

## Comparison Kinetic Analysis between Coats-Redfern and Criado's Master Plot on Pyrolysis of Horse Manure

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As a commonly used approach in kinetics analysis, the model-fit method is typically employed to determine the feedstock's reaction model undergoing thermal decomposition. There are several methods in the literature to obtaining the reaction model. However, very little research has been done to compare the discrepancies resulting from different model-fitting methods. In this study, two model-fitting methods, Coats-Redfern (CR) and Criado master plot were used to evaluate horse manure pyrolysis's kinetic reaction model. The feedstock was pyrolyzed in a thermogravimeter at a temperature ramp rate of 10 °C/min under N<sub>2</sub> atmosphere. Both methods indicated that the 2-D Diffusion (Anti-Jander) reaction model was most suited to describe the pyrolysis reaction, illustrating that the reaction rate was limited by the diffusion of components through the product layer at the interface of feedstock. The other two parameters of kinetic triplets as determined from the CR method are activation energy,  $E_a$  at 68.3 kJ/mol and pre-exponential factor,  $A$  at  $4.16 \times 10^6 \text{ s}^{-1}$ . The  $E_a$  value in this work is much lower than that obtained through the model-free method.

### 1. Introduction

Biomass is a potential renewable energy source, which is receiving a great deal of attention due to the superiority of vast resources, independent from climate, location, season and is green and sustainable. Among the various biomass energy conversion processes, pyrolysis is a thermal conversion pathway that heats biomass at high temperatures in an oxygen-free atmosphere that has received great attention (Mong et al., 2020). Pyrolysis stands out from other technological approaches because the process generally yields a lower number of pollutants and secondary products, making it a greener approach in conjunction with the global effort to cut down carbon emissions. The process can yield products with higher value in the form of solid, liquid, and gaseous that can be utilized as alternate fuels, bio-chemicals and even to produce advanced materials. Despite the attractiveness of this thermal conversion approach, the chemical reactions that occur during pyrolysis are extremely complicated and most often hard to predict, causing a delay in the advancement of the lab-to-industry route. The predictability of a process can be translated into a model, allowing it to be used for further optimization prior to setting up a reliable set of processing parameters.

To bridge this gap, a lot of researchers have been looking into the chemical kinetics of pyrolysis to investigate the detailed behaviour of feedstock during pyrolysis. The main goal in investigating chemical kinetics is to obtain the kinetics triplets, namely the apparent activation energy ( $E_a$ ), the pre-exponential factor ( $A$ ), and the kinetic model  $f(\alpha)$  (Acikalin, 2021). From the kinetics triplets', the reaction behaviors, mechanisms and characteristics of pyrolysis can be explored. This may provide a solution to overcome the barriers to up-scaling of biomass waste valorization, such as modelling of industrial processes, combustion in furnaces and boilers, and biomass

conversion methods (Marouani et al., 2021). Model-fitting and model-free methods are common approaches in evaluating kinetics properties. Model-free is mostly used to determine the  $E_a$  and  $A$  values disregarding the type of model it may possess. The approach is generally more reliable, but the full parameters of the kinetics triplets cannot be obtained. The model-fitting method provides information on the reaction model, but other parameters might suffer uncertainty. The reaction model employs a mathematical equation to establish the quantitative relationship between the rate and the degree of conversion (Farooq et al., 2021), providing an intuitive fitting method to detect the reaction mechanism by determining a suitable reaction model.

In the previous work, model-free methods Flynn–Wall–Ozawa (FWO), Kissinger-Akahira-Sunose (KAS) and Friedman methods were used to determine the activation and pre-exponential factor of horse manure, where the activation energy was determined as 199.3, 200.2 and 194.6 kJ/mol, respectively (Mong et al., 2019). The model-free method is more reliable to determine  $E_a$  and  $A$  values as it can evaluate the two kinetic parameters with a mathematical equation that is independent of the reaction model. Despite the results obtained, the absence of the reaction model still leaves a gap that is yet to be filled. There have been reports on other treatments for horse manure through anaerobic digestion (Hadin and Eriksson, 2016), gasification (Nanda et al., 2016) and carbonization (Tsai et al., 2015), but none of them investigated the reaction mechanism.

