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# Accelerating the Development of "Transformational" Solvents for CO2 Separations

## May 2016

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U.S. DEPARTMENT OF
ENERGY

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**Reporting Term:** Quarterly

**Signature:** Kevin Ghirardo

## I. Accomplishments and Milestone Update

### Synopsis of Accomplishments

Q2 of FY 15 focused on continued work primarily on subtasks 2.2, 2.3 and 3.1. The modeling team focused their efforts on revising the model to predict 30 of the first 100 candidate molecules. After studying the effects of hydrogen bonding in Q1, the team has been focusing on the impacts of ion pairing and stacking of the molecules. At this point it is not clear if stacking impacts viscosity or just promotes a phase transition from the $CO_2BOL$ liquids to a glass. The synthesis team has continued their work by synthesizing and characterizing 8 of the first 13 candidate molecules. Key targets of the synthesis team include silane and fluorine derived molecules, to serve as representative molecules for new classes of $CO_2BOLs$. These derivatives will be used as reference molecules to be used to derive new molecular libraries to study the impacts of cation/ion shielding and changes in acid/base strength. Currently 4 molecules have been tested visually for viscosity and $CO_2$ uptake. A few of these derivatives show promise of reduced viscosity compared to the reference compound. The promising candidates are being scaled up in the lab to provide enough material for testing in Task 4

### Milestones

The milestones for this program are shown in Table 1. 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 ongoing, with 30 of 100 candidate molecules simulated. Subtasks 3.1 and 3.3 are ongoing, while no work has begun on 3.2. Currently in 3.1, 8 of 13 molecules have been made in the gram scale, and scale up of promising derivatives is ongoing. Subtask 3.3 has started in part by the $CO_2$ uptake measurements of some of the 8 candidates that have been synthesized. The team is still scheduled to meet Milestone 4 in February of FY15.

**Table 1.** Major Milestones Relevant to BP1.

| Mile-stone Number | Milestone Description | Estimated Completion Timing | Performance Needed |
|---|---|---|---|
| 1 | Updated Project Management Plan | Mar, 2014 | |
| 2 | Construct Physical Property Model | September, 2014 | The model is complete and a regressed model also has enabled faster screening. 30 of 100 molecules have been tested |
| 3 | Synthesize and Characterize 13 Candidate $CO_2BOL$ Molecules | January, 2015 | 8 of 13 molecules have been made and are being scaled up for testing |
| 4 | Viscosity Reduction of 200 cP demonstrated | February, 2015 | |

| | | | |
|---|---|---|---|
| 5 | Go no-go presentation at NETL | March, 2015 | |
| 6 | Synthesize and Characterize 13 Candidate $CO_2$BOL Molecules | November, 2015 | |
| 7 | Viscosity Reduction of 400 cP Demonstrated | December, 2015 | |
| 8 | Synthetic Methodology of Optimal $CO_2$BOLs Demonstrated at $10/kg | February, 2016 | |
| 9 | Final report provided to NETL | March, 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

A 340 molecular library was developed based on variations of the initial formulation. The first variation focused on intermolecular compared to intramolecular hydrogen bonding to determine the effects of hydrogen bonding within the molecule itself or with partners. A second variation focused on steric crowding around the base and alcohol moieties as a means to shield the ions and in turn reducing cation/anion interactions within molecules. Lastly, the design team focused on tuning acid/base strengths with electron donating or reducing groups to determine the effect on viscosity and any (if any) impacts on $CO_2$ uptake. Currently around 30 molecules have been simulated and our intuition from this library has directed the synthesis team to work on the most promising 13 molecules from this library

### Subtask 2.2 Construct physical property prediction model

We are moving toward building a reduced model that will quickly estimate $CO_2$BOL viscosity based on the identified structural parameters, without having to perform time-consuming simulations to calculate viscosity. Reduced models, based on computational chemistry calculations have been successfully developed with ionic liquids to predict H-bond basicity and acidity (Niedermeyer *et al.*, 2013), temperature dependence of viscosity and conductivity (Eiden *et al.*, 2011), and models based on molecular volumes to predict viscosity and conductivity (Slattery *et al.*, 2007). These models will have to be tailored for $CO_2$BOLs, unlike the more common two-species ionic liquid combinations, by including the structural parameters obtained from the MD simulations.

