

Pyrolysis properties and kinetics of mandarin peel

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Abstract—The thermal property of the pyrolysis reaction of mandarin peel was studied using thermogravimetric analysis (TGA). Thermogravimetric analyses with temperature increases of 10, 20 and 40 °C/min showed large weight losses within the temperature range 150-590 °C. Differential thermogravimetric (DTG) analysis curves illustrated that the pyrolysis of mandarin peel was a multi-step process, consisting of water desorption, the decomposition of pectin, hemicellulose, cellulose and lignin, and devolatilization of the residual char. The apparent activation energies ranged between 119 and 406 kJ/mol, depending on the pyrolytic conversion. The pyrolysis products were analyzed, using pyrolyzer-gas chromatography/mass spectrometry (Py-GC/MS), to evaluate mandarin peel as a renewable source of valuable industrial chemicals. The pyrolysis products of mandarin peel contained high portions of methanol and acetic acid, as well as valuable compounds, such as limonene and vitamin E.

Key words: Mandarin Peel, Pyrolysis, TGA, Py-GC/MS

INTRODUCTION

The importance of renewable energy sources has rapidly increased due to the high price of crude oil and environmental concerns related to fossil fuels. Of various energy resources, biomass, in the form of bio-fuels (solid, liquid and gaseous), can directly replace fossil fuels (solid, liquid and gaseous), either fully or in blends of various fractions, and has attracted considerable interest as a promising renewable energy resource over the last few decades. Moreover, since biomass is CO₂-neutral, and contains negligible sulfur, nitrogen and ash components, its adverse effects on the environment on energy production and consumption are minimal compared to conventional fossil fuels. In general, biomass is defined as living and recently dead biological materials, which are being continuously produced by photosynthesis [1-5].

Mandarin farming is an important industry and main resource of local income on Jeju-Do, Korea. In response to the overproduction and circulation problem associated with mandarin since 2000, mandarin processing plants have now been formed as public corporations. In 2005, 125,343 tons (about 18% of total mandarin produced in Korea) of mandarin fruits were processed, with 55,000 tons of mandarin byproducts produced [6]. Accordingly, the disposal of mandarin byproducts has become a major issue in Jeju-Do. Many of the byproducts from the mandarin industry have been used as oriental medicine and animal feed, while a significant amount has been discharged to international waters. Ocean dumping, however, was re-

cently banned by the marine protection policy. Moreover, the demand of mandarin peel as an oriental medicine has decreased. Therefore, the development of a new method to treat mandarin byproducts is urgently required.

Studies on pyrolysis, a representative thermochemical method for the conversion of biomass, have been widely conducted for the conversion of waste biomass materials into liquid and gaseous hydrocarbons and a solid char residue [1-7]. The pyrolysis of mandarin peel has the potential as an eco-friendly treatment technique and sustainable energy source, especially in mandarin production areas, such as Jeju-Do, and some recently published papers can be found on the subject. To our knowledge, Aquiar et al. [8] studied the pyrolysis of orange peel residues in a fixed bed reactor and Miranda et al. [9] studied the pyrolysis of sweet orange dry peel using a thermogravimetric analyzer and bench-scale pyrolysis experiments. However, an analysis of the kinetic data and detailed research on the pyrolysis byproducts at different reaction temperatures remain to be reported. In addition, the chemical composition of orange peel is quite different from that of mandarin peel [10]. The thermal degradability is affected by the chemical composition, as the different components of the lignocellulosic material have different thermal behaviors [8,11]. Therefore, a fundamental investigation on the kinetic analysis and product characteristics for the pyrolysis of mandarin peel needs to be performed prior to its application in Jeju-Do.

The main objective of this study was to investigate the pyrolytic characteristics and determine the kinetic parameters during the pyrolysis of mandarin peel, using thermogravimetric and kinetic analyses via a model-free method. The pyrolysis products were also evaluated using pyrolyzer-gas chromatography/mass spectrometry (Py-GC/MS).

