Spring 6-11-2013

Novel Ni-based catalysts for the hydrotreatment of fast pyrolysis oil

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21-6-2014

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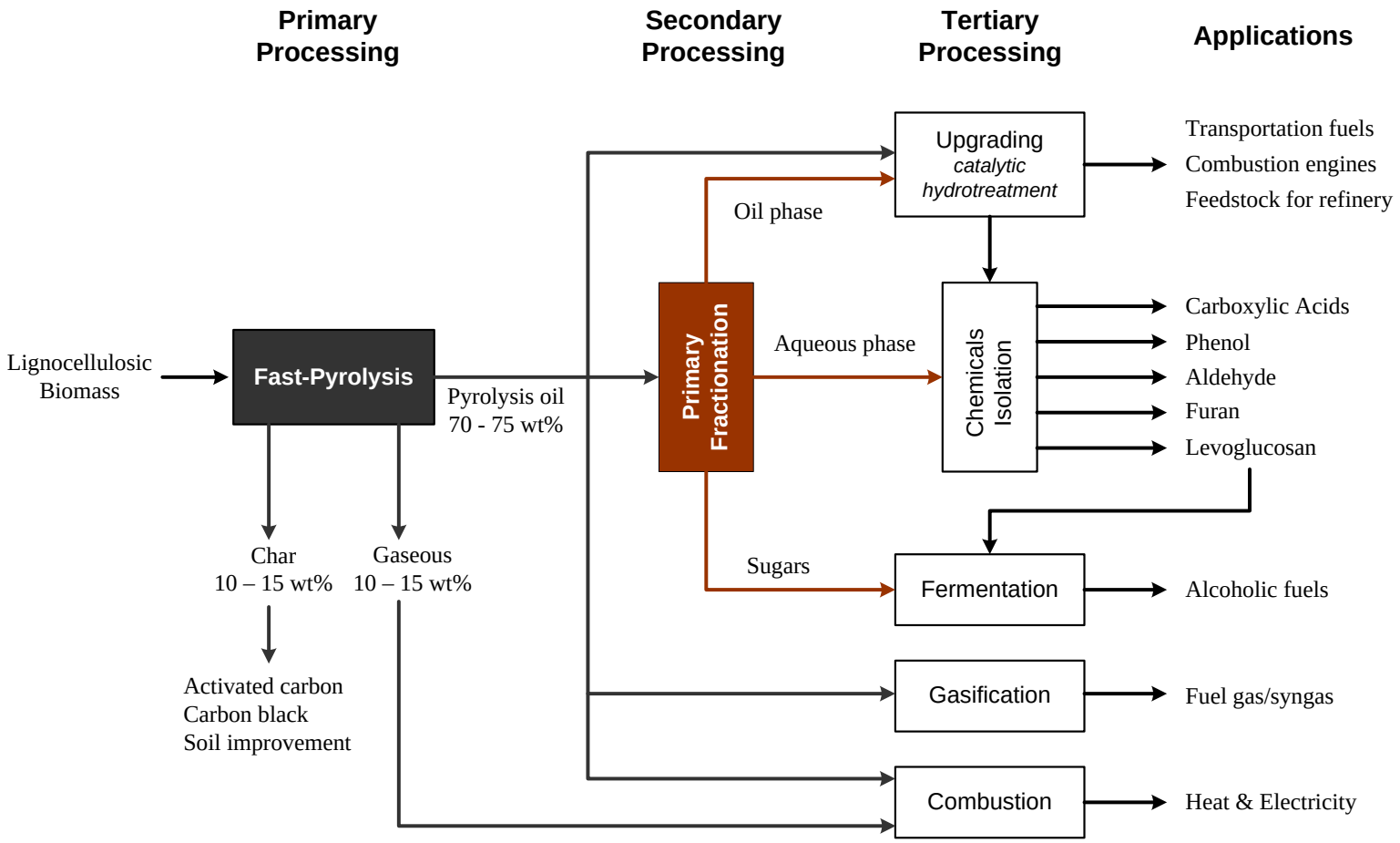
Robbie Venderbosch (BTG)

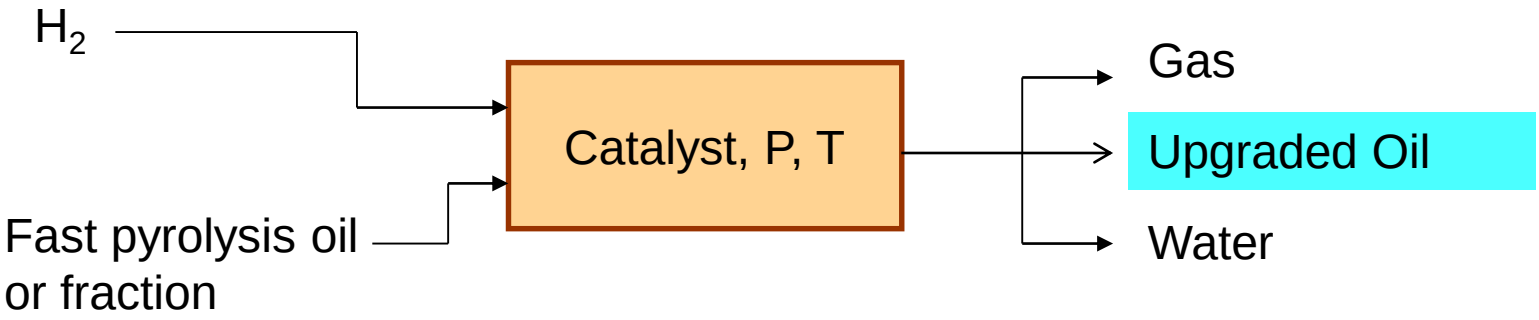
Content

- Introduction
  - Catalytic hydrotreatment
  - Objectives
- Results and discussion
  - Catalyst screening studies: identification of novel catalysts
  - Process studies
- Conclusions
- Acknowledgment

