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EVALUATION OF CNSL DERIVATIVE AS ECO-FRIENDLY FLOW IMPROVER FOR INDIAN CRUDE OIL

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ABSTRACT

Paraffin deposition is a serious flow assurance issue faced by the Petroleum industry which can be mitigated by different techniques among which chemical treatment is the most practical solution to reduce the pour point and improve the cold flow properties of crude oil. However, the utilization of environmentally hazardous chemicals for mitigation of this severe issue also causes additional threats. Thus, motivated by such a problem, current research endeavor to synthesize and application of ecofriendly products for the mitigation of paraffin deposition. Cashew nut shell liquid (CNSL) collected from cashew nut shells was esterified with ethanol amine. The CNSL derivative (CD) was tested as a pour point depressant and cold flow improver for paraffinic crude oils. The pour point of doped crude oil was significantly reduced reaching a maximum of 120C and viscosity was tremendously dropped up to 90%. CD demonstrated remarkable paraffin inhibition efficacy of up to 56%. Photomicrographs of treated crude oil were inspected, revealing changes to the wax shape and microstructure. Thus, CNSL can be utilized as a flow improver for waxy crude oil and it has potential as a renewable chemical feedstock for the manufacturing of pour point depressants and other oilfield chemicals.

Keywords: Pour Point Depressants, CNSL, Natural Product, Viscosity Reduction, Crude Oil.

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INTRODUCTION

Wax deposition in the oilfield is a critical flow assurance problem for the production of paraffinic crude oil.[1,2] Wax precipitation occurs when the temperature falls below the wax appearance temperature (WAT).[3] Wax formation in the oilfield has serious cost implications related to the cost of repairs of damaged equipment, mechanical and/or chemical removal of deposits, and loss of production.[4] Thus, it is critical for the petroleum sector to address the cumbersome issue of paraffin deposition on a priority.[5,6] Different methods viz. mechanical, thermal, chemical, or a combination of any of these methods are generally used for the inhibition and rectification of paraffin deposition in crude oil production systems.[7] Comparatively, mitigation of wax formation using chemical inhibitors is an efficient and cost-effective way to control wax formation in the oilfield and ensure continuous flow.[8] However, the unique nature of pour point depressants to oil wells, in addition to the expense of chemical additives, has fueled interest in developing better and less expensive chemical solutions to the wax formation problem. Recently the use of vegetable oils and plant-based surfactants as crude oil wax crystal modifiers, pour point depressants, and viscosity reducers either in their natural state or after simple derivatization, has been receiving increased research attention.[9–12] Green products viz. oil extracted from plant seeds can be utilized as green solutions for mitigation of paraffin deposition either as such or after derivatization.[9,13,14] However, the usefulness of plant seeds in edible oil restricts their utilization for fluid flow enhancement of waxy crude oils. The cashew nut shell liquid (CNSL) is a residue of the cashew nut industry and is constituted of components such as anacardic acid, cardol, and cardanol, which operate as a possible pour point depressant.[15,16] Cashew nut shell liquid, being a non-food source, offers an advantage over plant seed oils in terms of cost and sustainability. Chemical alteration of CNSL by esterification resulted in more effective pour point depressants.[15,17] In this study, CNSL was isolated from shells and derivatized by using diethanol amine (DEA) to obtain CNSL derivative (CD) which was evaluated as on waxy crude oil. Pour point and rheological investigations were

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used to assess the additives' effects on oil flow qualities. Cross-polarized microscopy was used to study their impact on wax shape and microstructure.

EXPERIMENTAL

Materials and Methods

The crude oil sample (CO) utilized in the current study was collected from the Western Onshore oil field, Oil and Natural Gas Corporation (ONGC), India. Cashew nut shells were collected from a local cashew factory, in India. Diethanol amine, acetone, xylene, concentrated sulphuric acid, and sulphamic acid were purchased from Loba Chemie, India.

General Procedures

Characterization of Crude Oil Samples

The characterization of crude oil was carried out as per the Institute of Petroleum (IP) and the American Society for Testing and Materials (ASTM) procedures. Cloud point or Wax Appearance Temperature (WAT) was determined using the viscosity-temperature curve (Sharma *et al.,* 2022). Further, carbon distribution of wax was carried out by High-Temperature Gas Chromatography (HTGC) and Fourier transform infrared (FTIR) analysis was also performed to detect components present in crude oil.

