The Impact of Disruptive Change in Feedstock Price and Availability on Chemical Process Development

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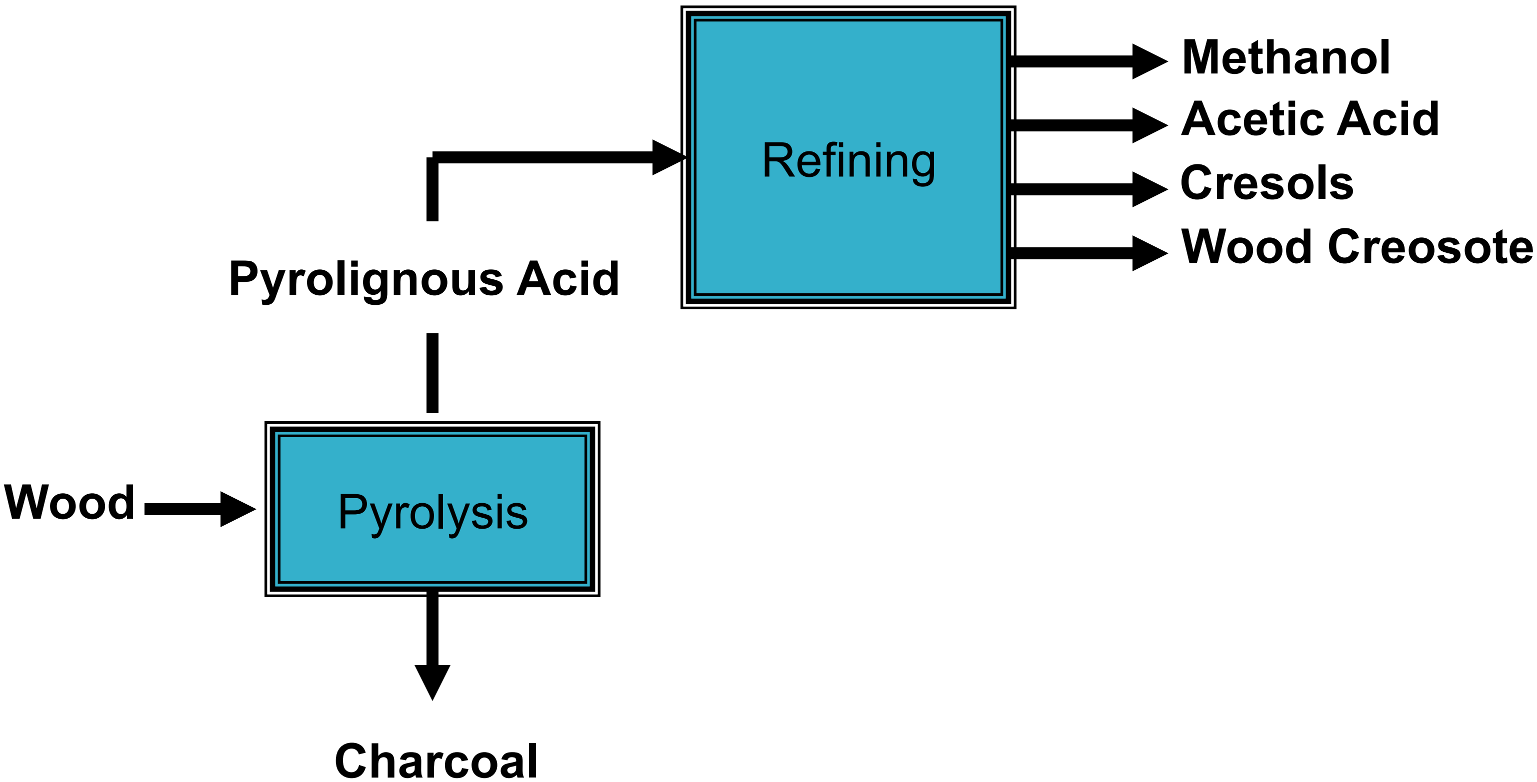
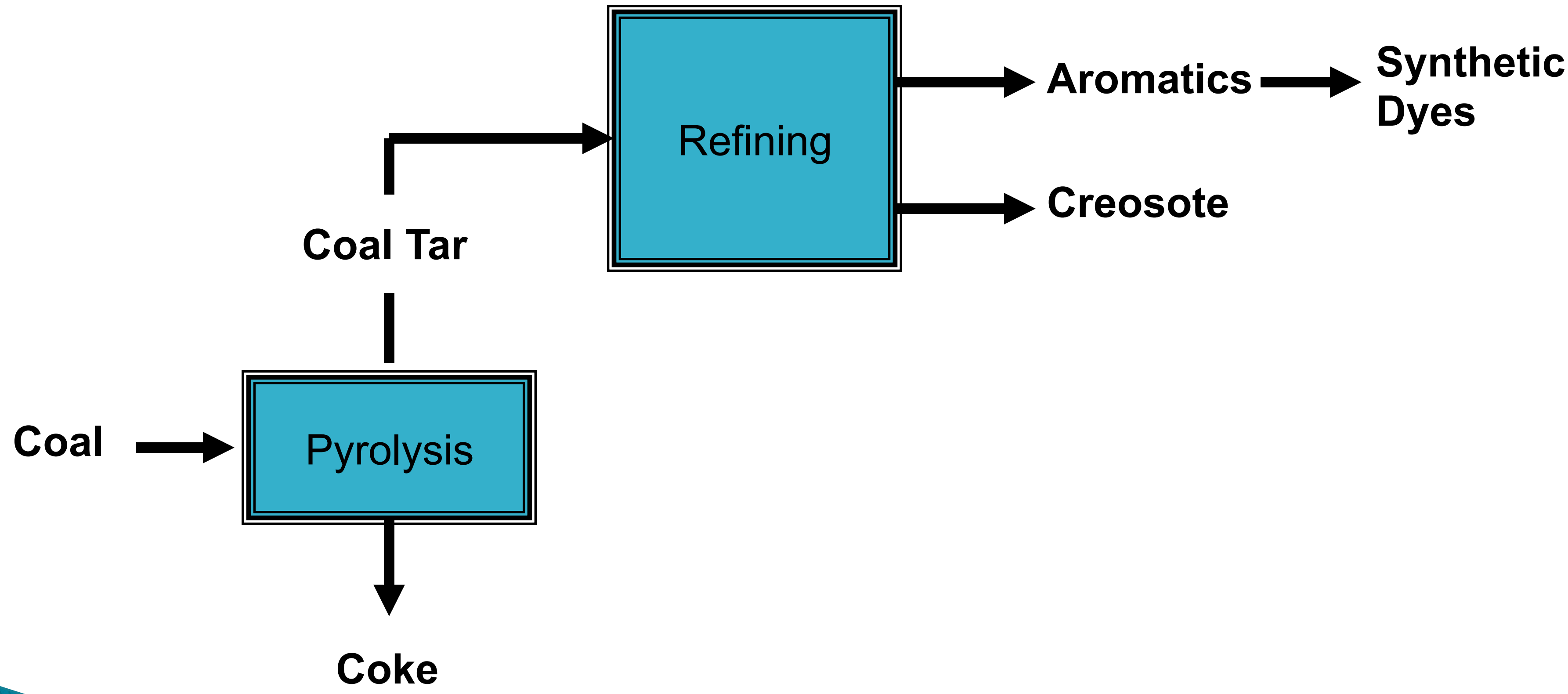
Outline

