Final Report to

GAME CHANGING TECHNOLOGY OF POLYMERIC-SURFACTANTS FOR TERTIARY OIL RECOVERY IN THE ILLINOIS BASIN

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ABSTRACT

A special class of polymeric surfactant designated Functional Polymeric Surfactant (FPS) a variant from conventional polyacrylamide, based upon theoretical and experimental study has proven to be a cost effective method for enhanced oil recovery (EOR). This technology shows a marked increase in cost savings as compared to conventional tertiary oil recovery methods such as polymer (P) flood, surfactant and polymer (SP) flood, or alkaline surfactant polymer (ASP) flood. Although FPS is a single component chemical, it can provide needed viscosity for improved mobility in a control water flood and decrease the oil water interfacial tension (IFT) required in obtaining microscopic displacement efficiency for tertiary oil recovery. FPS can effectively replace traditional multiple component SP-flooding or complicated ASP oil recovery methods, both very expensive and difficult for small oil producers to apply, thus potentially saving small and independent mature oil field producers millions of expenditure dollars.

A series of FPS chemicals were identified as possible candidates for EOR application testing based upon typical Illinois Basin field evaluation. Due to significant variety in molecular structures and chemical formulations of FPS, advanced laboratory procedures were systematically applied to a number of candidates to evaluate FPS performance relevant to the EOR application. Typical test parameters included solution viscosity, oil-water emulsion, interfacial tension (IFT), and oil displacement efficiency from cores. Initial screenings were conducted on a model oil sample, dodecane (C_{12}) and sixteen oil/brine samples from four mature Illinois oil fields were collected and tested with only potentially successful FPS candidates selected for further development. Advanced molecular modeling techniques were applied to improve fundamental understanding of the functionality of FPS as an EOR agent and assist in FPS formulation and synthesis. Three series of special FPS chemicals were evaluated during this project and their performance as FPS-flooding agents for EOR applications were tested by both in house and an independent EOR testing lab. Preliminary engineering and economic assessments of the FPS-EOR technology revealed that the oil recovery from FPS-flooding could yield an additional 12% Original Oil in Place (OOIP) in comparison with conventional P-flooding Hydrolyzed PolyAcrylaMide (HPAM) technology. FPS is a cost effective oil recovery method for domestic small oil producers without significantly increasing materials and operational costs.

TABLE OF CONTENTS

ABSTRACT 4

TABLE OF CONTENTS 5

EXECUTIVE SUMMARY 13

1. INTRODUCTION 15

1.1 Enhanced Oil Recovery (EOR) Overview 15

1.2 Our Approach of Selecting FPS Polymer 18

1.3 EOR in Illinois Basin 19

1.3.1 Field-scale Tertiary Oil Recovery Applications in the Illinois Basin 21

1.3.2 Applications of the FPS Flooding in the Illinois Basin 23

2 PROJECT OUTLINE 24

2.1 Objectives 24

2.2 Completed Tasks 25

2.2.1 Task 1 – Selections of Proper Functionalized Polymeric Surfactants 25

2.2.2 Task 2 – Laboratory Screening of Proper Functionalized Polymeric Surfactants 26

2.2.3 Task 3 – Technical Assessment of FPS-EOR Application in Illinois Basin 27

2.2.4 Task 4 – Economic Analysis of FPS-EOR for Illinois Basin 28

3 METHODOLOGIES 29

3.1 Molecular Modeling of Functionalized Polymeric Surfactant 29

3.1.1. Survey of Theoretical Aspects of Molecular Designs 29

3.2.2 Copolymerization *vs.* post-polymerization modifications 36

3.2.3 Copolymerization of Functionalize Polymeric Surfactants 36

3.3 EXPERIMENTAL METHODS 37

3.3.1 Phase Behaviors 39

3.3.2 Viscosity Measurements 40

3.3.3 Surface Tension and Interfacial Tension (IFT) Measurements 41

3.3.4 Adsorption Test 43

3.3.5 Filtration Test 43
3.3.6 Thermal Stability Test 44
3.3.7 Sand Pack Flooding 44
3.3.8 Core Flooding 46
4 RESULTS AND DISCUSSION 47
4.1 With Model Oil 47
4.1.1 Emulsion 47
4.1.2 Interfacial Tension (IFT) 50
4.1.3 Solubility 56
4.1.4 Viscosity 57
4.1.5 Thermal Stability 63
4.2 With Illinois Oil 64
4.2.1 Emulsion 64
4.2.2 Emulsion Type 69
4.2.3 Berea Sandstone Adsorption Tests 71
4.2.4 IFT 73
4.2.5 Filtration Test 75
4.2.6 Sand Pack Flooding 78
4.2.7 Core flooding 82
5 FIELD TESTING and TECHNOLOGY TRANSFER EFFORTS 98
5.1 Geologic Assessment of Potential Field Trial Site in Illinois Basin 98
5.2 Economic Assessment of the FPS-EOR Technology 101
5.3 Presentations and Conferences 104
5.4 Journal Publications 104
6 CONCLUSIONS 106

LIST OF TABLES

Table 2-1: Local and Geological Information of the Crude Oil/Brine Samples from Illinois Basin 27
Table 2-2: Comparisons of Engineering and Economics of the FPS-Flooding with Other EOR Methods 28
Table 3-1 List of the Laboratory Testing Procedures and Measurements 38
Table 4-1: Viscosity of FPS before and after 3-day 80℃ thermal test 63
Table 4-2: Emulsion test. Comparison shows emulsification before and after adding FPS into solution. . 67
Table 4-3: Emulsion test. Comparison shows excellent phase behavior of FPS-33 with oil/water sample. 68
Table 4-4: Emulsion test. Performance under high temperature..... 69
Table 4-5: Emulsion test. Compatibility with stimulation fluids (acidic condition 0.3 wt% KCl at 80℃).69
Table 4-6: Viscosity (cP) change of FPS solution wo/w stone over time 71
Table 4-7: Viscosity (cP) change of FPS solution in different salinity over time 72
Table 4-8: Water Permeability 79
Table 4-9: HPAM-1830 sand pack flooding data 79
Table 4-10: FPS-228-73 sand pack flooding data (1) 80
Table 4-11: FPS-228-73 sand pack flooding data (2) 80
Table 4-12: FPS-228-75 sand pack flooding data 81
Table 4-13: FPS-212-140 sand pack flooding data 81
Table 4-14: HPAM + FPS-212-156 core flooding results 83
Table 4-15 Brief summary of HPAM + FPS-212-156 core flooding results 83
Table 4-16: HPAM + FPS-212-181 core flooding results 84
Table 4-17: Brief summary of HPAM + FPS-212-181 core flooding results 86
Table 4-18: Second HPAM + FPS-212-181 core flooding results 88
Table 4-19: Brief summary of second HPAM + FPS-212-181 core flooding results 90
Table 4-20: Comparison of FPS and HPAM flooding 91
Table 4-21: Results from third party for HPAM followed by FPS core flooding 93
Table 4-22: Results from third party for FPS followed by FPS core flooding 94
Table 4-23: Results from a third party for HPAM & FPS core flooding 94
Table 4-24: FPS core flooding test under various controlled conditions 95
Table 4-25 Experiment summary 96
Table 5-1: Source of Oil Production in Illinois Basin 99
Table 5-2: Oil and Gas Production Statistics in the Illinois Basin 99
Table 5-3: Collected Oil/Brine Samples from Various Sites of Illinois Basin 99

Table 5-4: Field Data of the #11 Oil/Brine Sample 101
Table 5-5: Economic Analysis Input Parameters 102
Table 5-6: Chemical Injection Design 103
Table 5-7: Economic Analysis 103

LIST OF FIGURES

Figure 1-1: Typical Oil Desaturation (Recovery) Curve as Function of the Capillary Number N_c. 17
Figure 1-2: FPS on the oil-water interface 19
Figure 1-3: Map of the Illinois Basin (left) and EOR potentials (right, darker spots indicating greater OOIP) areas. 19
Figure 1-4: Annual Oil Production 1906-present 20
Figure 1-5: Oil prices adjusted for inflation using the headline CPI 21
Figure 1-6: Typical Reservoir Conditions (Temperature and Pressure) of Illinois Basin 23
Figure 3-1: Molecular Structure of Partial Hydrolyzed Polyacrylamine Polymer (HPAM). The degree of hydrolysis is defined as τ = [AA]/{[AA] + [AM]}, which [AA] and [AM] are the portions of the acrylic acid and acrylamine groups. 100 repeated units were made, and the molecular geometry was optimized using Drending force field molecular dynamic calculations. Increase of the [AA] ratio distort the special symmetry of polymer. 33
Figure 3-2: Calculated binding energies of HPAM of various degrees of hydrolysisτ, with an oily hydrocarbon compounds (modelled by C_{14}). The increase of τ values decreases the miscibility of HPAM with the C_{14} compound, suggesting that the HPAM towards more hydrophilic with increasing degree of hydrolysis. Note that $E_{bs} = E_{sb}$, so the simplest way to check the miscibility of base and screen will be that all three calculated energies E_{bb}, E_{ss}, and E_{bs} should have similar shape of the energy distributions. 35
Figure 3-3: Calculated interaction parameter,χ, as function of the degree of hydrolysis, τ of Partial Hydrolyzed Polyacrylamide (HPAM) polymers with an oily hydrocarbon alkane, C_{14}. 35
Figure 3-4: Chemical Structure of a Copolymer of $NaAMC_{14}S/Am$ 37
Figure 3-5: Laboratory of Power Environmental Energy Research (PEER) Institute in Covina, CA 39
Figure 3-6: Diagram exhibits the importance of micro-emulsion phase formation between aqueous and oil phase. This illustrates a procedure where the surfactant system is equilibrated with crude oil at different salinities. Based on the appearance of the phases, the optimum conditions for lowest IFT (Interfacial Tension) can be estimated. 40
Figure 3-7: Photographs of (a) Brookfield DV-II +Pro, and (b) DV-I prime digital viscometers from the PEER Institute laboratory. 41
Figure 3-8: Photograph of TX-500C full range spinning drop tensiometer 42
Figure 3-9: Photograph of the filtration apparatus 43
Figure 3-10: Lab oven used in this project 44
Figure 3-11: Sand pack flooding system 45

Figure 3-12: Sand pack by pusher under same injection rate, tubes collecting solution/oil from sand pack 45
Figure 3-13: Core flooding system 46
Figure 4-1: Emulsion test. FPS 228-73 in different solution with model oil. Salinities from left to right are as marks on the tubes. Results show a promising salinity range for 228-73 between 0 to 10%. 47
Figure 4-2: Emulsion test. FPS 212-205 in different solution with model oil. Salinities from left to right are as marks on the tubes. 48
Figure 4-3: Emulsion test. FPS 228-80 in different solution with model oil. Salinities from left to right are as marks on the tubes. Results show a curve with a peak on salinity 4.5%, which provides a guild of range to do further tests. 48
Figure 4-4: Emulsion test. FPS 212-158 in different solution with model oil. Salinities from left to right are as marks on the tubes. Results show a curve with a peak on salinity 3%, which provides a guild of range to do further tests. 49
Figure 4-5: Emulsion test. FPS 2019 in different solution with model oil. Salinities from left to right are as marks on the tubes. Emulsifications in almost all tested salinities are very successful. 50
Figure 4-6: IFT of FPS-228-73 in different brine concentrations with dodecane decreases along the time 51
Figure 4-7: Searching for the minimum IFT of FPS-228-73 in different brine concentrations with dodecane 51
Figure 4-8: IFT of FPS-212-205 in 3% KCl brine with dodecane decreases along the time 52
Figure 4-9: IFT of FPS-228-80 in different brine concentrations with dodecane decreases along the time 53
Figure 4-10: A summary for IFT of FPS-228-80 in different brine concentrations with dodecane 53
Figure 4-11: IFT of FPS-212-158 in different brine concentrations with dodecane decreases along the time 54
Figure 4-12: A summary for IFT of FPS-212-158 in different brine concentrations with dodecane 54
Figure 4-13: IFT of FPS-2019 in different brine concentrations with dodecane decreases along the time 55
Figure 4-14: A summary for IFT of FPS-2019 in different brine concentrations with dodecane 55
Figure 4-15: FPS-228-73, FPS-212-158, FPS-228-80 and FPS-212-205 dissolved in 2% KCl. 56
Figure 4-16: FPS-2019 dissolved in 2% to 4% KCl. Insoluble gels are floating on the surface. 56
Figure 4-17: Close look at FPS-2019 57
Figure 4-18: Viscosity of FPS-228-73 at 50℃ and 30 rpm in different concentration 58
Figure 4-19: Viscosity of FPS-228-80 at 50℃ and 30 rpm in different concentration 58
Figure 4-20: Viscosity of FPS-212-158 at 50℃ and 30 rpm in different concentration 59

Figure 4-21: Viscosity of FPS-212-205at 50℃ and 30 rpm in different concentration 59
Figure 4-22: Viscosity of FPS-228-73 at different temperatures and 30 rpm in 3.5% KCl..... 60
Figure 4-23: Viscosity of FPS-228-80 at different temperatures and 30 rpm in 4.5% KCl..... 61
Figure 4-24: Viscosity of FPS-212-158 at different temperatures and 30 rpm in 2.5% KCl..... 61
Figure 4-25: Viscosity of FPS-228-73 at 50℃ and different rpm in 3.5% KCl 62
Figure 4-26: Viscosity of FPS-228-80 at 50℃ and different rpm in 4.5% KCl 62
Figure 4-27: Viscosity of FPS-212-158 at 50℃ and different rpm in 2.5% KCl 63
Figure: 4-28 Viscosity of FPS through thermal test..... 64
Figure 4-29: Emulsion studies of FPS-140 in synthesized brine with 13 Illinois Basin field crude oils.... 64
Figure 4-30: Emulsion test. FPS-158 in synthesized brine with 13 Illinois Basin field crude oils..... 65
Figure 4-31: Emulsion test. FPS-159 in synthesized brine with 13 Illinois Basin field crude oils..... 65
Figure 4-32: Emulsion test. FPS-160 in synthesized brine with 13 Illinois Basin field crude oils..... 65
Figure 4-33: Emulsion test. FPS-161 in synthesized brine with 13 Illinois Basin field crude oils..... 66
Figure 4-34: Emulsion test. FPS-162 in synthesized brine with 13 Illinois Basin field crude oils..... 66
Figure 4-35: Emulsion test. FPS-163 in synthesized brine with 12 Illinois Basin field crude oils..... 66
Figure 4-36: Emulsion test. FPS-164 in synthesized brine with 11 Illinois Basin field crude oils..... 67
Figure 4-37: Emulsion test. FPS-185 in synthesized brine with 13 Illinois Basin field crude oils..... 67
Figure 4-38: FPS-212-90 emulsion type – oil external emulsion 70
Figure 4-39: FPS-212-99 emulsion type – oil external emulsion 70
Figure 4-40: FPS-212-116 emulsion type – water external emulsion..... 70
Figure 4-41: FPS-212-117 emulsion type – water external emulsion..... 71
Figure 4-42: Adsorption Test. Viscosity (cP) change of two FPS solution over time. 72
Figure 4-43: Adsorption Test. Viscosity (cP) change of FPS solution in different salinity over time. 73
Figure 4-44: FPS-153 in different salinity with #10 field crude oil..... 74
Figure 4-45: FPS-153 in corresponding produced water with different field crude oils. 74
Figure 4-46: FPS-134/140 in corresponding produced water with #11 field crude oil..... 75
Figure 4-47: HPAM 1830 filtration test..... 76
Figure 4-48: FPS-228-90 filtration test (1). 76
Figure 4-49: FPS-228-90 filtration test (2). 77
Figure 4-50: FPS-229-006 filtration test..... 77
Figure 4-51: FPS-229-007 filtration test..... 78
Figure 4-52: Visualized core flooding summary (1) of FPS-212-181 87
Figure 4-53: Visualized core flooding summary (2) of FPS-212-181. 87

Figure 4-54: Comparison of FPS and HPAM flooding 91
Figure 4-55 FPS core flooding tests under various controlled conditions 96
Figure 5-1 Illinois Basin, Area of Interest 98
Figure 5-2 Illinois Basin Sampling Sites 100
Figure 5-3 Crude Oil Prices during last 8 years 103

EXECUTIVE SUMMARY

Project Title: Game Changing Technology of Polymeric-Surfactants for Tertiary Oil Recovery in the Illinois Basin

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A special class of polymeric surfactant designated Functional Polymeric Surfactant (FPS) modified from conventional polyacrylamide is proving a cost effective method for enhanced oil recovery. The significant characteristics post application of these FPS chemicals were: (1) increased water viscosity at reasonable polymer concentration, (2) reduced oil and water interfacial tension (10^{-1} dyne/cm), (3) emulsified oil to form a water external oil in water emulsion, and (4) provided reasonable thermal stability under typical reservoir conditions. FPS-flooding can replace the use of multiple components systems of the EOR process, such as surfactant and polymer (SP) flooding or the more complicated alkaline, surfactant, and polymer (ASP) oil recovery methods, both expensive and difficult applications for small oil producers. Applications of FPS chemicals in tertiary EOR, especially in the domestic mature oil fields from the Illinois Basin have been further developed and evaluated through this DOE-RPSEA Small Producer program.

A functionalized polymeric surfactant is a high-molecular weight polymer, for example, polyacrylamide PAM and/or partial hydrolyzed polyacrylamide HPAM, incorporating various hydrophobic moieties that can be selected from anionic, cationic, nonionic, zwitterionic, betaine, and/or amphoteric ion pair. The key molecular designing concept for the functionalization of a polymeric surfactant is to create a surfactant characteristic for the polyacrylamide-based polymer backbone such that it can simultaneously lower the interfacial tension (IFT) of the oil and water when placed in the oil-water interface.

This breakthrough technology utilizes a single component rather than multiple components as in traditional SP or ASP-flooding and has an uncomplicated, low operational cost comparable to polymer (P) flooding. FPS-flooding can achieve the dual functions of a polymer, improving both sweep and microscopic displacement efficiency, approximately doubling the oil recovery efficiency of a conventional P-flooding. Use of FPS-flooding is a preferred, suitable EOR approach for domestic mature oil-field oil producers unable to afford expensive conventional SP or ASP processes for EOR.

Accomplishments of the RPSEA project follow:

- Development of three distinct series of FPS, including Class A, a lab-graded series with significant changes in chemical composition of FPS chemicals, Class B, specifically designed for improved oil recovery in the mature, tight sand, shale oil, and heavy oil fields, and Class C, a series that can be scaled-up for production with reduced costs for large-quantity field applications.

- In-depth understanding obtained from theoretical, experimental, and field application ascertaining the reasons that FPS are superior chemical agents.
- Implementation of a well-calibrated laboratory screening and evaluation procedure to identify and optimize FPS-flooding performance comprised of (1) screening and selecting FPS candidates based upon geological conditions of the specific test field, (2) conducting laboratory evaluations (emulsions, IFT, phase behaviors, etc.) to obtain optimized engineering parameters, (3) performing oil recovery core flood tests for tertiary oil recovery, and (4) testing in field applications.

The success of FPS-EOR technology was achieved by identifying and optimizing FPS chemicals with the best performance with respect to the specific reservoir conditions of each EOR application. While the capability to screen, synthesize, and evaluate the FPS compounds best suited for EOR under special geologic conditions has been strengthened through this DOE-RPSEA project, detailed understanding of the typical reservoir geologic conditions by evaluation of each reservoir's unique oil, brine, and mineralogical features is essential for widespread application of FPS-EOR technology.

Power Environmental Energy Research (PEER) Institute's ongoing cooperation with its small production partner and other oilfield chemical producers coupled with Illinois Basin field trials will further optimize the FPS-EOR process.

1. INTRODUCTION

1.1 Enhanced Oil Recovery (EOR) Overview

Primary recovery of hydrocarbon (e.g., oil) from a hydrocarbon-bearing (e.g., oil-bearing) reservoirs rely upon the use of differential pressure present in the reservoir as the main drive for the displacement of formation oil to production wells. However, this process recovers a minor portion of the Original Oil-in-place (OOIP). In the United States, total crude oil resources are 649 billion barrels. Of this, it is estimated that 377 billion barrels are still remaining in already-discovered reservoirs, and they are the target for enhanced oil recovery (EOR). Thus, a variety of supplemental recovery techniques have been employed to increase recovery of oil from subterranean reservoirs.

The viability of an oil recovery displacement process is depended on two important factors: volumetric sweep efficiency and microscopic displacement efficiency. Enhanced oil recovery (EOR) processes usually involve the injection of a fluid of some type into a reservoir. The injected fluids and processes supplement the natural drive present in the reservoir to displace oil to a producing well. In addition, the injected fluids interact with the reservoir rock and oil system to create conditions favorable for oil recovery. The mobility control process and chemical process are two commonly used EOR processes.

The widely applied mobility control process is the polymer flooding (P-flooding). In a typical P-flooding application, the polymer solutions are designed to develop a favorable mobility ratio between the injected polymer solution and the oil/water bank being displacement ahead of the polymer. The purpose is to develop a uniform volumetric sweep of the reservoir, both vertically and horizontally, in order to prevent water from fingering by the oil and moving by the shortest path to the production well. A number of polymer projects have been implemented since the 1960's. However, mobility control alone does not ensure that microscopic displacement efficiency is adequate and may result in a low recovery efficiency. Thus, incremental oil recovery is limited, usually under 10% OOIP of oil recovery. Manning et al. analyzed statistical data of field wide projects and found the median recovery of oil was 2.91% OOIP.[1] Schurz et al. summarized results from 99 projects initiated during 1980-1989 and the projected median incremental oil recovery ranges between 3.7% and 4.8%.[2] Gogarty et al explained that much of incremental recovery by polymer flooding is the result of accelerated oil production before the economic limit is reached.[3]

Chemical processes involve the injection of specific liquid chemicals that efficiently displace oil because of phase behavior properties, which result in decreasing the interfacial tension (IFT) between the displacing liquid and oil. The surfactant + polymer (SP) process has been demonstrated to have the potential for tertiary oil recovery. In this process, the primary surfactant slug, a micelle solution, is followed by a mobility buffer, a solution that contains polymer which is often graded in concentration, becoming more dilute in polymer as more of the solution is injected. The recovery efficiency primarily uses a displacing fluid that has an ultra-low IFT with the displaced oil. Green et al. specifically disclosed

[1] Manning R. K., Pope G. A. and Lake L. W. (1983) A Technical Survey of Polymer Flooding Projects. US Department of Energy DOE/BETC/10327-19, Bartlesville, Oklahoma.
[2] Schurz G. et al. (1989) Polymer Augmented Waterflooding and Control of Reservoir Heterogeneity. NMT 890029 Petroleum Technology into the Second Century Symposium, Socoko, NM pp. 263-75.
[3] Gogarty W. B. (1967) Rheological Properties of FPSeudoplastic Fluids in Porous Media, SPE 1566-A.

that the IFT of displacing fluid must be reduced to ultra-low, about 10^{-3} dyne/cm, before a large reduction in the waterflooding residue oil saturation is achieved.[4] There are drawbacks; however, the chemical solutions for generating ultra-low IFT, which need to contain surfactant, co-surfactant, and sometimes oil, electrolytes, and alkaline, are usually complicated and expensive, and may suffer from chromatographic separation during the EOR operation. In addition, the produced oil maybe easily to form tight emulsion (difficult to break), and also suffers from scale issues caused by alkaline solution will significantly limit the use of SP and ASP technologies.

Since the pioneering concept of polymeric soap published by Strauss et al. in 1951[5], there has been a vast amount of literature published on the polymerization of or in organized amphiphilic assemblies. To some extent, polymeric surfactants serve all the same functions as low molecular weight surfactants. Because of their high molecular weight and complex structures, however, they have some unique characteristics. For example, formation of monomolecular micelles in the dilute solution, and varies shapes of micelles at different concentrations. Applications utilize emulsion stabilizers in submicronic colloidal systems also have been published. Polymeric surfactants are a very attractive class of compounds since the presence of macromolecular chains at the surface of colloidal particles offer significant advantages. This combination of rheological features (e.g. thickening properties) and unique phase behavior properties has broad potential applications in super absorbency, latex paints, hydraulic fluids, flocculation, protein separation, controlled drug release, and biological and medical devices. However, there is only a limited amount of literature which explores the use of polymeric surfactant for enhance oil recovery.[6,7]

The common theory of chemical processes is that the microscopic displacement efficiency largely determines the residual oil saturation remaining in the reservoir rock at the end of the process, which is one of the key criteria in evaluating the success or failure of a chemical EOR process (Figure 1-1). Capillary and viscous forces govern phase trapping and mobilization of fluids in porous media and thus microscopic displacement efficiency. Green et al. studied the capillary number $N_c = \mu c^* \nu/\sigma$ wherein the N_c is the capillary number, μ is the interstitial velocity, ν is the displacing phase viscosity, and σ is the IFT between the displacing and displaced phases.[8] It has been widely accepted in the art that the residue oil saturation cannot be largely reduced unless σ becomes ultra-low at 10^{-3} dyne/cm level. Therefore, attempts of design polymeric surfactant have so far be concentrated on selecting the polymeric surfactant or preparing the polymer surfactant containing solution with co-surfactant or other additives to generate low or ultra-low IFT value between the oil and water phase.

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[4] Green D. W. and Willhite G. P. (1998) Enhanced Oil Recovery. SPE Textbook Series Vol. 6, pp. 35.

[5] Strauss U. P. and Jackson E. G. (1951) PolysoaFPS. I. Viscosity and Solubilization Studies on an *n*-dodecyl Bromide Addition Compounds of Poly-2-vinylpyridine. *J. Poly. Sci.* 6(5), 649-659.

[6] Elraies K. A., Tan I. M. Fathaddin M. T. and Abo-Jabal A. (2011) Development of a New Polymeric Surfactant for Chemical Enhanced Oil Recovery. Petroleum Science and Technology 29, 1521-1528.

[7] Elraies K. A. and Tan I. M. (2012) The Application of a New Polymeric Surfactant for Chemical EOR, in Introduction to Enhanced Oil Recovery (EOR) Processes and Bioremediation of Oil-Contaminated Sites. (Ed Romero-Zerón L) ISBN 978-953-51-0629-6. InTech.

[8] Green D. W. and Willhite G. P. (1988) *Enhanced Oil Recovery*. SPE Textbook Series Vol. 6, pp. 22 ISBN 1-55563-077-4.

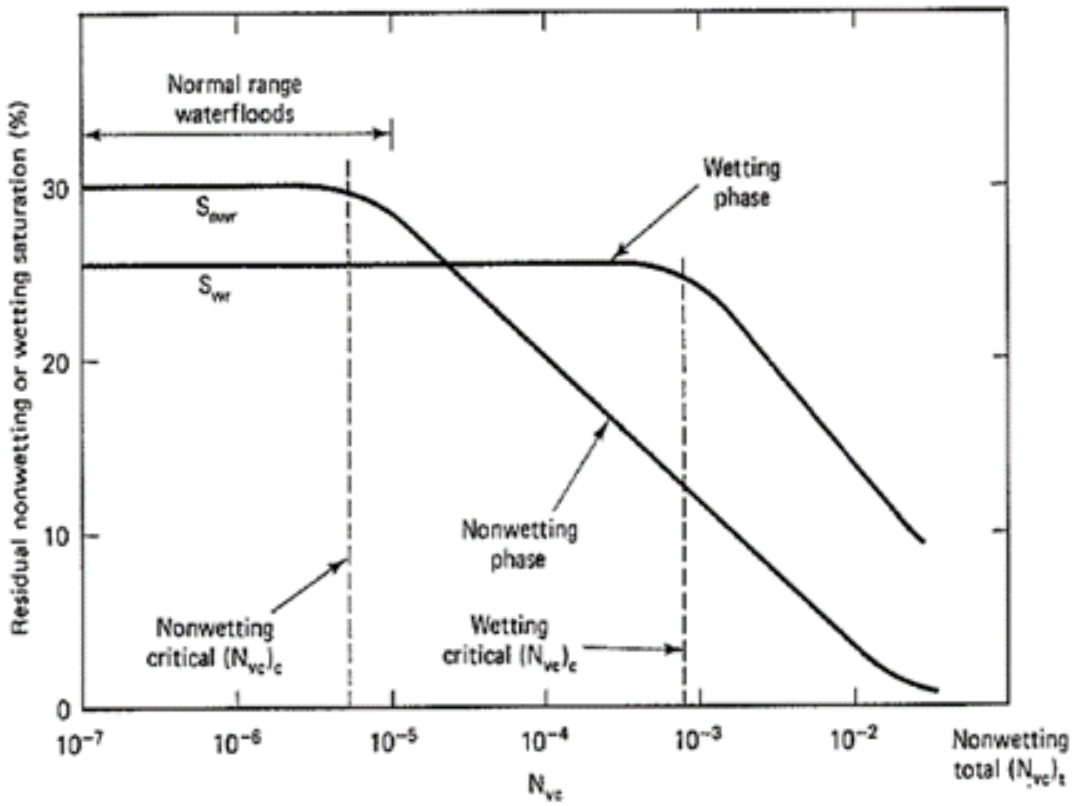

Figure 1-1: Typical Oil Desaturation (Recovery) Curve as Function of the Capillary Number N_c.

For example, in the early 80s, Chen et al. [9] disclosed a method for the injection of polymeric surfactant into a waterflooding operation. Chen et al. specifically emphasized that the interfacial tension between oil and water should be less than 0.1 dyne/cm (e.g., a preferred the oil-water IFT having a value of 0.005 dyne/cm or less) in order to reach an optimum microscopic displacement efficiency.

Cao et al. [10] identified a novel family of polymeric surfactants which might have potential for enhance oil recovery. The novel series of polymeric surfactants is based on carboxy methyl cellulose and alkyl poly (etheroxy) acrylate. The IFT properties of this kind of polymeric surfactant change little with increasing NaCl concentration. Under the influence of added alkali, the IFT of the polymeric surfactants, in aqueous solution, decreases to the level of less than 10^{-2} dyne/cm.

The idea of using polymeric surfactants for EOR application is aimed at the generation of a displacement fluid that has efficient and stable viscosity allowing for improved mobility control and therefore, improved reservoir sweep. Influenced by the conventional wisdom of employing ultra-low IFT displacing fluid in the chemical processes, even though the hydrophically modified water-soluble copolymers have

[9] Chen C. S. H. and Sheppard E. W. (1981) Oil Recovery by Waterflooding Employing Anionic Polymeric Surfactants. US-Patent 4,284,517; 4,317,893

[10] Cao Y. and Li H. (2002) Interfacial Activity of a Novel Family of Polymeric Surfactants. *European Polymer Journal* 38(7), 1457-1463.

recently attracted a great deal of interest, McCormick et al conducted fundamental, laboratory research to developing "smart" multi- functional polymers that can respond in situ to stimuli and result in significantly improved sweep efficiency in EOR processes.[11] McCormick et al. investigated the improvement of microscopic displacement efficiency and phase behavior of polymeric surfactants compared to polymers, but did not disclose the use of polymeric surfactants with oil-water with IFT values more than of 0.1 dyne/cm in EOR.

1.2 Our Approach of Selecting FPS Polymer

Instead of chasing ultra-low IFT of a surfactant solution, our FPS flooding technology aims at a balance of the volumetric sweeping efficiency and the microscopic displacement efficiency with a single compound. Specifically, our FPSs have been made through functionalized polyacrylamide and its derivatives, therefore just like normal polymer flooding to increase the fluid viscosity therefore the sweeping efficiency.[12] Our strategy is to evaluate FPS both on its ability to reduce IFT and ability to emulsify oil. The goal was to screen and identify the FPS chemicals with strong oil emulsification ability. In general, IFT is related to emulsification ability (the lower IFT, the higher the ability to emulsify oil) but not always. For example, unlike the conventional surfactants which can normally give very low IFT values, our FPS typically do not have ultra-lower IFT but can still exhibit much stronger emulsification potentials. Typically the water external emulsions at the oil and water interface have slightly higher viscosity than the bulk viscosity of FPS containing water. The higher viscosity of the water external emulsion caused by FPS at the oil and water interface can help exert an additional force on oil under reservoir condition (increasing capillary number). Of course, if a FPS forms an oil external emulsion with too high of viscosity, it would not be a good candidate for EOR (maybe a candidate for conformance control). . Thus a good FPS candidate can provide reasonable water viscosity, lower IFT, and strong emulsion ability. This can lead to decrease of the oil saturation even at the medium range oil-water IFT value, such as in 0.1 to 15 dyne/cm range.[13]

Another hypothesis proposed for our FPS-EOR technology is that the local oil displacement mechanism is stronger than in conventional surfactant flooding operations. Specifically, the molecular interaction of FPS chemical at the oil and water interface is quite different in comparison to conventional surfactants. (Figure 1-2). The highly concentrated hydrophobic and hydrophilic groups of FPS chemical could help to emulsify oil more much efficiently. Correspondingly, micro-viscosity is increased and sweep efficiency is improved. On the other hand, the micro-viscosity on the interface is moderately higher than the tested bulk viscosity of the aqueous phase owing to the surfactant groups that drive polymers to aggregate both into micelles and onto the interface.

[11] McCormick C. L. et al. (2004) (2005) Smart Multifunctional Polymers DOE Final Report DE-FC26-03NT15407.
[12] Sorbie, K.S. (1991). Polymer-improved Oil Recovery, CRC Press, Inc., Boca Raton, Florida.
[13] Wang, D., Cheng, J., Xia, H., Li, Q., & Shi, J. (2001, January 1). Viscous-Elastic Fluids Can Mobilize Oil Remaining after Water-Flooding by Force Parallel to the Oil-Water Interface. Society of Petroleum Engineers. doi:10.2118/72123-MS

Figure 1-2: FPS on the oil-water interface

To develop FPS chemicals, it is important to select a cost effective hydrophobic monomer to copolymerize with the acrlyamide monomer. The structure of the hydrophobic monomer, the weight percentage of hydrophobic monomer, the method of synthesis (random or block polymers) and the molecular weight of the overall polymer are critical factors to determine the FPS performance.

