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Synthesis of Wax Inhibitor and Assessment of Squeeze Technique Application for Malaysian Waxy Crude

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Abstract

Highly paraffinic (or waxy) crude oil can cause significant problems in the pipelines due to wax–oil gel blockage resulting from the precipitation of the wax components. Once blockage of the pipeline occurs and flow ceases, the pipeline flow cannot be restarted with the original steady state operating pressure but instead requires significantly higher pressures to restart the flow. Due to this, it is important to maintain the oil at a temperature above its natural pour point.

The incorporation of chemical products known as wax inhibitors and pour point depressant (PPD) reduce the pour point and viscosity of oil. This paper introduces an indigenously synthesized wax inhibitor from the hydrophobically modified polybetaines (zwitterionic) family for treating waxy crude A located in Peninsular Malaysia. The synthesized wax inhibitor had been evaluated as flow improver, crystal modifier and pour point depressant.

The wax inhibitor coded CRODDA-AA, works efficiently since it can reduce the pour point of waxy crude A by 12°C and the viscosity about half of the original value at 1000 ppm concentration, as well as lowering the yield stress by 8 Pa at 51°C. In order to assess the use of the CRODDA-AA wax inhibitor for squeeze applications, a core flood study was conducted to determine its adsorption capability onto formation. A formation damage study was also conducted to ensure that there is no formation damage coupled with the injection of wax inhibitor. It was found that wax inhibitor CRODDA-AA can be retained in the formation up to 88.5% without significant formation damage. As a next step, it is planned to run the core flood and wax inhibitor release tests to refine the design of squeeze treatment.

Keywords: Wax inhibitor, waxy crude, pour point, viscosity

1.0 Introduction

Paraffin wax deposition is a phenomenon that plagues the oil industry. It can choke the production lines thereby reducing the oil production to uneconomic levels. Apart from the reduced flow, shutdowns are necessary to apply various treatments to deal with the problem[1]. According to Pederson and Ronningsen, pretreatment of the crude oil with wax inhibitor is a method by which the rheological properties of the gelled waxy crude undergo changes for easier transportation. Wax inhibitor (WI), alternatively known as pour point depressant (PPD)/ wax crystal modifier, can reduce the growth of the wax crystal and form smaller crystals allowing large free space of the liquid fraction of the crude oil to flow freely[2]. The use of wax inhibitor available commercially on the market has not always been an efficient solution to paraffin waxes deposition problem. Thus, the development of new wax inhibitors that can solve or minimize such problems is of great interest for the petroleum industry in the whole world.

Based on Matlach et.al, the effects of various wax inhibitors to treat high wax content crude near Altamount area in Utah were analyzed based on pour point, viscosity and yield value analysis. A carefully tested additive shows both pour point and viscosity reduction of the waxy crude oil. This can lead to significant improvement in flow properties, especially near or below the pour point of the oil[3]. Mendell studied the effects of wax inhibition on crude oil flow improvement. Their findings revealed that the inhibiting mechanism for a pour point depressant was most likely related to crystal modification and/or dispersion. They also found that no single additive has proved to be effective for all crude types[4].

A squeeze technique has been introduced for applying the wax inhibitor in the field. The technique of squeeze application in scale control is well documented and proven in scale management and control[5]. This research study propose to develop certain chemistries in order to be able to apply the same rational in wax control activities. Benefits of the squeeze application procedure is that it creates an artificial adsorption/ desorption that slows treatment return and produces an effective longer lasting treatment life.

In some literatures produced by James B. Dobbs, they have presented a paper describing a technique for squeezing inhibitor into the reservoir matrix to get a slow return of inhibitor that provides an extended treatment for controlling deposition[6]. It is essential to analyse the molecular weight distribution of the wax being deposited as this can affect the method of inhibition and the selection of chemical inhibitors.

If a wax inhibitor could only be put into the formation in a form that is only slightly soluble in produced fluids, the squeeze life could theoretically be prolonged. This was achieved in 1981 in several West Texas wells as reported by Nalco in 1985[7]. Solid products were introduced into the producing formation as part of a fracturing treatment. Records indicated wax control lasted an average of eight to twelve months[7]. These applications were generally very successful in providing long-term wax inhibition by placing a slow dissolving solid chemical in the producing formation. However, this type of treatment is only pratical in conjuction with fracturing jobs[8].

In an extension of this work, Haynes and Lenderman developed a liquid inhibitor mixed with an “activator” to ensure a controlled release of chemical with the advantage that the mixture was liquid and therefore pumpable. However, the effectiveness and significance of this work has not been duly supported by literature[8]. Further extension of this research study would be on adsorption and desorption squeezes with the application of slow release surfactant technology available from its well bore cleaning work and also formulation and application of its wax dissolver chemistry[9].

The development chemistries which are truly charge distributed will then form bond with the formation rock which will allow the chemical to remain for a period while slowly being dissociated or released in a uniform way in order to provide a minimum inhibitor concentration (MIC). Zwitter ionic molecules offer an interesting arena of chemistry which are proposed for further investigation[10].

2.0 Experimental

2.1 Crude Characterization Study

Waxy crude A was provided for evaluating the performance of flow improvers. The physical characteristics and rheological behavior of the crude oil are provided in Figures 2 and 3 and Table 1.

Table 1 - Physical Characteristics of Waxy Crude A

Properties	Methods	Results
Density @15 ºC (kg/L)	Pyknometer	0.8882
API gravity (º)	Calculation	27.3
Pour Point (ºC)	ASTM D97/ D5853	57
WAT (ºC)	CPM	69.0
Wax content (%)	UOP 46	10.3
TAN (mg KOH/g)	ASTM 664	0.53
IBP (ºC)	ASTM 2887 (Sim Dis Method)	148.6
Asphaltene content (%)	ASTM D3279	0.73
Temperature/ Viscosity Profile, shear rate = 10s^{-1}	Haake Rheostress 6000	Refer to Fig 2
Carbon distribution (HTGC)	HTGC	Refer to Fig 3

