Before discussing Petrochemical Technology, let’s look at some history....

- A number of what we now call “petrochemicals” were originally extracted or transformed from coke oven gas. Others came from natural sources (e.g., acetic acid, ethanol).
- Acetylene made from calcium carbide was the original raw material for producing vinyl chloride, vinyl acetate, and acrylonitrile.
- Early manmade fibers (e.g., rayon, acetate) were produced from cellulose recovered from wood.
- There was little or no ethylene available to make derivatives.
The synthesis of ammonia in the early Twentieth Century in Germany is arguably the most important step in the development of industrial, continuous process chemistry.

In 1908, Fritz Haber, working at the Technische Hochschule in Karlsruhe “fixed” atmospheric nitrogen through the catalytic conversion of hydrogen and nitrogen at 500-600°C and 100-200 atmospheres. The Haber-Bosch process is still in use today!
Important research carried out before World War II led the way from early 20th century chemicals manufacture to today’s global petrochemical industry

• IGFarben affiliates were extremely active. Essentially all of this research was based on coal chemicals

• British, French and U.S. developers were also at work, researching polymer chemistry, synthetic fibers, resins and adhesives, solvents.

• Petrochemical research started in the 1920s by a few U.S. companies focused on refinery streams and natural gas liquids – both abundant in the U.S.
Styrene and SBR Rubber: IG Farben

- The German chemical industry led the world as firms like Bayer, BASF, Hoechst and others developed technologies to produce numerous organic chemicals and polymers.
- Its research was essential to make Germany self-sufficient as Europe prepared for war.
  - The Fischer-Tropsch process for diesel fuel and chemicals
  - High octane aviation gasoline from ethylbenzene
  - Buna synthetic rubber

But some firms were starting R&D on “petrochemicals”
Ethylene: Union Carbide and its Linde division

- Located in a hydrocarbon-rich area, Union Carbide bought natural gas liquids and condensate and built separation equipment to recover ethane and higher alkanes.

- In 1918, first experiments were carried out to crack ethane to ethylene, using an electrically heated silicon tube – the first ethylene produced directly from petroleum feedstocks!

Now, it’s deja vu all over again!
• Shell Chemical was another company developing petrochemicals during the prewar period, though its primary motivation was improving the octane rating of its gasoline

• Shell and Exxon started production of isopropyl alcohol (IPA) from cat cracker propylene; Shell produced acetone from IPA

• Shell also developed a synthetic glycerin process based on allyl chloride, made from propylene and chlorine

*Shell Chemical has, over the years, been the most active and successful division of oil companies in developing petrochemical technologies*
Polyamides (Nylon): Carothers at DuPont

• In the 1920s, Dr. Wallace Carothers at DuPont was assigned to work on polymerization by condensation in structures of high molecular weight.

• Eventually he found that by reacting adipic acid with hexamethylenediamine, a “superpolymer” termed nylon 6/6 was produced that could make a synthetic fiber. The first commercial nylon plant was built in 1938.

*IGFarben was carrying out similar research during the 1930s, culminating in the discovery of nylon 6, with relatively similar structure to nylon 6/6, but made from caprolactam*
• Imperial Chemical Industries (ICI) and a Dutch team carried out very high pressure chemical research (up to 20,000 atmospheres) in the 1920s.

• In 1932, 20 cubic centimeters of ethylene and benzaldehyde were brought up to 2000 atmospheres in a small autoclave. When it was opened, a white, waxy substance (polyethylene) was found on the walls. It was determined that a small amount of oxygen catalyzed the polymerization.
Naphtha Reforming: UOP

• With Russian and American scientists, UOP became a leader in the development of petroleum refining technology: Distillation, thermal and catalytic cracking, naphtha reforming, etc.

• UOP’s breakthrough research in naphtha reforming (using platinum catalyst) is key to the production of all aromatic petrochemical derivatives

• The design of petrochemical plants is closely related to the design of refinery units.
The U.S. and Canada were forced by circumstances to develop high performance fuels and novel chemical and synthetic rubber technology.

