Green Chemistry

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Cite this: *Green Chem.*, 2020, **22**, 4676

Two-step conversion of Kraft lignin to nylon precursors under mild conditions†

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Received 6th April 2020,
Accepted 27th June 2020

DOI: 10.1039/d0gc01220c

rsc.li/greenchem

This study explores the valorization of Kraft lignin by conversion into nylon precursors in a two-step process. First, lignin was depolymerized in dilute alkaline aqueous solution under atmospheric N_2 at 200 °C to give guaiacol with high selectivity (>80%) with a total monomer production of 13% based on lignin input. Solution and solid state NMR analyses and reactions of model compounds indicated that depolymerization took place *via* cleavage of β-O-4 bonds in lignin. In the second step, lignin-derived guaiacol was selectively converted to the nylon precursors cyclohexanol/cyclohexanone (KA oil) using Ru/C catalyst under 1 bar H_2 and 150 °C. This two-step process constitutes a low-temperature and low-pressure pathway for producing value-added chemicals from lignin using water as the reaction solvent.

Introduction

Lignin accounts for 10–35% of lignocellulosic biomass[1,2] and is the largest renewable source of aromatic building blocks in nature. Remarkably, it is also a massive industrial waste product. Indeed, the world's paper industry alone generates about 50 million tons of lignin waste annually,[3–5] with Kraft lignin being the predominant type.[6] Despite its potential as starting material for many chemicals and fuels,[7] the main method of lignin disposal is direct combustion with limited economic benefit and high carbon footprint.[8,9] This has triggered the development of processes that pursue the depolymerization of lignin into value-added small molecules.

The processes, which aim to break the C–C or C–O bonds in lignin structure include pyrolysis,[10,11] hydrolysis,[12] hydrogenolysis,[13–15] solvolysis,[16–18] and oxidation.[19–21] Among these, hydrogenolysis and oxidation of β-O-4,[15,22,23] β-1,[24] β-5,[24–26] and 5–5′[25,27] linkages have been abundantly investigated, both in lignin and model compounds. One of the challenges associated with these reactions is that they operate under harsh and environmentally challenging conditions, such as high temperatures or use of organic solvents like methanol,[13,15,28] dioxane,[29,30] and tetrahydrofuran (THF).[28,31] In addition, hydrogenolysis reactions typically require high H_2 pressures (>10 bar)[32,33] that imply high reactor cost and safety risks. Moreover, sulfur present in Kraft lignin can cause deactivation of the metal catalysts required for hydrogenolytic depolymerization.[34]

Whereas the solubility of lignin in water is low,[35] it can be significantly improved in alkaline media due to deprotonation of phenolic hydroxyls.[6] In fact, alkaline conditions are typically used in the pulping processes to isolate lignin from cellulose.[36–38] Furthermore, concentrated NaOH or KOH (0.5–4 M) can also cleave C–O or C–C bonds in lignin,[21,39,40] and there are even some examples of lignin conversion in dilute alkaline solutions.[16,41]

Another challenge in lignin depolymerization is posed by its heterogeneous structure, which results in low selectivity to a single type of product and therefore demands energy-intensive separations of complex mixtures. For example, more than three dozen compounds were detected when depolymerizing Kraft lignin at 380 °C.[42] Whereas recent efforts have focused on converting lignin derivatives to industrially relevant compounds with high selectivity,[43–47] only few of them involve processes that start from the raw lignin streams.[48]

In this study, we propose a two-step pathway for converting Kraft lignin to nylon precursors (Fig. 1). In the first step, Kraft

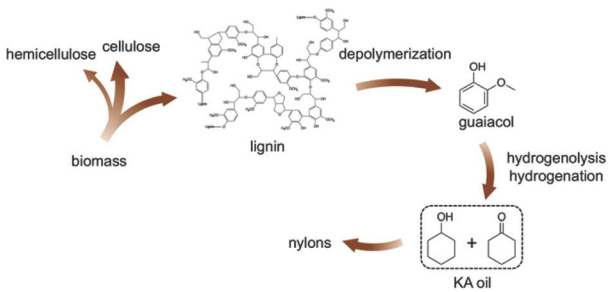

Fig. 1 Proposed pathway for producing nylons from lignin.

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† Electronic supplementary information (ESI) available: Experimental methods, chromatograms, additional spectra and tables. See DOI: 10.1039/d0gc01220c

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lignin is selectively converted into guaiacol in dilute alkaline solutions under 1 bar N_2. In the second step, guaiacol is upgraded to a cyclohexanone-cyclohexanol mixture, also known as KA oil, an industrial precursor for nylon.[49,50] To our best knowledge, this is the first time that KA oil is generated from lignin with high selectivity.

Results and discussion

Depolymerization of lignin in basic conditions

We first treated Kraft lignin (from Norway spruce, softwood with 100% guaiacyl units)[51] in methanol at 200 °C and 1 bar N_2. The treatment led to dissolution of about 33% of the raw lignin, and produced a low amount of monomers (1.1% after 8 h, Table S1,† Fig. 2(a) and Fig. S2†). The lignin was much more soluble in dioxane (*ca.* 83%), however very low amounts of monomers were detected when treating the solution under the same conditions (Fig. S3†). Whereas the reaction in 1 mM NaOH aqueous solution gave also moderate solubility and low monomer yields (55% and 1.1%, respectively), increasing the base concentration to 10 or 100 mM led to more than 90% lignin dissolution (Table S1 and Fig. S4†) and *ca.* 13% of monomers. Guaiacol selectivity was higher than 80%, and the remaining monomers were mainly phenol and 4-alkylguaiacols (Fig. 3 and S5†).