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EXPERIMENTAL

1. Raw Material

The mandarin peel was obtained from mandarins grown in Jeju-Do. The mandarin peel was dried under atmospheric pressure at ambient temperature. The dried mandarin peel was cryo-milled with liquid nitrogen and sieved to particle sizes between 200 and 300 μm . Proximate analyses of the samples were performed based on ASTM methods E871, E872-82 and D1102-84. The moisture was evaporated in an oven at 110 $^{\circ}\text{C}$ for 4 hours. The volatile matter was removed in a furnace, under an inert atmosphere, at 950 $^{\circ}\text{C}$ for 7 minutes. The ash content was then measured by burning the combustible matter in air at 600 $^{\circ}\text{C}$. The C, H, N and S contents of the samples were determined using an Elemental Analyzer (Flash EA 1112series/CE Instruments), which can burn up to 2 mg of sample at 1,100 $^{\circ}\text{C}$, using a BBOT standard (C 72.53%; N 6.51%; H 6.09%; S 7.44%; O 7.43%), with the oxygen content calculated by difference. The higher heating values (HHVs) of the samples were then estimated from the elemental composition, using the Dulong equation. The results of the proximate and ultimate analyses, as well as the HHV for the mandarin peel, are shown in Tables 1 and 2.

2. Thermogravimetric Analysis (TGA)

To investigate the kinetic properties of the pyrolysis reaction of mandarin peel, thermogravimetric analysis was performed using a thermogravimetric analyzer, in a nitrogen atmosphere, with three different heating rates; 10, 20 and 40 $^{\circ}\text{C}/\text{min}$.

3. Kinetic Analysis

The results of the thermogravimetric experiments were expressed as a function of conversion X , which was defined as:

$$X = (W_0 - W) / (W_0 - W_{\infty}) \quad (1)$$

where W_0 is the initial mass of sample, W the remaining mass of the pyrolyzed sample and W_{∞} the final residual mass.

The kinetic analysis of the thermal decomposition of biomass is usually based on the rate equation for solid state decomposition processes [12,13]:

$$dX/dt = A \exp[-E/RT] f(X) \quad (2)$$

where X is the conversion of the sample, $f(X)$ the reaction model, A the pre-exponential factor and E the activation energy.

The kinetic analysis using the 'model-free method' allows E to be estimated as a function of the conversion, without choosing a reaction model. Therefore, many investigations [14-17] have employed the model-free method in the analysis of the non-isothermal decomposition of biomass.

In this research, the Friedman method [17] was employed to obtain the pyrolysis kinetic parameters from the thermogravimetric data. The method involves taking logarithms of the Arrhenius rate equation, as shown below:

$$\ln(dX/dt) = \ln(\beta dX/dT) = \ln A + \ln f(X) - E/RT \quad (3)$$

A plot of $\ln(dX/dt)$ against $1/T$ for the same degree of conversion from the data taken at various heating rates will result in a series of lines, each with a slope equal to $-E/R$, corresponding to each value of conversion, X , at different heating rates, β . Thus, the activation energy, E , at each conversion, X , can be obtained.

4. Py-GC/MS Analysis

A vertical furnace type pyrolyzer (Py-2020D, Frontier-Lab Co.) was directly coupled with a gas chromatograph/mass spectrometer (7890A GC/5975C inert MSD, Agilent), which employed an ultra alloy capillary column (UA-5, 30 m \times 0.25 mm i.d.) coated with crossed linked 5% diphenyl 95% dimethyl-polysiloxane at a film thickness of 0.25- μm . About 6 mg of dried mandarin peel powder, taken in a deactivated metal sample cup, was introduced into the heated center of the pyrolyzer under a flow of helium carrier gas for the fast pyrolysis of the sample at 400, 500 and 600 $^{\circ}\text{C}$. A carrier gas flow rate of 50 ml/min at the pyrolyzer was reduced to 1 ml/min at the capillary separation column using an inlet splitter. The GC oven temperature was programmed to increase from 40 (5 min) to 320 $^{\circ}\text{C}$ (10 min) at a heating rate of 5 $^{\circ}\text{C}/\text{min}$. The identification of each peak on the program was carried out using the Nist 8th library (Nist).

