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Game Changing Technology of Polymeric Surfactants for Tertiary Oil Recovery in the Illinois Basin

10123-03
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Houston Research Center
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Project Objective

The main objective of this laboratory study is to develop functional polymeric surfactant (FPS) compounds that will be the next generation of EOR chemicals. The particular area that is intended for initial deployment of these new chemicals is the Illinois Basin. In addition to identifying the best technical design for such a chemical EOR project, the project will include a general economic analysis of the polymeric surfactant (PS) process as would be applied in typical small producer field in the Illinois Basin. We anticipate that these chemicals that are suitable there also will be favorable for small producers in other areas in the United States that have similar reservoir conditions.

SCOPE of WORK

The scope of this project is to further develop polymeric surfactant (PS) technology as an alternative chemical EOR approach. This breakthrough technology that uses a single component instead of multiple components as in traditional Surfactant Polymer (S+P) flooding has the potential of saving millions of dollars for mature field tertiary oil recovery operations. The typical oilfield reservoir conditions from the Illinois Basin will be used to test and evaluate the developing PS-EOR potential for this important mature oil field region.

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Tasks to be Performed

- Screening for Proper Functionalized Polymeric-Surfactants
- Laboratory Measurements to Characterize FPS Performance
- Technical Design for Typical Illinois Basin EOR Target Reservoirs
  - Identify field samples and injection waters
  - Testing the interfacial tension (IFT) of our FPS samples
  - Rheology testing for both commercial and synthesized polymeric surfactant
  - Thermal stability testing for both commercial and synthesized polymeric surfactant
  - Core flood testing and oil recovery experiments
- Economic Analysis of PS-EOR for the Illinois Basin

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Project Status

Detailed Project Schedule									
Task	Description	Completion Time (Quarter)							
		1	2	3	4	5	6	7	8
1	Project Management Plan								
2	Technology Status Assessment								
3	Technology Transfer								
4	Other Reports and Special Items								
5	Identification and Synthesis of Polymeric-Surfactants								
6	Laboratory Measurements to Characterize Polymeric-Surfactant Performance								
7	Technical Design for Typical Illinois basin EOR Target Reservoirs								
8	Economic Analysis of polymeric Surfactant EOR for the ; Final Report								
Milestones	1								
	2								
	3								
	4								

- Period – April 1, 2012 to March 30, 2014
- Organizations & Team:

    Power Environmental Energy Research Institute (PI: Yongchun Tang)

    American Energy Reserves, LLC (Co-PI: Gary Watts)

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Current Tertiary Recovery Technologies

Polymer Flood (P)

– Basic chemical flood.

(Mobility Controller to increase volumetric sweep efficiency)

Surfactant-Polymer Flood (SP)

– Advanced P flood.

(To increase volumetric sweep efficiency and microscopic displacement efficiency)

Alkali-Surfactant-Polymer Flood (ASP)

– Advanced SP flood.

(Using alkali as sacrifice agent to reduce surfactant usage)

Overall Competition Comparison

Aspect	P Flood	SP Flood	ASP Flood	PEER FPS
EOR Efficiency	★	★★	★★★	★★
Chemical Cost	★	★★	★★★	★
Operation Cost	★	★★	★★	★
Scaling Problem			★★	
Economics	☆	☆☆	☆☆	☆☆☆

Note: PEER FPS has more other good features according to lab and field evaluations.

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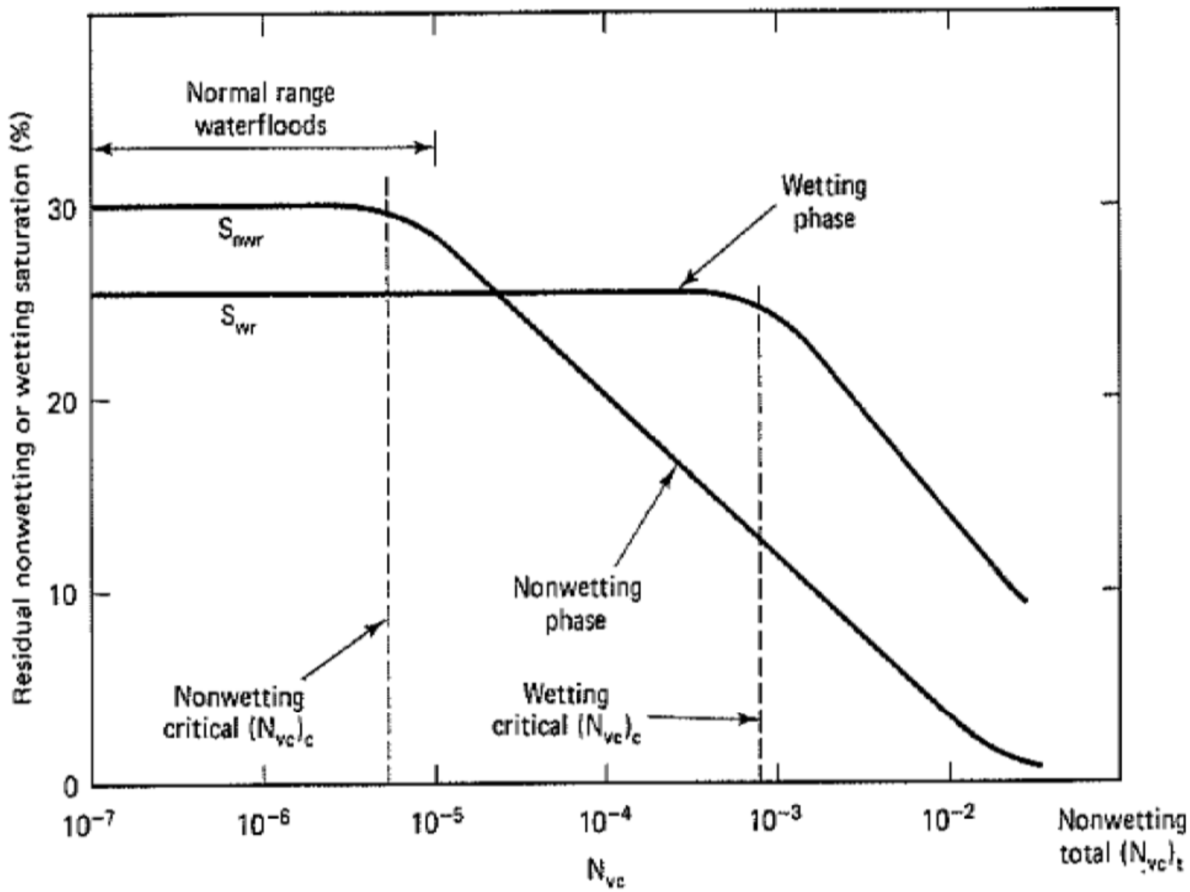
Schematic Capillary Desaturation Curve



