Framework for Solvent Recovery, Reuse, and Recycling in Industries

John D. Chea, Stewart Slater, Mariano Savelski, and **Kirti M. Yenkie**

Department of Chemical Engineering

Henry M. Rowan College of Engineering

Rowan University, Glassboro, NJ, 08028, USA

Sustainable Design and Systems Medicine Lab

Research Group Website: https://yenkiekm.com/

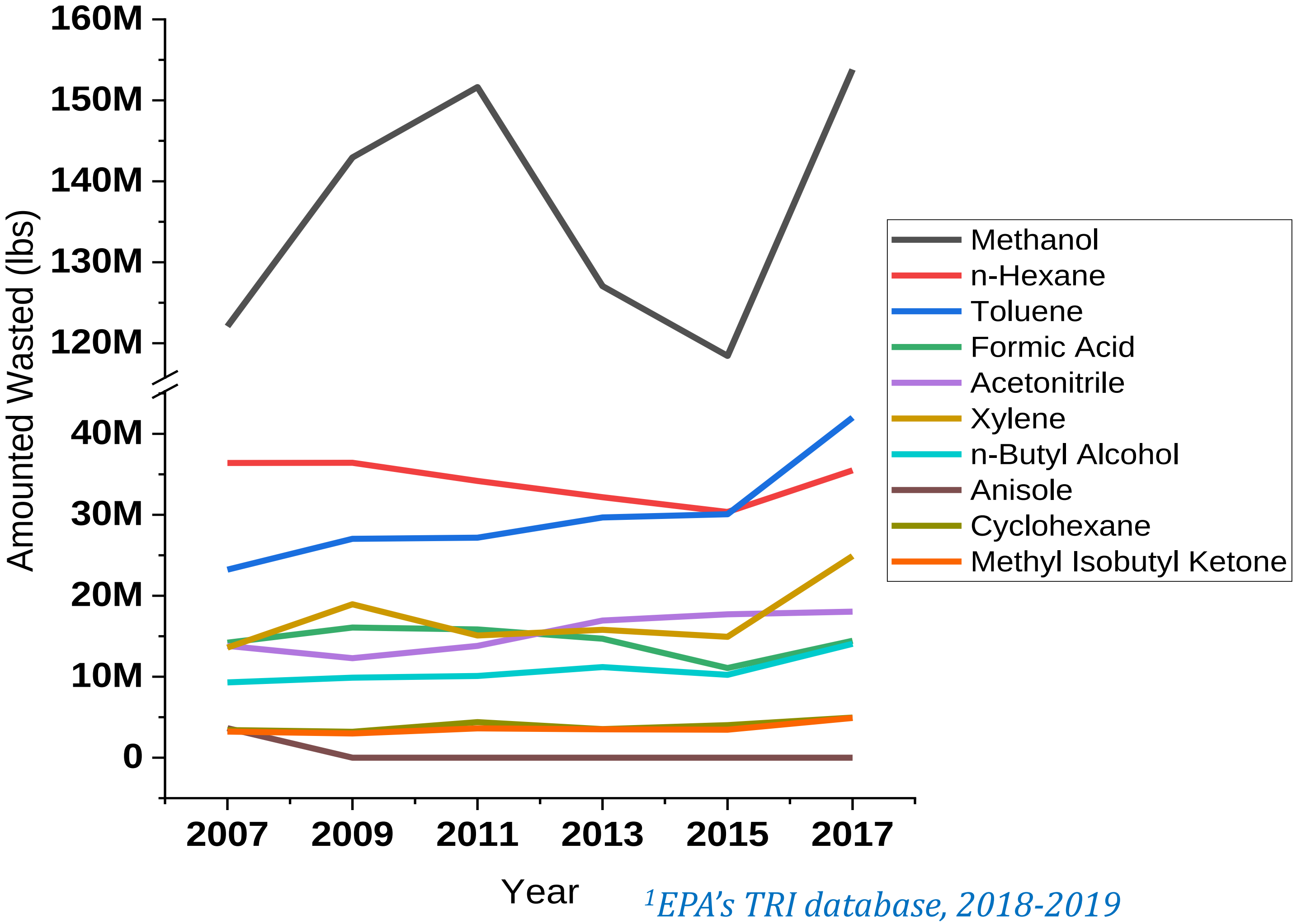
Overview

- Background on solvent use and waste
- Propose solutions for enhancing greenness and sustainability
- Example case study
- Results
- Summary
- Future work

Background

Trend of National Chemical Waste between 2007-2017[1]

Top 10 wasted chemicals and amounts



[1]*EPA's TRI database, 2018-2019*

- Rapid growth is projected in the Global Chemical Industry with production, capacity and sales almost doubling by 2030
- Growing concerns for chemical releases, wastes, safety, and environmental impact due to process inefficiencies
- Solvent recovery methods are expected to improve the greenness and sustainability of existing and future chemical processes

Industries Consuming Solvents

Industry	Solvents	Process/Application	Reference
Pharmaceutical	Isopropyl alcohol, methanol, dichloromethane, etc.	APIs, reactants, cleaning agents	(David J. C. Constable,Conchita Jimenez-Gonzalez, and Richard K. Henderson, 2007)
Adhesives and Sealants	Acetone, methyl ethyl ketone, toluene, xylene	To regulate viscosity, surface preparation and primers	(Manso et al., 2008; Nasar, Srinivasan, Mohan, & Radhakrishnan, 1998; Wypych, 2014a)
Cosmetics and Personal Care	Ethanol, acetone, isopropyl alcohol, toluene, etc.	Nail polishes, hair care, fragrances, etc.	(Balasundaram, Harrison, & Bracewell, 2009; Choi & Lee, 1999; Günerken et al., 2015)
Food Industry	Hexane, hexane isomers, heptane, etc.	Oil extraction and edible oil processing	(Grandison & Lewis, 1996; Vilkhu, Mawson, Simons, & Bates, 2008)

