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
2020 Integrated Review Webinar

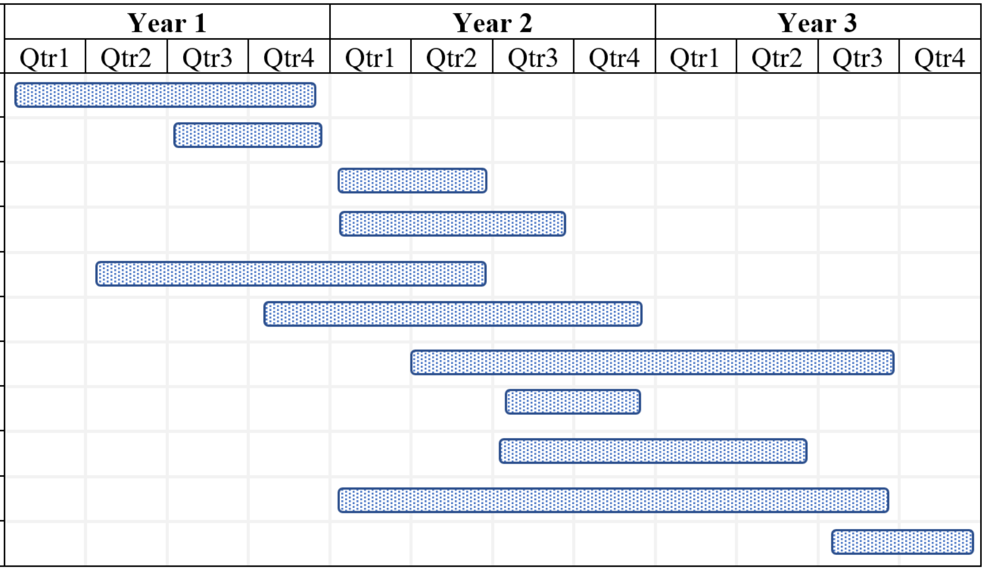
Program Overview

- ## 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
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
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

Program Overview

▪ Project Objectives

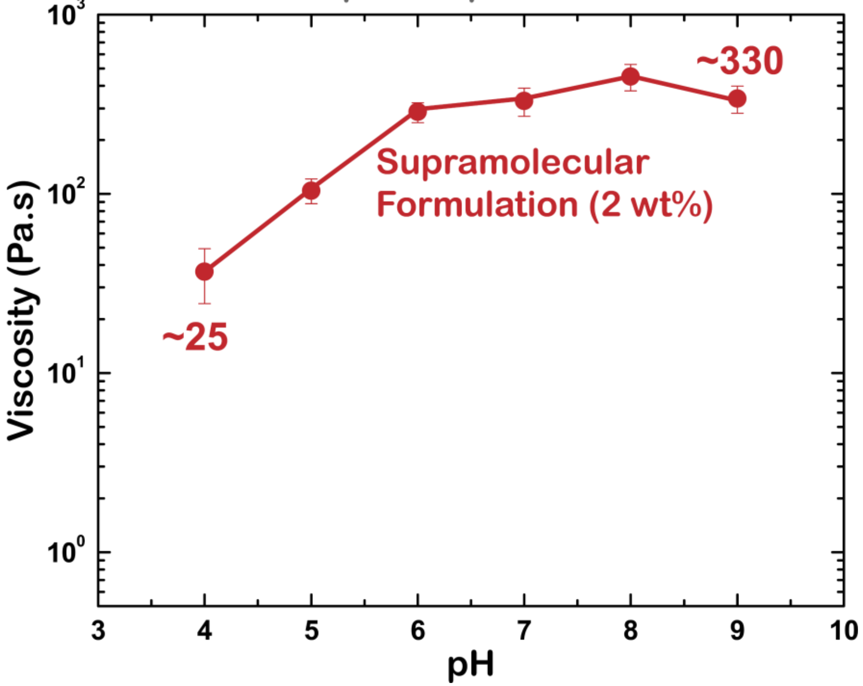
- To develop novel dynamic binary complexes to achieve super-adjustable, reversible viscosities and the implementation and wide-spread utilization of these novel viscosifiers in hydraulic fracturing fluids.
- To mature the Technology Readiness Level (TRL) of this concept from TRL 2-3 to TRL 5-6.
- To 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

Technology Background

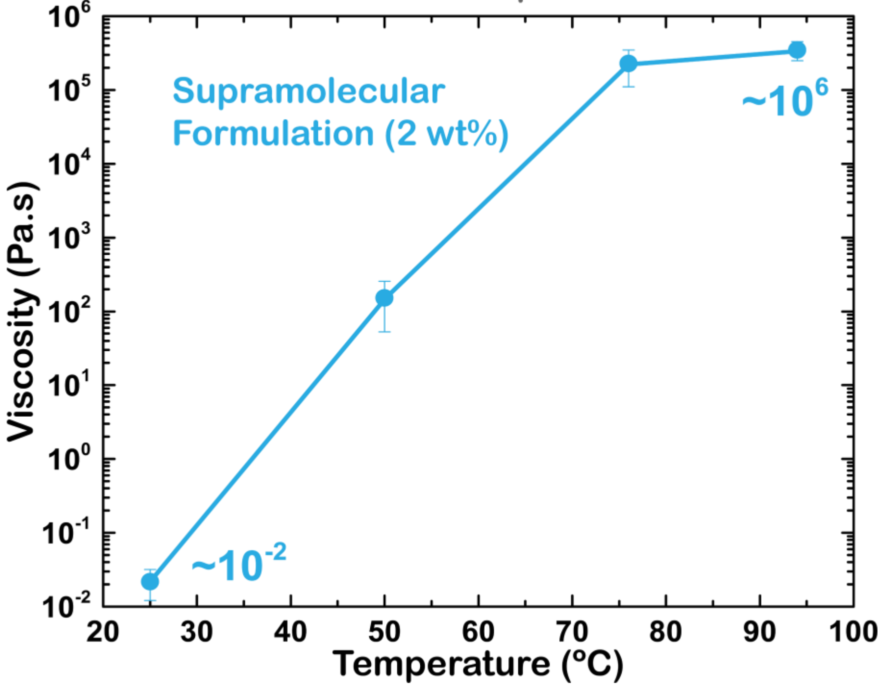
	Viscosity	Advantages	Disadvantages/Limitations
Water frac	2−5 cP	• Inexpensive • Insensitive to salinity	• Requires high pump rates • Poor proppant transport • Narrow fracture width
Linear aqueous gels	10-30 cP	• Environmentally friendly • Support transport of medium-sized proppants	• Not re-usable • Somehow narrow fracture width • Some residue leftover in fractures
Cross-linked aqueous gels	100-1000 cP	• Wide fracture width • Reduced fluid loss • Enhanced proppant transport	• Not re-usable • Corrosive/toxic breakers • Fracture damage by residues
Aqueous viscoelastic surfactant (VES)-based fluids	100-1000 cP	• Wide fracture width • Enhanced proppant transport • No residue leftover in fractures	• High-cost • Poor temperature/salt tolerance • High 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 formations • Lower formation damage	• Gelling and clogging problems • Higher cost • More toxic than water-based systems

Technology Background

pH-Responsive



Thermo-Responsive



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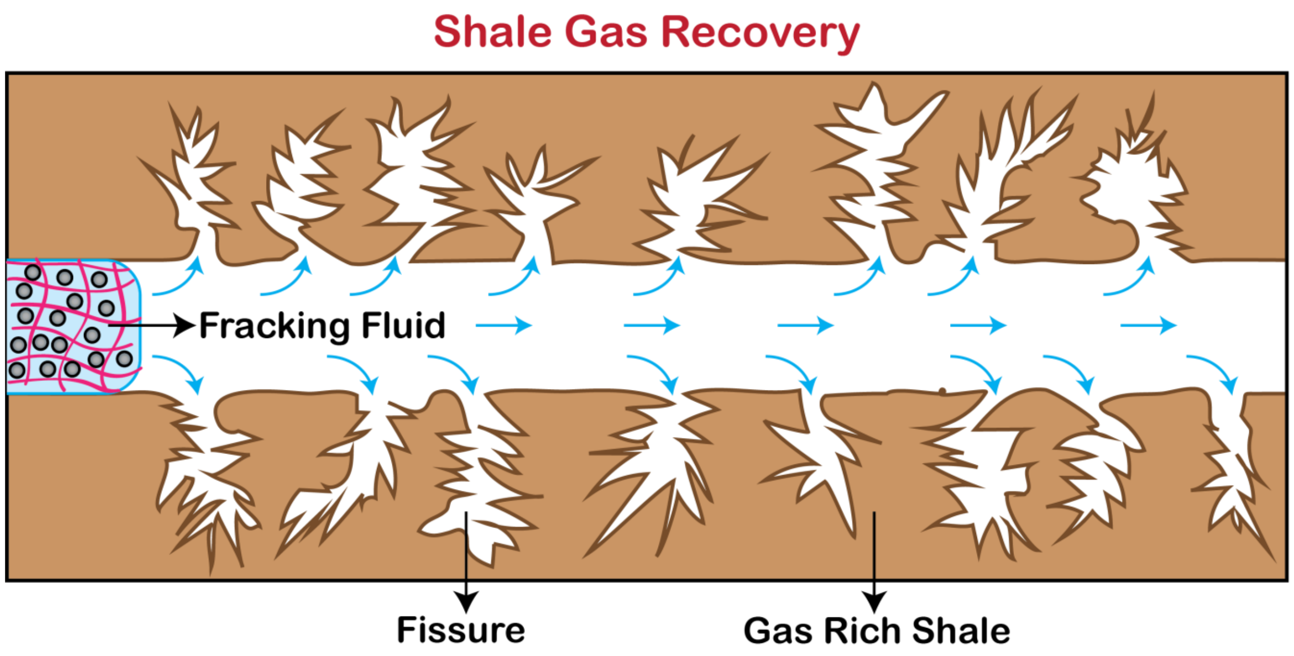
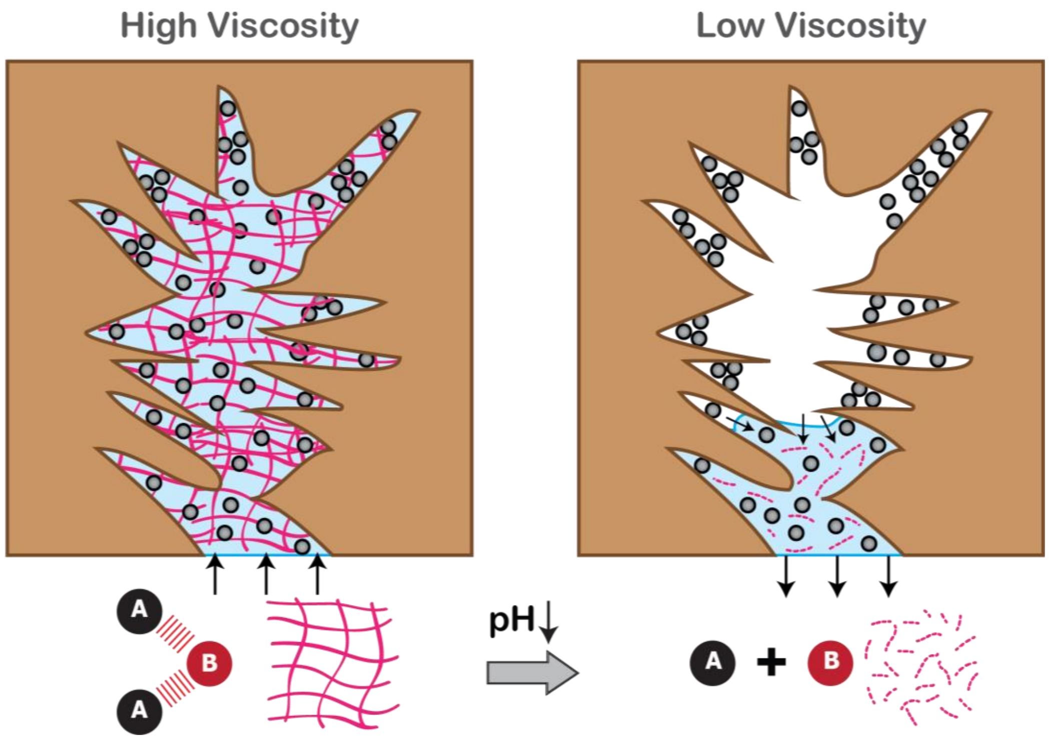
Technology Background

