# Kinetic Study on the Catalytic Pyrolysis of Decanter Cake from Palm Oil Milling Plant by using Thermogravimetry Data

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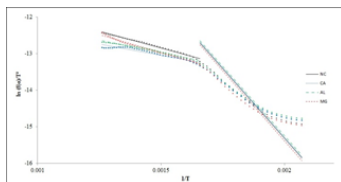[b]Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak 26300 Kuantan, Pahang, Malaysia

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**Graphical abstract**

**Abstract**

The kinetic study on the catalytic pyrolysis of decanter cake (DC) from palm oil milling plant was carried out using thermogravimetry method. Catalysts were added to dry DC in desired ratio and then mixed manually. Based on the thermogravimetric analysis (TGA) results, the main thermal decomposition of both non-catalytic and catalytic pyrolysis of DC occurred at 210–530°C. Coats-Redfern method was used in this study. Two stage reactions were identified during the main thermal decomposition, with the first stage at 210–330°C, while second stage occurred at 330–530°C. The pyrolysis reaction obeyed the first and second order kinetic model for first and second stage reaction, respectively. The presence of the catalysts reduced the activation energy of thermal decomposition in both stages. Minimum activation energy value was observed at 10 wt% of catalyst loading.

*Keywords*: Catalytic pyrolysis; kinetic; Coats-Redfern; thermogravimetry; decanter cake; biomass; renewable energy

**Abstrak**

Kinetik pemangkinan pirolisis penyiring kek (DC) daripada penyisaran minyak kelapa sawit telah dikaji dengan menggunakan kaedah termogravimetri. Mangkin ditambahkan ke dalam DC yang kering dengan nisbah yang diingini dan seterusnya digaul secara manual. Berdasarkan keputusan TGA, terma penguraian yang utama daripada DC dengan sama ada tanpa mangkin atau adanya mangkin pirolisis berlaku pada suhu 210–530°C. Kaedah Coats-Redfern telah digunakan dalam kajian ini. Dua tahap tindak balas telah dikenal pasti semasa terma penguraian utama, iaitu tahap pertama pada suhu 210–330°C dan tahap kedua pada suhu 330–530°C. Tindak balas pirolisis mematuhi model kinetik tertib pertama dan kedua untuk tahap pertama dan kedua, masing-masing. Kehadiran mangkin telah megurangkan tenaga pengaktifan daripada terma penguraian dalam kedua-dua tahap itu. Nilai tenaga pengaktifan yang minimum diperhatikan pada 10wt% daripada muatan mangkin.

*Kata kunci*: Pemangkinan pirolisis; kinetic; Coats-Redfern; termogravimetri; penyiringan kek; biojisim; tenaga yang boleh diperbaharu

## ■1.0 INTRODUCTION

Energy consumption has been increasing doubly with oil price hike and the depletion of oil reservoirs has encouraged our nation to find alternative energy resources. Biomass becomes an attractive alternative as it is easily obtained locally in huge amount at relatively cheap price. Biomass is also considered as carbon neutral when utilized as energy sources and hence, does not contribute towards global warming. Recently, biomass has been extensively employed as energy resources worldwide and it is the third primary energy resources after oil and coal. Agricultural sector in Malaysia, particularly oil palm industries, generates abundant biomass either from plantation or palm oil milling plant processing. In 2010, almost 80 million tons of biomass was generated from 500 million tons of oil palm plantation producing 18.91 million tons of crude palm oil [1-2]. Utilization of biomass as energy sources in Malaysia is supported by the government regulation through the 5th fuel policy introduced in the 8th Malaysia Plan (2001–2005). In this plan, renewable energy is considered as the fifth fuel in the energy supply mix [3].

The energies from biomass can be harvested through several methods, such as direct combustion and chemical or biological process. Thermochemical process of biomass, particularly pyrolysis, is well known as a method to convert biomass into biofuel such as charcoal, bio-oil or synthetic gases. In recent

years, application of catalytic pyrolysis in conversion of biomass into biofuels has received great interests. The kinetic of biomass thermal decomposition is important to develop efficient thermochemical processes to convert biomass into biofuels [4].

