Hydrodeoxygenation of lignin derived phenolic monomers and model bio-oils towards (alkyl)cyclohexane hydrocarbon fuels

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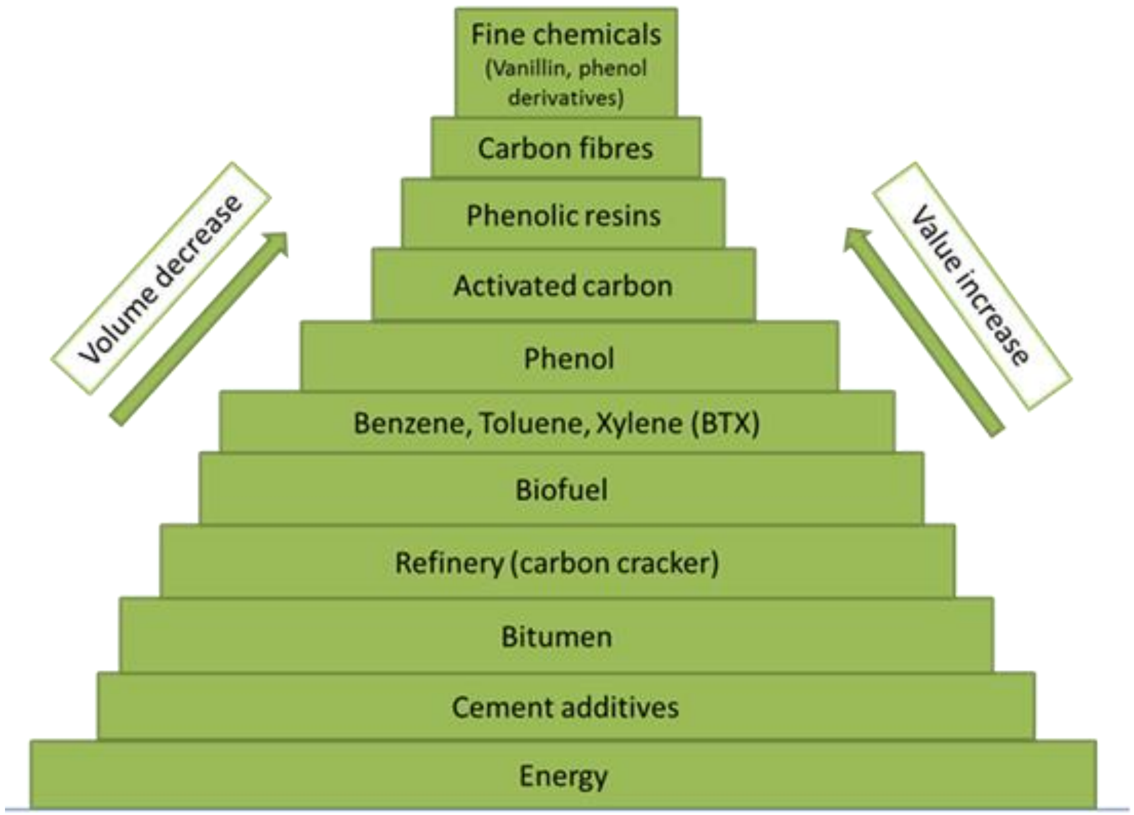
CA17128 LignoCOST Lignin Conference

May 31 – June 3, 2022

WICC, Wageningen, The Netherlands

Lignin applications (value vs. volume) & fast pyrolysis contribution



Gosselink R.J.A. 2011

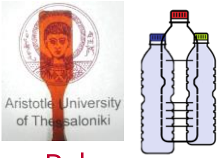
Lignin Fast Pyrolysis oils (bio-oils):

An abundant source of alkoxy/alkyl-phenols, BTX aromatics and naphthalenes

Platform chemicals

Applications:

- Platform chemicals
- Phenolic resins and plastics
- Bio-crude for co-processing to biofuels
- Drop-in hydrocarbon fuels

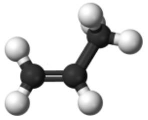


Polymers

Fuels/additives

Lignin derived bio-char

Light olefins in non-condensable gases



WAGENINGEN
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100years 1918 — 2018

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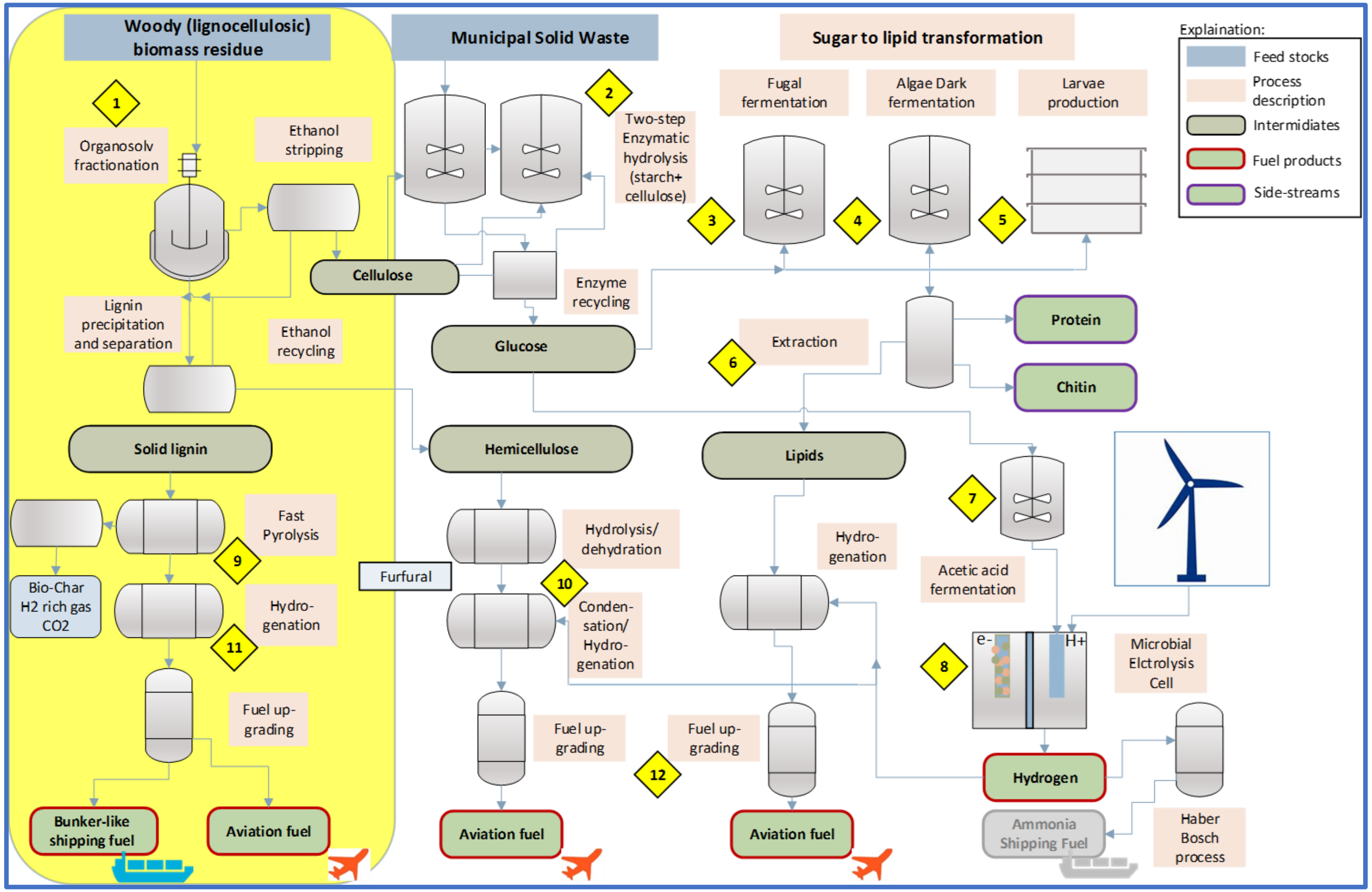
Flexible and resilient integrated biofuel processes for competitive production of green renewable jet and shipping fuels (FLEXI-GREEN FUELS)

WP5: Thermochemical and catalytic upgrading of hemicellulose, lignin and microbial lipids to jet/bunker fuels



- **Organosolv Lignins:**
  - ✓ hardwood (beech, birch)
  - ✓ softwood (spruce)
  - ✓ Wheat straw
- **Fast pyrolysis bio-oils**
- **Alkyl-cycloalkanes via HDO**

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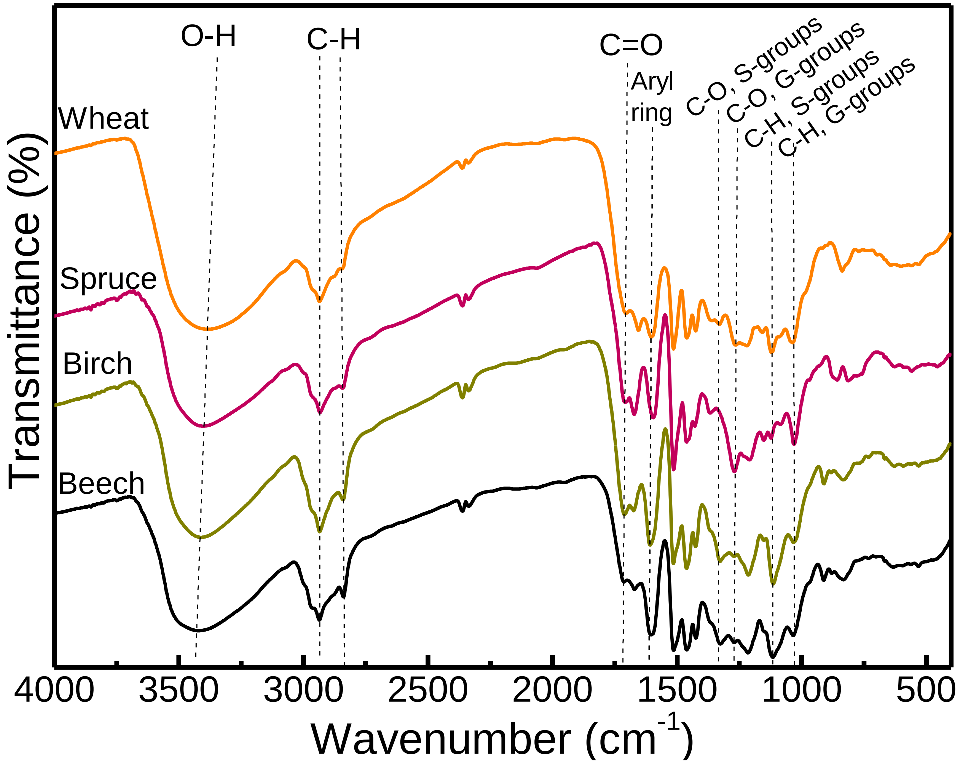
FLEXI-GREEN FUELS

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101007130

Characterization of Organosolv lignins (TGA, FTIR, Elemental analysis)



