Section: # Heavy oil

SPE WVPS

Bioreducer effect in heavy and extraheavy oil crudes.

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Abstract

Oil crude viscosity reduction is a very important issue for the oil industry, as it is considered the main feature regarding both, oil extraction and pipeline transportation. This reduction is directly linked to the design of less or smaller equipment and therefore to substantial savings in energy consumption. Oil viscosity together with other rheological properties, also plays an important role in reservoir simulation and calculation of the hydrocarbon structure in the solid matrix. Viscosity may vary due to changes in temperature and pressure and it depends on the origin, type and nature of crude chemical composition, particularly concerning polar compounds.

In this work the effects of three chemical products in heavy and extra heavy oil crudes are analyzed, and the results of several parameters are presented showing Newtonian deviation, °API growth, and changes in boiling point ranges among others. From these results it was possible to establish different asphaltenes or waxes interaction depending on oil crude types. It was also found an effect on oil-in-water dispersion usable in oil spills when the viscosity reducer is biodegradable.

1.0 Introduction

Asphaltenes are high molecular weight molecules found in crude oil. Their structure may contain from 4 to 20 benzene rings, which are linked together via alkyl chains, cycloalkanes, and heterocyclic compounds containing sulfur, nitrogen and oxygen [1, 2].

Because of being polar molecules, they tend to attract each other in an apolar medium as aggregates that in the presence of resins are stabilized by forming a colloidal suspension in crude oil. The increase in volume of the dispersed phase contributes to the increase in viscosity, affecting pumping costs. Moreover, this colloidal suspension can become unstable due to electro kinetic effects when crude oil flowed, causing the precipitation of asphaltenes in pipelines. Also due to its polar nature, asphaltenes increase the rate of droplet coalescence of crude dispersed in water systems that forms during oil spills at sea, decreasing the efficiency of biological treatments used for decontamination [3, 4, 5, 6].

The Viscosity Bioreducer (BRV) is a commercial product composed by fatty acid esters of low molecular weight hydrocarbons, used as a viscosity reducer and as a dispersing agent in the oil [7]. The present work aims to study the physical and chemical mechanisms that cause the effect of this compound on the properties of the crude oil. It has been structured as follows: in section 2 we theoretically study the effect of BRV on intermolecular distances corresponding to the paraffins and asphaltenes by using the tools of computational chemistry. Section 3 shows the experimental results that have been obtained in relation with the BRV influence on precipitation of asphaltenes in the presence of n-heptane; section 4 presents the results obtained by examining the effectiveness of BRV as dispersants of crude oil systems in water by applying a technique based on morphological characterization of the interface through the fractal dimension. Section 5 discusses the effect of BRV on viscosity and non-Newtonian behavior of the oil and reducing its effectiveness as losses of friction in pipes for both monophasic and biphasic flow. Conclusions are presented consequently after section 5.

Theoretical prediction of the BRV's effect over intermolecular interactions in asphaltenes and waxes

It has been reported [8, 9] that polar solvents decrease the attractive interactions between asphaltene molecules, leading to a decreased volume of the dispersed phase formed by the aggregates of asphaltenes. Rupture of these aggregates has been confirmed through the use of several diffraction techniques such as small angle x-ray scattering (saxs) [8, 9]. BRV contains polar compounds in its composition; it is expected that this effect may be the primary cause of the action exerted by the product as a viscosity reducer, causing the breakdown of aggregates and decreasing the volume of the disperse phase of these in the crude oil.

Computational techniques and theoretical chemistry were used to theoretically analyze the influence of BRV into intermolecular interactions, supported by the use of the software Arguslab 4.0 with a single point energy calculation Hamiltonian QM-AM1 [10]. Figure 1 shows the molecular structures BRV, the asphaltenes and paraffins were obtained theoretically [11, 12, 13, 14].

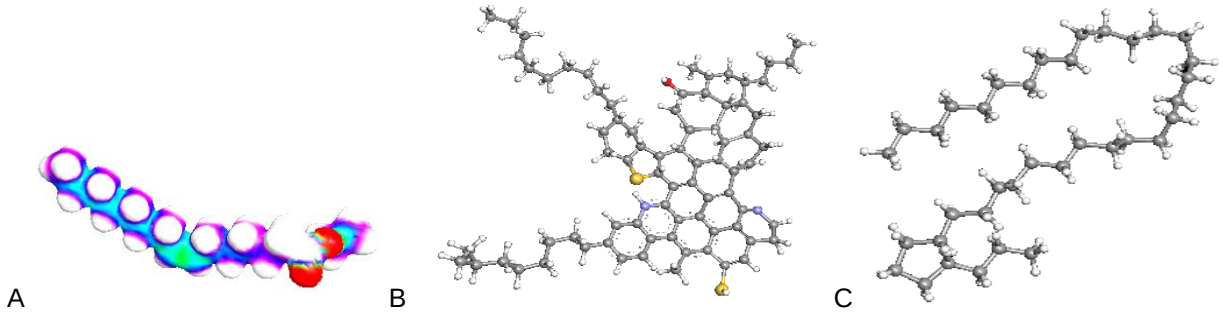


Figure 1. Simulated molecular structures: active principle of BRV polar agent, B: asphaltene, C: paraffin.

