BIOKET

The global conference dedicated to PROCESSES AND TECHNOLOGIES APPLIED TO BIOMASS

TROIS-RIVIERES, May 23-25, 2023

Valorization of bio-based molecules by hybrid catalysis: towards the synthesis of polymers and surfactants

Alexandra GIMBERNAT[1,2,3], Antoine LANCIEN[1,2], Jean-Sébastien GIRARDON[2], Franck DUMEIGNIL[2], R. WOJCIESZAK[2,] Egon HEUSON[1], Mickaël CAPRON[2], Pascal DHULSTER[1], Nicolas LOPES FERREIRA[3], Damien DELCROIX[3] and Rénato FROIDEVAUX[1]

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[3] *IFP Energies Nouvelles, France*

BioEcoAgro

UCCS UNITÉ DE CATALYSE ET CHIMIE DU SOLIDE

Brings catalysis over lightspeed REALCAT

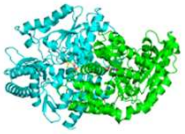
Université de Lille

IFP Energies nouvelles

Hybrid catalysis


Pd Au Ru Pt

Metal nanoparticles

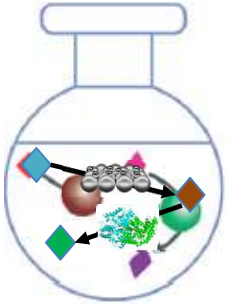


Enzymes

Microorganisms 

Main advantage

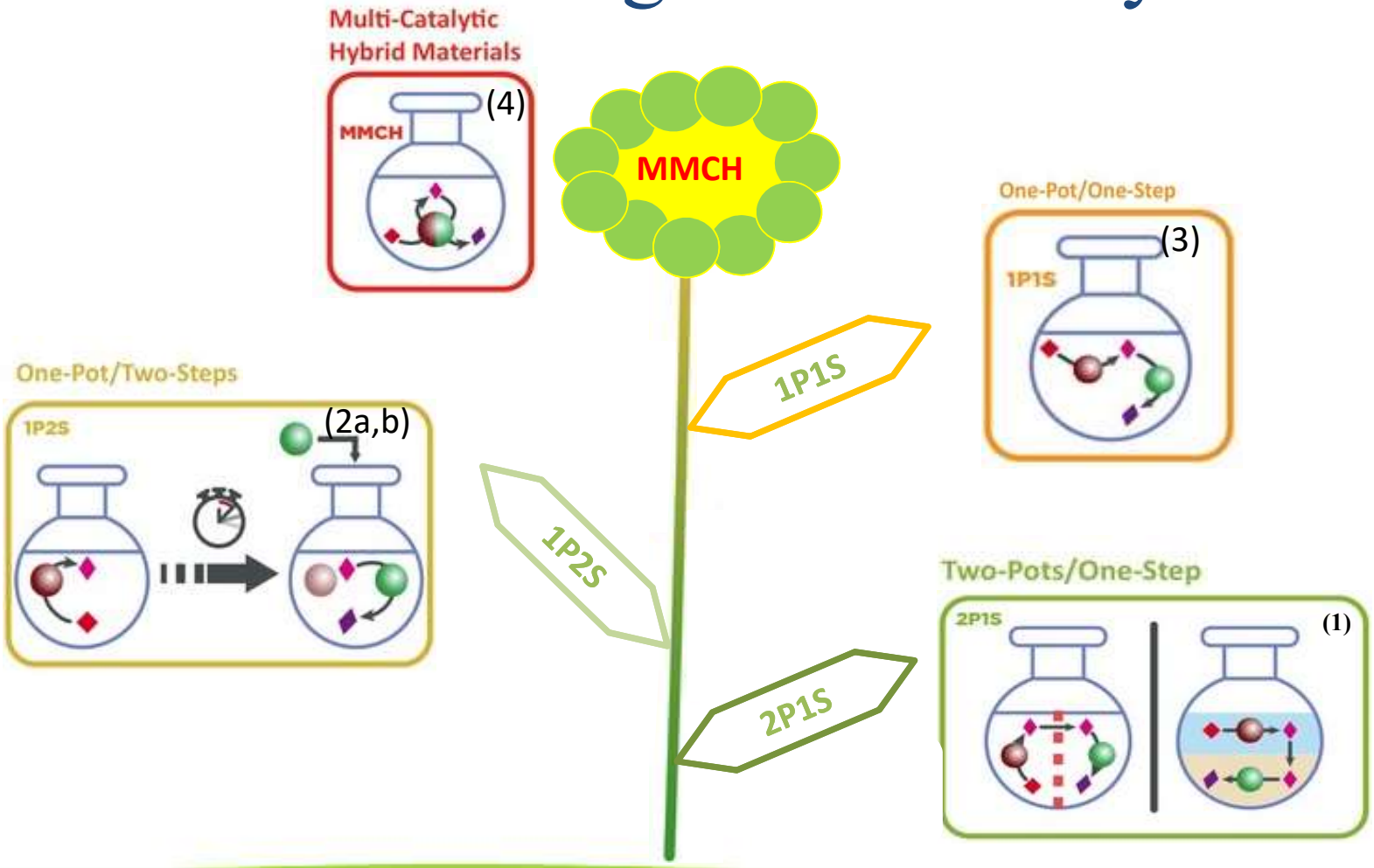
Green approach for opening of new reaction paths towards new synthesis difficult to achieve in only with chemical or enzymatic catalysts



Main challenge

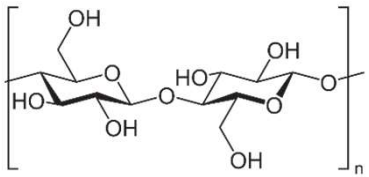
Compatibility between catalysts and reaction conditions

The different configurations of hybrid reaction



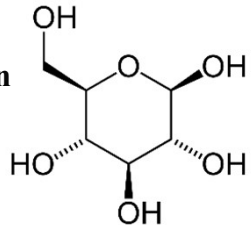
Heuson *et al.*, 2020, (1) Gimbernat *et al.*, 2018 (2) : (a) Paris *et al.*, 2019 (b) Lancien *et al.*, 2020 (3) Mutti *et al.*, 2010 (4) Dutta *et al.*, 2020

Biomass valorization through HMF and furfurylamines



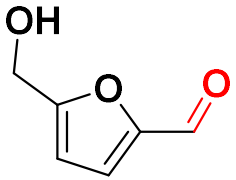
Cellulosic biomass

Degradation



D-Glucose

Example 1
Isomerization/Dehydration

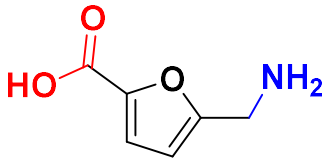


5-HMF

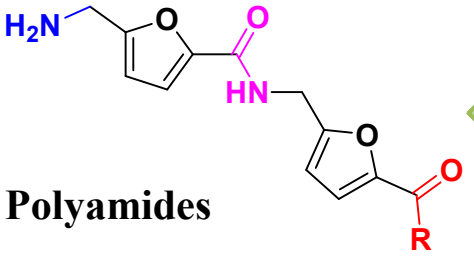
Polyesters
Polyamides
Polyurethanes

Example 2
Amination/Oxidation

Furfurylamine



2-furanoic 5-aminomethyl acid (AMFC)



Polyamides

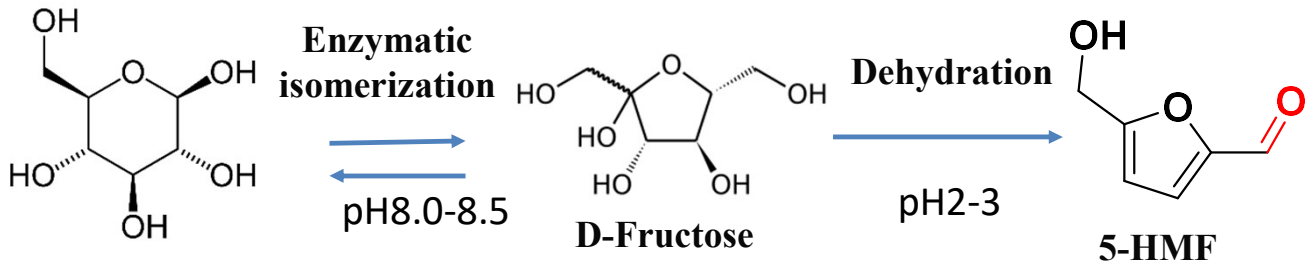
BioEcoAgro

Enzymes

UCCS

Metal nanoparticles

What challenges for HMF synthesis from D-glucose?



≈50% at thermodynamic equilibrium

1P1S
1 enzymatic step
+ 1 chemical step

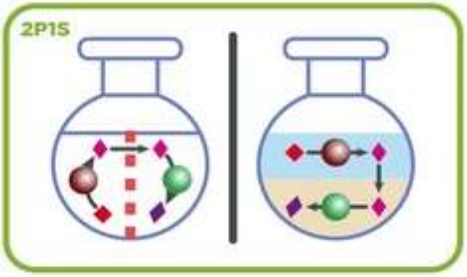
Glc isomerase Oxalic acid	H_2O +NaCl 2MTHF	70 110	**2h** **1h**	28.5%
Glc isomerase SO_3H-FMS	THF/H_2O (4:1)	90	**2h**	20%

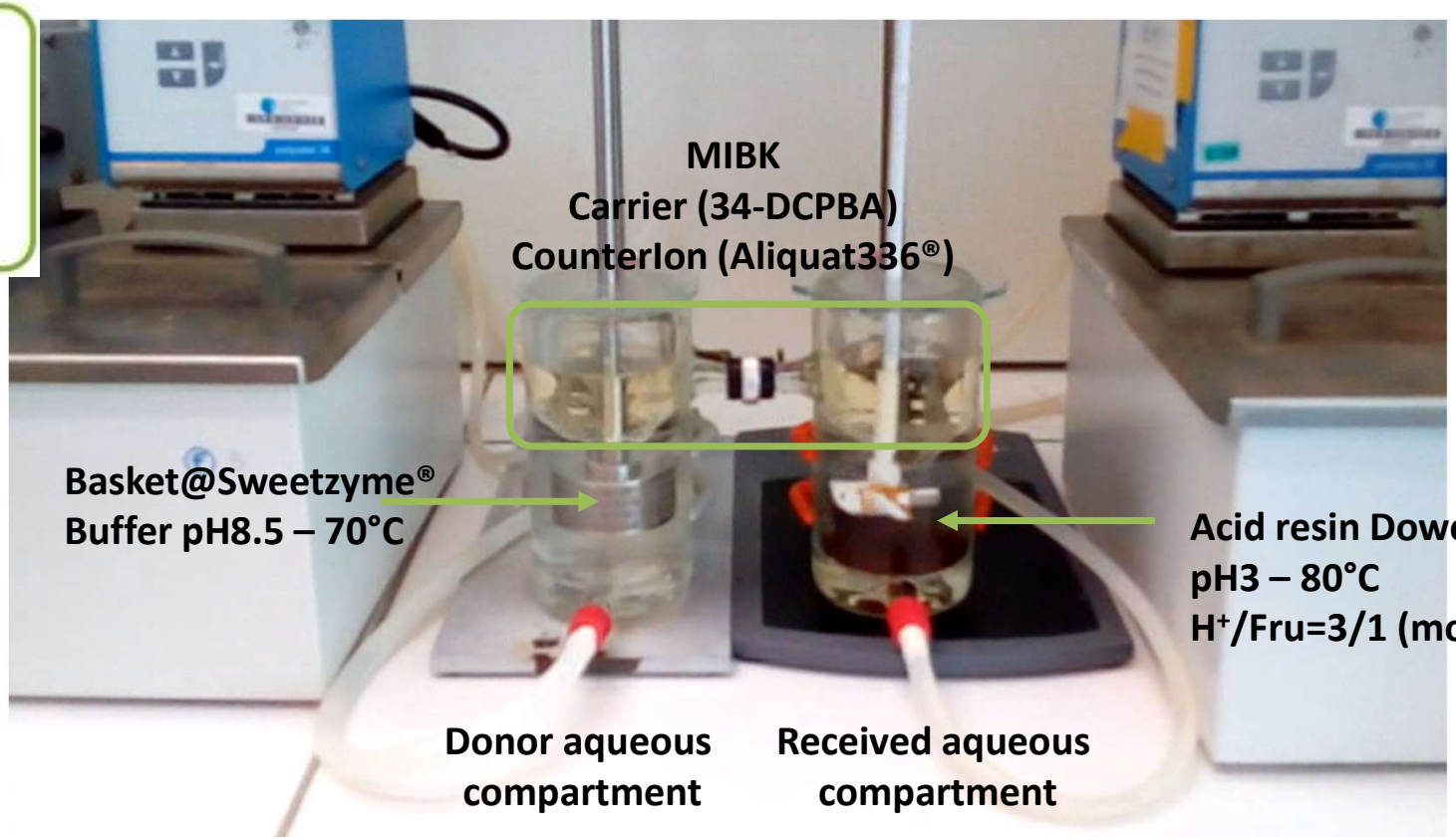
Inactivation of isomerase due to acid pH induced by chemical catalyst
⇒ 1P1S NOT POSSIBLE !!

Development of a « H-reactor » dedicated for 2P1S process hybrid

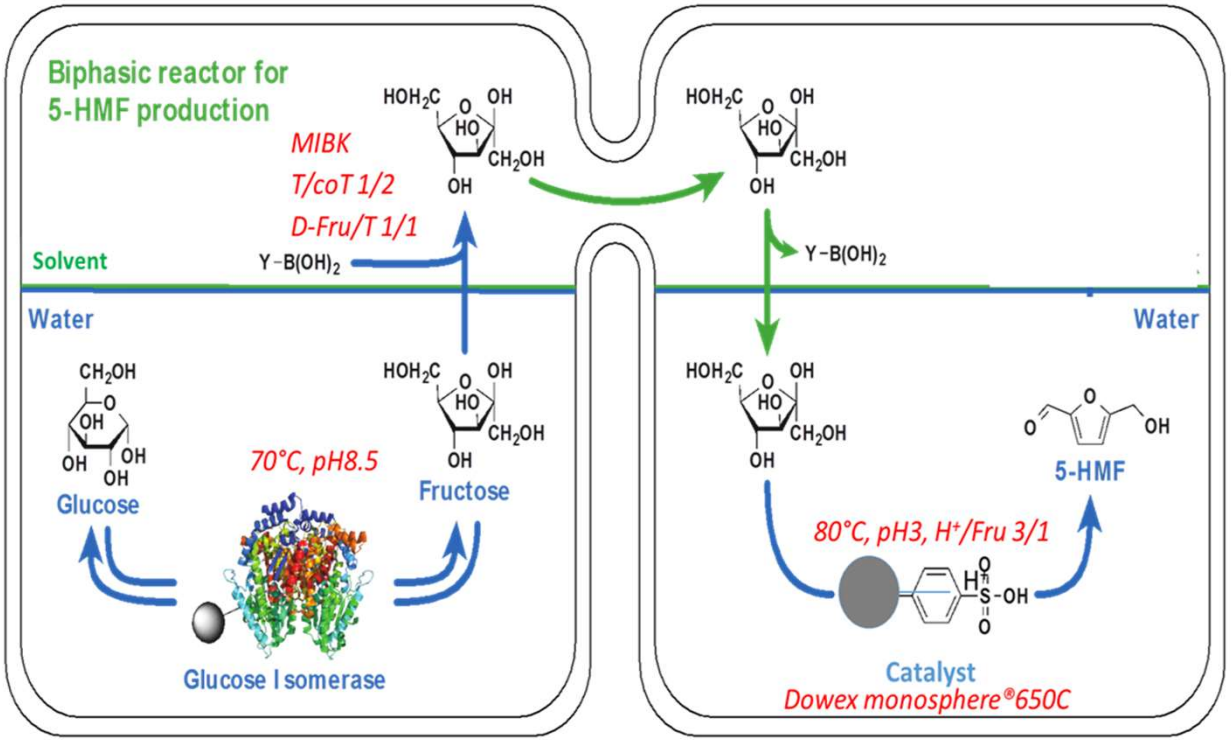
Pagán-Torres, Y. ACS Catal. 2, 930−934 (2012). Nikolla, E. ACS Catal. 1, 408−410 (2011)
Simeonov, S. ChemSusChem. Com. Grande, P. ChemSusChem 5, 1203 – 1206 (2012)

2P1S hybrid process

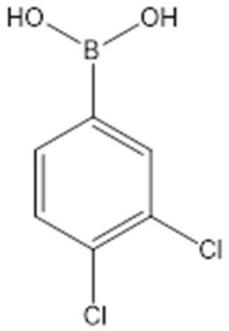




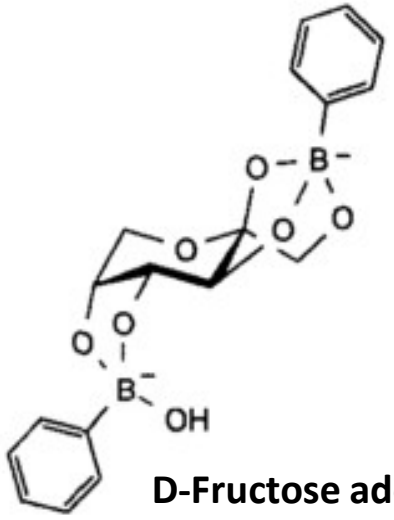
Extraction of D-fructose



Carrier (C)

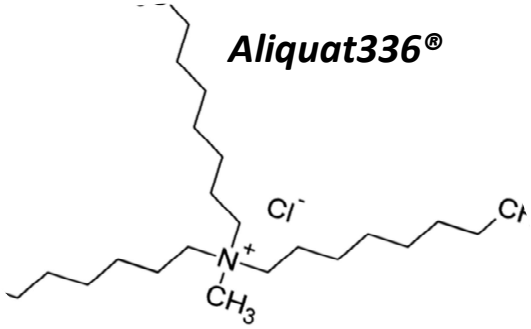


34-DCPBA



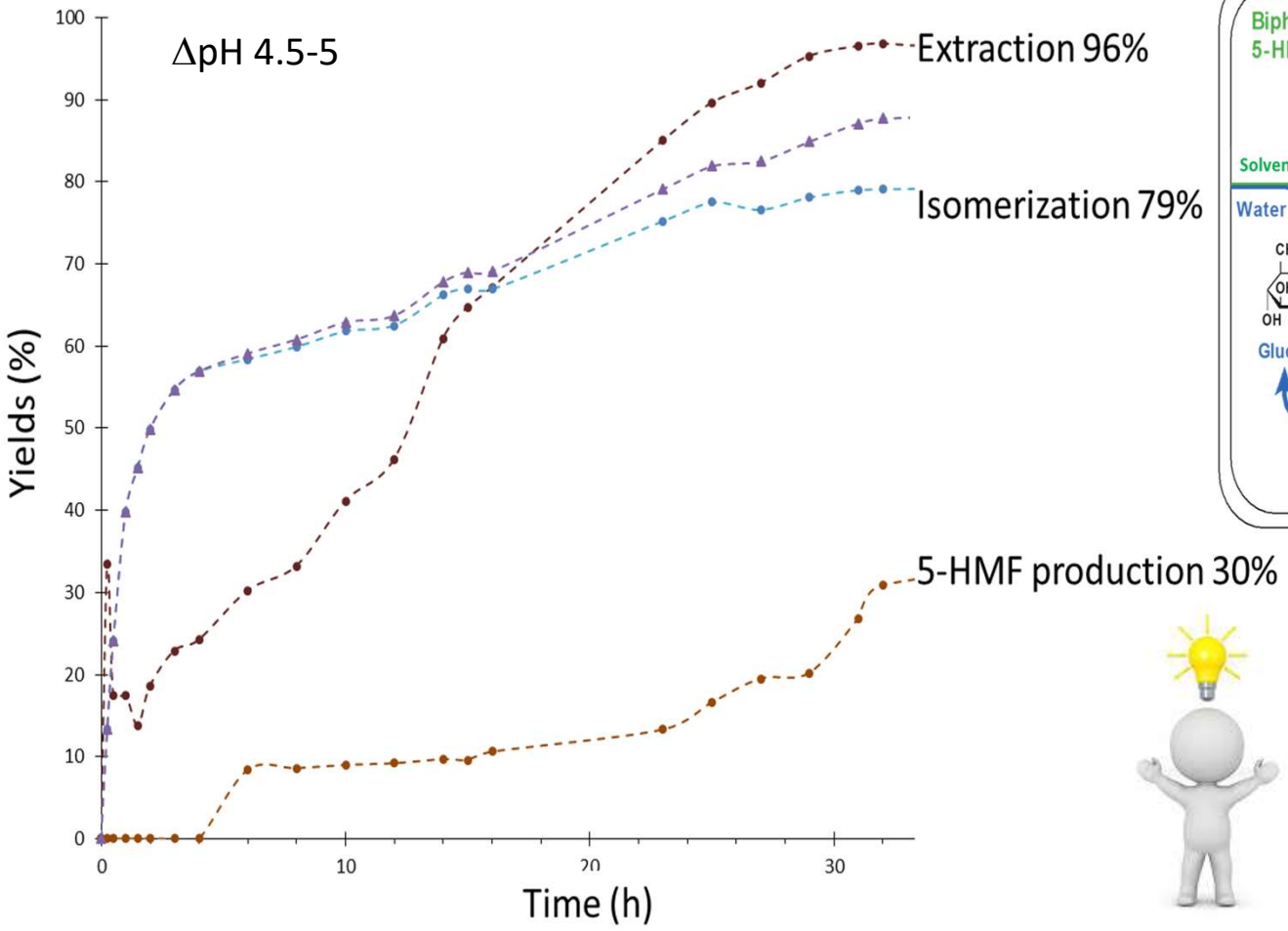
D-Fructose adducts

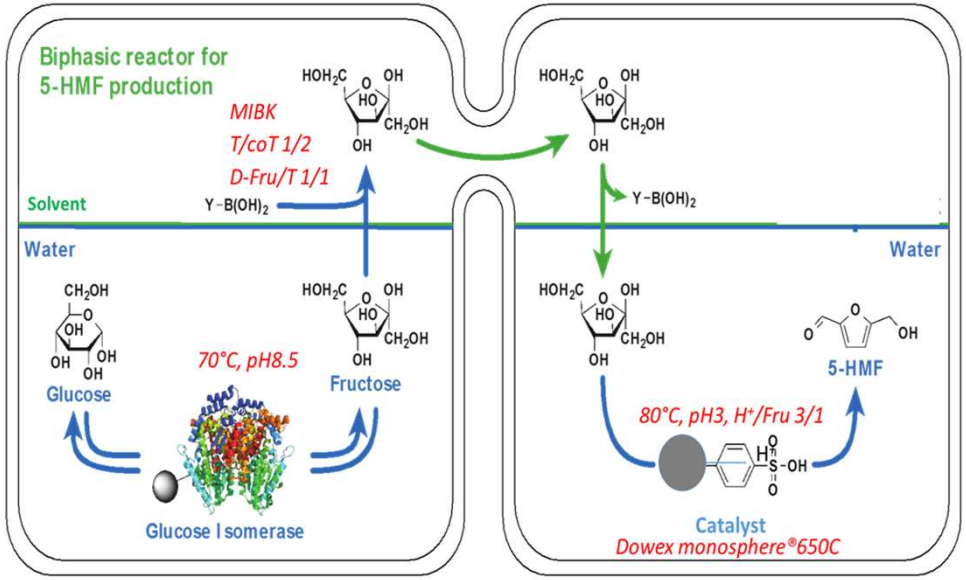
Aliquat336®



Westmark, P. R., Gardiner, S. J., Smith, B. D. J. Am. Chem. Soc. 118, 11093–11100 (1996).
Takeuchi, M., Koumoto, K., Goto, M., Shinkai, S. Tetrahedron 52, 12931–12940 (1996).

2P1S hybrid process



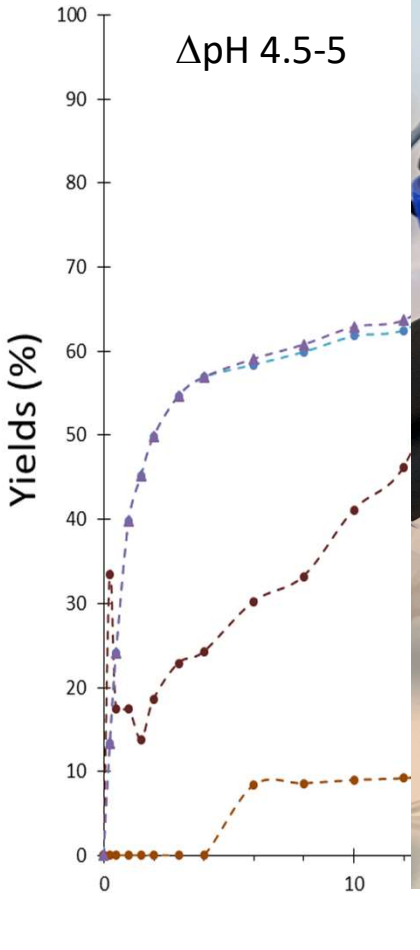


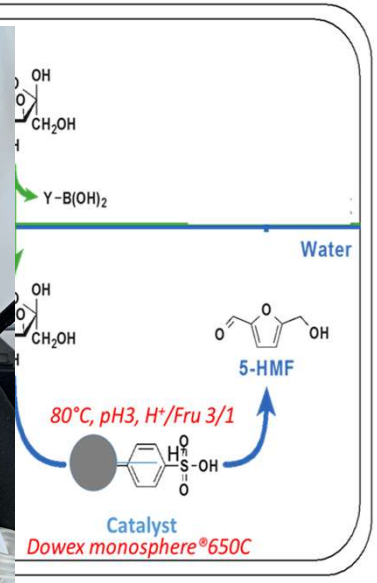
$Yield_{isomerization}$=79% (50% at thermo. equil.)

No enzyme inactivation during 32 hours !

$Y_{5\text{-}HMF}$=30% after 32h

Hybrid process in continuous flow





at thermo. equil.)

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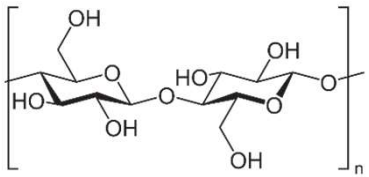
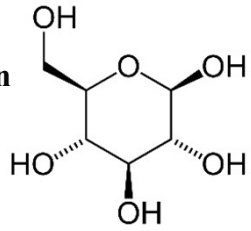
Biomass valorization through HMF and furfurylamines



Cellulosic biomass

Degradation



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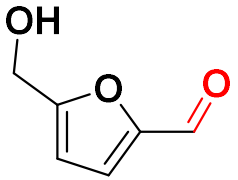
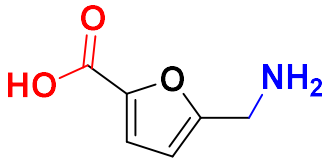


5-HMF

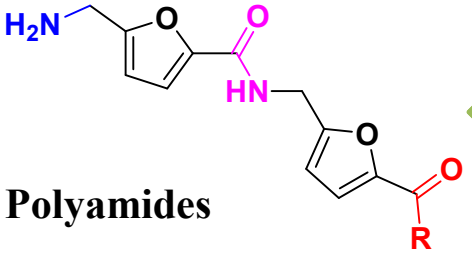
Polyesters
Polyamides
Polyurethanes

Example 2
Amination/Oxidation

Furfurylamine



2-furanoic 5-aminomethyl acid (AMFC)



Polyamides

BioEcoAgro

Enzymes

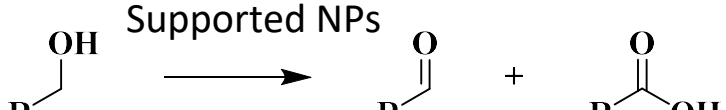
UCCS

Metal nanoparticles

Gimbernat *et al*, 2018

What challenges for furfurylamines synthesis from HMF ?

❑ **Supported nanoparticles**



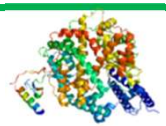
Alcohol — Aldehyde — Carboxylic acid

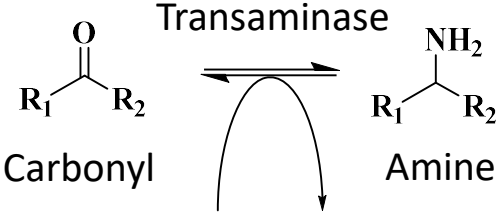
Gold NPs

Pt or Pd NPs

Bimettalic NPs

❑ **Transaminases**

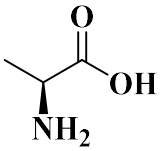




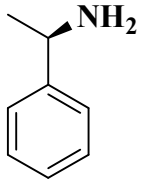
Carbonyl — Amine

Amine donor — Carbonyl co-products

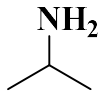
❑ Amine donors



L-alanine



(*S*)-MethylBenzyl Amine



IsoPropyl Amine

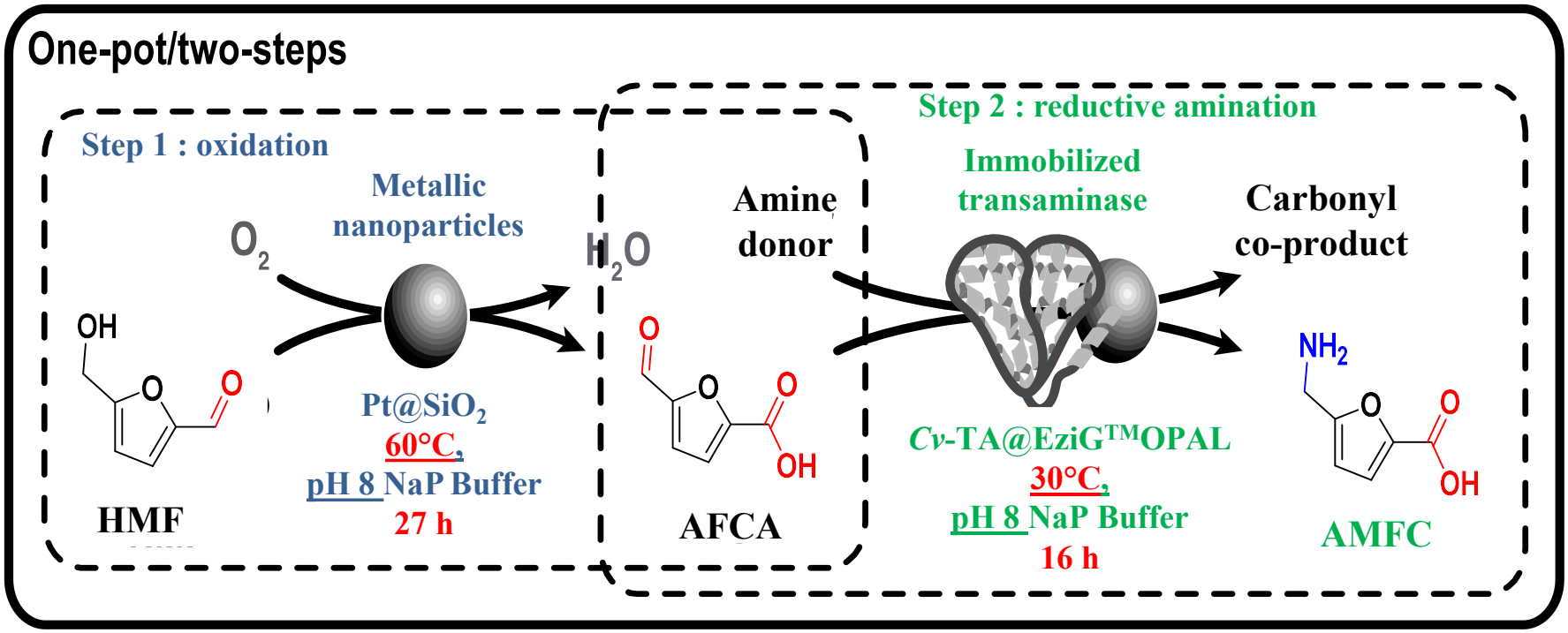
Hybrid catalysis

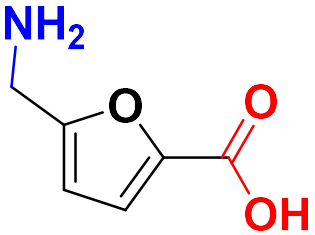
- ***Selectivity and specificity***
- ***Potential synergy***
- ***Opening to new reaction paths***

Ferraz *et al.*, 2018,
Grasset *et al.*, 2017,
Wojcieszak *et al.*, 2016,
Baldovino-Medrano *et al.*, 2016

Dunbabin *et al.*, 2017,
Simon *et al.*,2014,
Mathew *et al.*, 2012,
Höhne *et al.*, 2009,
Petri *et al.*, 2018

Hybrid one-pot/two-step process

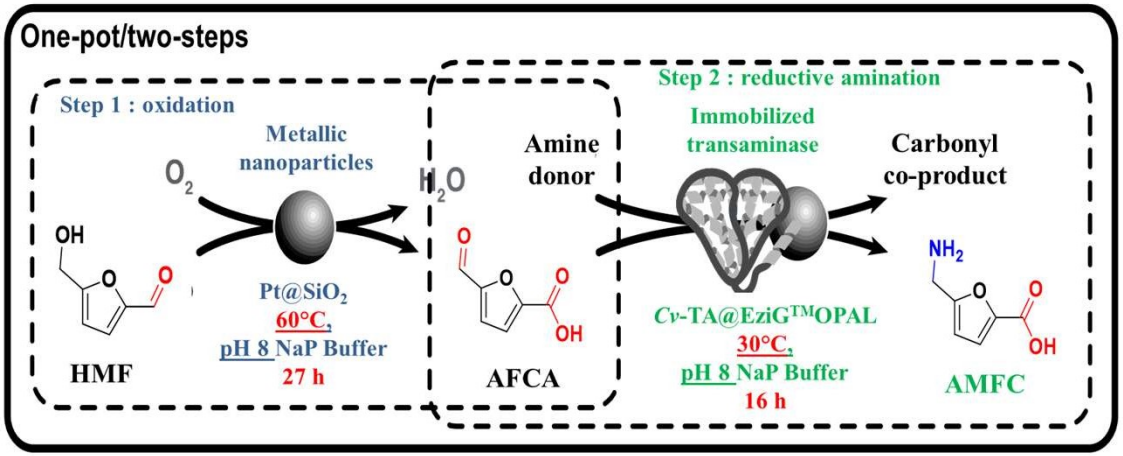




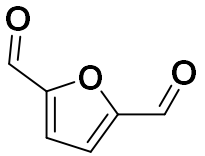
AMFC yield
77%

Lancien *et al*, 2020

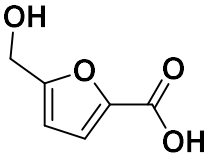
Towards a hybrid one-pot/one-step process



- Enzyme unstability at 60°C
- AMFC production limited by the low selectivity of step 1 in 1P2S
  ⇒ Presence of subproducts

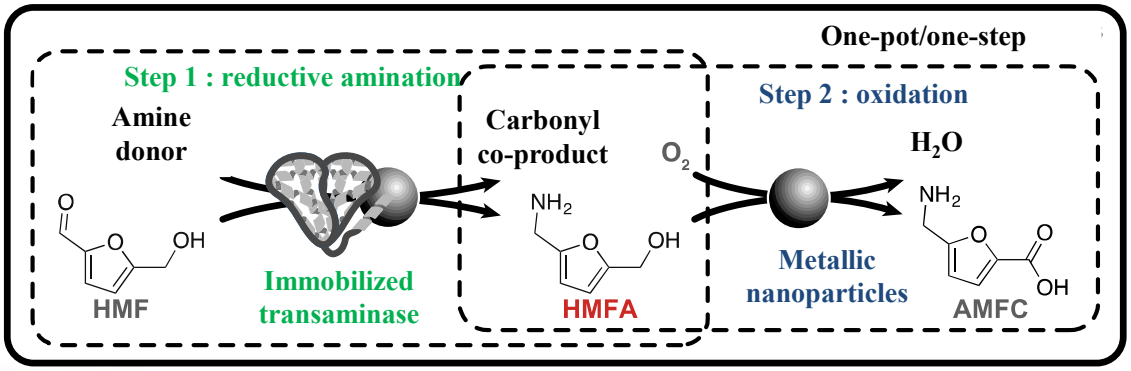


DCAF



HFCA

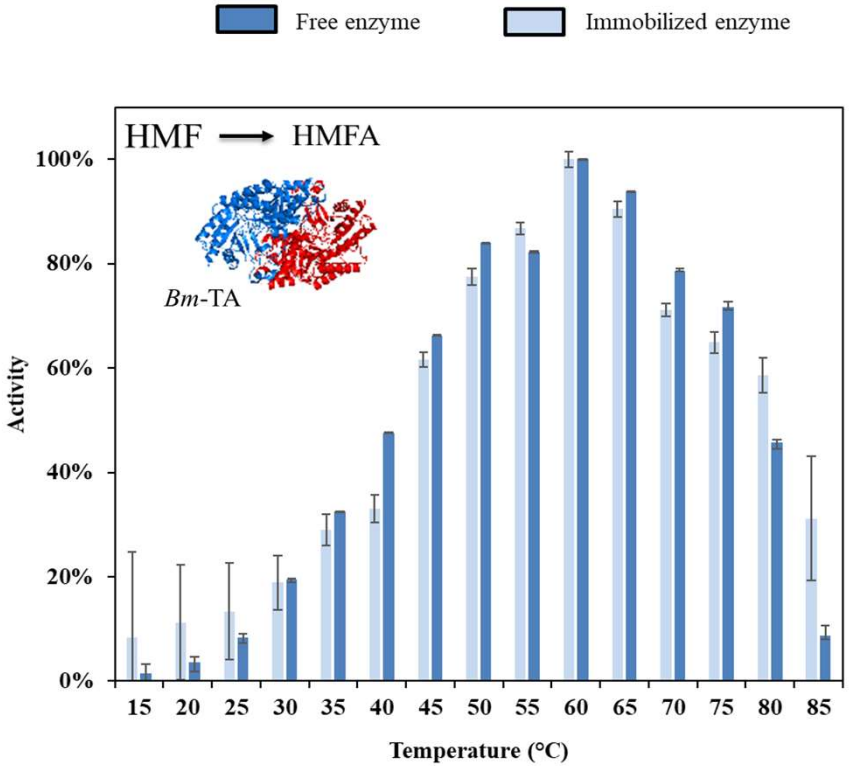
- New thermostable transaminase
- Heterogeneous catalyst with high specificity for HMFA



Production, characterization and immobilization of new transaminases

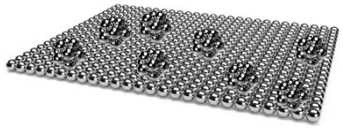
Pr U. Bornscheuer
Univ. Greifswald
Germany

1 : B9AZ94
2 : I2IXB4
3 : D1C7Z3
4 : A0KE01
5 : 3HMU

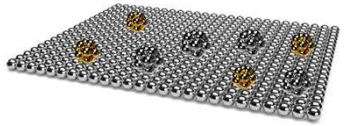


Production and characterization of new catalysts active on HMFA

Gold NPs



Palladium NPs

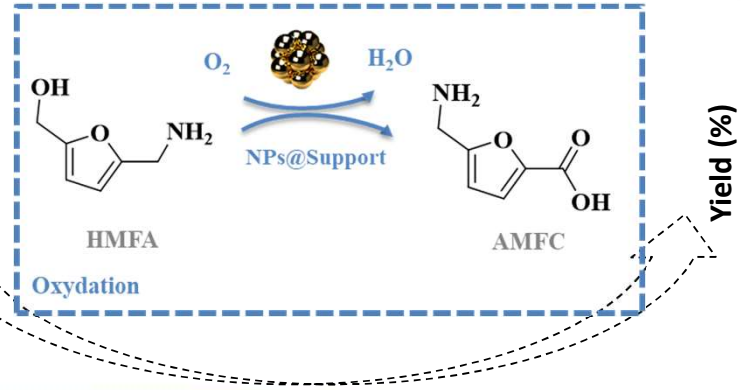


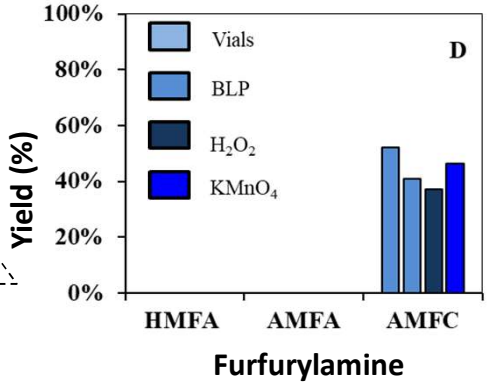
Bimetallic NPs

@CaO @TiO_2, @CeO_2

BioLector pro®

- 33 catalysts
- 150 conditions tested in microplates on REALCAT HT platform

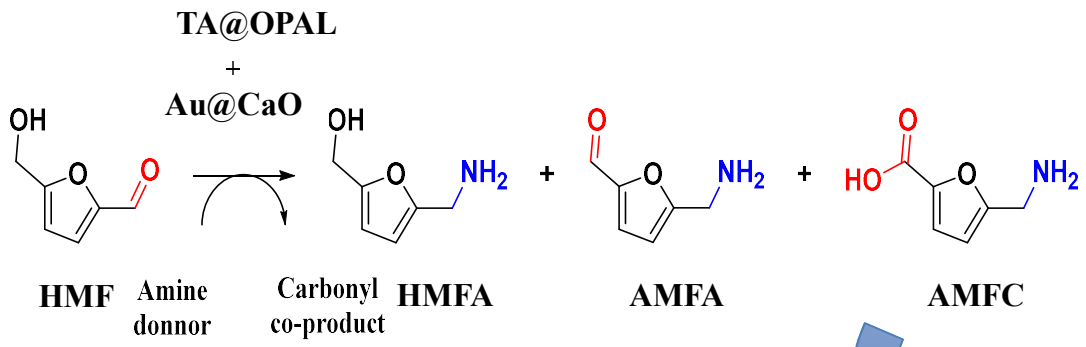




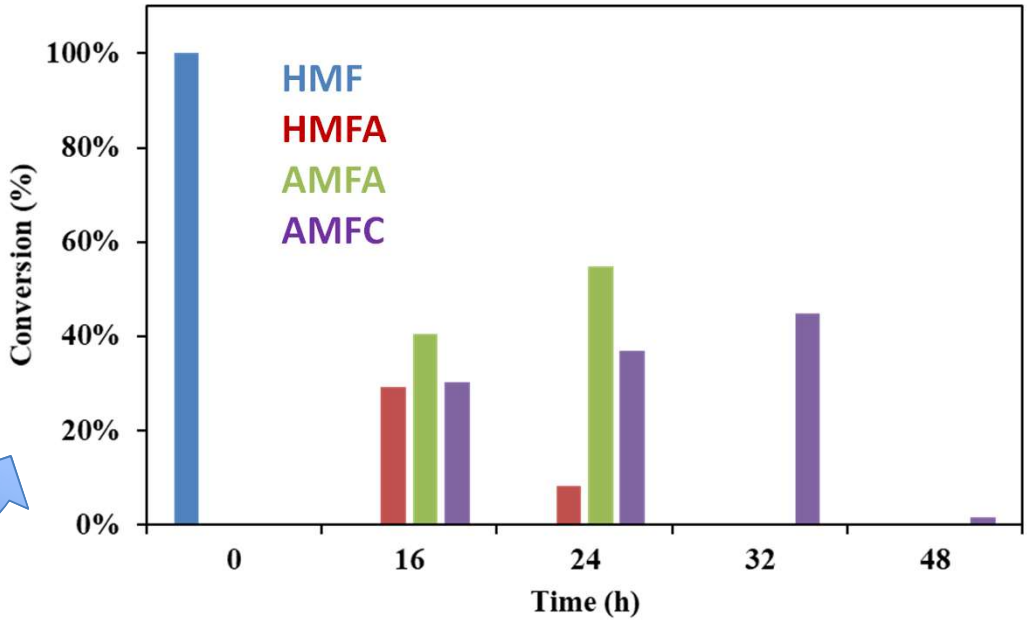
Brings catalysis over lightspeed
REALCAT

Au@CaO
Y(AMFC) ≈ 50%

Hybrid one-pot/one-step process



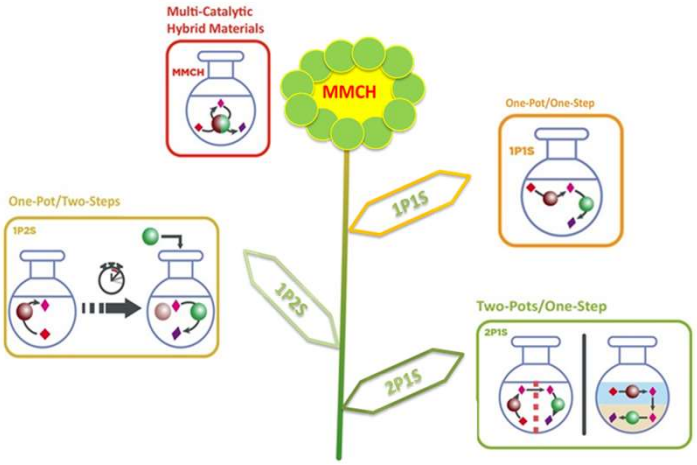
Kinetics
48 hours
50°C – pH8
400 rpm



- Complete conversion of HMF to HMFA
- Complete conversion of HMFA to AMFC

$\Rightarrow$ **Y(AMFC) = 50%**

Conclusion



NEW PATHS in CATALYSIS…… GREENER SYNTHESIS APPROACH

Acknowledgements

BioEcoAgro

Alexandra GIMBERNAT
Antoine LANCIEN
Nabil AIT RADI
Amandine LORTHIOS
Racym MEKKI
Pascal DHULSTER

UCCS

Jean-Sébastien GIRARDON
Egon HEUSON
Mickael CAPRON
Franck DUMEIGNIL
Sébastien PAUL
Robert WOJCIESZAK

Brings catalysis over lightspeed
REALCAT

Sébastien PAUL
Egon HEUSON
Quentin HAGUET
Svetlana HEYTE

Funders

ifp Energies nouvelles

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BIOKET

The global conference dedicated to PROCESSES AND TECHNOLOGIES APPLIED TO BIOMASS

TROIS-RIVIERES, May 23-25, 2023

Valorization of bio-based molecules by hybrid catalysis: towards the synthesis of polymers and surfactants

Rénato FROIDEVAUX

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UMRt BioEcoAgro 1158, Team Biotransformation/Enzymes and Biocatalysis, Lille, France

Université de Lille

BioEcoAgro

UCCS UNITÉ DE CATALYSE ET CHIMIE DU SOLIDE

Brings catalysis over lightspeed REALCAT

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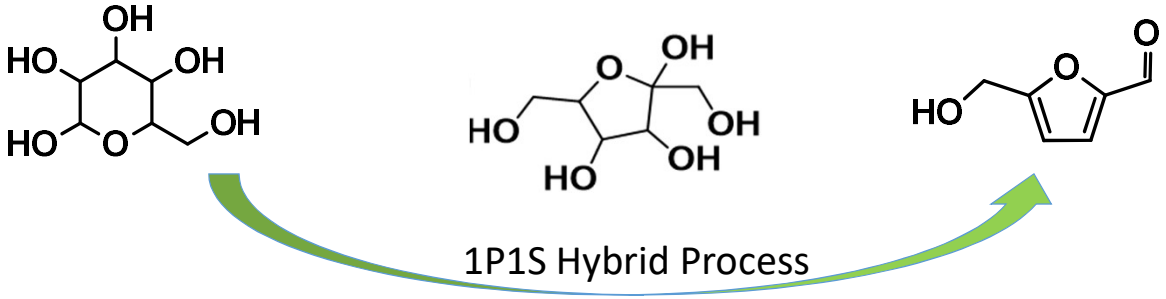
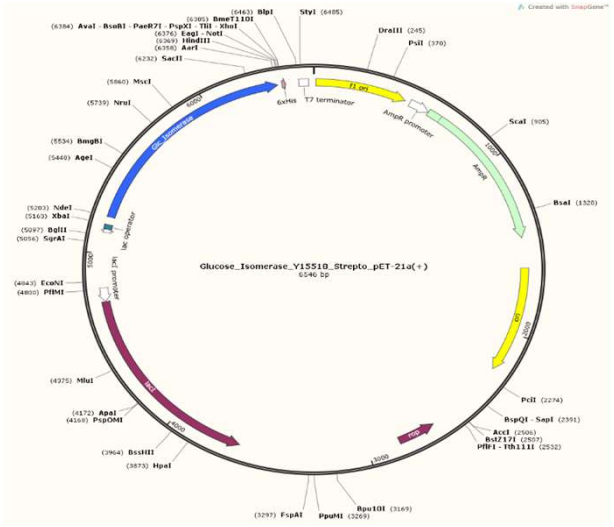
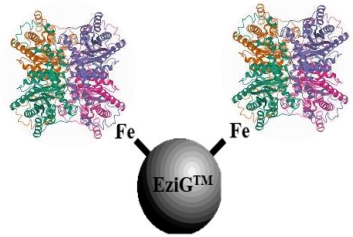
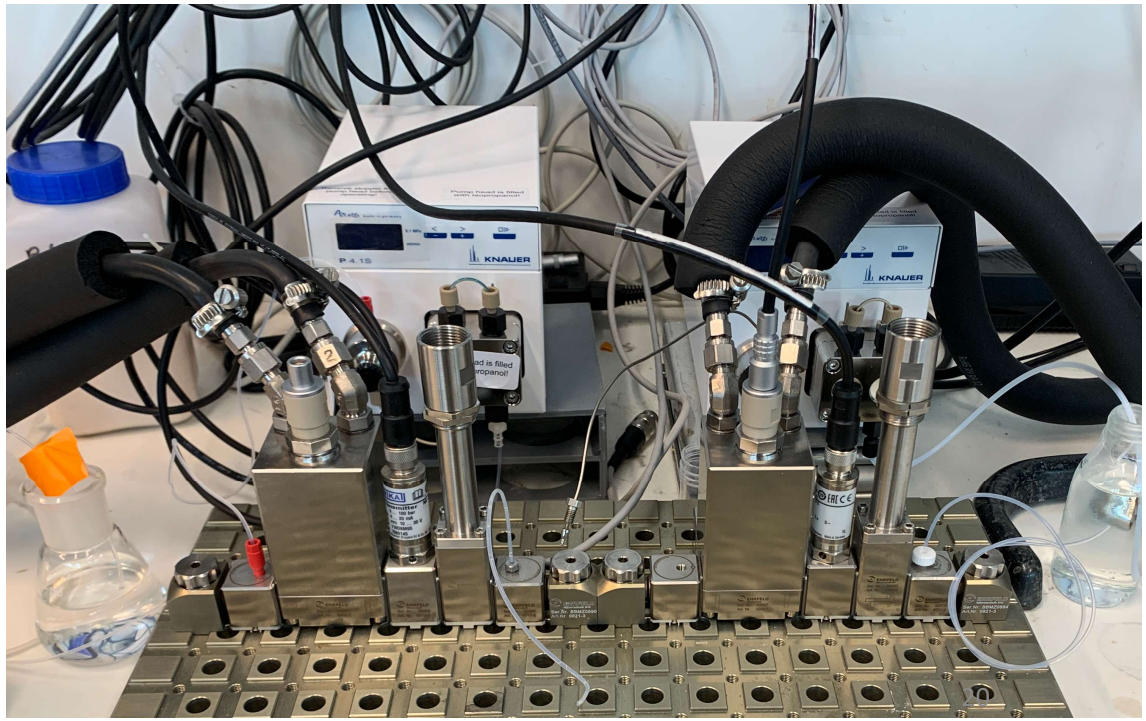




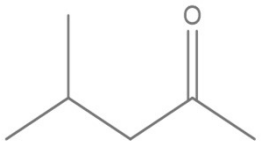
Plasmid pET-21a

Immobilization





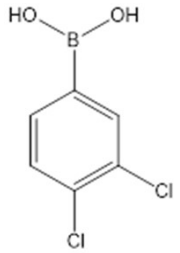
Development: extraction of fructose



MIBK

- Solvent

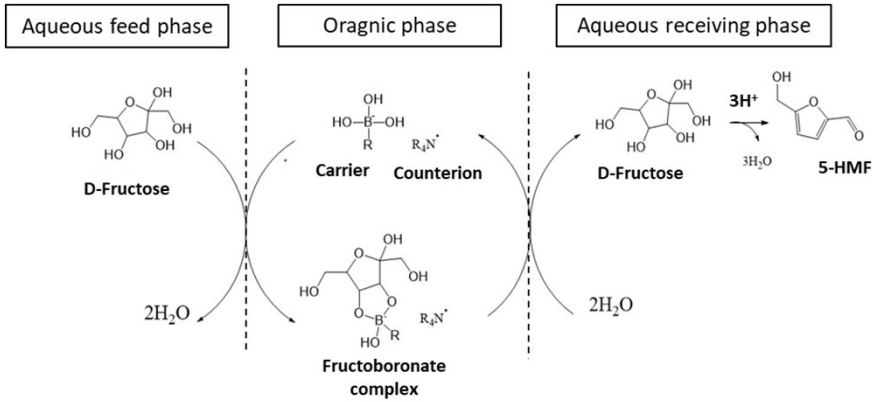
4-methylpentan-2-one (MIBK)



34-DCPBA

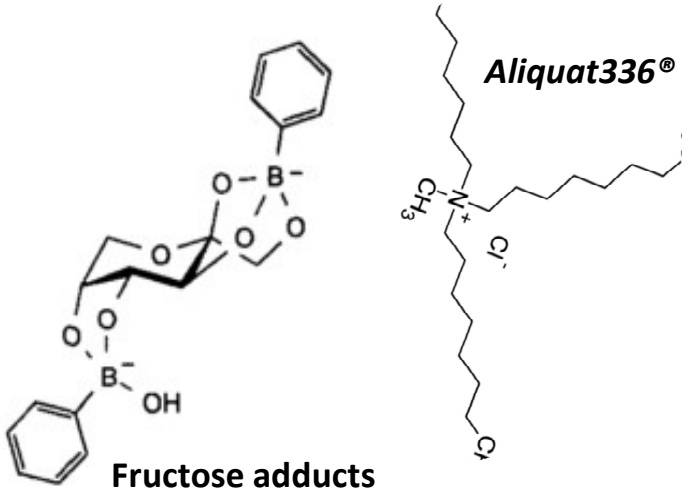
- Carrier (T)

23-DCPBA	35-DCPBA	3-TFMPBA	2-NNPBA
34-DCPBA	3-NPBA	4-B1nPBA	32-carboPBA
35-BTFMPBA	24-DCPBA	4-M21HPBA	
4-TFMeOPBA	2-TFMPBA	2-T5PBA	



Glucose and fructose adducts formed with boronic acids
Affinity $(34\text{-DCPBA})_{Fru}$ >> $(34\text{-DCPBA})_{Glc}$
This complex induces the negative ion on the bore

Ionic interaction with the counterion **Aliquat336®**
Formation of a lipophilic complex
Extraction in MIBK solvent



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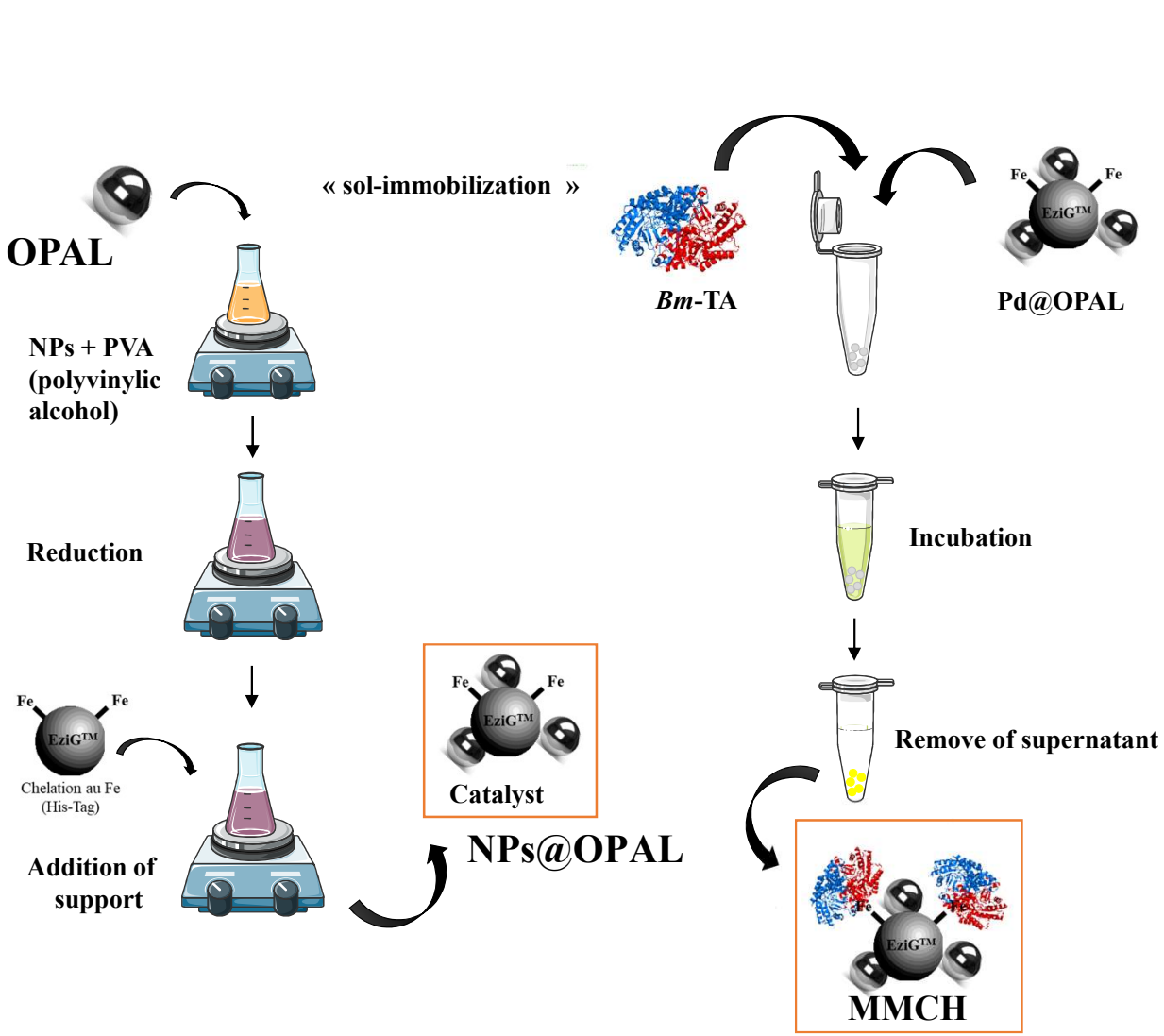
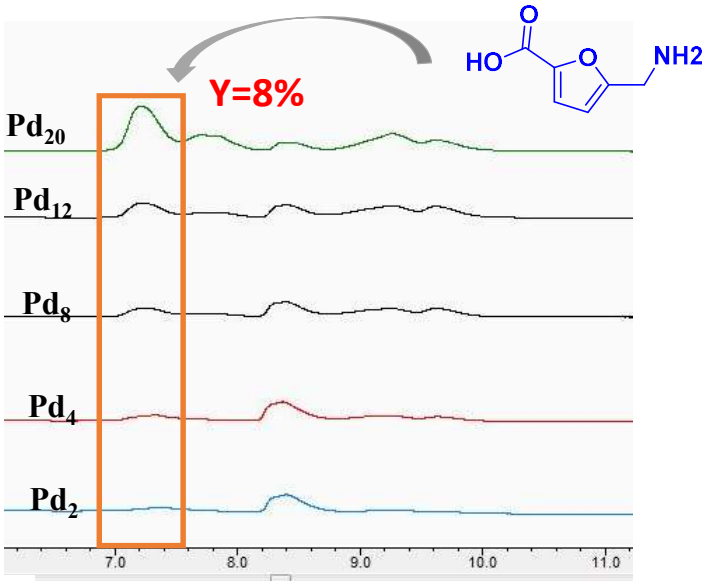
Construction of MMCH





Proof of concept with MMCH !!