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Catalytic hydrodeoxygenation of pyrolysis oil over nickel-based catalysts under H_2/CO_2 atmosphere

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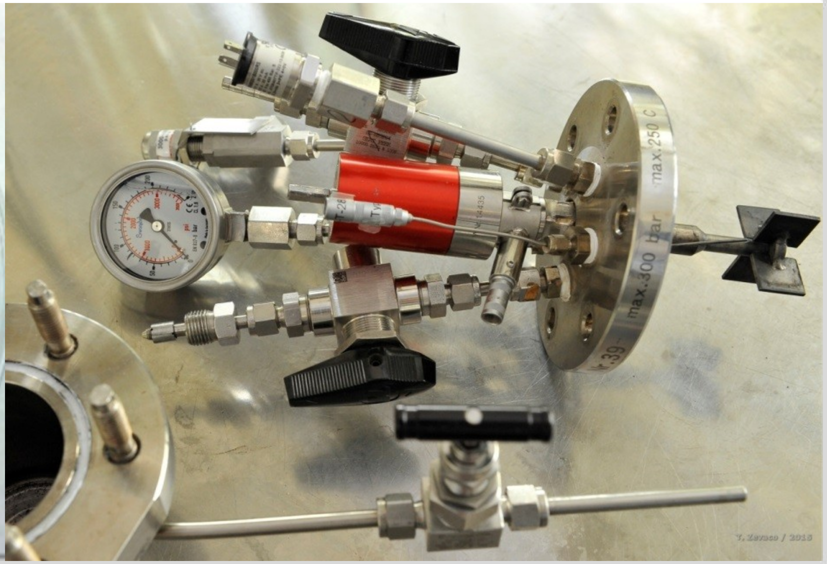
Institute of Catalysis Research and Technology (IKFT)



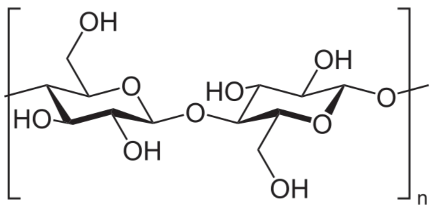


Contents

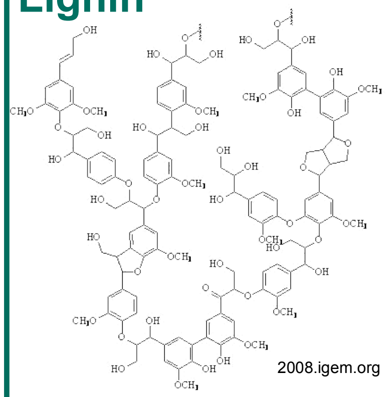
Renewable energy and fuels: fast pyrolysis oil

Biomass

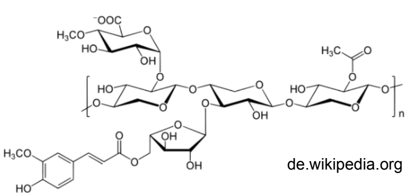
Cellulose



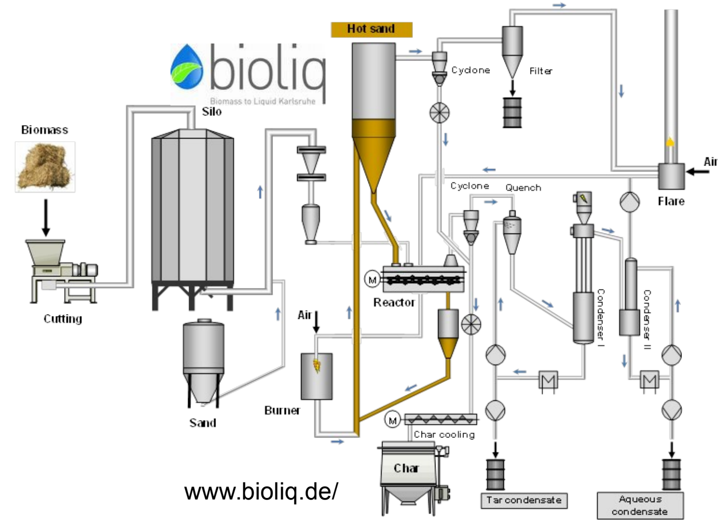
Lignin



Hemicellulose



FAST PYROLYSIS



- *short hot vapor **residence time** (typically **less than about 5 s**)*
- *typically at between **450 – 600 °C***
- ***at near atmospheric pressure** or below,*
- *in the **absence of oxygen.***

