

## Pyrolysis kinetics and product properties of softwoods, hardwoods, and the nut shell of softwood

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**Abstract**—The pyrolysis of softwoods (*Pinus (P) densiflora*, *P. koraiensis*), hardwoods (*Quercus acutissima* and *Liriodendron tulipifera*) and nut shell of *P. koraiensis* was investigated using a thermogravimetric analyzer and fixed bed reactor. Thermogravimetric analysis showed that the maximum decomposition temperature of each biomass was influenced by the ash content and lignocellulosic composition of biomass. The activation energy values also varied according to the content of hemicellulose and lignin of each biomass. Large amounts of acids, such as acetic acid, were recovered from the hardwood pyrolysis reaction due to their high hemicellulose content. The nut shell of *P. koraiensis* and softwoods with a higher lignin content produced higher yields of phenolic compounds than the hardwoods.

Keywords: Softwood Hardwood, Pyrolysis, Kinetics, Lignocellulosic Composition

### INTRODUCTION

The intensive use of fossil fuels has prompted a focus on biomass conversion technologies, such as fermentation, gasification, and pyrolysis [1-3]. These conversion techniques can provide a solution to issues such as oil shortage, environmental contamination, and global warming. Among them, pyrolysis is being considered as an appropriate tool for the production of bio-oil, which can be used as fuel and/or chemical feedstock [4]. Biomass pyrolysis has been investigated widely using various kinds of biomass, such as wood [5-7], algae [8,9], fruit peel [10-12], and so on [13,14].

Among various kinds of biomass, wood has been considered as the main object of attention to produce bio-oils via pyrolysis. Many researchers have focused on not only pyrolysis but also catalytic upgrading of bio-oils obtained from the pyrolysis of woods [15,16].

Generally, wood biomass can be classified as either softwood or hardwood depending on its lignocellulosic composition (hemicellulose, cellulose, lignin, and extractives) and shape (conifers and flowering plants), and their distribution is different in each country. For example, softwood and hardwood comprise 40.5% and 27.0% of the total forest area in Korea, respectively. *Pinus (P) densiflora* and *P. koraiensis* are typical softwoods, and *Quercus (Q.) acutissima* and *Liriodendron (L.) tulipifera* are representative hardwoods in Korea.

The chemical properties of products obtained from the pyrolysis of softwood and hardwood are different due to their lignocellulosic composition. Therefore, many studies have examined the different pyrolysis behaviors and products of softwoods and hard-

woods.

Gronli et al. [17] performed a comparison study of hardwoods and softwoods using by thermogravimetric (TG) analysis. They reported that softwoods decompose at lower temperatures and a wide pyrolysis region (hemicellulose and cellulose) due to the large amount of extractives and the difference in the hemicellulose reactivity. Wang et al. [18] examined the pyrolysis behavior of hemicellulose isolated from hardwoods and softwoods, and reported that the hemicellulose activation energy in hardwoods is higher than that of softwoods. They also found that furfural and acids are the main pyrolyzates in hardwood hemicellulose. In addition, 5-hydroxymethylfurfural and anhydro sugars were produced mainly from softwood hemicellulose. Previous studies [19-21] showed that the lignin isolated from softwood and hardwood also have very different thermal behavior and products. The pyrolysis researches using TG analyzer and FTIR spectroscopy [19,21] reported the key differences (thermal stability, char yield, and pyrolyzate) on the pyrolysis of hardwood and softwood due to their different compositions of the lignin monomer. Hardwoods have larger amounts of methoxyl groups than softwoods due to the large amount of syringol unit in hardwoods.

Although the pyrolysis properties of individual wood biomass have been studied intensively, the comparison studies of the pyrolysis of typical softwoods and hardwoods harvested in Korea have been limited. Therefore, it is important to comprehend the thermal behavior and pyrolysis product characterization to better understand the different pyrolysis behaviors of softwoods and hardwoods occupying large areas in Korea.

In this study, representative wood species in Korea, *P. densiflora*, *P. koraiensis*, *Q. acutissima*, and *L. tulipifera*, were pyrolyzed to obtain valuable information on the pyrolysis kinetics and product properties focusing on the differences between softwoods and hardwoods. For this, three different techniques were employed: TG analysis,

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evolved gas analysis-mass spectrometry (EGA-MS) measurements, and pyrolysis reaction with the product analysis using a fixed bed reactor and gas chromatography/MS (GC/MS). The nut shell (NS) of *P. koraiensis* was also used as a sample to determine the pyrolysis property of the nut shell of wood fruit, which also has a different lignocellulosic composition from softwood and hardwood.

## EXPERIMENTAL

### 1. Sample Preparation

Two wood groups, softwood (*P. densiflora* and *P. koraiensis*) and hardwood (*Q. acutissima* and *L. tulipifera*), and the NS of *P. koraiensis* were obtained from sawmill factories or pine nut plant located in Gangwon province in Korea. All samples were prepared in small particle form below 800  $\mu\text{m}$ , by grinding with a knife mill, sieving, and drying at 105  $^{\circ}\text{C}$  (4 h). The powder forms of hemicellulose, cellulose, and lignin were purchased from Sigma-Aldrich and Kanto

chemical. Proximate, ultimate analysis, and higher heating value (HHV) measurement of each sample were performed according to methodologies reported elsewhere [7,22–24].

