Article

Pyrolysis Kinetic Analysis of Biomasses: Sugarcane Residue, Corn Cob, Napier Grass and their Mixture

Kiattikhoon Phuakpunk[1,a,*], Benjapon Chalermsinsuwan[2,3,4,b], and Suttichai Assabumrungrat[4,5,6,c]

1 Energy Research Institute, Chulalongkorn University, Bangkok 10330, Thailand
2 Fuels Research Center, Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
3 Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University, Bangkok 10330, Thailand
4 Advanced Computational Fluid Dynamics Research Unit, Chulalongkorn University, Bangkok 10330, Thailand
5 Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand
6 Bio-Circular-Green-economy Technology & Engineering Center, BCGeTEC, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand
E-mail: [a]kiattikhoon.p@chula.ac.th (Corresponding author), [b]benjapon.c@chula.ac.th, [c]suttichai.a@chula.ac.th

Abstract. The aim of this study is to investigate pyrolysis kinetic parameters of three high potential energy biomasses including sugarcane residue (tops and leaves), corn cob and Napier grass via thermogravimetry analysis (TGA). In addition, those of their mixture at 1:1:1 by mass is explored. Activation energy and pre-exponential factor were the two considered parameters calculated by following the Ozawa-Flynn-Wall method using condition of 30-900°C with heating rates of 5, 10, 20 and 40°C/min. The derivative thermogravimetric (DTG) curves indicated that there might be at least three different component structures in corn cob. The effective values of the both parameters were almost similar as 214.54, 216.60, 212.51 kJ/mol and 1.510E+19, 1.575E+19, 1.562E+19 min^{-1} for the sugarcane residue, the corn cob, the Napier grass, respectively. Finally, the ternary diagram suggested that the increase of Napier grass proportion would slightly affect the conversion of pyrolysis by reducing the total activation energy of the biomass mixture.

Keywords: Pyrolysis kinetics, sugarcane residue, corn cob, Napier grass, Ozawa-Flynn-Wall method.

1. Introduction

Sugarcane tops and leaves are unused residues from agricultural field in Thailand. A survey about energy crop farming issued from the Department of Alternative Energy Development and Efficiency (DEDE), Ministry of Energy indicated that, in 2013, the sugarcane tops and leaves were produced about 17 million tons but were unused about 15 million tons [1]. This unused amount was in the top scale of unused agricultural residues besides rice husk and oil palm frond [1, 2]. The unused sugarcane residues have been always burnt in the fields because their leaves have sharp edges and are hard to handle for farmers. Burning the residues also emit greenhouse gas and produce air pollution, especially aerosol particles causing respiratory disease and other continual harm like PM2.5 (particulate matter with diameter of 2.5 micron and smaller) and PM10 (particulate matter with diameter of 10 micron and smaller).

Corn cob is another waste from both agriculture fields and industries with about 1.2 million tons produced in 2013. Although some of corn cob can be utilized as an ingredient in animal foods, a material of plywood, a substrate of drugs, etc., the corn cob still remains unused about 10%, according to the DEDE report [1]. In addition, the corn cob is found given high heating value and offered high yield of biooil in the 3rd place among 25 bioresidues in a research of Mythili et al. [3]. If considering only expected potential bioresidues in Thailand [1, 2], the corn cob got the highest in both heating value and biooil yield.

Another interesting biomass is Napier grass which is an easy-to-grow and fast-growing plant. At first, it was imported and mating designed for cattle food. Then, the Napier grass has been promoted from the Department of Livestock Development (DLD), Ministry of Agriculture and Cooperatives, Thailand [4]. Until the Napier grass has been promoted for compressed biogas (CBG) production and/or power generation in the last decade. Napier grass farming has been growing due to subsidies from Ministry of Energy, Thailand [5].

Pyrolysis is a thermal decomposition "process" of solid organic compounds like polymers and biomasses. The pyrolysis process differs from combustion because it is a non-oxidative process. In bioenergy conversion, the pyrolysis processes are applied for higher-heat-content biofuels such as charcoal, biooil and non-condensable gas [6-10]. Typically, pyrolysis processes were divided into three main types. First is "slow pyrolysis" or conventional pyrolysis which operates around 300-550°C with low heating rate. The slow pyrolysis can produce 20-50% wt. biooil and 25-35% wt. biochar as the main products [9, 10]. Second is "fast pyrolysis" or flash pyrolysis using extremely high and immediate heating. The fast pyrolysis can produce more biooil (60-75% wt.) and less biochar (10-25% wt.) than the slow pyrolysis [6, 9, 10]. Sometimes, "intermediate pyrolysis" has been classified as another process [9, 10]. The last type is "carbonization pyrolysis" which commonly known as char production. This process uses very low heating in mild condition and obtains biochar as only main product [7].

Besides, pyrolysis is also called for a thermal "reaction" which converts dry biomass into gases, tar and char. In pyrolysis reaction, the released mass is called volatile matter which includes condensable liquids and non-condensable gases. The actual pyrolysis may take place via different mechanisms depending on structure of the biomass. Some biomasses have noticeably single step of pyrolysis, while some involve double steps, especially woody biomasses or lignocellulosic biomasses [11, 12]. Lignocellulose consists of cellulose, hemicellulose and lignin that are biopolymers apart from protein and carbohydrate. Generally, agricultural wastes consist of 30-50% wt. cellulose, 15-35% wt. hemicellulose and 10-20% wt. lignin [3, 8, 10, 13].

In research field of biomass conversion, biomass compositions can be divided into four groups including 1) moisture 2) volatile matter 3) fixed carbon and 4) ash. Each composition can be analyzed by methods according to ASTM International standards [14, 15]. This characterization is proximate analysis. Besides ASTM methods, proximate compositions can be also calculated using thermogravimetric analysis (TGA) by temperature change with low heating rate via drying, pyrolysis and combustion, respectively [16, 17].

Furthermore, TGA has been also employed as a useful technique for kinetic studies in many thermal reactions such as degradation of polymers [18,19], reaction of metal oxides [20, 21] and combustion or pyrolysis of solid fuels [22-26]. The TGA curve indicates the mass change with the changing of temperature or time in specific atmosphere. The derivative of TGA curve is called derivative thermogravimetric (DTG) curve which shows the rate of change per temperature or time. The DTG curve could indicate the change more evidently than the TGA curve. With different heating rates, TGA and DTG curves were mutually applied for kinetic parameters i.e. activation energy and pre-exponential factor (frequency factor) according to Arrhenius equation. Furthermore, this technique could also identify the reaction order via verification of calculated values of the parameters.

There are many methods to calculate the activation energy and the pre-exponential factor from TGA/DTG results. The simple methods known as model free methods are based on isoconversional principle. The assumption for this method is that the conversion is dependent on only temperature. The free model methods had been used in kinetics studies in degradation of biomasses or biomaterials [27-29]. Furthermore, a new developed method like Distributed Activation Energy Model (DAEM) was also used for biomass degradation [24, 30]. One of the model free methods was Ozawa-Flynn-Wall (OFW) method which developed from original Ozawa method. Still, there was some literature indicating the restrictions and error correction when using OFW on kinetics calculation of complex materials like biomass [31-36]. However, the TGA with OFW has still been favorable to use for kinetics calculation in many

materials [18, 20, 21, 26, 37-39] because of its testing simplicity and adequately accurate results to apply in further simulations.

To develop new alternative solid fuels, the concept of mixing biomass with coal or other biomasses have been studied. In chemical properties studies of mixture, the coal-biomass mixtures have been studied more than the biomass-biomass mixtures [40-46]. There was a study about advantages and disadvantages of various biomasses comparing with coal [47]. The study of biomass-biomass mixture was found only in the study of Nozela et al. [48]. Their study indicated that the mixture of sewage sludge and pruning residues by 1:1 could reduce the activation energy and gave higher heating value than the pure ones.

In this study, the mentioned biomasses, i.e. corn cob, Napier grass and sugarcane residue were selected to investigate due to their differently notable potentials or advantages as energy supplies. The corn cob had very good properties for energy conversion and was quite highly produced. The Napier grass had been being more cultivated and was fast-growing. The sugarcane residue remained abundant as waste which needed to be proper eliminated or utilized. However, using single biomass can make problem to investment of the conversion processes. Because different time of harvesting, volatility in marketing, purchase prices, subsidies, etc. causes abundance or lack of each biomass in some season. That will make the production discontinued. Alternating feedstock cannot be good option in some processes due to unequal qualities of products. Thus, mixing the biomasses can solve the instability of feedstocks and the mixture may get better properties than the single one. The ternary mixture is novel and interesting. In the preliminary step, pyrolysis reaction kinetics is the first property to be investigated. In addition, the kinetic results of this study will be used in simulating and designing processes such as biooil production via slow pyrolysis and gasification. Therefore, the proposed biomasses and their mixture were tested by TGA/DTG technique to find the kinetic parameters of pyrolysis using OFW method and to investigate the effect of biomass mixture on their pyrolysis kinetics.

