Pyrolysis Kinetics of the Arid Land Biomass Halophyte Salicornia Bigelovii and Phoenix Dactylifera Using Thermogravimetric Analysis

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Abstract: Biomass availability in arid regions is challenging due to limited arable land and lack of fresh water. In this study, we focus on pyrolysis of two biomasses that are typically abundant agricultural biomasses in arid regions, focusing on understanding the reaction rates and Arrhenius kinetic parameters that describe the pyrolysis reactions of halophyte *Salicornia bigelovii*, date palm (*Phoenix dactylifera*) and co-pyrolysis biomass using thermo-gravimetric analysis under non-isothermal conditions. The mass loss data obtained from thermogravimetric analysis of *S. bigelovii* and date palm revealed the reaction rate peaked between 592 K and 612 K for *P. dactylifera* leaves and 588 K and 609 K for *S. bigelovii* at heating rates, 5 K/min, 10 K/min and 15 K/min during the active pyrolysis phase. The activation energy for *S. bigelovii* and *P. dactylifera* leaves during this active pyrolysis phase were estimated using the Kissinger method as 147.6 KJ/mol and 164.7 KJ/mol respectively with pre-exponential factors of 3.13×10^9/min and 9.55×10^{10}/min for the respective biomasses. Other isoconversional models such as the Flynn-Wall-Ozawa were used to determine these kinetic parameters during other phases of the pyrolysis reaction and gave similar results.

Keywords: halophytes; *Phoenix dactylifera*; *Salicornia bigelovii*; thermogravimetric analysis

1. Introduction

Any arid region biomass-based renewable energy form has to confront a number of challenges, such as the unavailability of enough arable land and lack of fresh water [1]. The two biomasses considered in this study were halophyte *Salicornia bigelovii*, which can be grown in arid lands using saltwater [2] and date palms (*Phoenix dactylifera*), a native arid land biomass and one of the most abundant agricultural residues in arid regions. Pyrolysis of biomass was identified as an effective way of producing pre-cursors for jet-fuel production. Pyrolysis of biomass yields pyro-oils, pyro-char and gases in varying proportions depending on process parameters [3–5]. Pyro oil yields of up to 35% have been obtained by various authors [6] while fast pyrolysis yields have reached up to 75% [5]. Other authors have studied the effects of temperature on pyrolysis oil yields [7,8].

Arid-land lignocellulose biomass pyrolysis literature is scarce [9–11], and co-pyrolysis of these types of biomass have not been reported before. Both *S. bigelovii* and date palm have attracted attention in the biorefinery of arid-land biomass [1,12,13]. From the sustainability perspective, both plants are addapted to the harsh conditions of arid-land. *S. bigelovii* can grow in arid-land coastal areas using seawater, thereby reducing the stress on freshwater demand [12,13]. Date palm leaf residues',

including leaflets and rachis, annual global production is estimated to be over 6 million tonnes [1]. Hence, the pyrolysis of this biomass is an opportunity to divert these residues from landfilling.

Understanding the kinetic parameters and effect of heating rates on reaction rate at different stages in the pyrolysis process is important in the design of pyrolysis reactors specifically for the investigated biomasses and in scaling up the process. It is also necessary in predicting the extent of reaction under different experimental conditions at different times. This work studies the pyrolysis reactions using thermogravimetric analysis for *S. bigelovii*, date palm, and co-pyrolysis of both at different mass ratios. The effects of the heating rate on the reaction rates were determined and key Arrhenius kinetic parameters, i.e., activation energy and pre-exponential factor, were determined. By obtaining thermal loss data from thermogravimetric analysis [14], these kinetic parameters were determined by using pre-determined non-isothermal models such as the Kissinger model, the Flynn-Wall-Ozawa model (FWO), and the improved Kissinger-Akahira-Sunose model (KAS) derived from the generalized Arrhenius model. Results from these methods are compared.

