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Evaluation of Asphaltenes Deposition Inhibition Factors in Heavy Crude Oil Pipelines

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Abstract

Asphaltenes deposition is considered as Achilles's heel in the oil industry. The nucleation, precipitation and deposition of asphaltenes reduce the production rate significantly in affected wells and sometimes it can completely block the flow by plugging the flowlines, tubing and process facilities, in severe cases. This chapter evaluates the extrinsic and the intrinsic (thermodynamic) factors within the heavy crude oil production system. The main consequences of asphaltenes deposition are discussed such as the solvent-to-crude oil dilution ratio, crude oil physical properties (cloud point, pour point and API gravity), chemical solvent type (carbon number, functional group), agitation time and temperature changes. This chapter is expected to become the means for understanding the factors affecting the asphaltenes nucleation, precipitation and deposition.

Keywords: heavy crude oil, flow assurance, asphaltenes, deposition, inhibition

1. Introduction

Oil industry has been increasing its activities of crude oil production in subsea environments, deep waters and cold environments [1]. However, the physical and chemical conditions of these unconventional reservoirs have been challenging in which oil industry needs to overcome flow assurance issue such as asphaltenes deposition [2].

Asphaltenes deposition will affect the oil production rate at all oil production stages [3]. For example, when asphaltenes deposit in reservoir rock, they change the rock wettability hence decrease the chances of having an effective oil recovery [4, 5]. In some enhanced oil recovery (EOR) methods such as carbon dioxide injection [6] and chemical (cEOR) [7], the guest chemical would interact with asphaltenes in crude oil and subsequently result in asphaltenes deposition. Crude oil which flows in flowlines, tubing or process facilities will create a temperature gradient within a specified boundary [8, 9]. This temperature change will weaken the molecular interactions of resins which hold the asphaltenes molecule in crude oil. Due to its polarity, asphaltenes molecule will accumulate and subsequently start to nucleate. In general, asphaltenes deposition is considered as the major problem for oil industries as it occurs in upstream, midstream and downstream.

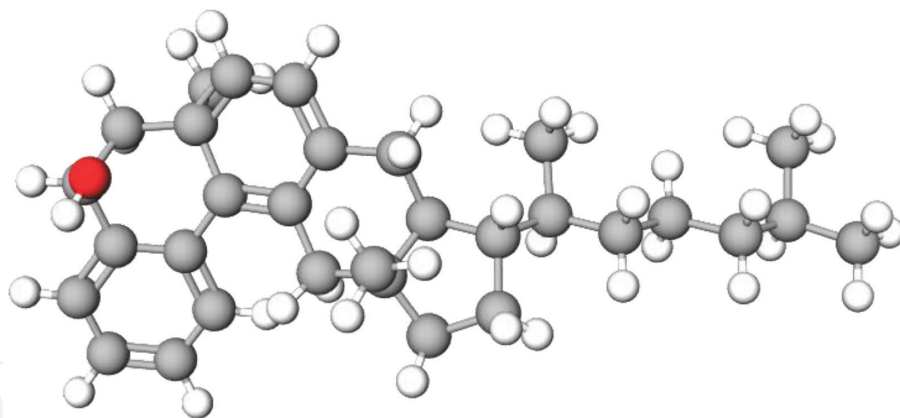


Figure 1.
Asphaltenes molecular structure.

Asphaltenes are the heaviest, polar hydrocarbon substances containing hetero-atoms such as nitrogen, sulfur and oxygen. Asphaltenes have an average molecular weight, MW_{ave} of 750 g/mol. **Figure 1** shows a schematic structure of the continental-model asphaltenes which obtained using MolView software v2.4.

There are several approaches for inhibiting deposition of asphaltenes such as via physical removal, use of dispersant and use of chemical solvent. Physical removal is done by using a pigging tool. It is however uneconomical because the collected solid asphaltenes must be properly disposed and the production must halt for the workers to conduct pigging. The use of dispersant is also uneconomical as the oil industry will need to use a large amount of dispersant for a long period of time. Chemical solvent such as benzene, toluene, chlorate or xylene as asphaltenes inhibitor is widely used as the base component of commercial chemical inhibitor. But, due to their low flash point and high toxicity level, these chemical solvents require extra safety precaution during handling and storage.

