Carbon Content Evaluation and Related Vocs Emission from Experimental Burn Of Tropical Biomass

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Abstract: *Tropical biomass burning contributes significantly to the global atmospheric pollutants. This study presents the compositional analysis and the associated volatile organic compound (VOC) emissions from ten tropical (Malaysian) biomass species by a developed on-line burning facility. In addition, the potential of the analysis method to estimate the emitted compounds and the emission factor were also demonstrated. The biomass species were selected based on their frequent exposure to natural and man-made fires. The smoke was withdrawn from the facility, conditioned and regulated to a constant flow; consequently, activated carbon traps adsorbed the trace gases to capture the VOCs. The sampling period for the gases from the burning facility was integrated over both smoldering and flaming phase course fires. The adsorbed VOCs were extracted by an organic solvent and quantified using a special program on gas chromatography/mass spectrophotometry (GC/MS). The on-line burning facility analysis results showed that a number of VOCs captured by the sampling method. The results also suggest that biomass burning emissions factor contributes significant amounts of benzene, toluene and m,p-xylene in relation to the biomass carbon content. Thus, over mass tropical burn great attention needed to address the emission impact.*

Keywords*: biomass, burning, experimental, emissions factor, GC/MS, sampling, tropical, VOCs,*

I.   Introduction

Given that they contribute to the oxidative capacity of the atmosphere, volatile organic compounds (VOCs) are of high interest for atmospheric chemistry and biogeochemistry studies [1, 2, 3, 4, 5, 6]. Still, our knowledge of the role of some dominant ecotypes of the world's burning emission factors is insufficient in spite of the fact that global emission budgets for vegetation exist [7, 8, 9, 10]. There are large regions of the world that have been poorly investigated, namely tropical rainforest ecosystems [11, 2, 12].

Relatively few studies exist regarding atmospheric VOC concentrations, fluxes and emission factors within the tropics [13, 5, 13, 10]. Emissions from open burning on a mass pollutant per mass fuel (emission factor) basis are greater than those from well-controlled combustion sources [14].

Some types of open burning (e.g., biomass) are large sources on the global emission scale, when compared with other broad classes of sources (e.g., mobile and industrial sources). Data available in the literature varies according to the source and class of air toxins of interest [15, 16, 7, 17]. On a mass emitted per mass burned basis, fewer VOCs are typically emitted from biomass open burning sources than from those with anthropogenic fuels, particularly fuels containing polymers [8, 2, 4]. Biomass open burning sources typically emit fewer semi volatile organic compounds and poly aromatic hydrocarbons (SVOCs and PAHs) than anthropogenic sources on a mass emitted per mass burned basis [18]. Based on very limited data, biomass open burning sources have typically produced higher levels of carbonyls than anthropogenic sources on a mass emitted per mass burned basis, probably due to the oxygenated structures resulting from the thermal decomposition of cellulose [19, 13, 5].

It must be noted that local burn conditions could significantly change these relative levels. The pollutant emitted from the burning of the uncontrolled fires in Asia, and particularly in Malaysia, in Southeast Asia, in 1997 and 1998, triggered the alarm of issues such as biomass burning and greenhouse gas emissions [3, 2, 5, 12]. Thus, this study highlights the importance of tropical biomass contribution to the global emission of VOCs. The selected species represent the major ecosystem in tropical Malaysian forests. The use of an experimental burning facility enabled the biomass burn to be conduct and quantify in a representative manner, making it possible to obtain accurate and detailed measurements of the combusted material. In addition, the on-line burning facility will allow determining different compounds during the combustion phases Therefore, accurate mission estimation possibly may achieve.

II.   Materials And Method

2.1 The burning facility

The main parts of the burning apparatus include hood in the form of inverted funnel and burning table placed of high-resolution (0.001 gm) weighting scale (Figure 1).Earlier version of similar burning facility used by [13,17].

