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Harnessing the Biosurfactant Trifecta to Mitigate Organic Solids Deposition

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Abstract

Asphaltenes are the heaviest and most polarizable ultracomplex fraction of crude oil. It is well known that asphaltene deposition is a common problem in the upstream oil and gas industry with significant economic implications. Asphaltene precipitation is due to pressure depletion and fluid compositional change, impacting petrophysical properties such as permeability and wettability in oil reservoirs. It can cause blockages, not only in the wellbore and near wellbore region but also in the pipeline; it restricts the flow of crude oil, which leads to reduced oil production, equipment damage, and decreased efficiency. Several strategies are commonly adapted to mitigate the effect of asphaltene deposition, such as asphaltene inhibitors, solvent wash, and physical removal. However, conventional oilfield chemical treatments are costly and can cause additional well damage, and the efficacy has been marginal at best. This paper describes the development of a novel ESG-friendly biosurfactant-mediated asphaltene inhibitor made from renewable raw materials with a carbon-neutral footprint**.** This represents a viable, cost-effective, and actionable approach for reducing the volume of chemicals required for flow assurance management in oil field applications.

The approach detailed here centers on building a fundamental understanding of the asphaltenic fraction of a given bitumen - followed by the rational design of a biosurfactant-mediated asphaltene inhibitor best suited to inhibit the asphaltene precipitation or delay the on-onset asphaltene precipitation. Analytical tools and techniques were used to characterize oil and its asphaltene molecules. Lastly, various asphaltene inhibitor screening methods were applied to identify and rationally design a suitable inhibitor to maximize its efficacy under lab and realistic field conditions. The ultimate result is the development of a novel biosurfactant inhibitor capable of significantly increasing asphaltene inhibition by >95% for more than two weeks, drastically reducing asphaltene deposition while utilizing a lower dosage than traditional chemical dosage deployed at the oil field.

Our results demonstrate that our biosurfactant inhibitors effectively mitigate asphaltene deposition for different crude oils. This could be due to the higher steric hindrance effect of the surfactant-containing polar head groups (heteroatoms) attached to the asphaltene polar surface, creating an asphaltene-solvent interaction. The alkyl end blocks or isolates the asphaltene molecules from further contact with other asphaltene molecules. In addition, the biosurfactant based inhibitor decreases the asphaltene aggregate size as shown by dynamic light scattering, which disperses asphaltene molecules and acts as resin molecules, hence preventing precipitation. It is assumed that there are strong interactions between inhibitors and asphaltene particles via the formation of hydrogen bonds. Our results provide initial evidence of the chemical interactions between asphaltenes and the biosurfactant-mediated asphaltene inhibitor.

Introduction

In the upstream oil and gas industry, specifically oil production facilities, asphaltenes are well known for clogging surface facilities (i.e., separators, pumps), flow pipelines, wellbores, and nearby regions. Throughout oil production operations, many challenges arise due to the deposition of asphaltene, which frequently hinders production operations and, thus, imposes substantial economic and technical challenges on the oil industry (Akbarzadeh, 2007). Usually, once asphaltene deposits accumulate all over the oil production facilities, they result in loss of production, safety problems, and a significant increase in production costs for cleaning and maintenance operations. In addition, in downhole, the adsorption of asphaltene deposits onto rock surfaces tends to significantly alter vital rock formation properties such as porosity, permeability, and rock wettability, which results in lower recovery and additional expenditures (Clementz, 1982; De Pedroza, 1996). Hence, the precipitation and deposition of asphaltenes during oil production operations have become a widespread problem worldwide with many devastating and economic consequences.

Mostly, the asphaltene precipitation is due to the destabilization of asphaltene molecules surrounded by resins, aromatics, and poor saturated solvents. This destabilization occurs due to changes in thermodynamic factors such as pressure, temperature, and change in oil composition. According to the Yen model (Yen, 1961), it is generally hypothesized that asphaltene molecules form nano-aggregates using a stack of polyaromatic hydrocarbons with an aggregation number of ~4-6 molecules, which is strictly governed by the presence of alkyl side chains on the fused aromatic rings that

form a layer of protection through steric hindrance around these structures (Mullins, 2010). Furthermore, it is anticipated that around eight nano aggregates are needed to form clusters of the nano-aggregates, eventually creating the micro-aggregates and the solid-like irreversible precipitated phase afterward. The asphaltene precipitation, resulting from the disturbance and destabilization of asphaltenes constituent in crude oil, is an essential condition for forming asphaltene deposits in the wellbore and the near wellbore regions.

The formation of asphaltenes deposits during oil production interferes with oil recovery as it often clogs wellbores and pipelines, reducing well productivity. The usage of chemical inhibitors has shown in recent years that it could offer at low concentrations a practical and economical solution for the precipitation of the asphaltenic fractions since they can effectively stabilize asphaltenes and potentially ensure a convenient and economical flow of crude oil from the reservoir to the point of sale (Hashmi and Firoozabadi, 2013; Karambeigi, 2016; Fogler, 1994; Jamaluddine, 2002).

