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On the Use of Solvent Blends to Remove Organic Deposits, Oil and Emulsions from Subsea Production Lines

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Abstract
Cleaning-up subsea production lines for decommissioning offshore production systems is a complex time-consuming operation, which often depends on costly pumping service boats or work-over rigs to be carried out. Besides being troublesome to remove organic materials from long subsea tie-backs, if such an operation is not well conceived it can bring on poten environmental serious environmental, economic and social problems. Therefore, it is necessary to discover new solvent formulations for the cleaning procedure of subsea lines and production. In this experimental work that has been carried out in lab of Petrobras, a series of organic solvent blends with different compositions of xylenes, marine diesel oil (MDO) and commercial demulsifier formulation, had their performance evaluated (by soaking) to address their capacity of cleaning organic emulsion. These assays, carried out at seabed temperature, showed that mechanisms of action of the solvent blends on the organic deposits and emulsions are two-folded: (i) dissolution; and (ii) permeation. The solvent soaking lab results also show a higher solving power for those solvent blends containing both a high xylenes content, and added with a selected demulsifier.

Keywords
Cleaning seabed production lines; Soaking operations; Oil emulsion removal.

Introduction
One is aware that decommissioning stage follows the last stage of the useful economic life cycle of an oil and gas production lease. Within the decommissioning domain, the facilities are due to be safely deactivated, the producing wells abandoned and plugged, all the production equipment are disassembled and removed from location. The decommissioning process is intended to clean up the whole leased area to return it in pristine condition to the leaser controller [1].
Decomissioning is an activity which is relatively new to the Brazilian offshore oil industry. So far, most of the decommissioning works performed in the Brazilian territory has been concentrated in small leases in different (onshore) terrestrial basins. In Brazil, the offshore production activities are much more recent than the onshore production ones. In fact, only in recent years have we started to deal with the decommissioning in our offshore scenarios. One may say that we are going through the early stages of decommissioning our oldest offshore fields [2].
Our offshore fields to be presently decommissioned are spread over shallow, deep, and ultra-deepwater. However, each production facility is intrinsically different from another, because they reflect the existing engineering concepts, characteristics, demand and limitations at the time they were set up. Another noteworthy point is that the deeper the water depth the more complex the production facilities are. One should also bear in/on mind that there are no two wells alike even if they were completed in the same field pay zone [2]. So, the whole decommissioning work must be carried out on a case-by-case basis.
Because decommissioning is an activity that does not produce cash, rigless pipe cleaning operations are always the operator's first option because of the relatively lower OPEX demanded. It goes without saying that a holistic approach must be taken to adapt highly efficient, techno-economically efficient chemical-enhanced solvent mixtures and well-planned and environmentally safe pumping operations. To capitalize on the efforts made to combat the problem, a well-detailed pipe cleaning pumping schedule must be drawn up.
Oil spills is not acceptable in offshore scenarios, because of the serious problems they can end up creating. In fact, this is a kind of situation that can lead to a series of far-reaching problems, such as: environmental degradation, economic losses to the fishery industry, and damage to the public image of the company. Besides, some heavy sanctions may be imposed by authorities, such as costly fines and forced production shutdowns [3].
In this experimental work, the performance of different solvent blends, with or without demulsifier added, was evaluated in petroleum emulsions from a Brazilian offshore well. All these tests were

carried out at 4°C, which is the minimum temperature at the bottom of the sea. These evaluation tests aimed at finding the best solvent blends for cleaning subsea (oil emulsion) production lines by soaking.

Methodology

Materials

A crude oil emulsion from a Brazilian offshore well, composed by a medium API grade crude oil (24.8°API) plus a prepared NaCl solution, was used in the experimental work. Sodium chloride P.A., purchased from Vetec, and deionized water, in-house produced with the aid of a Millipore Elix 5 deionizer apparatus, were used to formulate a Sodium Chloride solution at 50g/L concentration.

The chemicals and solvents used in this study, specifically: xylenes P.A. from VETEC; marine diesel oil (MDO) from Duque de Caxias refinery; and commercial formulations of petroleum demulsifiers; were used as received.

