Investigation of metalloporphyrin compound in maltenes of duri crude oil

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Abstract. Metalloporphyrin is one of the compounds that could potentially cause deactivation of catalysts in the process of catalytic cracking and hydrotreating. Knowledge of the structure of metalloporphyrin can be used as the basic information in overcoming the problem of catalyst poisoning. This work is performed to identify metalloporphyrins in the maltenes fraction of Duri crude oil. The low content of asphaltenes in Duri crude oil with a fractional weight of 0.79 %, allows a high level of metalloporphyrin in the fraction of maltenes which has a fractional weight of 82.73 %. Metalloporphyrin in the maltenes derive fraction, saturates, aromatics, and resin were separated using column chromatography. Saturates, aromatics and resins have fractional weight of 49.75; 34.92; and 15.33 %, respectively. Only resin contained metalloporphyrin based on the analysis of UV-Vis spectrophotometer and Fourier-transform infrared spectroscopy (FT-IR), thus metalloporphyrins in resin was further separated into fractions by column chromatography. The result of UV-Vis spectrophotometer analysis for resin separation showed an absorbance peak of metalloporphyrin at 480–700 nm, while FT-IR analysis showed the presence of pyrrole group as porphyrin base framework with vibrational region at 400–1100 cm⁻¹ The results of micro plasma-atomic emission spectrometer (MP-AES) analysis showed the presence of Fe, Ni, and V metals content. The liquid chromatography-mass spectrometer (LC-MS) analysis showed the molecular structure of the obtained compound was C33H34N4VO2. According to the results, metalloporphyrins presented in the maltenes fraction of Duri crude oil was vanadyl porphyrin.

Keywords: Metalloporphyrin, maltenes, Duri crude oil, vanadyl porphyrin

1. Introduction

In recent years, crude oil tends to be more difficult to process due to the increasing amount of acid and the fraction of heavy crude oil [1]. In addition, the presence of metal content in crude oil has the potential to cause product contamination and a catalyst poisoning in the crude oil refinery process. The metals will attach to the active surface- of catalyst and decrease its area by clogging the pores thus the catalyst becomes inactive [2]. The low content of metals in crude oil causes a deactivation in the desulfurization process and catalytic cracking [3].

Crude oil is grouped into maltenes and asphaltenes based on their solubility in n-heptane and n-hexane solvents [4]. Maltenes is a soluble crude oil fraction in alkane solvent consisting of saturates, aromatics, and resins. Asphaltenes are a fraction in crude oil with high molecular weight and insoluble
Asphaltenes tend to be soluble in aromatic solvents and form the colloidal dispersed asphalt in the maltenes fraction. In terms of polarity distribution, metals in crude oil mostly found in resins and asphaltenes [5]. Metals in crude oil can be either found in a free state or forming a metal complex such as metalloporphyrin. There are two types of porphyrin in crude oil, the one that has a large mass and large size while settling together with asphaltenes, and other that has a lower mass and prefer to bind with resin [3].

Porphyrin compounds, particularly vanadyl porphyrins in resins, affect the amount of asphaltenes in crude oil. Asphaltenes compounds are generally separated from crude oil through precipitation with hexane and n-heptane solvents. The higher concentration of vanadyl porphyrin in the resin, the quantity of asphaltenes deposited by the n-hexane mixture will decrease and vice versa [6]. The low value of asphaltenes fractional weight of Duri crude oil indicates a high content of metalloporphyrin in the resin fraction. However, there was a research showing that metalloporphyrin contained in the fraction of crude oil, especially in asphaltenes [7, 8].

This study examined more about the content of metalloporphyrin compounds in maltenes derivate fractions, saturates, aromatics, and resins. Metalloporphyrin in maltenes was analyzed by column chromatography method, and further characterized by UV-vis spectrophotometer, FT-IR, LC-MS, and MP-AES.