Most of the kinetic studies on biomass pyrolysis were performed by using thermogravimetry (TG) technique. Application of TG data on kinetic parameter determination was comprehensively reviewed by White *et al.* [5], particularly for agricultural residue cases. Thermogravimetry equipment precisely measures decrease in substrate's mass during the thermal decomposition. Pyrolysis of biomass is a complicated process and involves several chemical reactions. Phase transitions between solid materials into gaseous and liquid products also contribute to the complexity of this process. Several studies had been conducted previously to determine the kinetic parameters of pyrolysis by using various models. However, it is difficult to determine the model which is most suitable and consistent for the whole process. The Coats-Redfern integral method is widely used to describe the kinetic parameters of pyrolysis reaction, particularly for the assumption that the catalytic pyrolysis reaction follows apparent first order reaction kinetics [6]. However, there are still some researches that argued about how this approach sometimes is unsuitable to be applied [7].

The current paper presents the kinetic study on catalytic pyrolysis of decanter cake from palm oil milling plant. Coats and Redfern method was used to interpret the thermogravimetry data obtained from the pyrolysis process. The effect of catalyst to biomass ratio on the kinetic parameters was also presented and discussed.

# ■2.0 EXPERIMENTAL

## 2.1 Materials

Decanter cake was obtained from LKPP Sdn. Bhd., a palm oil milling plant in Lepar Hilir, Kuantan, Pahang. Fresh decanter cake was dried in oven at 105°C for 24 hours to remove moisture. Dried decanter cake was then ground and sieved to obtain average particle size of 100 μm. Calcium oxide (CaO) and magnesium oxide (MgO) were purchased from Sigma-Aldrich, while H-ZSM5 and gamma alumina ($\gamma$-$Al_2O_3$) were supplied by Zeolyst International and Merck, respectively.

## 2.2 Thermogravimetry Analysis Procedure

Five grams of the decanter cake was mixed with the required amount of catalyst and ground using ceramic mortar and pestle. The weight ratio of catalyst to decanter cake was varied at 5, 10, 15 and 20 %. About 5 mg of the sample was placed into a 70 μL alumina crucible and loaded into Mettler Toledo TGA/DSC for thermogravimetry analysis. The experiments were conducted in an inert atmosphere, which was achieved by flowing $N_2$ at a flow rate of 50 mL min$^{-1}$. The temperature of the furnace was increased from 25 to 1000 °C with heating rate of 10°C min$^{-1}$.

## 2.3 Kinetic Model

In this work, Coats-Redfern method was used to examine the kinetic of the pyrolysis. For first order reaction, the simplified form of Coats-Redfern method is expressed as:

$$\ln \frac{g(\alpha)}{T^2} = \ln \left| \frac{AR}{\beta E} \left( 1 - \frac{2RT}{E} \right) \right| - \frac{E_a}{RT} \tag{1}$$

Where

| | |
|---|---|
| $g(\alpha)$ | = kinetic functions |
| $T$ | = temperature |
| $A$ | = pre-exponential factor |
| $R$ | = gas constant |
| $E_a$ | = activation energy |
| $\beta$ | = heating rate |

$\alpha$ is the extent of the reaction, given by:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \tag{2}$$

Where $m_0$, $m_t$ and $m_\infty$ are initial sample mass, sample mass at time $t$ and sample mass at the end of reaction, respectively.

Equation (1) can be plotted in a graph as function of $g(\alpha)$ versus $1/T$. Linear regression of the plot gives $Ea$ and $A$ from the slope and intercept, respectively. Various forms of kinetic function $g(\alpha)$ used for the analysis are presented in Table 1. The accuracy of this model is indicated by the value of correlation coefficient ($R^2$) between experimental with calculated values, where values closer to 1 represent the better model than that of others.

