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CATALYTIC CONVERSION OF LIGNIN BY IMMOBILIZED Cu([H₄]SALEN AND [H₂]SALEN COMPLEXES UNDER HYDROTHERMAL CONDITIONS

A comparative investigation was made of the effect of catalysis by immobilized Cu([H₄]salen) on the hydrothermal conversion of organosolv lignin. The immobilization and hydrogenation of the complexes led to increased yield of liquid products compared with the corresponding unimmobilized and unhydrogenated complexes in catalytic conversion of lignin. In addition, the method of immobilization of the complexes affected the catalytic performance in lignin conversion, in which a higher yield of liquid products was obtained with the SB-immobilized complexes (ship-in-bottle method) than with the IM-immobilized complexes (impregnation method). The yield of liquid products obtained with Cu([H₂]salen) at 250°C and 4 MPa O₂ in water was 6.00%, compared with 16.80% and 22.08% respectively for Cu([H₄]salen)/IM and Cu([H₄]salen)/SB. Additionally, the addition of organic solvent had a marked effect on the catalytic performance of Cu([H₄]salen), and the highest yield of liquid products (27.06%) was observed with Cu([H₄]salen)/SB in water/methanol (80/20, v/v). The total yield of liquid products varied depending on temperature and oxygen pressure, and reached 46.01% under reaction conditions of 280°C and 6 MPa O₂ in water/methanol (80/20, v/v). GC-MS analysis showed the main compounds in the liquid products to be phenols, with a yield of 32.16%. Other compounds included alcohols, ketones, aromatics, olefins, cycloalkanes, and alkanes. A mechanism for their formation was proposed based on the oxidation of a lignin model compound under hydrothermal conditions.

Keywords: organosolv lignin; Cu([H₄]salen); Cu([H₂]salen); hydrothermal pyrolysis

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Introduction

Lignin is a complex heterogeneous aromatic polymer constituting up to 30% of plant material. Its aromatic structure suggests that it is a possible green feedstock for use in the production of biomass-based materials. However, because of the irregular three-dimensional network structure, the effective utilization of lignin has been greatly restricted. Therefore, more green processes are needed to explore possibilities of lignin conversion [Monteil-Rivera 2016].

In the past decades, several strategies have been employed for the transformation of lignin to value-added products, such as pyrolysis and gasification. Hydrothermal pyrolysis has been an important process in lignin conversion, as water is a unique and environmentally benign solvent [Cheng et al. 2017]. Atta-Obeng et al. [2017] prepared carbonaceous materials by hydrothermal carbonization (HTC) of technical lignin, and found that the condensation reaction promoted the carbonization in hydrothermal pyrolysis. Besse et al. [2015] studied the hydrothermal conversion of eugenol as a lignin model compound over a Pt/C catalyst and showed that the C=C double bond of the propenyl chain was hydrogenated, but the hydroxyl and methoxy groups of eugenol did not react under hydrothermal conditions. Some relevant reports focusing on the cracking of the inter-unit linkages and the effect of catalysts have stated that catalysis should be a key factor to fulfill the promise of lignin depolymerization to specific products. Oxidative pyrolysis has been widely applied in the conversion process due to its economic feasibility. Organometallic catalyzed oxidation, polyoxometalate (POM) catalyzed oxidation, biomimetic oxidation and enzyme-based oxidation have been studied, the aim being the cleavage of designated inter-unit linkages [Díaz-Urrutia et al. 2016; Chang et al. 2017; De Clercq et al. 2017; Abejón et al. 2018].

Meanwhile, in a new effective path, biomimetic catalysis is employed to solve the problem of selectivity and efficiency. Reactions have been studied by many researchers in biomimetic catalysis using lignin [Springer et al. 2016] and lignin model compounds [Badamali et al. 2011; Ambrose et al. 2013; Elder et al. 2013]. In addition, Tse et al. [2019] observed that immobilization of porphyrin into carbon-based materials prevented unwanted aggregation of the complex and increased oxidation. It was thus shown that biomimetic catalysis with salen and porphyrin complexes promoted the improvement of lignin transformation and specific product yield. It was also found in our previous research that lignin was increasingly degraded with the use of biomimetic catalysis, particularly the β -O-4, β -1, β -5 and β - β linkages, and improvements were obtained due to the immobilization of a biomimetic catalyst. The products obtained, such as aldehydes, ketones, alcohols, acids, phenols, furans, cyclohexadienone and biphenyls, were also found in biomimetic treatment of lignin, as detected by GC-MS [Tang and Zhou 2015; Zhou and Tang 2016]. In this study, the effects of biomimetic catalysis on lignin conversion under hydrothermal conditions were

investigated, where the [H₄]salen complex was used as a catalyst in comparison with the [H₂]salen complex. Their suitability for hydrothermal conversion at elevated temperature and in aqueous environments was evaluated, and fundamental research on understanding the oxidative process was carried out using lignin model compounds.

