PNNL-24530

Accelerating the Development of "Transformational" Solvents for CO2 Separations

Quarterly Progress Report, Budget Period 1, Q4, 2015

May 2016

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U.S. DEPARTMENT OF ENERGY

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I. Accomplishments and Milestone Update

Synopsis of Accomplishments

The team made contributions in three key areas in the last quarter. The modeling team continued to screen 100 molecules in order to meet Milestone 2, while also working on refinement of the reduced model to calculate viscosity without the time-intensive full-scale Classical Molecular Dynamics simulations. The team crafted a revised model that takes into account the hydrogen bond orientation and strength, without having to perform time-intensive calculations. The reduced model's performance is discussed in more detail below. The synthesis team had made 13 candidate molecules to meet Milestone 3 prior to the Go-No-Go and have been scaling up promising molecules for testing in task 4, and to meet Milestone 4. The experimental team has been working on shakedown testing of the new PVT cell, that will measure standardized VLE, kinetics and viscosity data, limiting sample volumes to 30 mL. A more detailed description of the shakedown can be found below.

Programmatically, the project output was cut by 1/3 due to a delay in the delivery of the June FIN Plan funds. The project team issued a stop work, and productivity suffered as a result. Details on the stop-work's impacts on schedule, task and budget are provided in more detail below.

Milestones

The project team completed Milestones 1-3 and 5, with work on Milestone 4 delayed due to the stop work. The team was working on the experimental testing of the new candidate compounds when the stop-work was issued, preventing experimental validation of viscosity for new CO_2BOL candidates using the new PVT cell. The team is slated to meet Milestone 4 in the next Quarter, and will ramp up efforts to meet Milestones 6 and 7 by the calendar year's end.

Table 1. Major Milestones Relevant to BP1.

Milestone	Milestone Description	Estimated Completion	Performance
1	Updated Project Management Plan	April, 2014	Complete
2	Construct Physical Property Model	October, 2014	Model is complete and 100 molecules have been modeled
3	Synthesize and characterize 13 Candidate CO_2BOL Molecules	May, 2015	13 molecules have been made and tested, 4 are scaled up for testing

4	Viscosity Reduction of 200 cP demonstrated	May, 2015	Viscometer/VLE cell is Assembled, Viscosity & loading tests underway
5	Go no-go presentation at NETL	April, 2015	Completed
6	Synthesize and Characterize 13 Candidate CO_2BOL Molecules	December, 2015	
7	Viscosity Reduction of 400 cP Demonstrated	January, 2015	
8	Synthetic Methodology of Optimal CO_2BOL Demonstrated at $10/kg	March, 2016	
9	Final report provided to NETL	April, 2016	

Project Accomplishments by Task:

Task 1. Project Management

Subtask 1.1 General Project Management

The PMP was updated and sent to DOE as required.

Task 2. Molecular Development

Subtask 2.1 Design 100 candidate molecules based on variations of current formulation

Subtask 2.1 was completed.

Subtask 2.2 Construct physical property prediction model

Model Findings:

Subtask 2.2 was completed in the last budget period.

Subtask 2.4 Revise performance targets and design the second 100 molecules

Computational efforts in the third quarter focused on the screening and compiling a computational library of 100 CO_2BOL structures, in their pristine (no CO_2) and loaded (with CO_2) states. In the first step, the CO_2 binding energy was determined in the gas phase and in the

presence of a dielectric continuum to obtain optimized structures and atomic charges to be used in the subsequent molecular dynamics (MD) simulations.

Predictions of viscosity are obtained from classical MD simulations performed on a subset of the screened compounds. Using knowledge from the initial MD simulations, a reduced model that approximates viscosity as a function of CO_2 loading was developed that included a structural parameter representing the internal Lewis acid/base pair formed upon CO_2 capture, $COO^{\cdots}H^{\cdots}N$, see equation (1), and Figure (1).

$$\eta = c_1 \ln\left(\frac{P_{int}}{1 - P_{int}}\right) e^{c_2 L}$$

where *Pint*=0.0001 if r_{OH}>2.0 Å and *Pint*=f(X) if r_{OH}<2.0 Å with $X = \frac{q_O q_H / r_{O-H}}{q_N q_H / r_{N-H}}$.

