Challenges for the Chemical Industry

John G. Pendergast

Fellow: Performance Materials

Formally: Fellow Process Separations Engineering & Process Sciences

The Dow Chemical Company

Center for Advanced Process Decisions

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Outline

- Dow Introduction
  - Company profile
  - Contributions and drivers
- Historical Perspective
  - Where do we come from
- Our Industry in Perspective
- Challenges
  - At least one suggestion for direction
    - » Bio-processing, chemicals from bio-processing √
    - » Distributed (small scale) manufacturing √
    - » Retrofit of existing processes√
    - » CO_2 Capture and Sequestration √
    - » Methane activation √
    - » Olefin recovery and separation √
    - » Low level heat recovery √
    - » New Realities √
- Questions, discussions

The Dow Chemical Company

- Diversified chemical company, harnessing the power of science and technology to improve living daily

1897 Founded Midland, MI

2000 Acquired Union Carbide

2008 Acquired Rohm & Haas

Dow by the numbers

- **35 Countries**
- **188 Sites**
- **5000+ Products**
- **50,000 WW Employees**
- **60++ Billion Annual Sales**

Unique perspective of commodity landscape <u>and</u> specialty chemicals

<u>Founded</u> on brine chemistry 116 years ago

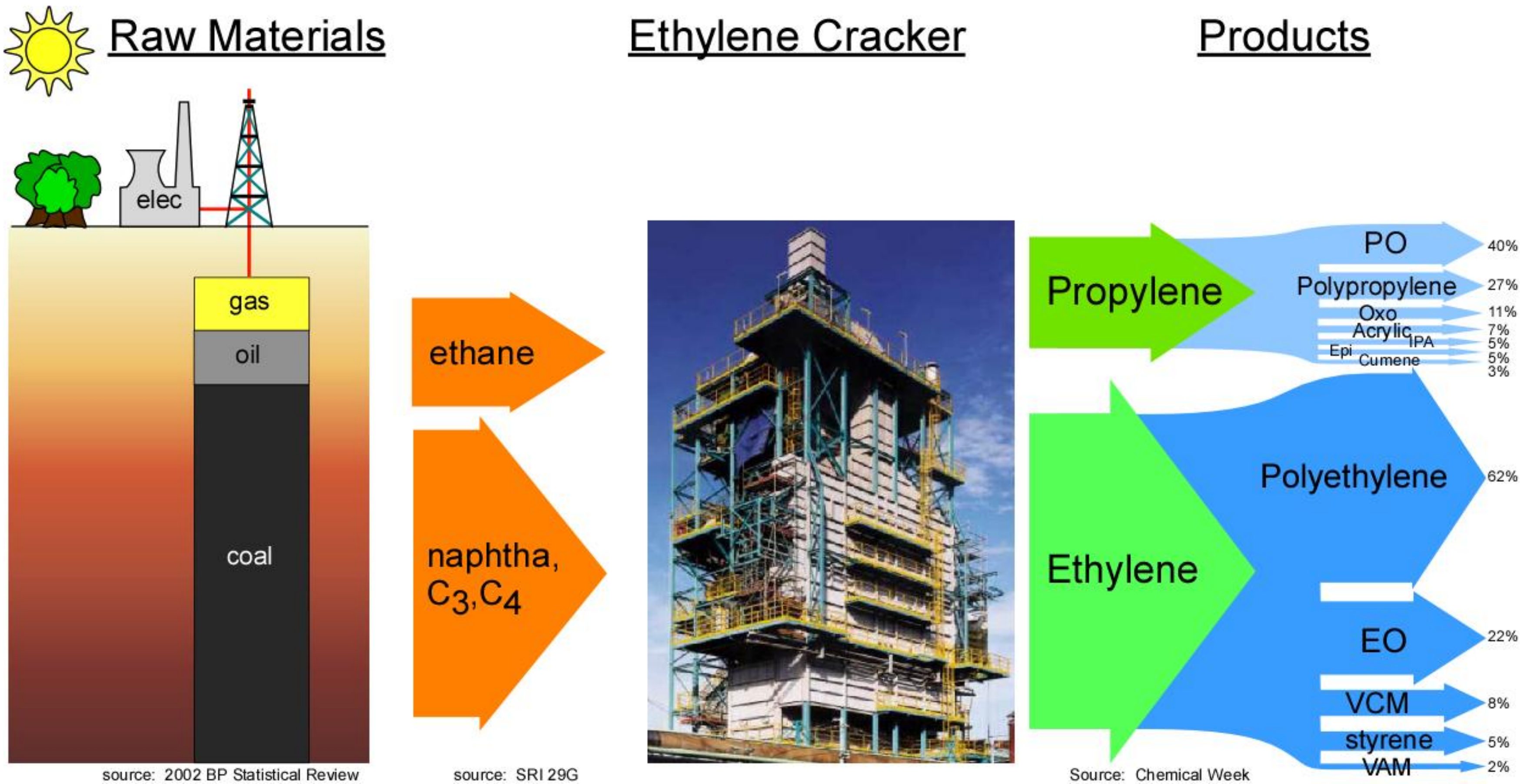
<u>Large Scale</u>
Ethylene and polyethylene
Chlorine and caustic
Ethylene oxide and ethylene glycol