2. Results and Discussion

### 2.1. Effect of Heating Rate on Conversion and Reaction Rate

Heating rates were varied for date palm biomass at 5 K/min, 10 K/min and 15 K/min to observe their effects on peak temperatures and also to obtain isoconversional data points for kinetic analysis. The mass loss curve for the two biomasses and co-pyrolysis are shown in Figure 1. Each mass loss curve (α) in Figure 1 is the resulting average of triplicates. The mass loss (α) is explained in Section 3.
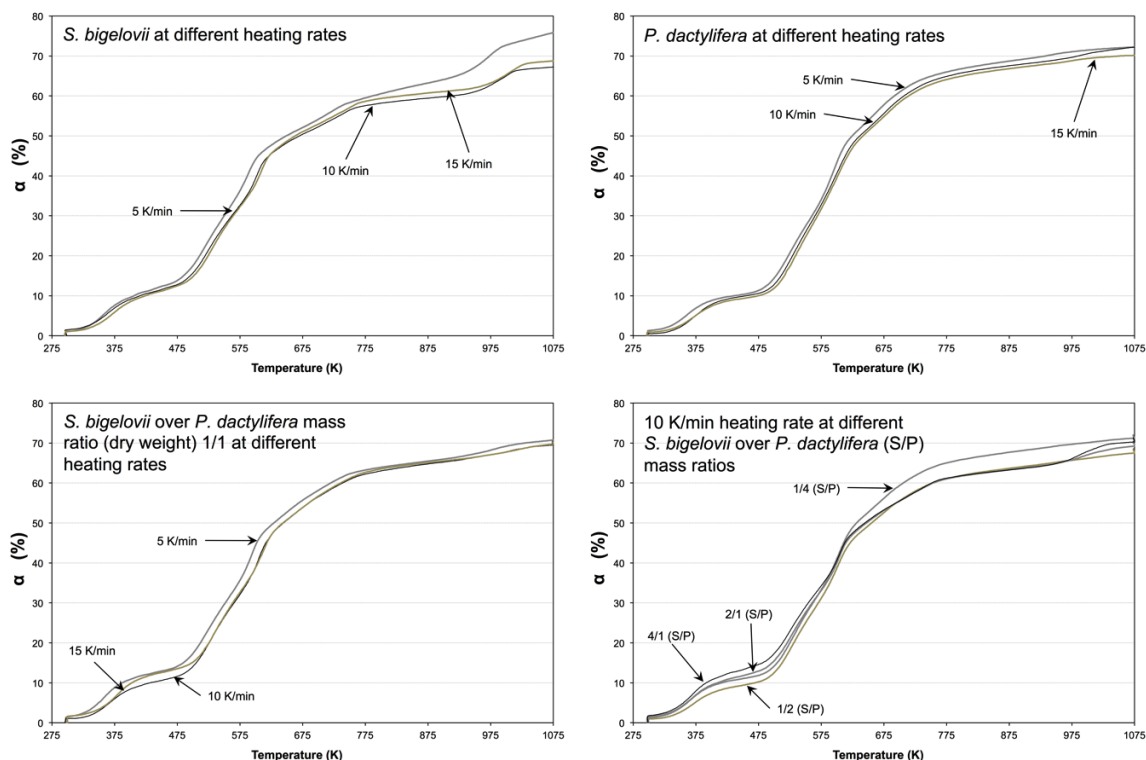
Figure 1. Comparison of the mass loss (α) curves of *S. bigelovii*, *P. dactylifera*, and mixtures of them, at different heating rates (K/min).

The mass loss curves for both biomasses show pyrolysis took place through an identical pathway. Co-pyrolysis biomass followed a pathway between the two pure biomasses as might be predicted; theoretical and kinetic parameters lie between those of the two pure biomasses. The pathway can be categorized into three main phases: Evaporation of water, passive pyrolysis and active pyrolysis