1.3 EOR in Illinois Basin

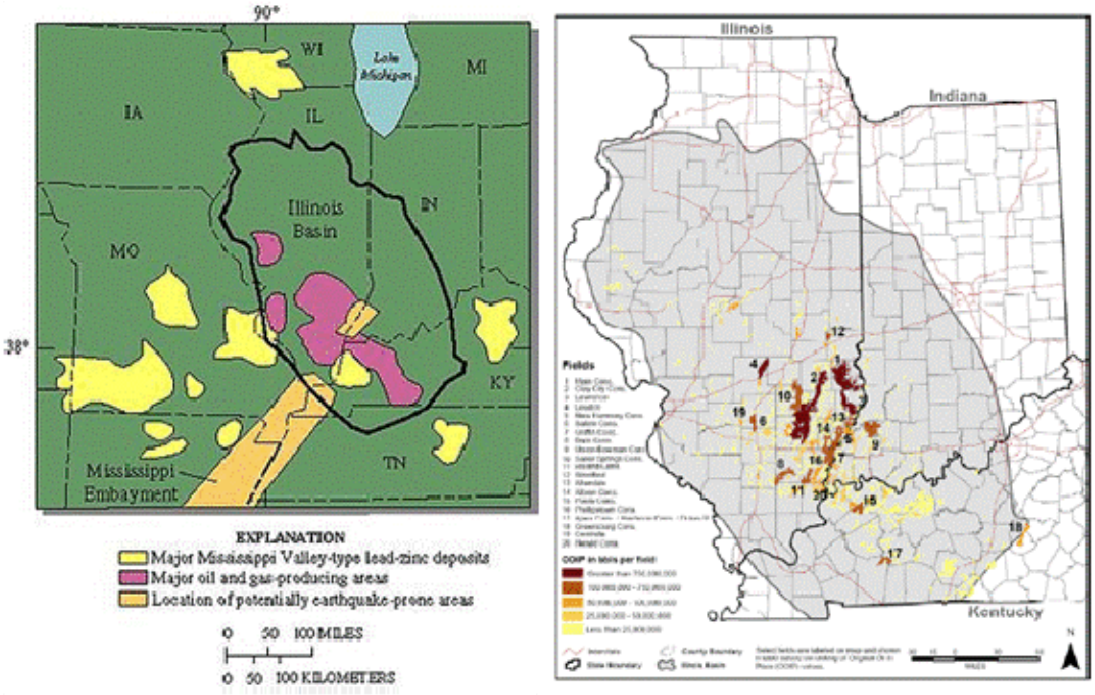

Figure 1-3: Map of the Illinois Basin (left) and EOR potentials (right, darker spots indicating greater OOIP) areas.

The Illinois Basin is a Paleozoic depositional and structural basin in the Midwest, US, underlying most of the state of Illinois, and extending into southwestern Indiana and western Kentucky (Figure 1-3). There are more than 1000 oilfields with ~ 14.1 billion barrels of Original Oil in Place (OOIP) in the Illinois Basin, and only 20~40% of OOIP has been recovered by the primary recovery (peaked in 1908, Figure 1-4) and the secondary water-flooding (in 1960, Figure 1-4). The Illinois Basin has a substantial amount of unrecovered oil. In addition, because it is dominated by very mature water-flooded reservoirs with small pattern spacing containing light crude oil, it has especially high potential for chemical EOR [14,15].

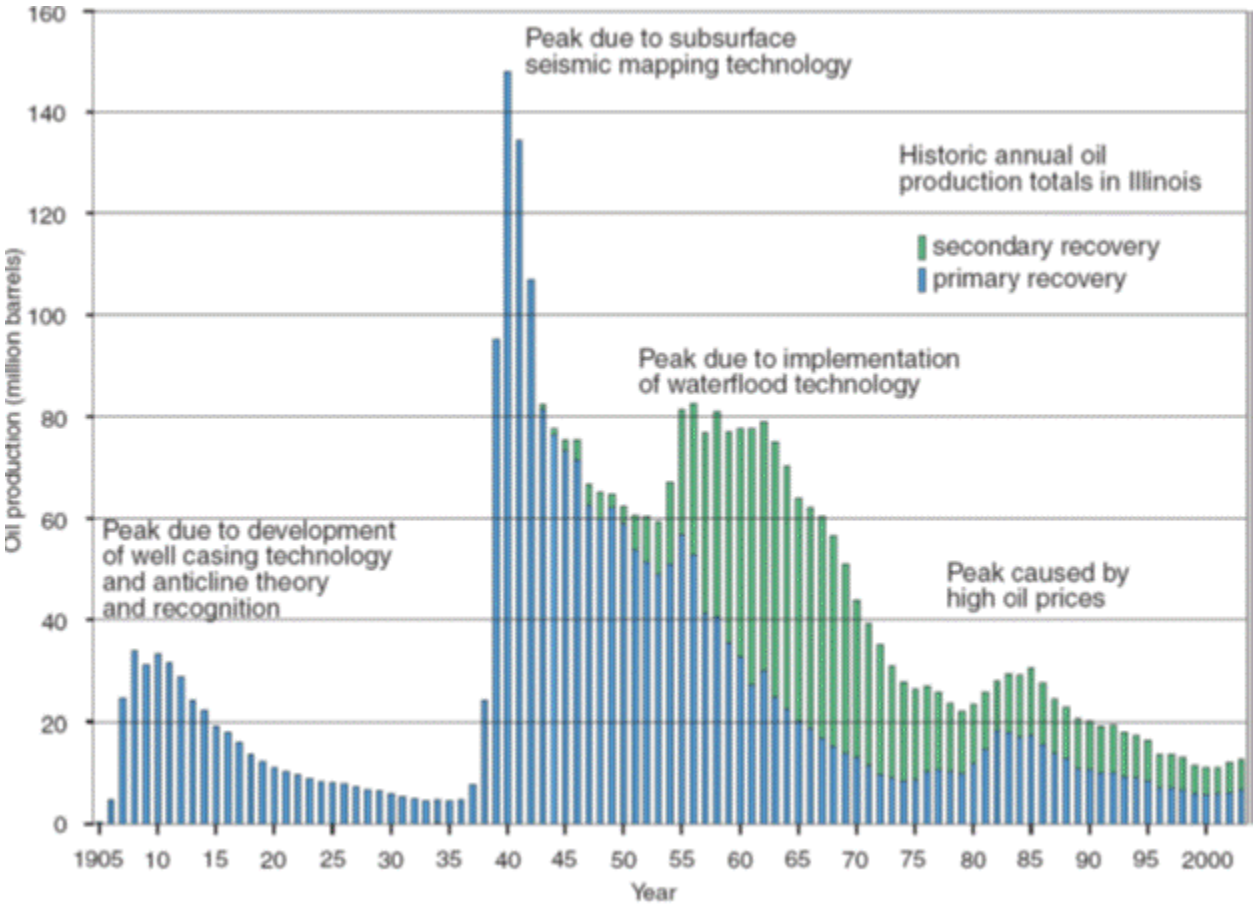

Figure 1-4: Annual Oil Production 1906-present[16]

[14] David H. Swann, "A Summary Geologic History of the Illinois Basin," in Geology and Petroleum Production of the Illinois Basin, Illinois Geologic Society, 1968, p.3-21.
[15] Jennie Ridgley, 'A Rebirth of the Illinois Basin', US Geological Survey, retrieved 29 October 2009.
[16] Scott M. Frailey, 'CO_2 Enhanced Oil Recovery in the Illinois Basin', Illinois State Geological Survey, April 2012

Oil production for the Illinois Basin reached a peak in the 1940's (Figure 1-4), when oil production was over 480 thousand barrels per day (140 Million barrels in 1940). Oil production declined under primary production until the introduction of waterflooding which yielded another peak of oil production in the 1960's. Production has subsequently declined to a recent 51 thousand barrels per day in 2004. Overall, the cumulative production through 2004 is approximately 9.1 million barrels of oil. However, the Illinois Basin still holds a rich resource of oil in the ground, with an estimated 11.5 billion barrels of oil that will be "stranded" due to lack of technology, high cost, and economic and technical risks. On the other hand, our developing FPS-EOR technology offers the path to deploying a low-cost and therefore lower-risk EOR method that is a good fit for the small produces there.

1.3.1 Field-scale Tertiary Oil Recovery Applications in the Illinois Basin

EOR activities are strongly related to the crude oil price (Figure 1-5). In the 1960's to 80's, a number of EOR field-trial projects using S+P floods were implemented in several fields in the Illinois Basin by Marathon, Texaco and Exxon in an attempt to recover a portion of the large percentage of OOIP that was being bypassed by the secondary recovery waterflooding. These projects reportedly were able to recover incremental oil reserves of 15% to 30% of OOIP.[17]

Figure 1-5: Oil prices adjusted for inflation using the headline CPI[18]

[17] Rex Energy Corporation 2013 Annual Report.
[18] Data from www.macrotrends.com.

Maraflooding was implemented in three pilots in the Lawrence Field in the 1970's and 1980's by Marathon Oil Corp.[19] The Maraflooding process is a micelle solution which contains surfactant, hydrocarbon and water, injected into an oil reservoir to improve displacement efficiency. Co-surfactants also may be added to provide some viscosity control to maintain mobility control with the displaced oil. The first project was the Kimmel-118-K Maraflooding surfactant flood implemented during the 1970's, which recovered an additional 30% of residual oil saturation (S_{OR}) after primary and secondary water-flooding productions. The second project, Robins 102-B Maraflooding surfactant flood, initiated in the 1980's. The production curve from that project shows an increase in oil cut from 1% to 20%. This was a 25 acre Bridgeport sandstone pilot project. The third project, 2.5 acre Bridgeport sandstone reservoir pilot project, was Robins 202-B Maraflooding surfactant flood. It achieved recovery of an additional 34 percent S_{OR} beyond primary and water-flooding productions (which recovered about 40% of OOIP). That is an additional recovery of ~20% OOIP. However, the success demonstration project did result in the widespread commercialization and was terminated in 1986 due to low oil prices (as shown in Figure 1-5).

Rex Energy Corporation is one of the largest oil producers in the Illinois Basin, with an average net production of 2,121 Barrels of Oil Per Day (BOPD) in 2013.[20] The Lawrence Field alkali-surfactant-polymer (ASP) flooding project was introduced in stages with the first flooding initiated in 2010. During 2011, initial and peak production from the project were received on its ASP Middagh unit in the Pennsylvanian Bridgeport B reservoir. Total pattern production increased from 16 BOPD and stabilized at a range of 65-75 BOPD in the last three months of 2011. Peak production rose to 100 + BOPD. Oil cut in the pilot increased for 1.0% to ~ 12.0% with an individual well showing oil cuts greater than 20%. However, production levels have been on a gradual decline since then. In 2012, ASP injection on the Perkins-Smith units was initiated, for an expectation of initial production response during the second or third quarter of 2014 and with peak production response during the first or second quarter of 2015. Chemicals used in the ASP Flooding Project include alkali, surfactants and polymer. The goal of this project is to duplicate the oil recovery performance of the surfactant polymer floodings conducted in the field in the 1980's, but at a significantly lower cost by using alkali in the formula, largely reducing the concentration of the more costly surfactant. Although ASP showed great promise from both core flood experiments and some field testing results, there are number of issues toward overall economic evaluation. ASP will generate extremely tight emulsions which are difficult to break, waste water treatment is much more difficult and also adding alkaline will generate additional scale problems. It is therefore, economically risky and operationally intensive for small oil producers to use the ASP process.

[19] Beverly Seyler et al. 2008-2012. Réservoirs Characterization of Bridgeport and Cypress Sandstones in Lawrence Field Illinois to Improve Petroleum Recovery by Alkaline-Surfactant-Polymer Flooding. DOE Final Report DE-NT0005664.
[20] Rex Energy Corporation 2013 Annual Report.

1.3.2 Applications of the FPS Flooding in the Illinois Basin

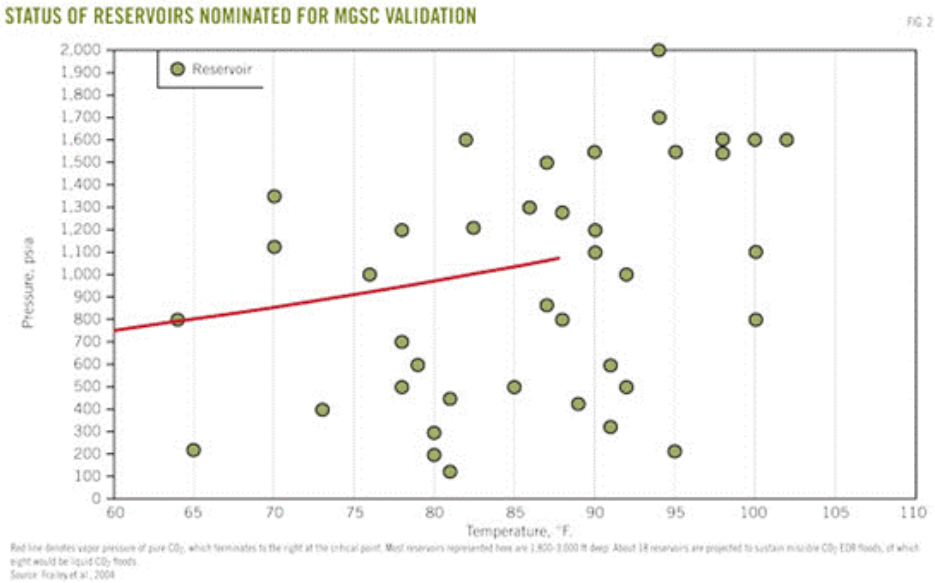

Figure 1-6: Typical Reservoir Conditions (Temperature and Pressure) of Illinois Basin

Oil Field Resources. Currently, no major oil companies and few or no large independent oil companies operate in the Illinois Basin. Most of the oil companies are small and medium-size with predominantly field employees, few geoscientists and engineers, limited capital and too few assets to commit to a large-scale EOR project. The simplified polymer flooding and/or FPS flooding could be easily implemented and therefore be attractive to smaller oil companies.

Reservoir Conditions. The Illinois basin is quite shallow (1000 ~ 4000 feet) and the reservoir temperatures are low (60~100°F/15~37°C) (Figure 1-6). Midwest has more sandstone than carbonate oil reservoirs. These make the conventional polymer/FPS flooding superior to CO_2-EOR.

Technical Challenges. In principal, the FPS flooding combines the dual functions of the polymer and surfactant (SP) that can simultaneously reduce the interfacial tension (IFT) and improve the sweep efficiency. Our laboratory studies have demonstrated that the properly-designed FPS-flooding could have comparable oil recovery potential to that of SP floodings.

Operational Challenges. The field application of the FPS flooding will be very similar to the conventional polymer flooding. A small scale FPS-EOR flooding instead of the large-scale CO_2-EOR can be easily accepted and implemented by small producers in the Illinois basin.

Regulatory challenges. Existing regulations and state laws regarding oil/gas production have been documented for the oil producing states in the Midwest. The permits for brine injections (including polymer flooding) is routine for most oil field operations.

2 PROJECT OUTLINE

2.1 Objectives

The overall objective of this project is to further develop the functionalized polymeric surfactant (FPS) as an advanced Enhanced Oil Recovery (EOR) agent. One of the special features of such a single component FPS-EOR approach is the utilization of the dual-functional single FPS component, instead of multiple components as in traditional Surfactant + Polymer (SP) and/or Alkali + Surfactant + Polymer (ASP) floodings. Consequently, the FPS-EOR technology offers 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 FPS-EOR potential for this important mature oil field region.

The great bulk of the "stranded oil" resource in the large oil reservoirs of the Illinois and Michigan Basin is amenable to chemical EOR. Application of FPS-EOR flooding would enable a significant portion of the "stranded oil" to be recovered. None of this "stranded oil" would become economically recoverable at oil prices of $30 per barrel as adjusted for gravity and location. Introduction of "State-of-the-art" FPS technology, risk mitigation incentives and lower chemical production costs would enable economically EOR in the Illinois Basin.

We expect the potential for the FPS-EOR technology is to be a minimum of 10% oil de-saturation where applied in good candidate mature oil fields. In the USA, it is estimated by the DOE that there are 377 billion barrels of oil that are not recoverable with conventional water injection, Therefore, almost 38 billion barrels of oil could be targeted for using our technology in mature oil fields.

Once developed, FPS technology may be applied first, by emphasizing collaboration with MidAmerican Energy LLC, and then those other operators in the Illinois Basin that are interested in deploying EOR methods. This technology then can be expanded to other petroleum basins with similar reservoir geological conditions as the Illinois Basin. Our preliminary laboratory data indicate that this approach may be a technical success in a large percentage of sandstone reservoirs. Generally, those reservoirs that have favorable attributes for conventional chemical EOR methods also are likely candidates for this FPS-EOR process.

2.2 The Scope of Works

The scope of this project is to further develop functionalized polymeric surfactant (FPS) technology as a promising alternative to current chemical EOR approach. The main advantages of this technology over conventional chemical EOR are 1) lower cost, 2) good oil recovery, 3) simpler implementations, and 4) because it is a single chemical component, it is not prone to chromatographic separation; thus a more robust process.

The project is targeted for small producers who manage oil production from mature oil fields. In order to have a reasonable project scope the study will emphasize developing this new technology opportunity for the Illinois Basin. The work conducted includes: (1) the assembly of several suites of functionalized polymeric surfactants, from both commercially available chemicals and laboratorial synthesis through working with several chemicals suppliers; (2) laboratorial measurements of key parameters necessary for evaluation of the suitability of each FPS candidate for EOR applications; (3) generic reservoir simulations with oil/water samples from Illinois Basin, under conditions representative of local small oil producers situations to predict the results of the field performance of the best FPS agents.

In addition to furthering the unique technical advantages of FPS as EOR agents, another key objective of this study is to examine the potential economic impact of deploying this technology. The laboratory results will indicate the reasonable expectation of oil recovery achieved for the target type of reservoirs. The field information and samples to be gathered will be important to enable the most realistic possible laboratory experiments. This data is also a key to create a reasonable reservoir engineering forecast for expected oil recovery in typical mature fields in the Illinois Basin. By integrating all of these laboratory and reservoir forecasts and different scenarios of project costs and oil prices, there will be created an economic sensitivity analysis of this FPS-EOR process.

The entire project will deliver a package of information that any small producer may use as a guide for considering the possible technical suitability and economic benefit of the FPS-EOR technology. For small producers in the actual project study area (Illinois Basin) the results may be directly applicable for judging if their operation is both a favorable technical and economic good candidate.

2.2 Completed Tasks

2.2.1 Task 1 – Selections of Proper Functionalized Polymeric Surfactants

First task of this project is to identify or synthesize FPS candidates for an EOR application. First considerations in the selection of the initial FPS chemistries include its compatibility in the target saline field brine composition and the reservoir temperature. Later selections of FPS will be guided by successful laboratory evaluation performance for efficient oil recovery. In addition, these results will provide guidelines regarding features of the chemical structures that are more likely to produce the solution properties that lead to good oil recovery for typical Illinois Basin conditions.

We have closely worked with several major chemical suppliers to synthesis and secure a full database of FPS chemicals. This includes three different classes of FPS:

Class A – Lab-grade FPS. Combining molecular design and laboratory testing approaches, we have assembled a series of FPS compounds with a large variation of chemical compositional changes, and with controllable molecular properties for easy screening, matching and optimizing;

Class B – Specified FPS Products. Designed FPS compounds for oilfield applications for geological customization to enhance performance, such as for high-temperature and high-salinity reservoirs, low-molecular weight FPS for tight-sand and shale oil recovery, and/or with special aromatic components for heavy-oil recovery applications.

Class C – Large-scale Producible FPS. We have also teamed up with the chemical production companies to customized co-polymerization and production processes for scale-up productions of special FPS chemicals, with reduced cost for field applications and improved field condition adeptness.

2.2.2 Task 2 – Laboratory Screening of Proper Functionalized Polymeric Surfactants

Laboratorial procedures for measurements of key parameters necessary for evaluation of suitability of selected FPS for EOR applications have been established. The parameters that have been measured include:

- Solubility in the target field brines,
- Solution viscosity versus salinity, temperature, and shear rate,
- Ability to emulsify target oil sample and brine,
- Phase behavior of brine solution containing FPS and the target crude oil,
- Interfacial Tension (IFT),
- Thermal stability – temperature and shear effects,
- Filtration tests – particle size and molecular weight effects,
- Chemical retention – rock surface effects,
- Sand pack and core flooding – oil displacement ability from cores.

Measurements and evaluations should be performed with the crude oil and water samples that are best representative of the typical reservoir conditions, as well as in the model oil/water compounds for initial fast-screening.

2.2.3 Task 3 – Technical Assessment of FPS-EOR Application in Illinois Basin

A total of 16 crude oil and brine samples from 4 different locations of the Illinois Basin have been collected and detailed laboratory tests were conducted for evaluation of the application of developing FPS-EOR technology for the mature oil field in Illinois Basin (Table 2-1). The most promising FPS candidates from the initial screening tests were further tested to optimize the oil recovery capacity.

Table 2-1: Local and Geological Information of the Crude Oil/Brine Samples from Illinois Basin

Sample Name	Location	Formation	Depth (m)
GIN#001	Gibson City, IN	Hardinsburg Sand	1340
GIN#002	Gibson City, IN	Pennsylvania Sand	1479-1507
GIN#003	Gibson City, IN	Waltersburg Sand	1918-1969
Gin#004	Gibson City, IN	Hardinsburg Sand	1950-1960
POS#001	Posey City, IN	Pennsylvania Sand	650
POS#002	Posey City, IN	Mansfield Sand	1200
POS#003	Posey City, IN	Mansfield Sand	1190-1209
POS#004	Posey City, IN	Palestine Sand	1937-1951
POS#005	Posey City, IN	Waltersburg Sand	1830
POS#006	Posey City, IN	Tar Springs Sand	1924-1942
POS#006	Posey City, IN	Renault Lime	2592-2506
VAN#001	Vanderburgh City, IN	Mansfield Sand	913-926
VAN#002	Vanderburgh City, IN	Biehl Sand	1351-1358
HEN#001	Henderson City, KY	Tar Springs Sand	1430-1440
HEN#002	Henderson City, KY	Bencist Sand	1890-1900
HEN#003	Henderson City, KY	Aux Vases Sand	1956-1962

2.2.4 Task 4 – Economic Analysis of FPS-EOR for Illinois Basin

Table 2-2: Comparisons of Engineering and Economics of the FPS-Flooding with Other EOR Methods

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

An estimate of incremental oil production for a number of different chemical designs was made using the laboratory data of the chemical physical properties and its capability of mobilizing oil in the core flooding experiments, plus the field description (reservoir geology, waterflooding performance, well information, etc.). From these reservoir calculations we can appreciate the sensitivity of this new EOR process to variables such as the concentration of the FPS injected, volume of chemical slug, well-spacing, etc. Oil viscosity, reservoir salinity, cost of chemicals, and most importantly the waterflood efficiency are important factors needed to be taken into account in the economic analysis, because they all contribute to the overall project costs and are associated with the expected incremental income of an EOR project. The evaluation of these cases provides a good picture of the sensitivity of overall economic analysis. A preliminary comparison of the engineering and economic factors of the FPS-flooding technology with the traditional EOR methods is given in Table 2-2. A FPS flooding only requires the injection of one single compound, such that the operational cost will be similar to that of the single polymer flooding (P-flooding). The oil recovery potential of the FPS-flooding is nearly doubled compared to the P-flooding. Our preliminary results shows that the FPS flood is almost comparable to the Surfactant + Polymer (SP) flooding process. Furthermore, because the chemical composition and manufacturing procedure of FPS is similar to that of the conventional partially hydrolyzed polyacrylamide (HPAM) polymer, the cost of the two is similar. Thus, the FPS-flooding operation offers an effective and cost-effective EOR approach for mature oil field operation, especially by the domestic small oil producers.

3 METHODOLOGIES

3.1 Molecular Modeling of Functionalized Polymeric Surfactant

3.1.1. Survey of Theoretical Aspects of Molecular Designs

Three different theoretical approaches based on the molecular designs were utilized to provide fundamental understandings of FPS at the molecular level. A brief summary is given in this section:

- *Quantitative Structure-Activity Relationship (QSAR) and Quantitative Property-Activity Relationship (QSPR) Approaches* – A method correlating the molecular structures such as molecular weights, surface areas, logP/logD and pKa values, with the experimentally measured data.
- *Molecular Dynamic Studies* – A method based on the computational Monte Carlo simulation to predict macroscopic properties of bulk and/or interfaced systems. A sufficiently large number of polymer molecules is confined in a 3-dimensional box, and their motions with respect to time are calculated stepwise according to pre-defined interactions.
- *Statistical Associated Fluid Theory (SAFT) based on the Equation of State (EoS)* – a fundamental method to predict, correlate the thermodynamic properties and phase equilibrium by applying the perturbation theory to predict bulk and interfacial properties of fluids. The method is based on the fundamental statistical mechanics theory by taking into account effects of various inter- and intramolecular forces on the free energy functional of density.

3.1.2 Molecular Properties of Monomers

Monomer selection is key factor in the molecular design of FPS. A few molecular property relationship parameters have been used to guide the monomer designs.

The Hydrophilic-Lipophilic Balance (HLB) – the HLB value of a molecule (surfactant) is a measure of the hydrophilic and lipophilic character of a surface active agent, which is determined by calculating values for the different regions of the molecule, as described by Griffin in 1949[21] and 1954[22]. For a non-ionic surfactant, the HLB is defined as:

$$HLB = 20 * M_h / M \quad (1)$$

Where M_h is the molecular mass of the hydrophilic portion of the molecule, and M is the molecular mass of the whole molecule. The HLB number is further scaled in between 0 to 20, where HLB = 0 means a completely hydrophobic molecule, and HLB = 20 corresponds to a molecule made up completely of hydrophilic components.

[21] Griffin W. C. (1949) Classification of Surface-Active Agents by 'HLB'. *J. Soc. Cosmetic Chemists* 1(5) 311-326.
[22] Griffin W. C. (1954) Calculation of HLB Values of Non-Ionic Surfactants. *J. Soc. Cosmetic Chemists* 5(4) 249-256.

In 1957, Davies[23] suggested a method based on calculating a value related to the chemical groups of the molecule. The advantage of this method is that it takes into account the effect of strongly and less strongly hydrophilic groups. The method works as follows:

$$HLB = 7 + m * H_h + n * H_l \quad (2)$$

where m and n are numbers of hydrophilic and hydrophobic groups in the molecule respectively, H_h and H_l are values of the hydrophilic and hydrophobic groups.

The partition coefficient (logP) – a partition coefficient is defined as the ratio of a substance distributed between two immiscible phases (i.e., water and oil phases). Specifically, a logP value is referred to that of an un-ionized compound, so the pH of the aqueous phase is adjusted such that the compound is un-ionized:

$$\log P_{oct/wat} = \log \{[Solute]_{octanol} / [solute]^{un\text{-}ionized}_{water}\} \quad (3)$$

The distribution coefficient (logD) – is the ratio of the sum of the concentrations of all forms of the compound (ionized plus unionized) in each of the two phases. For measurements of the distribution coefficient, the pH of the aqueous phase is buffered to a specific value such that the pH is not significantly perturbed by the introduction of the compound. The logarithm of the ratio of the sum of concentrations of the solute's various forms in one solvent, to the sum of the concentrations of its forms in the other solvent is called Log D:

$$\log D_{oct/wat} = \log \{[Solute]_{octanol} / [solute]^{ionized}_{water} + [solute]^{un\text{-}ionized}_{water}\} \quad (4)$$

There are several approaches to theoretically determine the logP/logD values of a molecule or a fragment of the molecule. A brief summary is as follows:

Atomic based prediction (atom contribution) – This is the simplest method to determine the logP of a monomer. It is based on the parameterizing the contributions of various atoms to the overall molecular partition coefficient using constrained least square fitting to a training set of compounds with experimentally measured partition coefficients. In general, the most common organic elements such as hydrogen, carbon, oxygen, sulfur, nitrogen and halogens are classified into several different atom-types based on the neighbor atoms they are connected to, and the overall logP of a molecule is the summary of the contribution of all atoms with different weights. This method is generally the least accurate, but it has the advantage of quickly providing a rough estimate of a wide variety of molecules.

Fragment based prediction (group contribution) – This widely used prediction method, is an improved approach from atomic based prediction. The logP values of a fragment, instead of an atom, is determined in a statistical method analogous to the atomic methods (least squares fitting to a training set). In addition, Hammett-type corrections[24] are also included to account for the electronic and steric effects. However, the fragment-based prediction method cannot be used if a molecule contains unusual functional groups without being properly parameterized.

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[23] Davies J. T. (1957) A Quantitative Kinetic Theory of Emulsion Type. I. Physical Chemistry of the Emulsifying Agent. Gas/Liquid and Liquid/Liquid Interface (Proceedings of the International Congress of Surface Activity) pp. 426-438.

[24] Hammett L. P. (1937) The effect of Structure upon the Reactions of Organic Compounds. Benzene Derivatives. *J. Am. Chem. Soc.* 59, 96-103.

Data mining prediction (statistic contribution) – A statistic method to predict the logP value of a molecule when used with compounds that have similar chemical structures and known logP values. The correlative methods such as support vector machines, decision trees, neural networks, etc. can be used. Such a method has been very successful when a large number of referencing monomer/molecular data is available.

First principle calculation (*ab initio)* - Molecular modeling techniques have been applied to determine the solvation energies of molecular compounds in water and in another organic phase (e.g., 1-octanol) solutions. In the first principle calculation, the logP of a compound is evaluated from:

$$\log P = [\Delta G_{solv}(\text{water}) - \Delta G_{solv}(\text{octanol})]/2.303RT \quad (5)$$

where ΔG_{solv}(water) and ΔG_{solv}(octanol) are the solvation energies of the compound in water and in octanol, respectively, T is the temperature and R is the thermal constant. The advantages of this approach include its feasibility to compute the logP values of almost all molecules. However, it is also noted that the solvation models as embedded in the modern molecular modeling techniques are mainly based on the classical perturbation treatments that rely on using a few parameters such as dielectric constant and the atomic Pauli's radius of a solvent. Consequently, the calculated logP value needs to be calibrated with the known experimental data.

3.1.3 Miscibility Prediction Model

In order to provide in-depth theoretical guidance for our laboratory design and synthesis of special FPS candidates, we have developed a novel molecular modeling technique to determine the partition coefficient of FPS through the miscibility prediction model. Typical, the miscibility of a binary mixture can be determined from the Flory-Huggins model[25]:

$$\frac{\Delta G}{RT} = \frac{\phi_b}{n_b} ln\phi_b + \frac{\phi_s}{n_s} ln\phi_s + \chi\phi_b\phi_s \quad (6)$$

Here ΔG is the Gibbs' free energy of mixing (per mole), ϕ_b and ϕ_s are the volume fractions of component b (base) and s (screen), n_b and n_s are the degree of polymerization of components b and s, χ is the interaction parameter, T is the absolute temperature and R is the universal gas constant.

The interaction parameter χ represents the degree of interaction of two components (base and screen), which can be determined from:

$$\chi = E_{mix}/RT \quad (7)$$

That E_{mix} is the mixing energy of two compounds, which is determined from:

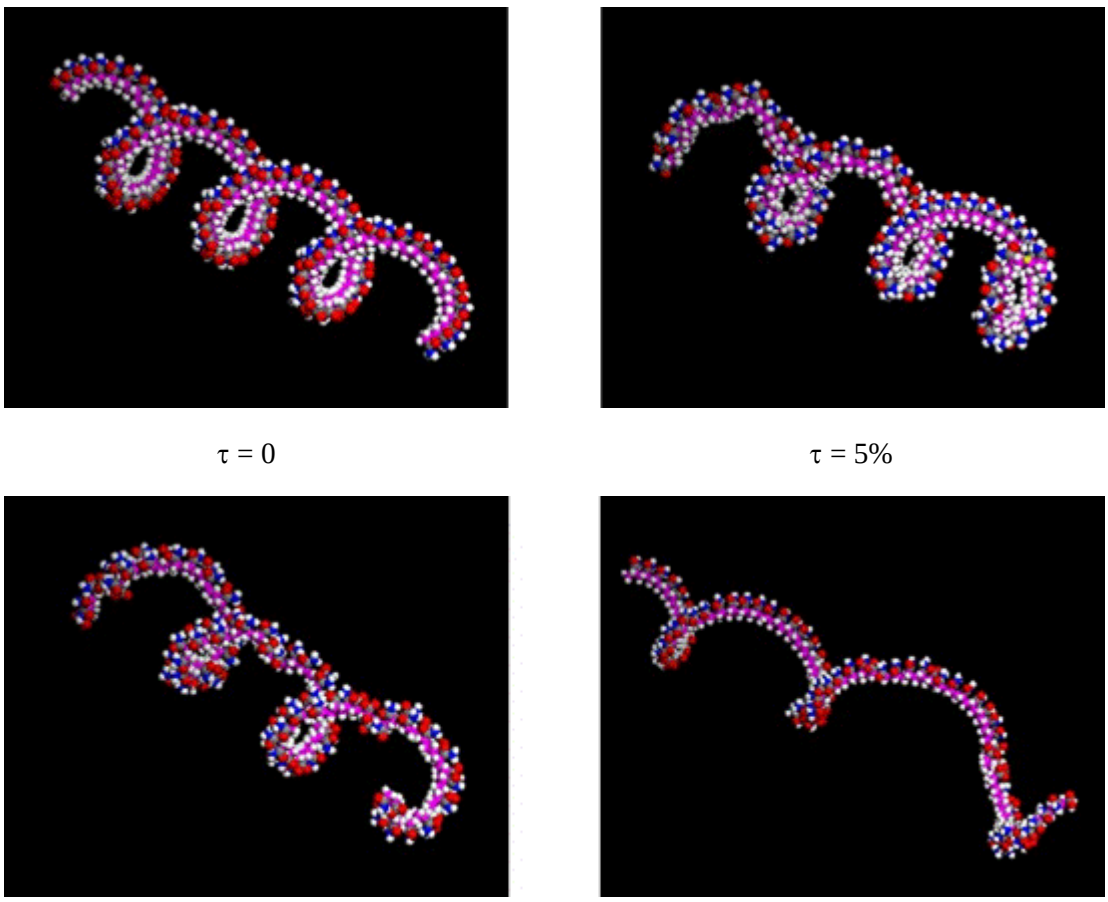
$$E_{mix} = ½ \{Z_{bs}\langle E_{bs}\rangle_\tau + Z_{sb}\langle E_{sb}\rangle_\tau - Z_{bb}\langle E_{bb}\rangle_\tau - Z_{ss}\langle E_{ss}\rangle_\tau\} \quad (8)$$

Here Z_{bs}, Z_{sb}, Z_{bb}, and Z_{ss} are the coordination numbers, and $\langle E_{bs}\rangle_\tau$, $\langle E_{sb}\rangle_\tau$, $\langle E_{bb}\rangle_\tau$, and $\langle E_{ss}\rangle_\tau$ are the average binding energies between base/screen, screen/base, base/base and screen/screen.

