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Catalytic Pyrolysis

Sasha R.A. Kersten

Catalytic Fast Pyrolysis for fuel production

S.R.A. Kersten

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Roel Westerhof, Stijn Oudenhoven, Pushkar Marathe, Daniele Castello, Caroline Lievens, Güray Yildiz, Wolter Prins

Some concerns I had

- Limited knowledge of chemistry
  - Which reactions are catalyzed?, which ones do we want to catalyze?
- Ill defined goal
  - Stabilization of oil (?)
  - Oxygen removal (yield often neglected)
  - Production of specific compounds – aromatics (yield and separation neglected)
  - **My goal = fuel precursor**
- Catalysts de-activation
  - Coke, interaction with K, Cl, Ca, S, etc..
- High reactivity of pyrolysis products
- Solid catalyst - solid biomass?
  - Catalysis of what? Vapors, Gases, Aerosols?

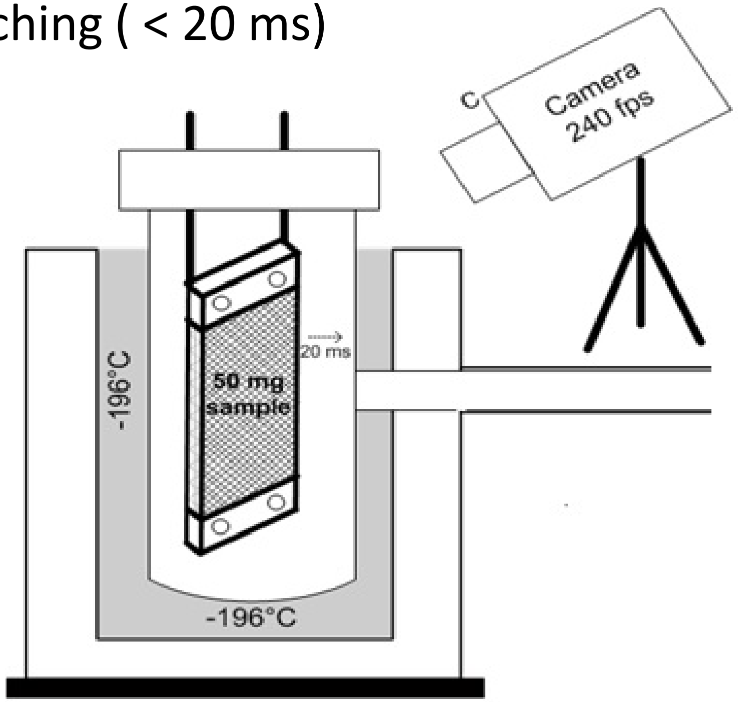
Agenda

Results of different feeds
using different catalyst (synthetic & ashes in feed)
in different reactors
showing that ……

Firstly I present experimental results without synthetic catalyst which are of interest for the interpretation of results obtained with catalyst

Equipment: pyrolysis

- 50 mg biomass
- Fast heating (5000 $^{o}C/s$) by hot screen
- Rate of products leaving the reaction zone controlled by pressure (5 Pa – 1 bar)
- Very fast quenching (< 20 ms)



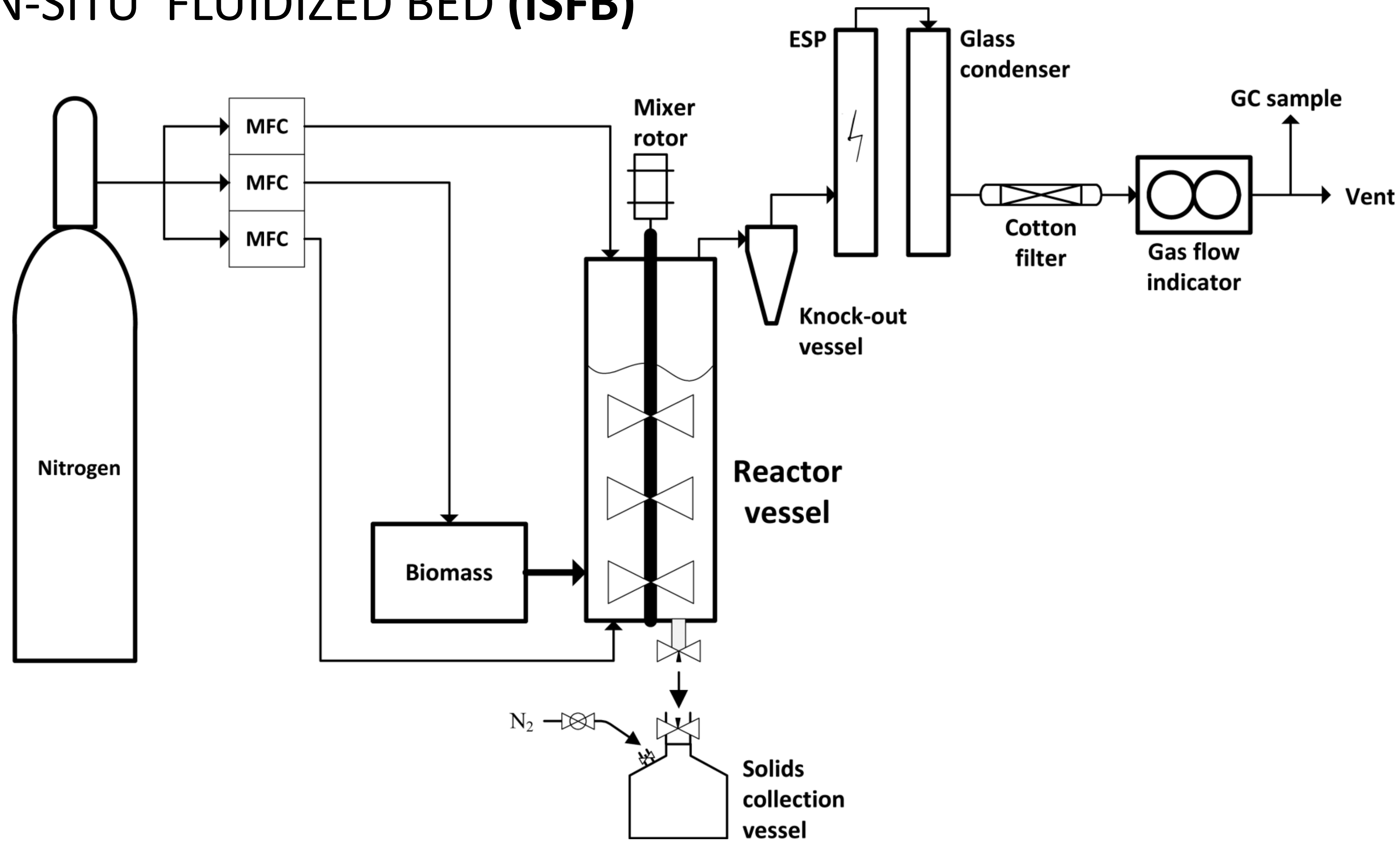
Screen-Heater **(SH)**

Fluidized Bed **(FB)**
In-Situ (CFP)
Ex-situ (CVUP)

- 1 kg/h feed
- Fluidized bed
- (also) fast heating (10,000 $^{o}C/s$)
- 0.5 – 1 bar
- Staged condensation
- 1- 2 s residence time of hot vapors

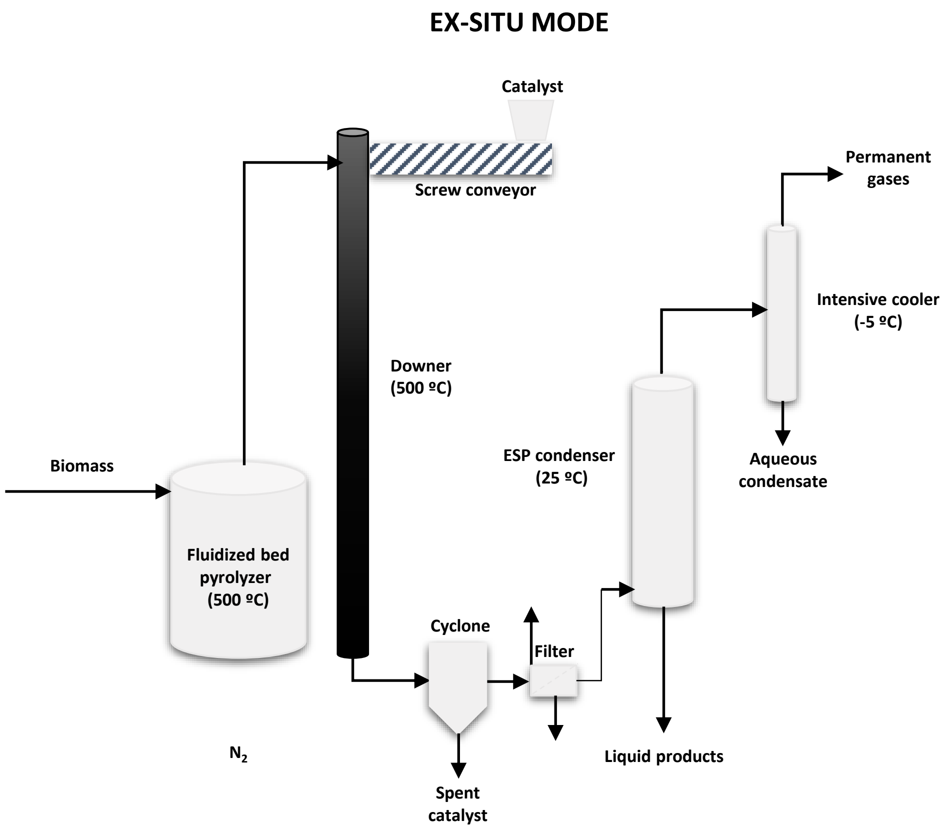
Equipment: fluidized bed for catalytic pyrolysis