### 2. Kinetic Analysis

To determine the pyrolysis kinetic properties, 10 mg of sample was heated non-isothermally from ambient temperature to 800  $^{\circ}\text{C}$  at three heating rates of 10, 20, and 40  $^{\circ}\text{C}/\text{min}$ , under a nitrogen flow of 120 mL/min using a TG analyzer (Pyris Diamond, Perkin Elmer Co.). A model-free kinetic method, ASTM E698-11 [25], was used to obtain the apparent activation energy of each biomass at each conversion (X).

### 3. EGA-MS Analysis

The thermal profiles of the specific pyrolyzates of hemicellulose, cellulose, and lignin contained in each biomass sample were obtained by EGA-MS using the same procedures reported elsewhere [7,11,12,22]. For EGA-MS, 2.0 mg of each biomass sample was heated from 100  $^{\circ}\text{C}$  to 800  $^{\circ}\text{C}$  at a heating rate of 20  $^{\circ}\text{C}/\text{min}$ .

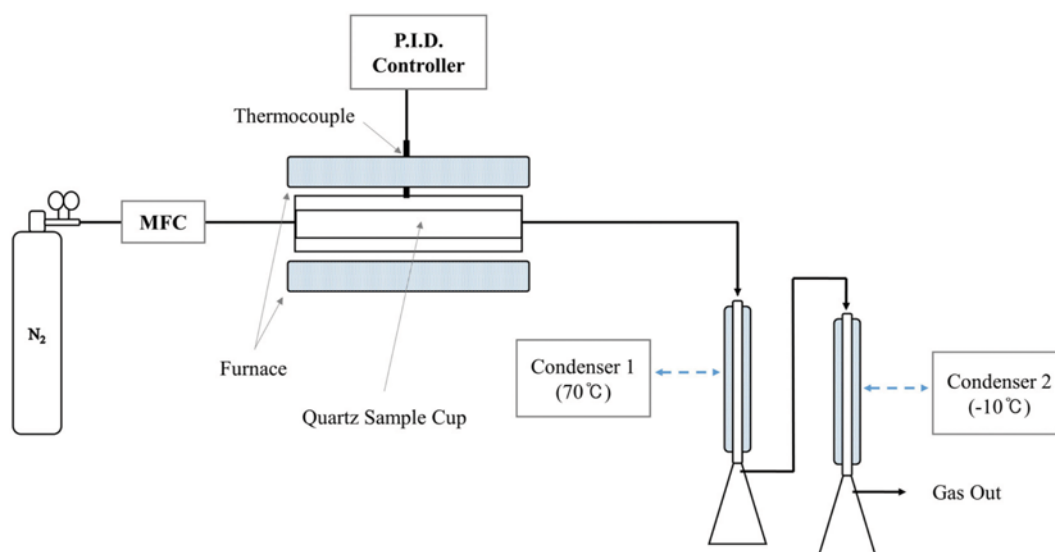


Fig. 1. Schematic diagram of the fixed bed type pyrolysis reactor system.

Table 1. GC/MS operation conditions for the analysis of liquid products

GC	
Inlet	320 $^{\circ}\text{C}$
Column	UA-5 (30 m $\times$ 0.25 mm i.d. $\times$ 0.25 $\mu\text{m}$ film)
Total flow	Helium 100 mL/min
Column flow	1 mL/min (Split 100 : 1)
Oven	40 $^{\circ}\text{C}$ (5 min) $\rightarrow$ 20 $^{\circ}\text{C}/\text{min}$ $\rightarrow$ 320 $^{\circ}\text{C}$ (10 min)
MS transfer line	300 $^{\circ}\text{C}$
MS	
Ion source	230 $^{\circ}\text{C}$
Quadrupole	150 $^{\circ}\text{C}$
Ionization current	70 eV
Scan range	15–550 amu
Scan speed	5.2 scans/sec
Peak identification	By NIST 8 <sup>th</sup> library (National Institute of Standards and Technology, USA)

**Table 2. Lignocellulosic composition of biomass used in this study**

Sample	Softwood		Hardwood		Nut shell
	<i>P. densiflora</i>	<i>P. koraiensis</i>	<i>Q. acutissima</i>	<i>L. tulipifera</i>	<i>P. koraiensis</i>
Reference	[26]	[27]	[5]	[28]	[22]
Hemicellulose	24.7	23.4	37.3	28.9	32.8
Cellulose	45.0	52.3	47.4	60.0	34.1
Lignin	30.3	24.3	15.3	11.1	33.1
Sum	100	100	100	100	100

#### 4. Pyrolysis Reaction

Fig. 1 shows a schematic diagram of the fixed bed type pyrolysis reactor used in this study for the pyrolysis of the samples. The system consisted of a temperature control, heating furnace, and two liquid condensation parts. For the reaction, approximately 6 g of each sample in the cylindrical quartz sample cup (30 cm length, 2.5 cm diameter) was inserted into the furnace. After 30 minutes of nitrogen purging, the sample was heated from ambient temperature to 500 °C at a heating rate of 10 °C/min under a nitrogen flow of 1 L/min. The liquid products were collected from the sequential condensers with the different condensing temperatures (70 °C at the 1<sup>st</sup>, and -10 °C at the 2<sup>nd</sup> condenser). The weight of the solid residue and liquid products was measured by the weight balance, and the gas yield was estimated by subtracting the summed weight of the solid residue and liquid products from the total weight of the input sample. The liquid products were also analyzed by GC/MS according to the conditions listed in Table 1.

