# Microwave-assisted depolymerization of various types of

1. **waste lignin over two-dimensional CuO/BCN catalysts**
2. Yang Cao,a,b Season S. Chen,b Daniel C.W. Tsang,\*b James H. Clark,c Vitaliy L.
3. Budarin,c Changwei Hu,d Kevin C.-W. Wu,e Shicheng Zhang\*a,f

5

1. a Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention (LAP3), Department
2. of Environmental Science and Engineering, Fudan University, Shanghai 200438, China.
3. b Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University,
4. Hung Hom, Kowloon, Hong Kong, China.
5. c Green Chemistry Centre of Excellence, Department of Chemistry, University of York, York,
6. YO10 5DD, UK.
7. d Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry,
8. Sichuan University, Chengdu 610064, China.
9. e Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan.
10. f Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, China.
11. Corresponding authors: E-mail: [dan.tsang@polyu.edu.hk](mailto:dan.tsang@polyu.edu.hk); E-mail: [zhangsc@fudan.edu.cn](mailto:zhangsc@fudan.edu.cn)

17

## Abstract:

1. Valorization of lignin towards valuable chemicals and biofuels increases the economic
2. viability of sustainable biorefineries. This work aimed at elucidating how the lignin
3. structures recovered from various agricultural and industrial residues governed the
4. downstream catalytic conversion. Three types of lignin, namely bio-enzymatic lignin
5. (BL), organosolv lignin (OL), and Kraft lignin (KL) were fully characterized by HSQC-
6. NMR, TGA, FTIR, and SEM to obtain a detailed description of the structures. In
7. consideration of redox-active CuO and highly active carbon-modified boron nitride
8. (BCN) in oxidative dehydrogenation, the two-dimensional CuO/BCN catalyst was
9. prepared and explored in the microwave-assisted lignin conversion to improve the
10. aromatic monomers yields. The BL achieved the highest yield of 10 wt% monomers
11. over the CuO/BCN catalyst after the 3rd cycle in 30 min under mild conditions (200 oC).
12. The yields of bio-oils reached 70 wt% in 10 min when BL and OL were used as the
13. substrate. High efficiency of microwave-assisted reaction was illustrated by comparing
14. with that of hydrothermal reaction. This work demonstrated strong dependence of
15. conversion efficiency on the interunit linkages and functional groups of lignin
16. structures. The strong metal-support interaction between CuO and BCN not only
17. facilitated lignin depolymerization *via* the promoted electron transfer, but also
18. enhanced the stability of Cu catalysts under hydrothermal conditions. In addition,
19. elucidation of catalyst redox evolution shed light on the role of the CuO/BCN catalyst
20. in lignin depolymerization in recycle runs.
21. **Keywords:** lignin biorefinery; sustainable waste management; copper catalyst;
22. oxidative dehydrogenation; metal-support interaction.

41

## Introduction

1. Sustainable utilization of biological resources, especially the wastes of agriculture,
2. forestry, and related industries, aims to address the limited fossil resource issue and
3. present an opportunity to make biorefinery profitable.1, 2 Valorization of lignocellulosic
4. biomass for the production of fuels and platform chemicals has attracted increasing
5. attention.3, 4 The cellulose and hemicellulose fractions of biomass have been
6. industrialized in food production, paper manufacturing (50 million tons a year), and
7. biorefinery to produce xylose, furfural and 2nd generation biofuels.5-8 Meanwhile, vast
8. amounts of wastes containing abundant lignin are generated, which has been considered
9. as a promising alternative to produce aromatic compounds with a higher energy density
10. and potential commercial value.9, 10 However, the mass-produced lignin residues are
11. often underused and burned as low-grade fuel. Retrieving values from waste lignin can
12. not only maximize the value of renewable carbon resource but also increase the
13. economic viability of the biorefinery industry.
14. Separation and recovery of lignin from lignocellulosic biomass is the foremost
15. challenging process towards effective utilization of lignin for valuable chemicals and
16. fuels production.11 In view of the complex and recalcitrant structure of biomass, various
17. fractionation technologies such as acid/base-assisted delignification, enzymatic process,
18. and organosolv pretreatment have been developed to isolate lignin from lignocellulosic
19. feedstocks.12-14 Classic Kraft pulping process employs high concentration of NaOH and
20. Na2S solvents, where the harsh condition can modify or damage the native lignin
21. structure.15, 16 On the contrary, enzymatic process rarely affects the native structure of
22. lignin owing to its mild operation condition.12 Organosolv pretreatment utilizing
23. different organic solvents (e.g., alcohols, organic acids, and ionic liquids) can enhance
24. enzymatic saccharification by the removal of soluble lignin, while it inevitably leads to
25. partial depolymerization of lignin.12-14 Therefore, the fractionation technologies should
26. be taken into account for the variation of lignin structure.10, 17 Detailed analysis of
27. interlinkages, repeat units, solubility, and thermochemical behaviour of lignin derived
28. from diverse technologies is important for understanding how the lignin structures
29. recovered from various biomass residues govern the downstream conversion.
30. Most lignin utilization strategies hinge on thermochemical conversion, mainly
31. involving oxidative/reductive depolymerization, fast pyrolysis, and gasification.18-22
32. Reductive depolymerization have shown a high activity and selectivity and could
33. produce aromatic alkane *via* H2 participated upgrading.23, 24 However, the high reaction
34. temperature (150-350 oC) and external H2 purification would add to the cost for factory
35. construction.25 Oxidation of lignin is usually performed under mild condition (150-250
36. oC) and focuses on the production of functionalized oxygen-containing biofuels,
37. ranging from aromatic aldehydes to carboxylic acids that are target chemicals.26 In view
38. of the rapid heating and energy-efficient features, microwave-assisted
39. depolymerization can reduce the demand of external H2 or O2 purification and offer
40. distinct advantages for green production of biorenewable products. 27-31
41. Advanced homogeneous and heterogeneous catalysts such as transition metal-based
42. catalysts, zeolites, and carbon-based catalysts have been widely explored for lignin
43. oxidation.32-36 Among which, the Cu-based catalysts have attracted considerable
44. interest in oxidative depolymerization of lignin due to their excellent catalytic activity
45. and low cost.32, 37 For example, homogeneous Cu(I) (CuCl/tetramethylpiperidine N-
46. oxide) and Cu(II) (CuCl2/polybenzoxazine) complexes can promote the cleavage of C-
47. C and C-O bonds in the oxidation of lignin model compounds.38, 39 Synthesized CuNiAl
48. catalysts were found to be active in the cleavage of C-O bond for improving the yield
49. of bio-oil during alkaline lignin conversion. However, the supported copper catalysts
50. often suffer from metal sintering or leaching during the hydrothermal reaction.40 The
51. improvement of structural stability is of particular importance for sustainable catalysts.
52. Currently, two-dimensional hexagonal boron nitride (h-BN), exhibits unique properties
53. such as superior chemical and thermal stability and has been developed for the oxidative
54. dehydrogenation (ODH) reaction.41 Unprecedentedly high selectivity of ODH of
55. propane to propene over BN has been reported, which sheds light on the active site of
56. oxygen-terminated armchair edge of BN.42 Due to superhydrophobic nature of h-BN,
57. significant efforts have been made regarding modifications of the BN (e.g., heteroatom
58. doping, vacancy defects) to achieve better dispersion and higher activity *via* tuneable
59. physicochemical properties.43, 44 For instance, the carbon-doped BN materials exhibited
60. high activity in ODH of ethylbenzene and excellent oxidation resistance.45 Hence, we
61. intend to fabricate and investigate the modified BN supported copper catalysts for the
62. oxidative depolymerization of lignin to achieve full utilization of waste biomass while
63. providing new solutions to key challenges of heterogeneous catalysts.
64. In the present study, the CuO anchored functionalized BN catalyst (CuO/BCN) was
65. prepared *via* soft urea strategy assisted by mechanochemical treatment and subsequent
66. pyrolysis.46, 47 We explored the bifunctional CuO/BCN catalyst in the alkaline oxidation
67. of three types of lignin-rich wastes from agriculture and forestry residues with
68. microwave radiation. Alkaline solvent is known to promote delignification by cleaving
69. C-O bonds and enhancing solubility of lignin. Through this study, we aim to: (a)
70. investigate the structures of lignin recovered from various methods; (b) evaluate the
71. catalytic activity and recyclability of CuO/BCN catalyst in the oxidative valorization
72. of lignin to monomers and bio-oil; (c) elucidate the relationship between the structures
73. of lignin wastes and conversion mechanisms; and (d) evaluate the influence of different
74. heating methods by measuring monomer yields *via* hydrothermal and microwave-
75. assisted depolymerization of lignin. Overall, utilization of lignin wastes towards target
76. chemicals and bio-fuels might be promising through identification of lignin structure
77. and their thermochemical reactions in microwave-assisted conversion with advanced
78. catalysts.
79. 121

## 2. Materials and Methods

1. **2.1 Sources and pretreatment of lignin**
2. Bio-enzymatic lignin wastes (BL) was obtained from Shandong Longlive Bio-
3. Technology Co., Ltd, China. This lignin was a byproduct from xylo-oligosaccharides
4. and bio-ethanol production from corncob. The Kraft lignin (KL, CAS number 471003)
5. was purchased from Sigma-Aldrich. The organosolv lignin (OL) were extracted in
6. laboratory for comparison.48 Briefly, almond shells purchased from Hebei Chengde
7. Lulu Co., Ltd were milled and Soxhlet-extracted by toluene/ethanol (2:1, v/v) for 24 h
8. and dried overnight, then 30 g extracted biomass, 300 mL ethanol/water (1:1 v/v)
9. solution and 3 mL HCl (6 M) were loaded into Parr pressure reactor and stirred at
10. 160 °C for 10 min. The OL was precipitated by adding an excess amount of deionized
11. water, and then the residual solid was dissolved in acetic acid-water mixture for further
12. purification.

## 2.2 Preparation of BCN and CuO/BCN catalysts:

1. h-BN (2 g, Saint-Gobain Ceramic Materials) and urea (4 g, Sigma-Aldrich) were mixed
2. inside a polytetrafluoroethylene milling container using a planetary ball mill at a
3. rotation speed of 800 rpm for 8 h. A desirable amount of Cu(NO3)2·3H2O and BN-urea
4. mixtures were added into 50% ethanol/water (v/v) solution at 120 °C to keep the boiling
5. state. Finally, the resulting gel-like product was pyrolyzed under the air atmosphere at
6. 550 °C (heating rate: 2 °C/min) for 3 h to obtain the CuO/BCN catalysts (CuO loading:
7. 10 wt%). The BCN sample was prepared by a similar procedure except not adding
8. Cu(NO3)2·3H2O precursor.

## 2.3 Catalytic conversion of lignin under microwave irradiation:

1. The conditions were optimized based on previous studies.32 In brief, we first conducted
2. the preliminary tests of lignin depolymerization in the absence of catalyst at 160 °C,
3. 180 °C, and 200 °C referring to the existing literature conditions and the microwave
4. capacity (Fig. S6a). We found that lignin depolymerization at 200 °C enhanced
5. monomer yield by 50% compared to that at 160 °C. Subsequently, NaOH concentration
6. at a relatively low range (0.4 to 4 wt%, compared to over 10 wt% in conventional
7. method) was evaluated to optimize the depolymerization condition (Fig. S6b). Hence,
8. the reaction temperature at 200 °C with 4 wt% NaOH was selected for the catalytic
9. evaluation tests. Lignin (0.2 g) was added into 10 mL solution (4 wt% NaOH and 0.1
10. mL of 30 wt% H2O2) with 0.1 g of CuO/BCN catalysts. It should be noted that the H2O2
11. was added into the NaOH solvent quickly before heating. The small amount of H2O2
12. quickly decomposed into oxygen and water during the heating process in the basic
13. environment, as indicated by the rapidly increasing pressure in the reactor monitored
14. by *in situ* pressure sensor. The primary role of H2O2 was to provide oxygen for
15. facilitating the oxidative depolymerization of lignin. For comparison, 0.1 g of BCN and
16. 0.03 g of Cu(NO3)2·3H2O as the catalysts were also evaluated under the same condition.
17. The mixtures were loaded in a closed vessel and heated to 200 °C with a ramp time of
18. 2 min in an Ethos Up Microwave Reactor with a maximum power of 1800 W. The same
19. temperature was maintained for 10-30 min under magnetic stirring. All the catalytic
20. reactions were conducted at least in triplicate. To examine the influence of different
21. heating methods, the hydrothermal depolymerization of lignin was conducted. The
22. heating rate of the reactor was 10 oC/min and all other conditions were the same as
23. above.
24. After the reaction, the solution pH values were adjusted to 2 with hydrochloric acid
25. and the bio-crude oil containing aromatic monomers were extracted by using ethyl
26. acetate for three times and subsequently analyzed by gas chromatography-mass
27. spectroscopy (GC-MS). The bio-oils were obtained and quantified after evaporation of
28. ethyl acetate. For the recyclability test, the catalysts were collected by centrifugation at
29. 3000 rpm. for 2 min, the recovered catalysts were washed with DI water and ethanol,
30. and then dried at 60 oC over overnight.

