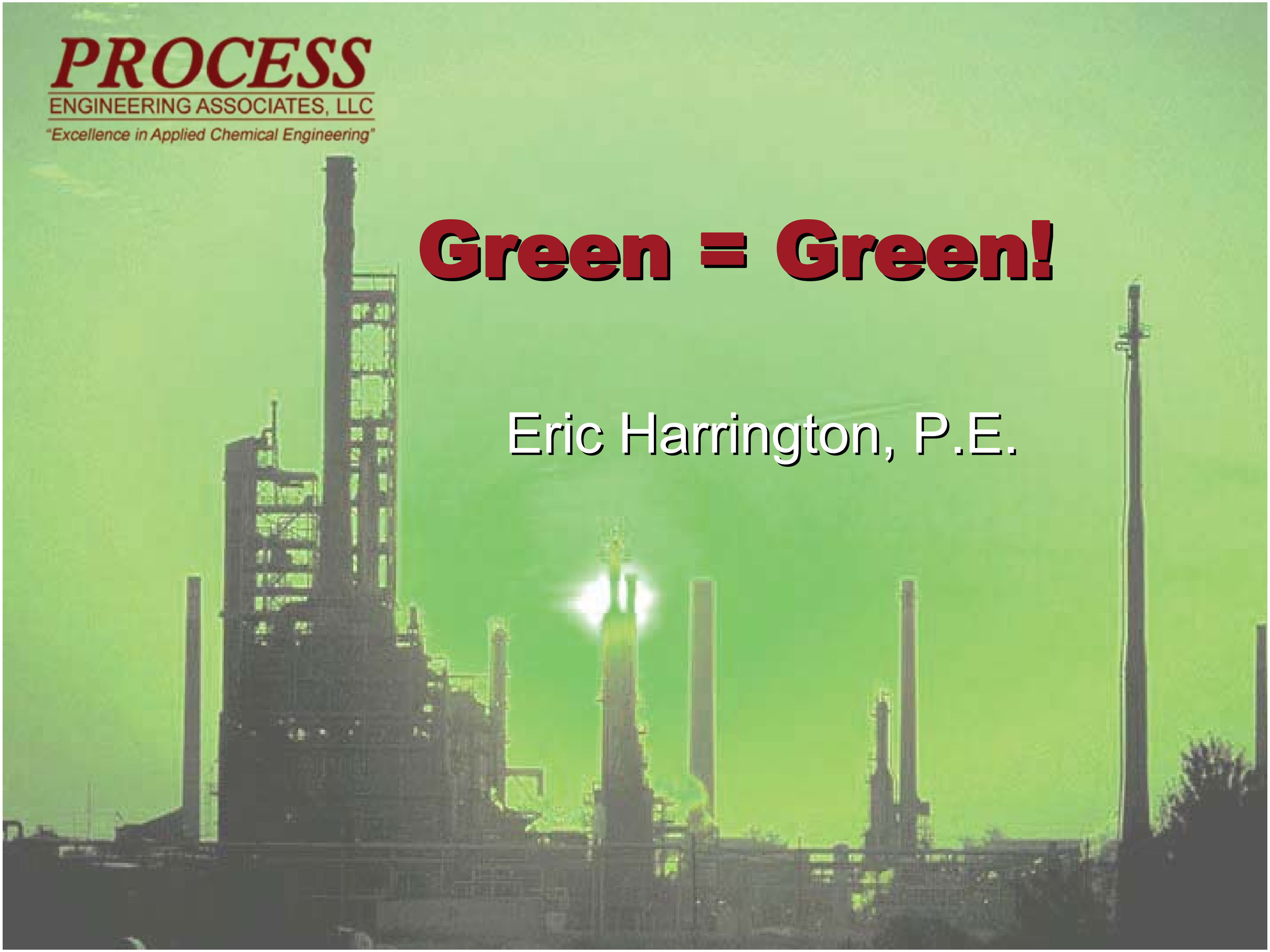

PROCESS
ENGINEERING ASSOCIATES, LLC
"Excellence in Applied Chemical Engineering"

Green = Green!

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Content

- Various concepts of sustainability
- Principles of green engineering
- Examples of green chemical engineering
- Design tools

Introduction

- Green Chemical Engineering is much more than a method for addressing environmental problems. It offers a framework for achieving innovation. Time and again, companies looking to the future through the lens of green chemical engineering have enjoyed tremendous environmental and economic returns.

