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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Shale Gas

- 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
- **Argentina**: 774
- **Poland**: 187
- **France**: 180
- **Algeria**: 231
- **Libya**: 290
- **Brazil**: 226
- **South Africa**: 485
- **Australia**: 396

**China**: 1,275 trillion cubic feet

**Note**: Data are shown only for countries included in the survey. Figures are estimates.

**Source**: U.S. Energy Information Administration

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Source: 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

<table>
<thead>
<tr>
<th>Well</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>CO2</th>
<th>N2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>79.4</td>
<td>16.1</td>
<td>4.0</td>
<td>0.1</td>
<td>0.4</td>
</tr>
<tr>
<td>2</td>
<td>82.1</td>
<td>14.0</td>
<td>3.5</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>3</td>
<td>83.8</td>
<td>12.0</td>
<td>3.0</td>
<td>0.9</td>
<td>0.3</td>
</tr>
<tr>
<td>4</td>
<td>95.5</td>
<td>3.0</td>
<td>1.0</td>
<td>0.3</td>
<td>0.2</td>
</tr>
</tbody>
</table>

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)

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

\[
\text{CH}_4 + \text{CO}_2 \xrightarrow{\text{cat.}} 2\text{CO} + 2\text{H}_2 \\
\text{Synthesis gas}
\]

Problems:  
(i) Low yield (~55%)  
(ii) Carbon deposit (~after 1 hour)

Our studies:  
- Reverse water-gas shift (RWGS) reaction over La\(_2\)NiO\(_4\) catalyst during CH\(_4\)/CO\(_2\) reforming by continuous wave cavity enhanced absorption spectroscopy (CEAS).

Associated reaction:  
\[
\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}
\]
CO2 use in chemicals production

- Carbon dioxide
  - NH₃
  - Phenol
  - Epoxide
  - Epoxide
  - CH₄
  - Butadiene
  - Urea
  - Hydroxy benzoic acids
  - Cyclic carbonates
  - Poly carbonates
  - Syn gas
  - Butene dicarboxylic acids
Fundamental studies on the synthesis of alcohols from CO/CO2 hydrogenation on metal/oxide catalysts

Best to optimize the performance of metal and oxide

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

Sinter resistant nano-Cu mixed metal oxides

NETL Nano Catalysts Outperform Commercial

Ceria on TiO2(110) 3nm x 3nm

Cu/TiO2(110)

Cu/ZnO

Cu / CeOx / TiO2(110)

Cu-Zn-Zr-Ga-Y

NSLS II @ BNL

Better dispersion of Cu

Low-phase

High-phase

Methanol Production Rate (mol/kgCu-h)

Position (nm)

Height (Angstrom)
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

**Pearl GTL**
- 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’