The use of chemical additives is an option to mitigate asphaltene deposition. They can act as dispersants and/or inhibitors. Inhibitors typically affect the flocculation onset point, whereas dispersants usually reduce the size of aggregates formed. Inhibitors can also act as dispersants, but in general, the inverse is not true; dispersants do not affect the flocculation onset point (Kelland, 2009). Inhibitors and dispersants are frequently combined in formulations applied in oil fields. Typically, dispersants have a polar head that interacts with asphaltenes and an alkyl tail that changes the polarity of the aggregate (Rogel, 2001). Examples of dispersants are alkylphenol resins, phosphoric esters, ether carboxylic acids, alkyl pyrrolidines, and alkyl benzene sulfonates, such as dodecyl benzyl sulfonic acid (Kelland, 2009). The chemicals often used to inhibit asphaltene deposition are generally toxic and non-biodegradable (Okafor, 2016), leading the oil community to look for cost-effective, non-toxic, environmentally friendly alternatives (Atta, 2017; Aguiar, 2013). To mitigate these challenges, here we describe the development of novel ESG-friendly biosurfactants, such as Sophorolipids (SLs) mediated asphaltene inhibitors, which are made from renewable raw materials with a carbon-neutral footprint.

Sophorolipids (SLs) are a class of non-ionic glycolipid bio-surfactants first reported in 1961 (Gorin, 1961). The most widely used organism for synthesizing SLs has been Candida Bambicola due to its high yield and productivity (de Oliveira, 2015). SLs consist of two molecules of glucose linked via a β-1,2 glycosidic bond (sophorose); another glycosidic bond connects this sophorose to a hydroxyl fatty acid. The sophorose acts as the hydrophilic head, while the long-chain hydroxyl fatty acid acts as the hydrophobic tail.

The production of SLs first requires biosynthesis of the hydroxy fatty acid from a fatty acid via enzymatic action of cytochrome P450 monooxygenase. This hydroxyl fatty acid is subsequently coupled to glucose by glycosyltransferase to yield a glucolipid. After that, a second glucose is attached, via a β-1,2 glycosidic bond, to the glucolipid to deliver an SL having a free carboxylic acid end group 1 (Figure 1). A further intermolecular esterification reaction (Develter, 2010) yields a lactonic sophorolipid (LSL) 2 (Fig. 1). The commonly attached fatty acids on the sophorose are those in the C16–C18 range and include palmitic, stearic, oleic, linoleic, and alpha-linolenic acids. Oleic acid is the most widely used of these acids because it is readily available and remains liquid (Jadhav,2019; Ceresa, 2020; Wang, 2020) at room temperature.

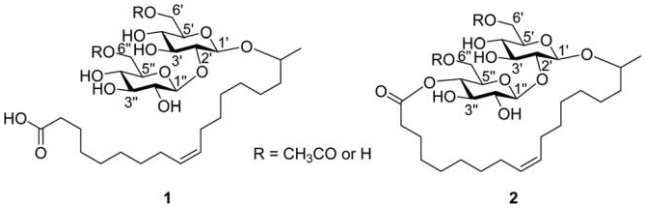
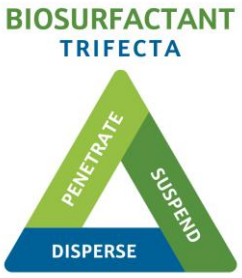


Figure 1: Free acid (1) and lactone (2) forms of sophorolipids.

SL biosurfactants have attracted commercial and academic interests for their applications (Ziemba, 2019; Gross, 2010; Mulligan, 2001) in detergency, surface enhancement of electro-spun fiber, bioremediation, enhanced oil recovery, medicine, home and personal care products, and antimicrobial agents. They are readily biodegradable, less toxic, and have low cytotoxicity compared to conventional non-ionic surfactants (Putro, 2019) such as Triton-X100, Pluronic L31, and polyoxyethylene lauryl ether. Our previous article presented the potential for sophorolipids to disperse asphaltenes (Aguiar, 2020) for the first time. Here, we present for the first time that sophorolipids have great potential to inhibit asphaltene precipitation due in part of the biosurfactant trifecta, which is the ability penetrate, disperse and suspend both organic and inorganic molecules or accumulated solids.



The main goal of this research study is to explore and compare the biosurfactant-based inhibitors with several commercial asphaltene inhibitors in mitigating the accumulation of asphaltene deposits in the wellbores through the inhibition of asphaltene precipitation for two different crude oils of medium and low API gravity. This research aims to enhance our fundamental understanding of biosurfactant-based inhibitors in preventing asphaltene precipitation and their interaction with asphaltene molecules. By doing so, it will significantly contribute to our knowledge of asphaltene

inhibition chemistry which is crucial for developing a novel precipitation inhibition process for innovative, cost-efficient, and environmentally friendly asphaltene inhibitors for oil production operations.