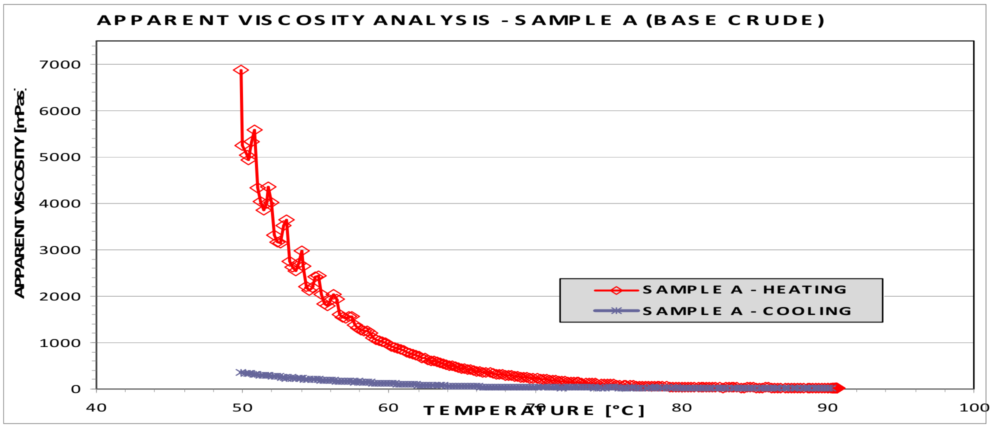


Figure 2 - Temperature/ Viscosity Profile for waxy crude A

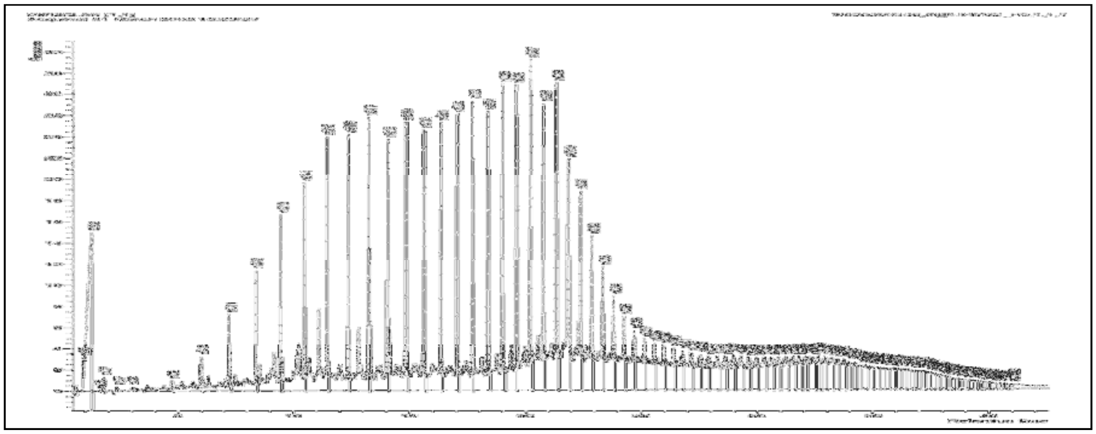


Figure 3 - Chromatographic profile of waxy crude A

2.2 Indigenous Synthesis Polybetaine Types of Wax Inhibitor

New wax inhibitors were synthesized indigenously based on the work of Didukh et.al[11]. This paper was selected since it has some potential for improvement of waxy crude fluidity due to micelles consisting of betaine groups and dodecyl group that retards growth of paraffin crystals. In addition to that this type of inhibitor is suitable for squeeze applications due to potential ionic bonding with the rock from zwitter ionic nature and potential adsorption/ desorption profiles from intramolecular H_2 bonding.

2.3 Evaluation Synthesized of Wax Inhibitors

Wax inhibitors were evaluated for improving the flow properties of waxy crude oil with high pour point in terms of pour point depression, viscosity and yield stress reduction and changes in paraffin morphology in the presence and absence of wax inhibitor in the crude. These tests include pour point analysis, paraffin morphology study, yield stress and dynamic viscosity under the effect of different temperatures, wax inhibitors concentrations and shear rates.

2.3.1 Pour Point (ASTM D97)

Pour Point test is conducted to assess the potential for gelling. It can be defined as the minimum temperature of a liquid when it ceases to flow on decreasing the temperature. After preliminary heating, the sample was cooled at a specific rate and examined at intervals of 3°C for flow characteristic.

2.3.2 Dynamic Viscosity and Yield Stress

Dynamic viscosity was measured by HAAKE Rheostress 6000 Viscometer. The oil viscosity cooled at a given test temperature depends on shear rate, thermal history and time. Prior to the test, the crude oil sample was heated to above its WAT at 75 ºC for approximately 1 hour to remove any thermal and shear history associated with the sample, and thoroughly mixed to ensure homogeneity. Then the crude was cooled at the cooling rate of 1°C/min from 90°C to 25°C at shear rates of $500s^{-1}$. The dynamic viscosity (cP) was plotted against Temperature (°C). Pour point result with applied shear rate also can be determined by HAAKE Viscometer which the reading is taken from the elbow of the viscosity profile.

The yield stress was simply defined as the minimum stress required to produce a shear flow[12]. In this study, the dynamic yield stress is dependent on the time scale of yielding and was measured with the controlled stress test. Ronningsen reported that the stress loading rate, cooling rate and aging time significantly affect the yield stress[13]. The dynamic yield stress value was determined by extrapolating the dynamic shear stress – shear rate data to the zero shear rate limits. The conditioning treatment prior to testing was the same as pretreatment of sample when conducting the dynamic viscosity test.

2.3.3 Paraffin Morphology Modification/ Reduction

Paraffin morphology was determined with two different equipment i.e cross-polarized microscope (CPM) and atomic force microscopy (AFM). In term of CPM utilization, special software was used to view image of paraffin crystals on the computer display as micrographs. Oil samples were heated up to 90 ºC and cooled at a rate of 5 ºC/min. The images of crude with presence and absence of wax inhibitor was captured at 45ºC.

For AFM imaging, the crude samples with the absence and presence of CRODDA-AA were spread on mica substrate. The imaging was performed in oscillatory amplitude modulation mode with simultaneous recording of topography and phase images. In attempt to smoothen the samples' surfaces, the samples were heated to around 50°C and then chilled to room temperature. This process had caused melting and re-crystallization of the materials.