Increasing the NaOH concentration to 1000 mM lowered the overall monomer yield. In fact, treating pure guaiacol with 1000 mM NaOH under the same conditions resulted in formation of coke on the reactor walls and a soluble polymer, as indicated by Q-TOF MS (Fig. S6†). Lastly, using KOH instead of NaOH did not lead to significant changes in the amount of dissolved lignin or monomer yield.

Whereas the monomer yields increased with reaction temperature in the 150 to 200 °C regime, higher temperatures led to a drop in the amount of monomers (Fig. 2b). Significant amount of residue was observed after reaction at 250 °C (Table S1†). The light color of the supernatant also suggested a lower amount of dissolved lignin after the reaction (Fig. S7†). It should be noted that higher temperatures changed the product selectivity by generating more phenol. This result suggested that demethoxylation of guaiacyl units could take place under these reaction conditions. This possibility is supported by a separate experiment where treatment of guaiacol with 100 mM NaOH at 250 °C led to formation of phenol (Fig. S8†). Importantly, however, the process also gave a considerable amount of solid residue. Replacing N_2 with air decreased the amount of monomers extracted by *ca.* 50%, most likely due to partial oxidation to organic acids.[6,52]

Compared to previous reports on lignin depolymerization, the method used in this study provides relatively mild conditions in dilute alkaline solution under ambient N_2 pressure. Eliminating the need for organic solvents and high pressure H_2 presents obvious advantages to both safety and cost. Importantly, previous studies on Kraft lignin depolymerization using more severe conditions than ours resulted in complex product mixtures and low single product selectivities.[30,53–55]

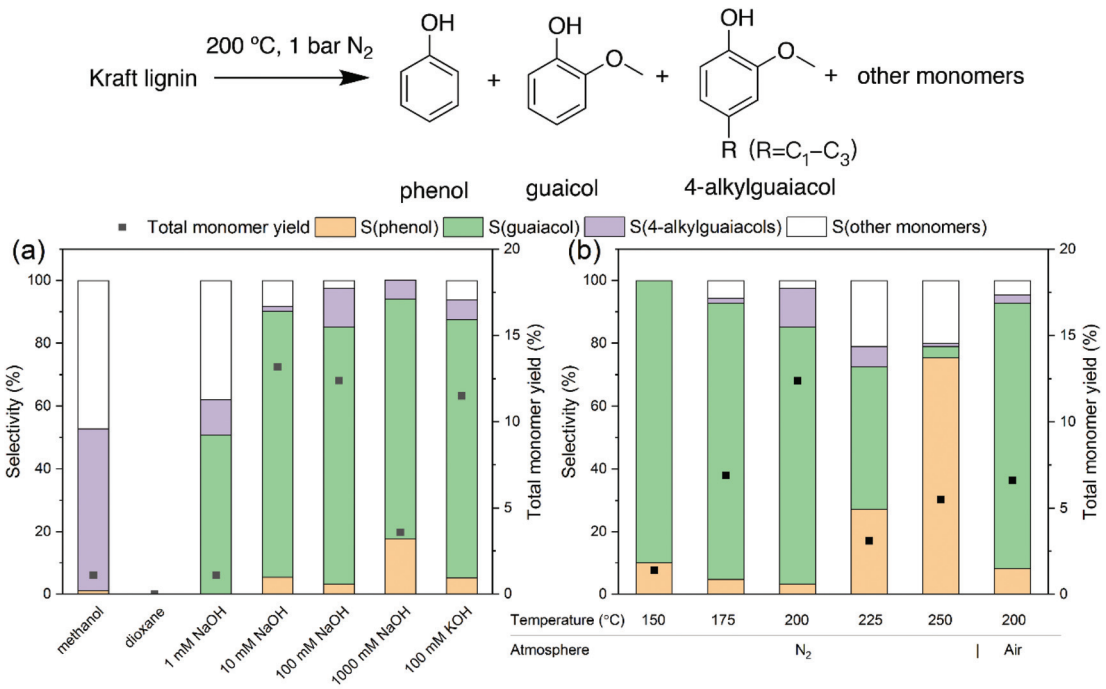

Fig. 2 Production of guaiacol, phenol, 4-alkylguaiacol and other monomers from lignin. (a) Reactions in different solvents (100 mg Kraft lignin, 25 mL solvent, 200 °C, 1 bar N_2, 8 h); (b) Reactions under different temperatures and atmospheres (100 mg Kraft lignin, 25 mL 100 mM NaOH solution, 1 bar N_2 or air, 8 h).

