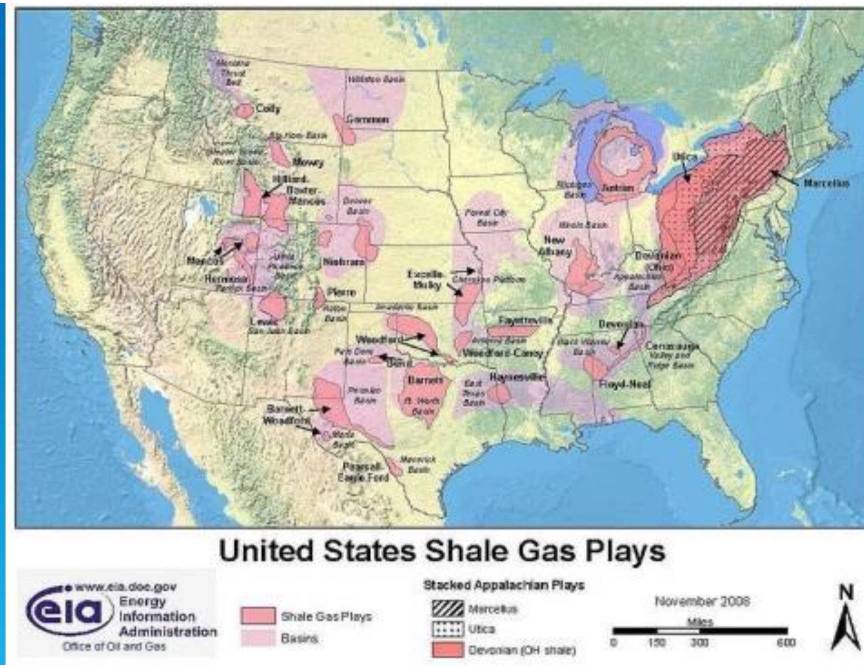
Co-conversion of Biomass, Shale-natural gas, and Process Derived CO_2 into Fuels and Chemicals