### RESULTS AND DISCUSSION

#### 1. Physico-chemical Properties

Table 2 lists the lignocellulosic composition of five biomass species reported in other literatures [5,22,26-28]. Although it is difficult to find any characteristics on the relative content of hemicellulose and cellulose distinguishing between softwoods and hardwoods,

the lignin content of softwoods is much higher than that of hardwoods. Among biomass, NS of *P. koraiensis* has the highest lignin content.

Different content of lignocellulosic components (hemicellulose, cellulose, and lignin) in biomass makes different thermal behavior and products during pyrolysis due to the different physico-chemi-

**Table 3. Physico-chemical properties of hemicellulose, cellulose, and lignin used in this study**

		Hemicellulose	Cellulose	Lignin
Proximate analysis <sup>a</sup> (wt%)	Volatiles	80.3	96.5	50.9
	Fixed carbon	17.3	2.1	33.0
	Ash	2.4	1.4	16.1
	Sum	100.0	100.0	100.0
Ultimate analysis <sup>a</sup> (wt%)	C	40.4	43.0	51.6
	H	5.9	6.3	4.6
	O <sup>b</sup>	53.7	50.7	42.0
	N	-	-	0.1
	S	-	-	1.7
	Sum	100.0	100.0	100.0
HHV <sup>a</sup> (kcal/kg)		3,754.0	4,147.1	4,919.3

<sup>a</sup>On a dry basis

<sup>b</sup>By difference

**Table 4. Physico-chemical properties of biomass used in this study**

		Softwood		Hardwood		Nut shell
		<i>P. densiflora</i>	<i>P. koraiensis</i>	<i>Q. acutissima</i>	<i>L. tulipifera</i>	<i>P. koraiensis</i>
Proximate analysis <sup>a</sup> (wt%)	Volatiles	82.1	81.5	81.0	83.2	72.2
	Fixed carbon	17.5	18.0	17.7	16.0	27.2
	Ash	0.4	0.5	1.3	0.8	0.6
	Sum	100.0	100.0	100.0	100.0	100.0
Ultimate analysis <sup>a</sup> (wt%)	C	47.0	47.5	46.1	46.1	50.8
	H	6.0	6.3	6.0	5.9	6.0
	O <sup>b</sup>	46.7	46.0	47.7	47.8	42.8
	N	0.3	0.2	0.2	0.2	0.4
	S	-	-	-	-	-
	Sum	100.0	100.0	100.0	100.0	100.0
HHV <sup>a</sup> (kcal/kg)		4,024.1	4,133.5	4,257.1	4,141.5	4,700.4

<sup>a</sup>On a dry basis

<sup>b</sup>By difference

cal properties of biomass components (Table 3). Therefore, it is also important to understand the characteristics of the biomass sample before the actual pyrolysis of biomass [29].

Table 4 lists the physico-chemical properties of five biomass samples used in this study. No distinct difference in the proximate analysis results was observed among the four wood samples; however, the NS of *P. koraiensis* had a much higher fixed carbon (27.2%) than four wood samples (16.0–18.0%). Elemental analysis showed that the softwoods (*P. densiflora* and *P. koraiensis*) had a slightly higher carbon content (47.0–47.5%) than those (46.1%) of the hardwoods (*Q. acutissima* and *L. tulipifera*). NS of *P. koraiensis* had a much higher carbon (50.8%) and lower oxygen content (42.8%) than the other woods. Owing to its higher carbon content, HHV of NS of *P. koraiensis* (4,700.4 kcal/kg) was also higher than those (4,024.1–4,257.1 kcal/kg) of the other four types of wood.

## 2. Pyrolysis Kinetics

Fig. 2 shows the TG and differential TG (DTG) curves of the hemicellulose, cellulose, and lignin. Hemicellulose, which consisted of two merged DTG peaks, decomposed between 200 °C and 330 °C. Cellulose showed a single sharp DTG decomposition peak between 250 °C and 380 °C. Lignin had a wider decomposition temperature zone ranging from 200 °C to 600 °C. Different thermal properties are related to the thermal stability derived by the network struc-

ture of an individual biopolymer. Hemicellulose has different kinds of sugar monomers as a polymer branch [30] and is more unstable than cellulose due to the unbranched anhydrous glucose structure [31]. Lignin, which decomposed over a wide temperature range, has a complicated three-dimensional structure [30,31]. The amounts of solid residue after TG analysis were 3% cellulose, 25% hemicellulose, and 51% lignin, respectively.

The different thermal behavior of woody biomass is also strongly related to not only the different content of biomass components but also to the content of inorganic compounds in biomass samples [32–34].

Fig. 3 shows the TG and DTG curves of five different biomass samples. The peak temperatures of the biomass samples tested were higher than that of pure cellulose (332.6 °C) due to the interaction of hemicellulose, cellulose and lignin. Yang et al. [32] compared the DTG curve of cellulose with those of cellulose mixed with hemicellulose and/or lignin, and found that the maximum temperature ( $T_{max}$ ) of cellulose decomposition was shifted to a higher temperature by mixing with hemicellulose and lignin.

