The effects of SKO on Assam crude oil

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Abstract
The energy demand for crude oil (CO) has increased globally which encourages the growth in the petroleum industry worldwide. When CO is transported through a pipeline over long distances, due to the change in environmental circumstances, the flow behavior of CO also changes. To improve the flowability of CO through the pipeline, a better understanding of the rheological behavior of CO is very important. In this paper, several experiments were conducted to improve the flowability of CO through pipeline transportation. Dilution of CO with its products like Superior Kerosene Oil (SKO) was selected as it improves the CO flowability through the pipeline and is economically affordable. In this study, the effect of SKO on oAPI gravity, Pour Point, Gel Point, Viscosity Gravity Constant, and rheological parameters were studied for the CO of Upper Assam Basin, Assam. SKO was mixed with CO in different ratios to examine the effect of SKO on it. The results obtained showed that with the addition of SKO, oAPI increases, the minimum limit of attaining paraffinic nature of CO samples can be determined, heavier CO may not always have high Pour Point and Gel Point. The variation in yield stress of CO with SKO was also observed. Herschel-Buckley Model (HBM) was used and from the three parameters of HBM, the shear-thinning or shear thickening behavior of CO was determined. Therefore, this paper attempts to study the flow behavior of CO and also to identify the % of SKO required for improving their flowability through the pipeline.

Keywords  API gravity · Pour point · Viscosity · Viscosity gravity constant · Rheological parameters

Abbreviations

| Abbreviation | Definition                                      |
|--------------|------------------------------------------------|
| CO           | Crude oil                                      |
| RPM          | Revolutions per minute                         |
| s            | Second                                         |
| cp           | Centi poise                                    |
| SKO          | Superior kerosene oil                          |
| API          | American Petroleum Institute                   |
| oAPI gr.     | API gravity                                    |
| dy/cm²       | Dyne/centimeter²                               |
| Pa           | Pascal                                         |
| MCO          | Medium crude oil                               |
| HCO          | Heavy crude oil                                |
| LCO          | Light crude oil                                |
| VGC          | Viscosity gravity constant                     |
| PP           | Pour point                                     |
| GP           | Gel point                                      |
| Sp. gr.      | Specific gravity                               |
| YS           | Yield stress                                   |
| PLM          | Power law model                                |
| BPM          | Bingham plastic model                          |

1 Introduction

With the fall in crude oil (CO) price in the international market due to the present global crises of Covid-19, the Assam oil and gas Exploration & Production (E&P) industries focus more on the transportation of all types of CO, be it heavy or light through the pipeline to the indigenous state refineries. Studies reveal that CO composition varies significantly from the reservoir to the reservoir [1, 2]. Besides many components of the CO may precipitate together with paraffin and the effect of each component on the rheological response of the gelled material may differ from oil to oil [3]. Theyab and Yahya, 2018 found that paraffins are the main components i.e. responsible for oil gelation and the waxy nature of CO [4]. Some waxy CO of Assam particularly, extracted from the Hansa Pung sand, create problems when the winter ambient temperature falls below the Wax Appearance Temperature (WAT), leading to precipitation of the waxy components of the CO on the inner walls of the pipeline.
thereby restricting the smooth flow through the pipeline [5, 6]. Singh et al. 2000 studied the effects of seasonal temperature variations on CO during pipeline transportation, which affects the crystallization rate of waxy CO more near the internal boundary wall of the pipeline than at the axis of the pipeline [7]. Singh et al. 2000, also found that further reduction in temperature causes gel formation in the inner wall of the pipeline, reducing the effective diameter of the pipeline and jamming of pipelines which results in a change in the CO’s rheological behavior from Newtonian to Non-Newtonian. Therefore, transportation of waxy CO through the pipeline is costly as it consumes high energy [7]. It was also observed that the transportation of CO through the pipeline from the production wells is expensive and involves difficulties during the winter months. Therefore, to improve the flowability of the CO, pre-treatment of CO is necessary for which the °API gravity (°API gr.), viscosity, and CO’s rheological parameters change for easier transportation [8].

Before pumping into the pipeline, to inhibit the wax deposition problem, different oil-soluble surfactants or polymeric chemical additives are used because these are the available method for the reduction of wax deposition in the pipeline transportation system [9]. Studies reveal that Assam CO is waxy and hence it causes difficulty in transportation through the pipeline [10]. Thus, the E&P industry associated with pipeline transportation systems are facing oil gelation problems for the past century [11].

Pour point (PP) is defined as the lowest temperature at which CO ceases to flow, for waxy COs the PP is in the range of 15–51 °C [12]. PP is a multiple of 3 °C or 5°F and gel point (GP) is defined as 3 °C lesser than the PP [13].

The PP and yield stress (YS) are two important flow properties i.e. related to the flow of waxy CO through the pipeline transportation system. The YS represents the gel strength of waxy CO which is a better parameter to define the flowability through the pipeline [14]. To restart a pipeline that is normally horizontal, the GP will be required to estimate the pump pressure through the YS of the CO [14]. Higher the GP means more will be the YS and hence more will be the pump pressure.

Viscosity gravity constant (VGC) as developed by Hill and Coats, 1928 is a great aid in defining and classifying COs [15]. It affords a convenient means for classifying CO as Paraffinic, naphthenic or aromatic. From the VGC chart of Houghton and J. A. Robb, 1931, the VGC of COs can be determined by knowing the Saybolt viscosity and °API or CO or vis a vis [16]. The empirical formula for VGC was generated by Kurtz et al. 1956 [17, 18].

