

# Kinetics analysis on isothermal torrefaction of sawdust in a fixed-bed reactor using the Coats-Redfern method and functional group analysis using FTIR spectroscopy

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## Abstract

In this study, torrefaction of sawdust was performed in a fixed bed reactor at different torrefaction temperatures and holding times of 200–300 °C and 20–60 mins respectively under inert nitrogen environment and isothermal condition. It was determined that the mass yield decreased upon increasing torrefaction temperature from 200 to 300 °C and holding time 20 to 60 mins. This could be contributed by the complete elimination of hemicellulosic fraction and slight removal of cellulosic fractions of sawdust which occurred at higher torrefaction temperature of 260–300 °C. The values of kinetics parameters such as activation energy,  $E_a$  and pre-exponential factor ( $\ln A$ ) for the torrefaction of sawdust at holding times of 20, 40, and 60 mins were evaluated using the Coats-Redfern method. The activation energy for torrefaction of sawdust reduced from 48.2054 to 41.7662 kJ/mol when the holding time for the reaction was increased from 20 to 60 mins. It was determined that the torrefaction of sawdust at 60 mins was more reactive than at 20 mins holding time. FTIR analysis on raw and torrefied sawdust showed the presence of OH hydroxyl group, C–H alkane, and C=O from ester or carboxylic acids groups.

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## 1.0 Introduction

Biomass is a source of sustainable energy which could improve the environment by reducing the dependency on non-renewable energy source as well as low detrimental impact on environment (Kumar et al., 2017). It was reported that approximately 3.4 million m<sup>3</sup> of wood waste such as sawdust, wood chips and bark were generated from timber industry (Syafie et al., 2017). This show abundant amount of sawdust which can be utilized as a source of energy. Torrefaction is a thermal treatment on biomass in the temperature range of 200 to 300 °C in the absence of oxygen under atmospheric condition (Nhuchhen, 2016). Torrefaction process on biomass has several advantages such as producing torrefied biomass with lower oxygen and water contents (Chen et al., 2014), lower particle length which leads to better grindability (Poudel et al, 2014). Dynamic non-isothermal torrefaction of biomass such as sawdust (Ren et al., 2013), rice husk (Lim et al., 2016) and birch spruce (Wang et al., 2014) have been reported with reaction kinetics such as Free-model

kinetics, iso-conversional Kissinger-Akaihiro-Sunose (KAS) or numerical methods. Among other kinetics analysis method, the Coats-Redfern method is an integral, model-free kinetics analysis that presumed the reaction follows the first order reaction kinetics that comply to the Arrhenius law with regard to the thermochemical degradation of biomass (Naqvi et al., 2015). This method has been used to analyse the kinetics parameters such as activation energy ( $E_a$ ) and pre-exponential factor ( $\ln A$ ) for the thermochemical decomposition of biomass such as date palm surface fibres (Raza et al., 2022), date seeds (Raza et al., 2023) and nut shell (Noszczyk et al., 2021).

However, the assessments on the kinetics parameters for isothermal torrefaction of sawdust using the Coats-Redfern method as well as functional groups change upon torrefaction are scarce. Therefore, this paper targets to report about the kinetics analysis on isothermal torrefaction of sawdust using the Coats-Redfern method with the change of functional groups analysis.

## 2.0 Methodology

### 2.1 Material

The feedstock for torrefaction process was sawdust, which was obtained from Jejawi, Perlis.

### 2.2 Methods

Torrefaction of sawdust was performed as described by Mohamed et al. (2019) and Singh et al (2019). Firstly, approximately 10.0 g of sawdust was weighed and located into the reactor tube. The reactor tube was placed inside a furnace where the temperature and time were set for the torrefaction process. Then, nitrogen gas was purged into the reactor tube at a flowrate of 150 ml/min for about 10 mins to ensure inert environment. Torrefaction was performed at several torrefaction temperatures of 200, 220, 240, 260, 280, and 300 °C for 20, 40 and 60 minutes at a constant heating rate of 20 °C/min for each experimental run. After the reaction has reach completion, the reactor tube was cooled down at room temperature under the nitrogen environment. The mass yield was calculated using Eq. (1).

$$\text{Mass yield} = \frac{\text{Mass of torrefied sawdust}}{\text{Mass of raw sawdust}} \times 100\% \quad (1)$$

### Kinetics analysis by Coats-Redfern method

Torrefaction process of sawdust follows the Coats-Redfern method. The study of this experiment involves the chemical reaction with respect to the reaction rate. Reaction rate  $\frac{d\alpha}{dt}$  is a function of progress of the reaction,  $\alpha$  as shown in Eq. (2):

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (2)$$

where  $k$  is reaction coefficient and  $\alpha$  is the progress of reaction as shown in Eq.(3):

$$\alpha = \frac{x_o - x}{x_o - x_f} \quad (3)$$

The rate constant,  $k$  is dependent on the activation energy,  $E_a$  as shown in Eq.(4):

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (4)$$

where:  $k$  is rate constant,  $A$  is pre-exponential factor,  $E_a$  is activation energy,  $R$  is universal gas constant, and  $T$  is temperature.

