Investigation of metalloporphyrins in Duri crude oil asphaltene fraction

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Abstract. Metalloporphyrins are a compound that leads the contaminant in catalytic cracking of crude oil. This study aims to investigate the metalloporphyrin in crude oil from Duri, Riau, Indonesia. The extraction process yielded maltene and asphaltene up to 71.87 % and 1.07%, respectively. Asphaltene fraction was extracted by soxhlet using methanol solvent. The separation of asphaltene fraction was perfomed by column chromatography using mixing of toluene: chloroform: methanol (5:5:1) eluents. The Fourier Transform Infrared (FTIR) spectrum of asphaltene indicated the presence of a pyrrole ring at 800 cm⁻¹ in the fingerprint region as a porphyrin-formed group. The UV-Vis absorption spectra of methanol separation showed free porphyrin at 580 nm and metalloporphyrins at 500–700 nm. The Microwave Plasma-Atomic Emission Spectrometer (MP-AES) qualitative analysis of asphaltene fraction showed the presence of vanadium, nickel, and iron. The Liquid Chromatography-Mass Spectrometry (LC-MS) analysis on asphaltene15th fraction showed the presence of C.H.N.V.O. compound.

1. Introduction

Crude oil is produced from the natural process of microorganism, animals, and plants and occurs slowly over a period of thousands of years. The main constituents of crude oil are hydrocarbons and organic compounds that contain sulfur, nitrogen, oxygen, and organometallics [1]. Hydrocarbons are classified into four main groups based on their polarity and solubility. This classification is known as SARA, which includes saturated, aromatic, resins, and asphaltene [2].

Almost 50% of the crude oil fraction can be used as renewable oil. The renewal oil from heavy fraction and remediation of soil pollution interested a lot of researchers to investigate, due to the presence of asphaltene [3]. Asphaltene fraction contains metal complexes, which is difficult to investigate and also responsible for the catalyst contaminant [4,5]. The metal complexes are mostly vanadium and nickel [6]. Vanadium and nickel are usually from napthenic acids in the form of organometallic complex such as metalloporphyrins [7].

As the result, in this study, metalloporphyrins were investigated from crude oil, and their structure and content in the oil were determined. Asphaltene was mixed with silica gel and extracted by soxhlet method with methanol. A column chromatography method was perfomed to separate the crude oil fraction using silica gel and the mixture of toluene: chloroform: methanol as mobile phase. A series of further soxhlet extractions and purification produced the target compounds. The separation results were characterized using Fourier Transform Infrared (FTIR) spectroscopy, UV-Vis spectrophotometry, Liquid Chromatography-Mass Spectrometry (LC-MS), and Microwave Plasma Atomic Emission Spectrometer (MPAES) to determine the metal content and metalloporphyrin structure in the crude oil.
2. Materials and methods

2.1. Materials
Crude oil was obtained from Duri, Riau, Indonesia. Methanol, n-heptane, toluene, silica gel 70–230 mesh were purchased from Merck (Germany), whereas double distilled water was used as a solvent.

2.2. Distillation of Duri crude oil
The crude oil was distilled at 260°C. The fraction with a boiling point greater than 260 °C was filtered and marked as the crude oil residue, whereas the metal content was determined [8].

2.3. Reflux of Duri crude oil residue
5 g of Duri crude oil residue was dissolved into 150 mL n-heptane and refluxed for an hour as reported by Keshmirizadeh [9]. The result of reflux was kept in the dark condition for 2 h, and then it was filtered and washed with warm n-heptane. The obtained residue and filtrate were used for further soxhlet extraction.

2.4. Soxhlet extraction of the Crude oil residue using methanol
Soxhlet extraction was performed by the method as reported in previous research [10]. Filter paper containing residues was placed in the extraction chamber. Round squash was filled with methanol solvent. Meanwhile, the round pumpkin containing the soxhlet extraction in n-heptane was evaporated at 60 °C.