The ability to quantify the rheological parameters of different COs is crucial for CO transportation, especially when dealing with off-shore deepwater fields and logistically difficult oil fields [2, 19, 20]. The large changes in temperature and pressure that arise during transportation scenarios result in the formation of several different solid precipitates, including clathrate hydrates, waxes, and asphaltenes, depending on the original composition of the CO [21]. The micro-structural state of these precipitates can then evolve with the shearing and thermal history profile experienced by CO flowing through the pipeline. Paraffinic components are one of the biggest issues that cause pipeline blockages and increase the risk of pipeline damage [22]. Paraffin wax is usually dissolved in the oil phase at the wellhead, but as the temperature of the CO decreases below a critical value known as the WAT, it starts to form wax crystals. The interaction between wax crystals is characterized by strong flocculation and strong attraction, as a consequence, when performing the shear on the CO samples, the wax crystals exhibit the entire motion and deformation behaviors, which was indicated by Dong et al. 2020 [23]. In this case, the individual motions of wax crystals were largely inhibited and the motion freedom of wax crystals was further reduced as observed. This perspective led to the formation of the inner structures of waxy CO at different initial temperatures.

The viscosities of COs were found in this research in the range of 4 cp—100 cp, when the °API gr. was in the range of 21–39, which is similar to the results obtained by Aske et al. 2002 as shown in Fig. 1 [24, 25]. As °API gr. increases, viscosity decreases as shown in Fig. 1.

But it was also found by several researchers that viscosity of CO less than 400 cp is considered as the traditional maximum viscosity required for heavy and extra heavy CO pipeline transportation system [26–28]. Studies were conducted to find useful techniques like heating or other applications to increase the °API gr. and to decrease the CO’s

![Fig. 1 Classification of CO by °API gr. and viscosity [24]](image-url)
The effects of SKO on Assam crude oil

viscosity flowing through the pipeline transportation system. But the heating process has certain disadvantages like heating requires a considerable amount of energy and high capital and operational cost, the base composition of CO may change during the heating process [29]. Some researchers also studied the effect of viscosity reduction on the addition of heavy CO with lighter oils, the addition of hydrocarbon gases or alcohols was done to decrease the viscosity of the heavy oils [30].

Ghannam and Esmail (2006) investigated different CO improving methods to improve the flow of Canadian conventional CO and found that the addition of kerosene enhanced the flow of CO more than the addition of other additives [31]. In this work also, Superior kerosene oil (SKO) was mixed with the CO samples to improve their rheology and hence enhance the flow through the pipeline.

Different researchers investigated the irreversibility of the material by imposing a maximum shear rate on the material and then returning to a lower shear rate [2, 32–34]. Mendes et al. 2015 observed that the high shear rates imposed on the waxy CO altered its structure irreversibly [35]. An irreversible fluid-structure breaks each time the fluid was sheared at a new maximum shear rate which causes a significant reduction of its apparent viscosity and YS as observed by Mendes 2015 [35]. As a result of that characteristic, heterogeneous viscosity profiles may appear in transient and steady-state flow [35]. Andrade et al. 2020 suggested the development of a specific model to focus on the irreversible circumstance as the macroscopic results of the waxy CO obtained from the conventional rheometers failed to consider the unsheared region [33]. Legnani et al. 2020 investigated the effect of the shear history on the flow of waxy COs and observed that the time-dependent elastoviscoplastic behavior of the waxy CO structure can be irreversibly modified by the shear [34].

The main focus of this paper was an attempt to study the rheological properties of CO for transportation through the pipeline. Hence, in this work, the irreversibility of the CO was not studied in detail. However, several authors investigated the irreversibility of the CO [2, 32–34]. So, the extension of this research work on irreversibility is kept for future work.

Several mathematical models are available to describe the rheology of non-Newtonian fluids which include but are not restricted to the Power Law model (PLM), Bingham Plastic Model (BPM), Herschel-Buckley Model (HBM), and Casson Model (CM). Researchers investigated different types of rheological models and observed that HBM characterized the rheology more accurately over the other BPM and PLM as these were not enough to describe the viscous fluids exhibiting yield point [36, 37]. So, modified PLM or HBM is used for this purpose which corrects this insufficiency using the power-law expression instead of the term plastic viscosity in the Bingham Plastic model [37]. Different researchers investigated the relationship between shear stress and rate and observed the necessity of conditioning the CO by adding different % of SKO to it, as a prerequisite for a proper rheological study of waxy COs [38, 39]. This paper attempts to study the effect of SKO on different CO samples, particularly on the variation in °API gr., VGC, PP & GP, and rheological properties.

2 Experimental

2.1 Materials and types of equipment

The materials and equipment used for the experiments are in Table 1 and Table 2, respectively.

Three samples named CO1, CO2, and CO3 were medium, heavy and light CO, respectively, and these samples were collected from three different wellheads of producing wells of Upper Assam Basin. The specifications of the samples are given in Table 3.