- Some chemistry history
  - Early fuels and feedstocks: coal and biomass
  - A disruptive change: petroleum and natural gas
  - Steam cracking: a paradigm-changing process
  - Chemical feedstock supply chains
  - Rhodium: a supply-chain-changing catalyst
- Natural gas
  - Impacts of natural gas supply, demand, and pricing policies
  - Interaction of electricity production and chemicals sectors
  - Shale gas and implications for chemical process development

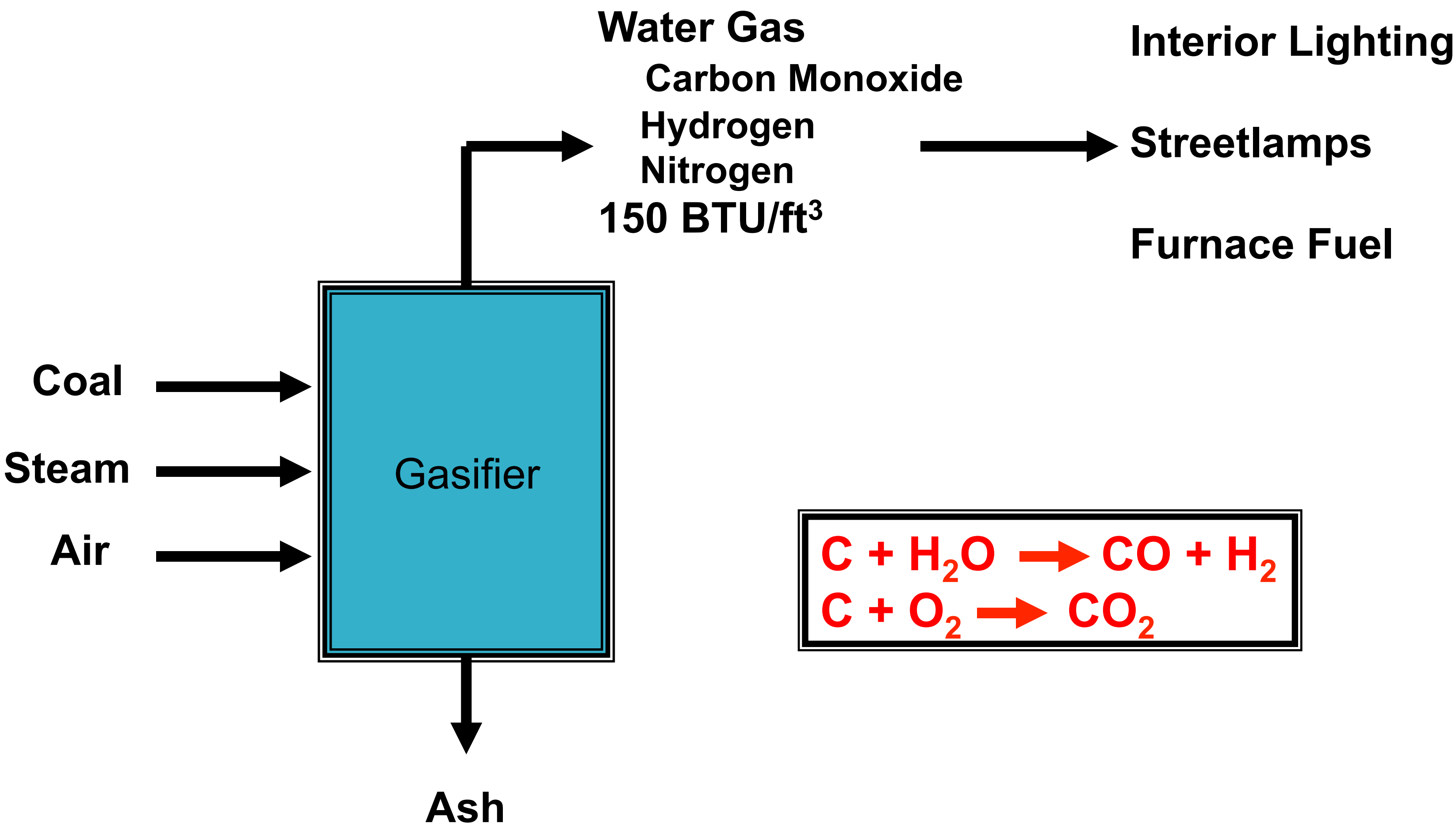
Wood as a Chemical Raw Material



Coal as a Chemical Raw Material



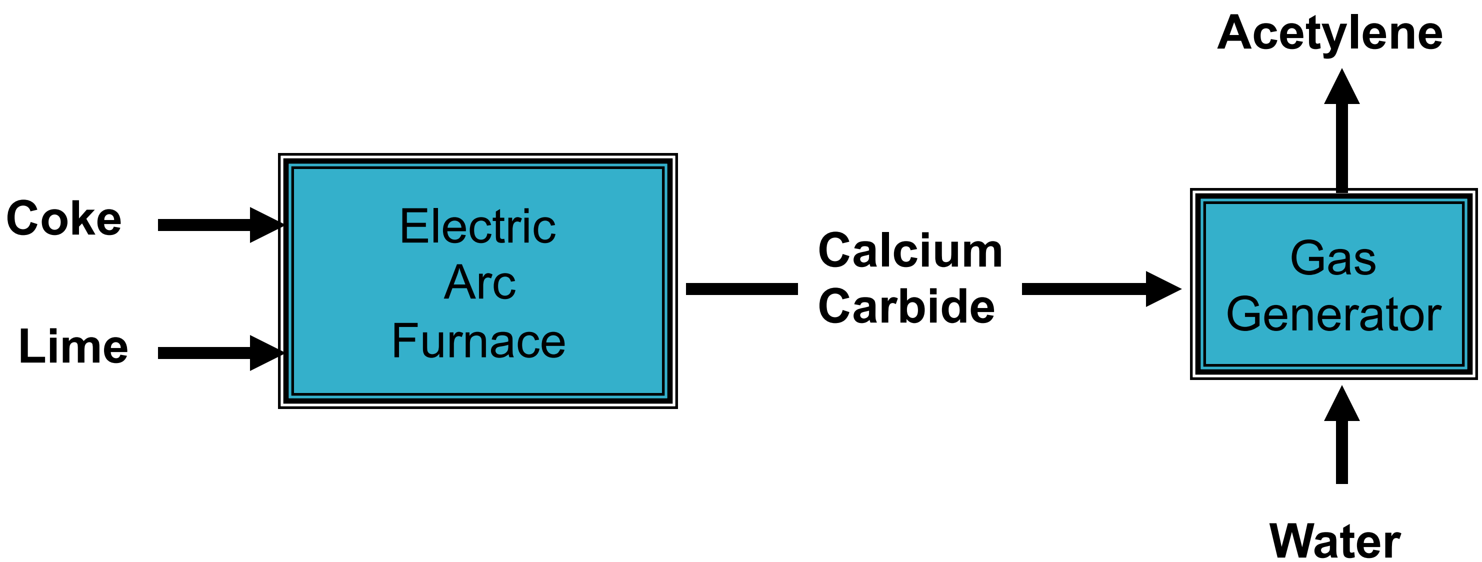
Coal as an Illumination Fuel



$$C + H_2O \rightarrow CO + H_2$$
$$C + O_2 \rightarrow CO_2$$

Reaction also used as a source of H_2 for NH_3 production

Coal as a Synthetic Organic Chemical Raw Material via Acetylene



$3C + CaO \rightarrow CaC_2 + CO$

$CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$

Acetylene Derivatives
Early Reppe Chemistry

Acetylene
HC≡CH

- → **Acetaldehyde** → **Aldol Condensation Products**
- → **Acrylic Acid** → **Acrylates (Paints)**
- → **Acrylonitrile** → **Acrylics (Fibers)**
- → **Chlorohydrocarbons** → **Trichloroethylene (Solvents)**
- → **Vinyl Acetate** → **PVA (Adhesives)**
- → **Vinyl Chloride** → **PVC (Vinyls)**
- → **Vinylacetylene** → **Chloroprene**

German Chemistry during World War II

- Fischer-Tropsch synthesis of diesel fuel from syngas ($CO + H_2$)