**Table 1** Kinetic functions used for kinetic analysis [7], [8]

| No. | Label | Reaction model | $g(\alpha)$ |
|---|---|---|---|
| 1 | P1/4 | Power Law | $\alpha^{1/4}$ |
| 2 | P1/3 | Power Law | $\alpha^{1/3}$ |
| 3 | P1/2 | Power Law | $\alpha^{1/2}$ |
| 4 | AE1/4 | Avrami-Erofeev | $[-\ln(1-\alpha)]^{1/4}$ |
| 5 | AE1/3 | Avrami-Erofeev | $[-\ln(1-\alpha)]^{1/3}$ |
| 6 | AE1/2 | Avrami-Erofeev | $[-\ln(1-\alpha)]^{1/2}$ |
| 7 | 1DD | One dimensional diffusion | $\alpha^2$ |
| 8 | JAN | Diffusion control (Janders) | $[1-(1-\alpha)^{1/3}]^2$ |
| 9 | CRA | Diffusion control (Crank) | $1-(2/3)\alpha-(1-\alpha)^{2/3}$ |
| 10 | N1 | Mampel (first order) | $-\ln(1-\alpha)$ |
| 11 | N2 | Second order | $(1-\alpha)^{-1}-1$ |
| 12 | CC | Contracting cylinder | $1-(1-\alpha)^{1/2}$ |
| 13 | CS | Contracting sphere | $1-(1-\alpha)^{1/3}$ |

# ■3.0  RESULTS AND DISCUSSION

## 3.1  First Order Kinetic Model

The kinetic parameters of catalytic pyrolysis were obtained from the analysis of TG data, using the approach associated to Equation (1). Since the pyrolysis process was assumed to obey the first order reaction (Model no. 10, Table 1), Equation (1) can be written as:

$$\ln\frac{-\ln(1-\alpha)}{T^2} = \ln\left(\frac{AR}{\beta E_a}\left(1-\frac{2RT}{E_a}\right)\right) - \frac{E_a}{RT} \qquad (3)$$

Since $2RT/E_a \ll 1$, thus Equation (3) can be simplified into:

$$\ln\frac{-\ln(1-\alpha)}{T^2} = \ln\frac{AR}{\beta E_a} - \frac{E_a}{RT} \qquad (4)$$

Correlation of ln [-ln (1-α)/T2] versus 1/T within temperature region of 210 to 530 °C is plotted in Figure 1. Each curve in this plot was divided into two sections according to its linearity. It proves that pyrolysis process involved multi-step reaction that cannot be explained by single kinetic model, which is in agreement with other researchers [6–8], [10], [11]. For both sections, slope and intercept of the linear plots were employed to determine the kinetic parameters of the pyrolysis process.

## 32  Thermogravimetry Analysis

Figure 2 shows TG and DTG plots of non-catalytic and catalytic pyrolysis of decanter cake using different catalysts. The curves indicate that the primary decomposition stage of biomass occurred from 220 to 500°C, for both non-catalytic and catalytic pyrolysis. However, two distinct mass decompositions were exhibited by CaO catalyzed pyrolysis, with one appearing at almost the same temperature with non-catalytic pyrolysis; while the other occurred at higher temperature of 600–700°C. The mass degradation in the second stage may be caused by the decomposition of carbonates [9].
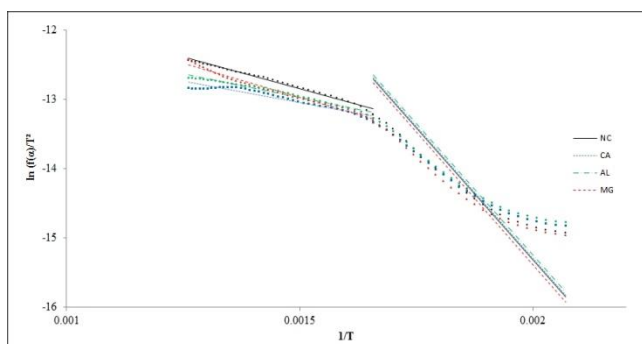


