Aalto University

天津大学 TIANJIN UNIVERSITY

Chemical and fuel commodities through catalytic solvolysis of lignin

A presentation on celebrating the 40th anniversary of CACS

Yongdan Li

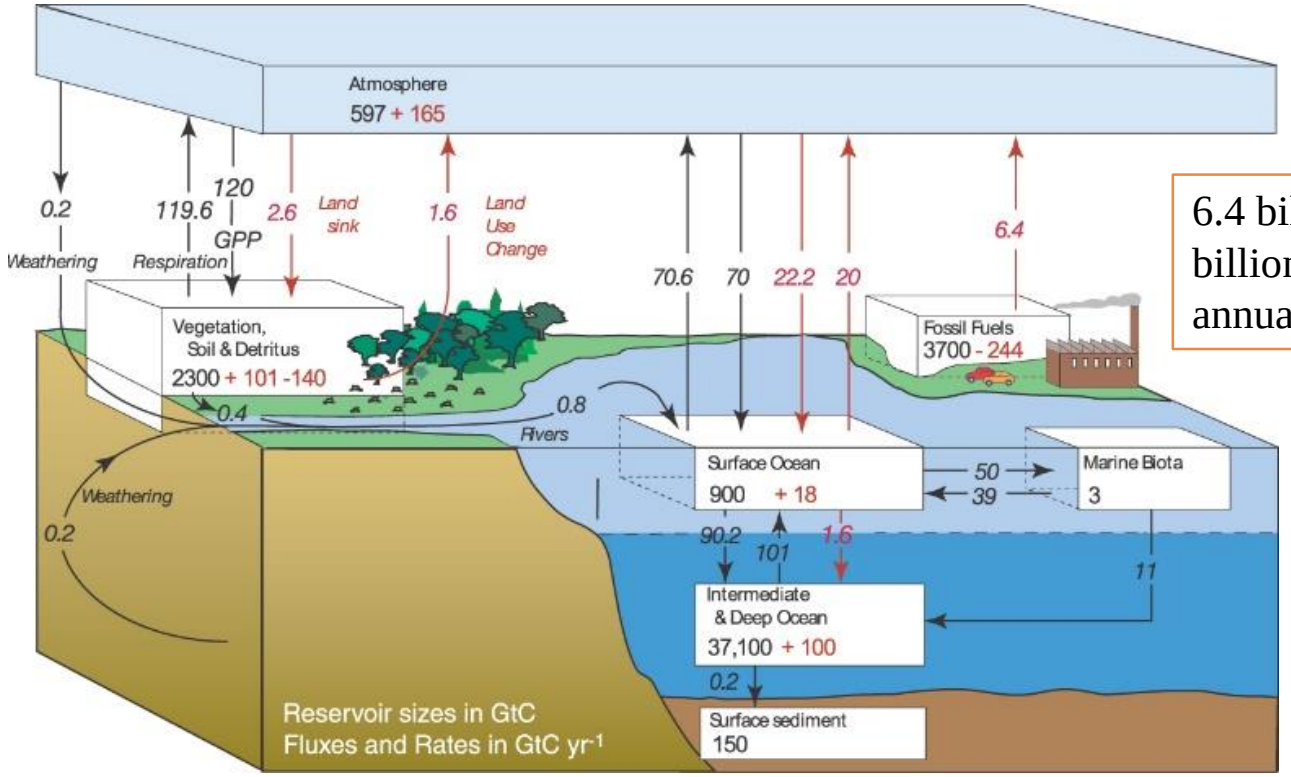
Professor of Industrial Chemistry
Department of Chemical and Metallurgical Engineering
School of Chemical Technology
Aalto University
Email: Yongdan.li@aalto.fi

And
Adjunct Chair Professor of Industrial Catalysis
Tianjin University

Contents

The next Grand Challenge

Global Carbon Imbalance



6.4 billion tons of carbon (23.5 billion tons of CO_2) are released annually

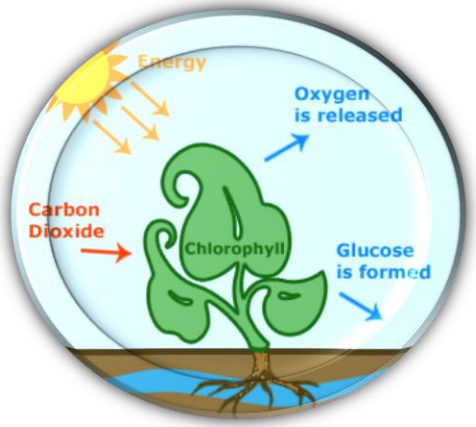
Nature carbon cycle (1750)

Human disturbance (the last decade of the 20th century)

IPPC AR-4, 2007

Background

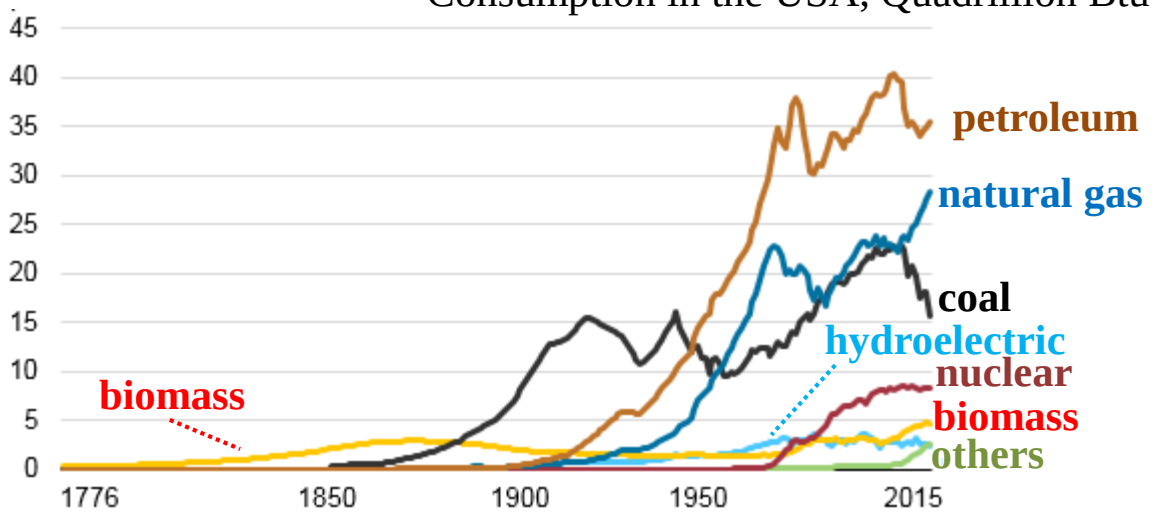
Biomass is enough for fuels and chemicals



