
Hanze
University of Applied Sciences
Groningen

# Catalytic pyrolysis towards BTX

**André Heeres, May 2019 (Hanzehogeschool/Syncom)**

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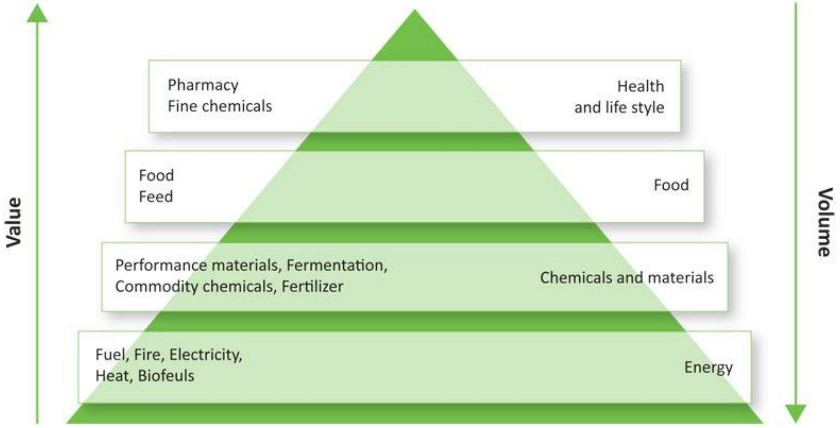
# Catalytic pyrolysis towards aromatics



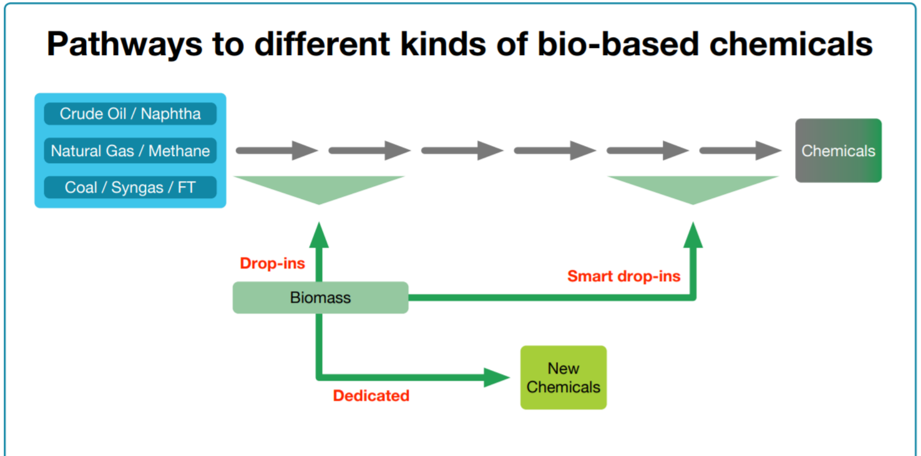
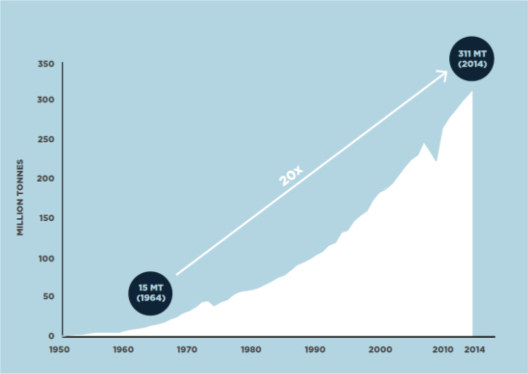




**Figure 1:** Schematic differentiation of pathways of drop-in, smart drop-in and dedicated bio-based chemicals

- Drop-in chemicals (aromatics)

# Drivers biobased transition





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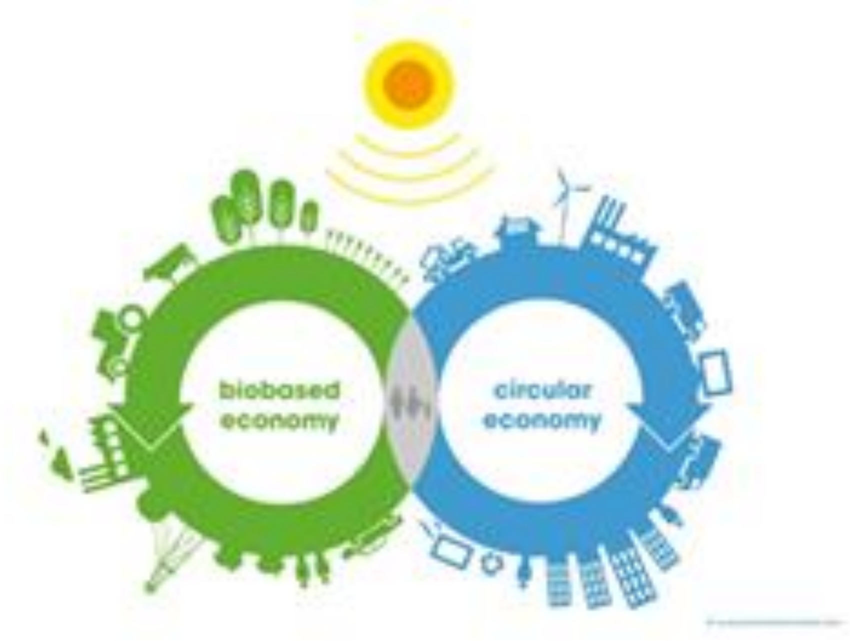
# Coupling biobased/circular ecnomy