Transition to Cleaner and Clean Energy

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July 31, 2013

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Shale Gas

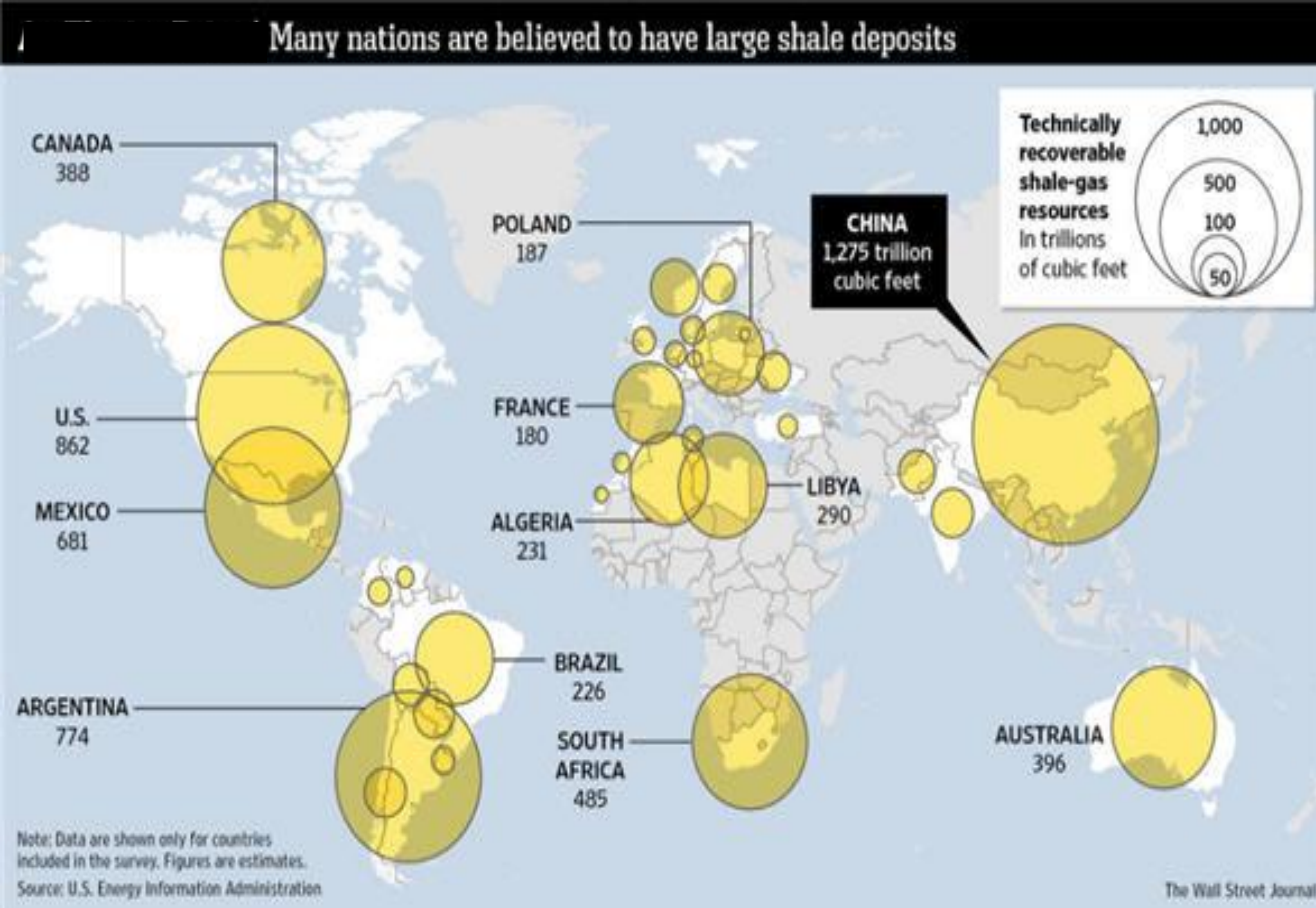
Wikipedia

- Unconventional Natural gas
- Contained in low permeability shales
- Accessible at depths of 2,000-7,000 feet
- Shale gas is generally sandwiched between two thick, black shale deposits
- Pennsylvania Marcellus Shale contains about 500 trillion cubic feet of natural gas
- 2,300 trillion cubic feet in U.S.
- Natural gas historically has only provided 22% of the total energy consumed.
- There is enough shale to support the U.S. gas needs for 90 years

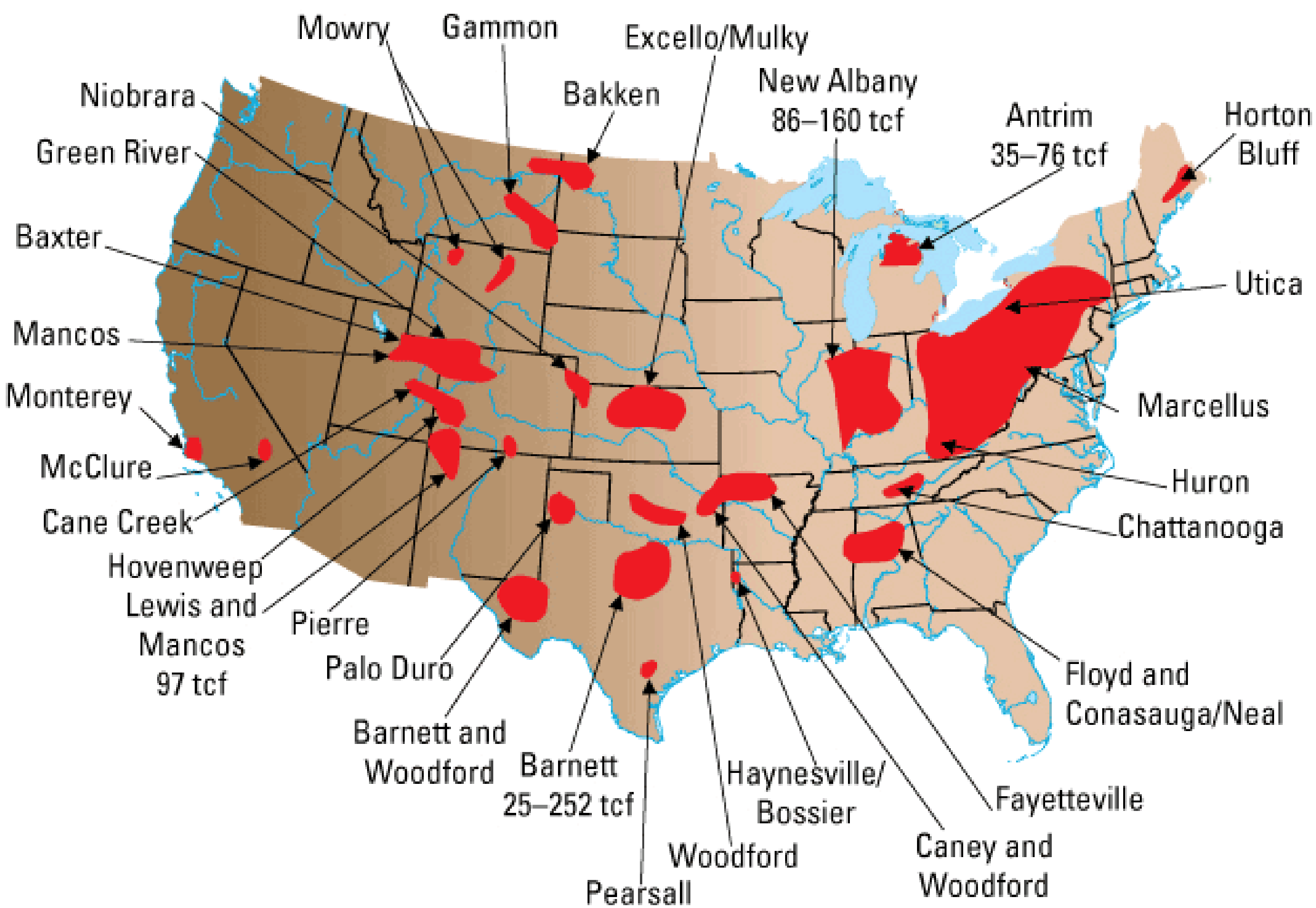
U.S. total natural gas consumption grows from 24.4 trillion cubic feet in 2011 to 29.5 trillion cubic feet in 2040 in the *AEO2013* Reference case.

