Combustion characteristics of biomass in SouthEast Asia

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Abstract
Gas emission during combustion of mixed tropical wood, bamboo, oil palm trunk, acacia, and rubber wood have been investigated by using TG–MS in presence of oxygen as well as FTIR. The weight decreasing profiles and the gas formation rates of oil palm trunk was significantly different among the samples although their elemental composition was almost the same from biomass samples. It was found that H2O is the main product formed for all samples. The evolving rates of the gaseous products during the combustion and infrared spectrums such as CO, H2O, CO2, CH4 and COOH+ were found. The DTG curves spectrums for biomass present four overlapping peaks.

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1. Introduction

Most commonly, biomass refers to plant matter grown for use as biofuel, but it also includes plant or animal matter used for production of fibres, chemicals or heat. It excludes organic material which has been transformed by geological processes into substances such as coal or petroleum. It is usually measured by dry weight. Biomass is part of the carbon cycle. At present, biomass share in the world’s total primary energy consumption is about 12% [1]. It is estimated to increase to near 15% by 2010 in developed countries [1]. With the depletion of fossil fuel sources as well as the global warming issues, the utilization of biomass attracted increased attention [2]. Combustion or burning is a complex sequence of exothermic chemical reactions between a fuel and an oxidant accompanied by the production of heat or both heat and light in the form of either a glow or flame. It is commonly accepted that the amount of carbon stored in biomass is approximately 50% of the biomass by weight [1]. Biomass combustion plumes impacting the measurement site are likely a significant contributor to the observed secondary organic aerosol (SOA). The results interpreted in terms of major sources are due to local build-up of organic contaminants from vehicular emissions, smoke from biomass burning, and natural background as a result of the atmospheric stability during the haze episode [3].

The Southeast Asian region has experienced high economic growth and social changes over the past few decades. This was based, in part, on the consumption of natural resources and development of agriculture-based industries, both of which involve renovation of forests and growth of land-uses. In fact fire is frequently used to prepare land and burn waste wood and crop residues. A prime example is the haze episode in 1997–1998, consequent of the combination of dry conditions during the El Nino Southern Oscillation (ENSO) cycle and the resulting atmospheric

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inversion. It produced a blanket of smoke or "haze" that spread and persisted over Indonesia and neighboring countries for months. The impacts of the atmospheric pollution on health, transport and tourism, largely were borne by Indonesia, Singapore and Malaysia. However, at times parts of southern Thailand and the Philippines also were affected, which helped make the fires and associated haze a major international environmental issue and media event [4]. The haze episodes that occurred in Malaysia in September–October 1991, August–October 1994 and September–October 1997 have been attributed to suspended smoke particulate matter from biomass burning in southern Sumatra and Kalimantan, Indonesia. On the basis of Abas [3] analysis, levoglucosan was found to be the most abundant organic compound detected in almost all samples. The mono-saccharides, a- and b-mannose, the lignin breakdown products, vanillic and syringic acids and the minor steroids, cholesterol and b-sitosterol were also present in some samples. The presence of the tracers from smoke overwhelmed the typical signatures of emissions from traffic and other anthropogenic activities in urban areas [5].

Thermogravimetry seems to be a promising technique to study biofuel properties while the mass losses considered by this method depend on the volatility (or molar mass) of the fractions investigated. This technique has been used to compare the evaporation and cracking behavior of different bio-oils and their fractions [6]. At present, most of researchers have assumed independent parallel decompositions of hemicellulose, cellulose, and lignin for biomass pyrolysis [1]. Since there are still inconsistent aspects in the reported works in terms of biomass degradation mechanism, there has been a lack of ability to confirm the presence of specific functional groups such as carbonate and the products. Besides, there is very little work on the degradation behavior under atmospheric pressure as would be encountered in true combustion. Therefore, in order to understand the combustion process, thermogravimetric analysis and infrared spectroscopy have been used. Otero et al. [7], conducted thermogravimetric analysis. Besides providing a means for the preliminary assessment of fuel values of biomass it allows for a prior knowledge of initial and final temperatures for their combustion as well as other relevant data such as maximum reactivity temperature or total combustion time. This information can then be used to forecast combustion efficiency, residence time, excess air, etc. On the other hand, the use of TG–MS techniques is well established for characterization of gaseous materials, allowing to relate weight loss signals and gaseous emission and FTIR provides the important data for the identification of the functional groups of the biomass, but it cannot provide molecular structure information. Hence it was also recommended for the evolved products collected to be analyzed using FTIR and GC–MS [7]. Jang and Wiklje [8] investigated the thermal degradation of polycarbonate under nitrogen atmosphere using TGA-FTIR, GC–MS and LC–MS as a function of mass loss. The gases evolved during degradation were inspected by in situ FTIR and evolved products were collected and analyzed using those equipments [8]. Matsuzawa et al. [9] carried out an extensive study on the degradation of cellulose with pyrolysis using TG–MS, FTIR and results from other studies. The fuel ratio of char was estimated by thermal analysis using a PVC–CE mixture to the biomass [9].

