

Viscosity Reduction of Sharqi Baghdad Heavy Crude Oil Using Different Polar Hydrocarbons, Oxygenated Solvents

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Abstract

This work studied the facilitation of the transportation of Sharqi Baghdad heavy crude oil characterized with high viscosity 51.6 cSt at 40 °C, low API 18.8, and high asphaltenes content 7.1 wt.%, by reducing its viscosity from break down asphaltene agglomerates using different types of hydrocarbon and oxygenated polar solvents such as toluene, methanol, mix xylenes, and reformat. The best results are obtained by using methanol because it owns a high efficiency to reduce viscosity of crude oil to 21.1 cSt at 40 °C. Toluene, xylenes and reformat decreased viscosity to 25.3, 27.5 and 28,4 cSt at 40 °C, respectively. Asphaltenes content decreased to 4.2 wt. % by using toluene at 110 °C. And best improvement in API of the heavy crude oil is 26.1 at 40 °C by using xylenes.

Keywords: Heavy crude oil; transportation; asphaltene content; viscosity reduction

Introduction

Petroleum transportation has become a complex and highly technical operation. One of the major difficulties in the pipeline transportation is the high viscous fluids that require efficient and economical ways to transfer the heavy crude. Heavy crude oils have a density approaching or even exceeding that of water. They are usually extremely viscous, with a consistency ranging from that of heavy molasses to solid at room temperature. Heavy crude oils are not pumped easily through the pipelines because of the high concentrations of sulfur and several metals, particularly nickel and vanadium. Crude oils are complex fluids that can cause a variety of difficulties during the production,

separation, transportation and refining of oil [1, 2].

Heavy crude is high viscosity, and high specific gravity as well as heavy molecular composition. It is dense and viscous due to the high presence of naphthenes and paraffines [3]. Heavy crude oil contains greater proportions of higher-boiling constituents such as (lubricating oil motor oils, lubricants, engine oil, cylindrical oil, and gear oil), greases and wax, and residue (residual fuel oils, coke, tar and asphalt). In addition, more aromatic, and heteroatom containing (N, O, S and metals) are contained in heavy petroleum than light petroleum [4].

Such asphaltening is considered as a ruthless problem within the petroleum industry due to their various costly problems in terms of production loss

and transport difficulties. Heavy crudes account for a large fraction of the world's potentially recoverable oil reserves. The viscosities of those crudes at room temperature vary from 100mPas to more than 10^5 mPas. Generally, crude oil with viscosity <400 mPas is the classical maximum desired pipeline viscosity [5-7].

The high viscosity of heavy oil is a crucial factor that strongly affects its up-stream recovering, down-stream surface transporting and refining processes. A better understanding of the origination of its high viscosity can greatly help to find more effective and economical methods for recovering the heavy oil and reducing the related capital and/or operating costs [8].

Therefore, different methods are used in order to reduce the viscosity of the heavy crude for the pipeline transportation. For instance, upgrading, dilution with lighter crudes or alcohols, heating, and the use of surfactants to stabilize emulsions are some of those common methods, oxidation and drag reduction. Heating is a common method utilized to overcome the above noted problems of transporting heavy oil by pipeline [1].

Another way to transport heavy oil is to heat the oil as the viscosity decreases very rapidly with increasing temperature. The basis for this method lies in the fact that as heavy oil is heated, the viscosity of the heavy oil is reduced and thus made easier to pump. Therefore, it is important to heat the oil to a point where the oil has a substantially reduced viscosity. A principle drawback to the use of heated pipelines is the high capital and operational cost of such a heated pipeline over long distances [5]. In addition, underwater pipeline transportation of heavy oil through a heated pipeline is very difficult due to the cooling effect of the surrounding water and the practical difficulty of

maintaining pumping stations and heating stations [9, 10].

Several experimental studies have shown that heavy oil viscosity is strongly dependent on the volume fraction, chemical structures, and physicochemical properties of its asphaltenes, which are the most polar and/or heaviest components in heavy oil [11, 12].

