Green Engineering Education in the United States: Environmentally Conscious Design of Chemical Processes

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What is Green Engineering?

- **Assessment** Defining what constitutes a green product or a green process is not simple
- **Improvement** Will new engineering design tools be necessary, or will our existing tools, that allow us to minimize mass and energy consumption be sufficient?
- **Implications for chemical engineering education**

(Allen and Shonnard, AICHE Journal, 47, 1906-1910, 2001)

What is Green Engineering?

Scale	**Assessment**	**Improvement**
Molecular		
Process		
System		

- Both assessment and improvement tools can be applied at a variety of design stages and at a variety of scales

Assessment:
What does it mean to be green?

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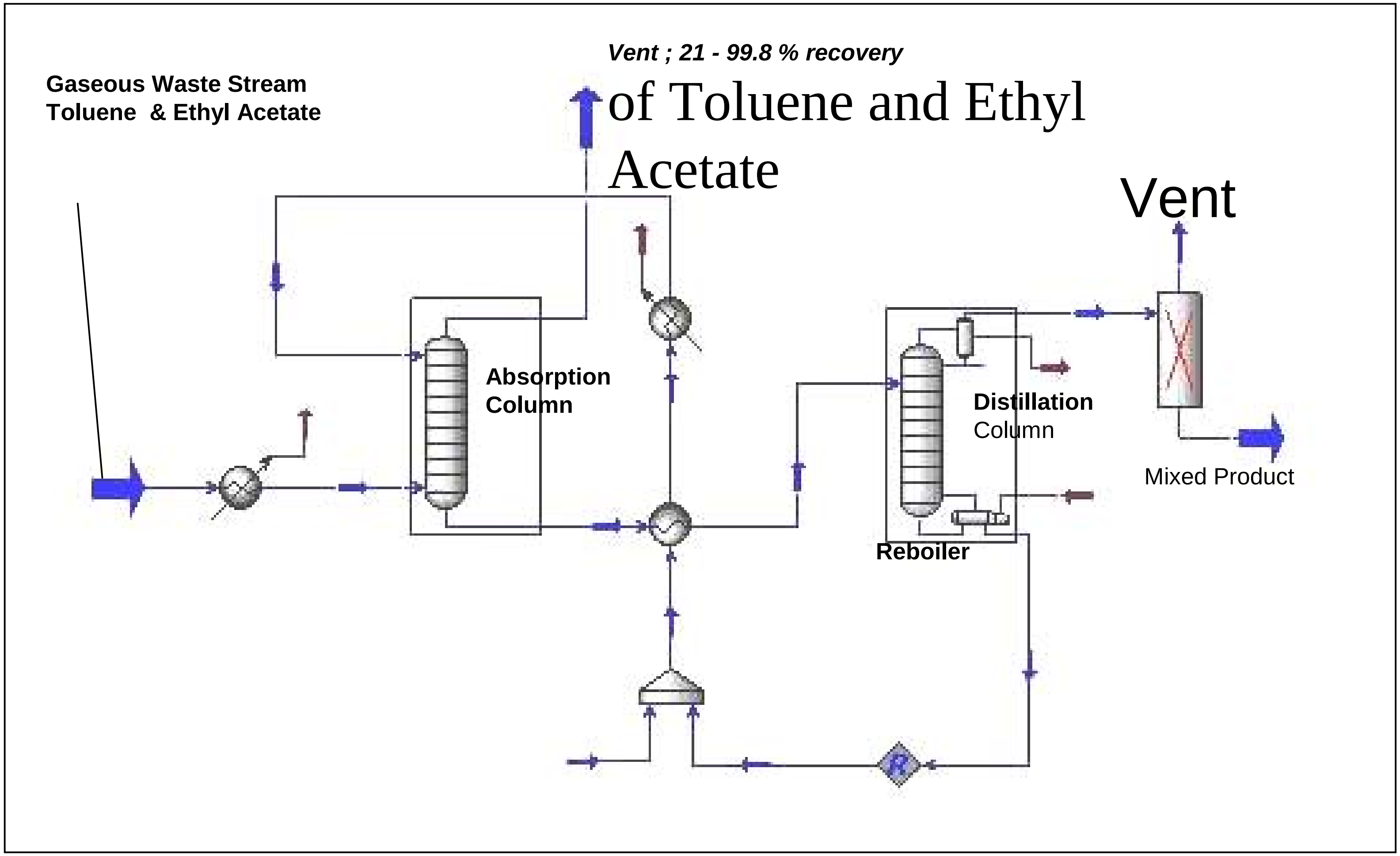
- Many different potential environmental impacts (global warming, stratospheric ozone depletion, smog formation, energy use, waterway eutrophication, and many more - general categories include human health impacts, ecosystem impacts and resource utilization)
- Most products or processes have a footprint and comparing products or processes is difficult
- Consider a simple process case study

