Enhanced Oil Recovery Institute

EORI Technical Evaluation #2022-01

An Evaluation of a Novel Product for Inhibition or Remediation of Paraffin Deposition

Eric Robertson

Contents

Executive Summary

Evaluating the effectiveness of products and/or methods that might improve oil and gas production in Wyoming is one of the functions of the Enhanced Oil Recovery Institute (EORI). As part of that effort, EORI sponsored an evaluation of a novel product that reportedly could help reduce the detrimental effects of paraffin precipitation and deposition in oil wells.

This novel product is produced from recycled tires and is under development by a clean-tech company that converts scrap rubber materials into several beneficial products. Although analyses have shown that this product in its current form does contain a significant quantity of aromatic solvents that may act either as inhibitors of paraffin wax deposition or as a paraffin solvent, tests using the novel, tire-recycled oil (TRO) product on three different paraffinic oils from Wyoming oil fields showed that the concentrations of these solvents in the product are insufficient to provide substantial benefits for that purpose.

Background

In May of 2021, a product development company that converts scrap rubber materials into beneficial products, contacted the Enhanced Oil Recovery Institute (EORI) requesting help with testing of a new product they were developing to inhibit or remediate paraffin problems in oil wells. Paraffin in crude oil can cause problems in oil wells when paraffinic molecules crystalize and form semi-solid deposits on downhole pumps, tubing, sucker rods, and aboveground flow lines. The solid or semi-solid paraffin deposits attract and entrap other debris such as dirt, rock fines, and asphaltenes. The paraffin mass can continue to grow and eventually choke off fluid flow paths from the bottom of the well to the surface and can also restrict movement of pumps and rods making the pumping process less efficient.

The new product under development and being evaluated in this report is a “green” paraffin solvent or dispersant produced during the pyrolysis of used rubber tires. “Green” is used as an adjective because the product potentially could be a value-added product resulting from recycling used tires and minimizing their contribution to landfills. The development company currently operates a demonstration plant capable of producing the product at a rate of 2 bbl/D. The feedstock of used tires is retorted and the resulting room-temperature liquid is the tire-recycled oil (TRO) product that is under development. Preliminary laboratory analyses of this initial phase of the novel TRO product suggests that it may be an effective paraffin remediation product. Because paraffin problems are significant for many operators of Wyoming fields, EORI agreed to work on the project, which consisted of following three phases:

Phase I. Review the laboratory work already completed by the development company on the TRO product and provide a report on findings with a go/no-go decision to proceed to Phase II. This phase was completed in 2021 with the writing of the Phase I report[1] the decision to proceed to Phase II.

Phase II. Design and complete additional laboratory work to determine efficacy of the TRO product to reduce or remediate paraffin deposition in a controlled, laboratory setting. The deliverable for Phase II is a report with an accompanying go/no-go decision to proceed to a Phase III.

[1] The full Phase I report can be obtained by contacting EORI.

Phase III. Assuming a successful Phase II outcome, work with the TRO development company and at least one Wyoming oilfield operator to test the application of TRO in working oil wells with documented paraffin issues.

This report discusses work and results of Phase II of the project. As a brief review of what was accomplished in Phase I and to set the stage for the Phase II work being reported herein, the conclusions of Phase I are listed below:

- Gas chromatograph/mass spectrometer (GC/MS) work indicated that the TRO product contains a significant quantity of aromatic solvents and may act as an inhibitor of paraffin wax deposition or as a paraffin solvent.
- The residual metals in the TRO product should not inhibit the ability of the product to dissolve paraffin.
- The asphaltenes present in the TRO product were at a concentration typical of a very low-density crude oil and should not hinder the solvation of paraffin.
- The cloud point testing done in 2014 to determine the ability of the TRO product to lower the cloud point of paraffinic oils was inconclusive, mainly because of poor samples and insufficient tests to determine optimal product concentrations.
- Based on these conclusions, it was recommended to proceed to Phase II and to design diagnostic tests in a controlled laboratory setting to determine the effectiveness of TRO as a paraffin solvent and dispersant.