Petroleum asphaltenes are defined as a solubility class of the heavy components in crude oil which are insoluble in nonpolar solvents. Asphaltenes exist in the form of colloidal dispersions stabilized by other constituents of the crude oil. These naturally occurring dispersions can be easily disturbed by a variety of mechanical and physicochemical conditions involved in oil field recovery and production. Changes in temperature and pressure, commingling of crude and condensate streams, and especially the use of enhanced recovery techniques can result in asphaltene destabilization, precipitation, and eventual deposition. Once deposited, asphaltenes pose a multitude of problems for crude oil producers [13].

Studies have shown that asphaltenes exhibit properties similar to colloids. These colloids exist in the heavy oil matrix in a micelle form. Since the mole fraction of resins is higher than asphaltenes in petroleum, micelles are richer in resins. Asphaltenes also exhibit properties of colloidal systems such as the 'critical micelle concentration' (CMC) at which aggregates begin to form. The breaking down of asphaltenes upon the addition of polar solvents can be rationalized in terms of a reduction in the solubility parameter or the polarity of the hydrocarbon medium [14-16].

The formation of micelles is believed to be primarily due to the interaction between asphaltene species or

asphaltene-resin fractions. The nature of the intermolecular or intramolecular forces that cause the formation of asphaltene micelles is not clear at present. It has been suggested that a number of forces may be involved including Van der Waals attraction, dipole-dipole interaction, hydrogen bonding, electron-transfer or charge transfer between aromatics (π - π bonding), and porphyrin interaction [17-18].

The aim of the present work is to study the reduction viscosity of heavy crude oil using different polar hydrocarbons and oxygenated solvents (toluene, methanol, mix xylenes and reformat) at different concentration (4, 8, 10 and 12 wt.%) and different temperature (40 °C and boiling point for each solvents except reformat at 100 °C) on the efficiency of viscosity reduction systems.

Experimental

Feedstock

The feedstock in this study was Sharqi Baghdad crude oil, obtained from Baghdad east oil fields. The properties of the crude are given in Table 1.

Table 1: Physical properties of Sharqi Baghdad crude oils

Test	Crude oil from east of Baghdad
Viscosity at 40°C	51.6 (cSt)
API at 60°F	18.8
Asphaltene content	7.1 wt.%
Sulfur content	5.0 wt.%
Vanadium	88 ppm
Iron	25 ppm
Nickel	38 ppm
Saturate compounds	42.2 ppm
Naphthene compounds	23.8 wt.%

Light Naphtha

Light naphtha was supplied from Al-Doura refinery, with viscosity and density 6.76×10^{-7} (stock) and 0.65 g cm^{-3} , respectively.

Reformat

Reformat was supplied from Al-Doura refinery, with boiling point 225 °C.

Toluene Solvent (C₇H₈)

Toluene was supplied from (GCC.Gainland chemical company). With molecular weight, boiling point and density are (92.14 kg/mole, 110 °C and 0.87 g/cm^3), respectively.

Methanol Solvent (CH₃OH)

Methanol was supplied from (POCH SA) company. With molecular weight, density and boiling point are 32.04, 0.79 g cm^{-3} and 65 °C, respectively.

Xylenes Mixture (C₈H₁₀)

Xylenes mixture of isomers, extra pure, is supplied from Al-Doura refinery. With molecular weight, density and boiling point are 106.17, 0.68 g cm^{-3} and 137.76 °C, respectively.

Distillation Stage

Two liters of Sharqi Baghdad heavy crude oil were subjected to the distillation using computerized laboratory apparatus (according ASTM 5236) (PIGNAT COMPANY, FRANCE) that consists of distillation flask, heating mantle, distillation column, condenser, thermometer and fraction collector as shown in Fig. 1. Distillation was carried out to remove naphtha from crude oil to obtain stripped crude oil; the initial boiling point was 75 °C to the end point of distillation was 175 °C. Distilled naphtha was represented 17% vol. based on crude oil.

