EHLCATHOL

Chemical transformation of enzymatic hydrolysis lignin (EHL)
with catalytic solvolysis to fuel commodities under mild conditions

Catalytic depolymerization of Kraft lignin and enzymatic hydrolysis lignin to chemicals and fuels

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http://ehlcathol.eu/

Literature Review:

Part 1: **Catalytic ethanolysis of Kraft lignin: the role of ethanol**

Part 2: **Catalytic depolymerization of enzymatic hydrolysis lignin (EHL): reactivity of EHL**

Literature Review:

Part 1: Catalytic ethanolysis of Kraft lignin over MoC_{1-x}

Ethanolysis of Kraft lignin over MoC_{1-x}/AC

Kraft Lignin (Sigma)

$280\ ^oC$, 6 h

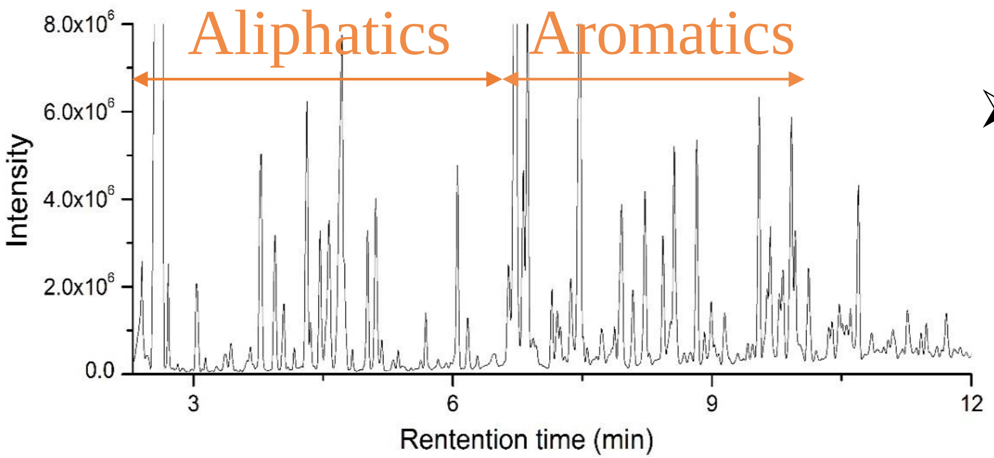
Ethanol, MoC_{1-x}/AC

Aliphatics
Higher alcohols and esters

Aromatics
Arenes, phenols and benzyl alcohols

Insoluble

No char



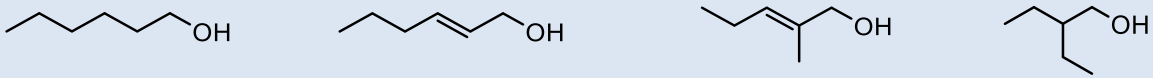
- Overall yield of quantified products **1.64 g/g** lignin.

