# Depolymerization of Lignin to Produce Monophenols and Oligomers Using a Novel Ni/Ce-CNT Catalyst

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A novel composite catalyst consisting of nickel, cerium, and carbon nanotube (CNT) was developed for native lignin and industrial lignin depolymerization. It was found that Ni and Ce had synergistic effects on the depolymerization. Native lignin was depolymerized to monophenols with a yield of 21.4% at 300 °C for 2 h under 2 MPa hydrogen pressure with serious coke formation. A milder condition set at 280 °C for 2 h under 2 MPa hydrogen pressure provided a monophenols yield of 13.5% with 78.6% lignin removal, but much less coke formation and better catalyst reusability. Even after running the trial four times, the catalyst presented high efficiency. Industrial lignin was depolymerized to oligomers, which are a series of aromatic micromolecules that could be extracted by specific organic solvents such as ethyl acetate. Those oligomers could be used as high calorific value bio-oil. After being depolymerized at 260 °C for 1 h under 2 MPa hydrogen pressure, the yields of oligomers were 56.0% and 11.6% extracted by ethyl acetate (EA) and petroleum ether (PE), respectively. After recycling four times, the catalyst still exhibited high activity. It was clear that the Ni/Ce-CNT was an effective catalyst in lignin depolymerization.

*Keywords: Native lignin; Industrial lignin; Depolymerization; Compound catalyst; Monophenols; Oligomers*

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## INTRODUCTION

Lignocellulose is one of the most abundant sources of biomass and has enormous potential to be a sustainable energy source for the production of chemicals and fuels (Huber *et al.* 2006). Lignocellulose primarily consists of three polymeric components: cellulose, hemicellulose, and lignin (Jae *et al.* 2010). Cellulose and hemicellulose are polysaccharides that can be hydrolyzed into monosaccharides (Jørgensen *et al.* 2007) or further converted into high-value chemicals such as furfural (Lange *et al.* 2012), hydroxymethylfurfural (Wang *et al.* 2011), and levulinic acid (Palmqvist and Hahn-Hägerdal 2000). During the past several decades, the conversion of carbohydrates has been widely studied, and both thermochemical and biological processes have been established (Kristianto *et al.* 2017). In contrast, the lignin conversion process is still in its infancy mainly due to its complex structures (Guo *et al.* 2017). Lignin is known as a highly branched aromatic polymer consisting of different phenyl propane units such as p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. All of its monomers are linked by C-C and ether bonds containing β-O-4, α-O-4, 4-O-5, β-β, β-5, β-4, and 5-5 linkages (Zhai *et al.* 2017), forming a recalcitrant structure that protects lignin from chemical and biological degradation (Kristianto *et al.* 2017). Despite difficulty in its conversion, lignin has the potential to produce high-value-added chemicals, such as 4-propylguaiacol (Zakzeski *et al.* 2010; Ouyang *et al.* 2015), and it is also a good precursor to produce higher calorific value liquefied fuel on account of its lower oxygen content compared with cellulose and hemicellulose (Piskorz *et al.* 1989; Ma *et al.* 2017). It is essential to develop effective processes to convert lignin to value-added chemicals and oligomers.

During recent decades, many thermochemical processes have been investigated to depolymerize lignin effectively (Pandey and Kim 2011). These methods include pyrolysis (Patwardhan *et al.* 2011), gasification (Wang *et al.* 2015), hydrogenolysis (Kärkäs 2017), chemical oxidation (Prado *et al.* 2016), and hydrolysis under supercritical conditions (Güvenatam *et al.* 2016). Among them, hydrogenolysis is considered to be a promising method because of less char and coke formation during the process (Huang *et al.* 2014, 2015). A large number of metals (*e.g.*, Ni, Pd, Pt, and Ru) loaded on specific carbon materials have been used in lignin depolymerization and have shown promising catalytic results (Galkin *et al.* 2014; Kristianto *et al.* 2017). For example, Jae *et al.* (2010) used Ru/C as a catalyst to depolymerize empty fruit bunch lignin, and 66.3 wt% bio-oil yield as well as 6.1 wt% aromatic monomer yields were obtained at 350 °C in supercritical ethanol. Shu *et al.* (2018) adopted Pd/C to depolymerize alkali lignin, and 58.5% liquefaction yield and 1.5% phenols yield were acquired at 260 °C for 5 h under 4 MPa $H_2$ in methanol. However, those depolymerization processes also present several issues that need to be overcome. For example, those reactions usually require high hydrogen pressure (> 3 MPa) (Macala *et al.* 2009; Zeng *et al.* 2015), high temperature (> 300 °C) (Wang *et al.* 2017), and a long reaction time (> 4 h), which result in a high demand for equipment and energy consumption. Therefore, the development of efficient depolymerization processes for lignin under low hydrogen pressure and low temperature with a high catalyst efficiency is needed.

