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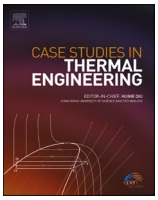

Kinetic and thermodynamic analyses for pyrolysis of hemp hurds using discrete distributed activation energy model

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ABSTRACT

In many counties, hemp is becoming a high-valued economic crop. Post-processing, more than 65% w/w of its starting material becomes waste. Herein, pyrolysis of hemp hurds/residues was investigated under low (10–50 °C/min) and intermediate (100–150 °C/min) heating rates using a discrete distributed activation energy model (DAEM). Thermochemical decomposition of hemp hurds occurred in three stages: drying, active pyrolysis, and char formation, accounting for 70–80% w/w overall weight loss. With the discrete DAEM, the model can be utilized for predicting pyrolysis behaviors of hemp hurds accurately with correlation coefficient of over 0.99. Different reaction mechanisms appeared between the low and intermediate heating rates with 60 and 25 parallel first-order pyrolytic reactions detected, respectively. Under low heating rates, the pyrolysis showed high reactivity. The activation energy (E) and enthalpy change (ΔH) varied within 240–320 kJ/mol. The Gibbs free energy (ΔG) was 120–200 kJ/mol. The entropy change (ΔS) was 120–300 J/mol•K. Under intermediate heating rates, the reactions were close to thermodynamic equilibrium and stability. The E and ΔH fluctuated from 80 to 250 kJ/mol. The ΔG was within 160–200 kJ/mol. The ΔS was between −100 and 100 J/mol•K.

1. Introduction

Global energy demand remains high even with the COVID-19 pandemic. Production of energy from fossil fuels has a negative impact on environmental health wellbeing and ecological balance [1]. Many countries are requested to achieve challenging emissions reductions targets that will result in global net zero by 2050 and keep 1.5 °C within reach. To achieve these targets, investment in renewables is one of the solutions. Among renewable energy resources, biomass will play a vital role [2]. Agricultural residues are lignocellulosic biomass considered to be major feedstocks for biorefineries [3]. In many counties, hemp, *Cannabis sativa* L., is becoming a high-valued economic crop. It is a herbaceous plant grown up under different climatic conditions [4]. Products from hemp include food (hemp proteins) [5] and pharmacy [6]. However, after processing two-thirds of starting raw materials become wastes, which are usually discarded or burned. Alternatively, hemp hurds/residues may be used as fuel, as they contain hemicellulose (~30% w/w) and cellulose (~45% w/w) [7]. Pyrolysis is a promising technology for converting hemp hurds into high-value products: biochar and

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bio-oils [8,9].

Determination of kinetic and thermodynamic parameters for pyrolysis of a specific feedstock is essential for the design, optimization, and operation of the pyrolysis system [8,10]. For kinetics of biomass pyrolysis, Onsree et al. [8] studied kinetics of corn residue pellets and eucalyptus wood ships pyrolyzed with heating rates of 5–15 °C/min using Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO) methods. They demonstrated that the kinetic parameters were a function of feedstock conversions. A discrete DAEM was also used to analyze kinetic parameters of pyrolysis of corn residues with high prediction accuracy [10]. It can be seen that, by varying kinetic parameters, different biomass materials would have different pyrolysis behaviors. For thermodynamic analysis of biomass pyrolysis, Singh et al. [11] investigated thermodynamic properties for pyrolysis of banana leaves at low heating rates of 10–30 °C/min and found that ΔH, ΔG, and ΔS fluctuated when the pyrolysis process proceeded.

To the authors' knowledge, very few studies on pyrolysis of hemp residues were reported, and conducted only at relatively low heating rates without considering thermodynamic properties. DAEM was rarely used in analyzing pyrolysis of hemp residues. Therefore, the current work aims to analyze kinetic and thermodynamic properties of pyrolysis of hemp hurds through the use of a discrete DAEM technique. Pyrolysis of hemp hurds was carried out from room temperature to 1000 °C at low (10, 25, and 50 °C/min) and intermediate (100, 125, and 150 °C/min) heating rates. Decomposition of hemp hurds during pyrolysis was characterized and discussed. By the discrete DAEM, the accuracy of the model for predicting pyrolysis behaviors of hemp hurds was evaluated. Effects of different heating rate ranges on kinetic and thermodynamic properties of pyrolysis of hemp hurds were discussed. Information on kinetic and thermodynamic parameters is crucial for designing a pyrolysis reactor for hemp hurds, especially in large-scale production of biochar.

