

The pyrolysis of waste mandarin residue using thermogravimetric analysis and a batch reactor

Jeong Wook Kim*, See-Hoon Lee**, Seong-Soo Kim**, Sung Hoon Park***,
Jong-Ki Jeon****, and Young-Kwon Park*****†

*Graduate School of Energy and Environmental System Engineering, University of Seoul, Seoul 130-743, Korea

**Korea Institute of Energy Research, Daejeon 303-343, Korea

***Department of Environmental Engineering, Sunchon National University, Suncheon 540-742, Korea

****Department of Chemical Engineering, Kongju National University, Cheonan 331-717, Korea

*****School of Environmental Engineering, University of Seoul, Seoul 130-743, Korea

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Abstract—A study on the pyrolysis of waste mandarin residue, with the aim of producing bio-oil, is reported. To elucidate the thermodynamics and temperature-dependency of the pyrolysis reaction of waste mandarin residue, the activation energy was obtained by thermogravimetric analysis. Mass loss occurred within the temperature range 200–750 °C, and the average activation energy was calculated to be 205.5 kJ/mol. Pyrolysis experiments were performed using a batch reactor, under different conditions, by varying the carrier gas flow rate and temperature. When the carrier gas flow rate was increased from 15 to 30 and finally to 50 ml/min, the oil yield slightly increased. Experiments performed within the temperature range 400–800 °C showed the highest oil yield (38.16 wt%) at 500 °C. The moisture content in the bio-oil increased from 35 to 45% as the temperature increased from 400 to 800 °C, which also resulted in reduction of the oxygenates content and increase in the phenolics and aromatics content, indicating that temperature is an important operating parameter influencing the yield and composition of bio-oil.

Key words: Waste Mandarin Residue, Pyrolysis, TGA, Bio-oil

INTRODUCTION

Biomass refers to all kinds of biological materials that come from living organisms, such as plants, animals, microorganisms and organic wastes, and includes byproducts of agriculture and forestry, sewage sludge and municipal solid wastes. Compared to other energy sources, biomass energy has several advantages. First, it is renewable and, hence, a limitless energy source. Second, it is environment-friendly, in that it often uses waste biomass as the energy source. Third, it is carbon-neutral if used in a sustainable manner. In particular, waste-to-energy technology has become an area of intensive research due to increased amounts of organic wastes, such as food wastes and sewage sludge, stemming from changes in food-related lifestyle and urbanization [1-3].

Mandarin farming is an important industry and a main resource of local income in Jeju Island, Korea. Since 2000, the problems of overproduction and distribution relating to mandarin have become worse. To mitigate these problems, mandarin processing plants were eventually established as public corporations. In 2005, 125,343 tons of mandarin (about 18% of total mandarin production) was processed from these plants, yielding 55,000 tons of mandarin byproducts [4]. Accordingly, the disposal of the mandarin byproduct, waste mandarin residue, has become an important issue on Jeju Island. A large amount of byproducts was discharged to international waters. However, discharging to the sea became illegal due to the marine protection policy [4]. Therefore, there is a great need for alternative

ways to treat mandarin byproducts on Jeju Island.

Difficulties can be encountered when a fruit waste containing rind is treated using microorganism-aided anaerobic digestion to produce bio-energy, due to a rapid pH reduction resulting from localized acid fermentation, scum conversion of cellulose due to differences in the acid fermentation rates, and the high salt content [5-7]. Therefore, the development of an improved process that can alleviate those problems would be desirable for the utilization of waste mandarin residue for bio-energy production. Of the thermochemical processes, pyrolysis has been used for the production of bio-energy using a variety of biomass wastes [8-17]. To the best of our knowledge, however, the pyrolysis of waste mandarin residue, which is of importance in terms of diversification in bio-energy source, has never been reported.

In this study, the pyrolysis of waste mandarin residue, mass-produced at the mandarin juice production plants on Jeju Island, was investigated. The waste mandarin residue was pyrolyzed in a lab-scale batch reactor at different temperatures. The yields and characteristics of the liquid and gaseous products were analyzed, with thermogravimetric analysis (TGA) used for a dynamics analysis.