2.2 Geometry type and dimensions in the viscometer

Shear stresses of the samples were measured at different shear rates (170.23 s⁻¹, 340.46 s⁻¹, 510.69 s⁻¹ &

| Table 1 | Materials used for the experiments |
|---|---|
| Sl. No. | Materials | Source |
| 1 | Three crude samples | Oil India Limited (OIL), Oil and Natural Gas Corporation Limited (ONGCL) |
| 2 | SKO | Locally purchased |

| Sl. No. | Equipments | Make | Model |
|---|---|---|---|
| 1 | Viscometer | Grace | M3600 |
| 2 | Hydrometer | | |
| 3 | Pour point apparatus | | |
| 4 | Constant temp. bath | USA | CT-500 series II |

| Table 3 | Sample specifications |
|---|---|
| Sl. No. | Samples | Sp. gr. at 15.6 °C/15.6 °C | °API gr | Type of CO |
| 1 | CO1 | 0.910 | 24 | MCO |
| 2 | CO2 | 0.927 | 21 | HCO |
| 3 | CO3 | 0.855 | 34 | LCO |
1021.33 s\(^{-1}\)) and at two temperatures (30 °C & 40 °C). The CO samples (CO1, CO2 & CO3) were used alone and with SKO that exhibit no wall slip condition to observe the effects of shear rates on the flow [40, 41]. When these phenomena are present in coaxial cylinder geometries with mechanical specifications and measurement range of the viscometer as given in Table 4 and Table 5, the shear stresses and shear rates may no longer be uniform across the radial extent of the geometry [42, 43].

### 2.3 Sampling of CO

Formation Water (FW) was separated from the CO samples collected from different wellheads of the Upper Assam Basin. Then 5%, 10%, and 15% SKO were added as in Table 6. A total of 12 samples were prepared. These samples were thermally pretreated at 66–70 °C to eliminate lighter ends [44].

#### 2.3.1 Determination of \(o\text{API gr.}\)

The Sp. gravities of CO samples were determined using ASTM D1298—12b [45]. The CO samples as in Table 6 were taken, one at a time in a measuring cylinder and kept in the temperature bath where the temperature was increased from 30 to 80°C. The values of Sp. gr. of the samples were plotted against a temperature range of 30–80 °C and Sp. gr. was determined at 15.6°C, which was used to calculate the \(o\text{API gr.}\), using equation (1) [46].

\[
\text{API}^o = \frac{141.5}{\text{Sp. gr. at 15.6°C/15.6°C}} - 131.5. \tag{1}
\]

#### 2.3.2 Calculation of VGC of the samples

The viscosity-gravity constant (VGC) is an important parameter that can be used for the approximate characterization of the viscous CO. VGC is related to COs composition which helps to identify the paraffinicity, naphthenicity, and aromaticity of CO. The VGC of the CO samples of Table 6 was calculated by equation (2) or (3) [18].

For light and medium COs

\[
\text{VGC} = \frac{10d - 1.0752\log(v - 38)}{10 - \log(v - 38)}, \tag{2}
\]

where, \(d = \text{Sp. gr. at 15.6 °C,}\)
\(v = \text{Saybolt viscosity at 37.78 °C.}\)
Saybolt viscosity can be expressed as
\(v = B \mu/\text{Sp. gr.}\)
\(= B \nu_{\text{centiStokes}}\)
where, \(\nu = \text{kinematic viscosity (SSU).}\)
\(B = 4.632 \text{ for temperature 37.78 °C}\)
\(\mu = \text{dynamic or absolute viscosity (cp)}\)
\(\nu_{\text{centiStokes}} = \text{kinematic viscosity (cSt)}\)
For heavy COs

\[
\text{VGC} = \frac{d - 0.24 - 0.022\log(v - 35.5)}{0.755}. \tag{3}
\]

#### 2.3.3 Determination of PP and GP

The PPs of CO samples in Table 6 were determined by ASTM D 97 [47]. The pretreated samples were heated from ambient temperature to 40 °C. The flowability of the tested

| Table 4 | Mechanical specifications of viscometer |
|---------|----------------------------------------|
| Sl. No. | Parameters | Specifications |
| 1       | Dimensions/footprint | 5” × 8” (12.7 × 20.3 cm) |
| 2       | Height | 16” (40.6 cm) |
| 3       | Weight | 12.5 lbs (5.7 kg) |

| Table 5 | Measurement range of the viscometer |
|---------|-------------------------------------|
| Sl. No. | Rotor Bob | R1 B1 |
| 1       | Rotor radius (cm) | 1.8415 |
| 2       | Bob height (cm) | 3.800 |
| 3       | Bob radius (cm) | 1.7245 |
| 4       | Shear gap in annulus (cm) | 0.1170 |
| 5       | Radii ratio \((R/R_o)\) | 0.9365 |
| 6       | Maximum use temperature (°C) | 93 |
| 7       | Minimum use temperature (°C) | 0 |
| 8       | Shear stress range (dynes/cm\(^2\)) | 1–2,000 |
| 9       | Shear rate constant \(k_r\), s\(^{-1}\) per rpm | 1.7023 |
| 10      | \(N=100\) rpm | 170.23 |
| 11      | \(N=600\) rpm | 1,021.38 |
| 12      | Minimum viscosity (cp) | 0.098 |
| 13      | Maximum viscosity (cp) | 10,000,000 |

| Table 6 | CO samples |
|---------|-------------|
| Sl. No. | CO samples | CO samples prepared with and without adding SKO (%) |
| 0      | 5          | 10         | 15         |
| 1      | CO1        | CO1 + 0    | CO1 + 5    | CO1 + 10   | CO1 + 15   |
| 2      | CO2        | CO2 + 0    | CO2 + 5    | CO2 + 10   | CO2 + 15   |
| 3      | CO3        | CO3 + 0    | CO3 + 5    | CO3 + 10   | CO3 + 15   |
samples was checked every 3 °C till the anticipated PP was reached at which the CO samples ceases to flow when the test tube was held horizontal or vertical for 5s. The PP is 3 °C above the temperature at which the sample remains stationary. To obtain more accurate PP and GP, the tests were carried out at least five times under the same condition, and the average values were recorded as the result [13].