Compared to the hardwoods (*Q. acutissima* and *L. tulipifera*), softwoods (*P. densiflora* and *P. koraiensis*) had lower initial decomposition temperatures ( $T_{initial}$ ), 183.6 °C and 188.4 °C, than those of

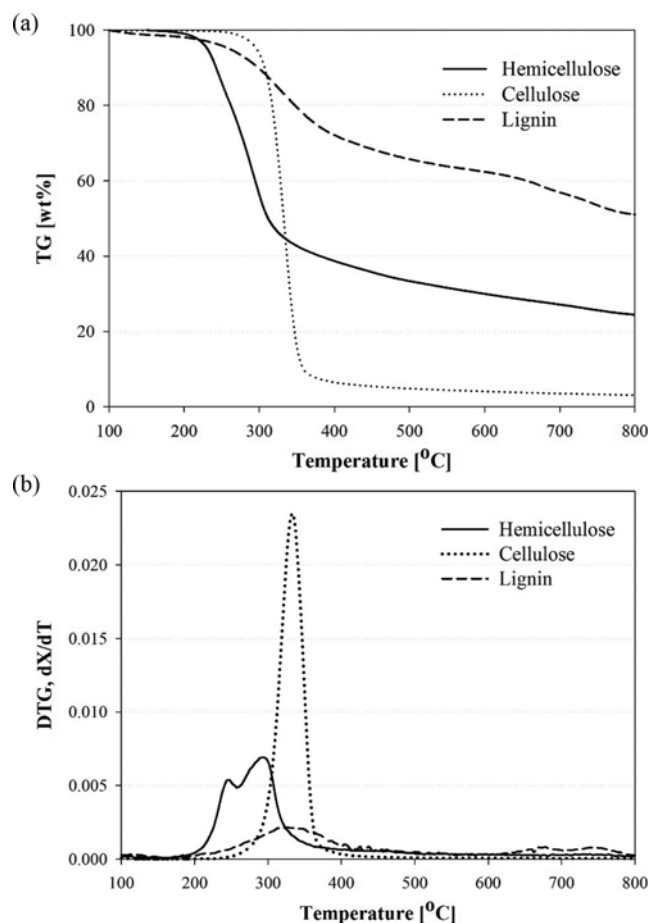


Fig. 2. (a) TG and (b) DTG curves of individual biopolymer at a constant heating rate of 10 °C/min.

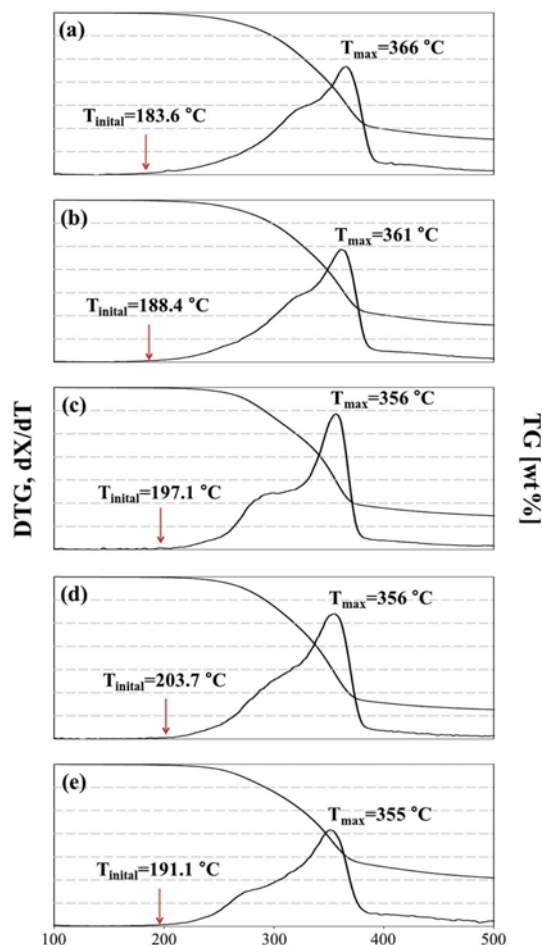


Fig. 3. TG and DTG curves of (a) *P. densiflora*, (b) *P. koraiensis*, (c) *Q. acutissima*, (d) *L. tulipifera*, and (e) NS of *P. koraiensis* at a heating rate of 10 °C/min.

hardwoods and NS of *P. koraiensis* (191.1–203.7 °C). This can be explained by the larger amount of extractives in the softwoods, which are thermally unstable components of biomass. Gronli et al. [17] also found a lower initial decomposition of softwoods than that of hardwood due to the larger amounts of extractives of softwoods (2–11 wt%) than those of hardwoods (2–4.5 wt%).

Maximum decomposition temperature ( $T_{max}$ ) of hardwoods (*Q. acutissima* and *L. tulipifera*) was lower (ca. 5–10 °C) than that of softwoods. This phenomenon can be explained by the different ash content (Table 4) and/or lignocellulosic composition of each biomass (Table 2). Eom et al. [33,34] conducted the demineralization of biomass to remove the inorganic metals, which act as a catalyst during pyrolysis, in biomass by acid or water extraction. As a result, the demineralized biomass sample has a higher  $T_{max}$  temperature. Although the ash content of NS of *P. koraiensis* (0.6%) is similar with that of softwoods (0.4–0.5%), it had a lower  $T_{max}$  than

the softwood samples, which can be explained by the larger amount of hemicellulose in the NS of *P. koraiensis* (32.8%) than softwoods (23.4–24.7%). Hemicellulose decomposition is initiated at a lower temperature than cellulose and lignin, however, its decomposition temperature zone overlaps with those of cellulose and lignin [11]. This means that the decomposition of hemicellulose can influence the decomposition of cellulose or lignin. Liu et al. [35] reported similar observations on the pyrolysis of fir. They compared the fir samples between before and after the extraction of hemicellulose from fir. The pyrolysis of fir containing hemicellulose was initiated earlier and showed a higher yield of residue than the hemicellulose-eliminated fir sample.