Materials and methods

Materials

The following commercially available reagents were used as received: guaiacol (Sigma-Aldrich, 99.0%), 1,4-dioxane (Sinopharm Chemical Reagent, analytical grade), acetone (Sinopharm Chemical Reagent, analytical grade), tetrahydrofuran (Sinopharm Chemical Reagent, analytical grade), acetonitrile (Sinopharm Chemical Reagent, analytical grade), acetic acid (Sinopharm Chemical Reagent, analytical grade), ethanol (Sinopharm Chemical Reagent, analytical grade), methanol (Sinopharm Chemical Reagent, analytical grade), anhydrous sodium sulfate (Sinopharm Chemical Reagent, analytical grade). The other chemicals used in the synthesis of lignin model compounds were reagent grade and were used as supplied by Aldrich Scientific. An organosolv lignin (Sigma-Aldrich, China) was used as a lignin sample; its sugar content, lignin content, ash content and molecular weight were 0.33%, 98.82%, 0.12% and 2832 respectively, and it contained 63.13% C, 5.27% H, 0.31% N, and 31.29% O.

Preparation of immobilized Cu[H₄]salen and [H₂]salen complexes

The immobilized Cu[H₄]salen and [H₂]salen complexes were prepared and characterized as reported in our previous publications. Their textural characteristics were as given in the reference [Zhou 2014].

Synthesis of lignin model compound

The lignin model compound (Fig. 1) was synthesized as in our previous work [Zhou and Lu 2016].

Catalytic experiments

20 g lignin, 1.0 g neat or 0.1 g immobilized complex (based on neat complex) and 100 ml solvent were added successively to a 300 ml Parr reactor. The reactor was evacuated with nitrogen three times, and filled with oxygen gas until a pressure of 4 MPa was maintained. The mixture was then heated to the desired temperature under stirring (600 rpm). In the course of the reaction, direct samplings were carried out at required intervals.

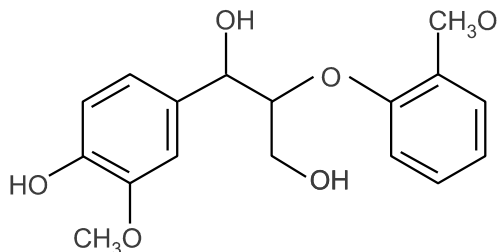


Fig. 1. Lignin model compound

The sample was filtered using a folded filter paper and washed with DI water. The liquid was extracted using an equal amount of diethyl ether to obtain a diethyl ether phase. The water phase obtained in the first extraction was then extracted using an equal amount of ethyl acetate to obtain an ethyl acetate phase. The two organic phases were dried with anhydrous sodium sulfate, filtered and dried in vacuum. Finally, the solid sample was dissolved in chloroform for GC-MS analysis.

The liquid products were quantitatively determined by GC-MS (Agilent HP6890-5973, equipped with an Rtx-5Sil MS column, 30 m × 0.25 mm × 0.25 μm), with undecane used as the internal standard. The temperature program for GC-MS was as follows: 40°C (10 min) → 280°C (10°C /min), hold for 5 min. Products were identified by means of the Wiley library HP G1035A and the NIST library of mass spectra and subsets HP G1033A.

The yield of compound was calculated based on the internal standard. Total yield was obtained by summing the yield of each compound.

Results and discussion

Effect of catalyst on lignin conversion

Biomimetic catalysts were used in this work for the hydrothermal depolymerization of organosolv lignin. The results are shown in Figure 2. The main products obtained in hydrothermal conversion included phenols, alcohols, alkanes, ketones, aromatics, olefins, cycloalkanes, and alkanes.

