Hydrogenation of biomass derived oxygenates to biochemicals

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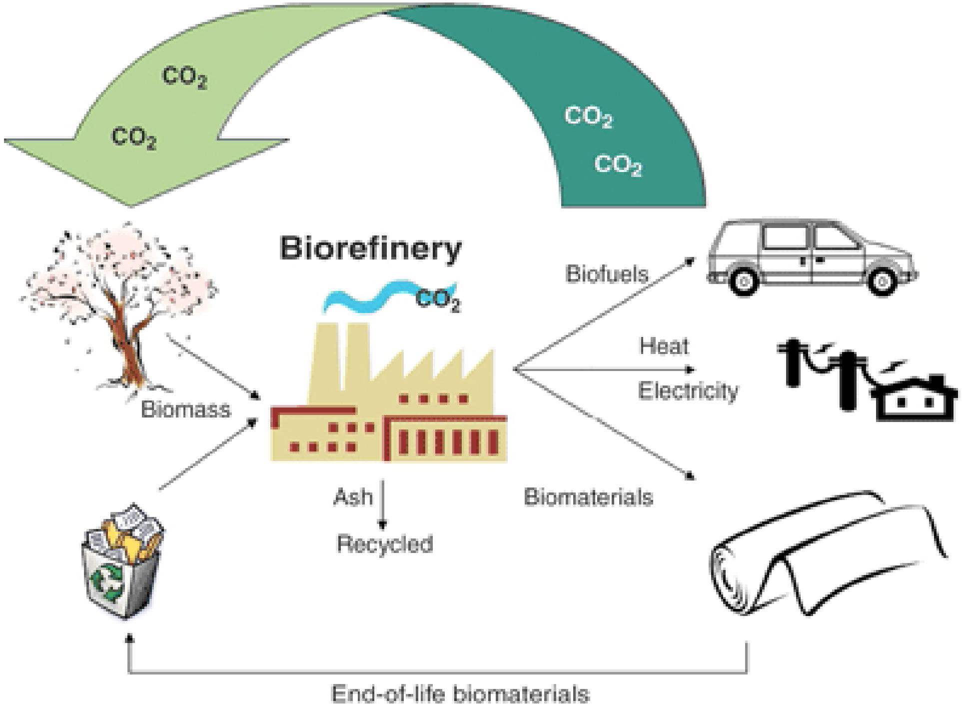
WP 2.4

