Synthesis and Systematic Evaluation of Solvent Recovery Pathways

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Expanding Chemical Market

- Global chemical industry projected to double in production, capacity, and sales between 2017 – 2030¹
- 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 Inventory¹

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 Methods¹

- 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 CO₂ / 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 processes²

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**

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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

Building a Database

Solvent	MW (g/mol)	Density (kg/m³)	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:

$$\sum_{j \in J_{ini}} F_{j,k} = \sum_{j \in J_{outi}} F_{j,k}$$

Minimum number of stages with Fenske's equation:

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

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:

$$R = 1.3R_{min}$$

Number of stages:

$$0.6N = N_{min}$$

Number of actual stages:

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

Costing variable of column;

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

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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

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Evaluation Framework for Case Studies

- 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

1. C. S. Slater, M. Savelski, D. Pilipauskas, F. Urbanski 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

- Aqueous Two-Phase Extraction – infeasible at specified condition
- Incineration: not economically viable and no material recovery

Cost Breakdown of PVP-UF

Environmental Impacts Analysis

Human Health (DALY)

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

Ecosystem ($\text{PDF} \cdot \text{m}^2 \cdot \text{yr}$)

Waste Handling Method	% Difference
Direct Disposal (Base Case)	0
Solvent Recovery	159
Incineration	90

Climate Change (kg CO₂ 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 to be completed for continuous framework enhancement
- Powerful tool to enhance solvent recovery practices in industry
 - Improve process optimization
 - Reduce global solvent consumption/waste (industrial collaboration required)

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Resource Conservation and Recovery Act (RCRA)

- Enacted in 1976 to address municipal and industrial solid waste generated nationwide
- Provides a general guideline for waste management (Regulations)
- RCRA Details
 - Gives EPA authority to control hazardous waste from “cradle-to-grave”
 - Identifies hazardous waste
 - Regulates nonhazardous solid waste
 - Collaborative partnership with stakeholders to encourage recycling
- Amendment to RCRA in 2015 – Redefined definition of solid waste
 - Recycled solvents may be excluded from regulations for hazardous waste
 - Incentive to recycle materials without increasing risk to human health and environment

1. US EPA, “Solvents in the Workplace - How to Determine if They Are Hazardous Waste,” Environmental Protection Agency, 2016.

Solvent Recovery Tool: R.SWEET

- A software toolbox that combines ASPEN Plus® simulation with SimaPro® and Ecosolvent Life Cycle Assessment (LCA) database
- Microsoft Excel Interface
- Strength: recommends and simulate recovery processes, performs economic analyses, customizable stream
- Limitation: Lack of simultaneous comparison against other options, iterative optimization process (see next slide)

1. Cavanagh, E., 2013. A new software tool to environmentally and economically evaluate solvent recovery in the pharmaceutical industry. Rowan University.

Solvent Recovery Tool: R.SWEET

Iterative process until the user
converged on a solution!
(Tedious, Time-consuming)

1. Cavanagh, E., 2013. A new software tool to environmentally and economically evaluate solvent recovery in the pharmaceutical industry. Rowan University.