Phenolic-Based Chemical Production from Catalytic Depolymerization of Alkaline Lignin over Fumed Silica Catalyst

S. Totong, P. Daorattanachai, N. Laosiripojana

Abstract—Lignin depolymerization into phenolic-based chemicals is an interesting process for utilizing and upgrading a benefit and value of lignin. In this study, the depolymerization reaction was performed to convert alkaline lignin into smaller molecule compounds. Fumed SiO_2 was used as a catalyst to improve catalytic activity in lignin decomposition. The important parameters in depolymerization process (i.e., reaction temperature, reaction time, etc.) were also investigated. In addition, gas chromatography with mass spectrometry (GC-MS), flame-ironized detector (GC-FID), and Fourier transform infrared spectroscopy (FT-IR) were used to analyze and characterize the lignin products. It was found that fumed SiO_2 catalyst led the good catalytic activity in lignin depolymerization. The main products from catalytic depolymerization were guaiacol, syringol, vanillin, and phenols. Additionally, metal supported on fumed SiO_2 such as Cu/SiO_2 and Ni/SiO_2 increased the catalyst activity in terms of phenolic products yield.

Keywords—Alkaline lignin, catalytic, depolymerization, fumed SiO_2, phenolic-based chemicals.

I. INTRODUCTION

LIGNIN is the second abundant composition in lignocellulosic biomass, woody, and agricultural residue. Most of lignin is generated from pulp and paper industry and become a waste from fractionation process. They are normally used as a low-grade fuel in a boiler for internal energy supply. Less than 5% of lignin has been used for other purposes or applications such as chemical production and material additives [1]. Nevertheless, lignin is an outstanding renewable resource for producing fuels, chemicals, and materials according to its potentials as a biopolymer structure, high carbon content, various functional groups/linkages and high-energy content. Therefore, the conversion of lignin into chemicals would be a choice to increase the value-added.

Many methods for the value-added chemical production from lignin have been studied such as gasification, pyrolysis, hydrolysis, chemical oxidation, and hydrogenation (hydrocracking) [2]. However, fine chemicals production from gasification and pyrolysis required many steps as lignin was degraded into syngas (H_2+CO) by gasification or pyrolysis

S. Totong is a PhD student at The Joint Graduate School of Energy and Environment (JGSEE), King Mongkut's University of Technology Thonburi (KMUTT), 126 Pracha Uthit Rd. Bangmod, Thungkru, Bangkok 10140, Thailand (e-mail: sansanee.tt@gmail.com).

P. Daorattanachai is a researcher and N. Laosiripojana is a professor at The JGSEE, Center for Energy Technology and Environment (CHE), KMUTT, 126 Pracha Uthit Rd. Bangmod, Thungkru, Bangkok 10140, Thailand (e-mail: p_pornlada@hotmail.com, navadol@jgsee.kmutt.ac.th).

followed by using further reaction to produce needed-chemicals. On the other hand, the lignin depolymerization is a process to convert the complex lignin compound to small molecule by direct transformation lignin on one step. Consequently, the depolymerization is an interesting process for converting lignin to value-added chemicals due to the simple transformation process.

Normally, depolymerization of lignin requires severe conditions regarding to the complicated and stability of lignin structure. Thus, the catalytic depolymerization has been employed to easily generate the phenolic compounds form lignin. The end products from catalyzed depolymerization of lignin is a diversity of phenolic monomeric and aromatic compounds such as phenol, syringol, guaiacol, vanillin, catechols, pyrocatechol, hydroxyacetophenone and their derivatives [3]-[8]. Most processes use homogeneous catalysts to enhance catalyst activities because it can be dissolved in system that became to the same phase resulting in a high interaction between themselves and reactant. However, it has enormous disadvantages such as it is difficult to separate from the reaction mixture and products and make a corrosive in reactor (in case concentrated acid catalyst). Then, heterogeneous catalysts have been applied to solve these problems. For instance, acid solid catalysts played an important role in catalytic cracking processes. Silica (SiO_2) was widely used as a catalyst due to high surface area, chemical-thermal stability, highly uniform pore volume and pore size distribution, and high adsorption capacity [9]. Many researches achieved that SiO_2 can be a catalyst or support material [10].

The aim of this study is to evaluate the potential of fumed SiO_2 catalysts for the lignin depolymerization to produce value-added and industrial-needed chemicals. In addition, the effects of conditions such as reaction temperature and reaction time on alkaline lignin depolymerization were also investigated. Moreover, lignin structure changes before and after catalytic-depolymerized were studied for understanding chemical changing of lignin during depolymerization reaction.

