VisRed

A single solution for multiple applications along the crude oil & petroleum fuel value chain

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INTRODUCTION AND KEY CONCLUSIONS

The accelerating green agenda, accentuated by the Covid-19 pandemic, is raising important questions regarding "peak oil", a flattening in demand growth and the prospect of oil reserves that are costly to commission into production being "orphaned". However, a comprehensive shift to renewable sources will take many years to complete, during which period there will be a continued demand for fossil fuels. Technologies that can help to mitigate some of the unacceptable environmental characteristics of oil, in terms of both its production and use, have significant value potential.

Given a relentless increase in overall energy demand, heavy crude oil reserves have become an important resource for oil and gas producers and will continue to be so during this transition to renewables. However, production and transportation are challenging due to the high viscosity of the crude oils. These challenges are typically addressed by using a viscosity reducer or by applying heat, sometimes in combination with each other. Nevertheless, many viscosity reducers are either toxic and/or expensive, while thermal methods (e.g. Steam Assisted Gravity Drainage, Cyclic Steam Stimulation) are energy and water intensive.

A proprietary chemical has been developed by Carbon Chain Technologies Limited ("CCTL") and tested in various formulations. As described below, its effect on heavy crudes has been studied at a range of low concentrations, without introducing heat; whilst its capability to increase the combustion efficiency of commercially available petroleum fuels in gasoline and diesel-powered road vehicles, improving miles per gallon ratios and reducing carbon emissions, has also been evaluated.

It has been concluded that the chemical, **VisRed** ("Viscosity Reducer"), shows potential to offer solutions for a range of applications at multiple points along the crude oil & petroleum fuel value chain.

In order to assess this potential, a team from the Department of Petroleum Engineering at Texas A&M University ("TAMU"), led by Dr Berna Hascakir, investigated the following:

- The performance of VisRed as a viscosity reducer
- Changes in Crude Oil Composition after interaction with VisRed
- Impact of Changes in Dose Ratios of VisRed on Viscosity Reduction
- Chemical and Physical Characterization of Heavy Crude Oils Before and After Blending with VisRed

Dr Hascakir also conducted coreflood experiments to assess VisRed's capability to enhance recovery of crude oil from porous media such as Canada oil sands.

In addition, the potential for one of the VisRed formulations to increase combustion efficiency in petroleum fuels was evaluated by a team from the Environment & Air Quality Division at the Texas A&M Transportation Institute.

SUMMARY RESULTS

1. Viscosity Reduction

a. Viscosity reductions at room temperature were observed in multiple crudes after blending with VisRed.
b. When applied to a bituminous Athabasca oil sample from the Fort McMurray area, VisRed was more effective at reducing the viscosity of this oil than toluene (a well-known viscosity-reducing solvent): at progressively higher dose ratios, this out-performance became more marked.
c. VisRed was found to reduce the impurity content of existing aromatics while increasing the overall content of aromatics having high solvent power.
d. Using SARA fractionation tests, viscosity reductions in VisRed blends were shown to correlate with increases in aromatic and/or resin fractions (increases in resins can also increase the solvent power).
e. VisRed was shown to have a catalytic effect in promoting this increase in aromatic content: and because a chemical change takes place in the oil, it does not subsequently revert to its previous state (c.f. the effect of cooling to ambient temperature following thermal processes, or separation from miscible diluents).

2. Concentration of impurities to facilitate removal

a. VisRed was dramatically effective at concentrating the impurities (metals, sulfur etc) found throughout the crude oil into the asphaltene fraction.
b. Adding a simple alkane (e.g. *n*-pentane) to the crude causes asphaltenes in solution to precipitate out. Precipitates can then be filtered away – this is a standard, well understood technique.
c. By loading the asphaltene fraction with substantially all the impurities and then filtering this away, the de-asphalted oil (DAO) produced will have an even lower viscosity.
d. As well as being easier to handle, the DAO will have a higher hydrocarbon content, beneficial to the refining process. Bituminous crudes are typically more costly and complex to refine.

3. Potential as an EOR fluid to enhance recovery of oil from porous media

a. Coreflooding experiments were performed on the Fort McMurray oil and another oil, Oil X.
b. Core-flooding is a laboratory test in which a fluid or combination of fluids is injected into a sample of oil-bearing rock or sand (“porous media”), simulating the use of the fluid in reservoir conditions.
c. For the Fort McMurray oil, the addition of VisRed increased the recovery of oil from the oil sand sample by approximately 33%, supporting the hypothesis that VisRed has potential as an EOR (Enhanced Oil Recovery) fluid.
d. In Oil X, another Athabasca crude, VisRed did not produce a decrease in viscosity but nevertheless showed a 50% increase in oil recovery, showing that VisRed’s mechanism for oil recovery in porous media is different from that observed blending with oil at the surface.

4. Fuel Combustion Enhancement

The use of VisRed to increase combustion efficiency in petroleum fuels was found to be highly effective, with reductions in consumption of 7.3% in gasoline and 13.7% in diesel observed.

A. Performance of VisRed as a Viscosity Reducer

SUMMARY

The performance of VisRed as a viscosity reducer was tested on 11 low API gravity, high viscosity crude oil samples. Four of these 11 crude oil samples are classified as bitumen, one as wax, four as heavy oil, and two as extra-heavy oil. The samples originated from wells in Texas, California, Alaska, Canada, Indonesia, Colombia and Venezuela. The tests were performed in May 2019.

Viscosities of the unblended crude oils and crude oil-VisRed blends (at 1:1000 vol/vol) were measured at four different temperatures and compared.

For nine of the crude oil samples (two of the bitumen samples, the wax sample, the heavy oil samples and the two extra-heavy oil samples), successful viscosity reduction was observed even at room temperature. This was further investigated by measuring the asphaltene content of the initial crude oil and the VisRed-crude oil blended samples. At room temperature, a decrease in the asphaltene content of those crude oil samples with significant viscosity reduction was observed. Hence, the preliminary conclusion was that VisRed chemically alters the crude oil samples even at room temperature, resulting in significant viscosity reduction.

The impact of time in the preparation of VisRed was also investigated and it was found that the waiting time (i.e. reaction time) is critically important for the viscosity reduction.

These first results were very promising in respect of viscosity reduction of high viscosity crude oils, particularly given the small proportion of VisRed used to prepare the blends and the low cost of the VisRed components. The results indicate that VisRed has potential to be used as Enhanced Oil Recovery fluid to extract high viscosity crude oils and for crude oil transportation.

MATERIALS AND METHODS

Changes in viscosity were tested for 11 different crude oil samples following blending of those samples with VisRed. Properties of the crude oil samples are listed below in Table 1 in terms of API gravity, viscosity at room temperature, n-pentane insoluble asphaltenes, and elemental analysis.

Table 1 Properties of 11 Crude Oil Samples

Oil Type	API Gravity	Viscosity at 21°C, cP	n-pentane insoluble asphaltenes, wt%	Elemental Composition					
				C, wt%	H, wt%	S, ppm	Ni, ppm	V, ppm	Na, ppm
Oil 1	8.19	53,200	34.30	80.3	10.3	68700	80	218	235
Oil 2	27.05	676	45.30	84.4	13.4	1190	7.46	0	14.8
Oil 3	17.12	607	12.57	81.3	11.5	32000	4.31	10.4	21.5
Oil 4	6.11	1,979,082	40.08	81.2	10.4	58200	9.76	258	504
Oil 5	7.97	384,482	22.26	83.5	10.6	36000	95.3	402	58.1
Oil 6	12.09	10,139	28.58	80.9	10.8	44100	68.1	172	23.3
Oil 7	18.84	884	23.76	81.0	11.0	14300	20	38.8	74.5
Oil 8	11.56	296,655	38.76	80.6	10.5	52400	88.4	469	8.46
Oil 9	12.56	263,273	38.08	72.91	10.53	8100	20.9	77.3	17
Oil 10	10.01	35,257,536	42.41	80.8	10.3	62200	100	512	209
Oil 11	12.19	237,794	23.35	80.9	11.0	23500	80.3	110	67

Oils 1, 4, 6 and 10 are categorized as bitumens. Oil 2 is wax. Oils 3, 7, 9 11 are heavy oils. Oils 5 and 8 are extra heavy oils. The samples originated from wells in Texas, California, Alaska, Canada, Mexico, Colombia, Venezuela and Indonesia.

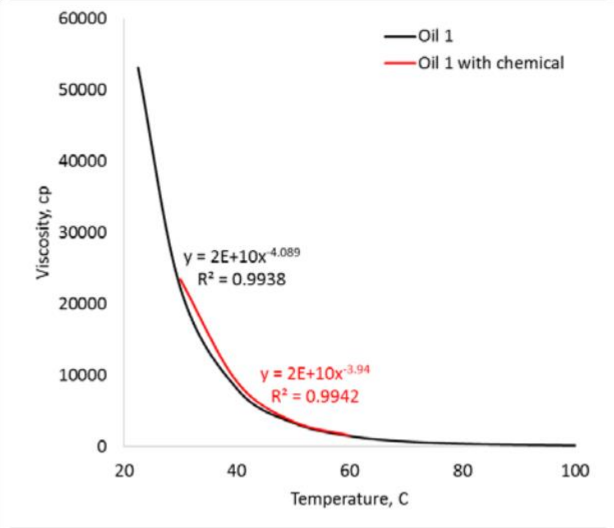
The VisRed was prepared first and allowed to remain at room temperature for at least 3 days (72 hours). 1 ml of VisRed was blended with 1,000 ml of each of the crude oil samples and the viscosity of the blends was measured using a Brookfield DV III Ultra Rheometer at four different temperature values (30°C, 40°C, 50°C, and 60°C).

