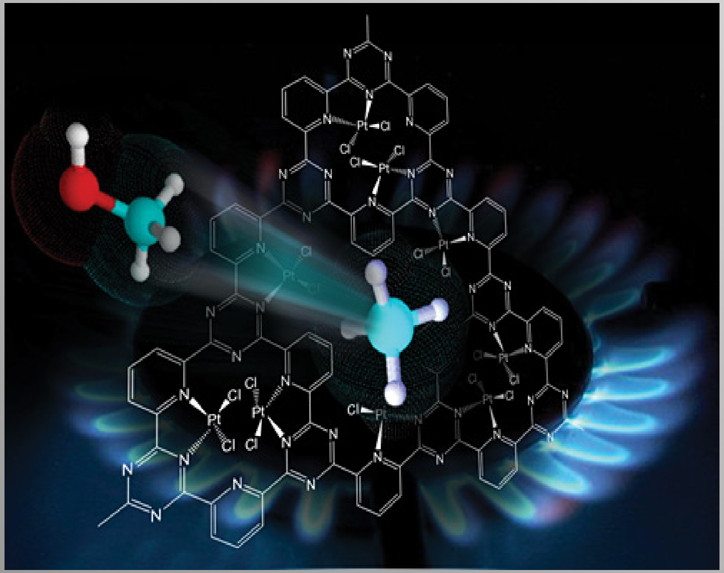



Pt-triazine-Polymer Catalyst for Low Temperature Methane to Methanol Conversion

# Historical Overview of Natural Gas (Methane) Conversion Technologies


**Charles E. Taylor,**
Associate Deputy Director, Office of Research and Development

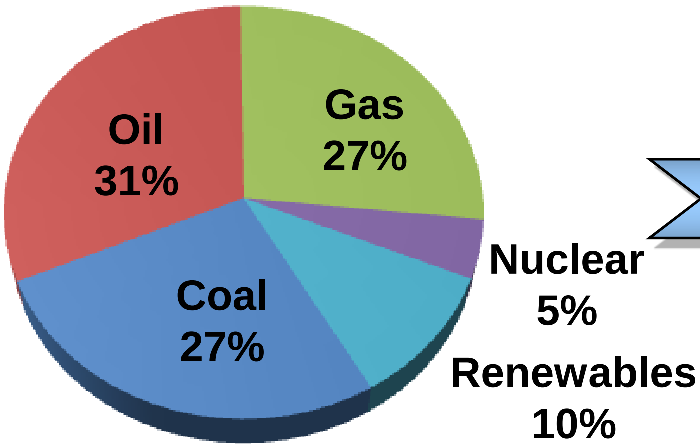

10/03/2013

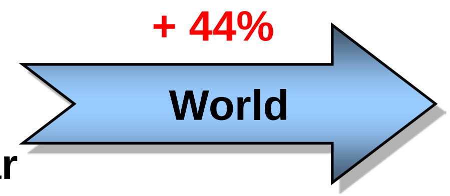
# National Energy Technology Laboratory

- **Only DOE national lab dedicated to fossil energy**
  - Fossil fuels provide 85% of U.S. energy supply
- **One lab, one management structure, five locations**
  - Government owned and operated
  - 3 R&D locations
- **>1,700 Federal and support-contractor employees**
- **Research spans fundamental science to technology demonstrations**

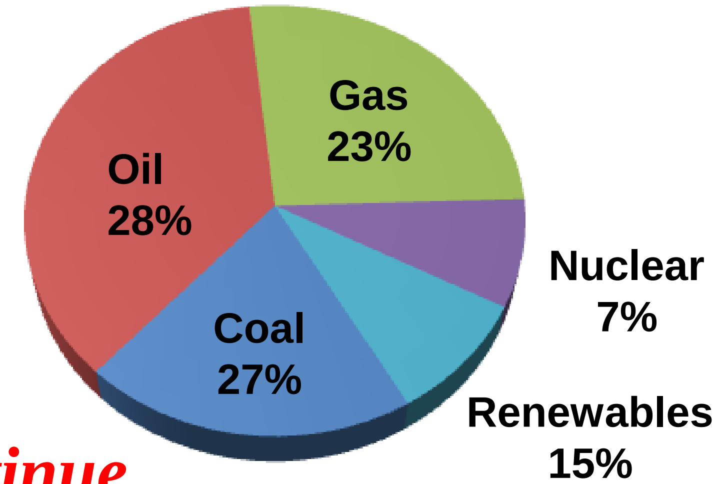
# Energy Demand 2011 | Energy Demand 2040

