Catalytic disassembly of an organosolv lignin via hydrogen transfer from supercritical methanol†

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A novel approach to disassembling biomass-derived lignin into processible units is described. This transformation is achieved in supercritical methanol, using a Cu-doped porous metal oxide as the catalyst, at a relatively mild temperature (300 °C). Hydrogen transfer from methanol to an organosolv lignin results in the complete hydrogenolysis of phenyl ether bonds, coupled with the hydrogenation of aromatic rings. The product is a complex mixture composed principally of monomeric substituted cyclohexyl derivatives with greatly reduced oxygen content and negligible aromatics. Notably, no char formation was observed. We also describe operational indices based on the 1H NMR spectra that facilitate holistic evaluation of the product distribution in this and other biomass transformations.

Introduction

Non-food biomass is an increasingly significant, renewable resource that has been estimated as having the potential to produce the annual equivalent of 3 billion barrels of liquid transportation fuel in the US alone.1 Thus, developing chemical approaches for transforming the lignocellulose component of this carbon-neutral energy source to liquid transportation fuels would have significant economic and environmental impacts.2 The two most plentiful biopolymers making up herbaceous biomass are cellulose and lignin. The latter is a complex material consisting largely of oxygenated 4-propylphenolic units cross-linked via phenyl ether bonds, as well as by C–C and other C–O bonds. Lignin serves to provide mechanical stability to plant tissues, and is very difficult to degrade by biochemical or chemical means.3 It makes up 15–30% of lignocellulose, and among biomass components has the highest carbon content potentially usable as liquid fuel. The difficulty in transforming lignin to liquid fuels originates mostly from its highly complex and diverse structure, as well as from the refractory behavior of phenolic ethers toward hydrolysis. Thus developing methods for the chemical processing of lignins is of crucial importance to effective utilization of biomass.

Reductive lignin disassembly has the advantage of increasing the fuel value of the product by adding H2 equivalents. Lignin hydrogenation was first described many decades ago by Harris et al., in high pressure/high temperature experiments,4 and it continues to be investigated for the conversion of lignins to fuel precursors.4 More recently explored reductive methods include pyrolysis with formic acid at temperatures above 350 °C to give bio-oils with significantly lower O/C ratios than the starting lignins.5 Similar results have been obtained in multi-step processes utilizing noble-metal catalysts,6 and Lercher et al.7 have demonstrated hydrodeoxygenation of bio-oil phenolic fractions to alkanes and methanol using a combination of a hydrogenation catalyst and a strong acid. These observations suggest that viable pathways for the production of liquid fuels and/or chemical precursors from lignins are becoming accessible, although multi-step processes and precious metal catalysts are generally involved.

We have developed a single-step approach using a non-precious metal catalyst for the hydrogenolysis-depolymerization of lignin and subsequent hydrogenation of aromatics. This method is based on our recent report of a process for the hydrogenolysis of phenyl ether bonds and subsequent aromatic ring hydrogenation, as demonstrated with the lignin model dihydroybenzofuran (DHBF, Scheme 1).8 The UCSB process utilizes supercritical methanol (sc-MeOH) as the reaction medium and is catalyzed by a copper-doped porous metal oxide (PMO) derived from an easily-prepared hydrotalcite precursor. The reducing equivalents for both steps originate from the solvent itself, which...
The organosolv lignin obtained in this manner has an average molecular weight of ca. 2.5 × 10^6 g mol⁻¹ and a polydispersity of 1.3, according to gel permeation chromatography (GPC) measurements in THF (Supporting Information, Figure S-1†). This molecular weight is consistent with the high solubility of organosolv lignin in various organic solvents, including methanol at room temperature, and is similar to that of the hypothetical structure depicted in Fig. 1 (3.1 × 10^6 g mol⁻¹, 15 aromatic units).