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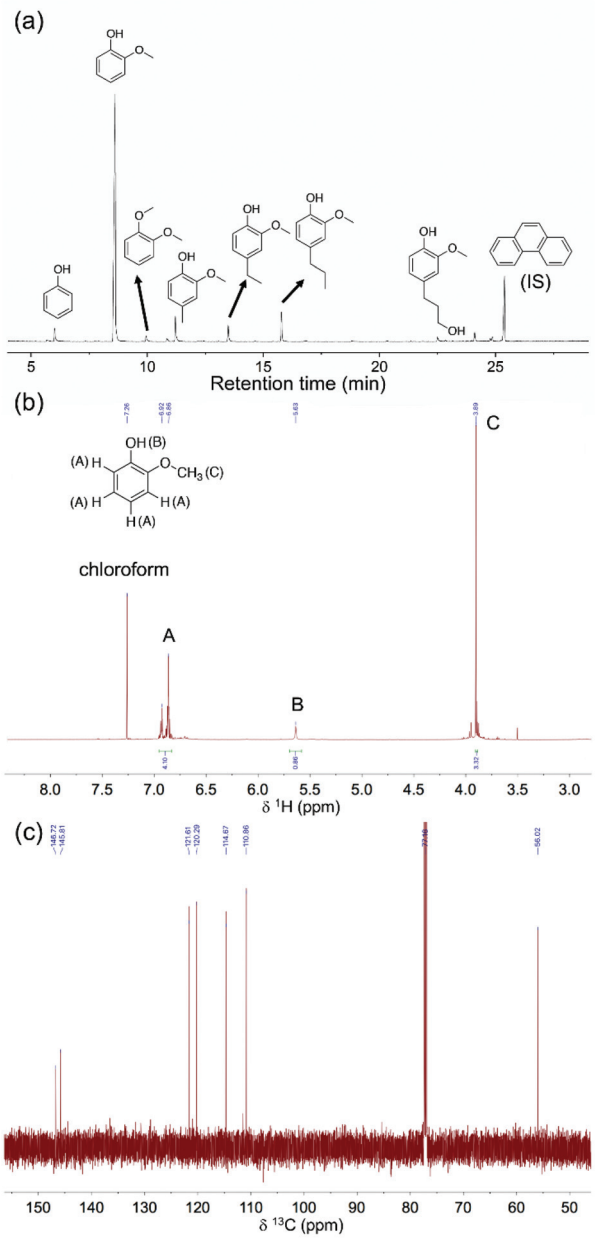

Fig. 3 Products of lignin treated with dilute NaOH solution. (a) Gas chromatogram showing the monomers obtained from the reaction; (b) and (c), ^{1}H and ^{13}C NMR spectra of $CDCl_3$ extracts from the NaOH solution. Reaction conditions: 100 mg Kraft lignin, 25 mL 100 mM NaOH solution, 200 °C, 1 bar N_2, 8 h.

Lignin depolymerization mechanisms

Because of its production method, Kraft lignin is composed of a mixture of oligomers and polymers with significant structural differences with respect to their natural source.[56,57] Typical molecular weights of Kraft lignin are below 5000 Da.[54] The material has abundant aromatic and methoxy groups, as identified by NMR analysis of its DMSO-d_6 solution (Fig. S9 and S10†). ^{13}C NMR analysis allows assignment of chemical shifts to resonances characteristic of the guaiacyl (G) units (Table S2†).[58] In contrast, the chemical shifts typically associated to *p*-hydroxyphenyl units (H) (158 and 128 ppm), and syringyl units (S) (154–152, 138.5, 134, 105–104 ppm) were not observed.[59] This result is consistent with reports that indicate softwood lignin is composed exclusively of G units.[6]

The ^{1}H–^{13}C HSQC analysis of the raw lignin dissolved in DMSO-d_6 confirmed the presence of the β-O-4 bonds and methoxy groups [Fig. 4(a)].[19,51] The amount of β-O-4 units was 20.6 per 100 C9 units from the semi-quantitative integration of relevant peaks in the HSQC NMR spectra (Fig. S11†).[60] DOSY