Preparation of the Synthetic Emulsion

A synthetic water-in-oil (W/O) emulsion, containing 70% (v/v) of saline water, was prepared in the laboratory by mixing and shearing the crude oil and water fractions. Both fluids were pre-heated at 80°C before mixing. The ultimate disperse (emulsion) system was prepared by stirring the mixture of fluids with the aid of the *Nova Ética* Pendulum Oven, at 100 motions per minute, for five minutes; followed by a shearing stage with the aid of the Ultraturrax T-18 homogenizer at 8,000 rpm for three minutes. The emulsion's stability was evaluated by gauging the water separation (bottle test), at 60°C for four hours.

Immersion Tests to Investigate the Effect of Solvent Blends on Synthetic Crude Emulsions

The five formulations of solvent blends (xylenes: MDO, v/v)) were prepared for the immersion tests, as follows: (a) 100:0; (b)75:25; (c) 50:50; (d) 25:75; (e) 0:100. Additional tests were carried out to address the commercial demulsifier ability to enhance the capacity of the solvent blends to resolve the synthetic crude emulsion. For that, the two solvent mixtures used were formulations (a) and (d) above, to which 2,000 ppm (v/v) of commercial demulsifier were added. The results of these tests were compared to the ones with no added demulsifier.

According to our lab procedures both the emulsion and the solvent blends are pre-cooled at 4°C, with the aid of a *Nova Técnica* NT 750 Cold Chamber. An aliquot of 40 mL of synthetic crude emulsion is transferred to a 100-mL graduated cylinder. Following that, an aliquot of 60 mL of solvent blend is carefully transferred to the top of the synthetic crude emulsion within the graduated cylinder, taking care to avoid swirling the emulsion. Every day, during the four consecutive weeks of cooling at 4°C, the supernatant part of the solvent (around the upper 10 mL) is vigorously hand-stirred with the help of a glass rod, for around 60 seconds.

Quantification of Crude Oil Concentration in the Supernatant Solvent Blend

At the end of each week, during consecutive four weeks, an aliquot of the supernatant fluid is collected to quantify the oil concentration in the solvent blend, by UV-Vis Spectrophotometry with the aid of the Thermo Scientific Evolution 300 Spectrophotometer, operating at 480nm wavelength. The aliquot of the supernatant solvent blend is diluted in xylenes P.A. prior to being analyzed.

Both xylenes and MDO present a low absorbance at 480 nm wavelength. Conversely, crude oil diluted in xylenes presents a strong absorbance at the same wavelength. An absorbance curve of known concentrations of 24.8 °API crude in xylenes versus absorbance was plotted using a linear regression technique.

Special care was taken to select a suitable range of concentrations for the 24.8 °API crude in xylenes, where a linear relationship of this parameter versus absorbance can be achieved. The co-relation coefficient of this curve (r^2) must be superior to 0.99 to end up generating an appropriate calibration curve.

Quantification of solvent action on emulsion viscosity

At the end of the four-week period, the solvent blend is carefully extracted from the graduated cylinder, and the viscosity of the crude oil emulsion is quantified at temperatures of 25°C, 10°C and 4°C, and at $250s^{-1}$ shear rate, with the aid of a Haake RS 6000 rheometer, using a coaxial geometry sensor (model #CC-25 DIM TI), equipped with a Julabo F500 chiller device. The viscosity of the synthetic 24.8°API crude oil emulsions, which remained still in the cold chamber for four weeks, was also quantified.

Results and Discussion

The synthetic 24.8°API crude oil emulsion containing 70% saline water, prepared in the laboratory, did not separate (visually) water when subjected to a temperature of 60°C for 4 hours. Therefore, this synthetic emulsion is considered to be very stable.

Figure 1 shows the appearance of the 24.8°API crude oil emulsion immersion tests in the solvent blends containing a xylenes:MDO ratio of 100:0 and 25:75.

