Novel High Capacity Oligomers for Low Cost CO_2 Capture

GE Global Research
GE Energy
University of Pittsburgh

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Annual NETL CO2 Capture Technology for Existing Plants R&D Meeting

March 24-26, 2009

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GE Global Research

World R&D Headquarters: Niskayuna, NY

First US industrial lab

Founding principle … improve businesses through technology

One of the world's most diverse industrial labs

Partnering with governments, industry, and academia

Program Objectives

For post-combustion CO_2 capture from a coal-fired power plant:

- Develop a novel, oligomeric solvent
- 90% Carbon capture efficiency
- Less than 35% increase in Cost of Energy Services

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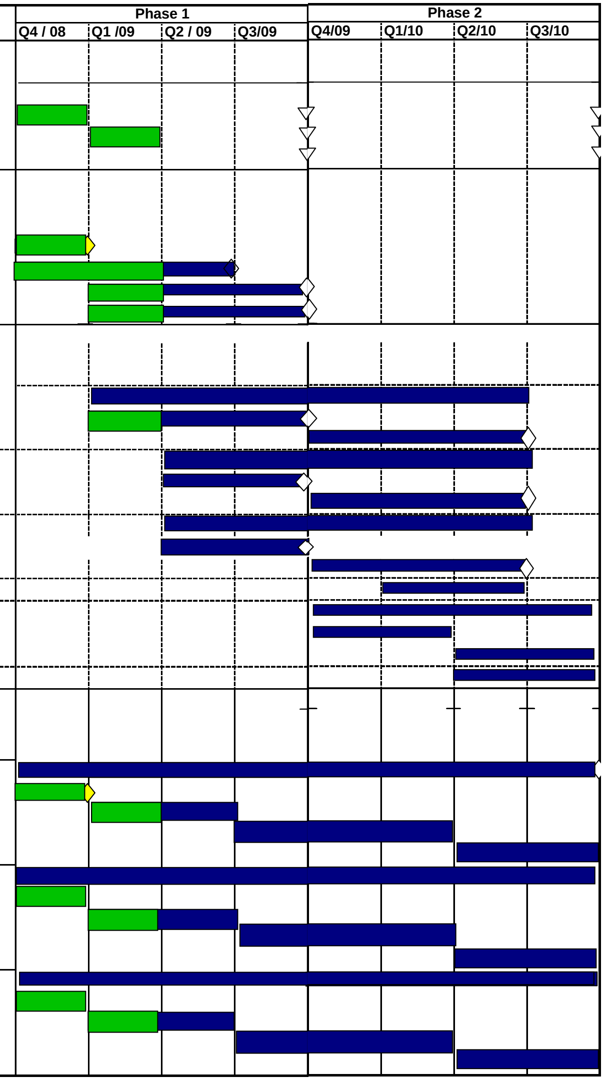
Schedule

	Participants
Task 1 Project Management and Planning	
Comprehensive topical reports delivered at the completion of each budget period.	**GE GRC** / GE Energy
Presentation of technical papers at the DOE/NETL annual contractor's review meeting	
Presentation of detailed briefings to the project officer at least once per year.	
Task 2 Screening and selection of solvent classes for CO2 capture	
2.1 Proposed solvent classes	**GE GRC** / U. Pitt
2.2 Selection of solvent classes	**GE GRC** / U. Pitt
2.3 Bench scale, multi-property determination of commercially available solvents	**GE GRC**
2.4 Synthetic strategy development for classes of solvent	**GE GRC**
Task 3 CO2 capture solvent synthesis, optimization and property testing	
3.1 Method development and high throughput synthesis of solvent libraries within the selected	**GE GRC**
3.1.1 Gen 1 Libraries	
3.1.2 Gen 2 Libraries	
3.2 High throughput evaluation of selected property within the synthesized solvent libraries	**GE GRC**
3.2.1 Gen 1 Libraries	
3.2.2 Gen 2 Libraries	
3.3 Multi-property modeling of lead candidates identified in 3.2 (vapor pressure, thermal stabili	**GE GRC**
3.3.1 Gen 1 Libraries	
3.3.2 Gen 2 Libraries	
3.4 Multi-property determination, and lead validation for the candidates selected from 3.2 and :	GE GRC / **U. Pitt**
3.5 Bench scale lead solvent performance evaluation (complete adsorption/desorption cycle de	**GE GRC**
3.5.1 Gen 1 lead lab demo	
3.5.2 Gen 2 lead demo	
3.6 Degradation testing / Enviromental testing	**GE GRC**
Task 4 Process modeling and cost of energy services	
4.1 Absorption & Stripping Cycles and Plant Simulation	GE Energy
4.1.1 Calibrated Plant Model	
4.1.2 Parametric Solvent and Plant integration study with class of materials	
4.1.3 Model "GEN 1" solvents in plant models	
4.1.4 Optimize plant around "GEN 2" Solvents	
4.2 Size layout & Operating Cost	GE Energy
4.2.1 Calibrated Plant Model	
4.2.2 Parametric Solvent and Plant integration study with class of materials	
4.2.3 Model "GEN 1" solvents in plant models	
4.2.4 Optimize plant around "GEN 2" Solvents	
4.3 Cost of Electricity calculations	GE Energy
4.2.1 Calibrated Plant Model	
4.2.2 Parametric Solvent and Plant integration study with class of materials	
4.2.3 Model "GEN 1" solvents in plant models	
4.2.4 Optimize plant around "GEN 2" Solvents	



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Two Year Program in Modeling and Experiments

Scope

Identify oligomeric solvents

Methods

- Molecular modeling to identify candidate solvents
- Synthetic chemistry to prepare solvents in the lab
- High throughput screening for relevant properties
- System modeling integrated with power plant model
- Cost of energy services analysis

Phase 1

- System model development
- Screening and selection of solvent classes
- Synthetic strategy development
- Development of Gen 1 solvents

Phase 2

- Synthesis & Test Gen 2 solvents
- Bench scale test most promising solvents
- Model refinement
- Degradation testing
- Predict overall solvent and plant performance

Milestones

Phase 1

Milestone	Completion Date	Status
Detailed Plant Model	12/31/08	Completed
Solvent property targets	12/31/08	Completed
Parametric studies/properties	6/30/09	
Synthetic strategy developed	9/30/09	

Go/No Go: Demonstrate capacity 25% greater than MEA w/ 50% increase in COE

Phase 2

Milestone	Completion Date	Status
COE understood for Gen 1 solvents	3/31/09	
Leads from Gen 2 solvents	6/30/09	
Bench tests/ physical properties	6/30/09	
Solvent lifetime / degradation	9/30/09	
COE target <35% at 90% capture	9/30/09	