Cerium (Ce) is a rare earth element with the ability to selectively break C-C bonds (Yu *et al.* 2010). In past research, Ce was used to depolymerize kraft lignin to produce bio-oil (Ma *et al.* 2017). A high yield of bio-oil with significant fuel performance was obtained during the process. Thus, Ce is regarded as a significant catalyst with the capacity to break many bonds in lignin. Nickel (Ni) is a conventional hydrogenation catalyst with good performance in lignin depolymerization (Shuai and Saha 2017; Xu *et al.* 2017). In recent years, Ni-M bimetallic catalysts using Ni compounds with other metals or metallic oxide have shown improved performance during some reaction processes (Huang *et al.* 2017; Zhai *et al.* 2017). Moreover, Ni-M bimetallic catalysts are considered to be effective in lignin depolymerization reactions because they have the potential to solve the bottleneck problem during the process. An important issue in lignin depolymerization reaction is the instability of the products. During the depolymerization process, products such as monophenols and oligomers with active radicals can polymerize easily, which shows negative effects on the result (Shuai *et al.* 2016). Thus, the development of bifunctional catalysts might solve this issue. In this research, Ce was used to break bonds in lignin and depolymerize it into small molecular products while Ni was used to passivate radicals to prevent repolymerization reactions. Carbon nanotube (CNT) has been used as a promising catalyst support (Wu *et al.* 2013; Chen *et al.* 2015). It is considered as a good hydrogen storage material (Zhou *et al.* 2014; Ryu *et al.* 2015), which might also benefit the hydrogenation reaction. Therefore, in this research, Ce and Ni loaded on CNT was synthesized and used to depolymerize lignin to produce high monophenol and oligomer yields.

The final products from the depolymerization of lignin largely depend on the types of lignin due to their different structural features. There are primarily two different types of lignin: native lignin and industrial lignin. Native lignin is a type of lignin that exists in raw biomass without being extracted. The structure and bonds in the native lignin are not damaged. Industrial lignin is a type of lignin extracted from biomass under various harsh conditions, including kraft lignin, organosolv lignin, soda lignin, as well as lignosulfonate lignin (Xu and Ferdosian 2017). During the extraction process, weak ether bonds are broken and stable carbon-carbon bonds are formed, making the subsequent depolymerization process difficult (Van den Bosch *et al.* 2015). Therefore, the yield of monophenols from industrial lignin depolymerization is quite low.

In this study, the lignin-first depolymerization method was applied in native lignin depolymerization. Lignin-first is a concept raised by Parsell's group (Parsell *et al*. 2015) and widely studied by some research groups such as Van den Bosch's group (2015). In their research, raw biomass was used as substrate and the lignin part was depolymerized directly in methanol solution during the reaction. After the process, a high yield of monophenols was obtained while cellulose was preserved in solid residue. The lignin-first process was considered to be an effective method to depolymerize native lignin. Therefore, this method was employed in this research to depolymerize native lignin into monophenols. The acidulated biphase solutions, dioxane-water-1wt% HCl solution (DWHS) and dioxane-methanol-1wt% HCl solution (DMHS) were employed instead of pure methanol to increase the lignin removal rate. For the depolymerization of industrial lignin, the target products were oligomers due to the difficulty to get monophenols from industrial lignin. The depolymerization was conducted in DMHS directly. The yield of oligomers was calculated based on the extraction process. Ethyl acetate (EA) and petroleum ether (PE) were used as extraction liquors to extract oligomers after the depolymerization process. The PE was used to extract oligomers with low molecular weight and low oxygen content while the EA extracted oligomers with a higher molecular weight.

## EXPERIMENTAL

### Materials

Corn stover was used as the source of native lignin. It was gathered from the northern Anhui province of Mengcheng, China. The biomass was washed, oven-dried, and milled to pass through a 40-mesh screen according to previous work (An *et al.* 2017). The original composition of raw biomass was determined as follows: 31.6% glucan, 20.5% xylan, 22.8% lignin, and 25.1% other components (Li *et al.* 2016). The industrial lignin, Indulin AT$^{TM}$, was bought from MeadWestvaco (Grover, NC, USA), and the chemical characteristics of it have been reported by Hu *et al.* (2016). The CNT (TNSM3) was purchased from Chengdu Organic Chemicals Co., Ltd. (Chengdu, China). Cerium nitrate, nickel nitrate, and ruthenium chloride were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai China). Other chemical reagents used in the paper were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

*Catalyst preparation*

The CNT was purified according to a previous study by Ma *et al.* (2017) to improve its adsorption property for metal catalysts. The Ce/CNT was produced *via* the impregnation method. Then, 5 g of CNT was impregnated with 0.3 g of cerium nitrate ($Ce(NO_3)_3•6H_2O$)

in 20 mL deionized water, corresponding to a cerium loading of 1.5%. The mixture was magnetically stirred and was kept in a draught cupboard at room temperature until it was dry. Next, the dried mixture was calcined under the protection of nitrogen at 550 °C for 3 h. The obtained Ce/CNT catalyst was ground before the next step. The Ce/CNT was added into a $Ni(NO_3)_2$ solution with the 1.5 wt% mass fraction of metal Ni. Then, a certain amount of polyvinyl pyrrolidone (PVP) was added into the solution with magnetic stirring at room temperature to protect the reduction of metal cation during the $NaBH_4$ reduction reaction. The mass ratio of metal Ni to $NaBH_4$ was 1:10. After stirring under room temperature for a certain time, the mixture was washed with deionized water and oven-dried at 80 °C for 12 h. The Ni/CNT, Pd/Ce-CNT, and Ru/Ce-CNT were prepared using the same method.

