Catalytic Conversion of Biomass to Biofuels

"Lignin Hydrogenation"

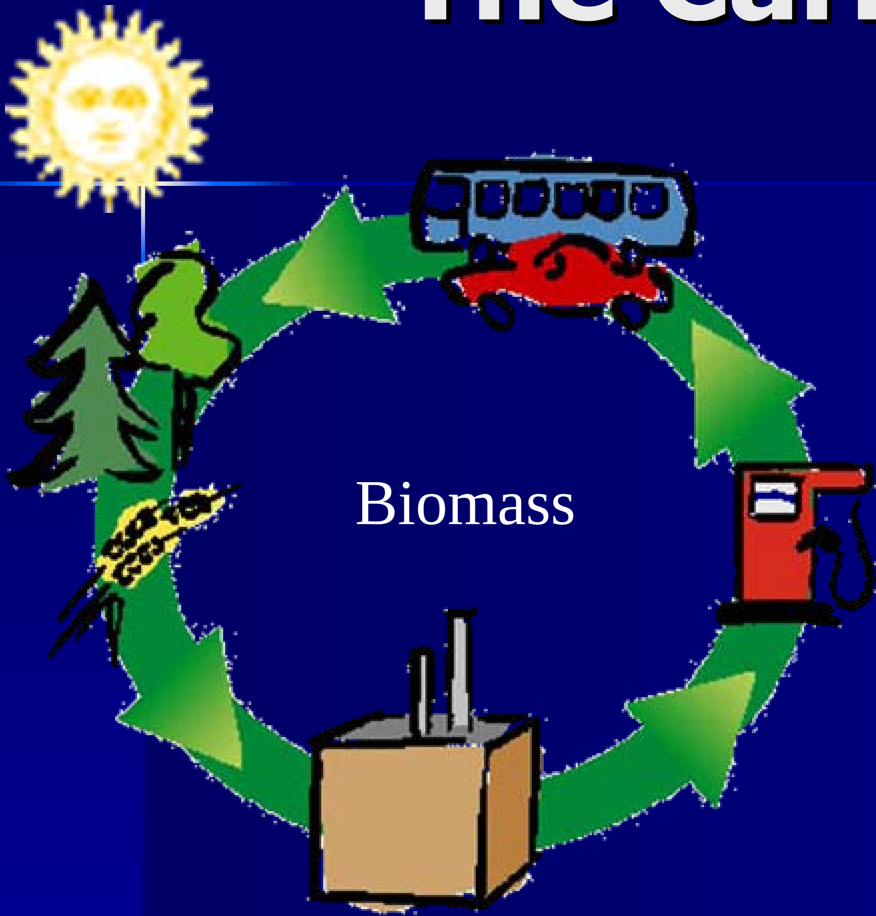
Mate Nagy

Georgia Institute of Technology

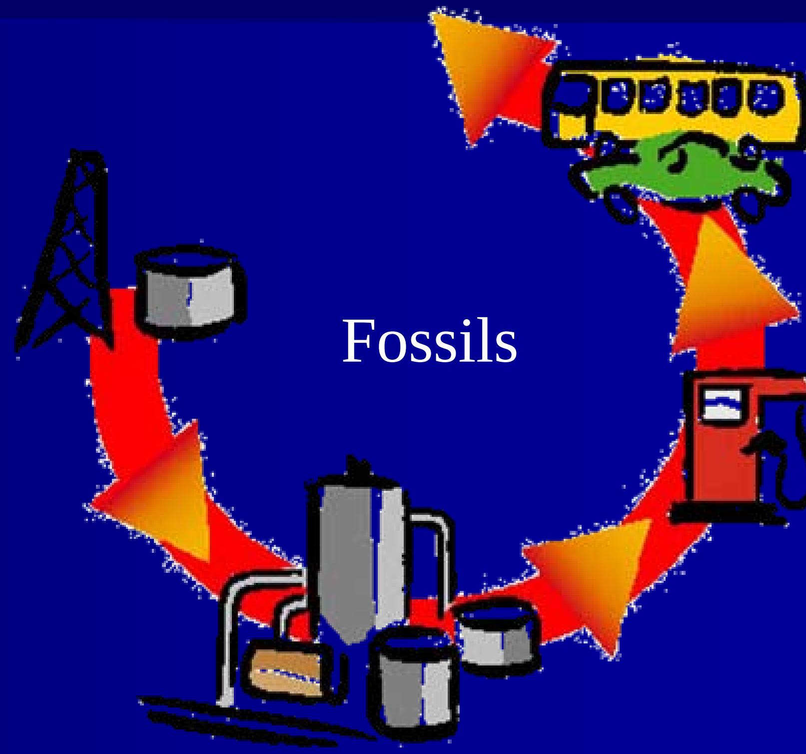
Overview

- Fossil fuels vs. Biofuels
- Available raw materials
- Experimental setup
  - Black liquor
  - Model compounds

The Carbon-cycle



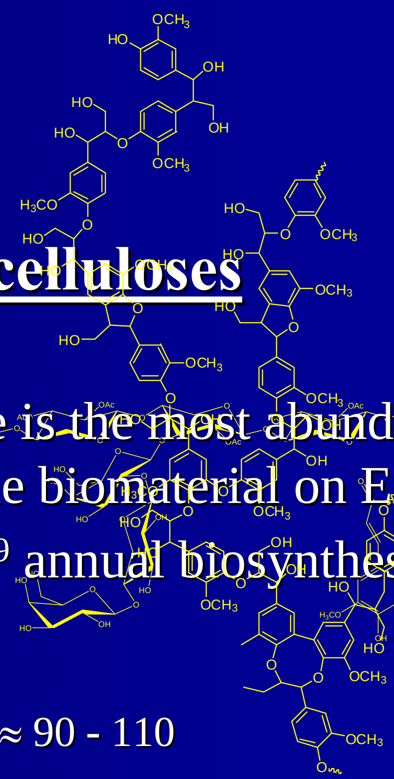
Closed cycle



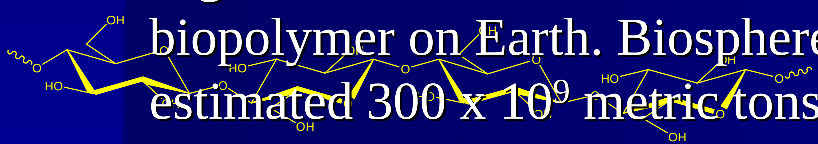
Broken cycle

Available raw materials

- From total annual biomass produced biosynthetically on Earth: 170 x 10^9 tons:
- Carbohydrates: ~70%
- Lignin: ~20%

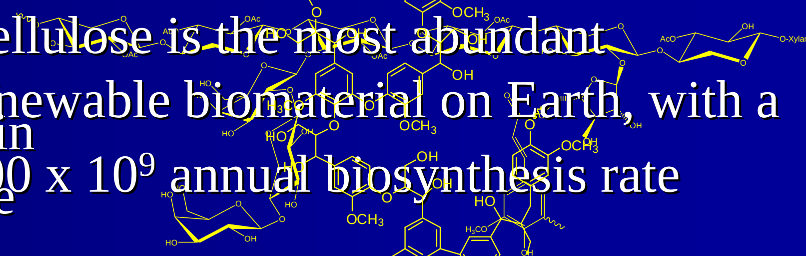


Cellulose



Lignin is the second most abundant biopolymer on Earth. Biosphere has an estimated 300 x 10^9 metric tons of lignin with a 20 x 10^9 annual biosynthesis rate

Hemicelluloses



Cellulose is the most abundant renewable biomaterial on Earth, with a 100 x 10^9 annual biosynthesis rate

DP ≈ 90 - 110

Differences between biomass based raw materials and gasoline or diesel

	Gasoline	Gas oil/diesel	Carbohydrate	Lignin
Carbon chain length	5-10	12-20	$[6-5]_n$	$[9-10]_n$
O/C molar ratio	0	0	1	0.3-0.4
H/C molar ratio	1-2	~2	2	0.7-1.1
Phase behavior (ambient T)	liquid	liquid	solid	liquid-solid
Polarity	a-polar	a-polar	polar	a-polar
Preferred structure	branched/aromatic /cyclic/unsaturated	linear/saturated	linear/cyclic	branched (3D)

