Furans as offspring for broad applications in chemical and polymer industry

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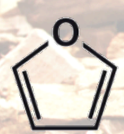
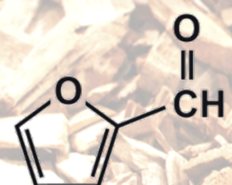
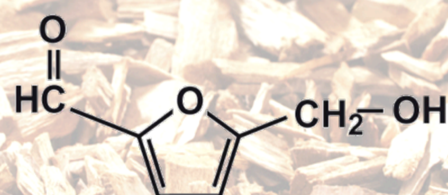


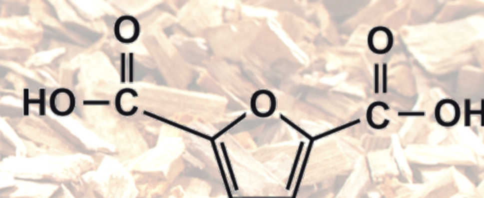
Furan



Furfural



5-Hydroxymethylfurfural



Furan-2,5-dicarboxylic acid

IIIrd Latin American Congress on Biorefineries, Pucón
November 19th-21st 2012

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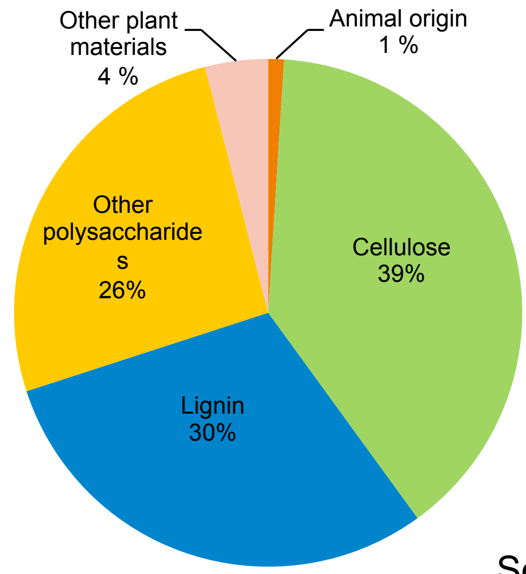
Outline

- Feedstock situation
- Applicability and derivatives
- Synthesis of furan compounds
- Results of functionalisation experiments
- Summary

Feedstock situation



Source: FNR

- Finiteness of fossil resources

  for fuels, plastics, chemicals and solvents

- Alternative: lignocellulosic biorefinery concept

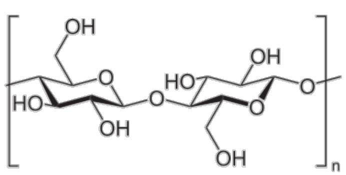
  lignin → aromatics; cellulose → glucose; hemicellulose → xylose

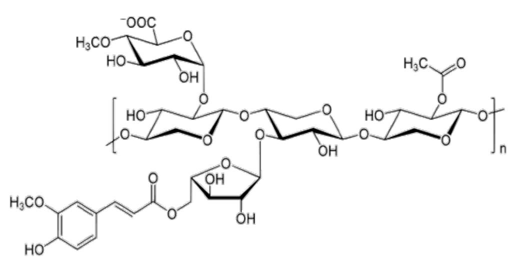
- Utilisation of residues from agriculture, forestry and food production with higher added value

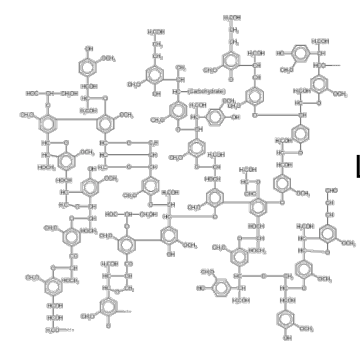
→ Production of **furan derivatives** for solvents, polymers, chemicals, resins, fuels, fuel additives, pharmaceuticals, herbicides and fertilzer as alternatives to products based on fossil oil