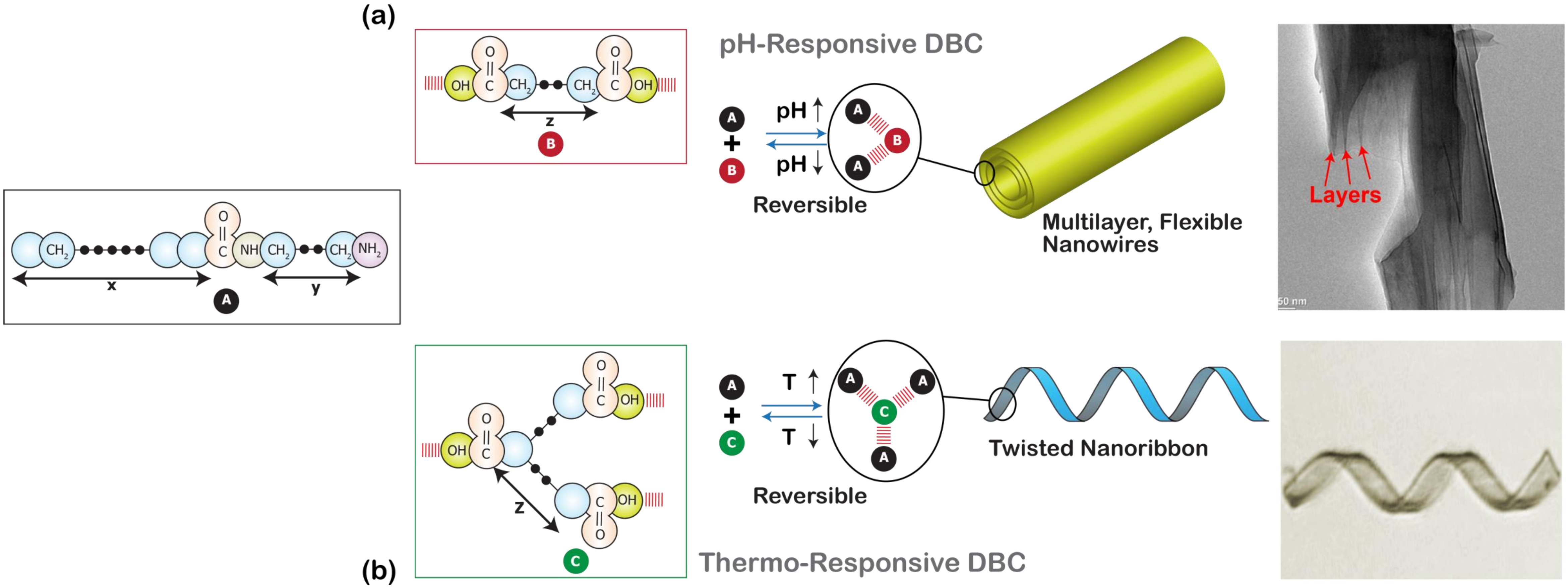




Region	Shale Depth (ft)	Temperature (°F)	Salinity (mg/mL)
Anadarko	4,000 – 11,000	140° to 280° F	<50
Appalachia	5,000 – 9,000	160° to 240° F	150-200
Bakken	6,000 – 12,000	180° to 300° F	200-300
Eagle Ford	4,000 – 14,000	140° to 340° F	50-100
Haynesville	10,000 – 13,000	260° to 300° F	<50
Niobrara	7,000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

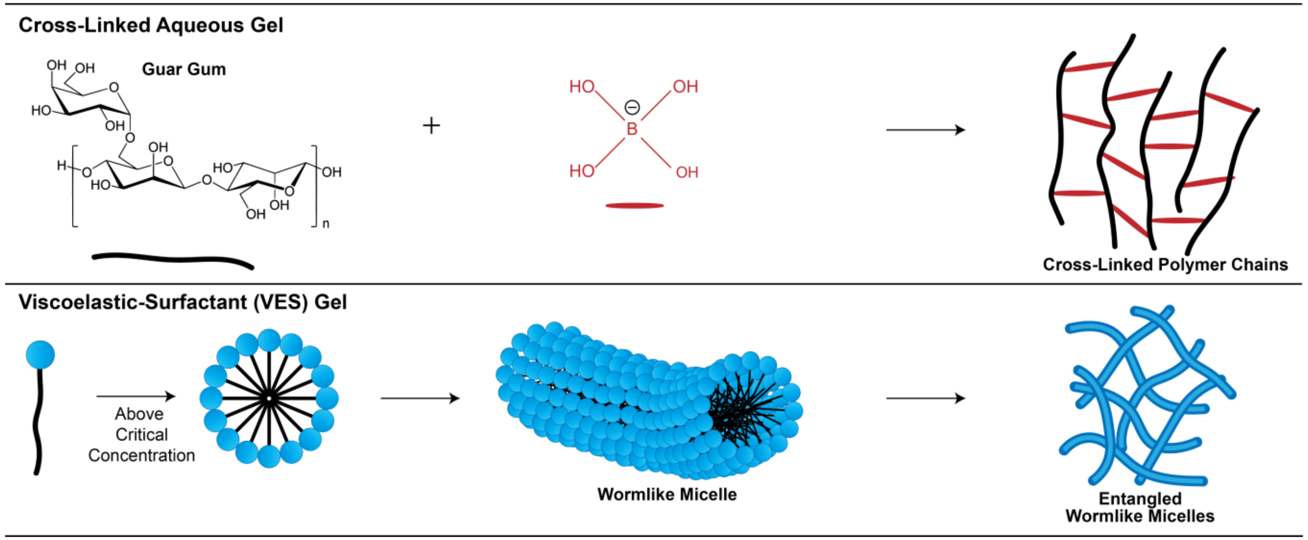
Target Conditions:
Temperature: 140°F to 280°F
Salinity: 50 mg/mL to 200 mg/mL
Depth: 4000 ft to 10,000 ft

