Practical Applications of Green Engineering

Solvent Recovery/Reuse in Pharmaceutical Processes

Nhan Nguyen / Kathy Davey / Sharon Austin
Office of Pollution Prevention and Toxics

US EPA

Expanding Business Value Through Pollution Prevention & Sustainable Practices
May 19, 2010
San Juan, Puerto Rico

Outline of Presentation

- Who are we?
- Green Engineering Pharma Project Goals, Status and Next Steps
- GSK Life Cycle Modules and Solvent Decision Support Tool (DST)
- Decision Support Tool (DST)
  - Tool framework, data input, and LCI / Business Models
  - Solvent, Process and Market Data
  - Community data / EJ impacts
  - Case studies (with environmental and economic benefits)

Who are we?

- Office of Pollution Prevention and Toxics (OPPT)
  - Toxic Substances Control Act (TSCA) and Pollution Prevention Act (PPA)
  - Multimedia
  - Serves as a gatekeeper/guardian to ensure chemical safety
  - Promotes environmental stewardship and sustainability
    - via collaborative programs (e.g. GC, GE, DfE) and educational activities
    - Develops tools and makes information available
  - Collaborates international to address chemicals
  - Consists of five divisions including Economics Exposure & Technology Division (EETD) and Pollution Prevention Division (PPD)
  - GE activities managed by the Chemical Engineering Branch (CEB) of EETD

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Project Overview

- Targets initially pharmaceutical processes, where large amounts of toxic solvents are used per mass of final product
- Large contributor to environmental footprint is disposal (incineration / cement kilns) of solvents.

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Project Goals

- Reduce environmental footprint and report measured results
  - Pounds of toxic materials reduced
  - Metric tons of CO_2 and BTUs reduced
  - Pounds of air, water and solid waste emissions reduced
  - Gallons of water and
  - $ saved.
- Facilitate information exchange on approaches and practices to rest of pharmaceutical sites and other chemical processes

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Status of Project

- Developed a Solvent Decision Support Tool (DST)
  - GSK Life Cycle module
  - Estimates energy, GHG and emissions to various media
  - Model to estimate savings corresponding to these reductions
- Identified approaches and practices to recover/reuse solvents
- Developed business case studies using available data collected
- Working closely with the regions and ORCR

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Next Steps

- Short-Term
  - Work with interested pharmaceutical plants in the regions (e.g. Region 2)
  - Pilot the approaches and practices
  - Apply Solvent Decision Tool using plant-specific data.
- Long-Term
  - Move upstream of the process (e.g. reaction, separation)
  - Stewardship initiative for the broader pharmaceutical industry
  - User-friendly tool for broader use by the Regions and industry
  - Expand to other chemical processes

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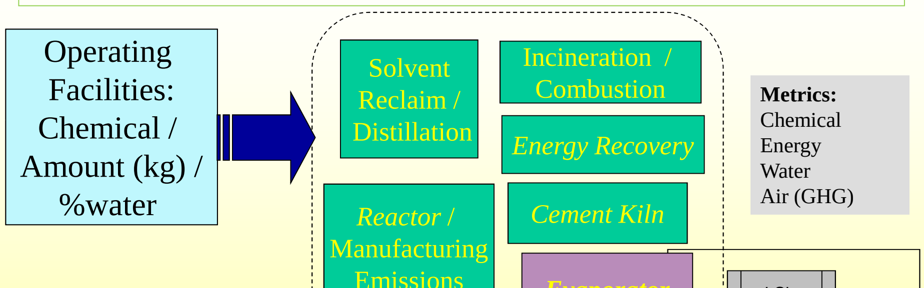
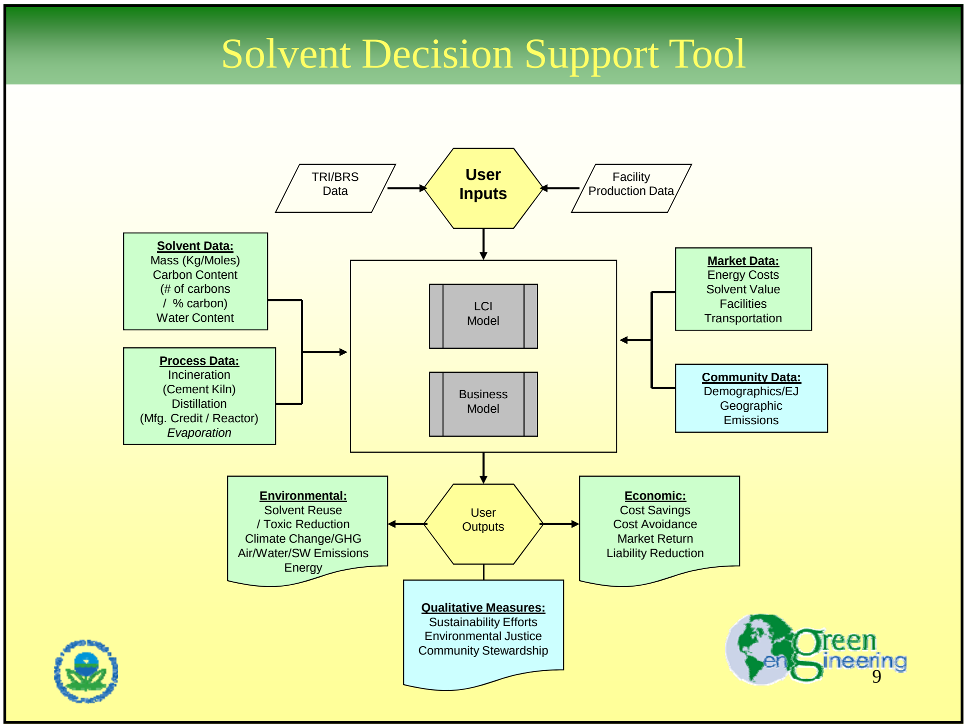
Adapted GSK Life Cycle Modules . . .

Material Flow . ...,…………………………………………Multiple Metrics



Modules developed by GlaxoSmithKline (GSK) and North Carolina State University's Chemical Engineering Department. Published in 2001 – publicly available.*

***Jimenez-Gonzalez C**, Overcash MR and Curzons AD. J. Chem. Technol. Biotechnol. 71:707-716 (2001). Model developers work with GE Program. Modules adapted and used by Ecoinvent / Swiss Zurich Institute