Energy from natural gas remains far less expensive than energy from oil through 2040

www.energytomorrow.org


Many nations are believed to have large shale deposits
CANADA
388
U.S.
862
MEXICO
681
POLAND
187
FRANCE
180
ALGERIA
231
LIBYA
290
CHINA
1,275 trillion cubic feet
Technically recoverable shale-gas resources in trillions of cubic feet
1,000
500
100
50
BRAZIL
226
ARGENTINA
774
SOUTH AFRICA
485
AUSTRALIA
396
Note: Data are shown only for countries included in the survey. Figures are estimates.
Source: U.S. Energy Information Administration
The Wall Street Journal

U.S. Shale Gas Plays



Impressive Figures (US EIA)

- (EIA) estimated that U.S. shale plays contain 827 Tcf of recoverable natural gas.
- Estimates of the size of the natural gas resource base are dynamic
- By 2035, shale gas production (12.2 Tcf) will represent 47% of U.S. production.
- In the seven most active shale plays producer estimates acknowledge that the potential production level could reach as high as 30 billion cubic feet (Bcf) per day by 2020

Marcellus Shale Gas Composition

Well	C1	C2	C3	CO2	N2
1	79.4	16.1	4.0	0.1	0.4
2	82.1	14.0	3.5	0.1	0.3
3	83.8	12.0	3.0	0.9	0.3
4	95.5	3.0	1.0	0.3	0.2

Note: ***Marcellus gas has sufficient liquids to require processing.***

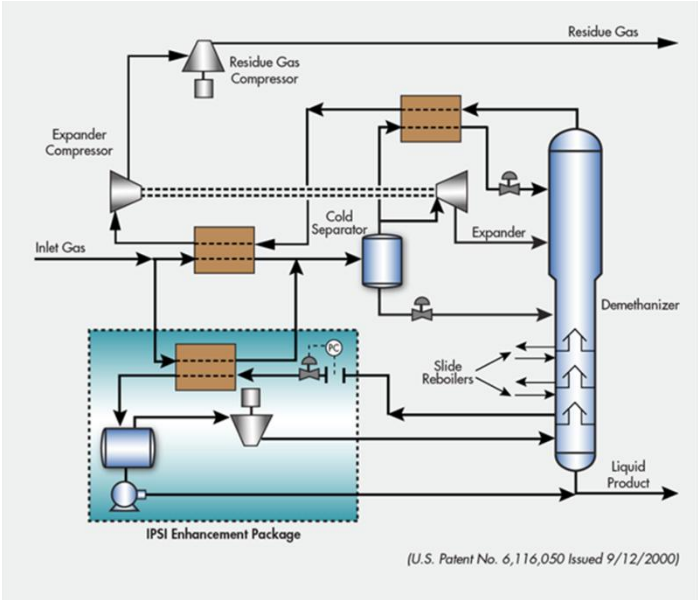
Flow-back water and criteria of irrigation and surface water