*Corn stover lignin depolymerization*

First, 1.5 g of corn stover was added into a 50 mL mechanically stirred autoclave with 0.3 g of catalyst. Second, the mixed solution, 25 mL dioxane mixed with 5 mL deionized water or 25 mL dioxane mixed with 5 mL methanol was put into the reactor. Then, 0.7 mL concentrated HCl (36.5 wt%) was added to increase the solution acidity, resulting in 1 wt% HCl concentration in the mixture solution. Finally, the reactor was sealed and 2 MPa hydrogen pressure was added. The effect of the reaction temperature was investigated. After the reaction, the reactor was cooled down by circulating water. The solid residue was washed and oven-dried after filtration; then it was analyzed to measure the lignin content to calculate the yield of lignin removal during reaction. The liquid was detected by gas chromatography (GC) to quantify the monophenols content. The yield of monophenols and lignin removal were calculated as follows,

$$\text{Yield of monophenols (\%)} = W_M / W_L \times 100 \quad (1)$$

$$\text{Yield of lignin removal (\%)} = (W_L - W_R) / W_L \times 100 \quad (2)$$

where $W_M$ is the total weight of all monophenols (mg), $W_L$ is the weight of lignin in raw corn stover (mg), and $W_R$ is the weight of lignin in residue after reaction (mg).

*Industrial lignin depolymerization*

At first, 1 g of lignin was dissolved completely in a mixed solution containing 25 mL of dioxane and 5 mL of methanol with stirring. Then, the solution was placed into the reactor with 0.5 g of catalyst, together with 2 MPa hydrogen pressure. After the reaction, the mixture was filtrated and the solid fraction was washed, dried, and weighed. The liquid fraction was divided into three equal parts. One part was analyzed by GC to measure the monophenols yield, second part was extracted by EA, and third part was extracted by PE. After extraction, the extract liquor was evaporated by a rotary evaporator and then the extraction products (oligomers) were weighed. The yields of liquefied products, monophenols, and oligomers were calculated as follows,

$$\text{Yield of liquefied products (\%)} = (W_{LL} - W_{LR}) / W_{LL} \times 100 \quad (3)$$

$$\text{Yield of monophenols (\%)} = W_{LM} / W_{LL} \times 100 \quad (4)$$

$$\text{Yield of oligomers (\%)} = W_{LO} / W_{LL} \times 100 \quad (5)$$

where $W_{LL}$ is the weight of lignin (1000 mg), $W_{LR}$ is the weight of solid residue after reaction (mg), $W_{LM}$ is the total weight of all monophenols, and $W_{LO}$ is the total weight of all oligomers (mg) .

## Methods

The monophenols were detected by GC-2010 gas chromatography (Shimadzu, Tokyo, Japan) equipped with a flame ionization detector (FID) and a Wonda-CAP5 column (Shimadzu, Tokyo, Japan). The oven temperature was set at 50 °C for 3 min, increasing to 250 °C at a speed of 10 °C/min and then held for another 10 min. The yield of monophenols was calculated using acetophenone as internal standard.

The lignin content was calculated by laboratory analytical procedures (LAP) established by the National Renewable Energy Laboratory (NREL) (Sluiter *et al.* 2008a; Sluiter *et al.* 2008b). The detailed process was performed in accordance with the authors' previous research (Liu *et al.* 2016).

Wide angle X-ray diffraction (WAXD; Rigaku SmartLab, Tokyo, Japan) was used to measure the metal loading condition of catalysts. The substrates were scanned in a range of 5° to 70° using an X'pert diffractometer (Philips, Almelo, Holland).

X-ray photoelectron spectroscopy (XPS; Thermo-VG Scientific ESCALAB 250, New York, USA) was used to measure metals' valence in catalysts.

The porosity of catalysts was also investigated. Specific surface area (SSA) was measured by $N_2$ adsorption/desorption isotherms using the Brunauer-Emmett-Teller (BET) method on a Tristar 11 3020M instrument of Micromeritics (Norcross, USA). The total pores volume was calculated by single point adsorption with a relative pressure ($P/P_o$) at 0.973.

## RESULTS AND DISCUSSION

### Catalyst Characterization

X-ray diffraction was utilized to understand the catalyst structures.