- Reppe carbonylation and oxo chemistry
  - Alcohols + CO => Carboxylic Acids
  - Esters + CO => Anhydrides
  - Olefins + CO + H_2 => Aldehydes
  - Cobalt catalysis, high temperatures, very high pressures

Cracking Processes (Petroleum)

- Thermal cracking
  - Developed in Russia (1891) and US (1908)
  - 375-400C (to produce light fractions)
  - 450C (to produce petroleum coke for electrodes)

- Catalytic cracking (1942)
  - Fluidized bed with catalyst regeneration
  - 670-760C
  - Originally low-activity alumina catalyst
  - Now high activity zeolite catalyst and short residence times

- Steam cracking (1920)
  - Non-catalytic hydrocarbon pyrolysis in the presence of steam to minimize coke formation
  - 850-1050C
  - Tend to produce olefin products (and hydrogen)

Paradigm Shift

- In World War II, steam cracking technology is applied to ethane (otherwise useless hydrocarbon) to produce ethylene for polyethylene for wire insulation and radar apps

- Realization that ethylene and oxygen behave like acetylene in many chemical reactions
  - Ethylene from ethane almost totally replaces acetylene from coal as the foundation of the organic chemical industry

Further Major Changes

- Steam methane reforming for H_2 and CO
  - Coal gasification virtually disappears
    (Except Fischer-Tropsch fuel in South Africa)
- Methanol synthesized from syngas and acetic acid synthesized from acetaldehyde
  - Wood distillation disappears
- Ethylene and propylene cracked from natural gas condensate (or refinery naphtha)
  - Acetylene as a specialty feedstock only
- Naphtha catalytic reforming for higher octane aviation and premium gasoline aromatics
  - Oil replaces coal tar as source for aromatics

Chemical Supply Chains

- C_1 – Methane (natural gas)
  - Hydrogen, Ammonia, Methanol, Formaldehyde
- C_2 – Ethane (condensate or naphtha)
  - Ethylene, ethylene oxide/glycol, acetaldehyde, acetic acid, vinyl acetate, vinyl chloride, styrene, propionaldehyde, propionic acid
- C_3 – Propane (condensate or naphtha)
  - Propylene, cumene, phenol, acetone, acrylates, methacrylates, butyraldehydes, butyric acids
- Aromatics (reformate)
  - Benzene, styrene, phenol, toluene, xylenes, terephthalic acid

Catalysis Innovation Can Change 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