II. MATERIALS AND METHODOLOGY

A. Materials

The commercial alkaline lignin was provided by Aldrich (M_w~10,000 g/mol, low sulfonate content ~4%, and pH ~10.5), which is used as raw material in this work. The CHNS elemental analyzer was used to analyze the elemental

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compositions of commercial alkaline lignin and the results were reported on dry and ash free basis as shown in Table I. Fumed SiO_2 is purchased from Sigma-Aldrich (0.007 µm, 390 m^2/g), which was used as catalyst. It was calcined in air at 400 ºC for 4 h before used for eliminating an impurity. Catalyst properties were analyzed by BET analysis and summarized in Table II. Metal nitrate salts in AR-grade such as $Cu(NO_3)_2 \cdot 3H_2O$ (99.5%, Qrëc) and $Ni(NO_3)_2 \cdot 6H_2O$ (BHD), which were used as metal precursor for synthesizing metal-doped SiO_2 catalysts. Furthermore, the standard phenolic compounds for example phenol, guaiacol, ethyl guaiacol, syringol and vanillin are obtained from Sigma-Aldrich.

TABLE I
ULTIMATE ANALYSIS OF ALKALINE LIGNIN (DRY BASIS)

Sample	Ultimate analysis (%)				
	C	H	N	S	O
Alkaline lignin	49.44	5.13	0.27	4.47	16.5

TABLE II
PHYSICAL PROPERTIES OF CATALYST

Catalyst	Surface Area (m^2/g) ^{a}	Pore Volume (cm^3/g) ^{b}	Pore Diameter (nm) ^{b}
SiO_2	302.3	0.61	3.7

^{a} Calculated by the BET equation;
^{b} BJH desorption pore volume and pore diameter.

B. Catalyst Preparation

The metal-doped SiO_2 catalysts were prepared by microwave-assisted impregnation method. The loading the amount of the metal precursor was set at 10 wt.% preferred to weight of SiO_2 support. $Cu(NO_3)_2 \cdot 3H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ were dissolved in deionized water and slowly added into calcined fumed SiO_2 support at 80 ºC. After that, the prepared catalysts were dried in microwave using power at 450 watt for 5 min. Then, the synthesized catalysts were calcined at 400 ºC for 4 h.

C. Catalytic Depolymerization of Alkaline Lignin

Initially, the catalytic depolymerization of lignin was conducted in 10 ml batch reactor equipped with thermocouple and gas inlet line. An experiment was carried out without catalyst (blank) as a reference. The system contained 0.0875 g of alkaline lignin and 5 ml of deionized water. The catalyst loading was set at 5 wt.% of initial lignin. After that, the reactor was sealed and nitrogen gas was flown several times for leak checking, purging and removing the air inside reactor. The reactor was heated to a required temperature and desired reaction time. The reaction initial pressure was atmospheric pressure. For keeping the system as homogeneous and well-mixed system, the electric stirrer was used to shake reactor at constant speed. After depolymerization, the reaction was immediately quenched in a water bath to stop further reaction. The reaction mixture will be fractionated and analyzed in product separation and analysis step.

D. Products Separation and Analysis

The reaction mixture in the reactor was separated into two phases, which were oil and solid phases by acidifying precipitation with 1 M of H_2SO_4 until pH below 2. Then the reaction mixture was centrifuged to separate liquid (aqueous) fraction from the solid fraction. The liquid fraction was extracted by using liquid-liquid extraction with ethyl acetate in order to extract phenolic monomer products. The phenolic products obtained from lignin depolymerization were extracted into organic phase. The phenolic monomer products from lignin depolymerization were identified and determined the products yield with external standard by using gas chromatography GC-2014 (Shimadzu, Japan) with a mass spectrometry (MS) and flame ionization detector (FID) equipped with a Petrocol® DH 50.2 Capillary column (50 m × 0.2 mm × 0.5 µm). The temperature program for analysis was initially set at 50 ºC with a hold of 5 min, ramped to 120 ºC at 10 ºC/min with a hold of 5 min and finally raised to 280 ºC at 10 ºC/min with a hold of 15 min. Standard calibration curve was made by using pure phenolic compounds; phenol, guaiacol, ethyl guaiacol, syringol, and vanillin. The solid phase was composed of residual lignin, oligomer, char, and catalyst.

