Thermogravimetric Analysis and Pyrolysis Kinetics of Malaysian Wood Species

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Abstract: The mass loss of three wood species in Malaysia, Shorea laevis, Koompassia malaccensis, and Shorea parvifolia were measured against time and temperature at three different heating rates (5, 10 and 20 °C/min) in nitrogen environment, through thermogravimetry analysis (TGA) technique. This measurement revealed that the decomposition of these wood generally occurred in three stages, the dehydration stage, the active stage, and the passive stage. The maximum decomposition peak in derivative thermogravimetric (DTG) analysis curve shifted towards higher temperature range with the expedition in heating rate. The kinetic decomposition parameters of the timbers were determined by adopting thermal kinetic method of Coats and Redfern. Principally, the density and moisture content of timber does not influence the kinetic parameters studied in this work. Overall, the thermal decomposition in the second-stage (active stage) was dominated by the hemicellulose and cellulose while the decomposition of lignin was apparent in the third-stage (passive stage) of pyrolysis. The higher activation energy in the second-stage indicates that more cellulose is contained in the sample. The activation energy of lignin is observed to be much lesser compared to the activation energy of the hemicellulose and cellulose for two species tested except for the Shorea parvifolia.

1. Introduction
The wood industry is one of the significant contributors to Malaysia’s economy, wherein 2018, the timber industry recorded RM22.3 billion in exports, contributing 1.6% to the country’s gross domestic product and 2.2% to total exports [1]. Due to their qualities, Malaysian wood is highly favored to be used as materials for furniture such as sofa, dining table, and cabinet. However, timber is considered as combustible material, which these surfaces may notably add to the fire loading of a compartment, promote the spread of flame, and speed up the outbreak of flashover. The thermogravimetric analysis (TGA) is the simplest way of investigating the thermal property of degradation for wood as it provides quantitative information on the decomposition of polymeric substance as it only requires a small amount of sample, which is less in cost. Hostikka et al. [2] evaluated the performance of three reaction schemes of wood pyrolysis in reproducing thermogravimetric experiments of birch wood and concluded that the
first-order single-step reaction scheme provides good prediction for the heat release rate. Sharma et al. [3] studied the thermal decomposition and the reaction mechanism of the eucalyptus wood and revealed that the reaction mechanism of wood pyrolysis overlaps the diffusion mechanism at lower conversion value ($\alpha = 0.05-0.4$). Lu et al. [4] examined the pyrolysis characteristics of raw/torrefied C. japonica and anthracite coal and found that the pyrolysis behavior of fuel blends can be determined in terms of the weight percentages of biomass and coal. The results obtained from TGA conversion curves are essential to develop kinetics models that are further used for completing the fire prediction models of the materials. Although many works have been done on fire properties of wood, the archival material related to the wood in Malaysia was found to be very limited in scope and incomplete [5]. Therefore, there is a reasonable need for the study of thermal degradations and pyrolysis kinetics of the local wood species in Malaysia. Thus, this work investigates the thermal degradations of three selected Malaysian solid wood material based on their application indoor and outdoor. Furthermore, the decomposition kinetic parameters are also determined by adopting thermal kinetics method, the Coats and Redfern (CR)[6].

2. Materials and methods

2.1. Samples preparation

Three Malaysian timber species were selected namely the Shorea laevis (Balau), the Koompassia malaccensis (Kempas) and the Shorea parvifolia (Light red meranti) as these species were listed by the Malaysian Timber Council (MTC) as 20 Malaysian commercial timbers based on the application, demand, and availability [7]. The specimens were prepared to be in fine fragment form in order to conduct the analysis.

2.2. Thermogravimetric analysis (TGA) technique

The thermogravimetric analysis of the three Malaysian timber species was performed using the Mettler Toledo equipment in Nitrogen atmosphere with the flow rate of 50 ml/min from 30 to 900°C. The samples were put on the platinum pan, then placed on a ceramic crucible and heated under three different heating rates of 5, 10 and 20°C/min. The mass loss of wood samples was recorded as a function of temperature and analyzed with STARe SW 12.10 thermal analysis software.

