Dynamic Binary Complexes (DBCs) as Super-Adjustable Viscosity Modifiers for Hydraulic Fracturing Fluids

DE-FE0031778

Texas A&M University Department of Chemical Engineering Texas A&M Energy Institute

U.S. Department of Energy National Energy Technology Laboratory Oil & Natural Gas 2021 Integrated Review Webinar

• Project Funding

	Federal	Cost Share	Total Costs	Cost Share %
Budget Period 1	\$492,699	\$124,683	\$617,382	20.20%
Budget Period 2	\$496,841	\$127,098	\$623,939	20.37%
Budget Period 3	\$510,169	\$123,209	\$633,378	19.45%
Total	\$1,499,709	\$374,990	\$1,874,699	20.00%

• **Project Performance Dates**

Task Name	Year 1	Year 2	Ye		
	Qtr1 Qtr2 Qtr3 Qtr4	Qtr1 Qtr2 Qtr3 Qtr4	Qtr1 Qtr2	2 Qtr3	Qtr4
Task 1: Investigation of Flow and Rheological Characteristics of DBCs					
Task 2: Determination of Proppant Dispersion Stability under Various Conditions					
Task 3: Obtaining an Understanding of Extent of Reversibility and Reusability					
Task 4: Investigation of Compatibility with Other Chemicals in Fracking Fluids					
Task 5: Development of Models to Describe Proppant Transport and Fracture Propagation					
Task 6: Construction of Models for Adsorption and Desorption of DBCs			1		
Task 7: Development of Models for Estimating Wastewater Recovery and Gas Production Rates					
Task 8: Selection and Optimization of DBC Formulations for Laboratory-Scale Tests					
Task 9: Carrying out Laboratory Experiments to Evaluate Hydraulic Fracturing Performance)	
Task 10: Scale-up, Manufacturing, and Field Testing of DBCs					
Task 11: Preparation of Cost-Benefit Analysis and Evaluation of Economic Impact					

Program Overview

Project Participants

Texas A&M University (Research and Development)

- Department of Chemical Engineering
- Texas AM& Energy Institute

Incendium Technologies (Commercialization)

Project Personnel

Mustafa Akbulut, Associate Professor, Texas A&M University Joseph Kwon, Assistant Professor, Texas A&M University Shuhao Liu, Graduate Student Silabrata Pahari, Graduate Student Yu-Ting Lin, Graduate Student Bhargavi Bhat, Graduate Student Spencer Doyle, Undergraduate Student Landry Ray, Undergraduate Student Ankit Anand, Undergraduate Student Sek Kai Leong, Project Technician

Cengiz Yegin, Product Development Engineer, Incendium Technologies

Project Objectives

- To develop novel dynamic binary complexes to achieve super-adjustable, reversible viscosities and the implementation and wide-spread utilization of these novel viscosifiers in hydraulic fracturing fluids.
- To mature the Technology Readiness Level (TRL) of this concept from TRL 2-3 to TRL 5-6.
- To investigate and optimize rheological properties of aqueous solutions containing DBCs with respect to shear rate, concentration, temperature, salinity, and pressure
- To evaluate and optimize the compatibility of DBCs with other chemicals used in fracking fluids such as clay stabilizers, corrosion inhibitors, scale inhibitors, friction reducers
- To develop computational models and frameworks for investigating the effect of DBC on proppant transport, fracture propagation, bank formation, and fluid leak-off during hydraulic fracturing
- To develop a 3D, three-phase black oil model for estimating the production rates of formation water, recovered DBC, and gas from the fractured wells
- To assess the efficiency of proppant transport into fissures and fractures and permeability enhancements using the selected optimum DBC formulations and to compare the performance of developed DBCs with that of currently available fracking fluids
- To outline comprehensive manufacturing design and strategy for the large-scale synthesis of the most optimum DBC formulation
- To carry out a comprehensive cost-benefit analysis considering the cost of raw materials, labor, capital investment of manufacturing equipment, operational costs, and percent improvements in shale gas recovery