In the present study, we focused on the gas emission during combustion of selected biomass. The main goal of this work was to characterize the composition of gas products obtained from combustion. To understand the thermal behavior of tropical biomass during combustion, thermogravimetric analysis was also performed. At present, tropical biomass used in this study will be burnt in the future to determine the carbon–sulphur–nitrogen fluxes during the burning of biomass commonly found in Malaysia.

2. Experimental

2.1. Materials

The materials selected for this study were Mixed Tropical Wood (MTW) residue from sawmill (off cut, slab processed into chip before particle board production), Bamboo, Oil palm trunk, Acacia and Rubber Wood (RW) which were collected from FIRM (Forest Research in Malaysia). These present biomass of the majority in south East Asia forest.

2.2. TG–MS analysis

The combustion experiments were performed in a sensitive thermobalance TGA-SDT A851® Ultramicro Balance with Mass Spectrometer QMS422 (MS) at a heating rate of 5 °C min\(^{-1}\) from 30 °C to a final temperature of 1000 °C under the air flow rate of 50 ml min\(^{-1}\). Prior to the experiments, the apparatus was purged with the carrier gas for 15 min. Samples were measured in an open Aluminum Oxide standard crucible of 70 μl volume. A mass spectrometer Thermo Star™ QMS422 (MS) coupled to the thermobalance was used for the evolved gas analysis. To avoid secondary reactions, a probe was placed very close to the sample pan of the thermobalance in the direction of the gas flow. The transfer lines between the TGA and MS were heated to 150 °C in order to avoid cold spots and thus prevent condensation of the gaseous products.

2.3. Principal component analysis

The MS ion intensities, with good signal-noise ratios, were integrated within the temperature range of decomposition. The m/z ratios of selected products were the following: m/z = 18, 43, 44, 45. Then the mass numbers were converted to the concentrations of H\(_2\)O, CO, CO\(_2\), and COOH\(^+\).

2.4. Fourier transform infrared spectrometry (FTIR)

To investigate functional groups in biomass, the FTIR analysis was employed. All the IR spectra were measured at 4 cm\(^{-1}\) resolution on an FTIR spectrometer (Bruker Optics IFS66vrs \(^{-1}\)). The IR Spectra of the raw biomass was measured by using KBr. 0.4 mg dry sample was milled with 40 mg IR grade KBr and was used to form the KBr disk for analysis. The background spectrum of pure potassium bromide was subtracted from that of the sample spectrum.
3. Results and discussion

3.1. Combustion of biomass

Initial weight loss, from ambient temperature to 150 °C, is due to moisture evaporation. The major weight loss (between 200 and 400 °C) is due to biomass volatilization and char oxidation processes. In this temperature range an extensive burning of large quantities of biomass was observed. The final, rather insignificant weight loss was detected between 405 and 1000 °C. It was due to oxidation of carbonaceous residues within inorganic solid particles [10]. When temperature was higher than 570 °C, almost no weight loss was observed. It is difficult to accurately establish a clear boundary between these stages because the regimes of volatiles release, char combustion and transformation are overlapping. It is possible to minimize the overlapping by applying much slower heating rate, say 5 °C min⁻¹, or using a smaller sample [10].

It is obvious, though, that as temperature increases during the heat-up and devolatilization of the biomass, the evolution of different products or groups of products occurs in segmented (but overlapping) phases. Initially, (T < 120 °C), it is associated primarily with moisture evaporation, then (120 < T < 450 °C) with the release of gases, primarily CO₂ and CH₄, and later (450 < T < 600 °C) it is connected with the release of chemically bonded CO₂ and chemically formed H₂O. Evolution of benzene, which was detected in small amounts in the gas phase, was associated primarily with moisture evaporation, volatilization and combustion of oil palm trunk.

Temperature end of this phase. The subsequent process, the DTG curves for biomass present four overlapping regions of combustion reactivity could be identified. They are associated with DTG peaks height and their location. Fig. 2 indicates that the derivative thermogravimetric (DTG) curves. It illustrates the sharp devolatilization process, the DTG curves for biomass present four overlapping peaks. Fig. 2 also shows a very different combustion behavior. Although the combustion reactions having the similar termination temperature except oil palm trunk, the major combustion of biomass started at 350 °C and the strongest weight loss occurred at 1000 °C. In addition, Oil palm trunk had a bigger weight loss at 1000 °C than others. Comparing curves in the Fig. 2 shows that the acacia has an increased combustibility, with greater T_min values at about 497 °C and DTG_max.