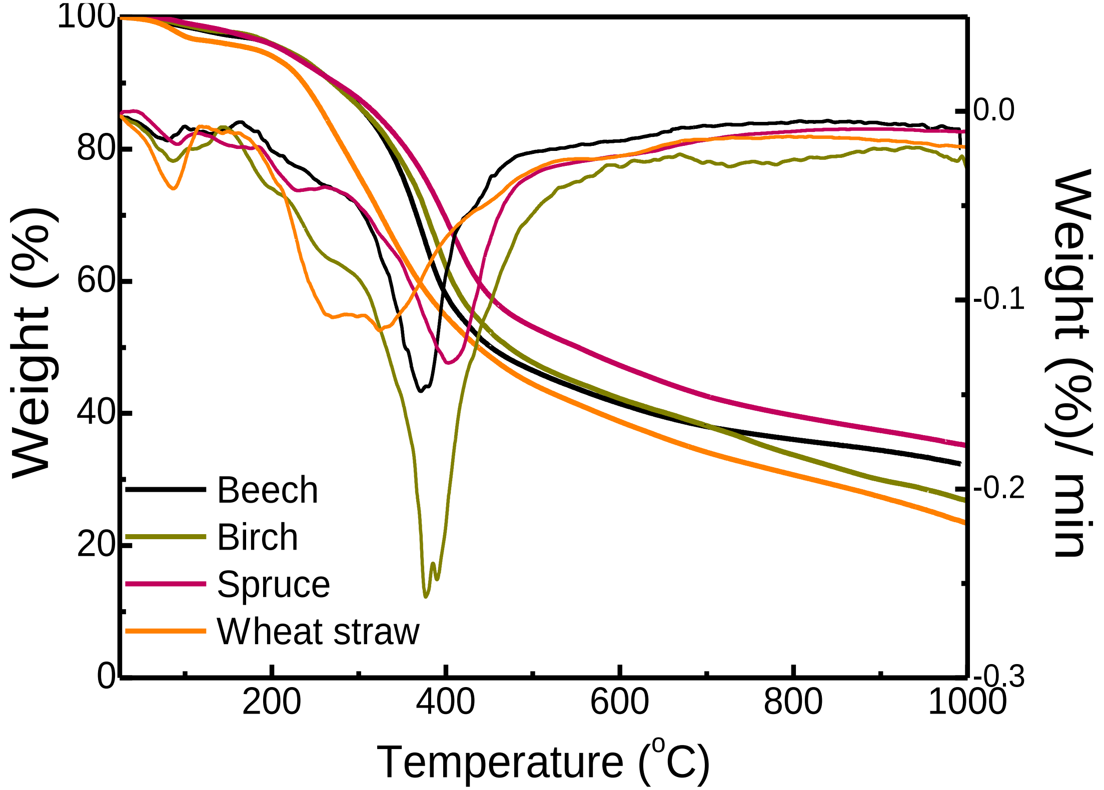
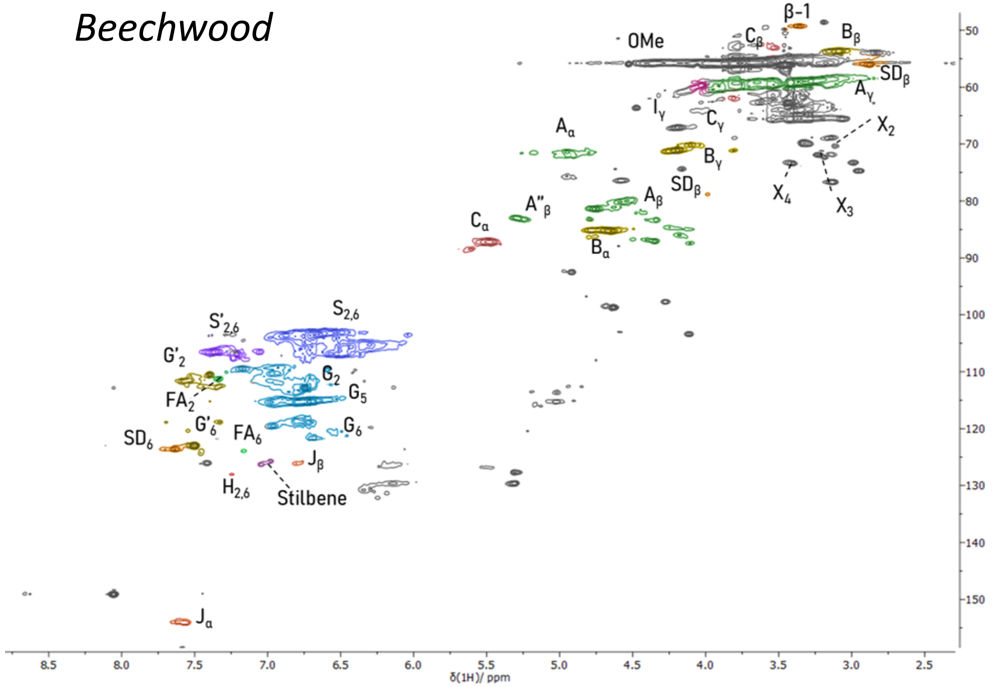
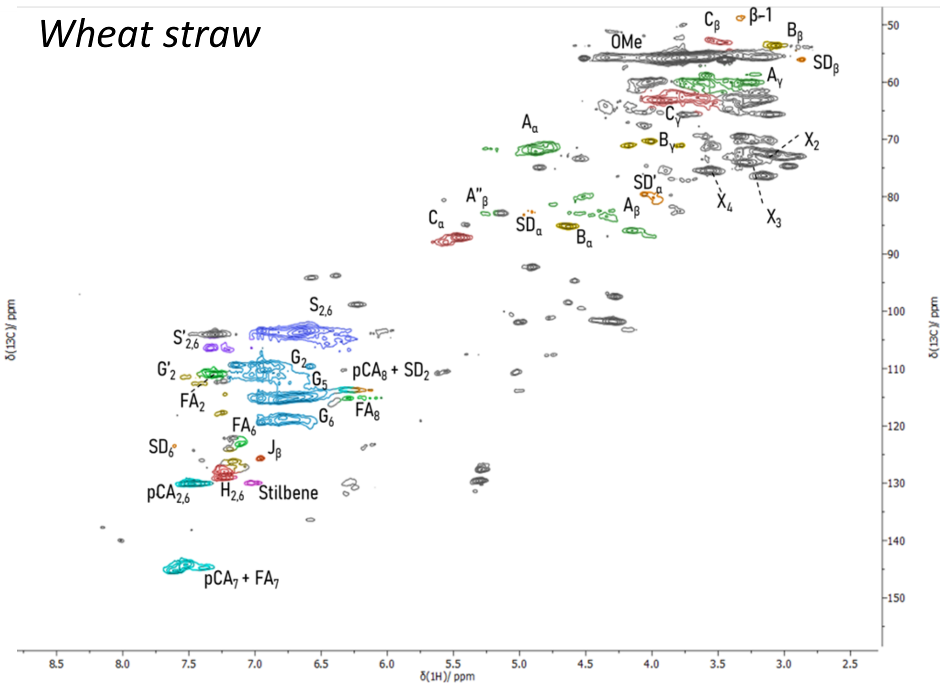


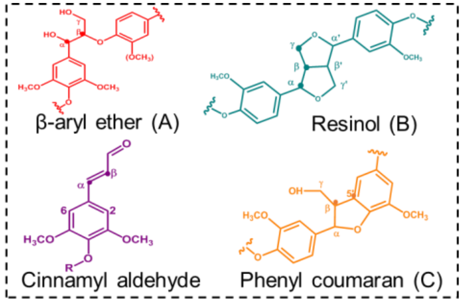
Table 2. Elemental analysis of organosolv lignins

Lignin Sample	C (wt.%)	H (wt.%)	S (wt.%)	N (wt.%)	O (wt.%)
Beechwood	67.09	6.09	0.00	0.01	26.81
Birch	68.10	6.09	0.00	0.00	25.80
Spruce	70.39	5.90	0.00	0.00	23.71
Wheat	59.93	5.99	0.00	1.68	32.39

Characterization of Organosolv lignins (2D HSQC NMR)







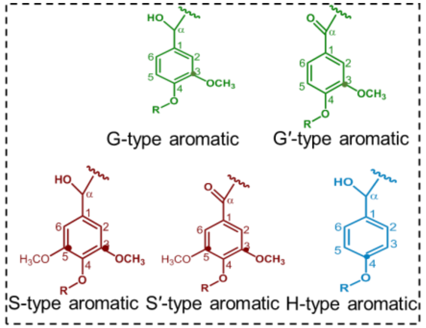
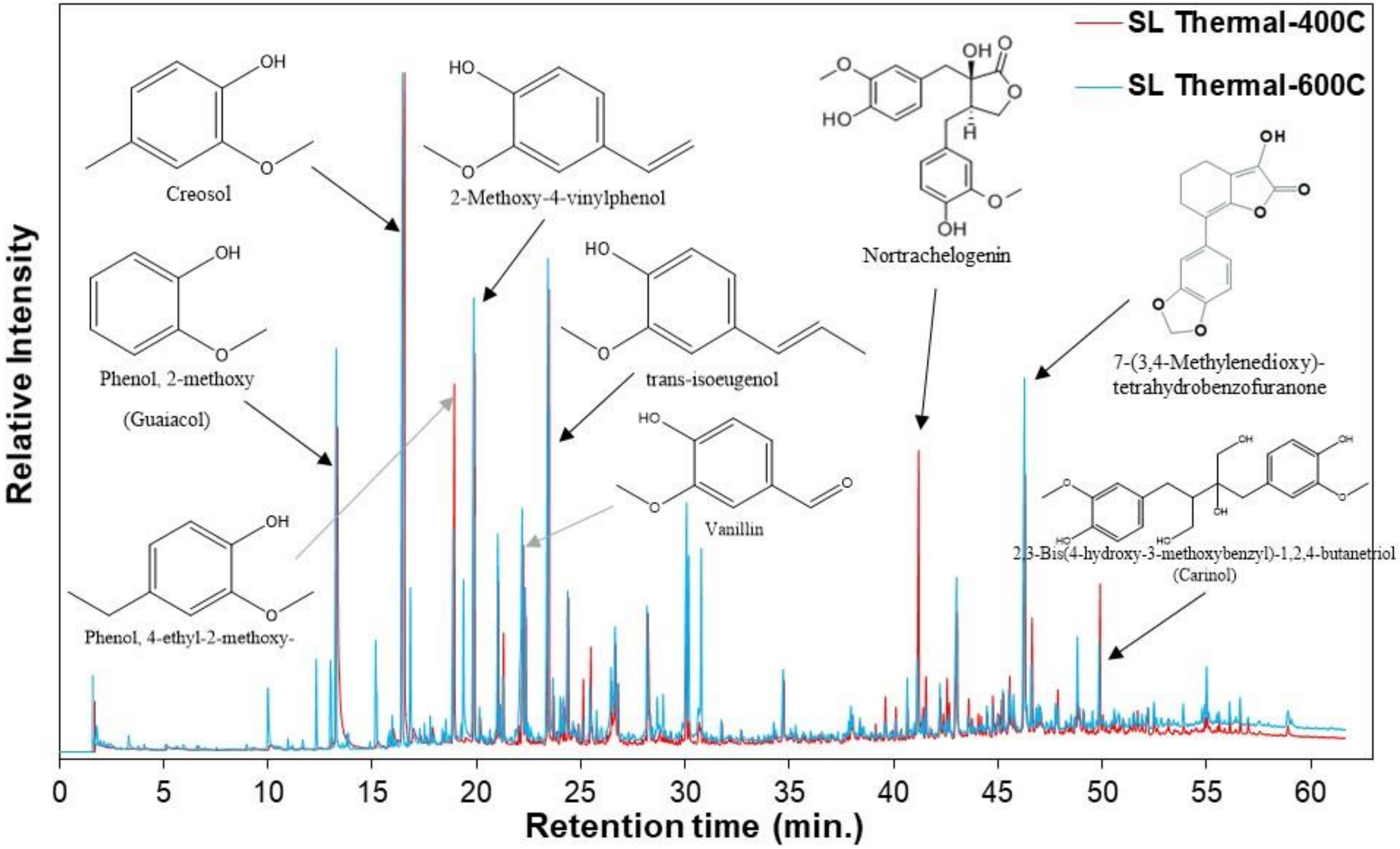


Table 1. Percentages of aromatic units (S, G, H) and inter-unit linkages (β-O-4, β-β, β-5) of the different organosolv lignin samples

