



Pacific Northwest
NATIONAL LABORATORY

Proudly Operated by Battelle Since 1965

Accelerating the Development of “Transformational” Solvents for CO₂ Separations

Quarterly Progress Report, Budget Period
1, Q3, 2014

May 2016

DJ Heldebrant
PK Koech

RJ Rousseau
V Glezakou

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes **any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.** Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST NATIONAL LABORATORY

operated by

BATTELLE

for the

UNITED STATES DEPARTMENT OF ENERGY

under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062;
ph: (865) 576-8401
fax: (865) 576-5728
email: reports@adonis.osti.gov

Available to the public from the National Technical Information Service,
U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161
ph: (800) 553-6847
fax: (703) 605-6900
email: orders@ntis.fedworld.gov
online ordering: <http://www.ntis.gov/ordering.htm>



This document was printed on recycled paper.

(9/2003)

Submitted to: U.S. Department of Energy (DOE)
Office of Fossil Energy

FWP Award: FWP-65872

Project Title: Accelerating the Development of “Transformational” Solvents
for CO₂ Separations

Quarterly Progress Report, Budget Period 1, Q3, 2014

Principal Investigators:

Dr. David J. Heldebrant
Phone: 509-372-6359
david.heldebrant@PNNL.gov

Dr. Phillip K. Koech
Phone: 509-372-6891
phillip.koech@PNNL.gov

Dr. Roger Rousseau
Phone: 509-372-6092
roger.rousseau@PNNL.gov

Dr. Vassiliki-Alexandra Glezakou
Phone: 509-375-6961
vanda.glezakou@PNNL.gov

Submitting Official: Contracting Officer

Date Submitted: April 31, 2015

Recipient Organization: Pacific Northwest National Laboratory
P.O. Box 999, MS K2-44
Richland, WA 99352

Project Period: May 1, 2014 through May 31, 2016

Reporting Period End Date: March 31, 2015

Reporting Term: Quarterly

Signature:



Laurie Martin
Contracting Officer

I. Accomplishments and Milestone Update

Synopsis of Accomplishments

The program team made significant progress in Q3 of FY 15. Subtasks 2.1 and 2.2 and 3.1 were completed. The modeling team developed a reduced model that was able to simulate material properties in a day within 90% accuracy of the full-scale molecular dynamics simulations that had previously taken up to 2 weeks each to complete. This reduced model enabled the team to predict materials properties of 100 candidate compounds and identify target molecules. This model also enabled us to discover the most critical elements of viscosity in these compounds, internal hydrogen bonding and molecular stacking. The synthesis team has synthesized 13 candidate molecules with steric tuning of candidates in addition to two new classes of CO₂BOL derivatives containing silanes (for charge solvation) and fluorine (for electronic tuning). The synthesis team has identified multiple candidates that show a reduced viscosity compared to the standard from the previous study. The engineering team has designed and assembled a new PTV cell that would allow for standardized testing for viscosity, density, vapor-liquid equilibria and kinetics all on a 20 mL sample volume. This PTV cell is the first of its kind, where equilibria data can be gathered running like a PTx cell, while adjusting volume of the cell with an internal mini wetted-wall contactor allows for measurements of CO₂ flux to be performed. This cell will allow testing of all materials properties at the same temperature and pressure in a single measurement, ensuring all data is collected at the same temperature, pressure, loading, viscosity etc... This cell will expedite testing to allow screening of material properties without having to go through formal scale up to 2-3 L to get kinetic data. This cell will be the main focus of testing in Task 4.

Milestones

Program milestones are tabulated in Table 1. As with previous reports, each milestone is provided with an estimated time and metrics needed for completion. Milestones 1 and subtasks 2.1 and 2.2 were completed in Q1. Subtask 2.3 is complete, with all 100 candidate molecules simulated. Subtask 3.1 is also complete with 13 candidates synthesized. Subtask 3.3 is ongoing. Work will begin on Task 4 and Subtask 3.2 next BP. Currently, the PTV cell is being assembled and shaken down on the 'Koechanol' to validate accuracy against our reference compound. The program team is slated to have met Milestones 1-4 prior to the go no-go presentation (Milestone 5).

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 ₂ BOL 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	April 8, 2015
6	Synthesize and Characterize 13 Candidate CO ₂ BOL Molecules	December, 2015	
7	Viscosity Reduction of 400 cP Demonstrated	January, 2015	
8	Synthetic Methodology of Optimal CO ₂ BOL 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:

Current engineering models rely on thermodynamic models for the prediction of physical properties such as viscosity. Viscosity however is highly dependent on molecular interactions that are completely absent in such models. Our molecular simulations reveal that CO₂BOL liquids become increasingly heterogeneous with loading. The heterogeneity arises from the coexistence of a glassy region within the liquid that is rich in ionic (CO₂ loaded) species and a 2nd region, which is rich in non-ionic (non-CO₂ carry molecules) species. The viscosity reduction relies on breaking up the former of the two regions by reducing molecular interactions between ionic species. Three local structural parameters have been identified that bear significant influence on the ionic species domain size and the overall viscosity of the CO₂BOLs: (i) intermolecular hydrogen bonding, (ii) top-bottom stacking, and (iii) adjacent stacking. We have identified the intermolecular NH⁺-COO⁻ hydrogen bond as the most critical structural parameter as reported in Q1. The species Koechanol shows a lower viscosity than a similar linear alkyl alcohol species because of a significant population of internal H-bonds, while keeping NH⁺-COO⁻ interactions with neighboring molecules to a minimum. Structural analysis from molecular dynamics trajectories show that 44% of Koechanol zwitterionic molecules at 15% mol CO₂-loading, and 34% of Koechanol zwitterionic molecules at 25% mol CO₂-loading, are involved in internal H-bonding. The high-viscosity, linear zwitterionic molecules have only 6% internal hydrogen bonds at 15% are observed CO₂-loading respectively. It is worth noting that as CO₂-loading increases, the probability that zwitterionic species will retain internal H-bonds decreases. This agrees with the hypothesis that internal H-bonds are critical for low viscosity and maximizing them needs to be one of the main design criteria. The internal hydrogen bond is disrupted as the size of ionic species domain increases with CO₂-loading due to the higher probability of having ionic first neighbors.