Angew. Chem. Int. Ed., **2014**, 126, 7438-7443

Ethanolysis of Kraft lignin over MoC_{1-x}/AC

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

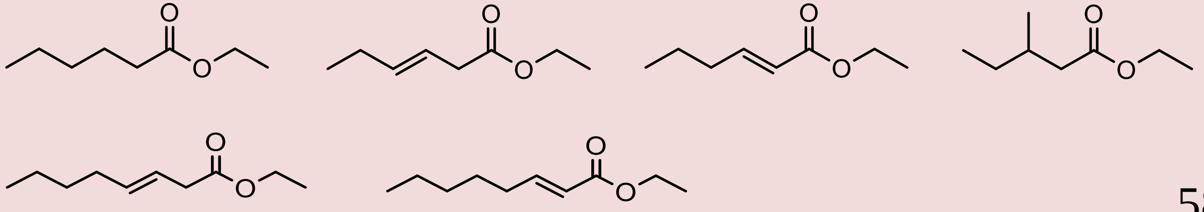
Alcohols – C6



25.2%

Esters – C8

Esters – C10



58.4%

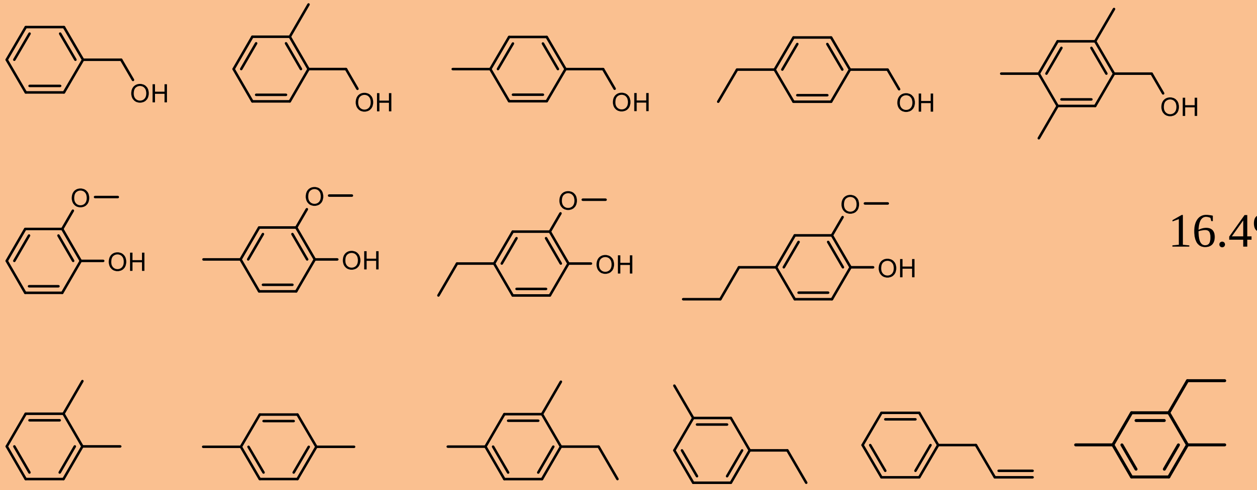
Aliphatics

Ethanol self-conversion

Benzyl alcohols

Phenols

Arenes



16.4%

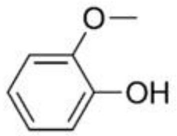
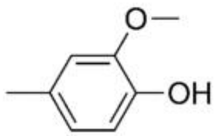
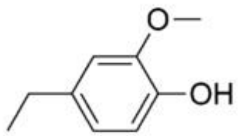
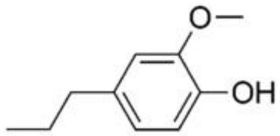
Aromatics

Lignin depolymerization

Angew. Chem. Int. Ed., **2014**, 126, 7438-7443

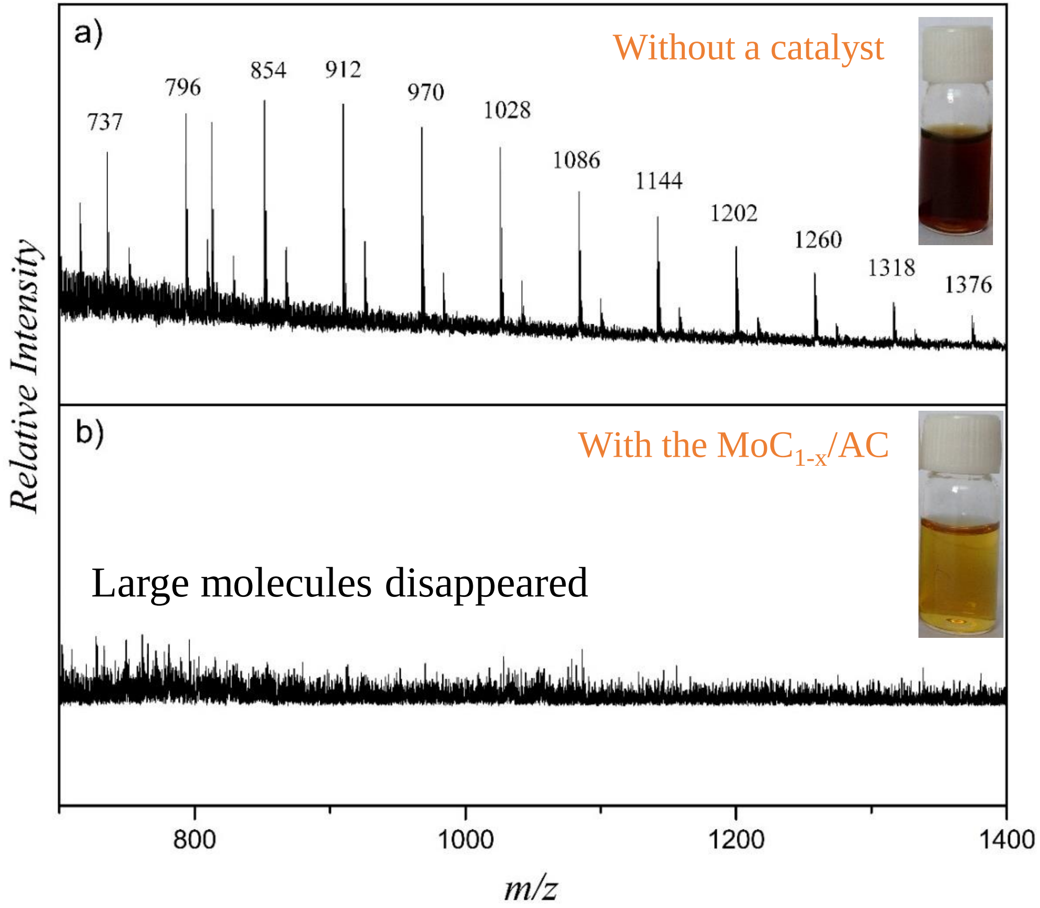
Ethanolysis of Kraft lignin over MoC_{1-x}/AC

