An In-Situ Thermogravimetric Study of Pyrolysis of Rice Hull with Alkali Catalyst of CaCO₃

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Abstract: Pyrolysis of rice hull (RH) with the presence of CaCO₃ catalyst was carried out in this study to understand the effect of alkali catalyst in the thermal degradation behaviour and evaluate the kinetic parameter of rice hull for bio-oil or syngas production. Five different heating rates of the pyrolysis experiments at 10, 20, 30, 50, and 100 Kmin⁻¹ were carried out in thermogravimetric analysis (TGA) equipment. Model fitting kinetic Coats Redfern integral method was applied in this study to estimate the activation energy (Eₐ) and pre-exponential (A) value of catalytic pyrolysis in RH. The results showed that the maximum degradation increased from 6.69 to 52.67 wt% min⁻¹ as heating rates increases from 10 to 100 Kmin⁻¹. Besides that, the Eₐ of the catalytic pyrolysis for RH using CaCO₃ catalyst 60.86 kJmol⁻¹ which is lower than other similar pyrolysis reaction reported in literature i.e. 77.4 kJ/mol. Meanwhile, the A value for the catalytic pyrolysis for RH using CaCO₃ catalyst was 4.68×10¹⁰ min⁻¹ which is significantly higher than 1.1×10⁶ min⁻¹ as reported in literature for non-catalytic pyrolysis of rice husk.

1. Introduction

Recently, the world’s energy consumption is mainly generated from fossil fuels and analysts have warned about the depletion of this non-renewable resources in the future. On the other hand, the environment awareness has increased due to greenhouse gas effect has restraint on fuel combustion emission, thus renewable energy has attracted plenty of attention in recent years [1]. Biomass (e.g. rice hull, coconut shell, microalgae) is one of the promising renewable sources since it is cheap, biodegradable and environmentally friendly [2]. The world production of biomass was estimated to be 146 billion metric tons per year [3]. The biomass energy source can be attained through thermochemical conversion method such as pyrolysis [4], gasification [5] and direct combustion [6].
Among all the thermochemical conversion, pyrolysis is considered one of most effective method to convert the biomass to energy since it could reduce the possibility of unwanted oxidation in the pyrolyzer and enhance the liquid (bio-oil) and gaseous (syngas) production [7]. Pyrolysis process is a thermal decomposition of materials in an inert atmosphere under non-isothermal conditions. Hence, kinetic study is fundamental for investigating the thermal degradation behavior of biomass to promote the product yield and obtain the energy recovery.

In recent studies, there are plenty of research studies on the catalysts implementation to the pyrolysis process to reduce the energy input and enhance the syngas production [8]. Zhang et al. (2013) [9] has reported that cracking with the presence of catalyst can increase liquid yield and reduce operation cost. There are three types of catalysts composition for biomass gasification process such as alkali metal (reduce tar content and methane content), dolomite (removal of hydrocarbons), and nickel (removal of hydrocarbons and gas composition adjustment) [10]. There are numerous discussions carried out by the research communities on the alkali minerals exploitation. Giudicianni et al. (2018) [11] has reported the addition of alkali ions in raw xylon pyrolysis produced high solid residue and Chen et al. (2018) [12] reported that pyrolysis of RH treated with alkali able to increase the yield of aromatics.

Kinetic parameters such as activation energy (E_A) and pre-exponential value (A) that obtained in catalytic pyrolysis can be used as a guidelines to design, optimize, and scale up the industrial plant level for this thermochemical process [13]. Chin et al. (2014) [14] had reported that thermogravimetric analysis (TGA) is one of the most convenient and widely used method to understand the thermal degradation behavior of biomass and determine the kinetic parameters in pyrolysis process. Meanwhile, Coats-Redfern integral is one of the non-isothermal model fitted method to describe kinetic parameters of non-catalytic pyrolysis and catalytic pyrolysis of biomass. Balasundrum et al. (2017) [8] has reported the kinetic study of catalytic pyrolysis of biomass for possible bio-oil production using Coats-Redfern integral method, and Naqvi et al. (2015) [15] has reported the kinetic study of catalytic pyrolysis of paddy husk using Coats-Redfern integral method.

To our best knowledge, most of the catalysts reported in previous study are transition element [16], acid catalysts [17] and mesoporous materials [18]. Meanwhile, there are only a few studies described the effect of alkali catalysts in catalytic pyrolysis of biomass. In our previous work, we had investigated the non-catalytic pyrolysis of rice husk using Kissinger-Akahira-Sunose method [19]. Therefore, the aim of this study is to investigate the effect of alkali metal of CaCO₃ catalyst in thermal degradation of catalytic pyrolysis of rice hull and determine the activation energy (Eₐ) and pre-exponential factor (A) using Coats Redfern integral method and compared with the Eₐ obtained in non-catalytic pyrolysis of rice hull that had been reported in previous literature.