Several variants (carbon side chains, ether groups, fluorinated groups) of the Koechanol species were also simulated with MD and their viscosities were calculated. Again, for compounds where the structural variation disrupted the internal H-bond, the viscosity increased, for example in Koechanol with a six-carbon side chains attached to the amine groups, a ~66% increase in viscosity was estimated. Compounds where internal H-bond was not disrupted, viscosity did not increase. An ether Koechanol species showed a ~30% viscosity reduction at 25% CO₂-loading, and this is being further investigated. MD simulations of fluorinated Koechanol species are also in progress, as they have shown a propensity for stronger internal H-bonding. However, while an internal H-bond is necessary for a low viscosity CO₂BOL, it is not sufficient for all compounds.

In a modified molecule with a second ring (Vandanol), the internal H-bond interaction occurs 100% of the time. Although Vandanol in the liquid phase could lead to ~45% viscosity reductions at 25% CO₂-loading, it can transition to a high-viscosity glassy state with slight pressure variations, beyond the ability of any theoretical method to predict accurately. Nevertheless, two structural parameters were developed to quantify and describe the glassy

state: top-bottom stacking and adjacent stacking. Stacking is defined as the dot product between two vectors normal to the three-nitrogen atom plane in each molecule, $X = x1 \cdot x2$ for top-bottom stacking, or $Y = x1 \cdot x3$ for parallel stacking. If $X(Y) = 0$ there is no stacking and if $X(Y) = 1$ there is complete stacking. A cutoff distance, evaluated from the radial distribution function of the center of masses of zwitterionic molecules, is used to count the molecules within the 1st association shell of each molecule in the solvent mixture. (See Figure 1)

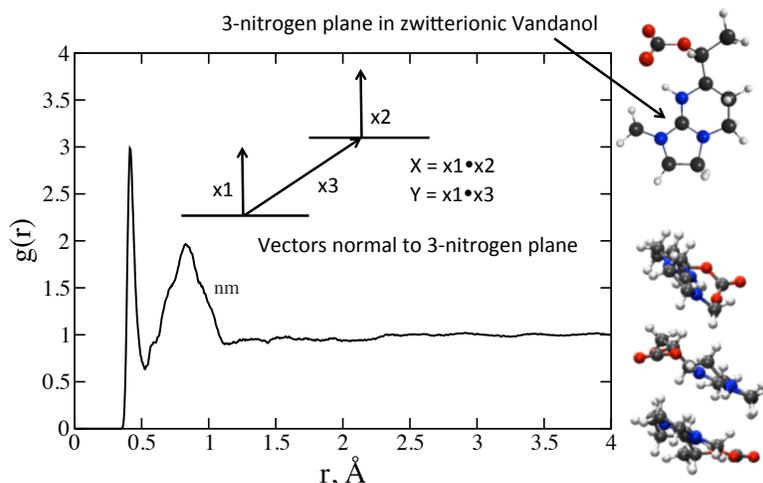


Figure 1. The radial distribution function of zwitterionic Vandanol molecules shows two solvation shells. Image shows Vandanol structures with a top-bottom stacking arrangement. The structural parameters are shown, calculated for all zwitterionic pairs in the 1st solvation shell.

We find that the stacking parameters are more of an indicator for local freezing of the structure into a solid form. A time-dependent analysis of the stacking (decay time of the pairing) during the MD simulations revealed that once zwitterionic pairs stack, it is likely they will remain so. As such, the stacking is an indicator of the freezing of the CO₂BOLs, but shows a poor correlation with the viscosity, for the liquid state. For instance CO₂-loaded Vandanol solvent mixtures show that ~33% of neighboring zwitterionic pairs display top-bottom stacking, compared to ~10% in Koechanol. Variants of the Vandanol structure were designed to suppress top-bottom stacking. Opening the 5-membered ring, or adding isopropyl groups close to the carboxylate, slightly reduced top-bottom stacking (~25% of neighboring zwitterionic pairs), however adding methyl groups to the second Vandanol ring, normal to the three-nitrogen atom plane, reduced stacking significantly (~10% of neighboring zwitterionic pairs). Although top-bottom stacking was reduced, no significant viscosity reduction was observed (See Table 3). Since the Vandanol liquid-glass state transition is very pressure sensitive (at 40 degrees C), more viscosity calculations are needed to distinguish between cases where structural variations changed liquid-state viscosity, or avoided the glassy state transition. Whether or not top-bottom stacking is a cause of liquid to glassy-state transition, it can still serve as a structural parameter that indicates a high-viscosity solvent mixture.

Construction and Validation of the reduced model:

The construction and validation of the first generation reduced model is based on a modular approach involving four distinct computational steps:

- (i) The electronic structure (optimized structures and atomic charges) of the basic solvent molecules is calculated by means of density functional methods.
- (ii) Classical molecular dynamics simulations (~50,000 atoms) were performed using refined parameters for the interatomic potentials (modified Universal OPLS parameters). Transport properties such as diffusion and viscosity can be calculated from analysis of the MD trajectories.
- (iii) The shear viscosity of a liquid in general is related to pressure fluctuations and can be calculated from a well-equilibrated simulation by integration of a Green-Kubo formula:

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle P_{xz}(t_0) P_{xz}(t_0 + t) \rangle_{t_0} dt.$$

Simulations for variants of the system Koechnol as well as other proposed systems were done to obtain estimates of the viscosity and used as guidelines for the validation on the reduced model.

- (iv) Based on our findings from the simulations regarding the interatomic hydrogen bonding and molecular stacking, the first generation reduced model was constructed, where the viscosity of the system is approximated as an exponential expression of the CO₂ loading (P) and the dipole moments of the pure (μ_l) and the loaded (zwitterion, μ_z) liquid:

$$\eta = c_1 \exp^{c_2 P (\mu_z / \mu_l)}$$

The coefficients c_1 and c_2 were fitted to reproduce the experimental data available for Koechnol. Figure 2 shows the validation of the first generation reduced model, where the viscosities (reduced) are compared to those from the MD simulation. This simplified model already captures ~2/3 of the underlying relationships ($R^2=0.67$).

