

RPPR submitted to the US DOE NETL
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**Small Molecular Associative Carbon Dioxide (CO₂) Thickeners for Improved Mobility
Control**

Quarterly Research Performance Progress Report

Start date: 10/1/13

End date: 12/31/13

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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 CO₂ thickener for CO₂ 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 CO₂ 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 CO₂ solubility and (for compounds that dissolve in CO₂) 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 CO₂ 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 CO₂-philic cores and aromatic associating groups at each end of the molecule. Type 2 refers to molecules with CO₂-philic cores and CO₂-reactive amine groups at each end of the molecule. Type 3 thickeners, which are two-component systems composed of a CO₂-philic compound with a pendent electron donating group (component 1) or a pendent electron-receiving group (component 2).

During this quarter we have received two letters of commitment for this project from two major CO₂ EOR operators; Denbury Resources and Kinder Morgan. Our contacts for obtaining these letters were David D'Souza, principal technical advisor for reservoir engineering at Denbury Resources; and Lanny Schoeling, VP of Engineering and Technical Development at Kinder Morgan CO₂ Company. The letters were signed by David D'Souza of Denbury and Walt True, Director of Reservoir Technologies at Kinder Morgan. We are continuing our discussions with David Smith, Conformance Engineering Advisor for Enhanced Reservoir Technology at ConocoPhillips. Further, Dr. Enick attended the 2013 CO₂ Conference in Midland Texas and had the opportunity to meet with two other CO₂ EOR operators; Rickey Coon, production Supervisor of Hess Corporation and Tracy Evans, Chief operating Officer of Tabula Rasa. Both companies are currently considering providing letters of support.

As noted previously, Denbury Resources appears to be particularly interested in this project because their CO₂ flooding strategy is focused on gas cycling (not WAG). Therefore Denbury Resources is particularly interested in CO₂-soluble additives such as surfactants (the objective of a separate NETL RUA project) and CO₂-thickeners (this NETL-funded project).

Dr. Enick and Beckman will continue to approach ConocoPhillips, Hess Corporation, and Tabula Rasa for similar letters.

2. ACCOMPLISHMENTS

Major goals:

The major goal of this project is to establish a relationship with several CO₂ EOR operators that will allow for the rapid and effective assessment of a CO₂ 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 CO₂ mobility control with a CO₂ thickener would be attractive to these operators.

The most important accomplishment during this quarter was obtaining two letters of commitment; one from Denbury Resources and one from Kinder Morgan.

The other accomplishment of this quarter was Dr. Enick's attendance at the 2013 CO₂ EOR Conference in Midland where he had the opportunity to discuss this project with numerous companies, two of which (Hess and Tabula Rasa) seem to have strong interest in the CO₂ thickener.

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 two letters of commitment.

Task 3 – Approaches for Laboratory Testing of Thickened CO₂

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 CO₂ flooding (unless, of course, the field under consideration was not waterflooded prior to CO₂ injection).
- Three core flooding experiments: (1) The baseline or "control" core flood shall employ continuous CO₂ injection. (2) The second run shall use a water-alternating-pure CO₂ WAG injection strategy at a 1:1 ratio. (3) Finally, thickened CO₂ 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 CO₂ thickener followed by CO₂. Check dispersion of the thickener in the CO₂.
- Use of the newly developed DOE-CO₂ simulator by U. T. Austin (or other simulator) for simulation of core floods with thickened CO₂. Add visualization (from CT scanner experiments and simulator results) to convince other operators that the injection of thickened CO₂ is a better option than the prolonged injection of pure CO₂ or WAG for the recovery of oil.

The plans shall be reviewed and agreed upon by the Recipient, the CO₂ EOR Operator(s) and NETL.

Task 4 – Technical Status of APRA-E Research

Our team has now synthesized several dozen 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 CO₂-philic cores and aromatic associating groups at each end of the molecule. Type 2 refers to molecules with CO₂-philic cores and CO₂-reactive amine groups at each end of the molecule. Type 3 thickeners, which are two-component systems composed of a CO₂-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. We have begun working on the “universal gelator” molecule bis-(R,β-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, 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 CO₂ solubility and viscosity enhancement of these compounds. We are achieving success in CO₂-solubility, but to date have not been able to simultaneously achieve self-assembly in solution that leads to viscosity enhancement.

Training and professional development

Dr. Enick spoke with numerous CO₂ EOR operators in Midland about this project and the implementation of a CO₂ thickener in the field.

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 CO₂ 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 CO₂ thickeners for the 2014 IOR conference in Tulsa, which has been accepted for presentation (the SPE paper is due Feb 10 2014).

Plans for next quarter

We intend to keep making CO₂ thickener candidate molecules under ARPA-E funding.

We intend to obtain a third letter of commitment.

We intend to visit one company (Denbury) during the next quarter.