Waste from Solvent Consuming Industries

$$\text{E-factor} = \frac{Total\ mass\ of\ Waste\ produced}{Total\ mass\ of\ Products\ manufactured}$$

Industry	Product (ton/yr)	E-factor
Food	$150x10^6$	0.1-5
Polymer	10^4-10^6	1-5
Cosmetics and Personal Care	100	4-9
Pharmaceutical	10-10^3	25-100

[2] *R. A. Sheldon, "The E Factor: fifteen years on," Green Chem., vol. 9, no. 12, pp. 1273-1283, 2007.*

Typical Solvent Disposal Methods

- **On-site methods:**
  - Direct release to air, water, or land
  - Scrubbers, incinerators, underground injection
- **Off-site methods:**
  - Transfer to alternative location before treatment, reuse or release
  - Purification for alternative industry
  - Incineration for energy recovery

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

Environmental Impact and Costs

- "By 2030, emissions from the solvents sector are expected to approximately double, reaching 10 million metric tons of carbon dioxide equivalent" …..US EPA
  - *Incineration – releases 6.7 kg CO_2/kg organic carbon*

- Cost example: 45 million kgs of methanol
  - *$124.7M to purchase and ~$47.3M to dispose of via incineration*

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.
"Global Mitigation of Non-CO2 Greenhouse Gases: Solvents," *EPA*, 09-Aug-2016. [Online].

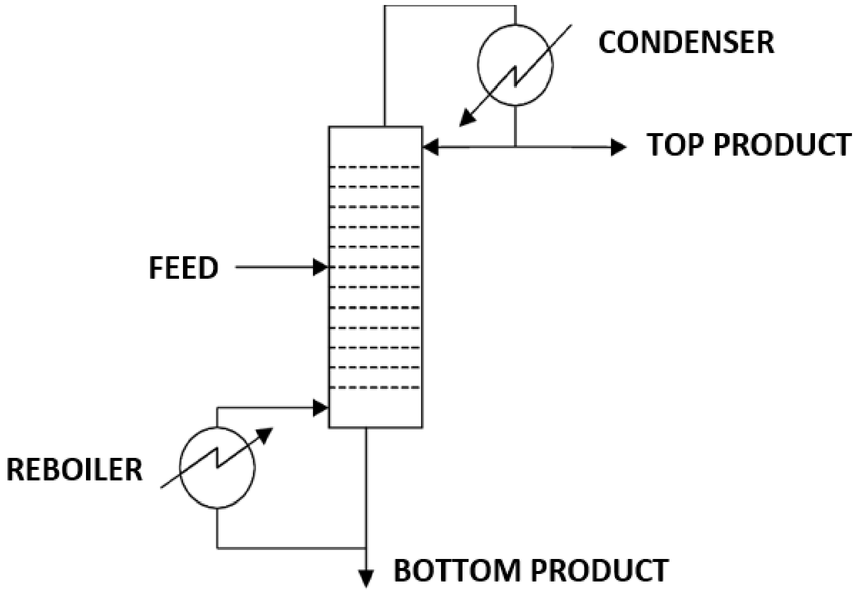
Solution?

- Efficient solvent recovery methods to minimize costs and improve sustainability of solvent-consuming industries
    - ✓ Common and novel separation technologies
    - ✓ Utilizing recovery train

Technology Information

Technology	Principle/Driving Force	Specifications
Distillation	Difference in volatility Boiling points	feed rate and composition, relative volatility, stages
Membranes	Particle/molecular size Diffusion Pressure gradient	Pore size, average flux
Aqueous Two-Phase Extraction	Molecular weight, miscibility	Concentration of separation agents
Liquid-Liquid Extraction	Selective partitioning of solutes	Partition coefficient, solubility of solutes Low solubility of added solvent in water
Common Disposal Method: Incineration	Heat of combustion	Energy recovery

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:

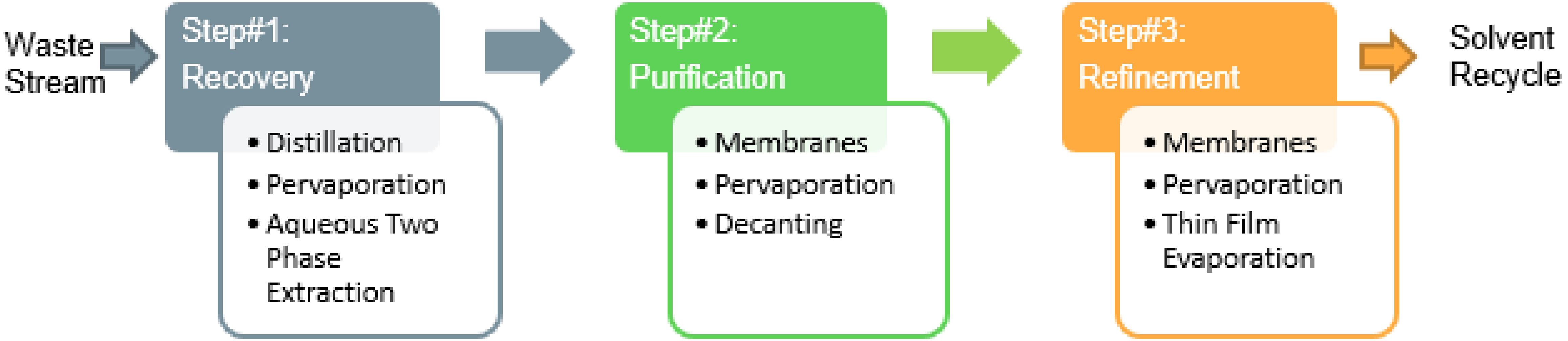
$$N_{act} = \frac{N}{\eta stage}$$

Costing variable of column;