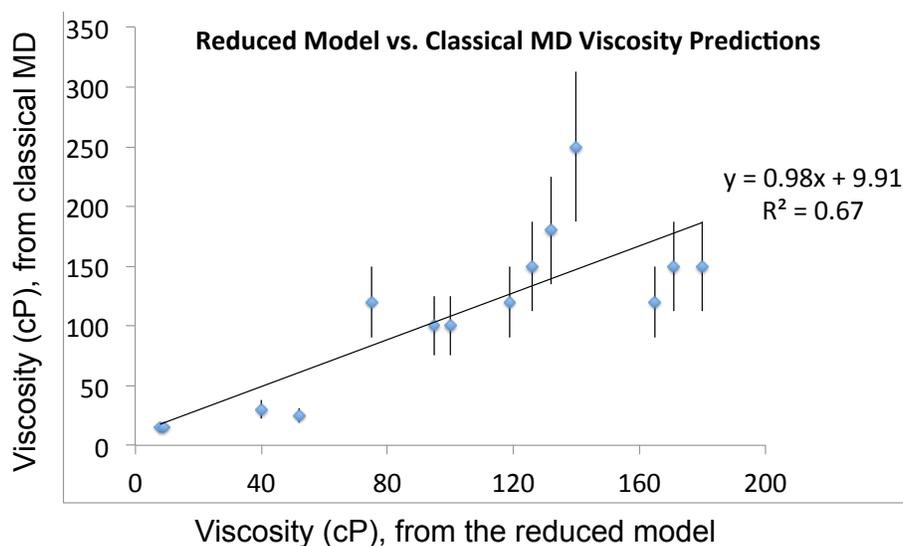


Figure 2. 1st generation reduced model showing 67% agreement with explicitly computed viscosities.

In the 2nd generation model, we modified the relationship to correlate the viscosity to the number of hydrogen bonds:

$$\eta = c_1 K_{eq} \exp^{c_2 P}$$

where $K_{eq} = X/(1-x)$, and x is the fraction of internal hydrogen bonds provides a much higher level of correlation, ~91% see figure 3. The population of internal hydrogen bonds can be inferred from charges obtained from the DFT calculations as this interaction is largely governed by electrostatic interactions and the close proximity of the amine and carbonate moieties. The improved fit is owing to the fact that it is the internal hydrogen bond more than the intermolecular dipole-dipole interactions which are the dominant structural feature which controls the size of the glassy region in the ionic portion of the liquid and hence the viscosity.

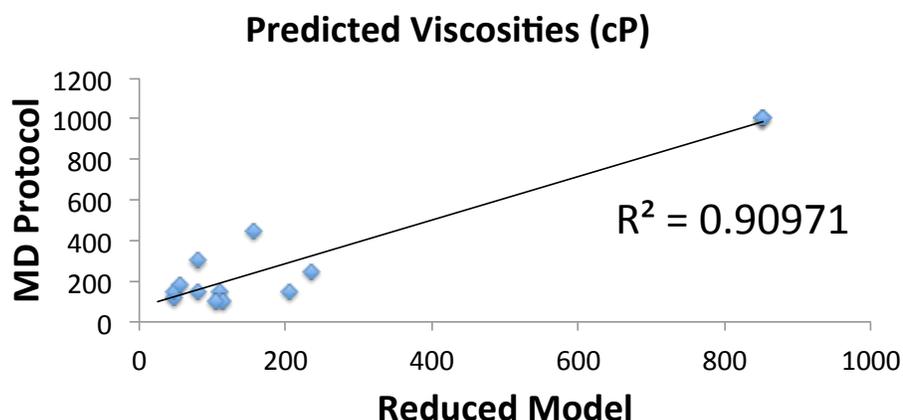


Figure 3. 2nd generation reduced model showing ~91% agreement with explicitly computed viscosities.

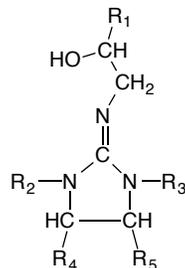
We are currently working on refining this model to explicitly include stacking and molecular shape factors that will help increase the goodness of the fit.

Subtask 2.3 Predict physical and thermodynamic properties of first 100 molecules

During this quarter, the modeling team used the reduced model to predict the physical and thermodynamic properties of 100 candidate compounds. The tables below show the structural variations and design motifs. Each candidate had properties modeled, notably the viscosity and CO₂ binding energy. The values are not provided in this report, as they need experimental validation to ensure the model's accuracy.

Molecules for computational screening

Table 2. Based on the Koechanol scaffold:



Compound	R1	R2	R3	R4	R5
KOL	CH3	CH3	CH3	H	H

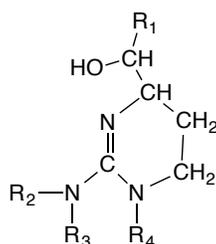
Blanks = CH3 in R1-R3, H in R4-5, for clarity

Ether-only Variants					
AKL		CH2-O-CH3	CH2-O-CH3		
BKL				CH2-O-CH3	CH2-O-CH3
CKL	CH2-O-CH3				
EKL		CH2-O-CH3			
IKL				CH2-O-CH3	
JKL	CH2-O-CH3			CH2-O-CH3	CH2-O-CH3
LKL				O-CH3	O-CH3
MKL	O-CH3				
OKL				O-CH3	
PKL	O-CH3			O-CH3	O-CH3
Fluoro-only Variants					
DKL		CH2-CF3	CH2-CF3		
FKL		CH2-CF3			
GKL	CH2-CF3				
QKL				CH2-CF3	CH2-CF3
RKL				CH2-CF3	
SKL	CH2-CF3			CH2-CF3	CH2-CF3
UKL		CF3	CF3		
VKL		CF3			
WKL	CF3				
XKL				CF3	CF3
YKL				CF3	

