

RPPR submitted to the US DOE NETL  
DE-FE0010799

**Small Molecular Associative Carbon Dioxide (CO<sub>2</sub>) Thickeners for Improved Mobility  
Control**

Quarterly Research Performance Progress Report

Start date: 1/1/14

End date: 3/31/14

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April 14, 2014

DUNS Number DUNS: 00-451-4360

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A handwritten signature in black ink, appearing to read "Robert M. Enick". The signature is written in a cursive style with a prominent flourish at the end.

## **DISCLAIMER**

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## **EXECUTIVE SUMMARY**

The objective of this project is to promote the application of a CO<sub>2</sub> thickener for CO<sub>2</sub> EOR, and to then test the thickener in a single injection well pilot test. During Phase 1 – the current and initial phase of this project - various CO<sub>2</sub> EOR operators will be contacted by email, phone, and during in-person meetings in an attempt to establish a relationship that will facilitate such a field trial should the thickener be successfully developed. The field test would be conducted during Phase 2 of this NETL award.

The design, synthesis, purification and initial assessments of CO<sub>2</sub> solubility and (for compounds that dissolve in CO<sub>2</sub>) viscosity enhancement are underway under separate ARPA-E funding. In all cases the thickeners are designed to be relatively small molecules that aggregate in solution to induce large increases in viscosity at low concentration. Ultrahigh molecular weight polymers are not being considered because our prior research has shown that only the prohibitive expensive and environmentally persistent fluoroacrylate-functionalized polymer can thicken CO<sub>2</sub> at reservoir conditions. Our team has begun the synthesis of Type 1, Type 2, and Type 3 small associative molecules under separate ARPA-E funding. Type 1 refers to molecules with CO<sub>2</sub>-philic cores and aromatic associating groups at each end of the molecule. Type 2 refers to molecules with CO<sub>2</sub>-philic cores and CO<sub>2</sub>-reactive amine groups at each end of the molecule. Type 3 thickeners, which are two-component systems composed of a CO<sub>2</sub>-philic compound with a pendent electron donating group (component 1) or a pendent electron-receiving group (component 2).

During this quarter we have received one letter of commitment for this project from one major CO<sub>2</sub> EOR operator; Tabula Rasa. Our contact for obtaining this letter was Tracy Evans. The letter was signed by Tracy Evans, Chief Operating Officer of Tabula Rasa Partners LLC. We successfully concluded discussions with Lillian Lo, reservoir Engineering Fellow of Enhanced Recovery Technology at ConocoPhillips. These discussions led to a verbal agreement for a letter of commitment, which should be obtained during the next quarter

As noted previously, Denbury Resources appears to be particularly interested in this project because their CO<sub>2</sub> flooding strategy is focused on gas cycling (not WAG). Therefore Denbury Resources is particularly interested in CO<sub>2</sub>-soluble additives such as surfactants (the objective of a separate NETL RUA project) and CO<sub>2</sub>-thickeners (this NETL-funded project).

## **2. ACCOMPLISHMENTS**

### **Major goals:**

The major goal of this project is to establish a relationship with several CO<sub>2</sub> EOR operators that will allow for the rapid and effective assessment of a CO<sub>2</sub> thickener in lab-scale tests that would provide enough information to give the operators confidence to conduct a pilot test of the thickener in the field. Therefore we intend to foster these relationships and to employ field data and fluid and rock samples from patterns in which CO<sub>2</sub> mobility control with a CO<sub>2</sub> thickener would be attractive to these operators.

The most important accomplishments during this quarter was obtaining one letter of commitment from Tabula rasa and obtaining one verbal agreement for a letter from Conoco Phillips.

### **Accomplishments under these goals**

#### **Task 1 – Project Management, Planning, and Reporting**

The PMP has been provided to NETL, and was sent along with this quarterly to verify its submission.

#### **Task 2 – Letters of commitment, Field Site Data and Samples**

During this quarter we received one more letter of commitment, bringing our total to three (Denbury, Kinder Morgan and Tabula Rasa).