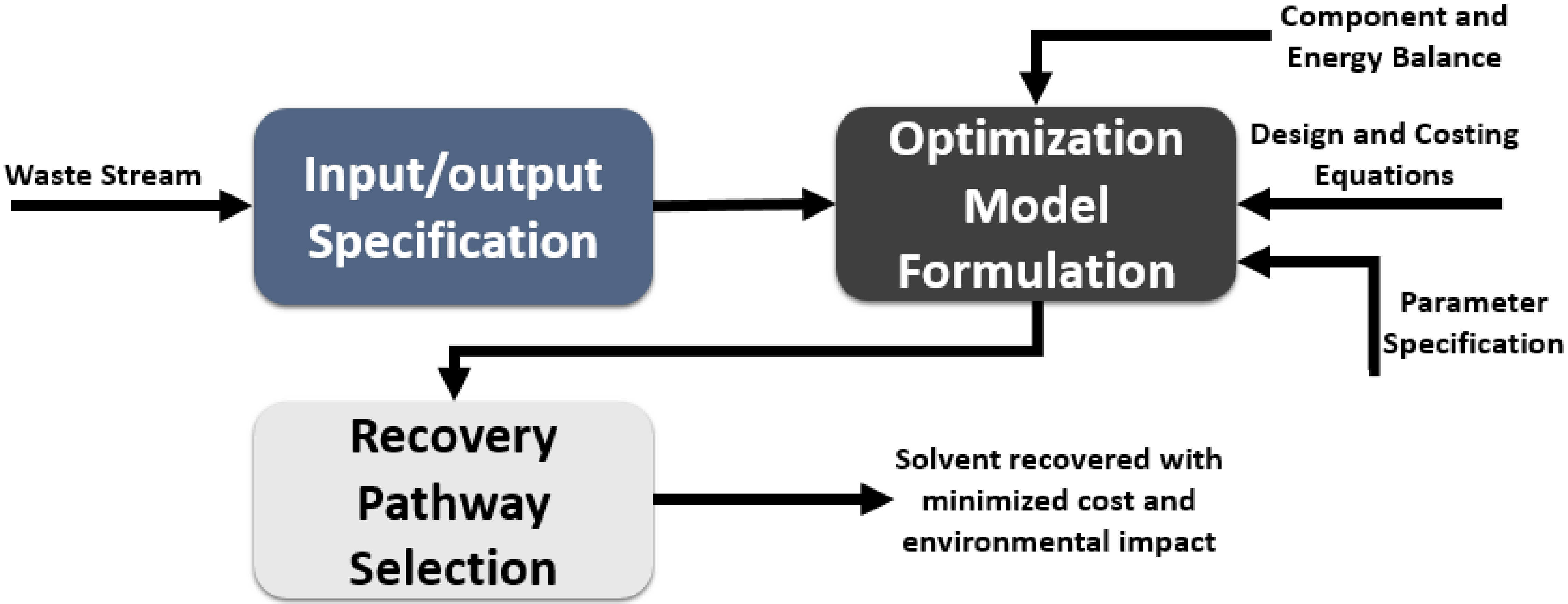
$$QS_{dst} = \frac{\pi}{4} D^2 H$$

Complexity of Designing a Recovery Process

- Number of possible pathways is dependent on the composition of the waste stream
- Additional stages of separation may be needed based on the purity requirements for reuse



