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# Thermogravimetric analysis and the fitting model kinetic evaluation of corn silk thermal decomposition under an inert atmosphere

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**Abstract.** The thermal behavior of corn silk pyrolysis under nitrogen atmosphere has been studied through the thermogravimetric analyzer. The drying process of the original sample was performed by means of an oven at 100 °C for 90 minutes. The dry sample subsequently ground and sieved for a mesh size of 60. Approximately 11 mg of the sample was weighed into the crucible. The constant heating program of 10 °C/min was imposed on the sample start from room temperature till to 900 °C. The 50 ml/min of nitrogen was continuously flowed into the inner of the chamber to ensure the inert conditions. The differential fitting model of Arrhenius was occupied to evaluate the kinetic parameters. The result shows that corn silk was decomposed into the three stages during the pyrolysis process. These three stages initiated by the dehydration process from room environment till to 154 °C and then followed by the most massive degradation of an organic component in the main devolatilization zone at the temperature range of 154-514 °C and finally rest of material was undergoing slow decomposition till to 900 °C. The respective activation energy ( $E$ ), logarithmic of the pre-exponential factor ( $\log A$ ) and reaction order ( $n$ ) of the corn silk pyrolysis were 207.37 kJ/mol, 19.15/min and 5.2.

## 1. Introduction

The scarcity of fossil-based fuel and its carbon dioxide emission into the atmosphere have become the critical barriers to the universe survival. For that reason, developing sustainable and environmentally friendly fuel to substitute or replace fossil fuel so that it is possible to mitigate the global warming has been receiving a significant concern. Several of renewable energy reserves such as geothermal, hydropower, solar, wind and biomass can be realized as sustainable and green energy for the future existence [1]. The power resulted from wind and solar energy have a high dependence on location and climate led to a significant lately developed. On the contrary, biomass fuel's utilization has grown substantially without any drawback in relation with its reserve and environment. Moreover, because of the carbon-containing in the biomass originated from carbon dioxide in the atmosphere that produced by means of the photosynthetic process, therefore it is considered to be a nearly CO<sub>2</sub>-neutral fuel and proposed as an emergency fuel towards the safely natural environment [2–4].



Indonesia as an agricultural country has great quantity in reserve of biomass derived from agriculture waste. One of the most abundant crops in Indonesia is corn plant. From the area point of view, the land for corn in the year 2017 stretch to 5,375,387 hectares [5] in which corn silk production per one hectare approximately 527 kg [6]. Therefore, the abundance of corn silk is around 2.85 million tonnes per annum [1]. Since the corn production continuously all over the year, hence the overall corn silk product is the precious amount that must be considered and dear to be ignored.

Research on corn silk has been carried out mainly related to its utility as a healthy food ingredient. Aukkanit et al., [7] examined the usefulness of corn silk as low-fat meatballs. The anti-obesity potential of corn silk has been studied by Chaiittianan et al., [8]. The physicochemical properties and antidiabetic effects of corn silk polysaccharides were investigated by Pan et al., [9]. According to the aforementioned literature, the potential of corn silk as an alternative fuel has never been revealed by the researchers. Therefore the characterization of corn silk as a fuel has novelty and will contribute to the advance of science related to the exploration of alternative fuels.

The common mode of thermal conversion of biomass to be energy is gasification, liquefaction, direct combustion, and pyrolysis. Among the various technique, pyrolysis provides the advantage for biomass conversion to be biofuels in which main results are easily stored and transported fuels such as gaseous fuel, bio-oil, and biochar [10]. The biomass pyrolysis is the process in which the material is subjected to the moderate temperature between 400-600 °C in the oxygen-free environment [11]. During the pyrolysis, the organical ingredient of the biomass undergoing kind of severe chemical changes due to the thermal attaches [3], hence it led to promote the thermal cleavage of the material and released as the volatile or partially form a liquid oil with the rest of biochar. The pyrolysis product is highly influenced by the origin of the biomass and operating condition such as reaction temperature, residence time and heating rate program. Therefore, a deep understanding of the thermal behavior and its kinetic parameters are critical so that it is possible to design a reactor appropriately.