Lignin Sample	Aromatic units			Inter unit linkages/100 Ar		
	S	G	H	β-O-4	β-β	β-5
Beechwood	54.2	45.3	0.5	9.5	14.8	9.9
Birch	60.5	39.0	0.5	0.0	7.5	0.0
Spruce	0.0	99.1	0.9	0.0	2.7	0.7
Wheat	38.7	54.4	6.9	24.5	5.9	15.3

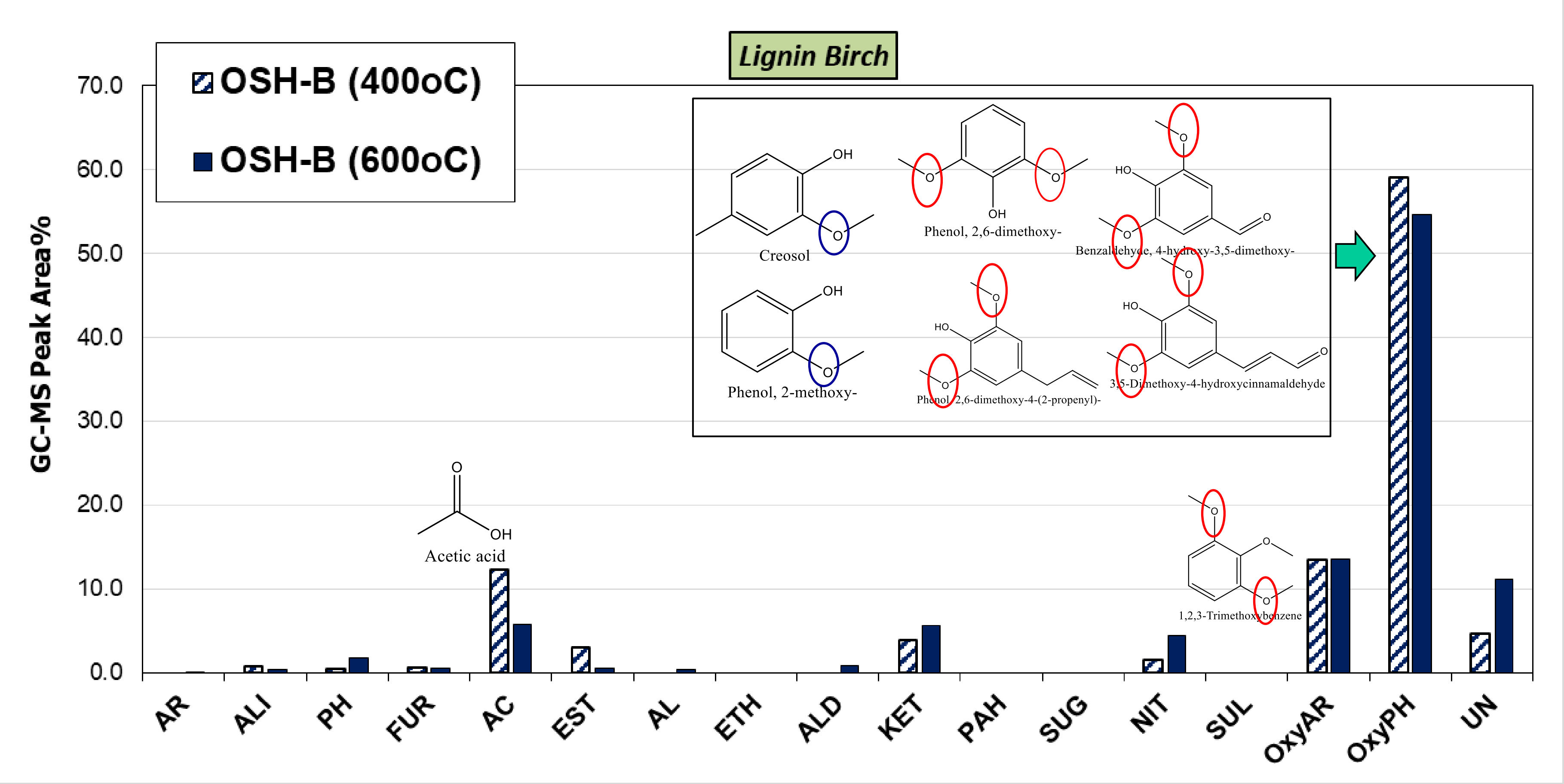
Thermal (non-catalytic) Fast Pyrolysis of Organosolv Lignin (Spruce) (Py/GC-MS, 600ºC)



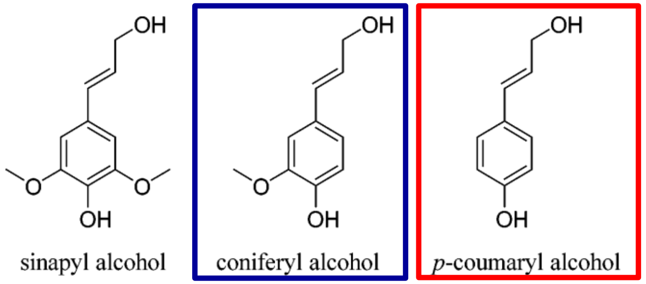
- **Lignin composition profile (S/G) is "transferred" to bio-oils**
- **Lignin derived bio-oil: Homogeneous mixture of alkoxy/alkyl-phenolics**

- Utilization in phenol-formaldehyde resins replacing petroleum phenol
- Homogeneous substrate for catalytic upgrading

Non-catalytic Fast Pyrolysis of Organosolv Lignin (birch)



	Lignin (wt.%)	Phenylpropane unit (%)		
		Coumaryl	Coniferyl	Sinapyl
Softwood	27-33	0.5-3.4	90-95	Very low
Hardwood	18-25	trace	25-50	50-75

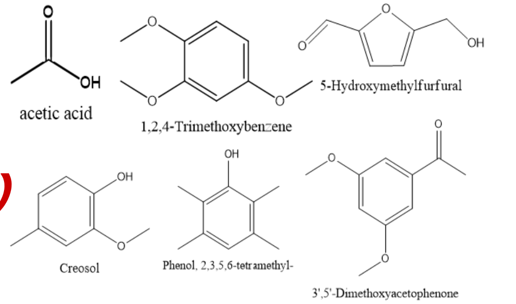


In situ upgrading of bio-oil via Catalytic Fast Pyrolysis (CFP)

Lignocellulosic biomass/lignin

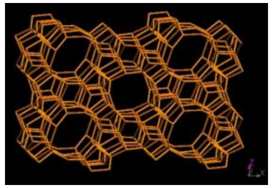
Initial degradation reactions:
thermal / non-catalytic

Depolymerization, Hydrolysis, Dehydration, Decarbonylation, Decarboxylation, C-O cleavage



Smaller oligomers and monomers
(non-catalytic biomass pyrolysis vapours)

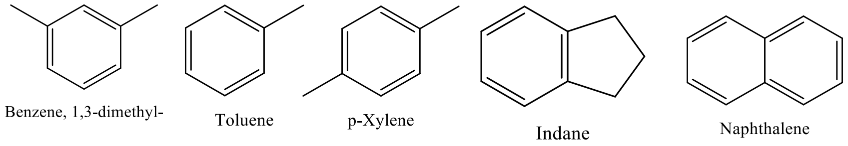
Catalytic Effect:
Porosity
morphology
active sites



MFI (ZSM-5)
5.1x5.5 & 5.3x5.6 Å

dehydration, decarbonylation, decarboxylation, ketonization, esterification, cracking, aromatization, condensation, coke formation

De-oxygenated, aromatic bio-oil



Gaseous products: **CO, CO_2, H_2, light hydrocarbons**
Solid products: **Char and reaction-coke on catalyst**

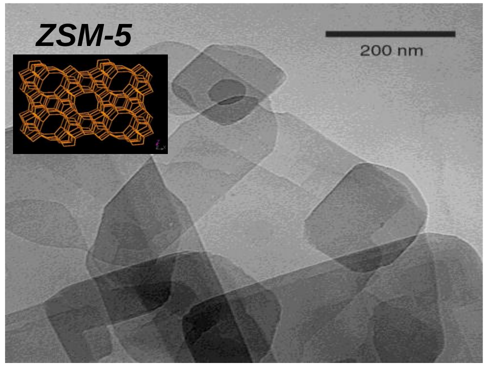
E.F. Iliopoulou, S.D. Stefanidis, K.G. Kalogiannis, A. Delimitis, A.A. Lappas, K.S. Triantafyllidis, Appl. Catal. B: Environ. 127 (2012) 281–290.
E.F. Iliopoulou, S. Stefanidis, K. Kalogiannis, A.C. Psarras, A. Delimitis, K.S. Triantafyllidis, A.A. Lappas, Green Chem. 16 (2014) 662–674.
S. Stefanidis, S. Karakoulia, K. Kalogiannis, E.Iliopoulou, A. Delimitis, H. Yiannoulakis, T. Zampetakis, A.Lappas, K. Triantafyllidis, Appli.Catal.B: Environ. 196 (2016) 155–173

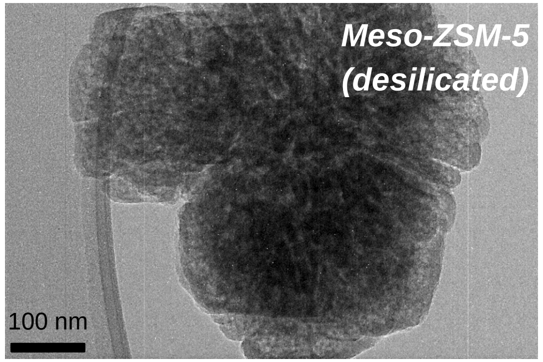
Characterization of ZSM-5 zeolite catalysts

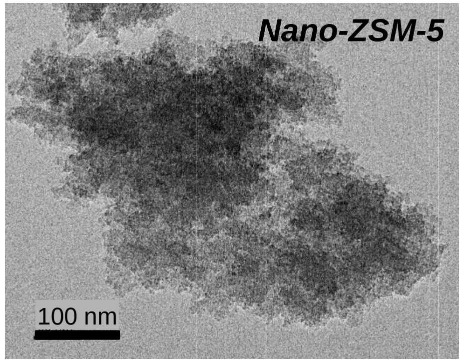
Catalyst	Total SSA [a] (m^2/g)	Micropore area [b] (m^2/g)	Meso/macropore and external area[c] (ml/g)	Average mesopore diameter [e] (nm)	Chemical composition (wt.%)		Acidity FT-IR/pyridine (μmol Pyr/g)		
					Al	Na	Brønsted	Lewis	B/L
ZSM-5 (40)	437	332	105	-	0.91	0.03	190	26	7.3
ZSM-5 (11.5)	424	349	75	-	3.20	0.06	430	123	3.5
Meso-ZSM-5 (9nm)	560	259	301	~ 9 & 90	0.82	0.05	192	21	9.1
Meso-ZSM-5 (45nm)	556	289	267	~ 45	3.00	0.09	385	76	5.0
Nano-ZSM-5	524	343	181[d]	macropores	0.86	0.08	100	53	1.9

[a] Multi-point BET method; [b] t-plot method; [c] Difference of total SSA minus micropore area; [d] Attributed mainly to macropores and external surface area; [e] BJH analysis using adsorption data.

