

Artigo

Improvement on Pour Point of Heavy Oils by Adding Organic Solvents

Santos, F. D.; Sad, C. M. S.; Bassane, J. F. P.; Neto, D. M. C.; Figueiras, P. R.; da Silva, M.; Silva, S. R. C.; Castro, E. V. R.; Romão, W.; Pereira, L. B.; Lacerda Jr., V.*

Rev. Virtual Quim., 2017, 9 (6), 2404-2413. Data de publicação na Web: 6 de novembro de 2017

<http://rvq.sbg.org.br>

Melhoria no Ponto de Fluidez de Óleos Pesados pela Adição de Solventes Orgânicos

Resumo: Este artigo descreve o comportamento do ponto de fluidez de três óleos pesados com adição de querosene, aguarrás, tolueno e condensado de gás. O estudo mostrou um decaimento no ponto de fluidez de todos os óleos que se relaciona com a composição química dos óleos. O óleo com menor grau API (maior quantidade de asfaltenos e resinas) apresentou maior decaimento do ponto de fluidez para todos os solventes, destacando o condensado de gás e a aguarrás. O uso de condensado de gás para reduzir o ponto de fluidez de óleos pesados é particularmente vantajoso, quando disponível no campo petrolífero. Previne a paralisação na produção de óleo, devido a obstrução e problemas de fluxo nos dutos, e facilita a logística, reduzindo os custos operacionais do processo.

Palavras-chave: Óleos pesados; ponto de fluidez; solventes orgânicos.

Abstract

This paper describes the pour point behavior of three heavy oils with the addition of kerosene, turpentine, toluene and gas condensate. The study showed a decrease in the pour point of all oils related to their chemical composition. The oil with the lowest API gravity (high amount of asphaltene and resins) showed the highest pour point decay for all solvents, highlighting gas condensate and turpentine. The use of gas condensate to reduce the pour point of heavy oils is particularly advantageous, when it is available in the oilfield. It also prevent halt in oil production, due to pipeline clogging and flow problems, and facilitate the logistics, reducing operational costs in the process.

Keywords: Heavy oils; Pour point; Organic solvents.

* Universidade Federal do Espírito Santo, Laboratório de Pesquisa e Desenvolvimento de Metodologias para a Análise de Petróleos (LabPetro), CEP 29075-910, Vitória-ES, Brasil.

✉ yljuniorqui@gmail.com

DOI: [10.21577/1984-6835.20170143](https://doi.org/10.21577/1984-6835.20170143)

Improvement on Pour Point of Heavy Oils by Adding Organic Solvents

Francine D. Santos, Cristina M. S. Sad, João F. P. Bassane, Dorval M. C. Neto, Paulo R. Filgueiras, Mayara da Silva, Samantha R. C. Silva, Eustáquio V. R. Castro, Wanderson Romão, Laine B. Pereira, Valdemar Lacerda Jr.*

Universidade Federal do Espírito Santo, Laboratório de Pesquisa e Desenvolvimento de Metodologias para a Análise de Petróleos (LabPetro), CEP 29075-910, Vitória-ES, Brasil.

* vljuniorqui@gmail.com

Recebido em 23 de maio de 2017. Aceito para publicação em 4 de novembro de 2017

1. Introduction

2. Materials and Methods

2.1. Sample Preparation

2.2. Experimental techniques applied for crude oils and solvents characterization

2.3. Pour Point Determination

2.4. Samples preparation (Crude oil with solvents)

3. Results and Discussion

4. Conclusion

1. Introduction

The basic difference between crude oils is the relative amounts of hydrocarbons classes present in it, which influences their physical chemical properties.¹ Heavy oils are crude oils with large amount of asphaltenes and resins.² These heavy molecules interact, being the principal responsible for the heavy and viscous character of this type of oil, a problem for the industry.³

An important property tested in the production step is pour point. Pour point is defined as the lowest temperature at which the oil does not flow under gravitational

action.⁴ Paraffins interfere directly in this property, but this class is not significant in heavy oils as asphaltenes and resins. Paraffins make the oil flow stop at highest temperatures when compared with oils with higher concentration of aromatic hydrocarbons.⁵ Pour point is used to define pipeline transfer conditions, allows process dimensioning and pumping calculations, and in preventive actions and process improvement, which facilitates oil flowing and reduces the incidence of incrustation due to paraffins and asphaltenes precipitation.⁶

A good option to prevent incrustations without the formation of stable water-oil emulsion, a common side effect in recovery

methods, is the dilution of heavy oils with organic solvents.^{7,8} The dilution method is especially applicable if cheap and large amounts of lighter hydrocarbons are available.^{9,10} In Brazil, much of the gas produced in oil fields is burned in the own production field.