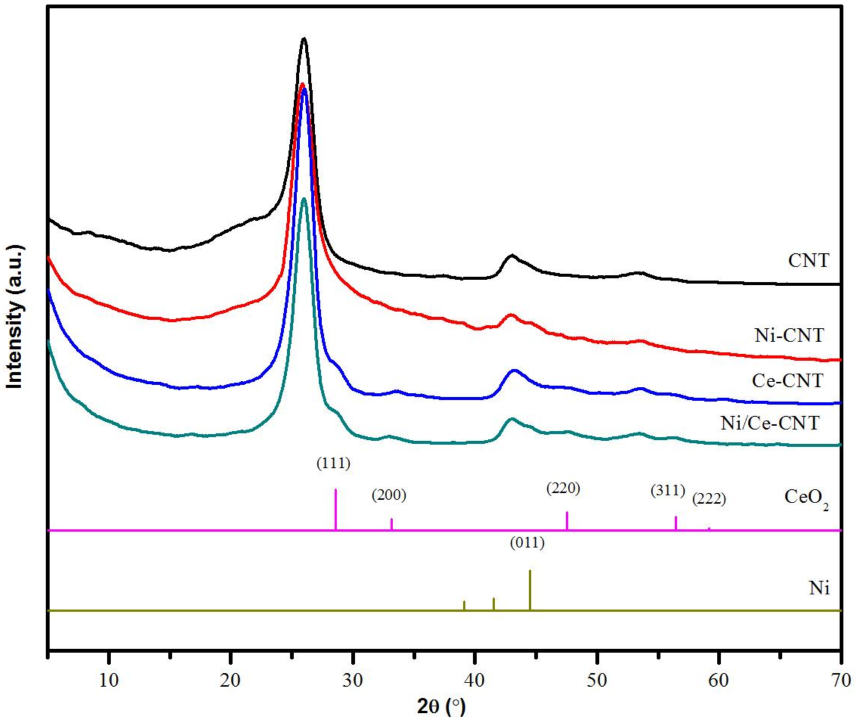

**Fig. 1.** XRD spectra of the CNT, Ni-CNT, Ce-CNT, and Ni/Ce-CNT

As shown in the XRD patterns in Fig. 1, the main peaks occurred at 26.0° and 43.0°, which corresponded to the CNT. Other diffraction peaks were relatively weak, which was ascribed to the low loading of the metal and metal oxide during catalysts synthesis (1.5 wt% Ce and Ni). It was clear that Ce-CNT and Ni/Ce-CNT presented a series of peaks at 28.6°, 33.1°, 47.6°, and 56.4°, in accordance with the (111), (200), (220), and (311) lattice planes of the cubic phase of $CeO_2$. However, characteristic peaks of metal Ce were not observed, indicating Ce exists in an oxidized form in the catalysts (Lawrence *et al.* 2011). Similarly, the characteristic peak at 44.5° from the (011) lattice plane of metal Ni was present in the catalysts of Ni-CNT and Ni/Ce-CNT, which indicated that Ni was a reducing metal in the catalysts.

