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Enhanced Catalytic Depolymerization of a Kraft Lignin by a Mechanochemical Approach

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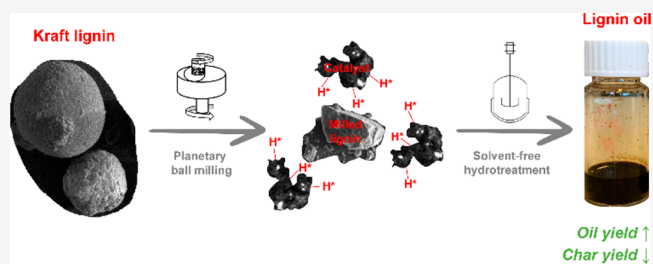


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Supporting Information

ABSTRACT: Kraft lignin is an abundantly available side product from the pulp and paper industry. It has a complex aromatic structure and has great potential to serve as a feedstock for renewable aromatic chemicals. In this communication, we show that a simple mechanochemical pretreatment (viz., ball milling) of commercial Indulin AT kraft lignin before solvent-free hydrotreatment results in a 15% increase in the recovered oil yield with 15% more alkylphenols and a 33% reduction in solids compared to the unmilled sample. This increase raises the carbon efficiency toward the oil based on elemental composition from 76 to 91%, respectively. This enhanced catalytic performance is attributed to improved heat transfer and allowing for better contact between the kraft lignin particles of reduced size and the catalyst particles, prompting enhanced depolymerization at an earlier stage of the reaction, thereby preventing charring.



Lignin is one of the most abundant natural polymers on Earth. A well-known lignin source is kraft lignin, an underutilized side product from the pulp and paper industry.¹ Kraft lignin has a complex structure with aromatic subunits connected by various linkages.^{2,3} This makes kraft lignin an attractive renewable source for aromatic chemicals.⁴ Processes, such as oxidative, base/acid-catalyzed, and (catalytic) fast pyrolysis, have also been explored for lignin depolymerization.⁵ Additionally, aromatic bulk chemicals, such as phenols and aromatics, can be obtained from kraft lignin using reductive processes, like catalytic hydrotreatment.^{6–9} In this communication, we show that a simple mechanochemical pretreatment (viz., ball milling) of kraft lignin before solvent-free hydrotreatment can lead to improved performance (i.e., 15% increase in the recovered oil yield, 15% more alkylphenols, and 33% reduction in solids) compared to unmilled kraft lignin.

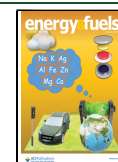
Our group has reported high yields of such alkylphenols and aromatics from kraft lignin via this solvent-free catalytic hydrotreatment approach.^{9,10} This approach was extended using multiple types of technical lignins and different lignin fractions obtained from solvent fractionation.^{11,12} Extensive catalyst screening studies have been conducted using the solvent-free catalytic hydrotreatment approach.^{9,13,14} The objective of all of these studies has been to enhance the yields of the liquid products and, particularly, the amounts of low-molecular-weight chemicals because these are deemed most valuable. A recent study shows that the use of a NiMoP/SiO₂ catalyst resulted in a lignin oil yield and monomer yield as high as 68.1 and 51.8 wt %, respectively.⁹

The structure and morphology of the lignin source are also expected to have a major impact on the hydrotreatment process. Both may be modified using a mechanochemical pretreatment of the lignin. For example, ball milling of kraft lignin before the reaction was found to increase the rate of polyesterification with ϵ -caprolactone. This was attributed to a higher surface area of the lignin as a result of a reduction of the lignin particle size by the pretreatment procedure.¹⁵ Here, we explore the use of ball milling, a grinding process widely employed in the industry,¹⁶ to increase the extent of depolymerization and, thus, the amounts of low-molecular-weight chemicals for the solvent-free catalytic hydrotreatment of kraft lignin. The effect of ball milling conditions, like milling times (5–60 min), on the lignin oil yield and composition was studied. Besides, the physicochemical properties of unmilled and milled kraft lignin were compared using scanning electron microscopy (SEM), N₂ physisorption, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), elemental analysis [CHNS and inductively coupled plasma mass spectrometry (ICP–MS)], gel permeation chromatography (GPC), two-dimensional heteronuclear single quantum coherence nuclear magnetic resonance (2D-HSQC NMR), X-

