Kinetic Analysis of Durian Rind Pyrolysis Using Model-Free Method

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Abstract. In this study, the thermal degradation behavior and kinetic parameters of durian rind were investigated by using the thermogravimetric analysis technique. The experiments were performed in the temperature range of 313 – 1,073 K with the heating rate of 5, 10, 20 and 40 Kmin⁻¹. Three model-free methods namely Friedman (FR) method, Kissinger-Akahira-Sunose (KAS) method, and Flynn-Wall-Ozawa (FWO) method were used to attain the kinetic parameters. The results show that the thermal degradation of durian rind exhibits 3 stages including dehydration stage (up to 380 K), active pyrolysis stage (380 – 680 K) and passive pyrolysis stage (above 680 K). A maximum rate loss shifts to a higher temperature with an increase in the heating rate. The values of kinetic parameters obtained from FR, KAS and FWO methods are in a good agreement with the experimental results. The average activation energies calculated by FR, KAS and FWO methods are reported at 243.02, 220.38 and 218.33 kJmol⁻¹, respectively. Combining with heating value and chemical structure of durian rind, it can be stated that durian rind can become a useful source of alternative fuels and/or chemical feedstocks.

1. Introduction
Thermochemical conversion processes, e.g. combustion, carbonisation, pyrolysis and gasification, are considered as a promising technology for biomass utilisation. By means of thermochemical conversion process, biomass can be converted into bio-fuels such as bio-oil and syngas, bio-char, and various useful chemicals. Biomass resources can be categorized into wood biomass, energy crops and agricultural waste. Particularly, agricultural residue has the potential to be used as renewable energy due to a large quantities produced annually worldwide. Additionally, agricultural waste is desirable feedstock since the cultivation of agricultural crops has less demand of area and cultivation period compared to wood biomass [1].

Durian known as the “king of fruits” is the most popular fruit in the South East Asia, especially in Malaysia, Indonesia, Singapore, Philippines and Thailand. Normally, durian rind accounts for 65 – 70 wt.% of the whole durian fruit. In particular, the production of durian in Thailand was approximately 753,000 tonnes in 2018 according to the Office of Agricultural Economics, Ministry of Agriculture and Cooperatives, consequently the volume of durian rind in excess of 527,000 tonnes were produced. Durian rind can be represented as a renewable and sustainable resource to be exploited rather than simply disposed by landfilling, composting and open burning. Yet, pyrolysis process is regarded as one of the most thermochemical conversion methods to convert durian rind into fuels and chemicals [2].
Although various notable studies were reported on durian residue investigations such as activated carbon derived from durian residue [3-6], carboxymethyl cellulose film from durian rind [7], biocharcoal briquette from durian peel [8] as well as durian rind fast pyrolysis [2], there are no data available to determine the pyrolysis reaction kinetic of durian rind. Information about biomass kinetics is important to evaluate biomass as a feedstock for fuel or chemical production and for efficient design and control of thermochemical processes. These lead us to investigate the thermal degradation behavior and pyrolysis kinetic of durian rind. The results discussed in this research work, durian rind pyrolysis in particular, may provide a useful basic data for thermochemical conversion system.

2. Experimental

2.1. Sample preparation and characterisation
The durian rind used in this study was collected from the local market of Mabkha City, Rayong Province, Thailand. The sample was first washed with water, cut into small pieces, sun-dried for 3-5 days, and then ground and sieved to an average size of 500 µm. The powder sample was stored in airtight glass container.

The proximate analysis including moisture content, volatile matter and ash content was determined according to ASTM E870 – 82, while the fixed carbon was calculated by subtracting the percentages of moisture content, volatile matter and ash content from 100%. In order to quantify the carbon, hydrogen, and nitrogen contents (oxygen content was determined by mass difference) in the durian rind sample, the elemental analysis was conducted by a Perkin-Elmer CHNS/O elemental analyser. The chemical functional groups presented in the durian rind sample was investigated by a Perkin-Elmer FTIR spectrometer. Furthermore, the calorific value of sample was calculated by the data obtained from the oxygen bomb calorimeter (Parr 1341).