Over **150 billion-tons** annual supply

>

Consumption in the USA, Quadrillion Btu

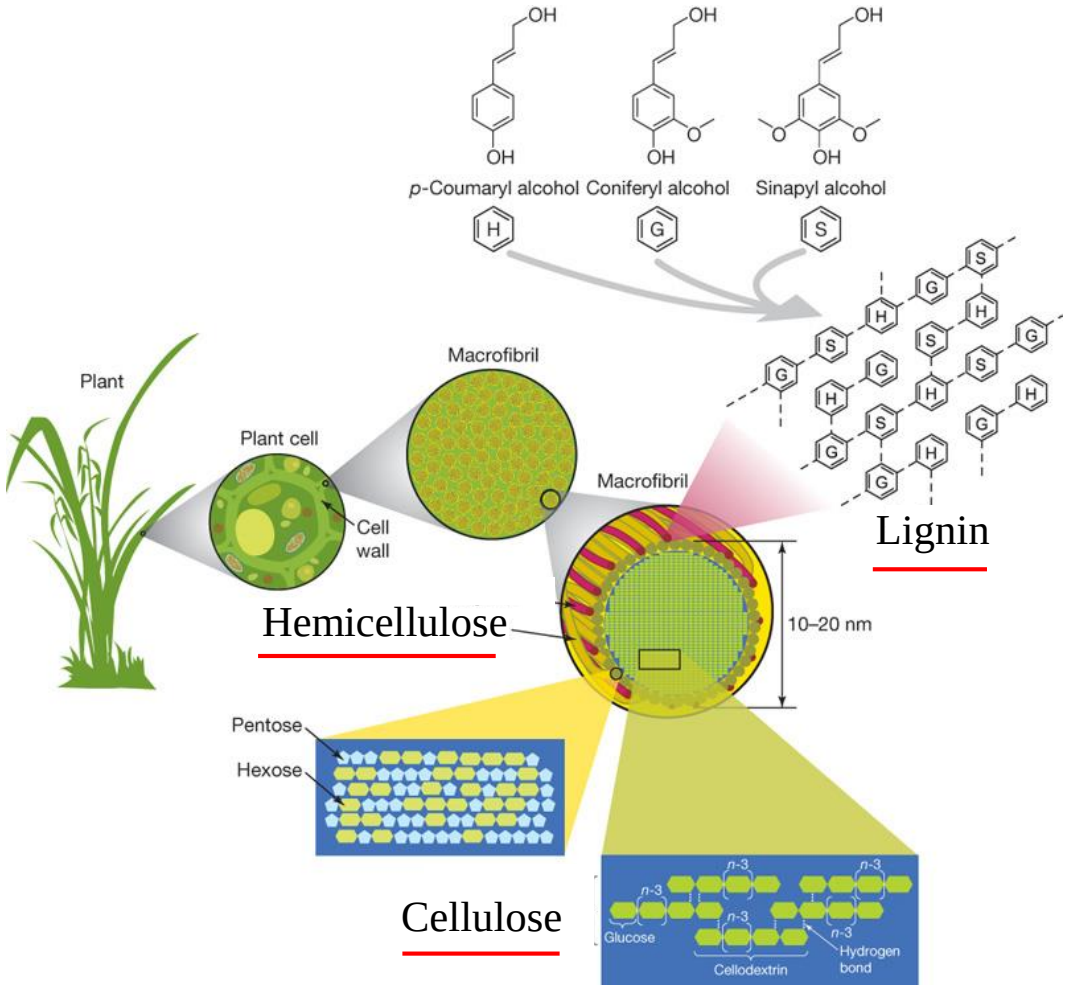


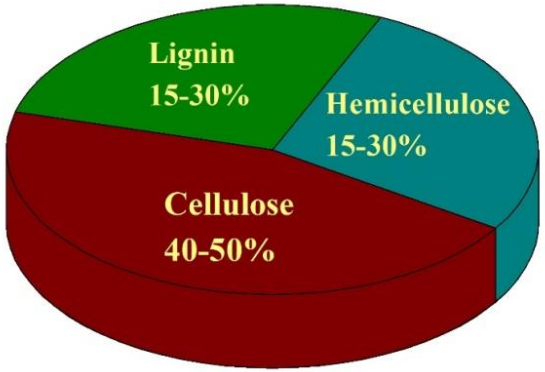
http://www.eia.gov/todayinenergy

Development of biofuel is urgent

Background

Lignin, the only renewable aromatic resource



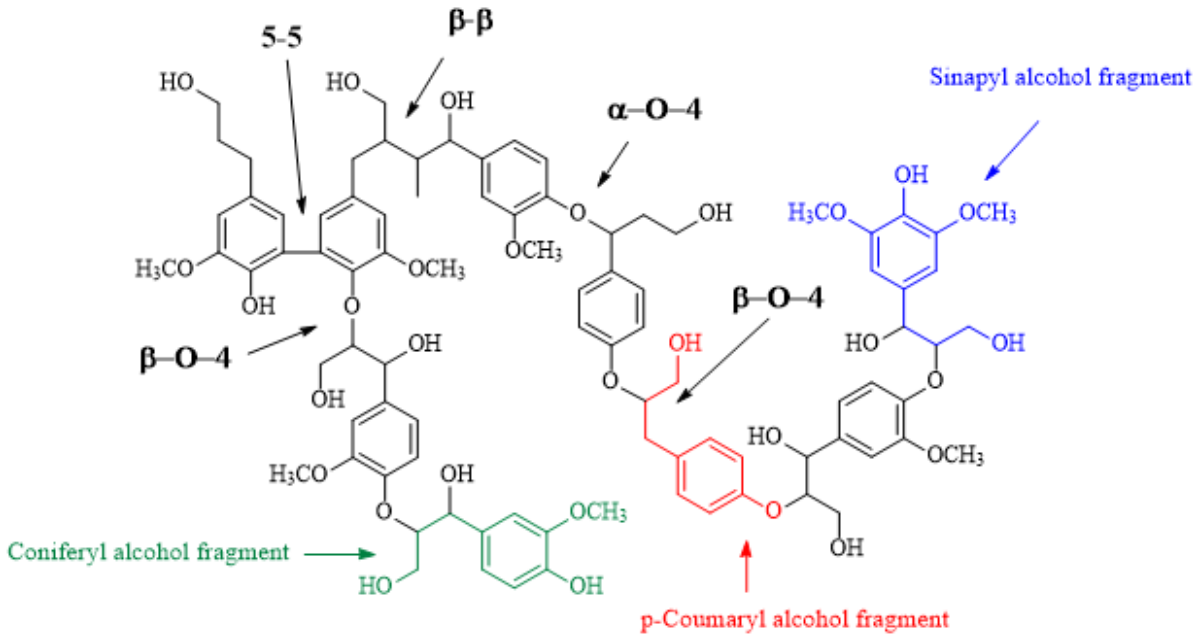


Low-heating-value fuel
13.5-15.5 MJ/kg

High value-added
platform chemicals

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

Background



Schematic representation of a soft wood lignin structure

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

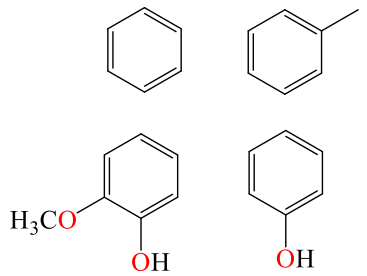
Chem. Rev., **2010**, 110, 3552-3599

Background

Potential applications of lignin

Chemicals

Platform chemicals



High

Value

Materials

- Polyurethane
- Phenolic resin
- Carbon fiber

Value added

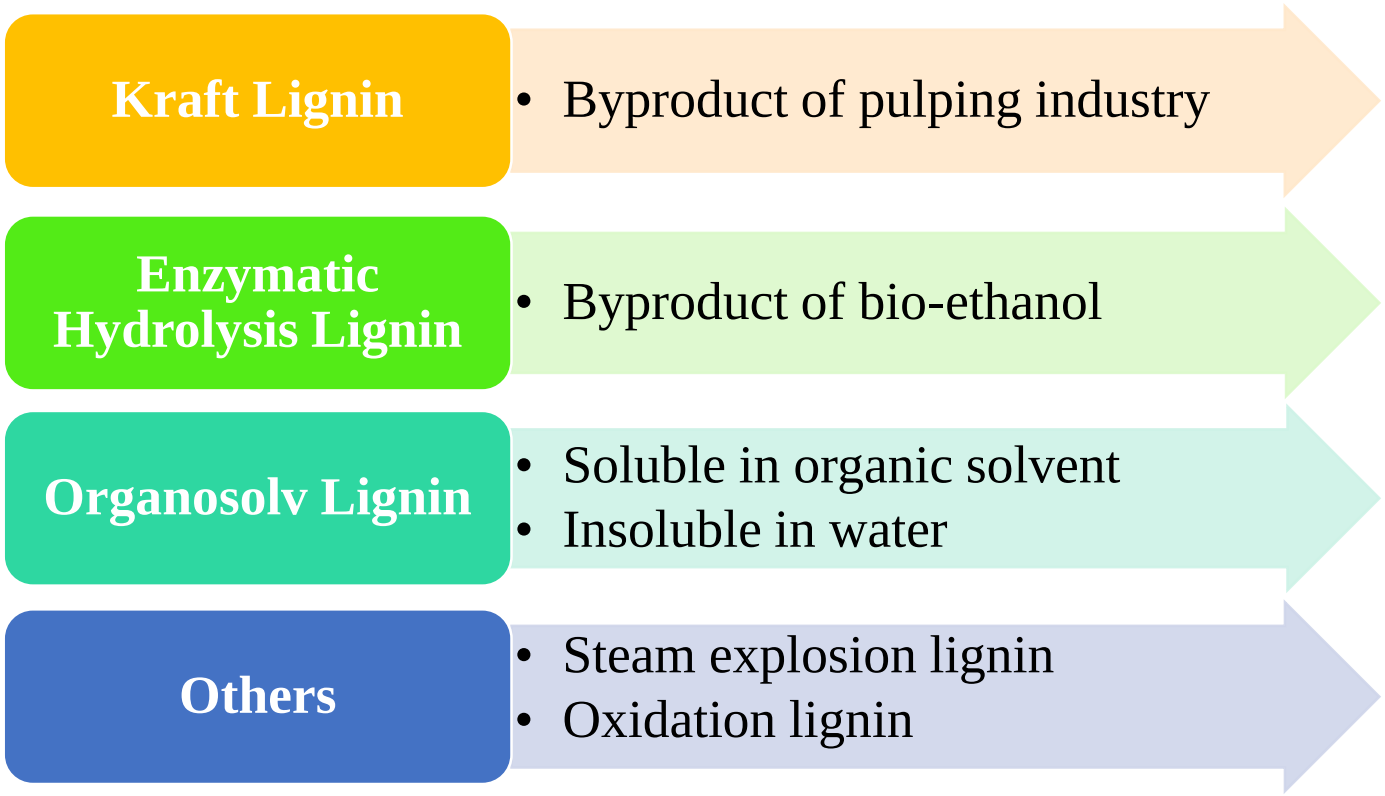
Fuels

- Low heating-value (*ca.* 13.5-15.5 MJ/kg)
- High ash content *Si, Ca, Mg, et al.*

Chem. Rev., **2015**, 115, 11559-11624

Background

Available lignin resources



- Only Kraft lignin is produced in an industrial scale.
- Enzymatic Hydrolysis Lignin probably become future major lignin raw stock

Part 1.1: Ethanolysis of Kraft lignin over MoC_{1-x}/AC

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

Kraft Lignin (Sigma)

280 °C， 6 h

Ethanol，MoC_{1-X}/AC

HAE

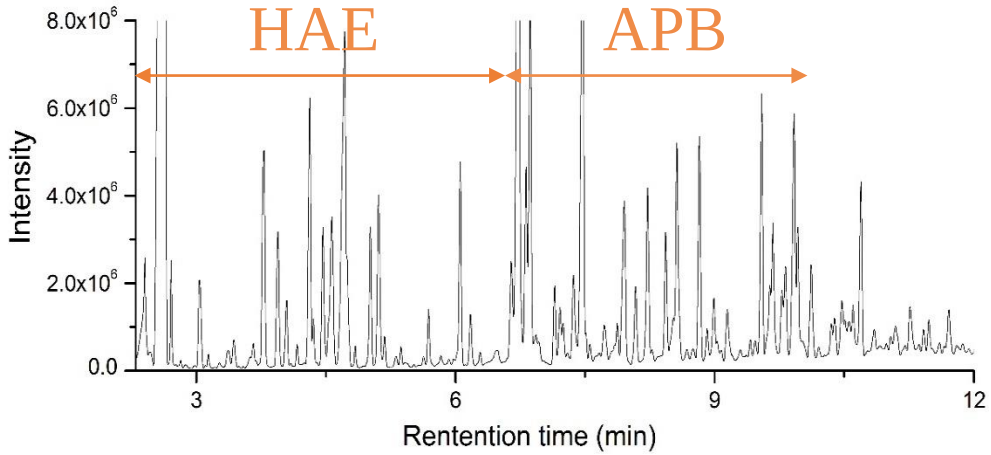
Higher alcohols and esters

APB

Arenes, phenols and benzyl alcohols

Insoluble

No char

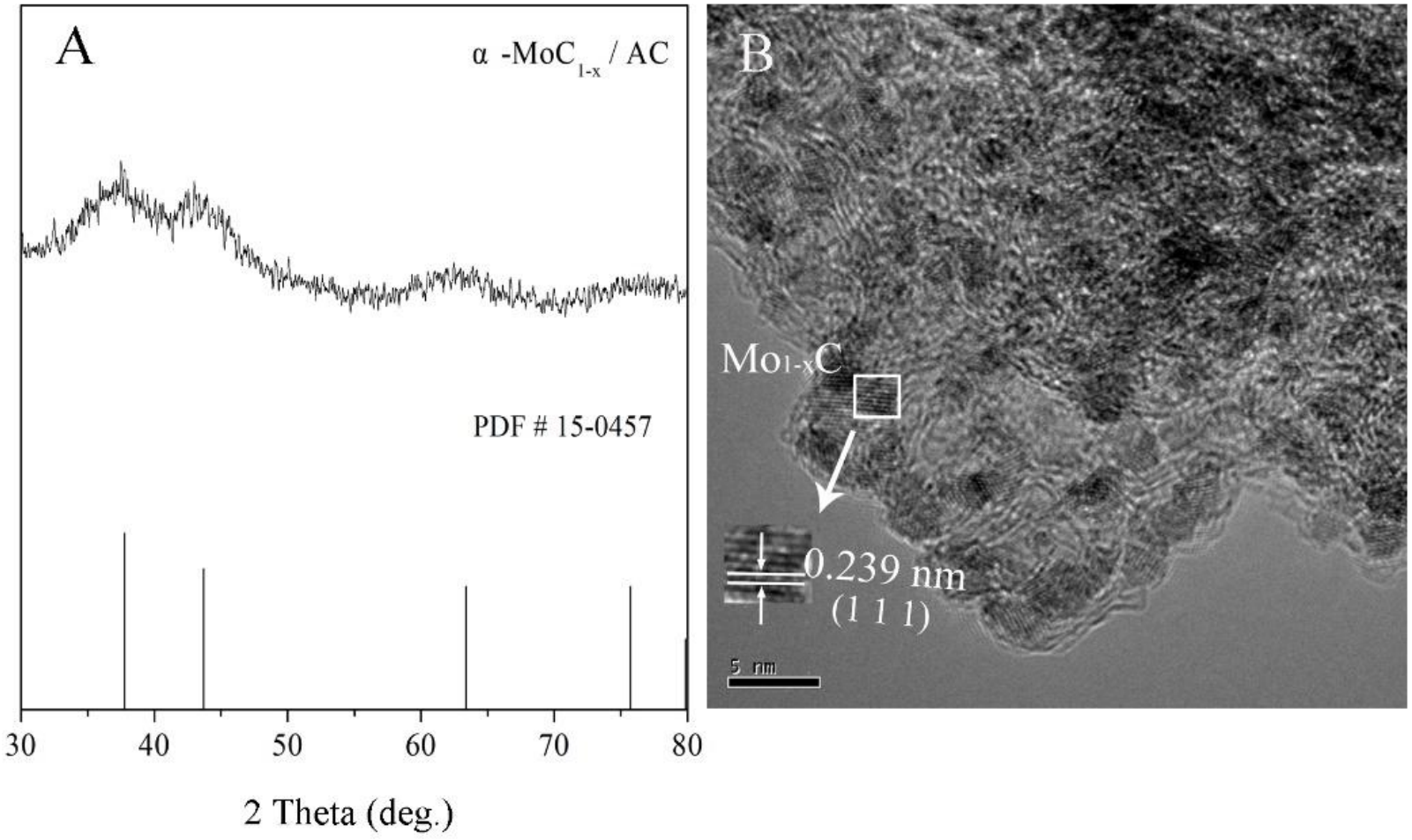


- 84 peaks related to Kraft lignin
- 52 peaks are qualified
- 25 peaks are quantified
- 32 peaks are still unknown

- 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



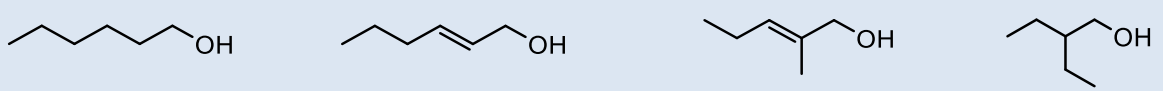
XRD pattern (A) and TEM image (B) of the α-MoC_{1-x} /AC.

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

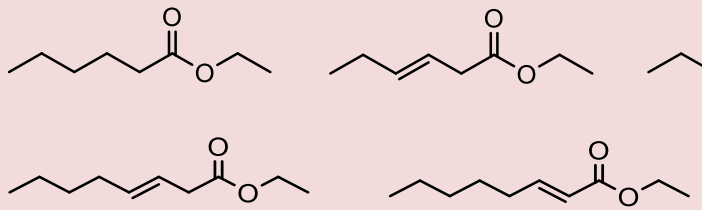
Alcohols – C6



25.2%

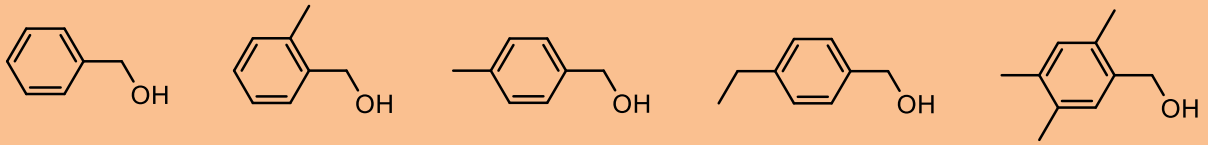
Esters – C8

Esters – C10

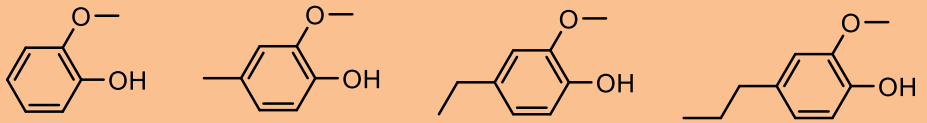


58.4%

Benzyl alcohols

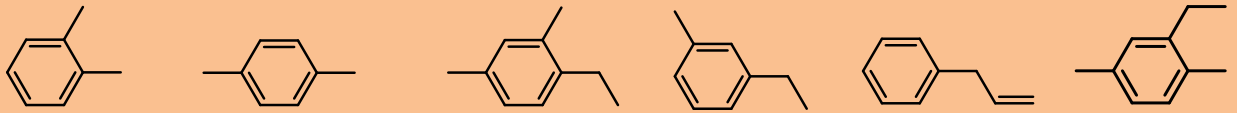


Phenols



16.4%

Arenes



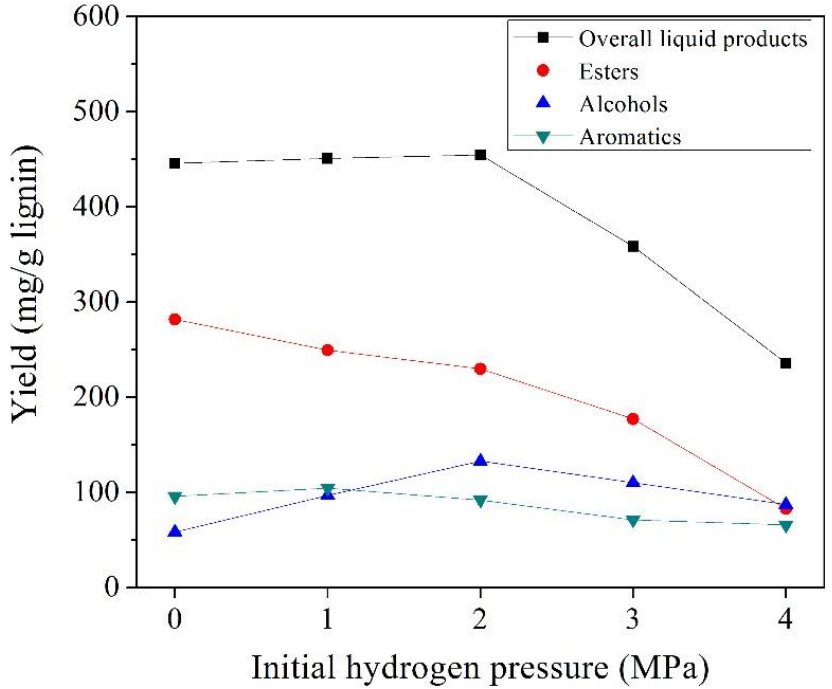
Angew. Chem. Int. Ed., **2014**, 126, 7438-7443