- Green chemical engineering is a way to not only improve the environment but positively impact the client's bottom line. Avoiding the generation of waste (including energy) or pollutants can often be more cost-effective than controlling or disposing of pollutants once formed.

- After all, aren't we, as engineers, supposed to be designing processes that give the client the best value for their money?

Intro (cont'd)

- Recently, for example:
  - A chemical company launched an entirely new branding opportunity from green chemistry efforts.
  - A pharmaceutical firm saved millions of dollars-- and millions of gallons of waste - through a redesign of their process.
  - An electronics firm added millions in shareholder value through a redesign of their process.

Sustainability

- In 1987, the United Nations World Commission on Environment and Development stated that sustainability is "meeting the needs of the present without compromising the ability of future generations to meet their own needs."
- Sustainable development is often used synonymously, but is more of an economic term describing how our economy should improve, and implying that an increase in quantity is not necessarily the goal, but rather an increase in quality. An analogy would be ourselves. As we grow older, we grow to a certain mature height and weight, and then, hopefully, stop growing. However, unless we avoid it, we never stop developing our skills, abilities, and knowledge.

Sustainability Concepts

- The Natural Step
- Pollution Prevention
- Design for Environment
- Eco-Efficiency
- Eco-Effectiveness
- Cradle-to-Cradle Design
- Industrial Ecology
- Environmental Management Systems/Sustainable Management Systems

The Natural Step

- TNS represents the ultimate principles of sustainability. The four system conditions of TNS are the basic "laws" that must be followed in order to achieve sustainability, and are stated as follows:

- In a sustainable society, nature is not subject to systematically increasing:
  - concentrations of substances extracted from the earth's crust;
  - concentrations of substances produced by society;
  - degradation by physical means
    and, in that society. . .
  - human needs are met worldwide."

- These conditions are based on our dearly-loved laws of thermodynamics (at least the first ones).

Pollution Prevention

- Pollution prevention incorporates the concepts of source reduction and recycling.

  - Source reduction is defined as those multimedia activities that prevent waste generation and contaminant release.
  - Recycling, for the purposes of pollution prevention, is defined as a process in which a waste material is reused in the original manufacturing process or another process.

Design for Environment

- Design for Environment (DfE) is defined as the systematic consideration during design of issues associated with environmental safety and health over the entire product life cycle.

Eco-Efficiency

- Eco-efficiency has been described as doing more with less. It involves minimizing waste, pollution and natural resource depletion (thus incorporating the concept of pollution prevention).
- Eco-efficiency is probably the easiest way to go, as well as the logical follow-up to the progress that has been made in the area of environmental management
  - Began with an era of no regulation
  - Followed by an era of regulation and strict compliance
  - After which is coming a time of “beyond compliance”, where businesses are finding that it can be to their benefit to not just adhere to the letter of the law, but to go beyond it.

Eco-Effectiveness

- In the words of William McDonough and Michael Braungart, “eco-efficiency is not a strategy for long-term success. It seeks to make the current, destructive system sustainable.”

- In other words, it is doing “less bad.”

- Proponents of eco-effectiveness point out that natural systems are not very efficient, but they sure are effective, and they represent the ideal systems which our systems must emulate in order to achieve sustainability. McDonough and Braungart point out the case of the cherry tree:
  - Each spring it makes thousands of blossoms, which then fall in piles to the ground - not very efficient. The same happens with the leaves every fall.
  - The leaves and blossoms become food for other living things.
  - The tree's abundance of blossoms is both safe and useful, contributing to the health of a thriving, interdependent system.
  - The tree spreads multiple positive effects-making oxygen, transpiring water, creating habitat, and more.