*L. tulipifera* had the lowest solid residue (12%) due to the lowest lignin content among the biomass samples tested. Although *Q. acutissima* had a similar solid residue to softwoods, it appears to be due to the higher content of ash (1.3%) and hemicellulose (37.3%)

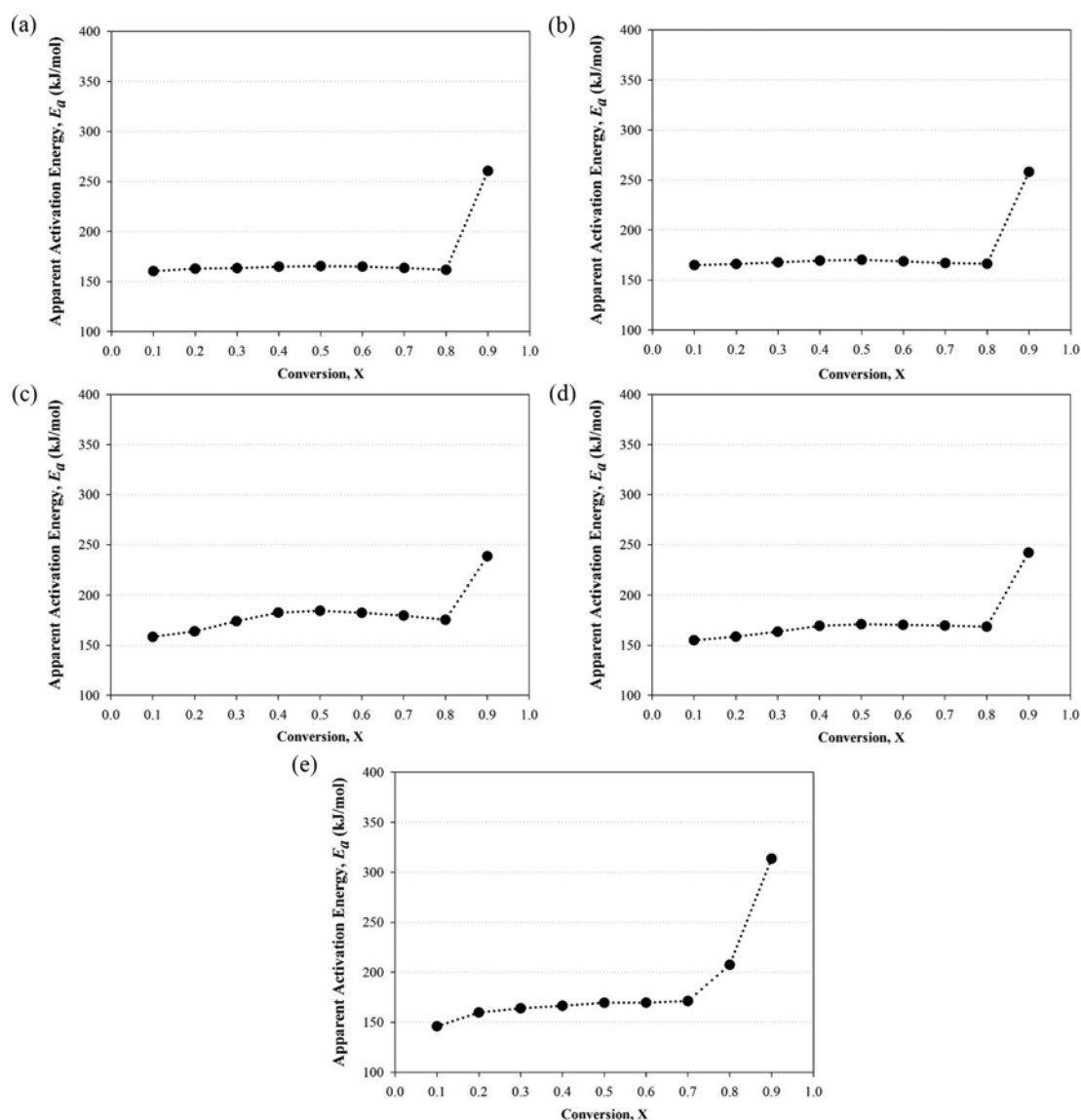


Fig. 4. Calculated apparent activation energies at different conversions of (a) *P. densiflora*, (b) *P. koraiensis*, (c) *Q. acutissima*, (d) *L. tulipifera*, and (e) NS of *P. koraiensis*.

than that of the other biomass (ash 0.4–0.8%; hemicellulose 23.4–32.8%) tested in this study.

