Efficient base-catalyzed decomposition and in situ hydrogenolysis process for lignin depolymerization and char elimination

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HIGHLIGHTS
- A promising process for lignin depolymerization and char elimination.
- Lignin decomposition and in situ oligomer hydrogenolysis responds to char reduction.
- The unsaturated oligomer was converted to more stable aliphatic alcohol.
- 92.5% conversion, 12.69% phenolic monomer and 6.12% aliphatic alcohol were achieved.
- Less than 14% solid was shown, which was far lower than the single catalyst system.

GRAPHICAL ABSTRACT
A novel and promising strategy for the efficient lignin depolymerization and char elimination was achieved via base-catalyzed decomposition of lignin and the in situ hydrogenolysis of phenolic oligomer.

ABSTRACT
Serious char formation caused by the repolymerization of unsaturated decomposition products is a considerable challenge for current lignin utilization. Here, a novel and efficient base-catalyzed depolymerization and in situ hydrogenolysis process for lignin decomposition and char elimination was proposed using the synergic catalyst of NaOH coordinated with Ru/C. In which, lignin was first depolymerized to phenolic monomer and its oligomer, and then the oligomer was further converted to more stable aliphatic alcohols simultaneously. The results showed that more than 92.5% of lignin was converted, giving 12.69% phenolic monomer, 6.12% aliphatic alcohol and less than 14.03% residual solid. This residual solid selectivity was far lower than it from the single catalyst condition. Furthermore, the products were analyzed using GC–MS, GPC, HPLC–MS and 1H NMR. The synergistic effect between depolymerization and hydrogenolysis was also investigated through comparative analysis of the feedstock, products, and the recovered lignin.

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1. Introduction

Lignin, a principal component of renewable biomass, consists of methoxylated phenylpropane structures and accounting for 15–30% of the weight and 40% of the energy of the lignocelluloses [1]. Therefore, lignin has been considered as a promising starting material for bulk aromatic chemicals and hydrocarbon (high quality biofuel) [2,3], considering on currently serious energy and resource crisis, CO₂ emission and air pollution. Unfortunately, this aromatic natural polymer is more recalcitrance than carbohydrate due to its complex structure and random chemical bonding. Most of it is combusted directly as a low value fuel, resulting in the significant deterioration of resource waste. Current technologies for this sustainable aromatic material include pyrolysis, liquefaction, hydrogenation and oxidation [4–8]. However, most of the reported processes suffer serious char formation, oligomer product repolymerization and relatively low phenolic monomers yield.

Compared with the acid catalyzed depolymerization, base-catalyzed process is insignificant carbon deposition [9–14]. For example, a series of alkali metal hydroxides such as KOH, CsOH and LiOH had proven to be efficient on the lignin depolymerization, but, it also exhibited more than 43% of ether insoluble char and tar [11]. Recently, Lavoie’s study [14] showed that 10% phenolic monomers and 60% oligomer could be obtained after the NaOH catalyzed depolymerization of the steam-treated lignin at 300–330 °C, however, more than 30% of char was generated. More recently, we found that organosolv pine lignin can be efficiently depolymerized in the presence of solid alkali MgO and THF as well. More than 32.2% yield of phenolic monomer was obtained due to the excellent lignin dissolution capability and the catalyst promotion effect [15]. However, the repolymerization of oligomer resulting in residual solid producing cannot also be neglected. Furthermore, it was reported that the producing of char and tar during lignin depolymerization process is caused by the repolymerization and condensation of oligomer followed by dehydration on the catalytic activity center with the thermal effect [16,17]. This repolymerization product has a significantly tighter internal structure and chemical bonding than original lignin, and is more difficult to be degraded.

Generally, aliphatic alcohol is more stable than phenolic compound due to its saturated structure. Therefore, the exploitation of novel and efficient strategy for the hydrogenolysis of phenolic oligomer to more inert aliphatic alcohol would be a promising approach for the comprehensive utilization of lignin with reduced char formation. Here, we construct an efficient, novel and integrated catalytic system for lignin depolymerization and char elimination at mild condition, in which, the ether bond, such as β-O-4 and C−OH, was first degraded giving phenolic monomer and unstable oligomer. This oligomer can be converted to more stable chemicals such as aliphatic alcohol in the self H-donating reagent CH₂OH with the hydrogenation catalyst Ru/C, reducing the char formation by the elimination of the unsaturated intermediate. Furthermore, the in situ hydrogenolysis process can also promote the depolymerization balance through the product consumption, resulting in high lignin conversion and phenolic monomer yield at mild condition.

2. Materials and methods

2.1. Materials

5 wt% Ru/C and 5 wt% Pd/C were purchased from Aladdin (Shanghai, China) and were used as received. THF and CH₂CN (high performance liquid chromatography (HPLC) grade) were provided by Acros (Belgium). NaOH, KOH, Na₂CO₃ and HCl were analytical grade. The organosolv South China pine lignin was isolated according to the reported procedure [18], Fourier Transform Infrared spectroscopy (FT-IR) and Nuclear Magnetic Resonance (¹H NMR, ¹³C NMR) results showed no obvious absorbance of the carbohydrate. There was also not any sugar be detected by HPLC analysis from the dilute acid hydrolysis. Therefore, the purity of the lignin was more than 97%.

2.2. Depolymerization and in situ hydrogenolysis of lignin

The depolymerization and in situ hydrogenolysis of lignin was conducted in a 100 mL stainless batch autoclave reactor (316L stainless, Weihai Chemical Machinery Co., Ltd.). In a typical process, 1.0 g lignin, 0.030 mol NaOH and 0.20 g Ru/C were added into the autoclave along with 40 mL anhydrous methanol as solvent. The reactor was purged with H₂ for three times and pressurized to 4.0 MPa. After that, it was heated to 260 °C for 4 h under the stirring of 800 rpm. When the reaction was finished, the autoclave was cooled to room temperature using electron fan.

