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Hybrid catalysis concept for the valorization of bio-based molecules to value-added chemicals for potential food-grade applications

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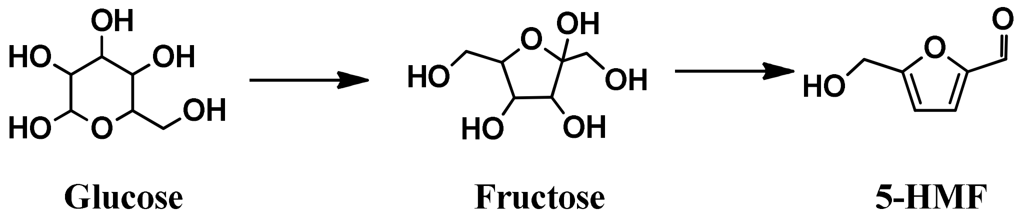


2 chemical steps

Catalyst	solvant	T (°C)	Time	Yield 5-HMF
Hydrotalcite Amberlyst15	DMF	300	2.5h 2h	45%
$AlCl_3$ + HCl	H_2O/2-sec-butylphenol	190	40 min	62%
Sn-β + HCl	H_2O/THF	180	70 min	57%

Limits =

1. **High temperatures**
2. **Formation of humins**
3. **Low selectivity**

1 enzymatic step + 1 chemical step

Catalyst	solvant	T (°C)	Time	Yield 5-HMF
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	24	20%

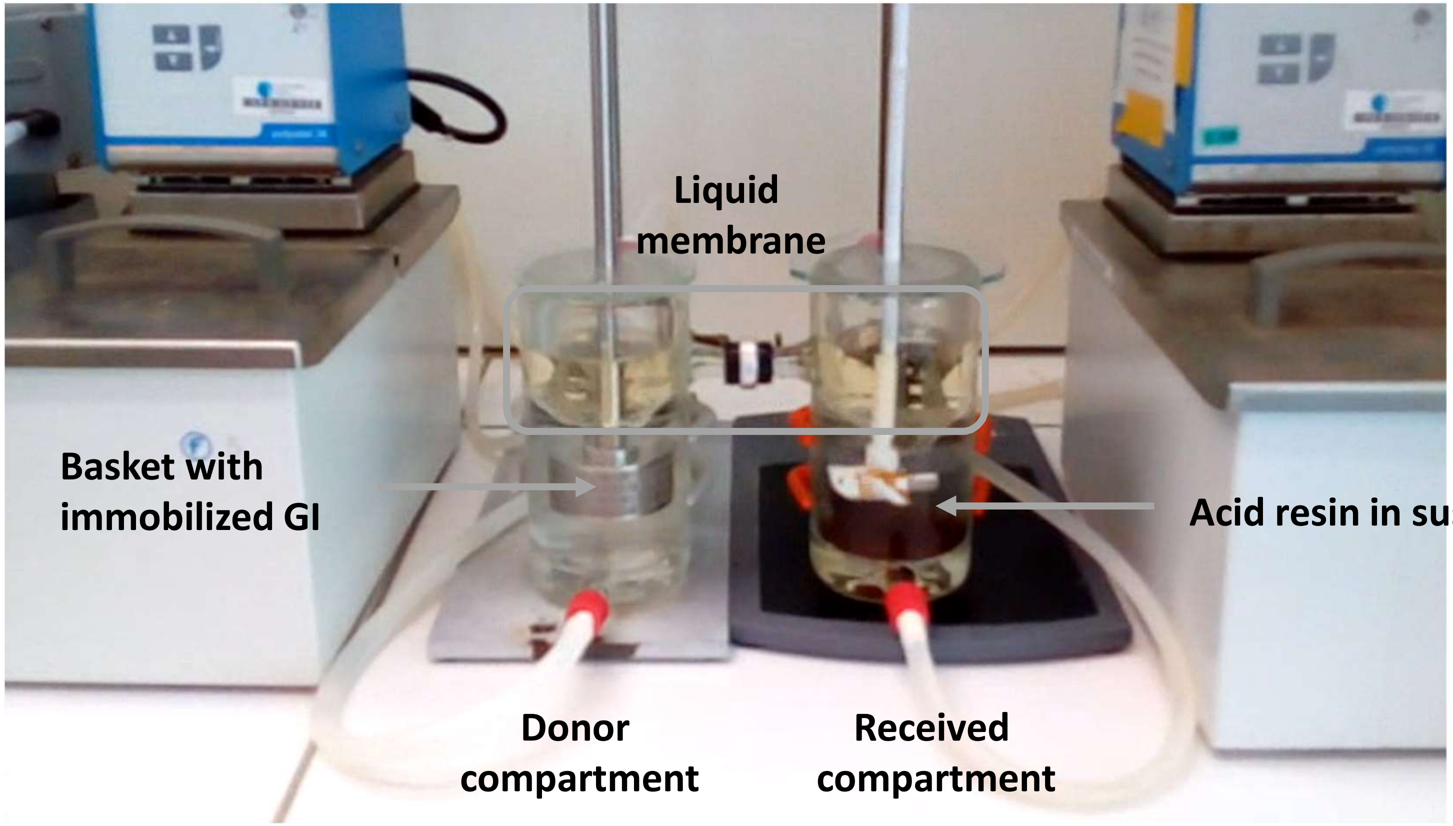
Limit =

1. **Inactivation of isomerase**

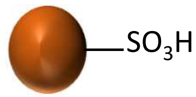
Simultaneous catalysis in a dedicated 2P1S hybrid catalytic reactor