Composition of wood and wood related substances

	Content	Structure	Function
Cellulose	40-55% (wood) 30-40% (straw)	Long-chain macromolecule with 1.000 – 10.000 glucose units	Frame substance of the cell wall, absorption of drag force
Hemicellulose	20-35% (wood) ~ 35% (straw)	Short-chain, branched macromolecule of e.g. pentoses	Cement substance and flexibiliser
Lignin	28-41% (softwood) 18-25% (hardwood) 12-20% (straw)	Threedimensional macromolecule of phenylpropane units	Binding agent, regulates water permeation, protection from microbiological attacks


Cellulose


Hemicellulose


Lignin

Composition of wood and wood related substances

	Fossil oil	Oils, fats	Lignocellulose
Carbon	85-90 %	76 %	50 %
Hydrogen	10-14 %	13 %	6 %
Oxygen	0-1 %	11 %	43 %

- Fossil compounds do not include oxygen, renewables do

- Different carbon / hydrogen / oxygen distribution requires new synthesis strategies for products

→ Use of functionality (e.g. sugar alcohols)

→ Reduction of photosynthetic OH-overfunctionalisation

→ Refunctionalisation

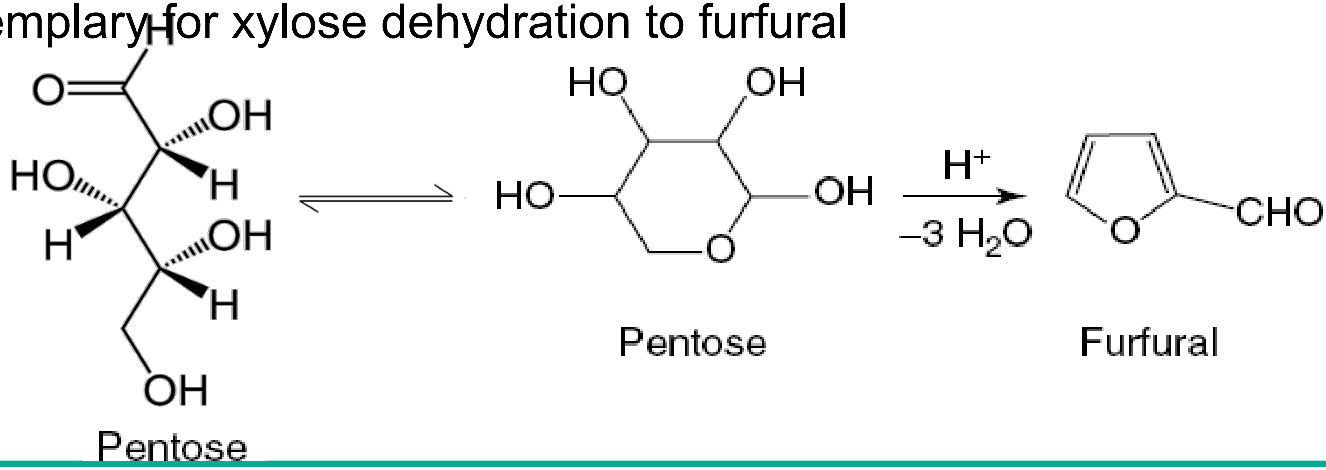
Production of furfural and 5-hydroxymethylfurfural

- Acid catalysed threefold dehydration of xylose (techn.: inorg. acids) and fructose

- State of the art: homogeneous catalysis, supercritical water, ionic liquids, organic solvents, ion exchange resins

