

Lignin Depolymerization to High-value Phenolic Products over NiMoReS₂

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Abstract: In this work, the depolymerization of organosolv lignin obtained from our own fractionation process from bagasse was studied. The effects of operating conditions including temperature (250-350°C) and time (1-5 h) in the presence of methyl isobutyl ketone (MIBK) were investigated. Moreover, bimetallic NiMo and trimetallic NiMoRe sulfides supported on γ -Al₂O₃ were also tested for comparison. Experiments revealed that at 350°C for 5 h, sulfided NiMoRe catalyst provided the highest phenolic product yield of 33.3%. The main phenolic monomers obtained are guaiacol and 4-ethylphenol. The result in this work suggested that NiMoRe sulfide catalyst is one of the alternative choices for catalytic depolymerization reaction in order to convert lignin to high value-added chemicals.

Keywords: Lignin depolymerization; Organosolv bagasse lignin; NiMoRe sulfide.

1. Introduction

On the basis of Thailand as an agricultural-based country, the successful utilization of local biomasses as feedstock to replace petroleum and petrochemical products would positively impact the overall economic of the country. Lignocellulosic biomass is one kind of biomass that refers to plant biomass. Plant biomass consists mainly of polysaccharides and lignin. Valorization of cellulose and hemicellulose via chemical and biotechnological conversion to various building block chemicals, biofuels, and bio-based material has been intensively studied since several years ago. In contrast, lignin application technologies are considerably less developed than those for polysaccharides. Usually lignin is discarded as waste or burned directly in boilers as a low-grade fuel.

The basic constituents of lignin are considered to be three types of phenyl propanoids; p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol [1]. The major inter unit linkage within the lignin macromolecule is the ether linkage β -O-4, consisting of more than half of the linkage structures of lignin [2]. Lignin can be efficiently converted to phenolic compounds, aromatic-based chemicals or industrial-needed chemicals which have significant potential as a source for the production of market products: adhesives, surfactants, phenolic resins, epoxy resins and various higher-value chemicals [3-5].

Currently, developing an efficient lignin depolymerization to aromatic compounds such as BTX (benzene, toluene, xylene), phenol, vanillin, guaiacol, and syringol involves wide range of conditions e.g. types of catalysts, reaction conditions, and solvent systems. For example, Joffres et al. [6] studied conversion of a wheat straw soda lignin in tetralin solvent with a NiMoS/Al₂O₃ catalyst under H₂ pressure. Oregui-Bengoechea et al. [7] studied thermocatalytic conversion of lignin in an ethanol/formic acid medium with NiMo catalysts. They found that the NiMo-sulfated alumina catalyst showed the best catalytic activity among all the catalysts studied. Jongerius et al. [8] studied the use of CoMo sulfide catalyst for hydrodeoxygenation of lignin model compounds at 50 bar hydrogen pressure and 300°C in dodecane, using a batch autoclave system. They found that hydrodeoxygenation (HDO), demethylation, and hydrogenation take place simultaneously. Moreover, they reported that yields and product distribution from lignin depolymerization vary depending on process conditions and catalyst. Therefore, this work aims to develop the process and catalyst for depolymerizing organosolv lignin from bagasse to produce the phenolic compounds by using bimetallic NiMo and trimetallic NiMoRe sulfides supported on γ -Al₂O₃ in the presence of methyl isobutyl ketone (MIBK) as a solvent.

2. Experimental section

2.1. Chemical and raw materials

The chemical standards of aromatic monomers (i.e. guaiacol, phenol, 2,6-dimethoxyphenol, p-cresol, vanillin, 4-ethylphenol, and 4-ethylguaiacol) were purchased from Sigma-Aldrich and Tokyo chemical industry Co. Ltd. For chemicals for catalyst synthesis, nickel (II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O), and ammonium perrhenate (NH₄ReO₄) were purchased from Sigma-Aldrich Chemical Co. LLC., Germany. Ammonium heptamolybdate tetrahydrate (NH₄)₆Mo₇O₂₄·4H₂O was obtained from Carlo Erba Reagent, Italy. The γ -Al₂O₃ with 1.8 mm diameter was purchased from Sasol Company, Germany. Organosolv lignin was extracted from sugarcane bagasse which was obtained from PTT Global Chemicals PCL, Rayong, Thailand. It was dried at 70 °C for 24 h and cut by Retsch ZM200 to be the average particles size of 0.5-0.85 mm in diameter. According to the standard NREL analysis [9], the biomass contained 38.3 wt% cellulose, 20.7 wt% hemicelluloses, 24.6 wt% lignin, and 4.3 wt% ash.