Since asphaltenes have a complex structure, differ depending on oil reservoirs and are not in any well-defined chemical group, it is difficult to predict the reason why asphaltenes became unstable and deposited out from crude oil [10]. Previous studies have revealed that asphaltenes deposition is a function of various parameters [11, 12]. Hence, this chapter evaluates the effect of asphaltenes deposition inhibition factors such as solvent-to-crude oil dilution ratio, crude oil physical properties (cloud point, pour point and API gravity), the chemical solvent type (carbon number, functional group), agitation time and temperature change on two types of Malaysia crude oils. The findings from this study are desirable to develop prevention and remediation methods for asphaltenes deposition problem.

2. Materials and methods

Pre-treated crude oil samples were collected from Malaysia oilfield with properties listed in **Table 1**. The crude oil samples contain negligible water and solids (such as sand, clay and corrosion debris).

Different types of liquid solvent were bought from Fisher Chemicals with a reported purity of 98–99%. The molecular structures of the solvents are shown in **Table 2**, used to control asphaltenes precipitation. Mixtures of solvent-to-crude oil dilution ratio of 1:1, 5:1, 10:1 and 15:1 were prepared for each solvent.

The method used to deposit the asphaltenes particles from crude oil is called “standard direct experimental” method. This method follows the modified ASTM 2007/ASTM D6560 standard procedure [13, 14]. Once the solvent and the crude

Properties	Sample 1	Sample 2
Cloud point (°C)	33.8	15.0
Pour point (°C)	−2.0	−18.0
API gravity (°API)	37.4	12.5
Wax content (%)	4.0	10.0
Phase	Liquid	Liquid
Color	Dark brown	Dark brown

Table 1.
Crude oil properties for the study.

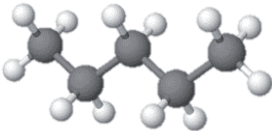
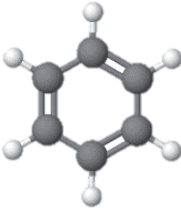
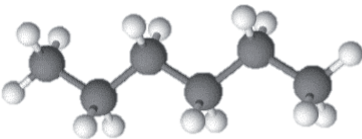
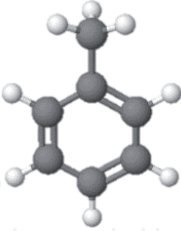
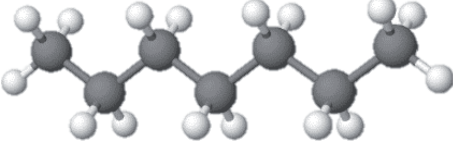
Solvent	Molecular formula (MW)	Molecular structure
n-Pentane	C ₅ H ₁₂ (72.15 g/mol)	
Benzene	C ₆ H ₆ (78.11 g/mol)	
n-Hexane	C ₆ H ₁₄ (86.18 g/mol)	
Toluene	C ₇ H ₈ (92.14 g/mol)	
Heptane	C ₇ H ₁₆ (100.21 g/mol)	

Table 2.
Molecular structure and molecular weight (MW) of solvents used for the study, in increasing carbon number.

oil were mixed together according to the desired dilution ratio, the resulted mixture was then placed in a water bath at room temperature and left for 3 h under agitation condition. Then, the aliquot was placed in a container and centrifuged at 10,000 rpm (SIGMA 3-18K, United Kingdom) with relative centrifugal force (RCF) of 16,000 times gravity. The deposited asphaltenes were filtered by using a Whatman® filter paper, grade number 42. Finally, the asphaltenes particles were dried in a vacuum oven at 100°C for 30 min and then weighed (with digital

instrument precision: ± 0.001 g) to determine the amount of asphaltenes precipitated. The entire procedure was repeated for different agitation time (6 and 9 h) and temperature (50 and 75°C).

3. Results and discussion

The observable deposited asphaltenes particle is shown in **Figure 2**. There have been a wide range of asphaltenes particle size as reported in literatures; 2–5 nano-micron [11] and 34–113 micron [13]. It is proposed that asphaltenes tend to self-aggregate by π - π interactions and originate the asphaltenes “nucleus” which consist of stacked nanoaggregates.

Figure 3a and **b** shows the plots for the deposited asphaltenes particles when n-pentane was used as the solvent type. Systematically, n-pentane is selected as the first stage of this study as recommended by the modified ASTM 2007 procedure.