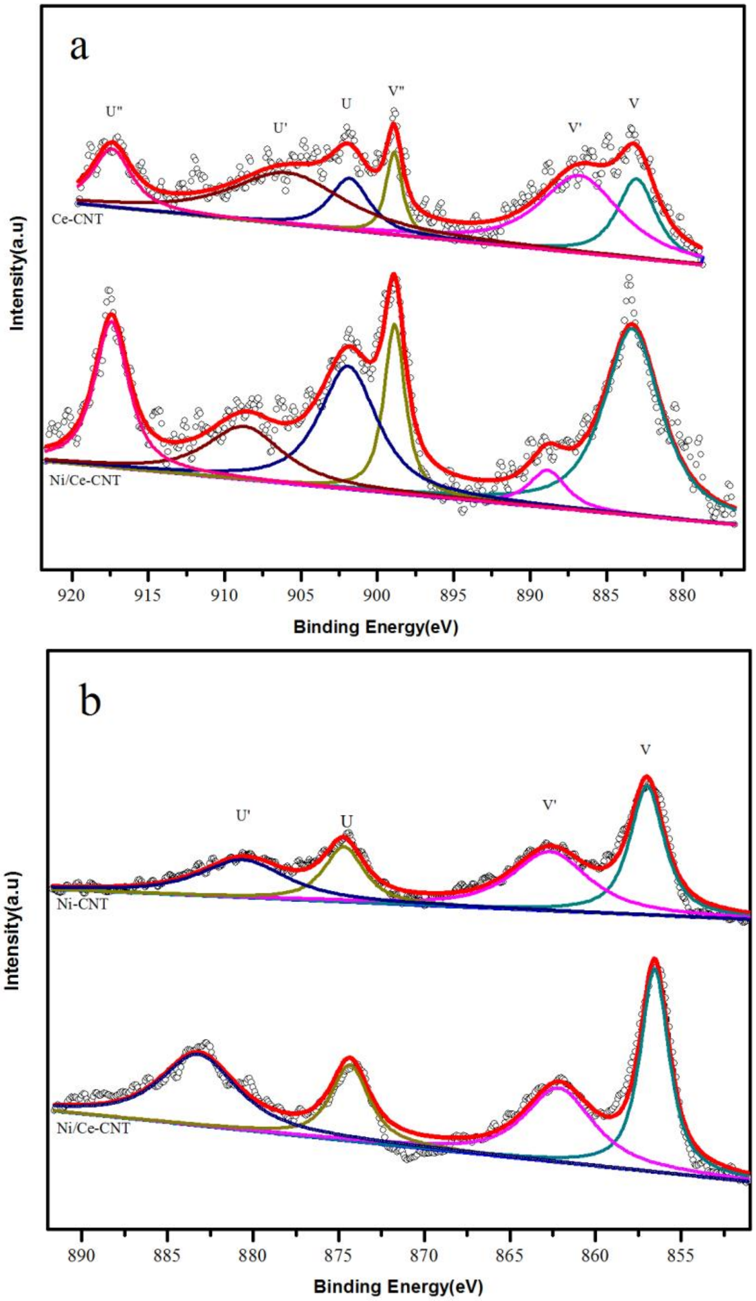

**Fig. 2.** XPS spectra of (a) Ce 3d for Ce-CNT and Ni/Ce-CNT and (b) Ni 2p for Ni/CNT and Ni/Ce-CNT

The catalysts were further analyzed by XPS to verify the oxidation states of the catalysts. On account of the charging effects during the analysis process, the binding energy scale was calibrated using adventitious carbon (284.6 eV) according to previous research (Li *et al.* 2011). The complex spectrum of Ce 3d was divided into six components and is shown in Fig. 2a. It is known that the Ce3d5/2 spectrum of Ce(IV) present peaks at the binding energies of 882.4 eV, 889.3 eV, and 897.7 eV (Zhang and Lin 2011), which are identical to the peaks of V, V', V" presented in Fig. 2a while U", U', and U are presented as peaks of Ce3d3/2. These results indicated that the cerium in Ce-CNT and Ni/Ce-CNT was present in Ce(IV) oxidation states, which was in agreement with the XRD observations. As shown in Fig. 2b, the peaks located at 856.3 eV and 874.5 eV are assigned to the binding energy of Ni 2p3/2 and Ni 2p1/2, respectively (Chen *et al.* 2012; Li *et al.* 2012). Those peaks reveal that the zero valent Ni is acquired after reduction from $Ni^{2+}$ (Li *et al.* 2012). The valence states of Ce and Ni measured by XPS was consistent with the result obtained by XRD.

The textural properties of the catalysts were analyzed using nitrogen adsorption/desorption isotherms. The specific surface area (SSA) and pore volume of CNT, Ni/CNT, Ce-CNT, and Ni/Ce-CNT were investigated, and the results are listed in Table S1. The SSA slightly decreased after the Ni or Ce catalyst was loaded on the CNT, from 156.4 $m^2/g$ to 144.6 $m^2/g$, 147.7 $m^2/g$, and 141.5 $m^2/g$ for Ni/CNT, Ce-CNT, and Ni/Ce-CNT, respectively. Similarly, the pore volume of catalysts experienced a parallel tendency. Pore volumes of catalysts decreased from initial 0.90 $cm^3/g$ to 0.83 $cm^3/g$, 0.86 $cm^3/g$, and 0.77 $cm^3/g$ with Ni/CNT, Ce-CNT, and Ni/Ce-CNT, respectively. These results indicated that loaded metals had a minor effect on the CNT structure. It was assumed that the remarkable hydrogen storage capacity of CNT was not damaged by the loading of metal catalysts.

## Catalytic Performance in Corn Stover Lignin Depolymerization

### *Effect of reducing conditions during catalyst preparation on catalyst performance*

Polyvinylpyrrolidone (PVP) is essential for the preparation of metal catalysts. It is a protector that stabilizes the reduced metal from polymerizing into large particles, resulting in a high dispersion of metal nanoparticles. During the catalyst preparation step, the amount of PVP dosage was optimized to a suitable level. When the PVP is insufficient, the aggregation of the metal catalyst will affect the catalytic performance of the lignin depolymerization. When the PVP is excessive, the reduced metal will be encompassed, which will also affect the catalytic performance. Therefore, different PVP amounts and reduction times during catalyst preparation were investigated to optimize their catalytic performance in the lignin depolymerization process. The results are listed in Table 1.

**Table 1.** The Effect of Reducing Condition on Catalyst's Preparation [a]

| Mole Ratio of PVP to Metal | Reducing Time (h) | Lignin Removal Yield (%) | Monophenols Yield (%) |
|---|---|---|---|
| 1:1 | 3 | 69.8 | 2.1 |
| 1:1 | 5 | 78.6 | 13.5 |
| 1:1 | 7 | 75.7 | 7.9 |
| 5:1 | 5 | 74.0 | 3.0 |
| 10:1 | 5 | 72.3 | 1.7 |

[a] Lignin depolymerization process condition: Ni/Ce-CNT, DWHS, 280 °C for 2 h under 2 MPa hydrogen pressure

The reaction results showed that when the mass ratio of PVP to reduced metal was 1:1, the highest lignin removal yield of 78.6% and monophenols yield of 13.5% were achieved when the catalyst was reduced for 5 h. The results suggested that an optimized reduction time was needed to prepare an efficient catalyst. It was found that when the amount of PVP increased, the lignin removal yield as well as monophenols yield decreased. This might have been because the superfluous PVP in the catalysts occupied the active sites. Therefore, the ratio 1:1 was regarded as the optimal reaction condition during catalyst preparation in the research.