$$N_c = \frac{\mu v}{\sigma}$$

μ - the viscosity,
v - the Darcy velocity
σ - the interfacial tension

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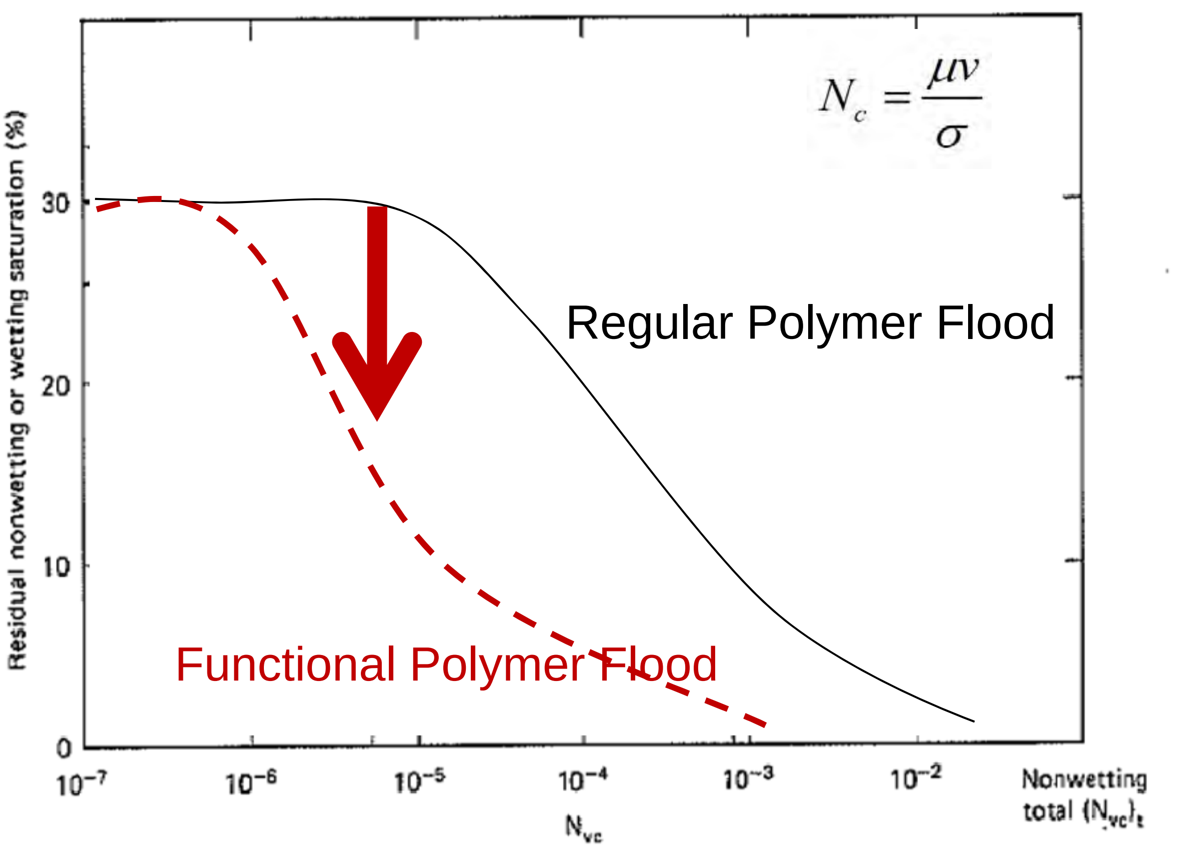
Schematic CDC Curves for Polymer Flood