RESULTS

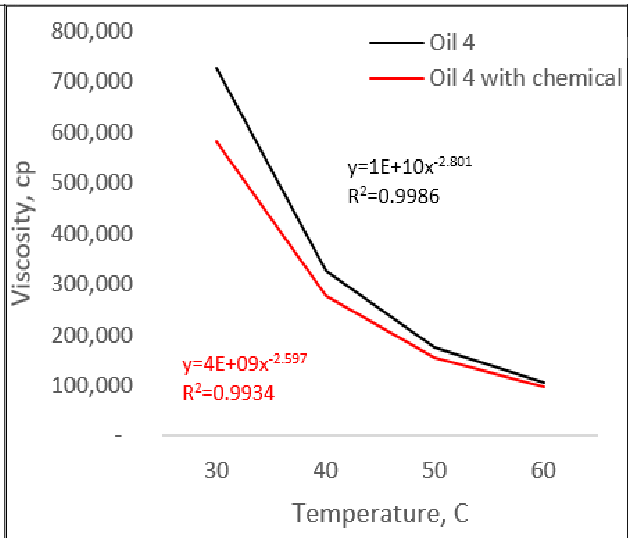
A. Viscosity Reduction by Crude Oil Type: results are grouped on the basis of crude oil types.

1. Results of Bitumen Samples

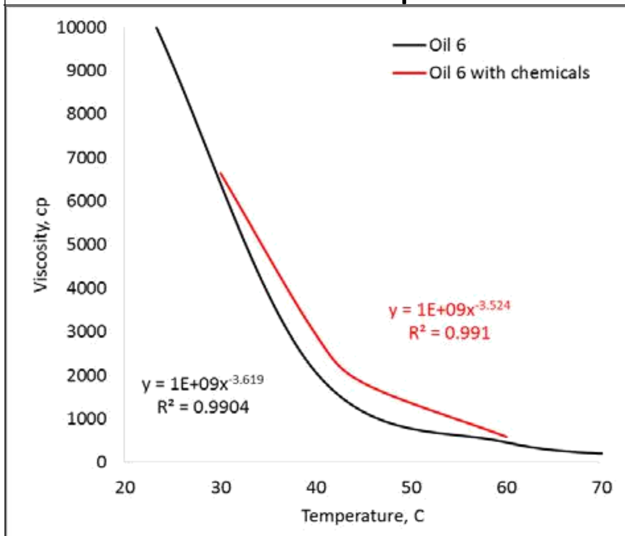
Figure 1 summarizes the viscosity results of all tested bitumen samples.



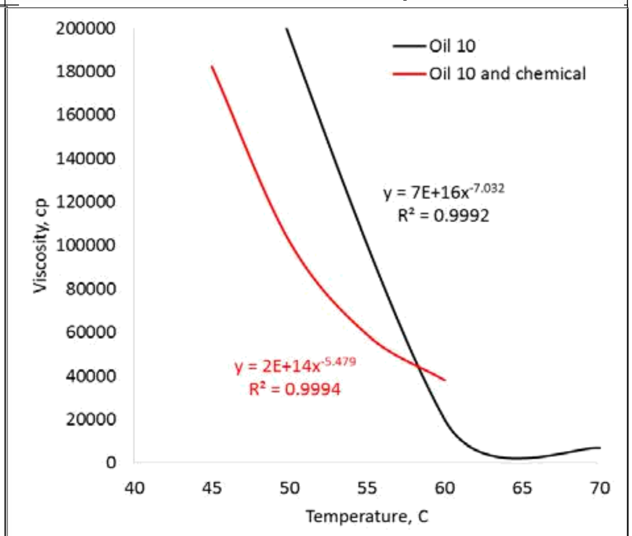
Viscosity of Oil 1 with and without chemical at different temperature



Viscosity of Oil 4 with and without chemical at different temperature



Viscosity of Oil 6 with and without chemical at different temperature



Viscosity of Oil 10 with and without chemical at different temperature

Figure 1 Viscosity Results of Bitumen Samples

The viscosity of Oils 4 and 10 showed significant falls after blending with VisRed, even at room temperature. The asphaltene content of these two crude oils before and after VisRed blending is shown in Figure 2 below. Accordingly, it can be preliminarily concluded that VisRed reduced the viscosity of these crude oils by chemically breaking asphaltene molecules. However, considering these results alongside the samples' properties (Table 1, page 5), it was not possible to determine why these crude oils responded better to VisRed than Oils 1 and 6. Oil 1 was re-tested using an alternative VisRed formulation and showed a 25-30% reduction in viscosity at room temperature.

Figure 2 suggests that the reason for these viscosity reductions is related more to the specific chemical structures of crude oils, rather than their physical properties shown in Table 1.

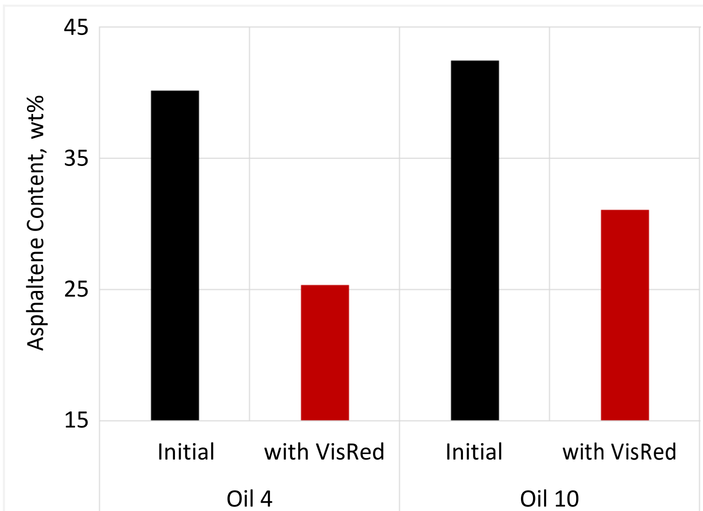


Figure 2: Asphaltene content of Initial Oil 4 and Initial Oil 10, and their blends with VisRed. The asphaltene content of the samples was determined through *ASTM D2007-11* standard (2011)

2. Results of Wax Sample

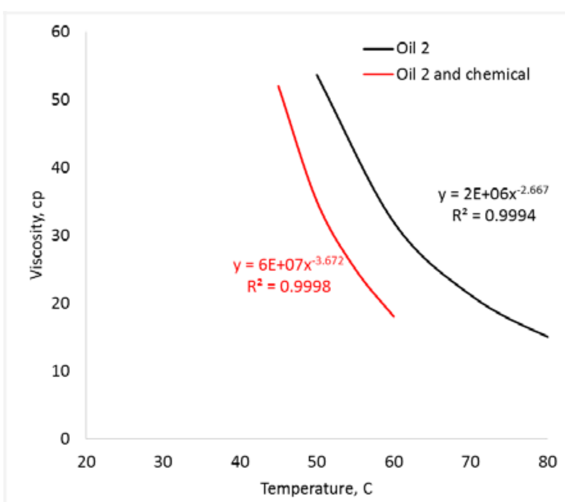
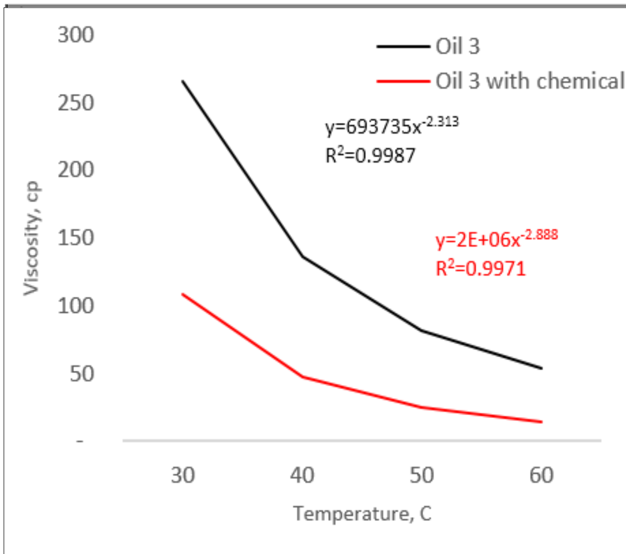


Figure 3 Viscosity Results of Wax Sample

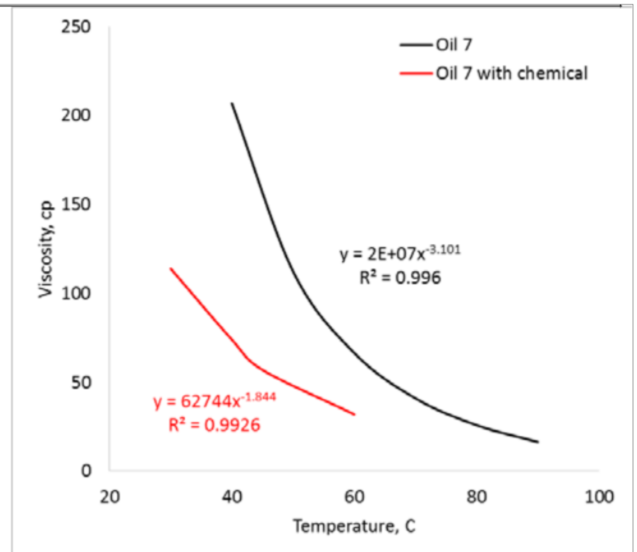
Wax in crude oil consists primarily of long chain, saturated hydrocarbons (linear alkanes/n-paraffins) with carbon chain lengths of C_{18} to C_{75+} (Garcia et al., 1998). At room temperature, the Oil 2 sample was in solid phase but, as it liquefied with increased temperature, viscosity was reduced after the addition of VisRed (Figure 3). Note that, per Table 1, Oil 2 also has a similarly high asphaltene content (more than 40wt%) to Oils 4 and 10.