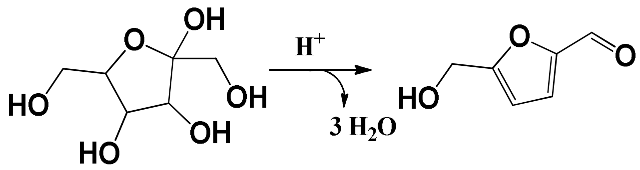
Pagán-Torres, Y. ACS Catal. 2, 930–934 (2012). Nikolla, E. ACS Catal. 1, 408–410 (2011)
Simeonov, S. ChemSusChem. Com. Grande, P. ChemSusChem 5, 1203 – 1206 (2012)

- 2P1S hybride reactor



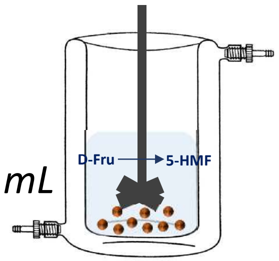
Heterogeneous chemical catalysis: dehydration of D-fructose with Dowex monosphere®650C



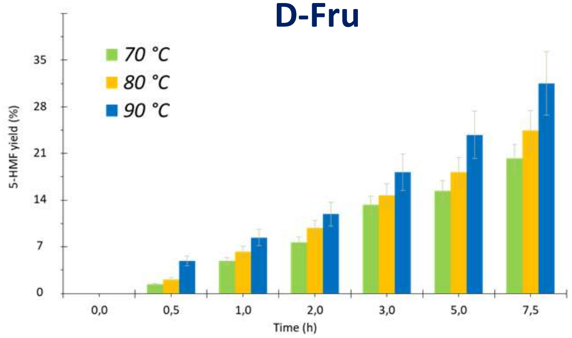


- Temperature:

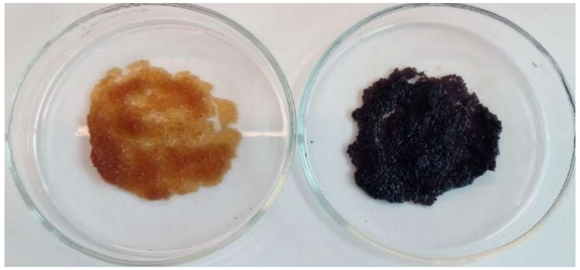
V= 100 mL



D-Fru



5-HMF



Better yield at **90 °C**

⇒ Choice **80 °C**

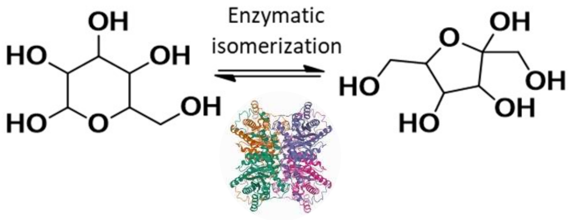
- Molar ratio H^+_{resin}/D-Fru:

  $n_{H^+_{resin}}/n_{D\text{-}Fru}$: 1/1 ; 2/1 ; 3/1

- pH of receiving aqueous phase:

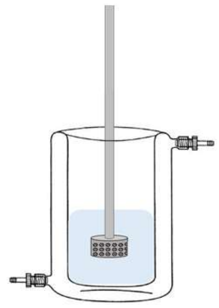
  pH : 3 ; 7

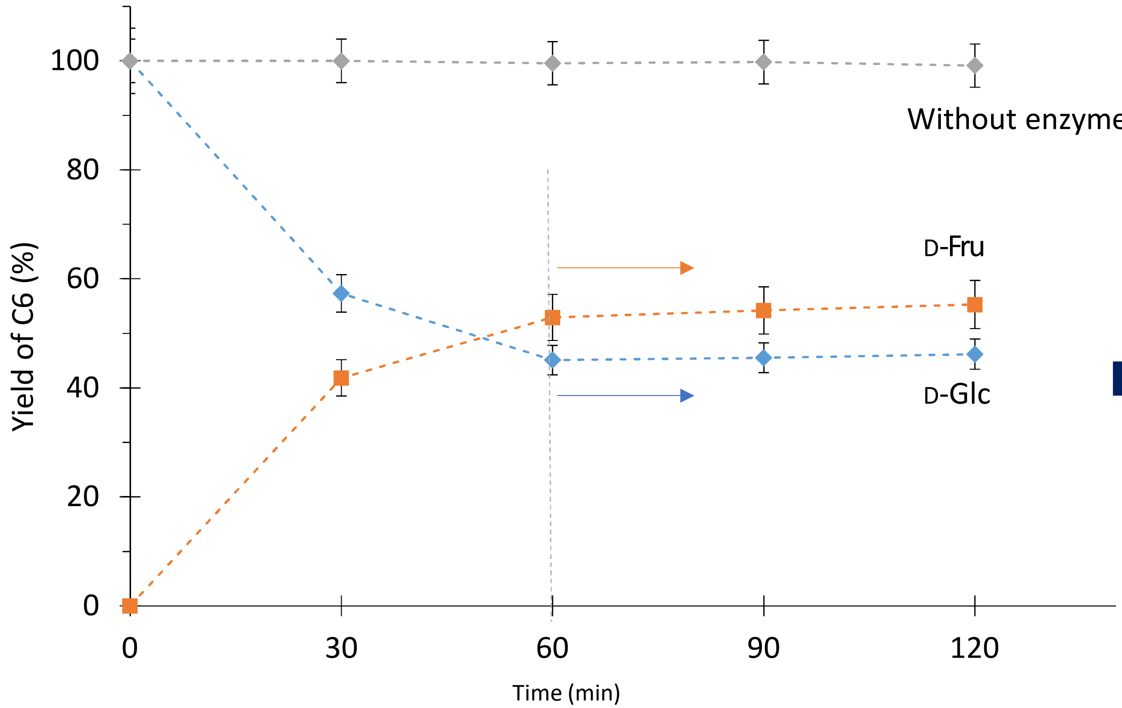
Enzymatic isomerization with Zweetzyme®



- Kinetics in optimal conditions (70 °C, pH=8.5)

100 mL
200 rpm
m_{IGI}= 500 mg
[D-Glc]=100 mM
[$MgCl_2$]=20 mM
[Na_2SO_3]=8 mM





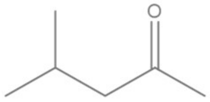
Yield after 60 minutes
Y_{iso} = 55%

✖ Thermodynamic equilibrium
Quantity of D-Fru is limited

Continuous extraction of D-fructose

Extraction of fructose : development of liquid membrane

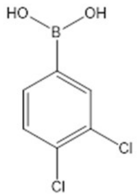
- Solvent



MIBK

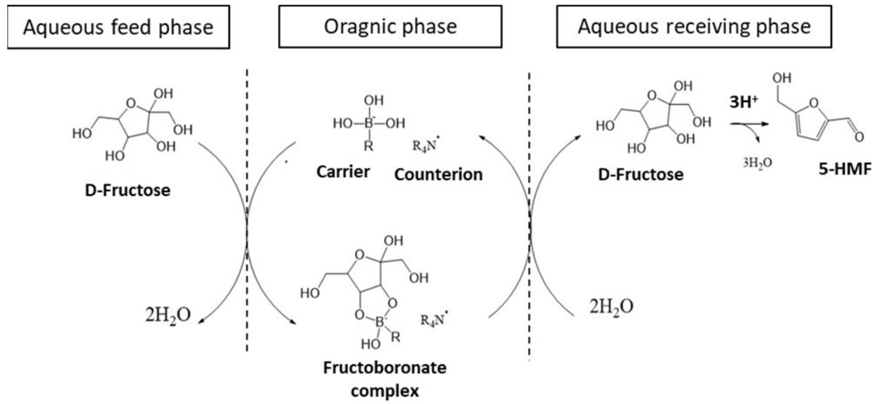
4-methylpentan-2-one (MIBK)

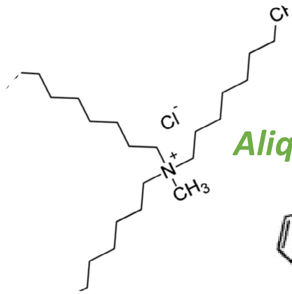
- Carrier (T)