Technology Background

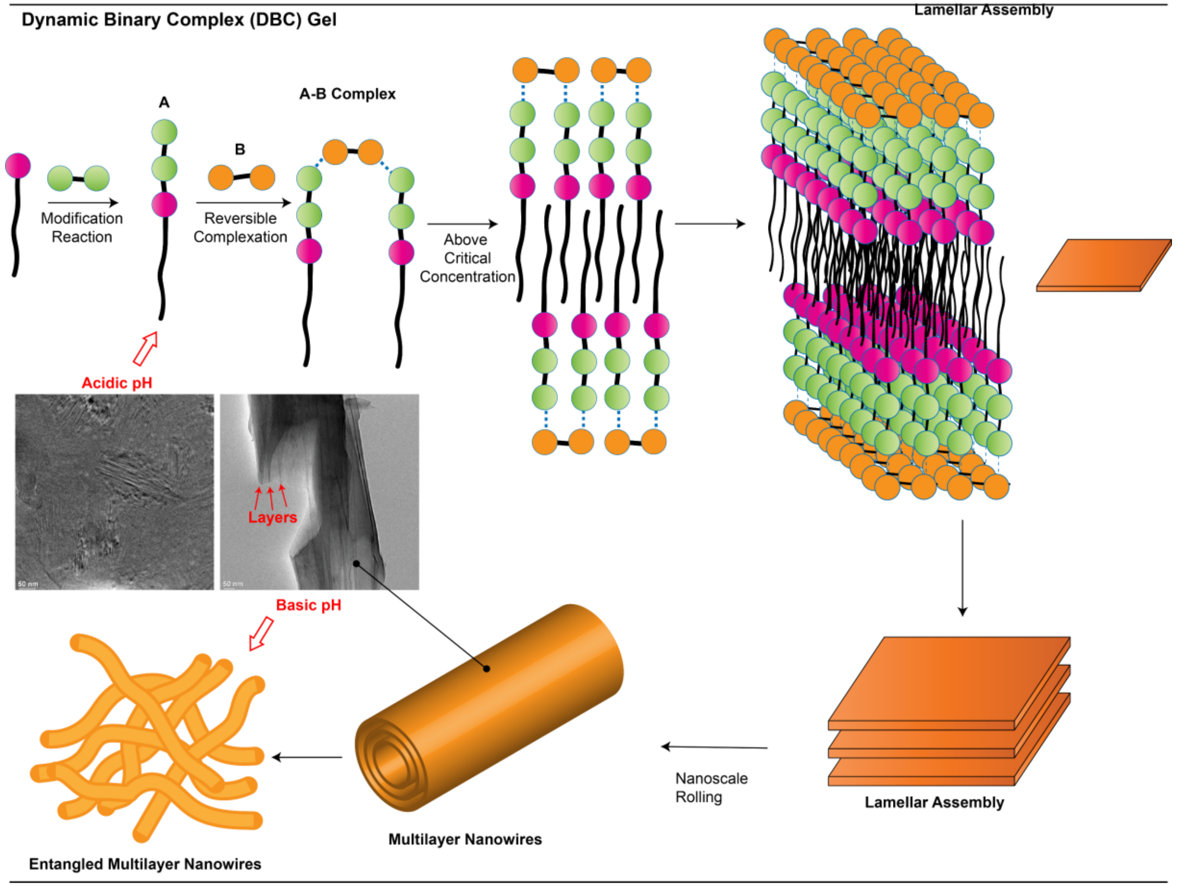


Technology Background

Current Viscosity Modifiers



Developed DBCs



Technology Background

Advantages of DBC Technology

- *Viscosity Adjustability*: Viscosity can reversibly be strongly controlled by adding acid or base.
- *Reusability*: DBC does not rely on permanent breakers and can be reused multiple times.
- *Environmentally Benign*: Building blocks are opted from nontoxic and biological-origin materials.
- *Superior Proppant Carrying Ability*: DBC can actively and passively interact with proppants.
- *High Durability*: DBCs can be used at elevated temperatures and salinity for prolonged periods.
- *Possibility of Eliminating Permeation Damage*: DBCs can be assembled and disassembled dynamically.

Challenges of DBC Technology

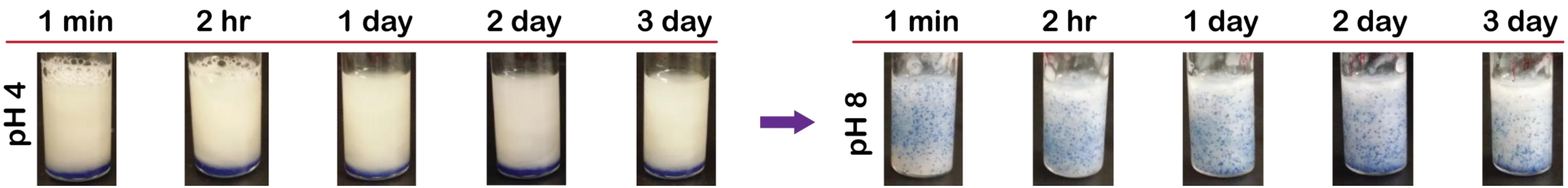
- *Current Economic Difficulties of Fracturing Industry*
- *Market Adaptation*
- *Material Cost*

Project Scope

- **Flow and Rheological Characteristics of Dynamic Binary Complexes (DBCs)**
  - Viscosity of a fracking fluid is critical to ensure carrying the proppant from the wellbore to the fracture tip, forcing proppant entrance into the fracture, and generating a desired net pressure to control proppant bank height growth.
  - Investigate viscosity as a function of DBC nanoarchitecture, DBC concentration, temperature, and salinity

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

- **Proppant Dispersion Stability**
  - Study the settling time of sand (proppant) in DBCs with respect to DBC nanoarchitecture and concentration, temperature, and salinity and maximize it



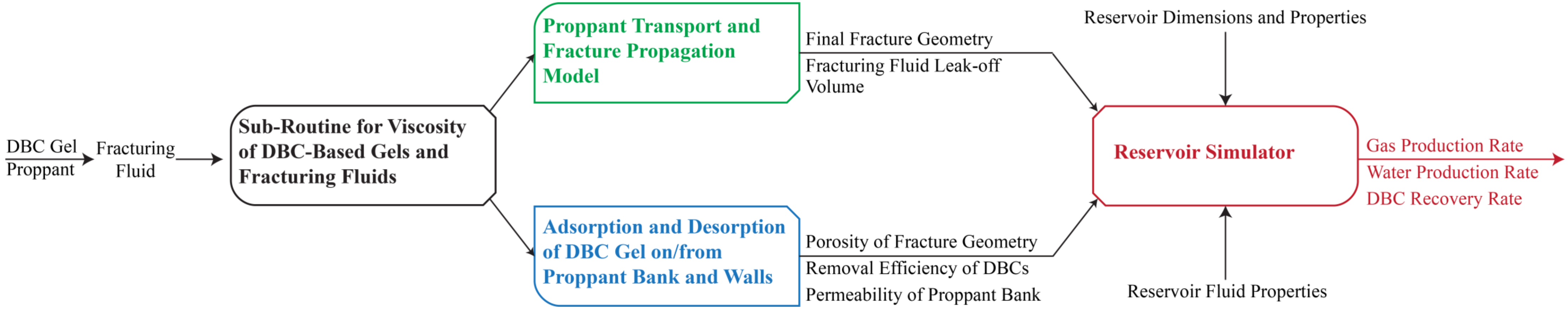
Project Scope

- **Extent of Reversibility and Reusability**
  - Evaluate the reversibility of DBCs against repetitive temperature and pH cycles

pH ↑ ↓ ↑ ↓ ↑ ↓ → Viscosity ? → Settling Time ?

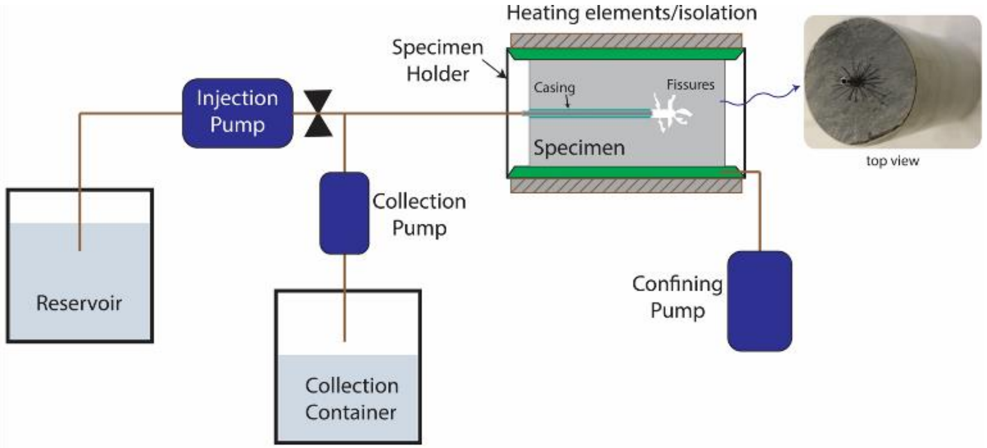
Temperature ↑ ↓ ↑ ↓ ↑ ↓ → Viscosity ? → Settling Time ?

- **Compatibility with Other Compounds in Fracking Fluids**
  - Fracturing Fluid Components: Biocide, Breaker, Clay Stabilizer, Corrosion Inhibitor, Friction Reducer, Iron Control, Emulsion Preventer, Scale Inhibitor
  - Investigate the compatibility of DBCs with other components of fracking fluids and identify the optimum compound with the highest compatibility for each function
- **Computational Models to Describe Proppant Transport and Fracture Propagation**



Project Scope

- **Computational Studies of Estimating Wastewater Recovery and Gas Production Rates after Fracking Fluid clean-up**
  - Develop a computational framework and sub-routines to enable the implementation of DBCs in the 3D, three-phase black oil model
  - Estimate gas production, water production, and DBC recovery rates
- **Selection and Optimization of DBC Formulations for Laboratory-Scale Fracturing Tests**
- **Laboratory Experiments to Evaluate Hydraulic Fracturing Performance**



- **Scale-up of DBC Production and Construction of Pilot Plant**
- **Field Tests**
- **Cost-Benefit Analysis**

Project Scope

▪ Milestones and Success Criteria

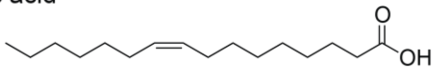
- *Achieve a viscosity of 50−1000 cP with 0.1−2% of DBC solutions at shear rates of 40−100 s^{-1}* [Year 1]
- *Obtain 50% improvements in proppant carrying capacity compared to three commercial fracturing fluids for a given concentration of DBC* [Year 1]
- *Accomplish a reversible re-adjustability of 20-fold in viscosity of DBCs at typical reservoir pressures, temperatures, and salinities via pH stimulus* [Year 1]
- *Achieve a maximum of 20% reduction in viscosity and proppant carrying capacity after 5 stimulus cycles* [Year 2]
- *Successful development of dynamic models for 3D, simultaneously growing multiple fractures with at least 2D proppant transport* [Year 2]
- *Determine all kinetic parameters of DBC formulation with the best laboratory-scale performance, which are the main scale-up parameters* [Year 2]
- *Obtain 50% enhancements in fracture permeability and conductivity using DBCs compared to four commercial fracturing fluids* [Year 2]
- *Realize 50 pounds/day production rate at a minimum yield of 85% in a pilot plant specifically designed manufacturing of DBC* [Year 3]
- *Achieve at least 50% improvements in the hydrocarbon recovery on the field tests compared to the current-state-of-art* [Year 3]
- *Prepare a comprehensive cost-benefit analysis considering raw material cost, production cost, deployment costs, durability, life-time, and potential benefits* [Year 3]

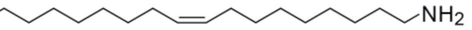
Progress and Current Status of Project

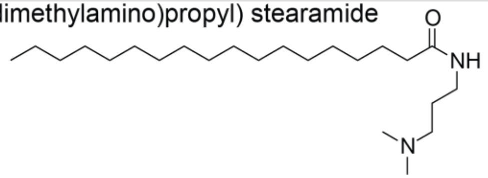
$$nA + mB \leftrightarrows DBC$$

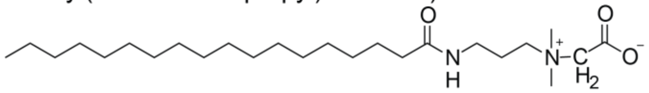
Long-Chain Building Block of DBC [A]

