Pyrolysis of Corn Residues: Kinetic Analysis using Discrete Distributed Activation Energy Model

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Abstract. Agro-residues are usually generated in large amount. These biomass materials may be utilized as renewable energy source via thermochemical conversion processes. Knowledge on kinetic of thermal decomposition behavior of biomass is important in reactor design and thermal process optimization. In this work, thermogravimetric (TG) data (35 to 900°C, at heating rates of 5 to 50°C/min) from pyrolysis of corn residues was analyzed using discrete distributed activation energy model (DAEM). Prediction accuracy of the simulated data was verified by comparing experimental with calculated data of conversion at selected heating rates. Kinetic parameters including activation energy and pre-exponential factor obtained from this method were found to give correct conversion curves for different heating rates simultaneously with correlation coefficients greater than 0.99, within the ranges considered. According to the discrete DAEM, variation in activation energy with conversion implied changes in mechanism during pyrolysis process. The activation energies were observed to be in the range of 100 – 120 and 80 – 180 KJ/mol for the macro-TG and typical TG analysers, respectively.

1. Introduction
Corn is a major economic crop in the world. It is widely planted for human food and animal feed. After harvesting, corn residues are usually left as waste. Some might be disposed of by burning openly in the fields, leading to high emissions of gaseous and particulate pollutants to atmospheric environment [1]. These agro-residues should be utilized for renewable energy, in which potentially 65,000 TJ per year was estimated for Thailand [2], [3].

Pyrolysis is a thermochemical process which converts raw biomass into valuable fuels. It is a promising method in utilization of biomass for renewable energy. By pyrolysis, the biomass material can be broken down to generate volatile gases, liquid products and solid char [4]. These products can be used as fuel or a source of useful chemicals [5]. It is therefore useful to understand the pyrolytic mechanism and its transformation process for subsequent generation of fuels, chemicals, and materials. Kinetic analysis is essential for engineering applications in views of design, building up, control and optimization of the thermal process. Kinetic parameters of reaction are necessary for characterizing and accurately predicting the thermal behaviours.

Kinetics of pyrolysis is usually investigated by a thermogravimetric (TG) analyser, which is among the most common and powerful instruments to study thermal behaviours of a few milligram of sample in the form of powder. It has been shown that pyrolysis is dependent on the biomass main components i.e. hemicellulose, cellulose, and lignin [6]. Thermal decomposition is strictly controlled by chemical
kinetics. However, at a commercial scale of pyrolysis plant, big particle size and large amount of biomass are used, the pyrolytic reaction is limited by transport phenomena [7].

In TG and macro-TG analysis experiments, the pyrolytic behaviours (mass loss and mass loss rate) are measured as functions of temperature and time in an inert atmosphere [8]. By using the experiments data, many mathematical methods such as model-fitting and model-free (iso-conversional model) were used [9–12]. However, these methods are still rather limited in applying to the kinetics of biomass pyrolysis because of the high heterogeneity such as catalysis of alkalis and secondary reactions of the pyrolysis process [13]. Distributed activation energy model (DAEM) is similar to model-fitting and shows good prediction for whole conversion range. The DAEM assumes that infinite irreversible independent parallel reactions occur simultaneously during pyrolysis. Such reactions share a constant pre-exponential factor (A) but the activation energy (E) is further assumed as a continuous distribution such as Gaussian distribution [14]–[16]. The infinite reactions are simplified by discretizing it to many but finite reactions as n parallel first-order reactions, known as discrete DAEM. Each of these reactions has its own activation energy and pre-exponential factor. Among these methods, the discrete DAEM is straightforward in making calculation and giving accurate prediction [17]–[20].

In the present study, pyrolysis of corn residues was investigated. The biomass residues in powdered form were tested in a typical TG analyser, while those in pelletized form were conducted in a macro-TG analyser. The kinetic behaviours of corn residue pyrolysis were evaluated using the discrete DAEM and the accuracy of predictions was examined.