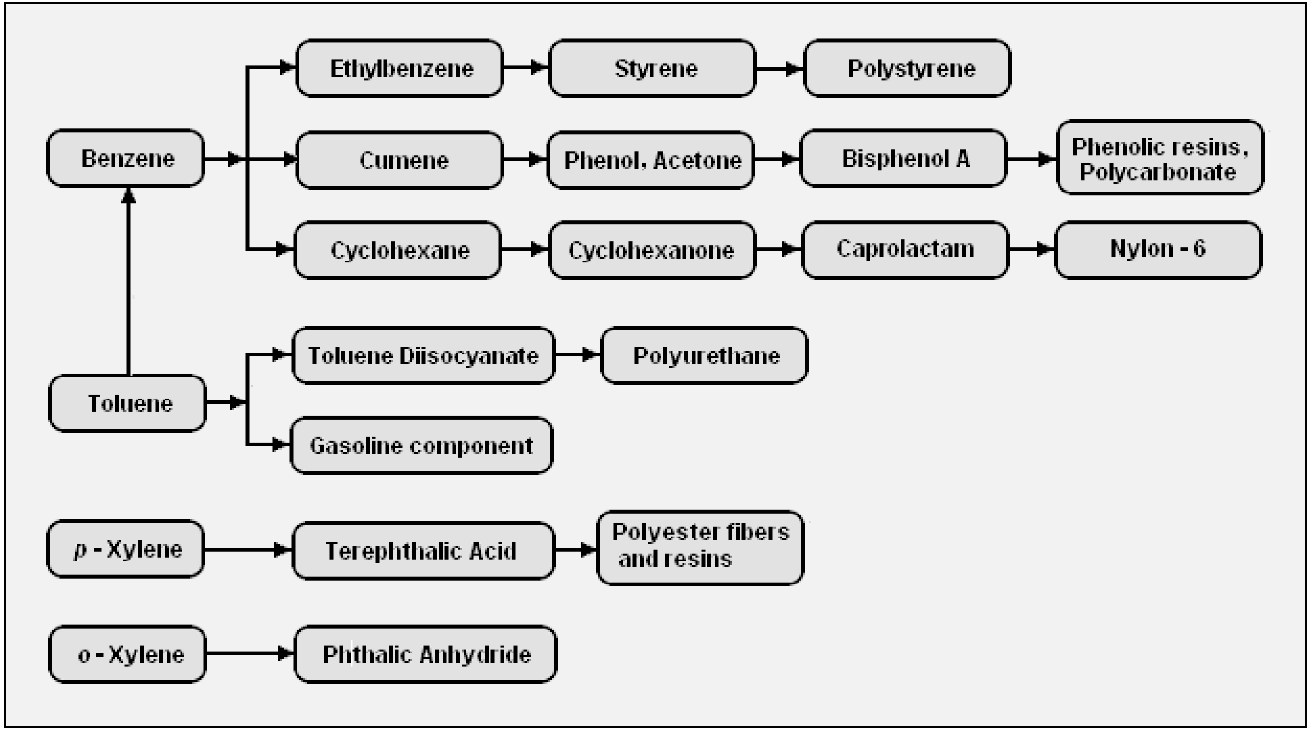


# Plastics from biomass

- Sustainable Consumption and Production, utilization of natural resources: an attractive alternative?

- About 40% of plastics contain aromatics.

# (Bio)aromatics: applications




Prices BTX strongly dependent on oil price (benzene $900/ton, toluene $800/ton, p-xylene $1050/ton (oil about $60 barrel))

# History

| | Event | |
|---|---|---|
| 2009 | BioBTX ideation: Bio-based, drop in aromatics | KNN |
| 2012 | Thermochemical conversions towards BTX | KNN, RUG, Syncom |
| 2012 | Consortium formed | KNN, RUG, Syncom |
| 2012 | Experimentation started (IAG subsidy) | KNN, RUG, Syncom |
| 2014 | BioBTX B.V. founded by KNN, Syncom | |