Fast pyrolysis oil

Circa 300 species detected

Common organic components include:

honeywellnow.com

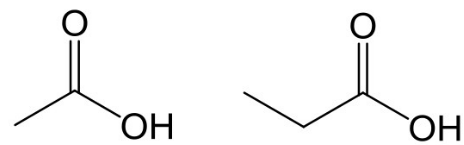
Bio-oil is a ***complex mixture*** *of* ***oxygenated hydrocarbon fragments derived from the biopolymer structures.***

Water

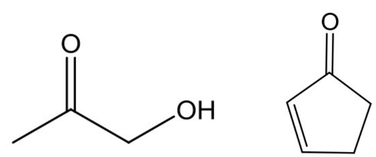
Alcohols

H_3C-OH

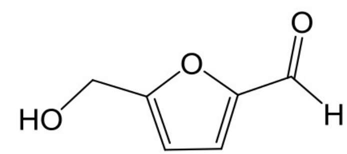
Carboxylic acids



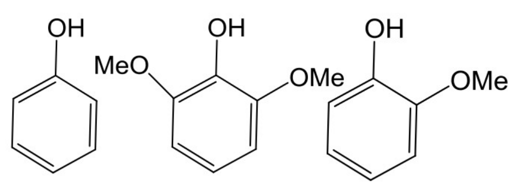
Ketones



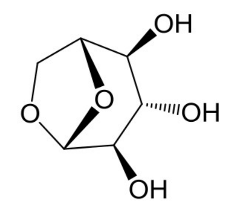
Aldehydes



Lignin derivatives



Sugar derivatives



+ pyrolytic lignin, sugars oligomers, etc.

Fast pyrolysis oil

honeywellnow.com

*Bio-oil is a **complex mixture** of **oxygenated hydrocarbon fragments derived from the biopolymer structures**.*

Problems for the direct use of bio-oil:

- High content of water
- Acidity
- Low heating value
- Phase instability

Upgrading is required for some applications

Pyrolysis oil production and characterisation

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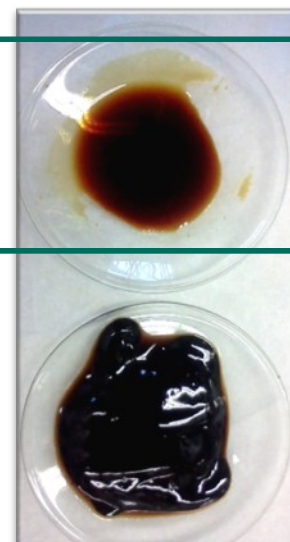
Straw

500°C

Fast Pyrolysis
in bioliq® plant
(Karlsruhe)

bioliq
Biomass to Liquid Karlsruhe

Phase separation



Light phase

Heavy phase

Advantages to work with **light phase:**

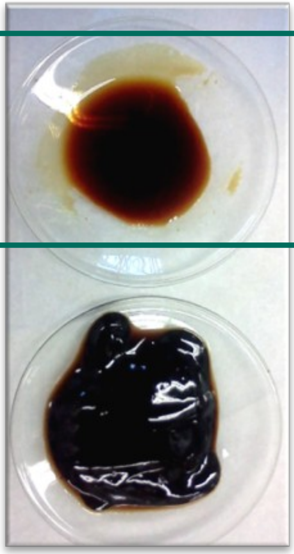
- One phase
- No solids
- Simpler system to follow the HDO reaction

Pyrolysis oil production and characterisation

500°C

Fast Pyrolysis in bioliq® plant (Karlsruhe)