BIO4FUELS

Norwegian University of Science and Technology

Biorefinery concept

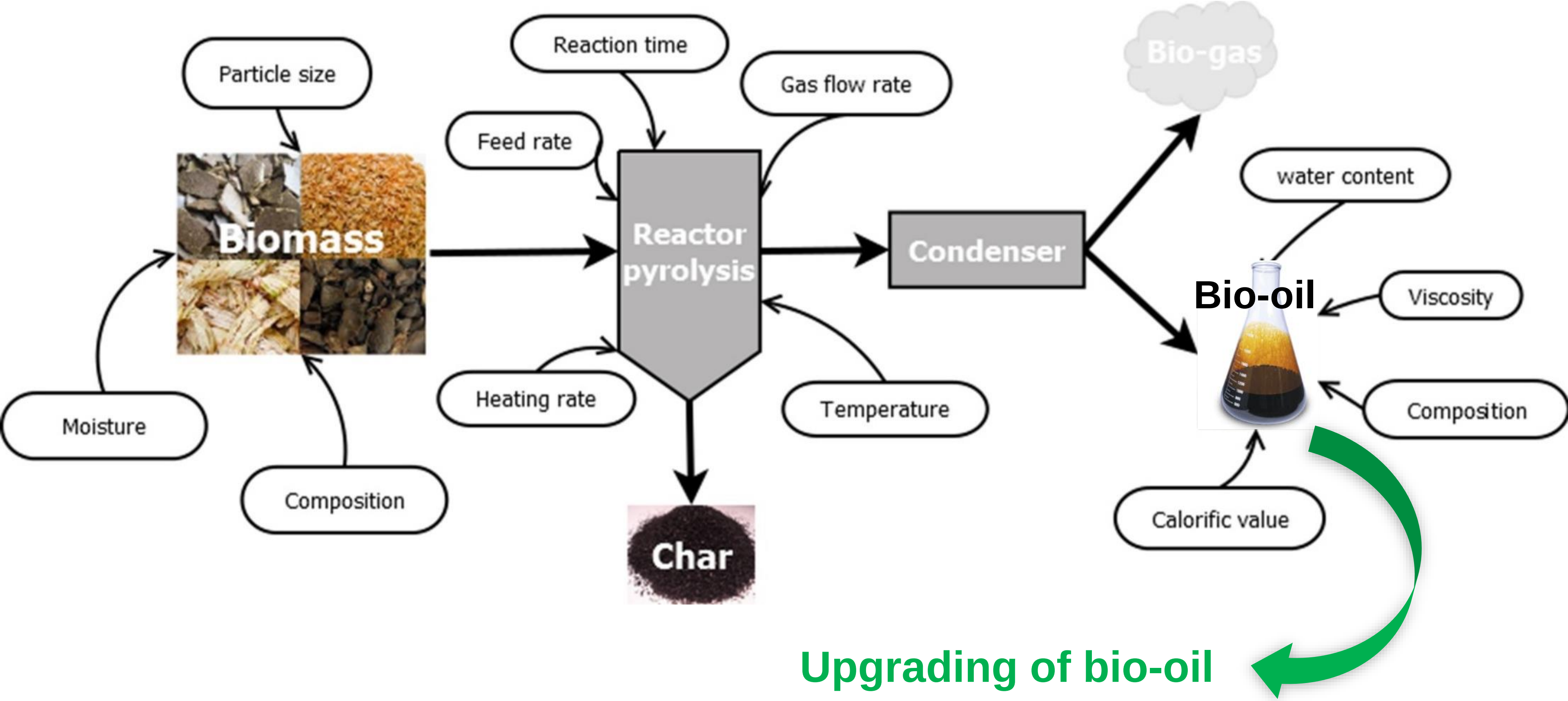


Integrated production
- Fuels
- Energy
- Chemicals
- Materials

↓

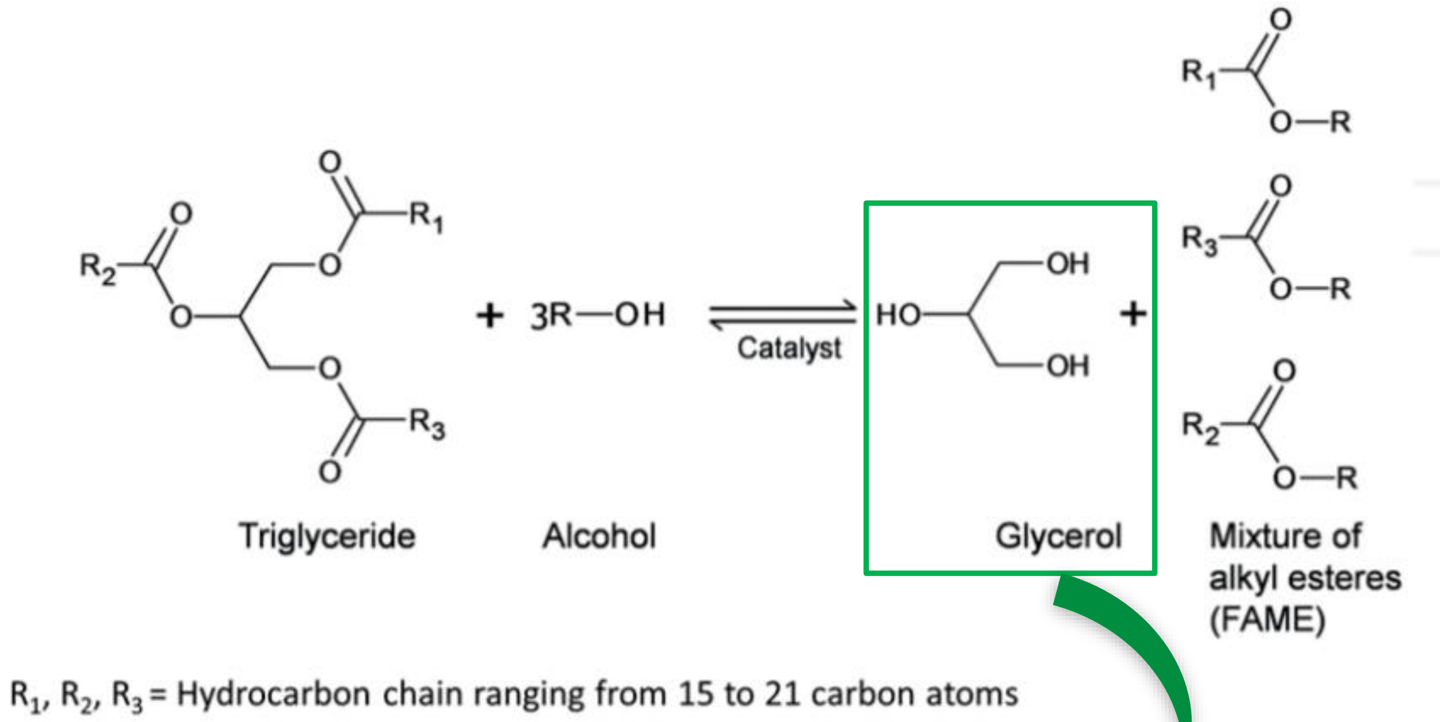
Increase
economic sustainability

Biomass pyrolysis



Raquel Escrivani Guedes, Aderval S. Luna, Alexandre Rodrigues Torres. Operating parameters for bio-oil production in biomass pyrolysis: A review. Journal of Analytical and Applied Pyrolysis, Volume 129, 2018, Pages 134-149

Trasesterification of vegetable oil for biodiesel production



Glycerol utilization

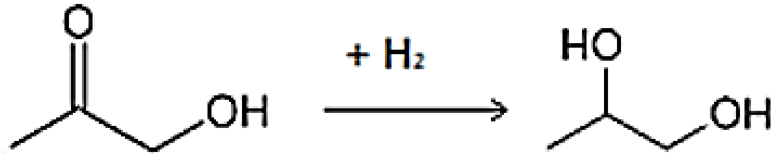
E Silva, Raphaela & Oliveira, Pâmella & Moraes, Gabriel & Alvarenga, Andre & Costa-Felix, Rodrigo. (2018). Ultrasound as a Metrological Tool for Monitoring Transesterification Kinetics. 10.5772/intechopen.70501.