**571 QBtu / Year**
**85% Fossil Energy**



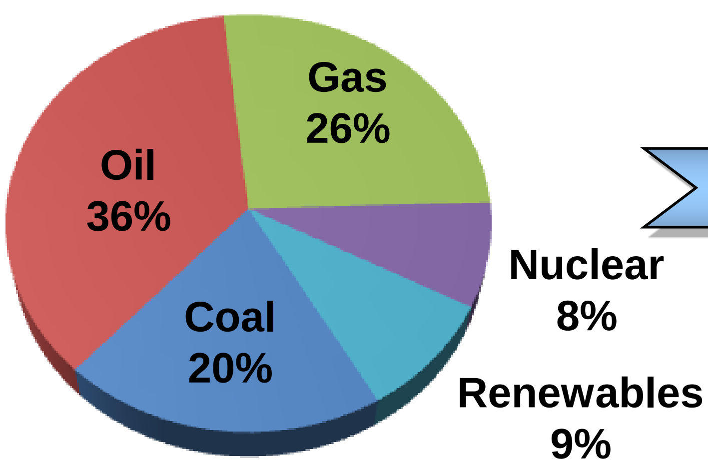



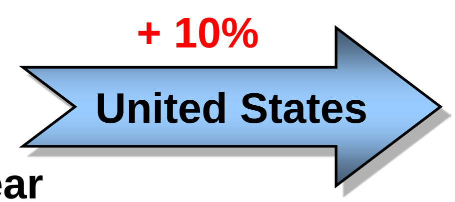

**820 QBtu / Year**
**78% Fossil Energy**



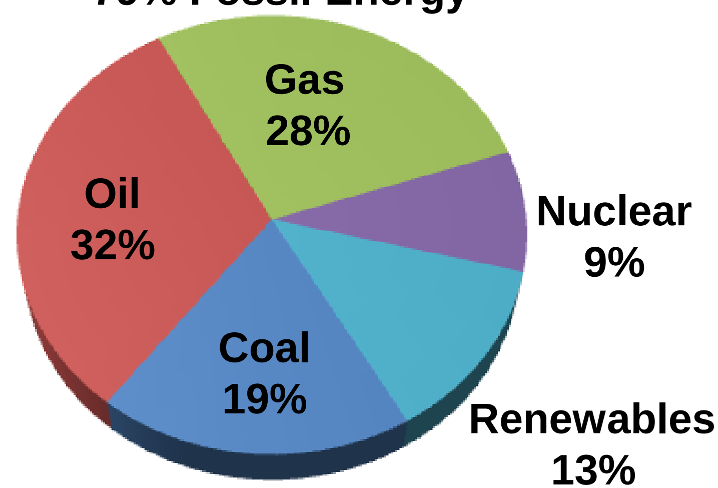

***Fossil Energy Will Continue to Provide Primary Supply***

**98 QBtu / Year**
**82% Fossil Energy**



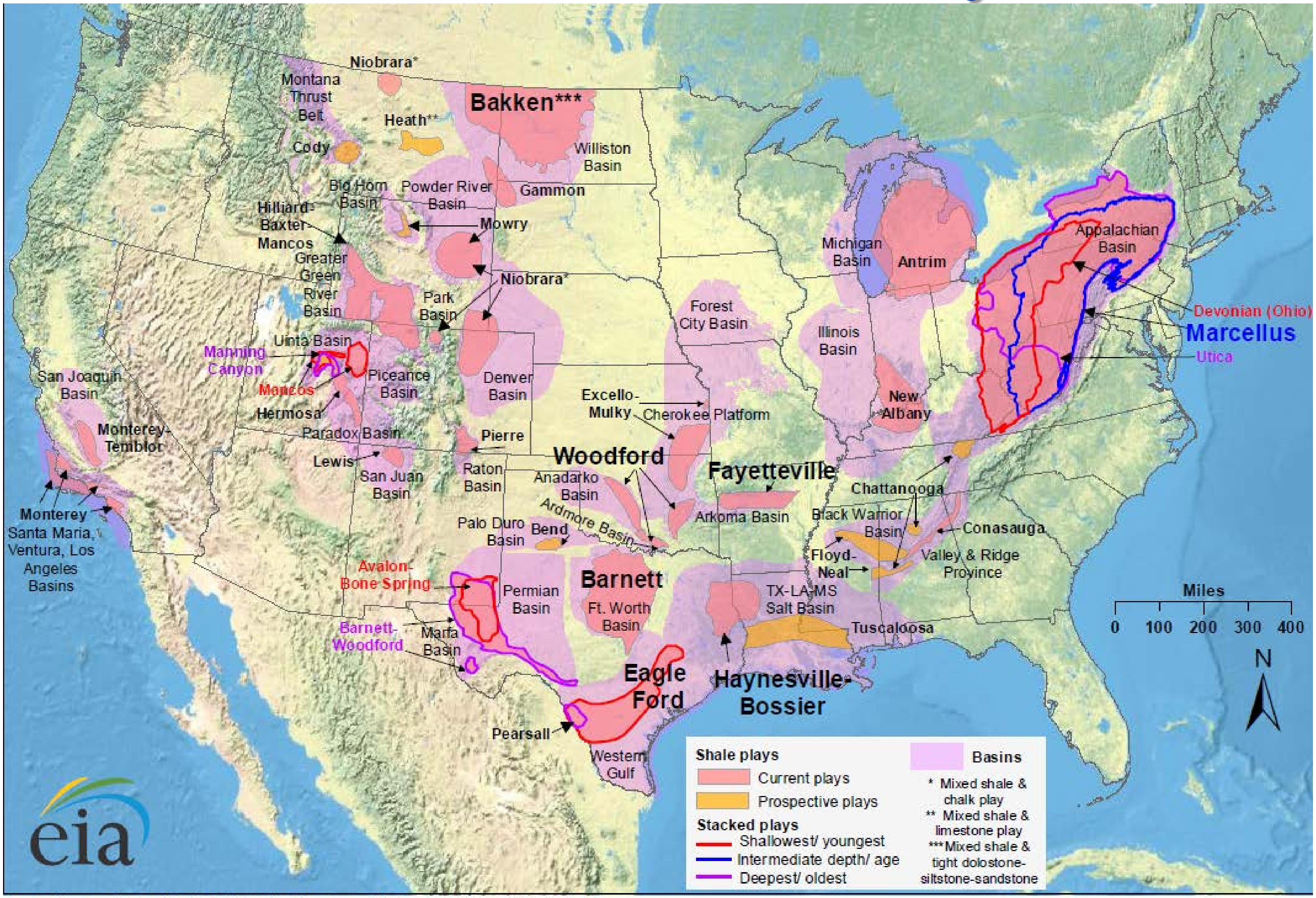




**108 QBtu / Year**
**79% Fossil Energy**



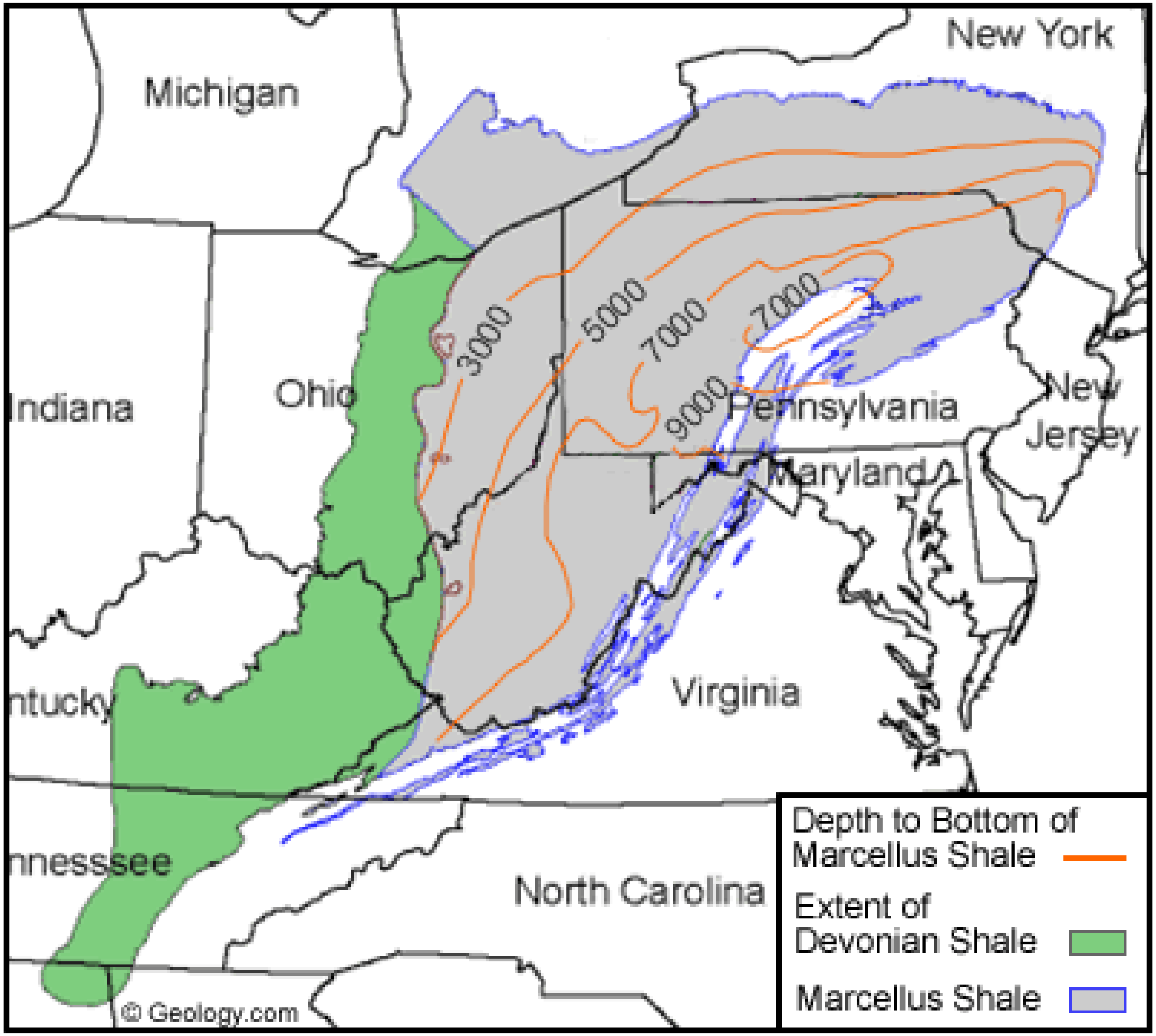

*U.S. data from EIA Annual Energy Outlook 2009 with Projections to 2030 Report #:DOE/EIA-0383(2009). World data from EIA International Energy Outlook 2009 Report #:DOE/EIA-0484(2009)*