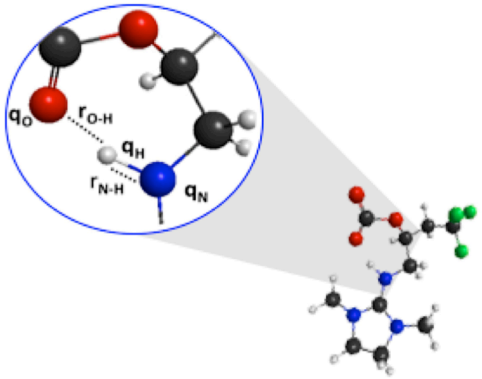


Figure 1. Structural parameters determining the functional form of hydrogen bonding and viscosity in the reduced model.

The correlation between MD-calculated viscosities from the initial subset (~15 viscosity calculations) and the viscosities predicted with the reduced model are shown below in Figure 2. We identified five promising candidates from the reduced model (Table 1), with viscosities at 25% loading all under 50 cP. These five molecules will be synthesized and tested in the next BP.

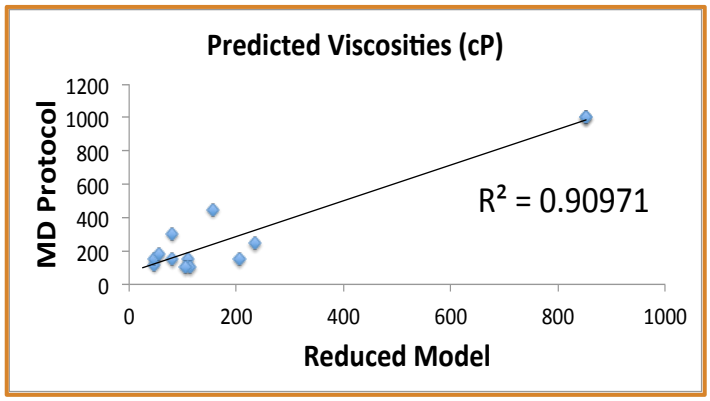
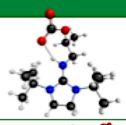
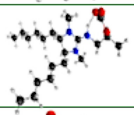
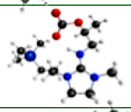
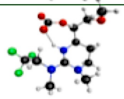
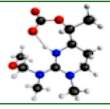


Figure 2. Correlation between the viscosities obtained from full MD simulations and the reduced model.

Table 1. Five top synthetic candidates based on predicted viscosity values from the reduced model.

Compound	Pint (Model predicted)	ΔΔE (kJ/mol) (CO_2 BE)	(cP)(25%) Reduced model
DJL 	87%	0.8	18
AJL 	79%	16.2	30
IDL 	75%	11.7	35
EWL 	75%	-8.2	37
EVL 	69%	-4.1	46

We also identified ten compounds from the 2nd subset so we can test the reduced model, and determine viscosities with classical MD, including silane-based CO_2BOLs and some with a new oxime functionality. Based on the resulting calculations, the model was corrected and parameters refined with the initial and 2nd datasets. The calculations of the ten compounds are ongoing.

Additionally, a series of optimizations on Zwitterionic dimers are in progress, along with analysis to extract structure relations that will help us predict stacking and 'glassy' transitions in the liquid phase.