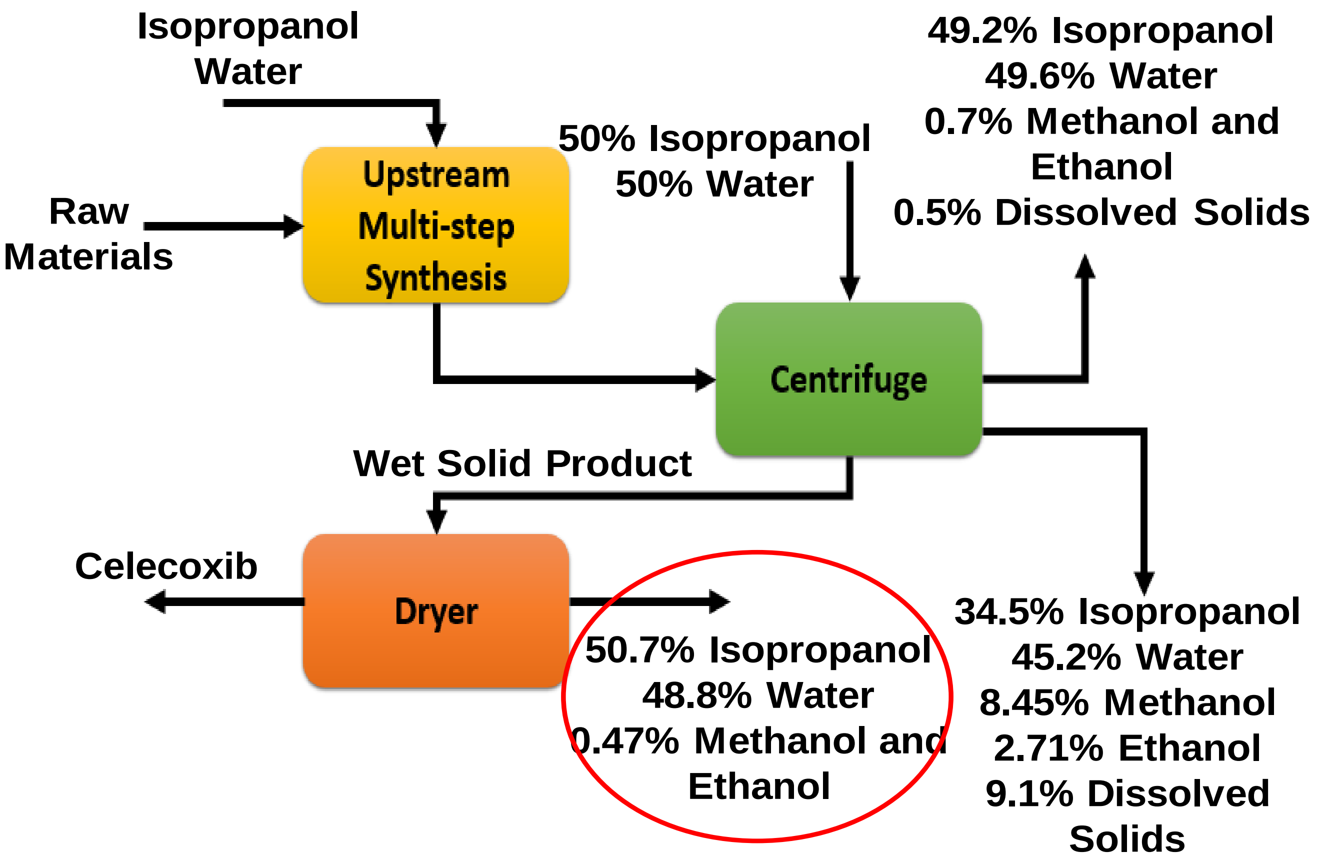
Evaluation Framework



- 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 Software (GAMS)
- Solver: Branch-And-Reduce Optimization Navigator (BARON)

Case Study: Pharmaceutical Waste Stream

- **Celecoxib[5]**
  - Arthritic pain medication active ingredient
  - 510 kg/hr of IPA
- **Incineration**
  - 14.51 kg of steam/kg IPA
  - 0.83 kWh of electricity/kg IPA
- **Life Cycle Analysis**
  - 2.19 total emissions (land, water, air)/kg of IPA



[5]*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.*

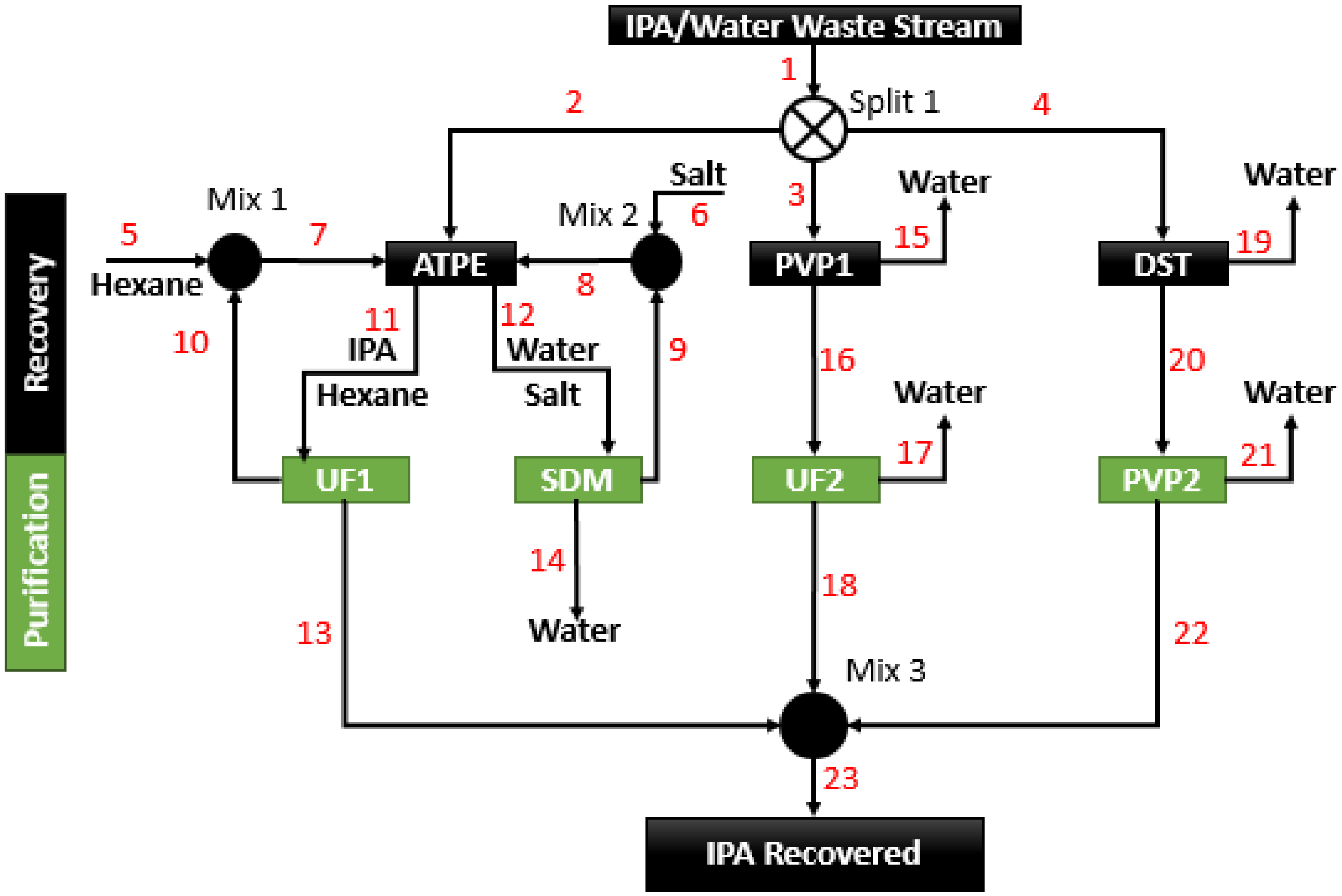
Specifications for Model Testing

- 0.5% trace solvents are negligible for model simplification
- Azeotrope at 80.37°C with 87.7 weight % IPA
- Compared results to additional incineration model developed in GAMS