For NMR spectral analysis, 100 mg organosolv lignin was fully dissolved in 0.7 mL CDCl₃. The ¹H NMR and ¹³C APT NMR spectra of this solution (Supporting Information, Figures S-2 and S-3†) show resonances characteristic of lignins.¹⁰ There are at least ten types of bonds present in a typical lignin structure.¹¹ As a starting point for the further discussion of NMR spectra and assessment of product streams from our reductive disassembly, we selected a hypothetical model for poplar lignin based on that proposed by Brunow.¹² It consists of syringyl and guaiacyl units, cross-linked mostly through β-O-4 linkages (see Supporting Information, Figure S-4, for the structures of such units).

Stoichiometry considerations

Ideally, a series of hydrogenolysis, hydrogenation and dehydration reactions will convert lignin exclusively to hydrocarbon products. The hydrogen equivalents originate from methanol by reforming (CH₃OH → CO + 2 H₂) and water-gas shift (CO → H₂O → CO₂ + H₂) of the resulting CO with any H₂O present to give three equivalents of H₂ per methanol consumed. Assuming sufficient water is formed or added, about half the methanol needed to generate the required H₂ would be formed in the reaction shown in eqn (1). If no C–C bonds are cleaved, one mole (3.14 kg) of the lignin model (Fig. 1) requires ca. 18 moles additional CH₃OH (0.58 kg) to produce 11 moles (1.64 kg) C₉ hydrocarbon and 2 moles (0.47 kg) C₁₅ hydrocarbon.

C₁₀H₁₉₃O₆₅ + 126 H₂ → 11 C₉H₁₈ + 24 CH₃OH + 41 H₂O

(1)

Model reactions in lignin disassembly

We propose the following hypothetical series of reactions for the stepwise reductive disassembly of lignin. In the first step, compounds 1–5 (Scheme 2) are created by selective hydrogenolysis of four β-O-4 linkages, one diphenyl ether-type linkage, and one dihydrobenzofuran unit. For compounds 1, 2 and 4, the alcohol group in the position alpha to the aromatic ring is likely to undergo dehydration to form a double bond that is conjugated with the aromatic system. In a reducing atmosphere, this double bond will be hydrogenated. Upon dehydration/hydrogenation of 1 and 2, compounds 6 and 7 are formed (Scheme 3), while compound 3 undergoes hydrogenation to 8. Compounds 6–8, upon hydrogenation of their aromatic rings, give the functionalized propylcyclohexanols 9–11.

If compounds 6 and 7 were to instead undergo loss of methoxy groups and hydrogenation of their aromatic rings, both would result in 4-(1-hydroxypropyl)-cyclohexanol (11). This could undergo subsequent dehydration/hydrogenation (Scheme 4) to form 4-propyl-cyclohexanol (12), as suggested.
Fig. 1  Hypothetical structure for organosolv lignin derived from poplar sawdust.

Scheme 2  Selective hydrogenolysis of aromatic ether linkages in lignin.
by the appearance of methyl resonances at ca. 0.9 ppm in the $^1$H NMR spectra (see below). Both 11 and 12 are saturated alcohols with low oxygen content, and could be used as fuel additives. The coexistence of both pathways (methoxy-loss and hydrogenation) is suggested by the reaction of guaiacol (2-methoxyphenol), which under these reaction conditions gives phenol, dihydroxybenzene and the corresponding ring hydrogenation products (see Supporting Information†). Dehydration/dehydrogenation of 12 gives propylcyclohexane, 13.

Accordingly, the products become more uniform with each stage of functionality removal, resulting eventually in the simple propylcyclohexyl skeleton of reduced lignin. Similar processes are envisaged for the reactivity of 4 and 5, as qualitatively proposed in Scheme 5.

Based on these scenarios, the compounds originating from different stages of these processes can be grouped according to their aromatic character and oxygen content, Table 1. (We note that they will not necessarily be formed in an easily identifiable sequence such as shown in the proposed steps.)

