

## **Thermochemical Conversion and Elemental Content Characterization of Tropical Biomass**

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**Abstract:** *This study presents recent unpublished characterization data on ten tropical biomass species. The experiments carried out to study the events taking place during thermal treatment in both oxidative and non-oxidative environments. In addition, this study also highlights some of the elemental contents of tropical biomass. The correlation between the elemental content of biomass and the thermal behavior was used to indicate the emission pattern. Devolatilization behavior of different tropical samples under steady heating condition also investigated. Thermogravimetric analysis (TGA) technique applied to study the thermo-chemical conversion processes (pyrolysis, combustion and gasification) of the tropical biomass samples. The thermograms showed two distinct reaction zones with different degradation rates. Some kinetic parameters such as activation energy and degradation rate were determined for these two reaction zones. It was found that during thermal zone large sample mass consumed (88, 95%) resulting in (11000, 237 J/g) energy released in both combustion and pyrolysis respectively. Characterizations of biomass samples such as Carbon, Nitrogen, Sulfur and Hydrogen contents were also determined using elemental analysis. It can be concluded that carbon content varies substantially among tropical species; hence the burning emissions and thus the impact differ accordingly. Furthermore, the 50% generic value as proposed in some tropical atmospheric static studies is an over simplified value in relation to the tropical biomass burning emissions estimations.*

**Keywords:** *Biomass, tropical, characterization, thermal degradation, combustion, pyrolysis, elemental analysis*

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### **I. Introduction**

One of the most promising sources of extracting energy from biomass materials is through thermochemical combustion processing, pyrolysis and gasification (Fine et al., 2004). Biomass today is known to be an important source of many trace gases affecting atmospheric chemistry (Satoshi et al., 2008; Crutzen et al., 1990). Despite its global significance, still more quantitative information is required about the emission of some emitted compounds (Simoneit et al., 2002). During the biomass combustion, series of thermal events occur, which may influence the release of toxic gases into the environment (Tietema et al., 1992). The chemical / physical form and concentration of these compounds depends on a number of factors including the elemental composition of the solid fuel and the combustion conditions (Wornat et al., 1995). Thus, the investigation of the possible thermal events occurring during solid fuel combustion is an essential factor as it may provide the ability to better understand the emission products. Thermoanalytical techniques, in particular thermogravimetry (TGA), allow this information to be obtained in a relative simple and straightforward manner (Branca et al., 2006). It can also obtain the measurement of weight loss of sample as a function of time and temperature. Generally biomass is consumed by both thermal decomposition (devolatilization) reactions and char oxidation. Large fractions of biomass are likely to be emitted as volatile gases during combustion process (Agrawal et al., 1985; Alves et al., 1988). These large volatile yields occur over a relatively short time and can influence the time required for complete combustion. Pyrolysis is the first and a major controlling stage in the process of gasification and combustion (Core et al., 1982). Ultimate analysis is used to determine carbon, hydrogen, nitrogen and sulfur (CHNS) is also important to estimate the calorific value of the biomass (Fine et al., 2001). Therefore, the material balance from the compositional analysis combined with other analysis data might lead to better understanding of biomass thermal behavior. Thus this study was mainly focused on tropical biomass characterization with the consideration of biomass elemental contents. The data obtained from this study is very useful to integrate with the tropical biomass emission inventory in which mostly needed in both regional and global biomass burning inventories. The selected biomass species in this work were sampled from Forest Research Institute Malaysia (FRIM) and were not previously studied in open literature. The biomass samples were mainly sampled from Malaysian dry forest.

## II. Sample Preparation

About 2.0 kg of each biomass samples obtained from forest research institute Malaysia (FRIM). Ten species were selected mainly due to their large distribution and repeated burnings occurrence in the Malaysian tropical forest namely *Koko*, *Kapure*, *Bakau*, *Acacia karoo*, *Acacia tortilis*, *Acacia melifera*, *Acacia reficiens*, *Surian*, *Kanaf* and *Sepetri* were investigated in this study. As recommended (Branca et al., 2006), samples were sun dried, and the dried material stored in a polyethylene bag for future use. For the elemental and thermal characterization, approximately 0.1 kg of each species was further oven dried at 105°C for 24 hours and ground in a laboratory ball mill. The grounded particles were further classified by using two sieves in the size range of 180- 600  $\mu m$ . This sieved powder sample was stored in dried condition for future analysis.

