

# Analysis of the Effect of D-Limonene on the Viscosity Reduction of Heavy Crude Oils Using FTIR-ATR Spectroscopy

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In Colombia, around 70% of the crude oil produced consists of heavy and extra-heavy crude oils, which pose various challenges during production, transportation, and refining stages due to their high viscosity values. To address this issue, naphtha has been applied as a diluent; however, its use can lead to high transportation and storage costs. For this reason, this research evaluated the use of natural additives as viscosity reducers for heavy crude oils. Specifically, D-Limonene, an extract from citrus fruits was utilized in this study, given its growing interest in various sectors of the hydrocarbon industry. Additionally, four heavy crude oils were selected for the preparation of the mixtures, identified as C1, C2, C3 and C4 with API gravity values of 11.9, 14.5, 14.0 and 16.9, respectively. The four heavy crude oils showed viscosities in the range of 968 to 16020 cP (@ 25 °C). These crudes also displayed a wide variation in their SARA compositional analysis (saturates, aromatics, resins, and asphaltenes), allowing for an in-depth analysis of D-Limonene as a viscosity-reducing agent and its chemical interaction with the crude components. Viscosity tests were performed at three different temperatures: 25°C, 45°C, and 60°C. Mixtures of each crude with D-Limonene were prepared at concentrations of 500, 750, 1000, and 1500 µL. The results showed that crudes C1, C2, C3, and C4 exhibited viscosity reductions in the ranges of 20.6% to 26.7%, 2.5% to 11.6%, 9.1% to 16.2%, and 16.2% to 81.7%, respectively. However, for higher concentrations of D-Limonene the difference in viscosity reduction is smaller. Finally, FTIR-ATR infrared spectroscopy analysis revealed that the efficiency of D-Limonene is related to the average molecular structure of the selected crudes. Notably, crude C4 demonstrated a higher affinity with D-Limonene, likely due to its higher resin/asphaltene content and the presence of -C=C functional groups.

## 1. Introduction

The increase in world energy demand has led to the search for alternatives to traditional fossil fuels. However, replacing oil with clean energy is difficult because of its sustainability and economic viability problems. Therefore, several studies predict that oil will continue to be the main energy source in the coming decades. In the same way, unconventional oil (heavy and extra-heavy crude oils) is highly interesting due to its abundance and contribution to the energy security of producing countries (Alotaibi et al., 2018; Sorokin et al., 2023). Heavy (API gravity 21.9-10) and extra heavy (API gravity less than 10) crude oils are classified based on different physicochemical properties such as molecular weight, distillation curve, pour point, and SARA compositional analysis (Saturated, Aromatics, Resins and Asphaltenes). Nonetheless, API gravity and viscosity play an important role in production, pipeline transportation, and oil recovery processes (Mironenko et al., 2017; Mateus et al., 2024). On the other hand, unconventional oil presents significant amounts of resins and asphaltenes, which require techniques to improve their mobility. Due to the viscosity tendencies of heavy and extra-heavy

crude oils, it is necessary to use different methods to reduce their viscosity. Some of these methods include physical heating, heating with catalysts, dilution with solvents, formulation of emulsions, and addition of viscosity reducers. These methods are important to improve the physicochemical properties of crude oil and condition them in the surface and refining stages (Ke et al., 2022). Viscosity reducers modify the physicochemical properties of heavy crude oil, facilitating its transportation; this, in turn, results in a decrease in cohesion between molecules and allows the heavy crude oil to flow easily through pipelines and processing equipment, which not only simplifies operations but also reduces the costs associated with handling heavy crudes. Zhang et al. (2022) evaluated the effect of viscosity reducers and their interaction mechanism in heavy crude oil with molecular dynamics simulation. The selected heavy crude oil presents a saturate content of 18.9 % by weight, aromatics 30.8 % by weight, resins 30.3 % by weight, and asphaltenes 20 % by weight. Therefore, branched polyaromatic macromolecules and heteroatoms produce strong non-covalent bonds, where the hydrogen bond has the strongest binding capacity. Also, these interactions between macromolecules increase the viscosity of the oil. For example, applying mixtures of octadecyl acrylate:styrene:acrylic acid and octadecyl acrylate:styrene:vinyl acetate produced viscosity reductions with values of 80 and 95 %, respectively. The results established that the viscosity-reducing molecules combine with the asphaltenes, and resins molecules through strong electronegativity. The formation of the new hydrogen bonds prevents the aggregation of the asphaltenes, resins and other macromolecules, favoring their dispersion and reducing the system's viscosity.

