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STUDY ON THE KINETICS AND PYROLYTIC CHARACTERISTICS OF NAVEL ORANGE RESIDUE BY THERMOGRAVIMETRIC ANALYZER

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ABSTRACT

Pyrolytic behaviors of biomass (navel orange residue, NOR) and kinetic parameters were investigated by a thermogravimetric (TG) analyzer in N₂ atmosphere. The results showed that the thermal degradation temperature range of NOR varied with heating rates; the slower heating rate, then narrower temperature range. The results indicated that total mass loss had to do with heating rate. Based on the DTG data with different heating rates, activation energy was calculated by three methods. The activation energy was from 104.75 to 178.85 kJ·mol⁻¹; the order of reaction was 1.19.

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INTRODUCTION

Energy requirement is increasing in the global, which indicates that research on a cheap, alternative energy source is necessary (Martínez *et al.*, 2014). Biomass is cheap and renewable and can be converted to gasoline and diesel, as well as chemical products. Renewable biomass-energy contributes to reduce global warming, and mitigates environmental and energy problems. Fruit residues biomass (FRB) is wastes from daily life and agricultural processes, and the annual amounts of that are increasing year by year. To date, land filling and discarding are by far the dominant approach for FRB treatment. Today, many cities in China are surrounded by garbage, and many landfills reach saturation. In order to protect environment and develop economy, an efficient method is needed to treat FRB. Of all the methods, thermal conversion of FRB is becoming popular. The two most common thermal conversion processes being considered are pyrolysis and gasification. In pyrolysis, biomass is fast heated to 873 K in an inert atmosphere to produce oil that can be used as a feedstock. Rapid thermal conversion is promising utilization method for the conversion of biomass toward a

clean fuel source that can substitute fossil fuels in turbine *et al* (Liu *et al.*, 2015; Du *et al.*, 2013; Bahng *et al.*, 2009). In order to design the necessary equipments for thermochemical process, it is crucial to understand the thermal behavior and kinetic parameters of a biomass during its thermal conversion. Thermo-analytical techniques such as TGA, DSC and DTG are useful tools for kinetic studies of biomass pyrolysis (Liu *et al.*, 2015; Flynn and, 1964; Lipska and Parker, 1966; Sørnum *et al.*, 2001; Shuping *et al.*, 2010). Traditionally, discrete isothermal methods of analysis can obtain kinetic data from biomass pyrolysis reactions. Interest in the methods, however, has gradually waned because they are considered toilsome (White *et al.*, 2011). Conversely, dynamic methods performed under non-isothermal conditions have attracted much appeal (Agrawal, 1992). Non-isothermal methods by multiple heating rates can provide more reliable estimates of kinetic parameters (Antal *et al.*, 1980). Compared the data from cellulose pyrolysis in nitrogen and steam as carrier gas, and there are apparent differences in the data. Ozawa (1992) applied iso-conversion methods to estimate activation energy. Starink (1996) compared three iso-conversion methods, and he thought the Kissinger method is generally the most accurate. Wight *et al.*, (1997) thought the kinetics of solid-state reactions generally cannot be assumed to follow simple rate laws that are applicable to gas-phase reactions. Hajimirsadeghi