2.3. Production separation

The gaseous fraction was collected in a 200 mL reservoir bag. The product mixture was filtered, and the solid fractions (include catalyst and residue) were first washed three times with 30 mL CH₃OH (10 mL × 3). Then, it was dried at 100 °C until constant weight. The filtrate was neutralized with 1.0 mol L⁻¹ HCl, then, 200 mL deionized water was poured to precipitate the undegraded and/or partly degraded lignin. Recovered lignin was obtained by the removal of solvent and freeze-drying overnight under vacuum. The phenolic monomers were extracted using CH₃Cl₂. The used catalyst (included in the residual solid fraction) was first neutralized by 1.0 mol L⁻¹ HCl, and then it was washed by deionized water for three times until no Cl⁻ was detected. After careful freeze-drying overnight under vacuum, the recycled Ru/C was used for the next run.

2.4. Analysis and measurement of the products

Detail product analysis could be found in the supplementary data. The quality and quantitative analysis of the gaseous fraction were carried on an Agilent 7890 GC with both thermal conductivity detector (TCD) and flame ionization detector (FID). The gas chromatography mass spectrometer (GC–MS) analysis of the volatile products was conducted on an Agilent 7890 GC with an Agilent 5975 inert mass-selective detector and was identified according to the NIST MS library. The quantitative analysis of these chemicals was carried out on an Agilent 7890 GC with a FID using acetophenone as internal standard at the same capillary column and temperature program as the GC–MS analysis. The FT-IR spectrum of water soluble fraction was obtained on a Nicolet is50 FT-IR spectrometer by KrBr pelleting method. ¹H NMR experiment was performed on a Bruker Advance 400 III spectrometer, where D₂O was used as solvent. And the HPLC–MS analysis was carried out on a Quadrupole-time of flight Liquid Chromatography–Mass Spectrometry (LC–MS, Agilent, USA) equipped with HiPac Sampler, Binary Pump and triple-quadrupole Mass Spectrometer (TOF/Q-TOF). The FT-IR analysis of the residual solid was conducted on a Nicolet is50 FT-IR spectrometer using KrBr pelleting method.

The conversion of lignin was measured by the weight comparison between the recovered and the original lignin as shown in Eq. (1). The yield of aliphatic alcohol and phenolic monomer were measured according to the following Eqs. (2) and (3) respectively based on the GC results. The yield of residual solid was obtained by Eq. (4). According to above separation procedure, the products were separated into gas (less than 1% weight of lignin for each
run, so it is neglectable), aliphatic alcohol, water soluble fraction, and residual solid. Therefore, the yield of water soluble fraction was calculated by the weight subtraction method (Eq. (5)). Three parallel experiments were conducted to reduce the relative error, and the reported data in this study were the average.

\[
C_l = \frac{(W_f - W_{RL})}{W_f} \times 100\% 
\]

(1)

\[
Y_A = \sum_{i=1}^{j} \left[ \frac{W_{Ai}/W_f}{} \right] \times 100\%
\]

(2)

\[
Y_P = \sum_{i=1}^{j} \left[ \frac{W_{Pi}/W_f}{} \right] \times 100\%
\]

(3)

\[
Y_R = \frac{W_{RS}/W_f}{} \times 100\%
\]

(4)

\[
Y_W = (C_l - Y_A - Y_P - Y_R) \times 100\%
\]

(5)

\[C_l: \text{ conversion of lignin}; \ Y_A: \text{ yield of aliphatic alcohol}; \ Y_P: \text{ yield of phenolic monomer}; \ Y_R: \text{ yield of residual solid}; \ Y_W: \text{ yield of water soluble fraction}; \ W_f: \text{ the weight of feed lignin}; \ W_{RL}: \text{ the weight of recovered lignin}; \ W_A: \text{ the weight of aliphatic alcohol}; \ W_P: \text{ the weight of phenolic monomer}; \ W_{RS}: \text{ the weight of residual solid}.
\]

2.5. Characterization of raw and recovered lignin

The molecular weights of raw and recovered lignin were determined by gel permeation chromatography (GPC) (Agilent 1260 HPLC) with a differential refraction detector (RID). The average molecular weight of the sample was measured according to the external standard method with narrow polystyrene as the standard compound. The measurement of main elements of raw and recovered lignin was carried out on a vario EL III element analyzer. Scanning electron microscope (SEM) images and FT-IR spectra were obtained on a Hitachi S-4800 instrument and on a Nicolet is50 FT-IR spectrometer respectively. 13C CP/MAS NMR was conducted on a Bruker AVANCE III 300 WB spectrometer (7.05 T). The pyrolysis gas chromatography mass spectrometer (Py-GC–MS) analysis was conducted on a Pyroprobe 5200 High Pressure Reactor directly connected with an Agilent 7890 GC/Agilent 5975 inert mass-selective detector. Detail characterization methods could be seen in the supplementary data.

2.6. Characterization of the fresh and used Ru/C

The Ru leaching of the catalyst in the CH2OH was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, OPTIMA 8000) and X-ray fluorescence (XRF, PANalytical Axios). The comparative characterization of the fresh and used Ru/C were conducted by X-ray diffraction radiation (XRD, X Pert Pro MPD with Cu Kα (λ = 0.154) radiation, Philip, the scanning angle (2θ) ranged from 5° to 80°), SEM (Hitach S-4800 instrument at 10 kV), transmission electron microscope (TEM, Tecnai G2F20S-TWIN) and X-ray photoelectron spectroscopy (XPS, Thermo ESCA-LAB 250Xi).

