EFFICIENT LIGNIN DEPOLYMERIZATION WITH RU MODIFIED COMPOSITE METAL OXIDE

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ABSTRACT

With the development of research on renewable energy, lignin, as the second abundant component in biomass, has attracted more and more attention. In this study, the effects of the catalyst compositions on lignin depolymerization were investigated. Ru-W/Sn-AlO$_x$, converted about 95% lignin into liquid product and 2/3 of the liquid product can be soluble in petroleum ether at 300 °C after 12 h reaction. It meant that 2/3 of the liquid product were depolymerized to a mixture whose number-average molecular weight (Mn) was about 364. Meanwhile, the catalyst effectively reduced the char to 2%. In detail, the monomers was characterized by GC and 6% phenolic compound was get at optimized condition.

Keywords: lignin depolymerization, composite metal oxide, hydrogenation, Ru-modified

1. INTRODUCTION

The increasing consumption of fossil feedstock (i.e. crude oil and natural gas) caused many environmental problems. Therefore, the concept of replacing the fossil feedstock has been researched increasingly. Lignin, the most abundant natural aromatic source, wasn't utilized adequately for its complex complex three-dimensional, amorphous polymeric structure [1]. To this day, lots of efforts have been devoted to developing efficient methods to utilize lignin, including reductive depolymerization, oxidative depolymerization, base- and acid-catalyzed depolymerization, solvolytic & thermal depolymerization and two-step lignin depolymerization [2]. However, there are many problems of industrial utilization of lignin, such as low yield of small molecular product, high char formation, poor product selectivity [3]. To solve these problems, a proper catalytic method is necessary.

Generally speaking, reductive depolymerization is a hydrogenation process with a catalyst (Ru or Pt) and a hydrogen donating species (hydrogen gas or methanol) [4]. It can effectively convert lignin to liquid product and reduce the char formation but its drawback is low yield of small molecular product [5]. Harsh hydroprocessing at high temperature (>320 °C) and hydrogen pressure (>35 bar) could solve this problem but it brought high energy consumption [6]. Acid-catalyzed depolymerization could primely result in a relatively high yield of small molecular product [7]. Nevertheless, it suffered from high char formation [2]. To improve the method, many researchers synthesized these two methods and get better bifunctional catalytic lignin depolymerization process [8-13]. The hydroprocessing could stabilize the intermediate to reduce the char formation and maintain the high yield of small molecular product from acid-catalyzed depolymerization [14].

Here we report a one-pot lignin conversion with a Ru-W/Sn-AlO$_x$ catalyst in 1, 4-dioxane and methanol. About 95% liquid product, 2% char and 60% small molecular product were got at optimized conditions. A gas chromatograph-mass spectrometer (GC-MS) and gas chromatograph (GC) were employed in product analysis. The effects of the acid and hydrogenation components of the catalyst were also investigated.

2. EXPERIMENTAL

2.1 Materials

The lignin, Indulin AT^{TM} was bought from MeadWestvaco. RuCl$_3$, acetophenone, phenol, guaiacol, veratrole, 4-ethylphenol, 2-methoxy-4-methyl-phenol, 3, 4-dimethoxytoluene, 2-methoxy-4-ethyl-phenol, syringol, 2-methoxy-4-propyl-phenol, vanilline,

isoeugenol, acetovanillone, BHT, 3, 4-dimethoxyacetophenone, homovanillic acid and Ru/C (Ru: 5 wt%) was purchased from Aladdin (Shanghai, China). $SnCl_4 \cdot 5H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $NH_3 \cdot H_2O$, $H_3O_{40}PW_{12} \cdot xH_2O$, ethanol, $NaBH_4$, methanol, acetone, 1, 4-dioxane, and petroleum ether were analytical reagents and produced by Sinopharm Chemical Reagent Co., Ltd., (Shanghai, China). All chemicals were used without further purification.