RESULTS AND DISCUSSION

1. Thermogravimetric (TG) and Differential Thermogravimetric (DTG) Analysis

Fig. 1 shows the degree of conversion versus temperature for the mandarin peel obtained at heating rates of 10, 20 and 40 $^{\circ}\text{C}/\text{min}$ for the TGA. The TG curves obtained at a heating rate of 10, 20 and 40 $^{\circ}\text{C}/\text{min}$ showed a first stage between 30 and 154 $^{\circ}\text{C}$ ($X=0\sim 0.12$), followed by second, third, fourth and final stages between 154 and 203 $^{\circ}\text{C}$ ($X\sim 0.16$), 203 and 322 $^{\circ}\text{C}$ ($X\sim 0.59$), 322 and 409 $^{\circ}\text{C}$ ($X\sim 0.84$) and 410 and 590 $^{\circ}\text{C}$ ($X\sim 0.97$), respectively. However, 22.7% solid residues (W_{∞}) remained in the sample cup after the TG analysis.

Three peaks and two shoulder peaks, corresponding to weight losses, were observed on the DTG curves (Fig. 2). For example, in the DTG curve for the rate of 40 $^{\circ}\text{C}/\text{min}$, the maxima of the peaks occurred at 84 (peak 1), 242 (peak 2), 280 (shoulder peak 1) and 371 $^{\circ}\text{C}$ (peak 3). The first peak was attributed to water vaporization. Peak 2, the shoulder peak, and peak 3 were assigned to the decompositions of pectin, hemicelluloses and cellulose, respectively [11]. A flat tailing section (Shoulder peak 2) of the DTG curve ap-

Table 1. Proximate analysis of mandarin peel

Components	Mass fraction (wt%)
Water	5.2
Volatile matter	74.6
Fixed carbon	18.4
Ash	1.8

Table 2. Ultimate analysis and higher heating value of mandarin peel

Ultimate analysis (wt%)	
C	52.5
H	6.5
O ^a	38.9
N	2.1
S	-
HHV ^b (MJ/kg)	20.5

^aBy difference, ^bCalculated

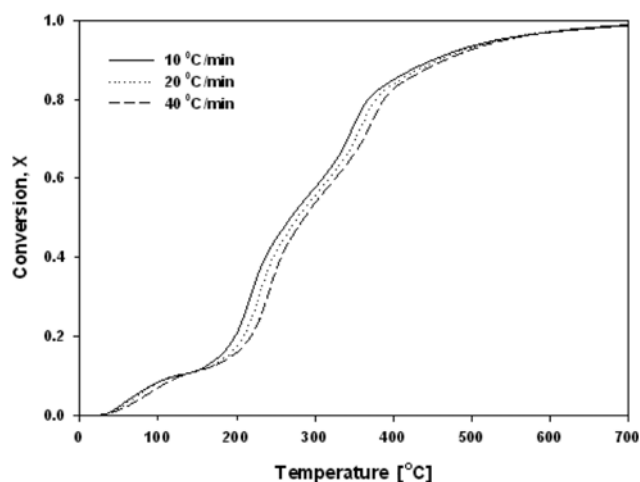


Fig. 1. The change in conversion of mandarin peel obtained at heating rates of 10 to 40 °C/min.

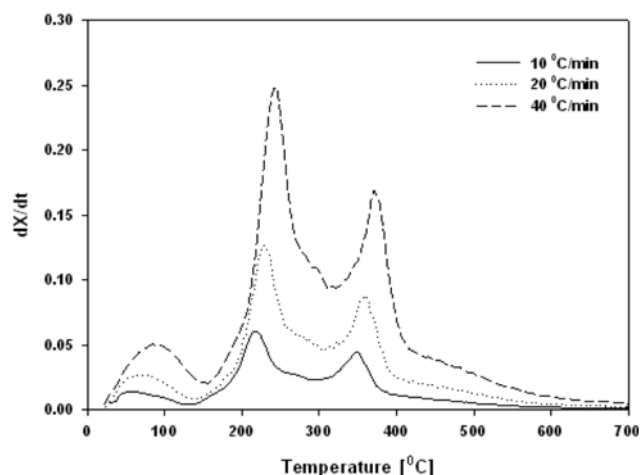


Fig. 2. Variation of the instantaneous reaction rate with temperature obtained at heating rates of 10 to 40 °C/min for the pyrolysis of mandarin peel.

