Identification of metal porphyrins in Duri crude oil

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Abstract. Crude oil comprises several complex hydrocarbon mixtures because of their slow natural formation process, including the toluene-soluble asphaltene component. The comparison result of Soxhlet extraction with and without silica was 55.15% and 86.75%, respectively. The Duri crude oil residue is mixed with silica gel, and Soxhlet extraction was performed with toluene. Further Soxhlet extractions and purifications obtain free porphyrin and two metal porphyrins. The Fourier Transform Infrared (FTIR) spectrum of n-heptane column chromatographic separation indicated the presence of a pyrrole ring at a wavenumber 800 cm⁻¹ in the fingerprint region as a porphyrin-formed group. UV-Vis absorption spectra of the n-heptane separation showed free porphyrin spectra at a maximum wavelength of 440 nm and those of metal porphyrins ranging 500–700 nm. The results of a qualitative analysis of toluene fraction and n-heptane fraction showed the presence of C, Si, S, Ni, V, Fe, and Al. With this combination of spectroscopic techniques (FTIR, UV-Vis), Liquid Chromatography–Mass Spectrometry (LC-MS), and Energy Dispersive X-Ray Spectroscopy (EDX), nickel porphyrin (C₃₆H₃₂Ni, 534 m/z) and etioporphyrinato vanadyl (IV) (C₃₆H₃₂VO, 541 m/z) are isolated and identified from the silica gel chromatography fraction of the n-heptane Soxhlet extract of the toluene Soxhlet extract obtained from the Duri crude oil residue.

Keywords: silica gel, crude oil Duri, metalporphyrin, toluene

1. Introduction

Almost 50% of the crude oil heavy fraction can be used as renewable oil [1]. The renewable oil is obtained from heavy fraction and remediation of soil pollution that are interesting to be investigated due to the presence of asphaltenes and resins. For example, the percentage of asphaltenes and resins in oil samples reaches from Mexico and China are 46% to 80% and 33% to 53%, respectively [2].

Crude oil is produced from the natural processing of microorganisms, animals, and plants, and this 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. The composition of crude oil depends on the location, age, and depth of the mine. Hydrocarbons are classified into four main groups based on their polarity and solubility. This classification is known as SARA, which includes saturated (alkanes and cycloparaffin), aromatics (hydrocarbons, monoatomics, diatomics, and polyatomics), resins (polar molecules with N, O, and S), and asphaltenes (large molecular weight resin with a polyatomic nucleus) [3].

It is difficult for metal complexes to be integrated into the asphaltenes fraction [4]. The amount of metal in crude oil varies, and as much as 10,000 ppm of metal has been observed. Commonly found...
metals include lithium, sodium, calcium, potassium, strontium, silver, copper, manganese, vanadium, zinc, lead, tin, cobalt, gold, nickel, chromium and titanium [5].

The metal complexes that cause problems in the organic fraction of fossil fuels are vanadium and nickel [6]. Vanadium and nickel usually form naphthenic acids in the form of organometallic complexes such as metalloporphyrins. Some of these destructive porphyrins can be isolated from oil. In addition to their destructive effects, these porphyrins also act as important geochemical markers [7].

In this study, metal porphyrins were isolated from crude oil, and their structure and content in the oil were determined. The Duri crude oil residue was mixed with silica gel, and Soxhlet was extracted with toluene. A series of further Soxhlet extractions and purifications resulted in the isolation of the target compounds. The resulting compounds were examined by Fourier Transform Infrared (FTIR) spectroscopy, Ultraviolet–Visible (UV-Vis) spectroscopy, Liquid Chromatography–Mass Spectrometry (LC-MS), and Energy Dispersive X-Ray Spectroscopy (EDX).

2. Experimental

2.1. Materials and methods
Crude oil was obtained from Duri, Riau, Indonesia. Methanol, n-heptane, and silica gel 60 (70–230 mesh) were purchased from Merck (Germany). Toluene was obtained from Mallinckrodt, and double distilled water was used as a solvent.

2.2. Distillation of Duri crude oil
The crude oil was distilled at 370 °C. The residue with a boiling point that was greater than 370 °C was filtered as the crude oil residue, and the metal content was determined.

2.3. Soxhlet extraction of the crude oil residue using toluene
The crude oil residue was mixed with pure silica (1:1) to form a dispersion. The mixture was Soxhlet extracted using toluene, filtered, and concentrated at 111 °C under reduced pressure. Soxhlet extraction of the crude oil residue without silica was also conducted under identical conditions.

2.4. Soxhlet extraction of the toluene fraction using n-heptane
The toluene fraction was mixed with pure silica to form dispersion. The mixture was Soxhlet extracted using n-heptane, filtered, and concentrated at 98.4 °C.

2.5. Soxhlet extraction of the n-heptane residue using methanol
The n-heptane fraction was mixed with pure silica (1:1) to form a dispersion. The mixture was Soxhlet extracted using methanol, filtered, and concentrated at 64.7 °C.

2.6. Silica gel column chromatography (Flash chromatography)
The n-heptane fraction was mixed with pure silica to form dispersion. The mixture was injected onto a silica-gel-filled column to perform chromatography. The eluent composition was n-heptane and ethyl acetate (8.5:1.5). The obtained fractions were characterized by UV–Vis spectroscopy to determine the compound-containing fractions. FTIR spectroscopy to identify the functional groups present in each fraction, EDX to determine the elemental content and composition of the fractions, LC–MS to investigate the determination of the molecular formula, and structural information through fragmentation pattern analysis.

