Aalto University

Depolymerization of enzymatic hydrolysis lignin into aromatic chemicals and fuels

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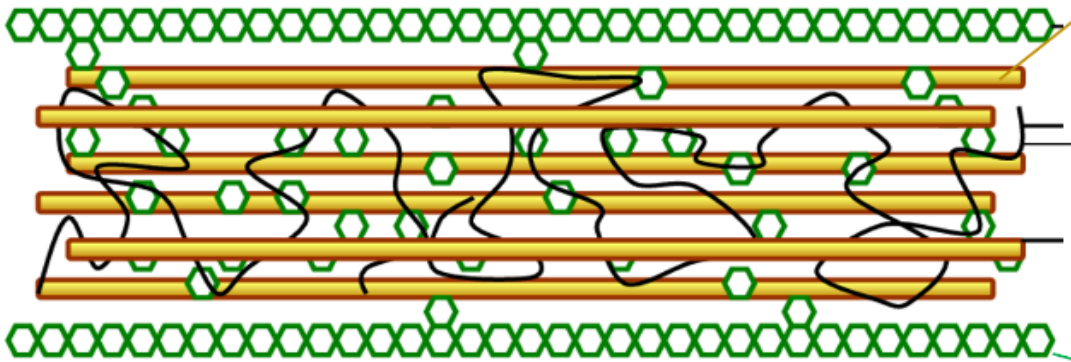
Supervisor: Professor Yongdan Li

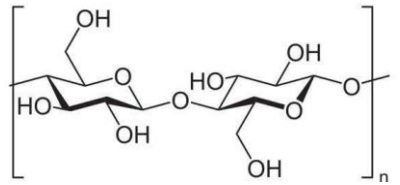
March 22, 2022

Lignocellulose

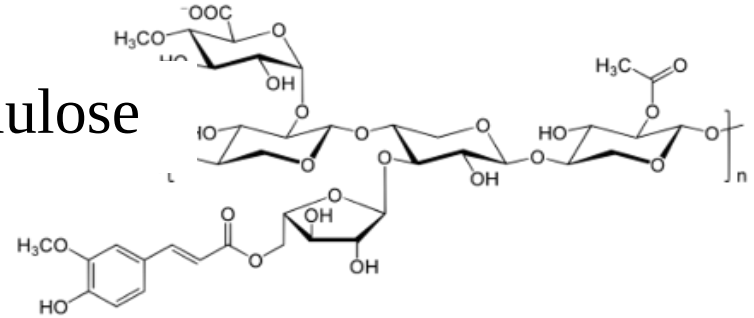
Lignocellulose



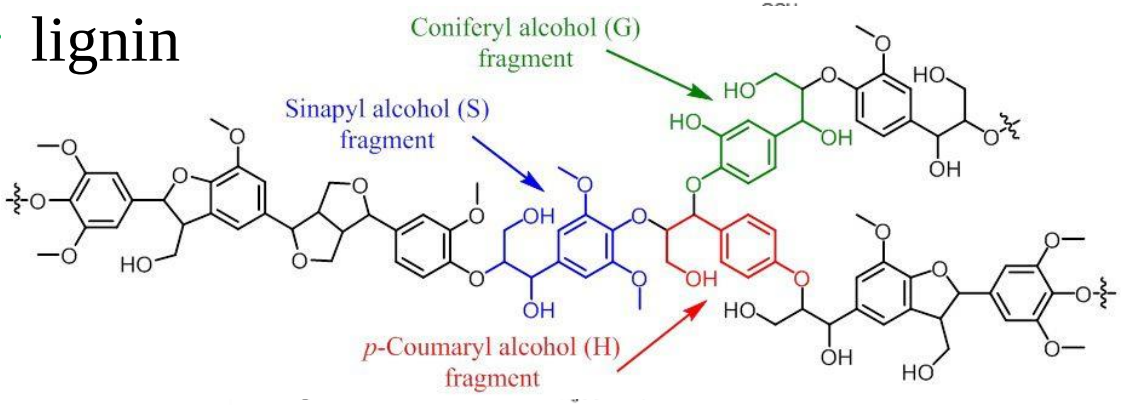
cellulose



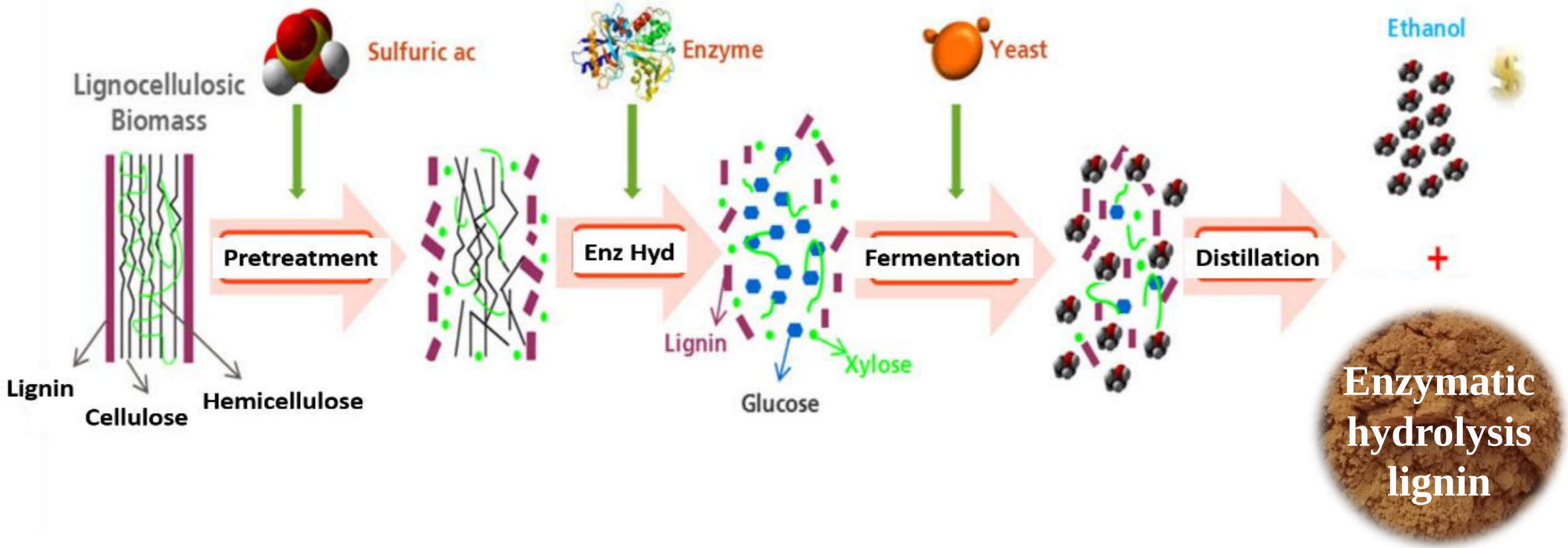
hemicellulose



lignin



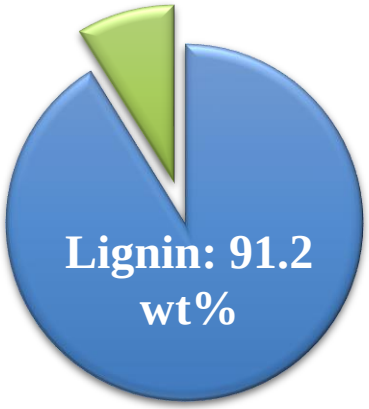
Bio-ethanol Production



EHL

EHL Characterization

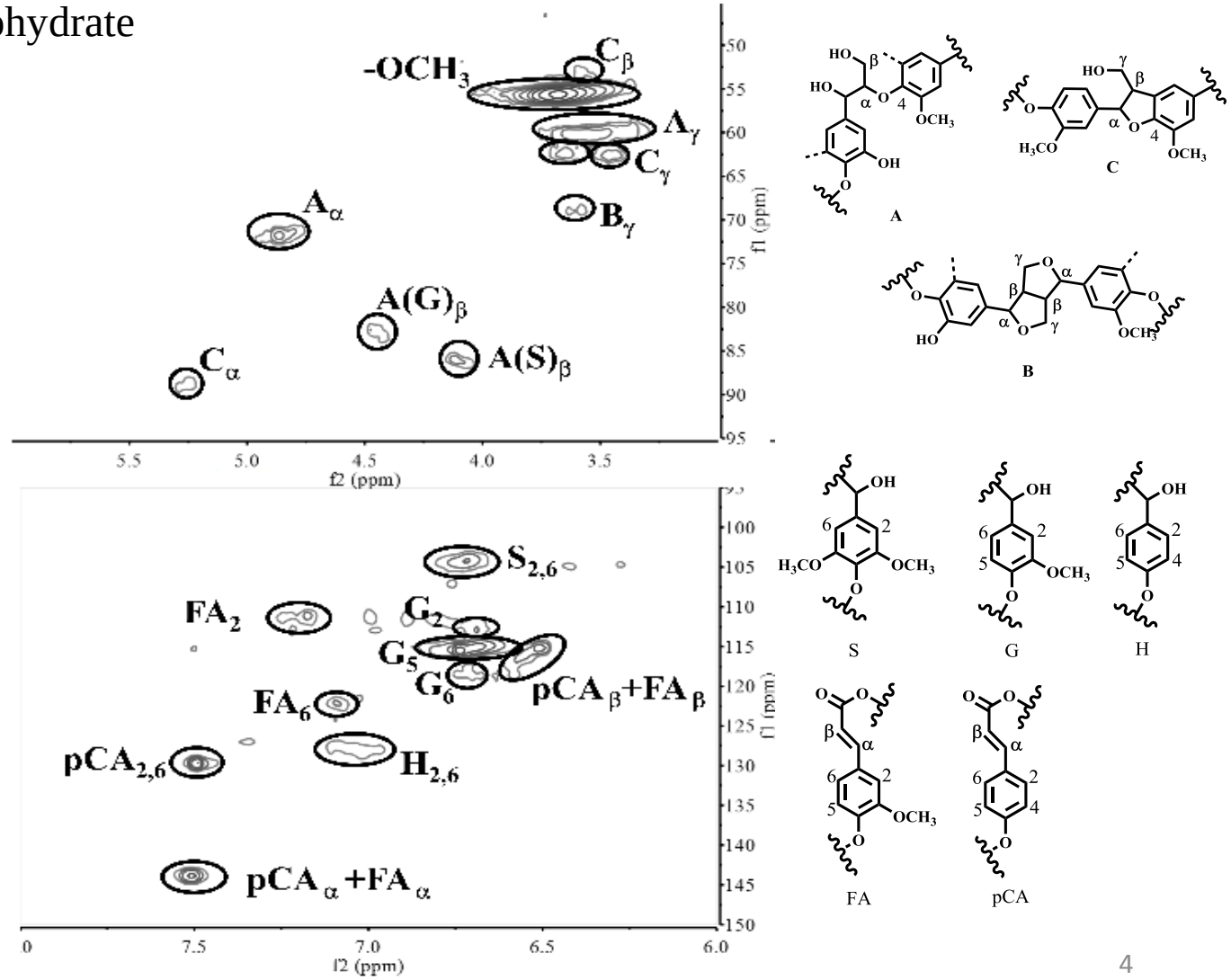
Others： : Ash, and residual carbohydrate