### 2.3.4 Determination of rheological properties

The rheological properties of CO samples in Table 6 were determined using M3600DAQ software of the Viscometer as in Table 2, by selecting the required test set up which included the temperature, rotational speeds in the set-up menu [48]. The test results were obtained in an excel sheet for speed (rpm), shear rate (s⁻¹), shear stress (dy/cm²), dynamic viscosity (cp) against the values given in the initial set-up. The graphs of shear stress (Pa) against shear rate (s⁻¹) were generated, in which shear stress values were in the SI unit i.e., in Pa since in this paper all calculations were done in the SI unit.

In this work, the Herschel Buckley model (HBM) was used to describe the rheology of non-Newtonian fluids and mathematically, this HBM is expressed as:

\[ \tau = \tau_o + k\gamma^n, \]  \hspace{1cm} (4)

where \( \tau \) is the shear stress (Pa),

\( \gamma \) = Shear rate (s⁻¹),

\( n \) = Flow behavior index (dimensionless),

\( k \) = Consistency index in (Pa.sⁿ),

\( \tau_o \) = YS (Pa).

This HBM is a three-parameter model which includes \( \tau_o \), \( n \) and \( k \) values. Whether the fluid is exhibiting Newtonian or non-Newtonian can be identified from this model.

So, taking logarithmic of equation (4), the following equation can be derived-

\[ \log(\tau - \tau_o) = \log k + n\log \gamma, \]  \hspace{1cm} (5)

YS can be calculated by measuring the shear stress at 3 rpm and 6 rpm i.e. at 5 s⁻¹ and 10 s⁻¹ shear rates. The equation used to measure \( \tau_o \) is given below [36, 49]—

\[ \tau_o = 2\tau_3 - \tau_6, \]  \hspace{1cm} (6)

where

\( \tau_3 \) & \( \tau_6 \) are the shear stresses at 3 and 6 rpm i.e. at 5 and 10 s⁻¹ shear rates, respectively, in Pa. A graph was plotted between \( \log(\tau - \tau_o) \) vs. \( \log \gamma \) and an equation (\( y = mx + c \)) was obtained from which the \( n \) and \( k \) values were obtained by regression analysis with the help of Eq. (5) [37]. After calculating \( \tau_o \), \( n \) and \( k \) values, HBM flow rheogram was obtained for each CO sample.

### 3 Results and discussion

#### 3.1 Effect of °API gr. when SKO was added to CO samples

Effects of °API gr. when different % of SKO was added to the CO samples were observed by their relationship between °API gr. and % of SKO as shown in Fig. 2. The values of °API gr. were tabulated in Table 7 and the relationship of °API gr. with the addition of % of SKO in CO1, CO2 and CO3 were plotted in Fig. 2. The effect of SKO was observed in both with and without the addition of SKO in CO.

From Fig. 2, it was observed that in the case of CO1, °API gr. first increases and then gradually decreases and again increases as the % of SKO in the sample increases. In the case of CO2 as % of SKO in the sample increases, °API gr. also increases indicating that gradually CO2 converted from heavy to lighter CO. For CO3, °API gr. increases with an increase in % of SKO and then becomes stable to 10% of SKO added and then again decreases with an increase in °API gr. of SKO in the CO sample. But CO3 remained lighter with and without the treatment of SKO but the value of °API gr. was higher when the addition of SKO was increased to 10%.

As per Pabón and Filho, 2019 the °API gr. of CO varies typically between10 to 50, usually CO can be classified as LCO when °API gr. >31.1, MCO when °API gr. lies between 31.1 and 22.3, and HCO when °API gr. <22.3 [50]. So, based on the °API gr. values obtained from the experiment, CO samples were classified as mentioned in Table 7. It was observed from Table 7 that the addition of SKO was beneficial as it converted the MCO into LCO for CO1 and
HCO to finally LCO in case of CO2. The exact % of SKO at which the CO samples changed from HCO to MCO or LCO was determined from Fig. 2. It was found from Fig. 2 that in the case of CO1, the addition of SKO from 0 to 13.1 % exhibited MCO and beyond that, it changed to LCO. Since CO2 changed from HCO to MCO and then to LCO, the addition of SKO from 0 to 5 % exhibited HCO, then from 5 to 13.4 % it exhibited MCO and beyond that, it changed to LCO. In the case of CO3, the addition of SKO from 015% exhibited LCO. Since viscosity is inversely proportional to °API gr. as observed in Fig. 1, and higher the °API gr. means lighter the CO. So, the minimum % of SKO required for maintaining the LCO nature of the CO is very important as it gives the lower viscosity value at the economic limit.

3.2 Effect of VGC when SKO was added to CO samples

VGC is an important parameter that is used to characterize CO. VGC values help to determine the nature of the samples as shown in Table 8 [17]. The paraffinic nature of CO indicates the presence of wax and causes a problem in the transportation of CO [51–53]. VGC is comparatively not sensitive to molecular weight but is associated with the composition of samples under test.

VGC values of the CO samples and their classifications based on VGC values were tabulated in Table 9. Variation of VGC with the % of SKO in CO1, CO2, and CO3 was plotted in Fig. 3.

As the % of SKO in CO1 increased up to 10%, VGC decreased and showed the naphthenic nature whereas beyond that showed the paraffinic nature. The maximum % of SKO up to which the naphthenic nature of the CO1 sample could be maintained was determined from Fig. 3. It was found that the addition of SKO from 0 to 11.19% exhibited naphthenic nature and beyond that exhibited paraffinic nature.

In the case of CO2, as the % of SKO in CO2 increased, VGC remained constant till the addition of SKO in CO2 was 5% and then decreased up to 15% of SKO in the sample. Therefore, the range of SKO % for exhibiting the naphthenic nature of CO2 was found from 0 to 10.99% and beyond that relatively paraffinic nature was observed.

