UT-BATTELLE

Alternative Feedstocks in Chemicals Manufacturing

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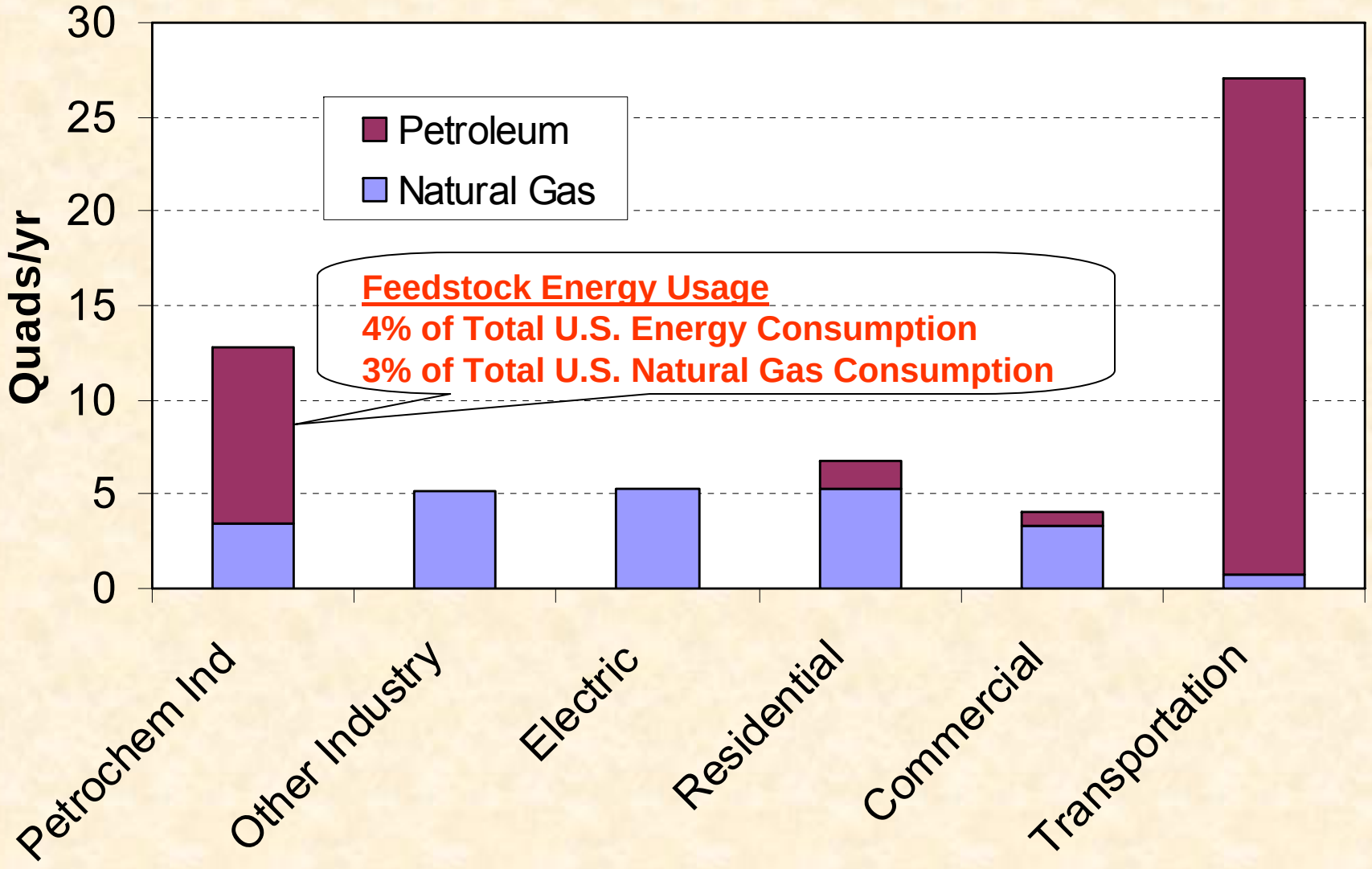
High Feedstock Prices Negatively Impact the Chemical Industry

- **The high cost of natural gas has eliminated the competitive advantage for U.S. chemical production**
- **As fuel prices rise, chemical manufacturers are shutting down domestic production and moving plants to Asia & Middle East**
  - **50% of methanol, 45% of ammonia, and 15% of ethylene capacities have been shut down in U.S. since 2000**
  - **U.S. import of fertilizers increased to 45% from 10% in 1990**
  - **In 2005 8,400 jobs were lost in the chemical industry**
  - **Industry went from an 80-yr trade surplus ($20B in 1995) to trade deficits beginning in 2002**