Pyrolysis 2.0: a biorefinery



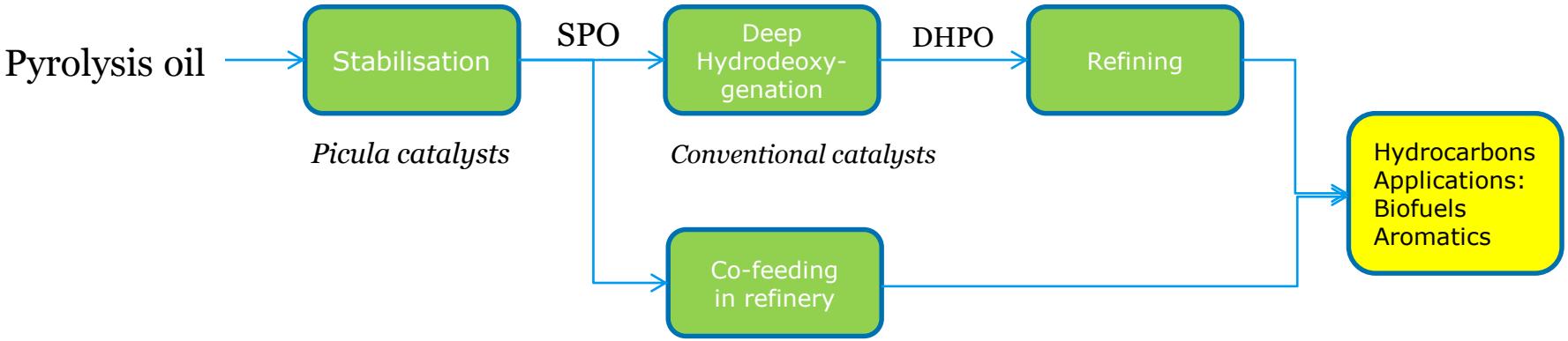
Catalytic hydrotreatment



$$-(CH_xO_y)- + c\ H_2 \rightarrow -(CH_x)- + (H_2O, CO_2, CH_4, CO)$$

Typical conditions: 125-400 C, 20-200 bar pressure

Two stage hydrotreatment



Objectives catalytic hydrotreatment

- Process considerations:
  - Low hydrogen consumption
  - Active, stable and cheap catalysts

- Product considerations
  - Reduced oxygen content, exact amount depending on product application
  - Low viscosity
  - Low water content
  - Low coking tendency (improved thermal stability)
  - Preferably miscible with hydrocarbons

Stabilisation: catalyst developments

- Benchmark: Ru/C
- Bimetallic noble metal catalysts[a]
- Ni-Cu catalyst on supports[b,c]
- Improved Ni-Cu catalysts (Picula)[d]

a. A.R. Ardiyanti, A. Gutierrez, M Honkela. O. Krause, H.J. Heeres, Applied Catalyis A 407(1-2) (2011) 56-66.
b. A.R. Ardiyanti, S.A. Khromova, R.H. Venderbosch,V.A. Yakovlev, I.V. Melián-Cabrera, H.J. Heeres, Applied Catalysis A 449 (2012) 121-130.
c. A.R. Ardiyanti, S.A. Khromova, R.H. Venderbosch, V.A. Yakovlev, H.J. Heeres, Applied Catalysis B: Environmental 117– 118 (2012) 105– 117.
d. Venderbosch and Heeres; Chapter 17: Pyrolysis Oil Stabilisation by Catalytic Hydrotreatment, Biofuel's Engineering Process Technology, **Free download:** http://www.intechopen.com, Patent application pending

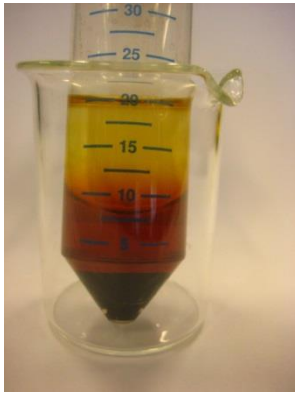
Picula catalysts

Table 2 Catalyst composition

Code	Active metal loading (wt%)	Support (wt%)
Picula Cat B	Ni 58.3 Pd 0.7	SiO_2 41
Picula Cat C	Ni 28.8 Cu 3.7	SiO_2 33.8 Kaolin 33.8
Picula Cat D	Ni 57.9 Cu 7	SiO_2 35.1
Picula Cat E	Ni 36.5 Cu 2.3	SiO_2 12.6 ZrO_2 37.2 La_2O_3 0.9

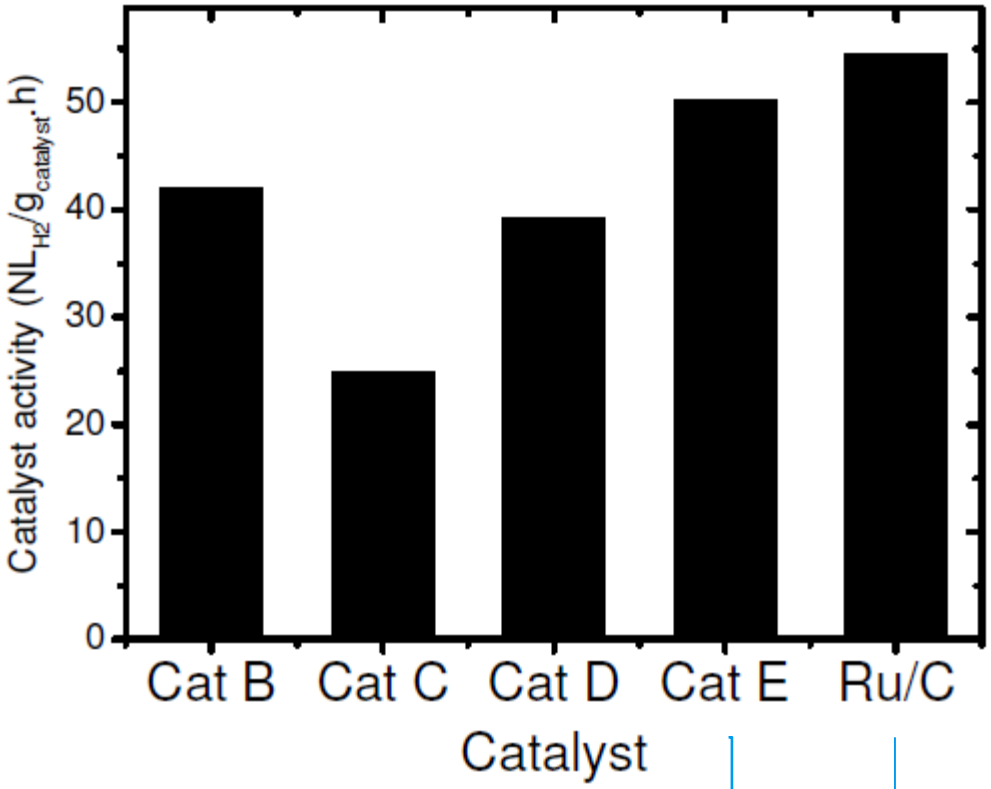
- High Ni content (29-58 wt%)
- Promoted with Cu, Pd
- Various supports

- Prepared by BIC



Venderbosch and Heeres; Chapter 17: Pyrolysis Oil Stabilisation by Catalytic Hydrotreatment, Biofuel's Engineering Process Technology, **Free download:** http://www.intechopen.com