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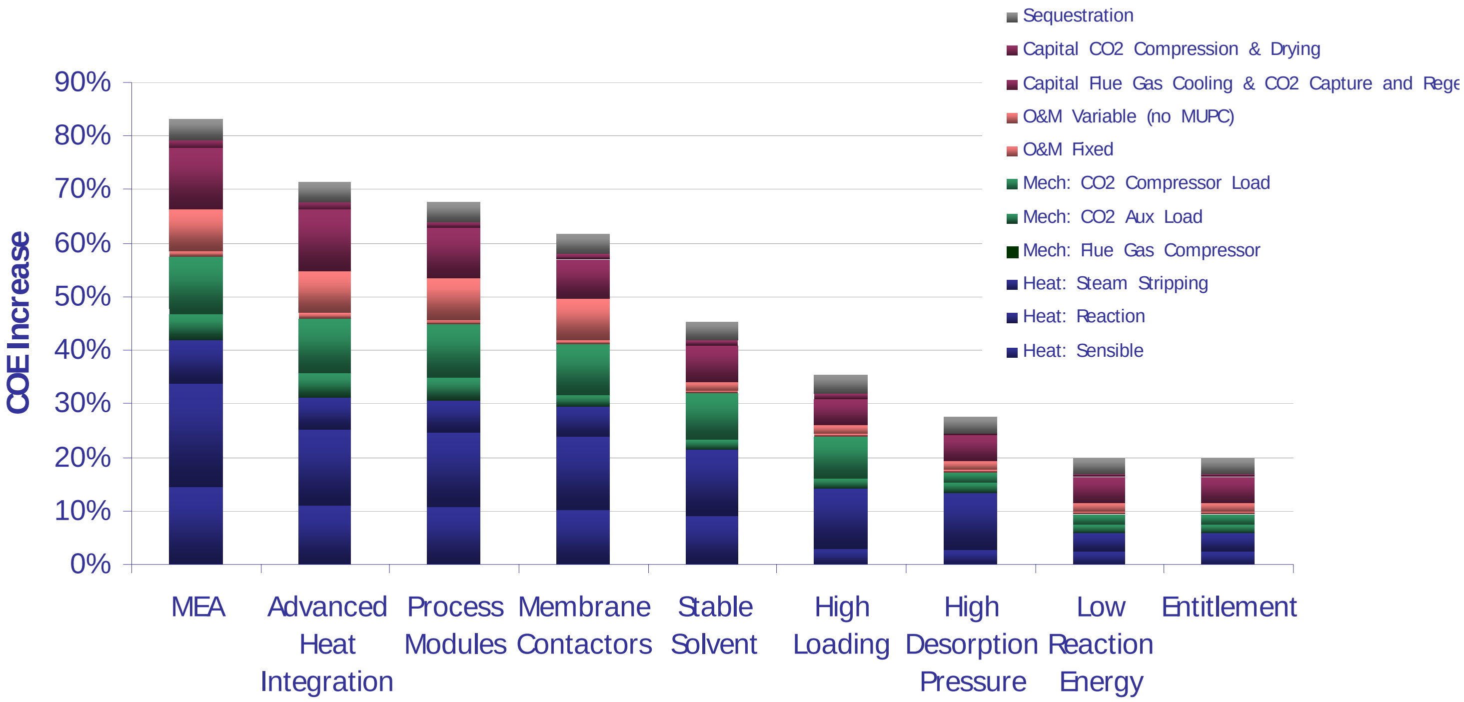
Budget

	BP1			BP2			Total		
	Gov't Funding	Cost Share	Total	Gov't Funding	Cost Share	Total	Gov't Funding	Cost Share	Total
GE Global Research	$982,676	$317,600	$1,300,276	$745,436	$236,302	$981,738	$1,728,112	$553,902	$2,282,014
GE Energy	$241,948	$0	$241,948	$253,102	$0	$253,102	$495,050	$0	$495,050
Univ. of Pittsburgh	$174,553	$32,194	$206,747	$75,447	$32,194	$107,641	$250,000	$64,388	$314,388
Total	$1,399,177	$349,794	$1,748,971	$1,073,985	$268,496	$1,342,481	$2,473,162	$618,290	$3,091,452

- $3 Million cost-shared program
- Finishing second quarter of program
- All teams up and running

Technology Intro

Cost of Electricity Components Define Critical Chemical Characteristics



Solvent properties – a significant influence on COE

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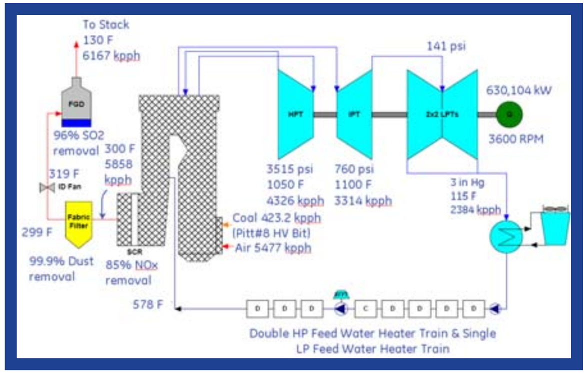
Relating Chemistry to COE

Chemical Parameters

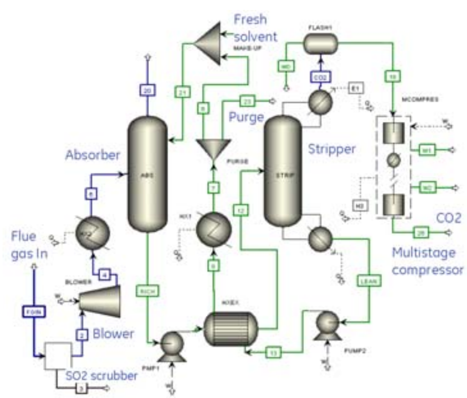
- Stable Solvent
- Low volatility
- High Loading
- Low Heat of Reaction
- High reaction rate
- High Desorption Pressure
- Low cost

Plant & Process Models

A detailed calibrated coal power plant model complete in Thermoflow & THB



Non-Aqueous chemistry requires new process designs in Aspen Plus



Cost of Electricity

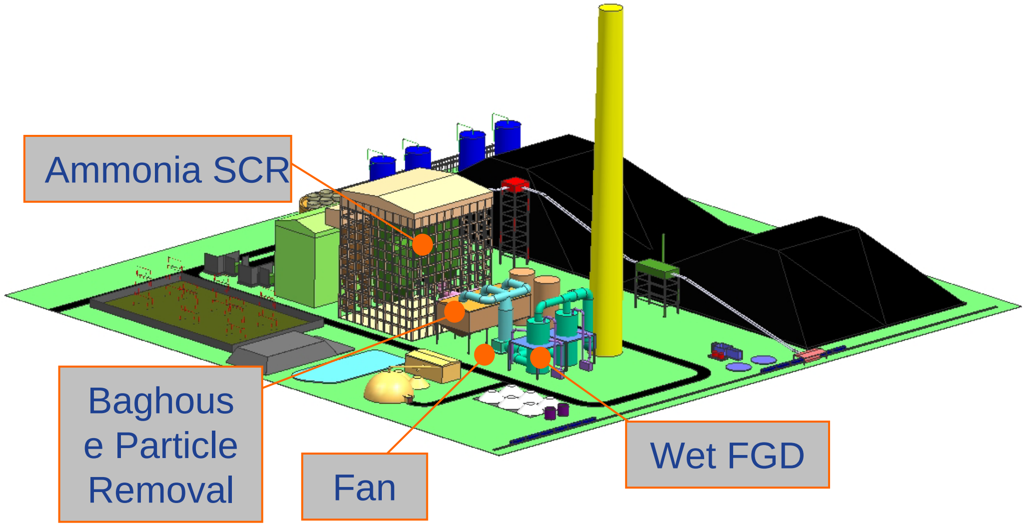
Cost of Electricity Model Complete, calibrated to DOE references

	2007 DOE COE Report	GE Energy Coal Plant
Plant Efficiency	39.1%	38.1%
Plant Output (MW	550	586
Plant Cost ($MM)	$866	$1,362
$ / kW	$1,575	$2,324
Capital Recovery	3.5	**5.3**
Fuel	1.9	2.0
O&M	1.0	1.1
Total	**6.3**	**8.4**