# Lower 48 Shale Gas Plays




Source: Energy Information Administration based on data from various published studies.
Updated: May 9, 2011

# Marcellus Shale Gas Recoverable (>141 TCF*)




**2012 U.S. Natural Gas Production = 25.3 TCF.****

**1.418 TCF of gas produced in PA during the first six months of 2013 – a 57% increase from the amount of gas produced in the same period of 2012.*****

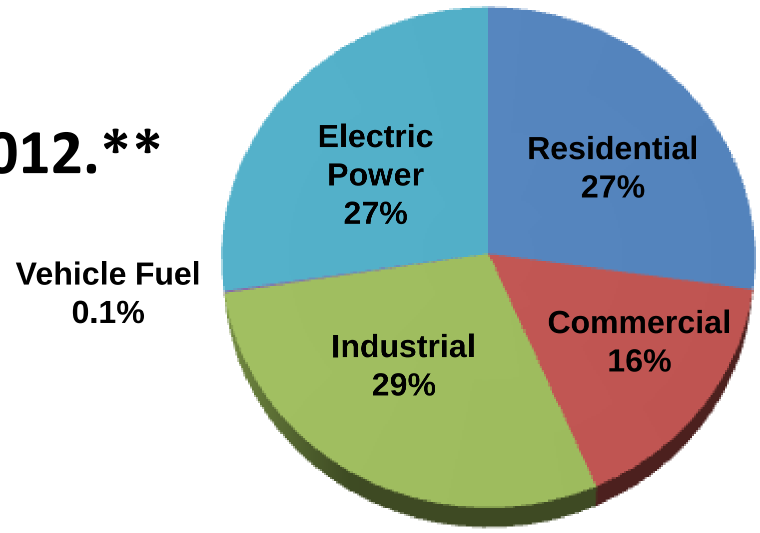
**http://www.eia.gov/forecasts/aeo/er/pdf/0383er(2012).pdf*