3. Results of Heavy Oil Samples

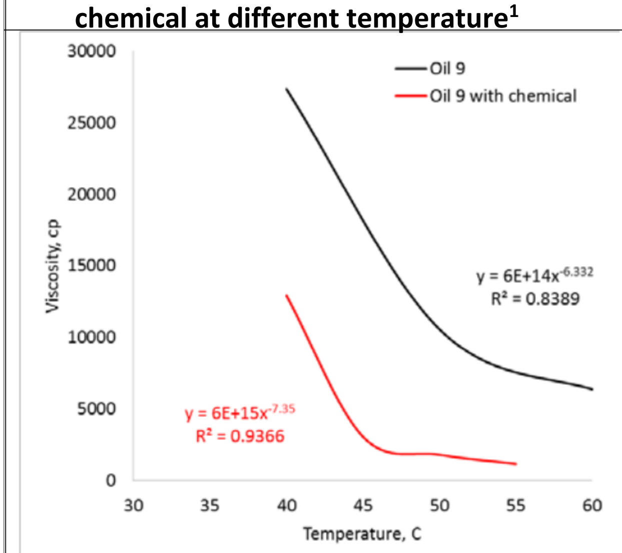
Four Heavy Oil samples were tested. Figure 4 summarizes the viscosity results of all tested heavy oil samples.



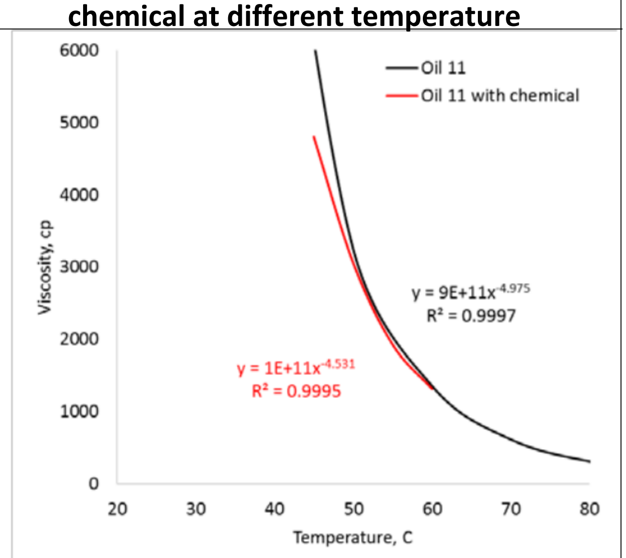
Viscosity of Oil 3 with and without chemical at different temperature[1]



Viscosity of Oil 7 with and without chemical at different temperature



Viscosity of Oil 9 with and without chemical at different temperature



Viscosity of Oil 11 with and without chemical at different temperature

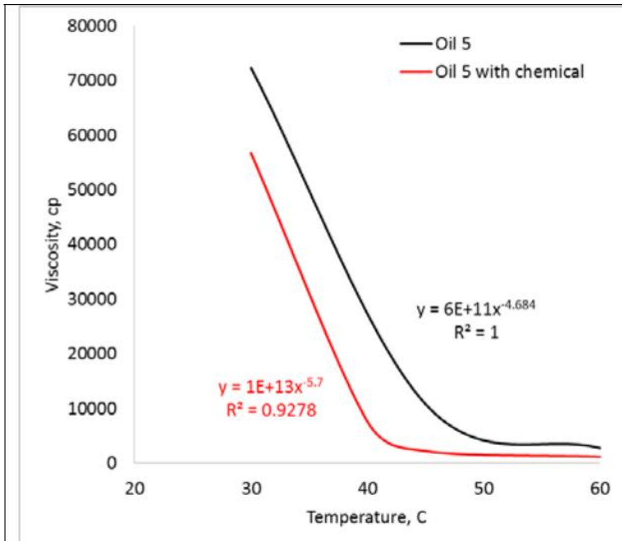
Figure 4 Viscosity Results of Heavy Oils Samples

[1] *Test performed in March 2019*

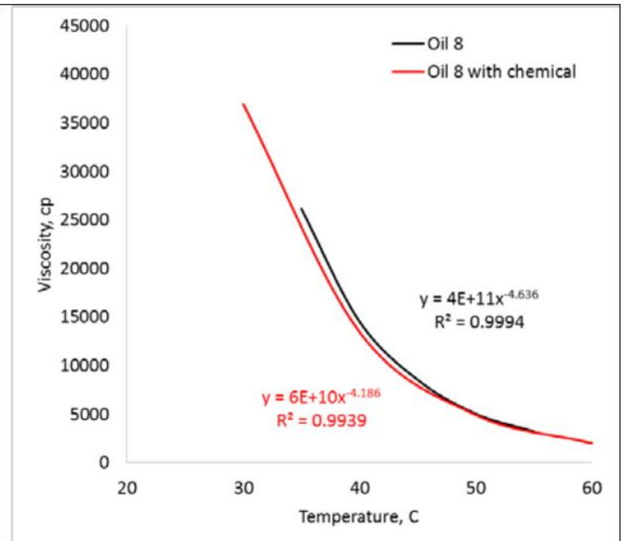
Viscosity reduction was observed in Oils 7, 9 and 11 after interacting with VisRed. Figure 4 includes the result of an earlier test in March 2019, in which Oil 3 also showed a reduction in viscosity after interacting with VisRed.

4. Results of Extra-Heavy Oil Samples

Two Extra-Heavy Oil samples were tested. Figure 5 summarizes the viscosity results of all tested extra-heavy oil samples.



Viscosity of Oil 5 with and without chemical at different temperature.



Viscosity of Oil 8 with and without chemical at different temperature.

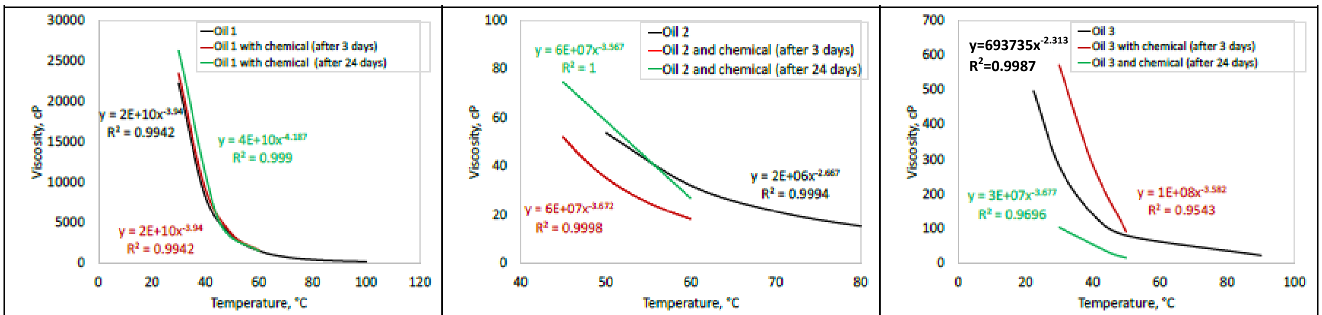
Figure 5. Viscosity Measurement of Extra Heavy Oils Sample

After blending with VisRed, the viscosity of both extra-heavy oils was reduced.

B. Time dependence of viscosity reduction reactions: The impact of time on VisRed preparation was also investigated. Accordingly, 3 days and 24 days respectively after VisRed was prepared, crude oil samples were blended with VisRed and then viscosity measurements were carried out. Results are summarized in Figure 6.

It can be observed from Figure 6 that the preparation/reaction time for VisRed is critical and its impact varies according to the composition of the crude oil.

(Note: further work was subsequently done to study the effect of reaction time, using two crude oil samples from the Athabasca Region, Canada (see E. on page 25). With these oils, the optimal reaction time for combining the components of VisRed before blending with the crudes was found to be three days for one oil and four days for the other [2].)



A-Results for Oil 1	B-Results for Oil 2	B-Results for Oil 3

Figure 6 Importance of time while preparing VISRED on Viscosity reduction

[2] *In tests to evaluate the use of a VisRed formulation to enhance combustion efficiency in petroleum fuels, no deterioration in terms of effectiveness was observed as a function of reaction time. See F. on page 26-27*

DISCUSSIONS

The viscosity change at 30 °C as a consequence of adding VisRed is shown in Table 2 below.