Elemental analysis of EHL

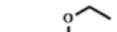
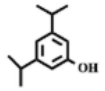
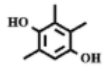
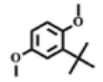
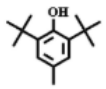
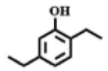
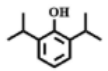
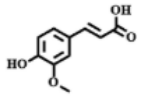
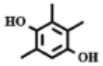
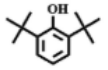
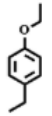
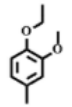
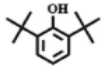
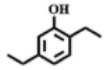
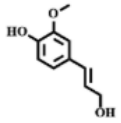
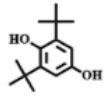
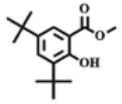
C	H	N	S	O
61.75%	6.48%	0.90%	0.58%	30.29%

HSQC-NMR of EHL



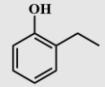
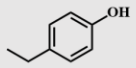
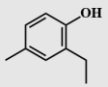
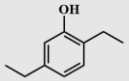
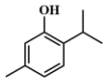
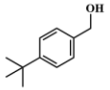
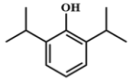
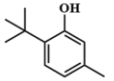
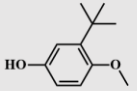
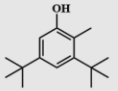
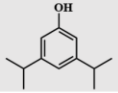
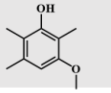
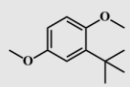
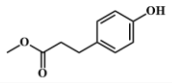
Our previous works

1 g $WO_3/\gamma\text{-}Al_2O_3$, 1 g EHL, 320 °C, 0 bar N_2, 8 h, ethanol solvent,

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

Total yield: 31.6 wt%

1 g $NiMo/\gamma\text{-}Al_2O_3$, 1 g EHL, 320 °C, 27.6 bar H_2, 7.5 h, ethanol solvent

No.	Structure	No.	Structure	No.	Structure	No.	Structure	No.	Structure
1		2		3		4		5	
6		7		8		9		10	
11		12		13		14		15	
16		17							

Total yield: 25.5 wt%

- No char is formed, and the EHL is completely liquified
- High yield of aromatic products are obtained, and alkylphenols are the main products

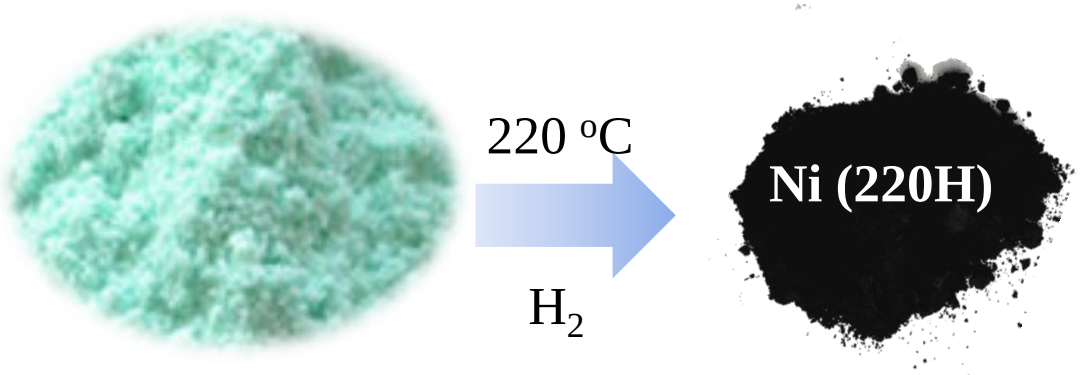
Ind. Eng. Chem. Res. **2019**, 58, 10255-10263

Part 1:

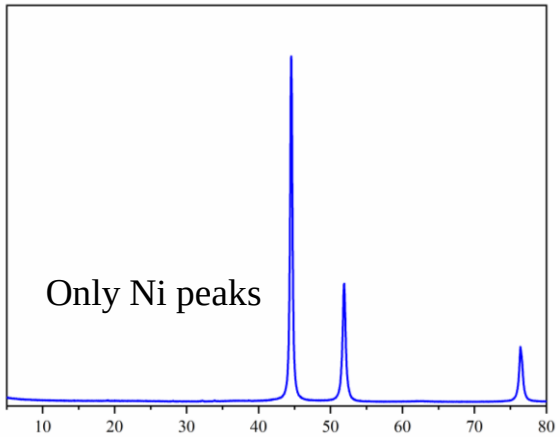
EHL depolymerization with unsupported Ni catalyst: the formation of monomers

EHL depolymerization with unsupported Ni catalyst

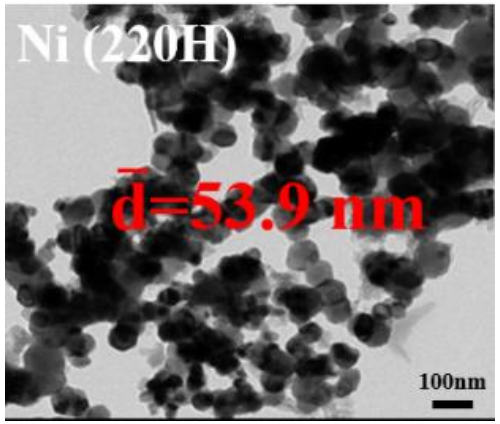
Catalyst preparation: Nickel formate decomposition