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

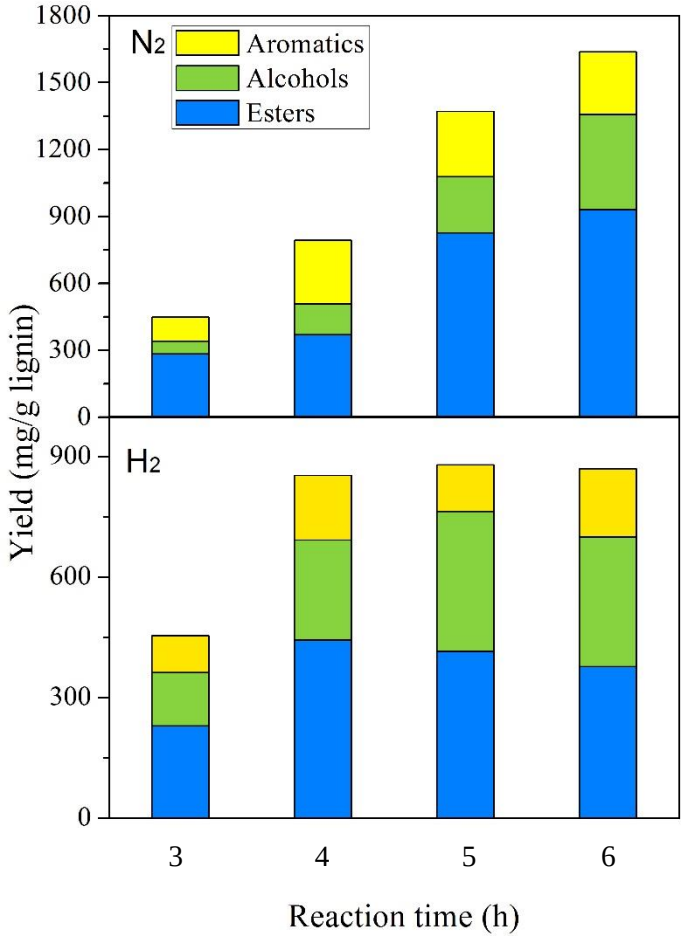
- **Gas atmosphere：**

  As H_2 increases, the yield decreases

  Yield in N_2 is higher than that in H_2



Effect of initial P_{H2} on yield

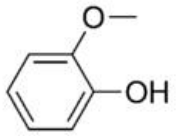
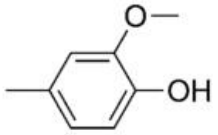
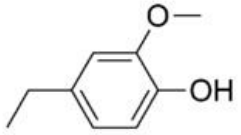
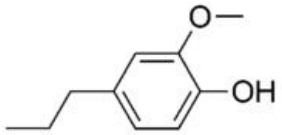


Yields comparison in N_2 & H_2

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

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

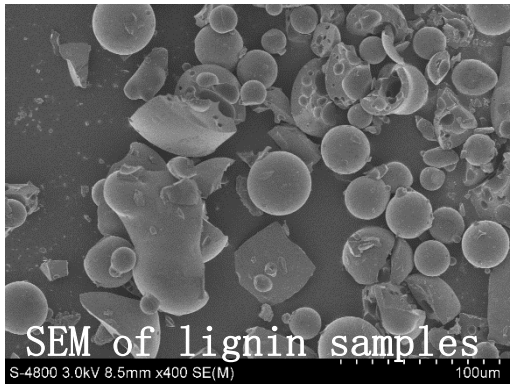
Ethanol is the most efficient solvent for Kraft lignin conversion

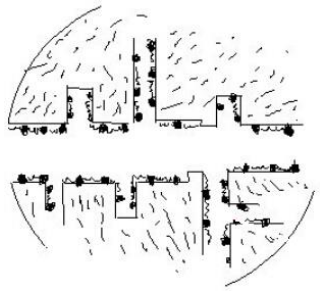
Products	Solvent			
	ethanol	water	methanol	isopropanol
	4	14	3	17
	35	3	8	2
	16	11	5	5
	23	8	2	4
other aromatics	202	9	2	3
alcohols	409	–	–	–
esters	949	–	–	–

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

Part 1.2: Reaction mechanism

Proposal of the reaction mechanism





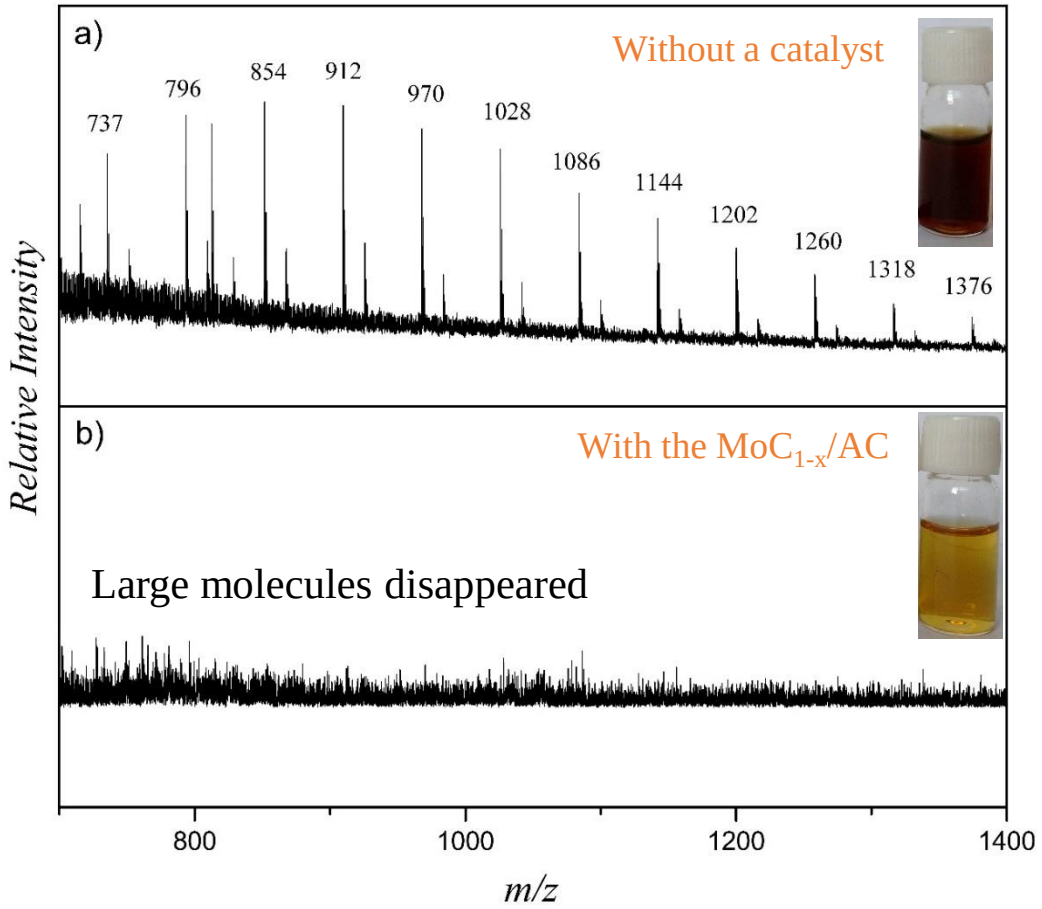
Lignin Partical Size 20-80 μm >> Catalyst Pore Diameter 7.9 nm

The pore diameter of MoC_{1-x}/AC catalyst

Sample	S_{BET} (m^2/g)	V_O (cm^3/g)	V_m (cm^3/g)	Pore diameter (nm)
MoC_{1-x}/AC	749	0.12	0.59	7.9

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.

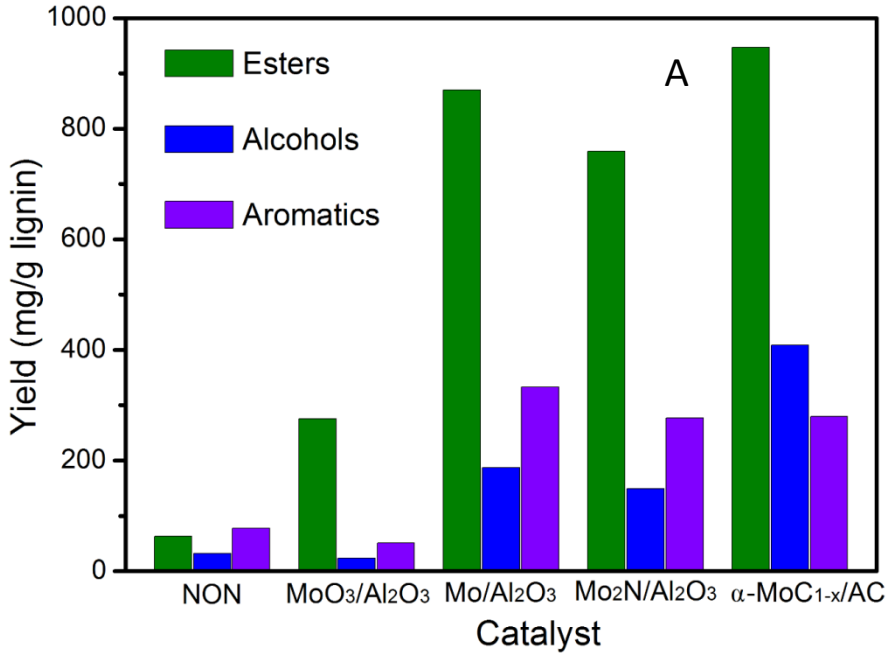
Angew. Chem. Int. Ed., **2014**, 126, 7438-7443