2. Methodology

2.1. Materials Preparation and Characterization

The fresh corn cob from Kamphaeng Phet Province in the north of Thailand was stripped kernel off and dried in the sun for 4-5 days. The fresh Napier Pakchong 1 grass from Saraburi Province in the middle of Thailand and the sugar tops and leaves from Chonburi Province in the east of Thailand were also dried in the sun at least a week. The sun drying was applied to all materials to ensure that they would not be moldy before collected as raw materials. Then, the raw materials were cut in a shredding machine, dried in an oven with 110°C atmosphere for a day, grinded in a ball mill into small particles and sieved with mesh sieve no. 80 (powder size not over 180 micron). The powder of

each biomass was collected and some amount of each was characterized by proximate and ultimate analyses.

2.2. Thermogravimetric Analysis

In this study, four samples including three pure materials (named SR100, CC100, NP100 for sugarcane residue, corn cob and Napier grass, respectively) and one mixture of all materials in weight equivalent (named Mix 1:1:1) were tested in METTLER's TG/SDTA analyzer-850e model. In every single test, 5 mg of the material in 70 μl alumina crucible was inserted then operated with 50 ml/min of N_2 flow. The sample was heated from 30 to 900°C with different heating rates of 5, 10, 20 and 40°C/min. TGA and DTG data were then plotted and calculated for kinetics of pyrolysis.

2.3. Kinetic Parameters Calculation

Generally, the rate of pyrolysis is defined as a function of temperature (T) and conversion (X);

$$\frac{dX}{dt} = k(T)f(X) \tag{1}$$

where the conversion is calculated from the mass change as

$$X = \frac{w_0 - w}{w_0 - w_f} = \frac{100 - wt\%}{100 - wt\%_f} \tag{2}$$

Typically, the function of conversion, $f(X)$, can be classified by assuming mechanism of solid-state reaction i.e. 1) nucleation, 2) geometrical contraction, 3) diffusion and 4) reaction order. In many studies of biomass pyrolysis kinetics, the reaction order model assuming that reaction is homogeneous, and the rate law is favorite to define $f(X)$ [23, 49] as

$$f(X) = (1-X)^n \tag{3}$$

The $f(X)$ can have different reaction order (n) depending on its mechanism. A proper reaction order would be investigated fitting to the experimental data. Cortés and Bridgewater collected previous works and found that the reaction order was about 1 to 3 for pyrolysis of many biomasses [23]. Herein, the reaction order would be chosen as integer of 1, 2 and 3.

The function of temperature is called rate constant (k) which can be defined as Arrhenius equation [23];

$$k(T) = A \exp(-\frac{E_a}{RT}) \tag{4}$$

so,

$$\frac{dX}{dt} = A \exp(-\frac{E_a}{RT})f(X) \tag{5}$$

To investigate kinetic parameters i.e. activation energy (E_a) and pre-exponential factor (A) of pyrolysis of

each material, the newly developed isoconversional method like OFW method was complied with TGA and DTG data with different heating rates (H) of 5, 10, 20 and 40°C/min [23].

$$T = T_0 + Ht \qquad (6)$$

Deriving derivative of conversion with temperature instead of time, gets

$$\frac{dX}{dT} = \frac{A}{H}\exp(-\frac{E_a}{RT})f(X) \qquad (7)$$

Defining dimensionless term of energy as α and integral form of $f(X)$ as $g(X)$ [23], gives

$$\alpha = \frac{E_a}{RT} \qquad (8)$$

$$g(X) = \int_0^X \frac{dX}{f(X)} = \frac{A}{H}\int_0^{T_X}\exp(-\frac{E_a}{RT})dT$$

$$= \frac{A \cdot E_a}{H \cdot R}\int_\alpha^\infty \frac{\exp(-\alpha)}{\alpha^2}d\alpha \qquad (9)$$

Next, defining integral term of α as $p(\alpha)$ [23];

$$p(\alpha) = \int_\alpha^\infty \frac{\exp(-\alpha)}{\alpha^2}d\alpha \qquad (10)$$

so,

$$g(X) = \frac{A \cdot E_a}{H \cdot R}p(\alpha) \qquad (11)$$

$$\log H = \log(\frac{A \cdot E_a}{R \cdot g(X)}) + \log p(\alpha) \qquad (12)$$

In OFW method, the approximation of $p(\alpha)$ has been developed and it is reliable in the range as below [23, 49].

$$\log p(\alpha) = -2.315 - 0.4567\alpha \quad ,20 \le \alpha \le 60 \qquad (13)$$

Replacing in Eq. (12), then

$$\log H = \log(\frac{A \cdot E_a}{R \cdot g(X)}) - 2.315 - 0.4567\frac{E_a}{RT} \qquad (14)$$

From Eq. (14), plotting the linear lines of $\log H$ versus $\frac{1}{T}$ at each conversion from 0.1 to 0.9. In many studies using model-free models, the increment of conversion should be 0.05-0.1, but 0.1 was proper and favorite [21, 23, 26, 38, 50]. The activation energy value can be calculated from the slope and the pre-exponential factor can be found from the intercept term. The intercept term involves $g(X)$ which is the integral of $f(X)$ as Eq. (8). So, $g(X)$ could get different expressions depending on chosen reaction order as shown in Table 1.

Table 1. Formula of $f(X)$ and $g(X)$ as a function of conversion and reaction order used for pre-exponential factor calculation.

Reaction order (n)	$f(X)$	$g(X)$
Order 1	$(1-X)$	$-\ln(1-X)$
Order 2	$(1-X)^2$	$(1-X)^{-1}$
Order 3	$(1-X)^3$	$\frac{1}{2}(1-X)^{-2}$

2.4. Mixture Analysis

Ternary diagrams would be created for analysis effect of mixing of the biomasses using four samples (three pure materials and one mixture). After getting constants of both the activation energy and the pre-exponential factor which verified with experiments, the constants would be plotted in ternary diagram of the activation energy and ternary diagram of the pre-exponential factor as function of mixture compositions. Using linear mixture method, linear contours would be created and analyzed by analysis of variances (ANOVA).

3. Results and Discussion

3.1. Materials Characterization

To prevent all the materials from mold, the raw materials had been sun-dried. Thus, the characterization of the raw materials as shown in Table 2 was excluded the actual moisture content. The proximate results showed that the dry Napier grass had more volatiles but less fixed carbon than the other two. In the ultimate analysis, C content of Napier grass was close to C content of the others. This meant that the high C content of Napier grass was not only found from the fixed carbon but also from the volatile matter. However, overall, the materials had slightly different elemental compositions.
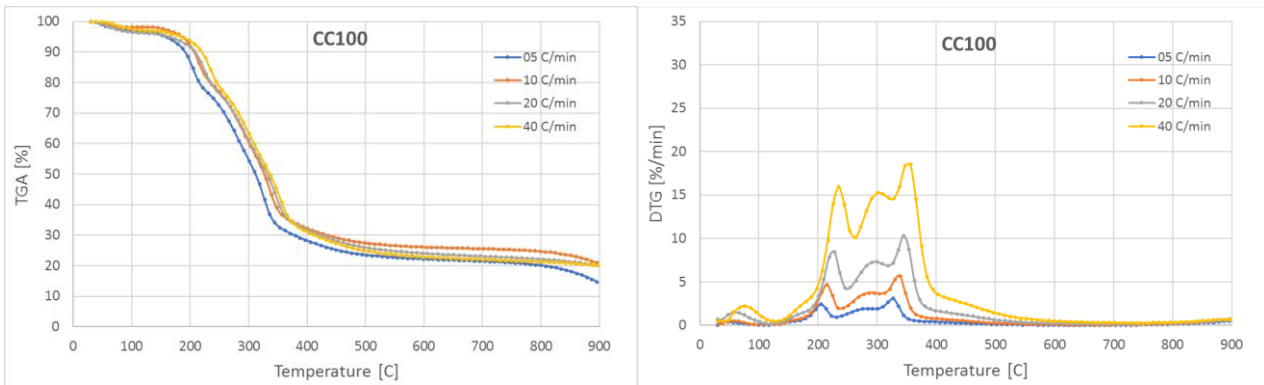
Table 2. Proximate and ultimate analyses of the raw materials.