2.4 Characterization of Optimum Wax Inhibitor

The optimum wax inhibitor was characterized in terms of chemical functional group using the FTIR spectra using a Perkin Elmer FTIR-ATR spectrometer. FTIR is the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is transmitted. The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. A sample of mixture is put on the plate. The cylinder is rotated slowly to produce gauge force on the sample. The reading of gauge force produced should be in the range of 90-100. Graphs which consist of many peaks will be obtained after scanning the sample.

2.5 Assessment of Squeeze Treatment

Assessment of squeeze treatment by core flood studies was presented to investigate adsorption capability of the synthesized wax inhibitor onto sandstone core. Remaining concentration of the wax inhibitor that coming out from core flood system was detected by refractive index measurements thus percentage of the inhibitor that still retained in the core can be determined. SEM was utilized to observe the core image after the wax inhibitor injection to ensure no formation damage happened to the core after the injection.

2.5.1 Core Flood Studies

Two core flood studies were conducted with Berea and actual core. Actual core from Field A could not be utilized due to unavailability of the core that is sufficient enough to be placed inside the core holder. Thus core from Field C was selected for this study as this core has similar properties as core from Field A.

2.5.2 Refractive Index Analysis

Determination of the wax inhibitor concentration was done using Refractive Index analysis by Rudolph Automatic Refractometer. The wax inhibitor concentration at the outlet of coreflood system will reflect the concentration of wax inhibitor that is flowing out straightly after the injection. On the other hand, the remaining concentration will reflect the concentration of wax inhibitor that is retained in the core or formation.

2.5.3 Scanning Electron Microscopy (SEM) Analysis

Scanning Electron Microscopy (SEM) analysis also was performed on the selected Berea core and core C using LEO 1430VP Scanning Electron Microscope to observe changes in structural and surface morphology of the core before and after the chemical injection. In this analysis, magnification used in capturing the core image was 100 times the magnification limit of the best light microscopes.

3.0 Results and Discussion

3.1 Indigenous Synthesis Polybetaine Types of Wax Inhibitor

Five wax inhibitors were indigenously synthesized namely:

1) CRODDA-AA (Crosslinked and Linear) or [(2-carboxyethyl)dodecylamino]-but-2-enoic acid ethyl ester
2) CROHDA-AA (Crosslinked and Linear) or [(2-carboxyethyl)hexadecylamino]-but-2-enoic acid ethyl ester
3) CRODDA-MAA (Crosslinked) or [(2-carboxymethyl)dodecylamino]-but-2-enoic acid methyl ester

For the sake of comparison, we had taken methacrylic acid instead of acrylic acid to synthesize the same type of additive. This was the case of a new series of wax inhibitor CRODDA-MAA. This additive differs from CRODDA-AA by methyl group branching in the backbone of the polymer.

3.2 Evaluation of Synthesized Wax Inhibitor

All the five synthesized wax inhibitors were evaluated in term of pour point depression and viscosity reduction based on this optimum concentration as illustrated in Figure 4 and Table 2.

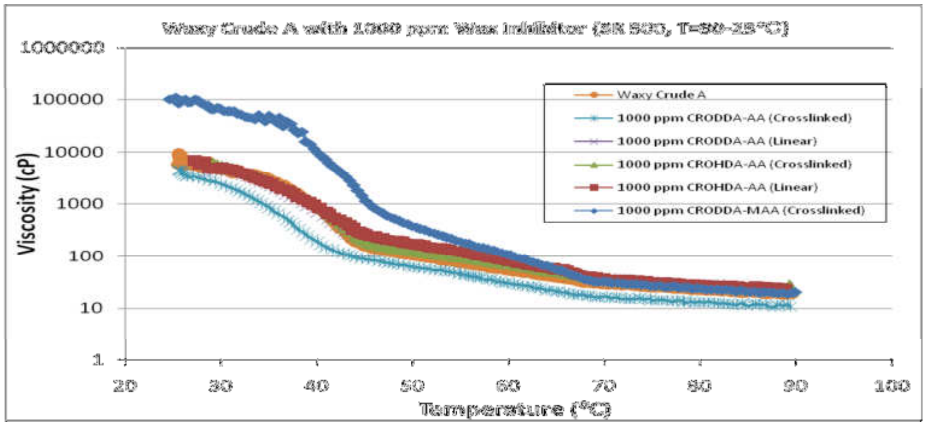


Figure 4 - Viscosity profile of waxy crude A with absence and presence of 5 wax inhibitors

Table 2 - Pour point and viscosity result of synthesized wax inhibitors

No	**Sample**	**Pour Point – Static (˚C)**	**Pour Point – Dynamic (˚C)**	**Viscosity @27ºC – Dynamic (cP)**
1	Original Waxy Crude A	57	45	5421
2	1000ppm CRODDA-AA (Crosslinked)	45	42	3220
3	1000ppm CRODDA-AA (Linear)	48	45	5702
4	1000ppm CROHDA-AA (Crosslinked)	54	45	7126
5	1000ppm CROHDA-AA (Linear)	60	45	6853
6	1000ppm CRODDA-MAA (Crosslinked)	54	46	102300

From the results, it can be observed that the optimum wax inhibitor is 1000 ppm CRODDA-AA (Crosslinked) due to the biggest reduction in pour point of 12ºC in static condition and 3ºC in dynamic condition with the applied shear rate of 500s^{-1}. The difference in the pour point value in static and dynamic condition has been ascribed to the different wax particles behavior in the static pour point test and in the measurements involving shearing. The viscosity also reduced abruptly with the addition of CRODDA-AA (Crosslinked) wax inhibitor from 5421 cP to 3220 cP at seabed temperature of 27ºC.

A structure of polybetaine in oil environment represents reverse micelles consisting of hydrophilic core (zwitterionic part) surrounded by hydrophobic edge (dodecyl group). The PPD mechanism suggests the adsorption of paraffin molecules on the surface of hydrophobic micelles inhibiting the formation of large wax crystal matrix and hindering the gelation mechanism[14]. Thus, the hydrophobically modified polybetaine acts both as wax deposition inhibitor and as PPD.