Table 2: Viscosity comparison between initial oil and VisRed/oil blend at 30 °C.

Oil Type	API Gravity	Viscosity at 30°C, cP	
		Initial	After VISRED addition
Oil 1	8.19	18,242	30,281
Oil 2	27.05	230	226
Oil 3	17.12	266	111*
Oil 4	6.11	728,758	583,413
Oil 5	7.97	72,329	38,055
Oil 6	12.09	4,511	6,232
Oil 7	18.84	525	119
Oil 8	11.56	56,771	39,348
Oil 9	12.56	266,084	83,428
Oil 10	10.01	2,870,657	1,613,922
Oil 11	12.19	40,324	20,284

* Using VisRed left to react for 24 days before blending: see Fig.6, p.10

Successful viscosity reduction after interaction with VisRed was observed for nine oil samples (Oil 2, Oil 3*, Oil 4, Oil 5, Oil 7, Oil 8, Oil 9, Oil 10, and Oil 11) out of 11 crude oil samples. No direct correlation was observed between the crude oil physical properties shown in Table 1 (page 5) and viscosity reduction. Hence, it is clear that it is the chemical composition of the crude oils that is critical in defining the success of these tests.

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B. Changes in Crude Oil Composition after Interaction with VisRed

SUMMARY

Following the work done to assess the changes in viscosity in crude oils after blending with VisRed, the impact of VisRed on crude oil composition was tested. Two different methods were used: **SARA fractionation** and **TGA/DSC**. The work was carried out between July and September 2019.

SARA fractionation identifies the weight percentage of saturated hydrocarbons (Saturates fraction), simple aromatic hydrocarbons (Aromatic fraction), and complicated polyaromatic hydrocarbons (Resins and Asphaltenes fractions) present in crude oils.

The Saturates fraction of crude oil contains saturated carbon chains (i.e. having no double or triple bonds between carbon atoms). Saturates can be in the form of straight, branched, or cyclic saturated hydrocarbon chains, but the hydrocarbon molecules may also have oxygen, nitrogen, or sulfur in their molecular structure.

The Aromatics fractions of crude oil may have one or two aromatic rings in their molecular structures, and may also contain oxygen, nitrogen, or sulfur.

The Resins and Asphaltenes fractions of crude oil have polyaromatic structures in their molecules and, while resins are liquid, asphaltenes are solid. They both have oxygen, nitrogen, sulfur, and metals in their molecular structure, with the concentrations of those impurities being particularly high in asphaltenes.

TGA/DSC (Thermogravimetric Analysis/Differential Scanning Calorimetry) tests were used to provide information on the combustion characteristics of the crude oil samples before and after addition of VisRed.

For the 11 crude oil samples, both SARA and TGA/DSC analysis were conducted on the initial crude oil and then on their blends with VisRed. The VisRed was prepared by following the same procedure as before (with a minimum 72 hours reaction time and 1: 1000 VisRed to crude oil ratio).

MATERIALS AND METHODS

This section considers how VisRed affected the chemistry of the crude oil samples in terms of the amount of SARA (saturates, aromatics, resins, and asphaltenes) fractions and combustion kinetics tests of crude oils through TGA/DSC (Thermogravimetric/Differential Scanning Calorimetry).

RESULTS

A. Change in Crude Oil S-A-R-A fractions after interacting with VisRed:

The numeric value of the weight percentage (wt %) measurements for each SARA fraction is shown for all 11 crude oil below in Table 3, together with the percentage change in each fraction.

Table 3 Summary of SARA content before and after interaction with VisRed

Oil Name	With VisRed?	SARA, wt %				SARA change				Viscosity reduced ?
		Saturates	Aromatics	Resins	Asphaltenes	Saturates	Aromatics	Resins	Asphaltenes	
Oil 1	No	23.7	20.1	21.9	34.3	-7.2%	24.4%	5.0%	-12.5%	No
	Yes	22	25	23	30					
Oil 2	No	24.3	25	5.4	45.3	15.2%	4.0%	11.1%	-11.7%	Yes
	Yes	28	26	6	40					
Oil 3	No	30	41.8	15.6	12.6	23.3%	-4.3%	-35.9%	3.2%	*No**
	Yes	37	40	10	13					
Oil 4	No	10.7	29.1	20.1	40.1	119.6%	11.0%	-5.5%	-37.2%	Yes
	Yes	23.5	32.3	19	25.2					
Oil 5	No	12.7	42.1	22.9	22.3	8.7%	-59.1%	69.9%	35.0%	Yes
	Yes	13.8	17.2	38.9	30.1					
Oil 6	No	16.4	37.7	17.1	28.8	9.8%	6.9%	-8.2%	-9.7%	No
	Yes	18	40.3	15.7	26					
Oil 7	No	22.6	37.6	16	23.8	0.9%	-29.5%	27.5%	27.3%	Yes
	Yes	22.8	26.5	20.4	30.3					
Oil 8	No	10.1	38	13.1	38.8	13.9%	-62.6%	135.1%	12.1%	Yes
	Yes	11.5	14.2	30.8	43.5					
Oil 9	No	11	44.8	20.8	23.4	35.5%	6.5%	-36.5%	3.4%	Yes
	Yes	14.9	47.7	13.2	24.2					
Oil 10	No	32	22	8	38	-60.9%	56.4%	118.8%	-6.3%	Yes
	Yes	12.5	34.4	17.5	35.6					
Oil 11	No	11	30.5	16.1	42.4	-14.5%	9.8%	0.0%	-3.3%	Yes
	Yes	9.4	33.5	16.1	41					

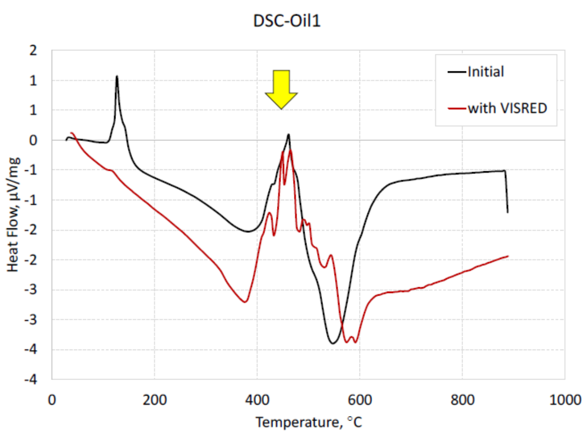
** May 2019 test: Oil 3 blended with VisRed having 72 hour reaction time. See Fig.6, page 10*

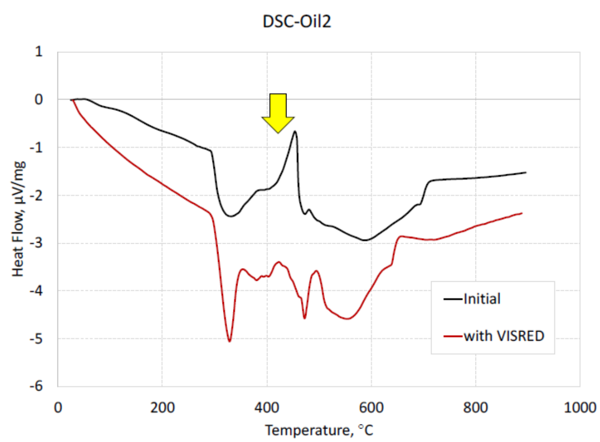
Typically, increases in Resins and Asphaltene would be undesirable, while increases in Saturates and Aromatics would be desired - because higher values of resins and asphaltenes indicate that crude oil composition changes towards more complicated hydrocarbon structures, while higher values of saturates and aromatics show that crude oils more complex structures are forming smaller and less complex hydrocarbons.

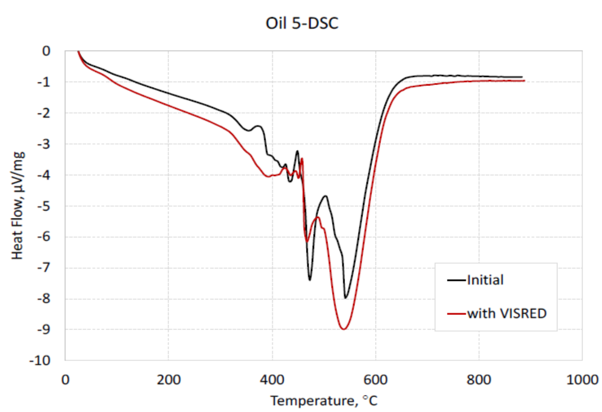
B. Change in combustibility of crude oils after the addition of VisRed:

Combustion analysis was carried out using TGA/DSC equipment. Initial crude oils and their VisRed blends were subjected to heated air increasing at 20 °C/min to a peak of 900 °C. A summary of the results in the form of Heat Flow curves is given below.

In these graphs, peaks show endothermic reactions (i.e. those requiring heat, such as water evaporation, thermal cracking of hydrocarbons), while valleys indicate exothermic reactions (i.e those generating heat, such as combustion). Black curves give TGA/DSC results of the initial oil samples and red curves give TGA/DSC results of crude oils after blending with VisRed. Accordingly, in Oils 1, 2 and 5, the deeper red valley shows that energy generation increased after VisRed addition while for the rest of the oils, the red valley was reduced when compared to the black valley for the initial oils.