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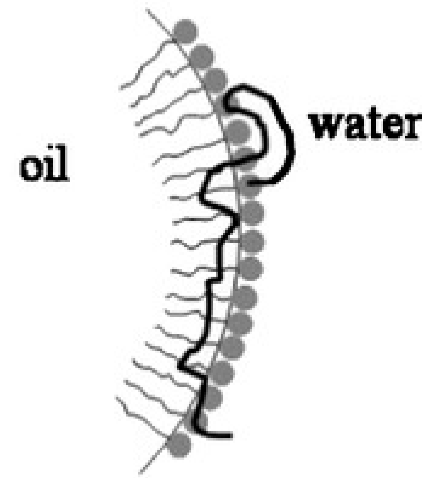
New Hypothesis of Functional Polymer

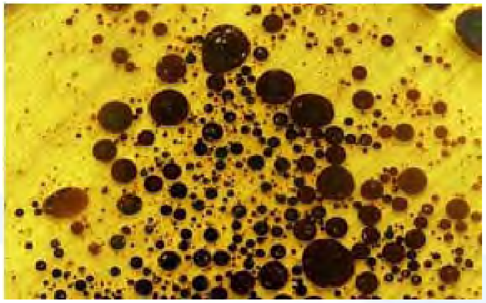
$$N_c = \frac{\mu v}{\sigma}$$

How to Increase Nc to 1000 times?



μ - at oil water interface, the micro-viscoisty of water is higher than the bulk viscosity of water

σ - the interfacial tension is at least 100 times lower than the oil water interfacial tension of regular polymer flood



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Viscosity Measurements of FPS in Brine

Photographs of (a) Brookfield DV-II +Pro, and (b) DV-I prime digital viscometers from the PEER Institute laboratory.

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Interfacial Tension (IFT) Measurement

Photograph of TX-500C full range tensiometer from the PEER Institute laboratory.

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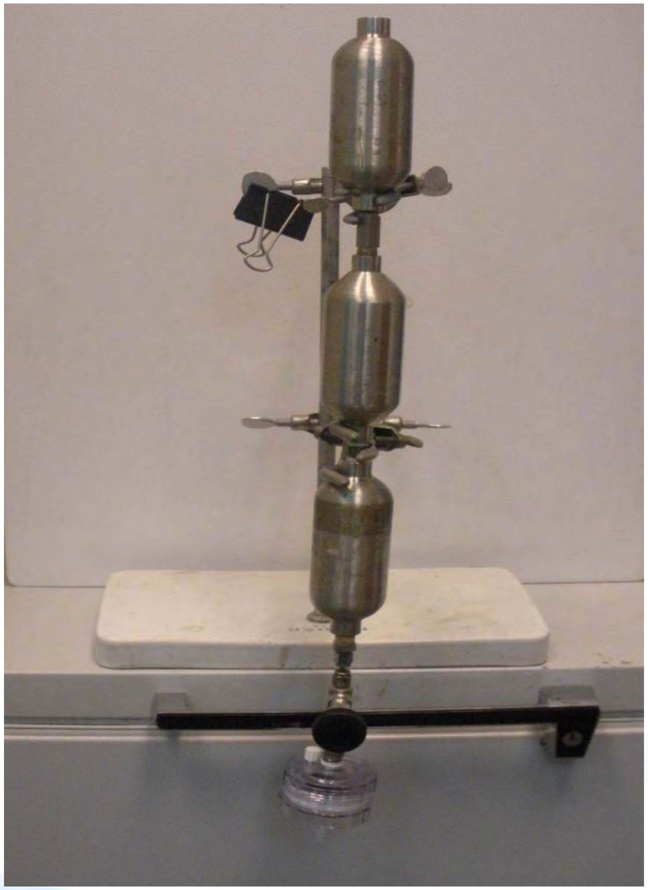
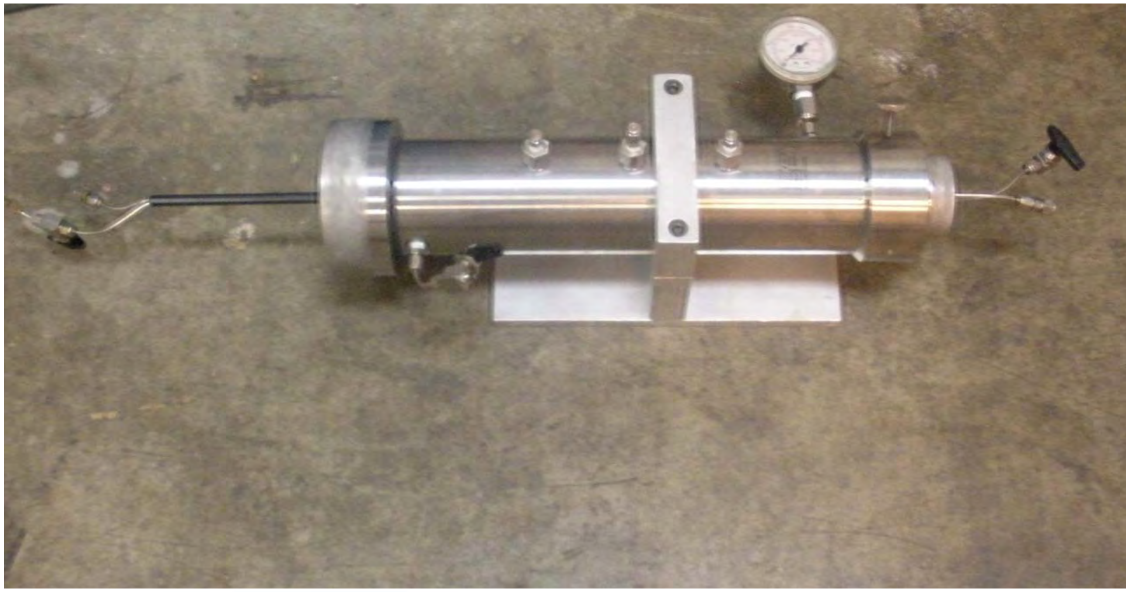
Filtration and Core Flood Experiments



Photograph of the filtration apparatus from the PEER Institute laboratory.



