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EFFECT OF A VISCOSITY BIO-REDUCER IN CRUDE OIL PERFORMANCE BY NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY.

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ABSTRACT
Heavy and extra-heavy crude production is increasing in Mexico, and this fact entails to deal with several issues especially due to transport. Some physical processes have been employed to reduce crude viscosity and friction drag in pipelines to achieve flow enhancement, and chemical products are also applied for this purpose. Even though several physicochemical processes are involved, the real intermolecular effects are barely known. In this work, Nuclear Magnetic Resonance Spectroscopy (NMR) was used to evaluate compositional changes of extra-heavy crude oil in which certain amount of a viscosity reducer was added. Adding 5% of the product, 66% viscosity reduction was obtained at 25 °C and the NMR spectra of this sample showed overlapping signals at 0.5 and 3.5 ppm, typical of crude oil, as well as a singlet at 3.6 ppm and a multiple signal at 5.34 ppm, which was different for the sample not dosed; this behavior is associated to the presence of the viscosity reducer in the mixture. Also, it was corroborated that the dosed product aggregates to the medium fraction of the crude without phase separation.

INTRODUCTION
Petroleum is constituted by a complex mixture of hydrocarbons that, in accordance with their functional group, are classified as saturated, aromatics, resins, and asphaltenes [1]. Experimentally, high viscosity crudes (with values between 10^3 and 10^6 cP and less than 10 °API for extra-heavy crude oil) present a considerable fraction of asphaltenes and paraffins whose tend to form aggregated and precipitations, produce transport problems. For this reason, some physicochemical procedures have been proposed [2,3] to deal with this problem. There are two basic process: the first one consists in increasing temperature of the crude [4], which causes a decrease of viscosity. The second one is based on addition of chemical products (viscosity reducers or flow enhancers) that interact with asphaltenes and the fraction that forms aggregated is decreased [5].

On July of 2017 (Fig. 1), crude production in Mexico, totaling the contributions of territorial and off-shore fields, reached 1988 KBPD of which 52% correspond to heavy and extra-heavy crudes [6]. According to prospective on national probable reserves [7], it is expected that the heavy and extra-heavy crude oil production for 2030 will diminish (Fig. 2), but this scenario could be modified considering that recent exploration of deep waters has showed that the crude in these zones is mostly of heavy kind [7].

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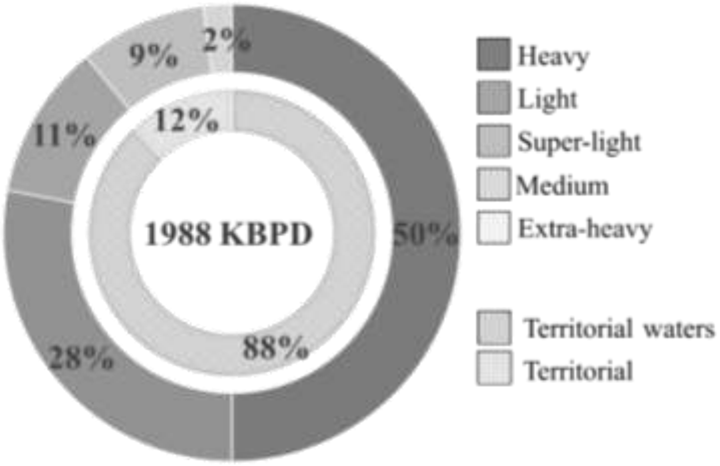

Figure 1. Crude oil Production in Mexico by type of crude (July 2017) [6].