IN-SITU FLUIDIZED BED **(ISFB)**

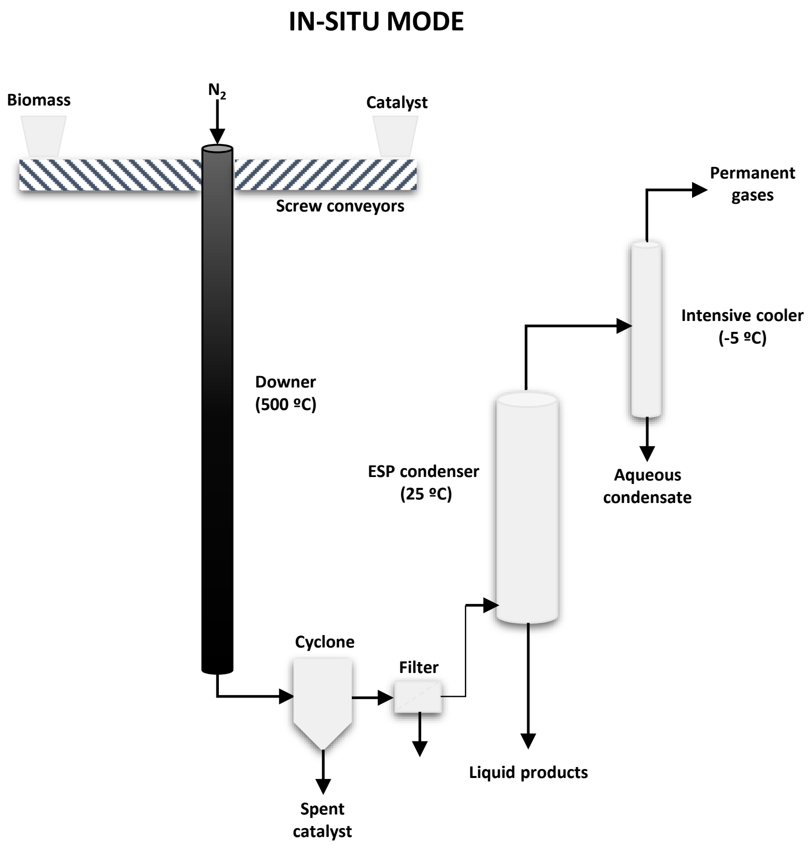


Equipment: downer for catalytic pyrolysis

EX-SITU downer **(ESD)**



IN-SITU downer **(ISD)**



Feeds and catalysts

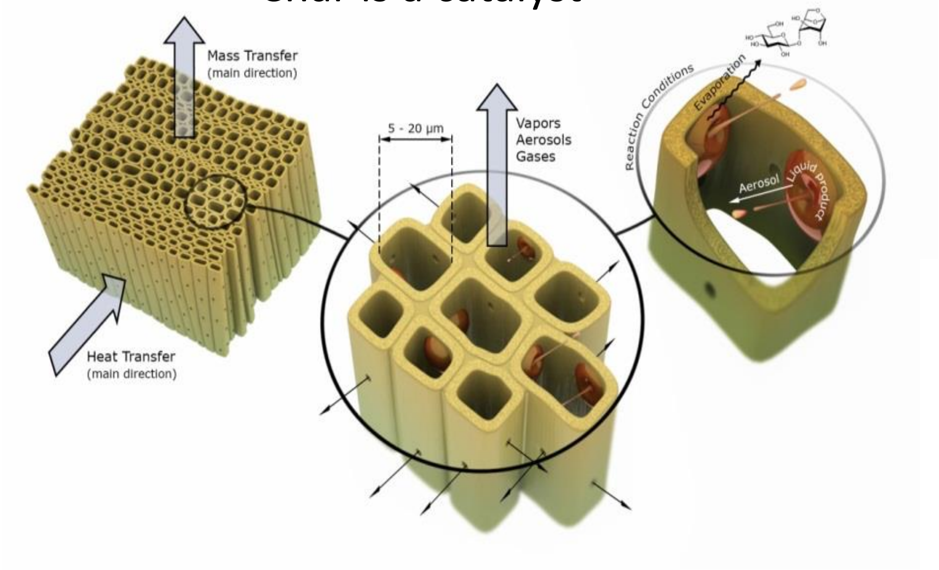
- Pine
- Straw
- Hay
- Bagasse
- Avicel cellulose
- Cotton
- Lignins

- ZSM-5
- Na_2O on Al_2O_3
- Ashes, K_2CO_3

All results at 500 – 530 ^oC, unless stated otherwise

My model of catalytic pyrolysis

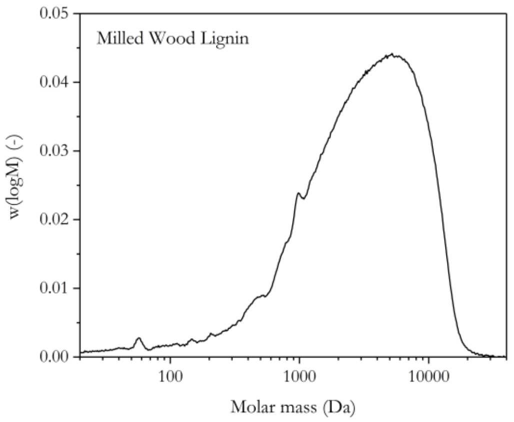
Processes at particle level
Mass and Heat transport
Pyrolysis reactions
Catalysis by AAEMs
Char is a catalyst