## 2.4 Product identification and quantification

𝑊𝑂

1. Yield of bio ― oil (wt%) = 𝑊𝐿 × 100%
2. where WO represents the weight of bio-oil extracted by using ethyl acetate, and WL is
3. the weight of initial lignin.
4. For lignin depolymerization, aromatic monomers were identified and quantitated by
5. GC-MS (Agilent GC7890N equipped with HP-5 MS column). The conversion and
6. yields were determined using an internal standard (decane) method on a basis of the
7. peak area in the GC chromatogram.18, 49

𝑊𝑚𝑜𝑛𝑜𝑚𝑒𝑟

183 𝐶𝑚𝑜𝑛𝑜𝑚𝑒𝑟 =

184 𝑌𝑚𝑜𝑛𝑜𝑚𝑒𝑟 =

𝑉

𝑊𝑚𝑜𝑛𝑜𝑚𝑒𝑟

𝑊𝐿𝑖𝑔𝑛𝑖𝑛

1. Ymonomer: the yield of monomer based on the weight of lignin.

## 2.5 Characterization of catalysts and lignin:

1. The surface morphology and element mapping were investigated by using scanning
2. electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX, TESCAN
3. VEGA3 XM). Brunauer-Emmett-Teller (BET) surface areas were determined by
4. nitrogen adsorption-desorption isotherm measurements using a gas sorption analyzer
5. (Micromeritics Accelerated Surface Area and Porosimetry system, ASAP 2020). The
6. crystalline structures of the catalysts were examined by X-ray diffraction analysis
7. (XRD; Rigaku SmartLab) in a scanning range of 5-90°. Structural characteristics of
8. lignin and obtained catalysts were determined by Fourier-transform infrared
9. spectroscopy (FTIR, Perkin Elmer, UATR Two). Thermogravimetric analysis (TGA)
10. was performed from 30 to 1000 °C at a heating rate of 10 °C/min under N2 atmosphere
11. (TGA, Rigaku Thermo Plus). The molecular weight distributions of various types of
12. lignin were measured using gel permeation chromatography (GPC) instrument (Agilent
13. 1260 HPLC systems) equipped with a refractive index detector (RID). The samples of
14. 2 mg were dissolved in 1 mL THF. The H2 temperature programmed reduction (H2-
15. TPR) illustrated the reducibility of catalysts. A 60 mg of sample was pretreated under
16. the N2 atmosphere, and then reduced in 10 vol% H2 of N2 (30 mL/min) at a ramp rate
17. of 10 oC/min to 900°C.
18. Two-dimensional heteronuclear single quantum correlation nuclear magnetic
19. resonance (2D HSQC NMR) spectra of various types of lignin were recorded on a
20. Bruker AVIII 400 MHz spectrometer at 25 °C. About 80 mg of lignin was dissolved in
21. 0.6 mL of DMSO-d6 (99.8%). The spectral widths were 11 ppm and 190 ppm for the
22. 1H- and 13C-dimension, respectively. The overall amounts of aromatic units (C9) were
23. selected as the internal standard and quantified based on the analysis of 2D HSQC
24. cross-signal.50, 51 Results of structural features present in various lignin were expressed
25. as percentage of per 100 aromatic units (Ar).

212 Hardwood lignin (OL): I(𝐶9)units = 0.5I(𝑆2,6) +I(𝐺2)

213 Grass lignin (BL): I(𝐶9)units = 0.5I(𝑆2,6) +I(𝐺2) + 0.5I(𝐻2,6)

214 Softwood lignin (KL): I(𝐶9)units = 0.5I(𝐺2)

𝐼𝑥

215 𝐼𝑥% = 𝐼𝐶9 × 100 %

216 I(C9): the integral value of the aromatic ring.

217

## 3. Results and Discussion

1. **3.1. Characterization of the catalyst**
2. The 2D sheet structures of BN, BCN and CuO/BCN samples were revealed by SEM
3. (Fig. 1). Pristine BN showed the smooth flake-like morphology (Fig. 1a), whereas
4. reduced lateral size and rough surface were clearly observed in the BCN and CuO/BCN
5. samples (Fig. 1b-c). These results evidenced that ball milling can effectively exfoliate
6. and generate defects on BN to improve its dispersibility in water.52 Urea was adopted
7. to introduce functional groups during ball milling and stabilize metal oxides during
8. calcination.46, 53 Mixing Cu(NO3)2·6H2O and BN-urea under a boiling state can
9. facilitate the formation of highly dispersed gel-like composites *via* metal-urea-BN
10. complexation. Thermal decomposition of urea could form a thin carbon nitride coating
11. over the BN surface, which can be applied to prevent metal agglomeration and modify
12. the BN surface for the oxidative conversion.46 The SEM-EDX mapping confirmed the
13. presence of carbon nitride modifiers and highly dispersed Cu species on the catalyst
14. surface without noticeable aggregation (Fig. 1d). The ball milling process together with
15. soft urea strategy successfully modified the surface of BN and gave rise to a highly
16. dispersed CuO species.
17. The XRD pattern verified the formation of crystalline CuO on the surface of BCN
18. support. The relatively low intensity of CuO phases in the XRD patterns indicated the
19. presence of highly dispersed and small sized particles of CuO on the BCN surface. The
20. crystallite size of CuO phase was approximately 13-17 nm calculated from XRD peaks.
21. Four diffraction peaks centred at 26.7°, 41.6°, 50.1°, and 55.1° can be ascribed to the
22. typical BN phases (Fig. 2a). The BCN and CuO/BCN catalysts showed that the
23. intensities of diffraction peaks of BN phase significantly decreased. The characteristic
24. peak at 26.7° shifted to a lower degree and became broader in the BCN as compared
25. with the pristine BN sample, corresponding to an increase in the interplanar distance
26. from 0.332 nm (BN) to 0.333 nm (BCN). The decreased thickness and increased lattice
27. spacing were probably a result of milling-induced exfoliation, corroborating the
28. presence of defects induced by carbon-heteroatom doped (Fig. S1).54 The reflection of
29. BN phase in CuO/BCN catalyst shifted back to the original position of BN, which may
30. be due to the structure contraction upon the introduction of metal oxides.55 In the FTIR
31. spectra (Fig. 2b), two strong FTIR bands at 1380 and 760 cm-1 were attributed to B-N
32. stretching and bending. Evidently, these two peaks shifted towards the higher
33. wavenumber in contrast with that of BN, which also implied the conjugative effect of
34. B-C-N in BCN and CuO/BCN catalysts. The Cu-O stretching at 520 cm-1 and 595 cm-
35. 1 were observed in the CuO/BCN catalyst.56 For BCN and CuO/BCN catalysts, two
36. small peaks at 3410 cm-1 and 3225 cm-1 could be assigned to the -OH and -NHx groups,
37. respectively, suggesting the presence of moisture-sensitive surface defects in the ball
38. milled samples.
39. The textural properties of the catalysts were evaluated by nitrogen adsorption-
40. desorption isotherm. The BET specific surface area of pristine BN is 2.0 m2/g, and the
41. corresponding pore size distribution based on the BJH model shows a primary
42. micropore width of 1-2 nm (Table S1). After the mechanochemical treatment and
43. calcination, the BET specific surface area of BCN increases to 45 m2/g, and the majority
44. of pore diameters fall into the range of 2-5 nm. The CuO/BCN catalyst shows type H4
45. hysteresis loops and a range of pore sizes from 2 to 10 nm, with a slight decrease of
46. specific surface area and volume in comparison with that of BCN (Fig. 2c). These
47. results suggest that the introduced CuO species are mainly loaded on catalyst surface
48. covering partial mesopores of BCN. For the 2D catalyst, the increased surface area
49. infers that more edges and defects derived from ball milling treatment were exposed on
50. the BCN and CuO/BCN catalysts. The significant enhancement of specific surface area
51. and pore volume (0.18 cm3/g) of CuO/BCN catalyst are anticipated to accommodate
52. more catalytic sites.
53. The XPS spectra of CuO/BCN catalyst are illustrated in Fig. 3. The XPS survey
54. spectrum showed the presence of B, C, N, O, and Cu elements. The peaks at binding
55. energies of 936.6 eV and 946.7 eV could be assigned to Cu 2p3/2 and Cu 2p1/2 along
56. with shake-up satellites, indicating the oxidation state of Cu2+.57 The Cu 2p3/2 binding
57. energy of CuO is typically reported around 933.5 eV, the higher binding energy might
58. suggest the presence of Cu2+ species with a higher cationic character, indicating a strong
59. interaction between Cu and BCN support.58-60 Hence, the surface defects caused by ball
60. milling together with urea can stabilize and confine CuO species on the catalyst surface.
61. The B 1s and N 1s full width at half maxima (fwhm) peak widths were detected at 2.6
62. eV, which is larger than the fwhm value of pristine BN (Fig. S2). Typically, such peak
63. broadening could be considered as a result of the superposition of multiple peaks.61 The
64. B 1s spectrum was deconvoluted into three peaks centred at 190.4 eV, 191.3 eV, and
65. 192.5 eV, corresponding to B-C, B-N, and B-O bonds, respectively.45 The primary B-
66. N peak originated from the BN structure, and the presence of B-C bond suggested the
67. presence of defect sites where partial B atoms could bind with C atoms. The
68. deconvolution of N 1s showed three types of N structures, consisting of N-B (398.6
69. eV), N-H (399.5 eV), and N-C (400.5 eV) bonds,62 where the N-H bonds could
70. represent the defect sites from urea formed carbon nitride or modified BN. The
71. spectroscopic evidence (i.e., XRD, FTIR, and XPS results) suggested that the defective
72. surface of BN after ball milling was strongly bound with the thin carbon nitride coating.
73. Therefore, it is likely that during the mechanochemical process, urea molecules could
74. react with defective surface and active edges of exfoliated BN, thus possibly forming
75. amine groups for the stabilization of CuO species. The highly dispersed CuO species
76. and modified surface of BCN *via* forming B-C and N-C bonds may provide more active
77. sites for the oxidation of lignin.

## 3.2. Characterization of various types of lignin.

1. In order to identify the authentic structure of various waste lignin feedstocks and
2. illustrate the relationship between lignin structures and depolymerization behaviour for
3. the production of aromatic monomers and bio-oil, three typical waste lignin feedstocks
4. (OL, BL, and KL) from biorefinery industries were selected for comparison. The
5. particle size and surface morphology of lignin were clearly distinctive and dependent
6. upon different extraction methods (Fig. 4a-c and Fig. S3). The SEM images showed
7. irregular bulks of OL and BL, while KL showed uniform spherical structure, indicating
8. destruction of the original structure and repolymerization of recovered lignin.63 Among
9. the three types of lignin, the OL showed the smallest particles (10 - 20 μm), followed
10. by BL (20 μm), and KL (20 - 40 μm). In addition, the increasing weight- and number-
11. average molecular weights (Mw and Mn) of KL listed in Table S2 illustrated the
12. repolymerization of lignin, while the mild treatments resulted in less defined particle
13. shapes, smaller particle sizes and molecular weights. The polydispersity index for OL
14. and BL value were 1.48 and 1.18, respectively, which indicated good uniformity that
15. could be beneficial for further selective depolymerization.
16. The solubility, abundance in functional groups, and linkages of recovered lignin also
17. varied. The elemental analysis showed that all three lignin samples had similar contents
18. of fixed carbon (48-57 wt%) (Table S3). Due to the use of hydrogen sulphide in the
19. extraction process, 3.06 wt% of sulphur was observed in KL (Table S3).16 The slightly
20. darker colour of KL compared to those of OL and BL samples (Fig. S4a) could be
21. attributed to the re-condensation of lignin.64 The modified structure of KL showed an
22. increase in water solubility as a result of the exposed OH groups and the incorporation
23. of sulphur species, whereas the dispersibility of OL and BL remained poor in water due
24. to the slight change of structure under mild treatment (Fig. S4b). All lignin samples
25. showed good dispersion in alkaline solution (4 wt% NaOH solution), which can provide
26. effective contact between the solid catalyst and lignin for reducing mass transfer
27. limitation.
28. The FTIR and NMR spectra were collected to illuminate the structures especially the
29. interunit linkages of various lignin feedstocks recovered from different extraction
30. methods. The FTIR showed broad signals at 3440 cm-1 and 2936 cm-1 for all three types
31. of lignin which can be ascribed to the stretching vibrations of O-H groups and C-H in
32. methyl and methylene groups, respectively (Fig. 4d). A notable band at 1740 cm-1 was
33. observed in BL, which can be attributed to the C=O stretching in conjugated aldehydes
34. and carboxylic acids groups, as an evidence of partial cleavage of β-O-4 linkage
35. resulting from steam explosion process before bio-enzymatic treatment. By contrast,
36. such a band was absent in KL and OL. All the lignin spectra showed bands at 1590,
37. 1505, and 1415 cm-1 assigned to aromatic skeletal vibrations,65 and one centred at 1460
38. cm-1 corresponding to C-H deformation with aromatic ring vibration. Two bands at
39. 1270 and 1215 cm-1 in all lignin samples represent C-O vibrations in the guaiacyl (G)
40. unit, while 1330 and 1120 cm-1 were assigned to C-O and C-H vibrations in syringyl
41. (S) unit, respectively.48 In addition, the distinct band of C-H vibrations in the S unit
42. observed in OL suggested an abundance of S-type of monomers. All the lignin spectra
43. showed C-O deformation and C-H out-of-plane deformation bands at 1030 cm-1 and
44. 830 cm-1 with different intensities,65 indicating that the native lignin structure was
45. affected to different extents by the extraction processes.
46. The 2D-HSQC analysis confirmed the presence of major lignin structures (β-O-4,
47. β-5, β-β linkages and S/G/H units), side-chain (δC/δH 50-90/2-6) and aromatic (δC/δH
48. 95-135/6-8) regions (Fig. 5). Three typical interunit linkages including (A) β-O-4, (B)
49. β-5, and (C) β-β linkages were identified by C-H correlation at δC/δH 72.6/4.85 (Cα- 346 Hα, A), 85.1/4.36 (Cβ-Hβ, A), 60.2/3.55 (Cγ-Hγ, A), 85.1/4.72 (Cα-Hα, B), 54.5/3.07 (Cβ- 347 Hβ, B), 87.9/5.50 (Cα-Hα, C), 53.9/3.52 (Cβ-Hβ, C), and 62.1/3.75 (Cγ-Hγ, C).66, 67 All
50. lignin samples exhibited a strong signal corresponding to methoxyl (δC/δH, 55.80/3.75)
51. in the side-chain regions. OL and BL presented more native-types of lignin with an
52. abundant amount of β-O-4 linkages. The β-O-4 bonds were the dominant linkages in
53. BL (grass lignin), suggesting that more native structure of lignin remained after the
54. enzymatic process (Table 1). Typically, β-O-4 linkage accounts for 40-50%, 50-60%,
55. and 35-45% of all linkages in softwood lignin, hardwood lignin and grass lignin,
56. respectively.68 The low content of β-O-4 linkage (11.2%) in OL (hardwood lignin)
57. sample was consistent with previous studies, which reported that β-O-4 bond could be
58. cleaved under the organosolvolysis pretreatment.14 By contrast, the major interunit
59. linkages of lignin were not detectable in KL, except for the methoxyl groups. Hence,
60. the NMR spectra verified that various extraction protocols could modify the lignin
61. structure *via* the cleavage of β-O-4 linkages and undesired condensation reactions.
62. In the aromatic region, S/G/H units were clearly distinguishable in all lignin samples.
63. The S units were defined by δC/δH 104.3/6.65, and the signals at δC/δH 106.1/7.22 and
64. δC/δH 128.5/7.25 were attributed to the Cα-oxidized S unit (S′) and C2,6-H2,6 aromatic
65. of H unit, respectively. The G units showed different correlations at δC/δH 112.1/7.09