#### **Task 3 – Approaches for Laboratory Testing of Thickened CO<sub>2</sub>**

We have no changes to our previously submitted lab testing plan. This outline has already been presented to David D'Souza of Denbury Resources, and is found below.

- Conducting the core floods at or near reservoir temperature and pressure that is commensurate with the fields that may be used in future field tests.
- The core shall be waterflooded and oil-flooded to emulate geologic history, and then waterflooded to emulate decades of waterflooding that often precedes CO<sub>2</sub> flooding (unless, of course, the field under consideration was not waterflooded prior to CO<sub>2</sub> injection).
- Three core flooding experiments: (1) The baseline or “control” core flood shall employ continuous CO<sub>2</sub> injection. (2) The second run shall use a water-alternating-pure CO<sub>2</sub> WAG injection strategy at a 1:1 ratio. (3) Finally, thickened CO<sub>2</sub> shall be continuously injected.
- Repeating each test to verify the reproducibility of the results.
- Conducting a displacement that accounts for the heterogeneity of most formations by using (a) a very heterogeneous core, or (b) a co-axial “core-within-a-core”, or (c) a core with longitudinal, irregular, rough-walled fracture(s) extending the length of the core, (d) or two fairly homogeneous parallel cores with different permeabilities.
- Use of a slug (fraction of a pore volume) of CO<sub>2</sub> thickener followed by CO<sub>2</sub>. Check dispersion of the thickener in the CO<sub>2</sub>.
- Use of the newly developed DOE-CO<sub>2</sub> simulator by U. T. Austin (or other simulator) for simulation of core floods with thickened CO<sub>2</sub>. Add visualization (from CT scanner experiments and simulator results) to convince other operators that the injection of thickened CO<sub>2</sub> is a better option than the prolonged injection of pure CO<sub>2</sub> or WAG for the

recovery of oil.

The plans shall be reviewed and agreed upon by the Recipient, the CO<sub>2</sub> EOR Operator(s) and NETL.

#### Task 4 – Technical Status of APRA-E Research

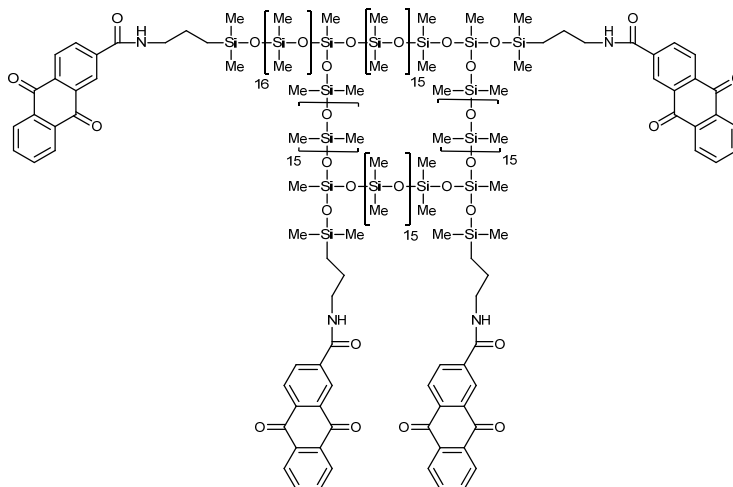
Our team has now synthesized over 100 Type 1, Type 2, and Type 3 small associative molecules thickeners. About half of the ARPA-E funding supports our collaborators at GE Global Research in Niskayuna NY. Type 1 refers to molecules with CO<sub>2</sub>-philic cores and aromatic associating groups at each end of the molecule, or small rigid sugar-based gelators. Type 2 refers to molecules with CO<sub>2</sub>-philic cores and CO<sub>2</sub>-reactive amine groups at each end of the molecule. Type 3 thickeners, which are two-component systems composed of a CO<sub>2</sub>-philic compound with a pendent electron donating group (component 1) or a pendent electron-receiving group (component 2).