XRD

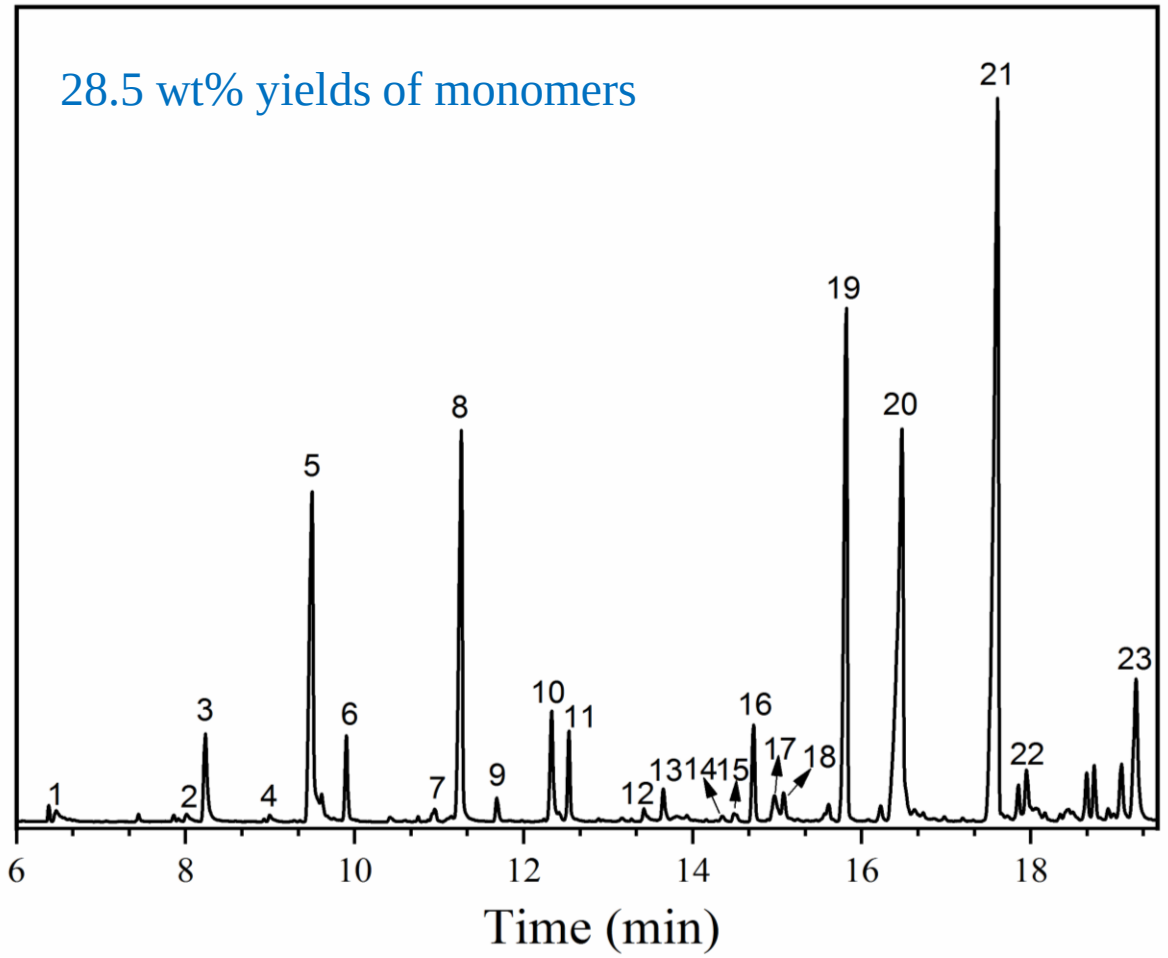


TEM



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

EHL depolymerization with unsupported Ni catalyst



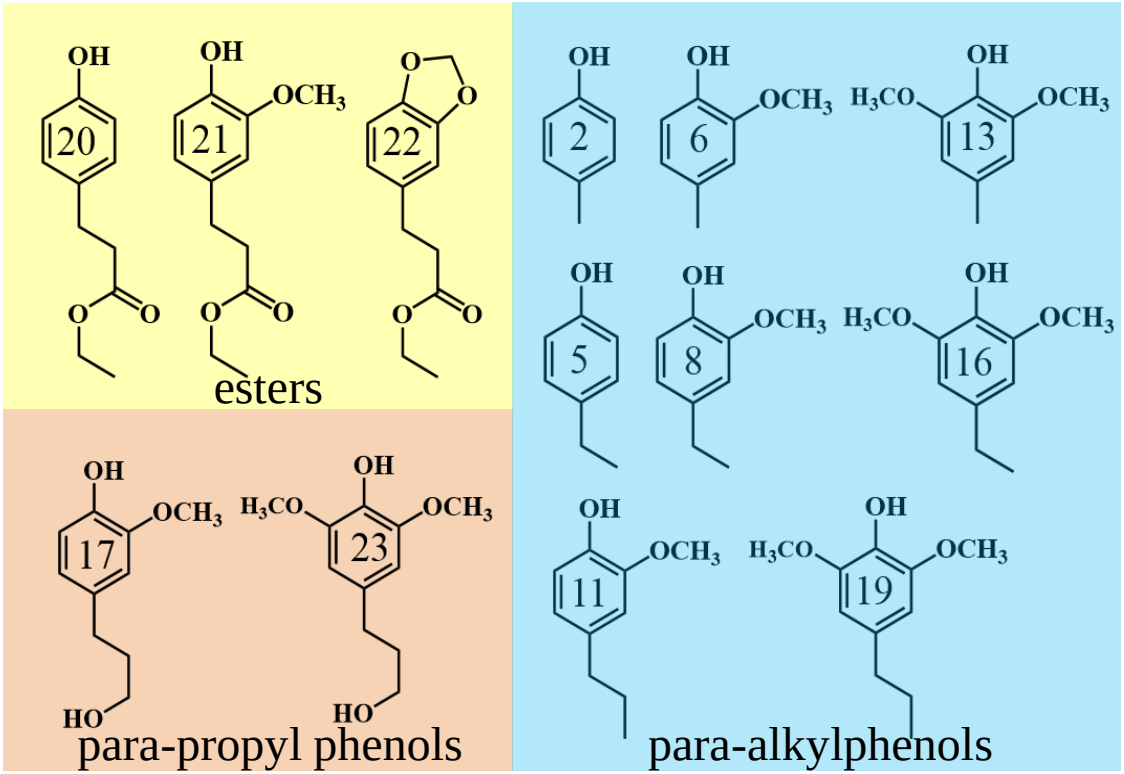
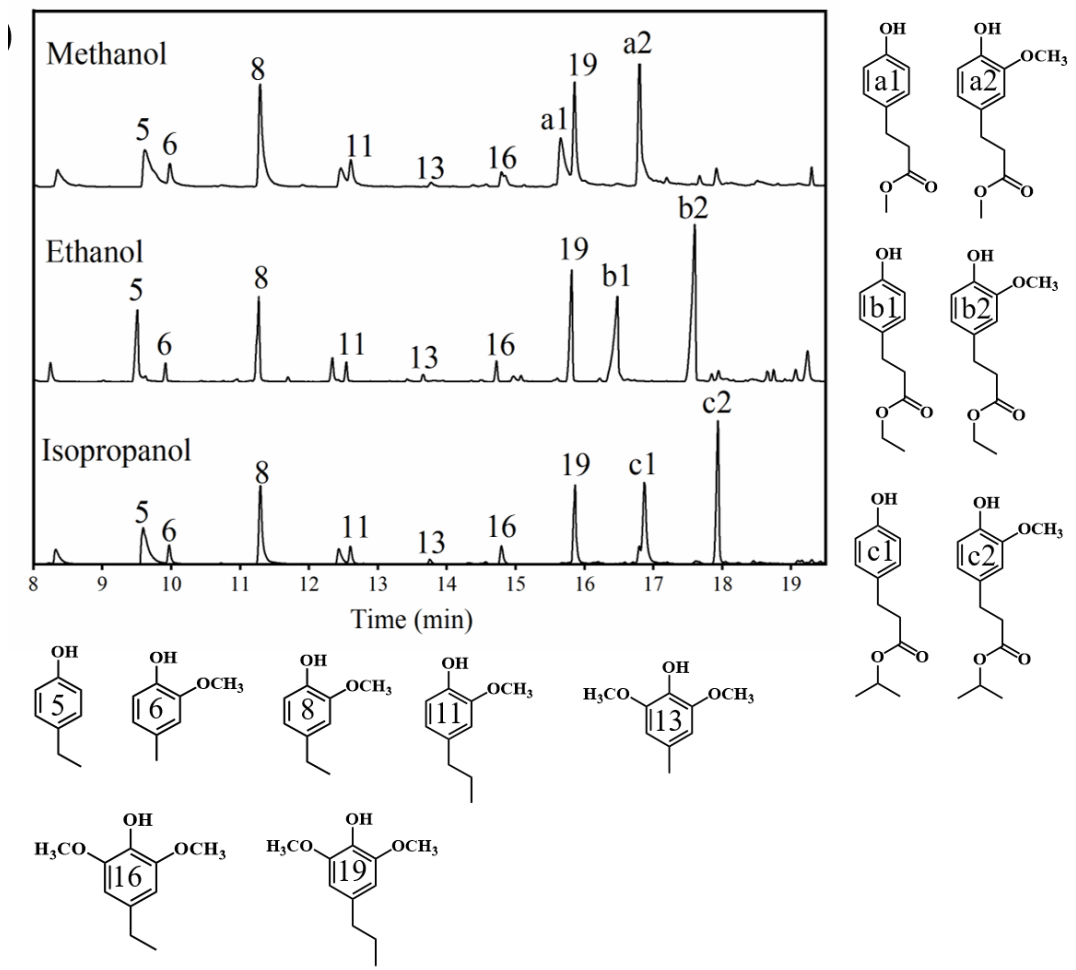
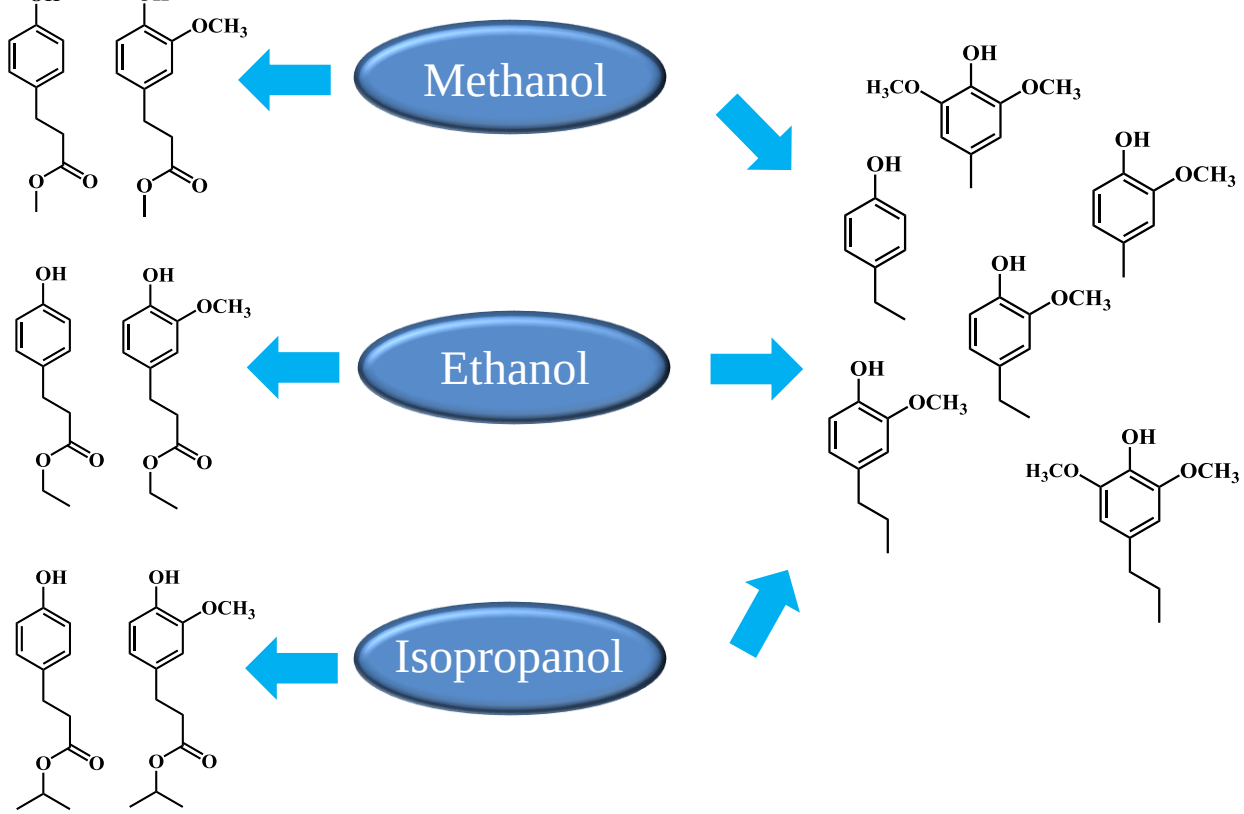


Fig. 5. Total-ion chromatogram (TIC) of the liquid product obtained from EHL depolymerization over Ni (220H) in ethanol at 280 ^{o}C for 6 h under 20 bar H_2.