E. Calculation

The lignin conversion and phenolic product yield were defined and calculated from following equations. In calculation, the weight of residual lignin can be determined by the different of total solid residue subjected weight of catalyst. Additionally, weight of phenolic products was determined from quantitative analysis by GC/FID. All of calculation was based on initial weight of lignin.

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

$$\text{Yield of product i (\%)} = \frac{\text{weight of product i (g)}}{\text{weight of initial lignin (g)}} \times 100\%$$

III. RESULTS AND DISCUSSION

To develop the performance of lignin depolymerization process, fumed SiO_2 catalyst was tested in this studied. It was found that fumed SiO_2 catalyst enhanced the higher activity and diversity of monomeric compounds when compared with an absence catalyst system. Furthermore, the total product yield was increased from 2.48 (no catalyst) to 4.62 wt.%. Moreover, the significant parameters including reaction temperature, residence time, and metal-doped catalysts were studied for optimizing and maximizing the catalytic activity on lignin depolymerization process.

A. Effect of Reaction Temperature on Catalytic Depolymerization of Alkaline Lignin

The effect of reaction temperature on catalytic activity depolymerization of lignin using fumed SiO_2 as a catalyst was varied from 250-300 °C at constant reaction time of 60 min (see Fig. 1). It was found that the reaction temperature was an important parameter for lignin depolymerization in term of lignin conversion, product yield, and product distribution. It can conclude that increasing temperature was simultaneously

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promoted the decomposition of lignin and repolymerisation of the intermediates. With the increase of temperature from 275 to 300 °C, the yield of phenolic products obtained by catalytic depolymerization of lignin using fumed SiO_2 was decreased. It is similar result studied by Ye et al.; they have found that the yield of liquid products decreased with increasing temperature from 225 to 300 °C for lignin depolymerisation in ethanol–water. This indicates that lower temperature favored depolymerisation reaction whereas with the increase of temperature formation of higher reactive radicals promoted repolymerisation [11]. Moreover, it probably resulted from acidity of SiO_2 that promoted the repolymerrization of intermediates to solid residue.
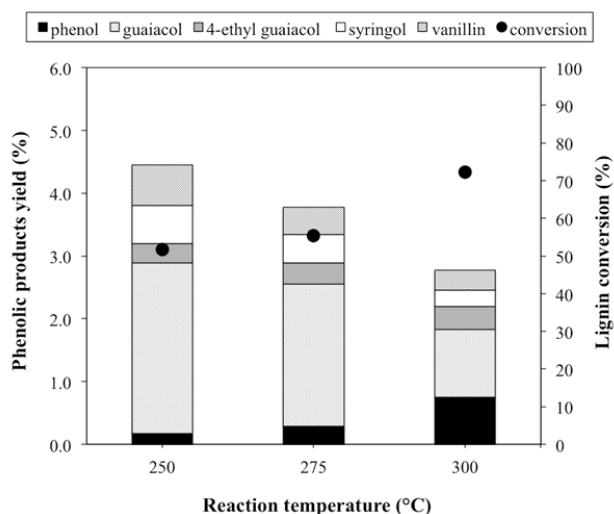

Fig. 1 The effect of reaction temperature on lignin conversion and phenolic products yield of catalytic depolymerization of alkaline lignin for 60 min of reaction time

B. Effect of Reaction Time on Catalytic Depolymerization of Alkaline Lignin

The efficient factor on lignin depolymerization and phenolic monomer product yield distribution was reaction time. The effect of reaction time on lignin conversion and phenolic monomer products yield was investigated at 250 ºC over fumed SiO_2 was shown in Fig. 2. The highest lignin conversion and phenolic monomer products yield over fumed SiO_2 were 51.7 and 4.62% by weight, respectively which was observed at 250 ºC for 60 min. It was found that phenolic monomer products yield from depolymerization of lignin over fumed SiO_2 was decreased when reaction time increased. Due to during lignin depolymerization reaction, the cracking reactions and repolymerization occurred continuously at the same time. In addition, these results may be concluded that the phenolic compounds (i.e. guaiacol, syringol, and vanillin) were reactive immediate and speedily reacted or degraded into other compounds. It was confirmed that concentration of phenol was higher with increased reaction time.
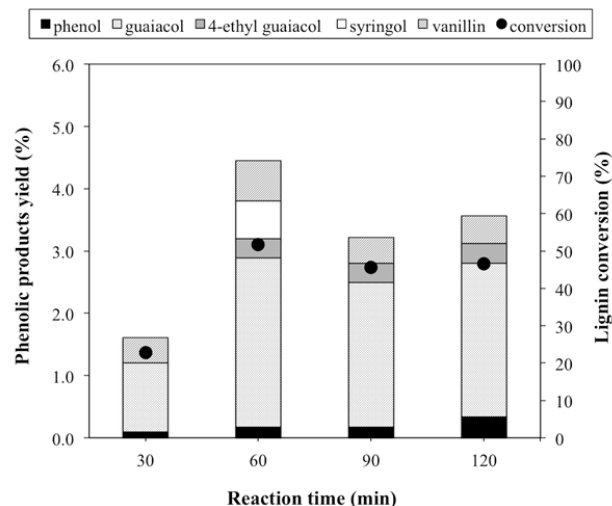