Ethanol is the most efficient solvent for Kraft lignin conversion

Products	Solvent			
	ethanol	water	methanol	isopropanol
	4	14	3	17
	35	3	8	2
	16	11	5	5
	23	8	2	4
other aromatics	202	9	2	3
alcohols	409	–	–	–
esters	949	–	–	–

Angew. Chem. Int. Ed., **2014**, 126, 7438-7443

Proposal of the reaction mechanism



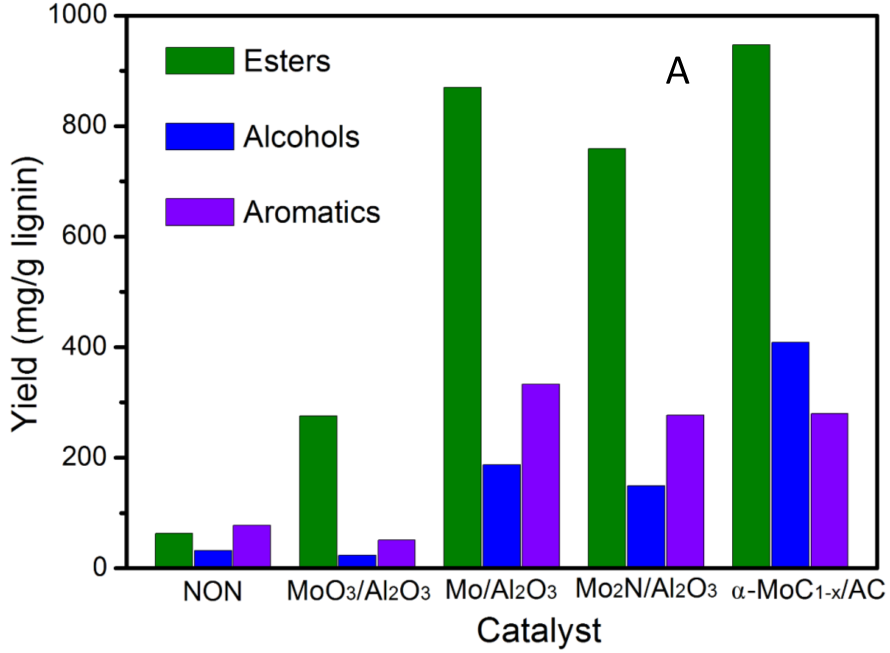
m/z	Difference
737	-
796	58
815	19
854	39
912	58
970	58
1028	58
1086	58
1144	58
1202	58
1260	58
1318	58

MALDI-TOF-MS profiles of various substrates：
(a) Kraft lignin treated in supercritical ethanol without catalyst,
(b) Kraft lignin treated in supercritical ethanol over the MoC_{1-x}/AC catalyst.

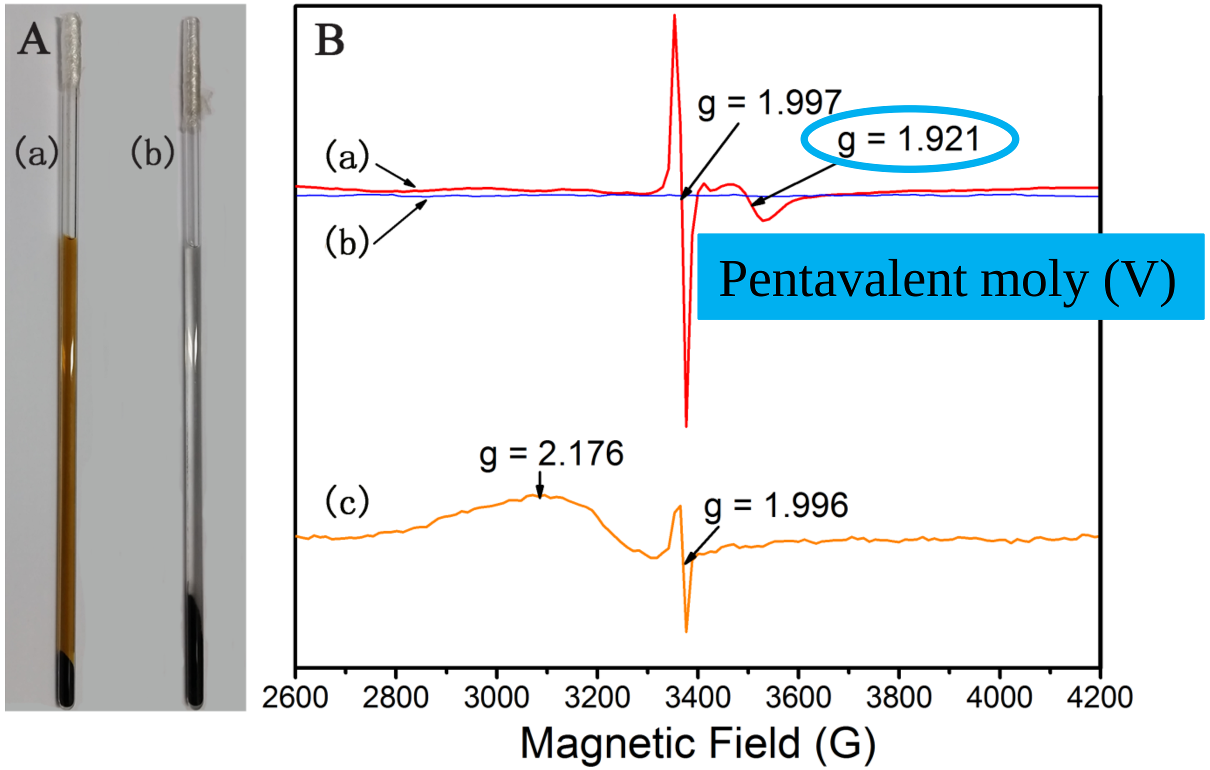
Angew. Chem. Int. Ed., **2014**, 126, 7438-7443