Work backwards from plant requirements to solvent

Plant Model

Plant Overview



630 MW Gross Super critical coal fired plant

South Eastern U.S.
- Ambient 95 F, Wet Bulb 80 F
- Relative Humidity 53%

Super Critical Steam Turbines
- HP 3515 psia, 1050 F
- IP 760 psia & 1100 F
- LP 141 psia

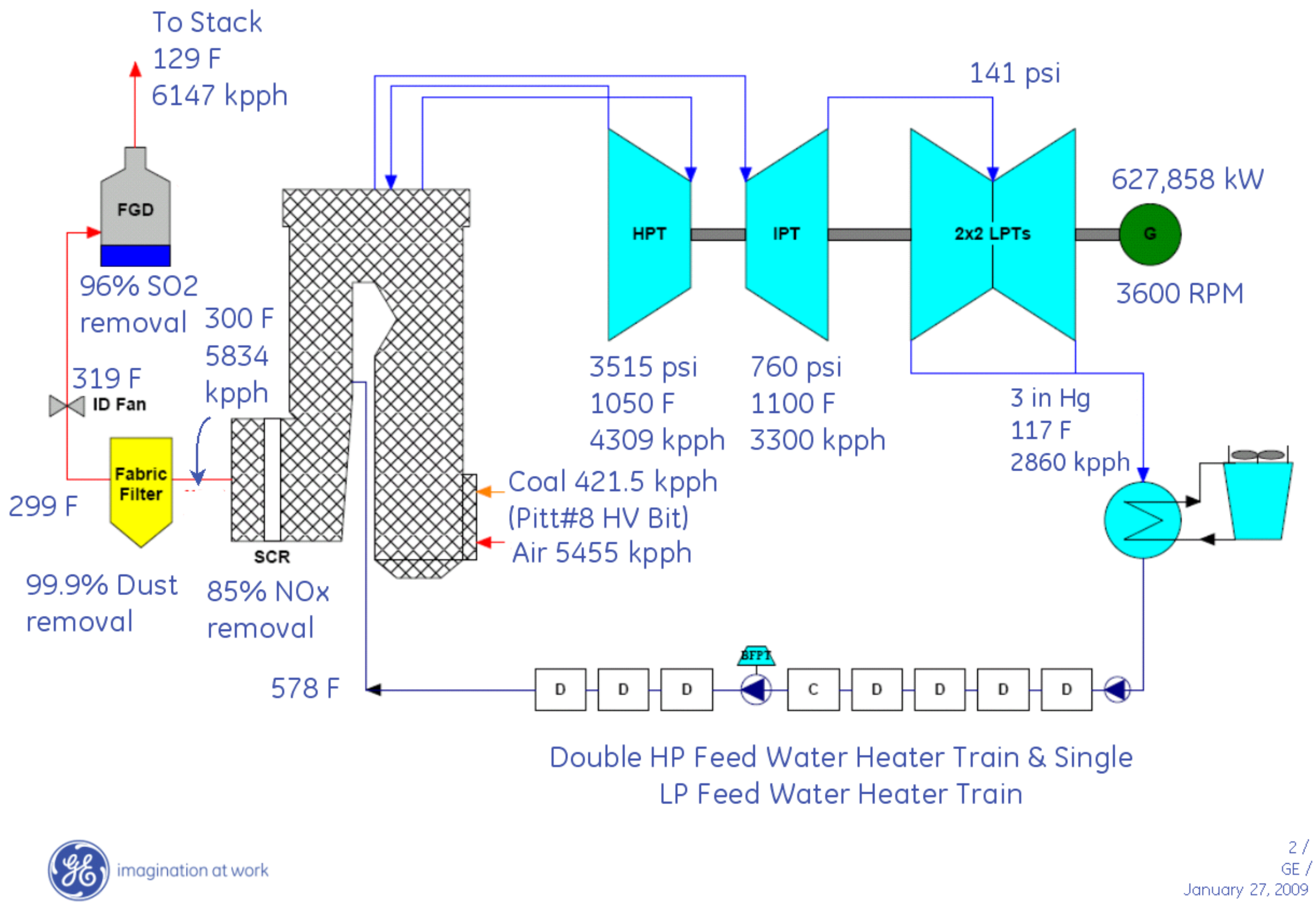
Generator 13.8 kV, Transmission 765 kV

Excess Air - 20%

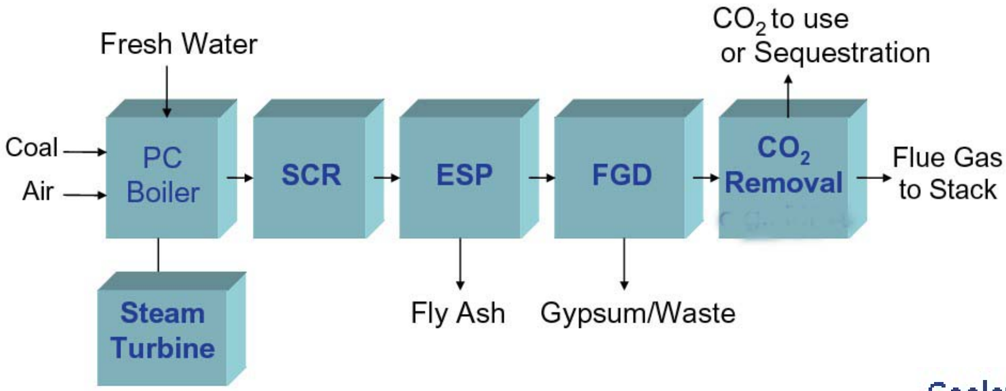
Pittsburgh No. 8
- Eastern High Volatile Bituminous Coal
- HHV – 12,450 Btu/lb
- 9.94% Ash
- 6% moisture
- 2.89% Sulfur

Emission Regulations
- NOx – 0.07 lb/mmBTU
- SOx – 0.182 lb/mmBTU
- PM – 0.035 lb/mmBTU