Effect of Solvent Type on Asphaltene Content

Figures 3, 4, 5 and 6 show the effect of different types of polar solvents with different concentration on the asphaltene content. The feedstock is exposed to different solvents at different concentrations and temperatures. These solvents reduced asphaltene content affected by temperature and the action of polar solvents to disperse asphaltene agglomerates. From Figures 3, 4, 5 and 6, the higher reduction in asphaltene content is obtained with toluene 4.3638 wt.% at 40°C, while 5.0071 wt.% asphaltene is obtained with reformat, 5.0381 wt.%, and 5.0392 wt.% asphaltene content is obtained with xylenes and methanol, respectively. It is well known that special types of compounds have the ability to break down asphaltene agglomerates. The presence of π electrons in the ring of solvents may play a role in the interaction between the compounds added and the n electrons in the polyaromatic systems of the asphaltene agglomerates. The compounds kept to one ring to keep the size of the molecules allow for a greater diffusion through the crude oil matrix and penetration into the asphaltene agglomerates.

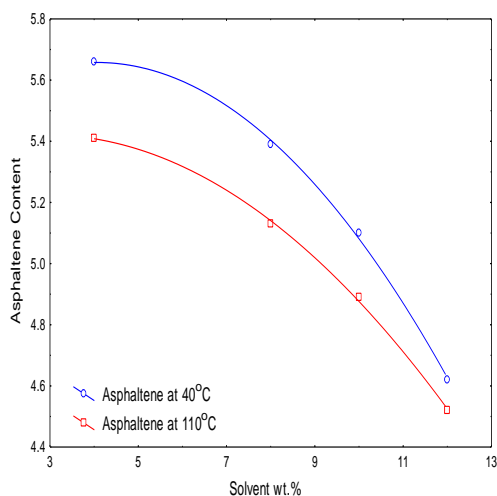


Fig. 3: Effect of toluene weight fraction on asphaltene content of crude oil

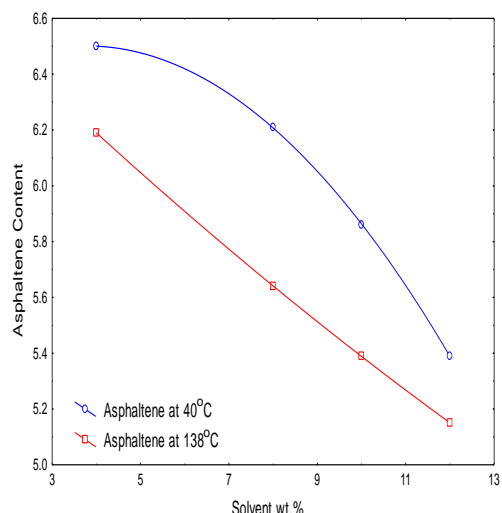


Fig. 4: Effect of xylene weight fraction on asphaltene content of crude oil

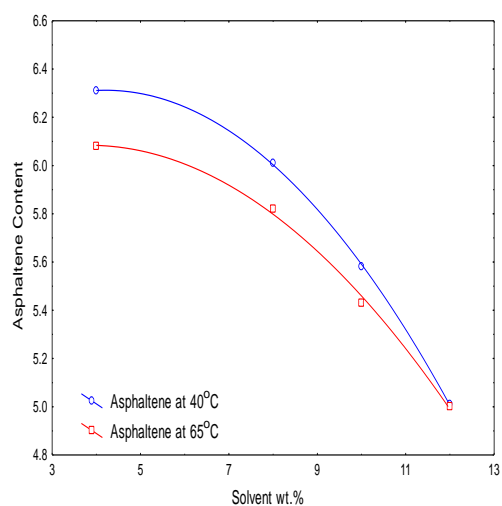


Fig. 5: Effect of methanol weight fraction on asphaltene content of crude oil

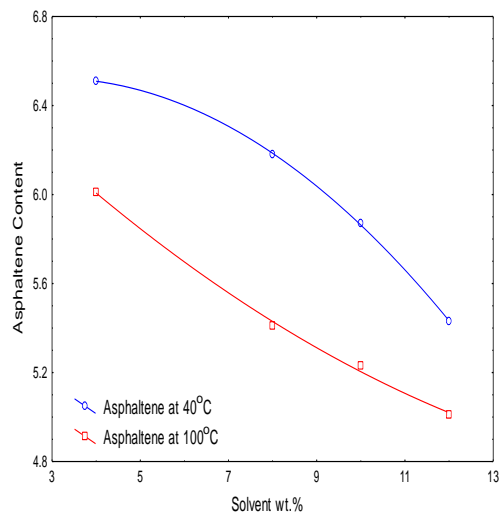


Fig. 6: Effect of reformat weight fraction on asphaltene content of crude oil

Effect of Solvent Type on Viscosity

The effect of solvent concentration at different temperature on viscosity reduction of Sharqi Baghdad heavy crude oil was studied. Figures 7, 9, 11 and 13 show the effect of different concentrations of toluene, methanol, xylenes, and reformat on viscosity of crude oil at different temperatures, respectively. The viscosity decreased with increasing solvent concentration. The heavy crude oil viscosity decreases maximally from 51.6 cSt to 21.7 cSt at 110 °C by using toluene, and to 21.1, 27.5, and 28.4 cSt at 40 °C by using methanol, xylenes, and reformat, respectively.