Photograph of core flooding instrument from PEER Institute laboratory

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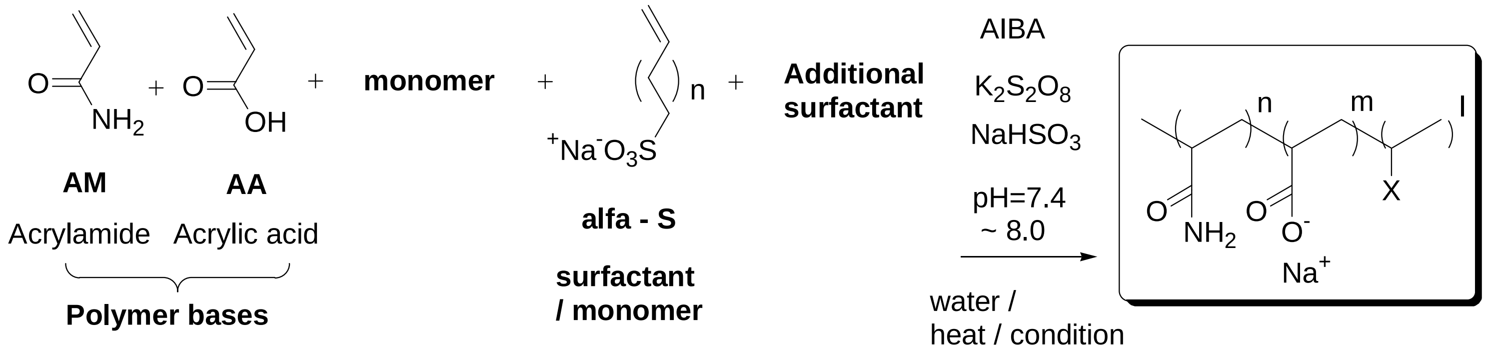
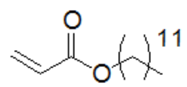
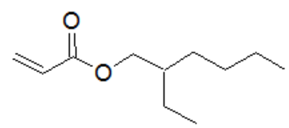
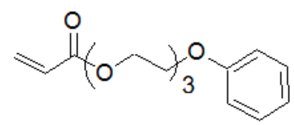
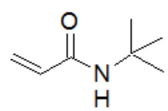
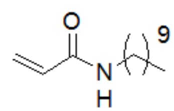
FPS Synthesis Routine



Monomers used		
n-Lauryl acrylate **1** 	2-Ethylhexyl acrylate **2** 	Poly (ethylene glycol) phenyl ether acrylate **3** 
N-tert-Butyl acrylamide **4** 	N-Decyl acrylamide **5** 	

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Modification of Molecular Composition of FPS

Six synthetic exemplary FPS samples ware prepared *via* free-radical initiated copolymerization. The ratios of the compositions of component parts of each FPS are given.

Monomer	FPS-1a	FPS-1b	FPS-1c	FPS-2a	FPS-2b	FPS-2c
acrylamide	6-~80%	6-~80%	6-~80%	0~40%	0~40%	0~40%
H1	0~35%	0~35%	0~35%	50~90%	50~90%	50~90%
H2		1~5%	1~5%			1~5%
H3	1~5%	1~5%		1~5%	1~5%	1~5%
L1			1~5%	1~5%		
L2		1~5%			1~5%	
L3	1~5%			1~5%		
L4	0~5%	0~5%	0~5%			1~5%
L5	1~5%		1~5%	1~5%	1~5%	1~5%

•FPS-1a, 1b, 1c each has molecular weight ranged from 5 mil to 10 mil, and FPS-2a, 2b, 2c each has molecular weight ranged from 0.2 mil to 3 mil;

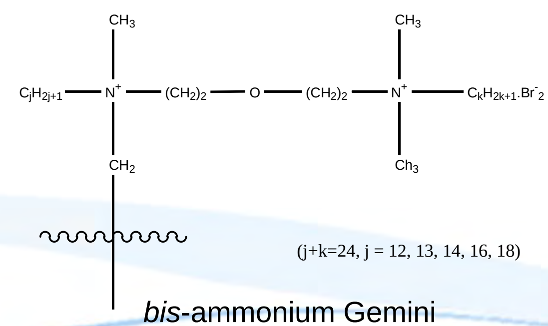
•H1, H2, H3 are hydrophilic monomers, and H1=[CH_2=CH-CO-OH], H2=[CH_2=CH-CO-NH-C$(CH_3)_2$-$CH_2SO_3^-Na^+$], H3=[CH_2=CH-CO-O-$(EO)_p$-$(CH_2)_n$-CH_3];