Compared with the neat complexes, the yields of liquid products obtained in the catalytic conversion of lignin by the immobilized complexes were significantly higher; the values were 7.64%, 9.47%, 16.80% and 22.08% for catalysis by Cu([H₂]salen)/IM, Cu([H₂]salen)/SB, Cu([H₄]salen)/IM and Cu([H₄]salen)/SB respectively. Metal [H₂]salen and [H₄]salen complexes immobilized in the pores and void spaces of NaY have been reported to show improved catalytic activity in oxidation compared with the corresponding neat complexes, which deactivated easily due to the formation of dimeric oxo- and peroxo-bridged species [Wang et al. 2017]. Moreover, the quantity of the

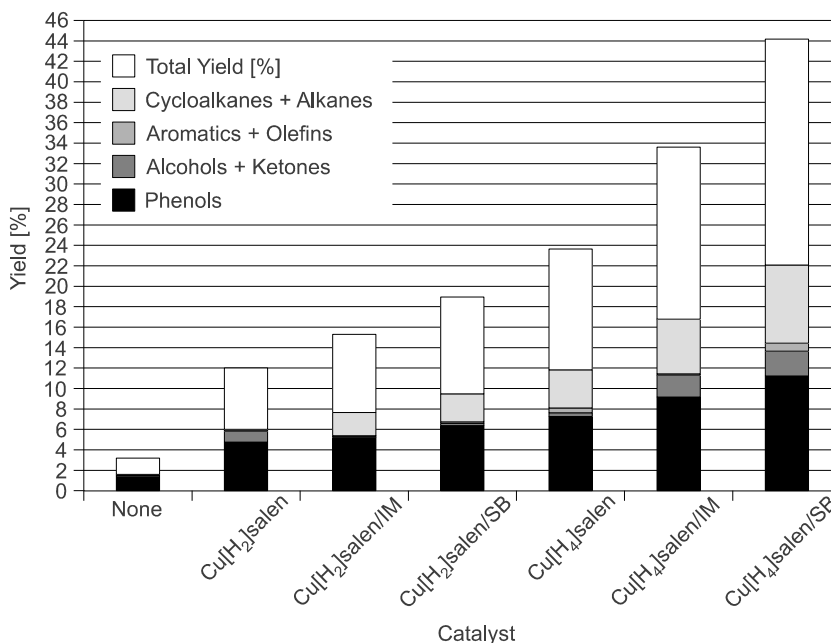


Fig. 2. Conversion of lignin with immobilized catalyst: lignin (2.0 g), catalyst (1.0 g), water (100 mL), 250°C, 4 MPa O₂, 120 min, 600 rpm

immobilized complexes used in the reaction was relatively low, in terms of the neat complex. Nevertheless, the hydrogenated complexes, both unimmobilized and the immobilized, were superior to the corresponding unhydrogenated complexes in catalytic performance according to the yield of liquid products (Fig. 2). For example, when the same dosage of the complex was used, Cu([H₂]salen) produced a yield of 6.00% of liquid products, Cu([H₂]salen)/IM gave a yield of 7.64% and Cu([H₂]salen)/SB gave 9.47%, while Cu([H₄]salen) gave a yield of 11.82% of liquid products, Cu([H₄]salen)/IM gave 16.80% and Cu([H₄]salen)/SB gave 22.08%. The explanation for this may be that the conversion of the [H₂]salen ligand to [H₄]salen with sodium borohydride afforded a more flexible complex due to the hydrogenation of C=N to C-N, thus enhancing catalytic performance [Yang et al. 2011].

In addition, the use of SB-immobilization in catalyst preparation led to an improvement in catalytic performance for lignin transformation (Fig. 2). It increased the yield of liquid products by 31.42% and 23.95% for Cu([H₄]salen)/SB and Cu([H₂]salen)/SB, respectively, compared with the corresponding IM complex. The most important factor leading to the improvement concerned the textural properties of the catalyst [Zhou 2014]: the high specific surface area and pore diameter of the SB complex increased the accessibility of reactants inside supercages [Shah et al. 2015].

