A study on cashew nut shell liquid as a bio-based flow improver for heavy crude oil

Sivakumar Pandian¹ · Patel Chintan Dahyalal¹ · Shanker Krishna¹ · S. Hari¹ · Deepalakshmi Subramanian²

Received: 24 February 2021 / Accepted: 7 April 2021 / Published online: 17 April 2021
© The Author(s) 2021

Abstract

Transportation of heavy crude oil through pipelines poses a great challenge in oil and gas industry. Crude oil chokes the pipelines when the temperature drops below the pour-point temperature. In the present study, a bio-based additive, i.e., Cashew Nut Shell Liquid (CNSL) has been tested as a flow improver for heavy crude. CNSL was obtained from waste cashew nut shell by means of mechanical extraction, and it was completely characterized. Similarly, the crude oil used in the study was characterized for its physio-chemical properties. Also, the crude oil was subjected to Saturates, Aromatics, Resins and Asphaltene analysis and Fourier Transform Infra-Red analysis. The raw and additive-treated crude oil with different CNSL dosages were subjected to pour-point and rheology measurements and optical micro-imaging analysis which indicated a remarkable improvement in flow whereby an optimum dose of 2000 ppm was observed. Furthermore, the effects of different parameters like shear rate, concentration of the flow improver and the effect of temperature on the crude oil flowability were studied. The process variables were optimized by means of Taguchi method, and the percentage contribution of each parameter was identified with the help of ANOVA table. The results indicate that a remarkable improvement in flow was observed at an optimum dose of 2000 ppm. The contribution of the concentration was found to be around 53%, whereas the contributions of the shear rate and the temperature were only 18.08 and 28.91%, respectively. Therefore, it has been observed that CNSL flow improvers extracted from cheap reasonable resources are more effective as they are cost-effective and eco-friendly when compared to conventional additives.

Keywords Bio-based additive · Flow improver · Taguchi method · ANOVA table · Heavy crude

Introduction

Over the years, global energy demand has witnessed a remarkable increase due to rapid economic and population growth. Crude oil serves as the cornerstone of a nation's economy playing a vital role in quenching the world's thirst for energy. It comprises a complex blend of hydrocarbon compounds with diverse physical characteristics based on which it is categorized into light and heavy crude (Coussirat et al. 2019). In recent years, the development of light crude oil resources has been experiencing a declining trend. Globally, this has led to a gradual increase in the development,

collection and transportation of heavy oil (Gu et al. 2018). These resources play a significant role in mitigating energy crisis (Sivakumar et al. 2020). Heavy oil fields are generally scattered throughout the world in different geological zones at far-fetched regions. Therefore, the production, storage and conveyance of heavy crude oil to the refineries and processing facilities have become extremely complex and technically a challenging operation. Based on the area from which the oil is produced, it may contain substantial quantity of waxes that are comparatively insoluble and precipitate when the oil comes in contact with the surface environment. These waxes may even solidify at places where facilities may not be available within their vicinity.

In general, crude oil is transported to refineries after production by truck, trains, ships and pipelines. When compared to other transportation methods, pipeline transfer has many advantages in terms of safety, energy efficiency and convenience. Moreover, a huge amount of crude can be transported through pipelines. The crude oil component that crystallizes

✉ Sivakumar Pandian
sivakumar.p@spt.pdpu.ac.in

¹ School of Petroleum Technology, Pandit Deendayal Energy University, Gandhinagar 382426, India

² Department of Engineering and Physical Sciences, Institute of Advanced Research, Gandhinagar 382426, India

as the temperature of the ambience or the pipeline wall drops below its Wax Appearance Temperature (WAT) is termed as wax (Deka et al. 2020). Its formation hinders crude oil movement through the pipelines ultimately, leading to significant economic loss (Admiral et al. 2016). WAT or cloud-point represents the temperature that marks the commencement of the separation of wax components from the crude oil which impedes the flow gradually with dropping temperature. Wax Precipitation Temperature (WPT) represents the temperature at which the wax crystallizes and touches the peak (Huang et al. 2011). Recently, there has been a worldwide increase in the production of waxy crude oils (Sun et al. 2016). The temperature and pressure within the reservoir are high so as to retain the solubility of the wax crystals in crude oil. The problems associated with the flow of hydrocarbon fluids are primarily due to wax deposition at low temperatures, especially in deep sea settings. The behavior of heavy oils and bitumen is non-Newtonian under conditions defined by very low temperature as well as very high shear rate (Ilyin and Strelets 2018). Wax crystal formation at low temperatures results in the impartation of non-Newtonian behavior to light oils. In order to improve the flow and solve such issues, several methods like mechanical removal by pigging, induction heating, chemical dosing, emulsification and dilution are generally applied. Wax deposition is a major flow assurance problem that has drawn widespread attention in the past few decades (Yang et al. 2020). The deposition of wax inside the subsea pipelines poses a serious threat during offshore hydrocarbon production. It is necessary to adopt an effective and appropriate method to treat the deposited wax in pipelines to maintain safe and economical transportation of oil (Pal et al. 2018, 2019).