Sources:
Guide to the Business of Chemistry 2005
Chemicals IOF Annual Report 2004

Energy Independence Issue: Industrial Use of Petroleum & Natural Gas



Alternative Feedstock Options for Producing Large-Volume Chemicals

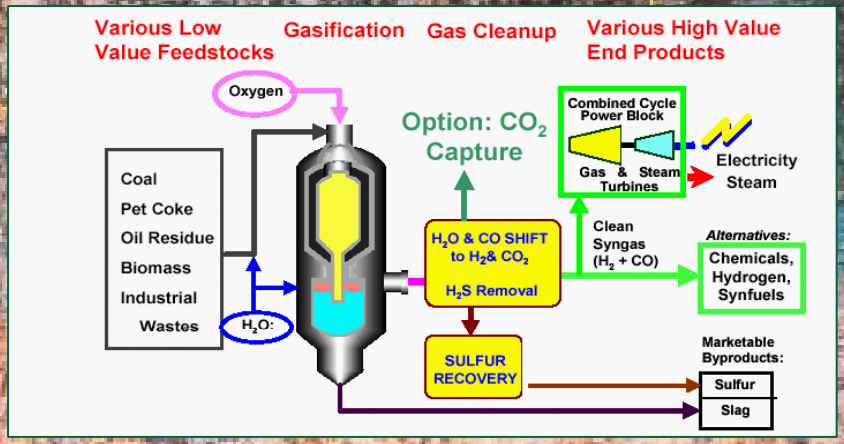
- **Coal – gasification and liquefaction**
- **Biomass – thermochemical, biological processes, pyrolysis**
- **Methane – stranded, unconventional, and hydrates**
- **Unconventional petroleum – oil shale, tar sands, heavy oil**
- **Novel pathways – CO_2/H_2O, methane, hydrogen to hydrocarbons**

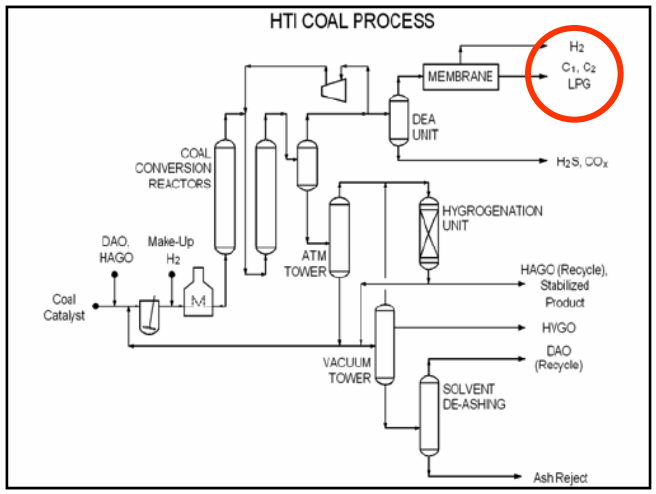
Selected Top Commodity Chemicals
(CMA 1998)

Chemical	Alternative Source	Industry/End Use	Volume (x10^6 tons) 1997 US production
Olefins:	Gasification of coal, biomass	R-Cl, oxide, polymers	
Ethylene	from methanol		24
Propylene			14
Aromatics:	Gasification	Polymers, cyclohexane	
Benzene	from methanol		7.5
Toluene	(gas-to-liquids)		4.1
Xylene			4.0
Paraffinic derivatives:	Gasification	Building blocks	
MTBE	Methanol	Fuel additives	
Butadiene	dehydrogenation	polymers	9.0
	Fischer-Tropsch		2.0
Acetone	Gasification	Intermediate	1.5
Formaldehyde	Methanol, CH_4	Olefin	4.2

Alternative Feedstocks Study - Coal

- **Overseas – large scale**
  - **Gasification – Sasol**
  - **Coal liquefaction – off shore (Choren and Shell - China)**
- **US technology at small/pilot scale**
  - **Gasification for energy production (e.g., Gilberton)**
  - **Chemicals/EOR/CO_2 sequestration (e.g., Dakota www.dakotagas.com)**