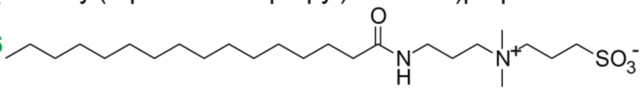
Octadecylamine
A1

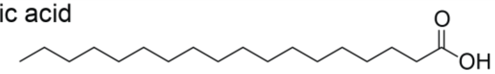

Oleic acid
A2


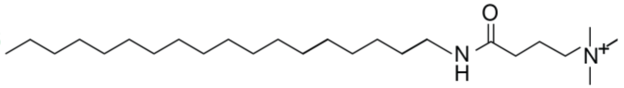
Oleylamine
A3


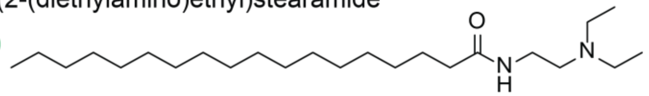
N-(3-(dimethylamino)propyl) stearamide
A4


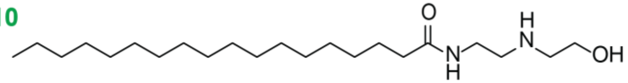
2-(dimethyl(3-stearamidopropyl)ammonio)acetate
A5


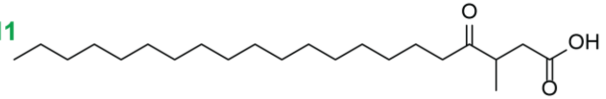
3-(dimethyl(3-palmitamidopropyl)ammonio)propane-1-sulfonate
A6


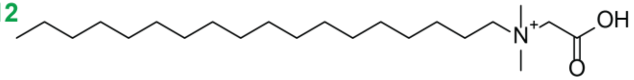
Stearic acid
A7


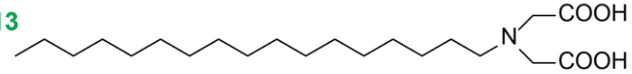
N,N,N-trimethyl-4-(octadecylamino-4-oxobutan-1-aminium
A8


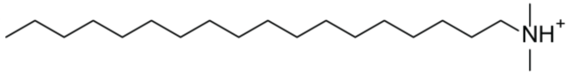
N-(2-(diethylamino)ethyl)stearamide
A9


N-(2-((2-hydroxyethyl)amino)ethyl)stearamide
A10


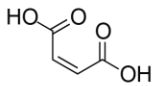
3-methyl-4-oxohenicosanoic acid
A11


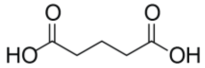
N-(carboxymethyl)-N,N-dimethyloctadecan-1-aminium
A12


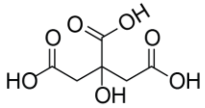
2,2'-(heptadecylazanediyl)diacetic acid
A13


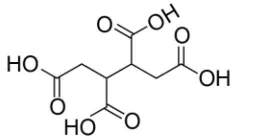
N,N-dimethyloctadecan-1-aminium
A14


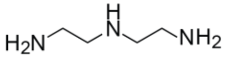
Short-Chain Building Block of DBC [B]

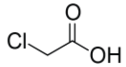
Maleic acid
B1


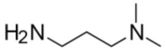
Glutaric acid
B2


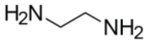
Citric acid
B3


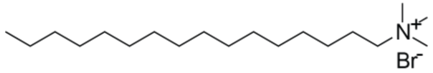
1,2,3,4-Butanetetracarboxylic acid
B4


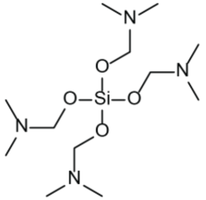
Diethylenetriamine
B5


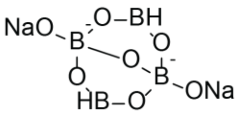
2-chloroacetic acid
B6


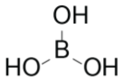
N,N-dimethylpropane-1,3-diamine
B7


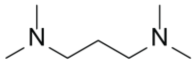
Ethane-1,2-diamine
B8


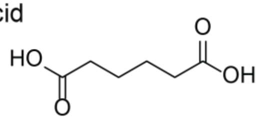
Cetyltrimethylammonium bromide
B9


Tetrakis((dimethylamino)methyl) silicate
B10


Sodium borate
B11


Boric acid
B12


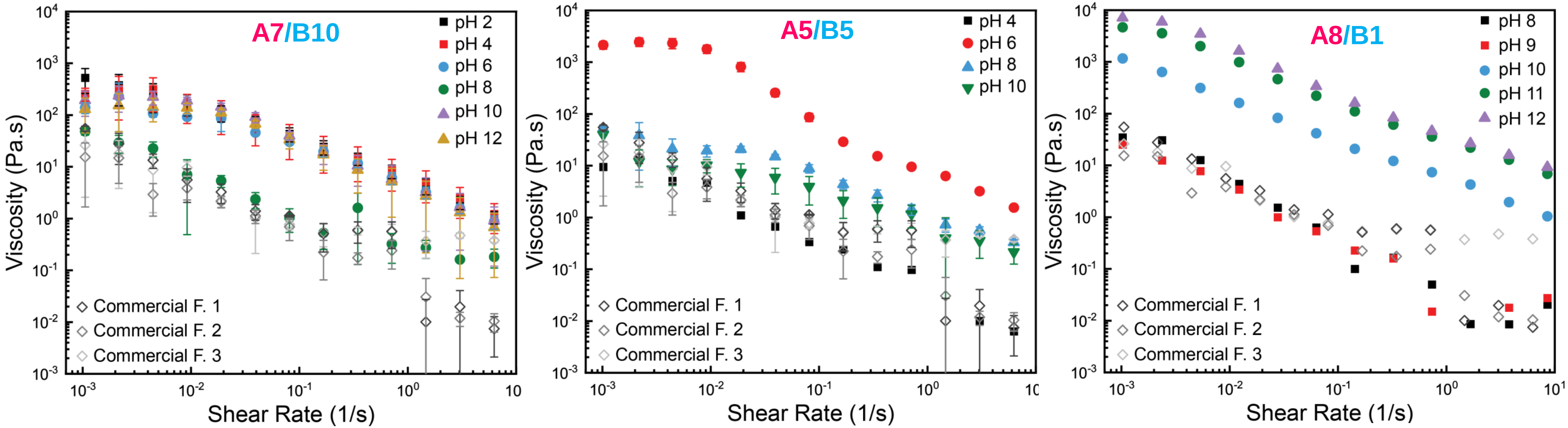
N,N,N′,N′-Tetramethyl-1,3-propanediamine
B13


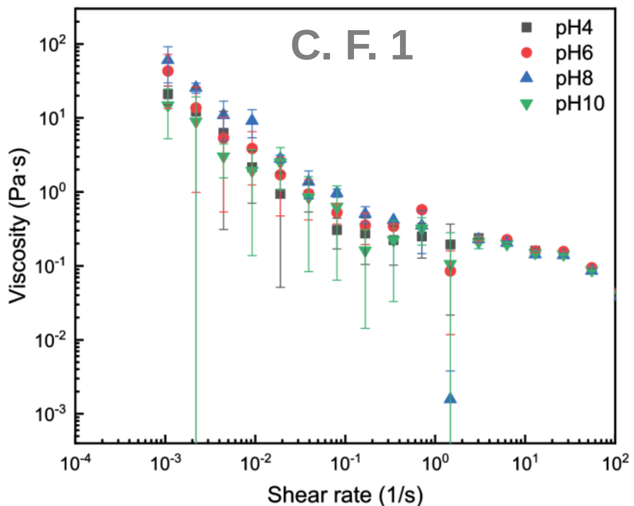
Adipic acid
B14


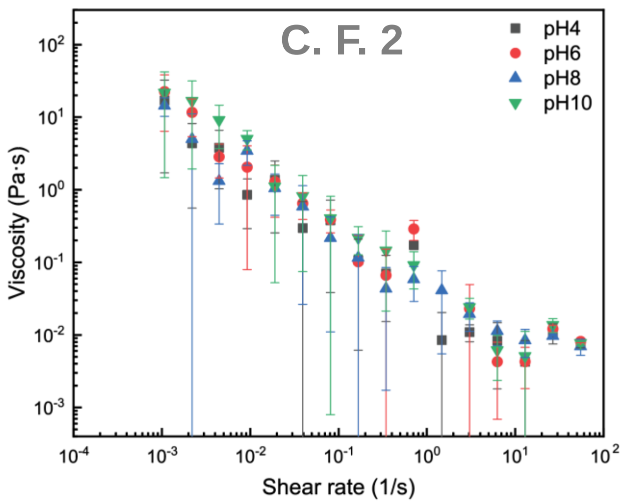
- 49 new formulations have been developed!
- 6 formulations with exceptional flow properties and proppant carrying ability have been identified.

Progress and Current Status of Project

pH-Adjustability of DBC Viscosifiers





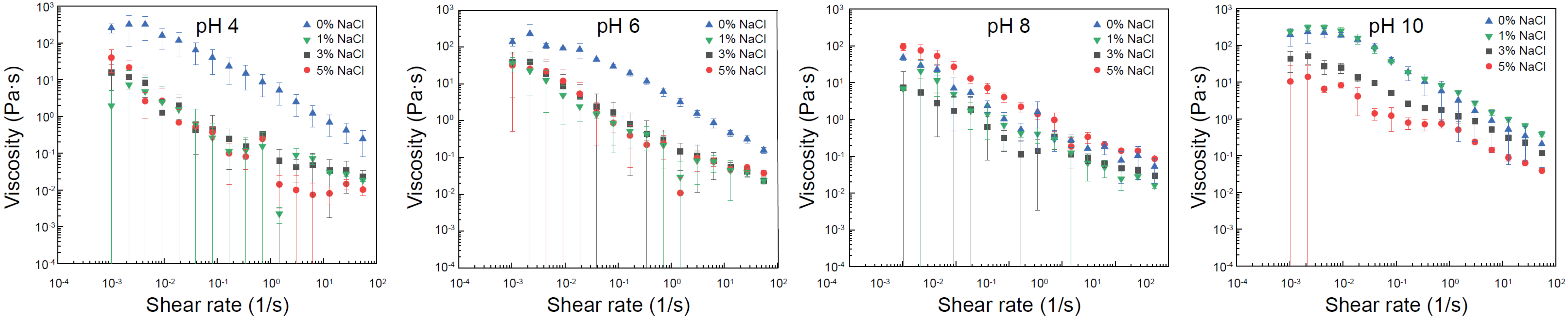


- *pH Adjustability for A7/B10*: 228-fold
- *pH Adjustability for A5/B5*: 1624-fold
- *pH Adjustability for A8/B1*: 284-fold
- *pH Adjustability for CF1*: ~1-3 fold
- *pH Adjustability for CF2*: ~1-3 fold