In the case of CO3, as the % of SKO in CO3 increased, VGC decreased drastically and changed from naphthenic to paraffinic nature. The maximum % that CO3 exhibited naphthenic nature was determined from Fig. 3 which was obtained 0.6% beyond which paraffinic nature was obtained.

Paraffin is the main component of the wax deposition so from Fig. 3, it was identified that increase of % of SKO above 11.19% and 10.99% for CO1 and CO2, respectively, increased the chances of wax deposition as it converted the CO1 and CO2 samples into paraffinic nature. But in the case of CO3, the addition of SKO above 0.6% converted it to paraffinic nature. Therefore, conditioning of CO3 with SKO was not effective as it enhanced the chances for wax deposition.
The effects of SKO on Assam crude oil

3.3 Effect of PP and GP when SKO was added to CO samples

The values of PP and GP were tabulated in Table 10 and the variation of PP with an increase in % of SKO was shown in Fig. 4. It was observed that in the case of CO1 on the addition of SKO from 0 to 5%, both PP and GP increased and then remained constant up to 10% of SKO followed by an increase in PP and GP with the addition of SKO from 10 to 15%.

In the case of CO2 also, on the addition of SKO from 0 to 5%, both PP and GP increased then decreased up to 10% of SKO followed by the increase of PP and GP up to 15% of SKO.

But in the case of CO3 on the addition of SKO from 0 to 10%, both PP and GP decreased first and then increased on the addition of SKO from 10 to 15%.

Tuttle, 1983 defined 15.55–51.67 °C as high PP CO, therefore, the PP obtained for CO1, CO2, and CO3 as shown in Fig. 4 and Table 10 predicted high PP CO samples, except CO2 without SKO [12]. High PP and high GP, were generally associated with high paraffin content indicating the presence of wax, thereby, affecting the flowability of CO through pipeline transportation [54]. The PP and GP changed w.r.t. the addition of SKO to CO samples as in Fig. 4, which is considered to be closely related to sample composition, such as wax, resins, and asphaltenes contents [13, 55–57].
In general, if wax present can be dissolved before the cooling starts, the resins and asphaltenes will have enough opportunities to build into the wax crystal structure and alter their morphology and surface characteristics, creating a tendency to interact at different heating temperatures leading to diverse flow behavior of the samples under study [13]. It was observed by Geest et al., 2019 that due to the temperature profile, the CO having high PP and GP would cool down more slowly in the center of the pipeline under a static condition, which generates a stronger crystalline structure [58]. Similarly, the gel formed near the pipeline wall would provide more space in which the crystals could grow, thus generating a stronger gel. Both situations tend to increase the gel strength, possibly explaining why the equilibrium time of CO flow through the pipeline is higher [58]. In general, COs with high PP values have higher YS values which creates difficulty to restart the flow through the pipeline [59].

In terms of PP and GP, treatment of SKO was not beneficial in the case of CO1 and CO2 as the PP and GP of these samples were lowest without the treatment with SKO. But in the case of CO3, the lowest value of PP and GP were observed when treated with 10% of SKO.

### 3.4 Effect of shear stress and shear rate when SKO was added to CO samples

Shear stress values at different shear rates of 102.138 s⁻¹, 510.69 s⁻¹, 340.46 s⁻¹, 170.23 s⁻¹, 10 s⁻¹, and 5 s⁻¹ were measured using a viscometer and tabulated in Table 11. Shear stress at shear rates 10 s⁻¹ and 5 s⁻¹ was measured to calculate the YS of the sample using equation (4). After calculating the YS value, \( \log(\tau - \tau_0) \) vs. \( \log \gamma \) was plotted where \( \log k \) defined the intercept value for each CO sample as shown in Fig. 5. So, the equation obtained from this relationship which in the form of \( y = mx + c \) was used to

![Variation of PP of different CO and SKO mixtures](image)

**Table 10** PP and GP at different % of CO and SKO mixtures

| Sl. No | CO Samples | CO + % of SKO | PP (°C) | GP (°C) |
|--------|------------|--------------|--------|--------|
| 1      | CO1        | CO1 + 0      | 24     | 21     |
|        |            | CO1 + 5      | 30     | 27     |
|        |            | CO1 + 10     | 30     | 27     |
|        |            | CO1 + 15     | 27     | 24     |
| 2      | CO2        | CO2 + 0      | 12     | 9      |
|        |            | CO2 + 5      | 27     | 24     |
|        |            | CO2 + 10     | 24     | 21     |
|        |            | CO2 + 15     | 27     | 24     |
| 3      | CO3        | CO3 + 0      | 24     | 21     |
|        |            | CO3 + 5      | 21     | 18     |
|        |            | CO3 + 10     | 18     | 15     |
|        |            | CO3 + 15     | 24     | 21     |

![Table 11](image)