•L1, L2, L3, L4, L5 are hydrophilic monomers, and L1=[CH_2=CH-CO-NH-CH(CH_2-SO_3Na)($(CH_2)_n$-CH_3)], L2=[CH_2=CH-CH_2-$N^+(CH_3)_2$-$(CH_2)_n$-$CH_3.X^-$], L3=[CH_2=CH-CO-NH-$(CH_2)_n$-$N^+(CH_3)_2$-$(CH_2)_n$-$CH_3.X^-$], L4=[CH_2=CH-CO-O-$(CH_2)_n$-CH_3], L5=[CH_2=CH-CO-G];

•n is an integer from 8 to 20; p is an integer from 6 to 20;

•EO represents –CH_2CH_2O-, X^- = Cl^-, Br^-,

•G represents a *bis*-ammonium Gemini surfactant moiety, covalent bonding with carbonyl group in the monomer as in Figure.



bis-ammonium Gemini surfactant moiety, G

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IFT Measurement and Comparison

Comparison of measured Interfacial Tension (IFT) (dyne/cm) of six synthesized PFS with commercial partially hydrolyzed polyacrylamide previously used in polymer flooding system (MO4000 by Mitsubishi) and the control system (*n*-heptane and 3% NaCl).

	IFT (dyne/cm)
FPS-1a	5.34
FPS-1b	7.29
FPS-1c	3.47
FPS-2a	0.91
FPS-2b	0.86
FPS-2c	1.36
MO4000	34.33
Control	44.8

Note: IFT values of these systems (Oil phase as *n*-heptane, aqueous phase as 1000 ppm FPS solution in 3% NaCl) were determined at 86 F using a spinning drop interfacial tensiometer.

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Comparison with Coreflood Tests

The resulting irreducible oil saturation data from coreflood tests. The chemical flood began with the injection of a 0.3 pore volume (PV) slug of 1500 ppm FPS sample prepared with 0.5% NaCl brine, followed by 0.5% NaCl brine to irreducible oil saturation (watercut 98%). A separate chemical flood used PAM-25 (polyacrylamide, hydrolysis degree = 23%, molecular weight 25 mil).

	Saturation
FPS-1a	0.30
FPS-1b	0.35
FPS-1c	0.32
FPS-2a	0.27
FPS-2b	0.29
FPS-2c	0.30
PAM-25	0.38

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Effects of Temperature on FPS Viscosity

Measured Viscosity of Different FPS (2500 ppm) in Brine

Unit: Cps	25°C/6rpm	25°C/30rpm	50°C/6rpm	50°C/30rpm	75°C/6rpm	75°C/30rpm
FPS-21-1	23.5	15.4	11.5	8.5	6.5	5.4
FPS-108	9.5	7.4	5	3.5	1.4	0.5
FPS-7-3	25	16.5	23	15	17.5	10.9
FPS-166	18	13.2	17	11.7	9	6.1

Unit: Cps	25°C/6rpm	25°C/30rpm	50°C/6rpm	50°C/30rpm	75°C/6rpm	75°C/30rpm
FPS-1	28.5	19.7	17.0	12.6	10.0	8.2
FPS-38	25.5	17.5	13.5	11.0	8.5	6.7
FPS-107	28.0	20.3	17.0	13.5	10.5	8.7
FPS-228	25.0	18.2	12.5	10.9	8.5	6.8
FPS-350	14.0	10.2	7.0	5.7	5.0	4.1
FPS-540	5.0	2.8	1.5	0.9	0.5	0.4

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Identify Field Samples and Injection Water

Recently receipts of the oil/water samples from Illinois Basin

Name	Location	Formation	Depth (m)	Note
Morgan#1	Township 3 South Range 9 West Section 3, Gibson County, Indiana	Hardinsburg Sand	1340	
Marx#1	Township 7 South Range 13 West Section 25, Posey County, Indiana	Waltersburg Sand	1830	
Schriefer #3A	Township 7South Range 12 West Section 18, Posey County, Indiana	Pennsylvanian Sand	650	
St Wendel Unit	Township 5 South Range 12 West Section 24, Posey County, Indiana	Mansfield Sand	1200	The field consists of 44 wells, 12 of which have been plugged

We are expecting to receive more oil/water samples from Illinois Basin soon.

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Synthesized Formation Water Composition

Synthesized Modeled Formation Water Composition used in Laboratorial Studies

Component	NaCl	Na_2SO_4	KCl	$CaCl_2 \bullet 2H_2O$	$MgCl_2 \bullet 6H_2O^-$
Molecular Weigh (gm)	58.5	142	74.5	147	203.3
Concentration (mg/L)	24000	4010	740	1520	10900

Formation Water Collected and Analyzed from a single well from Illinois Basin

Element		Na	Ca	Mg	K	Cl^-	SO_4^{2-}	Others
Concentration (mg/L)	Test 1	31300	5160	1940	271	62910	708	<500
	Test2	31500	5170	1950	271	62960	696	<500
	Test3	31000	5090	1940	305	62960	625	<500

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Initial Oil Sample Testing Results

FPS	Morgan#1	Marx#1	St Wendel Unit
FPS-01	3.20		
FPS-02	11.40		
FPS-03	2.80	7.2	3.1
FPS-04	7.80		
FPS-05	15.20		
Commercial-A	12.20		
Commercial-B	0.21	0.11	0.099
Commercial-C	3.10		