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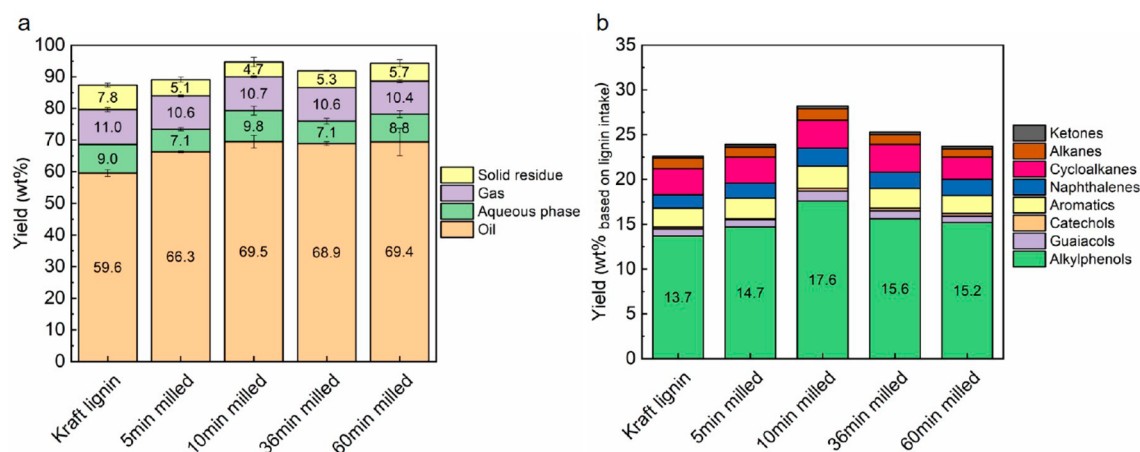


Figure 1. (a) Product yields (wt % on lignin intake) for catalytic hydrotreatment experiments (15 g of lignin, 0.75 g of NiMoP/SiO₂ catalyst, 400 °C, 2 h, and 100 bar H₂ initial pressure) of the unmilled and milled kraft lignin and (b) oil composition quantified by GC × GC–FID based on lignin intake. All reactions were conducted in duplicate, and average values are considered for product yields (see Figure S13 of the Supporting Information for unmilled kraft lignin data).