Finally, acid-zwitterion structure optimization and dynamic equilibrium of proton transfer are in progress using enhanced sampling techniques (metadynamics), allowing us to

determine the free energy landscape and equilibrium constant for these two forms. In the binding mechanism of CO_2 by CO_2BOLs, CO_2 reacts with the alcohol moiety, making n alkylcarbonic acid which the protonates the guanidine base component. As such, the acid/base equilibrium proton from the alcohol between the acid and base can be studied. If the proton moves form the acid to base, the zwitterionic liquid is formed, thereby increasing viscosity. If this proton does not exchange to the base, then there are no ions made in solution. We hypothesize that preventing the proton migration; we can control the viscosity by not having ions made in solution. We show the simulations of the acid/base equilibrium in Figure 3. Here, two cases are modeled where the neutral form (a) or the zwitterion (b) are favored. We are investigating ten compounds to understand what functionalities may favor the acid state (no proton transfer) and why. Preliminary data from MD viscosity calculations predict at least 30% viscosity reduction (due to the retardation of ion formation) if half of CO_2-bound species present are in an acid form.

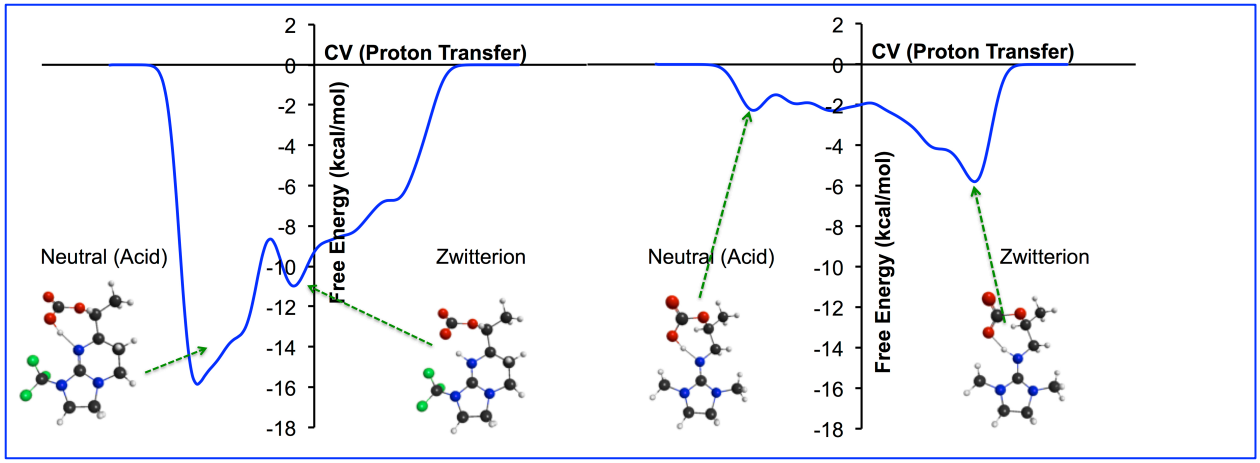


Figure 3. Free energy surface for proton transfer and equilibrium showing the shift towards a neutral loaded state, for solvents with appropriate electronic structure.

Ab initio molecular dynamics simulations of the acid-zwitterion equilibrium, and CO_2 binding mechanisms started.

Cluster-size analysis is in progress to describe the zwitterion clustering in solution.

Subtask 2.5 Predict physical and thermodynamic properties of second 100 molecules

No work has been performed on this subtask to date.

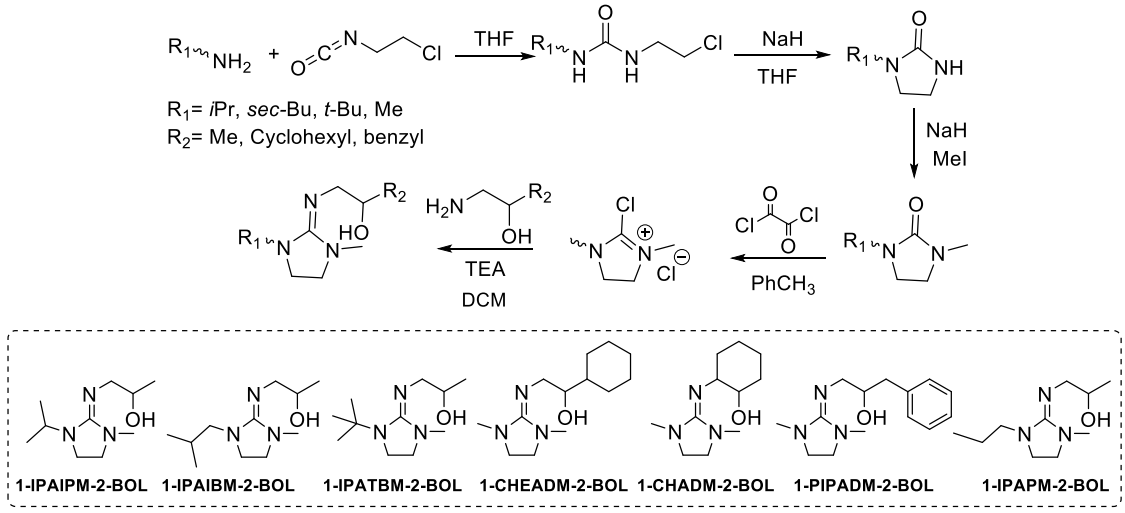
Task 3. Synthesis and Characterization of Candidate Molecules