It is widely assumed that the asphaltene molecules in oil agglomerate to form micelle-like cluster. Interactions between these clusters contribute towards the viscosity of the oil. By breaking these agglomerates apart, viscosity will be reduced. So, increasing polar solvent concentration had an essential role on increasing and acceleration of breaking down the asphaltene agglomerates, and thus achieved deeper viscosity reduction [19].

The addition of a polar solvent acted on the colloidal structure of the asphaltenes and the viscosity decreased. The higher the polarity parameter or the hydrogen bonding parameter of the solvent was, the greater the viscosity reduction was [20].

To access the extent of the viscosity reduction, the percentage of viscosity reduction VR % was introduced and it was calculated by Eq. 1[21].

$$VR\% = \frac{(\eta_r - \eta_c)}{\eta_r} * 100 \quad \dots(1)$$

Where η_r and η_c are the reference and corresponding viscosities of crude oil in cSt at 40°C. Figures 8, 10, 12, and 14 show the viscosity reduction

percentage vs. solvent concentration at different temperatures for different solvents. Figs. 7 and 8 show that toluene gave best viscosity reduction at 110 °C; toluene is a strong solvent that owns a high ability to disperse the asphaltene agglomerates.

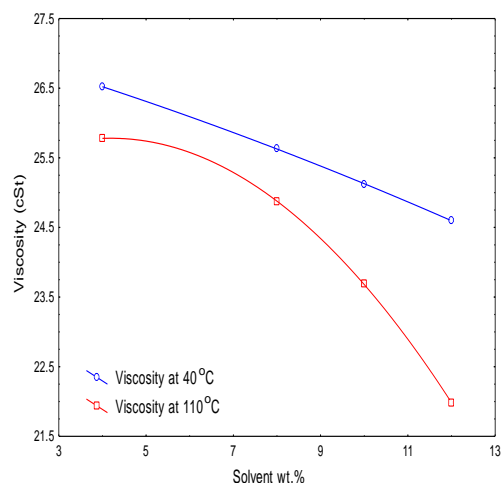


Fig. 7: Effect of toluene weight fraction on viscosity of crude oil

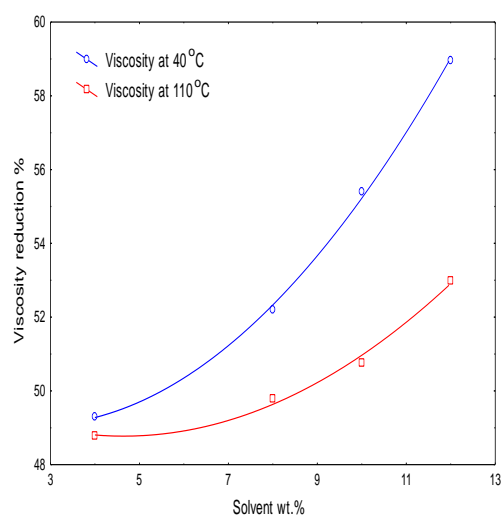


Fig. 8: Effect of toluene weight fraction on viscosity reduction percentage of crude oil

If partial solubility or phase separation is occurring such as methanol, then a lower than expected viscosity measurement will be recorded. This is because when phase separation occurs, then the more fluid phase, the additive compound, may tend to concentrate around the spindle of the viscometer, and thus lower apparent viscosity [22].