3. Results and discussion

3.1. Depolymerization and in situ hydrogenolysis of lignin

Table 1 showed the depolymerization and in situ hydrogenolysis of pine lignin with various catalysts. As seen from Table 1, about 45.7% lignin was converted with the single thermal effect. However, no more than 2.12% yield of phenolic monomer without any aliphatic alcohol was achieved, whereas 26.6% of it was converted to the residual solid (Table 1, entry 1). With the addition of alkali catalyst, both the conversion of lignin and the yield of phenolic monomers were significantly increased. It was reported that the ether bond of lignin could be efficiently broken with the base catalyst, resulting in more complete depolymerization of the lignin [14,15]. Therefore, this efficient promotion of the lignin depolymerization by NaOH was considered to be responsible for the increase of the degree of the lignin liquefaction and the phenolic monomer yield, and the decrease of the residual solid selectivity. This lignin can also be hydrogenolyzed by Ru/C, where 76.6% degree of depolymerization and 6.05% yield of phenolic monomer were obtained (Table 1 entry 3). Noticeably, 1.58% aliphatic alcohol was detected, which had not been detected during both base catalyzed and thermal depolymerization (Table 1, entry 1 and 2). The abovementioned catalytic processes were efficient for phenolic monomer producing. However, the selectivity of solid product was high. Furthermore, most of the aromatic product is easier to repolymerize [15]. When this process was conducted under the catalysis of NaOH coordinated with Ru/C, significant decrease on the solid and increase on aliphatic alcohol and phenolic monomer were shown (Table 1, entry 4). The base-catalyzed depolymerization and the simultaneous hydrogenolysis of lignin are responsible for it. Certainly, the fact that NaOH prevented the hydrogenation of lignin aromatic ring, and indirectly promoted the lignin depolymerization [19] was also contributed to the highest phenolic monomer yield with the synergic catalyst of NaOH and Ru/C.

The simultaneously catalytic depolymerization and in situ hydrogenolysis of lignin was also tested with 5 wt% Ru/C coordinated with other commercial alkalis, such as KOH and Na2CO3 respectively (Table 1, entry 5 and 6). The results showed that the base strength has a significant effect on both the lignin conversion and the product distribution. For example, 91.4% lignin was converted with the stronger alkali KOH, leaving 12.19% residual solid (Table 1, entry 5). However, it was sharply decreased to 85.3% with 27.44% of the undesired solid in the presence of Na2CO3 (Table 1, entry 6). The fact that the weaker base strength of Na2CO3 results in the insufficient decomposition of lignin is responsible for it. Table 1 also demonstrated that the hydrogenation activity of the Ru/C is influenced by the basicity. Higher base results in high Ru/C activity. For instance, 3.28% of the aliphatic alcohol was shown with Na2CO3, whereas 6.12 and 7.32 of it could be achieved with NaOH and KOH respectively. Pd/C is another powerful catalyst for lignin depolymerization and the depolymerization product hydrodeoxygenation (HDO) [20–22]. It had shown better catalytic activity than Ru/C in the lignin degradation products hydrogenation [20]. However, this phenomenon was insignificant during the lignin base-catalyzed depolymerization and in situ hydrogenolysis process, in which, almost the same level of conversion and product yields were exhibited (Table 1, entry 4, 7). It indicated that the original lignin and the phenolic oligomer rather than volatile monomer is converted in the presence of hydrogenation catalyst, which also accords well with the reported lignin liquefaction process [23].

Fig. 1 showed that this lignin base catalyzed depolymerization and in situ hydrogenolysis process is high temperature dependence. Both the lignin conversion and the product distribution were significantly influenced by the reaction temperature. For instance, the conversion of lignin was gradually increased with the elevating temperature, and 100% of it was converted at 300 °C (Fig. 1a). Simultaneously, the change of product distribution was various. For example, the aliphatic alcohol and phenolic monomer had a significant increase with the decline of solid fraction when the temperature was lower than 260 °C, and the opposite tendency was demonstrated at the elevated temperature. It is considered that there were at least two processes during lignin degra-
dation: base-catalyzed depolymerization and hydrogenolysis. The former was catalyzed by NaOH resulting in phenolic monomer and oligomer. And the oligomer and the raw feedstock could be further catalytic hydrogenated to give aliphatic alcohol (the later process). Nevertheless, the oligomer containing unsaturated chemical bond could also polymerize each other to give residual solid. And thus, the intense competition between hydrogenolysis and repolymerization was existed. At lower temperature (220°C), the hydrogenolysis is insignificant, therefore, lower aliphatic alcohol and higher residual solid were obtained. However, both the depolymerization and the repolymerization become much faster at higher temperature (for example, 280 and 300°C, Fig. 1). And further dehydration and carbonization of repolymerization products occurred on the metal catalyst surface, resulting in the deactivation of Ru/C (as detected by SEM, Fig. S1). Therefore, only 1.89% aliphatic alcohol and 7.81% phenolic monomer were achieved, though 100% lignin conversion was shown at 300°C. Compared with the influence of reaction temperature, it of time is insignificant (Fig. 1b). The increase of the residual solid fraction at prolonged time is attributed to the repolymerization and carbonization of lignin and oligomer.

Fig. 2 showed the influences of the catalyst dosages. With the increasing of NaOH dosage, lignin depolymerization was easier to occur with higher conversion, higher volatile products yield and less residual solid formation when it was less than 0.03 mol (Fig. 2a). However, NaOH catalyzes not only lignin depolymerization, but also the repolymerization of its part decomposition fraction (phenolic oligomer) [1]. Therefore, the conversion of lignin

![Table 1](image)