2.2 Preparation of catalyst

The support was prepared by coprecipitation method. 15.381g $SnCl_4 \cdot 5H_2O$ and 19.732 $Al(NO_3)_3 \cdot 9H_2O$ were dissolved in 200 mL ultrapure water. The PH was adjusted to 10 using NH_3H_2O and then stirred for 30 min. After 2 h precipitation, the solution was stirred at 80 °C in water bath for 6 h and then dried at 105 °C for 12 h, following by grinding and calcinations at 300 °C for 2 h and 500 °C for 3 h with a heating rate of 3 °C /min.

1.126 g phosphotungstic acid, 8 g Sn-AlO$_x$ powder and 80 mL distilled water were added in a 100 mL beaker. After 2 h stirring, the sample was impregnated for 2 h and then was put in 60 °C and 70 °C water bath 2 h respectively. After that, the sample was calcined at 300 °C for 2 h and 550 °C for 3 h with a heating rate of 3 °C /min and then grinded.

10 ml of $RuCl_3$ solution (0.1026 g $RuCl_3$) and 1 g of powder were added to the mixed solution of 40 ml ethanol and 60 ml distilled water. After 6 h stirring, 100 ml of $NaBH_4$ solution (2 g $NaBH_4$) was added to it dropwise. After 12 h stirring, filtrating and washing by ethanol and distilled water, the powder was dried in a vacuum at 70 °C for 12 h. After grinded, Ru-W/Sn-AlO$_x$ (Ru: 5 wt%) was got.

2.3 Depolymerization of lignin

The depolymerization method was like the method in Wang's paper [15]. The difference were that the mass of the catalyst was 0.1 g, the H_2 pressure was 2 MPa and the products were only dealt with petroleum ether. According to Jiang's paper [16], the petroleum ether soluble product consists of monomers, dimers, trimers or some little bigger multimers for its Mn is about 364. In this study, different catalyst component, reaction temperature (270, 290, 300, 310 °C), and reaction time (1, 3, 6, 12 h) were investigated.

2.4 Analysis methods

The GC and GC-MS analysis methods were like Wang's paper [15]. The kinds of internal standard substance were added several.

NH$_3$-Temperature Programmed Desorption (NH$_3$-TPD) measurements were carried out on an Automatic Chemical Adsorption Instrument (Quantachrome Instruments, American). 100 mg of catalyst sample was pretreated in a flow of helium (30 mL/min) at 300 °C for 1 hour, and after cooling to 100 °C, then saturated with 10% NH$_3$/He at 300 °C. Subsequently, the excessive, physically adsorbed ammonia was removed by purging with helium at a flow rate of 30 mL/min at 100 °C. Finally, the desorption process came up when the temperature rose to 1000 °C at a rate of 20 °C /min.

3. RESULTS

3.1 Catalyst characterization

The data of NH$_3$-TPD was shown in **Table 1**. The desorbed temperature represented the strength of the acid sites and the amount of desorbed NH$_3$ represented the amount of acid sites. Entry 1 demonstrated that there were two acid sites in Sn-AlO$_x$, named the weak acid site (205°C, WAS) and the strong acid site (550°C, SAS). After modified by W (entry 2), the first two acid sites changed a little. The WAS became slightly weaker and the SAS became slightly stronger. Besides, a super strong acid site (950 °C, SSAS) came out. After modified by Ru, the SSAS disappeared but the WAS and SAS were obviously enhanced (entry 3).

Table 1 The desorption of NH$_3$

NH3-TPD	Peak1/°C (μmol·g-1)	Peak2/°C (μmol·g-1)	Peak3/°C (μmol·g-1)
1　Sn-AlOx	205[a] (381.90[b])	550 (346.31)	-
2　W/Sn-AlOx	220 (320.76)	560 (380.61)	950 (28.17)
3 Ru-W/Sn-AlOx	240 (475.11)	560 (548.09)	-