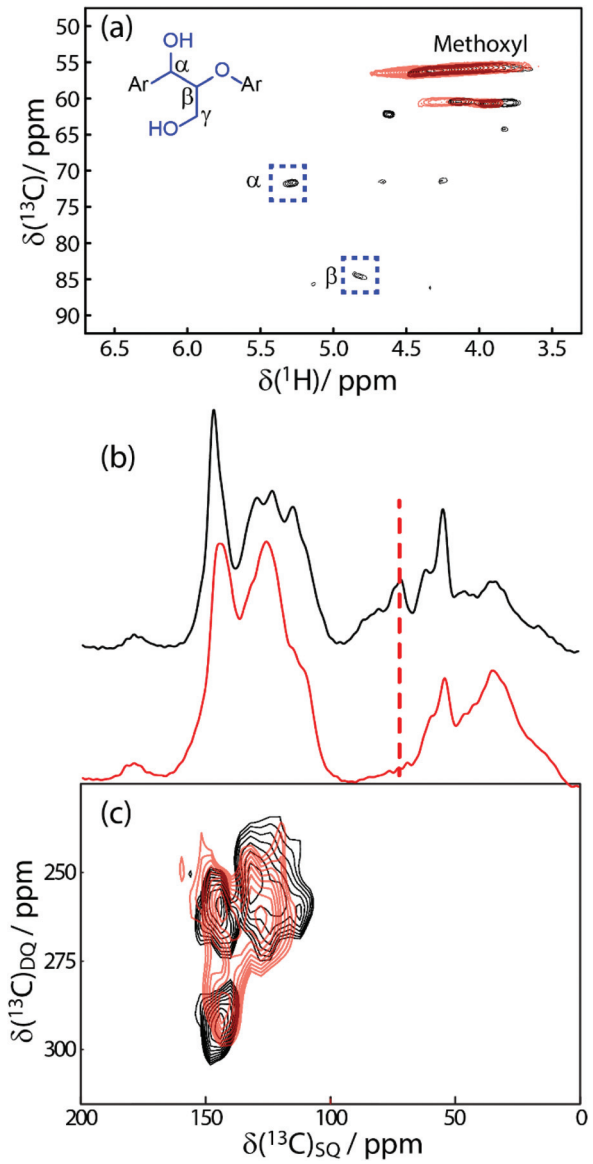

Fig. 4 (a) HSQC (in DMSO-d_6), (b) ^{13}C CPMAS, and (c) DNP-enhanced ^{13}C refocused INADEQUATE NMR spectra of lignin before (black) and after (red) depolymerization reaction. The loss of β-O-4 linkages is evident from the loss of HSQC (a, blue boxes) and CPMAS (b, dashed line) resonances after the reaction. Changes in the INADEQUATE correlations, see Table S3,† are consistent with the solid residue containing guaiacol polymerization products. Reaction conditions: 100 mg Kraft lignin, 25 mL 100 mM NaOH solution, 200 °C, 1 bar N_2, 8 h.

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NMR analysis showed an increase in the diffusion coefficient of lignin after the reaction in 100 mM NaOH suggesting a drop in its molecular weight (Fig. S12†),[61] which is consistent with partial depolymerization. After the reaction was completed, the solution was neutralized with 1 M HCl inducing precipitation of a black solid. The solid was redissolved in DMSO-d_6 for analysis. The signals indicative of β-O-4 bonds were no longer observed in the HSQC spectrum [Fig. 4(a)]. The loss of the β-O-4 bonds (70 ppm) was further confirmed by comparing the ^{13}C solid-state NMR of the original lignin and the solid residue [Fig. 4(b)].[62] These observations suggested that the cleavage of β-O-4 bonds was involved in lignin deconstruction and the generation of monomers. DNP-enhanced ^{13}C-refocused INADEQUATE measurements were also performed on the lignin and residual solid.[62–64] The correlations observed between the aromatic carbons of the lignin were in agreement with the expected shifts for the sites in the guaiacol moiety but there were some notable differences with the residual solid. For instance, the correlation between relatively low frequency carbons (DQ shift of 240 ppm) disappeared and there was new intensity at a DQ shift of 270 ppm. The INADEQUATE spectra are shown in Fig. 4c and the arrangement of the aromatic ^{13}C shifts is given in Table S3.† This observation suggests a major structural reorganization in the residual solid. A plausible assignment for these correlations is the formation of guaiacol polymers containing moieties akin to bisguaiacol;[65] this is in agreement with our observation of acetophenone condensation under these conditions, *vide infra.*

To further explore the depolymerization mechanism, lignin model compounds were treated under the same reaction conditions. Reaction of 2-phenoxy-1-phenylethanol (PPE) in 100 mM NaOH at 200 °C led to the formation of phenol and acetophenone (94% and 31% yields, respectively, Fig. 5(a)). Also formed was a solid residue possibly resulting from acetophenone self-condensation. A Q-TOF mass spectrum of a reaction using pure acetophenone under the same conditions suggested the formation of a polymer (Fig. S13†). The reaction of PPE in water (without any base) generated only a small amount of phenol (11.2% yield) and no acetophenone was detected [Fig. 5(b)]. Guaiacylglycerol-β-guaiacyl ether (GGE), a group commonly found in lignin structure,[66] was also tested using 100 mM NaOH solution. After 8 h at 200 °C, 84.3% of guaiacol was detected [Fig. 5(c) and S14†], confirming that β-O-4 bonds can be cleaved in NaOH solution. Therefore, some of the guaiacol observed in the depolymerization experiments was likely formed *via* β-O-4 bond cleavage of terminal guaiacyl units in the Kraft lignin (<5000 Da).[54] Additional types of cleavage not detectable by our methods may have also been involved in the production of guaiacol.

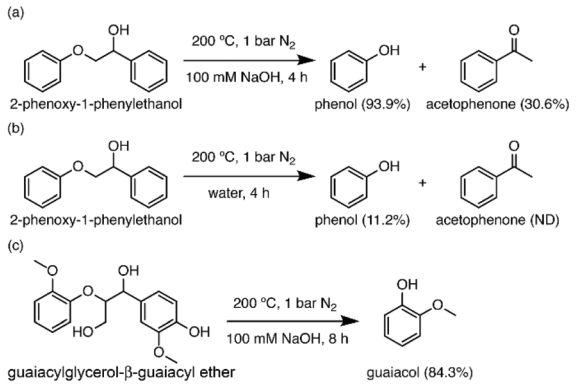

Fig. 5 Reactions of lignin model compounds. The yields (in parentheses) are based on the starting material.