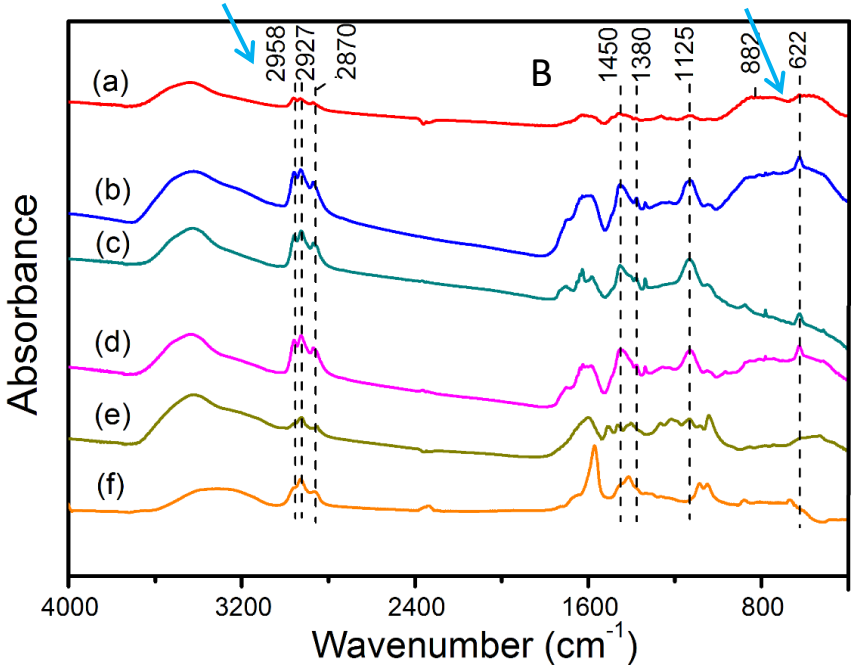
Proposal of the reaction mechanism

All the Mo-based catalysts show high and similar activities

$-CH_3$ and $-CH_2$ stretching vibration

Mo-O stretching vibration





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

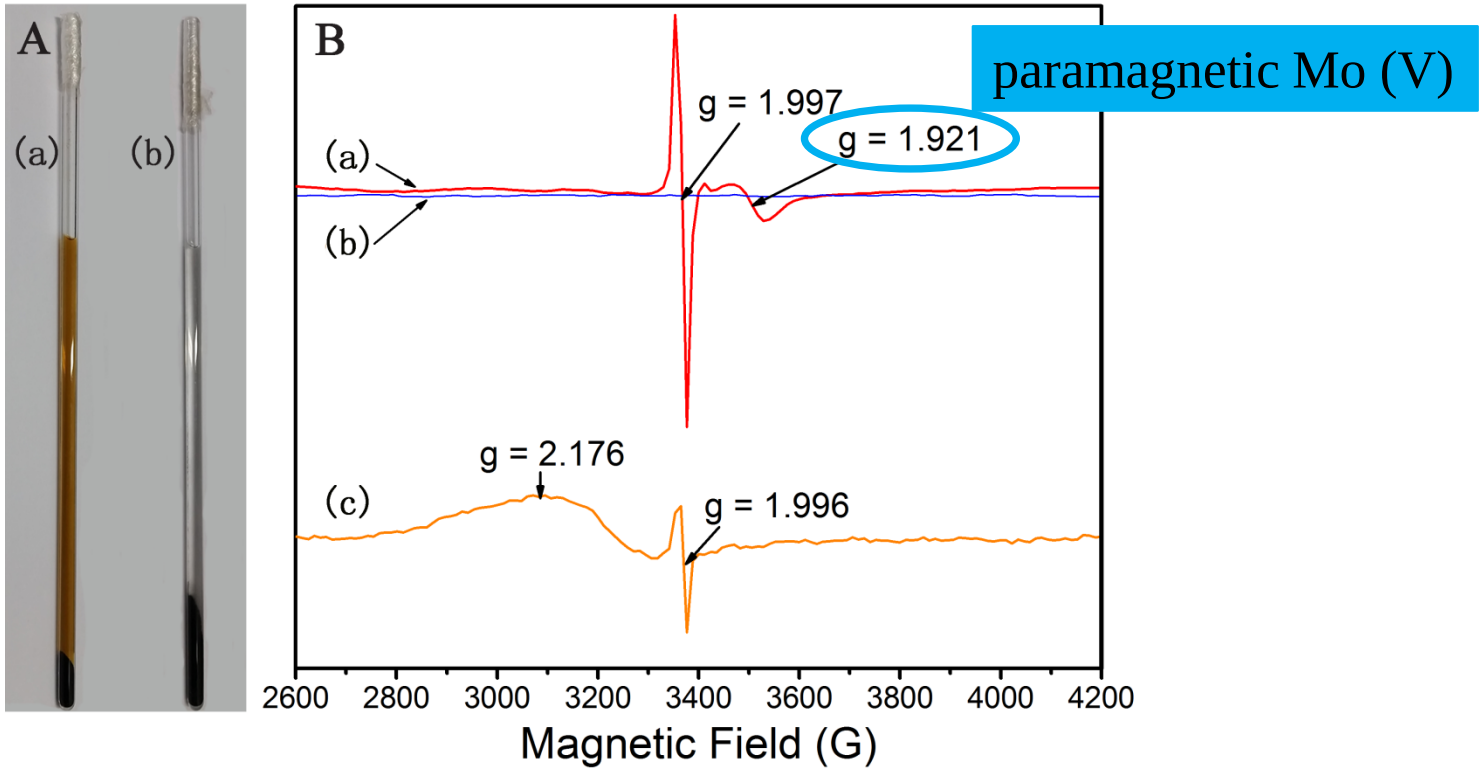
(B) The FT-IR spectra of the different samples before and after reaction

(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.

ACS Catal., **2015**, 5 , 4803–4813

Proposal of the reaction mechanism



paramagnetic Mo (V)

(A) Photographs of (a) used Mo/Al_2O_3 catalyst with liquid products, (b) fresh Mo/Al_2O_3 catalyst in ethanol in EPR sample cell.

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

Other used Mo-based catalysts with g tensor around 1.92 were also recorded, indicating the presence of Mo (V)

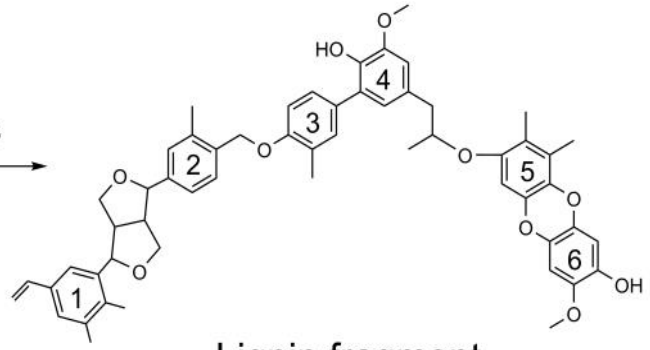
ACS Catal., **2015**, 5 , 4803–4813

Proposal of the reaction mechanism

Kraft lignin

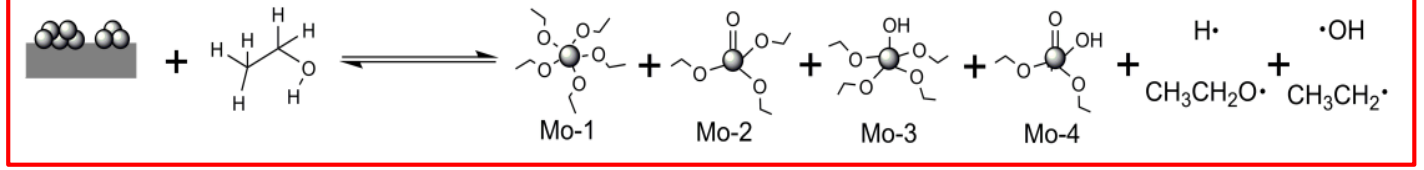
Mw = 60,000

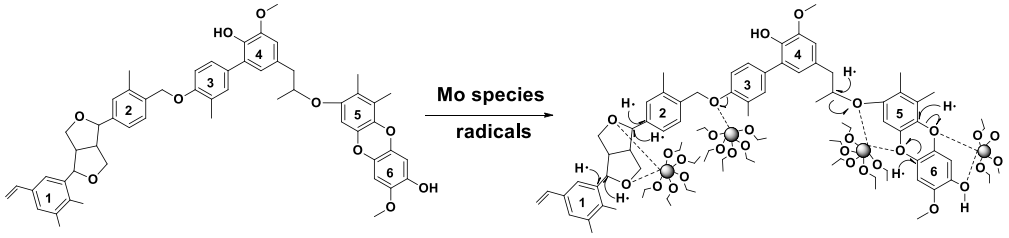
ethanolysis

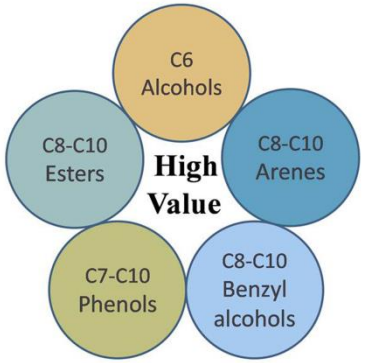


Lignin fragment

about 6 subunits, Mw = 891







ACS Catal., **2015**, 5 , 4803–4813

Part 1.3: Ethanolysis of Kraft lignin over MoC_{1-x}/Cu-$MgAlO_z$

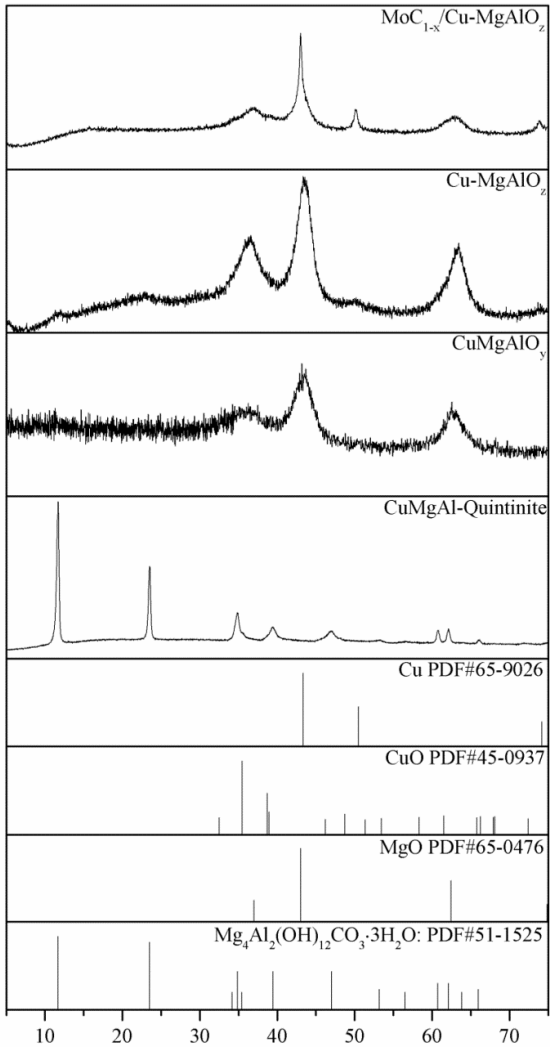
Ethanolysis of Kraft lignin over $MoC_{1-x}/Cu\text{-}MgAlO_z$

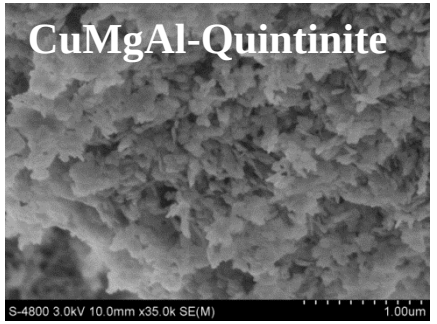
$CuMgAlO_y$

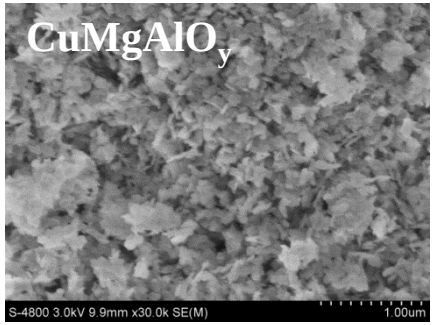
$(NH_4)_6Mo_7O_{24}$ impregnation

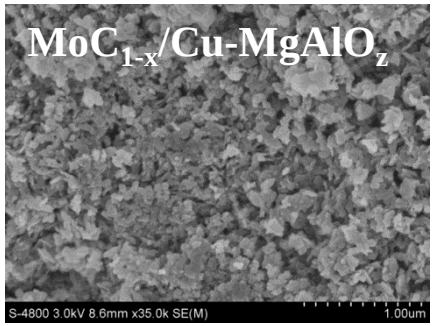
H_2/CH_4 TPR

$MoC_{1-x}/Cu\text{-}MgAlO_z$





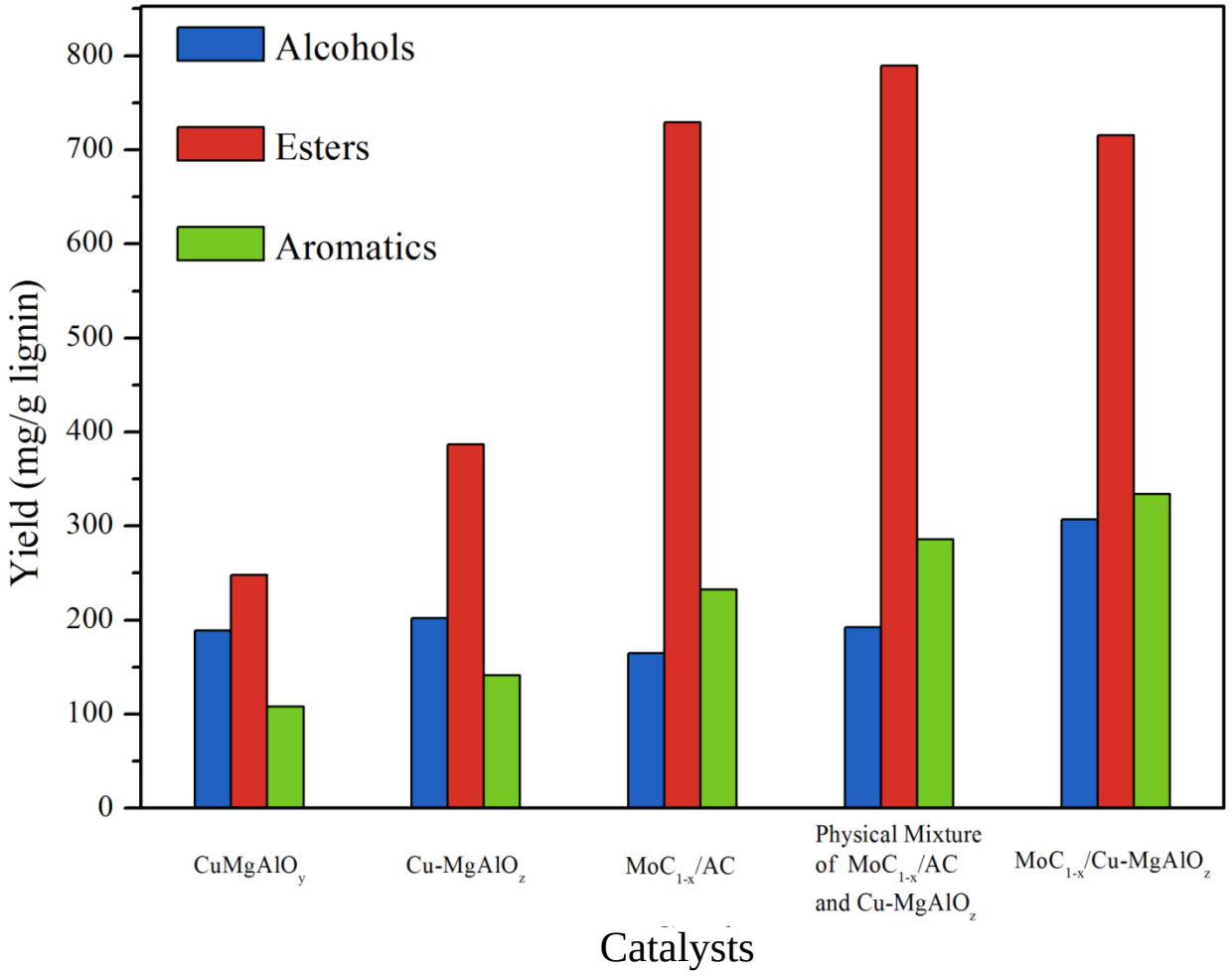




Appl. Catal. B, **2017**, 202, 305-313

Ethanolysis of Kraft lignin over $MoC_{1-x}/Cu\text{-}MgAlO_z$

Roles of components in catalyst



Activity of $CuMgAlO_y$ increased after reduction.