which corresponds to the first two phases having characteristic peaks associated with them on the DTG diagram in Figure 2. The evaporation of water occurs around 373 K, corresponding to the first peak on the curve. Active pyrolysis was observed to take place between 473 K and 633 K as seen with the two peaks in this region. Passive pyrolysis began after active pyrolysis and continued till the end of mass loss.
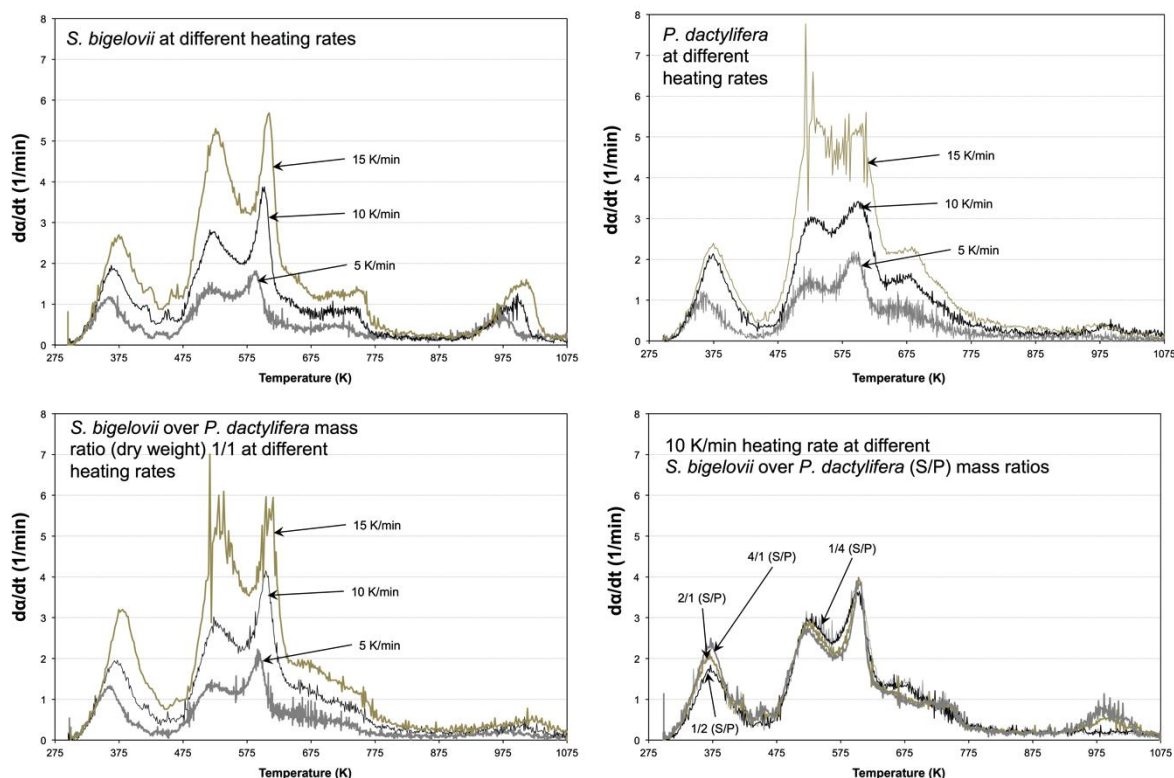
Figure 2. Decomposition rates ($d\alpha/dt$) of *S. bigelovii*, *P. dactylifera*, and mixtures of them, at different heating rates (K/min) showing peak temperatures.

Gasparovic et al. [15] studied the decomposition of hemicellulose, cellulose and lignin and concluded that the decomposition of these three components typically occurred at temperature ranges between 473 K to 653 K, 523 K to 653 K and 453 K up to 1075 K, respectively. This observation reveals that the decomposition of all hemicellulose and cellulose took place during active pyrolysis but decomposition of lignin took place in both active and passive pyrolysis phases.

Increasing heating rate increases the rate of reaction but does not significantly affect the conversion yields at the end of the experiment. Lower heating rates for *S. bigelovii* actually increased the total conversion at the end of the process although the rate of reaction was slower. The reaction rate for all heating rates peaked between 588 K and 602 K during the active pyrolysis phase. These peak temperatures were employed in the kinetic parameter determination using the Kissinger method.

From Figure 2, it is clear that the rate of reaction at all phases of pyrolysis increased with increasing heating rates. However, increased heating rates also led to a more non-uniform reaction decomposition process during the active pyrolysis phase. From the diagram, it can be seen that though the rate of decomposition generally increases with the heating rate and during the active pyrolysis phase, there are no distinct peaks.

2.2. Kinetic Analysis

2.2.1. Kinetic Analysis-*S. bigelovii*

Kinetic parameters were determined for different conversion rates corresponding to different segments of the pyrolysis reaction and the activation energy and pre-exponential factors were determined. The three utilized methods, i.e., Kissinger, FWO, and KAS, are explained in Section 3.