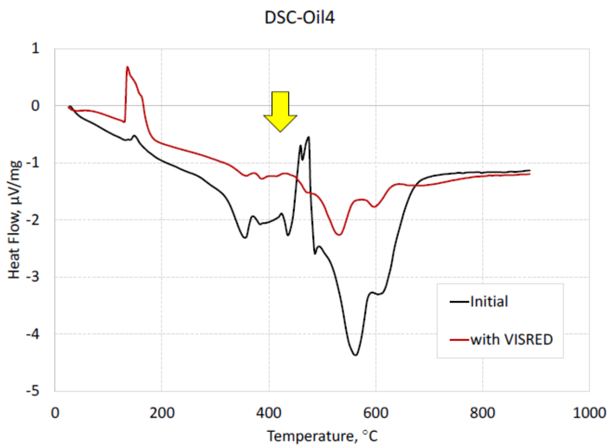


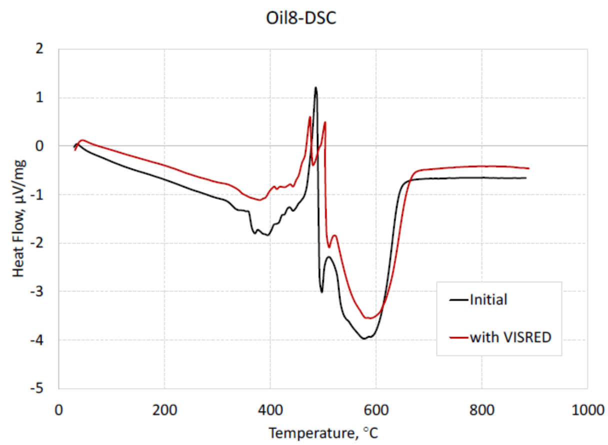




Combustion Reactions were observed between 400-500 °C. The occurrence of combustion reactions varied across the oil samples after the addition of VisRed, with some occurring earlier and some later.

Oils 2, 4 and 8 showed that the heat required to break bonds in order to initiate combustion reactions was significantly reduced after blending with VisRed. (Result for Oil 2 is shown above).





C. Impact of Changes in Dose Ratios of VisRed on Viscosity Reduction

SUMMARY

The purpose of this part of the study was to assess whether there is an optimum dosage rate for VisRed in terms of its capability to reduce viscosity, and to compare this with the performance of toluene, a well-known and powerful solvent.

VisRed was prepared in the laboratory as before. After preparation, 72 hours of reaction time was allowed before blending VisRed with a crude oil sample from the Fort McMurray area of the Athabasca Region, Canada. Tests were performed using VisRed-to-crude ratios of 1:1000, 1:500, 1:250 and 1:100. The tests were repeated using blends of toluene with the crude oil in the same ratios.

The viscosities were all measured at 25 °C. The results are shown in Chart 1 below. Data points at dosages of 1/166 and 1/125 were interpolated.

RESULTS

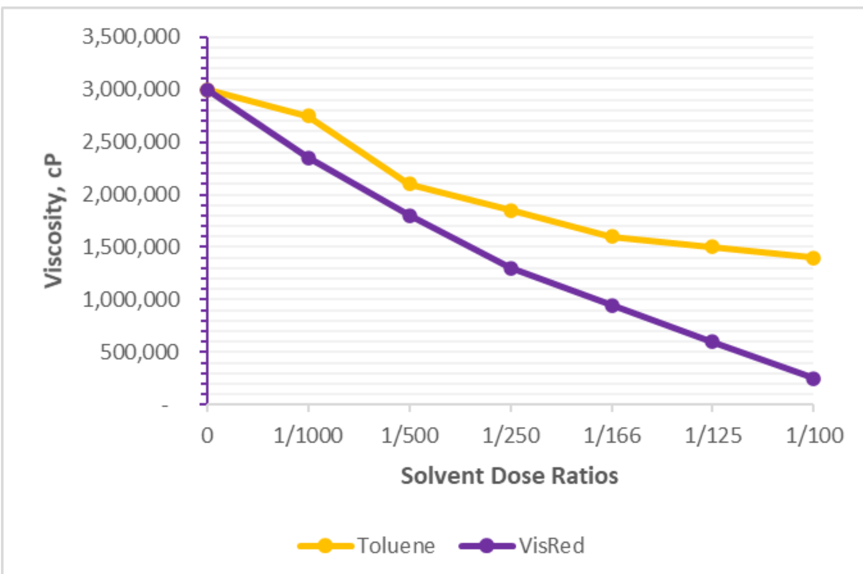


Chart 1: Viscosity of crude oil at varying dose ratios of VisRed and toluene

The results showed that VisRed was progressively more effective at reducing the viscosity of the crude oil as the dose ratio was increased, to a substantially greater extent than toluene. Accordingly, in terms of effectiveness, there is no optimum dosage rate[3].

[3] *This contrasts with what was observed when evaluating VisRed as a combustion enhancer in petroleum fuels, as described in F. below (page 27). 1:500 vol/vol was found to be the optimum dose for combustion enhancement, with reduced effectiveness observed at higher dose rates.*

D. Chemical & Physical Characterization of Heavy Crude Oils Before and After Blending with VisRed

SUMMARY

The purpose of this phase of the study (carried out during 2020-21) was to understand the mechanism by which VisRed reduces viscosity in crude oils. Several compositional analyses were conducted on the oil sample from the Fort McMurray area of the Athabasca Region used in C. above, and after its blending with VisRed. 72 hours reaction time were allowed in preparation of the VisRed, which was then blended with the oil sample in a ratio of 1:500 (c.f. previous tests in sections A and B, in which blending was done at 1:1000).

The results show that <u>VisRed does cause compositional changes to crude oil even at room temperature</u>. After blending with VisRed:

- while the H:C atomic ratio decreases overall for the Saturates fraction, the fraction has a higher proportion of lighter saturated hydrocarbons (C_{11}-C_{59}) after blending with VisRed.
- the Aromatics, Resins, and Asphaltenes fractions became more saturated with hydrogen.
- the Nitrogen, Sulfur, and Cation content of asphaltenes significantly increased.

A substantial proportion of the most undesirable non-hydrocarbon components of crude oil were concentrated in the asphaltenes fraction as a consequence of blending with VisRed. As is well known, asphaltenes are easy to remove from crude oils by using precipitants such as n-pentane, followed by filtration.

RESULTS

1. Viscosity Reduction

As per C. above, a c.40% viscosity reduction was obtained after VisRed addition to the Fort McMurray oil at 25 °C.

2. Compositional Changes

a. SARA Fractionation

First, SARA fractionation was conducted on the initial oil sample. It is important to note that little is known in the literature regarding the chemical composition of each SARA fraction. These fractions are typically grouped or classified based on their solubility in different solvents (Figure 7 overleaf).

Saturates are categorized as saturated hydrocarbons but some impurities are likely to be present in their composition. These “impurities” may comprise any substance other than hydrogen or carbon. In the aromatics fraction, aromatic structures (but not polyaromatic) should be observed; one or two aromatic rings are most common. In the resins fraction, polyaromatic structures with impurities such as nitrogen, sulfur, oxygen and heavy metal components are observed. In the asphaltenes fraction, polyaromatic structures along with similar impurities (nitrogen, sulfur, oxygen, heavy metals) present but in a greater proportions than in the resins fraction.

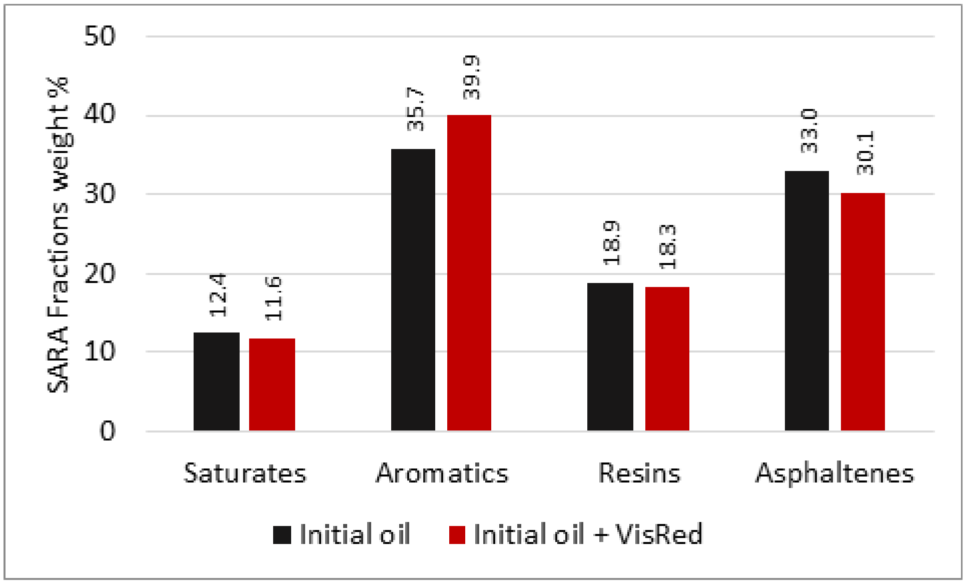


Figure 7: SARA Fractionations of initial oil and initial oil-VisRed blend

After blending the initial oil with VisRed, the weight percentage of the heavier fractions (resins and asphaltenes) reduced and the weight percentage of the lighter fractions (saturates and aromatics) increased.