a the desorbed temperature of the peak
b the amount of the desorbed NH$_3$

3.2 Effects of different catalyst compositions

The results were shown in **Table 2**. Considering the result in **Table 1** and the entry 1, 3, 6 in **Table 2**, the yield of petroleum ether soluble products and the strength of acid sites were in positive correlation. This correlation was more conspicuous at 270 °C (shown in entry 2, 5). Stronger acid benefited the formation of small molecular products. From entry 1, 3, 6, 8, it can be seen that the yield of liquid products increased and solid products decreased with the appearance of hydrogenation component (Ru). Besides, without acid, the yield of petroleum ether soluble products was relatively low (entry 8). The conclusions above were drawn in 1 h reaction time. When the reaction time is 12 h, the main influence factor of the yield was the appearance of

hydrogenation component (Ru) (entry 4, 7, 9). The acid can still increase the yield of petroleum ether soluble products but the increase was relatively small (entry 7, 9 46.99% to 59.86% compared with entry 4, 9 36.8% to 59.86%). In conclusion, acid enhanced the process that lignin depolymerized to monomers or dimers but it also polymerize more oligomers to solid products (char). The hydrogenation component could effectively stabilize the

intermediate and reduce the char formation. From the results, the monomers and dimers were more stable than the oligomers at mild conditions. Therefore, the catalytic effect of hydrogenation component wasn't obvious in short reaction time (1 h, entry 3, 4, 6, 7) or at low temperature (270 °C, entry 2, 3, 5, 6). From entry 6 and 10, Ru has a synergistic effect with W/Sn-AlO$_x$ for more petroleum ether soluble products.

Table 2 The effects of different catalyst compositions

Entry	Catalyst	Reaction time/h	Reaction temperature/°C	Solid products/%	Gas products/%	Liquid products/%	Petroleum ether soluble products/%
1	Sn-AlO$_x$	1	300	44.51	2.73	52.76	14.93
2	W/Sn-AlO$_x$	1	270	9.9	1.26	88.84	12.44
3	W/Sn-AlO$_x$	1	300	46.84	2.26	50.9	21.1
4	W/Sn-AlO$_x$	12	300	30.91	4.01	65.08	36.8
5	Ru-W/Sn-AlO$_x$	1	270	7.36	1.14	91.5	9.24
6	Ru-W/Sn-AlO$_x$	1	300	33.14	2.95	63.91	20.19
7	Ru-W/Sn-AlO$_x$	12	300	1.92	3.76	94.32	59.86
8	Ru/C	1	300	21.91	2.77	75.32	12.91
9	Ru/C	12	300	1.08	3.15	95.77	46.99
10	Ru/C & W/Sn-AlO$_x$[a]	1	300	33.51	2.13	64.36	17.85

Condition: 0.5 g lignin, 0.1 g catalyst, 2 MPa H$_2$, 900 rpm. a mechanical mixing 0.1 g Ru/C (Ru: 5 wt%) and 0.1 g W/Sn-AlO$_x$

3.3 Effects of reaction temperature

To research the effect of reaction temperature, the lignin depolymerization reactions catalyzed with Ru-W/Sn-AlO$_x$ were done at different temperature (270, 290, 300, 310 °C). This series of reaction was done in various reaction time (1, 3, 6, 12 h). For the limited space, only the data of 12 h reaction time was shown in **Fig. 1a** and **Fig. 1b**. As can be seen in **Fig. 1a**, the yield of liquid products decrease from 94.81% to 67.82% when the temperature increase from 270 °C to 290 °C. It may be attributed to the relatively low hydrogenation ability at the mild conditions. Then the yield rose to 95.28% at 310 °C. This indeed revealed the effect of hydrogenation component. The yield of petroleum ether soluble products first increased from 270 °C (20.47%), then reach the top at 300 °C (59.86%), and then declined (53.58%, 310 °C). It was demonstrated that excessive temperature would hinder the catalytic lignin depolymerization. **Fig. 1b** showed that the yield of total identified monomers increased from 5.46% to 8.27% along with rising temperature. However, the yield of the guaiacol (guaiacol, 4-methyl- guaiacol, 4-ethyl- guaiacol, 4-propyl-guaiacol) first increased from 2.4% (270 °C) to 4.92 (290 °C), and then decreased to 4.26% (310 °C). It could be explained that the guaiacol was converted to the corresponding dimethoxy-benzene at high temperature for the yield of dimethoxy-benzene (veratrole, 3, 4-