<u>Specialty Scale</u>
Metal organics, tri-methyl gallium, tri-methyl indium
OLED materials
Chemical mechanical planarization products, photoresists…

Current Dow Feedstock Utilization

Starting Materials = Ethylene & Propylene

Raw Materials | Ethylene Cracker | Products

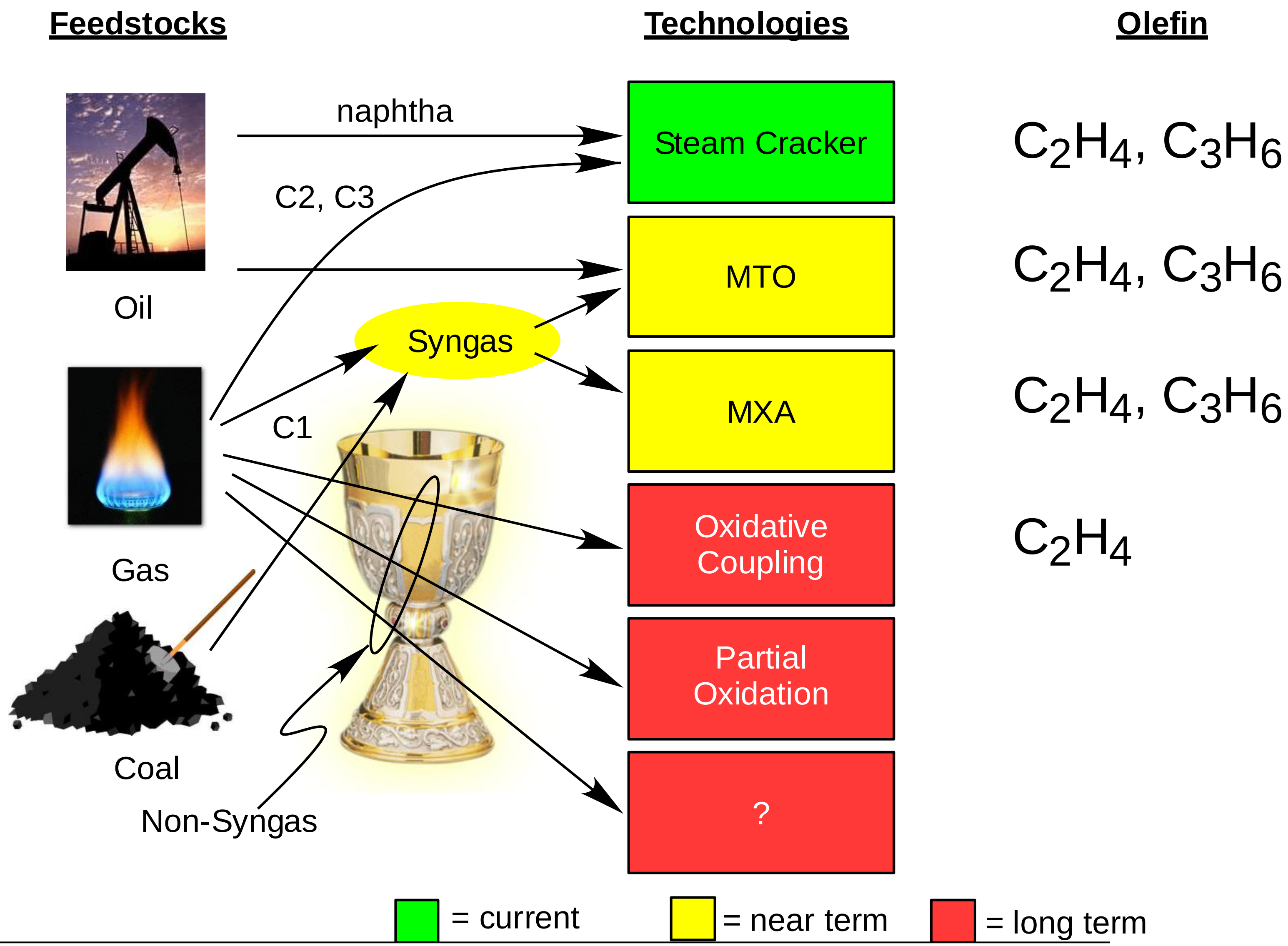


source: 2002 BP Statistical Review

source: SRI 29G

Source: Chemical Week

Technology Options: Fossil Feedstocks

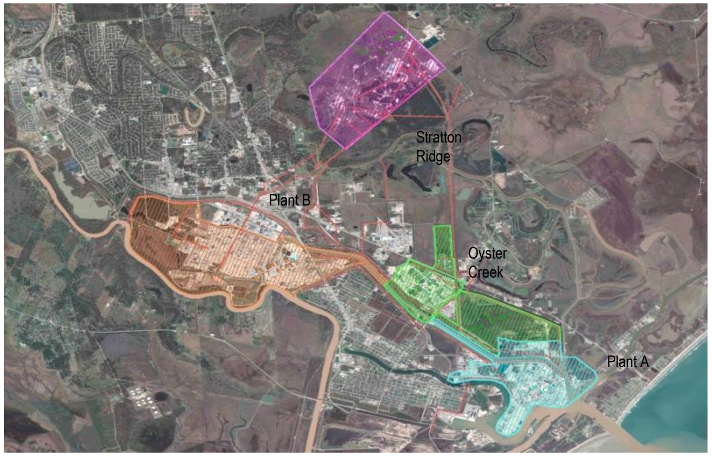


Large Integrated Manufacturing Sites

Plaquemine, U.S.A.

Terneuzen, Netherlands

Stade, Germany



Freeport, U.S.A.

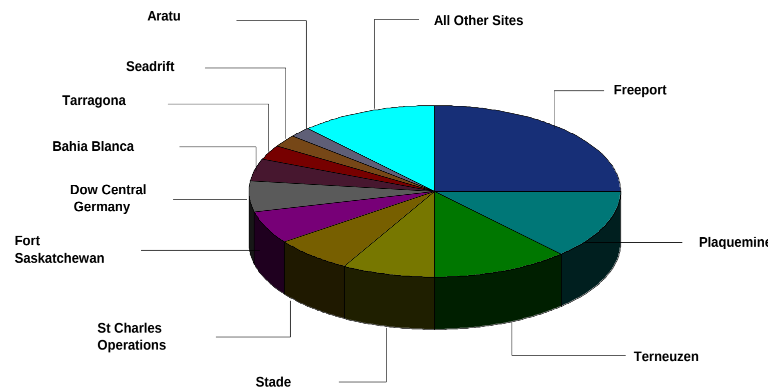
Sustainability is Crucial to Our Success

- One of the world's largest (non-utility) industrial consumer of power and steam

3,700 MW of electricity required to operate Dow plants

=

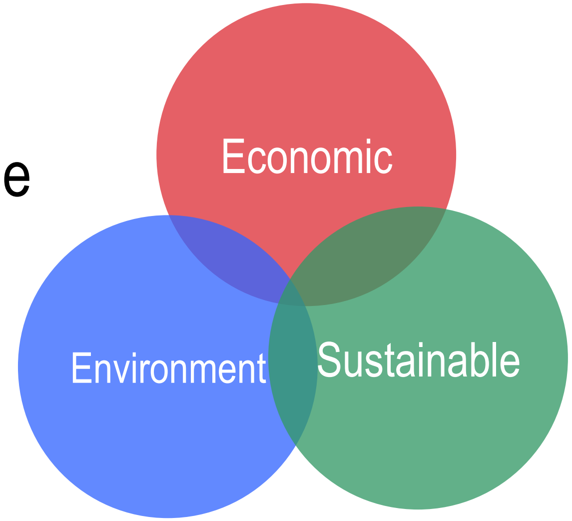
3,700 MW of electricity Used by San Francisco, San Diego, & Oakland <u>combined</u>



- Feedstock demand is **800,000 barrels/day**
- Leading innovator in cogeneration
  - Increased efficiency with reduced impact on the environment
  - Uses **20-40% less fuel**
- Self-generates **~75%** of all power & steam
- Operates over **$6.2 billion** in energy assets & supports **$2.5 billion** in JV assets
- Operate our own Wastewater treatment
- Operate our own incineration facilities
- We strive to be good stewards because it is good business

Sustainable Chemistry

- Integrated look at chemicals, processes and products
    - » Improve safety of manufacturing processes
    - » Maximize energy efficiency
    - » Maximize the efficiency of raw material use
    - » Minimize the use of scarce resources
    - » Minimize the return of anthropogenic substances to nature
    - » Minimize environmental impact
    - » Significantly enhance benefits to society
- Will change the way that some products are made
    - – We are seeing “sustainability issues” raised
        - » Zero water discharge requests
        - » Solvent recovery, solvent recycle
        - » Sustainability is good business
- It’s all about balance
- Our products must be profitable
    - – Alternatives must be supported financially