	Viscosity	Advantages	Disadvantages/Limitations
Water frac	2-5 cP	InexpensiveInsensitive to salinity	Requires high pump ratesPoor proppant transportNarrow fracture width
Linear aqueous gels	10-30 cP	 Environmentally friendly Support transport of medium-sized proppants 	 Not re-usable Somehow narrow fracture width Some residue leftover in fractures
Cross-linked aqueous gels	100-1000 cP	Wide fracture widthReduced fluid lossEnhanced proppant transport	 Not re-usable Corrosive/toxic breakers Fracture damage by residues
Aqueous viscoelastic surfactant (VES)-based fluids	100-1000 cP	Wide fracture widthEnhanced proppant transportNo residue leftover in fractures	High-costPoor temperature/salt toleranceHigh volume of fluid leak-off
Foam fluids	10-100 cP	 Very low fluid loss Mediocre proppant transport Reduced environmental impact 	 High-cost of gas Gas availability Depressurization damage in fractures
Gelled oil-based fluids	50-1000 cP	Compatible with all formationsLower formation damage	 Gelling and clogging problems Higher cost More toxic than water-based systems











Region	Shale Depth (ft)	Temperature (°F)	Salinity (mg/mL)
Anadarko	4,000 - 11,000	140° to 280° F	<50
Appalachia	5,000 - 9,000	160° to 240° F	150-200
Bakken	6,000 - 12,000	180° to 300° F	200-300
Eagle Ford	4,000 - 14,000	140° to 340° F	50-100
Haynesville	10,000 - 13,000	260° to 300° F	<50
Niobrara	7,000 - 8,000	200° to 220° F	50-100
Permian	6,700 - 11,300	190° to 280° F	100-150

Target Conditions:

Temperature: 140°F to 280°F Salinity: 50 mg/mL to 200 mg/mL Depth: 4000 ft to 10,000 ft





Developed DBCs

Dendrimer polymer \rightarrow - groups (carboxylic)

$nA + mB \leftrightarrows DBC$







• Optimum formulations: A5/B5, A8/B1, A10/B12, A12/B5

Task Name		Ye	ar 1			Yea	ar 2			Yea	nr 3	
	Qtr1	Qtr2	Qtr3	Qtr4	Qtr1	Qtr2	Qtr3	Qtr4	Qtr1	Qtr2	Qtr3	Qtr4
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Compatibility with Additives

- Additives are important functional components in the fracking fluid that could affect the viscosity of a fracking fluid.
- Based on most commonly used commercial formulations, different types and concentrations of additives were chosen to investigate the compatibility of the developed viscosity modifying agents

1: biocide	glutaraldehyde
2: breaker	ammonium persulfate
3: clay stabilizer	choline chloride
4: corrosion inhibitor	isopropanol
5: friction reducer	ethylene glycol
6: iron control	citric acid
7: emulsion preventer	isopropanol
8: scale inhibitor	sodium acrylate

Effect of Additives on viscosity of DBCs



- The additives have very limited influence on the viscosity of DBC formulas A8/B1 and A10/B12 within their working pH.
- The additives have a weak influence on the viscosity of DBC formula A5/B5



• The additives has a limited influence on the sand stability of A10/B12 DBC formula at its working condition pH 9

• The sand was stable in the A10/B12 for more than 6 hours at the working condition

- The additives have a weak influence on the sand stability of A5/B5 DBC formula at its working condition pH 6
- The sand was stable in the A5/B5 for more than 4 hours at the working condition with most of the additives

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Effect of DBC and commercial formula on service life of pipelines

- Two methods were carried out to determine the corrosion behavior of the DBC and Commercial formula
 - The weight loss of hot working steel was measured everyday after submerging in the solutions.
 - The corrosion rate of solution on hot working steel was detected through analyzing Tafel plot collected with the 3-probe electrochemical method.



Reduced friction between proppant and piping material:

- Frictional characteristics of proppant
 material against tubing material was
 carried out by high-precision
 tribometer.
- Decreased friction between proppant material and tubing material by DBC formula achieved very drastic reductions in friction.

Laboratory-Scale Fracturing Studies with Epoxy



Commercial Formula



DBC

Laboratory-Scale Fracturing Studies with Cement





Fracturing process and first-step setup in the lab scale



Fracturing process and first-step setup in the lab scale





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- A fracture propagation model for non-Newtonian fluids is developed to obtain the dynamic fracture growth and final fracture geometry as a function of fracturing fluid viscosity, pumping rate, and proppant concentration.
- Filter-cake formation during fracture propagation resulting due to fluid leak-off has also been considered alongside proppant transport.
- Fracture widths are found to vary significantly with fracturing fluid viscosity.





Fracture propagation, (a) temporal evolution of hydraulic fracture, (b) final fracture geometry for different fluid viscosities.



- A reservoir simulator is developed for production estimation.
- Multiphase (i.e., oil/water) flow simulation is performed with the simulator for a reservoir with complex geometry and heterogeneity.
- Time evolution of oil/water saturation profiles in the reservoir is observed for 1600 days.
- Owing to the good convergence and stability of the solutions, fractures and gel flow equations were further considered.