Polyethylene for radar shielding

Mass production of key war materials: antifreeze, solvents, nylon (parachutes), ammonia (explosives), vinyl tents

A synthetic rubber industry when Japan occupied Malaysian rubber plantations
The post-war (1950-1980) period saw intensive development of petrochemical technology

- New synthetic polymers (plastics, fibers, elastomers) had been developed for the war effort and were now in great demand for housing, apparel, cars, packaging.

- The traditional chemical companies were slow to build new plants and unwilling to license technologies.

- But, many companies in the oil and gas, paper, glass, rubber industries wanted to get into petrochemicals. This created an opening for independent engineering firms to develop licensable technologies.
During this fertile period for petrochemical R&D, companies approached new technology development from several directions:

### Less Expensive Feedstocks
- Ethylene instead of acetylene:
  - Vinyl chloride, vinyl acetate
- Butane instead of benzene:
  - Maleic anhydride
- Acrylonitrile from propylene

### New Organic Chemistry
- Propylene Oxide
- Terephthalic acid (TPA)
- Detergent Alcohols
- Acrylic Acid/Acrylates
- Nylon intermediates
- Acetic Acid
- Linear alpha olefins

### New Polymer Chemistry
- Polypropylene
- Epoxy resins
- ABS resins
- Polycarbonate
- Polyurethane
- Polyester

### Less Polluting Chemistry
- Terephthalic Acid
- Isocyanates (no HCN)

### Larger Scale Operations
- Ethylene
- Ammonia
- Methanol

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**MANAGING R&D DURING DIFFICULT TIMES: CREATING GLOBAL COMPETITIVENESS**
Single Train “Giant” Ethylene Plants

Relatively modest size ethylene plants were built in the 1950-1960 period, which had relatively low yields of ethylene and often needed to be shut down due to furnace tube coking.

- But, engineering contractors (notably Kellogg, Foster-Wheeler Stone and Webster, C.F. Braun) and equipment manufacturers were collaborating on developing a brand new flowsheet for ethylene plants that would solve the problems of plant size limitations and tube coking.

- In 1964, a paper presented by Shell gave a comparison as shown below.

<table>
<thead>
<tr>
<th>Year</th>
<th>Plant Size</th>
<th>Manufacturing Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>1955</td>
<td>20,000 TPY</td>
<td>81 £/ton</td>
</tr>
<tr>
<td>1965</td>
<td>100,000 TPY</td>
<td>32 £/ton</td>
</tr>
</tbody>
</table>

A new flowsheet created 1000 tons/day ammonia plants with excellent economics

As was the case for very large, single train ethylene plants, the developments that led to “giant” ammonia plants were a series of engineering breakthroughs rather than new chemistry.

- ICI’s development of high pressure reforming of hydrocarbons allowed synthesis gas to be produced at pressure similar to that in the ammonia converter
- Use of centrifugal instead of reciprocating compressors
- MWKellogg’s complete redesign of the steam system and use of a lot temperature shift catalyst

The new flowsheet and the design of much larger plants brought the production cost of ammonia down by 32 percent.
Producers kept innovating to reduce the cost of making vinyl chloride

- Initially, vinyl chloride (VCM) was made from acetylene and HCl in a very straightforward manner
- With ethylene available, VCM could be made by cracking ethylene dichloride, resulting in byproduct HCl. This was reacted with acetylene as before, thus halving the amount of acetylene required
- Researchers then had to work out how to eliminate the other half of acetylene, resulting in the oxychlorination step,

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Units/Lb</th>
<th>Price ($/Lb)</th>
<th>$/LB of VCM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene</td>
<td>0.424</td>
<td>0.35</td>
<td>0.148</td>
</tr>
<tr>
<td>Chlorine</td>
<td>0.580</td>
<td>0.04</td>
<td>0.023</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.017</td>
<td>0.25</td>
<td>0.004</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td><strong>0.175</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Units/Lb</th>
<th>Price ($/Lb)</th>
<th>$/LB of VCM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>0.468</td>
<td>0.18</td>
<td>0.084</td>
</tr>
<tr>
<td>Chlorine</td>
<td>0.599</td>
<td>0.04</td>
<td>0.024</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.141</td>
<td>0.02</td>
<td>0.003</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td><strong>0.111</strong></td>
</tr>
</tbody>
</table>
Sohio: Acrylonitrile via Ammoxidation