Bio-based Products

- Bio-based product are challenged to compete on a cost basis with hydrocarbon based products
  - The consumer has a very limited willingness to pay a premium for “green products”
    - In products far removed from the end user (commodity) , the consumer has even less willingness to pay
  - Several notable examples of this difficulty
    - Poly-lactic acid
    - Chitin and chitin derived materials
  - The lesson: simply providing a “renewable product” does not guarantee acceptance
    - Certainly does not guarantee financial success
- Chemicals and Energy
  - Chemicals have higher value add than fuels
  - In U.S. 3% of the fossil resources used for chemicals against In U.S. 97% for energy usage (1)
    - Added value of this 3% chemicals is $375 billion
    - $520 billion for the remaining 97%
- Energy (fuels) are the ultimate commodity
  - Bio-based fuels are at a huge disadvantage
- Specialty chemicals, in our opinion, have some promise for bio-derived materials
  - Higher margins, less commodity mentality
  - Some tolerance for a premium

(1) Bozell and Peterson, Technology Development for the Production of Biobased Products from Bio-refinery Carbohydrates – the US Department of energy’s “Top 10: Revisited

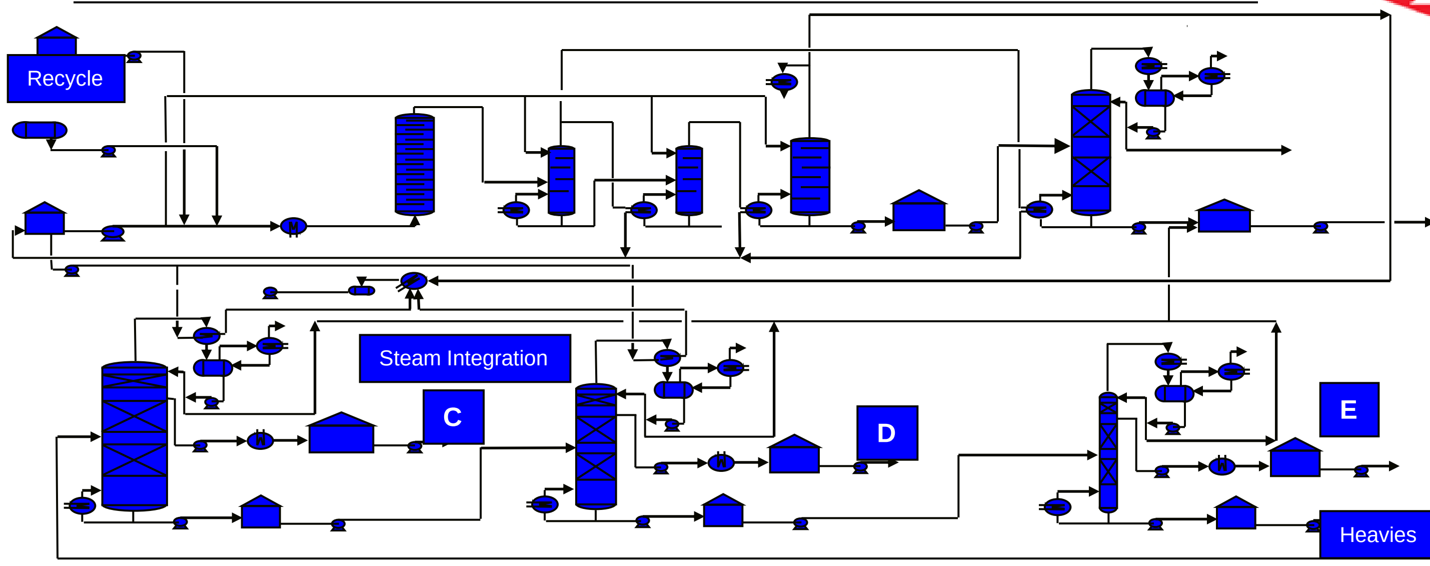
Distributed manufacturing

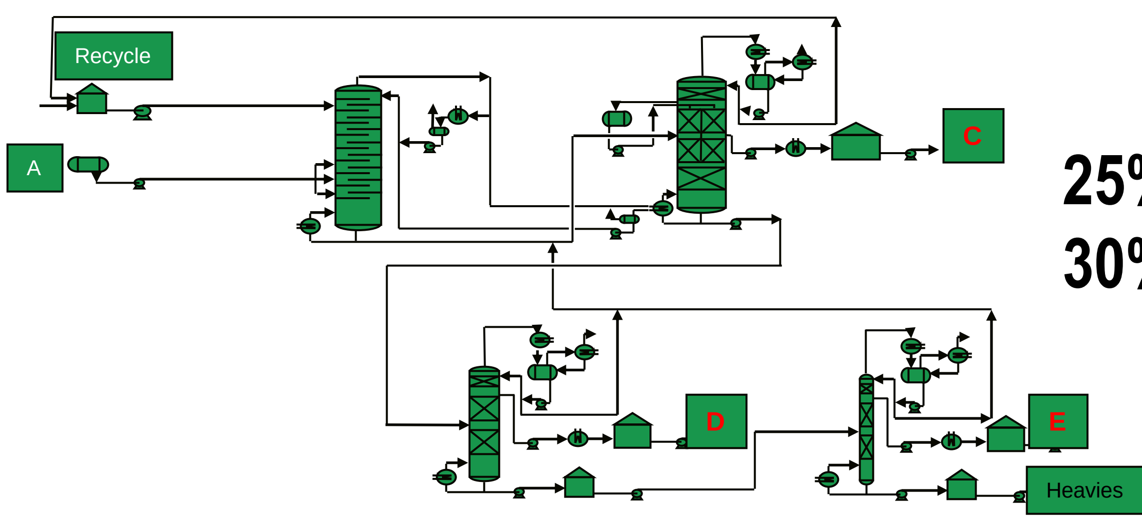
- Distributed manufacturing may be a partial solution to effective use of biomass
  - » Resource radius limitations
    - Biomass cannot economically be shipped past a certain radius
    - 80 – 100 kilometers
  - » Stranded resources