This paper presented the fundamental thermal characteristics and its kinetic parameters of the corn silk during the pyrolysis process through the thermogravimetric analyzer (TG). The kinetic parameters were evaluated at a single heating program of 10 °C/min by using the differential fitting model of Arrhenius.

## 2. Methods

### 2.1. *Material and properties*

The corn silk sample was gotten from Badas village, district of Kediri, East Java, Indonesia. The drying process of the raw material was performed by using the oven at 100 °C for 90 minutes. The dehydrated sample was ground and sieved to reach the mesh size of 60. The powder of corn silk then deposited in the tightly closed bottle. Prior to the TG test, the sample was characterized in relation to its chemical and physical properties, and the results were tabulated in Table 1.

### 2.2. *Thermogravimetric test*

To recognized the thermal degradation of the corn silk in relation to the temperature escalation, the thermogravimetric analyzer (METTLER TOLEDO TGA/DSC1) was occupied in the constant heating rate of 10 °C/min. To ensure the inert conditions during the pyrolysis process from room temperature till to 900 °C, the nitrogen continuously flowed into the chamber at a constant rate of 50 ml/min. The small sample of 11 mg was weighed into the crucible to minimize the effect of temperature gradient during thermal conversion. The computer which is working in synchronization with the furnace was recorded the mass loss of the sample in the course of the heating as a function of temperature and time. Subsequently, TG curve was achieved, and differential thermogravimetry (DTG) curve has resulted from the first derivative of the TG. In accordance with both TG-DTG curves, then thermal behavior and characteristic parameters of the corn silk pyrolysis were determined.

### 2.3. Kinetics model

The reaction rate of the solid in the course of heating can be modeled by using the Arrhenius equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = Ae^{\frac{-E}{RT}}f(\alpha) \quad (1)$$

in which

$t$  is the time (minute),

$k(T)$  is the constant of temperature-dependent rate,

$f(\alpha)$  is the function of conversion of temperature-independent,

$A$  is the pre-exponential factor ( $s^{-1}$ ),

$E$  is the activation energy (kJ/mol),

$R$  is the universal gas constant (kJ/mol K),

$T$  is the absolute reaction temperature (K).

The conversion ( $\alpha$ ), which represented the mass loss fraction of the sample material expressed as the following equation:

$$\alpha = 1 - \frac{m_t - m_f}{m_i - m_f} = \frac{m_i - m_t}{m_i - m_f} \quad (2)$$

where:

$m_i$  is the initial mass of the sample;

$m_t$  is the sample remaining mass at time  $t$ ;

$m_f$  is the final mass of the sample that refers to the end of the mass event of interest

For non-isothermal reaction, the change of temperature in connection with the time extension represented the rate of heating,  $dT/dt = \beta$ . Substituting Equation (1) with  $dt = dT/\beta$  and then by defining the  $n$ th order reaction model lead to non-isothermal expression as follow:

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} e^{\frac{-E}{RT}} dT \quad (3)$$

In accordance with Equation (3), subsequently, the kinetic parameters of the solid thermochemical conversion can be evaluated.

## 3. Result and Discussion

### 3.1. Thermal characteristics

The fundamentals properties of the corn silk sample as presented in Table 1 was adopted from Sumarli et al., [1]. The thermal degradation of the sample material as a function of temperature at a typical heating rate of 10 °C/min was depicted in the TG-DTG curve of Figure 1. The various stages could be taken place during the pyrolysis process. In this study, three stages of the corn silk degradation were determined, i.e., Stage I (dehydration zone), Stage II (main devolatilization zone) and Stage III (slow decomposition zone).

