

DETERMINATION OF ASPHALTENE AND C, H, N, O, S CONTENTS IN CRUDE OIL FROM X-OILFIELD IN SOUTH SUMATRA

By: **Tjuwati Makmur**

Researcher at "LEMIGAS" R & D Centre for Oil and Gas Technology

Jl. Ciledug Raya, Kav. 109, Cipulir, Kebayoran Lama, P.O. Box 1089/JKT, Jakarta Selatan 12230 INDONESIA

First Registered on 14 September 2009; Received after Corection on 2 November 2009

Publication Approval on : 26 November 2009

ABTRACT

All analyzed crude oil samples contain firstly, the carbon contents in a range of 75.2830 % wt – 83.5739 % wt. Secondly, asphaltene with in a range of 0.6930 % wt – 1.8260 % wt and it can deposit in the formation and block the pore throats, which may reduce the permeability significantly. Thirdly, the hydrogen contents in a range of 9.1948 % wt – 11.2339 % wt and it is impurities crude oil indicator. Fourthly, the crude oil samples have zero % wt nitrogen contents and don't result in corrosive properties. However, the existence of the oxygen contents (in a range of 5.1634 % wt – 14.0560 % wt) and the sulfur contents (in a range of 0.1334 % wt – 0.2533 % wt) in the crude oil samples may cause corrosion problem.

Key words: asphatene, carbon, hydrogen, nitrogen, oxygen, sulfur, plugging, corrosion

I. INTRODUCTION

Asphaltenes in oil industry are the heaviest constituents of crude oil. Under initial reservoir fluid conditions, they are believed to be dissolved in the crude oil as colloidal particles. This gives the oil a black-brown coloration. Numerous production problems encountered in oil production have been associated with asphaltenes. Several factors, like changes in reservoir pressure, temperature, and composition, may cause asphaltene to precipitate from the crude oil as a solid. Solid asphaltenes are often found in the form of sticky and deformable deposits.

Asphaltenes are considered to be the least valuable component of the crude oil. The presence of asphaltenes means additional difficulties related to transport and processing due to the increased crude oil viscosity caused by the asphaltenes. Asphaltenes have high resistance to cracking and they are therefore often held responsible for decreasing the yield of petroleum distillates. Because the asphaltenes usually contain heavy metal components, they are very hard to biodegrade. This makes them unpopular from a petroleum waste perspective. But most commonly,

asphaltenes represent a significant problem from a production and reservoir management point of view.

At sufficiently low reservoir pressure, asphaltenes can deposit within the formation and block the pore throats, which may reduce the permeability significantly. Asphaltenes adsorbing onto the rock surface may shift the wettability properties of the rock from water-wet to oil-wet, which may reduce the relative permeability.

Another problem is related to the high viscosity of asphaltene rich crude oils, which can cause problems associated with production rate, pumping energies, and transfer rates. Furthermore, asphaltenes contribute in stabilizing tight water in oil emulsions. This can also lead to higher viscosity, or even blocking of pore throats. Asphaltenes are also a common nucleation site for paraffin crystallization, and the two substances are often found within the same deposit.

Deposits of asphaltenes may also lead to wellbore plugging, flow restrictions in tubings, flowlines and production facilities, fouling of downhole safety valves, and solids build-up in storage tanks. Well interventions for cleaning out asphaltene restrictions

and restore well productivity often constitute significant expenses for the affected oil companies.

Precipitation of asphaltenes in the formation usually happens near the wellbore because of the significant pressure draw-down generated there. But theoretically, the precipitation can occur throughout the whole reservoir. Asphaltenes deposited within the reservoir formation may lessen the permeability and cause formation skin that is very hard to repair.

A common definition is that asphaltenes are the material that is (1) insoluble in n-pentane (or n-heptane) at a dilution ratio of 40 parts alkane to 1 part crude oil and (2) re-dissolves in toluene.