For petrophysical properties: Rwechungura R, Suwartadi E, Dadashpour M, Kleppe J, Foss B. The field case-A unique comparative case study. In SPE Intelligent Energy Conference and Exhibition

- Fracture propagation is modeled in the reservoir by the discrete fracture model.
- A three-phase oil/water/gel flow model is considered to calculate fluid flow back.
- The saturation profile inside the reservoir obtained after hydraulic fracturing (here, the gel saturation is highlighted), is the initial condition for fluid flow-back.
- Gel saturation and gel production is obtained after eight days of fluid production.

Reservoir length (m)

Point of production well The Reservoir length (m) Ē hydraulic-fracture Reservoir length Reservoir width (m) Reservoir length (m) (a) (b)

Fractured reservoir, (a) Unstructured fracture, (b) gel saturation before flow-back, (c) gel saturation profile after 8 days flow-back.





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- Fracture propagation model used to obtain varying fracture geometry.
- Formation damage is estimated after the fracture propagation is obtained from filter-cake formation, and gel saturation profile obtained after fracturing.
- Sensitivity of the hydrocarbon production with different fluid viscosities is obtained to identify the gel leading to maximum hydrocarbon recovery.



Wigth of reservoir (cm) 2

40

100

140

Production and saturation prediction, (a) reservoir production sensitivity, (b) gel saturation in reservoir after hydraulic fracturing, (c) gel saturation profiles inside fracture after flowback for different viscosities

- Specifically, gel that leads to maximum hydrocarbon recovery was considered to produce a fracture width of 1.7 cm and fracture half-length of 210 m.
- Optimal pumping schedule was determined to get target fracture geometry.
- However, to utilize the obtain framework to non-Newtonian fluids such as DBC gels microscopic model is necessary to predict the rheology of these gels.





Width and proppant concentration, (a) proppant concentration, (b) fracture width profile during hydraulic fracturing

- In order to accurately model the rheology and enhance the material properties, it is essential to study the structure and property relationships for DBCs.
- Coarse-grained Molecular simulations are performed to obtain the stable structures of the self-assembled DBCs.
- Predicted structures of DBCs vary with solution conditions and are quantified with small angle X-ray (SAXS) diffraction intensity.







Self-assembled structures, (a) initial simulation condition, (b) energy profile during simulation, (c) final equilibrium structure

- The obtained structures will be utilized in a mesoscale model to predict the rheology of the solution, thus giving the structure and property relationships.
- A mesoscale kinetic Monte Carlo (kMC) algorithm-based model is developed.
- A case study for wormlike micelles (WLMs) is done with this model. The model predictions are found to be in good agreement with experimental results.
- For rheology prediction of DBCs, molecular and kMC models would be combined.



Rheology prediction, (a) storage and loss modulus, (b) viscosity with varying salt concentration, (c) viscosity with varying pH.



Plans for Future Testing/Development/Commercialization

- Future Plans/Development
 - Further compatibility studies with other components of fracturing fluids
 - Investigation of permeation improvements
 - Determine kinetical parameters for scale-up studies
 - Large-scale fracturing tests
 - Computational studies to estimate the reductions in wastewater
 - Aging studies for storage over prolonged periods of time
 - Scale-up studies
 - Perform cost-benefit analysis

Plans for Future Testing/Development/Commercialization

Scale-up and Commercialization

- Incendium Technologies have performed reaction kinetics tests on two formulations received from Texas A&M and decided on going forward with the most promising formulation in terms of manufacturing cost and availability of raw materials (Feedback received from industry partners for such decision).
- Construction of a pilot reactor in in the progress. Quotes have been received from various companies for auxiliary parts (e.g., heating components, chillers, etc.) and the assembly will be finalized once those parts arrive.
- Non-confidential information on the developed viscosifying agents were shared with **Saudi Aramco**. They are interested in testing the developed material in their new fields. The provided information about the formulations is under review, and pending approval for field testing in near future.
- Incendium team visited facilities of Eastman Chemicals last month and discussed the progress of the project. In general, they are happy with the current progress, and requested some information on modeling efforts of the project.
 A big meeting will be held in September for further information exchange. They will support us in sourcing the raw materials once we get closer to the industrial scale production.