Sugars cracking

Sugars → Intermediates → biochemicals

- MEG (monoethylene glycol) via hydrogenation
- MVG (methyl vinyl glycolate) via retro-aldol chemistry

Hydroxyacetone hydrogenation to 1,2-propanediol



hydroxyacetone 1,2-propanediol

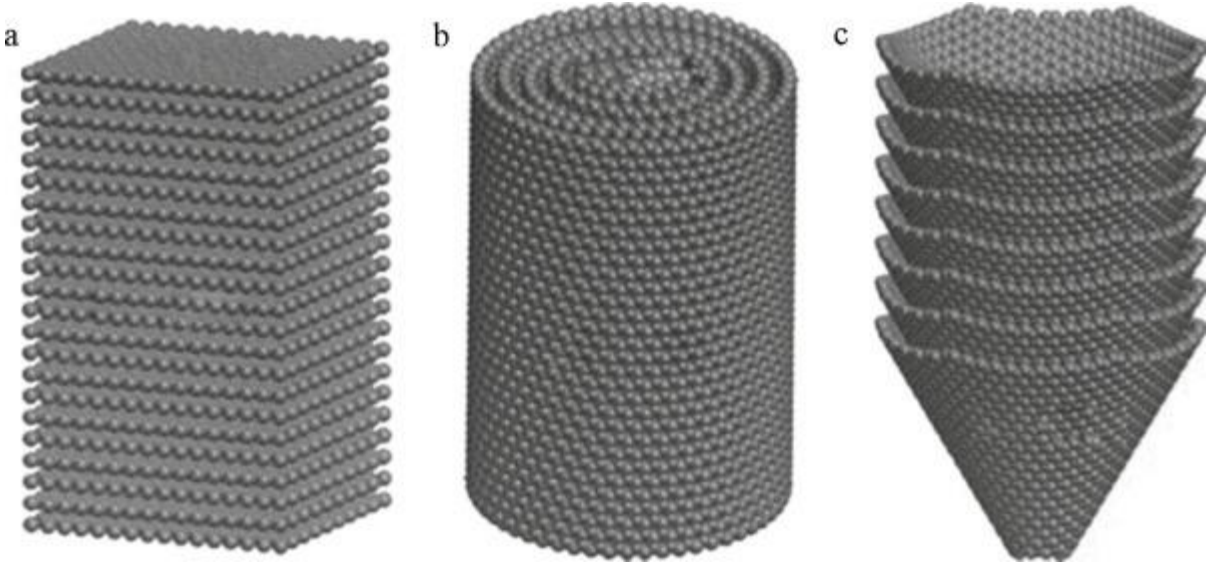
Copper catalyst

- ✓ Active
- ✓ Selective
- ✓ Stable

Catalyst preparation - *5wt% Cu*

support	*precursor*	*solvent*
SiO_2	Copper(II) nitrate $Cu(NO_3)_2$	H_2O
		EtOH
		iso-PrOH
	Copper(II) acetate $Cu(CH_3COO)_2$	H_2O
		EtOH
		iso-PrOH
	Basic Copper(II) carbonate $CuCO_3 \cdot Cu(OH)_2$	H_2O
		EtOH
		iso-PrOH