3. PRODUCTS

Our presentation at AIChE National Meeting was:

The CO₂-Solubility and Viscosity Enhancing Potential of CO₂-Philes Functionalized With Aromatic Groups, has been accepted for presentation 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. Lee¹, **Stephen Cummings**¹, Robert J. Perry², Eric J. Beckman¹ and **Robert Enick**³, (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 CO₂ 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 CO₂-soluble additives that will increase the effective viscosity of CO₂ 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 π - π 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 CO₂ 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 CO₂ thickening candidate consists of at least one non-fluorous CO₂-philic segments and at least two slightly CO₂-phobic functionalities that promote intermolecular aggregation (e.g. aromatic groups). Solubilities of a range of newly synthesized molecules in CO₂ and their associated viscosity enhancing abilities will be presented. Preliminary results indicate that it is possible to design such novel CO₂-thickening candidates that are up to 1wt% soluble in CO₂ at pressures commensurate with EOR.

The PI (Dr. Enick) completed a chapter on CO₂ 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.

The abstract for the April 2014 SPE IOR meeting in Tulsa was accepted

Development of Small Molecule Thickeners for CO₂ EOR and CO₂ Fracturing

The only known CO₂ thickener (a compound that dissolves in CO₂ 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 CO₂ 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% CO₂), 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 CO₂ at EOR conditions, we are assessing the use of novel small molecules that self-assemble into viscosity-enhancing supramolecular structures in dense CO₂. 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 CO₂ thickening candidates are designed, synthesized and assessed for solubility in CO₂ and viscosity-increasing capabilities. Each small molecule possesses a "CO₂-philic" segment that promotes dissolution in CO₂; the CO₂-philic segments are low-cost oligomeric versions of CO₂-soluble polymers. Three different types of slightly "CO₂-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 CO₂. A variety of prospective CO₂ thickeners have been synthesized and the solubility of these candidates in CO₂, and their ability to thicken CO₂, will be presented.

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, Hess 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 CO₂ 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 CO₂ EOR (including thickeners), has helped to re-invigorate interest in CO₂ 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



Date: 1/7/2014

Dr. Robert Enick
Dept. of Chemical and Petroleum Eng.
University of Pittsburgh
1249 Benedum Hall
Pittsburgh PA 15261
rme@pitt.edu

Dear Prof. Enick:

It is my understanding that you are researching small molecule CO₂ thickener for improved CO₂ 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, we would be interested in providing you with the following items related to a pattern in one of our CO₂ floods (West Heidelberg or other) with mobility control problems.

The reservoir temperature
The CO₂ Injection well – wellhead & flowing bottomhole pressure
The producing well bottomhole pressure
The MMP for the oil
Samples of 1" diameter and 2" diameters horizontal plugs form an oil-rich zone, or
Samples of 4" diameter vertical cores form an oil-rich zone
1 gallon of crude oil, 1 gallon of produced brine
A brief history of the pattern's production

It is my understanding that you would use this materials and information to conduct lab-scale tests that would demonstrate whether the CO₂ thickener would be a viable candidate for a single injection well field test.

This letter does not constitute any obligation on Denbury's part, but merely a strong interest in the CO₂ viscosifier project. Further, if the data above is provided to you, Denbury's agreement and permission would be required prior to publication of any data, information or results regarding its fields. A contract and confidentiality agreement would be executed prior to any data being provided to you for the project.

If the lab testing is successful, we would be very interested in testing the CO₂ thickener in the field.

Sincerely,

A handwritten signature in blue ink that reads "Walt S. True". The signature is fluid and cursive.

Walt S. True,
Director of Reservoir Technologies
5320 Legacy Drive
Plano, TX 75024
Phone: 972-673-2505



2 January 2014

Robert Enick
Dept. of Chemical and Petroleum Eng.
University of Pittsburgh
1249 Benedum Hall
Pittsburgh PA 15261

Dear Prof. Enick:

It is my understanding that you are researching small molecule CO₂ thickener for improved CO₂ 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, I would be able to provide you with the following items related to a pattern in a field with mobility control problems.

SACROC

The reservoir temperature

The CO₂ pressure at the injector wellhead

The CO₂ injection well flowing bottomhole pressure

The producing well bottomhole pressure

The MMP for the oil

Samples of 1" diameter and 2" diameters horizontal plugs form an oil-rich zone, *or (if available)*

Samples of 4" diameter vertical cores form an oil-rich zone (if available)

1 gallon of crude oil

1 gallon of produced brine

A brief history of the pattern's production

It is my understanding that you would use this materials and information to conduct lab-scale tests that would demonstrate whether the CO₂ thickener would be a viable candidate for a single injection well field test.

Sincerely,

A handwritten signature in cursive script that reads 'Lanny Schoeling'.

Dr. Lanny Schoeling, P.E.
VP of Engineering and Technical Development
Kinder Morgan CO₂ Company