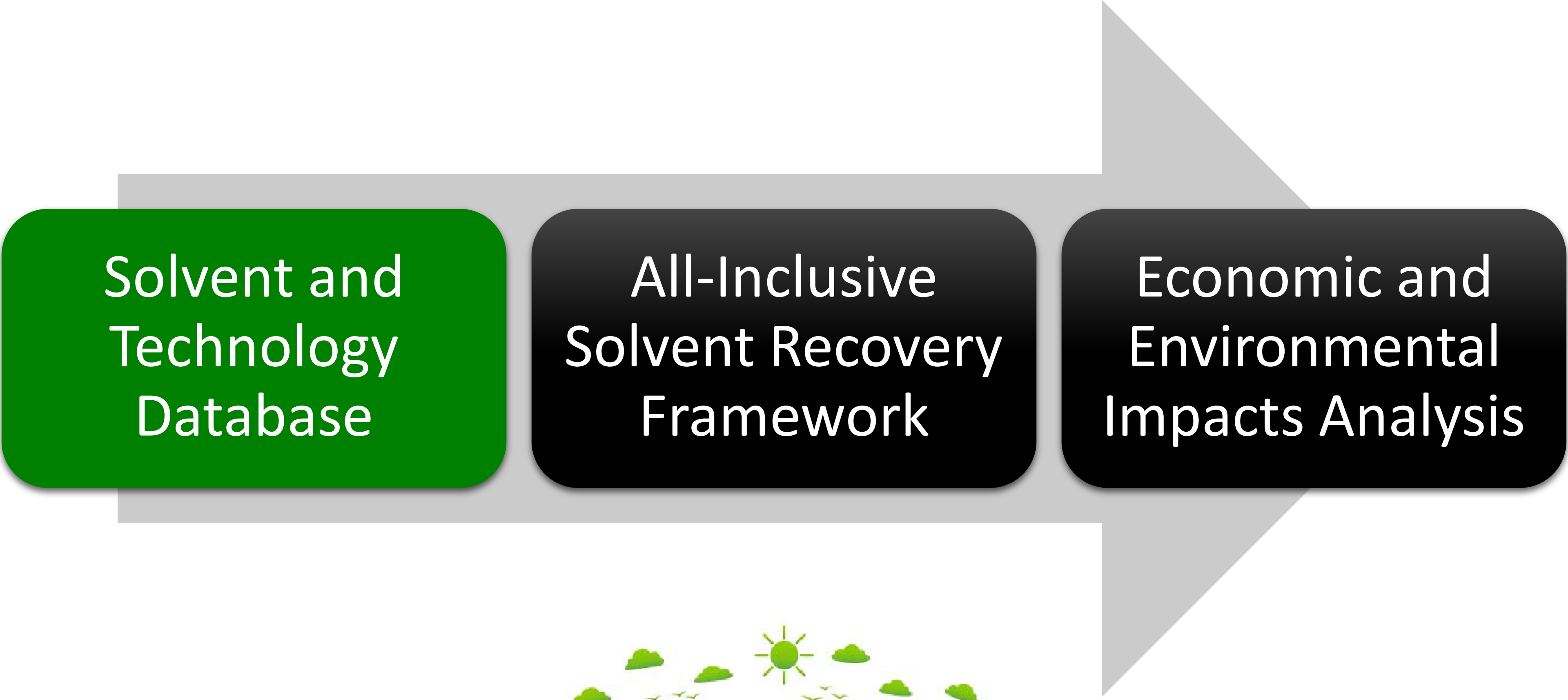
1. C. S. Slater, M. J. Savelski, W. A. Carole and D. J. Constable, "Solvent Use and Waste Issues," in Green Chemistry in the Pharmaceutical Industry, WIley, 2010, 49-82
2. C. S. Slater, M. Savelski, G. Hounsell, D. Pilipauskas, and F. Urbanski, “Green design alternatives for isopropanol recovery in the celecoxib process,” Clean Technol. Environ. Policy, vol. 14, no. 4, pp. 687–698, Aug. 2012

Optimizing Solvent Recovery

How do we make the design of solvent recovery process more efficient?

- Solvent and Technology Database
- All-Inclusive Solvent Recovery Framework
- Economic and Environmental Impacts Analysis

Optimizing Solvent Recovery



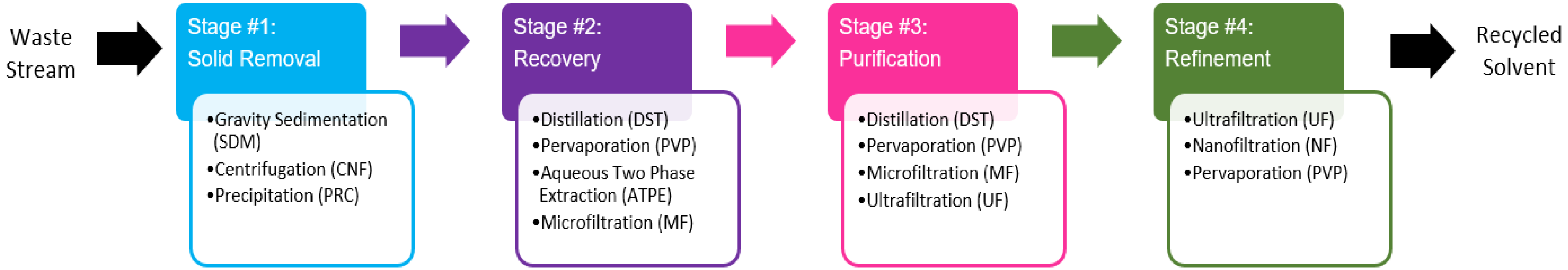
Solvent and Technology Database

All-Inclusive Solvent Recovery Framework

Economic and Environmental Impacts Analysis

Designing a Recovery Process

- Create a database of information
  - Many possible chemicals involved in a solvent waste stream
  - Multiple separation processes to consider
- Number of possible pathways dependent on waste stream composition
- Additional stages of separation added as required to meet purity requirements



Waste Stream

Stage #1: Solid Removal

- Gravity Sedimentation (SDM)
- Centrifugation (CNF)
- Precipitation (PRC)

Stage #2: Recovery

- Distillation (DST)
- Pervaporation (PVP)
- Aqueous Two Phase Extraction (ATPE)
- Microfiltration (MF)