Assessment:
What does it mean to be green?



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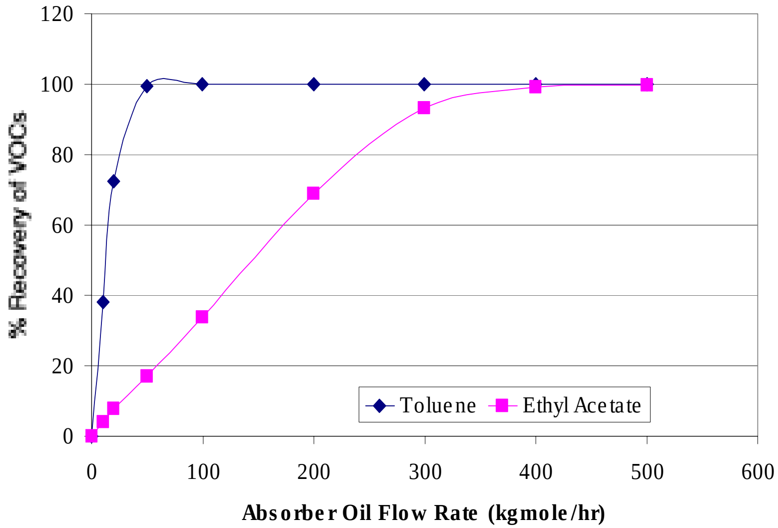