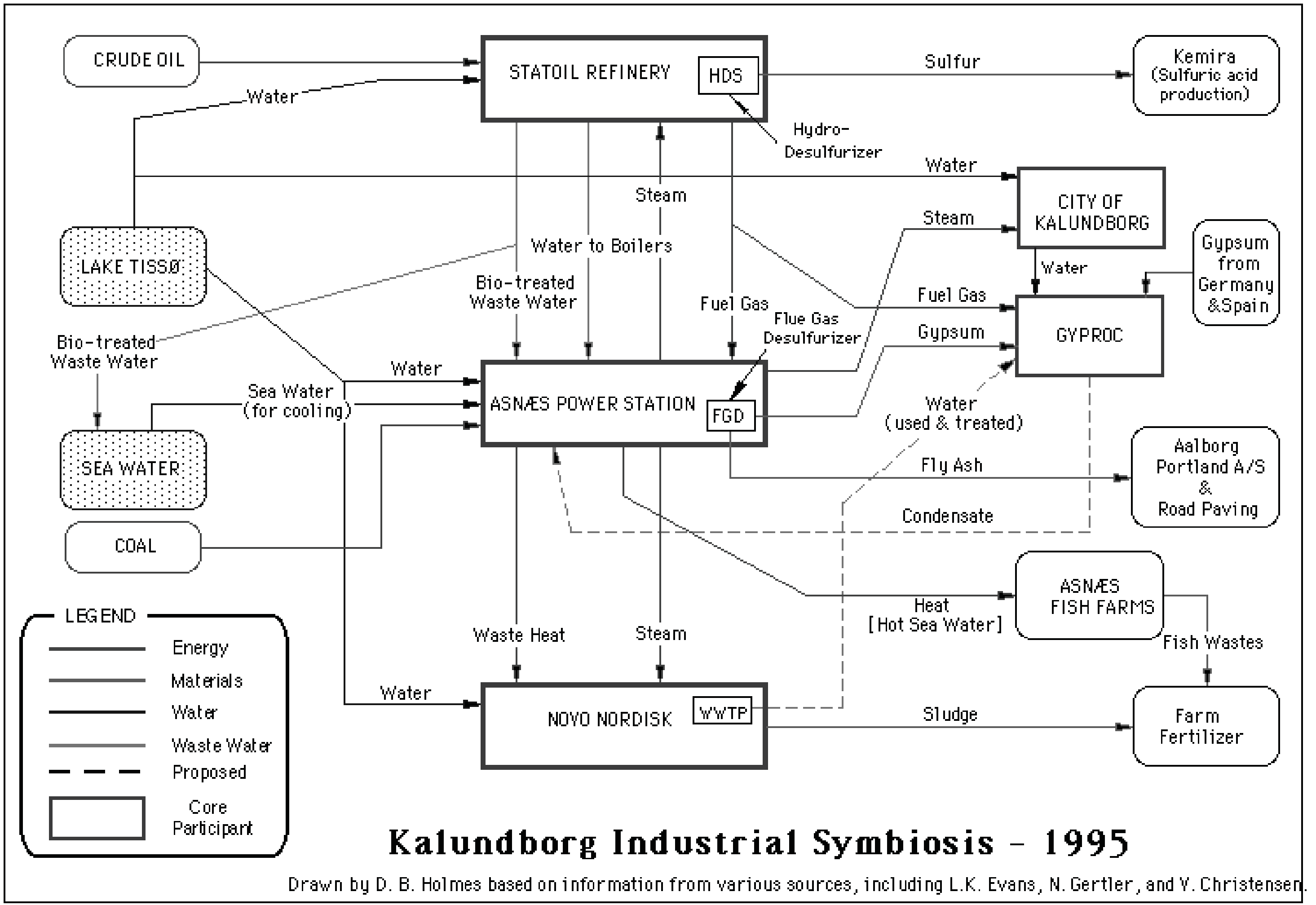
Cradle-to-Cradle Design

- C2C Design is an example of an eco-effective strategy.
- The C2C concept divides materials into biological nutrients and technical nutrients
- A biological nutrient is a material or product that is designed to return to the biological cycle.
- A technical nutrient is a material or product that is designed to go back into the technical cycle, into the industrial metabolism that made it. Isolating the technical nutrient from the biological nutrient allows it to retain its high quality in a closed-loop industrial cycle.
- Example: design of a new upholstery fabric
  - Initially considered a recycled PET/cotton combination that sounds great (recycled and natural) until one sees that the PET will not degrade and the cotton cannot recirculate in industrial cycles
  - Instead of filtering out mutagens, carcinogens, endocrine disrupters, persistent toxins, and bioaccumulative substances at the end of the process, a filter was applied to the design, rather than the waste stream
    - Eight thousand chemicals were eliminated for their negative effects; 38 were selected for their positive effects
  - A textile was created that can be thrown on the compost pile at the end of its useful life.