Considering the assumption of the Coats-Redfern method ( $2RT/E \ll 1$ ), Eq. (5) represents the kinetic

equation in order to calculate the value of activation energy,  $E_a$  and pre-exponential factor,  $\ln A$ .

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{BE_a}\left(1 - \frac{2R}{E_a}\right)\right] - \frac{E_a}{RT} \quad (5)$$

Upon plotting the  $\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]$  vs.  $1/T$ , and the values of  $E_a$  and  $\ln A$  can be obtained graphically. The correlation gives a straight line with the first order kinetics.

### Fourier transform infrared (FTIR) analysis

FTIR analysis on raw and torrefied sawdust was carried out using Perkin Elmer FTIR Spectrophotometer model Spectrum-65. Approximately 1 mg of sample was introduced by ATR technique, and it was analysed in the range of 4000 to 400  $\text{cm}^{-1}$  with a resolution of 2  $\text{cm}^{-1}$ .

## 3.0 Results and discussion

Fig. 1 shows the mass yield of sawdust upon torrefaction from 200 to 300 °C at 20, 40, and 60 minutes of holding times. It is apparent that the mass yield decreased upon increasing torrefaction temperature from 200 to 300 °C and holding time 20 to 60 minutes. The decreasing trend for torrefaction temperature of 200–240 °C corresponds to the thermochemical breakdown of the hemicellulosic fraction of sawdust that proceeded via decarboxylation and decarboxylation reactions producing carbon dioxide ( $\text{CO}_2$ ), carbon monoxide ( $\text{CO}$ ) as well as dehydration that released water ( $\text{H}_2\text{O}$ ) (Cai et al., 2013). The decreasing trend becomes more progressive at higher torrefaction temperature of 260–300 °C, which can be contributed by the complete elimination of hemicellulosic fraction and slight removal of cellulosic fractions of sawdust (Ghani et al., 2014).

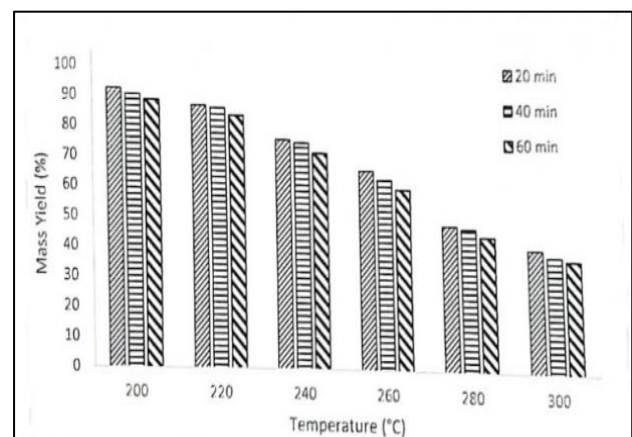


Fig. 1: Mass yield of torrefied sawdust against the torrefaction temperature

**Table 1:** Kinetics parameters for torrefaction of sawdust at several holding times

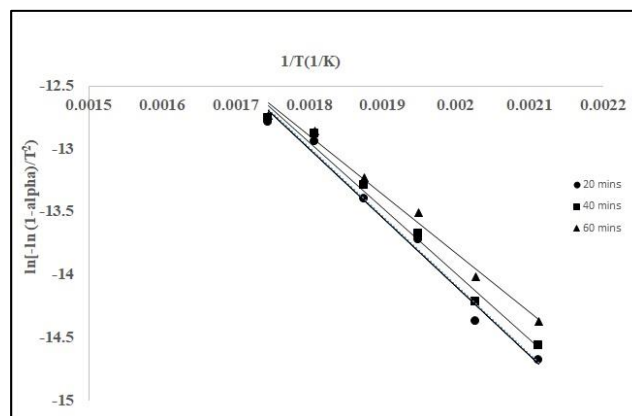
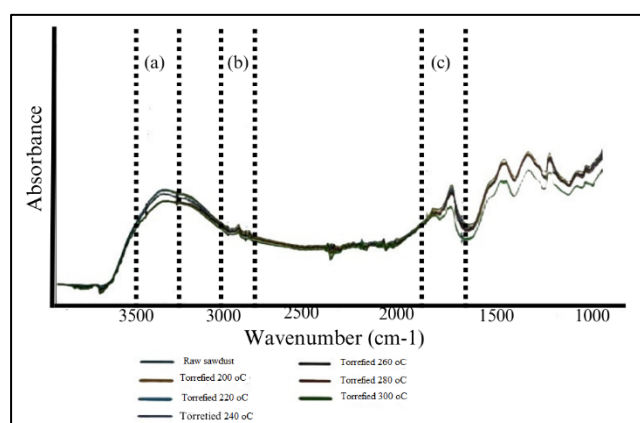
| Reaction                | Holding time (mins) | Equation              | R <sup>2</sup> | E <sub>a</sub> (kJ/mol) | ln A |
|-------------------------|---------------------|-----------------------|----------------|-------------------------|------|
| Torrefaction of sawdust | 20                  | $y = -5798.2x - 2.58$ | 0.9889         | 48.2054                 | 6.08 |
|                         | 40                  | $y = -5402.7x - 3.25$ | 0.9908         | 44.9181                 | 5.35 |
|                         | 60                  | $y = -5023.6x - 3.86$ | 0.9877         | 41.7662                 | 4.66 |