### Definitions of operational indices

Owing to the complexity of the reaction product mixtures, we created a set of numerical indices to provide metrics for classifying the chemical transformations in this and other biomass conversions.

$$H = \left\{ \frac{N_A}{N_A + N_O + N_H} \right\} \times 100$$

$$O = \left\{ \frac{N_O}{N_A + N_O + N_H} \right\} \times 100$$

where $N_A$ is the number of aromatic protons; $N_O$ is the number of protons on carbons that bear an oxygen (including –OH); and $N_H$ is the number of aliphatic protons. Thus, $H$ represents the fraction of protons bound to aliphatic carbons, $A$ the fraction at aromatic sites and $O$ those that are adjacent to or bonded to oxygen. The subscript “T” indicates theoretical values (i.e., $H_T$, $A_T$ and $O_T$), calculated simply by counting the various types of protons in the model compounds. Table 2 summarizes the values of the $H_T$, $A_T$ and $O_T$ indices for the hypothetical lignin model and for each of the compound classes in Table 1.

The subscript “E” designates experimentally determined values: $H_E$, $A_E$ and $O_E$. These were defined as shown from the ratios of the integrations of specific chemical shift regions ($R_i$) in
Table 2  $A_T$, $O_T$ and $H_T$ indices calculated for the lignin model (Fig. 1) and the proposed product groups

<table>
<thead>
<tr>
<th>Group</th>
<th>$A_T$</th>
<th>$O_T$</th>
<th>$H_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin model</td>
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</tr>
<tr>
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<tr>
<td>C</td>
<td>0</td>
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<td>D</td>
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<tr>
<td>E</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

For a particular sample, $R_A$ is the integrated area of proton resonances in the chemical shift range 7.2–5.0 ppm, $R_O$ is the area for the range 5.0–3.0 ppm, and $R_H$ is the area for the range 3.0–0.3 ppm. A test of this approach would be 4-(3-hydroxypropyl)-2-methylcyclohexanol, a compound that resembles likely intermediates in reductive lignin disassembly. Its calculated $O_T$ and $H_T$ values are 25 and 75, respectively, while the published $^1$H NMR spectrum in CDCl$_3$ [3.71–3.02 ppm (m, 5 H) and 2.03–0.64 ppm (m, 15 H)] has $O_T = 25$ and $H_T = 75$, in agreement with the prediction. Nonetheless, we note that there is some ambiguity in the determination of aliphatic and aromatic –OH protons, since they do not always appear in the 5–3 ppm range.

In general, the $H$ index reflects the extent of hydrogen transfer to the organosolv lignin, and is therefore at a minimum for unmodified substrate. The hypothetical structure portrayed in Fig. 1 has an $H_T$ index of 1.0, an $O_T$ index of 80.4 and an $A_T$ index of 18.5. Comparison to the experimental indices for organosolv lignin shows reasonable agreement (Fig. 2), although the $H_E$ value (12.9) is significantly higher than predicted by this model.

The average $A_T$, $O_T$ and $H_T$ indices for compound groups A–E are also displayed in Fig. 2. Group A has approximately the same $A_T$ value as the lignin model (Fig. 1), indicating little difference in their aromatic proton contents. The modestly elevated $H_T$ and lower $O_T$ values arise because of the methylene groups formed during hydrogenolysis. Compounds in groups B and C have nearly the same $O_T$ index, although $H_T$ and $A_T$ change as more aromatic rings are hydrogenated. Complete transformation of lignin to alkanes (group E) gives $H_T = 100$, since $A_T$ and $O_T$ both become zero.

**Time course of hydrogenation**

In order to follow the disassembly of the organosolv lignin substrate over the course of the reaction, a series of experiments was performed using different time intervals. In each, 50 mg substrate and 50 mg Cu$_2$O@PMO catalyst were heated to 300 °C in 3 mL CH$_3$OH in a 10 mL volume minireactor. The reactions were quenched by rapid cooling, and then the solvent and volatiles removed by rotary evaporation at room temperature. The remaining liquids were then completely dissolved in 1.0 mL CDCl$_3$, and $R_A$, $R_O$ and $R_H$ values were determined by integrating the defined $^1$H NMR spectral regions (see Fig. 3 and Figures S-6 to S-14 in the Supporting Information†).

