Lignin to Bio-fuels via Fast Pyrolysis Process Assisted by Volatiles Catalytic Upgrading

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Outline

- **Short introduction**

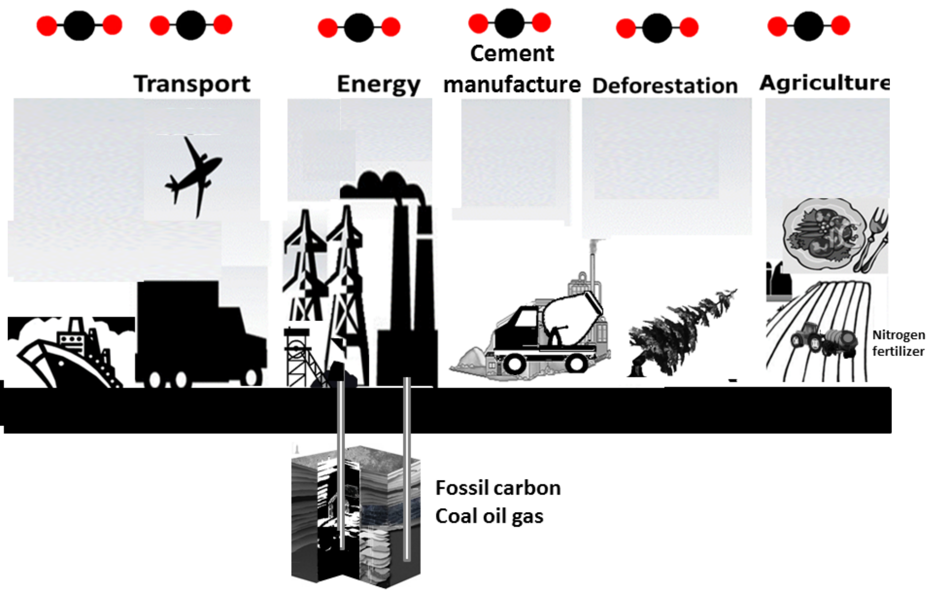
- **Py-GC/MS**
- **Fixed bed reactor flowsheet: brief description**

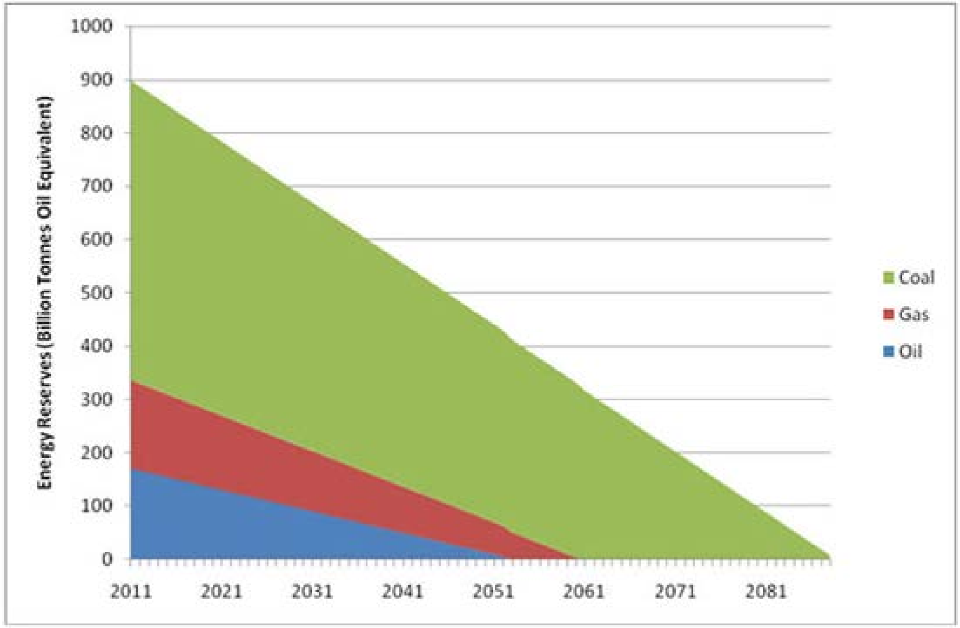
- **Py-GC/MS**:
  - Temperature Analysis
  - FP-CU on zeolites: HZSM-22, HZSM-5, HY, SAPO and Hβ

- **Fixed bed reactor:**
  FP vs FP-CU
  - Mass Balance
  - Gas analysis
  - Liquid analysis

- **Conclusions**

Sources of CO_2 emissions





Population Growth
Demand per capita

10 billion in 2056
11 billion in 2088

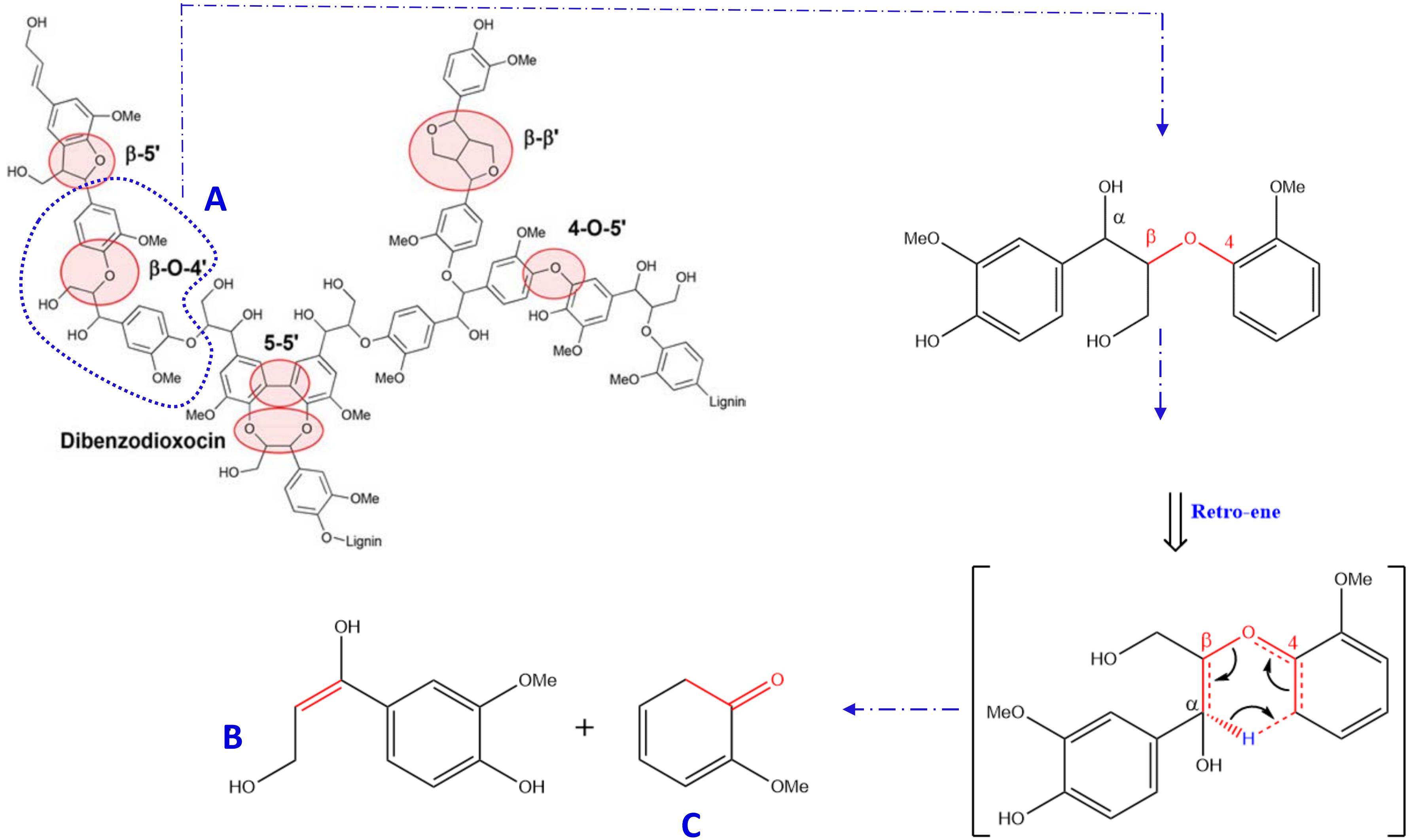
- First generation biofuel (sugar source, rapeseed, sunflower)