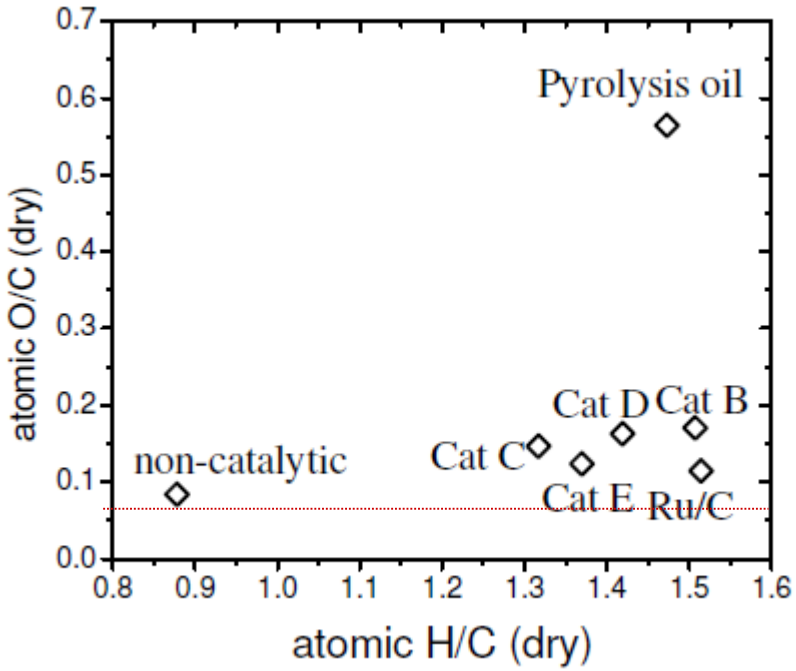
Batch studies

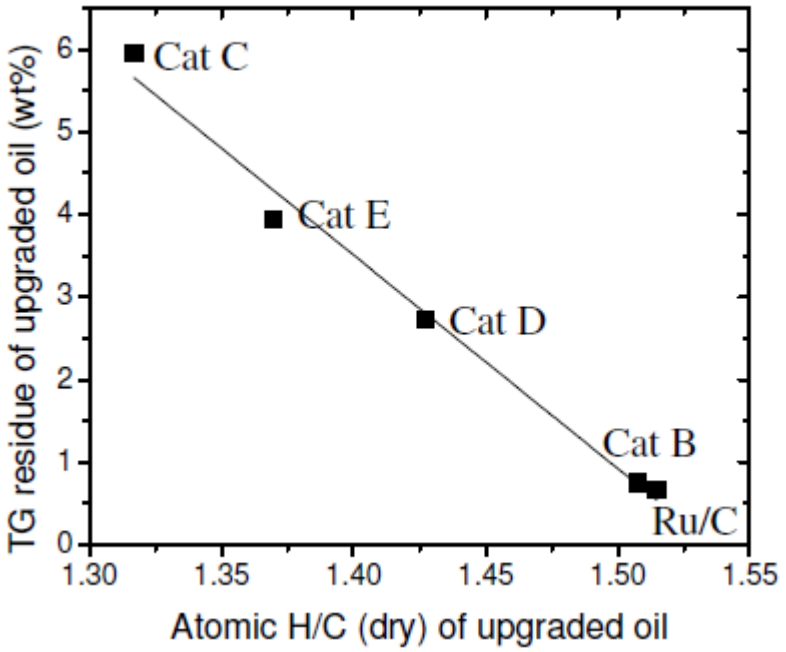


- 150 C, 1 h
- 350 C, 3 h
- 200 bar

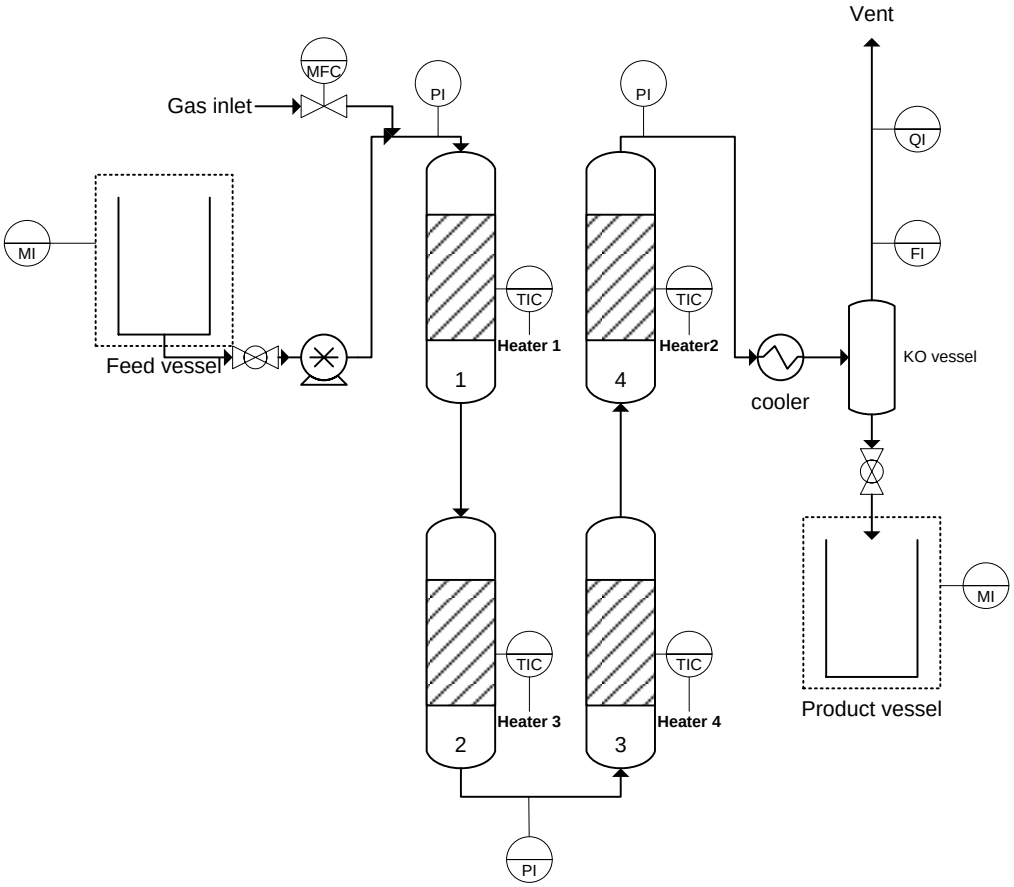
Methanation!