At 1:1 dilution ratio, the amount of asphaltenes deposited was 0.860 g when the agitation time was 3 h (as shown in **Figure 3a**). At 15:1 dilution ratio, the amount of asphaltenes deposited was 3.100 g, at the same agitation time. Result showed that the amount of deposited asphaltenes particle is increased with solvent-to-crude oil dilution ratio. This is due to the increasing formation of unstable asphaltenes aggregates. It is expected that a maximum asphaltenes yield would be produced at a dilution ratio of 40:1 [15].

The same trend was found at longer agitation time, i.e., 6 and 9 h. The increasing amount of deposited asphaltenes particles at higher dilution ratio was verified with published results [16, 17]. In the presence of n-pentane solvent, the asphaltenes particles became unstable and precipitated as primary particles. At higher volume of the solvent and longer agitation time, more resins which responsible for asphaltenes solubility in crude oil are “washed off” that lead to rapid aggregation of asphaltenes molecules. Consequently, macroparticles (i.e., heavier particles) asphaltenes are formed.

Interestingly, at lower region of dilution ratio (1:1 and 5:1), the amount of asphaltenes deposited from sample A crude oil having agitation time of 3 h is the same as that of 6 h (as in **Figure 3a**). As one may see, **Figure 3b** shows the same behavior despite having different physical properties. This indicates that the



Figure 2.
Filtered asphaltenes particles.

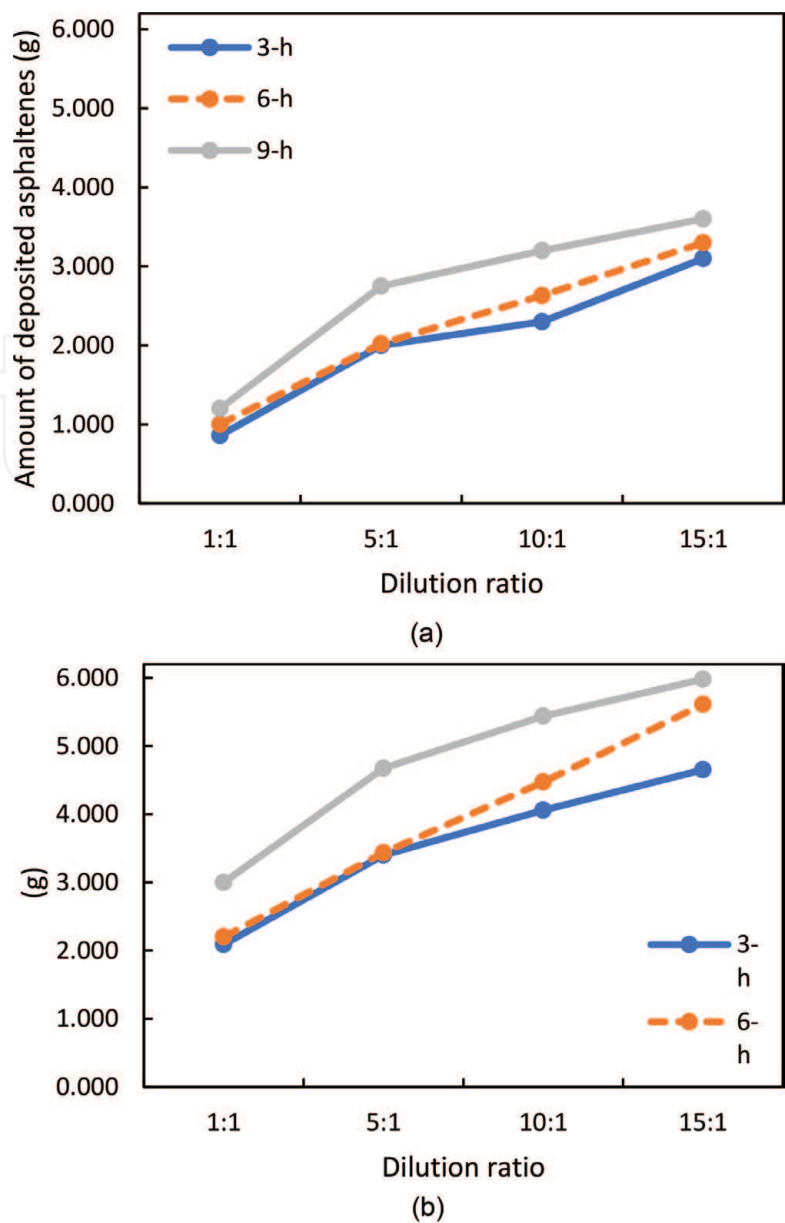


Figure 3. Amount of deposited asphaltenes at selected solvent-to-crude oil dilution ratio and different agitation time. The conditions of experiment were: chemical solvent type = *n*-pentane and $T = 30^{\circ}\text{C}$. (a) Sample A and (b) sample B.

solubility of asphaltenes in *n*-pentane solvent is approximately constant at low solvent concentration or in this case lower region of solvent dilution ratio. We proposed that this observation is due to the rapid diffusion and aggregation of asphaltenes molecules hence resulting in high precipitation rate at short mixing times. It is worth highlighting that future asphaltenes deposition studies should distinct between the lower and higher regions of solvent dilution ratio. Note that the kinetic effect is ignored here since the agitation time is constant (either at 3 or 6 h).

