BENCHMARKING CO₂ CAPTURE TECHNOLOGY (VOL. 2):
PRE-COMBUSTION AND OXY-COMBUSTION ROUTES

A Techno-economic investigation
commissioned by the members of the
Carbon Dioxide Capture & Conversion (CO₂CC) Program

Client Private
August 2011
The Carbon Dioxide Capture & Conversion (CO₂CC) Program

The CO₂CC Program is a membership-directed consortium whose members are involved in the development, monitoring and utilization of the “state-of-the-art” in technological progress and commercial implementation of carbon dioxide capture/clean-up and conversion. By the direction of the member companies (through balloting and other interactive means), the program delivers a range of timely and insightful information and analyses which are accessible exclusively to members and protected by confidentiality agreements. The objective is to document technically and commercially viable options for CO₂ capture/clean-up as well as its conversion into useful products which meaningfully address the challenges posed by CO₂ life-cycle and overall sustainability issues.

Members receive three in-depth CO₂CC Techno-economic Reports which are written by leading scientists and experienced industry professionals in areas selected by the membership (via ballot); weekly CO₂CC Communiqués (delivered via e-mail) which provide the latest updates on technical breakthroughs, commercial events and exclusive development opportunities; and attendance at the CO₂CC Program Annual Meeting.

The Carbon Dioxide Capture & Conversion (CO₂CC) Program is available on a membership basis from The Catalyst Group Resources (TCGR). For further details, please contact John J. Murphy at John.J.Murphy@catalystgrp.com or +1.215.628.4447 (x1121).

TCGR
THE CATALYST GROUP RESOURCES™

P.O. Box 680
Spring House, PA 19477 U.S.A
ph: +1.215.628.4447
CONTENTS

EXECUTIVE SUMMARY ........................................................................................................... xxiii

1. INTRODUCTION ................................................................................................................ 1
  1.1 SCOPE AND OBJECTIVES OF REPORT (VOL. 2) ....................................................... 1
  1.2 METHODOLOGY FOR TOPIC SELECTION/PRIORITIZATION ......................... 3
  1.3 REPORT CONTRIBUTORS ......................................................................................... 6