Industrial Ecology

- Industrial metabolism is the basic concept upon which industrial ecology is based.
- Industrial ecology is a means of designing and operating industrial systems as systems interdependent with natural systems.
- Industrial ecology involves application of systems science to industrial systems, proper definition of the system boundary to incorporate the natural world, and optimization of the systems under consideration.
- It is characterized by exchange of materials and energy within a network of industrial, commercial, or municipal facilities to the mutual benefit of each and all entities in the network.
- The prime example of the employment of industrial ecology concepts is located in Kalundborg, Denmark, where a number of industrial facilities are interconnected in such a manner that wastes or byproducts from one facility provide feedstock for other facilities.

Kalundborg, Denmark



Kalundborg Industrial Symbiosis - 1995

Drawn by D. B. Holmes based on information from various sources, including L.K. Evans, N. Gertler, and V. Christensen.

Environmental Management Systems/Sustainable Management Systems

- Environmental management systems include:
  - establishment of an environmental policy that contains commitments to continual improvement, compliance, and pollution prevention,
  - environmental planning to identify significant environmental impacts,
  - controlling these activities to minimize their impact on the environment; and
  - setting environmental performance objectives and targets and tracking progress toward meeting them.
- EMS are more methods of analyzing and tracking progress towards sustainability, rather than concepts that can be implemented to achieve sustainability.
- Sustainability management systems are similar, but go one step further in that they provide a sustainability-based framework on which to base the targets developed by the EMS. One example is the combination of TNS with EMS.

Principles of Green Engineering

- **1. Inherent Rather Than Circumstantial**
  Designers need to strive to ensure that all materials and energy inputs and outputs are as inherently nonhazardous as possible.

- **2. Prevention Instead of Treatment**
  It is better to prevent waste than to treat or clean up waste after it is formed.

- **3. Design for Separation**
  Separation and purification operations should be designed to minimize energy consumption and materials use.

- **4. Maximize Efficiency**
  Products, processes, and systems should be designed to maximize mass, energy, space, and time efficiency.

More Principles

- **5. Output-Pulled Versus Input-Pushed**
  Products, processes, and systems should be "output pulled" rather than "input pushed" through the use of energy and materials.

- **6. Conserve Complexity**
  Embedded entropy and complexity must be viewed as an investment when making design choices on recycle, reuse, or beneficial disposition.

- **7. Durability Rather Than Immortality**
  Targeted durability, not immortality, should be a design goal.

- **8. Meet Need, Minimize Excess**
  Design for unnecessary capacity or capability (e.g., "one size fits all") solutions should be considered a design flaw.

And Some More

- **9. Minimize Material Diversity**
Material diversity in multicomponent products should be minimized to promote disassembly and value retention.

- **10. Integrate Material and Energy Flows**
Design of products, processes, and systems must include integration and interconnectivity with available energy and materials flows.

- **11. Design for Commercial "Afterlife"**
Products, processes, and systems should be designed for performance in a commercial "afterlife.“

- **12. Renewable Rather Than Depleting**
Material and energy inputs should be renewable rather than depleting.

- ** Anastas, P.T., and Zimmerman, J.B., "Design through the Twelve Principles of Green Engineering", Env. Sci. and Tech., 37, 5, 95 ? 101, 2003.*

Chementator Listings

- The Chementator column in Chemical Engineering magazine continually includes examples of green engineering:
  - October 2003: Producing phenol from benzene without producing byproducts; design of a more energy-efficient centrifuge decanter; phosgene-free route to polycarbonate
  - September 2003: Making more methanol in one pass with new catalyst; new route to propylene oxide via hydrogen peroxide rather than chlorohydrin or styrene monomer routes
  - July 2003: Making methanol from methane using microbes rather than reaction of hydrogen and carbon monoxide at high temperature and pressure

More Listings

- May 2003: Producing biodegradable polymer from food waste; winning chromium compounds from chromite ore using liquid phase oxidation instead of roasting
- April 2003: Microfiltration to help a distillery to reuse a waste stream; turning driftwood into charcoal, vinegar, and gas
- March 2003: Reclaiming oilseed byproducts as active ingredients in hair gel; ash-recycling process to eliminate waste; production of hydrogen from food-processing wastewater
- February 2003: Wet methanation process that uses half the water; hybrid rocket fuel that is nontoxic and nonhazardous; fertilizer from swine waste
- January 2003: Sintering process to reduce carbon dioxide emissions in the production of pig iron; dye removal process to improve wastewater recycle in textile production