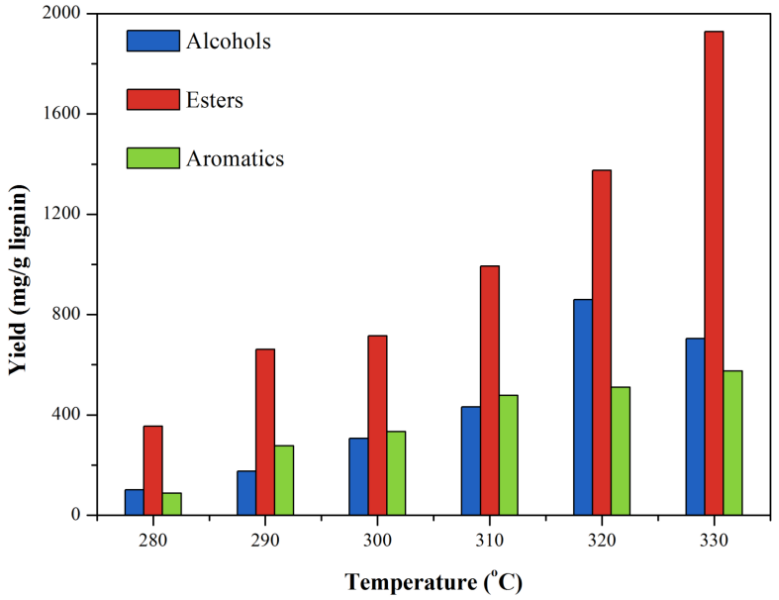
MoC_{1-x}/AC is more active.

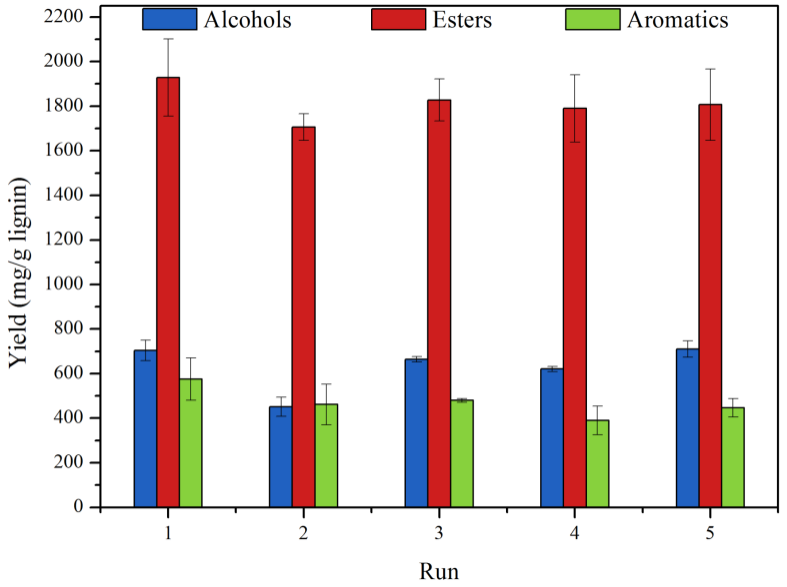
Physical mixture catalyst is better than either.

The combined catalyst shows the best activity.

Appl. Catal. B, **2017**, 202, 305-313

Ethanolysis of Kraft lignin over MoC_{1-x}/Cu-$MgAlO_z$





As temp. increased, the yield rise

Highest Yield: 3207 mg/g lignin
Aromatics 575 mg/g lignin
Alcohols 704 mg/g lignin
Esters 1928 mg/g lignin (330 °C, 6h)

successive run for 5 times

Appl. Catal. B, **2017**, 202, 305-313

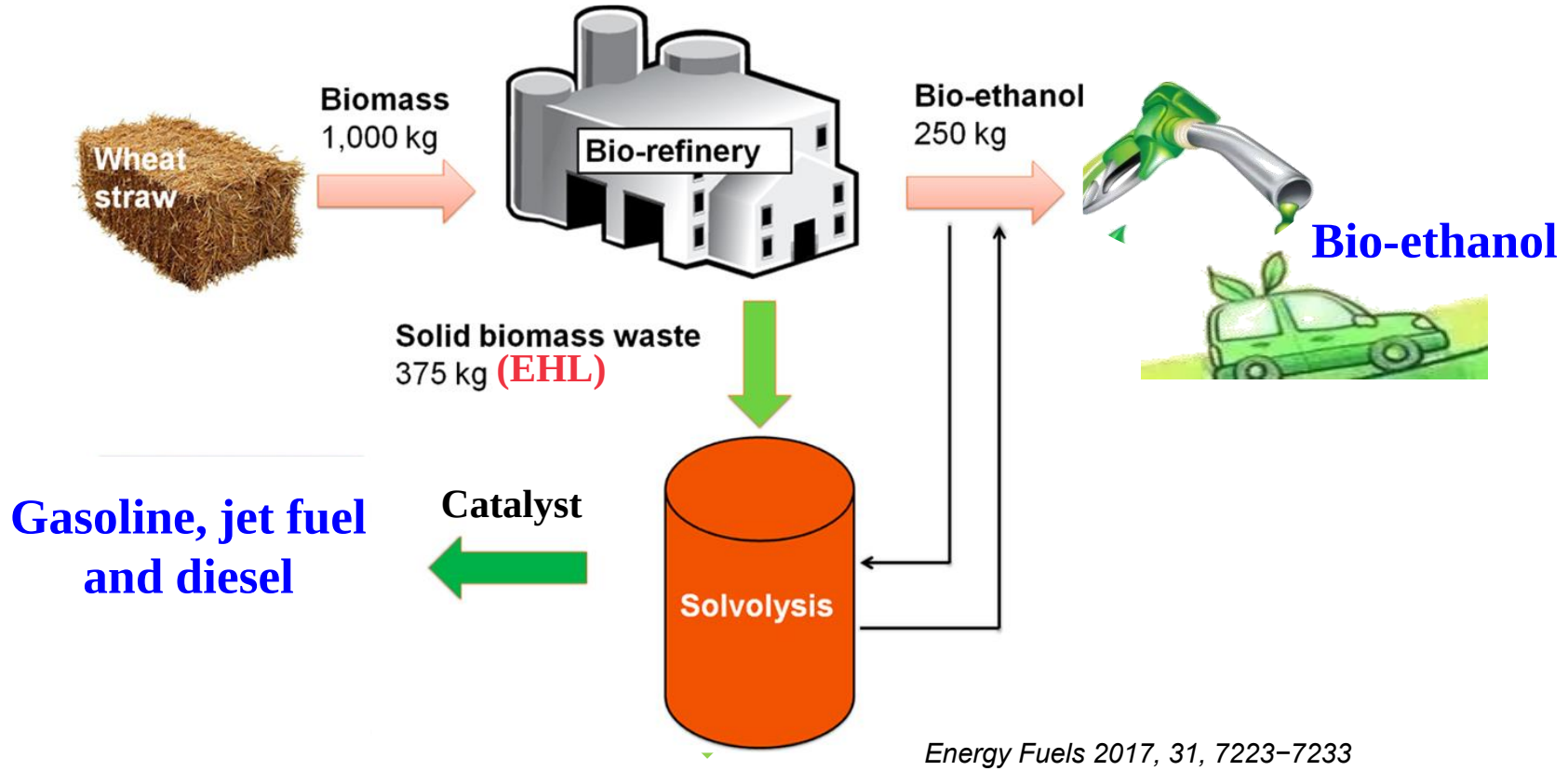
Summary of Kraft lignin ethanolysis over Mo-based catalysts

- **Complete catalytic ethanolysis of Kraft lignin to alcohols, esters and aromatics over MoC_{1-x}/AC with a yield of 1.64 g/g lignin.**

- **Ethanol itself depolymerizes Kraft lignin. The dissociative Mo (V) ethoxide facilitates the complete decomposition of the segments. Ethanol pieces are incorporated into the product molecules.**

- **The combination of MoC_{1-x} and Cu-$MgAlO_z$ maximizes the catalytic activity.**

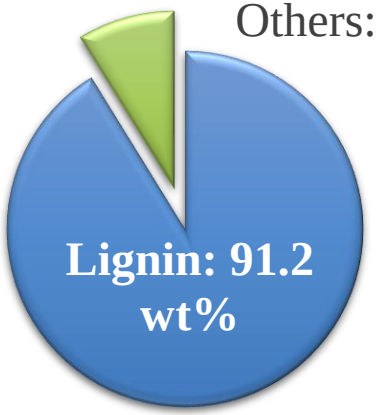
EHL



An emerging topic:
Catalytic solvolysis of enzymatic hydrolysis lignin (EHL)