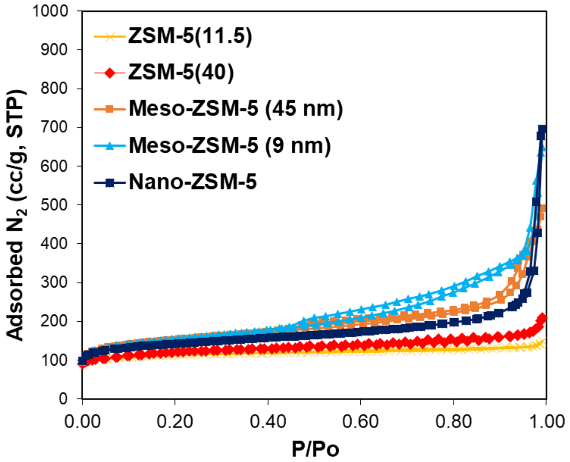
TEM images

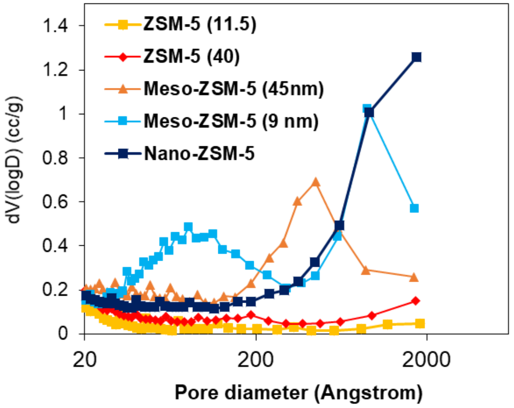




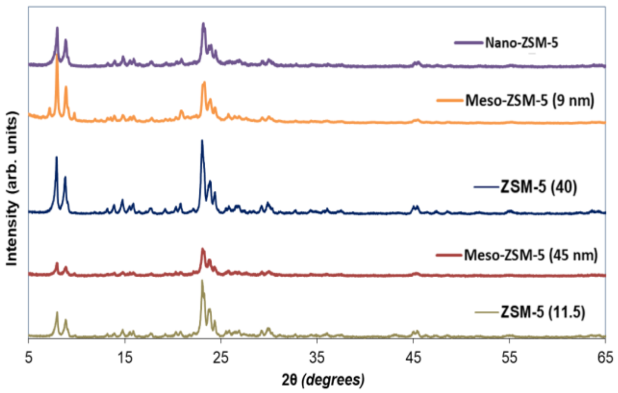


N_2 isotherms & BJH pore size distribution

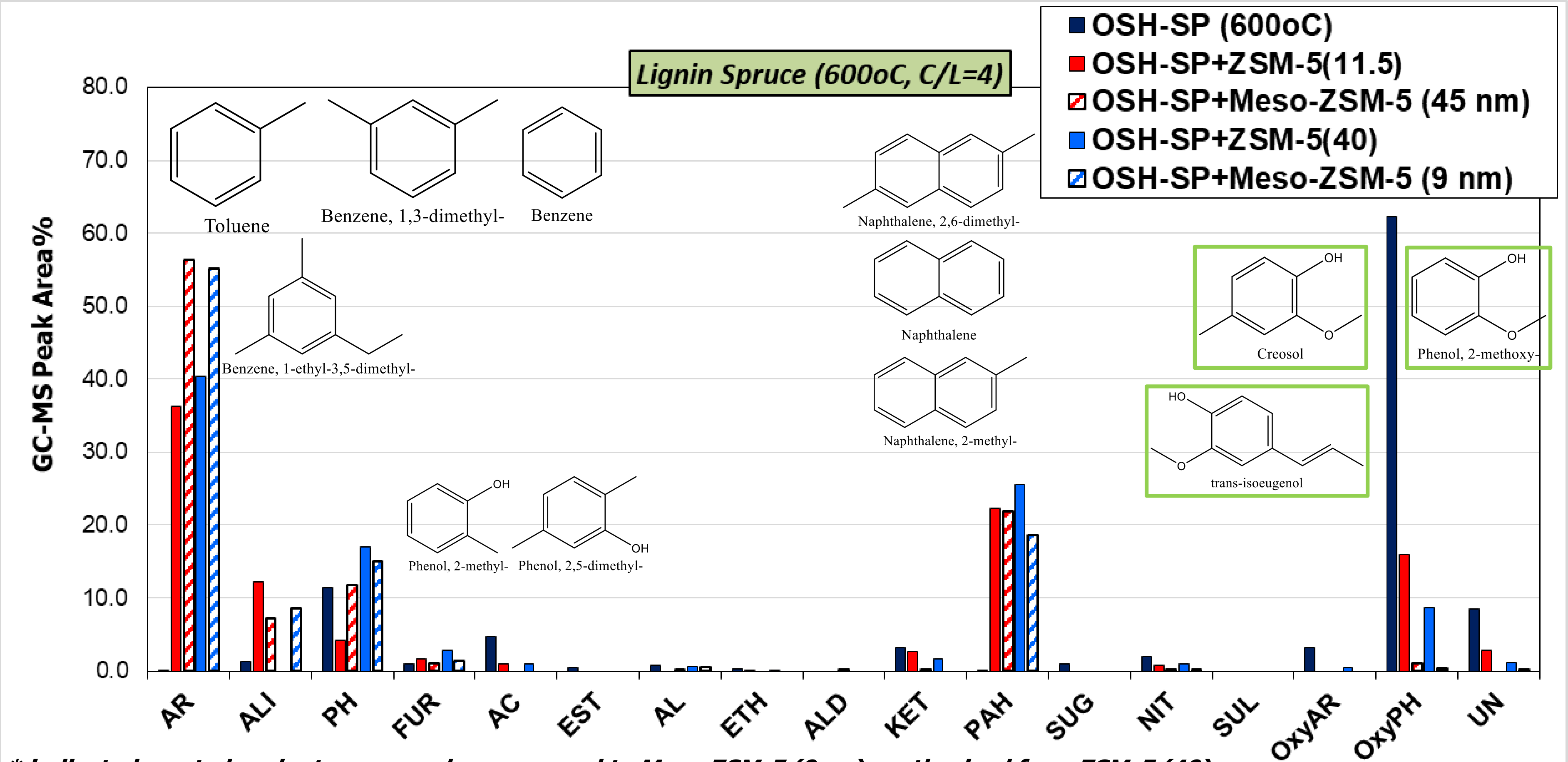




XRD patterns



CFP of Organosolv lignin (Spruce) with conventional and mesoporous ZSM-5 zeolite



** indicated most abundant compounds correspond to Meso-ZSM-5 (9nm) synthesized from ZSM-5 (40)*

- Increased conversion of alkoxy-phenols with ZSM-5 of higher Si/Al ratio (40 vs. 15)
- Enhanced reactivity activity of meso-ZSM-5
- Higher selectivity to BTX aromatics with meso-ZSM-5
- The higher BTX selectivity with meso-ZSM-5 does not induce higher PAHs (naphtalenes)

I. Charisteidis, P. Lazaridis, A. Fotopoulos, E. Pachatouridou, L. Matsakas, U. Rova, P. Christakopoulos, K. Triantafyllidis, Catalysts 2019, 9, 935

P. Lazaridis et al., Frontiers in Chemistry, 6:295. 2018. doi: 10.3389/fchem.2018.00295

A.G. Margellou, P.A. Lazaridis, I.D. Charisteidis, C.K. Nitsos, C.P. Pappa, A.P. Fotopoulos, S. Van den Bosch, B.F. Sels, K.S. Triantafyllidis, Applied Catalysis A, General 623 (2021) 118298

Hydrodeoxygenation (HDO) of lignin derived phenolics and bio-oils with Ni-based catalysts towards jet fuels

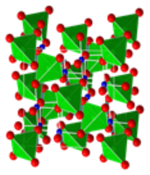
Catalyst selection: synthesis and characterization

- Bifunctional catalysts, transition (e.g. Ni, Co) or noble (e.g. Ru, Pd) metals supported on zeolites or other micro/mesoporous porous acidic materials

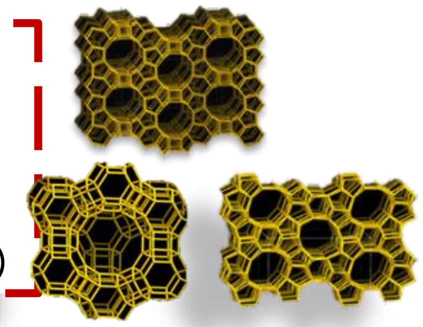
vs.

- *S*ulfided NiMo/CoMo hydrotreatment catalysts (which will be tested *by HULTEBERG*)

Oxides
- $NiAl_2O_4$ spinel
- WO_3/ZrO_2



Zeolites
- ZSM-5 (Si/Al=11.5, 40)
- Meso-ZSM-5
- Beta (12.5, 37.5, 150)
- Mordenite (10), USY (6), Ferrierite (10)



Increase of acidity

Preparation of supported metal catalysts
- Dry/Incipient wetness impregnation
- Use of metal oxalates or nitrate salts
- Calcination, in/ex-situ reduction

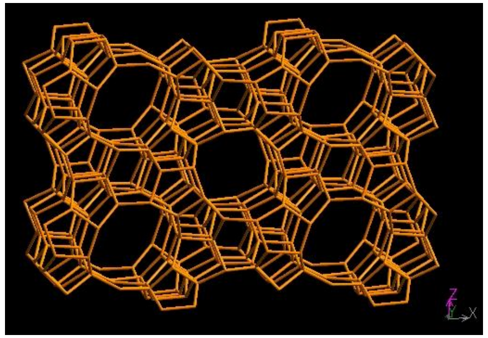
Catalyst characterization

XRD, FTIR, N_2 sorption, TGA, SEM, TEM, TPR, XPS, acidity measurements, etc.

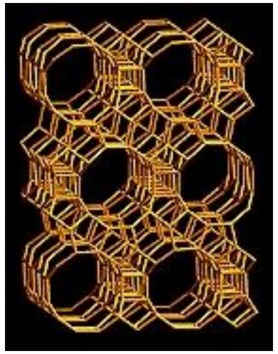
Physicochemical characteristics of supports

Catalyst (Si/Al)	Total SSA (m^2/g)	Micropore area (m^2/g)	Meso/macro pore/external area (m^2/g)	Average mesopore diameter (nm)	Chemical composition (wt.%)		Acidity FT-IR/pyridine (μmol Pyr/g)		
					Al	Na	Brønsted	Lewis	B/L
H-Beta (12.5)	596	376	220	~60 (broad)	2.73	0.01	176	229	0.8
H-Beta (37.5)	670	351	318	35	0.89	~0	135	65	2.1
H-ZSM-5 (11.5)	424	349	75	-	3.20	0.06	430	123	3.5
H-ZSM-5 (40)	437	332	105	-	0.91	0.03	190	26	7.3
Meso-ZSM-5 (40)	560	259	301	~9 & 90	0.82	0.05	192	21	9.1
15%WO_3-ZrO_2	99	-	99	7.3	-	-	13	60	0.2

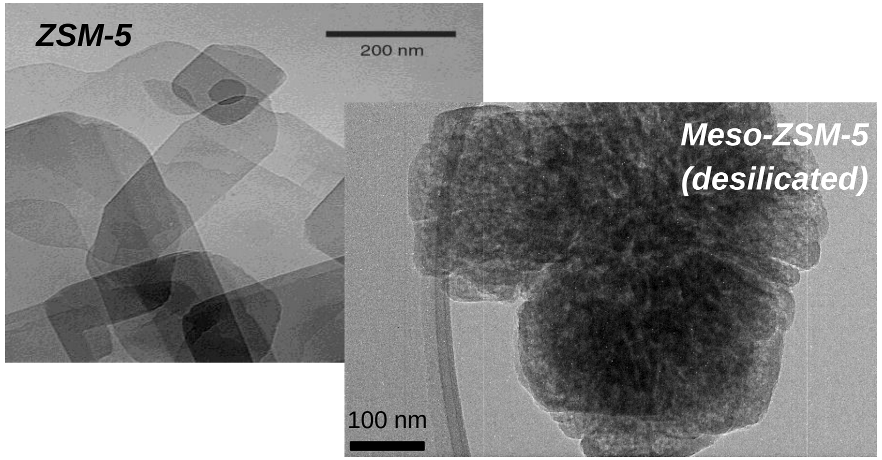
- **Conventional microporous zeolites**
- **Microporous ZSM-5 with intra-crystal mesopores**
- **Low acidity mesoporous WO_3-ZrO_2**