This work aims to identify the reaction model of horse manure pyrolysis through the model-fitting approach. There have been reports of utilizing different model-fit approaches in identifying the reaction models, but very little research evaluates the difference in approaches for the model-fitting method. The CR and Criado's master plot methods were chosen to investigate the horse manure pyrolysis reaction model, and the possible discrepancies between both methods were assessed. The Criado's master plot method integrates a series of model-fitting curves (theoretical) to be compared with the experimental curve, allowing the assessment of pyrolysis mechanism. The current work is conducted to probe the feasibility of kinetic triplets' determination of horse manure, utilizing the model-fit method individually, being one of the first studies investigating the reaction model of horse manure pyrolysis through a comparison of different model-fitting approaches.

## 2. Material and method

### 2.1 Feedstock characterization and thermogravimetric analysis

Horse manure is utilized as feedstock. The physiochemical properties are reported in the earlier work (Mong et al., 2019). Horse manure was pyrolyzed in a thermogravimeter with a temperature ramp rate of 10 °C/min under an  $N_2$  atmosphere, where the mass loss and rate of mass loss were recorded in TG and DTG forms.

### 2.2 Kinetics analysis

The kinetic analysis aims to determine three kinetic parameters, collectively referred to as the "kinetic triplets" (Acikalin, 2021). In general, the rate of conversion of solid feedstock during pyrolytic decomposition can be described as:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where  $f(\alpha)$  is the differential form of the reaction model as a function of conversion, and  $k(T)$  is the reaction rate constant as a function of temperature. The degree of conversion,  $\alpha$  in the thermal decomposition process can be expressed as:

$$\alpha = \frac{m_0 - m}{m_0 - m_f} \quad (2)$$

where  $m_0$ ,  $m_f$ , and  $m$  denote the mass of biomass at initial ( $t = 0$ ), final ( $t = \text{final}$ ), and any time ( $t > 0$ ).

The temperature dependence of the rate constant  $k(T)$  of biomass was given by the Arrhenius equation as follow:

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

where  $A$  is the pre-exponential factor ( $\text{min}^{-1}$ ),  $E_a$  is the apparent activation energy (kJ/mol),  $R$  is the universal gas constant, taken as 8.314 (J/mol K), while  $T$  is the absolute temperature (K). From Eq(1) and Eq(3), the rate of conversion of solid feedstock during pyrolytic decomposition can be rewritten as:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (4)$$

For non-isothermal condition, the heating rate  $\beta$  can be introduced as:

$$\beta = \frac{dT}{dt} = \frac{dT}{d\alpha} \times \frac{d\alpha}{dt} \quad (5)$$

The rate of conversion can be expressed as following with the combination of Eq(4) and Eq(5):

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E_\alpha}{RT}\right) f(\alpha) \quad (6)$$

Eq(6) can then be solved by integrating with respect to T as follows:

$$g(\alpha) = \frac{A}{\beta} \int_0^{T_\alpha} \left(-\frac{E_\alpha}{RT}\right) dT \quad (7)$$

where  $g(\alpha) = \int_0^\alpha [f(-\alpha)]^{-1} d\alpha$  is the integrated form of the reaction model.

### 2.3 Model fit

The model-fit methods, such as CR method and Criado's master plots method, can be used to study the pyrolytic degradation mechanism and kinetics of the process through the determination of the kinetic model  $f(\alpha)$ , which is one of the important parameters in the kinetic triplets.

#### 2.3.1 Coats–Redfern method

Coats–Redfern method is an integral method involving the thermal degradation mechanism in its formulation. This technique utilized the asymptotic series expansion of Eq(7) to estimate the temperature integral (Farooq et al., 2021), giving the following equation.

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\frac{AR}{\beta E_\alpha} - \frac{E_\alpha}{RT} \quad (8)$$

From the liner plot between  $\ln\left(\frac{g(\alpha)}{T^2}\right)$  and  $\frac{1}{T}$ , the slope and intercept can be used to evaluate the kinetic parameters of pyrolysis. The thermal degradation curves could be reconstructed via Eq(4) to evaluate the calculation performance.