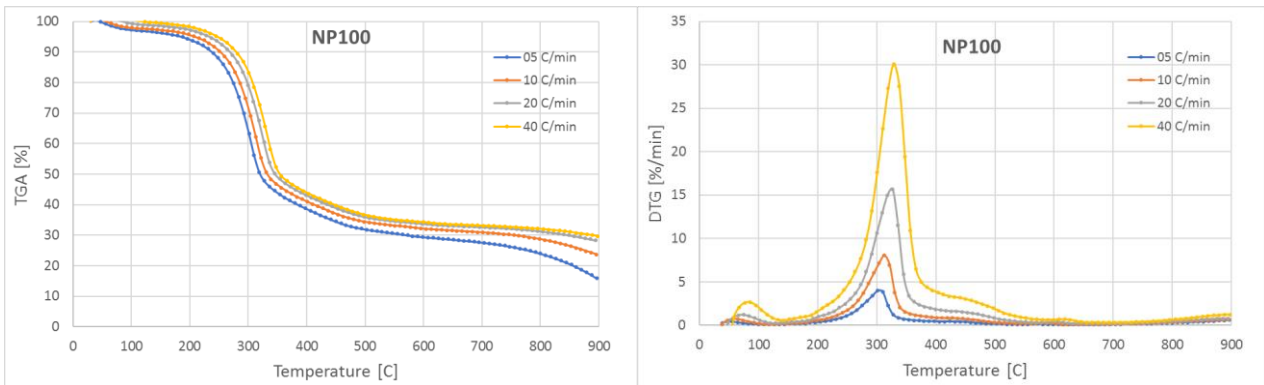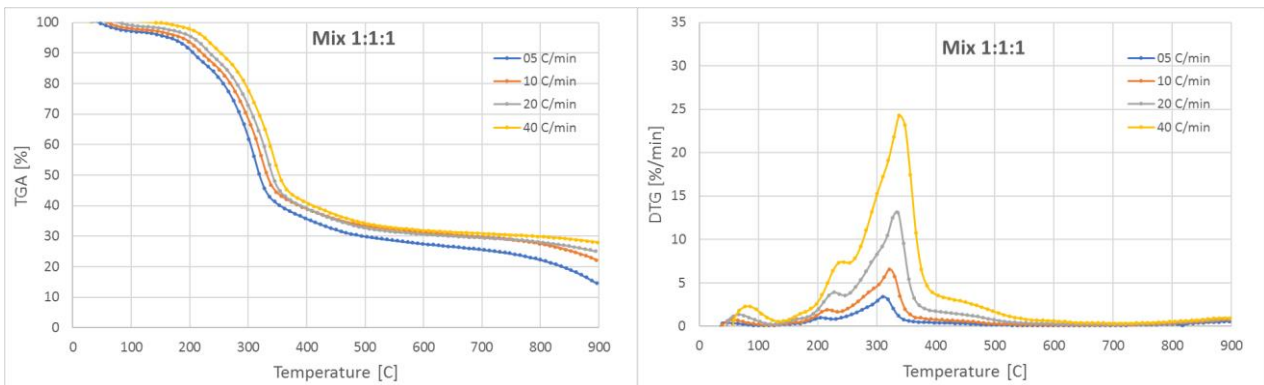|	Sugarcane residue	Corn cob	Napier grass
FC (% db.)	15.15	13.78	8.33
VM (% db.)	78.39	83.10	85.34
Ash (% db.)	6.46	3.12	6.33
C (% db.)	45.44	42.05	45.1
H (% db.)	6.23	6.35	5.94
N (% db.)	0.61	0.66	0.95
S (% db.)	0.14	0.47	0.17
O (% db.)*	41.12	47.36	41.51

* — O element was balanced = 100-C-H-N-S-Ash
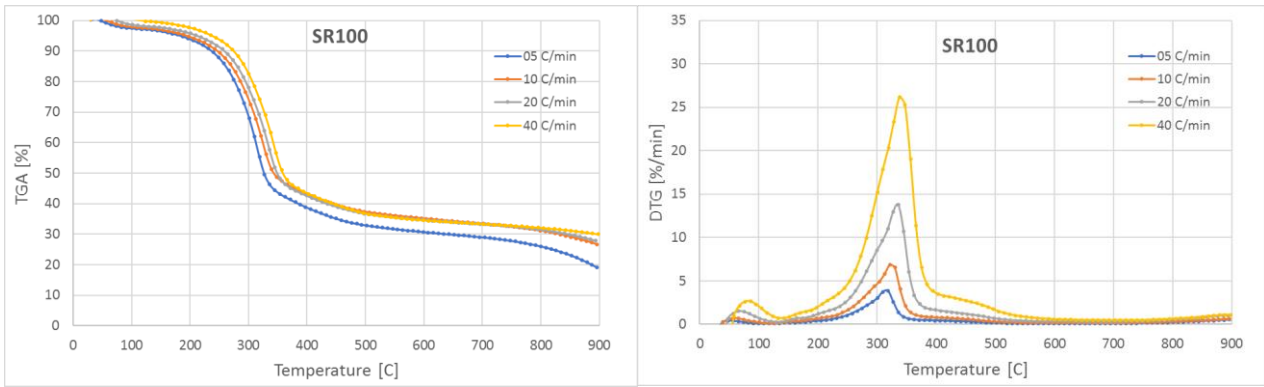
(a)

(b)

(c)

(d)

Fig. 1.   TGA and DTG curves of the biomasses: (a) sugarcane residue (b) corn cob (c) Napier grass and (d) mixture in 1:1:1 ratio.

3.2. Thermogravimetric Results

TGA curves and DTG curves of each sample are shown in Fig. 1. In all TGA curves, small amount of remaining moisture was released when temperature reached 100°C. When the temperature was up to 200°C, the pyrolysis started, and the volatiles were released increasingly. Until around 350°C, the decreasing of mass was slowed down and had small released after 500°C. DTG curves of sugarcane residue and Napier grass showed single peak of mass change while DTG curves of corn cob pointed three peaks. This could be indicated that there were three evidently different component structures inside which decomposed at different temperature ranges.

According to Yang et al. [51], initial decomposition belonged to pyrolysis of hemicellulose which mainly occurred at 220-315°C then decreasingly at higher temperature. While, pyrolysis of cellulose happened extremely at 315–400°C. But pyrolysis of lignin, which was hardly degradable, would decompose in wide range from 160 to 900°C. Considering DTG curves, cellulosic component was majority decomposed in sugarcane residue and Napier grass. In case of corn cob, the first peak indicated the decomposition of hemicellulose, and the top/last peak showed decomposition of cellulose. The middle peak might belong to 1) intercomponent between hemicellulose and cellulose, or 2) intermediate of double-stage pyrolysis of cellulose [52]. However, in some works which corn cob was analyzed by TGA, there were only double peaks which separately belonged to hemicellulose and cellulose [53, 54]. In case of Napier grass, the single peak was a merging peak [55, 56]. Similarly, the single peak of sugarcane residue also agreed with one in the previous work [57]. These quasi-single peaks of Napier grass and sugarcane residue indicated that main decomposition was the cellulose.

