On-line CO, CO₂ emissions evaluation and (benzene, toluene, xylene) determination from experimental burn of tropical biomass

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ABSTRACT

Atmospheric pollution and global warming issues are increasingly becoming major environmental concerns. Fire is one of the significant sources of pollutant gases released into the atmosphere, and tropical biomass fires, which are of particular interest in this study, contribute greatly to the global budget of CO and CO₂. This pioneer research simulates the natural biomass burning strategy in Malaysia using an experimental burning facility. The investigation was conducted on the emissions (CO₂, CO, and Benzene, Toluene, Ethylbenzene, Xylenes (BTEX)) from ten tropical biomass species. The selected species represent the major tropical forests that are frequently subjected to dry forest fire incidents. An experimental burning facility equipped with an on-line gas analyzer was employed to determine the burning emissions. The major emission factors were found to vary among the species, and the specific results were as follows. The moisture content of a particular biomass greatly influenced its emission pattern. The smoke analysis results revealed the existence of BTEX, which were sampled from a combustion chamber by enrichment traps aided with a universal gas sampler. The BTEX were determined by organic solvent extraction followed by GC/MS quantification, the results of which suggested that the biomass burning emission factor contributed significant amounts of benzene, toluene, and m,p-xylene. The modified combustion efficiency (MCE) changed in response to changes in the sample moisture content. Therefore, this study concluded that the emission of some pollutants mainly depends on the burning phase and sample moisture content of the biomass.

Introduction

Humans have used fire throughout history to improve crop production, hunting, cooking, heating, and lighting (Yang et al., 2004). These uses continue today on a large scale in the tropics where the population is rapidly increasing. The total emissions of (CO₂, CO, and Benzene, Toluene, Ethylbenzene, Xylenes (BTEX)) from burning tropical biomass contribute 30% to the total global emissions and thus influence the properties of the atmosphere (Chrysikou et al., 2008; Andreae and Merlet, 2001; Hallquist et al., 2009; Keith and Elliot, 2002; Christoffer, 2005; Crutzen and Andreae, 1990; Saleh et al., 2013). These emissions occur through the release/redistribution of carbon (Prather et al., 1994), which changes the oxidative capacity of the atmosphere and affects human health (Hobbs et al., 1997; Kaufman and Fraser, 1997; Lelieveld et al., 1997; Mason et al., 2001; Sharkey, 1997; Tan et al., 2012). Further studies are needed to obtain more
reliable emission estimates and to address accurate tropical biomass burn (Kurokawa et al., 2013; Goode et al., 2000; Yang et al., 2004; Zhang et al., 2008).

Earlier field and laboratory measurements were conducted other than Malaysia, where the smoke was trapped and characterized (Bertschi et al., 2003; Goode et al., 1999; Holzinger et al., 1999; Lobert et al., 1993; Yang et al., 2004; Yokelson et al., 1996, 1997, 1998) and these laboratory studies were in good agreement with field measurements (Sahu, 2012; Yokelson et al., 2003). All of the past studies suggested the importance of using an experimental burning strategy in order to correlate the experimental burn to a natural burn. In addition, the experimental burn provides details on the compounds that are below the detection limits in field studies.

Therefore, this experimental study investigates the burning emissions of common tropical biomass species in Malaysian forests where natural/manmade burning frequently occurs. To the best of our knowledge, implementation of the experimental burning facility used in this study was the first such research in Malaysia.

1. Experimental

1.1. Selection and sampling of Malaysian biomass

The tropical biomass samples used in this study were obtained from the Forest Research Institute Malaysia. These samples were selected by the Chemistry Division of Forest Research Institute Malaysia based on their wide existence in the Malaysian forest and their high exposure to forest fires. Ten types of tropical biomass were investigated in this study: namely Koko, Kapure, Bakau, Acacia karoo, Acacia tortilis, Acacia melifera, Acacia reficiens, Surian, Kanaf, and Sepetri.