Pulp and Paper Industry

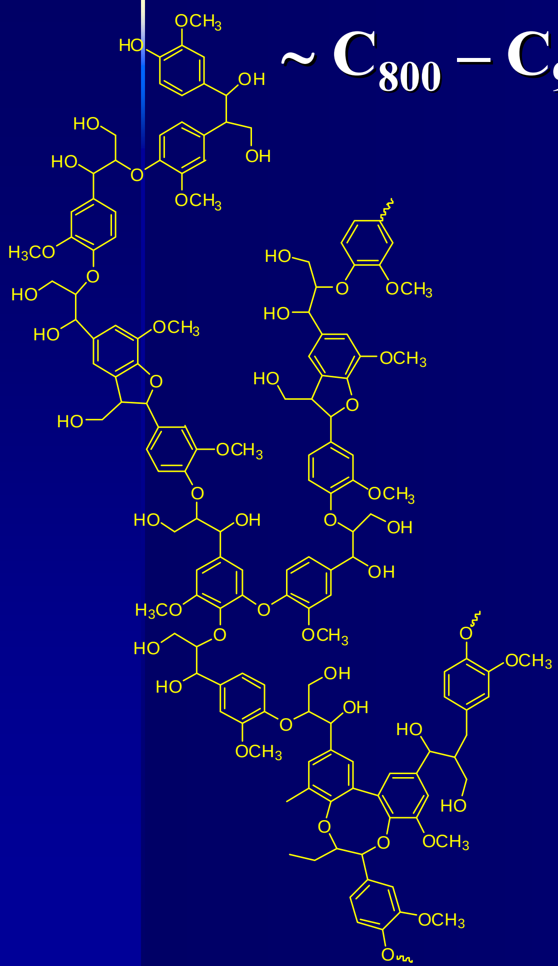
- Most abundant biopolymers are available in the form of lignocellulose matrix “wood”.
- US agriculture and forestry reserves have the potential to address at least 30% of the nation’s current petroleum demand.
- US timberland inventory is 21 10^9 dry tons, with an annual production of 368 10^6 tons and consumption of 142 10^6 tons.
- US Pulp and Paper industry collects and processes 108 10^6 tons anually.

Chemical Pulping "*Kraft*"

Component	Wood Components		Kraft Pulp Components	
	Pine	Birch	Pine	Birch
	As a % of Original Wood			
Cellulose	38 – 40	40 – 41	35	34
Glucomannan	15 - 20	2 - 5	5	1
Xylan	7 - 10	25 – 30	5	16
Other carbohydrates	0 - 5	0 – 4	-	-
Lignin	27 - 29	20 – 22	2 – 5	1.5 – 3
Extraneous compounds	4 - 6	2 - 4	0.25	< 0.5

Catalytic conversion of biomass to biofuels

Biofuel precursor:



~ $C_{800} - C_{900}$

Cracking Biopolymer

$C_9 - C_{18}$

Viable Biodiesel or Biogasoline Component

Current Research Activities:

- *Utilization of conventional heterogeneous hydrogenation catalysts*
- *Development of homogenous aqueous phase catalysis chemistry for hydrogenation cleavage of:*
  - *Aryl-O-Aryl*
  - *Aryl-O-Aliphatic Ethers*