In case of the mixture, DTG curves was merged among the materials and gave slightly separated peaks effluent by corn cob portion. Considering effect of heating rate, TGA curve with higher heating rate would shift to right, evidently in pyrolysis range (200-500°C). While DTG curve with higher heating rate would have higher peak(s), and the peak(s) would shift to right as well. These could be explained that higher heat would increase conversion rate but decrease conversion time affecting the conversion to delay.
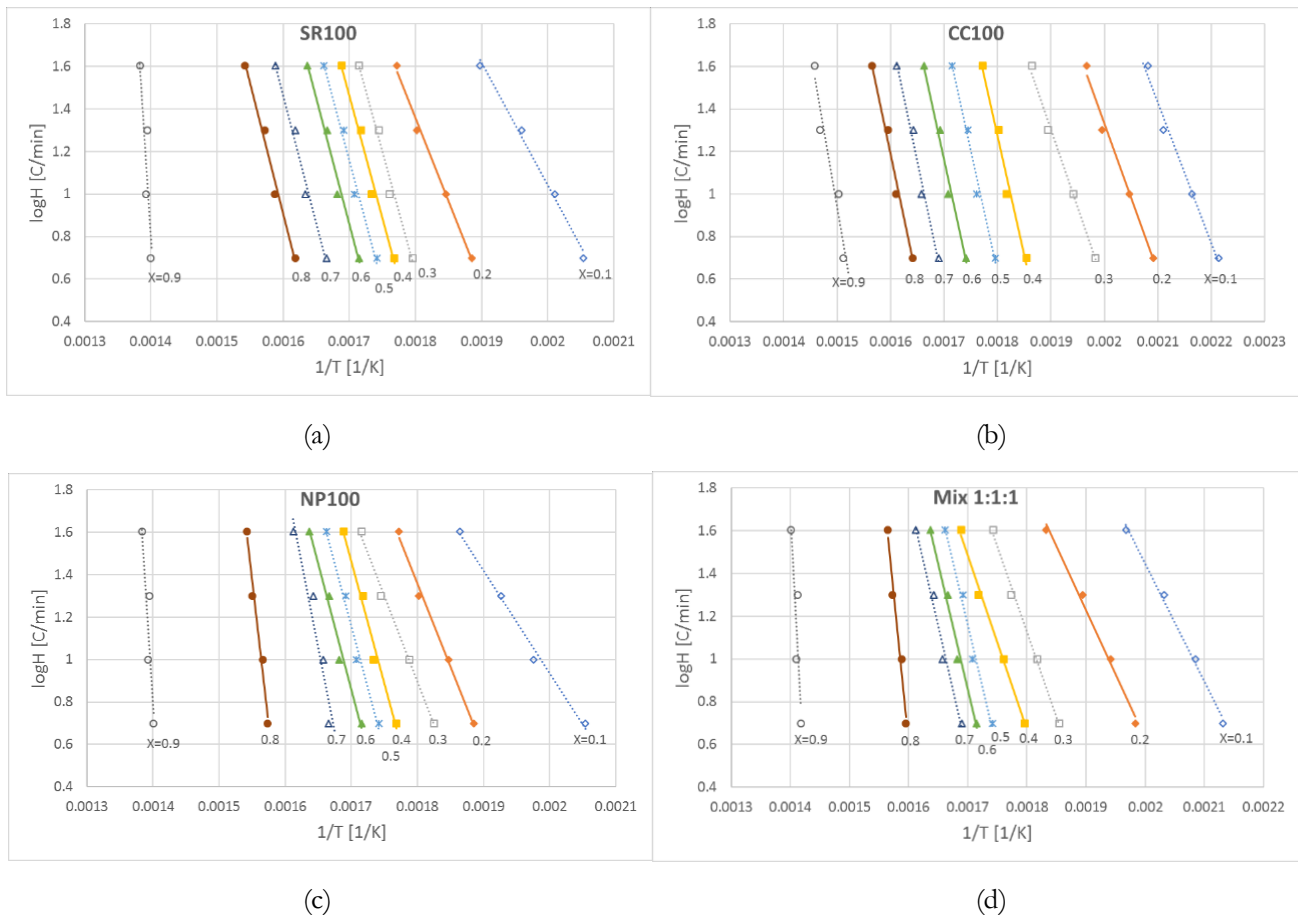

(a)

(b)

(c)

(d)

Fig. 2.   Isoconversional plots via Ozawa-Flynn-Wall method on (a) sugarcane residue (b) corn cob (c) Napier grass and (d) mixture in 1:1:1 ratio.

3.3. Kinetic Parameters Estimation

Complying to Eq. (14) using OFW method, the linear plots at various conversion of 0.1, 0.2 up to 0.9 of each sample are shown in Fig. 2. The slopes of each line were used to calculate the activation energy values, and all the results are shown in Fig. 3 and Table 3. But OFW method had accuracy limit of $20 \leq \dfrac{E_a}{RT} \leq 60$, the activation energy values at conversion of 0.9 of sugarcane residue and at 0.8-0.9 conversion of Napier grass were not reliable, as well as at 0.8-0.9 conversion of the mixture. While the pre-exponential factor values were calculated by the intercepts as a function of reaction order in $g(X)$ term. The estimated results of pre-exponential factor are shown in Fig. 4 and Table 3. All the pre-exponential factor values indicated independent to the reaction order. However, trends of the pre-exponential factor were similar with the activation energy, so the values at high conversion of sugarcane residue, Napier grass and the mixture were also unreliable. After cutting the unreliable values off, these indicated that the range of the activation energy were 104.5-222.7 kJ/mol for the sugarcane residue, 119.8-264.4 kJ/mol for the corn cob and 87.8-289.2 kJ/mol for the Napier grass. The pre-exponential factor was in the ranges of 6.06E+10 to 1.16E+19 min^{-1} for the sugarcane residue, 2.84E+13 to 3.41E+21 min^{-1} for the corn cob and 8.35E+8 to 3.72E+25 min^{-1} for the Napier grass.

Considering the activation energy of each biomass, the activation energy was low at initial conversion then increased and reached stable at conversion above 0.4. In middle range of conversion, the activation energy of all biomasses was similar. This might be because they were lignocellulosic biomass with very close components as discussed in Table 2. The activation energy was low at initial conversion because devolatilization started at about 200°C required not much energy to release the volatiles. The rank of the initial activation energy of these biomasses was likely contrary to the rank of their volatile matter (VM) content. At conversion of 0.1, Napier grass had the lowest activation energy related to its highest VM. Then, at conversion of 0.2-0.3, the activation energy of corn cob became a little lower than Napier grass and sugarcane residue had higher activation energy than the others in conversion of 0.1-0.3 due to its lowest VM.

The overvalues at 0.8-0.9 conversion in cases of sugarcane residue and Napier grass could be suspected due to degradation of lignin. Because lignin was harder to be decomposed than cellulose and hemicellulose, so it needed higher energy to degradation. As previously mentioned, lignin could be decomposed in wide temperature range, while the others were almost

decomposed under 400°C or in lower conversion range. In the previous similar works, some biomasses had the overvalues at high conversion, for examples, Miscanthus [23] and sugarcane leaves [57]. In case of corn cob, it might contain less lignin than the others, so it had no overvalues at 0.8-0.9 conversion. This case accorded to other works investigating kinetics of corn cob [29] and cellulose [39]. However, there was no clear evidence in this work.
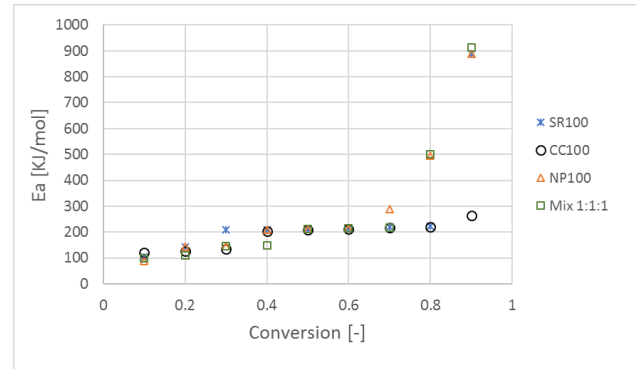

Fig. 3.   The activation energy values of biomasses as a function of conversion, which were calculated by Ozawa-Flynn-Wall method.

Table 3.   Estimated values of the activation energy and the pre-exponential factor from Ozawa-Flynn-Wall method at different conversion.

	X	SR	CC	NP	Mix 1:1:1
	0.1	104.5	119.8	87.8	100.2
	0.2	142.5	127.3	141.9	108.9
	0.3	208.2	134.7	146.7	144.3
	0.4	210.3	203.9	211.4	149.1
E_a	0.5	213.3	208.2	212.3	213.1
	0.6	214.4	212.3	215.1	213.4
	0.7	218.6	216.5	289.2	215.5
	0.8	222.7	220.6	494.3	500.8
	0.9	884.5	264.4	887.2	912.0
	0.1	24.83	30.98	20.54	24.70
	0.2	31.24	31.18	31.74	25.06
	0.3	44.39	31.36	31.38	31.48
	0.4	44.56	45.10	44.28	31.53
$*\ln A$	0.5	44.20	44.73	44.05	44.20
	0.6	44.43	44.42	44.17	44.57
	0.7	43.96	44.21	58.88	44.49
	0.8	43.90	44.13	96.00	98.67
	0.9	154.97	49.58	155.21	161.33

$*$ — values of $\ln A$ represented by $n = 2$

(a)   (b)