Different interactions of the active ingredient in BRV and molecules of asphaltenes and paraffins respectively, and intermolecular interactions on asphaltenes and paraffins were simulated [12, 13, 14], obtaining the structures shown in Figure 2.

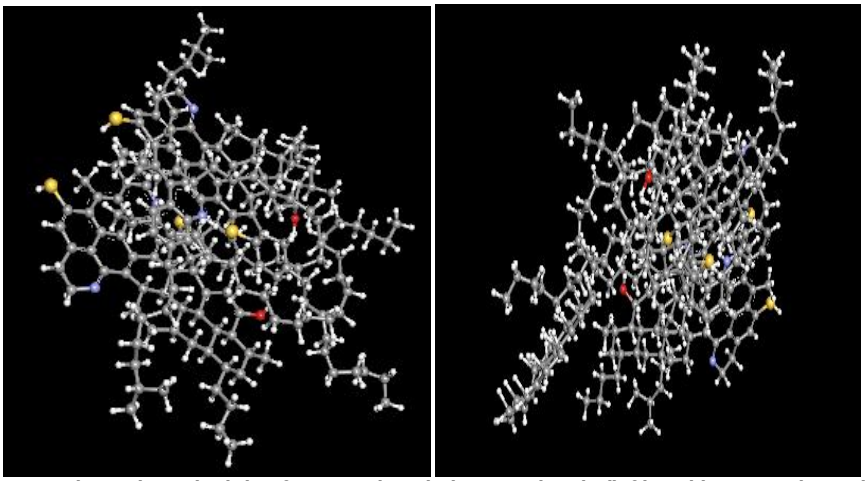


Figure 2. Interactions between the active principle of BRV and asphaltene molecule (left) and between the active principle of BRV and paraffins (right)

In this case it is predicted that the BRV significantly increases the minimum intermolecular distance between asphaltenes and paraffins, indicating a decrease in attractive interactions and, therefore, less likely for the formation of aggregates.

Table 1. Results of Molecular modeling from interactions between the BRV, asphaltenes and paraffins.

		Bond distance ($x10^{-10}$m)	Minimum intermolecular distance ($x10^{-10}$m)
Without BRV	Paraffin-Paraffin	1.5692	3.8700
	Asphaltene-Asphaltene	1.4650	3.7738
With BRV	Paraffin-Paraffin	1.5301	4.0010
	Asphaltene-Asphaltene	1.4497	3.8084

Experimental study of the influence of BRV on asphaltenes precipitation in presence of n-heptane

The asphaltenes precipitate in the presence of n-heptane, where the speed at which this process occurs is dependent on the temperature, pressure and composition of the system (1). According to the results predicted by simulations based on computational and theoretical chemistry presented in the previous section, it is expected that the presence of BRV will cause a significant decrease on the amount of asphaltene precipitates. To corroborate this experiment, a mixed composition of 1.8% asphaltenes in toluene was done, after which the solutions were prepared with n-heptane 1:1 at various percentages of BRV at 25ºC. Complex patterns formed by the precipitates were observed with a microscope Konus College # 5302, eyepiece WF 15x and 10X magnification and photographed with a camera SONY Cyber Shot DSC-W530 14.1-megapixel, Carl Zeiss lens, 4X optical zoom and 7 megapixels. The photographs obtained were converted into binary images obtaining a precipitated complex morphology, and which will determine the fractal dimension D capacity by ImageJ v1.46 [15] (see Figure 3).

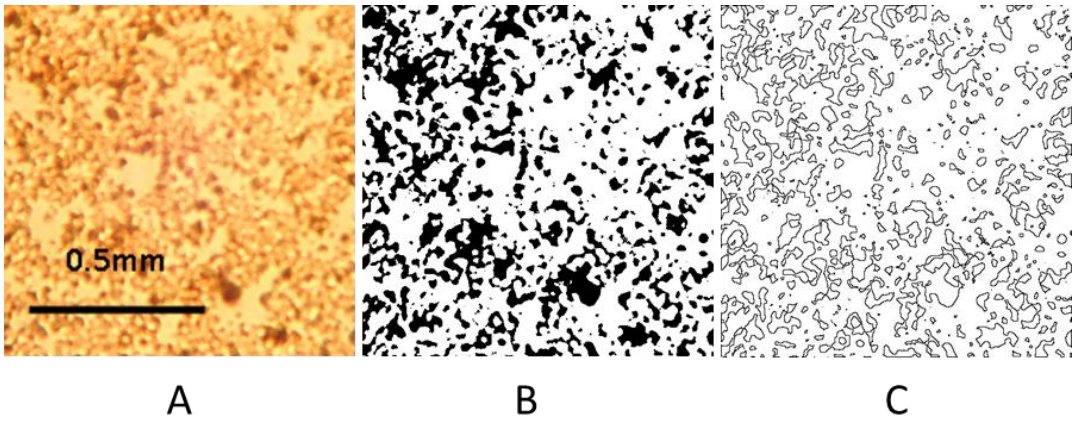


Figure 3. Pattern formed by the asphaltene precipitate, A: original photograph, B: binary image corresponding to A, C: precipitate pattern which will be determined the fractal dimension of capacity.