As for the remaining four wax inhibitors, the viscosities were higher than the original crude at seabed temperature of 27ºC thus considered as not effective even though their pour points at static condition were lower than the original crude. The most non suitable wax inhibitor for this type of crude is CRODDA-MAA whereby the viscosity increased drastically which up to 102300 cP at seabed temperature thus was changing the behavior of the crude to be very viscous.

The evaluation then continued with the yield stress analysis for the optimum wax inhibitor, CRODDA-AA. Figure 5 to 7 represent shear stress versus shear rate plots of untreated and treated crude oils at 51ºC, 54ºC and 57ºC for both dynamic and static yield stress determination. The data reveals that both the treated and untreated crude oils follow a non-Newtonian yield-pseudo plastic rheological behavior[15]. This non-Newtonian behavior is brought about by the ability of the precipitated waxes to form an interactive structure that must be broken down before the crude will flow[16].

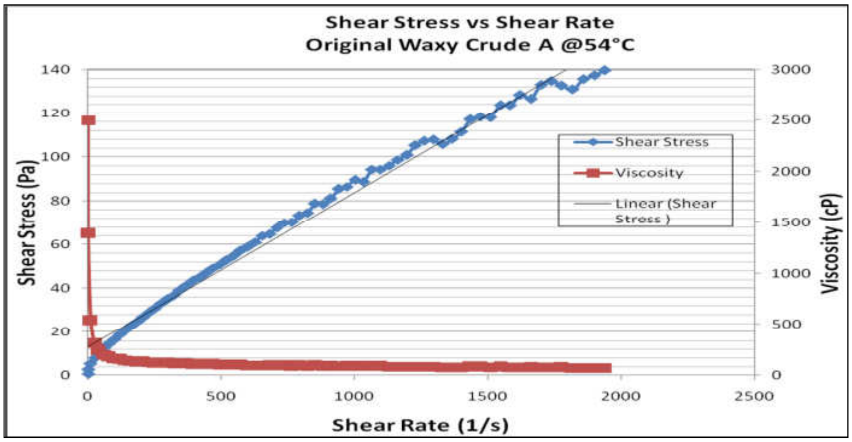


Figure 5 - Shear stress versus shear rate plot for original waxy crude A at 54℃ fo r dynamic yield stress determination

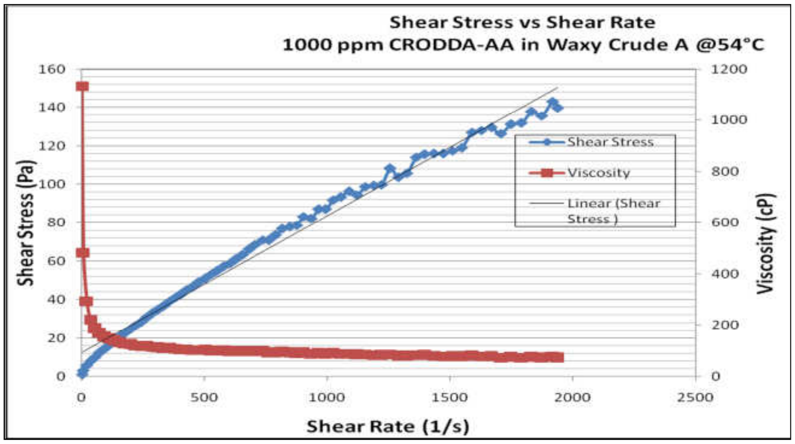


Figure 6 - Shear stress versus shear rate plot for waxy crude A treated with wax inhibitor CRODDA-AA at 54℃ for dynamic yield stress determination

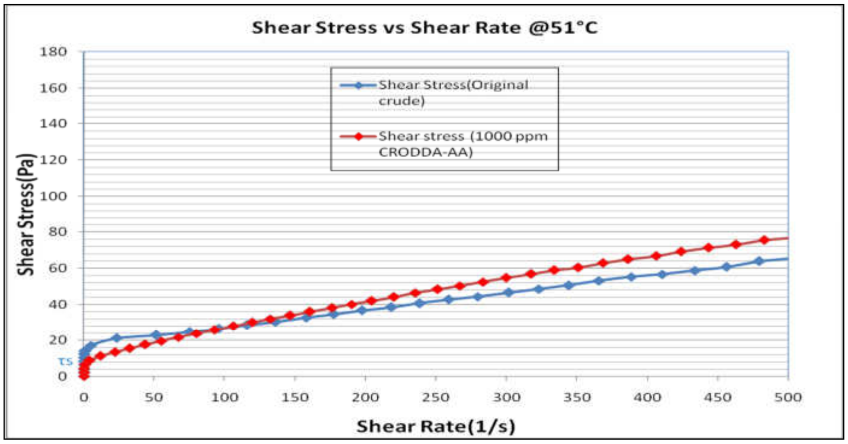


Figure 7 - Shear stress versus shear rate plot of both untreated and treated crude oils at 51℃ for static yield stress determination

Regarding the treated crude oil sample, the rheograms show the wax inhibitor changes the behavior of the oil by lowering the yield value. Table 3 shows yield values for the untreated and treated samples of crude oil at 51ºC, 54ºC and 57ºC. As the temperature increases, yield stress is decreased. With the presence of CRODDA-AA, the most reduction of static yield stress happened at 51ºC (8 Pa reductions). As for dynamic yield stress, the reduction can only be seen at 54ºC whereby the yield value drops by 2 Pa. The decrease in yield stress value has proved that the rheological characteristics of the crude oil are significantly improved.