Batch studies





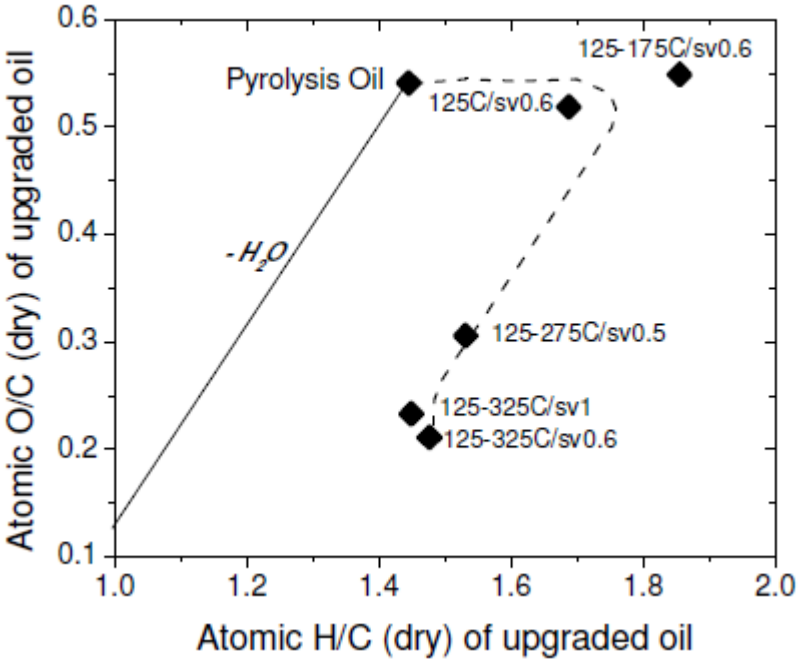
Continuous experiments

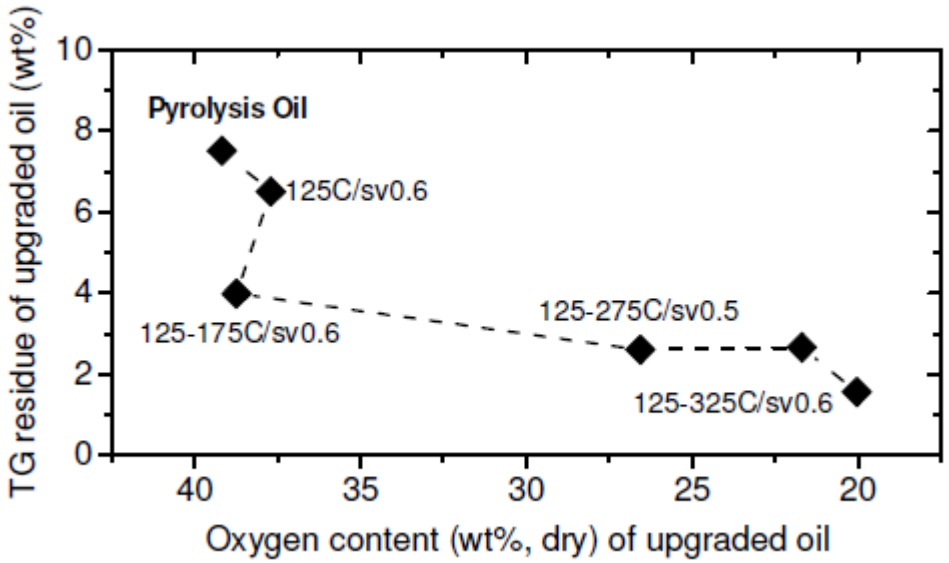


- 4 fixed-bed reactors in-series
- Catalyst: Picula catalyst D
- H_2 pressure: 200 bar
- WHSV = 0.6 – 1 h^{-1}
- Variable: T

- Analysis:
  - Elemental composition, TGA, GPC, TAN, CAN, 2D-GC

Continuous experiments

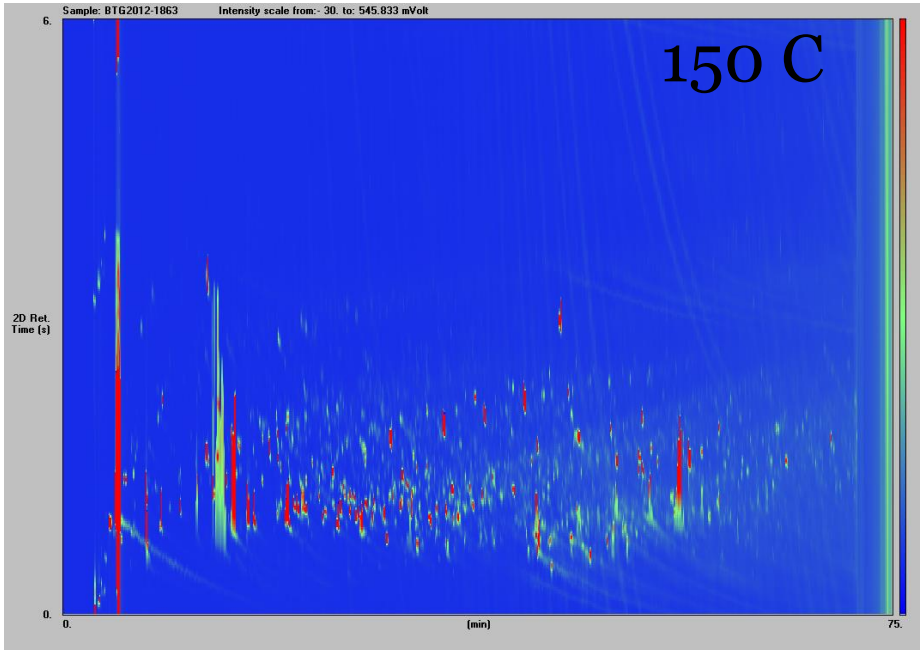


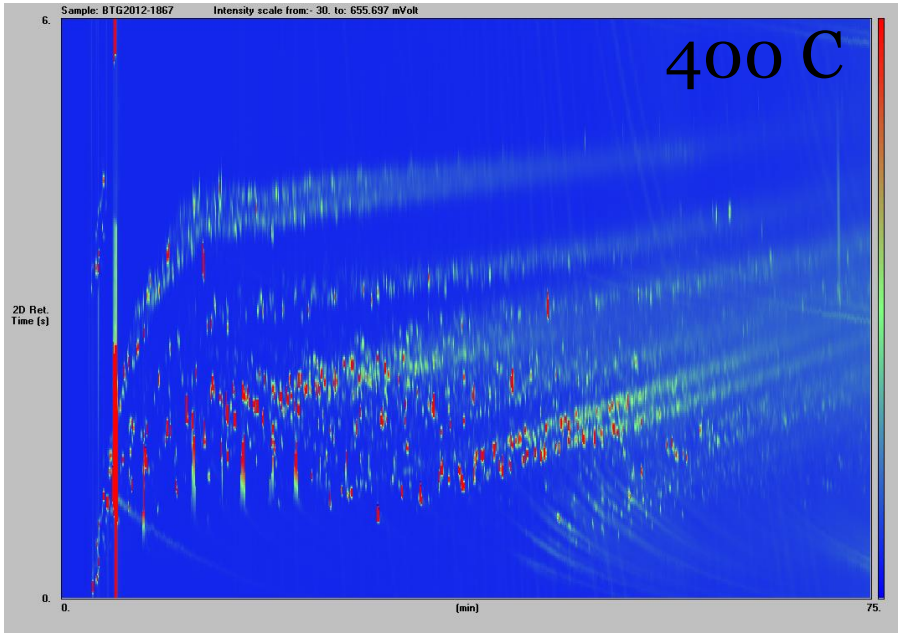


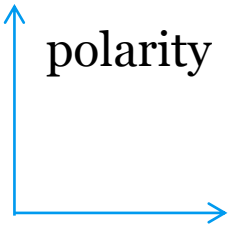
Visual appearance

Pyrolysis oil 150°C 400 °C distillates

2D-GC


Sample: BTG2012-1863
Intensity scale from:- 30. to: 545.833 mVolt
150 C
6.
2D Ret. Time (s)
0.
0.
(min)
75.