Figure 2.1
Crude oil contains no asphaltene

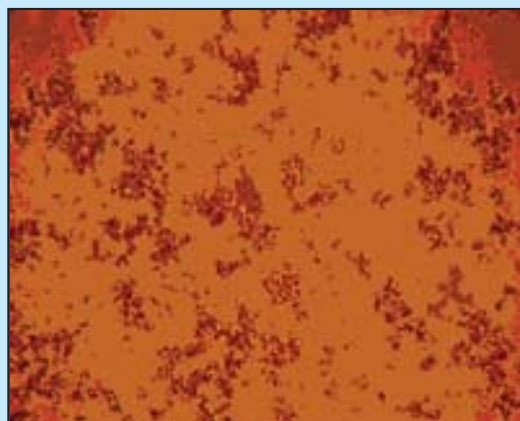


Figure 2.2
Example of the microscopic appearance
of asphaltene precipitated from
crude oils with n - C15

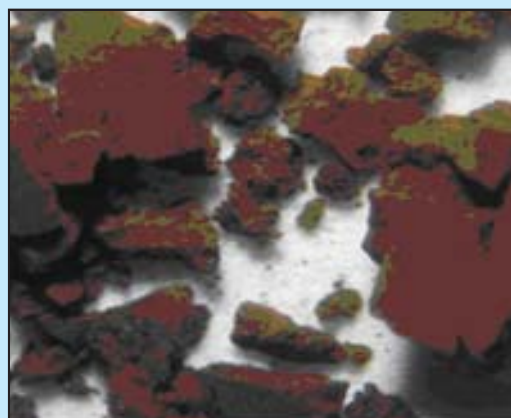


Figure 2.3
Example of the appearance of asphaltene
separated from Mars P - crude oils with
excess of n - C5

A wide variation in properties is found from the lightest crude oils to the highly asphaltenic crudes. The carbon content normally is in the range 83-87%, and the hydrogen content varies between 10 and 14%. In addition, varying small amounts of nitrogen, oxygen, sulfur are found in crude oils.

This paper is focused on determination of asphaltene, carbon, hydrogen, nitrogen, oxygen and total sulfur contents in several crude oil samples from X-oilfields, South Sumatra with using IP - 143 standard method. The results of laboratory tests will be able to give valuable information about its crude oil.

II. ASPHALTHENE

Buckley in 1996 carried out microscopic observation for identifying the onset of asphaltene flocculation. Crude oil contains no asphaltene (see in Figure 2.1). Example of the microscopic appearance of asphaltene precipitated from crude oils with n - C15 in Figure 2.2. Then, example of the appearance of asphaltene separated from Mars P - crude oils with excess of n - C5 can be seen in Figure 2.3 below.

The appearance of Figures 2.2 and 2.3 differ in color and in texture. Asphaltenes constitute a general class of aromatic-type substances which are defined on the basis of their solubility. Asphaltenes are soluble in carbon disulfide but insoluble in light alkanes such as n-pentane and n-heptane. Asphaltene molecules carry a core of stacked, flat sheets of condensed (fused) aromatic rings linked at