MFI (ZSM-5)
5.1x5.5 & 5.3x5.6 Å, 10-ring, 3-D

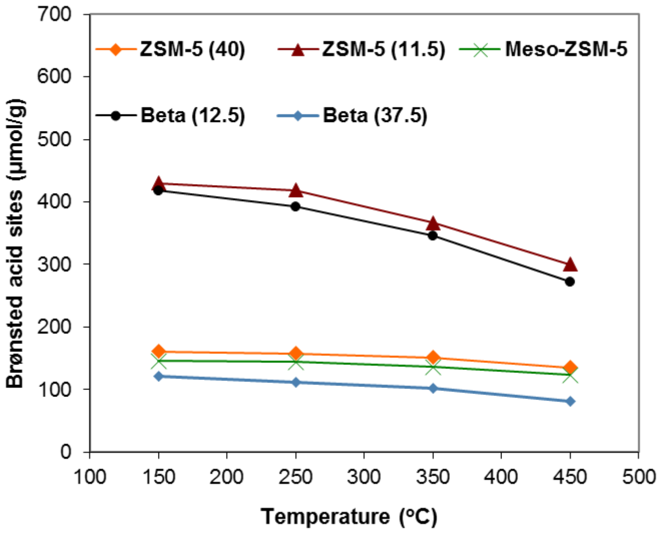


BEA (Beta)
6.6x6.7 & 5.6x5.6Å, 12-ring, 3-D



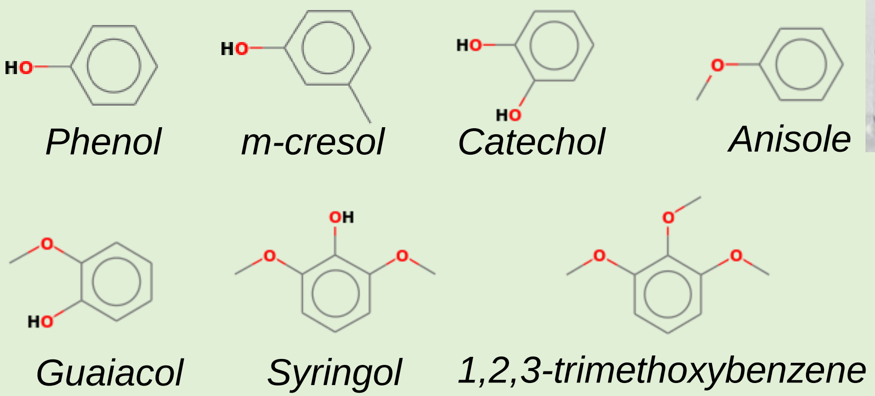
TEM images of ZSM-5

FTIR/pyridine adsorption



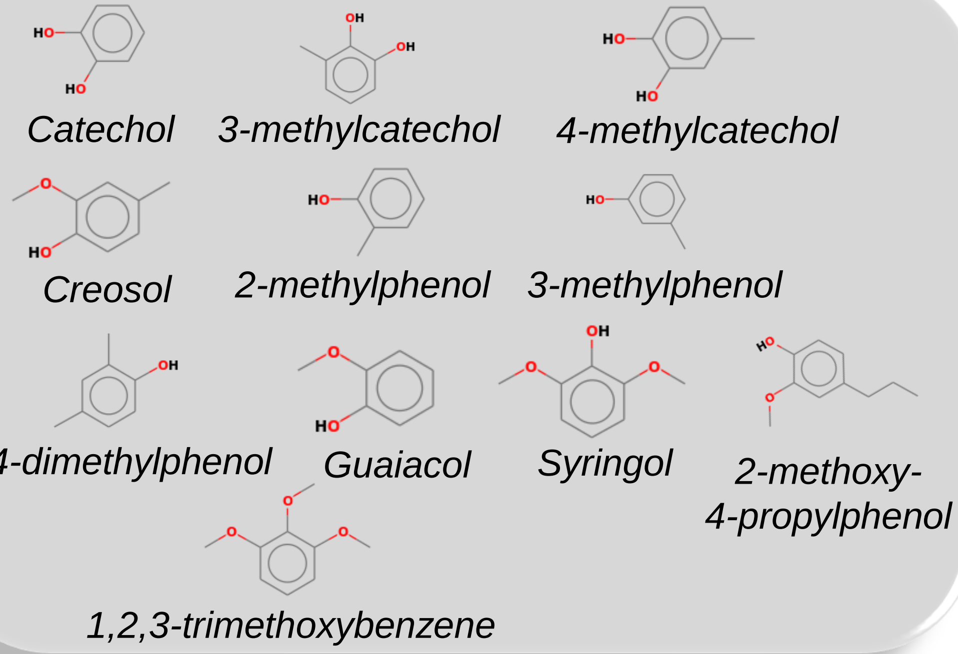
Reactants and feeds in HDO experiments

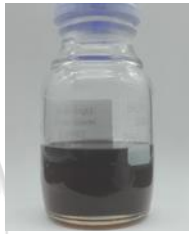
Model Compounds



Model compounds Mixtures

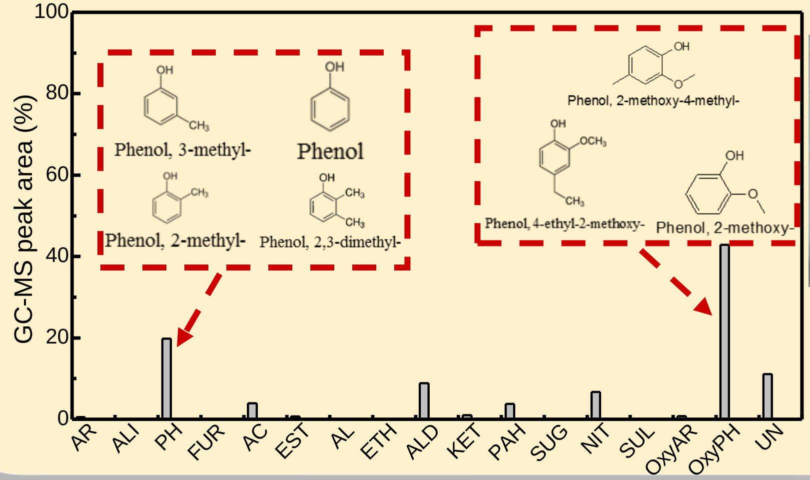
based on pyrolysis bio-oils composition

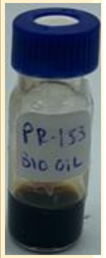




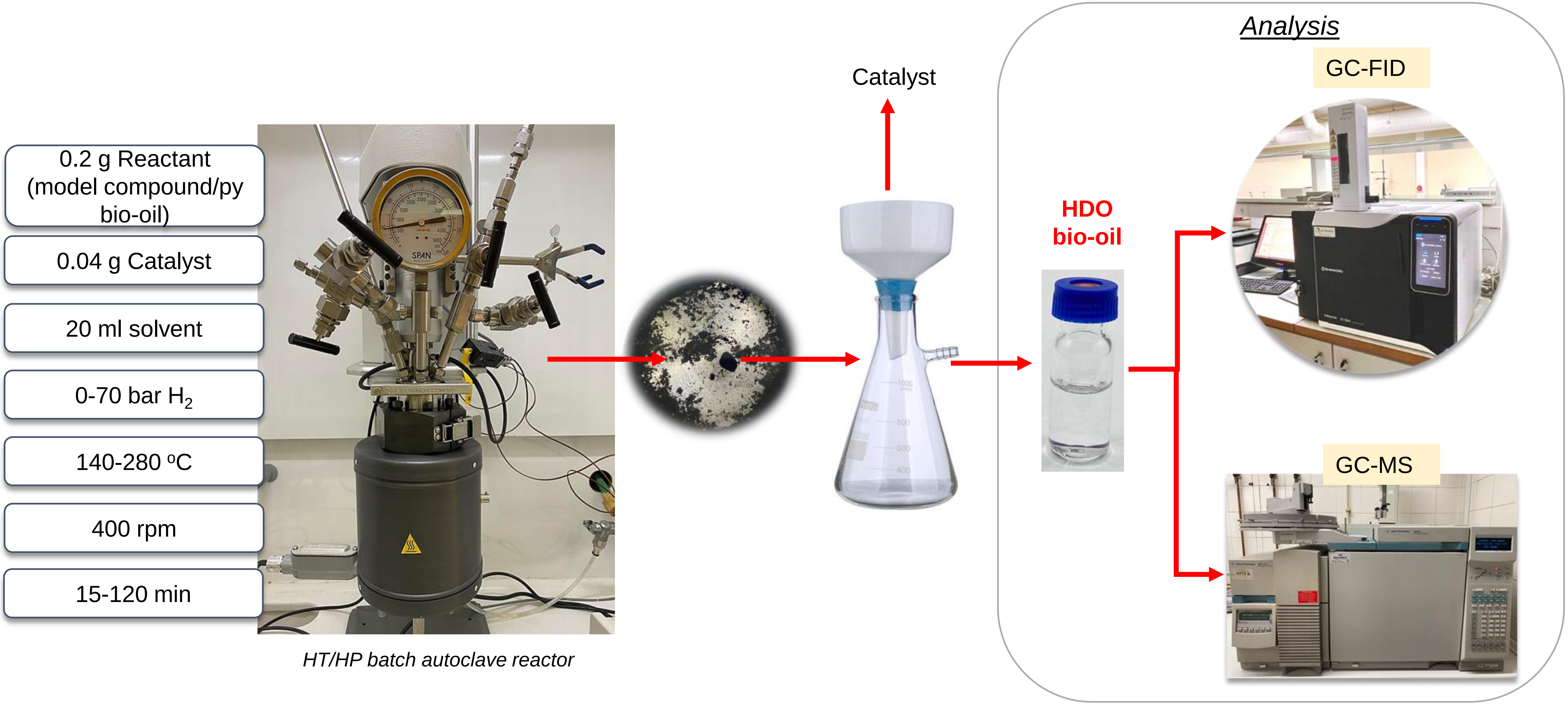
Actual bio-oil

