CatchBio

*Cat*alysis for Sustainable *Ch*emicals from *Bio*mass

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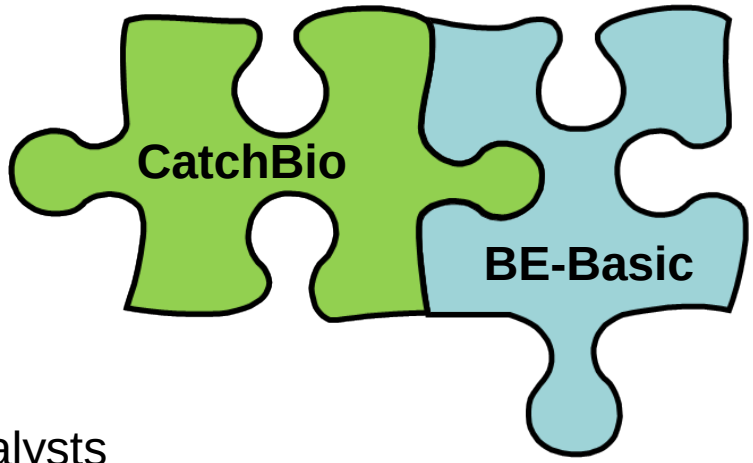
Focus

- CatchBio focuses on **chemocatalytic** conversion routes



Chemocatalysis:
Use of hetero- and homogeneous catalysts

Biocatalysis:
Use of enzymes and micro-organisms

CatchBio

Biomass

Feedstock: lignocellulose, oils and proteins

Sufficient food for everyone

Biorefinery

clean

selective

efficiënt

Chemo- & Bio-Catalysis
Hybrid Conversion Processes

Products

Energy, chemicals & materials for everyone

Our partners

CatchBio

Academic partners:

Universiteit Utrecht

WAGENINGEN UNIVERSITEIT
WAGENINGEN UR

TU Delft

University of Twente
The Netherlands

TU/e Technische Universiteit Eindhoven University of Technology

Universiteit van Amsterdam

RuG

Universiteit Leiden

Radboud University Nijmegen

ECN

Industrial partners:

DOW

DSM

ALBEMARLE

MSD

AVANTIUM

sabic

BASF
The Chemical Company

Shell Global Solutions

sasol
reaching new frontiers

VibSpec

Hybrid Catalysis

The grand challenge

apolar, unfunctionalized compounds of carbon and hydrogen

polar, **highly functionalized** compounds of carbon, hydrogen and **oxygen**

Catalytic toolbox should be adapted:

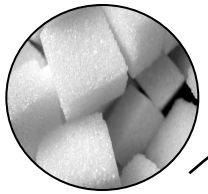
- selective defunctionalisation
- C-C cleavage vs. C-C making
- hydrophobicity/hydrophilicity
- catalysis in aqueous media

Research clusters

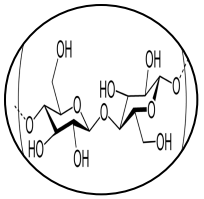
Themes

CatchBio

~ 65% of biomass



sugars



(hemi)cellulose

Formation of sugar derivatives

C-O (deoxygenation)
C-C (isomerization)

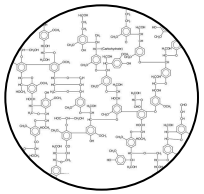
HMF
LA

Valorisation of sugar derivatives

Bulk products

Energy products

~ 25% of biomass



lignin, humins

Lignin & humines

- aromatics
- <u>others</u>

hydrogen production

~ 5% of biomass

vegetable oils

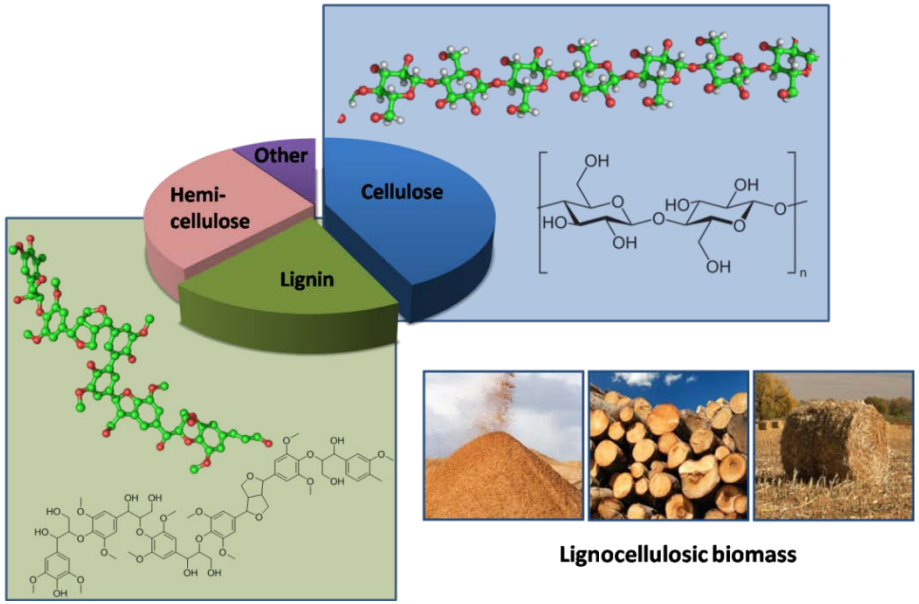
transesterification/ esterification/ decarboxylation

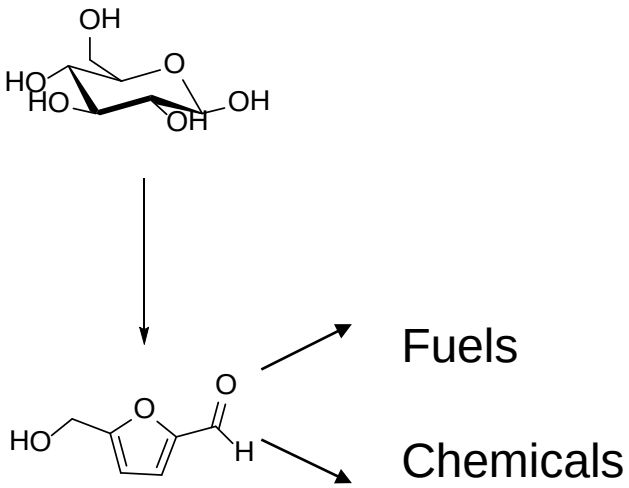
~ 5% of biomass

proteins

decarboxylation

Two highlights from the bulk cluster





Design of novel catalytic systems for the selective dehydration of glucose to HMF; HMF is desirable *platform* molecule (fuels and chemicals)