Food competition

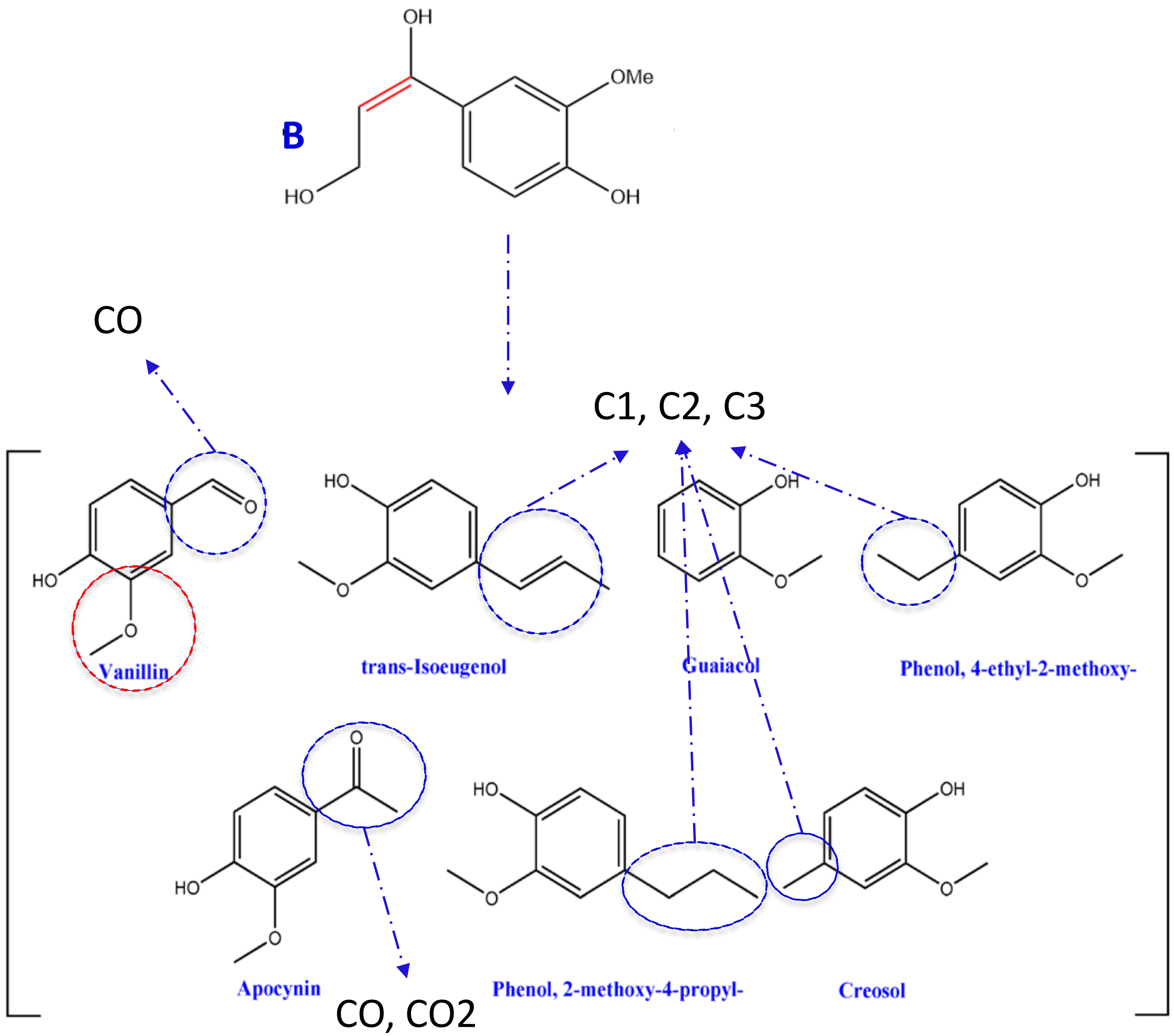
- Second generation biofuel (lignocellulose agriculture waste like sugarcane bagasse, wood, corn cobs, sawdust)

