Heterogeneous base catalyzed depolymerization of lignin into aromatic monomers

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Introduction

- Lignin is a natural amorphous three-dimensional polymer consisting of methoxylated phenylpropane structures that confers strength and rigidity to plants.[1]
- Lignin is generated as a major by-product during bio-ethanol production and having several aromatic rings linked together via various linkages (e.g. C-C bond, C-O-C bonds, etc).
- Most abundantly naturally occurring phenolic polymer in the world.

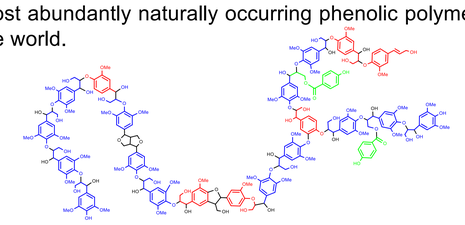
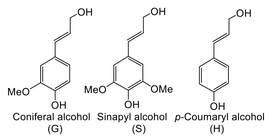


Figure 1. Schematic representation of lignin

- The composition of lignin (monolignols) varies considerably from plant to plant.[2]



Monolignols

Plant	G (%)	S (%)	H (%)
Softwood (gymnosperm)	>95	None or trace	<5
Hardwood (angiosperm)	25-50	46-75	0-8
Grasses (graminaceous)	33-80	20-54	5-33

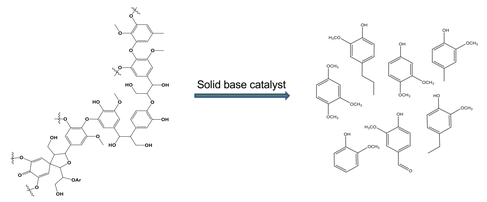
Motivation

- Absence of a systematic study of the depolymerisation of lignin into aromatic monomers.
- Most of the previous studies are limited to the use of homogeneous bases as catalyst.[3]

Objectives

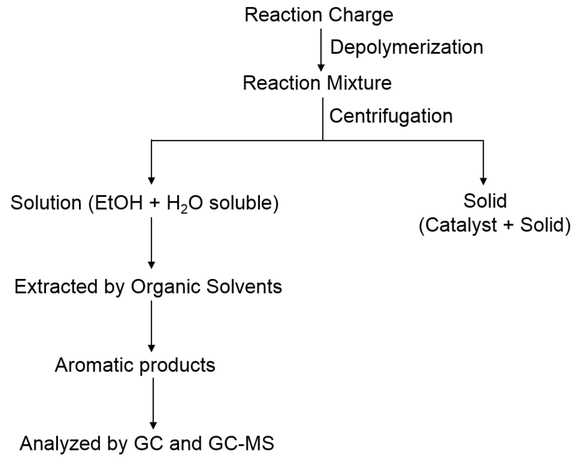
- Developing a method for the depolymerisation of lignin into aromatic monomers.
- Use of actual lignin substrate.
- Use of solid base catalysts at low temperature (T ≤ 250°C).

Reaction Scheme



Lignin — Aromatic monomers

Work-up procedure



Experimental Parameters

- Substrate: Lignin
- Catalyst: Various solid bases
- Solvent: Ethanol-water
- Temperature: 230-270°C
- Time: 20-120 min.

Experimental methodology

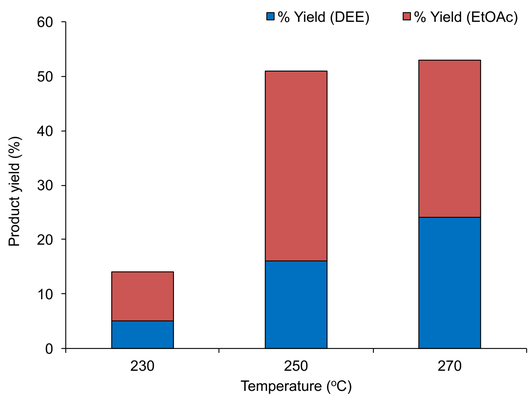
Base catalyzed depolymerization:

- Lignin depolymerization (LD) reactions were conducted in a batch mode at desired temperature and time. EtOH:H_2O was used as reaction media for all the reactions. After the reaction, catalyst was separated by centrifugation and washed thoroughly with EtOH:H_2O in order to remove any adsorbed lignin/ products on the catalyst. The work up of the reaction mixture was performed and later products were extracted from reaction mixture in different organic solvents.
- Analysis: Lignin and products were analysed by using GC, GC-MS, NMR, FT-IR, etc. Solid base catalyst (fresh and spent) were characterized using XRD, CO_2 TPD, N_2 sorption, etc. techniques.
- Product yield calculations:

$$\%\ \text{Yield (DEE / EtOAc)} = \frac{\text{Wt. of DEE / EtOAc soluble products (g)}}{\text{Wt. of lignin (g)}}$$