In other studies, a heavy crude oil dilution approach was employed using toluene, naphtha, heptane, and methanol as solvents. The solvents showed a favorable effect on the viscosity reduction of heavy crude oil crude in the order toluene>heptane>naphtha. However, the effect on viscosity reduction was less significant with increasing solvent concentration. On the other hand, adding methanol to heavy crude oil generated higher viscosity in heavy crude oil due to the formation of hydrogen bonds (Dehaghani et al., 2016). In general, viscosity reducers act mainly as dispersants and asphaltene stabilizing agents. The most common are reducers of aromatic compounds such as toluene and xylene, but they have environmental disadvantages. Piedra et al. (2020) determined that using natural viscosity reducers with concentrations between 1000 to 3000 ppm reduces viscosity in a heavy crude oil of 2590 cP between 65 and 69.2 %. In the same line of research, other authors have employed D-Limonene to replace commercial solvents such as acetone, toluene, n-hexane, and chlorinated organic compounds in the treatment of heavy crude oil and oil sands (Cortez et al., 2012; Lazenby., 2014). The results showed that D-Limonene is a green, sustainable, and environmentally friendly alternative due to its low toxicity compared to traditional solvents. This research aims to evaluate the effect of D-Limonene as a viscosity reducer in four Colombian heavy crude oils. Additionally, it is intended to relate the results with the chemical nature of heavy crude oils using the FTIR-ATR spectroscopy technique.

## 2. Materials and Methods

This work was carried out in three stages: first, a literature review was conducted to select the D-limonene concentration; then, the mixing and viscosity measurement experimental tests were designed; and finally, the data were analyzed and processed. Figure 1 shows the experimental diagram.

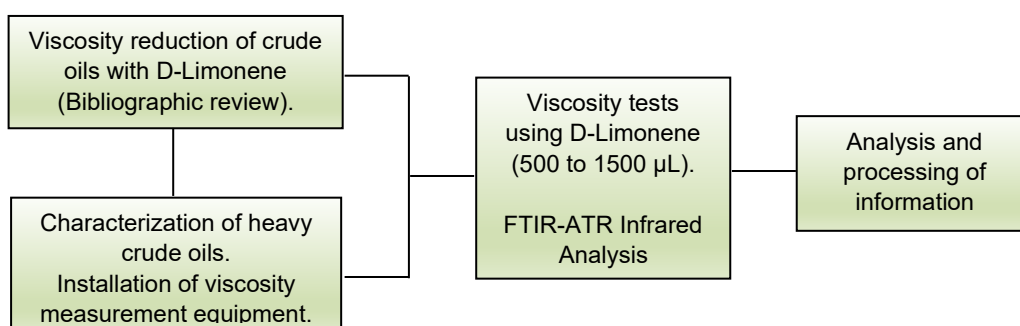


Figure 1: Experimental diagram.

### 2.3.1 Materials

Four Colombian heavy crude oils were selected with values of 11.9, 14, 14.5, and 16.9 °API, and D-limonene as a reducer. For the SARA analysis (saturated, aromatic, resins, and asphaltenes), n-heptane, methanol, and dichloromethane from the commercial company Sigma – Aldrich were used as solvents.

### 2.3.2 Analysis of viscosity reduction of heavy crude oils using D-Limonene

60 mL crude oil mixtures were prepared with 500, 750, 1000, and 1500  $\mu\text{L}$  D-Limonene doses. The crude oil/D-Limonene mixtures were prepared in a mechanical stirrer at 35 °C for 20 minutes for a uniform distribution of the D-limonene used as a reductant.

### 2.3.3 Characterization

#### 2.3.4 SARA compositional analysis

Asphaltenes and maltenes (saturates, aromatics, and resins) were separated according to ASTM D6560 and ASTM D2007. Asphaltenes were separated from each crude by adding n-heptane, using a volume ratio of 40:1. The mixture was refluxed for 1 h. It was then allowed to stand at room temperature for 24 h. After refluxing, asphaltenes were separated by filtration (Whatman #42 filter paper), and n-heptane was recovered. The saturates, aromatics and resins fractions were separated by elution with n-heptane, dichloromethane, and a dichloromethane/methanol solution using two glass columns (46 cm long  $\times$  1.25 cm inside diameter per column), which contain silica gel, alumina, and Florisil. Small amounts of glass wool were placed at the bottom of the columns to retain the absorbent materials (León et al., 2024).