Source: Jiang, 2013 (Marcellus, New York, USA)

Constituent	SGFW	Irrigation	Surface Water Discharge
TOC (Total Organic Carbon) (mg/L)	720		
TSS (Total Suspended Solids) (mg/L)	881		
TDS (Total Dissolved Solids) (mg/L)	48,000	2000	500
pH	6.85		
Alkalinity (mg/L)	205	510	200
Conductivity (μs/cm)	67,000	3000	
Turbidity (NTU)	770		
Na (mg/L)	12,200	920	
K (mg/L)	363	2	
Mg (mg/L)	104	122	
Ca (mg/L)	2935	800	
Ba (mg/L)	697		10
Sr (mg/L)	591		10
Al (mg/L)	105		
Fe (mg/L)	< 1		1
Mn (mg/L)	< 2	0.2	1.5
Cl (mg/L)	28,500	1064	230
Br (mg/L)	19		
F (mg/L)	< 1		
Sulfate (mg/L)	12.9	1920	250

NG Upgrading and NGL Recovery
Proven & Commercial

- Dehydration
- N2 rejection
- Gas sweetening
- NGL recovery
- Helium recovery
- CO2 separation



Source: Bechtel Corp.

Biomass Resources

Pause to Review Challenges

(Source: Several including - *klemow.wilkes.edu/Shalegas2.09.ppt*)

- Current shale gas recovery practices
  - Environmental issues
  - Water requirements (2 million to 4 million gallons of water to drill and fracture a horizontal shale gas well)
  - Targets for production are guided by 'gas supply' practices
- Protection of Groundwater
- Wildlife Impacts
- Community Impacts
- Surface Disturbances….Threat of quakes and tremors
- Gas quality
- Adaptability of existing technologies for co-conversion of shale gas and biomass to synthesis gas for fuels and chemicals

Opportunities

- Energy security & Less polluting fossil fuel
- Rapid deployment of NGVs
- NG – MeOH & FTL are commercial
- Prospects for CO_2 reformation and CO_2-shale fracture and sequestration
- Co-conversion is a 'clean bridge technology' to develop sustainable biomass feedstock infrastructure
- Innovations could relieve pressure on ground water & water requirement in general
- Regional opportunities for co-conversion with high-impact biomass
- Development of new industries and industrial jobs in addition to sustainable rural socio-economic opportunities (with energy plantations and feed preparation)

Background on dry reformation

- Numerous studies on CH_4/CO_2 reforming reaction using Ni-based catalysts.

$$CH_4 + CO_2 \xrightarrow{\text{cat.}} 2CO + 2H_2$$

Synthesis gas

Problems: **(i) Low yield (~55%)**

(ii) Carbon deposit (~after 1 hour)

Our studies:

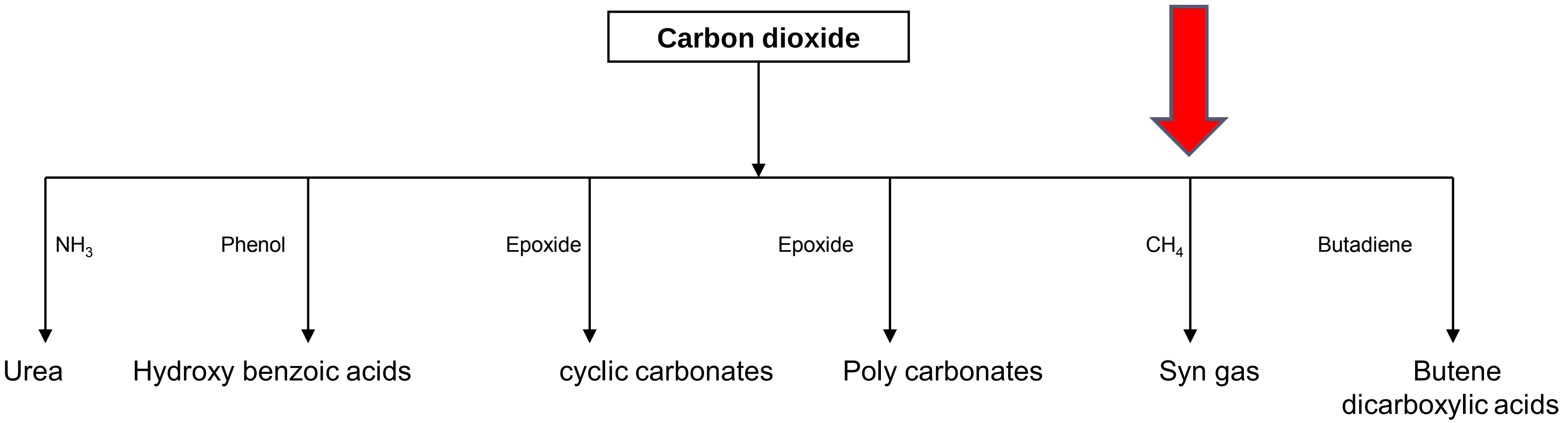
- Reverse water-gas shift (RWGS) reaction over La_2NiO_4 catalyst during CH_4/CO_2 reforming by continuous wave cavity enhanced absorption spectroscopy (CEAS).

