



# 유동층 열분해에 의해 생산된 바이오오일의 특성 Characteristic of bio-oil produced from fluidized bed pyrolysis

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### Introduction

#### 1. Biomass

##### Advantage

- Not strict limitations to the size and type of raw biomass used
- Variable use of the resultant product
- Less pollution problem (ex. CO<sub>2</sub> emission problem)

##### Application

- Direct combustion
- **Pyrolysis**
- Gasification
- Carbonization

Table 1. The range of main operating parameters for pyrolysis processes

	Conventional pyrolysis	Fast pyrolysis	Flash Pyrolysis
Temperature [K]	550-950	850-1250	1050-1300
Heating rate [K/s]	0.1-1	10-200	>1000
Particle size [mm]	5-50	<1	<0.2
Heating time[s]	450-550	0.5-10	<0.5

#### 2. Bio-oil

- Water soluble phase  
Low molecular compounds (low molecular acids)
- Water insoluble phase (Tar)  
High molecular compounds (aromatics)
- Application  
pitch, varnish, cement, antiseptic, sterilizer, medicine etc.

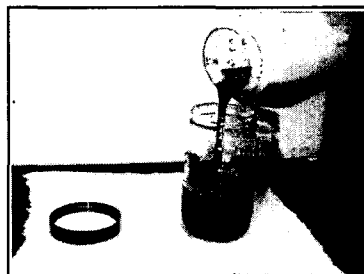


Fig. 1. Typical bio-oil produced produced by fast pyrolysis.

1. Main reaction of pyrolysis

- depolymerization, hydrolysis, oxidation, dehydration, decarboxylation etc.

2. Main composition of bio-oil

- Phenol, cresol, methyl cresol, catechol, guaiacol, creosol, phlorol, toluene, xylene, naphtalene etc.

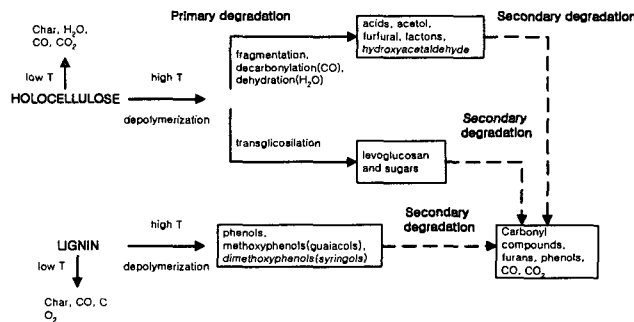


Fig. 2. A lumped reaction mechanism of wood decomposition (Branca et al., 2003).

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1. Fast pyrolysis

Biomass

Larch, *Quercus acutissima* sawdust 0.25~1mm

Bed material

white fused alumina 35 μm (NANKO, DN2343)

Table 2. Operating conditions of fluidized bed reactor

	experimental variable
Temperature [°C]	350, 400, 450, 500, 550
Feedrate[g/min]	2.0~5.0

\* L/D = 2.0,  $U_0/U_{mf} = 4.0$

Fluidized bed reactor

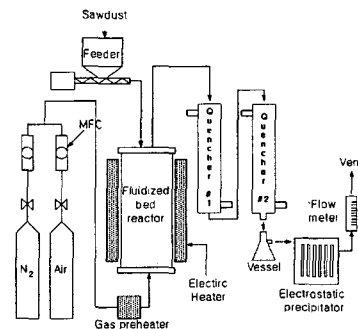


Fig. 3. Schematic diagram of bubbling fluidized bed reactor system.

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2. Analysis

Table 3. Analytical methods used this study

Biomass	Holocellulose	TAPPI Useful method 249
	Cellulose	TAPPI T17 wd 70(T 17m-55)
	Hemicellulose	Holocellulose%-cellulose%
	Lignin	TAPPI standard T222 om-83
Bio oil	pH	Digital pH meter
	Water content	Karl Fischer's titration [ASTM E 203]
	Qualification	HP-5973 MSD 5min at 40 °C, then at 5 °C/min to 300 °C and 10 min at 300 °C
	Quantification	HP-6890 FID 5min at 40 °C, then at 5 °C/min to 300 °C and 10 min at 300 °C Using RRF(Relatively Response Factor) from literature and STD.