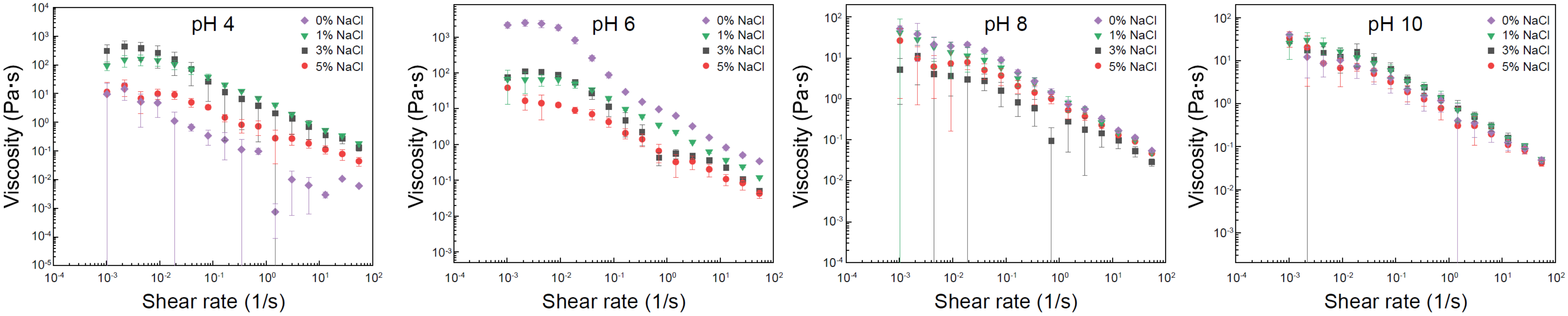
Progress and Current Status of Project

Effect of Salt on Viscosity of DBCs

A7/B10



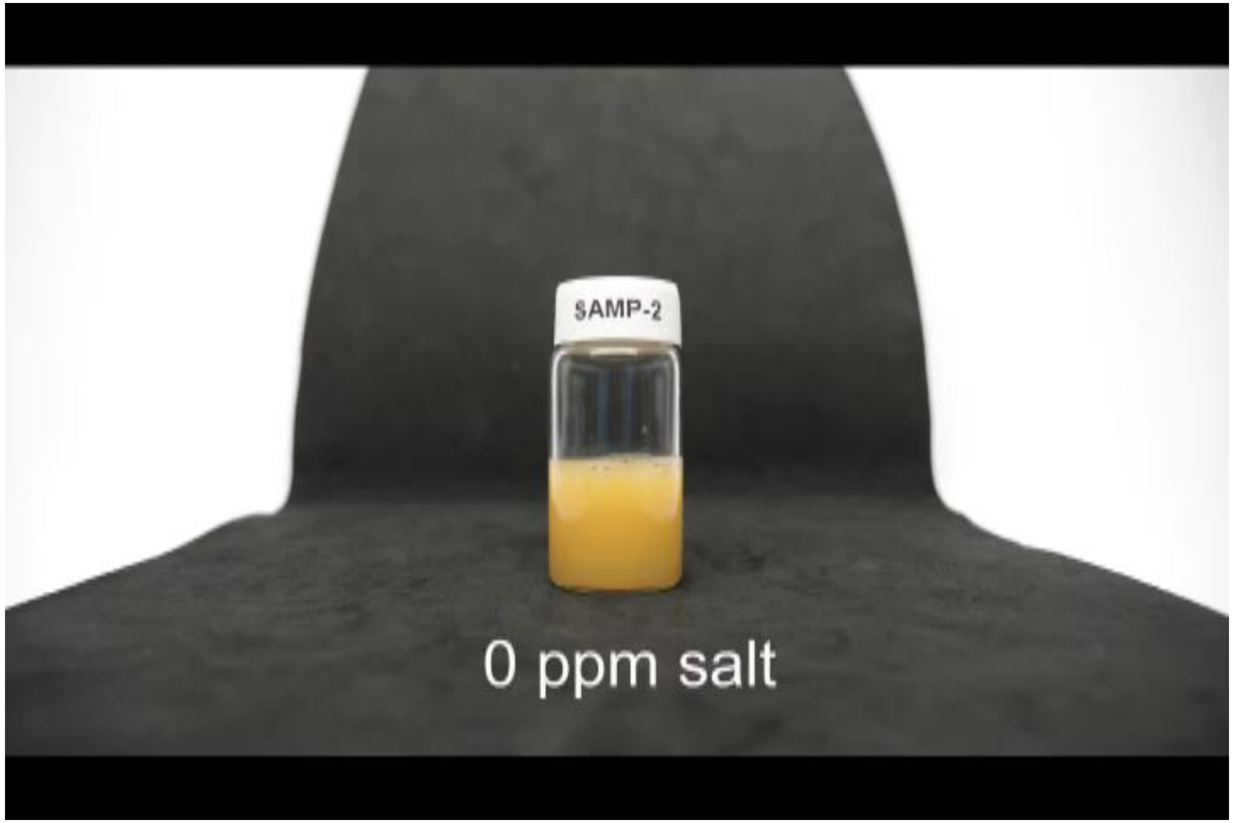
A5/B5

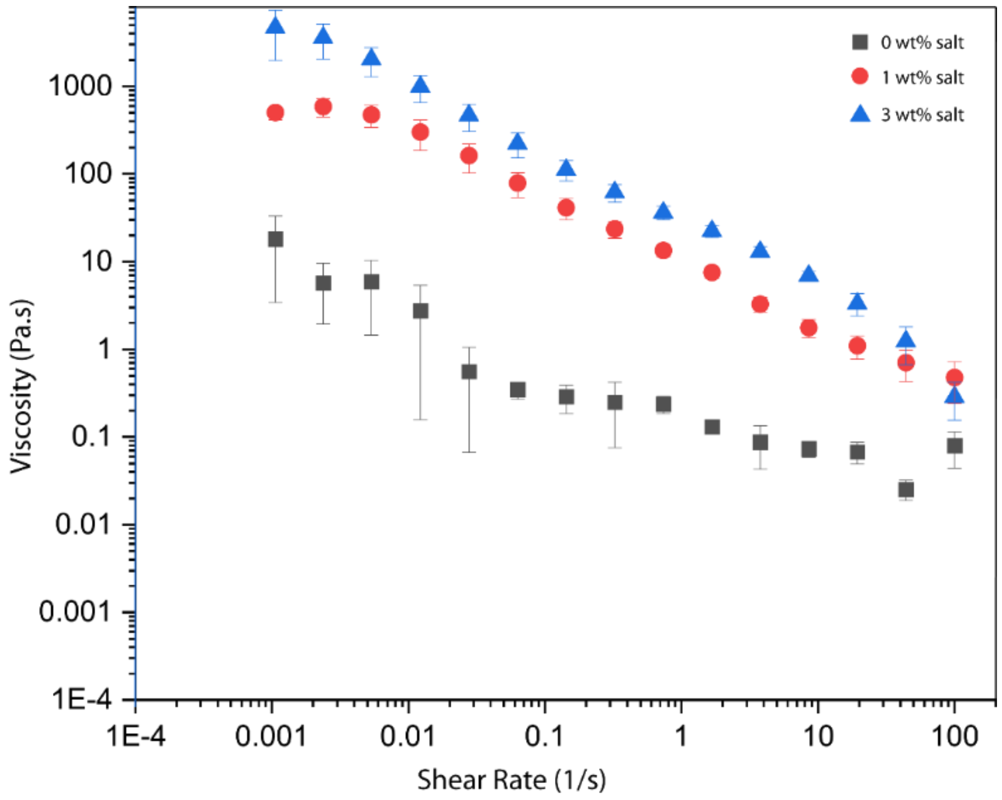


Progress and Current Status of Project

Salt-Induced Viscosification and Gelling of DBC A8/B1 !

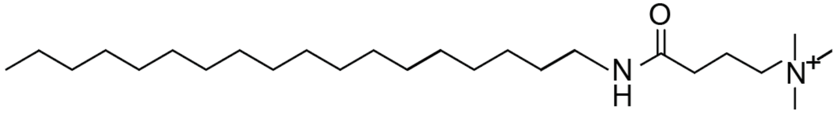
DBC A8/B1





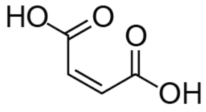
N,N,N-trimethyl-4-(octadecylamino-4-oxobutan-1-aminium