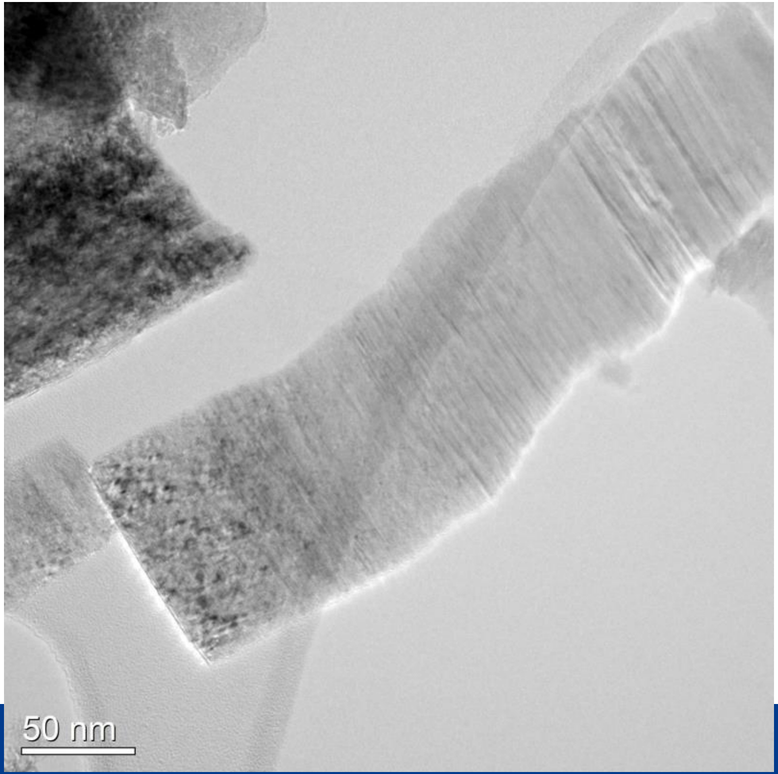
Catalyst support
Carbon Nanofibers



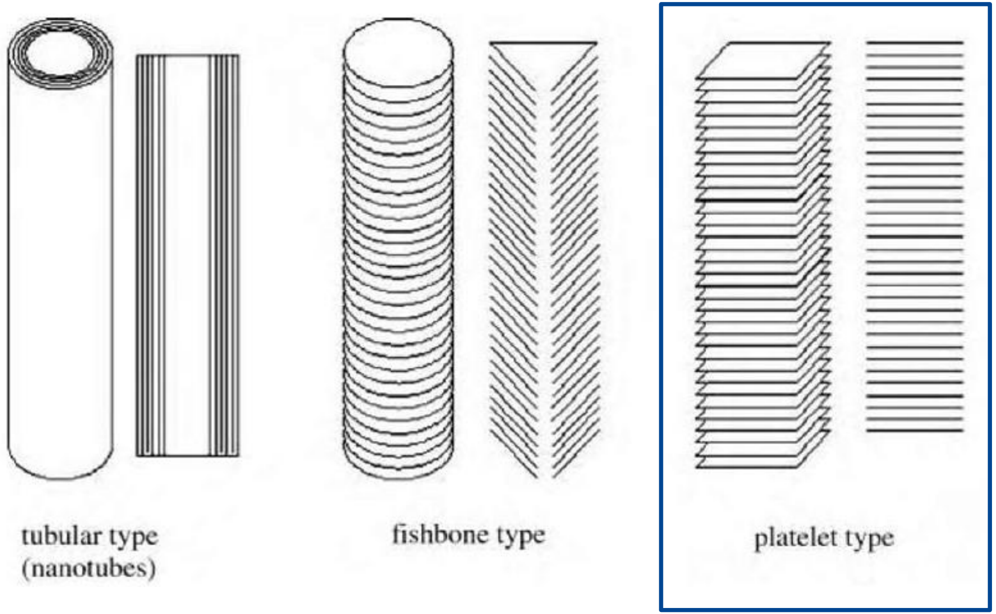
- high surface area:
  10-300 m^2/g
- large number of edges: anchoring sites for catalyst precursors
- surface properties adjusted by surface oxidation and foreign-ion doping

Catalyst support - *Carbon Nanofibers*

Platelet type



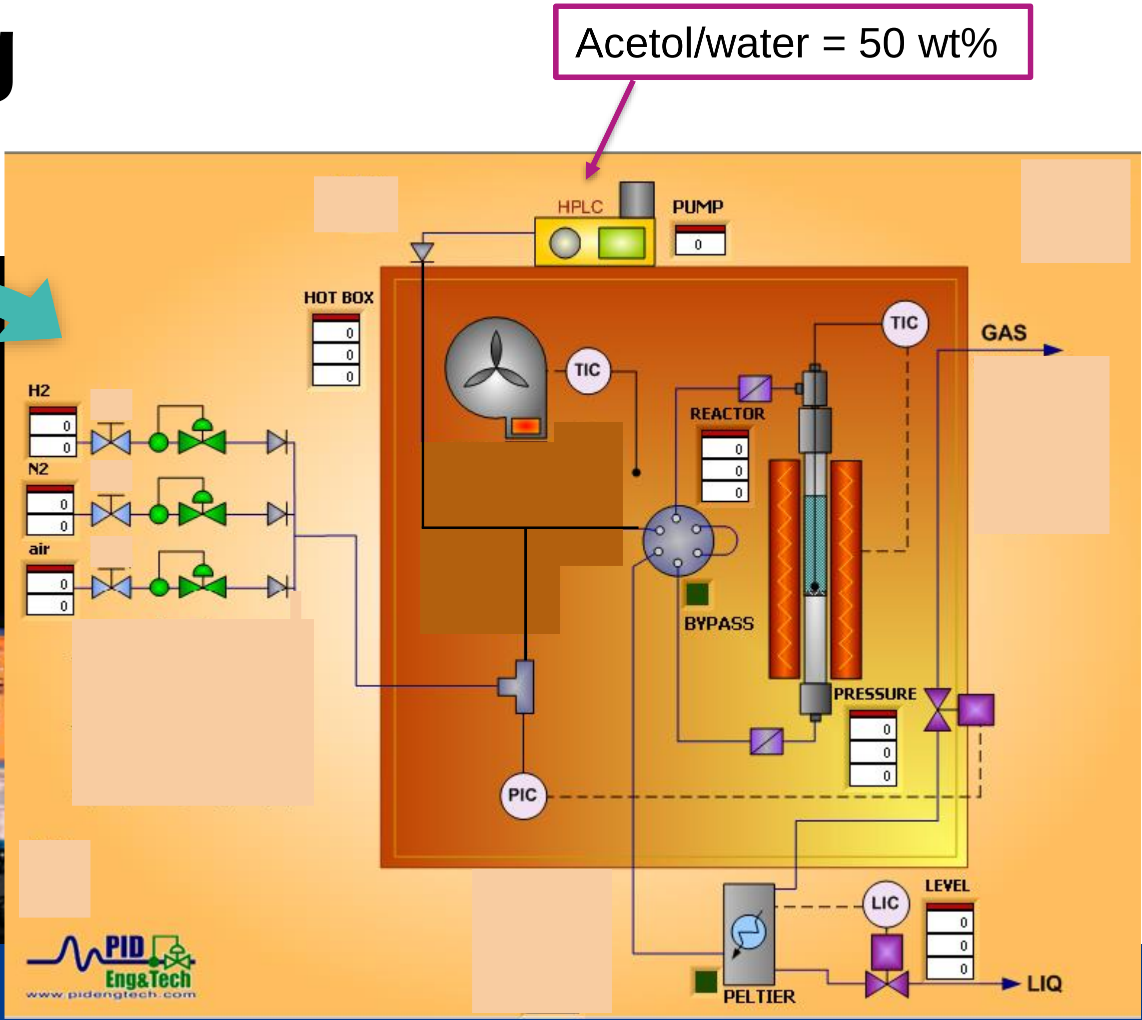
$$\frac{\textit{exposed edges sites}}{\textit{basal plane}} \text{ and basicity}$$