In the dehydration zone (Stage I), it is obviously known that at the temperature range of 65-135 °C the moisture content released rapidly and pronounced peak of DTG curve was noticed. This fast dehydration also indicated by declining line on TG curve due to a fair amount of moisture evaporated in line with increasing temperature. This declining line of the TG curve then followed by presenting a flat line at a temperature range of 135-154 °C, pointed out that moisture evaporation was completed.

In the main devolatilization zone (Stage II), the insignificant mass loss was encountered in the temperature range of 154-200 °C indicated by the undistinguished declining line of the TG curve. This

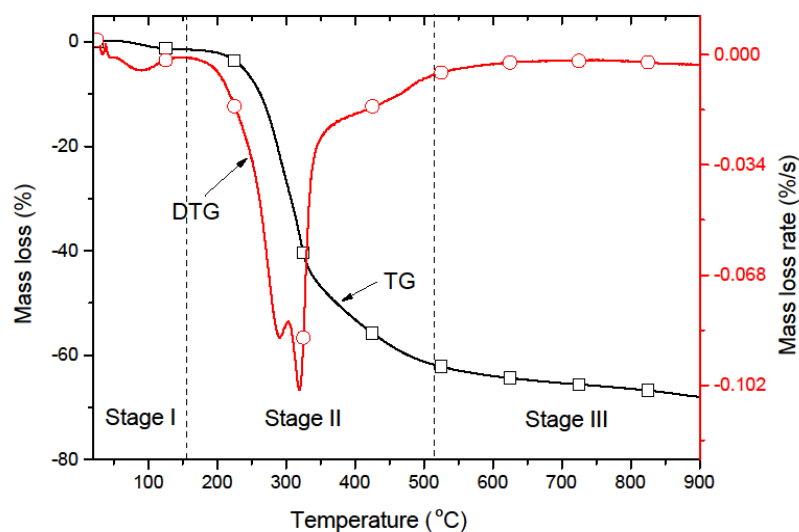
phenomenon was revealed that the corn silk material initially underwent a depolymerization process with the very small sample was decomposed. After that, a large amount of material was tremendously degraded through the complex thermochemical reaction in the temperature range of 200-370 °C, specified by the emergence of sharp slope on TG curve and very prominent basin of DTG curve. In this temperature range, the organic component of corn silk was decomposed and released to be volatile. This process continued till to 514 °C with a slight deceleration on declining of TG curve. It probably due to the degradation of the component which is hardly decomposed such as lignin. According to the DTG curve in Figure 1, it was encountered two peaks basin in Stage II where the first peak at 291 °C and the second one at 319 °C. The peak at low temperature was referring to the hemicellulose degradation whereas the peak at a higher temperature could be attributed to the cellulose decomposition. This result was in accordance with the result of Shen et al., [12].

Stage III was characterized by the presence of relatively flat of TG curve at a temperature range of 514-900 °C. The phenomenon in this stage was in correlation with slow decomposition lignin. Due to the thermal reactivity of lignin was lower than that of cellulose and hemicelluloses; hence lignin was decomposed in the large span of temperature [13].

**Table 1.** Chemical and physical properties of corn silk, adopted from Sumarli et al., [1]

Chemical elements		Physical properties		HHV (MJ/kg)
	(wt,%)		(wt,%)	
C	45.83 ± 4.01	Moisture	8.6 (ar)	19.50
O	46.43 ± 3.58	Volatile matter	72.2 (db)	
Mg	0.45 ± 0.30	Fixed carbon	22.4 (db)	
Al	0.44 ± 0.24	Ash	5.4 (db)	
Si	0.16 ± 0.15	Total sulfur	0.34 (db)	
P	1.26 ± 0.18			
Cl	0.99 ± 0.11			
K	3.53 ± 0.33			
Ca	0.31 ± 0.15			
S	0.60 ± 0.32			
ar: as received, db: dry basis				

ar: as received, db: dry basis



**Figure 1.** TG -DTG curves of corn silk pyrolysis at 10 °C/min

### 3.2. Evaluation of kinetic parameters

The evaluation of kinetic parameters was implemented on the main devolatilization zone (Stage II), in which thermal degradation of material have occurred massively. In accordance with TG-DTG curve, it could be determined the characteristic parameters which specified the pyrolysis of corn silk, here are onset temperature of reaction ( $T_o$ ), the burnout temperature ( $T_b$ ), the temperature in which material decomposed in the maximum rate ( $T_m$ ), the maximum reaction rate ( $M_m$ ) and the total mass loss at the end of the defined zone. These parameters were listed in Table 2.