*References:*

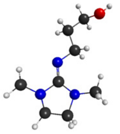
- P Eiden, S Bulut, T Kochner, C Freidrich, T Schubert, I Krossing (2011) In Silico Predictions of the Temperature-Dependent Viscosities and Electrical Conductivities of Functionalized and Nonfunctionalized Ionic Liquids. *J. Phys. Chem. B*, 115, 300-309.
- H Niedermeyer, C Ashworth, A Brandt, T Welton, PA Hunt (2013) A step towards the *a priori* design of ionic liquids. *Phys. Chem. Chem. Phys.*, 15, 11566-11578.
- JM Slattery, C Daguenet, PJ Dyson, TJS Schubert, I Krossing (2007) How to Predict the Physical Properties of Ionic Liquids: A Volume-Based Approach. *Angew. Chem.*, 119, 5480-5484.

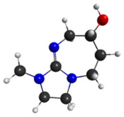
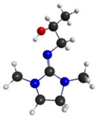
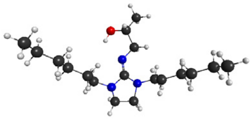
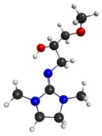
### Subtask 2.3 Predict physical and thermodynamic properties of first 100 molecules

During this quarter, we studied additional structural parameters for controlling $CO_2$BOL viscosity, and performed molecular dynamics (MD) simulations to calculated viscosities (methodology described in the Q1 report) on more compounds.

Three local structural parameters have been identified which influence ionic species domain size and the overall viscosity of the $CO_2$BOLs: (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 such internal H-bonds, while keeping NH-COO interactions with neighboring molecules to a minimum. Structural analysis from molecular dynamics trajectories show that 80% of Koechanol zwitterionic molecules at 15% mol $CO_2$-loading, and 50% of Koechanol zwitterionic molecules at 25% mol $CO_2$-loading, are involved in internal H-bonding. The high-viscosity linear zwitterionic molecules have only 20% and 15% internal hydrogen bonds at 15% and 25%-mol $CO_2$-loading respectively (See Table 2). It is worth noting that as $CO_2$-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 $CO_2$-loading due to the higher probability of having ionic first neighbors.

**Table 2**: Effect of internal H-bonds on viscosity. Black for carbon, white for hydrogen, red for oxygen, and blue for nitrogen.

| **Species** | **Loading** | **Probability of Internal H-Bond in Zwitterion** | **Viscosity (cP)** |
|---|---|---|---|
| Linear alcohol  | 15% | 20 | High (> 600) |
| | 25% | 15 | High (> 600) |

| | | | |
|---|---|---|---|
| Seven-Ring<br> | 15% | 20 | High (> 600) |
| | 25% | 15 | High (> 600) |
| **Koechanol and Structural Variants** | | | |
| Koechanol<br> | 0 | - | 15 |
| | 15% | 80 | 35 |
| | 25% | 50 | 150 |
| Two six-carbon chains<br> | 0 | - | 50 |
| | 15% | 25 | 150 |
| | 25% | 10 | 250 |
| Ether<br> | 0 | - | 8 |
| | 25% | 70 | 100 |
| Fluorinated | Work in Progress | | |

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 six-carbon side chains, a ~66% increase in viscosity was estimated. Compounds where internal H-bond was not disrupted, viscosity did not increase (See Table 2). An ether Koechanol species showed a ~30% viscosity reduction at 25% $CO_2$-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 $CO_2$BOL, 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% $CO_2$-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, $X=x1\bullet x2$ for top-bottom stacking, or $Y=x1\bullet x3$ for parallel staking. 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)