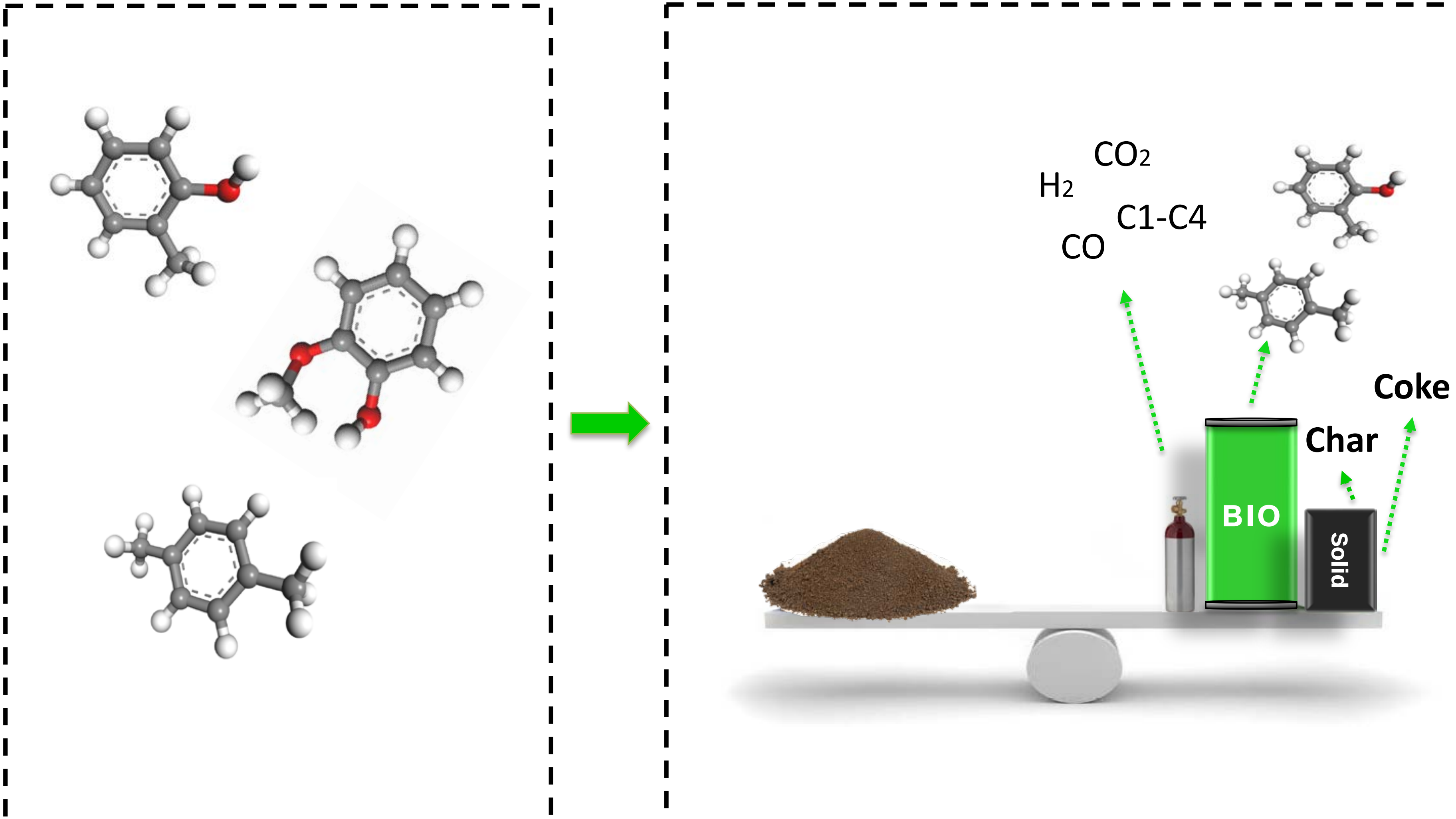
- Third generation biofuel (algae)

Lignin Structure



Choi, Y.S., et al., *Pyrolysis reaction networks for lignin model compounds: unraveling thermal deconstruction of β-O-4 and α-O-4 compounds.* Green Chemistry, 2016. **18**(6): p. 1762-1773.
Huang, J., et al., *Density functional theory studies on pyrolysis mechanism of β-O-4 type lignin dimer model compound.* Journal of Analytical and Applied Pyrolysis, 2014. **109**: p. 98-108.


B
OH
OMe
HO
OH
CO
C1, C2, C3
Vanillin
trans-Isoeugenol
Guaiacol
Phenol, 4-ethyl-2-methoxy-
Apocynin
CO, CO2
Phenol, 2-methoxy-4-propyl-
Creosol



Py-GC/MS

Qualitative analysis (liquid)

Fixed bed reactor-GC/FID/TCD/MS

Qualitative and quantitative analysis

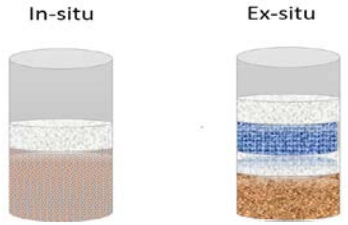
Pyrolyzer(Py)-Gas Chromatography (GC)/Mass Spectrometry (MS)

Pyrolyzer

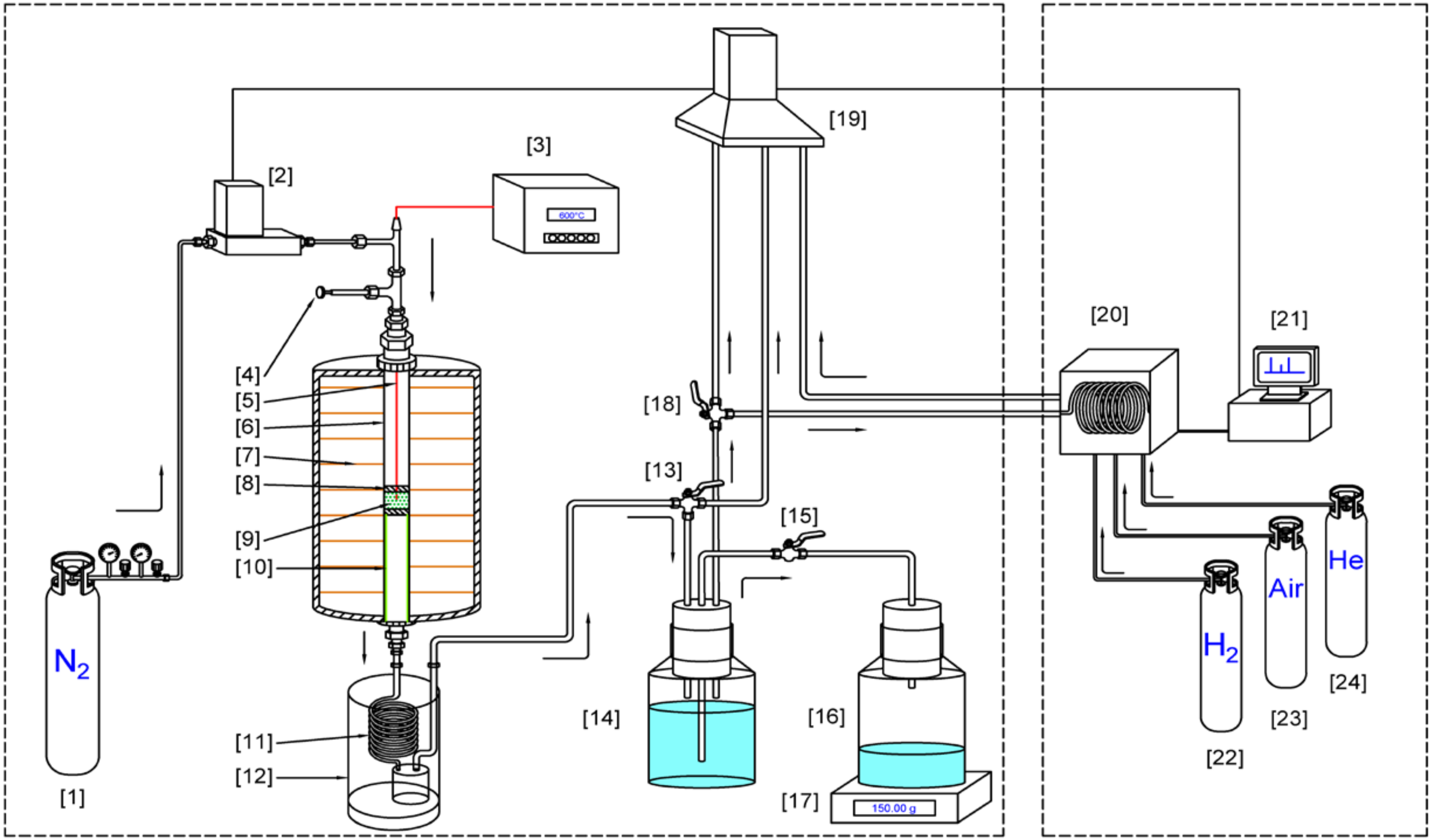
Gas Chromatography

Mass Spectrometry

Carrier gas – Helium
Ultra ALLOY® Capillary Column (30m × 0.25mm × 0.25 μm)
The lignin sample mass was kept constant for all analyzes (=0.5 mg)