**Figure 1**  Linearization of ln [−ln (1−α)/$T^2$] versus 1/$T$ plot at temperature range of 210–530°C. The dots and lines reflect the experimental data and calculated linear plot, respectively
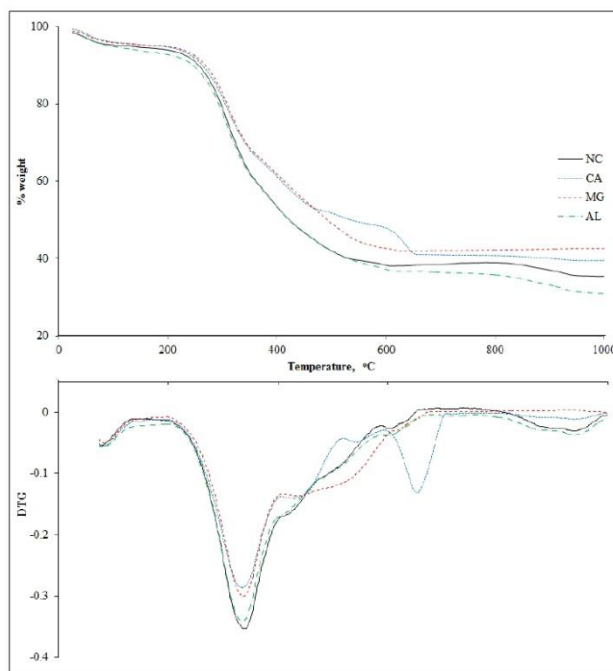


**Figure 2**  TG and DTG plots of non-catalytic and catalytic pyrolysis of decanter cake (NC: non catalytic, CA: CaO, MG: MgO, and AL: γ-Al₂O₃)

The presence of catalyst gave positive effect by lowering the activation energy of pyrolysis process, as indicated in Table 2. Addition of 10% catalysts reduced activation energy from 37.85 kJ/mol in stage 1 and 14.44 kJ/mol in stage 2 to lower values. CaO gave the lowest activation energy for stage 1, while the lowest energy activation for stage 2 was achieved by γ-Al₂O₃ catalyst. As seen in Table 2, the presence of catalyst exhibited various effects on the pre-exponential factor of pyrolysis reaction.

## 3.3  Comparison with Other Kinetic Models

In order to obtain the best approach for determining the kinetic parameters, other kinetic functions listed in Table 1 were also evaluated. Linearization method based on Coats-Redfern equation was used in the same way with first order reaction in *Section 3.2*. Figure 3 illustrates the linear correlation plots between the kinetic function and 1/T for non-catalytic pyrolysis at various kinetic models, while Table 3 provides the value of the kinetic parameters calculated. Some kinetic models gave unrealistic results by determining negative values of activation energy (Power and Aframi-Erofeev models). First order kinetic model provided the highest value of R² in both reaction stages. It can be concluded that the best approach for kinetic parameters evaluation of non-catalytic pyrolysis of decanter cake was first and second order reaction in stage 1 and stage 2 of reaction, respectively. Evaluation of catalytic pyrolysis kinetic parameters resulted in similar result with that of non-catalytic pyrolysis as shown in Table 4. First and second order kinetic models were best fitted for stage 1 and stage 2 of reaction, respectively.

**Table 2** Kinetic parameters for catalytic pyrolysis of decanter cake determined by first order reaction model using Coats-Redfern method

| Catalyst | Stage 1 (210 – 330 °C) | | | Stage 2 (330 – 530 °C) | | |
|---|---|---|---|---|---|---|
| | $E_a$, kJ/mol | ln A | $R^2$ | $E_a$, kJ/mol | ln A | $R^2$ |
| Non-catalytic | 37.85 | 2.0 | 0.982 | 14.44 | 3.2 | 0.991 |
| CaO | 30.82 | 3.7 | 0.967 | 9.92 | 9.2 | 0.921 |
| MgO | 35.21 | 2.4 | 0.972 | 10.81 | 5.6 | 0.989 |
| $\gamma$-Al$_2$O$_3$ | 34.06 | 13.4 | 0.988 | 7.41 | 3.1 | 0.990 |

