Thermogravimetric kinetics of catalytic and non-catalytic pyrolytic conversion of palm kernel shell with acid treated coal bottom ash

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Abstract. The catalytic and non-catalytic pyrolytic conversion kinetics of palm kernel shell with untreated (as received) and H2SO4 treated coal bottom ash as catalyst were investigated in this study. The activation energy was determined using Flynn-Wall-Ozawa (FWO) kinetic model and distributed activation energy model (DEAM) isoconversional kinetic models. The study was conducted using thermogravimetric analysis at 10, 20, 30 and 50 °C/min heating rates. The activation energy (Ea) ranged from 145.7-228.3 kJ/mol and 142.1-274.2 kJ/mol for FWO and DEAM, respectively. The use of acid treated ash reduced the activation energy compared to the non-catalytic process while the untreated ash increased the activation energy.

1. Introduction

Exploitation of palm kernel shell as one of the major biomass energy sources has received attention especially in Malaysia. Palm kernel shell is one of the biomass wastes considered to have high potential to contribute to the ever increasing energy needs of the society [1]. Utilization of palm kernel shell and coal bottom ash (CBA) in catalytic pyrolysis process, not only helps to preserve the environment but also generate useful products: biochar, pyrolysis oil and gas. Furthermore, coal ash could upgrade pyrolysis liquid product due to its alkali and alkali earth metal content [2], which has similarity with red mud that has been widely used as catalyst for biomass pyrolysis [3-5].

Palm kernel shell has high potential for energy applications due to its high-energy content, abundance and renewability [6]. Furthermore, it has excellent environmental impact properties that could result in a net zero greenhouse gas impact and has very low sulphur content [7]. In general, its excellent energy properties have propelled research and innovation for its possible utilization for fuel and power generation applications.

Utilization of ash for biomass conversion may be accompanied with attendant problems due to fusion of the ash at high temperatures predominant in gasification [8]. Ash fusion and agglomeration are common phenomena in thermochemical conversion due to the high operating temperature [9].
could affect the performance of ash used as catalyst in the process. Coal, biomass and ash have been treated in various ways to reduce the problems associated with ash fusion and agglomeration [8, 10]. Improvement in the surface area of ash could increase its suitability for application as catalyst. Higher surface area of ash reduces the possibility of sintering and formation of agglomerates [11]. Lu et al. [12] effectively prevented agglomeration resulting from potassium loading during gasification of coal in a pressurised fluidised bed gasifier. They reported that washing the ash with water removes the soluble potassium, which tends to combine with other metal oxide on heating thus resulting in agglomeration. Patrick et al. [13] studied the effect of water leaching on coal bottom ash and its influence on hydrogen and syngas production in biomass gasification. They observed that leaching of the ash in ionised water slightly improved the surface properties, especially the pore width. The ash also performed better than the untreated ash. The H\textsubscript{2} content of the of the syngas produced in the gasification of palm kernel shell using the leached ash (45.2 vol\%) [13] was comparable to that obtained using a more expensive Fe-Ni bimetallic catalyst (47.41 vol\%) in the same process [14]. Furthermore, the leached ash reduced the CO\textsubscript{2} produced. However, to the best of authors’ knowledge at present there are no studies reported in the literatures on the use of coal bottom ash as catalyst for palm kernel shell pyrolysis, thus this study intends to bridge this gap.

In this study, leaching of coal bottom ash in aqueous H\textsubscript{2}SO\textsubscript{4} is explored to develop it for application as a catalyst in palm shell pyrolysis. Treatment in aqueous H\textsubscript{2}SO\textsubscript{4} could increase the surface area by dissolving the silica/slag matrix [15], as well as functionalize (sulfonate) the by formation of SO\textsubscript{3}- functional group in the active sites [16]. The catalytic and non-catalytic pyrolytic conversion kinetics of palm kernel shell with untreated (as received) and H\textsubscript{2}SO\textsubscript{4} treated coal bottom ash as catalyst were also investigated.

2. Materials and methods

2.1. Material preparation and characterization

Waste palm kernel shell (PKS) used in the study was obtained from Kilang Sawit Felcra Nasarudin Sdn. Bhd., Bota, Perak, Malaysia. The waste was sun-dried for 4 days then further dried in an oven set at 105°C for 24 hours to ensure removal of free bond moisture. The dried PKS was crushed then milled and sieved to obtain 0.50 - 0.75 mm particle sized samples for the experiment [13].