Subtask 3.1 Synthesize 12-13 promising derivatives from first 100 molecules library

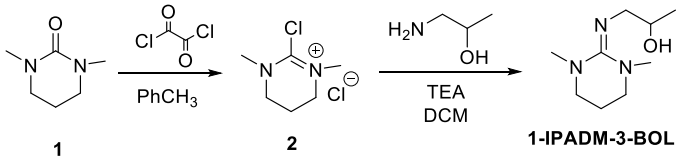
Completed

Subtask 3.3 Laboratory property testing completed for model validation

In Q3 we reported the results of our rational approach exploring the effect of steric tuning the anion. In that context, we synthesized six analogues of CO_2BOLs and are currently synthesizing a new derivative 1-IPAPM-2-BOL using the synthetic methodology shown in Scheme 1. This synthesis involved the nucleophilic addition of the amine to 2-chloro-ethylisocyante to generate a urea intermediate which underwent cyclization to form imidazolidinone. The imidazolidinone was methylated followed by our standard Vilsmeier salt chemistry to generate desired CO_2BOLs. In order to further explore the impact of sterics and stacking we have extended our substrate scope to six-membered, tetrahydropyrimidine core. To this end, we synthesized 1-IPAIPM-3-BOL using our standard Vilsmeier salt chemistry, i.e. condensation of 1-aminopropan-2-ol with Vilsmeier salt **2** (Scheme 2).



Scheme 1: CO_2BOLs based on steric tuning.

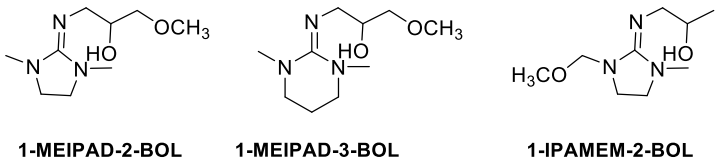


Scheme 2: Six-membered, tetrahydropyrimidine core based CO_2BOLs.

The CO_2 capture ability of 1-IPADM-3-BOL was evaluated gravimetrically by bubbling CO_2 through neat sample and the gas uptake was found to be 5.5 wt%. Nonetheless, the CO_2 uptake capacity of 1-IPADM-3-BOL was found to be relatively lower than our best case CO_2BOLs (IPADM-2-BOL, 10.5 wt% of CO_2) but the CO_2 bound 1-IPADM-2-BOL was found to be visually less viscous. The scale up of 1-IPADM-3-BOL to obtain 30 mL for material property testing has been completed.

Since, our preliminary gravimetric studies displayed improved viscosity for one of our ether-based CO_2BOL variants (designed for charge solvation), i.e. 1-MEIPAD-2-BOL (7.2 wt% CO_2 uptake). In this quarter, we have completed the scale up of 1-MEIPAD-2-BOL to obtain 30 mL of substrate for material properties measurements such as viscosity, density, vapor pressure, heat capacity, kinetic and thermodynamic bench scale testing. In the future, other CO_2BOLs-

containing ether functionalities will be synthesized to explore the impact of solvation of charges on viscosity reduction (Scheme 3). Currently, our synthetic efforts are focused on combining the fundamental learnings of sterics, stacking and solvation of charges towards designing less viscous CO_2BOLs.