Table 3 - Rheological Data for Waxy Crude A with Presence and Absence of Wax Inhibitor CRODDA-AA

No	Sample	Temperature (℃)	Static Yield Stress (Pa)	Dynamic Yield Stress (Pa)	Viscosity at Yield Stress (cP)
1	Original Waxy Crude A	51 54 57	14 3 1	20 14 8	559900 2501 1259
2	1000 ppm CRODDAA-AA (Crosslinked)	51 54 57	6 0 0	24 12 8	49370 1134 6491

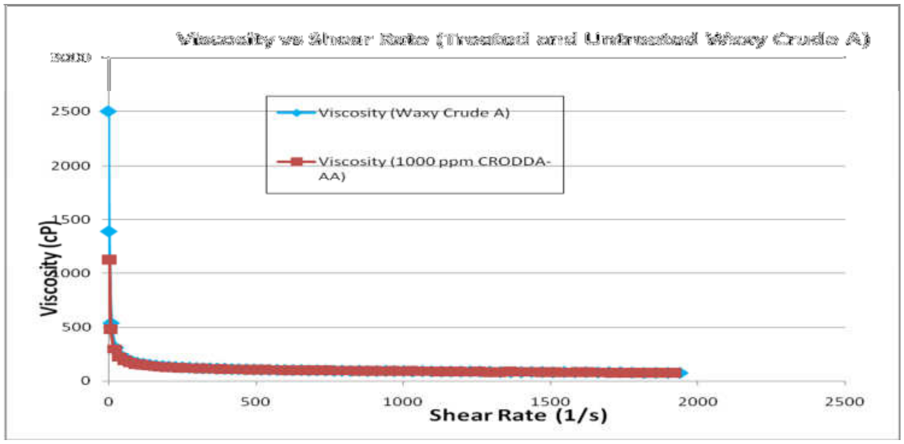
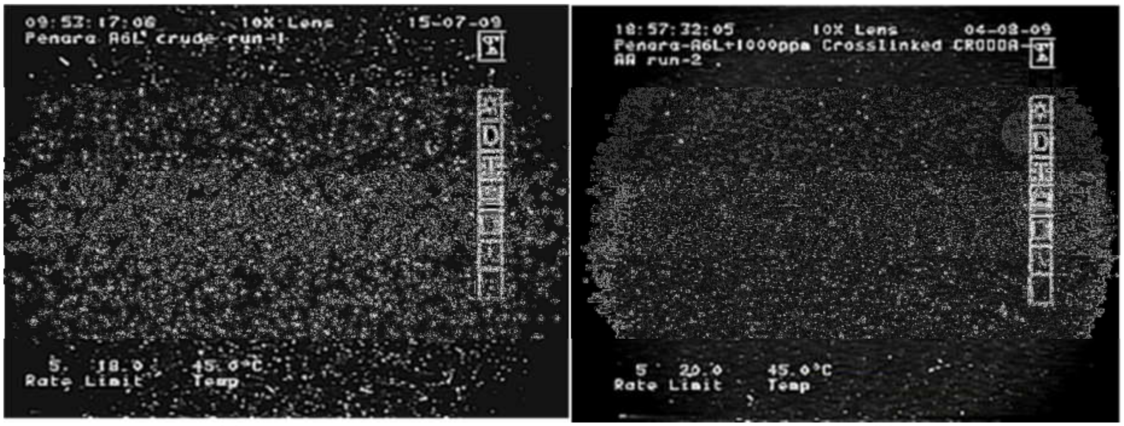


Figure 8 - Viscosity profiles of both untreated and treated crude oils with the variation of different shear rates from 0 to 2000s^{-1} at 54℃

Figure 8 illustrates the viscosity profiles of both untreated and treated crude oils with the variation of different shear rates from 0 to 2000s^{-1} at 54ºC. At high shear rates, the viscosity reached a constant value at which the equilibrium steady state was attained. With the presence of CRODDA-AA in the crude, at zero shear rates, the viscosity is less than half that of the original crude (1134 cP compared to 2501 cP). This result is in good agreement with data on the yield stress shown in Table 6 and in Figures 5 to 7.

In oil environment, CRODDA-AA represents the micelles consisting of hydrophilic core (betaine groups) and hydrophobic edge (dodecyl groups). The wax inhibitor mechanism of CRODDA-AA with respect to waxy crude oil suggests the adsorption of definite fractions of paraffin molecules on the surface of micelles and retarding further agglomeration. Thus, the micellar structure of CRODDA-AA is probably responsible for improvement of waxy crude oil fluidity. To understand effect of the wax inhibitor, morphology of the paraffin crystals formed in waxy crude A after cooling at 45ºC with and without 1000 ppm CRODDA-AA crosslinked was studied by cross polar microscopy. Representative micrographs are shown in Figure 9(a-b).

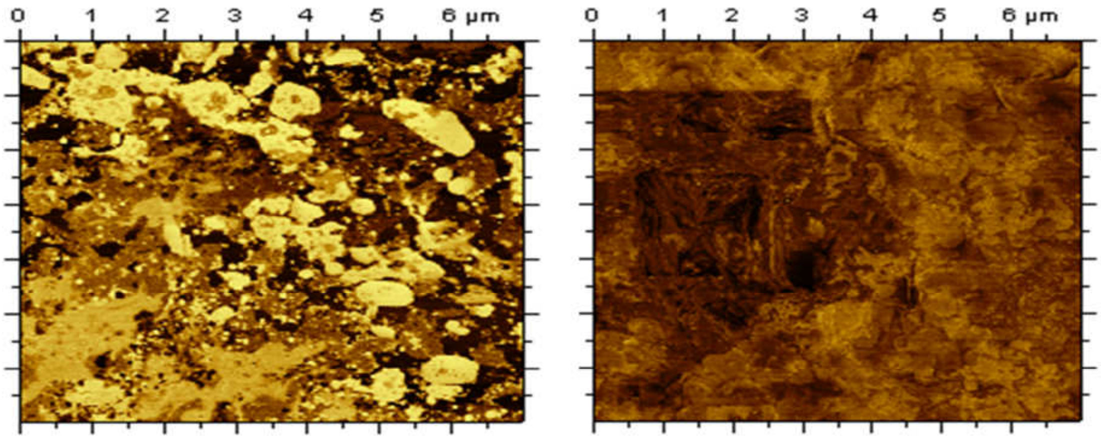


(a) (b)

Figure 9 - Morphology of waxy crude A before (a) and after treated with 1000 ppm wax inhibitor CRODDA-AA crosslinked (b)

From the figures above, in the presence of the new wax inhibitor, the amount of paraffin crystals formed is drastically reduced compared to the original waxy crude A. This new wax inhibitor works to immobilize the paraffins thus prevents them from forming a continuous three-dimensional network. This results in a large free space, which is available for the liquid fraction of the crude oil to flow freely. The zwitterionic part of the wax inhibitor is dissimilar to the wax crystals and blocks the extensive growth of wax matrices. As a result, pour point and viscosity of the crude also were reduced[14].