Solvent Decision Support Tool
TRI/BRS Data
User Inputs
Facility Production Data
Solvent Data:
Mass (Kg/Moles)
Carbon Content
(# of carbons
/ % carbon)
Water Content
Process Data:
Incineration
(Cement Kiln)
Distillation
(Mfg. Credit / Reactor)
Evaporation
LCI Model
Business Model
Market Data:
Energy Costs
Solvent Value
Facilities
Transportation
Community Data:
Demographics/EJ
Geographic
Emissions
Environmental:
Solvent Reuse
/ Toxic Reduction
Climate Change/GHG
Air/Water/SW Emissions
Energy
User Outputs
Economic:
Cost Savings
Cost Avoidance
Market Return
Liability Reduction
Qualitative Measures:
Sustainability Efforts
Environmental Justice
Community Stewardship
engineering
green
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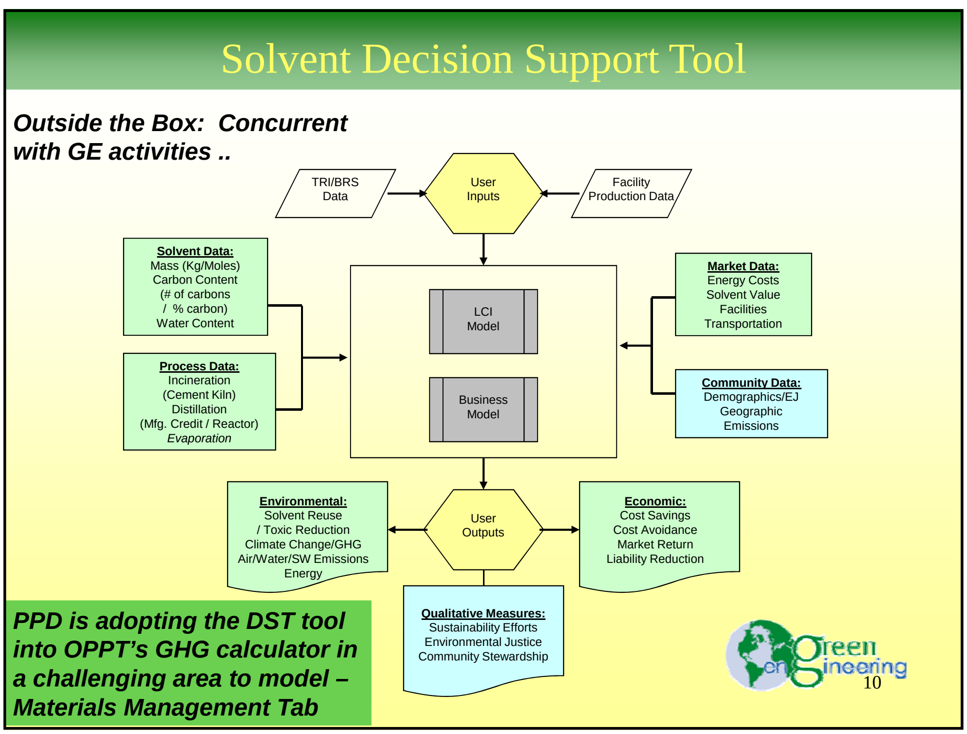
Solvent Decision Support Tool
Outside the Box: Concurrent
with GE activities ..
TRI/BRS Data
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Qualitative Measures:
Sustainability Efforts
Environmental Justice
Community Stewardship
PPD is adopting the DST tool
into OPPT's GHG calculator in
a challenging area to model –
Materials Management Tab
engineering
green
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Solvent Data – Mass & Carbon Balance

Solvent Data:
Mass
(Kg/Moles)
Carbon Content
(# of carbons
/ % carbon)
Water Content

TWO VARIABLES: How much Carbon and How much Water

Kg in -> Kg out (mass balance)

Carbon in → Carbon out (carbon balance)

Water in -> Water out

$$ in → $$ out

Isotainer

Solvent	Molecular Weight	Chemical Formula	# of Carbons	% Carbon	% Water	Kg in 5000 gallons
Methanol	32	CH_4O	1	37%	50%	7,481
Tetrahydrofuran	72	$C4H_8O$	4	67%	25%	12,642
Toluene	92	$C7H_8$	7	91%	0%	16,477

What do you do now? (dispose as waste – baseline & worst case)

Process change to extend solvent life?

DST provides metrics for each process change. (lbs, GHG, energy, $$)

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Process Data – Where Solvents Go . .

Disposal is worst case scenario – any change will provide numerous benefits

Process Data:
Incineration → *'Waste Disposal'*
(*Cement Kiln**)
Distillation → ***Substance Recovered / reused (with waste disposal)***
(Mfg. Credit / *Reactor*)*
*Evaporation** → ***Substance Dehydrated (energy recovered)***

- Toluene (like oil). High Carbon. No Water.
- Tetrahyrdrofuran (THF) Medium Carbon. Quarter Water.
- Methanol (like water) Low Carbon. Half Water.
- Demonstrate impacts of carbon and water through various processing / unit operations

** Adapting / Developing Models*

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Incinerator Module: Methanol (single carbon)

COMBUSTION!! More Carbon out then in!!! Shipping and Burning Water!!!!

Materials are put in the oven where air containing CO2 is heated and materials are 'baked' until destroyed. For methanol, energy extended (depleted) to burn water before combusting carbon in solvent.

1 carbon

Isotainer

7,481 kg Methanol
7,481 kg Water

14,962 kg

Air 25 ^oC — *390 ppm CO2*

Combustion Chamber
Methanol

25,000 kg CO2eq

871- 982 ^oC
Burning Natural Gas

Always need external fuel source to 'heat the oven'

	MillionBTUs	***MetricTons***
Solvent	MMBTU	MCO2eq
Methanol	161	**25**

Kg CO2 eq: 25,000
10,000 kg from combusting Methanol
15,000 kg from burning Natural Gas

Same in US – only way to get rid of methanol is to pay for cement kiln to dispose. (plant produces methanol as byproduct, searching for home)

Incinerator Module: Toluene (multi-carbon)

COMBUSTION!! Even more Carbon out then in!!!

For Toluene, all energy is extended to combust high carbon material, which is what makes it a good fuel (oil). Largest footprint with energy use and carbon emissions.

7 carbons

Isotainer

Toluene: 16,477 KG

16,477 kg

Air 25 ^oC — *390 ppm CO2*

Combustion Chamber
Toluene

113,000 kg CO2eq

Natural Gas
871- 982 ^oC

	MillionBTUs	***MetricTons***
Solvent	MMBTU	MCO2eq
Methanol	161	25
Toluene	614	**113**

Kg CO2 eq: 113,000
54,000 kg from combusting Toluene
58,000 kg from burning Natural Gas

Green engineering

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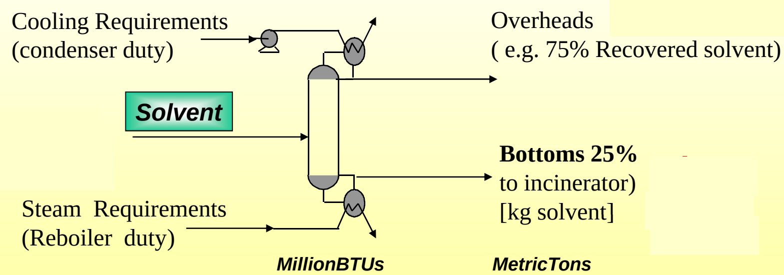
Solvent Distill / Reclaim Module

Solvent is fed into distillation column. Evaporated solvent goes to the top and is recovered. Model default recovery rate is 75%. Heavier components, including water, go to the bottom. Bottoms are typically disposed of as hazardous waste.



Whenever you distill you have bottoms to contend with . . Why this makes a difference? Waste can (currently) only be disposed in US with high manifest shipping and processing costs.

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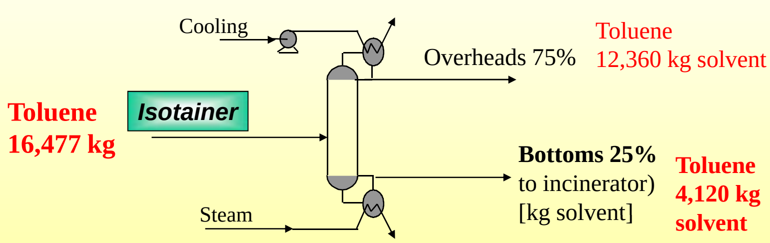
Toluene – Primary Distillation (Reclamation)

	MillionBTUs	*MetricTons*
Solvent	MMBTU	MCO2eq
Distill 100%	10.4 steam	1.1



It takes 15 times more Energy in natural gas and generates 25 times CO2eq when combusting 25% (bottoms) then it does to distill 100% with steam.