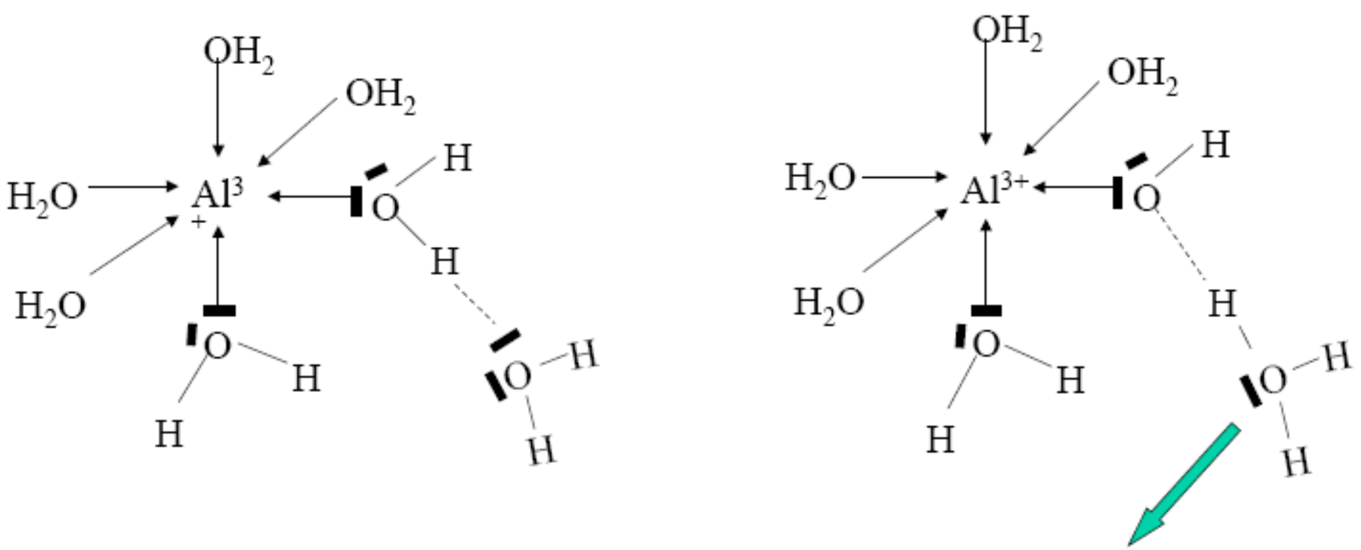
  → Often contamination of targeted product

- Exemplary for xylose dehydration to furfural



Production of furfural and 5-hydroxymethylfurfural

- Now: Heterogeneous catalysis
- Activation with highly charged electrical field of metal ions / salts

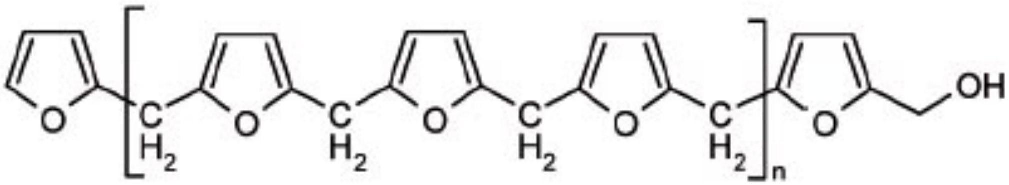


$$[Al(H_2O)_5(OH)]^{2+} + \boxed{H_3O^+_{(aq)}}$$

Applications and market for furfural

- Annual production: min. 400 000 t (2010)
- Main producer: China
  Over 300 facilities, increasing own consumption
- 60-70% for furfuryl alcohol, resins

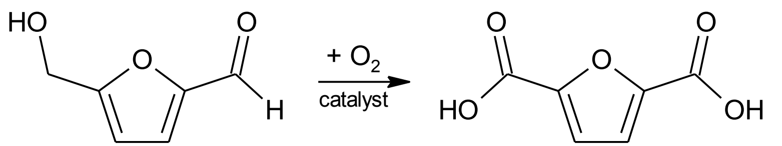
BioRez[TM] Thermoset resin



- Rest for
  - extractants for aromatics
  - cleaning agents for C_4 and C_5 hydrocarbons
  - reactive solvent and surfactant
  - basis for other furan derivatives