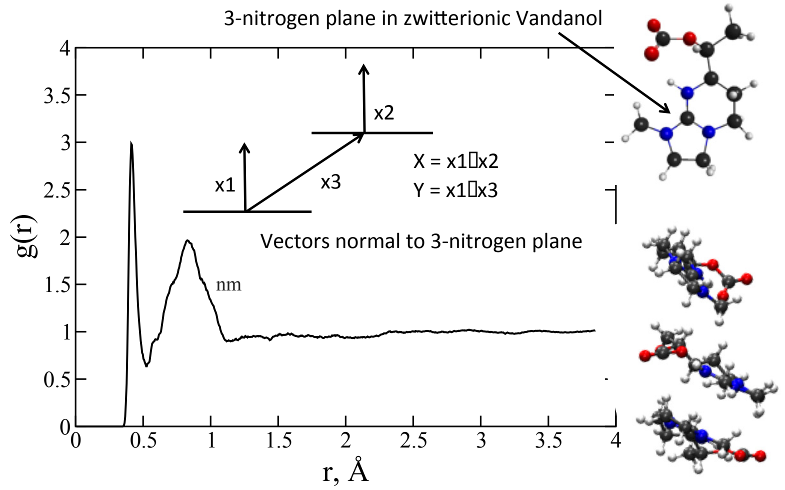
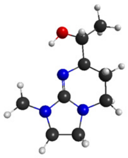
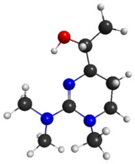
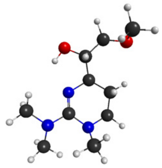
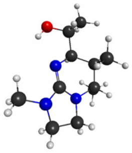
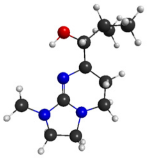


**Figure 1**: *The radial distribution function of zwitterionic Vandanol molecules shows two solvation shells. Image shows Vandanol structures with a top-bottom stacking arrangement. The structural parameters are shown, calculated for all zwitterionic pairs in the 1st solvation shell.*

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 $CO_2$BOLs but shows a poor correlation with the viscosity, for the liquid state. For instance $CO_2$-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.

**Table 3**: Top-bottom stacking in Vandanol and its structural variants, and its effect on viscosity. Black for carbon, white for hydrogen, red for oxygen, and blue for nitrogen. Numbers in parentheses are still being evaluated.

| **Vandanol and Structural Variants** | **Loading** | **Probability of Internal H-Bond in Zwitterion** | **% of Top-Bottom Stacked Zwitterionic Pairs** | **Viscosity (cP)** |
|---|---|---|---|---|
| Vandanol<br> | 0 | - | - | 15 |
| | 15% | 100 | 33 | 25 |
| | 25% | 100 | 34 | 80 |
| Open<br> | 0 | - | - | 35 |
| | 15% | 100 | 27 | 60 |
| | 25% | 70 | 24 | (400) |
| Ether Open<br> | 0 | - | - | 20 |
| | 25% | 100 | 22 | 120 |
| Ringmethyl<br> | 0 | - | - | 20 |
| | 15% | 100 | 7 | 60 |
| | 25% | 100 | 7 | 180 |
| Isopropyl<br> | 0 | - | - | 20 |

### Subtask 2.4 Revise performance targets and design the second 100 molecules

No work has been performed on this subtask to date.

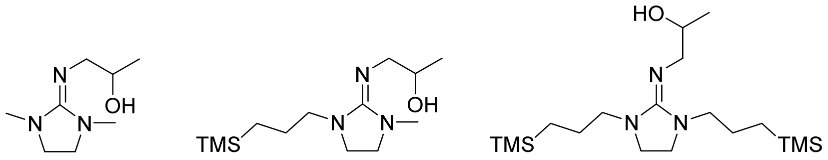
### Subtask 2.5 Predict physical and thermodynamic properties of second 100 molecules

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

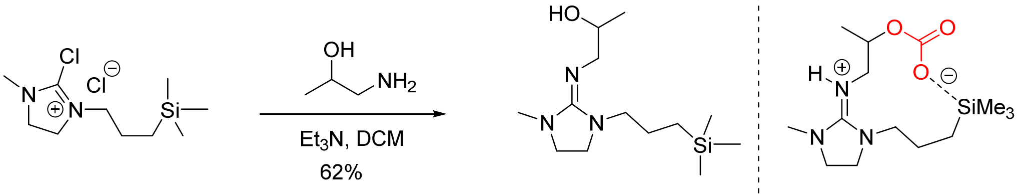
In the first quarter we reported a silane based $CO_2$BOLs i.e. 1-TMSIPADM-2-BOL which shows improved viscosity compared to our non-silane containing IPADM-2-BOL. Encouraged by this result, the synthetic team has designed other variants of silane based COBOLs in order to further lower the viscosity. These analogues include 1-IPATMSPM-2-BOL and 1-IPADTMSP-2-BOL as shown in Figure 2, which were identified as potential targets to explore the impact of molecular structure on the viscosity.