Materials and Methodology

Crude Oils and Chemicals. Two crude oil samples, one is crude oil A, and another is crude oil B, were considered in this study. However, a detailed analysis was carried out with crude oil A only. Several biosurfactant-mediated asphaltene inhibitors were evaluated compared to commercial inhibitors for their ability to inhibit asphaltene precipitation. Here, we report results from inhibitors A, B, C, and D, including three commercial inhibitors, E, F, and G. Here we report results from inhibitors A - G where B is the SL containing version of A, D is the SL containing version of C and E - G are commercial products.

Asphaltenes were precipitated from the crude oil using n-heptane (C7), oil/C7 ratio 1:40, extracted via a 0.45 µm filter and characterized using Fourier Transform Infrared Spectroscopy (FTIR). Sophorolipids (SLP) isolated and purified to >90% activity from a large-scale fermentation process were used after dilution in DI water. LC-MS analysis revealed that the sample was comprised mainly of acetylated and non-acetylated sophorolipids derived from stearic, oleic, and linoleic fatty acids.

The refractive index of the crude oil and hydrocarbon mixture was measured using a digital refractometer (Anton Paar, Abbemat 3000). Refractive index (RI) measurement is a powerful tool in determining the onset of asphaltene precipitation when a crude oil sample is titrated with a precipitant.

Table 1: Physical and Chemical Properties of Crude Oil A & B

Oil	Density, (20 °C) g/cm^3	Viscosity, (20 °C) cP	API Gravity	C_7 Asphaltene Wt.%
Oil A	0.9679	1,854.0	14.5	11.2
Oil B	1.012	144,000.0	8.3	35.0

Saturates, Aromatics, Resins, and Asphaltenes (SARA) Analysis. For SARA analysis, crude oil samples were submitted to Premier Corex (Houston, TX). Asphaltenes were heptane (C7)-precipitated from the fluids. The compositional contents of the crude oil were identified via Saturates, Aromatics, Resins, and Asphaltene (SARA) analysis. SARA fractions were determined for the crude oil using an open-column chromatography technique packed with silica and alumina. SARA fractionation initially separated asphaltenes by adding n-pentane to the crude oil. The remaining components, called maltenes, were separated via column chromatography, packed with silica and alumina, and flushed with various solvents (petroleum spirit and methanol).

Table 2: SARA fraction of Oil A

	% Saturates	% Aromatic	% Resin	% Asphaltene
Oil A	14.88	42.24	31.65	11.22

***Particle size distribution analysis*:** The effect of the inhibitor on the particle size distribution of asphaltene in the heptane solution was determined by dynamic light scattering (DLS, Anton Paar, Lightsizer). The resultant mixtures were agitated for 1 minute before standing at room temperature (22 °C). Samples of the asphaltene and heptane solution were added to a cuvette with a PTFE stopper after different aging times, such as 1 hour, 24 hours, and 1 week. This mixture was agitated by hand for 10 s before being immediately transferred to the DLS cuvette with a PTFE stopper.

Asphaltene Dispersion Test (ADT)

ADT is a method used to evaluate the ability of a given chemical to delay asphaltene sedimentation upon the addition of n-heptane. The ADT measures normal gravimetric sedimentation of asphaltene over a period of time after diluting the oil with an asphaltene precipitant, such as n-heptane.

The test also enables the determination of the efficacy of treatment chemicals. An aliquot of untreated and treated crude oil is added to ADT test tubes that contain 10 mL of heptane. Inhibitor test formulations and commercial samples were dosed at 500 and 1000 ppm by volume (based on crude oil) of the chemical. The gravity-assisted percentage sedimentation for up to seven days is observed and recorded. The sedimentation or precipitation is recorded in milliliters from the graduated ADT tubes. The reference of the blank (no chemical treatment) deposit level was evaluated and noted D_{Blank}. Different dosages of inhibitors were added to 10 ml of n-hexane, and the above procedure was repeated with the deposit level noted as $D_{Treatment}$. The efficiency of the inhibitors to reduce asphaltene precipitation at each concentration is reported at percent inhibition (% I) and is calculated through the following equation:

$$\%\, I = \left(\frac{D_{blank} - D_{treatment}}{D_{blank}} \right) X\ 100$$

Finally, the samples were left undisturbed for a specific period (also known as aging time), and the amount of sediment

obtained was recorded in mL at the end of the experiment. The aging times used were 1h, 24 h, and one week. When no deposition was observed, the data entry was recorded as ‘‘clear,” and when precipitation was observed but was not measurable, the data entry was recorded as ‘‘trace.” The criterion for evaluation of the performance of dispersants using the ADT consists of comparing the amount of sediment obtained in mL for the different chemicals and dosages with respect to the control or untreated oil, which was the mixture of crude oil and n-heptane without the addition of the dispersant.

RESULTS AND DISCUSSION

FTIR of Asphaltenes

Fourier transform infrared spectroscopy (FT-IR) was used as a fingerprinting method to investigate the presence of certain chemical functional groups in the separated asphaltenes. The technique was utilized to obtain infrared spectra of emission of the solid samples in the mid-infrared spectral region of 4000-500 cm^{-1}. FT-IR spectra were recorded using the IR-Tracer-100 by Agilent equipped with an Attenuated Total Reflection (ATR) method. The FT-IR spectra (Figure 2) were recorded using an ATR accessory with a high refractive index zinc selenide (ZnSe) prism. Solid samples were prepared by making thin films of the powdered samples in the ATR cell.