2500ppm Concentration

Tested Under Identify Fields Condition

More tests are undergoing

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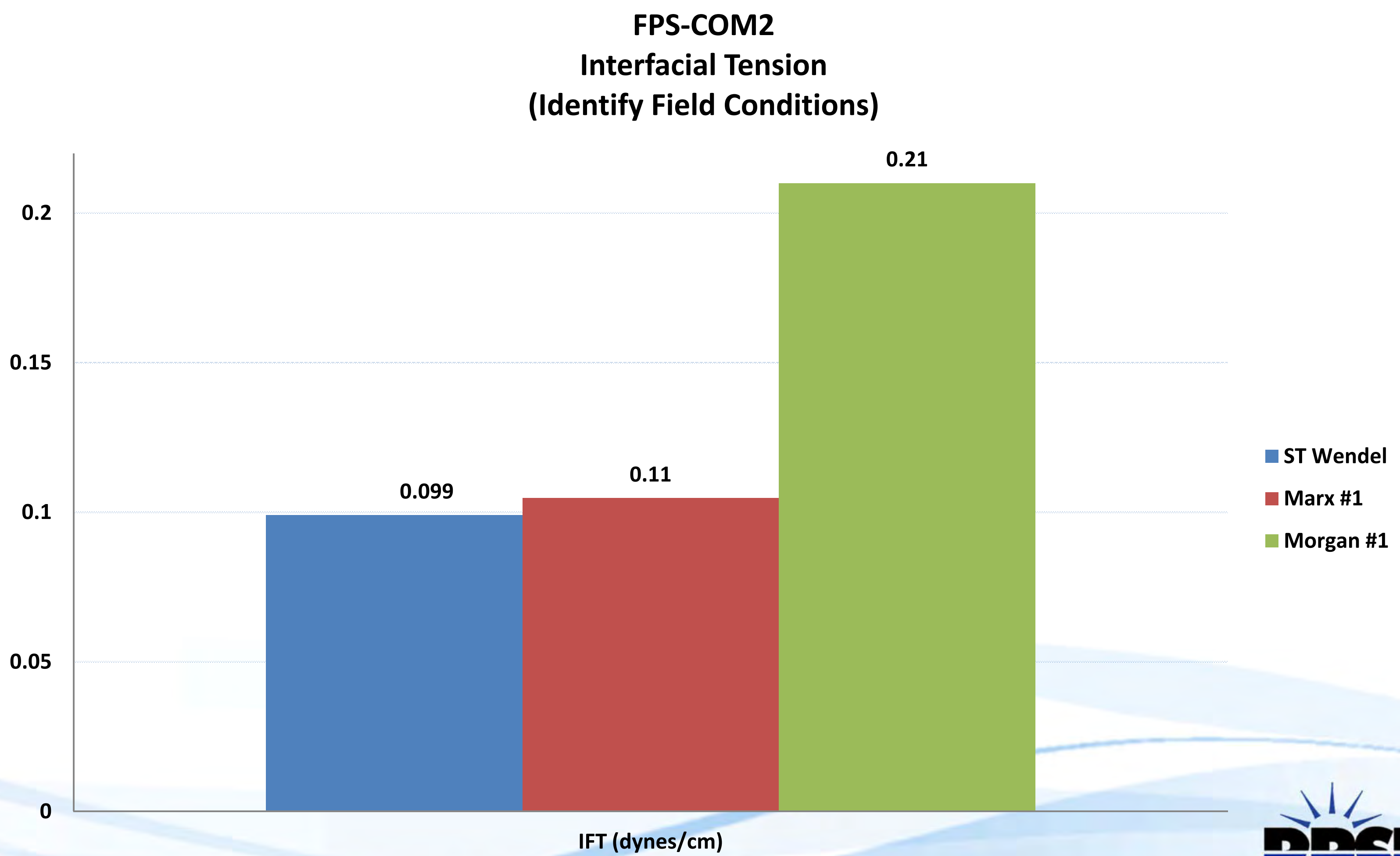
Interfacial Tension