Extraction of Cashew Nut Shell Liquid (CNSL)

Cashew nut shells obtained from a local cashew factory were first washed several times with water and dried for a week in a vacuum oven. After the complete removal of moisture, acetone was used to isolate the liquid from the cashew nut shell at refluxing for 3 hours. After extraction, the solvent was removed by vacuum distillation to obtain CNSL. It is to be noted that a low boiling solvent such as acetone was used for extraction to isolate CNSL containing a high amount of Anacardic acid.[18] Major components present in CNSL are shown in Fig.-1.

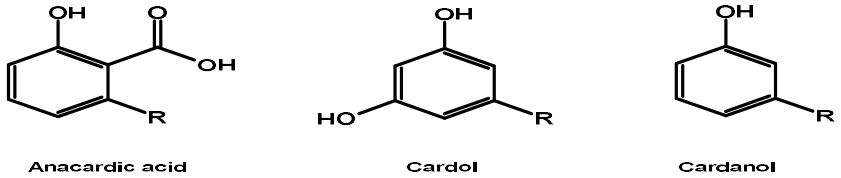

Fig.-1: Major Components Present in CNSL

Synthesis of CNSL derivative (CD)

The CD was synthesized by esterification of CNSL with diethanol amine (DEA) in the presence of sulphamic acid as a catalyst and then acidified with conc. Sulphuric acid.[19] CNSL and DEA were homogenized in xylene in a 1:2 molar ratio along with 1% sulphamic acid. The reaction mixture was refluxed for 2 hours generated during esterification and was removed by using a Dean-Stark trap. The reaction mixture was then kept in an ice bath to achieve a 2°C temperature. In the reaction mixture, 1/3rd of conc. sulfuric acid was added dropwise under stirring to achieve the final product. The schematic representation of the synthesis of the CNSL derivative is given in Fig.-2.

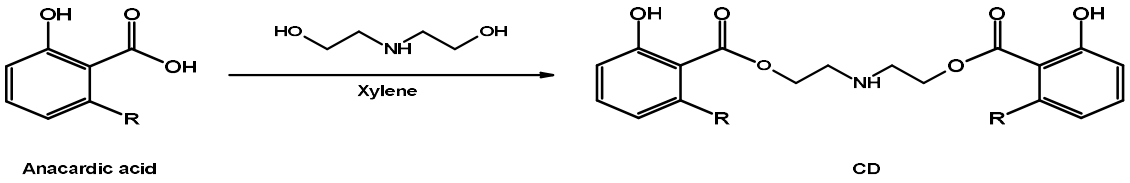

Fig.-2: Schematic Outline of the Synthesis of CNSL Derivative (CD)

Characterization of CD

Fourier transform infrared (FTIR) (Bruker RX-IFTIR, scanning range 400-4000 cm^{-1}) analysis was performed to confirm the synthesis of CNSL derivative.

Evaluation of CD

Before proceeding with the evaluation of CD, the thermal history of crude oil was removed by maintaining the crude oil above the cloud point for 30 minutes. The crude oil sample was then treated with 100, 300,

500, and 1000 ppm of 10% CD solution in xylene, and the pour point of the treated crude oil was determined. The optimum concentration was decided from pour point studies which were considered for further studies such as Rheological measurements, Cold finger test, and microscopic studies. Rheology of treated and untreated crude oil samples was carried out in Anton par MCR 102e at different temperatures and different shear rates. The cold finger test assesses the quantity of paraffin deposition in crude oil and evaluates the efficiency of chemical additives in lowering paraffin deposition (%PIE). Microscopic studies were conducted using an optical microscope (Nikon eclipse Ci POL with Linkam heating stage) with 10µm resolution at temperatures above and below the pour point of crude oil to understand the morphological changes in wax crystals.