- Sohio stunned the industry with an ammoxidation process that reacted propylene with ammonia in a fluid bed reactor system. An economic comparison of three successive technologies shows the dramatic advantage of the Sohio process. (Prices in table not current, but illustrative)

<table>
<thead>
<tr>
<th>Raw Materials</th>
<th>$/Lb</th>
<th>$/Lb of ACN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Ethylene Oxide</td>
<td>0.30</td>
<td>0.28</td>
</tr>
<tr>
<td>Hydrogen Cyanide</td>
<td>0.20</td>
<td>0.11</td>
</tr>
<tr>
<td>Acetylene</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>Propylene</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>Ammonia</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>0.39</strong></td>
<td><strong>0.29</strong></td>
</tr>
</tbody>
</table>
Phillips Chemical, Ziegler and Natta: Polypropylene

- Karl Ziegler developed the catalyst systems for high density polyethylene (HDPE). He was at first unable to make polypropylene and was beaten to this goal by Dr. Giulio Natta at Montecatini.

- However, it turned out that Phillips Petroleum, an HDPE producer, had been granted a composition of matter patent on polypropylene with priority over Ziegler and Natta, as was determined after a long patent fight.
Several engineering polymers were developed during this creative period

- An important example is polycarbonate, researched independently by GE and Bayer in the early 1950s and commercialized by both companies in the late 1950s.
- This is an instance where two companies with conflicting patent positions decided to join forces.
- While the original product was brown, innovation by both firms resulted in a clear product, now used almost exclusively for electronic and optical applications.
- Another opportunity for innovation was to develop a process that eliminated the use of phosgene, a highly toxic chemical.

*SABIC acquired GE Plastics in 2007*
Shell: Higher Olefins (SHOP) Process

Shell Chemical R&D did substantial research on metathesis, a technology that produces mixed oligomers from single or chain hydrocarbons. Shell’s objective was to maximize the amount of C\textsubscript{12} linear olefins from a mixture of higher olefins. This led to Shell Chemical’s entry into detergent alcohols.

Later, when C\textsubscript{6} and C\textsubscript{8} linear olefins started to be used as co-monomers in polyethylene production, Shell’s SHOP process provided a second commercial product.
Monsanto: Acetic Acid via Methanol Carbonylation (Rhodium catalyst)

Other Routes to Acetic Acid

- Ethylene + O₂ → Acetic Acid
- Ethane + O₂ → Acetic Acid
- Ethanol + O₂ → Acetic Acid

Source: IHS
Independent R&D firms saw a unique opportunity to help new producers to enter the petrochemical industry

- Scientific Design, UOP, and to a small extent, Chem Systems were conducting petrochemical R&D during this period

The authors of this paper worked at Scientific Design Company (Spitz) and Chem Systems (Spitz, Philpot) during the time when important petrochemical industry technology development was taking place.
Scientific Design (SD) had a number of R&D successes and failures over the 1955-1982 period.

**Success: Ethylene Oxide/Glycol**

**Background:** Demand for Automobile Anti-freeze and solvents (later also for Polyester fiber) rose rapidly. Companies in the U.S. and Europe wanted to enter the field but needed technology (UCC and Shell would not license competitors).

**Approach:** SD developed a silver catalyst for direct air oxidation of ethylene and improved the then state-of-the art flowsheet, leading to a patented ethylene oxide process. It was first commercialized by Naphtachimie in France and later licensed worldwide to twenty or more companies.
Scientific Design (SD) had a number of R&D successes and failures over the 1955-1982 period

**Success: Terephthalic Acid (Polyester fiber)**

**Background:** The existing technology used nitric acid oxidation to make dimethyl terephthalate (DMT) that was reacted with glycol to make polyester polymer. This was a relatively complex and somewhat polluting process.