From Beechwood organosolv lignin





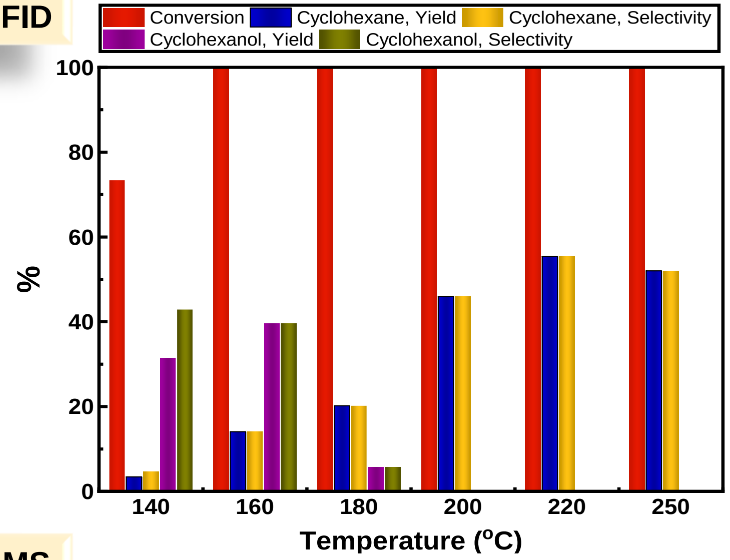
HDO experimental procedure



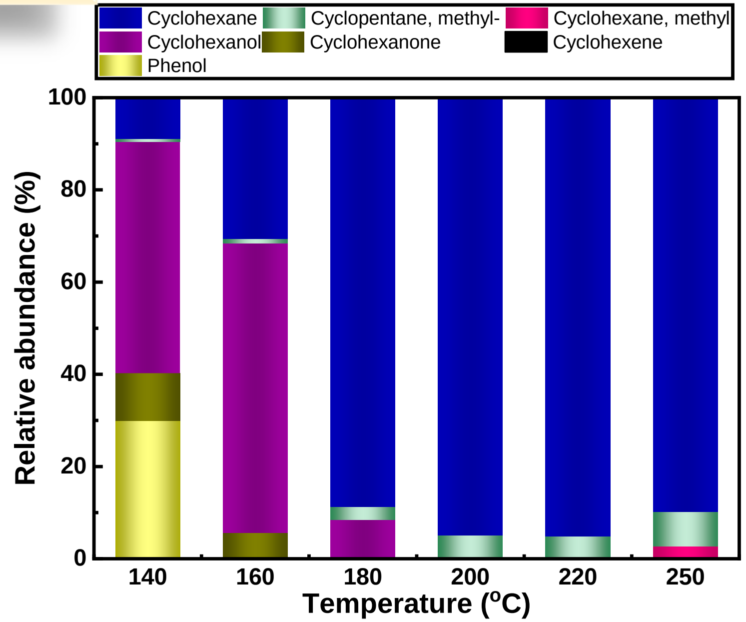
HDO of Phenol – Effect of temperature

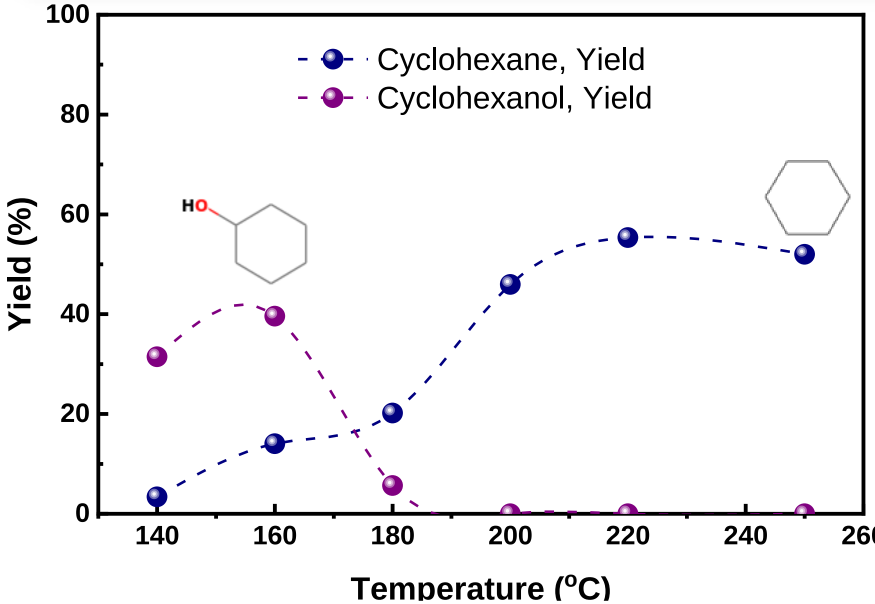
Phenol, Hexadecane, 10% Ni/ZSM-5 (40), 1 h, 50 bar H_2, C/P=0.2

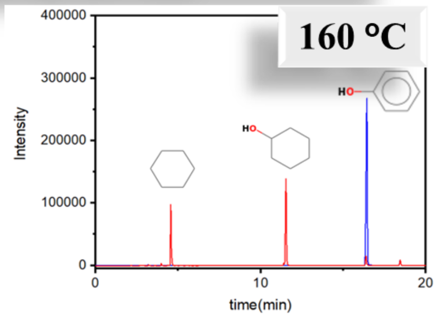
GC-FID

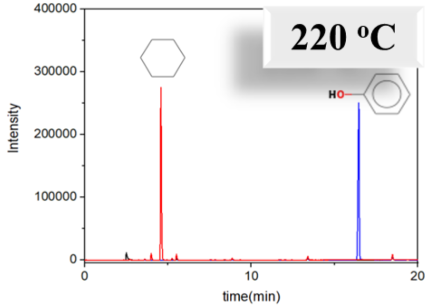


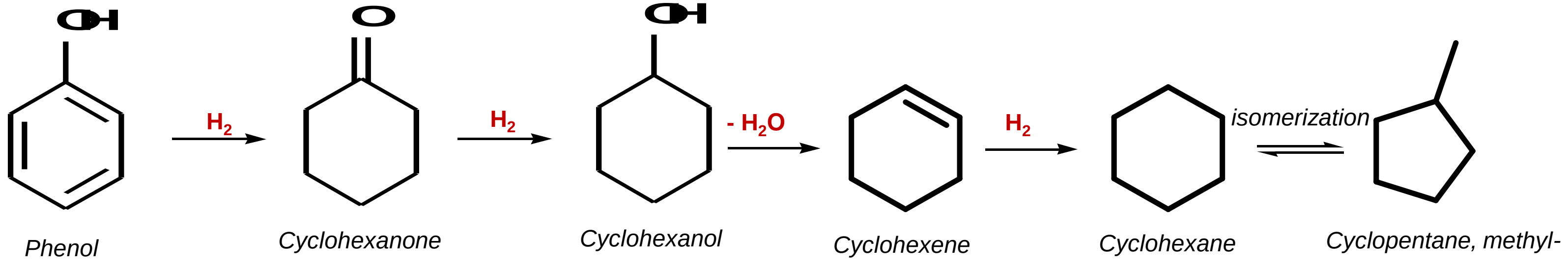
GC-MS





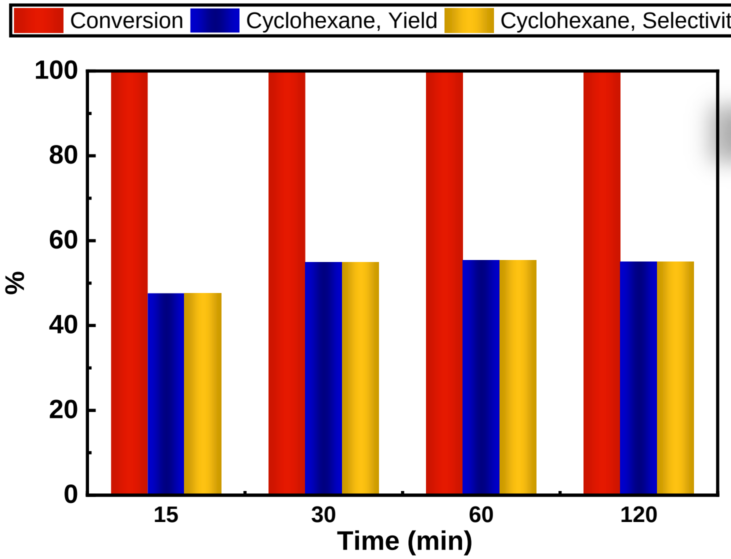






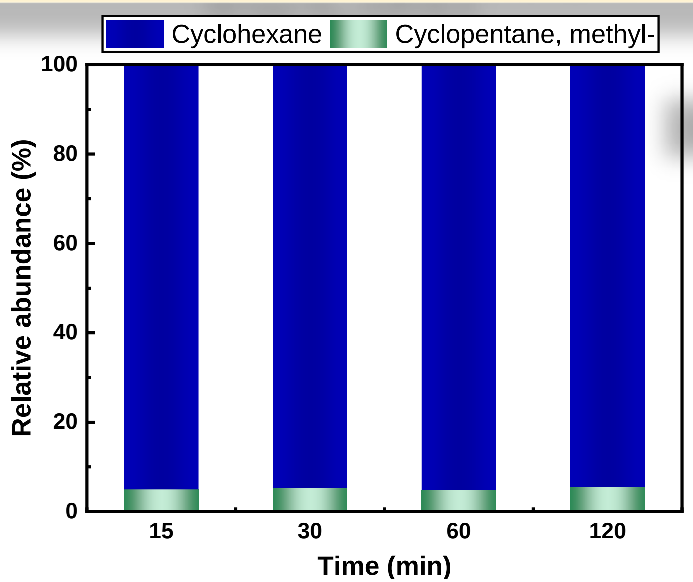
HDO of Phenol – Effect of time and H_2 pressure