Scheme 3: CO_2BOLs-containing ether functionalities.

<u>Task 4.</u> Measurement of Key Physical/Thermodynamic Data

The experimental team was working on validation of the new PVT cell by testing known 1st and 2nd generation CO_2BOL materials. The team tested the 1st generation CO_2BOL (DBU-1-hexanol) for shakedown because it is commercially available. 30 mL of the fluid was loaded into the cell and the PVT cell was shaken down. The fluid recirculation rate, leak checks, gas injection volumes and temperature controls were all validated. DBU-1-hexanol was then tested for isotherm behavior at 40, 60 and 73.6 ˚C, with the corresponding viscosity measured at the same conditions.. The cell was run in manual injection mode, meaning operators logged all data (Figure 4). One can see the high quality isotherms (corresponding to the right axis) indicating the cell's successful operation as a PT_x cell. The viscosity data (left axis) shows the observed non-linear behavior of viscosity with respect to CO_2 loading. In all, the cell's hardware and infrastructure shakedown was successful prior to the stop-work.

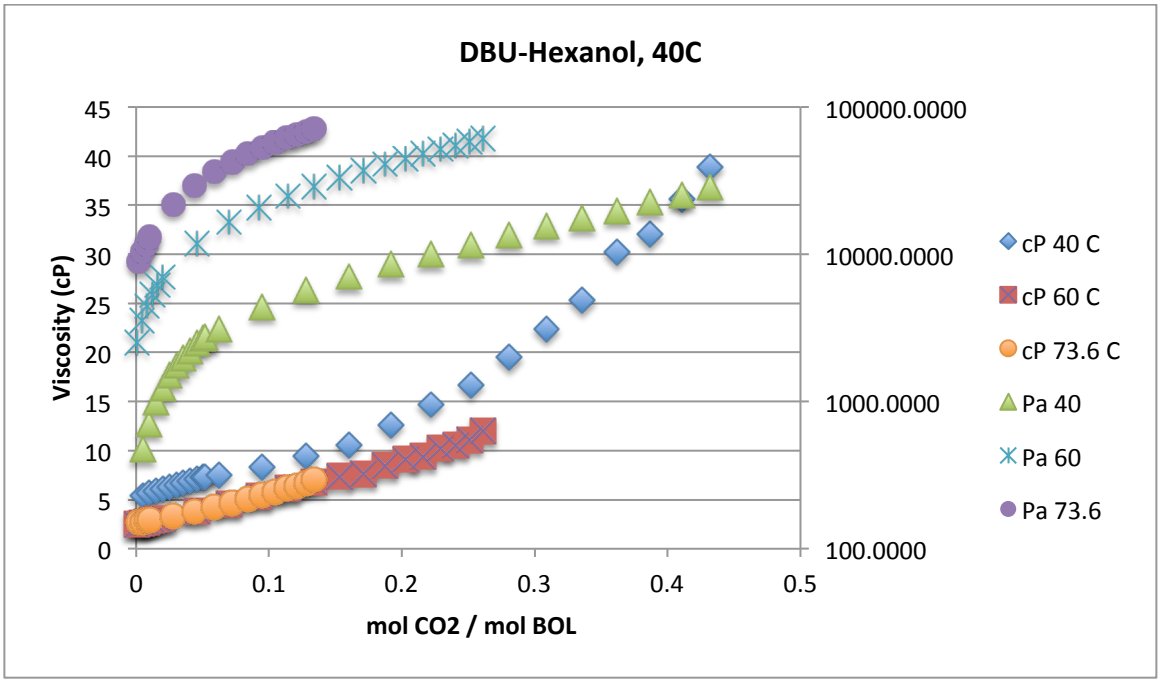


Figure 4. PTV testing of DBU-1-hexanol in manual mode operation. Viscosity in cP is on

the left axis, and P* CO_2 in Pa on the right axis.