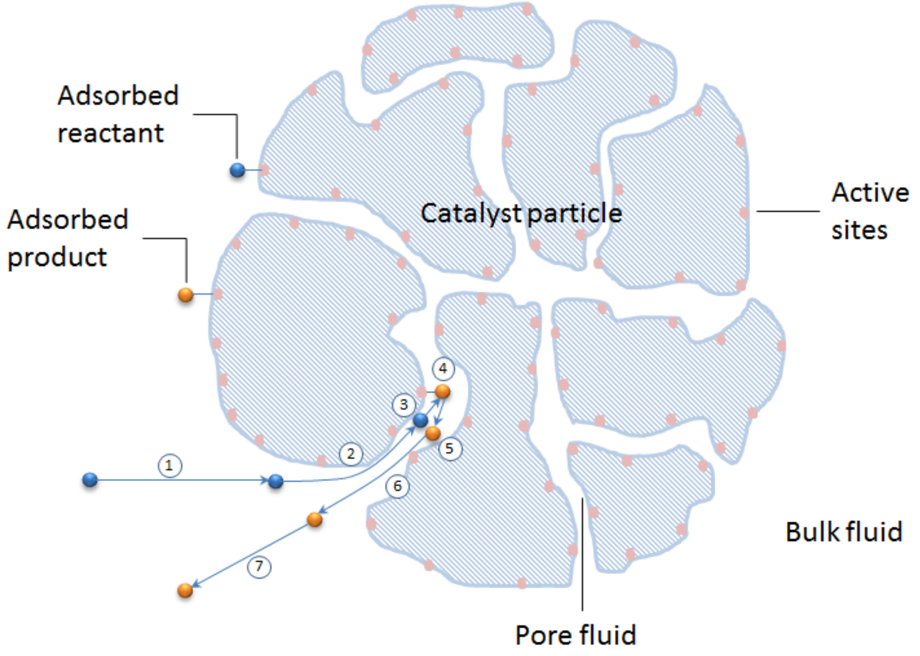
Can be studied in Screen -Heater

Processes in vapor phase
Homogeneous reactions

Gas, Vapors, Aerosols

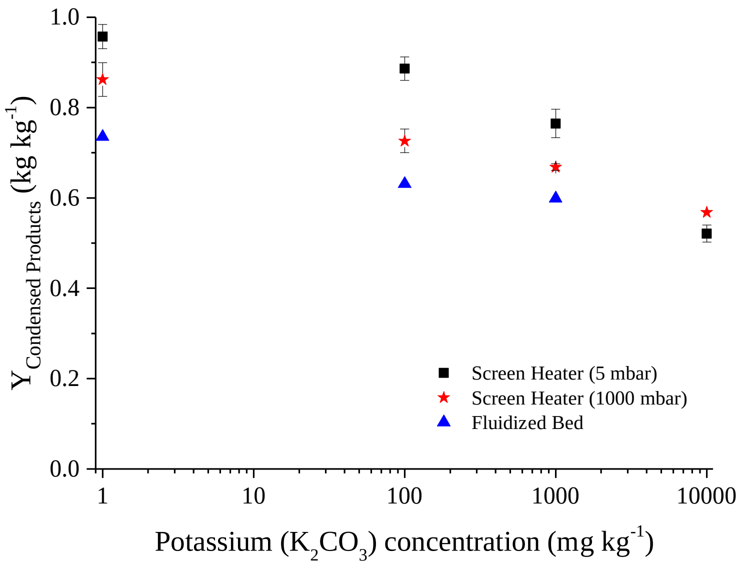


Processes on / in catalysts

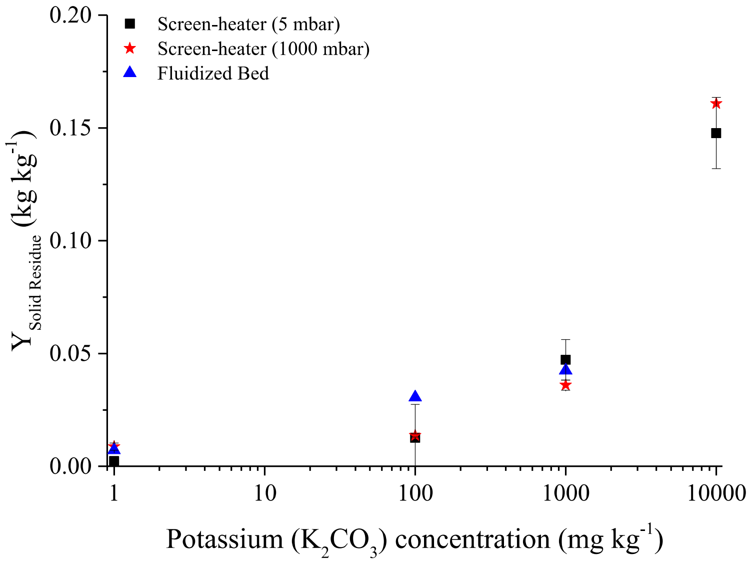


Influence of AAEMs on yields of lumped product

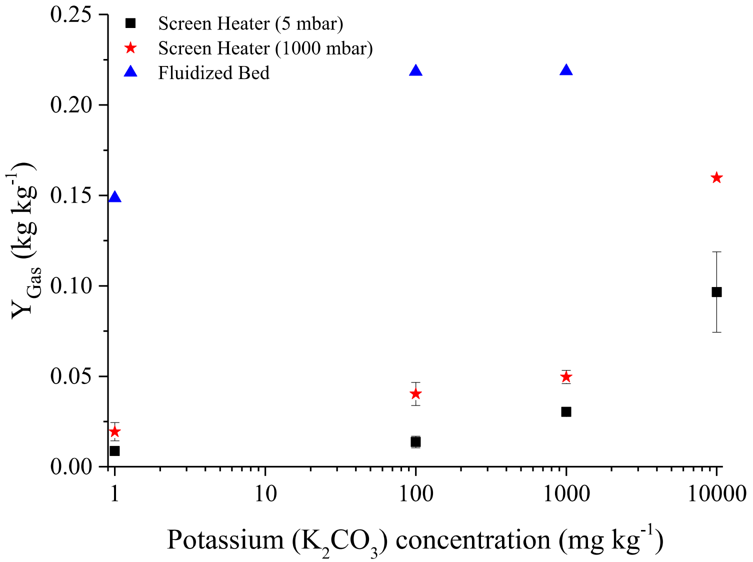
feed = cellulose



Liquid



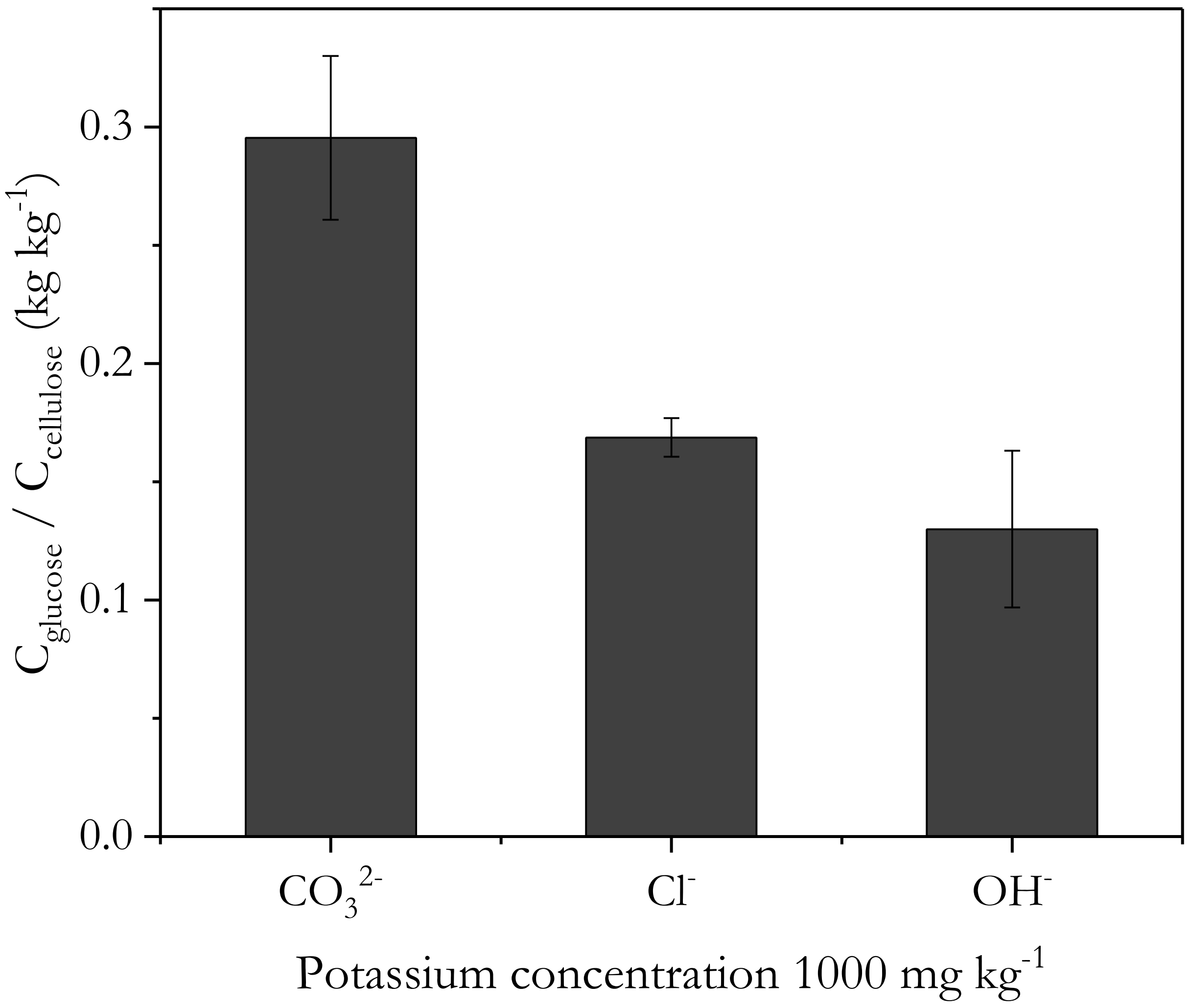
Solid



Gas

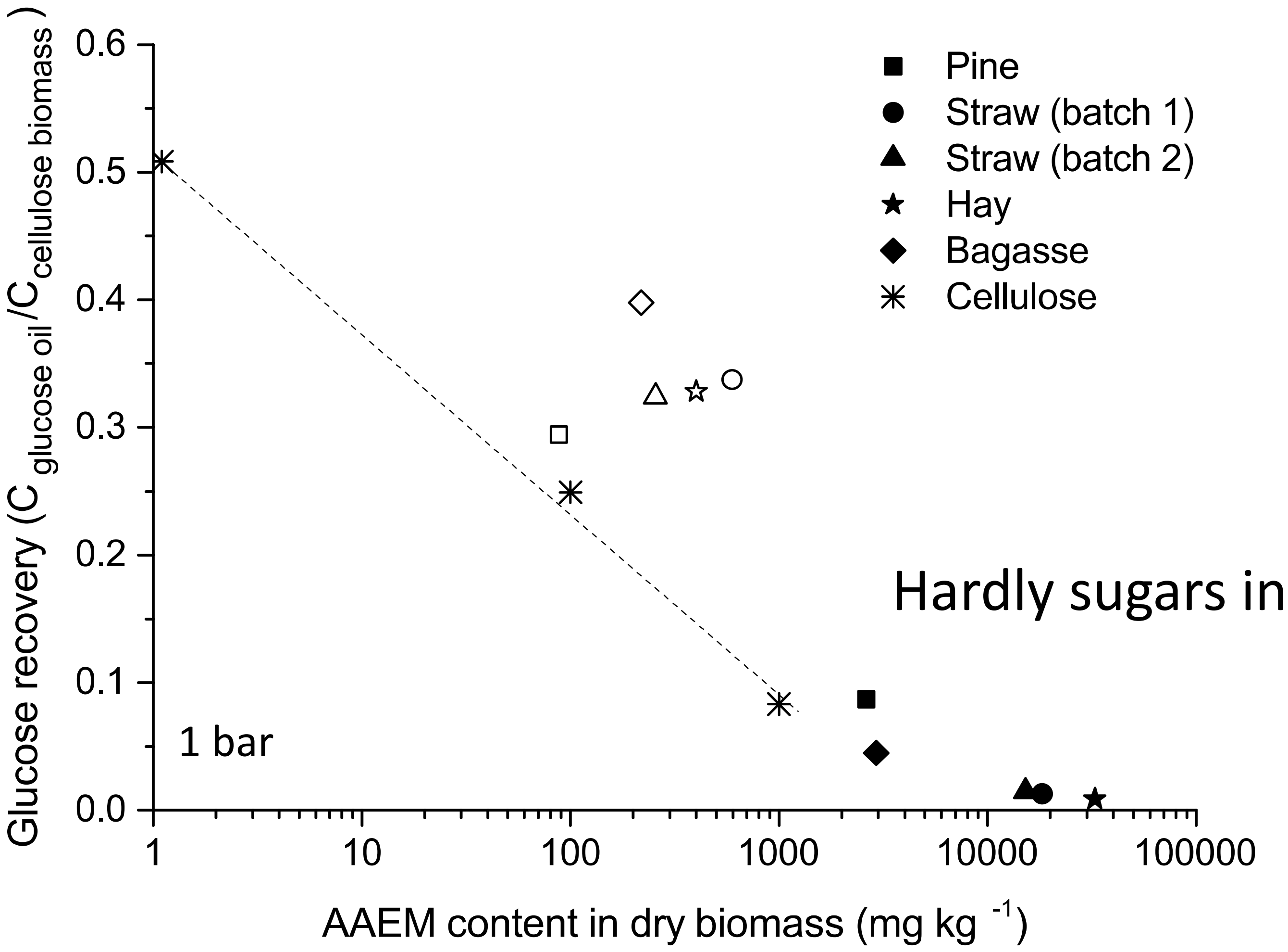
AAEMs = natural catalyst (they accumulate on the catalyst)