Associated reaction:

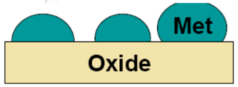
$$CO_2 + H_2 \rightarrow CO + H_2O$$

*Source: https://kb.osu.edu/dspace/bitstream/.../CH4**CO2**%20presentation2.**ppt**?...*

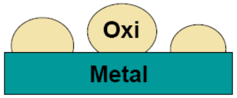
CO2 use in chemicals production



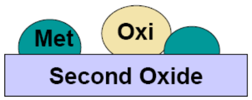
Fundamental studies on the synthesis of alcohols from CO/CO2 hydrogenation on metal/oxide catalysts



conventional



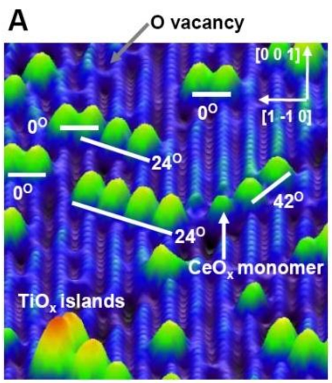
inverse

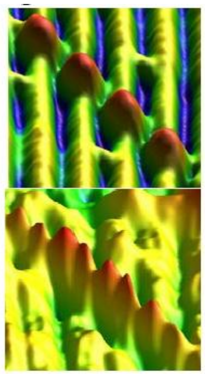


mixed-metal oxide

Best to optimize the performance of metal and oxide

Titania substrate imposes non- typical coordination modes on the ceria NPs

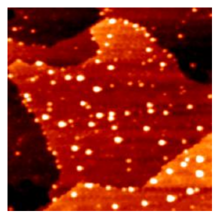




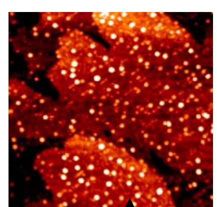
Ceria on TiO2(110)

3nm x 3nm

Cu/TiO2(110)

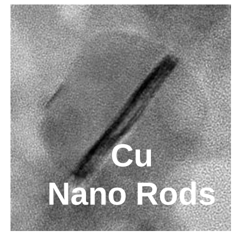


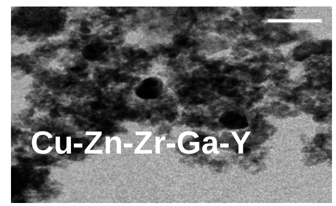
Cu / CeOx /TiO2(110)