Effect of solvent on lignin conversion

Additionally, the addition of organic solvent had a marked effect on the catalytic performance of Cu([H₄]salen), as shown in Figure 3. Acetone tetrahydrofuran and acetonitrile as solvents showed little solvolysis, and dioxane exhibited a negative effect in lignin conversion, as opposed to their normal roles. Meanwhile, under hydrothermal conditions, the organic solvents – including acetic acid, ethanol and methanol – used in solvent systems had a positive effect on the oxidative degradation of lignin. The highest yield of liquid products was observed in methanol (27.06%), followed by ethanol (25.32%) and acetic acid (23.34%). Peroxyacetic acid may be generated in situ in the presence of acetic acid. Then this oxidant (peroxyacetic acid) accelerated the oxidation of lignin. Similarly, methanol and ethanol might quench the reactive radicals of lignin fragments to prevent condensation between radicals, enhancing the depolymerization of lignin. Also, methanol may afford active H species for hydrogenolysis of the lignin substructures [Deng et al. 2015], increasing the yield of aromatic products such as phenols (Fig. 3).

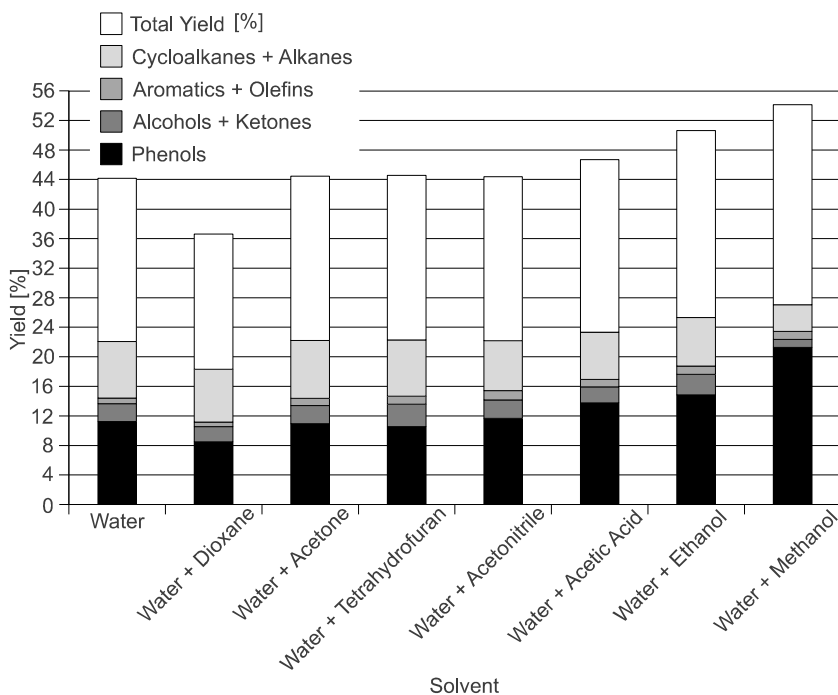


Fig. 3. Conversion of lignin with Cu([H₄]salen)/SB: lignin (2.0 g), Cu([H₄]salen)/SB (1.0 g), solvent (100 mL; 80% water + 20% organic solvent), 250°C, 4 MPa O₂, 120 min, 600 rpm

Effect of reaction temperature and oxygen pressure on lignin conversion

In order to further optimize the hydrothermal pyrolysis, the effect of temperature and oxygen pressure on lignin transformation was explored within specified ranges (240-320°C, 2-8 MPa). As the reaction temperature rose from 240°C to 320°C, the total yield of liquid products increased from 23.22 wt% to 40.21 wt%, and the phenol yield rose from 19.37 wt% to 28.06 wt% (Fig. 4a), which suggested a remarkable reaction selectivity due to the enzymatic properties of Cu([H₄]salen)/SB directed against the β -O-4 cleavage in lignin [Chen and Ma 2016; Jiang et al. 2017]. Moreover, increasing temperature favored the oxidation reaction, which led to a decrease of aromatics and olefins, and an increase of alkanes, including cycloalkanes, and oxygenated compounds (alcohols, ketones) in the liquid products. In addition, the catalyst was most reactive in terms of product yield when the peak temperature reached 280°C. Figure 4b clearly shows the influence of oxygen pressure on the pyrolysis behavior of the lignin samples. The increase in pressure in the range 5.0-6.0 MPa O₂ led to the evolution of distinctly higher yields of phenols, alcohols/ketones and cycloalkanes/alkanes, and therefore lower yields of aromatics/olefins, in pyrolysis. On the whole, while clear plateaus appeared in the other cases after certain pressure and temperature values were attained, the graphs of aromatics plus olefins were characterized by a reduced yield for the highest values. This may be due to the acceleration of secondary pyrolysis of some aromatics and olefins at high reaction temperature and oxygen pressure [Lui et al. 2017]. The kinetic model suggested by Forchheim et al. [2014] also confirmed that decomposition of aromatics and catechols often occurred under harsh conditions, such as high temperature and high pressure, during the hydrothermal depolymerization of lignin. Further explanation of the mechanism was provided with the use of a β -O-4 lignin model compound (see “Mechanism considerations”).