Pollution Prevention in Process Development and Design

- Avoid adsorptive separations where adsorbent beds cannot be readily regenerated.
- Provide separate reactors for recycle streams to permit optimization of conversions.
- Consider low-temperature distillation columns when dealing with thermally-labile process streams.
- Consider high-efficiency packing rather than conventional tray-type columns to reduce pressure drop and decrease reboiler temperatures.
- Consider continuous processing when batch cleaning wastes are likely to be significant.
- Consider scraped-wall exchangers and evaporators with viscous materials to avoid thermal degradation of product.

More…

- Seek to minimize the number of process steps
- Minimize potential for leaks
- Maximize process selectivity at each unit operation
- Minimize process utility requirements
- Segregate process streams where possible
- Design for operability
- Vessel design:
  - Ensure easy access to vessels to simplify cleaning
  - Design for complete drainage
- Piping design:
  - Recover waste streams separately
  - Minimize length of piping runs to reduce inventory
  - Minimize valves and flanges
  - Route drains, vents, relief lines to recovery or treatment
  - Specify bellow-seal or zero-emission valves

And more.

- Instrumentation design
  - Use in-line process analyzers
  - Use closed-loop sampling ports
  - Install predictive maintenance monitoring equipment
  - Instrument heat exchangers to permit real-time monitoring of fouling and leakage
  - Consider advanced control strategies such as model-based control
- Materials selection
  - Consider costs of waste disposal when selecting maximum allowable corrosion rates
  - Consider foul-resistant materials like Teflon on surfaces requiring frequent cleaning
  - Consider glass or polymer linings where frequent cleaning is required
- Cost estimation
  - Incorporate hidden waste costs in cost estimates

Pollution Prevention through Reactor Design

- Prevent pollution by modification of reactor parameters:
  - Kinetics
  - Mixing regimes
  - Temperature
  - Pressure
  - Batch versus continuous processing
  - Control schemes

Separations Technologies

- Removal or isolation of components from process streams to enable in-process recycling or recovery and reuse of the components
- Liquid separations
  - Suspended solids
  - Dissolved solids
  - Miscible and immiscible liquids
  - Dissolved gases
- Gas separations
  - Suspended solids
  - Miscible gases
  - Suspended liquids

Pollution Prevention through Process Control

- Optimize control system performance
  - Measurement accuracy, stability, repeatability
  - Sensor location
  - Controller response action
  - Process dynamics
  - Final control element characteristics and location
  - Overall system reliability

Pollution Prevention through Process Simulation

- Process simulation can enable engineers to consider environmental issues, such as waste generation and energy use, earlier in the design, as well as:
    - Characterizing the environmental properties of process waste streams
    - Taking into account environmental aspects of design, such as raw material and solvent selection, assembly of reaction and separation steps, and consideration of in-process recycling alternatives
    - Implementing methodologies and tools that identify and evaluate alternative environmentally benign reaction pathways
    - Integrating the design of manufacturing with treatment systems
    - Estimating the real costs of the process, including waste treatment and disposal, permitting, liability, etc.
    - Tracking trace components in process and waste streams

Pollution Prevention through Chemistry

- Alternative synthetic pathways
- Use of biological methods for reaction or catalysis
- Avoidance of toxic feedstocks, including intermediates
- Elimination of organic solvents

Design Tools

- Green Chemistry Expert System (GCES)
  - www.epa.gov/greenchemistry/tools.htm
  - Searchable literature database on green chemistry
  - For example,
    - Supercritical solvents
    - Solvents
    - Inherently safer chemical
    - Alternative pathways for partial oxidation reactions or Friedel Crafts reactions
- Indexing methods for evaluating alternative synthetic pathways using:
  - Composite environmental index based on reactant and product stoichiometry and weighting factors for toxicity, persistence, bioaccumulation, etc.