**Table 1**

Base catalyzed depolymerization and in situ hydrogenolysis of lignin.a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Weight yield (%)</th>
<th>Aliphatic alcohol</th>
<th>Phenolic monomer</th>
<th>Water soluble</th>
<th>Residual solid</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>45.7</td>
<td>2.12</td>
<td>16.66</td>
<td>26.92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.030 mol NaOH</td>
<td>90.8</td>
<td>7.56</td>
<td>49.19</td>
<td>34.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.20 g Ru/C</td>
<td>76.6</td>
<td>1.58</td>
<td>6.05</td>
<td>26.91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.030 mol NaOH/0.20 g Ru/C</td>
<td>92.5</td>
<td>6.12</td>
<td>12.69</td>
<td>59.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.030 mol KOH/0.20 g Ru/C</td>
<td>91.4</td>
<td>7.32</td>
<td>12.53</td>
<td>59.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.015 mol Na2CO3/0.20 g Ru/C</td>
<td>85.3</td>
<td>3.28</td>
<td>8.65</td>
<td>45.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.030 mol NaOH/0.20 g Pd/C</td>
<td>93.6</td>
<td>6.24</td>
<td>12.36</td>
<td>60.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.030 mol NaOH/0.20 g Ru/C</td>
<td>91.2</td>
<td>3.12</td>
<td>8.39</td>
<td>52.56</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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*Conditions: lignin: 1.0 g; solvent: CH3OH; H2: 4 MPa; temperature: 260 °C; time: 4 h.

a The conversion was determined via the weight comparison of initial and recovered lignin.

b The yields of aliphatic alcohol and phenolic monomer were measured by internal standard method using acetophenone as standard compound; and the yield of residual solid was determined by the weight comparison of it and the initial lignin.

d Ru/C was used for 3 runs.
was slightly decreased with the increase of residual solid and decrease of volatile products (including aliphatic alcohol and phenolic monomers) when the NaOH dosage increased to 0.060 mol (Fig. 2a). It is also good accordance with the recent reported work [19], where a significant decrease of the lignin model compound conversion and product yield were shown when the pH value of the solvent was increased from 13 to 14.

On the contrary, the effect of Ru/C dosage is insignificant on both the lignin conversion and residual solid yield (Fig. 2b). But, the selectivity of aliphatic alcohol was increased significantly when it was increased from 0.1 g to 0.2 g, because the hydrogenation process is accelerated at a large catalyst dosage (Fig. 2b).

CH3OH is an excellent H2 donating solvent for lignin depolymerization and has good dissolved capability for organosolv lignin. Therefore, the highest lignin conversion and volatile products yield were shown with the least residual solid yield (Table S1). The lower lignin liquefaction and volatile product yield in H2O and the apolar solvent naphthene can be attributed to the poor dissolved capability of the solvent for lignin, resulting in the insufficient contact of between the feedstock and catalyst.

Under the optimized condition, the recyclability of the Ru/C catalyst was further investigated. The result listed in Table 1, entry 8 showed that both the yield of aliphatic alcohol (3.12%) and the phenolic monomer (8.39%) were decreased after 3 runs. However, the yield of residual solid was increased to 27.13%. ICP-AES and XRF analysis on the CH3OH solvent after lignin hydrogenation showed no Ru leaching. XRD and XPS analyses (Figs. S2 and S3) also demonstrated that there were no obvious changes on the species and the surface valent state of the Ru metal. TEM images (Fig. S4) showed no obvious increase of the particle size as well. However, the SEM (Fig. S5) and TEM (Fig. S4) analyses showed an obvious carbon deposition coated on the Ru surface, due to the repolymerization of the phenolic oligomer (determined by FT-IR (Fig. S6)). It is good agreement with our previous study that repolymerization of phenolic oligomer was occurred on the catalyst surface [15]. Therefore, the product from the repolymerization of the phenolic oligomer on the surface is considered to be responsible for the catalytic activity declination of the Ru/C.

3.2. Analysis of the volatile products

Gaseous product generated from this process was determined by GC-TCD-FID. Interestingly, it was mainly composed of C1 to C6 saturated alkane, where almost the same level of CH4 and C2H2 was exhibited (Fig. S7). CO2, CO and unsaturated chemicals, the most common gaseous products from lignin depolymerization [15], had not been detected. The excellent hydrogenation capability of Ru/C is responsible for it. However, the total weight of the gaseous fraction collected each run was less than 1% of the feed lignin. Therefore, we considered that the gaseous products in this process are negligible, and had not taken it into account in the material balance.

GC–MS analysis of the volatile products demonstrated that the main components from various catalysts were significantly different (Tables 2 and S1–S3). In the absence of a catalyst, the identified volatile product was scarce on both the species and the contents. When NaOH or Ru/C was added, the decomposition was occurred more thoroughly, resulting in not only higher content guaiacol and syringol, but also their derivatives. In particular, a few of aliphatic alcohols such as 3-pentanol, 2-methyl propanol were detected with 5 wt% Ru/C. However, under the synergistic effect of base catalyzed depolymerization and hydrogenolysis, lignin was more prone to convert, generating phenolic monomer and aliphatic alcohol as listed in Table 2. Furthermore, 2-ethyl toluene and 1,2,3-trimethyl-benzene, which generally come from the hydrogenation of the C–O bond of phenolic monomer, were also detected. However, cyclohexane and its derivatives, which originated from the further hydrogenation of benzene ring [24], had not been observed, indicating that Ru/C is perfect for C–O bond breakage rather than C=C addition. Moreover, GC–MS results also displayed that the distribution of phenolic monomers was different significantly in the presence of various catalysts. As seen from Table S3, the phenolic monomer was mainly consisted of guaiacol and syringol from the NaOH catalytic process. However, when 5 wt% Ru/C was added, phenol and alkyl substituted phenol were found to be the most abundant (Table 2). It further confirmed that the C–O bond of lignin monomer is readily to be broken under the synergic catalysis of NaOH and Ru/C. Table 2 also exhibited that a lot of methyl phenols were detected, indicating the efficient methyl group transfer. These methyl phenols contain aromatic functional group and 6–12 carbon atoms, and advantage lower oxygen content and higher heat value than the lignocellulosic biomass. Therefore, they can be a potential feedstock for the sustainable aromatic fine chemicals and bio-jet fuel.