Catalyst preparation - *5wt%Cu*

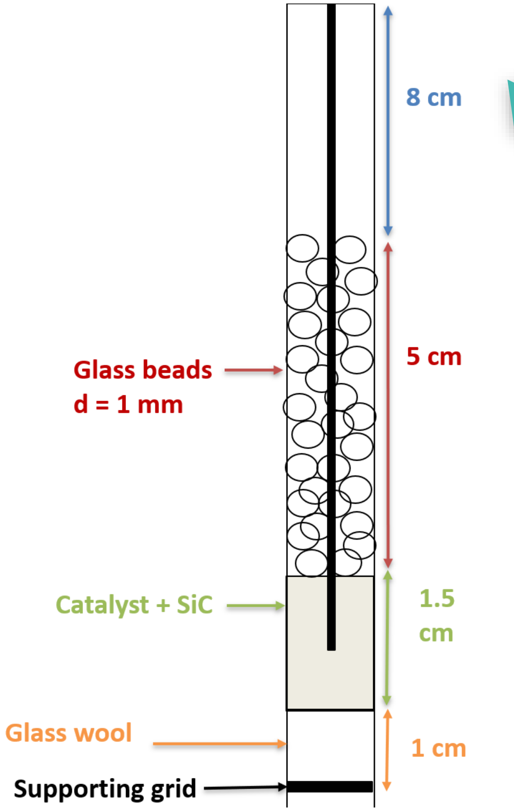
support	*precursor*	*solvent*	*CNF pretreatment*
PCNF	Copper(II) nitrate $Cu(NO_3)_2$	H_2O	/
		EtOH	/
		iso-PrOH	/
			HNO_3
			Ar @ 700°C
			HNO_3 Ar @ 700°C
			HNO_3 Ar @ 1000°C
	Basic Copper(II) carbonate $CuCO_3 \cdot Cu(OH)_2$	H_2O	/
		EtOH	/
		iso-PrOH	/