Design Tools

- Process heat integration
  - Uses the heat from streams that need cooling to heat streams that need heating
  - Prevents pollution by reducing the need for fuels and for cooling tower operation
  - Done by heat exchange network (HEN) synthesis
  - One method is to use a “pinch” diagram, which determines the extent to which heat transfer is possible and helps determine which hot stream should be paired with which cold stream

Design Tools

- Process mass integration
  - Use of materials that would otherwise be wasted
  - Tools include:
    - source-sink mapping
    - optimizing strategies for segregation, mixing and stream recycle
    - mass exchange network (MEN) synthesis (similar to HEN synthesis) (can use “water pinch” methodology)

Design Example

- In a refinery, process water is brought into contact with crude oil to remove salts and other solid contaminants that could disrupt downstream operations, then sent to wastewater treatment facility
- Problem is that solids accumulate in the boiler and excessive levels of suspended solids lead to fouling, efficiency decreases, and cleaning requirements
- Dissolved solids also accumulate in cooling tower blowdown
- When boiler blowdown meets tower blowdown, precipitation occurs and hazardous oily sludges are formed when blended with wastewater from desalter
- Solution uses reverse osmosis to remove dissolved solids from feed water to eliminate source of solids in oily sludge.
- Savings in disposal costs paid for pretreatment equipment and its operation
- Fewer boiler and tower chemicals were needed, and maintenance costs were reduced

Design Examples

- Problem: Non-optimal reactant addition can lead to segregation and excessive byproduct formation
- Solution: Premix liquid reactants and solid catalysts using inline mixers
- Benefit: More efficient mixing and reduced waste generation by side reactions for 2nd order or higher competitive-consecutive reactions
- Solution: Improve dip tube and sparger designs for tank reactors. Do not add low-density material above liquid surface. Control residence time of gases added to liquid reaction mixtures.
- Benefit: Control strategy reduced hazardous waste generation by 88% and saved $200K

Design Examples

- Problem: homogenous catalysts can lead to heavy metal contamination of water and solid waste streams
- Solution: use heterogeneous catalyst immobilized on solid support
- Problem: old catalysts designs emphasized conversion over selectivity
- Solution: consider a new catalyst that features higher selectivity and better physical characteristics
- Benefits: Lower downstream separation and waste treatment costs; e.g., new catalyst for phosgene minimized formation of carbon tetrachloride and methyl chloride, saving $1M and eliminating an end-of-pipe treatment device

Design Example

- Problem: reactants entering a fixed-bed reactor are poorly distributed. Flow preferentially travels down the center. Residence time in the center is too short and too long at the walls. Yield and selectivity suffer.
- Solution: Install a flow distributor at the entrance to ensure uniform flow across the reactor cross-section.

Design Examples

- Problem: Convention heat exchange design is not optimum for controlling reactor temperature.
- Solution: For highly exothermic reactions, use cocurrent flow of cooling fluid on external surface of tubular reactors at the inlet; use countercurrent flow near exit where reaction rates and heat generation rates are lowest.

- Problem: Diluents added to gas phase reactions, such as nitrogen or air help to dissipate heat but result in the generation of wastes such as nitrogen oxides
- Solution: Use a non-reactive substitute diluent, such as carbon dioxide or even water vapor.

Design Examples

- Wastewater from a solution polymerization process contained RCRA solvents and was incinerated. Distillation followed by extraction recovered more than 10 million lb/yr of solvent, reduced incineration loads by 4 million lb/yr, and had a 2-year payback.
- Waste ink from newspaper printing contained 20% organic solvent, 15% water, and 65% ink. Flash distillation separated the ink, binary distillation separated the solvent, and the ink and solvent were reused.
- Pure ethylene glycol was batch distilled from used antifreeze and reused in new antifreeze.
- In electroplating, spent acids from etching tanks, cleaning tanks, and pickling tanks can be distilled to recover pure acids such as hydrochloric acid and nitric acid.

Design Examples

- Triethylamine is used as a solvent to extract hydrocarbons from refinery wastewater and sludges for recycle back into the process.
- Reverse osmosis is used to recovery homogeneous metal catalysts (instead of chemical precipitation) and saves $300K/yr.
- Ultrafiltration recovers polymers from cleaning of polymerization reactors, such as polyvinyl alcohol from synthetic yarn manufacture.
- Molecular sieve absorbents are used to dehydrate natural gas, eliminating the use of a solvent (triethyleneglycol).
- Molecular sieve absorbents can replace azeotropic distillation by eliminating the azeotropic solvents such as benzene and cyclohexane.