To evaluate the effect of the properties of the crude oil such as the cloud point, pour point and density (reflected by the API gravity of crude oil), plots in **Figure 3a** and **b** were compared. Although sample B having higher wax content and heavier, i.e., more dense than sample A, both plots showed similar trend of increment of deposited asphaltenes particles at higher volume of solvent (i.e., higher region of solvent dilution ratio). At 1:1 dilution ratio, we found that the magnitude of increment for both sample A and sample B is 2.2–2.5, when the agitation time is 3–9 h. Surprisingly, at 5:1, 10:1 and 15:1 dilution ratio, the magnitude of increment is constant, i.e., ~1.7 when the agitation time is 3–9 h. Previous study [13] showed that

the amount of deposited asphaltenes was either reached a plateau value or reduced, when the dilution volume is higher than 15:1.

Figure 4a–d shows the plots for the deposited asphaltenes particles when different types of liquid solvent were added to sample A. For the molecular structure of these solvents, see **Table 2**. This study shows the effect of increment carbon number (n-pentane, C5, n-hexane, C6 and n-heptane, C7) and the effect of functional group (i.e., alkane group and benzene-ring group). Firstly, we observed the influence of n-pentane, n-hexane and n-heptane at 30°C (as in **Figure 4a**). At dilution ratio 1:1, 0.860 g of asphaltenes were deposited when n-pentane and n-heptane were added. A slight reduced (0.710 g) amount was observed when n-hexane was added. This result suggests that the solubility of asphaltenes decreases when higher solvent carbon number was used. As the viscosity of the solvent increases with carbon number, asphaltenes diffusion is slower. Subsequently, fewer asphaltenes-asphaltenes collision which then leads to lesser amount of deposited asphaltenes.

Meanwhile, at dilution ratio from 5:1 to 15:1 (as in **Figure 4b–d**), we observed that the highest amount of asphaltenes was obtained when n-pentane was added, followed by n-hexane and lastly n-heptane. Interaction between the long, planar molecules of n-heptane and the planar, supramolecular asphaltenes compound would have resulted in lower steric effect, and thus leading to a decrease in aggregation size [18].

Secondly, we found that both benzene and toluene do not significantly influence the deposition of asphaltenes, having measurements of less than 0.005 g. Despite typically reported by authors worldwide, the asphaltenes deposition was not affected by thermodynamic temperature variation. The reason anchoring this observation is due to the solvent chemical properties. Asphaltenes are known to be miscible in benzene (1 benzene ring) and toluene (1 benzene ring and 1 methyl branch), or other similar structure compounds such as ethylbenzene (1 benzene