**IPADM-2-BOL** **1-IPATMSPM-2-BOL** **1-IPADTMSP-2-BOL**

Figure 2: *Silane based $CO_2$BOLs.*

We have completed the synthesis and characterization of 1-IPATMSPM-2-BOL. This synthesis was performed using our standard protocol that is, condensation of 1-aminopropan-2-ol with Vilsmeier salt **1** (Scheme 1). The rationale behind silane based $CO_2$BOLs is that the oxo-philic silicon centers will form a dative bond with the carbonate anion (Scheme 1) consequently weakening the cation-anion interactions and thus reducing the viscosity of the molecular system. The scale up of this silane based $CO_2$BOL to generate enough material for material properties measurements such as viscosity, density, vapor pressure, heat capacity, kinetic and thermodynamic bench scale testing is underway in our laboratory.

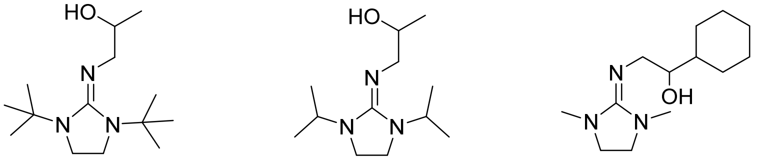


**1** **1-IPATMSPM-2-BOL** **$CO_2$ bound 1-IPATMSPM-2-BOL**

Scheme 1: Synthetic methodology for the synthesis of silane based $CO_2$BOLs and our hypothesis.

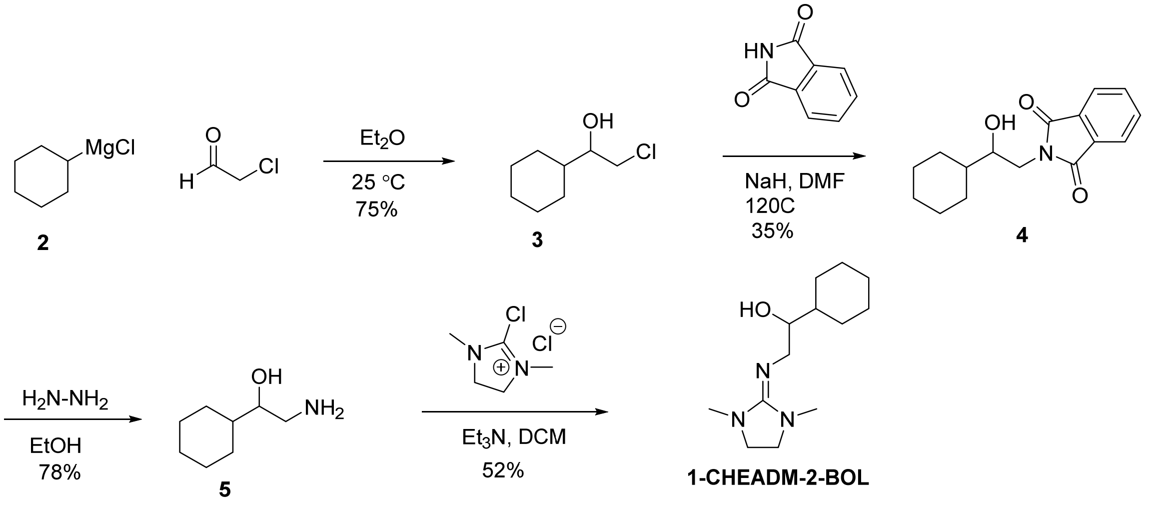
## Steric tuning

In order to investigate the impact of steric bulk on the anion we have designed molecular targets as shown in Figure 3. To this end we have synthesized 1-CHEADM-2-BOL using our standard synthetic methodology. This synthesis involves the addition of cyclohexylmagnesium chloride **1** to chloroacetaldehyde **2** to generate chlorocyclohexylethan-1-ol **3** at room temperature (Scheme 2). The corresponding aminocyclohexylethanol **5** was synthesized by the reaction of phthalimide with **3** in the presence of sodium hydride followed by the treatment with hydrazine hydrate under reflux conditions. The resulting compound aminocyclohexylethanol **5** underwent condensation with Vilsmeier salt to furnish 1-CHEADM-2-BOL in small scale. Currently, our efforts are focused on synthesizing other variants such as 1-IPADTB-2-BOL and 1-IPADIP-2-BOL to minimize the cation-anion electrostatic interactions. 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 $CO_2BOLs$ with lower viscosities.



