

**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).



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
2.1.2 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 CO ₂ -PSA Modified-Carbon-Adsorbent Development (TDA Research)	74

PROPRIETARY -- Do Not Reproduce or Redistribute!

This message is in red ink. If not, you have an unauthorized copy.

2.2.2.2.1 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/NETL)	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

2.3 REFERENCES	123
3. OXY-COMBUSTION CO₂ CAPTURE TECHNOLOGIES.....	129
3.1 POTENTIAL ADVANTAGES.....	129
3.2 COST/PERFORMANCE/TIMING GOALS	132
3.3 STATE OF TECHNOLOGY DEVELOPMENT.....	134
3.4 TECHNOLOGY OPTIONS.....	138
3.4.1 Atmospheric Combustion.....	138
3.4.2 Pressurized Combustion	138
3.5 APPLICATIONS AND DESIGN BASIS OPTIONS	139
3.5.1 Industrial Applications	139
3.5.2 Design Basis Options	140
3.6 R&D PROJECTS	140
3.7 SUPPORTING TECHNOLOGIES DEVELOPMENT	141
3.7.1 Air Separation.....	141
3.7.1.1 Cryogenic Air Separation.....	141
3.7.1.2 ITM-based Technology (Air Products and Chemicals)	144
3.7.1.2.1 Technology Benefits and Drivers.....	144
3.7.1.2.2 Technology Description	145
3.7.1.2.3 Competitive Position and Commercial Potential	150
3.7.1.2.4 Implications and Hurdles.....	151
3.7.1.3 OTM-based Technology (Praxair)	151
3.7.1.3.1 Background & Objectives	151
3.7.1.3.2 Technology Description and Status.....	152
3.7.1.3.3 Benchmarking/Economic Data.....	158
3.7.1.3.4 Implications and Hurdles.....	159
3.7.1.4 Chemical Looping Process (Alstom)	161
3.7.1.4.1 Background & Objectives	161
3.7.1.4.2 Technology Description and Status.....	162
3.7.1.4.3 Benchmarking/Economic Data.....	166
3.7.1.4.4 Implications and Hurdles.....	167
3.7.2 CO ₂ Purification	169
3.7.3 CO ₂ Compression	170

3.7.4	Integration of CO ₂ Purification and Compression.....	171
3.8	BENCHMARK PROJECTS.....	171
3.8.1	FutureGen 2.0	171
3.8.2	Lacq	174
3.8.3	Vattenfall	174
3.8.4	Callide.....	174
3.8.5	Compostilla.....	175
3.9	SUMMARY & RECOMMENDATIONS.....	175
3.10	REFERENCES	176
4.	INDEX.....	181

FIGURES

Figure 2.1.1.1.1.1	Process Flow Sheet for a Typical Rectisol® Process Prepared by Lurgi	12
Figure 2.1.1.1.2.1	Process Flow Diagram - UOP Selexol™ 2-stage Process.....	16
Figure 2.1.1.2.1.1	Block Flow Diagram – Texas Clean Energy Project (TCEP)	23
Figure 2.1.1.2.2.1	Block Flow Diagram - Hydrogen Energy California (HECA) Project....	29
Figure 2.1.1.2.3.1	Block Flow Diagram – Kemper County IGCC	35
Figure 2.1.1.2.3.2	Project Status/Timeline – Kemper County IGCC	40
Figure 2.1.1.3.1	Equilibrium Curves for CO ₂ in Methanol and Selexol™	44
Figure 2.2.1.1.1.1	Schematic of SRI AC-ABC Process within an IGCC Facility	52
Figure 2.2.1.1.1.2	SRI Data for High Pressure CO ₂ Regeneration from the Solvent	53
Figure 2.2.1.1.1.3	SRI Data for H ₂ S Regeneration Depicting H ₂ S Concentration vs H ₂ S Pressure.....	54
Figure 2.2.1.1.1.4	SRI Flowscheme for AC-ABC Process for Gasification Syngas	54
Figure 2.2.1.1.1.5	SRI Laboratory Absorber (left) and Regenerator (right) Sections	55
Figure 2.2.1.1.3.1	DOE/NETL Advanced CO ₂ Capture Timeline for Core R&D Programs	62
Figure 2.2.2.1.1.1	Single PSA Adsorber w Multiple Adsorbents (left) & PSA/TSA Pressure-Loading Cycle.....	63
Figure 2.2.2.1.1.2	5-Step PSA Process Cycle (dark--H ₂ /light--non-H ₂ Impurities)	63
Figure 2.2.2.1.1.3	APCI Sour PSA Diagram for H ₂ Production and CO ₂ Capture.....	64

PROPRIETARY -- Do Not Reproduce or Redistribute!

This message is in red ink. If not, you have an unauthorized copy.