Effect of the solvent on the structure of main monomers

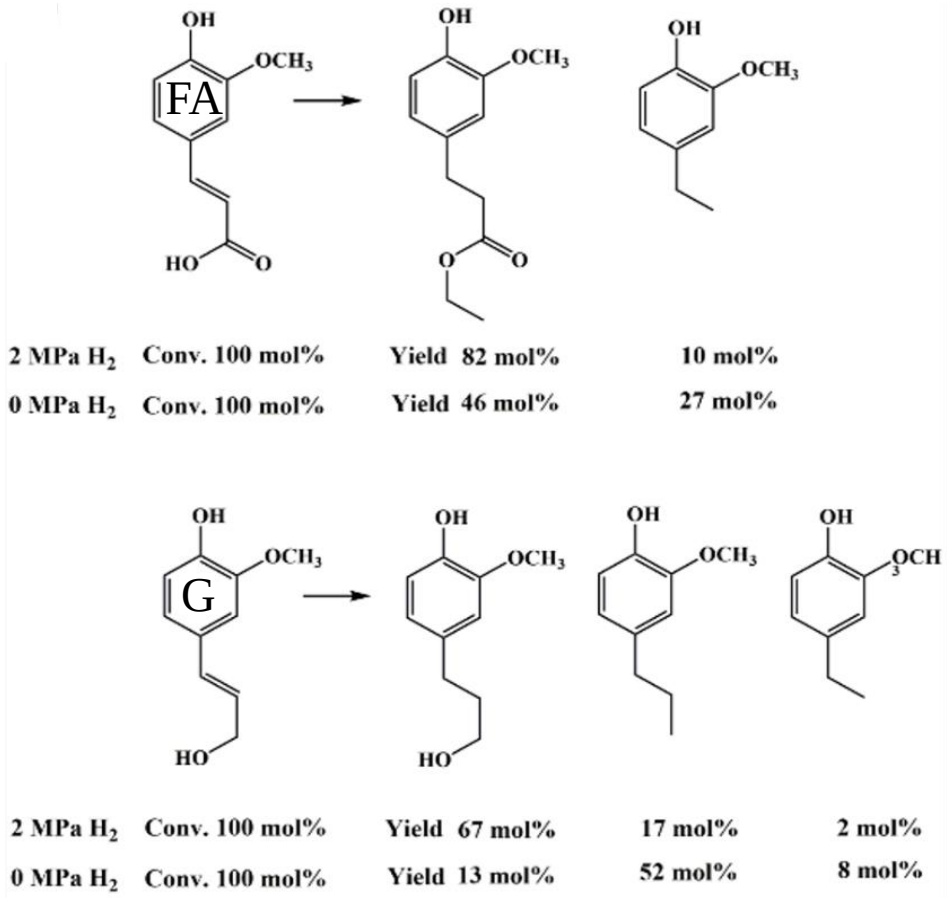




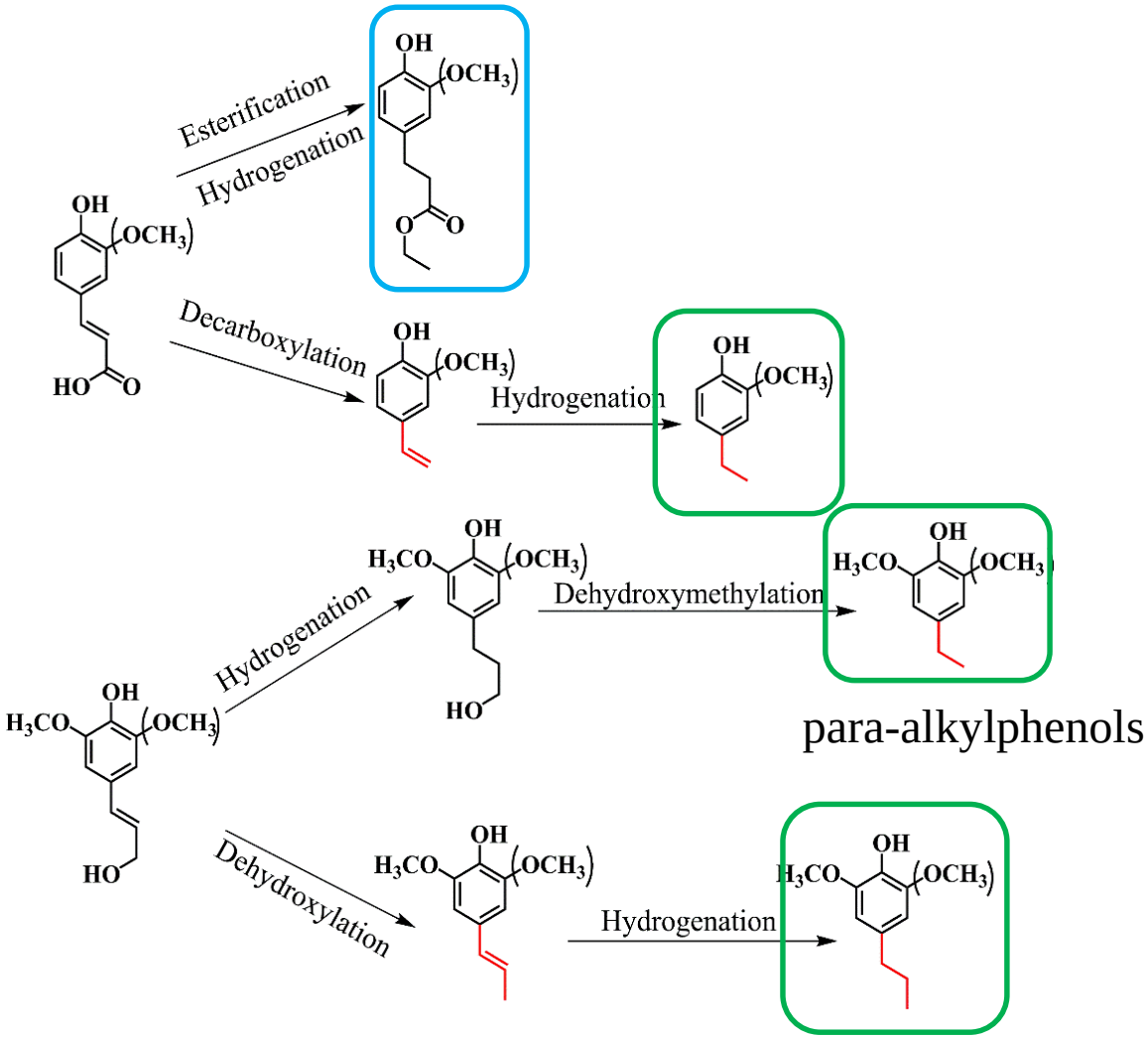
Ind. Eng. Chem. Res. **2020,** *59* (16), 7466-7474.

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.

Monomer formation



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



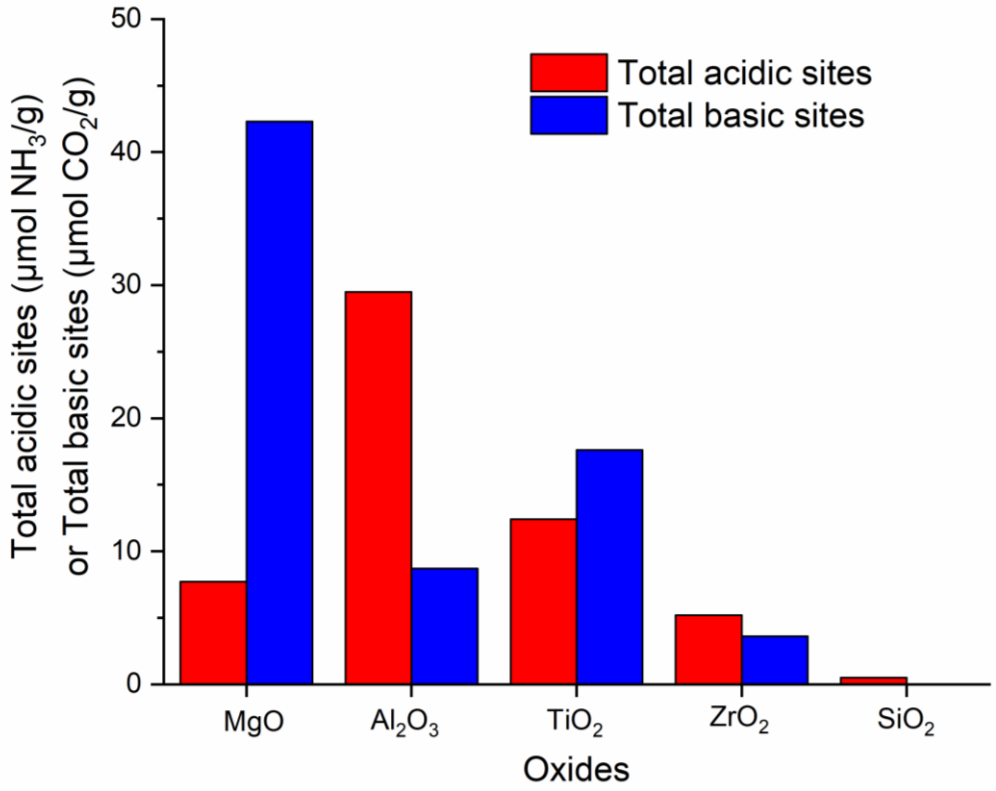
para-alkylphenols

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

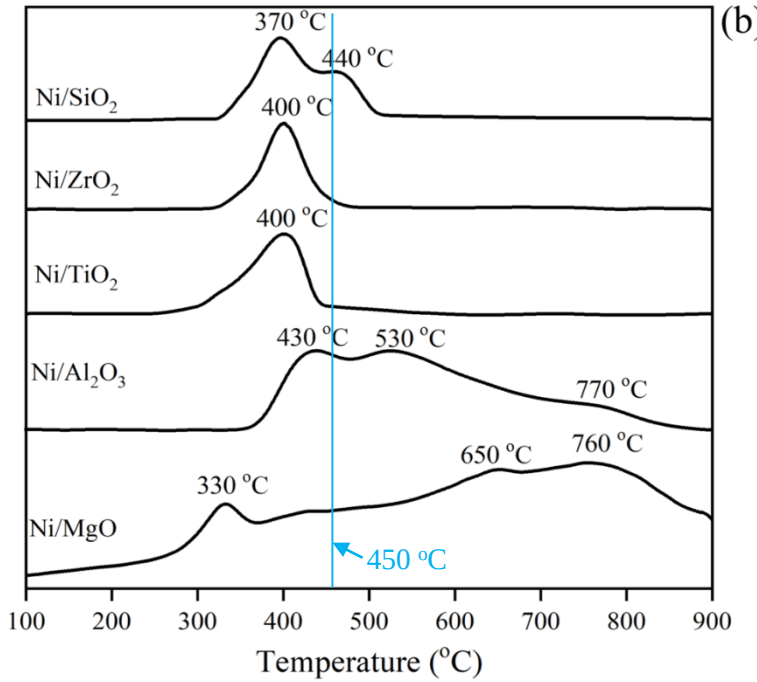
Part 2:

EHL depolymerization with supported Ni catalysts: the reaction pathways

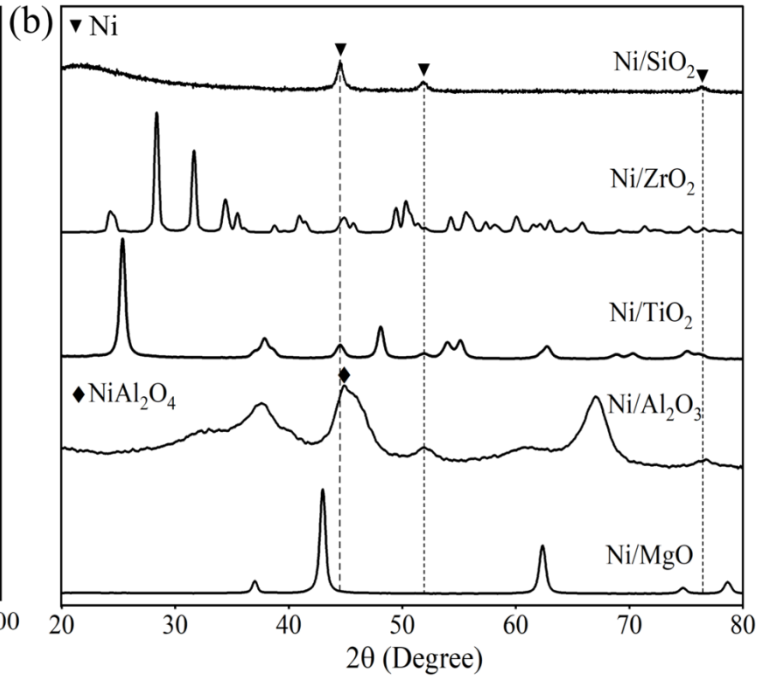
Ni catalysts supported on different oxides



TPR-H_2



XRD

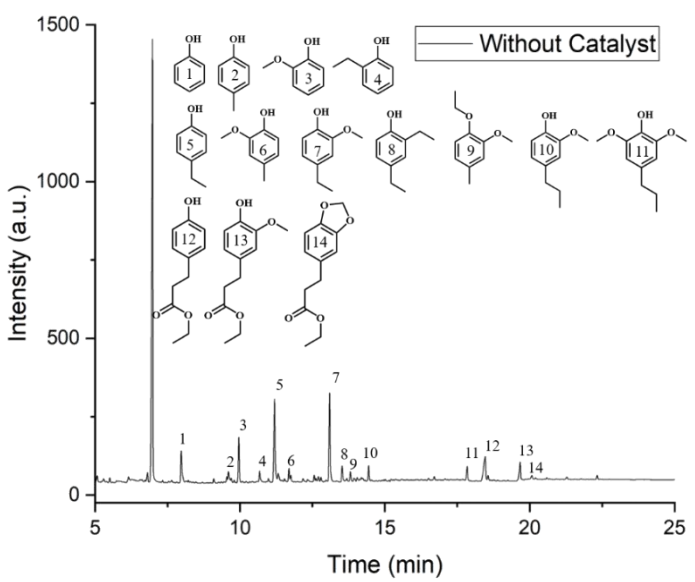


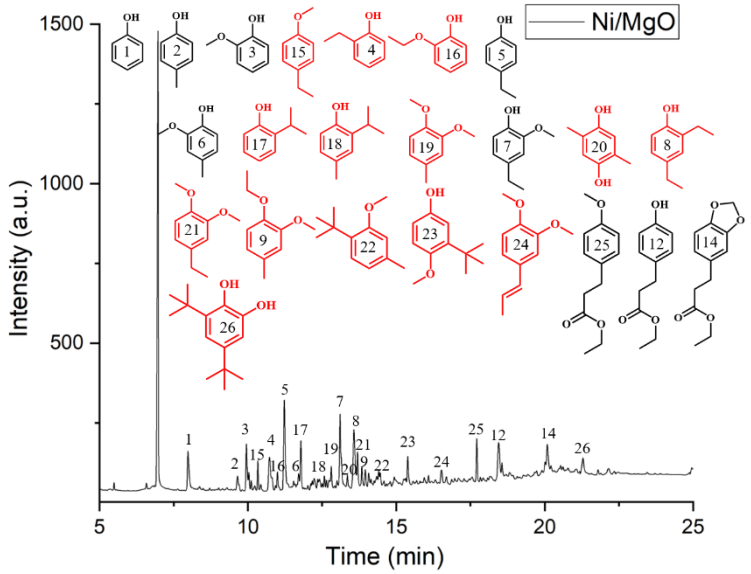
Catalyst	Ni loading (%)[a]	Ni dispersion (%)[b]
Ni/MgO	10.7	Not calculated
Ni/Al_2O_3	9.7	Not calculated
Ni/TiO_2	11.1	4.9
Ni/ZrO_2	9.5	6.1
Ni/SiO_2	10.6	12.0

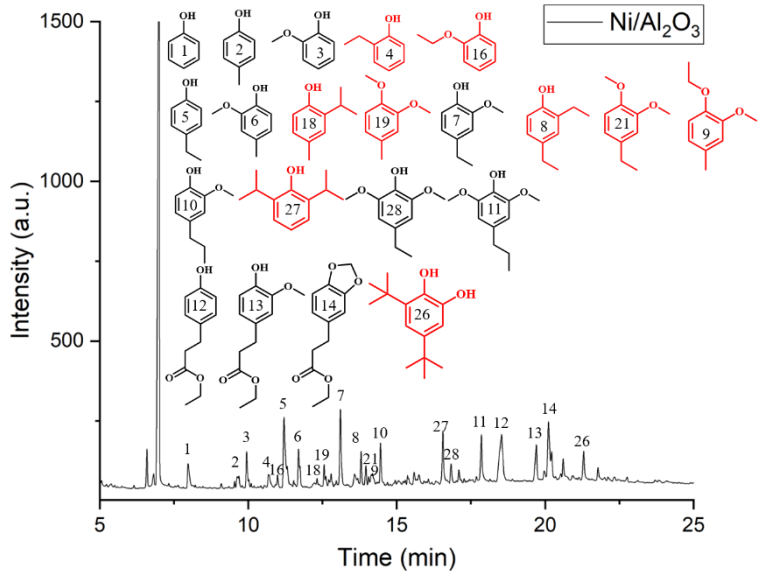
[a] Determined from ICP-OES;
[b] Determined from H_2 chemisorption;

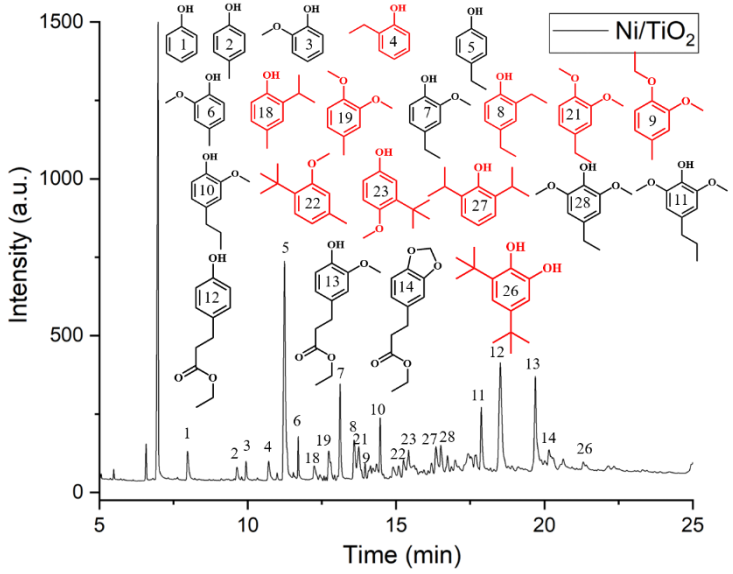
EHL depolymerization with supported Ni catalyst

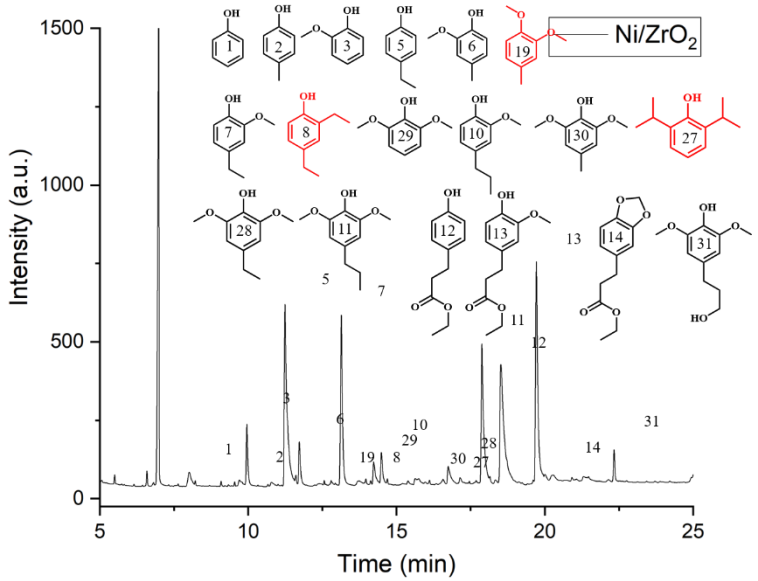
These catalyst are employed in EHL depolymerizationn in ethanol at 280 °C for 6 h under 20 bar H_2

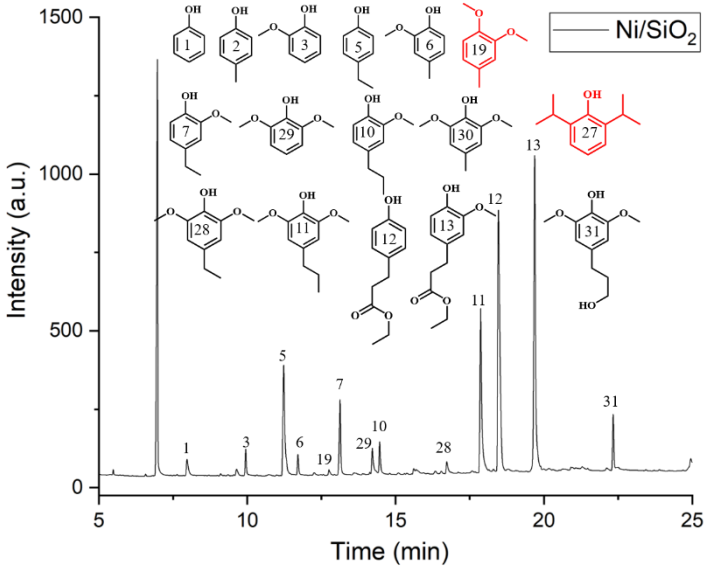




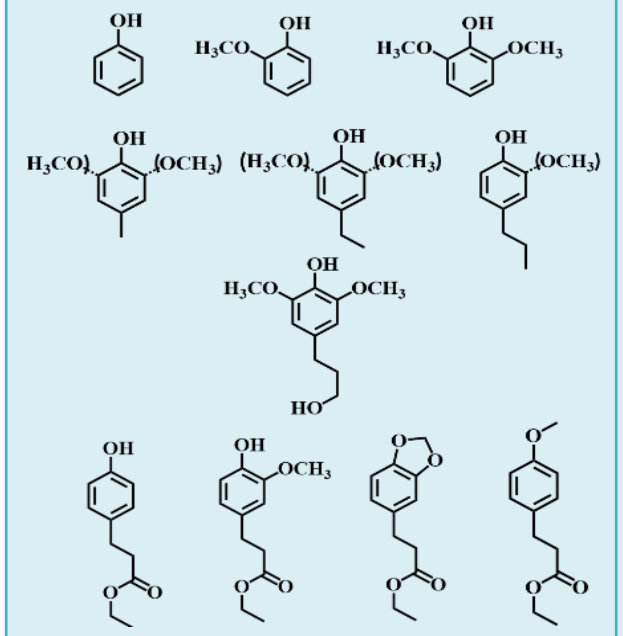
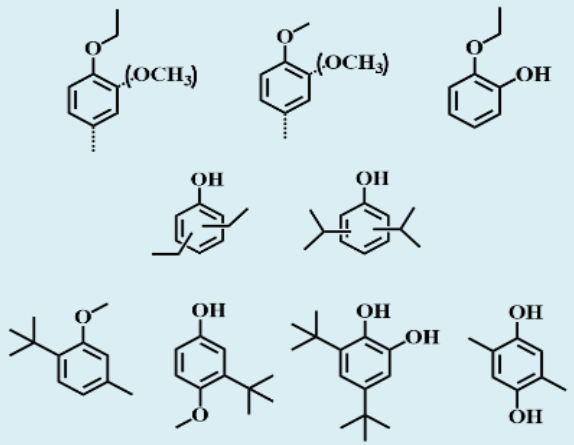