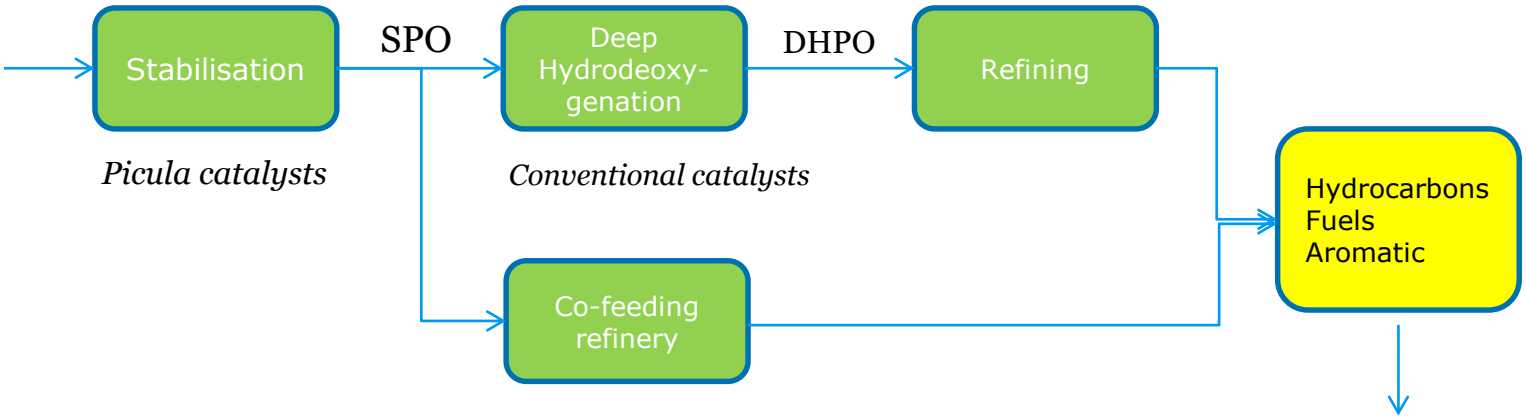

Sample: BTG2012-1867
Intensity scale from:- 30. to: 655.697 mVolt
400 C
6.
2D Ret. Time (s)
0.
0.
(min)
75.

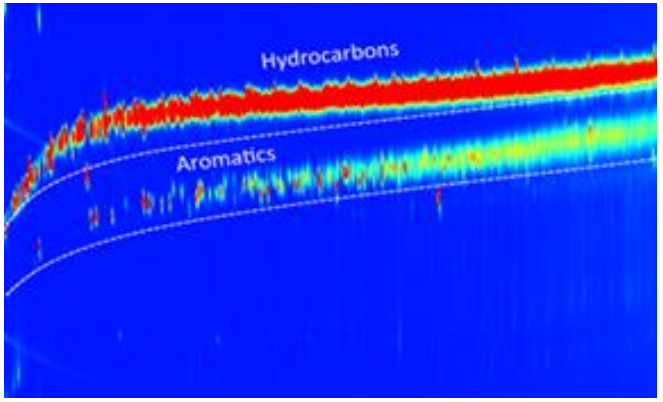

polarity

b.p

Product is distillable

Two stage hydrotreatment





Conclusions

- Novel catalysts for pyrolysis oil stabilisation by catalytic hydrotreatment have been identified
- Products are distillable, indicative for improved thermal stability
- Picula catalysts show unique performance
  - Improved product properties at low processing temperature
  - Low hydrogen consumptions due to limited methane formation
  - Good hydrothermal stability (run times up to 400 h have been demonstrated)
- Two stage hydrotreatment leads to deep deoxygenation and formation of hydrocarbons

Acknowledgement

BIOCOUP

Agentschap NL
Ministerie van Economische Zaken

SenterNovem

university of groningen

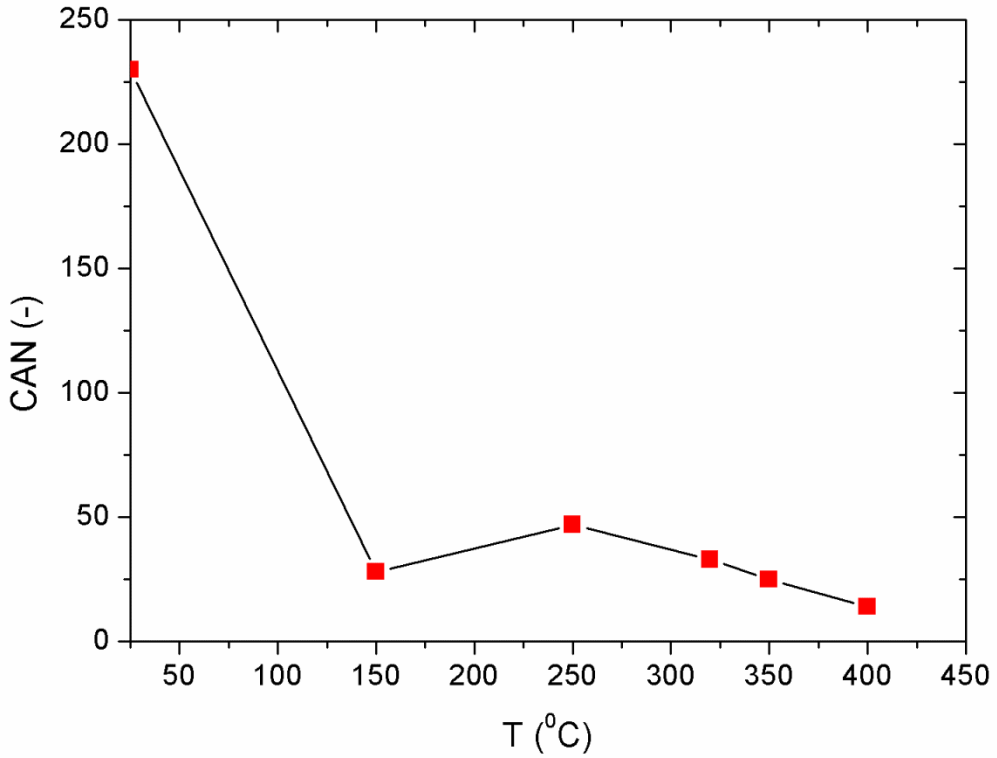
Vacancy

Tenure Track Assistant Professor Green Chemistry and Technology (1,0 fte)