The weighting scale was calibrated with standard weights. Simple mechanism allows adjustment of the burning table to an angle up to 60° in order to simulate different wind direction. Gas sample analyzer probe, sampling line and other temperature sensors were mounted in the stack. The locations of the sampling points calculated as US-EPA standards. The sample weight loss during the burn recorded and monitored at real time via software installed in adjustment computer at frequency of 2-5 sec^{-1}.

III.   Vocs Sampling System

Stack sampling occurred through ¼ " controlled heated Teflon lines (length 5m). This heated tube line was used to draw the smoke from stack above the burning table to the universal sampling system. The use of the heated sampling line was to prevent condensation in the sampling tube line.

Universal sampling system contains Teflon filters (47 mm diameter, 2 μm pore size) was employed to remove particulate matters from the smoke stream in addition to trap the moisture. The smoke flow inside the heated tube continuously monitored and controlled during the experiment time.

Calibrations and all recovery procedures were performed earlier to ensure the accuracy and recovery level during the test.
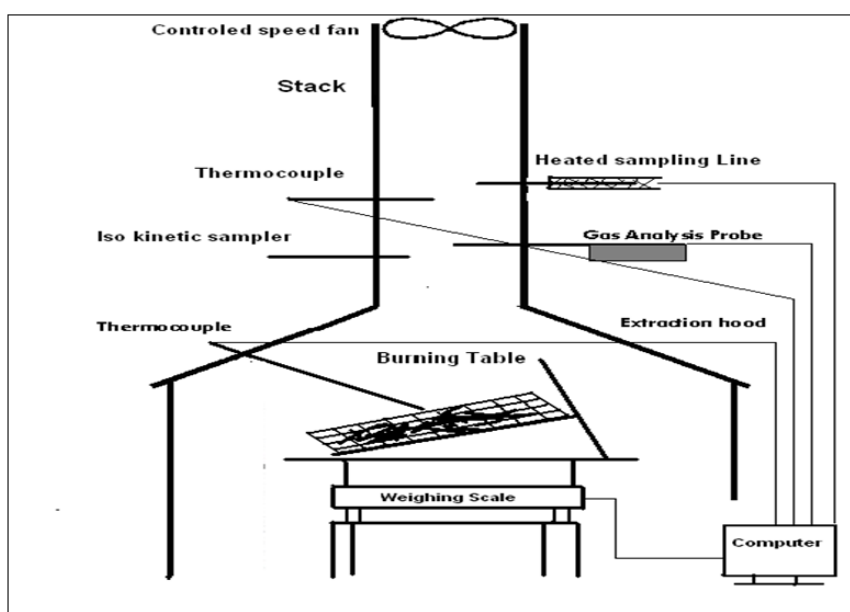

Fig. 1   Schematic diagram of open burning facility.

Methods of Collection of Volatile Organic Compounds (VOCs)

There are several techniques for collecting VOCs for analysis, including summa canisters, thermal desorption tubes, activated carbon tubes, and solid phase microextraction (SPME). All of these techniques are described in Table 1.For this project, a technique was needed that would be sensitive to chemicals that present in part per million ppm level [17, ,5, 9].

Each of the above technique has advantages and disadvantages. All of these techniques are sensitive enough to analyze VOCs emissions in the lower range of ppb and ppm. Our burning experiments require smoke sampling from the stack on top of the burning table for almost one hour period. This is due to the time needed for complete the burning of the tropical biomass sample.

Unfortunately, summa canisters have limited holding capacity. Moreover, SPME had disadvantage that it is capable of sampling a static headspace for limited period of time. Therefore, thermal desorption and carbon tubes offer better advantage that they can be used to collect VOCs over extended amount of time [14, 19, 14, 5,20].

Table 1 Summary of collection techniques. **Source** [13, 5].