***http://www.eia.gov/dnav/ng/hist/n9050us2m.htm*

****http://stateimpact.npr.org/pennsylvania/2013/08/19/marcellus-shale-gas-production-numbers-surge/*

# How Do We Currently Use Natural Gas?

- Electricity generation
  - 30% of U.S. power generation in 2012.**
- Residential
  - Space heating, water heating, and cooling.
- Commercial
  - Space heating, water heating, and cooling.
- Vehicle Fuel (CNG, LNG)
  - 115,863 CNG and 3,354 LNG in 2010.***
- Industrial
  - Raw material for the manufacture of such varied products such as plastic, fertilizer, anti-freeze, and fabrics.



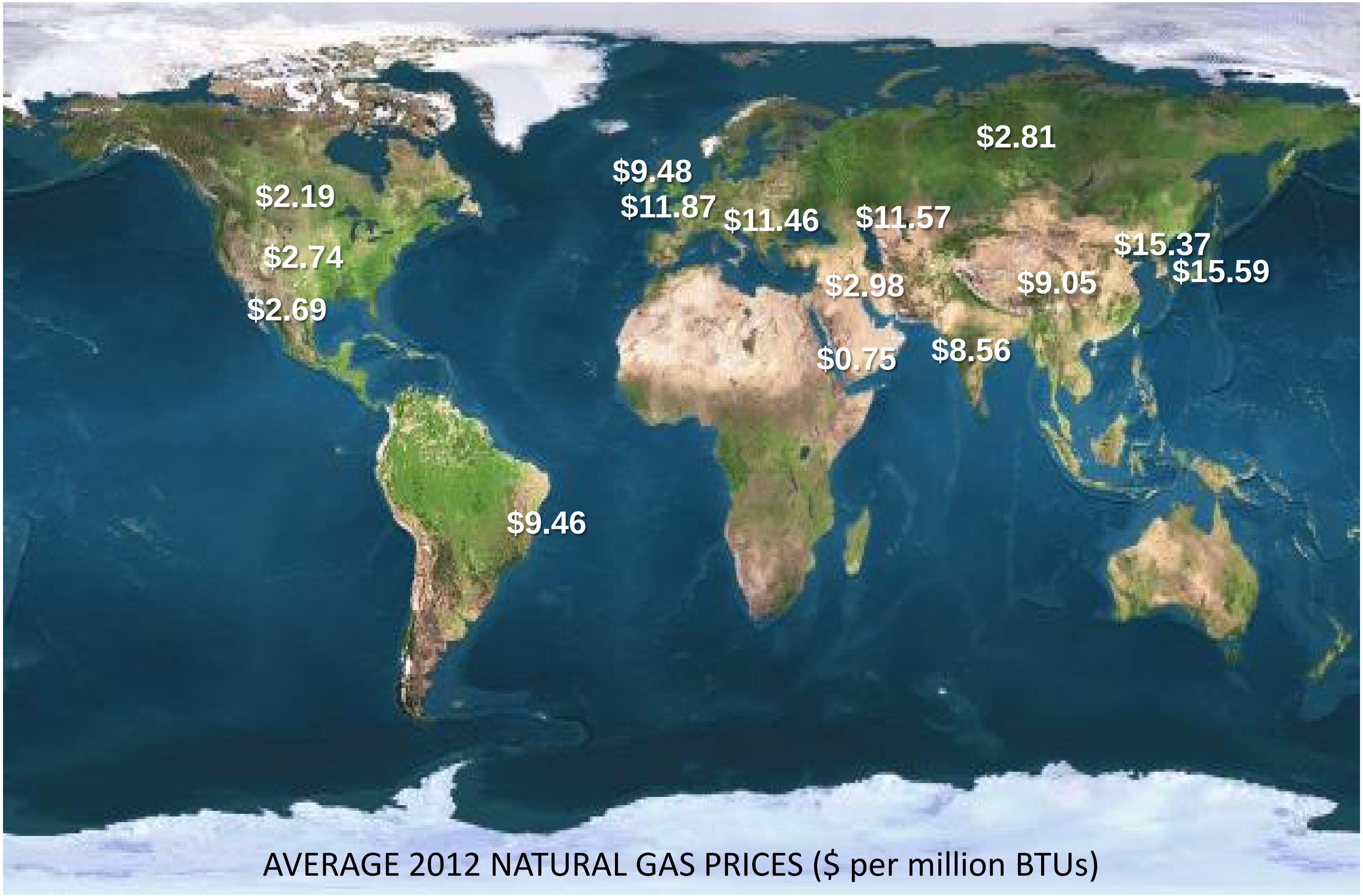

U.S. Average*
Dec 2012 – May 2013

2012 Annual consumption 25.5 TCF

*http://www.eia.gov/dnav/ng/ng_cons_sum_dcu_nus_m.htm

**http://www.eia.gov/electricity/data/browser/ ***http://www.afdc.energy.gov/data/#10300

# What to Do with This Resource?

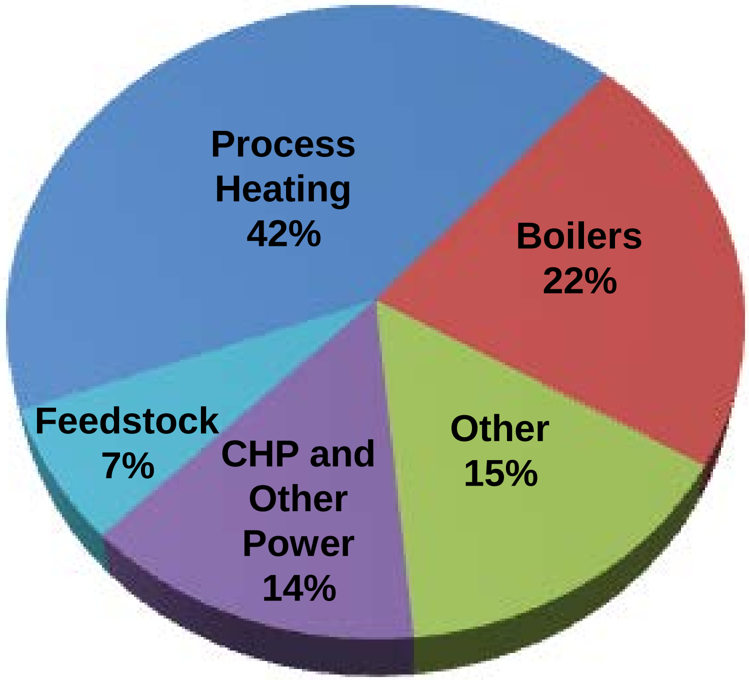



Note: Prices generally reflect domestic wellhead/hub prices or imported prices via pipeline. Some nations (e.g., Japan and Korea) import LNG. Thus, the higher prices. Other nations import LNG if it's a minor share of demand but these prices aren't generally reflected in the above.

NETL

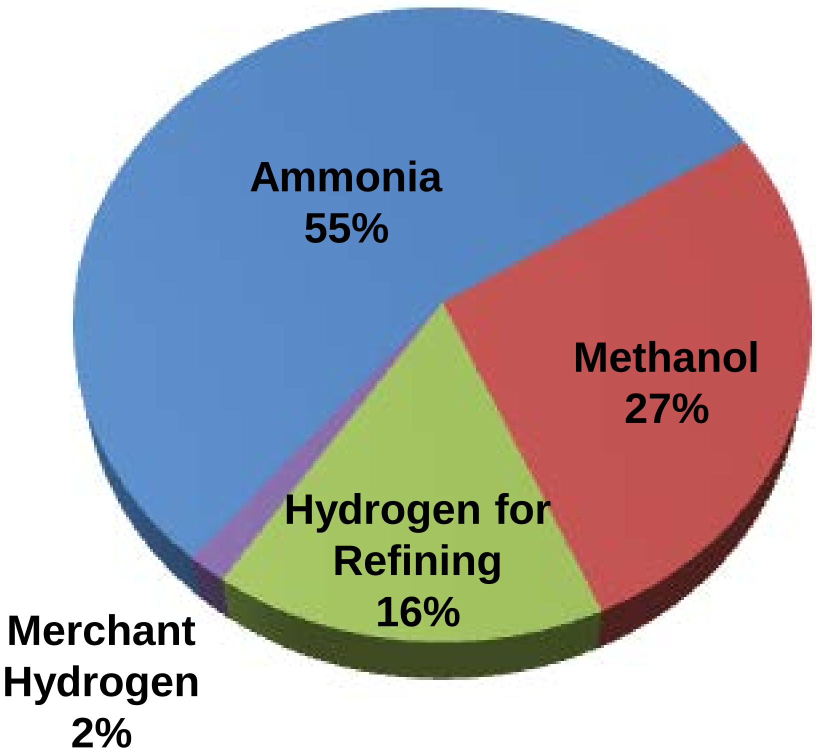
# How Much Natural Gas is Used for Chemicals?

- **Industry accounts for ~30% of natural gas consumption in the U.S. (7.1 TCF in 2012)**
- **Majority (78%) used for heating and power generation.**
- **0.5 TCF used as a feedstock in the manufacturing of chemicals (primarily ethane, propane, and butane separated from natural gas streams).**