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et al., (2009) reported effect of the ASTM and Ozawa methods, as well as particle size of samples on the values of the kinetic parameters. Zou et al., (2010) investigated pyrolysis characteristics and kinetics of the marine microalgae *Dunaliella tertiolecta* by thermogravimetric analyzer. Pareek et al. (2015) comprehensively reviewed the development of the reaction kinetics of pyrolysis biomass. Mahinpey et al [18] developed a new method to obtain the rate constant and activation energy independent of a kinetic model, which does not require any assumed kinetic model (Fang et al., 2015; Zhao et al., 2013). Calculated the values of average activation energies of biomass (macro-algae, paper sludge) by FWO and KAS method. Narayanan et al., 2013 analyzed thermal behaviour of biomass samples such as rice husk, saw dust in an inert nitrogen atmosphere from ambient temperature to 1073 K by a thermo-gravimetric analyzer. Ataíde et al., 2015 reported the kinetics of decomposition of this variety of lignocellulosic sorghum bagasse by the independent parallel reaction model. However, the kinetic parameters obtained do not only have with heating rates but also the type of biomass and calculated methods. Now, high heating rates (>10K/min) are adapted, and result in heat transfer lag. Moreover, the pyrolytic behavior of NOR is not reported. In this paper, the pyrolytic behaviors of NOR is investigated under a nitrogen atmosphere by a thermogravimetric analyzer. The kinetics parameters are calculated by different methods. This study aims to investigate the feasibility of biomass pyrolysis in solid waste disposal and to gather useful data in the solid waste treatment.

Experimental

MATERIALS

Navel orange residues are from Jiangxi Province in China. The samples are dried at 373 K for 8 h. Then they are ground and sieved to particle size between 150 μm and 200 μm for the experiments of pyrolysis analysis.

Thermogravimetric (TG) experiments

The TG instrument (SDT Q600) was used, and the sample mass-losses with changes of temperatures were recorded. Sample (ca.10mg) was tested a time under 100 mL·min⁻¹ N₂ flow from room temperature to 1173 K with a heating rate. From these tests, the evolution with temperature of mass loss (TG) and the mass-loss rate (DTG) were obtained for pyrolysis. To ensure the accuracy of results, all the experiments were carried out three times.

Pyrolysis kinetic analysis

The kinetics of biomass decomposition can be expressed by the following canonical equation (1) (Friedman, 1964).

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A \exp\left(\frac{-E_a}{RT}\right)f(\alpha) \dots\dots\dots (1)$$

Taking natural logarithms of each side from Eq. (1) yields:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln\left[\beta\left(\frac{d\alpha}{dT}\right)\right] = \ln[Af(\alpha)] - \frac{E_a}{RT} \dots\dots\dots (2)$$

Biomass degradation is independent of temperature and depends only on the rate of mass loss if the conversion function f(α) remains constant. A plot of ln [da/dt] versus 1/T

yields a straight line, the slope of which corresponds to E_a/R. Where t denotes time, α signifies the degree of conversion, or extent of reaction, da/dt is the rate of the isothermal process, and f(α) is a conversion function that represents the reaction model used and depends on the controlling mechanism. Non-isothermal rate expressions, which represent reaction rates as a function of temperature at a linear heating rate, β, can be expressed through an Eq. (3):

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt} \cdot \frac{dt}{dT} = \frac{d\alpha}{dt} \cdot \frac{1}{\beta} \dots\dots\dots (3)$$

An expression of the rate law for non-isothermal conditions can be obtained by substituting Eq. (1) into Eq. (3):

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(\frac{-E_a}{RT}\right)f(\alpha) = \frac{A}{\beta} \exp\left(\frac{-E_a}{RT}\right) (1 - \alpha)^n \dots\dots (4)$$

The Flynn–Wall–Ozawa (FWO) method (Flynn and Wall, 1964 and 1966; Ozawa, 1992 and 1965; Flynn, 1997) is an integral isoconversional technique that assumes the apparent activation energy remains constant throughout the reaction (i.e., from t = 0 to t_α, where t_α is the time at conversion α). Integrating Eq. (4) with respect to variables α and T:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^{t_\alpha} \exp\left(\frac{-E_a}{RT}\right) dT \dots\dots\dots (5)$$

$$g(\alpha) = \frac{AE_a}{\beta R} \int_\alpha^\infty \frac{\exp^{-x}}{x^2} dx = \frac{AE_a}{\beta R} p(x) \dots\dots\dots (6)$$

where p(x) representing the rightmost integrand in Eq. (6) is known as the temperature integral. p(x) is treated by Doyle’s approximation for the temperature integral, and then both sides of Eq. (6) are taken logarithms. FWO method is described by in following Eq. (7).

