STUDIES ON ALIPHATIC AND AROMATIC HYDROCARBONSOF MINAS AND DURI
CRUDE OILS USING GC-MS

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INTRODUCTION

Studies on the crude oils from Minas and Duri located in Riau Province, Indonesia are reported in this paper. Minas and Duri are well-known as oil producing area in Indonesia. The oil fields are located in central eastern part of Sumatra Island. Physical characteristics of those crude oil are available but the chemical characteristic of the petroleum hydrocarbons are not well documented. Characterization of crude oils were identified by GC-MS to get specific fingerprint is very important. Extensive spillage of crude oil and refined oil is a possible source of hydrocarbon pollution in marine environment. GC-MS are very powerful instrument to analyse crude oil (Wang, 2004). Using molecular markers as a tool to see the relationship of the crude oils. It would affect their fate in the environment (Blumer et al., 1973). This study focuses on the characterization of alkanes and polycyclic aromatic hydrocarbons (PAHs) for the crude oils using 1st step (5% H2O deactivated silica gel column) and 2^{ad} step (fully activated silica gel column) and then GC-MS analysis. The PAHs signature are useful as source material for future 'fingerprinting' studies in monitoring oil contamination especially in Riau Province, Indonesia.

EXPERIMENTAL SECTION

All the organic solvent such as Methanol, Acetone, Isooctane, Hexane, Dichloromethane and standard solution such as alkanes, hopanes and PAHs were purchased from Wako Pure Chemical, Chiron and Sigma. PAHs surrogate internal standard (SIS) consists of five PAHs namely naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_u and perylene-d_4. Internal Injection Standard (IIS) uses p-terphenyl-d_{14}. Deionized water purified by filtration through the Millipore-Q system was used in all experiment (Zakaria, et.al., 2000). Aliphatic (n-alkanes) and aromatics (PAHs) were identified by Hewlett Packard HP Series 6890 Gas Chromatograph (GC) interfaced with Mass Selective Detector (MSD) HP Series 7683-SIM (Selective Ion Monitoring) Mode. Helium was used as carrier gas at 100 kPa. The instrument was set at 70 eV ionization potential with the source at 200°C and electron multiplier voltage at —2000 eV. The injection port was maintained at 300°C. Exactly 1 [IL of the sample was injected in the splitless mode followed by 1 minute purge after the injection. The column temperature was held at 70°C for 1 minute then programmed at 20°C/min to 250°C and at 4°C/min to 310°C, and held for 20 minutes (Zakaria, et al., 2001). A Selected Ion Monitoring (SIM) mode was employed after an initial solvent delay of 4 minutes. In this study, 16 individual PAHs were analyzed. They had been chosen because of their carcinogenic and mutagenic effects.

RESULTS AND DISCUSSION

Table 1 ang Figure 1 shows the finding of the diagnostic ratios of aliphatic hydrocarbons (n-alkanes) in both crude oils from Central Sumatran Basin.

Table 1. Diagnostic Ratios of n-Alkanes Analysis in Crude Oils

Crude Oil	Diagnostic Ratio of n-Alkanes				
	EAlkanes (1.1g/g) [a]	UCM [b]	Pr/Ph '	L/H [d]	CPI '
Duni	1165	n.d	2.4	11.8	0.82
Minas	1270	n.d	2.1	13.0	0.77

[a] EAlkane=sum of n-C16 to n-C36. [b] UCM=unresolved complex mixture. Pr/Ph= a ratio of pristane to phytane. [d]L/H = sum of n-C_{16} — nC36 alkane relative to sum of n-C_{27}-nC36 alkane. 'CPI = 1/2 [(C25+C27+ 29+C31+C33)/(C24+C26+C28+ C30 +C32)]+[(C25+C27+C29+C31+C33)/(C26+C28+C30+C32+C34)]. n.d = not detected