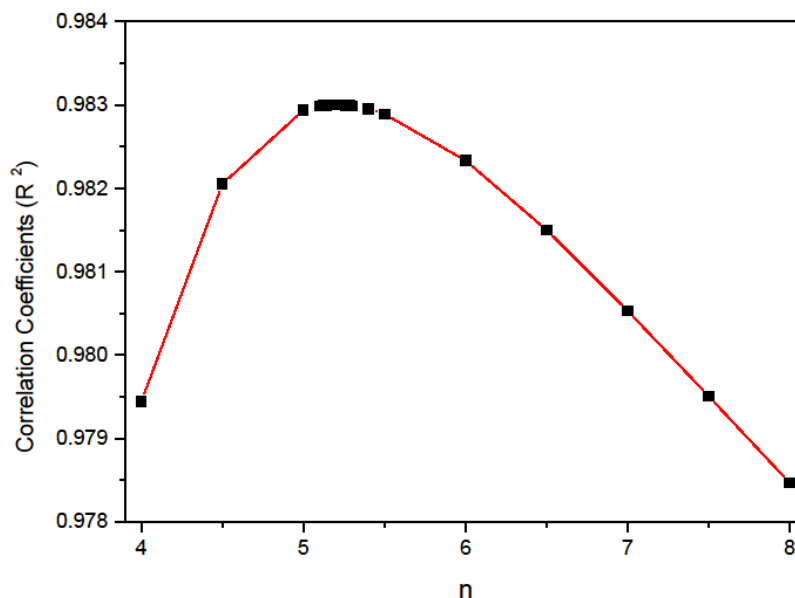
The pyrolysis reaction of corn silk was supposed as a particular reaction at a specific temperature region as a single step reaction of the  $n$ th order. Referring to this assumption then the expression for the pyrolysis reaction rate could be specified as in Equation (3). By taking the logarithm of Equation (3) and constructing some reordering, the Arrhenius equation for stating the reaction rate became a linear equation as follow:

$$\ln\left(\frac{d\alpha}{dT}\right) - n \ln(1 - \alpha) = \ln\left(\frac{A}{\beta}\right) - \frac{E}{RT} \quad (4)$$

Acikalin [14] had proposed the method for determining proper  $n$  value. Initially, any  $n$  values were selected then the plot of  $\ln(d\alpha/dT) - n \ln(1 - \alpha)$  versus  $(1/T)$  were drawn, resulted in a straight line with the related correlation coefficients ( $R^2$ ) and subsequently  $R^2 - n$  curve can be plotted. The peak of the  $R^2 - n$  curve represented the highest value of  $R^2$  and it associated with the most appropriate of the  $n$ . This most appropriate  $n$  value then was implemented to generate a final plot of  $\ln(d\alpha/dT) - n \ln(1 - \alpha)$  versus  $(1/T)$ . The activation energy and pre-exponential factor determined from the slope and intercept of this last plot.