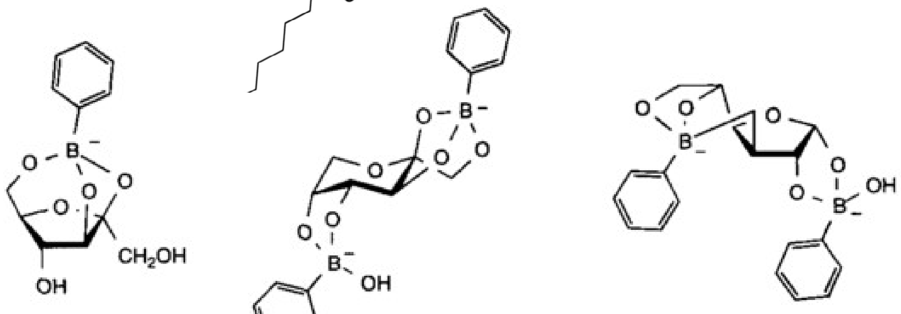
34-DCPBA

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	





Aliquat336®



1 2 3

Fructose Adducts

Glucose Adduct

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

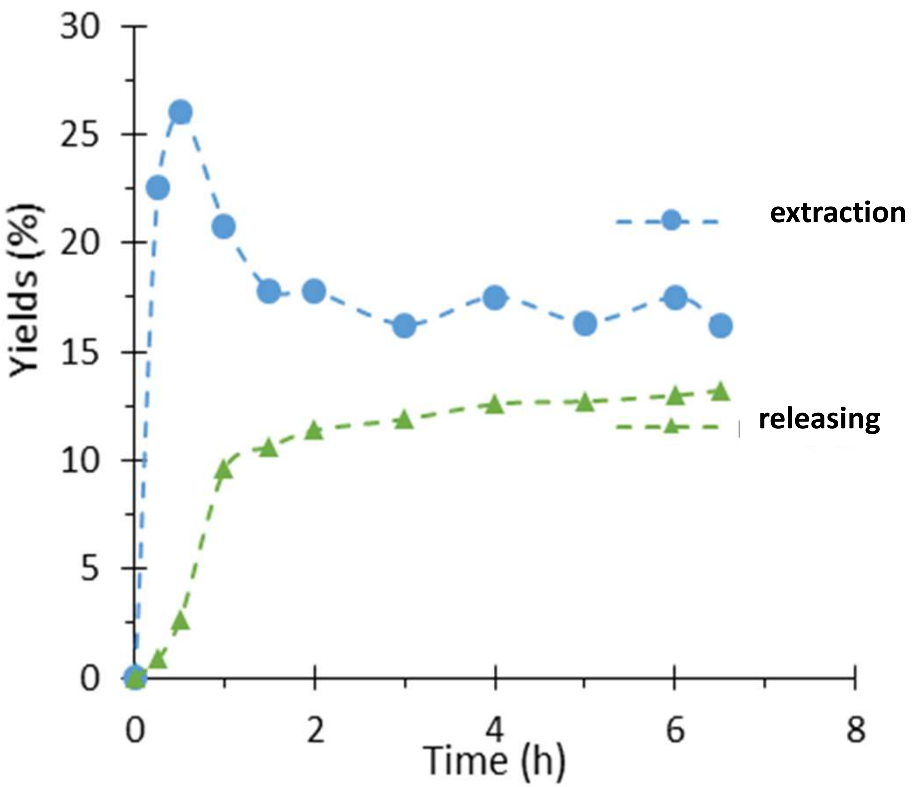
Ionic interaction with the counterion **Aliquat336®**

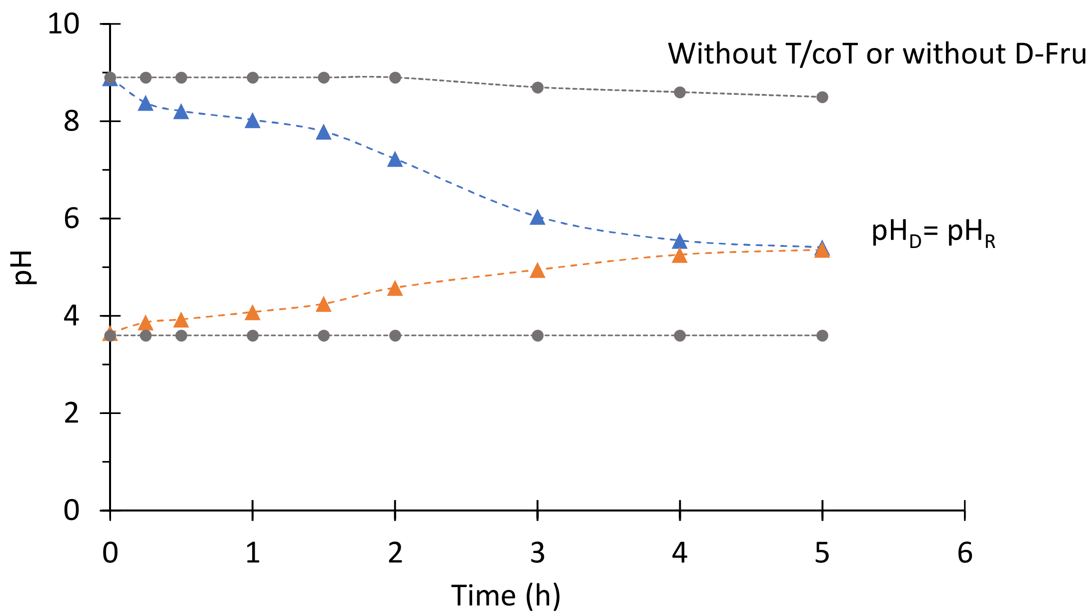
Formation of a lipophilic complex

Extraction in MIBK solvent

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).