[25] Flory P. J. (1941) Thermodynamics of High Polymer Solutions. *J. Chem. Phys.* 9(8), 660.

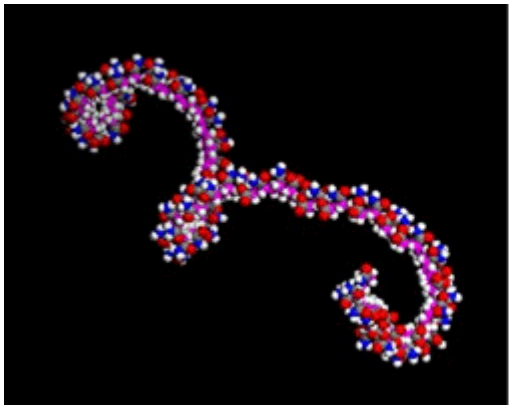
Note that $Z_{bb}<E_{bb}>_\tau + Z_{ss}<E_{ss}>_\tau$ is the total energy of the binary system before mixing and $Z_{bs}<E_{bs}>_\tau + Z_{sb}<E_{sb}>_\tau$ is the energy after mixing, E_{mix} represents the energy gain due to the mixing. If $E_{mix} > 0$, the mixed system is more energetically favorable than the separated system, so the base (solvent) and screen (solvate) are miscible. If $E_{mix} < 0$, the separated system is more energetically favorable than the mixed system, so the base (solvent) and screen (solute) are immiscible. The average binding energies can be computed from the Monte Carlo simulations.

The water soluble polyacrylamide (PAM) polymers are made from the polymerization of the repeated units of acrylamide (AM) monomers. When dissolved in the aqueous solution, the amide $–C=ONH_2$ group will undergo a certain degree of hydrolysis, and form –COOH (or $–COO^-$) groups. The degree of the hydrolysis τ reflects the number of the hydrolyzed amide group. To enhance the water solubility of a Hydrolyzed Polyacrylamide (HPAM), some acrylic acid (AA) monomers can be added in the initial polymerization stage. Therefore, the formed HPAM will have various ratios of [AM] and [AA] in the polymer both being dependent on the degree of hydrolysis (Figure 3-1).

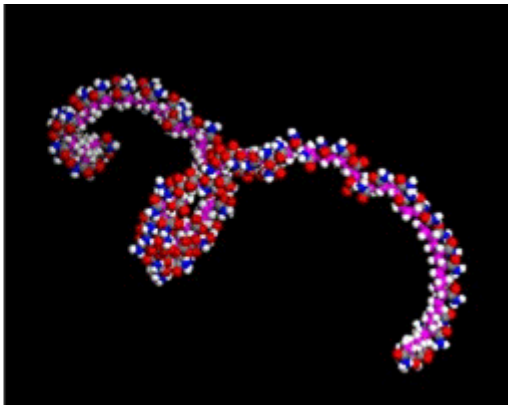


$\tau = 0$ $\tau = 5\%$

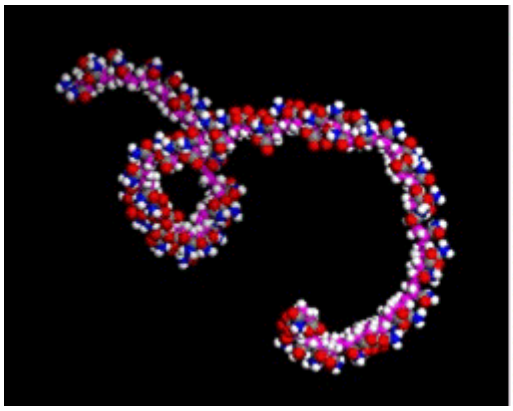
$\tau = 10\%$ $\tau = 15\%$



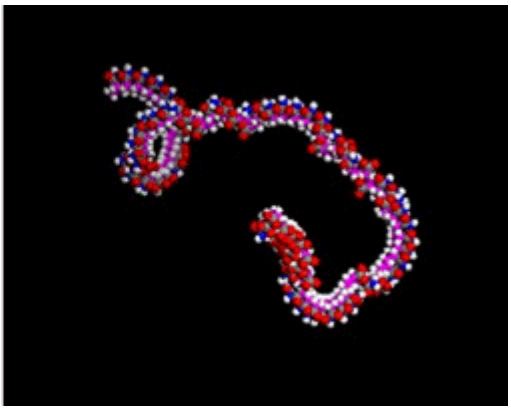
τ = 20%



τ = 25%

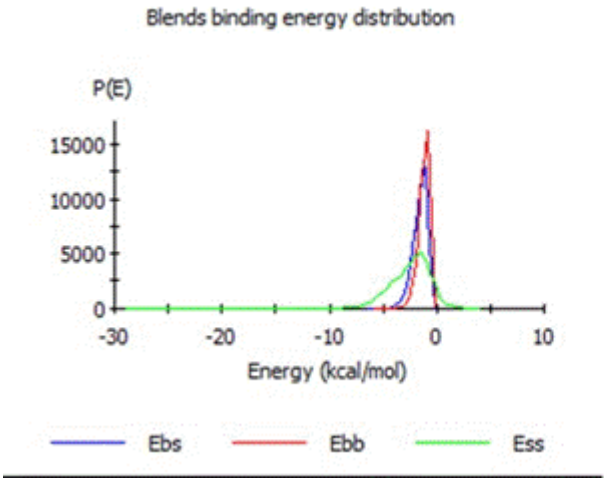


τ = 30%

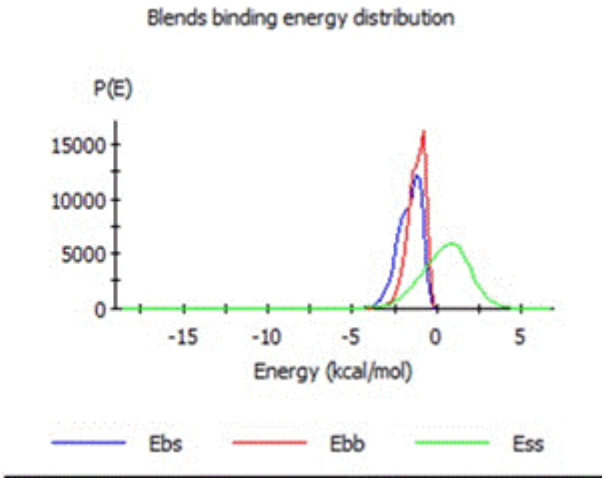


τ = 35%

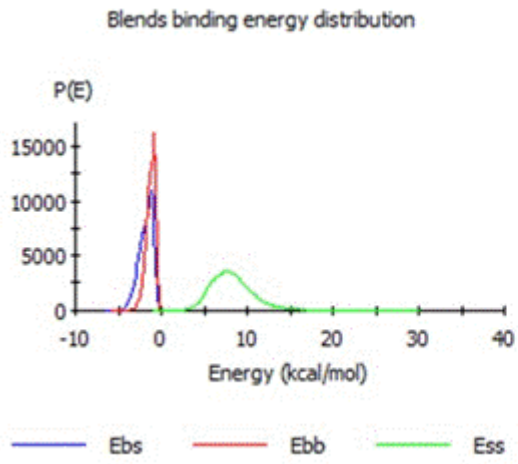
Figure 3-1: Molecular Structure of Partial Hydrolyzed Polyacrylamine Polymer (HPAM). The degree of hydrolysis is defined as τ = [AA]/{[AA] + [AM]}, which [AA] and [AM] are the portions of the acrylic acid and acrylamine groups. 100 repeated units were made, and the molecular geometry was optimized using Drending force field molecular dynamic calculations. Increase of the [AA] ratio distort the special symmetry of polymer.



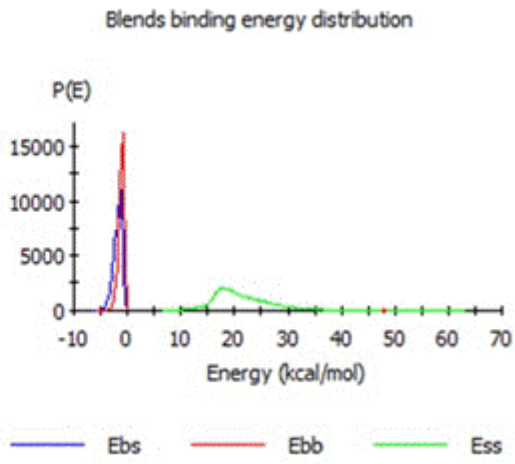
τ = 0



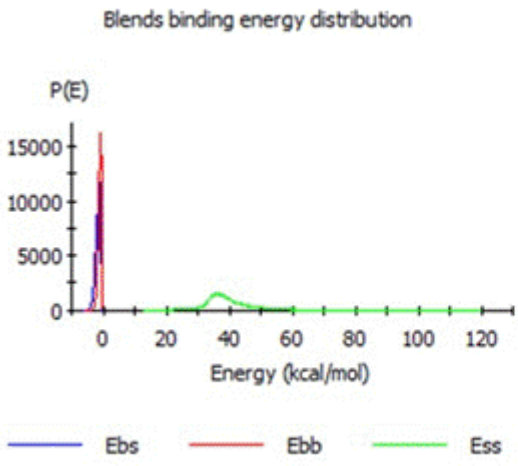
τ = 5%



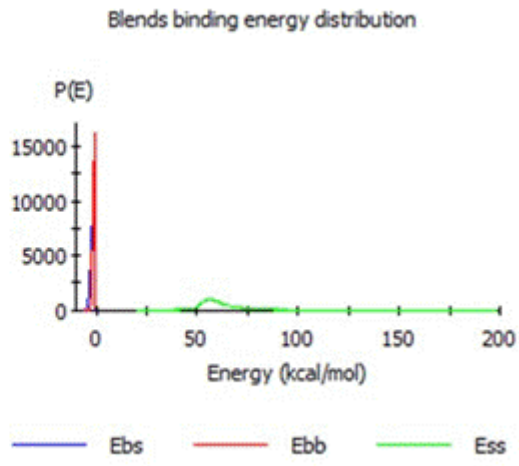
τ = 10%



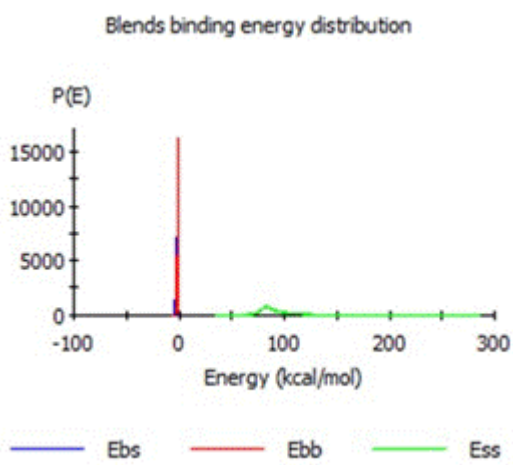
τ = 15%



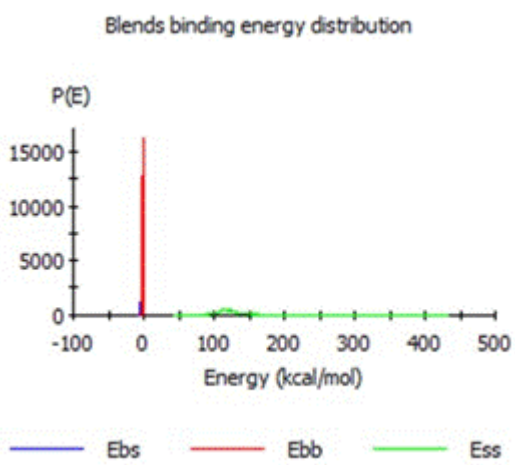
τ = 20%



τ = 25%



τ = 30%



τ = 35%

Figure 3-2: Calculated binding energies of HPAM of various degrees of hydrolysis τ, with an oily hydrocarbon compounds (modelled by C_{14}). The increase of τ values decreases the miscibility of HPAM with the C_{14} compound, suggesting that the HPAM towards more hydrophilic with increasing degree of hydrolysis. Note that $E_{bs} = E_{sb}$, so the simplest way to check the miscibility of base and screen will be that all three calculated energies E_{bb}, E_{ss}, and E_{bs} should have similar shape of the energy distributions.

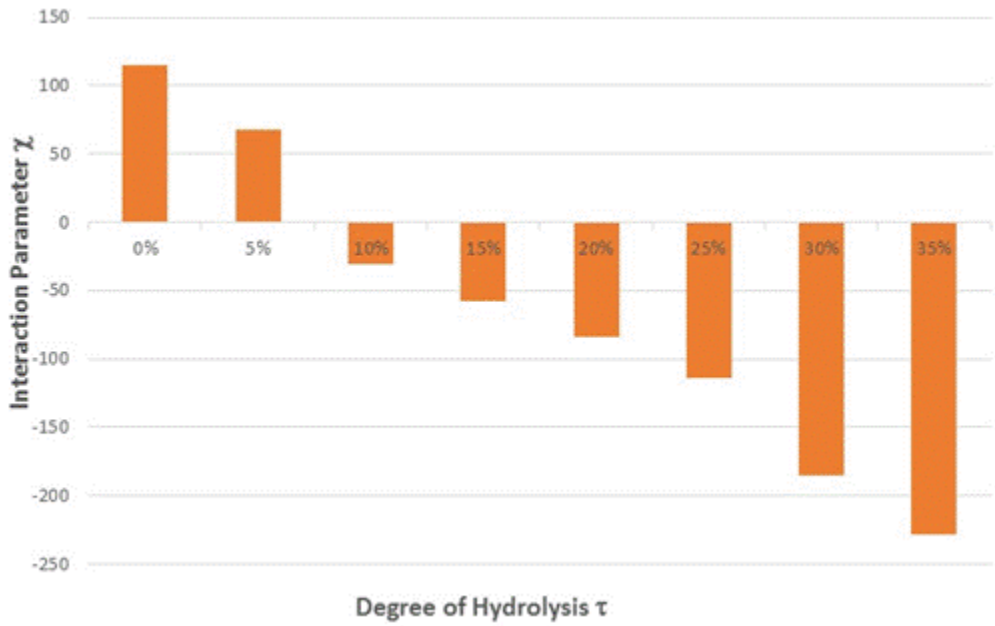


Figure 3-3: Calculated interaction parameter,χ, as function of the degree of hydrolysis, τ of Partial Hydrolyzed Polyacrylamide (HPAM) polymers with an oily hydrocarbon alkane, C_{14}.

3.2 Synthesis of Functionalized Polymeric Surfactant

Polymerization is a chemical process to form chemical bonds between monomers through a variety of reactions. A number of well-established methods are available for both the laboratory- and industry-scale to form polymers.

3.2.1 Addition Polymerization

Addition or chain growth polymerization, is a process whereby the unsaturated monomer molecules are added onto a growing polymer chain one at a time. It can be represented as:

$$\text{nM (monomer)} \dashrightarrow \text{-(-M-)n- (polymer)} \qquad (7)$$

Based on the method used to add the monomer, addition polymerization can be further classified as:

Free radical addition polymerization – The reactive center of a polymer consists of at least one radical. Emulsion polymerization is a special radical addition polymerization technique in which the reactive sites are kept separated by dispersing monomers in an aqueous medium.

Cationic addition polymerization – The addition reaction is initiated by electrophilic agents such as acids which are electron acceptors, or compounds capable of generating carbonium ions. Typically, Lewis acid initiators require the presence of either a proton donor (protogen) such as water, alcohol, and organic

acids; or a cation donor (cationogen) such as *t*-butyl chloride or triphenylmethyl fluoride, ultimately supplying the proton or cation which is added to monomer that initiates polymerization.

Anionic addition polymerization – The addition polymerization is initiated by a strong base and anion, such as alkali amide, or an organometallic compound. The reaction is typically fast and complete. The reaction only stops when all monomer is consumed or when another reaction takes over.

Coordination polymerization – At least one organometallic active center will be involved, such as the heterogeneous Ziegler-Natta catalyst based on titanium tetrachloride to generate the active catalytic center with an aluminum co-catalyst such as methyaluminoxane.

Condensation – or the step-growth polymerization process that involves the chemical reaction of multifunctional monomer molecules. In contrast to other addition polymerization processes, the monomers used in the condensation process should have at least two reactive sites, or two functional groups (like alcohol, amine, or carboxylic groups).

3.2.2 Copolymerization *vs.* post-polymerization modifications

One special type of our developing FPS polymer is the addition of the selected hydrophobic moieties (monomer) into the water-soluble polymer chains. There are two basic synthetic strategies (1) direct copolymerization of hydrophobic and water-soluble monomers, and, (b) post-polymerization functionalization. In the case of the Hydrophobically Modified Polyacrylamides (HMPAM), a commonly accepted method is the micelle copolymerization in which an appropriate surfactant is employed to solubilize both monomers. It is well known that the obtained polymers are characterized by (a) blocky distribution of the hydrocarbons; (b) compositional inhomogeneity; (c) strong dependence of solution properties on block length.

One major difficulty in the synthesis of HMPAM originates from the insolubility of the hydrophobic comonomer in water. Simply dispersing this insoluble monomer as fine particles in the aqueous medium under stirring ‘heterogeneous polymerization’ is not a satisfactory process. Two methods were devised to overcome this problem:

(1) Polymerization in an organic solvent or a water-based solvent mixture in which both monomers are soluble. (2). Micelle polymerization where an aqueous surfactant solution ensures the solubility of the hydrophobic monomer within the micelles.

In a related micelle process, a micelle-forming polymerizable surfactant can be used instead of the hydrophobic monomer.

3.2.3 Copolymerization of Functionalize Polymeric Surfactants

Direct copolymerization of hydrophobic and hydrophilic monomers to form the polymeric surfactants is the primary synthesized method. After attempts using heterogeneous, inverse emulsion, micro-emulsion, and precipitation copolymerization processes, the final method accepted is micelle free radical copolymerization. In this process, the hydrophobic monomer is solubilized within surfactant micelles, whereas the hydrophilic monomer is dissolved in the aqueous continuous medium. This situation contrasts with conventional solution copolymerization in which the different co-monomers are randomly dispersed within the reaction medium (homogeneous polymerization). In the case of influences of

HMPAM prepared by micellar polymerization, the main effects are the nature and molar ratio of the hydrophilic and hydrophobic monomers, the total monomer concentration, the nature and content of the surfactant, and the nature of the initiator and the temperature.

The chemical structure of the copolymer, sodium 2-acrylamido-tetradecane sulfonate ($NaAMC_{14}S$) / acrylamide (AM), is depicted in Figure 3-4. It is found that such a copolymer could strongly interact with the Gemini surfactant hexylene-1,6-*bis* (dodeccyldimethylammonium bromide) ($C_{12}C_6C_{12}Br_2$) in several respects as follows: (1) addition of $C_{12}C_6C_{12}Br_2$ enabled the copolymer $NaAMC_{14}S$/AM to produce intermolecular association below its critical association concentration in the absence of the $C_{12}C_6C_{12}Br_2$; (2) the mixed micelles of $NaAMC_{14}S$/Am and $C_{12}C_6C_{12}Br_2$ formed below the critical micellar concentration (CMC) of $C_{12}C_6C_{12}Br_2$; (3) for the aqueous solution of 0.30%(*w*) copolymer $NaAMC_{14}S$/AM, the apparent viscosity increased dramatically with an increase in the higher than the initial value without $C_{12}C_6C_{12}Br_2$ concentration, and the maximum value of the viscosity was enhanced three orders of magnitude higher than the initial value without $C_{12}C_6C_{12}Br_2$.

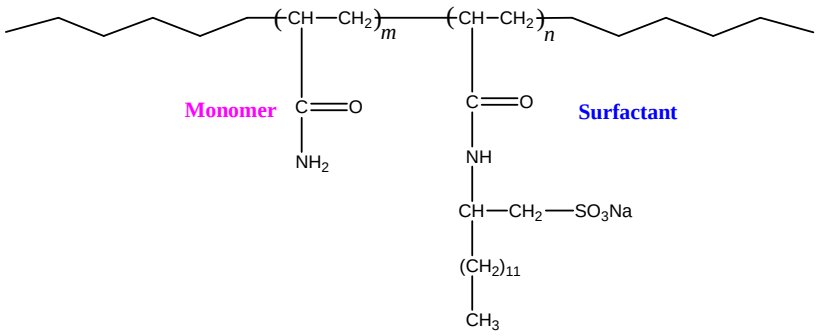


Figure 3-4: Chemical Structure of a Copolymer of $NaAMC_{14}S$/Am

3.3 EXPERIMENTAL METHODS

The laboratory work for this chemical EOR evaluation was performed at the Power Environment Energy Research Institute (PEER Institute) based in Covina, California. The PEER Institute has in house facilities capable of conducting a thorough chemical EOR assessment for a target reservoir. The laboratory provides different research services to many major oil companies in the world (Figure 3-5).

After screening a number of surfactants and polymers from the literature, a testing program was executed in the laboratory of PEER Institute. The laboratory evaluation program included a wide spectrum of measurements to determine the potential suitability of different FPS. The different experimental procedures to examine the quality of FPS are described below:

Table 3-1 List of the Laboratory Testing Procedures and Measurements

Number	Measurement	Functions and Descriptions
1	Phase behavior	All phases remain as low viscosity liquids – no gels
2	Viscosity	Measure increase of viscosity at different polymer concentrations. Prefer a low polymer concentration needed to reach target viscosity
3	IFT (Interfacial Tension)	Low IFT desired to mobilize residual oil
4	Chemical adsorption	Measure chemical adsorbed to reservoir rock
5	Filtration test	Determine risk of plugging during injection
6	Thermal stability test	Stability of polymeric surfactants at high temperatures
7	Sand Pack Flooding	Pressure to core flooding
8	Core Flooding	simulation of tertiary oil recovery

All of the desirable attributes above are maintained when blending individual chemicals together creating a final formulation suitable for field injection.

Figure 3-5: Laboratory of Power Environmental Energy Research (PEER) Institute in Covina, CA

3.3.1 Phase Behaviors

Phase behavior of different surfactants in association with crude oil at different water salinities are studied quantatively in the course of this project. The formation volume of the emulsion phases is measured at different salinities. A brief explanation of the importance of different volumetric emulsion phase formation is described in the figure below. Typically in emulsion tests, 4g of 2000ppm polymeric surfactant solution and 4g of crude oil are added to a test tube. The test tube is caped and shaken at 80 strokes/min for 10 min, then allowed to stand for 30 min. The emulsification results are then recorded.

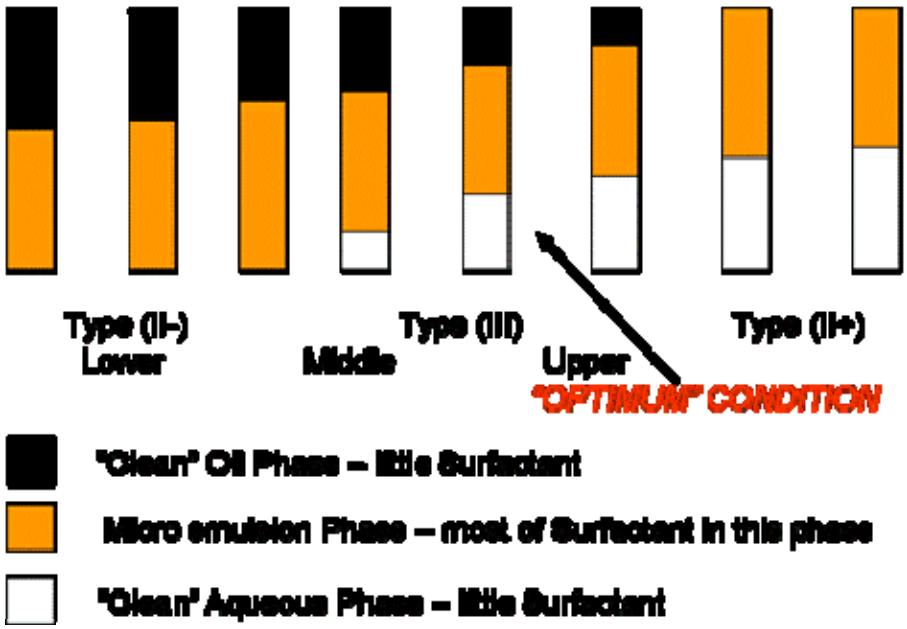


Figure 3-6: Diagram exhibits the importance of micro-emulsion phase formation between aqueous and oil phase. This illustrates a procedure where the surfactant system is equilibrated with crude oil at different salinities. Based on the appearance of the phases, the optimum conditions for lowest IFT (Interfacial Tension) can be estimated.

3.3.2 Viscosity Measurements

Viscosity is a measure of the resistance of a fluid to deform under shear stress. It is commonly perceived as "thickness", or resistance to flow. Viscosity describes a fluid's internal resistance to flow and may be thought of as a measure of fluid friction. Thus, water is "thin", having a lower viscosity, while vegetable oil is "thick" having a higher viscosity. All real fluids (except superfluids) have some resistance to shear stress, however a fluid which has no resistance to shear stress is known as an ideal fluid or inviscid flow.

Viscosity is measured with various types of **viscometers**. Close temperature control of the fluid is essential to accurate measurements, particularly in materials like lubricants, whose viscosity can change dramatically with temperature; for example a doubling of viscosity in only 5 ^{0}C. Commonly used viscometers are:

U-tube viscometer – These are also known as Ostwald viscometers or glass capillary viscometers. Common variations for particular sorts of liquid are the Cannon-Fenske and reverse flow viscometers for opaque liquids. In these it is the rise of liquid level up through a lower bulb which is measured

Falling Sphere Viscometers – In these, the fluid is stationary in a vertical glass tube. A sphere of known size and density is allowed to descend through the liquid. If correctly selected, it reaches terminal velocity, which can be measured by the time it takes to pass two marks on the tube. Electronic sensing can be used for opaque fluids. Knowing the terminal velocity, the size and density of the sphere, and the density of the liquid, Stokes' Law can be used to calculate the viscosity.

Vibrating viscometers – these are rugged industrial systems used to measure viscosity in the process condition. The active part of the sensor is a vibrating rod. The vibration amplitude varies according to the viscosity of the fluid in which the rod is immersed. These viscosity meters are suitable for measuring clogging fluid and high-viscosity fluids even with fibers (up to 1,000,000 cP).

Rotation viscometers – These uses the idea that the torque required to turn an object in a fluid, can indicate the viscosity of that fluid. The common Brookfield-type viscometer determines the required torque for rotating a disk or bob in a fluid at known speed

The PEER Institute is equipped with two digital viscometers (Brookfield DV-II +Pro, and DV-I prime digital viscometers) which have been available for this project. Both of the two instruments are featured by variable rotating speed capability (0.01-200 rpm for DV-II +Pro, and 3-100 rpm for DV-I prime digital), a continuous display of temperature, viscosity and shear stress, and has repeatability of 0.2% of full scale range.

The figure below provides a photograph of both of these viscometers.

Figure 3-7: Photographs of (a) Brookfield DV-II +Pro, and (b) DV-I prime digital viscometers from the PEER Institute laboratory.

3.3.3 Surface Tension and Interfacial Tension (IFT) Measurements

The surface tension is an effect within the surface layer of a liquid that causes that layer to behave as an elastic sheet. It is caused by the attraction between the molecules of the liquid by various intermolecular forces. The molecules at the surface are subject to an inward force of molecular attraction which can be balanced only by the resistance of the liquid to compression. Thus the liquid squeezes itself together until it has the locally lowest surface area possible.

Numerous laboratory measurement techniques have been developed to determine the surface tension.

- *Du Noüy Ring method*: The traditional method used to measure surface or interfacial tension. Wetting properties of the surface or interface have little influence on this measuring technique. Maximum pull exerted on the ring by the surface is measured.

- *Wilhelmy plate method*: A universal method especially suited to check surface tension over long time intervals. A vertical plate of known perimeter is attached to a balance, and the force due to wetting is measured.

- *Spinning drop method*: This technique is ideal for measuring low interfacial tensions. The diameter of a drop within a heavy phase is measured while both are rotated.

- *Pendant drop method*: Surface and interfacial tension can be measured by this technique, even at elevated temperatures and pressures. The geometry of a drop is analyzed optically.
- *Bubble pressure method* (Jaeger's method): A measurement technique for determining surface tension at short surface ages. The maximum pressure of each bubble is measured.
- *Drop volume method*: A method for determining interfacial tension as a function of interface age. Liquid of one density is pumped into a second liquid of a different density and the time between drops produced is measured.
- *Capillary rise method*: The end of a capillary is immersed into the solution. The height at which the solution reaches inside the capillary is related to the surface tension by the previously discussed equation.
- *Stalagmometric method*: A method of measuring the weight of the drops of the fluid falling from the capillary glass tube and then calculate the surface tension of the specific fluid which we are interested in *Sessile drop method*: A method for determining surface tension and density by placing a drop on a substrate and measuring the contact angle.

The PEER Institute is equipped with two digital spinning drop tensiometers. The interfacial tension measurement between surfactants and crude oil for this project can be performed in TX-500C full range tensiometer. This interfacial tension (IFT) measurement instrument is equipped with a microscope component along with CCD video. The whole system is attached to a PC. This enables real time viewing of an oil drop within the surfactant solution placed into a sample tube. The proprietary software (TX-500 tension calculation software) measures interfacial tension between oil and surfactant at specified temperature and at specified rotation (rpm) value of the sample tube. Figure 3-8 shows the TX-500C full range spinning drop tensiometer.

Figure 3-8: Photograph of TX-500C full range spinning drop tensiometer

Interfacial tension measurements for different surfactants solution and oils was done at different time intervals (such as at 5, 10, 20, 40, 60,100 minutes) at a specified rotation speed. The default rotation speed was 5,000 rpm. Typically, the surfactant concentration was 0.3 wt% and the test temperature was 50 ℃.

3.3.4 Adsorption Test

The adsorption tests of different products (FPS) are done in a static environment. FPS solutions with known concentrations (for polymer it is 1000 ppm) are kept in containers along with a known amount of ground reservoir sand materials (default is 30 grams solution and 10 grams of reservoir rock). Ground cuttings are used from sands A, B, C, and D as the test reservoir material.

The concentrations of FPS solution are measured at certain time intervals to measure the concentration change versus exposure time. For the polymer, the solution viscosity may decrease as polymer is adsorbed and removed from solution. A decrease in the solution viscosity may be related to the final concentration of the polymer left in solution. From the apparent decrease in the chemical concentration, and knowing the amounts of initial solid and polymeric-surfactants solution, one can calculate the loss of polymeric-surfactants due to solid adsorption.

3.3.5 Filtration Test

The PEER Institute laboratory has the equipment for filtration tests of different products (surfactant and/or polymer solutions). In the filtration test, the time required for the product solution (polymers/surfactants) is done at certain intervals of fluid collection (every 50 ml) after passing through a specified filter. In this process nitrogen gas is used to build pressure over the product solution to help the transmission of solution through the filter. A complete experimental set up of filtration test is shown in the Figure 3-9.

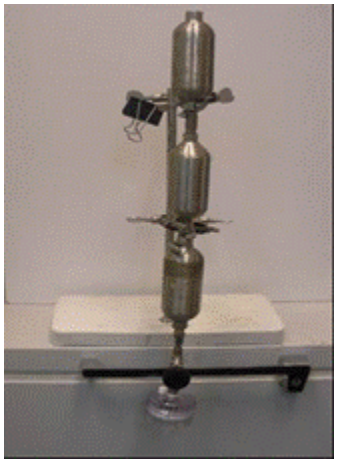


Figure 3-9: Photograph of the filtration apparatus

The default specifications for conducting this test are to load approximately 450 ml of test solution into the pressure cylinders, and then push with a constant pressure of 20 psig. The time to collect every 50 ml up to 400 or 450 ml is noted. The filters are Nucleopore Track-Etch Membrane filters from Whatman. Default. The pore size is 0.45-micron for brine or surfactant solution, and 5-micron for polymer or surfactant/polymer (SP) solutions. For polymer solutions the test concentration is adjusted so that the viscosity becomes between 15 – 20 cP at room temperature.