Industrial coal bottom ash waste was obtained from Tenaga Nasional Berhad, Janamanjung Sdn Bhd power plant, Manjung, Malaysia. The ash was oven-dried at 105°C for 24 hours and ground in preparation for treatment. It was treated by leaching in aqueous solutions of 2M H\textsubscript{2}SO\textsubscript{4} at 45°C for 6.5 h. Controlled leaching of ash was done to ensure partial dissolution of oxides encapsulated in the glass phase thus releasing them from the silicate/slag matrix [15]. Ash dissolution is influenced by the acid concentration (which also influences the pH), ratio of the volume of leaching solution to mass of ash, L/S, temperature of leaching solution and the time of leaching.

Proximate analysis of the palm shell was done using thermogravimetric analyser (Exstar TG/DTA 3200) while the ultimate analysis was carried out by following the ASTM D5373 standard method using LECO CHNS 932 elemental analyser, where carbon, hydrogen, nitrogen and sulphur content of the PKS were determined. The calorific value of PKS was determined using IKA C5000 oxygen bomb calorimeter. Standard operating procedure based on ASTM E711-87 was adapted for the test.

The untreated and treated coal ash samples were analysed using X-ray fluorescence (XRF) and the physisorption properties were also determined. The pore size and surface area were determined by Branauer-Emmett-Taylor (BET) method while the pore volume was measured using Barret-Joyner-Halenda (BJH) method.

2.2. Thermogravimetric analysis

Thermogravimetric analysis for devolatilization of PKS was performed at four different heating rates: 10, 20, 30 and 50 °C min\textsuperscript{-1} with untreated and treated ash, and without ash using thermogravimetric
analyser (Exstar TG/DTA 3200). During the experiment, nitrogen gas flowrate was maintained at 100 mL/min to purge out air and maintain an inert environment. For each experiment, a 10 mg of PKS sample was mixed with 0.07 wt% ash, placed in a ceramic crucible and heated from 50 to 800°C in an inert environment. The experimental conditions were chosen based on previous study [13]. The experiment was repeated thrice to ensure reproducibility.

2.3. Thermal degradation kinetic theory
Thermogravimetric analysis of the samples was conducted to acquire information in order to determine kinetic parameters, which can be used for the thermal degradation process and to optimize the conversion process [17].

2.3.1. The distributed activation energy model. The thermal degradation of various solid materials in both inert and oxidative environments have been successfully described by the distributed activation energy model (DAEM) [17-19]. It consists of a series of successive irreversible first order reactions and expressed as the kinetic formula in Equation (1).

\[
1 - \frac{V}{V_\infty} = \int_0^\infty \Phi(E, T) f(E) dE
\]  

where \( V = w_0 - w \), \( V_\infty = w_0 - w_\infty \) and \( \Phi(E, T) = \exp\left(-\frac{A}{\beta_2} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT\right) \). The terms \( w_0 \), \( w \) and \( w_\infty \) are the initial weight, weight at time, \( t \) and final weight, respectively.

\( V \) is the weight loss percentage at time \( t \); \( V_\infty \) is the total weight loss percentage; \( E \), \( A \), \( \beta \), \( T \), and \( R \) represent the activation energy, pre-exponential factor, heating rate, absolute temperature, and universal gas constant, respectively; \( f(E) \) is the normalized distribution function of the activation energy.

As pointed out by Miura (1995), \( \Phi(E, T) \) is a step function, which can be approximated as in Equation (2):

\[
\Phi(E, T) \cong \exp\left(-\frac{AR^2}{\beta R} \exp\left(-\frac{E}{RT}\right)\right)
\]

Substituting Equation 2 into Equation 1 and simplifying results the DAEM equation (Equation (3)).

\[
\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR^2}{R}\right) + 0.6075 - \frac{E}{RT}
\]

The plot of \( \ln(\beta/T^2) \) against \( 1/T \) in Equation (3) is a straight line for the same \( V/V_\infty \) at different heating rates corresponding to the occurrence of the first-order reaction. The activation energy, \( E_a \) and pre-exponential factor, \( A \) are determined from the slope and intercept of the linear-fitting plot, respectively.

2.3.2. Flynn-Wall-Ozawa (FWO) kinetic model. Biomass devolatilization process is often described by a one-step global model which proceeds as a single reaction [20] as shown in Equation (4).

\[
\text{Biomass} \rightarrow \text{Volatiles} + \text{Char} + \text{Tar}
\]

where volatiles refers to the gas generated and \( k \) is pyrolysis rate constant of a reaction with a temperature dependence expressed by the Arrhenius equation (Equation 5).