Table 1 indicates that the peaks are present within the temperature range of 30–1000 °C. These temperature ranges correspond to moisture evaporation, volatilization and combustion processes. It shows a starting combustion temperature of around 30 °C and a termination temperature of approximately 500 °C with a sharp weight loss at 320, 84, 310, 325, and 281 °C, respectively.

3.2. Thermogravimetry–mass spectrometric analysis during the combustion of biomass

One of the most useful tools available for studying the pyrolysis products of biomass is the thermogravimetry–mass spectrometric analysis. More than 20 types of pyrolysis products of biomass have been identified by TG–MS. Studies of the production of the major products, such as H₂O, CO₂, CO, C₆H₆, O₂, CH₄, and CH₃COO⁻ are essential to understand the function of pyrolysis of biomass.

The experiments indicated that the biomass ignition temperature was about 281 °C. Weight loss (approximately 84 wt.%) occurs in the oil palm trunk as a result of moisture evaporation, as well as volatilization and combustion of oil
palm trunk. In this stage, light organic volatiles present in the biomass samples are burned after moisture vaporization. FTIR spectra (Fig. 9) revealed the presence of CO$_2$, H$_2$O and CO, as well as small amounts of unidentified hydrocarbons (C$_x$H$_y$) at the beginning.

As temperature increases to 405 °C, both unidentified hydrocarbons and CO gradually disappear. At this temperature, char particles are formed as a result of biomass combustion. In the first stage, mixing and kinetic inadequacies may likely be the limiting factors for the observed destruction of organics

**Table 1** - TG and DTG behavior for TMW, Bamboo, Oil palm trunk, Acacia, RW.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Evaporating</th>
<th>Devolatization</th>
<th>Combustion</th>
<th>Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_r$ (°C)</td>
<td>$T_{min}$ (°C)</td>
<td>Weight loss%</td>
<td>MS Signal</td>
</tr>
<tr>
<td>MTW</td>
<td>30–153</td>
<td>80</td>
<td>4.88</td>
<td>18</td>
</tr>
<tr>
<td>Bamboo</td>
<td>30–163</td>
<td>50</td>
<td>4.56</td>
<td>18</td>
</tr>
<tr>
<td>Oil Palm Trunk</td>
<td>30–168</td>
<td>84</td>
<td>84.03</td>
<td>18,19,20</td>
</tr>
<tr>
<td>Acacia</td>
<td>30–158</td>
<td>55</td>
<td>8.45</td>
<td>18</td>
</tr>
<tr>
<td>RW</td>
<td>30–153</td>
<td>60</td>
<td>3.65</td>
<td>18</td>
</tr>
</tbody>
</table>

$T_r$: Weight Loss Temperature Range (TGA).

$T_{min}$: Min Temperature Range (DTG).

**Fig. 3** – Mass spectrometry results for H$_2$O = 18 m/z during combustion of biomass.

**Fig. 4** – Mass spectrometry results for CH$_3$CO$^+$ = 43 m/z during combustion of biomass.
in the combustion system. Relatively poor mixing between biomass and air may cause a scenario when not enough oxygen is available to sustain the oxidation rate required by the biomass samples [10]. In general, the biomass combustion process could not be completed in the first stage due to insufficient amount of oxygen. Higher excess oxygen and improved mixing may be helpful in controlling emissions of organics in the first combustion stage. The second stage is taking place between 154°C and 404°C. In this stage, unburned biomass finally decompose liberate CO₂. Char, formed in Stage 1, is oxidized to CO₂ as well.

The formation behavior of H₂O can be seen in Fig. 3. Of particular interest is the fact that H₂O was the main product formed for all the samples in the first weight loss of decomposition. It started to evolve at 30°C slightly, while it started to evolve dramatically at 30°C for oil palm trunk. Figs. 3–8 show the gas formation rates (H₂O, CO₂, CO, CH₃CO⁺ and COOH⁺) of MTW, Bamboo, Oil Palm trunk, Acacia, and RW. The feature common of the phenomenon, namely evolving behavior of the samples can be seen in Table 1. The formation behavior of oil palm trunk is certainly different from others. As can be seen in Figs. 3–9 for oil palm trunk, the formation rate of oxygenated gases such as H₂O and CH₄ start slowly. Furthermore, for oil palm trunk CO, CO₂, and COOH⁺ start smoothly at about 330°C, whereas for MTW and Bamboo, formation rate start considerably at 320 and 281°C, respectively (Figs. 3–8). A relatively large amount of CH₄ (m/z 16), H₂O (m/z 18), CO(m/z 12), CH₃CO⁺(m/z 43), CO₂ (m/z 44), and COOH⁺(m/z 45) is formed from all samples owing to the large number of hydroxyl groups and oxygen atoms present in the natural polymers that make up the cell walls (cellulose, hemicellulose and lignin). The H₂O evolution profile is similar for all the samples except oil palm trunk. It occurs over the entire temperature range of biomass decomposition, indicating the multiple origin of water. The release of adsorbed water accounts for the peak at around 100°C, whereas the main peak above 350°C correspond to the water formed in the decomposition of the polymeric cell wall constituents. Therefore, the most significant portion of mass signal in the second weight loss (Table 1) can be attributed to CO₂. The MS curves of CO₂ and CO are different for the given samples above 281°C. There is a noticeable evolution of no products between 361 and 1000°C.