# How Much Methane is Used for Chemicals?

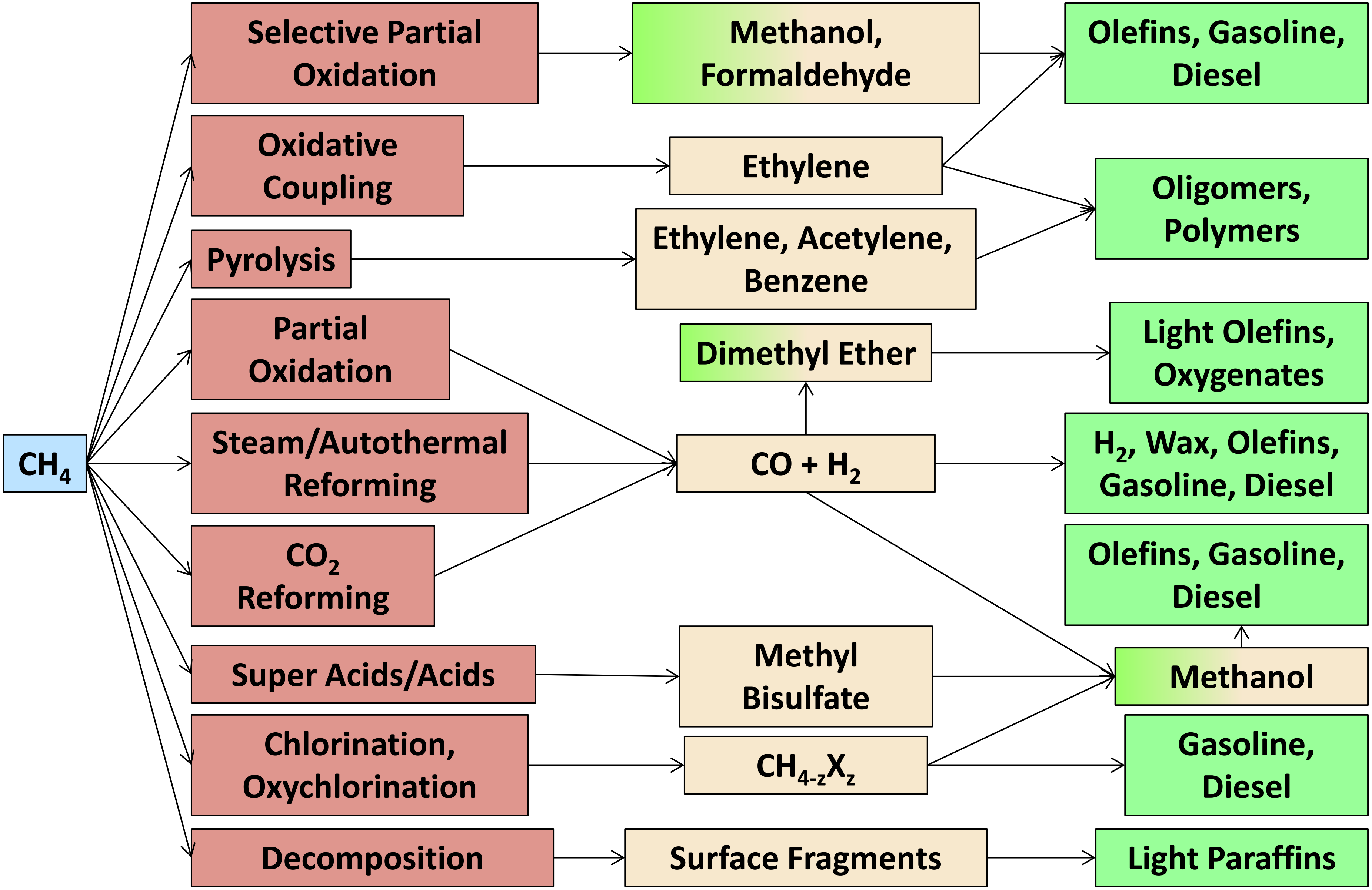
- Most common chemical use for methane (~1 TCF) is in the production of syngas ($CO + H_2$).
- Syngas is produced by the steam reforming of the methane.*
- The syngas can be further reacted to form chemicals.
- Additional hydrogen can be produced by the water-gas-shift reaction




*Additional chemicals produced from methane include: acetic acid, acetic anhydrid), acetylene, formaldehyde nitromethane, chloroform), carbon tetrachloride, and some freons*

**Reaction conditions: 700°C–1,000°C, 43–360 psi in the presence of a catalyst. Steam reforming is endothermic, heat must be supplied to the process for the reaction to proceed.*

# Pathways for Methane Utilization



# Why Do We Not Currently Convert Methane into Higher-Value Products?

- **Converting methane directly to valuable chemicals and liquid fuels is an industrial challenge that has defied the best minds in chemistry.**

- **Methane activation is difficult because of its thermo-dynamic stability with a noble gas-like electronic configuration. The strong tetrahedral C–H bonds (435 kJ/mol or 104 kcal/mol) offer no functional group, magnetic moments, or polar distributions to undergo chemical attack. This makes methane less reactive than nearly all its conversion products, and limits efficient utilization of natural gas, the world's most abundant petrochemical resource.**

# Methane Combustion Intermediates

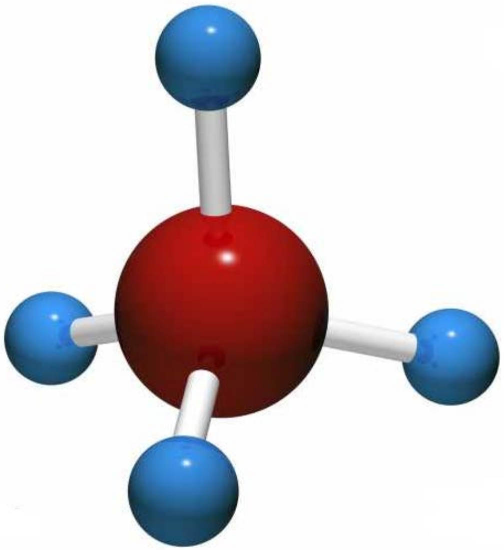
$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$ ($\Delta H = -891$ kJ/mol (at standard conditions))

*M* signifies an energetic third body, from which energy is transferred during a molecular collision*