    - No pipeline, gas flaring
  - » Distributed manufacturing may be used to reduce some transportation hazards
    - Drive to reduce “rail miles” for many chemicals
    - Some materials are too hazardous to routinely ship
    - Still must take place is a professional, tightly monitored environment
  - » Political instability
    - Move your asset
    - Walk away
- Challenge
  - » We must be realistic … distributed manufacturing is a huge challenge
    - Seeks to reverse ~100 years of consolidation
  - » Design philosophy
    - Simply making a plant smaller will not work
    - Design philosophy must be different
    - This is in sharp contrast to the paradigm shown earlier
  - » Safety must be a major consideration / concern
    - Certain processes should simply be out of consideration

Maintaining Efficiency Across Lifecycle

- Our processes (physical facilities) have long life spans
  - 30 years is not uncommon … 50 years not unknown
    - » Maintenance is performed and parts replaced
    - » Instrumentation upgraded
    - » Plants are by no means neglected …. but
  - Basic configuration may not have changed … in two generations!
- How do we find and implement process alternatives to improved that meet our economic criterion
  - Energy cost alone will not support total replacement
  - Additional capacity generally will support capital expenditure
  - It must fit into the existing framework
  - We must uncover "all" alternatives
  - Dow has done a great deal of work in Synthesis and Intensification
    - » Professor Rakesh Agrawal has done some very interesting work in the area of separations