Besides using cross polar microscopy, the microscopic images of waxy crude A in the absence and presence of wax inhibitor CRODDA-AA also was tested using Atomic Force Microscopy (AFM). Due to presence of the additives, the crystallization of the samples led to different crystalline morphologies as seen from Figure 10(a-b). The original waxy crude A exhibits large areas with amorphous material form strong interpenetrating networks. In the presence of polymer additive, their shapes have been modified, thereby producing smaller crystals of higher volume/ surface area ratio since the wax has remains in the dispersed state. This has resulting in reduced yield stress and improved flow of the crude oil.



(a) (b)

Figure 10 - Morphology of waxy crude A before (a) and after treated with 1000 ppm wax inhibitor CRODDA-AA (Crosslinked) by using Atomic Force Microscopy

3.2 Characterization of Optimum Wax Inhibitor

The proposed structure of CRODDA-AA is confirmed by FTIR spectroscopy (Figure 11). The bands of carbonyl group, symmetric, asymmetric, and rocking vibrations of *CH* groups, symmetric and asymmetric modes of carboxylate ions are appeared as described in Table 4. Peak at 1095 cm^{-1} is responsible for *C-O-C* groups.The intensive peak at 1712 cm^{-1} belongs to stretching vibrations of *C=O* groups. Asymmetric vibration of carboxylic groups is appeared at 1570 cm^{-1}.

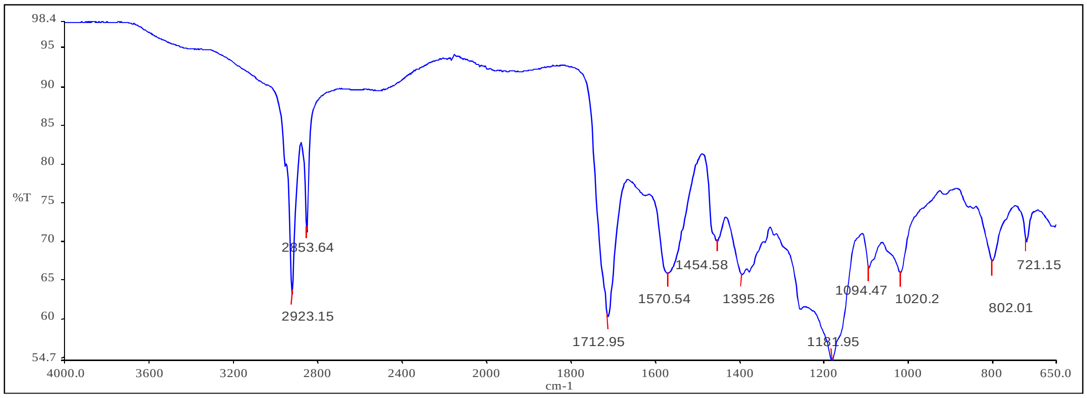


Figure 11 - FTIR spectrum of CRODDA-AA (Crosslinked)

Table 4 - Identification of FTIR Spectra of CRODDA-AA (Crosslinked)

Functional groups	Frequency,[a] cm^{-1}
$v(CH)_{as}$	2923 (vs)
$v(CH)_{s}$	2853 (s)
$v(C=O)$	1712 (vs)
$v(COO^{-})_{as}$	1570 (s)
$v(COC)_{as}$	1095 (w)

[a] Band intensities and vibration types: vs- very strong; s-strong; w-weak; $_{s}$-symmetric; $_{as}$-asymmetric

3.3 Application of Squeeze Treatment

3.3.1 Core Flood Studies Using Berea Core

As for the core flood studies using the Berea core, the synthesized wax inhibitor needs to be dissolved in the brine. However, the inhibitor could not be diluted in the brine since it was in solid form. Thus, CRODDA-AA was re-synthesized with some modifications in order for the product to be in liquid form thus can be dissolved in the brine.

Pour point analysis has been conducted to evaluate performance of the re-synthesized wax inhibitor CRODDA-AA and the results had been tabulated in Table 5 below. Based on the results, 100 ppm and 200 ppm of CRODDA-AA wax inhibitor in waxy crude A show the lowest pour point value of 41ºC with applied shear in dynamic condition. Due to this, 100 ppm CRODDA-AA wax inhibitor was utilized for the first core flood with Berea core whereas 200 ppm has been chosen for the second core flood study with core C.

Table 5 - Pour point results of the re-synthesized wax inhibitor CRODDA-AA

No	Sample	Pour Point – Static (˚C)	Pour Point – Dynamic (˚C)	Viscosity @27˚C – Dynamic (cP)
1	Original waxy crude A	57	45	5421
2	1000ppm CRODDA-AA *(l)*	51	42	3220
3	500ppm CRODDA-AA *(l)*	48	42	2991
4	200ppm CRODDA-AA *(l)*	48	41	2556
5	100ppm CRODDA-AA *(l)*	48	41	2967

Specification of the Berea core used in this study was described as below:

- Length: 48.41 mm
- Porosity (%): 12.191
- Vp: 12.043
- K_{air} (md): 358.187
- K_{∞} (md): 350.644

Initial *Kw* from the data plotted after flushing with brine was 492.9 md. Figure 12 shows total volume of brine collected after the wax inhibitor has been injected and aged in the core for overnight. Concentration of wax inhibitor in the brine was determined and compared before and after its injection to the core flood system. Concentration of wax inhibitor in the brine before injection is known to be 100 ppm. Concentration of wax inhibitor in the brine after injection is taken from the first tube as illustrated in Figure 12 since it has the highest wax inhibitor concentration compared to the second and third test tubes.

Figure 12 - Brine collected after wax inhibitor was aging overnight

Wax inhibitor concentration in the brine collected at the core flood outlet after the injection was determined using Refractive Index analysis. In order to start the analysis, a few concentrations of wax inhibitor CRODDA-AA in brine were prepared ranges from 40 to 100 ppm whereby the refractive index were determined for each of the concentration. The refractive index profile was illustrated in Figure 13.