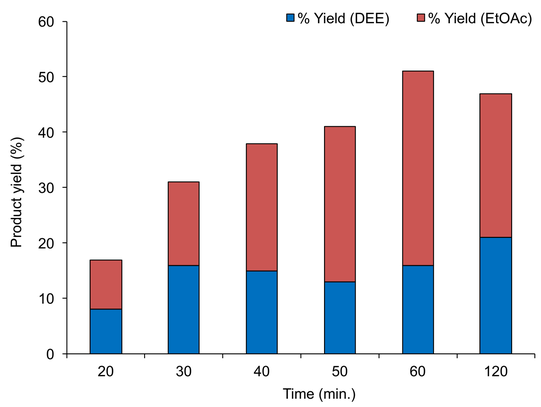
Results and Discussions

Effect of temperature



- It is apparent from the above figure that product yield increases with increase in the temperature.
- DEE = Diethyl ether, EtOAc = Ethyl acetate

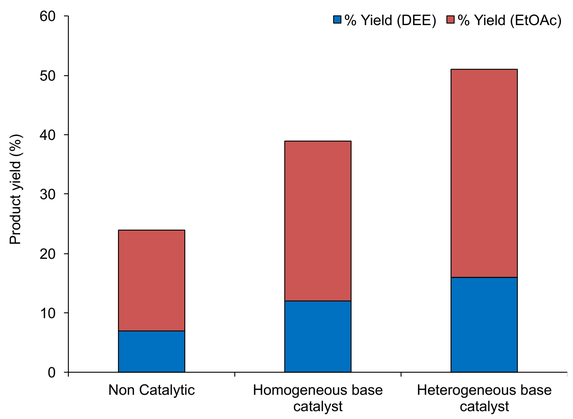
Effect of time



- With increase in time, the product yields increases (20-60 min.) while after 60 min. degradation of products was observed.

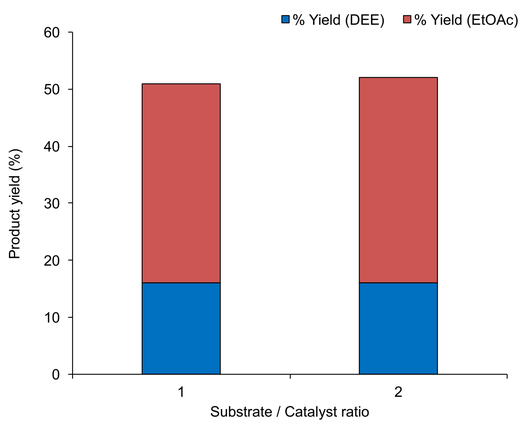
Results and Discussions

Catalyst evaluation for lignin depolymerization

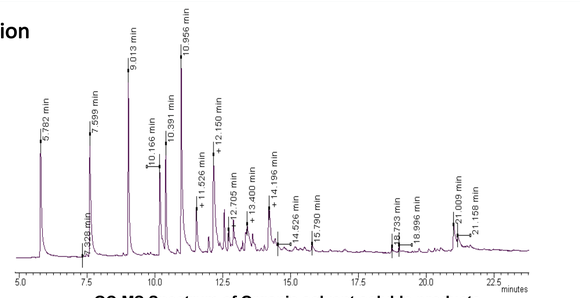


- It is noticeable from the figure that heterogeneous base catalysts shows more activity for the depolymerization of lignin into aromatic monomers.

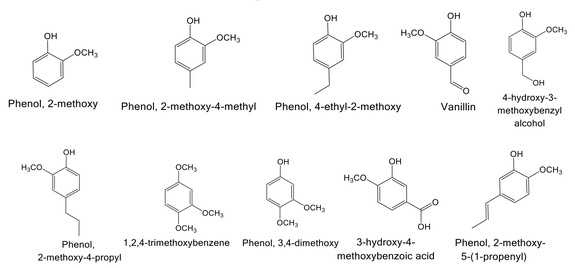
Effect of Substrate / Catalyst ratio on lignin depolymerization



- Substrate to catalyst ratio has negligible effect on the product yield.
- It is more beneficial to use lesser catalyst i.e. substrate to catalyst ratio of 2.



GC-MS Spectrum of Organic solvent soluble products



Products identified by GC-MS

Conclusions

- **Lignin (Mw. = 60,000 Da) depolymerization using solid base catalysts was done at milder reaction conditions (T ≤ 250°C).**
- **The yield of aromatic monomers varied strongly depending on the heterogeneous base catalyst used.**
- **Monomers yields were improved by optimizing reaction conditions (ca. 50%).**

References

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