Kissinger Method

The peak temperatures of the DTG curves for *S. bigelovii* and *P. dactylifera* at heating rates of 5 K/min, 10 K/min and 15 K/min were plotted according to the Kissinger model as shown in Figure 3. From the slope of the linear relationship, the calculated activation energy, E (kJ/mol) and the pre-exponential factor, A (1/min), were 147.6 kJ/mol and 3.13×10^9 (1/min) for *S. bigelovii*, respectively, and 164.7 kJ/mol and 9.55×10^{10} (1/min) for *P. dactylifera*, respectively. The peak temperature T_p (K) for *S. bigelovii* at 5, 10 and 15 K/min was 589, 602 and 609 K, respectively. For *P. dactylifera* it was 592, 603 and 612 K.
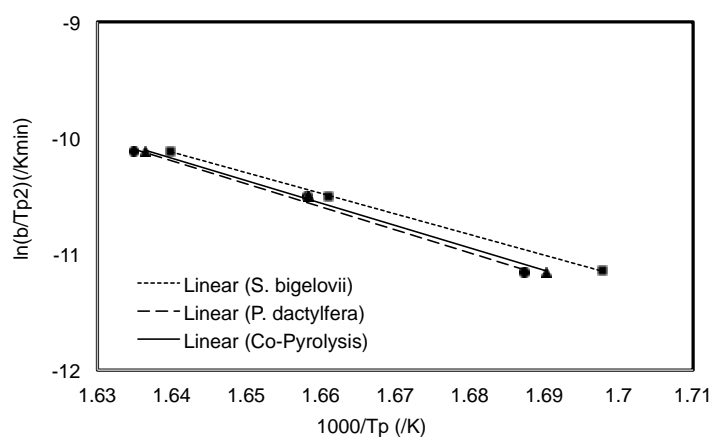

Figure 3. Kissinger curve for *S. bigelovii*, *P. dactylifera* and co-pyrolysis of them at a mass ratio of 1/1, at different isoconversional points.

FWO Method

A plot of $\ln b$ against $\frac{1000}{T_i}$ at the same conversions for heating rates 5 K/min, 10 K/min and 15 K/min was made for varying degrees of conversion of *S. bigelovii* and *P. dactylifera*.

The calculated activation energy, E (kJ/mol) and the pre-exponential factor, A (1/min), were 146.7 kJ/mol and 2.92×10^{20} (1/min) for *S. bigelovii*, respectively, and 204.3 kJ/mol and 1.93×10^{37} (1/min) for *P. dactylifera*, respectively. The FWO plot is shown in Figure 4.
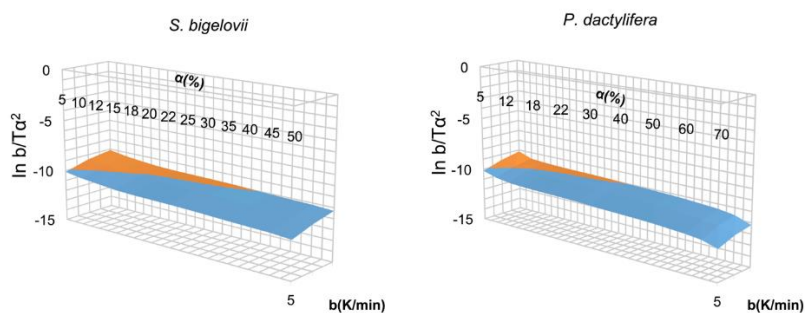
Figure 4. FWO Plot for *S. bigelovii*, *P. dactylifera*.

KAS Method

Figure 5 shows a plot of $\ln \frac{b}{T_\alpha^2}$ against $\frac{1000}{T_\alpha}$ at different heating rates 5 K/min, 10 K/min and 15 K/min at the same conversion for varying conversions from 5% to 50%, during which active pyrolysis takes in *S. bigelovii* and *P. dactylifera*. The calculated activation energy, *E* (kJ/mol), and the pre-exponential factor, *A* (1/min), were 147.3 kJ/mol and 3.57×10^{14} (1/min) for *S. bigelovii*, respectively, and 201.4 kJ/mol and 8.54×10^{31} (1/min) for *P. dactylifera*, respectively.
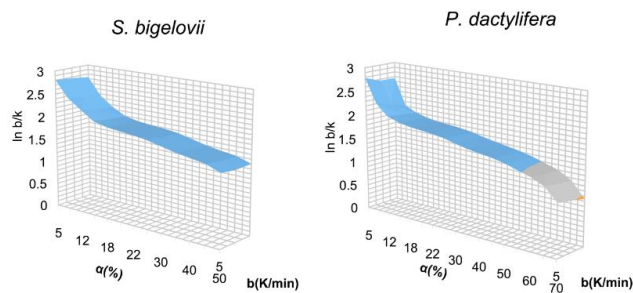

Figure 5. KAS Plot for *S. bigelovii*, *P. dactylifera*.