1. $CH_4 + M^* \rightarrow CH_3 + H + M$
2. $CH_4 + O_2 \rightarrow CH_3 + HO_2$
3. $CH_4 + HO_2 \rightarrow CH_3 + 2\ OH$
4. $CH_4 + OH \rightarrow CH_3 + H_2O$
5. $O_2 + H \rightarrow O + OH$
6. $CH_4 + O \rightarrow CH_3 + OH$
7. $CH_3 + O2 \rightarrow CH_2O + OH$
8. $CH_2O + O \rightarrow CHO + OH$
9. $CH_2O + OH \rightarrow CHO + H_2O$
10. $CH_2O + H \rightarrow CHO + H_2$
11. $CHO + O \rightarrow CO + OH$
12. $CHO + OH \rightarrow CO + H_2O$
13. $CHO + H \rightarrow CO + H_2$
14. $H_2 + O \rightarrow H + OH$
15. $H_2 + OH \rightarrow H + H_2O$
16. $CO + OH \rightarrow CO_2 + H$
17. $H + OH + M \rightarrow H_2O + M^*$
18. $H + H + M \rightarrow H_2 + M^*$
19. $H + O_2 + M \rightarrow HO_2 + M^*$

# Historical Methane Conversion Technologies

- Electrophilic Methane Conversion (super acids)
- Conversion of Methane into Ethylene, Acetylene and Ethane by the Chlorine-Catalyzed Oxidative-Pyrolytic (CCOP) Process
- Electrocatalytic Conversion of Light Hydrocarbons to Synthesis Gas
- Direct Methane Conversion
  - Direct Methane Conversion to Methanol by Ionic Liquid-dissolved Platinum Catalysts,
  - Methane to Methanesulfonic Acid
- Oxyhydrochlorination of Methane
- Plasma Conversion
- Oxidative Coupling
- Halogenation of Methane
- Dehydroaromatization of Methane to Benzene
- Biological Conversion of Methane
- Methane Reforming