Reactions of propylguaiacol or dihydroconiferyl alcohol under the same conditions (200 °C, 1 bar N_2, 100 mM NaOH, and 8 h) did not produce guaiacol (Fig. S15†), indicating that these conditions do not lead to removal of substituents at the *para* position. Therefore, guaiacol generated from this study did not originate from 4-alkylguaiacols.

Conversion of guaiacol obtained from lignin to KA oil

KA oil (a mixture of cyclohexanol and cyclohexanone) is a nylon precursor typically produced by oxidation of cyclohexane.[67,68] Guaiacol can be converted to KA oil *via* hydrogenolysis and hydrogenation using Ru, Pd or Ni catalysts.[43,44,69–73] In this study we scaled up the reaction using 1 g of lignin in 100 mM NaOH at 200 °C for 16 h, giving 79 mg monomers with 82% selectivity to guaiacol. We extracted the guaiacol-containing lignin depolymerization solution with ethyl acetate. After removal of ethyl acetate by rotary evaporation, the isolated residue was dissolved in water and treated with 1 bar H_2 at 150 °C using either Ru/Al_2O_3, Ru/C, Pd/C, or Ni/C as catalysts [Fig. 6(a)]. Ru/C catalyzed reactions gave a full conversion after 8 h, whereas only 50% conversion in the same timespan was obtained with Ru/Al_2O_3 as the catalyst. Moreover, the Ru/C catalyzed reaction produced exclusively KA oil (92.3% cyclohexanol and 7.7% cyclohexanone), proving a high efficiency for hydrodemethoxylation of the guaiacol substrate (Fig. S16†).

Because both the base-catalyzed hydrolysis of lignin and hydrogenolysis of guaiacol are performed in water, we attempted a one-pot, two step conversion. Ru/C was added to the crude aqueous reaction mixture, and was then heated under H_2, but this sequence did not produce KA oil. The lack of catalytic conversion may be due to the presence of impurities such as sulfur compounds from Kraft lignin (2.1 wt% S) in the mixture, which may cause the deactivation of the hydrogenolysis/hydrogenation catalysts.[34,74,75] However, extraction of the monomers in the two-step process solves this problem.

Ni/C was less effective than Ru/C for guaiacol conversion. Whereas Pd/C gave similar guaiacol conversion as Ru/C, its selectivity to KA oil was low (60.8%) giving a significant amount of unwanted 2-methoxycyclohexanol (MCH) byproduct. This MCH product is proposed to form *via* a second pathway during metal nanoparticles catalyzed-reactions of guaiacol and H_2, with selectivity for KA oil and MCH depending on the relative rates of demethoxylation and dearomatization.[44,76,77] If the rate of demethoxylation is faster the reaction proceeds to give KA oil *via* a phenol intermediate.

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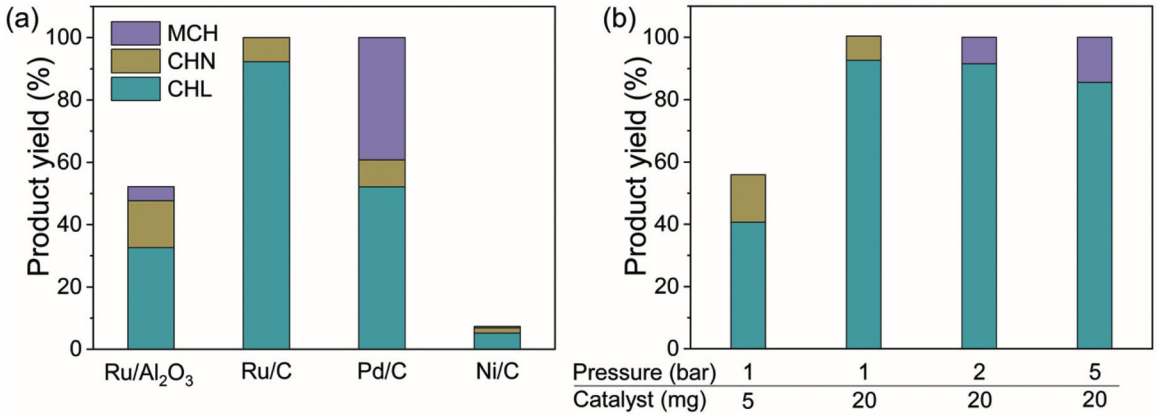

Fig. 6 Conversion of guaiacol obtained from the lignin reaction into KA oil (a) with different catalysts (1 : 20 mass ratio metal to guaiacol, 1 bar H_2, 150 °C, 8 h); (b) under different pressures with 5% Ru/C, 150 °C, 8 h. MCH: 2-methoxycyclohexanol; CHN: cyclohexanone; CHL: cyclohexanol.

However, if the rate of dearomatization is faster, the reaction leads to MCH, which is much more resistant to demethoxylation than guaiacol under reducing conditions.[44,77] Therefore, our results suggest that the rate of guaiacol demethoxylation is higher using Ru/C than Pd/C as a catalyst.