RESULTS AND DISCUSSION

Characterization of Crude Oil Samples

Some important characteristic parameters of CO are listed in Table-1. The data in Table-1 indicates that CO is waxy crude oil with a high pour point and low asphaltene content which might create transportation issues, particularly in the winter.[20] HTGC analysis (Fig.-3 (a)) of wax isolated from crude oil revealed that the average carbon number in the wax sample isolated from CO is 22. FTIR spectra represented in Fig.-3(b) confirm the presence of a high amount of saturates due to appearance of peaks at 721 cm^{-1}, 1375 cm^{-1}, 1461 cm^{-1}, 2852 $cm^{-1,}$ and 2921 cm^{-1}.[21]

Table-1: Physico-chemical Parameters of CO

Properties	Method	Results
Water content (% v/v)	ASTM D4006 81	Nil
Density @15^{0}C (g/cc)	ASTM D1298-12b	0.8458
Specific gravity @15^{0}C		0.8461
API (^{0})		35.74
Wax Appearance Temperature (^{0}C)	Viscosity-Temperature Curve	53
Pour point (^{0}C)	ASTM D97-17b	39
Initial Boiling Point (IBP) (^{0}C)		52
Wax content (% w/w)	UOP 46-64	33.61
Melting point of Wax (^{0}C)		68
Congealing point of Wax (^{0}C)		64
Saturate content (% w/w)		73.70
Aromatic content (% w/w)		17.83
Resin content (% w/w)		8.29
Asphaltene content (% w/w)	ASTM D6560	0.18

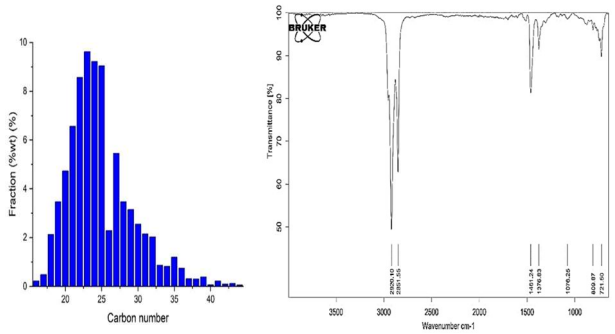

Fig.-3: (a) Carbon Number Distribution of Wax Sample Isolated From CO (b) FTIR of CO

Characterization of CD

FTIR spectra of CD are shown in Fig.-4. Figure-4 depicts the FTIR spectra of CNSL isolated from shells and CD. The broad band at 3300 cm^{-1} in the spectrum results due to the presence of phenolic O–H in CNSL and CD. Similarly, the bands at 3010 cm^{-1}, 2910 $cm^{-1,}$ and 2850 cm^{-1} are due to = C–H stretching and a long chain containing C15 carbons. The presence of a long chain is also confirmed by bending vibration at 718 cm^{-1} (Fig.-4). Also, corresponds to C–H vibrations of methylene and methyl groups of the 15-carbon

chain of CNSL. Methyl C–H stretch vibration of the aliphatic chain of CNSL is confirmed by the deformation vibrations at 1449.9 cm^{-1} in the spectrum of CD (Fig.-4).

The bands at 1605 cm^{-1} correspond to the benzene ring of Anacardic acid which arises due to the C=C stretch (Fig.-4). The sharp band at 1690 cm^{-1} and 1210 cm^{-1} in the spectrum of CNSL is a significant peak confirming the presence of anacardic acid in CNSL which shows the C=O stretching and C-O stretching of carboxylic acid respectively (Fig.-4). This band disappears after esterification with DEA and the new band appears at 1729 cm^{-1} in the spectra of CD due to C=O vibrations of ester (Fig.-4). Moreover, a new band at 1245 cm^{-1} appears due to esterification with DEA.[12,15]

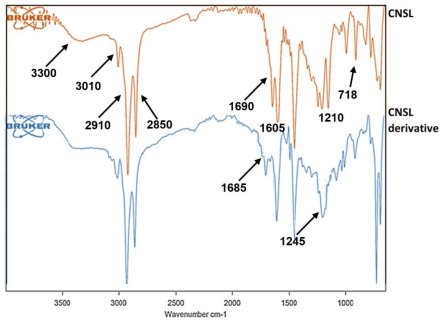

Fig.-4: FTIR of CNSL and CNSL Derivative (CD)

Evaluation of CD

Table-2 displays the pour point of CO treated with various concentrations of CD and Fig.-5 shows the comparative impact of CD on the pour points of CO.