Conventional methods available to improve the flowability at low temperatures are heating, dilution, emulsification, etc., whereas pigging is used for wax removal (Sivakumar et al. 2018). These methods are generally time consuming, energy intensive and expensive. Taking these constraints into consideration, some chemical methods have been developed where natural or synthetic chemicals are added to crude that undergoes different mechanisms like adsorption, nucleation, co-crystallization, enhanced wax dispersion, etc., to enhance the flowability of crude. For instance, Deshmukh and Bharambe (2008) synthesized and evaluated the performance of maleic anhydride and acrylic acid copolymer and found that they can be used as wax dispersant as well as a good pour-point depressant. Experiments conducted on flow improvers in Tuha crude oil showed that when the shear temperature became lower than WAT, the shear in pipeline and pump tends to increase the pour-point (Tao et al. 2012).

In order to protect the crude oil from being contaminated and to avoid any kind of adverse effects on the environment, bio-additives are being developed (Eke et al. 2021). These environmentally benign additives are basically the various

types of fatty acids, naturally obtained oils and occasionally, their combinations (Xu et al. 2018). As a part of efficiency improvement, they can be combined with other chemicals. Components derived from natural products enhance the flow characteristics of crude oil. The process can be carried out in an eco-friendly and cost-effective way. Heikal et al. (2017) stated that vegetable oils have a remarkable potential to replace mineral oils on account of their non-toxic behavior, renewability and eco-friendly and cost-effective nature. This paper offers a brief description of the different flow improvers that are developed from natural products such as canola oil, rapeseed oil, castor seed oil, soybean oil, jatropha seed oil, rubber seed oil. (Akinyemi et al. 2016, 2018; Chen et al. 2016; Zhang et al. 2018; Deka et al. 2020).

In the present study, an effort has been made to investigate the impact of CNSL used as a bio-based flow improver on a typical waxy crude oil. It also explores the effect of shear on the rheology and its relationship with different dosages and temperatures. The raw crude oil and crude oil treated with flow improver were subjected to pour-point and rheology measurements and optical micro-imaging and FTIR analysis. Further, the process variables affecting the viscous flow were finally optimized by means of Taguchi method (Taguchi and Konishi 1987). The percentage contribution of each parameter was identified using ANOVA table. Discussions have been carried out on the influence of shear on the rheology of waxy crude oil.

Materials and methods

The sample of crude oil employed in this investigation was collected from the western onshore Cambay basin in India and stored at 5 °C till its use in the study. Cashew nut shell is a commodity of low-value that was procured from cashew nut processing industries. Waste cashew nut shells were obtained from the local industry involved in cashew nut processing situated in Kadalur, India. Cashew nut is a product of cashew tree, an evergreen tree that is scientifically known as *Anacardium occidentale*. It belongs to the eastern parts of Brazil, and later the Portuguese introduced it to the tropical regions (Pimentel et al. 2009). It bears a fleshy pseudo-fruit with a kidney-shaped nut. The thickness of the cashew nut shell ranges from 0.25 to 0.3 cm, and the shell covers the nut. It has a honeycomb structure and forms the basis for CNSL.

Extraction and characterization of CNSL

Waste cashew nut shells were physically cleaned and dried under the sun for 5 days, and it was further dried in a hot air oven at 60 °C for a period of 5 h. CNSL was obtained from the dry shells by means of mechanical extraction process

using an EPS-602 model, table top spiral press oil extractor (EPS Exim, India). The physical and chemical characteristics of CNSL were found through the official analysis techniques prescribed by AOAC International (Latimer 2019). The major composition of CNSL was identified using a high-performance liquid chromatogram system (SPD-10A VP model, Shimadzu, Japan) coupled with a C-18 column and a LC-10AD VP Pump. The chromatogram has a UV–Vis detector with a mixer that enables the detection of UV and the whole visible light by means of high sensitivity wavelength programming. The mobile phase comprises acetonitrile and water along with acetic acid in the ratio of 80:20:1, respectively.

All the chemicals utilized in this investigation belonged to analytical grade and were purchased from Merk, Mumbai, India. The chemicals were used as such without any further purification.