2. Materials and methods

2.1. Experimental

In this study, corn residues were obtained from a local corn field in Chiang Mai, Thailand. The raw material was dried naturally. One part of the sample was then crushed and sieved with 120 mesh. The other part was densified in a pelleting machine to become 8 mm in diameter and 25 mm in length. Both samples were then stored in an airtight plastic bag at room temperature prior to experimentation. The powdered sample was pyrolyzed in a Mettler Toledo TG analyser model 851e with 0.1 μg resolution. An initial weight of about 10 mg was placed in an alumina crucible and then heated from room to the final temperature of 900°C at three different heating rates of 10, 30, and 50°C/min under high purity nitrogen with a flow rate of 20 mL/min. The pelletized sample with 40 g each was pyrolyzed in a macro TG analysis setup with 0.01 mg resolution, shown in Figure 1. High purity nitrogen at a flow rate of 5 L/min was used as a carrier gas. The pellet was loaded in a basket and then heated from room to the final temperature of 900°C at three different heating rates of 5, 10, and 15°C/min. The data of weight loss and temperature evolution were monitored and recorded continuously. Experiments were repeated in triplicate for all conditions.

2.2. Kinetic analysis

2.2.1. Distributed activation energy model

Kinetic of solid-state pyrolysis in non-isothermal conditions at linear heating rate can be explained using Arrhenius equation [13]. The differential form of the reaction rate (r) can be expressed as follows:

\[ r = \frac{d\alpha}{dT} = -\frac{A}{\phi} \exp\left(-\frac{E}{RT}\right)f(\alpha) \] (1)

where \( \alpha \) is the conversion, \( T \) is the absolute temperature (K), \( A \) is the pre-exponential factor (1/s), \( E \) is the activation energy (kJ/mol), \( R \) is the universal gas constant (8.314 J/mol·K), \( \phi \) is the linear heating rate (K/s), \( f(\alpha) \) is a reaction model and its independent variable, \( \alpha \), which can be defined as:

\[ \alpha = \frac{m_0 - m(t)}{m_0 - m_f} = \frac{v(t)}{v_0} \] (2)
where $m_0$ is the initial mass, $m(t)$ is the instant mass at any time $t$, and $m_f$ is the final mass of the sample remaining after the pyrolysis reaction. $v(t)$ and $v_0$ are the mass of volatiles at any time and the initial mass of volatiles. Integral form of equation (1) is given as:

$$g(\alpha) = \int_0^\alpha f(\alpha) = \frac{A}{\phi \beta} \exp \left( - \frac{E}{RT} \right) dT = - \frac{A}{\phi} \psi(E, T)$$

which $\psi(E, T)$ is a temperature integral without an analytical solution. Replacing $f(\alpha)$ by first-order reaction, $f(\alpha) = 1-\alpha$, equation (3) can be rewritten in the following form:

$$1 - \alpha = \exp \left[ - \frac{A}{\phi} \psi(E, T) \right]$$

DAEM assumes that infinite irreversible independent parallel reactions occur simultaneously during pyrolysis [21]. All the reactions share a constant pre-exponential factor, and the activation energy is further assumed as a continuous distribution [22]. According to equation (4), the conversion function of DAEM over the entire temperature range becomes:

$$x = 1 - \alpha = \int_0^\infty \exp \left[ - \frac{A}{\phi} \psi(E, T) \right] f(E) dE$$

where $x$ represents the remaining conversion, $f(E)$ is the probability density function (PDF) of the activation energy distribution. Several PDFs such as Gaussian, Weibull, Gamma and others have been reported [23].