Stage #3: Purification

- Distillation (DST)
- Pervaporation (PVP)
- Microfiltration (MF)
- Ultrafiltration (UF)

Stage #4: Refinement

- Ultrafiltration (UF)
- Nanofiltration (NF)
- Pervaporation (PVP)

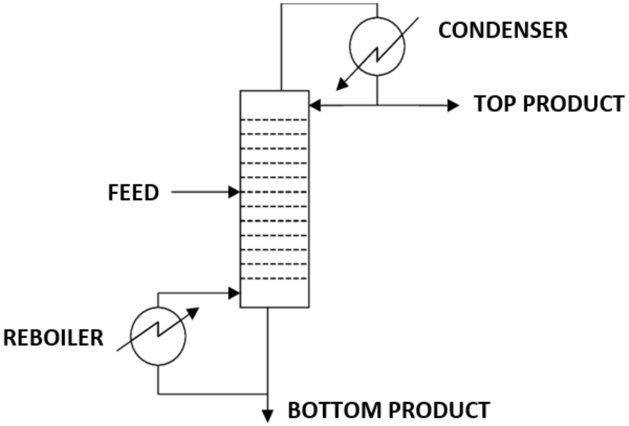
Recycled Solvent

Building a Database

Solvent	MW (g/mol)	Density (kg/m^3)	Physical State	MP (°C)	BP (°C)	Solubility in water (g/100g)	Toxicity (potential side effects)
Methanol	32.042	792	Liquid	-97.6	64.7	Miscible	Dizziness, nausea, blurred vision, vomiting, GI bleeding
Acetone	58.08	784	Liquid	-94.8	56	Miscible	Skin/eye irritant; dizziness, blurred vision, headaches
Benzene	78.114	876	Liquid	5.5	80.1	0.18	Carcinogen

Technology	Principle/ Driving Force	Specifications and Important Conditions
	Membrane Processes	
Membranes	Particle/molecular size Sorption/Diffusion Pressure	Pore size, Mol. wt. cut-off, average flux, Pressure gradient, type of membranes – MF, UF, NF and RO
Pervaporation	Sorption/Diffusion Partial pressure	Heat of vaporization, pressure gradient, average flux, membrane selectivity

Example Model: Distillation



Molar flow rates:

$$F_{j,k} = \frac{M_{j,k}}{MW_k}$$

Component balance:

$$\sum_{j \in Jini} F_{j,k} = \sum_{j \in Jouti} F_{j,k}$$

Minimum number of stages with Fenske's equation:

$$N_{min} \log(\alpha_B) = \log[\left(\frac{Xm_{2,B}}{Xm_{2,A}}\right)\left(\frac{Xm_{3,A}}{Xm_{3,B}}\right)]$$

Underwood's variable:

$$(1-q) = \sum_{k \in K^{dst}} \frac{\alpha_k Xm_{1,k}}{\alpha_k - U_v}$$

Assume feed is a saturated liquid (q=1):

$$\sum_{k \in K^{dst}} \frac{\alpha_k Xm_{1,k}}{\alpha_k - U_v} = 0$$

Minimum reflux ratio:

$$R_{min} = \sum_{k \in K^{dst}} \frac{\alpha_k Xm_{2,k}}{\alpha_k - U_v} - 1$$

Reflux ratio:

$$R = 1.3 R_{min}$$

Number of stages:

$$0.6N = N_{min}$$

Number of actual stages:

$$N_{act} = \frac{N}{\eta stage}$$

Costing variable of column;