dimethoxytoluene) increased from 0.18% (270 °C) to 0.53% (310 °C). In summary, 300 °C is an appropriate temperature for lignin depolymerization with Ru-W/Sn-AlO$_x$.
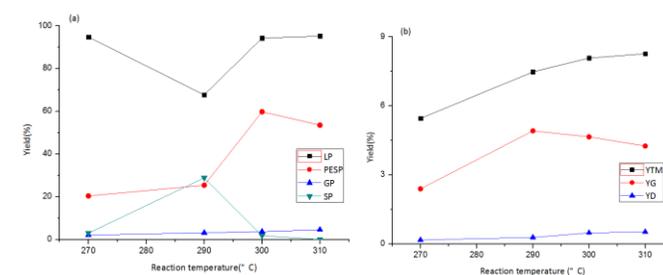

Fig. 1 Product distribution with different temperature (a) Distribution of gas products (GP), solid products (SP), liquid products (LP) and petroleum ether soluble product (PESP). (b) Distribution of yield of total monomer (YTM), guaiacol (YG) and
dimethoxy-benzene (YD).

3.4 Effects of reaction time

Reaction time is an important factor for lignin depolymerization. The results of different reaction time were shown in **Fig. 2a** and **Fig. 2b**. From **Fig. 2a**, it can be seen that the yield of liquid products rose rapidly from 63.91% (1 h) to 82.57% (3 h) and then rose relatively slowly to 94.32% (12 h). The trend of solid products was just the reverse. The char yield declined from 33.14% (1

h) to 14.11% (3 h) fast and then slowly decreased to 1.92% (12 h). The yield of gas products and petroleum ether soluble products increased steadily from 2.95% and 20.19% (1 h) to 3.76% and 59.86% (12 h). **Fig. 2b** demonstrated similar results to **Fig. 2a**. The yield of total identified monomers increased from 6.15% to 8.08% along with prolonging reaction time. The change rules of the yield of the guaiacol and dimethoxy-benzene were also similar. This illustrated that prolonging reaction time vastly benefited the formation of monomer and the char elimination. The reason may be that hydrogenation was a slower process than depolymerization and it need more reaction time. Besides, the guaiacol would be converted to corresponding dimethoxy-benzene at harsh conditions. In conclusion, prolonging reaction time improves lignin depolymerization a lot.
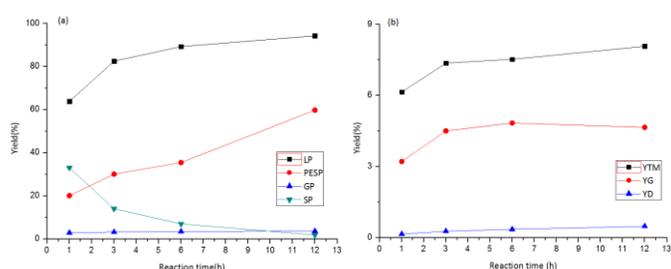

Fig. 2 Product distribution with different reaction time (a) Distribution of gas, solid, liquid and petroleum ether soluble product. (b) Distribution of yield of total monomer, yield of guaiacol and yield of dimethoxy-benzene.

4. Conclusion

In the study of catalyst component, it can be known that the strength of the acid component has positive correlation with the formation of small molecular products and the catalytic effect is more conspicuous at mild conditions such as low temperature (270 °C), short reaction time (1 h). The benefit of hydrogenation component becomes significant at high temperature (300°C) and long reaction time (12 h). In general, Ru-W/Sn-AlO$_x$ is an effective catalyst for the lignin depolymerization. At optimized conditions (300 °C, 12 h), it converted about 95% lignin into liquid product and 2/3 of the liquid product were monomers, dimers, and some oligomers. Meanwhile, the catalyst effectively reduced the char to less than 2%.