# Catalytic pyrolysis towards aromatics/BTX

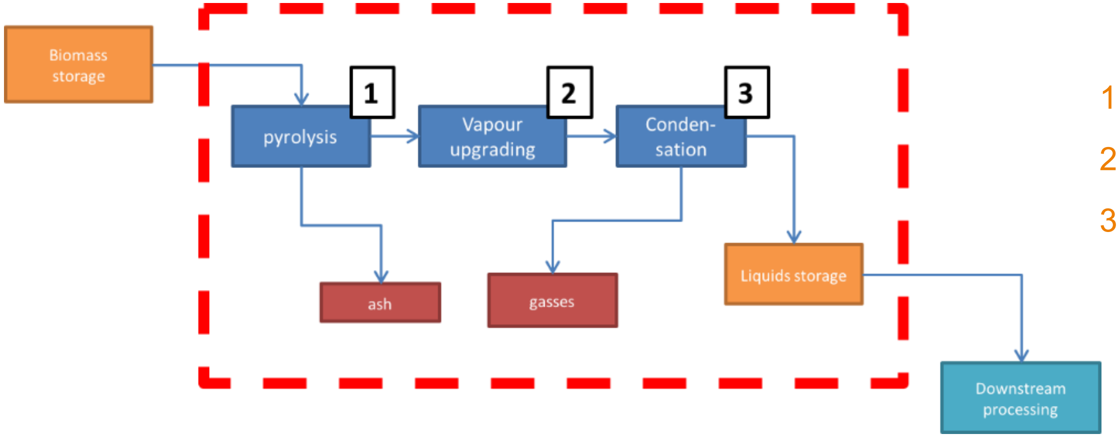
- *In situ* catalytic pyrolysis

- Efficient one-step process
- Sustainable, low carbon footprint
- Non food and cheap biomass
- Conventional zeolite catalysts
- Moderate yields of BTX (5-25%, depending on biomass/conditions)

…….. but the “life time” of the catalyst??

- Restricted to dry biomass containing low amounts of inorganics.

# *Ex situ* aromatization

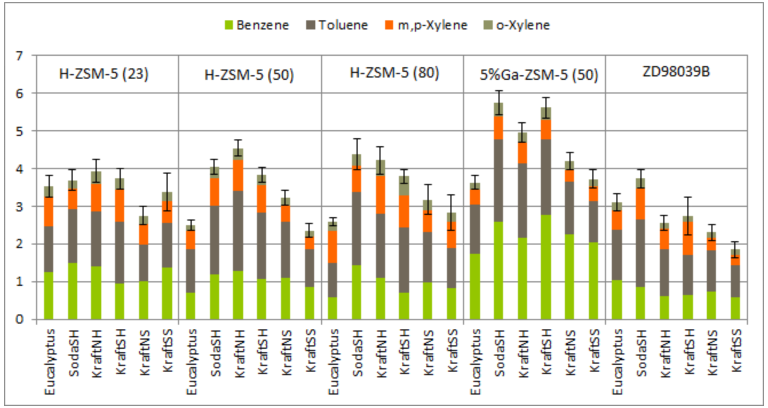


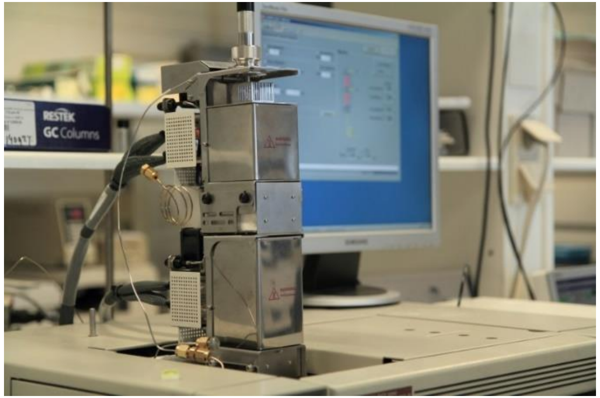

1. Thermal cracking
2. Catalytic conversion
3. Liquids collection

- Extended life time of the catalyst
- Ability to use highly contaminated/wet biomass streams
- More “tools” for optimization

# Ex situ catalytic pyrolysis Black Liquor

- Tandem Micro reactor ($T_1$ = 500° C, $T_2$ = 600° C)

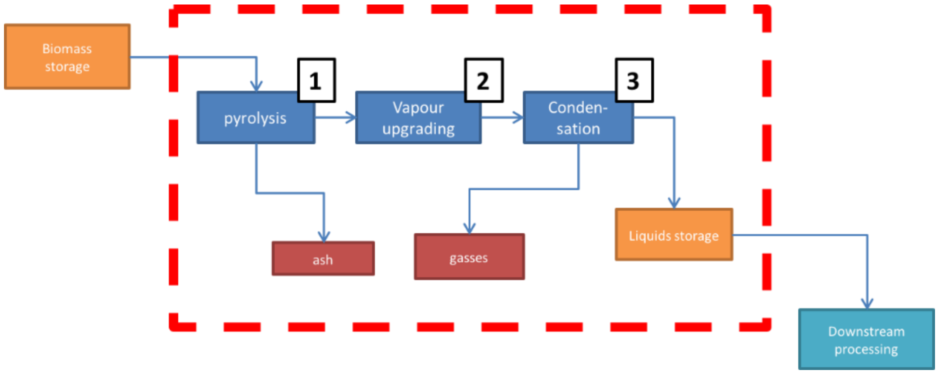



André Heeres, Niels Schenk, Inouk Muizebelt, Ricardo Blees, Bart De Waele, Arend-Jan Zeeuw, Nathalie Meyer, Rob Carr, Erwin Wilbers, Hero Jan Heeres, *ACS Sustainable Chem. Eng.*, 2018, 6 (3), pp 3472–3480