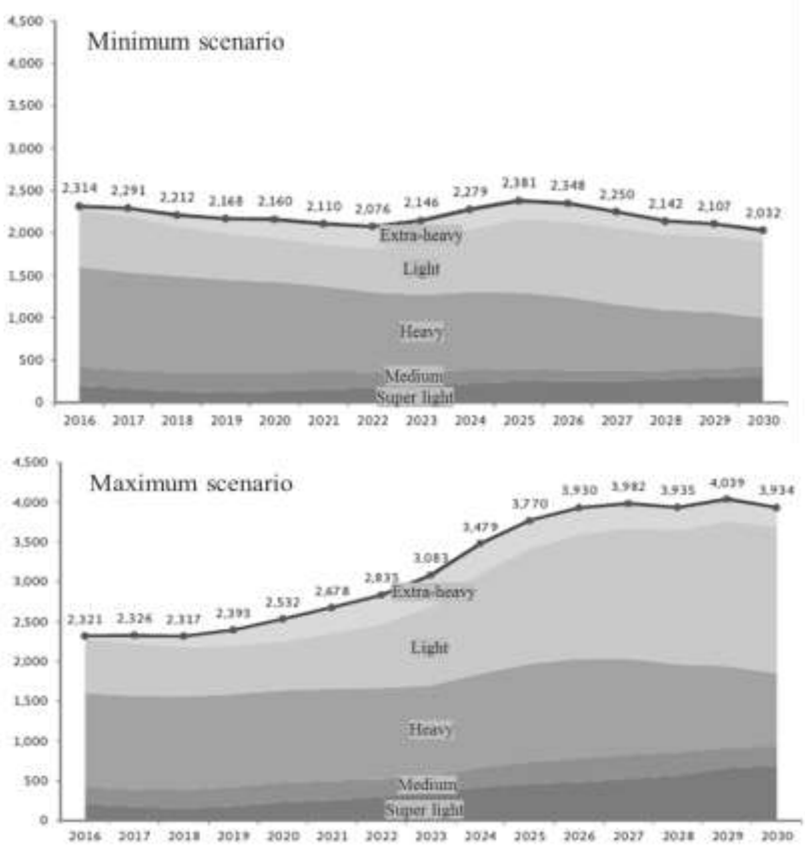

Figure 2. Prospective on crude production by type in KBPD, at minimum and maximum scenario [7].

Nuclear Magnetic Resonance spectroscopy (NMR) is an analytical method employed in the study of molecules structure analysis in a wide variety of research areas, being a tool that allows to work with solids and liquids. Almost all the atomic nuclei possess a property called nuclear spin and if submitted to the influence of an external magnetic field with a specific intensity, suffer the resonance effect (inversion of the nuclei orientation). The instrument registers information about the interaction of the nuclei and the magnetic field resulting in a spectrum that represents the defined frequency absorption of the molecules by narrow peaks [8-10].

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NMR technique has been used to characterize organic and inorganic materials, from proteins to polymers [11]. For ninety years, this method has proved to be a useful tool for petroleum and gas industry in well evaluation. First applications focused on porosity and permeability properties of sediments [12,13]. Further, the application extended to petroleum, gas and brine typification, as well as the determination of saturation degree of the compounds of the crude [14].

Advances in structural characterization by NMR of crude constituents and contaminants has become more important every time because of the direct relation of the content of this compounds to the physicochemical properties of oil, mainly viscosity and, as mentioned above, such properties reflect their effects on cost-benefit production [15].

Hence, the use of formulations and chemical products that act as viscosity reducers is increasing constantly because of the growing production of heavy and extra-heavy crude oil in fields. These kind of materials, are widely used to enhance the flow in pipes, making transportation easier. However, it is important to verify that the integrity of crude is not compromised. Hence, this work discusses the effect of crude viscosity diminution by addition of a viscosity bio-reducer, also measuring the implication of temperature rise.

MATERIALS AND METHODS

For this study, a duplicated sample from a well located at northern Veracruz in Mexico was considered. Both samples were mixed to get one, achieving homogenization by mechanic stirring (1 h). The final mix was divided into two equal parts that were identified as samples A and B. The first one is representative of original crude (100%) and the second was added with the chemical formulation of the reducer at 0.5, 1 and 5% v/v. Sample B was also treated with mechanical stirring for homogenization (1 h). The viscosity bio-reducer (BRV®) used in this work, is essentially an organic formulation of esters and is a product manufactured by Geo Estratos SA de CV and which has been considered as part of a research project of the Mexican Council of Science and Technology (CONACYT, Project number: 166923)

Viscosity determinations were performed with a parallel plates Brookfield viscometer. Part of the characterization of the samples involved the analysis of the light, medium and heavy fractions to detect possible differences in the composition of the crude constituents by effect of the presence of the viscosity reducer. These determinations were performed under current Mexican legislation (NMX-AA-134-SCFI-2006, NMX-AA-141-SCFI-2007, NMX-AA-105-SCFI-2008 and NMX-AA-145-SCFI-2008).

Spectroscopy analysis were performed with a NMR spectrometer Bruker Avance III, at 400 MHz frequency. Deuterated chloroform ($CDCl_3$) was used as solvent and tetramethylsilane (TMS) as internal reference materials. Chemical changes are presented in parts per million units (ppm) in δ scale.

RESULTS AND DISCUSSION

For each dosage case (0.5, 1.0 and 5.0%), it was observed the same behavior with similar results. However, for the 5% dosage, a better NMR resolution was obtained, and therefore (in obvious of space), just the results of such experiment are reported. Table 1 shows the viscosity measurements in a range of temperatures from 25 to 90 °C with increments of 5 °C. Effect of the addition of the viscosity reducer is clearly evident at the lowest temperature, reaching a viscosity reduction of 66% and an increase of 16% of API. This means that the interaction between the asphaltenes and the molecules of the bio-reducer is efficient.