2. Materials and methods

2.1. Thermal decomposition experiment

Hemp hurds were collected from rural Chiang Mai, Thailand. They were cleaned to remove dirt and dried under sunlight. The dried sample was ground and sieved to about 0.1 mm. The sample was then sealed in Ziploc bags and kept at room temperature until analyzed. Table 1 presents properties of the biomass sample. Thermal decomposition of the samples was investigated up to 1000 °C with two different ranges of heating. Low heating rates of 10, 25, and 50 °C/min were performed with a PerkinElmer simultaneous thermal analyzer (STA8000 model). Intermediate heating rates of 100, 125, and 150 °C/min were reached by a thermogravimetric analyzer (Mettler Toledo). Nitrogen was applied at fixed flow rates of 20 and 60 mL/min for low and intermediate heating rates, respectively. Mass losses were recorded. All test conditions were repeated at least three times to ensure reproducibility which was found, in terms of standard error of mean, to be within 5% of its average.

2.2. Kinetic analysis

One-step global reaction is applied for modeling biomass pyrolysis kinetics. Conversions, $\alpha = (m_0 - m_t)/(m_0 - m_\infty)$, where m_0, m_t, and m_∞ are the initial, any time t, and final mass of the sample before, during and after pyrolysis, respectively. The kinetics of biomass pyrolysis can be explained as

$$d\alpha / dt = kf(\alpha) \tag{1}$$

where k is the reaction constant, which can be represented by Arrhenius' equation, and $f(\alpha)$ is a function of biomass conversions [12]. Integrating Equation (1) provides

$$g(\alpha) = \int \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int \exp\left(\frac{-E}{RT}\right) dT \tag{2}$$

where A is the preexponential factor (Hz), E is the activation energy (J/mol), R is the universal gas constant (8.314 J/mol•K), T is the

Table 1
Physico- and biochemical properties of the hemp hurd sample.

Properties[a]	Analysis	Value	Unit
C	Ultimate analysis, ASTM D3176	45.1	% w/w
H		6.0	% w/w
N		0.5	% w/w
O		45.7	% w/w
Moisture	Proximate analysis, ASTM D7582	9.6	% w/w
Volatile matter		71.8	% w/w
Fixed carbon		16.0	% w/w
Ash		2.6	% w/w
Cellulose	Detergent method, AOAC 1998	61.7	% w/w
Hemicellulose		20.6	% w/w
Lignin		10.1	% w/w
Organic extractives and inorganic minerals		7.6	% w/w
Higher heating value	Bomb calorimetry, ASTM D5865	3847.4	kcal/kg

[a] Note that CHNO and heating value were based on dry basis, while the others were on as received basis.

absolute temperature (K), and β is a heating rate (°C/s).

A discrete DAEM assumes that many parallel first-order reactions, related to different chemical groups in raw biomass, take place simultaneously during biomass pyrolysis [10]. Each reaction i has its own activation energy (E_i) and pre-exponential factor (A_i). From Equation (2), the function of conversions for the discrete DAEM over the entire temperature range is

$$x = 1 - \alpha = \sum_{i=1}^{n} f_{i,0} \exp\left(-\frac{A_i}{\beta_j} \psi(E_i, T_i) \right) \tag{3}$$

where $f_{i,0}$ is the initial mass fraction of reaction i and $\psi(E,T) = \int \exp\left(\frac{-E}{RT}\right) dT$ is a temperature integral (without an analytical solution) [10]. The value E of each reaction i can be calculated from $\psi(E_1, T_1) = \psi(E_2, T_2)$ by assuming that the same reaction should occur at a single value of x under different heating rates (e.g., β_1 and β_2). Then, the value A_i can be determined as follows:

$$\ln \ \Psi_i = -1 = \frac{A_i}{\beta_1} \left[T_0 \exp\left(-\frac{E_i}{RT_0} \right) - \frac{E_i}{R} \int_{u_0}^{\infty} \frac{\exp(-u)}{u} du - T_2 \exp\left(-\frac{E_i}{RT_2} \right) + \frac{E_i}{R} \int_{u_2}^{\infty} \frac{\exp(-u)}{u} du \right] \tag{4}$$

where $u = \frac{E}{RT}$ and T_0 is the initial temperature of the pyrolyzed sample (K). Using an assumption of $\ln \ \Psi_i = -1$ refers to that the conversion of reaction i would maximize the rate of thermochemical decomposition [12]. Once E_i and A_i are known, the value $f_{i,\,0}$ can be calculated from

$$x = \begin{bmatrix} \Psi_1(E_0, T_0) & \Psi_2(E_0, T_0) & \cdots & \Psi_{n-1}(E_0, T_0) & 1 \\ \Psi_1(E_1, T_1) & \Psi_2(E_1, T_1) & \cdots & \Psi_{n-1}(E_1, T_1) & 1 \\ \Psi_1(E_2, T_2) & \Psi_2(E_2, T_2) & \ldots & \Psi_{n-1}(E_2, T_2) & 1 \\ \vdots & \vdots & \ddots & \vdots & 1 \end{bmatrix} \times \begin{bmatrix} f_{1,0} \\ f_{2,0} \\ f_{3,0} \\ \vdots \end{bmatrix} \tag{5}$$

where $\Psi(E_i, T_i) = exp\left(-\frac{A}{\beta} \psi(E_i, T_i) \right)$ is the double exponential term. The resulting $f_{i,\,0}$ must be guaranteed with the following constraints: $f_{i,\,0} \in (0, 1)$ and $\sum f_{i,\,0} = 1$.

2.3. Thermodynamic analysis

From kinetic parameters obtained, thermodynamic properties for biomass pyrolysis can be calculated as follows [13]:

$$\Delta H_i = E_i - RT_i \tag{6}$$

$$\Delta G_i = E_i + RT_m ln\left(\frac{k_b T_m}{hA_i} \right) \tag{7}$$

$$\Delta S_i = (\Delta H_i - \Delta G_i) / T_m \tag{8}$$

where T_m is the temperature at the maximum value of $d\alpha/dt$, k_b is Boltzmann's constant (1.381×10^{-23} J/K), and h is Plank's constant (6.626×10^{-34} J s). Enthalpy change, ΔH, denotes the amount of heat evolved or absorbed in a reaction. It is an energy difference between the activated complex and the reagent. Gibbs free energy difference, ΔG, is the available energy of the process proceeding reactions. Entropy change, ΔS, indicates the degree of disorder in a process. It is also an indication of the spontaneity of the process. A process with a small value of ΔS has less reactivity than others with a higher value of ΔS.

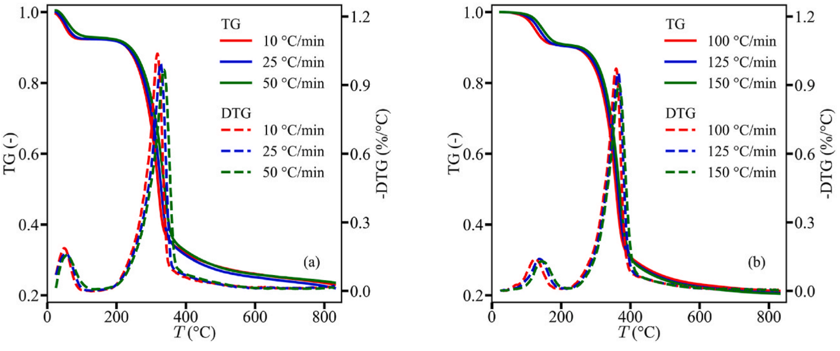

Fig. 1. TG and DTG curves of hemp hurds pyrolyzed at (a) low and (b) intermediate heating rates.