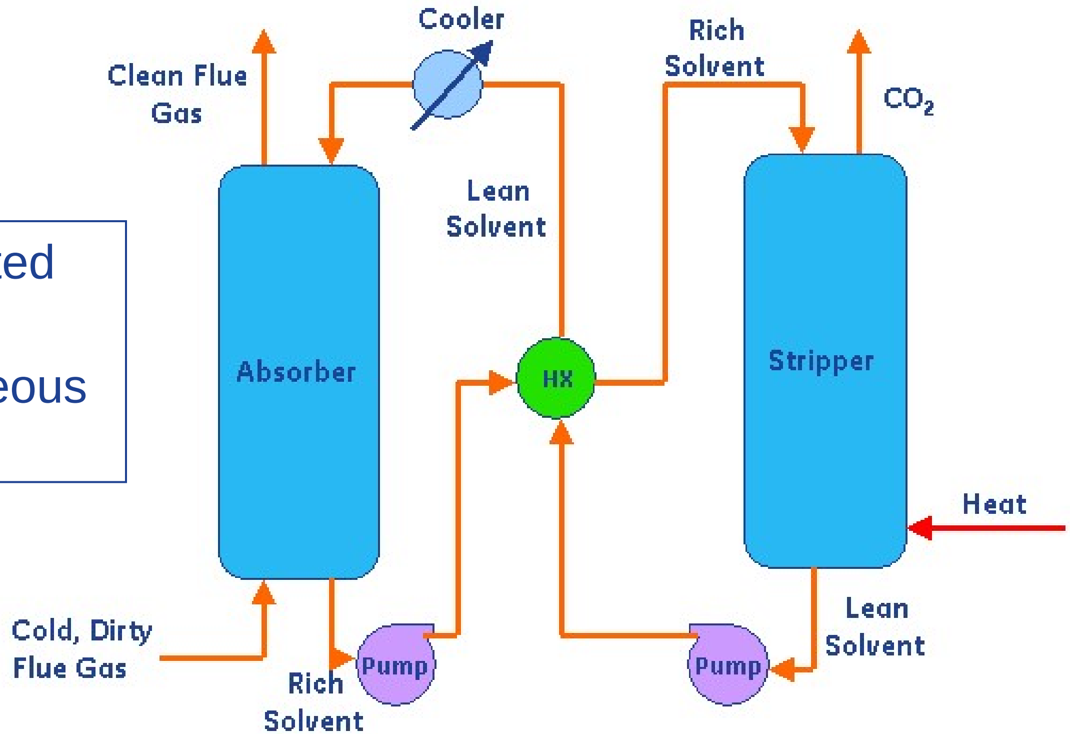
Overall Plant Summary



Capture Plant Schematic



- Capture plant added to overall model
- Unit operations changeable



- ASPEN model validated with MEA
- Modified for non-aqueous solvent

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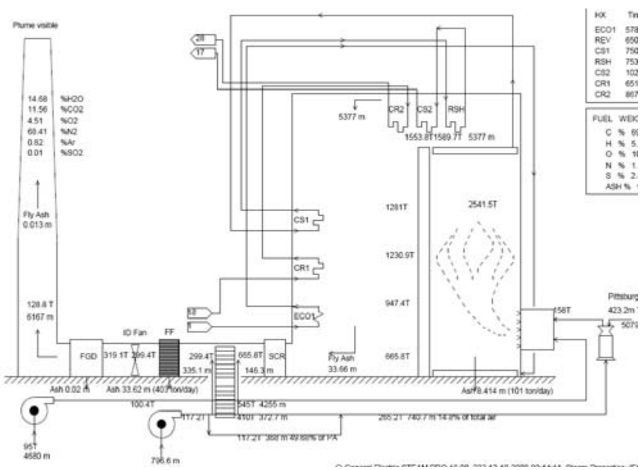
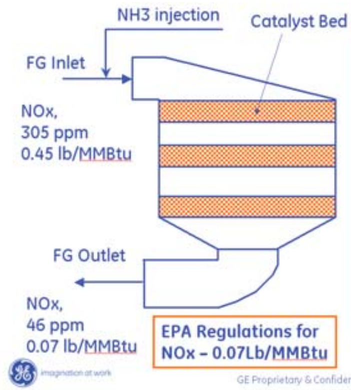
Detailed Process Models

Thermoflow process models calibrated with external references

Boiler



SCR

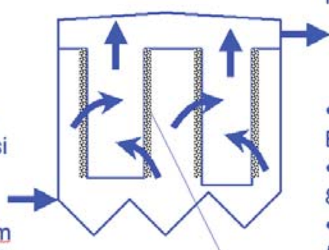


Vol, Mcfm	2.53
Mass*, kpph	5410
Temp, F	666
Pressure, psia	14.6
Number of reactors	3
Gas Velocity	16
NOx reduction	85%
Pressure Drop, in H2O	7
NOx removed, kpph	2.03
NH3 consumed, kpph	0.75
NH3 Slip, kpph	0.009
Power, kW	213

*5626 kpph for Santee Cooper Pee Dee, ~615 MW Gross

Baghouse

PM – 0.006 lb/MMBtu
Fly Ash – 0.03 kpph



- Flue Gas Inlet
- PM – 6.4 lb/MMBtu
- Pressure – 14.14 psi
- Temp – 300 F
- Mass – 5899 kpph
- Volume – 1.93 mcfm
- Fly Ash – 33.81 kpph

- Dust Collection Efficiency 99.9%
- Power Consumption 832 kW
- W x D x H = 296 ft x 54 ft x 70 ft

Fly Ash removed – 33.78 kpph

- Type – Pulse-jet
- Material – Fiberglass
- Number of Casings – 4
- Total Cloth Area – 0.58 M ft^2

EPA Regulations for PM 0.035 Lb/MMBtu. Further Particles removed by FGD

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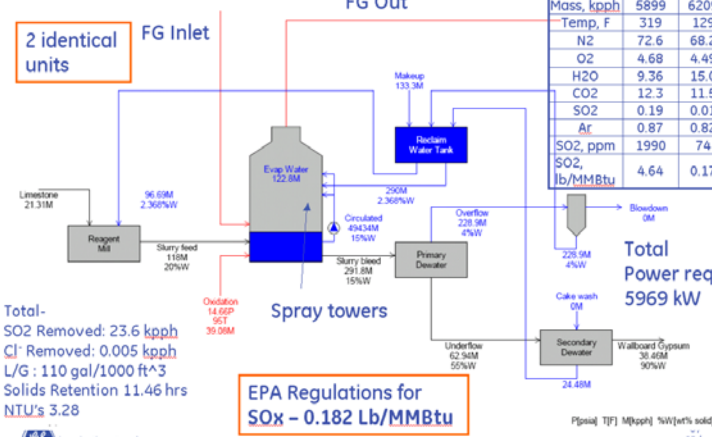
January 16, 2009

FGD

	FG In	FG Out
Mass, kpph	5899	6209
Temp, F	319	129
N2	72.6	68.2
O2	4.68	4.49
H2O	9.36	15.0
CO2	12.3	11.5
SO2	0.19	0.01
Ar	0.87	0.82
SO2, ppm	1990	74
SO2, lb/MMBtu	4.64	0.17



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Power

Plant model captures key auxiliary energy flows affected by carbon capture

Details	DOE Report	% of Gross	Current Model	% of Gross
Gross Power, kW	**586,980**	**100.00%**	630,107	100.00%
Coal Handling, kW	2,590	0.44%	3,411	0.54%
Ash Handling, kW	2,070	0.35%	841	0.13%
Primary Air Fans, kW	1,220	0.21%	1,406	0.22%
Forced Draft Fans, kW	2,550	0.43%	1,996	0.32%
Induced Draft Fans, kW	9,160	1.56%	9,574	1.52%
SCR, kW	300	0.05%	212	0.03%
Baghouse, kW	100	0.02%	806	0.13%
FGD Pumps & Agitators, kW	6,620	1.13%	5,934	0.94%
Condensate Pumps, kW	780	0.13%	1,015	0.16%
Circulating Water Pumps, kW	4,170	0.71%	5,265	0.84%
Cooling Tower Fans, kW	2,370	0.40%	2,265	0.36%
Misc. BOP, kW	5,270	0.90%	8,820	1.40%
Total Auxiliaries, kW	37,280	6.35%	41,545	6.59%
Net Power, kW	**549,700**	**93.65%**	**588,562**	**93.41%**
Net Efficiency (HHV) %	**39.50**		**38.11**	
Net Heat Rate (HHV), Btu/kWhr	8,646		8,953	
Type of Coal	IL#6 HV Bit		Pitt#8, East HV Bit	
Ash in Coal, wt%	9.7		9.9	
Moisture in Coal	11.1		6	
Sulfur in Coal	2.51		2.89	

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Cost of Electricity (COE) Calculation