Fig. 2 The effect of reaction time on lignin conversion and phenolic products yield of catalytic depolymerization of alkaline lignin at reaction temperature 250 °C

C. Structure Changes in Residual Lignin after Catalytic Depolymerization

The FT-IR was used to determine information on the lignin types and functional groups (i.e. methoxyl groups, carbonyl groups, and hydroxyl groups) that usually found in lignin and the influence of structural variations on these groups. For this experiment, FT-IR analysis was used to assess the structure of initial lignin and structure changed after detpolymerization process. The FT-IR spectra of commercial alkaline lignin and residual lignin after deporimerization process using fumed SiO_2 as catalyst were shown in Fig. 3.
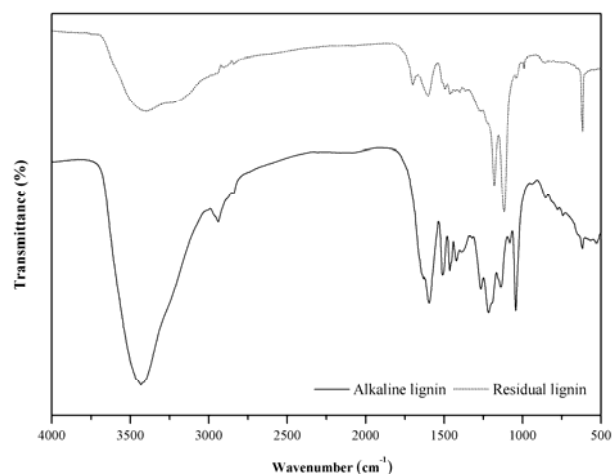

Fig. 3 FT-IR spectra of commercial alkaline lignin (solid line) and residual lignin after deporimerization process over fumed SiO_2 at 250 ºC for 60 min (dot line)

The commercial alkaline lignin showed a strong broad in the range of 3100-3600 cm^{-1}, which indicated to phenolic and aliphatic OH group. After depolymerization, it was found that the FT-IR spectra of residual lignin have a similar pattern but an intensity in each peak dramatically decreased since the lignin after depolymerization process was decomposed into

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small and low molecular weight compounds.

D. Effect of Metal Doped on Catalytic Depolymerization of Alkaline Lignin

The synthesized Cu/SiO_2 and Ni/SiO_2 catalysts were candidate catalysts in lignin depolymerization for studying the efficiency of metal on catalytic activity. The effect of metals on catalytic depolymerization of alkaline lignin was shown in Fig. 4. It was discovered that Cu and Ni enhanced the phenolic product yield and product selectivity. The metals Cu and Ni are least expensive, earth abundant metals, and have highly catalytic performance. They have been widely used in many catalytic reactions, such as hydrogenation of alkane and aromatics compound, methane reforming, ethanol steam reforming, and water-gas shift reaction. Zhao and Lercher reported a Ni-based SiO_2 catalyst to cleave aryl ethers bonds of aromatic lignin-derived and hydrogenation of oxygenated-intermediates in the aqueous phase [12]. Moreover, Jeong et al. studied catalytic performance of various transition metal catalysts on depolymerization reaction of Protobind lignin to monoaromatic compounds [13]. They found that the presence of Ni and Cu doped on ZSM-5 can enhance the lignin depolymerization and the yield of monoaromatic compounds was increased.
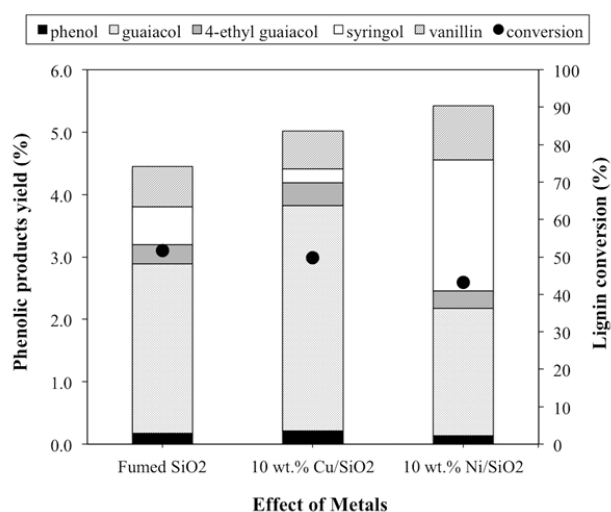