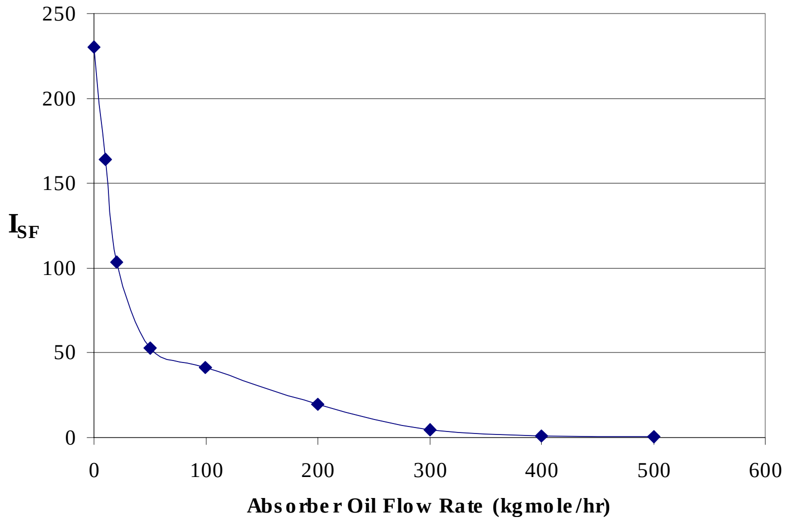

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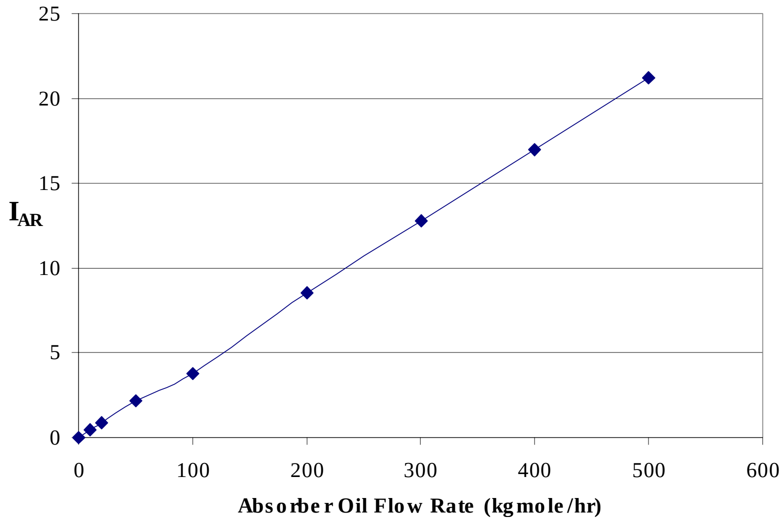
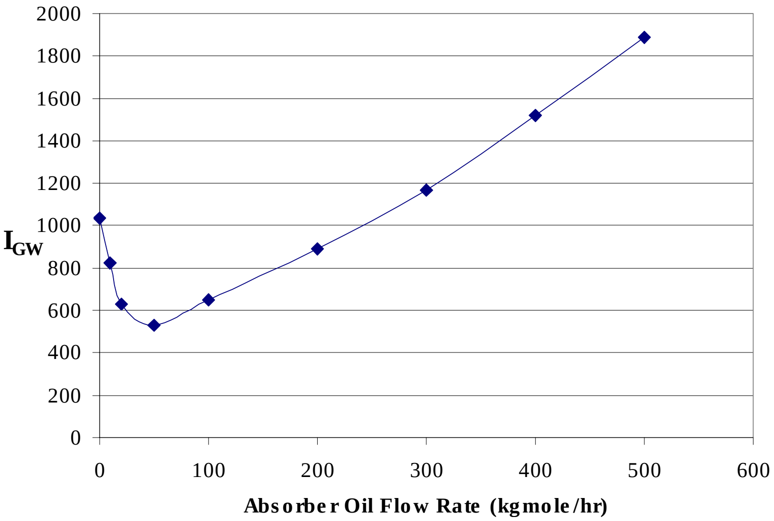




So, assessment tools may give us ambiguous information, nevertheless, we proceed

Systematically examine assessment tools at each scale

Scale	**Assessment**	**Improvement**
Molecular	**X**	
Process	**X**	
System	**X**	

- Both assessment and improvement tools can be applied at a variety of design stages and at a variety of scales

Assessment: What does it mean to be green?

- Consider an example at a molecular level - comparing two reaction pathways for producing the same chemical
- Here we have a decision that occurs early in the design process where we have limited information

Assessment:
What does it mean to be green?

$$(CH_3)_2\ C{=}O + HCN \rightarrow HO\text{-}C(CH_3)_2\ \text{-}CN$$

(Acetone + hydrogen cyanide → acetone cyanohydrin)

$$HO\text{-}C(CH_3)_2\ \text{-}CN + H_2SO_4 \rightarrow CH_3\text{-}(C{=}CH_2)\text{-}(C{=}O)\text{-}NH_2(H_2SO_4)$$

(acetone cyanohydrin → methacrylamide sulfate)

the methacrylamide sulfate is then cracked forming methacrylic acid and methylmethacrylate

$$CH_3\text{-}(C{=}CH_2)\text{-}(C{=}O)\text{-}NH_2(H_2SO_4) + CH_3OH \rightarrow CH_3\text{-}(C{=}CH_2)\text{-}(C{=}O)\text{-}OH$$

$$\rightarrow CH_3\text{-}(C{=}CH_3)\text{-}(C{=}O)\text{-}O\text{-}CH_3$$

Assessment:
What does it mean to be green?