Type 1 molecules made to date include triphenoxymethanes, simple organogelators, silicone oligomers with aromatic end groups, and polyether (specifically polypropylene glycol, PPG) oligomers with aromatic end groups, and sugar-based small molecule thickeners. We have begun working on the “universal gelator” molecule bis-(R, $\beta$ -dihydroxy ester (an oxygenated hydrocarbon molecule with two hydroxyls and an isopropyl group on each end) which is capable of thickening an incredibly diverse set of solvents (2H,3H-perfluoropentane (HPFP) and 1H,1H-heptafluorobutanol (HFB), water, toluene, cyclohexane, a 10:1 hexane-chloroform-hexane mixture, dichloromethane, water, CS<sub>2</sub>, and even lager and wine! These solvents were gelled with less than 1wt% of the universal gelator, with the exception of the dichloromethane, which required about 5wt%.

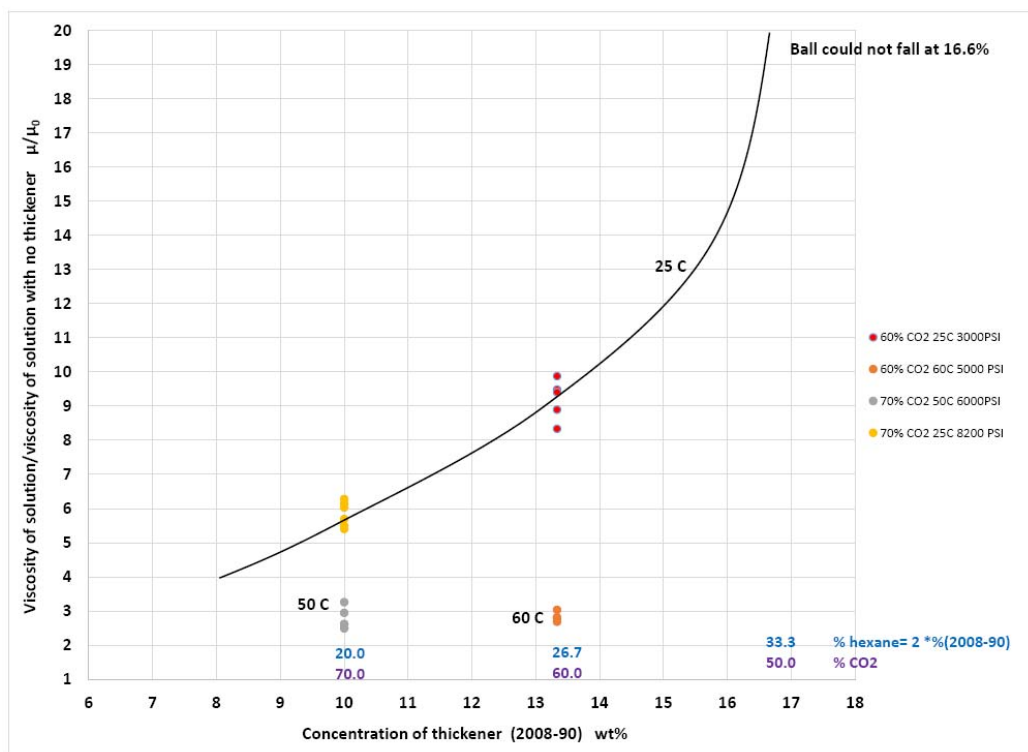
Type 2 molecules made to date include silicone oil oligomers with terminal primary and/or secondary amines, PPG oligomers with terminal primary and/or secondary amines, and silicone oil oligomers terminated with amide groups leading to aromatic groups.

Type 3 thickeners have been made solely with silicone oil based A and silicon oil based B compounds. About a dozen A + B combinations have been made to date.