2. Experimental

2.1. Materials
The materials used for this study were Duri crude oil, toluene (Merck), n-heptane (Merck), methanol (Merck), chloroform (Merck), filter paper Whatman no.42 (GE), silica gel 60 (70-230 mesh) (Merck), aluminum foil. The characterization equipment for this research were FT-IR spectroscopy Prestige 21 Shimadzu, UV-Vis spectrophotometer Shimadzu 2600, LC-MS Agilent 1200, MP-AES Agilent 4210.

2.2. Sample preparation
The sample preparation of Duri crude oil followed the procedure of ASTM D6560. Sample preparation was performed to separate maltenes and asphaltenes based on their solubility in n-heptane [9].

2.3. Separation of saturate, aromatic, and resin
The column for separation with silica gel was activated at 250 °C for 24 h using a wet method. Maltenes were separated into its derived fractions through the adsorption method on silica. The sample was orderly eluted with 150 mL of heptane for saturates, 150 mL of toluene for aromatic and 300 mL of toluene: chloroform: methanol (1:1:1) (v/v) for resins. 25 mL of each separation was collected into fractions and characterized by UV-Vis spectrophotometer and FT-IR.

2.4. Resin separation by column chromatography
The resin was mixed with the silica gel and inserted into the column as reported in our prior work [10]. The first eluent was a mixture of toluene: chloroform: methanol with a volume ratio of 1:1:0.1. The second eluent was toluene: chloroform: methanol with a volume ratio of 1:1:1 to bring the sample retained in the stationary phase. The separation results were collected into fractions every 5 mL and characterized by UV-Vis spectrophotometer, FTIR, MP-AES, and LC-MS.

3. Results and discussion
According to the sample preparation, the fractional weight of maltenes and asphaltenes in crude oil were 82.73 and 0.79 %, respectively. The composition of saturates, aromatics, and resins of each type of crude oil were varied. Based on the calculation result, the fractional weight of saturates, aromatics, and resin from maltenes of Duri crude oil were 49.75; 34.92; and 15.33 %, respectively. The porphyrins
compounds have peaks at 390–425 nm for free porphyrins and 480–700 nm for porphyrin-bound metals [11]. The UV-Vis absorption spectra of the saturates and aromatics in figure 1a and figure 1b do not show a typical uptake of porphyrin. This result indicates that saturates and aromatics contain no porphyrins. Meanwhile, figure 1c shows the presence of porphyrins in both fractions 2 and 3 by evaluating the different pattern at 50–700 nm.

The vibrational mode of pyrroles porphyrin base framework is in the wavenumber region of 450–1100 cm$^{-1}$ [12]. Figure 2 shows the presence of pyrrole symmetric folding at 785 cm$^{-1}$, and pyrrole asymmetric folding with bending vibration types at 669 cm$^{-1}$. The column chromatography separation of 2$^{nd}$ and 3$^{rd}$ resin fractions resulted in 17 subfractions. The eluent consisting of toluene: chloroform: methanol with a volume ratio of 1:1:0.1 was used to separate the subfraction of 1–11, while the eluent consisting of toluene: chloroform: methanol with a volume ratio of 1:1:1 was used to separate the subfractions of 12–17.

![Figure 1](image1.png)

Figure 1. UV–Vis absorption spectra of (a) saturates, (b) aromatics (c) resin fractions of 1–6, and (d) resin fractions of 7–12.
3.1. UV-vis spectrophotometer characterization of resin separation
The subfractions of resin separation obtained by column chromatography were characterized. Figure 3a and figure 3b show the absorption spectra for the subfractions of 1–11 do not show any distinctive peak.

Figure 2. FTIR spectra of 2nd and 3rd resin fraction.

Figure 3. UV−vis absorption spectra subfraction (SF) of (a) 1–6, (b) 7–11 (c) 12–17 and (d) 15–17.
of metalloporphyrin, while the analysis results for the subfractions of 12–17 show the existence of a typical absorption peak, particularly in the subfractions of 15, 16, and 17 as presented in figure 3c. These three subfractions have a different pattern from other subfraction spectra. This result indicates the presence of the same compounds in those three subfractions. Therefore, they were combined for further characterization. Absorbance peaks for fractions 15, 16, and 17 tend to go down because the blank evaporated during the measurement process as shown in figure 3d. Hence, the solvent of the sample was replaced with methanol to prove the formation of the maximum absorption peak. The result of the UV-vis spectrophotometer measurements exhibits a typical absorption peak at maximum wavelength of 515 nm and 673 nm as shown in figure 4a. This result corresponds to the wavelength range of metalloporphyrin which is 480–700 nm.

