BASIC STUDIES ON THE PYROLYSIS OF LIGNIN COMPOUNDS

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SUMMARY

By pyrolyzing lignin model compounds 1-lV at 315°C, an investigation was carried out with some results. In the pyrolysis of lignin model compound I and 11, 0.47 mol of guaiacol, 0.57 mol of dimethoxyphenol (DMP), and 0.12 and 0.23 mol of dimethoxyaceton ophenone (DMAP) were produced respectively. In the pyrolysis of lignin model compound lll and lV, 0.26 mol of guaiacol, 0.30 mol of DMP, and 0.09 and 0.15 mol of trimethoxy acetonphenone (TMAP) were produced respectively. The results show that pyrolysis mechanism of lignin model compounds were dehydrated at first, and then guaiacol, DMP, DMAP arid TMAP were formed by cleavage of ß-o-4 linkage one after another.

keyword : lignin compounds, ß-o-4 linkage, pyrolysis, guaiacyl ring, syringyl ring, veratryl ring, guaiacol

1. INTRODUCTION

To get the alternative resources to fossil resources, many researches have been performed actively to secure precious materials of chemical industry or produce energy from woody biomass. The purpose of those researches is to make a systematic investigation and put to practical use by separating Cellulose, Hemicellulose, Lignin from woody biomass in Europe and America. Especially, they have applied lignin of its aromatic ring to basic experiment to use properly by combining several lignin compounds.

The purpose of studying lignin among them is not only to examine chemical structure but also serve to reveal various reactions in relation to number chemical industry. This could improve the device for the progress of work as well. Besides, we could take advantages from exploitation of it.

Among each kind of lignin model compounds, the compound of arylglycerol-ß-arylether structure has a phenylpropane linkage pattern which is the most important in lignin. This kind of ß-o-4 linkage accounted for about 30% to 50% in the whole lignin phenypropane unit. Because this compound whose structure is aryl-glycerol-ß-arylether as a linkage pattern of lignin phenylpropane unit, is much in quantity and contains relatively abundant ß-ether, it has been used as a basic model compound to hold an inquest over the reactivity of lignin or the interpretation of the structure of lignin through analyzing various reactions of resolution in the process of the dissociation of pulp and bleaching by many viewers for ages.

Nowadays, a composition of lignin model compound is also under investigation in various ways abroad.

The recent researches on the pyrolysis of lignin model compound were performed by Domburg[2], Klein[6] and Brezny[1]. The mechanism of resolution is shown in *Figures.* This paper, by consulting these literatures, examined pyrolysis reaction from these materials in compounding with recently developed fastest method and high possibility by synthesizing nonphenolic dimer lignin. However, unfortunately only five pieces of research articles on synthesis and analysis of lignin were presented by Yoon[7] and Hwang[3,4,5,7,] and nothing was done about pyrolysis of lignin in Korea, so far. The purpose of this paper is to provide materials for examination on pulp and every kind of reactivity and to secure basic resources for exploiting biomass in the field of woody resources. The process of this experiment is as follows: arylglycerol-ß-arylether linked compound which exists in lignin of high probability was synthesized first and then pyrolysized at 250-500°C and lastly the quantitative analysis was attempted by GC-MS, which served to reveal pyrolysis reaction mechanism. Such researches have

seldom been carried out in Korea. Therefore, we need to look into the level of the research through this experiment.

2. MATERIALS AND METHODS

2.1 Synthesis of lignin model compound

KP lignin and lignin dimer model compound which is the sample materal for the characteristics of lignin pyrolysis were synthesized through a synthesis process which is indicated in *Fig. 1, 2.*

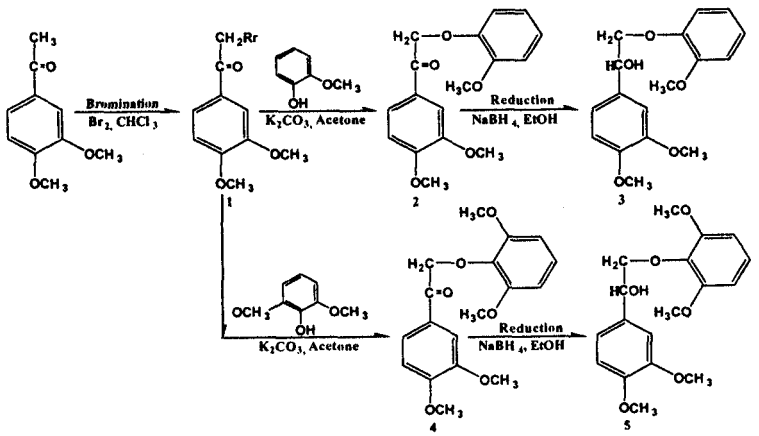

Fig. 1. Synthesis pathway of the ß-O-4 compounds. (V-G and V-S copolymers).