2.2.2. Summary of Parameters

The kinetic parameters obtained for *S. bigelovii* and *P. dactylifera* leaves from all three methods are summarized in Table 1. The Kissinger method gives one value for the activation energy for the whole process. This value tends to correspond more closely with conversion near peak values at which the Kissinger model was developed. Kinetic parameters for the FWO and KAS method vary with conversion with low values of activation energy at stages prior to active pyrolysis. Activation energy rises during the active phases but tends to reduce at higher conversions during the passive phase for both KAS and FWO methods.

There is very scarce or no literature study on the kinetic parameters of these two biomasses using these methods to compare. Sait et al. [9] have reported activation energies below 44 kJ mol^{-1} for date palm biomass, which significantly deviates from the values reported here, 146–204 kJ mol^{-1}. The activation energy values reported here are in the same order of what has been reported for other non-arid-land lignocellulosic biomass [15–17]. Gasparovic et al. [15] determined the kinetic parameters of wood chip using the generalized isoconversional method and activation energy values of between 131.56 and 215.94 kJ mol^{-1} depending on the conversion. Kongkaew et al. [17] also determined the kinetic parameters for pyrolysis of rice straw using Kissinger, FWO and and KAS methods and obtained 172.62 kJ mol^{-1} for the Kissinger method and activation energy values between 180.54 to 220.27 kJ mol^{-1} and 181.95 to 221.72 kJ mol^{-1} for FWO and KAS, respectively [17]. The same author also obtained 1.46×10^{11} min^{-1} as the pre-exponential factor using the Kissinger method as well. Bartocci et al. [16] have reported activation energies for the three main components of lignocellulosic biomass, 154.1 kJ mol^{-1}, 224.7 kJ mol^{-1}, and 190.5 kJ mol^{-1} for hemicellulose, cellulose, and lignin, respectively.

This shows the activation energy values obtained for both *P. dactylifera* leaves and *S. bigelovii* are within the range of values obtained by other authors using other non-arid-land lignocellulosic biomasses as reactants. Since the Kissinger method adopts the same method to obtain an average value of activation during active pyrolysis, these values are more comparable with values obtained from other authors using different biomasses. FWO and KAS methods, though generally more accurate than the Kissinger method [18], tend to cite averages which also depend on data points. These estimates, however, help to understand the pyrolysis reaction and calculate reaction constants at various stages of the pyrolysis. Also, the fact that the present results are similar to those obtained for non-arid-land lignocellulsic biomass, has interesting implications, e.g., the scale up of the studied arid-land biomass can benefit from the non-arid-land technology.

Table 1. Sumary of kinetic parameters E (kJ/mol) and A (1/min) for *S. bigelovii*, *P. dactylifera* by different methodologies.

Method	*S. bigelovii*		*P. dactylifera*	
	E (KJ/mol)	A (min^{-1})	E (KJ/mol)	A (min^{-1})
Kissinger	147.6	3.13×10^{9}	164.7	9.55×10^{10}
FWO	146.7	2.92×10^{20}	204.3	1.93×10^{37}
KAS	147.3	3.57×10^{14}	201.4	8.54×10^{31}

3. Materials and Methods

Dried *S. bigelovii* (whole plant) were obtained from ISEAS farms in Abu Dhabi. Dried *P. dactylifera* leaves were also obtained from a farm in Abu Dhabi. All feedstock were shredded, milled and filtered through a sieve to obtain particle sizes below 0.5 mm. A sample of *S. bigelovii* and *P. dactylifera* were milled together in the ratio 1:1 for co-pyrolysis. Thermogravimetric analysis was conducted with a Netzch STA 449F3 STA449F3A-0625-M instrument and an aluminum crucible (Al_2O_3) under a Nitrogen atmosphere. The mass loss of biomass (α) was observed over a temperature program from 283 K to 1073 K. For each test, the mass loss (α) was performed in triplicates. The heating rate was kept constant at 10 K/min. Isothermal conditions were created at the start and end of the temperature program to eliminate noise. The heating rate was then varied at 15 K/min and 5 K/min respectively for both biomasses.