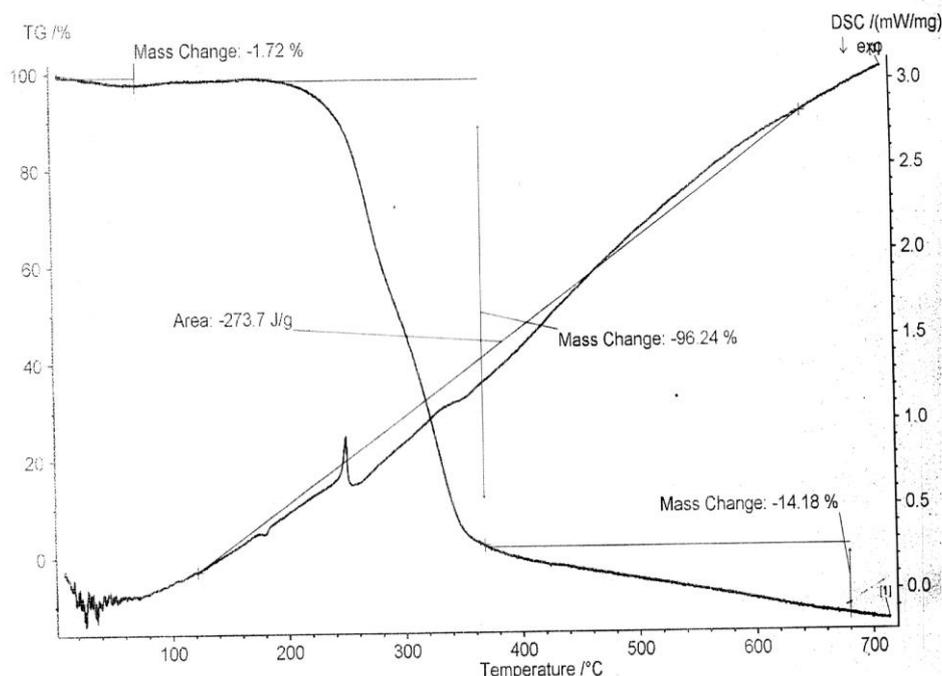
## III. Experimental protocol

Experiments conducted using computer controlled Thermogravimetric analyzer (TGA) NETZSCH TA with data acquisition system. The sample environment was both air and nitrogen atmospheres to obtain combustion and pyrolysis characteristics. In TGA, a sample is heated at specified heating rate, mass is measured with an electronic microbalance and the temperature is recorded with a thermocouple. The results can then be used to determine the ash content, the dry loss, the ignition temperature, and the kinetics of devolatilization. The principal experimental variables which could affect the pyrolysis characteristics in a TGA are the pressure, the purge gas flow rate, heating rate, weight of the sample and sample size fraction (Kozinski et al., 2006; Mansaray et al., 1999; Core et al., 1982). In the present study, the operating pressure was kept constant at atmospheric pressure. The purge gas used was pure nitrogen to prevent the presence of air in the pyrolysis zone and to remove gases which evolved during the pyrolysis. A constant flow rate was maintained at 100 ml/min and the heating rate was 5 °C/min. The microbalance was calibrated by following manufacturer instructions. The uniformity of the sample was maintained by using a 10-15 mg sample from the stored lot of size fraction 180-600  $\mu m$  (Branca et al., 2007; Erlich et al., 2006; Calvo et al., 2004) and spreading it uniformly over the crucible base in all the experiments. The furnace temperature in the TG thermo balance was controlled in such way that sample temperature followed the desired profile. For this purpose, the temperature equilibration function between the furnace and sample was provided by the manufacturer. Other wood combustion properties such as the development of smoke (including soot and toxic gases) and gaseous products are not covered in this paper. Perkin Elmer elemental analyzer was used to quantify total carbon, hydrogen, nitrogen and sulfur contents of the biomass samples. Each sample (~1mg) of dry wood powder was weight into a clean, dry tin container (~33 mg tin, 20mm diameter. Circle crimped into cup) using AD-6 Autobalance (calibrated precision 0.0001mg). The crucible was placed in the combustion/reduction column of the analyzer. Full chromatographic resolution of the total carbon, nitrogen and sulfur was achieved using CHNS combustion/reduction column. The analyzer was calibrated with standard method and triplicates of each biomass samples were repeated to assure high accuracy of the analysis data.