Reactive Distillation plus Dividing Wall Columns



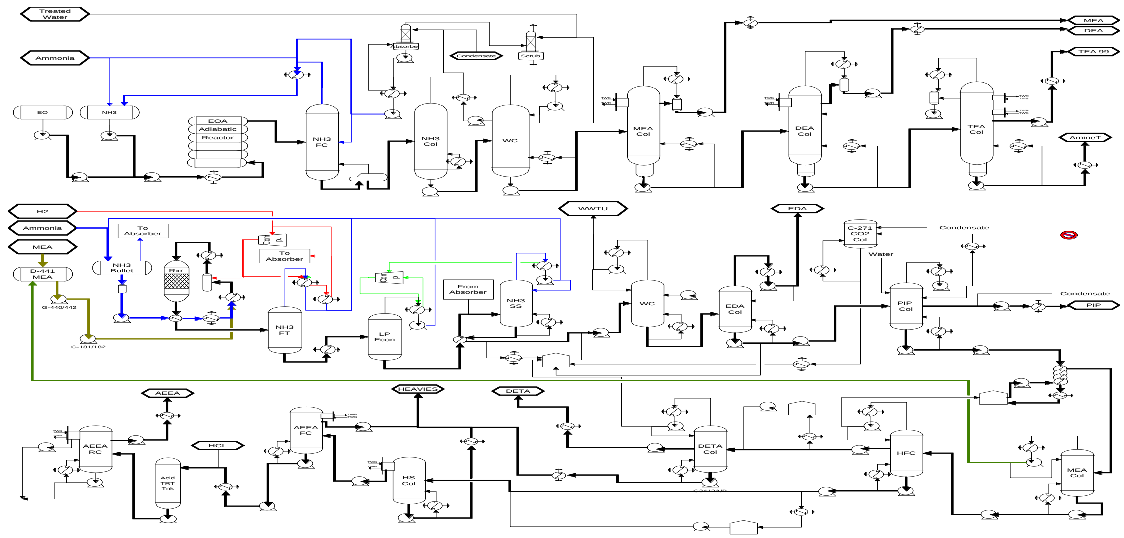


25% Capital Reduction
30% Energy Savings

Advanced Separations

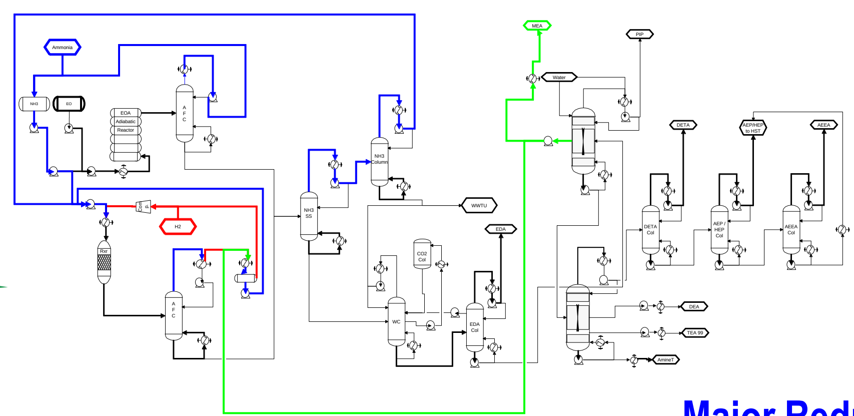
Current Design

19 Columns Total



Proposed Design

13 Columns Total



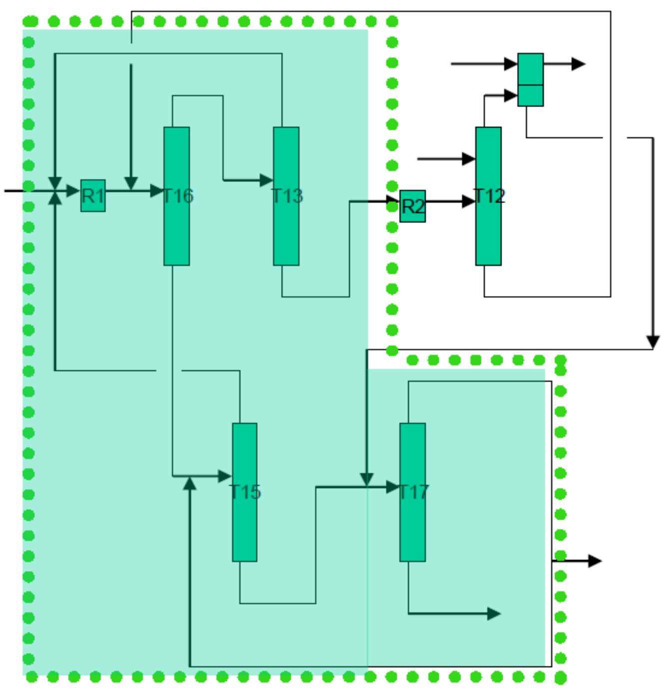
Major Reduction in Capital and Energy Costs by Separation sequencing and DWC

Reactive Distillation

Where applicable, one of the most powerful intensification techniques available

- Reaction must take place at approximately the same conditions as the separation
- Generally thought of as being applicable to reacting away azeotrope
- Generally thought of as driving equilibrium limited reactions