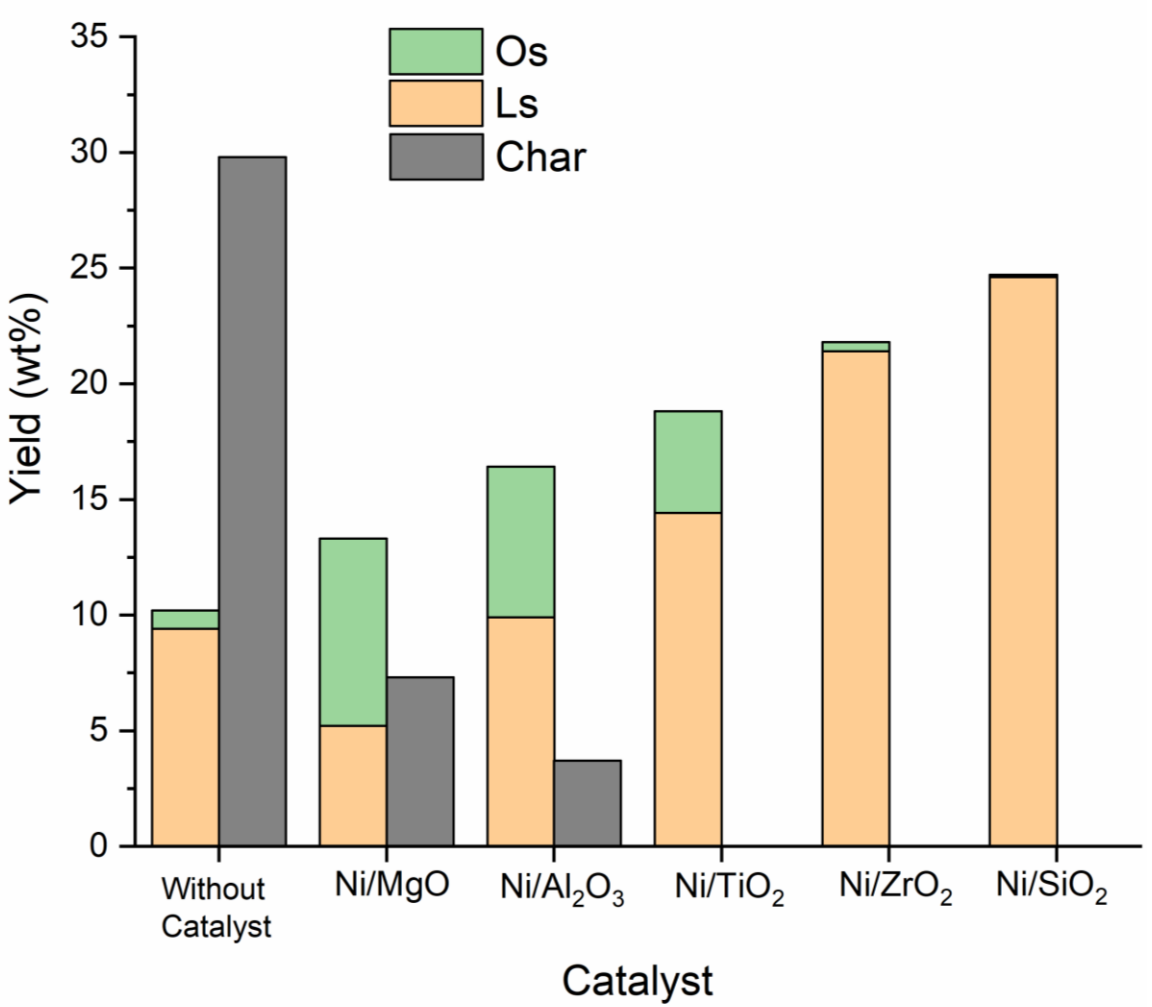






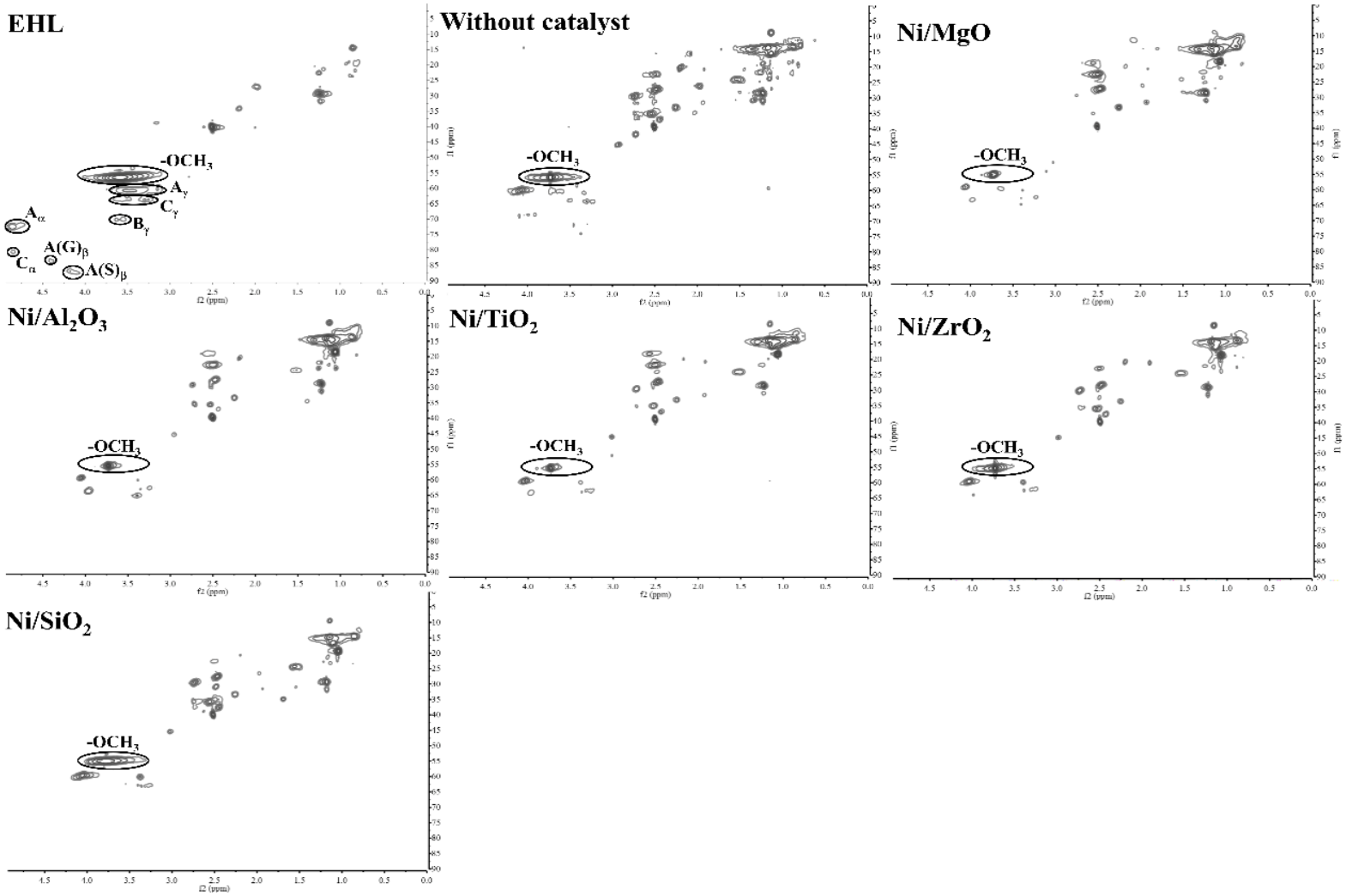
EHL depolymerization with supported Ni catalyst

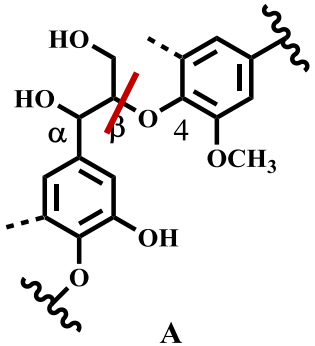
Ls	Os
	



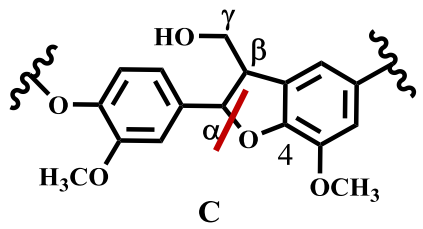
EHL depolymerization with supported Ni catalyst