The results of insight^{...}

- Novel gelling agents with super-adjustable viscosity have been developed.
- Nanoarchitecture of building blocks of DBCs can tuned to alter the target pH for stimuli-responsiveness
- DBCs have demonstrated high-tolerance against temperature.
- Salinity has a weak influence on the viscosity of DBCs.
- DBCs have demonstrated exceptional ability to suspend proppants.
- DBCs have very desirable lubricity characteristics.
- DBCs have a reduced corrosion on pipelines compared to commercial formulations.

Appendix

Organizational Chart



Gantt Chart

Task Description	Mile- stone	Milestone Description	Milestone Verification Process	Expected Quarter	Adsorption and Desorption of DBCs on/from Proppant and	F1	Successful development of dynamic models describing adsorption and	Laboratory-scale studies to verify the models with a criterion of 20%	8
Flow and Viscosity	A1	Achieve a viscosity of 50-1000 cP with	Rotational and oscillatory	1	Fracture Surfaces		desorption of DBCs on proppant surfaces	accuracy	
Properties of DBCs		0.1-2% of DBC solutions at shear rates of $40-100$ s ⁻¹	rheometry measurements with three repeats for each sample		Laboratory Experiments to Evaluate Hydraulic Fracturing	G1	Obtain 50% enhancements in fracture permeability and conductivity using DBCs	Tests using specimens obtained unconventional reservoirs from	8
	A2	Accomplish a reversible re-adjustability of 100-fold in viscosity of DBCs at	High-pressure rheometry studies with three replicate	2	Performance		compared to four commercial fracturing fluids	Texas	
		typical reservoir pressures, temperatures, and salinities via pH stimulus	measurements for each sample		Go/No-Go Decision Point 2		Go if Milestones 3.1–7.1 are successfully completed.	No-Go if there are challenges associated with these Milestones. We will modify nanoarchitectures	8
Proppant Dispersion Stability	B1	Obtain 100% improvements in proppant carrying capacity compared to four commercial fracturing fluids for a given concentration of DBC	Static and dynamics sand settling experiments	3	estimating wastewater recovery and gas production rates after	H1	Develop a subroutine for non-Newtonian fluid to compute the modified viscosity due to DBCs and use this subroutine for	of DBCs. Experimental studies to confirm the validity of models with a criterion of 20% accuracy	9
	B2	Realize 3 orders of magnitude reversible control over the proppant settling	Static and dynamics sand settling experiments	4	fracking fluid clean-up		calculating gas production and water recovery rates		
		velocity in situ			Scale-up, Large-Scale	I1	Determine all kinetic parameters of DBC	Time-resolved spectroscopic	9
Go/No-Go Decision Point 1		Go if Milestones 1.1, 1.2, 2.1, and 2.2 are successfully completed.	No-Go if there are challenges associated with these Milestones. We will modify	4	Manufacturing, and Field Testing of DBCs		formulation with the best laboratory-scale performance, which are the main scale-up parameters	analysis	
			nanoarchitecture of DBCs.			I2	Realize 100 pounds/day production rate at		10
Extent of Reversibility and Reusability	C1	Achieve a maximum of 20% reduction in viscosity and proppant carrying capacity after 5 stimulus cycles	High-pressure rheometry and sand settling measurements verified with three different	5			a minimum yield of 85% in a pilot plant specifically designed manufacturing of DBC	determining the reaction yield and digital balances for measuring the production rates	
		capacity after 5 stillulus cycles	samples			I3	Achieve at least 50% improvements in the	Coriolis flow meter measurements	11
	C2	Achieve a maximum of 10% reduction in viscosity and proppant carrying	High-pressure rheometry and sand settling measurements	6			hydrocarbon recovery on the field tests compared to the current-state-of-art	of natural gas production in the selected well over 10 days	
		capacity after 10 stimulus cycles	verified with three different samples		Cost-Benefit Analysis	J1	Prepare a comprehensive cost-benefit analysis considering raw material cost,		12
Compatibility with Other Chemicals in Fracking	D1	Identify at least one compound that is compatible with DBCs for all functions	Aging and phase behavior experiments, visual	7			production cost, deployment costs, durability, life-time, and potential benefits		
Fluids		of clay stabilization, friction reduction, corrosion inhibition, scale inhibition, and iron control suitable for hydraulic fracturing	inspection, and chemical spectroscopy		Go/No-Go Decision Point 3		Go if Milestones 8.1–11.1 are successfully completed. Apply for the Phase II project to reach TRL 8–9.	No-Go if there are challenges associated with these Milestones.	12
ComputationalModelstoDescribeProppantTransportandFracturePropagationFracture	E1	Successful development of dynamic models for 3D, simultaneously growing multiple fractures with at least 2D proppant transport	Experimental validation within 20% accuracy	6					