3.2. FTIR characterization of resin separation

The result of the FTIR analysis of subfractions 15, 16, and 17 indicates the presence of a pyrrole group at 677 cm⁻¹ as shown in figure 4b. Thus, it can be seen that the porphyrin compound could be separated and purified with the resin separation process by column chromatography.

3.3. MPAES characterization of resin separation

Characterization with MP-AES gives information about the number of metals contained in the sample. It shows that there were 3 types of metals, V, Ni, and Fe that bind to porphyrin. The subfraction of resin separation contain 3 types of metals as shown in table 1. This result demonstrates that the porphyrin contained in the resin subfractions 15–17 was in the form of metalloporphyrin.

![Figure 4](image.png)

**Figure 4.** (a) UV-vis absorption spectrum of the mixture of resin separation fraction of 15–17 and (b) FTIR spectra of resin and resin separation.

| Sample                  | Concentration (ppm) |
|-------------------------|----------------------|
|                         | Fe       | Ni       | V        |
| Resin                   | 7.776    | 4.948    | 0.104    |
| Resin separation        | 2.969    | 0.760    | 0.051    |

**Table 1.** MP-AES analysis of resin and resin separation.
3.4. LC-MS characterization
Based on the LC analysis in figure 5a, there was a peak at a retention time of 14.52 min. The MS result at a retention time of 14.52 min in figure 5b has the m/z value of 572. The obtained m/z value is the positive ion of the target compound. Therefore, the molecular weight of the target compound was 571. This result was conformed to the previous result [13] that the vanadyl porphyrin compounds with the m/z value of 571 has a structure as shown in figure 6.

4. Conclusion
Metalloporphyrin have been identified in resins by column chromatography separation method. Resins are the only derived fraction of maltenes containing metalloporphyrin compounds. The results of the analysis with LC-MS showed the presence of vanadyl porphyrin in the form of C₃₃H₃₄N₄VO₂.
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References
[1] Moeini F, Hemmati-Sarapardeh H, Ghazanfari M H, Masihi M and Ayatollahi S 2014 *Fluid Phase Equilib.* **375** 191-200
[2] Rodriguez M A, Elizalde I and Ancheyta J 2012 *Fuel* **100** 152-62
[3] Dechaine G P and Gray M R 2010 *Energ. Fuel.* **24** 2795-808
[4] Reisch M 1999 *Chem. Eng. News* **77** 70
[5] Zhao S, Kodyar L S, Woods J R, Sparks B D and Chung K H 2000 *Petrol. Sci. Technol.* **18** 587-606
[6] Yakubov M R et al. 2016 *Energ. Fuel.* **30** 8997-9002
[7] Luz M S and Oliveira P V 2019 *Talanta* **199** 147-54
[8] Chainet F, Lienemann C P, Courtiade M, Ponthus J and Donard O F X 2011 *J. Anal. At. Spectrom.* **26** 30-51
[9] Affendi T, Yulizar Y, Haerudin H, Kurniawaty I and Apriandanu D O B 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **763** 012017
[10] Kurniawaty I, Yulizar Y, Gamar I, Haerudin H and Apriandanu D O B 2018 *AIP Conf. Proc.* **2023** 020087
[11] Kumolo S T, Yulizar Y, Haerudin H, Kurniawaty I and Apriandanu D O B 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **496** 012038
[12] Rio Y, Rodriguez-Morgade M S and Torres T 2008 *Org. Biomol. Chem.* **6** 1877-94
[13] Mishra S, Kaur S, Tripathi S K, Mahajan C G and Saini GS 2006 *J. Chem. Sci.* **118** 361-9.