Pour Point Tests Experimental Design and Results

Some of the work in Phase I focused on measuring cloud point changes using a clear, single-component paraffin as a proxy for paraffinic crude oil. The cloud point is the temperature at which paraffin crystals start to form and is deduced by visual inspection as the clear liquid begins to become cloudy. The tests in Phase I to determine the effectiveness of the TRO product to lower cloud point proved to be inconclusive.[2]

To follow-up with the inconclusive cloud point tests in Phase I, alternative tests (pour point) were designed that also can be used to determine the effectiveness of an additive to lower paraffin deposition. Cloud point tests cannot be done with paraffinic crude because crude oils are generally not clear, making determination of the cloud point (first paraffin crystallization) impossible. The pour point of a paraffinic crude oil is the temperature at which the oil no longer pours (complete paraffin crystallization). The accuracy of the pour point tests is ± 5°F.

Table 1 lists the locations of the wells where the crude oil samples were collected that were used in the pour point tests as well as the pour point of each unadulterated crude oil. The crude oils were collected from three different basins and three different formations, ensuring that each oil was unique and distinctive. Each of the operators involved with collecting the crude oil samples indicated that paraffin issues were routinely needing to be addressed in the normal operation of these fields and wells.

[2] Complete details of the cloud point tests can be found in the Phase I report.

Wyoming Crude Oils Used in Pour Point Test Matrix

County	Natrona	Converse	Carbon
Basin	Wind River	Powder River	Hanna
Formation	Cody	Teapot-Teckla	Sundance
Field	Raderville	Well Draw	Elk Mountain
Well Name	Federal 1-22-B	Fed Larson 1-1	UPRR Anschutz Ranch 1
API # of well	49-025-23399	49-009-20784	49-007-05452
Pour Point	-5°F	-20°F	95°F

Table 1. Information pertaining to the crude oils used in the pour point experimental matrix of Phase II of this project.

The three crude oil samples were subjected to pour point testing by ASTM method D-97-09 conducted by Energy Laboratories, Casper, Wyoming. After establishing a baseline pour-point for each sample, the TRO product was added at mass concentrations of 250 ppm, 1000 ppm, 5000 ppm, 10,000 ppm (1%), and 50,000 ppm (5%). Pour points were established for each concentration of TRO for all three crude oils. A commercially available cloud point depressant from an oilfield service company was also tested at a concentration of 1000 ppm[3] in all three crude samples.

The tests showed that the addition of TRO at any of the concentrations tested did not produce a statistically significant change in the pour points for any of the crude oils used in the experimental matrix. All the results were contained within the accuracy of the experimental error of the tests. The addition of the commercial pour point depressant at the one concentration tested did show a drop in pour point temperature for one of the crude oils, but not for any of the others.

Paraffin Dissolution Tests Experimental Design and Results

The paraffin dissolution experimental matrix (discussed below) was developed to test TRO's effectiveness as a paraffin ball solvent. The dissolution tests measured the amount of a ball of paraffin of known mass that was dissolved by 20 mL of a test solvent inside a gently agitated, sealed glass bottle. The paraffin ball was weighed initially and then again after 60 hours of gentle agitation inside the glass bottle with the test solvent followed by 24 hours of drying in a fume hood. The percent dissolved was obtained by the following equation:

$$M_{P_D} = \frac{M_{P_i} - M_{P_f}}{M_{P_i}} \times 100,$$

where M_{PD} is the mass of paraffin dissolved by the test solvent (as a percent of initial mass), M_{Pi} is the initial mass of the paraffin ball and M_{Pf} is the final mass of the paraffin ball after drying. The solvent experimental matrix tested the performance of the TRO product compared to three proprietary commercial solvents (CS) provided by an oilfield service company and also to 100% xylene, which is an aromatic solvent frequently used to resolve paraffin problems in oil wells. The composition of the three commercial solvents was not known. Three different types of paraffin were used in the test matrix: paraffin from collected from the Teapot Formation, paraffin from the Turner Formation, and a generic paraffin collected from an eastern Wyoming pipeline. The amount of paraffin in each dissolution test was roughly the same at about 2.5 grams. In order for the tests to quantitatively measure paraffin solvation, there must be some amount of paraffin remaining in all tests. Accordingly, the amount of

[3] The concentration of 1000 ppm used for the commercial pour point depressant was recommended by the supplier.

paraffin initially added to the system was designed to be more than could be dissolved by any solvent. Results from the paraffin dissolution tests are shown in Table 2.