Cost of Electricity Calibrated to DOE rates, capital cost differs

		Symbol	Units	GE Calculation	DOE Reference
Inputs	Present Worth Discount Rate	i	-	10.5%	10.5%
	Annual Escalation Rate	e	-	2.5%	2.5%
	Number of Years (Period)	n	-	20	20
	Capital Charge Factor	FCR	-	16.4%	16.4%
	Net Power Output	P	kW	586,239	550,150
	Plant Net Efficiency (HHV)	h	-	38.12%	39.10%
	Capacity Factor	f	-	0.85	0.85
	Fuel Cost (HHV)	c_{fuel}	USD/MMBtu	1.803	1.803
	Variable O&M Cost	c_{var}	USD/MWh	4.0	4.9
	Fixed O&M Cost	c_{fix}	USD/kW	39.0	25.2
	Plant Total Capital Investment	TCI	USD	1,362,000,000	865,936,100
Levelization Factors	Capital Recovery Factor	CRF	-	12.1%	12.1%
		K	-	0.93	0.93
	Levelization Factor	F_L	-	1.21	1.21
Plant Performance	Annual Operating Hours	T	hrs	7,446	7,446
	Annual Energy Output	PT	kWh	4,365,135,594	4,096,416,900
	Fixed Annual Operating Cost	C_{fix}	USD	22,863,321	13,847,276
Levelized COE	COE - Fixed O&M		cents/kWh	0.63	0.41
	COE - Variable O&M		cents/kWh	0.48	0.59
	COE - Fuel		cents/kWh	1.95	1.90
	COE - Capital Recovery		cents/kWh	5.12	3.47
	COE - Total		**cents/kWh**	**8.19**	**6.37**

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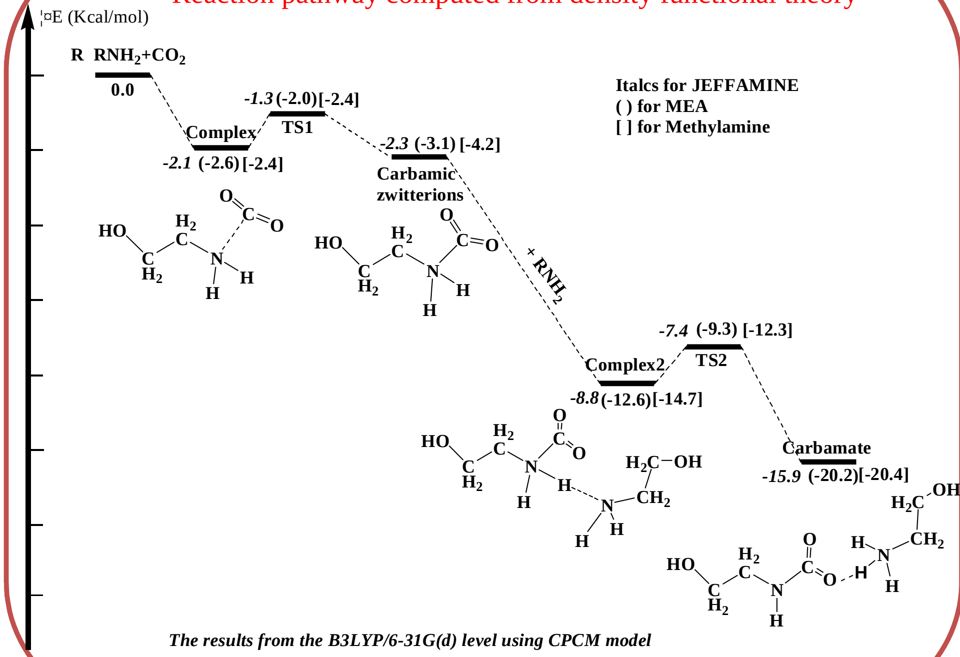
Molecular Modeling

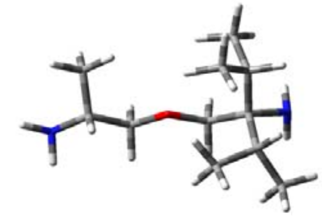
Molecular Modeling

Reaction pathway computed from density functional theory



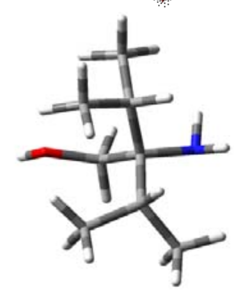
Design

New compounds with lower heats of reaction



1,1-di-isopropyl JEFFAMINE

Heat of reaction = -9.4kcal/mol



1,1-di-isopropyl MEA

Heat of reaction = -10.4kcal/mol

Calculations for designing new amines that have heats of reaction in a desirable range (~-8.5 to -10 kcal/mol)

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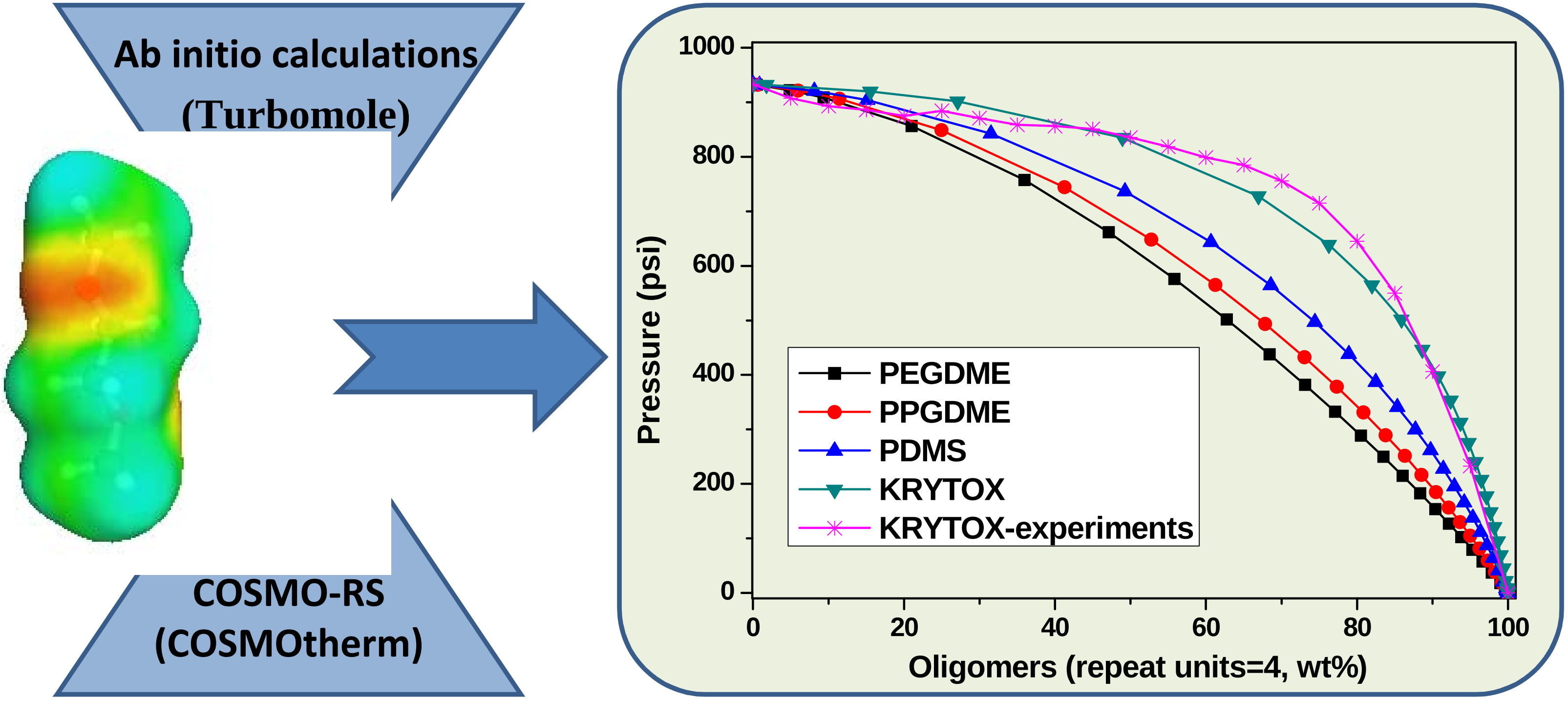
Molecular Modeling