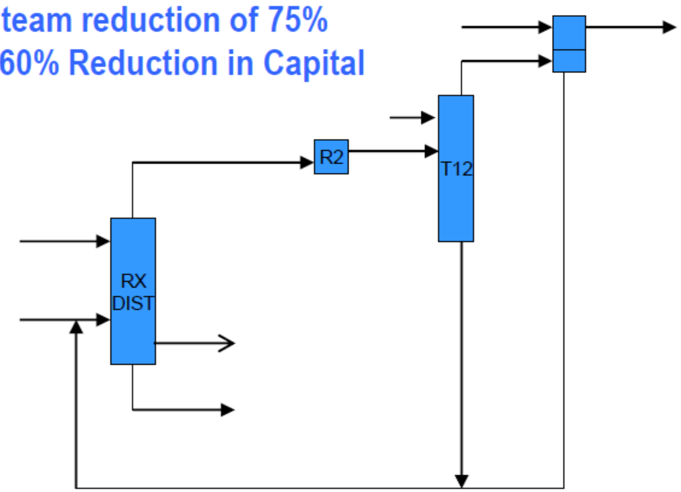
Legacy Process



New Flowsheet with Reactive Distillation

Steam reduction of 75%

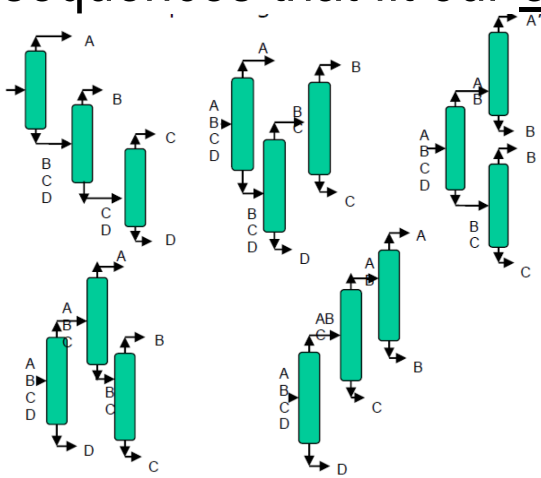
>60% Reduction in Capital

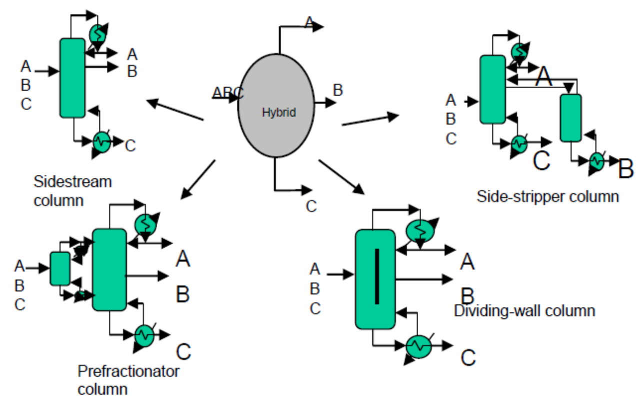


Separation Sequencing

- We have the tools and the techniques to
  - » Generate all sequences
  - » Simple plus complex
  - » Heat integrated sequences
  - – Use optimization tools to decide the “best” sequence
- Our challenge
  - – Use these tools to build new plants
  - – Even more challenging: Use these tools to find better sequences that fit our existing facilities

Extremely challenging but very important





CO2 Capture and Sequestration (CCS)

- The Chemical Process Industry is not the bulk of the problem
  - Our industry is not trivial
  - We are in an excellent position (perhaps the best) to do our share
  - Depending on the accounting method 5% [1] of global CO_2
    - » Many of our larger products produce roughly one mass unit of CO_2 per mass unit of product
- CCS is not a technical issue
  - CCS is an economic issue
    - » Credible estimates $70 - $200 per ton
    - » We compete in a global market
    - » Unilateral application puts us at an economic disadvantage
  - CCS is a litigation / risk management issue
- Potential fruitful areas of development
  - Enriched oxygen (membranes / PSA) and CO_2 capture on furnace vents
    - » Reduces flow requirements
  - Optimize fractional recovery for economic benefit
    - » We simply do not believe that 90% capture is the optimum number
- (1) Technology Roadmap Energy and GHG Reductions in the Chemical Industry via Catalytic Processes 2013 Rights IEA

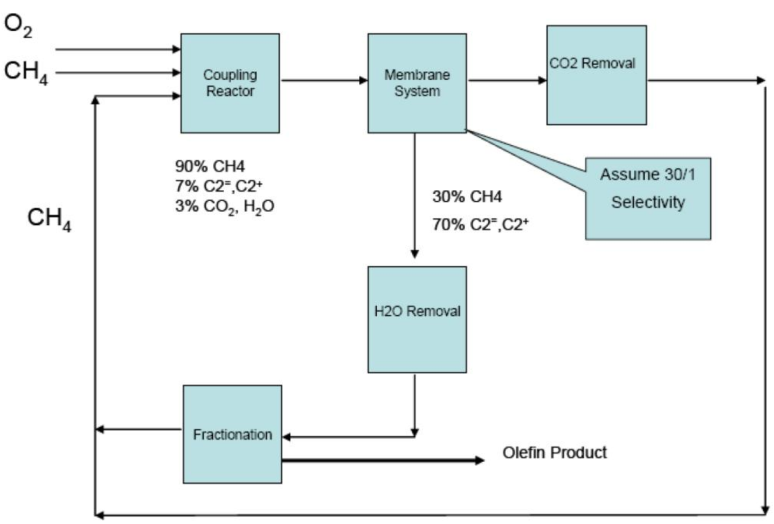
Methane Activation

- Direct coupling of methane without syn-gas
  - In the interest of full disclosure: Many companies believe in methane to products through syn-gas
    - » Fischer–Tropsch process
    - » Methanol to Gasoline process (MTG)
    - » Syngas to gasoline plus process (STG+)
    - » Dow process US8129436B2
      - Our focus is different because our focus is C_2=, C_3=
- Oxidative Coupling or Direct Coupling of Methane (OCM)
    - » The Holy Grail of Hydrocarbons
    - » Fundamental problem: the intermediate is more reactive than either the reactant or final product
    - » Conventional wisdom says 30-40% conversion to C_2 is the minimum for economic viability