Phase separation



Light phase

Heavy phase

Composition

- Water: 56.5 wt%
- pH around 4
- $C_1 H_{1,90} O_{0,64}$ (40% wt oxygen, dry basis)
- HHV: 9.2 MJ/kg (wet basis)

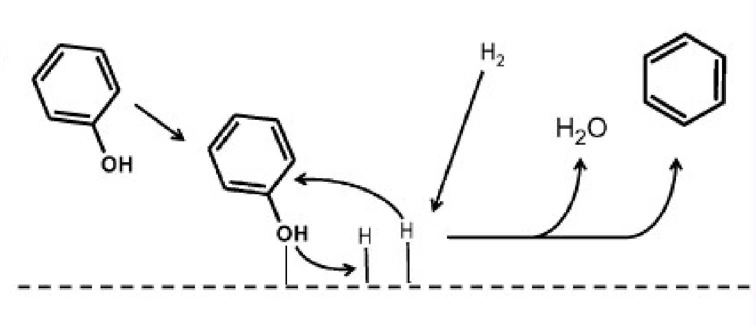
Upgrading of a bio-oil: hydrodeoxygenation

$$CH_xO_y + (1+y-x/2)\ H_2 \rightarrow 1\ \text{"}CH_2\text{"} + y\ H_2O$$

Complete HDO...

- decreases the oxygen content of the bio-oil;
- increases the heating value and the stability;
- permits to obtain an upgraded product of higher quality which is more similar to a fossil fuel.

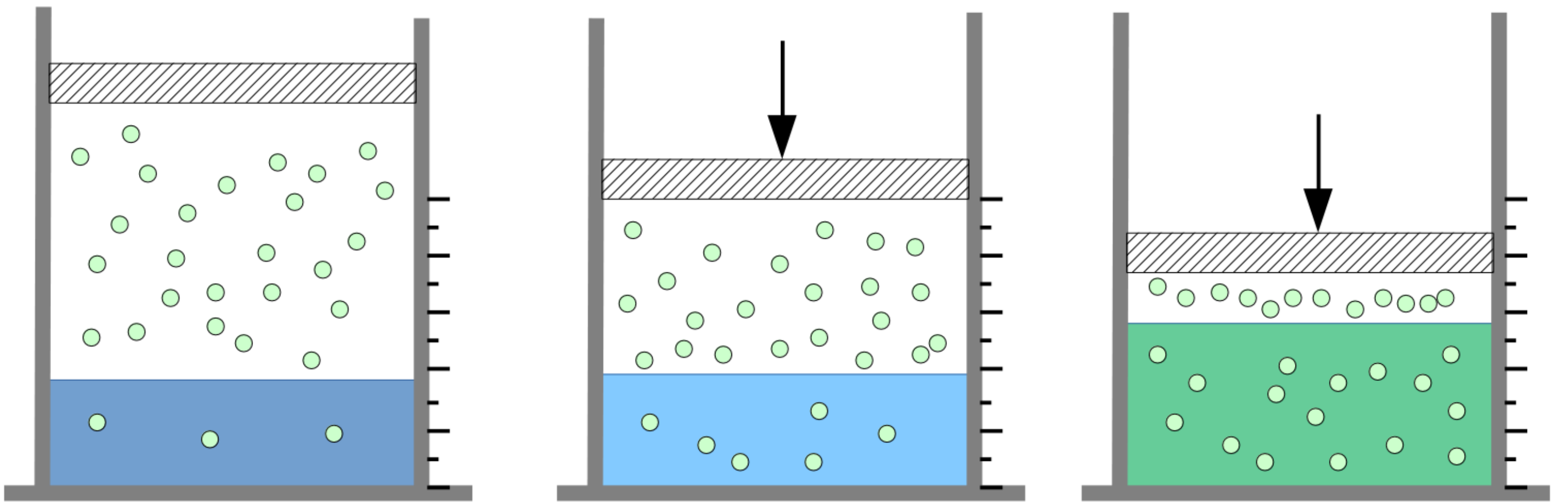
HDO (H_2 pressure 150-400 bar)	
Stabilisation or mild HDO	Temperature up to 250°C
Deep HDO	Temperature up to 400°C