Characterization of crude oil

For determining the physical characteristics of the sample, standard methods were adopted. Specific gravity test was carried out with the help of a specific gravity bottle as well as a weighing machine from which the API was calculated. Standard ASTM technique was followed to determine the pour-point of the sample (ASTM D97-15 2016). For this, a pour-point apparatus comprising a test jar, water bath, jacket and thermometer was employed. After the sample was subjected to initial heating, it was cooled in a test apparatus and the movement was monitored at every drop in temperature (measured in °C) by horizontally tipping the jar. Pour-point was reported to be the lowest value of temperature corresponding to which the flow stopped. Similarly, the water content was measured using Dean Stark method.

The SARA compositions of the sample were found with the help of column chromatography method. It is a sequential leaching of the different components of crude oil using different solvents through a stationary phase (silica gel). After extraction, the solvents were removed by vacuum evaporation and the individual composition was found using gravimetric analysis.

Differential Scanning Calorimetry (DSC) was employed to identify WPT and WAT. It was performed in an 822e model DSC instrument (Mettler Toledo Ltd, Switzerland) by reducing the temperature to 10 °C from 70 °C at a cooling rate of 5 °C min^{−1}.

FTIR spectroscopic analysis for raw crude, CNSL and crude with CNSL was conducted in a Nicolet™ iS™ 10 FTIR spectrometer (Thermo Scientific, USA). It was used to spot the different functional groups present in the sample. The absorbance spectra in terms of percentage transmittance were between the wave numbers ranging from 4000 to 400 cm^{−1}.

The wax crystal in crude oil was studied with the help of Motic BA310MET series cross polar microscope. The sample was analyzed under partially polarized light with varying magnifications of 5–50×. Transmitted light option with a camera adapter aided in viewing the transparent samples. In order to study the crude sample, it was placed on a slide with a thickness of 20 mm which was subjected to a temperature of 65 °C and observations were made under decreasing temperatures that decreased to room temperature. The samples were placed on a hot plate built in with an auto-heating controller.

The study of the rheological characteristics of the sample and the sample added with additives was carried out using an MCR 102 series rheometer (Anton Paar, Austria). The reading was taken at different temperatures ranging from 30 to 40 °C. At a constant shear rate between 100 and 1000 s^{−1} with an interval of 100, a reading was taken. All the rheological studies were repeated for raw crude with additive at different concentrations ranging from 1000 to 5000 ppm.

Determination of optimum condition

The three key parameters that have an impact on the flowability of the crude are shear rate, concentration of the flow improver and temperature. Therefore, optimization of these parameters is necessary. In this study, Taguchi optimization and ANOVA table were employed to find the optimum condition and percentage contribution of each parameter.

In Taguchi optimization, the characteristic lower values represent better performance. In quality engineering, this idea is appropriately represented with the help of “Lower is Better.” For determining the significant parameter, an effectual representation is found to be the S/N (signal to noise) ratio wherein the maximum variance is evaluated. It is calculated using Minitab 18.1.0 software in accordance with Eq. (1).

$$\left(\frac{S}{N}\right)_{LB_n} = -10 \log \left[\frac{1}{n} \sum_{m=1}^n m^2 \right] \quad (1)$$

here n indicates the number of trails, while m denotes the yield that is found at every level of the experiment. LB_n denotes the “Lower is Better” condition in this case.

In this study, L18 array having a configuration of $6^1 \times 3^2$ experiments was constructed on the basis of the combination of the parameters as shown in Table 1. Corresponding to the optimized values, the plots for these parameters were obtained.

Results and discussion

Description of the characteristic features of CNSL

Cashew nut shells contain 24.3 wt% of CNSL which was obtained by mechanical extraction process. It was a light

Table 1 Levels of parameters

Levels	Factor 1 (shear rate, s ⁻¹)	Factor 2 (concentration, ppm)	Factor 3 (temperature, °C)
L1	500	1000	30
L2	600	2000	35
L3	700	5000	40
L4	800		
L5	900		
L6	1000		

Table 2 Physical and chemical properties of the CNSL

Property	Values
Density (kg m ⁻³)	0.995
Viscosity @ 40 °C (mm ² s ⁻¹)	37.92
Iodine value (I ₂ 100 g ⁻¹)	73.29
Saponification value (mg KOH g ⁻¹)	194
Peroxide value (meq kg ⁻¹)	11.2
Free fatty acid (% oleic acid)	3.12
pH	5.1
Moisture content (wt%)	0.673

amber-colored viscous oil. The major compositions of the mechanically expelled CNSL are monoene-, diene- and triene- of anacardic acid (65.34%), cardol (15.29%) and cardanol (13.1%), and the rest (6.27%) were undetectable. These results were at par with the findings reported previously, and the minor variations in the components may be due to the extraction method or the geographical area where it is grown (Anilkumar 2017; Lomonaco et al. 2017).