Mechanism considerations

A lignin model compound with β -O-4 linkage was used as the substrate for considerations of the mechanism of lignin conversion by Cu([H₄]salen)/SB under hydrothermal conditions. The dehydrogenation to phenoxy radicals initiated the degradation of the lignin model compound by L-Cu-O-O \cdot , and β -O-4 was cleaved simultaneously, producing phenols [Shimazaki and Yamauchi 2011], as shown in Schema 1. Correspondingly, the side-chain oxidation of the lignin model compound contributed to the production of alkanes, alcohols and ketones. Further oxidation of quinones derived from phenoxy radicals resulted in a ring-opening reaction, giving cycloalkanes and olefins. In addition, epoxidation on double bonds in side-chains by L-Cu-O-O \cdot led to aromatics [Elder and Bozell 1996], such as compound 1, compound 2, compound 3, and compound 4.

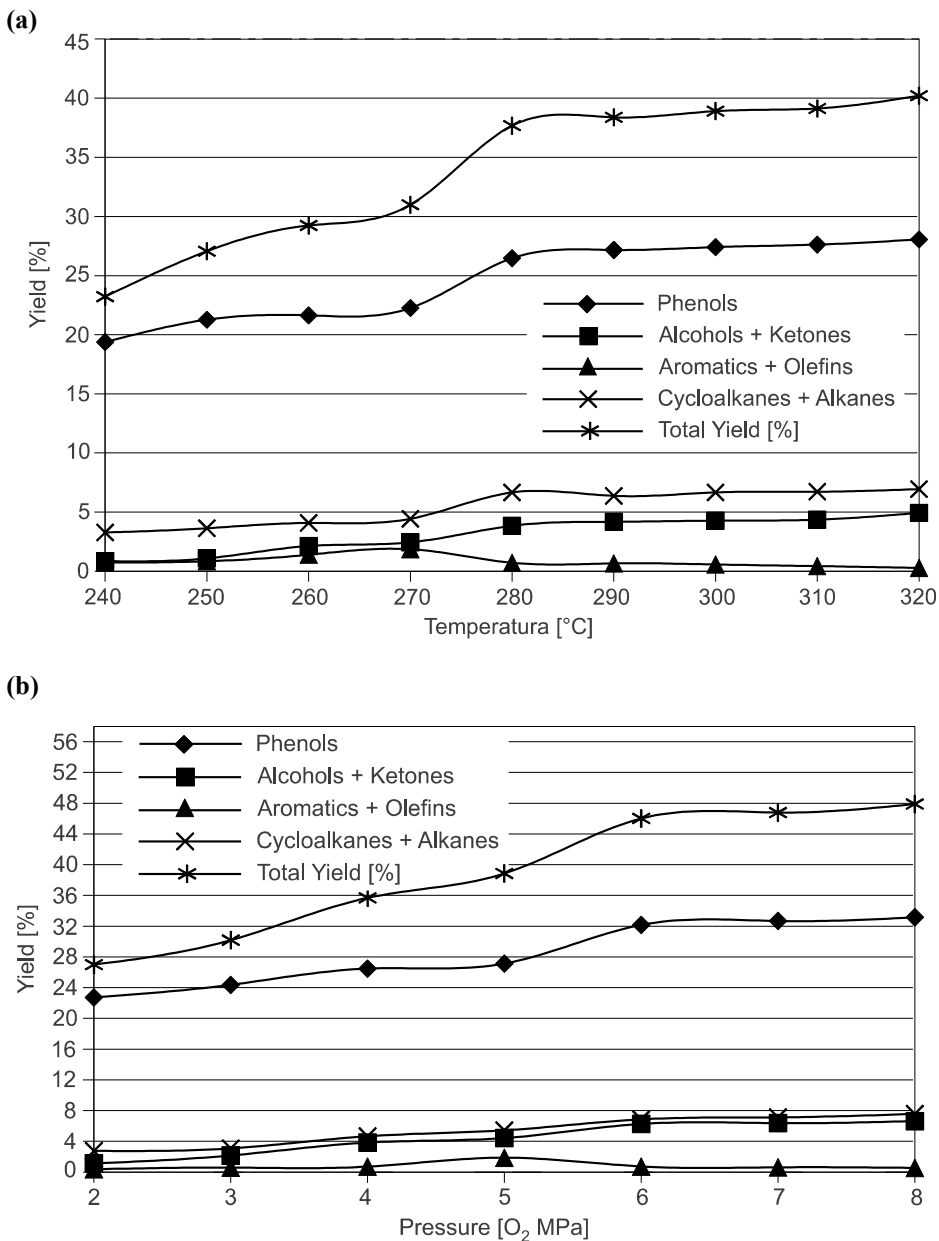
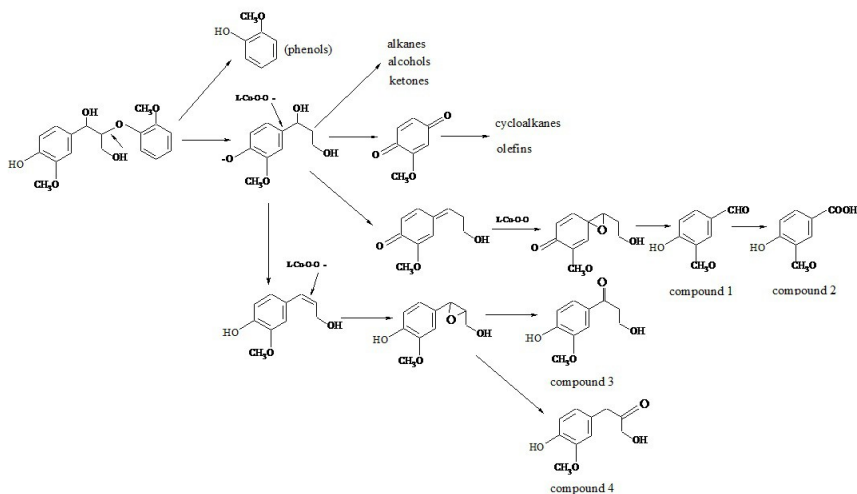