**Approach:** In the late 1950s p-xylene became an article of commerce. SD developed a proprietary catalyst based on cobalt and manganese bromides in acetic acid which could oxidize p-xylene directly to terephthalic acid. The process (called “Mid-Century”) was commercialized by Amoco Chemical, which built many TA plants around the world.
Scientific Design (SD) had a number of R&D successes and failures over the 1955-1982 period.

**Success: Propylene Oxide**

**Background for R&D:**

Propylene oxide was originally produced via the chlorhydrin route. SD and Arco Chemical independently researched similar routes that produced propylene oxide by first making a hydroperoxide of ethylbenzene or isobutane, and producing a substantial amount of “co-product” in the form of styrene or t-butyl alcohol.

**The Chemistry:**

Halcon/Arco process with styrene co-product.

![Chemical reaction diagram]
Scientific Design (SD) had a number of R&D successes and failures over the 1955-1982 period

Failure: Ethylene Glycol (direct process)

- A number of companies researched this technology which would have replaced the traditional ethylene oxide process b
- SD/Halcon in joint venture with Arco Chemical built a 360,000 Tpa unit at the Houston ship channel, with design based on large scale pilot plant work.
- Impurities from the Tellurium/Br catalyst system could not be fully removed from the product stream. There was serious plugging in a reboiler and serious corrosion of equipment items. The plant was eventually scrapped.
Chem Systems’ laboratory followed SD’s business model with mixed results

**Success: Maleic anhydride from n-butane**

**Background for R&D**
Until the 1970s, maleic anhydride was produced via vanadium oxide catalyzed oxidation of benzene. By adding additional components to the catalyst, it was possible to oxydehydrogenate n-butane to butylenes and then to maleic anyhydride.

**Commercialization**
Amoco Chemical became interested in broadening its petrochemical portfolio and agreed to sponsor pilot plant and other work in return for an option to purchase the technology. The company was satisfied with the results and became sole owners of the process, building a successful commercial plant at its Chicago refinery.
Chem Systems’ laboratory followed SD’s business model with mixed results

**Limited Success: methanol**

**Background for R&D**

With experience on a DOE project to make substitute natural gas from naphtha, Chem Systems, with funding by DOE, EPRI and Fluor, developed on a pilot plant scale a process to react synthesis gas to methanol in a liquid slurry reactor.

**Demonstration Plant**

Air Products and Eastman Chemical joined the consortium. A 10 tons/day plant was built next to Eastman Chemical’s coal-based methanol plant in Kingsport, Tennessee where the technology was successfully demonstrated. However, continued improvement and optimization of the conventional fixed bed process precluded commercialization.

*This is a good example of the fact that a new technology with excellent economics may not obsolesce an existing technology, since it is just not that much better!*
Chem Systems’ laboratory followed SD’s business model with mixed results

**Failure: Propylene Oxide**

**Background for R&D**

Many researchers have worked on technologies that would produce propylene oxide directly with only minor amounts of co-products. Chem Systems laboratory worked at laboratory scale on a new route that showed considerable promise.

**Chemistry:** The first step was acetoxylation of propylene using an iodine catalyst. The resultant product was then converted to propylene oxide with small amounts of acetaldehyde byproduct.

**Scale-up in large pilot plant**

Chem Systems granted BASF a license. A large pilot plant was built at Ludwigshafen. Unfortunately, it was not possible to remove iodine-based impurities and so BASF discontinued the work.
Let’s now move beyond 1980 and look at some more recent developments.

**Olefin Metathesis**

- Phillips Petroleum developed its Triolefin process to make ethylene and 2-butene from propylene.
- The process is also reversible to make more propylene from ethylene.
- LyondellBasell built the first large unit of this kind in Houston.

**Propane Dehydrogenation**

- UOP’s Oleflex and Lummus’ Catofin processes are now in broad use, converting propane to propylene. Oleflex consists of a fluid bed reactor and a fluid bed regenerator where the coke is burned off the circulating catalyst.
- Four of the largest plants were built in Saudi Arabia, which mostly cracks ethane and therefore needed more propylene for derivatives production.
Methanol to Olefins (MTO) Technology has emerged and could be a real game-changer (No hydrocarbon liquid feedstock)!