Gas condensate, also called natural gasoline, is composed mostly of pentane, hexane, heptane and other compounds of saturated branched and cyclic saturated chain.¹¹ So, it is important to highlight that the addition of light paraffins (pentane, hexane, heptane), such as gas condensate, to these oils, could lead to asphaltene precipitation, which may cause problems during oil production.¹² Therefore, the aim of this study was to improve the pour point of heavy oils with the addition of organic solvents as gas condensate, kerosene, turpentine and toluene, without precipitation of compounds.

2. Materials and Methods

2.1. Sample Preparation

Three heavy crude oil samples (named A, B, and C) were selected from production fields located in the Brazilian coast. The physicochemical properties of the oils and of the organic solvents: kerosene, turpentine, toluene and gas condensate (named I, II, III and IV, respectively) were determined (Table 1). The samples were prepared and handled in according to the ASTM D5854.¹³ For oil treatment, the free water (non-emulsified water) was previously separated from the crude by gravitational settling, and the water content was determined in the water-in-oil emulsions according to ASTM D4377 using a Metrohm KF titrator (model 836 Titrandu)

equipped with a double-platinum electrode.¹⁴ Oils with water content over 1% (v/v) were dehydrated by using 200 μ L of a concentrated commercial demulsifier (composed of surfactants containing isoprene and glycol propylene oligomer species) at 60 °C and centrifuged at 1600 rpm for 15 minutes. After demulsification, the water content was determined to verify if it was below 1.0% (v/v) for all oils. The characterization properties were then determined (Table 1) for the dehydrated crude oils, according to each standard ASTM methods.

2.2. Experimental techniques applied for crude oils and solvents characterization

Density was determined in compliance with ISO 12185 by injecting the sample into the digital automatic analyzer Stabinger SVM 3000 (Anton Paar).¹⁵ API gravity was also reported according to ASTM D1250.¹⁶ Total acid number (TAN) was determined in compliance with the ASTM D664 by potentiometric titration (Metrohm 836 automatic titrator) of the sample, using an alcoholic solution of KOH.¹⁷ Maximum and minimum pour point (PPmax e PPmin) determined according to ASTM 5853 for the oils and by ASTM D97 for the solvents, by the use of a semi-automatic equipment (CAPPV-Petrotest).^{4,18} Total sulfur content was analyzed according to ASTM D4294 using the automatic analyzer HORIBA, model SFLA-2800.¹⁹ Elemental analysis for the oils was determined by a LECO CHN-1000 analyzer. SARA (saturates, aromatic, resins and asphaltene) content was obtained by chromatographic analysis following the ASTM D2549 standard.²⁰ The chromatographic profile of the gas condensate (Table 2, Figure 1) was determined by chromatography using a GC-MS 5050 Shimadzu.