2.5. Column chromatography
Column chromatography method was adapted from the previous reports [11]. The asphaltene fraction was mixed with pure silica to form dispersion. The mixture was injected into a silica gel-filled column chromatography with the eluent composition of toluene: chloroform: methanol (5:5:1). The obtained fractions were characterized by UV-Vis spectrophotometer (Shimadzu 2600) to determine the constituent compounds, FTIR spectroscopy (IR Prestige-21 Shimadzu) to identify the functional groups, MP-AES (Agilent 4210) to determine the elemental content and composition of the fractions, LC-MS (Agilent 1200) to investigate the molecular formula and chemical structure of the compound in the fractions.

3. Results and discussion
The distillation process was conducted to separate the oil from the crude oil to the each fraction based on the boiling point. The percentages of maltene and asphaltene fractions in crude oil were 71.87 % and 1.07%, respectively. The methanol soxhlet extraction of asphaltene was investigated using UV-Vis spectrophotometer. The use of methanol is highly considered due to its inability to mix with oil and is an appropriate solvent for extraction of metallophorphyrin [11]. Figure 1 shows a weak peak in
The visible range of 480–700 nm that indicated the presence of porphyrin in the methanol fraction as described in the previous report [3].

The asphaltene fraction was further separated by column chromatography and each fraction was characterized by UV-Vis spectrophotometer as shown in figure 2. Figure 2a shows there was no peak at all in fractions at the visible range, whereas figure 2b shows absorption peak around 666 nm that indicated the presence of metalloporphyrins at fraction 12, 15 and 26. Metalloporphyrin has typical absorption around 480–700 nm [12]. Fraction 15 has the highest absorbance and lowest maximum wavelength. This result assumes that the presence of metalloporphyrins could be significant at fraction 15. Moreover, it was further characterized by FT-IR, MP-AES, and LC-MS.

The comparison of FTIR spectra of the asphaltene and the 15th fraction after column chromatography is presented in figure 3. The presence of C-H groups was indicated by a band at 2865 cm$^{-1}$. The bands at 2865, 1500, 1116, and 800 cm$^{-1}$ corresponds to the presence of C-H, C = C aromatic, C-N, and pyrrole groups, respectively. The presence of pyrrole group illustrates the typical vibration mode of porphyrin at 800 cm$^{-1}$ as reported by Mishra et al. [13]. Therefore, the presence of a porphyrin in the fractions is clearly revealed.

Figure 2. UV-Vis Absorption Spectra of Metalloporphyrin

Figure 3. FTIR Spectra of asphaltene and the 15th fraction
Table 1. Elemental composition of asphaltene fractions after column chromatography

| Sample     | Concentration (ppm) |
|------------|---------------------|
|            | Ni  | Fe  | V   |
| 12\textsuperscript{nd} Fraction | 0.042 | 0.015 | 0.011 |
| 15\textsuperscript{th} Fraction  | 0.026 | 0.010 | 0.074 |
| 26\textsuperscript{th} Fraction  | 0.034 | 0.012 | 0.110 |

Figure 4. (a) Liquid chromatogram and (b) Mass spectrogram of 15\textsuperscript{th} fraction

Figure 5. Molecular structure of C\textsubscript{34}H\textsubscript{39}N\textsubscript{4}VO\textsubscript{2}
Table 1 shows the MP-AES data that reveals the presence of elements commonly observed in asphaltene fractions. LC analysis shows a peak at retention time of 14.89 min as presented in figure 4a. Figure 4b shows the value of m/z represented by the pseudomolecular peak ion (M + H + ACN) is 628. Therefore, the compound has a molecular weight of 586. This indicates compatibility with the previous research [14] that the molecular weight of 586 is C,H,N,VO as a porphyrin compound bound to vanadium metals as shown in figure 5. This result was supported by the UV-Vis absorption spectrum, which shows metal bonds to porphyrin.

4. Conclusions
Metalloporphyrrin has been investigated in asphaltene fraction of Duri crude oil with the chemical structure of C,H,N,VO confirmed by LC-MS analysis. FTIR spectrum confirmed a pyrrole ring appears at 800 cm⁻¹, which corresponds, to porphyrin groups. UV-Vis absorption spectrum also showed a vanadium bond porphyrin at 666 nm.

Acknowledgements
This work was funded by Pertamina Join Research Grant between Departement of Chemistry Faculty of Mathematics and Natural Science Universitas Indonesia and Research & Technology Center PT. Pertamina (Persero) 2018.

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