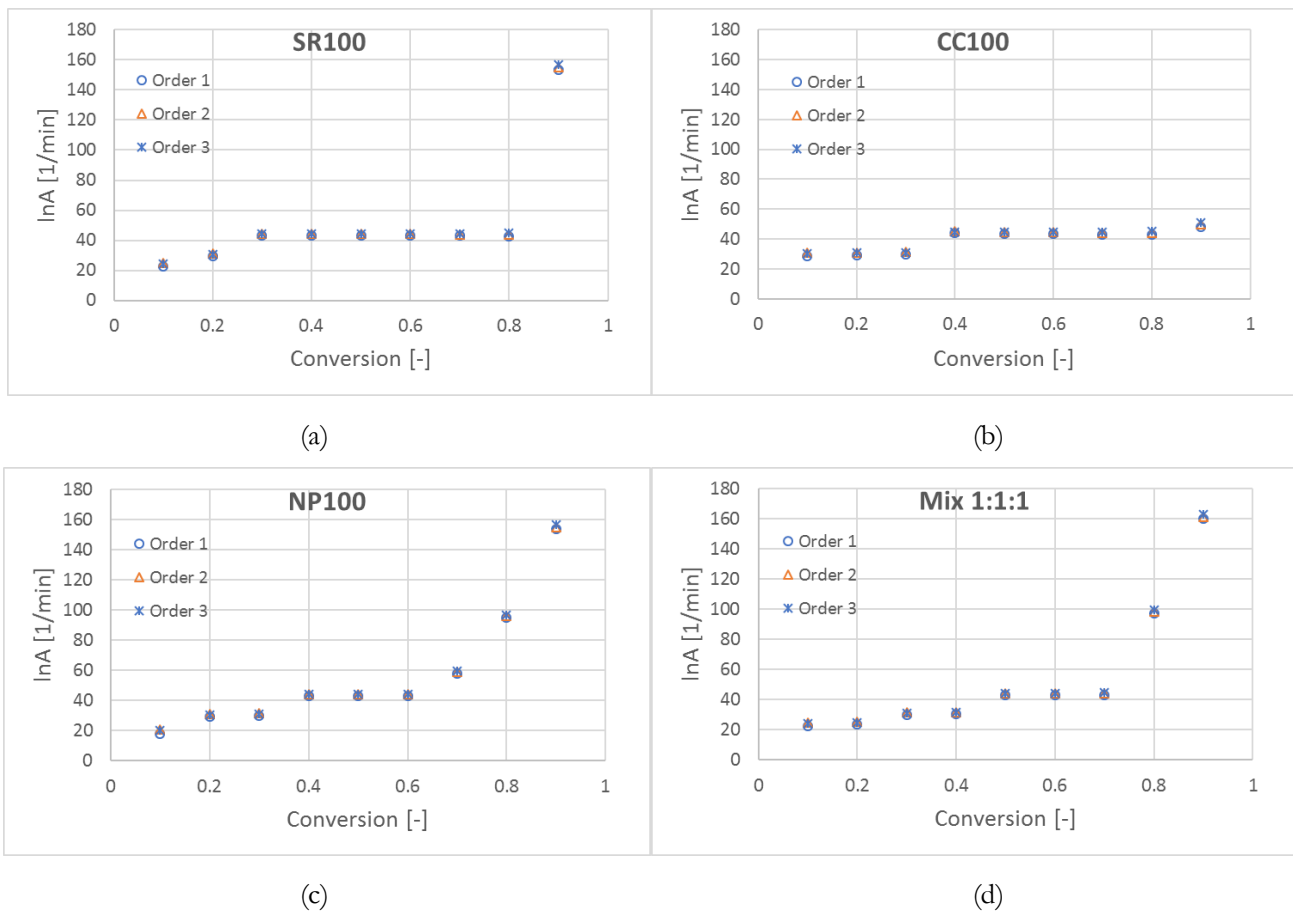(c)   (d)

Fig. 4. The pre-exponential factor values of (a) sugarcane residue (b) corn cob (c) Napier grass and (d) mixture in 1:1:1 ratio as a function of conversion, which were calculated by Ozawa-Flynn-Wall method.

3.4. Model Verification

As seen in Fig. 3 and 4, the activation energy and the pre-exponential factor changed at different conversion. But using constant values had been more convenience to apply in other modelling and to compare among biomasses. Thus, herein, the values at top peak of DTG was selected to be representative values (the all values are shown in Fig. 7). According to Eq. (5), almost parameters were fixed except the $f(X)$ term. Various reaction orders were investigated as shown in Fig. 5 and verified with experimental data as shown in Fig. 6. In Fig.5, the higher reaction order would reduce the conversion rate in high conversion range. In these cases, there was no significant different on R^2 at reaction order of 3 to 6. Overall, the 5th order was found the most proper with the highest R^2 and fitted with the curves at high conversion over 0.7. However, varying reaction order could not affect the curves in low conversion range.

In Fig. 6, the calculated conversion curves which used the parameter values at the DTG peak and reaction order of five, were almost fitted with the experimental curves along the middle conversion to the final conversion but not fitted in initial conversion range (conversion less than 0.2-0.3). These mismatch lines always occurred because of using single values of the parameters, similar

with a work of Cortés et al. [23]. The values of activation energy and pre-exponential factor should use less in the initial range. Thus, to completely fit the calculated curves to experiment, complicated equations of each parameter as a function of conversion should be created in the future.

3.5. Mixture Analysis

After investigating the proper values of the kinetic parameters, the activation energy and the pre-exponential factor, including 216.60 kJ/mol and 1.575E+19 min^{-1} for the corn cob, 212.51 kJ/mol and 1.562E+19 min^{-1} for the Napier grass, 214.54 kJ/mol and 1.510E+19 min^{-1} for the sugarcane residue, were plotted in corners of the ternary diagrams as shown in Fig. 7. All the pure biomasses show values of both parameters very close to each other. This is because of the similar structure or compounds in the biomasses, according to the properties as discussed in Table 2. However, in case of the activation energy, difference of 216.60 and 212.51 kJ/mol could shift the temperature of conversion curve about 10°C when used in the modeling while there was rarely changed in case of difference of 1.510E+19 and 1.575E+19 min^{-1} of the pre-exponential factor.
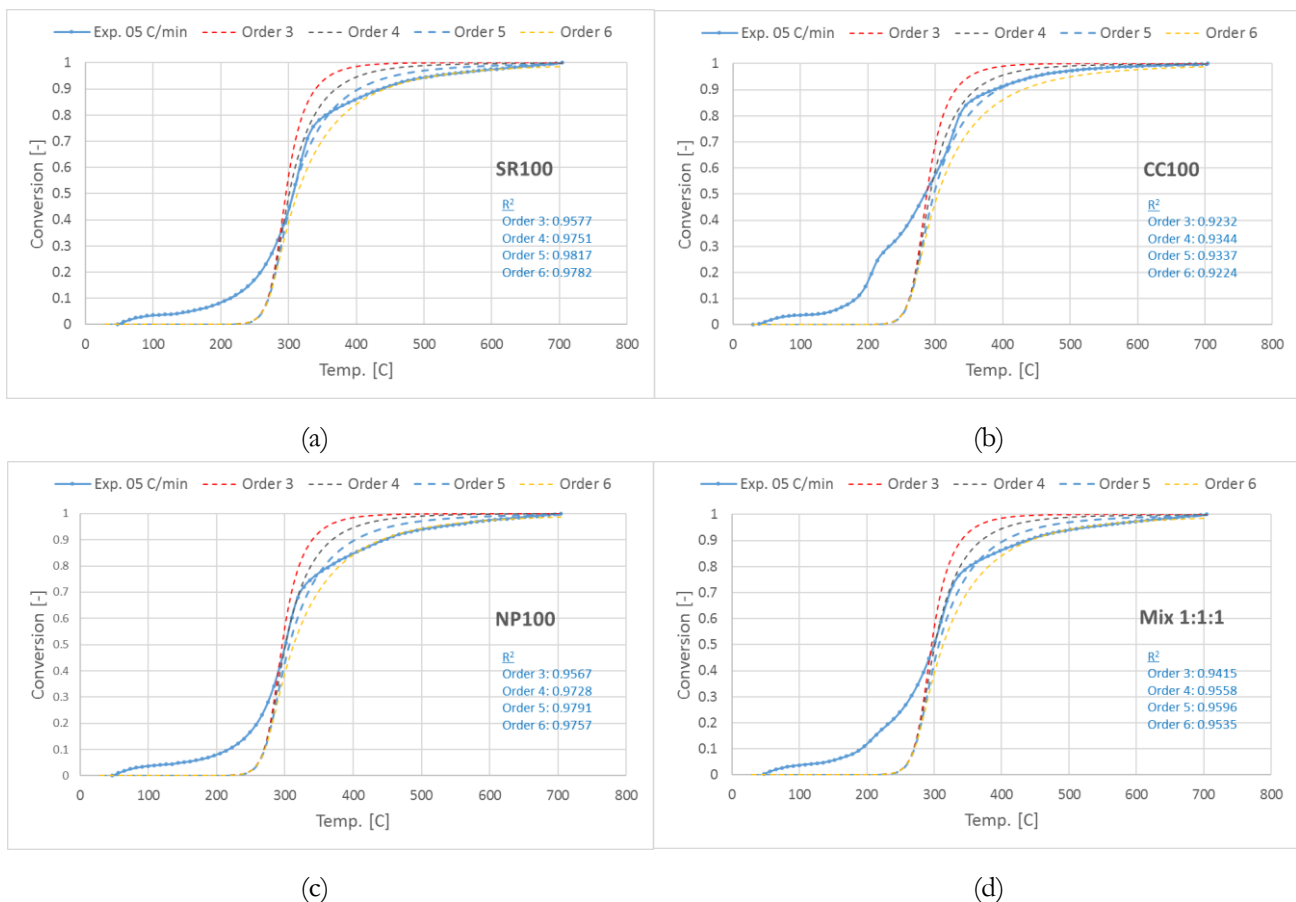
(a)