The fractal dimension *D* is determined using the software ImageJ v1.46 through the ratio (15:16):

$$D = \lim_{r \to 0} \frac{\ln N_0(r)}{\ln\left(1/r\right)} \tag{1}$$

Where *r* is the size of the *N* sites in which the image is divided and *N0* is the number of sites at which there is the presence of precipitates. If taken into consideration that *D* is a measure of the amount of substance Φ that is present a plane of characteristic length *L*:

$$\Phi \equiv L^D \tag{2}$$

It is expected that the value of *D* will increase with the amount of precipitates formed. Table 2 shows the behavior of the fractal dimension with respect to BRV concentration obtained experimentally. In this case it is seen that the fractal dimension decreases by increasing the BRV concentration, implying that the quantity of asphaltene precipitates decreases. This experimental result confirms the theoretical result predicted that the BRV causes a decrease in the attractive interactions between asphaltene molecules.

Table 2. Experimental fractal dimension

BRV Concentration (%)	Average Fractal Dimension
0	1.62 ± 0.05
1	1.64 ± 0.05
2	1.51 ± 0.07
3	1.42 ± 0.07
4	1.18 ± 0.20
5	1.20 ± 0.08
7	1.20 ± 0.10

BRV's influence on the dispersion of crude oil in water

Generally dispersed systems liquid-liquid are metastable, in the sense tending to a free minimum energy that corresponds to the minimum of the area of the interface. The degree of dispersion is calculated from the specific surface area, defined as the quotient between the total area of the interface and the volume of the dispersed phase. The interface area is inversely proportional to the droplet size in all systems where dispersed droplets have equal size (monodisperse systems); when the droplets are of different sizes (polydisperse systems) the degree of dispersion depends on the average radius, and the distribution of particle size.

It is possible to obtain the pattern formed by the interface 2D observed through a program appropriate image processing in systems where there is a clear distinction between the dispersed droplets and the dispersion medium, as in the case of the dispersion of crude oil in water (see Figure 4). In this case, the fractal dimension f of the line observed in 2D maintains reasonably proportional to the total area of the interface, such that an increase in the fractal dimension is an indication of increasing the degree of dispersion.

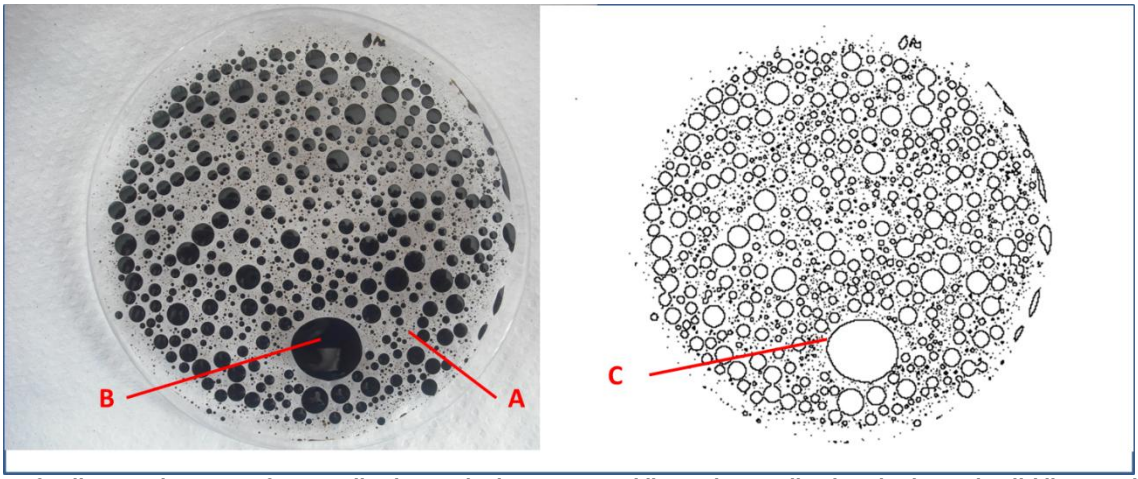


Figure 4. Images of a dispersed system of water-oil, where A is the sea water (dispersion medium) and B is crude oil (dispersed phase). C is the oil-water interface, which corresponds to the outer edge of the crude oil droplets.

This technique was used to experimentally evaluate the effectiveness of BRV as dispersant. For this study, three kinds of oil whose characteristics are shown in Table 3 were selected. Crude samples and sea water having a composition of 1.25% by weight of oil were used as control samples and samples of seawater-oil-BRV having a composition of 1.25% by weight of oil and 1.25% by weight of BRV. The samples were stirred at 700 r / min and then placed on a watch glass, which were photographed after 2 min, 5 min and 10 min with a digital camera FUJIFILM PinePix J12, 8 mega-pixel resolution. The size distribution of the droplets and the fractal dimension were determined using the ImageJ software v1.46.

Table 3. Crude oil characteristics used in scattering experiments

Sample	Viscosity cP @ 25°C	°API	% (P/P) Asphaltenes	% (P/P) Waxes

Crude #1	**6826**	**14,1**	**26,9**	**24,6**
Crude #2	**9356**	**11,1**	**33,0**	**20,0**
Crude #3	**118000**	**8,6**	**38**	**16,5**

Specific surface area was estimated from the particle size distribution determined using the ImageJ according to the ratio:

$$A_{total} = \sum_i 4\pi R_i^2 n_i \tag{3}$$

Where *ni* is the number of particles of radius *Ri* in Figure 5 shows the experimental behavior found between the estimated surface area and the fractal dimension, which shows that the positive correlation between the two variables indicating that the fractal dimension can be used to quantify the degree of dispersion of the system.