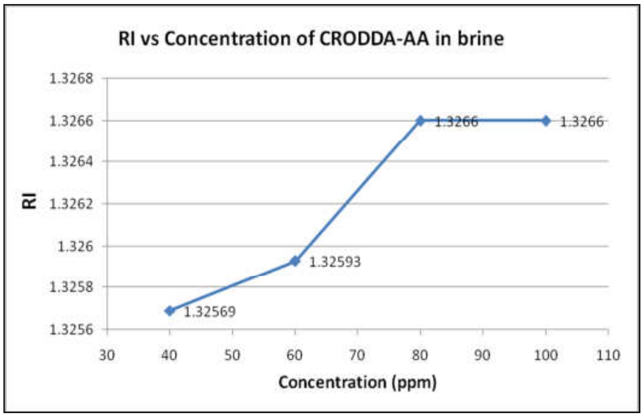


Figure 13 - Graph of RI versus concentration of wax inhibitor CRODDA-AA in brine

Once the refractive index profile was developed, refractive index (RI) of the wax inhibitor CRODDA-AA in the first tube collected at the core flood outlet was determined and the RI showed the value of 1.32616. When the RI value was plotted in the graph, the concentration was found to be 68 ppm as read from the red arrow in Figure 14 and Table 6.

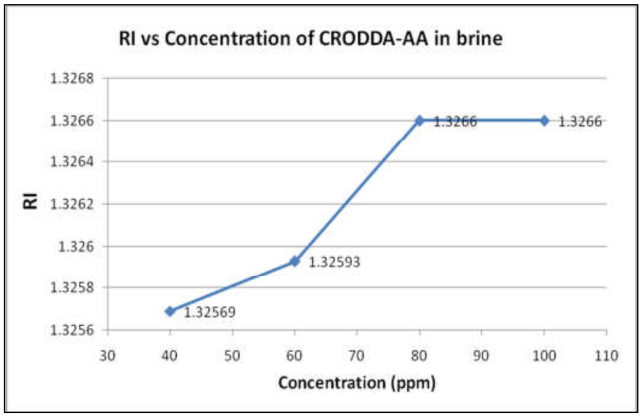


Figure 14 - Concentration of wax inhibitor CRODDA-AA in brine that collected at core flood outlet

Table 6 - Refractive index for various concentration of wax inhibitor CRODDA-AA in brine

WI Concentration in Brine (ppm)	RI
40	1.32569
60	1.32593
68	1.32616
80	1.32660
100	1.32660

Wax inhibitor CRODDA-AA concentration of 68 ppm at the outlet of core flood system reflects concentration of wax inhibitor that is flowing out straightly after the injection. On the other hand, the remaining concentration which is 32 ppm reflects concentration of wax inhibitor that is retained in the core or formation. This indicates that the adsorption capability of this inhibitor is quite high since 32% of the wax inhibitor CRODDA-AA still retained in the formation.

3.3.2 SEM Analysis of Berea Core

Figure 15 represents the SEM image of the original Berea core. This image illustrates a three dimensional view of the core sample at a microscopic level. Figure 16 describes the topography of the surface of the Berea core which had been restored implying that these areas are completely washed by the wax inhibitor. The wax inhibitor injection was not totally blocked the core since the pores still visible indicates that no formation damage occurs after the treatment.

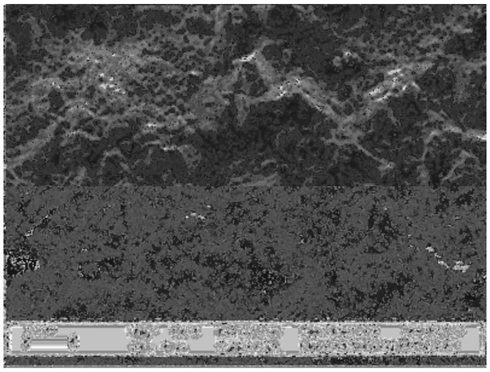


Figure 15 - SEM Image of Original Berea core

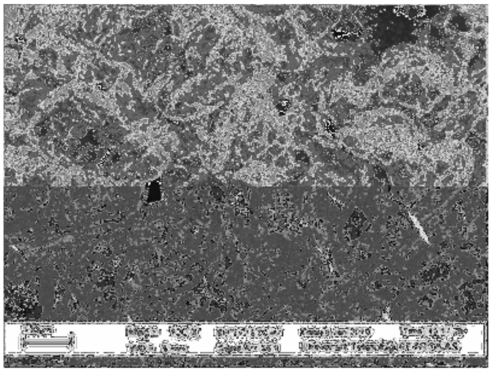


Figure 16 - SEM Image of Berea core after wax inhibitor injection

3.3.3 Core Flood Studies Using Actual Core C

Specification of the actual core C used in this study was described as below:

- Length: 44.42 mm
- Porosity (%): 24.350
- Vp (cc): 12.087
- K_{air} (mD): 336.035
- K_{∞} (mD): 316.938

Initial Kw, Kw_i from the data plotted after flushing with brine was 299 mD. After Kw_i has been established, 200 ppm wax inhibitor CRODDA-AA in waxy crude A (crude) was injected at the flow rate of 1 ml/min until irreducible water was determined. After this step, the crude was aging for seven days at the temperature of 110°C in an oven. Next, the crude was flushed with 3.2% NaCl (brine) until no more crude was coming out from the system to determine $Kw_{@SOR}$. Fluid samples, crude and brine, were collected in test tubes at the outlet of the core floods system as described in Figure 17.

Figure 17 - Crude and brine were collected in test tubes at the outlet of core floods system after crude aging and flushing with brine

From the data, $Kw_{@SOR}$ value was taken to be 251 mD. Compared with the initial Kw of 299 mD, the reduction of permeability after the wax inhibitor injection was only 48 mD which is equals to 16%. No significant reduction in the permeability shows that no formation damage occurs to the core caused by the wax inhibitor injection.

In addition to that, concentration of wax inhibitor in the crude was determined and compared before and after its injection to the coreflood system. Concentration of wax inhibitor in the crude before injection is known to be 200 ppm. Concentration of wax inhibitor in the crude after injection is taken from the first tube as illustrated in Figure 17 since it has the highest wax inhibitor concentration.

Wax inhibitor concentration in the crude collected at the core flood outlet after the injection was determined using Refractive Index analysis. Same as the previous refractive index analysis, a few concentrations of wax inhibitor CRODDA-AA in crude were prepared ranges from 10 to 200 ppm whereby the refractive index were determined for each of the concentration. The refractive index profile was illustrated in Figure 18 and Table 7.