EXPERIMENTAL

1. Sample Preparation

The samples for pyrolysis were sieved to obtain samples of 1-2 mm in size. For each experiment, a 7 g sieved sample was used after drying at 110 °C for at least 24 hours. Two elemental analyzers, a TruSpec Elemental Analyzer (LECO Co., USA) and SC-432DR Sulfur Analyzer (LECO Co., USA), were used to analyze the C,

†To whom correspondence should be addressed.
E-mail: catalica@uos.ac.kr

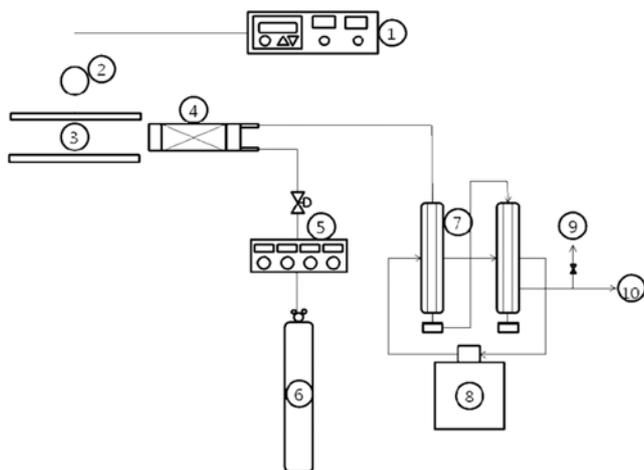


Fig. 1. Schematic of pyrolysis reactor system.

- | | |
|--------------------------|-----------------------|
| 1. P.I.D Controller | 6. N ₂ gas |
| 2. Thermocouple | 7. Condenser |
| 3. Furnace | 8. Circulator |
| 4. U-type quartz reactor | 9. Gas sampling |
| 5. MFC | 10. To vent |

H, O, N and S content. A proximate analysis was performed using a pyris1 TGA (Perkin Elmer). The heating value of the sample was obtained using a Parr 6320EF Calorimeter (PARR Co., USA).

2. Thermogravimetric Analysis

Thermogravimetric analysis was carried out using a pyris1 TGA (Perkin Elmer) to measure the thermal characteristics of the waste mandarin residue and determine an appropriate pyrolysis temperature. The temperature of the sample was raised from room temperature to ~900 °C, using three different temperature rising rates, 10, 20 and 30 °C/min, under N₂ gas at a flow rate of 60 ml/min. To minimize the heat transfer effect, samples were pulverized and sieved into 0.15 mm or smaller sizes. For each analysis, a 6–11 mg sieved sample was used.

3. Pyrolysis in the Batch Reactor

Fig. 1 shows the schematic of the pyrolysis batch reactor system used in this study. The system consisted of a gas control system, a temperature control system, a pyrolysis system, an oil collection system and a gas sampling system. The reactor was a U-type quartz reactor, with a volume, height, and inlet and outlet diameters of 50 ml, 160 mm, and 15 mm, respectively. The reactor was purged with a nitrogen gas flow of 50 ml/min for about 30 minutes before each experiment to create oxygen-free conditions. The furnace temperature was controlled with a PID controller.

Gaseous and liquid products were collected by using two condensers, which were cooled to –20 °C with a coolant circulator to promote condensation of the bio-oil species. The product gas passing through the condensers was captured with a Teflon gas bag. Experiments were performed for one hour, under different conditions, by varying the flow rate (15, 30 and 50 ml/min) and temperature (400, 500, 600, 700 and 800 °C).

4. Product Analysis

The product gas captured by the Teflon gas bag was analyzed by GC (ACME 6000, Young Lin Instrument Co., Ltd.), equipped with TCD and FID. CO, CO₂, H₂ and CH₄ were analyzed by TCD, with a Carboxen 1000 column, while hydrocarbons were analyzed by FID, with an HP-plot Al₂O₃/KCl column. The response factor

needed for analysis was calculated using the Kaiser equation.

