The Impact of Shale Gas and Oil on the Chemical Industry

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Chemical Industry Feedstocks

- Since WWII …
  - The widespread development of natural gas distribution infrastructure
  - The development of steam cracking of natural gas condensate and refinery light naphtha to olefins
  - Catalytic reforming of middle naphtha to aromatics

- Methane, ethylene, propylene, butadiene, benzene, toluene, and the xylenes became the principal feedstocks of the organic chemicals industry
  - Replacing wood, coal tar, and acetylene
Post War Chemical Supply Chains

- $C_1$ – Methane (natural gas)
  - Hydrogen, Ammonia, Methanol, Formaldehyde

- $C_2$ – Ethane (condensate or light naphtha)
  - Ethylene, ethylene oxide/glycol, acetaldehyde, acetic acid, vinyl acetate, vinyl chloride, styrene, propionaldehyde, propionic acid

- $C_3$ – Propane (condensate or light naphtha)
  - Propylene, cumene, phenol, acetone, acrylates, methacrylates, butyraldehydes, butyric acids

- Aromatics (oil reformate)
  - Benzene, styrene, phenol, toluene, xylenes, terephthalic acid
US Organic Chemical Industry

- Supply chains were fairly stable

- Led to the development of many large volume products, especially polymers

- Rapid growth of the American chemical industry

- Chemicals contributed significantly to a positive balance of trade
  - Those with access to condensate considered economically advantaged
Catalysis Innovation Can Alter Supply Chains

- In 1968, Monsanto discovered that cobalt-catalyzed Reppe carbonylation chemistry could be rhodium-catalyzed at much milder conditions.

- First application was a route to acetic acid from methanol:
  \[ 2H_2 + CO \rightarrow \text{MeOH} \]
  \[ \text{MeOH} + CO \rightarrow \text{HOAc} \]
  - Acetic acid becomes a C\textsubscript{1} chemical from methane via methanol instead of a C\textsubscript{2} chemical from ethane via ethylene and acetaldehyde.
Occasional Supply Chain Hiccups

- Price controls and cold winter of 1977 lead to gas shortages, industrial curtailments, and institutional closings for lack of heat
  - Restrictions on industrial and powerplant gas use, orderly and eventually complete price decontrol, order-of-magnitude increase in gas price, then two decades of relative price stability

- 1992 Clean Air Act Amendments, FERC Orders decoupling pipeline transportation, and Energy Policy Act allowing unregulated non-utility cogenerators
  - Huge increase in natural gas powerplant construction
Electric generating capacity additions, 1995 - 2010
gigawatts

Source: U.S. Energy Information Administration Forms EIA-860 and BA-860M
Note: data for 2010 are preliminary.
US Natural Gas Price (1976-2001)
Impacts of Increasing Natural Gas Prices

- **Chemicals from methane**
  - Methanol production moves offshore to sources of stranded gas
  - MTBE abandoned as gasoline oxygenate
  - Ammonia moves to Canada
  - Hydrogen becomes expensive (and ultra-low-sulfur diesel at the pump becomes more expensive than regular)
  - Some consider alternative lignite and petcoke gasification routes to hydrogen

- **Chemicals from condensate**
  - Condensate price tied to natural gas
  - Ethylene price spikes
  - Propylene price finally rises higher than ethylene
Chemical Industry Responses

- Some abandon commodity ethylene and propylene polymers
- Research C1 routes (from coal) to previous C2 and C3 chemicals like ethylene glycol and propylene
- Flight to off-shore production (to sources of stranded methane and condensate - Persian Gulf)
- Bio-based feedstocks (ethylene from sugar-based bioethanol dehydration - Brazil)
- Feedstocks from coal gasification and liquefaction (China)
- Greater interest in chemicals and fuels from biomass including chemicals from carbohydrates and the need for water-tolerant refinery catalysts
- Calls for increased US LNG import infrastructure
- Application of directional and horizontal drilling, hydraulic fracturing, and microseismic monitoring technologies to develop impermeable hydrocarbon-containing shale formations

Ethylene and propylene prices returned to traditional levels
Crude Oil and Natural Gas Prices
Ratio of Crude Oil Price ($/bbl) to Natural Gas Price ($/MBTU)