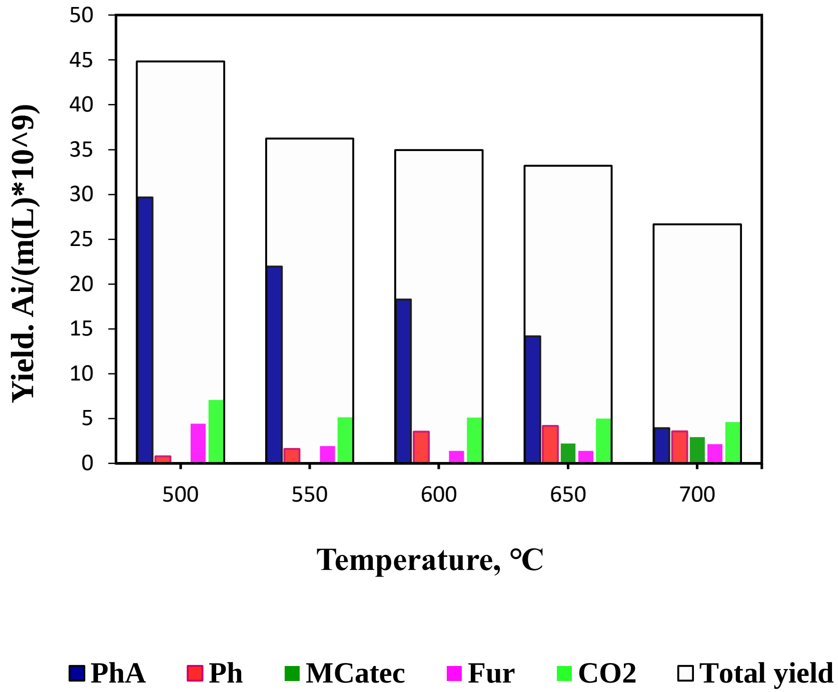
Tailor made entrained flow fast-pyrolysis reactor suitable for complete mass balance@NTNU

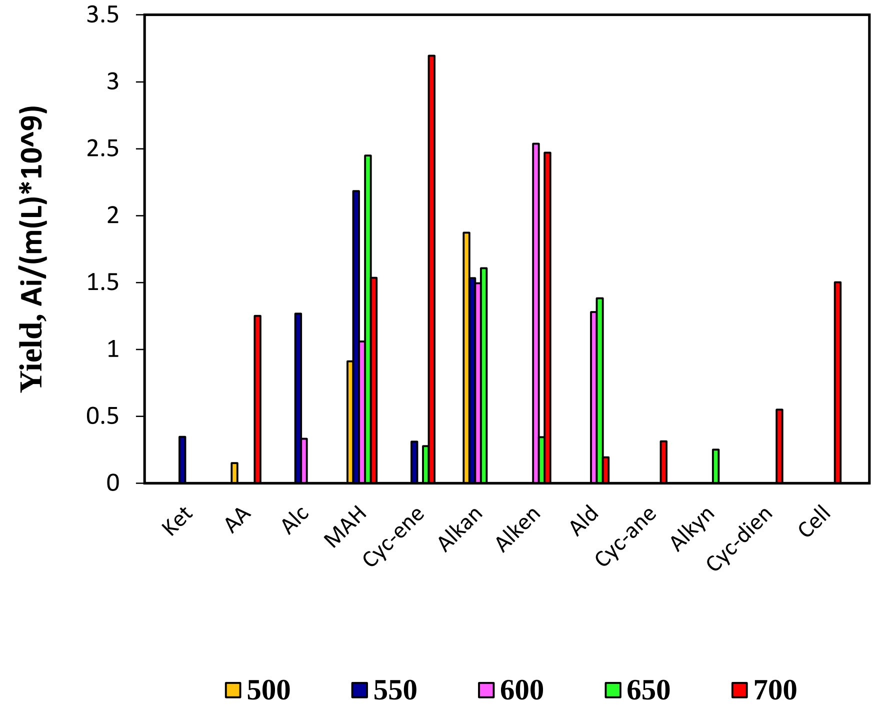


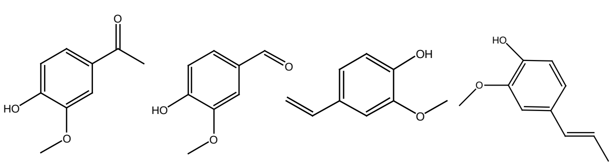
Nr.	NAME OF PART	Nr.	NAME OF PART	Nr.	NAME OF PART
1.	Nitrogen tank	9.	Catalyst / inert heat carrier material	17.	Scale
2.	Mass flow controller	10.	Metal support	18.	3-way valve
3.	Temperature controller	11.	Spiral glass condenser	19.	Ventilation
4.	Piston	12.	Ice cooling bath	20.	Gas chromatograph - FID/TCD
5.	Thermocouple	13.	3-way valve	21.	PC
6.	Fixed bed tubular reactor	14.	Gas cylinder with 3-hole rubber plug	22.	Hydrogen tank
7.	Furnace	15.	2-way valve	23.	Air tank
8.	Quartz wool	16.	Water collector	24.	Helium tank