Given these observations, it should be noted that the oils showing viscosity reduction and then SARA tested in May 2019 all showed increases in those fractions with carbon rings, as follows:

Oils with viscosity reduction observed	2	4	5	7	8	9	10	11
Aromatics increased	✓	✓				✓	✓	✓
Resins increased	✓		✓	✓	✓		✓	
Asphaltenes increased			✓	✓	✓	✓		

An increase in resins has the potential to increase solvent power in the same way as aromatic fractions.

b. Hydrogen to Carbon Atomic Ratio

In petroleum processing, it is important to consider hydrocarbon saturation. A high H:C atomic ratio is always desirable. The H:C ratio provides an idea of the chemical stability and processing characteristics of the crude oil. For this reason, the H:C atomic ratio was also analyzed (Figure 8).

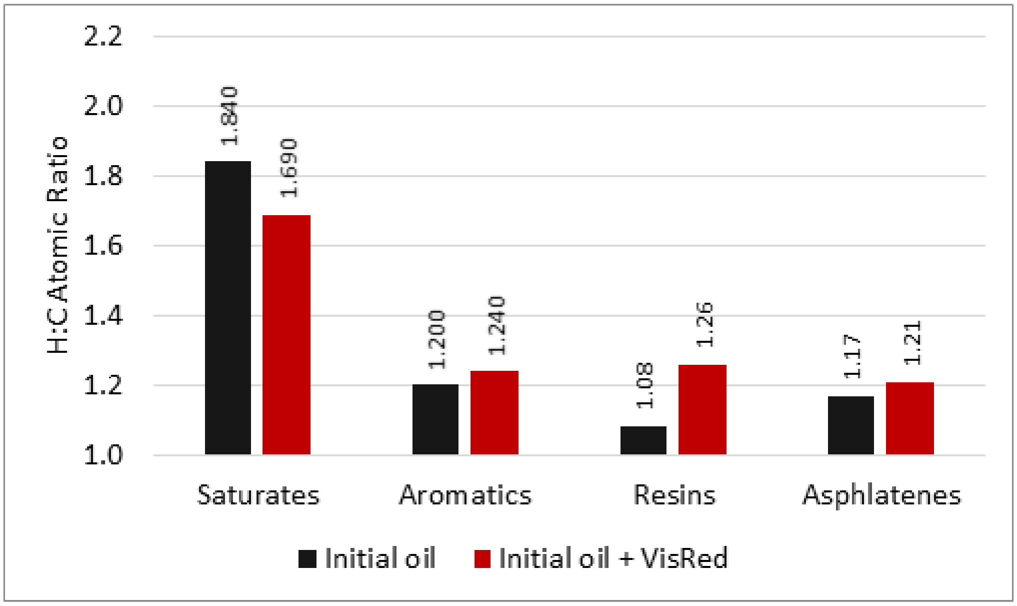


Figure 8. H:C Atomic Ratio of Initial Oil and Initial oil-VisRed Blend.

As shown in Figure 8, the H:C atomic ratio in the Saturates fraction decreased; that is to say, the saturates fraction of the crude oil became less hydrogenated, while hydrogen saturation decreased with the addition of VisRed. Following a mass balance approach, it can be concluded that hydrogen atoms in the saturates fraction travelled to or became part of other fractions: this can be supported by the increase in H:C atomic ratio observed in the remaining fractions.

In other words, the addition of VisRed to the oil sample triggered the transfer of hydrogen atoms to the non-saturate oil fractions. As a result, the heavier fractions became more saturated: their hydrogenation increased. This has positive implications for the handling characteristics of the heavier fractions in the refining process.

c. C_1 to C_{60+} Components

Compositional analysis was performed to better understand how the composition of the crude oil changes with the addition of VisRed. Any significant reductions or increases in weight percent of a specific group of alkanes could help limit the scope of the analysis or provide a better understanding as to why the hydrogen saturation or de-saturation mentioned in b. above and shown in Figure 8 occurred.

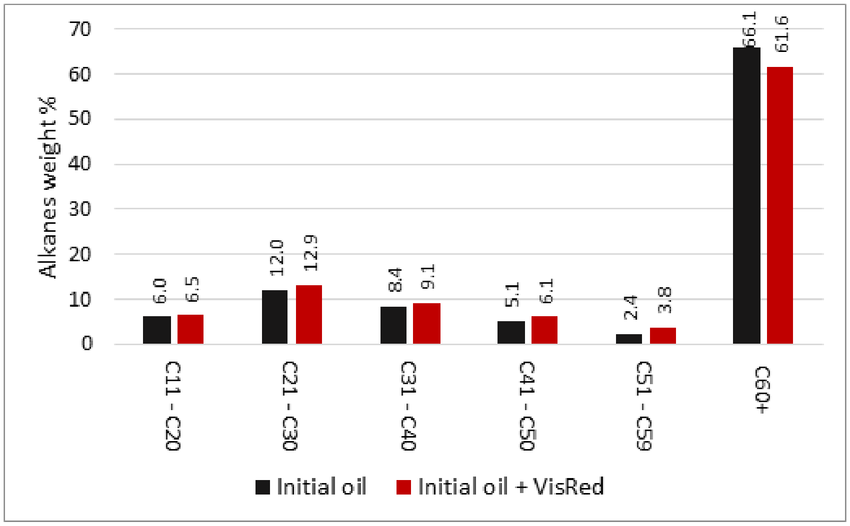


Figure 9 Alkanes weight % of Initial oil and its VisRed blend

No substantial overall change in weight percentages of each hydrocarbon group was observed as seen in Figure 9. However, the small changes shown are observed to comprise an increase in the lighter hydrocarbon components (C_{11}-C_{59}) and a reduction in heavier alkanes (C_{60+}) after adding VisRed. This supports the finding that the addition of VisRed increases the lighter components of the saturated hydrocarbons and decreases the heavier component of the saturated fractions of crude oil.

3. Elemental Analysis

a. Carbon

The carbon distribution in each fraction before and after the addition of VisRed can be seen in Figure 10. After the addition of VisRed, the weight percentage of carbon in the aromatics and resins fractions increased, while the percentage in the saturates and asphaltenes decreased. In other words, the asphaltenes fraction of the crude oil accumulates more non-carbon elements.

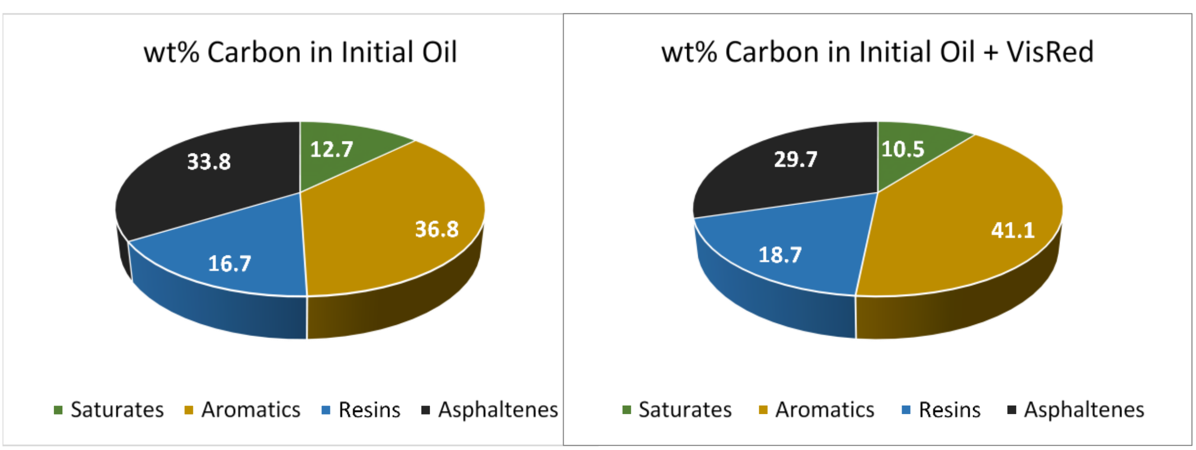


Figure 10 Weight percent change of Carbon in initial oil (L) and after blending with VisRed (R)

b. Nitrogen

As noted above, any substance other than carbon or hydrogen in crude oil may be considered an impurity. In Figure 11, nitrogen distribution in the initial oil and in the oil/VisRed blend is shown. Nitrogen content moves mainly from the resins fraction to the asphaltenes fraction after the addition of VisRed. Thus, de-asphalted oil (DAO) after VisRed addition contains less nitrogen than the initial oil sample. However, note that the saturates and aromatics fractions were enriched with nitrogen after VisRed addition[4].