The moisture content of the biomasses was determined in oven drying procedure accordance (USDA Forest Products Laboratory, Wood Handbook, 1999). Biomass sample was placed in an oven (105°C) and initial weight was recorded. Periodical weighing (every 3 hr) was performed until constant weight was achieved.

1.2. Combustion facility, CO and CO2 sampling, and analysis

The burning facility used in this study (Fig. 1) was significantly modified from the earlier versions (Lobert et al., 1991; Manö and Andreae, 1994; Holzinger et al., 1999). The main component is a hood in the form of an inverted funnel and a burning table placed on a high-resolution balance (0.01 g). An online gas analyzer was attached to the facility to measure the emissions of CO and CO2 gases. Real-time monitoring and data capturing software were used to store the data for further analysis. A universal gas sampler probe was installed in the stack for BTEX collection. Temperature sensors and sample weight loss data during the burning process were monitored and captured by the online software. The data collection frequency was set to three to five seconds to obtain accurate burning behavior monitoring.

During the burning process, the biomass mainly utilized in the flaming phase produced less smoke than in the smoldering phase (Kurokawa et al., 2013; Peterson, 1987; Peterson and Sandberg, 1988).

The flaming phase normally was recognizable by high moving flames that dominated the burning process. This phase usually consumed more than 80% of the sample weight and was followed by a smoldering phase. Minimum of triplicate burning cycles were obtained with 4–5 kg of sample. The duration of a complete burning cycle (flaming and smoldering) was relatively 45–60 min.

1.3. BTEX sampling, extraction, and analysis

The BTEX emissions were captured by activated coconut-shell carbon tubes (Supelco, Bellefonte, USA). This type of complete sample burning is time-intensive (Andreae and Merlet, 2001;
Chrysikou et al., 2008; Fine et al., 2004; Keith, 1991; Keith and Elliot, 2002; May et al., 2013). Sample extraction was done by carbon disulfide (CS$_2$). Then, the extract was injected quantitatively into a GC/MS type (Hewlett-Packard 6890/5972) gas chromatograph with the following conditions: MS Transfer line: 28WC, Injector: 250°C, Split ratio 10. Column: 2–20 m x 0.18 mm ID DB-624, J&W Scientific, Inc., with a 1.0 μm film thickness. GC Temperature Program: Oven initial 40°C, hold 8 min. Ramp to 100°C at 10°C/min., hold 1 min, ramp to 240°C at 12°C/min, hold 2.0 min. Flows: Column: He, 1.6 ml/min, column pressure 80 kPa (velocity: 35.7 cm/sec). Adequate BTEX sensitivity of (20 ppb) was achieved with an average precision of 14% at 200 ppb level. Quality control for the analysis was done carefully to determine the blank and background for the results calculation. Thus, preliminary cycles on the sampling system and extraction followed by GC/MS analysis were conducted.

2. Results and discussion

2.1. Effect of moisture content on the burning emissions

Several factors may influence biomass burning emissions. One of the most often identified factors was the sample moisture content. The distribution of the burning stages is also highly dependent on the type of biomass (e.g., grass or solid and moister content). The biomass moisture content generally varies between 5% (e.g., dead grasses during dry season) and 20% (e.g., fresh biomass) (Andreae and Merlet, 2001; Kamalak Kannan et al., 2004; Lobert et al., 1991). Past emission estimate studies recommended the use of CO/CO$_2$ as the actual indicator for combustion quality (Yang et al., 2001). Therefore, this ratio was implemented in the calculations of this study.

