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

Hui Zhou, a,b Hsin Wang, a,b Frédéric A. Perras, a Pranjali Naik, a,b Marek Pruski, b Aaron D. Sadow a,b and Igor I. Slowing a,b

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 N₂ 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 H₂ 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 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, and Kraft lignin being the predominant type. Despite its potential as 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. Whereas recent efforts have focused on converting lignin derivatives to industrially relevant compounds with high selectivity, only few of them involve processes that start from the raw lignin streams.

In this study, we propose a two-step pathway for converting Kraft lignin to nylon precursors (Fig. 1). In the first step, Kraft lignin can cause deactivation of the metal catalysts required for hydrogenolytic depolymerization.

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

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. Whereas recent efforts have focused on converting lignin derivatives to industrially relevant compounds with high selectivity, only few of them involve processes that start from the raw lignin streams.

In this study, we propose a two-step pathway for converting Kraft lignin to nylon precursors (Fig. 1). In the first step, Kraft lignin being the predominant type. Despite its potential as 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. Whereas recent efforts have focused on converting lignin derivatives to industrially relevant compounds with high selectivity, only few of them involve processes that start from the raw lignin streams.

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Results and discussion
Depolymerization of lignin in basic conditions

We first treated Kraft lignin (from Norway spruce, softwood with 100% guaiacyl units) in methanol at 200 °C and 1 bar N₂. 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 N₂ 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 N₂ pressure. Eliminating the need for organic solvents and high pressure H₂ 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 N₂, 8 h); (b) Reactions under different temperatures and atmospheres (100 mg Kraft lignin, 25 mL 100 mM NaOH solution, 1 bar N₂ or air, 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.\textsuperscript{56,57} Typical molecular weights of Kraft lignin are below 5000 Da.\textsuperscript{54} The material has abundant aromatic and methoxy groups, as identified by NMR analysis of its DMSO-\textit{d}_6 solution (Fig. S9 and S10\textsuperscript{†}).\textsuperscript{13}C NMR analysis allows assignment of chemical shifts to resonances characteristic of the guaiacyl (G) units (Table S2\textsuperscript{†}).\textsuperscript{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.\textsuperscript{59} This result is consistent with reports that indicate softwood lignin is composed exclusively of G units.\textsuperscript{6}

The \(^1\)H–\(^{13}\)C HSQC analysis of the raw lignin dissolved in DMSO-\textit{d}_6 confirmed the presence of the \(\beta\)-O-4 bonds and methoxy groups [Fig. 4(a)].\textsuperscript{15,51} The amount of \(\beta\)-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\textsuperscript{†}).\textsuperscript{60} DOSY
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†).41 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-d6 for analysis. The signals indicative of β-O-4 bonds were no longer observed in the HMQC spectrum [Fig. 4(a)]. The loss of the β-O-4 bonds (70 ppm) was further confirmed by comparing the 13C 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 13C-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 no new intensity at a DQ shift of 270 ppm. The INADEQUATE spectra are shown in Fig. 4c and the arrangement of the aromatic 13C 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 acetoephone 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-phenoxyl-1-phenylethanol (PPE) in 100 mM NaOH at 200 °C led to the formation of phenol and acetoephone (94% and 31% yields, respectively, Fig. 5(a)). Also formed was a solid residue possibly resulting from acetoephone self-condensation. A Q-TOF mass spectrum of a reaction using pure acetoephone 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 acetoephone 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.

Reactions of propylguaiacol or dihydroconiferyl alcohol under the same conditions (200 °C, 1 bar N2, 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.13,44,69-71 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 KA oil (92.3% cyclohexanol and 7.7% cyclohexanone), proving a high efficiency for hydrodemethylation 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 H2, 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 H2, with selectivity for KA oil and MCH depending on the relative rates of demethylation and dearomatization.14,76,77 If the rate of demethylation is faster the reaction proceeds to give KA oil via a phenol intermediate. 

Fig. 5 Reactions of lignin model compounds. The yields (in parentheses) are based on the starting material.
However, if the rate of dearomatization is faster, the reaction leads to MCH, which is much more resistant to demethoxyla-
tion than guaiacol under reducing conditions. 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 H2 pressure led to
converting all CHN into CHL. Interestingly, however, the
higher pressures also led to formation of MCH (i.e. decreased
the KA oil selectivity), suggesting that the rate of dearomatiza-
tion has a larger dependence on H2 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 H2
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 N2.
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 depo-
lymerization 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 H2. The use of low H2 pressure proved critical to
ensure full selectivity to KA oil, without formation of the unde-
sired methoxy-cyclohexanol byproduct. Importantly, the de-
activation 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 pro-
cessing into other chemical commodities in an integrated
refinery for waste Kraft lignin.

Conflicts of interest

There are no conflicts to declare.

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