Methanol owns high polarity more than the other solvent used in this study. So the lowest crude oil viscosity was achieved by this solvent. The effect of methanol concentration on viscosity is better at low temperature 40 °C than at its boiling point or high temperature, and this is more economical point of work as shown in Figure 9. Figure 10 clarify VR% of methanol.

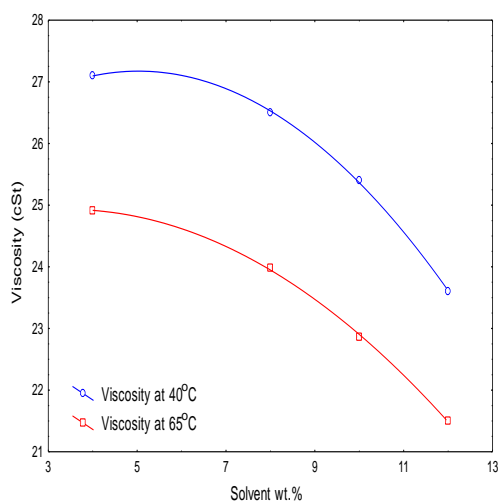


Fig. 9: Effect of methanol weight fraction on viscosity of crude oil

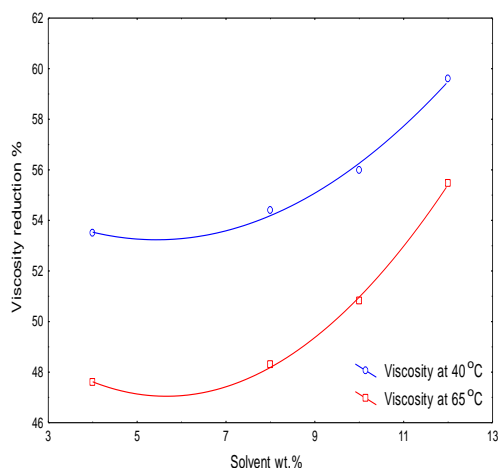


Fig. 10: Effect of methanol weight fraction on viscosity reduction percentage of crude oil

Xylenes mixture gives good results on reducing the viscosity of heavy crude oil. Pure isomers of xylenes are more efficient at low temperature, 40 °C, than high temperature, 138 °C, as shown in Figure 11; Figure 12 clarifies VR%.

Figure 13 shows the effect of using reformat to reduce viscosity in crude oil at different concentrations and different temperature; viscosity of the crude at 40 °C is better than 100 °C. Figure 14 clarifies VR% of reformat .