The results showed that the ratio of CO/CO$_2$ increased from 2 to 10 when the fuel moisture was varied from 6% to 15%, which can be explained by the fact that the water in the biomass generally exists as bound and free water (Malcolm and Tina, 2012; Yang et al., 2001, 2004). Free water evaporates easily and travels to the surface to maintain the equilibrium vapor pressure while bound water is hard to evaporate (Yang et al., 2004). A high moisture content sample contributes more water to the burning zone, which enhances the smoldering stage (high CO emission). Similar work by Yang et al. (2001, 2008) also agreed with our results (i.e., a wetter biomass produces a thinner flame zone). It appears that higher biomass moisture content lowers the combustion efficiency (0.9 to 0.8), shortens the flaming stage (25 to 15 min) and prolongs the smoldering stage (25 to 35 min), which directly impacts the emissions. Therefore, biomass moisture content increases the emissions of CO.

2.2. Emissions of CO and CO$_2$

The typical burning behavior of biomass acacia is illustrated Fig. 2. The biomass moisture content was between 5%–8% on average. In addition, the emissions magnitude was generally similar for all the biomass types. Various physical properties of biomass may affect the burning process, such as the burning bed density, the sample size, and the compactness of the fuel bed. The flaming stage normally dominates the beginning of the burning process in all the biomass species. Fig. 2 clearly shows the well-isolated peaks for both of the main emission gases for all the biomass samples under study.

As shown in Fig. 2, the CO$_2$ and CO peaks were clearly separated, reflecting the flaming and smoldering phases. In addition, the transition between these phases was easily distinguishable (Chakrabarty et al., 2010). The Modified Combustion Efficiency (MCE) was higher than (average 0.9 ± 0.031) during the flaming phase. On the other hand, when the flames ceased, a decrease in CO$_2$ emissions was noticed, causing a decrease in the MCE (average 0.8 ± 0.015), which was expected as the CO$_2$ emissions decreased against the CO increment during this period of the burn.

Another factor could have affected the MCE value, such as the bed and the wood density. The Acacia karoo, Bakau, Sepetri, Acacia reficiens Koko, Surian, Acacia tortils and Acacia melifera all burned with a lower MCE (0.9 to 0.94) than the Kapure and Kanaf (0.97 and 0.98). Biomass species Kapure and Kanaf have less density than other species and thus burned faster and with more flames, resulting in a higher value of MCE (Hosseini et al., 2009). The obtained emission factor values were in reasonable agreement with the savanna biomass reported by Lobert et al. (1991), Warneke et al. (1999), and Yang et al. (2001). In fact, our results were also in a range similar to that observed in Brazil (0.98 to 0.84) by Hobbs et al. (1997), which could imply the nature of tropical species (Yokelson et al., 1997; Yang et al., 2001).

The emission factors were calculated for both flaming and smoldering phases. Table 1 presents the Malaysian biomass emission factors. The classical definition of the emissions factor as described by Christian et al. (2003), where defined as a mass of pollutant emitted over the mass of dry fuel consumed. Homogenized samples were assumed in this well mixed small stack as suggested by US-EPA. In this method, concentration of the target gas and the volumetric flow rate, through the stack during the smoldering stage were all considered (Dhammapala et al., 2006).

The experimental burning facility was equipped with an accurate weighting scale terminal balance (detection limit 0.001 g), which recorded the loss in weight during the burn. Thus, the EF values are reported per the weight of the sample. In addition, the data are reported separately for each phase of

![Fig. 2 – Typical emissions trend of CO$_2$% and CO during a burn. Example of flaming (CO$_2$) and smoldering (CO) peaks for acacia species. The points are average of triplicates with standard deviation of less than 15%](image-url)
the burn (smoldering and flaming), which was accomplished by classifying the data for each phase and then calculating it accordingly through a data logging system that captured the gas analyzer reading every 3 to 5 sec.

This study conducted the first simulated burning of Malaysian biomass. To the best of our knowledge, there are no experimental measurements of emissions from Malaysian biomass fires for comparison. This simulated burning suggests that the results of these laboratory fires may be representative of Malaysian biomass.