2. PRE-COMBUSTION CO₂ CAPTURE TECHNOLOGIES ............................................. 9
  2.1 PRE-COMBUSTION TECHNOLOGY BENCHMARKS ............................................... 10
    2.1.1 Commercial and Demonstration Projects ..................................................... 10
    2.1.1.1 Commercial Projects ............................................................................... 10
    2.1.1.1.1 Coal/Coke Gasification Using Rectisol® .............................................. 10
    2.1.1.1.2 Coal/Coke Gasification Using Selexol™ .............................................. 14
    2.1.1.2 Demonstration Projects ............................................................................ 19
    2.1.1.2.1 Summit Texas Clean Energy IGCC – Rectisol® (DOE/NETL) ............... 19
    2.1.1.2.2 Hydrogen Energy California – Rectisol® (DOE/NETL) ...................... 26
    2.1.1.2.3 Southern Company Kemper IGCC – Selexol™ (DOE/NETL) ............... 33
    2.1.1.3 Comparison & Implications Selexol™ and Rectisol® .................................. 41
  2.2 PRE-COMBUSTION TECHNOLOGY ADVANCES ..................................................... 51
    2.2.1 Solvent Absorption .............................................................................................. 51
    2.2.1.1 Ammonium Carbonate-Ammonium Bicarbonate Process (SRI International) ... 51
    2.2.1.1.1 Description & Status ........................................................................... 51
    2.2.1.1.2 Techno-Economic Benchmarking Data .............................................. 57
    2.2.1.1.3 Commercial Potential ....................................................................... 59
    2.2.2 Solid Adsorption ................................................................................................. 62
    2.2.2.1 Advanced PSA for Sour Syngas (Air Products & Chemicals) ...................... 62
    2.2.2.1.1 Description & Status ........................................................................... 62
    2.2.2.1.2 Techno-Economic Benchmarking Data .............................................. 72
    2.2.2.1.3 Commercial Potential ....................................................................... 73
    2.2.2.2 CO₂-PSA Modified-Carbon-Adsorbent Development (TDA Research) ....... 74
2.2.2.1 Description & Status................................................................. 74
2.2.2.2 Techno-Economic Benchmarking Data................................. 83
2.2.2.3 Commercial Potential ............................................................ 85
2.2.2.3 Mg(OH)_2 High-Temperature Adsorbent (DOE/NELT) ........ 87
  2.2.2.3.1 Description & Status....................................................... 87
  2.2.2.3.2 Techno-Economic Benchmarking Data............................ 91
  2.2.2.3.3 Commercial Potential ..................................................... 92
2.2.2.4 Sorbent-Enhanced Water Gas Shift – SEWGS (URS Group) ... 93
  2.2.2.4.1 Description & Status....................................................... 93
  2.2.2.4.2 Techno-Economic Benchmarking Data............................ 97
  2.2.2.4.3 Commercial Potential ..................................................... 97
2.2.3 Hydrogen Transport Membranes............................................. 99
  2.2.3.1 Polymeric Membrane (Los Alamos National Lab, LANL) ..... 99
    2.2.3.1.1 Background & Objectives.......................................... 99
    2.2.3.1.2 Technology Description and Development Status .......... 100
    2.2.3.1.3 Benchmarking/Economic Data.................................... 103
    2.2.3.1.4 Implications and Hurdles ......................................... 104
  2.2.3.2 Hydrogen Transport Membrane (Praxair) ......................... 105
    2.2.3.2.1 Background & Objectives.......................................... 105
    2.2.3.2.2 Technology Description and Development Status .......... 106
    2.2.3.2.3 Benchmarking/Economic Data.................................... 109
    2.2.3.2.4 Implications and Hurdles ......................................... 110
  2.2.3.3 Dense Metallic Membrane (Eltron Research & Development) 111
    2.2.3.3.1 Background & Objectives.......................................... 111
    2.2.3.3.2 Technology Description and Development Status .......... 112
    2.2.3.3.3 Benchmarking/Economic Data.................................... 115
    2.2.3.3.4 Implications and Hurdles ......................................... 116
  2.2.3.4 Ceramic-based Membrane (Argonne National Laboratory) ... 117
    2.2.3.4.1 Background & Objectives.......................................... 117
    2.2.3.4.2 Technology Description and Development Status .......... 118
    2.2.3.4.3 Benchmarking/Economic Data.................................... 121
    2.2.3.4.4 Implications and Hurdles ......................................... 122
3. OXY-COMBUSTION CO\textsubscript{2} CAPTURE TECHNOLOGIES

3.1 POTENTIAL ADVANTAGES

3.2 COST/PERFORMANCE/TIMING GOALS

3.3 STATE OF TECHNOLOGY DEVELOPMENT

3.4 TECHNOLOGY OPTIONS

3.4.1 Atmospheric Combustion

3.4.2 Pressurized Combustion

3.5 APPLICATIONS AND DESIGN BASIS OPTIONS

3.5.1 Industrial Applications

3.5.2 Design Basis Options

3.6 R&D PROJECTS

3.7 SUPPORTING TECHNOLOGIES DEVELOPMENT

3.7.1 Air Separation

3.7.1.1 Cryogenic Air Separation

3.7.1.2 ITM-based Technology (Air Products and Chemicals)

3.7.1.2.1 Technology Benefits and Drivers

3.7.1.2.2 Technology Description

3.7.1.2.3 Competitive Position and Commercial Potential

3.7.1.2.4 Implications and Hurdles

3.7.1.3 OTM-based Technology (Praxair)

3.7.1.3.1 Background & Objectives

3.7.1.3.2 Technology Description and Status

3.7.1.3.3 Benchmarking/Economic Data

3.7.1.3.4 Implications and Hurdles

3.7.1.4 Chemical Looping Process (Alstom)

3.7.1.4.1 Background & Objectives

3.7.1.4.2 Technology Description and Status

3.7.1.4.3 Benchmarking/Economic Data

3.7.1.4.4 Implications and Hurdles

3.7.2 CO\textsubscript{2} Purification

3.7.3 CO\textsubscript{2} Compression
3.7.4 Integration of CO₂ Purification and Compression

3.8 BENCHMARK PROJECTS

3.8.1 FutureGen 2.0

3.8.2 Lacq

3.8.3 Vattenfall

3.8.4 Callide

3.8.5 Compostilla

3.9 SUMMARY & RECOMMENDATIONS

3.10 REFERENCES

4. INDEX

FIGURES

Figure 2.1.1.1.1 Process Flow Sheet for a Typical Rectisol® Process Prepared by Lurgi

Figure 2.1.1.2.1 Process Flow Diagram - UOP Selexol™ 2-stage Process

Figure 2.1.1.2.1.1 Block Flow Diagram – Texas Clean Energy Project (TCEP)

Figure 2.1.1.2.2.1 Block Flow Diagram - Hydrogen Energy California (HECA) Project

Figure 2.1.1.2.3.1 Block Flow Diagram – Kemper County IGCC

Figure 2.1.1.2.3.2 Project Status/Timeline – Kemper County IGCC

Figure 2.1.1.3.1 Equilibrium Curves for CO₂ in Methanol and Selexol™

Figure 2.2.1.1.1.1 Schematic of SRI AC-ABC Process within an IGCC Facility

Figure 2.2.1.1.1.2 SRI Data for High Pressure CO₂ Regeneration from the Solvent

Figure 2.2.1.1.1.3 SRI Data for H₂S Regeneration Depicting H₂S Concentration vs H₂S Pressure

Figure 2.2.1.1.4 SRI Flowscheme for AC-ABC Process for Gasification Syngas

Figure 2.2.1.1.5 SRI Laboratory Absorber (left) and Regenerator (right) Sections

Figure 2.2.1.1.3.1 DOE/NETL Advanced CO₂ Capture Timeline for Core R&D Programs

Figure 2.2.2.1.1.1 Single PSA Adsorber w Multiple Adsorbents (left) & PSA/TSA Pressure-Loading Cycle

Figure 2.2.2.1.1.2 5-Step PSA Process Cycle (dark--H₂/light--non-H₂ Impurities)