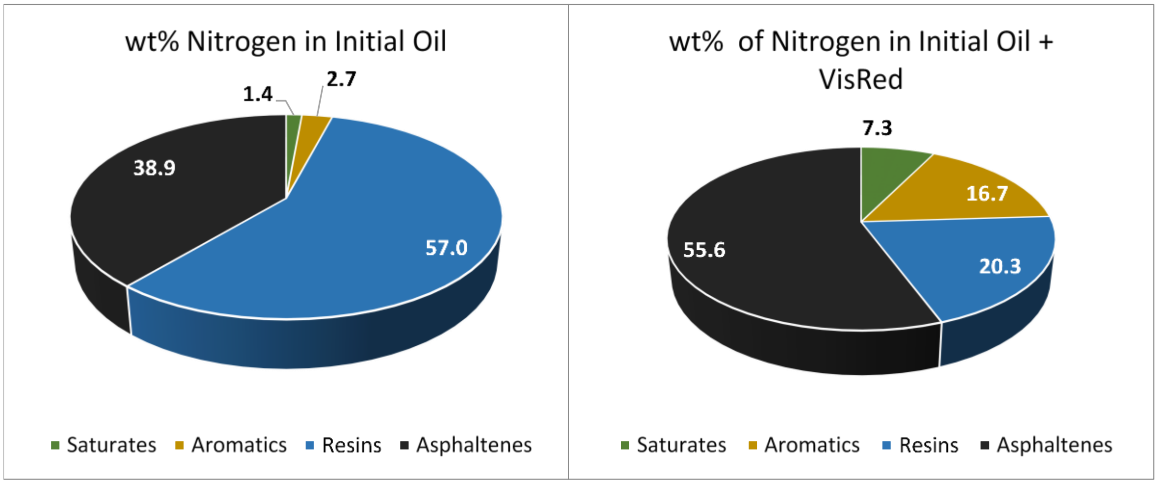


Figure 11 Weight percent change of Nitrogen in initial oil (L) and its blend with VisRed (R)

c. Oxygen

Oxygen is another impurity in crude oil. Figure 12 shows the oxygen distribution in the initial and oil/VisRed blend. The saturates and aromatics fractions became more oxygenated after the addition of VisRed, while the weight percentages of oxygen in the asphaltenes and resins fractions decreased.

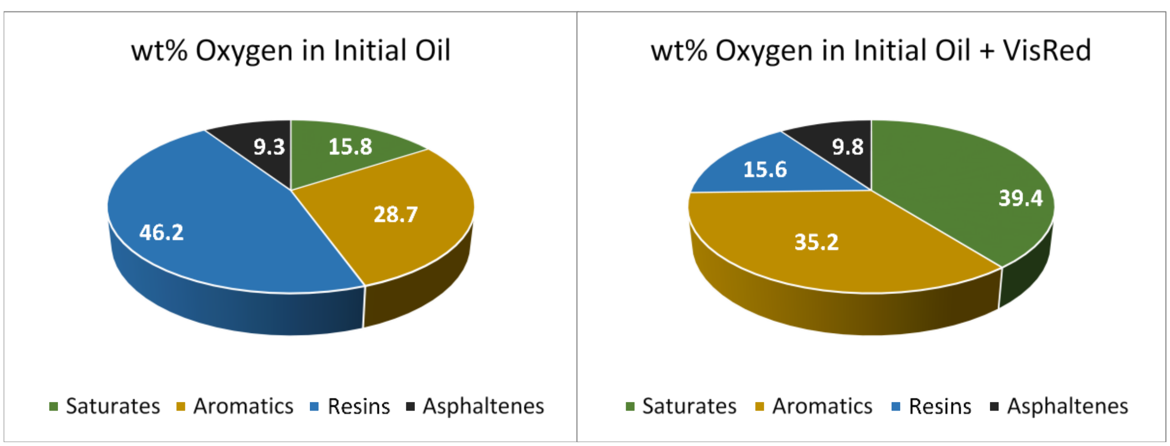


Figure 12 Weight percent change of Oxygen in initial oil (L) and its blend with VisRed (R)

[4] *This could be of benefit in, for example, amines production*

d. Sulfur

As with oxygen and nitrogen, sulfur is also considered to be an impurity in crude oil. Figure 13 gives the sulfur distribution in crude oil before and after adding VisRed. While the sulfur content of the resins fraction decreases, the sulfur content of the asphaltenes fraction increases after the addition of VisRed.

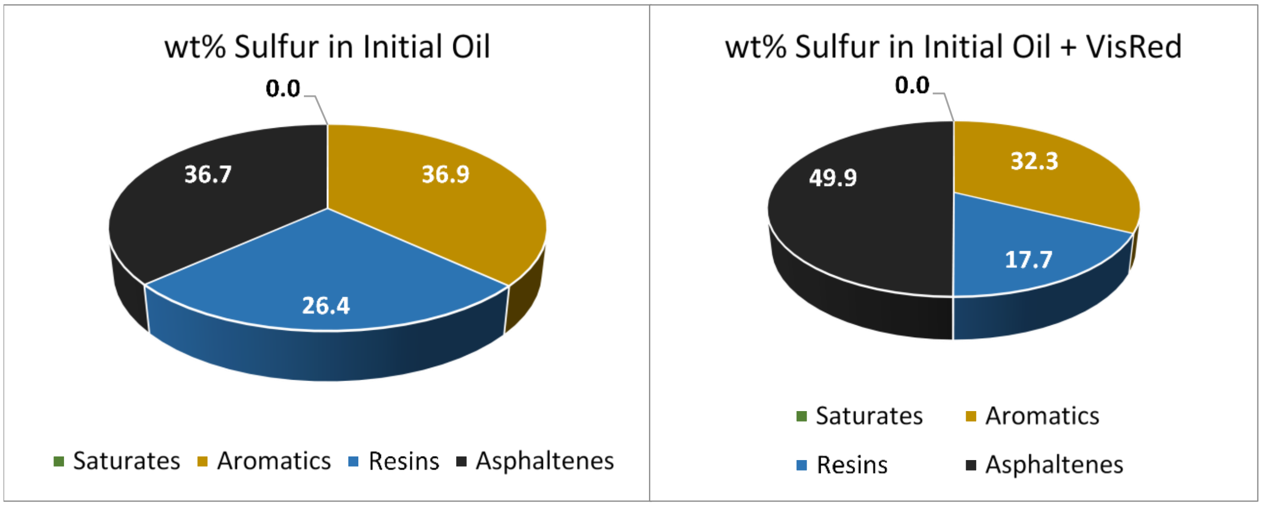


Figure 13 Weight percent change of Sulfur in initial oil (L) and its blend with VisRed (R)

e. Ash

Ash is also an impurity and mainly composed of metals. All the non-hydrocarbon components - heavy metals and inorganic materials present in the crude oil - are very difficult to extract without introducing heat. Ash is the result of the extraction of those impurities left over after the crude oil has been combusted out. The content of the ash (anions and cations) allows a better understanding of the elemental composition of each SARA fraction. Figure 14 summarizes the ash content of each fraction.

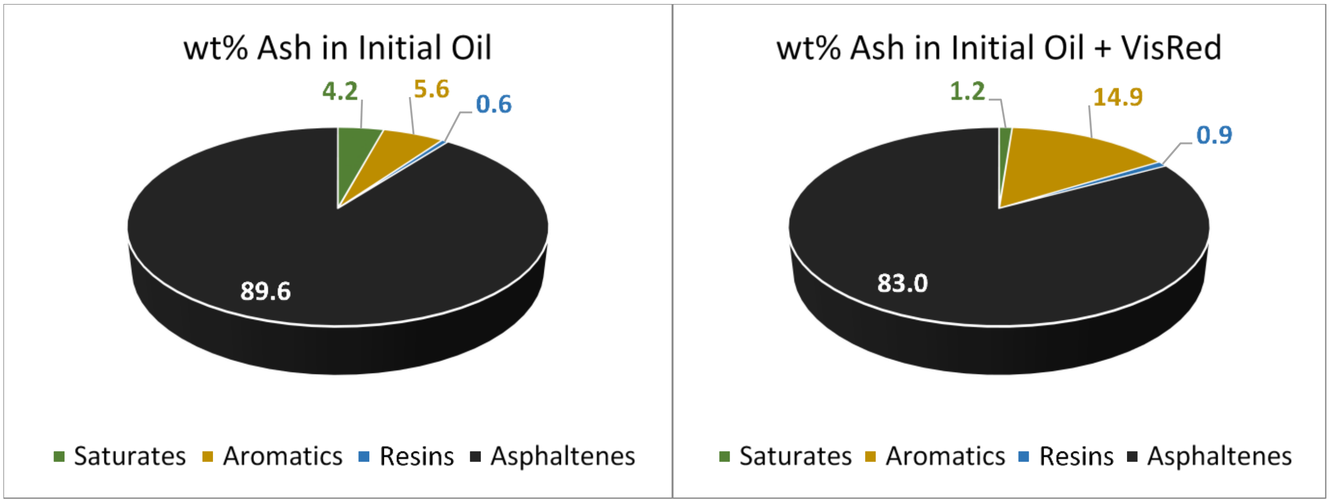


Figure 14 Weight percent change of Ash in initial oil (L) and its blend with VisRed (R)

Most of the ash content is found in the asphaltenes fraction and after the addition of VisRed, this content is reduced. Note, however, that some accumulation is seen in the aromatics fraction (this could be caused by the chloride or other anions present).

f. Cations

The cations present in the crude oil were analyzed. These cations may be an integral part of the crude oil and are often called organo-metallic components. The following cations were analyzed: Al, Ba, B, Cd, Ca, Cr, Cu, Fe, Pb, Li, Mg, Mn, Ni, P, K, Si, Na, Sr, and Zn.