$$QS_{dst} = \frac{\pi}{4} D^2 H$$

Optimizing Solvent Recovery

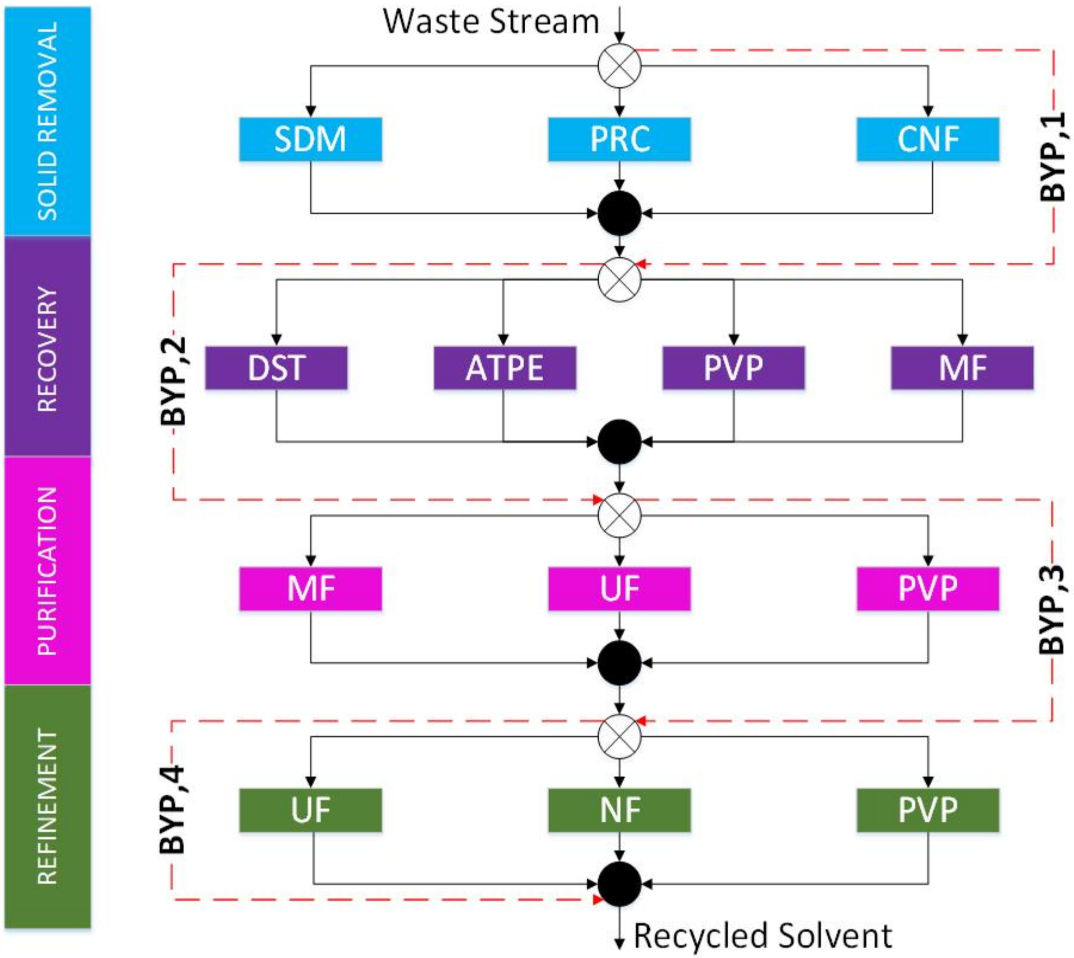
Solvent and Technology Database

All-Inclusive Solvent Recovery Framework

Economic and Environmental Impacts Analysis

Generalized Solvent Recovery Framework

- Superstructure-based
  - Considers multiple options to reach a desired goal
  - Advantage over one-by-one approach
- Stages
  - Solid Removal
    - SDM: Sedimentation
    - PRC: Precipitation
    - CNF: Centrifugation
  - Recovery, Purification, and Refinement
    - DST: Distillation
    - ATPE: Aqueous Two-Phase Extraction
    - PVP: Pervaporation
    - MF: Microfiltration
    - UF: Ultrafiltration
    - NF: Nanofiltration
  - Additional steps to each stage can be added for multicomponent separation



Optimizing Solvent Recovery

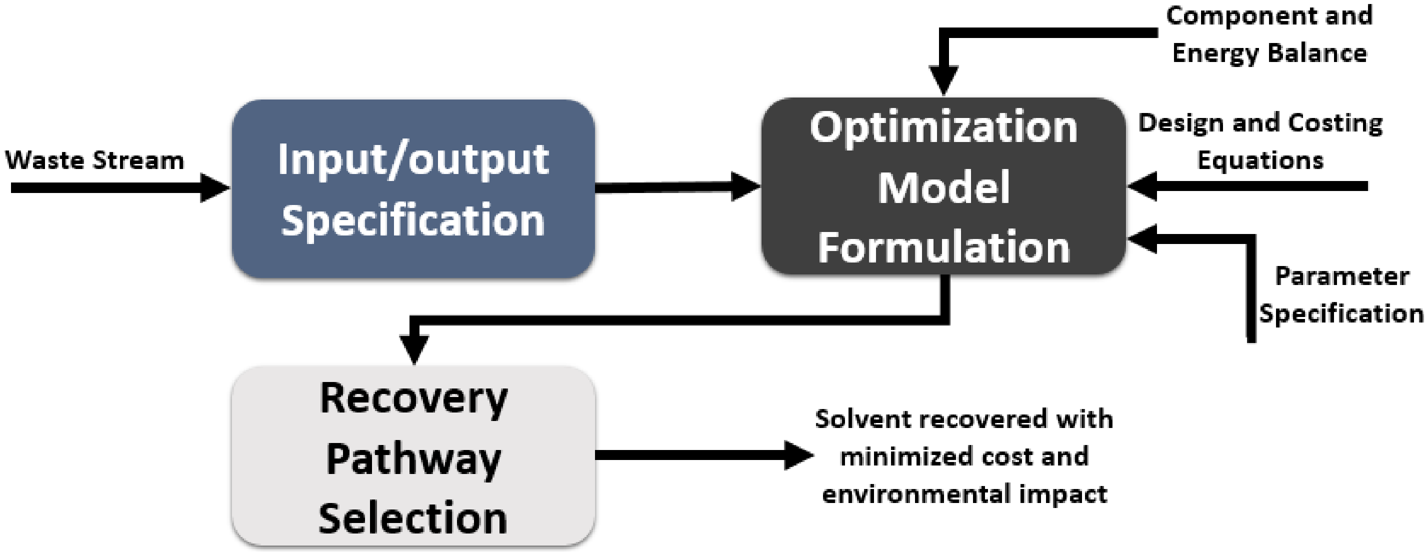
Solvent and Technology Database

All-Inclusive Solvent Recovery Framework

Economic and Environmental Impacts Analysis

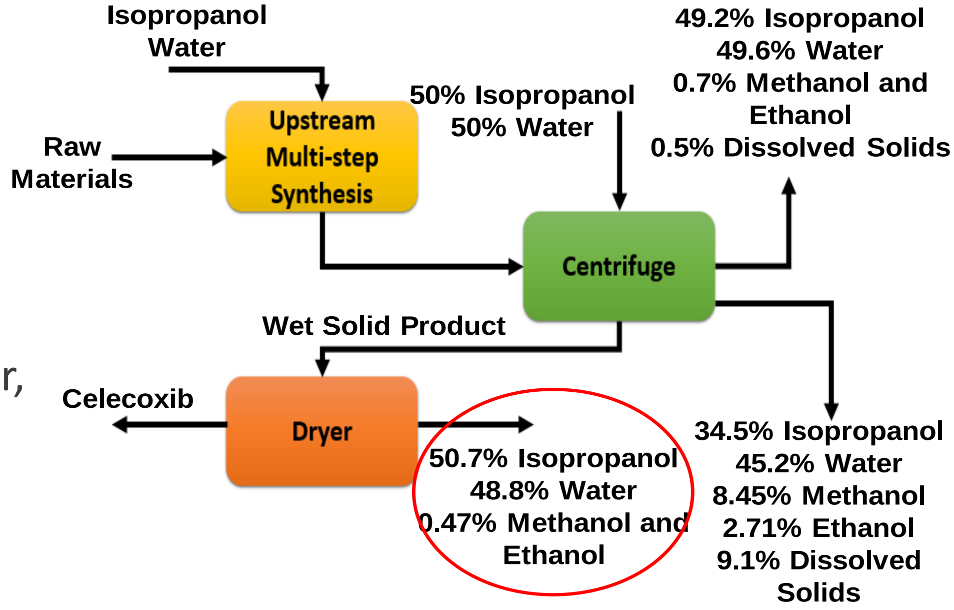
Evaluation Framework

- Mathematical models for process technology help to minimize cost and maximize process efficiency while still reaching target values for safe reuse of solvents
- Programming tools: General Algebraic Modeling Systems (GAMS)
- Solver: Branch-And-Reduce Optimization Navigator (BARON)
- Life Cycle Analysis tool: SimaPro