The moisture content in the oil was analyzed by using a Karl Fischer titrator (Metrohm 787 KF Titrator), based on the ASTM E 203 method [18]. HYDRANAL-Composite 5 and HYDRANAL-METHANOL Dry were used as the titrant and the titration solvent, respectively.

The bio-oils produced at different temperatures were analyzed by GC/MS (HP 6890N Gas Chromatography; HP 5973 inert Mass Spectral Detector), with an HP-5MS (30 m×0.25 mm×0.25 μm) column. The obtained mass spectra were interpreted with an automatic library (NIST05a).

RESULTS AND DISCUSSION

1. Characterization of Waste Mandarin Residue

The characteristics of the waste mandarin residue are summarized in Table 1. In this table, oxygen and carbon are seen to be the two most abundant elements. The sulfur content was very low (0.03%), implying that the bio-oil derived from waste mandarin residue may be used as a low-emissions fuel.

2. Thermogravimetric Analysis

Fig. 2 shows the results of the thermogravimetric analysis of waste

Table 1. Characteristics of waste mandarin residue

Proximate analysis (wt%)	
Water	4.88
Volatiles	72.28
Fixed carbon	12.24
Ash	10.60
Ultimate analysis (wt%)	
C	39.30
H	6.08
O	42.84
N	1.15
S	0.03
HHV(kcal/kg)	3,660

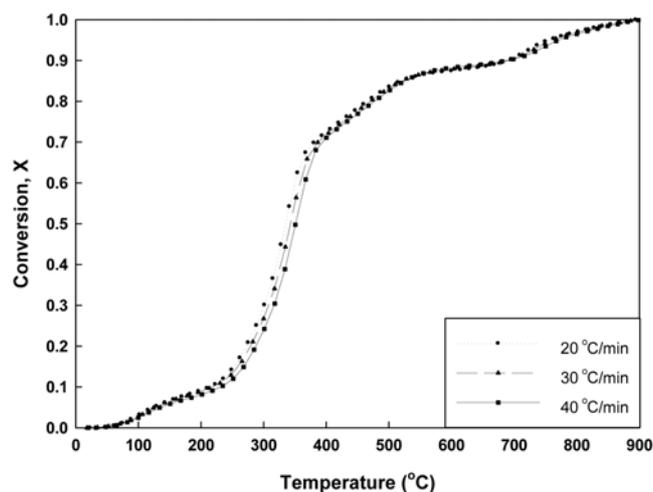


Fig. 2. Decomposition of waste mandarin residue observed with different heating rates.

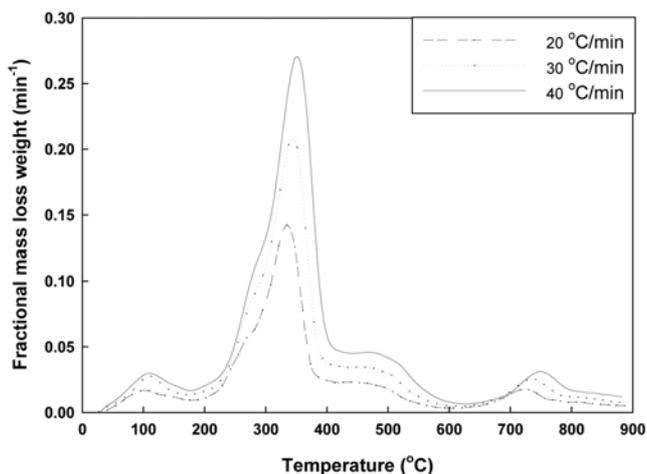


Fig. 3. DTG Curves of waste mandarin residue obtained with different heating rates.