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1. Composition of biomass

Table 4. Typical composition of different biomass species

	Ash	Lignin	Holocellulose	
			Cellulose	Hemicellulose
<i>Quercus acutissima</i>	-	15.02	46.35	36.49
Larch	0.58	39.97	76.78	
* <i>Quercus variabilis</i>	Sapwood	0.57	21.76	
	Heart wood	1.00	18.14	
* <i>Quercus serrata</i>	Sapwood	0.26	14.11	
	Heart wood	0.27	19.19	

\* Moon(1982)

2. Bio-oil

Table 5. Physical properties of tar residue and bio oil (at 400 °C)

Fast pyrolysis oil	pH	Water content [%]
<i>Quercus acutissima</i>	2.67	15.02
Larch	2.16	39.97

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3. Yield of products (Temperature effect)

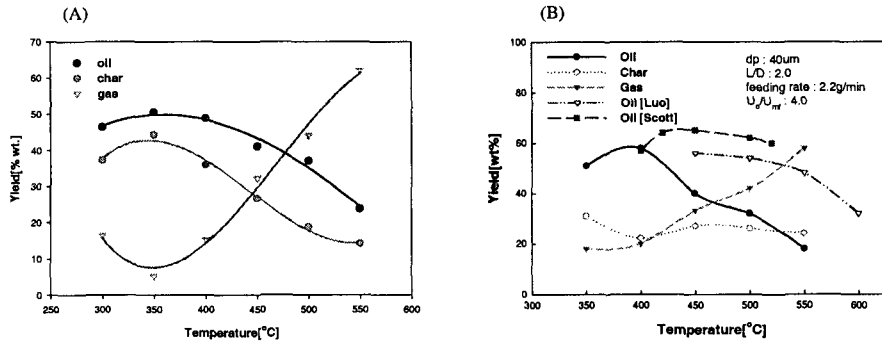


Fig. 4. Effect of temperature on the product yield of (A) *Quercus acutissima* and (B) Larch.

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3. Yield of products (Feed rate effect)

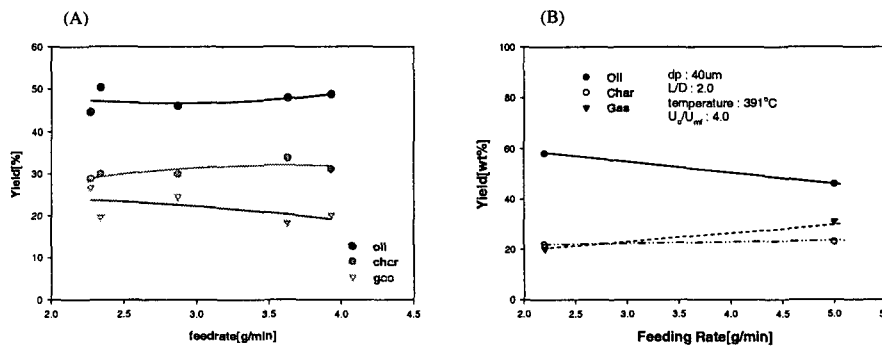


Fig. 5. Effect of feed rate on the product yield of (A) *Quercus acutissima* and (B) Larch.

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3. Composition of bio-oil

Qualification (GC/MS) & Quantification (GC-FID)

Peak identification & Classification (Branca et al.)

•Furans



•Phenols



•Guaiacols (methoxyphenols)



•Syringols (dimethoxyphenols)

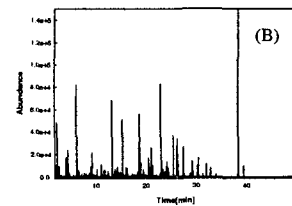
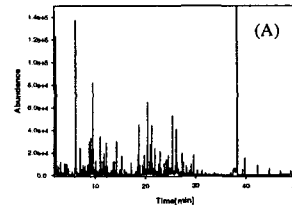
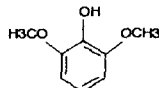


Fig. 6. Total ion chromatograms of (A) *Quercus acutissima* and (B) Larch bio-oil (at 400 °C).