IPA Recovery Case Study

- Recovery of Isopropanol from a Celecoxib waste stream
  - Celecoxib – arthritic pain medication active pharmaceutical ingredient (API)
  - 510 kg/hr IPA waste
- Incineration
  - 14.51 kg steam / kg IPA
  - 0.83 kWh electricity / kg IPA
- Life Cycle Analysis
  - 2.19 kg total emissions (land, water, air)/ kg IPA waste



Isopropanol
Water

Raw Materials

Upstream Multi-step Synthesis

50% Isopropanol
50% Water

Centrifuge

49.2% Isopropanol
49.6% Water
0.7% Methanol and Ethanol
0.5% Dissolved Solids

Wet Solid Product

Dryer

Celecoxib

50.7% Isopropanol
48.8% Water
0.47% Methanol and Ethanol

34.5% Isopropanol
45.2% Water
8.45% Methanol
2.71% Ethanol
9.1% Dissolved Solids

1. C. S. Slater, M. Savelski, D. Pilipauskas, F. Urbanksi and G. Housell, "Green design alternatives for isopropanol recovery in the celecoxib process," *Clean Technologies and Environmental Policy*, vol. 14, pp. 687-698, 2012.

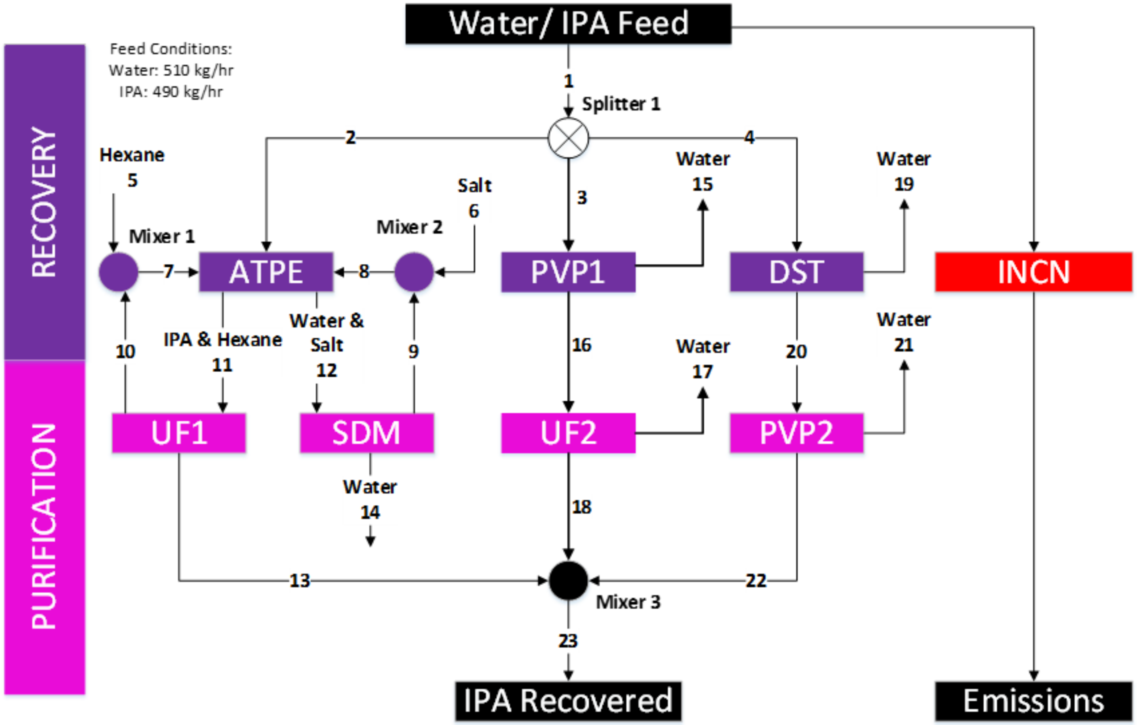
Specifications for Model Testing

- Assume trace solvents are negligible for model simplification
- Azeotrope at 80.37°C and 87.7 wt% IPA
- Solvent recovery results compared to incineration

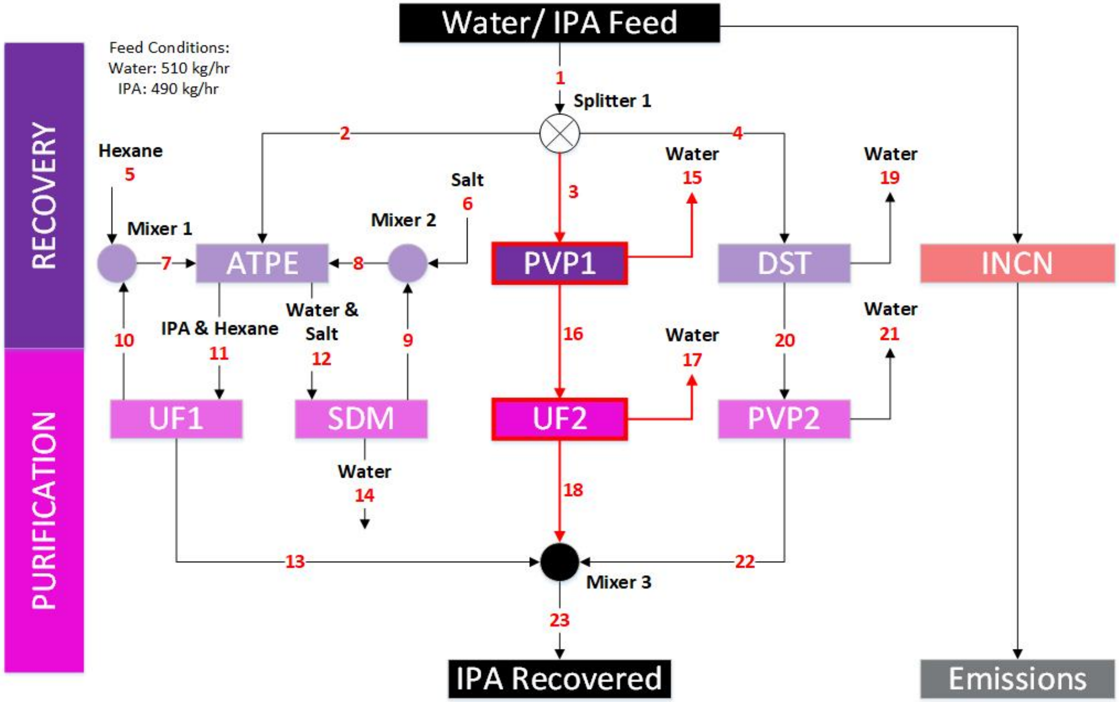
Feed Condition	Feed Rates (kg/hr)	Output Requirements
Isopropanol (51%)	510	Recovery: 99.5%
Water (49%)	490	Purity: 99%