Selected hydrogenation catalysts

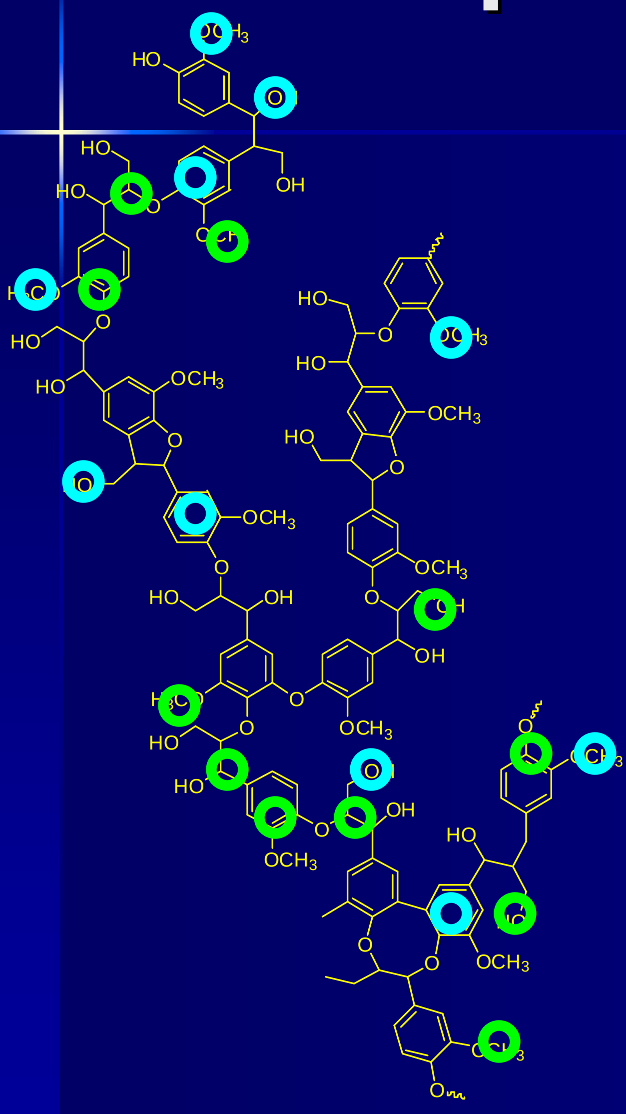
Complexes	**Non-water-soluble hydrogenation complexes**	**Water-soluble hydrogenation complexes**
Ruthenium		
	$Ru(Cl)_2(PPh_3)_3$	$[Ru(Cl)_2(TPPMS)_2]_2$
	$Ru(H)(Cl)(PPh_3)_3$	$Ru(H)(Cl)(TPPMS)_3$
	$Ru(H)_2(PPh_3)_3$	$Ru(H)_2(TPPMS)_3$
	$Ru(Cl)(H)(CO)(PPh_3)_3$	
Rhodium		
	$RhCl(PPh_3)_3$	$RhCl(TPPMS)_3$
Other hydrogenation catalysts	**Non-water-soluble**	**Water-soluble**
Nickel		
	Raney-nickel (hetero)	
Platinum		
	Pt/C (Carbon supp./hetero)	
Palladium		
	Pd/C(Carbon supp./hetero)	
Ruthenium		
		Ru-(PVP) nanoparticle