Table-2: Pour Point of Neat and CD Beneficiated Crude Oil

Concentration (ppm)	PP of CO = 39^0C	
	PP (^{0}C) (After treatment)	ΔPP (^{0}C)
100	33	6
300	30	9
500	27	12
1000	33	6

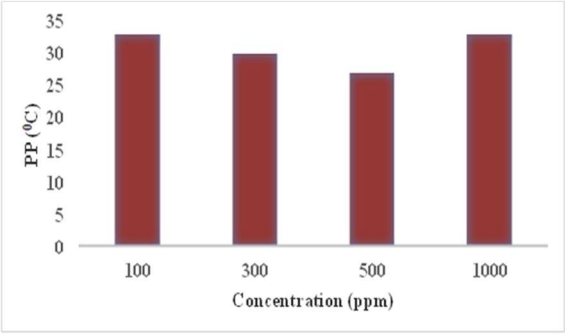

Fig.-5: Effect of CD on Pour Point of CO

The pour point of CO is 39^0C which depresses significantly when treated with CD. Up to 500 ppm of CD, a maximum depression of 12^0C was achieved however, a further increase in concentration results in, rise in pour point which suggests that the optimum concentration of CD is 500 ppm. The structural features of the CNSL derivative lead additive molecules to interact with waxes, lowering the oil pour point. Long alkyl chains and functional groups such as benzene, hydroxyl, and ester groups hinder wax agglomeration, which is where the additive molecules are adsorbed. Because of the relatively polar nature of hydroxyl and ester groups, electrostatic repulsion may arise between microscopic nucleates of wax crystals in the oil, thereby facilitating wax dispersion [22] as shown in Fig.-6.

For further studies, the crude oil sample was treated with an optimum concentration of CD i.e., 500 ppm. The effects of CD on the yield value and viscosity of crude oil at different shear rates and temperatures are shown in Fig.-7.