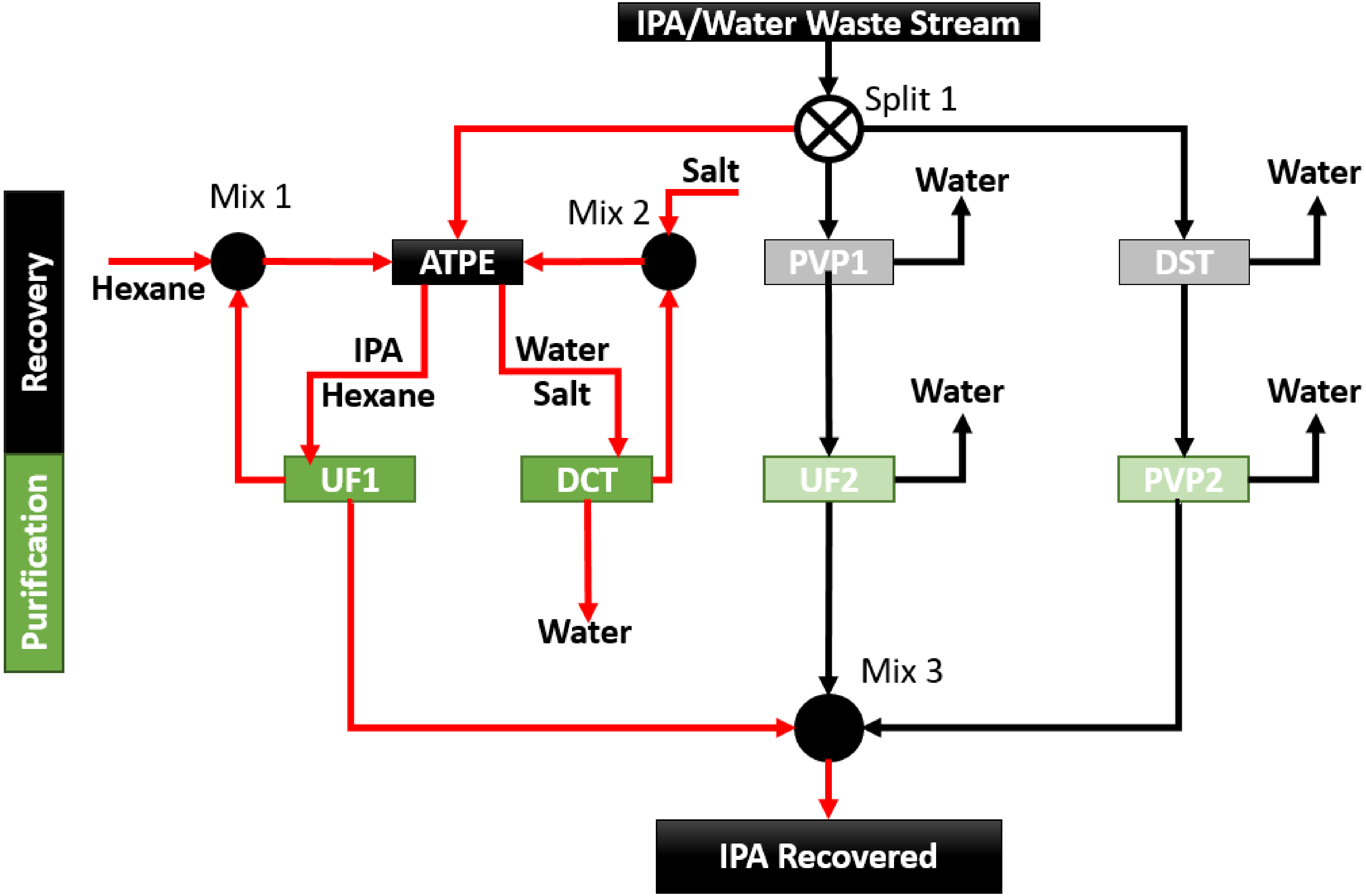
Feed Condition	Feed Rates (kg/hr)	Outlet Requirements
Isopropanol (51%)	510	Recovery: 99.5%
Water (49%)	490	Purity: 99%

Summary of the GAMS Model

- **3** paths to solvent recovery, **7** technologies, **23** streams
- Technologies included:
  - ATPE: Aqueous Two-Phase Extraction
  - PVP: Pervaporation
  - DST: Distillation
  - UF: Ultrafiltration
  - SDM: Sedimentation