The team had started running a 2nd generation CO_2BOL IPADM-2BOL from the prior program as another reference compound to validate the isotherm and viscosity data against prior to the stop-work. The cell was setup to run in its fully automated mode, being the injections, sampling and data collection were fully automated. Results from this shakedown will be provided in the next budget period once the stop-work is over.

Subtask 4.1 Key process data measured for process performance projections

No work has been performed on this subtask to date.

Task 5. Process Performance Projections

No work has been performed on this subtask to date.

Subtask 5.1 Project reboiler heat duty, regeneration temperatures and net power outputs for candidate molecules

No work has been performed on this subtask to date.

Subtask 5.2 Project equipment sizing and costing for candidate molecules

No work has been performed on this subtask to date.

Task 6. Alternative Synthetic Methodology Identified

No work has been performed on this subtask to date.

Task 7. Translation of Development Capabilities to Other Transformational Solvent Systems

No work has been performed on this subtask to date.

Cost Status:

Table 6 details the project accruals through 6/26/15. Total accrued costs are $1,054,635 with $440 in commitments for chemicals and laboratory supplies. The program transitioned into BP2 at the beginning of the next quarter, with $633,000 in funding coming in for the May and June FIN plans.

Table 6. Total project budget summary to-date (3/31/15)

Project Summary	Total Project Budget	Total Cost to Date	Commitments	Balance Remaining

		06/26/2015)		
Federal Share	$1,761,000	$1,054,635	$440	$705,925
Totals	$1,761,000	$1,054,635	$440	$705,925

Q4 in BP2 contained April through June of 2015. The planned and earned value costs for Q3 are outlined below in Figure 11 and in Table 2. The actual value costs (BCWP) were $332k, climbing back from a low value in Q2. This ramp up was the program pickup after the holiday break and low funding in the end of Q2. The earned value costing increased in Q3 to $704k due to continued productivity of the synthesis and modeling efforts. The cumulative cost and schedule variances were 54% and 17% respectively.