**Table 11** Shear stress (Pa) values at different shear rates (s⁻¹) of all CO samples

| Sl. No | CO | CO + % of SKO | Shear stress (Pa) at different shear rates (s⁻¹) |
|--------|----|--------------|-----------------------------------------------|
|        |    |              | 1021.38  | 510.69  | 340.46  | 170.23  | 10   | 5   |
| 1      | CO1 | CO1 + 0      | 33.4    | 23.9    | 16.8    | 13.9    | 21.9 | 21.8|
|        |     | CO1 + 5      | 4.4     | 2.5     | 1.7     | 0.9     | 1.8  | 1.7 |
|        |     | CO1 + 10     | 0.2     | 0.1     | 0.1     | 0.1     | 1.6  | 1.5 |
|        |     | CO1 + 15     | 5.7     | 3.4     | 2.3     | 1.4     | 19.9 | 19.8|
| 2      | CO2 | CO2 + 0      | 41      | 21.8    | 14.6    | 7.6     | 1.9  | 1.5 |
|        |     | CO2 + 5      | 3.4     | 1.9     | 1.5     | 1.3     | 0.9  | 0.7 |
|        |     | CO2 + 10     | 3.9     | 2.5     | 1.8     | 0.9     | 0.8  | 0.6 |
|        |     | CO2 + 15     | 4.5     | 3.3     | 2.2     | 1.2     | 1    | 0.9 |
| 3      | CO3 | CO3 + 0      | 6.9     | 5.2     | 3       | 1.3     | 0.95 | 0.9 |
|        |     | CO3 + 5      | 6.6     | 3.9     | 2.8     | 1.7     | 0.9  | 0.81|
|        |     | CO3 + 10     | 7       | 3.6     | 2.5     | 1.3     | 0.3  | 0.21|
|        |     | CO3 + 15     | 6.9     | 3.7     | 3.1     | 2       | 1.1  | 1.05|
determine the $k$ and $n$ values. The three parameters of HBM along with their respective HBM equations of all the prepared samples at 30°C and 40°C were given in Table 12 and Table 13.

It was observed from Table 12 that all the CO samples exhibited shear thinning behavior at 30°C as $n < 1$. The highest and lowest YS values of CO samples at 30°C were observed in the case of CO1 + 0 and CO1 + 10, respectively. It was also observed from Table 12 that as % of SKO increased up to 10% for CO1, CO2, and CO3, the YS value decreased and increased at 15% of SKO. Highest YS among all the CO samples at 30°C means that CO1 without SKO forms a gel, thereby requiring maximum YS to start the flow; while the lowest YS means that CO1 with 10% SKO requires minimum YS without much affecting the flow. It was also observed that n values of CO1 + 10 and CO1 + 15 were negative. Padmanabhan and Bhattacharya, 1991 also observed a negative $n$ value and they explained that molecular degradation of the sample, viscous indulgence, sample slip, and presence of YS could be the reason for the negative values of $n$ [60]. Fraiha et al. 2011 considered the negative $n$ value ‘meaningless’ as it occurs due to the slipping out of the sample while performing the rheological experiments [61]. But in this work, it was stated that the experiments did not present the wall slip, so molecular degradation of the sample, viscous indulgence, and presence of YS could be
the reason for the negative n values. Since negative n value was observed in the case of CO1 + 10 and CO1 + 15; so, the Herschel-Bulkley equation was not fitted and shown in the results for these two samples at 30 °C.

But in the case of 40 °C, except CO2 + 0, CO3 + 10, and CO3 + 15, all other CO samples exhibited shear-thinning behavior as n < 1. But CO2 + 0, CO3 + 10, and CO3 + 15 exhibited shear thickening behavior as n > 1. The highest and lowest YS values among all the CO samples at 40 °C were observed in the case of CO1 + 0 and CO3 + 10, respectively. YS value of CO1 gradually decreased with an increase in % of SKO up to 10% and then increased at 15% of SKO. But in the case of CO2, as % of SKO increased up to 10%, the YS value also increased and then decreased at 15% of SKO. In the case of CO3, the YS value increased from 0 to 5% of SKO and then decreased at 10% followed by an increase in YS at 15% of SKO at 40 °C. Here also the highest YS was observed in the case of CO1 without SKO treatment. Higher the YS means higher the tendency to exhibit the pipeline wall shear stress which increases the resistance to flow. The variation of flow resistance is higher for Herschel-Bulkley compared to others indicating that the flow resistance is directly proportional to n and k values. An increase in ‘n’ value causes flows resistance to rise considerably as compared to the value of k [62].

Finally calculating the three parameters needed for the HBM, shear stress at different shear rates for all the prepared CO samples except CO1 + 10 and CO1 + 15 at 30 °C were measured using equation (iv) at both the temperatures 30 °C and 40 °C as shown in Table 14 and Table 15. Rheograms of HBM for each CO sample except CO1 + 10 and CO1 + 15 at 30 °C were plotted in Fig. 6 as these two samples CO1 + 10 and CO1 + 15 exhibited a negative n value. It was also observed from the flow curves of HBM fluid in Fig. 6 that minimum stress was required for each CO sample to start the flow.

It is also important to consider the influence of wax chemical structure on the YS since it is promoted by interlocking networks maintained by Van der Waals forces among wax crystals [55, 63]. Due to CO multi-component, variable