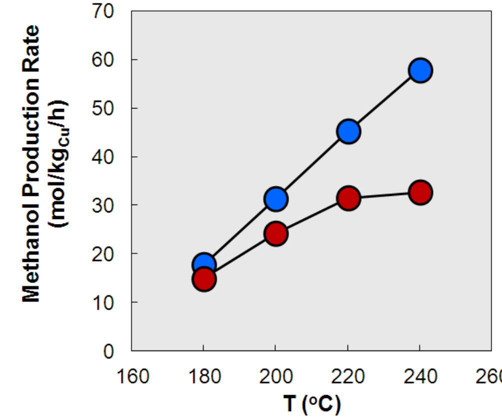
Better dispersion of Cu

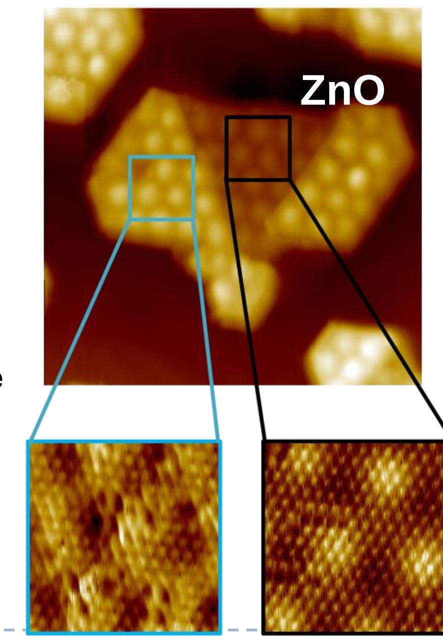
Sinter resistant nano-Cu mixed metal oxides

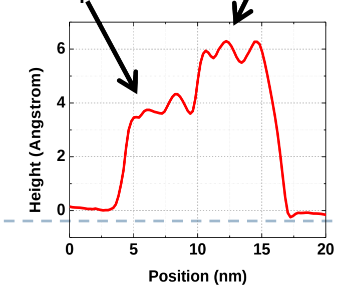




NETL Nano Catalysts Outperform Commercial







NOTES

- **SPE 26925: CO2/Sand Fracturing in Devonian Shales**

A.B. Yost 11, U.S.DOE- METC;R.L.Mazza, Petroleum Consulting Services; and J.B. Gehr, Natural Gas Resources Corp.

- **Fracking could be combined with carbon capture plans**

14:54 31 August 2012 by Phil McKenna

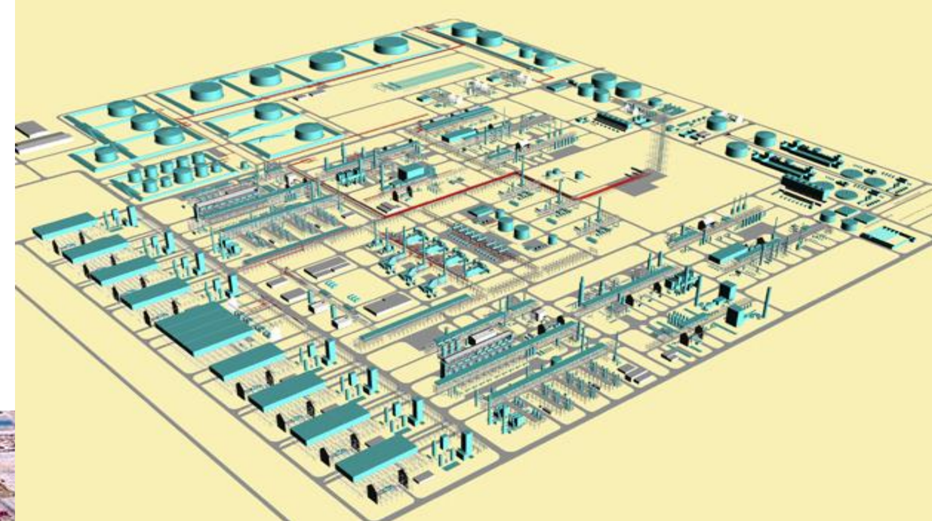
- **Welcome to the Sasol Lake Charles gas-to-liquids (GTL)**

AMERICAN PRESS: Sasol executive touts company's $21 billion investment in Westlake - 06.26.13 | NEWS CLIPPING

Shell GTL from Laboratory Bench to World Scale Plant

<u>Pearl GTL</u>

- 1,600 MMscf/d well head gas
- ~120,000 b/d Condensate, LPG & ethane
- 140,000 b/d GTL products



Pearl GTL, Qatar World Scale Plant - first commercial shipment from the Pearl GTL was made on 13 June 2011

Bintulu Commercial Plant - 1993

Amsterdam Pilot Plant - 1983

Amsterdam Laboratory – 1970’s

Stakeholders

"From Cracks to Crankshafts"

(British Quotation)

- **USDOE (FE & EERE) and US EPA -** Policy & R&TD
- **Industrial Partners -**
  ANGA, AGA, Chemical, and oil and gas industries:
  Tech. Integration, Scale-up and Commercialization
- **Catalyst Developers –**
  Industry, National Labs, and Academia:
  Develop Novel, Robust, and Low-cost Catalysts
- **Rural Participation –**
  Develop Sustainable Supply of QC/QA
  Biomass from Sustainable Energy Plantations

In closing.. let's remember 'Gas Hydrates' →