#### 2.3.2 Criado's master plot method

This method is a direct model-fitting approach to identify the kinetic reaction mechanism of the pyrolysis process, and the equation can be shown as follows:

$$\frac{Z(\alpha)}{Z(0.5)} = \frac{f(\alpha) \times g(\alpha)}{f(0.5) \times g(0.5)} = \left(\frac{T_\alpha}{T_{0.5}}\right)^2 \frac{\left(\frac{d\alpha}{dt}\right)_\alpha}{\left(\frac{d\alpha}{dt}\right)_{0.5}} \quad (9)$$

where  $T_{0.5}$  and  $(d\alpha/dt)_{0.5}$  represent temperature and conversion rate at  $\alpha = 0.5$ .

Each reaction mechanism is represented by a reduced theoretical curve on the left side of Eq(9) as  $\frac{f(\alpha)g(\alpha)}{f(0.5)g(0.5)}$ .

The experimental data could be determined from the right side of the equation, which is related with the lower rate. For a specific solid-state reaction, the expression of  $f(\alpha)$  depends on the reaction mechanism. Some of the pyrolysis reaction models are recorded elsewhere (Marouani et al., 2021).

## 3. Results and discussion

### 3.1 Model-fit methods

The reaction models use a mathematical equation to describe the quantitative relationship between the rate and the degree of conversion (Farooq et al., 2021). They describe a specific reaction type and convert it into a rate equation for solid-state processes. Different models have been created and presented in solid-state kinetics based on mechanistic assumptions, some of which were used in this work. Model-fit methods determine the  $E_\alpha$  and  $A$  values after finding the best statistical match reaction model. The CR and Criado's master plot methods were chosen to find the kinetic reaction model of pyrolytics degradation because the reaction mechanisms were involved in their formulations (Marouani et al., 2021). By fitting different models into the theoretical formulations such as Eq(8) and Eq(9), the best-fitted model can be determined according to a higher linear correlation coefficient value ( $R^2 \sim 1$ ) in the CR method and through a master plot. A single heating rate and constant kinetic parameters assumption were employed.

### 3.2 Coats–Redfern method

The TG and DTG of horse manure was analyzed by the CR method. All 21 solid-state reaction models have been fitted into Eq(8), and a group of linear graphs are fitted on the plots of  $\ln\left(\frac{g(\alpha)}{T^2}\right)$  versus  $\frac{1}{T}$ , as shown in Figure 1. The detail equation of each mathematical models can be found elsewhere Marouani et al. (2021) and Vyazovkin and Wight (1999) and only a selected few models has been displayed in Figure 1 to demonstrate the comparison technique. The model with the highest correlation (largest  $R^2$  value) indicates the best-fitted linear line, which will be selected as the most appropriate model to describe the reaction. From the results, the Anti-Jander 2-D diffusion model (labelled as D2-AJ in Figure 1) achieved the highest  $R^2$  of 0.9646 among all other models. From the linear plot utilizing the Anti-Jander 2-D diffusion model, the  $E_a$  was calculated at 68.295 kJ/mol. Finally, the A value was determined using Eq(4). These values indicate that horse manure is required to be supplied with an activation energy of 68.295 kJ/mol during pyrolysis and the number of molecular collisions required for a successful reaction is estimated at  $4.16 \times 10^6 \text{ s}^{-1}$ .