EHL

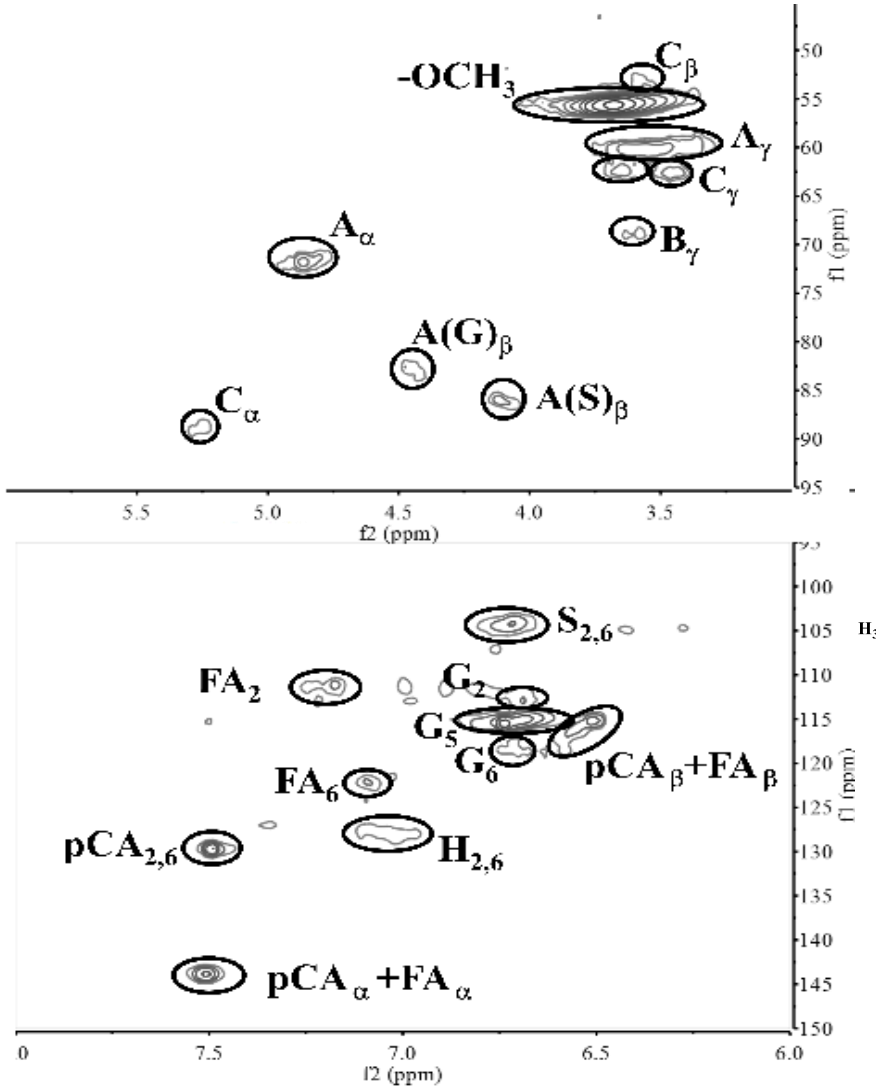
Lignin source: Corn stover

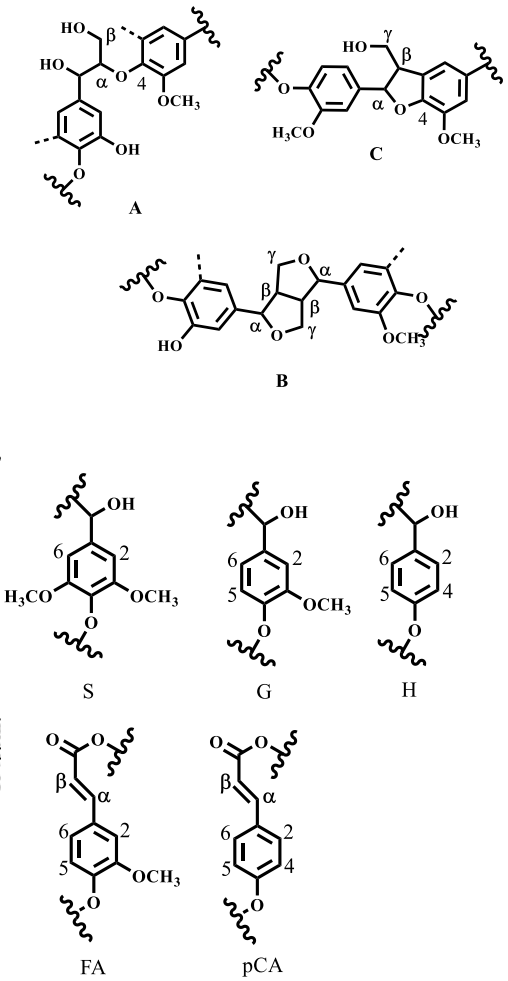


Elemental analysis of EHL

C	H	N	S	O
61.75%	6.48%	0.90%	0.58%	30.29%

2D-HSQC of EHL

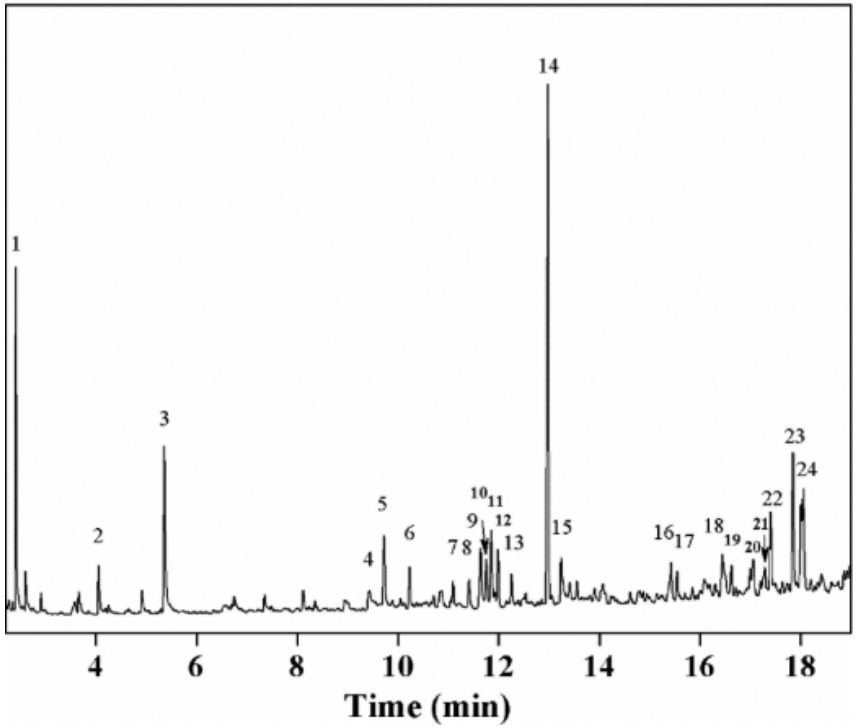




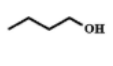
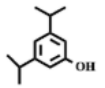
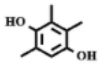
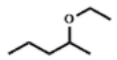
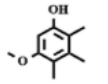
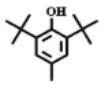
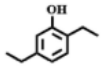
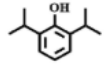
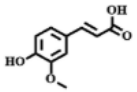
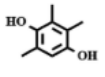
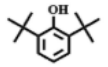
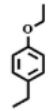
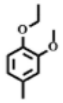
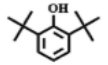
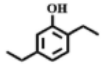
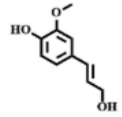
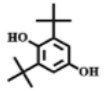
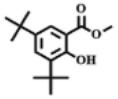
Part 2.1: Catalytic ethanolysis of EHL without H_2

Catalytic ethanolysis of EHL without H_2

WO_3/γ-Al_2O_3 catalyzed EHL ethanolysis at 320 °C under 0 bar N_2



31.6 wt% yields of monomers

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 tar or char is formed, and the EHL is completely liquified
- Complex alkylphenols are the main products

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

Catalytic ethanolysis of EHL without H_2

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	γ-Al_2O_3	Ethanol	19.3	2.4	43.7	65.5
4	WO_3/γ-Al_2O_3	Ethanol	32.9	26.3	245.2	315.8
5	WO_3/γ-Al_2O_3	Methanol	16.2	3.5	160.2	179.6
6	WO_3/γ-Al_2O_3	Isopropanol	26.8	5.7	96.0	128.2

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

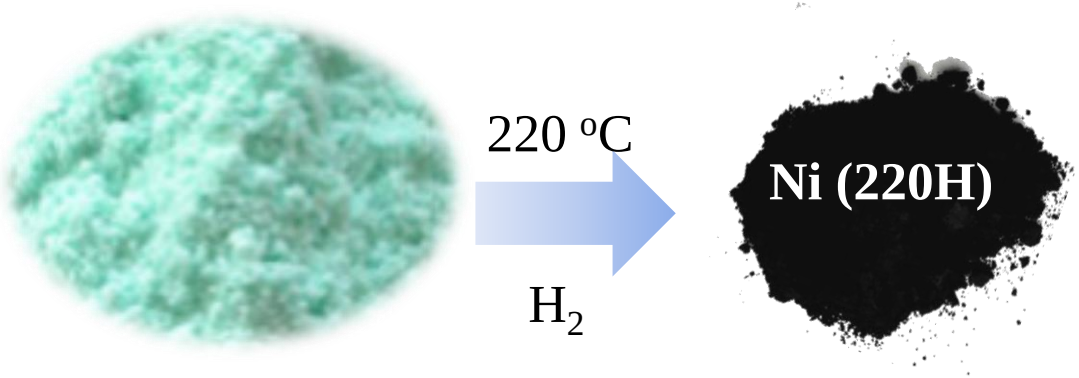
- The WO_3/γ-Al_2O_3 catalyst gave highest yield
- Ethanol gave higher aromatic product yield than other alcohols

Part 2.2: Catalytic ethanolysis of EHL with H_2

Catalytic ethanolysis of EHL with H_2

Part 2. Unsupported Ni catalyst catalyzed EHL ethanolysis with H_2

Catalyst preparation: Nickel formate decomposition



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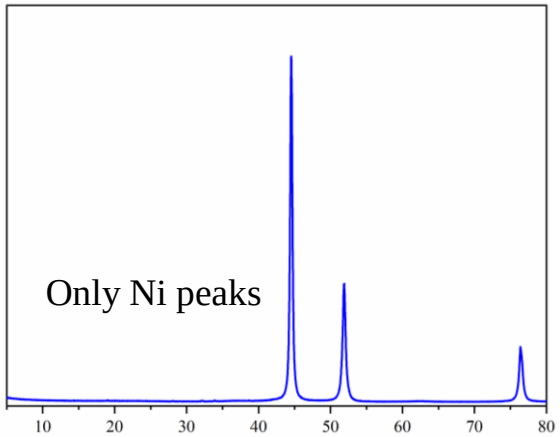

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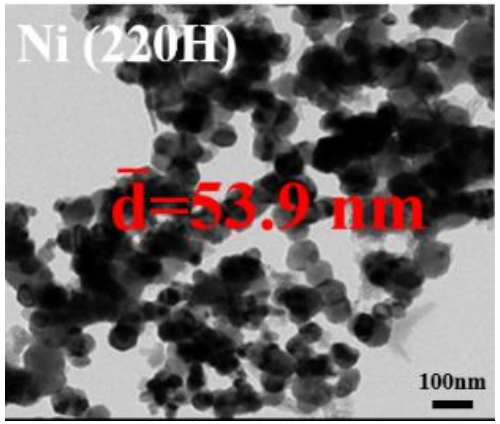


Ind. Eng. Chem. Res. **2020,** *59* (16), 7466-7474.

Catalytic ethanolysis of EHL with H_2

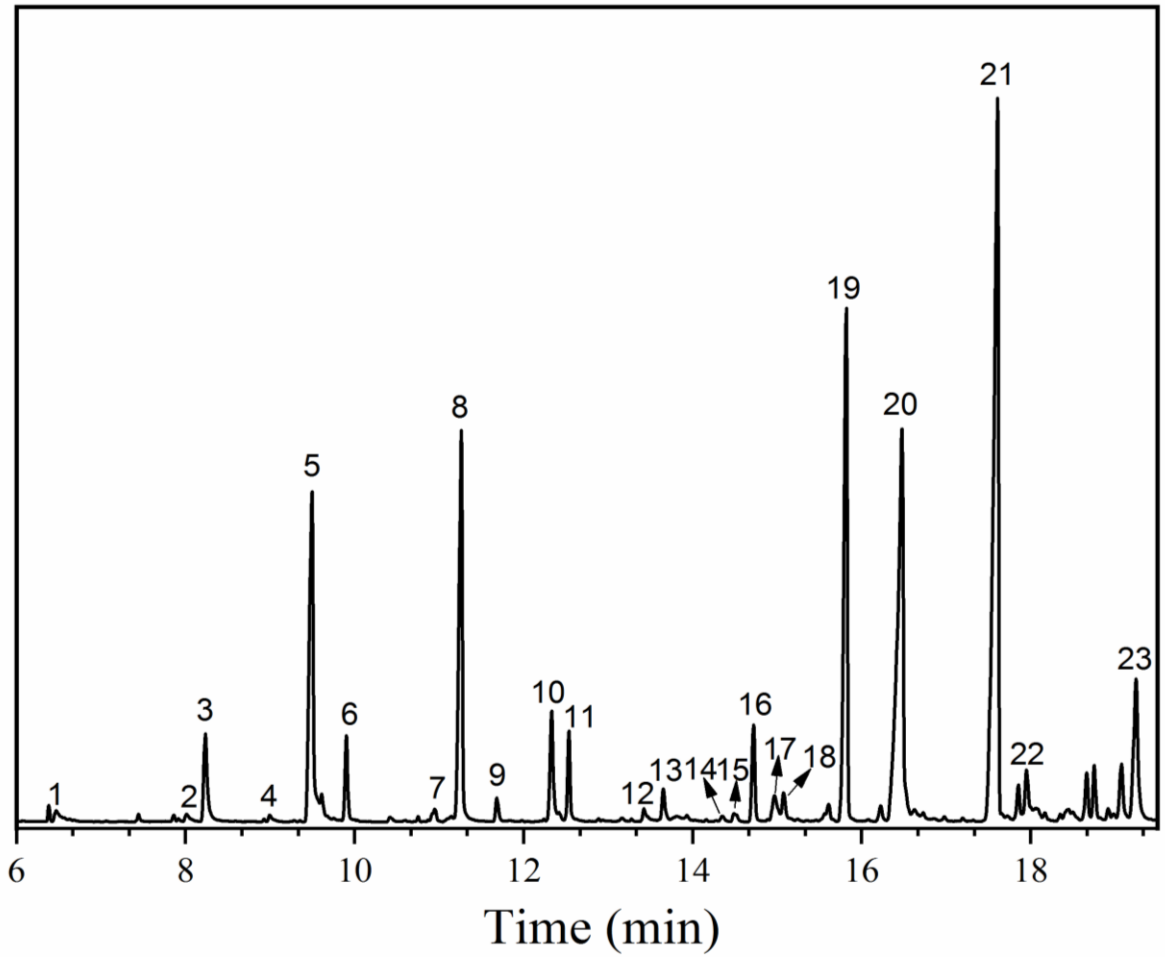
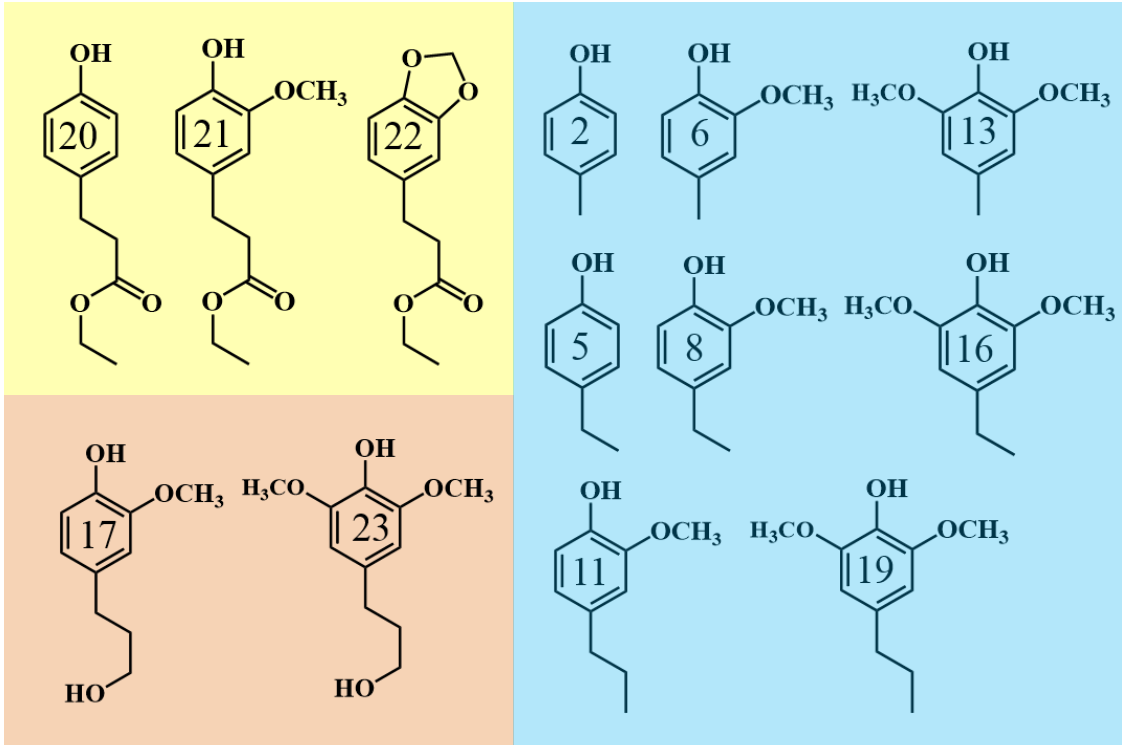


Fig. 5. Total-ion chromatogram (TIC) of the liquid product obtained from EHL depolymerization over Ni (220H) in ethanol over Ni (220H) at 280 °C for 6 h with 2 MPa H_2.