- Gram scale reactor 4-6% BTX, 10-20% higher aromatics

# Integrated Cascading Catalytic Pyrolysis (ICCP)

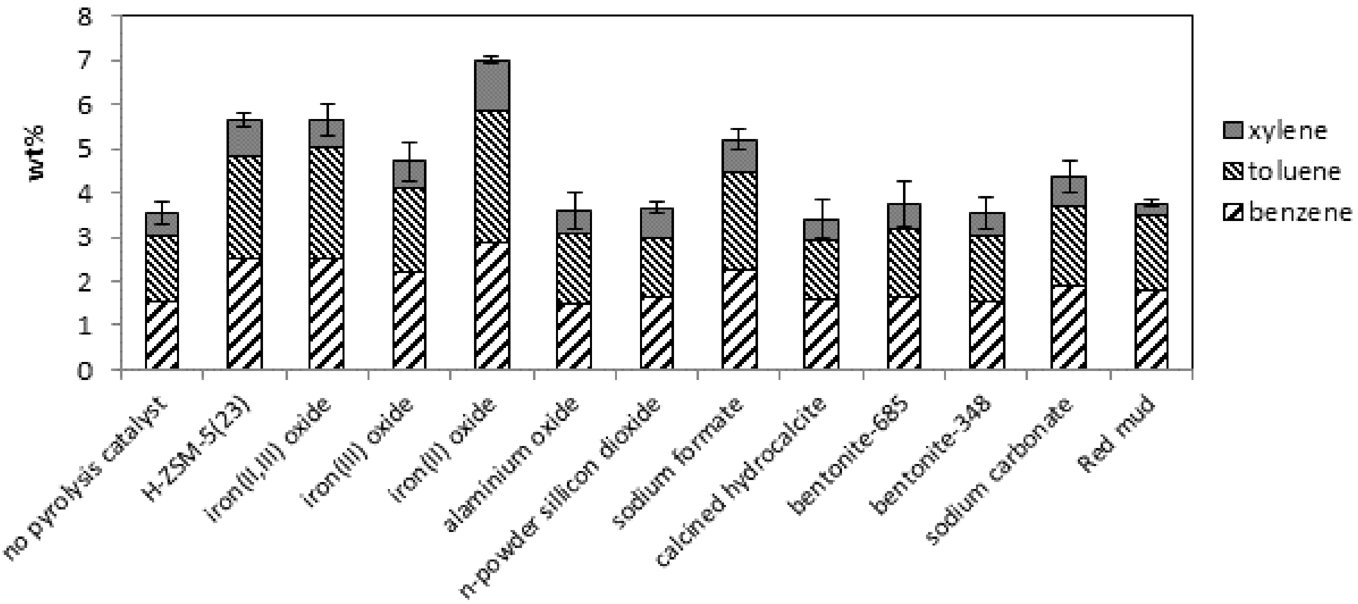



1. Thermal cracking
2. Catalytic conversion
3. Liquids collection

- Hypothesis: A (cracking) catalyst could influence both the composition and amount of the gaseous phase.

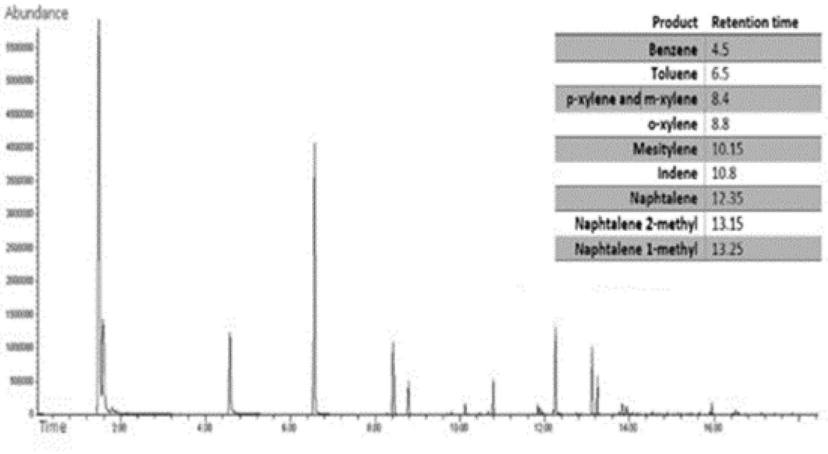
*Schenk, N.J., Biesbroek, A., Heeres, A., Heeres, H.J., Process for the preparation of aromatic compounds, WO2015047085*

# Significant effects “cracking” catalyst on yields BTX




TMR; pinewood : pyrolysis catalyst : (H-ZSM-5 (23), $T_1$ = 550 ºC, $T_2$ = 575 ºC)