(b)

(c)

(d)

Fig. 5. The experimental (solid) and calculated (dash) conversion curves with different reaction orders of (a) sugarcane residue (b) corn cob (c) Napier grass and (d) mixture in 1:1:1 ratio as a function of temperature when heated at 5°C/min.

When putting the mixture point with the activation energy of 214.53 kJ/mol and the pre-exponential factor of 1.523E+19 min^{-1} in the middle of diagrams, the contours could be created as can be seen in Fig. 7. For the ANOVA, the diagram of the activation energy had p-value of linear mixture method of 0.0063 but the diagram of the pre-exponential factor had p-value of 0.422 which much over p-value of reliability limit at 0.05. Thus, the biomass mixture had an affected on the activation energy but not had an affected on the pre-exponential factor. Focusing on the diagram of the activation energy, decrease of the activation energy had direction to the Napier grass corner. This indicated that the increasing of the Napier grass ratio in the mixture would reduce the total activation energy and shift the conversion curve.

4. Summary

In this study, three raw materials which had potential for energy utilization in Thailand were selected i.e. sugarcane residue, corn cob and Napier grass. They were investigated their pyrolysis kinetics using TGA and DTG technics with temperature range of 30-900°C and N$_2$ atmosphere. The kinetic parameters such as the activation energy and the pre-exponential factor were calculated using the isoconversional method developed by Ozawa-Flynn-Wall (OFW) with 5, 10, 20 and 40°C/min.

Furthermore, the mixture of the raw materials in equivalent ratio was also investigated the kinetics.

The TGA and DTG results showed that pyrolysis of all samples occurred in about 200-500°C. The DTG curve of the corn cob had three visible peaks indicated that there might be at least three different component structures inside the corn cob, while the other raw materials had only one peak.

Using OFW method, the activation energy and the pre-exponential factor was calculated. Range of the activation energy of the sugarcane residue was 104.5 to 222.7 kJ/mol, the corn cob was 119.8 to 264.4 kJ/mol, and the Napier grass was 87.8 to 289.2 kJ/mol. Range of the pre-exponential factor of the sugarcane residue was 6.06E+10 to 1.16E+19 min^{-1}, the corn cob was 2.84E+13 to 3.41E+21 min^{-1}, and the Napier grass was 8.35E+8 to 3.72E+25 min^{-1}. In verification, single values of the activation energy and the pre-exponential factor (214.54 kJ/mol and 1.510E+19 min^{-1} for the sugarcane residue, 216.60 kJ/mol and 1.575E+19 min^{-1} for the corn cob and 212.51 kJ/mol and 1.562E+19 min^{-1} for the Napier grass) were simple to use, and reaction order of five had a little better fitting than the order numbers nearby. The calculation curves could get good agreement with the experiments in conversion range over 0.3. In comparison, the parameters' single values of each raw material were very close to values of the others because the

compositions of the raw material were very close to each other. In addition, the rate of pyrolysis might be further calculated as a function of conversion to cover all range of conversion.

Next, ternary diagrams dependent on weight percentage of the three raw materials were plotted for the activation energy and the pre-exponential factor. The diagram of activation energy showed that the mixture with more Napier grass would slightly decrease the total activation energy which could shift temperature of conversion.

In conclusion, the single values of the activation energy and the pre-exponential factor could be applied in simulations. The kinetic parameters of these biomasses were very close to each other due to their analogous compositions. Lastly, the mixing of biomass seemed to have a little better effect on the pyrolysis reaction. Thus, more calculation methods and more ratios of the mixture should be investigated for more accurate and clear effect of the ternary mixing.
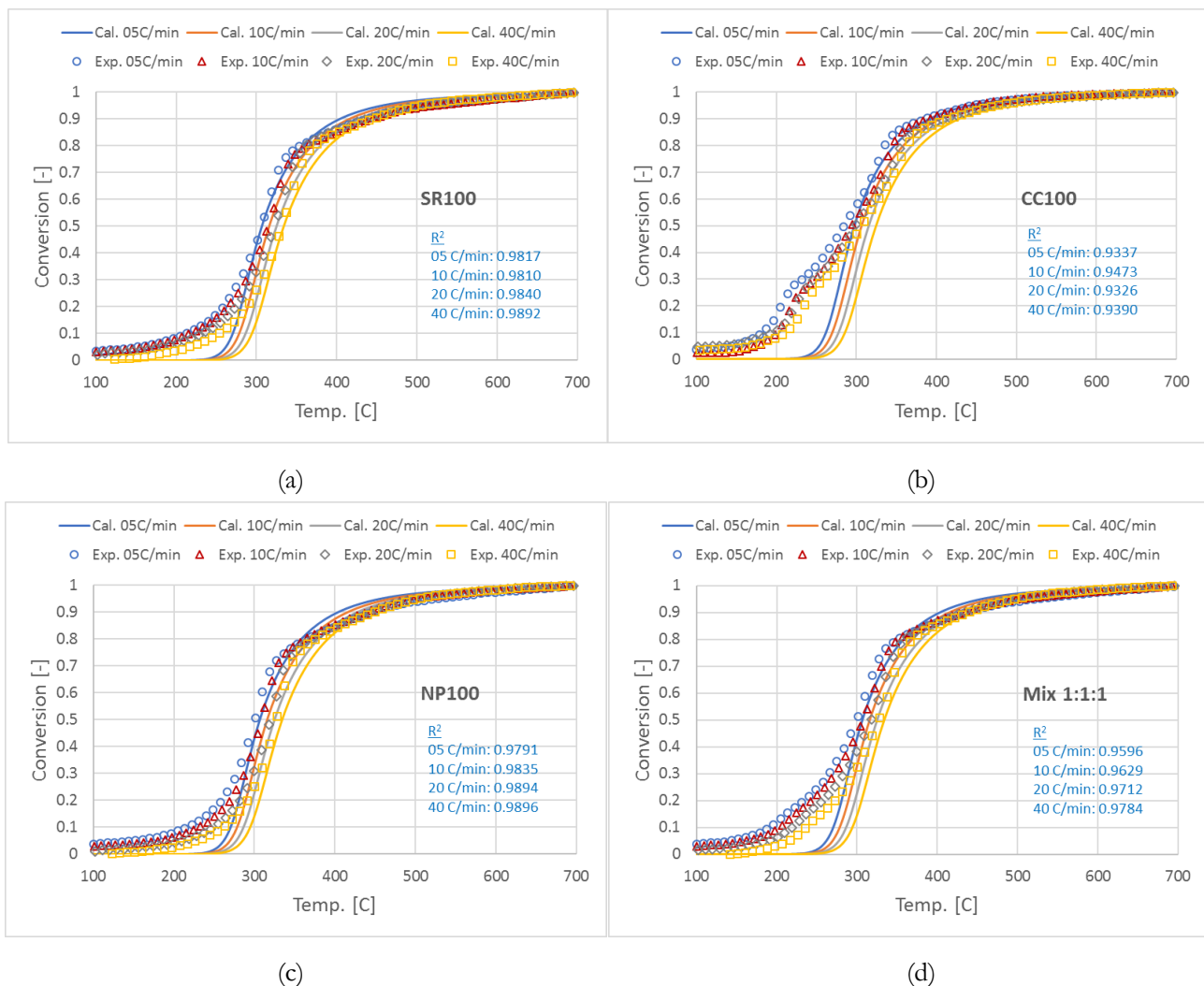
Acknowledgement