Figure 1 shows the solvent blends used to immerse the 24.8°API crude oil emulsion at 4°C, became darker over time, at a temperature of 4°C. This darkening process of the solvent blend was associated with the solvent blend's action to dissolving the 24.8°API crude oil contained in the emulsion. It can be also visually observed that the darkening kinetics of the solvent blend was greater the higher the xylenes content in the solvent blend composition. The solvent blend containing only xylenes, from the very first day, showed a strong darkening profile. However, visually, after 7 days of testing, all solvent blend compositions became dark so that it was no longer possible to visually identify differences in the color of the solvent blends over other solvent blends and over time.

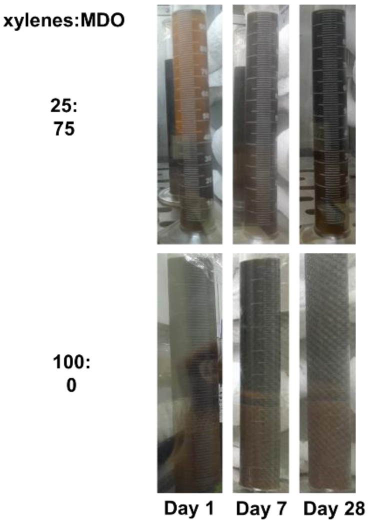

Figure 1. Aspect of the crude oil emulsion immersion tests in the solvent blends with a xylenes:MDO ratio of 25:75 and 100:0.

Table 1 shows the variation of the 24.8°API crude oil emulsion dissolution in the solvent blends as a function of the immersion time.

Table 1. Crude oil dissolution kinetics at different solvent compositions, at 4°C.

Solvent Composition xylenes:MDO	Oil Concentration (mg/L)			
	Week			
	1	2	3	4
100:0	26.5	34,4	37,4	38,4
100:0 + desemulsifier	14.1	22,4	28,5	34,2
75:25	14.2	16,4	23,2	25,8
50:50	10.7	17,1	20,8	24,4
25:75	5,0	10,1	12,1	14,0
25:75 + desemulsifier	6,4	9,6	12,6	14,5
0:100	2,3	4,1	4,8	5,8

From the results presented in Table 1, there is an increase in the dissolution of the oil in the solvent blends as a function of the emulsion immersion time. It is also possible to verify that the increase in the xylenes content in the solvent mixture was accompanied by a greater dissolution of crude oil in the solvent mixture. On the other hand, pure marine diesel, formulation (e), was the least efficient solvent for crude oil, dissolving about 15% of the oil fraction dissolved in xylenes. In formulation (a), the presence of 2,000 ppm of commercial demulsifier showed a lower crude oil dissolution efficiency than in the absence of demulsifier. However, these results may have been falsified by the presence of water in the solvent. In formulation (d), the addition of the demulsifier promoted an increase in the dissolution kinetics of crude oil by the solvent, when compared to the test in the absence of demulsifier. On the other hand, the demulsifier did not significantly increase the dissolution of crude oil in the solvent mixture at the end of the test.

Table 2 and Fig. 2 and 3 show the effect of solvent blend composition and immersion on the crude oil emulsion viscosity after completion of the tests, at temperatures of 25°C, 10°C and 4°C and at a shear rate of 250s^{-1}. The emulsion, at the same condition, that was not immersed in any solvent, which was kept four weeks at 4°C, is listed for reference.

Table 2. Effect of different solvent blends composition on the viscosity of the 24.8°API crude oil emulsions

Solvent Composition xylenes:MDO	Temperature (°C)		
	25	10	4
	Viscosity @250s^{-1} (mPa.s)		
Emulsion without immersion on solvent	4,791	11,489	17,765
100:0	262.7	427.9	598.5
100:0 + desemulsifier	130.1	217.9	287.8
75:25	432.6	769.0	1,112
50:50	809.6	1,554	2,308
25:75	927.1	1,886	2,872
25:75 + desemulsifier	309.6	481.3	609.2
0:100	1,684	3,841	5,828

As per the results depicted in Table 2, one can be observed that the emulsion of crude oil has high viscosity, especially at 4°C. The effect of immersing the emulsion in solvent blends for four weeks at 4°C significantly reduced the viscosity of that emulsion. This viscosity reduction can be associated with the permeation of the solvent mixture molecules in the crude oil emulsion, arguably promoting compositional changes in its external phase.