Influence negative ion



SH @ 500 Pa

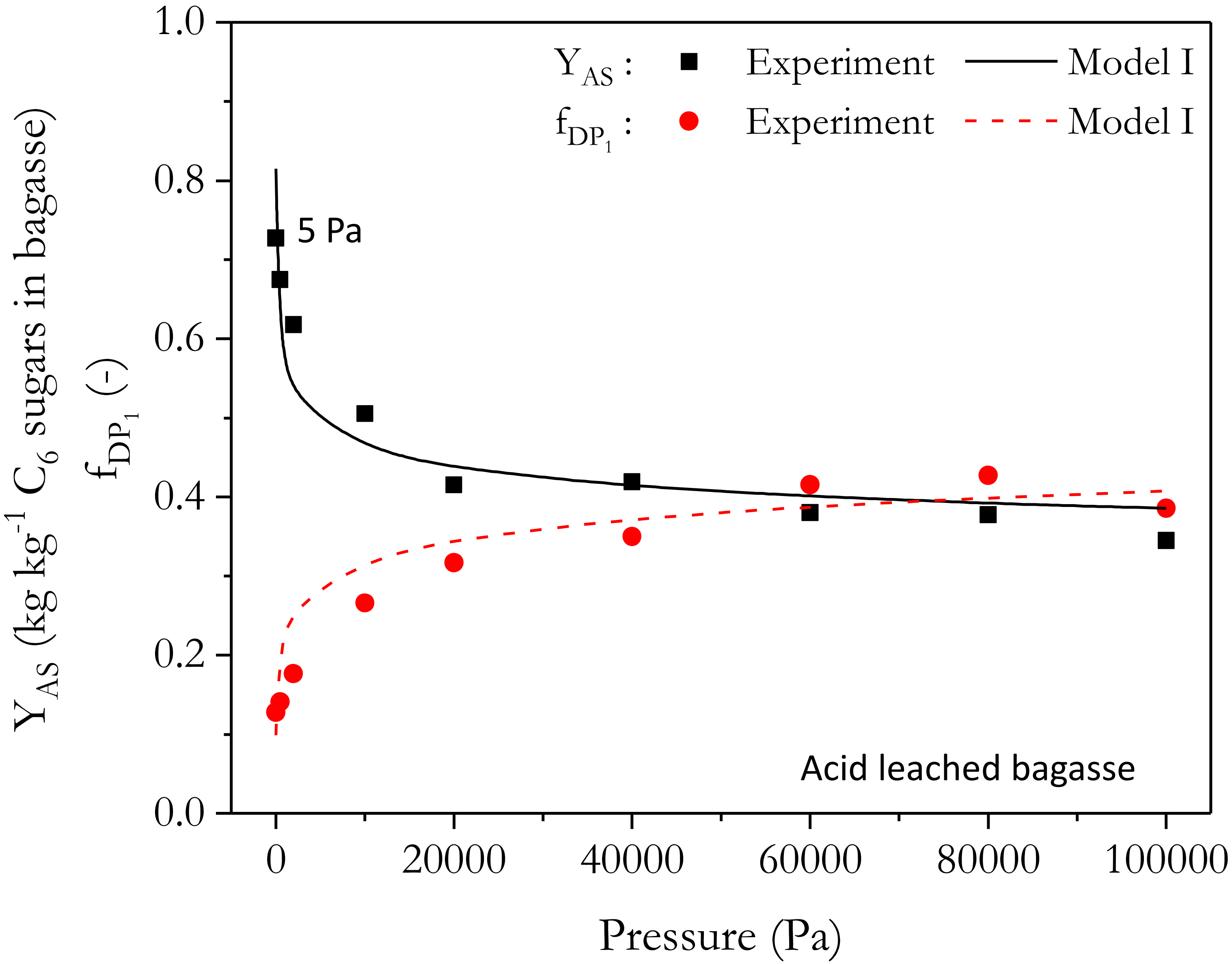
Influence of AAEMs on sugar chemistry



Hardly sugars in contact with catalyst

FB

Production of sugars – effect of pressure



SH

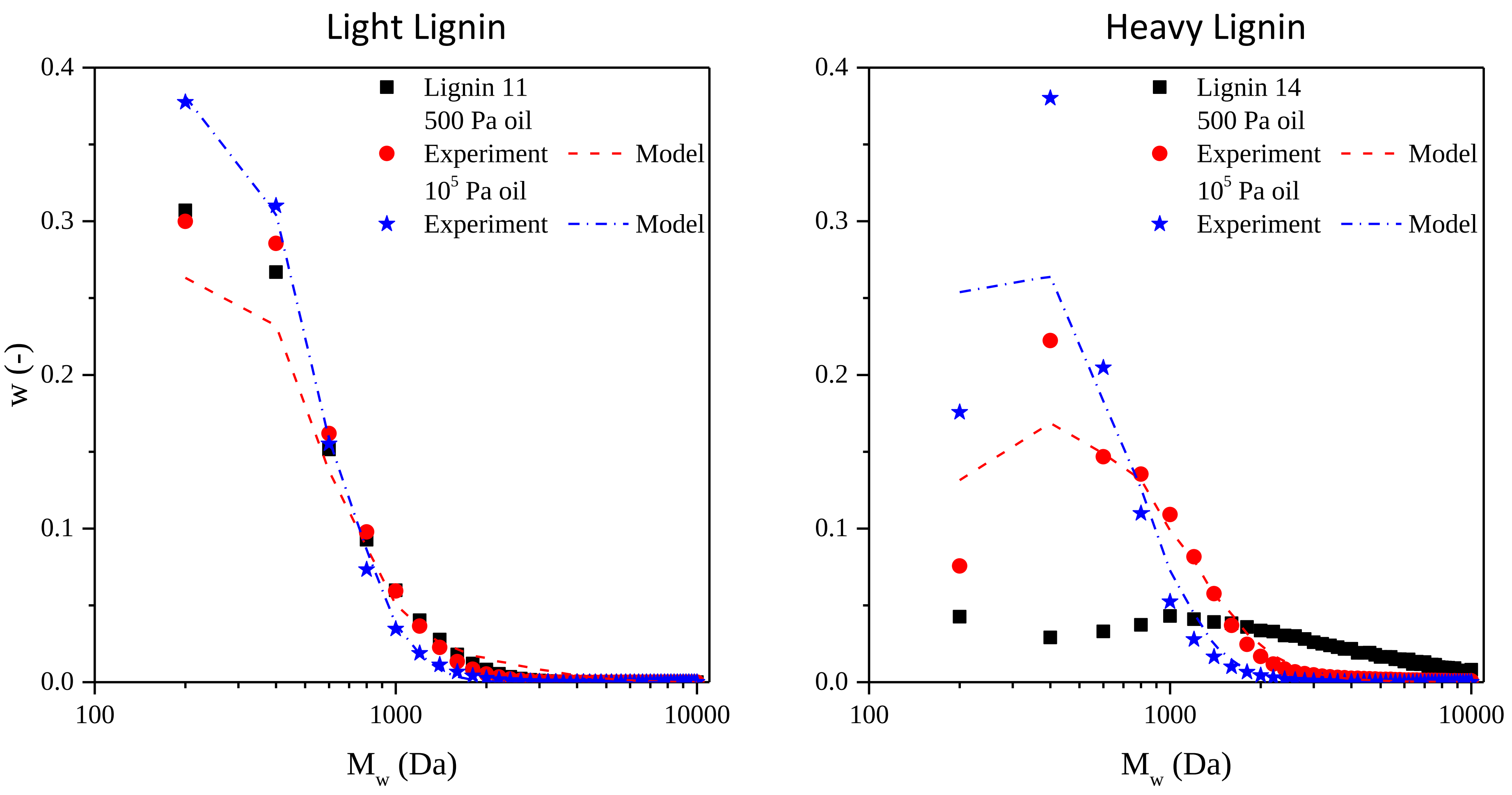
Pyrolysis of Lignin

- Processed/extracted lignins
  - Solvolysis
  - Pyrolytic
- Milled wood lignin (closest to native)
- Similar C, H, O
- 600 –3600 Da (weight averaged)
- 0 – 35% β-O-4

Lignin	Code	C	H	O *	N	H/C	$\langle M_w \rangle$ **	Đ	β-O-4 linkages
(-)	(-)	(% on mass basis, dry)				(mole mole^{-1})	(Da)	(-)	(per 100 Ar units)
SL	1	66.9	6	27	0.1	1.1	2515	2.1	1.8
L-SL	2	-	-	-	-	-	1591	1.7	-
H-SL	3	-	-	-	-	-	3462	1.8	-
WSL	4	64.8	5.8	28.6	0.8	1.1	2043	2.0	8.6
L-WSL	5	-	-	-	-	-	1449	1.7	-
H-WSL	6	-	-	-	-	-	2601	2.0	-
PL1	7	68.1	6.3	25.5	0.1	1.1	725	1.5	-
L-PL1	8	-	-	-	-	-	670	1.5	-
H-PL1	9	-	-	-	-	-	1047	1.6	-
PL2	10	64.8	6.5	28.6	0.1	1.2	616	1.6	0
L-PL2	11	-	-	-	-	-	588	1.6	-
H-PL2	12	-	-	-	-	-	1241	2.0	-
SOL	13	63.9	5.7	30.3	0.1	1.1	1858	2.2	7.8
MWL	14	60.7	6.3	33	<0.1	1.2	3596	2.5	34.5