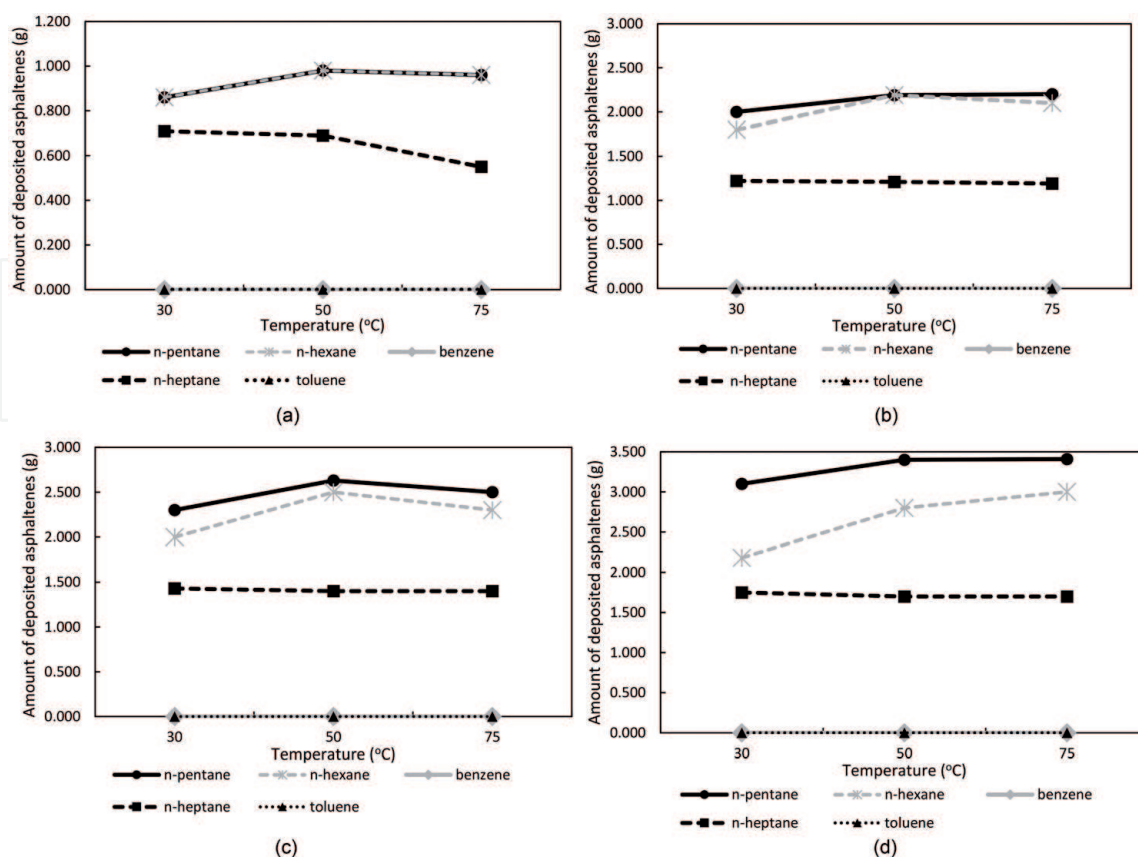


Figure 4. Amount of deposited asphaltenes as a function of solvent type and temperature. The conditions of experiment were: crude oil type = sample A, agitation time = 3 h. (a) 1:1, (b) 5:1, (c) 10:1, and (d) 15:1 dilution ratio.

ring and 1 ethyl branch) and xylene (1 benzene ring, 2 methyl branches). These solvents would interact with asphaltenes and give similar value of enthalpy of mixing ($+\Delta H_{\text{mix}} = 0.5 \pm 0.2 \text{ kJ}$) [19]. In asphaltenes mitigation strategy application, these benzene-based chemicals are applied as dispersants.

Temperature factor plays an important role in preventing or reducing asphaltenes deposition [20]. **Figure 4a** illustrates that 0.860, 0.980 and 0.960 g of asphaltenes particles were deposited at 30, 50 and 75°C, respectively when n-pentane was added. Consecutively, n-hexane follows the same trend, while n-heptane had resulted in 0.710, 0.690 and 0.550 g of asphaltenes deposits at 30, 50 and 75°C, respectively. In general, it was noted that a discontinuity increment in the amount of deposited asphaltenes occurs at increasing temperature. Heating process or existence of sufficient thermal energy hinders the mechanism of asphaltenes aggregation. This is due to the weak force of interparticle attraction between asphaltenes molecules and between asphaltenes and constituents (such as saturates and resins) [21] hence lowers the ability for the asphaltenes particles to coalesce. The influence of temperature effect on asphaltenes deposition was similar with earlier study [13].

4. Conclusions

For the two samples of Malaysia crude oil, the amount of deposited asphaltenes increased as the solvent-to-crude oil dilution ratio and the agitation time increased. Similar trend was observed for both samples despite having distinctive physical properties (cloud point, pour point and API gravity). Results also showed that the amount of deposited asphaltenes is solvent-dependent (carbon number and functional group) and temperature-dependent. Also, we suggest that future studies on asphaltenes deposition should be linked to low/high region of solvent dilution ratio.

Acknowledgements

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Nomenclature

MW	molecular weight, g/mol
CP	cloud point, °C
PP	pour point, °C
API	The American Petroleum Institute gravity
RCF	relative centrifugal force, g
ΔH_{mix}	enthalpy of mixing, J/mol

Abbreviations

cEOR	chemical enhanced oil recovery
API	The American Petroleum Institute gravity
ASTM	American Society for Testing and Materials

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