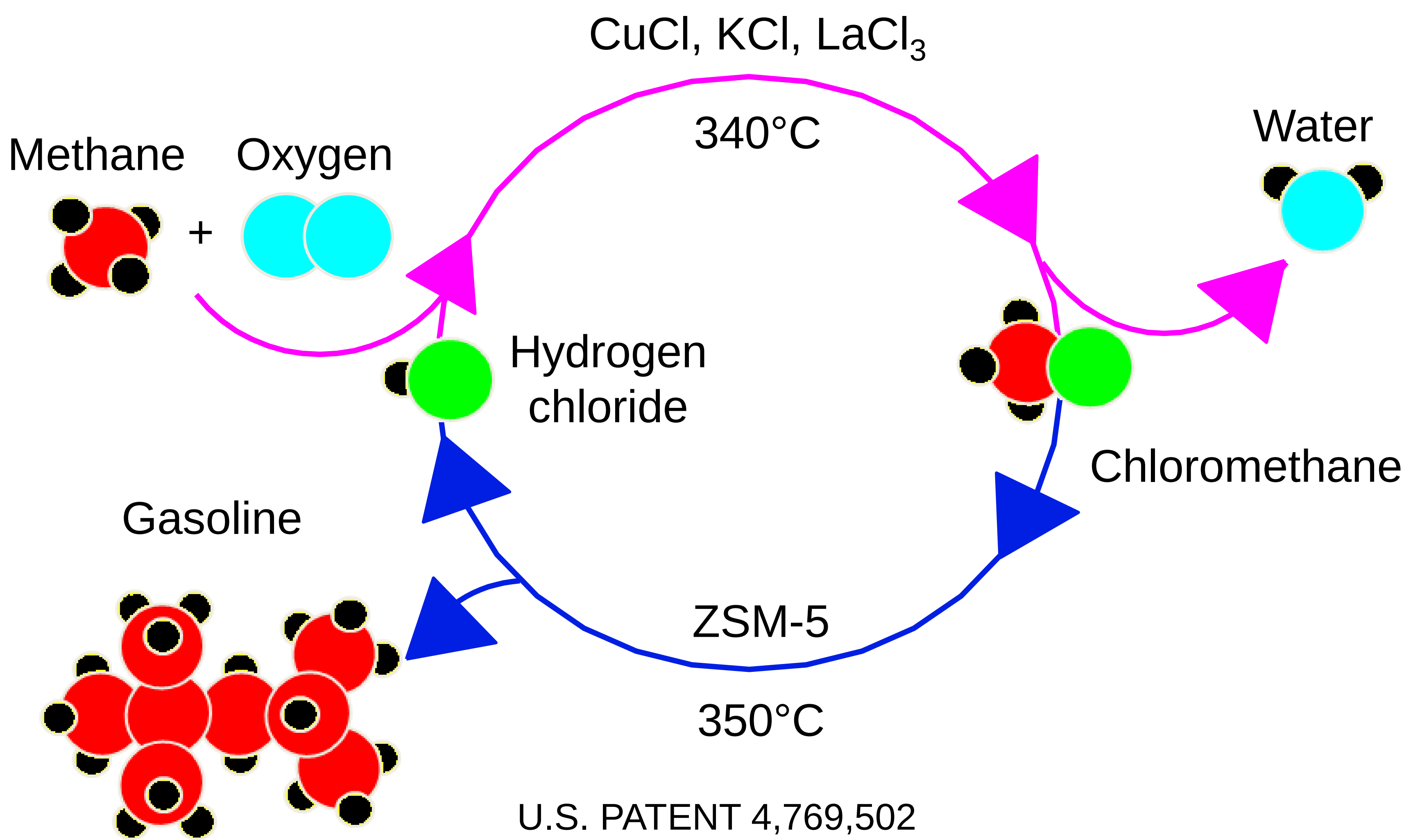


# Historical Methane Conversion Technologies

| Process | Desired Product | $CH_4$ Conversion (%) | Product Selectivity (%) |
|---|---|---|---|
| Biological Oxidation | $CH_3OH$ | >1 | 23 |
| Bromination | $CH_3Br$ | 40 - 90 | 77 - 50 |
| Chlorination | $CH_3Cl$ | 7 - 58 | 90 - 75 |
| Dehydroaromatization | Benzene, Toluene, Naphthalene | 10 - 30 | 90 - 50 |
| Dry Reforming | $CO + H_2$ | 17 - 70 | 25 - 10 |
| Liquid-Phase Oxidation | $CH_3OSO_3$ | 72 - 90 | 81 |
| | $CH_3SO_3H$ | 3 - 6 | N/A |
| Oxidative Coupling | $C_2H_6 + C_2H_4$ | 10 - 20 | 85 |
| Oxyhydrochlorination + Oligermerzation | Gasoline | 34 - 60 | 34 - 60 |
| Partial Oxidation | $CH_3OH$ | 10 - 90 | 90 - 10 |
| Plasma | $C_1$ Oxygenates, $C_2$+ | 3 - 40 | 80 - 20 |
| Methane Reforming* | $H_2 + CO_X$ | 1 - 99 | 1 - 95 |

** Includes Steam Reforming, Autothermal Reforming, and Partial Oxidation Reforming,*

# NETL's Methane-to-Gasoline Process

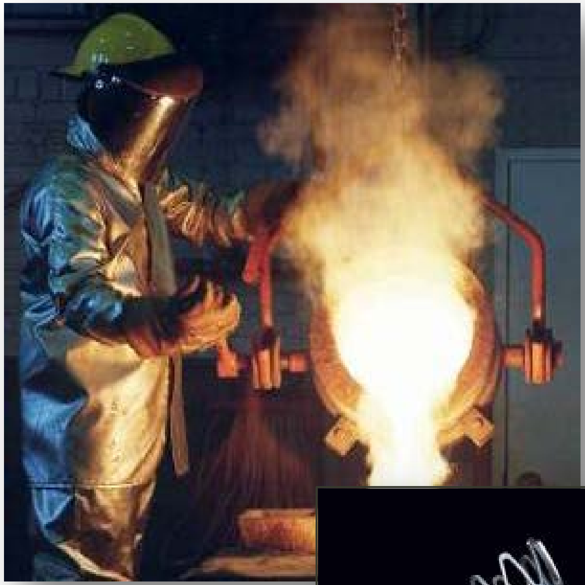


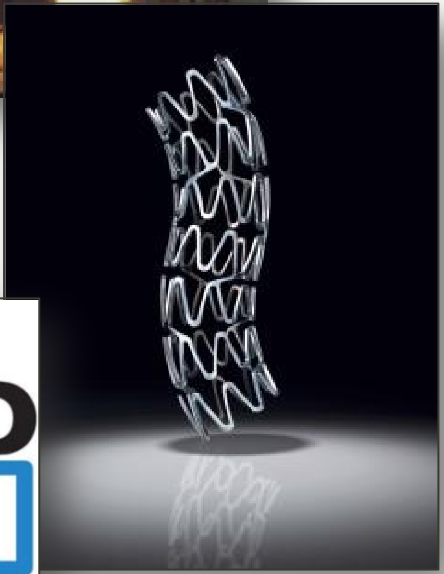

U.S. PATENT 4,769,502

# Leveraging NETL Capabilities through Work For Others

## Platinum/Chromium Alloy for Coronary Stents (2011 R&D 100 award and 2012 DOE Secretary's Honor Award)

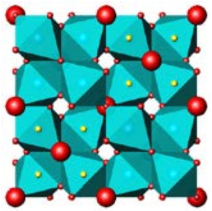
Jointly developed by NETL and Boston Scientific, this novel alloy is the first austenitic stainless steel formulation to be produced for the coronary stent industry having high visibility with x-ray scanning, while being flexible enough to navigate through arteries.



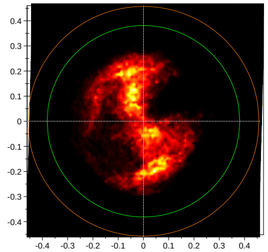