IPA Recovery Superstructure

- 3 major pathways, 6 technologies, 23 streams
- Technologies
  - ATPE: Aqueous Two-Phase Extraction
  - PVP: Pervaporation
  - DST: Distillation
  - UF: Ultrafiltration
  - SDM: Sedimentation
  - INCN: Incineration



Optimal Recovery Path



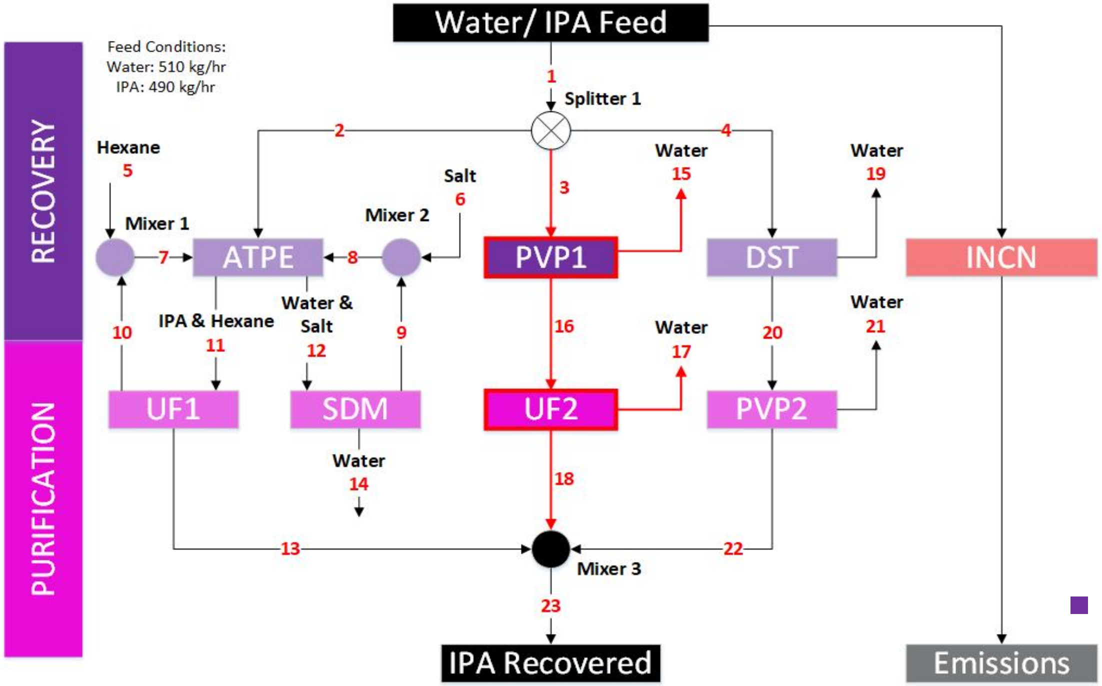
GAMS Model & Solution Statistics

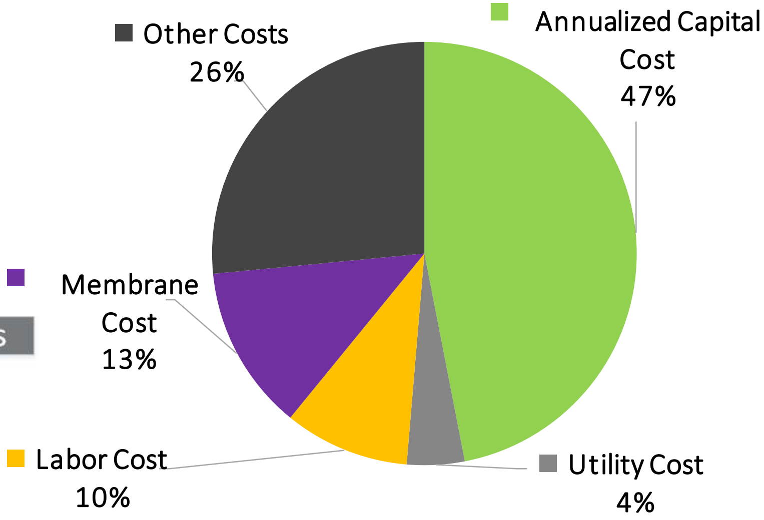
Model Statistics	Values
Equations	258
Variables	238
Discrete Variables	4
Solution Time	2.48 s

Pathways	Annualized Cost ($ million/yr)	Prices ($/kg processed)
ATPE-UF1-SDM	Infeasible	Infeasible
PVP1-UF2	**0.524**	**0.14**
DST-PVP2	0.862	0.25
Incineration	8.1	2.01