Table 1. Physicochemical properties of the oils and organic solvents

Properties	A	B	C	I (kerosene)	II (turpentine)	III (toluene)	IV (gas condensate)
Water (%) v/v)	0.050 (0.002)	0.050 (0.001)	0.301 (0.003)	0.050 (0.002)	< 0.050	< 0.050	< 0.050
Density (g.cm ⁻³)	0.920 (0.002)	0.938 (0.003)	0.970 (0.003)	0.7888 (0.005)	0.7875 (0.002)	0.8383 (0.001)	0.6734 (0.002)
API	21.6	18.7	13.7	46.9	47.2	36.3	76.9
TAN (mg KOH.g ⁻¹)	0.840 (0.008)	1.871 (0.010)	0.580 (0.030)	<0.010	<0.010	<0.010	<0.010
Viscosity (Pa.s)	0.0820 (0.0023)	0.1055 (0.0030)	2.7319 (0.0080)	0.0006	0.0006	0.0004	0.0002
PPmax (°C)	12 (3)	-27 (3)	10 (2)	-69 (3)	-69 (3)	-69 (3)	-69 (3)
PPmin (°C)	-33 (3)	-27 (3)	7 (2)	-	-	-	-
SARA content (wt %)							
Saturates	57.2 (0.06)	49.0 (0.03)	36.0 (0.02)	79.6 (0.02)	83.3 (0.04)	<0,01	88.7 (0.04)
Aromatics	26.9 (0.02)	31.1 (0.05)	25.0 (0.03)	20.1 (0.01)	15.7 (0.02)	99.5 (0.04)	11.1 (0.02)
Resins	12.9 (0.02)	19.0 (0.01)	32.0 (0.01)	<0.01	0.70 (0.01)	<0.01	0.10 (0.010)
Asphaltenes	3.14 (0.02)	0.98 (0.01)	7.10 (0.02)	<0.01	<0.01	<0.01	<0.01
Element analysis (wt %)							
C	86.0 (0.4)	85.8 (0.3)	87.0 (0.3)	87.3 (0.2)	87.6 (0.1)	87.8 (0.4)	87.9 (0.2)
H	13.6 (0.1)	13.5 (0.1)	12.5 (0.2)	12.3 (0.2)	12.0 (0.2)	12.2 (0.4)	12.1 (0.10)
N	0.17 (0.02)	0.25 (0.04)	0.24 (0.02)	<0.0001	<0.0001	<0.0001	<0.0001
S	0.3200 (0.0020)	0.5103 (0.0010)	0.3566 (0.0020)	0.3721 (0.0010)	0.3910 (0.0010)	0.0016 (0.0003)	0.01802 (0.0003)

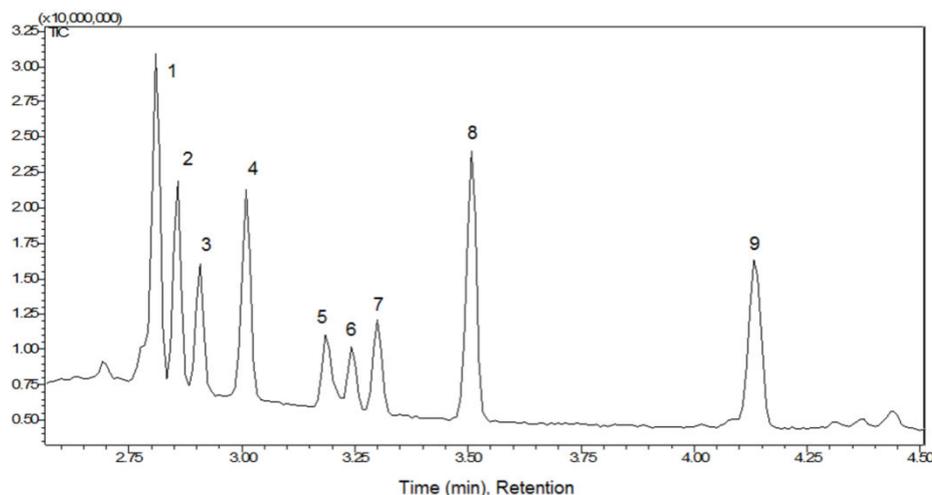


Figure 1. Chromatographic profile of the gas condensate sample

Table 2. Compounds found in gas condensate chromatogram (Figure 1)

No.	Hydrocarbon
1	Cyclohexane
2	2-methylhexane
3	2,3-dimethylpentane
4	3-methyl hexane
5	1,3-dimethyl cyclopentane
6	1, cis, 2 - dimethylcyclopentane
7	1,2 trans-dimethylcyclopentane
8	Heptane
9	Methylcyclohexane

2.3. Pour Point Determination

The ASTM D5853 is specific for determining maximum (upper) and minimum (lower) pour points of crude oils. After preliminary heating, the oil samples are cooled and examined at intervals of 3 °C for checking the flow characteristics. Therefore, the lowest temperature at which movement of the sample is observed is reported as its pour point. The maximum and minimum pour point temperatures provide a temperature window, where a crude oil, depending upon

its thermal history, might appear as liquid or solid states. The accuracy for pour point determination of this method follows the repeatability criteria of 3 °C for the maximum pour point and 6 °C for the minimum pour point, with 95% confidence of result acceptability.