Mortensen, P. M., Grunwaldt, J.-D., Jensen P. A., Jensen A. D. A C S Catalysis, Vol. 3, No. 8, 2013, p. 1774-1785

Gas expansion with CO_2

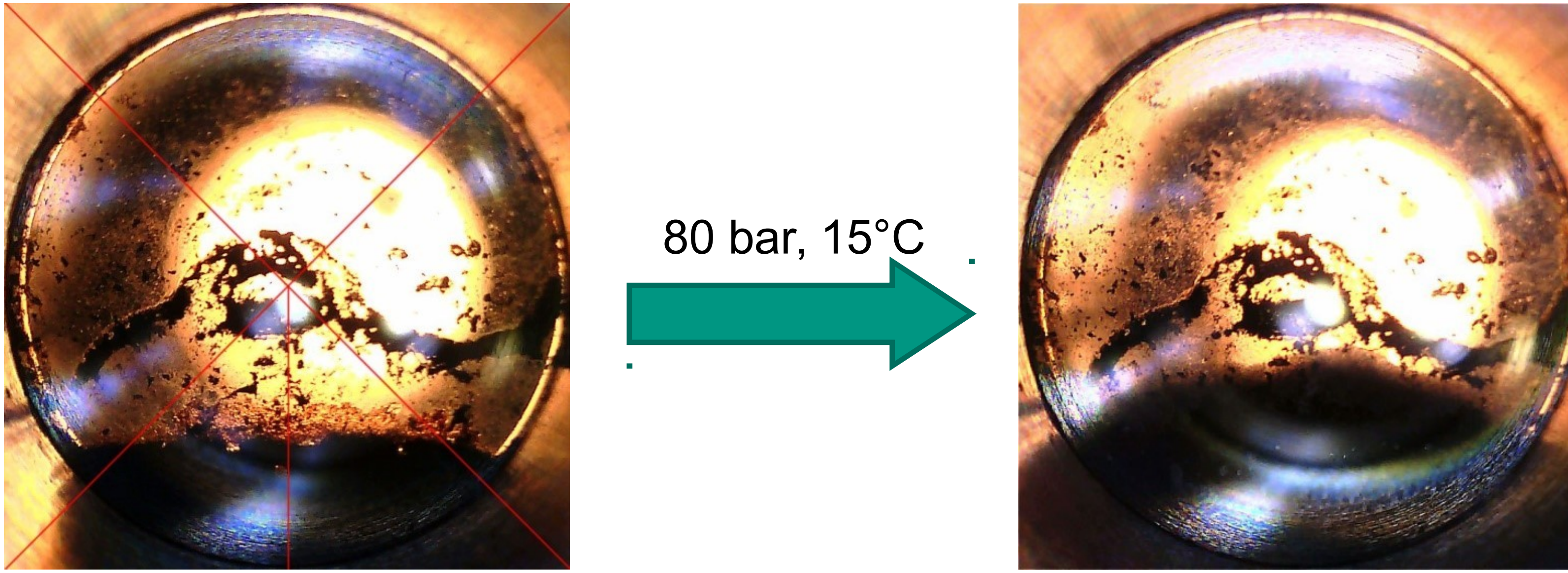
Under near critical conditions the solubility of a gas in a liquid can increase by several orders of magnitude. The liquid undergoes significant changes in properties.



→ ***gas expanded liquid (GXL)***

→ **improved properties like diffusion & viscosity help to overcome transport limitations in heterogeneous catalysis**

Gas expansion with CO_2



H. Zang, „Chemical and physical behavior of Pyrolysis oil in a CO2 atmosphere at elevated pressure and temperature“, Karlsruhe Institute of Technology, Karlsruhe, 2015.