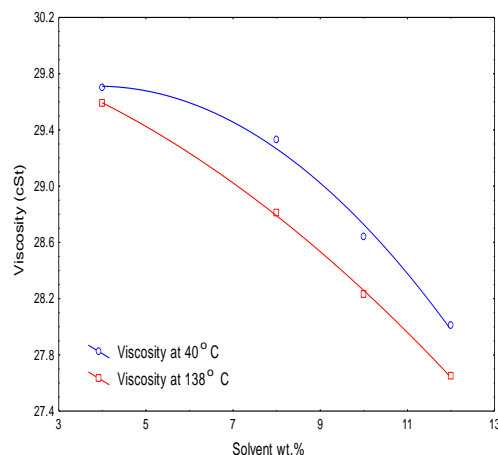


Fig. 11: Effect of xylenes weight fraction on viscosity of crude oil

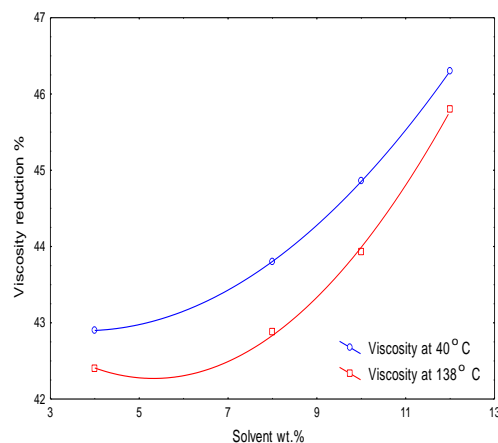


Fig. 12: Effect of xylenes weight fraction on viscosity reduction percentage of crude oil

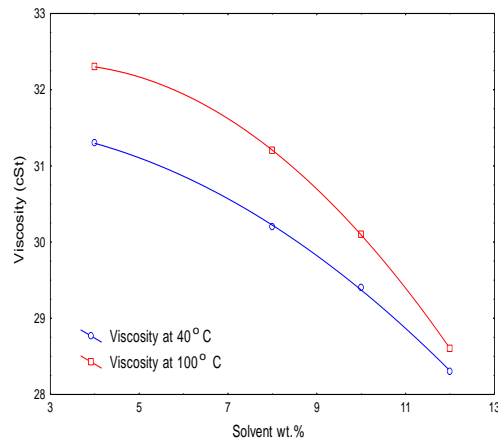


Fig. 13: Effect of reformat weight fraction on viscosity of crude oil

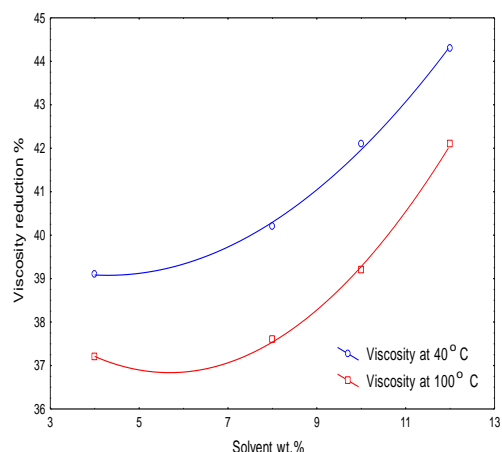


Fig. 14: Effect of reformate weight fraction on viscosity reduction percentage of crude oil

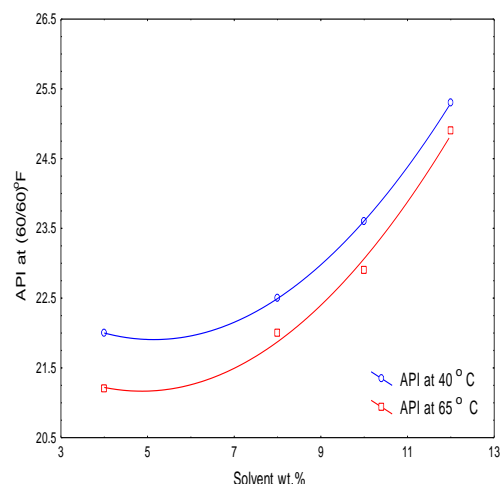


Fig. 16: Effect of methanol weight fraction on API of crude oil

API Gravity

The API of heavy crude oil was increased with increasing solvent concentration at different temperatures. Figures 15, 16, 17 and 18 show the effect of solvents concentration on improvement of API values at difference temperatures.

It is clear that the breaking down of asphaltenes agglomerates and reducing presence of micelle-like clusters had an essential role in the improvement of API for heavy crude oil, where the polar solvents played on dispersion of asphaltenes molecules, reduction of their molecular size, and decreasing of asphaltenes content, which led to the increasing of API of heavy crude oil.