### *Effect of different catalysts on lignin depolymerization*

To investigate the function of Ni and Ce in Ni/Ce-CNT during the lignin depolymerization, a series of catalysts were synthesized and performed for the lignin depolymerization reaction. The Ni-CNT, Pd/Ce-CNT, and Ru/Ce-CNT were synthesized using the same method as described earlier. The results are presented in Table 2.

**Table 2.** Effect of Different Catalysts on Lignin Depolymerization

| Catalyst | Lignin Removal Yield (%) | Primary Products Weight (mg) | | | | Monophenols Yield (%) |
|---|---|---|---|---|---|---|
| | | A | B | C | D | |
| Blank | 61.2 | -- | -- | -- | -- | -- |
| CNT | 60.1 | -- | -- | -- | 0.2 | 0.1 |
| Ce-CNT | 76.8 | 0.5 | 0.2 | -- | 0.3 | 0.3 |
| Ni/CNT | 78.5 | 2.5 | 1.7 | 6.5 | 3.8 | 4.9 |
| Ni/Ce-CNT | 78.6 | 3.6 | 5.1 | 11.2 | 4.5 | 13.5 |
| Ni/Ce-CNT [a] | 73.0 | 0.7 | 1.9 | 1.7 | 0.9 | 7.9 |
| Ni/Ce-CNT [b] | 63.9 | 26.5 | 7.8 | 13.0 | 10.1 | 21.4 |
| Pd/Ce-CNT | 79.1 | 0.3 | 0.6 | 0.7 | 0.8 | 1.0 |
| Ru/Ce-CNT | 78.1 | 3.8 | 8.1 | 11.9 | 9.4 | 13.4 |
| Ni/Ce-CNT [c] | 59.7 | 2.4 | 3.6 | 4.0 | 3.8 | 15.7 |

A: Guaiacol; B: 1-Ethyl-4-hydroxybenzene; C: 4-Propylphenol; D: Guaethol; Reaction condition if not specifically mentioned: DWHS, 280 °C, 2 h, 2 MPa hydrogen pressure; [a] 260 °C; [b] 300 °C; [c] DMHS

Table 2 indicates that Ce-CNT, Ni-CNT, and Ni/Ce-CNT all affected the lignin removal (approximately 78%) at 280 ℃. The control experiments without a catalyst or using CNT as a catalyst also had relatively high lignin removal (approximately 60%) but negligible monophenols yield. A much higher monophenols yield at 13.5% was achieved by Ni/Ce-CNT compared to Ce/CNT and Ni/CNT (0.3% and 4.9%, respectively). The results showed that Ce had the ability to remove lignin but did not affect the monophenols production. This is because Ce can break bonds in lignin effectively but the products repolymerize quickly due to the presence of active radicals. Ni has the function of catalytic hydrogenation, which can produce more stable products during the hydrogenation process with limited bonds-broken ability. When Ni/Ce-CNT was used as a bifunctional catalyst in the process, the synergistic effects between two metals promoted the monophenols production.

The effect of the reaction temperature on lignin depolymerization catalyzed by Ni/Ce-CNT was studied at 260 °C, 280 °C, and 300 °C in DWHS. The results demonstrated that temperature had critical effects on lignin removal and monophenols yield. Namely, when the temperature was increased from 260 °C to 300 °C, monophenols yield increased from 7.9% to 21.4%. However, coke formation also became more serious with increasing temperature, which resulted in decreased lignin removal yields.

The Ru/Ce-CNT and Pd/Ce-CNT were synthesized to formulate a comparison with Ni/Ce-CNT. The Ru/Ce-CNT yielded 13.4% monophenols during the process, which was similar to Ni/Ce-CNT. However, a small monophenols yield (1.0%) was achieved when Pd/Ce-CNT was employed. This could mean that Ru may also have a noticeable synergistic effect with Ce compared with Ni. Nevertheless, taking material cost into consideration, Ni is more attractive than Ru.

### *Effect of different reaction solutions on lignin depolymerization*

Solutions often have a vital effect on the reaction. In this paper, two different solutions, DWHS and DMHS, were investigated. The Ni/Ce-CNT was employed to depolymerize lignin at 260 °C for 2 h in the two solutions. The results demonstrated that a higher yield of monophenols was achieved in DMHS (15.7%) compared with DWHS (7.9%). This could be because methyl alcohol acts as a hydrogen source as well as hydrogen gas in reactor during the hydrogenolysis reaction (Van den Bosch *et al.* 2015). However, the lignin removal yield was lower (59.7%) in DMHS than DWHS (78.6%). Even the reaction without a catalyst could reach 61.2% in DWHS. Those results indicated that DWHS was effective at removing lignin while DMHS promoted the monophenols production. In addition, Table 2 shows that increasing the reaction temperature increased the lignin liquefied yield as well as monophenols outputs. Unfortunately, the pressure in the reactor with DMHS quickly increased to more than 5 MPa when the temperature went above 260 °C due to the supercritical state of methanol. The high pressure at high temperature poses severe requirements on equipment, which is dangerous as well as uneconomical. Thus, DWHS was considered to be a better solution during the reaction.