# Higher aromatics formed

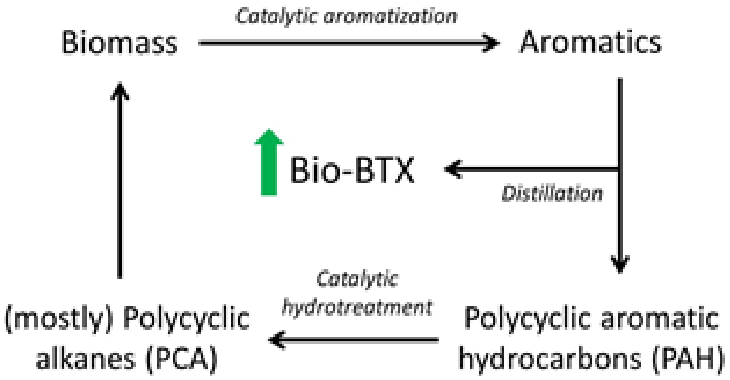


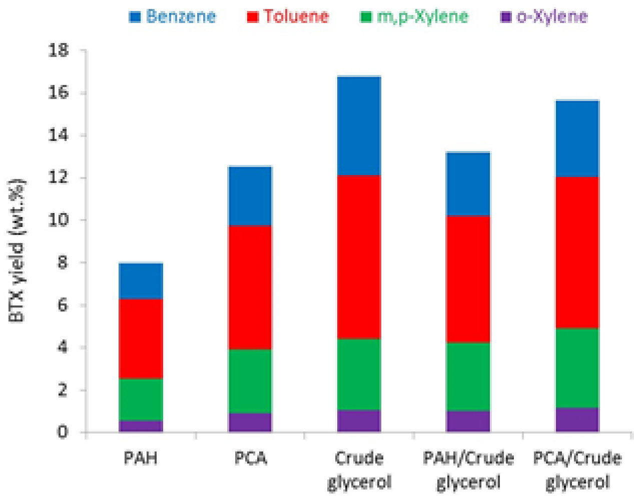

- Gram scale unit, H-ZSM-5 (23), T = 550 ºC

| *source* | *BTX yield (%)* | *bio-oil (%)* | *ratio* |
|---|---|---|---|
| | | | |
| glycerol | 15.48 | 33.46 | 2.16 |
| sucrose | 3.82 | 13.71 | 3.59 |
| cellulose | 4.48 | 13.95 | 3.11 |
| jatropha oil | 23.71 | 53.34 | 2.25 |
| lignin | 2.14 | 12.19 | 5.70 |
| wood | 3.02 | 16.03 | 5.30 |

- Valorization higher aromatics

# Co-feeding (reduced) higher aromatics



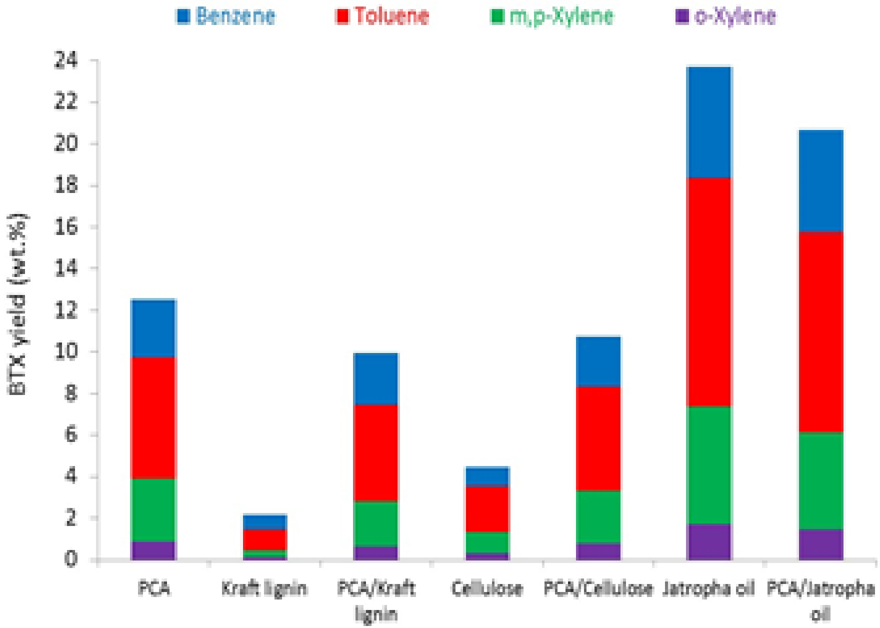




- Decrease $H/C_{eff}$ by hydrogenation

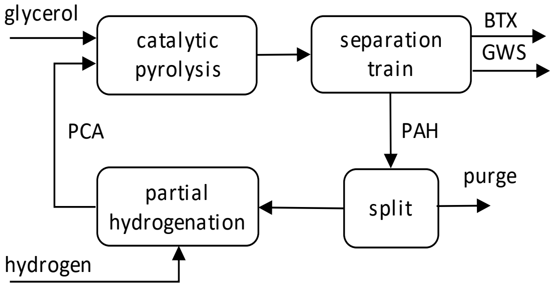
BTX yields (wt.% relative to feed intake) obtained after *ex situ* catalytic pyrolysis of crude glycerol and co-pyrolysis with PAH or PCA (1:1 wt. ratio, total weight of 1 g) in the presence of H-ZSM-5 catalyst (1:3 feed mix:catalyst wt. ratio, 550 oC).