364 (C2-H2), 116.2/6.92 (C5-H5), and 120.0/6.80 (C6-H6). Additionally, p-coumaric acid (P)

1. and ferulic acid (F) were detected in the spectra of BL sample, as discussed in the FTIR
2. results.67 The presence of P and F signals was attributed to the enzymatic delignification
3. enhanced by steam explosion pretreatment. As shown in Table 1, the higher S/G ratio
4. in OL than that in BL, i.e., more S units in OL, was consistent with the primary unit of
5. hardwood lignin. Theoretically, a higher amount of S-type lignin units is favourable for
6. the formation of β-O-4 linkage and facilitates the yield of aromatic monomer. In G/S-
7. rich BL and G-dominant KL, the exposed C5 position in G unit may be prone to fast
8. monomer coupling again *via* re-condensed C-C bond during the subsequent
9. depolymerization process. The observed difference in monolignol distribution may
10. influence the effectiveness of depolymerization of lignin.
11. The TGA measurements showed that oxygen-containing functional groups (e.g.,
12. OCH3, OH, and COOH) and various linkages in lignin are associated with different
13. bond energies in lignin and corresponded to different cleavage temperatures.69, 70 As
14. shown in Fig. 6a, the weight loss of OL, BL, and KL samples was 68.2%, 69.7%, and
15. 49.5%, respectively. The KL sample showed the highest char residue, indicating that
16. more stable and condensed structure formed via C-C bond repolymerization during the
17. extraction process. These results also corroborated with the structure identification by
18. FTIR and NMR analysis. As shown in Fig. 6b, OL and BL rich in β-O-4 linkages
19. decomposed at a lower temperature than KL due to the lower bond energies of C-O
20. linkages in comparison to those of C-C bonds. Therefore, preserving the native
21. structure of lignin with abundant β-O-4 linkage is possibly conducive to catalytic
22. conversion at a lower temperature.65 The native-like structure of OL and BL can
23. provide a higher possibility for achieving a low-temperature selective conversion of
24. lignin.
25. 389

## 3.3. Depolymerization of lignin

1. The three types of lignin feedstocks showed totally different monomer distributions and
2. yields under microwave-assisted oxidative depolymerization, highlighting the
3. significance of lignin structure in its downstream conversion. The yields of aromatic
4. monomers and bio-oil were greatly improved in the presence of CuO/BCN catalyst,
5. while the product distribution was not much different than the control without catalysts
6. (Fig. 7a). The main monomers (aromatic compounds 1-9) produced during lignin
7. depolymerization are displayed in Fig. S5 and Table 2, consisting of vanillin (6),
8. syringaldehyde (8), acetosyringone (9), as well as other phenols and aromatic ketones.
9. Higher contents of aromatic monomers obtained from BL and OL depolymerization
10. were attributed to the relatively abundant β-O-4 linkages preserved in the lignin
11. structure, as supported by the 2D NMR analyses and TG results. In comparison, the
12. relatively low monomer yield from KL reflected the known difficulty in valorization of
13. the lignin waste from widely used industrial process because of repolymerized C-C
14. bonds in the modified structure. In addition, catalytic conversion of BL over both BCN
15. and Cu(NO3)2 showed an increase in monomer yields (Fig. S7). The modified BCN
16. could induce unique electronic structures and provide more active sites for promoting
17. the catalytic performance, while dispersed CuO under alkaline condition at 200 oC was
18. also active for lignin depolymerization.45 A combination of BCN and CuO species in
19. the catalyst showed synergistic effects to enhance lignin depolymerization, which
20. highlights the promotional effect of strong metal-support interaction on the catalytic
21. performance, as discussed in the section on XPS analysis.
22. As the reaction time increased from 10 to 30 min, the monomer yields significantly
23. increased (Fig. 7b), while the growth of bio-oil was marginal (less than 10%) (Fig. 7c).
24. The total yield of monomers from BL reached up to 9.4 wt% (1865 mg/L) in 30 min,
25. which was much higher than the monomer yield from KL (5.1 wt%). These results
26. demonstrated fast depolymerization of lignin under microwave radiation. Although the
27. content of β-O-4 linkages was much less in OL than that in BL, the higher S/G ratio in
28. OL may mitigate the formation of inactive C-C bonds and increase monomer yields
29. mainly consisting of S-type monomers.71 Higher bio-oil yields could be achieved from
30. the conversion of BL (73%) and OL (74%), as compared to that from KL (39%). The
31. spent CuO/BCN catalyst after the conversion of KL was analyzed by XRD (Fig. S8),
32. where no sulphur-containing species was detected on the catalyst surface. This result
33. confirmed that the lower yield of monomer and bio-oil from KL conversion mainly
34. resulted from its inert structure rather than catalyst deactivation by sulphur. These
35. results revealed that more native-like lignin structures preserved in the feedstocks (such
36. as BL and OL) are favourable for higher product yields of oxidative depolymerization,
37. and the CuO/BCN catalysts are effective for the production of aromatic monomers. To
38. examine the influence of different heating methods, the hydrothermal and microwave-
39. assisted depolymerization of lignin were performed for comparison (Fig. S9).
40. Microwave energy could homogeneously heat the whole biomass which is important
41. for processing poorly thermal-conducting feedstocks. Rapid heating of the substrates
42. can shorten the reaction time and prevent over-reaction of the obtained products. The
43. results further confirmed synergistic effects of microwave radiation on the lignin
44. depolymerization towards high yield and product selectivity.
45. In view of the high yields of monomers and bio-oil, the recyclability test of
46. CuO/BCN catalyst was conducted for oxidative depolymerization of BL. The high
47. yields of bio-oil were maintained after three cycles (Fig. S10). The results indicated
48. that the CuO/BCN catalyst had no apparent loss of activity in the three cycles (Fig. 8a).
49. Nevertheless, the monomer yields slightly increased to 10 wt% in the 3rd cycle. The
50. XRD patterns showed that different redox dynamics were involved during the oxidative
51. reactions. The CuO species were the only detectable Cu species observed in the fresh
52. CuO/BCN catalyst (Fig. 2a), while Cu2O species appeared after the 1st cycle due to
53. partial reduction of CuO (redox cycle: CuO-Cu2O) (Fig. 8b). After the 2nd cycle, the
54. peak intensity of Cu2O species decreased and metallic Cu phase was formed (redox
55. cycle: Cu2O-Cu2O/Cu). After the 3rd cycle, no Cu2O phase were detected, suggesting
56. the transformation of Cu2O to Cu species. The slightly improved yields in the 3rd recycle
57. run might be attributed to the stronger redox capability of Cu2O/Cu pair as reported by
58. previous studies.32, 72, 73
59. Furthermore, H2-TPR profiles illustrated the surface interaction between various
60. CuOx species and BCN support (Fig. 8c). In fresh CuO/BCN catalyst, two reduction
61. peaks can be distinguished at 309 oC and 420 oC. The peak at the lower temperature
62. corresponded to the reduction of highly dispersed CuO phase, and such kind of Cu
63. species could be readily reducible.74, 75 The peak at the higher temperature (420 oC)
64. represented bulk CuO which had weaker interaction with the BCN surface. The peak
65. decreasing from 309 oC to 290 oC indicated that a large amount of highly dispersed
66. CuO species could participate in the oxidative reaction and be reduced in the first cycle,
67. while the peak decreasing from 420 oC to 370 oC represented the reduction of bulk
68. CuO.74 The total intensity and temperature of reduction peaks decreased gradually after
69. the second and third cycles, implying the formation of metallic Cu, which is consistent
70. with the XRD patterns. To further shed light on redox evolution of the CuO/BCN
71. catalyst during lignin depolymerization, a comparative reaction was conducted under
72. the same condition in the absence of lignin (200 oC, 10 mL solution, 0.1 g catalyst, 30
73. min). The XRD patterns (Fig. S11) showed that CuO species were not reduced in this
74. comparative test. These results demonstrated CuO could act as the solid oxidant during
75. the selective oxidation of lignin.76 The SEM images and EDX mapping of the recovered
76. catalysts after the 3rd cycle (Fig. S12) showed similar structure to the fresh CuO/BCN
77. catalyst and highly dispersed Cu species, illustrating superior hydrothermal stability of
78. the catalyst and strong metal-support interaction to inhibit Cu aggregation during the
79. oxidative depolymerization of lignin.
80. In light of the above experimental results, possible reaction mechanisms are proposed
81. for the oxidation depolymerization of native lignin (β-O-4 linkage) over the CuO/BCN
82. catalyst in this study (Scheme 1). The selective cleavage of Cα-Cβ and Cβ-O bonds was
83. the most commonly recognized pathway.77 Typically, the β-O-4 alcohol could be
84. oxidized to β-O-4 ketone over the CuO/BCN surface under alkaline condition, and the
85. formation of ketone intermediates could lower the Cβ-O bond energy for the subsequent
86. depolymerization (Step Ⅰ).78 The Cβ-O bond cleavage facilitated the production of
87. acetovanillone (7) and acetosyringone (9), while the yields of vanillin (6) and
88. syringaldehyde (8) were significantly promoted by CuO/BCN catalyst; thus, the Cα-Cβ
89. cleavage might contribute to the production of aldehydes through retro-aldol reaction
90. (Step ⅠⅠ). Meanwhile, the Cu(II) species were reduced to Cu(I) in the absence of
91. sufficient oxygen. The oxidative capability of copper-based catalysts on the activation
92. of C-C bond was consistent with previous studies,38, 39 whereas the modified BN
93. support and the strong metal-support interaction could promote the catalytic conversion
94. of electron-rich aromatic substrates and intermediates. Therefore, the synergistic effect
95. of redox-active CuO and active modified BCN support enabled efficient oxidative
96. depolymerization of lignin.
97. 487

## 4. Conclusions

1. In this work, microwave-assisted depolymerization of lignin derived from various
2. fractionation methods was conducted over CuO/BCN catalyst. The aromatic monomers
3. yield from lignin containing more native structures (e.g., BL and OL) could reach up to
4. 10 wt% in 30 min, which was twice as high as that of KL with significantly modified
5. structure. The CuO/BCN catalyst showed synergistic advantage of metal-support
6. interaction of redox-active CuO and carbon-modified BN support for the oxidative
7. depolymerization of lignin. Overall, these results highlight the importance of green and
8. energy-efficient approach for achieving full utilization of waste lignin with adequate
9. biomass fractionation protocols.
10. 498

## Acknowledgements

1. This study was supported by the International Cooperation Project of Shanghai
2. Municipal Science and Technology Commission (No. 18230710700), National Key
3. Research and Development Program of China (No. 2017YFC0212205), National
4. Natural Science Foundation of China (No. 21876030), Royal Society International
5. Exchanges 2016 Round 2 - IE160441, Hong Kong Research Grants Council (PolyU
6. 15217818), and Hong Kong International Airport Environment Fund (Phase 2).
7. 506

## References

1. 1. Z. Sun, G. Bottari, A. Afanasenko, M. C. A. Stuart, P. J. Deuss, B. Fridrich and K. Barta, *Nat.*

509 *Catal.*, 2018, 1, 82-92.

1. 2. S. Y. Lee, H. U. Kim, T. U. Chae, J. S. Cho, J. W. Kim, J. H. Shin, D. I. Kim, Y.-S. Ko, W. D.
2. Jang and Y.-S. Jang, *Nat. Catal.*, 2019, 2, 18-33.
3. 3. J. Remón, J. Randall, V. L. Budarin and J. H. Clark, *Green Chem.*, 2019, 21, 284-299.
4. 4. L. Petridis and J. C. Smith, *Nat. Rev. Chem.*, 2018, 2, 382-389.
5. 5. L. Wang, R. Templer and R. J. Murphy, *Energy Environ.Sci.*, 2012, 5, 8281.
6. 6. Y. Li, P. Liu, J. Huang, R. Zhang, Z. Hu, S. Feng, Y. Wang, L. Wang, T. Xia and L. Peng,

516 *Green Chem.*, 2018, 20, 2047-2056.

517 7. I. K. M. Yu and D. C. W. Tsang, *Bioresour. Technol.*, 2017, 238, 716-732.