Influence of CO_2 on the viscosity of pyrolysis oil at 52°C:

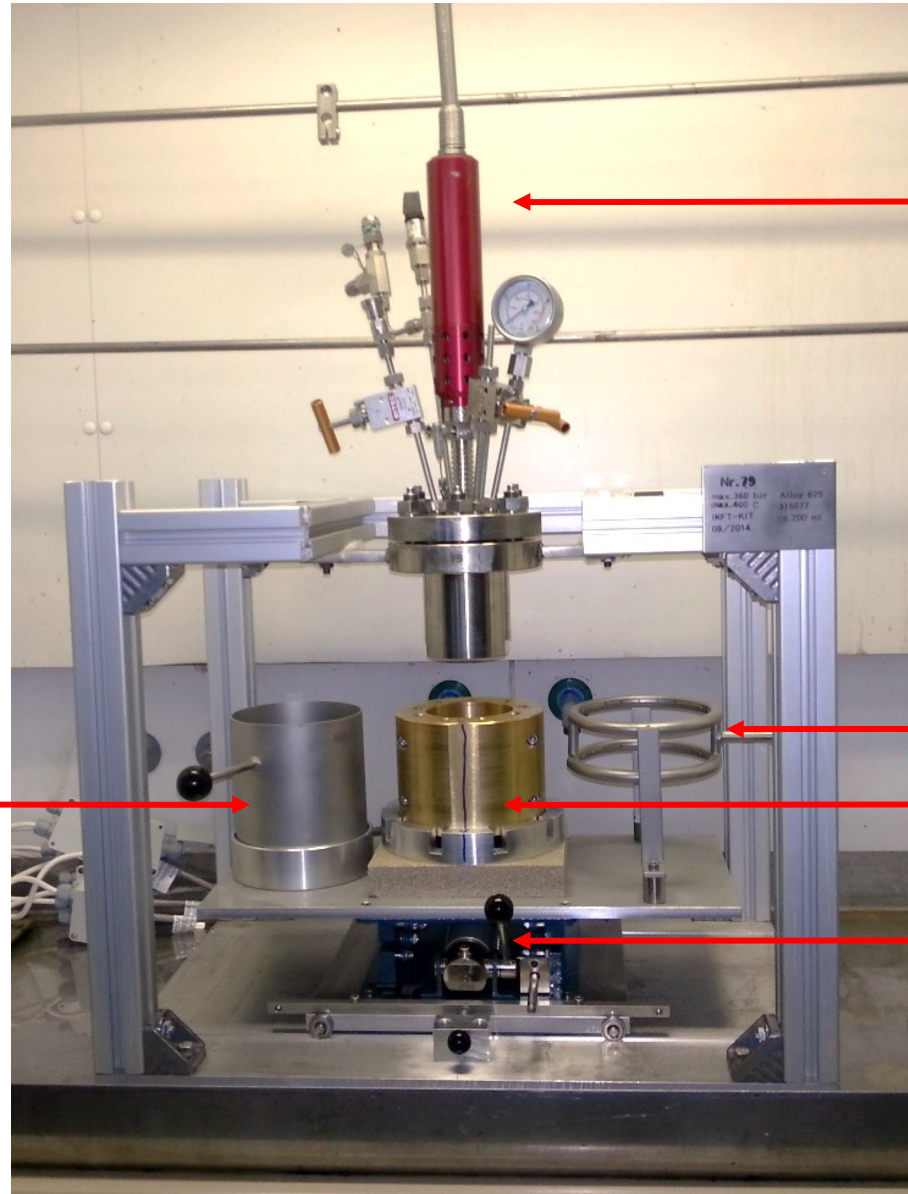
→ at 5 bar the viscosity decreases by 30%

→ at **40 bar** the viscosity decreases **by 60%**.

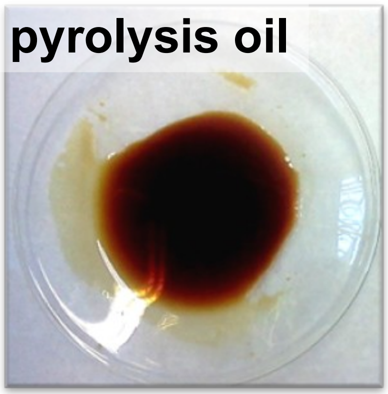
CO_2 and pyrolysis oil form a promising system for GXL-enhanced catalysis.

