Characterization of Hydrocarbons in Smoke Aerosols from Burning of Three Tropical Wood Species
(Pencirian Hidrokarbon dalam Zarah Asap daripada Pembakaran Tiga Spesies Kayu Tropika)

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ABSTRACT
A study has been carried out to characterize hydrocarbons emitted from the burning of three tropical wood species. The woods were burned to ember and smoke aerosols emitted were sampled using high volume sampler fitted with a pre-cleaned glass fibre filters. Hydrocarbons were extracted using ultrasonic agitation with dichloromethane-methanol (3:1 v/v) as solvent and the extracts obtained were then fractionated on silica-alumina column. Detection and quantification of aliphatic and polycyclic aromatic hydrocarbons (PAHs) compounds were carried out using GC-MS. The results indicated that the major aliphatic hydrocarbons characterized were straight chain n-alkanes in the range of C$_{12}$-C$_{35}$ with C$_{\text{max}}$ in the range of C$_{27}$-C$_{33}$. Rhizophora apiculata and Hevea brasiliensis wood smoke exhibited a weak odd to even carbon number predominance with carbon preference index (CPI) values greater than one whereas Melaleuca cajupati wood smoke aerosols did not exhibit similar pattern with CPI obtained close to one. The results obtained also indicated that burning of these wood resulted in formation of PAHs compounds in their smoke aerosols with predominance of three to four rings PAHs over the two, five and lesser of six rings PAHs. PAH diagnostic ratios calculated except for Flan/(Flan+Py) and Indeno/(Indeno+BgP) were consistent with the ratios suggested for wood combustion source as reported in literatures. In the case of the latter, two diagnostic ratios, the values were generally lower than the range normally reported for wood combustion.

Keywords: Biomass burning; combustion process; diagnostic ratios; polycyclic aromatic hydrocarbons; smoke aerosols

INTRODUCTION
Biomass burning has been widely known as one of the important primary source of soot and organic particulate matter, which influence the atmospheric chemical, optical and radiative properties through direct and indirect mechanisms (Crutzen & Andreae 1990; Levine et al. 1995; Oros & Simoneit 2001a; Simoneit 2002). Biomass burning that occurred through natural (forest fire and volcanoes) and anthropogenic (man-made fire, slash and burn of forest trees) activities, had significantly increased the input of organic pollutants to the atmosphere including the carcinogenic and mutagenic compound, like polycyclic aromatic hydrocarbons (PAHs). The knowledge on the chemical composition of these aerosols is important to understand the role of biomass burning emissions on the atmospheric chemistry processes. In general, each individual plant species emits ‘chemical fingerprint’ of natural (unaltered) and thermally altered (pyrolysis) organic constituents which is source specific and unique in composition upon burning, thus, they can
be utilized as specific indicators for identifying fuel source inputs, transport mechanisms and receptor fate in samples of atmospheric fine particulate matter (Oros & Simoneit 2001a). In Malaysia, biomass burning is mainly practiced through clearing of agricultural wastes, garden refuse and in rural areas, through domestic cooking. The charcoal processing industry found at the coastal areas of Terengganu uses paper bark tea tree (*Melaleuca cajupati*) wood for charcoal making. In contrast, similar industry in the west coast of Peninsular Malaysia uses mangrove tree (*Rhizophora apiculata*) wood as raw material for charcoal making. Terengganu is also popular with ‘keropok lekor’ or fish cake industry which can be found along the coastal areas (e.g. Penarik, Merang, Batu Rakit, Chendering) or fish cake industry which can be found along the coastal areas (e.g. Penarik, Merang, Batu Rakit, Chendering).

**EXPERIMENTAL DETAILS**

**SAMPLING**

*Melaleuca cajupati* wood was sampled at Kg. Bukit Tunggal, located few kilometers away from major roadside whilst *Rhizophora apiculata* wood was sampled from a mangrove area located at Kg. Merang, Setiu, Terengganu. For both wood samples, only trunk part was taken for burning process. *Hevea brasiliensis* wood was collected from a ‘keropok lekor’ shop located at Kg. Batu Rakit, Kuala Terengganu. All woods sampled were kept in a box lined and covered with aluminium foils to prevent from contamination during transportation to the laboratory. Once in the laboratory, the woods were cleaned from unwanted debris and kept in separate paper boxes. The woods were later air dried in aluminium line boxes for a period of two to three weeks before subjected to burning process.

**SAMPLING OF WOOD SMOKE AEROSOLS**

Each type of wood samples was burnt completely to ember. The smoke emitted throughout the burning process were collected using a high-volume air sampler (HVS) fitted with a pre-cleaned glass fibre filter, placed approximately 1 m diagonally above and to the side of the flames in the smoke plume.