Deadline for applications: June 28, 2013

Contact: h.j.heeres@rug.nl

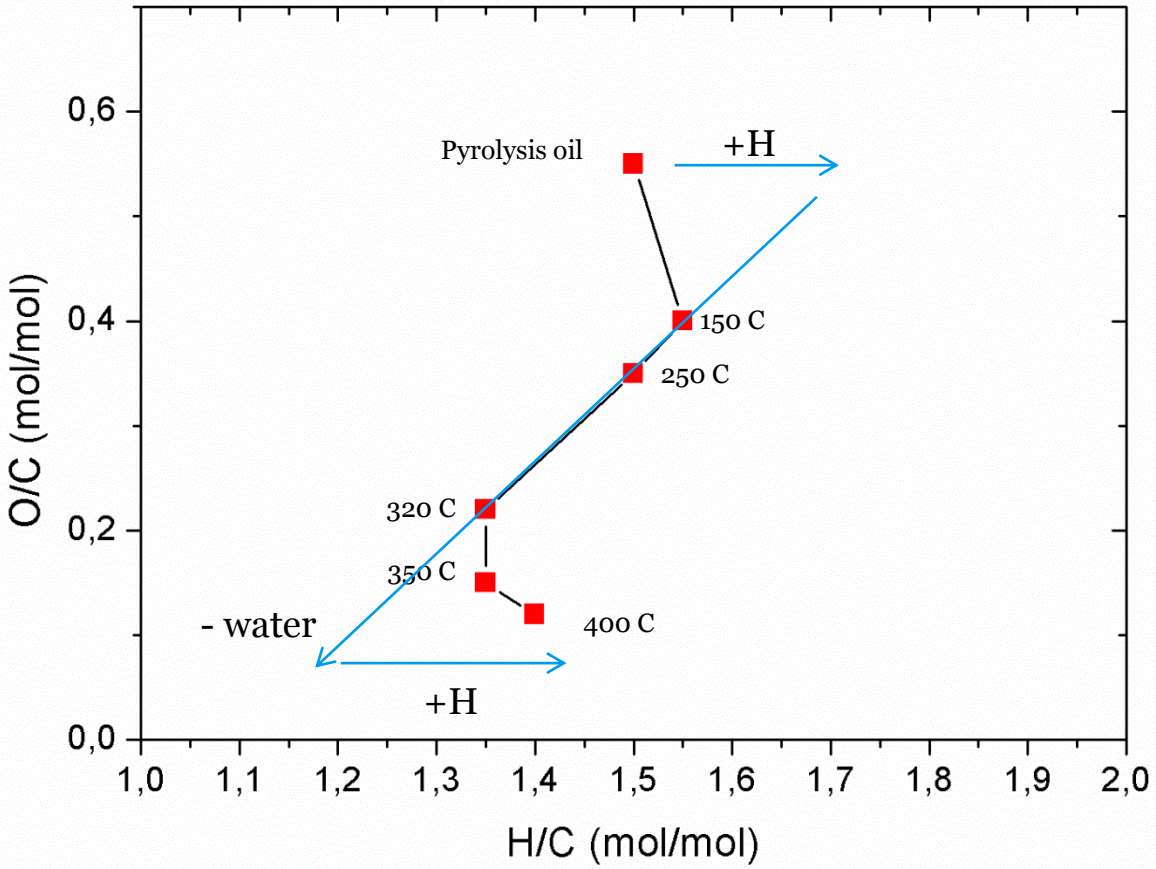
Carbonyl number



Alehydes and ketones are very reactive at low temperature

Formation of new compounds at about 250 °C

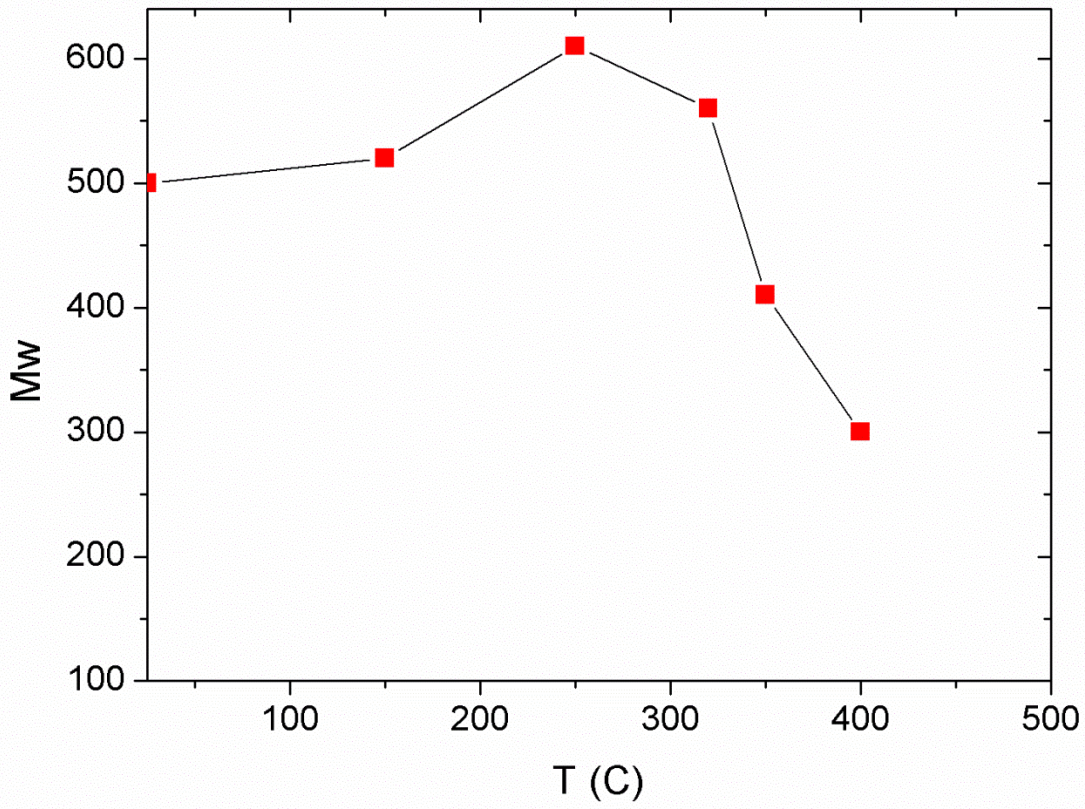
Elemental composition



Sequence:

- Hydrogenation
- Dehydration
- Hydrogenation

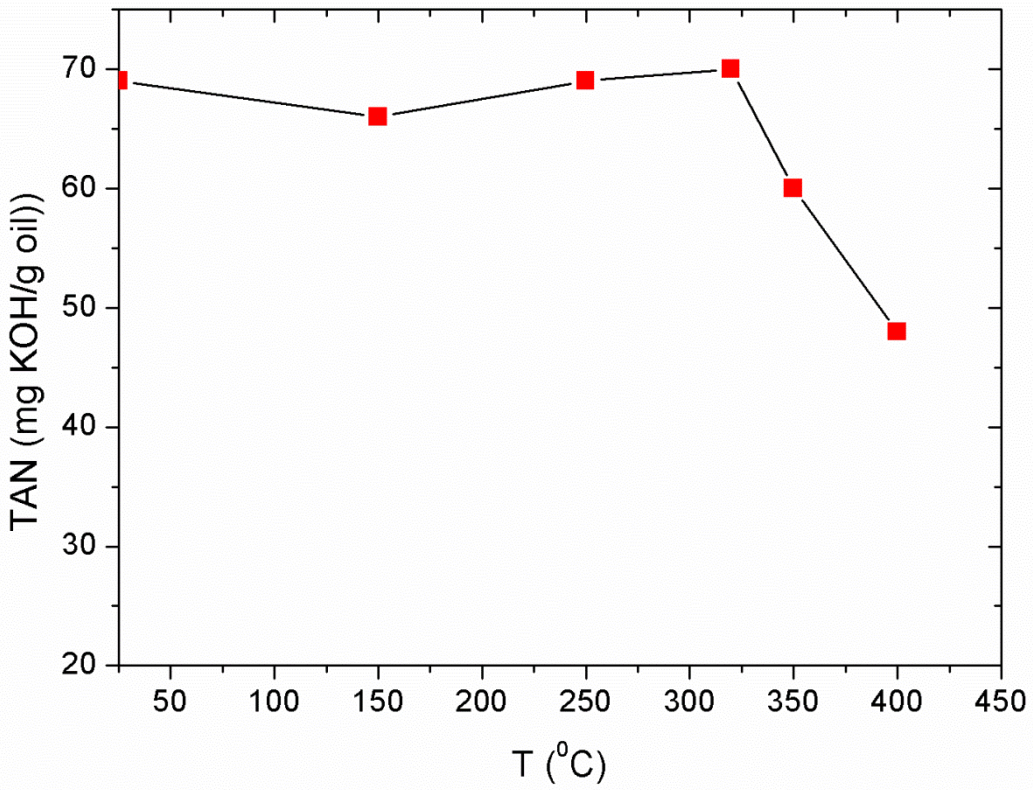
Molecular weight (GPC)



Sequence:

- Limited polymerisation till 250 °C
- Hydrocracking above 300 °C

Total acid number



Acids are very persistent, reactive only above 300 ^{o}C

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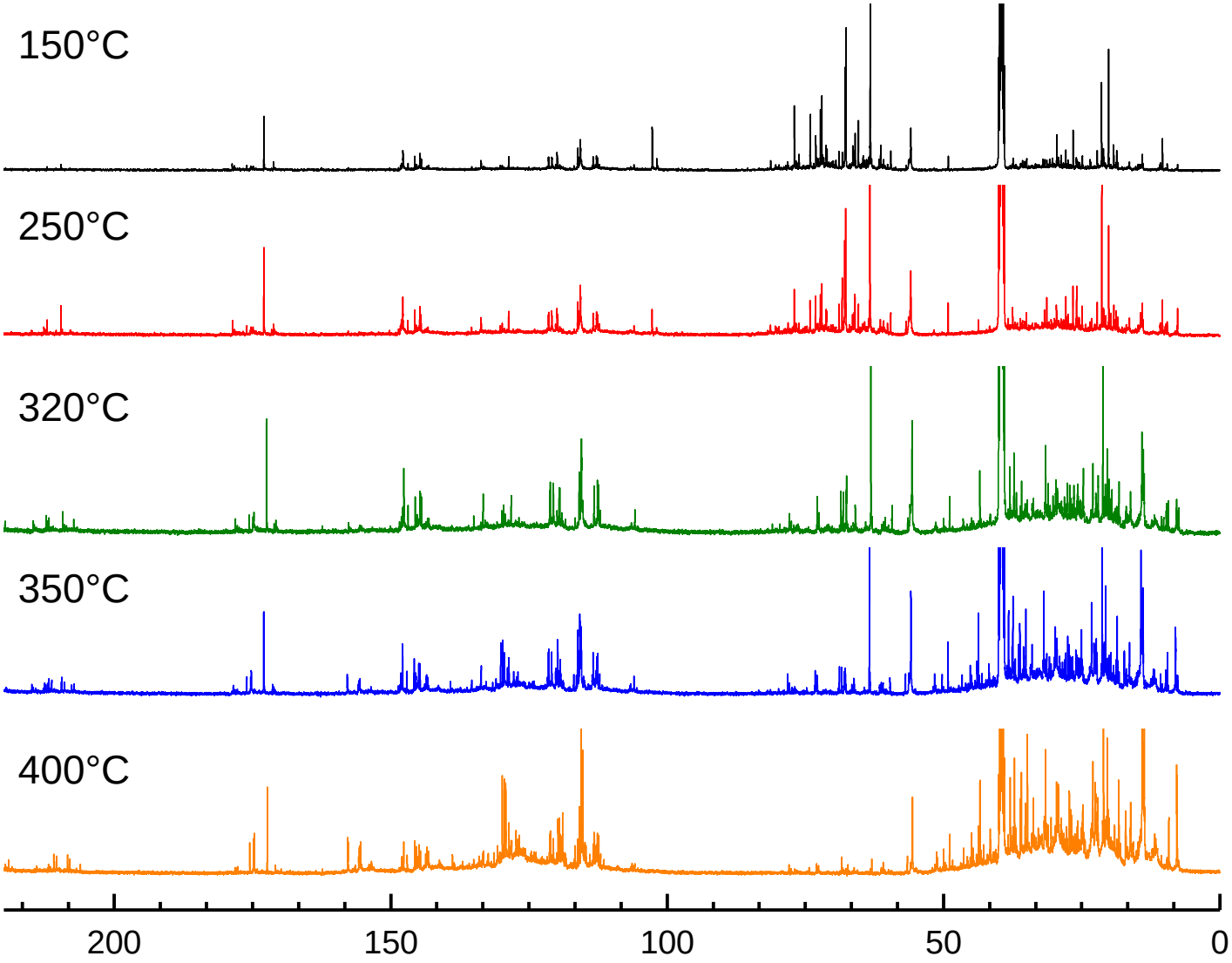
^{13}C NMR

btg



Overview

Stabilisation (< 250 ^{0}C)

Competition between hydrogenation and polymerisation

Water formation by condensation reactions

Slight increase in Mw

Hydrogenation of aldehyde/ketones

Sugar chemistry dominates

Mild hydrotreatment (250-350 ^{0}C)

hydrogenation-dehydration

Reduction in Mw

Water formation by alcohol dehydration

Breakdown of higher Mw fractions

Sugar-sugar alcohol chemistry dominates

Deep hydrotreatment (> 350 ^{0}C)