3.3.6 Thermal Stability Test

Figure 3-10: Lab oven used in this project

In this process, polymer/surfactant solutions individually or in combination are prepared and placed into vials sealed. Before sealing, the vials are filled with nitrogen to insulate from potentially reacting gases. A series of these bottles are made up for each product. The bottles are placed into an oven and held at 80 ℃. Bottles are taken from the oven one at a time at selected intervals and tested. These viscosity are compared to the values with fresh samples that were not aged. A decreased viscosity versus time indicates the system is not stable at that time at test temperature.

3.3.7 Sand Pack Flooding

The experimental setup (Figure 3-11) for sand pack flooding tests consisted of four components: sand pack holder, displacement pump (Teledyne Isco), cylinders for holding crude oil and chemical/brine, and the collector. The sand particles (>100 mesh) were filtered and dried. For each test, fresh sand was packed to ensure the same wettability for all tests. Then it was placed under high vacuum for 3hrs and saturated with 0.3% NaCl aqueous solution overnight. The absolute permeability was measured by injecting brine solution at a constant flow rate. It was next flooded with crude oil at an injection rate of 0.09ml/min to irreducible water saturation, and the oil saturation was measured by material balance. Water-flooding was then continued at a 0.09ml/min injection rate until the water cut reached above 95%. A substantial amount of oil was recovered during this water/brine flood. The remaining oil was recovered by different polymer flooding at 0.09ml/min followed by chase water flooding. The recovered fluids were collected by a fraction collector at regular intervals.

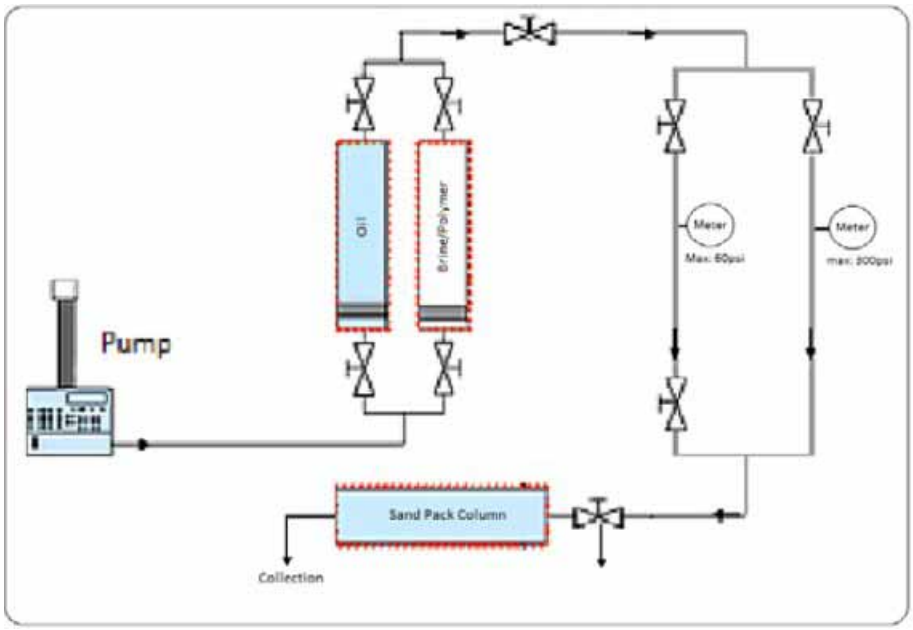


Figure 3-11: Sand pack flooding system

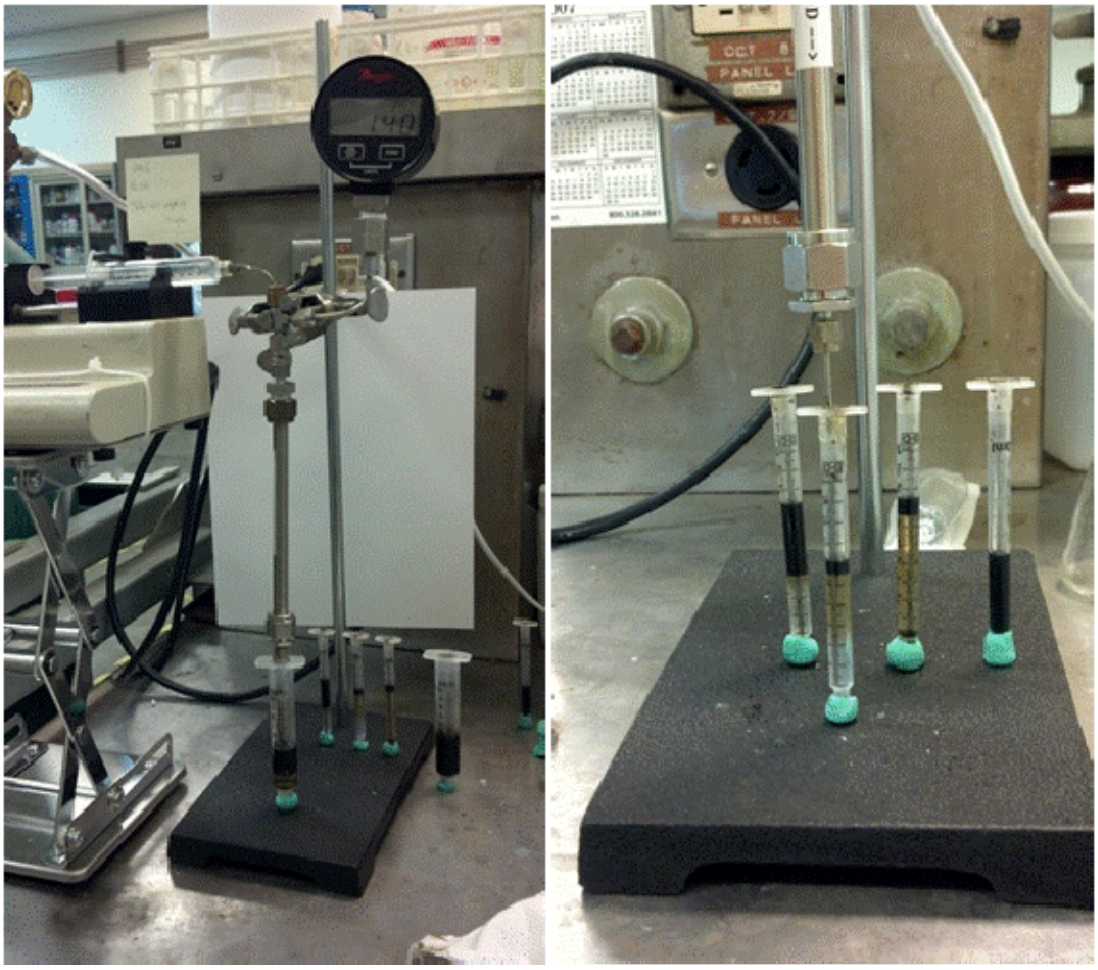


Figure 3-12: Sand pack by pusher under same injection rate, tubes collecting solution/oil from sand pack

3.3.8 Core Flooding

Core flood tests are essential for measuring tertiary oil recovery under laboratory conditions. The experimental setup (Figure 3.14) for core flooding tests consists of four components: core column, displacement pump (Teledyne Isco), cylinders for injecting crude oil and chemical/brine, and the collector. The Berea sandstone core was first heated at 120°C for 3hrs, and then inserted into the rubber tube in the column. The core column was closed. The column surrounding pressure was increased to 100psi by deionized water. Then the inner core column was placed under high vacuum for 6hrs and saturated with synthesized Illinois basin brine overnight. Absolute permeability was measured by injecting brine solution at a constant flow rate. It was next flooded with crude oil to irreducible water saturation, and the initial oil saturation was measured by material balance. It was then water-flooded until the water cut reached above 99%. A substantial amount of oil was recovered during this water/brine flood (typically more than 50% of OOIP recovered from this water flood process). The remaining oil was recovered using 1 PV of different FPS flooding followed by 1 PV chase water flooding. The recovered fluids were collected by switching the fraction collector at regular intervals. By properly calculating the volume of oil recovered, the correspondingly derived tertiary recovery rate or OOIP% can show the products' oil recovery performance.

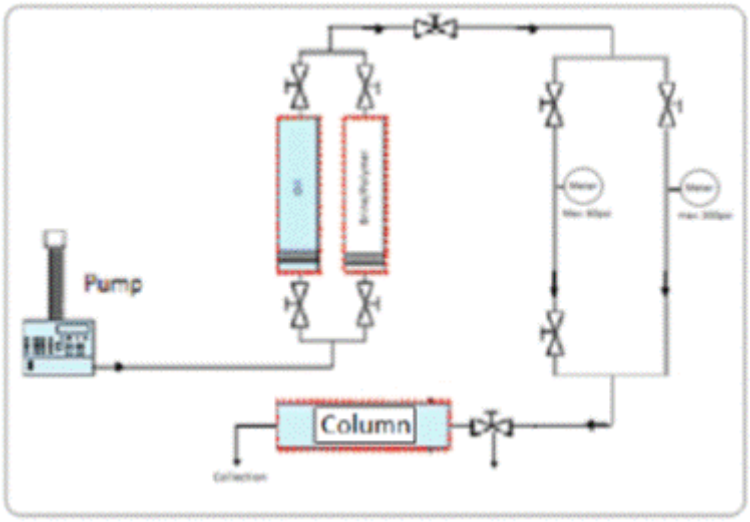


Figure 3-13: Core flooding system

4 RESULTS AND DISCUSSION

4.1 With Model Oil

The task is to identify or screen best suited FPS products which may be candidates for an EOR application. First selection of the polymeric-surfactants includes performance in various salinities and at reservoir temperature. Later selection of FPS is guided by their successful laboratory evaluation performance such as efficient oil recovery. A considerable number of the potentially successful products go through a system of ladder screening tests, but only few can pass the final round and become the potential candidates for Illinois Basin conditions. In addition, these results will provide guidelines regarding features of the chemical structures that are more likely to produce the properties that lead to good oil recovery for typical condition of the Illinois Basin.

Tests were conducted with model oil, dodecane. Dosages of all FPS discussed here are 2 gallons per thousand gallons, gpt.

4.1.1 Emulsion

Initially, in order to establish the general effect salinity has on FPS products, FPS were dissolved in a broad range of salinities, from deionized water to 20% KCL, with model oil, as shown in Figure 4-1. Results show a promising performance of FPS-228-73 in solution with salinities of less than 10% KCl. The emulsion is unsatisfactory with 15%KCL and 20% KCL solutions.

Figure 4-1: Emulsion test. FPS 228-73 in different solution with model oil. Salinities from left to right are as marks on the tubes. Results show a promising salinity range for 228-73 between 0 to 10%.

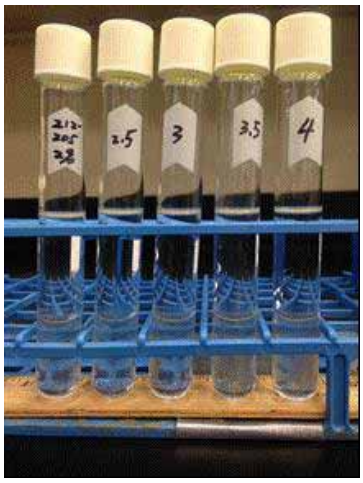


Figure 4-2: Emulsion test. FPS 212-205 in different solution with model oil. Salinities from left to right are as marks on the tubes.

For FPS-212-205 (Figure 4-2), the emulsion tests fail as little to no emulsification occurs. Because the emulsification performance indicates little potential for added recovery, 212-205 is not considered for further tests including IFT, viscosity or core flooding.

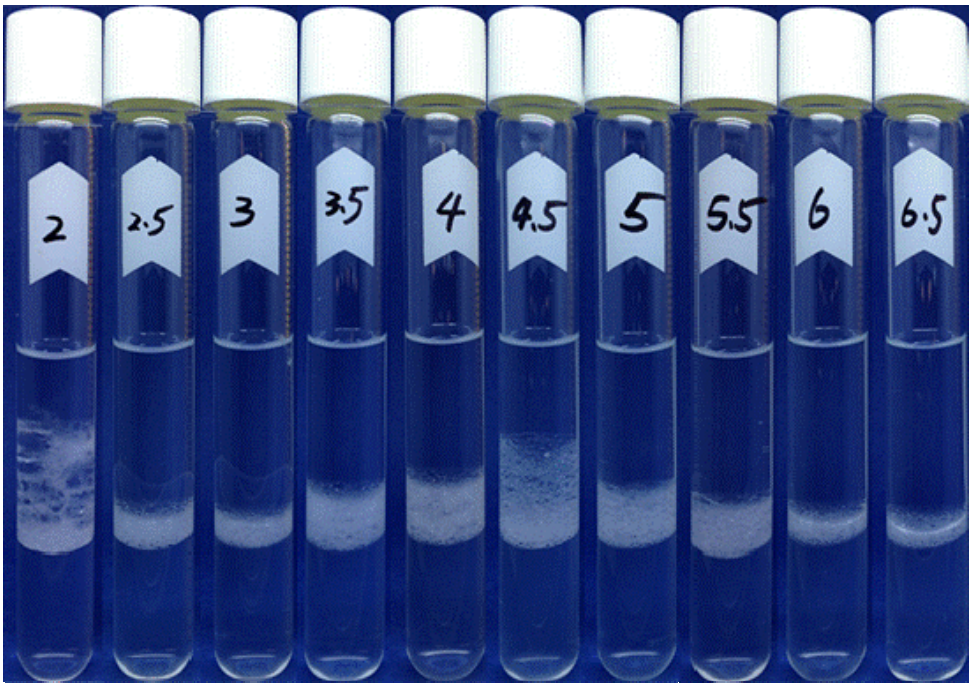


Figure 4-3: Emulsion test. FPS 228-80 in different solution with model oil. Salinities from left to right are as marks on the tubes. Results show a curve with a peak on salinity 4.5%, which provides a guild of range to do further tests.

For FPS-228-80 (Figure 4-3), the emulsion test shows results with maximum emulsification at salinity 4.5%. Therefore, for the following tests, we confine the salinity range from 3.5 ~ 5.5%.

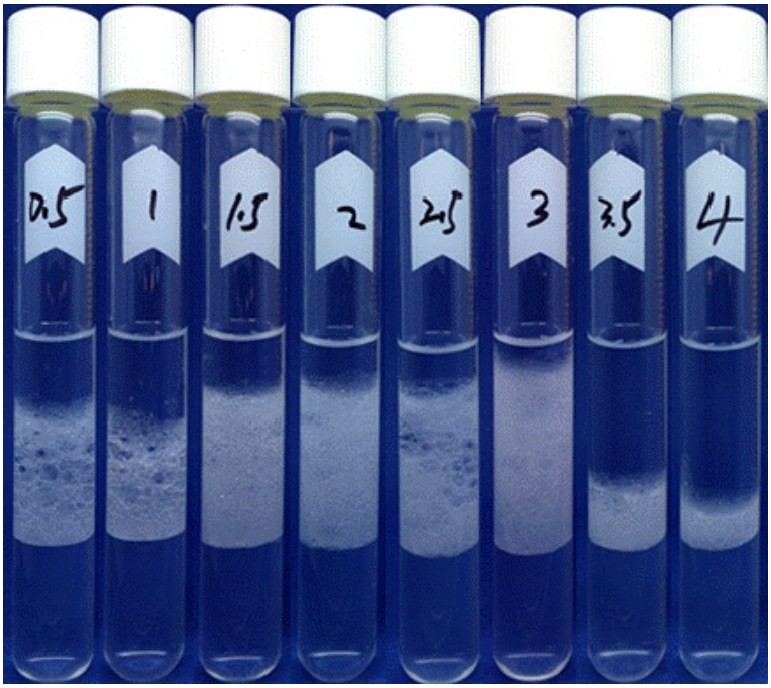


Figure 4-4: Emulsion test. FPS 212-158 in different solution with model oil. Salinities from left to right are as marks on the tubes. Results show a curve with a peak on salinity 3%, which provides a guild of range to do further tests.

FPS-212-158 emulsion test indicates best results at salinity 3% (Figure 4-4), with an even better emulsification than that from FPS 228-80.

Figure 4-5: Emulsion test. FPS 2019 in different solution with model oil. Salinities from left to right are as marks on the tubes. Emulsifications in almost all tested salinities are very successful.

For the FPS-2019, emulsion tests are very successful and emulsifications in almost all tested salinities are good. The above experiments show that phase behavior tests are important screening tools. Different FPS chemicals will show different phase behavior.

4.1.2 Interfacial Tension (IFT)

Oil and water Interfacial tension (IFT) altered by FPS is a critical measure of tertiary oil recovery potential. One requirement for IFT reduction is that the FPS should reside at oil and water interface. If the FPS is too water soluble, one needs to add salt to push the FPS to the oil phase ("salting out" effect). If the FPS is too oil soluble, reduce salinity or add co-solvent to increase FPS solubility into the water phase. The following figures show the IFT changes with different salinities:

FPS 228-73

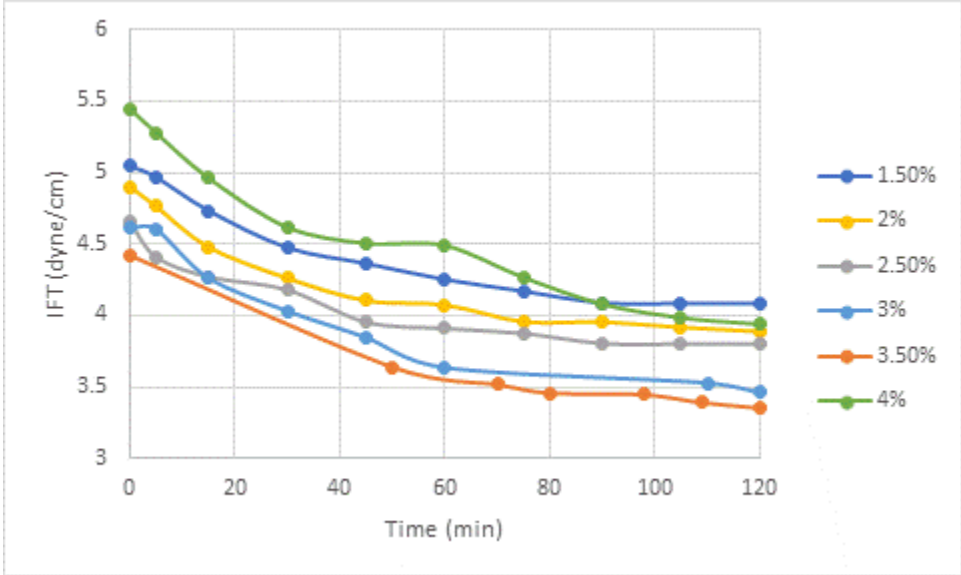


Figure 4-6: IFT of FPS-228-73 in different brine concentrations with dodecane decreases along the time

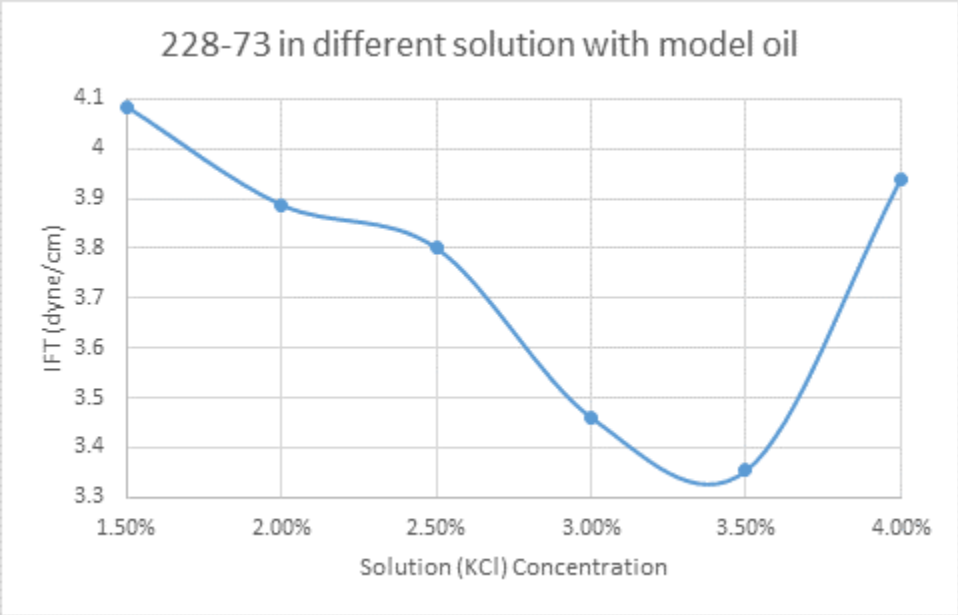


Figure 4-7: Searching for the minimum IFT of FPS-228-73 in different brine concentrations with dodecane

The results show an obvious curve of IFT which is decreasing from 1.5% to approximately 3.5% KCl brine and increasing afterwards. It can be concluded that FPS-228-73 works best around 3.5% salinity with dodecane

FPS-212-205

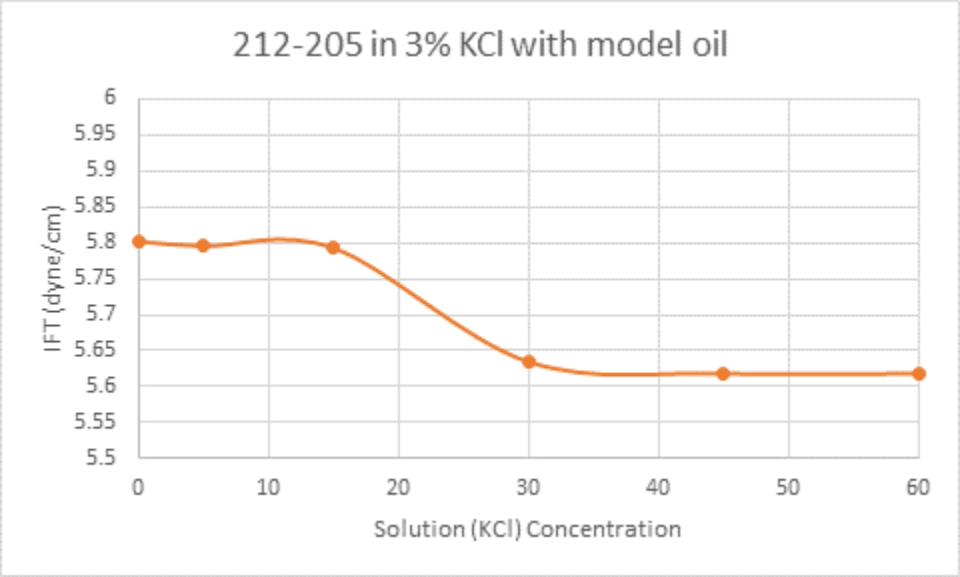


Figure 4-8: IFT of FPS-212-205 in 3% KCl brine with dodecane decreases along the time

Due to the failure of the emulsion test, only one set of IFT experiments is conducted to confirm the results.

FPS-228-80

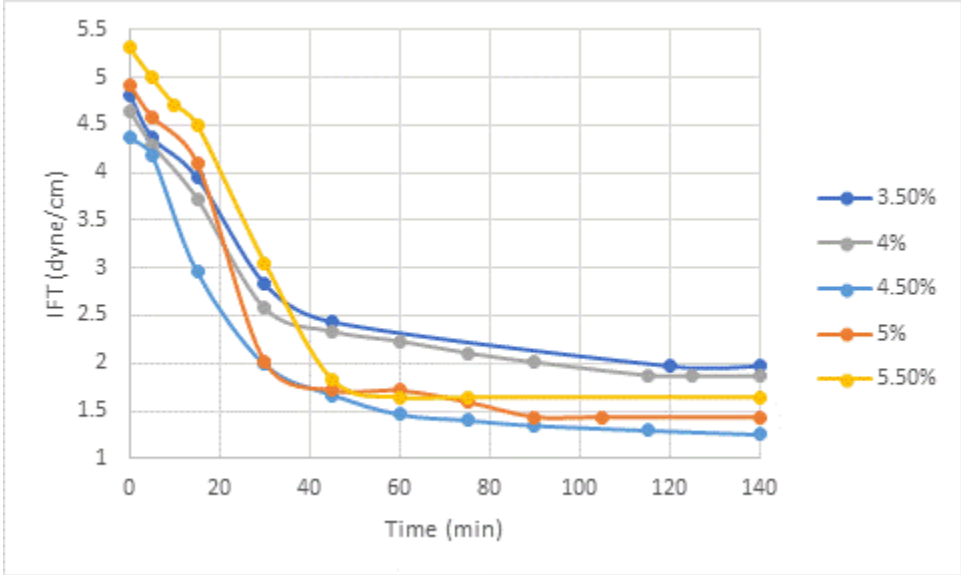


Figure 4-9: IFT of FPS-228-80 in different brine concentrations with dodecane decreases along the time

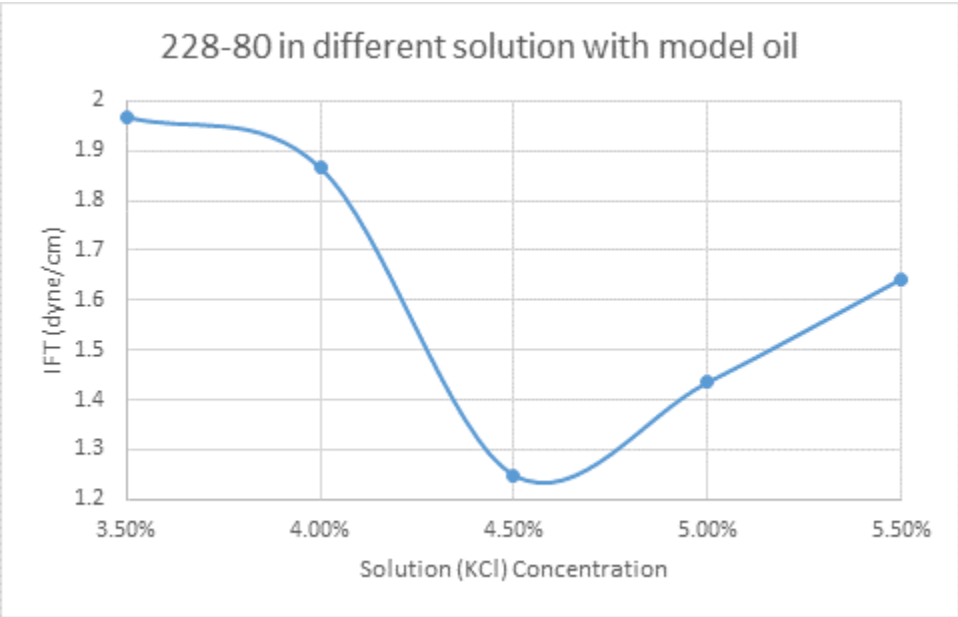


Figure 4-10: A summary for IFT of FPS-228-80 in different brine concentrations with dodecane

The water-dodecane IFT with the FPS-228-80 solution varies with the sale concentration. And the minimum IFT occurs at a 4.5% salt concentration.

FPS-212-158

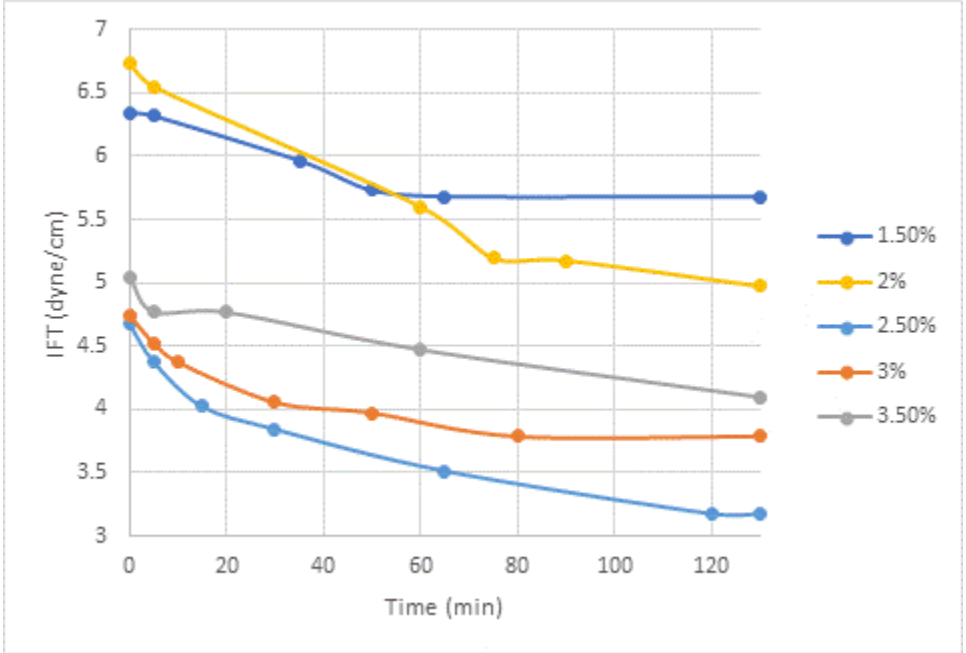


Figure 4-11: IFT of FPS-212-158 in different brine concentrations with dodecane decreases along the time

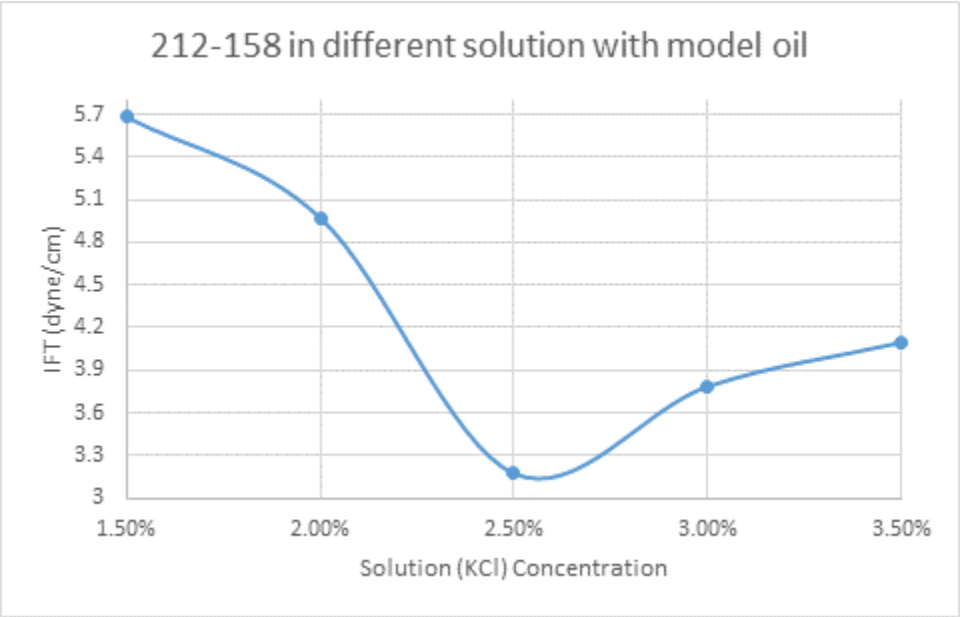


Figure 4-12: A summary for IFT of FPS-212-158 in different brine concentrations with dodecane

The results show an obvious curve of IFT which is going down from 1.5% to 2.5% KCl brine and up afterwards. It can be therefore concluded that FPS-212-158 works best at 2.5% salinity with dodecane.

FPS-2019

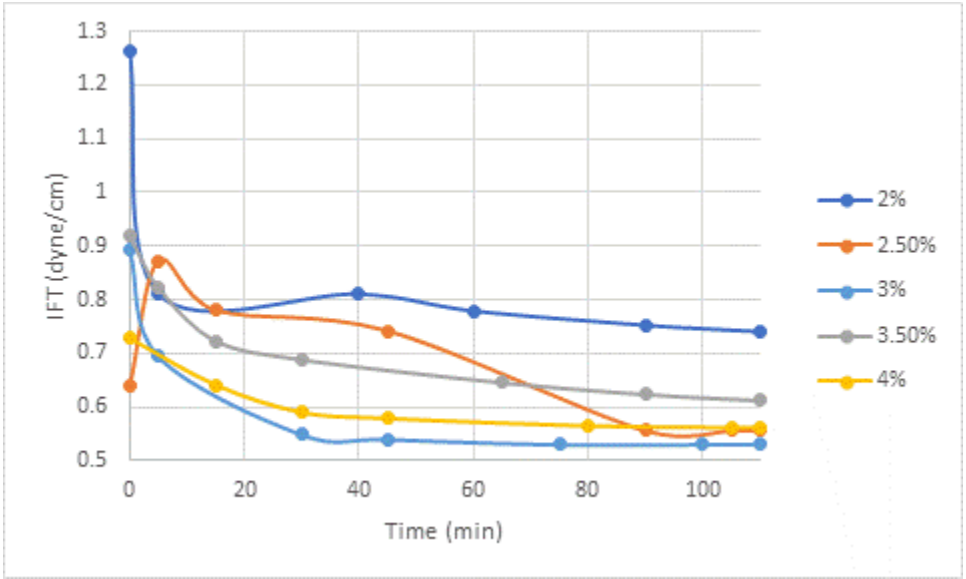


Figure 4-13: IFT of FPS-2019 in different brine concentrations with dodecane decreases along the time

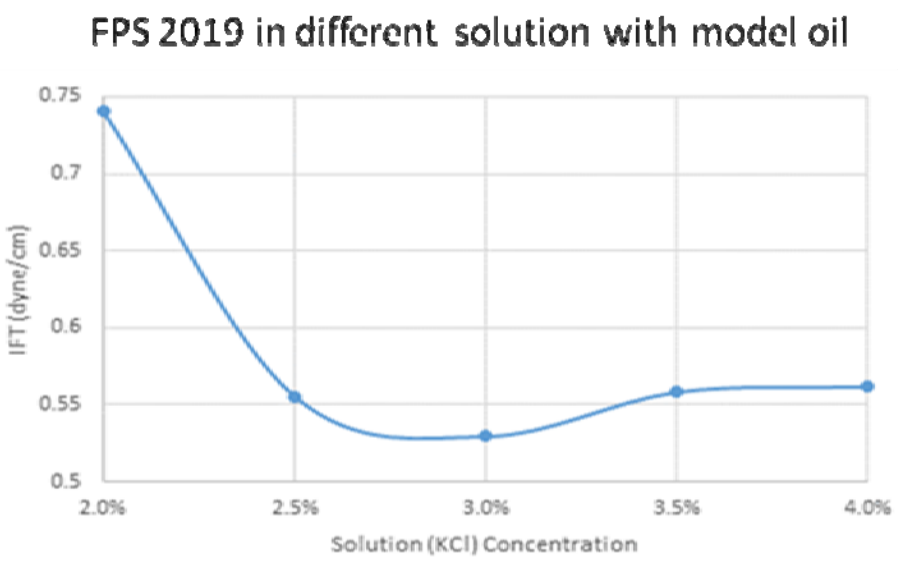


Figure 4-14: A summary for IFT of FPS-2019 in different brine concentrations with dodecane

FPS-2019 has a very good IFT performance at salinity from 2% to 4% with dodecane.