2.3. BTEX emission factors

Generally, in all types of fires, the transition from the flaming phase to the smoldering phase does not occur quickly. In fact, most of the measured BTEX are emitted primarily during the smoldering phase and thus relate better with the CO emission pattern rather than with the CO2 (Akagi et al., 2011; Hallquist et al., 2009). The smoldering phase instantly commences after the flaming phase. The maximum emissions are released at the beginning of the smoldering phase while the temperature is still high with little or no flames. The BTEX sampling carried for 30–40 min, which started directly after the flaming ceased. During the smoldering period, the emission intensity also decreases quickly due to the sharp decrease in the fuel available to burn. Table 2 shows the emission factors for the BTEX. It is clear that the higher BTEX emissions produced may have been due to the slower burning process of wood and thus its higher volatile release (Cohen, 1996; Keith and Elliot, 2002; Kurokawa, et al., 2013). The increase in BTEX emissions suggests a less complete combustion and it therefore relates well with the increase in CO emissions during the smoldering phase (Gullett et al., 2007). The density of the biomass also had a significant impact on the BTEX emissions due to the fact that harder woods have a longer smoldering phase and thus higher BTEX emissions. According to Karl et al. (2007), the targeted BTEX were the major emission compounds reflected in the biomass burning emissions. Other VOCs with minor emission rates also were noticed during the analysis; however, they were not included due to the low detection limits utilized. The moisture content of the biomass contributes significantly to the water vapor in biomass burning emissions, and thus influences the emission. Higher moisture content in the biomass burn results in higher CO thus, higher BTEX emissions.

The emissions of benzene and toluene were within the emission range given by Andreae and Merlet (2001), Baker et al. (2010) and Bertoni et al. (2000). The xylenes in this study were close to the sum of the emission factors of these compounds reported by Andreae and Merlet (2001) and Karl et al. (2007). Our results were in good agreement (±15%) with the measurements of savanna tropical species by Lobert et al. (1991) and Yang et al. (2001, 2004). The ratio of benzene to toluene obtained in this study (1.8) was also in well compatibility with Yokelson et al. (2003), who reported a ratio of (1.7) for wood stove burning emissions.

3. Conclusion

The findings from the experimental burning indicated different emission patterns for the burning of different species. However, the emission quantities still varied slightly among the species. The experimental burning facility proved that the two major phases of burning could be simulated in a small-scale sample and produced the following observations. The emitted compounds during each phase of biomass burning had better correlations to either CO or CO2. The mixing phase area between the phases suggests that the emitted compound existed in both phases of burning could be simulated in a small-scale sample and the subsequent emission patterns for the burning of different species. However, the emission quantities still varied slightly among the species. The experimental burning facility proved that the two major phases of burning could be simulated in a small-scale sample and the subsequent emission patterns for the burning of different species. However, the emission quantities still varied slightly among the species. The experimental burning facility proved that the two major phases of burning could be simulated in a small-scale sample and the subsequent emission patterns for the burning of different species.

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<table>
<thead>
<tr>
<th>Species</th>
<th>Compounds emission factor (mg/kg C)</th>
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<tbody>
<tr>
<td></td>
<td>Benzene</td>
</tr>
<tr>
<td>Bakau</td>
<td>220 ± 30</td>
</tr>
<tr>
<td>Acacia melifera</td>
<td>180 ± 20</td>
</tr>
<tr>
<td>Acacia tortilis</td>
<td>170 ± 30</td>
</tr>
<tr>
<td>Acacia reficiens</td>
<td>190 ± 25</td>
</tr>
<tr>
<td>Koko</td>
<td>170 ± 30</td>
</tr>
<tr>
<td>Surian</td>
<td>160 ± 20</td>
</tr>
<tr>
<td>Kanaf(s)</td>
<td>180 ± 20</td>
</tr>
<tr>
<td>Sepetri</td>
<td>200 ± 30</td>
</tr>
</tbody>
</table>

Data are presented as average means ± SD.
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