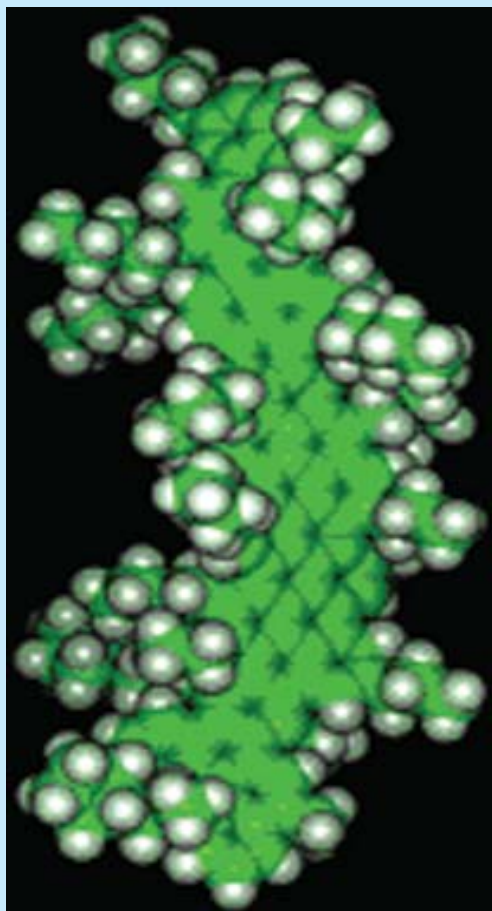


Figure 2.4
Sulphur, vanadium, and asphaltenes
contents in crude oil

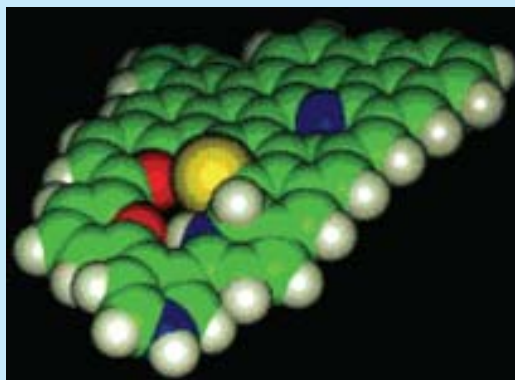


Figure 2.5
The form of a non-homogeneous
flat sheet of asphaltene

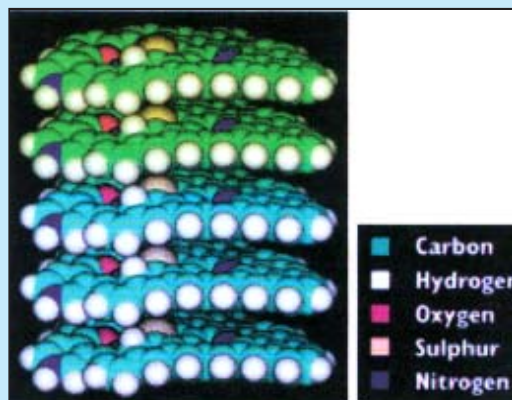


Figure 2.6
The structure of agglomeration
of asphaltene

their edges by chains of aliphatic and/or naphthenic-aromatic ring systems. The condensed sheets contain NSO atoms and probably vanadium and nickel complexes (see Figure 2.4).

The present trend in the petroleum industry is an increasing demand for light products. In order to meet the market demand, refineries convert a portion of their residuals into light fractions. This conversion results in the production of modern heavy fuels which contain a greater concentration of sulphur, vanadium, and asphaltenes. Asphaltenes are considered as part of the "bottom of the barrel". They constitute the non-volatile, high molecular weight fraction of petroleum. In addition, since they are non-soluble in heptane, they remain in solid form in the crude as well. The condensed aromatic rings exist in the form of a non-homogeneous flat sheet (See Figure 2.5).

In the crude, the asphaltene sheets remain dispersed. However, they have the tendency to be attracted towards each other thus resulting in the formation of an agglomeration. The structure of the agglomeration is similar to that of a book: a compact stack of thin sheets (See Figure 2.6).

In general, solids in crude oil fall into two classes: "basic sediment" and "filterable solids". These particles have an economic impact on petroleum industry. Carried along in the oil, they can cause fouling, foaming, erosion, corrosion, etc. Depending on the case, coagulants (molecular weight < 10,000.) or flocculants (molecular weight > 10,000.) might provide an indirect aid in solids removal [Schantz and

Table 3.1
The results of asphaltene contents determination

| No. | Crude oil from different wells | Unit | Asphaltene contents |
|-----|--------------------------------|------|---------------------|
| 1 | W1 | % wt | 1,2230 |
| 2 | W2 | % wt | 1,2300 |
| 3 | W3 | % wt | 1,2510 |
| 4 | W4 | % wt | 1,1980 |
| 5 | W5 | % wt | 1,2400 |
| 6 | W6 | % wt | 1,5780 |
| 7 | W7 | % wt | 1,2230 |
| 8 | W8 | % wt | 0,6930 |
| 9 | W9 | % wt | 1,8260 |

Table 3.2
The results of carbon contents determination

| No. | Crude oil from different wells | Unit | Carbon contents |
|-----|--------------------------------|------|-----------------|
| 1 | W1 | % wt | 83,5739 |
| 2 | W2 | % wt | 75,8561 |
| 3 | W3 | % wt | 81,1371 |
| 4 | W4 | % wt | 77,0970 |
| 5 | W5 | % wt | 75,2830 |
| 6 | W6 | % wt | 77,8952 |
| 7 | W7 | % wt | 78,2833 |
| 8 | W8 | % wt | 83,0332 |
| 9 | W9 | % wt | 76,4602 |

Elliot, 1994]. Coagulants are molecules with strong polar charge which act to disrupt charges on the surface of the oil droplet that would otherwise prevent coalescence. Flocculants, act to coalesce oil droplets, because they are very soluble in oil, but in some cases they can have drastically reduced solids removal, that is to say, solids never die, they just move around. Resins are not known to deposit on their own, but they deposit with asphaltenes as it will be elaborated later. The reasons for the asphaltene deposition can be many factors including variations of temperature, pressure, composition, flow regime, and wall and electrokinetic effect. When various heavy organic compounds are present in a petroleum fluid their interactive effects must be also considered in order to understand the mechanisms of their collective deposition or lack of it. This is specially important when one of the interacting heavy organic compounds is asphaltene. For example a regular waxy crude containing minute amounts of asphaltene will behave differently at low temperatures (below the wax cloud point) compared with a clean waxy crude with no other heavy organics