ZKL	CF3			CF3	CF3
Alkane-only Variants					
AJL				(CH2)5-CH3	(CH2)5-CH3
HKL		(CH2)5-CH3	(CH2)5-CH3		
TKL	t-Butyl				
BJL	i-Propyl				
CJL	(CH2)5-CH3				
DJL		t-Butyl	t-Butyl		
EJL				t-Butyl	t-Butyl
FJL		i-Propyl	i-Propyl		
GJL				i-Propyl	i-Propyl
HJL		t-Butyl			
IJL			t-Butyl		
JJL				i-Propyl	
Mixed Variants					
KJL	CH2-O-CH3	CH2-CF3	CH2-CF3		
LJL	CH2-O-CH3			CH2-CF3	CH2-CF3
MJL	CH2-O-CH3	CF3	CF3		
NJL	CH2-O-CH3			CF3	CF3
OJL	O-CH3	CH2-CF3	CH2-CF3		
PJL	O-CH3			CH2-CF3	CH2-CF3
QJL	O-CH3	CF3	CF3		
RJL	O-CH3			CF3	CF3
SJL	CH2-CF3			CH2-O-CH3	CH2-O-CH3
TJL	CH2-CF3	CH2-O-CH3	CH2-O-CH3		
UJL	CH2-CF3			O-CH3	O-CH3
Silane Variants					
DOL	CH2-Si-(CH3)3				
EDL		CH2-Si-(CH3)3			
FDL				CH2-Si-(CH3)3	

GDL				CH ₂ -Si-(CH ₃) ₃	CH ₂ -Si-(CH ₃) ₃
HDL	(CH ₂) ₃ -Si-(CH ₃) ₃				
IDL		(CH ₂) ₃ -Si-(CH ₃) ₃			
JDL				(CH ₂) ₃ -Si-(CH ₃) ₃	
KDL				(CH ₂) ₃ -Si-(CH ₃) ₃	(CH ₂) ₃ -Si-(CH ₃) ₃
Aryl Variants					
ARL	CH ₂ -Benzene				
FRL	CH ₂ -Benzene-F				

Table 3. Based on the Open-Vandanol scaffold:



Compound	R1	R2	R3	R4
OVL	CH ₃	CH ₃	CH ₃	CH ₃

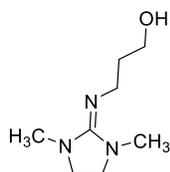
Blanks = CH₃ for clarity

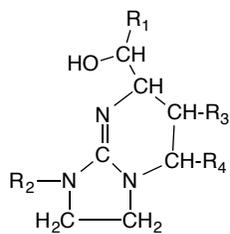
Ether-only Variants				
CVL	CH ₂ -O-CH ₃			
AVL	CH ₂ -O-CH ₃		CH ₂ -O-CH ₃	
BVL			CH ₂ -O-CH ₃	CH ₂ -O-CH ₃
DVL			CH ₂ -O-CH ₃	
EVL		CH ₂ -O-CH ₃		
GVL	O-CH ₃			
Fluoro-only Variants				
MVL	CH ₂ -CF ₃			

NVL		CH2-CF3		
PVL			CH2-CF3	CH2-CF3
QVL			CH2-CF3	
SVL	CF3			
UVL		CF3		
VVL			CF3	CF3
WVL			CF3	
Alkane-only Variants				
TVL	t-Butyl			
XVL	i-Propyl			
YVL			t-Butyl	
ZVL			i-Propyl	
Mixed Variants				
AWL	CH2-O-CH3		CH2-CF3	
BWL	CH2-O-CH3		CF3	
CWL	O-CH3		CH2-CF3	
DWL	O-CH3		CF3	
EWL	CH2-O-CH3	CH2-CF3		
FWL	CH2-O-CH3	CF3		
GWL	O-CH3	CH2-CF3		
HWL	O-CH3	CF3		
IWL	CH2-CF3		CH2-O-CH3	CH2-O-CH3
JWL	CH2-CF3		CH2-O-CH3	
MWL	CF3		CH2-O-CH3	CH2-O-CH3
NWL	CF3		CH2-O-CH3	

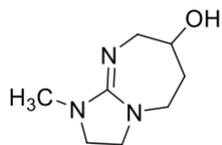
Table 4. Other compounds

COL: Linear alcohol





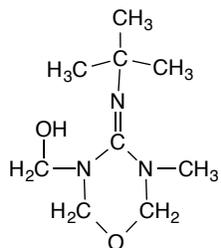
ROL: Seven-member ring



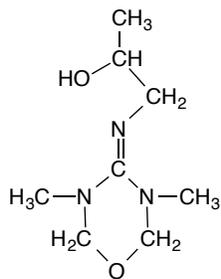
Vandanol (VOL) and Variants

	R1	R2	R3	R4
VOL	CH3	CH3	H	H
FVL	CH3	CF3	H	H
HVL	CH2-O- CH3	CH3	H	H
IVL	i-Propyl	CH3	H	H
JVL	CH2-CF3	CH3	H	H
RVL	CH3	CH3	CH3	CH3

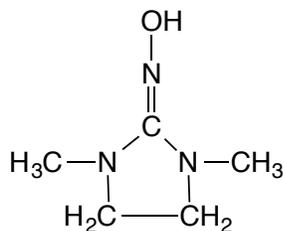
HOL



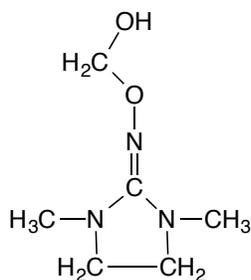
AHL



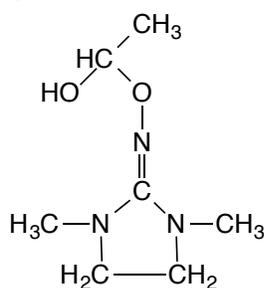
AXL



BXL



CXL



Subtask 2.4 Revise performance targets and design the second 100 molecules

No work has been performed on this subtask to date.

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 molecule library

In the first and second quarters we reported silane based CO₂BOLs i.e. 1-TMSIPADM-2-BOL, 1-IPATMSPM-2-BOL, and 1-IPADMSP-2-BOL. CO₂BOLs 1-TMSIPADM-2-BOL and 1-IPATMSPM-2-BOL show improved viscosity compared to our non-silane containing IPADM-2-BOL (Figure 1). In this quarter we completed the synthesis of another silane-based CO₂BOL 1-DMSPAM'DM-2-BOL containing internal silane and a primary alcohol (Figure 4). The synthesis is if

this new compound followed previously reported protocol. We have completed the scale up of 1-IPATMSPM-2-BOL to obtain 20 mL for material property testing.