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

where \( A \) is the pre-exponential factor (min\(^{-1}\)), \( E_a \) is the activation energy (kJ.mol\(^{-1}\)), \( R \) is the gas constant (8.314 J.K\(^{-1}\).mol\(^{-1}\)) and \( T \) is temperature in Kelvin (K). Solid-state devolatilization kinetics is expressed as:

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

\[
g(\alpha) = k(T)t
\]
where $\alpha$, $t$, $k(T)$, $f(\alpha)$, $g(\alpha)$ are conversion fraction, reaction time, rate constant, differential reaction model and integral reaction model, respectively. The conversion fraction, $\alpha$, for non-isothermal thermogravimetric analysis at any temperature is defined as the weight loss of the sample and given by Equation (8):

$$\alpha = \frac{m_i - m_t}{m_i - m_f}$$

where $m_i$, $m_t$ and $m_f$ are initial mass, substrate mass at a given time, $t$, and final substrate mass remaining after pyrolysis reaction. Substitution of Equation (5) into Equations (6) and (7) gives the expression of reaction rate as shown in Equations (9) and (10):

$$\frac{da}{dt} = A e^{\frac{E_a}{RT}} f(\alpha)$$

$$g(\alpha) = A e^{\frac{E_a}{RT}} t$$

Non-isothermal method is used for solid-state kinetics and the equation of heating rate, $\beta = \frac{dT}{dt}$ can be used to develop the model free (isocconversional) kinetic models. Substituting the $\beta$ into Equations (9) and (10), results in Equations (11) and (12).

$$\beta \frac{da}{dt} = A e^{\frac{E_a}{RT}} f(\alpha)$$

$$g(\alpha) = \int_0^\alpha \frac{da}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T e^{\frac{E_a}{R \alpha dT}}$$

Flynn-Wall-Ozawa (FWO) kinetic model is one of the common global kinetic method used to determine the kinetic parameters of thermal degradation process of biomass. An isocconversional integral form of Equation (12) was developed for non-isothermal data by obtaining the logarithmic form given in Equation (13) [21].

$$\ln g(\alpha) = \ln \frac{AE_a}{\beta R} + \ln p(x)$$

where $p(x)$ is the integral of the exponential $e^{\frac{E_a}{R \alpha dT}}$. Applying Doyle’s approximation [22], $\ln p(x) \approx -5.331 - 1.052x$, to Equation (13) yields Equation (14)

$$\ln g(\alpha) = \ln \frac{AE_a}{\beta R} - 5.331 - 1.052x$$

and substituting $x = \frac{E_a}{RT}$ into the equation gives Equation 15

$$\ln g(\alpha) = \ln \frac{AE_a}{\beta R} - 5.331 - 1.052 \frac{E_a}{RT}$$

A straight-line plot of $\ln g(\alpha)$ against $1/T$ will give a slope of $-1.052E_a/\beta R$. This is used to evaluate the value of activation energy ($E_a$).

### 3. Results and Discussion

3.1. Physicochemical Characterization of PKS

The ultimate analysis indicates that the C, H, N, S and O contents of the PKS sample contains 51.65 wt% carbon, 5.53 wt% hydrogen, 1.22 wt% nitrogen, 0.13 wt% sulphur, and 41.47 wt% oxygen, respectively. PKS is considered as a sustainable feedstock with low pollution impact on the environment due to possible low emission of NOx, HCl, and SO2 during pyrolysis as a result of the low nitrogen and sulphur contents [23]. From the proximate analysis of the PKS, the moisture content is 4.69 wt%, which make it ideal for utilization in pyrolysis process [24], since it fall below 30% thus making it ignitable and having a potential for generation of high calorific value from the product [25]. The volatile matter and fixed carbon of PKS are 74.27 and 19.81 wt%, respectively, while the ash content is 1.23 wt%. It is therefore expected that the sample will release high volume of vapor during pyrolysis due to the volatile matter content [23]. The low ash content of the sample is beneficial
because it helps to reduce or eliminate agglomeration and slagging problem in the pipelines [25, 26]. The higher heating value (HHV) of 19.05 kJ/kg gives an indication that it is suitable for use in small scale second generation biofuel application [27].