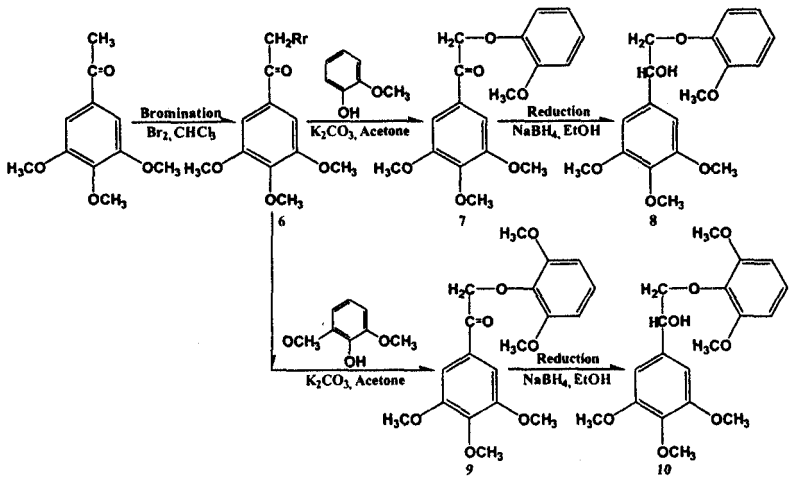

Fig. 2. Synthsis pathway of the ß-O-4 compounds. (T-G and T-S copolymers).

2.2 Pyrolysis of Lignin model compound

2.2.1 Sample material for lignin pyrolysis

The sample material for pyrolysis of compound synthesized from the process 1) are 1 -(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-ethanol [V-G, 1], 1-(3,4-dimethox y-phenyl)-2-(2,6-dimethoxyphenoxy)-ethanol [V-S,11], 1-(3,4,5-tri-methoxyphenyl) -2-(-methoxyphenoxy)-ethanol [T-G, lll], and 1-(3,4,5- trimethoxyphenyl)-2-(2,6-di-methoxypheno xy)-ethanol [T-S, lV].

Its structural formula is as follows.

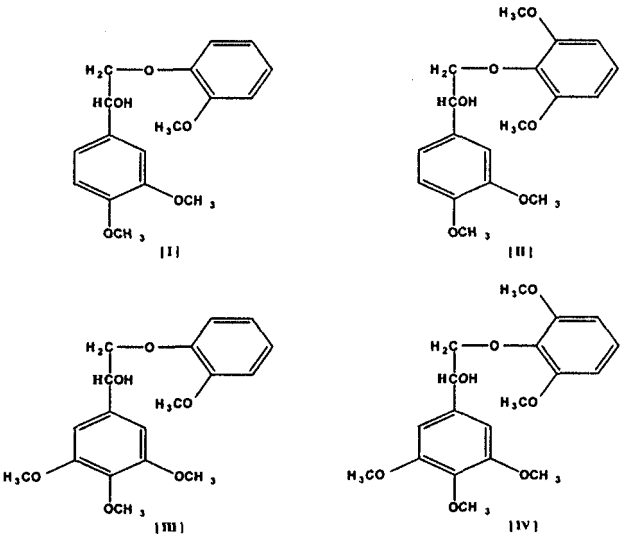

Fig. 3. Pyrolysis samples of the ß-O-4 lignins.

2.2.2 Pyrolysis Conditions

There was a preliminary examination at 250-500°C attempted to sustain an appropriate temperature for pyrolysis of sample material. The result was shown to be 315°C. A glass tube (about 10 cm in length, 5 mm in diameter) for pyrolysis and an oil bath equipment was provided to keep the temperature 1000°C as a pyrolysis apparatus. It was certain that the examination was pyrolysized after adjusting at 315°C.

2.2.3 Pyrolysis Test

After putting each sample material which was scaled at 10-20 mg into a pyrolysis tube, substituting it into N_2 and sealing it, we pyrolysized at the intervals of 5, 10, 15, 20, 25, 30, 60 minutes in the oil bath equipment adjusted at 315°C. Finally the pyrolysis tube was cut, being chloroform eluted with and filtrated, which is based on the quantitative analysis by GC-MS.

3. RESULTS AND DISCUSSION

Table 1-4 shows the results of this experiment which we pyrolysized four sample materials of lignin compounds adjusted at 315°C from 5 min. to 60 min. and analyzed by GC-MS to find out the characteristics for pyrolysis of lignin model compounds. The data by diagrammatizing is indicated in *Fig. 4-7* so that we can recognize better.

Table 1. Yield of pyrolysis products of the V-G copolymer (I)

	GOH[a]	DMAP	V-G[b]
0	0.00	0.00	1.00
5	0.11	0.05	0.40
10	0.23	0.09	0.31
20	0.38	0.12	0.28
30	0.40	0.11	0.27
40	0.42	0.10	0.23
50	0.45	0.13	0.20
60	0.47	0.12	0.20

[a] guaiacol
[b] veratryl-guaiacol

An A ring of lignin model compound 1 and 11 is veratryl nucleus and an A ring of lignin model compound lll and lV is trimethoxyphenol. The results show the productivity of aromatic ring with high possibility in which guaiacol and DMP was produced more in the experimental material of veratryl nucleus than in that of trimethoxyphenol under condition at 3 15°C. In other words, in the lignin model compound 1 and 11, 0.47mol of guaiacol, 0.57mol of DMP, and 0.12 and 0.23mol of DMAP were produced respectively.