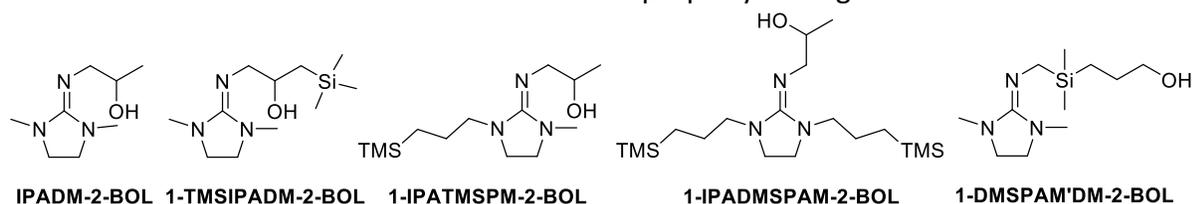


Figure 4. Silane based CO₂BOLs.

Fluorinated CO₂BOLs

In order to reduce the electrostatic cation-anion interaction in CO₂ rich solvent we have designed CO₂BOL derivatives based on fluorine motif as it has been shown in literature that fluorine based solvents exhibit reduced viscosity compared to analogous hydrocarbon solvents. To validate our hypothesis, we selected targets such as 1-TFEIPA-2-BOL, 1-PFPIPADM-2-BOL, 1-IPATFEM-2-BOL and 1-TFIPADM-2-BOL for synthesis and testing (Figure 5). To date we have synthesized 1-TFIPADM-2-BOL and 1-PFPIPADM-2-BOL previously reported in Q2 using our standard Vilsmeier salt chemistry protocols in gram scale and successfully characterized it using NMR spectroscopy. Our current synthesis efforts are focused on the synthesis of other fluorine-based variants such as 1-TFEIPA-2-BOL, 1-IPATFEM-2-BOL and the corresponding products will be characterized using ¹H and ¹³C NMR and FTIR analysis. 1-TFEIPA-2-BOL has been shown by computation that it is 33% less viscous than our best-case IPADM-2-BOL at 50% loading at 40 °C.

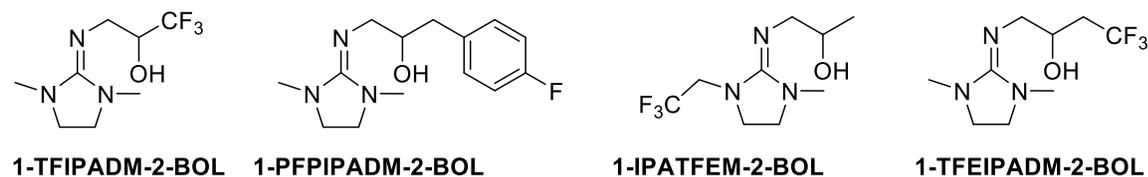


Figure 5. Fluorine based CO₂BOLs.

Ether –Containing CO₂BOLs

We have designed another class of CO₂BOLs containing ethers functionalities, which are known to solvate charges resulting in decreased viscosity (Figure 6). These CO₂BOLs include 1-MEIPAD-2-BOL, 1-IPAMEM-2-BOL, and 1-IPADME-2-BOL. Computation has shown that 1-MEIPAD-2-BOL is 33% less viscous than our current CO₂BOL IPADM-2-BOL at 25% loading at 40 °C. We have completed the synthesis of 1-MEIPAD-2-BOL and preliminary evaluation shows improved viscosity over our best case solvent.

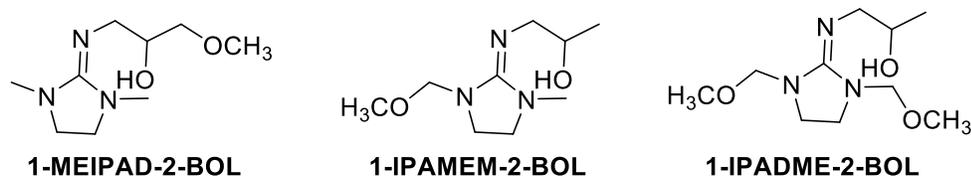


Figure 6. Ether-Containing CO₂BOLs.

Steric tuning

In Q2 we initiated studies to investigate the impact of steric bulk on the anion we have designed molecular targets as shown in Figure 7. To this end we have synthesized six CO₂BOL molecules include one reported in Q1 using our standard synthetic methodology. In this set of CO₂BOL molecules IPAIBM-2-BOL shows improved viscosity over our best-case compound IPADM-2-BOL. Currently, our efforts are focused on scale up of IPAIBM-2-BOL and developments of derivatives with different size cyclic core such as cyclohexyl base guanidine core. The insight gained from studying these molecular targets will support fundamental understanding of the impact of the steric environment of both cation and anion centers. These results will be utilized to guide our efforts towards designing an optimal synthetic model for the identification of viable CO₂BOLs with lower viscosities.

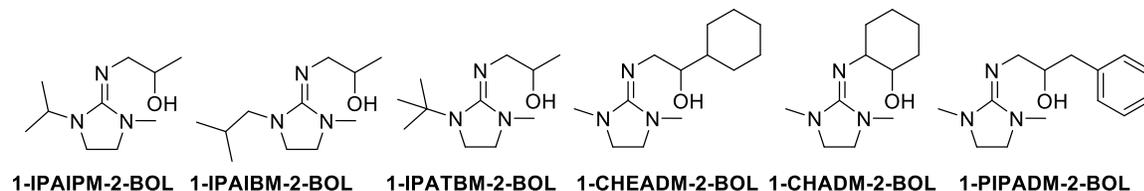


Figure 7. Synthesized the steric tuning CO₂BOL molecules.

Subtask 3.2 Synthesize 12-13 promising derivatives from second 100 molecule library

No work has been performed on this subtask to date.