**1-IPADTB-2-BOL** **1-IPADIP-2-BOL** **1-CHEADM-2-BOL**

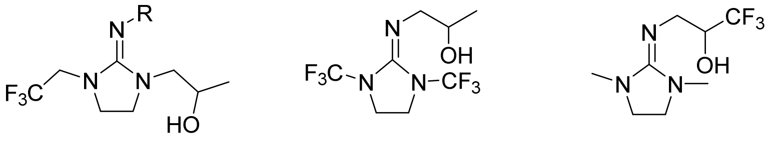
Figure 3: *Selected targets for the steric tuning.*



Scheme 2: Synthetic methodology for the synthesis of 1-CHEADM-2-BOL.

## Fluorinated $CO_2BOLs$

In order to reduce the electrostatic cation-anion interaction in $CO_2$ rich solvent we have designed $CO_2BOL$ derivatives based on fluorine motif as it has been shown in literature that fluorine based solvents can reduce the viscosity. To validate our concept we have selected targets such as 1-TFEIPA-2-BOL, 1-IPADTFM-2-BOL and 1-TFIPADM-2-BOL for synthesis and testing (Figure 4). To date we have synthesized 1-TFIPADM-2-BOL by the condensation reaction of trifluoroaminoalcohol with the Vilsmeier salt on gram scale and successfully characterized it using NMR spectroscopy. Since our compound 1-TFIPADM-2-BOL was solid at room temperature, preliminary $CO_2$ gravimetric uptake studies were performed using 67% by weight diglyme as inert solvent. Our initial result shows the $CO_2$ uptake capacity of 1-TFIPADM-2-BOL is 1.9 wt%. This low uptake, is attributed to the low solubility of this compound in diglyme. In future our efforts will be focused on the synthesis of other fluorine based variants such as 1-TFEIPA-2-BOL, 1-IPADTFM-2-BOL and the corresponding products will be characterized using $^1H$ and $^{13}C$ NMR and FTIR analysis.



**1-TFEIPA-2-BOL** **1-IPADTFM-2-BOL** **1-TFIPADM-2-BOL**

Figure 4: *Fluorine based $CO_2$BOLs.*

### $CO_2$ uptake studies

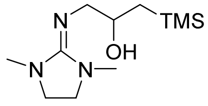
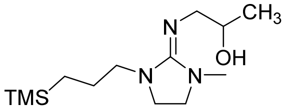
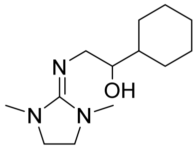
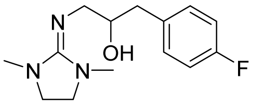
### Subtask 3.2 Synthesize 12-13 promising derivatives from second 100 molecule library

No work has been performed on this subtask to date.

### Subtask 3.3 Laboratory property testing completed for model validation

Preliminary gravimetric $CO_2$ uptake and visual viscosity measurements have been performed to assess if candidate molecules warrant scale up for testing in Task 4. To date, the $CO_2$ capture ability of four representative $CO_2$BOLs comprising of silane, bulky cyclohexyl groups and fluorine i.e. 1-TMSIPADM-2-BOL, 1-IPATMSPM-2-BOL, 1-CHEADM-2-BOL, and 1-FPIPADM-2-BOL has been evaluated gravimetrically by bubbling $CO_2$ through the neat samples (Table 4). The $CO_2$ 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 $CO_2$ bound 1-IPATMSPM-2-BOL demonstrated slightly reduced viscosity over the $CO_2$ bound 1-TMSIPADM-2-BOL which is promising for designing less viscous $CO_2$BOLs. On the other hand, $CO_2$BOLs i.e. 1-CHEADM-2-BOL containing a steric hindered alcohol by the cyclohexyl group, and 1-FPIPADM-2-BOL bearing fluorine motif did not show improvement and the $CO_2$ capture ability was rather found to be lower i.e. 3.4 wt% and 3.0 wt %, respectively.