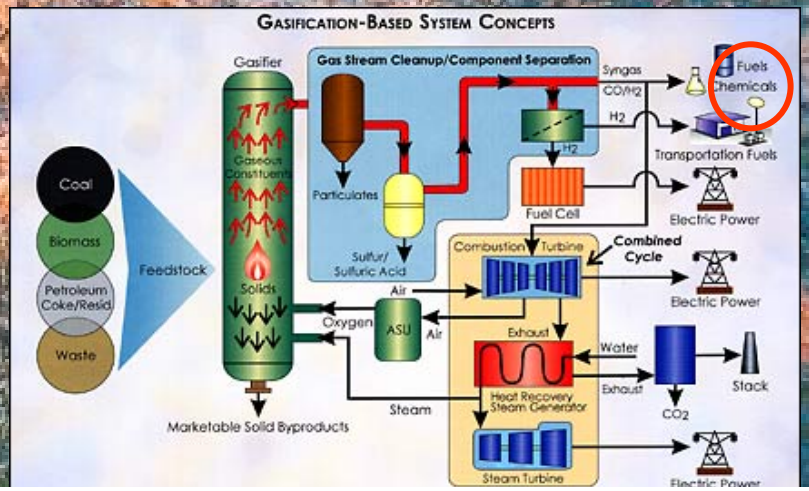


Shenghua Group Corporation, Coren, Shell

Chemicals from Coal: Liquefaction and Gasification

- **Separations:**
  - **pretreatment**
  - **waste minimization, byproducts**
  - **gases (novel membrane technology), CO_2 sequestration**
- **Couple production of energy and chemicals**
  - **advanced controls**
- **Mixed feedstocks:**
  - **biomass, coal, petrochemical residues**
- **New chemical pathways:**
  - **optimized Fischer-Tropsch catalysis**

The technologies are fairly mature, but improvements are needed to make coal an economical feedstock for large-scale production of chemicals in the US.



http://www.fe.doe.gov/programs/powersystems/gasification

Alternative Feedstocks Study – Biomass to Chemicals

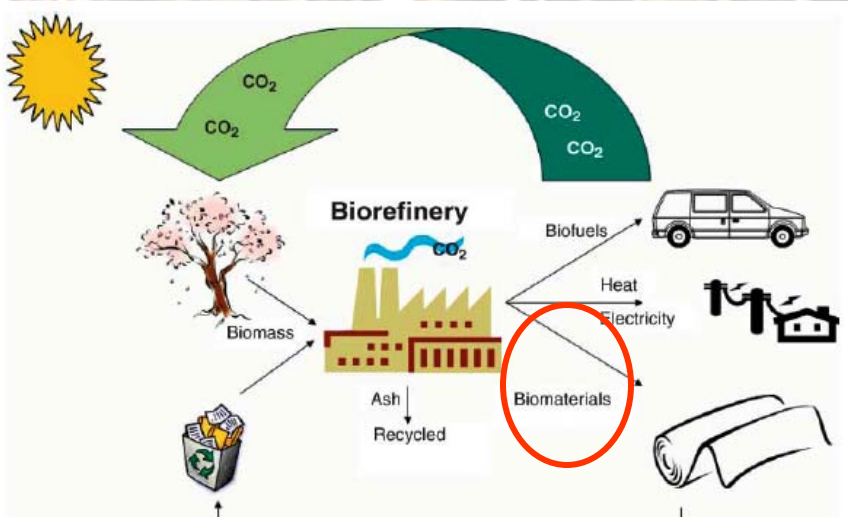
- 1st-generation fermentation technology (sugar based)
  - Niche chemical production (Eastman, Dupont)
  - Can leverage off alternative fuels
    - ethanol, biodiesel production
    - glycerine production
  - Potential for production of specialty chemicals
- Biorefining, pulping, wet and dry milling
  - Sugars to polyols (China, 10,000 MT facility)
  - Vegetable oils to lubricants

Adipic acid
Ascorbic acid
Diacids
Aspartic acid
Itaconic acid
FCDA 2,5 furan dicarboxylic acid
Glutaric acid
Levulinic acid
HPA – hydroxy propionic acid
Xylitol
Sorbitol
Hydroxybutyrolactone

Werpy, T., Peterson, G., DOE Office of Biomass Program, EERE, August 2004.