3. Results and discussion

3.1. Thermochemical decomposition characteristics

Fig. 1 illustrates TG and DTG curves of hemp hurds pyrolyzed at low and intermediate heating rates. Similar patterns of TG and DTG curves in both ranges of heating rate were evident. The DTG curves comprise one small peak, one pronounced peak, and one long tailing, referring to different reactions taking place during pyrolysis of hemp hurds, evaporation of physical water in the sample, devolatilization (active pyrolysis), and carbonization or passive pyrolysis [8,12]. An increase in heating rates not only affected the decomposition rates but also caused the shifting of TG and DTG curves to higher temperatures. This was because a higher heating rate causes the lagging of heat and mass transfer [8]. The main pyrolytic reaction occurred within 200–380 °C for the low heating rates and within 220–400 °C for the intermediate heating rates. The datasets in these ranges were considered for calculating kinetic parameters of the discrete DAEM. It accounted for approximately 60–70% in TG curves.

3.2. Modeling and validation

Two datasets at different heating rates are required to calculate the kinetic parameters. In the present work, the datasets from 10 to 50 °C/min were applied for a low range, while those from 100 to 150 °C/min were used for an intermediate range. Fig. 2 depicts theoretical (simulation) decomposition data in comparison with experimental data measured at the corresponding heating rates, using kinetic parameters obtained from the discrete DAEM. It can be seen that the model perfectly fitted the data used at 15, 50, 100, and 150 °C/min and accurately predicted the pyrolysis behavior of hemp hurd samples at 25 and 125 °C/min. By regression analysis, the correlation coefficients were over 0.99. The accuracy of the discrete DAEM for pyrolysis of hemp hurds was comparable to other types of biomass pyrolysis [10,12,14].

3.3. Discrete DAEM kinetic parameters

Fig. 3 shows the kinetic parameters (E_i, A_i, and $f_{i,0}$) calculated by the discrete DAEM for two ranges of low and intermediate heating rates. For both ranges, E_i and A_i appeared to have a similar trend as the x increased. Their values decreased with increasing x to 0.2. The E_i and A_i values were then increased, when x was increased from 0.2 to 0.92 for the low heating rates and from 0.2 to 0.7 for the intermediate heating rates. After that, the E_i and A_i dropped with increasing x. For low heating rates, the E_i values were between 240 and 320 kJ/mol, and the A_i values were within 10^{18}–10^{32} Hz. For intermediate heating rates, the E_i values varied from 80 to 250 kJ/mol, and the A_i values fluctuated from 10^{8} to 10^{20} Hz.

An interesting phenomenon was observed that 60 parallel first-order reactions ($i = 60$) were detected for pyrolysis of hemp hurds under low heating rates, compared to only 25 reactions ($i = 25$) in the intermediate heating rates. For low heating rates, the most dominating reactions occurred after x was higher than 0.4, in which the highest $f_{i,0}$ value was slightly over 0.1 at x of about 0.55. For intermediate heating rates, the dominating reactions took place at x between 0.3 and 0.5, and the maximum $f_{i,0}$ value was about 0.2 at x of 0.45. Similar to the E_i and A_i, there appeared to have three ranges in the $f_{i,0}$ for both heating ranges. Based on those kinetic parameters obtained from the discrete DAEM, pyrolytic behavior of hemp hurds in the low heating rate zone was clearly different from that in the intermediate heating rates. Many different reactions occurred during pyrolysis of hemp hurds under low heating rates. Meanwhile, those reactions would be combined to be other dominating reactions found under intermediate heating rates. These two pyrolysis processes underwent different heat and mass transfers. The hemp hurd sample pyrolyzed under low heating rates would have

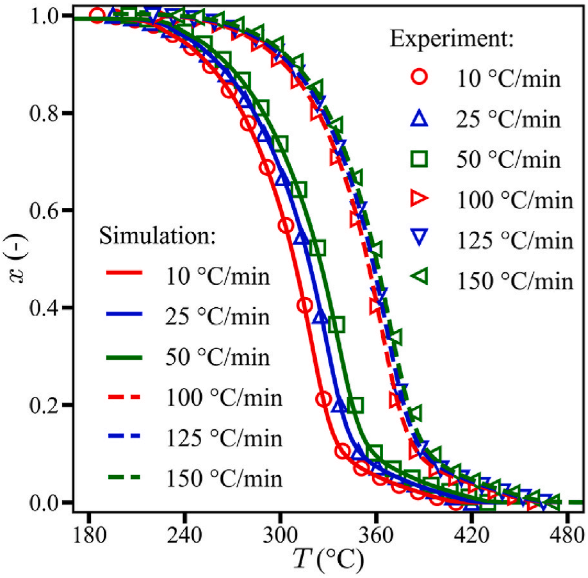

Fig. 2. Comparison of experimental data and simulation using the discrete DAEM.