**Table 4**: $CO_2$ uptake studies for selected $CO_2$BOLs.

| $CO_2$BOLs | Wt% ($CO_2$) | Mol% ($CO_2$) |
|---|---|---|
| <br>**1-TMSIPADM-2-BOL** | 5.5 | 30 |
| <br>**1-IPATMSPM-2-BOL** | 6.0 | 37 |
| <br>**1-CHEADM-2-BOL** | 3.4 | 19.5 |
| <br>**1-FPIPADM-2-BOL** | 3.0 | 18.5 |

## Task 4. Measurement of Key Physical/Thermodynamic Data

Design work has been started to assemble an advanced cell that is capable of measuring vapor-liquid equilibria (VLE), viscosity, density, and kinetics of $CO_2$ absorption. This new cell is a variant of the cell used for our previous program. Advances in this cell will include real-time viscosity and density measurements during equilibrium loading. This cell also allows for gas-phase sampling to determine the composition of the gas-headspace of the cell enabling more accurate VLE data collection. Assembly of this cell will be performed in Q3.

### 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:

Project accruals through 12/31/14 are listed in Table 5. The total accrued costs total $458,929 with $5,083 in commitments for chemicals and laboratory supplies. The program received money in the November FIN plan and has enough funding to continue up through the go-no go period in spring of FY15.

**Table 5.** Total project budget summary to-date (12/31/14)

| Project Summary | Total Project Budget | Total Cost to Date 12/31/2014 | Commitments | Balance Remaining |
|---|---|---|---|---|
| Federal Share | $1,761,000 | $458,929 | $5,083 | $1,296,988 |
| Totals | $1,761,000 | $458,929 | $5,083 | $1,296,988 |

Q2 of the first budget period contained October through December of calendar year 2014. Planned, actual and earned value costs for Q2 are provided in Figure 5 and in Table 6. The actual value costs (BCWP) were $160k, which was low in Q2 due to the delay in funding and the holiday break. The carryover of ~$32k from Q1 was enough to cover post-doctoral research associates, but all other staff had not been charging to the program until additional funds came in mid November. Many of the staff also took time off for the holidays, which also resulted in less charging for the quarter. The earned costs during Q2 went up to $528k due to higher than expected productivity of the synthesis and modeling efforts with lower charging.

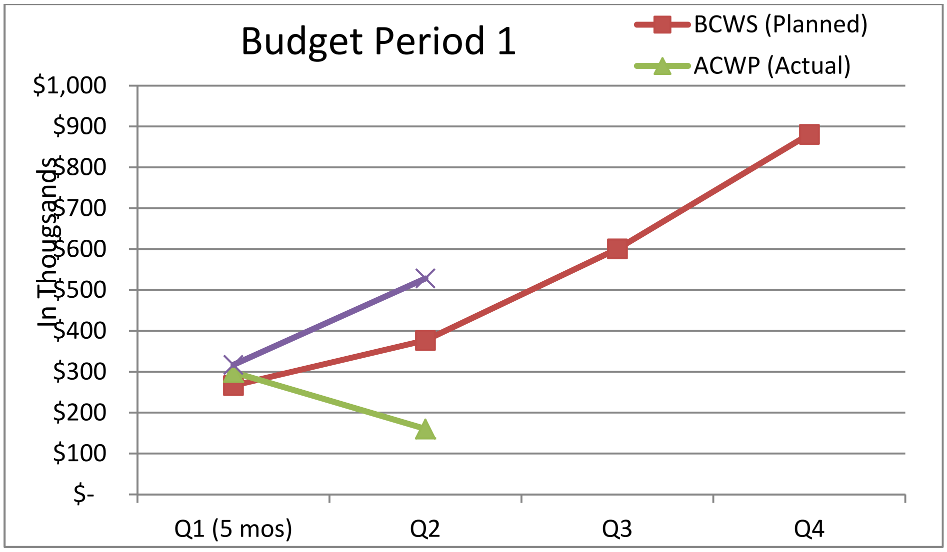


**Figure 5.** Performance Measurement Graph for BP1

**Table 6.** 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 | | |
| **BCWP (Earned)** | $317 | $528 | | |
| **Cum Cost Variance** | 18.28 | 368.08 | | |
| **Cum Scheduled Variance** | 50.58 | 151.39 | | |
| **Cum % Cost Var** | 6% | 70% | | |

Further costing breakdowns by quarter in BP1 are provided in Table 7, and by Task in Table 8. Task 1 (project management) was lower than Q1 due to Q1 having five months compared to 3 months in Q2. Tasks 2 ($69,639) & 3 ($62,802) are currently moving forward with low costing again due to the post-doctoral research associates as the primary staff charging during this quarter. Tasks 2 and 3 are on schedule and on budget according to the project schedule as full time modeling and synthesis staff will be ramping up charging in Q3. There currently has been no work started on Tasks 4-7, however Task 4 will begin in Q3 and Tasks 5-7 will begin after the go-no go at the end of BP1.