Collection	Description	Collection substrate	Method of analysis
Suma Canisters	Air sampled into stainless steel canister	Canister	GC analysis
Thermal desorption tubes	Air passed through thermal adsorbent tube	Activated carbon	Thermal GC analysis
Activated carbon tubes	Air adsorbed on activated carbon	Activated carbon	GC analysis
Solid phase Microextraction (SPME)	Air sampled with highly adsorbent fiber	Special collection fiber	GC analysis

Several inorganic and organic sorbents are available as passive samplers. Examples of inorganic sorbents are silica gel, alumina magnesium, aluminium silicate and molecular sieves [5]. These types of sorbents are effective at collecting polar organic compounds however; in instances where the relative humidity is high the adsorption capacity may be affected [2, 14, 16]. The advantage of organic sorbents is their low affinity for water never the less; they also tend to collect water as easily leading to rapid sorbent deactivation. In addition, inorganic sorbents can cause isomerization of organic compounds. For these reasons, inorganic sorbents are not often used when collecting VOCs [14]. After comparison of all analytical aspects, activated coconut-shell carbon tubes were used (Supelco, Bellefonte, PA, USA) [3, 2, 14, 5]. Also, activated charcoal trap proved to have great recovery and absorption capacity toward VOCs [21, 14, 16, 13].

Sample Extraction And Analysis

Once the adsorbent tube disconnected from the sampling system after the burning completed, the contaminants were extracted for analysis. Solvent extraction method employed carbon disulphide (CS_2) as extraction solvent from the sorbent material. The analysis implies only a portion of the solution to analyze, allowing replicate analysis as well as further analysis [22, 16, 5, 13].

Quantitative analysis performed by injecting accurate amount from the extracted solution in the gas chromatograph mass selective detector GC/MS (Hewlett-Packard Network), with the following conditions; MS Transfer line: 28WC, Injector: 250 "C, Split ratio 10, Liner 4 mm straight liner with glass wool. Column: 2 - 20m X 0.18mm ID DB-624, J&W Scientific, Inc., with a 1.0 um film thickness. GC Temperature Program: Oven initial 40 ^{o}C, hold 8 min. Ramp to 100 "C @ 7 ^{o}C/min., hold 1 min., ramp to 240 ^{o}C @ 12 ^{o}C/min., hold 2.0 min. Flows: Column: He, 1.6 ml/min, column pressure 80kpa. (velocity: 35.7cm/sec).

Biomass Elemental Analysis

The Malaysian biomass species were characterized by a PerkinElmer elemental analyzer to quantify the total carbon, hydrogen, nitrogen and sulphur contents; these results are shown in Table 2. Each sample (~1mg) of dry wood powder was weighed into a clean, dry tin container (~33 mg tin, 20mm diameter. Circle crimped into cup) using an AD-6 Auto balance (calibrated precision 0.0001mg). The analyzer was calibrated with standard methods, and triplicates of each biomass sample were repeated to assure high accuracy of the analyzed data. The carbon contents in biomass also play an important role in their emissions [18,5, 13].

IV. Results And Discussion

As previously mentioned, emissions from the flaming phase are dominated by highly oxidized products, such as CO_2. Generally, the high diversity of VOC emissions is produced during the smoldering phase of the combustion process [2,14, 4, 13]. Nevertheless, most compounds that are measured mainly in the smoldering phase are also emitted during flaming, but, to a greater or lesser extent they are oxidized by the flames [2, 5, 13, 4]. An ultimate analysis of ten tropical biomass species under this study showed that the carbon content among the species ranged from 43.9 to 49.1% (w/w), as illustrated in Table 2 below.

Table 2 Compositional analysis of dried biomass.

Species	Carbon %	Carbon* %	Nitrogen %	Hydrogen %	Sulphur %	Ash %	C/N ratio
Kapur (s)	46.43	48.2	0.59	6.02	1.51	21.4	78.6
Acacia karoo	47.81	49.1	0.52	6.16	1.65	23.2	91.9
Bakau	47.24	43.8	0.67	5.27	1.3	14.8	65.97
Acacia tortilis	45.72	46.7	0.55	5.21	1.28	23.5	83.09
Acacia melifera	46.56	47.3	0.57	5.3	1.36	24.1	81.68
Acacia reficiens	46.83	47.6	0.61	5.17	1.35	22.8	76.77
Koko	45.5	43.9	0.68	5.08	1.28	22.1	61.02
Surian	45.94	44.1	0.59	5.11	1.26	21.7	77.86
Kanaf(s)	46.28	44.5	0.54	5.64	1.32	21.5	85.7
Sepetri	45.37	44.15	0.58	5.5	1.19	23.1	78.1

C* is the average carbon content of the particular component of the tree (trunk, branch, etc.), (s) softwood. All data were taken as dried weight % , species name were according to Forest division Malaysia.