No obvious deactivation of the Ru/C was observed in the stability tests over 3 cycles (Fig. S17†). Lowering the amount of Ru/C catalyst from 20 to 5 mg decreased guaiacol conversion to less than 60%; however, the selectivity to KA oil remained at 100% [Fig. 6(b)]. As expected, increasing H_2 pressure led to converting all CHN into CHL.[49] Interestingly, however, the higher pressures also led to formation of MCH (*i.e.* decreased the KA oil selectivity), suggesting that the rate of dearomatization has a larger dependence on H_2 pressure than the rate of demethoxylation over the Ru/C catalyst. Therefore, in addition to its reduced energy cost and system safety, the use of low H_2 pressures (1 bar) is advantageous in terms of maximizing the selectivity to the desired product (KA oil).

Conclusions

We demonstrated a mild and selective pathway for producing nylon precursors from waste lignin using water as a solvent. In the first step, Kraft lignin was depolymerized in dilute alkaline solution at relatively low temperature (200 °C) under 1 bar N_2. Guaiacol was produced with high selectivity (>80%) with a total monomer amount of 13% based on the lignin input, along with phenol and alkylguaiacols as byproducts. The depolymerization involved cleavage of β-O-4 bonds in the original structure according to HSQC and INADEQUATE NMR analyses of the raw and reacted lignin. The cleavage of β-O-4 bonds under our reaction conditions was confirmed by experiments using model lignin compounds. In the second step, lignin-derived guaiacol was converted to KA oil using Ru/C catalyst under 1 bar H_2. The use of low H_2 pressure proved critical to ensure full selectivity to KA oil, without formation of the undesired methoxy-cyclohexanol byproduct. Importantly, the deactivation of Ru/C catalyst observed in the direct treatment of lignin, was avoided in the two-step procedure. Thus, the method reported in this paper provides a new option for lignin utilization in the production of high-demand value-added chemicals. We envision this process as a low-energy step that leaves the remaining oligomers available for downstream processing into other chemical commodities in an integrated refinery for waste Kraft lignin.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research is supported by the Laboratory Directed Research and Development Program (LDRD) of the Ames Laboratory. Solid-state NMR/DNP experiments (FP, MP) were supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences. The Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. DE-AC02-07CH11358.

References

1 C. Li, X. Zhao, A. Wang, G. W. Huber and T. Zhang, *Chem. Rev.*, 2015, **115**, 11559–11624.
2 M. Hara, K. Nakajima and K. Kamata, *Sci. Technol. Adv. Mater.*, 2015, **16**, 034903.
3 C. Heitner, D. Dimmel, J. Schmidt, D. Dimmel and J. Schmidt, *Lignin and Lignans : Advances in Chemistry*, CRC Press, 2016.
4 Z. Sun, B. Fridrich, A. de Santi, S. Elangovan and K. Barta, *Chem. Rev.*, 2018, **118**, 614–678.