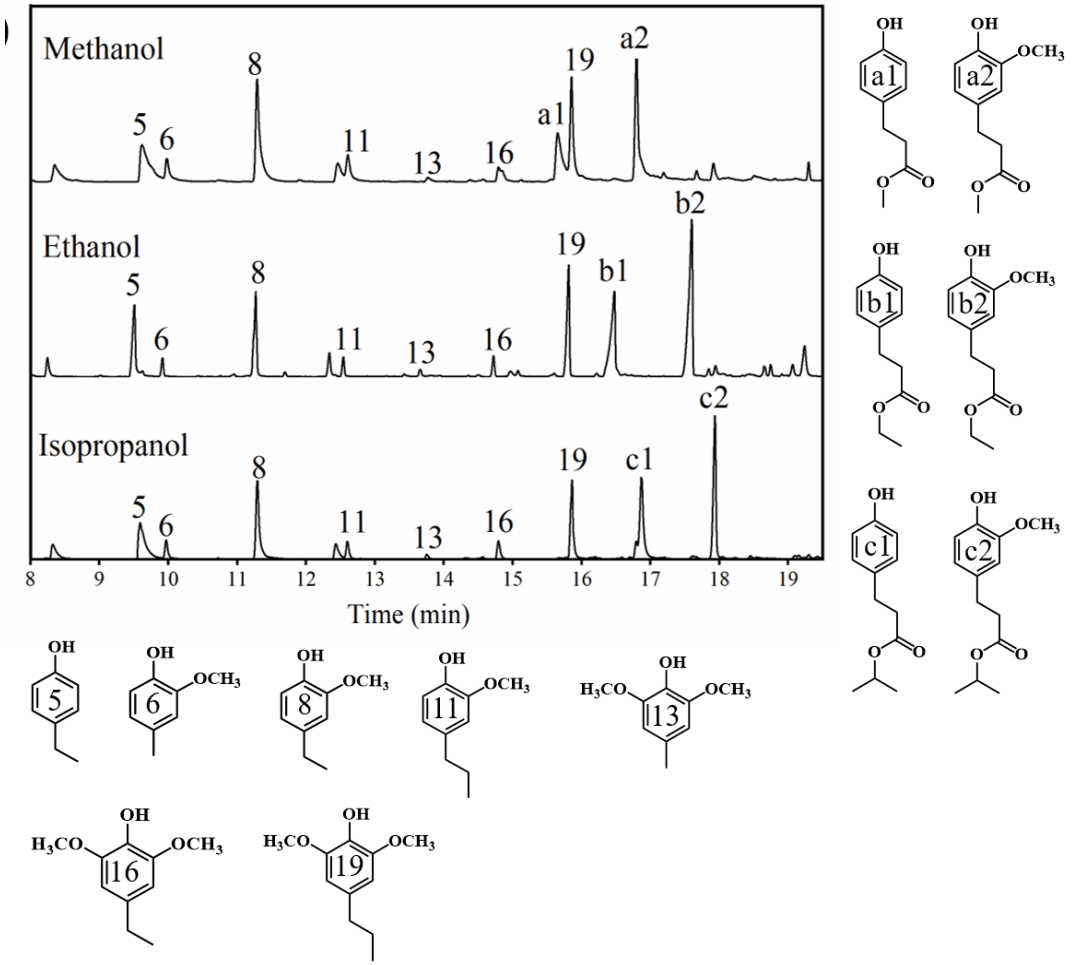
28.5 wt% yields of monomers

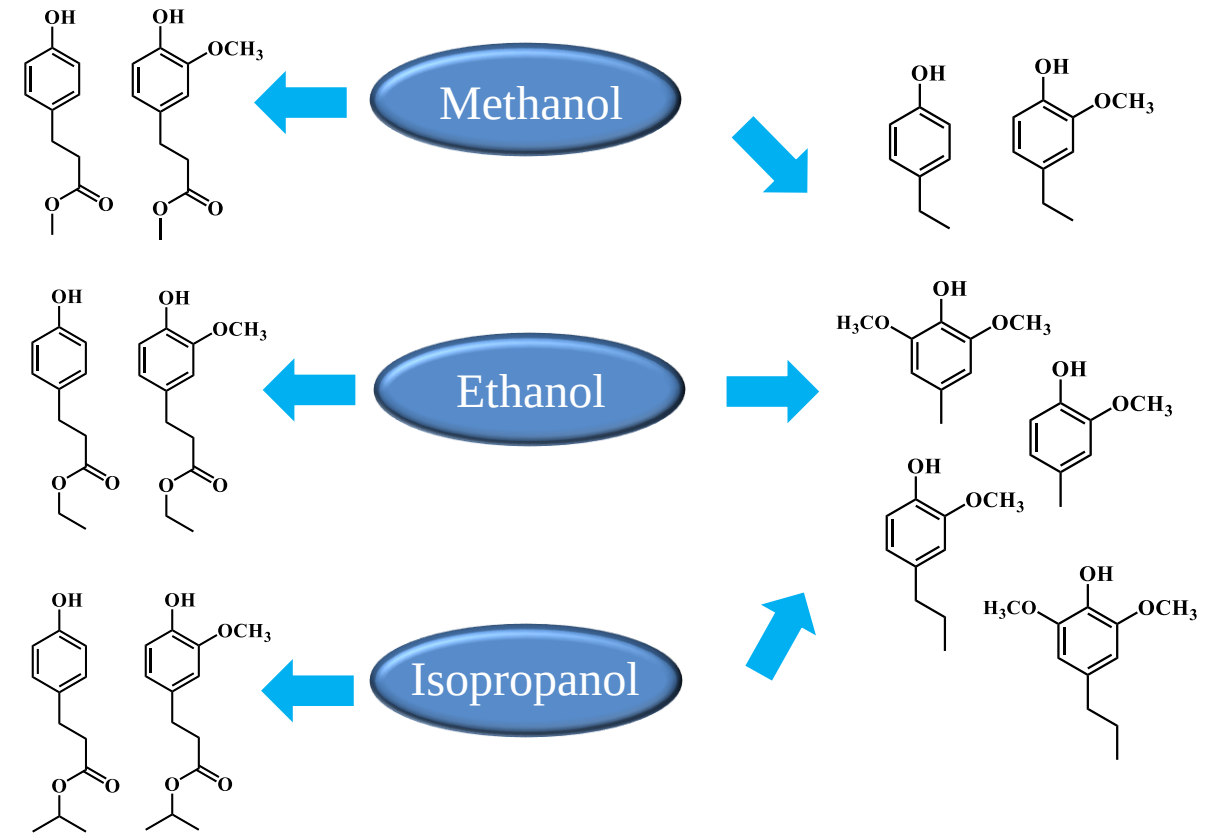


- High yields of esters were detected
- The alkylphenols only contain para-alkyls

Catalytic ethanolysis of EHL with H_2

Effect of the solvent on the structure of main monomers.



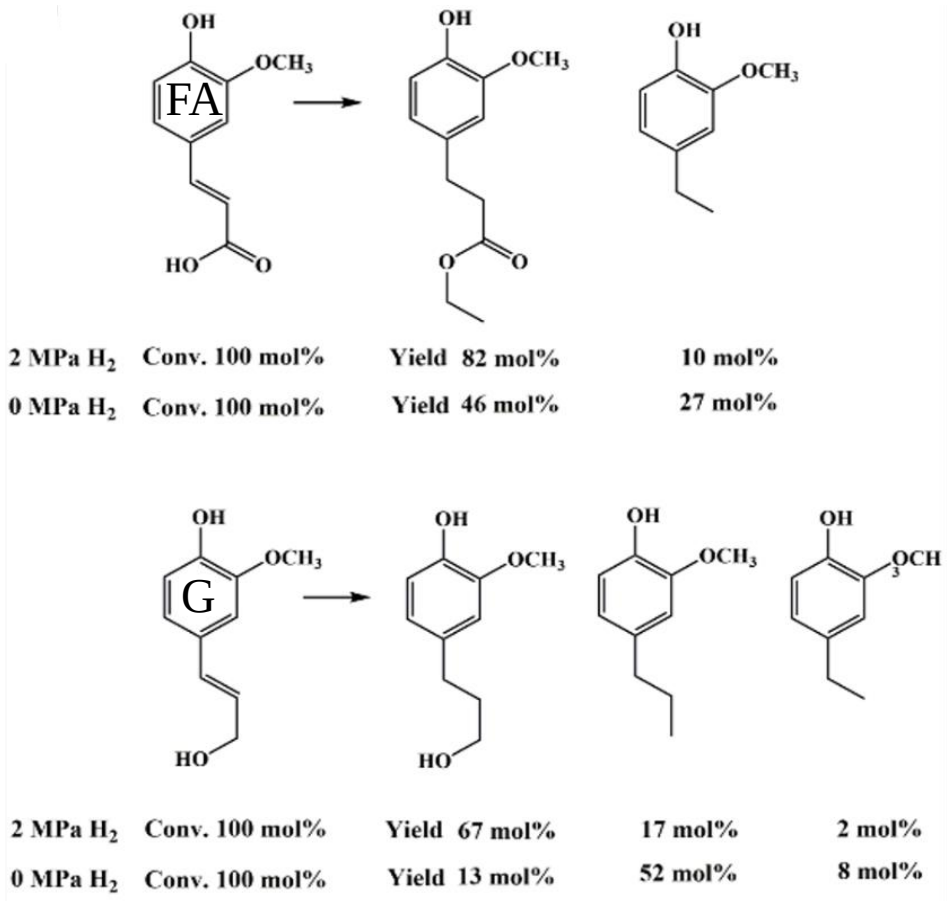


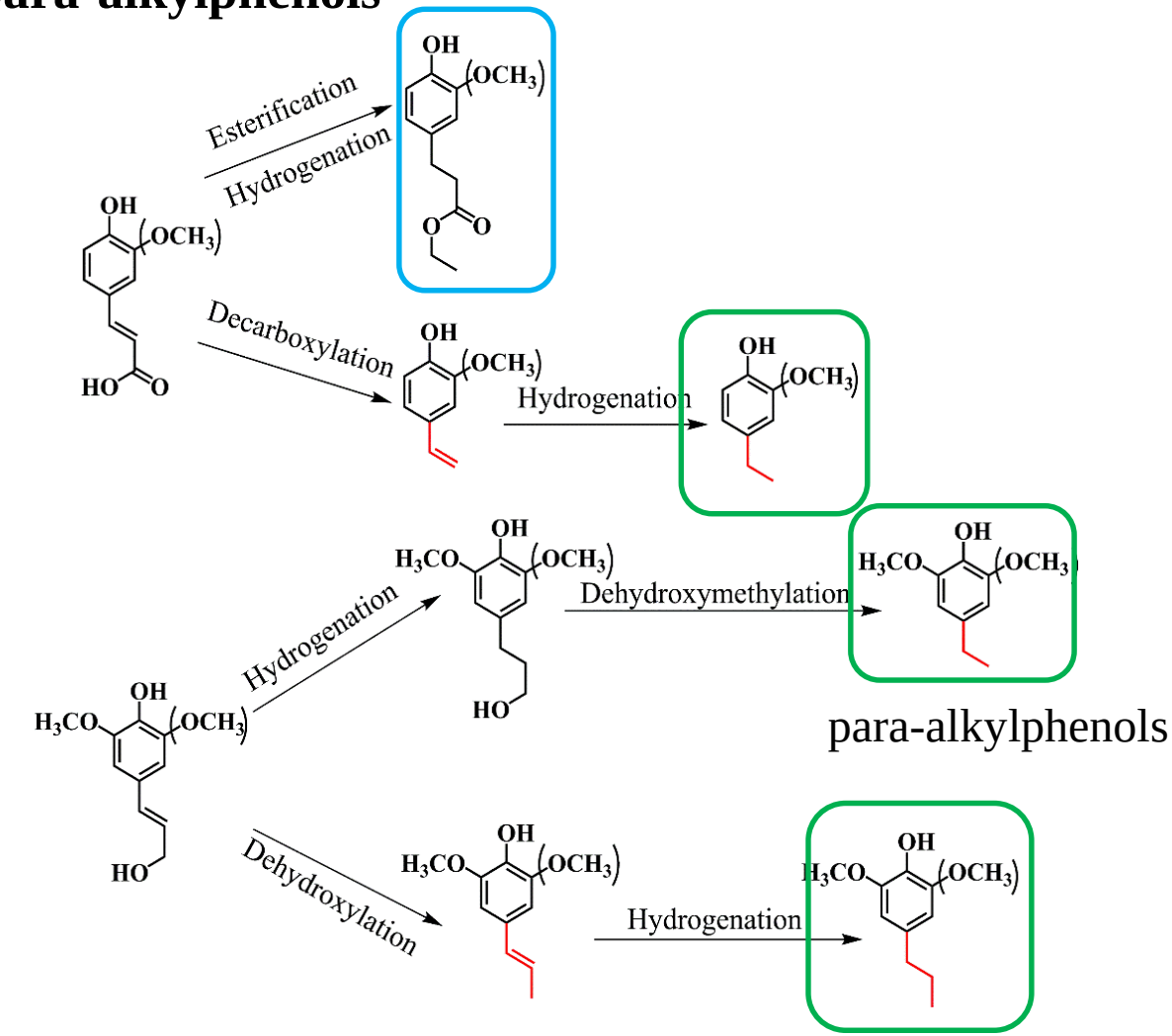
TIC of products and structures of main monomers obtained from EHL depolymerization with Ni (220H) at 280 °C for 6 h with 2 MPa H_2.