Carbon content of the species varies due to the lignin and extractives contents [12, 7]. Therefore, the impact of different carbon contents among species will be further pronounced on the carbon emissions rate. The hydrogen contents ranged from 5.5 to 6.2% (w/w), whilst nitrogen and sulphur were also analysed. Their contents ranged between 0.52-0.68% and 1.19-1.65 % (w/w), respectively. All of these results are in a similar range with other tropical data published elsewhere [2].

It can correlate from Figure 2 that biomass species with higher carbon content emit more m,p-xylene compounds and thus higher emission factor. However, biomass spices Acacia Karoo, Melifira and Rificiens emit less carbon tetrachloride. There are few factors play vital rule in the emission intensity such wood density and moisture [23]. More investigation can carry on to identify the cause of low emissions of these compounds with that two species.

In addition, in all types of fires the transition from flaming to smoldering combustion did not occur quickly. In fact, most measured VOCs were emitted predominantly during the smoldering stage. Thus, it relates better with CO than with CO_2 [4, 24, 13].

Usually, the maximum emission level reached at the beginning of the smoldering phase, while the temperature is still high with few or no flames. Thus, this phenomenon also affects the burn efficiency and thus impact the emission.

The emission pattern also supports this fact, as it quickly declines after a sharp rise as the remaining fuel mostly burnt up. Table 3, below, shows the emission factors for four VOC compounds for ten types of biomass samples [25]. It was clear that higher VOC emissions might be due to the slower burning of the wood, and thus higher volatile releases [14, 5]. The increase in VOC emissions suggests less complete combustion, and therefore relates well to the increase in CO emissions during the smoldering stage [18, 24, 5].
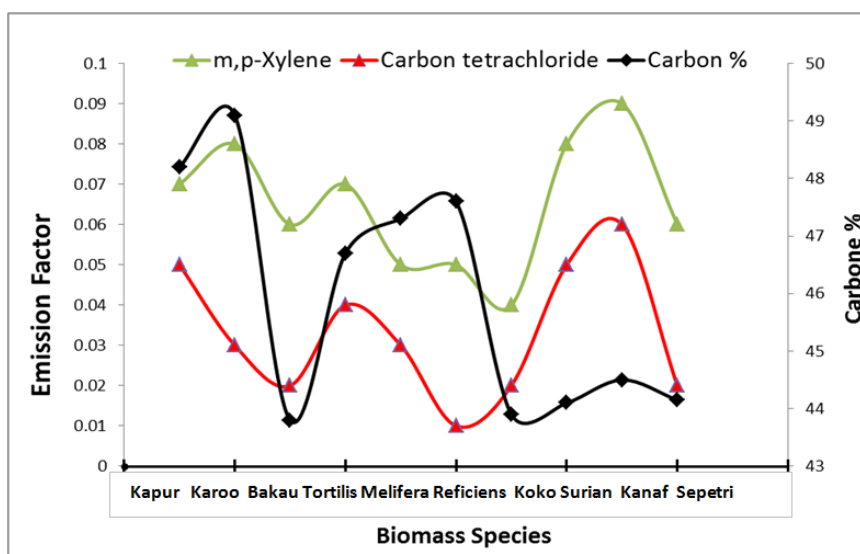

Fig 2 Correlation between carbon content and emission factor for carbon tetrachloride and m,p-Xylene.

The emissions of benzene and toluene are within the emission range given by [21, 3]. The compound xylenes, in this study, are close to the emission factors reported by [19, 13, 16, 9].

Table 3 Emission factors (gm/kg) for four VOCs compounds for different biomass samples.