Alternatively, methyl methacrylate can be manufactured with isobutylene and oxygen as raw materials.

$$CH_3\text{-}(C{=}CH_2)\text{-}CH_3 + O_2 \rightarrow CH_3\text{-}(C{=}CH_2)\text{-}(C{=}O)H + H_2O$$

isobutylene + oxygen → methacrolein

$$CH_3\text{-}(C{=}CH_2)\text{-}(C{=}O)H + 0.5\ O_2 \rightarrow CH_3\text{-}(C{=}CH_2)\text{-}(C{=}O)\text{-}OH$$

methacrolein → methacrylic acid

$$CH_3\text{-}(C{=}CH_2)\text{-}(C{=}O)\text{-}OH + CH_3OH \rightarrow CH_3\text{-}(C{=}CH_2)\text{-}(C{=}O)\text{-}O\text{-}CH_3 + H_2O$$

methacrylic acid + methanol (in sulfuric acid) → methylmethacrylate

Traditional screening metrics are based on cost

Compound	*Pounds produced or pounds of raw material required per pound of methyl methacrylate**	*Cost per pound*[1]
Acetone-cyanohydrin route		
Acetone	-.68	$0.43
Hydrogen cyanide	-.32	$0.67
Methanol	-.37	$0.064
Sulfuric acid	-1.63	$0.04
Methyl methacrylate	1.00	$0.78
Isobutylene route		
Isobutylene	-1.12	$0.31
Methanol	-0.38	$0.064
Pentane	-0.03	$0.112
Sulfuric acid	-0.01	$0.04
Methyl methacrylate	1.00	$0.78

Need parallel environmental screening metrics

- Consider multiple indicators (e.g. atom efficiency, PBT performance)
- Develop indicators that can be used as a new chemistry evolves from the benchtop, to the pilot plant, to final process design

Multiple Environmental Criteria (PBT)

Stoichiometric, persistence, toxicity and bioaccumulation data for two synthesis routes for methyl methacrylate

Compound	Pounds produced or pounds required per pound of Methyl methacrylate[1]	Atmospheric half-life / Aquatic half-life[1]	1/TLV[4] (ppm) $^{-1}$	Bioconcentration factor[5] (conc. in lipids/conc.in wate
Acetone-cyanohydrin route				
Acetone	-.68	52 days/weeks	1/750	3.2
Hydrogen cyanide	-.32	1 year/weeks	1/10	3.2
Methanol	-.37	17 days/days	1/200	3.2
Sulfuric acid[3]	-1.63		1/2(est.)	
Methyl methacrylate	1.00	7 hours/weeks	1/100	2.3
Isobutylene route				
Isobutylene	-1.12	2.5 hours/weeks	1/200 (est)	12.6
Methanol	-0.38	17 days/days	1/200	3.2
Pentane	-0.03	2.6 days/days	1/600	81
Sulfuric acid[3]	-0.01		1/2 (est)	
Methyl methacrylate	1.00	7 hours/weeks	1/100	2.3

Assessment:
What does it mean to be green?

- Consider an example at the process level - comparing two processes for producing the same chemicals
- Here we have a more information than at the reaction pathway level, but still not enough information to perform a complete environmental impact assessment

What metrics should be used? CWRT Sustainability Metrics

- Material use per unit product (or per unit sales or per unit value added)
- Water use per unit product
- Energy use per unit product
- Emissions per unit product (greenhouse gas, toxics, ozone depleting chemicals)

Sample sustainability metrics

Compound	Process	Material lb/ lb prod.	Energy KBTU/ lb prod.	Water gal/ lb prod.	Toxics lb/ lb prod.	Pollutants lb/ lb prod.	Pollutants +CO2 lb/ lb prod.
Acetic Acid	from MeOH by low pressure carbonylation process, Rh catalyst	0.100	1.82	1.24	0.00011	0.00005	0.07588
Acrylonitrile	by the ammoxidation of propylene process	0.493	5.21	3.37	0.01514	0.00781	0.65682
Adipic acid	from cyclohexane by conventional Process	0.281	11.38	3.52	0.00008	0.00000	0.00003
Sulfuric acid	from pyrometallurgical sulfur dioxide	-0.345	0.07	0.57	-0.65303	-0.65303	-0.65303
Sulfuric acid	from sulfur	-0.672	-0.87	0.69	0.00195	0.00195	0.00477
Sulfuric acid	from sulfur (actual data)	-0.672	-2.54	0.69	0.00195	0.00195	0.00477

How can we use these data?

- Practical minimum energy project case study
- Assess energy metric for base case flow sheet and flow sheets that incorporate state of the art or emerging technologies
- Consider maleic anhydride case

Maleic anhydride base case

Base case Energy Requirements for Maleic Anhydride Production;
Base Case: From n-butane via fixed bed with dibutyl phthalate solvent.
Energy requirements in BTU per pound of maleic anhydride.