HDO autoclave

- Max temperature 400°C, max pressure 360 bar
- Labview program to control and record the temperature



HDO experiments



- CO_2 (0 / 20 / 40 bar at RT)
- H_2 added to total pressure of 80 bar at RT
- 250°C or 340°C

- 2 h reaction time in batch autoklave
- catalyst: Ni/Al2O3 Ni-loading = 20%

products

aqueous phase (80-82%)

oil phase (7-9%)

+ gases, (<2%)

+ solids (<2%)

Analysis of the products

Aqueous phase

Oil phase

Gas

Aqueous phase and oil phase:

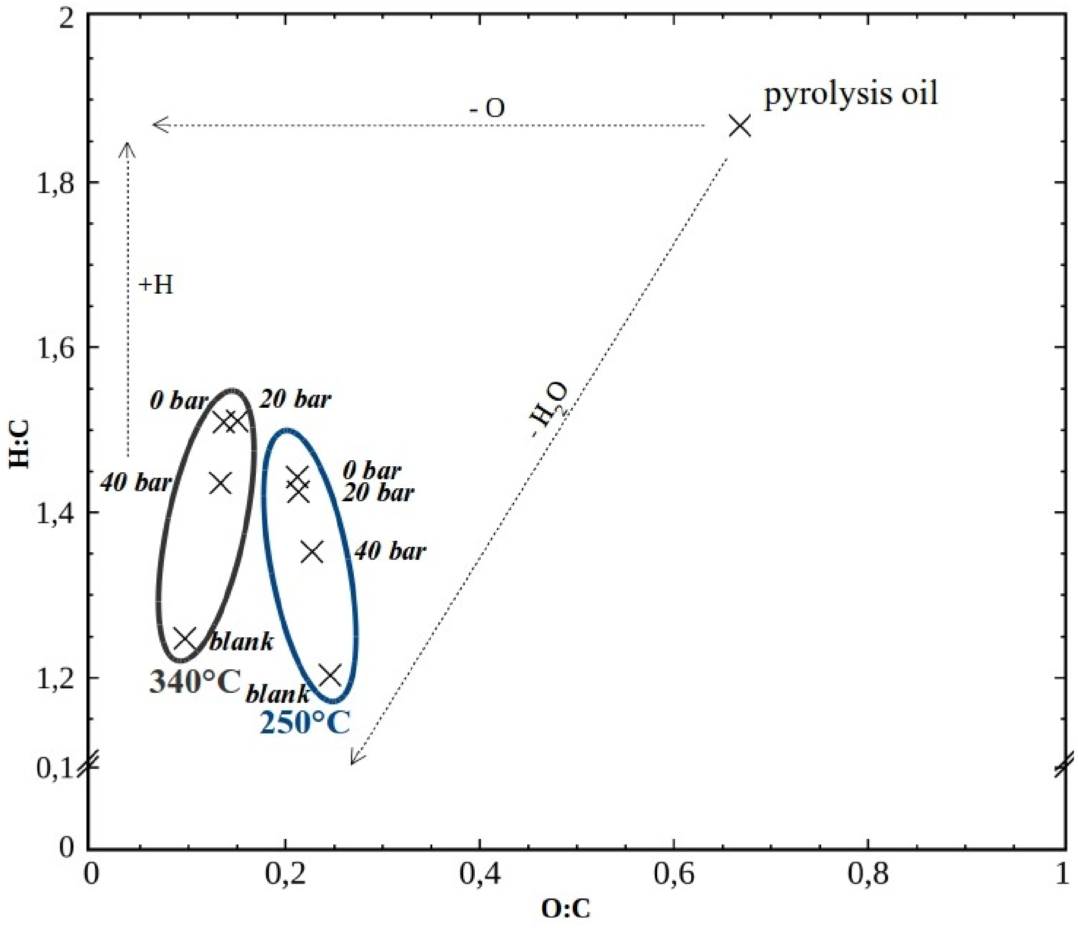
- Elemental analysis
- Karl Fischer Titration
- NMR
- GC-MS

Gas:

- GC-FID-TCD

Upgraded oil characterization

Van Krevelen diagram of the oil phase (dry basis)



deoxygenation degree:
70 %

carbon recovery:
60 %

Densification in energy:
9.2 MJ/kg → **30 MJ/kg**

< 10% water

^{1}H-NMR analysis for upgraded products

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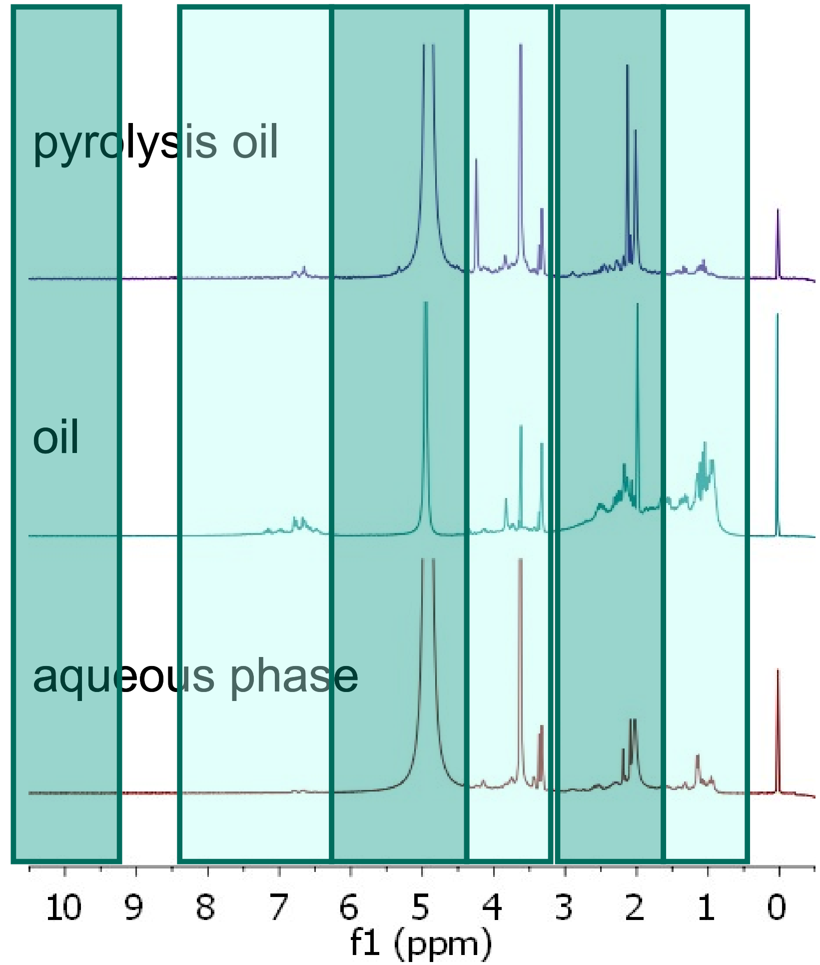
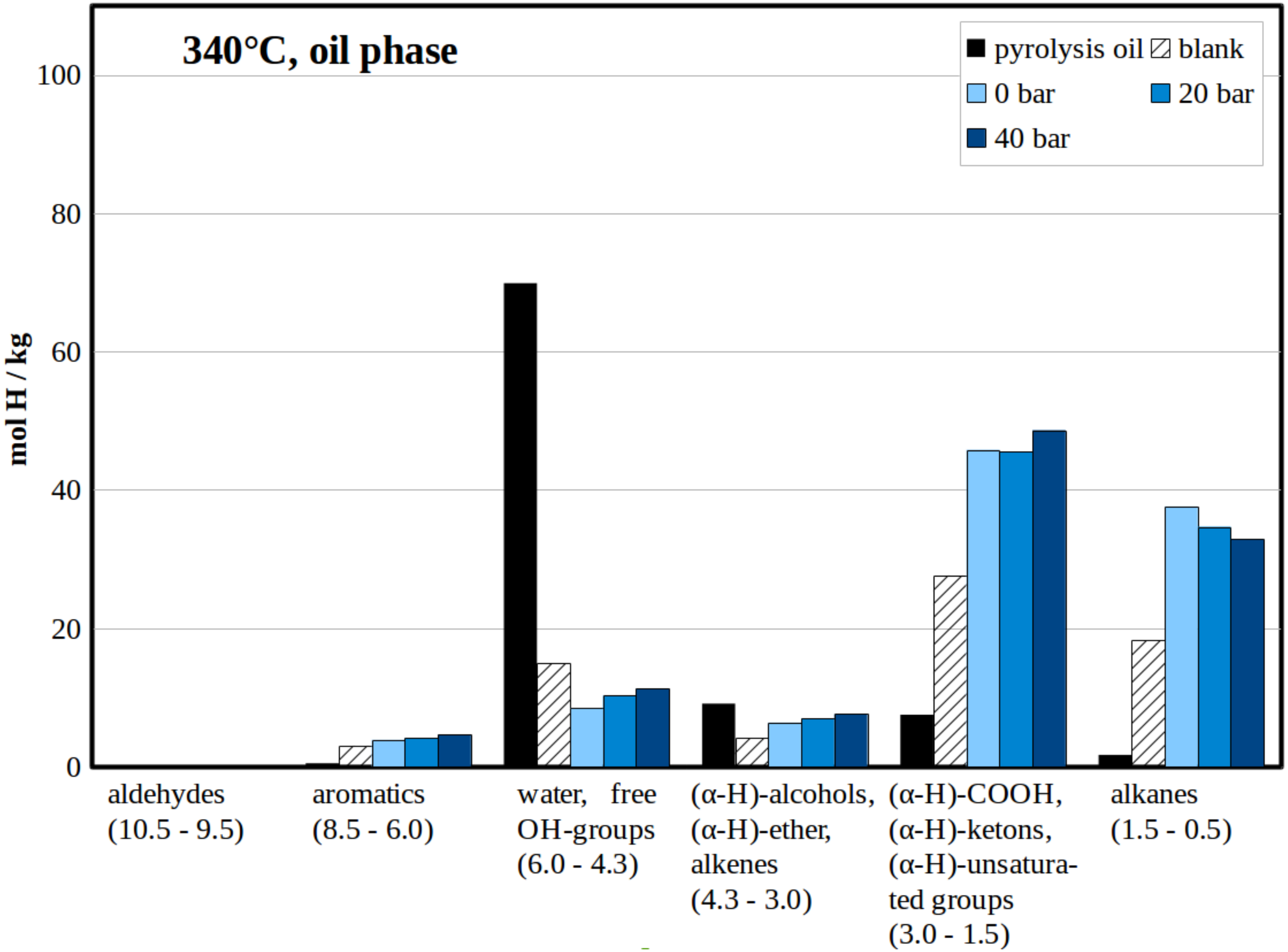
Integration range of ^{1}H-NMR spectra	Proton assignment
10.1-9.5	Aldehydes
8.5-6.0	(Hetero-)aromatic
6.0-4.3	Carbohydrates, water, O-H exchanging group
4.3-3.0	Alcohols, ethers, alkenes
3.0-1.5	α proton to carboxylic acid or keto-group, α proton to unsaturated groups
1.5-0.5	Alkanes



[1]H-NMR analysis for upgraded products



Conclusions

- A successful hydrodeoxygenation was achieved.
- The expansion with CO_2 was not effective as expected.
- No negative effect could be observed, except an indirect weakening of the hydrogenation reactions due to the lower partial pressure of H_2. → Direct use of HCOOH possible!
- A positive finding is that nickel-based catalysts are not active for the methanation of CO_2 when they are used together with pyrolysis oil.
- Further investigations will focus on the heavy phase and lower temperature.

Acknowledgements

- Helmholtz Research School Energy-related Catalysis

- **IKFT-KIT** and **ITCP-KIT**: B. Rolli, G. Zwick, A. Lautenbach, H. Köhler, J. Maier, J. Heinrich, D. Neumann-Walter and A. Beilmann, E. Kehrwecker and V. Meinzer.

Thank you for your kind attention!

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