Fig. 6. The comparison between the experimental (pointed) curve and the calculated (lined) curve (using the approximate kinetic parameter values at peaks of DTG and reaction order of five) of each heating rate of (a) sugarcane residue (b) corn cob (c) Napier grass and (d) mixture in 1:1:1 ratio.
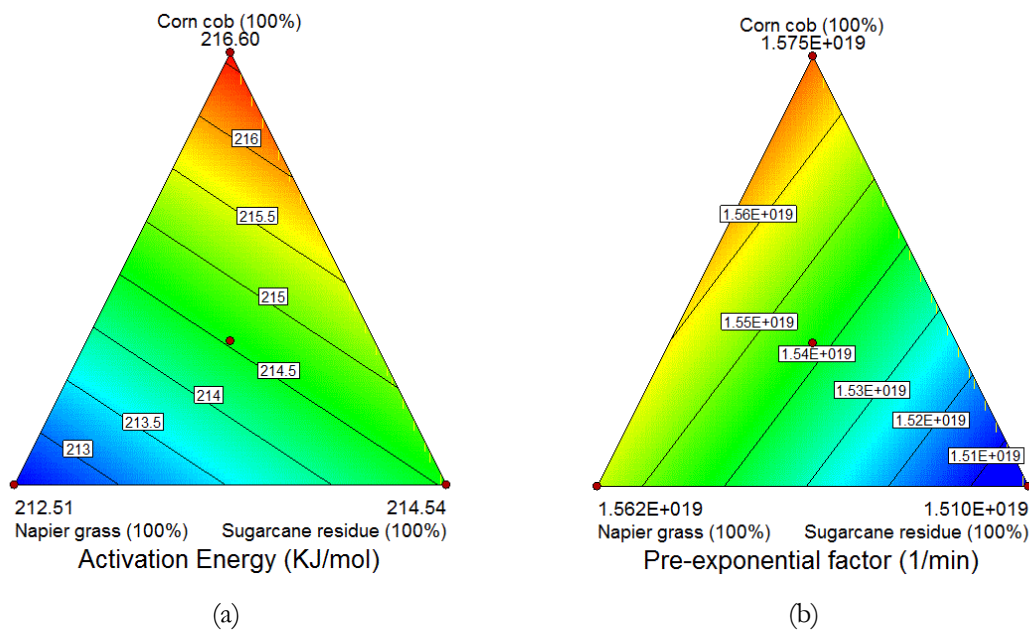
Fig. 7. The ternary diagrams of (a) the activation energy (b) the pre-exponential factor with linear contours as a function of weight percentage of sugarcane residue, corn cob and Napier grass.

References

[1] *Database of annual potential biomass in Thailand in 2013*, Department of Alternative Energy Development and Efficiency, Thailand, 2014. Accessed: 6 February 2019. [Online]. Available: http://biomass.dede.go.th/biomass_web/index.html

[2] "Thailand alternative energy situation 2018," Dept. of Alt. Energ. Devel. and Effic., Bangkok, Thailand, Rep. no. 16, 2018.

[3] R. Mythili, P. Venkatachalam, P. Subramanian, and D. Uma, "Characterization of bioresidues for biooil production through pyrolysis," *Bioresour. Technol.*, vol. 138, pp. 71–78, 2013.

[4] *Napier Pakchong 1 grass growing (in Thai)*, Department of Livestock Development, Thailand, 2017. Accessed: 6 February 2019. [Online]. Available: http://secretary.dld.go.th/index.php/information dld/article-dld/2625-1-5-2560

[5] *Napier grass: the green energy plant in (Thai)*, Department of Alternative Energy Development and Efficiency, Thailand, 2015. Accessed: 6 February 2019. [Online]. Available: http://webkc.dede.go.th/testmax/node/152

[6] A. V. Bridgwater, "Review of fast pyrolysis of biomass and product upgrading," *Biomass Bioenerg.*, vol. 38, pp. 68−94, 2012.

[7] T. Kan, V. Strezov, and T. J. Evans, "Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters," *Renew. Sust. Energ. Rev.*, vol. 57, pp. 1126−1140, 2016.

[8] S. Wang, G. Dai, H. Yang, and Z. Luo, "Lignocellulosic biomass pyrolysis mechanism: A state-of-the-art review," *Prog. Energy Combust. Sci.*, vol. 62, pp. 33−86, 2017.

[9] P. Roy abd G. Dias, "Prospects for pyrolysis technologies in the bioenergy sector: A review," *Renew. Sust. Energ. Rev.*, vol. 77, pp. 59−69, 2017.

[10] V. Dhyani and T. Bhaskar, "A comprehensive review on the pyrolysis of lignocellulosic biomass," *Renew. Energ.*, vol. 129, pp. 695−716, 2018.

[11] S. Gerber, F. Behrendt, and M. Oevermann, "An Eulerian modeling approach of wood gasification in a bubbling fluidized bed reactor using char as bed material," *Fuel*, vol. 89, pp. 2903–2917, 2010.

[12] M. G. Grønli. "A theoretical and experimental study of the thermal degradation of biomass," Ph.D. thesis, NTNU Trondheim, Trondheim, Norway, 1996.

[13] S. I. Mussatto and G. M. Dragone, "Biomass pre-treatment, biorefineries, and potential products for a bioeconomy development," in *Biomass Fractionation Technologies for a Lignocellulosic Feedstock Based Biorefinery*. Amsterdam, Netherlands: Elsevier, 2016, ch. 1, sec. 1.2, pp. 2–6.

[14] J. Parikh, S. A. Channiwala, and G. K. Ghosa, "A correlation for calculating elemental composition from proximate analysis of biomass materials," *Fuel*, vol. 86, pp. 1710–1719, 2007.

[15] A. Ozyuguran and S. Yaman, "Prediction of calorific value of biomass from proximate analysis," *Energy Procedia*, vol. 107, pp. 130–136, 2017.

[16] J. Cai, Y. He, X. Yu, S.W. Banks, Y. Yang, X. Zhang, Y. Yu, R. Liu, and A. V. Bridgwater, "Review of physicochemical properties and

analytical characterization of lignocellulosic biomass," *Renew. Sust. Energ. Rev.*, vol. 76, pp. 309–322, 2017.

[17] R. García, C. Pizarro, A. G. Lavín, and J. L. Bueno, "Biomass proximate analysis using thermogravimetry," *Bioresour. Technol.*, vol. 139, pp. 1–4, 2013.

[18] L. Zhang, M. Huang, and C. Zhou, "Thermal stability and decomposition kinetics of polysuccinimide," *Am. J. Anal. Chem.*, vol. 4, pp. 749-755, 2013.

[19] H. Cui, J. Jiu, T. Sugahara, S. Nagao, K. Suganuma, H. Uchida, and K. A. Schroder, "Using the Friedman method to study the thermal degradation kinetics of photonically cured electrically conductive adhesives," *J. Therm. Anal. Calorim.*, vol. 119, pp. 425–433, 2015.

[20] A. Aboulkas and K. El Harfi, "Study of the kinetics and mechanisms of thermal decomposition of Moroccan Tarfaya oil shale and its kerogen," *Oil Shale*, vol. 25, no. 4, pp. 426–443, 2008.

[21] V. Georgieva, L. Vlaev, and K. Gyurova, "Non-isothermal degradation kinetics of $CaCO_3$ from different origin," *J. Chem.*, vol. 2013, pp. 1-12, 2013, Art. no. 872981.

[22] F. Thurner and U. Mann, "Kinetic investigation of wood," *Ind. Eng. Chem. Process Des. Dev.*, vol. 20, pp. 482-488, 1981.

[23] A. M. Cortés and A.V. Bridgewater, "Kinetic study of the pyrolysis of miscanthus and its acid hydrolysis residue by thermogravimetric analysis," *Fuel Process. Technol.*, vol. 138, pp. 184–193, 2015.

[24] T. Onsree, P. Sittisun, R. Sasaki, and N. Tippayawong, "Pyrolysis of corn residues: Kinetic analysis using discrete distributed activation energy model," in *IOP Conf. Ser. Earth. Environ. Sci.*, City of Conf., 2018, vol. 159, pp. 1-8, Art. no. 012036.

[25] E. Grieco and G. Baldi, "Analysis and modelling of wood pyrolysis," *Chem. Eng. Sci.*, vol. 66, pp. 650–660, 2011.