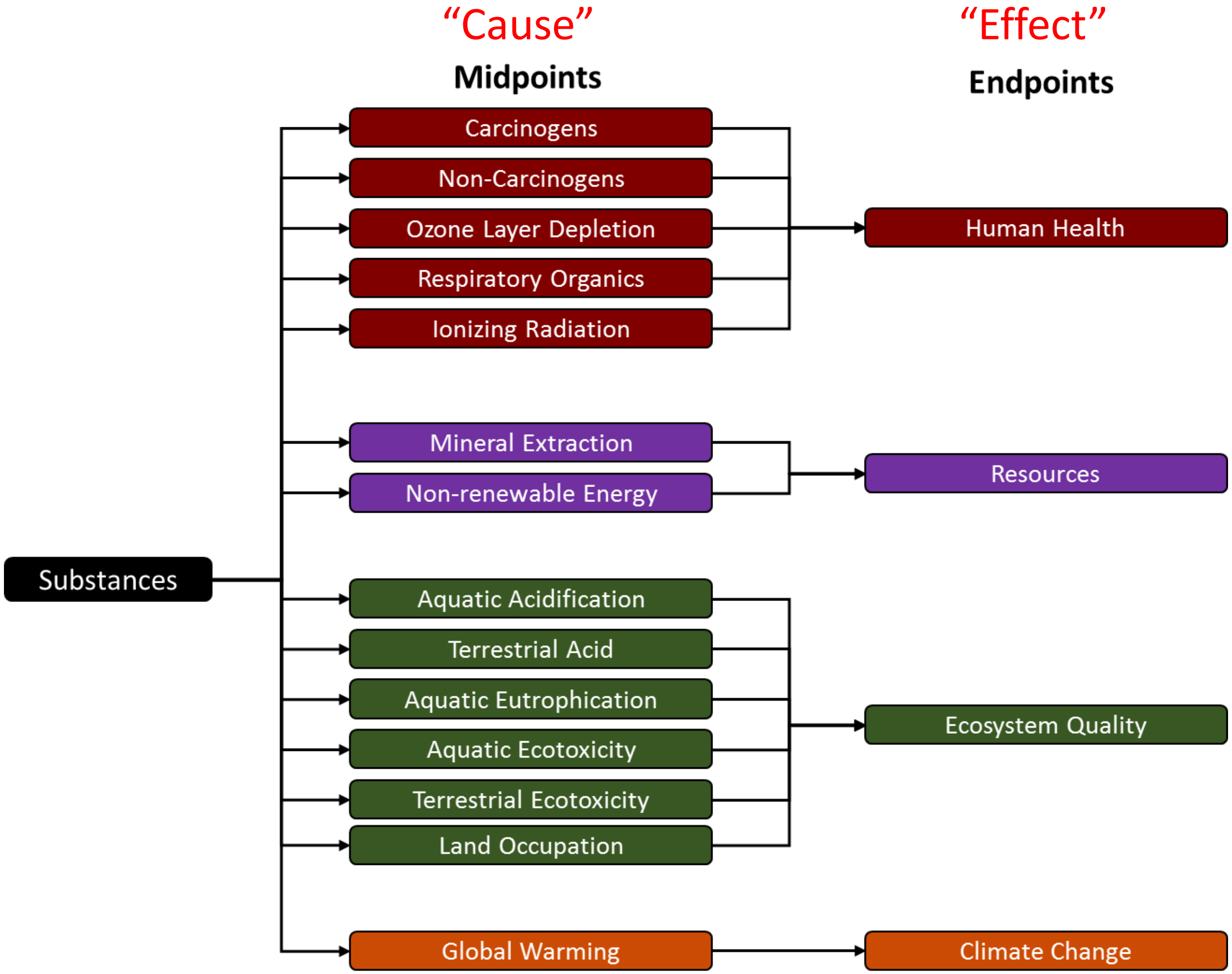
- Pervaporation followed by ultrafiltration is the best path
- Aqueous Two-Phase Extraction – infeasible at specified condition
- Incineration: not economically viable and no material recovery

Cost Breakdown of PVP-UF





Environmental Impacts Analysis



“Cause”

Midpoints

“Effect”