518 8. I. K. M. Yu, X. Xiong, D. C. W. Tsang, L. Wang, A. J. Hunt, H. Song, J. Shang, Y. S. Ok and

519 C. S. Poon, *Green Chem.*, 2019, 21, 1267-1281.

520 9. M. Talebi Amiri, G. R. Dick, Y. M. Questell-Santiago and J. S. Luterbacher, *Nat. Protoc.*, 2019,

521 14, 921-954.

522 10. E. M. Anderson, M. L. Stone, R. Katahira, M. Reed, W. Muchero, K. J. Ramirez, G. T. Beckham

523 and Y. Roman-Leshkov, *Nat. Commun.*, 2019, 10, 2033.

524 11. S. Kasakov, H. Shi, D. M. Camaioni, C. Zhao, E. Baráth, A. Jentys and J. A. Lercher, *Green*

525 *Chem.*, 2015, 17, 5079-5090.

526 12. Z. Zhang, M. D. Harrison, D. W. Rackemann, W. O. S. Doherty and I. M. O'Hara, *Green Chem.*,

527 2016, 18, 360-381.

528 13. C. G. Yoo, M. Li, X. Meng, Y. Pu and A. J. Ragauskas, *Green Chemistry*, 2017, 19, 2006-2016.

529 14. X. Ouyang, X. Huang, B. M. S. Hendriks, M. D. Boot and E. J. M. Hensen, *Green Chem.*, 2018,

530 20, 2308-2319.

531 15. C. S. Lancefield, H. L. J. Wienk, R. Boelens, B. M. Weckhuysen and P. C. A. Bruijnincx, *Chem.*

532 *Sci.*, 2018, 9, 6348-6360.

1. 16. C. Gioia, G. Lo Re, M. Lawoko and L. Berglund, *J. Am. Chem. Soc.*, 2018, 140, 4054-4061.
2. 17. A. Rahimi, A. Ulbrich, J. J. Coon and S. S. Stahl, *Nature*, 2014, 515, 249-252.
3. 18. M. Wang, X. Zhang, H. Li, J. Lu, M. Liu and F. Wang, *ACS Catalysis*, 2018, 8, 1614-1620.
4. 19. T. Kleine, J. Buendia and C. Bolm, *Green Chem.*, 2013, 15, 160-166.
5. 20. S. Kudo, Y. Hachiyama, Y. Takashima, J. Tahara, S. Idesh, K. Norinaga and J.-i. Hayashi,

538 *Energy Fuels*, 2013, 28, 76-85.

539 21. W. Wang, M. Wang, J. Huang, X. Zhao, Y. Su, Y. Wang and X. Li, *Bioresour. Technol.*, 2019,

540 278, 464-467.

541 22. L. Cao, C. Zhang, H. Chen, D. C. W. Tsang, G. Luo, S. Zhang and J. Chen, *Bioresour. Technol.*,

542 2017, 245, 1184-1193.

543 23. E. M. Anderson, M. L. Stone, M. J. Hülsey, G. T. Beckham and Y. Román-Leshkov, *ACS*

544 *Sustainable Chem. Eng.*, 2018, 6, 7951-7959.

545 24. M. L. Stone, E. M. Anderson, K. M. Meek, M. Reed, R. Katahira, F. Chen, R. A. Dixon, G. T.

546 Beckham and Y. Román-Leshkov, *ACS Sustainable Chem. Eng.*, 2018, 6, 11211-11218.

547 25. C. Zhang, C. Jia, Y. Cao, Y. Yao, S. Xie, S. Zhang and H. Lin, *Green Chem.*, 2019, 21, 1668-

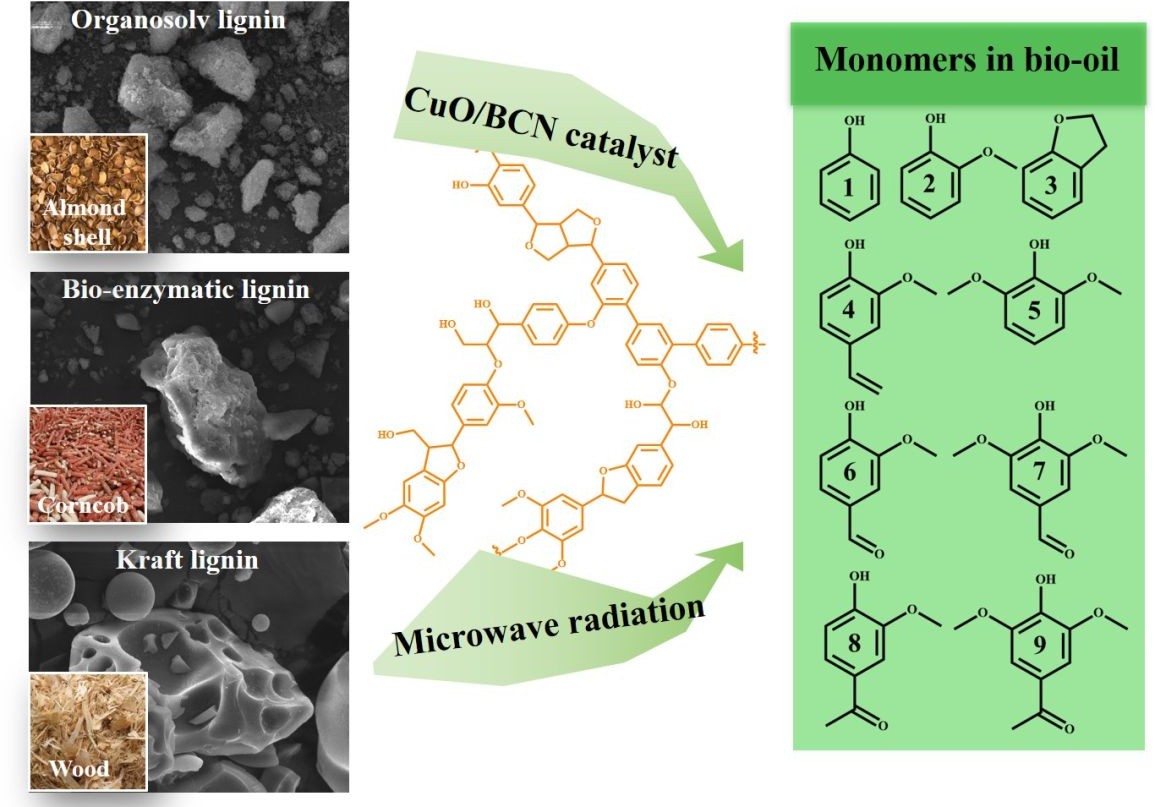
548 1679.

|  |  |  |
| --- | --- | --- |
| 549 | 26. | J. Dai, G. N. Styles, A. F. Patti and K. Saito, *ACS Omega*, 2018, 3, 10433-10441. |
| 550 | 27. | S. S. Chen, T. Maneerung, D. C. W. Tsang, Y. S. Ok and C.-H. Wang, *Chem. Eng. J.*, 2017, |
| 551 |  | 328, 246-273. |
| 552 | 28. | S. S. Chen, I. K. M. Yu, D.-W. Cho, H. Song, D. C. W. Tsang, J.-P. Tessonnier, Y. S. Ok and |
| 553 |  | C. S. Poon, *ACS Sustainable Chem. Eng.*, 2018, 6, 16113-16120. |
| 554 | 29. | I. K. M. Yu, D. C. W. Tsang, A. C. K. Yip, A. J. Hunt, J. Sherwood, J. Shang, H. Song, Y. S. |
| 555 |  | Ok and C. S. Poon, *Green Chem.*, 2018, 20, 2064-2074. |
| 556 | 30. | I. K. M. Yu, X. Xiong, D. C. W. Tsang, Y. H. Ng, J. H. Clark, J. Fan, S. Zhang, C. Hu and Y. |
| 557 |  | S. Ok, *Green Chem.*, 2019, DOI: 10.1039/c9gc00734b. |
| 558 | 31. | L. Cao, I. K. M. Yu, D. W. Cho, D. Wang, D. C. W. Tsang, S. Zhang, S. Ding, L. Wang and Y. |
| 559 |  | S. Ok, *Bioresour. Technol.*, 2019, 273, 251-258. |
| 560 | 32. | R. Panyadee, P. Posoknistakul, W. Jonglertjunya, P. Kim-Lohsoontorn, N. Laosiripojana, B. M. |
| 561 |  | Matsagar, K. C. W. Wu and C. Sakdaronnarong, *ACS Sustainable Chem. Eng.*, 2018, 6, 16896- |
| 562 |  | 16906. |
| 563 | 33. | B. Sedai, C. Díaz-Urrutia, R. T. Baker, R. Wu, L. A. P. Silks and S. K. Hanson, *ACS Catal.*, |
| 564 |  | 2013, 3, 3111-3122. |
| 565 | 34. | A. K. Deepa and P. L. Dhepe, *ACS Catal.*, 2014, 5, 365-379. |
| 566 | 35. | M. Oregui-Bengoechea, N. Miletić, W. Hao, F. Björnerbäck, M. H. Rosnes, J. S. Garitaonandia, |
| 567 |  | N. Hedin, P. L. Arias and T. Barth, *ACS Sustainable Chem. Eng.*, 2017, 5, 11226-11237. |
| 568 | 36. | X. Xiong, I. K. M. Yu, L. Cao, D. C. W. Tsang, S. Zhang and Y. S. Ok, *Bioresour. Technol.*, |
| 569 |  | 2017, 246, 254-270. |
| 570 | 37. | Y. Shao, K. Sun, Q. Li, Q. Liu, S. Zhang, Q. Liu, G. Hu and X. Hu, *Green Chem.*, 2019, 21, |
| 571 |  | 4499-4511. |
| 572 | 38. | B. Sedai, C. Díaz-Urrutia, R. T. Baker, R. Wu, L. A. P. Silks and S. K. Hanson, *ACS Catal.*, |
| 573 |  | 2011, 1, 794-804. |
| 574 | 39. | X. Ren, P. Wang, X. Han, G. Zhang, J. Gu, C. Ding, X. Zheng and F. Cao, *ACS Sustainable* |
| 575 |  | *Chem. Eng.*, 2017, 5, 6548-6556. |
| 576 | 40. | M. Zhou, B. K. Sharma, P. Liu, H. Xia, J. Xu and J.-c. Jiang, *ACS Sustainable Chem. Eng.*, |
| 577 |  | 2018, 6, 11519-11528. |
| 578 | 41. | S. Chen, R. Xu, J. Liu, X. Zou, L. Qiu, F. Kang, B. Liu and H. M. Cheng, *Adv. Mater.*, 2019, |
| 579 |  | 31, e1804810. |
| 580 | 42. | J. T. Grant, C.A. Carrero, F. Goeltl, J. Venegas, P. Mueller, S. P. Burt, S. E. Specht, W. P. |
| 581 |  | McDermott, A. Chieregato and I. Hermans, *Science*, 2016, 354, 1570–1573. |
| 582 | 43. | C. N. R. Rao and M. Chhetri, *Adv. Mater.*, 2019, 31, e1803668. |
| 583 | 44. | M. Fan, J. Wu, J. Yuan, L. Deng, N. Zhong, L. He, J. Cui, Z. Wang, S. K. Behera, C. Zhang, J. |
| 584 |  | Lai, B. I. Jawdat, R. Vajtai, P. Deb, Y. Huang, J. Qian, J. Yang, J. M. Tour, J. Lou, C. W. Chu, |
| 585 |  | D. Sun and P. M. Ajayan, *Adv. Mater.*, 2019, 31, e1805778. |
| 586 | 45. | F. Guo, P. Yang, Z. Pan, X. N. Cao, Z. Xie and X. Wang, *Angew. Chem., Int. Ed.*, 2017, 56, |
| 587 |  | 8231-8235. |
| 588 | 46. | T. Jin, X. Sang, R. R. Unocic, R. T. Kinch, X. Liu, J. Hu, H. Liu and S. Dai, *Adv. Mater.*, 2018, |
| 589 |  | 30, e1707512. |
| 590 | 47. | W. Zhu, Z. Wu, G. S. Foo, X. Gao, M. Zhou, B. Liu, G. M. Veith, P. Wu, K. L. Browning, H. |
| 591 |  | N. Lee, H. Li, S. Dai and H. Zhu, *Nat. Commun.*, 2017, 8, 15291. |
| 592 | 48. | L. Yao, C. Chen, C. G. Yoo, X. Meng, M. Li, Y. Pu, A. J. Ragauskas, C. Dong and H. Yang, |