	Reaction Section	Recovery & Purification Section	**Total Process**
Electricity Requirement	1,377	44	**1,421**
Heat Requirement	411	2,446	**2,857**
Process Heat & Power Req.	1,788	2,490	**4,278**
Fuel for Electricity	4,439	142	**4,581**
Fuel for Steam/Dowtherm	675	4,361	**5,036**
Fuel for Waste Incineration	-	3,227	**3,227**
Total Fuel Required	*5,114*	*7,730*	***12,844***
Fuel Credit	-12,077	-	**-12,077**
Total Process Energy	-6,963	7,730	**767**

Maleic anhydride – state of art

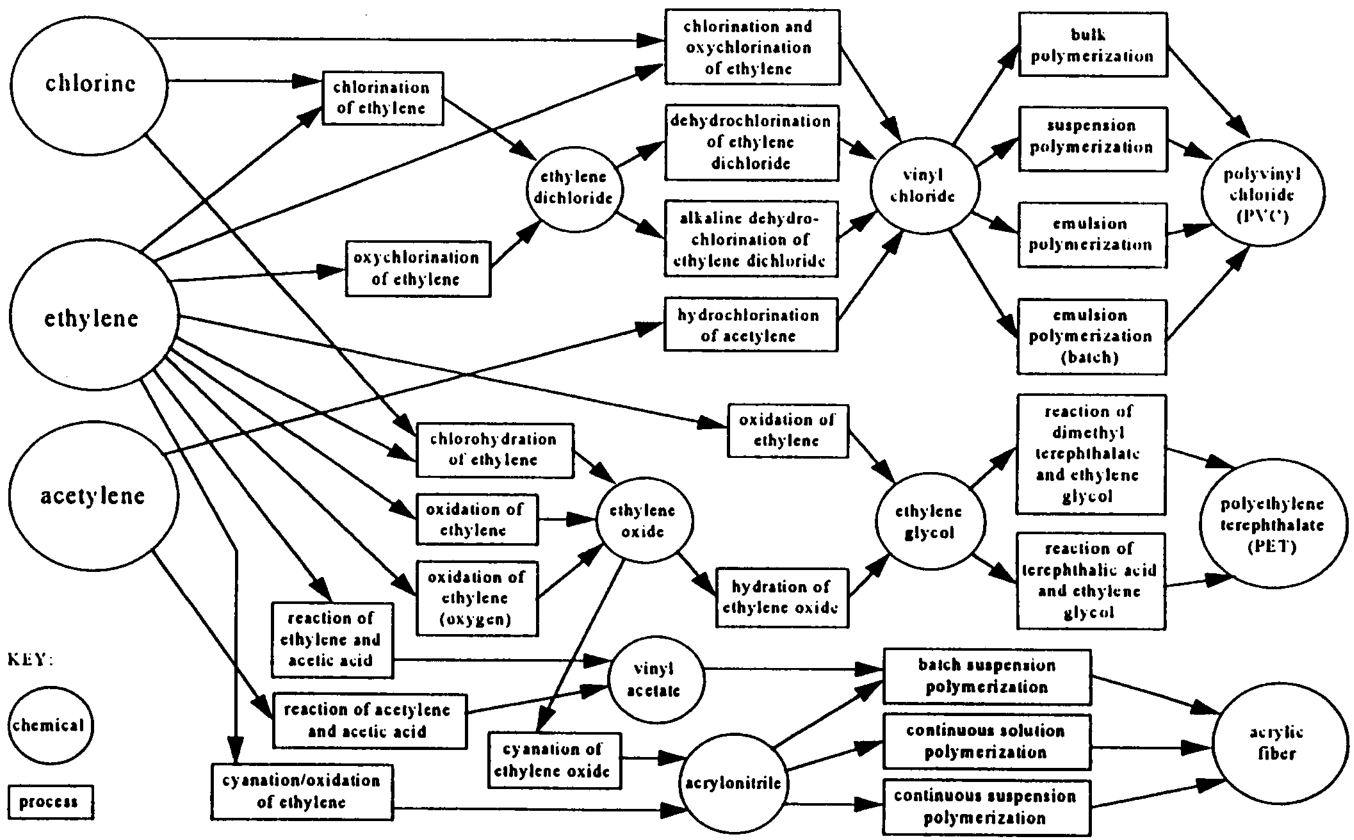
Energy requirements in BTU per pound of maleic anhydride.