[26] S. Kumar, M. Kumar, S. Lal, S. Kumar, and S. Arora, "Model free multiple heating rate degradation kinetic studies of modified celluloses," *Chem. Sci. Trans.*, vol. 4, no. 1, pp. 181-193, 2015.

[27] S. Arora, M. Kumar, and G. P. Dubey, "Thermal decomposition kinetics of rice husk: Activation energy with dynamic thermogravimetric analysis," *J. Energy Inst.*, vol. 82, no. 3, pp. 138–143, 2009.

[28] F. Yao, Q. Wu, Y. Lei, W. Guo, and Y. Xu, "Thermal decomposition kinetics of natural fibers: Activation energy with dynamic thermogravimetric analysis," *Polym Degrad Stabil.*, vol. 93, pp. 90–98, 2008.

[29] S. Arora, S. Lal, S. Kumar, M. Kumar, and M. Kumar, "Comparative degradation kinetic studies of three biopolymers: Chitin, chitosan and cellulose," *J. Arch. Appl. Sci. Res.*, vol. 3, no. 3, pp. 188–201, 2011.

[30] J. Cai, W. Wu, R. Liu, and G. W. Huber, "A distributed activation energy model for the pyrolysis of lignocellulosic biomass," *Green Chem.*, vol. 15, pp. 1331–1340, 2013.

[31] S. Vyazovkin, A. K. Burnham, J. M. Criado, L. A. Pérez-Maqueda, C. Popescu, and N. Sbirrazzuoli, "ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data," *Thermochim. Acta*, vol. 520, pp. 1–19, 2011.

[32] S. Vyazovkin, K. Chrissafis, M. L. Di Lorenzo, N. Koga, M. Pijolat, B. Roduit, N. Sbirrazzuoli, and J. J. Suñol, "ICTAC Kinetics Committee recommendations for collecting experimental thermal analysis data for kinetic computations," *Thermochim. Acta*, vol. 590, pp. 1–23, 2014.

[33] S. Vyazovkin, "Modification of the integral isoconversional method to account for variation in the activation energy," *J. Comput. Chem.*, vol. 22, pp. 178–183, 2001.

[34] J. Cai, W. Wu, and R. Liu, "Isoconversional kinetic analysis of complex solid-state processes: parallel and successive reactions," *Ind. Eng. Chem. Res.*, vol. 51, pp. 16157−16161, 2012.

[35] A. Ortega, "A simple and precise linear integral method for isoconversional data," *Thermochim. Acta*, vol. 474, pp. 81–86, 2008.

[36] T. Wanjun and C. Donghua, "An integral method to determine variation in activation energy with extent of conversion," *Thermochim. Acta*, vol. 433, pp. 72–76, 2005.

[37] V. Mamleev, S. Bourbigot, M. Le Bras, and J. Lefebvre, "Three model-free methods for calculation of activation energy in TG," *J. Therm. Anal. Calorim.*, vol. 78, pp. 1009–1027, 2004.

[38] Y. Han, "Theoretical study of thermal analysis kinetics," Ph.D. thesis, Mech. Eng., Univ. of Kentucky, Lexington, Kentucky, 2014.

[39] D. Q. Viet and V. S. Tho, "Study on kinetics of pyrolysis reaction (degradation) of rice husk, corn corb and sugarcane bagasse as agricultural residues in Vietnam," *Vietnam J. Sci. Technol.*, vol. 55, no. 4, pp. 436–442, 2017.

[40] L. Roendahl, "Biomass resources, fuel preparation and utilization for improving the fuel flexibility of advanced power plants," in *Advanced Power Plant Materials, Design and Technology*. Cambridge, UK: Woodhead Publishing, 2010, ch. 12, pp. 312–331.

[41] N. J. Simms, "Solid fuel composition and power plant fuel flexibility," in *Power Plant Life Management and Performance Improvement*. Cambridge, UK: Woodhead Publishing, 2011, ch. 1, pp. 3-37.

[42] D. Tillman, D. Duong, and N. S. Harding, "Blending coal with biomass: cofiring biomass with coal," in *Solid Fuel Blending: Principles, Practices, and Problems*. Oxford, UK: Butterworth-Heinemann, 2012, ch. 4, pp. 125-200.

[43] J. B. Królczyk, A. Rezwiakow, and M. Tukiendorf, "Mixing of biomass and coal in a static mixer as an example of technological solutions involving implementation of renewable energy sources," *Sources, Ecol. Chem. Emg. S.*, vol. 21, no. 4, pp. 685-696, 2014.

[44] E. Manzanares-Papayanopoulos, J. R. Herrera-Velarde, A. Arriola-Medellín, A. M. Alcaraz-Calderón, J. A. Altamirano-Bedolla, and M. Fernández-Montiel, "The co-gasification of coal biomass mixtures for power generation a comparative study for solid fuels available in Mexico," *Energ. Source. Part A*, vol. 36, pp. 104-111, 2014.

[45] N. J. Simms, "Plant integrity in solid fuel-flexible power generation," in *Fuel Flexible Energy Generation: Solid, Liquid and Gaseous Fuels*. Cambridge, UK: Woodhead Publishing, 2016, ch. 8, pp. 201–240.

[46] A. C. Kokossis, "Design of integrated biorefineries," *Comput. Aided Chem. Eng.*, vol. 34, pp. 173-185, 2014.

[47] S. V. Vassilev, C. G. Vassileva, and V. S. Vassilev, "Advantages and disadvantages of composition and properties of biomass in comparison with coal: An overview," *Fuel*, vol. 158, pp. 330-350, 2015.

[48] W. C. Nozela, C. E. M. Braz, S. Almeida, C. A. Ribeiro, and M. S. Crespi, "Mixture of biomass to energy reuse," *J. Therm. Anal. Calorim.*, vol. 131, pp. 765-769, 2018.

[49] J. E. White, W. J. Catallo, and B. L. Legendre, "Biomass pyrolysis kinetics: A comparative critical review with relevant agricultural residue case studies," *J. Anal. Appl. Pyrol.*, vol. 91, pp. 1–33, 2011.

[50] A. F. Santos, L. Polese, M. S. Crespi, and C. A. Ribeiro, "Kinetic model of poly(3-hydroxybutyrate) thermal degradation from experimental non-isothermal data," *J. Therm. Anal. Calorim.*, vol. 96, no. 1, pp. 287–291, 2009.

[51] H. Yang, R. Yan, H. Chen, D. H. Lee, and C. Zheng, "Characteristics of hemicellulose, cellulose and lignin pyrolysis," *Fuel*, vol. 86, pp. 1781−1788, 2007.

[52] D. Shen, R. Xiao, S. Gu, and H. Zhang, "The overview of thermal decomposition of cellulose in lignocellulosic biomass," in *Cellulose - Biomass Conversion*: IntechOpen, 2013, ch. 9, pp. 193–226.

[53] E. R. D. Padilla, G. T. Nakashima, A. L. S. Hansted, L. R. O. Santos, J. L. Barros, A. C. De Conti, and F. M. Yamaji, "Thermogravimetric and FTIR analyzes of corn cob pyrolysis," *Quím. Nova*, vol. 42, no. 5, pp. 566−569, 2019.

[54] G. K. Gupta, M. Ram, R. Bala, M. Kapur, and M. K. Mondal, "Pyrolysis of chemically treated corncob for biochar production and its application in Cr(VI) removal," *Environ. Prog. Sustain. Energy*, vol. 37, no.5, pp. 1606−1617, 2018.

[55] T. H. Boon, A. Raheem, A. Karim, S. A. Hussain, and D. Ng Kok Sum, "Thermogravimetric study of Napier grass in inert and oxidative atmospheres conditions," *J. Phys. Sci.*, vol. 28, no.1, pp. 155−169, 2017.

[56] I. Y. Mohammed, Y. A. Abakr, F. Kabir, and S. Yusup, "Effect of aqueous pretreatment on pyrolysis characteristics of Napier grass," *J. Eng. Sci. Technol.*, vol. 10, no.11, pp. 1487−1496, 2015.

[57] M. Kumar, S. Sabbarwal, P. K. Mishra, and S. N. Upadhyay, "Thermal degradation kinetics of sugarcane leaves (*Saccharum officinarum* L) using thermo-gravimetric and differential scanning calorimetric studies," *Bioresour. Technol.*, vol. 279, pp. 262−270, 2019.

Kiattikhoon Phuakpunk, photograph and biography not available at the time of publication.

Benjapon Chalermsinsuwan, photograph and biography not available at the time of publication.

Suttichai Assabumrungrat, photograph and biography not available at the time of publication.