#### 2.3.5 Viscosity analysis

The viscosities of the heavy crude oils and their blends with D-limonene were measured at 25, 35, and 60 °C temperatures using a FIRST PRO-PLUS® rotational viscometer (Lamy Rheology®, France). During the tests, a circulation jacket connected to a VWR AD07R-20-V12E® thermal bath (VWR International, USA) was used for temperature control. A water and propylene glycol mixture in a 3:1 volumetric ratio was used as the coolant.

#### 2.3.6 Acquisition of FTIR-ATR infrared spectra

Infrared spectra of heavy crude oil samples and D-Limonene were acquired on a Nicolet™ Summit™ FTIR Spectrometer (Thermo Scientific) in the 400 - 4000  $\text{cm}^{-1}$  region at 32 scans. Spectral data were acquired using OMNIC PARADIGM software.

## 3. Results and discussion

Table 1 shows the physicochemical properties of the four selected heavy crude oils.

Table 1. Physicochemical properties of Colombian heavy crude oils.

Property	Crude oil C1	Crude oil C2	Crude oil C3	Crude oil C4
°API Gravity	11.9	14.5	14	16.9
Saturates, % by weight	43.2	47.8	31.2	43.3
Aromatics, % by weight	20.1	17.2	21.5	23.1
Resins, % by weight	30.4	20.5	30.1	30.9
Asphaltenes, % by weight	6.3	14.5	17.2	2.7
viscosity cP, (@ 25 °C)	968 $\pm$ 5.6	2207 $\pm$ 12.5	4063 $\pm$ 19.3	16020 $\pm$ 20.7

The results show that the selected crude oils correspond to heavy crude oils (10 to 22.3 °API). Additionally, the viscosity values and the SARA compositional analysis indicate that the crude oils present a significant variation in their composition and physicochemical properties.

Figures 2a – 2d show the viscosity curves of the four heavy crude oils and their mixtures with D-Limonene. The graphs show a variation in viscosity reduction for the four heavy crude oils. The trend of the results allows us to show that the use of D-Limonene is an alternative for improving the properties. The results indicate that adding D-Limonene influences the decrease in the viscosity of heavy crude oils in the order C4 > C1 > C3 > C2. The above allows to clarify that the effect of D-Limonene has a close tendency with the relationship between the resin/asphaltene content where the C1, C2, C3 and C4 crudes present values of 4.83, 1.41, 1.75 and 11.4, respectively. Additionally, it can be indicated that the effect of D-Limonene on viscosity reduction depends on the composition of heavy crude oil. The viscosity curves show that temperature and D-Limonene characteristics are two interactive factors. These results are consistent with the work reported by other researchers (Dehaghani et al., 2016, Perez et al., 2019).

Figure 2e shows the viscosity reduction (measured at 25 °C) of heavy crude oils with D-Limonene compared to the initial heavy crude oils. The results confirm that D-Limonene allows significant viscosity reductions for C1 and C4 heavy crude oils. Meanwhile, the effect of D-Limonene is similar for C2 and C3 heavy crude oils.