The results above indicate that although IFT and emulsification do not have direct relationship, in most of cases, they do show some correlations (i.e., the higher the IFT, the lower the ability to emulsify oil).

4.1.3 Solubility

Dissolution plays an important role in industrial applications in various ways, and a better understanding of products solubility allows for the optimization of design. On the other hand, insolubility may prevent a polymeric-surfactant from performing effectively. Therefore, every product was tested for solubility and results are as follows.

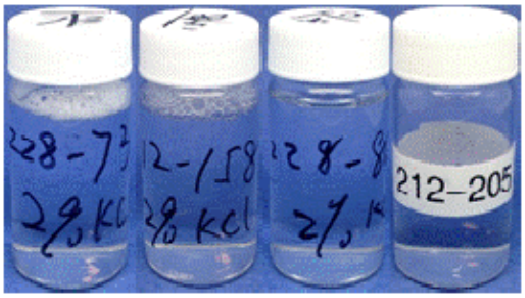


Figure 4-15: FPS-228-73, FPS-212-158, FPS-228-80 and FPS-212-205 dissolved in 2% KCl.

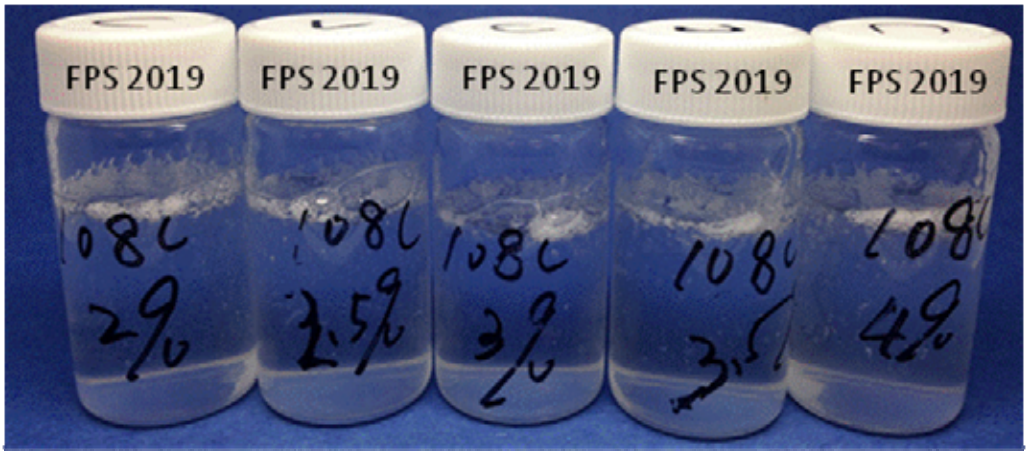


Figure 4-16: FPS-2019 dissolved in 2% to 4% KCl. Insoluble gels are floating on the surface.

Figure 4-17: Close look at FPS-2019

As seen in Figure 4-15, FPS 228-73, 212-158, 228-80 and 212-205 can be dissolved well in brine. However, even if under a high rate of vibration and a long time of intensive shaking, FPS-2019 solutions in various salinities are cloudy with visible insoluble gel, which indicates poor dissolution (Figure 4-17).

4.1.4 Viscosity

Numerous viscosity tests were set up trying to characterize the behavior of FPS properties. These include viscosity versus salinity, temperature and shear rate (rpm). An ideal viscosity profile of polymeric surfactants helps improve sweep efficiency. All the results were generated from a Brookfield DV-II + Pro digital viscometer which is a rotation viscometer.

Viscosity versus salinity

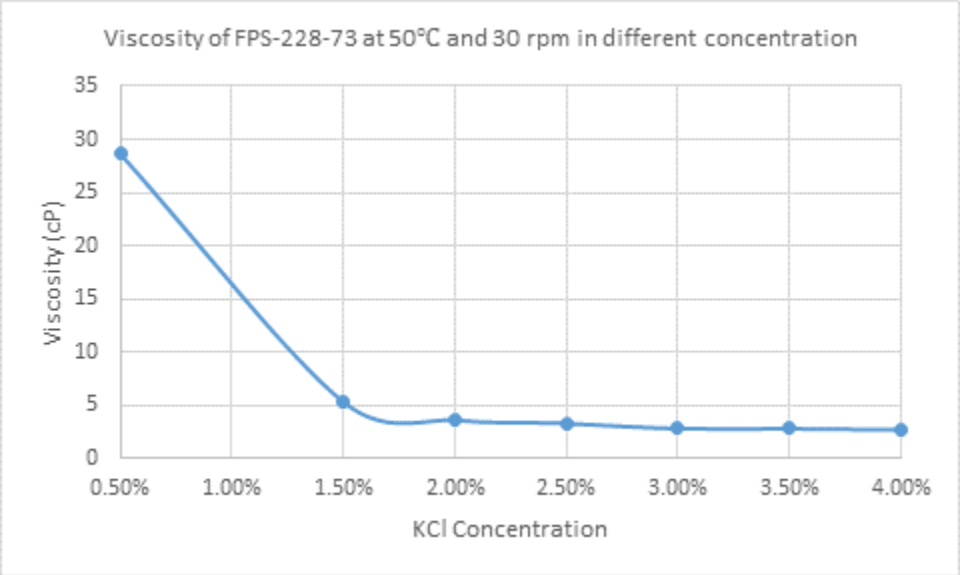


Figure 4-18: Viscosity of FPS-228-73 at 50℃ and 30 rpm in different concentration

The viscosity of FPS-228-73 is approximately 28 cP in the 0.5% KCL solution. The viscosity decreases sharply as salinity increases to 1.5% and then remains stable at a value of 2 to 4 cP as salinity is increased to 4.0%.

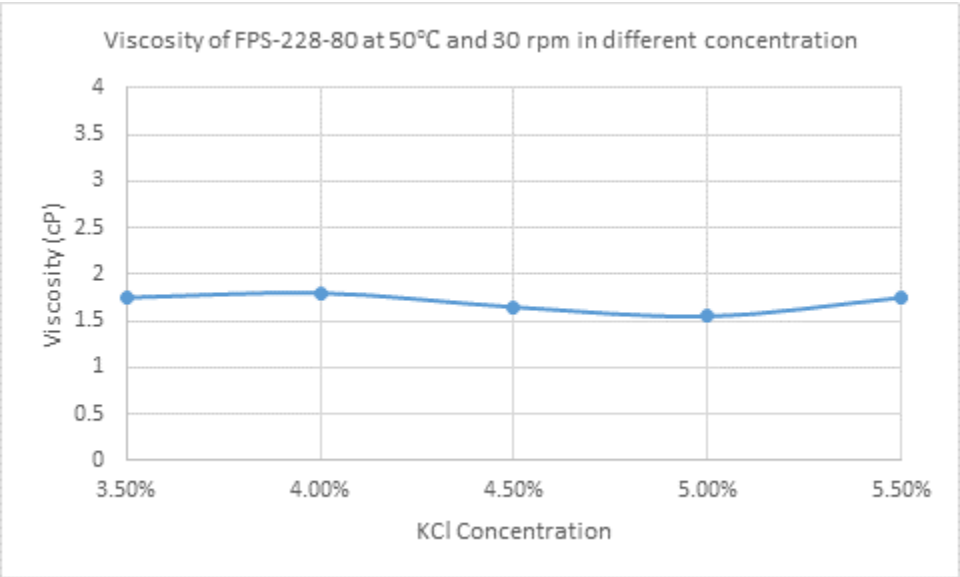


Figure 4-19: Viscosity of FPS-228-80 at 50℃ and 30 rpm in different concentration

The viscosity of FPS-228-80 is quite stable as brine concentration varies, staying in the range of 1.5 to 1.8 cP.

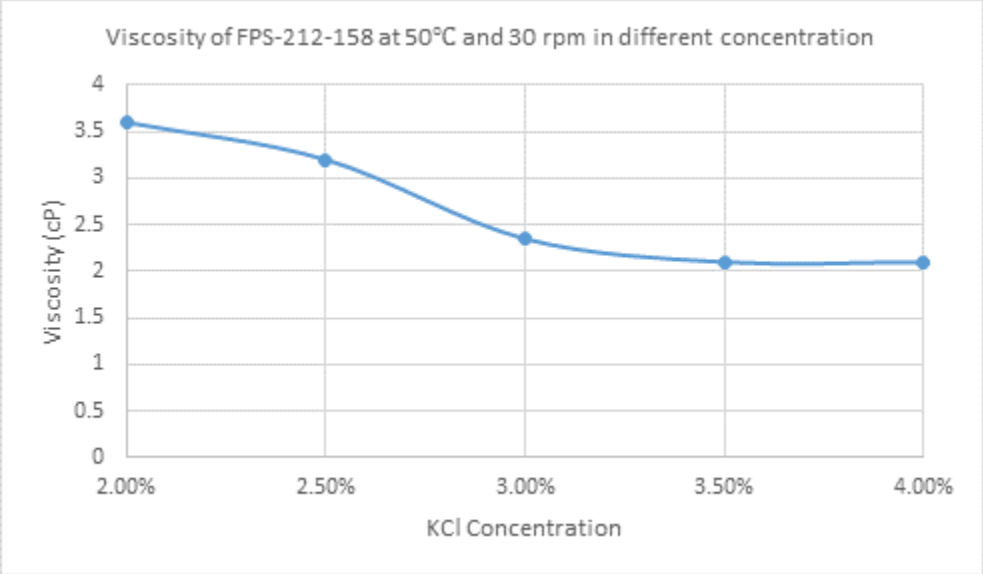


Figure 4-20: Viscosity of FPS-212-158 at 50℃ and 30 rpm in different concentration

Results of the viscosity test for FPS-212-158 show decreasing viscosity from about 3.5 cP at 2.0% to 2.1 cP with salinity higher than 3.5%.

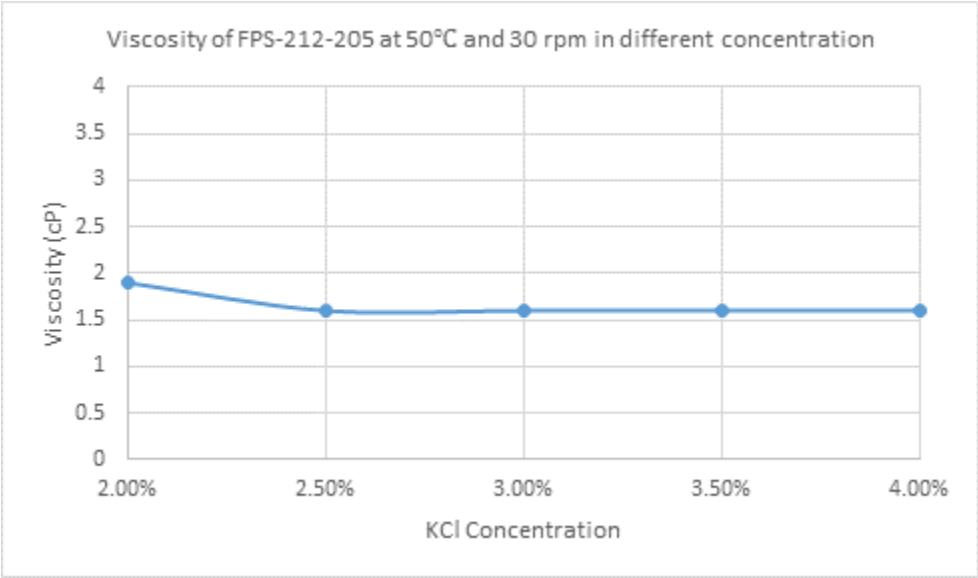


Figure 4-21: Viscosity of FPS-212-205at 50℃ and 30 rpm in different concentration

The viscosity of FPS-212-205 is quite stable as brine concentration increases. Except the initial 1.9 cP at 2% salinity, viscosity is fixed at 1.6 cP afterwards.

The preceding tests indicate that, for the FPS formulations tested, viscosity has a tendency to decrease as salinity increases and that in most cases, the reduction is not dramatic.(in the last three case the decreases are within 1.5 cP and last one is in 0.3 cP).

Viscosity versus temperature

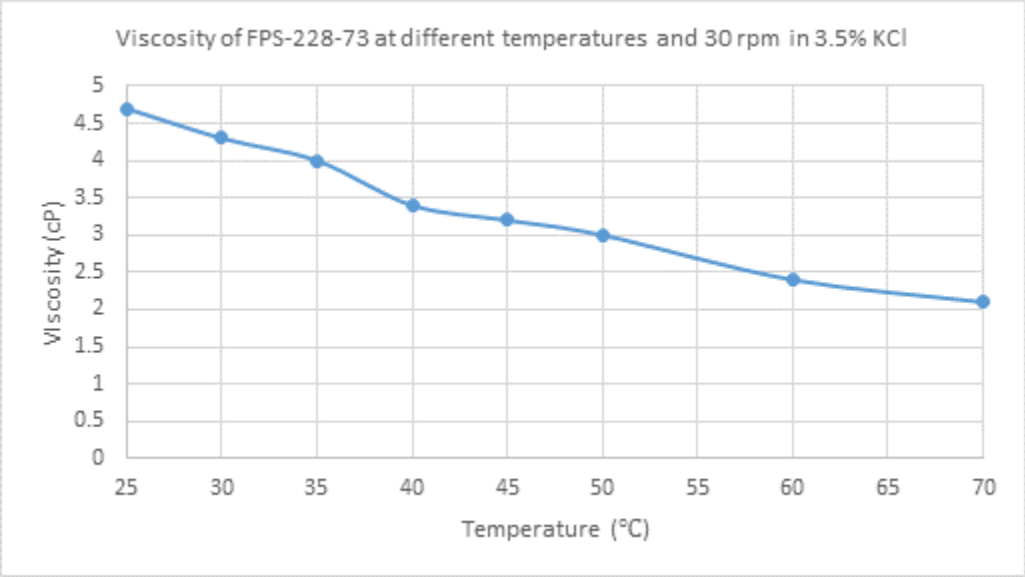


Figure 4-22: Viscosity of FPS-228-73 at different temperatures and 30 rpm in 3.5% KCl

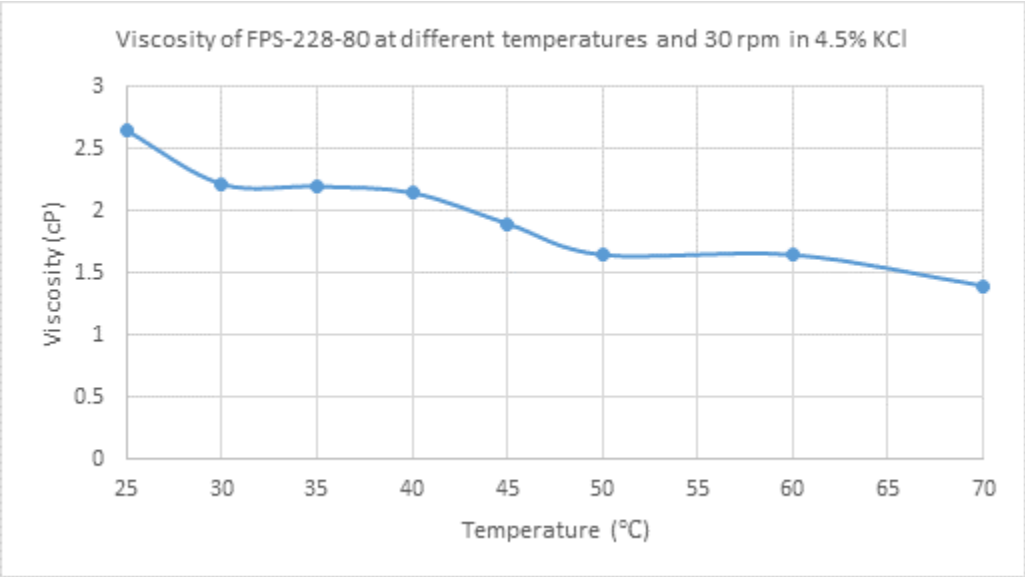


Figure 4-23: Viscosity of FPS-228-80 at different temperatures and 30 rpm in 4.5% KCl

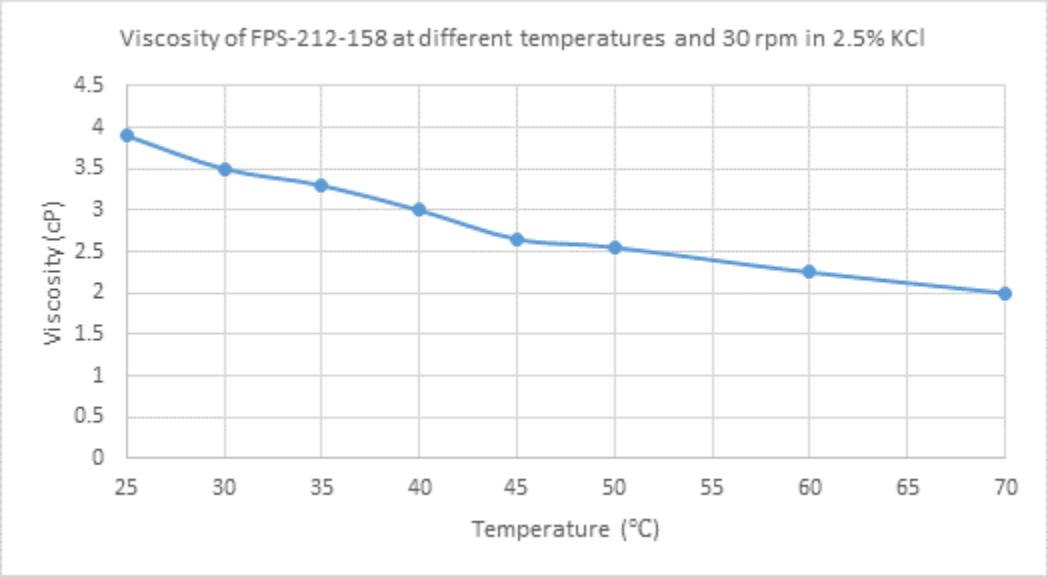


Figure 4-24: Viscosity of FPS-212-158 at different temperatures and 30 rpm in 2.5% KCl

Viscosity of polymeric surfactant decreases as temperature increases. Most of tested FPS show reduced viscosity by half as temperature goes from 25 to 70℃.

Viscosity versus shear rate (rpm)

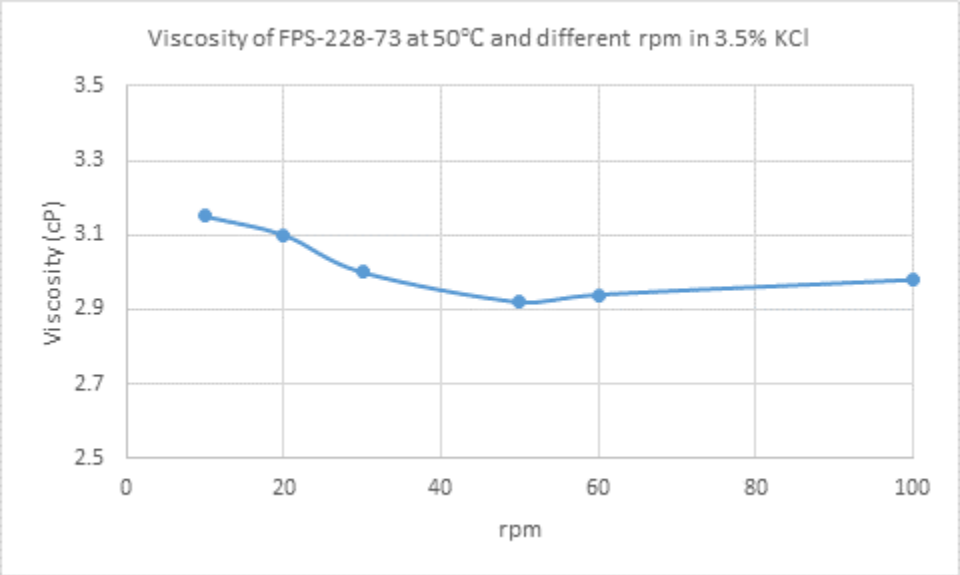


Figure 4-25: Viscosity of FPS-228-73 at 50℃ and different rpm in 3.5% KCl

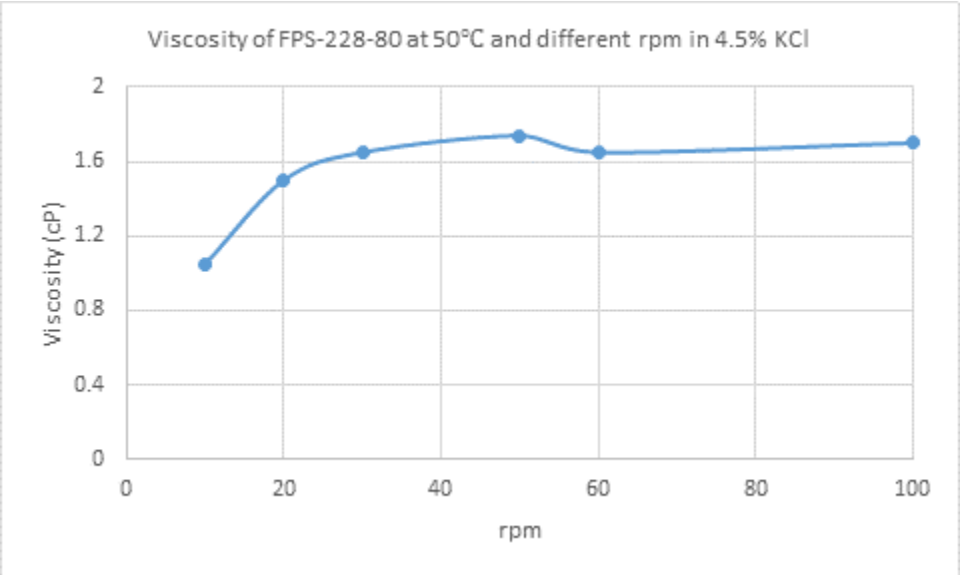


Figure 4-26: Viscosity of FPS-228-80 at 50℃ and different rpm in 4.5% KCl

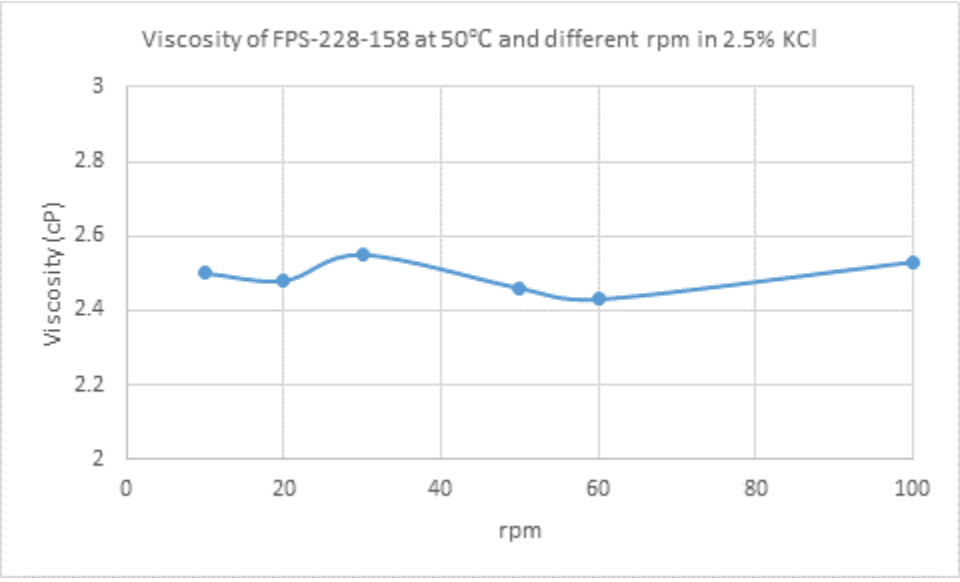


Figure 4-27: Viscosity of FPS-212-158 at 50℃ and different rpm in 2.5% KCl

For FPS solution, non-Newtonian fluids, the viscosity should drop at high shear rates – known as shear thinning. However, from Figure 4-25 and Figure 4-27 the results roughly show the viscosity changes with shear rate is quite different than normal polyacrylamide. It is worth mentioning that we have to be careful about that viscosity study. The lower viscosity at below 25 RPM is due to shear slip on measurement by using a Brookfield.

4.1.5 Thermal Stability

Table 4-1: Viscosity of FPS before and after 3-day 80℃ thermal test

	228-73	228-80	212-158
Viscosity before thermal treatment (cP)	3.6	4	3.6
Viscosity after thermal treatment (cP)	2.4	2.7	2.45

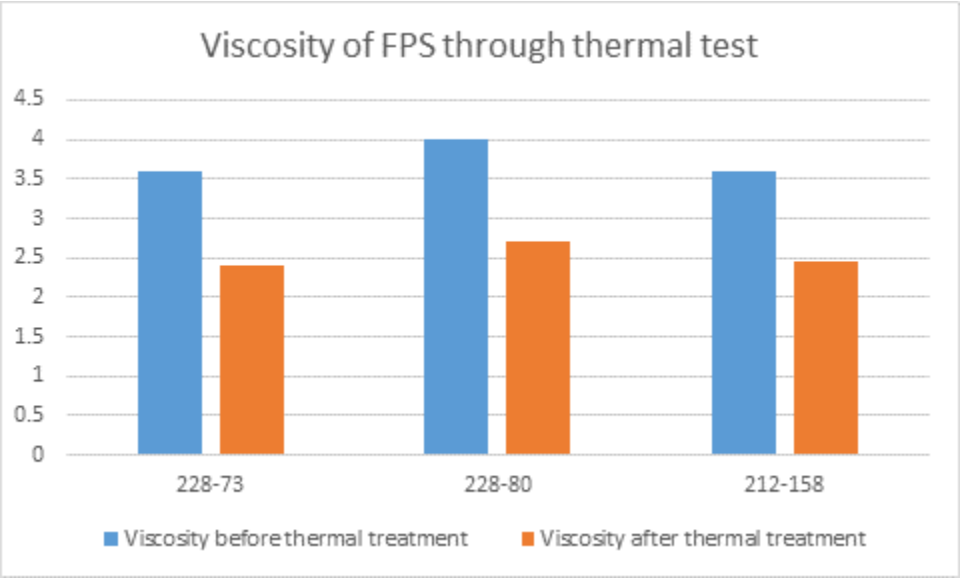


Figure: 4-28 Viscosity of FPS through thermal test

Table 4-1 and Figure: 4-28 show most FPS products' viscosity has decreased by 1/3 after 3 days of 80℃ thermal treatment, demonstrating acceptable thermal stabilities.

4.2 With Illinois Oil

4.2.1 Emulsion

The emulsification performance of 13 different Illinois Basin oils with many FPS products were measured. The measurement was made under Illinois Basin oil field conditions (in lab synthesized Illinois Basin produced water). Comparisons of emulsification performance before and after adding FPS to the oil/brine solutions under various conditions are also attached below (Table 4-2 to Table 4-5)

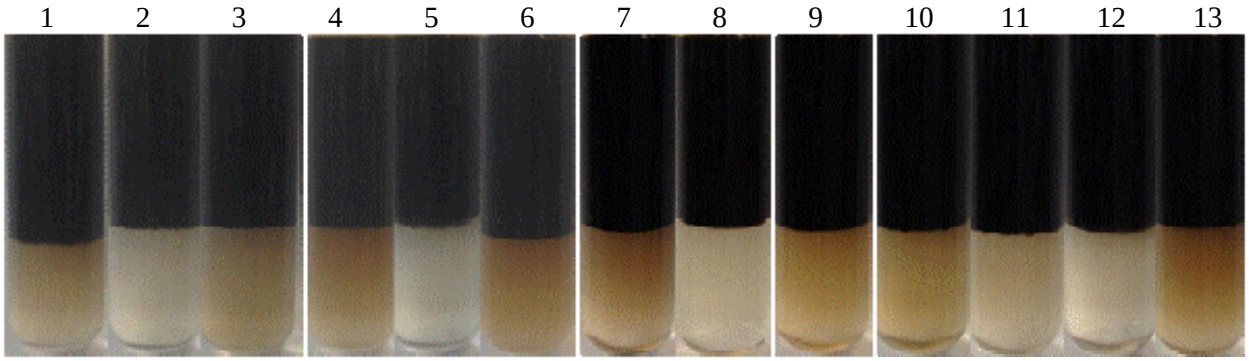


Figure 4-29: Emulsion studies of FPS-140 in synthesized brine with 13 Illinois Basin field crude oils.

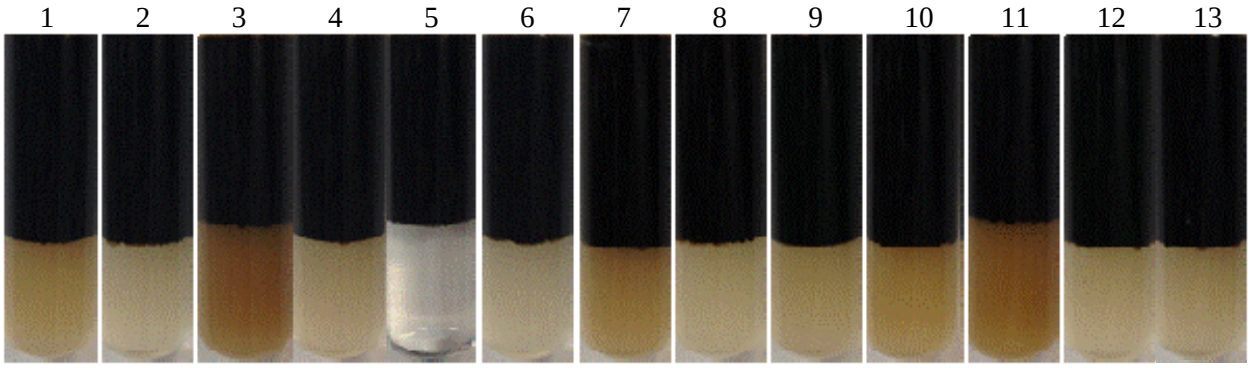


Figure 4-30: Emulsion test. FPS-158 in synthesized brine with 13 Illinois Basin field crude oils.

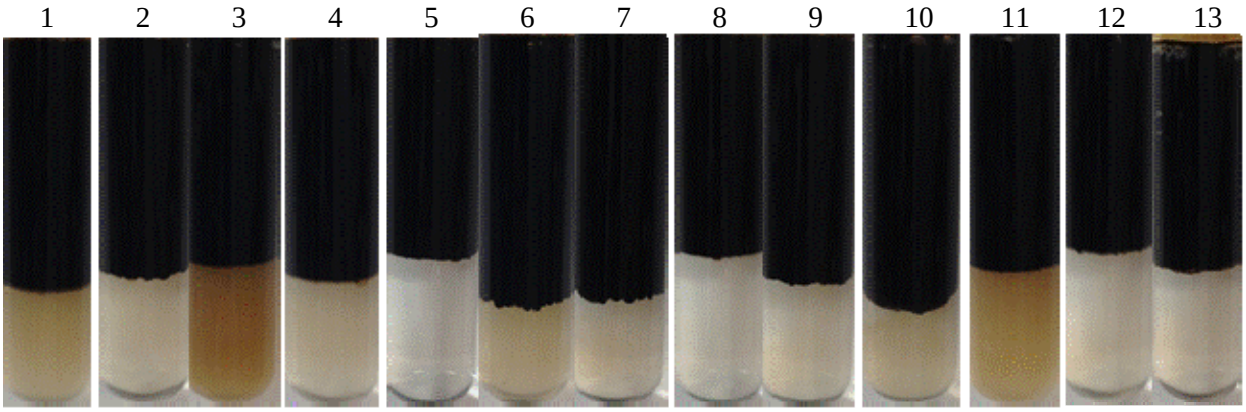


Figure 4-31: Emulsion test. FPS-159 in synthesized brine with 13 Illinois Basin field crude oils.