GC-FID

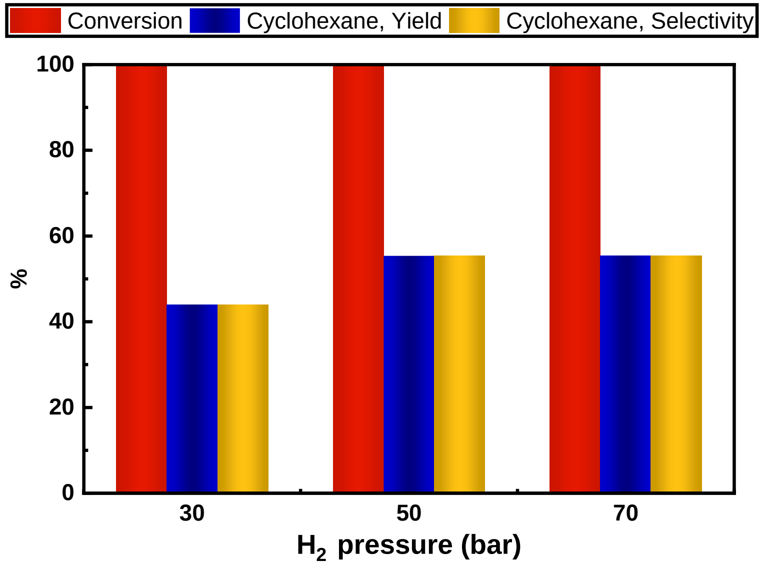


Phenol, Hexadecane, 10% Ni/ZSM-5 (40), 220 ^oC, 50 bar H_2, C/P=0.2

GC-MS

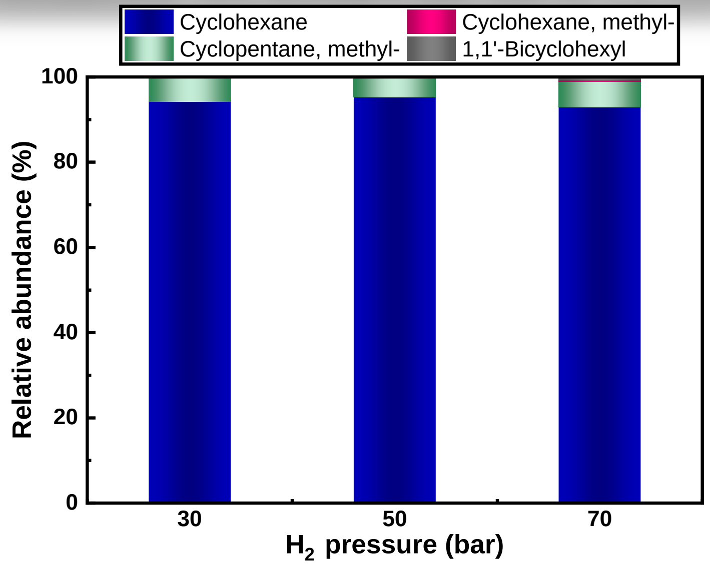


GC-FID



Phenol, Hexadecane, 10% Ni/ZSM-5 (40), 220 ^oC, 1 h, C/P=0.2

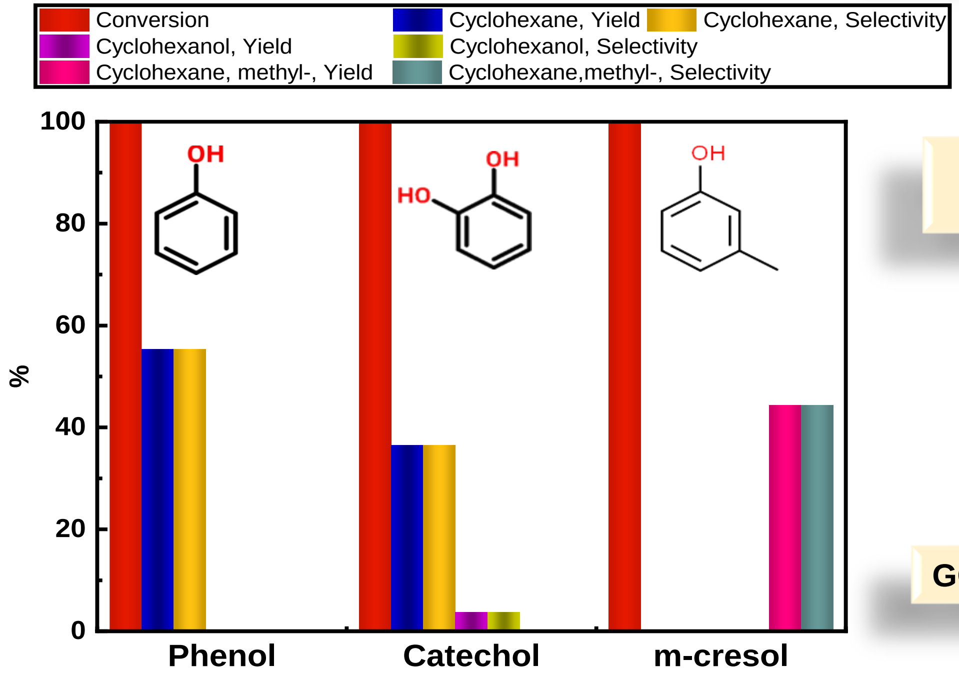
GC-MS



HDO – Effect of model compound structure

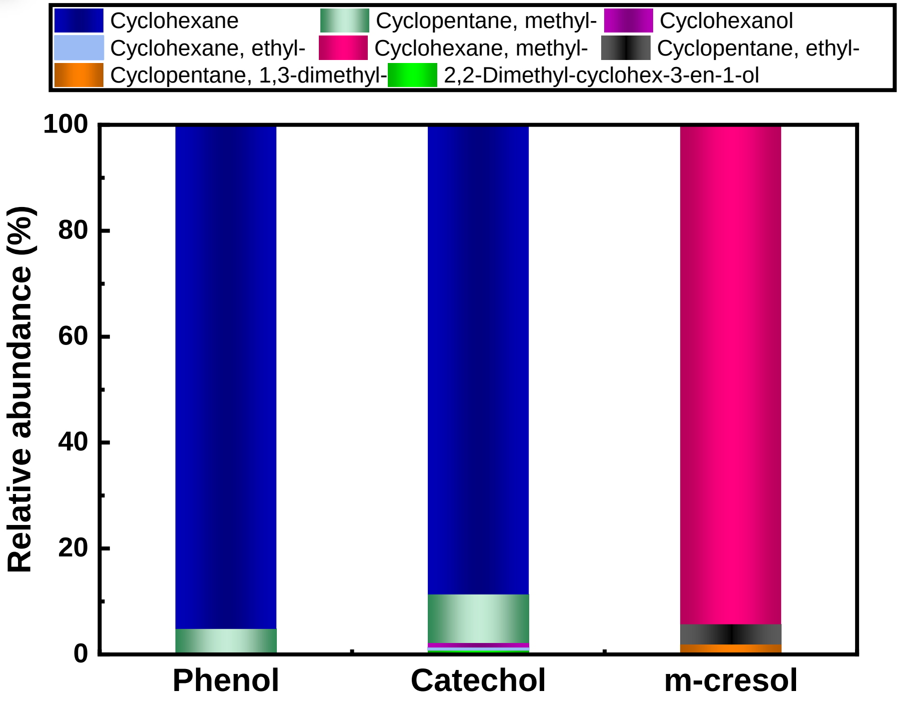
Effect of –OH and CH_3– group

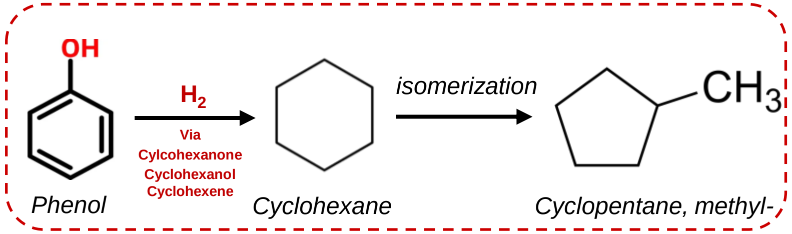
Hexadecane, 10% Ni/ZSM-5 (40), 220 °C, 1 h, 50 bar H_2, C/P=0.2