Figure 2.2.2.1.1.4	Single-Adsorber Life Test Apparatus (top) & 2-Bed PSA Pilot Plant (bottom)	65
Figure 2.2.2.1.1.5	Spent Adsorbent Samples/EERC Adsorber (Left-Bottom-Feed/ Right-Top-Product)	66
Figure 2.2.2.1.1.6	H ₂ S Capacity at EERC Pilot Plant from H ₂ S Breakthrough Tests	66
Figure 2.2.2.1.1.7	Sour PSA Tailgas Combustion/Purification/Compression Flowscheme	67
Figure 2.2.2.1.1.8	Sour PSA Combusted Tailgas Compression & Purification Flowscheme	68
Figure 2.2.2.1.1.9	Air Products CPU---CO ₂ Purification Schematic (Cold Box)	69
Figure 2.2.2.1.1.10	APCI Sour PSA Tailgas H ₂ S Processing by a Claus SRU	70
Figure 2.2.2.2.1.1	TDA Sorbent Pore Volume vs Pore Width	75
Figure 2.2.2.2.1.2	Calculated and Measured Heat of CO ₂ -Adsorption for TDA Sorbent	75
Figure 2.2.2.2.1.3	TDA Sorbent Equilibrium Loading Isotherms with Langmuir-Freundlich Correlation	76
Figure 2.2.2.2.1.4	CO ₂ Working Capacity and Removal Efficiency for Flow Experiments	76
Figure 2.2.2.2.1.5	CO ₂ Adsorbent Breakthrough & Saturation Capacities for Flow Experiments	77
Figure 2.2.2.2.1.6	CO ₂ Breakthrough Tests on TDA Adsorbent w and w/o H ₂ S Present (left) CO ₂ Loading on Adsorbent vs Cycle Number with 300 ppmv H ₂ S Present in Syngas (right)	77
Figure 2.2.2.2.1.7	Arsine (Arsenic) and Mercury (Hg) Adsorption Breakthrough Tests	78
Figure 2.2.2.2.1.8	TDA Adsorption-Regeneration PSA Cycle at Elevated Temperature & Pressure	78
Figure 2.2.2.2.1.9	PSA Cycle with Beds in Adsorption/Pressure Equalization/Blowdown/ Purge Steps	79
Figure 2.2.2.2.1.10	4-Bed PSA Cycle with Step Times & Syngas Recovery & Working Capacity	79
Figure 2.2.2.2.1.11	TDA CO ₂ -PSA Followed by CO ₂ Compression/Purification Block Flow Diagram	80
Figure 2.2.2.2.1.12	CO ₂ Compression / Purification Process Flowscheme	80
Figure 2.2.2.2.2.1	~690MW IGCC Coal-based Power Plant Block Flow Diagram w/ TDA CO ₂ -PSA	83
Figure 2.2.2.2.3.1	DOE/NETL Advanced CO ₂ 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) ₂ Adsorbent Process	89
Figure 2.2.2.3.3.1	DOE/NETL Advanced CO 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 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 ₂ Production and Targets for HTM Development (Schwartz, 2007).....	107
Figure 2.2.3.2.2.3	H 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

PROPRIETARY -- Do Not Reproduce or Redistribute!

This message is in red ink. If not, you have an unauthorized copy.

Figure 2.2.3.3.2.1	Schematic of Eltron's Hydrogen Transport Membrane (Jack, 2007; Technology Opportunities, 2009).....	112
Figure 2.2.3.3.2.2	Impact of Membrane Thickness and Temperature on Flux (Jack, 2008)	113
Figure 2.2.3.3.2.3	Flux Stability in the Presence of H ₂ S (Technology Opportunities, 2009).....	113
Figure 2.2.3.3.2.4	Flux Stability in Coal Derived Syngas (Evenson, 2010).....	114
Figure 2.2.3.3.2.5	(a) As Received Uncoated Tubes (b) Tubular Membrane as-Received (bottom) and with Deposited Catalyst (top) (Evenson, 2010).....	114
Figure 2.2.3.3.3.1	Process Flow Diagram for Integration of HTM with IGCC for CO ₂ Capture (Jack, 2008; Evenson, 2010).....	116
Figure 2.2.3.4.2.1	ANL's Three Approaches to HTM Membranes (Balachandran, 2008).....	119
Figure 2.2.3.4.2.2	H ₂ Flux Comparison of the Three Types on ANL Membranes (Balachandran, 2008)	119
Figure 2.2.3.4.2.3	Pd based HTM Sulfur Stability (ANL Annual Report, 2009).....	120
Figure 2.2.3.4.2.4	Composite HTM Membranes at ANL (Balachandran, 2008)	121
Figure 2.2.3.4.2.5	H ₂ Flux through Thin Film Cermet Membrane on Porous Al ₂ O ₃ Substrate (Balachandran, 2008)	121
Figure 3.1.1	Process Schematic of Coal-based Power Generation with CO ₂ Capture via Oxy-combustion (U.S. Department of Energy/National Energy Technology Laboratory (DOE/NETL), 2010)	130
Figure 3.1.2	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
Figure 3.2.1	DOE/NETL Timeline for CCS RD&D including Oxy-combustion (DOE/NETL, 2010).....	133
Figure 3.2.2	One pathway to Achieve DOE/NETL's Cost/Performance Goal (Ciferno, 2010)	134
Figure 3.3.1	Progression of Oxy-combustion Technology Development and Demonstration (IEA Clean Coal Centre, 2010)	135
Figure 3.5.1	Oxy-combustion Applied to FCC (Source: CO ₂ Capture Project, 2010).....	139
Figure 3.7.1.1.1	Oxygen Requirements for Oxycoal CO ₂ Capture (Fogash et al., 2010).....	143
Figure 3.7.1.1.2	Air Products Oxycoal "Reference ASU" Cycle (Fogash et al., 2010).....	143