$$\log \beta = \log\left(A \frac{E_a}{Rg(\alpha)}\right) - 2.315 - 0.4567 \frac{E_a}{RT} \dots\dots\dots (7)$$

In the FWO method, plots of logβ versus 1/T for different heating rates produce parallel lines for a constant conversion. The slope (0.4567E_a/R) of these lines is proportional to the apparent activation energy. Eq. (6) is treated by another empirical approximation derived by Doyle, and KAS method (Kissinger, 1957; Starink, 2013; Chunxiu et al., 2004) is described by Eq. (8).

$$\ln\left(\frac{\beta}{T_m^2}\right) = -\frac{E_a}{R} \left(\frac{1}{T_m}\right) - \ln\left[\left(\frac{E_a}{AR}\right) \int_0^\alpha \frac{d\alpha}{f(\alpha)}\right] \dots\dots\dots (8)$$

Where T_m is the temperature at the maximum reaction rate. Assuming α has a fixed value, E_a can be determined from the slope of the straight line obtained by plotting ln(β/T_m) versus 1/T_m. The integral method based on the Coats and Redfern (CR) Eq. (9) (White et al., 2011; Coats and Redfern, 1964) was criticized for the non-unique or indistinguishable kinetic triplet, and the modified Coats–Redfern (CR*) method (Brown et al., 2000; Burnham and Braun, 1999), which provides an integral isoconversional technique equivalent to those of FWO and KAS, has been advanced.

$$\ln\left(\frac{-\ln(1 - \alpha)}{T^2}\right) = \ln\left[\frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT} \dots\dots\dots (9)$$

The CR* method rearranges terms in Eq. (9) to yield:

$$\ln\left[\frac{\beta}{T^2(1 - 2RT/E_a)}\right] = \ln\left[\frac{AR}{g(\alpha)E_a}\right] - \frac{E_a}{RT} \quad \dots\dots\dots (10)$$

The order of reaction *n* is determined by Eq.(11), where S is defined by Eq. (12). The value of S can be determined from the derivation of DTG curve. After getting the values of *n* and *E_a*, the frequency factor *A* can be solved from Eq. (4) (Jiang *et al.*, 2010).

$$S = 0.63n^2 \quad \dots\dots\dots (11)$$

$$S = \frac{\left(\frac{d^2\alpha}{dT^2}\right)_{left}}{\left(\frac{d^2\alpha}{dT^2}\right)_{right}} \quad \dots\dots\dots (12)$$