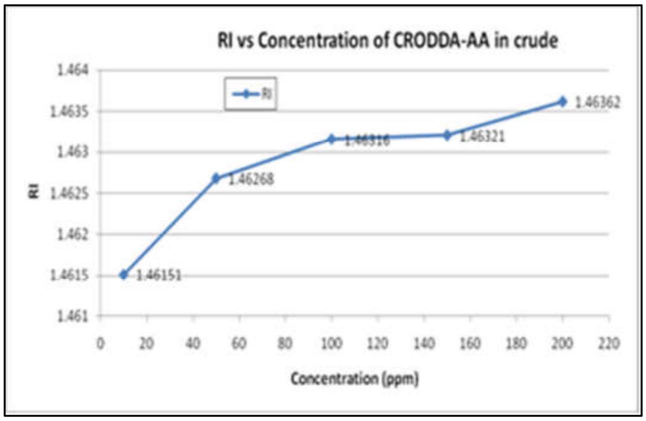


Figure 18 - Graph of RI versus concentration of wax inhibitor CRODDA –AA in waxy crude A

Table 7 - Refractive index for various concentration of wax inhibitor CRODDA-AA in crude

WI Concentration in Crude (ppm)	RI
10	1.46151
20	1.46190
50	1.46268
100	1.46316
150	1.46321
200	1.46362

Once the refractive index profile has been developed, refractive index (RI) of the wax inhibitor CRODDA-AA in the first tube collected at the core flood outlet was determined and the RI showed the value of 1.4619. When the RI value was plotted in the graph, the concentration was found to be 23 ppm as read from the red arrow in Figure 19.

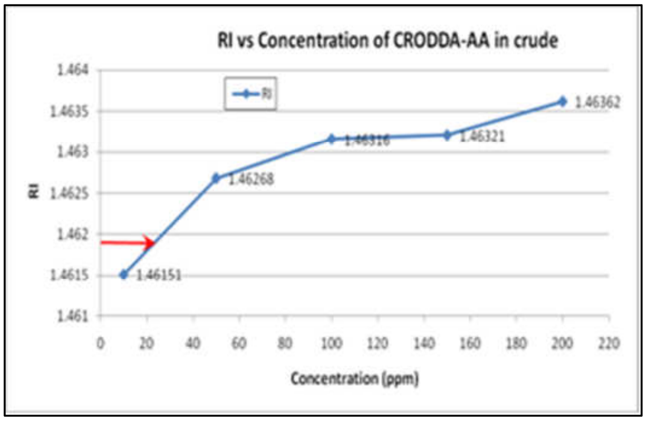


Figure 19 - Concentration of wax inhibitor CRODDA-AA in crude collected at core flood outlet

Wax inhibitor CRODDA-AA concentration of 23 ppm at the outlet of core flood system reflects concentration of wax inhibitor that is flowing out straightly after the injection. On the other hand, the remaining concentration which is 177 ppm reflects concentration of wax inhibitor that is retained in the core or formation. This indicates that the adsorption capability of this inhibitor is very high since 88.5% of wax inhibitor CRODDA-AA still retained in the formation which implies a potential for longer treatment lifetime.

3.3.4 SEM Analysis of Actual Core C

Figure 20 represents the SEM image of the original core C. Figure 21 illustrates the SEM image of the core after the wax inhibitor injection whereby an adsorbed layer of the inhibitor can be observed on the rock surface. Like the Berea core, image of the actual core C also shows no significant damage since the pore openings are still visible. This had supported the result of small permeability reduction after the wax inhibitor injection which is only 16% from the original K_w thus considered insignificant damage.

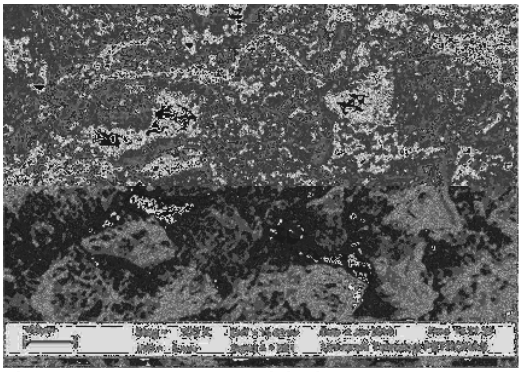


Figure 20 - SEM Image of original Core C

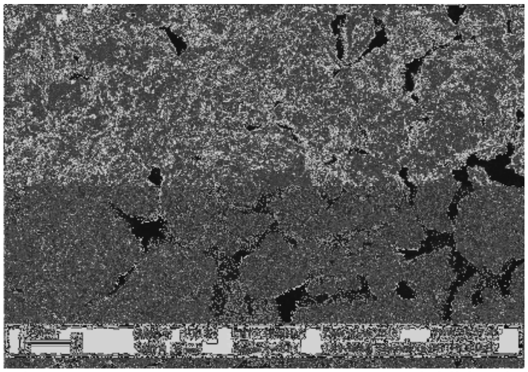


Figure 21 - SEM Image of Core C after wax inhibitor injection

4.0 Conclusions

As a conclusion, the crude analysis indicates that the waxy crude A is waxy and has high paraffinic content thus cause a flow assurance problem that can deteriorate the flow passage of the oil. Polybetaine types of wax inhibitors had been successfully synthesized, characterized and evaluated in order to solve the flow assurance problem in waxy crude A. It has been concluded that 1000 ppm concentration of the optimum wax inhibitor, CRODDA-AA in the crude can reduce the pour point by 12ºC from 57ºC to 45ºC and lower down the viscosity at seabed temperature about half of the original value from 5421 cP to 3220 cP. This can lead to the improvement in flow properties, especially near or below the pour point of the crude oil.

In term of adsorption capability of wax inhibitor CRODDA-AA to retain in the formation, from the core flooding study, adsorption of CRODDA-AA is higher in the actual core compared to the Berea core. From the results, amount of inhibitor that is still retained in the actual core is 88.5% without significant formation damage. As a next step, it is planned to run the core flood and wax inhibitor release tests to refine the design of squeeze treatment.

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