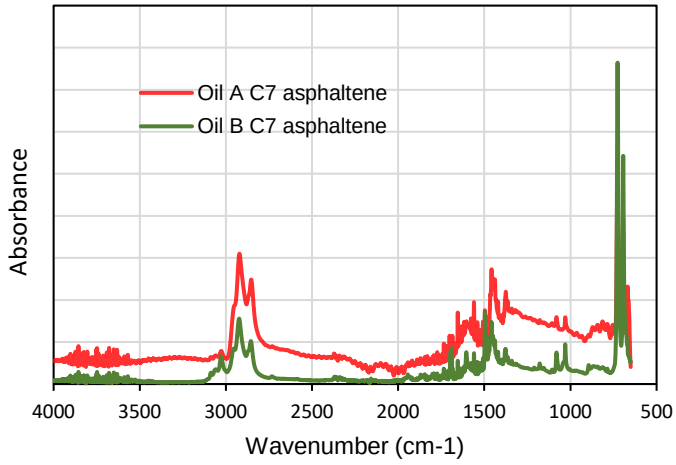


Figure 2: FT-IR spectrum of the asphaltene for both oils

FTIR demonstrates pure asphaltene spectra extracted from crude oil using the ASTM D6560 method. A wide-intense peak at the wavenumber of 3419 cm^{-1} corresponds to the O–H or N–H stretching banding. It is necessary to mention that to determine the type of peaks accurately, access to elemental analysis results of the asphaltene sample is required. The peak will correspond to the O–H stretching bond if the sample has oxygen. Otherwise, it will correspond to the N–H stretching band (Silverstein and Bassler, 1962). In Figure 2, the 3000–3800 cm^{-1} peak corresponds to the molecule's poly-aromatic structure, and methylene could just be observed as a side alkyl chain bound to central aromatic nuclei. The asphaltene in the crude oil samples has a functional group of esters attached to the aromatic ring. Carbonyl C=O stretching vibration was identified by a peak at the wavenumber of 1695 cm^{-1}. The peak in frequency of 1259 cm^{-1} corresponds to C–C (=O) –O, while if it appears in the frequency range between 1159 cm^{-1} to 1299 cm^{-1}, it will correspond to esters bound to aromatics. There are also two peaks at a range of 1020 cm^{-1} to 1090 cm^{-1} in the fingerprint region, which correspond to the O–C–C bands of esters (steric carbon-oxygen stretching) (Silverstein and Bassler, 1962; Taheri-Shakib et al., 2018; Smith, 2011). In aromatic compositions such as asphaltene, the S=O sulfoxide peak is usually present in 1030 cm^{-1} to 1164 cm^{-1}.

Determining On-Set Asphaltene Flocculation by RI

The flocculation studies were carried out by adding n-heptane to the crude oil in toluene. Different volumes of n-heptane are added to 10 mL of the asphaltene in a toluene solution to induce the asphaltene flocculation. All the experiments were conducted at a controlled temperature of 25 ^{o}C. The refractive index of a mixture such as crude oil before precipitation is a linear combination of refractive indexes of the individual components. In contrast, this relation does not hold after asphaltene precipitation (Wattana, 2003). Changes of RI with asphaltenes flocculation for Oil 1 Asphaltene (Figure 3) are presented. The plot shows a nonlinear behavior of the RI as a function of the n-heptane added.

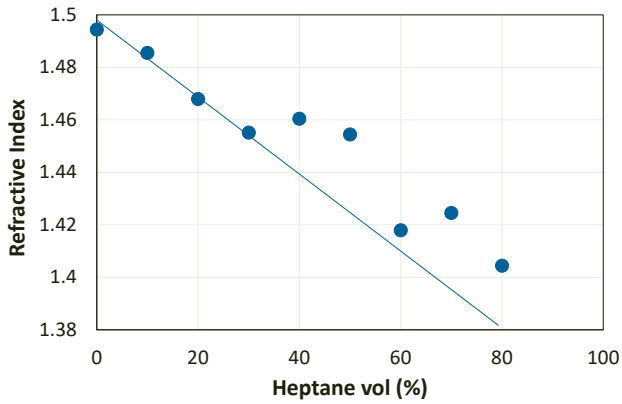


Figure 3. RI plots for Oil 1 asphaltenes (2000 mg/g) in the toluene-heptane mixture.