A8

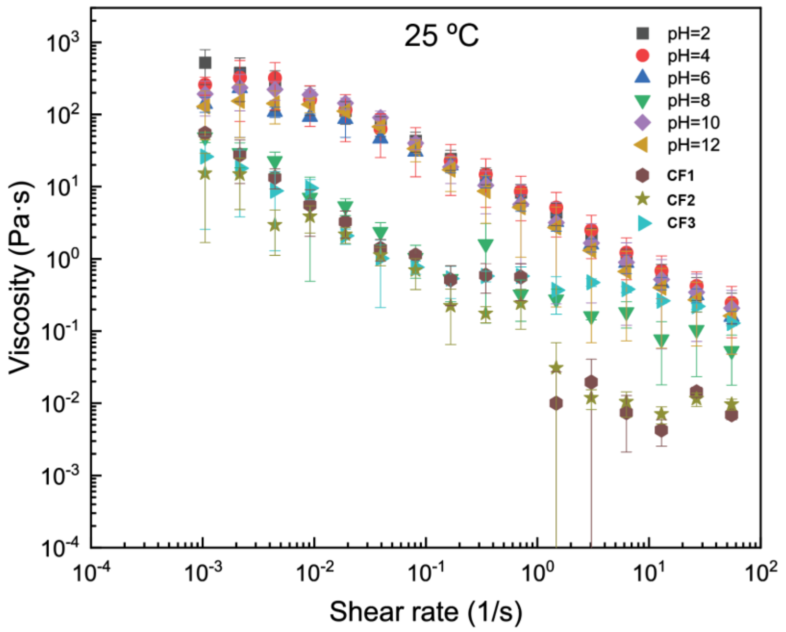


Maleic acid

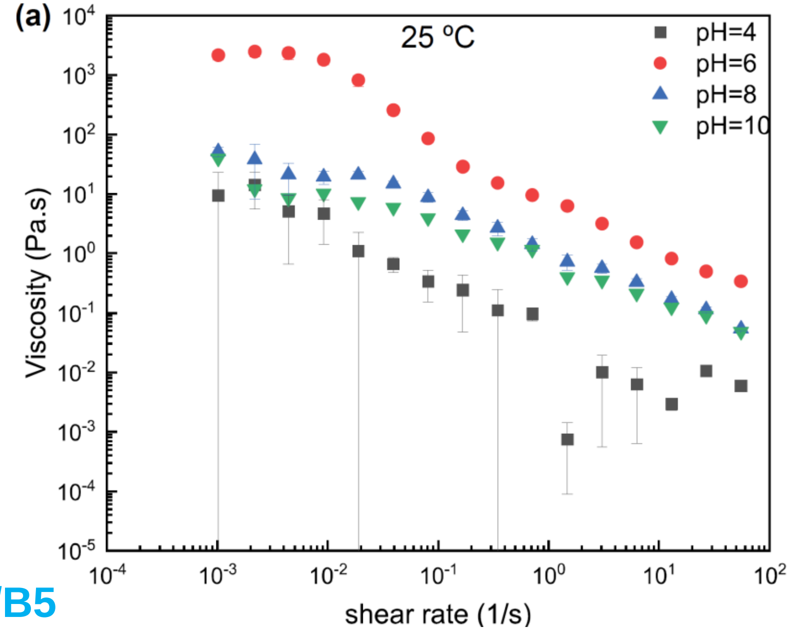
B1



Progress and Current Status of Project

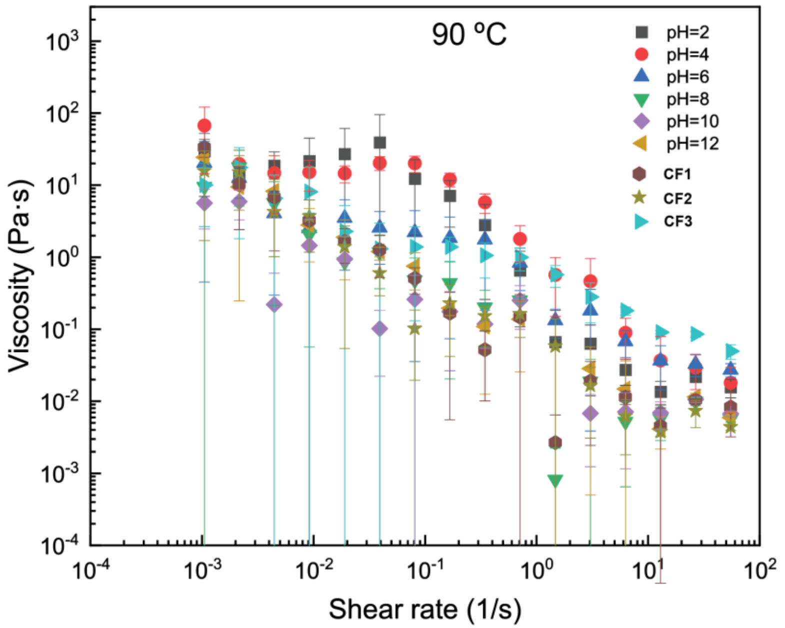


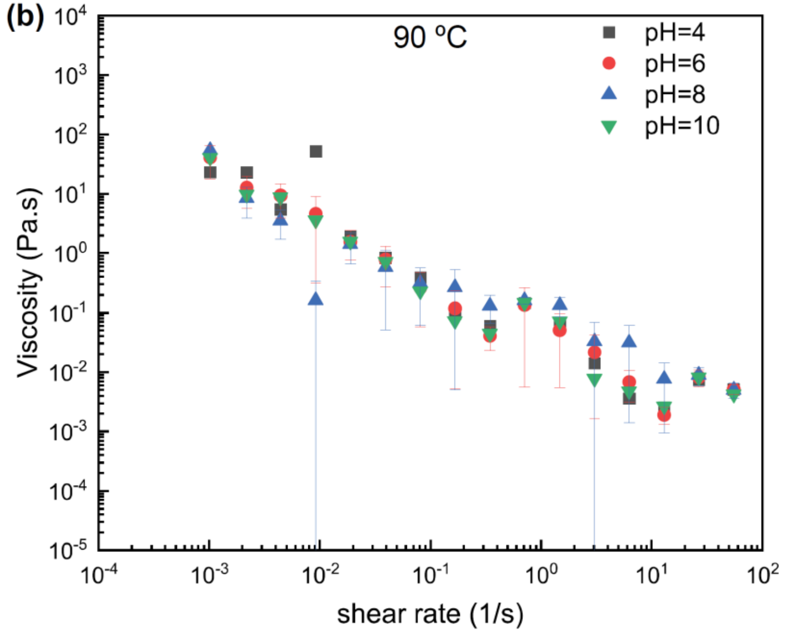
Effect of Temperature on Viscosity of DBCs



A7/B10

A5/B5





Progress and Current Status of Project

Characteristics of "a Dream" Fracking Fluid:

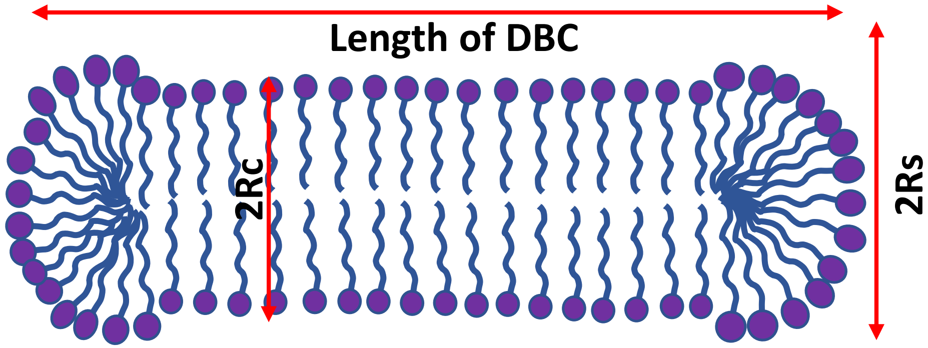
- large proppant carrying capacity at elevated temperatures
- large proppant carrying capacity at high salinity
- high adjustability to precisely control proppant transport and deposition

DBC A8/B1

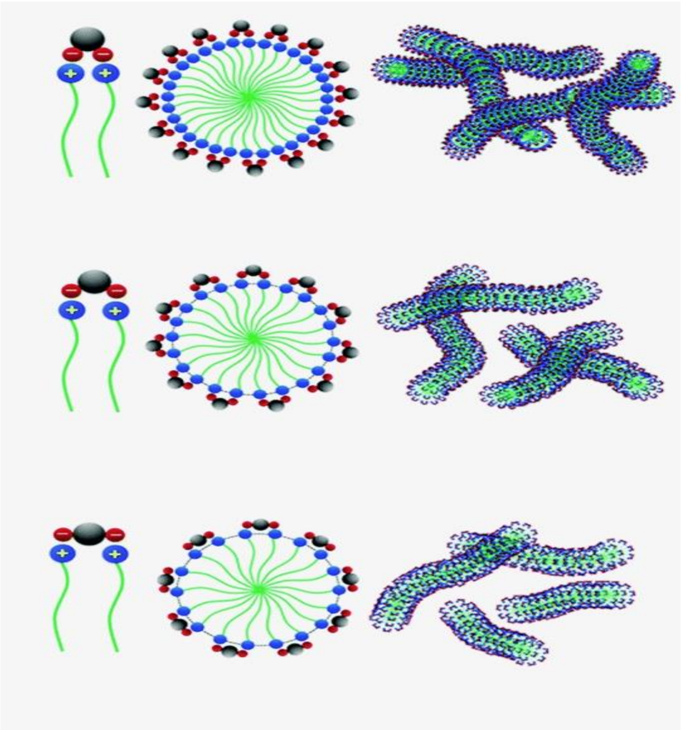
Formulation	Proppant Settling Time
CF1 @25 °C	8 min
CF2 @25 °C	< 30 sec
CF3 @25 °C	~ 1 min
DBC A8/B1 @25 °C	~ 3 days
DBC A5/B5 @25 °C	~ 2 days
DBC A7/B10 @25 °C	~ 1 day
CF1 @90 °C	3 min
CF2 @90 °C	< 30 sec
CF3 @90 °C	< 30 sec
DBC A8/B1 @90 °C	**~ 8 hr**
DBC A5/B5 @90 °C	90 sec
DBC A7/B10 @90 °C	**~ 15 min**

Progress and Current Status of Project

- A thermodynamic model has been developed by considering all the components of the free energy in a cylindrical DBCs.
- The model is able to predict packing fraction of the micelles in response to varying pH.
- Equilibrium dimensions are used to predict the length of DBCs. This length is used as an input for the rheology model discussed in the next slide.



Size considerations of the thermodynamic model.