*For the first time, allows methane and/or coal to be used as feedstocks for olefins production.*

This concept was discovered accidentally by Mobil in their methanol-to-gasoline (MTG) plant in New Zealand in the mid 1980’s.

Source: IHS
Many CTO/MTO Projects in China

- Multiple plants are in operation
- Many more are under construction
- CTO and CTMEG projects are built in coal-rich west
- MTO projects are built along east coast
- Some planned projects will not be built

Source: IHS
Saudi companies have been active in petrochemical development and commercialization:

- SABIC and IFP (Institute Francaise de Petroles) joined to commercialize a process to dimerize ethylene to 1-butene
- Sabic built the first LPG to Aromatics plant using UOP’s Cyclar process.
- Chevron and a private Saudi group used Chevron’s Aromax technology to build a plant at Al Jubail to convert light naphtha to benzene and cyclohexane – a first-of-its kind plant
- An isobutylene-to-MTBE plant was built in cooperation with Snam Progetti
- SABIC and LINDE cooperated to develop and commercialize a competitive LAO technology now also being licensed
- SABIC used its own technology to build plants to make acetic acid from ethane

The question for the worldwide petrochemical industry is: where are the new opportunities for significant innovation?
Most existing technologies have been improved and optimized to the point where no more breakthroughs are expected.

<table>
<thead>
<tr>
<th>Process</th>
<th>Typical Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene (Ethane)</td>
<td>85%</td>
</tr>
<tr>
<td>Styrene</td>
<td>94%</td>
</tr>
<tr>
<td>VCM</td>
<td>95%</td>
</tr>
<tr>
<td>Ethylene Oxide</td>
<td>80%</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>81%</td>
</tr>
<tr>
<td>Terephthalic acid</td>
<td>95%</td>
</tr>
</tbody>
</table>
Novel lower production cost technologies face a major hurdle versus existing (large) plants

- The situation in the 1960-1980 period
  - Small plants shut down as much larger plants were built
  - A new process could be the basis of a small first plant at relatively low investment. In some cases, this was an expensive learning lesson

- 1990 to present: The first plant for a “breakthrough technology” now has to be huge to achieve “shutdown” economics (i.e. to obsolesce) large, depreciated plants using the current technology. Companies are generally unwilling to risk the large amount of capital to build that first plant.
The long-standing problem facing developers of a new ethylene process

• From the first time this olefin was produced by cracking a saturated hydrocarbon at high temperature to the present time, the technology is essentially unchanged. It can be likened to “hitting a molecule with a hammer and separating the products”

• Many researchers have looked at this “not-very-elegant” process and wanted to develop a more selective, catalytic route. But, they have not been commercialized because
  - The byproducts of cracking (propylene, butadiene, benzene, isoprene, etc.) from the traditional process have substantial value
  - The first plant needs to be in the billion pound per year range to achieve scale economics—therefore very high investment for a first-of-a-kind plant that may not work well or be economical
Current Petrochemical Research: It has been difficult to find new breakthroughs

- When an industry is new, innovation is rampant and new products are discovered.
- No new important (multimillion lbs/year) polymer has been commercialized over several decades and none are expected.
- As noted, current processes have been greatly optimized. Accordingly, most chemical company R&D efforts are now aimed in different directions:
  - Chemicals from biomass, Specialty chemicals, The energy sector (e.g., energy storage), Electronics, Sustainability, Health

But there are still opportunities, as China and UOP have shown with C1 chemistry.
Some new petrochemical chemistry may be on the horizon

- Direct methane coupling to ethylene: Siluria (a small private company) and Linde are working on a promising oxidative coupling program first pioneered at MIT. Aramco has made a substantial investment in Siluria’s work.
- One-step styrene: Researchers at the University of Virginia use a rhodium catalyst achieving 100% selectivity.
- A phenol process without byproduct is being developed by Japan Chemical Innovation Institute and Tosoh. Acetic acid forms phenyl acetate, which is then hydrolized to recover the acetic acid.
- Methanol-to-aromatics: Chinese researchers are working on this
The Rich History of Petrochemical R&D

It’s never over!