

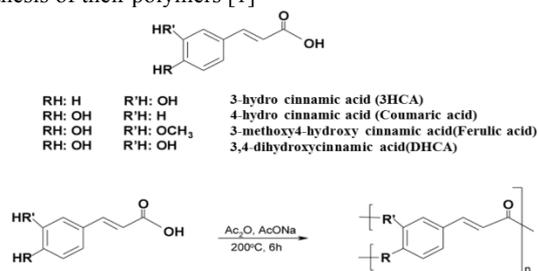
# Production of monomers for biodegradable plastics with lignin as raw material

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## 1. Introduction

Bio-base polyesters exhibiting smooth degradation have been widely studied as environmentally friendly polymeric material. They can be derived from renewable feedstock, thereby reducing greenhouse gas emissions. For instance, polyhydroxyalkanoates and lactic acid (raw materials for polylactic acid) can be produced by fermentative biotechnological processes using agricultural products and microorganisms. However the rate of these fermentative reactions is small, so production of these monomers in bulk is still difficult.

Kaneko et al. [1] reported that coumaric acid derivative homo-polymers which are one type of bio-base polyester showed smooth in-soil degradation. **Figure 1** shows chemical structures of various coumaric acid derivative monomers and synthesis of their polymers [1]



**Figure 1:** Chemical structures of various coumaric acid derivative monomers and synthesis of their homo-polymers

These coumaric and ferulic acids are contained as the main phenyl propane construction monomers in lignin [2]. Lignin is one of the major substances in plant together with cellulose and hemicellulose; however there are a great quantity of lignin residue in the world such as rice straw and pulp industry residue. Production of biodegradation plastics from lignin residue is one of effective methods to resolve the environmental problems.

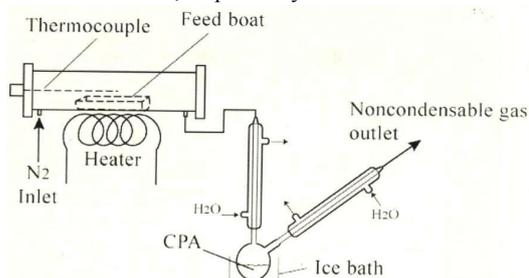
In this work, the preparation of coumaric and ferulic acids from lignin is studied. The pyrolysis of lignin under steam atmosphere was conducted to decompose the complexity construction of lignin structure to simple substances. Liquid products from pyrolysis of lignin were analyzed by UV spectroscopy and high performance liquid chromatography (HPLC) to study the existence of coumaric acid and ferulic acid. After that, extraction experiment was conducted to recover the obtained acids. Moreover, the pyrolysis of the agriculture residue of rice straw, which contains about 19~21% lignin by mass, was also studied.

## 2. Experimental

**Material.** Lignin powder was purchased from Kasei Kanto Co. Coumaric acid and ferulic acid were purchased from Wako pure chemical Co. Rice straw was obtained from Hiroshima. Dried rice straw was ground and sieved to obtain particles ranging between 1.7 and 0.35 mm.

**Pyrolysis.** **Figure 2** shows the schematic diagram of pyrolysis experimental system. The sample holder was filled with lignin or rice straw, and placed at the center of the pyrolysis reactor. Nitrogen and water were supplied during the pyrolysis. All of the gases flowing out from the end of the reactor were sent to the liquid product trap to obtain the liquid product of crude pyrolytic acid (PCA). Non-condensable gases were discharged to open air. The experimental conditions for pyrolysis of lignin and rice straw are showed at **Table 1**. The thermal decomposition of lignin should take place at

temperature above 350°C [4] and the temperatures of pyrolysis were fixed at 500°C, 600°C, 700°C, 800°C with lignin, and at 600°C with rice straw, respectively.