**Table 2.** Characteristic parameters of corn silk pyrolysis at 10 °C/min.

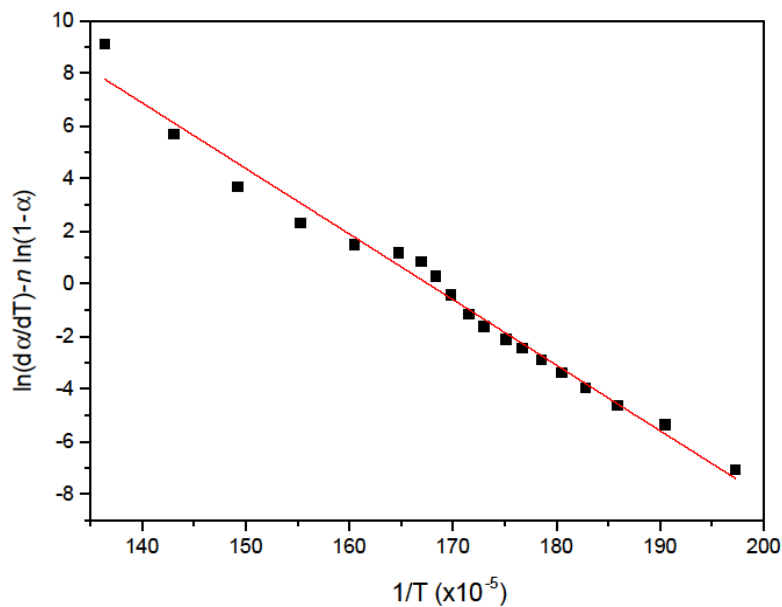
Characteristic parameters				
$T_o$ (°C)	$T_b$ (°C)	$T_m$ (°C)	$M_m$ (%/s)	Total mass loss (%)
154	514	319	0.103	60.31



**Figure 2.** The  $R^2 - n$  curve resulted from the Arrhenius method.

By adopting the aforementioned method, any  $n$  values were selected in the range of 4-8, then it was used for computing the  $\ln(d\alpha/dT) - n \ln(1 - \alpha)$  with the conversion ( $\alpha$ ) extended between 0.05-0.95. The  $\ln(d\alpha/dT) - n \ln(1 - \alpha)$  versus  $(1/T)$  at every  $n$  value was plotted to generate  $R^2$  and afterward  $R^2 - n$  curve was drawn as depicted in Figure 2. The peak of  $R^2 - n$  curve indicated the highest  $R^2$  (0.983) in correlation with the most proper  $n$  value of 5.2. According to this most proper  $n$  value then the final plot of  $\ln(d\alpha/dT) - n \ln(1 - \alpha)$  versus  $(1/T)$  was plotted as shown in Figure 3. The activation energy and pre-exponential factor of the main devolatilization zone of corn silk pyrolysis were tabulated in Table 3.

As shown in Table 3, it was recognized that activation energy in main devolatilization zone of the corn silk pyrolysis was 207.37 kJ/mol. This value was comparable with agro-industrial waste, in which their activation energy for the active pyrolysis stage in the range of 133–275 kJ/mol [15]. Comparing kinetic parameters of corn silk pyrolysis with the other part of corn plants, it was known that this result of activation energy was higher than that of corn stover pyrolysis that was between 58-63 kJ/mol [16] and in the range of activation energy of corn stalk pyrolysis that varied from 148 to 473 kJ/mol [17].



**Figure 3.** Linear regression of the plot  $\ln(d\alpha/dT) - n \ln(1 - \alpha)$  versus  $(1/T)$

**Table 3.** The kinetics parameters of the devolatilization zone of corn silk

$\beta$ (°C/min)	Trendline equation	$R^2$	Kinetics parameters		
			$E$ (kJ/mol)	$\log A$ (1/min)	$n$
10	$y = -24942.37x + 41.799$	0.983	207.37	19.15	5.2

#### 4. Conclusions

From the thermogravimetric analysis of the corn silk pyrolysis, it has been recognized the three stages decomposition process during a thermal attack from room temperature til to 900 °C. The moisture was released firstly, then an organical component of corn silk degraded tremendously in the second stage

(main devolatilization zone), and the last was slowly decomposition of the solid residual. The kinetic parameters resulted from the Arrhenius method were indicated that the possible mechanism could be modeled as a function with  $f(\alpha) = (1 - \alpha)^{5.2}$ ;  $\log A = 19.15/\text{min}$  and  $E = 207.37 \text{ kJ/mol}$ .

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