Proposal of the reaction mechanism

All the Mo-based catalysts show similar activities and give similar products



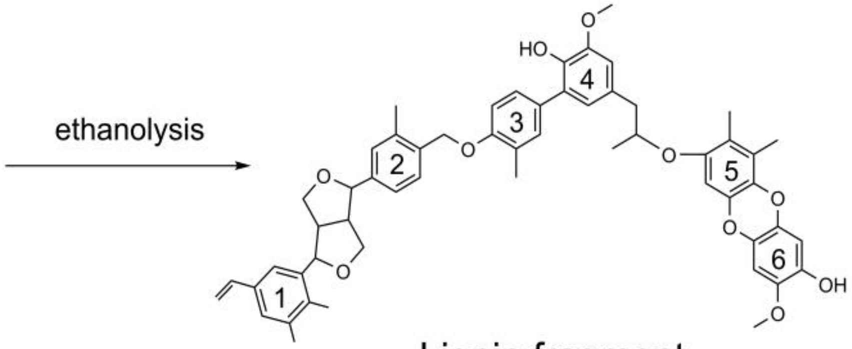
Liquid product yields of lignin conversion over different Mo-based catalysts



EPR spectra of (a) used Mo/Al_2O_3 catalyst, (b) fresh Mo/Al_2O_3 catalyst and (c) Kraft lignin.

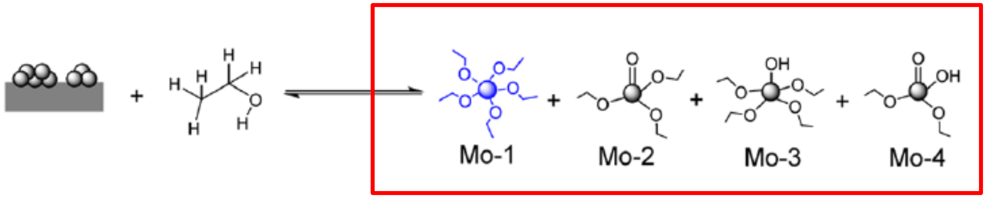
ACS Catal., **2015**, 5 , 4803–4813

Proposal of the reaction mechanism

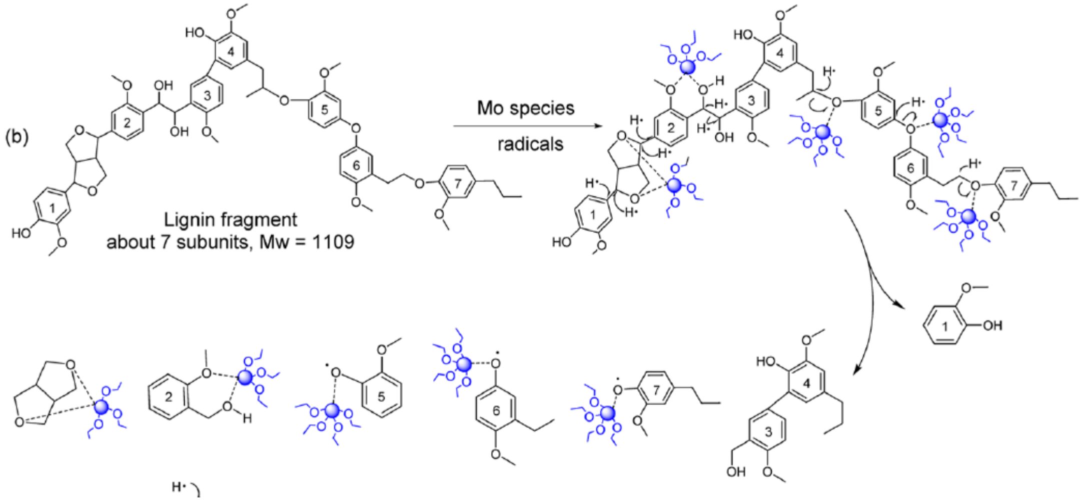


Kraft lignin
Mw = 60,000

Lignin fragment
about 6 subunits, Mw = 891



Ethanolyzed Mo species



ACS Catal., **2015**, 5 , 4803–4813

Literature Review:

Part 2: Catalytic depolymerization of enzymatic hydrolysis lignin (EHL)

EHL

Lignin source: Corncob

Component	Lignin	Carbohydrate	Ash
Mass content (wt%)	91.2	0.12	0.59

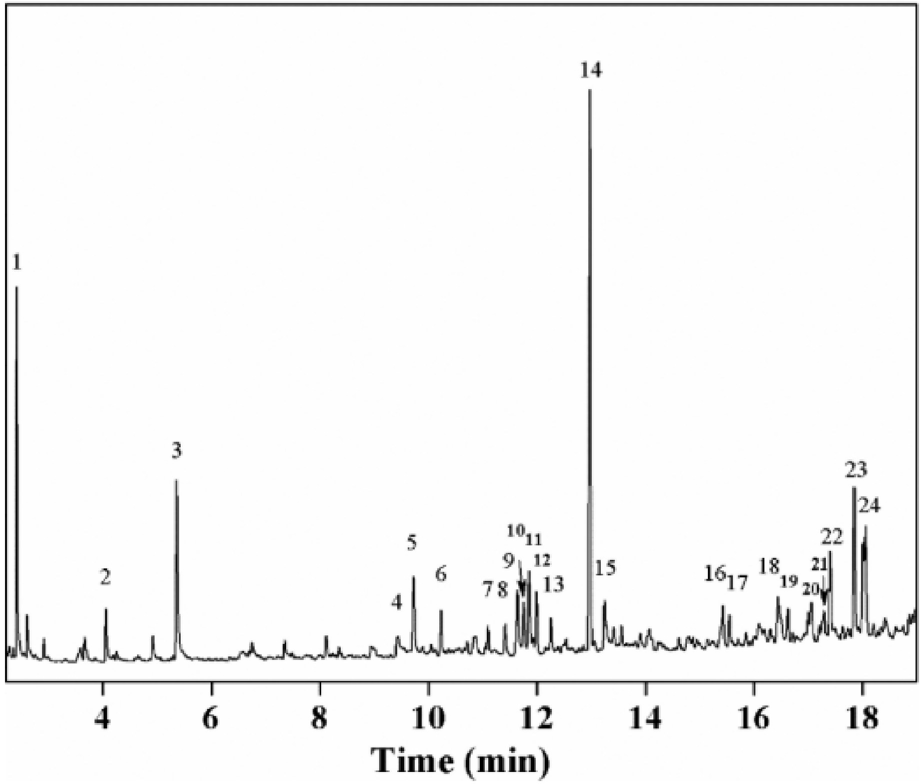
Elemental analysis of EHL

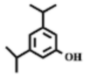
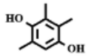
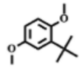
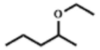
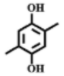
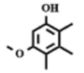
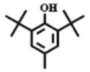
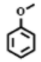
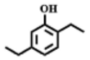
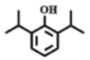
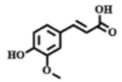
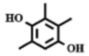
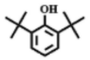
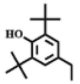
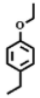
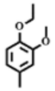
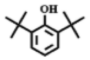
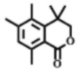
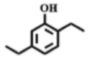
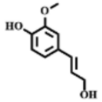
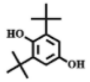
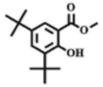
C	H	N	S	O
61.29%	6.69%	0.98%	0.01%	29.61%

Cl	Na	p	Fe	Si
0.797%	0.089%	0.089%	0.050%	0.045%

Catalytic ethanolysis of EHL without H_2

$WO_3/\gamma\text{-}Al_2O_3$ catalyzed EHL ethanolysis at 320 °C under 0 bar N_2



No.	Structure	Yield	No.	Structure	Yield	No.	Structure	Yield	No.	Structure	Yield
1		39.4	7		3.1	13		5.3	19		5.4
2		8.2	8		6.5	14		89.3	20		12.7
3		-	9		13.0	15		11.6	21		5.7
4		4.9	10		7.7	16		10.3	22		13.0
5		13.8	11		13.7	17		4.6	23		26.3
6		6.6	12		9.3	18		15.3	24		37.6

- No char is formed
- High yield of aromatic products (315.8 mg/g EHL with 36.3% alkylphenols)