For a particular sample, $R_A$ is the integrated area of proton resonances in the chemical shift range 7.2–5.0 ppm, $R_O$ is the area for the range 5.0–3.0 ppm, and $R_H$ is the area for the range 3.0–0.3 ppm. A test of this approach would be 4-(3-hydroxypropyl)-2-methylcyclohexanol, a compound that resembles likely intermediates in reductive lignin disassembly. Its calculated $O_T$ and $H_T$ values are 25 and 75, respectively, while the published $^1$H NMR spectrum in CDCl$_3$ [3.71–3.02 ppm (m, 5 H) and 2.03–0.64 ppm (m, 15 H)] gives $O_T = 25$ and $H_T = 75$, in agreement with the prediction. Nonetheless, we note that there is some ambiguity in the determination of aliphatic and aromatic –OH protons, since they do not always appear in the 5–3 ppm range.

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Fig. 2  Comparison of $A_T$, $O_T$ and $H_T$ indices for the lignin model (Fig. 1) and for the compound groups arising from its hydrogenation. The corresponding $A_E$, $O_E$ and $H_E$ indices for organosolv lignin are also shown.

Table 3 and Fig. 4 illustrate the temporal progression of $A_E$, $O_E$ and $H_E$ during the reaction. After only 2 h, the value of $A_E$ declines from 12.9 for organosolv lignin to 4.3 in the product mixture, while $O_E$ drops from 74.3 to 17.2, and $H_E$ increases markedly from 12.9 to 78.6. This value of $H_E$ is close to $H_T$ for compound group D, suggesting that after only 2 h, the substrate
The exchangeable O–H protons remain.

The differences between the results for experiments 8 and 9 are minor (Figures S-13 and S-14†) suggesting that surprisingly few evaluate the content of readily exchangeable product protons.

The elevated HE index of the final product mixture, compared to the HE index for Group D, suggests that ring alkylation may occur concurrently with the reduction; methylated byproducts were seen previously in the analogous reactions of DHBF. The temporal evolution of the HE/AE and HE/OE ratios (Table 3) emphasizes the markedly increasing fraction of aliphatic (vs. aromatic) protons, and the decreasing oxygen content of the products. The reproducibility of the behavior in Table 3 and Fig. 4 was demonstrated by an independent series of experiments with another sample of organosolv lignin (Supporting Information, Table S-5 and Figure S-15†).

**Mass balance**

A more detailed investigation of the product mixture, including gases, was conducted to evaluate the mass balance. Each experiment consisted of a deep brown solution of 100 mg organosolv lignin with 100 mg Cu20PMO in 3 mL methanol, heated to 300 °C for 24 h. After quenching by rapid cooling, the gas phase was collected and analyzed by gas chromatography. The liquid phase was then recovered quantitatively and centrifuged. The resulting colorless solution was decanted and the solid catalyst residue dried in vacuo at room temperature for several days.

The gases (550 mL at room temperature, ambient pressure) obtained after 24 h reaction consisted of H2 (18.2 mmol), CH4 (1.8 mmol), CO (2.0 mmol) and CO2 (0.89 mmol). The H2 and CO originate largely from catalytic methanol reforming (CH3OH → 2H2 + CO), while the CO2 results from water-gas shift (CO + H2O → CO2 + H2). The amount of water generated is apparently insufficient to give complete conversion of CO to CO2. There are several likely sources for the methane, including hydrogenolysis of O–CH3 linkages in the organosolv lignin and hydrogenation of one of the C1 components of the system, including CH3OH. Based on the model in Fig. 1, a maximum of 1 mmol CH3 can originate from the substrate itself, therefore the larger observed value implies that C1 hydrogenation is significant.

The originally green catalyst was purple when recovered from the reactor. When the used catalyst was dissolved in nitric acid, the resulting solution contained no black particulates. The absence of char or other insoluble materials was demonstrated by gravimetric analysis of the residual solid. Its average weight after reaction was (102 ± 5) mg (Supporting Information, Table S-3†); thus, there was negligible weight gain.