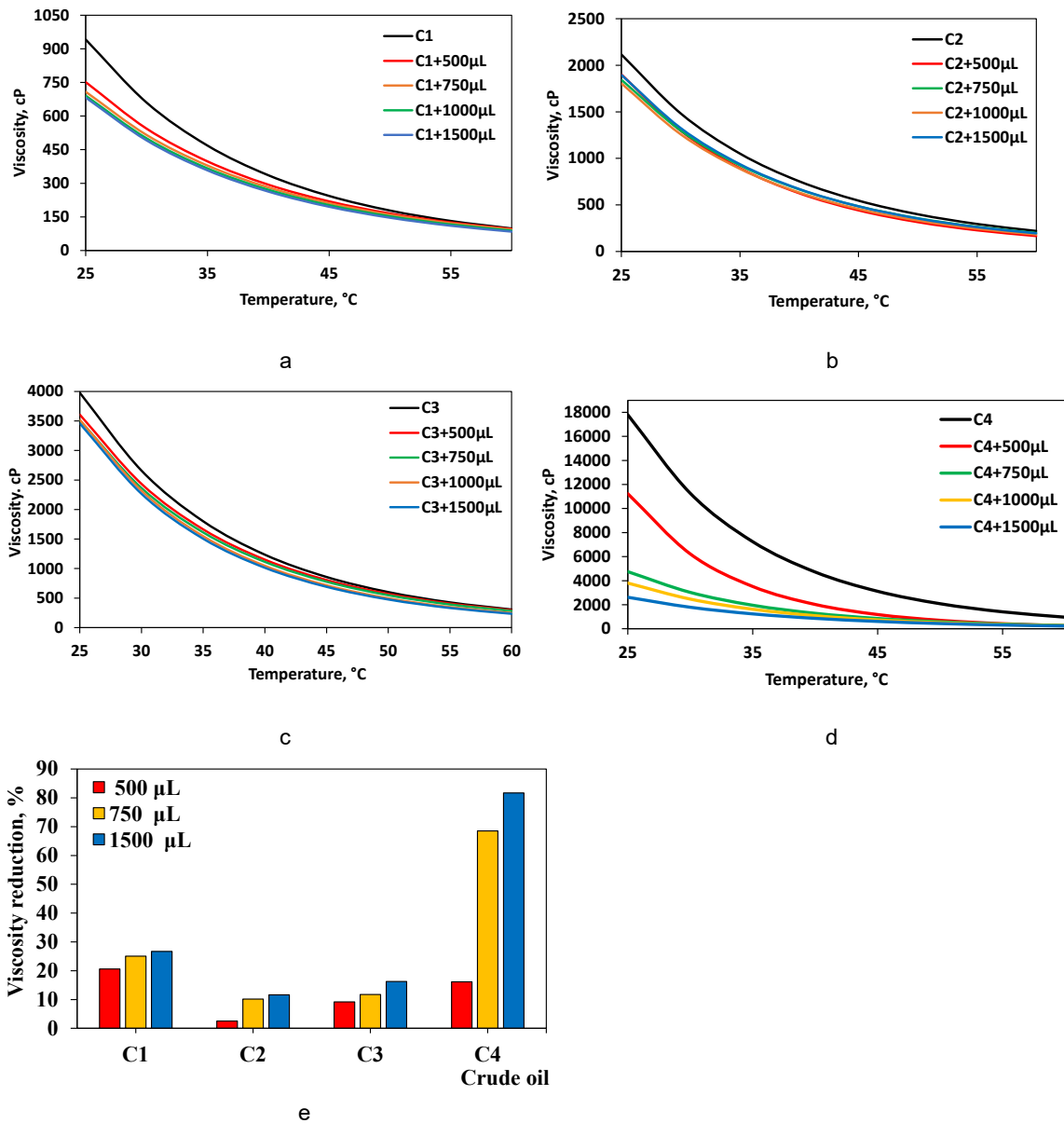


Figure 2: Viscosity of heavy crude oils with D-Limonene: a-Crude oil 1 (C1), b-Crude oil (C2), c-Crude oil 3 (C3), d-Crude oil 4 (C4), and e- Viscosity reduction (@ 25 °C).

To complement the viscosity analyses, in this work the effect of the concentration of D-Limonene and heavy crude oil on the viscosity of the final mixture was correlated using the Lederer model (Sheng et al., 2015) represented by equation 1.

$$\log \mu_m = \left(1 - \frac{\alpha v_o}{\alpha v_o + v_s}\right) \log \mu_s + \left(\frac{\alpha v_o}{\alpha v_o + v_s}\right) \log \mu_o \quad (1)$$

Where  $V_o$  and  $V_s$  correspond to the volumes of crude oil and D-Limonene in ml. The parameters  $\mu_o$ ,  $\mu_s$  and  $\mu_m$  represent the viscosities of heavy oil, D-Limonene and the mixture. The parameter  $\alpha$  for crude oils C1, C2, C3, and C4 in the presence of D-Limonene (500 to 1500 µL) presented values in the range of 0.24 to 0.49, 0.58 to 1.68, 0.68 to 1.42 and 0.17 to 0.1, respectively. Other investigations determined that the parameter  $\alpha$  takes values greater than 0 for organic solvents such as toluene, naphtha, heptane, and methanol at room (Dehaghani et al., 2016). Therefore, the parameter  $\alpha$  depends on the interaction of the reductant and the crude oil. This work determined that the parameter  $\alpha$  changes with the temperature and nature of the heavy crude oil.