  $$2H_2 + CO \rightarrow MeOH$$

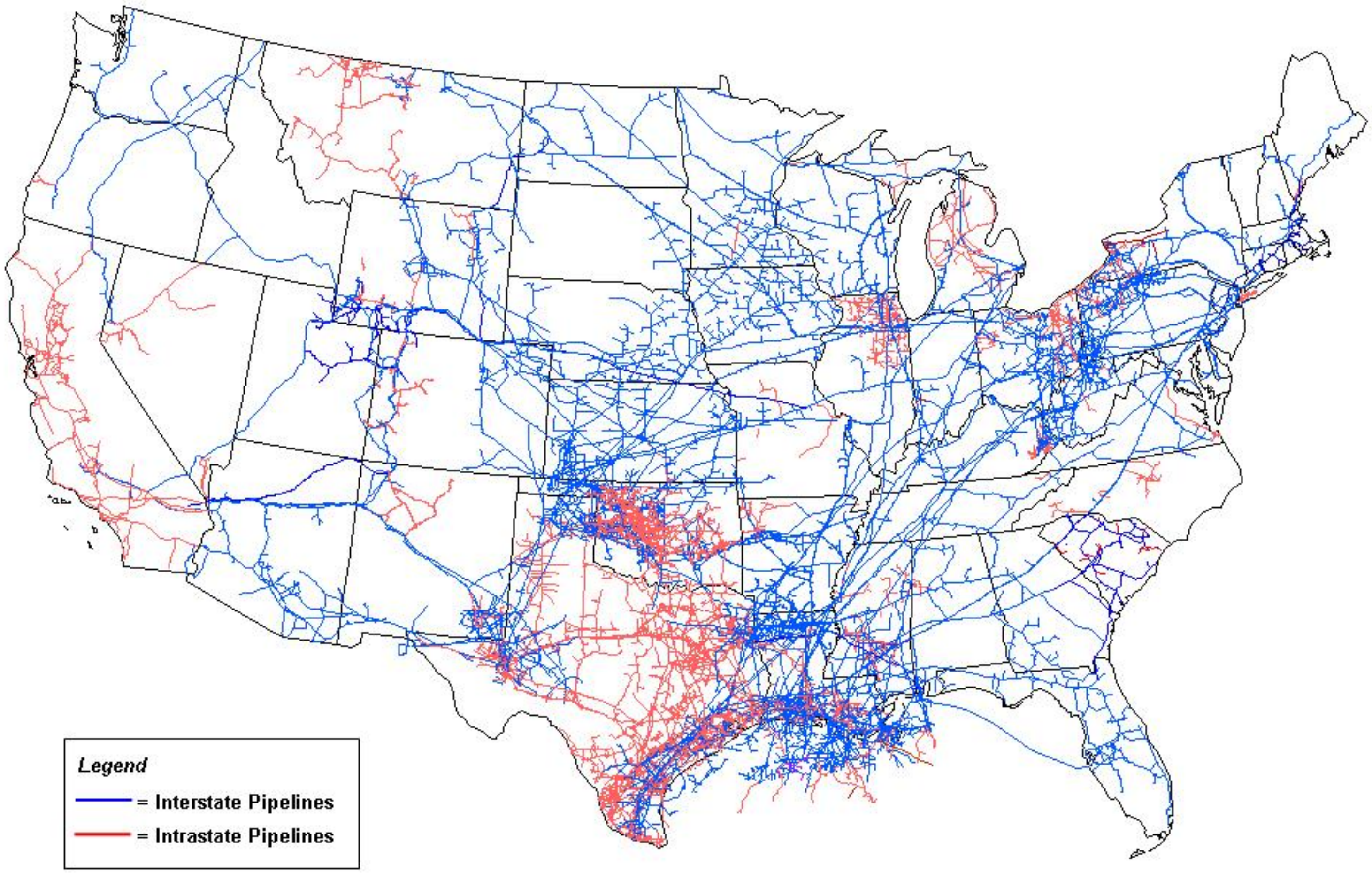
  $$MeOH + CO \rightarrow HOAc$$

  - Acetic acid becomes a C_1 chemical from methane via methanol instead of a C_2 chemical from ethane via ethylene and acetaldehyde

Natural Gas as Fuel and Feedstock

- Natural gas is the fuel that powers most (but not quite all) US chemical and refining processes
- Natural gas methane is the feedstock for hydrogen production (for hydrocracking, hydrodesulfurization, and ammonia) and for syngas (for methanol, and its derivatives MTBE, formaldehyde, and acetic acid)