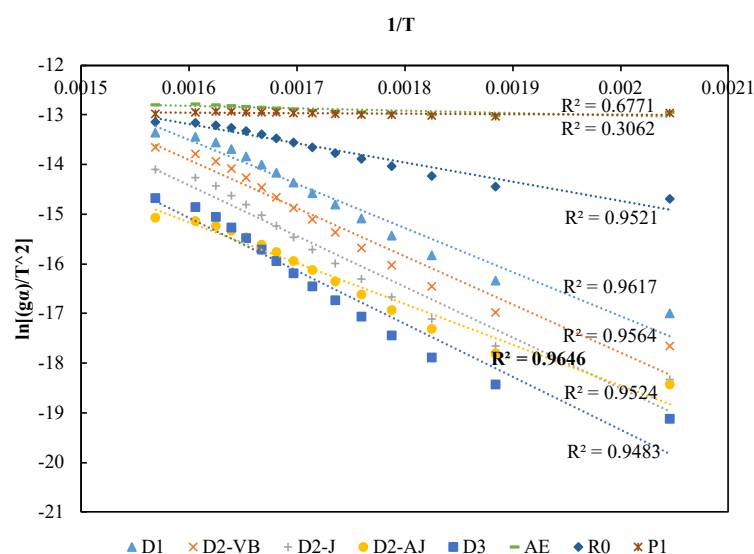


Figure 1:  $\ln\left(\frac{g(\alpha)}{T^2}\right)$  versus  $\frac{1}{T}$  plot with correlation coefficient  $R^2$  using CR method (Note: Numbers in the figure refers to a different reaction model)

Although the CR method provides a very direct way to analyse the reaction model and other kinetics parameters, there are two main non-ignorable hypotheses that may lead to uncertainty of results. The pre-assumption of the reaction model in this method and the selection of the best-fitted line, as indicated by the highest correlation coefficient, which may induce unforeseen errors. Other kinetics parameters, like  $E_a$  and A, are only determined after the pre-assumption of reaction model has been placed. There has been literature report that the sole usage of best-fitted line approach may not yield accurate results. For instance, Marouani et al. (2021) reported that through the CR method, the best-fitted model was found to be the First Order Chemical Reactions (F1) with the highest  $R^2$  of 0.9885. However, when the Criado's master plot was implemented, a different reaction model, the Second Order Chemical Reactions (F2), was found to be more appropriate to describe the reaction model for the degradation of loquat kernels (Marouani et al., 2021). The  $R^2$  of the F2 model was 0.9692 in the CR method, which was lower than that of model F1. This brings to light that the probability of identifying a different reaction model using different approach might be present, requiring a countercheck by comparing different model-fitting methods.

Meanwhile, the  $E_a$  derived from the CR method was very much different from what was previously being reported (Mong et al., 2019). This is because  $E_a$  is allowed to be estimated at an increasing conversion value without modelistic assumptions in the model-free approach. It has also been regarded by the ICTAC Kinetics Committee as the most trustworthy methods for computing the activation energy of thermally activated reactions. Compared with the  $E_a$  value of the horse manure as obtained from various model free methods, like FWO, KAS and Friedman, which are 199.3, 200.2 and 194.6 kJ/mol (Chong et al., 2019), the  $E_a$  value in this study is much lower at 68.3 kJ/mol. Vyazovkin et al. (2011) claimed that a single heating rate model-fitting value  $E_a$  rarely matches the model-free activation energy value with good accuracy. There are two main reasons that may

contribute to the highly ambiguous kinetic triplets when apply model-fitting method to non-isothermal data. One is that the ambiguity is peculiar to the model-fitting method itself, and the other is that the temperature and conversion contributions of the reaction rate are not separated in a non-isothermal experiment (Vyazovkin and Wight, 1999). Sánchez-Jiménez et al. (2013) also discovered that the use of a set of curves recorded under different heating schedules instead of a single curve was necessary if the model-fitting approach was used in non-isothermal conditions. This proposed method may generate results closer to the model-free method when multiple heating rates were incorporate to evaluate the kinetics data.

### 3.3 Criado's master plot method

The Criado's method integrates the experimental data from the TGA to be compared with a set of common solid-state reaction models through Eq(9). The models and the expressions for the associated functions  $g(\alpha)$  and  $f(\alpha)$  were shown elsewhere (Marouani et al., 2021). The master curve plots  $\frac{Z(\alpha)}{Z(0.5)}$  versus  $\alpha$  for different mechanistic models according to the Criado's method, were illustrated in Figure 2. The experimental curve is plotted from the rate of mass loss as directly obtained from the DTG curve. Specifically, the  $dm/dt$  values (Deriv. Weight / %/min) from DTG data were employed here to replace  $da/dt$  in the experimental part of Eq(9). Both theoretical and experimental curves were compared visually and the model which best describes (similar curve) the experimental curve was selected as the reaction model.