The COOH⁺(m/z 45) ion (Fig. 6) is a characteristic fragment of the decomposition of both cellulose and hemicellulose [11]. Although it can also be a fragment of hydroxyacetaldehyde and low molecular weight carbonyl
compounds represented by the m/z-143 ion (CH$_3$CO$^+$) (Fig. 4). This latter compound is one of the characteristic products of the main cellulose decomposition pathway [11]. In the oil palm trunk sample the 16 m/z profile exhibits one visible maxima around 30 and 150°C. The first process can mostly be attributed to the decomposition of lignin methoxyl groups [12].

3.3. FTIR analysis of biomass

In this section the changes in the functional groups of raw biomass were examined by utilizing the FTIR analysis. Conditions for the degradation and transition of FTIR spectra at each biomass are shown in Fig. 9. Assignment of absorbance bands, are reported by [13–15] and Bruker Optics Guide are as follows:

(a) O–H Stretching (3200–3610 cm$^{-1}$)
(b) C–H Stretching (2940 cm$^{-1}$)
(c) C=O Stretching (1720 cm$^{-1}$)
(d) C–C Stretching (1640–1670 cm$^{-1}$)
(e) H–C–H Deformation (1430 cm$^{-1}$)
(f) C–OH Stretching and deformation (1100–1000 cm$^{-1}$)

With the application of heat, the evolution profile of (a), (b), (e) and (f) decreased, while (c) and (d) increased. Fig. 8 shows the changes in the FTIR spectra (700–4000 cm$^{-1}$) for all biomass studied. The amount of OH groups (3200–3610 cm$^{-1}$) and aliphatic C–H groups (2900–3000 cm$^{-1}$) decreased significantly when the temperature is about at 300 °C. The amount of ester groups (1750–1800 cm$^{-1}$) gradually increased. Worasuwannarak [16] suggested that ester groups increased when the temperature exceeded 250 °C, but started to decrease above 330 °C [16]. These results indicated that the ester groups were formed at around 250 °C and ester groups were decomposed at above 330 °C.

4. Conclusion

The devolatilization behavior of five biomass materials (mixed tropical wood, bamboo, oil palm trunk, acacia, and rubber wood) was investigated by thermogravimetry/mass spectrometry within the range of slow pyrolysis. The thermogravimetric data and the evolution profiles of the low molecular mass products evidenced the particular thermal behavior of regular wood biomass. The wood samples evolved more organic products (aldehydes, acids, Alcohol, phenyl, benzene, furan derivatives, etc.) due to their high polysaccharide content. The characteristic DTG data and the mass spectrometric intensities of the major volatile products revealed specific differences in the thermal decomposition and in the product distribution, due to the different type of sample. It was found that H$_2$O was the main product formed from all the samples. The differences in the gas formation rates were found to be due to their differences in the composition of hemicellulose, cellulose, and lignin. It was found that, among the biomass samples, oil palm trunk produced the largest amount of H$_2$O. The
most significant portion of mass signal in the second weight loss (Table 1) can be attributed to CO$_2$. The MS curves of CO$_2$ and CO are different for the given samples above 281 °C. There is a noticeable evolution of no products between 361 and 1000 °C. In general, the biomass combustion process could not be completed in the first stage due to insufficient amount of oxygen. Higher excess oxygen and improved mixing may be helpful in controlling emissions of organics in the first combustion stage. The second stage is taking place between 154 °C and 404 °C. In this stage, unburned biomass finally decompose liberate CO$_2$. Char, formed in Stage 1, is oxidized to CO as well. From FTIR analyses of the raw samples, it can be considered that the suppression of tar formation during the combustion of biomass. At present, tropical biomass used in this study will be burned in next future to determine the carbon–sulphur–nitrogen fluxes during the burning of biomass commonly found in Malaysia.

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