2500ppm Concentration

Tested Under Identify Fields Condition

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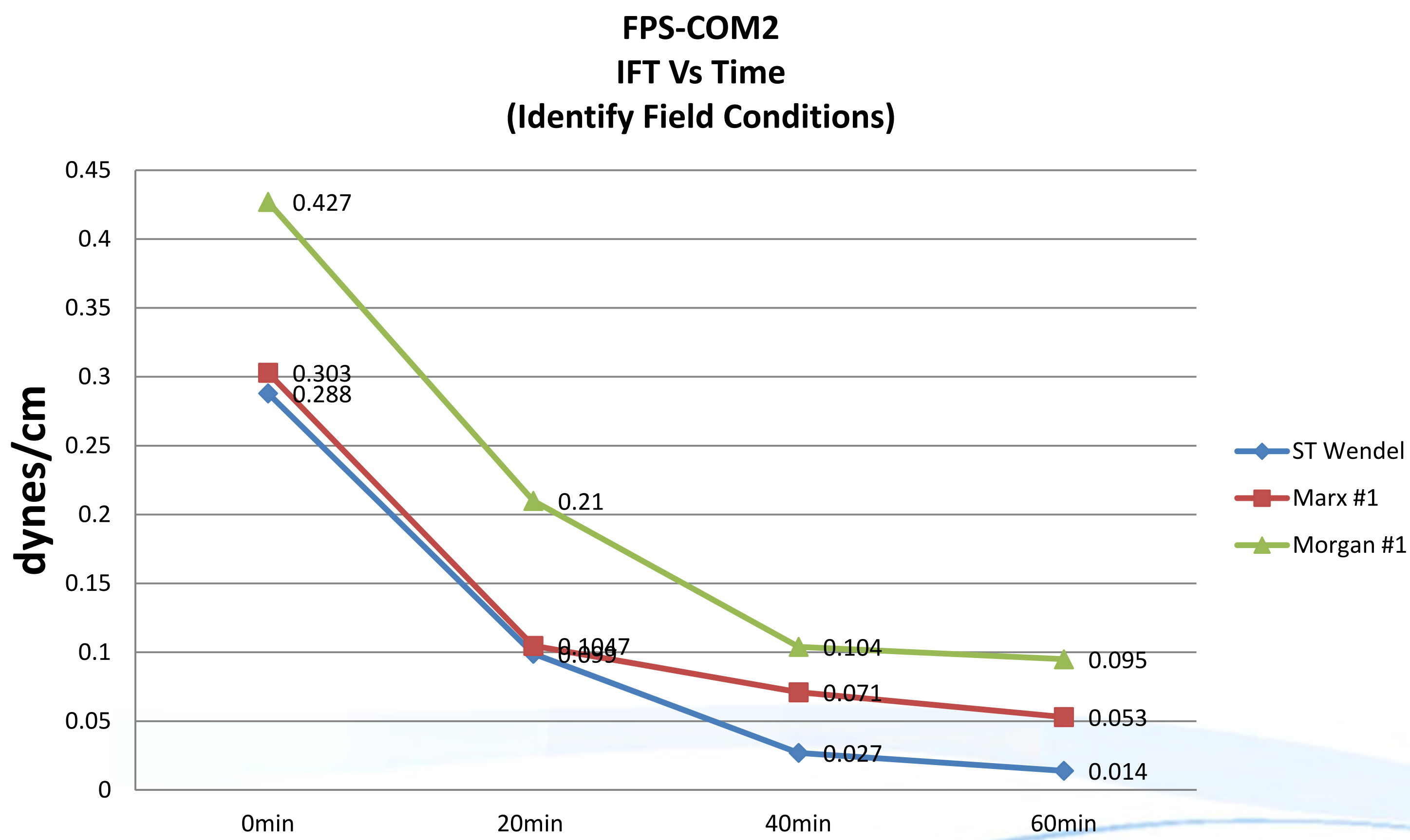
Interfacial Tension Vs Time



2500ppm Concentration
Tested Under Identify Fields Condition

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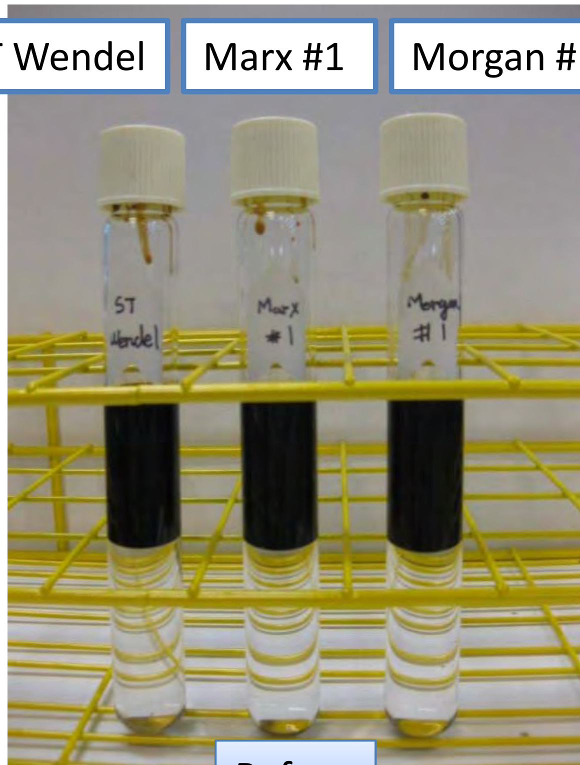
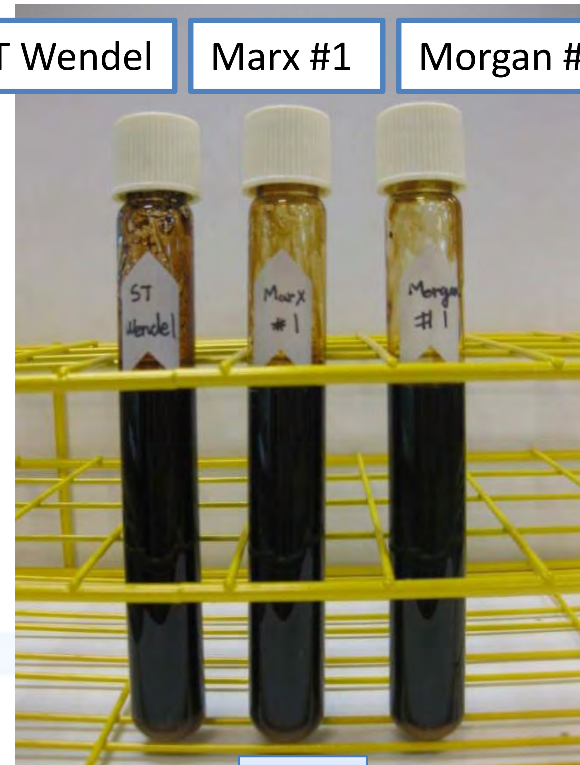
Crude Oil/Water Emulsification