3.3. Chemical structure of nonvolatile products

The main functional group and chemical structure of water soluble nonvolatile fraction from the lignin base-catalyzed depolymerization coordinated with in situ hydrogenolysis process were intensively analyzed using FT-IR, 1H NMR and HPLC–MS. As shown in Fig. S8, the characteristic infrared absorbance of the phenolic hydroxy group (3424 and 1237 cm−1), benzene ring (1614, 1462, 928, 883, 773 and 701 cm−1) can be found clearly [18]. The strong absorbencies at 2965, 2935, 2868 and 2833 cm−1 suggested the existence of −OCH3 and −CH3. 1776 cm−1 was regarded as the characteristic stretching vibration of the carbonyl group. The peak at 2718 cm−1 could be attributed to the existence of aldehyde [25]. Therefore, the FT-IR spectrum indicated that the water soluble fraction is also phenolics, which contained characteristic functional group of lignin (for example, phenolic hydroxy and methoxy) and unsaturated bond (such as aldehyde) derived from the depolymerization of lignin molecule.

1H NMR spectrum was recorded with D2O as solvent, and was annotated with peak assignments based on the previous publication (Table S5) [26]. As shown in Fig. S9, the chemical shift at 0.79−1.22 was ascribed to the aliphatic alicyclic on the side chain of lignin. The strong absorbance of the single peak at 1.81 ppm indicated that the existence of large amounts of CH3 directly attached to the benzene ring. It is good agreement with the above GC–MS analysis results, where many multiple methyl substituted benzenes were detected (Table 2). Namely, it further confirmed the conclusion of the existence of methyl transfer during the synergic catalysis process. The chemical shifts at 2.08 and 2.29 could also be designated as the characteristic absorption of alkyl group on the aromatic ring. The appearance of the single chemical shift signal at 2.58 ppm indicated the aliphatic H connected on the phenylcoumarane substructure. The strong single peak with chemical shift of 3.56 ppm suggested the abundant −O−C−OH unit in the phenylcoumarane substructure. The strong single peak with chemical shift of 3.05 ppm was assigned to H3 in the phenylcoumarane substructure. The absorption at 3.83 ppm was also displayed because of the existence of methoxyl group. The signal at 4.05 ppm was identified as H6 in p-hydroxyxcinnamyl alcohol end group. And the signals with chemical shift of 8.11–8.59 ppm confirmed the existence of aromatic ring. Summarily, the 1H NMR spectrum demonstrated clearly that the nonvolatile products are composed of aromatic chemicals with the characteristic structure of lignin. The appearance of H5 and H6 indicated that the hydroxy-phenyl structural unit of lignin is much more flexible to be degraded [27].

HPLC–MS analysis (Fig. S10) demonstrated that the water soluble products had a molecular weight ranged from 115 to
525 g mol\(^{-1}\). GPC results also demonstrated that its weight-average molecular weight was 382 g mol\(^{-1}\) (Table 3). The qualified results through the comparative analysis with the library demonstrated that this fraction contained 9–22 carbon atoms in the molecule. Therefore, the FT-IR, \(^1\)H NMR and HPLC–MS results clearly indicated that the water soluble fraction is phenolic dimer and trimer originated from the incomplete decomposition of lignin and the repolymerization of unsaturated monomer.

FT-IR spectrum of the residual solid (Fig. S7) showed an obvious lignin characterization infrared absorption. The strong absorption at 3411 cm\(^{-1}\) is assigned as the stretching of phenolic OH. The peaks at 2965, 2914 and 2863 cm\(^{-1}\) are attributed to the stretching vibration of OCH\(_3\), CH\(_3\) and CH\(_2\) respectively. Benzene ring and the Ar—O, which showed infrared absorptions at 1629, 1574, 1442, 1341, 1082, 1041, and 839 cm\(^{-1}\) could also be observed clearly. Furthermore, the FT-IR spectrum of this fraction showed a similar profile as it of the water soluble products (Fig. S8). Therefore, we think that the residual solid coated on the surface of the Ru/C was mainly consisted of the repolymerization products from phenolic oligomer. This part overburden can also be detected by the SEM analysis, where a more hardened surface was shown after the reaction (Fig. S5). It is also a main cause for the decrease of the hydrogenation activity of the Ru/C (Table 1, entry 8).

Table 2
GC–MS analysis of volatile products of the synergic catalysis process.\(^{a}\)