pearing between 410 to 590 °C was attributed to lignin, which is known to be decomposed slowly over a very broad temperature range [18]. This result was also in accordance with the pyrolyses of pure pectin (210–270 °C [19], 250 °C [20]), hemicellulose (268 °C) and cellulose (355 °C) [21].

As pointed out by Mohan et al. [22], it is well known that under a slow heating regime, the decomposition of cellulose is complete at around 360 °C: hemicellulose decomposes between 200 and 260 °C, with most of the decomposition happening under 180 °C, and lignin decomposes between 280 and 500 °C, which is the compound that produces the highest amounts of char and tar. Less information is available on the pyrolytic behavior of other compounds, but in the work of Sharma et al. [23], the decomposition of citrus pectin is also observed to be complete below 400 °C.

2. Kinetic Parameters

Fig. 3 shows the plots of $\ln(dX/dt)$ versus $1/T$ for each conversion. The R^2 values for each conversion were over 0.99. The variations in the apparent activation energies as a function of the mandarin

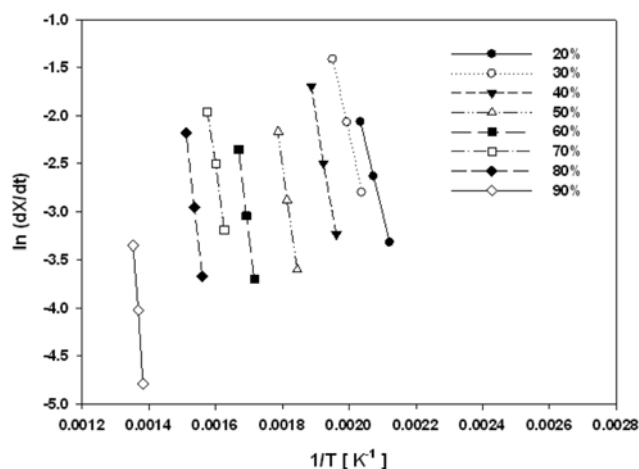


Fig. 3. Plots of $\ln(dX/dt)$ versus $1/T$ at different conversions.

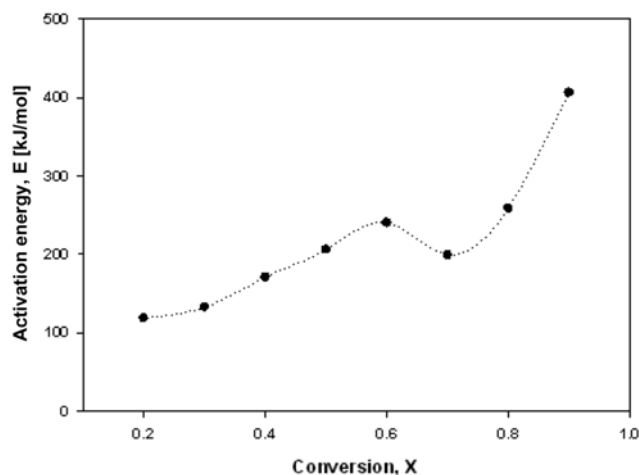


Fig. 4. Calculated activation energies at different conversions via the pyrolysis of mandarin peel.

peel conversion are shown in Fig. 4.

The range of apparent activation energies for the pyrolysis reaction of mandarin peel was between 119 and 406 kJ/mol, and increased with increasing conversion. The average activation energy was 217 kJ/mol. The apparent activation energies up to 80% conversion were lower than 260 kJ/mol. The trend of the activation energy confirmed that the decomposition of mandarin peel proceeded via a multi-step process comprised of numerous complex reactions.