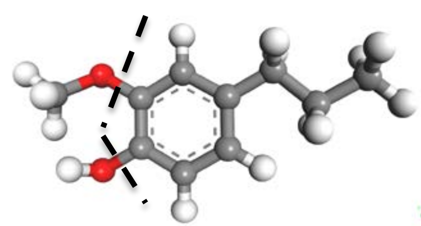
Py-GC/MS results

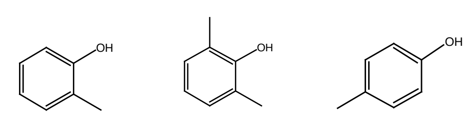
Temperature analysis



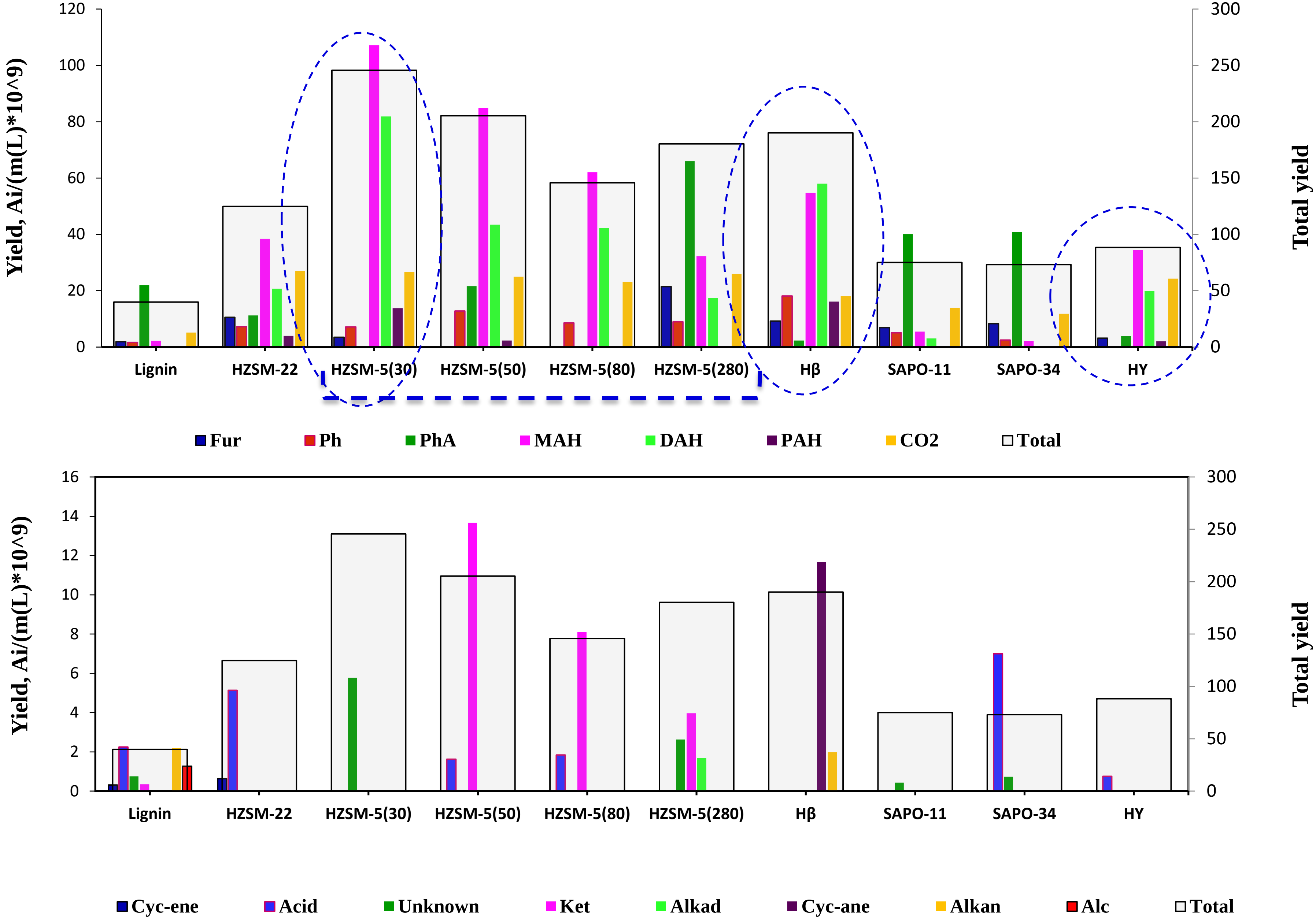




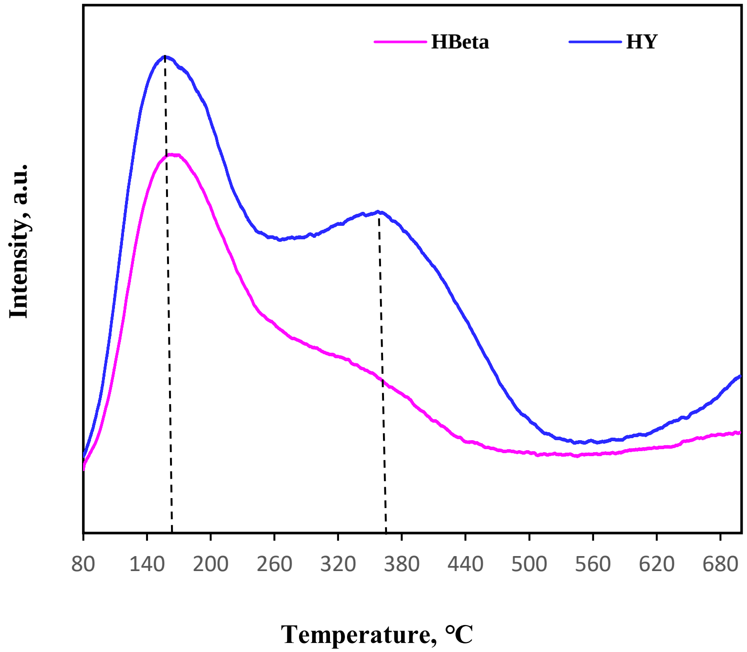


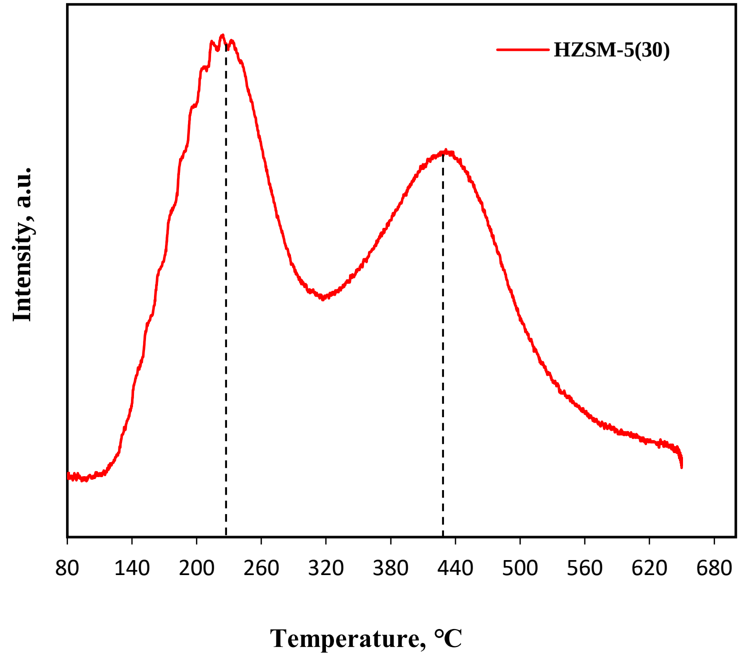


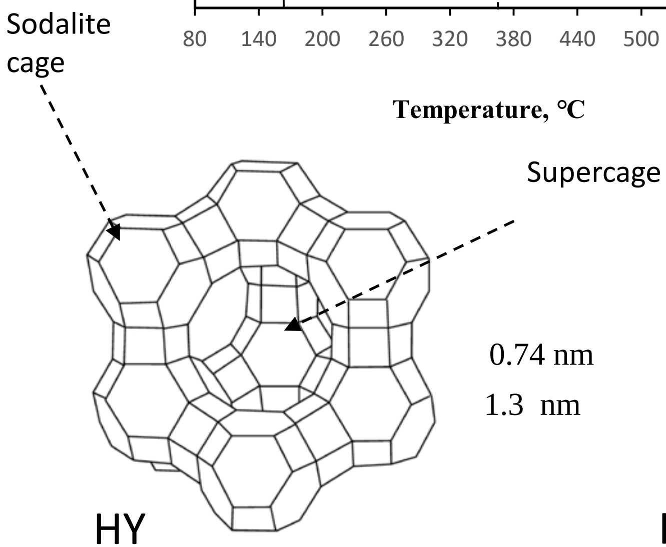
Temperature: 600°C; Catalyst to lignin ratio: 3:1

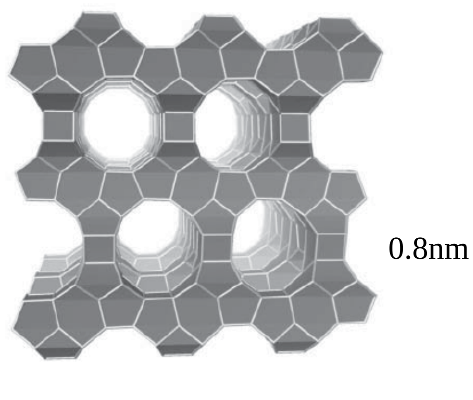


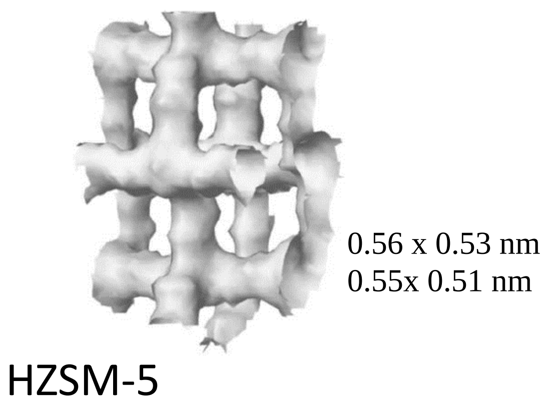
NH_3-Temperature Programmed Desorption