**Figure 2.** Schematic diagram of pyrolysis experimental system  
**Table 1** Experimental condition of thermal treatment of lignin

Feed	Lignin (Rice straw)	
Mass of feed	$m_{Feed}$ [g]	12~15
Atmosphere	$N_2$	
Flow rate of atmosphere	$f_{N_2}$ [mL/min]	50
Flow rate of moisture	$f_{H_2O}$ [mL/min]	1
Temperature	$T$ [°C]	500, 600, 700, 800
Holding time	$t$ [h]	1

### Extraction of coumaric acid from liquid products.

At extraction experiment, ether and then aqueous sodium hydrogen carbonate solution were added in liquid products one by one. The obtained acids in liquid products should be converted to sodium salt forms after reacting with sodium hydrogen carbonate, and dissolved in aqueous phase. Each phase of this process was analyzed by UV spectroscopy. The experimental condition of extraction is showed at **table 2**

**Table 2** Experimental condition of extraction of liquid products

Feed	Liquid products	
Aqueous phase	Aqueous solution of $NaHCO_3$	
Organic phase	Ether	
Concentration aqueous solution of $NaHCO_3$		
	$C_{NaHCO_3, aq, 0}$ [kmol/m <sup>3</sup> ]	0.01
Volume of feed	$V_{feed}$ [m <sup>3</sup> ]	$3.0 \times 10^{-5}$
Volume of aqueous phase	$V_{aq}$ [m <sup>3</sup> ]	$3.0 \times 10^{-5}$
Volume of organic phase	$V_{org}$ [m <sup>3</sup> ]	$3.0 \times 10^{-5}$
Temperature	$T$ [°C]	298

**Analysis of liquid products.** Liquid products from the pyrolysis were analyzed by UV Probe 2.43 and HPLC (Shimada. Co). At HPLC analysis, the mobile phase is methanol. The mobile phase was delivered at a rate of 0.5 mL/min. The detection was monitored at 280nm.

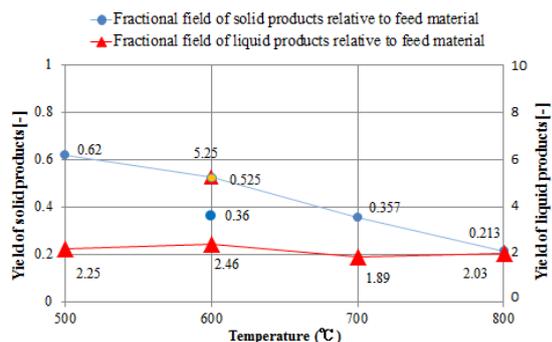
## 3. Results and Discussion

### Pyrolysis

The products obtained from the pyrolysis were solid, liquid, and gas ones. Because of the quantity of moisture supplied during heat treatment, mass of liquid products were greater than mass of feed material. In **Figure 3**, the blue and red points show the yield of solid products and fractional yield of liquid products relative to material.

In pyrolysis of lignin, there was a significant reduction in yield of solid products at higher temperature. In contrast, it only had a little change in the fractional yield of liquid products relative to feed material. Therefore, it was considered that the

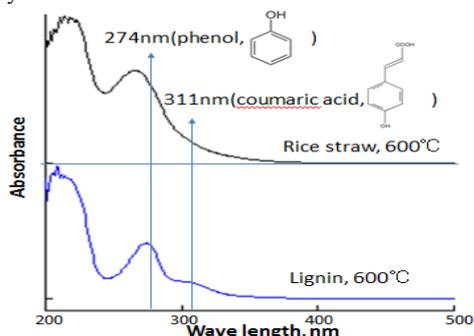
gas products increased proportionally at higher temperature. In the temperature range from 500°C to 800°C, the pyrolysis temperature had significant effects on the yields of solid and gas products, but it had little effects on the yield of liquid products.



**Figure 3.** Fractional yield of solid products and liquid products relative to feed material

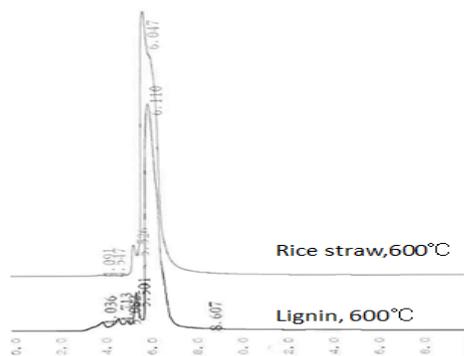
Comparing between pyrolysis of lignin and rice straw at 600°C, rice straw was degraded more than lignin. Liquid products from pyrolysis of rice straw were more than two times to these from lignin. It might be caused by the degradation of hemicellulose and cellulose in rice straw. These substances were degraded at lower temperature than lignin.