As shown in the TG curves, pectin, hemicellulose and cellulose were decomposed with less than 84% conversion, and the corresponding activation energies were between 119 and 259 kJ/mol for their decompositions, which was in accordance with Vamvuka et al. [18], who reported the pyrolysis characteristics of biomass residual mixtures with lignite. The kinetics of the thermal decomposition was modeled using a scheme consisting of three independent first-order parallel reactions of the main biopolymer components: hemicellulose, cellulose and lignin. They reported activation energies between 145 and 285 kJ/mol for cellulose, 90 and 125 kJ/mol for hemicellulose and 30 and 39 kJ/mol for lignin. The variation in the apparent activation energy for cellulose showed a similar trend to that of our data. Also, Fisher et al. [20] reported that pectin melted

Table 3. Main compounds from the pyrolysis of mandarin peel indentified by Py-GC/MS

No.	Identified compound	400 °C (Area %)	500 °C (Area %)	600 °C (Area %)
1	Carbon dioxide	15.01	16.70	18.70
2	Formaldehyde	3.12	1.21	4.29
3	Acetaldehyde	4.82	3.57	4.26
4	Methanol	14.14	11.14	4.42
5	Acetone	5.69	5.61	6.06
6	2, 3-Butanedione	2.95	1.13	2.30
7	2-Butanone	1.05	1.66	1.11
8	2-Methylfuran	1.37	1.01	0.83
9	Glycolaldehyde	2.85	1.19	2.29
10	Acetic acid	15.03	15.39	11.72
11	Hydroxyacetone	6.32	8.08	8.40
12	Pyruvic acid, methyl ester	2.05	2.58	1.38
13	Furfural	1.28	1.81	2.87
14	2-Hydroxycyclopent-2-en-1-one	2.23	2.24	2.25
15	Phenol	0.83	1.14	1.88
16	Limonene	1.66	1.67	1.92
17	3-Methyl-1, 2-cyclopentanedione	0.72	1.13	1.32
18	2, 5-Dimethyl-4-hydroxy-3(2H)-furanone	1.31	1.28	1.80
19	3, 5-Dihydroxy-6-methyl-2, 3-dihydro-4H-pyran-4-one	1.88	1.74	0.75
20	5-Hydroxymethylfurfural	3.19	2.96	2.21
21	2-Methoxy-4-vinylphenol	3.02	3.17	3.40
22	Ethyl α -D-glucopyranoside	2.39	3.13	2.25
23	n-Hexadecanoic acid	0.50	0.57	0.55
24	Vitamin E	0.30	0.25	0.29

at around 150 °C, with a heat of melting of about 75 J/g, and then underwent primary decomposition above 200 °C, with a corresponding endothermic reaction energy of about 90 J/g. The highest apparent activation energy (406 kJ/mol) at the highest conversion (0.9) appeared to be due to further devolatilization of the residual char.

3. Py-GC/MS

Table 3 shows the area fractions of the main pyrolytic products indentified by Py-GC/MS, respectively. As shown in the results of pyrolysis at 400 °C, the yields of methanol (>14%) and acetic acid (>15%) were particularly high via the pyrolysis of mandarin peel. Compared to other biomass, mandarin peel has a considerably higher citrus pectin content, resulting in high selectivity to methanol and acetic acid [24].

Another characteristic of the pyrolysis of mandarin peel was the production of high-value-added compounds, such as limonene and vitamin E. Limonene is a colorless liquid hydrocarbon, classified as a cyclic terpene, which releases a strong scent of oranges, and is used in chemical synthesis as a precursor to carvone, cosmetic products, and biofuel. Also, vitamin E is a natural compound and well known antioxidant.