The colorless solution phase was further treated by removing methanol and other low-boiling volatiles in vacuo. The remaining oily material weighed (58 ± 2) mg (Supporting Information, Table S-4†), and was further analyzed by NMR spectroscopy, GC-MS and gel permeation chromatography. Notably, if that sole product were a propylcyclohexanol, the yield would be 68 mg; the recovered liquid product represents 86% of that quantity. For GPC analysis, the crude mixture was dissolved in 1 mL THF. Less than 2% of the original 100 mg substrate remained, based on a lower detection limit of ca. 1 mg polymer per mL. The observed average molecular weight (191 g mol⁻¹, polydispersity 1.48) corresponds to the monomer-dimer range of 186–387 g mol⁻¹ (Supporting Information, Figure S-5†).

GC-MS analysis revealed a relatively complex mixture of compounds (Supporting Information Figure S-15†). Several components were identified qualitatively by their fragmentation patterns to be cyclohexanols (Supporting Information, Figure S-16). GC-MS results after 2, 4, 12 and 24 h reaction times confirm that, although the product composition evolves, cyclohexyl-derivatives are present. There are only modest changes after the first 4 h, consistent with the behavior seen with the NMR indices.

**Table 3** Indices for liquid reaction products, defined operationally and obtained from 1H NMR measurements. For each experiment, 50 mg substrate and 50 mg Cu20PMO catalyst were heated to 300 °C in 3 mL CH3OH in a 10 mL volume minireactor for a specific time period, and the liquid products were separated and analyzed by 1H NMR. No insoluble char was formed except in experiment 10.

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<th>H&lt;sub&gt;e&lt;/sub&gt;</th>
<th>H&lt;sub&gt;e&lt;/sub&gt;/O&lt;sub&gt;e&lt;/sub&gt;</th>
<th>H&lt;sub&gt;e&lt;/sub&gt;/A&lt;sub&gt;e&lt;/sub&gt;</th>
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<td>46.2</td>
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<td>3.6</td>
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</table>

* This solution was somewhat inhomogeneous. * Data for experiment 9 was generated from the sample used in experiment 8, which was shaken with a small amount of D2O in order to evaluate its content of readily-exchanged protons. * Reaction conducted under analogous conditions but with 100 mg substrate and without catalyst; 40 mg insoluble “char” was also formed.

**Fig. 4** Temporal evolution of the A<sub>e</sub>, O<sub>e</sub> and H<sub>e</sub> indices during organosolv lignin hydrogenolysis/hydrogenation under standard conditions.

has been largely disassembled, with most of its aromatic rings hydrogenated and significant deoxygenation having already taken place. Longer reaction times lead to a slow increase in H<sub>e</sub>, to 86.2 after 24 h, and further declines in A<sub>e</sub> and O<sub>e</sub> to 1.5 and 11.8, respectively. The 24 h values represent the average of runs 7 and 8, the reasonable agreement of which (Table 3) provides a measure of the technique’s reproducibility. In experiment 9, the liquid product of experiment 8 was shaken with D2Ot o to evaluate the content of readily-exchanged protons.

The temporal evolution of the H<sub>e</sub>/A<sub>e</sub> and H<sub>e</sub>/O<sub>e</sub> ratios (Table 3) emphasizes the markedly increasing fraction of aliphatic (vs. aromatic) protons, and the decreasing oxygen content of the products.

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A control reaction with 100 mg catalyst and 3 mL methanol but no substrate was carried out under analogous conditions. However, no higher boiling liquid products were detected by GC-MS analysis.

Fig. 5 compares the $^1$H NMR spectrum of the liquid phase after 24 h reaction to that of the original organosolv lignin. The result for a control reaction performed under the same conditions but without added catalyst is also shown. In the aliphatic chemical shift region, the spectra suggest that the majority of the protons occur in methylene groups (1–2 ppm), consistent with formation of cyclohexyl rings. There is significant intensity below 0.9 ppm, characteristic of aliphatic methyl groups, possibly the termini of propyl chains or methyl substituents on cyclohexyl rings. The latter may arise by aromatic methylation, as seen previously with the model compound DHBF. The relatively low intensity in the 5–3 ppm region indicates that most methoxy groups in the original lignin structure are lost during the reaction.