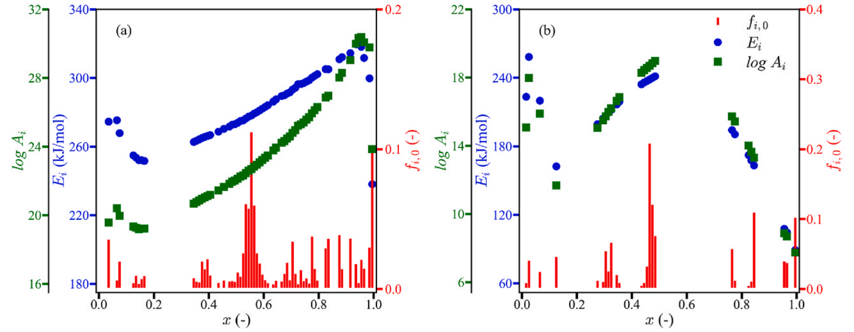

Fig. 3. Kinetic parameters (activation energy, pre-exponential factor, and initial mass fraction) from the discrete DAEM at two ranges of (a) low and (b) intermediate heating rates.

a more uniform temperature distribution [8].

Generally, pyrolysis of lignocellulosic biomass is affected by decomposition of hemicellulose, cellulose, and lignin. Hemicellulose decomposes effectively at low temperatures of 220–315 °C, while the others do well at higher temperatures [15]. Therefore, for low heating rates, pyrolysis of hemp hurds at x less than 0.2 would refer to decomposition of chemicals/elementals ($i = 1$–8) in lignin, and at x between 0.2 and 1.0, it became a combined decomposition of chemical groups ($i = 9$–60) in hemicellulose and cellulose. On the contrary, for intermediate heating rates, chemical groups and/or elementals in hemicellulose, cellulose, and lignin were decomposed individually. Chemicals/elementals of lignin ($i = 1$–4), cellulose ($i = 5$–17), and hemicellulose ($i = 18$–25) were decomposed at $x < 0.2$, 0.2–0.7, and >0.7, respectively.

3.4. Thermodynamic properties

Fig. 4 illustrates thermodynamic properties for pyrolysis of hemp hurds under different ranges of heating rates. Note that, in the current work, T_m at heating rates of 25 and 125 °C/min was used as a representative in calculating ΔG_i and ΔS_i for low and intermediate heating rate zones, respectively. ΔH_i and ΔS_i values had a similar trend to the kinetic E_i value, while ΔG_i appeared to have decreased values with increasing x. ΔH refers to the amount of heat changed during a process progressed under constant pressure. For low heating rates in Fig. 4 (a), ΔH_i was increased significantly from about 240 to 320 kJ/mol, when x changed from 1.0 to 0.9. Then, it gradually dropped to slightly over 240 kJ/mol over x of 0.2–0.9. After that ($x < 0.2$), the ΔH_i was increased and ended with 270 kJ/mol. Similarly, for intermediate heating rates in Fig. 4 (b), ΔH_i was increased from about 80 to 200 kJ/mol when x changed from 1.0 to about 0.7. It dropped to around 150 kJ/mol when x decreased to 0.2. Before the end of the process, the ΔH_i jumped to over 240 kJ/mol. These indicate that the active pyrolysis stage of hemp hurds was endothermic for both ranges of heating rates. On the whole, when pyrolysis of hemp hurds proceeded, endothermicity decreased for low heating rates. Meanwhile, it increased for intermediate heating rates. However, more energy was required for pyrolysis of hemp hurds with low heating rates, in comparison with performing the process with intermediate heating rates. Furthermore, the conversion of the reactants to pyrolytic products was expected to be easy because low differences between E_i and ΔH_i were found to be within 4.9–5.5 kJ/mol for low heating rates and within 4.2–6.0 kJ/mol for intermediate heating rates, in agreement with previous works [16].