<table>
<thead>
<tr>
<th>RT (min)</th>
<th>Compound</th>
<th>Structure</th>
<th>Content (%)</th>
<th>RT (min)</th>
<th>Compound</th>
<th>Structure</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.14</td>
<td>2-Hexanone, 4-methyl-</td>
<td><img src="image1" alt="Structure" /></td>
<td>0.38</td>
<td>13.44</td>
<td>Phenol, 4-methoxy-3-methyl-</td>
<td><img src="image2" alt="Structure" /></td>
<td>0.51</td>
</tr>
<tr>
<td>3.48</td>
<td>Pentanoic acid, methyl ester</td>
<td><img src="image3" alt="Structure" /></td>
<td>1.86</td>
<td>13.48</td>
<td>Benzyl alcohol</td>
<td><img src="image4" alt="Structure" /></td>
<td>2.74</td>
</tr>
<tr>
<td>3.62</td>
<td>1-Propanol, 2-methyl-</td>
<td><img src="image5" alt="Structure" /></td>
<td>8.63</td>
<td>13.84</td>
<td>Phenol, 2,6-dimethyl-</td>
<td><img src="image6" alt="Structure" /></td>
<td>3.25</td>
</tr>
<tr>
<td>4.07</td>
<td>Butanoic acid, 2- methyl-, methyl ester</td>
<td><img src="image7" alt="Structure" /></td>
<td>1.42</td>
<td>14.33</td>
<td>Phenol, 2-methoxy-4-methyl-</td>
<td><img src="image8" alt="Structure" /></td>
<td>0.85</td>
</tr>
<tr>
<td>4.22</td>
<td>1-Butanol</td>
<td><img src="image9" alt="Structure" /></td>
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<td>14.43</td>
<td>Benzaldehyde, 2-hydroxyl-5-methoxy-</td>
<td><img src="image10" alt="Structure" /></td>
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<tr>
<td>4.47</td>
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<td><img src="image11" alt="Structure" /></td>
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<td>14.76</td>
<td>Phenol, 2,4,6-trimethyl-</td>
<td><img src="image12" alt="Structure" /></td>
<td>1.98</td>
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<tr>
<td>4.77</td>
<td>Hexanoic acid, methyl ester</td>
<td><img src="image13" alt="Structure" /></td>
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<td>14.79</td>
<td>Phenol, 2-methyl-</td>
<td><img src="image14" alt="Structure" /></td>
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<td><img src="image15" alt="Structure" /></td>
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<td>14.84</td>
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<td><img src="image16" alt="Structure" /></td>
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<td>15.07</td>
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<td>15.20</td>
<td>Phenol, 2,4,6-trimethyl-</td>
<td><img src="image20" alt="Structure" /></td>
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<td><img src="image21" alt="Structure" /></td>
<td>2.25</td>
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<td><img src="image22" alt="Structure" /></td>
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<tr>
<td>6.32</td>
<td>1-Pentanol, 2-methyl-</td>
<td><img src="image23" alt="Structure" /></td>
<td>2.21</td>
<td>15.55</td>
<td>Phenol, 3,5-dimethyl-</td>
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<td>15.83</td>
<td>Phenol, 2-methoxy-4-propyl-</td>
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<td>4-methoxybutan-2-ol</td>
<td><img src="image27" alt="Structure" /></td>
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<td>16.22</td>
<td>Phenol, 5-methoxy-2,3,4-trimethyl-</td>
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</tr>
<tr>
<td>6.98</td>
<td>Hexane, 3,4-dimethyl-</td>
<td><img src="image29" alt="Structure" /></td>
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<td>16.45</td>
<td>Phenol, 3,4-dimethyl-</td>
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<td>1-Hexanol</td>
<td><img src="image31" alt="Structure" /></td>
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<td>16.55</td>
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<td><img src="image34" alt="Structure" /></td>
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<td>Phenol, 3,4,5-trimethyl-</td>
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<tr>
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<td>16.90</td>
<td>Phenol, 2,3,5-trimethyl-</td>
<td><img src="image38" alt="Structure" /></td>
<td>1.84</td>
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<tr>
<td>12.04</td>
<td>2-ethoxy-5-methoxy-4-methylphenol</td>
<td><img src="image39" alt="Structure" /></td>
<td>1.91</td>
<td>18.60</td>
<td>Phenol, 2-(1,1-dimethyl ethyl)-6-methyl-</td>
<td><img src="image40" alt="Structure" /></td>
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<td>3,4-Dimethoxytoluene</td>
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<td>18.72</td>
<td>Phenol, 2-methyl-5-(1-methylethyl)-</td>
<td><img src="image42" alt="Structure" /></td>
<td>0.86</td>
</tr>
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<td>13.34</td>
<td>Phenol, 2-methoxy-</td>
<td><img src="image43" alt="Structure" /></td>
<td>0.87</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) Conditions: capillary column: HP-INNOWAX, 30 m × 0.25 mm × 0.25 μm; programmed oven temperature: 60 °C, hold 2 min at 60 °C and then ramped up with 10 °C min\(^{-1}\) to 260 °C and hold for another 10 min; injector: kept at 280 °C in split mode with a split ratio of 5:1; 99.999% helium as the carrier gas.

\(^{b}\) Determined by GC-FID.
and lignin molecule was hydrogenated by Ru/C. Table 4 also demonstrated the highest carbon and hydrogen and lowest oxygen contents. It is noticeable that the catalytic process showed more similar elemental contents and high heat value as raw material than others. It is evident that the degree of unsaturation of raw lignin was 5.42, while it was declined significantly, because of its excellent hydrogenation capability.

SEM images (Fig. 3) showed that the surface of raw lignin was loose and regular, featuring many uniform globes with an approximate diameter of 200 nm (Fig. 3a). Under the single thermal effect, the globe was enlarged significantly because of the repolymerization, but no obvious tar and char were observed (Fig. 3b). After the catalysis of NaOH (Fig. 3c), the surface morphology of recovered lignin was remarkably changed. For example, its surface became irregular, where a smooth and tar-like surface coated by smaller particle was displayed, suggesting that lignin decomposes and repolymerizes of oligomer followed by dehydration for tar and char formation occurred simultaneously. This tar formation process was gentle with 5 wt% Ru/C (Fig. 3d), because of the hydrogenation of unsaturated lignin structure and the different decomposition mechanism of the base-catalyzed depolymerization and hydrogenolysis [1,28]. It also accords well with the above elemental analysis results that the highest carbon and hydrogen and lowest oxygen content were shown with the Ru/C catalyst (Table 4). However, when it was degraded with integrated catalyst (Fig. 3e), no obvious char and tar like surface morphology was displayed. Comparatively, it showed much more similar surface as the feedstock, though the particle was insignificantly large.