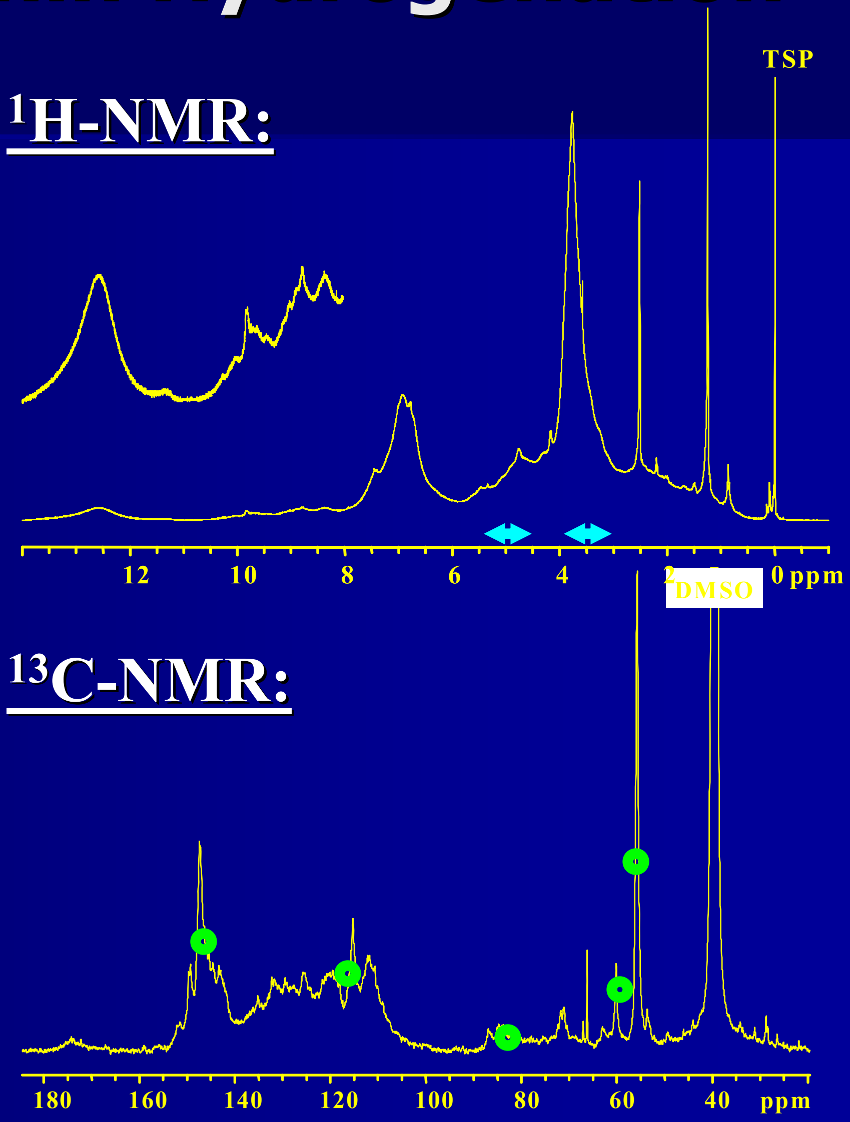
Experimental setup

- 4560 Mini Parr reactor equipped with a 4842 temperature controller.
- Pressurized with UHP Hydrogen gas.
- Under on-line controlled time and pressure.