Other products of the pyrolysis of mandarin peel include alcohols, acetone, ketones, phenolics and carboxylic acids, which resulted from the pyrolysis characteristics of pectin, hemicellulose, cellulose and lignin components of mandarin peel. It was clear that the pyrolysis products of the major components of biomass were substantially affected by the chemical structure of the materials. From our results, the pyrolysis products were in good accordance with the main composition of mandarin peel, i.e., pectin, hemi-cellulose,

lignin and cellulose. It was recently reported that acetic acid was mainly formed from hemicellulose [25]; whereas, levoglucosan was from cellulose [26], phenols from lignin [27], and furfural and 1-hydroxy-propanone from holocellulose [28]. Zhou et al. [24] studied the formation mechanism of the pyrolysis gases released during the pyrolysis of pectin under conditions that simulated a cigarette smoldering. They used thermogravimetric analysis, coupled to Fourier transform infrared spectrometer (TG-FTIR) and flash pyrolysis, with high performance liquid chromatography (FPy-HPLC). Their TG-FTIR results illustrated that the product gas formed by the flash pyrolysis was mainly composed of CO₂, H₂O, CO, methanol and methane, as well as carbonyl compounds, such as formaldehyde, acetaldehyde, acetone, acrolein, propionaldehyde, crotonaldehyde, methyl ethyl ketone and butyraldehyde.

Fig. 5 shows the area fractions of the different chemical groups in the pyrolytic product of mandarin peel obtained at different temperatures, where ketones accounted for the highest fraction. The carbon dioxide content increased with increasing temperature. Conversely, alcohols, the most abundant of which was methanol, decreased with increasing temperature. It was presumed that as the decomposition of pectin was complete at a low temperature, the generation of other products at higher temperatures hindered the formation of alcohols. The fraction of acids, composed mainly of acetic acid, was highest at 500 °C. In contrast, the yield of phenols, the main products of decomposition of lignin [27], increased with increasing temperature. The yields of ketones and furan derivatives also increased with increasing pyrolysis temperature.

The area fractions of limonene and vitamin E did not change much

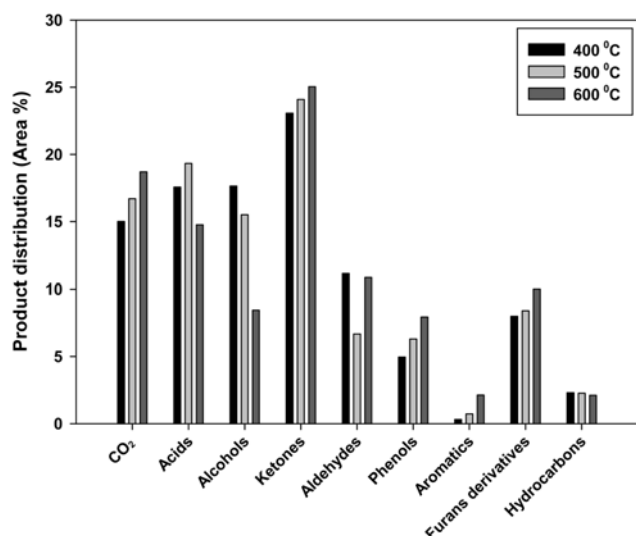


Fig. 5. Product distribution from the pyrolysis of mandarin peel.

with changes in temperature above 400 °C, probably because these two compounds were produced by the thermal desorption from mandarin peel, and not by the pyrolysis of the bio-polymer content of the mandarin peel.

CONCLUSIONS

The TG curves of mandarin peel showed three different weight loss regimes, due to water vaporization, the decomposition of the bio-polymers, such as citrus pectin, hemicellulose, cellulose and lignin, and devolatilization of the residual char. The range of apparent activation energies for mandarin peel determined by the differential method was between 119 and 406 kJ/mol. The average activation energy was 217 kJ/mol. The activation energy increased with increasing conversion. The trend of the activation energy mandarin peel confirmed that the decomposition of mandarin peel proceeded via a multi-step process, comprised of numerous complex reactions. The pyrolytic products contained valuable compounds, including methanol, acetic acid, limonene and vitamin E. The yield of alcohols, the main pyrolysis products of pectin, was highest at 400 °C, while acids, including acetic acid, showed their highest yield at 500 °C. The yields of ketones, phenolics and furan derivatives increased with increasing pyrolysis temperature.

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