To determine the maximum pour point, the sample was kept resting in a test jar for 24 h at room temperature to reach the equilibrium between the dissolved wax and the crystallized wax, to enhance gelation of wax crystals and solidification. Before starting

the test, the resting state must be broken with a gentle stirring of the sample. The minimum pour point was measured after submitting the sample to a 105 °C heating in a pressure vessel for 30 minutes, to delay gelation of wax crystals and solidification.

The differential treatment under which the sample was submitted for determining the maximum pour point leads to an increase in the wax gelation and crystallization, favoring a faster solidification of the sample. On the other hand, the different treatment performed to determine the minimum pour point allows the delay of wax crystallization, which results in slower solidification of the sample.

2.4. Samples preparation (Crude oil with solvents)

The oil samples prepared for this study consisted on crude oil with the addition of different concentrations of organic solvents (kerosene, turpentine, toluene and gas condensate). Previously, the crude oil sample was homogenized for 3 minutes. Then,

aliquots of the crude oils were separated into flasks and each of the flasks received different volumes of the solvent in order to obtain a mixture, with solvent concentration ranging from 0 to 32.6% (v/v). After the solvent addition, the mixture was submitted to a mechanical stirring with rotation of 7500 rpm, by using a Turrax (model IKA T25). These mixtures were submitted to density and maximum and minimum pour points analysis.

3. Results and Discussion

The results (Figure 2) show that all solvents were effective in reducing the pour point of the oils when compared to the pour point values of the oils without the addition of solvents. The higher the volume of added solvent, varying the concentration of the solvents (I – IV) from 0 to 32%(v/v), the higher was the pour point reduction. During the tests it was not visually observed any kind of precipitation that could be related to paraffins and asphaltenes.

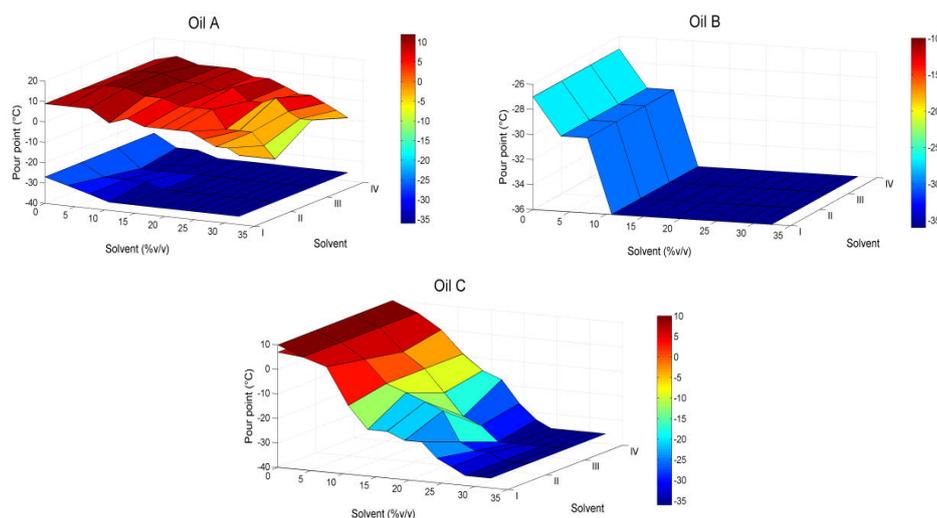


Figure 2. Diagram of the pour point behaviors of oils A, B and C mixed with different concentrations (% v/v) of solvents I, II, III and IV

Oil A (Figure 2) showed a different behavior between the results of minimum and maximum pour point with the solvents addition, which corresponds, respectively, to the top surface (reddish tones) and lower surface (blue tones). While for oils B and C this behavior was not observed and the maximum and minimum pour point surfaces are overlapped.

Oil B is noteworthy for presenting an initial pour point (without solvent addition) corresponding to $-27\text{ }^{\circ}\text{C}$, and its variation in the pour point of the mixture with the solvents was small in comparison with oils A and C (Table 3). This behavior is clear visible on Figure 2. It is important to highlight that according to ASTM D5853, test is discontinued when the sample remains fluid to $-36\text{ }^{\circ}\text{C}$ and the pour point is reported as less than $-36\text{ }^{\circ}\text{C}$. Whereas the pour point is the lowest temperature that oil stops flowing, below -36 it is desirable for flow assurance.