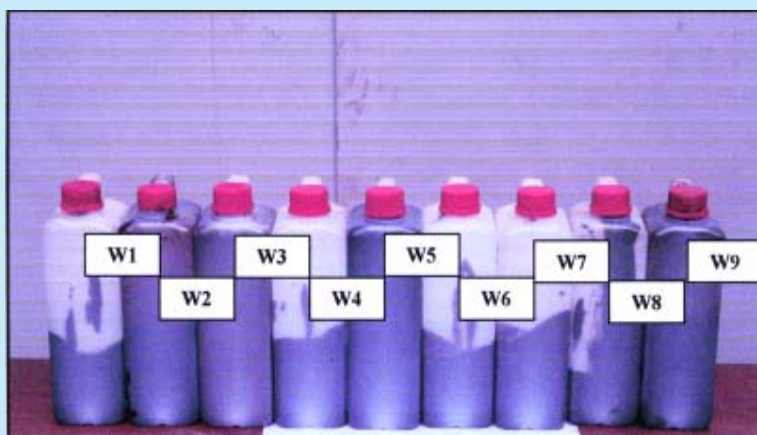


Figure 3.1
Crude oil samples from different wells

present in it, an asphaltenic crude containing some paraffin / wax, or a purely asphaltenic crude containing no paraffin / wax.

III. RESULTS AND DISCUSSION

According to corrosion and water technology for petroleum producers text book by Jones. L.W, the contents of sulfur, oxygen and nitrogen in crude oil may result in corrosive properties of crude oil. While, hydrogen content factor in crude oil indicates impurities of crude oil.

In this research, determination of asphaltene, carbon, hydrogen, nitrogen, oxygen and total sulfur contents in the crude oil were carried out on nine crude oil samples (W1 to W9) from nine different wells (shown in Figure 3.1). The results of asphaltene contents are presented in Table 3.1. Generally, the asphaltene contents are in a range 0.6930 % wt – 1.8260 % wt. When, the result of asphaltene content of the W8 sample is compared with W1, W2, W3,

W4, W5, W6, W7 crude oil samples, the W8 crude oil sample has the lowest asphaltene content (0.6930 % wt). Next, the asphaltene contents in W1, W2, W3, W4, W5, W6, W7 crude oil samples are twice higher than W8 crude oil sample. The W9 crude oil sample contains the highest asphaltene content (1.8260 % wt) and is almost three times higher than the asphaltene content in W8 crude oil sample. Asphaltenes can deposit within the formation and

Table 3.3
The results of hydrogen contents determination

| No. | Crude oil from different wells | Unit | Hydrogen contents |
|-----|--------------------------------|------|-------------------|
| 1 | W1 | % wt | 11,1220 |
| 2 | W2 | % wt | 9,9335 |
| 3 | W3 | % wt | 11,2339 |
| 4 | W4 | % wt | 9,3102 |
| 5 | W5 | % wt | 9,1948 |
| 6 | W6 | % wt | 10,4667 |
| 7 | W7 | % wt | 10,0855 |
| 8 | W8 | % wt | 10,9147 |
| 9 | W9 | % wt | 9,7128 |

Table 3.4
The results of nitrogen contents determination

| No. | Crude oil from different wells | Unit | Nitrogen contents |
|-----|--------------------------------|------|-------------------|
| 1 | W1 | % wt | 0,0000 |
| 2 | W2 | % wt | 0,0000 |
| 3 | W3 | % wt | 0,0000 |
| 4 | W4 | % wt | 0,0000 |
| 5 | W5 | % wt | 0,0000 |
| 6 | W6 | % wt | 0,0000 |
| 7 | W7 | % wt | 0,0000 |
| 8 | W8 | % wt | 0,0000 |
| 9 | W9 | % wt | 0,0000 |

Table 3.5
The results of oxygen contents determination

| No. | Crude oil from different wells | Unit | Oxygen contents |
|-----|--------------------------------|------|-----------------|
| 1 | W1 | % wt | 5,1634 |
| 2 | W2 | % wt | 14,0560 |
| 3 | W3 | % wt | 7,4887 |
| 4 | W4 | % wt | 13,4422 |
| 5 | W5 | % wt | 15,3808 |
| 6 | W6 | % wt | 11,5047 |
| 7 | W7 | % wt | 11,4821 |
| 8 | W8 | % wt | 5,8926 |
| 9 | W9 | % wt | 13,5737 |