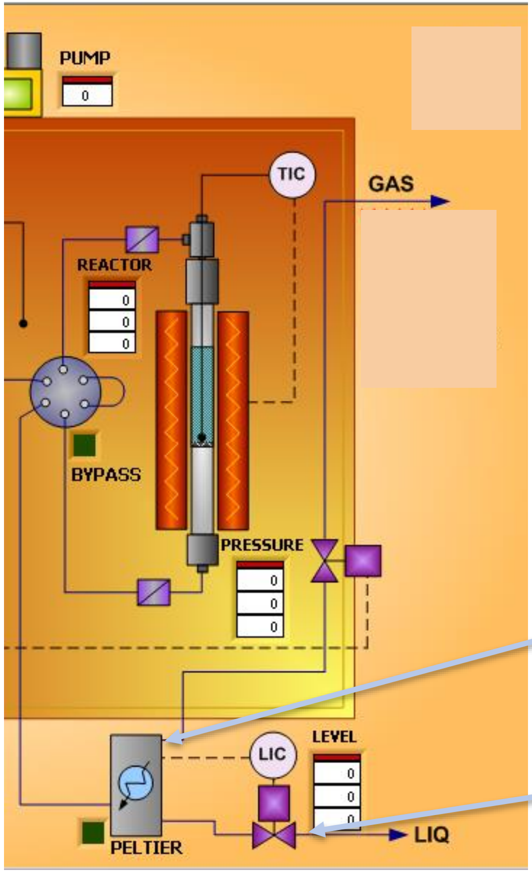
Catalyst testing



Catalyst testing

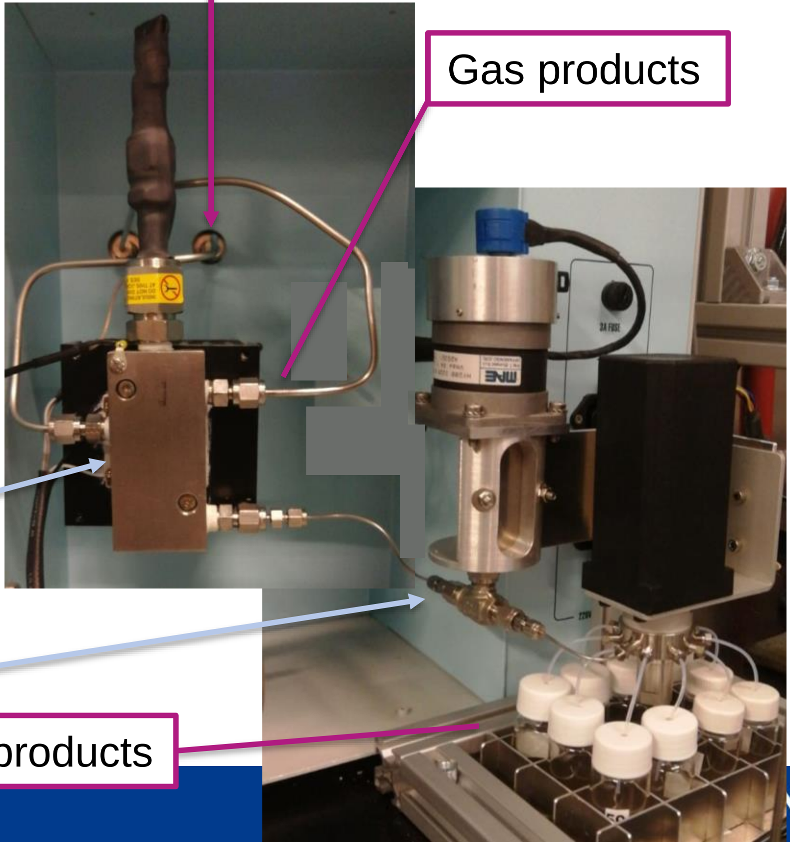
Catalyst testing





Products mixture from reactor

Gas products



Liquid products

Catalyst testing

NTNU

	Conversion		Selectivity		TOF	r	TOS	N_2O-chemisorption		*BET*		
	end	loss	start	end	end	end	end	dispersion	$d_{p,Cu}$	$S_{A,cat}$	V_{pore}	d_{pore}
					[1/h]	[mol/(h*g_{cat})]	[h]	[%]	[nm]	[m²/g]	[cm³/g]	[nm]
SNW	23%	30%	98%	97%	74.8	3.0E-03	49.5	5.0	11.6	570.2	0.8	5.5
SNE	24%	25%	97%	94%	85.9	3.3E-03	44	4.8	11.9	534.5	0.8	5.4
SNI	25%	36%	96%	95%	119.9	3.7E-03	49	3.9	14.7	529.2	0.8	5.8
SAW	30%	30%	96%	96%	128.6	3.9E-03	49	3.8	15.1	550.7	0.8	5.8
SAE	9%	28%	95%	95%	62.5	1.5E-03	49			585.0	0.9	6.8
SAI[a]	5%	0%	72%	90%		5.7E-04	47			580.5	0.8	5.7
SCW	1%	34%	41%	0%	2.8	9.3E-05	49	4.2	13.6	561.6	0.7	5.2
SCE	1%	0%	17%	39%	4.8	1.8E-04	49			523.8	0.7	5.7
CNW	17%	3%	95%	94%	27.0	2.0E-03	46	9.5	6.0	81.5	0.3	13.1
CNE[b]	11%	23%	92%	92%	8.3	1.4E-03	47	22.2	2.6	95.2	0.1	5.1
CNI	17%	0%	93%	94%	31.5	2.1E-03	46	8.4	6.8	96.0	0.1	5.1
CNI_at700[a]	31%	39%	94%	96%		3.6E-03	47					
CNI_at1000	27%	40%	96%	97%		3.0E-03	47					
CCW	1%	0%	48%	17%	3.4	1.5E-04	49	5.5	10.5	95.2	0.1	5.0
CCE	0%	35%	0%	0%		8.8E-05	49			89.4	0.1	5.0

1st letter = S/C = SiO_2 / CNF
2nd letter = N/A/C = nitrate/acetate/carbonate
3rd letter = W/E/I = water/ethanol/isopropanol

Experiments performed at 240°C, 6bar (442mbar acetol, 3.4bar H_2) for 48h
[a] 6 bar (355mbar acetol, 3.3 bar H_2)
[b] 7bar (515 mbar acetol, 4 bar H_2)