2.2. Thermogravimetric experiments
Thermal degradation behavior of durian rind sample was carried out with TA Instrument Q50 analyser under an inert atmosphere. Prior to the TGA experiments, the fine durian rind powder, ca. 10 mg, was placed in a small platinum crucible and thermally purged under a nitrogen stream at 313 K for 10 min. TGA profiles were attained by heating the sample from 313 to 1,073 K using a nitrogen flow of 60 mlmin⁻¹. The heating rates of 5, 10, 20 and 40 Kmin⁻¹ were used to understand the thermal degradation behaviour. In order to ensure repeatability and accuracy, each experiment was repeated at least two times. Data obtained from TGA experiments were also used for kinetic parameter analysis.

2.3. Kinetic procedure
The primary pyrolysis process is represented by the following reaction mechanism:

\[
\text{Biomass (Solid)} \xrightarrow{k(T)} \text{Volatile (tar + gases)} + \text{Char (solid residue)}
\]  

(1)

The rate of conversion \((d\alpha/dt)\) from solid-state to the volatile product can be expressed by the following equation:

\[
\frac{d\alpha}{dt} = k(T) f(\alpha)
\]  

(2)

where \(k(T)\) is the reaction rate constant, \(T\) is the absolute temperature, \(f(\alpha)\) is the function of reaction mechanism and \(\alpha\) is the fractional change in solid mass due to thermal degradation at any time \(t\) or conversion, defined as:

\[
\alpha = \frac{m_0 - m_f}{m_0 - m_i}
\]  

(3)
where \( m_0 \), \( m_i \) and \( m_f \) are the initial mass, the instantaneous mass and the final mass of the solid sample, respectively. According to Arrhenius equation, the reaction rate constant is almost always strongly dependent on temperature. The temperature dependence of the reaction rate constant could be correlated by the equation of

\[
k(T) = A e^{\left(-\frac{E_a}{RT}\right)}
\]

where \( A \) is the pre-exponential factor or frequency factor, \( E_a \) is the activation energy and \( R \) is the universal gas constant. By combining equation (2) and (4) gives:

\[
\frac{d\alpha}{dt} = A e^{\left(-\frac{E_a}{RT}\right)} f(\alpha)
\]

Under constant heating rate \( (\beta = \frac{dT}{dt}) \), the rate of conversion can be expressed as the function of temperature:

\[
\frac{d\alpha}{dT} = \frac{A}{\beta} e^{\left(-\frac{E_a}{RT}\right)} f(\alpha)
\]

Integration of both sides of equation (6) gives:

\[
g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{\beta_0}^{T} e^{\left(-\frac{E_a}{RT}\right)} dT
\]

where \( g(\alpha) \) is the integral form of the conversion dependence function \( f(\alpha) \). The equation (7) does not have an analytical solution, a various approximation techniques can be used for approximated values. The most method used to determine the kinetic parameters is the isoconversional method or model-free method. Isoconversional method has been proven particularly effective for kinetic analysis and was recently strongly recommended by the Kinetics Committee of the International Confederation for Thermal Analysis and Calorimetry (ICTAC) \[9\]. The isoconversional method has the ability to reveal complexity of the process in the form of a functional dependence of the activation energy on the extent of conversion. The basic assumption of this method is that the reaction rate for a constant extent of conversion depends only on the temperature.

2.3.1. Friedman (FR) method

Friedman method is the simplest and one of the most widely used differential isoconversional method for kinetic analysis. By applying natural log on both sides of equation (6). The Friedman equation is stated as follows,

\[
\ln\left(\beta \frac{d\alpha}{dT}\right) = \ln\left[A f(\alpha)\right] - \frac{E_a}{RT}
\]

The activation energy can be calculated from the slope of the plot of \( \ln\left(\beta (\frac{d\alpha}{dT})\right) \) versus \( (1/T) \).