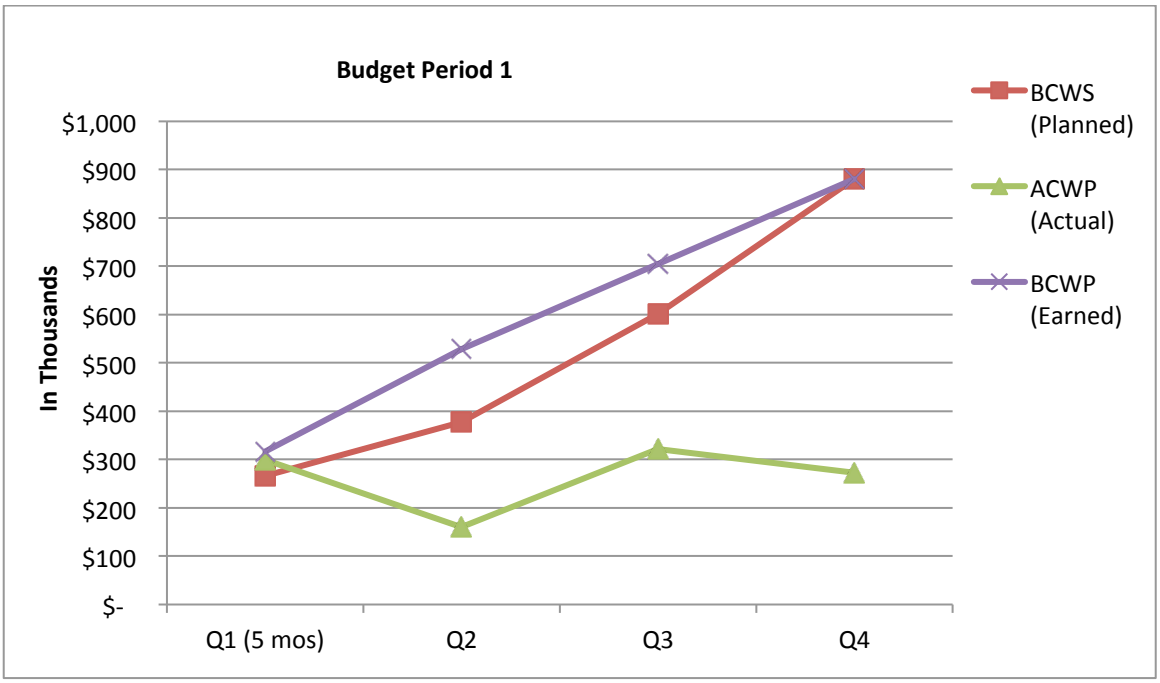


Figure 11. Performance Measurement Graph for BP1

Table 2. BP1 Cost and Schedule Variance by Quarter

Job to Date All BP	Q1 (5 mos)	Q2	Q3	Q4

Quarterly Amounts	Q1 (5 mos)	Q2	Q3	Q4
BCWS (Planned)	**$266**	**$111**	**$224**	**$280**
ACWP (Actual)	$266	$377	$601	$881
BCWP (Earned)	$299	$160	$322	$273
Cum Cost Variance	$317	$528	$704	$881
Cum Scheduled Variance	18.28	368.08	382.00	607.20
Cum % Cost Var	50.58	151.39	103.65	-0.35
Cum % Sch Var	6%	70%	54%	69%

Breakdowns of costs by quarter are provided in Table 3, and broken out by Task in Table 4. Task 1 (project management) contained travel for three staff to present at the NETL program meeting in Pittsburgh, PA. The planned and earned costs for the program lined up during this period, with the actual value cost staying constant with previous quarters. Task 3 ($116,163) was high as we were in the process of scaling up many of the candidate molecules for testing on the new PVT cell, corresponding to testing in Task 4. Other program expenditures were low due to the stop-work in June. Tasks 2 and 3 are on budget and schedule. The majority of current testing and program efforts in the next quarter will be on Tasks 2 and 4.

Table 3. Project Costing by Quarter (BP1)

Baseline Reporting Quarter	Budget Period 1 (05/01/2014-04/30/2015)							
	FY14		FY15		FY15		FY15	
	Q1	Project Total	Q2	Project Total	Q3	Project Total	Q4	Project Total
Total Planned	$ 266,403	$ 266,403	$110,508	$376,911	$ 223,842	$ 600,753	$ 280,092	$ 880,844
Quarterly Cost	$ 298,705	$ 298,705	$160,224	$458,929	$ 322,404	$ 781,333	$ 273,302	$ 1,054,635
Plan/Actual Variance	$ (32,302)	$ (32,302)	$(49,716)	$(82,018)	$ (98,562)	$(180,581)	$ 6,789	$ (173,791)

Table 4. Project Costing by Task BP1

Task	Task Title	BP1				
		Q1 (5 mos)	Q2	Q3	Q4	Total BP1
1	Project Management	$49,002	$27,782	$11,439	$19,772	$107,995
2	Molecular Development	$145,636	$69,639	$214,965	$86,261	$516,502
3	Synthesis & Characterization of Candidate Molecules	$104,066	$62,802	$96,000	$116,163	$379,032

4	Measurement of Key Physical/Thermodynamic Data	$-	$-	$-	$51,105	$51,105
5	Process Performance Projections	$-	$-	$-	$-	
6	Alternative Synthetic Methodology Identified	$-	$-	$-	$-	
7	Translation of Development Capabilities to Other Transformational Solvent Systems	$-	$-	$-	$-	
	TOTAL - ALL TASKS	**$298,705**	**$160,223**	**$322,404**	**$273,302**	**$ $1,054,634**

Schedule Status

II. Issues, Risks, and Mitigation

During the period of June 26-July 24th the project team had a stop-work issued and work was discontinued. Details of the project output and resolution of the stop-work will be provided in the next quarter's report.

Risk 1: Program budget

The project's funds were delivered incrementally in May's FIN plan ($100,000) and (~$533,000) in June's FIN plan. Unfortunately there was an issue getting the June FIN plan's WAS out in time, a such the program did not receive the June FIN plan funds till July 24.