ΔS can be used to describe the possible numbers of different arrangements of particle positions and energies, in which the disorder of a process/system is generally stated. A higher (positive) ΔS value indicates high reactivity as the stage of materials is far from their own thermodynamic equilibrium [17]. Therefore, pyrolysis of hemp hurds with low heating rates was far away from thermodynamic equilibrium, and reactions started to take place rapidly. The ΔS_i values were within 120–320 J/mol•K. Whereas, both positive and negative ΔS_i values were found from the pyrolysis of hemp hurds under intermediate heating rates. The ΔS_i values fluctuated between −100 and 100 J/mol•K. The negative ΔS_i values were at x of 0.1–0.2 and 0.9–1.0. A negative ΔS_i value points out a lower degree of disordered nature of the products than those of the initial reactants. It also depicts thermodynamic equilibrium state during the

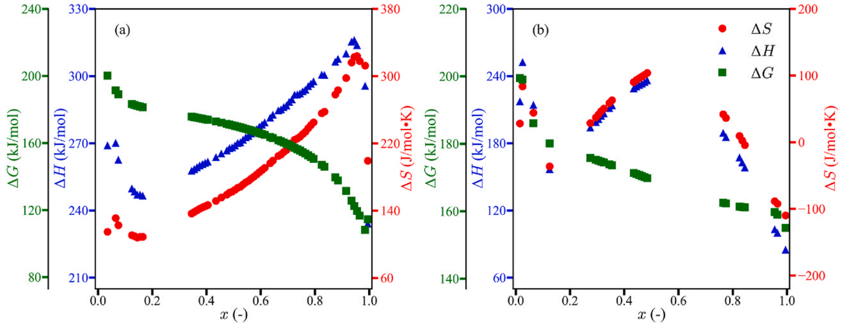

Fig. 4. Thermodynamic properties for pyrolysis of hemp hurds with (a) low and (b) intermediate heating rates.

pyrolysis process, which was also supported from previous studies [18].

ΔG is generally utilized for describing the equilibrium or tendency of a reaction to proceed in a specific direction. In the current work, all ΔG_i values obtained were positive. This means that the active pyrolytic reactions of hemp hurds under both ranges did not occur spontaneously, and energy input was necessary for those pyrolytic reactions. With pyrolysis of hemp hurds proceeding, ΔG_i was increased from about 120 to 200 kJ/mol for low heating rates and from 160 to 200 kJ/mol for that of intermediate heating rates. A higher ΔG_i value implies that there were lower pyrolytic reaction favorability and significant energy requirement for decomposition of hemp hurds [19]. Different rates of ΔG_i changes were found over the range of x for both ranges of heating rates, in which it would be corresponding to thermochemical decomposition of lignin, cellulose, and hemicellulose, respectively.

4. Conclusion

Pyrolysis of hemp hurds was carried out under low (10, 25, and 50 °C/min) and intermediate (100, 125, and 150 °C/min) heating rates. Decomposition of hemp hurds was classified into three stages: drying, active pyrolysis, and char formation, accounting for 70–80% w/w overall weight loss. The discrete DAEM can be utilized for predicting behaviors of hemp hurds pyrolysis accurately with very high correlation. Different reaction mechanisms between low and intermediate heating rates were observed. On the whole, the kinetic and thermodynamic parameters from pyrolysis of hemp hurds under low heating rates were significantly higher than those from the pyrolysis under intermediate heating rates. Our finding is useful in future utilization of hemp hurds via pyrolysis for bioenergy and biochemical production. For future works, yield distribution, characterization, and application of products obtained from pyrolysis of hemp hurds should be considered.

Credit authorship contribution statement

P.M. was responsible for investigation, methodology, and original draft. **T.O.** was responsible for formal analysis, software, visualization, and original draft. **S.R.N.** was responsible for the methodology. **S.S.** was responsible for supervision and reviewing and editing of the manuscript. **N.T.** was responsible for conceptualization, funding acquisition, supervision, and reviewing and editing of the manuscript.

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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