2.2.2. Discrete DAEM

The infinite reaction is simplified by discretizing it to finite reactions as $n$ parallel first-order reactions. Each of these reactions has its own activation energy and pre-exponential factor [24]. For the pyrolysis of biomass under non-isothermal conditions, biomass decomposes via several such first-order reactions:

$$\frac{dm_i}{dT} = - \frac{A_i}{\phi_j} \exp \left( - \frac{E_i}{RT} \right) m_i$$

where $m_i$, $A_i$, and $E_i$ are the instantaneous mass, pre-exponential factor, and activation energy of $i$-th reaction, respectively. The integral form of equation (6) is:
\[ M_i = M_{i,0} \exp \left[ -\frac{A_i}{\phi_j} \Psi(E_i, T) \right] \]  

(7)

where \( M_i \) is the mass of \( i \)-th reaction, \( M_{i,0} \) is the initial value of \( M_i \). From equations (6) and (7), the discrete DAEM can be expressed as:

\[
x = \frac{\sum_{i=1}^{n} M_i}{\sum_{i=1}^{n} M_{i,0}} - \frac{\sum_{i=1}^{n} w_{\text{char},i}}{\sum_{i=1}^{n} f_{i,0}} \exp \left[ -\frac{A_i}{\phi_j} \Psi(E_i, T_i) \right] 
\]

(8)

where \( f_{i,0} \) is the initial mass fraction of \( i \)-th reaction, \( T_i \) and \( w_{\text{char},i} \) are the corresponding temperature and char mass of \( i \)-th reaction, respectively. Subscripts run from 1 to \( n \) for \( i \) and 1 to 2 which \( j = 1 \) and 2 means \( \phi = 5 \) and 10°C/min, respectively. If the values of \( E_i \) and \( A_i \) are known, the unknown, \( f_{i,0} \), in equation (8) will be solved by using linearly equation (9) as:

\[
x = \begin{bmatrix}
\Psi_1(E_0, T_0) & \Psi_2(E_0, T_0) & \ldots & \Psi_n(E_0, T_0) & 1 \\
\Psi_1(E_1, T_1) & \Psi_2(E_1, T_1) & \ldots & \Psi_n(E_1, T_1) & 1 \\
\vdots & \vdots & \ddots & \vdots & \vdots \\
\Psi_1(E_n, T_n) & \Psi_2(E_n, T_n) & \ldots & \Psi_n(E_n, T_n) & 1 \\
\end{bmatrix}
f_{i,0} 
\]

(9)

where \( T_0 \) is the initial temperature of biomass and \( \Psi(E_i, T) \) is the double exponential term:

\[
\Psi(E_i, T) = \exp \left[ -\frac{A_i}{\phi_j} \Psi(E_i, T_i) \right] 
\]

(10)

To calculate the initial mass fractions decomposing in each reaction \( i \), a set of reactions must be generated first with a known value of \( E \) and \( A \) by assuming that there will be a single reaction dominating at the same \( x \) under two different heating rates (e.g. \( \phi_1 \) and \( \phi_2 \)). And one characteristic \( x \) represents the only reaction taking place at this \( x \). Then, \( f_{i,0}(\phi_1, T_1) = f_{i,0}(\phi_2, T_2) \) at two particular temperature, \( T_1 \) and \( T_2 \) so that the \( E_i \) can be calculated by:

\[
\Psi_i(E_1, T_1) = \Psi_i(E_2, T_2) 
\]

(11)

To determine the pre-exponential factor, \( A_i \), once \( E_i \) already known from equation (11) is used with the assumption of \( \Psi_i = e^t \approx 36.86\% \) which a value of \( \Psi_i = e^t \) means that the conversion of a single first-order reaction would reach a maximum in the decomposition rate [17]. This allows \( A_i \) to be calculated from the double exponential term as equation (12) below:

\[
\ln(\Psi_i) = -1 = \frac{A_i}{\phi_i} \left[ T_0 \exp \left( -\frac{E_i}{RT_0} \right) - \frac{E_i}{R} \int_{u_0}^{\infty} \frac{\exp(-u)}{u} du - T_2 \exp \left( -\frac{E_i}{RT_2} \right) + \frac{E_i}{R} \int_{u_2}^{\infty} \frac{\exp(-u)}{u} du \right] 
\]

(12)

where \( u_i = E_i/(RT_i) \). When \( A_i \) and \( E_i \) are known, the initial mass fraction, \( f_{i,0} \), in equation (9) can, then, be solved by non-negative linear least squares method which is the lsqlinnonneg algorithm in Matlab software version 7.11.0; R2010b and the results must be guaranteed via the following constraints.
\[
\begin{align*}
\begin{cases}
f_{i,0} \in [1] \\
\sum_{i=1}^{n} f_{i,0} = 1
\end{cases}
\end{align*}
\]