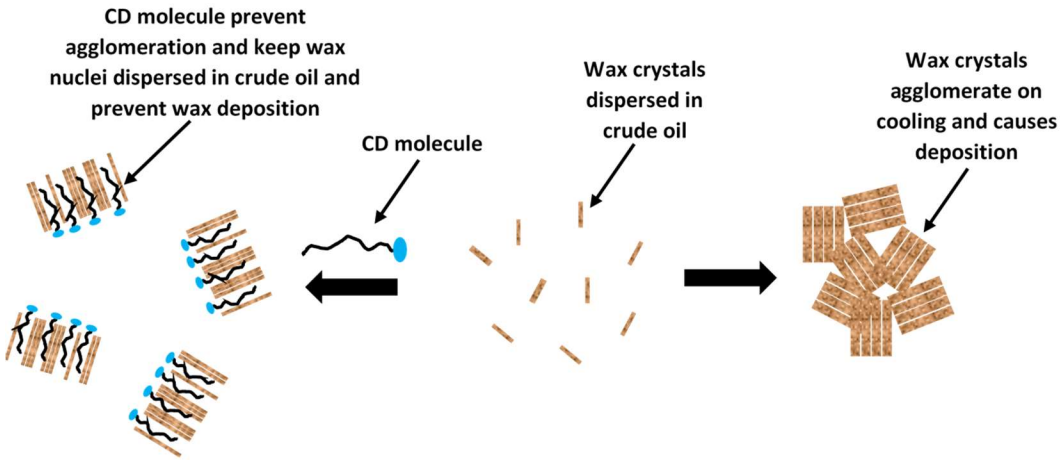

Fig.-6: Mechanism of Interaction of CD with Wax Crystals

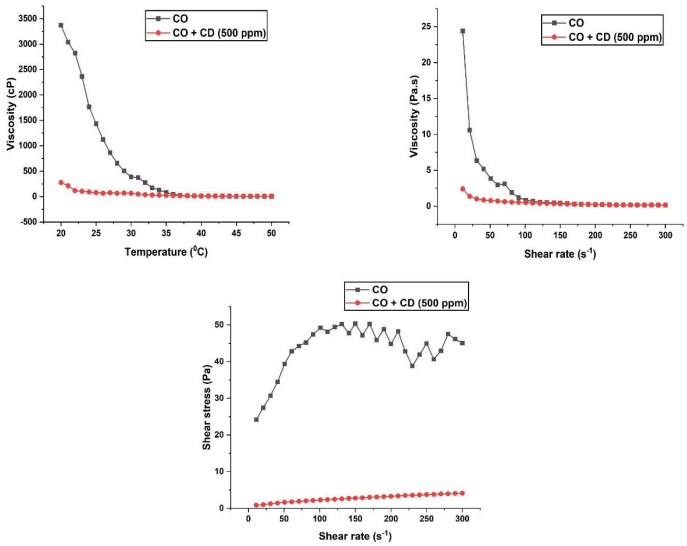

Fig.-7: Effect of CD on Rheology of CO

It can be seen that the viscosity of crude oil shows an inverse relationship with temperature. At low temperatures, the viscosity of crude oil is quite high which signals crude oil transportation issues, especially in winter. The viscosity of neat crude oil is 3400 cP at 20^0C at a constant shear rate which dramatically reduced to 250 cP after treatment with 500 ppm CD solution. Thus, CD causes an excellent reduction in viscosity up to 92%. Moreover, the neat crude oil exhibits Bingham plastic characteristics which require minimum stress for its flowability. The yield value of untreated crude oil was 20 Pa which has significantly reduced to 0.15 Pa after treatment with CNSL derivative. This clearly indicates the improvement in flow characteristics of treated crude oil. Thus, pour point and rheology data prove that CD can be implemented as a flow improver for such waxy crude oil. A cold finger test was also performed to supplement the results obtained by pour point and rheological studies. The amount of wax deposit in untreated crude oil was 5.3 g however, the amount of wax deposit in CD treated crude oil considerably decreased to 2.1 g which revealed 60% paraffin inhibition efficiency (PIE) of CNSL derivative. These findings may be associated with how additives combine with wax crystals under dynamic conditions, inhibiting their deposition, and also support the results obtained by pour point and rheological studies. The rheology enhancement and reduction in the pour point of CD are attributed to their impact on the morphology of wax crystals in the oil. The images obtained by microscopic studies of crude oil treated with 500 ppm of CD are represented in Fig.-8.

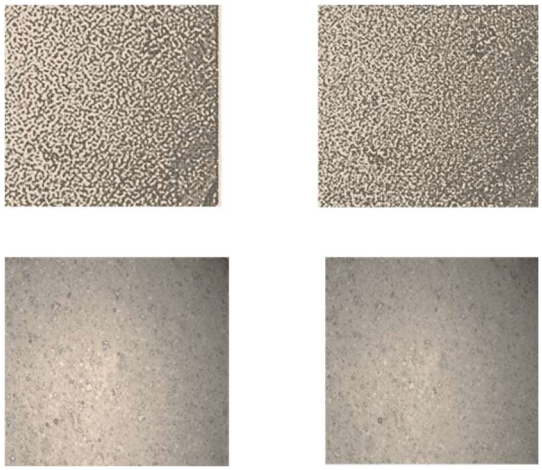

Fig.-8: Microscopic Studies of Treated and Untreated Crude Oil Samples(a, b, c, d clockwise)

The wax crystals nucleate at WAT to form a network structure below WAT (45^0C) as shown in Fig.-8(b). The networking of wax crystals intensifies with a further decrease in temperature which can be clearly observed from Fig.-8 (a) which shows irregular interconnected waxy crystals at 30°C which entraps crude oil and obstructs the flow of crude oil.[23–25] When the crude oil is treated with optimum concentration of CD, the change in shape and size of paraffin crystals is observed which prevents the aggregation of paraffin crystals which ultimately prevents networking of wax crystals and keeps them dispersed in oil as represented in Fig.-8 (c and d). On further increase in temperature, tiny wax crystals are observed which cannot aggregate to form wax crystals nucleate at WAT to form a network structure below WAT (45^0C) as shown in Fig.-8 (b). Thus, instead of larger flocs, a significant number of small wax crystals are observed improving rheological properties at temperatures WAT.

CONCLUSION

The crude oil sample utilized in the investigation contains a high wax content, indicating pipeline transportation issues. The impacts of CNSL derivative on waxy crude oil were evaluated by pour point, rheology, and paraffin inhibition efficiency which showed significant improvements in all parameters as compared to virgin crude oil. The maximum pour point depression of 120C occurred at extremely low doses of around 500 ppm. Rheological investigations demonstrated a significant decrease in crude oil viscosity of up to 92% at 500 ppm. The cold finger test demonstrated a large degree of wax inhibition produced by CNSL derivative, which was around 60%. Microscopic analysis indicated a dense network of wax crystals which was significantly damaged in the presence of CNSL derivative. Thus, highly effective and low dosage of CNSL derivative gives satisfactory results for all the parameters evaluated.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID IDs, given below:

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