2.2 Fractionation process

Organosolv bagasse lignin was prepared according to a procedure described elsewhere [10]. Briefly, bagasse (10% (w/v)) was pulped in a ternary mixture (79% (v/v)) of ethyl acetate:ethanol:water (32:25:43) with 21% (v/v) of formic acid at 164°C for 45 min under 20 bar N₂. The lignin was recovered from the organic solvent by filtration, solvent evaporation and drying to constant weight at 45°C.

2.3 Catalyst synthesis and characterization

Bimetallic (3%Ni-10%Mo) and trimetallic (1%Re-3%Ni-10%Mo) sulfide catalysts supported on γ -Al₂O₃ were prepared by impregnation technique. The commercial γ -Al₂O₃ was milled and sieved to obtain the desirable particle size 0.425 mm. The metal precursors were weighted and dissolved in deionized water to obtain the aqueous solutions. The metal aqueous solutions were dropped on γ -Al₂O₃ to make the alumina pore full with metal solution. Then, materials were dried overnight in at 105°C and calcined at 500°C for 5 h. Before testing reaction, synthesized materials were sulfided at 400°C for 4 h under a flow of 4 Lh⁻¹ of H₂S/H₂ (10/90) mixture.

The specific surface area and porosity of catalysts were characterized by BET experiment (Belsorp-max Bel, Japan) while the H₂-TPD was performed to determine the distribution of metal sulfide catalyst samples. The temperature programmed

oxidation (TPO) was used to identify the carbon species which deposited on the surface of the catalysts after post-reaction.

2.4 Lignin depolymerization

The reactions were carried out in batch-type reactor with inner volume of 10 mL, from which 0.0875 g of organosolv lignin and 10 %w/w of sulfide catalyst were mixed in 5 mL of MIBK. After reaching the reaction time required, the reaction was stopped instantly by quenching the reactor in an ice-cool water bath. The liquid fraction was separated from solid fraction (including char, unconverted lignin, and catalyst) by centrifugation at 5,000 rpm for 10-15 min. Next, the liquid fraction was acidified with 1 M HCl. In this step, residual lignin fraction was precipitated as a solid form. The solid form was separated by centrifugation and dried overnight at 60°C. In case of liquid fraction (containing phenolic monomers) was filtered through a 0.45 µm syringe filter and characterized by GC-FID (Shimadzu GC-2014, Japan) with a Petrocol™ DH 50.2 fused silica capillary column (Supelco, USA). The phenolic products were quantified using the calibration curves of guaiacol, phenol, 2,6-dimethoxyphenol, p-cresol, vanillin, 4-ethylphenol, and 4-ethylguaiacol. The yields of the all dried fractions (liquid acid soluble fraction, residual lignin fraction, and char/unconverted lignin fraction) were measured by weighting and calculating with the initial weight of lignin.

The yields of phenolic monomers, residual lignin, liquid acid soluble, char/unconverted lignin, and lignin conversion were calculated using the following equations:

$$\text{Phenolic monomer yield (\%)} = \frac{\text{weight of phenolic monomers (g)}}{\text{weight of initial lignin (g)}} \times 100 \quad (1)$$

$$\text{Residual lignin yield (\%)} = \frac{\text{weight of residual lignin in acid insoluble (g)}}{\text{weight of initial lignin (g)}} \times 100 \quad (2)$$

$$\text{Liquid acid soluble yield (\%)} = \frac{\text{weight of liquid fraction (g)} - \text{weight of residual lignin (g)}}{\text{weight of initial lignin (g)}} \times 100 \quad (3)$$

$$\text{Char/Unconverted lignin yield (\%)} = \frac{\text{weight of solid fraction (g)} - \text{weight of solid catalyst (g)}}{\text{weight of initial lignin (g)}} \times 100 \quad (4)$$

$$\text{Lignin conversion} = \frac{\text{weight of initial lignin (g)} - \text{weight of residual lignin (g)}}{\text{weight of residual lignin (g)}} \times 100 \quad (5)$$

3. Results and Discussion

3.1 Organosolv lignin characterization

Before reaction testing, the characteristics of isolated bagasse lignin were examined and compared to commercial organosolv lignin. The organosolv lignin samples were analyzed by Klason lignin method. From Table 1, the proportional of acid insoluble lignin of isolated bagasse lignin (92.3%) in this study was slightly higher than commercial organosolv lignin (91.7%).

Table 1 Comparison of lignin composition in this work.