Before



After

-2500ppm Concentration in Identify Field Conditions
-3 Testing Tubes Were Rotated 10 Rounds and Recorded Simultaneously

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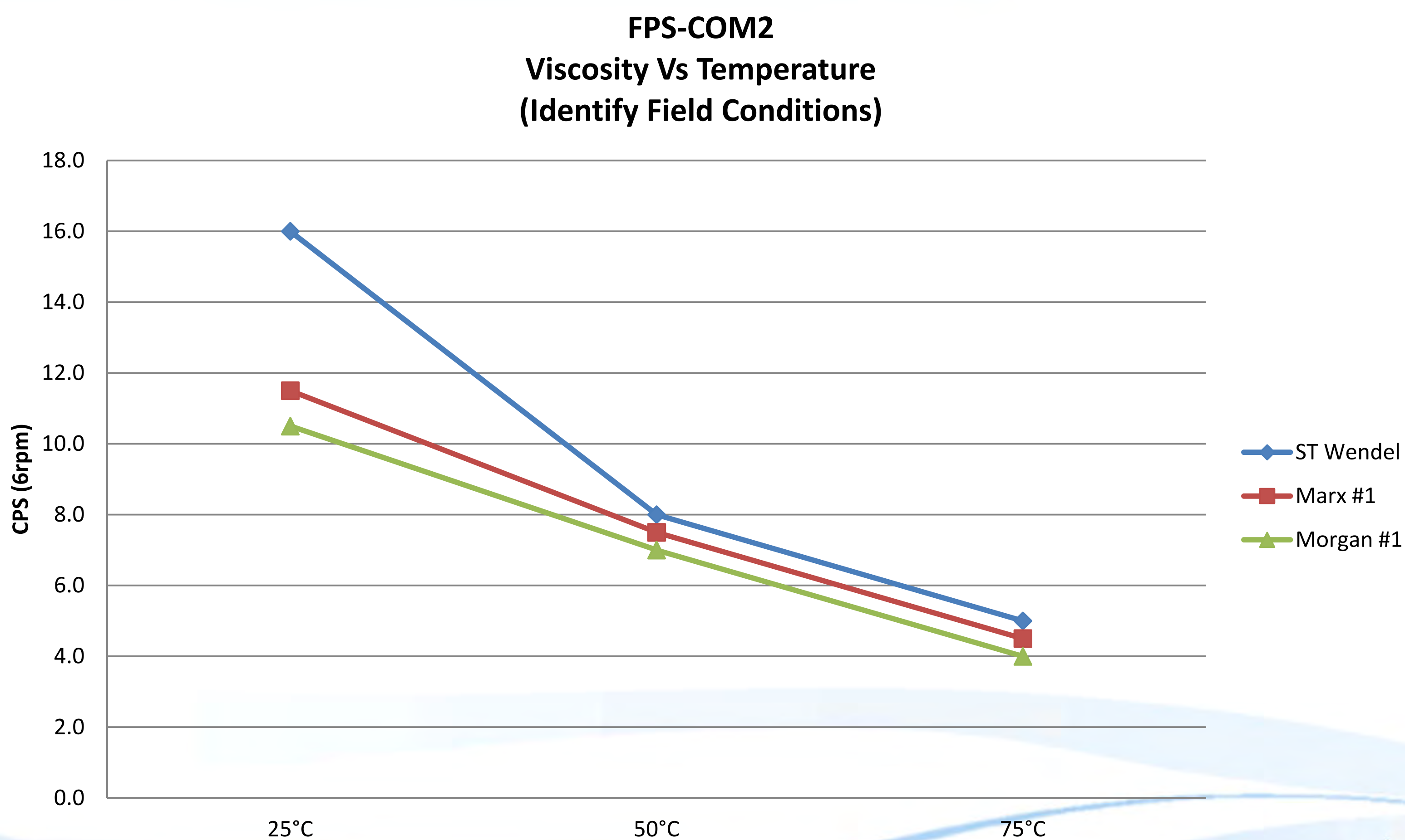
Viscosity in Identify Field Brine



2500ppm Concentration in Identify Field Brine

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Project Interim Summary

SUMMARY

- Preliminary laboratorial studies have demonstrated that a large variety of functionalized polymeric surfactants could be obtained, and that may lead to the oil field application for enhanced oil recovery (EOR)
- Although premature, our laboratorial tests shown promises to using a single FPS chemical to achieve the similar oil sweeping efficiency of commercially available S+P chemical flooding.
- A number of the oil field samples provided from our industrial partners are now available for more extensive studies; and we are expecting to secure more samples in the near future.
- A few potential FPS candidates, available from both commercial and lab-synthesized, have been identified for further investigated, especially for the oil/water samples from the Illinois basin.

Future Work

- Laboratorial evaluations of other physical/chemical properties such as viscosity changes, degree of association, thermal and salt tolerant of the selected FPS candidates.
- Further tests of the selected FPS with the oil/water samples, including the adsorption and flirtation studies.
- Continue screen for commercial FPS polymers and synthesized FPS compounds, if needed.
- Plan to do core flood for the identify commercial FPS samples.
- Compare with Polymer + Surfactant flood with FPS flood

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