Fig. 4 The effect of metals on lignin conversion and phenolic products yield of catalytic depolymerization of alkaline lignin at reaction temperature 250 °C

IV. CONCLUSION

The study aimed to produce high value-added phenolic monomer compounds from lignin depolymerization. It was found that the guaiacol compound was easy to produce under experiment carried out without catalyst. Catalytic depolymerization in the presence of fumed SiO_2 can greatly promote the lignin conversion and phenolic-based product yields. The reaction temperature and reaction time also strongly affected the lignin depolymerization, the optimized conditions were observed at 250 °C for 60 min in the presence at 5 wt.% of fumed SiO_2 catalyst. Furthermore, the metal loaded on fumed SiO_2 (i.e. Cu and Ni) increased the catalyst

activity in terms of phenolic products yield and product distribution. It can indicate that Cu and Ni metal was promotional material for improving lignin depolymerization.

REFERENCES

[1] Kleinert, M., and Barth, T. (2008). Phenols from lignin. *Chemical Engineering & Technology*, *31*(5), 736-745.
[2] Zakzeski, J., Bruijnincx, P. C., Jongerius, A. L., & Weckhuysen, B. M. (2010). The catalytic valorization of lignin for the production of renewable chemicals. *Chemical reviews*, *110*(6), 3552-3599.
[3] Gardner, D. J., Schultz, T. P., and McGinnis, G. D. (1985). The pyrolytic behavior of selected lignin preparations, *Journal of wood Chemistry and Technology*, *5*(1), 85-110.
[4] Windt, M., Meier, D., Marsman, J. H., Heeres, H. J., and de Koning, S. (2009). Micro-pyrolysis of technical lignins in a new modular rig and product analysis by GC–MS/FID and GC×GC-TOFMS/FID, *Journal of Analytical and Applied Pyrolysis*, *85*(1), 38-46.
[5] Saisu, M., Sato, T., Watanabe, M., Adschiri, T., and Arai, K. (2003). Conversion of lignin with supercritical water-phenol mixtures, *Energy & Fuels*, *17*(4), 922-928.
[6] Sricharoenchaikul, V. (2009). Assessment of black liquor gasification in supercritical water, *Bioresource technology*, *100*(2), 638-643.
[7] Elliott, D. C., Hallen, R. T., and Sealock, L. J. (1984). Alkali catalysis in biomass gasification, *Journal of analytical and applied pyrolysis*, *6*(3), 299-316.
[8] Villar, J. C., Caperos, A., and Garcia-Ochoa, F. (2001). Oxidation of hardwood kraft-lignin to phenolic derivatives with oxygen as oxidant, *Wood Science and Technology*, *35*(3), 245-255.
[9] Soled, S. (2015). Silica-supported catalysts get a new breath of life. *Science*, *350*(6265), 1171-1172.
[10] Armor, J. N., & Zambri, P. M. (1982). Silica as an oxidation catalyst. *Journal of Catalysis*, *73*(1), 57-65.
[11] Ye, Y., Zhang, Y., Fan, J., Chang, J. (2012). Novel method for production of phenolics by combining lignin extraction with lignin depolymerization in aqueous ethanol. *Industrial & engineering chemistry research*, *51*, 103-110.
[12] He, J., Zhao, C., & Lercher, J. A. (2012). Ni-catalyzed cleavage of aryl ethers in the aqueous phase. *Journal of the American Chemical Society*, *134*(51), 20768-20775.
[13] Jeong, S., Yang, S., & Kim, D. H. (2017). Depolymerization of Protobind lignin to produce monoaromatic compounds over Cu/ZSM-5 catalyst in supercritical ethanol. *Molecular Catalysis*, *442*, 140-146.