Ind. Eng. Chem. Res. **2019**, 58, 10255-10263

Catalytic solvolysis of EHL over $WO_3/\gamma\text{-}Al_2O_3$

Product yield and distribution over different catalysts

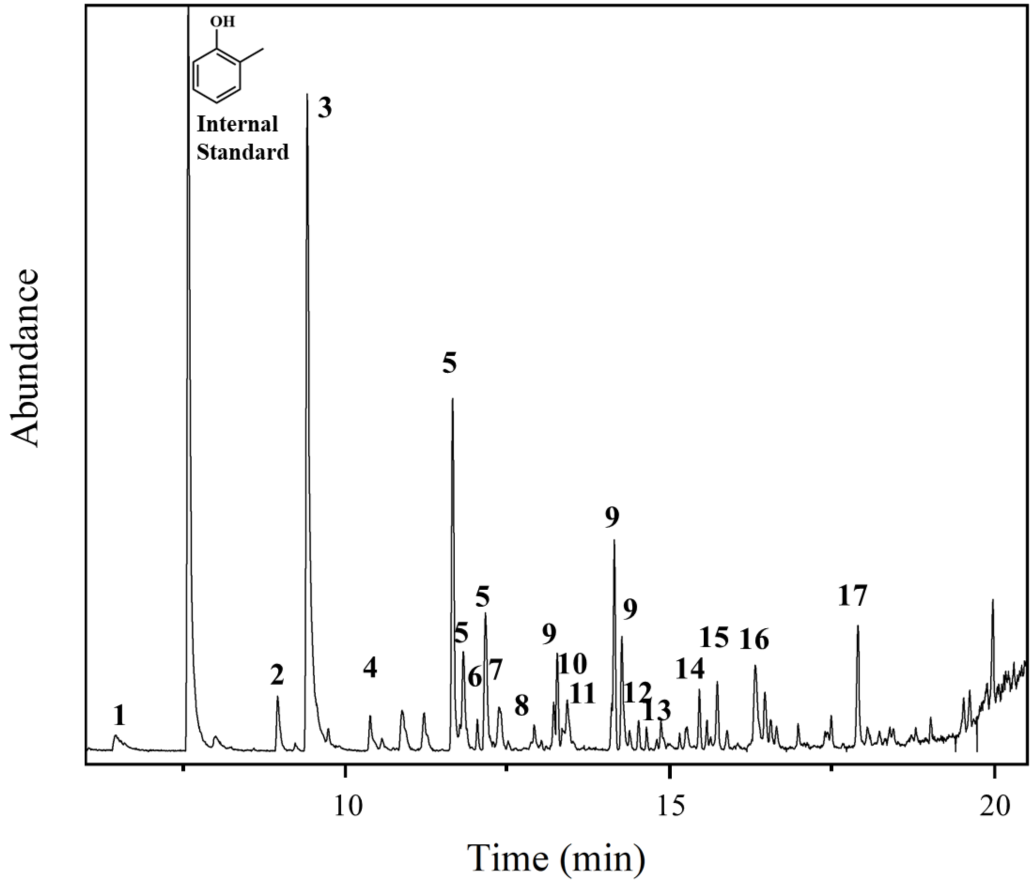
Entry	Catalyst	Solvent	Yield (mg/g EHL)			
			Aromatic Ethers	Aromatic Esters	Phenolic Compounds	Overall Aromatic Compounds
1	WO_3	Ethanol	51.1	43.6	123.3	218.0
2	H_2WO_4	Ethanol	23.1	11.5	128.3	169.1
3	$\gamma\text{-}Al_2O_3$	Ethanol	19.3	2.4	43.7	65.5
4	$WO_3/\gamma\text{-}Al_2O_3$	Ethanol	32.9	26.3	245.2	315.8
5	$WO_3/\gamma\text{-}Al_2O_3$	Methanol	16.2	3.5	160.2	179.6
6	$WO_3/\gamma\text{-}Al_2O_3$	Isopropanol	26.8	5.7	96.0	128.2

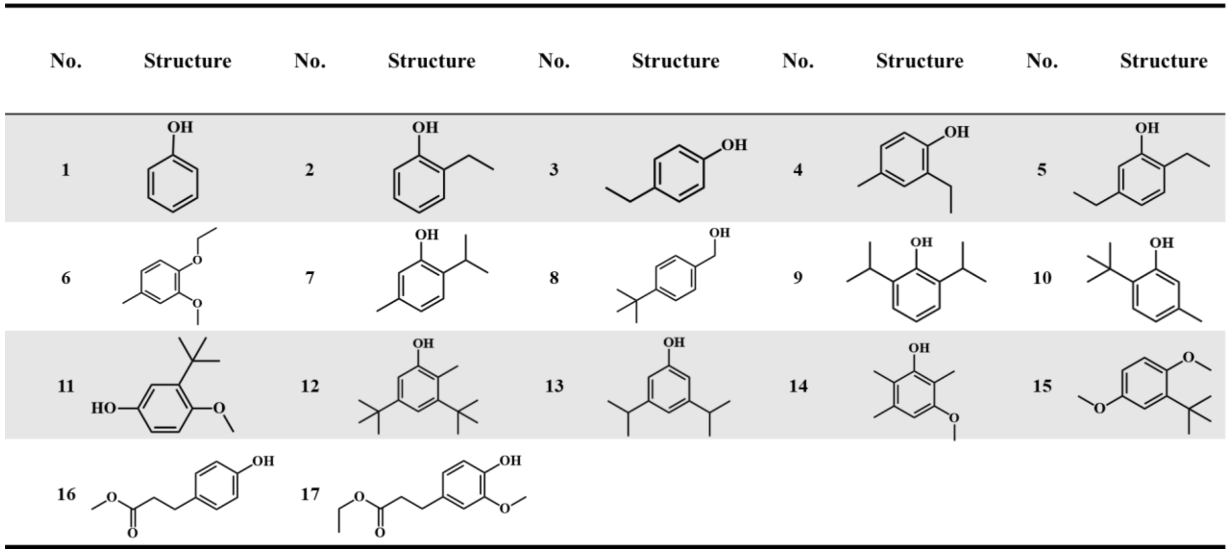
- The $WO_3/\gamma\text{-}Al_2O_3$ catalyst gives highest yield
- Ethanol gives higher aromatic product yield than other alcohols