Polar affinity between molecules could explain this behavior because, theoretically, the viscosity reducer should avoid asphaltene precipitation. Nevertheless, this process should not be reflected in viscosity reduction but in remaining with a constant value, so it seems that such interactions have also a redispersion effect of the heavy compounds that are already precipitated or agglomerated. This behavior turns more relevant for heavy and extra-heavy crude oil production because it allows petroleum industry to avoid or significantly reduce thermal treatment in the process, accomplishing a substantial reduction of operational costs [16].

Table 1. Experimental viscosity and °API results of samples without (A) and with (B) bio-reducer added.

Temperature (°C)	Viscosity (cP)		Reduction (%)	°API		Enhancement (%)
	A	B		A	B	
25	372.000	125.000	66,40	6,80	8,10	16,05
30	298.000	99.872	66,49	7,20	8,30	13,25
35	165.000	76.480	53,65	8,00	8,50	5,88
40	98.341	49.256	49,91	8,30	9,20	9,78
45	58.410	31.418	46,21	9,00	9,60	6,25
50	32.708	19.261	41,11	9,60	9,80	2,04
55	14.171	8.473	40,21	10,00	10,20	1,96
60	10.351	4.517	56,36	10,20	11,60	12,07
65	7.168	3.116	56,53	10,70	12,20	12,30
70	3.642	2.024	44,43	12,10	13,40	9,70
75	2.598	1.520	41,49	12,50	13,70	8,76
80	1.742	1.145	34,27	12,80	13,90	7,91
85	1.336	810	39,37	13,00	14,10	7,80
90	1.142	672	41,16	13,20	14,30	7,69

Compositional analysis results are shown in Table 2. It can be observed a slight diminution in the concentration profile of the constituents of the sample containing the bio-reducer (B) that is proportional to the increase of the compounds between C11 and C22, which clearly indicates the presence of the chemical product. In all dosage cases, there was an increment of medium fraction.

Table 2. Analyses results of light, medium and heavy fractions of the crudes without (A) and with (B) bio-reducer added.

Constitute	% weight	
	A	B
C6	0,7453	0,7080
Mcycle-C6	0,5674	0,5390
Benzene	0,6845	0,6503
cycle-C6	0,7231	0,6869
C7	0,4737	0,4500
Mcycle-C6	0,5324	0,5058
Toluene	0,5124	0,4868
C8	0,4218	0,4007
C2-benzene	0,8436	0,8014
m,p-xylene	0,6243	0,5931
o-xylene	0,4536	0,4309
C9	0,7435	0,7063
C10	1,2435	1,1813
C11	1,9657	2,2311

C12	1,9745	2,2394
C13	1,4535	1,7445
C14	1,8234	2,0959
C15	1,8452	2,1166
C16	1,6435	1,9250
C17	1,4525	1,7435
C18	1,6747	1,9546
C19	1,3325	1,6295
C20	1,4239	1,7163
C21	1,2120	2,1514
C22	1,4524	1,7434
C23	1,3398	1,2728
C24	1,2125	1,1519
C25	1,6623	1,5792
C26	1,1231	1,0669
C27	1,4122	1,3416
C28	1,2345	1,1728
C29	1,2388	1,1769
C30+	62,9539	59,8062
TOTAL	100	100

Based on the results above, the effect of the viscosity reducer on the crude viscosity diminution can be established. When the addition of a flow enhancer or viscosity reducer in the production of crude oil is unknown, it is possible to apply NMR spectroscopy to prove the addition of chemicals. In the spectrum of each sample (figure 3), it was found the presence of low defined aromatic compounds signals in the range between 6.5 and 8.5 ppm and some overlapping signals between 0.5 and 3.5 ppm. The general aspect of the spectra matches with the one expected for a crude [17-20]. In NMR analysis, the crude sample containing 5% of BRV, presented an additional singlet at 3.66 ppm and a multiple signal at 5.34 ppm that indicate the presence of a compound uncommon to the crude. Such signals are related to methyl groups linked to an oxygen atom, most probably to be ester and methylic ether type, corresponding to the bio-reducer composition and are in accordance with some NMR studies reported for the same kind of material [21-25]. In relation with the fractional composition analysis of crude, the increase on the content profile of compounds containing C11 to C22, confirm the presence of the biodiesel based reducer, and can be detected by NMR.