Fig. 4. Effect of reaction temperature (a) and oxygen pressure (b) on lignin conversion: (a) lignin (2.0 g), Cu([H₄]salen)/SB (1.0 g), solvent (100 mL; 80% water + 20% methanol), 4 MPa O₂, 120 min, 600 rpm; (b) lignin (2.0 g), Cu([H₄]salen)/SB (1.0 g), solvent (100 mL; 80% water + 20% methanol), 280°C, 120 min, 600 rpm



Schema 1. Postulated oxidation of lignin model compound over biomimetic catalyst: lignin model compound (0.50 g), Cu([H₄]salen)/SB (15 mg), solvent (100 mL; 80% water + 20% methanol), 6 MPa O₂, 280°C, 120 min, 600 rpm

Conclusions

The extent of hydrothermal conversion of the studied organosolv lignin depended upon the type of the biomimetic catalysts and the method of immobilization of the complexes, namely, Cu([H₂]salen), Cu([H₄]salen), Cu([H₂]salen)/IM, Cu([H₄]salen)/IM, Cu([H₂]salen)/SB and Cu([H₄]salen)/SB. Immobilization and hydrogenation of the complexes resulted in high yield and selectivity of the liquid products obtained in catalytic conversion of organosolv lignin under hydrothermal conditions, while immobilization of the complexes with the SB method also resulted in improvement in the yield and selectivity of the liquid products. On the other hand, organic solvent, temperature and oxygen pressure affected the hydrothermal pyrolysis and reaction selectivity of organosolv lignin. The mechanism was also considered, using a lignin model compound with β -O-4 linkage. With regard to the real-world applicability of the proposed system on an industrial scale, consideration should be given to further study using lower catalyst:lignin ratios (from 1:10 to 1:200).

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