Ind. Eng. Chem. Res. **2019**, 58, 10255-10263

Catalytic ethanolysis of EHL with H_2

Reaction condition: NiMo/γ-Al_2O_3, ethanol solvent, 320 ^oC, 30 bar H_2, 7.5 h





- ➢No tar or char is formed
- ➢255.4 mg/g EHL of aromatic monomers
- ➢57.9 % selectivity of alkylphenols

Energy Fuels, **2019**, 33, 8657-8665.

Catalytic solvolysis of EHL over NiMo/γ-Al_2O_3

The yields of liquid products obtained from EHL depolymerization over different catalysts.

Entry	Catalyst	Overall Aromatic yield (mg/g EHL)	Alkylphenol yield (mg/g EHL)
1	γ-Al_2O_3	62.4	59.8
2	Ni/γ-Al_2O_3	102.8	17.7
3	Mo/γ-Al_2O_3	127.9	120.8
4	Mixture of Mo/γ-Al_2O_3 and Ni/γ-Al_2O_3	164.7	121.7
5	NiMo/γ-Al_2O_3	255.4	147.9

- The NiMo/γ-Al_2O_3 catalyst exhibits much higher activity than other catalysts

Energy Fuels, **2019**, 33, 8657-8665.

Catalytic ethanolysis of EHL with H_2

Nickel formate decomposition

200-280 ^{o}C

H_2 or N_2

X: decomposition temperature (200-280)
Y:decomposition atmosphere (H or N)