- Natural gas condensate (ethane and propane) becomes the advantaged raw material via ethylene and propylene to much of the organic chemicals industry (compared to crude-oil-derived naphtha)

US Natural Gas Pipeline Network



Source: Energy Information Administration, Office of Oil & Gas, Natural Gas Division, Gas Transportation Information System

Partial History of Natural Gas Regulation in the US

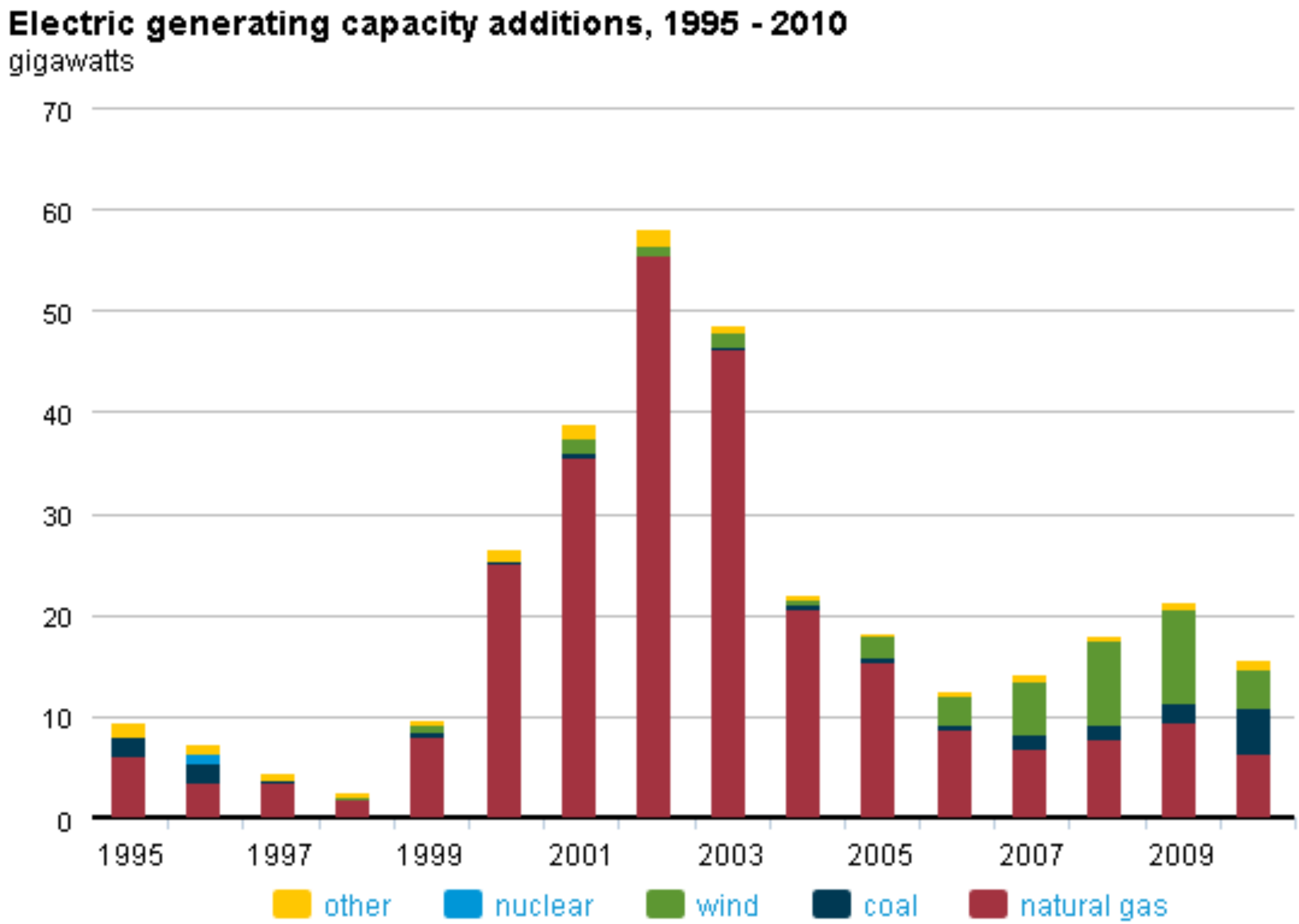
- 1954 Phillips Supreme Court Case
  - Federal Power Commission (now FERC) has jurisdiction to regulate wellhead price of interstate natural gas
  - Ceiling set at to protect consumers from monopolistic pricing
  - US natural gas consumption and production steadily expand