**Table 3** Activation energy of non-catalytic pyrolysis obtained by various kinetic models

| Model | Stage 1 (210-330 °C) | | Stage 2 (330-530 °C) | |
|---|---|---|---|---|
| | Activation energy, kJ/mol | $R^2$ | Activation energy, kJ/mol | $R^2$ |
| N1 | 37.85 | 0.982 | 14.29 | 0.992 |
| N2 | 37.94 | 0.937 | 38.36 | 0.995 |
| P1/4 | -16.48 | 0.000 | -8.68 | 0.988 |
| P1/3 | 2.97 | 0.759 | -7.71 | 0.979 |
| P1/2 | 8.94 | 0.920 | -5.79 | 0.939 |
| AE1/4 | 1.29 | 0.375 | -5.10 | 0.984 |
| AE1/3 | 4.72 | 0.807 | -2.95 | 0.945 |
| AE1/2 | 11.56 | 0.912 | 1.36 | 0.715 |
| 1DD | 62.68 | 0.968 | 11.56 | 0.863 |
| JAN | 69.54 | 0.962 | 28.49 | 0.985 |
| CRA | 67.17 | 0.964 | 21.59 | 0.963 |
| CS | 29.40 | 0.954 | 5.96 | 0.881 |
| CC | 30.28 | 0.953 | 8.46 | 0.948 |

**Table 4** Activation energy of catalytic pyrolysis obtained by various kinetic models

| Model | Stage 1 (210-330 °C) | | | | | | Stage 2 (330-530 °C) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | CA | | MG | | AL | | CA | | MG | | AL | |
| | Ea | $R^2$ | Ea | $R^2$ | Ea | $R^2$ | Ea | $R^2$ | Ea | $R^2$ | Ea | $R^2$ |
| N1 | 30.82 | 0.967 | 35.21 | 0.972 | 34.06 | 0.988 | 9.92 | 0.905 | 10.81 | 0.941 | 9.61 | 0.977 |
| N2 | 38.17 | 0.957 | 41.49 | 0.947 | 38.56 | 0.951 | 23.65 | 0.979 | 30.96 | 0.983 | 27.99 | 0.999 |
| P1/4 | 0.36 | 0.124 | 1.13 | 0.445 | 0.32 | 0.090 | -8.65 | 0.986 | -8.16 | 0.993 | -8.64 | 0.989 |
| P1/3 | 3.47 | 0.865 | 4.51 | 0.866 | 3.43 | 0.844 | -7.68 | 0.976 | -7.02 | 0.988 | -7.67 | 0.981 |
| P1/2 | 9.71 | 0.952 | 11.25 | 0.942 | 9.63 | 0.944 | -5.74 | 0.929 | -4.75 | 0.962 | -5.73 | 0.946 |
| AE1/4 | 1.53 | 0.563 | 2.33 | 0.650 | 1.55 | 0.529 | -6.27 | 0.971 | -4.47 | 0.993 | -5.89 | 0.984 |
| AE1/3 | 5.03 | 0.877 | 6.10 | 0.869 | 5.06 | 0.860 | -4.50 | 0.922 | -2.10 | 0.934 | -4.01 | 0.957 |
| AE1/2 | 12.04 | 0.943 | 13.64 | 0.932 | 12.08 | 0.935 | -0.97 | 0.235 | 2.62 | 0.876 | -0.23 | 0.044 |
| 1DD | 64.75 | 0.940 | 71.92 | 0.953 | 65.45 | 0.957 | 11.71 | 0.842 | 15.68 | 0.914 | 11.78 | 0.887 |
| JAN | 71.86 | 0.945 | 78.19 | 0.948 | 71.88 | 0.951 | 23.45 | 0.945 | 33.31 | 0.915 | 25.16 | 0.979 |
| CRA | 69.76 | 0.947 | 76.04 | 0.950 | 69.66 | 0.953 | 18.93 | 0.922 | 26.23 | 0.911 | 19.92 | 0.961 |
| CS | 30.66 | 0.940 | 33.81 | 0.942 | 30.62 | 0.946 | 4.29 | 0.678 | 8.30 | 0.912 | 4.89 | 0.837 |
| CC | 31.44 | 0.939 | 34.61 | 0.941 | 31.45 | 0.944 | 5.94 | 0.795 | 10.87 | 0.922 | 6.79 | 0.917 |
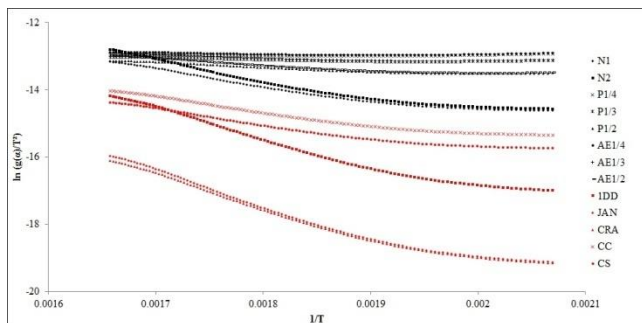