We have begun the testing of CO<sub>2</sub> solubility and viscosity enhancement of these compounds. We are achieving success in CO<sub>2</sub>-solubility, and recently found that the anthraquinone group is particularly effective at intermolecular associations. For example, in the following molecule the structure of a thickener is shown. The silicone portions -(Si-CH<sub>3</sub>CH<sub>3</sub>O)<sub>n</sub>- (shown as -(Si-MeMeO)<sub>n</sub>-) promote solubility in CO<sub>2</sub>, while the aromatic group anthraquinone composed of three benzene rings and two =O groups provide intermolecular associations.



This compound forms transparent rigid gels in liquids like hexane in dilute concentration; and while not soluble in CO<sub>2</sub>, the compound (which is designated as 2008-90) was capable of thickening CO<sub>2</sub>-rich solutions (mixtures of CO<sub>2</sub> and hexane) as in the following figure.



We continue modifying this compound and developing new compounds that can thicken CO<sub>2</sub> without the need for a co-solvent.

## **Training and professional development**

### **Dissemination of results**

As described in the accomplishment section, we have made five companies aware of our three-pronged (Types 1,2 and 3) approach for development of a CO<sub>2</sub> thickener.

We gave a presentation on our work at the AIChE conference in San Francisco.

We submitted an abstract of our ARPA-E + NETL funded work on CO<sub>2</sub> thickeners for the 2014 IOR conference in Tulsa, which has been accepted for presentation (the SPE paper is due Fen 10 2014).

### **Plans for next quarter**

We intend to keep making CO<sub>2</sub> thickener candidate molecules under ARPA-E funding.  
We intend to obtain a fourth letter of commitment.

### 3. PRODUCTS

1. Our presentation at AIChE National Meeting was:

*The CO<sub>2</sub>-Solubility and Viscosity Enhancing Potential of CO<sub>2</sub>-Philes Functionalized With Aromatic Groups*, was presented at the 2013 AIChE Annual Meeting in San Francisco, CA.

Date: **Wednesday, November 6, 2013**

Wednesday, November 6, 2013: 8:30 AM  
Union Square 14 (Hilton)

**Jason J. Lee**<sup>1</sup>, **Stephen Cummings**<sup>1</sup>, Robert J. Perry<sup>2</sup>, Eric J. Beckman<sup>1</sup> and **Robert Enick**<sup>3</sup>, (1)Chemical Engineering, University of Pittsburgh, Pittsburgh, PA, (2)Global Research, General Electric, Niskayuna, NY, (3)University of Pittsburgh, Department of Chemical and Petroleum Engineering, Pittsburgh, PA

The low viscosity of CO<sub>2</sub> at typical enhanced oil recovery (EOR) conditions is responsible for a poor mobility ratio that causes viscous fingering and poor sweep efficiency, leading to reduced efficiency and yield. To overcome this problem, there is a need to develop CO<sub>2</sub>-soluble additives that will increase the effective viscosity of CO<sub>2</sub> without the use of a co-solvent. The only known polymeric direct thickener poly(fluoroacrylate-co-styrene) (polyFAST) has been shown to significantly increase the viscosity measured by falling cylinder viscometry and Berea sandstone core mobility experiments. The proposed mechanism of aggregation responsible for this viscosity enhancement is believed to be  $\pi$ - $\pi$  stacking between aromatic rings. However, high molecular weight polymers like polyFAST require significant amounts of expensive fluorinated moieties in order to impart solubility. In addition to their cost, fluorinated compounds have undesirable environmental impacts. Therefore, this work focuses on the development of less expensive and safer hydrocarbon-based CO<sub>2</sub> thickeners. Because our prior studies have demonstrated that unacceptably high pressures are required to dissolve non-fluorous polymers, this study entails the use of small, associating compounds to create a thermodynamic illusion of a polymer. Each CO<sub>2</sub> thickening candidate consists of at least one non-fluorous CO<sub>2</sub>-philic segments and at least two slightly CO<sub>2</sub>-phobic functionalities that promote intermolecular aggregation (e.g. aromatic groups). Solubilities of a range of newly synthesized molecules in CO<sub>2</sub> and their associated viscosity enhancing abilities will be presented. Preliminary results indicate that it is possible to design such novel CO<sub>2</sub>-thickening candidates that are up to 1wt% soluble in CO<sub>2</sub> at pressures commensurate with EOR.

