Investigation of metalloporphyrin in maltenes phase of crude oil Duri

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Abstract. The presence of metals and organometals in heavy crude oil is interesting research to study. The most abundant heavy metals and undesirable presence of heavy metals in crude oil are nickel and vanadium. Organometals such as metalloporphyrin can inhibit the catalyst performance in cracking process. Crude oil is classified into asphaltenes and maltenes phases. In this study, isolation of metalloporphyrin in maltenes was performed by column chromatography using eluent of n-heptane: ethyl acetate (8:5:1.5) (v/v). The isolated metalloporphyrin was characterized using Ultraviolet-Visible (UV-Vis) spectrophotometry, FTIR (Fourier Transform Infrared), and Liquid Chromatography-Mass Spectrometry (LC-MS). UV-Vis spectrophotometry characterization showed the presence of metalloporphyrin at the maximum wavelength of 480–700 nm. FTIR characterization showed the existence of pyrrole rings vibration, which described as porphyrin compound at the wavenumber of 800 cm⁻¹. LC-MS characterization showed the presence of vanadium bound at porphyrin in maltenes with the molecular formula of C₉H₈N₄VOS.

Keywords: asphaltenes, crude oil Duri, heavy crude oil, maltenes, organometal, porphyrine.

1. Introduction
The components of the crude oil consists of hydrocarbons, organic compounds such as sulfur, oxygen, nitrogen, and metals such as nickel and iron. The negative effects of metals in petroleum have been known for a long time. Metals contaminate not only the product but also catalyst. A chelate metals can poison a catalyst and cause the pollution, as well as an excess gas formation [1]. The presence of metal in fluid catalytic cracking causing the serious problems potentially. Although the sulphur can be converted to a gas, but non-volatile substances will accumulate in the unit. This causes a change in the structure of the catalyst. Crude oil contains a large metal mainly vanadium, iron and nickel [2–3]. The metal content in crude oil is classified in to asphaltenes and maltenes phases. The metal can bound porphyrins and impede the process of hydrocracking in crude oil. Much research focuses on vanadium porphyrins and nickel porphyrins in crude oil. This research aims to detect the effect of catalyst poisoning and study the nature of the vanadyl porphyrins and nickel porphyrins [4].

Metalloporphyrin was the first compound isolated from petroleum [5]. Petroleum and asphalt contains porphyrins [6]. Since then, the researchers investigate a porphyrin compound on crude oil in several places. The asphaltenes and maltenes phases on crude oil can be separated by extraction and spectrophotometry methods [7]. The extraction used a variety of solvents. The solvents which can solute a crude oil properly is n-alkanes. The results showed that the oil contains some complex metal-
porphyrins. The metal on porphyrin compounds was dominated by iron \[8\]. Metalloporphyrin compounds in Duri crude oil should be removed due to its toxicity. It can reduce the catalyst performance in the residue catalytic cracking (RCC) process.

In this research, the investigation of metalloporphyrin compound in maltenes phase of crude oil Duri is developed by extraction and column chromatography methods, then characterized using Ultraviolet-Visible (UV-Vis) spectrophotometer, Fourier Transform Infrared (FTIR), and Liquid Chromatography-Mass Spectrometry (LC-MS). It aims to get an effective and efficient ways to overcome the problem of catalyst poisoning in the cracking process.

2. Materials and methods

2.1. Materials
Crude oil was obtained from Duri, Riau, Indonesia. N-heptane, ethyl acetate, and toluene were purchased from Merck, Germany.

2.2. Distillation of Duri crude oil
Crude oil was distilled at 370 °C. The residue boiling point that was greater than 370 °C was filtered as crude oil residue, and the metal was determined \[9\].

2.3. Preparation of maltenes and asphaltenes
Samples were fractionated using Pilodist (ASTM D-6560) into several fractions at topped to an oil temperature of 260 °C to get maltenes and asphaltenes.

2.4. Isolation of metalloporphyrin
Maltenes of 0.5 g were added into silica. The mixture was put slowly into column chromatography using the eluent comparison of n-heptane: ethyl acetate (8.5:1.5) (v/v).

2.5. Characterization
The UV-Vis absorption spectrum of metalloporphyrin was examined using UV-Vis spectrophotometer at range of 200–800 nm. The pyrrol rings of metalloporphyrin was investigated using FTIR. LC-MS was used for determination of metalloporphyrin structure.

3. Results and discussion
The purpose of distillation is to obtain the oil fraction from crude oil. Then, the oil fraction is separated maltenes and asphaltenes fraction by ASTM D-6560 method. The percentage of maltenes and asphaltenes in Duri crude oil was 61.16 and 1.004 % respectively. This result is smaller than % asphaltenes fraction from several countries as shown in table 1.

The UV-Vis absorption spectra of isolated metalloporphyrin is shown in figure 1a. The result shows the presence of absorption spectrum at maximum wavelength of 550–650 nm. This absorption indicates to metalloporphyrin compound. It has the conformity that metalloporphyrine has an UV-Vis absorption at maximum wavelength area of 480–700 nm \[10\].

FTIR characterization was conducted to investigate a pyrrol ring in isolated metalloporphyrin. Figure 1b shows the FTIR spectra of maltenes and isolated metalloporphyrin from extraction and column chromatography results. There are three mains vibration bands, the vibration of C-H stretching appears at the wavenumber of 2900 cm\(^{-1}\), the vibration of C-C aromatic is also available at the wavenumber of 1450 cm\(^{-1}\). The absorption band at the wavenumber of 800 cm\(^{-1}\) shows the vibration of pyrrol rings, indicating a porphyrine framework in isolated metalloporphyrin. The FTIR results have the conformity with the previous research \[11\].

| Crude Oil          | Asphaltenes (wt.%) |
|--------------------|--------------------|
| Venezuela (Boscan) | 18.0               |
| Mississippi (Baxterville) | 17.2          |
| California (Belridge)  | 5.1                |
| Indonesia (Duri)    | 1.0                |
Figure 1. (a) UV-Vis absorption spectra of isolated metalloporphyrin and (b) FTIR spectra of maltenes and isolated metalloporphyrin.

Figure 2. (a) Mass spectrogram of isolated maltenes (b) molecular structure of C$_{39}$H$_{36}$N$_4$V$_1$O$_1$S.

Metalloporphyrin compound was identified by LC-MS characterization as shown in figure 2a. m/z value by a pseudomolecular ion peak analysis [M + H + NH$_3$] is 677. So, metalloporphyrin compound has a molecular weight of 659. According to the determination of molecular formula in previous reports [12–13], the molecular weight of 659 is C$_{39}$H$_{36}$N$_4$VOS. The result indicates that porphyrin are bound to vanadium (figure 2b).
4. Conclusions
Metalloporphyrin was successfully investigated by extraction and column chromatography method in maltenes phase from Duri crude oil. It has the molecular formula of C_{39}H_{36}N_{4}VOS due to the presence of vanadium bound at porphyrine proved by LC-MS. There is a pyrrole rings vibration, indicating the presence of porphyrine at the wavenumber of 800 cm^{-1} as the result of FTIR characterization. Characterization using UV-Vis spectrophotometry also strengthen the evidences that metalloporphyrin appears at the maximum wavelength of 550–650 nm.

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