Vapor liquid equilibrium of CO_2+ Oligomers

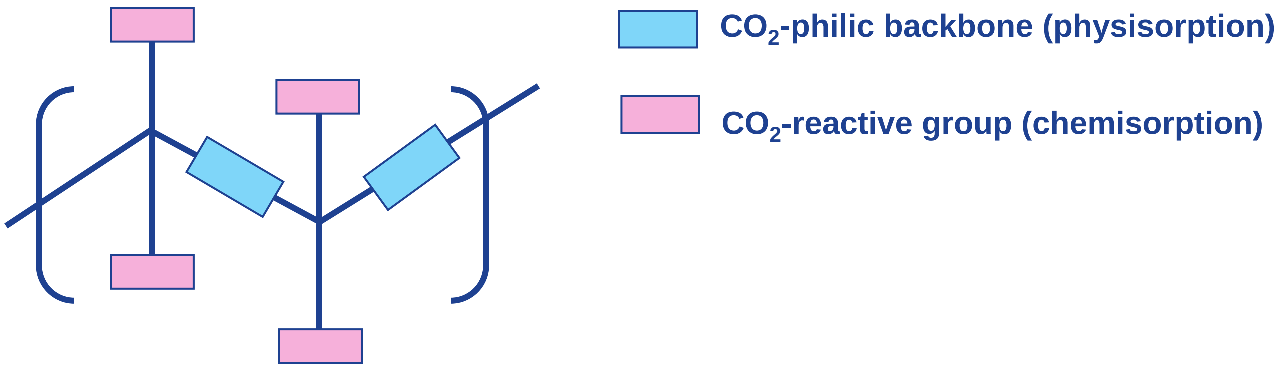


Calculations from COSMOtherm quantitatively predict the solubility of CO_2 in various oligomers. Future work: Design new materials that have higher solubility of CO_2.

Proposed Solvent Classes and Physical Property Targets

Background

Concept Solvent

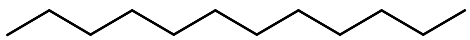


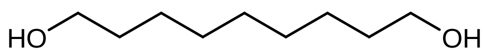
- Backbone or core that is CO_2-philic
- Reactive functional groups that chemically combine with CO_2
- Chemical experience and modeling to generate promising leads

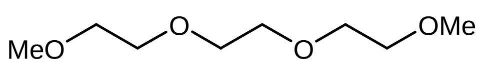
Proposed Solvent Classes

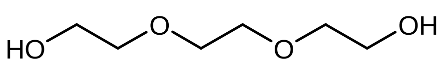
Model Compounds

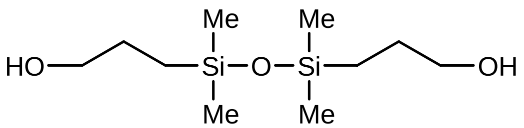
Physisorption

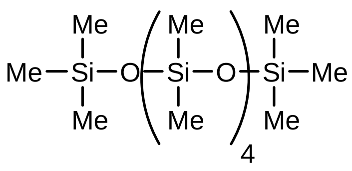




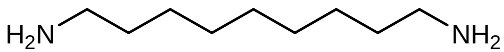


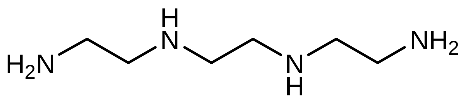




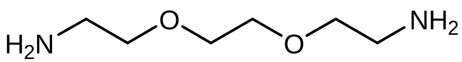


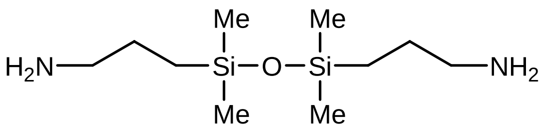
Chemisorption





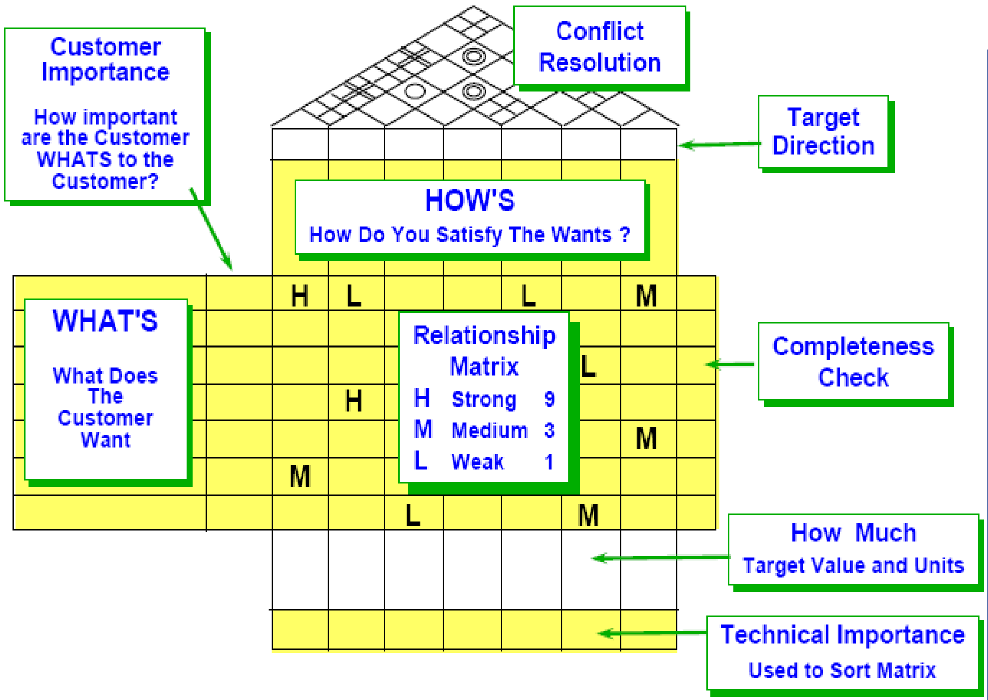
Both





- **Commercially available model compounds for benchmarking**
- **Determination of backbone effect and functional group reactivity**
- **Decouple physisorption from chemisorption**
- **Validate concepts and testing protocols**

Quality Function Deployment (QFD)



The 9 Elements of a QFD House of Quality

Quality Function Deployment (QFD)

- Structured methodology to identify and translate desirable features, measurable targets, and characteristics into technical requirements for reasearch and development
- Rank testing process
- Improve likelihood of meeting requirements
- Validate hypothesis in testing against highest attribute scores
- Reduce product development time

