CELLULOSE CHEMISTRY AND TECHNOLOGY

HYDROGENATION OF ASPEN ETHANOL LIGNIN IN SUPERCRITICAL ETHANOL IN THE PRESENCE OF NI/C CATALYST

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Lignin is the largest renewable source of aromatic chemicals and has great potential for the production of high value-added chemicals. In this work, we describe the process of hydrogenation of aspen wood ethanol-lignin in supercritical ethanol in the presence of Ni/C catalyst and in the absence of added catalysts. It is shown that at a temperature of 250 °C, the catalyst reduces the yield of solid residue from 7.3 to 1.9 wt%. The total yield of phenolic compounds during non-catalytic hydrogenation does not exceed 5.8 wt%. The bifunctional nickel-containing catalyst increases almost twofold (up to 10.1 wt%) the yield of liquid phenolic products, among which 4-propylsyringol predominates. Increasing the process temperature of catalytic hydrogenation to 300 °C leads to an increase in the yields of monomeric phenolic compounds to 13.4 wt%. In the presence of a catalyst, the molecular weight distribution of liquid products of ethanol lignin hydrogenation shifts to the low molecular weight region, due to an increase in the content of monomeric phenolic compounds in the liquid products.

Keywords: ethanol lignin, aspen, hydrogenation, nickel catalyst

INTRODUCTION

Biomass is an important resource for the production of biofuels and biochemicals. Compared with other renewable resources (such as solar and wind energy), biomass is the only renewable resource containing organic carbon on earth,[1] which makes it promising for the production of high-value chemicals that can effectively alleviate the global energy crisis and solve the related environmental problems caused by the increasing use of fossil resources – thus, it is beneficial for the sustainability of energy supply.[2] Lignocellulosic biomass (LB) is regarded as an ideal substitute for fossil carbon resources due to the advantages of environmental protection, sustainability and low cost, and is widely used in the production of biofuels and high-value chemicals.[3] Lignocellulosic biomass is mainly composed of three polymeric components: cellulose, hemicelluloses and lignin, of which hemicelluloses (accounting for 20–30%) and cellulose (accounting for 40–50%) are polymers of C5 and C6 sugars, respectively.[4] Currently, most advanced biofuel production strategies focus on the conversion of cellulose and hemicelluloses, which have been intensively studied and have led to mature technologies in the industrial production of biofuels and important chemicals, such as bioethanol, 5-hydroxymethylfurfural, furfural and levulinic acid.[5]

Among the three main components of lignocellulose, lignin provides structural integrity and strength to plants. About 170 billion tons of lignin are produced annually worldwide;[6] it is an undesirable component in the pulp and paper

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industry and is traditionally treated by direct combustion and discharge. As the most abundant natural aromatic material in the world, lignin has great potential for producing chemicals and fuels through various processes.[7]

Over the past few decades, a series of studies on lignin depolymerization (LD) processes have grown rapidly, including non-catalytic, catalytic pyrolysis, enzymolysis, catalytic depolymerization and oxidation.[8] Although the traditional processes can effectively depolymerize lignin, they require relatively high energy inputs, such as higher temperature or pressure, with external hydrogen or oxygen. In addition, the organic solvents used in these processes are always unfriendly to the environment. Due to its relative cheapness and high efficiency in breaking the bonds in lignin (*e.g.*, C–O–C and C–C), catalytic chemical conversion with various catalysts becomes a very competitive method for producing bioenergy and valuable chemicals.[9]

Catalysts are a key factor determining the effect of LD reaction, and their selection and design directly affect the product yield, distribution and selectivity. The most common type of catalyst is metal catalyst due to its diversity, constructability and outstanding catalytic effect.[10] Various metals have been used in the LD process, including transition metal catalysts, noble metal catalysts and bimetallic catalysts. As a transition metal, nickel is more cost-effective compared with noble metals. Meanwhile, several studies have shown that Ni-based catalysts are effective in breaking CO and CC bonds in lignin molecules.[11,12] In this paper, the hydrogenation processes of aspen ethanol lignin in the presence of bifunctional Ni/C catalyst were investigated to establish the effect of the catalyst on lignin depolymerization, liquid, solid and gaseous product yields.