From the results presented in Fig. 2, it can be seen that the crude oil viscosity reduction, after the immersion tests in solvent blends, was greater with the increase of the xylenes fraction in the solvent blend, although there appears to be no linear, and nor exponential correlation between the xylenes content itself and the crude oil emulsion viscosity. In fact, the crude oil emulsion viscosity, after being immersed in xylenes alone, dropped 97% of its original value. Likewise, the crude oil emulsion viscosity dropped 67% of its original values after being immersed in MDO The reduction of the crude oil emulsion viscosity after immersion in both 50:50 and 25:75 xylenes:MDO blends, were very similar, but both results were significantly lower than that one of the crude oil emulsions after immersion in pure MDO. These results seem to indicate that the viscosity reduction efficiency obtained by increasing the xylenes content in the solvent blend composition is associated with dimly understood factors, such as solvent viscosity, solvent aromaticity and Hildebrand solubility parameter.

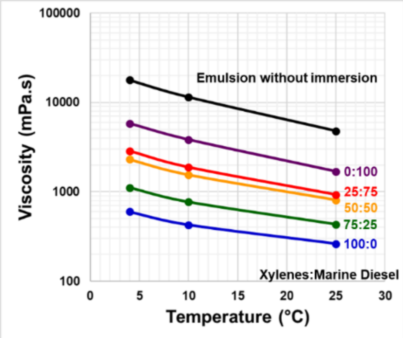

Figure 2. Effect of immersion of solvent blends with different xylenes to MDO ratios on the viscosity of the crude oil emulsion

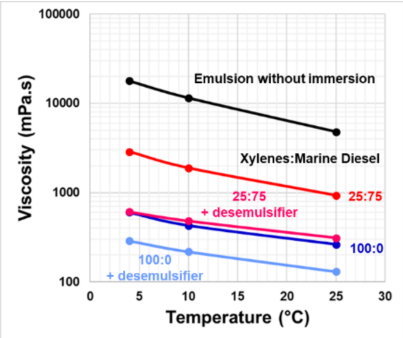

Figure 3. Effect of solvent blends immersion with and without the presence of demulsifier on the viscosity of the crude oil emulsion

From the results presented in Fig. 3, one can see that the presence of demulsifier in the solvent blend composition, when compared to the same solvent blend with no added demulsifier, increases the viscosity reduction of the crude oil emulsion. The viscosity reduction efficiency, provided by the presence of demulsifier in the solvent blend, was greater when the xylenes content in the solvent blend is low. It is believed that the demulsifier acts on the crude oil emulsion by resolution of crude emulsion which ends up reducing its viscosity, thus facilitating the solvent blend permeation.

Conclusions

Decommissioning stage of subsea production lines is relatively innovative for the Brazilian offshore oil industry. Furthermore, these activities still require a case-by-case assessment of entrepreneurship to obtain satisfactory technical, economic and environmental results. The use of solvents by soaking is still an important technique for cleaning those lines.

To evaluate the action of solvents in soaking operations, for cleaning production lines, a stable high viscosity emulsion was used, with Brazilian offshore crude oil of 24.8°API and brine, and different blends of solvents, obtained from different proportions of xylenes and MDO. The test results showed that the solvents act by (i) dissolving the crude oil in the solvent and (ii) reducing the viscosity of the emulsion due to the permeation of the solvent in the emulsion. It was also possible to observe an increase in the dissolution efficiency of crude oil by the solvents and a reduction in the viscosity of the emulsion due to the increase in the xylenes content in the composition of the solvent blend. The application of a demulsifier in the solvent blends only provided a greater reduction in the viscosity of the emulsion.

Therefore, it would be interesting if soaking operations with solvent blends in the production lines, at low temperatures, were carried out with solvent blends with the highest-possible xylenes content. Also, the presence of demulsifier in the solvent blend composition eases the emulsion removal, and the pipe cleaning job.

It is worth mentioning that, although pure xylenes are more efficient in cleaning operations in production lines, their use may be unfeasible due to the high acquisition and transportation costs (economic aspects) and very low flash point (security aspects).

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Responsibility Notice

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