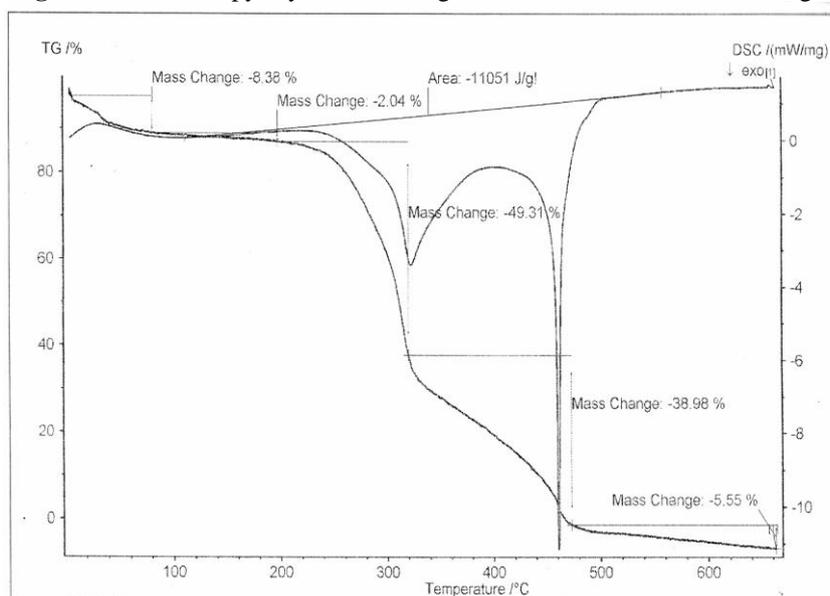
## IV. Results and discussion

The thermal dissociation of biomasses is a very complex process which occurs in a hetero-phase system in which several stages can be distinguished (Liu et al., 2008). These stages are associated with both heat transport as well as discharge of vapor gas products of decomposition or development of a new solid phase (Saade et al., 1998). The results of the performed experiments of the TGA showed the correlation between the degree of decomposition and the time constitute of each combustion/ pyrolysis phase. The changes in phases are in fact sum results of all physical phenomena and chemical reactions (Reina et al., 2006). These reactions had taken place during the decomposition process with varying degrees depending on each sample properties (Wornat et al., 1995). Tropical biomass acacia species was used as model for biomass samples due to its vast distribution in the tropical forests (Mohan et al., 2006; Coughenour et al., 1990). From both TG curves (Figs.1 and 2) which indicate the combustion in air and the pyrolysis in N<sub>2</sub> gas respectively. The initial small weight loss in combustion (8.3%) that occurred up to 130 °C, was mainly due to release of some volatile compounds from the samples (Nakamura et al., 2007; Boateng, 2007; Moilanen et al., 2006). All the treatments showed significant differences at 5% probability level in weight loss and active decomposition temperature at heating rates of 5 C min<sup>-1</sup>. Starting at temperatures of 100°C, dehydration (chemical release of water vapor leaving behind the amorphous carbon for char) accompanied by decarboxylation (release of carbon dioxide leaving behind aromatic or aliphatic char) begins to occur and then increases more rapidly (49%) around 280°C (Satoshi et al., 2008).

**Figure 1:** The TGA combustion chromatogram of biomass acacia under air.



**Figure 2:** The TGA pyrolysis chromatogram of biomass acacia under N<sub>2</sub> gas.



As the temperature increases under atmospheric pressure, these samples will thermally degrade by releasing light gases such as carbon monoxide and low-molecular weight gaseous (Nolte et al., 2001). During this zone the much of the sample energy released sharply with (11051 j/g). This energy emission mainly due to an extensive combustion of large sample mass (88%) at temperature above 200°C as shown in Fig 1. However, it's much smaller in the case of pyrolysis under N<sub>2</sub> gas as in Fig 2. This trend is due to high volatile content and low fixed carbon content in the biomass samples (Moilanen et al., 2006; Shafizadeh et al., 1984). This is also attributed to the strength of the molecular structure of the biomass. The polymer of cellulose, hemicelluloses and lignin, which constitute the macromolecular structure of the biomass and other woody materials, are linked together with relatively weak ether bonds (R-O-R, bond energy of 380-420 kJ.mol<sup>-1</sup>) (Liu et al., 2008; Parham et al., 1984; Wornat et al., 1995). These bonds are less resistant to heat at low temperature (400-500°C) (Aboulkas, et al., 2009; Varhegyi et al., 2006). Generally the total degradation and average degradation rate were lower in the second reaction zone as compared to those of the first reaction zone Table 1.