The physical and the chemical characteristics of CNSL are shown in Table 2. The iodine value classifies it under non-drying oil category, whereas the saponification value indicates the presence of lower molecular weight fatty acids in it. The occurrence of non-isoprenoid phenolic lipids in CNSL accounts for its mild phenolic odor. This is evident from the high peroxide value which causes hydrolytic rancidity.

Crude characterization

The physical and the chemical features of the crude oil are tabulated in Table 3. According to the API standard, the crude oil can be categorized as light oil. Since the water content was relatively lower, all the experiments were carried out without removing it. The result indicated that the raw crude oil sample had high wax content.

The SARA analysis results of the crude oil are tabulated in Table 4. A high amount of long chain saturates (paraffins) causes the wax crystal to show up and choke the lines.

Table 3 Physical and chemical properties of crude oil

Properties	Values
API gravity	33
Pour point (°C)	36
Water content (v/v%)	4
Wax content (wt%)	11
Free water	Nil

Table 4 SARA analysis

Parameter	Values
Saturates (wt%)	77.45
Aromatics (wt%)	15.23
Resin (wt%)	5.67
Asphaltene (wt%)	0.10
CII (wt%)	3.71
Resin: Asphaltene	56.7

Hence, these long chain structures agglomerate to form wax depositions in pipelines. Moreover, it can be inferred that the distortion of these long chain structures by adding flow improvers will be the best solution. Colloidal Instability Index (CII) of the crude is calculated as 3.71 which shows higher resin to asphaltene ratio. This higher value indicates the lesser possibilities of asphaltene deposition. This is mainly because these asphaltene components are surrounded by resin which allows them to disperse in crude oil (Deka et al. 2018). CII value remains high for higher saturates containing crude oil. When asphaltene is stabilized by resin, CII value becomes higher due to the non-polar saturate components. The appearance of imperial saturate components accounts for the higher viscosity of the crude oil sample. Moreover, it can also give information on any chemical reaction taking place during the addition of the flow improver.

FTIR analysis

FTIR confirms the presence of polymeric O–H, alkanes, carboxylic acid and alkenes in CNSL, and these results are in accordance with the findings of Balgude et al. (2014). FTIR spectrums of neat crude, CNSL and crude with 5000 ppm CNSL are shown in Fig. 1. The peak region at 3172 cm⁻¹ is justified by the occurrence of the hydroxyl group in CNSL. Acardic acid exhibits the characteristic of the broadening of this peak. It is a carboxylic acid, and the occurrence of a tiny peak at 2595 cm⁻¹ supports its occurrence which is an indication that the substituted carbonyl gets absorbed by the aromatic group. The loss of C=O group from an acardic acid can be deduced from the peak loss at 2595 cm⁻¹ and the hydroxyl peak-sharpening on cardanol at 3334 cm⁻¹. The stretching vibration of C=C bond in aromatic compounds

Fig. 1 FTIR spectrum of neat crude, CNSL and crude with 5000 ppm CNSL

Table 5 Pour-point of crude at different concentrations of CNSL

CNSL (ppm)	Pour-point (°C)	Pour-point depression (°C)
0 (Raw crude)	36	0
1000	35	1
2000	30	6
3000	31	5
4000	31	5
5000	31	5

can be confirmed from the peak at 1601 cm^{-1} . Ifiok et al. (2014) and Silverstein et al. (2014) have stated that this may be due to the occurrence of asphaltic structure in crude oil.

Pour-point analysis

The pour-point of raw crude oil with different concentrations of CNSL is shown in Table 5. It was observed that a maximum drop in pour-point was achieved for 2000 ppm, i.e., $30\text{ }^{\circ}\text{C}$, whereas a further increase in the concentration slightly reduced the pour point. This may be due to the fact that the rise in the concentration of CNSL results in the co-crystallization of CNSL with the paraffin wax which causes modification in the crystal structure. Therefore, at optimum concentrations of 2000 ppm, sideways growth becomes difficult for wax crystals (Sharma et al. 2014).