2.3 Kinetics theory

The reasons for the kinetics analysis of wood pyrolysis were eventually to evaluate the activation energy, the pre-exponential factor, and the reaction mechanism. The kinetics parameters in this study were determined by embracing the CR method, assuming $n = 1$ and the value of $2RT/\varepsilon$ is minimal which can be expressed as:

$$\ln\left[\frac{-\ln(1-X)}{T^2}\right] = \ln\frac{AR}{\beta E_a} - \frac{E_a}{RT}$$  \hspace{1cm} (1)

Where $X$ is the fuel conversions, $T$ is the absolute temperature in K, $A$ is the pre-exponential factor, $E_a$ is the activation energy, and $R$ is the gas constant (8.314 J/K mol). The plot of $\ln[-\ln(1-X)/T^2]$ versus $1/T$ becomes a linear line where the $E_a$ and the $A$ are to be determined from the slope and the intercept of the regression line, respectively.

3. Results and discussions

The thermal degradations and the pyrolysis kinetics characteristic for three species of Malaysian wood were evaluated in this work. The characteristic reaction temperatures, devolatilization rates, and mass fractions were used to describe the TGA and DTG analysis curves at various heating rates. For the determination of kinetics parameters, the first-order reactions of the CR method were calculated, and the discussion of each result is provided in the following sections.
3.1 Thermal decompositions of Malaysian wood species

3.1.1 Thermal decomposition of heavy hardwood: Shorea laevis. The mass fraction and the time derivative of the mass fraction showed as TGA and DTG curves for Shorea laevis were as displayed in Figure 1 (a), (b), and (c). In concurrence with previous findings [8], generally, the DTG curves show two primary regions. The determination of wood pyrolysis stage is based on the mechanism of superposition of the individual wood structure components; starting with the decomposition of hemicellulose at 180-350°C (approximate range for first-stage of wood pyrolysis), followed by the decomposition of cellulose at 275-350°C (approximate range of second-stage of wood pyrolysis), and lastly the decomposition of lignin at 250-500°C (approximate range of third-stage of wood pyrolysis) [3, 4]. In this work, the Shorea laevis encountered the loss of moisture content at ~100 - 240°C. The main decompositions mostly take place at the second-stage of ~ 200°C-440°C due to the depletion of the cellulose [9]. The peak temperature at which the decomposition intensity is the highest or where the primary degradation occurred were at 358 (intensity rate = 0.9435 wt%/°C), 367 (intensity rate = 0.17 wt%/°C) and 378 °C (intensity rate = 0.35 wt%/°C) due to heating rates of 5, 10 and 20°C/min respectively. It is also observed that the higher the heating rate, the higher the decomposition intensity rate and the peak shifted to higher temperature. The decomposition of lignin occurred at the third stage of pyrolysis, at ~390 to 600 °C without showing any characteristic peak.

3.1.2 Thermal decomposition of medium hardwood: Koompassia malaccensis. The TGA and DTG curves of the Koompassia malaccensis were as disclosed in Figure 1 (d), (e) and (f). The decompositions of the Koompassia malaccensis was paramount at the second-stage (~200°C-480°C) due to the depletion of cellulose. The peak temperatures for Kempas were 341 (intensity rate:0.0896 wt%/°C), 363 (intensity rate:0.1755 wt%/°C) and 362 °C (intensity rate:0.3378 wt%/°C) at 5, 10 and 20 °C/min heating rates respectively. The decomposition of lignin samples demonstrated a volatile evolution due to decomposition of lignin at the temperature of 573 °C/min at the heating rate of 5°C/min.

3.1.3 Thermal decomposition of light hardwood: Shorea parvifolia. The TGA and DTG curves of the Shorea parvifolia were as exhibited in Figure 1 (g) (h) and (i). At the second-stage (~220 – 500 °C), this species demonstrated its peak temperature of cellulose decomposition particularly at 354 (intensity rate: 0.11wt%/°C), 374 (intensity rate: 0.20wt%/°C) and 385 °C (intensity rate: 0.38wt%/°C) under the heating rates of 5,10 and 20°C/min. It is noted that the expedition of heating rates accompanied the acceleration of peak temperatures. The third-stage of Shorea parvifolia pyrolysis does not indicate characteristic peak at all three different heating rates tested.

3.2 Pyrolysis Kinetics

In this work, the \( E_a \) and the \( A \) of all species were determined by adopting the iso-conversional kinetics method of Coats and Redfern (CR). The results were as tabulated in Table 1. The values of \( R^2 \) were found to be between 0.81 to 0.99, which reflects that the pyrolysis processes are well correlated whether in the second or third-stage.