2. The PI (Dr. Enick) completed a chapter on CO<sub>2</sub> EOR state-of-the-art for The Catalyst Group newsletter. This report, which includes a highlight the thickener developments, was distributed to the subscribers of the newsletter in the fall of 2013.

3. The abstract for the April 2014 SPE IOR meeting in Tulsa was accepted and is being presented by Jason Lee.

#### **Development of Small Molecule Thickeners for CO<sub>2</sub> EOR and CO<sub>2</sub> Fracturing**

The only known CO<sub>2</sub> thickener (a compound that dissolves in CO<sub>2</sub> and increases its viscosity significantly when present in dilute concentration) is a fluoroacrylate-styrene random copolymer that is probably too expensive for commercial application. High pressure CO<sub>2</sub> has also been thickened via the dissolution of high molecular weight polydimethylsiloxane (PDMS, silicone oil) or polyvinyl acetate (PVAc), but this strategy requires several wt% of the polymer and the addition of large concentrations of an organic solvent (e.g. 20% toluene + 80% CO<sub>2</sub>), which is also impractical for commercial use. Because the utilization of high molecular weight polymers no longer appears to be a viable strategy for affordably thickening CO<sub>2</sub> at EOR conditions, we are assessing the use of novel small molecules that self-assemble into viscosity-enhancing supramolecular structures in dense CO<sub>2</sub>. Small molecules can actually increase fluid viscosity just as effectively as high molecular weight polymers when compared at similar concentrations. For example, tributyltin fluoride and hydroxyaluminum di(2-ethyl hexanoate) are remarkable thickeners of light hydrocarbons even when present at concentrations well below 1wt%. In this presentation, three types of novel CO<sub>2</sub> thickening candidates are designed, synthesized and assessed for solubility in CO<sub>2</sub> and viscosity-increasing capabilities. Each small molecule possesses a "CO<sub>2</sub>-philic" segment that promotes dissolution in CO<sub>2</sub>; the CO<sub>2</sub>-philic segments are low-cost oligomeric versions of CO<sub>2</sub>-soluble polymers. Three different types of slightly "CO<sub>2</sub>-phobic" functional groups known to promote intermolecular associations in hydrocarbon and/or aqueous systems are also included in the thickener structure. The foremost challenge in the molecular design is selecting the appropriate type and number of associating groups needed to enhance viscosity, while not rendering the compound insoluble in CO<sub>2</sub>. A variety of prospective CO<sub>2</sub> thickeners have been synthesized and the solubility of these candidates in CO<sub>2</sub>, and their ability to thicken CO<sub>2</sub>, will be presented.

4. We will be presenting our work at a poster session in Midland in May 2014 at the AAPG Section Meeting

**Robert Enick**  
**Abstract for Southwest AAPG section meeting**  
Sunday 11-May-14 8:00 AM to Wednesday 14-May-14 5:00 PM CDT  
Midland Center