3.2. Characterization of Coal Bottom Ash

The chemical composition of the ash in terms of oxide as determined using XRF is depicted in Table 1. The treatment process reduced the concentration of all oxides apart from SO₃. The SiO₂ is significant in both sample and could contribute to the increase in surface area of the ash [28] especially when amorphous SiO₂ content is high. The treated CBA contains appreciable amount of alkali, alkali earth and transition metal oxides (AAETM), which are known to be effective catalysts. Furthermore, the reduction in the alkali oxides (K₂O and Na₂O) raise the melting temperature of the ash thus reducing problems associated with ash melting and agglomeration raw ash [12].

| Table 1. Chemical composition of CBA |
|-------------------------------------|
| Samples                             | Components (wt%) |
|                                     | SiO₂ | CaO | Fe₂O₃ | Al₂O₃ | SO₃ | MgO | P₂O₅ | TiO₂ | K₂O | Na₂O | Others |
| Untreated ash                       | 36.60 | 21.70 | 21.40 | 11.00 | 0.61 | 3.57 | 0.98 | 1.21 | 1.06 | 0.67 | 1.20 |
| Treated ash                         | 24.95 | 18.89 | 15.65 | 5.72  | 29.67 | 1.77 | 0.80 | 0.64 | -   | 1.02 |

Results of physisorption properties showed significant increase in surface area and pore volume of the treated ash (Table 2). This is likely due to the partial dissolution of the ash, which tends to eliminate the solidified silicate matrix [15] encapsulating the various metal species in the ash. This results in an increase in surface area, pore volume and pore width due to migration of the dissolved material from the ash structure.

| Table 2. Physisorption properties of CBA |
|----------------------------------------|
| Parameters                             | Raw Ash | Leached Ash Residue | Percentage Increase (%) |
| BET surface area (m²/g)                | 4.79    | 23.33               | 387.06                  |
| Pore volume (cm³/g)                    | 0.0082  | 0.046               | 460.98                  |
| Mean Pore Size (nm)                    | 6.83    | 7.71                | 0.13                    |

3.3. Kinetic analysis

The kinetic parameters were evaluated from the results of thermogravimetric analysis using the distributed activation energy model (DAEM) and Flynn-Wall-Ozawa (FWO) kinetic model. The activation energy obtained using DAEM and FWO methods were calculated based on Equations 3 and 15 for a given value of conversion. Variation in conversion with changes in heating rate are illustrated in Figs. 4, 5 and 6 for PKS pyrolysis without CBA and, with untreated and treated CBA, respectively. The activation energy was determined by choosing same values of conversion (from range of 0.2 to 0.7) for the different heating rates, determining their corresponding temperatures and applying them to Equation 3 and 15. The E_a can be determined from the slopes plots of ln(β/²) vs. 1000/T and ln(α) vs. 1000/T for DEAM and FWO methods, respectively.
The result shown in Figure 1 depicts the effect of catalyst on activation energy at different conversion for the non-catalytic and catalytic pyrolysis using both the treated and the untreated coal ash. A comparison of the three processes show that the treated ash reduce the activation energy after 40% conversion was attained. The untreated ash on the other hand, generally raise the activation energy throughout the process. The distribution of activation energy shows excellent agreement for FWO and DEAM models. This implies that for the DAEM model, which considers multiple $E_a$ of parallel reactions [29, 30], only one of the reactions significant, thus the $E_a$ agrees closely with that evaluated using FWO model. Furthermore, the close agreement of the $E_a$ values evaluated indicates that the data is reliable [31]. The $E_a$ changes also coincide when compared at the same conversion. Others researchers [32, 33] also reported similar results. Furthermore, the trend is similar to that obtained by Ma et. al. [34], corresponding to stages of degradation of hemicellulose, cellulose and lignin.

The use of acid treated ash reduced the activation energy compared to the non-catalytic process but the untreated ash increased the activation energy. This is an indication that acid treatment enhances the catalytic properties of the ash when it was used as catalyst for pyrolysis of palm kernel shell.

![Figure 1. Activation energies of isoconversional kinetic analysis using Flynn-Wall-Ozawa (FWO) and distributed activation energy models (DAEM) for non-catalytic pyrolysis of PKS (no CBA) and, PKS pyrolysis with untreated CBA (RCBA) and acid treated CBA (SCBA)](image)

4. Conclusion
This study evaluated the non-catalytic and catalytic kinetic parameters of palm kernel shell volatilization using isoconversional methods (DAEM and FWO). Thermogravimetric analysis was conducted at 10, 20, 30 and 50°C, used to evaluate conversion, and carryout the kinetic studies. The temperature range, peak height and positions for the active stage of PKS decomposition stages are influenced by the heating rate. The values of kinetic parameters obtained are in close agreement and appropriately describe the pyrolysis process. Catalytic pyrolysis using treated ash resulted in a lower $E_a$ with an average of 142.1033 and 145.7242 kJ mol$^{-1}$ for DAEM and FWO, respectively. This will result in a faster rate of reaction compare to the untreated ash.
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