Lignin sample	Klason lignin (%)	Sugar (%)			Ash (%)	Moisture (%)
		Glucose	Xylose	Arabinose		
Commercial lignin	91.7	0.92	0.12	0.12	0.86	<0.1
Isolated lignin	92.3	0.16	0.52	0.27	0.22	<0.1

Table 2 Physicochemical properties of the catalysts.

Catalyst	BET surface area (m ² g ⁻¹)	Metal dispersion (%)
NiMoS ₂ /γ-Al ₂ O ₃	117.0	6.9
NiMoRe/γ-Al ₂ O ₃	140.8	7.2

The compositions of C₆ sugars and ash contents of isolated bagasse lignin were much lower than that of commercial organosolv lignin while the content of C₅ sugars especially arabinose was relatively higher.

3.2 Effects of reaction temperature and time

The effects of reaction temperature and reaction time on product yield of phenolic monomers in non-presence of catalyst using MIBK as solvent were investigated in order to maximize the phenolic yield. As illustrated in Figure 1, the reaction time showed strong impact on the product yield. It was found that the product yield dramatically increased from 5.3% to 24.5% at longer reaction time at 350°C and maximize at 5 h, while the proportions of char and residual lignin contents significantly increased due to the repolymerization of degraded product into residue [11-13]. When increasing the reaction time from 5 h to 6 h, we found that the product yield considerably dropped to 7.6% but the char and residue also increased because the phenolic products decomposed into small molecules, gaseous compounds, and repolymerization products.

Moreover, the reaction temperature also plays an important role in the product yield. As presented in Figure 2, the reaction temperature was investigated between 250-350°C for 5 h in non-presence of catalyst by using MIBK as a solvent. The result showed that at 250°C the desired phenolic products were not found, while the product yield sharply increased at higher temperature. In addition, the char and residue lignin significantly decreased. The reason for this is because the increasing of the reaction temperature not only greatly promotes the rate of depolymerization but also gradually increases the diffusion and the dissolution of the solvent [14-15].

3.2. Catalytic activities toward lignin depolymerization

Lignin depolymerization reaction was operated at 350°C for 5 h under atmospheric pressure in MIBK with and without the presence of catalysts. The phenolic yields from the reaction are illustrated in Figure 3. It was found that 24.5% of total phenolic yield was observed without the presence of catalyst. The additional of trimetallic NiMoReS₂ catalyst can promote depolymerization reaction. Interestingly, the depolymerization reaction in the presence of trimetallic NiMoReS₂ can produce higher phenolic yield than bimetallic NiMoS₂ catalyst. From the study, NiMoReS₂ provided the highest phenolic monomers of 33.3% with the high selectivity of guaiacol and 4-ethylphenol.

According to the H₂-TPD and BET analysis, we found that NiMoS₂ showed both lower specific surface area and metal dispersion than those of NiMoReS₂ (see in Table 2). Moreover, the TPO experiments to determine the carbon deposition on the surface of NiMoS₂ and NiMoReS₂ catalysts were investigated. From TPO results, we found that NiMoS₂ and NiMoReS₂ were 3.76 and 2.35 g_{cat}⁻¹, respectively. Therefore, it can be concluded that the additional of Re into sulfided NiMo catalyst can greatly improve the catalytic activity toward the depolymerization of organosolv lignin.

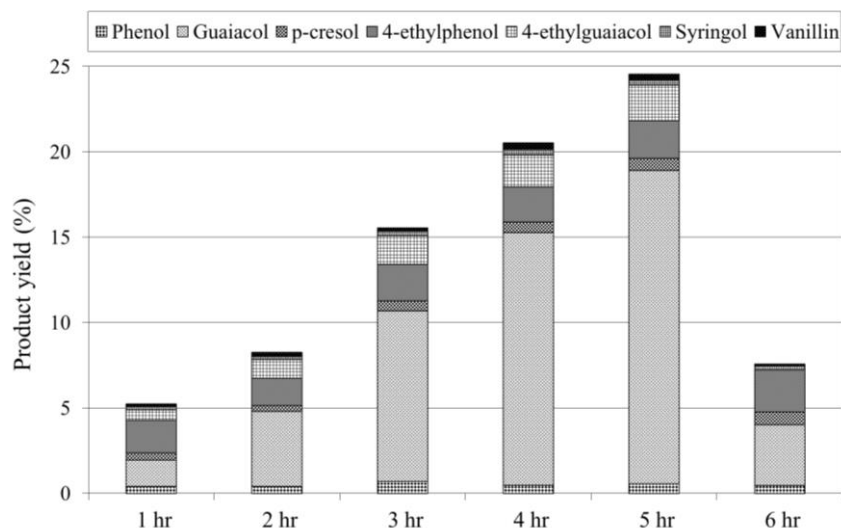


Figure 1. Effect of reaction time on product distribution from depolymerization of organosolv lignin from bagasse in MIBK at 350°C in the non-presence of catalyst.