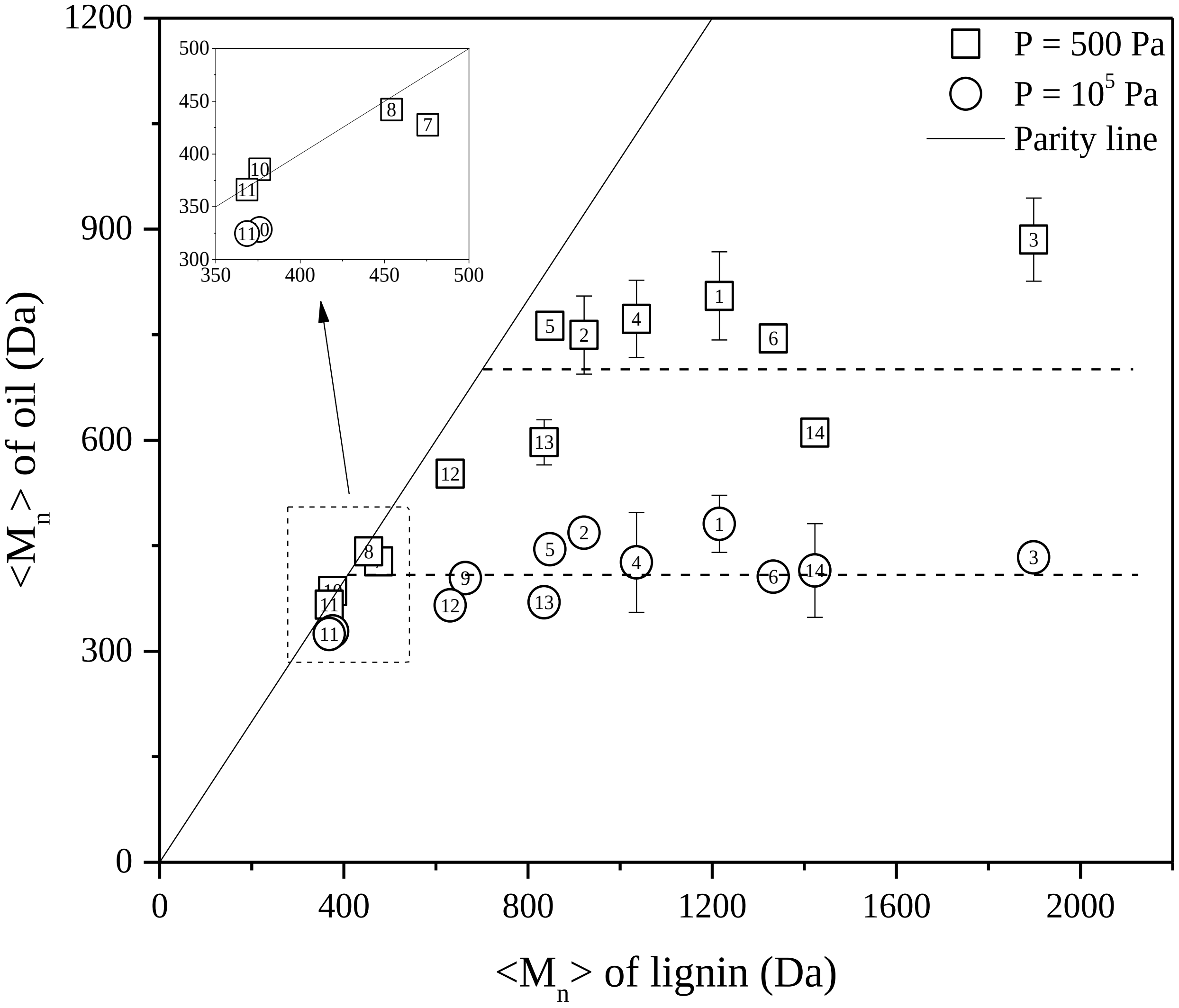
* Oxygen content by difference: (100 – C – H – N); ** $\langle M_w \rangle$ is calculated from UV detector response; – Not measured

Molecular weight distribution



SH

MW of oil vs. MW of Lignin



'Lignin' on contact with catalyst is of rather small MW

SH

Bond balance

Oxygen Bonds	Milled wood lignin	Oil at 500 Pa	Oil at 1 bar
β-aryl ether	34.4	9.9	0.0
Phenylcoumaran	14.1	4.3	0.6
Resinol	11.1	1.6	0.6
Total	59.5	15.8	1.3

‘Lignin’ that is in contact with the catalyst hardly contains C-O-C bonds, instead it is C-C bonded

Intermediate conclusion

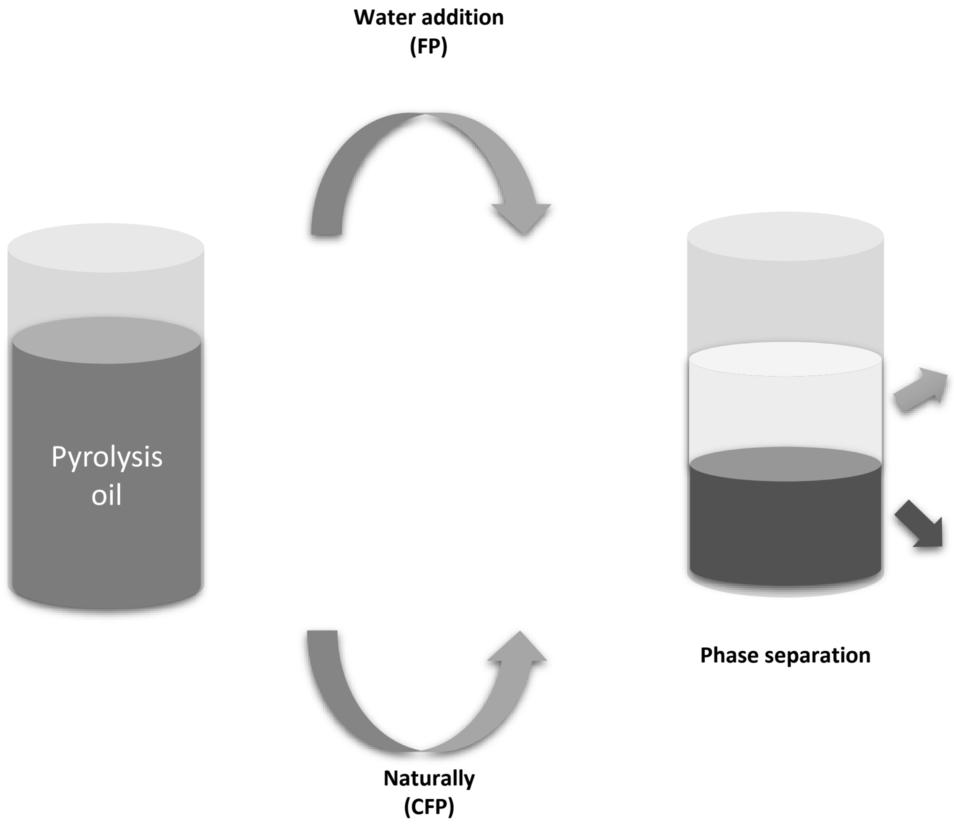
The catalyst is in contact with:

Light decay products of sugars (highly oxygenated)

Re-polymerized C-C bonded Lignin of ~ 500 Da

Most likely aerosols

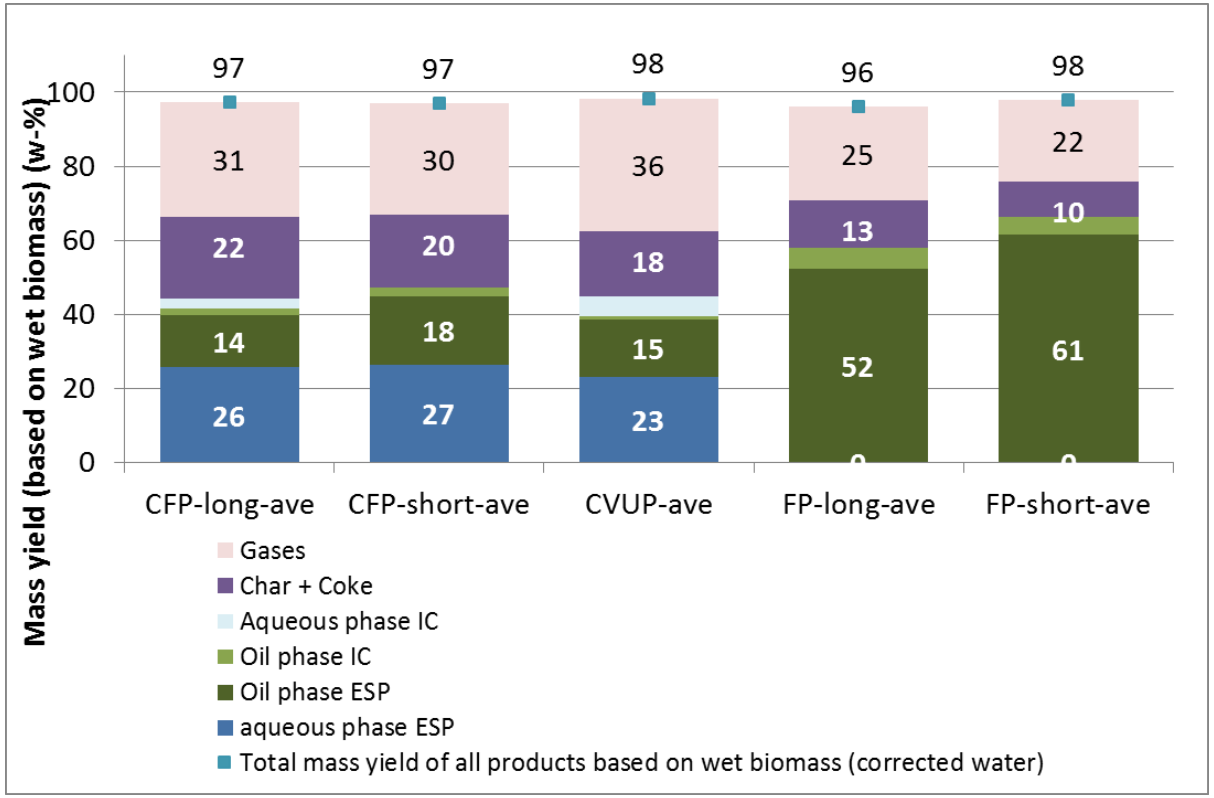
Interpretation of catalytic fast pyrolysis experiments