Biomass to Chemicals

- **Alternative Processing Options**
  - **Thermochemical: gasification**
  - **Fermentation of cellulose, hemicellulose and lignin.**
  - **Pyrolysis (high temperature) of waste biomass to produce oils**



Ragauskas et al. Science 311, 484-489 (2006)

- **Alternative feedstock use poses issues that are unique to chemical manufacture**
  - **Separations: pretreatment (cellulose, lignin, etc.), byproducts**
  - **Development of new chemical pathways as starting from more oxidized material than petrochemicals**
  - **Biological science: *omics, microbiology, crop development, cell metabolism**
  - **Logistical issues: diversified supply, scale-up difficult**

Alternative Feedstocks Study - Tar Sands and Heavy Oil

- **Potential long-term supply**
  - **US (Colorado, Utah oil shale deposit), pilot scale wells will be drilled in 2006.**
  - **Canada (Athabasca tar sands) in production**
  - **Venezuela (Orinoco) @ 500,000 bbl/d**
- **High capital costs, remote, expensive to operate (need power, natural gas for upgrading)**
- **Feasibility, environmental analysis for in situ pyrolysis, or steam extraction planned for oil shale**

Conversion of Tar Sands and Shale Oil to Chemicals

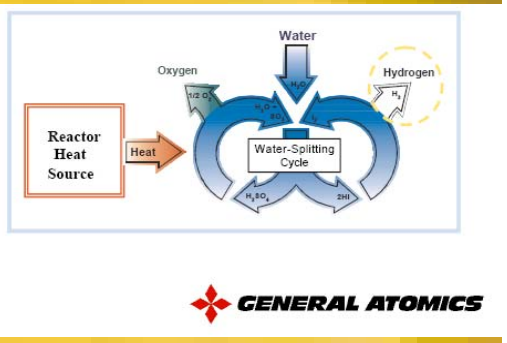
- **Current focus is on fuel production; need R&D into chemical feedstock manufacture**
- **Need robust ring-opening catalysts, such as selective cycloparaffinic ring opening, to break down polyaromatic tar compounds into smaller molecules**
  - **Resistant to impurities such as sulfur and nitrogen-containing compounds**
  - **Resistant to coating with ultra-fine particles**
- **Need chemical processes that minimize the use of hydrogen and natural gas**
- **Physical properties measurement and prediction**
- **Viscous, high molecular weight hydrocarbons from tar sands – need blending to adjust physical properties**

Alternative Feedstocks Study - Stranded Natural Gas

- **Gas that is uneconomical to transport by pipeline or tanker: remote, coal bed methane, hydrates, anaerobic fermentation - landfills**
- **Convert to liquid for transportation and end use**
  - **methanol best near-term opportunity, pathways known**
  - **methanol to olefin production offshore**
- **Energy policy needed to take advantage of these unconventional sources**
- **R&D needed to reduce dependence on natural gas at chemical plants, optimize energy efficiency**

Alternative Feedstocks: CO_2/H_2O and Methane to Chemicals

- **Develop radical new chemical processing concepts using solar or nuclear energy**
  - **Photocatalysis of CO_2 and H_2O to CO, H_2, CH_4,..**
  - **Nuclear generation of H_2 for heavy crude upgrading, O_2 for coal liquefaction**
- **Develop methods for on-platform conversion of methane to useful, easily condensable products (such as methanol) at high yield**
  - **Direct oxidation in H_2SO_4 to form acetic acid**
  - **On catalyst (supported vanadium, MoO_2/SiO_2) to give formaldehyde**



Alternative Feedstocks Study - Conclusions

- **Changing to alternative feedstocks in the chemical industry is a major shift as risky as the move of the auto industry to new fuels**
  - **Technology development needed for favorable economics**
  - **An energy policy will be needed to assist with the risks associated with large capital investments for new feedstock facilities in an environment of fluctuating energy prices.**
  - **Develop post-oil economy**
- **Multidisciplinary R&D investment is required**
  - **Leverage alternative liquid fuels development efforts, but address unique aspects associated with feedstock**
  - **New chemical pathways, from more oxidized starting materials to commodity chemicals**
  - **Novel separations, materials development, control technologies**

Alternative Feedstocks Study - The Team

- **Industrial Participants**
  - **Shell, Brendan Murray (Lead)**
  - **Air Products, Phillip Winkler**
  - **BP, Dave Söderburg**
  - **Dow, Mark Jones & Tyler Thompson**
  - **DuPont, John Carberry**
  - **Eastman, Jeff Siirola & Joe Zoeller**
  - **GE, Terri Grocela-Rocha, David Mobley, & Cheryl Sabourin**
  - **Innovene, Clark Simmons**
  - **Praxair, Ravi Prasad**
  - **Rohm & Haas, Frank Lipiecki**
- **Oak Ridge National Laboratory**
  - **Sharon Robinson (Industrial Technologies Program Manager for ORNL)**
  - **Joanna McFarlane**
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Questions?