It has been observed that the reaction model of Anti-Jander 2-D diffusion (labelled as D2-AJ in Figure 2) is most likely to represent the pyrolysis process of horse manure. It should be noted that this proposed model has a close similarity with the experimental curve only for the conversion range between 0.2–0.55. Beyond the conversion of 0.55, the Anti-Jander 2-D diffusion model might not fully represent the pyrolysis mechanism of horse manure. This observation indicates that there might be a multi-step reaction model, representing the pyrolysis reaction. Further analysis is necessary for a comprehensive evaluation on the suitable reaction model.

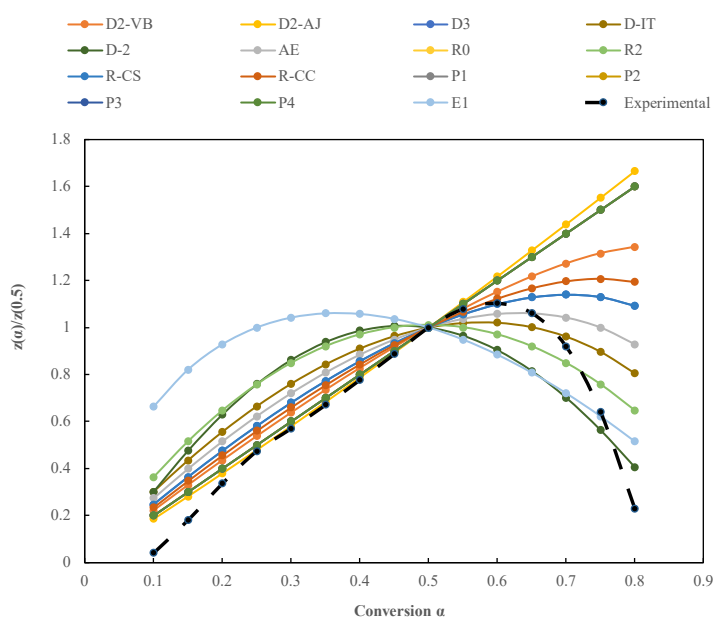


Figure 2: Criado's master plot of horse manure at 10 °C/min

Criado's master plot method provides a straight-forward and intuitive fitting method, which only uses experimental data for the models' assumption. There is no indication of  $E_a$  value in the analysis method. In this case, the results might not be entirely accurate as not all kinetic triplets as described in Eq(6) are considered. Eventually, both the CR and Criado's methods pointed towards the 2-D Anti-Jander diffusion reaction model, which can be considered as the relevant primary model to describe the degradation mechanism of horse manure, explaining that during the horse manure degradation process, the diffusion was slower than the chemical processes occurring at the reaction interface, becoming the limiting factor during reaction. The decomposition rate of solid was controlled by the diffusive escape of volatile products. The Anti-Jander 2-D diffusion model here explains the solid particles were in the shape of cylindrical, and the diffusion occurred radially through a cylindrical shell with an increasing reaction zone (Ammar and Flanagan, 2006). Raza et al. (2022) reported that among all models, the two diffusion models: Anti-Jander diffusion and 4-D diffusion were the best

fitted models with highest regression coefficient values ( $R^2 > 0.99$ ) in the degradation process of date palm surface fibers, which is also a biomass source.

#### 4. Conclusion

Kinetics analysis on horse manure pyrolysis at 10 °C/min using model-fit methods under non-isothermal conditions was conducted to explore the reaction model. By employing CR and Criado's master plot methods, Anti-Jander 2-D diffusion was determined as the most fitted model to describe the pyrolysis reaction mechanism of horse manure, where the reaction rate was limited by the diffusion of components through the product layer at the interface of feedstock. Comparatively, the  $E_a$  value obtained from model-free methods, the model-fitting CR method presented a lower value of 68.3 kJ/mol due to the problem of ambiguity caused by model-fit method itself and the combined action of temperature, conversion, and heating rate. This model determination is beneficial to reveal the entire kinetic behavior of horse manure and serves as a reference required for optimization and parametric study. The model-free method can obtain  $E_a$  with higher accuracy while the model-fit method can aid the identification of the reaction model. It is recommended that both methods are adopted together to ascertain a good solution. Other forms of the Criado's master plot can also be integrated in the future work to investigate the effectiveness in combining both methods. For example, by using the  $E_a$  obtained from model-free methods to be integrated into the model-fitting approach of master plot.

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