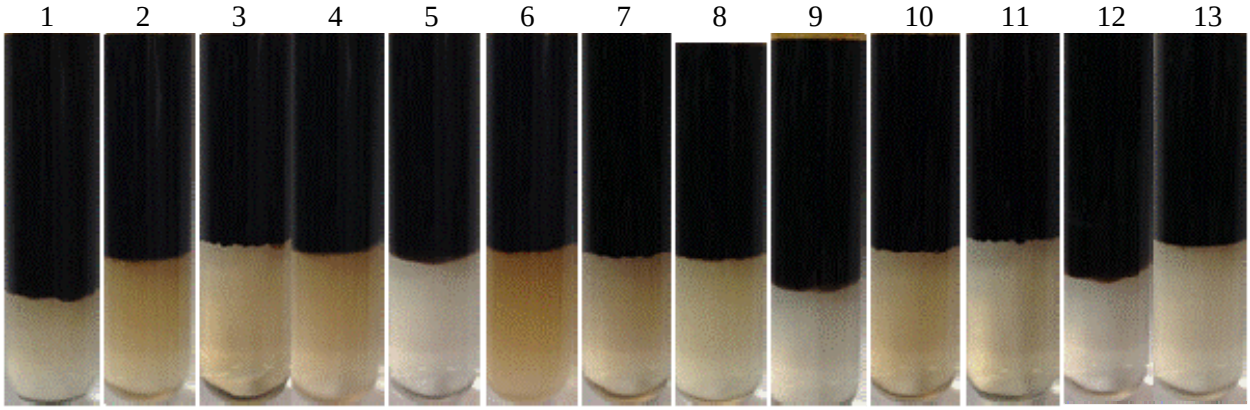


Figure 4-32: Emulsion test. FPS-160 in synthesized brine with 13 Illinois Basin field crude oils.

1 2 3 4 5 6 7 8 9 10 11 12 13

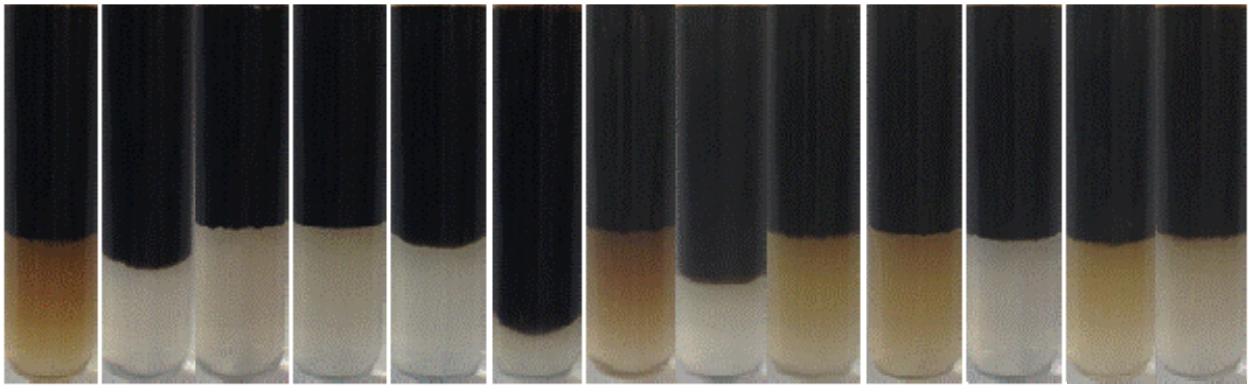


Figure 4-33: Emulsion test. FPS-161 in synthesized brine with 13 Illinois Basin field crude oils.

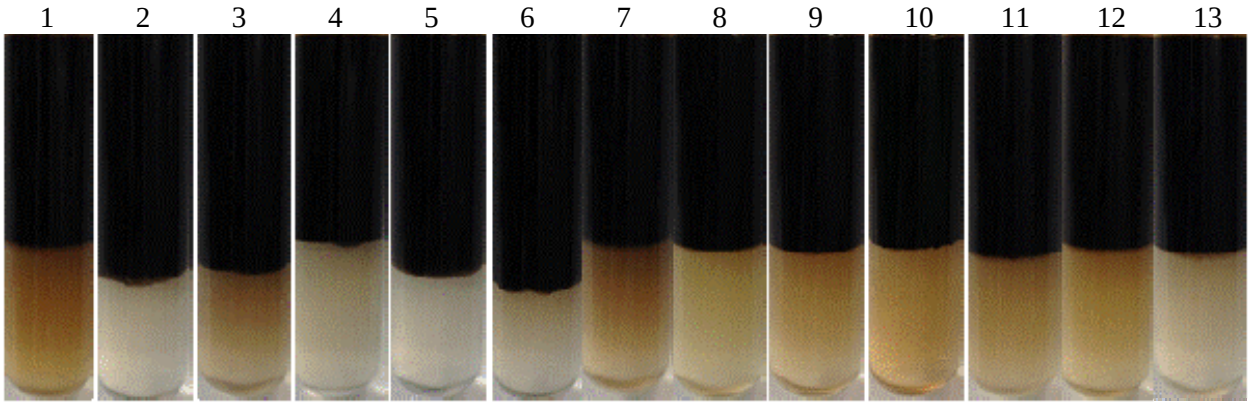


Figure 4-34: Emulsion test. FPS-162 in synthesized brine with 13 Illinois Basin field crude oils.

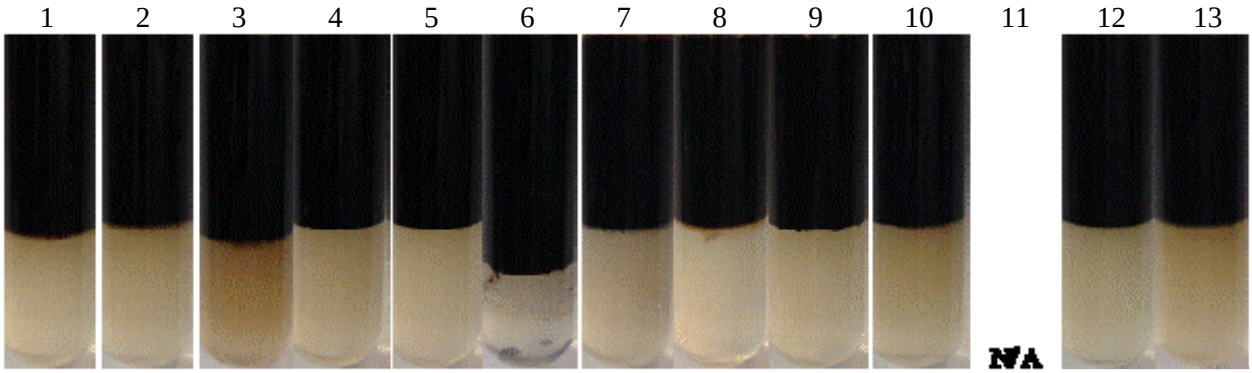


Figure 4-35: Emulsion test. FPS-163 in synthesized brine with 12 Illinois Basin field crude oils.

1 2 3 4 5 6 7 8 9 10 11 12 13

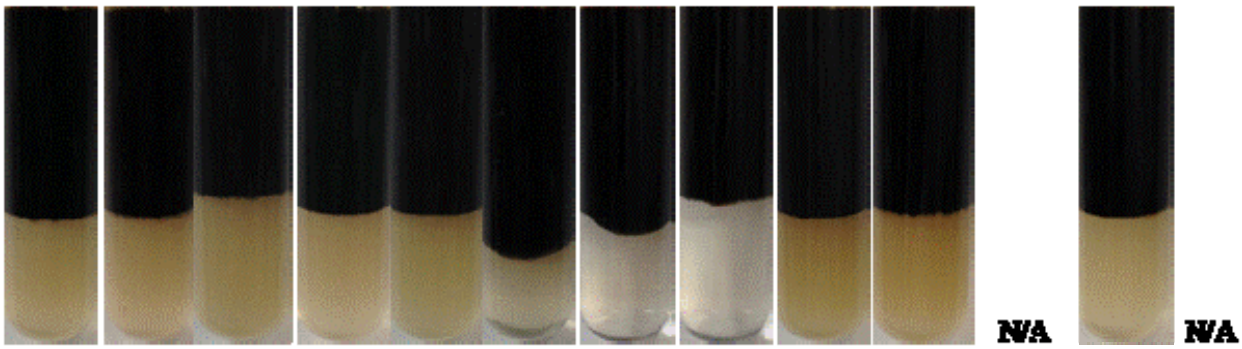


Figure 4-36: Emulsion test. FPS-164 in synthesized brine with 11 Illinois Basin field crude oils.

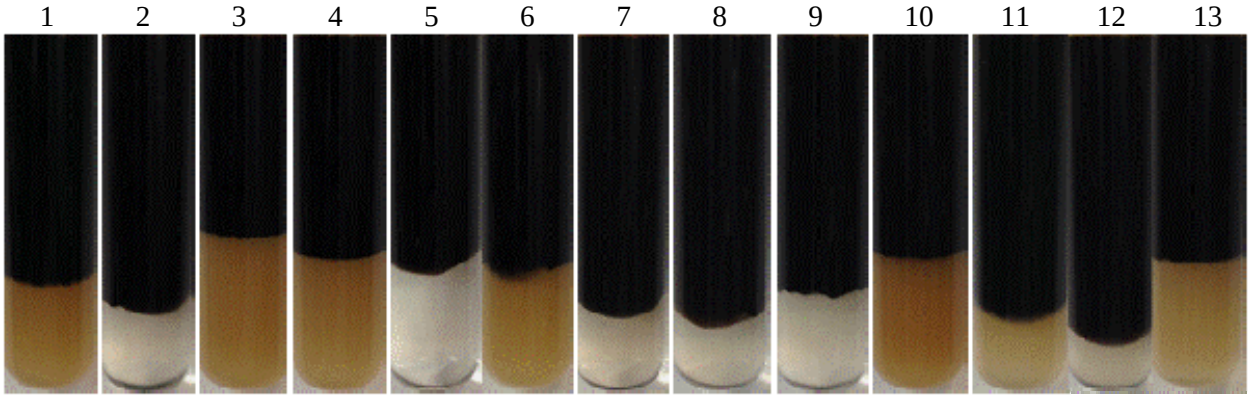


Figure 4-37: Emulsion test. FPS-185 in synthesized brine with 13 Illinois Basin field crude oils.

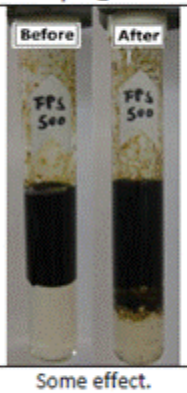
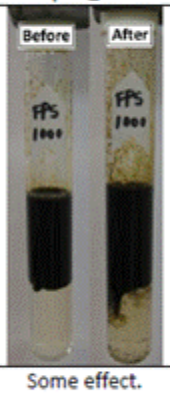
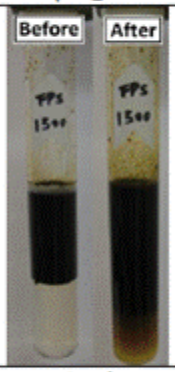
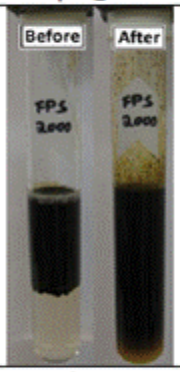
Table 4-2: Emulsion test. Comparison shows emulsification before and after adding FPS into solution.

212-158 2000ppm	2% KCl	Illinois Synthetic Brine
Viscosity*	5.0 cps @ 35˚C	2.2 cps @ 35˚C

Result:		
Note	Good emulsification	Good emulsification

Table 4-3: Emulsion test. Comparison shows excellent phase behavior of FPS-33 with oil/water sample.

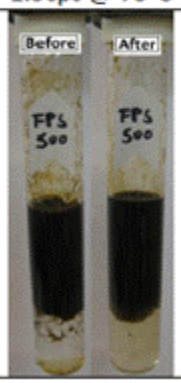
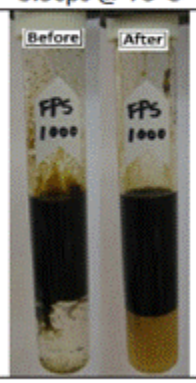
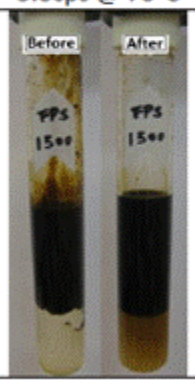
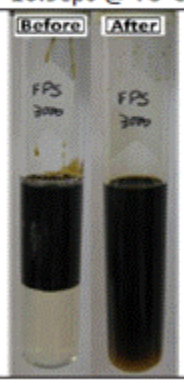
-Results

FPS-33 con.	500ppm	1000ppm	1500ppm	2000ppm	3000 ppm
Viscosity*	3.8cps @ 25˚C 1.5cps @ 75˚C	6.8cps @ 25˚C 3.5cps @ 75˚C	10.1cps @ 25˚C 5.8cps @ 75˚C	14.9cps @ 25˚C 8.7cps @ 75˚C	29.4cps @ 25˚C 16.9cps @ 75˚C
Result: @ 25˚C/30min					
Note	Some effect. Good emulsification in the first 5 min	Some effect. Good emulsification in the first 10 min	Good Emulsification	Great Emulsification	Great Emulsification

*DV-II+ pro #18 spindle, 30rpm

Table 4-4: Emulsion test. Performance under high temperature.

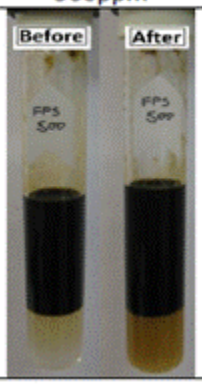
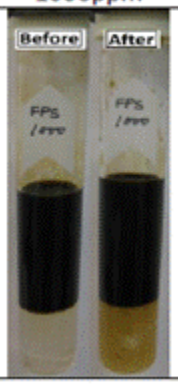
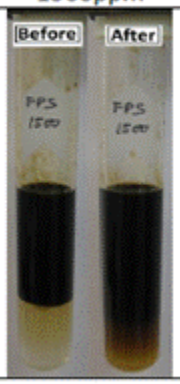
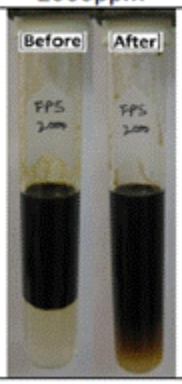
-Results

FPS-33 con.	500ppm	1000ppm	1500ppm	2000ppm	3000 ppm
Viscosity*	3.8cps @ 25˚C 1.5cps @ 75˚C	6.8cps @ 25˚C 3.5cps @ 75˚C	10.1cps @ 25˚C 5.8cps @ 75˚C	14.9cps @ 25˚C 8.7cps @ 75˚C	29.4cps @ 25˚C 16.9cps @ 75˚C
Result: @ 80˚C/30min					

*DV-II+ pro #18 spindle, 30rpm

Table 4-5: Emulsion test. Compatibility with stimulation fluids (acidic condition 0.3 wt% KCl at 80 ℃).

-Results

FPS-33 con.	500ppm	1000ppm	1500ppm	2000ppm	3000ppm
Result: @ 80˚C/30min					

4.2.2 Emulsion Type

Emulsion type refers to if water is the continuous external phase (oil in water) or oil is the external phase (water in oil). Since water viscosity is low, the water external phase is desired for our FPS chemicals. The oil external phase will cause a significant increase in viscosity which will lead to the plugging of the oil producing zone. Figure 4.39 and 4.40 show examples of oil external emulsion.

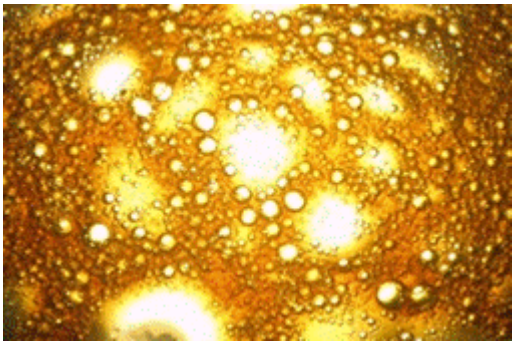


Figure 4-38: FPS-212-90 emulsion type – oil external emulsion

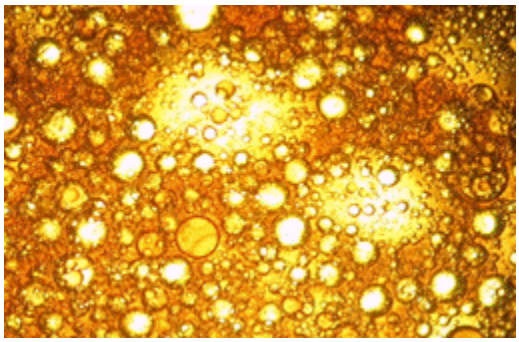


Figure 4-39: FPS-212-99 emulsion type – oil external emulsion

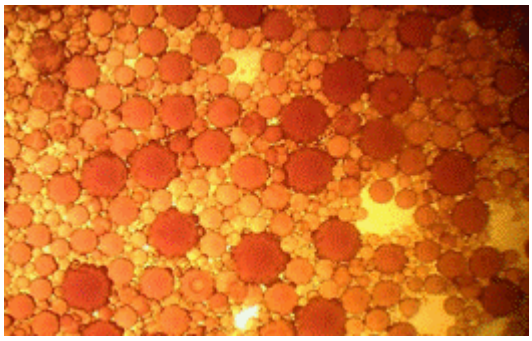


Figure 4-40: FPS-212-116 emulsion type – water external emulsion

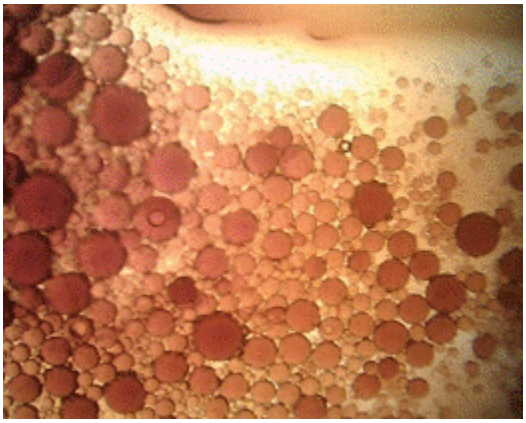


Figure 4-41: FPS-212-117 emulsion type – water external emulsion

A water external emulsion type is needed for increased oil recovery. Careful design and modeling of the FPS structure was used to achieve a water external emulsion (Figure 4-40 – Figure 4-41).

4.2.3 Berea Sandstone Adsorption Tests

The viscosity of the FPS solution is measured at certain time intervals to measure the concentration change versus exposure time. The solution viscosity may decrease as polymer is adsorbed by stone and removed from solution. A decreasing solution viscosity can be related to the final concentration of the polymer left in solution. From the apparent decrease in the chemical concentration, and knowing the amounts of initial solid and polymeric-surfactants solution, one can calculate the loss of polymeric-surfactants due to solid adsorption and consider the results as references for valuing performances.

Table 4-6: Viscosity (cP) change of FPS solution wo/w stone over time

Shaking @ r.t.	0hrs	2hrs	4hrs	6hrs	4days
212-116 3000ppm Blank	30.4	30.6	30.8	30.5	29.2
212-116 3000ppm with 10% crushed Berea stone	30.1	28.9	27.8	26.8	22.5

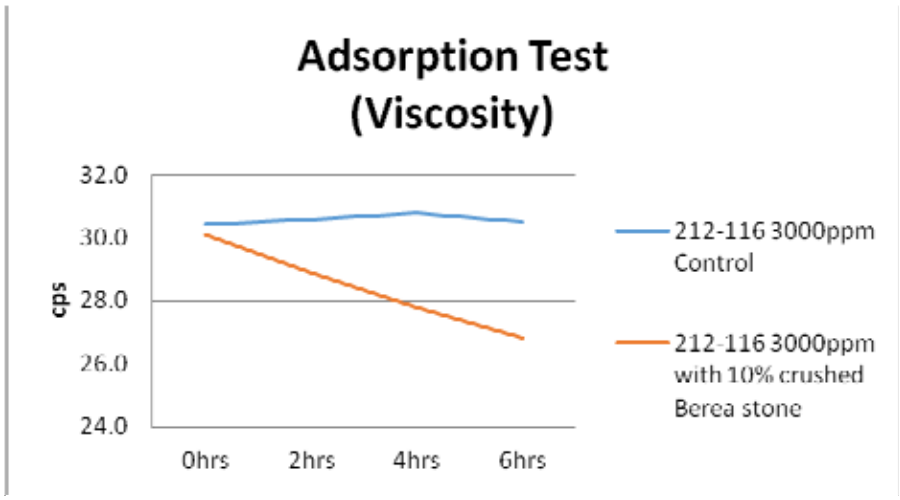


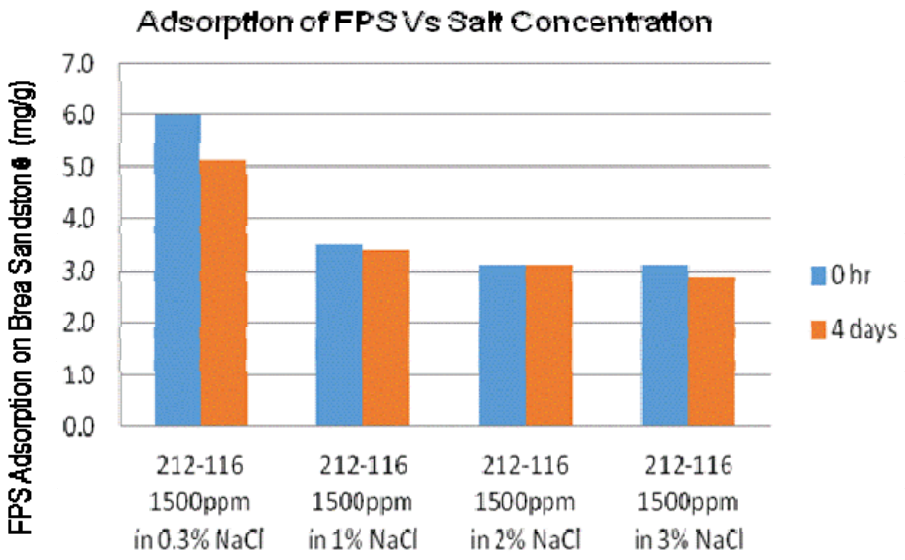
Figure 4-42: Adsorption Test. Viscosity (cP) change of two FPS solution over time.

The first set of tests indicate that part of the polymer is adsorbed onto Berea sandstone, as shown in Figure 4-42 as the viscosity, of the FPS solution continuously decreases with time.

Table 4-7: Viscosity (cP) change of FPS solution in different salinity over time

Shaking @ r.t. w/ 10% crushed Berea stone	0hrs	4 days
212-116 1500ppm in 0.3% NaCl	6.0	5.1
212-116 1500ppm in 1% NaCl	3.5	3.4
212-116 1500ppm in 2% NaCl	3.1	3.1
212-116 1500ppm in 3% NaCl	3.1	2.9

Figure 4-43: Adsorption Test. Viscosity (cP) change of FPS solution in different salinity over time.



This set of experiments shows us a result that at various concentrations of brine (

Figure 4-43, 212-116 1500ppm in 0.3% NaCl), FPS concentration decreases significantly which means increased adsorption by the stones. At salinities of 1% and greater, the FPS solution concentration is very stable, indicating little to no adsorption.

4.2.4 IFT

3 kinds of IFT measurements were done for screening – IFT versus salinity, oil samples and FPS products. Experiments were conducted by spinning drop methods.

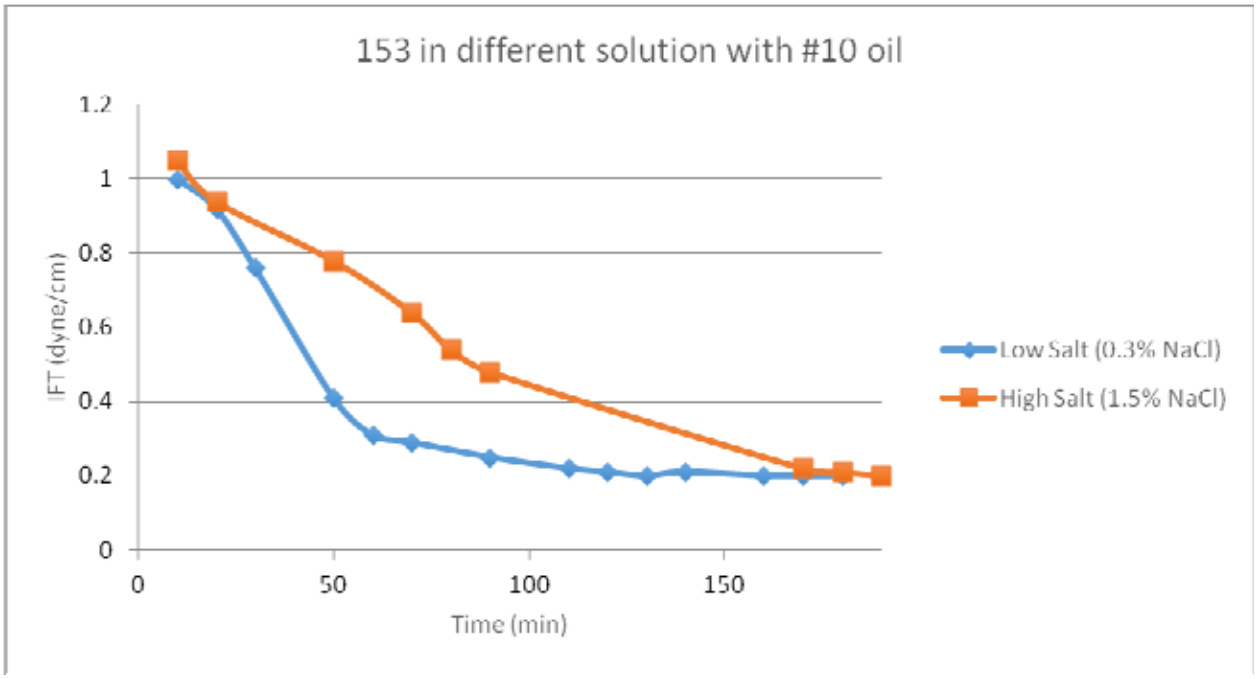


Figure 4-44: FPS-153 in different salinity with #10 field crude oil

Using the spinning drop IFT machine, Figure 4.45 shows the IFT changes with time. The FPS polymer with high salt concentration requires a longer time to reach a minimum IFT value.

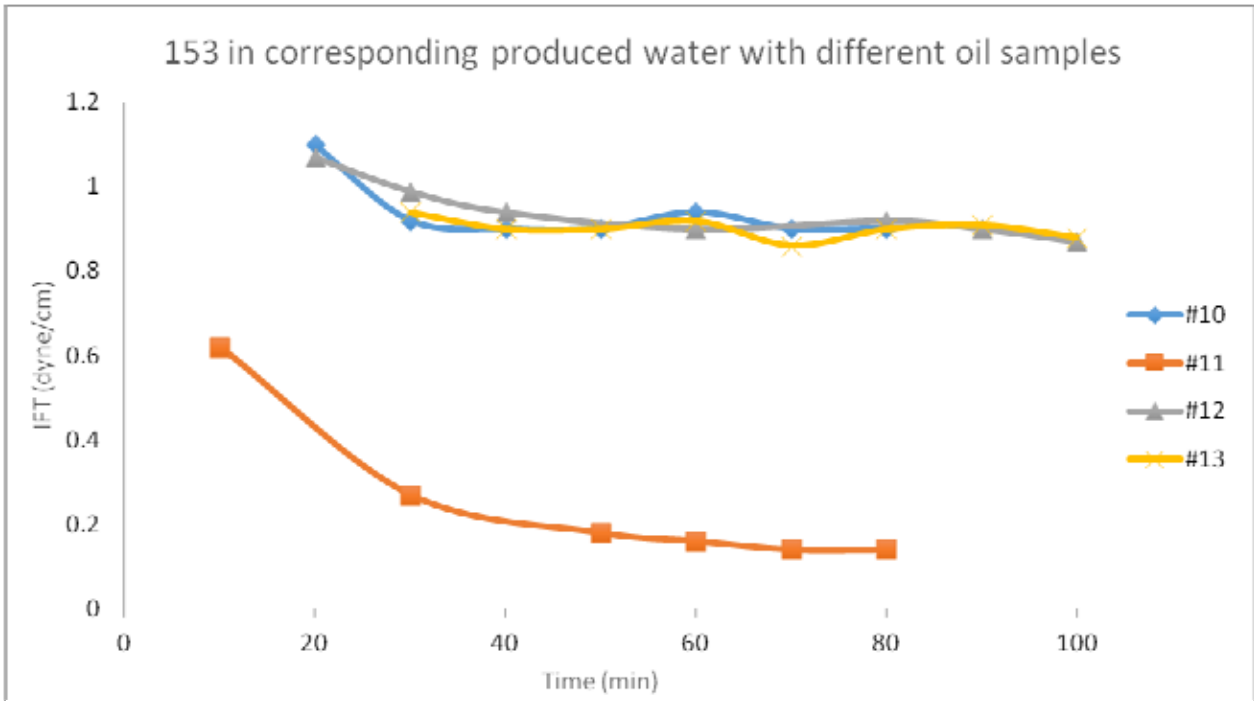


Figure 4-45: FPS-153 in corresponding produced water with different field crude oils.

In order to identify what kinds of oils allow the FPS-153 product to perform best, IFT tests of it with #10-13 oils were done. From the results, (Figure 4-45) FPS-153 with #11 oil shows far superior performance, achieving IFT of under 2 dynes/cm compared with that of over 8 with the other oils tested.

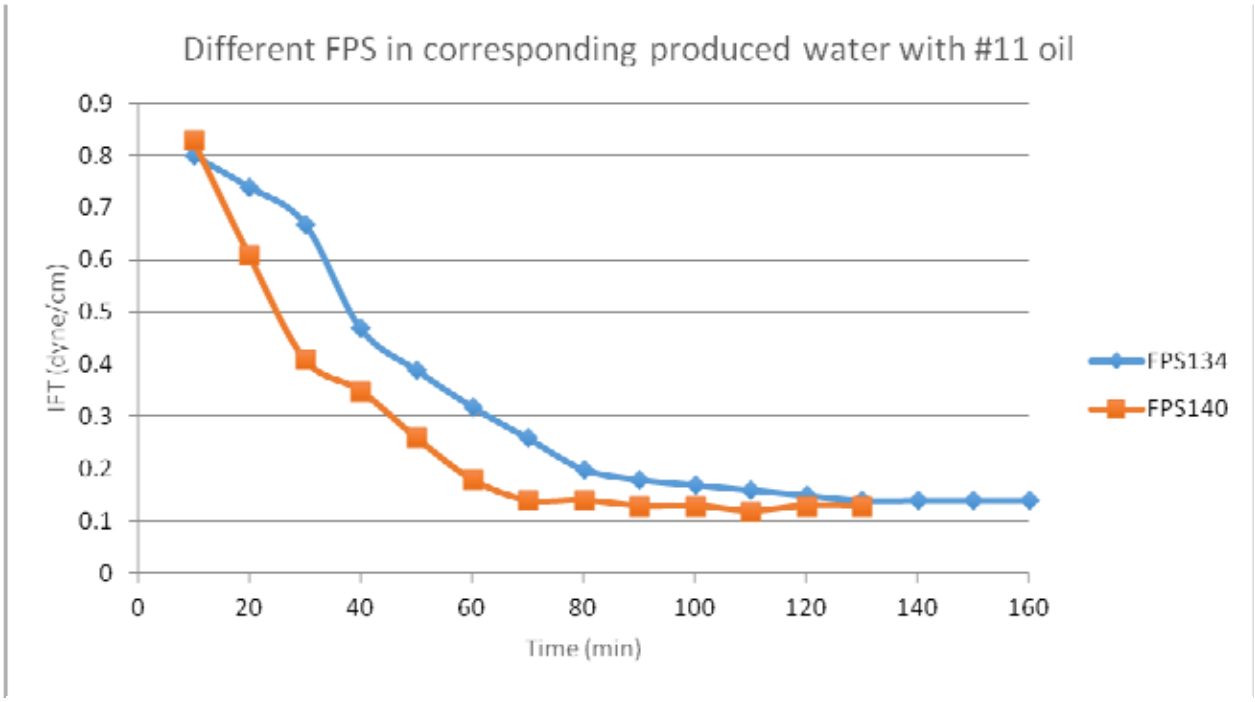


Figure 4-46: FPS-134/140 in corresponding produced water with #11 field crude oil.

For specific oil samples from field #11 of the Illinois Basin, we also evaluate FPS performance under specific temperature and salinity conditions, Figure 4-46 suggests that with regard to IFT, FPS-140 is a better fit under Illinois Basin conditions than FPS-134.

4.2.5 Filtration Test

The filtration test is comprised of 3 filtrate trials conducted using the same procedure. The purpose of the filtration test is to make sure that the product can successfully pass through the sand without plugging the formation.. The rate of flow of the FPS solution through the sand under a constant pressure is recorded. After the initial trial, the repeat of experiments (trial 2 and trial 3) in same tube may show decreasing flow rates, suggesting the sands have been affected by the flooding. The results have also been significant references for further tests, sand pack flooding and core flooding.