**EXTRACTION AND FRACTIONATION**

Hydrocarbon compounds were extracted using ultrasonic agitation with dichloromethane-methanol (3:1 v/v) as solvent. Before extraction, two internal standards consisted of predeuterated tetracosane-d50 (C50D50) for aliphatic fraction and predeuterated perylene-d12 (C36D12) for aromatic fraction was spiked into the filter paper for recovery assessment. The extracts were concentrated to about 1 mL using rotary evaporator and concentrated extracts were then fractionated on a silica-alumina column (silica: 5% deactivated (230-400 mesh); alumina: 2% deactivated (70-230 mesh)) using n-hexane to elute the aliphatic compounds and PAHs compounds were eluted using a combination of 10% DCM in hexane followed by 50% DCM in hexane.

**GC/MS ANALYSIS**

Identification and quantification of the aliphatic and 17 USEPA priority PAHs compounds were carried out using Shimadzu-QP2010 GC-MS in EI mode (70eV). The compounds determined for aliphatic hydrocarbons were n-alkanes ranging from n-dodecane (C12) to n-hexatriacontane (C36), whilst the 17 priority PAHs compounds were as follows: napthalene (Naph), acenaphthylene (Acena), acenaphthene (Ace), fluorene (Fluo), phenanthrene (Phen), anthracene (Anth), fluoranthene (Flan), pyrene (Py), benzo[a]anthracene (BaA), chrysene (Chry), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), benzo[e]pyrene (BeP), indeno[1,2,3-cd]pyrene (Indeno), dibenz[a,h]anthracene (Dibenzo), benzo[g,h,i]perylene (BghiP). The sum of n-alkanes is referred as total n-alkanes (TNA) whist the sum of 17 USEPA priority PAH compounds is known as total identified PAHs (TIP). The GC was used in splitless mode using helium as carrier gas at a rate of 1.20 mL/min. Column temperature for aliphatic compounds quantification was programmed at 70°C (1 min hold) to 140°C at a rate of 8°C/min, then up to 300°C at a rate of 7°C/min and hold isothermal for 10 min. Meanwhile, for PAHs compounds column temperature was programmed at 70°C (hold 2 min) to 180°C at a rate 25°C/min, then up to 280°C at a rate of 6°C/min and hold isothermal for 10min. Verification of peaks was carried out based on key fragment ions, retention times compared to those of external aliphatic hydrocarbons and PAHs standards and/ or mass spectra.

**RECOVERY BLANKS**

The recovery of the multi-step procedure for tetracosane-d50 ranged from 78-112% whilst perylene-d12 ranged from 68-95%. Appropriate corrections were made to the measured concentrations. Procedural blanks as well as solvent blanks were analyzed and quantified to ensure that there were no significant background interferences; no aliphatic and PAH compounds of interest were detected in these blanks.

**RESULTS AND DISCUSSION**

The following section present the result of hydrocarbon compounds obtained from wood smoke aerosols studied. It must be conceded that distributions and abundances of n-alkanes and PAHs compounds quantified from *Rhizophora apiculata*, *Melaleuca cajupati* and *Hevea*...
**brasilienis** wood smoke aerosols are strongly dependent on combustion conditions (e.g. smoldering versus flaming duration) and although attempt has been made in this study to sample aerosols under similar condition (during both smoldering and flaming conditions), uncertainty remains with respect to the duration of each combustion phase. Since the burning of wood samples were not carried out in a controlled combustion chamber the values reported in this study should not be used as absolute value but as a relative chemical fingerprints for each wood sample.