3. Results and discussion
The distillation process was conducted to separate the oil fractions from the Duri crude oil. The crude oil residue was Soxhlet extracted using toluene with and without the added silica gel. The mass percentages of the crude oil residue Soxhlet extracted using toluene are presented in Table 1.

| Table 1. The percentage of toluene fraction in crude oil residue. |
|---------------------------------------------------------------|
| Toluene Fraction     | Percentage  |
|----------------------|-------------|
| Crude oil residue with silica | 55.15%      |
| Crude oil residue without silica | 86.75%      |

The distillation process was conducted to separate the oil fractions from the Duri crude oil. The crude oil residue was Soxhlet extracted using toluene with and without the added silica gel. The mass percentages of the crude oil residue Soxhlet extracted using toluene are presented in table 1. The
smallest percentage value was observed for the crude oil residue that was mixed with silica. This indicated that silica adsorbed the polar organic compounds from the crude oil and prevented toluene from extracting these compounds. The addition of silica can enlarge the contact surface area of metal porphyrin and asphaltenes with solvents during separation.

The methanol Soxhlet extraction of the n-heptane residue on silica was investigated (figure 1). No UV–Vis absorption peaks were observed in the visible range. This indicated that there were no porphyrins in the methanol fraction. The presence of free porphyrins have been reported between 380 and 450 nm, whereas free porphyrins were absent in the methanol fraction [8].

The n-heptane fraction was further separated by column chromatography, and 11 fractions were collected. Each fraction was characterized by UV–Vis spectroscopy (figure 2). Figure 2a depicted no peak in the visible range, whereas figure 2b depicted an absorption peak at 440 nm. The presence of free porphyrins is indicated by the peak at 440 nm [8]. Figure 3 depicts that the concentrated fractions (6 and 7) display an absorption maximum at 575 and 627 nm, respectively; this indicated the presence of a metal porphyrin [8].
Table 2. Elemental composition of the crude oil and residues.

| Sample                                         | % wt | C   | Si | O   | S   | V   | Fe  | Ni  | Al  | Total |
|------------------------------------------------|------|-----|----|-----|-----|-----|-----|-----|-----|-------|
| Crude oil                                      |      | 97.28 | -  | -   | 0.23 | -   | 0.27 | -   | 2.22 | 100   |
| Crude oil residue                              |      | 97.07 | 0.19 | -   | 0.20 | -   | 0.49 | -   | 2.04 | 100   |
| Toluene Soxhlet extract of oil residue without silica gel | | 96.96 | -  | -   | 0.21 | 0.08 | 0.46 | 1.35 | 2.94 | 100   |
| Toluene Soxhlet extract of oil residue with silica gel | | 15.5 | 26.5 | 57.9 | -   | -   | -   | -   | -   | 100   |
| n-Heptane Soxhlet extract                      |      | 77.38 | 0.33 | -   | 0.20 | 0.09 | 0.54 | 0.44 | 20.04 | 100   |

Figure 3. UV–Vis absorption spectra of column chromatography fractions 6 and 7 after the eluent was removed by evaporation.

FTIR characterization was conducted to identify the functional groups in each fraction. The FTIR spectra comparison of the concentrated crude n-heptane Soxhlet extract and concentrated fractions 6 and 7 after column chromatography are presented in figure 4. The presence of C–H groups was indicated by the peaks at 2850 and 2922 cm⁻¹. The presence of C–C groups was indicated by the peak at 1490 cm⁻¹. The presence of a pyrrole C–N bond was indicated by the peak at 775 cm⁻¹. Therefore, the presence of a porphyrin in these fractions was clearly indicated [9].

EDX characterization was conducted to determine the elemental composition of the sample. EDX data depicted the presence of elements that are commonly observed in petroleum, as presented in table 2.

LC–MS characterization was conducted to determine the molecular formula and structures of the isolated products. Figure 5 depicts the peak of the pseudo molecular ion [M+H+ACN]+ at 576 m/z. The true compound exhibits a molecular weight of 534. According to Liu et al. [10], the molecular weight peak at 534 m/z can be assigned to C₃₂H₃₆N₄Ni, a nickel-bound porphyrin compound [10]. Using the method described by Liu et al. [10], we observed a porphyrin compound with a molecular weight of 541 m/z. The molecular weight indicated that the nickel ions were replaced with vanadium oxide. In figure 5, the pseudo molecular ion peak [M+H+ACN]+ can be observed at 583 m/z. This indicated that the compound was etioporphyrinato vanadyl (IV), with a molecular formula of C₃₂H₃₆N₄VO, as depicted in figure 6. These results were supported by the UV–Vis characterization in figure 3, which indicated the presence of a metal porphyrin.
Figure 4. FTIR spectra of the concentrated crude n-heptane soxhlet extract and concentrated fractions 6 and 7 after performing column chromatography.

Figure 5. Mass spectrogram of fraction 7 from the heptane soxhlet extract that was subjected to column chromatography.

Figure 6. Molecular structure of etioporphyrinato vanadyl (IV).
4. Conclusions
The toluene Soxhlet extracts of the Duri crude oil residue, both aided and unaided by silica gel, accounted for 55.15% and 86.75% of the crude residue, respectively. The addition of silica caused the polar organic compounds to be adsorbed and increased the contact surface area of porphyrin and asphaltenes with the solvents during separation. UV–Vis spectroscopy of the n-heptane Soxhlet fraction indicated the presence of a free porphyrin with absorption maximum at 440 nm and metal porphyrins at 575 and 627 nm. The mass spectrum result of LC–MS indicated the presence of Ni(II) porphyrin (C₃₂H₃₆N₄VO, 534 m/z) and etioporphyrinato vanadyl (IV) (C₃₂H₃₆N₄VO, 541 m/z).

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