|  |  |  |
| --- | --- | --- |
| 593 |  | *ACS Sustainable Chem. Eng.*, 2018, 6, 14767-14773. |
| 594 | 49. | L. Shuai, M. T. Amiri, Y. M. Questell-Santiago, F. Heroguel, Y. Li, H. Kim, R. Meilan, C. |
| 595 |  | Chapple, J. Ralph and J. S. Luterbacher, *Science*, 2016, 354, 329-333. |
| 596 | 50. | B.-C. Zhao, B.-Y. Chen, S. Yang, T.-Q. Yuan, A. Charlton and R.-C. Sun, *ACS Sustainable* |
| 597 |  | *Chem. Eng.*, 2016, 5, 1113-1122. |
| 598 | 51. | J.-L. Wen, S.-L. Sun, B.-L. Xue and R.-C. Sun, *Materials*, 2013, 6, 359-391. |
| 599 | 52. | W. Lei, V. N. Mochalin, D. Liu, S. Qin, Y. Gogotsi and Y. Chen, *Nat. Commun.*, 2015, 6, 8849. |
| 600 | 53. | L. Zhao, Y. Zhang, L. B. Huang, X. Z. Liu, Q. H. Zhang, C. He, Z. Y. Wu, L. J. Zhang, J. Wu, |
| 601 |  | W. Yang, L. Gu, J. S. Hu and L. J. Wan, *Nat. Commun.*, 2019, 10, 1278. |
| 602 | 54. | W. Zhu, X. Gao, Q. Li, H. Li, Y. Chao, M. Li, S. M. Mahurin, H. Li, H. Zhu and S. Dai, *Angew.* |
| 603 |  | *Chem., Int. Ed.*, 2016, 55, 10766-10770. |
| 604 | 55. | S. Henke, A. Schneemann, A. Wutscher and R. A. Fischer, *J. Am. Chem. Soc.*, 2012, 134, 9464- |
| 605 |  | 9474. |
| 606 | 56. | S. Konar, H. Kalita, N. Puvvada, S. Tantubay, M. K. Mahto, S. Biswas and A. Pathak, *J. Catal.*, |
| 607 |  | 2016, 336, 11-22. |
| 608 | 57. | Y.-C. Chen, Z.-J. Wu and Y.-K. Hsu, *J. Catal.*, 2019, 370, 224-231. |
| 609 | 58. | L. Pino, A. Vita, M. Laganà and V. Recupero, *Appl. Catal. B*, 2014, 148-149, 91-105. |
| 610 | 59. | W. H. Wanna, R. Ramu, D. Janmanchi, Y.-F. Tsai, N. Thiyagarajan and S. S. F. Yu, *J. Catal.*, |
| 611 |  | 2019, 370, 332-346. |
| 612 | 60. | Z. He, H. Lin, P. He and Y. Yuan, *J. of Catal.*, 2011, 277, 54-63. |
| 613 | 61. | S. Beniwal, J. Hooper, D. P. Miller, P. S. Costa, G. Chen, S. Y. Liu, P. A. Dowben, E. C. Sykes, |
| 614 |  | E. Zurek and A. Enders, *ACS Nano*, 2017, 11, 2486-2493. |
| 615 | 62. | S. Shang, P.-P. Chen, L. Wang, Y. Lv, W.-X. Li and S. Gao, *ACS Catalysis*, 2018, 8, 9936- |
| 616 |  | 9944. |
| 617 | 63. | H. Luo and M. M. Abu-Omar, *Green Chem.*, 2018, 20, 745-753. |
| 618 | 64. | C. K. Nitsos, K. A. Matis and K. S. Triantafyllidis, *ChemSusChem*, 2013, 6, 110-122. |
| 619 | 65. | J. Ho Seo, H. Jeong, H. W. Lee, C. S. Choi, J. H. Bae, S. M. Lee and Y. S. Kim, *Bioresour.* |
| 620 |  | *Technol.*, 2019, 275, 368-374. |
| 621 | 66. | H.-M. Wang, B. Wang, J.-L. Wen, T.-Q. Yuan and R.-C. Sun, *ACS Sustainable Chem. Eng.*, |
| 622 |  | 2017, 5, 11618-11627. |
| 623 | 67. | G. Wang, X. Liu, B. Yang, C. Si, A. M. Parvez, J. Jang and Y. Ni, *ACS Sustainable Chem. Eng.*, |
| 624 |  | 2019, 7, 10112-10120. |
| 625 | 68. | C. Li, X. Zhao, A. Wang, G. W. Huber and T. Zhang, *Chem. Rev.*, 2015, 115, 11559-11624. |
| 626 | 69. | K. Friedel Ortega, R. Arrigo, B. Frank, R. Schlögl and A. Trunschke, *Chem. Mater.*, 2016, 28, |
| 627 |  | 6826-6839. |
| 628 | 70. | S. Zhao, M. Liu, L. Zhao and L. Zhu, *Ind. Eng. Chem. Res.*, 2018, 57, 5241-5249. |
| 629 | 71. | A. J. Ragauskas, G. T. Beckham, M. J. Biddy, R. Chandra, F. Chen, M. F. Davis, B. H. Davison, |
| 630 |  | R. A. Dixon, P. Gilna, M. Keller, P. Langan, A. K. Naskar, J. N. Saddler, T. J. Tschaplinski, G. |
| 631 |  | A. Tuskan and C. E. Wyman, *Science*, 2014, 344, 1246843. |
| 632 | 72. | I. Weinrauch, I. Savchenko, D. Denysenko, S. M. Souliou, H. H. Kim, M. Le Tacon, L. L. |
| 633 |  | Daemen, Y. Cheng, A. Mavrandonakis, A. J. Ramirez-Cuesta, D. Volkmer, G. Schutz, M. |
| 634 |  | Hirscher and T. Heine, *Nat. Commun.*, 2017, 8, 14496. |
| 635 | 73. | Z.-z. Zhou, M. Liu and C.-J. Li, *ACS Catal.*, 2017, 7, 3344-3348. |
| 636 | 74. | Y. Xie, J. Wu, G. Jing, H. Zhang, S. Zeng, X. Tian, X. Zou, J. Wen, H. Su, C.-J. Zhong and P. |

|  |  |  |
| --- | --- | --- |
| 637 |  | Cui, *Appl. Catal. B*, 2018, 239, 665-676. |
| 638 | 75. | A. Davó-Quiñonero, D. Lozano-Castelló and A. Bueno-López, *Appl. Catal. B*, 2017, 217, 459- |
| 639 |  | 465. |
| 640 | 76. | G. Yin, Z. Huo, X. Zeng, G. Yao, Z. Jing and F. Jin, *Ind. Eng. Chem. Res.*, 2014, 53, 7856- |
| 641 |  | 7865. |
| 642 | 77. | M. Wang, M. Liu, H. Li, Z. Zhao, X. Zhang and F. Wang, *ACS Catal.*, 2018, 8, 6837-6843. |
| 643 | 78. | M. Wang, J. Lu, X. Zhang, L. Li, H. Li, N. Luo and F. Wang, *ACS Catal.*, 2016, 6, 6086-6090. |

## Graphical Abstract



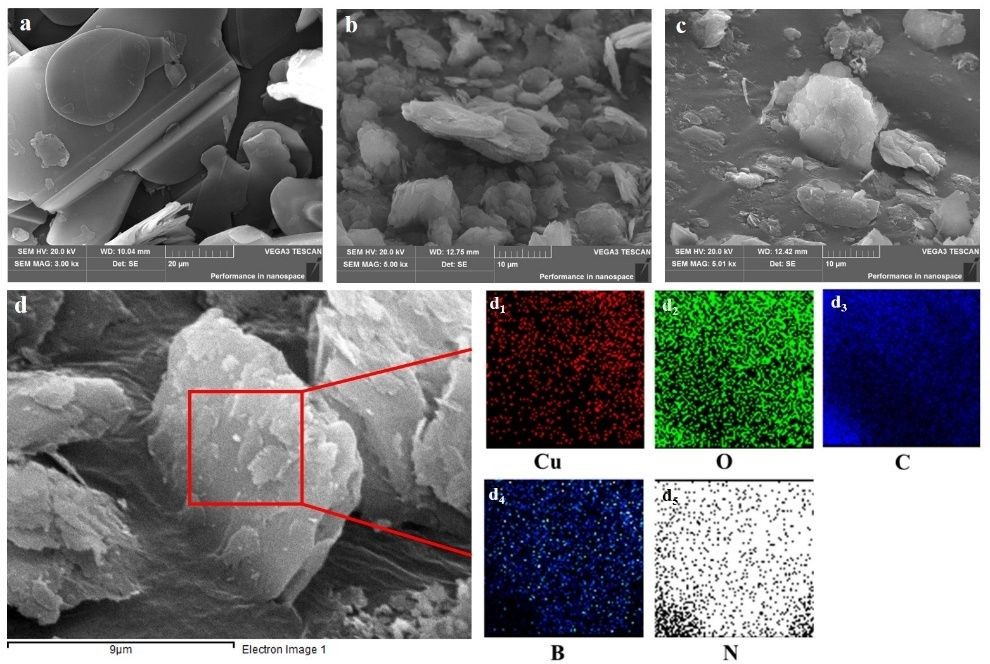


Fig. 1. SEM images of (a) BN, (b) BCN and (c) CuO/BCN catalyst and (d) elemental mapping results of CuO/BCN catalyst.

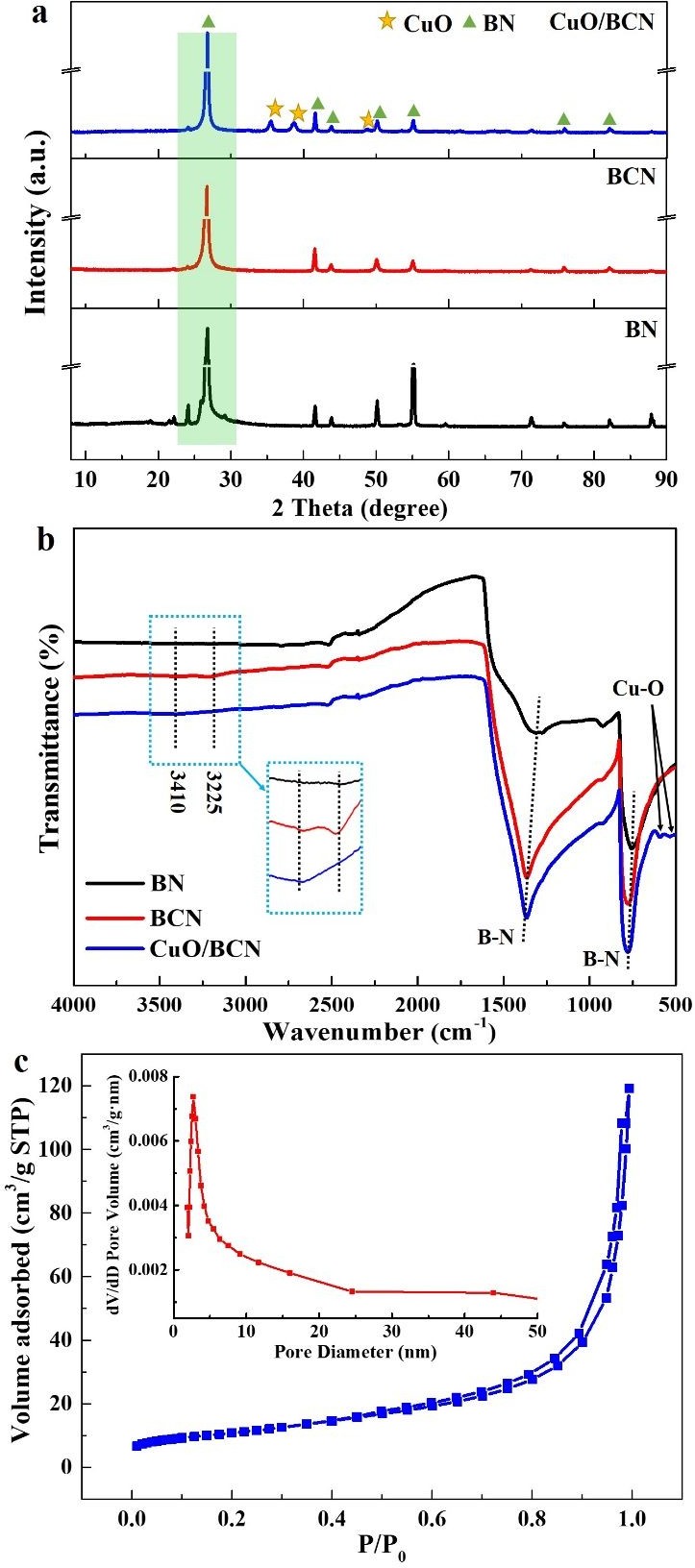


Fig. 2. (a) XRD patterns and (b) FTIR spectra of various samples, (c) N2 adsorption-desorption isotherms of CuO/BCN catalyst.

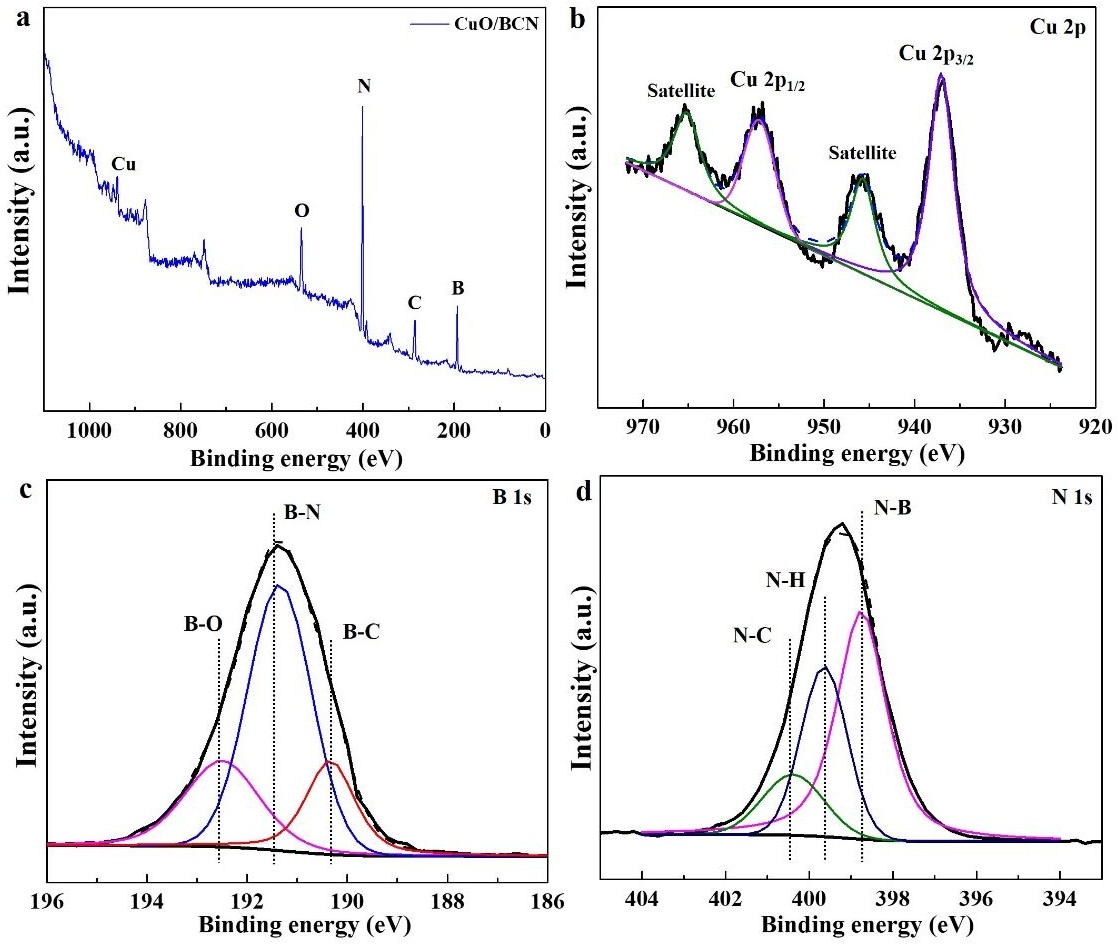


Fig. 3. XPS spectra of CuO/BCN catalyst (a) survey spectrum, (b) Cu 2p, (c) B 1s, and (d) N 1s.