6σ six sigma

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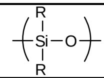
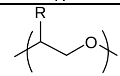
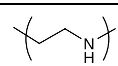
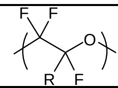
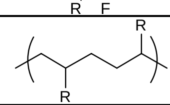
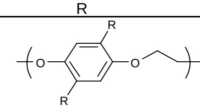
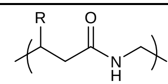
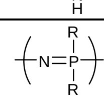
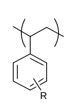
Proposed Solvent Classes

QFD Matrix of Solvent Backbones

backbone	Structure	attribute: physical state	cost (inexpensive)	synthetic availability	ease of derivatization	CO2-philic	stability	total
siloxane		9	5	9	9	9	9	**50**
alkyl ether		9	9	9	5	5	9	**46**
alkyl amino		5	9	9	5	9	9	**46**
perfluoroether		9	1	5	1	9	9	**34**
alkyl		9	9	9	5	1	9	**42**
aryl ether		1	5	5	5	5	5	**26**
alkylamido		5	5	9	5	5	5	**34**
phosphazene		5	1	5	5	5	1	**22**
Polystyrene		1	9	9	9	1	9	**38**

physical state	must be low vicoisty liquid	9=liquid, 5=viscous liquid, 1=solid
cost (inexpensive)	should be < $10/lb	9=<$10/lb, 5=$10-2-/lb, 1=>$20/lb
synthetic availability	able to be made on large scale	9=commercial, 5 = small scale, 1 = laboratory
ease of derivatization	must be easily functionalized	9=easy, 5 = moderate, 1 = difficult
CO2-philic	physisorption	9=high, 5=moderate, 1=low

- **Down-selection of most promising core structures**
- **Based on properties, availability and chemistry**

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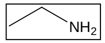
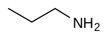
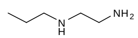
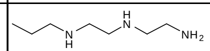
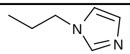
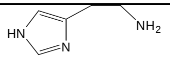
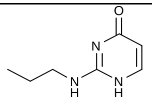
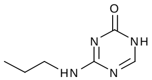
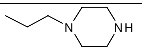
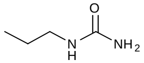
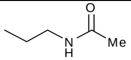
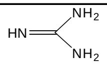
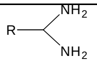
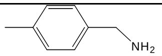
Proposed Solvent Classes

QFD Matrix of CO_2-reactive Functionality

Functional Group	Structure	attribute					Total
		CO2 capacity	Heat of reaction	Kinetics	Ease of attachment	Cost	
Aminoethyl		5	5	9	5	9	**33**
Aminopropyl		5	5	9	9	9	**37**
Aminoethylaminopropyl		9	9	9	9	9	**45**
Bis(aminoethyl)aminopropyl		9	9	9	9	9	**45**
Imidazole		1	1	1	9	5	**17**
Histamine		5	9	1	5	1	**21**
Isocytosine		5	5	5	5	1	**21**
5-Azacytosine		9	5	5	5	1	**25**
Piperazine		9	9	9	9	5	**41**
Urea		5	5	1	5	9	**25**
Acetamide		1	5	1	5	5	**17**
Guanidine		9	5	9	1	5	**29**
Amidine		9	5	9	9	5	**37**
Benzylamine		5	9	5	9	5	**33**

CO2 capacity	9=high, 5=moderate, 1=low	
Heat of reaction	9=moderate, 5=low, 1=high	
Kinetics	9=fast, 5=moderate, 1=slow	(reaction with CO2)
Ease of attachment	9=easy, 5=doable, 1=difficult	

- **Down-selection of most viable candidates**
- **All reactive sites are amine-derived**
- **Green have highest attribute score**

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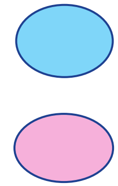
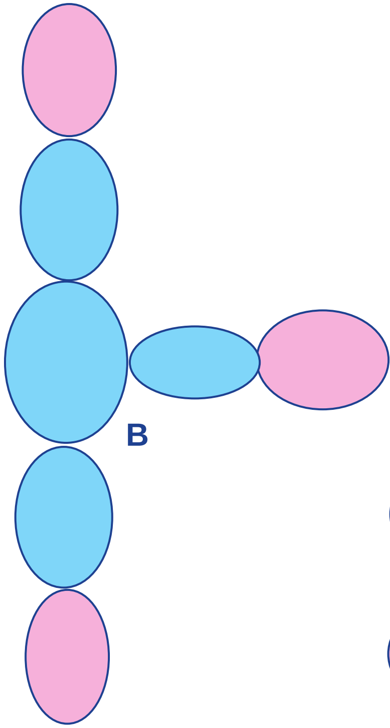
Proposed Solvent Classes





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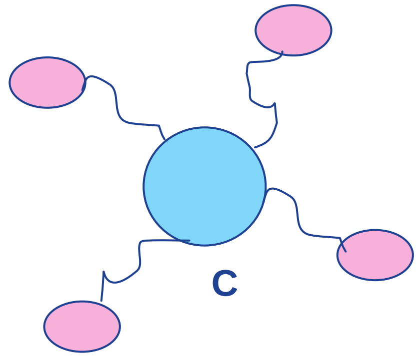
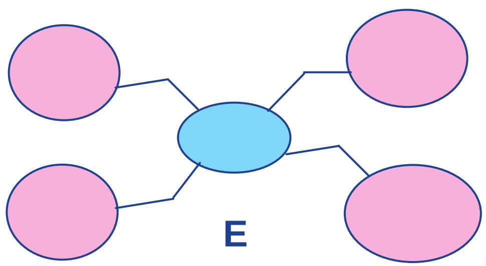
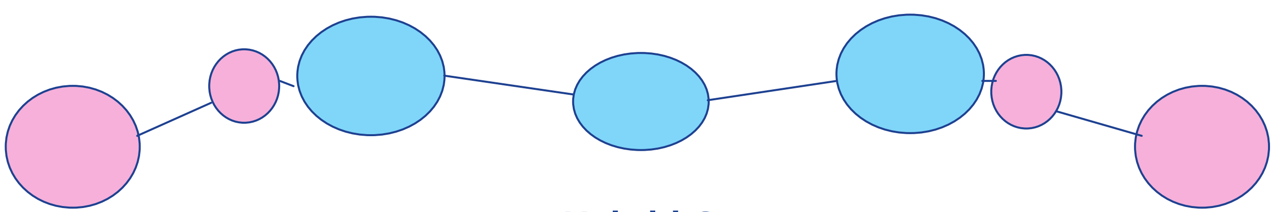


C



E

Target Solvent	Theoretical CO_2 wt % gain
30% MEA (Baseline)	10.8
Silicone target A	15.8
Silicone target B	16.3
Silicone target C	18.8
Silicone target D	25.9
Silicone target E	44.7
Carbon/Hybrid target A	18.9
Carbon/Hybrid target B	21.2
Carbon/Hybrid target C	23.8
Carbon/Hybrid target D	29.5