At low n-heptane ratios, the decrease in the RI is linear with the n-heptane volume added. When the precipitation onset is reached, an abrupt change in the plot is observed, and the RI increases (Figure 3). This change in the RI is due to the growth of the asphaltene colloids forming flocculates. After 40% of heptane is added, the flocculation sediments and the signal return to the predicted value for an ideal mixture. Precipitation of asphaltenes reduces the polarity properties of the remainder of the oil phase, and the asphaltene solution's RI value will be reduced. This confirms that Oil 1 asphaltene precipitation starts beyond 30% heptane, as reported in the literature. Adding a precipitant to a crude oil reduces the RI of the mixture in a linear trend. This behavior continues until the onset of asphaltene

precipitation. After this point, the polarity of the remaining oil is reduced due to the reduction of suspended asphaltene particles; therefore, RI deviates from its linear trend. According to the data published by Wattana et al. (2003), a jump will be observed in the RI curve at the onset of asphaltene precipitation if the asphaltene precipitation process occurs wholly and suddenly.

Role of Biosurfactants as Asphaltenes Dispersants

Initially, an asphaltene dissolution test was carried out by introducing a co-solvent, such as ethanol, that improves the primary solvent in dissolving and dispersing asphaltene deposits. Co-solvents may not necessarily contribute to the solvency of the asphaltene deposits but can act to disperse, suspend, or water wet the rock surfaces (Trbovich and King, 1991). Due to its water-wetting characteristics, ethanol has been applied as a co-solvent to heptane solvents. The primary motivation of the study is to determine if biosurfactants can help dissolve asphaltene in heptane solvent. As we know, asphaltene is not soluble in heptane as it is non-polar.

Figure 4: Effect of biosurfactant on asphaltene dissolution (Vial B1: asphaltene + heptane, B2: B1 + ethanol, and B3: B2 + biosurfactant)

As evidenced by the above solubility test, asphaltene is not soluble in heptane or the mixture of ethanol and heptane. However, the addition of biosurfactant significantly improves the solubility of the asphaltenes. This indicates biosurfactants help asphaltene solubility in non-miscible solvents like heptane and ethanol. This is due to the presence of surface-active sites and the H-bonding interaction of surfactant (Figure 5) with asphaltene molecules.

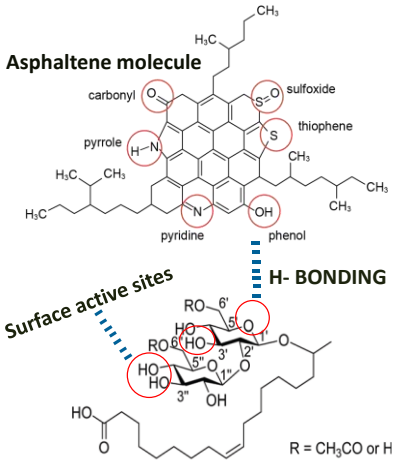


Figure 5: Asphaltene and Biosurfactant interaction

Effect of Biosurfactant on Asphaltene Size Distribution

In another test method, the solubility of asphaltenes was evaluated by the Accelerated Solubility Test (AST) at 25 °C, 5000 RPM for 10 minutes. Different ratios of n-heptane/toluene were tested: 90, 80, 70, and 60% V/V of n-heptane, and the final concentration of asphaltenes was 0.5% w/V. The effect of biosurfactants on the particle size distribution of asphaltenes at different volume fractions of heptane was investigated by DLS, as shown in Figure 6. In the absence of biosurfactants, it is observed that the addition of heptane results in the aggregation of asphaltene and increased particle sizes. Particles greater than 1um in diameter (black) are observed at 60 vol% heptane and above – the volume fraction of asphaltene existing as particles of this size increases with increasing heptane vol%. The solubility behavior of asphaltenes in toluene is enhanced when it has a lower amount of heptane concentration.

Table 3: Testing condition of asphaltene dissolution in a heptane-toluene solvent

Samples	Control	Biosurfactant
n-Heptane (%v/v)	60, 70, 80, 90	60, 70, 80, 90
Asphaltene (%w/v)	0.5	0.5
Chemical dosage	-	1000 ppm

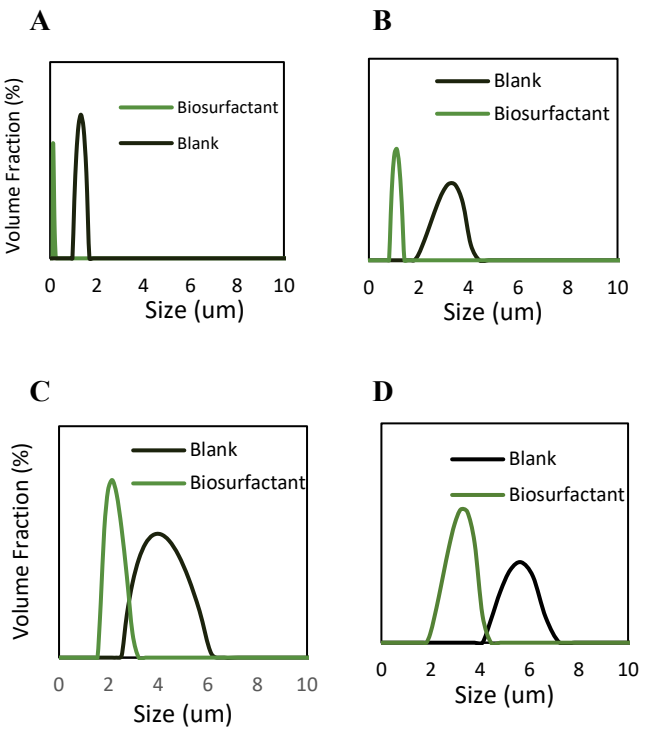


Figure 6: Particle size distribution determined by DLS for 0.1 gL^{-1} asphaltene in heptane-toluene. A: 60% Heptane, B: 70% heptane, C: 80% heptane and D: 90% heptane with no inhibitor (black line) and 1000 ppm biosurfactant dispersant (green line) at destabilization times of 10 min.