**CO<sub>2</sub> soluble surfactants and thickeners for CO<sub>2</sub> IOR**

There have been over a dozen field tests of SAG (aqueous surfactant solution-alternating-CO<sub>2</sub> gas) conformance and mobility control in the 1980s and 1990s. Most of these tests were technical successes but the economics of the process were hampered by the extremely low price of oil. Given the large amount of oil that remains in the ground after CO<sub>2</sub> EOR and the current price of oil, it's not surprising that there has been renewed interest in additives for improved conformance and or mobility control during CO<sub>2</sub> EOR. For example, there have been recent developments in the dissolution of surfactants in the high pressure CO<sub>2</sub> (rather than, or in addition to, the use of additives in the injected brine). The first example is the use of a slightly CO<sub>2</sub>-soluble (0.02-0.2 wt%) non-ionic surfactant designed to stabilize CO<sub>2</sub>-in-brine foams that are generated in-situ. This can allow an operator to continuously inject only CO<sub>2</sub> with dissolved surfactant (GS), with foam formation occurring as the soapy CO<sub>2</sub> mixes with the in-situ brine. Alternately, one can alternately inject brine and CO<sub>2</sub> gas containing dissolved surfactant (WAGS). Finally, one could consider injecting a brine-based soap solution containing an ionic surfactant alternately with CO<sub>2</sub> containing a non-ionic surfactant (SAGS). CO<sub>2</sub>-soluble surfactants are already available on a commercial scale for use in such processes. A second CO<sub>2</sub> additive of interest to CO<sub>2</sub> EOR operators is a CO<sub>2</sub> thickener. The ideal thickener would be an inexpensive, safe compound that could be added to high pressure CO<sub>2</sub> in dilute concentration (~0.1 wt%), where it would dissolve without the need to heat the CO<sub>2</sub>. The resultant transparent, stable solution could be easily tailored to have a viscosity that is the same as the oil being displaced simply by varying the concentration of the dissolved thickener. This would eliminate all of the problems associated with the low viscosity (i.e. high mobility) of CO<sub>2</sub>, possibly eliminating the need for WAG during CO<sub>2</sub> EOR. Although it is simple to thicken water and oils, CO<sub>2</sub> is notoriously difficult to thicken. A review of the long history of failed attempts to thicken CO<sub>2</sub> will be presented, along with an overview of the only CO<sub>2</sub> thickener identified to date (an expensive proof-of-concept compound), and the new inexpensive compounds currently being assessed in our labs.

#### **4. PARTICIPANTS & OTHER COLLABORATING ORGANIZATIONS**

Dr. Eric Beckman and Dr. Enick are supported by this NETL project.

Collaborators solely related to thickener development (funded by ARPA-E) include Steven Cummings (post doc at Pitt), Jason Lee (PhD student at Pitt), Aman Dhuwe (PhD student) Robert Perry, Michael O'Brien and Mark Doherty (GE chemists).

Informal collaborations have also been made with engineers at Denbury, Kinder Morgan, ConocoPhillips, and Tabula Rasa.

Collaborations with SCAL (core flooding) will not commence until Phase 2 of this project.

Name:	Robert Enick
Project Role:	PI
Nearest person month worked:	1
Contribution to Project:	Leading the project, contacting companies..
Funding Support:	NETL (this award) and ARPA-E
Collaborated with individual in foreign country:	No
Country(ies) of foreign collaborator:	No
Travelled to foreign country:	No
If traveled to foreign country(ies), duration of stay:	N/A

Name:	Eric Beckman
Project Role:	PI
Nearest person month worked:	1
Contribution to Project:	Thickener development and strategies for introducing thickeners into CO <sub>2</sub> for lab- and field-tests.

Funding Support: NETL (this award) and ARPA-E  
Collaborated with individual  
in foreign country: No  
Country(ies) of foreign collaborator: No  
Travelled to foreign country: No  
If traveled to foreign country(ies),  
duration of stay: N/A

Name: Jason Lee  
Project Role: PhD  
Nearest person month worked: 6  
Contribution to Project: Thickener synthesis and testing  
Funding Support: ARPA-E  
Collaborated with individual  
in foreign country: No  
Country(ies) of foreign collaborator: No  
Travelled to foreign country: No  
If traveled to foreign country(ies),  
duration of stay: N/A

Name: Aman Dhuwe  
Project Role: PhD  
Nearest person month worked: 6  
Contribution to Project: Thickener synthesis and testing  
Funding Support: ARPA-E  
Collaborated with individual  
in foreign country: No  
Country(ies) of foreign collaborator: No  
Travelled to foreign country: No  
If traveled to foreign country(ies),  
duration of stay: N/A

Name: Steve Cummings  
Project Role: PhD  
Nearest person month worked: 6  
Contribution to Project: Thickener synthesis and testing  
Funding Support: ARPA-E  
Collaborated with individual  
in foreign country: No  
Country(ies) of foreign collaborator: No  
Travelled to foreign country: No  
If traveled to foreign country(ies),  
duration of stay: Visited his family in Great Britain for vacation