**ALIPHATIC HYDROCARBONS (n-ALKANES)**

Table 1 shows the total n-alkanes (TNA) concentration calculated for all smoke aerosols samples, their respective carbon maximum (C\text{max}) and carbon preference index (CPI) values. The n-alkanes detected in all smoke aerosols samples were of straight chain n-alkanes in the range of C\text{12}-C\text{35} (Figure 1). It can be observed that *Rhizophora apiculata* wood smoke exhibited the highest TNA concentration of 49015 \(\mu gg^{-1}\), with C\text{max} at C\text{29} and CPI value of 1.44. *Hevea brasiliensis* wood smoke on the other hand exhibited TNA concentration of 4172 \(\mu gg^{-1}\) with C\text{max} at C\text{14} and CPI of 1.22 while *Melaleuca cajupati* wood smoke emitted TNA concentration of 2401 \(\mu gg^{-1}\) with C\text{max} at C\text{26} and CPI of 1.02. Carbon preference index (CPI) is defined as the concentration ratio of the sum of odd carbon number homologues over the sum of even carbon number homologues across a specified carbon number range and is generally used for identifying the source of n-alkanes. According to Simoneit (1984), carbon number profiles of n-alkanes derived from natural sources show CPI value greater than two, while those derived from fossil fuel combustion show a pattern with no carbon predominance and CPI value lesser than one. In this study, the CPI value calculated for n-alkanes in the chain length between C\text{12}-C\text{36} for the respective smoke sample were in the range of 1.02-1.44. *Rhizophora apiculata* and *Hevea brasiliensis* wood smoke exhibited weak odd-to-even carbon number predominance whereas *Melaleuca cajupati* wood smoke did not exhibit any carbon predominance. The CPI values obtained in this study were significantly less than typically reported values for CPI associated with leaf burning (Tay et al. 2007), probably due to the lesser amount of wax/resins materials present in the wood sample whereby this bark that contain the most waxes only attribute small percentage from the whole wood sample. This could be the reason for low CPI value especially in *Melaleuca cajupati* wood smoke aerosol. *Melaleuca cajupati* is papery or tissues like in structure and very easy to absorb water or moisture in the air, which makes it contain only a small amount of wax material in their bark. In addition, the low CPI obtained in this study could be due to the differences in chemical composition of wood compared to leaves/grasses. Leaves contain more of cellulosic material whereas wood were mainly made up of lignin materials. Although the CPI value of *Melaleuca cajupati* obtained is close to one and shows weaker odd-to-even carbon predominance, the C\text{max} obtained was still in the range of C\text{25}-C\text{33}. Vascular plants synthesize epicuticular waxes which often contribute up to 90% of all paraffin found in plant waxes (Eglinton & Hamilton 1963; Eglinton et al. 1962; Kollattukudy 1970; Pelejero 2003; Riele et al. 1991; Simoneit & Mazurek 1982). Consequently, the signature of odd C\text{max} in the range of C\text{25} to C\text{33} have also been reported on numerous studies relating to biomass burning of different vegetation, namely wood (Oros & Simoneit 2001a, 2001b; Tan et al. 2004), grass and litter falls (Tay et al. 2007).

**POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)**

Polycyclic aromatic hydrocarbon (PAH) compounds are generally formed by thermal decomposition of any organic matter containing C and H atom through either incomplete combustion (pyrolysis) or carbonization process and in the case of biomass burning it is formed either from high temperature thermal alteration of natural product precursors in the source organic matter or process of recombination of molecular fragment in the smoke. Figure 2 shows the distribution of individual PAH compounds found in the studied wood smoke aerosols samples. Seventeen PAHs were quantified in this study, but not all of the seventeen PAHs were detected in smoke aerosols in the samples analyzed. Thirteen and fifteen PAHs were detected for *Rhizophora apiculata* and *Melaleuca cajupati*, respectively, whilst *Hevea brasiliensis* wood

**TABLE 1. Concentration of aliphatic hydrocarbons in wood smoke aerosols samples**

<table>
<thead>
<tr>
<th></th>
<th>Mangrove tree (Rhizophora apiculata)</th>
<th>Paper bark tea tree (Melaleuca cajupati)</th>
<th>Rubber tree (Hevea brasiliensis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total identified resolved aliphatic hydrocarbons (TIRAH), (\mu g g^{-1})</td>
<td>49015</td>
<td>2401</td>
<td>4172</td>
</tr>
<tr>
<td>C\text{max}</td>
<td>C29</td>
<td>C27</td>
<td>C31</td>
</tr>
<tr>
<td>Carbon Preference Index (CPI), (C_{n-1}C_{n+1})</td>
<td>1.44</td>
<td>1.02</td>
<td>1.22</td>
</tr>
</tbody>
</table>

\(C_{n-1}C_{n+1}\): Carbon maximum, \(CPI = \frac{\sum (C_{n-1}C_{n+1})}{\sum (C_{n-1}C_{n})}\)
smoke exhibited the most PAH compounds with sixteen compounds detected. The major PAH compound emitted in the wood smoke aerosols were phenanthrene, fluoranthene and pyrene with pyrene exhibited the highest compound emitted in all smoke aerosols studied. Table 2 presents the total identified PAHs (TIP) concentration found in the wood smoke ranging from 1485 to 1981 μg g⁻¹ with *Hevea brasiliensis* emitted the highest TIP concentration and *Melaleuca cajupati* the lowest. Compared to the number of ring for PAHs compound emitted, PAHs with 3 and 4 rings exhibited the highest PAH emitted followed by two and five rings PAH and 6 rings PAH. The low concentration and percentage of 2-ring PAHs obtained in all smoke samples were probably due to their higher tendency to evaporate. These lighter low molecular weight PAHs tend to remain in the gaseous phase rather than the particulate phase of

![Figure 1: Distribution of individual n-alkaes compounds present in wood smoke aerosols samples](image1)

