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Reaction pathways of catalytic lignin ethanolysis



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Background

Previous work: Reaction pathways of Kraft lignin ethanolysis

Reaction pathways of enzymatic hydrolysis lignin ethanolysis

Background

Lignin, the only renewable aromatic resource





Nature **454**, 841-845 (2008)

Background



Lignin shows lower O/C, higher energy content among lignocellulosic biomass, indicating it is more promising as a petroleum alternative.

Background

Available lignin resources

Kraft Lignin	• Byproduct of pulping industry
Enzymatic Hydrolysis Lignin	• Byproduct of bio-ethanol
Organosolv Lignin	Soluble in organic solventInsoluble in water
Others	Steam explosion ligninOxidation lignin

- Enzymatic Hydrolysis Lignin probably become future major lignin raw stock

Previous work



Overall yield of quantified products **1.64 g/g** lignin.

• **O** 25 main products cover 84% of the total area in the GC-FID

Previous work

Ethanolysis of Kraft lignin with different Mo-based catalysts



- (A) Liquid product yields of lignin conversion over different Mo-based catalysts
- The FT-IR spectra of the different samples before and after reaction **(B)**
 - (a) Used MoO_3/Al_2O_3 , (b) Used Mo/Al_2O_3 , (c) Used α -MoC_{1-x}/AC, (d) Used Mo_2N/Al_2O_3 (e) Kraft lignin, (f) Dried liquid product from lignin catalyzed by Mo/Al_2O_3 .

Ma et al., ACS Catal., 2015, 5, 4803–4813

Previous work



MALDI-TOF-MS profiles of various substrates:

(a) Kraft lignin treated in supercritical ethanol without catalyst,(b) Kraft lignin treated in supercritical

(b) Kraft lignin treated in supercritical ethanol over the MoC_{1-x}/AC catalyst.

EPR spectra of (a) used Mo/Al_2O_3

and (c) Kraft lignin.

catalyst, (b) fresh Mo/Al₂O₃ catalyst



Ethanolysis enzymatic hydrolysis lignin (EHL)

Enzymatic hydrolysis lignin (EHL)



Microbial Biotechnology, 2016, 9, 585–594

Composition of Kraft lignin and EHL



Elemental analysis of Kraft lignin

С	Η	Ν	S	0
49.5 %	4.71 %	0.15 %	2.8 %	42.8 %



С	Н	Ν	S	0
61.8%	6.48%	0.90%	0.58%	30.3 %

EHL Characterization



EHL Characterization

HSQC-NMR of EHL



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Reaction pathways of enzymatic hydrolysis lignin ethanolysis

EHL ethanolysis with unsupported Ni catalyst



Ind. Eng. Chem. Res. 2020, 59 (16), 7466-7474.

EHL ethanolysis with unsupported Ni catalyst



Effect of the solvent on the structure of main monomers



TIC of products and structures of main monomers obtained from EHL depolymerization with Ni (220H) at 280 °C for 6 h with 20 bar H_2 .

Conversion of primary monomers





The conversion of syringol, guaiacol and phenol over Ni (220H) at 280 °C for 6 h in ethanol under 20 bar H_2

The conversion of primary monomers over Ni (220H) at 280 °C for 6 h in ethanol

The reaction pathways of monomer formation





Summary

EHL ethanolysis happens at 280 °C without a catalyst. The ether linkages in EHL are completely cleaved and 10.8 wt% monomers are produced.

With unsupported Ni catalyst, EHL ethanolyzes completely. The esters come from the esterification of acid units in EHL, and para-alkyl phenols come from the conversion of primary units in EHL instead of from alkylation routes.





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