Figure 2.2.2.1.1.3 APCI Sour PSA Diagram for H₂ Production and CO₂ Capture
Figure 2.2.1.1.4 Single-Adsorber Life Test Apparatus (top) & 2-Bed PSA Pilot Plant (bottom)........................................................................................................65
Figure 2.2.1.1.5 Spent Adsorbent Samples/EERC Adsorber (Left-Bottom-Feed/ Right-Top-Product) .................................................................................. 66
Figure 2.2.1.1.6 H2S Capacity at EERC Pilot Plant from H2S Breakthrough Tests........... 66
Figure 2.2.1.1.7 Sour PSA Tailgas Combustion/Purification/Compression Flowscheme..................................................................................................... 67
Figure 2.2.1.1.8 Sour PSA Combusted Tailgas Compression & Purification Flowscheme........................................................................................................ 68
Figure 2.2.1.1.9 Air Products CPU---CO2 Purification Schematic (Cold Box) ................. 69
Figure 2.2.1.1.10 APCI Sour PSA Tailgas H2S Processing by a Claus SRU ....................... 70
Figure 2.2.2.1.1 TDA Sorbent Pore Volume vs Pore Width .............................................. 75
Figure 2.2.2.1.2 Calculated and Measured Heat of CO2-Adsorption for TDA Sorbent..... 75
Figure 2.2.2.1.3 TDA Sorbent Equilibrium Loading Isotherms with Langmuir- Freundlich Correlation ............................................................................. 76
Figure 2.2.2.1.4 CO2 Working Capacity and Removal Efficiency for Flow Experiments ........................................................................................................ 76
Figure 2.2.2.1.5 CO2 Adsorbent Breakthrough & Saturation Capacities for Flow Experiments ........................................................................................................ 77
Figure 2.2.2.1.6 CO2 Breakthrough Tests on TDA Adsorbent w and w/o H2S Present (left) CO2 Loading on Adsorbent vs Cycle Number with 300 ppmv H2S Present in Syngas (right)................................................................. 77
Figure 2.2.2.1.7 Arsine (Arsenic) and Mercury (Hg) Adsorption Breakthrough Tests...... 78
Figure 2.2.2.1.8 TDA Adsorption-Regeneration PSA Cycle at Elevated Temperature & Pressure ............................................................................................ 78
Figure 2.2.2.1.9 PSA Cycle with Beds in Adsorption/Pressure Equalization/Blowdown/ Purge Steps ............................................................................................... 79
Figure 2.2.2.1.10 4-Bed PSA Cycle with Step Times & Syngas Recovery & Working Capacity ........................................................................................................ 79
Figure 2.2.2.1.11 TDA CO2-PSA Followed by CO2 Compression/Purification Block Flow Diagram........................................................................................................ 80
Figure 2.2.2.1.12 CO2 Compression / Purification Process Flowscheme.......................... 80
Figure 2.2.2.1.13 ~690MW IGCC Coal-based Power Plant Block Flow Diagram w/ TDA CO2-PSA ....................................................................................... 83
Figure 2.2.2.3.1 DOE/NETL Advanced CO2 Capture Timeline for Core R&D Programs ........................................................................................................... 87
Figure 2.2.2.3.1.1 HT Sorbent Process Replaces Cooling/Acid Gas Removal/Heating in IGCC ................................................................. 88
Figure 2.2.2.3.1.2 NETL Preliminary Process Flowscheme for Mg(OH)\textsubscript{2} Adsorbent Process .................................................................................. 89
Figure 2.2.2.3.3.1 DOE/NETL Advanced CO\textsubscript{2} Capture Timeline for Core R&D Programs ........................................................................................................... 93
Figure 2.2.2.4.1.1 Thermodynamic Equilibrium Analysis / CO-Shift Conversion vs Temperature ........................................................................................................... 94
Figure 2.2.2.4.1.2 IGCC Block Flow Diagrams of IGCC with Conventional CO-Shift and SEWGS ............................................................................................................. 94
Figure 2.2.2.4.1.3 Identification and Selection Criteria for SEWGS Adsorbents ............................................................... 95
Figure 2.2.2.4.1.4 Equilibrium CO\textsubscript{2} Partial Pressure vs Temperature for 7 Candidate SEWGS Sorbents .......................................................................................... 95
Figure 2.2.3.1.2.1 Chemical Structure of Polybenzimidazole Used in Membranes (Berchtold 2006) ................................................................. 100
Figure 2.2.3.1.2.2 Performance of Polymer Membrane Developed by LANL (Project Facts, NETL, 4/2008) .................................................................................. 100
Figure 2.2.3.1.2.3 Cross-Section of PBI Membrane Coated on Outside of Metal Composite Tube (SEM) and a Multi-tube Module (Berchtold 2005; O’Brien 2010) ........................................................................... 101
Figure 2.2.3.1.2.4 Stability of PBI Composite Membranes on Metallic Substrate (O’Brien 2010) ................................................................. 101