mandarin residue, which shows that the decomposition began at 200 °C, with further mass reduction observed up to about 800 °C. Four peaks were observed in the DTG curves (Fig. 3). The peak appearing at <100 °C was due to the evaporation of the moisture contained in the sample. The peak appearing around 300 °C was mainly the result of the decompositions of pectin and hemicellulose. The largest peak, appearing over the temperature range of 320-380 °C, was the typical signal of the rapid decomposition of cellulose [19]. The reason for the decomposition temperature of hemicellulose being lower than that of cellulose can be explained as follows. Cellulose polymer is a homogeneous polysaccharide composed of a one unit monomer, D-glucopyranose; therefore, the intramolecular bonds in the cellulose polymer lead to a regular crystal shape. In contrast, hemicellulose is a heterogeneous polysaccharide composed of various pentose and hexose unit monomers, resulting in a lower degree of polymerization and a weaker bond strength compared to cellulose [20]. The species decomposed at temperatures higher than 400 °C was believed to be lignin. Lignin begins to decompose slowly at over 200 °C with significant mass reduction at temperatures higher than 330 °C. Lignin is believed to be a complex polymer material, and thus the temperature range for its decomposition should be relatively wide [21].

2-1. Activation Energy

TGA analysis is widely used for investigating the temperature dependence of the properties of polymer materials. TG plots are determined from the dynamics of the pyrolysis expressed by the activation energy, Arrhenius frequency factor and reaction order.

The results of thermogravimetric experiments are expressed as a function of a conversion, X, which is defined as:

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

where W_0 is the initial sample mass, W the pyrolyzed sample mass 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 [20,21].

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

where X is the conversion of the sample, $f(X)$ the reaction model, A

the pre-exponential factor and E the activation energy. $f(X)$ is given by:

$$f(X) = (1-X)^n \quad (3)$$

In this study, Friedman's method, an iso-conversional method, was used to obtain the activation energy among various methods [22]. By substituting Eqs. (2) and (3) into Eq. (1), and taking natural logarithms of both sides, the following is obtained:

$$\ln\left(\frac{dX}{dt}\right) = \ln A + n \ln(1-X) - \frac{E}{RT} \quad (4)$$

By plotting $\ln(dX/dt)$ as a function of $1/T$, the activation energy, E, can be obtained from the slope.

Fig. 4 shows plots of $\ln(dX/dt)$ as a function of $1/T$ for different conversions. The activation energy values obtained are shown in Fig. 5. The higher apparent activation energy (484 kJ/mol) at the higher conversion of 0.9 appeared to be due to further devolatilization of residual char. The activation energy of the waste mandarin residue was determined to be within the range 90-485 kJ/mol, with an average of 205.1 kJ/mol.

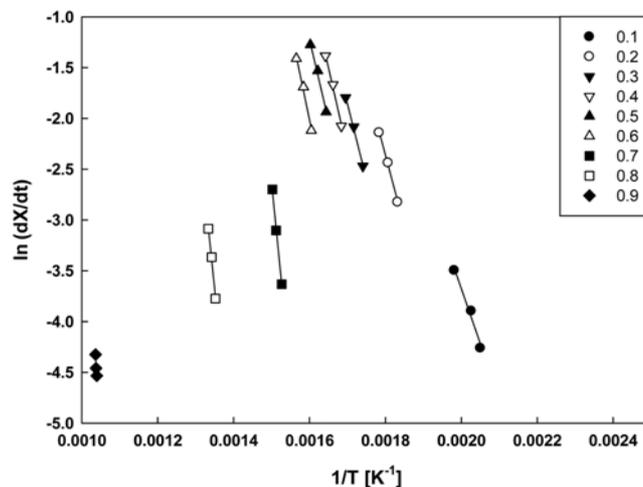


Fig. 4. Plot of $\ln(dX/dt)$ versus $1/T$ at each conversion.

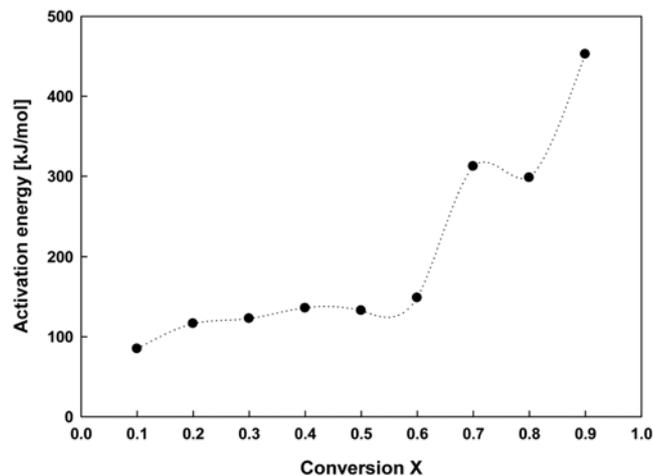


Fig. 5. Calculated activation energies at different conversions for pyrolysis of waste mandarin residue.