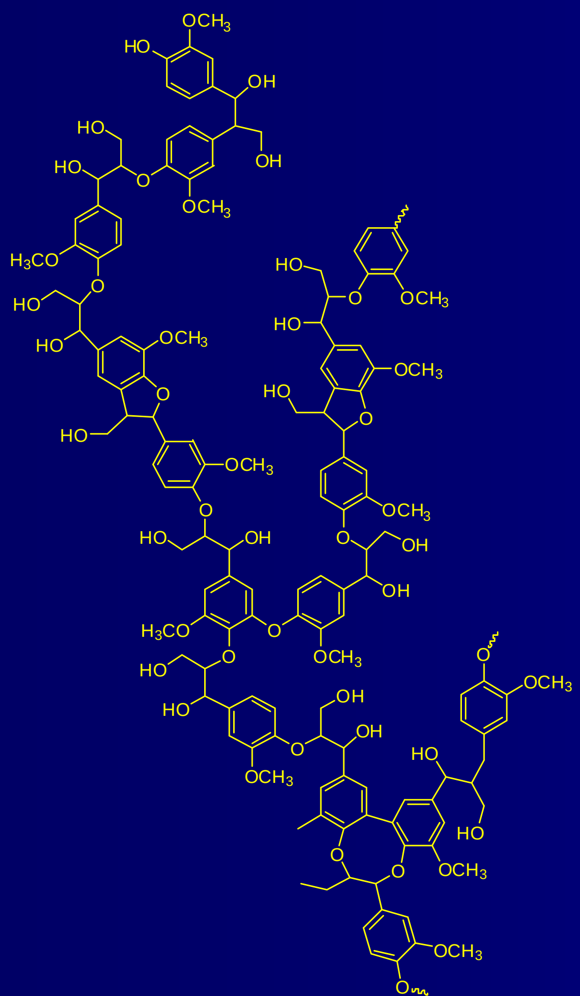
Black Liquor Lignin Hydrogenation

Black Liquor Lignin Hydrogenation

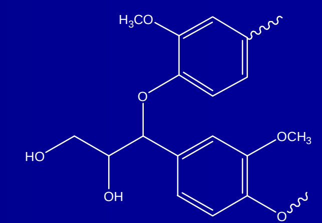




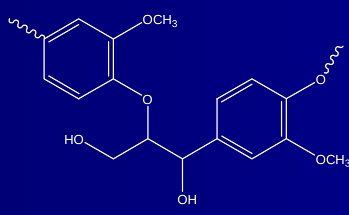
Modelling the lignin polymer



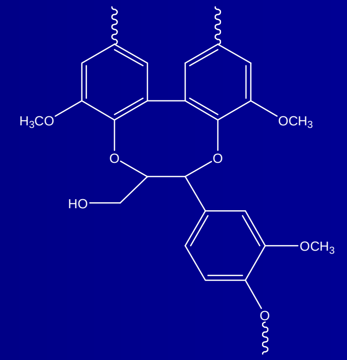
5-5



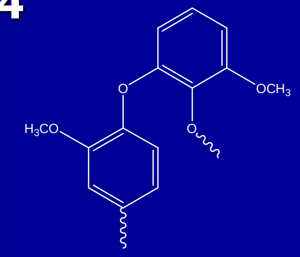
α-O-4



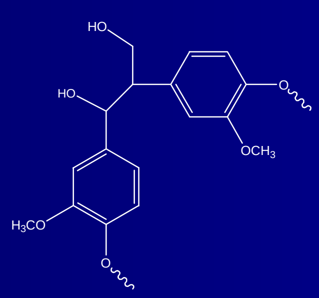
β-O-4



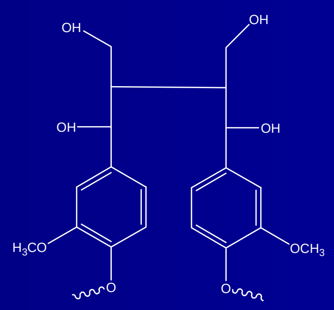
Dibenzodioxocin



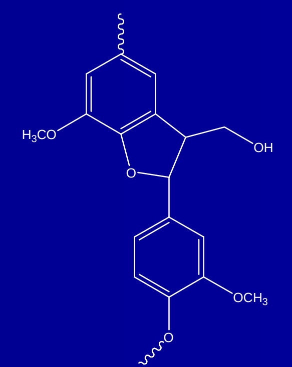
4-O-5



β-1



β-β

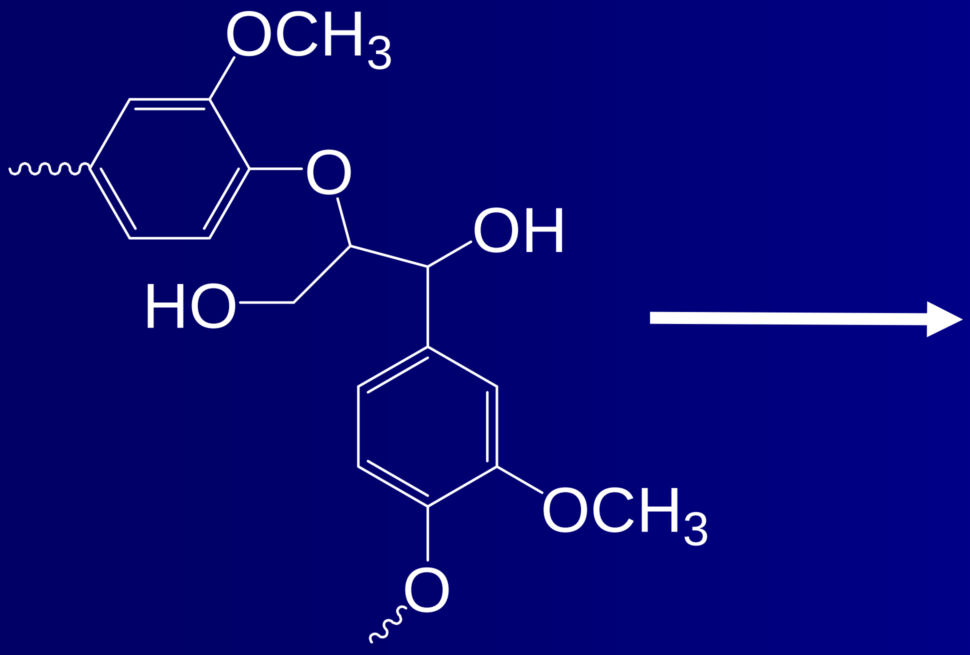


β-5

Modelling the lignin polymer

Linkage type	Dimer structure	Approximate percentage
β-O-4	Phenylpropane β-aryl ether	45-50
α-O-4	Phenylpropane α-aryl ether	6-8
β-5	Phenylcoumaran	9-12
5-5	Biphenyl and dibenzodioxocin	18-25
4-O-5	Diaryl ether	4-8
β-1	1,2-Diaryl propane	7-10
β-β	β-β-Linked structures	3