Solvent	MMBTU	MCO2eq
Combust 25%	154 natural gas	28.2

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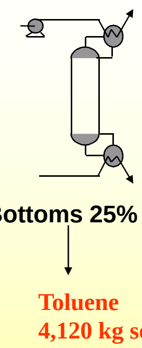
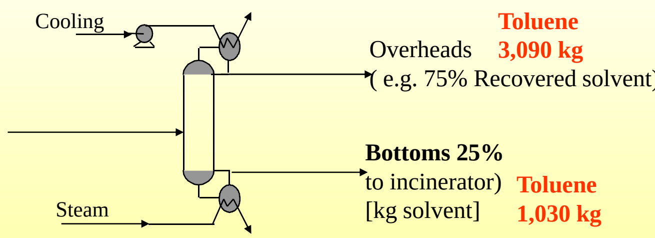
Toluene – Secondary Distillation (Reclamation)

Solvent	MMBTU	MCO2eq
Distill 25%	2.6 steam	0.3
Combust 8%	38.4 natural gas	7.0





Toluene 16,477 kg	Kg Recovered (%)	Steam MMBTU	Natural Gas MMBTU	MCO2eq
Primary	12,360 (75%)	10.4	154	29.3
Secondary	15,450 (92%)	13	38.4	8.4

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Effective bottoms management increases yield and reduces footprint

Solvent Recovery Module Manufacturing Emissions

- A reused solvent replaces solvent that would have otherwise been purchased. A reused solvent thus avoids disposal and manufacturing emissions.
- Highly processed chemicals, such as THF, have higher manufacturing emissions as compared to basic building block chemicals, such as toluene.
- Estimations of manufacturing emissions (cradle to gate) are similar from different sources. (GSK / Zurich Institute Paper) Currently have manufacturing emissions for all 33 F solvents.

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Toluene – Distillation Manufacturing Emissions

Distillation Emissions

MMBTU	MCO2eq
10.4	1.1

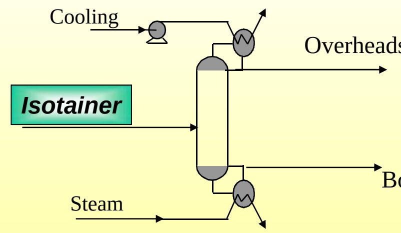
Manufacturing Emissions

	MMBTU	MCO2eq
Toluene	96	14.4

12,360 kg solvent

Recovered $0.30/lb
Bill Of Lading (BOL)

Toluene
16,477 kg



4,120 kg solvent

MMBTU	MCO2eq
154	28.2

For toluene, energy and GHG is lower to distill then to manufacture, and highest to combust.

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THF – Distillation Manufacturing Emissions

Distillation Emissions

	MMBTU	MCO2eq
Toluene	10.4	1.1
THF	10	1.0

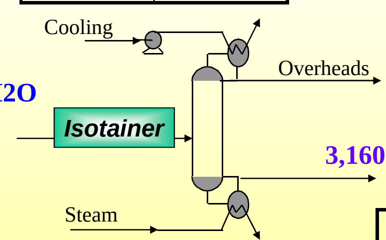
Manufacturing Emissions

	MMBTU	MCO2eq
Toluene	96	14.4
THF	1135	153

9,481 kg THF

Recovered $1.10/lb
Bill Of Lading (BOL)

THF & 25% H2O
12,642 kg
4,214 kg water
16,856 kg total



3,160 kg THF & 4214 kg water*

Bottoms (Incineration)

	MMBTU	MCO2eq
Toluene	154	28.2
THF	112	18.3

WWT

The high manufacturing emissions and resale cost for recovered THF are so high that they dwarf both distillation and incineration impacts.

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Methanol – Distillation Manufacturing Emissions

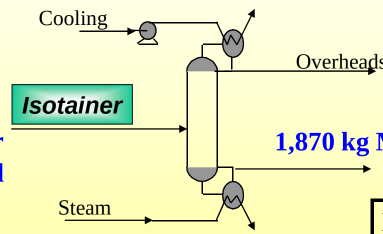
Distillation Emissions

	MMBTU	MCO2eq
THF	10.0	1.0
Methanol	14.7	1.0

Manufacturing Emissions

	MMBTU	MCO2eq
THF	1135	153
Methanol	66	9.6

Methanol
7,481 kg
7,481 kg water
14,962 kg total



5,611 kg Methanol

Recovered $0.08/lb
Bill Of Lading (BOL)

1,870 kg Methanol & 7481 kg water*

Bottoms (Incineration)

	MMBTU	MCO2eq
THF	112	18.3
Methanol	61	7.0

WWT

Even if one could remove the water it is not worth distilling and not best use of this piece of capital equipment.

* Note negative impact of water in incineration, and distillation

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What to do with the Methanol? What to do with the Water?

- **Methanol Denitrification**: Methanol Institute: Methanol serves as a carbon source for bacterial bugs in Waste Water Treatment Plants (WWTP), accelerating the anaerobic bacteria's conversion of the nitrate to harmless nitrogen gas at a fraction of the cost of nitrate removal. (*www.Methanol.org*)
- **Raw Material**: Windshield washer fluid; Methyl acetate (produced by esterifying methanol and separating w/ toluene)
- **Chemical Wash**: Methanol 'baths' are common in specialty chemical industry and already use recovered methanol (color)
- **Energy Recovery:**
  - **Miscible**: Most soluble – alcohol / water. Can be used in non- contact heating / cooling in place of water at any dilution
  - **Evaporative Technology**: Can process large amounts of material and operates on 'waste' / recovered steam

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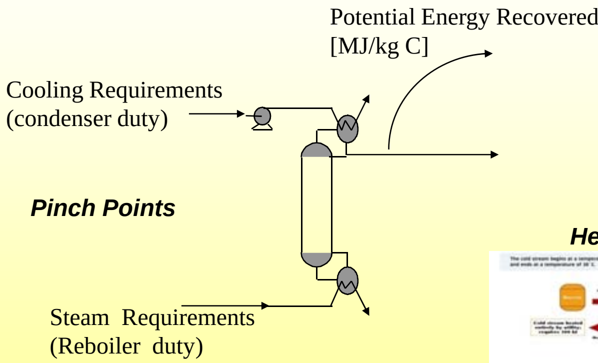
Distillation – Energy Recovery Opportunities

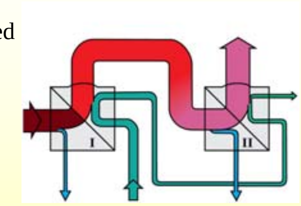
Energy Recovery opportunities

Pinch Points

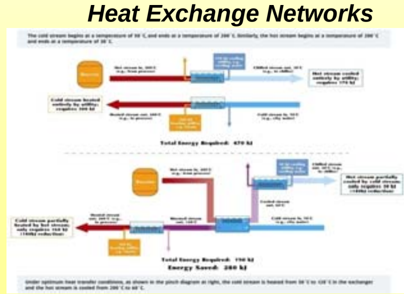


Distillation LCI module can calculate 'pinch points' for optimum use of recovered energy