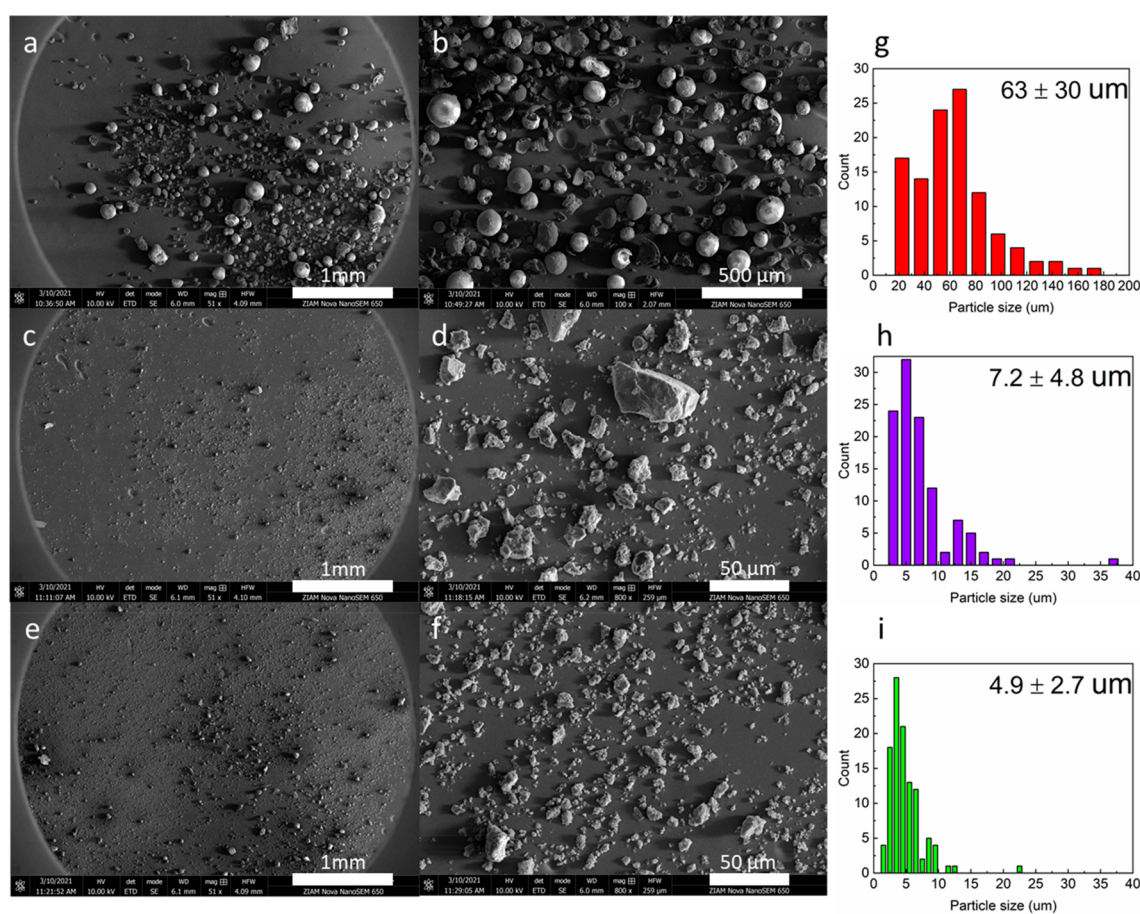


Figure 2. SEM micrographs of (a) kraft lignin (scale bar = 1 mm), (b) kraft lignin (scale bar = 500 μm), (c) 10 min milled (scale bar = 1 mm), (d) 10 min milled (scale bar = 50 μm), (e) 60 min milled (scale bar = 1 mm), and (f) 60 min milled (scale bar = 50 μm). PSDs of (g) kraft lignin, (h) 10 min milled, and (i) 60 min milled. The number in the graph is the mean particle size.

ray diffraction (XRD), and X-ray fluorescence (XRF) to obtain relations between lignin properties and catalytic performance.

Several ball-milled Indulin AT kraft lignin samples were prepared using different milling times (5–60 min) with 5 large ZrO₂ balls (5 × 15 mm) and 10 small ZrO₂ balls (10 × 5 mm), and details are given in Table S1 of the Supporting Information. The visual appearance of the samples differed

considerably. The original kraft lignin is much darker and less cohesive (Figure S1 of the Supporting Information), indicating a major difference in the particle size distribution (PSD), with smaller particles for the ball-milled kraft lignin. However, the particles were too cohesive to separate using analytical sieves, and thus, the PSD could not be determined this way. Thus,

SEM micrographs were used for obtaining the PSD of lignin samples (*vide infra*).

Catalytic hydrotreatment of unmilled and milled lignins was conducted in a batch reactor at 400 °C for 2 h and 100 bar initial H₂ pressure without an external solvent, using a NiMoP/SiO₂ catalyst (the detailed characterization of the NiMoP/SiO₂ catalyst is presented in the Supporting Information).⁹ Typically, the hydrotreatment led to the formation of gas-phase products and a liquid phase with suspended solids. The latter was separated by centrifugation followed by acetone extraction to obtain an organic product oil, an aqueous phase, and a solid residue (Scheme S1 of the Supporting Information). The recovered oil yield of unmilled kraft lignin was 59.6 wt %, whereas a significant improvement (*p* value of a *t* test is 0.003) was found at 66.3–69.5 wt % when using the ball-milled kraft lignin samples (Figure 1). As such, ball milling has a positive effect on the recovered oil yield.

The amount of gas-phase products and aqueous phase were similar when using unmilled and milled kraft lignin. A major difference is found in the solid residue yield, which is 7.8 wt % for unmilled lignin and much lower (4.7–5.7 wt %) when using ball-milled lignin. The mass balance closure is satisfactory for all experiments (87.4–94.7 wt %), although slightly better for hydrotreating experiments using ball-milled lignin also showing a positive effect here.

The molecular weight (GPC; Figure S2 of the Supporting Information) and elemental composition (see Figure S3 of the Supporting Information for a van Krevelen plot) results of the product oils showed considerable depolymerization and hydrodeoxygenation when compared to the feed. However, no significant differences or clear trends were found between unmilled and milled samples in these analyses, showing minimal changes in the oil characteristics. Characterization by comprehensive two-dimensional gas chromatography with flame ionization detection (GC × GC–FID; typical chromatogram in Figure S4 of the Supporting Information) showed that the product oils qualitatively have a similar composition for GC-detectable low-molecular-weight products (Figure S5 of the Supporting Information). The major components are alkylphenols, followed by cycloalkanes and aromatics, as well as minor amounts of guaiacols, catechols, naphthalenes, alkanes, and ketones. Quantification based on kraft lignin intake showed that alkylphenols are the major oil component, with 13.7 wt % yields for unmilled kraft and 14.7–17.6 wt % for milled kraft lignin (Figure 1b), and when corrected for the elemental composition (Table S5 of the Supporting Information), 76 and 91% of the carbon intake ends up in the oil for the unmilled and 60 min milled sample, respectively. The overall oil compositions are similar (Figure S5 of the Supporting Information); thus, the increased yield of valuable bio-based chemicals (e.g., alkylphenols and aromatics) is mainly due to the increased overall recovered product oil yield and decreased solid residue.