**Figure 3** Linear correlation plots between ln $(g(\alpha)/T^2$ against 1/T. Details on the legend is given in

### 3.4 Effect of Catalyst to Biomass Ratio on the Kinetic Parameters

The effect of catalyst to biomass ratio on the kinetic parameters of pyrolysis was also studied, particularly for CaO and $\gamma$-Al$_2$O$_3$ catalysts. Figure 4 shows the effect of catalyst loading on the activation energy of pyrolysis process. Addition of catalyst decreased the activation energy in both stages of reaction. It can be concluded that 10% catalyst loading is the optimum loading in terms of minimum activation energy.

### ■4.0 CONCLUSION

Thermal decomposition of decanter cake from palm oil milling plant occurred in the temperature range of 220 to 500°C. The kinetic of pyrolysis was modeled successfully using Coats-Redfern method. Two reaction stages were identified during the main thermal decomposition of substrate. First and second order reaction models were fitted to be applied in first and second stage

of reactions, respectively. The presence of catalyst reduced the activation energy of pyrolysis, either in the first stage or second stage of the thermal decomposition. CaO and γ-Al₂O₃ catalysts showed the best performance in terms of lowest activation energy for first and second stages, respectively. Optimum activation energy for pyrolysis of PDC was achieved at 10 wt% catalyst loading.
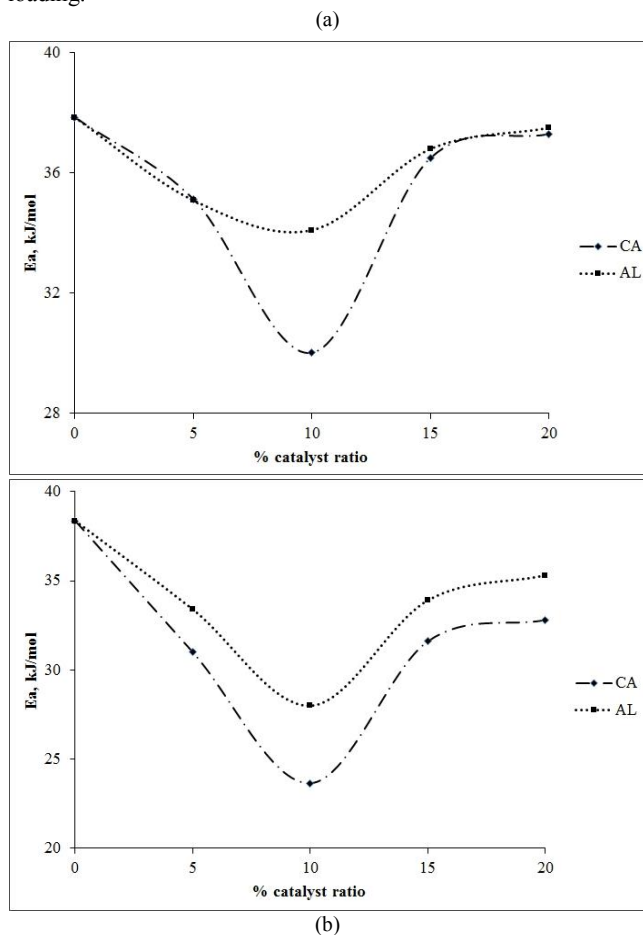
(a)



(b)

**Figure 4** The effect of catalyst loading on the activation energy of decanter cake pyrolysis: (a) stage 1 (210–330°C) and (b) stage 2 (330–530°C)

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