Figure 3.7.1.1.3	Oyxcoal ASU Machinery and Driver Considerations (Fogash et al., 2010)	144
Figure 3.7.1.2.1.1	ITM Oxygen Phases 3 and 4 Overview (Steele et al, 2010).....	145
Figure 3.7.1.2.2.1	ITM Oxygen Membrane Schematic and Module (Steele et al, 2010)....	146
Figure 3.7.1.2.2.2	ITM Oxygen Scale-up (Repasky et al, 2011)	147
Figure 3.7.1.2.2.3	ITM Oxygen--Wafers and Modules Scaled Up to Commercial Size (Steele et al, 2010)	147
Figure 3.7.1.2.2.4	Expansion of Ceramic Processing Infrastructure at Cerametec (Steele et al, 2010)	148
Figure 3.7.1.2.2.5	ITM Oxygen 100 Ton/Day Test Unit Process Schematic (Steele et al, 2010)	148
Figure 3.7.1.2.2.6	ITM Oxygen Program (Repasky et al, 2011)	149
Figure 3.7.1.2.2.7	ITM Oxygen Timeline (Repasky et al, 2011).....	150
Figure 3.7.1.3.2.1	Principle of Operation of OTM Membrane (Li, 2006)	153
Figure 3.7.1.3.2.2	Tubular OTM Membrane Made at Praxair (Christie, 2010).....	154
Figure 3.7.1.3.2.3	OTM Based Oxy-combustion (Christie, 2010)	154
Figure 3.7.1.3.2.4	Operation of OTM Tubes in Natural Gas Combustion (Shah, 2009)....	155
Figure 3.7.1.3.2.5	Praxair's Advanced Boiler Concept (Christie, 2009)	155
Figure 3.7.1.3.2.6	OTM Advanced Power Cycle (Christie, 2010)	156
Figure 3.7.1.3.2.7	Improved OTM Performance via Improved Substrate and Materials (Christie, 2010; Wilson, 2009)	157
Figure 3.7.1.3.3.1	Comparison of COE from Advanced OTM Power Cycle with Nearer Term Options (Shah, 2009)	159
Figure 3.7.1.4.2.1	Principle of Chemical Looping (Chiu, 2009)	162
Figure 3.7.1.4.2.2	Calcium based Chemical Looping Process (Chiu, 2009)	163
Figure 3.7.1.4.2.3	Chemical Looping Combustion Process (Andrus, March 2009).....	163
Figure 3.7.1.4.2.4	Chemical Looping for Hydrogen from Coal (Andrus, 2008)	164
Figure 3.7.1.4.2.5	A Concept for Retrofit of CLP into Existing PC Boiler (Andrus, 2008)	165
Figure 3.7.1.4.2.6	Alstom's Development Timeline (Andrus, March 2009).....	166
Figure 3.7.1.4.3.1	COE from New Plants with CLP and Other Capture Options (Chiu, 2009)	166
Figure 3.7.1.4.3.2	COE from Retrofit Coal Power Plant with CLP (Andrus, 2010)	167

PROPRIETARY -- Do Not Reproduce or Redistribute!

This message is in red ink. If not, you have an unauthorized copy.

Figure 3.7.2.1	NOx/SO ₂ Reactions in the CO ₂ Compression System (Fogash, 2009)	169
Figure 3.7.2.2	Air Products' CO ₂ Compression and Purification System: Removal of SO ₂ , NOx and Hg (Fogash, 2009)	170
Figure 3.7.3.1	Ramgen 2-Stage Process (Lawlor, 2010)	170
Figure 3.7.3.2	Ramgen CO ₂ 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 2.2.2.1.2.1	Sour PSA Economics for H ₂ to Product or Fuel (power) (APCI / GTC Conference – Nov 2010)	72
Table 2.2.2.2.1.1	2-Year Project Schedule – TDA Research (TDA / NETL Technology Meeting – Sept 2009)	82
Table 2.2.2.2.2.1	Power and Efficiency Analysis for a ~690MW IGCC Coal-based Power Plant (Alptekin, TDA/NETL Technology Meeting – Sept. 2010)	84
Table 2.2.2.4.3.1	Heat of Reaction - CO ₂ with Various Metal Salts at Standard Temperature & Pressure (Ind. Engr. Chem. Res., 48(2009), 48: 2135-2141).....	98
Table 2.2.3.1.1.1	Funding Sources and Partners	99
Table 2.2.3.1.3.1	COE from IGCC Cases with and without CO ₂ 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 CO ₂ Removal with Other Options (Jack, 2008).....	116

PROPRIETARY -- Do Not Reproduce or Redistribute!

This message is in red ink. If not, you have an unauthorized copy.

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