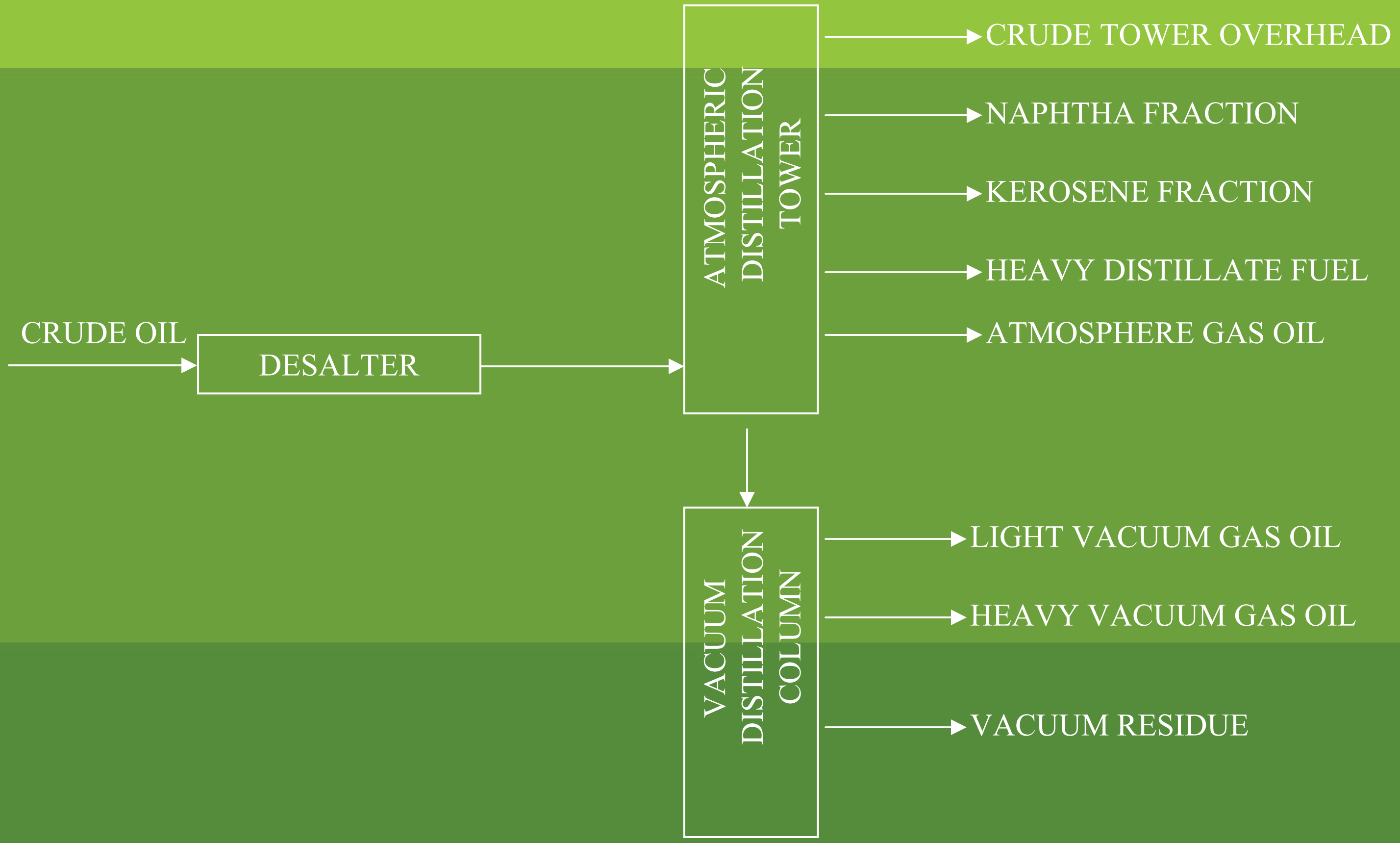
Design Examples

- Gas membranes can recovery and recyle high-value volatile organic compounds, such as olefin monomer from polyolefin processes, gasoline vapor recovery from storage tanks, vinyl chloride recovery from PVC reactor vents, and CFC recovery from process vents and transfer operations.
- Pervaporation is a membrane process used to recover organics from low flow and moderate concentration wastewater.
- Membrane can recover metal ions from aqueous waste streams.