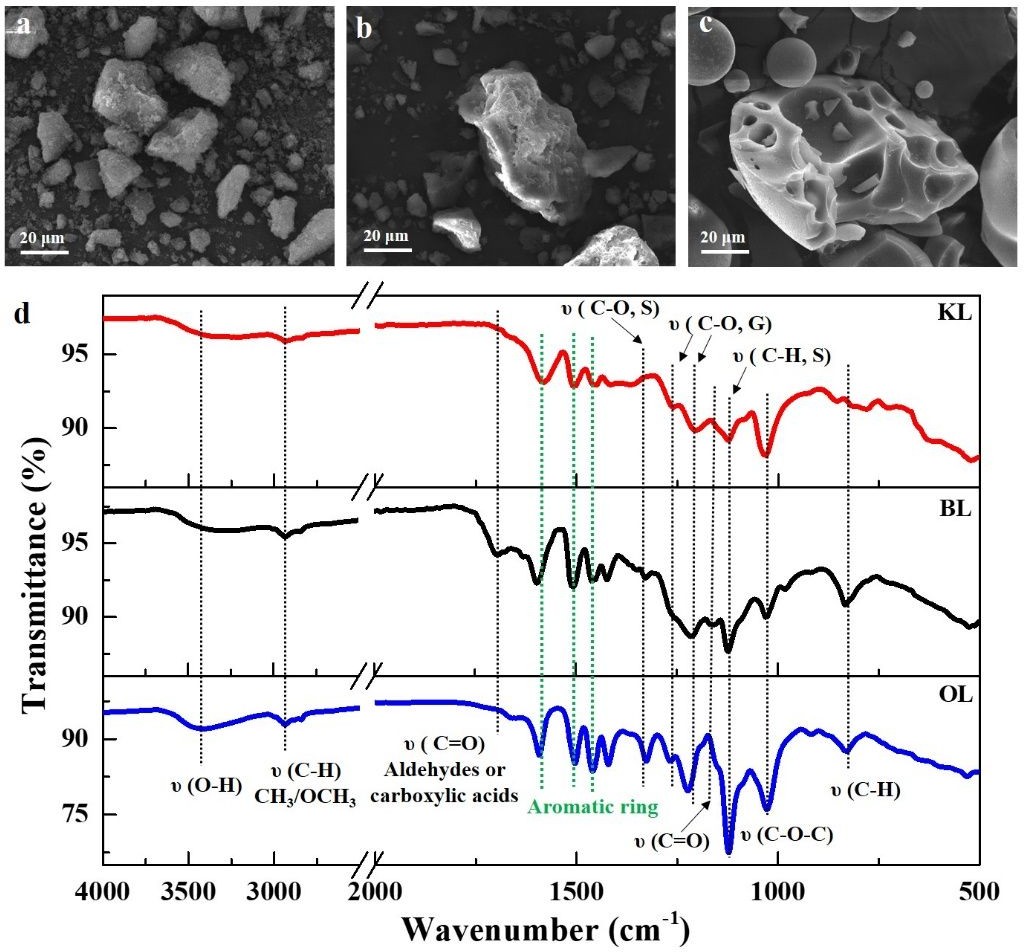


Fig. 4. SEM images of (a) OL; (b) BL and (c) KL samples; (d) FTIR spectra of various types of lignin.

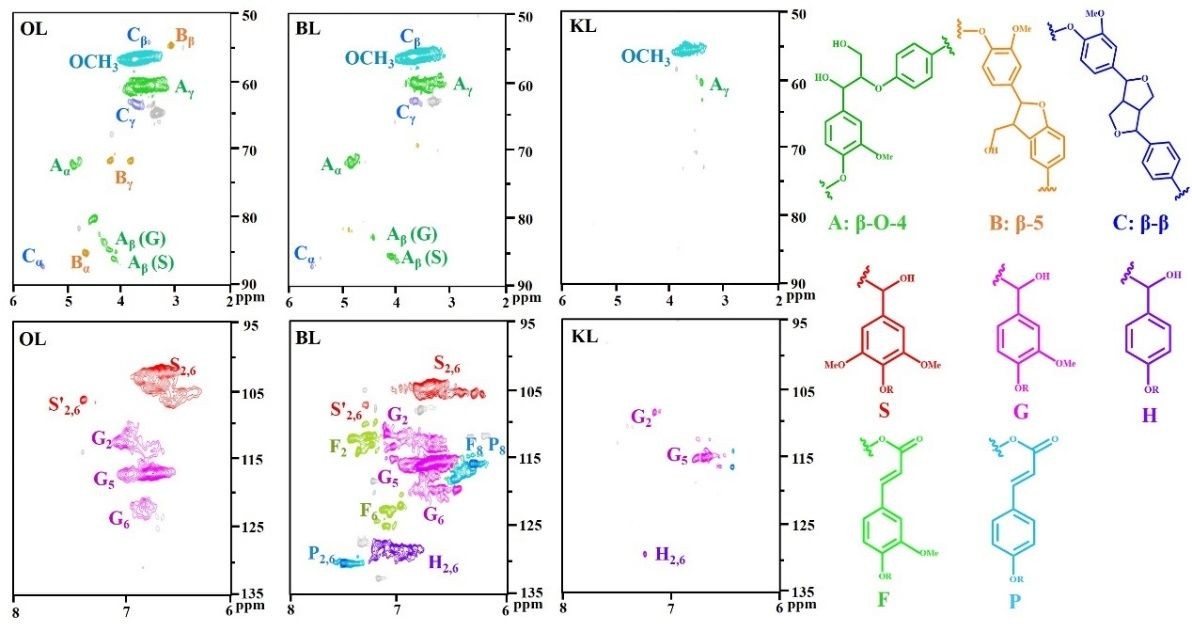


Fig. 5. Side-chain and aromatic region in 2D HSQC NMR of various lignin samples. Main substructures identified by 2D NMR: A: β-O-4 linkage; B: β-5 linkage; C: β-β linkage; S: syringyl unit; G: guaiacyl unit; H: p-hydroxyphenyl unit; F: ferulic acid unit; and P: p-coumaric acid unit.

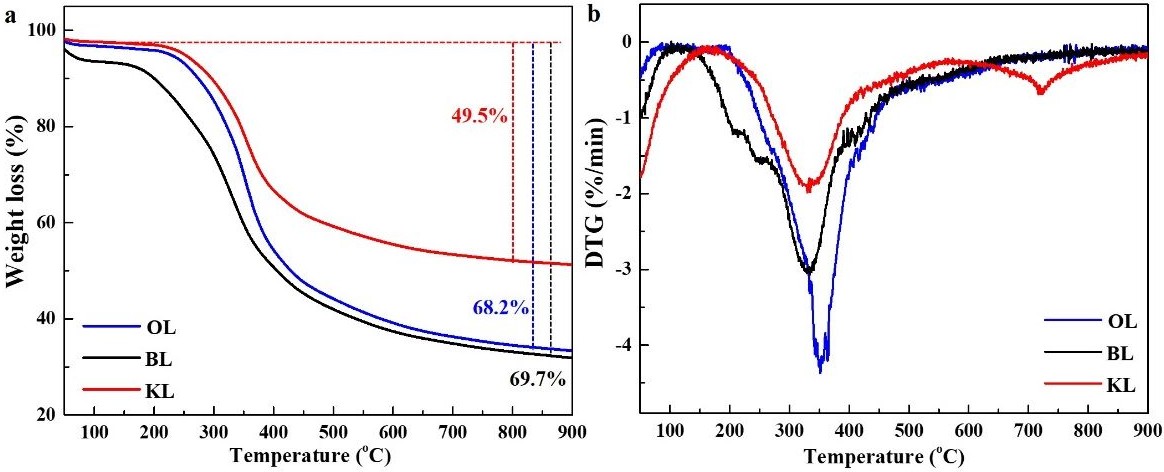


Fig. 6. (a) TGA and (b) DTG profiles of three types of lignins.

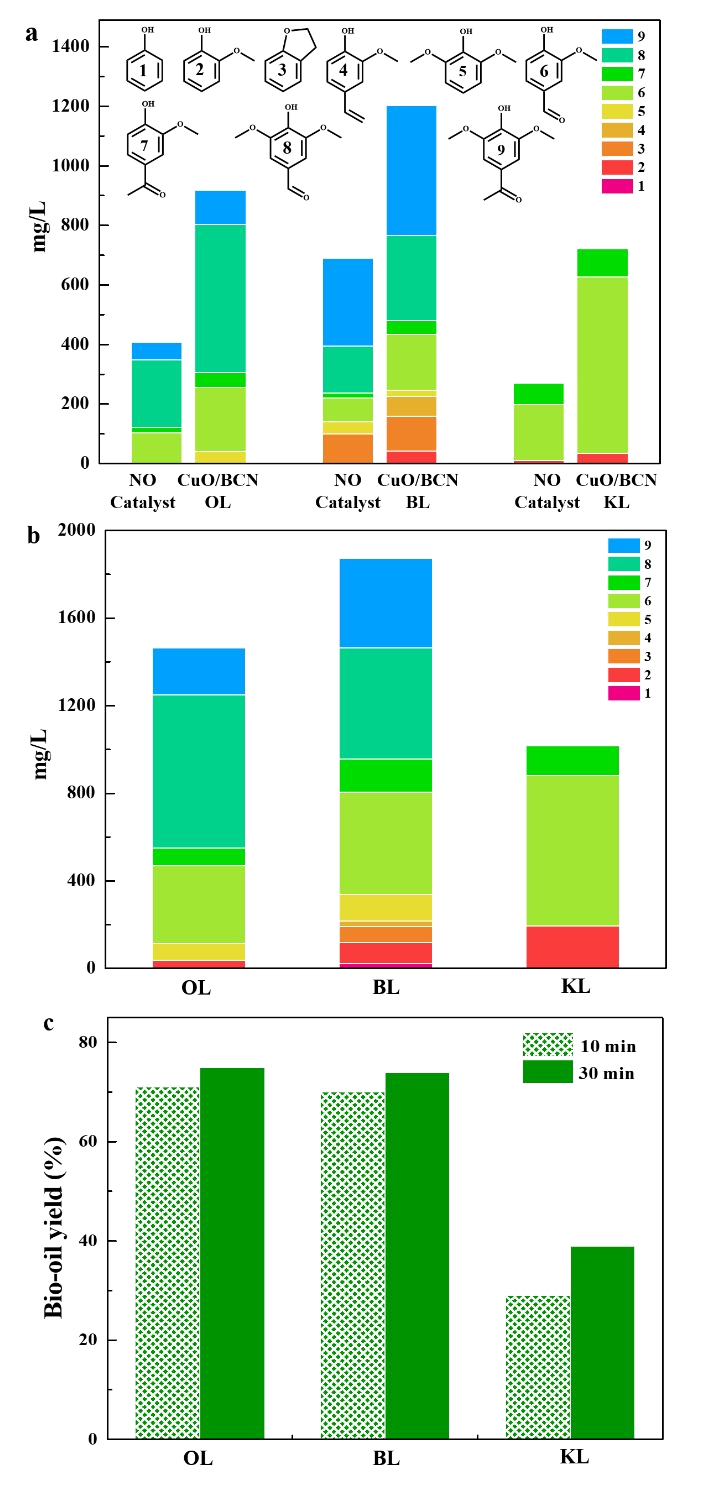


Fig. 7. Monomeric yields at (a) 10 min and (b) 30 min, and (c) yields of bio-oil from depolymerization of three types of lignin. Reaction conditions: 200 oC, 0.2 g lignin, 10 mL solution and 0.1 g CuO/BCN catalyst.