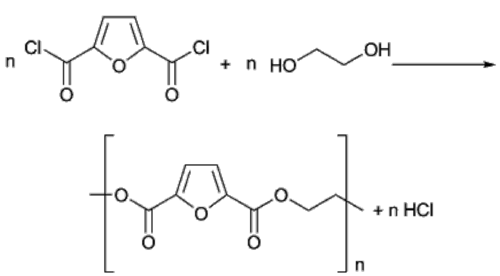
Applications for 5-hydroxymethylfurfural

- Specialty chemicals, polymers, fuel additives
- Compound thermally not very stable
  → soon conversion to the dicarboxylic acid

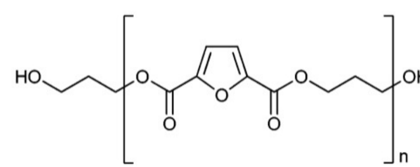


5-hydroxymethylfurfural furan-2,5-dicarboxylic acid

- Derivatisation of the acid, then polymerisation



Poly(ethylene-2,5-furanoate) PEF

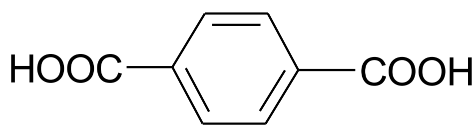


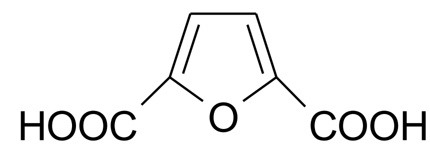
Poly(trimethylene-2,5-furanoate) PTF

2,5-furandicarboxylic acid FDCA

- Heteroaromatic building block, synthesis biobased

- Big physical and chemical similarity to fossil based terephtalic acid

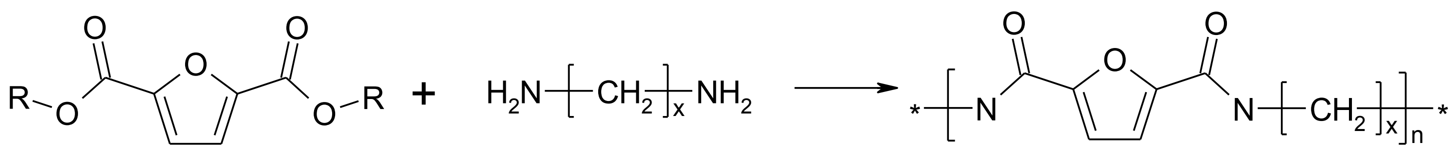




Melting point	subl. ≈ 300 °C	320 °C
Boiling point	392,4 °C	419,2 °C
Flash point	205,3 °C	207,3 °C
pK_A	3,49	2,28
Vapor pressure (25 °C)	73,5 $*10^{-8}$ Torr	8,9 $*10^{-8}$ Torr
Solubility	DMF, DMSO, Acetic acid	
	chemically stable, non-toxic	

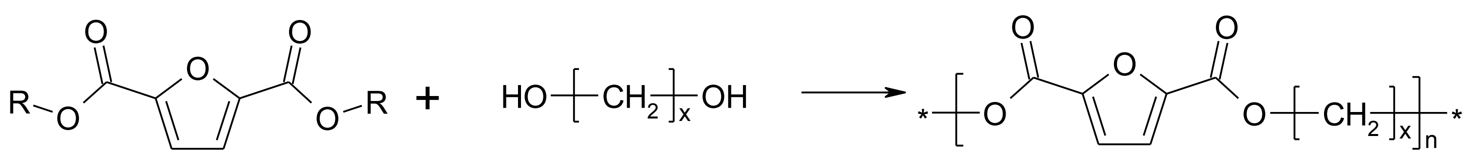
2,5-furandicarboxylic acid FDCA

Polyamide Synthesis:



R = -CH_3 –H or –Cl   x = 2 , 6, 8, 10, 12

Polyester Synthesis:



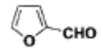
R = -CH_3 –H or –Cl   x = 2, 3, 4, 6, 10, 12, 18