Hybrid C

CO_2 Capture Solvent Synthesis, Optimization and Property Testing

48-Well Reactor for Rapid Throughput Screening of CO2 Solvents

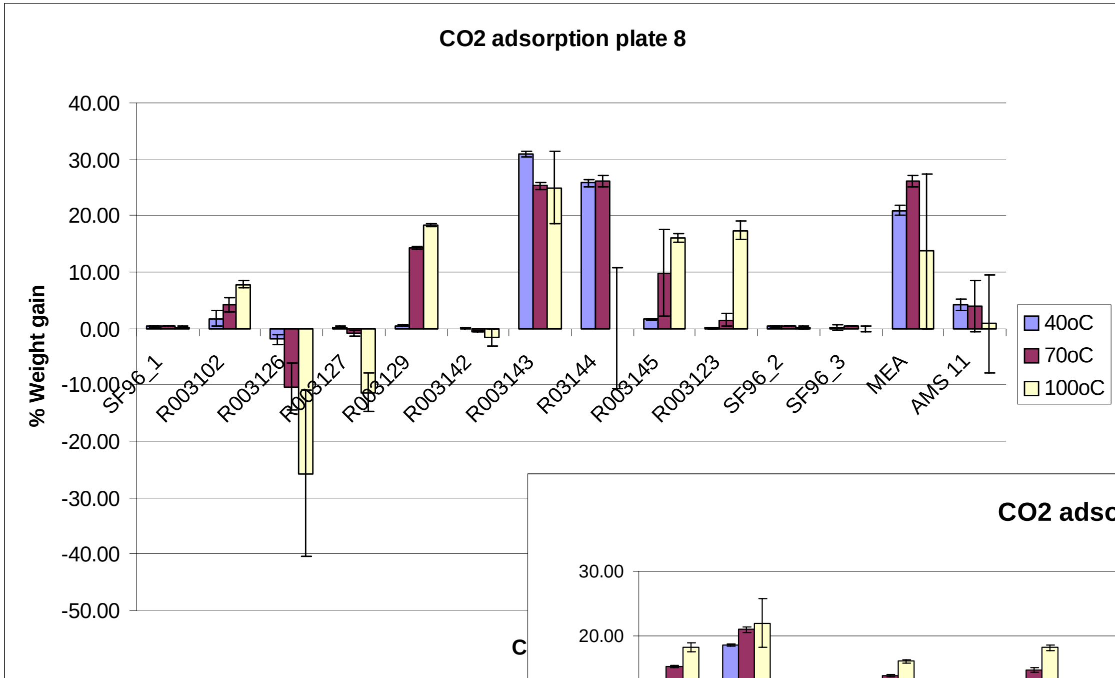
System

- Temperature controlled
- Multiple gas input capabilities
- Coupled to robot for sample weighing
- Screen ~10 samples/day with replicates and controls

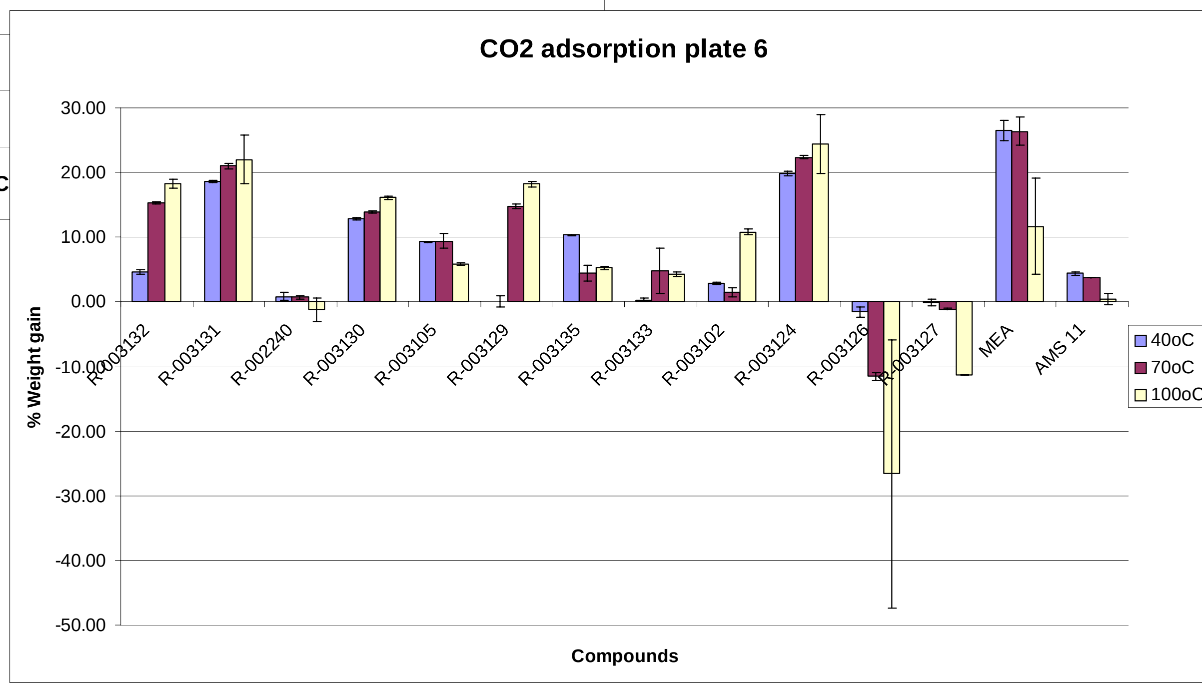
Strategy

- Synthetic strategy begun
- Screening readily available solvents
- Allow information generation to learn quickly
- Predict & understand factors

Initial Screening Results



- 1 atm CO_2
- 3 temperatures (40, 70, 100 ^oC)
- Replicate samples
- Control samples included



- 100% MEA as control
- Organic amine controls and silicone-based materials
- Loss of wt = volatile solvents

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Risk Analysis

High risk

Moderate risk

Low risk

Risk	Likelihood	Severity	Total risk
Synthesis and scale up			
high cost	9	9	**81**
Unavailability of starting materials/no toller/excessive synthetic steps/low yield	5	9	**45**
Ease of synthesis/hazardous by-products/false responses/low yield	5	5	**25**
Physico chemical properties of lead candidates			
High viscosity of reaction products/poisoning of amine	9	9	**81**
hydrolytic, thermal, oxidative, pH stability, toxicity	5	9	**45**
Non-Newtonian fluid/low solvent volatility/collateral emissions	5	5	**25**
too volatile/high freezing point	1	9	**9**
CO2 adsorption/desorption (Activity)			
Slow CO2 absorption,desorption kinetics/high heat of reaction/degradation of solvent	9	9	**81**
Low working capacity in design space (net loading)/poor CO2 capture at low pressure	5	9	**45**
Insufficient data to develop useful model & process design/CO2 prematurely desorbing	5	5	**25**
Need to separate water and CO2 after desorption	9	1	**9**
Process/plant			
Proposed process too costly/footprint to large	9	9	**81**
Low accuracy of the plant model/unit operations require significant modifications	5	9	**45**
Scale-up demonstration issues/poor integration with power plant/variation in exhaust from one facility to another	5	5	**25**
IP issues			
Prior IP on composition of matter or process that limits freedom of practice	5	9	**45**
Prior art on composition of matter, process found that prevents patenting	5	5	**25**
Jointly developed IP lead to GE/Upitt issues	1	5	**5**
EHS			
disposal/operation	5	9	**45**

Possible Abatements

- Similar, readily available material
- Chemistry change, engineering option
- Viscosity improve, contacting equip.
- Model optimization

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Summary

- Solid plan in place for program execution
- Reliable plant model to guide experimentation
- Sound molecular modeling capabilities for property prediction
- Viable chemistry options for solvent synthesis
- Analytical tools in place for rapid screening
- Bench scale adsorption apparatus being assembled
- Desorption protocol being examined
- Focus on absorption parameters

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