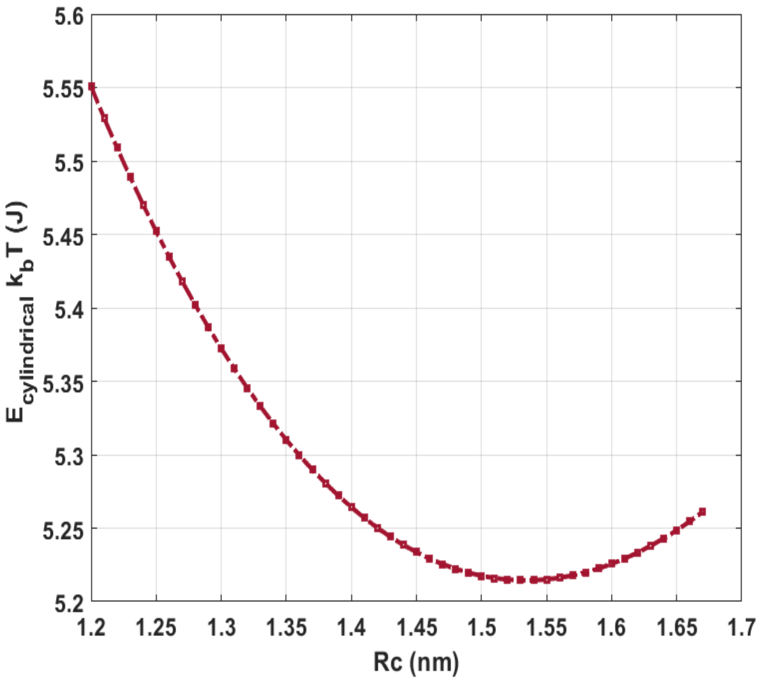


pH: 10.
Packing fraction 0.44

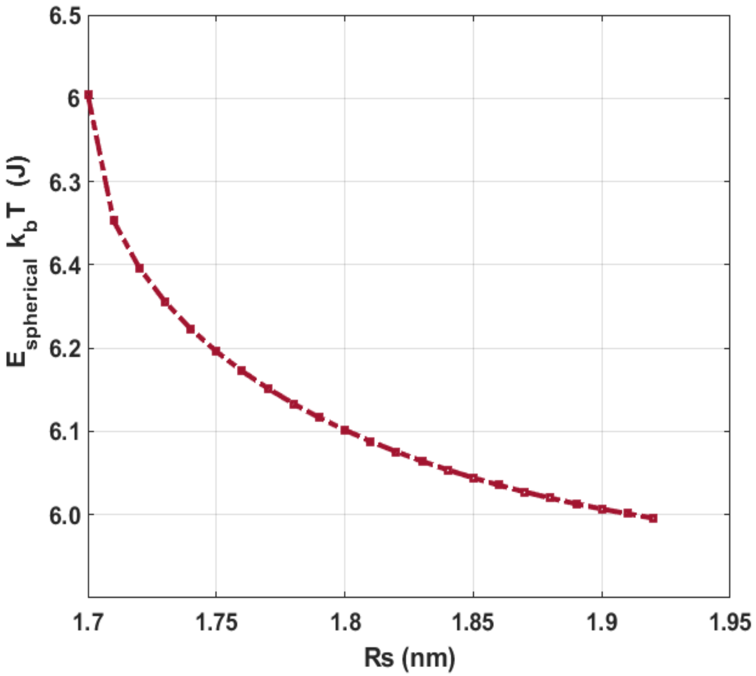
pH: 09.
Packing fraction 0.39

pH: 08.
Packing fraction 0.34

The altering packing fraction in DBC in response to different pH.



The change of free energy with varying Rc.

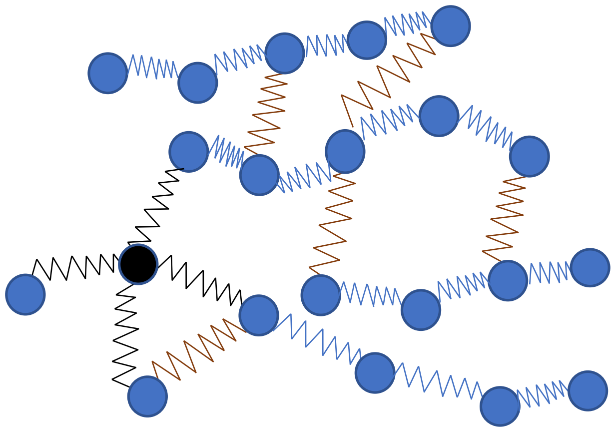


The change of free energy with varying Rs.

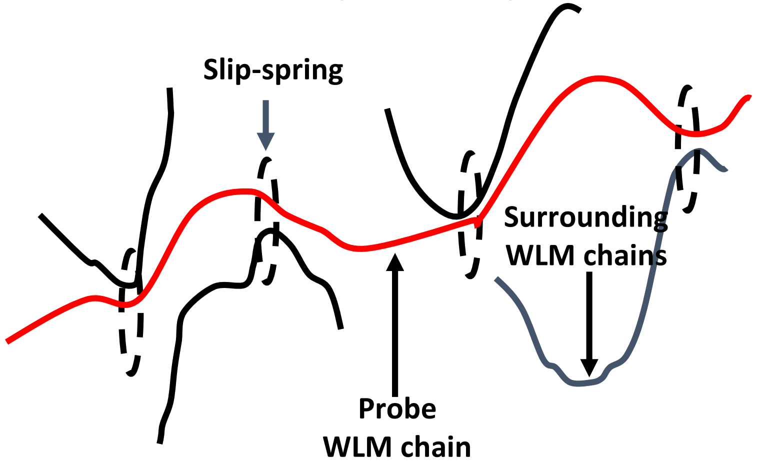
Progress and Current Status of Project

Novel coarse-grained Brownian dynamics(BD)/kinetic Monte Carlo (kMc) model developed for predicting rheology of DBCs

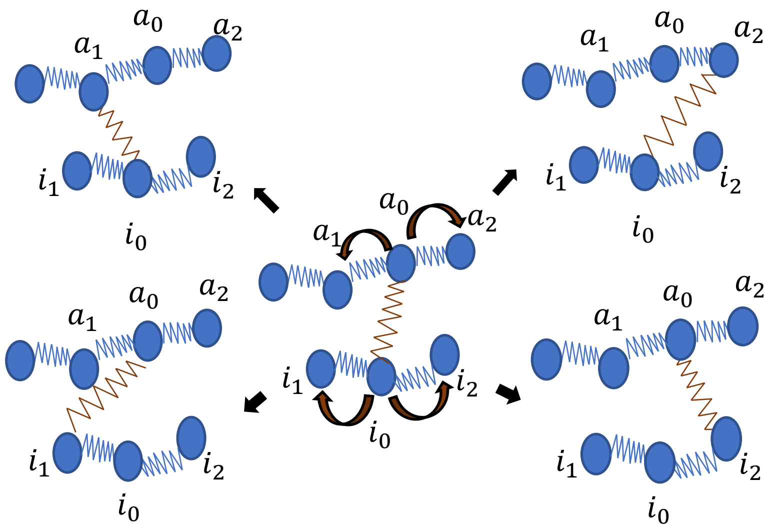
- In this model, DBC chains are represented by springs and beads while the entanglements are represented by slip-springs.
- Simulation of stress relaxation is modeled through mechanisms like reptation, contour length fluctuations, constraint release, and dynamic union and scission, which are executed by the kMC method using the standard metropolis algorithm.
- The kMC algorithm simulates the reptation mechanism by the process of slip spring hopping.



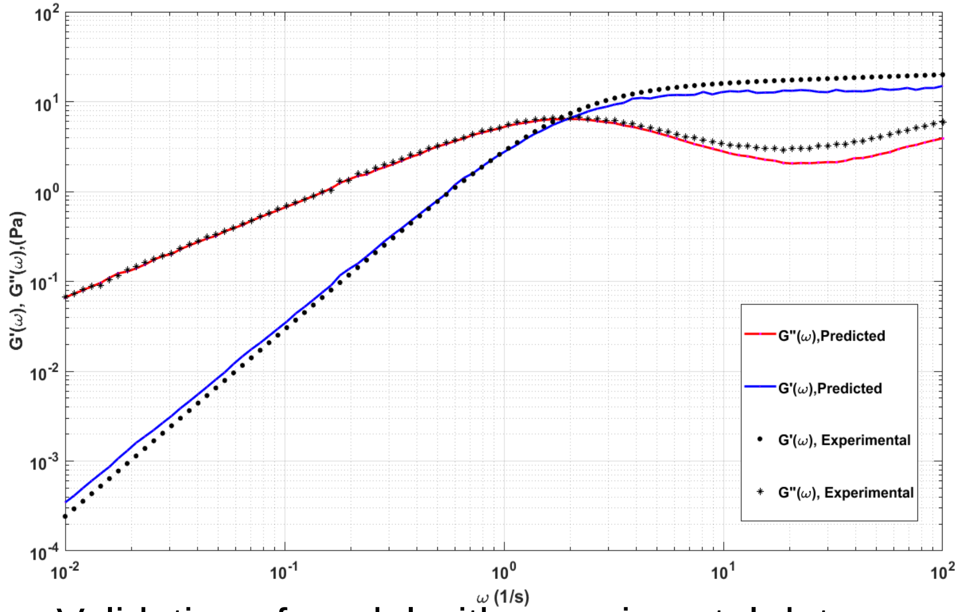
Coarse-grained representation of WLM melt



Entanglements in WLMs modeled with slip springs



Considered kMC events to model reptation in WLMs



Validation of model with experimental data

The Coarse grained BD/kMC rheology model simulations are compatible with the experimental data, which demonstrates that reptation, constraint release, contour length fluctuations, and dynamic union and scission are the major relaxation mechanisms in the WLMS.

Progress and Current Status of Project

Impact of using VES fluids

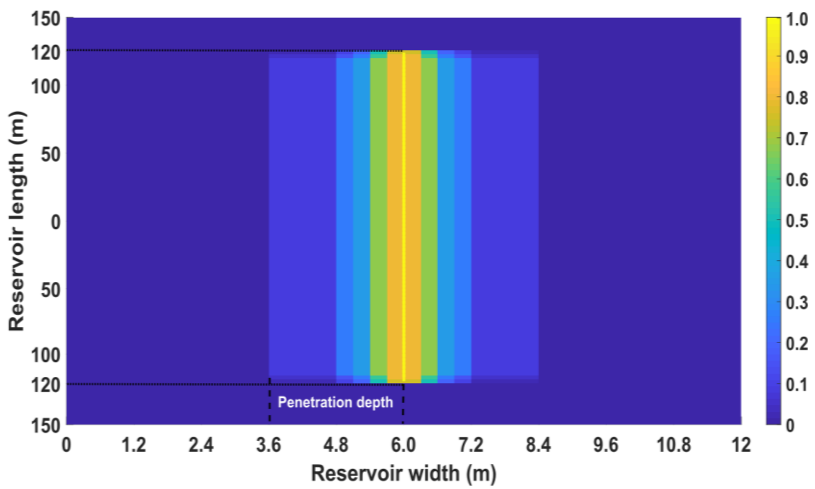
A three-dimensional, multiphase production simulator is developed to predict the production from a reservoir, hydraulic fractured with VES fluids, by considering the impact of formation damage, fracture geometry, and fluid flowback.