Subtask 3.3 Laboratory property testing completed for model validation

Preliminary gravimetric CO₂ uptake and visual viscosity measurements have been performed to assess if candidate molecules warrant scale up for testing in Task 4. To date, the CO₂ capture ability of nine representative CO₂BOLs comprising of silane, bulky cyclohexyl groups, fluorine and ether i.e. 1-TMSIPADM-2-BOL, 1-IPATMSPM-2-BOL, 1-CHEADM-2-BOL, 1-PFPIPADM-2-BOL, 1-IPADTMSP-2-BOL, 1-MEIPADM-2-BOL, 1-IPAIPM-2-BOL, 1-IPAIBM-2-BOL, and 1-CHADM-2-BOL have been evaluated gravimetrically by bubbling CO₂ through the neat samples (Table 5). The CO₂ uptake of asymmetric silane derivative 1-IPATMSPM-2-BOL (6.0 wt%) was found to be slightly better than 1-TMSIPADM-2-BOL (5.5 wt%). Interestingly the CO₂ bound 1-IPATMSPM-2-BOL demonstrated slightly reduced viscosity over the CO₂ bound 1-TMSIPADM-2-BOL which is promising for designing less viscous CO₂BOLs. The ether-containing CO₂BOLs 1-MEIPADM-2-BOL and the asymmetric 1-IPAIBM-2-BOL gave the highest uptake at 7.2% and 7.5% by weight respectively and both showing improved viscosity over IPADM-2-BOL

our best-case compound.

Table 5. CO₂BOL CO₂ Gravimetric uptake

CO ₂ BOLs	Wt% (CO ₂)	Mol% (CO ₂)
1-TMSIPADM-2-BOL	5.5	30
1-IPATMSPM-2-BOL	6.0	37
1-CHEADM-2-BOL	3.4	19.5
1-PFPIPADM-2-BOL	3.0	18.5
1-IPADTMSP-2-BOL	3.7	32.7
1-MEIPADM-2-BOL	7.2	35.5
1-IPAIPM-2-BOL	4.7	22.6
1-IPAIBM-2-BOL	7.5	39
1-CHADM-2-BOL	4.4	22

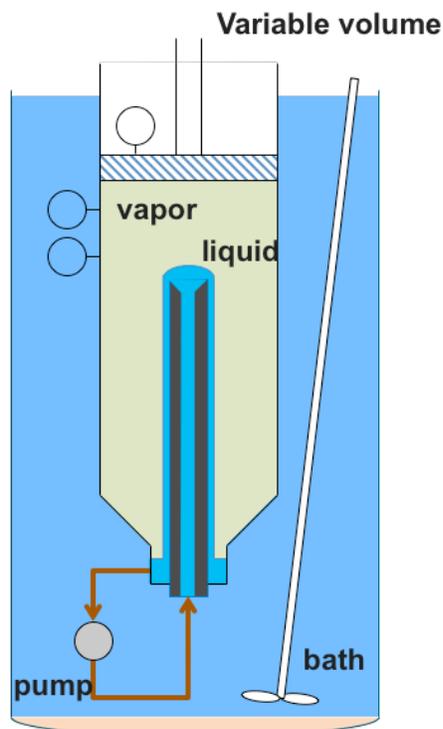


Figure 8. Internals of PVT cell.

Task 4. Measurement of Key Physical/Thermodynamic Data

Design work, fabrication and assembly of an advanced PTV cell started. This new PTV cell was envisioned to measure vapor-liquid equilibria (VLE), viscosity, density, and kinetics of CO₂ absorption all on a small sample size. This new PTV cell is a variant of the cell used for our previous program with real-time viscosity, density measurements and kinetics during equilibrium loading. The cell contains a miniature wetted-wall column (dark blue cylinder) inside, with a recirculation pump and in-line viscometer with pressure transducers and thermocouples. Assembly and shakedown of this cell will be performed in next quarter. Figure 8 to the left shows the internals, while Figure 9 shows the cell's design and gas manifolds, mass flow controllers and pressure transducers.

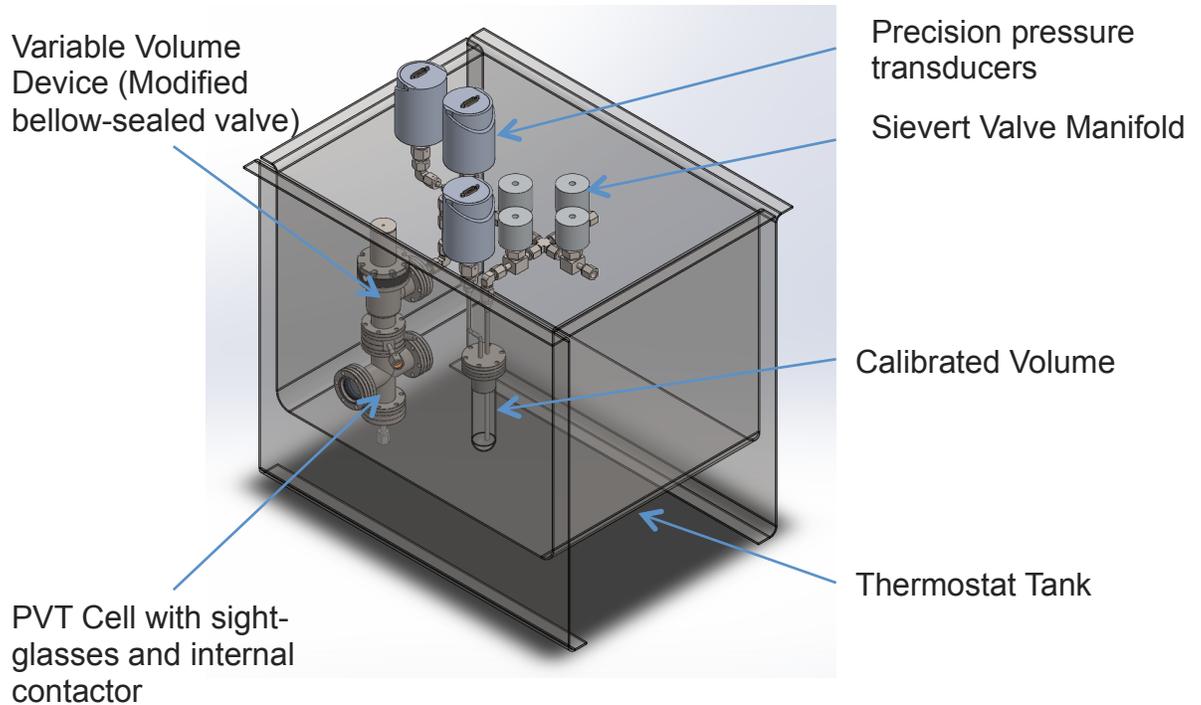


Figure 9. PVT cell design and components.