Aqueous phase organics (APO)
O = 50 wt%
MW = 100 Da
Mainly sugar based

Oil phase organics (OPO)
O = 35 wt%
MW = 600 Da
Mainly lignin based

Our first results with ZSM-5

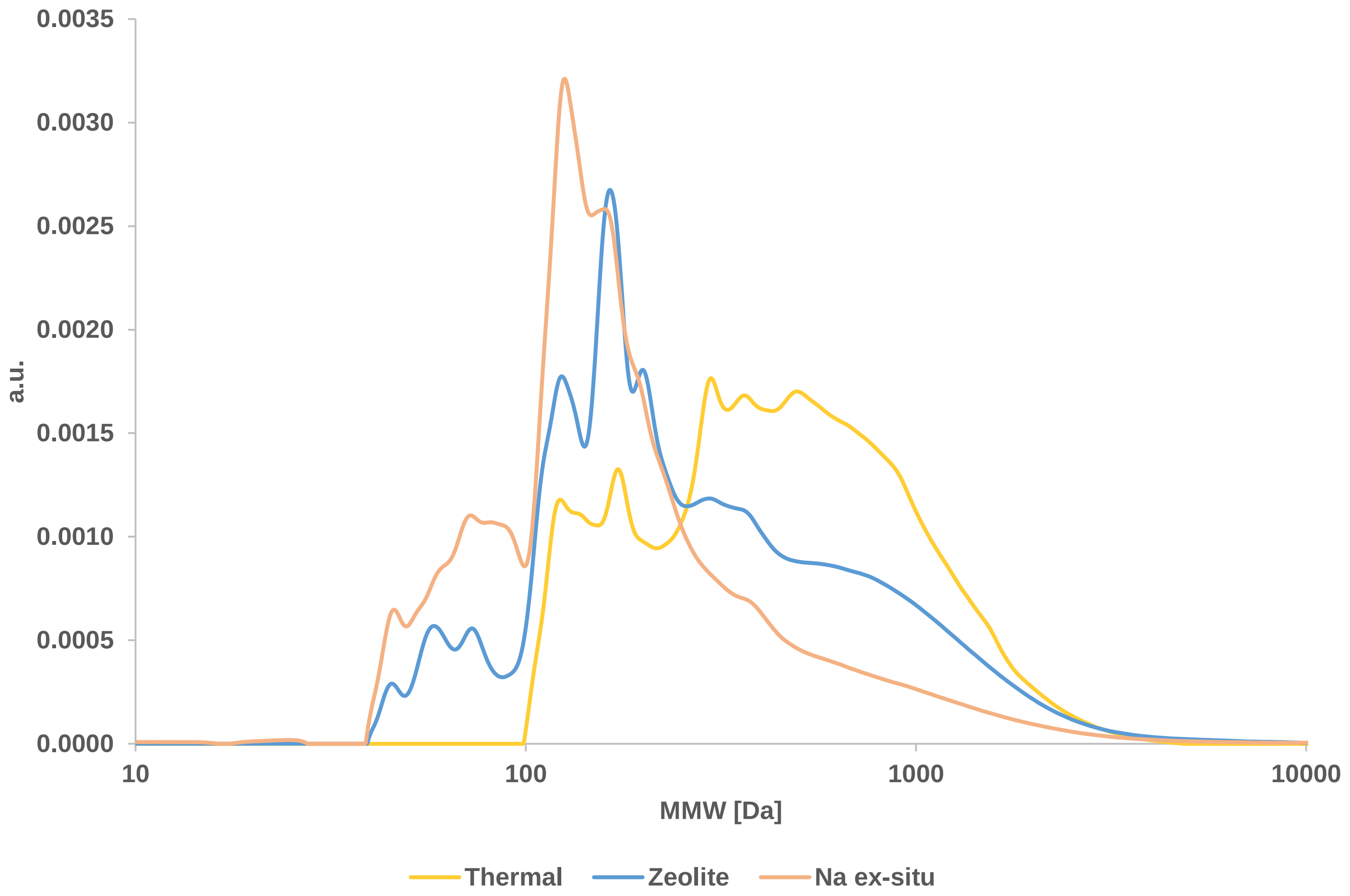


< 20 wt% oil yield

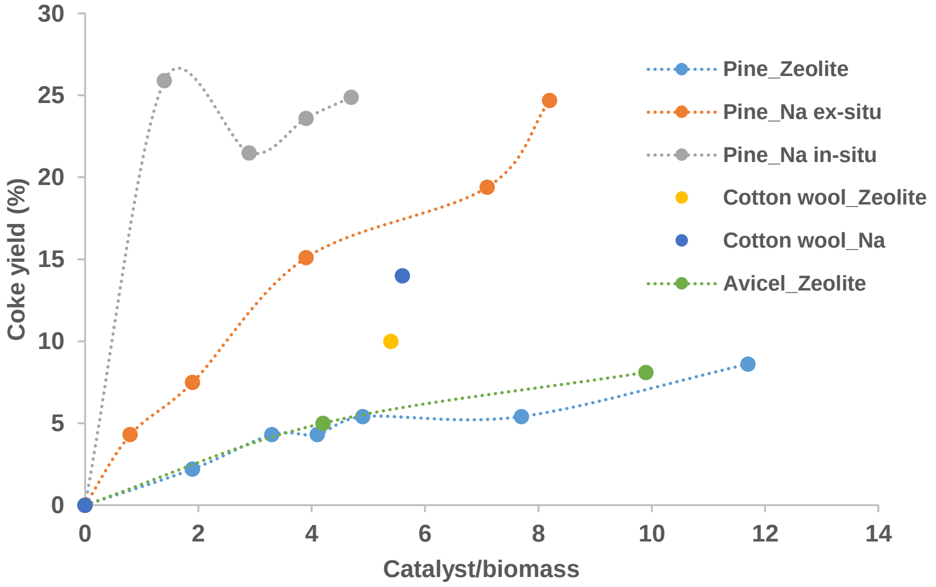
Oxygen content of 20 wt%

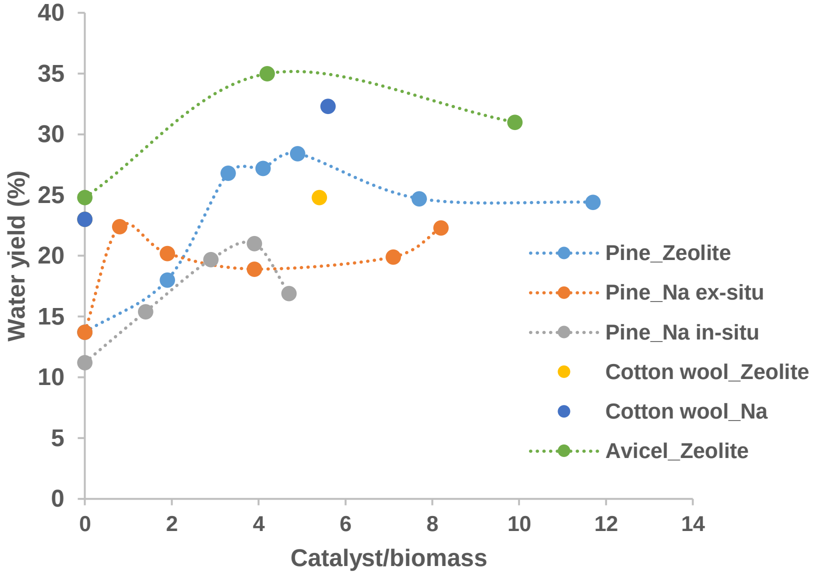
CFP and CVUP

Cracking: MWD of oils



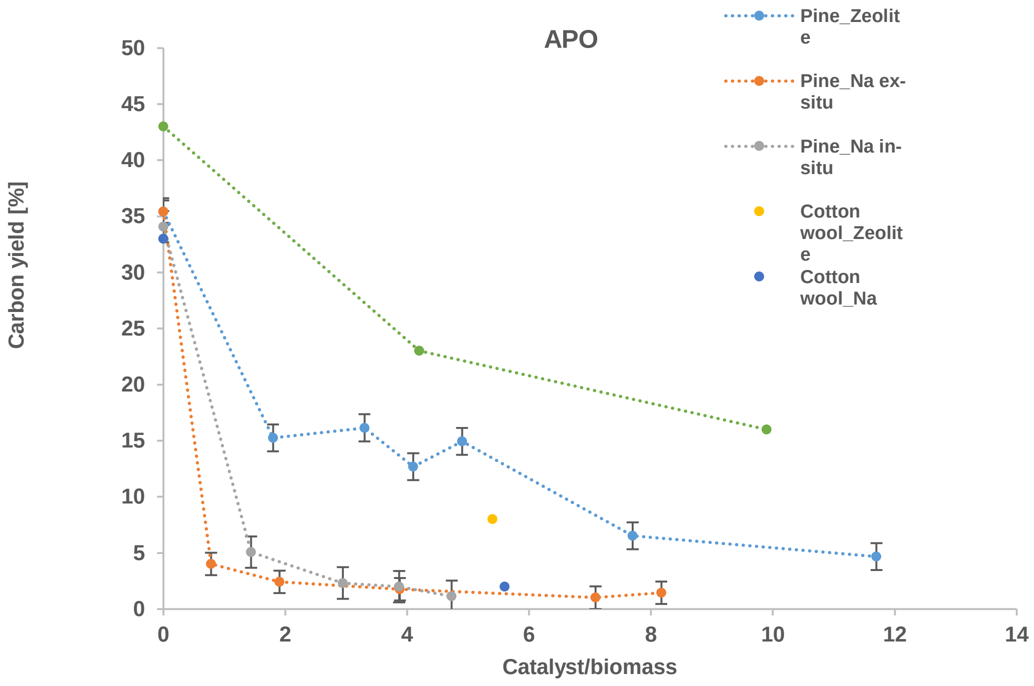