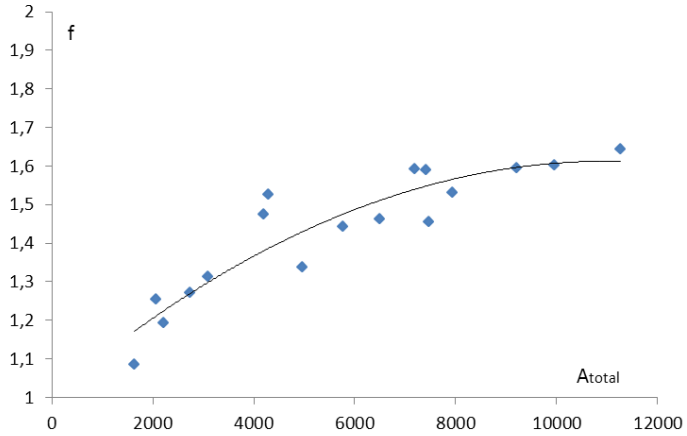
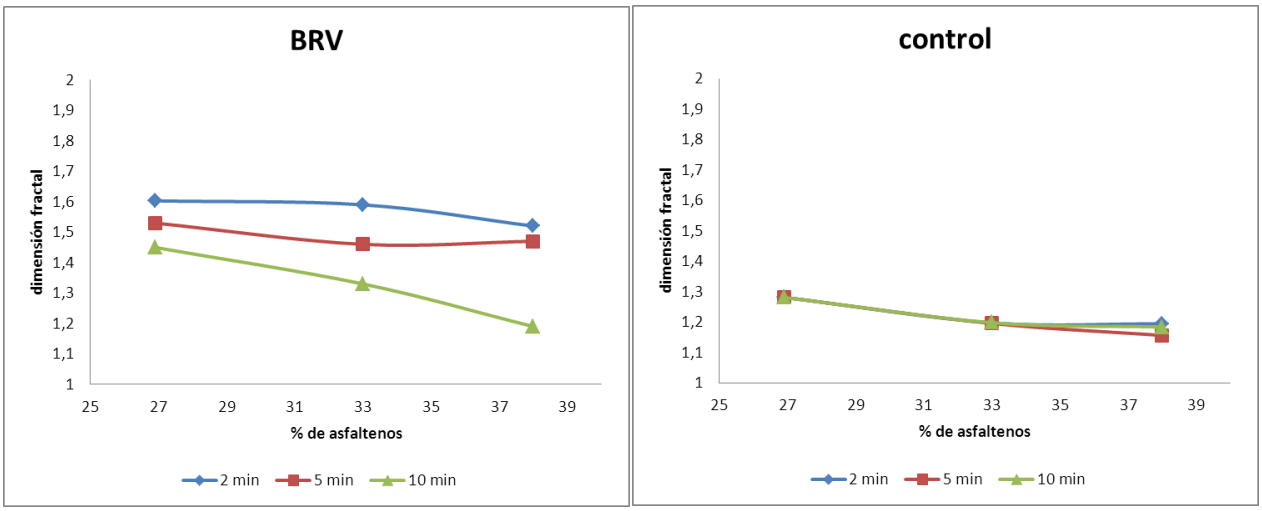


Figure 5. Experimental dependence found between the area of the interface and the fractal dimension.

Figure 6 shows the experimental behavior found between the fractal dimension and the percentage of asphaltenes present in crude at different time values for the control sample (0% of BRV) and for samples to which is added BRV.



6.a **6.b**

Figure 6. Behavior of the fractal dimension of the oil-water interface as a% of asphaltenes for different values of time. 6th: 1.5% of BRV; 6.b: 0% of BRV

As seen in Figure 6, the fractal dimension is found significantly higher in samples in which BRV was added compared with control samples, which shows the action of BRV as dispersant. Moreover, the fractal dimension decreases with the percentage of asphaltenes, which is expected if the influence of the attractive interactions between these molecules on the rate of coalescence of the crude oil

droplets is taken into account. It is observed that there is a fractal dimension change appreciably with time in the presence of the BRV, whereas the control samples were almost independent of this. The f decreased over time constitutes a representation of the evolution of the system to the minimum free energy, which corresponds to the minimum area of the interface. This result suggests that the system evolved more quickly to the lowest energy state in the case of samples with 0% BRV, so that not only BRV had a significant increase of the degree of dispersion, but also significantly increased the stability of the system, which is due to the action of its effect on the net forces of attraction between the asphaltene molecules.

BRV effect on rheological behavior of crude oil

A rheological study was conducted in two crudes, to analyze the feasibility of the use of BRV as viscosity reducer of crude oil, whose characteristics are shown in Table 4. Apparent viscosity measurements were made using a Brookfield Model DV-2. It was found that both crudes had a non-Newtonian behavior characterized through the apparent viscosity model potential given by:

$$\eta = m(\gamma)^n \tag{4}$$

Where η is the apparent viscosity (Pa.s), γ is the velocity gradient (s-1), m is consistency and n is the flow order.

Table 4. Characteristics of the crude oil.

Crude oil	A	B
ρ [kg.m3]	938.6	998
%asphaltenes	20.7	25.8
%waxes	18.1	10.9
% asphaltenes + % waxes	38.8	36.7

Table 5a. Behavior of the consistency and flow order for crude analyzed

BRV	A	B
25 C		
m [Pa.s^n]	65.478	39.176
n	0.940	0.954
R^2	0.698	0.743
60 C		
m [Pa.s^{n-1}]	2.951	1.962
n	0.990	0.980
R^2	0.654	0.934
80 C		
m [Pa.s^{n-1}]	1.108	0.445
n	0.970	1.066
R^2	0.930	0.925

Table 5b. m$\Delta P/L$ [Pa.m^{-1}] for monophasic flow and 0% de BRV

	Temperature		
Crude Oil Type	25 °C	60 °C	80 °C
A	5.649	0.210	0.069
B	3.161	0.135	0.035

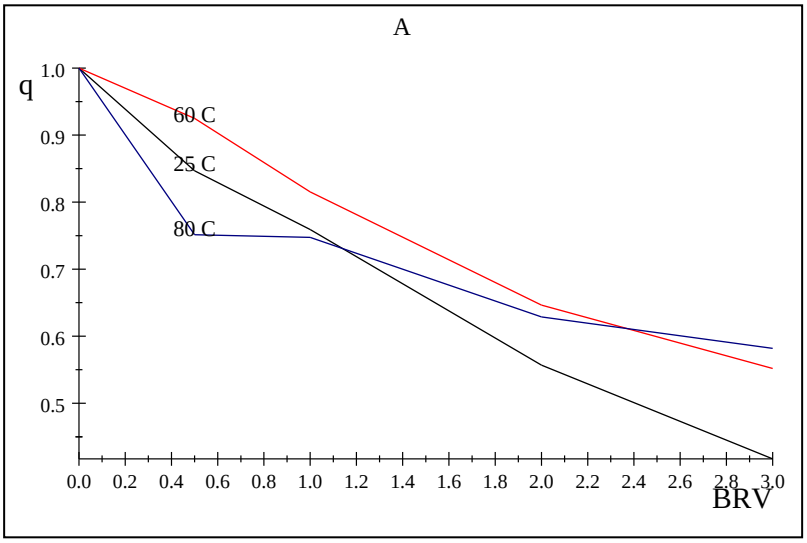
The results, shown in Table 5a and 5b, indicate that both crude oils exhibit viscoelastic behavior where the consistency decreases significantly with increasing temperature, being greater in the crude A, presenting a greater percentage of asphaltenes and paraffins. Reasonably assuming that the volume of asphaltenes found in the form of colloidal aggregates present in the oil is proportional to the amount of asphaltenes paraffins present, then it can be assumed that this increase in the volume of the dispersed phase is expressed in

the increased consistency. Moreover, viscoelastic behavior slightly observed in both crude oils (n <1), may be explained by considering that aggregates of asphaltene will be rearranged and flow more easily.

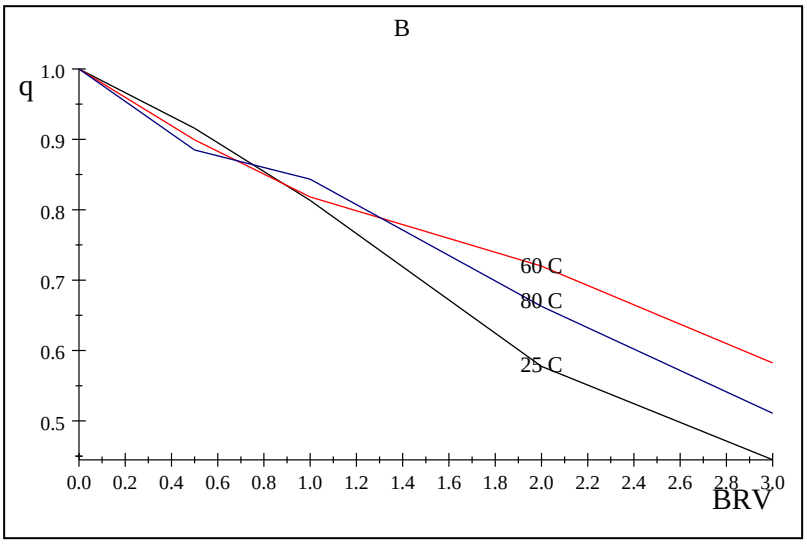
Samples with different percentages of crude oil and BRV were prepared to study the effect of this product, performing the corresponding rheological study to determine the influence of the concentration of BRV on the consistency and order flow for different temperatures. The effect of the consistency BRV was quantified using the parameter *q*, which is determined as:

$$q = \frac{m(x)}{m(0)} \tag{5}$$

Where *m(x)* is the consistency obtained for concentration *x* of BRV and *m(0)* is the consistency of crude with 0% of BRV. The results are shown in Figure 7, which shows that BRV significantly reduces the consistency to both crude oils.



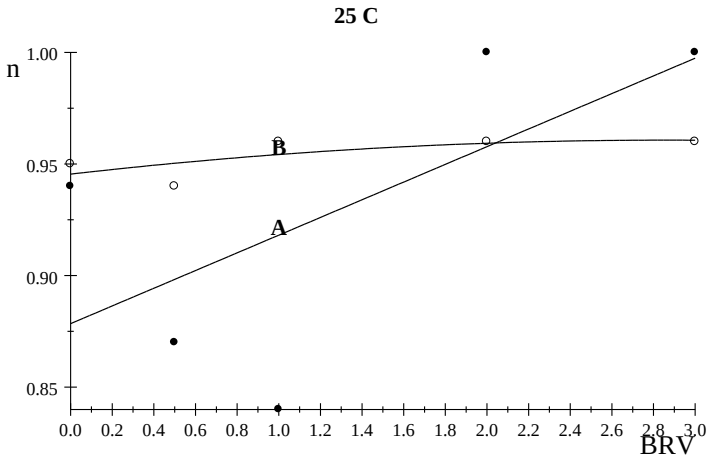
7.a



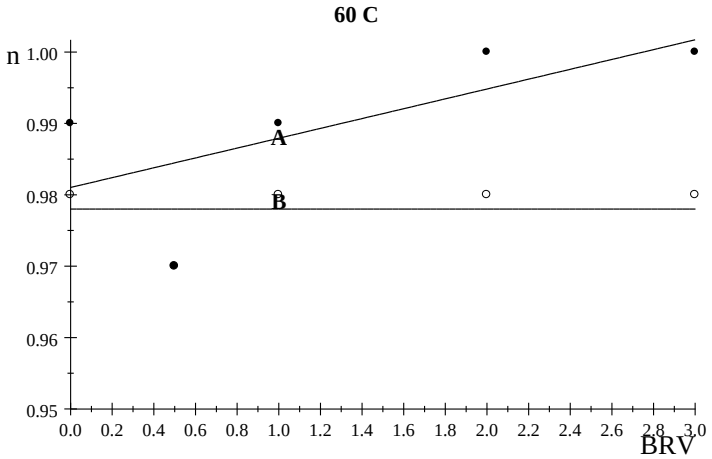
7.b

Figure 7. Influence of the concentration of BRV consistency on both crude oils. a: crude oil type A; b: crude oil type B

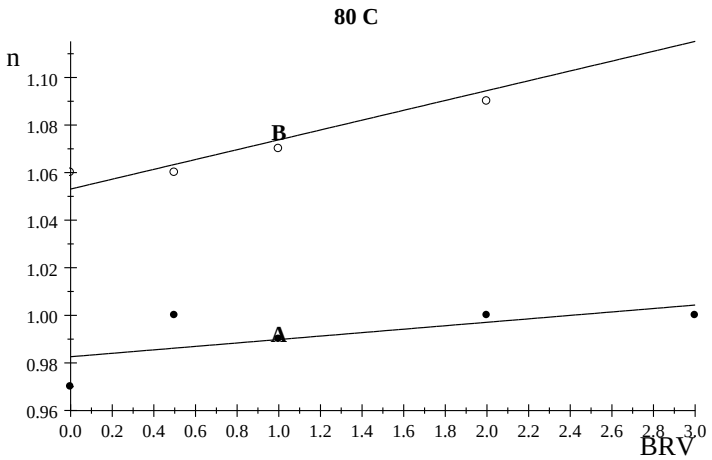
Figure 8 shows the effect of concentration of BRV on the order flow. As can be seen, we found that the flow order is increased relatively to the concentration of BRV, and the fluid may even slightly exhibit dilatant behavior, as is the case presented for crude B to 80ºC. The order flow behavior can be evidence that, by decreasing the level of aggregates of asphaltene will lose the effect of orientation of these easier flow and confers the viscoelastic behavior observed at 0% BRV.



8.a. order flow T = 25ºC



8.b. order flow T = 60ºC



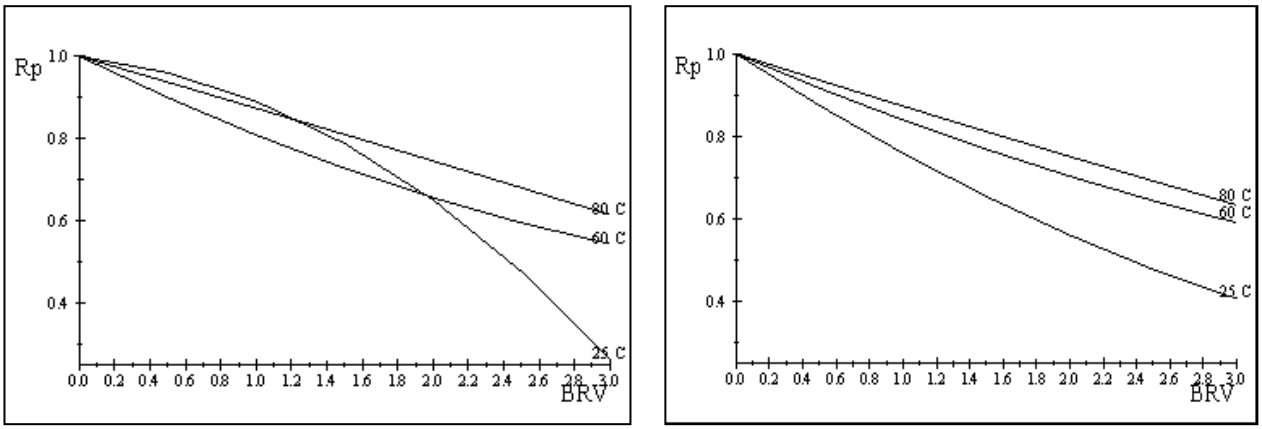
8.c. order flow T = 80 C

Figure 8. Influence of concentration BRV on the order flow

This complex rheological behavior, where the increase in concentration of BRV causes a decreased consistency and an increased order, requires the simulation of the frictional pressure losses in this system for analyzing the feasibility of the use of BRV to reduce transportation costs of crude.

A tube diameter of 0.254 m, a length L of 1000 m roughness of 0.006 m with a flow rate of 0.1ms-1 was considered to carry out the simulation. The results obtained for the pressure gradient in monophasic flow in both crude oils are presented in Table 6.

The Rp quotient between the pressure gradient at the given concentration of BRV and gradient to 0% of BRV, both considered at the same temperature, was determined to analyze the effect of BRV. The results obtained in this case are shown in Figure 9.

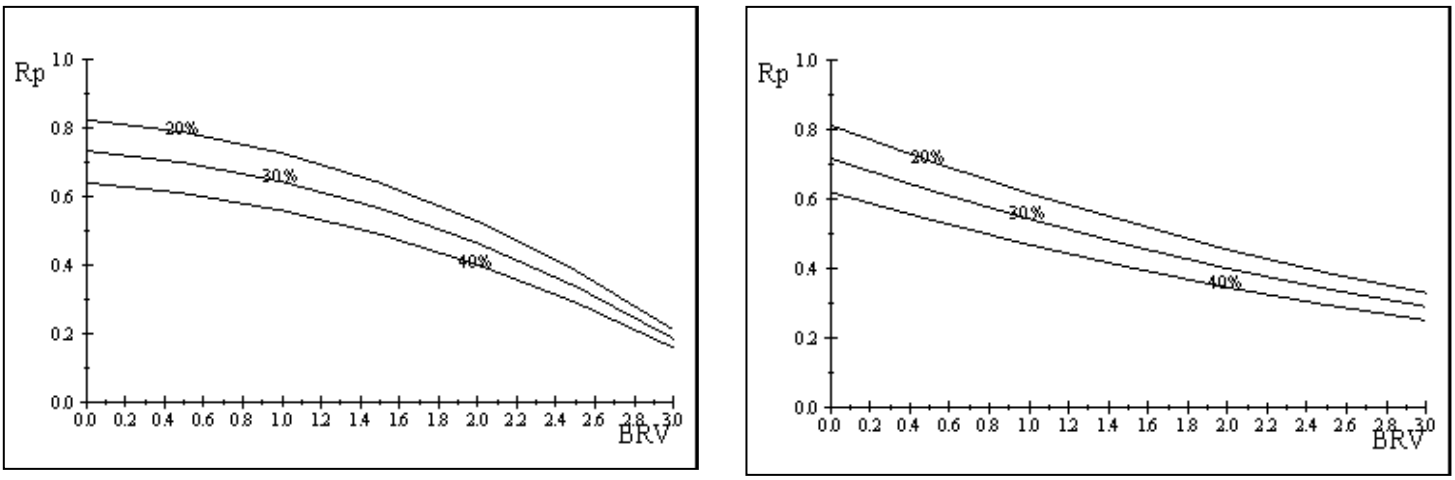


9.A Crude oil type A Monophasic **9.B crude oil type B monophasic**

Figure 9. Effect of the concentration of BRV on pressure drop by frictional in monophasic flow

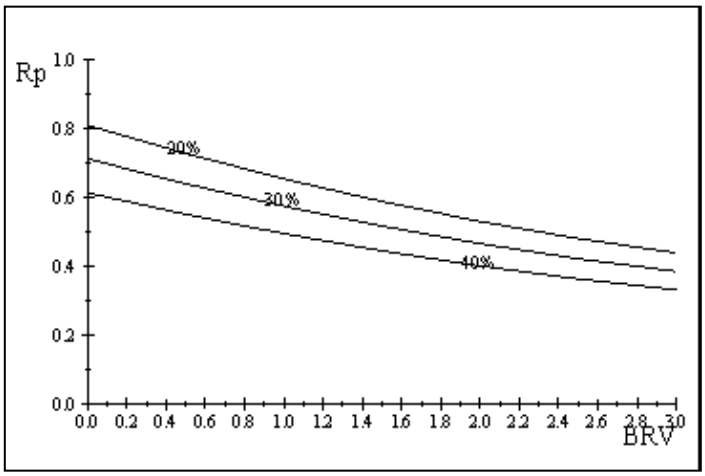
In this case it is seen that increased concentration of BRV causes an appreciable reduction in the pressure gradient for both crude oils, indicating that the increase in the order flow that can be caused by the breakdown of aggregates and loss asphaltene orientation of these would facilitate the flow, is not significant. The most important effect is reducing the consistency which is achieved by reducing the volume of the dispersed phase.

A simulation of the behavior of the pressure gradient using the method of Lockhart-Martinelli [17] was performed to check whether if into the biphasic flow also can the BRV be used to reduce pressure losses, considering a gas with viscosity of 0.2 10 - 2 Pas, molecular weight equal to 23 and a compressibility factor of 0.9577 for both crude oils. The BRV effect on reducing the pressure drop for different percentages of gas mass flow is determined using the ratio Rp, representing the ratio of the pressure drop for a two phase flow at a given concentration of BRV and pressure drop for single-phase flow and 0% of BRV, both considered at the same temperature. The results obtained are shown in Figure 10.

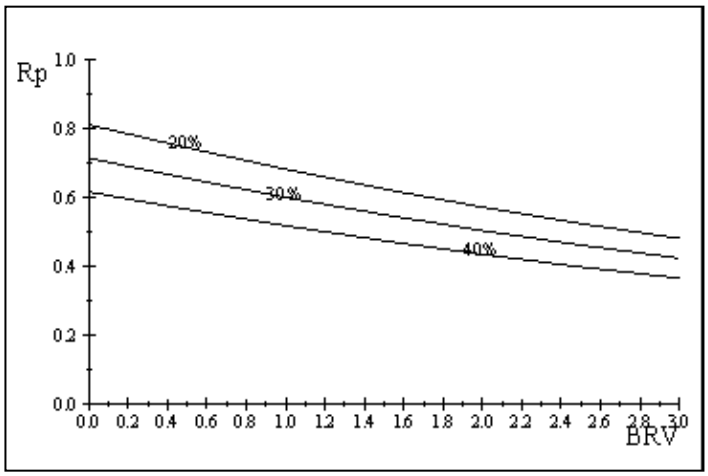


10.A 10.B

Figure 10. BRV influence on the pressure drop in two-phase flow for different % of gas volume.



10.C



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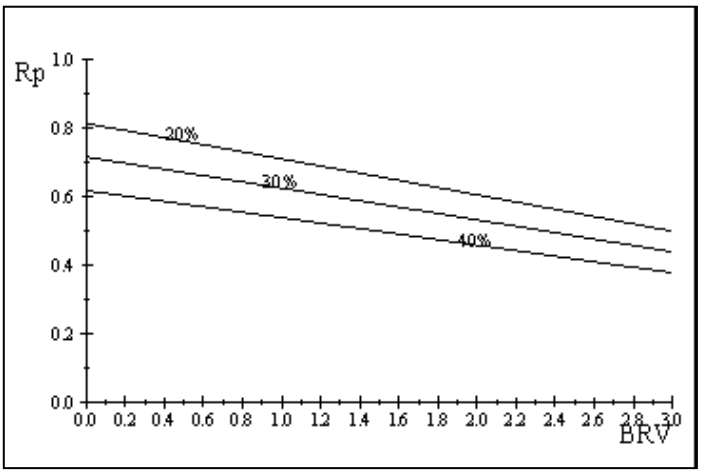
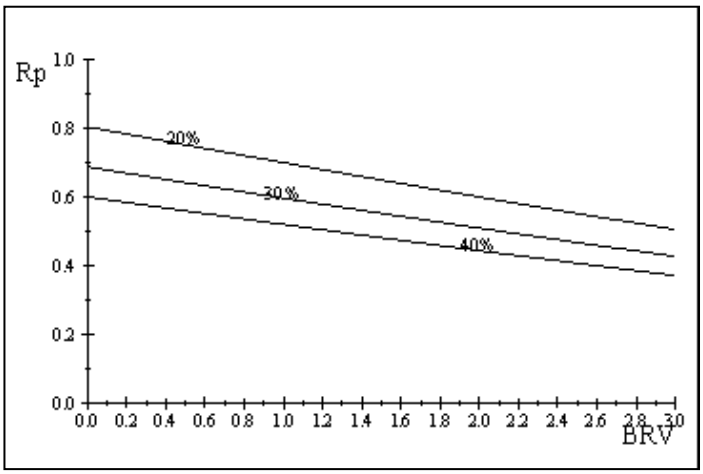


10.E



10.F

Figure 10 (cont…). BRV influence on the pressure drop in two-phase flow for different % of gas volume.

In this case it is appreciated that increasing the concentration of BRV, as in the case of mono-phase flow, causes a significant decrease in the pressure gradient in biphasic flow.

2.0 Conclusions

A computer simulation using the methods of theoretical chemistry to predict the influence of this compound on attractive interactions between the asphaltenes and paraffin was conducted to study the effect of BRV on physical-chemical behavior of crude oil, which predicted that the molecule that makes up the active ingredient of this compound causes an increase in bond distance between these molecules, reflecting a decrease in net attractive force. As it experimentally observed, decreasing asphaltenes and speed of droplets coalescence in crude oil systems dispersed in water, may be a theoretical confirmation of the result obtained.

Moreover, by performing an experimental rheological study was found that analyzed crudes have a slightly viscoelastic non-Newtonian behavior, which can be explained if considering that asphaltene aggregates tend to self-organize to facilitate the flow, which is manifested by reducing the flow order. The increase in the BRV concentration on rheological behavior causes a decreased consistency (due to a decrease in the volume of the dispersed phase formed by the aggregates) accompanied by an increase of the order (product loss of orientation effect aggregates that facilitates the flow). When performing simulations on the behavior of the frictional pressure gradient, it is obtained that the increase in the concentration of BRV cause an appreciable reduction of these losses both for monophasic and biphasic flow.

Acknowledgments

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