Napier Grass Pyrolysis: Kinetic and Thermodynamics Analysis

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Abstract

The pyrolysis behavior, kinetics and thermodynamics analysis of Napier grass were studied. A thermogravimetric analyzer (TGA) and differential thermal analyzer (DTA), at four heating rates: 5, 10, 20 and 30 ^{o}C/min were used in the experiments. Pyrolysis parameters were determined using model-fitting with the Coat-Redfern method. The results showed that the grass was roughly decomposed into moisture removal and volatiles release zones. The approximate peak temperature occurred in the major stage during 298 to 337 ^{o}C. The characteristic temperatures moved to a higher temperature during thermal degradation. The apparent activation energy and pre-exponential factor also increased with increasing heating rate. The positive values of enthalpies (ΔH), Gibbs free energies (ΔG) and the negative value of entropies (ΔS) exhibited that the Napier grass was endothermic but some exothermic reactions were also found, due to the presence of oxygen in its original components.

Keywords: Napier Grass; Pyrolysis; Kinetic Models; Thermodynamics Parameters

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Introduction

Napier grass is known as elephant grass (*Pennisetum purpureum*) or Uganda grass [1]. It is one type of perennial grasses that include Miscanthus, Switch grass and Reed canary grass [2] that can be used as a renewable resource. Napier grass originates from Africa and it is planted in many countries such as India, China, Brazil, the USA and some European countries [3]. The advantages of Napier grass include easy planting, fast growth, high yield and a mature height approaching 3 - 5 feet [4]. It can be cultivated up to four times in a year with a ratio of energy output to energy input of around 25 : 1 [1] and an annual yield in the range of 10 - 20 oven dry tons per hectare, with some nutrient input required during cultivation [5] - [6].

Fuel products from Napier grass include bioethanol, pyrolysis oil and biogas [7]. The production of bioethanol and pyrolysis oil are more efficient than that of biogas because they are easy to store and transport. The production of pyrolysis oil has more ways of waste recycling and energy recovery than that of bioethanol [7].

Pyrolysis is a thermal conversion process involving biomass, with the feedstock (biomass) converted into solid (biochar), liquid (bio-oil, pyrolysis oil) or gas (biogas) to produce heat, power, or other high value chemical products [2]. During pyrolysis, largely complex hydrocarbon molecules of the biomass decompose into smaller molecules [8]. Moisture release, hemicellulose decomposition, cellulose decomposition and lignin decomposition occur during the process [9]. Thermogravimetric analysis (TGA) is one of the most common and simplest methods to investigate the kinetics and thermodynamics properties of biomass during the pyrolysis process [10].

In kinetic analysis, an iso-conversional model (model-free) and model fitting are applied to simulate kinetic parameters. The model-free methods are accurate and time saving compared to other model-fitting methods [10] when the mass transfer resistance is not counted. It also shows various mechanisms on the conversion process by using many heating rate data [11].The Kissinger-Akahira-Sunose (KAS), the Flynn-Wall-Ozawa (FWO) or Friedman methods [2], [10] are examples of the model-free methods that are mainly used to evaluate the activation energy on conversion. Model-fitting methods are matched with choosing experimental results with the best statistical fit of kinetic factors [12]. Magalhães, D., et al. [11] and Freeman, E. S. and Carroll, B. [13] developed model-fitting methods. Many studies on grass and biomass pyrolysis with model-free and model-fitting have been reported in the literatures.

Mohammed, I. Y., et al. [1] studied the effects of temperature, heating rate and nitrogen flow rate on the intermediate pyrolysis of Napier grass in a vertical fixed-bed tubular reactor. They applied a response surface methodology with a central composite design to model the process and to optimize the process parameters. They found that the optimum bio-oil yield of 50.57 wt% occurred at 600 °C, 50 °C/min with 5 L/min of nitrogen flow.