III. Changes in Approach

There are no current changes in approach as the program.

The team has met with GE to discuss potential partnerships or collaborative efforts on modeling and testing of their aminosilicone and their phase change programs. GE has asked for PNNL's expertise in molecular modeling and use of our experimental infrastructure to aid their current programs in NETL's portfolio. The team is scheduled to visit GE in July to discuss options for partnerships.

IV. Key Personnel

Mark Bearden, our ASPEN Plus modeler will be retiring at the end of the calendar year after a storied and successful career at DOW and PNNL. Mark's 30 years of experience at DOW and 6 years modeling CO_2 capture are invaluable and cannot be replaced. We are currently working with Mark to continue his work on this program, either by reducing to 50% time or being hired back as a consultant. We have 6 more months prior to his retirement, and are working on ways to continue his involvement on this program.

V. Project Output

There were no outputs for this quarter other than the Go-No-Go and the oral and two poster presentations at the NETL project meeting in Pittsburgh, June, 2015.

Project Schedule Status

Table 5 shows the project's Gantt chart, with all Tasks and Subtasks broken out by quarter. Task 1, as usual, was completed (quarterly report). Milestones 1 and 2, and subtasks 2.1 and 2.2 were completed previously Q1 while subtasks 2.3-2.4 and Subtask 3.1 were completed in Q3. The team has met Milestones 1-3 and 5. A status update on Milestone 4 will be discussed in the next quarterly report. Work has begun on Task 4 with shakedown testing on the new PTV cell. With the stop-work, there may be a month long delay for remaining project deliverables and milestones. As such, Tasks 4-7 have been pushed back in Table 5 and the team asks for a no-cost time extension to cover the lost time on the project.

Table 5. Project timeline

Task 1. Project Management	BP1				BP2			
1.1 General project management								
Milestone 1 Updated Project Management Plan								
Task 2.Molecular Development	**BP1**				**BP2**			
2.1 Design 100 candidate molecules based on variations of current formulation								
2.2 Construct physical property prediction model								
Milestone 2 Construct physical property model								
2.3 Predict physical and thermodynamic properties of first 100 molecules								
Milestone 3 synthesize and characterize 13 candidate CO2BOL molecules								
Milestone 4 Viscosity reduction of 200 cP demonstrated								
2.4 Revise technology performance targets and design the second 100 molecules								
2.5 Predict physical and thermodynamic properties of the second 100 molecules								
Milestone 5 Go/No Go decision from initial feasibilty study								
Task 3. Synthesis and Characterization of Candidate Molecules	**BP1**				**BP2**			
3.1 Synthesize 12-13 promising derivatives from first 100 molecule library								
3.2 Synthesize 12-13 promising derivatives from second 100 molecule library								
3.3 Laboratory property testing completed for model validation (e.g. B.P., viscosity, CO2 capacity)								
Milestone 6 synthesize and characterize 13 candidate CO2BOL molecules								
Task 4. Measurement of Key Physical/Thermodynamic Data	**BP1**				**BP2**			
4.1 Key process data measured for Process Performance Projections (e.g. VLE, kinetics)								
Milestone 7 Viscosity reduction of 400 cP demonstrated								
Task 5. Process Performance Projections	**BP1**				**BP2**			
5.1 Project reboiler heat duty, Regen Temp, and net power output for candidate molecules								
5.2 Project equipment sizing and costing for candidate molecules								
Task 6. Alternative Synthetic Methodology Identified	**BP1**				**BP2**			
6.1 Provide alternative synthetic methdology (& projected costs) for optimal candidate solvents								
Milestone 8 Synthetic methodology for candidate molecules demonstrated at $10/kg								
Task 7. Translation of Development Capabilities to Other Transformational Solvent Systems	**BP1**				**BP2**			
7.1 Apply knowledge from Tasks 2-5 to current formulations in DOE's portfolio								
Milestone 9 Delivery of final report to client								