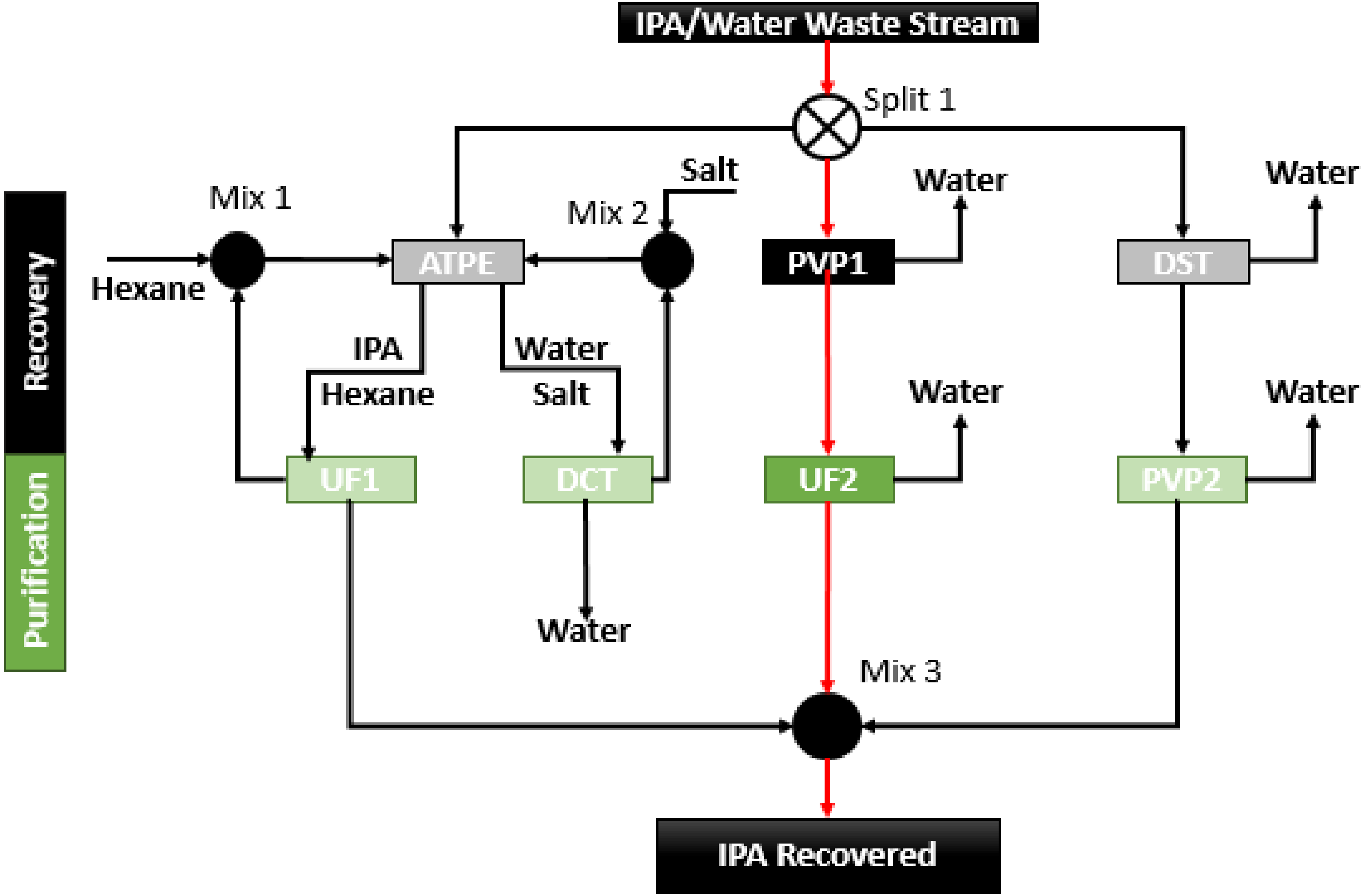


IPA Recovery Pathway#1

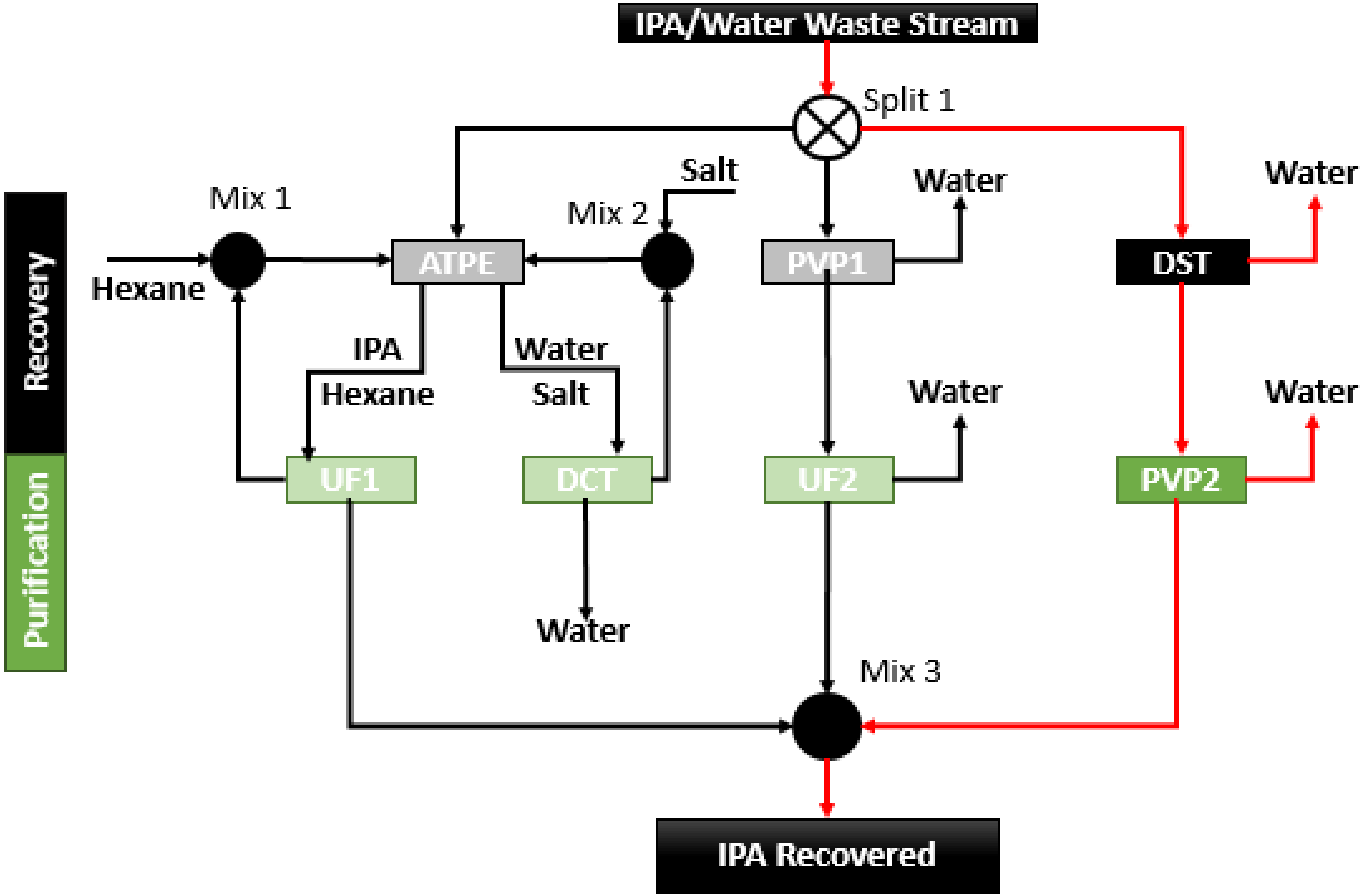


IPA Recovery Pathway#2

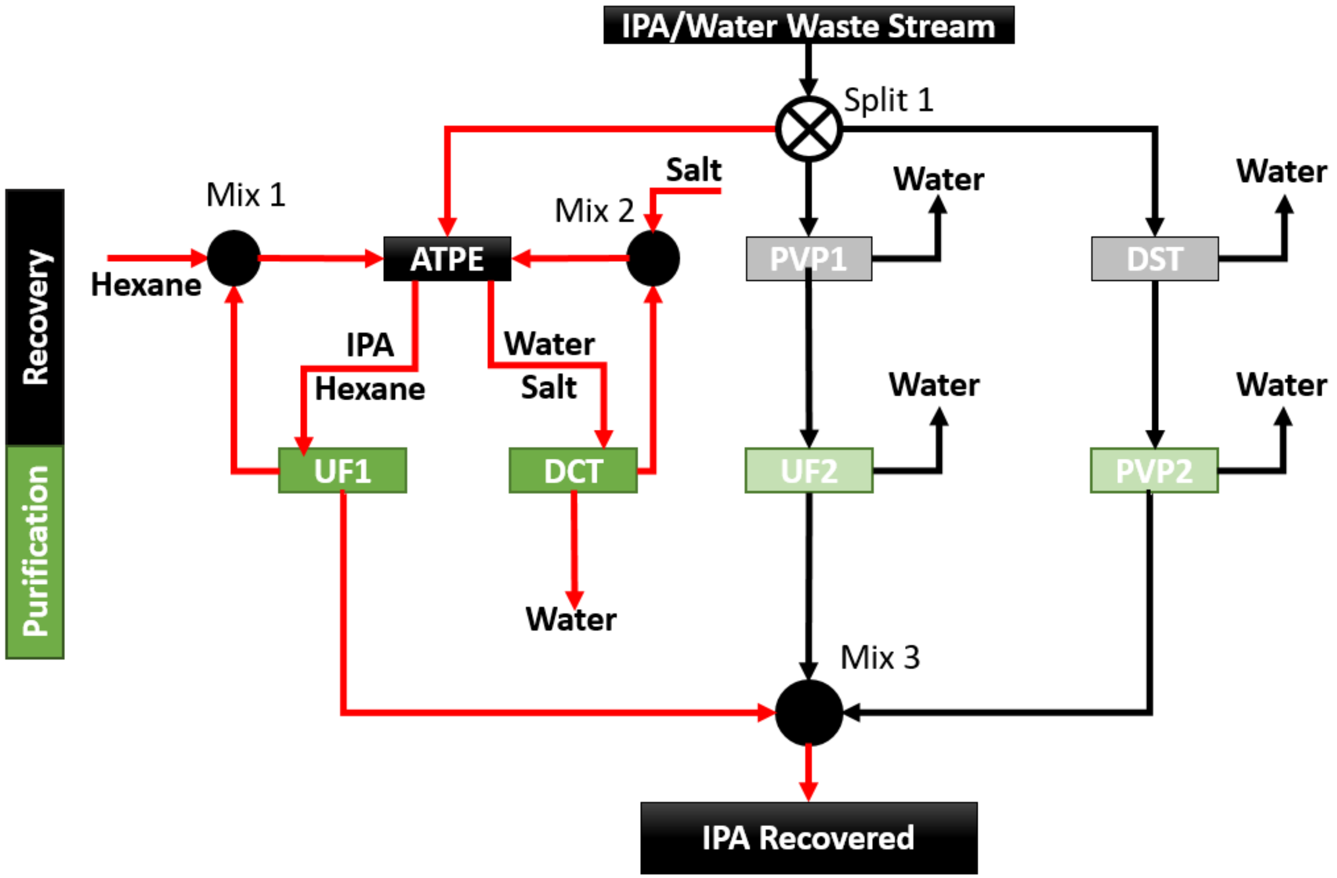
Rowan University



IPA Recovery Pathway#3



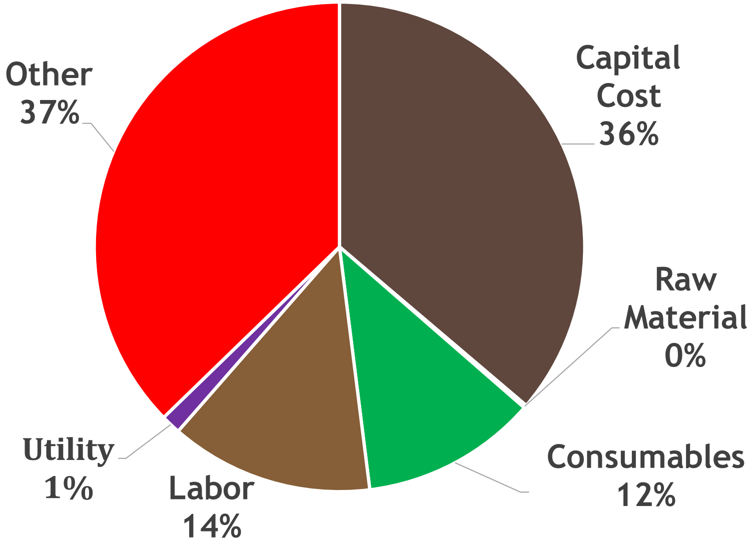
Result: Optimal Recovery Path



GAMS Model & Solution Statistics

Model Statistics	Values
Equations	73
Variables	21
Discrete Variables	6
Solution Time	0.390 seconds
Total cost	$9.36 MM/annum
Cost per kg solvent	2.36
Incineration costs	$8.06 MM/ annum