Detailed Case Study

- Generic crude oil processing unit
  - Desalter
  - Atmospheric distillation tower
  - Vacuum distillation column
- Feed materials are crude oil, water
- Products are crude tower overhead, light naphtha fraction, kerosene fraction, heavy distillate fraction, atmospheric gas oil fraction, light vacuum gas oil, heavy vacuum gas oil, and vacuum residue

Flowsheet



CRUDE OIL

DESALTER

ATMOSPHERIC DISTILLATION TOWER

CRUDE TOWER OVERHEAD

NAPHTHA FRACTION

KEROSENE FRACTION

HEAVY DISTILLATE FUEL

ATMOSPHERE GAS OIL

VACUUM DISTILLATION COLUMN

LIGHT VACUUM GAS OIL

HEAVY VACUUM GAS OIL

VACUUM RESIDUE

Desalting

- Desalting
  - Crude oil mixed with partially-treated wastewater, then heated
  - Two-stage desalter creates a dispersed mixture of oil and water
  - Water extracts salts from oil and the brine is separated from the oil using an electric field
  - Brine from 2nd stage serves as washwater for 1st stage
  - Brine from 1st stage goes to wastewater treatment after being cooled by heat exchange with desalter feed water and cooling water
  - Desalted crude is sent to a series of heat exchangers

Atmospheric Distillation

- Fuel-fired heater provide energy to the tower
- Two side streams are sent to secondary strippers, contacted with steam, and sent to other operations
- Overhead product is cooled with incoming crude oil and cooling water; collected in a drum, and fuel gases in vapor phase are withdrawn, compressed, and sent elsewhere
- Part of gasoline in condensed phases is used as a reflux
- Bottom stream is sent to the vacuum distillation column

Vacuum Distillation

- Bottoms are further fractionated
- Fuel-fired heater provides energy
- Overhead stream is contacted with steam, cooled, and separated into oil and water in an overhead drum
- Water stream goes to sour water stripper
- Oil is sent to storage

Options

- Reboil with hot oil rather than steam to avoid oil/water contacting operations; requires two additional side strippers to meet product specifications
- Add liquid ring vacuum pump to reduce vacuum tower pressure, which reduces allowable operating temperature, which results in reduced cracking and fouling of furnace tubes, so that production of sour water is reduced
- Replace burners with low-NOx burners and retrofit for flue gas recirculation to reduce NOx emissions
- Reduce fugitive emissions with stringent inspection and maintenance, leakless valves, , etc.
- Segregate mildly-contaminated water and treat for reuse

Solution

- Pinch analysis to reduce external energy requirements showed that air emissions could be reduced substantially by increasing surface of the existing preheaters by 8% by adding three additional preheaters. Cost was $2.3M, fuel cost savings was $1.7M/yr, with a payback of 1.3 years.
- Decreased nitrogen oxide emissions by 60% and VOC emissions by 93%
- Halved oil and grease in wastewater, decreased TSS by 32%, and reduced sulfides by 19%
- Reduced hazardous solid waste by over 90%, and generated a nonhazardous solid waste stream

Assignment

- Imagine that you have been assigned to design the Industrial Revolution, retrospectively. The assignment would read something like this; design a system of production that would:
  - Put billions of pounds of toxic material into the environment every year
  - Produce some materials so dangerous they will require constant vigilance by future generations
  - Result in gigantic amounts of waste
  - Put valuable materials in holes all over the planet where they cannot be retrieved
  - Require thousands of complex regulations – not to keep people and natural systems safe- but to keep them from being poisoned too quickly
  - Measures productivity by how few people are working
  - Creates prosperity by digging up or cutting down natural resources and then burning or burying them
- Of course, this was never the intent – just the way it turned out.

Challenge!

- Design products and processes with goals of zero waste, which includes pollution and energy.
- Design products and processes that are restorative.
- Use the intellectual and material resources of chemical engineering to create a world that is sustainable, in which what we have today is still there for members of the seventh generation in the future.

Resources

- AIChE Center for Waste Reduction Technology
- AIChE Sustainable Engineering Forum
- Chemical Engineering, Chemical Engineering Progress, and other magazines and journals
- Allenby, *Industrial Ecology*
- Freeman, *Industrial Pollution Prevention Handbook*
- Allen and Shonnard, *Green Engineering: Environmentally Conscious Design of Chemical Processes*
- McDonough and Braungart, *Cradle to Cradle*
- Internet
- Many other resources are out there just for the looking!