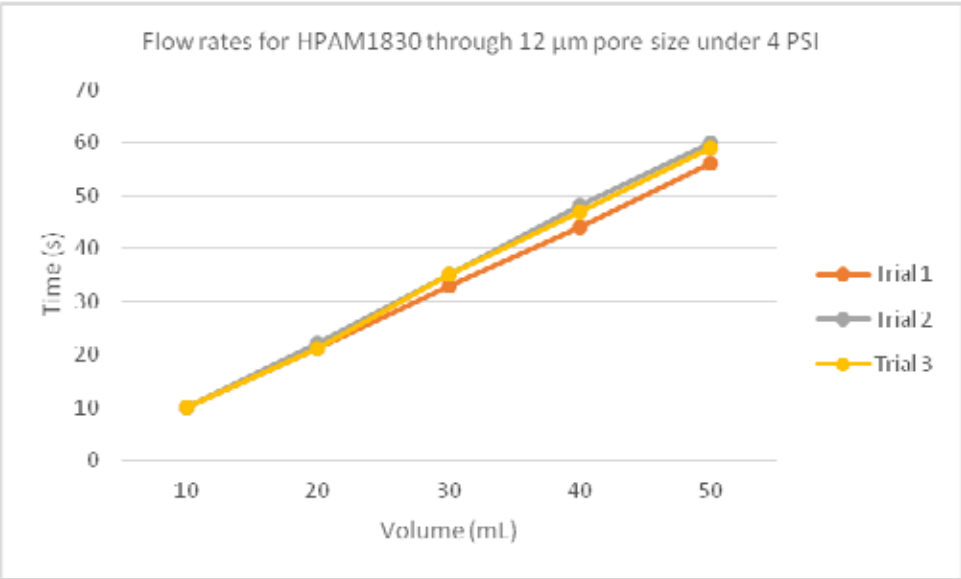


Figure 4-47: HPAM 1830 filtration test.

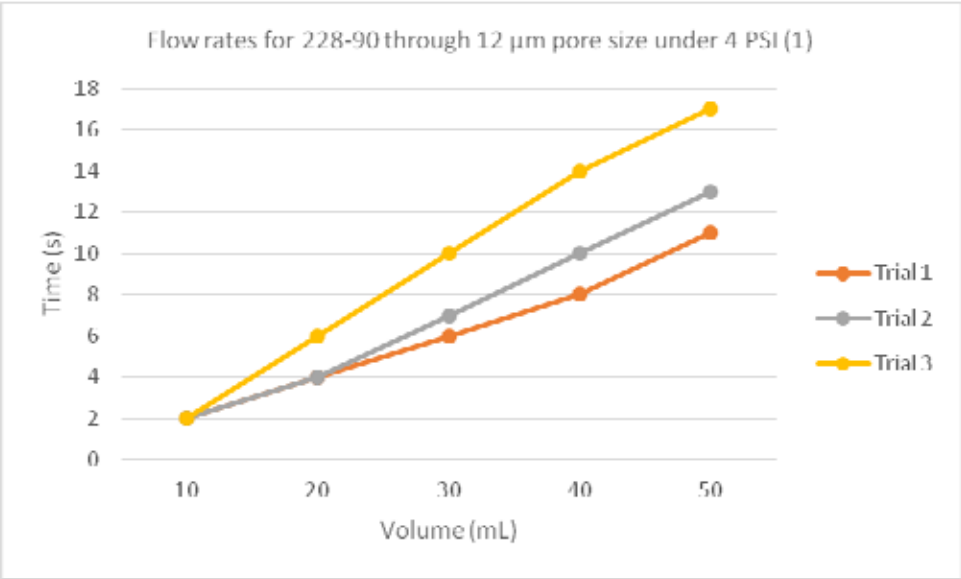


Figure 4-48: FPS-228-90 filtration test (1).

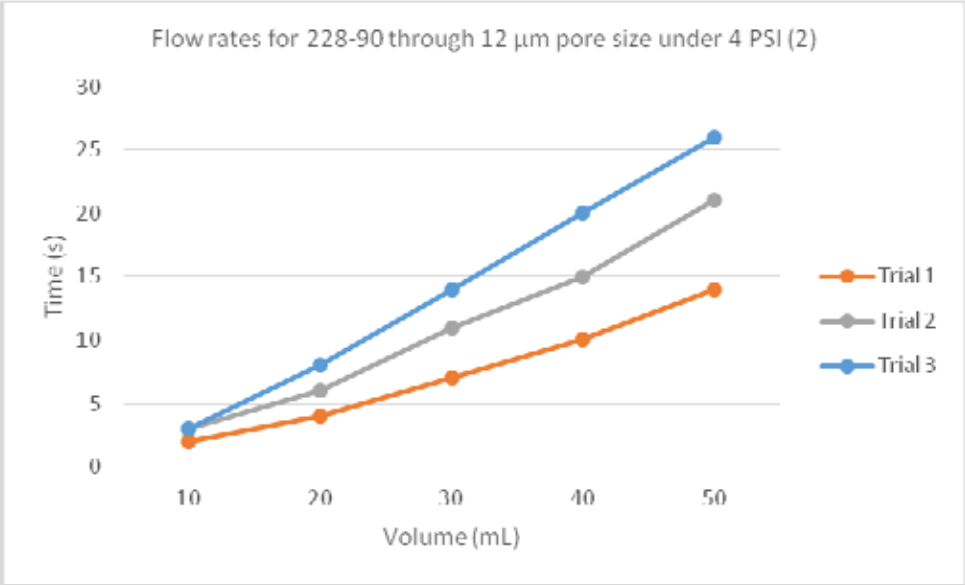


Figure 4-49: FPS-228-90 filtration test (2).

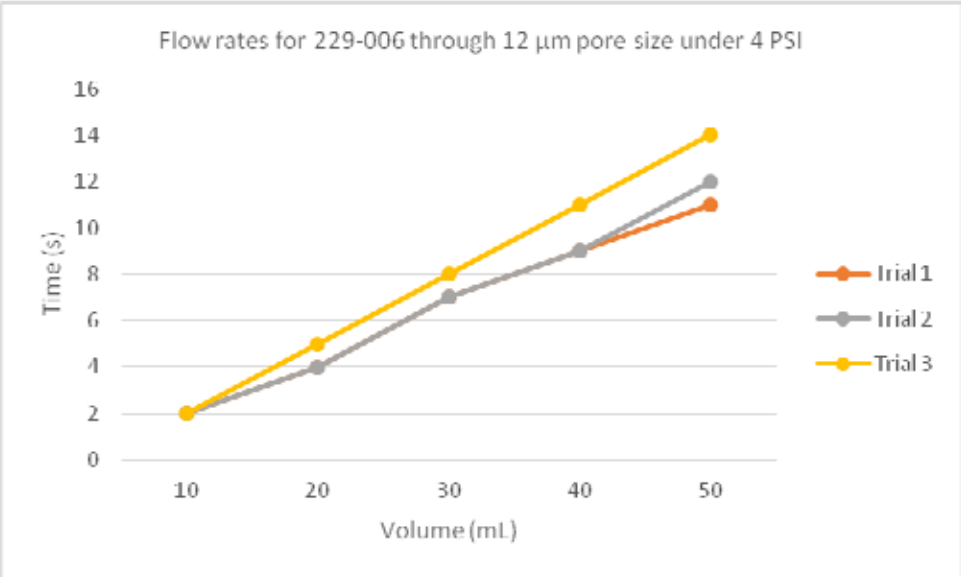


Figure 4-50: FPS-229-006 filtration test.

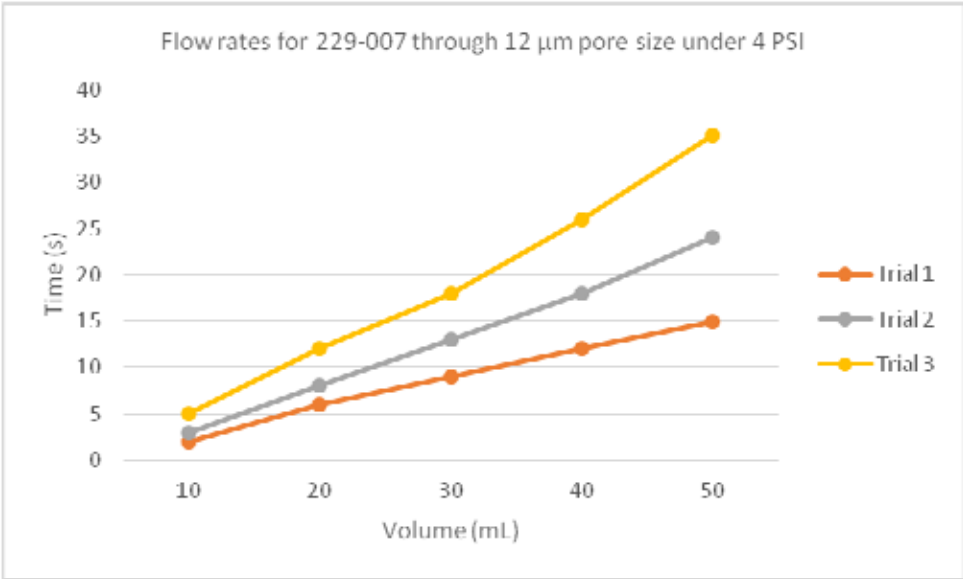


Figure 4-51: FPS-229-007 filtration test.

FPS chemicals that do not pass the filtration tests will not be considered for core flood analysis.

4.2.6 Sand Pack Flooding

Parameters for the sandpack columns are as follows: Packing is with Silica Sand F-95 (w/o sieving); the column is 16 cm x 0.64 cm length x ID; PV is 2.4 to 2.8 mL; and permeability (kw) is 3000 to 4000 mD. A general experimental procedure is as follows: Fill the column with sand and pack the column; repeat until column cannot be packed any further; vibrate the column to pack further; saturate the column with brine and weigh it before and after, the difference taken as the pore volume; next inject into the column a selected oil at a desired rate at two pore volumes, sufficient for oil saturation, and collect the effluent stream into a graduated cylinder (being finely marked, this and all others), where the amount of displaced brine is taken as a laboratory representation of original oil in place (OOIP); then push with brine initially at two pore volumes at the same rate as before, and collect into a different cylinder, followed by one pore volume of a chemical or dispersion being tested at the same rate and collecting; finally flush with one pore volume of brine and collecting; the amount of oil recovered from the chemical and final brine injections together over OOIP is % OOIP. In sequential injections, the final brine flush is replaced with either a polymer solution or a particles dispersion.

The sandpack flooding results can provide significant guidance for core flooding as the procedures and equipment are similar, but with advantages of saving time.

Table 4-8: Water Permeability

Q:	1	ml/min
dP:	3.08	Psi
Viscosity:	1	mPA.s
L:	12	Cm
A:	0.31752936	cm^2
Kw:	2963.8	mD

Table 4-9: HPAM-1830 sand pack flooding data

F-95 Sand (0.625 cm x 12 cm)		Condition	25˚C
PV=	2.32		
Permeability (Kw)=	1023	(2.31psi @ 1ml/min)	

Flow Rate: 0.25/min

	Aq. (ml)	Oil (ml)	Oil Sat.	Pressure	Total PV
Oil Sat.	1.85	5.6	79.74%	4.31	3.21

Flow Rate: 0.25/min

	Aq. (ml)	Oil (ml)	OOIP	Pressure	Total PV
Brine Flooding	6.5	1.3	70.27%	1.85	3.36
1830 Flooding	2.2	0.3	16.22%	9.00	1.08
W.C.	2.5	0.005	0.27%	3.40	1.08

1830 OOIP Recovery	16.49%
Tertiary%	55.45%

Compared to the core flood, sandpack flooding has lower porosity and higher permeability; therefore a higher tertiary recovery might be observed in the sandpack flooding experiment. Nevertheless, the sandpack flooding study can serve as a primary screening method before more expensive and lengthy

core floodings. In here our main focus is to relatively compare the FPS-flooding with the regular HPAM flooding. As shown in *Table 4-9*, by injecting one pore volume (PV) of regular HPAM (2000 ppm) solution right after the standard water-flooding, one can recover an additional 55.45% of remaining oil.

On the other hand, as shown in Table 4-10 and Table 4-11, the oil recovery of remain oil after water flooding by applying the FPS 228-73 flooding can achieve to as high as 77.78% and 73.53%, suggesting that the FPS-flooding efficiency is much higher than that of the regular HPAM flooding (55.45%).

Table 4-10: FPS-228-73 sand pack flooding data (1)

F-95 Sand (0.625 cm x 12 cm)			Condition	25˚C	
PV=	2.74				
Permeability (Kw)=	**3029**	(0.72psi @ 1ml/min)			

Flow Rate: 0.25/min

	Aq. (ml)	Oil (ml)	Oil Sat.	Pressure	Total PV
Oil Sat.	1.8	5.7	65.69%	9.8 psi	2.73 PV

Flow Rate: 0.25/min

	Aq. (ml)	Oil (ml)	OOIP	Pressure	Total PV
Brine Flooding	6	0.9	50.00%	2.14 psi	2.5 PV
228-73 Flooding + WC	5.2	0.7	38.89%	6.49 psi 4.97 psi	1.0 PV 1.0PV

228-73 OOIP Recovery	38.89%
Tertiary%	77.78%

Table 4-11: FPS-228-73 sand pack flooding data (2)

F-95 Sand (0.625 cm x 12 cm)			Condition	25˚C	
PV=	2.5				
Permeability (Kw)=	912	(2.59psi @ 1ml/min)			

Flow Rate: 0.25/min

	Aq. (ml)	Oil (ml)	Oil Sat.	Pressure	Total PV
Oil Sat.	2.28	5.02	91.20%	4.41	2.92

Flow Rate: 0.25/min

	Aq. (ml)	Oil (ml)	OOIP	Pressure	Total PV

Brine Flooding	6.7	1.6	70.18%	1.42	3.32
228-73 Flooding	2	0.2	8.77%	9.2	0.88
W.C.	2.2	0.3	13.16%	3.4	1.00

228-73 OOIP Recovery	21.93%
Tertiary%	73.53%

However, the oil recovering efficiency of the FPS flooding varies with different FPS chemicals. As can be seen from Table 4.12 and Table 4.13, both FPS 228-75 and FPS 212-140 shown worse results than the regular HPAM flooding.

Table 4-12: FPS-228-75 sand pack flooding data

F-95 Sand (0.625 cm x 12 cm)		Condition	25˚C
PV=	2.9		
Permeability (Kw)=	1170	(2.02psi @ 1ml/min)	

Flow Rate: 0.25/min

	Aq. (ml)	Oil (ml)	Oil Sat.	Pressure	Total PV
Oil Sat.	2.6	4.9	89.66%	4.44	2.59

Flow Rate: 0.25/min

	Aq. (ml)	Oil (ml)	% oil recovered	Pressure	Total PV
Brine Flooding	6.3	1.7	65.38%	1.64	2.76
228-75 Flooding	3	0.3	11.54%	3.3	1.14
W.C.	3	0.1	3.85%	1.4	1.07

228-75 OOIP Recovery	15.38%
Tertiary%	44.44%

Table 4-13: FPS-212-140 sand pack flooding data

F-95 Sand (0.625 cm x 12 cm)		Condition	25˚C
PV=	2.82		
Permeability (Kw)=	984	(2.40psi @ 1ml/min)	

Flow Rate: 0.25/min

	Aq. (ml)	Oil (ml)	Oil Sat.	Pressure	Total PV

Oil Sat.	2.6		92.20%	4.15	0.92

Flow Rate: 0.25/min

	Aq. (ml)	Oil (ml)	OOIP	Pressure	Total PV
Brine Flooding	6.4	1.5	57.69%	1.54	2.80
212-140 Flooding	2.8	0.1	3.85%	1.43	1.03
W.C.	2.9	0.1	3.85%	1.3	1.06

212-140 OOIP Recovery	7.69%
Tertiary%	18.18%

In summary, the sand pack method over estimated both secondary and tertiary oil recovery significantly. However it can still provide a quick and semi quantitative evaluation method toward FPS products optimization. Some FPS showed significant improvements in additional oil recovery in comparison to regular polymer flood but some show poor results even when the IFT is low. We feel emulsion might be the key measure toward FPS tertiary oil recovery.

4.2.7 Core flooding

Core Material: 1.5" x 12" Synthetic Sandstone Core (Permeability: 400mD)

-**Saturate core with synthetic formation brine**: The synthetic core was vacuumed to around -30psi for 6 hrs and then saturated with synthetic brine for overnight. Weighted the core before and after to calculate pore value (PV).

-**Flood with reservoir crude oil until S_{wr} approached**: Crude oil was then injected to the core until no more water coming out (less than 1%). Recorded total brine volume in this step as the oil saturation value. (1ml pushed out brine = 1ml remaining crude oil in the core)

- Flood with formation brine until S_{or} approached: Synthetic brine was then injected until water cut of 99%. Recorded total oil volume as brine flooding recovery.

-**Inject 1 PV of polymer in synthetic brine solution**: polymer solution was then injected to the core for 1 pore value. Total oil volume was recorded as chemical oil recovery.

-**Inject 1 PV of synthetic brine:** Finally, 1 PV of brine was injected to push/wash out all remaining polymer. Total oil volume was recorded as 2nd brine flooding oil recovery, which can be added up to chemical flooding as a set.

FPS-212-156 core flooding test

Table 4-14 and Table 4-15 record the core flooding results with FPS-212-156. After water flooding with Illinois synthetic brine, HPAM + brine was injected in an attempt to further increase oil recovery. Then FPS and brine flooding followed to see if it could improve oil recovery beyond that of polymer flooding

Table 4-14: HPAM + FPS-212-156 core flooding results

Receiver #	Time	Oil (ml)	Brine (ml)	Total (ml)	Flow Rate (ml/min)
Oil-1	14:37	0	0	N/A	0.25
Oil-1	15:28	19.5	16.5	36	1.0
Oil-2	15:29	0	0	N/A	1.0
Oil-2	15:57	39.75	0.25	76	2.0
Brine-3	16:21	0	0	N/A	0.05
Brine-3	7:37	10.5	38	124.5	0.05
Brine-4	7:39	0	0	N/A	0.25
Brine-4	13:14	0.5	24.5	149.5	0.05
HPAM-5	13:28	0	0	N/A	0.25
HPAM-5	15:00	2	15.5	17.5	0.25
WC-6	15:01	0	0	N/A	0.04
WC-6	12:59	0.25	21.75	39.5	0.25
FPS-7	13:21	0	0	N/A	0.25
FPS-7	14:59	2.5	22.5	64.5	0.25
WC-8	15:00	0	0	N/A	0.04
WC-8	16:30	0.01	10	74.51	0.04

Table 4-15 Brief summary of HPAM + FPS-212-156 core flooding results

Synthetic Core	PV=16.75 ml	Oil = IL #11
Permeability of Core	790.95 mD	
Brine Flooding	65.67% OOIP	Brine = IL Synthetic Brine
HPAM + Brine	13.43% OOIP	HPAM= 750 ppm 1830 in IL S.W.
FPS + Brine	14.99% OOIP	FPS= 2000 ppm 212-156 in IL S.W.

Results from Table 4-15 show that water flooding recovered 65.67 % OOIP during the core flooding test, followed by HPAM + brine flooding which improved recovery by an additional 13.43% OOIP. Following the polymer flood with the FPS flood resulted in an additional recovery of 14.99% OOIP. Therefore, a total of 94.09% of OOIP was recovered.

FPS-212-181 core flooding test (1)

Similar to the FPS-212-156 test, Table 4-16 records the core flooding results of FPS-212-181. After water flooding with Illinois synthetic brine, HPAM + brine flooding was performed to recover more oil. Then FPS + brine flooding was conducted in order to further improve oil recovery.

Table 4-16: HPAM + FPS-212-181 core flooding results

Flooding Type	Total PV injection	Total % OOIP Recovery
1st Brine Flooding	0.13	13.40%
	0.29	29.30%
	0.47	37.68%
	0.64	41.69%
	0.82	44.04%
	0.99	45.96%
	1.16	47.64%
	1.33	49.31%
	1.50	50.82%
	1.66	52.08%
	1.83	53.42%
	2.00	54.84%
	2.17	55.34%
	2.34	57.02%
	2.50	57.69%
	2.67	59.19%
	2.83	59.86%
	3.01	61.37%
	3.17	62.04%
	3.34	63.38%
	3.51	63.55%
	3.68	64.89%
	3.85	65.56%
	4.01	65.89%
	4.18	66.23%
	4.34	66.24%
	4.51	66.58%
	4.68	66.74%
HPAM Flooding	4.83	67.08%

	4.98	67.25%
	5.12	67.50%
	5.26	68.34%
	5.40	70.01%
	5.54	71.68%
	5.69	73.36%
	5.84	74.36%
	6.00	75.54%
	6.15	76.88%
	6.31	77.71%
	6.46	78.55%
	6.61	79.39%
2nd Brine Flooding	6.83	79.72%
	6.98	80.06%
	7.14	80.14%
	7.31	80.22%
	7.47	80.31%
	7.64	80.39%
	7.81	80.48%
	7.97	80.56%
	8.14	80.58%
FPS Flooding	8.27	80.58%
	8.42	80.91%
	8.53	81.16%
	8.66	81.41%
	8.79	81.50%
	8.94	82.00%
	9.09	82.50%
	9.24	83.00%
	9.38	83.67%
	9.53	84.34%
	9.69	85.01%
	9.84	85.52%
	10.01	85.85%
	10.16	86.02%
	10.29	86.19%
3rd Brine Flooding	10.45	86.35%

10.61	86.52%
10.79	86.86%
10.96	87.02%
11.13	87.19%
11.29	87.27%
11.44	87.36%
11.60	87.37%

Table 4-17: Brief summary of HPAM + FPS-212-181 core flooding results

Synthetic Core	PV=82	Oil = IL #6
Oil Saturation	72.83% PV	
Brine Flooding	66.74% OOIP	Brine = IL Synthetic Brine
HPAM + Brine	13.81% OOIP	HPAM= 1500 ppm 1830 in IL S.W.
FPS + Brine	6.82% OOIP	FPS= 1500 ppm 212-181 in IL S.W.

Results from Table 4-20 show that water flooding recovered 66.74% OOIP during the core flooding test, followed by HPAM + brine flooding which improved 13.81% OOIP more oil. After the HPAM flood, FPS + brine flooding was done and recovered an additional 6.82% OOIP. Although the results are not as good as we expected but it still indicates a promise for additional oil recovery by FPS.

The tested results are further illustrated in Figure 4-52 and Figure 4-53. With the Y-axis as the cumulated oil recovery percentages while the X-axis as the list of the collected tubes, Figure 4-52 shows the entire oil recovery process of (i) brine flooding, (ii) HPAM flooding + water chasing, and (iii) FPS flooding + water chasing. Even after the polymer flooding which recovered an additional 13.81% of OOIP, the FPS flooding can still recover a substantial amount of oil (6.82% OOIP).

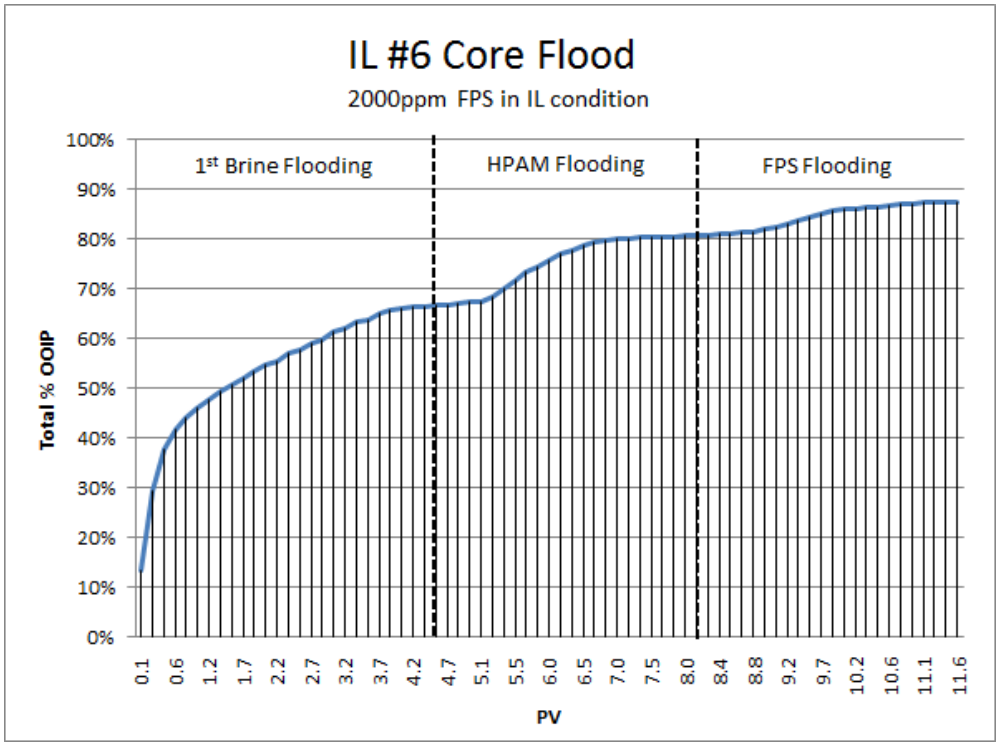


Figure 4-52: Visualized core flooding summary (1) of FPS-212-181

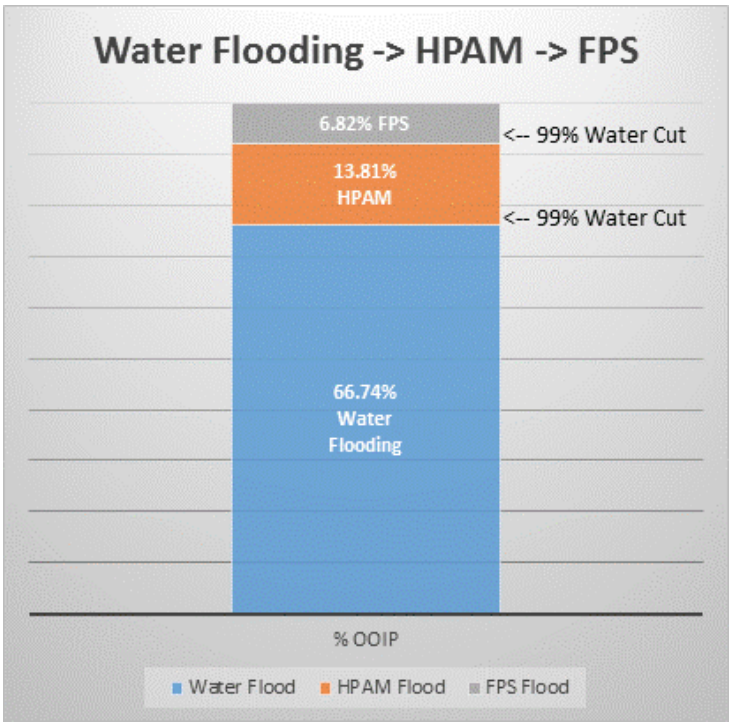


Figure 4-53: Visualized core flooding summary (2) of FPS-212-181.

FPS-212-181 core flooding test (2)

Table 4-18: Second HPAM + FPS-212-181 core flooding results

Flooding Type	Total PV injection	Total % OOIP Recovery
1st Brine Flooding	0.05	4.72%
	0.12	12.48%
	0.31	28.84%
	0.50	34.74%
	0.68	38.11%
	0.85	40.81%
	1.03	43.34%
	1.21	45.70%
	1.39	47.89%
	1.56	49.92%
	1.74	51.60%
	1.91	53.29%
	2.08	54.97%
	2.26	56.32%
	2.43	58.01%
	2.61	59.19%
	2.78	60.46%
	2.94	61.21%
	3.11	61.72%
	3.28	62.39%
	3.45	63.07%
	3.62	63.74%
	3.78	64.25%
	3.94	64.76%
	4.11	65.09%
	4.23	65.43%
	4.39	65.60%
	4.56	65.77%
FPS Flooding	4.77	65.94%
	4.97	66.19%
	5.14	66.53%
	5.28	67.54%
	5.44	68.72%

	5.60	70.07%
	5.76	71.25%
	5.93	72.43%
	6.09	73.69%
	6.26	74.87%
	6.43	75.89%
	6.59	76.90%
	6.76	77.91%
2nd Brine Flooding	6.86	78.58%
	7.03	79.60%
	7.26	80.86%
	7.42	81.87%
	7.59	82.55%
	7.75	82.88%
	7.91	83.22%
	8.03	83.47%
	8.12	83.64%
	8.30	83.81%

Table 4-19: Brief summary of second HPAM + FPS-212-181 core flooding results

Synthetic Core	PV=82.84	Oil = IL #6
Oil Saturation	71.58% PV	
Brine Flooding	65.77% OOIP	Brine = IL Synthetic Brine
FPS + Brine	18.04% OOIP	FPS= 1.5gpt 212-181 in IL S.W.

Instead of injecting FPS solution after polymer flooding, as in the first test, a second FPS-212-181 core flooding test was conducted directly after water flooding (*Table 4-18* and

Table 4-19) with a result of 18.04% OOIP recovered from core.

FPS vs HPAM

Table 4-20: Comparison of FPS and HPAM flooding

Core Flooding	Oil Saturation % PV	Brine Flooding % OOIP	*Polymer Flooding % OOIP	*Polymer Flooding % Tertiary	Polymer Injection Pressure
HPAM	72.82%	66.74%	13.81%	41.5%	12 PSI
FPS	71.58%	65.77%	18.04%	52.7%	6.5 PSI

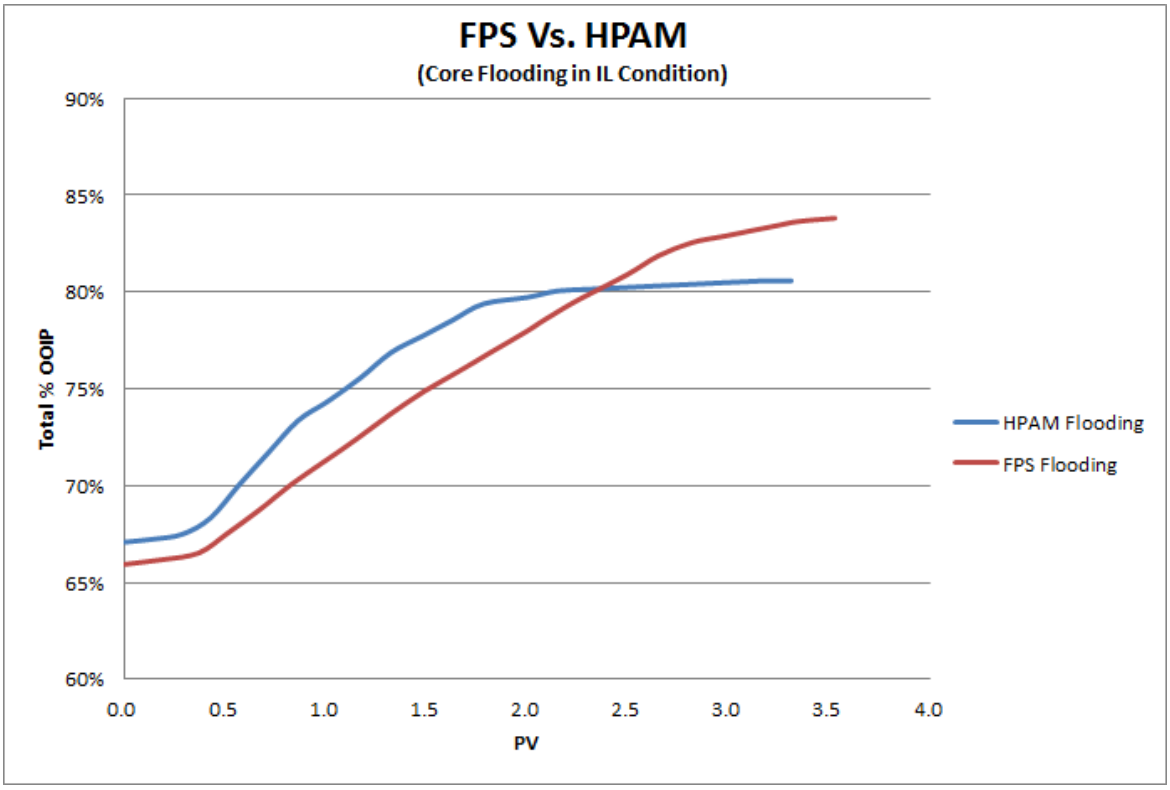


Figure 4-54: Comparison of FPS and HPAM flooding

The two tests of FPS-212-181, show the comparison of the performance of FPS and HPAM. Figure 4-54 suggests that after water flooding, instead of using polymer flooding with a recovery of 13.81% OOIP and 41.5% Tertiary, FPS flooding demonstrates a stronger ability to drive oil out (18.04% OOIP and 52.7% Tertiary).

FPS vs HPAM tests results from a third party

To further validate our results, we selected the PTS Laboratories, Inc. as a third party to conduct the standard core flooding tests (Table 4-21 and Table 4-22); and the results are summarized in Table 4-23.

The core flooding procedure includes (1) the initial oil saturation (S_{wi}), followed by (2) the water-flooding to achieve (S_{or}), then followed by a regular HPAM flooding (as shown in Table 4-21) or by a FPS flooding (as shown in Table 4-22). Evidently, the regular HPAM flooding recovered an additional portion (8.15%) of OOIP, while the FPS flooding nearly doubled the additional oil recovery (15.67%) of OOIP.

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Table 4-21: Results from third party for HPAM followed by FPS core flooding

PTS Laboratories, Inc.