This study shows the largest particle size in 90% heptane as the asphaltene is less soluble; hence, bigger aggregates were found. The addition of biosurfactant alters the particle size distribution and reduces the asphaltene particle size. The ability of the biosurfactant to disperse and suspend organic molecules prevents the agglomeration of asphaltenes and hence inhibits precipitation.

Asphaltene Inhibition Test (AIT)

The study used two crude oils to examine the efficiency of chemicals for asphaltenes inhibition in the oil phase. Table 1 reports American Petroleum Institute (API) gravities for the crude oils used in this work. Crude oil A is a medium oil, and crude oil B is a heavy oil. ADT was performed on both oils using the biosurfactant-mediated asphaltene inhibitor, as described in Methods.

Inhibitor B was added to the crude oil sample via a micropipette. The sample was agitated using a vortex mixer and heated for 1 hour at 60 °C before injection into the ADT tube. A total of 50 µL of the untreated and treated crude oil was injected into 10 mL of heptane. Table 4 reports gravity-assisted sedimentation at 10 minutes, 60 minutes, and 24 hours for the blank crude oil A and the crude oil treated with Inhibitor B.

To understand the effect of the dosage of Inhibitor B, studies with different concentrations at 500 ppm and 1000 ppm were performed, at 25 ºC and 24 h aging time. Lower dosages of inhibitors are desirable for field applications to minimize the treatment cost and chemical volume.

Table 4 shows that no precipitation was observed in the treated samples, and a significant percentage inhibition (%I) was achieved relative to the untreated crude oil. %I increased with increasing dosage (Juyal P et al. 2012) of Inhibitor B.

Table 4: Standard AIT Results for Crude Oil A & B

Sample	Inhibitor B dosage in (ppm)	Deposition (mL)			% Inhibition @ 24h	Turbidity (ntu)	Particle Size (um)
		10 min	*1h*	*24 h*			
Oil A	0	0.7	0.9	1.2	0	52	6.8
	500	clear	clear	0.2	83.3	124	1.8
	1000	clear	clear	0.1	91.7	146	0.87
Oil B	0	0.8	1.0	1.4	0	55	5.9
	500	clear	clear	0.3	78.6	135	1.6
	1000	clear	clear	0.2	85.7	158	1.1

Table 5: Standard ADT Results for Crude Oil A at different aging time

Centrifuge Tube	Sample	dosage (ppm)	% Inhibition		
			10 min	*1 day*	*1 week*
a	control	0	0	0	0
b	Inhibitor A	1000	100	57.1	13.0
c	Inhibitor B	1000	99.0	86.0	72.0
d	Inhibitor C	1000	99.0	79.0	56.0
e	Inhibitor D	1000	96.0	64.3	19.0

The AIT results confirm that the stability of asphaltene increases with the concentration of the biosurfactant-mediated inhibitor. Thus, it is evident that Inhibitor B effectively stabilizes asphaltenes against precipitation for crude oil A and B at both treatment rates tested. The turbidity increase with treatment rate supports that more asphaltenes remain in solution, while the low turbidity of the blank is consistent with the asphaltenes precipitating out of the bulk solution. Finally, the decreasing particle size with increasing Inhibitor B concentration is evidence of the ability of the biosurfactant to disperse and suspend particles.

Stability Study of Inhibitors for Crude Oil A

To evaluate the performance and effectiveness of different inhibitors with and without biosurfactant for controlling asphaltene precipitation, the ADT test was carried out for one week. The crude oil was treated with inhibitors at equal concentration, 1000 ppm, in an excess of heptane. The amount of sediment with different inhibitors is presented in Figure 7, and the % of inhibition is presented in Table 5. The lower amount of sediment collected means the dispersion of asphaltenes is more efficient.