Applicability and derivatives of furan compounds

C_6 derived

5-hydroxymethylfurfural
HMF

C_5 derived



furfural

Source: B. Kamm „Biorefineries - Industrial Processes and Products", 2006

Experimental setup

- 100 mL batch autoclave, stirred
- 50 mL educt solution with 5 % xylose or fructose

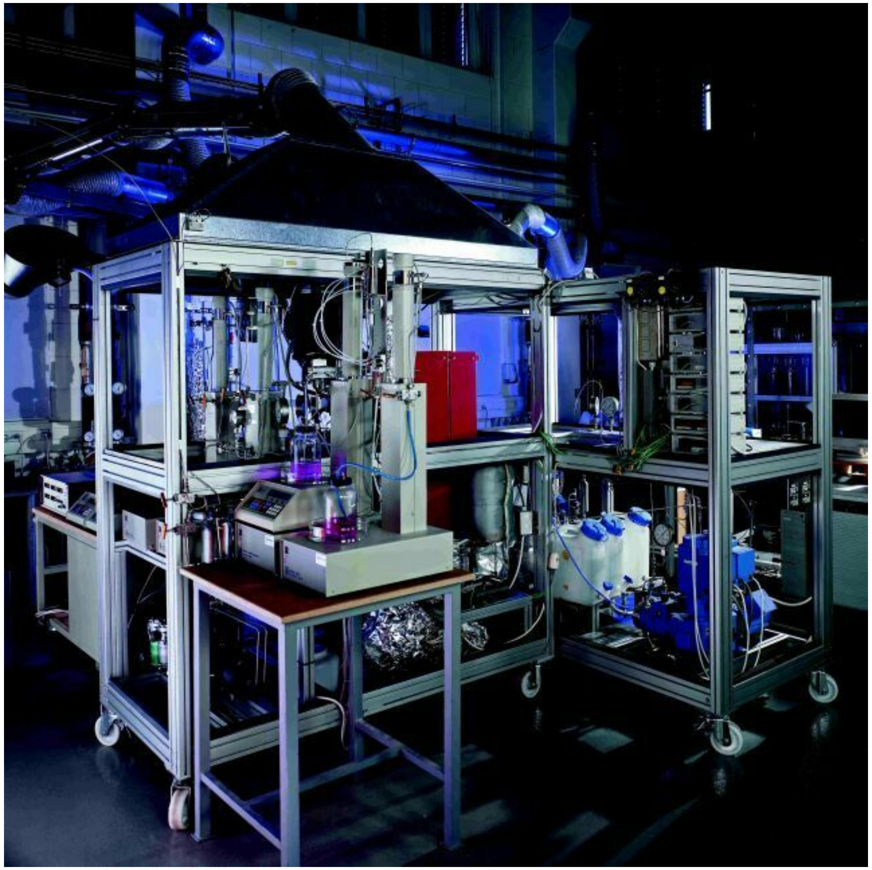
  0,5 g catalyst

  → liquor ratio 1:5

- Dwell time 10 – 240 min
- Temperature 140 – 200 °C
- Analysis: quant. HPLC

Experimental setup
Continuous operation

- 100 mL CSTR
- 1 g of catalyst, dispersed
- 50 bar pressure
- Dwell time 5 – 30 min
- Temperature 180 – 200 °C
- Analysis: quant. HPLC