(13)

3. Results and discussion

3.1. Thermal degradation characteristics

TG and derivative TG curves are shown in Figures 2a and b for the macro- and typical TG analysers. Both sets of curves showed similar patterns. Higher heating rates appeared to delay devolatilization to higher temperatures. For the same heating rate, temperature lagging effect was more apparent for pyrolysis in the macro TG than in the typical TG analysers. This was pointed out by Becidan et al. [7] that for the same degree of conversion, the macro-TG analyser took longer time, compared to typical TG analyser. It was also reported that the pyrolysis of wood occurred faster in micro TG than in macro-TG analysers because of the heat- and mass-transfer limitations of the larger samples used in the macro-TG analyser causing a lag in the temperature evolution of the biomass samples [25].

![Figure 2](image)

**Figure 2.** Remaining conversion and reaction rate for devolatilization of corn residues at different heating rates in (a) the macro-TG and (b) typical TG analysers.

3.2. Discrete DAEM kinetics

3.2.1. Modelling and simulation results

According to the discrete DAEM, each remaining conversion represents one first-order reaction which has a characteristic activation energy and pre-exponential factor. In this work, 39 parallel first-order reactions were assumed. From the discrete DAEM, three decomposition curves were obtained at 10, 30 and 50°C/min for the typical TG data and other three curves were obtained at 5, 10 and 15°C/min for the modified macro-TG data. Effect of temperature lag or delayed conversion on pyrolysis was taken into account when applying the discrete DAEM to the macro-TG data by shifting experimental TG curves to lower temperatures. The kinetic parameters obtained from the discrete DAEM were used in predicting pyrolysis behaviour of corn residue pellets. Results of simulated data from the pyrolysis of corn residues were subsequently compared with the corresponding experimental data, as shown in Figures 3a and b. It can be seen that the simulated data were closely similar to the experimental data. Correlation coefficients from regression analyses between the simulated and experimental data were evaluated to be greater than 0.99. The model was shown to be greatly accurate and effective in predicting pyrolysis behavior of corn residues.
Figure 3. Comparison of simulated and experimental date at three different heating rates for (a) macro-TG and (b) TG analysers.

3.2.2. Kinetic parameters
Figures 4a and b show the kinetic parameters (activation energy, pre-exponential factor and initial mass fraction) derived from the macro-TG and typical TG experimental data. The activation energy was found to vary with conversion. For pyrolysis in the macro-TGA, as $x$ increased, $E$ was initially decreased from about 220 to 110 kJ/mol, changed slightly, and then increased to 190 kJ/mol towards the end of devolatilization step. The opposite trend was observed for pyrolysis in the typical TGA, whose $E$ was varied between 40 to 180 kJ/mol. Variations of pre-exponential factor with conversion were similar to those of the activation energy. It should be noted that variation of activation energy with conversion can indicate change in decomposition mechanisms [20]. Although 39 reactions were assumed for the discrete DAEM, only several reactions contributed to the pyrolysis process, as can be seen from significant initial mass fractions shown in Figures 4a and b.

Figure 4. Discrete DAEM kinetic parameters (activation energy, pre-exponential factor and initial mass fraction) from (a) macro-TG and (b)TG analysers.

4. Concluding remark
Pyrolysis of corn residues in typical and macro-TG analysers was investigated. The thermal degradation behaviours were found to differ between the chemical kinetically controlled and the physically influenced reactions in typical and the macro-TG analysers, respectively. For a given conversion, effect of temperature lag was observed in the macro-TG cases, resulting from mass and heat transport limitation. Pyrolysis kinetics were also evaluated using the discrete DAEM. Simplification of the prediction process of thermal degradation of corn residues and good fits to the
experimental data were obtained. The kinetic parameters derived from the discrete DAEM were found to simulate correctly the whole conversion curves simultaneously for different heating rates with high correlation coefficients.

5. References

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