**Table 1:** Thermal events of biomass samples combustion.

Biomass samples	Initial Degradation Temperature (°C)	Final Temperature (°C)	Total Degradation %	Average degradation rate (% min <sup>-1</sup> )	Residual weight at 600 °C (%)
koko	315	470	31.5	3.1	18.5
kapure	312	481	32.1	2.6	20.1
Acacia karoo	318	475	28.8	2.8	19.3
bakau	316	478	32.8	3.4	17.6
Acacia tortilis	320	476	30.2	2.8	18.6
Acacia melifera	317	480	30.6	2.9	17.3
Acacia reficiens	322	477	31.4	2.7	19.5
surian	319	472	30.4	3.2	18.2
kanaf	318	475	29.7	2.7	17.4
sepetri	316	471	31.3	2.5	18.8

In the second reaction zone the total degradation was in the range of 31 to 35 % depending on the variety. The average degradation rates were around 2.5% for all biomass samples. The thermal degradation of all biomass samples was almost complete at the end of the second reaction zone. At the temperature above 510 °C very slight decomposition was recorded. Biomass moisture content is the major factor that influences the burning process (Otero et al., 2008). If the moisture content is too high, an appreciable amount of energy is needed to vaporize water, reducing combustion efficiency, which in turn increases smoke formation (Nunoura et al., 2006). On the other hand, biomass with low moisture content burns faster eventually causing O<sub>2</sub> deficient conditions that lead to incomplete combustion also with increased smoke particle formation (Skaar, C. 1984). When acacia species is heated, its constituents start to hydrolyze, oxidize, dehydrate, and pyrolyze, and with increasing temperature to form combustible volatiles, tarry substances, and highly reactive carbonaceous char (Branca et al., 2006). At the ignition temperature of the volatile and tarry substances, exothermic reactions known as combustion start to take place (Guerrero et al., 2005). Interstitial compounds and decomposition products of cellulose, hemicelluloses, and lignin, together with water vapor are stripped off, and then undergo partial to complete combustion in the flaming zone (Rogge et al., 1989). During the smoldering process, enough heat is produced to propagate charring with release of additional volatile decomposition products (Schauer et al., 2001). In addition the emissions from the combustion of any type of fuel depend directly on the chemical composition of that fuel and the combustion conditions (Core et al., 1982). For biomass burning most data are available for wood combustion (Nakamura et al., 2007). Plants develop markedly different biopolymers consisting of lignin and cellulose for structural support. Based on these smoke compositions grasses appear to contain more lignin than cellulose. Lignin is an irregular polymer of variously bonded hydroxyl- and methoxy-substituted phenylpropane units (Alves et al., 1988). It is biosynthesized from the precursor's p-coumaryl, coniferyl and sinapyl alcohols and contains mainly anisyl, vanillyl (guaiacyl) and syringyl nuclei (Fine et al., 200; Simoneit et al., 1993)).

It is worth to mention that during the pyrolysis process, char is the major product from the biomass pyrolysis due to the lignin content (Guerrero et al., 2005). The char accounts for about 40 wt.% of the sample. Analysis of ten tropical wood species showed that carbon content ranged from 41.5 to 47.8% (w/w) as per Table 2 below. Hydrogen contents ranged from 5.5 to 7.2% (w/w), whilst nitrogen and sulfur were also analyzed and its contents range between 1.3-1.7% and 1.3-1.5 % (w/w) respectively. All of these results similar range with the previous data published elsewhere (Fine et al., 2002; 2004).

**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 (Fine et al., 2004; Lamlo et al., 2003).

During biomass combustion, a series of thermal events take place, which may influence toxic gases release into the environment. The type and the quantities of these gases were strongly related to elemental contents of biomass samples under the burning process. It was found that total degradation was relation to the biomass carbon content. Thus, the species *koko* and *bakau* showed relatively high degradation rate due to their high carbon content. Other species can be seen to be in similar trend although with some fluctuations. This relation can further contribute to the emission factor. This might not be the case in other biomass species. In addition, wood composition may vary from one species to another and even within species, nevertheless some biomass species showed remarkable uniformity in their elemental composition (Fine et al., 2004; Lamlom et al., 2003). Thus recent research dealing with carbon in tree has assumed the 50% value has to be corrected.

## V. Conclusion

A total of ten biomass species representing Malaysian tropical forest were characterized in terms of their thermal behavior. The carbon content was found to vary significantly from (41.5- 47.81%), which indicate that 50% generic value of carbon content in most calculation is over simplified. The TGA profile revealed that the initial weight loss, from ambient temperature to 150°C, is due to moisture evaporation. The major weight loss (between 200 and 350°C) is due to volatilization and char oxidation processes. In this temperature range an extensive burning of large amount of sample mass was observed. The energy released in this stage indicates the break of lignin bonds in biomass structure. Rate of degradation also varied according to the weight loss. The final, rather insignificant weight loss was detected between 900 and 1000°C. It was due to oxidization of carbonaceous residues within inorganic solid particle. It was observed that some correlation between the higher carbon content and the higher degradation rate. Therefore, further investigation needs to be undertaken to clarify this relation and it might lead to better prediction toward the emissions.

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