Cost Distribution Chart



- Over 8,800 metric tons/yr of CO_2 emissions can be prevented
- Although incineration cost less, materials are not recovered and cannot be reused

Summary

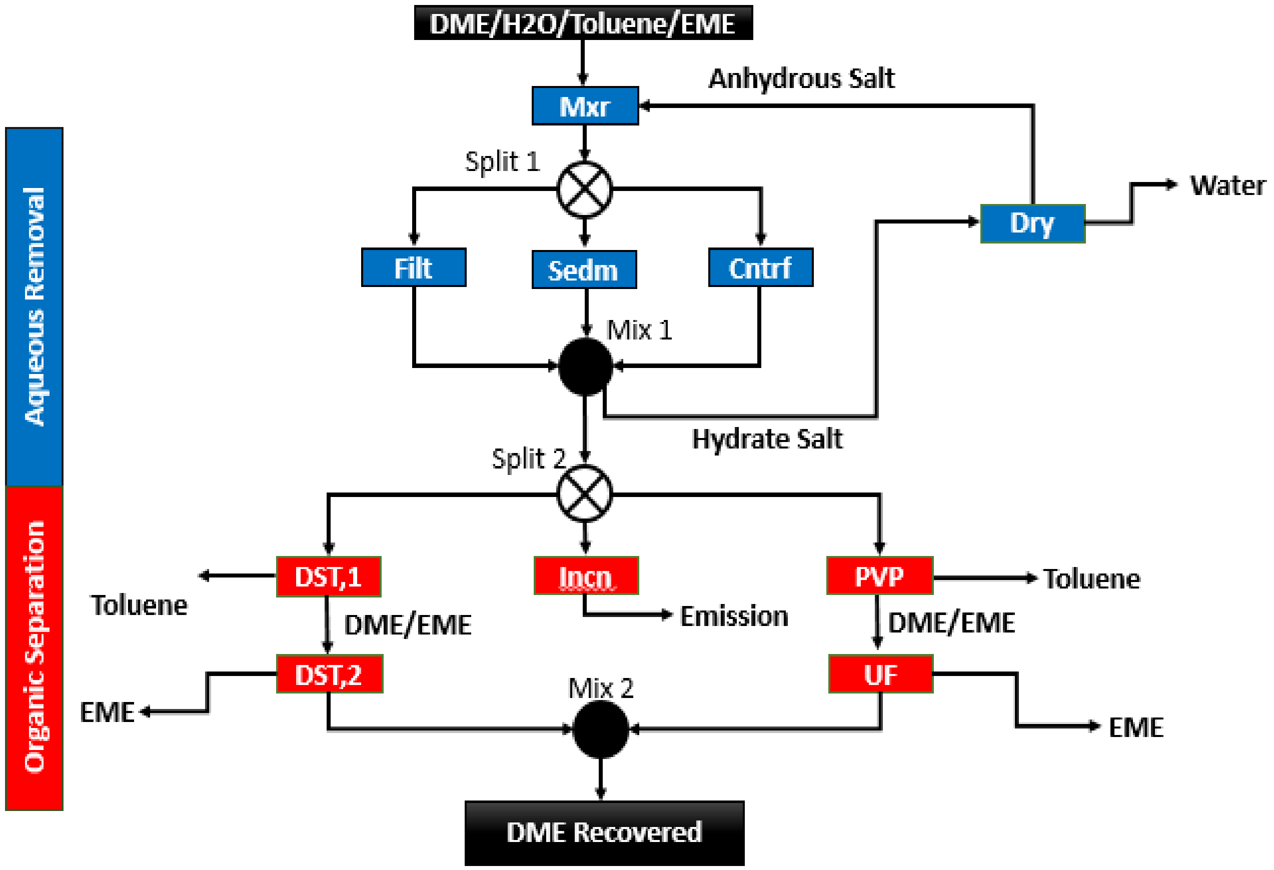
- Developed a systematic framework for comparing solvent recovery options
- Information Collection
  - Solvent use, properties, general disposal/recovery trends
  - Recovery technologies and model development
- Advantage over detailed simulators: multiple options compared simultaneously and reduction in computation time

Future Work

Rowan University

→ Additional case studies:

Specialty Chemical Waste



→ Life Cycle Analysis

- Include environmental impact analysis for each recovery pathway
- Compare the impacts with releases due to incineration or direct disposal

Acknowledgments

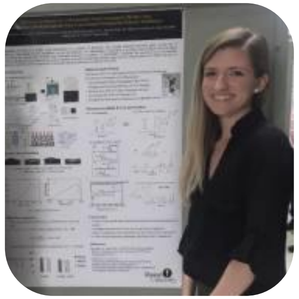
- This research has been supported by a grant from the U.S. Environmental Protection Agency's Pollution Prevention (P2) Program (NP96259218-0)
- Rowan University Chemical Engineering Department

Project Team

John D. Chea

Graduate Student

Amanda Christon



Undergraduate Student

Vanessa Pierce

Undergraduate Student

Maxim Russ

Undergraduate Student

Jake Stengel

Undergraduate Student

Kirti M. Yenkie, PhD

Principal Investigator

C. Stewart Slater, PhD

Co-Investigator

Mariano J. Savelski, PhD

Co-Investigator

Framework for Solvent Recovery, Reuse, and Recycling in Industries

John D. Chea, Stewart Slater, Mariano Savelski, and **Kirti M. Yenkie**

Department of Chemical Engineering

Henry M. Rowan College of Engineering

Rowan University, Glassboro, NJ, 08028, USA

Sustainable Design and Systems Medicine Lab

Research Group Website: https://yenkiekm.com/