	Best Practice	**Case C-1**	**Case C-2**
Electricity Requirement	1,421	1,494	**1,271**
Heat Requirement	901	1,059	**1,487**
Process Heat & Power Req.	2,322	2,553	2,759
Fuel for Electricity	4,581	4,815	**4,097**
Fuel for Steam/Dowtherm	1,574	1,841	**2,711**
Auxiliary Fuel for Steam Generation	3,227	265	**252**
Total Fuel Required	*9,382*	*6,921*	***7,060***
Fuel Credit	-12,077	-10,579	**-19,477**
Total Process Energy	-2,695	-3,658	**-12,417**
Hc Feedstocks – Hc Products	16,763	16,111	**21,934**
Primary Energy Consumed	14,068	12,453	**9,517**

Assessment:
What does it mean to be green?

- Consider an example at the systems level – evaluating how processes impact the entire system of chemical manufacturing
- These types of analyses, which rely heavily on optimization tools, first emerged for systems energy evaluations

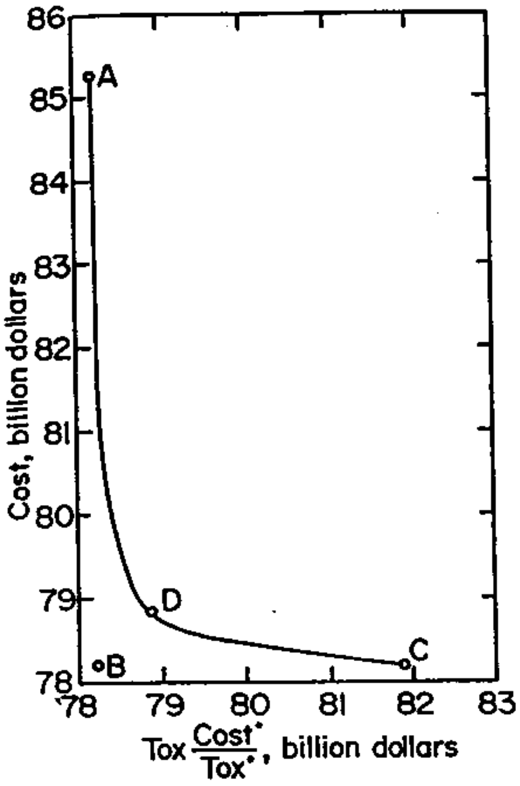
Many technology mixes are possible for a fixed set of raw materials and products