During the second-stage of pyrolysis, only the \( E_a \) of the Koompassia malaccensis increased from 30 to 49.05 kJmol\(^{-1}\) as the heating rate accelerates from 5 to 10°C/min. At this stage, the Shorea parvifolia has the highest \( E_a \) of 62kJmol\(^{-1}\) when heated at the rate of 10°C/min and lowest \( E_a \) of 27.26kJmol\(^{-1}\) at the heating rate of 5°C/min. In the third-stage of pyrolysis, the \( E_a \) of the Shorea laevis and Koompassia malaccensis seems to decrease as the heating rates increased. The Shorea laevis exhibited lowest \( E_a \) of 8.97kJmol\(^{-1}\) while the Shorea parvifolia has the highest \( E_a \) of 95.59 kJmol\(^{-1}\), both at the heating rate of 20°C/min. The assessment of \( A \) has a secure connection to the \( E_a \); the higher the \( E_a \) indicates higher value of \( A \).
Figure 1. The mass fraction (TGA) and the time derivative of the mass fraction (DTG) as functions of temperature for Shorea laevis, Koompassia malaccensis, and Shorea parvifolia at 5 [(a), (d), (g)], 10 [(b), (e), (h)], and 20 [(c), (f), (i)] °C/min heating rates.
Table 1. Thermal degradations and chemical kinetics of Malaysian wood at the heating rates of 5, 10, and 20°C/min from 30 to 900°C.

| Row | Species | Shorea laevis | Koompassia malaccensis | Shorea parvifolia |
|-----|---------|--------------|------------------------|------------------|
| 1   | Classification | Heavy hardwood | Medium hardwood | Light hardwood |
| 2   | Density kg/m³  | 905          | 862                    | 440              |
| 3   | Moisture content % | 14          | 16                     | 14               |
| 4   | Heating rate °C/min | 5           | 10                     | 20               |
| 5   | Temp. at the 1st peak °C | 358       | 367                    | 378              |
| 6   | Temperature at the 2nd peak * °C | -       | -                      | 573              |
| 7   | Peak MLR wt%/(°C) | 0.94       | 0.17                   | 0.35             |

**Second-stage reaction**

| 8   | Eα kJ mol⁻¹ | 41.28 | 49.11 | 31.41 | 30 | 45.54 | 49.05 | 27.26 | 63 | 45.06 |
| 9   | A s⁻¹ | 4.89x10⁹ | 1.85x10¹⁰ | 6.22x10¹⁰ | 4.81x10⁹ | 9.78x10¹⁰ | 1.62x10¹⁰ | 2.39x10¹⁰ | 2.5x10¹⁰ | 7.15x10³ |
| 10  | R²   | 0.93 | 0.96 | 0.90 | 0.86 | 0.92 | 0.96 | 0.85 | 0.98 | 0.93 |

**Third-stage reaction**

| 11  | Eα kJ mol⁻¹ | 17.22 | 16.55 | 8.97 | 26.68 | 14.86 | 12.87 | 57.51 | 46.95 | 95.59 |
| 12  | A s⁻¹ | 9.2x10¹⁰ | 7.23x10¹⁰ | 4.75x10¹⁰ | 4.2x10¹⁰ | 5.89x10¹⁰ | 2.73x10¹⁰ | 1.36x10¹⁰ | 1.95x10¹⁰ | 1.13x10² |
| 13  | R²   | 0.81 | 0.82 | 0.93 | 0.91 | 0.8 | 0.81 | 0.86 | 0.87 | 0.99 |

Notes:
* = Second peak temperature due to volatile evolution of extractive at the third-stage of pyrolysis.

4. Conclusions

The pyrolysis of Malaysian wood; (1) BalauShorea laevis (Balau); (2) Koompassia malaccensis (Kempas); and (3) Shorea parvifolia (Light red meranti) have been investigated through TGA technique in an inert atmosphere of nitrogen gas at three different heating rates. The results disclosed that the maximum decomposition temperature peaks shifted towards higher temperature when the heating rates of the wood samples accelerates. Further, the activation energies were determined by adopting the Coats and Redfern (CR) method, assuming n = 1. Generally, the density and moisture content does not influence the kinetics parameter studied in this work. Overall, the thermal decomposition in the second-stage was dominated by the hemicellulose and cellulose while the lignin was eminent in the third-stage. The higher activation energy in the second-stage indicates more cellulose is contained in the sample. From the results obtained, it can be said that in this work, the activation energy of lignin is much less than the hemicellulose and cellulose except for the Shorea parvifolia. The present study is useful to understand the complete degradation process and the pyrolysis kinetics involved in the thermal degradation of the Malaysian wood as indoor and outdoor furniture material.

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