Alkaline Oxidation of Lignin Using Reversibly-Soluble Bases

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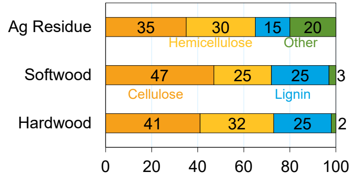
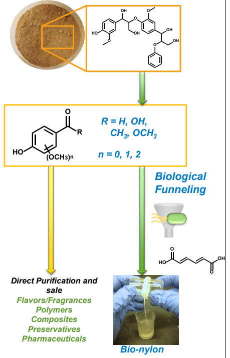
Production of oxidized aromatic monomers from lignin has been an intriguing process for decades, but widespread implementation has been inhibited by the high hydroxide:lignin ratios required for significant aldehyde yields. The high hydroxide loading in most scenarios renders the process uneconomical even for high-value products such as vanillin. In this work, we explore alkaline oxidation of a lignin-rich enzymatic hydrolysis residue isolated from corn stover, using alkaline earth metal hydroxides, such as $Sr(OH)_2$ and $Ba(OH)_2$ as base promoters. These materials are soluble at reaction temperature, but mostly insoluble at room temperature, allowing recovery and reuse by simple filtration. We show that monomer yields and profiles using these bases is similar to that obtained using NaOH as base, and that $Sr(OH)_2$ can be recovered in yields above 90%. Preliminary TEA and LCA suggest that replacing NaOH with $Sr(OH)_2$ can decrease monomer production costs by 40% and decrease global warming potential in lignin depolymerization by 30%, enabling a more economical and sustainable process.

$Sr(OH)_2$ can replace NaOH in alkaline oxidation of lignin with significant economic and environmental benefits

Background

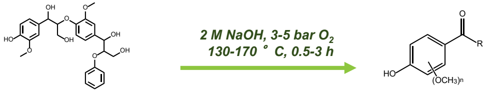




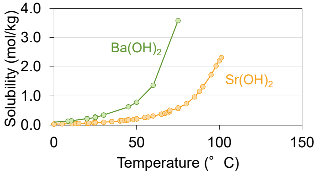
- Lignin is a heterogeneous aromatic polymer that comprises > 15 % of lignocellulosic biomass.[1]
- Valorization is critical for biorefinery economics.
- Depolymerization and further upgrading is promising valorization strategy.
- Depolymerized lignin can be purified and sold directly, or biologically-funneled into versatile intermediates, such as muconic acid, that can be upgraded into polymers, such as nylon.[2]

Component	Corn Stover	DMR Lignin
Glucan	40.3	9.4
Xylan	25.0	10.8
Other Sugars	5.3	4.1
Acetate	3.9	0.9
Lignin	**16.1**	**53.5**
Ash	3.3	1.9
Other/unknown	6.2	19.4
Total	100.0	100.0

- The focus of this work is depolymerization of native and isolated corn stover lignin.
- The deacetylation, mechanical refining, and enzymatic hydrolysis (DMR-EH) process preserves the lignin in a native like state

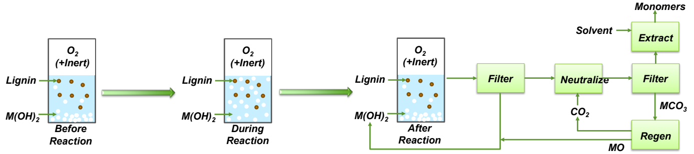


- Lignin depolymerization by alkaline aerobic oxidation is promising because it generates relatively high yields of monomers that are biologically available
- High hydroxide ion concentrations (~2 M) are required for high monomer yields, but most is wasted during neutralization for monomer recovery.
- Neutralization creates a high-salt solution that is not suitable for biological upgrading, while wasted NaOH decreases economic and environmental standing.