2.3.2. Kissinger-Akahira-Sunose (KAS) method

Kissinger-Akahira-Sunose method uses the Murray and White’s approximation. The KAS equation is expressed as:

\[
\ln\left(\frac{\beta}{T^2}\right) = \ln\left[\frac{AR}{E_a g(\alpha)}\right] - \frac{E_a}{RT}
\]

\[\text{(9)}\]
The activation energy can be obtained from the slope of the plot of $\ln \left( \beta / T^2 \right)$ versus $(1/T)$.

2.3.3. Flynn-Wall-Ozawa (FWO) method

Flynn-Wall-Ozawa method uses the Doyle’s approximation. The FWO equation is expressed as:

$$
\ln \beta = \ln \left[ \frac{AE}{Rg(\alpha)} \right] - 5.331 - 1.052 \frac{E}{RT}
$$

The plot of $\ln \beta$ versus $(1/T)$ should be a straight line whose slope can be used to evaluate the activation energy.

In order to find the pre-exponential factor, the general thermal degradation reaction represented by $f(\alpha) = (1 - \alpha)$ or $g(\alpha) = -\ln(1 - \alpha)$ was used in this study.

3. Results and discussion

3.1. Sample characterisation

The results of proximate analysis, ultimate analysis and calorific value of durian rind sample are presented in Table 1. It was observed that the durian rind is dominated by volatile matter (68.31 ± 0.71 wt.%), and fixed carbon content (20.04 ± 0.33 wt.%) and it contains only small amounts of moisture content (5.58 ± 0.05 wt.%), and ash content (6.07 ± 0.01 wt.%). Normally, both H/C and O/C values affect the heating value as the H/C ratio increases and O/C ratio decreases, the heating value will increase accordingly. It can be seen that the durian rind shows the H/C and O/C ratios of 2.00 and 0.75, respectively. A high value of H/C ratio indicates a considerable amount of aliphatic hydrocarbon compound such as alkanes and alkenes. The presence of these hydrocarbons suggests that the durian rind is a viable and potential candidate for a resource of energy and chemical feedstocks. Furthermore, the calorific value of durian rind was calculated as 15.34 MJkg$^{-1}$. This value is similar to those reported for the other biomass residues [10].

| Table 1. Characteristics of durian rind. |
|----------------------------------------|
| **Proximate analysis (wt.%)** |
| Moisture content | 5.58 ± 0.05 |
| Volatile matter  | 68.31 ± 0.71 |
| Fixed carbon     | 20.04 ± 0.33 |
| Ash content      | 6.07 ± 0.01  |
| **Elemental analysis (wt.%)** |
| Carbon           | 45.83        |
| Hydrogen         | 7.61         |
| Nitrogen         | 0.62         |
| Oxygen and others (by difference) | 45.94 |
| H/C molar ratio  | 2.00         |
| O/C molar ratio  | 0.75         |
| Calorific value (MJkg$^{-1}$)         | 15.34 ± 0.26 |

Figure 1 shows the infrared spectrum of durian rind. A very strong and broad band at 3401 cm$^{-1}$ can be attributed to the stretching of O-H that indicates the presence of alcohol, phenol and acid derived from the cellulose component. The transmittance peak detected at 2929 cm$^{-1}$ can be ascribed to compounds with C-H stretching of methylene group of an alkane compound that also presents in the cellulose component. The transmittance peak at 1736 cm$^{-1}$ can be associated with the alkyl ester of acetyl group in hemicellulose structure and/or the linkage between hemicellulose and lignin. The transmittance peak shown at 1618 and 1420 cm$^{-1}$ can be assigned to the deformation within the methoxyl groups of lignin, whereas the peak detected at 1377 cm$^{-1}$ can be referred to alkane compounds containing the
methyl group. The transmittance peak observed at 1249 cm$^{-1}$ can be ascribed to the stretching of C-O in the lignin component. The overlapping strong transmittance peak presented between 920 – 1200 cm$^{-1}$ can be attributed to compounds containing C-O-C and C-O-H stretching of primary and secondary alcohols those present in the cellulose and hemicellulose [11-13]. The result obtained from FTIR analysis shows that the durian peel is dominated by oxygenated compounds and aliphatic hydrocarbons and small amount of aldehydes and ketones, suggests that this agricultural waste could potentially be converted into liquid fuel as well as hydrogen gas which is used as a chemical feedstock.