3.4. Comparative characterization of original and recovered lignin

The decomposition of lignin was significantly improved with the synergistic catalyst (Table 1). Furthermore, the product distribution was varied under different catalytic systems (Tables 2 and S1–S3). The reason for this phenomenon thereby was further examined through an intensive comparative study of the molecular weight distribution and structure change of the initial and recovered lignin. Table 3 showed that the raw lignin had a weight average molecular weight of 1360. After the treatment in CH3OH without or with single Ru/C catalyst, both the average molecular weight and dispersion degree were enlarged because of the simultaneous depolymerization and repolymerization. This repolymerization becomes more serious under the catalysis of NaOH. However, it was converted in the presence of NaOH coordinated with Ru/C, the change of molecular weight was insignificant. It indicated the relative gentle repolymerization of oligomer and raw lignin, resulting in the less residual solid yield (Table 1). Elemental analysis (Table 4) exhibited the same trend. For example, the recovered lignin from NaOH coordinated with Ru/C catalytic process showed more similar elemental contents and high heat value as raw material than others. It is noticeable that the recovered lignin from depolymerization process with Ru/C exhibited the highest carbon and hydrogen and lowest oxygen contents. It can be ascribed to the reason that some unsaturated structure in lignin molecule was hydrogenated by Ru/C. Table 4 also demonstrated that the degree of unsaturation of lignin was changed significantly under different catalytic systems. As shown in Table 4, the degree of unsaturation of raw lignin was 5.42, while it decreased to 5.02 in the recovered lignin from the NaOH catalytic system, because of the decomposition to unsaturated products as listed in Table S3. Noticeably, when 5 wt% Ru/C was used singly or as cocatalyst, the degree of unsaturation of recovered lignin was declined significantly, because of its excellent hydrogenation capability.

FT-IR was also used for the investigation of lignin structure change. According to previous literatures [25,26], the peaks at 3435 cm−1 was assigned to the stretching vibration of the aromatic OH group. The peak at 2937 and 2896 cm−1 was designated as the characteristic absorption of −OCH3 and −CH3 bonds, respectively [29]. 1710 cm−1 was regarded as the characteristic absorption of the carbonyl [26]. The peaks at 1612, 1507, and 1459 cm−1 were assigned as the characteristic vibrations of the benzene structure [29,30]. The strong absorption peak at 1113 cm−1 indicated clearly the abundant guaiacyl lignin. And 869 cm−1 was considered to be the characteristic vibrations of lignin-carbohydrate complex (LCC) [1].

As shown in Fig. 4, the FT-IR spectra of feedstock and recovered lignin from various catalytic systems were changed remarkably. For example, compared with the benzene structure in lignin, the peak strength of carbonyl group (1710 cm−1) was decreased obviously under the thermal effect (Fig. 4, curve b) or catalysis of NaOH (Fig. 4, curve c and e). It indicated that some carboxyl-contained ingredients such as ferulic acid, a general product of lignin depolymerization [31], were separated. Fig. 4 also demonstrated that the FT-IR spectra of recovered lignin without catalyst (Fig. 4, curve b) or with the synergic catalyst (Fig. 4, curve e) were as much nearer as it of raw lignin. But, it of lignin recovered from NaOH (Fig. 4, curve c) or Ru/C (Fig. 4, curve d) catalytic process was obviously different, suggesting the partly damage of the lignin structure.

The differences of 13C NMR spectra between raw and recovered lignin with or without integrated catalyst were displayed in Fig. 5. As shown in Fig. 5, lignin from the cooperative catalytic system

### Table 3
Average molecular weight of water soluble product, raw and recovered lignin.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Mw</th>
<th>Mz</th>
<th>Mn</th>
<th>D*</th>
</tr>
</thead>
<tbody>
<tr>
<td>WPs</td>
<td>215</td>
<td>382</td>
<td>503</td>
<td>1.78</td>
</tr>
<tr>
<td>Recovered lignin A</td>
<td>794</td>
<td>1592</td>
<td>1732</td>
<td>2.01</td>
</tr>
<tr>
<td>Recovered lignin B</td>
<td>1028</td>
<td>1881</td>
<td>2859</td>
<td>1.83</td>
</tr>
<tr>
<td>Recovered lignin C</td>
<td>869</td>
<td>1614</td>
<td>2301</td>
<td>1.86</td>
</tr>
<tr>
<td>Recovered lignin D</td>
<td>653</td>
<td>1342</td>
<td>1537</td>
<td>2.06</td>
</tr>
<tr>
<td>Raw lignin</td>
<td>892</td>
<td>1360</td>
<td>1579</td>
<td>1.52</td>
</tr>
</tbody>
</table>

a. Mn: number average molecular weight; Mz: weight average molecular weight; Mw: Z-average molecular weight; D: dispersion degree.
b. WPs: water soluble products.
c. Recovered lignin A: lignin from depolymerization process without catalyst; recovered lignin B: lignin from depolymerization process with NaOH; recovered lignin C: lignin from depolymerization process with 5 wt% Ru/C; recovered lignin D: lignin from depolymerization process with the integrated catalyst NaOH coordinated with Ru/C.

### Table 4
The main composed elements of raw and recovered lignin.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Elemental content</th>
<th>Experimental molecular formula</th>
<th>HHV (MJ kg−1)</th>
<th>Degree of unsaturation</th>
</tr>
</thead>
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<tr>
<td>Recovered lignin A</td>
<td>69.12 5.82 24.90</td>
<td>C6H10O2·3.15N0.02S0.01</td>
<td>27.23</td>
<td>5.46</td>
</tr>
<tr>
<td>Recovered lignin B</td>
<td>68.47 6.32 24.92</td>
<td>C6H10O2.67N0.02S0.01</td>
<td>27.72</td>
<td>5.02</td>
</tr>
<tr>
<td>Recovered lignin C</td>
<td>73.80 7.05 18.96</td>
<td>C6H10O2.17N0.02S0.01</td>
<td>31.62</td>
<td>4.84</td>
</tr>
<tr>
<td>Recovered lignin D</td>
<td>66.03 6.31 27.36</td>
<td>C6H10O2.86N0.02S0.01</td>
<td>26.45</td>
<td>4.84</td>
</tr>
<tr>
<td>Raw lignin</td>
<td>65.33 5.55 28.75</td>
<td>C6H10O2.78N0.02S0.01</td>
<td>24.88</td>
<td>5.42</td>
</tr>
</tbody>
</table>