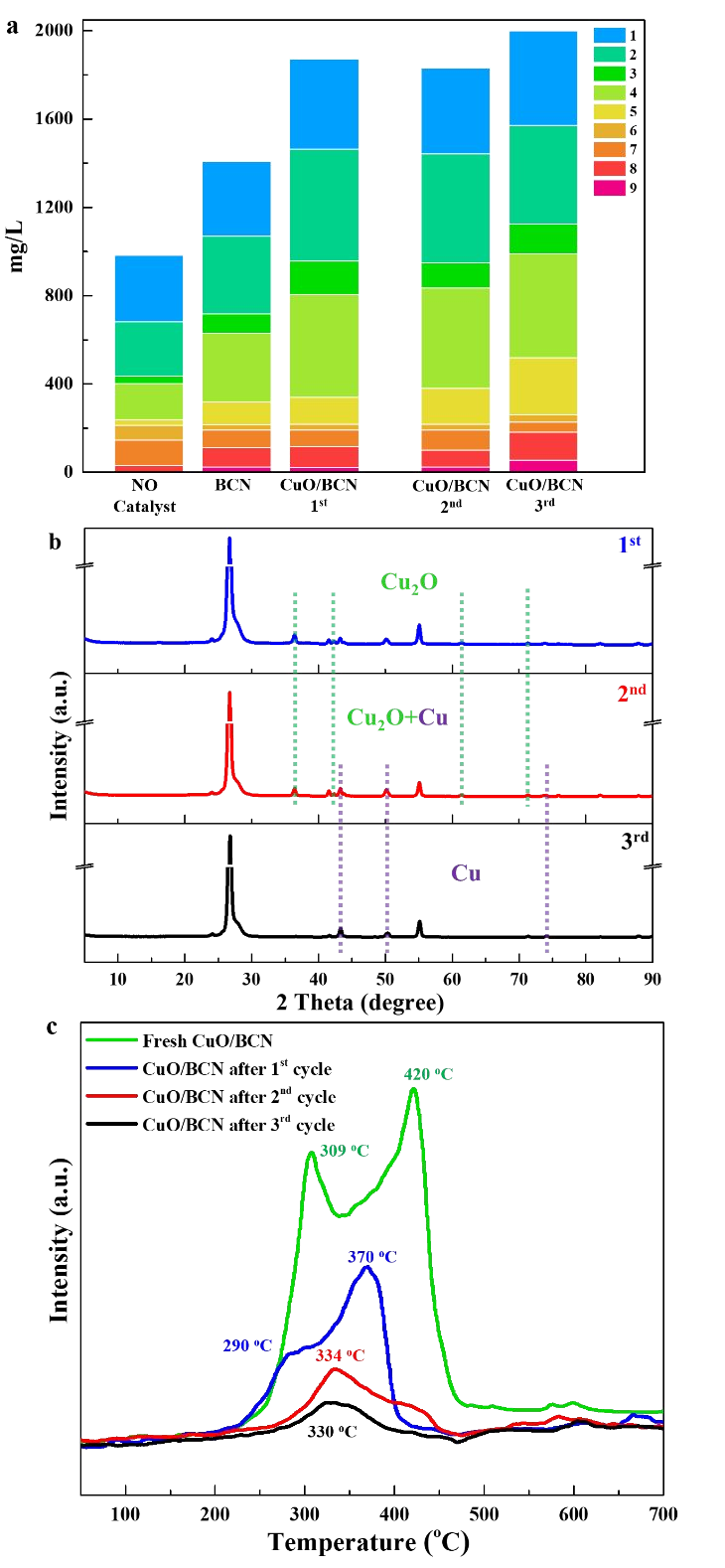
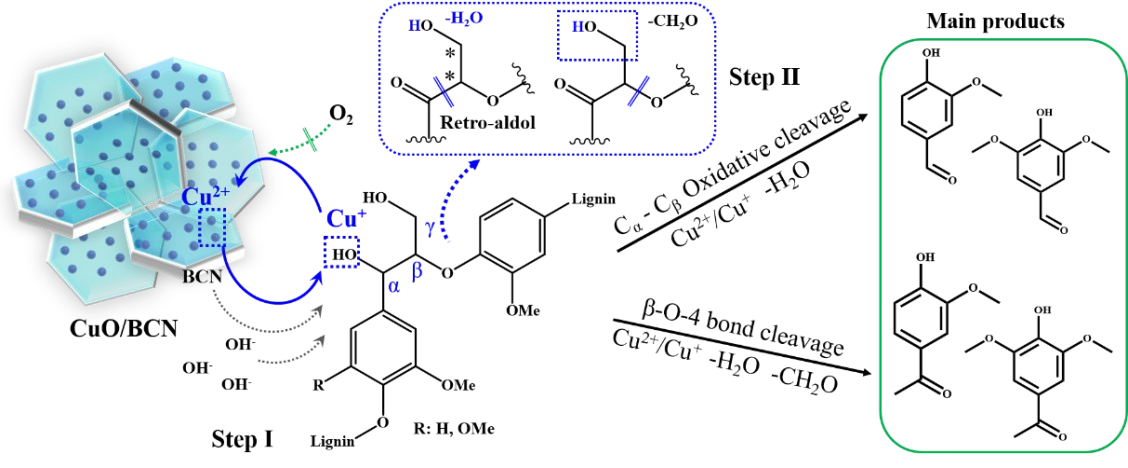


Fig. 8. (a) Recyclability test for the depolymerization of BL over CuO/BCN catalyst. Reaction conditions: 200 oC, 0.2 g BL, 10 mL solution and 0.1 g catalyst, 30 min. (b) XRD patterns, and (c) H2-TPR profiles of the fresh and recovered catalysts after each cycle.



Scheme 1. Proposed reaction mechanisms for the oxidation of native type lignin.

Table 1. Quantification of structures and interunit linkages of lignin.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Lignin Sa Ga Ha S/G | | | | | β-O-4a | β-5a | β-βa | β-O-4b | β-5b | β-βb |
| OL | 57.6% | 42.4% | ND | 1.35 | 11.2% | 8.3% | 4.0% | 47.6% | 35.3% | 17.1% |
| BL | 34.2% | 49.2% | 16.6% | 0.70 | 19.2% | 3.4% | Trace | 84.9% | 15.1% | Trace |
| KL | ND | 80.3% | 19.7% | - | ND | ND | ND | ND | ND | ND |

a Results expressed per 100 Ar based on quantitative 2D-HSQC spectra. b Amount of specific functional group was expressed a percentage of β-O-4+β-5+β-β. ND: Not Detect.

Table 2. The yielda of aromatic monomers from depolymerizationb of various lignin.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Entry | 1  H | 2  G | 3  G | 4  G | 5  S | 6  G | 7  G | 8  S | 9  S | Total |
| OL 10 min | - | - | - | - | 0.25 | 1.07 | 0.26 | 2.49 | 0.58 | 4.49 |
| OL 30 min | - | 0.19 | - | - | 0.37 | 1.78 | 0.40 | 3.50 | 1.07 | 7.32 |
| BL 10 min | - | 0.21 | 0.58 | 0.33 | 0.11 | 0.93 | 0.23 | 1.43 | 2.19 | 6.02 |
| BL 30 min (1st) | 0.11 | 0.48 | 0.37 | 0.13 | 0.61 | 2.34 | 0.76 | 2.54 | 2.05 | 9.37 |
| KL 10 min | - | 0.17 | - | - | - | 2.96 | 0.47 | - | - | 3.61 |
| KL 30 min | - | 0.97 | - | - | - | 3.34 | 0.68 | - | - | 5.08 |
| BL 30 min (2nd) | 0.12 | 0.38 | 0.45 | 0.13 | 0.81 | 2.27 | 0.58 | 2.47 | 1.94 | 9.16 |
| BL 30 min (3rd) | 0.18 | 0.64 | 0.22 | 0.17 | 1.30 | 2.36 | 0.66 | 2.25 | 2.14 | 10.00 |

a wt%, based on the initial lignin. b Reaction conditions: 10 mL solution, 0.1 g CuO/BCN catalyst.

**Supporting Information:**

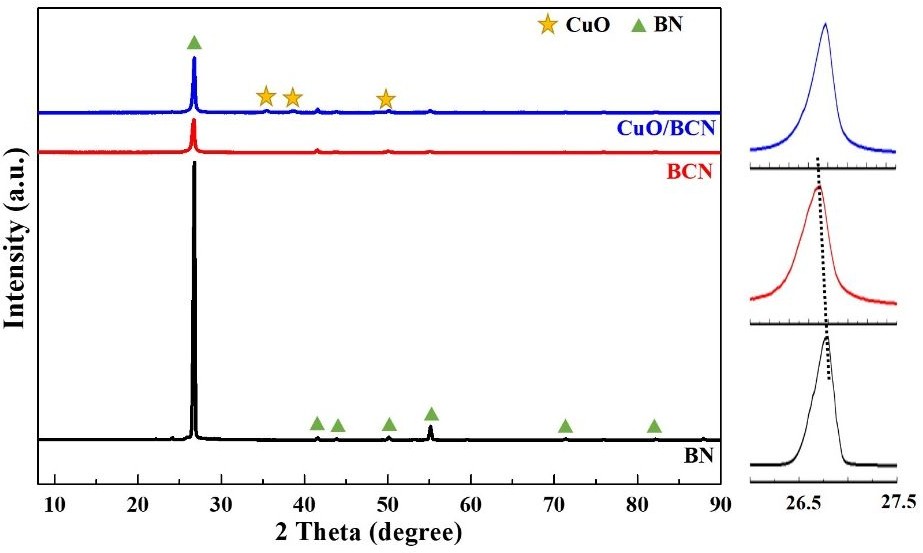


Fig. S1. XRD patterns and enlarged regions of the catalysts.

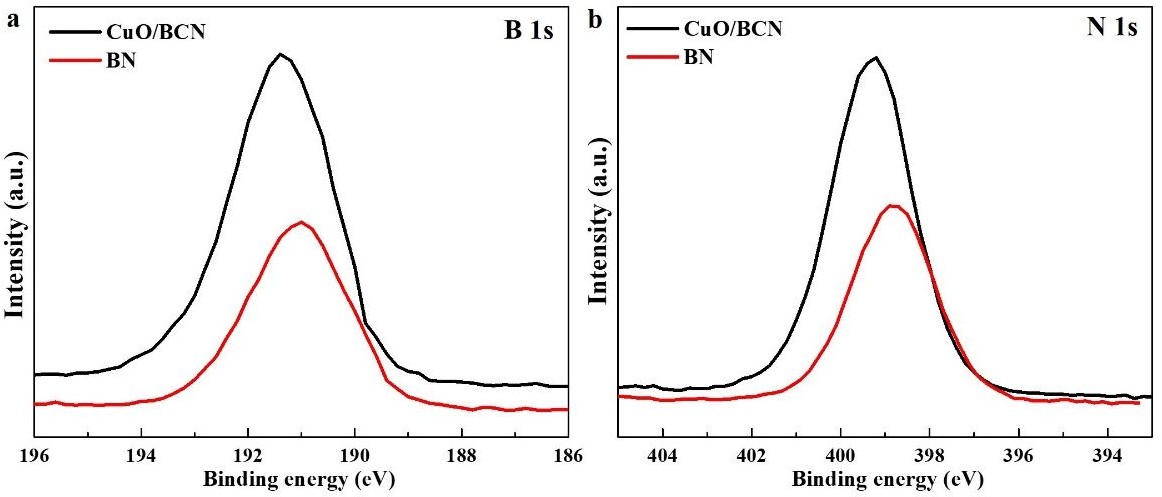


Fig. S2. XPS spectra of BN and CuO/BCN catalyst: (a) B 1s and (b) N 1s.

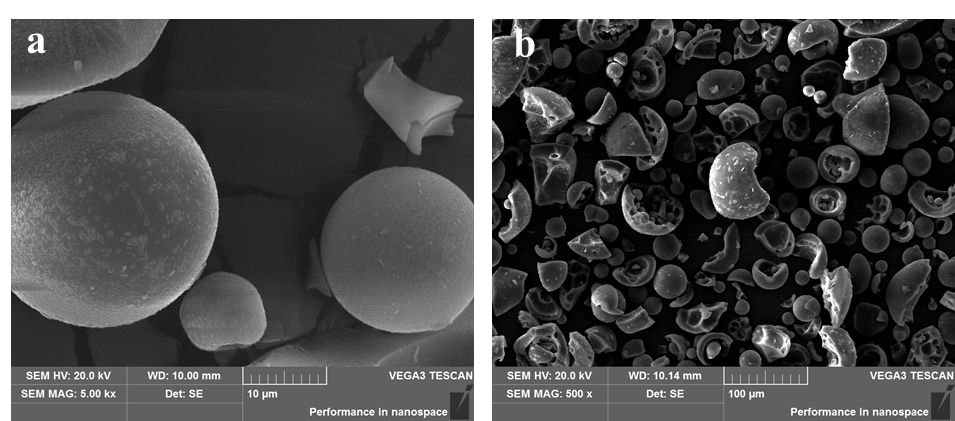


Fig. S3. SEM images of KL sample (horizontal bars indicated 10 µm and 100 µm).

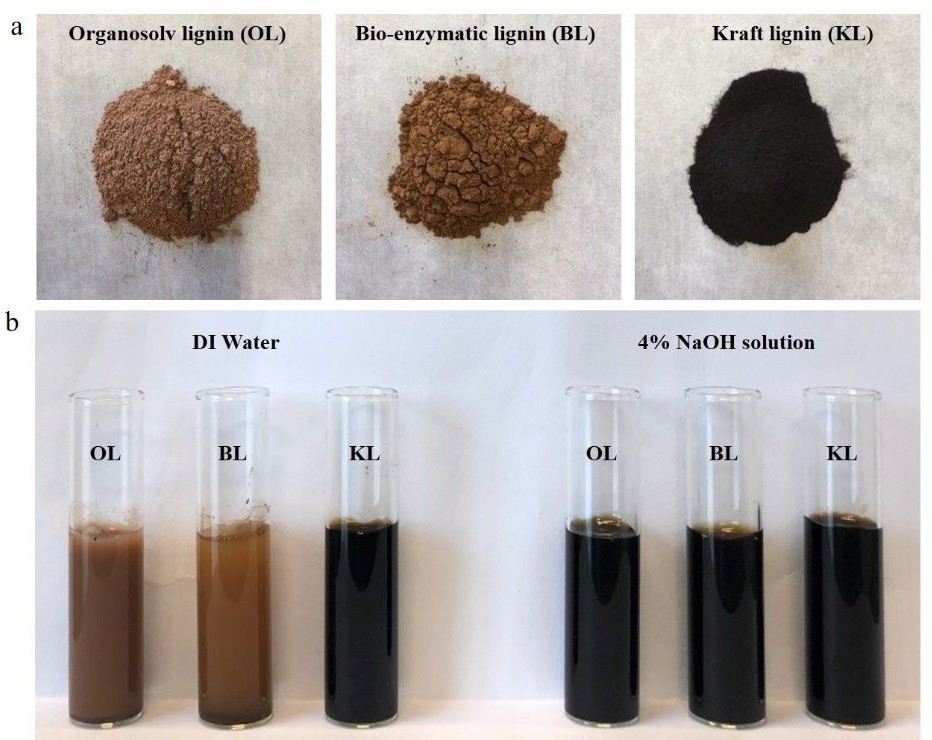


Fig. S4. (a) Photographs of various types of lignin with diffierent extraction methods and (b) solubility of various lignins in DI water and 4% NaOH solution (40 mg lignin, 2 mL solution).