Collazzo, G. C., et al. [2] investigated the thermal degradation and kinetics of elephant grass in an inert atmosphere using a non-isothermal thermogravimetric analysis method. Model-free methods including KAS and FWO were applied to evaluate the kinetic parameters. The average activation energy of KAS and FWO were 183.8±11.3 kJ/mol and 183.8±10.4 kJ/mol from the conversion of 0 to 0.6 respectively. The activation energies of hemicellulose, cellulose and lignin decomposition were 46.5 - 65.5 kJ/mol, 108 - 127.2 kJ/mol, and 45.6 - 53.5 kJ/mol respectively.

Manatura, K., et al. [14] performed the thermogravimetric analysis method of raw and torrefied *Cryptomeria japonica* at 250 °C and 350 °C in a pure CO_2 environment at three heating rates of 10, 15 and 20 °C/min. They pointed out that thermal degradation occurred in three different stages consisting of dehydration, hemicellulose-cellulose and lignin decomposition at 30.2 - 102.6 °C, 222.6 - 422.1 °C and 426 - 847.2 °C with activation energies of 77, 114 and 50 kJ/mol, respectively. They concluded that increasing the heating rate shifts the mass loss toward a higher temperature, increasing the activation energy and the pre-exponential factor.

The aim of this research is to establish the thermal characteristics of the Napier grass and to describe the pyrolysis characters by fitting a model using Coat-Redfern method. TGA and DTG experiments were addressed in an inert environment at different heating rates. While many reports have considered the kinetic behaviours and parameters of Napier grass, there is still a lack of description of the thermodynamic parameters for the biomass. Thus, this study contributes to the thermodynamic parameters and the gained activation energies can be used to determine the changes of enthalpy (ΔH), free Gibbs energy (ΔG), and entropy (ΔS). The results are useful for the understanding of the Napier grass pyrolysis process and the optimal design of corresponding pyrolysis and gasifier reactors especially downdraft gasifiers.

Materials and methods

Biomass characteristics

Napier grass (Pakchong 1) was used in this study. It was cultivated and collected from the Kasetsart University Kamphaeng Saen campus, Nakhonpathom, Thailand. The Napier grass was sun-dried for two days before being chopped and sieved to a particle size of approximately 1 - 2 mm.

The proximate analysis and ultimate analysis of the grass were characterized according to ASTM D 7582, D 5373, D 4239 and D 5865 and the results are shown in Table 1. These results were close to the values reported by Mesa-Pérez, J. M., et al. [15]. It should be noted that the volatile matter of Napier grass is high (67.50 wt.%), indicating Napier grass is a potential feedstock for the pyrolysis processes.

Table 1 Proximate and ultimate analysis of Napier grass

Characteristics	This study	Mesa-Pérez, J. M., et al. [15]
Proximate analysis (wt%, ar)		
Moisture	10.94	12.20
Volatile matter	67.50	67.34
Fixed carbon	15.21	15.54
Ash	6.35	4.92
Ultimate analysis (wt%, dry)		
C	40.03	41.16
H	6.44	5.55
O	46.49	46.59
N	0.58	1.78
S	0.11	-
HHV(MJ/kg)	15.75	-

Thermogravimetric analysis

The pyrolysis characteristics of the Napier samples were performed using a TGA analyzer (SDT 2960 Simultaneous, USA) in a nitrogen environment with a flow rate of 100 mL/min. Each Napier grass sample (7 - 10 mg) was placed in an aluminum pan in order to minimize heat and mass transfer phenomena. The sample was heated from 30 ^{o}C to 800 ^{o}C at four different heating rate (5, 10, 20 and 30 ^{o}C/min). The experiment was conducted three times to confirm acceptable results. During the heating process, variations of the mass loss and its derivative with respect to the time and temperature were recorded.