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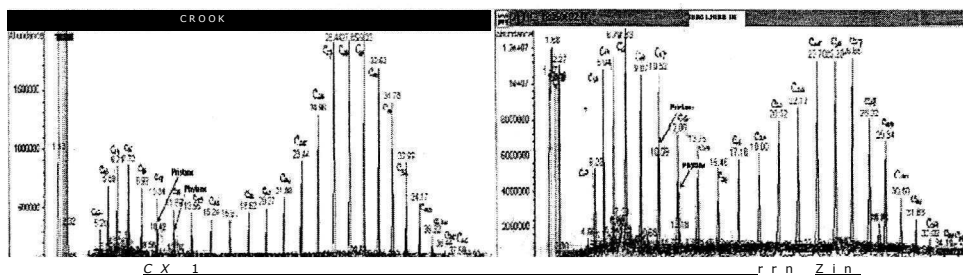
Figure 1. Typical Chromatograms of n-Alkanes from Minas (a) and Dun (b) Crude Oils

The typical GC chromatogram of n-alkanes distribution (C_{16}-C_{34}), as well as the isoprenoid alkanes: pristane and phytane are presented in Figure 1. It is identified that the distributions of the odd and even carbon number n-alkanes ranges C16-C36 were nearly identical peaks. The concentrations of total n-alkanes in Riau Province's crudes are Dun 1165 p.g/g and Minas 1270 pg/g, respectively as shown in Table 1. The low molecular weight relative to high molecular weight (L/H) n-alkane ratios indicate that Minas and Dun crude oils tend to be more abundant in low molecular weight of alkanes indicating the freshness of the oil.

Table 2. Diagnostic Ratios of PAHs Analysis in Crude Oils

Crude Oil	Diagnostic Ratio of PAHs		
	EPAHs (ug/g) [a]	L/H ratio [b]	MP/P ratio
Duri	4061	0.68	1.46
Minas	7335	3.67	4.07

[a]E PAHs = sum of concentration of dibenzothiophene + phenanthrene + anthracene + 3-methyl-phenanthrene + 2-methyl-phenanthrene+ 9-methyl-phenanthrene + 1-methyl- phenanthrene + 2methyl-anthracene + fluoranthene + pyrene + 1-methyl-pyrene + benzo(a) anthracene + chrysene + benzo(k) fluoranthene + benzo(e)acephenanthrylene + benzo(e)pyrene + benzo(a) pyrene + dibenzo(a,h)anthracene. [b]L/H ratio = a ratio of sum of concentration of dibenzo thiophene to pyrene relative to sum of concentration of 1-methyl-pyrene to dibenzo (a,h) anthracene. [c]MP/P ratio = a ratio of sum of 3-methyl-phenanthrene + 2-methyl-phenanthrene + 9-methyl-phenanthrene + 1-methyl-phenanthrene
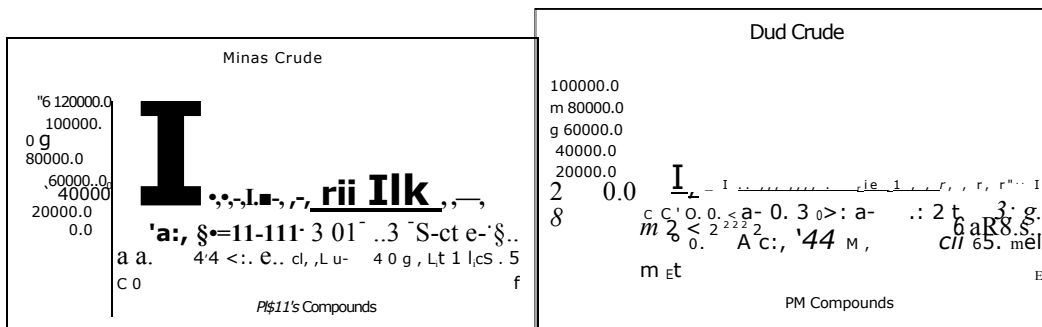

Figure 2. Individual PAHs Concentrations Determined in Minas (a) and Duri (b) Crudes

PAHs profile's distribution from dibenzothiophene to benzo(a,h)anthracene in the crude oils shows in Figure 2. The crudes are mostly dominated by 4-ring PAHs from fluoranthene, pyrene, 1-methyl pyrene, chrysene, and benzo(a)antracene. Low molecular weight of PAHs (2-, 3-ring PAHs) also detected lower than 4-ring PAHs. So, the L/H ratios for the crude oils are 0.68 (Duri) and 3.67 (Minas) and with the absence of UCM. The dominant of high molecular weight of PAHs, they would be expected to be South East Asia crude oil (SEACO).