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5 I. Mordor, Global Lignin Products Market – Segmented by Product Type, Source, Application, and Geography – Growth, Trends and Forecast (2017–2022), 2017.
6 W. Schutyser, T. Renders, S. V. d. Bosch, S. F. Koelewijn, G. T. Beckham and B. F. Sels, *Chem. Soc. Rev.*, 2018, **47**, 852–908.
7 J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius and B. M. Weckhuysen, *Chem. Rev.*, 2010, **110**, 3552–3599.
8 A. Demirbas, *Prog. Energy Combust. Sci.*, 2004, **30**, 219–230.
9 T. Renders, S. Van den Bosch, S. F. Koelewijn, W. Schutyser and B. F. Sels, *Energy Environ. Sci.*, 2017, **10**, 1551–1557.
10 H. Zhou, C. Wu, J. A. Onwudili, A. Meng, Y. Zhang and P. T. Williams, *Energy Fuels*, 2014, **28**, 6371–6379.
11 P. R. Patwardhan, R. C. Brown and B. H. Shanks, *ChemSusChem*, 2011, **4**, 1629–1636.
12 N. Mahmood, Z. Yuan, J. Schmidt and C. C. Xu, *Bioresour. Technol.*, 2015, **190**, 416–419.
13 E. M. Anderson, R. Katahira, M. Reed, M. G. Resch, E. M. Karp, G. T. Beckham and Y. Román-Leshkov, *ACS Sustainable Chem. Eng.*, 2016, **4**, 6940–6950.
14 Q. Song, F. Wang, J. Cai, Y. Wang, J. Zhang, W. Yu and J. Xu, *Energy Environ. Sci.*, 2013, **6**, 994–1007.
15 S. V. d. Bosch, W. Schutyser, R. Vanholme, T. Driessen, S. F. Koelewijn, T. Renders, B. D. Meester, W. J. J. Huijgen, W. Dehaen, C. M. Courtin, B. Lagrain, W. Boerjan and B. F. Sels, *Energy Environ. Sci.*, 2015, **8**, 1748–1763.
16 J. Long, Y. Xu, T. Wang, Z. Yuan, R. Shu, Q. Zhang and L. Ma, *Appl. Energy*, 2015, **141**, 70–79.
17 X. Huang, T. I. Korányi, M. D. Boot and E. J. M. Hensen, *ChemSusChem*, 2014, **7**, 2276–2288.
18 Z. Jiang, T. He, J. Li and C. Hu, *Green Chem.*, 2014, **16**, 4257–4265.
19 A. Rahimi, A. Azarpira, H. Kim, J. Ralph and S. S. Stahl, *J. Am. Chem. Soc.*, 2013, **135**, 6415–6418.
20 R. Ma, Y. Xu and X. Zhang, *ChemSusChem*, 2015, **8**, 24–51.
21 J. Gierer, *Wood Sci. Technol.*, 1986, **20**, 1–33.
22 M. V. Galkin, A. T. Smit, E. Subbotina, K. A. Artemenko, J. Bergquist, W. J. J. Huijgen and J. S. M. Samec, *ChemSusChem*, 2016, **9**, 3280–3287.
23 P. J. Deuss, C. S. Lancefield, A. Narani, J. G. d. Vries, N. J. Westwood and K. Barta, *Green Chem.*, 2017, **19**, 2774–2782.
24 Z. Fang and M. S. Meier, *Org. Biomol. Chem.*, 2018, **16**, 2330–2341.
25 L. Shuai, M. T. Amiri and J. S. Luterbacher, *Curr. Opin. Green Sustain. Chem.*, 2016, **2**, 59–63.
26 A. L. Jongerius, R. Jastrzebski, P. C. A. Bruijnincx and B. M. Weckhuysen, *J. Catal.*, 2012, **285**, 315–323.
27 C. Crestini, R. Saladino, P. Tagliatesta and T. Boschi, *Bioorg. Med. Chem.*, 1999, **7**, 1897–1905.
28 L. Shuai, M. T. Amiri, Y. M. Questell-Santiago, F. Héroguel, Y. Li, H. Kim, R. Meilan, C. Chapple, J. Ralph and J. S. Luterbacher, *Science*, 2016, **354**, 329–333.
29 K. M. Torr, D. J. van de Pas, E. Cazeils and I. D. Suckling, *Bioresour. Technol.*, 2011, **102**, 7608–7611.
30 L. Shuai, J. Sitison, S. Sadula, J. Ding, M. C. Thies and B. Saha, *ACS Catal.*, 2018, **8**, 6507–6512.
31 J. S. Luterbacher, A. Azarpira, A. H. Motagamwala, F. Lu, J. Ralph and J. A. Dumesic, *Energy Environ. Sci.*, 2015, **8**, 2657–2663.
32 J. Zhang, J. Teo, X. Chen, H. Asakura, T. Tanaka, K. Teramura and N. Yan, *ACS Catal.*, 2014, **4**, 1574–1583.
33 S. V. d. Bosch, W. Schutyser, S. F. Koelewijn, T. Renders, C. M. Courtin and B. F. Sels, *Chem. Commun.*, 2015, **51**, 13158–13161.
34 J.-P. Lange, *Angew. Chem., Int. Ed.*, 2015, **54**, 13186–13197.
35 C. Schuerch, *J. Am. Chem. Soc.*, 1952, **74**, 5061–5067.
36 M. Ek, G. Gellerstedt and G. Henriksson, *Pulping chemistry and technology*, Walter de Gruyter, 2009.
37 M. Ragnar, G. Henriksson, M. E. Lindström, M. Wimby, J. Blechschmidt and S. Heinemann, *Pulp in Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, 2014, pp. 1–92.
38 J. Gierer, *Wood Sci. Technol.*, 1980, **14**, 241–266.
39 C. Fargues, Á. Mathias and A. Rodrigues, *Ind. Eng. Chem. Res.*, 1996, **35**, 28–36.
40 P. C. R. Pinto, C. E. Costa and A. E. Rodrigues, *Ind. Eng. Chem. Res.*, 2013, **52**, 4421–4428.
41 T. Renders, W. Schutyser, S. Van den Bosch, S.-F. Koelewijn, T. Vangeel, C. M. Courtin and B. F. Sels, *ACS Catal.*, 2016, **6**, 2055–2066.
42 X. Huang, T. I. Korányi, M. D. Boot and E. J. M. Hensen, *Green Chem.*, 2015, **17**, 4941–4950.
43 G.-Y. Xu, J.-H. Guo, Y.-C. Qu, Y. Zhang, Y. Fu and Q.-X. Guo, *Green Chem.*, 2016, **18**, 5510–5517.
44 Y. Nakagawa, M. Ishikawa, M. Tamura and K. Tomishige, *Green Chem.*, 2014, **16**, 2197–2203.
45 B. Feng, H. Kobayashi, H. Ohta and A. Fukuoka, *J. Mol. Catal. A: Chem.*, 2014, **388–389**, 41–46.
46 H. Ohta, H. Kobayashi, K. Hara and A. Fukuoka, *Chem. Commun.*, 2011, **47**, 12209–12211.
47 K. Liu, C. Liang, Q. Ma, R. Du, Y. Wang, J. Mao, Z. Chen and H. Li, *Mol. Catal.*, 2017, **428**, 24–32.
48 N. Yan, C. Zhao, P. J. Dyson, C. Wang, L. t. Liu and Y. Kou, *ChemSusChem*, 2008, **1**, 626–629.
49 N. C. Nelson, J. S. Manzano, A. D. Sadow, S. H. Overbury and I. I. Slowing, *ACS Catal.*, 2015, **5**, 2051–2061.
50 M. T. Musser, *Cyclohexanol and cyclohexanone in Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, 2011, pp. 49–58.
51 Z. Sun, G. Bottari, A. Afanasenko, M. C. A. Stuart, P. J. Deuss, B. Fridrich and K. Barta, *Nat. Catal.*, 2018, **1**, 82–92.
52 A. G. Demesa, A. Laari, I. Turunen and M. Sillanpää, *Chem. Eng. Technol.*, 2015, **38**, 2270–2278.
53 V. Molinari, G. Clavel, M. Graglia, M. Antonietti and D. Esposito, *ACS Catal.*, 2016, **6**, 1663–1670.
54 S.-C. Qi, J.-i. Hayashi, S. Kudo and L. Zhang, *Green Chem.*, 2017, **19**, 2636–2645.
55 A. Narani, R. K. Chowdari, C. Cannilla, G. Bonura, F. Frusteri, H. J. Heeres and K. Barta, *Green Chem.*, 2015, **17**, 5046–5057.