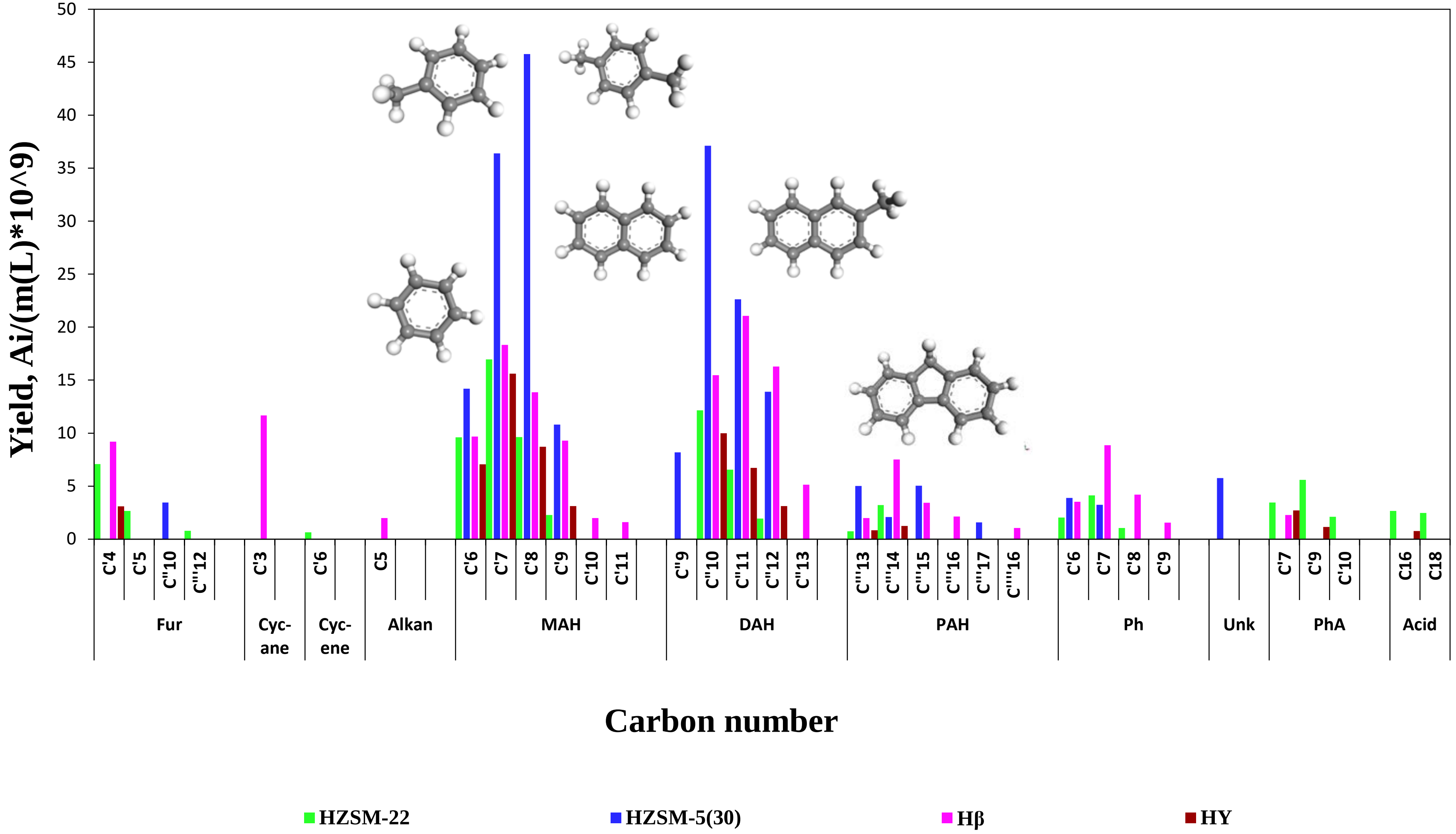








[1]Kulprathipanja, S. Zeolites in Industrial Separation and Catalysis, John Wiley & Sons.
[2]Henrique S. Cerqueira a, P. A. a., Jerzy Datka b, Michel Guisnet a,* (1999). "Influence of coke on the acid properties of a USHY zeolite." ELSEVIER.
[3]Lutz, W. (2014). "Zeolite Y: Synthesis, Modification, and Properties—A Case Revisited." Advances in Materials Science and Engineering **2014**: 1-20.