Fig. 4 presents the apparent activation energies in regard to the conversion obtained by the model-free kinetic analysis of each biomass sample. Although the average activation energies for all samples were in a narrow range (174 to 185 kJ/mol), the variation patterns of the activation energy of each sample were quite different with conversion. Softwood containing a small amount of hemicellulose had a very narrow variation ranging from 160 to 165 kJ/mol for *P. densiflora* and from 165 to 170 kJ/mol for *P. koraiensis* between conversions of 0.1 and 0.8. The hardwood samples, however, showed wide variations, from 158 to 184 kJ/mol for *Q. acutissima* and from 155 to 171 kJ/mol for *L. tulipifera* between 0.1 and 0.8. The NS of *P. koraiensis* also had a wide range of activation energies between 0.1 and 0.7 conversion. Interestingly, the hardwoods and NS of *P. koraiensis* had distinct tendency differences for the before and after specific conversions: conversion of 0.4 for hardwoods and conversion of 0.2 for NS of *P. koraiensis*. These changes in activation energy can be explained by the change in the main pyrolysis reaction from hemicellulose to cellulose. The pyrolysis of hemicellulose and cellulose had different activation energies [36]. Sharp distinctions

were observed with the hardwoods and NS of *P. koraiensis*, which have higher hemicellulose content than softwood. The conversion point showing a sharp increase in the apparent activation energies was also different and moved to the lower conversion when the biomass contained a larger amount of lignin. Owing to the higher lignin content, softwoods and NS of *P. koraiensis* had a higher activation energy than the hardwoods with lower lignin content at a conversion of 0.9. This suggests that a higher energy is required for the pyrolysis of lignin and char stabilization.

### 3. EGA-MS Analysis

Fig. 5 shows the total ion thermograms (TTIs) of each biomass sample and the extracted ion thermograms (EITs) for the specific pyrolyzates of hemicellulose, cellulose, and lignin. As expected, the  $T_{max}$ s and  $T_{ini}$  temperatures of each biomass were similar to those of the DTG curves (Fig. 3). *Q. acutissima* and *L. tulipifera* had larger peak heights for the primary ion of acetic acid ( $m/z$ : 43), the specific pyrolyzate of hemicellulose, than that of other biomass. The primary ion of levoglucosan ( $m/z$ : 60), the specific pyrolyzate of cellulose, was observed between 300 °C and 400 °C. Although the *L. tulipifera* has the highest amount of cellulose (Table 2), its peak height for  $m/z$  60 between 300 °C and 400 °C was not higher than