Taguchi optimization method

The highest value of S/N ratio gives the optimum value for the response parameter. Here, the “Smaller is Better”

principle forms the basis for finding the lowest value of viscosity. The value of viscosity corresponding to the different combinations of shear rate (rpm), concentration (ppm) and temperature ($^{\circ}\text{C}$) is represented in Table 6. According to the Taguchi optimization method, the highest value of S/N ratio gives the optimum value for the response parameter without performing a large number of experiments to find the lowest value of viscosity. As per Fig. 2, the lowest value of viscosity can be obtained with a combination of 1000 rpm of shear rate value, 2000 ppm of the concentration of CNSL and $40\text{ }^{\circ}\text{C}$ of temperature and this condition was found to be the optimum. The value of viscosity estimated under this optimum condition is 0.039293 Pa.s . This is the lowest value of viscosity that can be achieved in this setting which is obtained by the addition of 2000 ppm of the concentration of CNSL. The effect of a particular factor on viscosity is discussed later in the section that describes rheology.

ANOVA

As per Table 7, the effects of the concentrations of CNSL nearly consume 53.00622% and have an F value of 13.69 whereby it contributes the highest when compared to all other parameters. It indicates that a change in concentration will directly and effectively alter viscosity. Shear rate has a very negligible effect of only 18.08339% , and this indicates that for a constant concentration of CNSL, i.e., 2000 or 5000 ppm at a constant temperature (i.e., $40\text{ }^{\circ}\text{C}$), the viscosity remains constant even after the shear rate is increased. It represents the Newtonian behavior which is described in detail later in the paper. Temperature has an intermediate effect on viscosity which is around 28.91039% which is not a negligible value. With the increase in temperature, the curve shifts toward the horizontal axis and attains a straight-line

Table 6 L18orthogonal array data required for optimizing Taguchi technique

Levels	Shear rate (rpm)	Concentration (ppm)	Temperature (°C)	Viscosity (Pa.s.)
1	500	1000	30	0.06318
2	500	2000	35	0.05367
3	500	5000	40	0.06696
4	600	1000	30	0.05980
5	600	2000	35	0.05220
6	600	5000	40	0.06561
7	700	1000	35	0.10183
8	700	2000	40	0.03999
9	700	5000	30	0.08641
10	800	1000	40	0.04520
11	800	2000	30	0.05122
12	800	5000	35	0.08010
13	900	1000	35	0.05885
14	900	2000	40	0.03933
15	900	5000	30	0.07856
16	1000	1000	40	0.04477
17	1000	2000	30	0.04894
18	1000	5000	35	0.07329

shape for an optimum concentration of 2000 ppm of CNSL. As per the optimization technique, in order to get the lowest value of viscosity, the experiment must be carried out at 2000 ppm of the concentration of CNSL, 40 °C temperature and a 1000 rpm of shear rate.

Rheology studies

As per the optimization technique, the optimum value for shear rate is 1000 rpm at which rate a maximum reduction in viscosity is observed. Table 8 shows the value of viscosity for temperatures 30, 35 and 40 °C along with the reduction percentage for all the concentrations of CNSL at an optimum shear rate of 1000 rpm. Generally, it is observed that viscosity reduces with increase in temperature (Qin et al. 2018). However, with an increase in the concentration of CNSL, viscosity reduced to 49.01% (optimum condition) at 2000 ppm and a further increase does not improve the viscosity. This trend may be due to the recrystallization of co-precipitated crystals.

Effect of CNSL concentration on viscosity v/s shear rate

From the viscosity v/s shear rate graphs as indicated in Figs. 3, 4 and 5, it is evident that the viscosity of crude oil drops as the shear rate increases. This is observed for all the temperature values of 30, 35 and 40 °C. Thus, shear thinning

Fig. 2 Main effects plot for different SN ratios **Table 7** Percentage contribution of each factor

Source	DF	SS	MS	F value	P value	Contribution (%)	Rank
Shear rate (s ⁻¹)	5	0.000785	0.000157	1.87	0.206	18.08339092	3
Concentration (ppm)	2	0.002301	0.001151	13.69	0.003	53.00621977	1
Temperature (°C)	2	0.001255	0.000628	7.47	0.015	28.91038931	2
Error	8	0.000672	0.000084				
Total	17	0.005013					

DF degree of freedom, SS sum of squares, MS mean square variance

behavior is identified which indicates pseudo-plastic behavior of crude. As shown in Figs. 3, 4 and 5, without any additives, a rapid increase in viscosity can be observed with decreasing shear rate, specifically, at a lower value of shear rate. However, in the presence of CNSL, viscosity v/s shear rate curve tends to incline toward the horizontal line, i.e., even with a decreasing shear rate, there is no rapid increase in viscosity. Figure 5 shows that for a temperature of 40 °C

and a shear rate below 400 rpm, a sharp rise in viscosity is observed, whereas, for crude with an optimum concentration of 2000 ppm of CNSL, the curve totally inclined toward the horizontal line. Also, lower values of shear rate do not allow a sharp increment in viscosity which indicates that in the presence of CNSL, crystals of wax break into smaller crystals thereby decreasing the viscosity of crude oil effectively and providing flowability. For an optimum