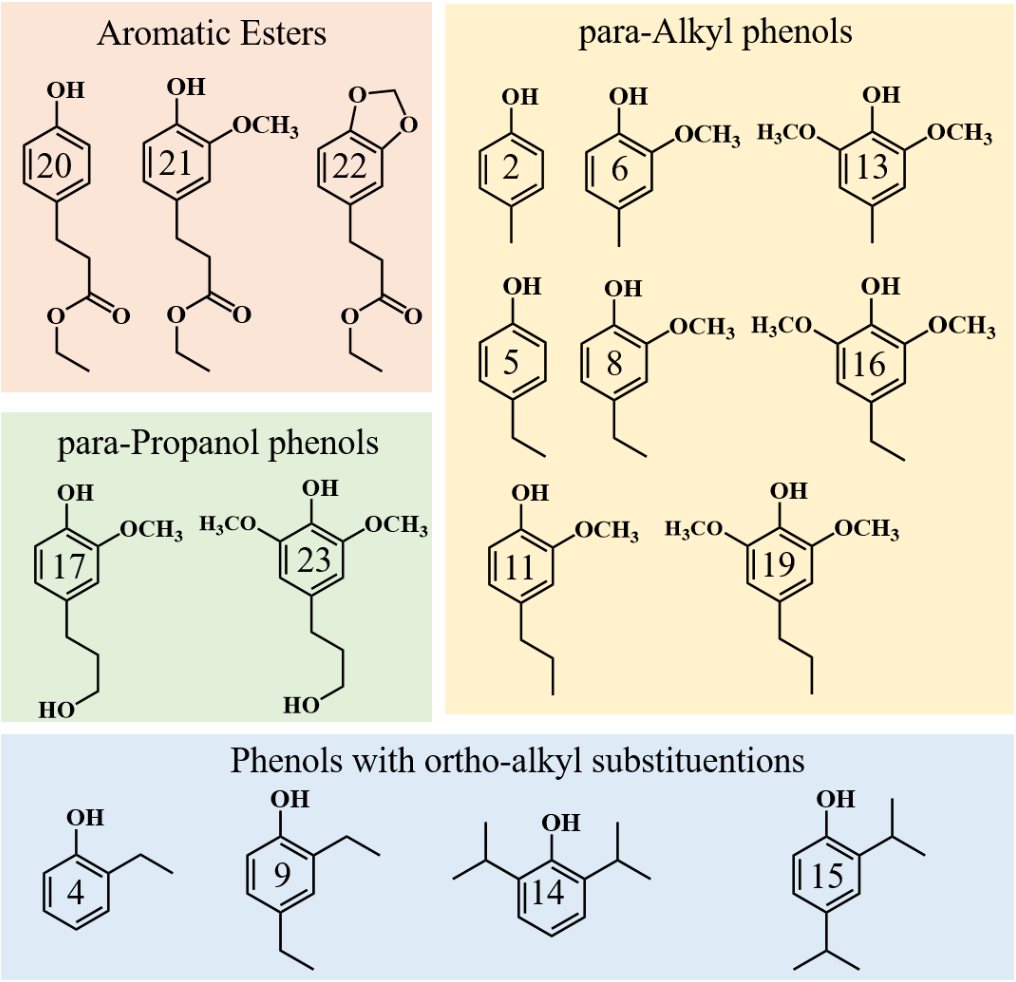
EHL depolymerization

Catalyst

280 ^{o}C 20 bar H_2
Ethanol

EHL is completely liquified

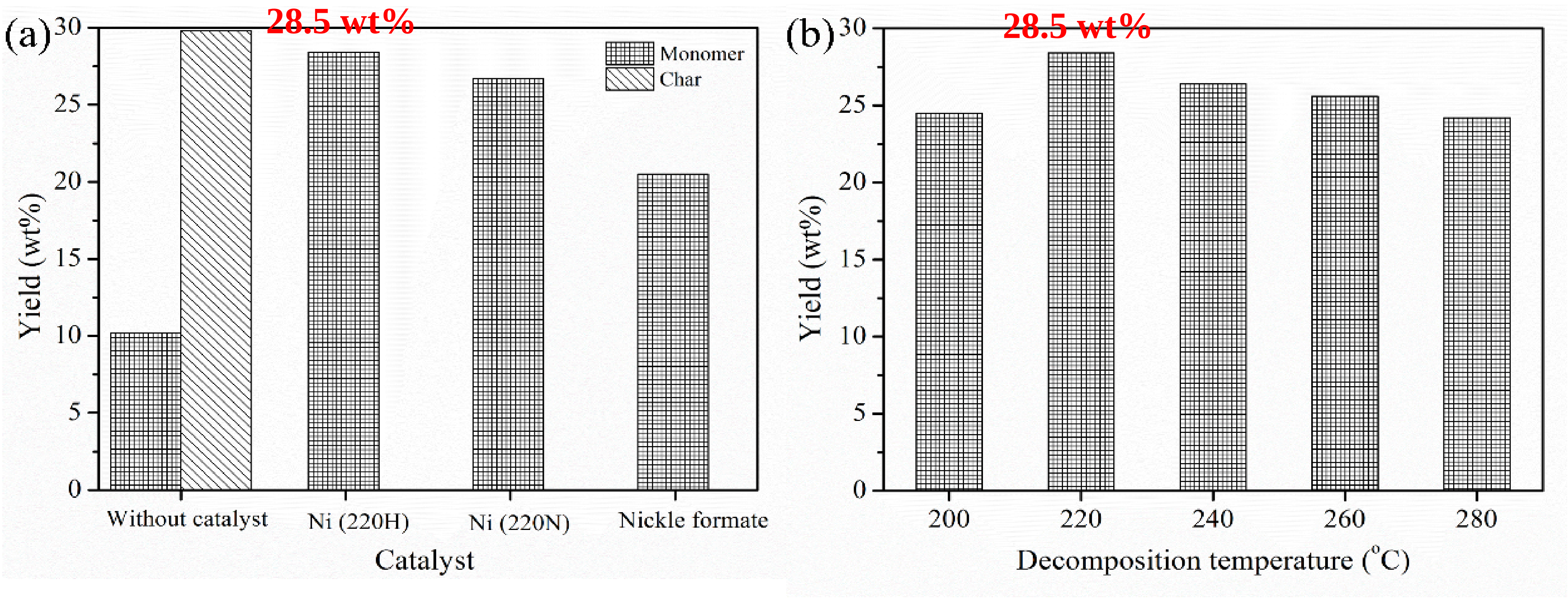
Product distribution



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

Catalytic ethanolysis of EHL with H_2

The effect of (a) catalyst and (b) decomposition temperature of nickel formate.



- High yield of Char was obtained in reaction without adding catalyst
- Highest phenolic monomer yield of 28.5 wt% was achieved with Ni (220H)

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

Catalytic depolymerization of EHL in cyclohexane

Reaction condition: 320 ºC, 30 bar H_2, 7.5 h, cyclohexane

Entry	Catalyst	Atmosphere	Element content (wt%)			Heating Value (MJ/kg)
			Carbon	Hydrogen	Oxygen	
1[a]	–	–	61.29	6.69	29.61	25.0
2	NiMo/γ-Al_2O_3	H_2	85.78	14.22	–	49.3
3	NiMo/γ-Al_2O_3	N_2	77.57	7.43	15.00	34.1

[a] EHL feedstock without treatment.

Bioresource Technology 323 (2021) 124634

After reaction catalyzed with NiMo/Al_2O_3 under H_2

- The O in monomers was completely removed
- The heating value was significantly improved

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 101006744. The content presented in this document represents the views of the authors, and the European Commission has no liability in respect of the content.

Waard Davey de from Eindhoven University of Technology also contribute to these slides