Comparing the solvents influence over the oils maximum and minimum pour points reduction (Table 3), it was calculated the

maximum and minimum variation (Δ_{max} and Δ_{min}) of the pour points of the oil/solvent mixtures. Results show that oil C, with less API gravity (13.7) and a highest resin (32.01 wt%) and asphaltenes (7.10 wt%) content, showed the highest variation in the value of minimum and maximum pour point with all solvents. Oils A and B showed different behavior for each solvent added. Oil B, which presented a low pour point without the addition of solvents, presented the smallest variation in the values of maximum and minimum pour point in the mixtures with all solvents. This behavior may be associated with the high content of aromatics (31.10 wt%) in its composition. Oil A, the one with the highest API gravity (21.6) and the highest saturates content (57.20 wt%), showed a larger variation of the maximum pour point with solvent II (turpentine) and IV (gas condensate) and presented the same value of minimum pour point variation. This was obtained because the two solvents were very effective in reducing the pour point until reaching the minimum value measured by method.

Table 3. Maximum and minimum pour point variations (Δ_{max} and Δ_{min}) in oils/solvents mixtures

	Oil A		Oil B		Oil C	
	Δ_{max} ($^{\circ}\text{C}$)	Δ_{min} ($^{\circ}\text{C}$)	Δ_{max} ($^{\circ}\text{C}$)	Δ_{min} ($^{\circ}\text{C}$)	Δ_{max} ($^{\circ}\text{C}$)	Δ_{min} ($^{\circ}\text{C}$)
Oil/Solvent I	18	9	9	9	46	43
Oil/Solvent II	24	9	9	9	46	43
Oil/Solvent III	12	9	9	9	46	43
Oil/Solvent IV	18	9	9	9	46	43

The mean variance analysis, with a 95% confidence interval, of the maximum and minimum pour point in the oil/solvents mixtures (Figure 3) shows that the four solvents were effective in reducing the pour point of oils A and C, but solvent II (turpentine) and IV (gas condensate) are noteworthy for presenting the largest variance in the pour points reductions. This behavior was not observed in oil B, which

presented similar mean variance for maximum and minimum pour point in the mixtures. The subtle change in oil B pour point was observed due to the low pour point of the oil even before the solvents addition. Thus, with small quantities of the four solvents, it was possible to lower the pour point of the oils until the technique limit ($-36\text{ }^{\circ}\text{C}$).

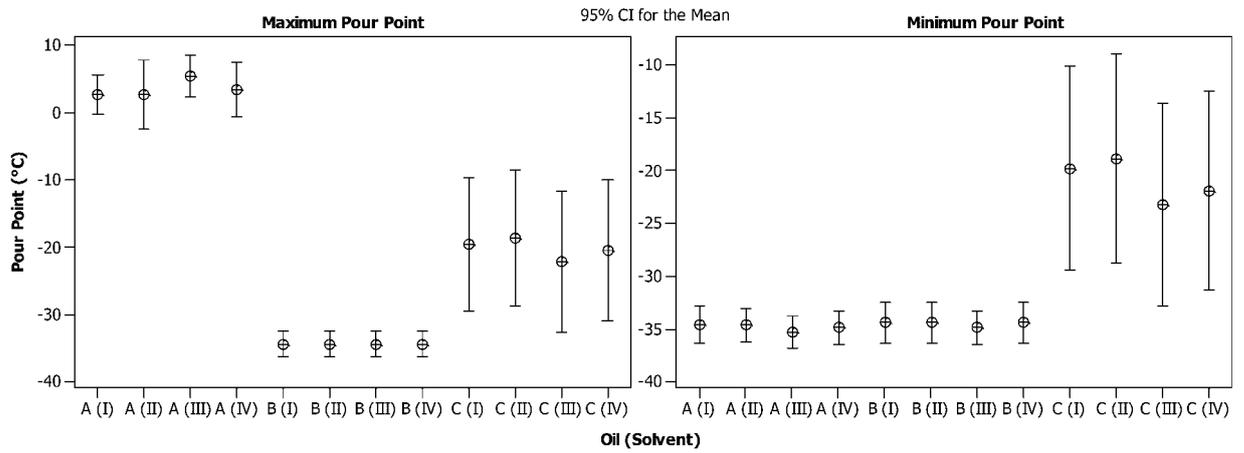


Figure 3. Mean variance graph of the maximum and minimum pour point results, separated by oil/solvent, with a confidence interval of 95%

The mean variance analysis, with a 95% confidence interval, of the density (Figure 4) of the oil/solvents mixtures was also evaluated. The results show that the mean

variance of the densities was more pronounced by the addition of gas condensate (IV) with a density reduction for all oils.