To complete the analysis of crude, the integration of the different zones of the NMR spectra according to Fergoug and Bouhadda [26] was made. For an 1H-NMR spectrum, chemical changes due to aromatic compounds should be solved between 6.5 and 9.5 ppm, that is different from the aliphatic type that are commonly solved between 0.5 and 4.5 ppm. These aliphatic peaks are subdivided in three types of protons: α, β and γ, depending on their position referent to aromatic core. It has been suggested [27,28] that α protons produce signals between 0.5 and 1 ppm, β protons in the range from 1 to 1.85 ppm, while γ protons appear between 1.85 and 4.5 ppm (Table 3). Taking as a reference this classification, it was calculated the relative percentage of each type of proton in samples A and B (Table 4), and these results are in accordance with NMR spectrum in which the domain of aliphatic compounds is observed. Such a behavior was the same for all dosage cases, finding modifications only in concentration directly proportional to quantity dosage. Heteroatoms or presence of metals that could affect chemical changes were not considered.

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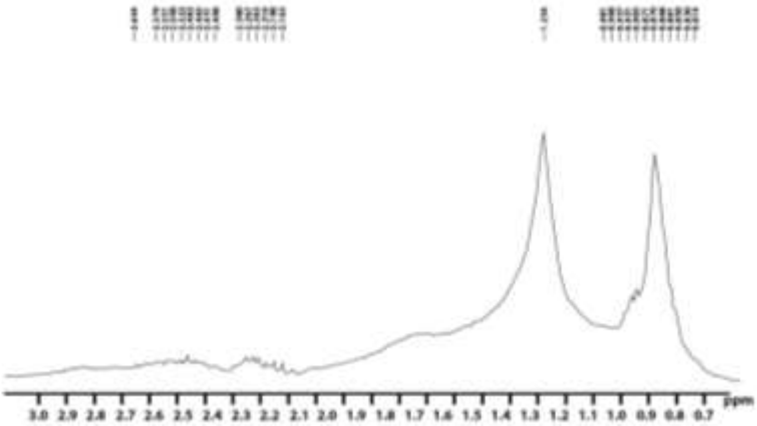
Table 3. Proton classification for hydrocarbons mixtures related to aromatic signals [26].

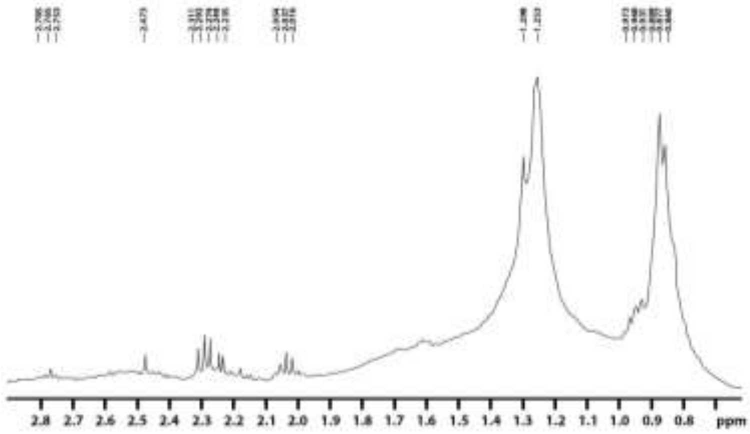
Range (ppm)	Descriptor	Classification
6.50-9.50	H_{ar}	Aromatic protons
1.85-4.50	H_{γ}	Protons linked to a saturated carbon in γ position
1.00-1.85	H_{β}	Protons linked to a saturated carbon in β position
0.50-1.00	H_{α}	Protons linked to a saturated carbon in α position

Table 4. Relative percentage of different protons in crude samples without (A) and with (B) reducer added.

Proton	A		B	
	Relative integration	% relative	Relative integration	% relative
H_{ar}	1,00	7,16	12,59	5,37
H_{γ}	2,23	15,97	40,54	17,29
H_{β}	7,55	54,08	127,23	54,26
H_{α}	3,18	22,78	54,01	23,04
Total	13,96	99,99	234,44	99,96



(A)



(B)

Figure 3. Representative 1H-NMR spectrum of samples without (A) and with (B) reducer dosage.

CONCLUSIONS

- A substantial viscosity reduction and increment of °API were obtained in the crude samples analyzed, by the effect of the addition of a viscosity bio-reducer and raise of temperature in the crude.
- The addition of the product that acts as a flow enhancer, caused a linear increase of the medium fraction

of crude, so it can be established that the product (BRV) incorporates to the crude without phase separation.

- 1H-RMN spectra of samples, indicated a mixture of hydrocarbons with a low percentage of aromatic protons. Signals suggest the presence of methyl group linked to oxygen atoms due to the chemical changes of ester and methylic ether compounds.
- NMR technique is useful to identify mixtures of chemical products and hydrocarbons, and allows to reveal if the crude goes under chemical treatment to enhance flow and the type of product employed.

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