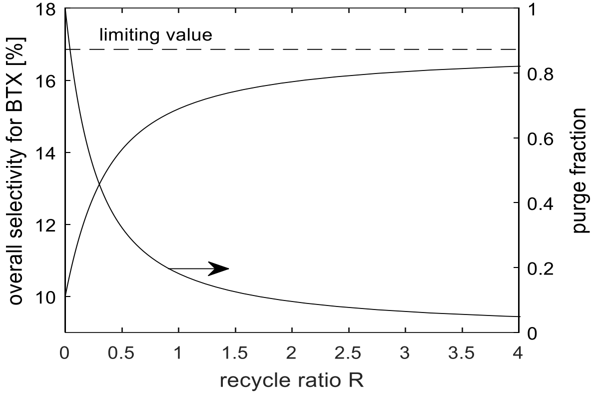
*Homer C. Genuino, Inouk Muizebelt, André Heeres, Niels J. Schenk, Jos G. M. Winkelman, and Hero J. Heeres, submitted for publication in Green Chem.*

# Co-feeding (reduced) higher aromatics




- Synergism observed



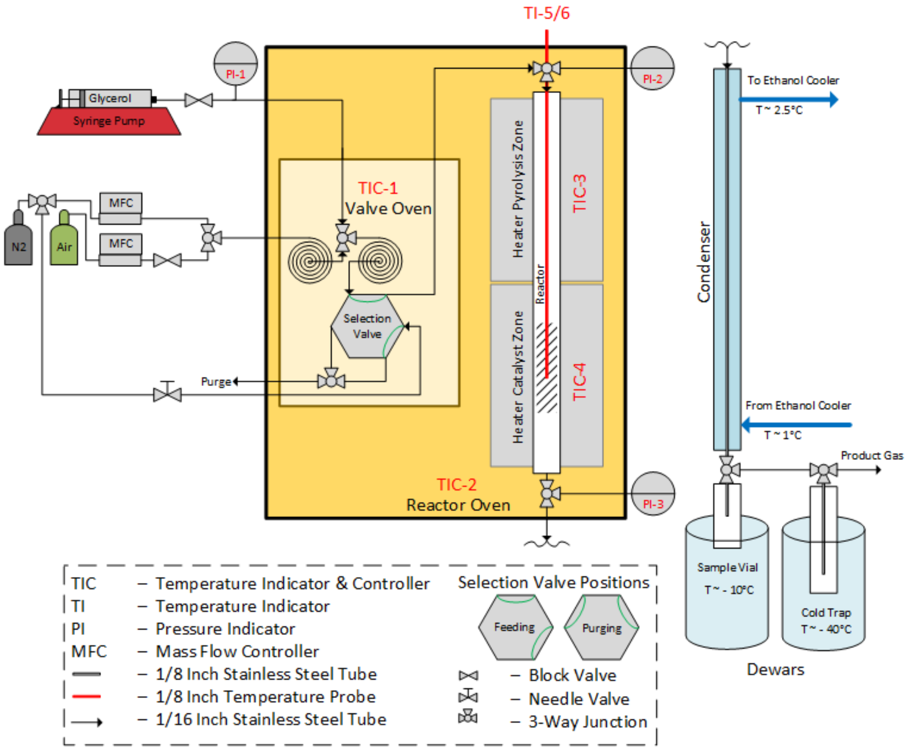




- Higher BTX yields obtained

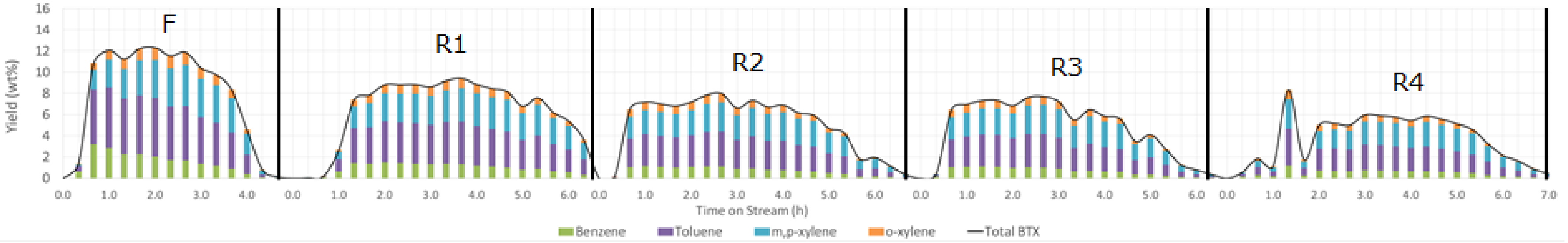
# Catalyst stability

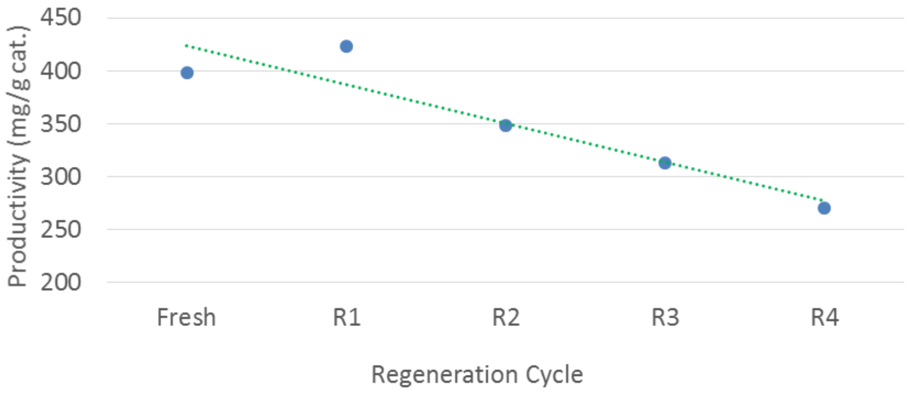
- Continuous set-up
- Pure glycerol, H-ZSM-5
- Optimized conditions