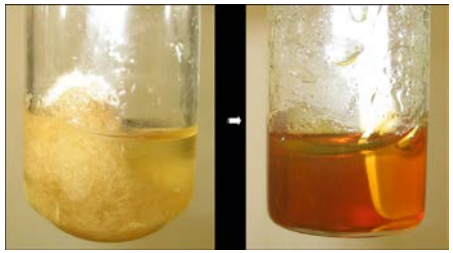
Technische Universiteit Eindhoven University of Technology

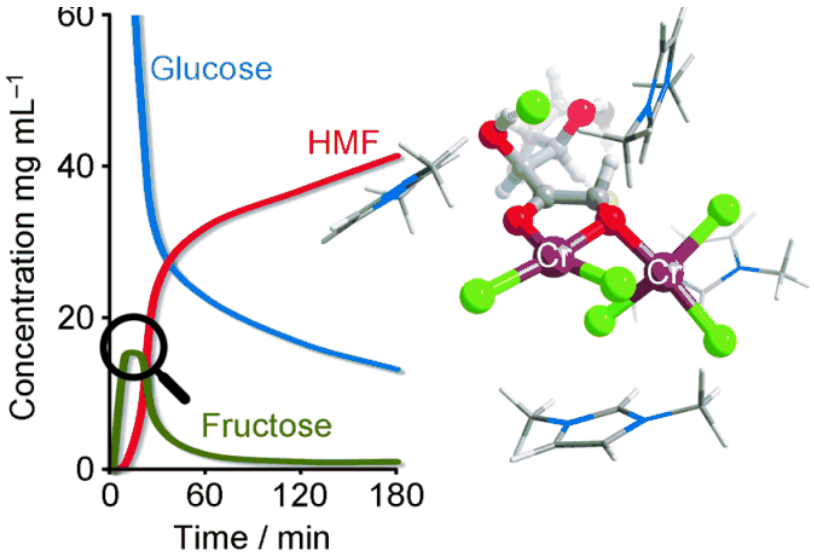
Prof. dr. Emiel Hensen
Dr. Evgeni Pidko

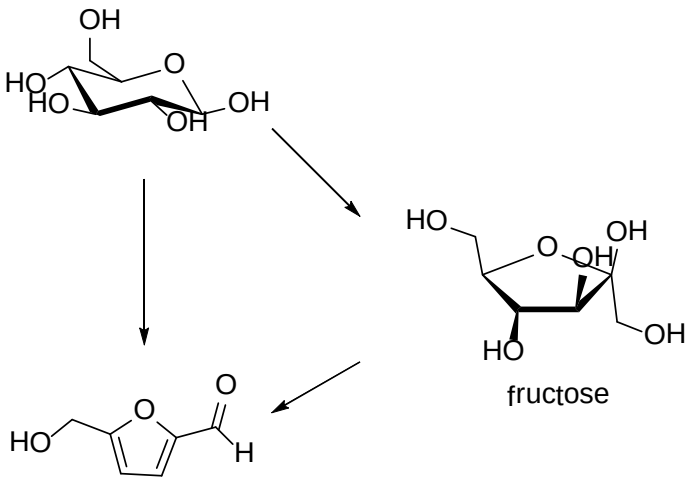
Two highlights from the bulk cluster

CatchBio

- HMF: **a key platform molecule**
- glucose isomerisation and dehydration







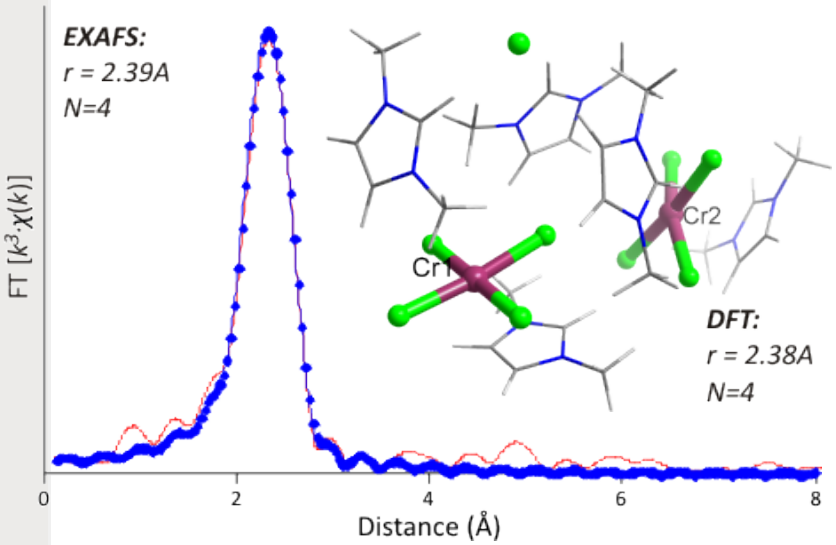
- Chromium salts give exceptional HMF yields in ionic liquid