	Percent of Paraffin Dissolved		
Test Solvent	Teapot	Turner	Pipeline
TRO	5	20	14
CS-A	61	60	66
CS-B	55	57	60
CS-C	46	58	54
Xylene	67	66	54

Table 2. Results of paraffin dissolution tests showing the percent of paraffin dissolved after drying. The highlighted cells performed the best for the paraffin/solvent combinations tested.

Paraffin Dispersant Tests Design and Results

The paraffin dispersant experimental matrix and tests (discussed below) were developed to test TRO's effectiveness as a paraffin dispersant and were designed to simulate dispersion of paraffin already deposited on downhole tubulars. These tests were qualitative (visual) inspections of how well a test fluid dispersed a ball of paraffin suspended in water inside a sealed glass container.

The test procedure was as follows: a ball of paraffin was placed inside a glass container filled with 100 mL of produced water.[4] One milliliter of a test dispersant was added and then the container was sealed. The sealed bottle containing water, paraffin, and the test dispersant was placed on a shaking machine, which provided continuous, gentle agitation. The bottles were removed from the shaker after 18 hours for final evaluation.

The test matrix included paraffin from the same locations as in the solvent tests (Teapot, Turner, and Pipeline) and six different test dispersants: one was the TRO product, another was plain water, and the other four were commercial dispersants (CD) supplied by an oilfield service company. Table 3 shows the experimental matrix and lists the sample identification labels for the paraffin dispersant tests.

	Sample Identification		
Test Dispersant	Teapot	Turner	Pipeline
TRO	TP1	T1	P1
CD-A	TP2	T2	P2
CD-B	TP3	T3	P3
CD-C	TP4	T4	P4
No Additive (water only)	TP5	T5	P5
CD-D	—	T6	P6

Table 3. Experimental matrix and sample identification used for testing the efficacy of certain test-dispersants.

The results of the dispersant tests are grouped by paraffin source: Teapot paraffin, Turner paraffin, and generic pipeline paraffin. Figure 1 through Figure 3 contain photos and qualitative descriptions of the results after 18 hours of gentle agitation. The bottles in these figures are labeled according to the nomenclature in Table 3.

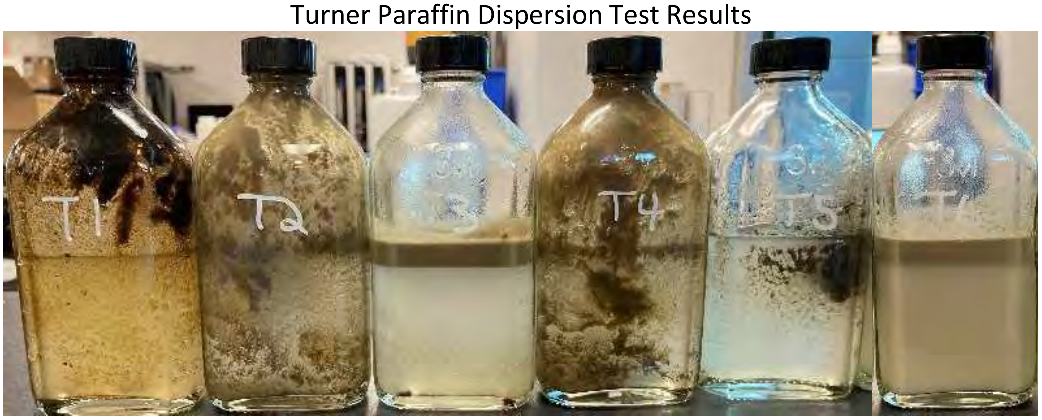
[4] The produced water used in these tests was a mixture of produced water from around the Powder River Basin, Wyoming.