RESULTS AND DISCUSSION

TG and DTG analysis of NOR

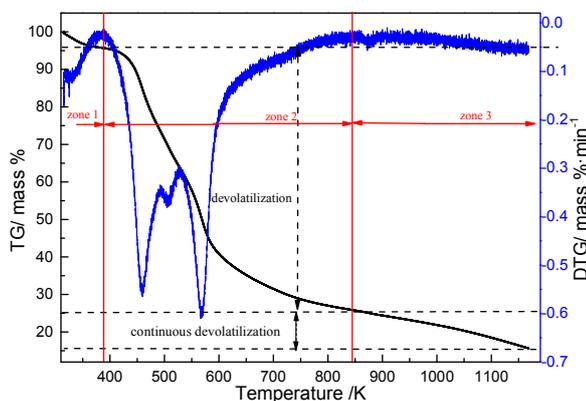


Fig. 1. TG and DTG of NOR with 1K/min

Fig. 1 shows the TG mass-loss and DTG analysis curves of NOR during pyrolysis. Here, a slow heating rate is programmed to avoid the temperature differences between samples and heating device. Four peaks centered at 333-353, 458, 512 and 569 K are distinguished, which indicates that NOR undergoes four significant mass loss processes during pyrolysis. Four peaks correspond to the loss of free water, hemicellulose, cellulose, and lignin, respectively. Peak at 333-353K (zone 1) corresponds to the loss of moisture. Peak centered at 458 K represents the major loss of hemicellulose, most of whose largest fraction decomposes between 180 and 573 K (Shen *et al.*, 2010; Mansaray and Ghaly, 1998). The peak at around 512 K is attributed to the loss of lignin, since lignin decomposes over a wide temperature range from 413 to 873K (Vamvuka *et al.*, 2013; Stefanidis *et al.*, 2014; Zhou *et al.*, 2013). The peak at around 569 K is attributed to the loss of cellulose, most of which decomposes between 553 and 653K (Shen *et al.*, 2010; Mansaray and Ghaly, 1998). The pyrolysis of hemicellulose, cellulose and lignin mainly occurred at zone 2. Our result is inconsistent with the reported results for heating rate, but the result obtained with high heating rate is in accord with the aforementioned, which is attributed to heat transfer limit. The area of peaks is normalized to approximate the initial mass fraction of each component. Hemicellulose and cellulose are major chemical components of NOR, and content of lignin is

lower than that of hemicellulose and cellulose. The TG curve of sample shows an initial slight mass loss between ambient temperature and 373 K (dehydration). In the stage, mass loss was attributed to the elimination of physically absorbed water in the sample and superficial or external water bounded by surface tension. After this stage, a very slight loss of mass followed up to a temperature of 383-453 K depending on the heating rate used. Then a major mass loss (where the main degradation occurred,) occurred, which ended by approximately 453-823 K depending on heating rate used and corresponded to the devolatilization stage referred to as the active pyrolysis zone. The highest mass loss occurred in the stage and was about 84% of the total mass-loss. Most of the cellulose, hemicellulose, and lignin in the sample were degraded and volatilized, during which carbon, hydrogen, and oxygen compounds are released. After the devolatilization stage, the TGA curves became flattened; mass loss continued to occur, and the ash mass at the final temperature of 1173 K was approximately 12% by mass of the original NOR. In the stage, mass-loss was from decomposition of mineral salt.

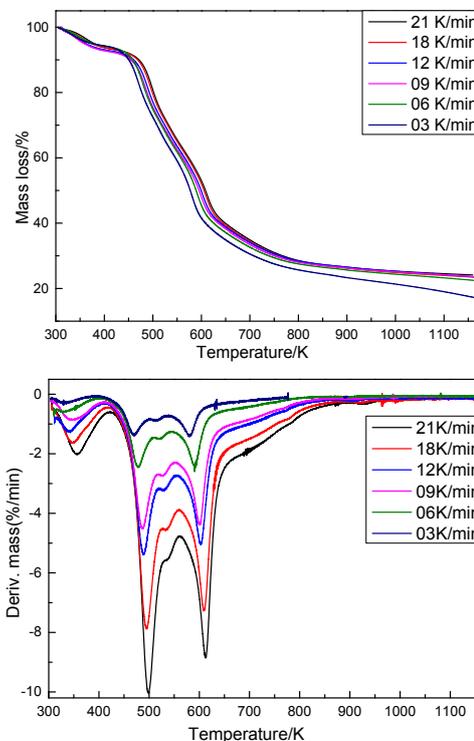


Fig. 2. TG and DTG curve of NOR with different heating rates

It is found that total mass-loss increases with heating rate while decreases (Table 1), and temperature interval increases at the same mass-loss. Namely, temperature shifts to high temperature when heating rate increases. Amount of ash increases with heating rate used, which is attributed to mass transfer limit. This indicated that sufficient time was not available for the consecutive pyrolytic reactions (fragmentation, formation of combustible volatiles, dehydration and the formation of carbonaceous char) to occur at higher heating rate. Thus, larger percentages of samples were left unconverted at higher heating rates (Shen *et al.*, 2010; Lipska-Quinn *et al.*, 1985).