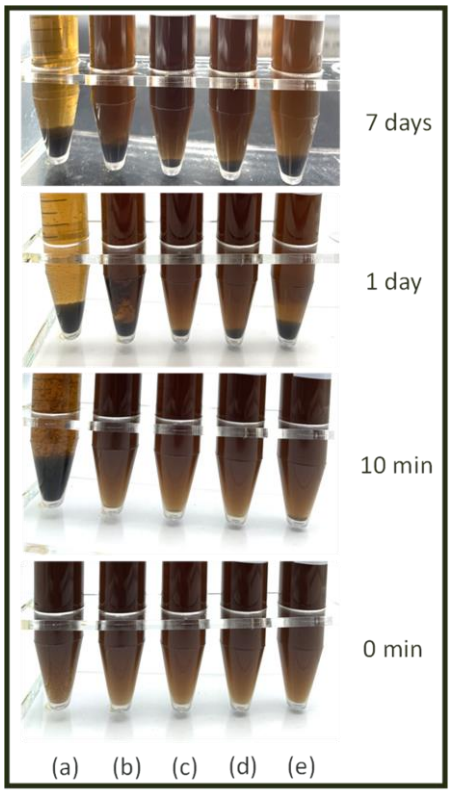


Figure 7. ADT results for crude oil A were treated with Inhibitor A, B, C and D at 1000 ppm for aging times of 0 h, 1h, 24h, and one week.

It is observed that all the inhibitors show diminished inhibition capacity with increased aging time. Still, inhibitor B was the most resilient over time with the least sedimentation.

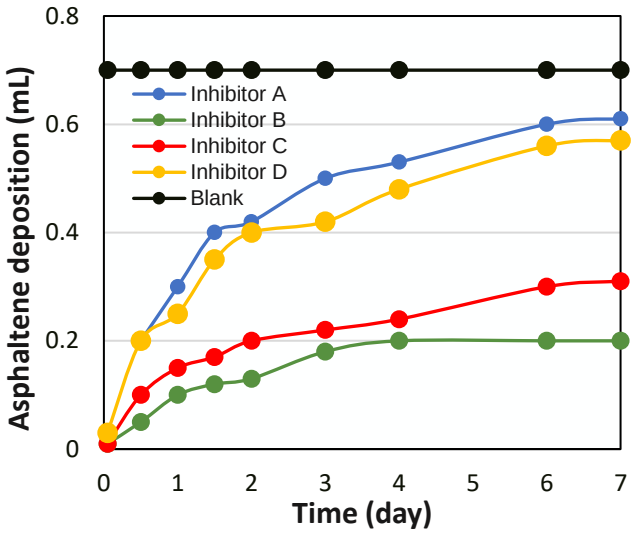


Figure 8. Rate of asphaltene deposition with aging time

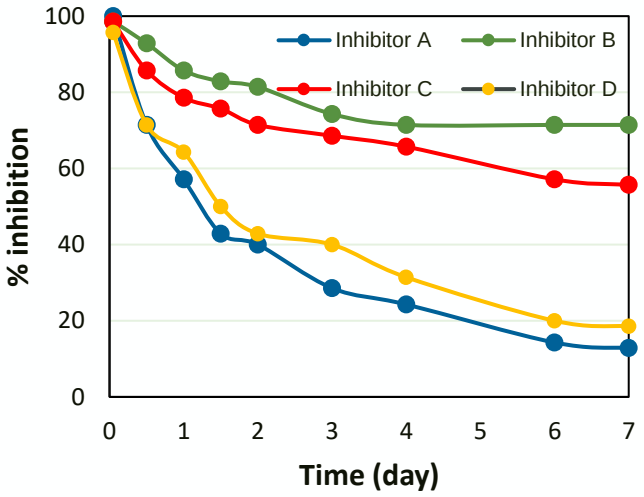


Figure 9. Efficiency of inhibitors with aging time

Inhibitor B is combination of Inhibitor A with biosurfactant. It is clear from the results presented in Figure 7 and Table 5 that the addition of SL significantly improved Inhibitor A. Inhibitor B showed asphaltene inhibition of more than 71% after one week and successfully redispersed and stabilized the precipitated asphaltenes for crude oil A. On the other hand, the performance of Inhibitor D, which is the combination of Inhibitor C and biosurfactant did not show improved performance over the non-SL containing Inhibitor C. Observed trends could be due to the negative synergistic effect of

biosurfactants with acids. Biosurfactant enhances the asphaltene inhibition for polymers and shows the best activity.

Based on the ADT experiments conducted with a suite of dead crude oils, biosurfactant-mediated asphaltene treatments can be highly effective in stabilizing asphaltenes in the hydrocarbon phase and can improve inhibition capacity. The chemicals were effective even after the mixture of crude oil and heptane was allowed to age for an extended period. The chemical effectively controlled the migration of destabilized asphaltene in the heptane phase.