Fig. 2 shows the linearisation curves of  $\ln \left[ \frac{-\ln(1-\alpha)}{T^2} \right]$  against  $1/T$  for isothermal torrefaction of sawdust at holding times of 20, 40, and 60 minutes according to the Coats-Redfern method. The torrefaction process of sawdust follows the first order reaction for torrefaction of sawdust at holding times of 20, 40, and 60 minutes.

Table 1 shows the values of kinetics parameters such as activation energy,  $E_a$ , and pre-exponential factor (ln A) for the torrefaction of sawdust at holding times of 20, 40 and 60 mins. The  $R^2$  values for each equation are all above 0.90 which indicates that there was high correlation between the independent and dependent parameters. The activation energy for torrefaction of sawdust reduced from 48.2054 to 41.7662 kJ/mol when the holding time for the reaction was increased from 20 to 60 minutes. The lower value of activation energy indicates that the reaction has higher reactivity (Ren et al., 2013). Therefore, it can be suggested that the torrefaction of sawdust at 60 minutes is more reactive than at 20 minutes holding time.

Fig. 3 illustrates the overlapped spectra of raw and torrefied sawdust. The torrefaction temperature was increased from 200 to 300 °C, at a heating rate of 20 °C/min and constant holding time of 20 mins. The presence of a single broad peak in the wavenumber range of 3400 to 3200  $\text{cm}^{-1}$  which is denoted by (a) region is identified that indicates the presence of OH hydroxyl group which could originates from alcohol or phenols (So & Eberhardt, 2018). The existence of small peaks in the wavenumber range of 3000 to 2800  $\text{cm}^{-1}$  and denoted by (b) suggests the presence of C–H stretching bond that corresponds to alkane functional group (Kumar et al., 2017).

It is also determined a peak denoted with (c) in the wavenumber range of approximately 1800 to 1600  $\text{cm}^{-1}$  that indicates the presence of C=O bond which is attributed either by the ester or carboxylic acids groups (Liu & Han., 2015). Generally, it is also observed that the intensity of each peaks reduced when

**Fig. 2:** Linearisation curves of  $\ln \left[ \frac{-\ln(1-\alpha)}{T^2} \right]$  vs  $1/T$ **Fig. 3:** The spectra for raw and torrefied sawdust

torrefaction temperature is increased. This could be due to removal of hemicellulosic fraction that increased as the torrefaction temperature is increased.

#### 4.0 Conclusions

In conclusion, torrefaction of sawdust was conducted in a fixed bed reactor at different torrefaction temperature and holding times of 200 to 300 °C and 20 to 60 minutes, respectively in a fixed bed reactor under nitrogen atmosphere. The mass yield decreased when torrefaction temperature was increased from 200 to 300 °C and holding time from 20 to 60 minutes. It was contributed by the devolatilization of hemicellulose and partial cellulose fractions at higher torrefaction temperature of 260 to 300 °C. From the Coats-Redfern kinetics analysis, torrefaction of

sawdust followed the first order reaction with  $E_a$  values of 48.2054, 44.9181 kJ/mol that reduced to 41.7662 kJ/mol for 20, 40, and 60 minutes of torrefaction time, respectively. Torrefaction of sawdust at 60 minutes from 200 to 200 °C was more reactive than that at 20 and 40 minutes since its value of  $E_a$  was the lowest. From FTIR analysis, several functional groups were identified on raw and torrefied sawdust such as OH hydroxyl group, C–H alkane and C=O from ester or carboxylic acids groups. However, the intensities for these peaks decreased when the torrefaction time was increased from 20 to 60 minutes. It was apparent that, increasing the torrefaction time from 20 to 60 minutes had allowed progressive cellulosic and hemicellulosic devolatilization process that resulted in the increasing amount of volatiles removal that contributed to higher reactivity process and reduced the intensities of functional groups on the surface of torrefied biomass. Overall, it can be concluded that the reduction in the values of  $E_a$  as determined from the Coats-Redfern method showed that torrefaction of sawdust within the studied torrefaction temperature and torrefaction time had higher reactivity with reduced intensities on the existence of functional groups, especially O–H.

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These two criteria are important assessment that indicated torrefied sawdust as a potential solid fuel.

## Authorship contribution statement

**Alina Rahayu Mohamed:** Conceptualization, Methodology and Writing-Original Draft. **Noor Hasyierah Mohd Salleh:** Writing-Reviewing and Editing. **Nur Nadhirah Nordin:** Investigation and Data Curation.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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