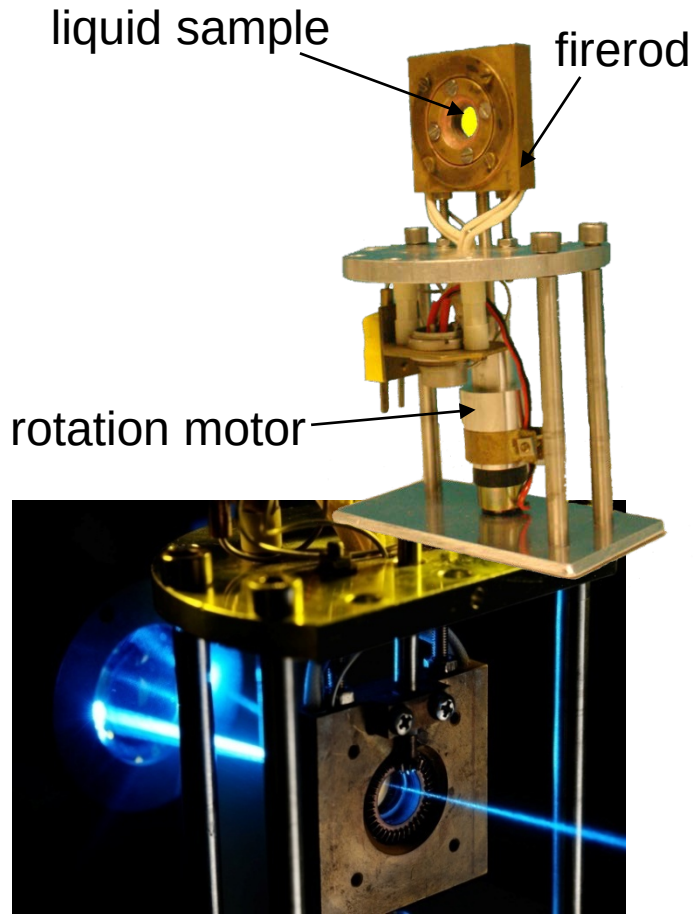
- The Eindhoven group elucidated the **mechanistic details** by a combination of kinetic, spectroscopy, and computational studies