Endpoints

Substances

Carcinogens

Non-Carcinogens

Ozone Layer Depletion

Respiratory Organics

Ionizing Radiation

Mineral Extraction

Non-renewable Energy

Aquatic Acidification

Terrestrial Acid

Aquatic Eutrophication

Aquatic Ecotoxicity

Terrestrial Ecotoxicity

Land Occupation

Global Warming

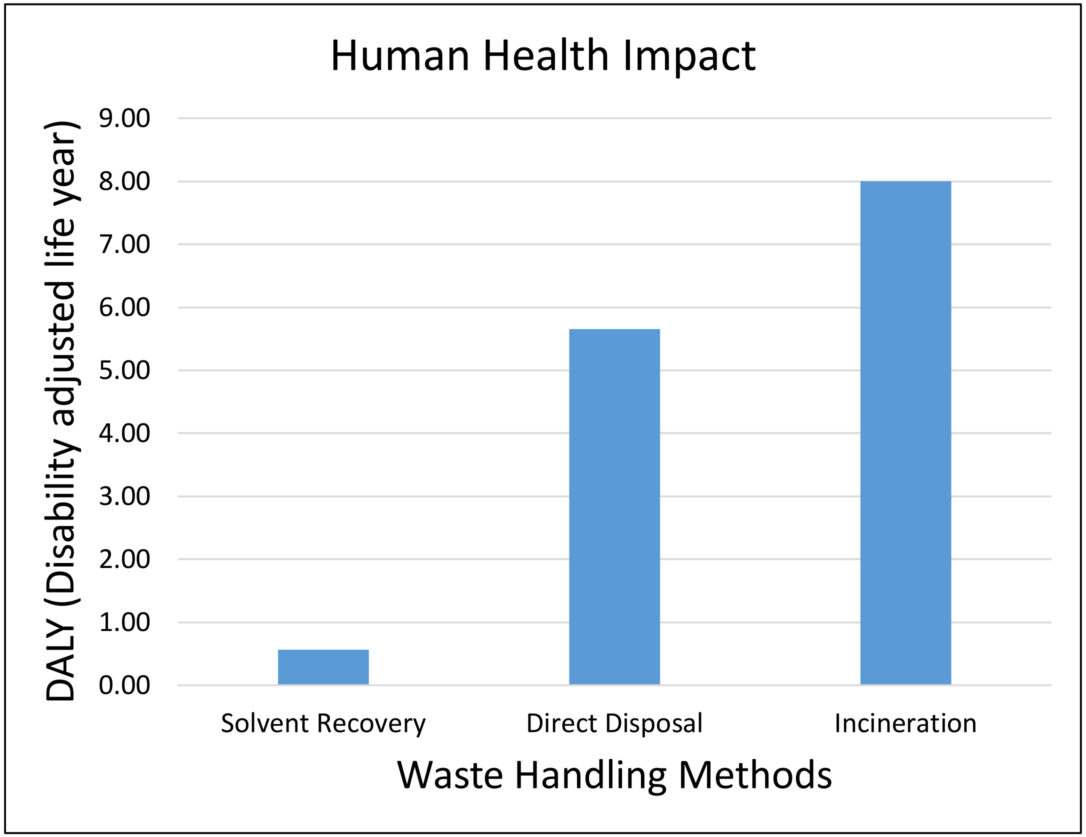
Human Health

Resources

Ecosystem Quality

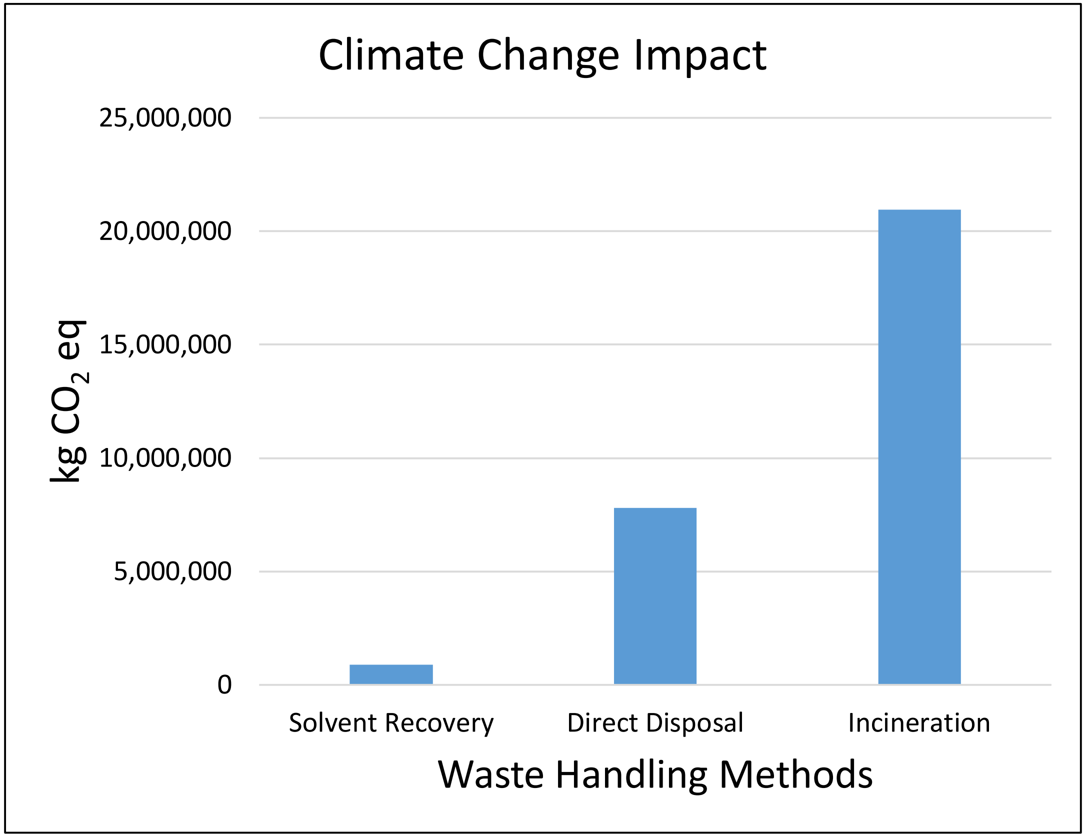
Climate Change

Human Health (DALY)



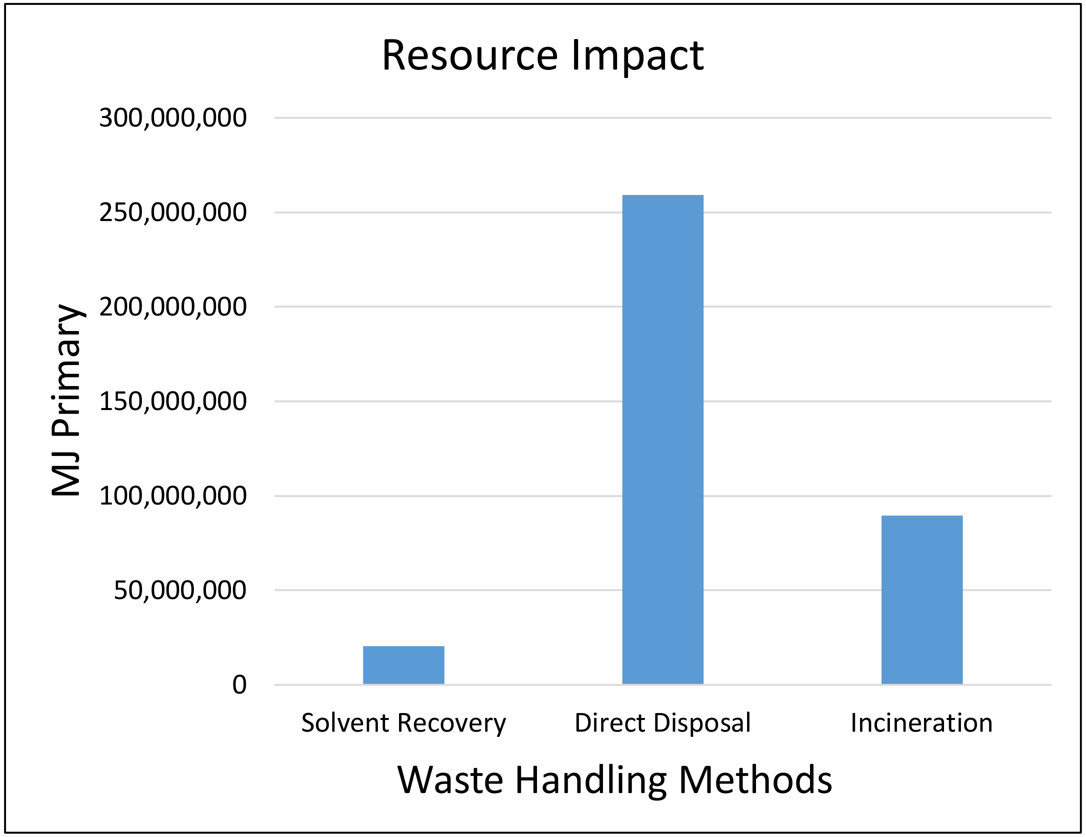
Waste Handling Method	% Difference
Direct Disposal (Base Case)	0
Solvent Recovery	164
Incineration	34

Climate Change (kg CO_2 eq.)