Table 1 mass loss of NOR with different heating rates

Heating rate K/min	3	6	9	12	16	18	21
Total mass-loss %	82.9	79.4	78.6	77.4	76.8	76.1	75.9

Fig. 2 shows the DTG curves of NOR at different heating rates. In all the processes, it is found the general shift to high temperature when the heating rate increases (Table 2). The heating rate increases, T_p (peak temperature) shifts to higher temperature and reaction interval increases (Table 2). In general, temperature shifts to higher temperature when heating rate increases, which is attributed to heat transfer limit. At first temperature intervals, intervals vary from 367 to 409 K. Elimination of moisture and volatilization of small molecular compounds from NOR are observed at the stage. At second one, intervals vary from 651 to 833 K. The main reaction region appears within the range of 393-873K, in which devolatilization occurs. In fact, another peak centered at 853-973K is attributed to continuous devolatilization process, in which char and some inorganic compounds formed in the process are degraded. An amount of ash depends on heating rate.

Table 2 effect of heating rates on temperature and reaction intervals

Heating rate	3	6	9	12	18	21
T_p (K)/(K/min) Zone						
1	328	332	339	343	349	357
2	466	477	483	486	497	499
	514	521	525	530	534	539
	581	591	599	601	611	612
Reaction intervals/K						
1	84	103	110	112	130	136
2	378	441	447	452	458	460

Note: peak temperature (T_p)

Kinetic analysis of NOR pyrolysis

In fact, the process mainly consists of elimination of moisture, degradation (hemicellulose, cellulose, and lignin), and char pyrolysis. It is important to select an appropriate temperature range to calculate parameters, so data of devolatilization stage (zone 2) were applied.

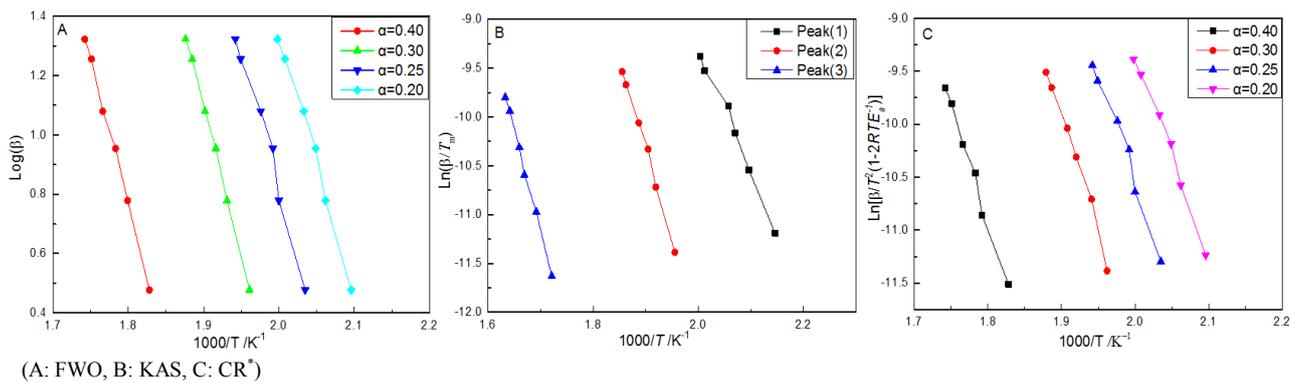


Fig. 3. Activation energy calculated by different methods

Table 3. E_a and $\ln A$ calculated by FWO, CR, and KAS methods

Heating rate(°C)	3	6	9	12	18	21	Average
Parameter							
S	0.879	0.975	0.951	0.826	0.803	0.902	0.889
n	1.18	1.24	1.20	1.14	1.13	1.20	1.19