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4. Composition of bio-oil (Temperature effect)

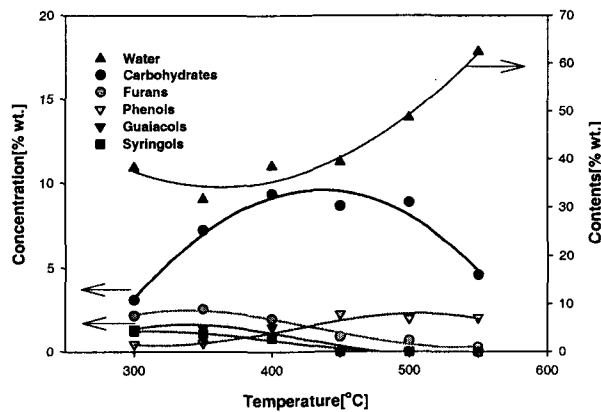


Fig. 7. Effect of temperature on composition of bio-oil (*Quercus acutissima*).

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4. Composition of bio-oil (Feed rate effect)

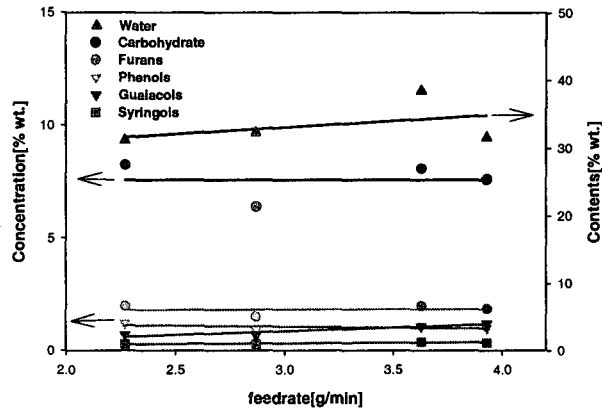


Fig. 8. Effect of feed rate on composition of bio-oil (*Quercus acutissima*).

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- 각 수종의 리그닌, 셀룰로오스 함량은 상수리 나무가 낙엽송에 비해 셀룰로오스 함량은 높고, 리그닌 함량이 적은 것으로 나타났다. 이는 열분해오일의 수율최적온도와 조성에 영향을 끼쳐 상수리나무의 경우가 최적온도가 낮고, 유기산의 함량이 높은 것으로 사료된다.
- 상수리나무와 낙엽송 각각의 바이오오일은 pH 2.16과 2.67로 강한 산성을 나타냈다.
- 온도가 올라갈수록 액상, 고상 생성물의 수율은 전체적으로 감소하는 경향을 보이나 기상 생성물은 증가하는 경향을 보였다. 이는 온도가 올라갈수록 열에 의한 분해가 더욱 진행되어 고상 액상에서 기상 생성물로 전환되었기 때문이라 사료된다. 바이오오일의 최대수율은 상수리나무와 낙엽송이 각각 350도와 400도에서 나타났고, 상수리나무의 높은 셀룰로오스 함량때문이라고 사료된다. 주입량이 증가함에 따른 생성물의 수율은 온도에 대한 영향보다 작게 나타나 유동층 열 분해 시 보다 주요한 인자는 온도인 것으로 사료된다.
- 바이오오일의 조성을 관찰해보면 바이오오일의 최대수율인 350도에서 수분함량이 가장 적은 것으로 나타났고, 오일의 수율과 반비례하는 경향을 보였다. carbohydrate 류의 농도는 약 400도에서 최대를 보였고 온도가 증가함에 따라 감소하는 경향을 보였다. Phenol 류의 농도는 온도가 증가함에 따라 증가한 반면 furan, guaiacol, syringol 류는 온도가 증가함에 따라 감소하는 경향을 보였다. 이는 온도가 증가함에 따라 고분자 페놀 화합물인 syringol, guaiacol 류의 hydroxy기와 methoxy기가 분해되어 저분자 화합물인 phenol류로 전환되기 때문이라 사료된다.

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