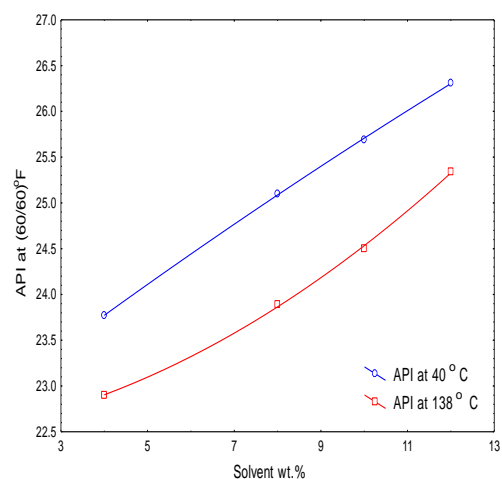


Fig. 17: Effect of xylenes weight fraction on API of crude oil

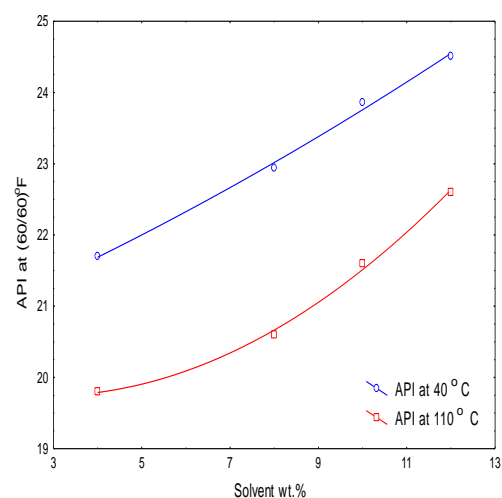


Fig. 15: Effect of toluene weight fraction on API of crude oil

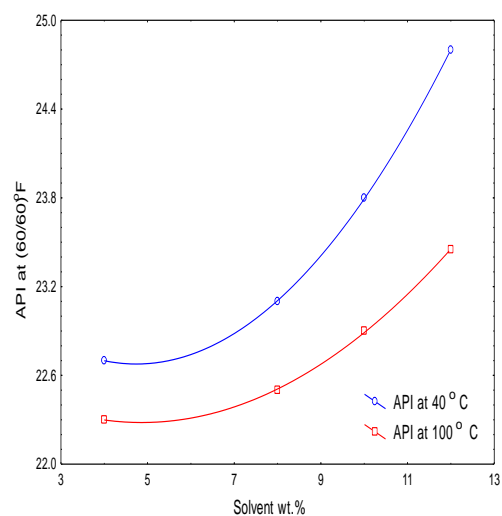


Fig. 18: Effect of reformate weight fraction on API of crude oil

Conclusion

From rheological and structure measurements heavy oils can be described as aggregation of agglomeration asphaltene particles; heavy viscosities of this type of crudes are due to the entanglement of solvated asphaltene particles. Some ways that will limit the entanglement will likely reduce the viscosity.

According to the results obtained from this study, the following conclusions are obtained:

1. Treatment of the heavy crude oil with different polar solvents gave high reduction in viscosity and asphaltene content; methanol owned a high efficiency to reduce viscosity of crude oil to 21.109 cSt at 40 °C. Toluene, xylenes and reformat decreased viscosity to 25.37, 27.510 and 28.407 cSt at 40 °C, respectively.
2. API of heavy crude oil improved to 26.193 at 40 °C by using xylenes, toluene, methanol and reformat improvement API to 23, 25.374 and 24.753 at 40 °C, respectively.
3. Asphaltenes content decreased to 4.259 wt. % by using toluene at 110 °C. Methanol, xylenes and reformat decreased asphaltene content to 5.0392, 5.0381 and 5.0071 wt. % at 40 °C, respectively.
4. Crude oil viscosity decreased with decreasing asphaltene content.
5. Crude oil viscosity was decreased with increasing polar solvent concentration.

References

- 1- Al-Besharah JM, Salman OA, Akashah SA., (1987), "Viscosity of crude oil blends". *Ind Eng Chem Res* 1987; 26:244, pp 5–9.
- 2- Speight JG., (1998), "Petroleum chemistry and refining". Philadelphia: Taylor and Francis.
- 3- Petroleum- Wikipedia, the free encyclopedia. Retrieved April 12,

(2007), from <http://en.wikipedia.org/wiki/petroleum>.