The trend of the activation energy confirmed that the decomposition of the waste mandarin residue proceeded via a multi-step process comprised of numerous complex reactions. Vamvuka et al. [23] reported the pyrolysis characteristics of biomass residual mixtures of 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 energy values 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. [24] reported that pectin melts at around 150 °C, with a heat of melting of about 75 J/g; it then undergoes primary decomposition above 200 °C, with a corresponding endothermic reaction energy of about 90 J/g. The higher apparent activation energy (484 kJ/mol) at the higher conversion of 0.9 appeared to be due to further devolatilization of residual char.

3. Batch Pyrolysis Reaction

3-1. Effect of Carrier Gas Flow Rate

To investigate the effect of the nitrogen carrier gas flow rate, three different flow rates were used in the pyrolysis experiments: 15, 30

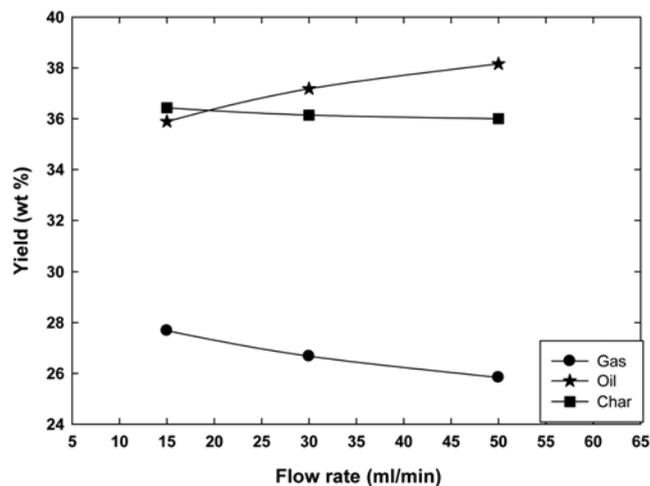


Fig. 6. Product yields as functions of carrier gas flow rate.

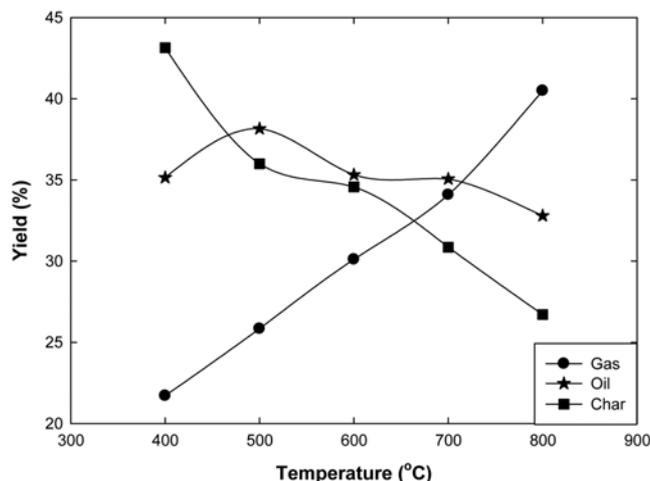


Fig. 7. Product yields as functions of pyrolysis temperature.

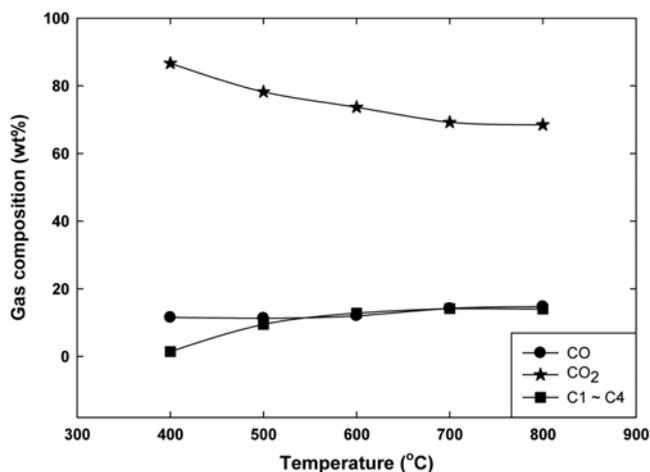


Fig. 8. Product gas compositions as a function of temperature.