Kinetic analysis

During the pyrolysis process, the conversion (X) of biomass can be represented by

$$X = \frac{w_i - w_t}{w_i - w_f} \tag{1}$$

where w_i, w_t and w_f are the initial sample mass, the sample mass at time t, and the final sample mass, respectively. The rate of conversion was expressed as:

$$\frac{dX}{dt} = k(T)f(X) \tag{2}$$

where k is the decomposition rate constant, and $f(X)$ is the reaction model which expresses the dependence of the conversion rate on the conversion. A heterogeneous function of uniform kinetic reactions of the first order, $f(X)$ can be written as:

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

The rate constant (k) is temperature dependent which generally is described by the Arrhenius equation as [16]:

$$k = Ae^{-E_a / RT} \tag{4}$$

where A is the pre-exponential factor (s^{-1}), E_a is the activation energy of the decomposition reaction (kJ/mol), R is the universal gas constant, 8.314 J/(mol.K), and T is the absolute temperature (K). Thus, the rate constant can be expanded to:

$$\frac{dX}{dt} = Ae^{-E_a / RT}(1 - X)^n \tag{5}$$

In non-isothermal analysis, the heating rate varies with the reaction time and temperature at a constant heating rate $\left(\frac{dX}{dt} = \beta\right)$ and can be rewritten as [2]:

$$\frac{dX}{dt} = \frac{A}{\beta}e^{-E / RT}(1 - X)^n \tag{6}$$

This method is a model fitting method that has been widely used in the kinetics of coal and biomass combustion/pyrolysis [11]. It is known that the Coat-Redfern method and can be written as:

For n = 1, $$\ln\left[-\frac{\ln(1 - X)}{T^2}\right] = \ln\left[\frac{AR}{\beta E_a}\right] - \frac{E_a}{RT} \tag{7}$$

For n ≠ 1, $$\ln\left[\frac{1 - (1 - X)^{1-n}}{T^2(1 - n)}\right] = \ln\left[\frac{AR}{\beta E_a}\right] - \frac{E_a}{RT} \tag{8}$$

For a plot of Z with $-\frac{1}{T}$ using linear regression with a high correlation coefficient (R^2), E_a can be calculated from the slope. In this case, Z is $\left[-\frac{\ln(1-X)}{T^2}\right]$ for n = 1 or $\ln\left[\frac{1-(1-X)^{1-n}}{T^2(1-n)}\right]$ for n = 1. The intercept $\left[\frac{AR}{BE_a}\right]$ can also be calculated as A.

Thermodynamic analysis

In this study, the thermodynamics parameters of enthalpies (ΔH), Gibbs free energies (ΔG) and entropies (ΔS) were evaluated using Equation (9) - (11).

$$\Delta H = E_a - RT \tag{9}$$

$$\Delta G = E_a + RT_p \ln\left(\frac{K_B T_p}{hA}\right) \tag{10}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_p} \tag{11}$$

where K_B, h and T_p are the Boltzmann constant = 1.381×10^{-23} J/K, Plank constant = 6.626×10^{-34} J.s and peak temperature, respectively.

Results and Discussion

Pyrolysis characteristics

The mass loss (TGA) and the rate of mass loss (DTG) for the Napier samples in an inert environment with different pyrolysis temperatures at four heating rates (5, 10, 20 and 30 ^{o}C/min) are shown in Figure 1 and 2 respectively.

The characteristics of the samples can be divided into three different stages. The first stage (stage I) represents the moisture removal zone. It occurs at temperatures from 30.2 to 120.1 ^{o}C. The mass loss was 8.6 % which agreed with the moisture content in Table 1. The rate of mass loss was quite low in the range 0.1 - 0.21 ^{o}C/min.