Modelling the lignin polymer



β-O-4

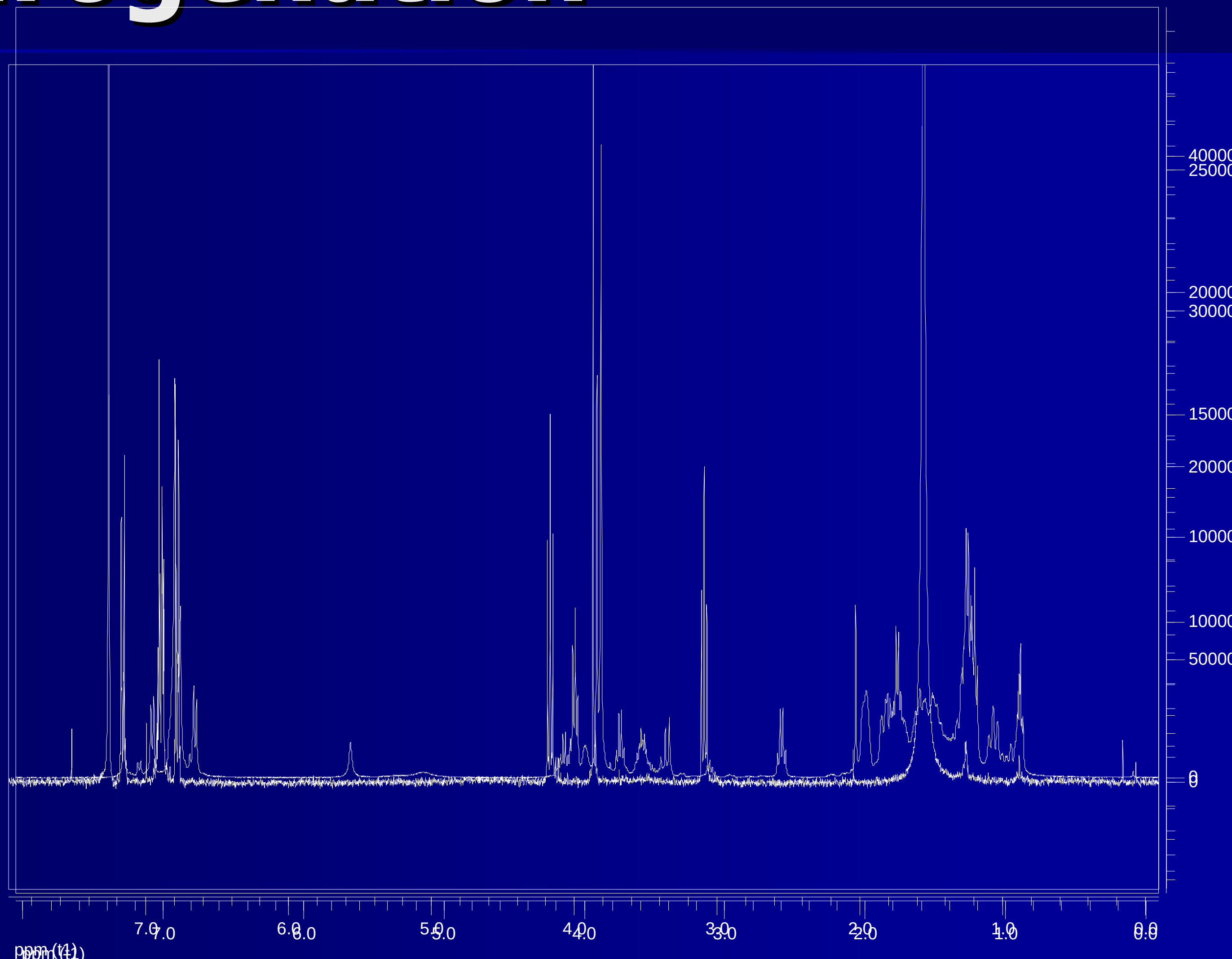
Phenol, 4-[2-(2-methoxyphenoxy)ethyl])