Methane Activation

- How do you change the paradigm?
  - » Fractionation under current conversions is not practical
- Remove the intermediate olefin and concentrate the olefin for purification
  - – Membrane
    - » Larger species permeating
    - » High flux more critical than high selectivity
  - – Reactive absorption
    - » Selectivity, safety and size are issues

http://www.sciencemagazinedigital.org/sciencemagazine/09_may_2014?folio=616#pg90



Olefin Recovery and Separation

- Olefin manufacturing dominated by separation landscape
  - Risk aversion is enormous … <u>and understandable</u>
  - Cryogenic separation rule
  - Separation of olefin product away from cracked gas would change paradigm
- Can also be extended to olefin recovery from process vents
  - Recycle
    - » Places false load on ethylene plant
    - » High risk of contamination and / or fouling
  - Adsorption, absorption, membranes
    - » Often economically challenged
- Potentially fruitful area
  - Reactive absorption
    - » There are safety considerations that <u>must</u> be considered
      - Scales well
        - » Could open the door for smaller, more compact olefins production
        - » This will be an uphill struggle
    - » Facilitated membrane transport

Low Level Heat Recovery

- Large facilities generally have large quantities of low level heat
  - Process facilities are generally well integrated with respect to high level heat
    - Within unit boundaries … reactors to separations
    - Across facilities … electricity, boilers, steam generation, boiler feed water … etc.
  - Condensing temperature limitations
  - Equipment limitations
- Many techniques known for low level heat recovery…
  - Difficult to deliver economic justification
    - In a strange twist, improved energy cost make justification more difficult!
    - May need justification from other sources … carbon credits … etc.
- Well known methods [(1)]
    - Direct utilization … drying, heating
    - Vapor Compression Heat Pump
    - Organic Rankine
    - Thermo-compressor
    - Refrigeration Cycles
- Utilization of absorption refrigeration cycles
  - Integration with site infrastructure
    - Lower pressure in equipment … improved safety
    - Use on satellite areas
  - Provide to commercial / residential as chilled water
    - Fraught with litigation concerns … cross-contamination risks may make this impossible
- Overarching concern
  - What is our failsafe position?
  - If we design our cooling water for 7-10 C, what happens if the chillers fail?

(1) Ankur Kapil, Igor Bulatov, Robin Smith, Jin-Kuk Kim *Advanced Process Integration for Low Grade Heat Recovery*

New Realities

- Water consumption
  - Historically, simulations have not even counted water
  - Large integrated sites consumption
  - Are we taking water from farms, urban areas?
- Water is a precious commodity in some areas
  - Water cost
  - New facilities may need to optimize around water
- Environmental constraints becoming more rigorous
  - Requests for zero liquid discharge are not uncommon <u>now</u>
- Current approach to combustion not rigorous enough
  - Furnaces, flares, combustion devices receive increased scrutiny
  - Present simulation approach may simply call for “duty”
  - Often ignore the “fired side” of the heat supply
    - » NOX per unit of heat?
    - » VOC per unit of heat?
  - What is the cost of a “unit of improvement”?

Thank You
Questions

BACK UP SLIDES

- BACK UP

Perspective

Technology development for the production of biobased products from biorefinery carbohydrates—the US Department of Energy's "Top 10" revisited

Joseph J. Bozell*[a] and Gene R. Petersen[b]

Biorefinery development has two strategic goals: the displacement of imported petroleum in favor of renewable domestic raw materials (an *energy* goal) and the establishment of a robust biobased industry (an *economic* goal). The energy goal is addressed by the current effort on ethanol, biodiesel and advanced biofuel production (butanol, algal biodiesel, *etc.*) to displace a portion of the huge amount of transportation gasoline (~142 × 10^9 gallons) and diesel (~60 × 10^9 gallons) used annually in the US.[1] But despite its high volume, fuel is a low value product.

High value, lower volume biobased chemicals provide this incentive. Even though chemical production accounts for only 7–8% of oil imports in the US,[3–5] analyses reveal that a biorefinery integrating biofuels and chemicals offers a much higher return on investment and meets its energy and economic goals simultaneously.[6,7] Such projections have prompted efforts to add coproducts into existing biorefinery models, such as corn wet and dry mills or pulp and paper operations, as a means to enhance revenue or repurpose existing underutilized infrastructure.[8] However, incorporating chemical products into the biorefinery's portfolio faces two primary challenges:

Moreover, the production of chemicals from biomass is economically interesting since it has an extremely large added value compared to energy production, while it demands only a fraction of the resources [1]. It has been estimated that in the United States, only 3% of the fossil resources are currently used for the production of chemicals, against 97% for energy usage. However, the added value of this 3% chemicals is $375 billion, against $520 billion for the remaining 97% directed at energy usage [1].

Abstract

The Chemical Process Industry (CPI) has seen a revitalization in the United State in the last several years, due primarily to the shale gas revolution and the abundance of low cost feedstocks. However, challenges exist for our industry, and this talk will address some of the challenges from the perspective of Dow Chemical. Dow has the unique perspective, both from a historical perspective of being 117 years old, and from the perspective of being involved in the entire spectrum of the CPI from the production of basic chemicals to the production of specialty products such as OLED's. This talk will discuss some of those challenges as well as some possible solutions.