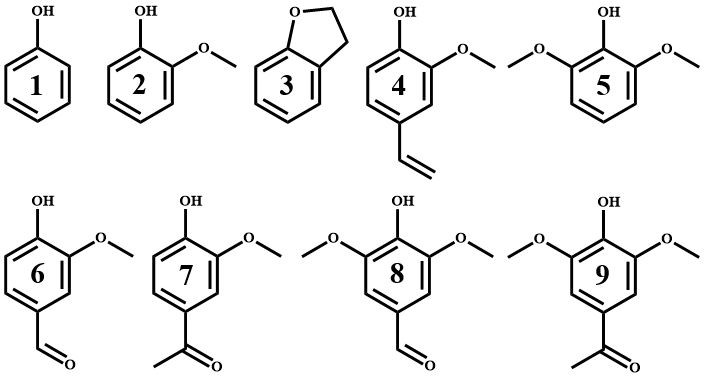


Fig. S5. Chemical structures of main aromatic monomers from depolymerization of lignin (1: Phenol; 2: Guaiacol; 3: 2,3-Dihydrobenzofuran; 4: 2-Methoxy-4-vinylphenol; 5: Syringol; 6:

Vanillin; 7: Acetovanillone; 8: Syringaldehyde; 9: Acetosyringone).

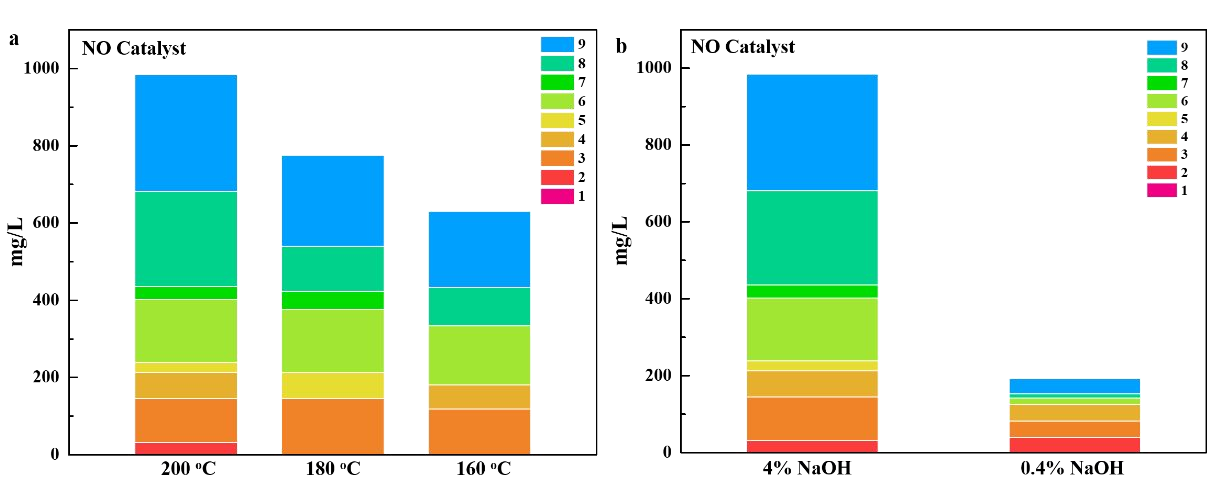


Fig. S6. (a) Temperature and (b) NaOH concentration effect on monomers yields from the depolymerization of BL (reaction conditions: 0.2 g lignin, 10 mL solution, 30 min).

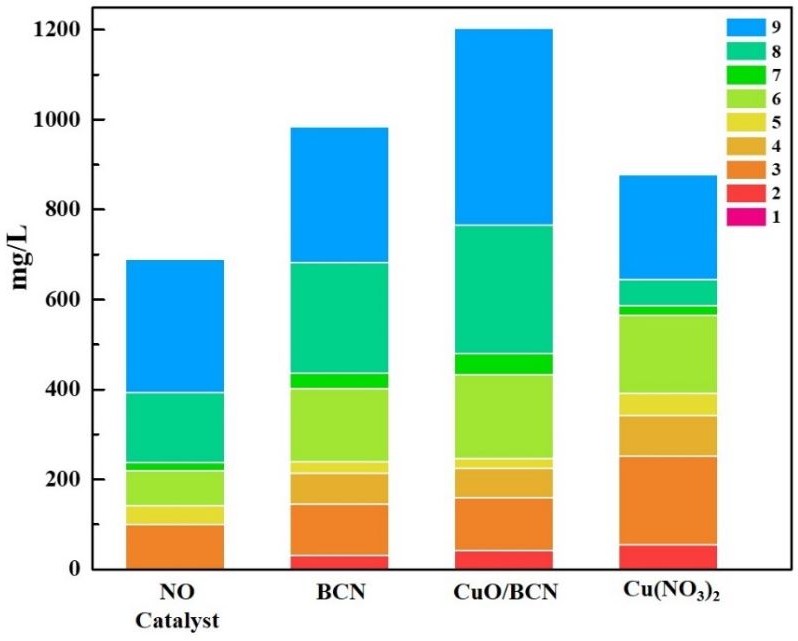


Fig. S7. Monomers yields from the depolymerization of BL over various catalysts (reaction conditions: 200 oC, 0.2 g lignin, 10 mL solution, and 0.1 g CuO/BCN catalyst/30 mg Cu(NO3)2·3H2O, 10 min).

During the reaction, the Cu(NO3)2·3H2O could be transformed into CuO species in the alkaline solution at 200 oC. The CuO loading of CuO/BCN catalyst was 10 wt%, Cu(NO3)2·3H2O (30 mg) as the catalyst was explored for comparison.

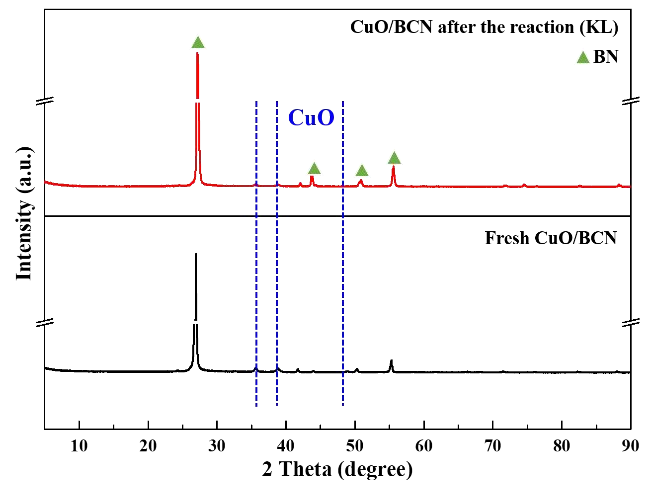


Fig. S8. XRD patterns of the catalysts after the conversion of KL.



Fig. S9. Monomers yields from the depolymerization of BL by microwave and hydrothermal process (reaction condition: 0.2 g lignin, 10 mL solution, 0.1 g CuO/BCN catalyst, 30 min).

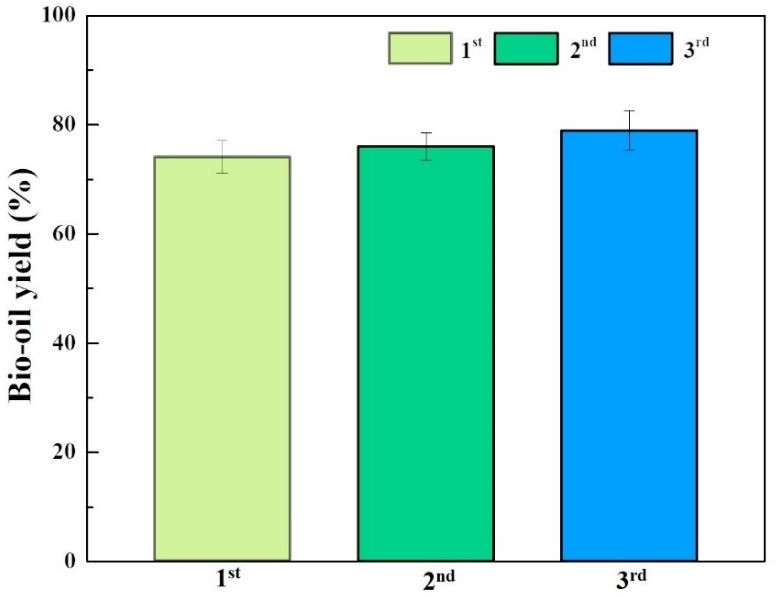


Fig. S10. Bio-oil yield from depolymerization of BL (reaction conditions: 200 oC, 0.2 g lignin, 10 mL solution, 0.1 g recovered catalyst, 30 min).

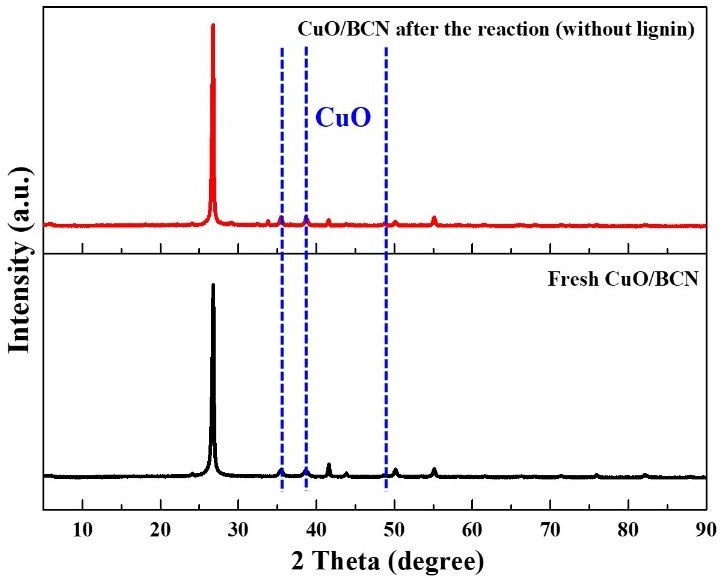


Fig. S11. XRD patterns of the catalysts.

We evaluated the spent catalyst by XRD (Fig. S11), and the experimental evidence indicated that no sulphur-containing species were detected after the depolymerization of KL. The sulphur species should be incorporated in the KL structure as the sulphur-containing functional groups would be difficult to remove at the tested temperature. Therefore, the lower yield of monomer and bio-oil from KL was mainly related to the its inert structure rather than catalyst deactivation.

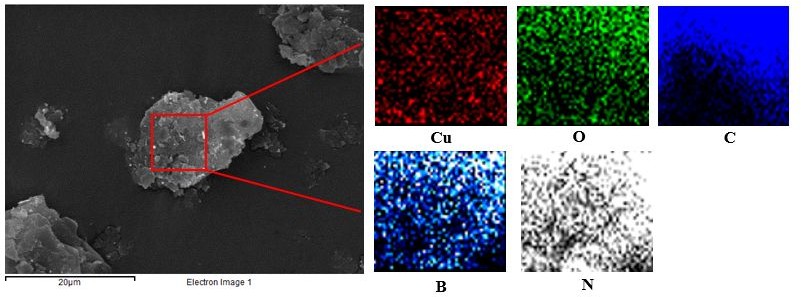


Fig. S12. SEM images and elemental mapping results of CuO/BCN catalyst after three cycles.

Table S1. Physicochemical properties of various catalysts.

|  |  |  |  |
| --- | --- | --- | --- |
| Sample | BET (m2/g) | Pore Volume (cm³/g) | Pore Diameter (nm) |
| BN | 2.1 | 0.0082 | 1.5 |
| BCN | 45 | 0.19 | 2.4 |
| CuO/BCN | 39 | 0.18 | 4.0 |

Note: pore diameter was computed from the desorption branch of the isotherm using the BJH method.

Table S2. GPC analysis of various types of lignin.

|  |  |  |  |
| --- | --- | --- | --- |
| Lignin | Mw (Da) | Mn (Da) | Polydispersity Index |
| OL | 1935 | 1311 | 1.48 |
| BL | 899 | 762 | 1.18 |
| KLa | ~10000 | - | - |

a results obtained from Sigma-Aldrich.

The harsh treatment conditions could lead to a significant decrease or even complete loss of β- O-4 structural units in KL, together with an increase of C-C linkages, which will alter the thermal stability and pyrolytic behaviour of the recovered lignin.

Table S3. Element analysis of various types of lignin (wt%).

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Lignin | N | C | H | S | O |
| OL | 0.17 | 56.11 | 5.57 | 0 | 38.15 |
| BL | 0.85 | 56.38 | 5.68 | 0 | 37.09 |
| KL | 0.11 | 48.86 | 5.26 | 3.06 | 42.71 |