Hydrocracking

Further reductions in Mw

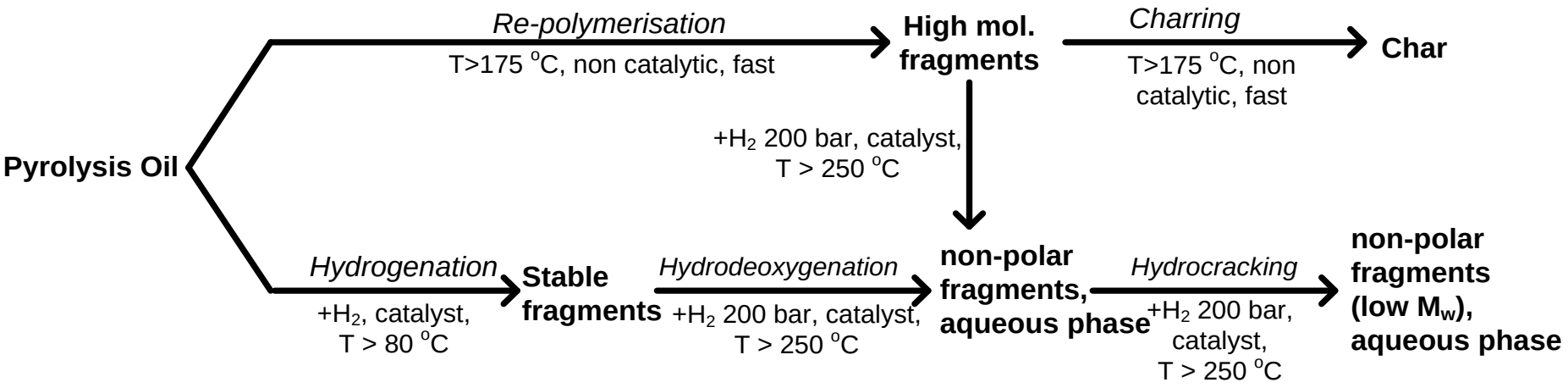
Formation of aromatics and aliphatic hydrocarbons

Acid conversion

Lignin chemistry dominates

Temperature

Reaction pathway



Venderbosch, Heeres et al., 2010, Stabilization of biomass-derived pyrolysis oil, J. of Chem.Techn. & Biotech., 85(5), 674-686

Catalytic biomass conversions RUG/CRE

Biofuels

- Catalytic pyrolysis oil upgrading
- Biodiesel from *Jatropha Curcas*
- Green gas by supercritical gasification in water

Biobased chemicals

Platform chemicals
- hydroxymethylfurfural
- levulinic acid/lactic acid
- methanol
- furanics based diols
- phenolics

Bio-based performance materials

- Starch modifications in non-conventional solvents
  - alcohols
  - supercritical CO_2

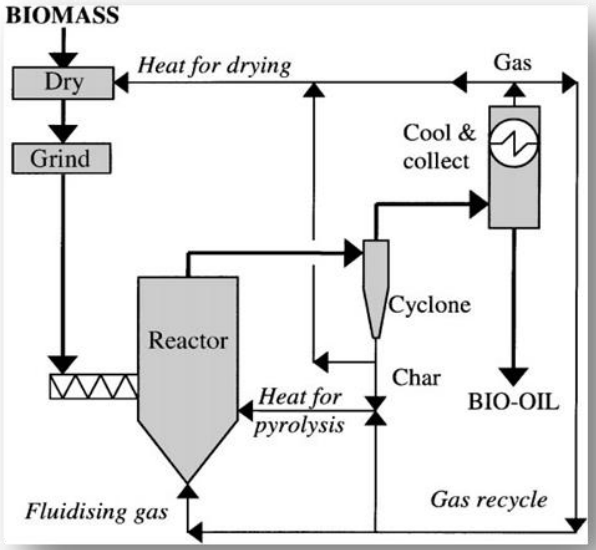
Enabling science and technology

- Catalyst development
- Process intensification using centrifugal contactor separators

Fast Pyrolysis Oil

Lignocellulosic biomass → Fast Pyrolysis → Volatiles, Condensables, *Fast Pyrolysis Oil*, Char

450-600 °C, 1-2 s

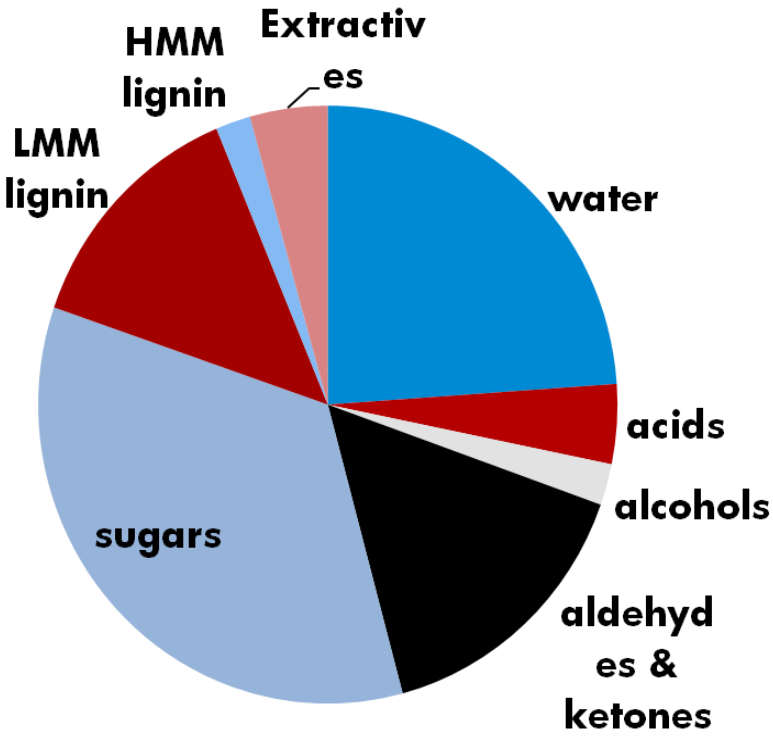


BTG, Enschede

Fast pyrolysis oil characteristics

- High oxygen content (up to 50%)
- Immiscible with petroleum products
- Limited stability upon heating and storage (coke formation, repolymerization)

Pyrolysis oil composition	
C (wt%)	40.1
H (wt%)	7.6
O (wt%)	52.1
Moisture (wt%)	23.9



Biomass application platforms

High T platform
Combustion
Gasification
Pyrolysis

Low T platform
Pre-treatment /hydrolysis
Fermentation
Separation in fractions

Secondary conversions

Heat and Power

Transportation fuels

Biobased Chemicals

Biobased Performance materials