Name: Robert Perry  
Project Role: Chemist at GE  
Nearest person month worked: 6  
Contribution to Project: Thickener synthesis and testing  
Funding Support: ARPA-E  
Collaborated with individual  
in foreign country: No  
Country(ies) of foreign collaborator: No  
Travelled to foreign country: No  
If traveled to foreign country(ies),  
duration of stay: N/A

Name: Michael O'Brien  
Project Role: Chemist at GE  
Nearest person month worked: 6  
Contribution to Project: Thickener synthesis and testing  
Funding Support: ARPA-E  
Collaborated with individual  
in foreign country: No  
Country(ies) of foreign collaborator: No  
Travelled to foreign country: No  
If traveled to foreign country(ies),  
duration of stay: N/A

Name: Mark Doherty  
Project Role: Chemist at GE  
Nearest person month worked: 6  
Contribution to Project: Thickener synthesis and testing  
Funding Support: ARPA-E  
Collaborated with individual  
in foreign country: No  
Country(ies) of foreign collaborator: No  
Travelled to foreign country: No  
If traveled to foreign country(ies),  
duration of stay: N/A

## **5. IMPACT**

The most obvious impact of this work will be the improved rate of oil recovery and increased amount of recoverable oil should a thickener be designed.

This work, along with the PI's recent NETL-sponsored review of mobility control and upcoming review of CO<sub>2</sub> EOR (including thickeners), has helped to re-invigorate interest in CO<sub>2</sub> mobility control. Specifically, this project is providing a springboard for the introduction of a research product into a rapid field application.

This project combines basic research, chemistry, chemical engineering, and petroleum engineering, and is an excellent example of how a team consisting of chemists, chemical engineers and petroleum engineers can address energy-related problems.

## **6. CHANGES/PROBLEMS**

None to date.

## **7. SPECIAL REPORTING REQUIREMENTS**

Under the ACCOMPLISHMENTS section we have reported on our progression the ARPA-E sponsored project related to the synthesis of a thickener.

## **8. BUDGETARY INFORMATION**





## Tabula Rasa PARTNERS

January 20, 2014

Robert Enick  
Department of Chemical and Petroleum Engineering.  
University of Pittsburgh  
1249 Benedum Hall  
Pittsburgh PA 15261  
[rme@pitt.edu](mailto:rme@pitt.edu)

Dear Prof. Enick:

As per our discussion at the Midland CO<sub>2</sub> Conference, it is my understanding that you are researching a small molecule CO<sub>2</sub> thickener for improved CO<sub>2</sub> mobility control, with funding from ARPA-e (for the design of the molecule itself) and NETL (for lab-scale testing and core studies to demonstrate viability in porous media). In order for your NETL-sponsored lab tests to closely replicate meaningful field conditions, TRP is willing to provide you with the following items related to Seminole East Field, Gaines County, Texas.

The reservoir temperature – 108 deg F

The CO<sub>2</sub> pressure at the injector wellhead – 1,800 psig

The CO<sub>2</sub> injection well bottom-hole injection pressure – 3500 psi

The producing well bottom-hole pressure – 1,500 psi

The MMP for the oil – Approximately 1,350 psi

Samples of 1" diameter and 2" diameters horizontal plugs from an oil-rich zone,

1 gallon of crude oil

1 gallon of produced brine

A brief history of the pattern's production

TRP's information will be used to conduct lab-scale tests that are designed to demonstrate whether the CO<sub>2</sub> thickener would be a viable candidate for a single injection well field test. After TRP has had an opportunity to evaluate the tests and experiments conducted we would be willing to discuss the possibility of performing a field test of the thickener

Sincerely,

A handwritten signature in blue ink, appearing to read 'Ronald T. Evans', with a long horizontal line extending to the right.

Ronald T. Evans

Chief Operating Officer

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Allen, Texas 75002

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