A control reaction run with 100 mg substrate but no catalyst led to the formation of ca. 40 mg of a black, char-like material. This material is insoluble in all common organic solvents. Elemental analysis showed it contains 69.3% C; 4.3% H and 0.4% N (O not determined). This composition was not dramatically different from that of the organosolv lignin itself, so we conclude that the “char” is largely polymerized lignin. The liquid phase was separated, methanol removed and the brown oily product analyzed by $^1$H NMR. From its spectrum (Fig. 5, top), it is clear that although some transformations had taken place, little aromatic ring hydrogenation had occurred ($\Delta_H = 12.7$, Table 3).

The expected solvent-to-substrate hydrogen/deuteron transfer was demonstrated by conducting an experiment in methanol-$d_4$. Fig. 6 shows the $^1$H and $^2$H NMR spectra of the liquid product mixture. In the $^1$H spectrum, there is little change in the aliphatic proton region (3.0–0.3 ppm) from that of unprocessed organosolv lignin (Fig. 5, bottom). However, the same aliphatic region of the $^2$H NMR spectrum of the same sample reveals extensive deuteration, strongly suggesting that the cyclohexyl rings generated by aromatic ring hydrogenation also underwent extensive exchange between the aromatic protons of the substrate and the reactive solvent medium.

**Summary**

The bio-oligomer organosolv lignin is disassembled to monomeric units with little or no formation of insoluble char by hydrogen transfer from supercritical methanol. The process is catalyzed by a copper-doped porous metal oxide, and the products contain virtually no aromatics and have greatly reduced oxygen content. Such products may be further processed to give liquid hydrocarbon fuels or fuel additives. A scheme for rationalizing lignin disassembly is discussed, and operational indices based on $^1$H NMR properties that describe the progressive transformation from oxygenated aromatics to aliphatic alcohols are introduced. It should be emphasized that the exact structure of the lignin model utilized has only modest influence on the overall conclusions since the use of the indices focuses on the holistic nature of the transformations rather than the specific products formed.

While there is increasing interest in utilizing supercritical fluids, including sc-MeOH, for biomass solubilization, a key advantage of doing so in the presence of a reforming catalyst is the absence of accompanying char formation. Hydroxalate-derived PMOs doped with Earth abundant metals are air- and moisture-stable catalysts and are ideal candidates for optimization. We are extending the application of this promising system to other biomass materials.

**Experimental section**

**Materials**

Organosolv lignin was extracted from sanded poplar sawdust (100 g) with 800 mL methanol (containing 1% HCl) following literature procedures. The 20% Cu-doped hydrotalcite catalyst precursor was prepared and characterized as described previously, with slight modifications described in the Supporting Information. This material was calcined at 460 °C for 24 h to give the catalyst used in these experiments.
Catalysis procedures
In a typical run, the organosolv lignin substrate (100 mg) was dissolved in methanol (3 mL) and combined with the metal oxide catalyst (100 mg) in a 10 mL stainless steel bomb. After purging the vessel with argon, the microreactor was sealed. It was placed in a heating block and heated to 300 °C for the indicated reaction time, after which it was rapidly cooled by immersing in a water bath. Once the pressure was released, the solid and liquid contents of the reactor were transferred to a centrifuge tube and centrifuged at 7000 rpm for 5 min. The liquid phase, containing the reaction products, was decanted. The solid was washed 3 times with methanol, centrifuged, and the methanol washings were collected. The remaining solid was dried in vacuo and weighed. The methanol solvent was removed from the liquid phase by rotary evaporation at room temperature. The remaining, higher boiling liquid was weighed and then further analyzed by NMR, GC-MS and GPC methods.

Instrumentation

GPC measurements were carried out using a Waters 2690 Separation Module instrument equipped with a 2414 Differential Refractometer and a Waters 2998 Photodiode Array Detector, with DMF as the solvent. GC-MS experiments were carried out on a programmable Agilent 5890 GC-MS instrument with a Refractometer and a Waters 2998 Photodiode Array Detector, and a 2414 Differential Analysis Module instrument equipped with a 2414 Differential Analysis Module.

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Elemental analyses were carried out by the UCSB Marine Science Analytical Laboratory.

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