2. Experimental

2.1 Material preparation

RH was obtained from Malaysia rice mill. The RH was ground and sieved to a particle less than 710 µm. The ultimate analysis of the RH was estimated using LECO CHNS-932 elemental analyzer and proximate analysis was analyzed using BS EN 14774-3:2009, BS EN 15148:2009 and BS EN 14775:2009, respectively [20]. Alkali metal catalyst of CaCO₃ was collected from Calrock Sdn. Bhd., Malaysia. The elemental analysis of the CaCO₃ catalyst was estimated using X-ray fluorescence (XRF) S8 Tiger Bruker.

2.2 Experimental procedure

In the present study, an approximate of 5.0 mg of RH was placed on a ceramic crucible with 0.5 mg of CaCO₃ catalyst which is 10% of the total weight of the RH. The experiments were conducted using
TGA under inert environment of nitrogen (N\textsubscript{2}) gas. Before the experiments were conducted, a 100mL/min flowrate of N\textsubscript{2} was introduced into the TGA system to remove unwanted gaseous. This could minimize the unwanted gaseous presence in the system that could cause coke formation on the catalysts and oxidation on the samples. Subsequently, all the samples were heated from temperature 323 to 1173 K at five different heating rates of 10, 20, 30, 50, and 100 Kmin\textsuperscript{-1} respectively. All the experiments were carried more than 3 times to ensure the accuracy of the data obtained.

2.3 Kinetic study

In this study, Coats-Redfern method was applied to study the kinetics of the catalytic pyrolysis of RH using MATLAB software R2015b. Coats-Redfern method uses the integral form of the non-isothermal rate law derived from Eq. (1) and integrate into Eq. (2).

\[
\frac{da}{dt} = \frac{A}{\beta} e^{-\frac{E_A}{RT} f(a)}
\]  
(1)

\[
g(a) = \int_0^a \frac{da}{f(a)} = \frac{A}{\beta} \int_0^T e^{-\frac{E_A}{RT} dT}
\]  
(2)

It utilized the asymptotic series expansion for approximating the temperature integral, \(p(x)\), Eq. (3) and derived Eq. (4) shown in below:

\[
\ln p(x) = \frac{AE_B}{RT}
\]  
(3)

\[
\ln \left( \frac{g(a)}{T^2} \right) = \ln \left( \frac{AE_A}{\beta E_A} \left[ 1 - \left( \frac{2RT_{exp}}{E_A} \right) \right] \right) - \frac{E_A}{RT}
\]  
(4)

where \(T_{exp}\) is the mean experiment temperature. In this study, twenty integral functions, \(g(a)\) represents different reaction models and the expression of \(g(a)\) were collected from previous studies tabulated in Table 1 [10]. By plotting the \((\ln \left( \frac{g(a)}{T^2} \right))\) versus \(\left( \frac{1}{T} \right)\) graph, the \(E_A\) and \(A\) can be obtained from the slope and intercept respectively. According previous studies, first order reaction is widely used as integral function model to determine the kinetic parameters [21].

### Table 1: Reaction model functions and its mechanism [8, 22].

| Model | Model name | Differential form, \(f(a) = \frac{1}{da} \) | Integral form, \(g(a) = kt\) |
|-------|------------|-----------------------------------|------------------|
| Nucleation model | Power law (P2) | \(2a^{1/2}\) | \(a^{1/2}\) |
|       | Power law (P3) | \(3a^{1/2}\) | \(a^{1/2}\) |
|       | Power law (P4) | \(4a^{1/2}\) | \(a^{1/2}\) |
|       | Avrami-Erofe’ev (A2) | \(2\left[1 - (1 - a)^{1/2}\right]\) | \([-ln(1 - a)^{1/2}\) |
|       | Avrami-Erofe’ev (A3) | \(3\left[1 - a\right]-ln(1 - a)^{1/2}\) | \([-ln(1 - a)^{1/2}\) |
|       | Avrami-Erofe’ev (A4) | \(4\left[1 - a\right]-ln(1 - a)^{1/2}\) | \([-ln(1 - a)^{1/2}\) |
|       | Prou-Tompkins (B1) | \(a(1 - a)\) | \(in\left[ln(1 - a)\right]\) |
| Geometrical contraction model | Contracting area (R2) | \(2\left[1 - (1 - a)^{1/2}\right]\) | \([1 - (1 - a)^{3/2}\) |
|       | Contracting volume (R3) | \(3\left[1 - (1 - a)^{3/2}\right]\) | \([1 - (1 - a)^{3/2}\) |
|       | 1-D diffusion (D1) | \(2a^{1/2}\) | \(a^{1/2}\) |
|       | 2-D diffusion (D2) | \([-ln(1 - a)\]^{-1}\) | \([1 - (1 - a)](1 - a)\) |
|       | 3-D diffusion-Jander equ. (D3) | \(3\left[1 - (1 - a)^{3/2}\right]\) | \([1 - (1 - a)^{3/2}\) |
|       | Anti-Jander equ. (D4) | \(2\left[1 - (1 - a)^{3/2}\right]\) | \([1 - (1 - a)^{3/2}\) |
|       | Gansring-Braunstein (D4) | \(3\left[2 - (1 - a)^{-1/2} - 1\right]\) | \([-2a/3 - (1 - a)^{3/2}\) |
| Reaction-order models | Zero-order (F0/R1) | \(1\) | \(1\) |
|       | Chemical reaction (n = 1) | \((1 - a)^{-2}\) | \((1 - a)^{-1}\) |
|       | First-order (F1) | \(1 - \left(1 - a\right)^{1}\) | \(ln(1 - a)\) |
|       | Second-order (P2) | \((1 - a)^{2}\) | \((1 - a)^{-1}\) |
|       | Third-order (P3) | \((1 - a)^{3}\) | \(0.5(1 - a)^{-1} - 1\) |
3 Results and Discussion