Until…

- The incremental price of natural gas production eventually exceeded the US controlled price
- The ceiling price provided inadequate incentives to explore for or develop new fields
- Production leveled off
- Resulted in gas shortages (especially in interstate markets)
  - In the cold winter of 1976-77, productive capacity supply could not meet demand
  - Upset freezing consumers and closed facilities
  - Industrial customers curtailed

Eastman Response (as an example)

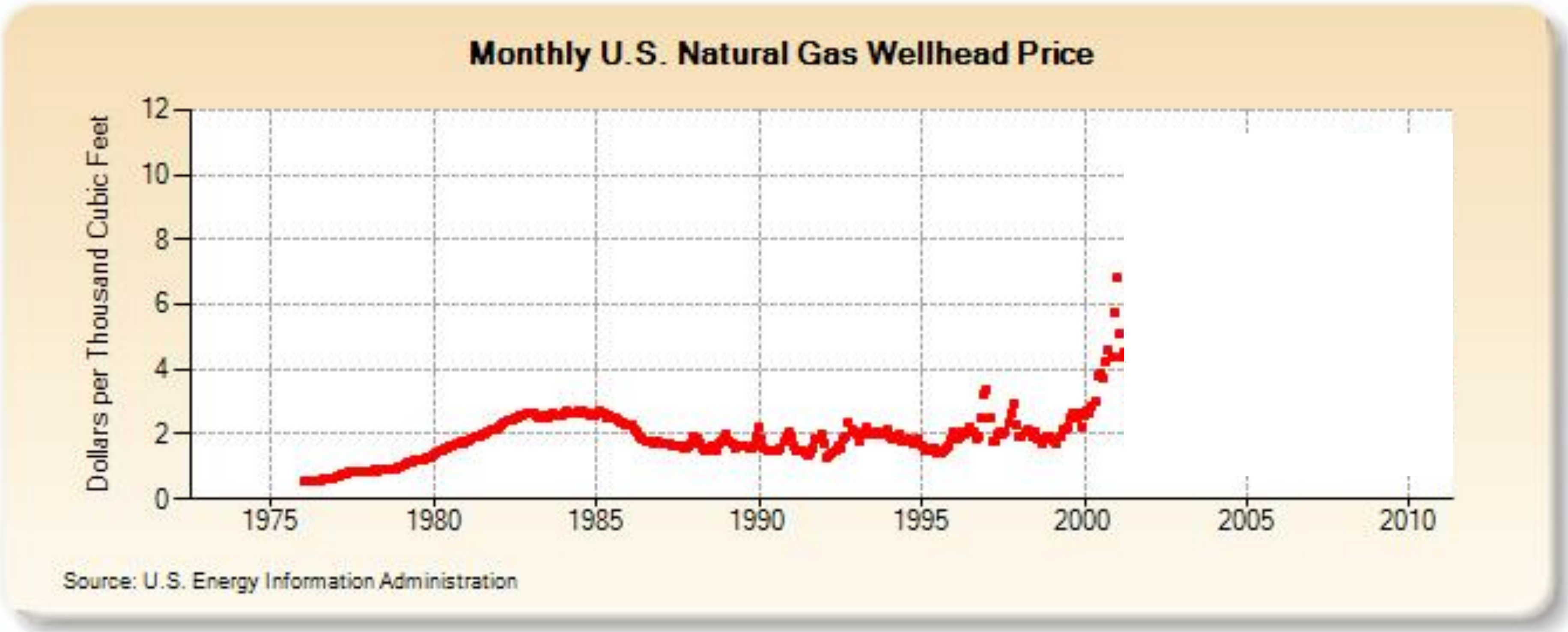
- Mostly coal-fired, but did use some natural gas to fire hot oil and cracking furnaces
- Substituted fuel oil where possible
- Considered coal gasification to town gas to fire cracking furnaces
- Ultimately used coal gasification for syngas feedstock and entirely new rhodium chemistry to avoid cracking reactions
- Chemicals from Coal complex started up in 1983 and expanded in 1991



Sources: U.S. Energy Information Administration Forms EIA-860 and EIA-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 low-sulfur diesel at the pump becomes more expensive than regular)

- Chemicals from condensate
  - Condensate price rises with natural gas
  - Ethylene price spikes
  - Propylene price finally rises higher than ethylene