**Table 7.**Project Costing by Quarter (BP1)

| | **Budget Period 1 (05/01/2014-04/30/2015)** | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **FY14** | | **FY15** | | **FY15** | | **FY15** | |
| **Baseline Reporting Quarter** | **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 | | | | |
| **Plan/Actual Variance** | $ (32,302) | $ (32,302) | $(49,716) | $(82,018) | | | | |

**Table 8.**Project Costing by Task BP1

| | | BP1 | | | | |
|---|---|---|---|---|---|---|
| **Task** | **Task Title** | **Q1 (5 mos)** | **Q2** | **Q3** | **Q4** | **Total BP1** |
| 1 | Project Management | $49,002 | $27,782 | | | |
| 2 | Molecular Development | $145,636 | $69,639 | | | |
| 3 | Synthesis & Characterization of Candidate Molecules | $104,066 | $62,802 | | | |
| 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** | **$160,223** | **-** | **-** | **$ -** |

## Schedule Status

## II. Issues, Risks, and Mitigation

There are currently no technical issues or risks associated with this program; the synthesis is proceeding as expected, and the model is working as predicted.

As mentioned in Q1's report, there remains a budgetary risk due to the delayed allocation of FY15 funds. The funding for Q2 was anticipated to come October 1, but came in the FIN plan in mid November. The program carried over $35,000 to cover the full-time post-doctoral research associates, however other staff members were not able to charge time to the program. As a result, the project productivity was reduced due to the month-long delay in funding. This delay is not likely to impact the project scope as the other staff members associated with this work were 25-50% time, and can now allocate a larger time commitment to this program over the next quarter to make up scope.

### *Risk 1: Program budget*

The project received $600,000 in November and little was charged due to the end of year holidays and vacation. Project funding is currently 450,000 and the team will be ramping up spending to meet the go-no go decision March 31, 2015.

## III. Changes in Approach

The team has not identified any necessary changes in approach for either the synthesis or molecular development as progress is being made with respect to each major component. We are eager to attend the external peer review in March to get valuable feedback from expert reviewers in the field.

As mentioned in the Q1 report, the team is keeping poor-performing materials to send to Livermore for their micro-encapsulation program efforts.

## IV. Key Personnel

In happy news, our synthetic postdoctoral research associate Dr. Deepika Malhotra is expecting, and will be taking maternity leave in the beginning of Q4. She is currently working on meeting the key program deliverables with respect to the synthesis of 13 candidate molecules prior to taking her leave. Her leave coincides with the project go-no go decision, where the first 13 candidate molecules will be tested for materials performance. Her leave will not impact the program deliverables, as she will return after the second library of 100 new molecules will have been constructed. She will return and begin synthesis on new materials in the end Q4.

## V. Project Output

There are no outputs for the second quarter. The project team is making progress towards 2-3 manuscripts will be submitted for publication. We anticipate submission of two manuscripts in Q3 (Jan-Mar) of FY15. As mentioned previously in Q1's report, we anticipate at a synthesis manuscript in *Green Chemistry* or *Environmental Science and Technology* and one molecular modeling manuscript will be submitted to the *Journal of the American Chemical Society*.

### Project Schedule Status

Table 9 is a Gantt chart that outlines by Quarter, all major tasks and subtasks with their projected completion dates. Task 1 was completed, as the quarterly report (here) has been provided to DOE by Jan 31, 2015. Milestones 1 and 2, and subtasks 2.1 and 2.2 were completed in Q1. Subtasks 2.3-2.4 have begun (with 30 molecules predicted), concurrently with subtask 3.1 (8 of 13 molecules synthesized). No work was started for Tasks 4 -7, however sample measurement work will be begin in Q3. All tasks and subtasks are all on track to be completed in the original project schedule.

**Table 9.** 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** | | | | | | | | ■ |