Figure 1. FTIR spectrum of durian rind.

3.2. Thermal degradation behavior

Figure 2 and 3 show the TG and DTG profiles of durian rind at the heating rates of 5, 10, 20 and 40 Kmin$^{-1}$. According to the loss rate, the thermal degradation behavior of durian rind can be distinguished into three stages as expected. This is the fact that durian rind is a lignocellulosic biomass composed of cellulose, hemicellulose and lignin. Each component has different thermal degradation temperature region. In the first stage, the removal of moisture as bound water on the surface and the hydrolysis of some extractive molecules are observed at the temperature up to 380 K. This stage is known as the dehydration stage. The second stage is active pyrolysis stage involved the thermal degradation of hemicellulose, cellulose and some part of lignin at the temperature range of 380 – 680 K. The first weight loss of the second stage is corresponded to the thermal degradation of hemicellulose and amorphous cellulose while the second weight loss of this stage is ascribed to the thermal degradation of α-cellulose. The last stage is passive pyrolysis stage involved the thermal degradation of cellulose and lignin. Lignin undergoes gradual thermal degradation over a wide temperature interval (500 – 900 K) without characteristic peak. The residue remaining is about 23.8 wt.% which corresponded to the proximate analysis result. It should be noticed that there are nuanced in weight loss curves of durian rind at different heating rates and the increasing in heating rates made TG curves shift to higher temperature. This might be due to the fact that a decrease in heat transfer efficiency at higher heating rates. Similar phenomena were also found in the cases of soybean straw [14], sawdust [15], oil-palm shell [16] and castor [17]. Moreover, it can be noticed that the relationship between the maximum weight loss rate ($DTG_{\text{Max}}$) and heating rate can be expressed as $DTG_{\text{Max}} = 0.6066\beta$ (with $R^2 = 0.9995$).
3.3. Kinetic analysis

Figure 3 shows the FR plot, KAS plot and FWO plot for the kinetic parameter calculations and Table 2 summarises the kinetic parameters calculated by using the different three isoconversional methods. It was found that the activation energies calculated by FR, KAS and FWO are in the range of 192.98 – 336.90, 157.82 – 250.51 and 157.56 – 247.82 kJmol\(^{-1}\), respectively. It should be noticed that the value of average activation energy achieved by FR method is larger than those obtained by KAS and FWO methods: \(E_{a,\text{avg}}^{\text{FR}} > E_{a,\text{avg}}^{\text{KAS}} \approx E_{a,\text{avg}}^{\text{FWO}}\) (243.02 > 220.38 ≈ 218.33 kJmol\(^{-1}\)). This might be because the difference in the kinetic model between differential and integral isoconversioal methods. Similar phenomenon was also found in the case of sawdust pyrolysis, with the mean activation energies obtained from FR, KAS and FWO were 168, 158 and 153 kJmol\(^{-1}\), respectively [18]. Nevertheless, all three isoconversional methods are suitable for determining the activation energy for durian rind pyrolysis, based on the data of calculated \(R^2\).