Hensen et al. *Angew. Chem. Int. Ed.* **2010**, *49*, 2530

Chromium (II) chloride in ionic liquid

Liquid phase EXAFS and DFT

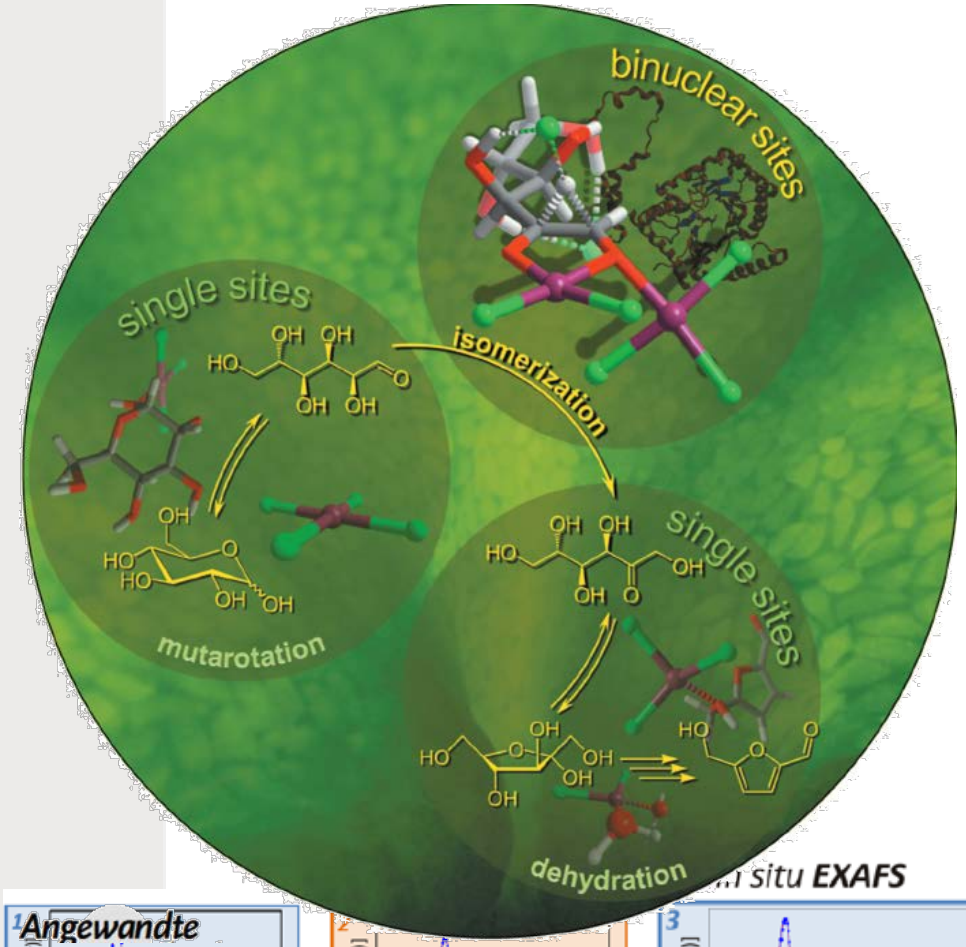


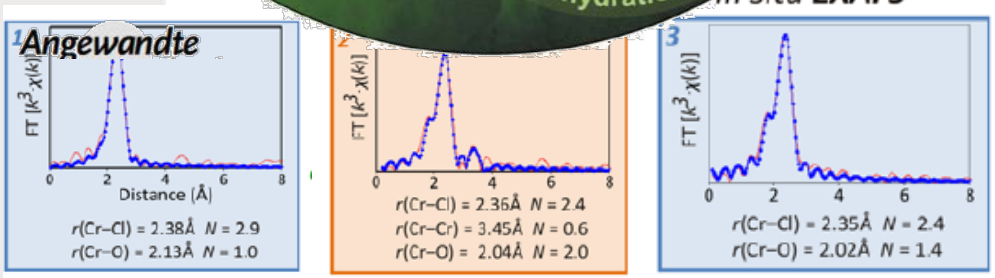


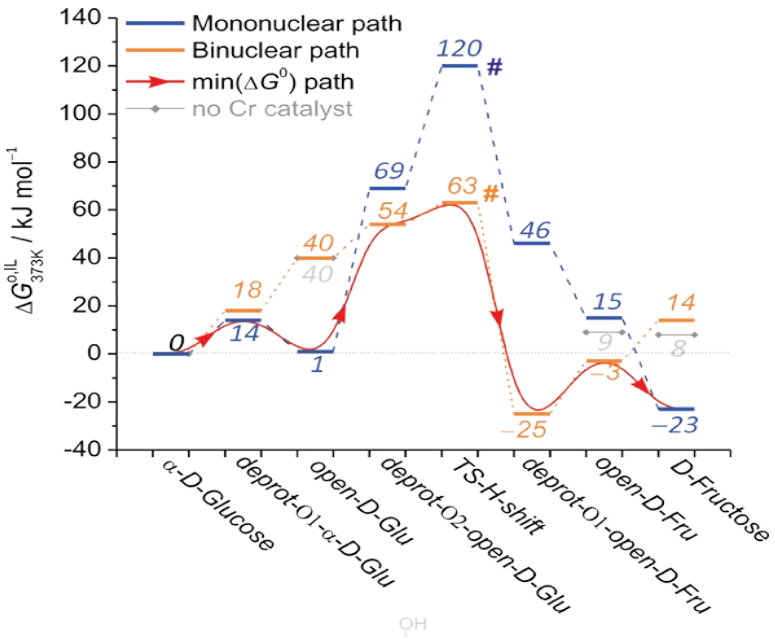
- **EXAFS**
  - Isolated $CrCl_4^{2-}$
  - No Cr-C coordination
- **DFT**
  - Multinuclear species are prohibited
  - Isolated square planar $CrCl_4^{2-}$
  - Perfect match with experiment

Hensen et al., *Inorg. Chem.* 2011, 49, 10081

Two highlights from the bulk cluster

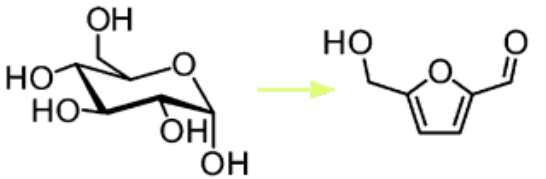


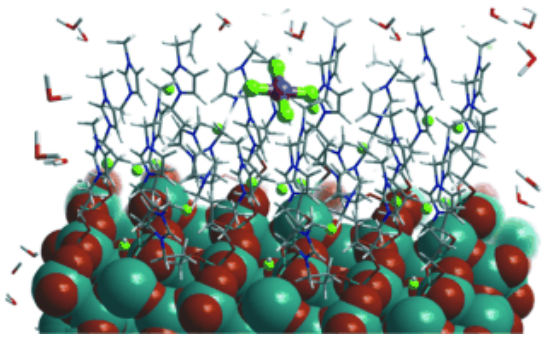


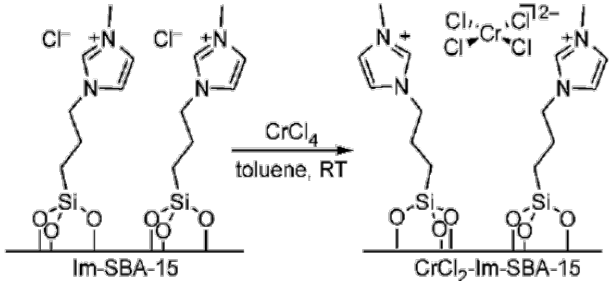


- Ring opening/closure catalyzed by a single chromium ion
- Hydrogen transfer (rds) catalyzed by transient **dimeric chromium species**
- **Enzyme like chemistry**

Two highlights from the bulk cluster







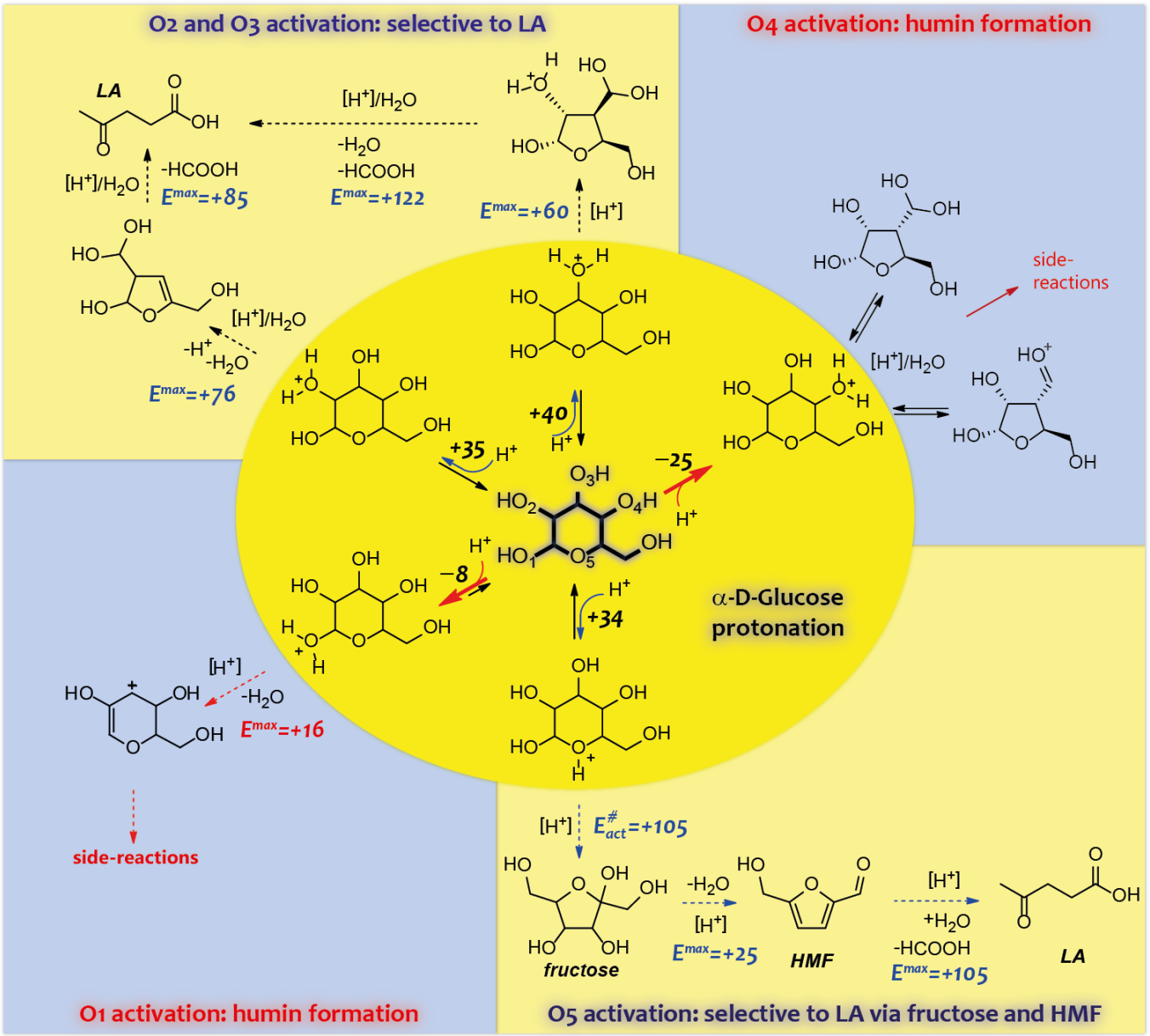
Detailed understanding led to **design of new catalysts**:

- immobilization of chromium salts in an ionic liquid film on a mesoporous support
- Conversion 50%, selectivity 65% (yield 33%) in water
- use of cheaper solvents including water/organics
- current focus: further stabilization of the catalyst

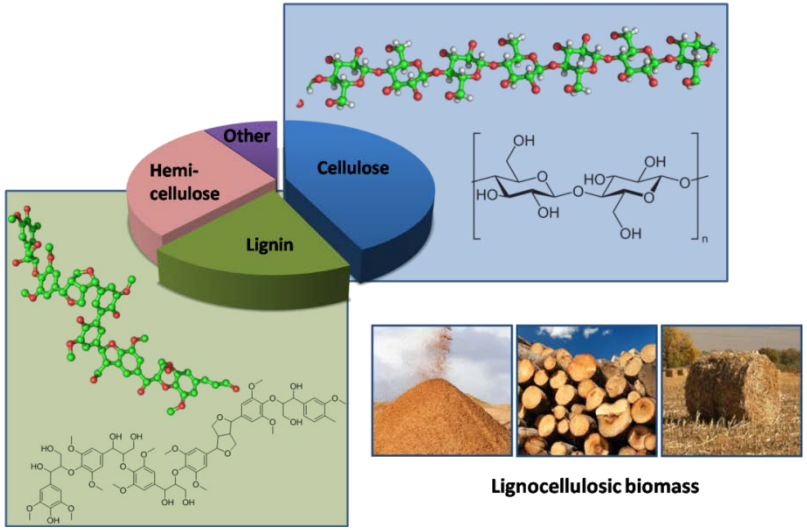
Hensen et al., *Chem. Eur. J.* **2011**, *17*, 5281
Hensen et al., *ChemCatChem* **2011**, *3*, 969

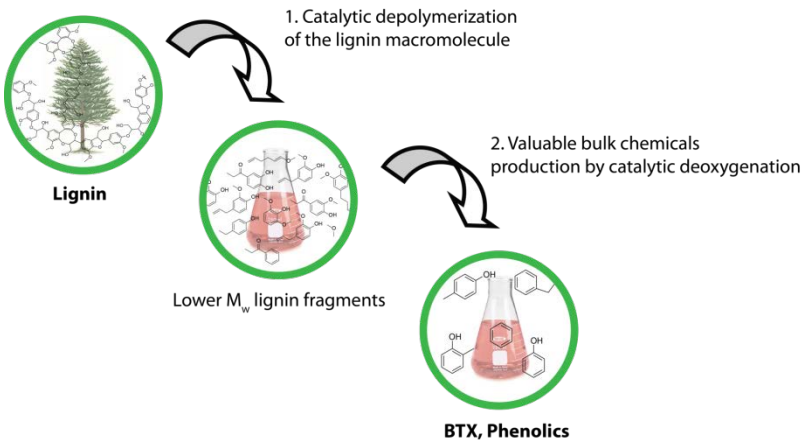
Yang, Pidko, Hensen, *under revision*

Proton catalyzed conversion of glucose



Two highlights from the bulk cluster





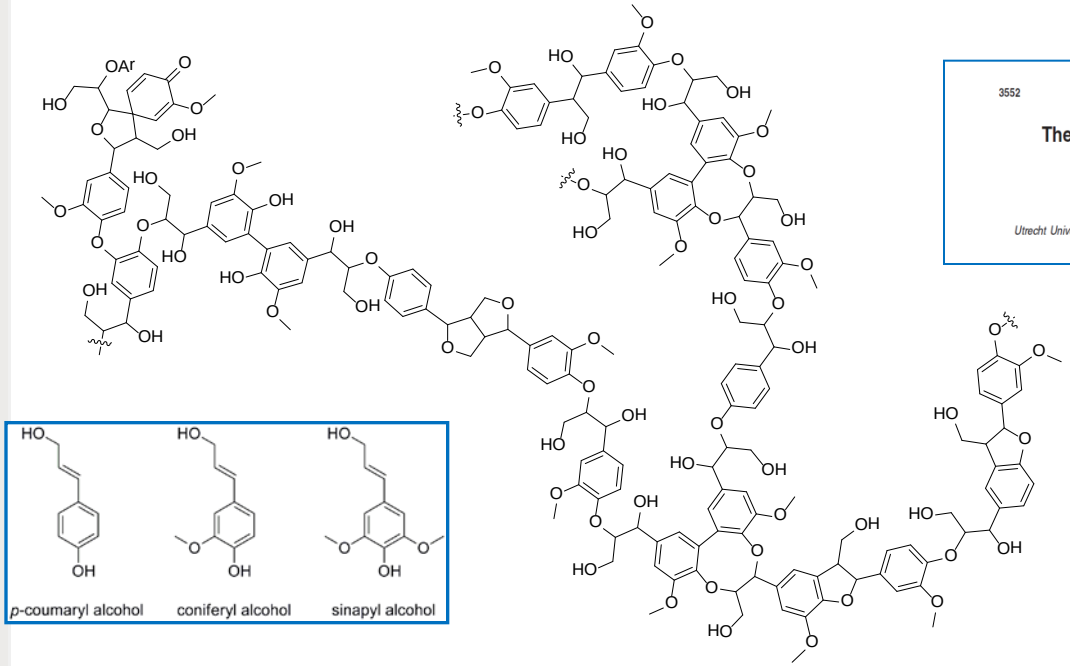
Two-stage catalytic depolymerization of lignin to bulk chemicals

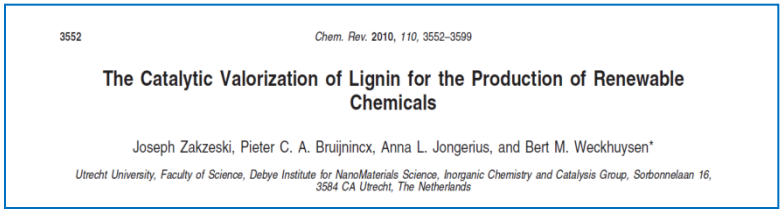
Universiteit Utrecht



Prof. dr. ir. Bert Weckhuysen
Annelie Jongerius MSc
Dr. Joseph Zakzeski

Two highlights from the bulk cluster





3552 *Chem. Rev.* **2010**, *110*, 3552–3599

The Catalytic Valorization of Lignin for the Production of Renewable Chemicals

Joseph Zakzeski, Pieter C. A. Bruijnincx, Anna L. Jongerius, and Bert M. Weckhuysen*

Utrecht University, Faculty of Science, Debye Institute for NanoMaterials Science, Inorganic Chemistry and Catalysis Group, Sorbonnelaan 16, 3584 CA Utrecht, The Netherlands

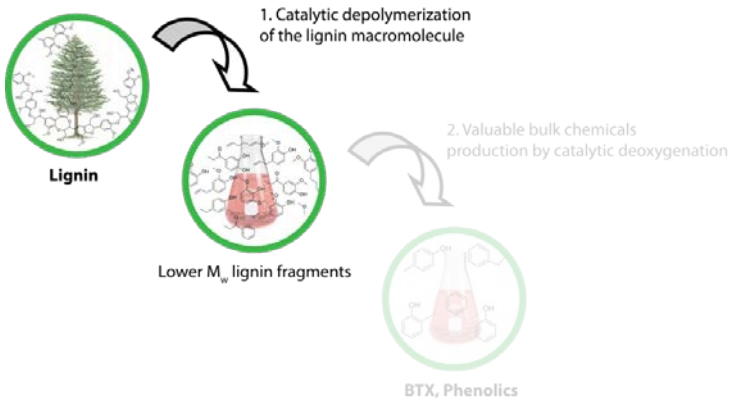
- **Large lignin streams** generated by pulp- and paper industry, future streams available from biorefinery operations

- **Current use**: 98%: low value heating fuel
  2%: chemicals and materials

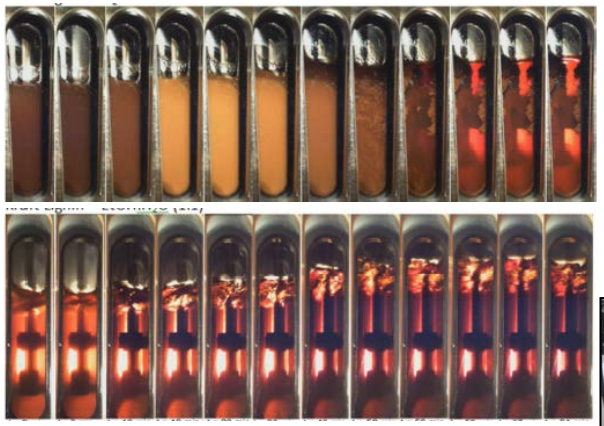
- **Chemocatalytic lignin valorization** reviewed in *Chem. Rev.* **2010**, *110*, 3552

Two highlights from the bulk cluster

- An integrated approach to the valorization of lignin is under study

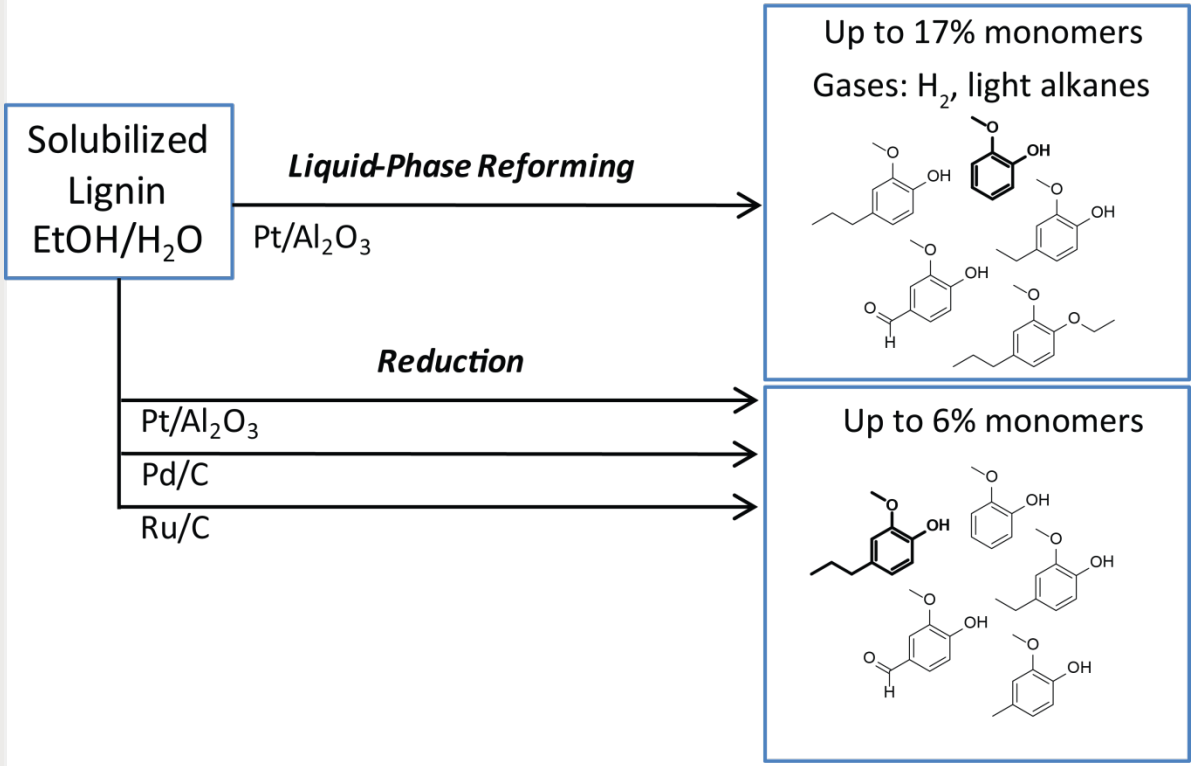


- Different lignins are **nearly 100% soluble** in a mixture of ethanol/water
- No agglomeration of solids
- This allows **further catalytic conversion** of the soluble lignin



Zakzeski, Jongerius, Bruijnincx, Weckhuysen, *to be submitted*

Two highlights from the bulk cluster



Typical conditions:

498K, 90 min, 59 bar He
1/1 v/v EtOH/H_2O

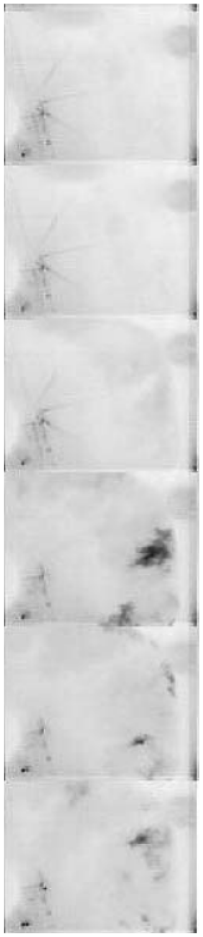
473K, 4h, 30 bar H_2
1/1 v/v EtOH/H_2O

- Various catalytic processes tested to convert solubilized lignin feed
- Product yield and composition depends on the **process/catalyst combination**

Zakzeski, Jongerius, Bruijnincx, Weckhuysen, *to be submitted*

Lignin to Cyclox fuel (reverse engineering)

regular diesel

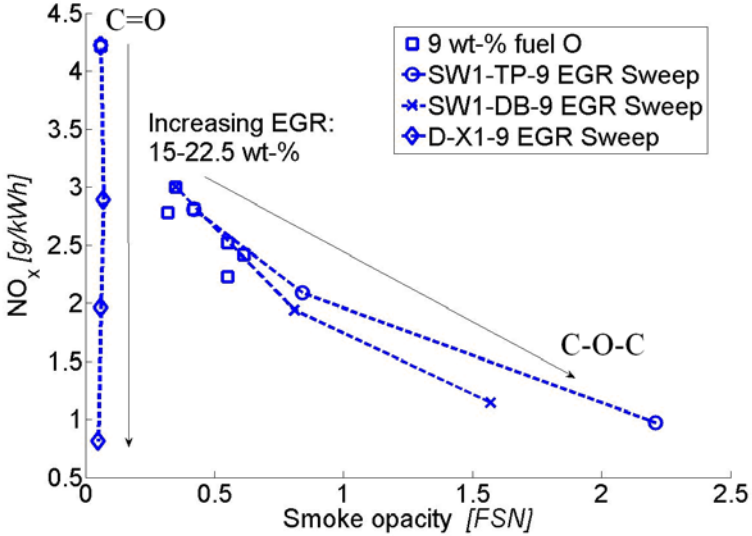


regular diesel
+ **cyclohexanone**

Results

Simultaneous near-zero NO_x and soot with various engines & burners

Patented technology



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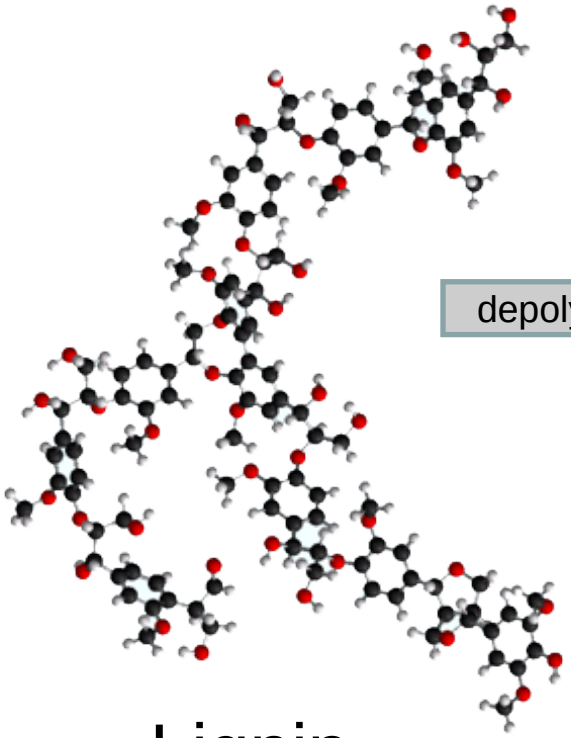
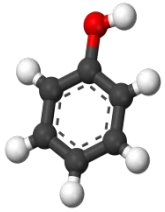
Lignin to Cyclox fuel (reverse engineering)



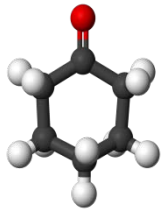
Lignin
(recalcitrant biomass fraction)

depolymerization



Phenolics

upgrading



Mixture
Oxygenated
Aromatics
=
Cyclox

KIC InnoEnergy

BOM
Brabant Development Agency

Technische Universiteit Eindhoven University of Technology

Projects

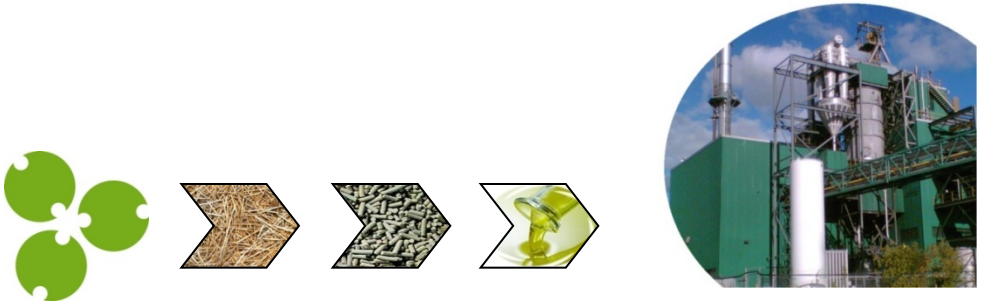
- **First phase** (2008): 19 research projects
- **Second phase** (2009): 17 research projects

    - 37 PhD students
    - 17 Postdoc years
    - WUR/FBR & ECN

- **Third phase** (2012-2015):

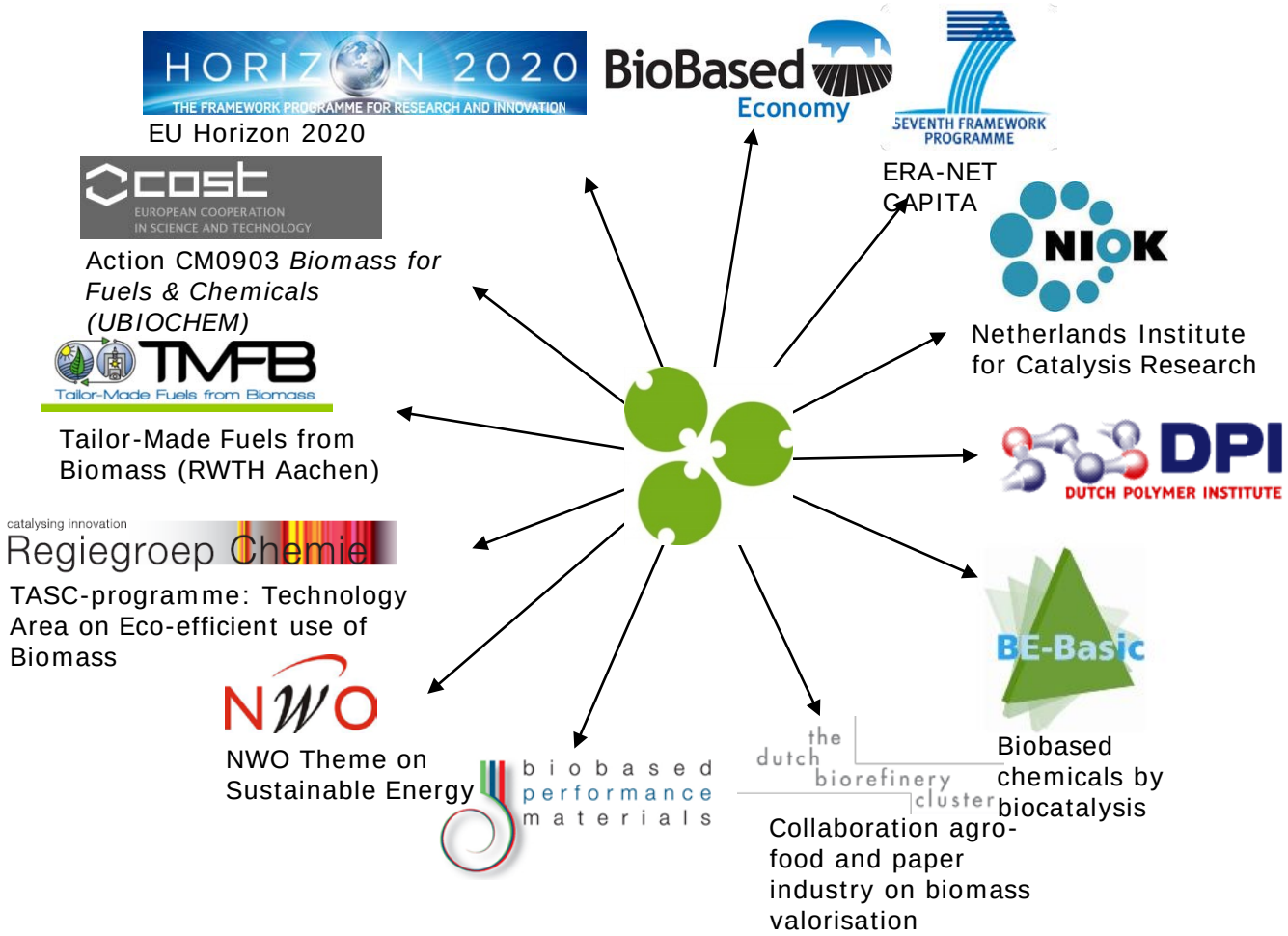
Develop integrated process concepts that will be offered to industry for further development. Based on:

- Delivered proof-of-principles
- Socio-economic assessment
- Interest from industry



(Inter)national positioning

CatchBio should function as a catalyst itself as well: generate **new research lines** and **spur collaboration**.



Topics to be considered for collaboration

CatchBio

General

- Chemocatalytic biomass conversion: robust catalysts for liquid phase processes
- Development in-situ spectroscopy & computational modeling (liquid phase processes)
- Hybrid concepts for biomass conversion: bio- & chemocatalysis
- Catalytic pyrolysis/Fischer-Tropsch Synthesis of biosynthesis gas
- Green diesel production (upgrading of triglycerides, O removal with or w/o H_2)

Cellulose/hemicellulose

- Elementary reaction steps C-O, C-C and O-H bond activation
- Aqueous phase reforming (cheap catalysts, high selectivity to hydrocarbon fuels)
- Catalytic chemistry of sugar valorization (dehydration vs. decarboxylation)
- Catalytic chemistry along the chain: sugars → furfural → levulinic acid → fuels

Lignin

- Depolymerization lignin to fuels and chemicals
- Lignin upgrading to cyclic oxygenates