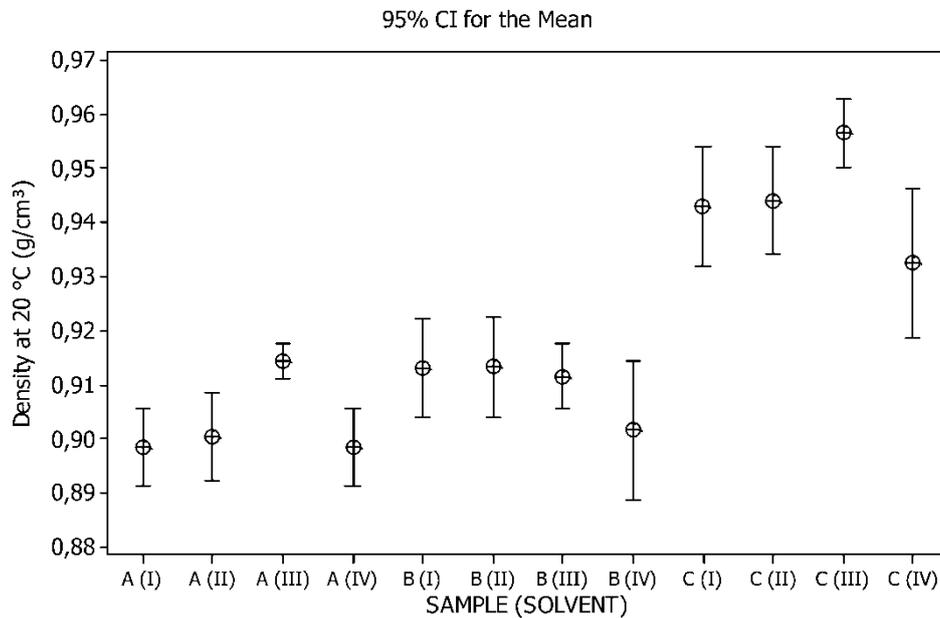


Figure 4. Mean variance graph of the density at 20 °C results, separated by oil/solvent, with a confidence interval of 95%

4. Conclusion

It may be concluded that the four organic solvents chosen were efficient to reduce the pour point of the oils and, consequently, to improve the heavy oils flow. For concentrations until 32.6% (v/v) no kind of deposits were observed, what could indicate instability in the mixture and precipitation of asphaltenes. Oil C, the one with the highest density (lowest API gravity), highest asphaltenes and resins content, and lowest content of saturated in its composition, had the highest reduction in maximum and minimum pour point with all solvents, with the highest mean variance for gas condensate and turpentine.

Oil A, with the lowest density (highest API gravity), lowest asphaltenes and resins content, and highest saturates content in its composition, showed a good reduction in maximum pour point with turpentine and gas condensate. It could be observed that oils with higher pour point is indicative of high content of asphaltenes and resins, and in the presence of saturated or aromatic organic solvents, the maximum and minimum pour point presented a significant reduction. It was also verified that the very low pour point of the oils can be related to the presence of high aromatic hydrocarbons content, and when adding organic solvents to these oils, it was observed a little decrease of the maximum and minimum pour point.

Acknowledgments

The authors are grateful to the Research and Development Laboratory of Petroleum Analysis Methodologies (LabPetro/UFES), the National Council for the Scientific and Technological Development (Conselho Nacional de Desenvolvimento Científico e Tecnológico - CNPq), the Coordination for the Improvement of Higher Education Personnel (Coordenação de Aperfeiçoamento de Pessoal do Nível Superior - CAPES) and the

Espírito Santo Research Foundation (Fundação de Amparo à Pesquisa do Espírito Santo - FAPES) for the support.