Table 8 Viscosity at different temperatures

CNSL conc. (ppm)	Viscosity (Pa)			Viscosity reduction (%)		
	30 °C	35 °C	40 °C	30 °C	35 °C	40 °C
0000	0.09616	0.0964575	0.069405	0	0	0
1000	0.05248	0.057945	0.044768	45.424293	39.9269	35.498
2000	0.048938	0.0472225	0.039293	49.108257	51.0432	43.387
3000	0.07378	0.0776025	0.059805	23.27371	19.5475	13.832
4000	0.06631	0.076455	0.061725	31.042013	20.7371	11.065
5000	0.075285	0.073285	0.062214	21.708611	24.0235	14.361

Fig. 3 Effect of CNSL concentration on viscosity versus shear rate at 30 °C

Fig. 4 Effect of CNSL concentration on viscosity versus shear rate at 35 °C

Fig. 5 Effect of CNSL concentration on viscosity versus shear rate at 40 °C

concentration of CNSL, which is 2000 ppm, the growth of crystals is prevented and this is evident from the alteration in the behavior of crude from non-Newtonian to Newtonian fluid in which the viscosity remains almost constant with shear rate. Without CNSL additives, the behavior of crude shifts toward non-Newtonian behavior which is because a decreasing shear rate results in the deposition of wax crystals and crystal growth. Consequently, a constant increase in the viscosity can be observed which hinders the flow.

Effect of CNSL concentration on shear stress v/s shear rate

Similarly, the slope of the curve in shear strain v/s shear rate indicates the apparent value of viscosity. On the same note, when the slope of the curves inclines toward a straight line, it denotes Newtonian behavior wherein no further change in viscosity is observed. According to Fig. S1–S3, as the concentration of CNSL moves toward the optimum condition, there is a reduction in the slope of the curves whereby

a reduction in the viscosity is observed. At an optimum concentration of 2000 ppm, there is a perfect straight-line curve which indicates Newtonian behavior and a constant value of viscosity.

As discussed, at an optimum shear rate of 1000 rpm and an optimum concentration of 2000 ppm, a maximum reduction in viscosity is observed which gives the lowest value of viscosity. The percentage reduction in viscosity was found to be around 49.108257%, 51.0432% and 43.387% for temperature values of 30, 35 and 40 °C, respectively, as shown in Table 8. The reduction in viscosity decreases while moving toward a higher concentration of CNSL, i.e., from 2000 to 5000 ppm. Maximum reduction in viscosity was observed at 35 °C temperature with 2000 ppm concentration, but the lowest value of viscosity of 0.039293 Pa.s was observed at 40 °C with 2000 ppm of CNSL concentration and at 1000 rpm shear rate.

Fig. 6 DSC thermogram of neat crude and crude with 2000 ppm CNSL

DSC analysis

Appearance of wax and precipitation temperature for neat crude and crude with 2000 ppm CNSL are shown in Fig. 6. The DSC thermograms show two distinct peaks in which the broad first peak represents the presence of a wide distribution of wax molecules. It was observed that there was significant change in WAT for both neat crude and crude with 2000 ppm of CNSL, and the difference between them was 8.7 °C. Similarly, a shift in the lower WPT can be observed and the difference between them is 5.9 °C. A significant reduction in WPT indicates that the temperature at which the precipitation of wax occurs at its maximum rate has reduced. This shows that the additive may alter the wax crystallization phenomenon and extend the WPT, thus, enhancing the cold flow property (Wu et al. 2012). Therefore, the flow improver has a significant influence on the total quantity of wax crystals that precipitate from crude on WAT and also it can be concluded that after WPT, CNSL may act as a crystal growth inhibitor and a crystal modifying agent for the precipitated wax crystals.

Polarization microscopy analysis

Polarization microscope images in Fig. 7a–c show the size of wax crystals in neat crude and crude with 2000 and 5000 ppm of CNSL, respectively. The crystal size is maximum for neat crude, and it decreases with the addition of CNSL up to 2000 ppm. Further addition induces co-crystallization of CNSL with the paraffin wax modifying the crystal structure as seen in Fig. 7c. At an optimum concentration of 2000 ppm, the flow improver may behave as a nucleating agent or an agent that inhibits crystal growth to retain the critical size of paraffin crystals (Marie et al. 2005). Similarly, the development of a large number of sub-critical sized wax nuclei lessens the growth of a single huge wax crystal by making the wax particulate too small to be stable in crude oil-phase (Yang et al. 2015). However, above 2000 ppm of CNSL, an increase in the size of wax crystals was observed. Beyond this optimum concentration, CNSL may co-crystallize with the paraffin wax modifying the crystal structure to promote sideways growth (Sharma et al. 2014). This result is at par with the outcomes of pour-point, rheology and DSC studies.