| CO | CO + %SKO | (Y = mx + C) | τo | log k | k | n | τ = τo + ky^n |
|----|-----------|--------------|----|-------|---|---|----------------|
| CO1 | CO1 + 0   | y = 0.026x + 0.983 | 9.5 | 0.983 | 9.616 | 0.026 | τ = 9.5 + 9.616y^{0.026} |
| CO1 | CO1 + 5   | y = 0.106x - 0.016 | 0.3 | -0.016 | 0.964 | 0.106 | τ = 0.3 + 0.964y^{0.106} |
| CO1 | CO1 + 10  | y = -0.663x + 0.617 | 0.05 | 0.617 | 4.140 | -0.663 | - |
| CO1 | CO1 + 15  | y = -0.435x + 1.507 | 0.7 | 1.507 | 32.137 | -0.435 | - |
| CO2 | CO2 + 0   | y = 0.840x - 0.979 | 1.1 | -0.979 | 0.104 | 0.840 | τ = 1.1 + 0.104y^{0.840} |
| CO2 | CO2 + 5   | y = 0.412x - 0.934 | 0.5 | -0.934 | 0.116 | 0.412 | τ = 0.5 + 0.116y^{0.412} |
| CO2 | CO2 + 10  | y = 0.463x - 1.004 | 0.4 | -1.004 | 0.099 | 0.463 | τ = 0.4 + 0.099y^{0.463} |
| CO2 | CO2 + 15  | y = 0.631x - 1.446 | 0.8 | -1.446 | 0.036 | 0.631 | τ = 0.8 + 0.036y^{0.631} |
| CO3 | CO3 + 0   | y = 0.892x - 1.961 | 0.85 | -1.961 | 0.011 | 0.892 | τ = 0.85 + 0.011y^{0.892} |
| CO3 | CO3 + 5   | y = 0.743x - 1.538 | 0.72 | -1.538 | 0.029 | 0.743 | τ = 0.72 + 0.029y^{0.743} |
| CO3 | CO3 + 10  | y = 0.781x - 1.579 | 0.12 | -1.579 | 0.026 | 0.781 | τ = 0.12 + 0.026y^{0.781} |
| CO3 | CO3 + 15  | y = 0.873x - 1.903 | 1 | -1.903 | 0.013 | 0.873 | τ = 1 + 0.013y^{0.873} |

Table 12 HBM equations to predict non-Newtonian behavior of CO samples at 30 °C with different % of SKO mixtures

| CO | CO + %SKO | (Y = mx + C) | τo | log k | k | n | τ = τo + ky^n |
|----|-----------|--------------|----|-------|---|---|----------------|
| CO1 | CO1 + 0   | y = 0.770x - 2.345 | 2.78 | -2.345 | 0.005 | 0.77 | τ = 2.78 + 0.005y^{0.77} |
| CO1 | CO1 + 5   | y = 0.951x - 2.360 | 0.26 | -2.360 | 0.004 | 0.951 | τ = 0.26 + 0.004y^{0.951} |
| CO1 | CO1 + 10  | y = 0.554x - 2.328 | 0.2 | -2.328 | 0.005 | 0.554 | τ = 0.2 + 0.005y^{0.554} |
| CO1 | CO1 + 15  | y = 0.919x - 2.326 | 0.36 | -2.326 | 0.005 | 0.919 | τ = 0.36 + 0.005y^{0.919} |
| CO2 | CO2 + 0   | y = 1.119x - 1.790 | 0.9 | -1.790 | 0.016 | 1.119 | τ = 0.9 + 0.016y^{1.119} |
| CO2 | CO2 + 5   | y = 0.347x - 0.475 | 1.5 | -0.475 | 0.335 | 0.347 | τ = 1.5 + 0.335y^{0.347} |
| CO2 | CO2 + 10  | y = 0.433x - 0.771 | 1.8 | -0.771 | 0.169 | 0.433 | τ = 1.8 + 0.169y^{0.433} |
| CO2 | CO2 + 15  | y = 0.706x - 1.474 | 0.2 | -1.474 | 0.034 | 0.706 | τ = 0.2 + 0.034y^{0.706} |
| CO3 | CO3 + 0   | y = 0.770x - 1.868 | 0.85 | -1.868 | 0.014 | 0.77 | τ = 0.85 + 0.014y^{0.77} |
| CO3 | CO3 + 5   | y = 0.877x - 1.919 | 1.15 | -1.919 | 0.012 | 0.877 | τ = 1.15 + 0.012y^{0.877} |
| CO3 | CO3 + 10  | y = 1.216x - 2.864 | 0.19 | -2.864 | 0.001 | 1.216 | τ = 0.19 + 0.001y^{1.216} |
| CO3 | CO3 + 15  | y = 1.020x - 2.418 | 1.06 | -2.418 | 0.004 | 1.02 | τ = 1.06 + 0.004y^{1.02} |

Table 13 HBM equations to predict non-Newtonian behavior of CO samples at 40 °C with different % of SKO mixtures
The effects of SKO on Assam crude oil

composition, the gel formation mechanism is quite complex and wax structure plays an important role in this regard [64].

Rheological behavior of the CO samples was observed while flowing at a constant temperature of 30 °C and 40 °C and a comparison of the results with different flow conditions was done to distinguish the fluid–structure evolution.

Rheogram of all the CO samples except CO1 + 10 and CO1 + 15 at 30 °C were plotted in Fig. 6 where the rheogram showed the YS values, shear-thinning, and shear thickening behavior. From Fig. 6, it was also observed that at 30 °C, all the CO samples exhibited shear-thinning behavior while at 40 °C, CO2 + 0, CO3 + 10, and CO3 + 15 CO samples exhibited shear thickening behavior. After the sample starts to flow there is a linear relationship between shear stress and shear rate in the case of BPM [49]. But the linear relationship was not observed in the case of HBM indicating that the shear stress of waxy CO shows sophisticated non-Newtonian characteristics in the shear rate of range 0–1021.38 s\(^{-1}\), in which the shear stress vs. shear rate appears a non-linear behavior. Therefore, the non-linear behavior indicates that the waxy CO has a yielding property in shearing at the experimental temperature, caused by the microstructure of wax in the CO as observed by Huang et al. 2008 [65].

