Energy Production In a Carbon-Constrained World

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**CO₂ Summit: Technology and Opportunity**
Vail, Colorado, June 6-10, 2010

Engineering Conferences International
The World Needs Affordable Energy

[Map showing GDP per capita and annual commercial energy consumption per capita, with countries like Bangladesh, Ethiopia, China, Mexico, Poland, South Korea, Japan, U.S., and UK marked. The map illustrates a correlation between affluence and poverty, with Bangladesh and Ethiopia clustered near the poverty line and the U.S. and Japan near the affluence line.]
Energy Demand 2006

- 100 QBtu / Year
- 85% Fossil Energy
- 5,892 mmt CO₂
- 465 QBtu / Year
- 81% Fossil Energy
- 28,100 mmt CO₂

Energy Demand 2030

- 113 QBtu / Year
- 79% Fossil Energy
- 675 QBtu / Year
- 81% Fossil Energy
- 42,300 mmt CO₂ (51%)

**United States**

- Coal 23%
- Gas 22%
- Nuclear 8%
- Oil 40%
- Renewables 7%

**World**

- Coal 26%
- Gas 21%
- Nuclear 6%
- Oil 34%
- Renewables 13%

**United States**

- Coal 23%
- Gas 22%
- Nuclear 8%
- Oil 34%
- Renewables 13%

**World**

- Coal 29%
- Gas 22%
- Nuclear 5%
- Oil 30%
- Renewables 14%

*Data from EIA, Annual Energy Outlook 2009 early release; world data from IEA, World Energy Outlook 2008*
CO₂ Management Options

- Increase efficiency of energy use
- Increase conservation
- Reduce reliance on carbon-based fuels
  - Renewable energy
  - Nuclear energy

- Sequester carbon & utilization
  - Enhance natural carbon sinks
  - Capture and store CO₂ from fossil fuels
  - CO₂ “re-use”
Sequestration = Stabilization

Plausible Scenario to Stop GHG Emissions Growth

GHG Emissions Reductions

- Advanced Sequestration
- Value-Added Sequestration
- Non-CO2 GHGs
- Forestation and Agriculture
- Efficiency and Renewables

EIA Annual Energy Outlook 2002; EPA special studies; DOE/FE/NETL Sequestration Benefits Model
Carbon Capture and Sequestration

**Terrestrial Capture**
CO$_2$ absorbed from air

**Terrestrial Storage**
Trees, grasses, soils

**Point Source Capture**
Power plants
Ethanol plants
Cement & steel Refineries
Natural gas processing

**Transportation Pipelines**

**Geologic Storage**
Saline formations
Depleted oil & gas fields
Unmineable coal seams
Basilts and shales

Capture and storage of CO$_2$ and other greenhouse gases that would otherwise be emitted to the atmosphere
The current capture technology

- Amine solvent scrubbing: familiar; widely used and studied.
- Essential energy inputs: sensible, vaporization, chemical reaction: \( Q = Q_{\text{sens}} + Q_{\text{vap}} + Q_{\text{react}} \)
- What can be done to reduce the energy penalty?
The current technology

- Amine solvent scrubbing: familiar; widely used and studied.
- Essential energy inputs: sensible, vaporization, chemical reaction: \( Q = Q_{\text{sens}} + Q_{\text{vap}} + Q_{\text{react}} \)
- What can be done to reduce the energy penalty?

- **Sensible:** reduce the crossover temperature difference, increase loading.
- **Vaporization:** linked to the solvent CO2 and water vapor pressure
- **Reaction:** different chemistry…but can be linked to vaporization – oops!
- **System options:** pressurized regeneration schemes, etc.

Reducing the energy penalty
Eliminate/reduce the vaporization and sensible heat

• **Aqueous solvents:**
  – Adding heat reverses the capture reaction.
  – Adding heat creates (somewhat desirable) water vapor.

• **Alternatives:**
  – Dry sorbent
  – Non-aqueous solvent
Dry Sorbents

- **The advantages:**
  - Potentially lower sensible energy to heat and cool.
  - Potential elimination of vaporization heat.

- **The challenges**
  - Requires high CO$_2$ loading.
  - Requires handling solids with thermal management.
Basic energy requirements for dry sorbents

- Heat balance on the sorbent, process.
- Need to manage absorbed/desorbed water!
- Bottom line: working loading range ~2 gmol CO\textsubscript{2}/kg (8.8wt%) is very good!

\[
\frac{Q}{m_c} = \frac{m_e}{m_c} \cdot C_e \Delta T + \frac{B}{L} \cdot C_s \Delta T + C_{p,c} \cdot T_2 - C_s \cdot T_1 + \frac{Q_r}{m_c} + C_{p,w} \cdot T_2 - C_s \cdot T_1 + \frac{Q_w}{m_c}
\]

- Heat duty
- Heating the "equipment"
- Heating the sorbent
- Enthalpy change between gaseous CO\textsubscript{2} and sorbent
- CO\textsubscript{2} Heat of reaction
- Enthalpy change between gaseous H\textsubscript{2}O and sorbent
- H\textsubscript{2}O Heat of reaction
Status of dry sorbents

- Sorbents have been developed by multiple organizations
- Common tests completed in NETL contract with ADA, Inc.
- Sorbents that meet 1st level performance metrics identified.
- Stable lab performance 8 wt% – 250 cycles, 10 ppm SO₂
Example of sorbents

- **Two different formulations studied at NETL:**
  - Clay substrate, amine impregnated.
  - Silica (catalyst support).
- **Both manufactured with commercial processes/partner.**
Process and Component Development
In progress right now!

• NETL experimental system.
  – Lab size/scale allows rapid screening of component options.
  – circulating absorber & regenerator
  – validates thermal, hydrodynamic, transport, and kinetic performance

• Validating data: enabling rapid numeric scale-up.

Predicted absorber gas fraction *

* Prediction from a different design than shown schematically
Summary of Sorbent Potential & Progress

• Sorbent advantages are possible:
  – Sufficient capacity (loading) demonstrated.
  – Reactor designs, simulation proceeding!

• Other chemistries may be useful:
  – Pursue even lower reaction heat.
  – Greater impurity tolerance, oxidative resistance.

• What about non-aqueous solvents?

Investigation of solid supported amino acid for CO₂ capture: Arginine crystal and PSS/Arginine complexes of same mass.

Baseline

Inert:Sorbent 4:1

Reactor design concepts/tradeoffs studied at NETL

Non-aqueous solvents
Oxy-fuel Combustion
(Next generation – or this generation?)

- Oxygen + flue gas recycle = easy CO₂ capture.
- Innovative oxygen production/integration helps!
- Validated simulation tools:
  - Enabling rapid & multiple retrofit and greenfield.
  - Requires establishing simulation appropriate to new combustion environment.

Example of predicted gas radiation absorption. Three different published radiation models.

Selection of radiation model depends on speed/accuracy needed.

Measurement of oxy-fuel flame radiation properties.
Chemical Looping

- Shares advantages of oxy-fuel
  - Product is just CO₂ and H₂O
- No separate oxygen production is needed
- Significant interest/development worldwide

\[ \text{Carbon + metal oxide} = \text{CO}_2 + \text{metal} \]

\[ \text{Metal + air (oxygen)} = \text{metal oxide} \]
NETL on-site Research on Chemical Looping

- **Evaluating carrier behavior & options**
  - Physics of solid-fuel & MeO reaction.
  - Evaluation of metal “commodity” carriers from waste or natural sources.

- **Leverages NETL capability in multi-phase flow:**
  - Cold Flow Facility
    - Investigating *ash, coal, carrier separation* and handling.
    - Validate model predictions.
  - Hot Flow Facility
    - Address reaction performance
    - Detailed design in progress.
  - Reactor simulations.
    - Accelerate understanding & scale-up
Comparison of CFD and Cold Flow Rig

Oxygen carrier

Lighter ash carried out with fluidizing steam or CO₂

Solid fuel into this bed

Oxygen carrier

Air reactor

EXPERIMENT
Comparison of CFD and Cold Flow Rig
How can we accelerate technology development for carbon capture and storage?

Key differences in the design process used to create these two machines:
better science, more engineers…..and also large-scale simulations
Actual Trend of FGD Capital Cost

Climbing the “technology readiness” ladder
Faster with Simulations – a NETL Initiative

The Simulation Initiative:
• Enables rapid and reliable adaptation of most promising concepts.
• Reduces the number and size of experimental projects.
• Accelerates learning from successive generations of technologies to speed up the “learning curve”.

Emerging Innovations:
• Lab studies & demonstrations.
• Discovery computations and experiments.

Increasing Technology Readiness Level

Information

Actual Power plant

Pilot scale test (needed?)

System Engineering (process & integration)

Engineering Science (reactors/ components)

Applied Science (lab-scale)

Basic Science & Ideas (fundamentals)

Research activity

Knowledge gap
Geological Sequestration
Storing CO$_2$ in underground rock formations
What does a CO\(_2\) storage site look like?

- Power plants typically emit on the order of \(10^6 - 10^7\) tons CO\(_2\)/year and, hence, \(~10^7 - 10^8\) tons total

- \(10^8\) tons of CO\(_2\) is roughly...
  - \(10^{-1}\) km\(^3\) (~1 km\(^3\) reservoir at 10% porosity)
  - \(10^9\) barrels
  - \(10^0\) TCF

- Several sites inject CO\(_2\) at scales comparable to power plant emissions
  - CO\(_2\) enhanced oil recovery
  - CO\(_2\) sequestration
  - Acid-gas injection

- Many natural analog sites are sized comparable to power-plant emissions

- IPCC (2005) estimated global CCS potential
  - \(~10^9\) tons/year by 2020
  - \(~10^{11} - 10^{12}\) tons CO\(_2\) total
Key Challenges to Carbon Capture and Storage
Focus Infrastructure to Address Both Types of Issues

**Technical Issues**
- Capture Technology
  - Existing Plants
  - New Plants (PC)
  - IGCC
- Cost of CCS
- Storage Capacity
- Permanence
- Best Practices
  - Storage Site Characterization
  - Monitoring/Verification
  - Site Closure
  - Etc etc …

**Legal/Social Issues**
- Regulatory Framework
  - Permitting
  - Treatment of CO₂
- Infrastructure
- Human Capital
- Legal Framework
  - Liability
  - Ownership
    - pore space
    - CO₂
- Public Acceptance (NIMBY → NUMBY)
**U.S. DEPARTMENT OF ENERGY • OFFICE OF FOSSIL ENERGY**

**NATIONAL ENERGY TECHNOLOGY LABORATORY**

**CARBON SEQUESTRATION PROGRAM with ARRA Projects**

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### Core R&D
- Pre-combustion Capture
- Geologic Storage
- Monitoring, Verification, and Accounting (MVA)
- Simulation and Risk Assessment
- CO₂ Use/Reuse
- ARRA: University Projects

**Benefits**
- Reduced cost of CCS
- Tool development for risk assessment and mitigation
- Accuracy/monitoring quantified
- CO₂ capacity validation
- Indirect CO₂ storage

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### Infrastructure
- Regional Carbon Sequestration Partnerships
  - Characterization
  - Validation
  - Development
- ARRA: Development of Technology Transfer Centers
- ARRA: Site Characterization

**Benefits**
- Human capital
- Stakeholder networking
- Regulatory policy development
- Visualization knowledge center
- Best practices development
- Public outreach and education

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### Global Collaborations
- North America Energy Working Group
- Carbon Sequestration Leadership Forum
- International Demonstration Projects
  - Canada (Weyburn, Zama, Ft. Nelson)
  - Norway (Sleipner and Snovhit)
  - Germany (CO₂Sink)
  - Australia (Otway)
  - Africa (In-Salah)
  - Asia (Ordos Basin)

**Benefits**
- Knowledge building
- Project development
- Collaborative international knowledge
- Capacity/model validation
- CCS commercial deployment

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### Other Large-Scale Projects
- ARRA: Site Characterization
- ARRA: Development of Technology Transfer Centers
- ARRA: University Projects

**Benefits**
- Knowledge building
- Project development
- Collaborative international knowledge
- Capacity/model validation
- CCS commercial deployment

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**Demonstration and Commercialization Carbon Capture and Storage (CCS)**
Regional Carbon Sequestration Partnerships
Developing the Infrastructure for Wide Scale Deployment

Seven Regional Partnerships
350 + distinct organizations, 43 states, 4 Canadian Provinces

Characterization Phase (2003-2005)
- Search of potential storage locations and CO₂ sources
- Found potential for 100’s of years of storage

Validation Phase (2005-2010)
- 21 injection tests in saline formations, depleted oil, unmineable coal seams, and basalt

- 9 large scale injections (over 1 million tons each)
- Commercial scale understanding
- Regulatory, liability, ownership issues

- Engage regional, state, and local governments
- Determine regional sequestration benefits
- Baseline region for sources and sinks
- Establish monitoring and verification protocols
- Address regulatory, environmental, and outreach issues
- Validate sequestration technology and infrastructure
National Atlas Highlights (Atlas II)
Adequate Storage Projected
U.S. Emissions ~ 6 GT CO$_2$/yr all sources

North American CO$_2$ Storage Potential
(Giga Tons)

<table>
<thead>
<tr>
<th>Sink Type</th>
<th>Low</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saline Formations</td>
<td>3300</td>
<td>13000</td>
</tr>
<tr>
<td>Unmineable Coal Seams</td>
<td>160</td>
<td>180</td>
</tr>
<tr>
<td>Oil and Gas Fields</td>
<td>140</td>
<td>140</td>
</tr>
</tbody>
</table>

Conservative Resource Assessment

Hundreds of Years of Storage Potential

NRAP: National Risk Assessment Partnership

NRAP is developing a science-based methodology to quantify risk profiles at storage sites, using integrated assessment models to link various subsystems at a storage site.

- Storage site described by subsystems
- Subsystem behavior can be treated in detail
- Uncertainty/heterogeneity handled by stochastic descriptions of subsystems

**Potential Receptors or Impacted Media**

**Release and Transport**

**Storage Reservoir**

- Lawrence Berkeley National Lab
- Lawrence Livermore National Lab
- Los Alamos National Lab
- National Energy Technology Lab (lead)
- Pacific Northwest National Lab
A successful storage project will require predicting the site’s performance beyond the injection phase.

Schematic description of risk assuming probability of CO$_2$ release relates to reservoir pressure and phase-distribution of CO$_2$ (Benson, 2007).

Site Characterization, Site Operation (e.g., CO$_2$-EOR), Post Closure, Long-Term Stewardship

10$^0$ 10$^1$ 10$^2$ 10$^3$

Time (yrs)
NRAP research efforts are coordinated across several interdependent topical areas.

**Systems Modeling for Risk Assessment**
- quantification of site-specific risk profiles
- identification of key uncertainty drivers to direct research
*goal*: validated, science-based methodology for risk profiles

**Ensuring protection of groundwater**
- comprehensive assessment of potential impacts (CO₂/O₂/…)
- identification of early signals for strategic monitoring
*goal*: ensure protection by early detection

**Wellbore integrity & natural-seal integrity**
- open/close conditions of pathways; effective permeability
- methods to identify potential pathways
*goal*: quantitative estimate of potential release

**Strategic monitoring**
- optimization tied to risk assessment
- dynamic integration of monitoring and prediction
- quantification of reservoir stress
*goal*: risk-based monitoring protocol
A Future Option to Consider?

- Combining CO₂ sequestration with co-gasification
- Coal energy used to “reform” *renewable* carbon

Life-Cycle GHG Emissions for 15wt% CBTL with CCS

Net to Atmosphere + 2,015 t_c/d

Credit for Upstream CHG Emissions for Producing Naptha from Petroleum

Electric Credit Grid

Electricity

Transportation of Synthetic Diesel Fuel

Coal Mining and Transportation

Biomass Cultivation and Transportation

Soil/Root Carbon

Char

Carbon Storage

91.5% Capture

9,9% Energy HHV

Biomass

Photosynthesis

- 848 t_c/d

407 t_c/d

265 t_c/d

79 t_c/d

848 t_c/d

8,091 t_c/d In

8,091 t_c/d Out

F-T Products

9,425 BPD Synthetic Diesel
20,575 BPD Synthetic Naphtha

Naphtha with Zero Upstream Life Cycle CHG Emissions

Naptha

6 t_c/d

-158 t_c/d

0 t_c/d

Sulfur

Dioxides

Nitrogen Oxides

Particulate Matter

Carbon Dioxide

Combustion Emissions from Synthetic Diesel

3240 t_c/d

976 t_c/d

7243 t_c/d

81 t_c/d

4363 t_c/d

Coal

848 t_c/d
Can we mix coal + biomass (a.k.a “co-gasification”)?

Affordable, Low-Carbon Diesel Fuel from Domestic Coal and Biomass, Available at www.netl.doe.gov, DOE/NETL-2009/1349
Coal Gasification Plants in the United States

Coal Areas
- Eastern
- Interior
- Western

Solid Fuel Gasification Plants
- Existing
- Proposed

Primary Product
- Chemicals
- Electricity
- Electricity/Steam
- Fuels
- Hydrogen
- SNG

Biomass Energy Content (1,000 GJ/Year)
- 10,063 to 55,375
- 4,783 to 10,063
- 2,391 to 4,783
- 969 to 2,391
- 0 to 969

Summary

• Significant research progress and potential for advancing CCS performance:
  – Solid sorbents
  – Non-aqueous solvents
  – Oxy-fuel combustion
  – Chemical Looping

• Simulation and modeling tools: a key enabler for rapid development.
  – Captures knowledge, enables what if?

• Sequestration program addressing key issues:
  – Storage capacity, integrity, risk
  – Legal, regulatory, and public acceptance

• Coal + Biomass + CCS
  – A low-carbon liquid fuel option.
BACKUP SLIDES
Non-aqueous solvents

- Could reduce/eliminate water vaporization heat in thermal swing systems.
- Different solvents are possible; discuss just ionic liquids:
  - Negligible vapor pressure
  - Thermally stable above 200 °C
  - High CO₂ solubility relative to CH₄, N₂, and H₂
  - But water absorption matters!

### Ionic Liquid Reactor

**Supported Ionic Liquid Membrane test**

Do we synthesize and test all of the candidates?

### Ionic liquid reactor

(many cations) X (many anions) = (many)² options & possibilities

Ideal for humid syngas membrane......

.................water exclusion can be addressed...
Computational Methodology: Ab Initio & Molecular Simulation

**Ab initio QM**

1. energy, structure
2. charges, force field parameters
3. mechanism, etc.

**Classical force-field**

\[ V_{tot} = \sum_{\text{bonds}} k_b (r - r_0)^2 + \sum_{\text{angles}} k_\theta (\theta - \theta_0)^2 \]

\[ + \sum_{\text{dihedrals}} k_\chi [1 + \cos(n\chi - \delta)] + \sum_{\text{improvers}} k_\psi (\psi - \psi_0)^2 \]

\[ + \sum_{i=1}^{N-1} \sum_{j>i}^N \left[ 4\varepsilon_{ij} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 + \frac{q_i q_j}{4\pi \varepsilon_0 r_{ij}} \right] \]

\[ + U_{\text{pol}} \]

*Thermodynamic properties* from Monte Carlo

*Transport properties* from Molecular Dynamics

- Henry’s law constant, mixed gas selectivity, transport coefficients;
- Permeability, permeability selectivity;
- Other process related properties such as heat of mixing, heat capacity;
- Interaction mechanism: physical, chemical, intermolecular complex.

- Search for better ILs
- Modify IL functionality
- Discover new IL

A new ionic liquid has been identified from molecular simulations which exhibits high CO₂ permeability and high CO₂/H₂ selectivity. The initial experimental data from NETL (David Luebke Group) verified this prediction.
Detailed CFD of Reacting Components  
(Chalmers Quartz Reactor)  

- Used as a validation case for numeric simulation.
- Petcoke and Metal Oxide are well mixed
- Only small quantities of H$_2$ leak through bubbles


- Fuel Consumption: 50/50 wt% H$_2$O/N$_2$
- Carrier Oxidation: 10/90 wt% O$_2$/N$_2$

- d = 45mm
- d = 30mm
- d = 10mm
- 100mm
- 20mm
- 250mm

Petcoke
Vol. Frac.
0.0-0.006

Carrier
Vol. Frac
0.0-0.6

CO$_2$ wt%
0-40

H$_2$ mole%
0-12

600 mL/min
~0.55 m/s