As well as these organo-metallic compounds that are part of the crude oil molecule, it is important to point out that other cations may have an inorganic origin (reservoir rock, reservoir waters-brines).

Both categories of cation are considered impurities. Their distribution is shown in Figure 15.

In the initial oil sample, most of these cations accumulated in the asphaltenes and aromatics fractions. After the addition of VisRed, most of the cations were found to have concentrated in just the asphaltenes fraction.

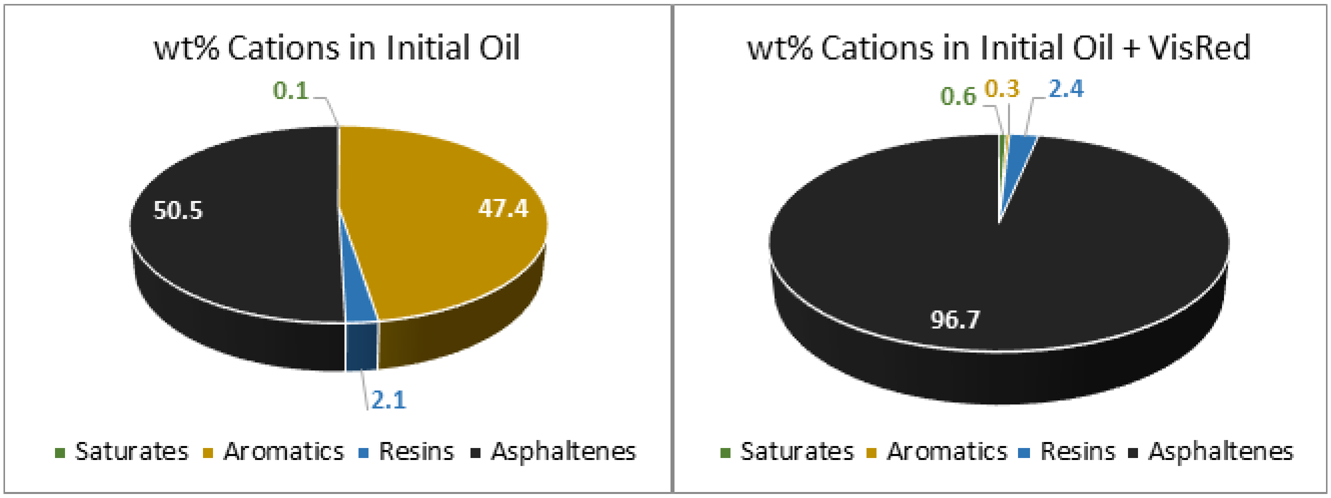


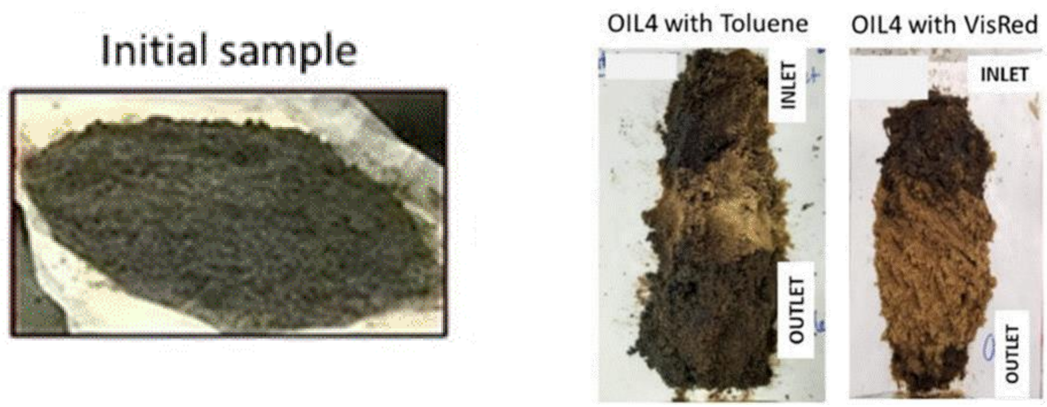
Figure 15 Weight percent change of Cations in initial oil (L) and its blend with VisRed (R)

As with the other type of impurities, VisRed helps gather the majority in just a single fraction. **By adding VisRed and then precipitating and filtering out the asphaltene, the result will be a "cleaner" and less viscous De-asphalted Oil.**

E. Coreflood experiments

Coreflooding is a laboratory test in which a fluid or combination of fluids is injected into a sample of oil-bearing rock or sand (“porous media”), simulating the use of the fluid in reservoir conditions.

For the Fort McMurray Athabasca sample used in C. and D. above (identified below as “Oil 4”), the addition of VisRed increased the recovery of oil from the oil sand sample by approximately 33%, outperforming the use of toluene and supporting the hypothesis that VisRed has potential as an EOR (Enhanced Oil Recovery) fluid.



The experiment was repeated using Oil X, a crude from outside the sample group used for the other experiments in this paper. VisRed did not produce a decrease in the viscosity of Oil X, yet showed an even higher (+50%) increase in oil recovery, showing that VisRed’s mechanism for oil recovery in porous media is different from that observed blending with crude oils at the surface.

The increased oil recovery occurs as a result of the EOR helping to unblock the pore spaces. The higher effectiveness with Oil X is likely to be because of a reaction with the rock itself.

F. Combustion Enhancement

a. Fuel economy and in-use emissions tests were performed using light-duty gasoline vehicles (LDGVs) and class 8b Heavy-Duty Diesel Vehicle (HDDV-8b). The purpose of this testing program was to evaluate the performance of VisRed as a combustion enhancer in commercially available gasoline and diesel, blended at 1:500 vol/vol [5].

b. The tests were conducted by a team from the Environment & Air Quality Division of the Texas A&M Transportation Institute ("TTI"), led by Dr Joe Zietsman, at the Pecos Research and Testing Center (RTC) outside Pecos, Texas. They were based on the SAE J-1321 protocol using gravimetric methods. SAE J-1321 is the standard testing procedure for fuel consumption in the US.

c. For each vehicle category, fuel consumption in a test vehicle was compared to fuel consumption in an identical control vehicle before and after VisRed treatment at the recommended dose rate of 1:500 vol/vol. Improved fuel economy, together with reduced exhaust emissions, was found to be optimised after two tanks full of treated fuel (this may be due to VisRed's first eliminating accumulated carbon deposits on engine and cylinder walls). Each segment of testing consisted of a gravimetric fuel consumption testing followed by emissions testing using SEMTECH-DS manufactured by Sensors Inc. and Montana-2100 manufactured by Clean Air Technology International Inc. (CATI) portable emissions measurement units.

d. The results of the tests demonstrated that, based on the SAE J-1321 procedure, the VisRed-treated diesel fuel improved the fuel consumption of the tested vehicle by 13.7%. The results also show statistically significant changes of CO_2. Recorded CO_2 reduction was 5.4%. Changes in CO and NOx levels were found to be statistically insignificant. Because the vehicles were equipped with diesel particulate filters, the PM (particulate matter) emissions levels were very low and inconclusive.

e. The tests also showed that VisRed-treated gasoline improved the fuel consumption of the tested vehicle by 7.3%. The results showed statistically significant changes of CO_2, CO and NOx. Recorded CO_2 reduction was 6.9%, and for CO, 27.1%. NOx was shown to have increased by 13.3%; note, however, that the exhaust gases used for measurement were drawn from directly below the manifold and consequently had not passed through the test vehicle's catalytic converter.

f. In contrast to observations noted on page 10, there was no indication that reaction time is a critical factor in respect of producing the VisRed formulation capable of enhancing combustion. Anecdotally, VisRed stored in ambient conditions shows no decline in effectiveness as a combustion enhancer over even extended periods.

g. In tests carried out by an accredited testing agency, a blend of VisRed and automotive diesel at 1:125 was found to remain fully compliant with EN590 and relevant ASTM fuel specifications. One of the measured metrics in these tests, lubricity, was observed to improve by 2.6% using the VisRed blend.

[5] *In contrast to the effect of VisRed on viscosity described in C. above (page 16), 1:500 vol/vol was found to be an optimum dose for combustion enhancement in fuels, with reduced effectiveness observed at higher dose rates.*

Although small in magnitude, this is a positive, given that the removal of sulfur in fuels to produce LSD/ULSD reduces fuel lubricity, requiring the introduction of lubricating additives to compensate[6].

h. It is believed that fuels refined from crudes that have already been blended with VisRed may inherit the characteristics described above, in terms of the capability to improve combustion efficiency. This may reflect the observation shown in Figure 9 on page 20, viz. that the addition of VisRed increases the lighter components of the saturated hydrocarbons and decreases the heavier component of the saturated fractions of crude oil.

i. On this basis, were a substantial proportion of the components of VisRed to be recovered for recycling as part of the refining process, VisRed's environmental and economic credentials would be further enhanced.

[6] *Some commentators have observed that the refining process that removes the sulfur also reduces the aromatic content and density of the fuel, resulting in a minor decrease in the energy content, by about 1%. This decrease in energy content may result in slightly reduced peak power and fuel economy. VisRed would provide a compensating benefit.*