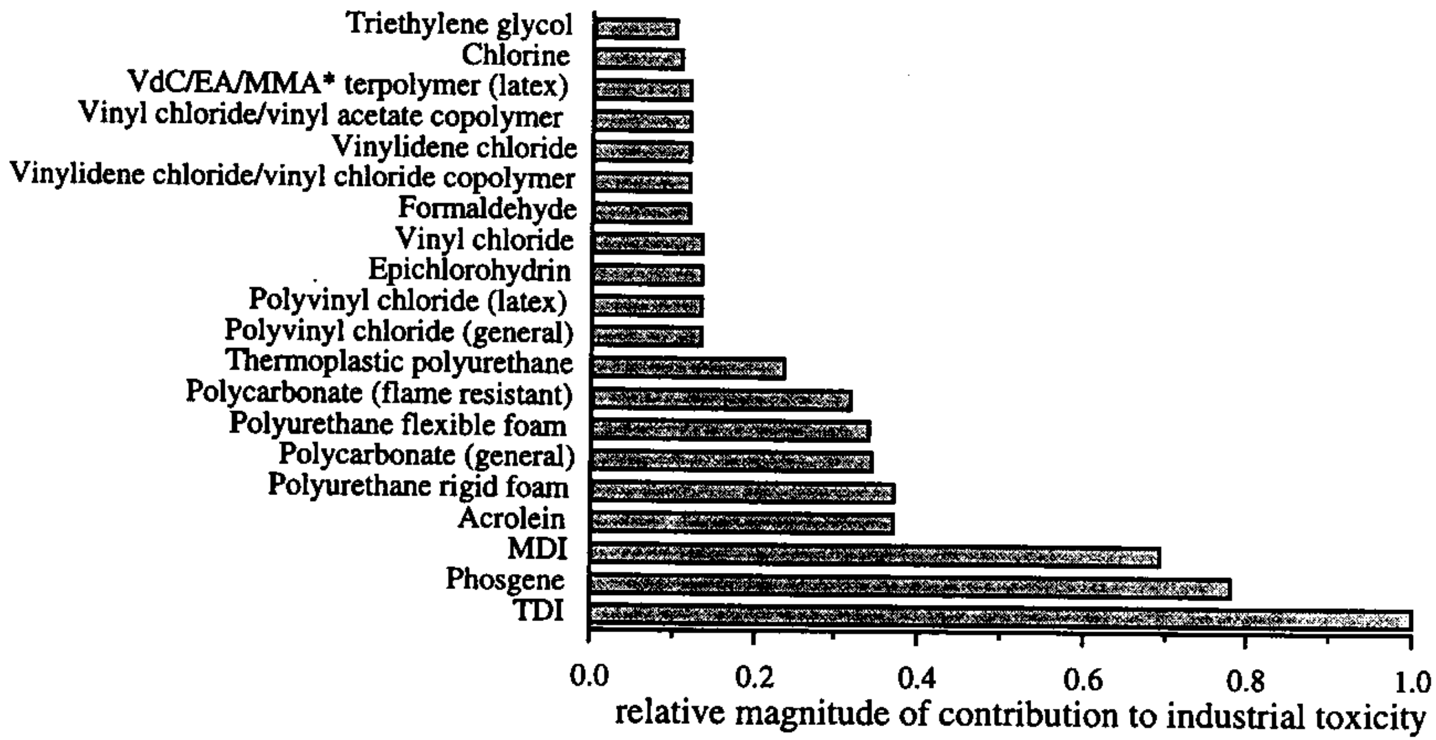
Formulate as a mathematical programming problem

- Each technology has energy and mass input requirements
- Each has a different set of environmental performance indices
- Consider the performance indices of cost and toxicity of chemicals used (as measured by TLV)

Select a set of technologies that minimize cost, or a set that minimizes toxicity of intermediates



Identify the sources of residual toxicity; these are candidates for alternative reaction pathways



*VdC/EA/MMA: Vinylidene chloride/ethyl acrylate/methyl methacrylate

New systems – New tools

Scale	Assessment	Improvement
Molecular		
Process		
System		

- We have examined assessment tools for our traditional systems
- Most of the improvement tools for our traditional systems are the conventional tools of process design – BUT – to the extent that we are examining new systems, we will need new tools

Green Engineering

New Systems

- National flows of materials and energy
- Byproduct synergy (wastes as raw materials)

New Tools

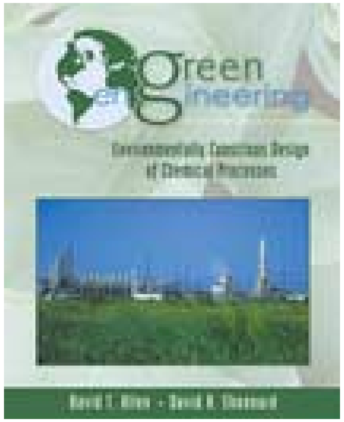
- Tools are needed for integrating material and energy flows across industrial sectors; spatial information must also be incorporated

Implications for chemical engineering education

- New courses (Green Engineering textbook)
- Incorporate concepts and tools into existing courses (Course Modules)

Green Engineering Textbook

- **Part I: A Chemical Engineer's Guide to Environmental Issues and Regulations**
- **Part II: Environmental Risk Reduction for Chemical Processes**
- **Part III: Moving Beyond the Plant Boundary**



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GREEN ENGINEERING RESOURCES

- Textbook
- Modules
- Software
- Websites

www.epa.gov/oppt/greenengineering