Transport of fructose: control of pH in aqueous phases

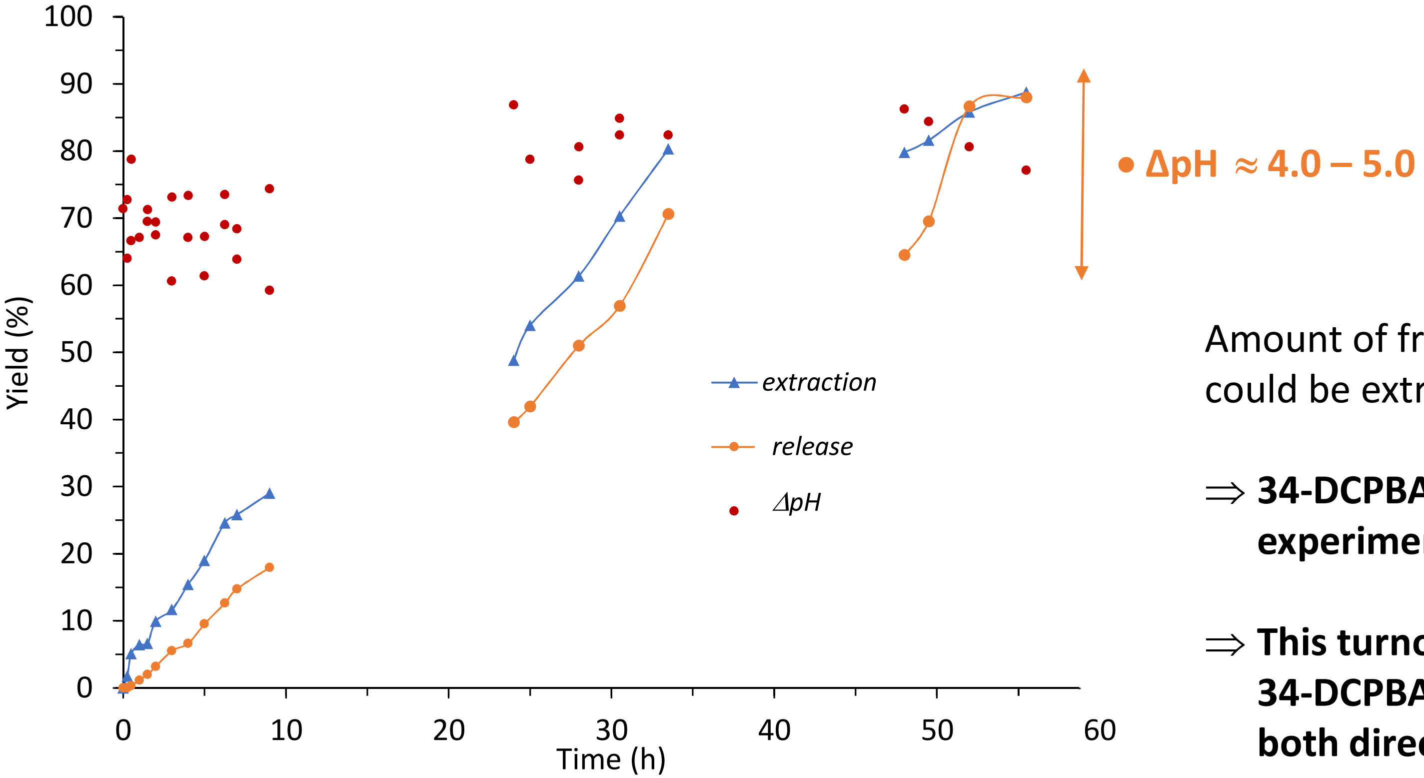




➡ pH unstable during the simultaneous process

→ Control of pH in each aqueous phase

Transport of fructose: Recycling of 34-DCPBA / Aliquat336®



Y_{ext}= 89%
Y_{rel}= 88%
30 regulated hours

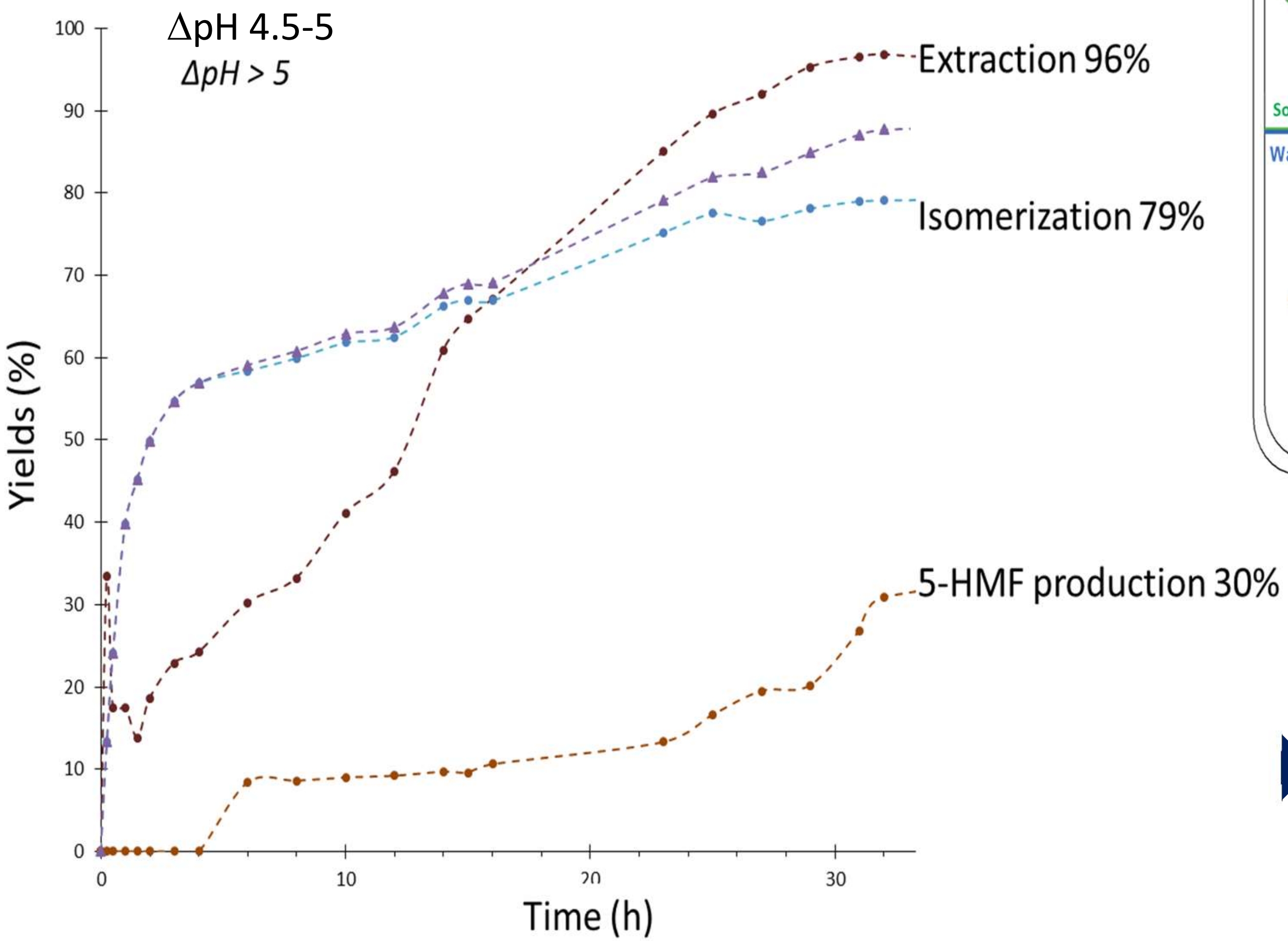
$n_{D\text{-}Fru}/n_T$ = 1/0.25

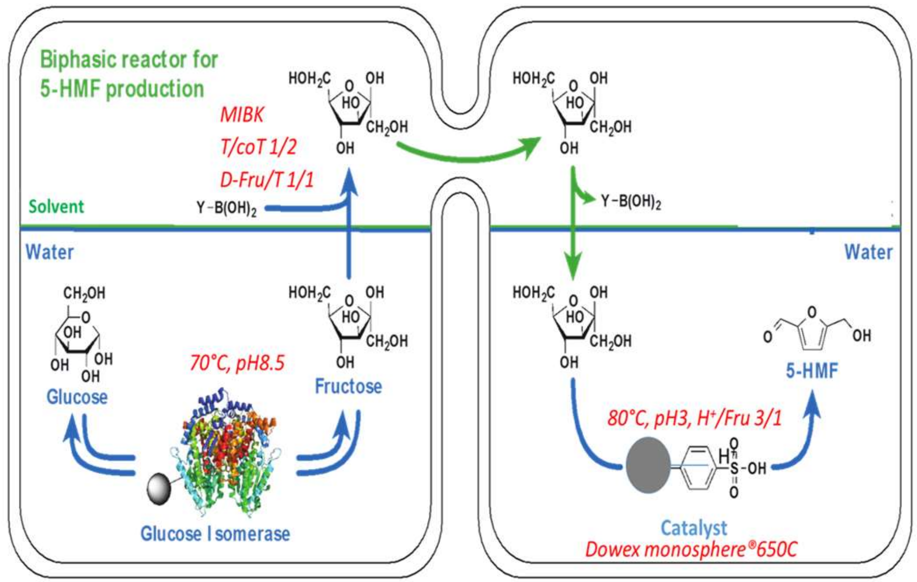
Amount of fructose extracted > Amount of fructose that could be extracted during 1 extraction cycle

⇒ **34-DCPBA - Aliquat336® pair is recycled during the experiment**

⇒ **This turnover also highlights the movement of the 34-DCPBA (T) and Aliquat336® (coT) molecules in both directions**

2P1S hybrid reactor implementation

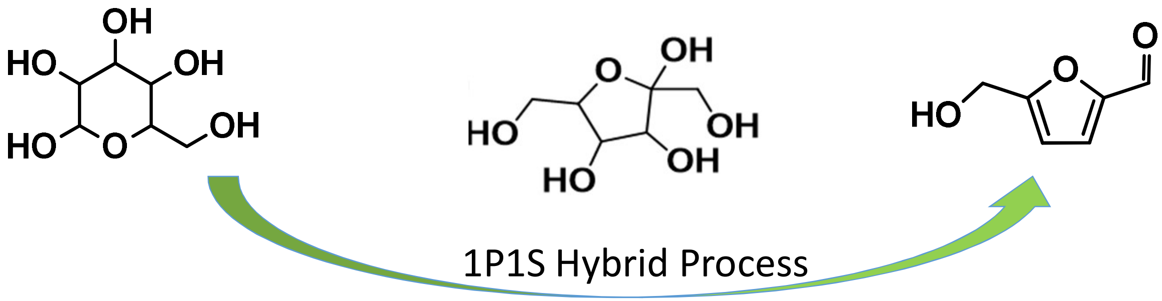


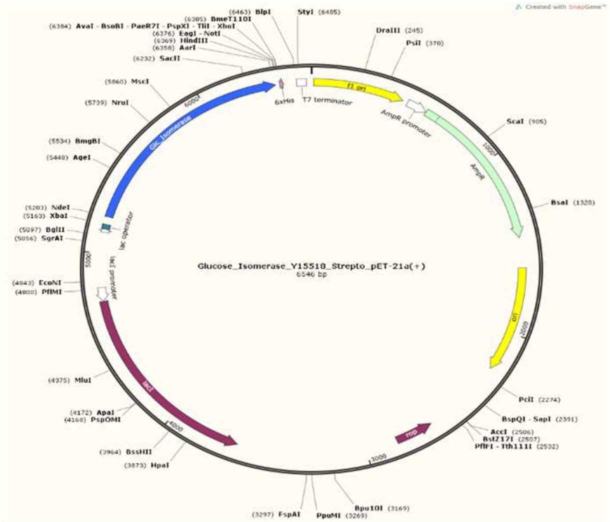


$\text{Yield}_{\text{isomerization}}$=79% (55% at thermo. equil.)

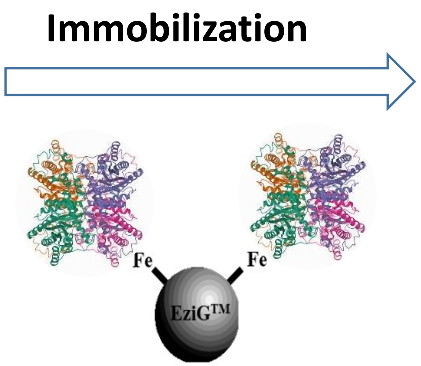
No enzyme inactivation during 32 hours !

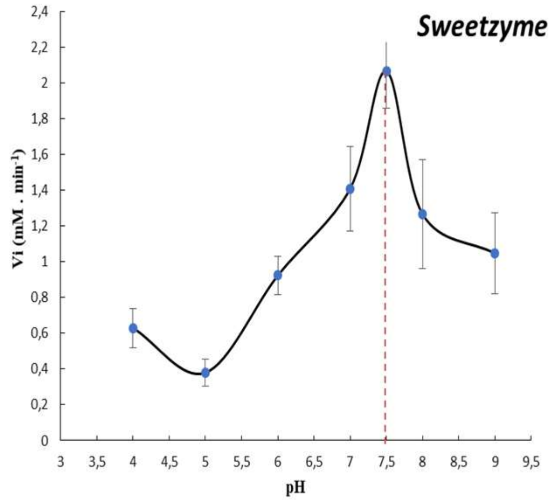
$Y_{5\text{-HMF}}$=30% at 32h

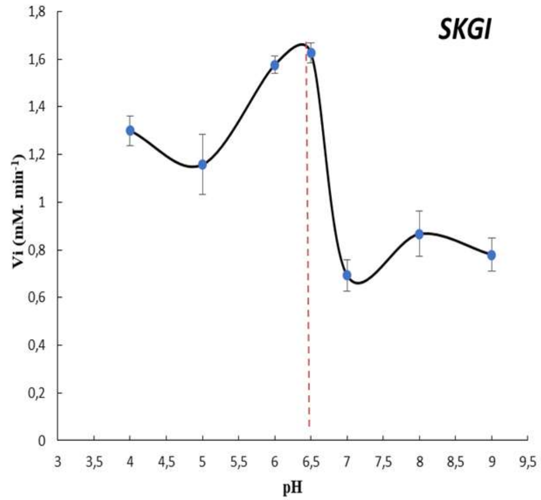


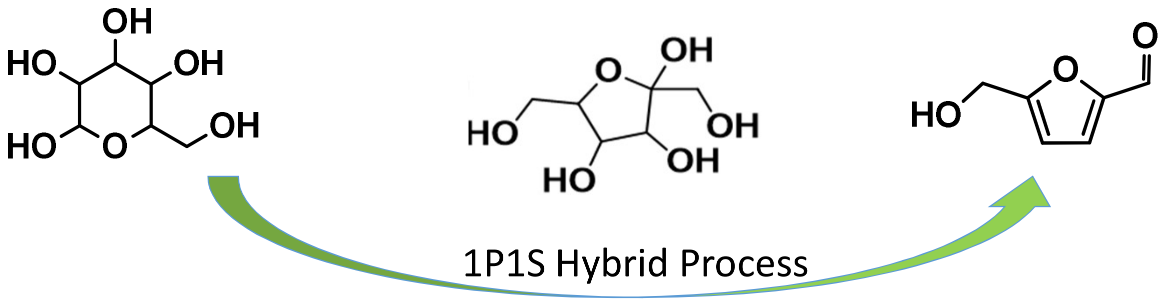


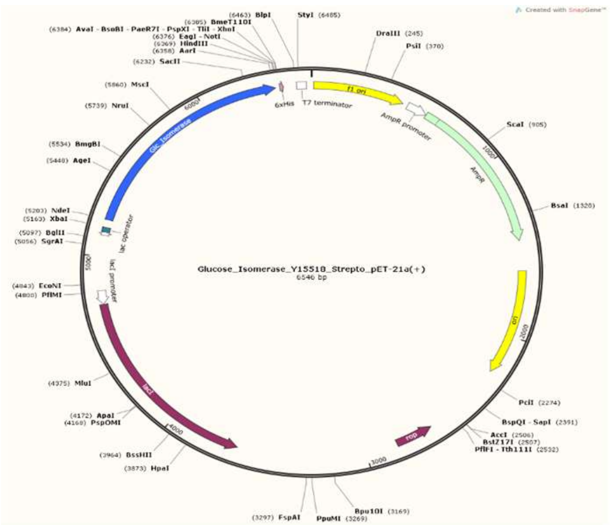
Plasmid pET-21a



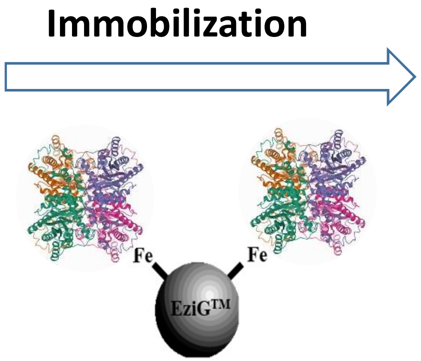


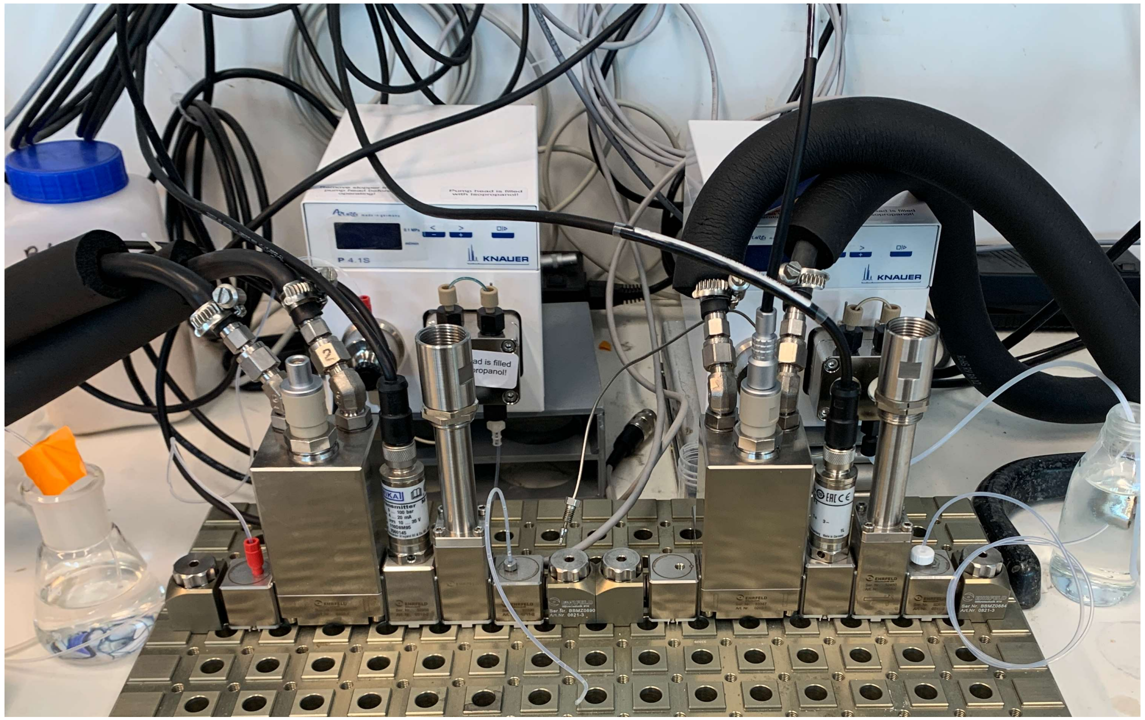


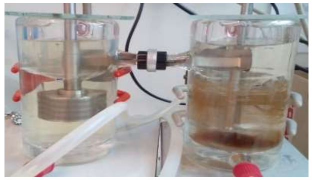




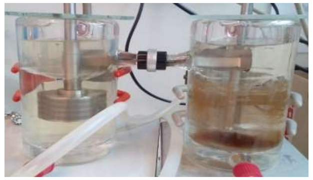
Plasmid pET-21a



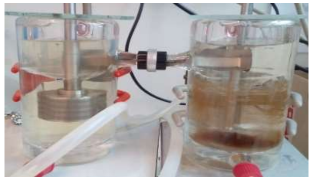




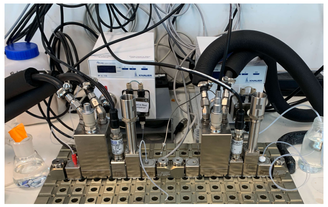
⇒ Design of the reactor « H » for 2P1S hybrid process ⇒ Proof of concept of simultaneous (bio)catalytical reactions



⇒ Shifting of isomerization thermodynamic equilibrium (25%)



⇒ Yield of 5HMF of 30% after 32 hours of process



⇒ **Synthesis of 5HMF in 1P1S hybrid process**

Acknowledgements

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Sébastien PAUL

Brings catalysis over lightspeed
REALCAT

STAND in ISGC !

Sébastien Paul
Egon HEUSON
Quentin HAGUET
Svetlana HEYTE

ifp Energies nouvelles

Hélène OLIVIER-BOURBIGOU
Nicolas LOPES-FERREIRA
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