Figure 4 shows the UV spectroscopy of liquid products from pyrolysis of lignin and rice straw at 600°C. The wavelengths of the absorptions were observed at 311nm of coumaric acid, 322nm of ferulic acid and 274 nm of phenol, respectively.



**Figure 4.** UV-spectroscopy of liquid products from pyrolysis of lignin and rice straw at 600°C

There were broad absorption bands with peaks around 260-280 nm in both the samples. Because the absorption at 322 nm was relatively small, only little amount of ferulic acid could be generated. The absorption at around 311nm was observed in liquid products obtained from pyrolysis of lignin. The absorption of coumaric acid was also at 311nm, as shown above.



**Figure 5.** HPLC of liquid products from pyrolysis of lignin and rice straw at 600°C

It was found that the aqueous solutions of coumaric sodium salt showed absorption at around 286 nm. Mixture of liquid

products and sodium hydrogen carbon solution presented the peak of 5.5 min which did not present at liquid products sample only. The result of HPLC analysis is showed at **Figure 5**

Then, the concentration of coumaric acid was quantified. The fractional yields of coumaric acid relative to feed material were shown in **Table 2**.

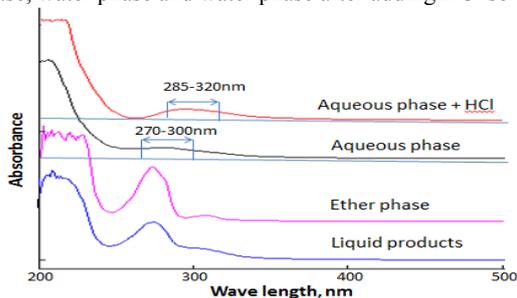
**Table 2** Concentration of sodium salts of coumaric acid

Samples	Concentration coumaric acid in liquid products[mg/ml]	Fractional yield of coumaric acid relative to feed
Lignin 500°C	0.465	0.0010
Lignin 600°C	0.488	0.0012
Lignin 700°C	0.430	0.0008
Lignin 800°C	0.459	0.0009
Rice straw 600°C	0.464	0.0024

Although rice straw contained lignin with only about 0.2 by mass fraction, the yield of coumaric acid was greater than that with lignin. For examples, from these results, it could obtain about 2.4 g of coumaric acid from 1kg feedstock of rice straw. The yield of coumaric acid exceeded slightly in liquid products heat treatment at 600°C than other temperature. Therefore, operating heat treatment of lignin at 600°C should be preferable. However yield of coumaric acid from lignin heat treatment products was still small.

#### Extraction of coumaric acid from liquid products.

Figure 6 shows UV spectroscopy of liquid products, ether phase, water phase and water phase after adding HCl solution.



**Figure 6.** UV spectroscopy of liquid products, ether phase, water phase and water phase +HCl

The distribution coefficient,  $D_i$ , was defined as,

$$D_i = \frac{\text{Absorbance of substance in water phase} \times \text{Concentration in water phase}}{\text{Absorbance of substance in ether phase} \times \text{Concentration in ether phase}}$$

Phenol was considered as the major impurity for the recovery of coumaric acid from liquid products. The  $D_i$ s of coumaric acid and phenol were measured as 2.2 and 0.055, respectively with liquid products of thermal treatment of lignin at 600°C.

Coumaric acid was extracted in the aqueous phase while most of phenol remained in ether phase. Although the purity of coumaric acid is still problem, this extraction experiment method can remove a quantity of impurities in liquid products away coumaric acid.

#### 4. Conclusions

It can be concluded that coumaric acid exits in liquid products from thermal treatment of lignin. Thermal treatment lignin at 600°C is most adequate to obtain more quantity of coumaric acid. Separation of sodium salt of coumaric acid from liquid products by HPLC is analytically succeeded. Small quantity of coumaric acid is extracted from main impurities in liquid products. It is necessary to take account of more efficient extraction method or thermal treatment experimental conditions to obtain more quantity and pure of coumaric acid.

#### References

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