Table 2. Yield of pyrolysis products of the V-S copolymer(II)

	DMP	DMAP	V-S [a]
0	0.00	0.00	1.00
5	0.21	0.13	0.53
10	0.41	0.19	0.34
20	0.54	0.20	0.24
30	0.55	0.24	0.16
40	0.57	0.22	0.08
50	0.58	0.22	0.03
60	0.57	0.23	0.01

[a] veratryl-syringyl

And in the lignin model compound lll and lV, 0.26mol of guaiacol, 0.30 mol of DMP, and 0.09 and 0.15mol of TMAP were produced respectively.

Table 3. Yield of pyrolysis products of the T-G copolymer(III)

	GOH	TMAP	T-G[a]
0	0.00	0.00	1.00
5	0.05	0.04	0.40
10	0.09	0.06	0.13
20	0.13	0.07	0.10
30	0.17	0.08	0.10
40	0.19	0.08	0.09
50	0.23	0.08	0.08
60	0.26	0.09	0.04

[a] trimethoxyphenyl-guaiacol

Table 4. Yield of pyrolysis products of the T-S copolymer(IV)

	DMP	TMAP	T-S[a]
0	0.00	0.00	1.00
5	0.11	0.09	0.39
10	0.16	0.11	0.24
20	0.23	0.13	0.20
30	0.28	0.13	0.18
40	0.28	0.12	0.15
50	0.28	0.15	0.13
60	0.34	0.13	0.16

[a] trimethoxyphenyl-syringyl

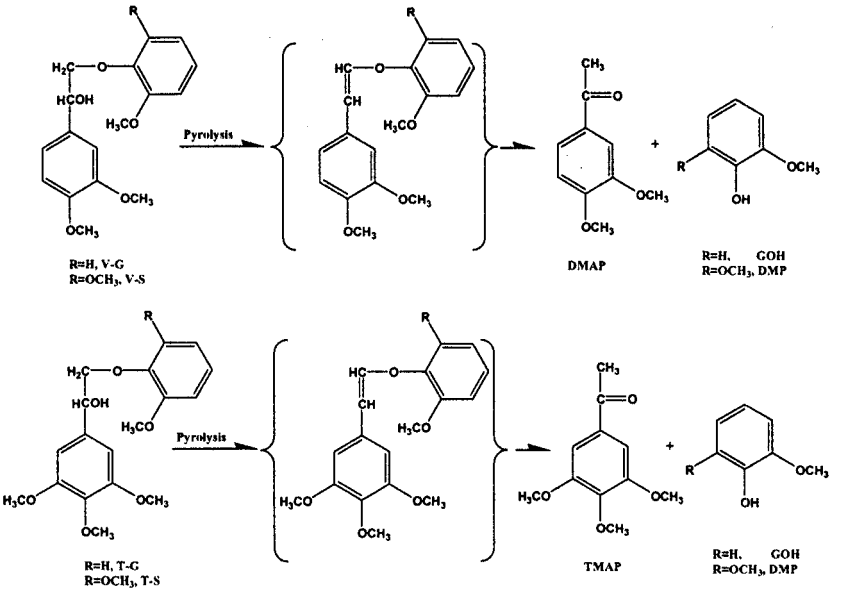

Fig. 8 Pyrolysis products of the ß-O-4 lignins.

The reaction mechanism which was expected by pyrolyzing lignin compound was explained in Fig. 8. It can explain that the experiment is dehydrated at a, b first and converted into an intermediate compound and then formed DMAP, guaiacol and DMP in the experimental material 1 and 11 by cleavage of the combination of arylglycerol-ß-arylether. Also in the experimental material lll and lV, dehydration was occured first. After converting into and intermediate compound, TMAP, guaiacol and DMP were formed by cleavage of 8-0-4 linkage one after another.

4. CONCLUSION

Lignin model compounds 1-lV were pyrolyzed at 315 °C . The mixture compounds pyrolized were analyzed by GC-MS spectrometry. The results are as follows:

1. In the pyrolysis of lignin model compound I and 11, 0.47mol of guaiacol, 0.57mol of dimethoxyphenol(DMP), and 0.12 and 0.23mol of dimethoxyacetonophenone(DMAP) were produced respectively.

2. In the pyrolysis of lignin model compound 111 and lV, 0.26mol of guaiacol, 0.30mol of DMP, and 0.09 and 0.15mol of trimethoxyacetonphenone(TMAP) were produced respectively.

3. Pyrolysis mechanism of lignin model compounds are dehydrated at first, and guaiacol, DMP, DMAP and TMAP were formed by cleavage of ß-O-4 linkage one after another.

The above results show that lignin model compound I and 11 produce more aromatic compounds than lignin model compound 111 and lV. This is the reason that the structures of veratryl unit may pyrolyze easier than that of trimethoxyphenol unit. Further empirical and formal investigation will be needed to settle this issue.

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