The cell can be used as a PTx cell with a static volume, yielding equilibrium data and viscosity. If the cell's volume is changed, the changes in volume will either force CO₂ in or out of the liquid. The ability to extract rate-based data from these perturbations in volume was modeled, with linear changes in volume showing the most accurate flux data. The equations and model simulations (Figure 10) for a linear displacement are outlined below.

- Governing Equation
 - Linear volume displacement:
 - Ideal gas law:
 - 1st order rate equation:

(We can ignore gas film mass transfer resistance)

- Simplify to differential equation of pressure:
 - Further, assume negligible liquid loading change, $dP^*/dt \approx 0$.
 - Closed-form solution:

$$V = V_0 + v \cdot t$$

$$PV = nRT$$

$$n \dot{V} = k_g A (P^* - P)$$

$$P \dot{V} (V_0 + v \cdot t) + P(v + v \cdot t) - P^* v = 0$$

$$v = 0$$

$$P|_{t=0} = P_0$$

$$P - P^* \left(\frac{v}{v_0} \right) / P_0 - P^* \left(\frac{v}{v + v_0} \right) = (1 + v_0 t / V_0) \uparrow - (1 + v / v_0)$$

KEY:

- k_g - closed-form solution negligible liquid loading
- P^* - vapor liquid equilibrium pressure
- V_0^* - vapor liquid equilibrium
- n - vapor liquid equilibrium
- P - vapor liquid equilibrium
- T - vapor liquid equilibrium
- v_0 - rate of vapor volume displacement
- v of liquid film mass transfer coefficient expressed in volume velocity unit, $v = RT k_g A$

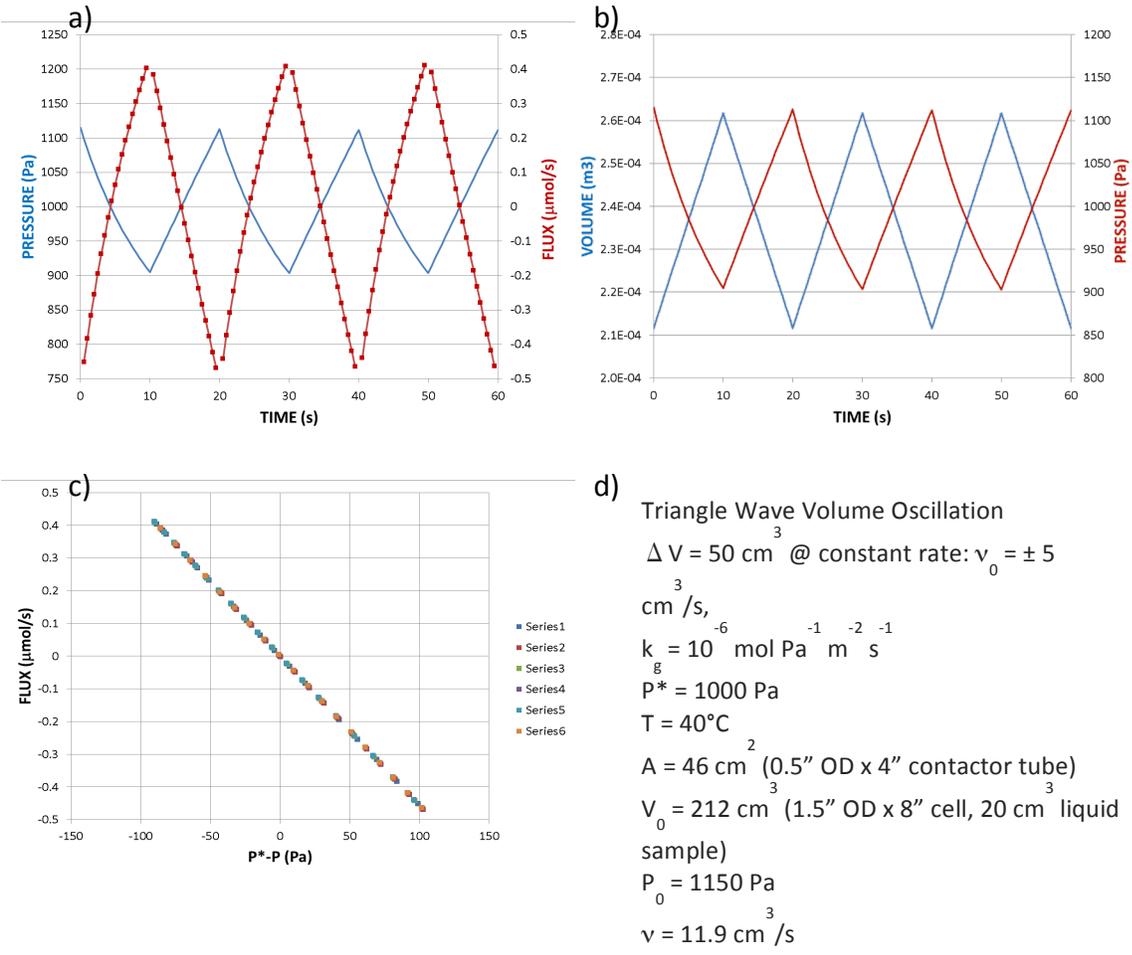


Figure 10. a) Simulation of cell pressure VS flux, b) Simulation of cell volume VS pressure, c) Model calculation of CO₂ flux data from changes in a). d) Calculation inputs.

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 13/31/15. Total accrued costs are \$781,333 with \$1,388 in commitments for chemicals and laboratory supplies. The program has money to carry through early May, after the anticipated go-no go decision, marking the end of BP1. The program will transition into BP2 at the beginning of the next quarter.

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

Project Summary	Total Project Budget	Total Cost to Date 12/31/2014	Commitments	Balance Remaining
Federal Share	\$1,761,000	\$781,333	\$1,388	\$978,279
Totals	\$1,761,000	\$781,333	\$1,388	\$978,279

Q3 in BP1 contained January through March of 2015. The planned, actual and earned value costs for Q3 are outlined below in Figure 11 and in Table 7. 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.