HSQC-NMR

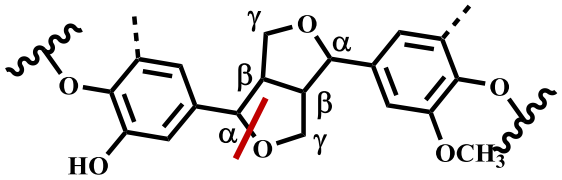




A

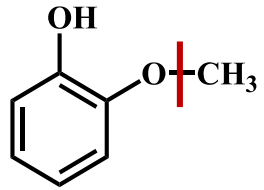


C



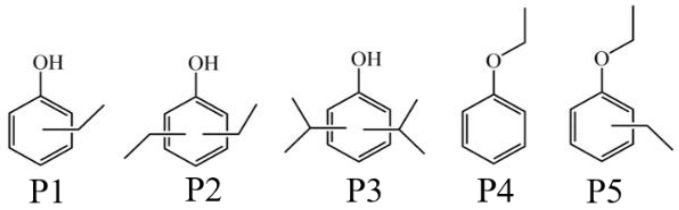
B

Ni/MgO, Ni/Al_2O_3 and Ni/TiO_2

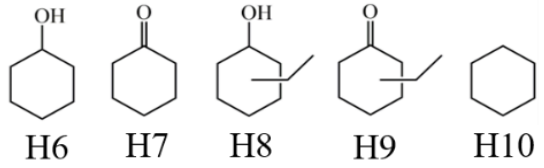


demethylation

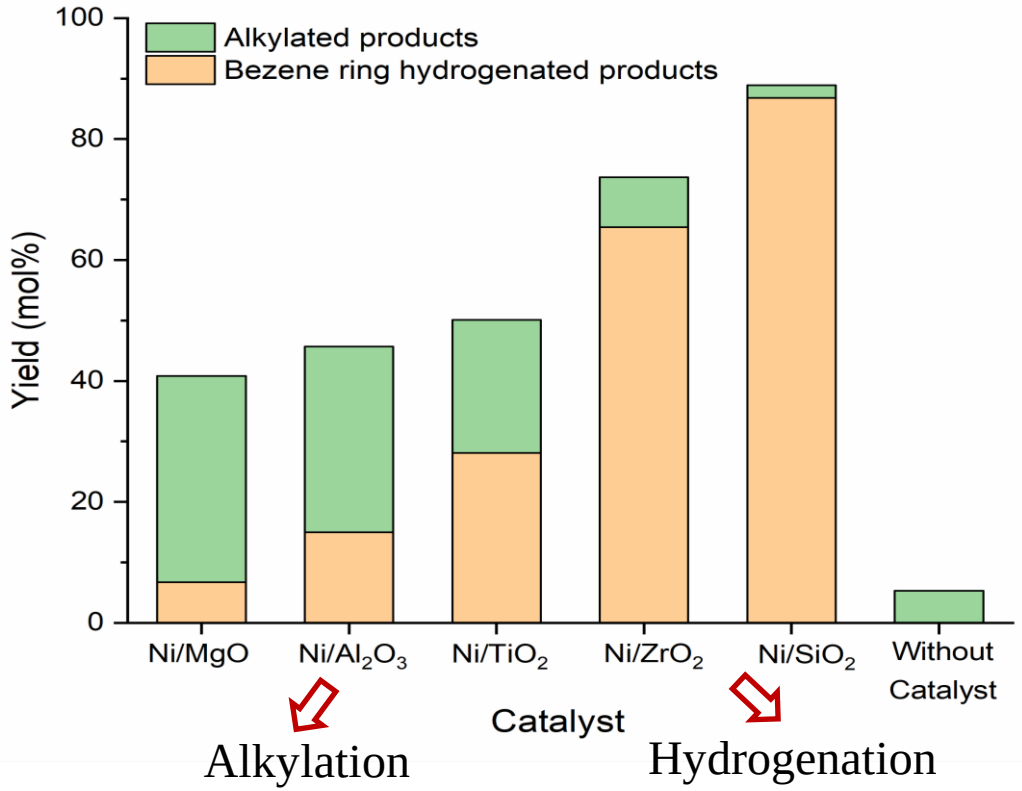
Phenol conversion



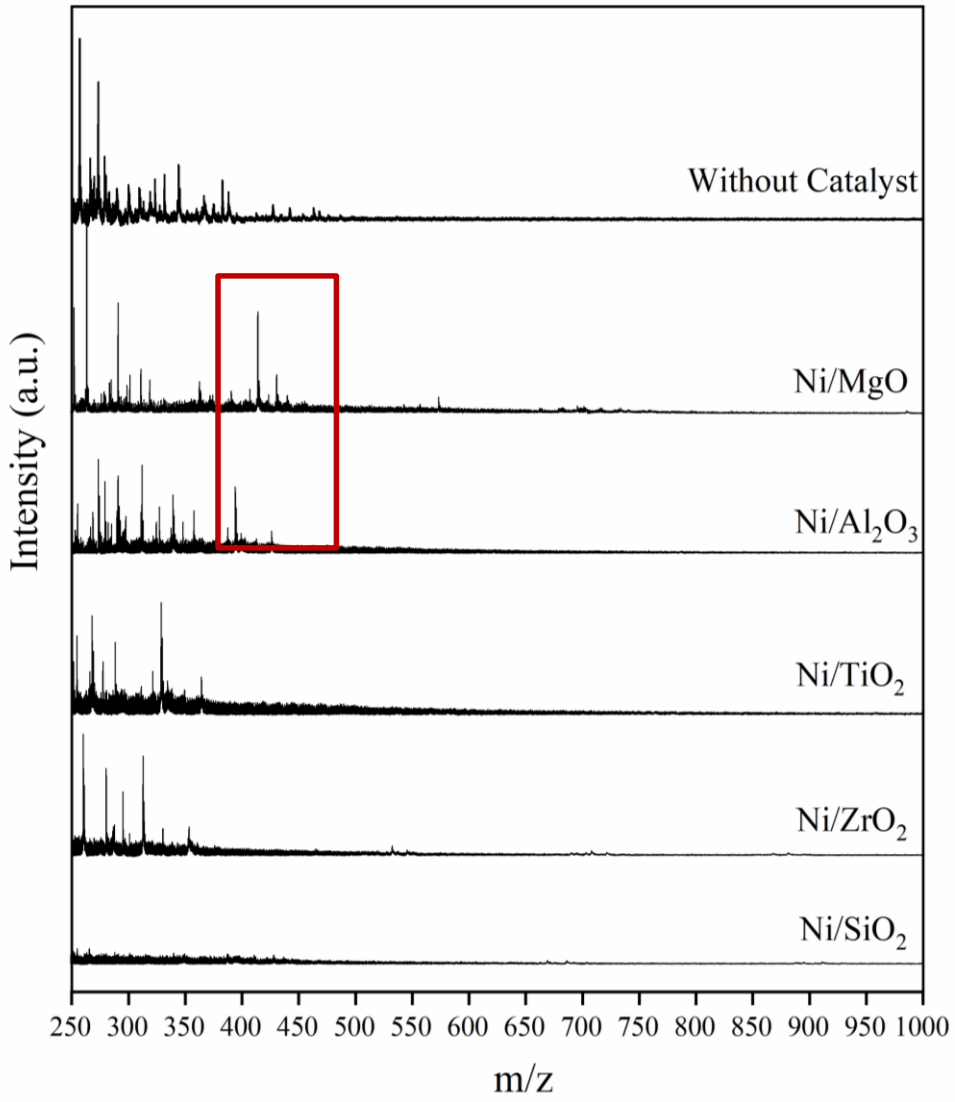
Alkylated products



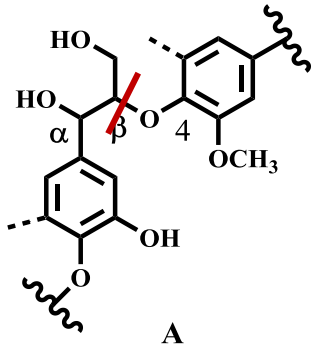
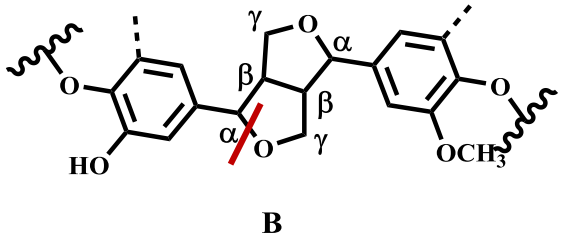
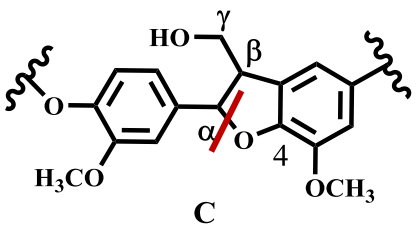
Benzene ring hydrogenated products



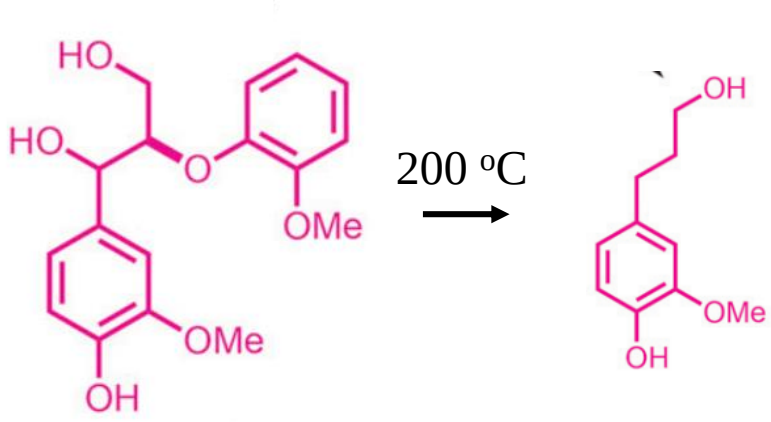
MALDI-TOF-MS

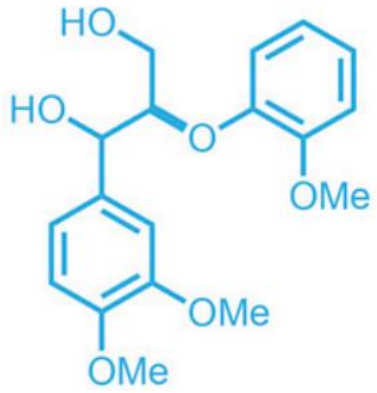


Reaction pathways of lignin depolymerization

Structure	 A	 B	 C	CH_3CH_2OH
Bond Dissociation Energies (BDEs, kcal/mol)	54-72	68-80	42-57	94-110

- Ethanol decomposition into free radicals is more difficult than the homolysis of ether linkages