Conclusions

The present work investigates the role of a bio-based flow improver to enhance the flow characteristics of waxy crude oil. In this study, Taguchi statistical method was employed for the optimization of every influencing parameter, whereas

Fig. 7 **a** Microscopic image of wax crystals in neat. **b** Microscopic image of wax crystals in crude with 2000 ppm of CNSL. **c** Microscopic image of wax crystals in crude with 5000 ppm of CNSL

ANOVA supported in the process of finding the influence of individual parameter. FTIR and pour-point-based studies confirmed that after the addition of CNSL, there was no chemical alteration in the crude oil though there was a mild reduction in pour point. Optimum parameters that improve

the viscous flow are 2000 ppm of CNSL concentration, 40 °C temperature and 1000 rpm of shear rate. A maximum contribution of around 53% was from the concentration of CNSL. A significant viscosity reduction from 0.069405 to 0.039293 Pa.s. was achieved for CNSL treated crude oil. The results from microscopic investigation confirmed that there was distortion of the wax structure and that CNSL acted as a good crystal modifier. A significant reduction in WPT of around 5.9 °C indicates the control on maximum wax deposition rate. Hence, it is proved that the maximum reduction in viscosity contributed by the concentration of CNSL is not accidental. Therefore, it can be concluded that CNSL functions as a mild pour-point depressant, viscosity reducer, crystal growth inhibitor and a modifier agent. On the whole, CNSL is found to be a good bio-based flow improver.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s13202-021-01162-w>.

Funding This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- Admiral A, Abdullah MK, Ariffin A (2016) Evaluation of emulsified acrylate polymer and its pour point depressant performance. *Procedia Chem* 19:319–326
- Akinyemi OP, Udonne JD, Efeovbokhan VE, Ayoola AA (2016) A study on the use of plant seed oils, triethanolamine and xylene as flow improvers of Nigerian waxy crude oil. *J Appl Res Technol* 14:195–205
- Akinyemi OP, Udonne JD, Oyedeko KF (2018) Study of effects of blend of plant seed oils on wax deposition tendencies of Nigerian waxy crude oil. *J Pet Sci Eng* 161:551–558
- Anilkumar P (ed) (2017) *Cashew nut shell liquid: a goldfield for functional materials*, 1st edn. Springer, Cham
- ASTM D97-15 (2016) ASTM international. West Conshohocken, USA
- Balgude D, Konge K, Sabnis A (2014) Synthesis and characterization of sol-gel derived CNSL based hybrid anti-corrosive coatings. *J Sol-Gel Sci Technol* 69:155–165
- Chen G, Bai Y, Zhang J et al (2016) Synthesis of new flow improvers from canola oil and application to waxy crude oil. *Pet Sci Technol* 34:1285–1290
- Coussirat V, Amarilla F, Peruzzo PJ, Cortizo MS (2019) Dioctyl fumarate-co-vinyl benzoate copolymers preparation and their performance as flow improvers in waxy crude oils. *J Pet Sci Eng* 182:106290. <https://doi.org/10.1016/j.petrol.2019.106290>
- Deka B, Sharma R, Mahto V (2020) Synthesis and performance evaluation of poly (fatty esters-co-succinic anhydride) as pour point depressants for waxy crude oils. *J Pet Sci Eng* 191:107153
- Deka B, Sharma R, Mandal A, Mahto V (2018) Synthesis and evaluation of oleic acid based polymeric additive as pour point depressant to improve flow properties of Indian waxy crude oil. *J Pet Sci Eng* 170:105–111
- Deshmukh S, Bharambe DP (2008) Synthesis of polymeric pour point depressants for nada crude oil (Gujarat, India) and its impact on oil rheology. *Fuel Process Technol* 89:227–233
- Eke WI, Kyei SK, Ajiinka J, Akaranta O (2021) Effect of bio-based flow improver on the microscopic and low-temperature flow properties of waxy crude oil. *J Pet Explor Prod* 11:711–724
- Gu X, Zhang F, Li Y et al (2018) Investigation of cationic surfactants as clean flow improvers for crude oil and a mechanism study. *J Pet Sci Eng* 164:87–90
- Heikal EK, Elmelawy MS, Khalil SA, Elbasuny NM (2017) Manufacturing of environment friendly biolubricants from vegetable oils. *Egypt J Pet* 26:53–59
- Huang Z, Lee HS, Senra M, Scott Fogler H (2011) A fundamental model of wax deposition in subsea oil pipelines. *AIChE J* 57:2955–2964
- Ifio U, Imeh J, Clement O (2014) Discerning group-type analysis of crude oils from osso platform, Nigeria, using vibrational spectroscopy with multivariate statistics. *Int J Eng Sci* 3:6–16
- Ilyin SO, Strelets LA (2018) Basic fundamentals of petroleum rheology and their application for the investigation of crude oils of different natures. *Energy Fuels* 32:268–278. <https://doi.org/10.1021/acs.energyfuels.7b03058>
- Latimer GW (ed) (2019) *Official methods of analysis of AOAC International*, 21st edn. AOAC International
- Lomonaco D, Mele G, Mazzetto E (2017) Cashew nutshell liquid (CNSL): from an agro-industrial waste to a sustainable alternative to petrochemical resources. In: Anilkumar P (ed) *Cashew nut shell liquid: a goldfield for functional materials*, 1st edn. Springer International Publishing AG, Cham, pp 19–38
- Marie E, Chevalier Y, Eydoux F et al (2005) Control of n-alkanes crystallization by ethylene-vinyl acetate copolymers. *J Colloid Interface Sci* 290:406–418
- Pal N, Samanta K, Mandal A (2019) A novel family of non-ionic gemini surfactants derived from sunflower oil: synthesis, characterization and physicochemical evaluation. *J Mol Liq* 275:638–653. <https://doi.org/10.1016/j.molliq.2018.11.111>
- Pal N, Saxena N, Laxmi KVD, Mandal A (2018) Interfacial behaviour, wettability alteration and emulsification characteristics of a novel surfactant: implications for enhanced oil recovery. *Chem Eng Sci* 187:200–221. <https://doi.org/10.1016/j.ces.2018.04.062>
- Pimentel MF, De-Lima DP, Martins R et al (2009) Ecotoxicological analysis of cashew nut industry effluents, specifically two of its major phenolic components, cardol and cardanol. *Pan-Am J Aquat Sci* 4:363–368
- Qin Y, Wu Y, Liu P et al (2018) Experimental studies on effects of temperature on oil and water relative permeability in heavy-oil reservoirs. *Sci Rep*. <https://doi.org/10.1038/s41598-018-31044-x>
- Sharma S, Mahto V, Sharma VK (2014) Effect of flow improvers on rheological and microscopic properties of Indian waxy crude oil. *Ind Eng Chem Res* 53:4525–4533