3.1 Ultimate and proximate analysis of rice hull

The ultimate and proximate analysis for RH was shown in Table 2. The carbon, hydrogen, nitrogen, sulphur and oxygen content of the RH were estimated to be 39.65 wt%, 5.21 wt%, 1.20 wt%, 0.02 wt% and 53.92 wt% in dry and ash free basis respectively. From the proximate analysis, it showed that RH contained a high volatile content (69.20 wt%) and low ash content (1.23 wt%) can increase the bio-oil production which indicated it is suitable for fuel production [23].

| Ultimate analysis (wt %)\(^a\)  |
|-------------------------------|
| Carbon                        | 39.65 |
| Hydrogen                      | 5.21  |
| Nitrogen                      | 1.20  |
| Sulphur                       | 0.02  |
| Oxygen                        | 53.92 |

| Proximate analysis (wt %)\(^b\) |
|-------------------------------|
| Moisture content              | 4.29  |
| Volatile matter               | 69.20 |
| Fixed carbon\(^a\)            | 19.45 |
| Ash                           | 1.23  |

\(^a\) dry and ash-free basis
\(^b\) dry basis

3.2 Chemical Characterisation for Alkali Catalyst CaCO\(_3\)

The elemental analysis of alkali metal catalyst of CaCO\(_3\) was listed in Table 3. The magnesium, calcium, iron, silicon, and other content of the alkali metal catalyst of CaCO\(_3\) were estimated to be 1.05 wt%, 91.20 wt%, 2.63 wt%, 4.67 wt%, and 0.45 wt% respectively. It can be noticed that calcium content has the highest weightage in CaCO\(_3\) which indicates the purity of CaCO\(_3\). Sutton et al. (2001) [10] has reported that higher purity of Ca in CaCO\(_3\) may increase in the reactivity of decomposition.

| Chemical characterisation of CaCO\(_3\). |
|-----------------------------------------|
| Elemental analysis (wt %)               |
| Magnesium                               | 1.05  |
| Calcium                                 | 91.20 |
| Iron                                    | 2.63  |
| Silicon                                 | 4.67  |
| Others                                  | 0.45  |

3.3 Thermal Degradation Behavior of RH

Figure 1(a) and 1(b) show the thermogravimetric (TG) analysis in wt% and derivative thermogravimetric (DTG) analysis in wt% min\(^{-1}\) for catalytic pyrolysis of RH under five different heating rates of 10, 20, 30, 50, and 100 Kmin\(^{-1}\) respectively. It was observed that the curves in the TG profile for the catalytic pyrolysis of RH showed similar trend of weight loss and almost identical in all heating rates studied. The TG-DTG curves were divided into three phases of thermal degradation: vaporization of moisture developed at temperature less than 450 K (Phase I), followed by Phase II which is the devolatilization phase of volatile matter at temperature range of 450 to 800 K and Phase III which is the lignin decomposition of biomass at temperature range of 800 to 1173 K. Moreover,
there is a small peak can be observed in Fig.1(b) at temperature around 1023 to 1123 K was associated to carbonization of CaCO$_3$ as shown in Eq. (5).

\[
\text{CaCO}_3 \leftrightarrow \text{CaO} + \text{CO}_2
\]

From Figure 1(a) and 1(b), it can be observed that the mass loss curves shifted to the right as heating rates increased from 10 to 100 Kmin$^{-1}$. Also, it can be noticed there was lateral shift in temperature of the maximum degradation peak as heating rate increased. These right lateral shift occurrences were due to the combined effect of heat transfer at different heating rates and the heat conductive property of the biomass particle [24]. The maximum degradation rate has rose from 6.69 wt% min$^{-1}$ to 59.37 wt% min$^{-1}$ for the heating rate of 10 to 100 Kmin$^{-1}$. The rise of the maximum degradation peak showed that heating rate may affect the degradation rate of pyrolysis process. The residue produced from the catalytic pyrolysis of RH has increased compare to raw RH studies reported by Ahiduzzaman et al. (2015) [25]. This occurrence was good agreement with the studies reported by Giudicianni et al. (2018) [11] where the elimination of tar has converted to char.