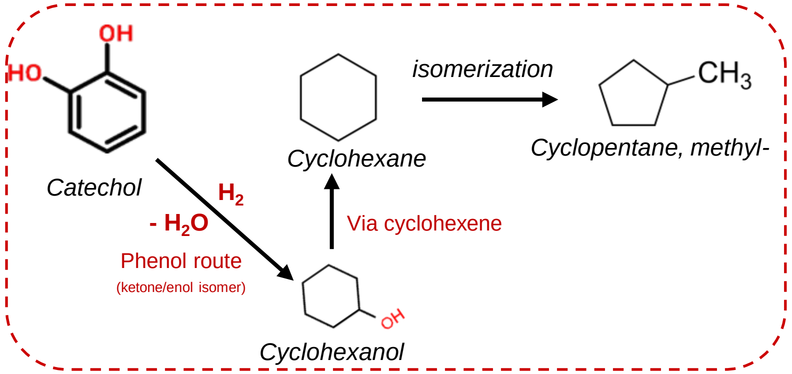


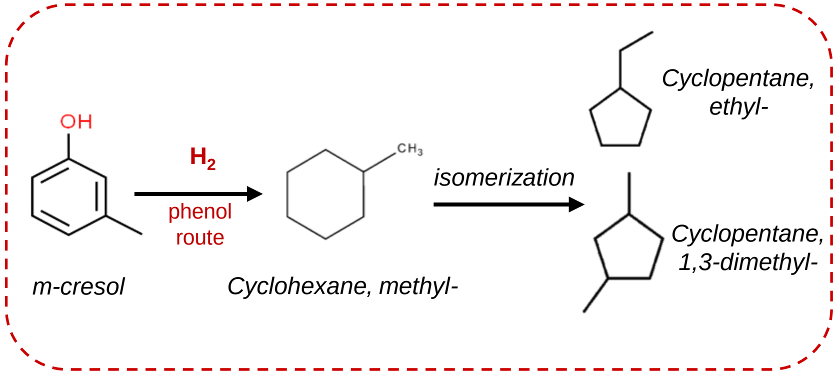
GC-FID

GC-MS





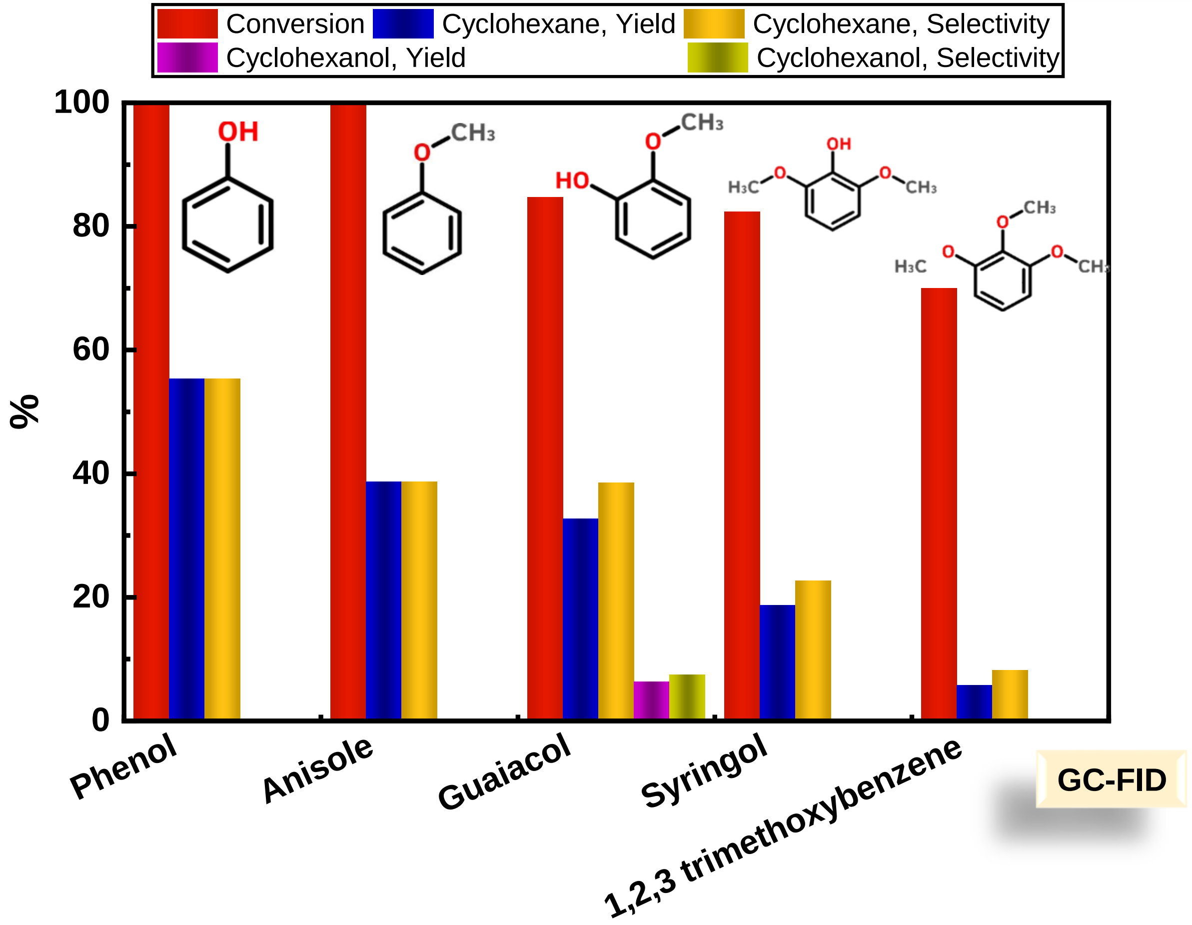


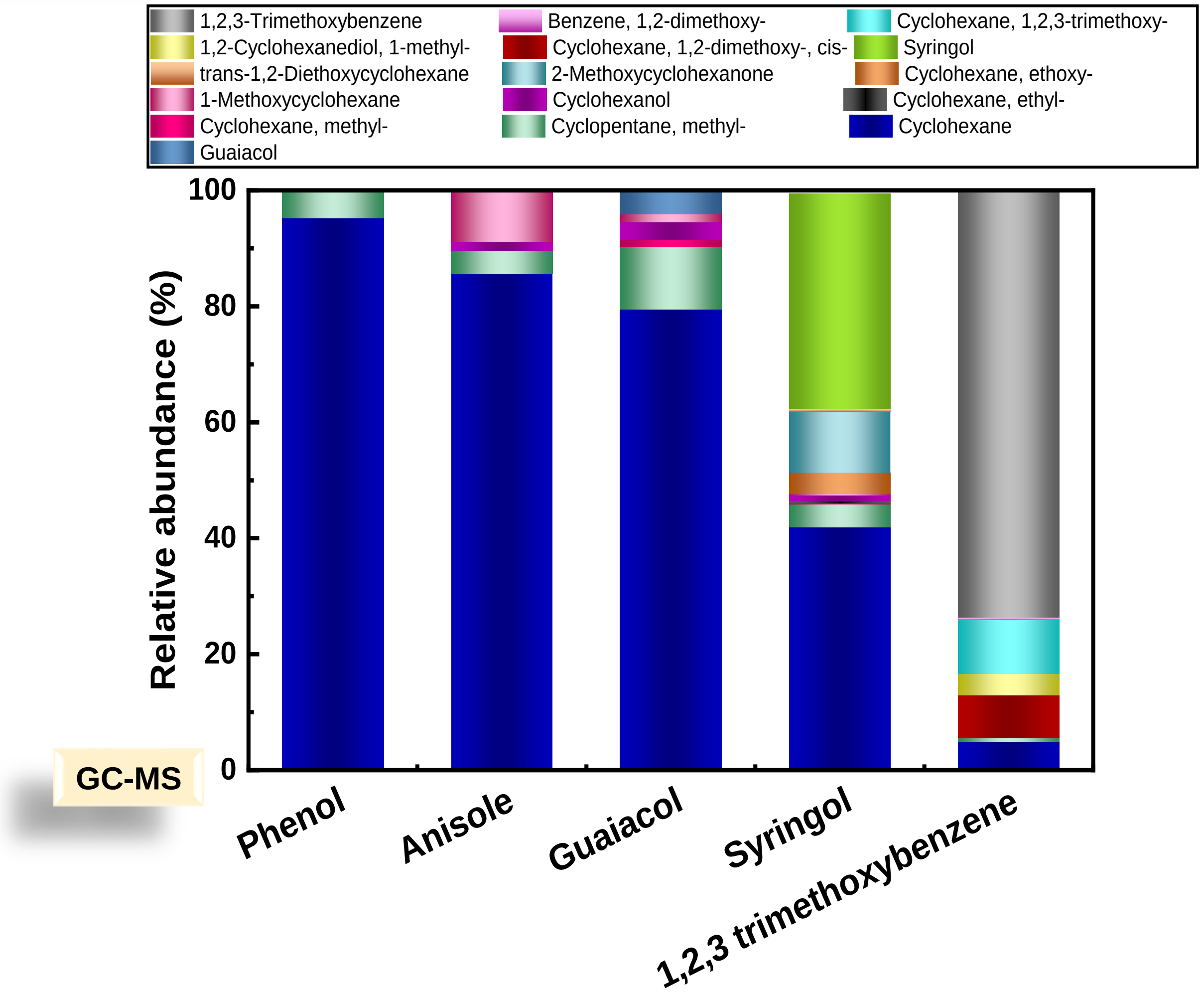


HDO-Effect of model compound structure

Effect of –OCH_3 groups

Hexadecane, 10% Ni/ZSM-5 (40), 220 °C, 1 h, 50 bar H_2, C/P=0.2

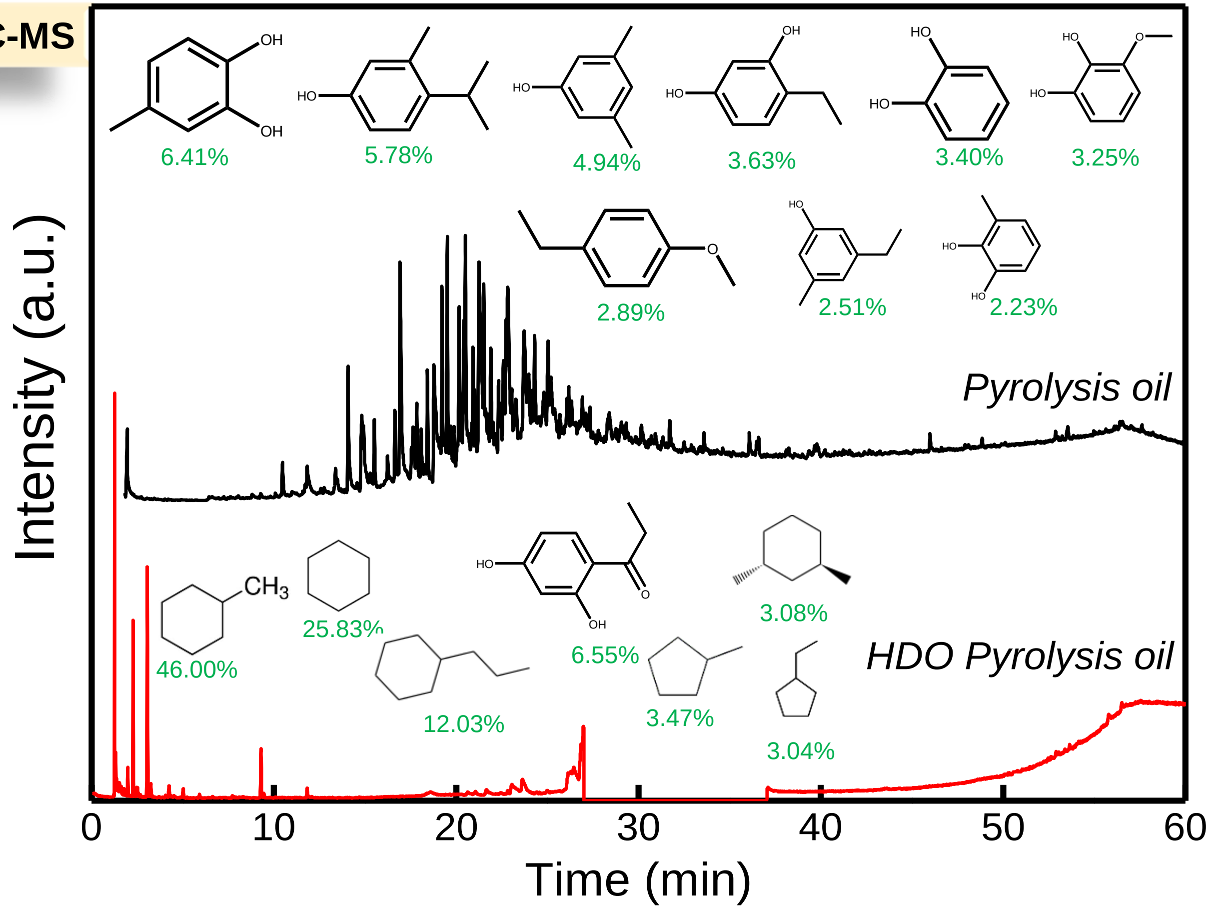




HDO of lignin pyrolysis bio-oil

Thermal (600°C) pyrolysis bio-oil of beechwood Organosolv lignin

GC-MS



Reaction conditions:

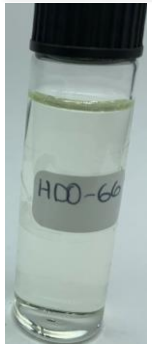
- 220 °C
- 50 bar H_2
- 1 hour
- 400 rpm

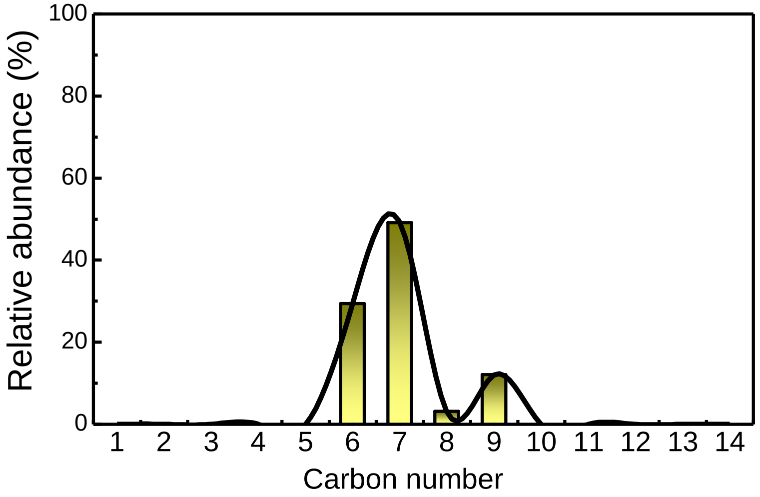
10%Ni/Beta(12.5)

Oxygenated products: 6.55%
Deoxygenated products: 93.45%

Before HDO

After HDO

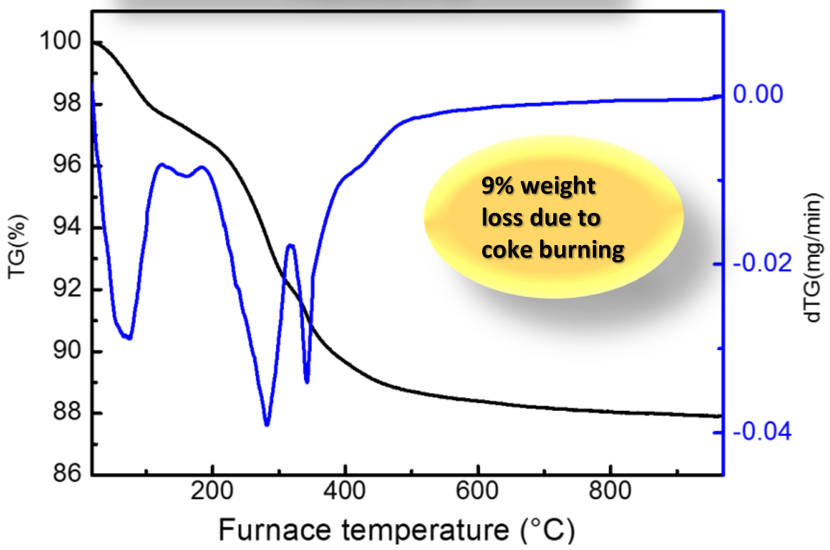




Characterization and reusability of catalyst

10%Ni/ZSM-5 (40)

TGA/DTG



Elemental analysis:
Coke: < 2 wt.% on feed

Porosity

	S_{BET} (m^2/g)	S_{mic} (m^2/g)	V_{tot} (cm^3/g)	V_{mic} (cm^3/g)
Fresh	370	240	0.325	0.106
Used after 1 run	356	230	0.322	0.104

Acid sites

	FT-IR/pyridine (μmol Pyr/g)		
	Bronsted	Lewis	B/L
Fresh	99	246	0.4
Used after 1 run	90	256	0.3

Reusability (HDO phenol)

	Conversion (%)	Cyclohexane, Yield (%)	Cyclohexane, Selectivity (%)
Fresh	100	55.4	55.4
Used after 1 run	100	52.7	52.7

Conclusions & outlook

- **Tuning acidity (amount, strength) and micro/mesoporosity of ZSM-5 and Beta zeolites as Ni supports leads to efficient HDO of alkoxy/alkyl-phenolics at mild conditions (T, P / 220^{o}C, 50 bar)**
- Less acidic supports induce similar reactivity/selectivity but at slightly higher temperatures (ca. 280^{o}C)
- Phenol HDO pathway: cyclohexanone → cyclohexanol → cyclohexene → cyclohexane → methyl-cyclopentane
- Methoxy-groups inhibit reactivity and induce alternative hydrogenation/hydrogenolysis pathways
- Alkyl-groups are not prone to hydrogenolysis thus leading to higher carbon number alkyl-cyclohexanes
- **Light (model) phenolic mixture and real lignin bio-oils lead to C6-C10 alkyl-cyclohexanes/pentanes**
- **Coking/stability/regeneration of zeolite-based catalysts needs to be further evaluated**

Acknowledgements

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Thank you for your attention!
Thessaloniki, April 2015