Species	Compounds Emission factor gm/kg C, (average ± SD 0.89)			
	Benzene	**Toluene**	**m,p-Xylene**	**Carbon tetrachloride**
Kapur (s)	0.23	0.10	0.07	0.05
Acacia karoo	0.19	0.11	0.08	0.03
Bakau	0.17	0.12	0.06	0.02
Acacia tortilis	0.18	0.11	0.07	0.04
Acacia melifera	0.22	0.1	0.05	0.03
Acacia reficiens	0.19	0.09	0.05	0.01
Koko	0.17	0.1	0.04	0.02
Surian	0.16	0.08	0.08	0.05
Kanaf(s)	0.18	0.1	0.09	0.06
Sepetri	0.20	0.11	0.06	0.02

The emissions from different Malaysian biomass species produced mostly the same types of VOCs, but with different emission factors. This also could be attributed to the carbon content of the species. VOC emissions from these burning processes mostly oxygenated hydrocarbons [24]. The emissions are mainly from smoldering combustion. However, emission factors given for fire plumes are integrated over all stages of combustion.

One of the goals of VOC collection was to accumulate enough VOCs in the carbon tubes that GC/MS analyses could be performed. Thus, a large volume of smoke would compensate for this fact [5]. The GC/MS analyses demonstrated that samples emit a significant amount of VOCs. Another task of VOC collection was to collect as many VOCs as possible within the burning period without losing any due to oversaturation of the activated carbon. The GC/MS data analyses confirmed that there was no breakthrough of chemicals from the first to the second in-line carbon tube. Although a significant amount of compounds were inherent to the chamber and found during the VOC collection, it was encouraging to find unidentified peaks. The fragmentation pattern of the unidentified peaks suggests C_5 alkene is most similar to isoprene. The match quality is not high enough within the GC-MS library to firmly conclude it is isoprene, but it may suggest isoprene or a closely related isomer. Moreover, the presence of a C_5 hydrocarbon from biomass burning emissions is consistent with the extant literature. It was found that tea-leafed willows emit alkenes, such as terpenes, propene, 1-butene and isoprene [22, 19, 5, 26]. The sampling and the analysis method prove significant capability of qualitative and quantitative determinations.
Good agreement (±15%) was found with others measurements of tropical savannah biomass species [16, 17, 28, 5].In addition, the ratio of benzene to toluene in this study (~1.8) related to the ratio (1.7) from wood stove burning emission by [15, 5, 27].

In most experiments, the transition from flaming to smoldering combustion did not occur rapidly, and thus a large fraction of the emissions emitted during the mixed phase [14, 28, 15]. To account for the totality of the emissions, the mixed phase usually assumed to contribute equally (50:50) to both the flaming and smoldering phases. Flaming combustion consumed approximately 90% of the fuel in soft wood (kanaf and kapur) fires and 70% in all other biomass types [4, 13, 26, 5, 29]. Moreover, in soft wood fires more than half of the total emissions of almost all compounds actually emitted in the flaming phase (MCE ~0.98).

V.   Conclusion

Biomass fires have been responsible for several global and regional haze episodes in Southeast Asia and most of the fires in areas dominated by tropical biomass. Samples were burnt at an experimental burning facility to simulate both smoldering and flaming combustion products. The advantage of the burning facility was that it made it possible to achieve accurate mass emission per mass burned measurements, and therefore reliable emission factor data. Analyses of carbon biomass contents were useful to relate the burning conditions to the emissions. Adsorption of the smoke on the sorbent media that is capable of capturing VOCs followed by extraction and GC/MS analyses quantified the most prevalent compounds, thus emission factors were calculated. Aldehydes and PAHs were not detected in the combustion products; however, these may have been present at levels below the method detection limits. The emission factors determined in this study provide a quantitative basis for assessing the impact of biomass burning in Southeast Asia and to the global carbon budget, as they useful as input parameters for VOC inventories in various environmental models. The preliminary study reported here could be extended to investigate a greater variety of emission products over a wider range of biomass species.

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