EXPERIMENTAL

Materials and methods

Ethanol lignin was extracted from aspen wood by means of an ethanol-water mixture at a temperature of 185 °C and subsequent precipitation with cold water according to a previously described method.[13]

Preparation of nickel catalysts

Carbon samples were prepared from commercial mesoporous carbon material Sibunit®-4(S4) (Center for New Chemical Technologies, Institute of Catalysis SB RAS, Omsk). The carbon material (CM) was pre-washed with hot deionized water to remove possible metal impurities and dried in an argon stream at 150 °C. To obtain a fraction with a carbon particle size of 56-94 μm, the CM was ground in a porcelain mortar and sieved. To obtain oxidized samples, Sibunit was oxidized with humid air. Oxidation was carried out in a quartz cell placed in a furnace. The cell filled with CM was pre-purged with argon (200 mL/min, 0.5 h), then a mixture of 20 vol% O_2 in N_2 in the presence of water vapor was fed into the cell at a given temperature (450 °C) (saturation at 90 °C, vapor pressure 70.1 kPa, flow 200 mL/min, 2 h).[14] Nickel catalysts based on oxidized Sibunit-4 CM were obtained by incipient wetness impregnation with an aqueous solution of nickel (II) chloride hexahydrate ($NiCl_2$ $6H_2O$), followed by drying at room temperature for 3 h and at 60 °C for 12 h.

The active component was reduced in a quartz reactor in a hydrogen stream (flow 30 mL/min) at 450 °C for 2 h, the temperature was increased at a rate of 8 °C/min, after cooling to room temperature in a hydrogen atmosphere, the catalyst was passivated with a gas mixture of 1% O_2 in N_2 (flow 200 mL/min, 0.5 h).[14]

We selected a catalyst with a Ni content of 10 wt%, which had previously shown high efficiency in the hydrogenation of flax shives.[15] Catalyst characteristics: Ni particle sizes: d_{min} 63 nm, $<d_l>$ 152 nm, dmax 351 nm; textural characteristics: S_{BET} 315 m^2/g, V_{por} 0.51 cm^3/g, $<d_{por}>$ 5.61 nm.

Methods of experiment

The hydrogenation process was carried out in a ChemReSYStem R-201 autoclave (Korea) with a volume of 300 mL according to the method described in the work.[16] The reactor was loaded with 50 mL of ethanol, 5.0 g of substrate and 0.5 g of catalyst. Then, the autoclave was hermetically sealed and purged with argon to remove air. Hydrogen was supplied, the initial pressure of which was 3 MPa. The reaction was carried out with constant stirring at a speed of 1000 rpm at a temperature of 250 and 300 °C for 1 hour. The rate of temperature rise was 10 °C/min, the time to reach the required temperature was 20-25 minutes. The operating pressure in the reactor was 9.0 MPa. After cooling the reaction mixture to room temperature, the gaseous products were collected in a gasometer, their volume was measured, and the composition was determined by gas chromatography. Then, the reaction products were quantitatively discharged from the autoclave by washing with ethanol, and the resulting mixture of liquid and solid products was separated by filtration.

The solid was washed with ethanol until the solvent became colorless. The solvent was removed from the liquid product using a rotary evaporator, and the product was brought to constant weight by drying under vacuum (1 mm Hg) at room temperature. The solid product was dried at a temperature of 80 °C to constant weight. The yield of liquid products (α1), the yield of solid product (α2), the total yield of gaseous products (α3) and the degree of lignin conversion (χl) were determined using the relations below:

$$\alpha_1 = \frac{m_l\,(g)}{m_i\,(g)} \times 100\% \qquad (1)$$

$$\alpha_2 = \frac{m_s\,(g) - m_{cat}\,(g)}{m_i\,(g)} \times 100\% \quad (2)$$

$$\alpha_3 = \frac{m_g\,(g)}{m_i\,(g)} \times 100\% \quad (3)$$

$$\chi_l = \frac{m_i\,(g) + m_{cat}\,(g) - m_s\,(g)}{m_i\,(g)} \text{ x } 100\% \quad (4)$$

where χ_l – conversion of ethanol lignin, %; m_l – mass of liquid products (g), m_i – mass of the original sample (g), m_{cat} – catalyst mass (g), m_g – mass of gaseous products (g), m_s – mass of solid residue.