4 Conclusion

(a) The highest °API gravity was observed in CO3 + 5 and CO3 + 10 but lowest in CO2 + 0. To convert the CO samples to LCO, % of SKO > 13.1% for CO1, > 13.4% for CO2 were required for the treatment of CO samples using SKO. But in the case of CO3, both with and without SKO treatment, the sample remained LCO thus SKO had no influential effect on °API gr. of the sample. CO3 appeared to be a lighter CO as the °API was in the range of 34–39, but from VGC, CO3 was found paraffinic, which is an indication of the waxy nature of CO. Lighter the CO means lower the viscosity value so

| Sl. No. | CO | CO + % of SKO | Shear Stress (Pa) at different Shear rates (s\(^{-1}\)) |
|--------|----|---------------|---------------------------------------------------|
|        |    |               | 1021.38 | 510.69 | 340.46 | 170.23 | 10 | 5 |
| 1      | CO1 | CO1 + 0       | 21.014  | 20.808 | 20.690 | 20.49  | 19.709 | 19.527 |
|        |     | CO1 + 5       | 2.309   | 2.167  | 2.088  | 1.962  | 1.531  | 1.443  |
|        |     | CO1 + 10      | -       | -      | -      | -      | -      | -      |
|        |     | CO1 + 15      | -       | -      | -      | -      | -      | -      |
| 2      | CO2 | CO2 + 0       | 39.985  | 29.913 | 14.522 | 8.102  | 1.992  | 1.797  |
|        |     | CO2 + 5       | 2.515   | 2.014  | 1.781  | 1.463  | 0.800  | 0.725  |
|        |     | CO2 + 10      | 2.848   | 2.176  | 1.872  | 1.468  | 0.688  | 0.609  |
|        |     | CO2 + 15      | 3.652   | 2.641  | 2.226  | 1.720  | 0.954  | 0.899  |
| 3      | CO3 | CO3 + 0       | 5.490   | 3.824  | 3.127  | 2.266  | 0.903  | 0.800  |
|        |     | CO3 + 5       | 5.711   | 3.702  | 2.927  | 2.038  | 0.881  | 0.816  |
|        |     | CO3 + 10      | 5.943   | 3.509  | 2.589  | 1.557  | 0.277  | 0.211  |
|        |     | CO3 + 15      | 6.508   | 4.007  | 3.111  | 2.153  | 1.097  | 1.053  |

Table 15 Shear stress values for rheogram of CO samples at 40 °C with different % of SKO mixtures

| Sl. No. | CO | CO + % of SKO | Shear stress (Pa) at different shear rates (s\(^{-1}\)) |
|--------|----|---------------|---------------------------------------------------|
|        |    |               | 1021.38 | 510.69 | 340.46 | 170.23 | 10 | 5 |
| 1      | CO1 | CO1 + 0       | 3.818   | 3.389  | 3.225  | 3.041  | 2.809  | 2.797  |
|        |     | CO1 + 5       | 3.169   | 1.765  | 1.283  | 0.789  | 0.296  | 0.279  |
|        |     | CO1 + 10      | 0.432   | 0.358  | 0.326  | 0.286  | 0.218  | 0.212  |
|        |     | CO1 + 15      | 3.274   | 1.901  | 1.422  | 0.921  | 0.402  | 0.382  |
| 2      | CO2 | CO2 + 0       | 38.174  | 18.061 | 11.802 | 5.919  | 1.110  | 0.997  |
|        |     | CO2 + 5       | 5.209   | 4.416  | 4.033  | 3.492  | 2.245  | 2.086  |
|        |     | CO2 + 10      | 5.195   | 4.315  | 3.910  | 3.363  | 2.258  | 2.139  |
|        |     | CO2 + 15      | 4.729   | 2.976  | 2.285  | 1.478  | 0.373  | 0.306  |
| 3      | CO3 | CO3 + 0       | 3.755   | 2.554  | 2.097  | 1.581  | 0.932  | 0.898  |
|        |     | CO3 + 5       | 6.377   | 3.996  | 3.144  | 2.236  | 1.240  | 1.199  |
|        |     | CO3 + 10      | 4.752   | 2.154  | 1.390  | 0.706  | 0.206  | 0.197  |
|        |     | CO3 + 15      | 5.753   | 3.374  | 2.590  | 1.815  | 1.102  | 1.081  |
the minimum % of SKO required for maintaining the LCO nature of the CO is very important as it reduces the consequences of viscous flow through the pipeline. (b) Paraffin deposition is the main problem of the CO pipeline transportation system and so to alleviate this problem, SKO treatment was done with the CO samples. The maximum % of SKO for the treatment of CO samples were determined as 11.19%, 10.99%, and 0.6% for CO1, CO2 and CO3, respectively, beyond which they converted into paraffinic nature. Therefore, VGC helps to determine the limitation of using SKO for conditioning the CO samples.

(c) PP and GP were obtained high > 15.5 °C for all CO samples, except CO2 + 0, which was < 15.5 °C. So, it cannot be accomplished that heavier CO will always have high PP and GP. In terms of PP and GP, treatment of SKO was beneficial for CO3, up to the addition of 10% of SKO at which the lowest PP and GP of the sample were observed.

d) Since the PP of almost all the CO samples were near 30 °C, so 30 °C, and 40 °C test temperatures were considered to study the rheological behavior of the CO samples, and a comparison of the results obtained from the experiments was done to identify the effects of SKO.
on CO. HBM was used to observe the flow behavior and flow behavior can be well explained with the help of the three parameters of HBM i.e. Y.S., n and k values. Higher the YS means more pumping pressure is required to start the flow. So, the treatment of SKO will reduce the YS to an extent. So, the rheological study of CO will help to evaluate the consequences of fluid flow behavior, and then significant decisions can be made for continuous transportation.

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Declarations

Conflict of interest
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