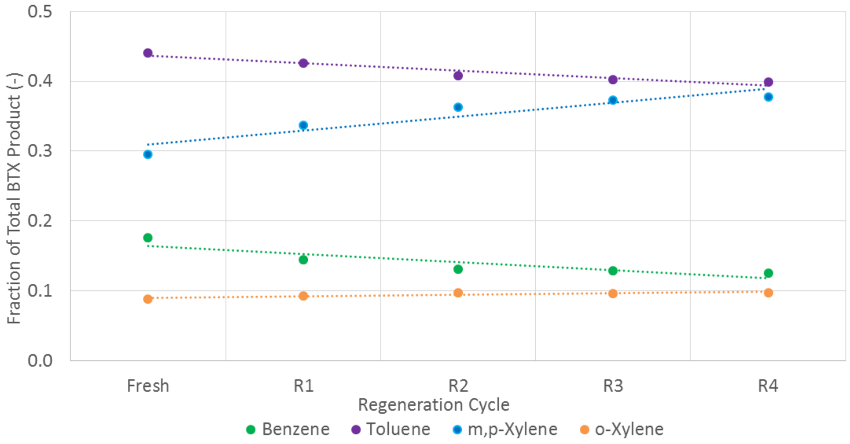
- WHSV 1 h-1 (1 g cat.)
- $T_{Pyrolysis}$ = 400 ºC
- $T_{Aromatization}$ = 500 ºC
- Glycerol Feed Rate 1 g hr-1



# Catalyst stability

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# Analysis

- $NH_3$-TPD & XRD
- Nitrogen Physisorption
- Micropore analysis
- TEM, ICP, EDX, $^{27}$Al-SS-NMR

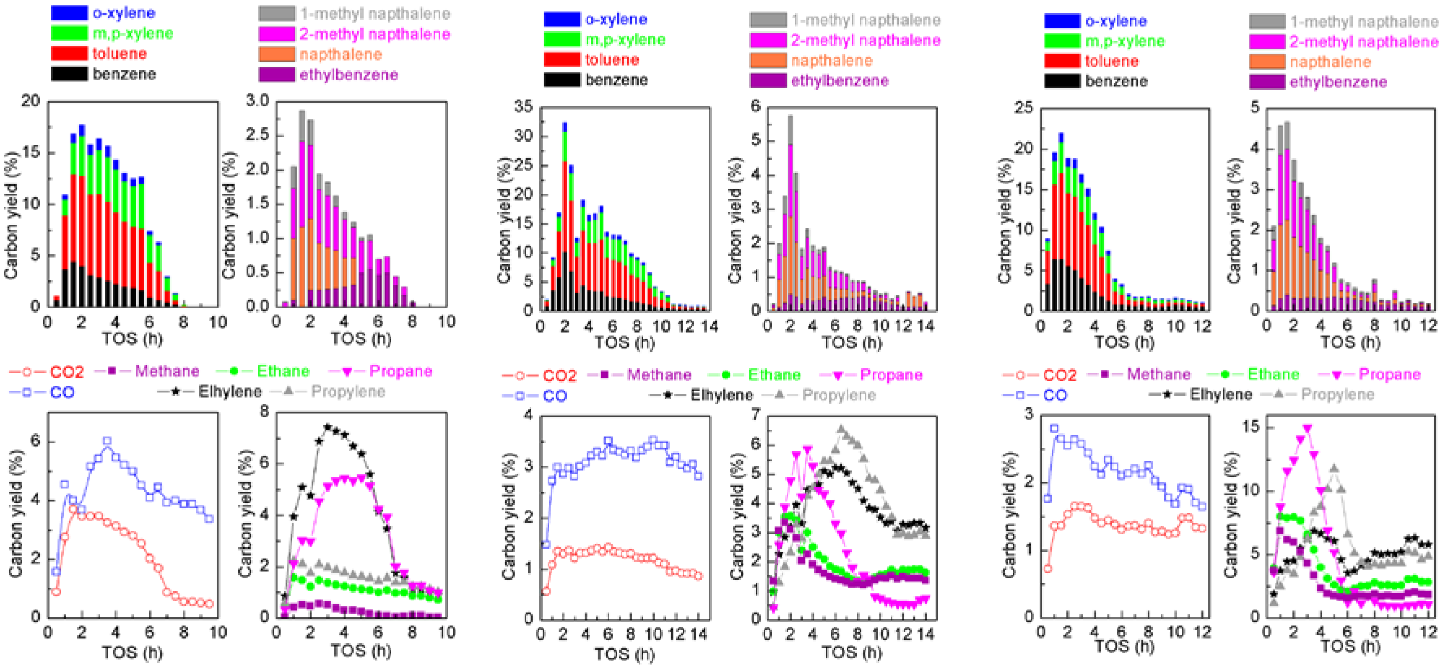
| *Catalyst Name* | *Acidity (µmol $g^{-1}$)* |
|---|---|
| *H-ZSM-5* | 1464 |
| *Cat-D* | 131 |
| *Cat-R1* | 516 |
| *Cat-R5* | 281 |