To rationalize the higher oil yield when using ball-milled kraft lignin, relevant physicochemical properties (e.g., PSD, surface area, molecular weight, and interunit linkages) of unmilled and milled kraft lignin samples were determined. Because PSD was unsuccessful by sieving (*vide supra*), SEM micrographs were used to observe the morphology and particle size changes before and after ball milling. Macro overview SEM images of three samples (unmilled, 10 min milled, and 60 min milled) showed a significant decrease in the particle size for ball-milled lignin (panels a, c, and e of Figure 2). In addition,

unmilled lignin contains mainly spherical particles, likely the result of spray drying,¹⁷ while ball-milled lignins are made up of fragmented particles (panels b, d, and f of Figure 2). The PSD for each sample was determined, showing a drastic reduction in the average particle size upon ball milling (63 μm for unmilled to 7.2 μm for 10 min milling and 4.9 μm for 60 min milling; see panels g, h, and i of Figure 2). This phenomenon was also reported in the literature when kraft lignin was milled with glass balls.¹⁵

Ball milling also resulted in major changes in the specific surface area and pore volume of the samples (Table S4 of the Supporting Information). The unmilled kraft lignin has a very low surface area (1.0 m²/g) and limited pore volume (0.004 cm³/g), while these numbers are significantly higher for milled samples (surface areas of 3.4–3.5 m²/g and pore volumes in the range of 0.015–0.026 cm³/g). Besides, the “melting” behavior of kraft lignin was optically observed using a M-560 (Büchi) device, and all kraft lignin samples “melted” at around 180 °C.¹⁰ Accurate insights into this phase transition were obtained using DSC (Figure S6 of the Supporting Information). It shows a clear effect at about 150 °C, associated with a glass transition temperature (*T*_g).

The moisture, ash, volatiles, fixed carbon, and CHONS contents of the unmilled and ball-milled samples are similar (≤1% difference), as shown in Table 1. The slight decrease of

Table 1. Proximate Analysis, Ultimate Analysis, Weight Average Molecular Weight (*M*_w), and Linkages of Unmilled and 60 min Ball-Milled Kraft Lignin

| analysis | parameter | unit | kraft lignin | 60 min ball-milled |
|--------------------|-----------------------|---------------------------|--------------|--------------------|
| proximate analysis | moisture | wt % (ar) ^a | 3.2 | 2.5 |
| | ash | wt % (db) ^b | 1.8 | 2.1 |
| | volatile | | 62.2 | 61.8 |
| | fixed carbon | | 36.0 | 36.1 |
| ultimate analysis | C | wt % (db) ^b | 63.7 | 62.7 |
| | H | | 6.2 | 6.1 |
| | O ^c | | 25.9 | 26.9 |
| | N | | 0.8 | 0.8 |
| | S | | 1.6 | 1.4 |
| GPC | <i>M</i> _w | g/mol | 1630 | 1550 |
| HSQC ^d | β–O–4 | per 100 aromatic C9 units | 11.7 | 12.1 |
| | β–5 | | 4.9 | 5.4 |
| | β–β | | 5.0 | 4.6 |

^aOn an as-received (ar) basis. ^bOn a dry basis (db). ^cDetermined by the difference. ^dThe data were calculated by the semi-quantitative method and based on 100 aromatic C9 units.

C, H, and S contents upon milling could be due to some oxidation that was previously observed during milling.^{18,19} The weight-average molecular weight of milled lignin is only slightly lowered (about 5%), and the molecular weight distributions are about similar (Figure S7 of the Supporting Information). The 2D-HSQC NMR of the samples showed a condensed guaiacyl aromatic structure with some stilbenes and the expected low amounts of β–O–4, β–5, and β–β linkages (Figure S8 of the Supporting Information).^{2,11} Some very minor resonances from, for example, enol ethers disappeared after ball milling, possibly as a result of some repolymerization or degradation induced by intensive ball milling.^{15,20} Overall, differences in integration data of the signals in the linkage region are minimal (Table 1),¹⁹ indicating that the ball milling

under the prevailing conditions did not significantly alter the lignin chemical structure.

