Effect of solvents on reactions of lignin-related compounds over iron-oxide based catalyst for selective production of phenol

Takuya Yoshikawa,[a,*] Kanta Yamaguchi,[a] Yuki Kawamata,[a] Yuta Nakasaka,[a] Yoshihito Koyama,[a,b] Eri Fumoto,[c] Shinya Sato,[c] Teruoki Tago,[d] Takao Masuda,[a]

[a] *Faculty of Engineering, Hokkaido University, Sapporo, 060-8628, Japan*

[b] *Advanced Technology Research Laboratories, Idemitsu Kosan Co.,Ltd., Sodegaura, 299-0293, Japan*

[c] *Research Institute of Energy Frontier, National Institute of Advanced Industrial Science and Technology, Tsukiba, 305-8569, Japan*

[d] *School of Materials and Chemical Technology, Tokyo Institute of Technology, 152-8550, Tokyo, Japan*

**Corresponding author: (+81)-11-706-6552, yoshikawa@eng.hokudai.ac.jp*

Abstract: The effect of solvents on the reactions of lignin model compounds and reagent lignin-derived substrate was investigated over iron-oxide based catalyst. As compared with the result using 1-butanol solvent, which was conventionally employed for organosolv treatment of biomass in our group, substituted phenols derived from 1-butanol decreased, and phenol increased in the reactions of model compounds using benzene as a solvent. Moreover, quinoline was applied for solvent of reagent lignin-derived substrate because it has both the good solubility and low reactivity toward iron-oxide based catalyst, resulting in a higher yield of phenol.

Keywords: Lignin, Phenol, Solvent.

1. Introduction

Lignin can be an alternative source of phenol because it is composed of alkylphenol unit. Many researchers have focused on catalytic reactions of lignin model compounds containing various types of functional group and linkage between lignin units[1]. Because lignin extracted from raw biomass is solid or paste-like substance in many cases, some solvent for supplying the feedstock to flow type reaction system is needed. However, study on the solvents having both good solubility of lignin-related compounds and low reactivity toward the employed catalysts is limited.

Our group have developed two-step process for producing phenols from reagent lignin, in which lignin was treated in water/1-butanol (hereafter BuOH) mixture and thus obtained lignin-derived liquid was reacted over an iron-oxide catalyst[2,3]. About 40% of the phenols were substituted with butyl group derived from BuOH solvent. For this reason, it is expected that replacement of solvent from BuOH to that with low reactivity toward the catalyst leads to improve the yield of phenol in 2nd step of the process. In this study, therefore, the effect of solvents on the reactions of lignin model compounds and reagent lignin-derived substrate was investigated over iron-oxide based catalyst.

2. Experimental

Based on the chemical structure of lignin, 1-phenoxy-2-phenylethane and guaiacol were selected as lignin model compounds containing alkyl ether bond and methoxy group, respectively, and diluted with BuOH or benzene. Catalytic reactions of the model compounds were carried out using high pressure fixed bed flow type reactor over TiO_2-FeO_X catalyst, which was prepared by co-precipitation method, and reaction conditions were as follows: T=400 °C, P=15 MPa, *Time*=2 h, W/F=0.5 h, F_{H2O}/F=2.5, where W is the amount of catalyst, F is the flow rate of feedstock and F_{H2O} was the flow rate of steam. After the reaction, liquid product was analyzed by GC-FID, GC-MS and HPLC.

Water/BuOH treatment of reagent lignin (Tokyo Chemical Industry) was carried out in a batch type reactor using silica-alumina catalyst. After evaporating the solvent from BuOH phase containing lignin-derived compounds, the concentrate were re-solubilized in BuOH or quinoline. The catalytic reaction were

carried out using fixed bed flow type reactor under atmospheric pressure. Other reaction conditions and analytical procedure were the same with that using the above lignin model compounds.

3. Results and discussion

Benzene was confirmed inert over in advance TiO_2-FeO_X catalyst. Table1 shows the conversion of 1-phenoxy-2-phenylehtane and the yield of phenol and C4 substituted phenols including butyl phenol. As compared with the result using BuOH solvent, C4 phenols didn't formed and phenol was selectively produced using benzene as a solvent. Similarly, in the reaction of demethoxylation of guaiacol to phenol, the yield of C4 phenols drastically decreased, and that of phenol increased using benzene. Therefore, it is expected that application of solvent with lower reactivity toward catalyst leads to improve the selectivity of phenol in catalytic reactions of lignin. However, it is difficult to employ benzene as a solvent for extracted lignin and lignin-derived substrates from raw biomass because of its lower solubility to non-polar benzene.

Table 1. Conversion and yields of mono- and C4 phenols after reaction of 1-phenoxy-2-phenylehtane.

Solvent	Conversion [C-mol%]	Yield [C-mol%]	
		Phenol	C4 phenols
1-BuOH	19	1.3	1.3
Benzene	27	9.3	0

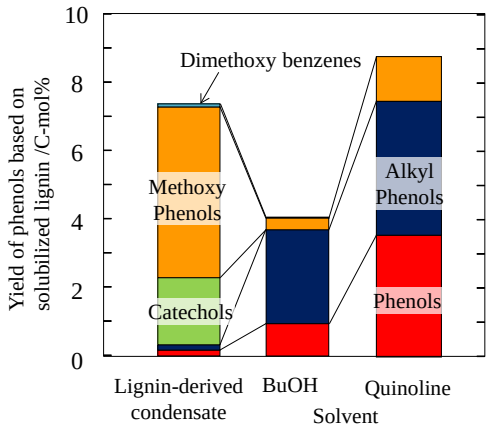

Figure 1. Yield of phenols after reactions of solubilized lignin over TiO_2-FeO_X with different solvents.

Based on the investigation of various organic solvents containing heteroatoms such as oxygen and nitrogen, quinoline was found to be a good solvent of lignin-derived substrate and show low reactivity toward TiO_2-FeO_X catalyst. Lignin-derived concentrate after water/BuOH treatment was re-solubilized in BuOH or quinolone and fed into the reactor. Fig.1 shows the product yields after the catalytic reactions. As shown in Fig.1, the formation of phenol was promoted using quinoline solvent. From the above, it is shown that quinoline is effective for catalytic reaction of lignin-related compounds over TiO_2-FeO_X catalyst for selective production of phenol.

4. Conclusions

The effect of solvents on the reactions of lignin model compounds and reagent lignin-derived substrate was investigated over TiO_2-FeO_X catalyst. Application of inert solvent toward the catalyst was found to be effective for suppressing undesirable substituted phenols in the reaction of lignin model compounds. In addition, quinoline, having both good solubility of lignin-derived substrate and low reactivity toward TiO_2-FeO_X catalysts, could be applied as solvent of reagent lignin-derived substrate, resulting in the higher yield of phenol as compared with conventional BuOH.

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