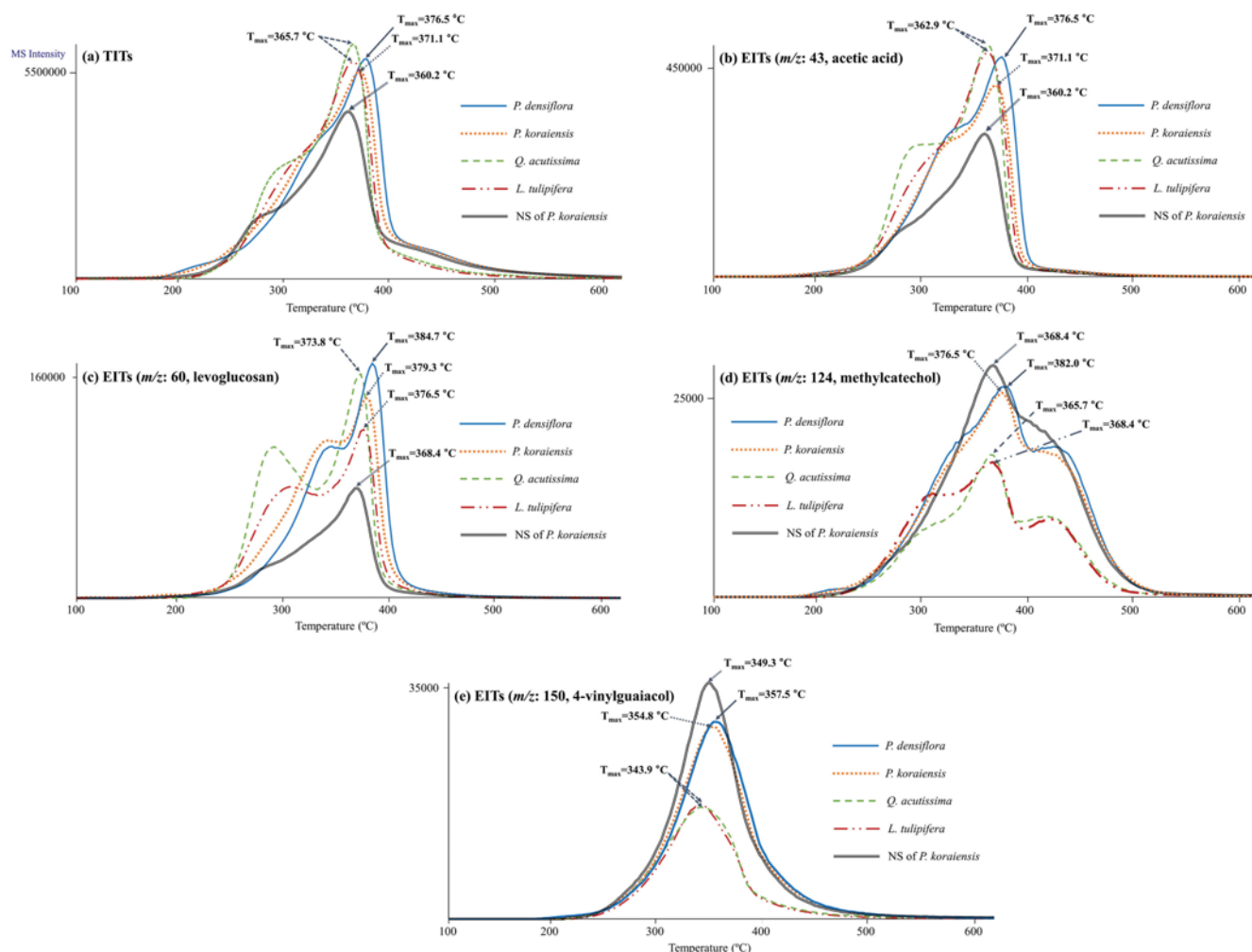


Fig. 5. Total ion thermograms (TTIs) and extracted ion thermograms (EITs) for specific pyrolyzates of hemicellulose (acetic acid,  $m/z$ : 43), cellulose (levoglucosan,  $m/z$ : 60), and lignin (methylcatechol,  $m/z$ : 124; 4-vinylguaiacol,  $m/z$ : 150) obtained from the EGA-MS analysis.

those of the other biomass samples except for the NS of *P. koraiensis*. Methylcatechol ( $m/z$ : 124) and 4-vinylguaiaicol ( $m/z$ : 150), which are generally considered to be the specific pyrolysis products of lignin (Fig. 5(d)-(e)) [22], were observed over a broad temperature region from 200 °C to 500 °C. Although each EIT of lignin pyrolyzate had a different thermal profile and peak temperature, the total peak areas of  $m/z$  124 and  $m/z$  150 were highest on the EITs of N.S

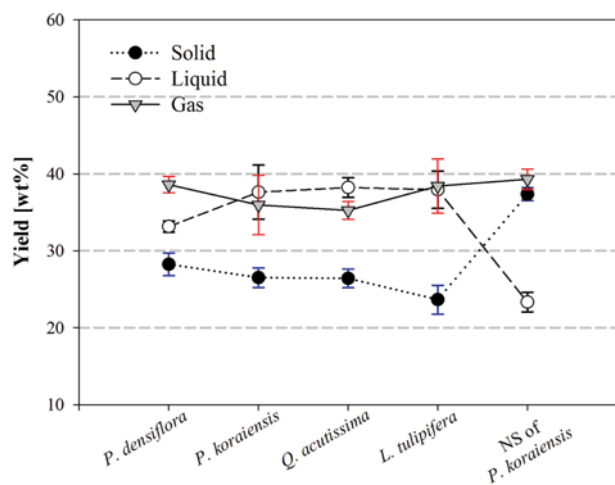


Fig. 6. Product yields for solid, liquid, and gas product from the non-isothermal pyrolysis of five biomass samples (pyrolysis up to 500 °C at a heating rate of 10 °C/min).

of *P. koraiensis*, which means that NS of *P. koraiensis* produces a large number of phenolic compounds due to the high lignin content [22].

#### 4. Fixed Bed Type Pyrolysis Reaction

##### 4-1. Gas, Liquid, and Solid Yields

Fig. 6 presents the yields of gas, liquid, and solid products obtained from the non-isothermal pyrolysis of five biomass samples up to 500 °C. Among the biomass samples tested, *L. tulipifera* produced the smallest amount of solid product and large amounts of liquid and gas product. The NS of *P. koraiensis*, which has a higher

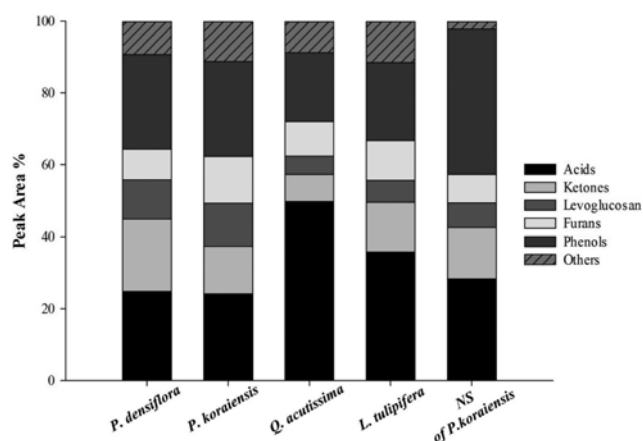


Fig. 7. Product distribution from the pyrolysis of five biomass samples.

Table 5. GC/MS area % of main compounds obtained from the pyrolysis reaction of five biomass samples