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

Catalytic ethanolysis of EHL with H_2

Formation of esters and para-alkylphenols





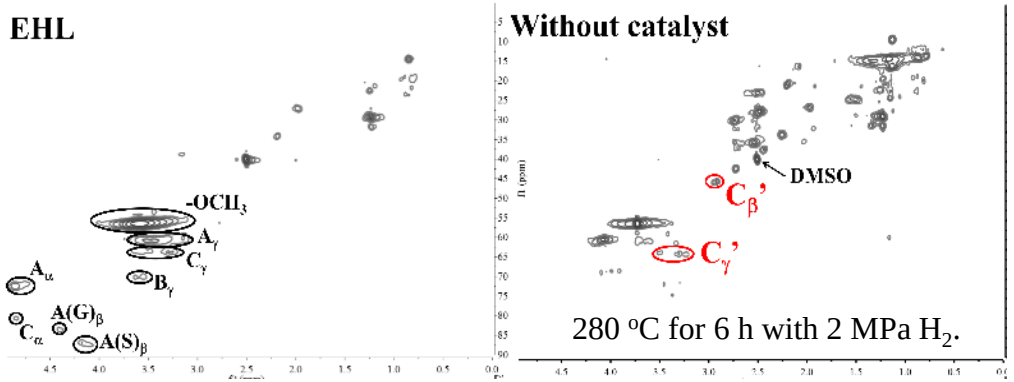
para-alkylphenols

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

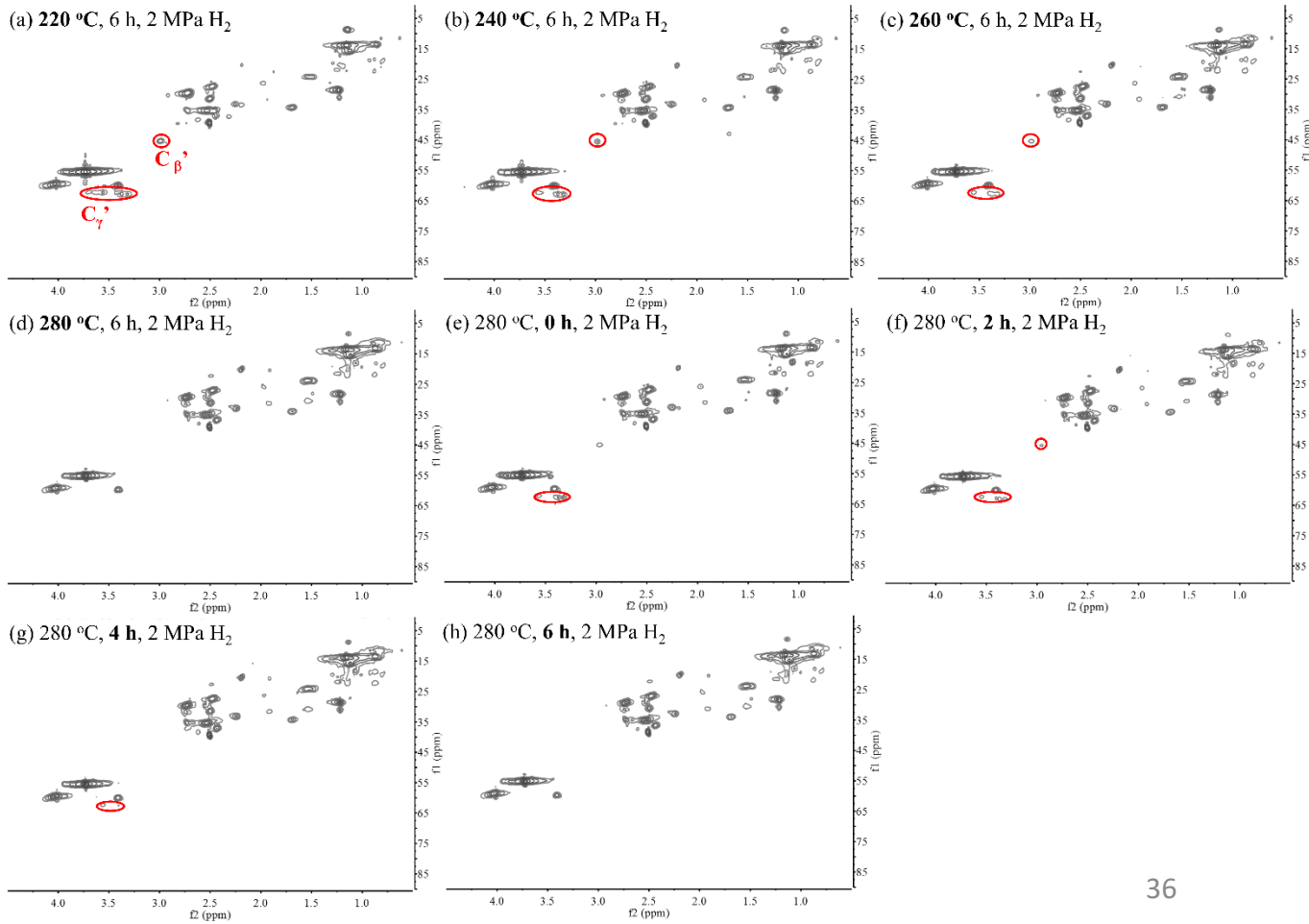
Ind. Eng. Chem. Res. **2020,** *59* (16), 7466-7474.

Catalytic ethanolysis of EHL with H_2

Cleavage of linkages in EHL (2D-NMR analysis)



Ni(220H) catalyzed EHL depolymerization.



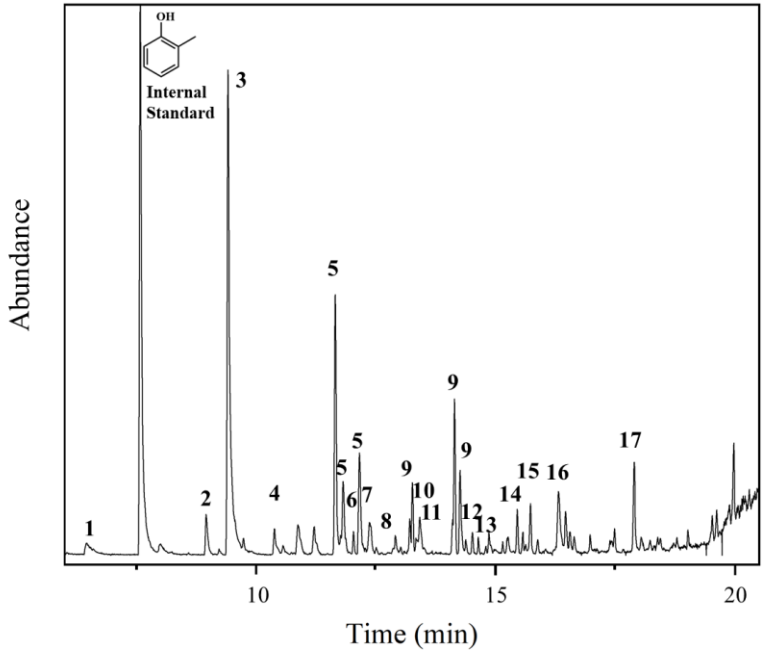
- Ether linkages can be cleaved without catalyst
- C-C linkages in C' are gradually cleaved during Ni(220H) catalyzed reaction

Part 2.3: The effect of solvent for EHL depolymerization

The effect of solvent for EHL conversion

NiMo/γ-Al_2O_3 catalyzed depolymerization of EHL in ethanol

Reaction condition: 320 °C, 27.6 bar H_2, 7.5 h, ethanol solvent, NiMo/γ-Al_2O_3



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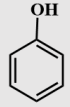
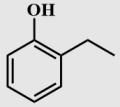
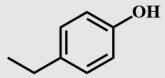
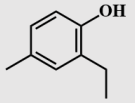
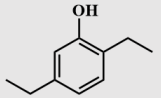
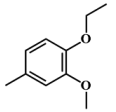
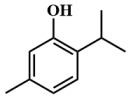
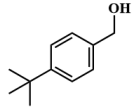
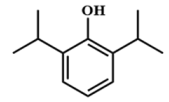
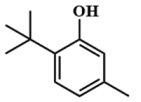
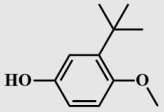
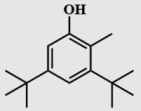
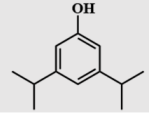
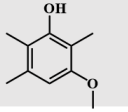
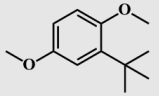
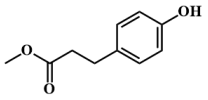
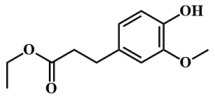
1		2		3		4		5	
6		7		8		9		10	
11		12		13		14		15	
16		17							

25.5 wt% yields of monomers

- Complex alkylphenols were the main products

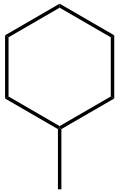
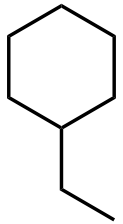
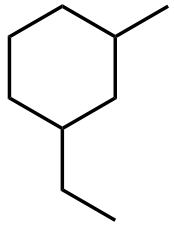
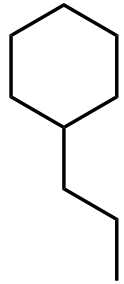
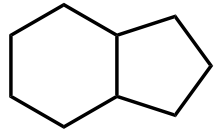
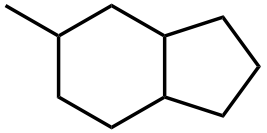
Energy Fuels, **2019**, 33, 8657-8665.

The effect of solvent for EHL conversion

NiMo/γ-Al_2O_3 catalyzed depolymerization of EHL in cyclohexane

Same reaction condition: 320 °C, 27.6 bar H_2, 7.5 h, ethanol solvent, NiMo/γ-Al_2O_3

Products Yields

1.5 wt%	4.6 wt%	0.3 wt%	3.3 wt%	0.2 wt%	0.4 wt%
					

Total: 10.4 wt%

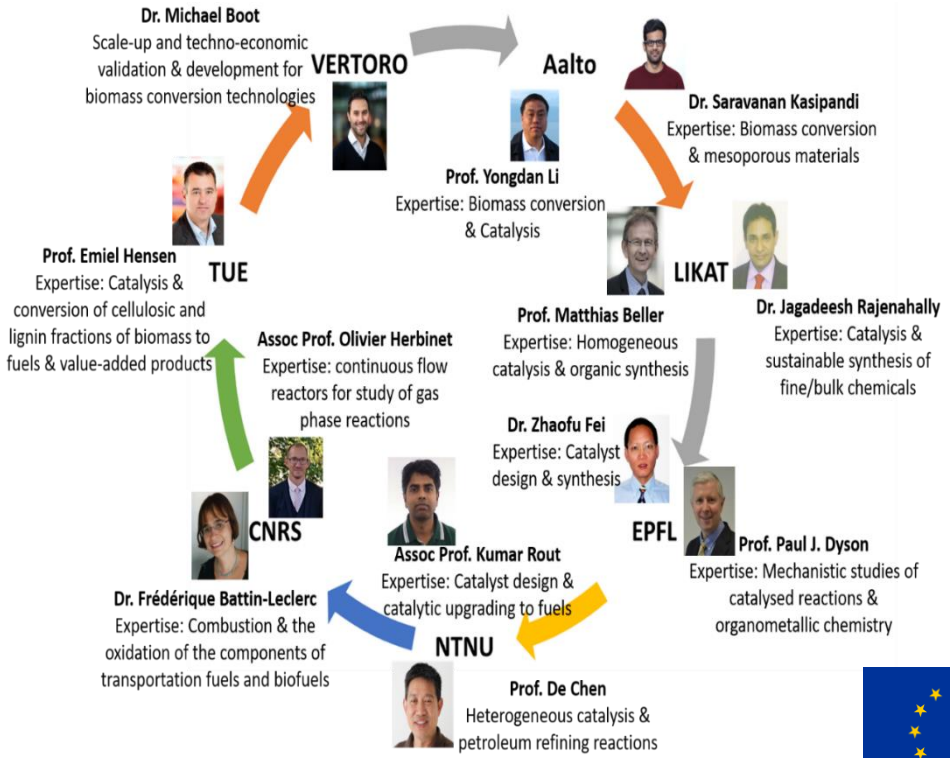
- The benzene rings in products was completely hydrogenated
- The O in products was completely removed

Bioresource Technology 323 (2021) 124634

Summary: EHL catalytic depolymerization

- **The product distribution strongly depends on the solvent, catalyst, with or without hydrogen.**
- **In $WO_3/\gamma\text{-}Al_2O_3$ catalyzed reaction without H_2, complex alkylphenols are the main products. In Ni catalyzed reaction with H_2, esters and para-alky phenols are the main products.**
- **EHL was depolymerized into phenolic monomers in ethanol, but produced cycloalkanes in cyclohexane.**

EU Horizon 2020 project 101006744
EHLCATHOL website: www.ehlcathol.eu;
Welcome to join us!



Since 2010, the research on lignin chemical conversion has received funding from:

Ministry of Science and Technology of China
Natural Science Foundation of China
Ministry of Education of China
China Scholarship Council
European Union's Horizon 2020 research and innovation program under grant agreement no 101006744

Aalto University

Congrats for the 40th Anniversary of CACS!

Let us expect a prosperous future!