The second stage (stage II), temperature varied from 200 to 370 ^{o}C. The mass loss was about 53 % in this stage while the rate of mass loss was quite high (0.6 to 1 mg/^{o}C). The maximum lost occurred at 335 ^{o}C. It was clear that the main volatiles released in this range were in line with Yahiaoui, M., et al. [16] and the volatile content of the sample in Table 1. According to [10], the decomposition of hemicellulose and cellulose occurs in the temperature range 180 - 285 ^{o}C and 250 - 360 ^{o}C, respectively. Thus, the decomposition of hemicellulose and cellulose occurred in this second stage. The third stage, (stage III) had a long tail with small values of mass loss and the rate of mass loss. Lignin decomposition occurred in this stage from 350 to 600 °C and furthermore, the temperature until the end of the process left a final solid residue including fixed carbon and ash [10].

The influence of heating rate is also shown in Figure 1 and 2. Raising the heating rate leads to serving a large amount of thermal energy into the system and a longer time may be consumed for the carrier gas to reach an equilibrium state. Thus, the temperature required to decompose the sample also raises causing the maximum rate (peak) curve to move to the right [17]. Increasing the heating rate from 5 to 30 °C/min did not affect the shape of DTG, but shifted peaks to the higher temperature.

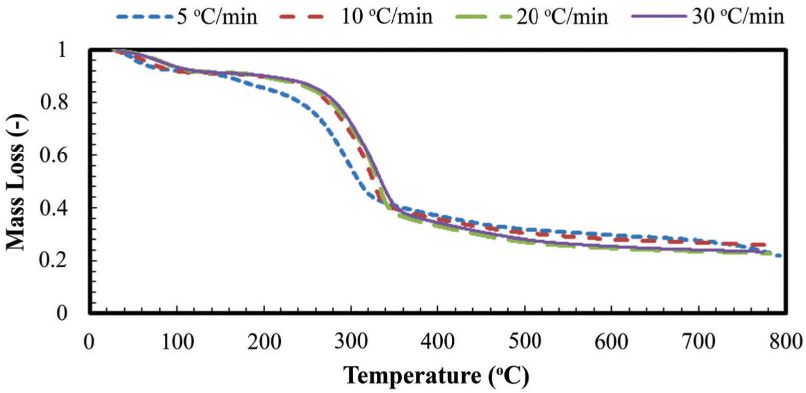

Figure 1 Mass loss curve for heating rates of 5, 10, 20 and 30 °C/min

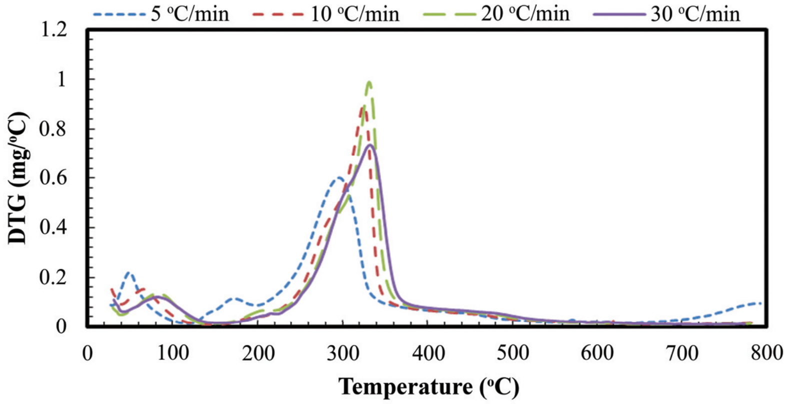

Figure 2 Rate of mass loss curve for heating rates of 5, 10, 20 and 30 °C/min

Kinetic analysis

The results from the TGA and DTG of Napier grass were used to simulate kinetic parameters including the activation energy (E_a), pre-exponential factor (A) and reaction order (n). The fitting methods of Coat-Redfern using Equation (7) and (8) was applied in this study.