- Silverstein RM, Webster FX, Kiemle DJ, Bryce DL (2014) Spectrometric identification of organic compounds eighth. Wiley
- Sivakumar P, Krishna S, Hari S, Vij RK (2020) Electromagnetic heating, an eco-friendly method to enhance heavy oil production: a review of recent advancements. *Environ Technol Innov* 20:1–24
- Sivakumar P, Sircar A, Deka B et al (2018) Flow improvers for assured flow of crude oil in midstream pipeline: a review. *J Pet Sci Eng* 164:24–30
- Sun G, Zhang J, Ma C, Wang X (2016) Start-up flow behavior of pipelines transporting waxy crude oil emulsion. *J Pet Sci Eng* 147:746–755
- Taguchi G, Konishi S (1987) Taguchi methods: orthogonal arrays and linear graphs-tools for quality engineering. American Supplier Institute
- Tao Y, Jiandong G, Binggang Y et al (2012) The effects of shear history on the physical properties of tuha oils in west pipelines. *Oil Gas Storage Transp* 31:71–74
- Wu Y, Ni G, Yang F et al (2012) Modified maleic anhydride co-polymers as pour-point depressants and their effects on waxy crude oil rheology. *Energy Fuels* 26:995–1001
- Xu J, Guo Z, Zhang F et al (2018) Preparation of crude oil flow improver from vegetable oil and the performance evaluation. *Key Eng Mater* 777:226–231
- Yang F, Zhao Y, Sjöblom J et al (2015) Polymeric wax inhibitors and pour point depressants for waxy crude oils : a critical review. *J Dispers Sci Technol* 36:213–225
- Yang J, Lu Y, Daraboina N, Sarica C (2020) Wax deposition mechanisms: is the current description sufficient? *Fuel* 275:117937
- Zhang J, Guo Z, Du W et al (2018) Preparation and performance of vegetable oils fatty acids hydroxymethyl triamides as crude oil flow improvers. *Pet Chem* 58:1070–1075

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.