- 4- Speight, J. G., (2001), "Handbook of Petroleum", John Wiley and Sons Inc., Canada, pp: 1- 82.
- 5- Nunez G, Briceno M, Mata C, Rivas H, Joseph D., (1996), "Flow characteristics of concentrated emulsions of very viscous oil in water systems". *J Rheol* 1996, 40:405-23.
- 6- Fruman DH, Briant J. (1983), "Investigation of the rheological characteristics of heavy crude oil-in-water emulsions". In: International conference on the physical modeling of multi-phase flow. England: Coventry.
- 7- Schumacher MM. (1980), "Enhanced recovery of residual and heavy oils". New Jersey: Park Ridge, Noyes Press.
- 8- Peng Luo, Yongan Gu, (2006), "Effects of asphaltene content on the heavy oil viscosity at different temperatures" Petroleum Technology Research Centre (PTRC), Petroleum Systems Engineering, Faculty of Engineering, University of Regina, Regina, Saskatchewan, S4S0A2 Canada, pp 1096.
- 9- Ali MA, Nofal WA. (1994), "Application of high performance liquid chromatography for hydrocarbon group type analysis of crude oils". *Fuel Sci. Technol. Int.*, 12(1):21–33.
- 10- Zaki NN, Butz T, Kessel D. Rheology, (2001), "particle size distribution, and asphaltene deposition of viscous asphaltic crude oil-in-water emulsions for pipeline transportation". *Petrol Sci. Technol.*; 19:425–35.
- 11- Khan MAB, Mehrotra AK, Svrcek WY. (1984) , "Viscosity models for gas-free Athabasca

- bitumen". *J Can Pet Technol*; 23:4, pp7–53.
- 12- Puttagunta VR, Miadonye A, Singh B. (1993), "Simple concept predicts viscosity of heavy oil and bitumen". *Oil Gas J*; 91:7 pp 1–3.
- 13- Manek M.B., Nallo/Exxon, (1995), "Asphaltene Dispersants as Demulsification Aids", *Energy Chemicals L.P. , SPE International Symposium on Oilfield Chemistry*, pp 14-17.
- 14- Storm, D.A.; Barresi, R, J.; DeCanio, S.J., *Fuel*, (1991), "Colloidal nature of vacuum residue", pp 779-782.
- 15- Speight, J.G., (1991), "The Chemistry and Technology of Petroleum", 2^{ed.}, Marcel Dekker: New York, NY.
- 16- Wiehe, I.A., (1992), "Solvent-resid phase diagram for tracking resid conversion", *Ind. Eng. Chem. Res.*, pp. 530-536.
- 17- Wiehe, I.A., (1993), "A phase-separation kinetic model for coke formation", *Ind. Eng. Chem. Res.*, pp 2447-2454.
- 18- Li, S.; Liu, C.; Que, G.; Liang, W.; Zhu, Y., (1997), "A study of the interactions responsible for colloidal structures in petroleum residua", *Fuel*, pp 1459-1463.
- 19- Mark W. Badger and Harold H. Schobert, "Viscosity Reduction in Extra Heavy Crude Oils", *The Laboratory for Hydrocarbon Process Chemistry The Energy Institute. 209 Academic Projects Building, the Pennsylvania State University*, pp 461.
- 20- P. Gateau , I. Hénaut , L. Barré and J.F. Argillier, (2004), "Heavy Oil Dilution", Vol. 59, No. 5, *Oil and Gas Science and Technology – Rev. IFP*, pp. 503-509.
- 21- Ghannam MT, Esmail N., (2006), "Flow enhancement of medium-viscosity crude oil", *J Pet Sci Technol*; 24(8):9, pp85-99.
- 22- Brian Clark, (2007),"Heavy Oil, Extra-Heavy Oil and Bitumen Unconventional Oil", national petroleum council, working document of the NPC Global Oil and Gas Study ,topic paper 22,pp 4.