## Catalytic Performance in Industrial Lignin Depolymerization

Industrial lignin is difficult to depolymerize into monophenols due to the decreased content of ether bonds and increased amount of C-C bonds during the lignin extraction process (Van den Bosch *et al.* 2015). However, industrial lignin could be depolymerized into oligomers of good quality (Ma *et al.* 2017).

During the native lignin depolymerization process, DMHS had better performance at monophenols production but a poorer performance at lignin removal. Because industrial lignin is the part that has been separated from biomass, DMHS was employed in this process. Table 3 demonstrates that temperature had a remarkable effect on the depolymerization result. Taking the Ce-CNT catalytic reaction for instance, when the reaction temperature was increased from 260 °C to 300 °C, the petroleum ether extraction yield and the monophenols yield increased from 16.8% to 31.4% and 1.5% to 6.8%, respectively, while almost no change was found in the liquefied yield or ethyl acetate extraction yield, which indicated that high temperatures had a positive effect on the hydrodeoxygenation reaction. Increasing the temperature will produce smaller low-oxygen oligomers and monophenols that can be easily extracted by PE when catalysts Ni/Ce-CNT and Ru/Ce-CNT are utilized in the process. Although a higher monophenols yield (3.4% and 3.1%) was obtained using Ni/Ce-CNT and Ru/Ce-CNT, respectively, a distinct lower extraction yield was gained (56.0% and 50.5% by ethyl acetate and 11.6% and 8.1% by petroleum ether, respectively) compared with the Ce-CNT catalytic process at 260 °C. Therefore, it was thought that the addition of Ni or Ru increased the lignin depolymerization. Thus, more lignin was depolymerized into oligomers and monophenols.

However, Ni or Ru was unable to stabilize all unstable products and some oligomers and monophenols underwent a re-polymerization reaction. The monophenols protected by Ni or Ru were reserved and presented a higher monophenols yield compared with Ce-CNT. In addition, coke formation became more serious and a decrease in liquefied and oligomers yield was achieved when catalyzed by Ni/Ce-CNT and Ru/Ce-CNT.

**Table 3.** Effect of Different Catalysts on Lignin Depolymerization [a]

| Catalysts | Liquefied Yield (%) | Ethyl Acetate Extraction Yield (%) | Petroleum Ether Extraction Yield (%) | Monophenols Yield (%) |
|---|---|---|---|---|
| Ce-CNT | 75.9 | 66.3 | 16.8 | 1.5 |
| Ce-CNT [b] | 73.6 | 66.8 | 31.4 | 6.8 |
| Ni/Ce-CNT | 71.7 | 56.0 | 11.6 | 3.4 |
| Ru/Ce-CNT | 72.3 | 50.5 | 8.1 | 3.1 |

[a] 1 g Indulin AT, 0.5 g catalyst, 30 M DMHS, 260 °C, 1 h, 2 MPa hydrogen pressure
[b] 300 °C

## Catalyst Recycles

After being depolymerized with Ni/Ce-CNT, the solid residue was washed with deionized water for 2 h. Then, the residue was milled with mortar and pestle for 5 min before use. Next, the residue was used as a catalyst to do cycle experiments. The lignin removal and monophenols yield of native lignin during the four circulations in DWHS at 280 ℃ for 2 h are shown in Fig. 3a, while liquefied EA and PE extractions and monophenols yields of industrial lignin after being depolymerized with Ni/Ce-CNT in DMHS at 260 ℃ for 1 h are shown in Fig. 3b.

In Fig. 3a, the lignin removal yield did not obviously decrease during circulation, but the monophenols yield showed a slight drop from 13.5% to 10.2% after four-times circulation. This can be explained as follows: it was not the catalyst itself but the reaction solvent that was the dominant factor during native lignin depolymerization. The catalyst affected the monophenols production more than the lignin removal. After the reaction, the property of the catalyst slightly decreased, and there was a minimal decrease of the monophenols yield. In addition, research recently conducted by Van den Bosch *et al.* (2017) shows that the primary role of the catalyst in lignin-first depolymerization is not to depolymerize lignin, but to stabilize the monomeric products through hydrogenation (Gan *et al.* 2016), which is in agreement with the current results.

Industrial lignin depolymerization presented similar results to native lignin depolymerization. After circulation, the yield of liquefied lignin as well as EA extraction do not obviously decrease (from 71.7% to 69.4% and 56.0% to 55.5%). However, the yield of PE extraction and monophenols decreased a lot from 11.6% to 3.0% and 3.4% to zero, respectively. The results indicated that the hydrogenation ability of the catalyst decreased during circulation. However, because liquefied and ethyl acetate extraction did not decrease much, the depolymerization ability of the catalyst was still in good condition. The catalyst is of a high reactivity during lignin depolymerization.