Table 3.6
The results of total sulfur contents determination

| No. | Crude oil from different wells | Unit | Total sulfur contents |
|-----|--------------------------------|------|-----------------------|
| 1 | W1 | % wt | 0,1407 |
| 2 | W2 | % wt | 0,1544 |
| 3 | W3 | % wt | 0,1403 |
| 4 | W4 | % wt | 0,1506 |
| 5 | W5 | % wt | 0,1414 |
| 6 | W6 | % wt | 0,1334 |
| 7 | W7 | % wt | 0,1491 |
| 8 | W8 | % wt | 0,1595 |
| 9 | W9 | % wt | 0,2533 |

block the pore throats, which may reduce the permeability significantly

The results of carbon contents analysis of nine crude oil samples (W1 to W9) are in a range of 75.2830 % wt – 83.5739 % wt as presented in Table 3.2.

Subsequently, the W1 to W9 crude oil samples contain hydrogen contents in a range of 9.1948 % wt – 11.2339 % wt presented in Table 3.3. All crude oil samples indicate high impurities of crude oil, because the analyzed crude oil samples have more than 1 % wt high hydrogen contents.

The analyzed crude oil samples (W1 to W9) have zero % wt nitrogen contents as tabulated in Table – 3.4 and don't show corrosive crude oil samples.

Next, the obtained oxygen contents in the W1 to W9 crude oil samples are in a range 5.1634 % wt – 14.0560 % wt and show corrosive crude oil. W1, W3 and W8 crude oil samples have less corrosion than W2, W4, W5, W6, W7 and W9 crude oil samples.

The sulfur contents in W1 to W9 crude oil samples are in a range of 0.1334 % wt – 0.2533 % wt and have potential to occur corrosion problem.

IV. CONCLUSIONS

Based on the results of laboratory tests, literature and also performance of crude oil visually after sampling can be concluded as follows:

1. The W1 to W9 crude oil samples contain:
 - a. The asphaltene contents in a range of 0.6930 % wt – 1.8260 % wt.
 - b. The carbon contents in a range of 75.2830 % wt – 83.5739 % wt.
 - c. The hydrogen contents in a range of 9.1948 % wt – 11.2339 % wt.
 - d. zero % wt nitrogen contents.
 - e. The oxygen contents in a range of 5.1634 % wt – 14.0560 % wt.
 - f. The sulfur contents in a range of 0.1334 % wt – 0.2533 % wt.
2. The asphaltene exists in the W1 to W9 crude oil samples and it can deposit in the formation and block the pore throats, which may reduce the permeability significantly.

3. The W1 to W9 crude oil samples have corrosive properties, because the contents of sulfur and oxygen are found in the crude oil samples.
4. The contents of nitrogen in the nine crude oil samples are zero % wt, so that these don't have corrosive properties.
5. Factor of the obtained hydrogen contents in the W1 to W9 crude oil samples is an indicator of impurities crude oil samples.

REFERENCES

1. Buckley, J.S., Wang, J.X., and Creek, J.L.: "Solubility of the Least Soluble Asphaltenes," Chapter 16 in *Asphaltenes, Heavy Oils and Petroleomics*, O. Mullins, E. Sheu, A. Hammami, and A. Marshall, eds., Springer (2007) 401-437.
2. Cimino, R., Corraera, S., Del Bianco, A., and Lockhart, T.P.: "Solubility and Phase Behavior of Asphaltenes in Hydrocarbon Media," *Asphaltenes: Fundamentals and Applications*, E.Y. Sheu and O.C. Mullins (eds.), NY: Plenum Press (1995) 97-130.
3. IP 143/04: "Determination of asphaltenes (heptane insolubles) in crude petroleum and petroleum products."
4. Long, R.B.: "The Concept of Asphaltenes," *Chemistry of Asphaltenes*, J.W. Bunger and N.C. Li (eds.), ACS, Washington, DC (1981) 17-27.
5. Sirota, E.B.: "Physical Structure of Asphaltenes," *Energy & Fuels* (2005) **19**, 1290-1296.
6. Wang, J.X. and Buckley, J.S.: "An Experimental Approach to Prediction of Asphaltene Flocculation," paper SPE 64994 presented at the 2001 OCS, Houston, 13-16 Feb.
7. Wang, J.X. and Buckley, J.S.: "Asphaltene Stability in Crude Oil and Aromatic Solvents-The Influence of Oil Composition," *Energy & Fuels* (2003) **17**, 1445-1451.
8. Wang, J.X., Creek, J.L., and Buckley, J.S.: "Screening for Potential Asphaltene Problems," paper SPE 103137 presented at the 2006 ATCE, San Antonio, 24-27 Sep.