TGA, which can serve as an indicator of the types of linking structures, showed no significant changes (Figure S9 of the Supporting Information).²¹ Only slightly more residue is left for unmilled lignin, also indicating minimal changes to the chemical structure induced by the milling. This observation further supported the results obtained from HSQC, GPC, and DSC analyses. Finally, the XRF and XRD analyses were used to check contamination from the ZrO₂ jar and balls. The Zr signal is below the detection limit for XRF, and XRD patterns of unmilled and milled lignin (Figure S10 of the Supporting Information) are almost the same, indicating no ZrO₂ is present in the milled lignin.

The solvent-free hydrotreatment in a batch setup starts out with lignin as a solid, which is mixed with the catalyst, and then is heated to the desired reaction temperature (e.g., 400 °C). During heating, the lignin will soften and “melt” at some stage (140–170 °C) and then, together with the low-molecular-weight products (oligomers) formed, act as the solvent. Considering a previously established reaction network (Figure S11 of the Supporting Information),¹⁰ the char formation is the most crucial part of this study, because the decreased char formed directly led to the increased recovered oil yield.

The inhibition for char formation as a result of the ball milling should happen at a low temperature (≤ 200 °C) because, beyond this melting temperature, the impact of different physical properties of particles should be minimal as a result of the more efficient mixing of molten lignin and solid catalyst particles under vigorous stirring in the batch setup. Heat transfer can play a role in the melting process, which can influence the stabilization of reactive intermediates. It is found that less heat flow is needed in the heating ramp of milled lignin (DSC result; Figure S6 of the Supporting Information), suggesting more rapid heating of milled lignin in the batch setup considering the constant power input during the initial stages of the hydrotreatment. The rapid melting can improve the contact between lignin and catalyst, which benefits the stabilization.

The close contact between milled lignin and catalyst particles may also have an effect at a low temperature, and it is known that non-catalytic thermal treatment under the same conditions leads to excessive char formation.²² It is anticipated that during the very beginning of the hydrotreatment (≤ 200 °C) the reduced size milled kraft lignin particles (7.2 μm for 10 min milled lignin) are close to the size of the catalyst particles (average particle size of 6.8 μm ; Figure S16 of the Supporting Information). This allows for more efficient interactions compared to the case of unmilled kraft lignin (63 μm). Increased exposure to the hydrogen species on the Ni catalyst leads to reduced char formation (Figure S12 of the Supporting Information) by hydrogenation and, thus, stabilization of reactive intermediates (radicals and double bonds) already formed at low temperatures (≤ 200 °C) as a result of thermal bond cleavage.²³ According to this, unstable intermediates formed under the solvent-free condition at the heating phase require stabilization by hydrogen species on the catalyst, and a smaller particle size now allows for close intimacy between the catalyst and increased surface of the smaller lignin particles. Overall, the improved exposure promotes depolymerization at low temperatures or, at the very least, affects the competing reactions (depolymerization versus repolymerization of reactive intermediates) during lignin hydrotreatment.

In conclusion, the particle size of Indulin AT kraft lignin can efficiently be decreased by ball milling. It is shown to be a simple and effective method to inhibit char formation and, thus, improve the oil recovery and valuable monomer (e.g., alkylphenols) yields in a solvent-free catalytic hydrotreatment approach. This finding provides a strategy that can improve value generation from this abundant residue from the paper industry.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.energyfuels.2c01109>.

Experimental section and catalyst characterization, ball milling conditions, gas-phase composition, elemental analysis, physical properties of lignins, carbon content and yield, workup procedure, visual images, GPC data, van Krevelen plot, GC \times GC–FID chromatogram, oil composition, DSC curves, 2D-HSQC NMR spectra, thermogravimetric (TG) and derivative thermogravimetric (DTG) curves, XRD patterns, proposed reaction network, schematic illustrations, reproducibility data, N₂ adsorption–desorption isotherms, temperature-programmed desorption of ammonia (NH₃-TPD) profile, SEM micrograph and PSDs, and high-angle annular dark-field scanning transmission electron microscopy–energy-dispersive X-ray spectroscopy (HAADF-STEM–EDS) images (PDF)

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Notes

The authors declare no competing financial interest.

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