No.	Identified compound	Peak area (%)				
		<i>P. densiflora</i>	<i>P. koraiensis</i>	<i>Q. acutissima</i>	<i>L. tulipifera</i>	NS of <i>P. koraiensis</i>
1	Hydroxy-acetaldehyde	4.7	5.7	1.6	4.9	2.3
2	2-Oxo-butanoic acid	0.6	0.9	1.1	1.9	0.6
3	Acetic acid	22.5	21.7	48.6	33.9	27.7
4	1-Hydroxy-2-propanone	17.3	10.5	7.6	10.8	14.1
5	1-Hydroxy-2-butanone	0.7	0.8	-	3.0	-
6	Acetoxyacetic acid	1.8	1.6	-	-	-
7	1,4-Butanedione	2.2	3.6	2.6	-	-
8	Methyl pyruvate	2.0	1.9	-	-	-
9	Tetrahydro-4H-pyran-4-ol	2.5	1.9	-	-	-
10	2-Furanmethanol	2.5	6.4	4.6	5.1	1.6
11	2-Hydroxy-2-cyclopenten-1-one	6.0	6.6	5.0	6.0	6.4
12	Guaiaicol	4.5	4.7	4.4	2.4	9.2
13	Creosol	5.7	5.2	1.5	1.8	9.3
14	Ethylguaiaicol	3.2	3.6	0.5	1.4	7.0
15	Vinylguaiaicol	4.5	4.1	2.3	2.2	7.0
16	Syringol	-	-	5.1	6.5	-
17	Isoeugenol	8.5	8.9	2.2	2.7	7.9
18	Levoglucosan	10.8	11.9	5.2	6.0	6.9
19	3,4,5-Trimethoxy-toluene	-	-	2.0	3.1	-
20	3,5-Dimethoxyacetophenone	-	-	2.6	3.6	-
21	Methoxyeugenol	-	-	3.1	4.7	-
Sum		100.0	100.0	100.0	100.0	100.0



lignin content in its cell wall, produced a larger amount of solid residue than the other test samples. Although their difference was not so high, the softwoods produced larger amounts of solid residue than the hardwoods. These trends were also in accordance with the amounts of solid residues remaining after TG analysis (Fig. 3).

#### 4-2. GC/MS Analysis of Oil Products

The pyrolysis oil quality is also strongly influenced by the lignocellulosic composition [22] and ash content of each biomass [33,34]. Fig. 7 shows the area fractions of the acids, ketones, levoglucosan, furans, phenols, and other compounds in the bio-oils obtained from the pyrolysis of biomass and detailed GC/MS peak area % of each product was shown in Table 5. Compared to the hardwoods having the lower lignin contents than 16%, softwoods produced higher content of phenolic compounds due to their high lignin content (>24%). The NS of *P. koraiensis* showed the highest content of phenols due to the larger lignin contents (33.1%) in the NS of *P. koraiensis*.

Levoglucosan is produced mainly from the pyrolysis of cellulose in biomass, and the highest levoglucosan yield would be expected from the pyrolysis of *L. tulipifera* because it has the highest proportion of cellulose. On the other hand, the levoglucosan yield from the pyrolysis of *L. tulipifera* was not higher than that of the softwood samples (*P. densiflora* and *P. koraiensis*). This can be explained by the interactions between cellulose pyrolyzates and the pyrolyzates of hemicellulose and lignin [37] or the enhanced secondary cracking due to the larger amount of ash [38] during pyrolysis. Much higher content of acids, mainly acetic acid, was obtained from the pyrolysis of the hardwood samples because of its higher hemicellulose content than softwood [39].

#### 4-3. Characterizations of the Solid Products

Table 6 lists the characteristics (proximate, ultimate analysis, and HHV measurements) of the solid products obtained from the non-isothermal pyrolysis reaction up to 500 °C. Compared to the carbon content of raw biomass materials (mean: 47.5%), those of the solid products after the pyrolysis reaction were increased dramatically (mean: 76.8%). In addition, the oxygen content of the solid residue decreased with increasing HHV. According to the charac-

teristics of the solid residue produced from the fixed bed reactor, it was also confirmed that pyrolysis of the solid products of biomass can be used as useful renewable sources, such as soil amendment, activated carbon, and pulverized coal in a blast furnace because of its high energetic value.

## CONCLUSION

The pyrolysis of softwood, hardwood, and NS of *P. koraiensis* was different due to the different lignocellulosic compositions (hemicellulose, cellulose, lignin, and extractives) and ash content. TG analysis indicated different thermal decomposition profiles: 1) lower initial decomposition temperature of softwoods due to the higher amounts of extractives than those of hardwoods, and 2) lower maximum decomposition temperature of hardwoods and NS of *P. koraiensis* due to the larger ash and/or hemicellulose content. The NS of *P. koraiensis* showed higher yields of phenolic compounds, which are normally considered to be lignin pyrolyzates, followed by softwood and hardwood. The higher carbon content and heating value of the solid products highlights their potential use as an alternative energy source.

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**Table 6. Physico-chemical properties of the solid products after pyrolysis reaction**

		Softwood		Hardwood		Nut shell
		<i>P. densiflora</i>	<i>P. koraiensis</i>	<i>Q. acutissima</i>	<i>L. tulipifera</i>	<i>P. koraiensis</i>
Proximate analysis <sup>a</sup> (wt%)	Volatiles	23.2	18.3	11.3	18.6	16.6
	Fixed carbon	76.1	79.9	84.8	78.8	81.0
	Ash	0.7	1.8	3.9	2.6	2.4
	Sum	100.0	100.0	100.0	100.0	100.0
Ultimate analysis <sup>a</sup> (wt%)	C	74.8	77.4	75.6	77.3	78.8
	H	3.7	3.2	3.0	3.1	3.1
	O <sup>b</sup>	21.1	19.0	20.9	19.3	17.6
	N	0.4	0.4	0.5	0.3	0.5
	S	-	-	-	-	-
	Sum	100.0	100.0	100.0	100.0	100.0
HHV <sup>a</sup> (kcal/kg)		6,393.5	6,505.2	6,586.5	7,237.8	6,529.4

<sup>a</sup>wt% On a dry basis

<sup>b</sup>By difference



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