Yield, Ai/(m(L)*10^9)
50
45
40
35
30
25
20
15
10
5
0
C'4
C'5
C''10
C'''12
C'3
C'6
C5
C'6
C'7
C'8
C'9
C'10
C'11
C''9
C''10
C''11
C''12
C''13
C'''13
C'''14
C'''15
C'''16
C'''17
C'''16
C'6
C'7
C'8
C'9
C'7
C'9
C'10
C16
C18
Fur
Cyc-
ane
Cyc-
ene
Alkan
MAH
DAH
PAH
Ph
Unk
PhA
Acid
Carbon number
HZSM-22
HZSM-5(30)
Hβ
HY

Fixed bed reactor

Mass Balance

FP vs FP-CU

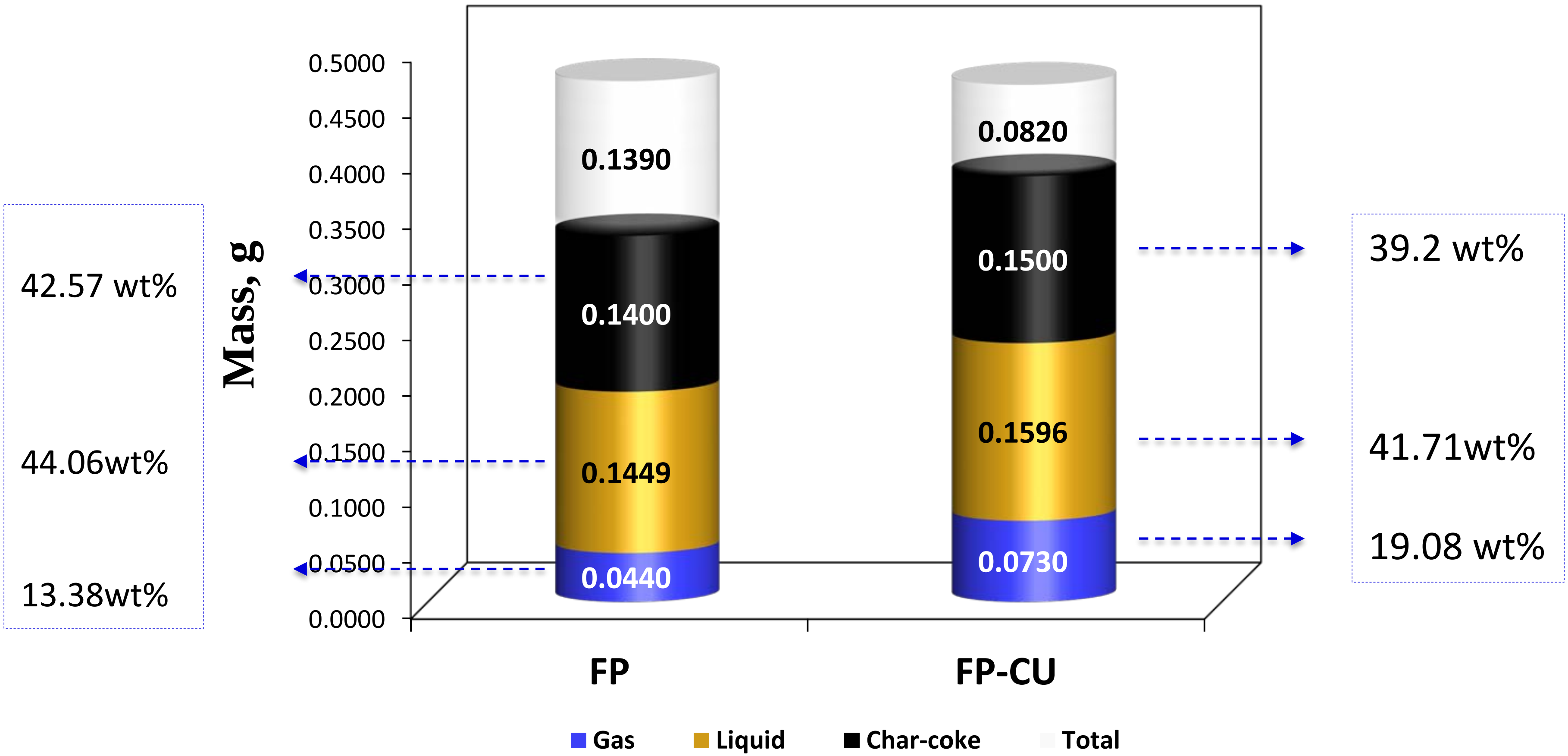
t=600 ^{o}C

CU: HZSM-5(SiO_2/Al_2O_3=30), particle size: 250-500 μm

Nitrogen flowrate=40 mL/min

Catalyst to lignin ratio = 1

Lignin=0.5 g



Fixed bed reactor

Gas analysis

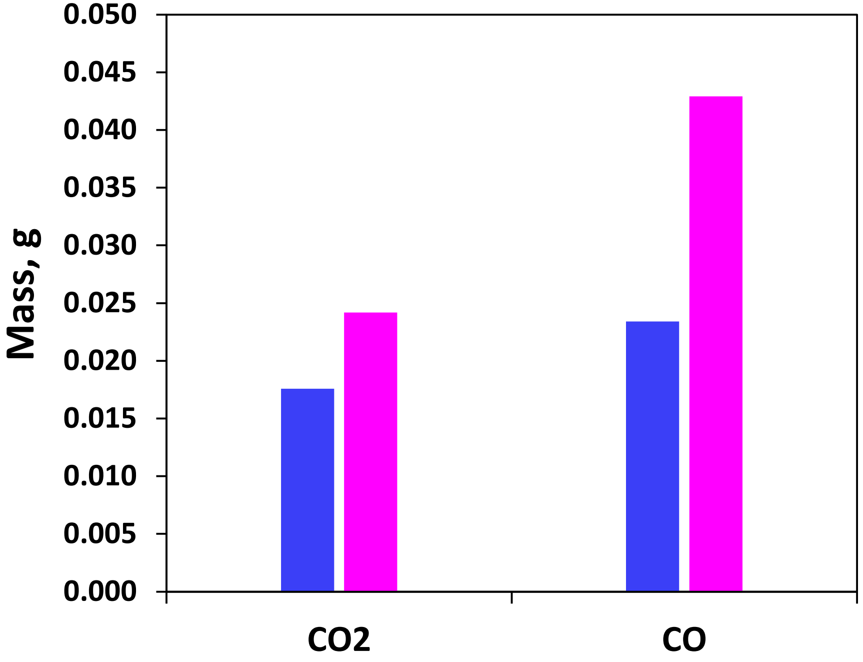
FP vs FP-CU

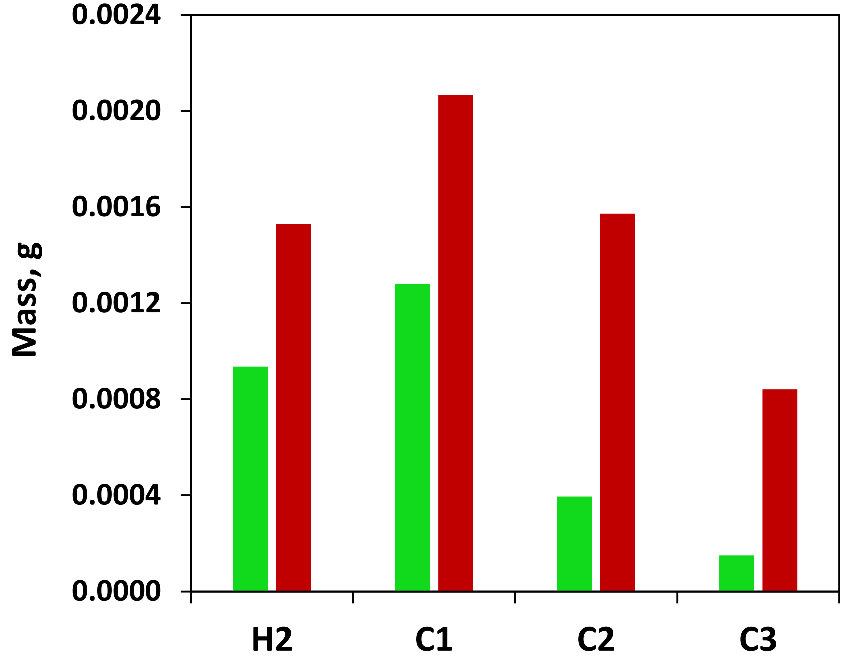
t=600 ^{o}C

CU: HZSM-5(SiO_2/Al_2O_3=30), particle size: 250-500 µm

Nitrogen flowrate=40 mL/min

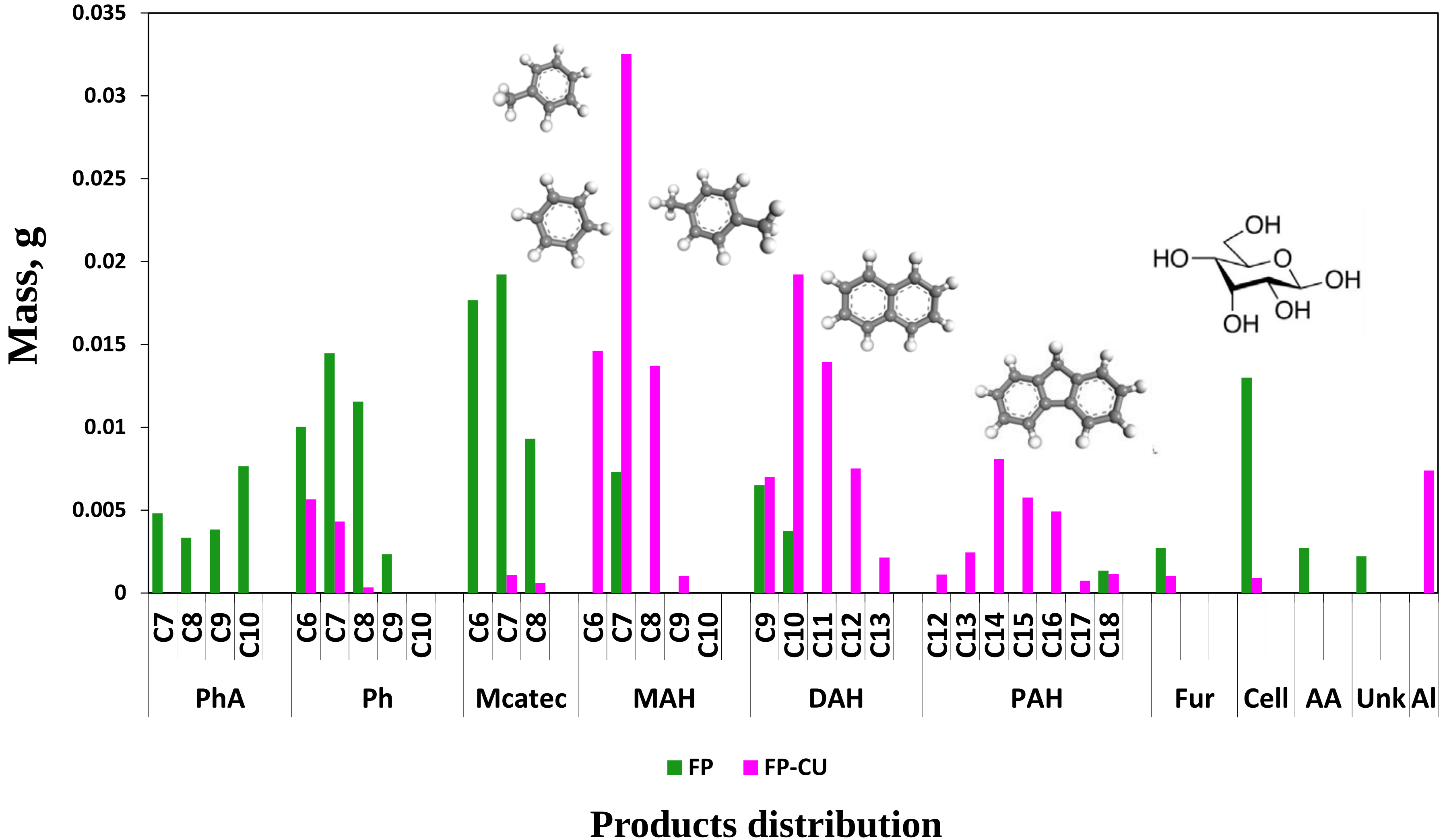
Catalyst to lignin ratio of 1





Fixed bed reactor

Liquid analysis
FP vs FP-CU
t=600 °C
CU: HZSM-5(SiO_2/Al_2O_3=30), particle size: 250-500 µm
Nitrogen flowrate=40 mL/min
Catalyst to lignin ratio of 1



Conclusions

- The distribution analysis of the FP and FP-CU products was quite similar for the both set-ups Py-GC/MS and Tailor-made Entrained Flow Fast Pyrolysis reactor, indicating that Tailor-made Entrained Flow Fast Pyrolysis reactor is an useful set-up for fast screening of catalysts and biomass with detailed quantitative product analysis.

- The Tailor-made Entrained Flow Fast Pyrolysis reactor is also suitable for the kinetic study, since this can provide both qualitative and quantitative analysis.

- Biomass can be fed as a semi-continuous manner to the Tailor-made Entrained Flow Fast Pyrolysis reactor, that can be helpful to get primary insights of catalyst deactivation.

- By analysing various zeolites with different pore structure and different internal pore architecture, it was noticed that HZSM-5 has the proper size for generating high yield of aromatic hydrocarbons, especially the MAH.

Acknowledgments

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St1

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Thank you