# Partnering with NETL

- **Leverage Lab Directed (Mission Related) Technology Development and Deployment**
  - Licensing opportunities (PCC)
- **Leverage Lab Core Competencies to Achieve Strategic Technological Goals**
  - Technological Goals Fall within Lab Mission (Current Locator)
  - Technological Goals are not within Lab Mission but the Lab Competencies Change the Development Landscape (Medical Stents)
- **Mechanisms to Partner with NETL**
  - Research Agreements (CRADAs, CFAs, etc)
  - Licensing of IP
  - Partnering on Solicitations
  - Joint Program Building



*Individual surface atoms in the Pyrochlore Catalyst impart unique properties desirable for certain reforming applications*




*The Electric Current Locator allows one to identify current paths in a furnace utilizing the magnetic field generated by the conducting path.*

*Coronary stent co-developed by Boston Scientific Corporation and NETL reached the US market in 2010.*

# Natural Gas-4-Prosperity (NG4P)

*A Partnership to Develop Technology Enabling Demand*

- **Shale gas represents a "generational" opportunity.**
  - Abundant, affordable, domestic.
- **Development of "downstream market" through regional partnership.**
- **Partnership focused on "technology-pull" innovation and solutions.**
- **The NETL, and its RUA partners, has tremendous level of expertise, facilities, and success in reaction engineering.**
- **NETL is establishing a framework to leverage opportunity, expertise, and facilities.**
  - Planning several "industry-laboratory" workshops.

NATIONAL ENERGY TECHNOLOGY LABORATORY

# *Find more information at www.netl.doe.gov*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