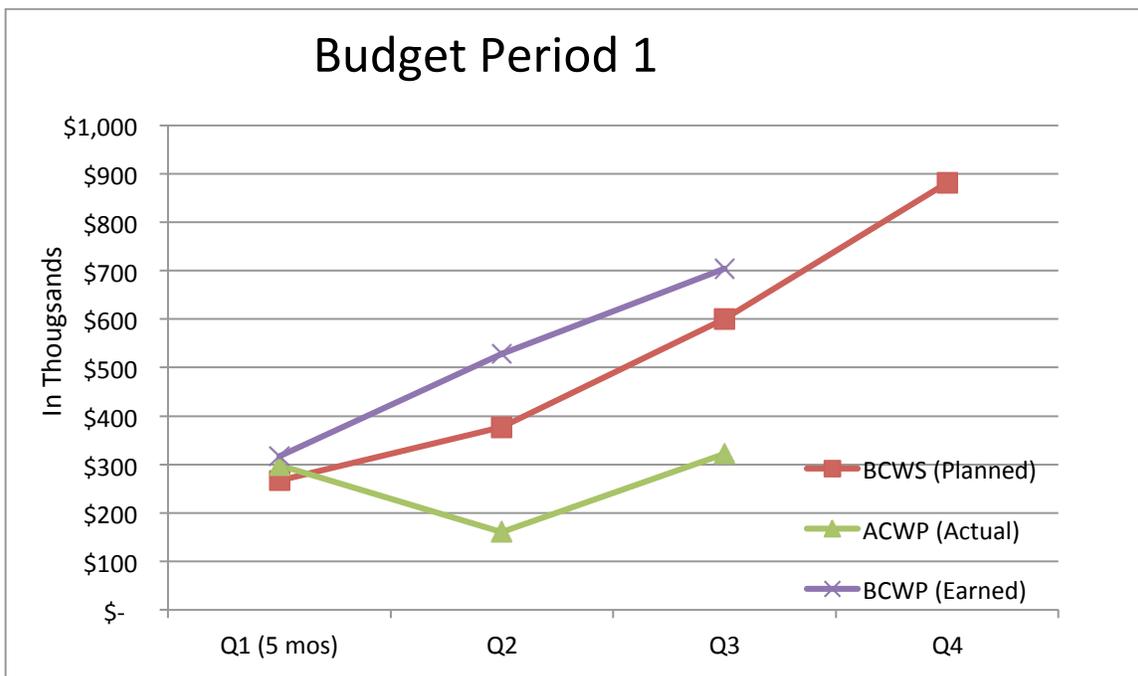


Figure 11. Performance Measurement Graph for BP1

Table 7. BP1 Cost and Schedule Variance by Quarter

Job to Date All BP	Q1 (5 mos)	Q2	Q3	Q4
Quarterly Amounts	\$266	\$111	\$224	\$280
BCWS (Planned)	\$266	\$377	\$601	\$881
ACWP (Actual)	\$299	\$160	\$322	
BCWP (Earned)	\$317	\$528	\$704	
Cum Cost Variance	18.28	368.08	382.00	
Cum Scheduled Variance	50.58	151.39	103.65	
Cum % Cost Var	6%	70%	54%	
Cum % Sch Var	19%	40%	17%	

Breakdowns of costs by quarter are going in Table 8, and also by Task in Table 9. Task 1 (project management) contained travel for two staff to attend an external peer review in Pittsburgh, PA. Task 2 (\$214,965) was the bulk of the charging for the program as the model development and validation were ramped up during this period. Task 3 (\$96,000) was also high as 13 of 13 candidate molecules were made during this period. Tasks 2 and 3 are on budget and schedule as the program transitions into BP2. Charging will ramp down on modeling as the

program begins transitioning into experimental testing in Task 4.

Table 8.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		
Plan/Actual Variance	\$ (32,302)	\$ (32,302)	\$(49,716)	\$(82,018)	\$ (98,562)	\$(180,581)		

Table 9.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		
2	Molecular Development	\$145,636	\$69,639	\$214,965		
3	Synthesis & Characterization of Candidate Molecules	\$104,066	\$62,802	\$96,000		
4	Measurement of Key Physical/Thermodynamic Data	\$-				
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	-	\$ -

Schedule Status

II. Issues, Risks, and Mitigation

There are currently no identified technical issues or risks.

Risk 1: Program budget

The project has sufficient funds as it transitions into BP2. Funding for BP2 will be arriving in the May FIN plan.

III. Changes in Approach

There are no current changes in approach as the program passed its go no-go and is transitioning into BP2.

The team is scheduling a visit from colleagues at LBNL up for a site visit to discuss encapsulation of poor-performing materials using LBNL's micro-encapsulation technology.

IV. Key Personnel

The team is excited to announce that Dr. Deepika Malhotra is currently on Maternity Leave following the birth of her daughter. Dr. Malhotra will be out of the office for the next 6 weeks as of April 22 (date of this report being drafted). Her leave will not impact the program deliverables, as she is slated to return once the second library of 100 new molecules has been assembled. She will return and begin synthesis on new materials near the end Q4 as Task 4 ramps up its experimental testing.

V. Project Output

There were no outputs for the second quarter, though each team is currently drafting a manuscript with their respective inputs. The molecular development team will be drafting a manuscript on the model construction and findings for the *Journal of the American Chemical Society*. The synthesis team will be drafting two manuscripts for journals like *Green Chemistry* or *Environmental Science and Technology*. The engineering team will be drafting a manuscript on the experimental validation and accuracy of the new PTV cell.

Project Schedule Status

Table 10 shows the Gantt chart breaking all Tasks and Subtasks by quarter. Task 1 was completed, with the only output being the quarterly report (here). Milestones 1 and 2, and subtasks 2.1 and 2.2 were completed in Q1. Subtasks 2.3-2.4 and Subtask 3.1 were completed. Milestones 1-3 were completed, with Milestones 4 and 5 scheduled for April in Q4. Work has just started for Task 4 with the design and assembly of the new PTV cell. All tasks and subtasks are all on track to be completed in the original project schedule.

Table 10. 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 feasibility 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 methodology (& 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		