REFERENCE
[1] Sun Z, Fridrich B, de Santi A, et al. Bright side of lignin depolymerization: toward new platform chemicals[J]. Chemical reviews, 2018, 118(2): 614-678.
[2] Schutyser W, Renders T, Van den Bosch S, et al. Chemicals from lignin: an interplay of lignocellulose fractionation, depolymerisation, and upgrading[J]. Chemical society reviews, 2018, 47(3): 852-908.
[3] Rinaldi R, Jastrzebski R, Clough M T, et al. Paving the way for lignin valorisation: recent advances in bioengineering, biorefining and catalysis[J]. Angewandte Chemie International Edition, 2016, 55(29): 8164-8215.
[4] Zakzeski J, Bruijnincx P C A, Jongerius A L, et al. The catalytic valorization of lignin for the production of renewable chemicals[J]. Chemical reviews, 2010, 110(6): 3552-3599.
[5] Van den Bosch S, Schutyser W, Vanholme R, et al. Reductive lignocellulose fractionation into soluble lignin-derived phenolic monomers and dimers and processable carbohydrate pulps[J]. Energy & environmental science, 2015, 8(6): 1748-1763.
[6] Kloekhorst A, Heeres H J. Catalytic hydrotreatment of Alcell lignin fractions using a Ru/C catalyst[J]. Catalysis Science & Technology, 2016, 6(19): 7053-7067.
[7] Zhang X, Zhang Q, Long J, et al. Phenolics production through catalytic depolymerization of alkali lignin with metal chlorides[J]. BioResources, 2014, 9(2): 3347-3360.
[8] Shu R, Long J, Xu Y, et al. Investigation on the structural effect of lignin during the hydrogenolysis process[J]. Bioresource technology, 2016, 200: 14-22.
[9] Parsell T H, Owen B C, Klein I, et al. Cleavage and hydrodeoxygenation (HDO) of C–O bonds relevant to lignin conversion using Pd/Zn synergistic catalysis[J]. Chemical Science, 2013, 4(2): 806-813.
[10] Yan F, Ma R, Ma X, et al. Ethanolysis of Kraft lignin to platform chemicals on a MoC1-x/Cu-MgAlOz catalyst[J]. Applied Catalysis B: Environmental, 2017, 202: 305-313.
[11] Ma H, Li H, Zhao W, et al. Selective depolymerization of lignin catalyzed by nickel supported on zirconium phosphate[J]. Green Chemistry, 2019, 21(3): 658-668.
[12] Murugappan K, Mukarakate C, Budhi S, et al. Supported molybdenum oxides as effective catalysts for the catalytic fast pyrolysis of lignocellulosic biomass[J]. Green Chemistry, 2016, 18(20): 5548-5557.
[13] Shao Y, Xia Q, Dong L, et al. Selective production of arenes via direct lignin upgrading over a niobium-based catalyst[J]. Nature communications, 2017, 8: 16104.
[14] Bjelić A, Grilc M, Huš M, et al. Hydrogenation and hydrodeoxygenation of aromatic lignin monomers over Cu/C, Ni/C, Pd/C, Pt/C, Rh/C and Ru/C catalysts: Mechanisms, reaction micro-kinetic modelling and quantitative structure-activity relationships[J]. Chemical Engineering Journal, 2019, 359: 305-320.
[15] Wang J, Li W, Wang H, et al. Liquefaction of kraft lignin by hydrocracking with simultaneous use of a novel dual acid-base catalyst and a hydrogenation catalyst[J]. Bioresource technology, 2017, 243: 100-106.
[16] Jiang X, Savithri D, Du X, et al. Fractionation and characterization of kraft lignin by sequential precipitation with various organic solvents[J]. ACS Sustainable Chemistry & Engineering, 2016, 5(1): 835-842.