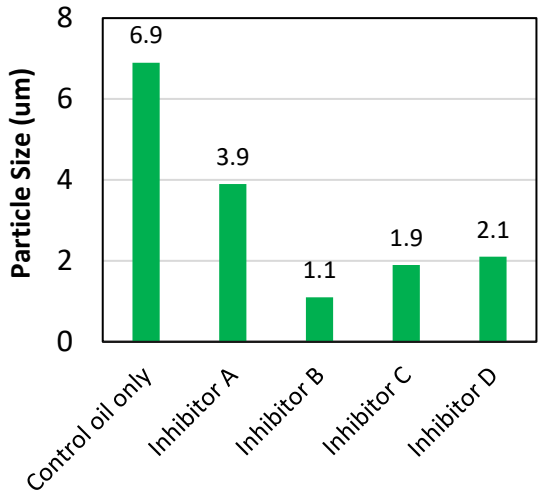


Figure 10. Particle size of asphaltenes in n-heptane with/out Inhibitors

The experimental data using ADT suggested that the biosurfactant-mediated asphaltene inhibitor stabilizes the asphaltene particles due to its unique ability to interact between asphaltene particles and asphaltene inhibitor molecules via π-π interactions and hydrogen bonding. The additive stabilizes the asphaltenes in the medium, inhibiting the molecular aggregation process. It can be observed that (Figure 10) the average sizes of the aggregates of these asphaltenes decreased with biosurfactant for inhibitor B, compared to inhibitor A, where there is no biosurfactant. However, no significant change in particle size was observed for inhibitors C and D. The asphaltene aggregate size is almost double that of inhibitor B.

Figure 11 illustrates the asphaltenes inhibition percentage for the three commercial inhibitors (i.e., E, F, and G), including biosurfactant-mediated inhibitors. The results indicate that inhibitors B and C have the highest asphaltenes inhibition efficiency of 86% and 79%, respectively. On the other hand, the asphaltenes inhibition percentage of A is 57%. In comparison, the minimum asphaltenes inhibition percentage was obtained using inhibitor F at a value of 50%, and similar performance was observed for other commercial inhibitors. Therefore, both B and C are relatively more effective in delaying asphaltenes precipitation than others.

Our experimental results provided initial evidence of the chemical interactions between asphaltenes and the biosurfactant-mediated asphaltene inhibitor. Also, it decreases the asphaltene aggregate size evidenced by DLS, which disperses asphaltene molecules and acts as resin molecules, hence preventing precipitation.

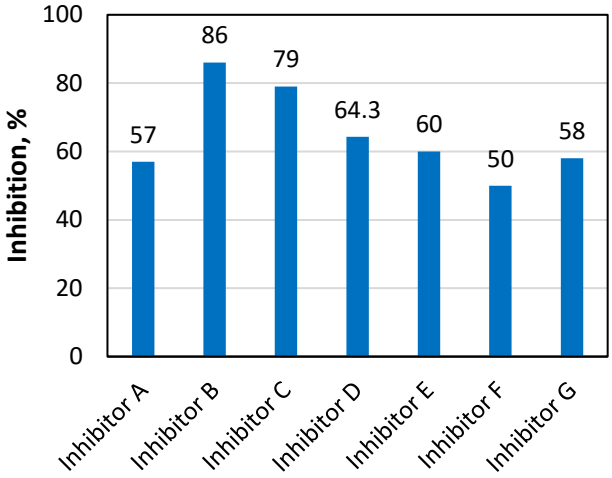


Figure 11. Asphaltene inhibition was % for the ADT test of crude oil with n-heptane with different inhibitors, including commercial ones.

Conclusions

The approach detailed here centers on building a fundamental understanding of the asphaltenic fraction of a given crude oil - followed by the rational design of a biosurfactant mediated asphaltene inhibitor best suited to inhibit the asphaltene precipitation or delay the onset asphaltene precipitation in down-hole, wellbore, and pipelines. We explored the potential utilization of a glycolipid bio-surfactant, Sophorolipids, as asphaltene precipitation inhibitors combined with synthetic copolymers. We optimized the ratio of copolymers to biosurfactant in each formulation and its dosage to maximize its efficacy for the asphaltene inhibition study.

The ultimate result is the development of a novel biosurfactant inhibitor capable of significantly increasing asphaltene inhibition by >85% for more than one week, drastically reducing asphaltene deposition. In the absence of a biosurfactant, the synthetic copolymer is not significantly effective in inhibiting asphaltene precipitation. Our results demonstrate that when biosurfactants are combined with specific chemistries, they effectively mitigate asphaltene deposition for different crude oils by significantly decreasing the asphaltene aggregation size (6x smaller size). The mechanism behind the enhanced inhibition capacity is due to the ability of the biosurfactant to disperse and suspend particles, resulting in nanosized asphaltene molecules, as evidenced by DLS analysis. The nanosized asphaltene molecule has a great tendency to disperse and hence prevents asphaltene precipitation. It is assumed that the higher steric hindrance effect of the surfactant-containing polar head groups attaches to the asphaltene polar surface, thereby creating an asphaltene-solvent interaction. The non-polar moiety of biosurfactant

blocks or isolates the asphaltene molecules from further contact with other asphaltene molecules.

The biosurfactant-mediated asphaltene inhibitor can be applied to the wellbore, near wellbore regions, and pipelines. Due to its high performance and longevity, harnessing the biosurfactant trifecta for asphaltene inhibition could be a viable, cost-effective, and actionable approach for reducing the toxic chemicals required for flow assurance management in oil field applications.

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Nomenclature

ESG =Environmental, Social, and Governance
SL = Sophorolipids (SLs)
ADT = Asphaltene Dispersion Test
FTIR = Fourier Transform Infrared Spectroscopy
AST = Accelerated Solubility Test
AIT = Asphaltene Inhibition Test
RI = Refractive Index

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