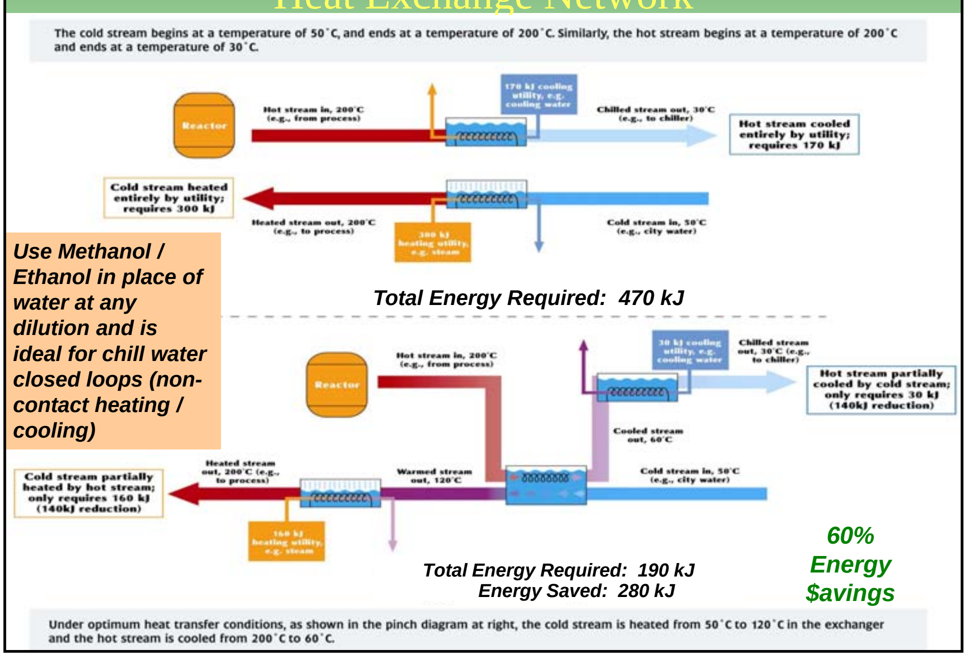
Evaporative Technology



Heat Exchange Networks



Heat Exchange Network



Use Methanol / Ethanol in place of water at any dilution and is ideal for chill water closed loops (non-contact heating / cooling)

Total Energy Required: 470 kJ

Total Energy Required: 190 kJ
Energy Saved: 280 kJ

60% Energy $avings

Energy Recovery Example

Dow Chemical's Louisiana division energy-savings projects:

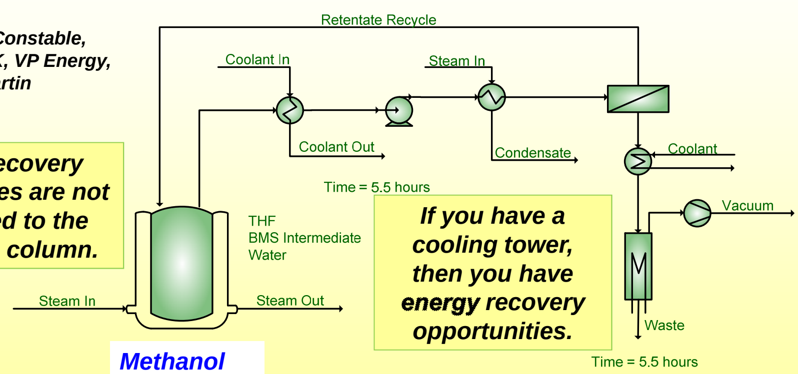
Projects involved more sophisticated thermodynamic "pinch" analysis, which allowed engineers to figure out where to place heat exchangers to capture heat emitted in one part of a chemical process and transfer it to a different part of the process where heat is needed. The first year, 1982, required a total capital investment of $1.7 million with an average annual return on investment of 173 percent. The second year required a total capital investment of $2.2 million and a 340 percent return -- a savings of $7.5 million in the first year and every year after that.

GE Opportunities: Energy and the UTILITY PLANT

70% of all energy consumed is for steam and cooling*

**** David J.C. Constable, formerly GSK, VP Energy, Lockheed Martin***

Energy recovery opportunities are not just limited to the distillation column.

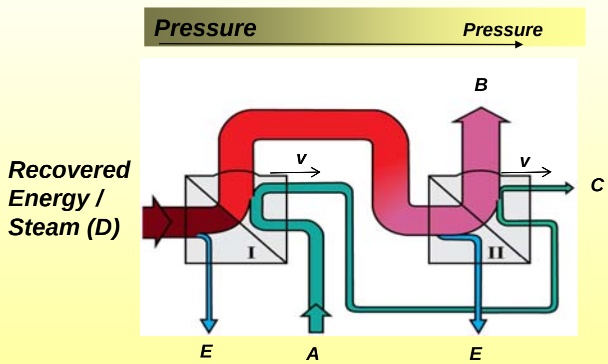


If you have a cooling tower, then you have energy recovery opportunities.

A single batch reactor and separation diagram. Methanol is commonly fed to reactor @85%. Energy from this stream can be used to help heat steam in or cool steam out based on its temperature.

Evaporation – Water removal and Energy Recovery

Multiple Effect Arrangement: In a multiple effect evaporation plant, the vapor produced in the first effect by the live steam is not lost to the condenser, but is reutilized as the heating medium of the second effect. This effectively reduced the steam consumption by about 50%.



A: Product to be evaporated
B: Residual vapor
C: Concentrate
D: Motive Steam
E: Heating steam condensate
F: Vapor condensate
V: Heat Loss

The main advantage of the multi-effect system is the high steam efficiency, which can be as high as 5.5 lbs water evaporated per lb of steam for a six effect system. (Smook, Handbook for Pulp & Paper Technologies)

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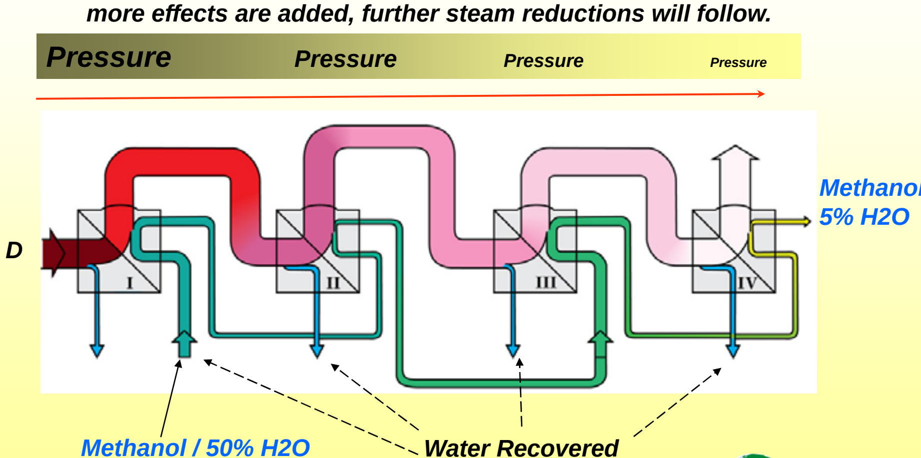
Multi-Effect Evaporation: Methanol

Evaporator with Four Effects

Single effect effectively reduces steam consumption by about 50%. As more effects are added, further steam reductions will follow.



Benefits of concentrated chemical, recovered water and energy saved.

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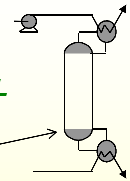
Evaporation for Tetrahydrofuran (THF) / Energy Recovery

THF evaporated for water removal – 25% to 5%.

Feedstock $0.10/lb BOL

12642 kg THF / 5% H20

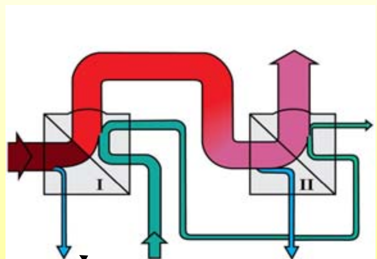


Distill

Recovered $1.10/lb BOL

Recovered Heat

From Distillation



Tetrahydrofuran (THF)
12,642 kg / *25% H20*

Water Recovered

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Solvent Recovery Module

Distillation Emissions

	MMBTU	MCO2eq
Toluene	10.4	1.1
THF 25%	10	1.0
THF 5%	12.2	1.3

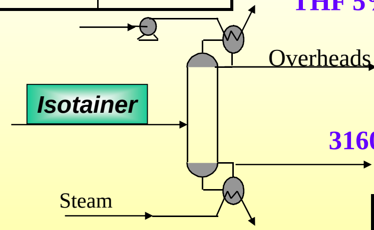
Manufacturing Emissions

	MMBTU	MCO2eq
Toluene	96	14.4
THF 25%	1135	153
THF 5%	1390	188

THF 5%

16,013 kg THF
843 kg water
16,856 kg total

Isotainer



12,009 kg THF
(9,481 kg recovered at 25%)

3160 kg THF & 843 kg water
Bottoms (Incineration)

	MMBTU	MCO2eq
Toluene	154	28.2
THF 25%	112	18.3
THF 5%	110	19.8

THF 25%

12,642 kg THF
4,214 kg water
16,856 kg total

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Market Data – Parameters that effect costs . .

Market Data:
Energy Costs
Solvent Value
Facilities
Transportation

Where recovered? In our out of manufacturing?
Manifest versus Bill of Lading (BOL)?

Business case models:

- Logistics
  - US Waste / Manifest ($0.14 / lb)
  - US Substance / BOL ($0.12 / lb),
  - Puerto Rico Substance / BOL ($0.01 lb)
- Processing (waste disposal, batch distill)
- Market Value (Virgin/SPEC, recovered, blend)

Where Recovered?? Solvent Waste Stream (#6)

Material Streams and Descriptions

ID#	Description
1	Raw Material Solvent Feed to Batch Reactor
2	Pharmaceutical Products
3	Solvent emissions to air pollution control unit (APC)
4	Solvent washdown from Seperation batch reactor
5	Solvent washdown from APC regeneration cycle

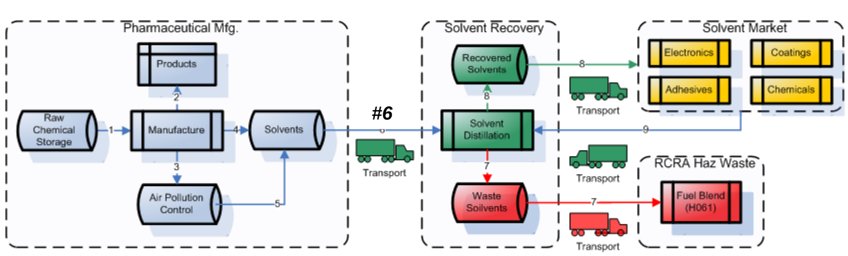
ID#	Description
6	Discarded solvent material (Crude Feedstock)
7	Solvent Bottoms (Waste Solvent)
8	Solvent Distillate (Recovered Toluene for Resale)
9	Discarded solvent material (Next Generation)

Material Streams and Economics (Case 2)

ID#	Description	Cost Component	Mass (Pound)	Unit Price (Pound)	Ext Price (Pound)
6	Crude Feedstock	Transport	36,192	$ (0.120)	$ (4,344)
6	Crude Feedstock (50% Toluene)	Processing	18,096	$ (0.150)	$ (2,714)
7	Distillation Bottoms	Disposal	22,620	$ (0.017)	$ (375)
8	Recovered Solvent	Market Resale	13,572	$ 0.300	$ 4,072
				Net Total	$ (3,361)
				Per Gallon	$ (0.67)

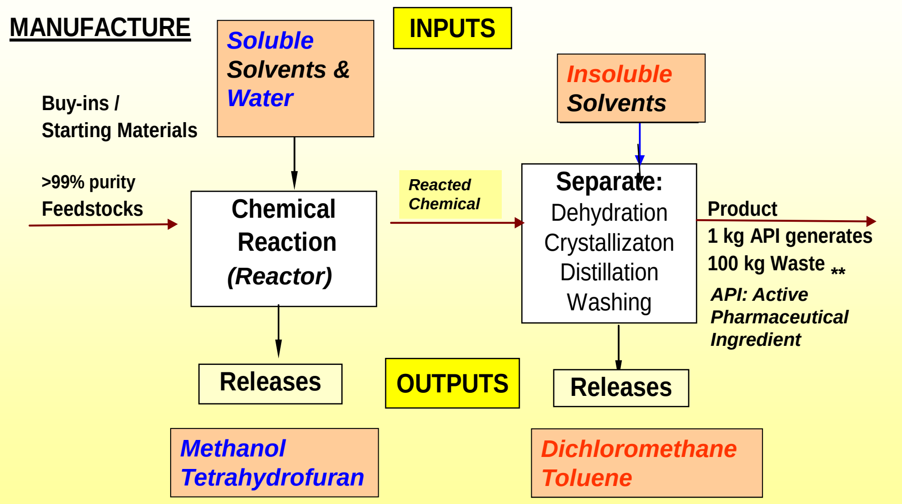
Crude Feedstock Composition (ID # 6)

Material	Conc.	SG
Toluene	50.0%	0.88
Methanol/Ethanol	30.0%	0.79
Ethyl-Acetate	10.0%	0.90
Water	5.0%	1.00
Solids	5.0%	1.00
Total	**100.0%**	**0.87**



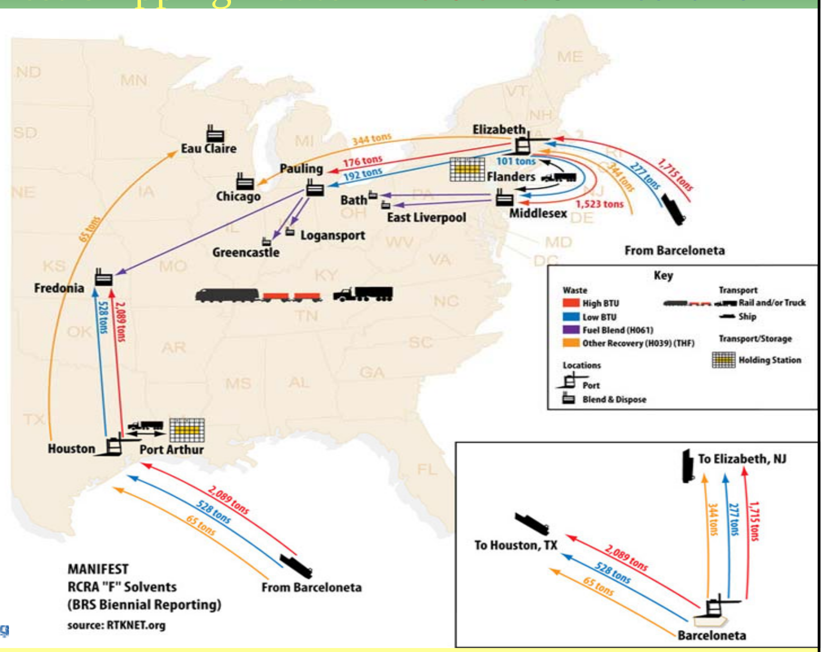
Recovered Outside of Manufacturing 'Box'

Where Recovered?? Byproduct Streams (Output)



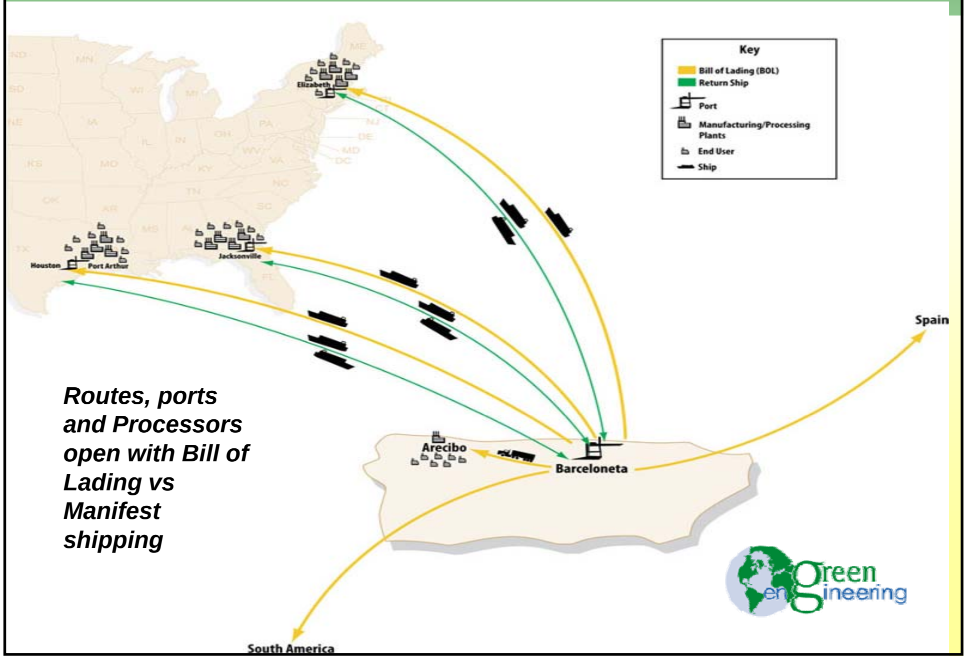
Recovered Inside of Manufacturing 'Box'

Manifest Shipping Route – Toluene & Methanol



MANIFEST
RCRA "F" Solvents
(BRS Biennial Reporting)
source: RTKNET.org

Bill of Lading (BOL) Shipping Routes and Processors



Routes, ports and Processors open with Bill of Lading vs Manifest shipping

Toluene Business Model - Benefits Table Worksheet

Toluene 36,192 lbs (5000 Gallons)
Recovered: $0.30 / lb
SPEC: $0.40 / lb

	Waste / US - Manifest		Houston **- Bill of Lading (BOL)**			Puerto Rico **- Bill of Lading (BOL)**	
			BOL Houston: $0.12			*BOL Puerto Rico: $0.01*	
	Fuel Baseline Waste	Primary Distill Recovered Waste	Primary Distill Recovered Substance	$0.30	Prim/Secondary Distill Recovered Substance	Primary Distill Recovered Substance	Prim/Sec Distill Recovered Substance
LOGISTICS	($5,110)	($5,110)	($4,343)		($4,343)	($400)	($400)
$/lb	($0.14)	($0.14)	($0.12)		($0.12)	($0.01)	($0.01)
PROCESING	($600)	($9,198)	($5,578)		($5,476)	($5,578)	($4,476)
$/lb	($0.02)	($0.25)	($0.15)		($0.15)	($0.15)	($0.15)
Isotainer **MARKET VALUE**	-	$8,143	$8,143		$9,989	$8,143	$9,989
yield&conc $/lb		$0.23	$0.23		$0.28	$0.23	$0.28
NET RETURN	($5,710)	($6,165)	($1,780)		$169	$2,164	$4,112
$/lb	($0.16)	($0.17)	($0.08)		$0.00	$0.06	$0.12
$ / Gallon	($1.14)	($1.23)	($0.36)		$0.03	$0.43	$3.29
Advantage to Fuel		($0.09)	$0.79		$1.18	$1.57	$4.43

Current scenario in column 1 – waste fuel. Column 2 – primary distill – demonstrates why cost prohibitive to recover as waste (Manifest).

BOL: (cost per isotainer for same material)
Logistics – 2 cents more a pound ($5110 vs $4343)
Processing – 10 cents more a pound ($9198 vs $5578)

Toluene Business Model - Benefits Table Worksheet

Toluene 36,192 lbs (5000 Gallons)
Recovered: $0.30 / lb
SPEC: $0.40 / lb

	Waste / US - Manifest		Houston - **Bill of Lading (BOL)**		Houston BOL	Puerto Rico
	Fuel Baseline Waste	Primary Distill Recovered Waste	Primary Distill Recovered Substance ($0.30)	Prim/Secondary Distill Recovered Substance	*use / reuse* Filter *Recovered* Substance ($0.30)	*use / reuse* Filter *Recovered* Substance
LOGISTICS	($5,110)	($5,110)	($4,343)	($4,343)	($4,343)	($400)
$/lb	($0.14)	($0.14)	($0.12)	($0.12)	($0.12)	($0.01)
PROCESING	($600)	($9,198)	($5,578)	($5,476)		
$/lb	($0.02)	($0.25)	($0.15)	($0.15)		
Isotainer **MARKET VALUE**	-	$8,143	$8,143	$9,989	$10,858	$10,858
yield&conc $/lb		$0.23	$0.23	$0.28	$0.30	$0.30
NET RETURN	($5,710)	($6,165)	($1,780)	$169	$6,514	$10,458
$/lb	($0.16)	($0.17)	($0.08)	$0.00	$0.18	$0.29
$ / Gallon	($1.14)	($1.23)	($0.36)	$0.03	$1.30	$2.09
Advantage to Fuel		($0.09)	$0.79	$1.18	$2.44	$3.23

Use / Reuse – Some of the toluene captured could be put directly back onto the market without any distillation / reclamation. Use / reuse activities include filtering, where a substance can be lightly processed and reused for its original intention. (amanda will cover later)

Though recognized limited markets, the returns are attractive enough to seek out these opportunities.

Toluene Business Model - Benefits Table Worksheet

Toluene 36,192 lbs (5000 Gallons)
Recovered: $0.30 / lb
SPEC: $0.40 / lb

	Waste / US - Manifest		Houston - **Bill of Lading (BOL)**		Houston - **Bill of Lading (BOL)**	
	Fuel Baseline Waste	Primary Distill Recovered Waste	Primary Distill Recovered Substance ($0.30)	Prim/Secondary Distill Recovered Substance	Prim/Sec Distill **SPEC** Substance ($0.40)	Prim/Sec Distill **SPEC** Substance Return Boat
LOGISTICS	($5,110)	($5,110)	($4,343)	($4,343)	($4,343)	($3,475)
$/lb	($0.14)	($0.14)	($0.12)	($0.12)	($0.12)	($0.10)
PROCESING	($600)	($9,198)	($5,578)	($5,476)	($5,476)	($5,476)
$/lb	($0.02)	($0.25)	($0.15)	($0.15)	($0.15)	($0.15)
Isotainer **MARKET VALUE**	-	$8,143	$8,143	$9,989	$13,319	$13,319
yield&conc $/lb		$0.23	$0.23	$0.28	$0.37	$0.37
NET RETURN	($5,710)	($6,165)	($1,780)	$169	$3,499	$4,367
$/lb	($0.16)	($0.17)	($0.08)	$0.00	$0.09	$0.12
$ / Gallon	($1.14)	($1.23)	($0.36)	$0.03	$0.70	$0.87
Advantage to Fuel		($0.09)	$0.79	$1.18	1.84	2.02

Other Scenarios:

- ***Waste Treatment on Island (no US disposal costs and transport)***
- ***Bottoms are used on site as fuel (no disposal costs)***
- ***Use/Reuse: toluene filtered, BOL, no wastes***

Return SPEC:

$913,000 for 210 isotainers of Toluene

Tetrahydrofuran Business Model - Benefits Table

Terahydrofuran (THF) @25%water (5000 gallons)

Recovered (<500 ppm H20)	$1.10 / lb
Feedstock 95%/5% Water	$0.10 / lb

	Waste / US - Manifest		Houston - Bill of Lading (BOL)			Puerto Rico
	Fuel Baseline Waste	Primary Distill Recovered Waste	Primary Distill Recovered Substance	Evap 5% Distill Recovered Substance	Evap 5% Distill Recovered Substance Return Boat	Evap 5% Distill Recovered Substance
LOGISTICS	($5,110)	($5,110)	($4,343)	($4,343)	($3,475)	($400)
$/lb	($0.14)	($0.14)	($0.12)	($0.12)	($0.10)	($0.01)
PROCESING	($600)	($11,704)	($9,415)	($11,766)	($11,766)	($11,766)
$/lb	($0.02)	($0.31)	($0.25)	($0.31)	($0.31)	($0.31)
Isotainer **MARKET VALUE**	-	$23,597	$23,597	$29,890	$29,890	$29,890
yield&conc $/lb		$0.62	$0.62	$0.62	$0.62	$0.62
NET RETURN	($5,710)	$6,784	$9,838	$13,780	$14,649	$17,728
$/lb	($0.16)	($0.17)	$0.26	$0.36	$0.38	$0.46
$ / Gallon	($1.14)	$1.36	$1.97	$2.76	$2.93	$3.54
Advantage to Fuel		$0.21	$0.83	$1.61	1.79	$2.40

Evap/Distill:

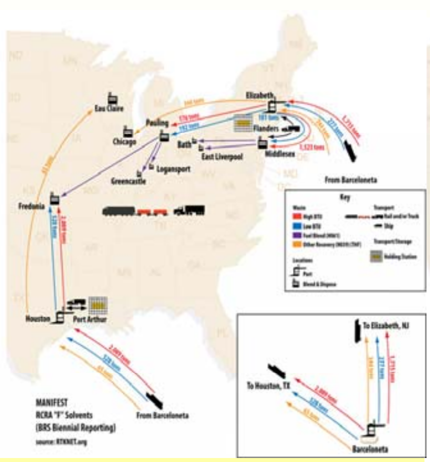
$311,000 for 21 isotainers of Toluene

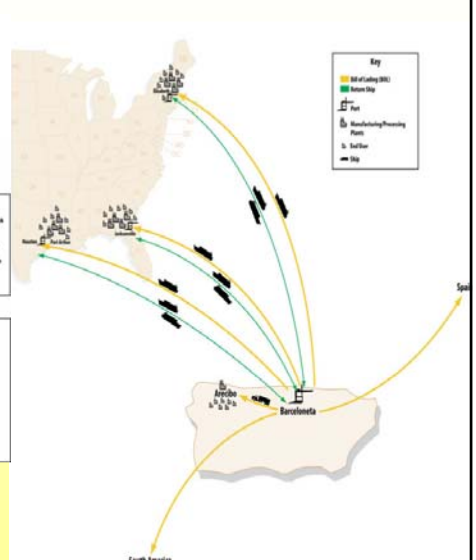
1000 gallons water recovered per isotainer

With high costs of THF any recovery method does provide. Evap / Distill provides greatest return.

Environmental Justice

Manifest – Hazardous Waste ***BOL – Hazardous Substance***





Toluene Business Model – Benefits Table Worksheet

Toluene 36,192 lbs (5000 gallons)
Recovered: $0.30 / lb
SPEC: $0.40 / lb

	Waste / US - Manifest: Fuel Baseline Waste	Waste / US - Manifest: Primary Distill Recovered Waste	Houston - Bill of Lading (BOL): Primary Distill Recovered Substance	$0.30	Houston - Bill of Lading (BOL): Prim/Secondary Distill Recovered Substance
LOGISTICS	($5,110)	($5,110)	($4,343)		($4,343)
$/lb	($0.14)	($0.14)	($0.12)		($0.12)
PROCESING	($600)	($9,198)	($5,578)		($5,476)
$/lb	($0.02)	($0.25)	($0.15)		($0.15)
Isotainer **MARKET VALUE**	-	$8,143	$8,143		$9,989
yield&conc $/lb		$0.23	$0.23		$0.28
NET RETURN	($5,710)	($6,165)	($1,780)		$169
$/lb	($0.16)	($0.17)	($0.08)		$0.00
$ / Gallon	($1.14)	($1.23)	($0.36)		$0.03
Advantage to Fuel		($0.09)	$0.79		$1.18

TOLUENE 100%
16,477 kg / 5000 Gallons Isotainer

KG material recovered	0	12,360	15,450
Manufacturing Credit MCO2 eq		-14.4	-18
Processing MCO2eq	113	29	8
TOTAL Metric Ton CO2eq	**113**	**14.6**	**-10**
Manufacuting Credit MMBTUs		-96	-120
Processing MMBTUs	370	164	51.4
Total Million BTUs	**370**	**68**	**-68.6**

THF Business Model – Benefits Table Worksheet

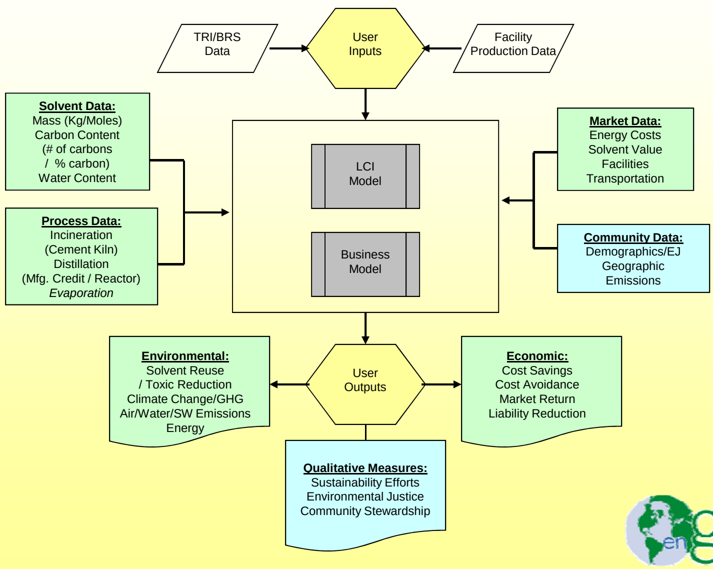
Terahydrofuran (THF) @25%water (5000 gallons)
Recovered (<500 ppm H20) $1.10 / lb
Feedstock 95%/5% Water $0.10 / lb

	Waste / US - Manifest: Fuel Baseline Waste	Waste / US - Manifest: Primary Distill Recovered Waste	Houston - Bill of Lading (BOL): Primary Distill Recovered Substance	Houston - Bill of Lading (BOL): Evap 5% Distill Recovered Substance
LOGISTICS	($5,110)	($5,110)	($4,343)	($4,343)
$/lb	($0.14)	($0.14)	($0.12)	($0.12)
PROCESING	($600)	($11,704)	($9,415)	($11,766)
$/lb	($0.02)	($0.31)	($0.25)	($0.31)
Isotainer **MARKET VALUE**	-	$23,597	$23,597	$29,890
yield&conc $/lb		$0.62	$0.62	$0.62
NET RETURN	($5,710)	$6,784	$9,838	$13,780
$/lb	($0.16)	($0.17)	$0.26	$0.36
$ / Gallon	($1.14)	$1.36	$1.97	$2.76
Advantage to Fuel		$0.21	$0.83	$1.61

Tetrahydrofuran (THF) 25% H2O
16,856 kg / 5000 Gallons Isotainer

KG material recovered	0	9,481	12,010
Manufacturing Credit MCO2 eq		-153	-194
Processing MCO2eq	66	8.6	11
TOTAL Metric Ton CO2eq	**66**	**-144.4**	**-183**
Manufacuting Credit MMBTUs		-1135	-1438
Processing MMBTUs	370	122	155
Total Million BTUs	**370**	**-1013**	**-1283**

Solvent Decision Support Tool



Summary

- Do as much on island as possible . . including processing, water removal and use / reuse.
- Devise different treatment strategies for solvent types such as soluble methanol and insoluble toluene
- Manage bottoms / wastes material minimizing materials that are disposed.
- Apply DST to assess best process changes and concurrent economic and environmental benefits
- Trace solvents streams to point of usage to determine best opportunities to reduce their use and/or extend solvent life
- Waste → Product. Cost → Net Return.