Figure 3 shows the infrared spectra (FTIR-ATR) for heavy crude oils and D-Limonene. The spectra shows that heavy crude oils vary around the wavelength of  $1600\text{ cm}^{-1}$ , mainly attributed to C=C bonds of aromatic rings. This characteristic is more intense for C2, C3, and C4 crude oils, possibly due to the high content of resins and asphaltenes. In the region between  $2800$  and  $3000\text{ cm}^{-1}$ , it is observed that heavy crude oils present a variation in their symmetric and asymmetric stretching intensities. These intensities are associated with alkyl structures with -CH, -CH<sub>2</sub> and -CH<sub>3</sub> bonds. Additionally, significant differences are observed in the intensities around  $1710\text{ cm}^{-1}$ , possibly corresponding to the carbonyl group C=O bond. This functional group may be attributed to esters, acids or ketones, among others.

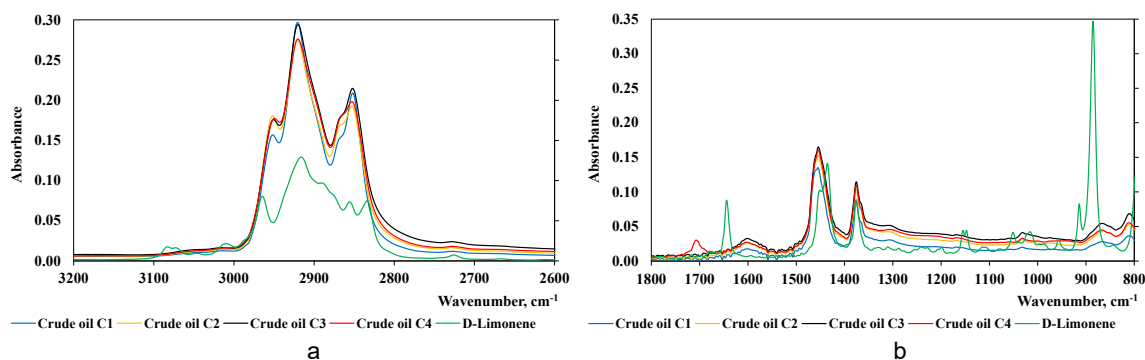


Figure 3: FTIR-ATR infrared spectra for crude oils and D-Limonene: a- $3200$ - $2600\text{ cm}^{-1}$ , and b- $3200$ - $2600\text{ cm}^{-1}$ .

The infrared spectrum of D-Limonene is similar to the spectrum reported in the literature (Derdar et al., 2019). The intensities around  $800 - 880\text{ cm}^{-1}$  correspond to groups with terminal double bond  $=\text{CH}_2$ . The peaks around  $1375 - 1250\text{ cm}^{-1}$  are associated with the C=C double bonds of limonene. The presence of a characteristic band corresponding to the double bond stretching band at  $1643\text{ cm}^{-1}$  and an intense band at  $2920\text{ cm}^{-1}$  corresponding to the methylene bond -CH is also shown. The results of FTIR-ATR infrared spectroscopy indicate that heavy crude oils present a certain degree of aromaticity due to the presence of aromatics, resins and asphaltenes. Furthermore, in terms of chemical composition, it can be said that the affinity of D-Limonene varies with the distribution of aromatic and aliphatic species present in crude oils. In general, it can be said that D-Limonene is soluble in heavy crude oil due to its chemical structure, and at the same time it offers stability of macromolecules dispersed in crude oil samples. In conclusion, the results of this research show that D-Limonene can be applied as a potential viscosity reducer in heavy crude oils. In turn, its affinity depends on the chemical nature of the crude oil species and its synergy with temperature.

#### 4 Conclusions

The results of this research demonstrated that D-limonene can be used as a viscosity reducer in heavy crude oils. The affinity of the mixture depends on the D-limonene concentration and the physicochemical properties of the heavy crude oil. The viscosity reduction for heavy crude oils C4, C1, C3, and C2 ranged from 16.2 to 81.7%, 20.6 to 26.7%, 2.5 to 11.6%, and 9.1 to 16.2%, respectively. The varying viscosity reduction behavior is possibly due to D-limonene acting as a viscosity reducer for heavy crude oils C1 and C4, and as a solvent for heavy crude oils C2 and C3. FTIR-ATR infrared spectroscopy analysis revealed that D-limonene has some functional groups that are similar to heavy crude oils. C4 crude oil exhibits a greater affinity for D-Limonene, possibly due to its high resin/asphaltene ratio and the presence of C=O groups. Finally, it can be indicated that D-Limonene is a potential candidate for viscosity reduction.

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