	Conversion		Selectivity		TOF	r	TOS	N_2O-chemisorption		*BET*		
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SAW	30%	30%	96%	96%	128.6	3.9E-03	49	3.8	15.1	550.7	0.8	5.8
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CCW	1%	0%	48%	17%	3.4	1.5E-04	49	5.5	10.5	95.2	0.1	5.0
CCE	0%	35%	0%	0%		8.8E-05	49			89.4	0.1	5.0

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Catalysts screening

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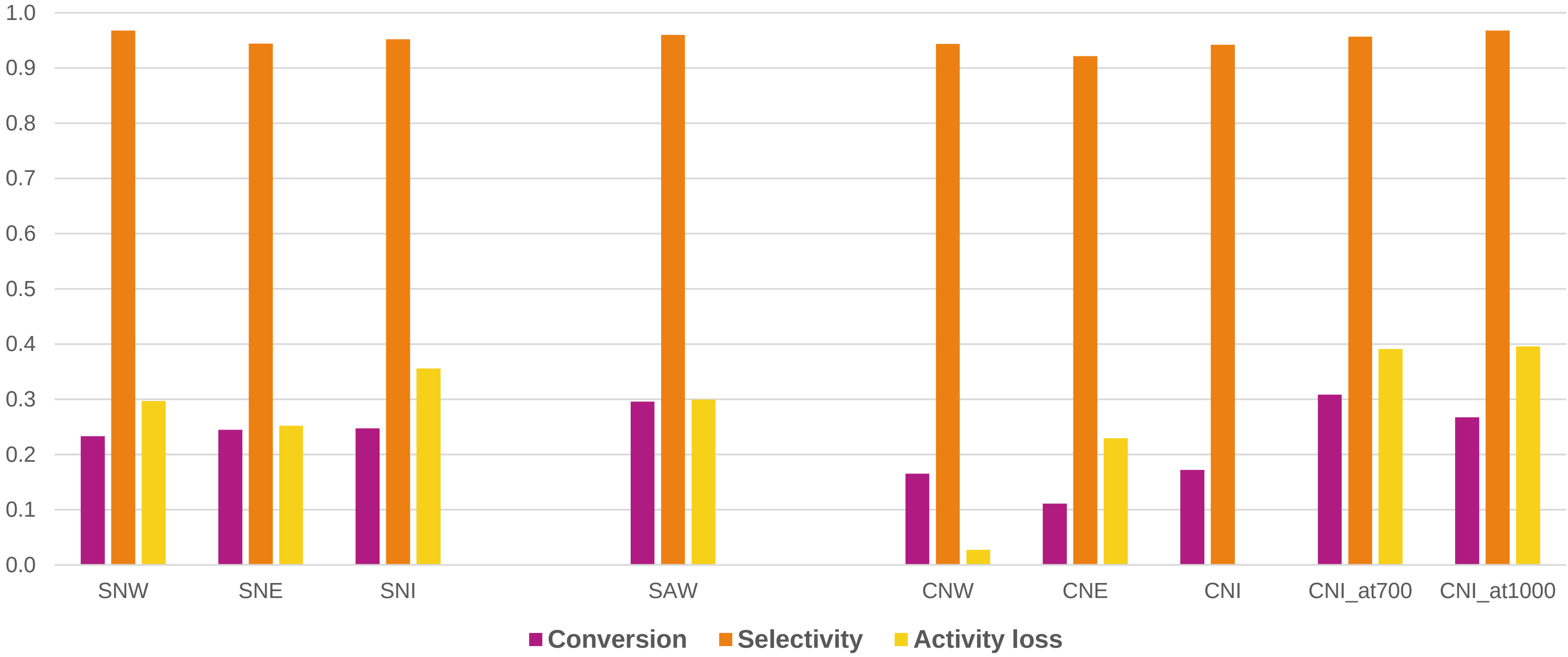
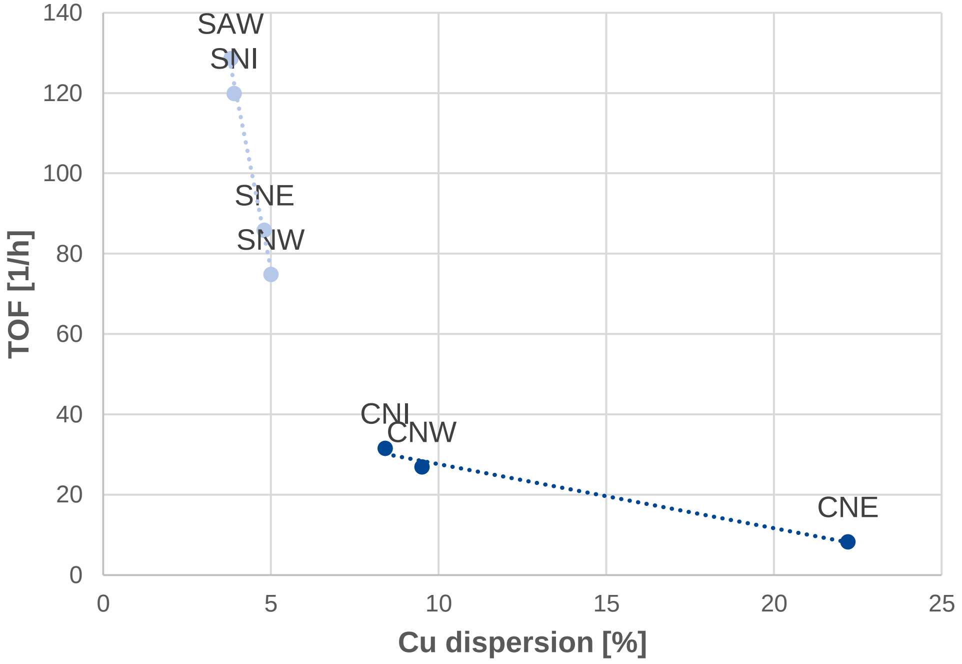