REFERENCE NOT PART OF PRESENTATION

Reference / question slides

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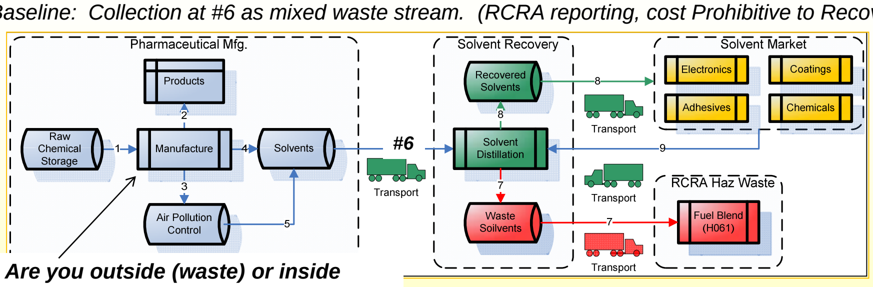
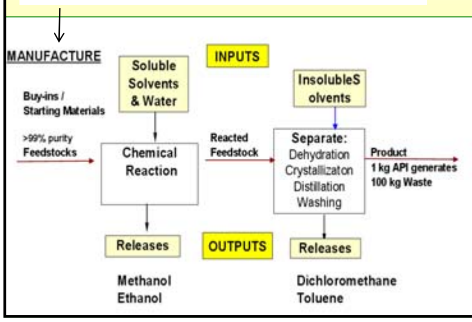
Final thought .. When is it Waste and When is it By-Product?

Baseline: Collection at #6 as mixed waste stream. (RCRA reporting, cost Prohibitive to Recover.)



Are you outside (waste) or inside (byproduct) the manufacturing box?



Under the Inventory Update Rule (IUR), a material recovered for commercial use (OUTPUTS) may be required to be reported as a listed substance.

The only one that can answer this question is you - - but we can help you get to that answer and demonstrate why it is worth the trip! ;-)

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Solvent Incinerator Module: Tetrahyrdrofuran (THF)

For THF, part of energy is extended to combust water and other portion to combust carbon materials. High recovered sale costs and manufacturing emissions provides multiple benefits to extend life vs. disposal.

4 carbons

Isotainer

12,642 kg THF
4,7214 kg H_2O

16,856 kg

Air 25 ºC

390 ppm CO_2

Combustion Chamber
THF

25,000 kg CO_2eq

Natural Gas
871- 982 ºC

	MillionBTUs	MetricTons
Solvent	MMBTU	MCO2eq
Methanol	161	25
Toluene	614	113
THF	**370**	**66**

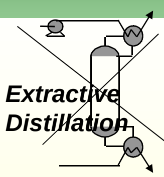
Kg CO2 eq: 66,000
31,000 kg from combusting THF
35,000 kg from burning Natural Gas

Evaporation for Soluble Solvents / Energy Recovery

1. Multiple Effect Arrangement

In a multiple effect evaporation plant, the vapour produced in the first effect by the live steam is not lost to the condenser, but is reutilized as the heating medium of the second effect. This effectively reduces the steam consumption by about 50%.

As this principle is repeated, further steam reductions follow.

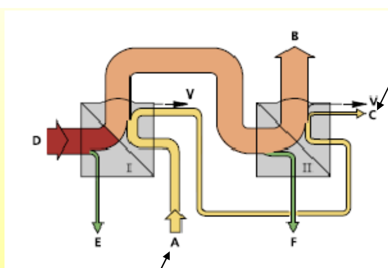


Extractive Distillation

Methanol / THF / 5% H2O

Recovered Heat

From Distillation



A product to be evaporated
B residual vapour
C concentrate
D motive steam
E heating steam condensate
F vapour condensate
V heat loss

Heat flow diagram of a double-effect, directly heated evaporator

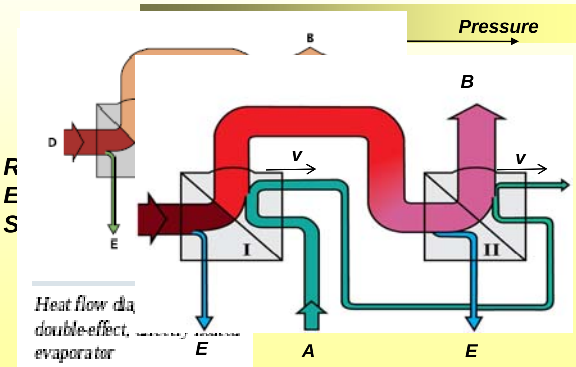
Methanol / 50% H2O & THF @ 75%

Double benefits of purer solvent and reduced heating load

Incidental Processing – out of RCRA jurisdiction

Evaporation – Water removal and Energy Recovery

Multiple Effect Arrangement: In a multiple effect evaporation plant, the bapour produced in the first effect by the live steam is not lost to the condenser, but is reutilized as the heating medium of the second effect. This effectively reduced the steam consumption by about 50%.



A: Product to be evaporated
B: Residual vapor
C: Concentrate
D: Motive Steam
E: Heating steam condensate
F: Vapour condensate
V: Heat Loss

The main advantage of the mulit-effect system is the high steam efficiency, which can be as high as 5.5 lbs water evaporated per lb of steam for the sextuplet system. (Smook, Handbook for Pulp & Paper Technologies)

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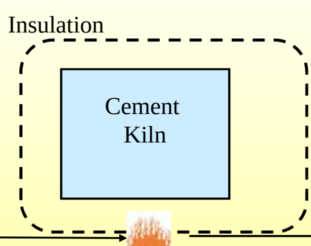
Cement Module (Adaption in progress)

Solvents are used as Fuel to power cement kiln.



67,753 kg HEV
4.1 isotainers
Insoluble
HEV/Toluene

67,753 kg HEV

Use exhaust gas for steam

50% Energy Recovery

13,137 kg less material generated same amount of energy.

	MillionBTUs	*MetricTons*
Solvent	MMBTU	$MCO2_{eq}$
HEV/LEV	1,480	228
HEV	1,480	224
HEV / ER	1,480	76

Recovered energy can be used to preheat the HEV generating further savings

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Cement Module (Adaption in progress)

Solvents are used as Fuel to power cement kiln.

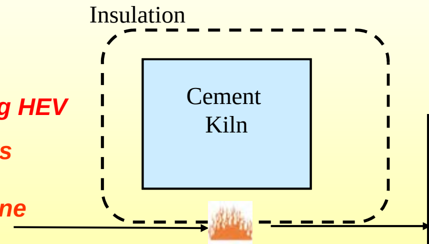
Common practice is to blend high energy value (HEV) with low energy value (LEV) solvents are used as Fuel to power cement kiln. (HO61)

65,908 kg HEV

4 isotainers Insoluble HEV/Toluene

1 isotainer LEV/Methanol

7,481 kg LEV & H_2O



80,870 Total kg

	MillionBTUs	*MetricTons*
Solvent	MMBTU	MCO2eq
HEV/ LEV	1,480	228

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Methanol Business Case (needs updating)