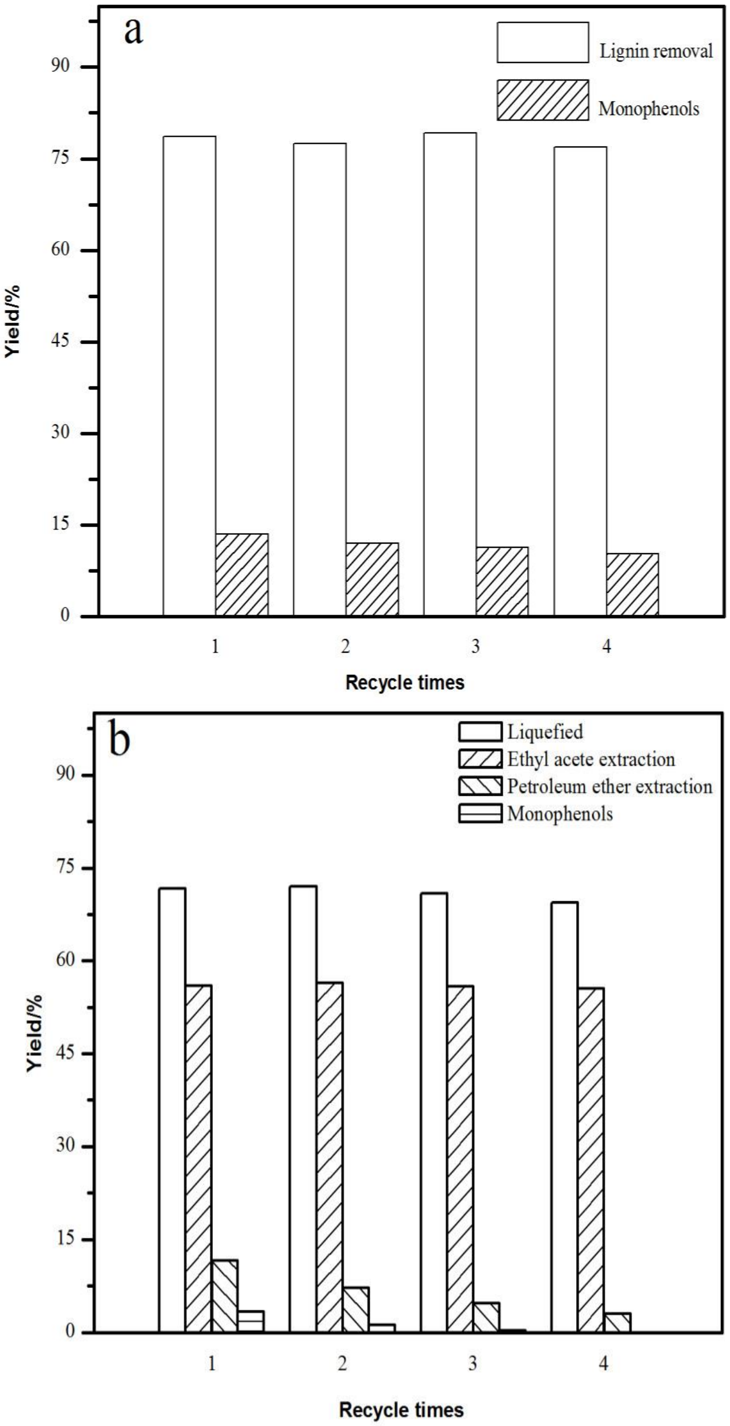

**Fig. 3.** Catalyst cycle experiment: (a) native lignin depolymerization: Ni/Ce-CNT, DWHS, 280 °C for 2 h under 2 MPa hydrogen pressure; (b) Ni/Ce-CNT, DMHS, 260 °C for 1 h under 2 MPa hydrogen pressure

The result showed that although the catalytic hydrogenation ability decreased upon recycle, the depolymerization function (attributed to the $CeO_2$) showed good stability. Therefore, Ni/Ce-CNT had good cyclicity in native lignin, as well as in the industrial lignin depolymerization process.

## CONCLUSIONS

1. A novel catalyst Ni/Ce-CNT was synthesized, and it improved the depolymerization effect on industrial lignin and native corn stover lignin.
2. Hydrogenation metal Ni presented synergistic effects with rare earth metal Ce during the process.
3. 21.4% monophenols yield was obtained at 300 °C for 2 h with native corn stover lignin. Industrial lignin was processed at 260 °C for 1 h. Following these treatments, 56.0% and 11.6% oligomers yield could be extracted by ethyl acetate and petroleum ether, respectively.
4. During the cycle experiment, the catalytic hydrogenation ability decreased while depolymerization function showed good stability.

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## APPENDIX

### Supporting Information

**Table S1.** Porosity of CNT, Ni/CNT, Ce-CNT and Ni/Ce-CNT

| | CNT | Ni/CNT | Ce-CNT | Ni/Ce-CNT |
|---|---|---|---|---|
| SSA ($m^2/g$) | 156.41 | 144.56 | 147.70 | 141.52 |
| Pore volume ($cm^3/g$) | 0.90 | 0.83 | 0.86 | 0.77 |