a. On a dry basis (the sample was dried under vacuum at 80 °C until without further weight loss occurred).
b. The oxygen content was estimated by the conservation of mass based on the assumption that the samples only contain C, H, N, S and O.
c. Evaluated by Dulong formula: HHV (MJ kg−1) = 0.3383 × C + 1.422 × (H – O)/8.
d. Recovered lignin A: lignin from depolymerization process without catalyst; recovered lignin B: lignin from depolymerization process with NaOH; recovered lignin C: lignin from depolymerization process with 5 wt% Ru/C; recovered lignin D: lignin from depolymerization process with the integrated catalyst NaOH coordinated with Ru/C.
Fig. 3. SEM images of raw and recovered lignin with various catalysts. (a) Raw lignin; (b) without catalyst; (c) NaOH; (d) 5 wt% Ru/C; (e) NaOH coordinated with Ru/C.

Fig. 4. FT-IR spectra of raw and recovered lignin with various catalysts. (a) Raw lignin; (b) without catalyst; (c) NaOH; (d) 5 wt% Ru/C; (e) NaOH coordinated with Ru/C.

(Fig. 5c) has almost the same $^{13}$C chemical shifts as the feedstock (Fig. 4a). Nevertheless, the recovered lignin from the thermal conversion process was significantly different (Fig. 5b). For example, the proportion of CH$_3$ with a chemical shift at 12–15 ppm in the recovered lignin was increased significantly, due to the efficient dehydration on the lignin surface. The reduced signal at 56 ppm was attributed to the degradation of A'OCH$_3$[32,33]. The reduced signal at 72 ppm suggested the cleavage of $\beta$-O-4 during the thermal conversion process. The sharp decrease of signal strength at 133–147.3 ppm indicated the decomposition of etherified bond and conjugated C=C bond in guaiacyl lignin [34], giving guaiacol and its derivatives as detected by GC–MS (Table S2). And the disappearance of signals at chemical shift of 106–114 ppm was attributed to the stripping of aromatic methane carbons [35]. Therefore, $^{13}$C NMR spectra suggested that the lignin structure and the main chemical bond, such as $\beta$-O-4, were cleaved under the thermal effect. However, with the integrated catalyst, the structural change is insignificant.

Generally, recovered lignin from the single thermal process was composed of at least two parts: undecomposed lignin and repolymerized lignin [15]. The former has the characteristic structure, chemical bond and functional group of raw lignin. But, the latter was originated from the repolymerization of phenolic oligomer. This molecular recombination process generally results in looser and more unordered structure. Furthermore, the repolymerization lignin is facilitated to dehydrate at high temperature. And thus, different carbon atom is existed. However, as for recovered lignin from the base-catalyzed depolymerization and in situ hydrogenolysis process, the generated oligomer was converted rapidly to much more thermal-stable small molecular chemicals such as aliphatic alcohol and phenolic monomers (Table 2). This process competes well with the repolymerization. Therefore, the recovered lignin is almost composed of the unreacted feedstock, showing more similar properties than others on molecular weight distribution (Table 3), elemental composition (Table 4), surface morphology (Fig. 3), functional group (Fig. 4) and molecular carbon atom species (Fig. 5). Simultaneously, the hydrogenolysis of oligomer promotes significantly the lignin depolymerization process, giving a high lignin conversion and volatile product yield, leaving less solid (Table 1).

Py-GC/MS is rapid and highly sensitive for characterizing the chemical structure of lignin[36,37]. It was thereby adopted for further comparative characterization of the original and recovered lignin from various catalyst conditions. As shown in Fig. S11 and Table S6, the main products from the fast pyrolysis of lignin were changed remarkably. As for raw lignin, ethanol, alkyl and aromatic hydrocarbon, acid, and phenolic compounds were found to be the primary. Furnas which generally originated from the LCC[38,39] of the lignin molecular was also detected. When it was treated with or without catalyst, the product distribution was varied. Especially, the contents of long chain acid and methyl substituted chemicals were increased significantly, confirming the proposed methyl transfer and aromatic structure cleavage process as discussed in above GC–MS analysis (Tables 2 and S1–S3), and FT-IR and NMR characterization of water soluble products (Figs. S8 and S9) and recovered lignin (Figs. 4 and 5). The absence of fuse ring compounds, the main ingredients of bio-tar, may attribute to the partially broken and loose molecular structure of recovered lignin. It must be noticed that, compared with others, the Py-GC–MS results of recovered lignin from the cooperative catalytic system showed more similar product distribution as the raw feedstock. For example, the LCC derived furans and benzofuran was disappeared thoroughly at single thermal effect and with either NaOH or Ru/C catalyst. However, they could be found in the products of recov-
ered lignin with cooperative catalyst (Table S6), indicating the reserve of lignin original structure. Therefore, Py-GC–MS results further confirmed above mentioned conclusion that lignin is first degraded to phenolic monomers and its oligomer, and the Ru/C is more likely to convert the oligomer to the monomer and the aliphatic alcohols during this synergic process.

4. Conclusions

A novel and promising strategy for efficient lignin depolymerization and char elimination was achieved via the lignin depolymerization and in situ hydrogenolysis of phenolic oligomer. Results showed a sharp decrease of residual solid in the presence of the integrated catalyst NaOH coordinated with Ru/C. Further characterizations of the original and recovered lignin demonstrated that phenolic oligomer generated from lignin depolymerization rather than the initial lignin is hydrogenolyzed with Ru/C. It thereby is responsible for the less residual solid formation. And thus, this novel route and method would be a beneficial reference for future utilization of this sustained and energy-potential aromatic material.

Acknowledgements

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apenergy.2014.12.025.

References

Catalysts.

as an efficient catalyst