![Figure 2: Distribution of individual polycyclic aromatic hydrocarbons present in the wood smoke samples](image2)
the smoke aerosols. This observation is consistent with the results reported by Zou et al. (2003) which detected the lower molecular weight PAHs (molecular weight ≤ 200) in the gaseous phase of firewood smoke aerosols. Since only smoke aerosol particulates were trapped to the fibre filter paper, it was not surprising that higher concentration of 3-rings and above PAHs was observed in this study. Besides, combustion temperature was also important in determining the formation of these medium to high molecular weight PAHs. Grimmer (1983) and Jauhiainen et al. (2005) has shown the effect of temperature on the formation of PAHs compounds. At high temperature combustion (T°C>700°C) and in insufficient of oxygen condition, the combustion happened simultaneously with pyrolysis reaction which enhances the formation of PAHs compounds. As the combustion temperature increased, the formations of higher molecular weight PAH increase with decreasing of lower and unstable molecular weight PAH (Jauhiainen et al. 2005). Lu et al. (2009) also reported in their study, as temperature increased, the emissions of benzog,h,i]perylene from burning of rice straw and bean straw had increased by 94% due to the breakup of unstable lower molecular weight PAH as temperature increased and recombined into larger and more stable compound with higher molecular weight.

PAHs DIAGNOSTIC RATIOS

PAHs ratios have been used to determine PAH sources; clarify sample by location and estimate the importance of combustion- and petroleum derived PAH (Yunker et al. 2002a, 2002b). The usual index of combustion and/ or anthropogenic input is an increase in the proportion of the less stable and/or kinetically produced parent PAH isomers relative to the thermodynamically stable isomers (e.g. fluoranthene relative to pyrene) or to the molecular mass totals (Yunker et al. 2002b). Such ratio calculations are traditionally restricted to PAH within given molecular mass to minimize confounding factors such as differences in volatility, water solubility and adsorption (Yunker et al. 2002a). Yunker et al. 2002b have evaluated and suggested four PAH isomer ratios as a diagnostic indicators to identify the possible major source of PAH compounds based on the ratio value (Table 3). Table 4 shows the ratios calculated for the three wood smoke samples analyzed in this study. For comparison, several ratios reported in the literature were also included. The ratios of Anth/(Anth+Phen) and BaA/(BaA+Chry) calculated in this study for the three wood species are consistent with the range suggested by Yunker et al., 2002b for biomass burning. In addition, Phen/(Phen+Anth) ratios obtained in this study are also in the range obtained for burning of leaves and twigs of Melaleuca cajupati (Wong 2007) and wood burning (Oanh et al. 1999; Santos et al. 2006; Tan et al. 2004). However, in the case of Flan/(Flan+Py) and Indeno/(Indeno+BgP) ratios, not all samples exhibited values that are generally accepted as indicative of biomass burning (ratio>0.5). At present, because of limited studies on wood combustion, it was uncertain whether the observed results reflect probable diagnostic ratios of tropical wood smoke aerosols. Thus more work is needed to ascertain whether the results obtained was a true reflection of differences in types of wood (tropical vs. temperate) or due to differences in combustion temperature.

CONCLUSION

The results obtained showed that Rhizophora apiculata, Hevea brasiliensis and Melaleuca cajupati wood smoke aerosols samples exhibit n-alkanes distribution in the range of C_{15} - C_{36} with C_{max} at C_{21}, C_{29} and C_{31}; CPI value of 1.02, 1.44 and 1.22, respectively. It is interesting to note

<table>
<thead>
<tr>
<th>Source</th>
<th>PAH isomer ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petroleum (unburned)</td>
<td>&lt; 0.10</td>
</tr>
<tr>
<td>Petroleum combustion</td>
<td>0.40 - 0.50</td>
</tr>
<tr>
<td>Petroleum &amp; Combustion (mixed)</td>
<td>0.20 – 0.35</td>
</tr>
<tr>
<td>Combustion</td>
<td>&gt; 0.10</td>
</tr>
<tr>
<td>Biomass &amp; coal combustion</td>
<td>&gt; 0.50</td>
</tr>
</tbody>
</table>

Yunker et al. (2002b)
that, despite the burning process, the signature/marker of epicuticular waxes or terrigenous plant input is still retained. Dominant PAH compounds found in the smoke samples were 3 to 4 rings PAH with lesser amount of 2, 5 and 6 rings PAH. This could be a reflection of burning temperature which exerts an important role in the formation of PAH compounds. The PAH diagnostic ratios calculated except for Flan/(Flan+Py) and Indeno/(Indeno+BgP) ratios, were consistent with the ratios generally associated with general combustion source and also within the ratios suggested for wood combustion source as reported in literatures. In the case of the latter two diagnostic ratios, the values obtained for Melaleuca cajupati and Hevea brasiliensis wood aerosols were generally lower than the range normally reported for wood combustion. At present, it is still unclear whether these values are a true reflection of different wood species or burning temperature, thus, based on the information obtained so far, there is a need to exercise some degree of caution when trying to interpret sources from combustion groups of sources using these diagnostic ratios.

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