Catalysts screening
Activity vs. dispersion

1st letter = S/C = SiO_2 / CNF
2nd letter = N/A/C = nitrate/acetate/carbonate
3rd letter = W/E/I = water/ethanol/isopropanol



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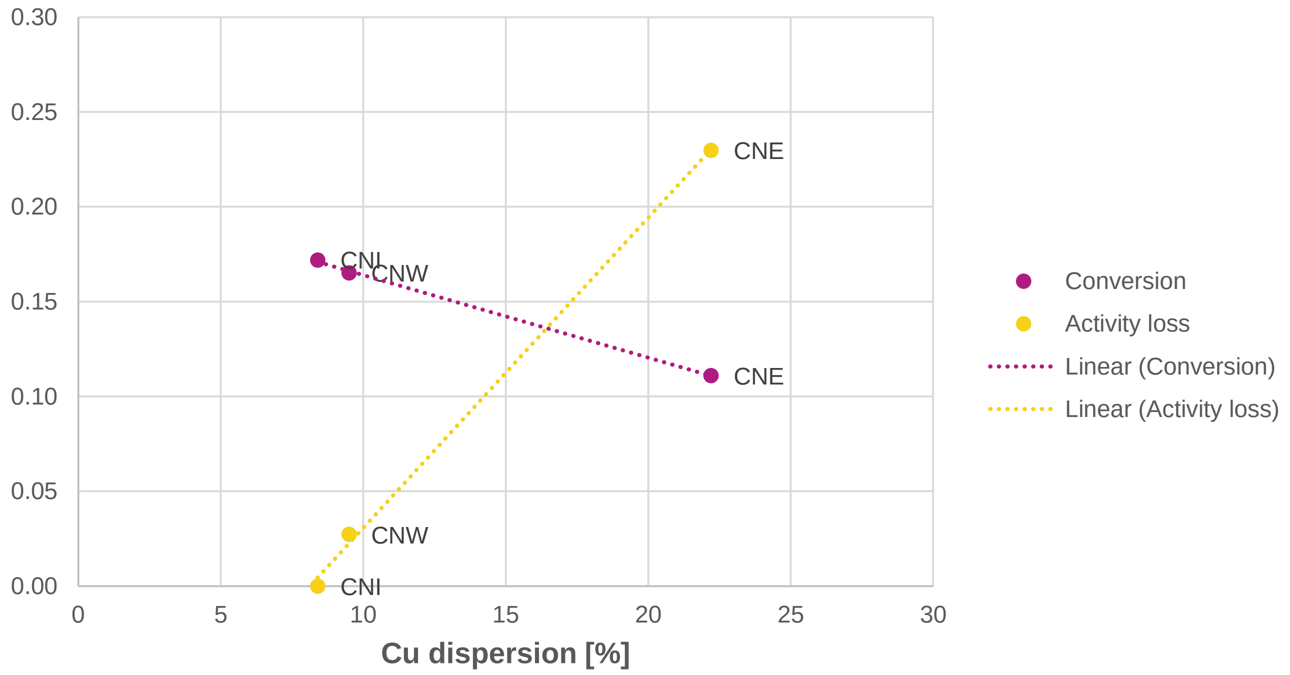
Catalysts screening
Activity and activity loss

1st letter = S/C = SiO_2 / CNF
2nd letter = N/A/C = nitrate/acetate/carbonate
3rd letter = W/E/I = water/ethanol/isopropanol



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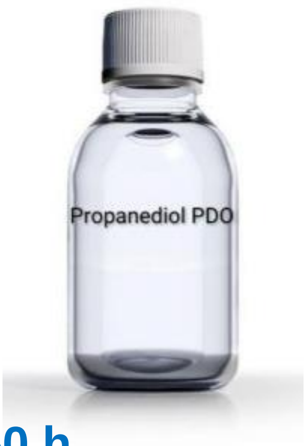
Highlights of WP2.4 Catalysis

New Cu catalyst developed



Active, high selectivity (>95%)
Stable: no deactivation observed within 50 h

- ✓ Fundamental understanding of Cu catalysts in terms of particle size and support effects on the reaction
- ✓ Kinetic model of acetol hydrogenation

Future work

Preparation

Catalysts with higher Cu loading (15wt%)

Characterization

Complete properties study

Testing

- Selectivity study at higher conversion levels
- DMO hydrogenation

Writing

Publications and PhD thesis

Thank you!