Coke, water & gas yields

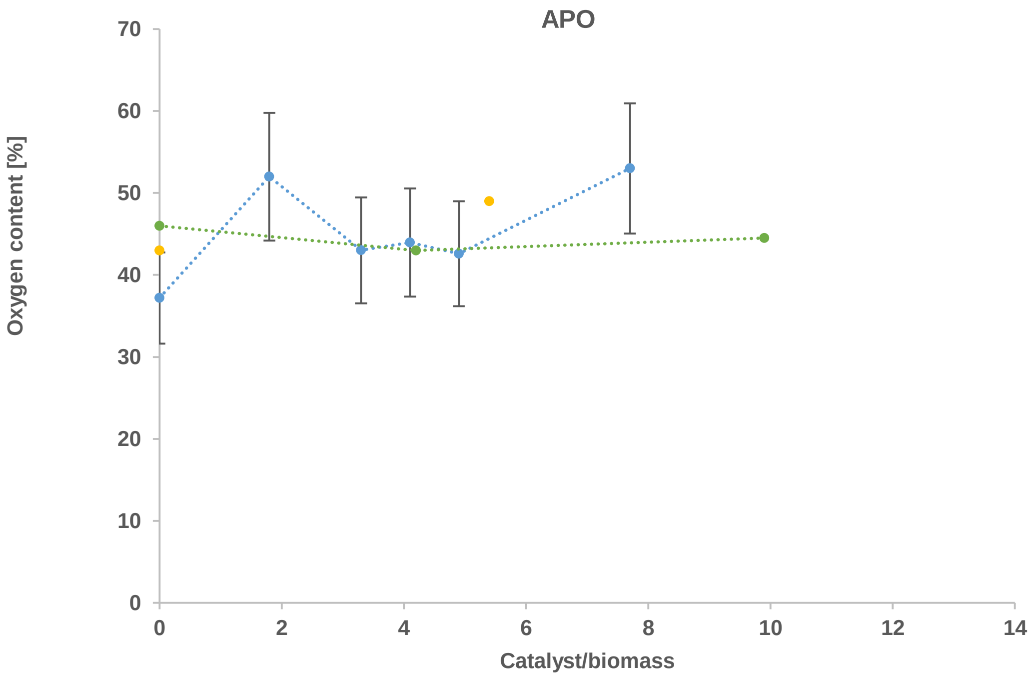




(ESD & ISD)

Yield and Oxygen % of the aqueous phase organics



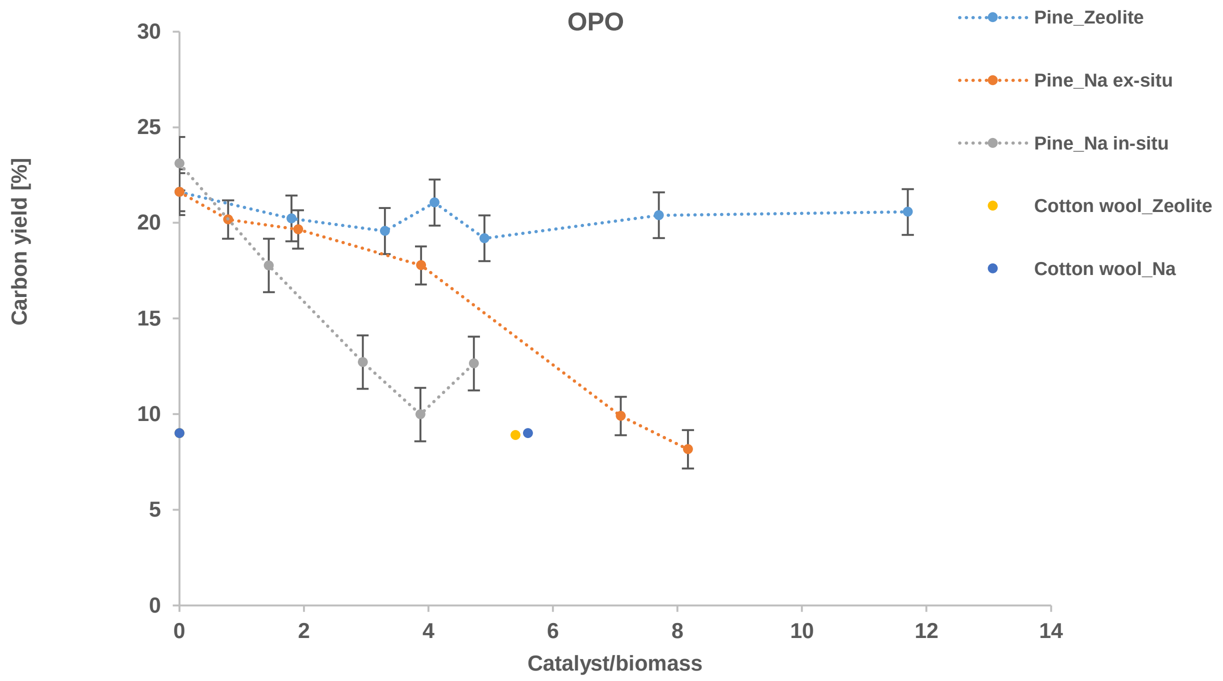


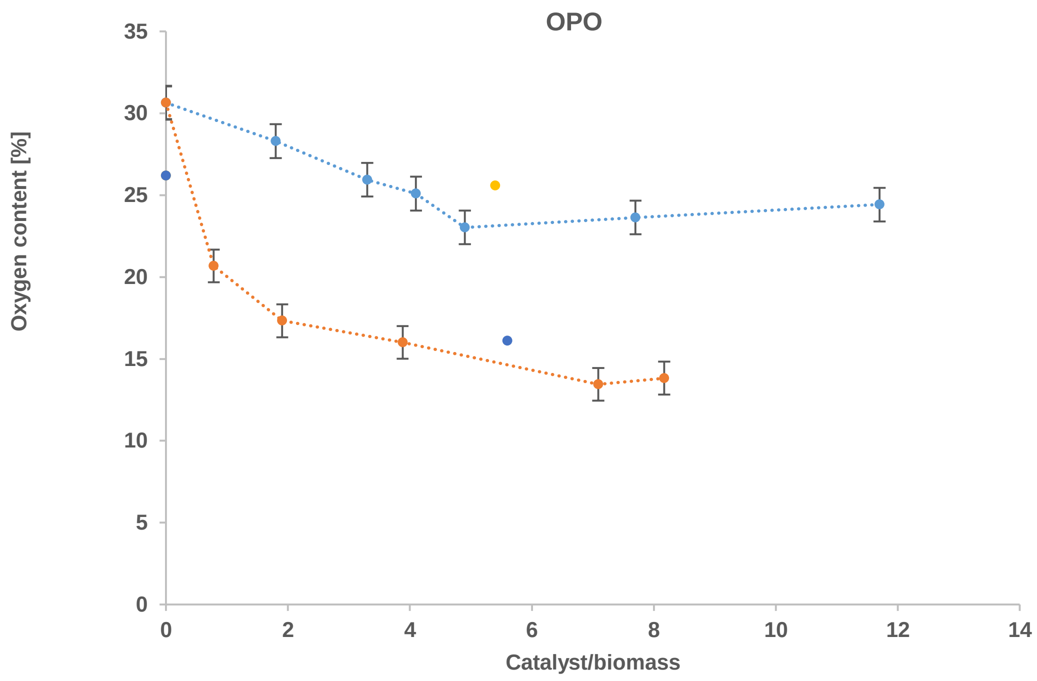
Aqueous phase organics (APO) → coke + water + gas

No de-oxyygenation of APO

(ESD & ISD)

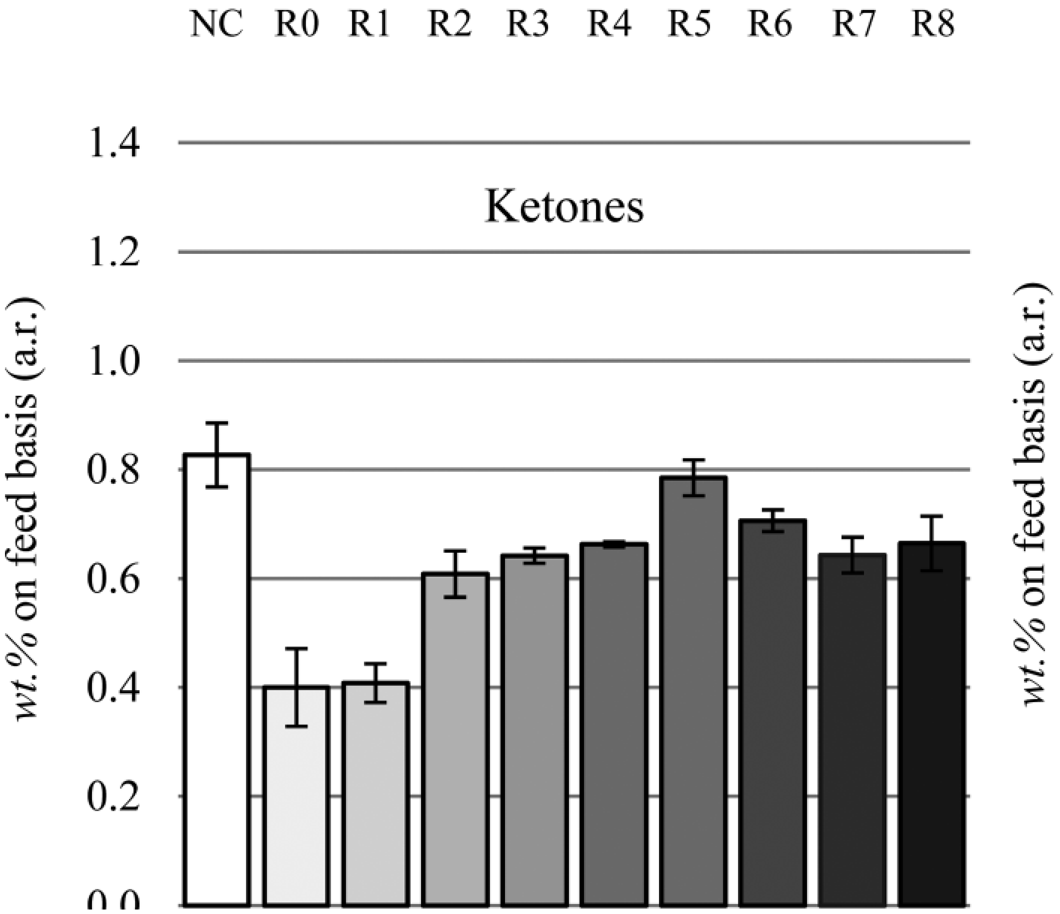
Yield and Oxygen % of the oil phase organics