Figure 2.2.3.1.2.5 SEM Picture of the Cross Section of a PBI Hollow Fiber with Separation Layer on the Inside Surface and a Small Test Module (O’Brien 2010) ........................................................................... 102
Figure 2.2.3.1.2.6 Performance of PBI Hollow Fiber Membranes (O’Brien 2010) ................................................................. 102
Figure 2.2.3.2.2.1 SEM of Cross Section of HTM Membrane (left) and Substrate Tubes Before and After Metal Film Deposition (right) (Schwartz, 2008) ..... 106
Figure 2.2.3.2.2.2 Process for H\textsubscript{2} Production and Targets for HTM Development (Schwartz, 2007) ................................................................. 107
Figure 2.2.3.2.2.3 H\textsubscript{2} Flux Through a Ternary Pd Alloy HTM - Lab Data and Model Predictions (Schwartz, 2011) ........................................................................... 108
Figure 2.2.3.2.2.4 Impact of Thermal Cycling and Conditioning on Membrane Flux (Schwartz, 2008) ........................................................................... 109
Figure 2.2.3.2.2.5 Improved Sulfur Resistance Using MembraGuard (Schwartz 2011) ........................................................................... 109
Figure 2.2.3.2.3.1 Cost Performance Index vs Membrane Thickness (Schwartz, 2010) ........................................................................... 110
<table>
<thead>
<tr>
<th>Figure 2.2.3.3.2.1</th>
<th>Schematic of Eltron’s Hydrogen Transport Membrane (Jack, 2007; Technology Opportunities, 2009) ........................................................... 112</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 2.2.3.3.2.2</td>
<td>Impact of Membrane Thickness and Temperature on Flux (Jack, 2008) .......................................................... 113</td>
</tr>
<tr>
<td>Figure 2.2.3.3.2.3</td>
<td>Flux Stability in the Presence of H₂S (Technology Opportunities, 2009) ................................................................. 113</td>
</tr>
<tr>
<td>Figure 2.2.3.3.2.4</td>
<td>Flux Stability in Coal Derived Syngas (Evenson, 2010) ........................................................................ 114</td>
</tr>
<tr>
<td>Figure 2.2.3.3.2.5</td>
<td>(a) As Received Uncoated Tubes (b) Tubular Membrane as-Received (bottom) and with Deposited Catalyst (top) (Evenson, 2010) ................. 114</td>
</tr>
<tr>
<td>Figure 2.2.3.3.3.1</td>
<td>Process Flow Diagram for Integration of HTM with IGCC for CO₂ Capture (Jack, 2008; Evenson, 2010) ........................................................................ 116</td>
</tr>
<tr>
<td>Figure 2.2.3.4.2.1</td>
<td>ANL’s Three Approaches to HTM Membranes (Balachandran, 2008) ................................................................. 119</td>
</tr>
<tr>
<td>Figure 2.2.3.4.2.2</td>
<td>H₂ Flux Comparison of the Three Types on ANL Membranes (Balachandran, 2008) ................................................................. 119</td>
</tr>
<tr>
<td>Figure 2.2.3.4.2.3</td>
<td>Pd based HTM Sulfur Stability (ANL Annual Report, 2009) ................................................................. 120</td>
</tr>
<tr>
<td>Figure 2.2.3.4.2.4</td>
<td>Composite HTM Membranes at ANL (Balachandran, 2008) ........................................................................ 121</td>
</tr>
<tr>
<td>Figure 2.2.3.4.2.5</td>
<td>H₂ Flux through Thin Film Cermet Membrane on Porous Al₂O₃ Substrate (Balachandran, 2008) ........................................................................ 121</td>
</tr>
<tr>
<td>Figure 3.1.1</td>
<td>Process Schematic of Coal-based Power Generation with CO₂ Capture via Oxy-combustion (U.S. Department of Energy/National Energy Technology Laboratory (DOE/NETL), 2010) ................................................ 130</td>
</tr>
<tr>
<td>Figure 3.1.2</td>
<td>Comparison of Cost Metrics for Different Types and Configurations of Power Plants With and Without CCS [LCOE = Levelized Cost of Electricity] (Source: DOE/NETL, 2010) ................................................ 131</td>
</tr>
<tr>
<td>Figure 3.2.1</td>
<td>DOE/NETL Timeline for CCS RD&amp;D including Oxy-combustion (DOE/NETL, 2010) ................................................ 133</td>
</tr>
<tr>
<td>Figure 3.2.2</td>
<td>One pathway to Achieve DOE/NETL’s Cost/Performance Goal (Ciferno, 2010) ................................................ 134</td>
</tr>
<tr>
<td>Figure 3.3.1</td>
<td>Progression of Oxy-combustion Technology Development and Demonstration (IEA Clean Coal Centre, 2010) ................................................ 135</td>
</tr>
<tr>
<td>Figure 3.5.1</td>
<td>Oxy-combustion Applied to FCC (Source: CO₂ Capture Project, 2010) ................................................ 139</td>
</tr>
<tr>
<td>Figure 3.7.1.1.1</td>
<td>Oxygen Requirements for Oxycoal CO₂ Capture (Fogash et al., 2010) ................................................ 143</td>
</tr>
<tr>
<td>Figure 3.7.1.1.2</td>
<td>Air Products Oxycoal “Reference ASU” Cycle (Fogash et al., 2010) ................................................ 143</td>
</tr>
</tbody>
</table>
Figure 3.7.2.1 NOx/SO2 Reactions in the CO2 Compression System (Fogash, 2009) ....... 169
Figure 3.7.2.2 Air Products’ CO2 Compression and Purification System: Removal of SO2, NOx and Hg (Fogash, 2009) .......................................................... 170
Figure 3.7.3.1 Ramgen 2-Stage Process (Lawlor, 2010) ....................................................... 170
Figure 3.7.3.2 Ramgen CO2 Compression (Lawlor, 2010) .......................................................... 171

TABLES

Table 1.2.1 Initial (39) and Selected (21) List of Technologies for “Case Study/Benchmarking” Evaluation (technologies in bold selected for coverage in this report) ................................................................. 4
Table 2.1.1.3.1 Physical Solvent Solubility Data (London Management, Inc.) ...................... 45
Table 2.1.1.3.2 Results Comparison: DPEG AGR vs. New Process (Patent Pending) (London Management, Inc.) .......................................................... 49
Table 2.1.1.3.3 Simulation Results for Changes in Methanol Circulation Rates (London Management, Inc.) .......................................................................................... 50
Table 2.2.1.1.1.1 DOE/NETL’s Summary of Current and Targeted Parameters for the SRI Technology (DOE/NETL Technology Update Report – May 2011) ............. 57
Table 2.2.1.1.2.1 SRI Preliminary Economic Comparison for IGCC Service (SRI/NETL Meeting – Sept 2010) ..................................................................................... 58
Table 2.2.1.2.1 Sour PSA Economics for H2 to Product or Fuel (power) (APCI / GTC Conference – Nov 2010) ................................................................................ 72
Table 2.2.2.1.2.1 2-Year Project Schedule – TDA Research (TDA / NETL Technology Meeting – Sept 2009) ..................................................................................... 82
Table 2.2.2.2.1.1 Power and Efficiency Analysis for a ~690MW IGCC Coal-based Power Plant (Alptekin, TDA/NETL Technology Meeting – Sept. 2010) ................. 84
Table 2.2.3.1.1.1 Heat of Reaction - CO2 with Various Metal Salts at Standard Temperature & Pressure (Ind. Engr. Chem. Res., 48(2009), 48: 2135-2141) ..................... 98
Table 2.2.3.1.3.1 COE from IGCC Cases with and without CO2 Capture using PBI Membrane (O’Brien 2010) ................................................................. 104
Table 2.2.3.2.1.1 Summary of Praxair’s HTM Development Programs ........................................ 106
Table 2.2.3.2.2.1 HTM Development Targets (Schwartz, 2007) ................................................. 107
Table 2.2.3.3.1.1 HTM Development Targets at Eltron (Peer Review Meeting, NETL, 2010)........................................................................................................... 111
Table 2.2.3.3.1.2 Funding Sources and Partners ................................................................. 111
Table 2.2.3.3.3.1 Comparison of Economics of HTM Based CO2 Removal with Other Options (Jack, 2008) ................................................................. 116
Table 2.2.3.4.1.1  ANL’s Targets for HTM Development (DOE/FE, NETL, 2010) ............... 118
Table 2.2.3.4.1.2  Development Programs, Funding and Partners ........................................... 118
Table 2.2.3.4.2.1  Fracture Toughness of Pd/YSZ (Balachandran, 2008) ............................... 120
Table 3.7.1.3.3.1  Comparison of OTM-based and Conventional Power Generation
(Christie, 2009) .................................................................................................................... 158