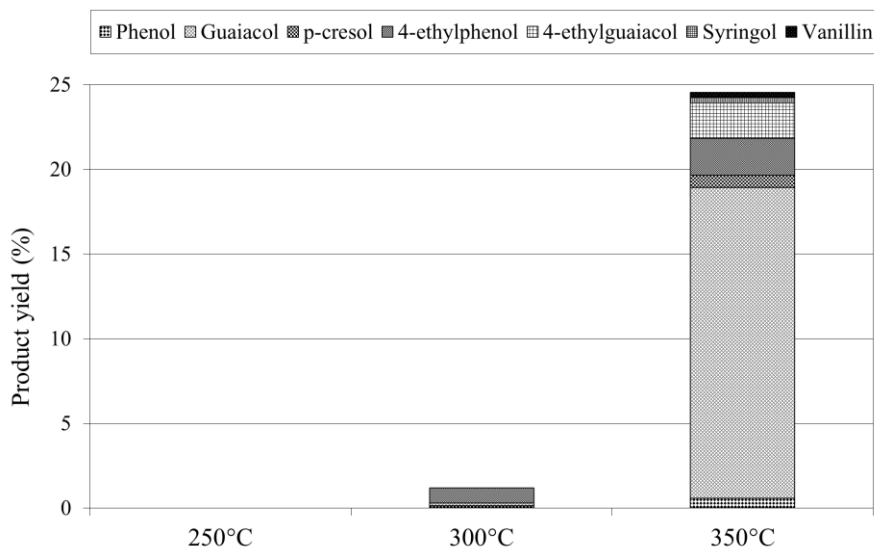


Figure 2. Effect of reaction temperature on product distribution from depolymerization of organosolv lignin from bagasse in MIBK for 5 h in the non-presence of catalyst.

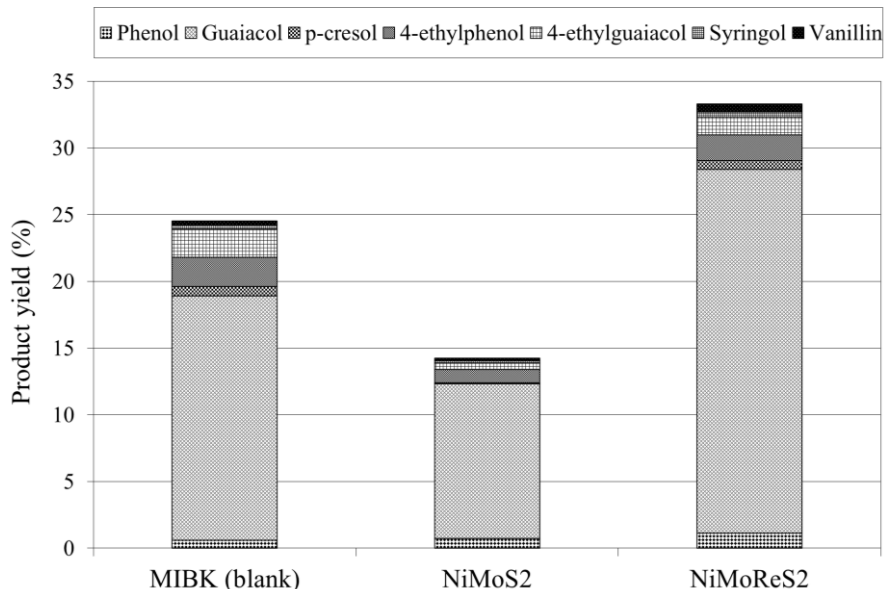


Figure 3. Effect of catalyst on product distribution from depolymerization of bagasse lignin at 350°C in MIBK for 5 h.

4. Conclusions

The catalytic depolymerization of organosolv lignin from bagasse was investigated in this study under several operating conditions. It can be clearly seen that the reaction temperature, reaction time, and catalyst also plays a vital role on phenolic product yield. At 350 °C for 5 h in MIBK system, sulfided NiMoRe catalyst provided the highest total phenolic product yield of 33.3%. The main phenolic monomers obtained are guaiacol and 4-ethylphenol.

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