Liquid products of aspen ethanol lignin hydrogenation were analyzed by GC-MS, using an Agilent 7890A chromatograph, with HP-5MS capillary column (30 m), temperature programming in the range of 40-250 °C, and an Agilent 7000A Triple Quad selective mass detector. Compounds were identified using the NIST MS Search 2.0 instrument database. Standard substances, such as phenol, guaiacol, vanillin, syringaldehyde, 4-methylphenol, propylguaiacol, syringol, methylsyringol and allylsyringol, were used for quantitative assessment of the yield of monomeric compounds. Phenanthrene was used as an internal standard.

The molecular weight distribution of liquid product samples was determined by gel permeation chromatography using an Agilent 1260 Infinity II Multi-Detector GPC/SEC System with triple detection: refractometer (RI), viscometer (VS) and light scattering (LS). Separation was performed on a PLgel Mixed-E column using tetrahydrofuran stabilized with 250 ppm butylhydroxytoluene as a mobile phase. The column was calibrated using polydisperse polystyrene standards (Agilent, USA). The eluent flow rate was 1 mL/min, the injected sample volume was 100 µL. Before analysis, the samples were dissolved in THF (1 mg/mL) and filtered through a 0.22 µm PTFE membrane filter (Millipore). Data collection and processing were performed using Agilent GPC/SEC MDS software.

The elemental analysis of the samples was performed on a ThermoQuest FlashEA-1112 elemental analyzer (Italy).

RESULTS AND DISCUSSION

The yield of liquid products of aspen ethanol lignin hydrogenation without a catalyst was 90.4 wt% (Table 1). The use of Ni/C catalyst leads to a decrease in the yield of liquid products to 77.7 wt%, solid product to 5.9 wt% and an increase in the yield of gases to 16.4 wt%. The presence of the catalyst contributed to the rupture of ether bonds in the lignin structure, with the formation of alcohol-soluble products and the intensification of decarbonylation and cracking reactions associated with the formation of CO and methane. Increasing the temperature of catalytic hydrogenation of aspen ethanol lignin to 300 °C leads to an insignificant increase in the yield of the solid product to 6.2 wt%, which is probably due to an increase in the repolymerization reactions of ethanol lignin hydrogenation products. The use of Ni/C catalyst at a temperature of 300 °C also leads to a decrease in the yield of liquid products to 69.5% and an increase in the yields to 24.3 wt%.

The use of the Ni/C catalyst in the process of aspen ethanol lignin hydrogenation at 250 °C and 300 °C leads to an increase in the gas yield by 7 and 10.5 times, respectively, as well as a change in their composition (Table 2). An increase in gas formation in the presence of the Ni/C catalyst occurs mainly as a result of a significant increase in the yield of CO and methane. It can be assumed that the catalyst intensifies the reactions of decarbonylation of Hibbert ketones,[17] formed during the destruction of aliphatic structural fragments and substituents of aromatic rings of lignin.[18,19] Also, on the acidic centers of the Ni/C catalyst,[20] the reactions of hydrolysis of ester bonds between lignin fragments and subsequent decarboxylation of the resulting acids with the release of CO_2 are intensified. Methane is apparently formed mainly during hydrocracking of aliphatic structural fragments of lignin and methoxyphenols.[21] Thus, an increase in the yield of CO and CO_2 in the presence of catalysts indicates an intensification of the reactions of deoxygenation of structural fragments of lignins.

Table 1
Effect of process conditions on the yield of aspen ethanol lignin hydrogenation products

Sample	Solid products, wt%	Liquid products, wt%*	Gas, wt%
Without catalyst[24]	7.3	90.4	2.3
Ni/C (250 °C)	2.1	79.0	16.7
Ni/C (300 °C)	2.3	71.2	23.5

* Including boiling up to 100 °C

Table 2
Composition of gaseous products of hydrogenation of aspen wood ethanol lignin

Sample	CO, wt%	CO_2, wt%	CH_4, wt%
Without catalyst	0.5	1.5	0.3
Ni/C (250 °C)	8.2	5.6	2.6
Ni/C (300 °C)	10.4	8.6	4.7