and 50 ml/min (Fig. 6). The oil yield increased with increasing carrier gas flow rate. It is presumed that the high flow rate and resulting low residence time reduce the chances for both char formation and decomposition into gas. The product gas composition was hardly affected by the carrier gas flow rate (data not shown).

3-2. Effect of Temperature

Fig. 7 shows the gas, oil and char yields as functions of the temperature. The highest oil yield was obtained at 500 °C, but decreased with increasing temperature thereafter. An increase in temperature also led to increased gas and reduced char yields. Generally, if the temperature is too high, the amount of heat supplied will exceed that required for oil generation by pyrolysis, resulting in overcracking of the feed biomass and the production of gaseous species with lower molecular masses. Secondary cracking of oil products due to high temperature also leads to its conversion to gases, thereby reducing the oil yield.

Fig. 8 shows the composition of the product gas as a function of the temperature. CO and CO₂ accounted for most of the mass of the product gases, indicating active decarboxylation and decarbonylation reactions in the temperature range examined. As the temperature increased, the CO₂ content decreased. The yield of CO remained relatively constant, while those of C1-C4 compounds increased slightly. This gas composition behavior was similar to that for the pyrolysis of macro algae [12]. The moisture content in the bio-oil is known to influence, either positively or negatively, the viscosity, heating value, density, stability, pH and homogeneity of the oil [25]. A reduction of the viscosity due to a high moisture content enhances the fluidity, thereby enabling atomization. A high moisture content is also known to reduce the production of pollutants upon combustion. On the other hand, a high moisture content causes a reduction of the heating value and occasionally phase separation of the bio-oil, and will also vaporize below the ignition temperature, causing additional preheating, a longer ignition delay time and higher cost [26]. In this study, the moisture content in the bio-oil increased with temperature: 36.10, 40.36, 43.90, 43.75 and 44.83% at temperatures of 400, 500, 600, 700 and 800 °C, respectively. This can be attributed to an enhanced deoxygenation reaction at a higher temperature. The moisture content reported in this study was higher than typical moisture content values of the bio-oils obtained from

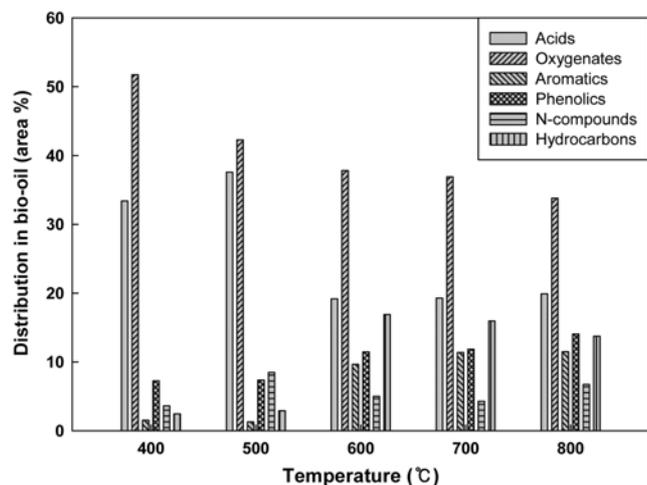


Fig. 9. Categorized composition of bio-oil produced at different temperatures.

the pyrolysis of wood biomass, 20-30% [20,21].

Another factor known to be involved in determining the moisture content is the carrier gas flow rate: a lower flow rate leads to a higher moisture content. In this study, the moisture content in the bio-oil also decreased with increasing flow rate: 48.38, 41.88 and 40.36% at flow rates of 15, 30 and 50 ml/min, respectively. Therefore, it is crucial to choose an appropriate flow rate and temperature to control the moisture content in the oil.