Chart Source: ICIS.com
Shale Gas Impact

- Shale gas now reclassified as conventional gas
  - US conventional gas reserves doubled
- Relative price of natural gas compared to oil reduced at one point by eighty percent (now closer to fifty percent)
- Electric power fuel switching from coal to natural gas accelerated
  - Interest in coal as a C1 and hydrogen feedstock on hold
- Shuttered US methanol and ammonia production restarted and new plants under construction
- Condensate crackers restarted
  - Sometimes at the expense of naphtha crackers
- Restored US feedstock advantage for many organic chemicals and intermediates
New US Chemical Plants

- Over 200 projects announced
  - Valued greater than $125B

- Ten new ethylene crackers (plus an equal number of expansions)
  - If all built would increase US ethylene capacity by more than 50%

- The expectation is that the majority of this product will be for export
  - Many of these projects will not be built
What to do with Marcellus Shale Gas Liquids

- Shell studies Monaca PA for ethylene plant (shale gas condensate cracker)
- Follow-up ethylene (and propylene) derivatives plants may soon follow (polyethylene, polypropylene, ethylene oxide/glycol, etc.)
- $C_1$ derivatives plants (methanol, formaldehyde, acetic acid, etc.) from shale gas also possible
- Interesting $C_1$ vs $C_2$ process competition

- How about aromatics from shale gas?
Stranded Marcellus Shale Gas Condensate Dilemma

- Build new cracking infrastructure?
- Build additional olefins derivatives capacity?
- For what markets?
  - Export?
  - Transportation infrastructure?

- Pipeline to existing cracking infrastructure?
  - New pipelines to Midwest?
  - Reverse pipelines to Gulf Coast?
Hydraulic Fracturing can also Stimulate Tight Oil Plays

- Bakken Field in the Williston Basin of North Dakota
  - Dolomite between two layers of shale
  - 200,000 square miles, 130 feet thick
  - Light oil and associated natural gas

- Eagle Ford Field in Texas
  - Brittle carbonate-containing shale
  - 50 miles wide, 400 miles long, 250 feet thick
  - Light oil and associated natural gas
Impact of Shale Oil on Chemical Industry

- Initial interest in exploiting shale gas through gas-to-liquids technologies now on hold

- Aromatics will continue to be supplied from refinery reformate streams
  - Less interest in C1 routes to aromatics
  - Current lack of production discipline keeping aromatic feedstocks uncharacteristically low, but not likely so in the longer term
New Shale Hydrocarbon Impacts

- New shale gas capacity can be absorbed by new gas demand from coal-fired powerplant fuel switching
- Extensive US shale gas reserves limit new offshore deepwater gas development
- Natural gas price expected to be relatively stable (given production discipline) at perhaps one-third to one-half historic extrapolations
- Total US oil demand is stable or slightly decreasing
- New shale oil capacity offsets crude oil imports
- New shale oil production can be absorbed only as fast as import commitments can be unwound
- Current low oil prices are the result of lack of production discipline and record high inventories and are not sustainable and likely will increase
What is Likely to Happen

- Natural gas substitution for coal will be the primary carbon management technique in the power industry.
- Increased deployment of highly efficient natural gas turbines for electricity production (NGCC) and chemical plant cogeneration will support increased electrification of transportation and domestic heating sectors.
- Increased US production and export of chemicals from both price-advantaged gas and oil.
- Aromatics will continue to be made from oil reformate.
- Research that was done when natural gas was expensive (to exploit coal syngas) is also applicable when shale gas is plentiful.
- For many intermediates, depending on local availability of wet or dry gas, interesting competition between C₁ (methane) and C₂ (ethylene) chemistries may result from advances in chemical catalysis and process engineering optimization.
An Unexpected Shale Gas Impact

- Increased availability and decreased cost of shale gas condensate has decreased the use of refinery light naphtha in US crackers for olefins
- Greater use of lighter feedstocks results in relatively less production of coproduct propylene
- This will require on-purpose production of propylene for the first time
  - C3 route: 1-Step catalytic propane dehydrogenation
  - C1 route: Multi-step methane-to-methanol-to-propylene
  - Depends on the relative cost of methane and propane
Outlook

- US oil and condensate output at highest level in 45 years
  - Shale will assure conventional feedstocks remain economically advantaged for some time even with production discipline

- In locations with wet shale gas but no ethane processing history, new $C_2$-based chemical infrastructure is possible
  - Only if additional product capacity is needed
  - Otherwise ethane pipelines will be built to existing crackers

- $C_1$ and $C_2$ chemistries will compete with each other
  - Extracting benefits from shale gas and shale oil is not contingent on new chemistry, catalysis, or process innovation
  - But innovations will occur and may alter the preferred shale gas or oil resource for any particular application
Thank You