Waste Handling Method	**% Difference**
Direct Disposal (Base Case)	0
Solvent Recovery	158
Incineration	91

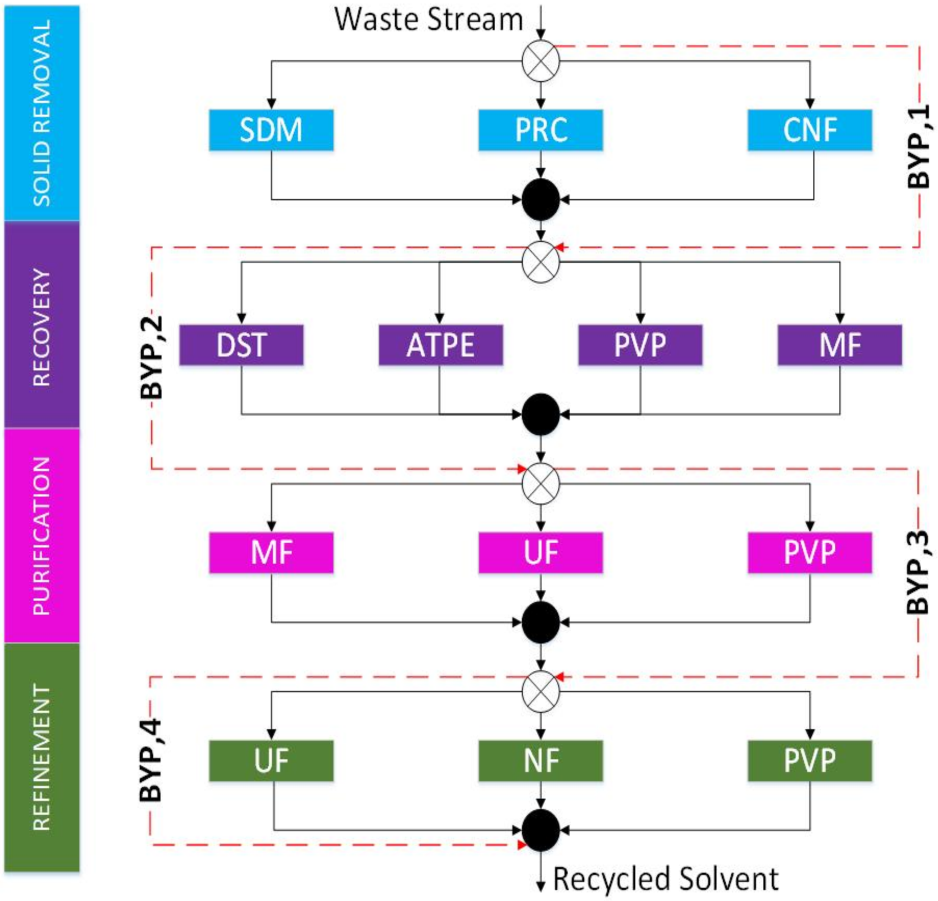
Resource



Waste Handling Method	**% Difference**
Direct Disposal (Base Case)	0
Solvent Recovery	171
Incineration	97

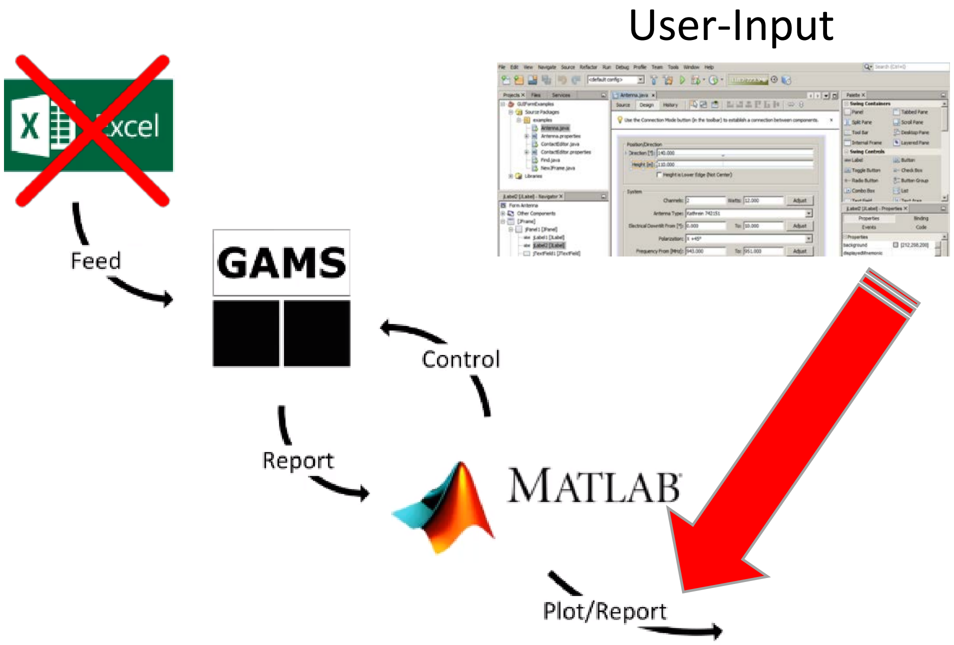
Summary

- Developed a systematic framework for comparing solvent recovery options
  - Simultaneous assessments of economic and environmental impacts
  - Additional case studies from other industries are being analyzed
- Powerful tool to enhance solvent recovery practices in industry
  - Improve process optimization
  - Reduce global solvent consumption/ waste (industrial collaboration required)



Future Work

- A user-friendly solvent recovery tool
    - Considers the optimization of solvent recovery pathways from economics and environmental impacts perspectives
    - Use the developed solvent recovery framework as a backbone
    - Does not require the user to know coding or Chemical Engineering



Current Project Team

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Co-Investigator

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Student Achievements

- Austin Lehr and Jake Stengel earned the 3rd place in Computing and Process Control (Undergraduate Poster Session) at 2019 AIChE Annual Student Conference, Orlando, FL
- They were ranked in top 5 among 149 participants in the Computing and Systems Technology (CAST) poster session at 2019 AIChE Annual Meeting, Orlando, FL
- A peer-reviewed journal paper published in Industrial & Engineering Chemistry Research

  Chea, J.D., Lehr, A., Stengel, J., Savelski, M.J., Slater, C.S., ***Yenkie, K.M.****, 2020. Evaluation of Solvent Recovery Options for Economic Feasibility through a Superstructure-Based Optimization Framework. Industrial & Engineering Chemistry Research.*

  https://doi.org/10.1021/acs.iecr.9b06725
- A peer-reviewed conference paper published in 2019 FOCAPD (Foundations of Computer-Aided Process Design) Conference, Copper Mountain, CO Proceedings.

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