The variation of activation energy with respect to conversion is also shown in Figure 4. It can be seen that the value of \(E_a\) is almost constant in the conversion range of 0.2 – 0.5. While in the conversion between 0.5 and 0.7, a steady increase in \(E_a\) values is observed. This might be due to the fact that the reaction mechanism of durian rind pyrolysis is not the same in the whole thermal degradation process and that activation energy is dependent on conversion as well as temperature regime. At low temperature region (< 773 K), the pyrolysis of hemicellulose and lignin involved exothermic reactions, while that of cellulose presumed endothermic reactions. On the contrary, at high temperature region (> 773 K), the pyrolysis of hemicellulose and lignin is endothermic, while that of cellulose is exothermic [19]. The values of calculated pre-exponential factor also show the variation in a wide range: \(4.56 \times 10^{17} – 1.69 \times 10^{20}\), \(3.30 \times 10^{14} – 1.74 \times 10^{20}\) and \(3.19 \times 10^{14} – 9.98 \times 10^{19} \text{ s}^{-1}\) for FR, KAS and FWO methods, respectively. This phenomenon can be attributed to the complex compositions of durian rind and the complex reactions that occur during the thermal degradation process.
Figure 4. FR, KAS and FWO plots and variation of activation energy with respect to conversion.

Table 2. Values of the kinetic parameters for durian rind obtained by FR, KAS and FWO methods.

| α   | $E_a$ (kJmol$^{-1}$) | $A$ (s$^{-1}$) | $R^2$ |
|-----|----------------------|----------------|-------|
| FR method |
| 0.1 | 192.98               | 5.44 × 10$^{17}$ | 0.9850 |
| 0.2 | 223.69               | 1.79 × 10$^{19}$ | 0.9971 |
| 0.3 | 228.86               | 8.09 × 10$^{18}$ | 0.9997 |
| 0.4 | 220.89               | 4.56 × 10$^{17}$ | 0.9995 |
| 0.5 | 232.66               | 2.51 × 10$^{18}$ | 0.9999 |
| 0.6 | 265.16               | 7.55 × 10$^{20}$ | 0.9796 |
| 0.7 | 336.90               | 1.69 × 10$^{26}$ | 0.9514 |
| Average | 243.02 |
| KAS method |
| 0.1 | 157.82               | 3.30 × 10$^{14}$ | 0.9680 |
| 0.2 | 225.77               | 1.74 × 10$^{20}$ | 0.9953 |
| 0.3 | 226.59               | 2.49 × 10$^{19}$ | 0.9994 |
| 0.4 | 220.90               | 1.81 × 10$^{18}$ | 0.9989 |
| 0.5 | 222.07               | 9.79 × 10$^{17}$ | 0.9978 |
| 0.6 | 239.03               | 1.53 × 10$^{19}$ | 0.9956 |
| 0.7 | 250.51               | 4.68 × 10$^{19}$ | 0.9960 |
| Average | 220.38 |
| FWO method |
| 0.1 | 157.56               | 3.19 × 10$^{14}$ | 0.9708 |
| 0.2 | 222.87               | 9.98 × 10$^{19}$ | 0.9956 |
| 0.3 | 224.09               | 1.57 × 10$^{19}$ | 0.9995 |
| 0.4 | 218.99               | 1.28 × 10$^{18}$ | 0.9990 |
| 0.5 | 220.31               | 7.19 × 10$^{17}$ | 0.9980 |
| 0.6 | 236.63               | 1.01 × 10$^{19}$ | 0.9959 |
| 0.7 | 247.82               | 3.00 × 10$^{19}$ | 0.9962 |
| Average | 218.33 |

4. Conclusions
It can be concluded that durian rind thermal degradation behavior can be distinguished into three stages consisted of dehydration stage (up to 380 K), active pyrolysis stage (380 – 680 K) and passive pyrolysis stage (above 680 K). The relationship between the maximum weight loss rate and heating rate can be observed as $DTG_{\text{max}} = 0.6066\beta$. Kinetic studies show that the average apparent activation
energies of durian rind pyrolysis calculated from FR, KAS and FWO are reported at ca. 243.02, 220.38 and 218.33 kJmol$^{-1}$, respectively. Regardless of the model-free method used, the activation energy is practically constant in the conversion range of 0.2 – 0.5 while it increases with the increase in the conversion range from 0.5 to 0.7, suggesting a complex reaction mechanisms of durian rind pyrolysis. The isoconversional method seems suitable for evaluating the kinetic parameters as well as for describing the dependence of kinetic parameters on the degree of conversion for durian rind pyrolysis.

5. References

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