Table 4. The order of reaction n

E_a (KJ/mol)	0.23	0.25	0.39	0.47
α (lnA) Methods				
FWO	107.0(17.5)	157.8 (28.6)	167.7 (29.3)	172.9(27.7)
CR	117.9(20.2)	164.7(30.2)	179.3(30.2)	178.8 (28.7)
KAS	$\alpha=0.17$ 104.7(21.4)	$\alpha=0.34$ 157.4(31.8)	$\alpha=0.54$ 173.1(31.1)	

Fig.3 shows activation energy calculated from the fitting curves. The kinetic parameters calculated with the help of the three different above-mentioned methods lie within the confidence limits of the results from each method. The activation energy of NOR was calculated by FWO, KAS, and CR* methods. Plots of $\log \beta$, $\ln(\beta/T_m^2)$ and $\ln[\beta/T_m^2(1-2RT/E_a)]$ versus $1/T, 1/T_m$ and $1/T$ with a certain conversion give straight lines with slopes of $-0.4567E_a/R$ and $-E_a/R$, the activation energy can be determined. Results were listed in Table 3. It was found that the activation energy depended on conversion of NOR. The activation energy increased with conversion, which was attributed to the fact that the decomposition of hemicellulose is a dominant reaction at a low temperature; the decomposition of cellulose was a major reaction at a high temperature. Moreover, the results calculated by three methods were consistent, because the essence of equations was same though the forms of them were different.

Especially the activation energy was calculated by CR*, an iterative process must be used by assuming an initial value for E_a and then re-evaluating $-E_a/R$ and slope of a line until the desired level of convergence. The value of S did not change markedly with heating rates for NOR, indicating that the order of reaction n did not vary significantly with heating rate. An average value of S was used for calculating n by Eq. (11). The frequency factor (A) was calculated by Eq. (4) after obtaining the values of E_a and n . The kinetic parameters are given in Table 3 and 4. The activation energy of NOR were in the range of 104.75–178.85 kJ/mol, which depends on conversion (α), indicating that the pyrolysis of NOR contains different processes. The activation energy of biomass calculated here different from the values reported (Liu et al., 2015; Wilson et al., 2011; Mu et al., 2015), which was attributed to heating rate (Caballero et al., 1997), biomass species (Aboulkas and El Harfi, 2009; Jauhiainen et al., 2004), particle size (Sovizi et al., 2009), and models (Tonbul, 2007).

The data from Table 3 shows that there is a strong correlation between the kinetic model that is used to calculate E_a and the resulting value. Another probable cause of variance in data might result from changes of reaction mechanisms occurring at different temperatures. The compositional complexity of NOR results also in the inconsistent E_a values. The data from Table 4. Shows the consistent n values, indicating that the order of reaction does not vary with heating rate in the pyrolysis process of NOR. The mean value of n (1.19) was used to evaluate the frequency factor. It was found that $\ln A$ varies dramatically for the changes of E_a , which indicates the effect of the physical and chemical composition of NOR and the used models on the values.

Conclusions

The pyrolytic and kinetic behaviors of NOR were investigated by a thermogravimetric analyzer. The DTG curves revealed the presence of two major peaks, which corresponded to hemicellulose and cellulose decomposition, respectively. As heating rate increased from 3 to 21 K·min⁻¹, there was a shift to higher temperature for the maximum rate of mass loss for the DTG and amount of ash increases. The kinetic parameters were evaluated. The activation energy was calculated using the Friedman, CR, and KAS method, which ranged from 104.7 to 179.3 kJ/mol and depended on conversion. The order of reaction of NOR is 1.19 and is not impacted by heating rate. $\ln A$ ranges from 17.5 to 31.8. The data from this study are useful for preliminary assessment of NOR as a feedstock for thermochemical conversion systems.

The definition of nomenclature

Nomenclature	
α conversion	n reaction order
β heating rate (K/min)	T absolute temperature (K)
R universal gas constant (J/mole K)	A frequency factor (/min ⁻¹)
E_a activation energy (kJ/mole)	k rate constant

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