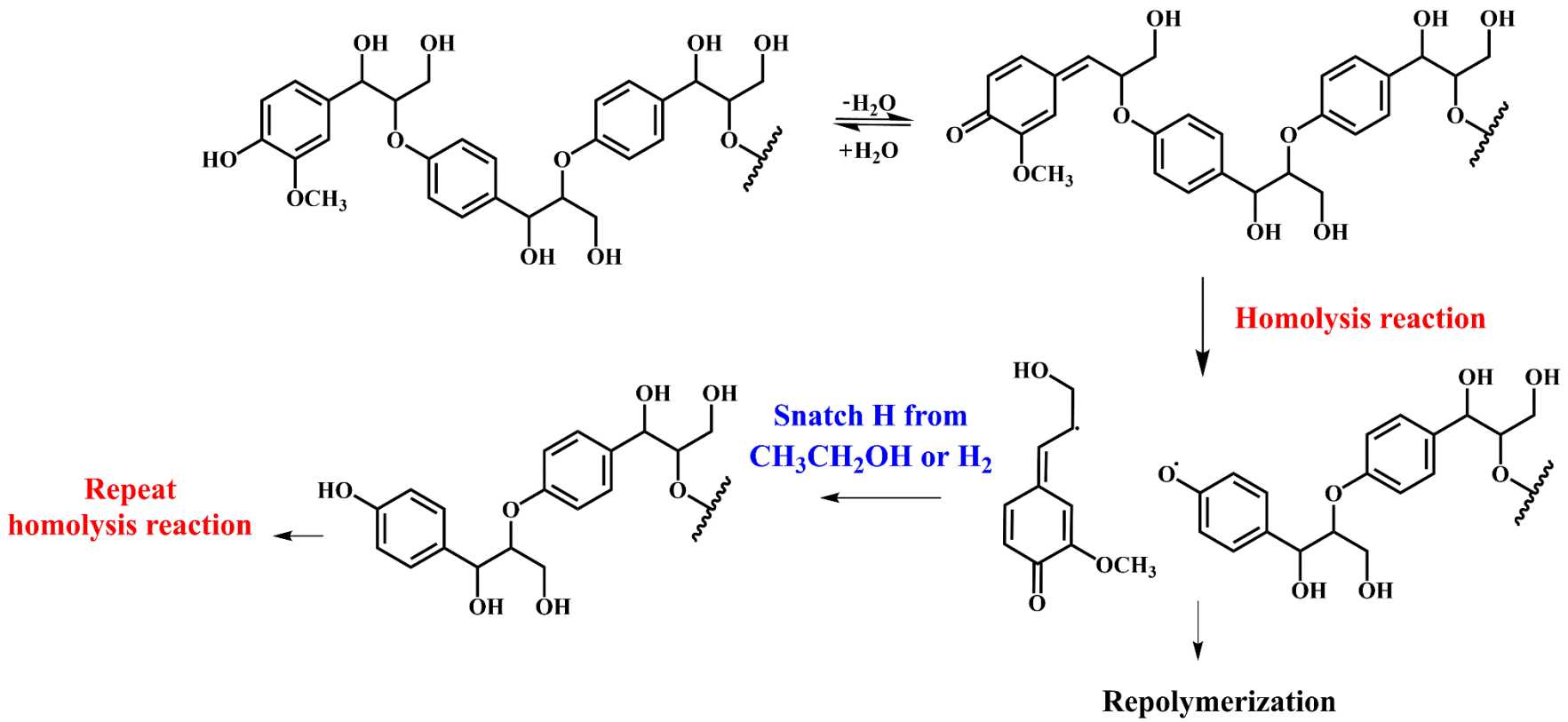




200 °C → No monomers

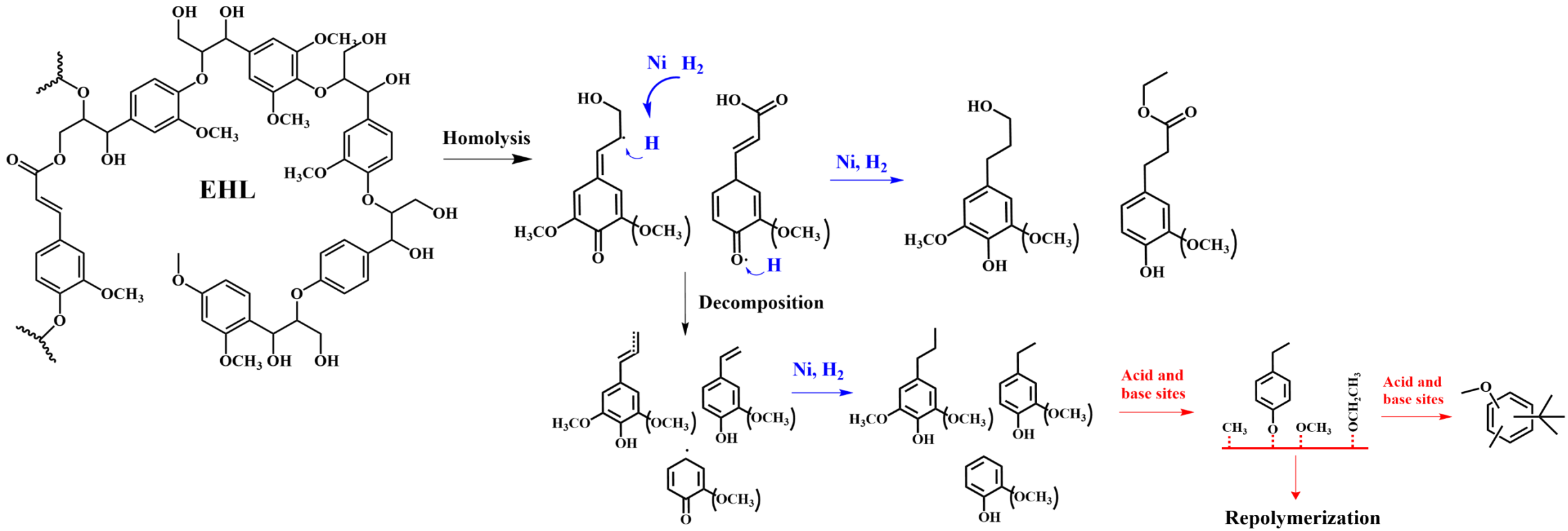
Green Chem., 21 (2019) 3561-3572.

Reaction pathways of lignin depolymerization



- Reaction starts from the unit with phenolic hydroxyl which undergo a homolysis reaction first
- The radicals formed snatch H from ethanol or H_2, and then repeat homolysis reaction.

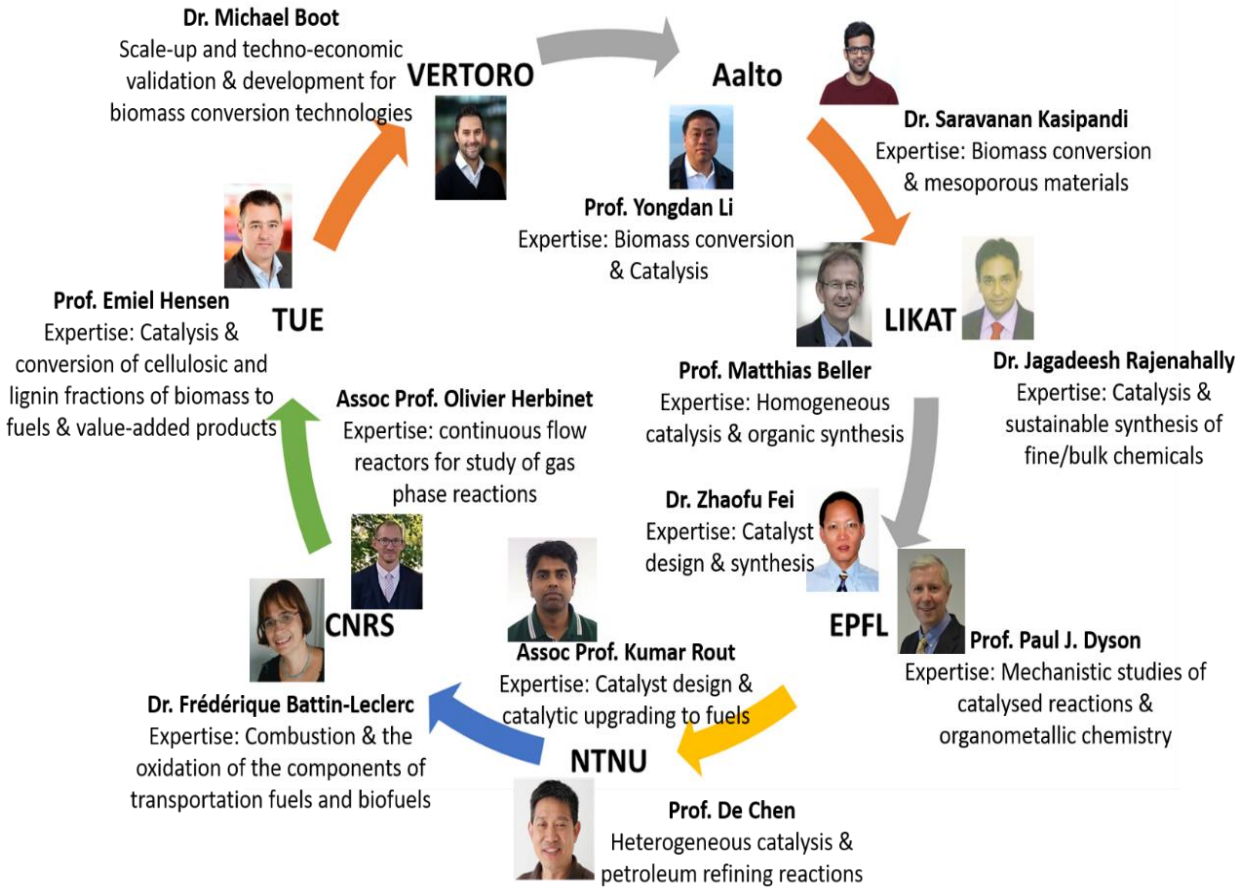
Reaction pathways of lignin depolymerization



- Ni sites hydrogenated active intermediates into stable monomers, suppressing the repolymerization reaction
- Acidic and basic sites promote the demethylation reactions and alkylation of monomers, and also promote repolymerization

Conclusions

- Esters come from the esterification of acid units in EHL
- para-alkyl phenols come from the conversion of primary units in EHL, instead of alkylation reaction.
- The cleavage of ether linkages can be achieved without a catalyst.
- Ni sites stabilize active intermediates, suppressing repolymerization reaction.
- Acidic and basic sites promote the second-conversion of monomers, and also promote repolymerization reaction



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

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

Thank you for your attention