Table 3
Elemental analysis data for aspen ethanol lignin samples, solid and liquid products of aspen ethanol lignin hydrogenation in supercritical ethanol (temperature 250 °C)

Sample	C, wt%	H, wt%	O, wt%	O/C	H/C
Initial ethanol lignin	64.61	6.79	26.76	0.31	1.31
Liquid products of non-catalytic hydrogenation	65.11	6.91	26.19	0.28	1.34
Liquid products of hydrogenation in the presence of Ni/C catalyst	66.21	7.49	24.36	0.25	1.45
Solid products of non-catalytic hydrogenation	67.24	7.76	23.21	0.24	1.15
Solid products of hydrogenation in the presence of Ni/C catalyst	68.15	8.11	21.96	0.21	1.22

According to the elemental analysis data, the O/C atomic ratio in the liquid products of non-catalytic and catalytic hydrogenation of ethanol lignin is lower than in the original lignin (Table 3). Moreover, the most significant decrease in O/C is observed in the liquid products obtained by catalytic hydrogenation of ethanol lignin. The O/C and H/C atomic ratios in the solid products of ethanol lignin hydrogenation are noticeably lower than in the case of the original ethanol lignin (Table 3). The observed changes also indicate that the Ni/C catalyst intensifies the reactions of hydrodeoxygenation of aspen wood ethanol lignin, leading to the formation of monomeric and dimeric products from lignin.[22,23]

According to GC-MS data (Table 4), the use of 10% Ni/C catalyst in the process of aspen ethanol lignin hydrogenation at a temperature of 250 °C leads to an increase in the yield of phenolic monomers from 5.8 to 10.1 wt%. A further increase in temperature to 300 °C leads to an increase in the total yield of monomeric phenols to 13.4 wt%.

The GC-MS results showed that the liquid products of aspen ethanol lignin hydrogenation with the 10% Ni/C catalyst are dominated by syringyl-type methoxyphenols, and the total yield of monomers reaches 10.1 wt% at a process temperature of 250 °C and 13.8 wt% at 300 °C. The main content is 4-propyl syringol. The predominance of 4-propylsyringol is probably associated with both the presence of acidic centers in the catalyst and the high temperature of the process, as a result of which the cleavage of the γ-OH group from 4-propanolsyringol is possible, with the formation of propyl syringol.[24]

The results obtained are comparable with the results obtained on more expensive platinum and ruthenium catalysts.[25] During aspen ethanol lignin hydrogenation under conditions of 250 °C, 4 H_2, 3 h, with the Pt/ZrO_2 catalyst, the yield of monomers from lignin reached 10.2 wt%.[16] It was previously shown that the use of a cheaper nickel-based catalyst $NiCuMo/SiO_2$ in the process of hydrogenation of Abies ethanol lignin under similar conditions to those used in the present work resulted in a monomer yield of 9.2 wt%.[26]

The extraction of lignin leads to changes in its structure due to a decrease in the content of reactive β-O-4 bonds, which probably affects both the yield of monomers and the selectivity for propyl and -propanol-substituted compounds. Thus, compared to the depolymerization of native lignin from wood, the yield of monomers is significantly lower. For example, earlier, during hydrogenation of Abies wood with a $NiCuMo/SiO_2$ catalyst,[25] the yield of monomers reached 37 wt% with high selectivity for 4-propanolguaiacol (16 wt%).

Table 4
Yield of phenolic monomers formed during the hydrogenation of ethanol lignin with 10% Ni/C catalyst

Compound	Yield, wt%		
	Without catalyst,[24] 250 °C	250 °C	300 °C
Phenol	0.2	0.3	0.6
Guaiacol	0.2	0.1	0.5
4-Methylphenol	0.4	0.2	0.6
3-Methoxycatechol	traces	traces	0.3
4-Ethylguaiacol	0.3	0.2	0.4
Syringol	0.4	0.4	0.9
4-Propylguaiacol	0.7	0.8	1.8
4-Propenylguaiacol	traces	0.5	traces
4-Methylsyringol	0.8	0.4	0.9
4-Ethylsyringol	0.6	0.5	0.7
4-Propylsyringol	1.8	3.1	4.8
4-Propenylsyringol	0.1	1.5	0.4
4-Propanolsyringol	0.1	1.2	traces
Other monomers	0.2	0.9	1.5
Total	5.8	10.1	13.4