3.1. Isoconversional Methods for Kinetic Parameter Estimation-Theory

The pyrolytic reaction of biomass converts biomass to char, oil and gases. The kinetics of the reaction can be described by defining a degree of conversion and using the Arrhenius equation. The isoconversional method is based on the fact that activation energy and pre-exponential are not constant throughout the decomposition but depend on the degree of conversion. Data points at the same conversion are gathered for different heating rates and each isoconversional curve is used to estimate the kinetic parameters at that conversion.

If m_i is the initial mass of sample placed in the crucible, and m_f is the mass of sample left after pyrolysis, a degree of conversion (α) for a given sample mass m at any temperature T during the process can be defined as:

$$\alpha = \frac{m_i - m}{m_i - m_f} \tag{1}$$

From the Arrhenius equation,

$$k(T) = A e^{\frac{-E}{RT}} \tag{2}$$

where k is the reaction rate constant (varies with temperature), E is the activation energy, A is the pre-exponential factor, R is the gas constant, and T is temperature in Kelvin.

The rate of decomposition can then be defined as a function of conversion and temperature:

$$\frac{d\alpha}{dt} = f(\alpha)k(T)$$

$f(\alpha)$ can be expressed as:

$$f(\alpha) = (1 - \alpha)^n,$$

where n is the reaction order.

Since the temperature program was run with a constant heating rate from 298 K to 1073 K, the temperature at any time t can be written as:

$$T = Ti + bt$$

where T = initial temperature = 298 K and b is the constant heating rate.

The rate of decomposition can be written as:

$$\frac{d\alpha}{dt} = (1-\alpha)^n A e^{\frac{-E}{RT}} \tag{3}$$

3.1.1. Kissinger Method

For a predetermined reaction order, the rate of decomposition can be plotted at the same conversion for different heating rates. Also the decomposition rate is maximum at peak temperatures (T_p).

$$\frac{d}{dt}\frac{d\alpha}{dt} = \frac{d}{dt}\left((1-\alpha)^n A e^{\frac{-E}{RT}}\right) = 0 \tag{4}$$

$$\ln\frac{b}{T_p^2} = -\frac{E}{RT_p} + \ln\frac{AR}{E} \tag{5}$$

A plot of $\ln\frac{b}{T_p^2}$ against $\frac{1000}{T_p}$ gives a straight line with slope $-\frac{E}{R}$.

3.1.2. FWO Method

Flynn-Wall-Ozawa developed a method where the activation energy is found by plotting the heating rates against the temperature at which a given conversion is obtained at that heating rate.

$$\ln b = -1.052\frac{E_\alpha}{RT_\alpha} + \ln\frac{A_\alpha E_\alpha}{Rf(\alpha)} - 5.331 \tag{6}$$

A plot of $\ln b$ against $\frac{1000}{T_i}$ gives a straight line with slope $-1.052\frac{E_\alpha}{R}$. This is used to find E_α.

3.1.3. KAS Method

The Kissinger-Akahira-Sunnose Method

$$\ln\frac{b}{T_\alpha^2} = -\frac{E_\alpha}{RT_\alpha} + \ln\frac{A_\alpha R}{E_\alpha f(\alpha)} \tag{7}$$

A plot of $\ln\frac{b}{T_\alpha^2}$ against $\frac{1000}{T_\alpha}$ at different heating rates at the same conversion gives a straight line with slope $-\frac{E_\alpha}{R}$. The activation energy at that conversion E_α is found from the slope.

4. Conclusions

Activation energy obtained using the Kissinger method for *S. bigelovii* and *P. dactylifera* leaves were 147.6 KJ/mol and 164.7 KJ/mol, respectively, while pre-exponential factors of 3.13×10^9/min and 9.55×10^{10}/min for *S. bigelovii* and *P. dactylifera* leaves were obtained from DTG data. Other values at different stages during the pyrolysis process were also obtained using other isoconversional methods like the FWO, KAS and the generalized isoconversional theories. The mass loss data also revealed the peak temperatures at which reaction is fastest during active pyrolysis. Results of DTG also showed the reaction proceeded in similar phases for the two sampled biomass types, and co-pyrolysis of them at different mass ratios.

Conflicts of Interest: The authors declare no conflict of interest.

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