ChemEOR
PTS File No. 43136

Sample No. Buff Berea SS 02 (12" long, Fired): Crude Oil Drive to Swi, Water flood followed by Polymer Injection

Sample Type: Berea Sandstone, Fired (Block Q8)
Porosity, % BV: 21.4
PV : 73.41

CRUDE OIL DRIVE TO SWI

Receiver #	Date	Time	Injection Pressure, psi	Injected Crude, ml	Produced Brine, ml	Temp. °F	~Rate, cc/min	Total H2O	Swi, %	PVs Through	Comments/Observations
1	14-May-13	1634	18.8	44.0	44.0	75	0.1	44.0	40.1	0.6	
2	14-May-13	0834	41	36.5	2.8	75	0.2	46.8	36.2	1.1	
3	14-May-13	1037	64	48.0	2.1	75	0.4	48.9	33.4	1.8	
4	14-May-13	1130	120	45.3	0.85	75	0.8	49.75	32.2	2.4	
5	14-May-13	1200	190	64.5	0.45	75	1.6	50.2	31.6	3.2	
6	15-May-13	0840	26	56.0	0.17	110	2	50.37	31.4	4.0	Begin Heating
7	15-May-13	0940	40	51.0	0.18	115	2 & 3.3	50.55	31.1	4.7	Bump & flow, continue heating.
8	15-May-13	1520	19	82.5	0.08	170	2 & 3.3	50.63	31.0	5.8	Bump & flow, continue heating to final temperature.
				427.75	50.63						

WATER FLOOD TO SOR AT 80°C

Receiver #	Date	Time	Injection Pressure, psi	Produced Fluid Crude, ml	Produced Fluid Brine, ml	Rate, cc/min	Water, Inject, ml	Total H2O	Cumulative H2O cut	PVs Through	Comments/Observations
											Start at 1200
1	16-May-13	1455	3.1	20.2	0.7	0.12	20.90	0.7		0.28	
2	16-May-13	1636	3.8	0.22	12.7	0.13	33.82	13.4	39.6	0.46	
3	16-May-13	1830	4.1	0.12	13.8	0.12	47.74	27.2	57.0	0.65	
4	17-May-13	0700	4.3	1.75	86.8	0.12	136.2	114.0	83.6	1.86	
5	17-May-13	0843	5.3	0.10	13.3	0.13	149.6	127.3	85.0	2.04	
6	17-May-13	1040	4.9	0.08	13.6	0.12	163.3	140.8	86.2	2.22	
7	17-May-13	1230	4.5	0.08	12.7	0.12	176.0	153.5	87.2	2.40	
8	17-May-13	1423	4.6	0.07	13.7	0.12	189.8	167.2	88.1	2.59	
9	17-May-13	1627	4.6	0.10	14.4	0.12	204.3	181.6	88.9	2.78	Reduce rate to 0.06 cc/min for overnight
10	17-May-13	1837	3.5	0.10	9.2	0.07	213.6	190.8	89.3	2.91	
11	18-May-13	745	3.5	0.20	49.0	0.07	262.8	239.8	91.2	3.58	Water Flood Instantaneous Water Cut = 99.6%
				23.02	239.77						Set Rate at 0.05cc/min (~1.5ft/day) - switch to polymer injection.

PTS Laboratories, Inc.

ChemEOR
PTS File No. 43136

Sample No. Buff Berea SS 02 (12" long, Fired): Crude Oil Drive to Swi, Water flood followed by Polymer Injection

Sample Type: Berea Sandstone, Fired (Block Q8)
Porosity, % BV: 21.4
PV : 73.41

POLYMER INJECTION AT 80°C

Receiver #	Date	Time	Injection Pressure, psi	Produced Fluid Crude, ml	Produced Fluid Brine, ml	Target Flow Rate, ft/day	Target Flow Rate, ml/min	Actual Flow Rate, ml/min	Total Fluids	PVs Through	Comments/Observations
P1	18-May-13	1300	9.21	0.02	14.6	1.5	0.050	0.046	14.62	0.20	750 ppm HPAM in 0.3% NaCl, start at 0745
P2	18-May-13	1740	13.28	0.02	13.2	1.5	0.050	0.047	27.84	0.38	
P3	19-May-13	0720	18.05	2.00	39.5	1.5	0.050	0.051	69.34	0.94	
P4	19-May-13	1140	19.19	0.05	14.0	1.5	0.050	0.054	83.39	1.14	Switch to 0.3% NaCl after 1 PV of Polymer
P5	19-May-13	1630	17.32	0.02	14.1	1.5	0.050	0.049	97.51	1.33	
P6	19-May-13	2135	16.37	0.01	15.0	1.5	0.050	0.049	112.52	1.53	
P7	20-May-13	0730	15.31	0.03	30.5	1.5	0.050	0.051	143.05	1.95	
P8	20-May-13	1220	15.01	0.01	14.3	1.5	0.050	0.049	157.36	2.14	Switch to 2000 ppm 212-73 in 0.3% NaCl after 1 PV
P9	20-May-13	1700	34.00	0.01	14.5	1.5	0.050	0.052	171.82	2.34	of 0.3% NaCl
P10	20-May-13	2055	53.00	0.01	12.2	1.5	0.050	0.052	184.03	2.51	
P11	21-May-13	0755	110.5	0.02	34.5	1.5	0.050	0.052	218.55	2.98	
P12	21-May-13	1155	128.0	0.01	12.5	1.5	0.050	0.052	231.06	3.15	Switch to 0.3% NaCl after 1 PV of 2000ppm 212-73 Polymer
P13	21-May-13	1650	64.5	0.01	15.3	1.5	0.050	0.052	246.37	3.36	
P14	21-May-13	2045	66.5	0.01	11.5	1.5	0.050	0.049	257.88	3.51	
P15	22-May-13	0745	66.5	0.02	33.5	1.5	0.050	0.051	291.40	3.97	
P16	22-May-13	1310	66.5	0.00	16.3	1.5	0.050	0.050	307.70	4.19	
P17	22-May-13	1615	67.5	0.00	9.2	1.5	0.050	0.050	316.90	4.32	
				2.25	314.7						Discontinue Test

Polymer: 750 ppm HPAM in 0.3% NaCl (5/17/13)
Brine Flush: 0.3% NaCL degassed and filtered to 0.45 microns
Polymer: 2000 ppm 212-73 in 0.3% NaCl
Brine Flush: 0.3% NaCL degassed and filtered to 0.45 microns
Note: Produced oil <0.01 ml or trace reported as 0.01 ml.

Table 4-22: Results from third party for FPS followed by FPS core flooding

PTS Laboratories, Inc.

ChemEOR
PTS File No. 43136

Sample No. K3-5 (12" long, Fired): Crude Oil Drive to Swi, Water flood followed by Polymer Injection

Sample Type: Berea Sandstone, Fired (Block K3)
Porosity, % BV: 21.4
PV : 73.8

CRUDE OIL DRIVE TO SWI

Receiver #	Date	Time	Injection Pressure, psi	Injected Crude, ml	Produced Brine, ml	Temp. °F	~Rate, cc/min	Cumulative H2O Produced	Swi, %	PVs Through	Comments/Observations
1	25-Sep-13	1700	30.8	43.9	43.5	75	0.1	43.5	41.1	0.6	
2	26-Sep-13	1005	62.2	30.5	3.7	75	0.2	47.2	36.0	1.0	
3	26-Sep-13	1300	127	71.0	3.6	75	0.4	50.8	31.2	2.0	Begin Heating.
4	26-Sep-13	1420	34	67.5	0.7	100	0.8	51.5	30.3	2.9	
5	26-Sep-13	1510	47	77.5	0.5	101	1.6	51.9	29.6	3.9	
6	26-Sep-13	1600	53	89.0	0.23	103	2.0	52.2	29.3	5.1	
7	26-Sep-13	1615	75	48.0	0.21	102	3.3	52.4	29.1	5.8	Heat to 176°F.
8	27-Sep-13	0845	2	83.5	0.15	176	3.3	52.5	28.8	6.9	Bump & flow.
				510.9	52.5						

WATER FLOOD TO SOR AT 80°C

Receiver #	Date	Time	Injection Pressure, psi	Produced Fluid Crude, ml	Produced Fluid Brine, ml	Rate, cc/min	Water, Inject, ml	Cumulative H2O Produced	Cumulative H2O cut	PVs Through	Comments/Observations
											Start at 1030
1	30-Sep-13	1310	3.3	27.2	0.16	0.17	27.4	0.16		0.37	
2	30-Sep-13	1430	4.1	0.25	14.3	0.18	41.9	14.5	34.5	0.57	Reduce rate to 0.10 cc/min for overnight
3	30-Sep-13	1555	4.4	0.10	13.7	0.16	55.7	28.2	50.5	0.75	
4	30-Sep-13	1753	4.4	0.02	18.8	0.16	74.5	47.0	63.0	1.01	Water Flood Instantaneous Water Cut = 99.9%
5	30-Sep-13	1945	3.2	0.01	11.1	0.10	85.6	58.1	67.8	1.16	Water Flood Instantaneous Water Cut = 99.9%
6	1-Oct-13	1000	5.4	0.35	89.5	0.11	175.5	147.6	84.1	2.38	Water Flood Instantaneous Water Cut = 99.6%
				27.93	147.56						Set Rate at 0.05cc/min (~1.5ft/day) - switch to polymer injection.

PTS Laboratories, Inc.

ChemEOR
PTS File No. 43136

Sample No. K3-5 (12" long, Fired): Crude Oil Drive to Swi, Water flood followed by Polymer Injection

Sample Type: Berea Sandstone, Fired (Block K3)
Porosity, % BV: 21.4
PV : 73.8

POLYMER INJECTION AT 80°C

Receiver #	Date	Time	Injection Pressure, psi	Produced Fluid Crude, ml	Produced Fluid Brine, ml	Target Flow Rate, ft/day	Target Flow Rate, ml/min	Actual Flow Rate, ml/min	Total Fluids	PVs Through	Comments/Observations
P1	1-Oct-13	1500	6.7	0.12	14.0	1.5	0.050	0.056	14.12	0.19	2000ppm 212-140-SC in 0.3% NaCl, start at 1000 20131001
P2	1-Oct-13	1930	9.0	0.20	13.4	1.5	0.050	0.050	27.72	0.38	
P3	1-Oct-13	0700	9.8	3.00	37.0	1.5	0.050	0.058	67.72	0.92	
P4	2-Oct-13	0845	10.0	0.08	6.7	1.5	0.050	0.065	74.50	1.01	Switch to 0.3% NaCl after 1 PV of Polymer
WC1	2-Oct-13	1115	9.0	0.10	14.0	1.5	0.050	0.094	88.60	1.20	Brine Flush
WC2	2-Oct-13	1315	8.0	0.05	13.7	1.5	0.050	0.115	102.35	1.39	Brine Flush
WC3	2-Oct-13	1600	5.7	0.01	13.2	1.5	0.050	0.080	115.56	1.57	Brine Flush
WC4	2-Oct-13	2010	5.3	0.01	13.4	1.5	0.050	0.054	128.97	1.75	Brine Flush
WC5	3-Oct-13	0615	5.1	0.05	31.5	1.5	0.050	0.052	160.52	2.18	Brine Flush
WC6	3-Oct-13	0810	5.1	0.01	5.6	1.5	0.050	0.049	166.13	2.25	Switch to 2000ppm 212-140-NP in 0.3% NaCl
P11	3-Oct-13	1240	11.8	0.01	13.0	1.5	0.050	0.048	179.14	2.43	
P12	3-Oct-13	1630	15.7	0.01	10.6	1.5	0.050	0.046	189.75	2.57	
P13	3-Oct-13	2030	18.0	0.00	11.9	1.5	0.050	0.050	201.65	2.73	
P14	4-Oct-13	0630	19.3	0.20	38.3	1.5	0.050	0.064	240.15	3.25	Switch to 0.3% NaCl after 1 PV of Polymer
WC7	4-Oct-13										Brine Flush
WC8											
WC9											
WC10											
				3.85	236.3						Discontinue Test

Polymer: 2000 ppm 212-140-SC in 0.3% NaCl
Brine Flush: 0.3% NaCL degassed and filtered to 0.45 microns (to follow 212-140-SC); Scheduled for 10/2
Polymer: 2000 ppm 212-140-NP in 0.3% NaCl; Scheduled for 10/3
Brine Flush: 0.3% NaCL degassed and filtered to 0.45 microns; Scheduled for 10/4

Table 4-23: Results from a third party for HPAM & FPS core flooding

Core Flooding	Oil Saturation % PV	Brine Flooding % OOIP	Polymer Flooding % OOIP	Polymer Flooding % Tertiary
HPAM	73.41%	45.47%	4.44%	8.15%
FPS	73.80%	53.20%	7.33%	15.67%

Other core flooding results summary

Other than the core flooding candidates discussed above, more FPS products have been put into the core flooding test for best matching with Illinois oil.

Table 4-24: FPS core flooding test under various controlled conditions

Core Type	Synth. Sandstone								F-95 sand w/1% clay		
Temp (*C)	30-40										80
Product Tested	212-162	212-158 (dry)		212-158	212-140	212-161	212-140	212-158	212-140	1830	1830 followed by 212-156
Brine Type	Synth. Brine										0.3% NaCl
Oil Type	#1	#3	#3	#3	#6	#7	#10	#10	#11	#11	#11
Brine OOIP %	65.9	51.3	53.3	62.9	61.3	64.3	59.7	64.2	55.9	61.9	65.7
1st Chemical OOIP %	12.5	31.0	19.3	21.4	18.6	11.9	17.5	15.7	29.7	21.7	13.4
1st Chemical Leftover Recovery %	36.7	63.6	41.3	57.7	47.9	33.3	43.5	43.7	67.3	57.0	39.1
2nd Chemical OOIP %	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	15.0
2nd Chemical Leftover Recovery %	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	43.7
Good/ Bad?	G	G	B	G	G	G	G	G	B	G	G

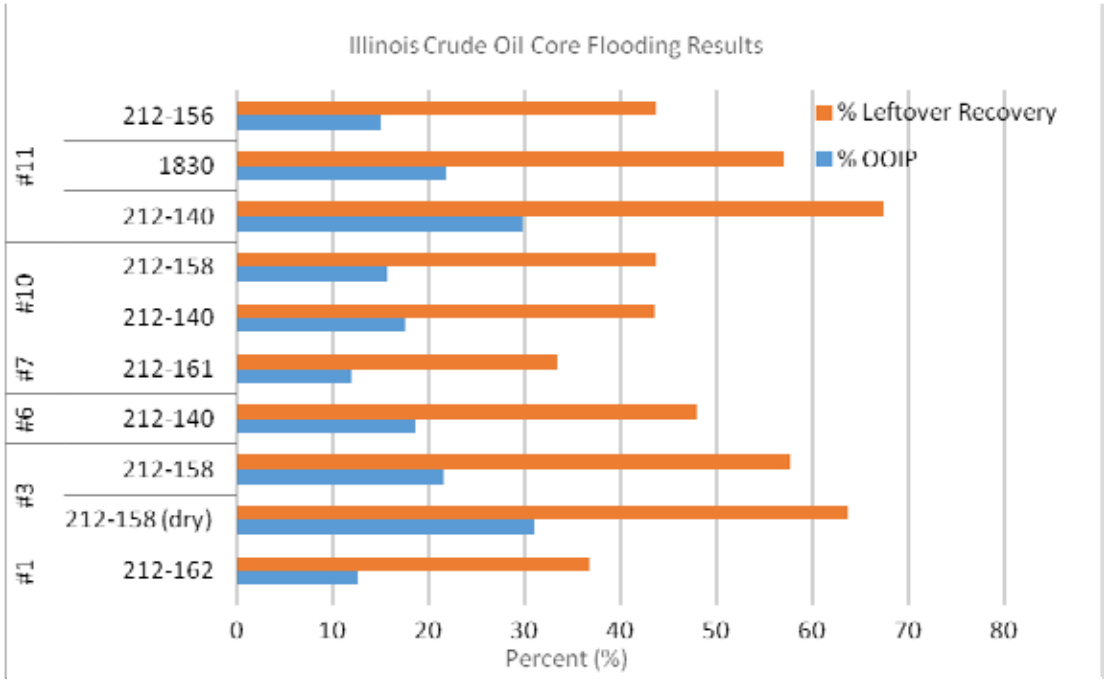


Figure 4-55 FPS core flooding tests under various controlled conditions

The results above show that most FPS flooding post water flooding can recover more than 10% OOIP, with a highest value of 31% to #3 Illinois oil. At temperature 80 ℃, FPS flooding was shown to recover an additional 15% OOIP even after water flooding and polymer flooding, demonstrating great abilities to extract oil and resist high temperature.

<u>Summary</u>

Table 4-25 Experiment summary

ID	Polymer	Dissolution	Dissolution After Drying	Emulsification	Emulsion type	IFT	Sand Pack Flooding	Core Flooding (Third-Party Lab)
212-73	ok	Good	-	Good	Oil/Water	0.06	-	Stuck
212-90	ok	Good	-	Good	Water/Oil	0.075	-	low recovery
212-91	ok	Good	-	Good	-	-	-	-
212-92	ok	Good	-	-	-	-	-	-
212-93	ok	Bad	-	-	-	-	-	-
212-94	Too hard	Bad	-	-	-	-	-	-
212-95	ok	Good	Bad	-	-	-	-	-
212-96	Too hard	Bad	-	-	-	-	-	-
212-97	ok	Good	Bad	Good				
212-98	Very Soft	Good	-	-	-	-	-	-
212-99	Soft	Good	-	-	Water/Oil	-	-	-

212-100	ok	Good	Bad					
212-102	Bad	-	-	-	-	-	-	-
212-103	ok	Good	Good (3000ppm 183 cps)	Good	-	-	-	-
212-107	ok	Good	-	Good	Water/Oil	-	-	-
212-108	ok	Good	-	Good	Water/Oil	-	-	-
212-109	Soft	Good	-	OK	Water/Oil	-	-	-
212-110	ok	Bad	-			-	-	-
212-111	Not good	-	-	-	-	-	-	-
212-112	ok	Not good	-	-	-	-	-	-
212-113	ok	Not good	-	-	-	-	-	-
212-114	ok	Good (3000ppm, 38cps)	-	Good	Oil/Water	-	-	-
212-115	ok	Not good	-	-	-	-	-	-
212-116	ok	Good (3000ppm, 31cps)	-	Good	Oil/Water	0.078	19% Recovery Kw= 589 (>100 meshes F-95) 20% Recovery Kw=887 (Silica Gel+ F-95, **2:1**)	TBD
212-117	ok	Good (3000ppm, 43.5cps)	-	Good	Oil/Water	0.07	-	-
212-118	ok	Good	-	Good	Oil/Water	-	-	-
212-119	ok	Good	-	Good	Oil/Water	-	-	-

5 FIELD TESTING and TECHNOLOGY TRANSFER EFFORTS

With the successful research and development of FPS series chemicals, PEER is also actively initiating planning for pilot-scale field trials in the Illinois Basin.

Before a FPS-EOR project can be launched in the Illinois Basin, it is necessary to carefully survey the geological conditions and evaluate the economic benefit for applying FPS-EOR technology in a targeted field. It is necessary to match the right kind of specific FPS to the formation in order to achieve economic success. Therefore, with the great efforts dedicated by our industrial partner, Gary Watts, geologic assessment of sampling sites was made followed by an economic evaluation.

5.1 Geologic Assessment of Potential Field Trial Site in Illinois Basin

Figure 5-1 Illinois Basin, Area of Interest

Table 5-1: Source of Oil Production in Illinois Basin

By System:	Upper Mississippian (Chesterian) 60%
	Ste. Genevieve Limestone (Valmeyeran) 18%
	Pennsylvanian 13%
By Lithology:	Sandstone 75%
	Carbonates 25%

Table 5-2: Oil and Gas Production Statistics in the Illinois Basin

OIL AND GAS STATISTICS	
Estimated OOIP	12 billion barrels
Historic Oil production	4.5 billion barrels
Historic Gas production	4 trillion cubic feet
Estimated future recoverable reserves	4.1 billion barrels
Current Oil production	15.2 million barrels (2004)
Overall recovery efficiency	36% [a]
Percentage recovered by secondary recovery	33% [b]

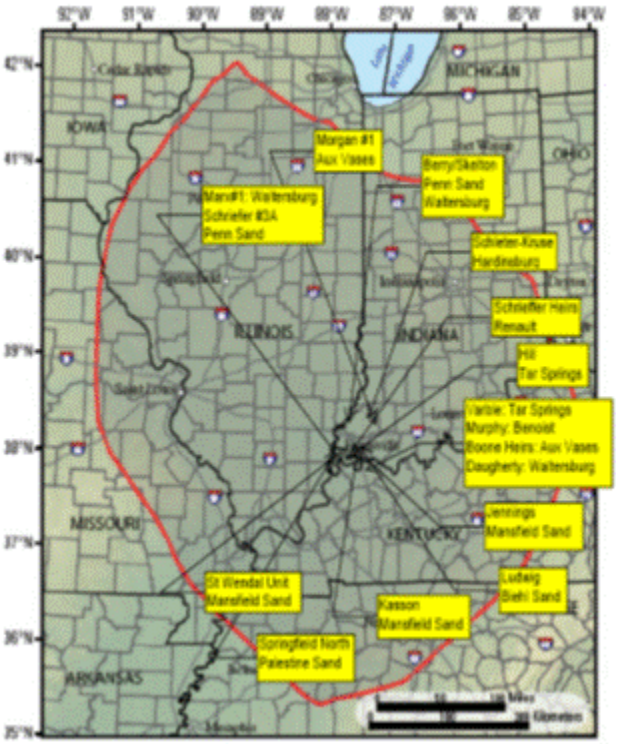
[a]*: The Illinois basin has the most onshore recovered oil ratio with respect to its OOIP in US.*
[b]: *Implementation of the secondary oil recovery technique is the key for the oil production in the Illinois Basin.*

Table 5-3: Collected Oil/Brine Samples from Various Sites of Illinois Basin

Sample Name	**Location**	**Formation**	**Depth (m)**
#1	Gibson City, IN	Pennsylvania Sand	1479-1507
#2	Gibson City, IN	Waltersburg Sand	1918-1969
#3	Gibson City, IN	Hardinsburg Sand	1950-1960
#4	Posey City, IN	Renault Lime	2592-2506
#5	Posey City, IN	Tar Springs Sand	1924-1942
#6	Henderson City, KY	Tar Springs Sand	1430-1440
#7	Henderson City, KY	Benoist Sand	1890-1900
#8	Henderson City, KY	Aux Vases Sand	1956-1962
#9	Henderson City, KY	Waltersburg Sand	1330-1340
#10	Posey City, IN	Mansfield Sand	1190-1209
#11	Vanderburgh City, IN	Biehl Sand	1351-1358
#12	Vanderburgh City, IN	Mansfield Sand	913-926
#13	Posey City, IN	Palestine Sand	1937-1951

The Illinois basin is an asymmetrical shaped structural depression that trends northwest-southeast and is filled with more than 14,000 feet of paleozoic sediment at its deepest point. The basin is bounded to the north by the Wisconsin arch, to the east by the Cincinnati arch, to the southeast by the Nashville dome, to the southwest by the Ozark dome and to the northwest by the Mississippi River arch. The layers of sedimentary strata dip gently from these boundaries toward the deepest and thickest part of the basin.

The Department of Energy (DOE) estimates for the Illinois Basin are roughly 25% of the oil remaining in place in Indiana and Illinois fields after conventional recovery is unswept (bypassed) mobile oil. This represents approximately 2.0 billion barrels of bypassed mobile oil.



Sampling sites were chosen by contacting interested operators and discussing the merits of individual fields. We concentrated more on the Pennsylvanian and Mississippian Sands, collecting information from over 20 fields, as
[a]*: The Illinois basin has the most onshore recovered oil ratio with respect to its OOIP in US.*
[b:] *Implementation of the secondary oil recovery technique is the key for the oil production in the Illinois Basin.*

Figure 5-2 Illinois Basin Sampling Sites

Heterogeneities in the basin's reservoirs, coupled with standardized well spacing, account for much of the bypassed oil. Reservoir architecture, primarily pore-space geometries, controls the distribution of fluids. Faults and impermeable barriers (shale breaks) compartmentalize fields and channel fluids. A better understanding of reservoir characteristics should lead to better predictions of both quantity and location of bypassed oil. This would lead to a more logical analysis of well locations and spacing.

The State of Indiana will grant 5 acre spacing to mature oil fields for in-fill drilling. Also the advent of horizontal drilling combined with properly designed water injection systems and the use of chemicals and polymers will greatly enhance the recovery rates of the residual oil in place.

By combining the field data and FPS screening results for the corresponding oil, a more detailed and valuable report can be generated for better EOR feasibility assessment. For example, our key research site, #11, whose oil is most frequently used in this study, was invested and some important data are listed below as Table 5-4.

Table 5-4: Field Data of the #11 Oil/Brine Sample

Sand Area	75	acres	**Average Pay Thickness**	15	Feet
Average Porosity	16.0%		**Original Oil Sat.**	72%	
Sand Volume	49,005,000	$Feet^3$	**Pore Volume**	7,840,800	$Feet^3$
Original Oil in place	1,117,209	BO	**Oil Produced**	65,450	BO
Estimated Rec. Polymer	89,377	BO	**Estimated Value $100/BO**	$8,937,672.00	

Structurally, the southern portion of the reservoir is higher in well number 52731, at a subsea depth of -946, and well number 52835, at a subsea depth of -953, and the thickest part of the reservoir in well number 52731, 23' thick.

Log data shows a very homogenous reservoir with very few shale streaks. Higher permeability numbers can be 250+ md, while lower numbers being around 20 md or less. Induction logs show that oil saturation is higher in the top and middle of the Biehl Sand, with up to 40 Ohms resistivity. Water flooding has been initiated in the north or structurally low portion of the reservoir. It is estimated that about 20% of oil has been recovered from the original oil in place.

Overall, the Biehl Sand is very attractive for Tertiary Recovery methods and would be a good candidate for FPS Polymer enhanced oil recovery. It would require reworking each well and establishing a new injection system with perha-FPS 5 acre spacing for 5th spot injection/production wells.

5.2 Economic Assessment of the FPS-EOR Technology

Comparison of the Net Present Value (NPV) Curves has been done to evaluate the economics of the FPS-EOR technology *vs* the traditional Polymer-Flooding (P-Flooding) and Surfactant + Polymer (SP) Flooding procedures. A number of factors including reservoir and economic conditions are essential in the determination of an economically successful operation. Typically, the "baseline" and "enhanced" NPV are defined as:

$$NPV^{bas} = \sum_{t=1}^{T^{bas}} \frac{p_o * Q_o (1 - f^R)(1 - f^{SP}) - C_o(Q_o)}{(1+r)^t} \qquad (10)$$

$$NPV^{eor} = \sum_{t=1}^{T^{eor}} \frac{p_0 * Q_e(1-f^R)(1-f^{SP}) - C_0(Q_e) - p_c Q_c}{(1+r)^t} - K \quad (11)$$

Where NPV^{bas} and NPV^{eor} are NPV values of the "baseline" operation, which is taken from continuous water-flooding; and of an EOR operation, which could be P-flooding, FPS-flooding, or S+P-flooding, etc. The other related parameters as:

$\boldsymbol{p_0}$ **–** the current and project oil price, which is usually taken as a constant,
$\boldsymbol{p_c}$ **–** chemical price of the additional usage of chemical agents,
$\mathbf{Q_0}$ **–** total oil recovery in the period *t* under the continuous waterflooding conditions,
$\mathbf{Q_e}$ **–** total oil recovery in the period *t* under the chemical flooding conditions,
$\mathbf{Q_c}$ – is the quantity of chemical usage,
$\mathbf{f^R}$ - is the pre-tax oil revenues any royalties rate,
$\mathbf{f^{SP}}$ – is the severance and property taxes rate,
r – is the monthly discount rate,
$\mathbf{C_0}$ **–** is the additional operational costs which is related to the oil recovery mechanism, which is as a function of waterflooding (0) or chemical flooding (e), etc,
K – is the up-front investment for the additional chemical flooding.

An economic analysis was made using the discounted cash flow (DSF) method to determine the net present value (NPV)[26]. An economic model was built up especially for chemical flooding. And the data used in this model included time (years), pore volumes (PV) injected, injected chemicals concentrations, oil price, and reservoir information shown in Table 5-4. Economic data included crude oil price, chemical costs, discount rate, annual inflation rate, tax rates, and operating costs.

Many parameters have been assumed in order to analyze the economics of EOR, as listed in Table 5-5. The assumed oil price of $100 per barrel is estimated based on crude oil prices during last 8 years (Figure 5-3). Prices for blended surfactant (surfactant, co-surfactant and co-solvent), polymer and FPS are also included.

Table 5-5: Economic Analysis Input Parameters

Capital and Operating Costs	Equipment Cost	$100,000
	Operating Cost	$5,000 per month
	Chemical Injection Cost	$0.1 per barrel
	Fluid Treatment Cost	$0.1 per barrel
Oil and Chemical Prices	Oil Price	$100 per barrel
	Blended Surfactant Price	$2.5 per pound
	Polymer Price	$1.0 per pound
	FPS Price	$1.5 per pound
General Rates	Inflation Rate	3%
	Real Discount Rate	10%

[26] Anderson G.A. et al. (2006) Optimization of Chemical Flooding in a Mixed-Wet Dolomite Reservoir. *Society of Petroleum Engineers* 10082

Figure 5-3 Crude Oil Prices during last 8 years[27]

Although different values of the chemical flooding can strongly affect the economic results of the project, in order to provide general concepts for small producers, commonly used assumptions were made in this study (Table 5-6) and the NPV ($) and internal rate of return (IRR) for each analysis case were therefore calculated using economic model (Table 5-7). Economic limit (years) means the point when the project starts to have negative discounted cash flow.

Table 5-6: Chemical Injection Design

Surfactant Slug Size (% PV)	25.00
Surfactant Concentration (wt. %)	1.00
Cosurfactant Concentration (wt. %)	0.10
Polymer Slug Size (% PV)	100.00
Polymer Concentration (ppm)	1000

Table 5-7: Economic Analysis

	S+P	P	FPS
NPV (MM$)	4.29	0.8	2.64
% IRR	52.9	48.6	112.4
Oil Reserve (MMbbl)	0.219	0.059	0.12
% Recovery	22.4	6	12.3
Economic Limit (years)	21	27	24
Chemical Cost per Barrel of Oil ($/Bbl)	19.65	8.3	6.1
Total Chemical Cost ($MM)	4.3	0.49	0.73
Capital Cost (MM$), Before Tax	0.1	0.1	0.1

[27] Data from Informine.com

The NPVs for SP flooding, P flooding and FPS flooding are 4.29, 0.8 and 2.64 MM dollars, respectively, which reflects S+P flooding has the highest revenue, FPS flooding follows, and P flooding is the last. Correspondingly, for oil reserve, SP flooding ranks the first, with 0.219 MMbbl oil recovered, i.e., 22.4% OOIP, followed by FPS flooding that recovered 0.12 MMbbl oil. On the other hand, a high revenue does not result in a high internal rate of return, compared to as high as the 112.4% IRR of FPS flooding, SP and P flooding indicate 52.9% and 48.6% IRR, almost half the value. That result will be explained by overall considering the chemical cost, oil recovery and the oil reserve. S+P flooding needs high chemical investment (4.3 MM$), yet has the highest oil recovery and is the most profitable; Polymer flooding requires initial chemical cost as low as 0.49 MM$ and correspondingly has the lowest payback which is 0.8 MM$ and 48.6%IRR, with a recovery of 6%. FPS flooding result is between these two, with 0.73 MM$ chemical cost and 2.64 MM$ NPV. What's noticeable is, FPS flooding, who only needs 1/6 chemical cost, can render more than half the profit of S+P flooding. With high IRR and low chemical cost, FPS flooding would be very economic feasible for small producers in Illinois basin who ask EOR for improving oil recovery.

5.3 Presentations and Conferences

- RPSEA Onshore Production Conference: Technology Keys to Enhance Production Operations. November 29, 2012. Houston, Texas

- RPSEA Onshore Production Conference: Technology Keys to Enhance Production Operations. October 17, 2013. Long Beach, California

- RPSEA Onshore Production Conference: Illinois Basin and Surfactant Flooding. April 30, 2014. Evansville, Illinois

- IOGA 67th Annual Convention & Trade Show, Illinois Oil & Gas Association, Evansville, Illinois.

5.4 Journal Publications

- Q. Ma et al., "Shale Gas Storage Model and Phase Behaviors: Effects of BETX Aromatic Hydrocarbon Compounds", Submitted to *Chemical Geology.*

- Q. Ma et al., "Hydrolysis and Stability of Polyacrylamide Polymers: Theoretical Studies on Effects of Divalent Cations", to be submitted to *Polymer*.

- Zijie Zhang et al., "Functionalized Polymer Surfactant for Enhanced Oil Recovery in Illinois Basin", to be submitted to *the SPE Journal*.

- Q. Ma et al., “Molecular Modeling for Designing Functionalized Polymeric Surfactant Flooding”, to be submitted in *Journal of Molecular Modeling.*

6 CONCLUSIONS

1. A method of using a special polymeric surfactant, designated functional polymeric surfactant (FPS), based upon both theoretical and experimental studies, is proving cost effective for small oil producers operating in tertiary oil recovery.

2. The most important features of these FPS chemicals are (1) the ability to lower oil water interfacial tension, (2) the capability of making water external oil in water emulsion with reasonable emulsion viscosity, (3) the capability for attaining viscosity reduction for higher viscosity oil, and (4) minimal adsorption onto the reservoir rock.

3. Sand pack experiments proved a quick screen of FPS performance and are in general agreement with core flood experiment oil recovery results.

4. The mechanism of FPS-flooding for oil desaturation may be a result of FPS chemicals having strong emulsion capability at the oil water interface, thus forming a microscopic emulsion phase with higher viscosity than the bulk water phase thereby increasing sweep efficiency.

5. Comparing FPS to P-flooding results reflect FPS provides an increased sweep efficiency and microscopic displacement yielding an additional 10% OOIP recovery.

6. Geological assessments conducted on 13 potential trial sites in the Illinois Basin indicate most are suitable candidates for tertiary recovery methods utilizing FPS-flooding.

7. Economic assessments of FPS as compared to SP and P-flooding EOR technology indicate FPS-flooding yields a higher NPV and the best IRR percentage and are economically and technologically feasible for small producers who choose to implement EOR in their mature water flood reservoirs.