Teapot Paraffin Dispersion Test Results

Sample ID	Description
TP1 (TRO)	100% dispersed, stuck to glass, sticky, thin HC layer on surface of water phase
TP2	100% dispersed, clean glass, nice HC layer, deeper tone of HC phase
TP3	100% dispersed, clean glass, nice HC layer
TP4	100% dispersed, stuck to glass, chunky HC layer
TP5 (water)	Polished ball, clean glass, no HC layer

Figure 1. Teapot paraffin ball photo and description of glass containers after 18 hours of gentle agitation. The hydrocarbon (HC) layer is on the surface of the water. The highlighted samples are those with the most favorable results.

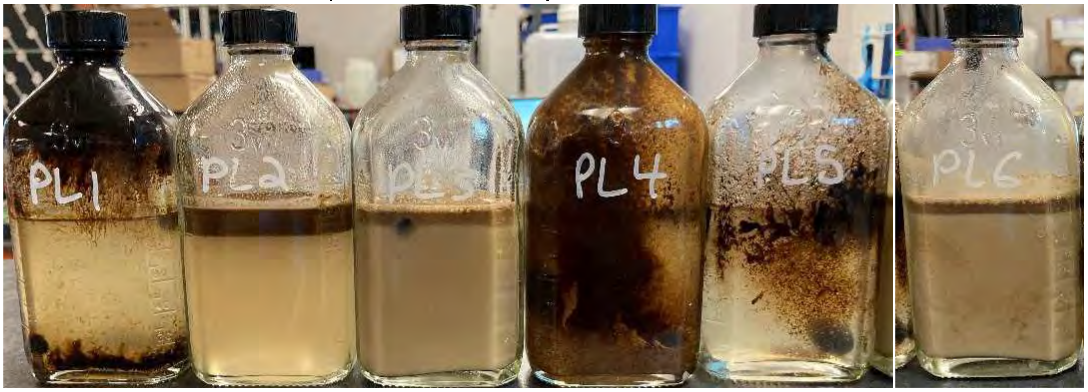
Turner Paraffin Dispersion Test Results



Sample ID	Description
T1 (TRO)	95% dispersed, stuck to glass, sticky, no HC layer
T2	100% dispersed, stuck to glass, soft, hydrated, chunky HC layer
T3	100% dispersed, clean glass, nice HC layer
T4	100% dispersed, stuck to glass, hydrated
T5 (water)	30% dispersed, stuck to glass, sticky, no HC layer
T6	100% dispersed, clean glass, nice HC layer

Figure 2. Turner paraffin ball photo and description of glass containers after 18 hours of gentle agitation. The highlighted samples are those with the most favorable results.

Pipeline Paraffin Dispersion Test Results



Sample ID	Description
PL1 (TRO)	80% dispersed, stuck to glass, sticky, no HC layer
PL2	100% dispersed, clean glass, nice HC layer
PL3	50% dispersed, clean glass, nice HC layer
PL4	100% dispersed, stuck to glass, sticky, no HC layer
PL5 (water)	30% dispersed, stuck to glass, sticky, no HC layer
PL6	95% dispersed, clean glass, nice HC layer

Figure 3. Pipeline paraffin ball photo and description of glass containers after 18 hours of gentle agitation. The highlighted sample is that with the most favorable results.

Discussion of Results

Pour Point Tests

The pour point test results showed no statistically significant drop in pour point temperature with the addition of TRO at any of the mass concentrations tested (from 0 to 5%). Perhaps, if higher concentrations of TRO were added, a lowering of the pour points might have been achieved.

The tests with a commercial pour point depressant at a concentration of 1% resulted in a statistically significant drop in pour point for one of the crude oils, but not for the other two. Due to miscommunication, the given procedures to test the commercial depressant at the same concentrations as those for the TRO (from 0% to 5%) were not followed. The pour point tests were inconclusive because both the TRO product and the commercial product failed to lower the pour points of the crude oils at the concentrations tested. Tests designed with higher concentrations of the TRO and commercial depressants could be done in the future to achieve definitive results.