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56 C. Crestini, H. Lange, M. Sette and D. S. Argyropoulos, *Green Chem.*, 2017, **19**, 4104–4121.
57 C. S. Lancefield, H. L. J. Wienk, R. Boelens, B. M. Weckhuysen and P. C. A. Bruijnincx, *Chem. Sci.*, 2018, **9**, 6348–6360.
58 J.-L. Wen, S.-L. Sun, B.-L. Xue and R.-C. Sun, *Materials*, 2013, **6**, 359–391.
59 R. E. Hage, N. Brosse, L. Chrusciel, C. Sanchez, P. Sannigrahi and A. Ragauskas, *Polym. Degrad. Stab.*, 2009, **94**, 1632–1638.
60 I. Panovic, C. S. Lancefield, D. Phillips, M. J. Gronnow and N. J. Westwood, *ChemSusChem*, 2019, **12**, 542–548.
61 A. Siouffi and G. Guiochon, in *Encyclopedia of Separation Science*, ed. I. D. Wilson, Academic Press, Oxford, 2000, pp. 915–930.
62 F. A. Perras, H. Luo, X. Zhang, N. S. Mosier, M. Pruski and M. M. Abu-Omar, *J. Phys. Chem. A*, 2017, **121**, 623–630.
63 H. Takahashi, D. Lee, L. Dubois, M. Bardet, S. Hediger and G. De Paëpe, *Angew. Chem., Int. Ed.*, 2012, **51**, 11766–11769.
64 A. Lesage, M. Bardet and L. Emsley, *J. Am. Chem. Soc.*, 1999, **121**, 10987–10993.
65 T. Periyasamy, S. P. Asrafali, S. Muthusamy and S.-C. Kim, *New J. Chem.*, 2016, **40**, 9313–9319.
66 M. Thierry, A. Majira, B. Pégot, L. Cezard, F. Bourdreux, G. Clément, F. Perreau, S. Boutet-Mercey, P. Diter, G. Vo-Thanh, C. Lapierre, P.-H. Ducrot, E. Magnier, S. Baumberger and B. Cottyn, *ChemSusChem*, 2018, **11**, 439–448.
67 R. Zhao, D. Ji, G. Lv, G. Qian, L. Yan, X. Wang and J. Suo, *Chem. Commun.*, 2004, **0**, 904–905.
68 A. J. Kumalaputri, C. Randolph, E. Otten, H. J. Heeres and P. J. Deuss, *ACS Sustainable Chem. Eng.*, 2018, **6**, 3419–3425.
69 N. Nelson, Z. Wang, P. Naik, J. S. Manzano, M. Pruski and I. I. Slowing, *J. Mater. Chem. A*, 2017, **5**, 2016–2018.
70 W. Schutyser, G. Van den Bossche, A. Raaffels, S. Van den Bosch, S.-F. Koelewijn, T. Renders and B. F. Sels, *ACS Sustainable Chem. Eng.*, 2016, **4**, 5336–5346.
71 X. Wang and R. Rinaldi, *Energy Environ. Sci.*, 2012, **5**, 8244–8260.
72 J. Yi, Y. Luo, T. He, Z. Jiang, J. Li and C. Hu, *Catalysts*, 2016, **6**, 12.
73 W. Schutyser, S. Van den Bosch, J. Dijkmans, S. Turner, M. Meledina, G. Van Tendeloo, D. P. Debecker and B. F. Sels, *ChemSusChem*, 2015, **8**, 1805–1818.
74 N. T. Kulishkin and A. V. Mashkina, *React. Kinet. Catal. Lett.*, 1991, **45**, 41–47.
75 N. Munakata and M. Reinhard, *Appl. Catal., B*, 2007, **75**, 1–10.
76 H. Zhou, H. Wang, A. D. Sadow and I. I. Slowing, *Appl. Catal., B*, 2020, **270**, 118890.
77 X. Liu, L. Xu, G. Xu, W. Jia, Y. Ma and Y. Zhang, *ACS Catal.*, 2016, **6**, 7611–7620.

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