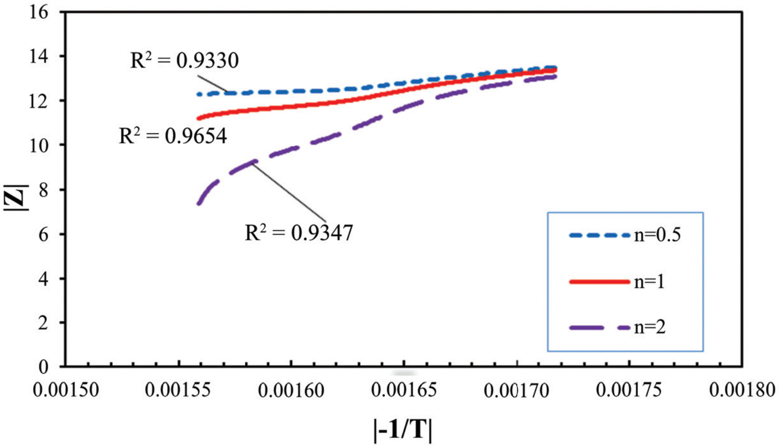

Figure 3 Reaction orders, n = 0.5, 1 and 2 at a heating rate of 20 °C/min

Figure 3 displays the reaction orders (n) of the relationship between Z and -1/T for heating rate of 20 °C/min. It can be seen that most values of n had high values of R^2 (> 0.9) in the range of 0.9330 - 0.9660. It was found that $n = 1$ produced the highest value of R^2 compared with the other values.

Table 2 also shows the kinetic parameters from the various values of reaction orders at a heating rate of 20 °C/min. Various values of n affected the kinetic factors as seen from Table 2. Raising n from 0.5 to 2 led to increase in E_a and A. It should be noted that the reaction order of 1 represented the case for heating rate of 20 °C/min that was also confirmed by the calculation from Figure 3.

Table 2 Kinetic parameters of Napier grass for reaction orders of 0.5, 1 and 2

n	E_a (kJ/mol)	A (s^{-1})	R^2 (-)
0.5	97.63	2.70×10^6	0.9330
1	114.09	1.29×10^8	0.9654
2	163.62	1.28×10^{13}	0.9347

Table 3 Kinetic parameters of Napier grass obtained using Coat-Redfern model for heating rates of 5, 10, 20 and 30 °C/min

Heating rate (°C/min)	T_i* (°C)	T_p** (°C)	T_f*** (°C)	E_a (kJ/mol)	A (s^{-1})	n (-)	R^2 (-)
5	200	298.1	353	90.91	5.84×10^5	1	0.9725
10	201	325.2	357	102.16	7.84×10^6	1	0.9758
20	227	333.8	370	114.09	1.28×10^8	1	0.9654
30	228	337.5	375	113.79	1.58×10^8	1	0.9637

*T_i : Initial decomposition temperature

**T_p : Maximum decomposition rate temperature

***T_f: Final decomposition temperature

Table 3 presents the characteristics of temperature and kinetic parameters of Napier grass at different heating rates. The data in this table can simulate the mass loss using integral numeration with Equation (5) for the selected stage as shown in Figure 4.

When the heating rate was raised, the temperature characteristics (T_i, T_p and T_f) moved up to a higher degree during thermal degradation. The kinetic parameters also increased with the rising heating rate from 10 to 30 °C/min. It can be noticed that the kinetic parameters at 5 °C/min were lower than at 10 °C/min. This may have been caused by the low reaction order at 10 °C/min leading to lower values of the parameters. The thermal characteristics of Napier starting from initial temperature (T_i) to final temperature (T_f) relates to moisture removal and light volatile releasing. The complex hydrocarbon molecules start to break down when the pyrolysis temperature increases.