Dissolution Tests

The paraffin dissolution tests were quantitative tests that determined the mass of the paraffin that was dissolved after being submerged in a test solvent for 60 hours and then dried. Xylene (an aromatic solvent) was the best performing solvent for the Teapot and Turner paraffins at 66% and 67% dissolution respectively, and the commercial solvent CS-A was best for the pipeline paraffin at 67%. The TRO product’s average paraffin dissolution was significantly lower—13% for all three paraffins—than the average paraffin dissolution of the commercial solvents—59%.

Note that certain solvents performed better with different paraffins, indicating the need to individualize the selection of the solvent and match it to a particular paraffin. Each paraffin has a different molecular composition, as does each solvent. Selecting an appropriate solvent for a given paraffin will require testing an array of solvents—a one-size-fits-all approach to paraffin solvent selection is not recommended.

Potential options for improving TRO's effectiveness as a paraffin solvent include:

- Increasing the concentration of aromatic solvents. The TRO product contains about 50% aromatic solvents by mass.[5] Increasing the amount of solvent in the product, if possible, may result in a better paraffin solvent.
- Tailoring the composition of the solvents in the product. The version of TRO tested herein contains a number of different aromatic solvents. Given that each crude oil-based paraffin is different, being able to tailor a product by manipulating the dominant solvent to target a specific paraffin may be important.

Dispersion Tests

The paraffin dispersion tests were qualitative tests based on visual findings:

- Cleanliness of the glass
    - Clean glass indicates that the product is able to remove and keep paraffin from redepositing on flow surfaces.
- Dispersion of Paraffin Sample
    - The percentage of the original paraffin ball that is broken down.
- Water Quality
    - The quality of the water (cloudy, dark, clear, etc.) can provide insight into how difficult it may be to separate the dispersed paraffin from the produced water.
- Quality of Hydrocarbon Phase
    - The color and thickness of the hydrocarbon phase on the water's surface provides insight into how well the dispersant removes the dispersed paraffin from the water phase. A thick hydrocarbon phase formed by the dispersed or dissolved paraffin deposit is ideal.

Effective paraffin dispersants necessarily contain both effective solvents and surface-active agents: solvents to dissolve the paraffin, and surface-active agents to prevent the dissolved paraffin from redepositing onto solid surfaces. As with the paraffin dissolution tests, different dispersants performed better with different paraffins. Selection of the most appropriate dispersant for a given paraffin will require an array of tests as done in this work. The TRO product did show the ability to disperse more than 80% of the paraffin present in all three tests because of the solvents it contains. However, it did not create a manageable hydrocarbon phase in two of the three tests probably because it did not contain an appreciable volume of surface-active agents. In the test where it did create a thin hydrocarbon layer (Teapot), it left almost all of the dispersed paraffin redeposited on the glass surface. The TRO product outperformed the water sample, was roughly equivalent to CD-C, and significantly underperformed against the better commercial dispersants tested.

Potential options for improving TRO's effectiveness as a paraffin dispersant include:

- Increasing the concentration of aromatic solvents. The best dispersants tested were able to break down the whole paraffin ball, but the TRO was able to break down or dissolve only 80% of

[5] Contact EORI for detailed information on TRO product composition.

the paraffin. Increasing the amount of solvent in the product, if possible, may allow the product to fully break down the paraffin.

- Adding a surface-active agent. There was no evidence of surface-active agents (surfactants) in the chemistry of the TRO product. However, if an effective surfactant(s) could be added to the product, it may keep the dissolved portion of the paraffin in solution in a hydrocarbon phase instead of being re-deposited on a solid surface.

Summary

Assuming application costs were equivalent between TRO (with no improvements) and commercial treatments, these tests show that the TRO product would not compete well with the best-performing commercial paraffin solvents and dispersants. However, we see promise for the product as a paraffin solvent if further development is undertaken to increase the aromatic solvent concentration, or as a paraffin dispersant if the solvent and surfactant concentrations were increased.

Go/No-Go Decision to Proceed

Based on the results and discussion of these tests, EORI does not see a compelling reason to proceed with a Phase III (field test) of the TRO product at this time. If future refinements to the product increase its ability to lower crude oil pour point, or to dissolve or disperse paraffin, EORI would be willing and desirous to re-engage with the manufacturer to conduct further tests.