![Figure 1](a) TG of Rice Husk with CaCO$_3$ (b) DTG of Rice Husk with CaCO$_3$

3.4 Determination of kinetic parameters from Coats-Redfern method
The kinetic parameters of pyrolysis of RH with the presence of alkali metal catalyst of CaCO$_3$ were estimated using Coats-Redfern integral method. The $E_A$ and A for different heating rates of 10, 20, 30, 50, and 100 Kmin$^{-1}$ were tabulated in Table 4. The predicted $E_A$ values ranged between 59.08 and 65.80 kJ mol$^{-1}$ while the average $E_A$ value attained was 60.86 kJ mol$^{-1}$. The calculated pre-exponential values range from $2.7 \times 10^9$ to $189.4 \times 10^9$ min$^{-1}$.

The comparison of $E_A$ from pyrolysis of different biomass using Coats-Redfern integral method were shown in Table 5. From the previous literature, the $E_A$ and A values of non-catalytic RH using Coats-Redfern kinetic model was 77.4 kJ mol$^{-1}$ and $1.1 \times 10^9$ min$^{-1}$ respectively [25]. It is found that the $E_A$ value in the present study of catalytic RH was reported 21.36 % lower compared to non-catalytic pyrolysis of RH, which explained the addition of catalyst has the effect to enhance the degradation rate of biomass. The reduced of $E_A$ has the effect on the plant design specification, optimization process and the operation cost [26].
Table 4: Kinetics determined with Coats-Redfern equation for pyrolysis of rice husk with alkali metal catalyst of CaCO₃.

| Heating rate, Kmin⁻¹ | Fitted equation | R²   | Tave (K) | Eₐ (kJmol⁻¹) | A (min⁻¹) |
|----------------------|-----------------|------|----------|--------------|-----------|
| 10                   | y = -7106x - 1.715 | 0.9858 | 555.0    | 59.08        | 5.52 × 10⁹ |
| 20                   | y = -7444x - 1.654 | 0.9879 | 562.5    | 61.89        | 1.88 × 10¹⁰ |
| 30                   | y = -7367x - 1.896 | 0.9964 | 566.3    | 61.25        | 17.5 × 10⁹   |
| 50                   | y = -6770x - 3.056 | 0.9979 | 571.1    | 56.29        | 2.70 × 10⁹   |
| 100                  | y = -7914x - 1.477 | 0.9923 | 577.5    | 65.80        | 1.89 × 10¹¹   |

Average | 0.9921 | 60.86 | 4.68 × 10¹⁰ |

Table 5: Comparison of EA using Coats-Redfern method from previous studies.

| Biomass | Heating rate (Kmin⁻¹) | Activation energy (kJmol⁻¹) | Pre-exponential factor (min⁻¹) | Reference |
|---------|------------------------|----------------------------|--------------------------------|-----------|
| RH      | 10 – 100               | 60.86                      | 4.68 × 10¹⁰                    | Present study |
| RH      | 20                     | 77.4                       | 1.1 × 10⁶                     | [25]        |
| Coal    | 10                     | 92.6                       | 3.31 × 10²³                   | [27]        |
| Coal    | 5 – 30                 | 83.46–93.41                | 3.94 × 10⁵ – 5.44 × 10⁵       | [28]        |

4. Conclusions

The study of the thermal degradation behavior of catalytic pyrolysis for rice hull was carried out using thermogravimetric analysis (TGA) equipment. The Coats-Redfern integral model was chosen to perform the kinetic study and determine the kinetic parameters of RH with the presence of alkali metal of CaCO₃ catalyst in the pyrolysis process from heating rate of 10 to 100 Kmin⁻¹. Coats-Redfern is a single step method which aimed to extract a single value of Eₐ for an overall process and compare the catalytic result to the non-catalytic result at given heating rate. The calculated activation energy, Eₐ for catalytic pyrolysis of RH was 60.86 kJmol⁻¹. It is found that the heating rate of the pyrolysis process and the presence of alkali metal catalyst of CaCO₃ have strong relation to the degradation rate. The higher the heating rate and the addition of catalyst to the pyrolysis process may increase the rate of degradation of pyrolysis process. High degradation rate can minimize char formation and increase bio-oil and syngas production.

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