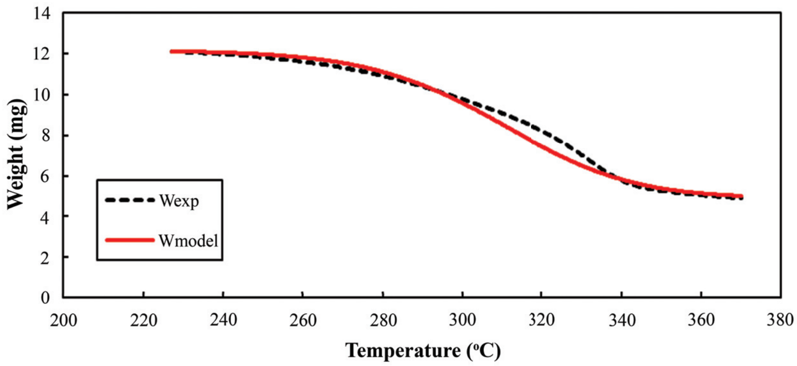

Figure 4 Predicted (Wmodel) and experimental (Wexp) values of mass loss at 20 °C/min

Figure 4 presents the comparison between the simulated and measured data at 227 - 370 ^{o}C at 20 ^{o}C/min. The simulated curve had a good fit for the range 227 - 300 ^{o}C. However, the simulated curve gradually diverted from 300 - 335 ^{o}C, because the reaction in this range was quite rapid due to cellulose degradation [2]. Another value of *n* between 1 and 2 can be used to modify this case to represent the 5 - 10 % error resulting from using the kinetic model for biomass conversion in a linear heating environment [14].

Thermodynamic analysis

To design the large scale pyrolysis process efficiency, not only the kinetic factors but also the thermodynamics factors should be known [9]. In this study, new knowledge of Napier grass in terms of its thermodynamics parameters are presented. The thermodynamic parameters (ΔH, ΔG and ΔS) were determined at peak temperature (T_p) because it represented the maximum rate of Napier process [9]. Table 4 shows the thermodynamic parameters including ΔH, ΔG, and ΔS from the pyrolysis of Napier grass on T_p at 20 ^{o}C/min.

Table 4 Thermodynamic parameters of Napier grass on characteristics temperature for heating rate of 20 ^{o}C/min

Sample	T_p (^{o}C)	E_a (MJ/kmol)	ΔH (MJ/kmol)	ΔG (MJ/kmol)	ΔS (MJ/(kmol.K))
Rice bran [9]	301.43	164.78	159.96	167.18	-12.46
Chicken manure [9]	330.55	175.33	170.03	175.30	-8.26
Napier (This study)	333.80	114.03	131.40	168.12	-60.52

The ΔH was the deviation of energy between the reagent and the activated complex depended on activation energies [9]. According to Table 4, the positive values of ΔH represented an endothermic reaction which requires an external heat source to convert the samples to their transition state [18] - [19].

The ΔG value is the amount of available energy for biomass in pyrolysis process [18], [20]. The ΔG of Napier grass was 131.40 MJ/kmol which was lower when compared with the ΔG values of the rice bran (167 MJ/kmol) and chicken manure (175 MJ/kmol). It pointed that the pyrolysis of Napier grass consumed less energy compared to the rice bran, and chicken manure.

The ΔS value referred to disorder or randomness of energy and matter in a system [9]. It showed how a state of the sample was near or far from its own thermodynamic equilibrium. Entropy also showed the degree of arrangement of the carbon layers in samples [9].

Their negative values showed exothermic reaction which implied an amount of energy was transferred out of the system to environment. It can be noticed that the absolute values of ΔS and ΔG were contrasted. These may refer to the fact that the absolute values of ΔS for the pyrolysis of Napier was higher than that of the other samples, thus this indicated that Napier grass required more energy to reduce its degree of arrangement.

Conclusions

The kinetic and thermodynamics characteristics of Napier grass on the pyrolysis process were identified using TGA experiments with the model-fitting method. The process can be roughly decomposed into moisture and volatiles components. The temperatures of decomposition and activation energies occurred in the ranges of 200 to 338 ^{o}C and 102 to 136 MJ/kmol at heating rate of 5, 10, 20 and 30 ^{o}C/min. An endothermic reaction represented the Napier grass pyrolysis due to the positive ΔH and ΔG and the negative ΔS at characteristic temperatures. The existence of oxygen in the Napier grass represented some exothermic reactions.

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