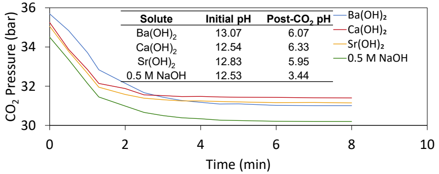


- Some hydroxides show low solubility at room temperature but high solubility under reaction temperatures.[3]
- **Hypothesis: $Ba(OH)_2$ and $Sr(OH)_2$ should allow excess hydroxide recovery by filtration rather than neutralization.**

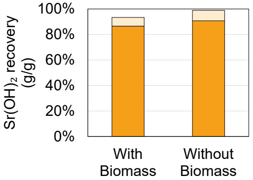
Process Concept



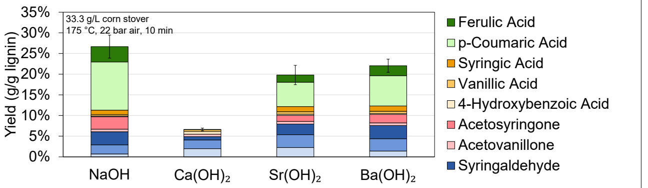
- The necessary excess of base is loaded into the reactor before reaction, but most is insoluble.
- During reaction, the insoluble portion of base becomes soluble, generating the high base concentration needed for high lignin monomer yields.
- After reaction the reactor is cooled down, precipitating most of the excess base, which can be directly recycled by filtering.
- Most of the remaining base can be precipitated as the corresponding carbonate, which is even less soluble than the base, leaving a neutral (pH 6-7) solution that is well suited for direct monomer extraction or biological upgrading.
- Neutralization occurs within 5 min, and > 90% of the base (Sr shown) can be recovered.



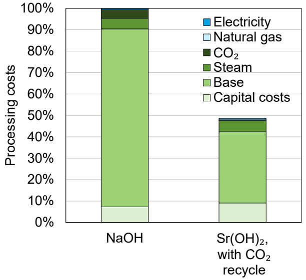
Solute	Initial pH	Post-CO_2 pH
$Ba(OH)_2$	13.07	6.07
$Ca(OH)_2$	12.54	6.33
$Sr(OH)_2$	12.83	5.95
0.5 M NaOH	12.53	3.44

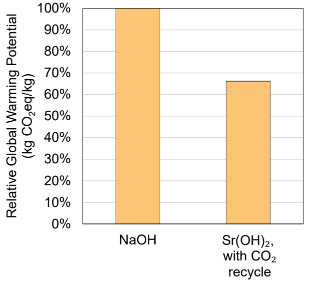


Results



- Monomer yields using $Sr(OH)_2$ and $Ba(OH)_2$ are similar to NaOH
- $Ca(OH)_2$, which does not exhibit the same extent of temperature-reversible solubility
- Main difference between NaOH and $Sr(OH)_2$/$Ba(OH)_2$ is in yield of coumaric and ferulic acid
- Similar trends observed with corn stover DMR-EH residue
- $Sr(OH)_2$ may be preferable to $Ba(OH)_2$ due to lower solubility of the corresponding carbonate, lower toxicity of Sr than Ba, lower calcination temperature required to regenerate precipitated carbonate to the oxide, and lower mass of Sr





- Replacing NaOH with $Sr(OH)_2$ could reduce processing costs by > 50% and global warming potential by > 30%.
- Additional savings available if lignin loading increases (assuming monomer yields can be maintained).

Conclusions

- DMR-EH processing preserves lignin in a native-like state
- Alkaline oxidation generates high-value, biologically-available monomers from lignin
- Replacing NaOH with $Sr(OH)_2$ shows similar monomer yields, but should decrease production costs and increase process sustainability

References
[1]Kumar et al., *Ing Eng Chem Res*, **2009**, 48:3713-3729
[2]Vardon et al., *Green Chem*, **2016**, 18:3397-3413
[3]Lambert et al., Alkaline Earth Hydroxides in Water and Aqueous Solutions, *IUPAC Solubility Series*, Vol 52, **1992**

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