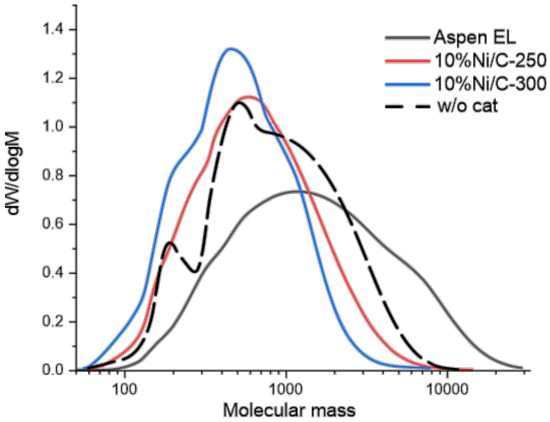

Figure 1: Molecular mass distribution curves of initial aspen ethanol lignin and of liquid products obtained by hydrogenation of aspen ethanol lignin with 10%Ni/C as catalyst at 250 °C and 300 °C

According to the gel permeation chromatography data of liquid aspen lignin hydrogenation products in the non-catalytic process, there is some shift of the molecular weight distribution curve to the low-molecular region (Fig. 1). It is worth noting that the molecules of the original lignin with a mass of more than 10,000 completely disappear, but the main part of the lignin molecules remains in the range of 1000-10,000. At the same time, two characteristic peaks appear in the region of 150 and 400 amu. Probably, these regions are represented by mono- and dimers of methoxyphenols. In the case of adding 10% Ni/C catalyst to the system at a temperature of 250 °C, the molecular mass distribution curve profile changes significantly. A decrease in the total molecular weight of the system is observed – the aspen lignin hydrogenation products in this case are represented by molecules with masses less than 6000, and the low-molecular region broadens. Such changes may be associated with selective cleavage of bonds in lignin and formation of a wide range of mono-, di- and trimers of methoxyphenols. Such a change correlates with GC-MS data, which show a 2-fold increase in the proportion of phenolic monomers compared to the non-catalytic process.

The data presented in Table 5 confirm a significant increase in lignin depolymerization on the 10% Ni/C catalyst, compared to the non-catalytic process, and an increase with increasing temperature. Probably, the monomer peak corresponds to the region of about 200. However, a peak is clearly visible on the curve of liquid products, located in the region from 400 to 500, related to dimers. Some shift in the peak position and scattering of the data are due to the difference in the compositions of the products.

Table 5
Molecular weight characteristic of aspen ethanol lignin (EL) and its liquid products

	M_N	M_W	PD
EL Aspen	910	1910	2.10
w/o cat	750	1480	1.97
10%Ni/C as catalyst at 250 °C	560	1100	1.96
10%Ni/C as catalyst at 300 °C	490	980	2.00

Increasing the temperature of the catalytic process of aspen lignin hydrogenation in the presence of 10% Ni/C to 300 °C leads to even more significant depolymerization of large lignin molecules, while the proportion of monomers increases significantly. The peaks in the range of 150-500 overlap, probably due to a wide variety of mono- and oligomeric fractions of the products.

CONCLUSION

It has been established that the use of the bifunctional Ni/C catalyst in the process of aspen ethanol lignin hydrogenation in a supercritical ethanol medium in the temperature range of 250-300 °C makes it possible to obtain up to 81 wt% yield of liquid products with an increased content of dimeric and monomeric phenolic compounds. The main monomeric component of the liquid products of the catalytic hydrogenation of aspen ethanol lignin is 4-propylsyringol. In this case, the total yield of monomers and dimers increased twice, and 4-propylsyringol by more than 2.5 times compared to the non-catalytic process. The increase in the monomer yield in the presence of the bifunctional Ni/C catalyst probably occurs due to the intensification of the reactions of β-O-4 bond rupture in lignin on Lewis acid sites and hydrogenation of the formed intermediate compounds with hydrogen on the metal sites of the catalyst. The observed increase in the yield of CO and CO_2 in the presence of a catalyst indicates the intensification of the deoxygenation reactions of structural fragments of lignin. The resulting methoxyphenols can be used as components of epoxy resins, fuel additives, and in other areas.

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