Determine optimal viscosity

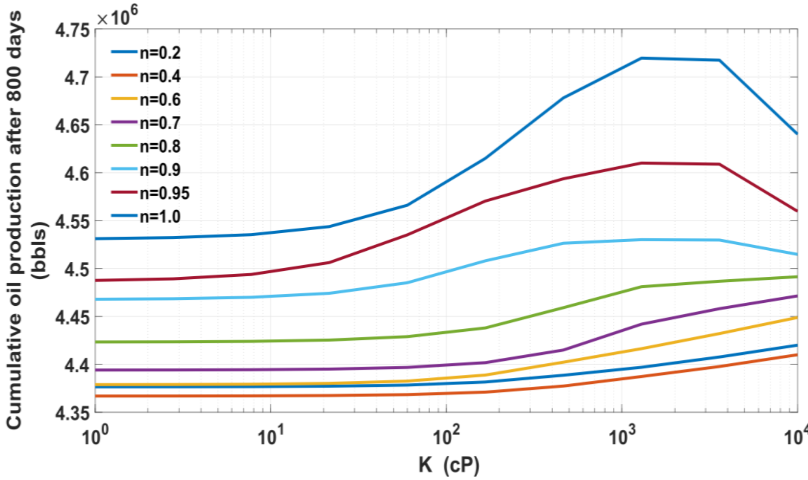
The production simulator is used to carry out the sensitivity analysis for determining the optimal viscosity of fracturing fluids, for a specific reservoir.

Obtaining a pumping schedule

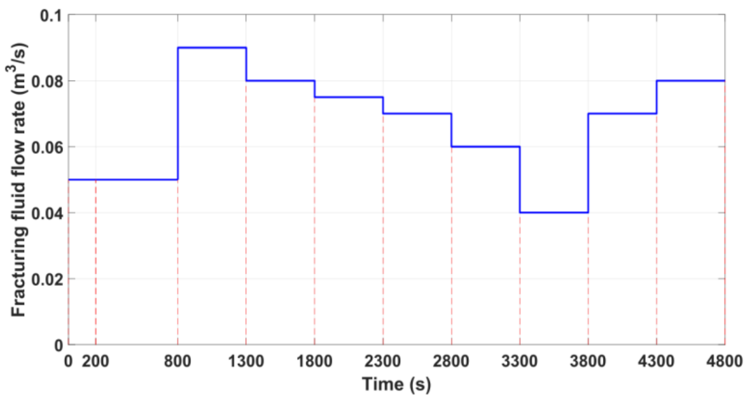
A closed-loop optimization problem is formulated and solved to obtain the optimum pumping schedule necessary for obtaining the final fracture geometry with uniform proppant concentration inside the hydraulic fractures.



The 2D view of the production simulator



Sensitivity analysis to determine optimal viscosity prediction



Optimal pumping schedule to attain target fracture geometry

Plans for Future Testing/Development/Commercialization

Future Plans/Development

- Compatibility studies with other components of fracturing fluids
- Investigation of permeation improvements
- Laboratory scale fracturing tests
- Large-scale fracturing tests
- Development of models for estimating fracturing performance of DBCs
- Aging studies for storage over prolonged periods of time
- Scale-up studies

Plans for Future Testing/Development/Commercialization

Scale-up and Commercialization

- As a first step in scale-up, **Incendium Technologies** are obtaining kinetical parameters for reactions of the most promising three formulations.
- Pilot reactor is being designed and will be built based on the kinetical parameters obtained.
- The sourcing of raw materials for pilot scale production will be established.
- The energy consumption and operational costs will be monitored to be able to estimate the cost of novel viscosifiers.
- After confirming enhanced fracturing efficiency and pilot scale production, Incendium Technologies and **Eastman Chemicals** will establish agreements for large scale production.

INCENDIUM TECHNOLOGIES

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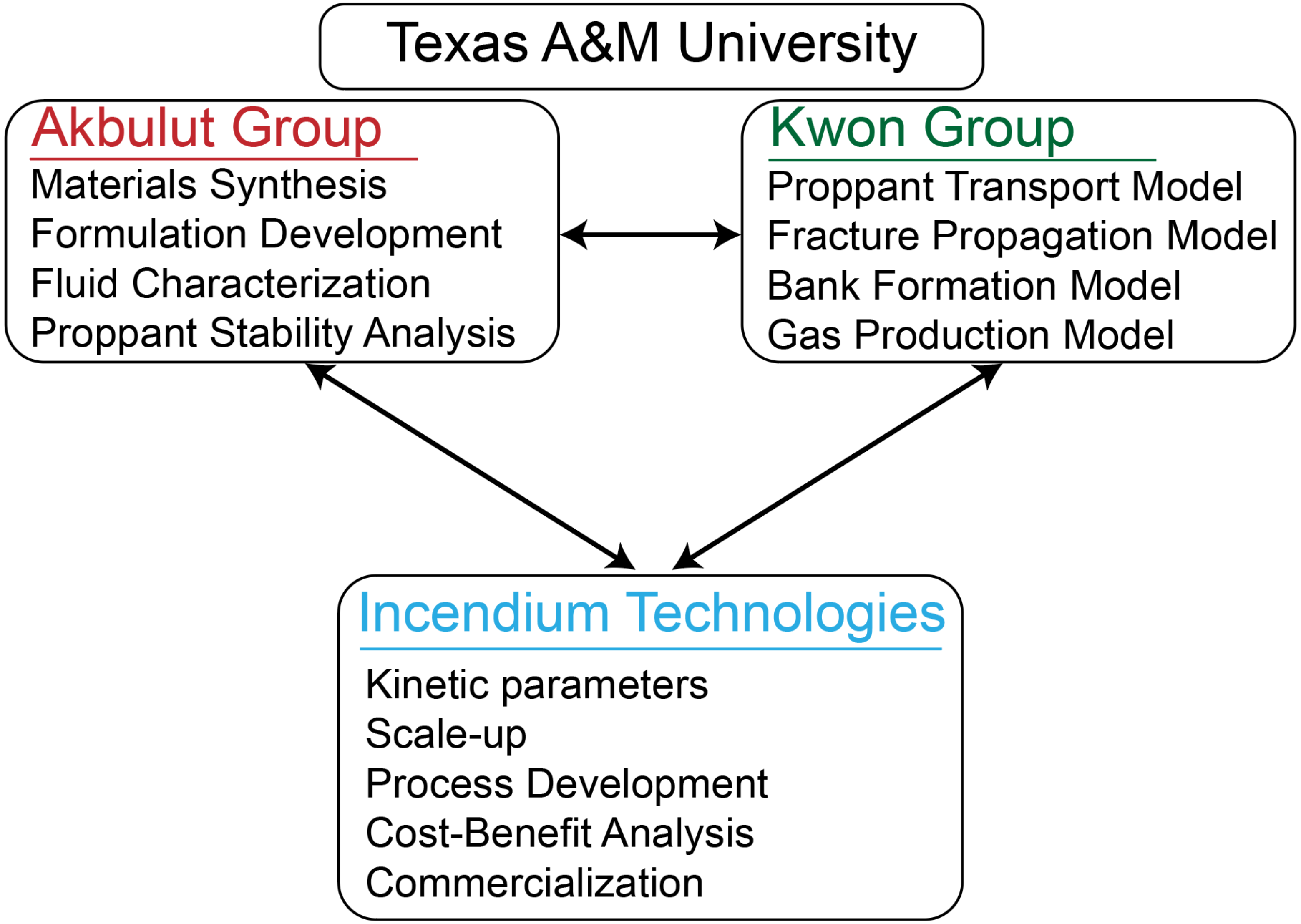
Summary

- 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.
- One particular formulation has been discovered to have increased viscosity with increasing salinity.
- DBCs have demonstrated exceptional ability to suspend proppants.
- Synergistic influence of viscosity and intermolecular interactions (DBC mesh adhering to proppant particles) are responsible for enhanced proppant stability.

Appendix

Organizational Chart



Appendix

Gantt Chart

Task Description	Mile-stone	Milestone Description	Milestone Verification Process	Expected Quarter
Flow and Viscosity Properties of DBCs	A1	Achieve a viscosity of 50−1000 cP with 0.1−2% of DBC solutions at shear rates of 40−100 s^{-1}	Rotational and oscillatory rheometry measurements with three repeats for each sample	1
	A2	Accomplish a reversible re-adjustability of 100-fold in viscosity of DBCs at typical reservoir pressures, temperatures, and salinities via pH stimulus	High-pressure rheometry studies with three replicate measurements for each sample	2
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
	B2	Realize 3 orders of magnitude reversible control over the proppant settling velocity in situ	Static and dynamics sand settling experiments	4
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 nanoarchitecture of DBCs.	4
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 samples	5
	C2	Achieve a maximum of 10% reduction in viscosity and proppant carrying capacity after 10 stimulus cycles	High-pressure rheometry and sand settling measurements verified with three different samples	6
Compatibility with Other Chemicals in Fracking Fluids	D1	Identify at least one compound that is compatible with DBCs for all functions of clay stabilization, friction reduction, corrosion inhibition, scale inhibition, and iron control suitable for hydraulic fracturing	Aging and phase behavior experiments, visual inspection, and chemical spectroscopy	7
Computational Models to Describe Proppant Transport and Fracture Propagation	E1	Successful development of dynamic models for 3D, simultaneously growing multiple fractures with at least 2D proppant transport	Experimental validation within 20% accuracy	6
Adsorption and Desorption of DBCs on/from Proppant and Fracture Surfaces	F1	Successful development of dynamic models describing adsorption and desorption of DBCs on proppant surfaces	Laboratory-scale studies to verify the models with a criterion of 20% accuracy	8
Laboratory Experiments to Evaluate Hydraulic Fracturing Performance	G1	Obtain 50% enhancements in fracture permeability and conductivity using DBCs compared to four commercial fracturing fluids	Tests using specimens obtained unconventional reservoirs from Texas	8
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 nanoarchitecture of DBCs.	8
Computational studies of estimating wastewater recovery and gas production rates after fracking fluid clean-up	H1	Develop a subroutine for non-Newtonian fluid to compute the modified viscosity due to DBCs and use this subroutine for calculating gas production and water recovery rates	Experimental studies to confirm the validity of models with a criterion of 20% accuracy	9
Scale-up, Large-Scale Manufacturing, and Field Testing of DBCs	I1	Determine all kinetic parameters of DBC formulation with the best laboratory-scale performance, which are the main scale-up parameters	Time-resolved spectroscopic analysis	9
	I2	Realize 100 pounds/day production rate at a minimum yield of 85% in a pilot plant specifically designed manufacturing of DBC	Spectroscopic analysis for determining the reaction yield and digital balances for measuring the production rates	10
	I3	Achieve at least 50% improvements in the hydrocarbon recovery on the field tests compared to the current-state-of-art	Coriolis flow meter measurements of natural gas production in the selected well over 10 days	11
Cost-Benefit Analysis	J1	Prepare a comprehensive cost-benefit analysis considering raw material cost, production cost, deployment costs, durability, life-time, and potential benefits		12
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