3-3. Bio-oil Composition

Bio-oil is a mixture of various species that are impossible to totally quantify. Therefore, a promising approach is to group the species into several categories to compare the composition of bio-oil [15,16].

Fig. 9 shows the categorized composition of the bio-oil produced in this study. It was observed that acids and oxygenated compounds accounted for the majority of the bio-oil mass at 500 °C or below. Generally, it is undesirable for bio-oil to contain acids, such as acetic acid, and oxygenates, including aldehydes and ketones, because these can cause engine corrosion and oil instability. In contrast, hydrocarbons, aromatics and phenolics are desirable products in terms of their octane values, and therefore have additional value. The contents of the valuable chemicals were shown to be high at 600 °C and higher, while the acids and oxygenated contents were low. It was presumed that acids and oxygenated compounds were decomposed by deoxygenation and additional reactions and converted into hydrocarbons and aromatics at high temperature. Although 500 °C was shown to be the optimal temperature in terms of oil yield, it seems to be more desirable to perform the pyrolysis at 600 °C or higher to produce good quality bio-oil. Considering the energy cost, it is recommended to perform the pyrolysis at 600 °C. In Table 2 some main compounds of bio-oil are shown.

CONCLUSIONS

The pyrolysis of waste mandarin residue was investigated for the first time. The average activation energy for the decomposition of waste mandarin residue was shown to be 205.1 kJ/mol. The carrier gas flow rate and temperature were the two parameters that most affected the bio-oil yield. The bio-oil yield was highest at 500 °C. The CO₂ content in the product gas, which was the most abundant species, decreased with increasing temperature, while those of CO and C₁-C₄ compounds increased. An analysis of the oil produced showed that the moisture content increased with increasing temperature, indicating the deoxygenation effect at high temperature.

Table 2. Major compounds of bio-oil obtained at 600 °C

Compound	Area %	Compound	Area %
Acetic acid	8.19	2-Methoxy-4-vinylphenol	1.05
Oleic acid	6.38	Phenol, 2-methyl-	0.76
n-Hexadecanoic acid	3.08	Phenol, 2-methoxy-	0.67
2-Cyclopenten-1-one, 2,3-dimethyl-	2.85	Phenol, 2-ethyl-	0.47
2(5H)-Furanone, 3-methyl-	1.66	Phenol, 3-ethyl-	0.46
2-Dodecen-1-yl(-)succinic anhydrid	1.53	Phenol, 4-ethyl-	0.39
1,2-Ethanediol, monoacetate	1.39	Phenol, 2-methoxy-3-(2-propenyl)-	0.35
1-Hydroxy-2-butanone	1.38	Phenol, 2-ethyl-6-methyl-	0.32
Ethyl Oleate	1.35	Phenol, 2-propyl-	0.27
2-Cyclopenten-1-one, 2-methyl-	1.18	2,5-Diethylphenol	0.16
1,2-Ethanediol	1.1	Docosane	3.31
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	0.97	Stigmastan-3,5-diene	2.05
2-Cyclopenten-1-one, 3-methyl-	0.93	Tetradecane	1.32
1H-Indene, 1-methyl-	1.01	Hexadecane	0.9
o-Xylene	0.74	Tricosane	0.89
Toluene	0.35	Heptacosane	0.75
Benzene, 1,2,3-trimethyl-	0.34	Hexacosane	0.56
Naphthalene, 1,2,3,4-tetrahydro-1,4-dimethyl-	0.29	Cyclododecane	0.55
Phenol	1.3	1-Tetradecene	0.47
Phenol, 4-methyl-	1.27	Hexacosane, 9-octyl-	0.44
Phenol, 2,4-dimethyl-	1.16	3,4-Octadiene, 7-methyl-	0.4

As the temperature increased, the acids and oxygenated contents were largely decreased; whereas, those of phenolics and aromatics were increased, suggesting that high temperature is favorable for the production of good-quality bio-oil. Considering both the bio-oil yield and oil quality, the optimal temperature for the batch-reactor pyrolysis of waste mandarin residue should be 600 °C.

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