(β-O-4)-model compound hydrogenation

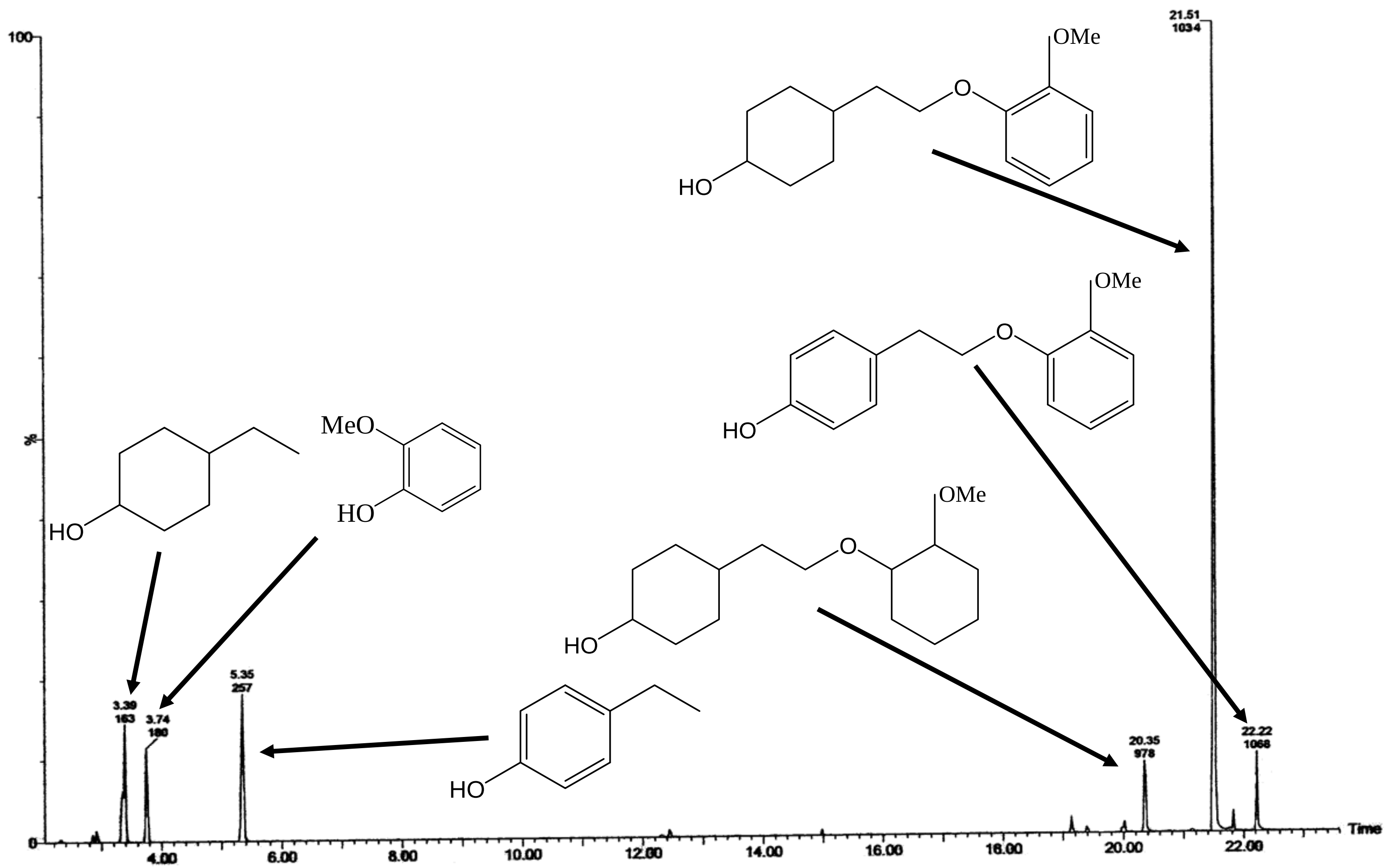
^{1}H-NMR:

Blank run

Raney Ni



(β-O-4)-model compound hydrogenation



Acknowledgments

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Questions: