Solvent Treatment on Cloud Point for Dewaxing in Crude Oil Industries

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Phase change in dewaxing of crude oil is controlled at a certain temperature where solids are dissolved in the fluid producing hazy appearance called cloud point formed by the processes of precipitation. Ultrasound techniques was applied in Indian crude oil to confirm an optimum blended chemical which changes the thermo dynamical equilibrium with a suitable operating environment capable to decrease the cloud point temperature to improve the quality of crude oil analysis. Three solvent to crude oil ratios of 10:1, 15:1 and 20:1 within 10°C to 50°C range were ultrasonically treated with solvent blends verified experimentally as separated bright spots with black background. The dewaxing process was compared with two different diluents in a common extractant in terms of the efficiency of extraction and microscopic observation for wax appearance in crude oil. The data recorded with diluents of low carbon chain was found more suitable as compared to immediate higher carbon chain and discussed in terms of different influencing factors like oil solvent ratio, effect of temperature, settling time and influence of ultrasonic wave.

Keywords: Acoustic parameters, Blended chemicals, Cloud point, Dewaxing, Ultrasonic wave

NOMENCLATURE

C Ultrasonic velocity
X_A, X_B mole fraction
Y acoustic parameters
Y Wax yield
W_e weight of the extract
W_o weight of crude oil sample
ED extract dilute pair

Introduction

Transportation and exploration of crude oil through subsea pipelines is always linked with diverse challenges.[1] Precipitation of wax in these flow lines at cold temperature is a major concern during the transportation of crudes from sea to refinery causing deposits on the wall that reduces the flow diameter of pipeline leading to blockage and valve failure.[2] The majority of crude oil contains paraffin waxes which are sparingly soluble in it and crystallise at lower temperatures contributing to wax deposits. Transportation in such gravity fluids is not just hampered by wax deposits but also linked with removal techniques like pigging or heating.[3] In refining, storage and processing industries, as an important guide factor cloud point has been considered to be potential parameter for acceleration of dewaxing process.

Since the cloud point temperature determines the crude oil quality calibrated on API gravity, the designing of reservoir and pipelines are constructed to reduce the cloud point. With reservoir temperature maintained below the cloud point, oil becomes dense due to high viscosity associated with merge oil recovery. Hence the vitality of cloud point plays a significant role in shaping of high pour point oil reservoirs. Though there are many techniques[4–8] supporting to measure the cloud point temperature and some of them are found to be accurate, yet no definite conclusions are confirmed to reduce the temperature. The work embedded describes the dewaxing of crude oil compatible with suitable extractant- diluents (ED) pair in the influence of ultrasonic wave. Estimation of acoustic parameters determines the compatible blended ED pair for thermo dynamical equilibrium condition for the wax precipitation with effect of temperature.[9,10] The experimental data confirms the cloud point decreases with increase of oil to solvent ratio with addition of light hydrocarbons.

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Basic Theory for Application of Ultrasonic Wave

High frequency and small wavelength of ultrasonic wave makes it possible for interacting at atomic and subatomic region of waxy crude oil, by changing the thermodynamic characteristics of solvent mixture used for dewaxing. Ultrasonic wave often visualized as oscillating particles as in elastic springs is influenced by inertial and elastic restoring forces. Such waves in any treatment medium generate pressure by pushing molecules together as in Fig. 1. As per Hooke's law, the force enacted on propagating medium is

$$F \alpha - x$$
$$F = -Kx \qquad \qquad \dots (1)$$

with a constant K influenced by the nature and intermolecular interaction in the propagating medium. Equation of a wave in elastic medium is given by

(a)

(b)

Liquid molecule   Liquid molecule

Ultrasonic Wave

F

x

(c)

Ultrasonically Active Liquid

Stainless steel nose piece

Ground connection

Electrode

Electrical Insulator

Attachment of the nose piece by vacuum brazing with copper

Aluminium coupling mass

Piezoelectric driving elements

Steel back mass

Compression Bolt
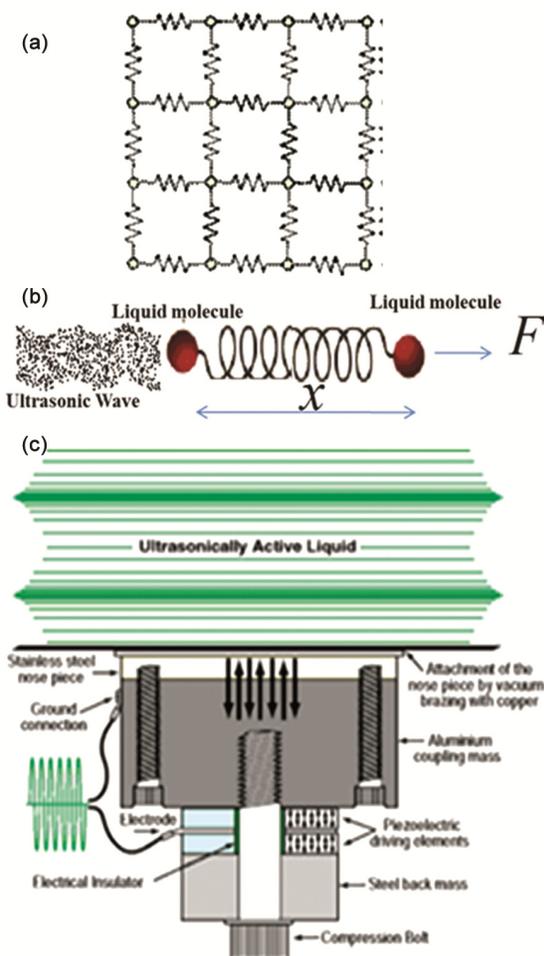
Fig. 1 — (a) Visual elastic medium (b) Effect of ultrasonic wave in liquid medium (c) Ultrasonically active medium

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{1}{C^2} \frac{\partial^2 \psi}{\partial t^2} \qquad \qquad \dots (2)$$

where C being the velocity of propagating ultrasonic wave. The high pressure wave produced due to periodic oscillation of the medium generates unstable micro bubbles which collapse spreading shock waves with high localized temperature promoting acoustic cavitations. Crude oil and ED blends subjected to rarefaction cycle of ultrasonic wave, with wave pressure below ambient, impresses pockets that expand to collapse due to the high stresses at the walls. These pockets are generally molecules finely dispersed throughout the liquid volume located as quasi crystalline structure of the liquid.

Materials and Methods

Materials

Chemicals were purified through standard procedure and redistilled before their usage. Samples of high purity and analytical grades of n-pentane, n-heptanes 99% (GC) and acetone 99 % (GC) were procured from CDH chemicals, India. Sealed bottles kept in desiccators were used to reduce the intimacy of hygroscopic chemicals with moist air. A suitable solvent mixture is used which increases the cloud point temperature. As a result of which the interaction of solvent mixture with wax decreases the viscosity converting the Non-Newtonian flow into Newtonian flow. Sample purities were ascertained by GLC. The oil samples used in our study were brought from Mathura Oil Refinery, with density ranging from (857–869) kg/m^3, wax 20.27 weight %, sulphur 0.051–1.5 weight % through ASTM.

Sample Preparation and Estimation of Acoustic Parameters

Air tight bottles were used for binary blends with their mass measurements calibrated on precision of ± 0.001 mg with a digital balance. Usually two solvents are used: liquid-1, which maintains fluidity at low temperatures, and liquid-2, which dissolves little of wax at low temperatures and acts as a wax precipitating agent. Wax precipitating agent/crystal modifiers act at the molecular level to reduce the networking tendency of wax molecules, and prevent them from forming lattice structures within the oil. They reduce oil viscosity and lower the wax gel strength. Dispersants are a type of liquids that acts to disperse the wax crystals into the produced oil or

water, thereby preventing wax deposition and effect positively on the viscosity and gel strength. Dispersants breaks up deposited wax into smaller particles capable of being carried in the oil stream. Density measurements of pure and mixture blends were done by double distilled pyknometer, accuracy of ± 0.01 kg/m^3. The uncertainty in mole fraction was ± 0.001. Measurement of ultrasonic speed with an accuracy of ± 0.01 ms^{-1} in the liquids mixtures was initiated with multi-frequency ultrasonic interferometer (Mittal Enterprises, New Delhi, Model-MX-3). As the low frequency ultrasonic wave can better interact at the atomic and molecular level so the present work is assembled with 2 MHz frequency. The temperature control of circulating water maintained at ±0.01 K using a bath having accuracy of ±0.001 K. Measured values of C, density and viscosity were used to estimate different acoustic parameters along with their excess values which might predict the physicochemical properties of the medium using Eq. 3.[11]

$$\left(Y^E\right) = Y_{mix} - \left(X_A Y_A + X_B Y_B\right) \qquad \dots (3)$$

where X_A, X_B are the mole fractions, Y_A, Y_B and Y_{mix} represents the (β_s) isentropic compressibility, (L_f) inter molecular free length, (Z) acoustic impedance, of n-pentane, n-heptane, acetone and mixture respectively.

Dewaxing With Different Solvents to Crude Oil Ratio

Blends of solvents mixed with a fixed amount of crude oil were prepared as experimental samples in the wax solvent extraction process as shown in Fig. 2. In the first set of experiment, (5 g of crude + 50 g of solvent blends) corresponding to 1:10 oil to solvent ratio were mixed in a beaker of 150 ml
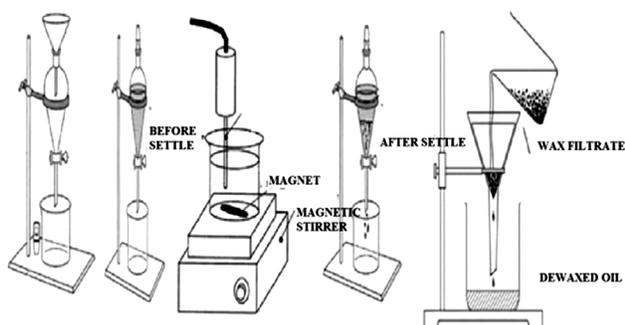
Fig. 2 — Schematic diagram for separation of dewaxing oil from wax filtrate

capacity for a temperature of (10°C–50°C). An ultrasonicator, frequency 125 kHz, power 60 W allows the sample dispersion in the solvent oil blend in presence of ultrasonic wave. Same experiment was repeated with second set of 75 g of solvents in oil to solvent ratio of 1:15 and the third set of 100 g mixed with oil to solvent ratio 20:1. Mixing repetitively with magnetic stirrer which heats the sample, it was allowed to cool on dry ice bath for wax crystallization and vacuum-filtered using 45 µm Whatmann filter paper. Then, ultrasonic waves irradiated a new sample of the residue oil for span of 5 to 15 minutes. After removing filter paper a settling time of 20 minutes was given allowing volatile solvent to evaporate. The wax yield % post treatment is by relation

$$Y = \frac{W_e}{W_o} X 100 \qquad \dots (4)$$

where Y = wax yield % of the total weight of the sample; W_e = the weight of the extract and W_o = the weight of the crude. The whole procedure for dewaxing is shown with flow diagram in Fig. 3.

Results and Discussion

Determination of ultrasonic velocity in pure acetone, n-pentane, n-heptane and their blended solution was used extensively to predict the acoustic parameter shown in Fig. 4. Results confirm C in pure n-pentane is lower than n-heptane and then has a decrement with increase of mole fraction of acetone up to 0.80.

This contributes to strong hydrogen bonding between the long hydrocarbon chain and C=O of acetone. There is a restricted motion in solvent molecule that declines the ultrasonic velocity. Regions rich in acetone bring high dispersion in similar molecules lowering ultrasonic velocity.[11]

Negative variation of excess isentropic compressibility and free length[12] as in Fig. 5 and Fig. 6 for different mole fractions of acetone indicates the strong bonding between acetone and n-pentane blend than n-heptane acetone blend. This may be due to the dominance of hydrogen bond in mixture than pure liquids.

It shows high interacting liquid mixture which is highly compressible possibly due to tight binding in
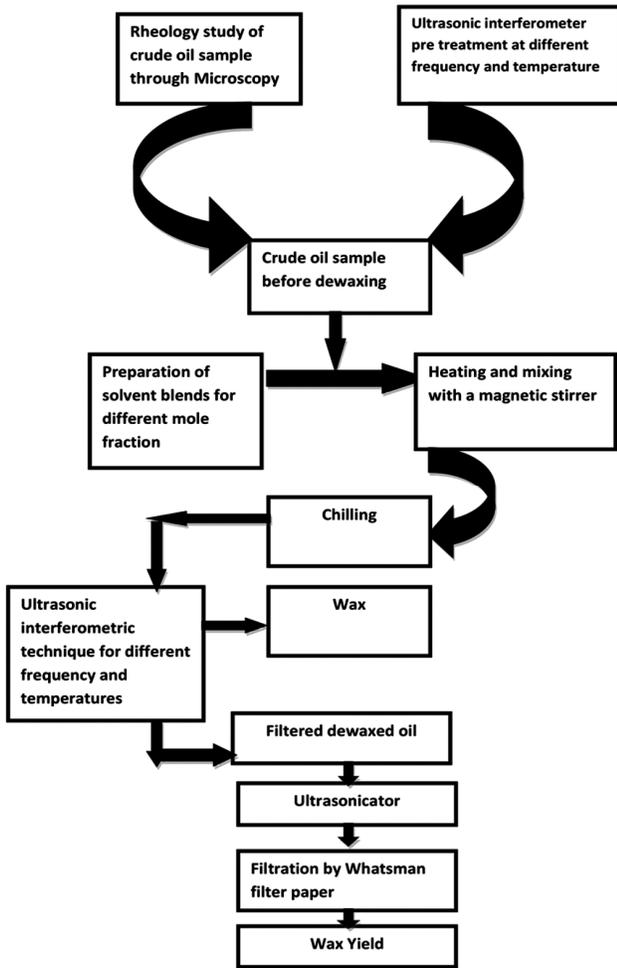
Fig. 3 — Block diagram of the dissimilation procedure
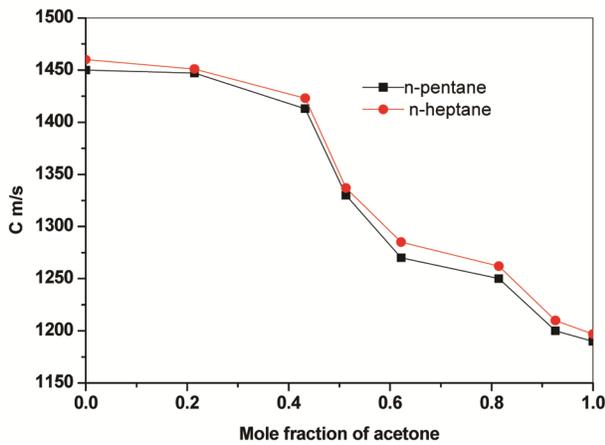
Fig. 4 — Variation of C with mole fraction of acetone

Fig. 5 — Variation of excess β_s with mole fraction of acetone

Fig. 6 — Variation of excess L_f with mole fraction of acetone
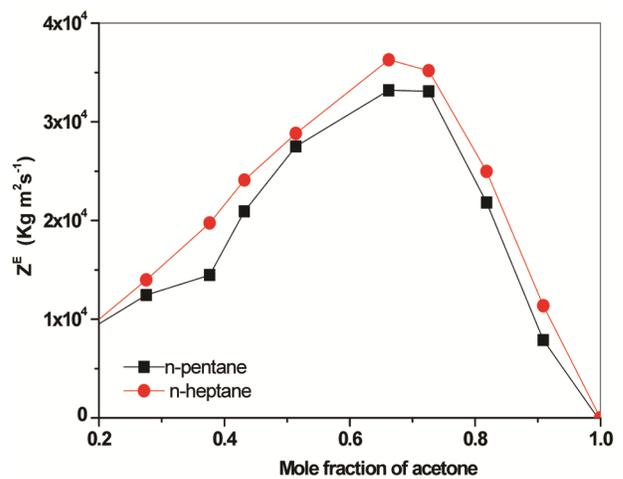
Fig. 7 — Variation of excess Z with mole fraction of acetone

dissimilar molecules. Negative L_f^E reflects strong molecular association. In Fig. 7, maximum positive deviation of Z shows high interacting liquid mixture which is highly compressible possibly due to tight binding in dissimilar molecules. Negative L_f^E reflects strong molecular association. In Fig. 7, maximum

positive deviation of excess Z at 0.6 to 0.7 mole fraction of acetone, which signifies strong binding in polar non-polar molecules. However, association has a declining trend with increase in polar component of acetone.[13]

Effect of Weight of Crude Oil on Wax Yield

From Fig. 8, it was observed that maximum wax was produced[14] under the condition of acetone/n-pentane ratio 20:1. Solvent oil ratio of (10:1), (15:1) and (20:1) in acetone/ n-pentane increased the quantum of wax removal. Increasing initial weight of crude oil from 5 g to 35 g increased the wax yield attributed due to more of long carbon chains.[14]

Effect of Temperature of Crude Oil on Wax Yield

Addition of chemical solvents in a suitable amount changes the thermodynamic of the waxy crude oil by lowering its energy. The molecular motion of the oil particles and other chemical constituents get slow down at low temperature and with increase of temperature the molecules are quickly diffuses to different regions forming instability in the systems.[15–17]

From the Fig. 9 it was observed that with decrease of temperature from 20°C to near about 4°C, the amount of wax increased due to decrease of magnitude of diffusion of the larger size hydrocarbon molecule towards the lower carbon molecules. The results also indicate that at high temperature filtration cannot be applied, due to increase of viscosity. The crystality of wax is also affected by addition of chemical inhabitants in presence of ultrasonic wave as the interaction of the wave decreases the cloud point by lowering the temperature of the mixture. This interaction enhances the large number of crystallization site which accelerates the formation of crystal below the cloud point for better filtration of the wax from the oil.

Effect of Settling Time of Crude Oil Filtrate on Wax Yield

The settling time of crude oil is one of the prime factors which affect wax deposition.[18–19] As the extractant-diluent mixed with crude oil is in the presence of ultrasonic wave; the dispersion of ED pairs in to the crude oil separates the wax due to frequency instability. It was observed that as the settling time increases the interaction of ED pairs with crude oil increases with a constant rate which separates the wax and crystallizes them in separating from crude oil and hence increases the wax contents. As the time increased from one hour to two hours the

amount of wax produced also increased as shown in Fig. 10.

The wax separated in the crude oil was observed and analyzed before treatment and after treatment through a light microscope (Metzer5000BM, resolving power 40X–1000X, with camera 3 Megapixel CMOS SENSOR) as shown in Fig. 11

From the observation it was clear that when there is no ED mixture added the wax are well dispersed within the crude oil. Increasing oil to ED mixture, the interaction site is increases which assemble the hydrocarbons to form the wax crystal separating from the crude oil easily. An increase in the solvent volume decreases the viscosity inducing crystal growth and consequently better filtration.
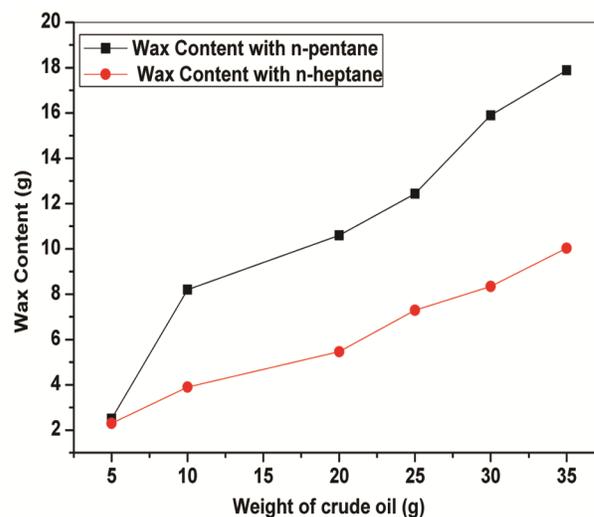
Fig. 8 — Variation of wax content in crude oil with different ED pair
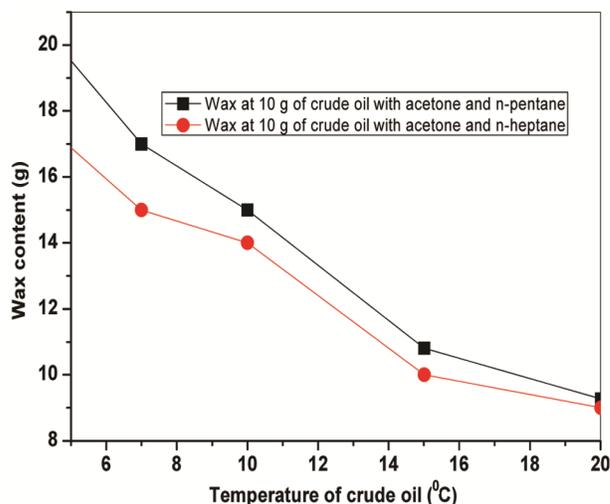
Fig. 9 — Variation of wax content with temperature of crude oil

Fig. 10 —Effect of settling time of crude oil filtrate on wax yield

Wax appearance before treatment
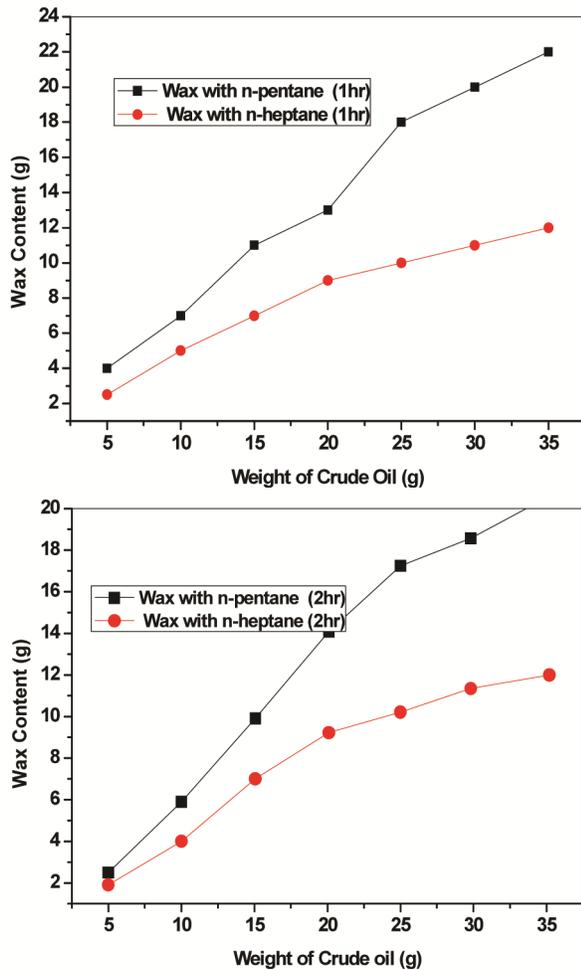
Wax appearance at 1:1

Wax appearance at 2:1

Wax appearance at 3:1
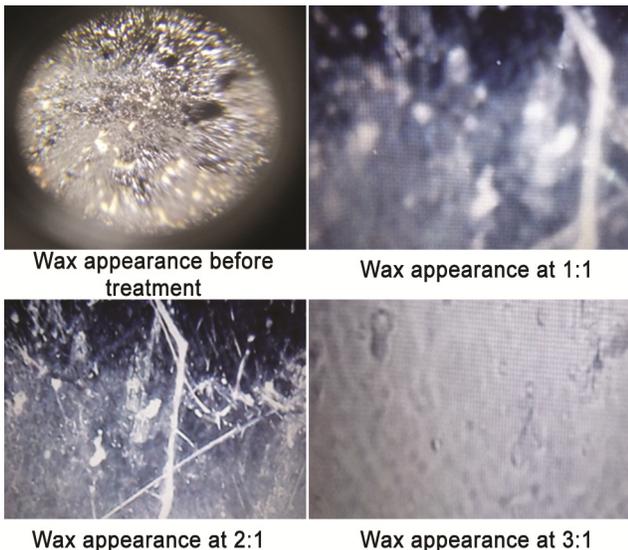
Fig. 11 — Wax appearance in crude oil before and after treatment with solvent mixtures

Conclusions

Choice of solvent blends for dewaxing process establishes different operational parameters through the ultrasonic wave. A trend in acoustic parameters reveals strong interactions in the solvent mixture with the treatment aiming at more coagulation of wax for a particular solvent to oil ratio. It is remarkable to conclude that with increase in initial weight of the crude oil and increased solvent ratio, amount of wax produced increased but not beyond the optimized value. Economic evaluation of solvent composition may lead to high oil recovery and optimization of rates of filtration. Otherwise phase separation may make the filtration impossible. The methodology is simple, environmentally safe, and non-destructive and is successful for the appropriate types of crude oil up to 85–90%. Knowledge of ultrasonicated solvent dewaxed crude may address to the cost-effective approach in flow assurance. It is desirable to have the solvent volume not more than optimized as its recovery and total operational cost may increase.

Acknowledgement

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