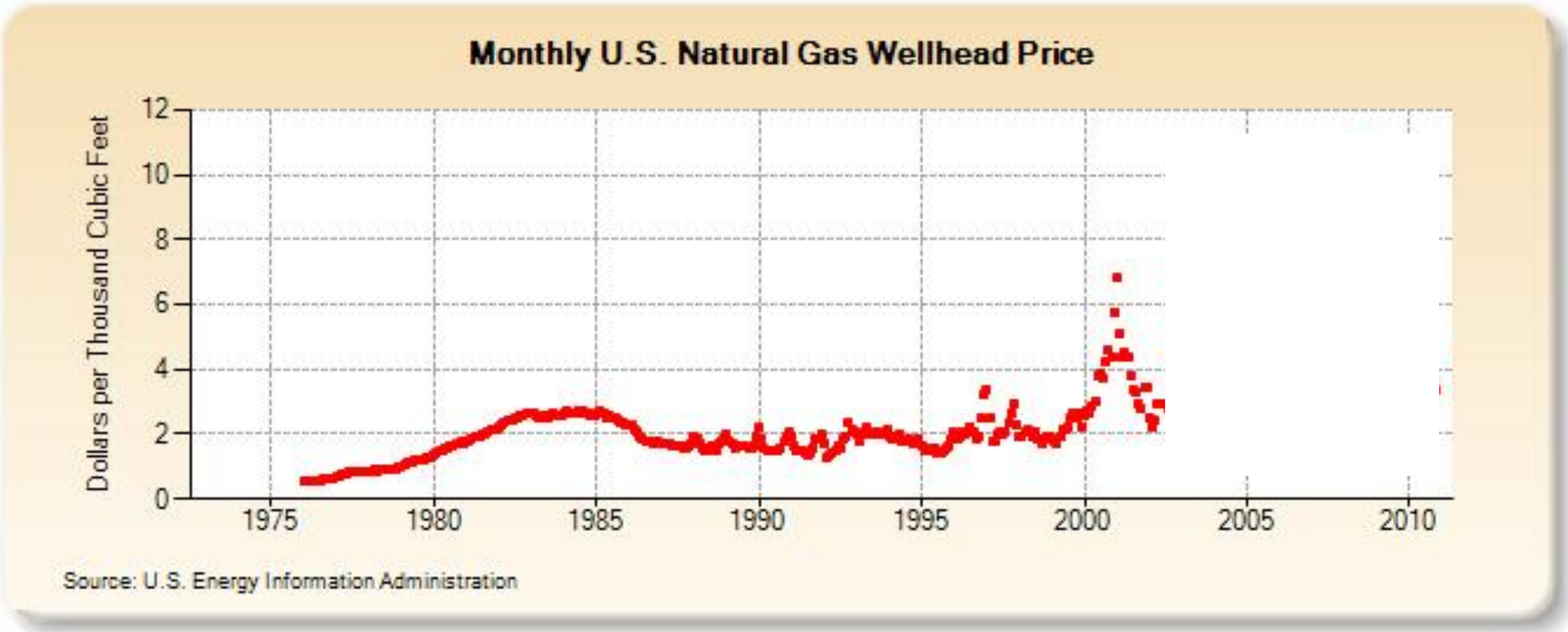
Eastman Response (again as an example)

- Shut down older cracker capacity
- Abandon some ethylene derivatives (polyethylene) and seek C_1 routes to others (ethylene glycol, acetaldehyde, vinyl acetate) as was done previously for acetic acid and acetic anhydride)
- Abandon polypropylene
- Seek C_1 routes to propylene (MTP) for existing oxo derivatives and other intermediates currently made from propylene (acrylics, methacrylics, acetone, etc.)
- Developed process for the large-scale gasification of petcoke, lignite, or coal as source of syngas for C_1 chemistries and refinery hydrogen in TX and LA

Other Responses

- 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 and especially chemicals derived from carbohydrates and water-tolerant refinery catalysts (energy independence)
- Calls for increased US LNG import infrastructure
- Application of directional and horizontal drilling and hydraulic fracturing technologies to develop hydrocarbon-containing shale formations