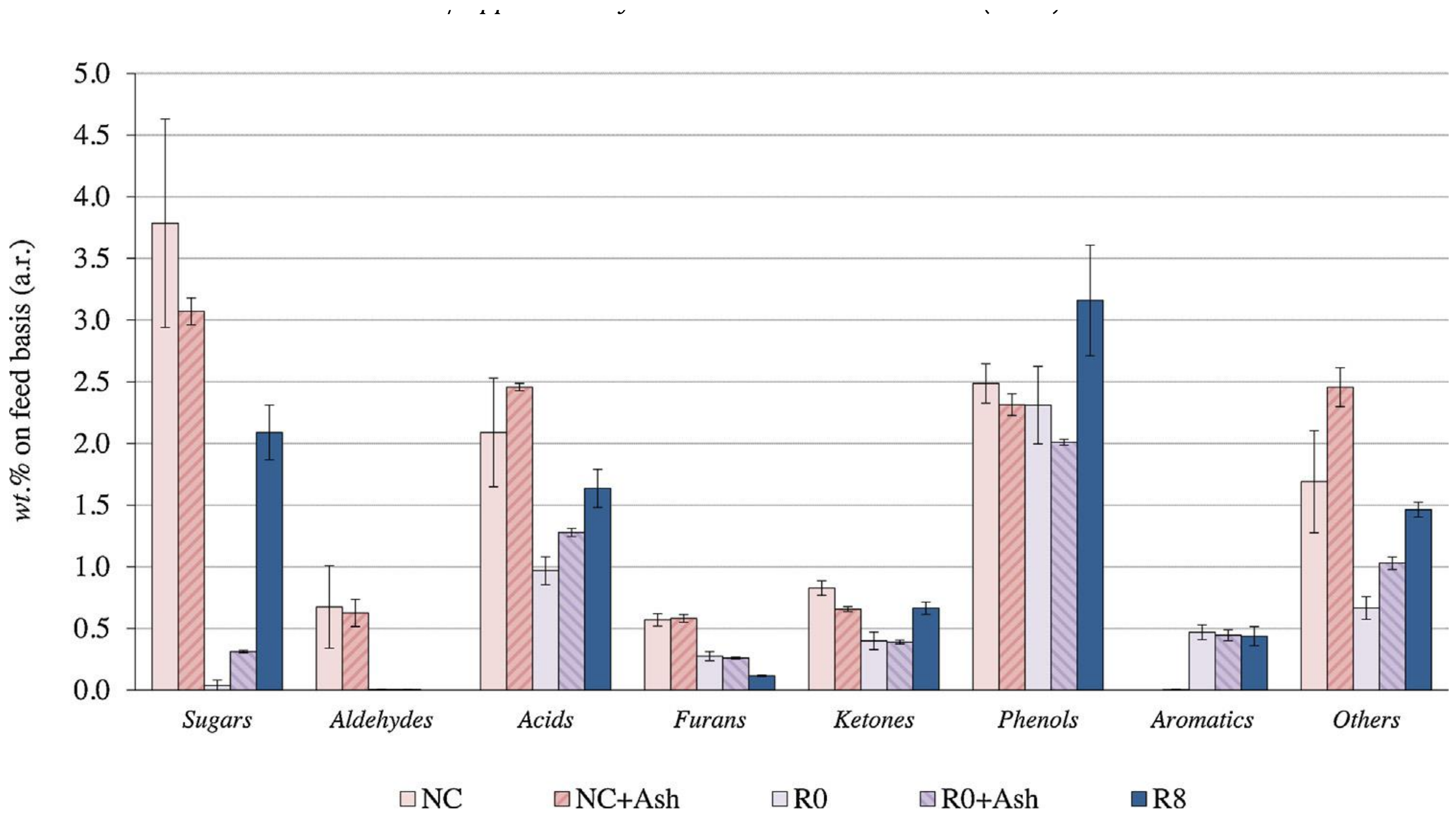
(ESD & ISD)

Conversion of sugars over regenerated ZSM-5



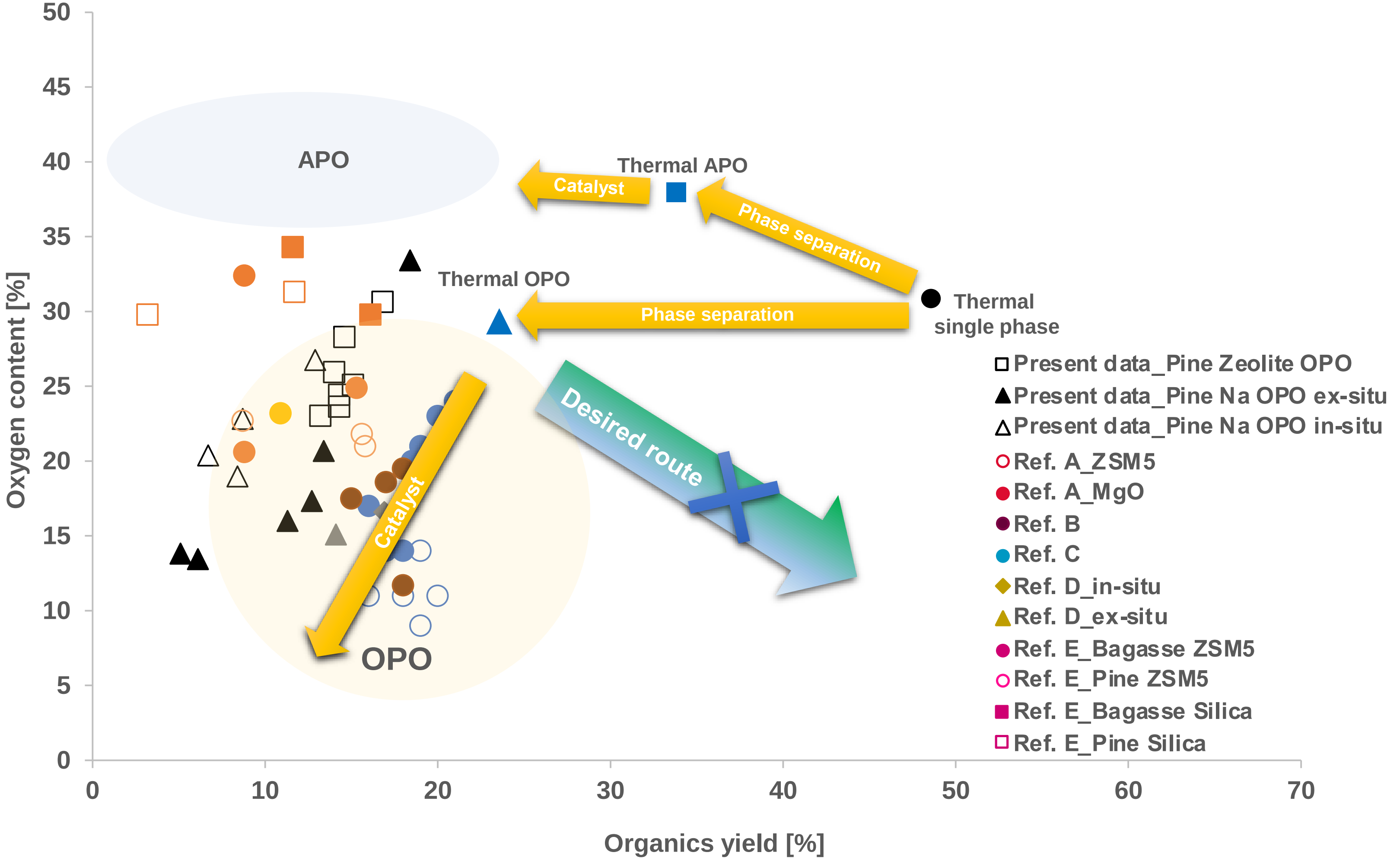
ISFB

ZSM-5 + ashes



5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
wt.% on feed basis (a.r.)
Sugars
Aldehydes
Acids
Furans
Ketones
Phenols
Aromatics
Others
NC
NC+Ash
R0
R0+Ash
R8

Catalytic pyrolysis



Take home messages

- Different reactor, different feedstocks, different contacting modes: never more that 20C% yield and lowest O content was 15% (10)

- The whole sugar fraction (2/3 of initial thermal oil) is lost to coke, water and gas.

- Only solution: new catalysis converting the sugar fraction into fuel.

... It is not easy being green...