References

- ¹ Riazi, M. R.; *Characterization and properties of petroleum fractions*. 1st ed., ASTM: West Conshohocken, 2005.
- ² Speight, J. G.; *Handbook of Petroleum Product Analysis*. 2nd ed., Wiley Interscience: Hoboken, 2002.
- ³ Mansoori, G. A.; A unified perspective on the phase behavior of petroleum fluids. *International Journal of Oil, Gas and Coal Technology* **2009**, *2*, 141. [CrossRef]
- ⁴ ASTM D5853-16, Standard Test Method for Pour Point of Crude Oils, ASTM International, West Conshohocken, PA, 2016. [CrossRef]
- ⁵ Sad, C. M. S.; Lacerda Jr., V.; Filgueiras, P. R.; Rigoni, V. S.; Bassane, J. F. P.; Castro, E. V. R.; Pereira, K. S.; Santos, M. F. P.; Limitations of the Pour Point Measurement and the Influence of the Oil Composition on Its Detection Using Principal Component Analysis. *Energy & Fuels* **2014**, *28*, 1686. [CrossRef]
- ⁶ Martínez-Palou, R.; Mosqueira, M. L.; Zapata-Rendón, B.; Mar-Juárez, E.; Bernal-Huicochea, C.; Clavel-López, J. C.; Aburto, J.; Transportation of heavy and extra-heavy crude oil by pipeline: A review. *Journal of Petroleum Science and Engineering* **2011**, *75*, 274. [CrossRef]
- ⁷ Gateau, P.; Hénaut, I.; Barré, L.; Argillier, J. F. Heavy Oil Dilution. *Oil & Gas Science and Technology* **2004**, *59*, 503. [CrossRef]
- ⁸ Dehagani, A. H. S.; Badizad, M. H. Experimental study of Iranian heavy crude oil viscosity reduction by diluting with heptane, methanol, toluene, gas condensate and naphtha. *Petroleum* **2016**, *2*, 415. [CrossRef]
- ⁹ Shigemoto, N.; Al-Maamari, R.; Jibril, B. Y.; Hirayama, A.; A Study of the Effect of Gas Condensate on the Viscosity and Storage Stability of Omani Heavy Crude Oil. *Energy & Fuels* **2006**, *20*, 2504. [CrossRef]
- ¹⁰ Bassane, J. F. P., Sad, C. M. S.; Neto, D. M. C.; Santos, F. D.; Silva, M.; Tozzi, F. C.;

- Filgueiras, P. R.; Castro, E. V. R.; Romão, W.; Santos, M. F. P.; Silva, J. O. R.; Lacerda Júnior, V. Study of the effect of temperature and gas condensate addition on the viscosity of heavy oils. *Journal of Petroleum Science and Engineering* **2016**, *142*, 163. [\[CrossRef\]](#)
- ¹¹ Becker, J. R.; Crude Oil Waxes, Emulsions and Asphaltenes. 1st ed., Pennwell Books: Tulsa, 2001.
- ¹² Speight, J. G.; Petroleum Asphaltenes. *Oil & Gas Science and Technology* **2004**, *59*, 467. [\[CrossRef\]](#)
- ¹³ ASTM D5854-96(2015), Standard Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products, ASTM International, West Conshohocken, PA, 2015. [\[CrossRef\]](#)
- ¹⁴ ASTM D4377-00(2011), Standard Test Method for Water in Crude Oils by Potentiometric Karl Fischer Titration, ASTM International, West Conshohocken, PA, 2011. [\[CrossRef\]](#)
- ¹⁵ ISO12185(1996), Crude Petroleum And Petroleum Products-Determination Of Density-Oscillating U-Tube Method, International Organization for Standardization, Geneva, SWZ, 1996. [\[Link\]](#)
- ¹⁶ ASTM D1250-08(2013)e1, Standard Guide for Use of the Petroleum Measurement Tables, ASTM International, West Conshohocken, PA, 2013. [\[CrossRef\]](#)
- ¹⁷ ASTM D664-11ae1, Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration, ASTM International, West Conshohocken, PA, 2011. [\[CrossRef\]](#)
- ¹⁸ ASTM D97-17. Standard Test Method for Pour Point of Petroleum Products, ASTM International, West Conshohocken, PA, 2017. [\[CrossRef\]](#)
- ¹⁹ ASTM D4294-08, Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry, ASTM International, West Conshohocken, PA, 2008. [\[CrossRef\]](#)
- ²⁰ ASTM D2549-02, Standard Test Method for Separation of Representative Aromatics and Nonaromatics Fractions of High-Boiling Oils by Elution Chromatography, ASTM International, West Conshohocken, PA, 2012. [\[CrossRef\]](#)