Decrease performance catalyst originates from:

- Reduction in acidity
- Partial structure collapse and dealumination

# Evolution… (an example)

| Glycerol : Oleic acid (weight ratio) | 10:0 | 8:2 | 6:4 | 4.5:5.5 | 2:8 | 0:10 |
|---|---|---|---|---|---|---|
| $H/C_{eff}$ (molar ratio) | 0.667 | 0.995 | 1.233 | 1.372 | 1.553 | 1.667 |




glycerol

glycerol : oleic acid (45 : 55)

oleic acid

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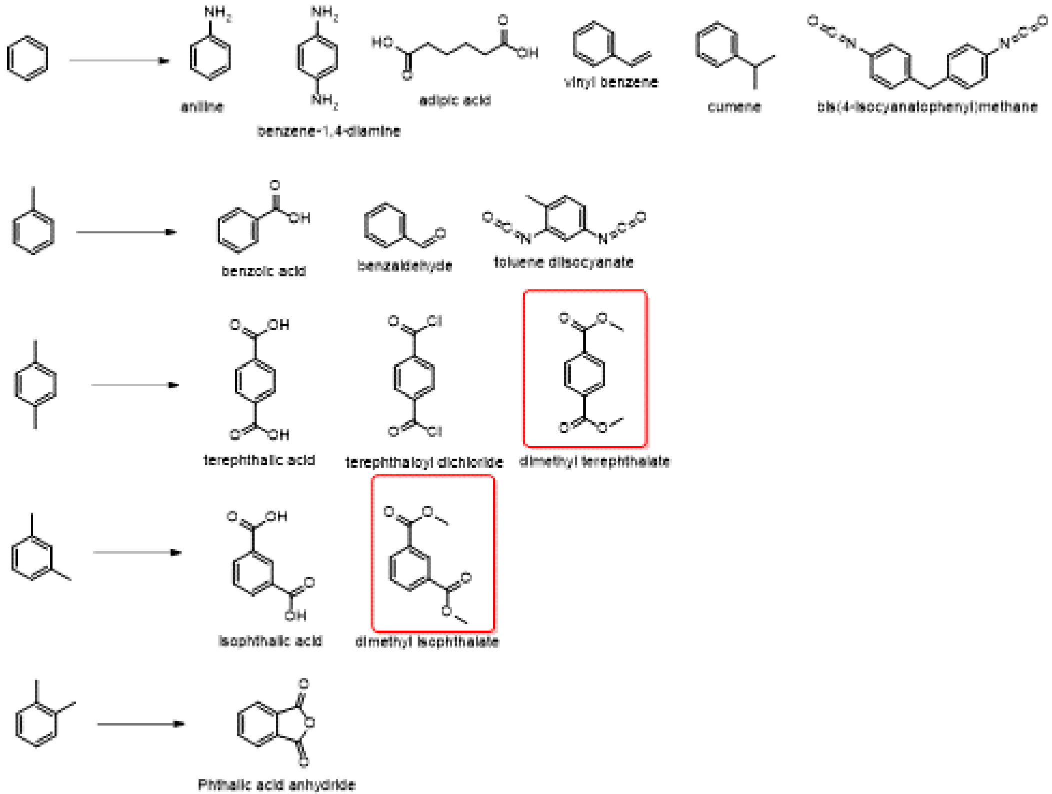
# …. and to scale-up

# Downstream to plastics

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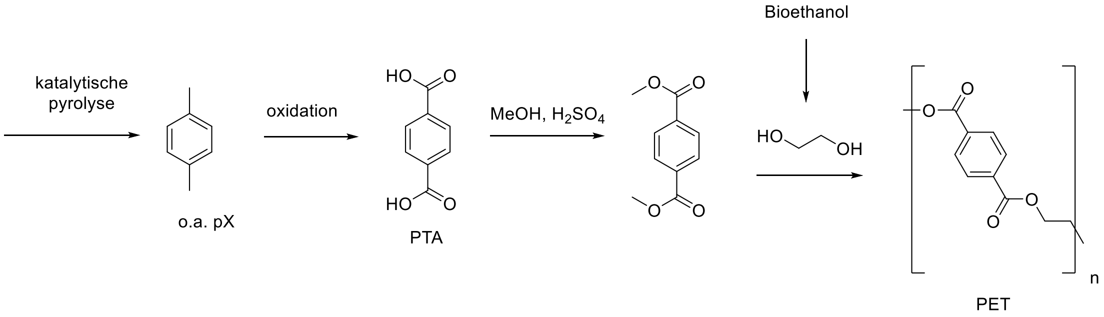
# An example: BioPET100




# Conclusions

- Catalytic pyrolysis has potential for the synthesis of aromatics (BTX) from renewables.
- The University of Groningen, Hanze and BioBTX have developed novel strategies in order to increase the yields of bioaromatics from biomass.
- The catalyst performance (ex situ, glycerol, H-ZSM-5) decreased after several cycles of regeneration.
- The preparation of sustainable plastics was demonstrated with BioPET100.

# Acknowledgements

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BioBTX

- Inouk Muizebelt, Pieter Imhof, Henk van de Bovenkamp, …