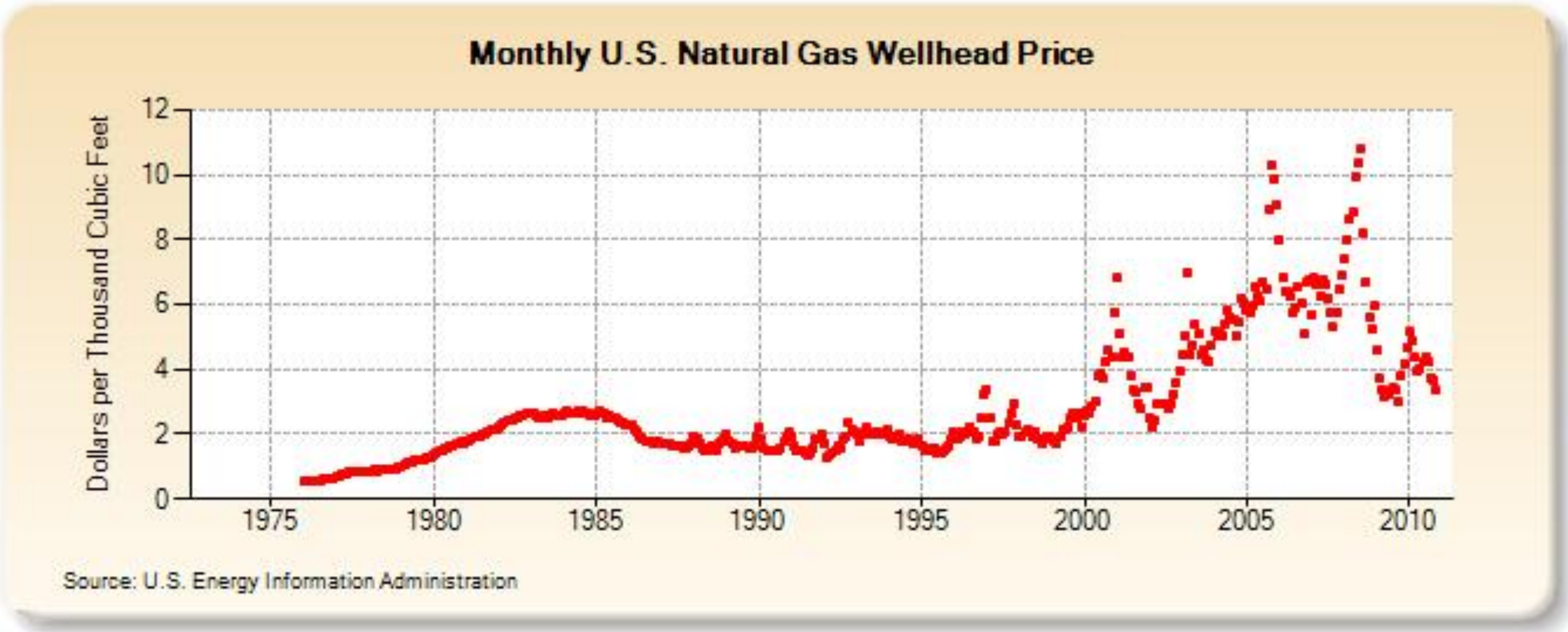
US Natural Gas Price (1976-2003)



Ethylene and propylene prices returned to traditional levels

US Crude Oil Price (1978-2012)

US Natural Gas Price (1976-2012)



Shale Gas

- Unconventional natural gas (as is coalbed methane, tight sandstone gas, and methane hydrates)
- Found in relatively thin shale formations of very low permeability
- Economic production enabled by two technological innovations:
  - Directional drilling
  - Hydraulic fracturing
- Technology and field development encouraged by high natural gas prices

Shale Gas Impact

- Shale gas now reclassified as conventional gas
- US conventional gas reserves therefore doubled
- Relative price of natural gas reduced by two-thirds
- Electric power fuel switching from coal to natural gas accelerated
- Killed proposed Eastman petcoke gasification project
- Shuttered US methanol and ammonia production restarted and new plants under construction
- Condensate crackers restarted and new crackers proposed in regions with wet gas
- Restored advantaged US feedstock position for many organic chemicals and intermediates

What is Likely to Happen

- Natural gas replacement for coal as the primary carbon management technique (source reduction)
- Increased deployment of highly efficient natural gas turbines for electricity production (NGCC) and chemical plant cogeneration
- Increased US production and export of chemicals decreasing the trade deficit
- For many intermediates, depending on local availability of wet or dry gas, interesting competition between C_1 (methane) and C_2 (ethylene) chemistries may result from advances in catalysis and process design optimization

What could go Wrong?

- Electricity power plant fuel switching could dominate the rate of shale gas development
- Amount of gas producible from shale formations might be less than predicted
- Additional shale formations might be more expensive to produce than first experiences suggest
- Some shale formations might be geologically inappropriate for development (e.g. shallow formations near sensitive groundwater supplies)
- Production technologies (especially hydraulic fracturing) might have unintended environmental consequences leading to political or regulatory restrictions

Outlook

- Shale-sourced feedstocks may be economically advantaged for some time (or maybe not)
- In locations with wet shale gas but without a previous ethane infrastructure, new C_2-based chemical production is possible
  - C_1 and C_2 routes will compete with each other
  - Benefits of shale gas feedstocks are not contingent on new catalytic or process innovations
  - But innovations will occur and may alter the preferred shale gas component for any particular application
- In locations with shale gas but not crude oil, new chemical production of aromatics possible
  - New processes and catalysis will be essential

Conclusions

- Chemical feedstock price and availability occasionally change in dramatic and disruptive ways
  - Such changes serve as the impetus for new chemistry new process and new catalysis developments

- In the most recent past, the preferred alternative for some commodity chemicals has shifted from gas to oil to coal to biomass and back to gas again
  - Each time these shifts have been accompanied renewed interest in new chemistries and catalysis

- Shale gas has doubled US gas reserves
- Such an increase in potential supply has altered traditional feedstock price ratios
  - Which persist but the shale gas advantage is decreasing given increased production discipline
- Shale gas will likely accelerate shift of electricity generation away from coal
  - Especially given anticipated greenhouse gas emission restrictions
  - This potentially large additional increment of demand could erase current natural gas price advantage

- Many opportunities will be local
  - Depending on local gas composition (wet or dry)
  - Local feedstock alternative availability
  - Local product demand

- There will be some interesting C_1 vs. C_2 chemistry/process competition
  - Not new (we have been here before)

- There may even be some interest in gas to aromatics
  - That would be new

Thank You