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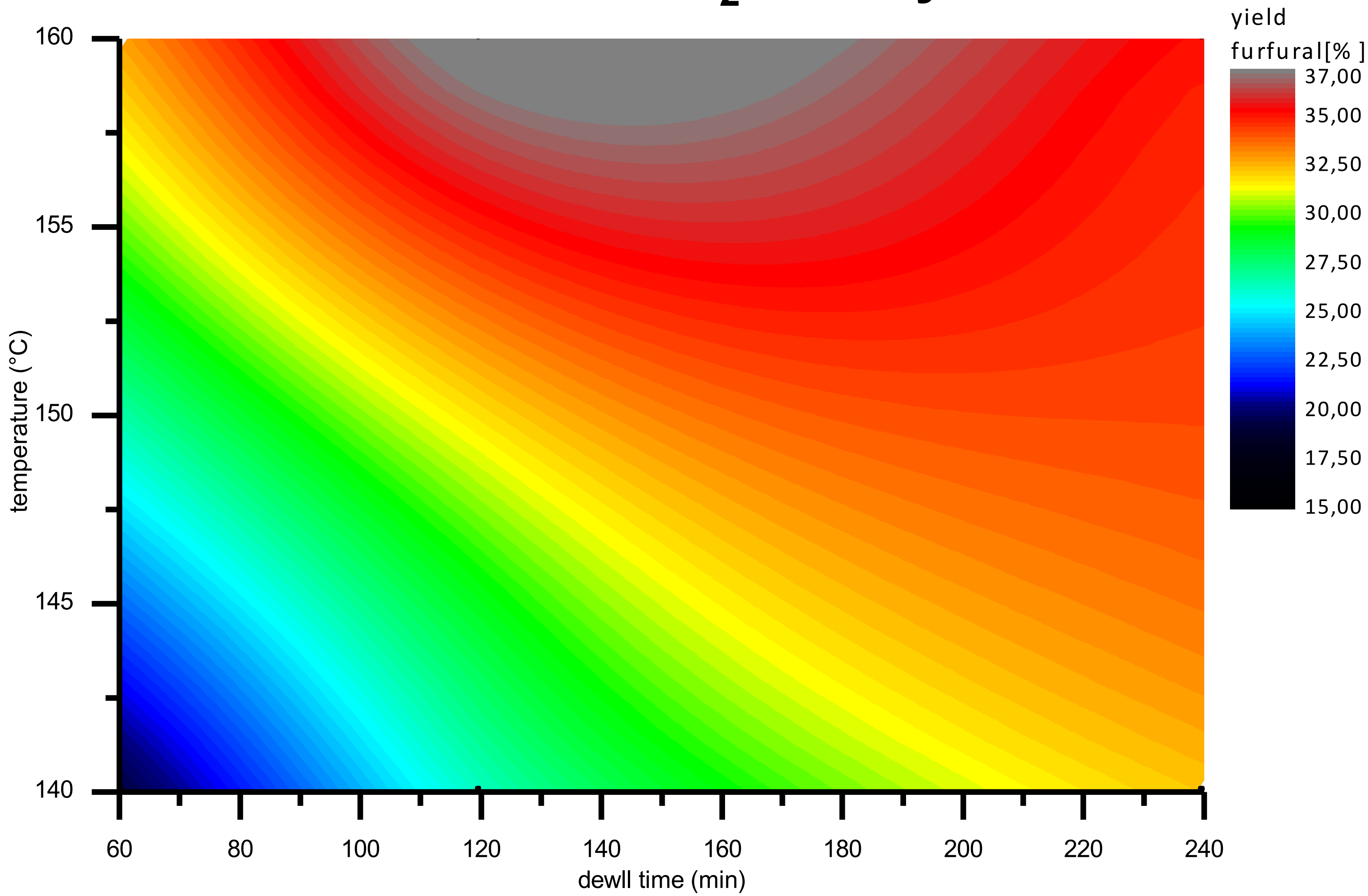
Results
Furfural synthesis (extract)

Catalyst	Conditions T [°C] / t [min]	Conversion Xylose [%]	Selectivity Furfural [%]	Yield Furfural [%]
no catalyst	160 / 60	7,91	78,89	6,24
H_2SO_4	160 / 60	70,52	48,98	34,54
Al_2O_3	160 / 60	83,99	21,77	18,28
TiO_2	160 / 60	79,94	40,74	32,57
AlP- complex	160 / 60	17,50	59,89	10,48
AlP- complex	180 / 30	27,13	66,66	18,08
AlP- complex	200 / 30	89,02	52,17	46,44

Results
Furfural with commercial TiO_2 - catalyst



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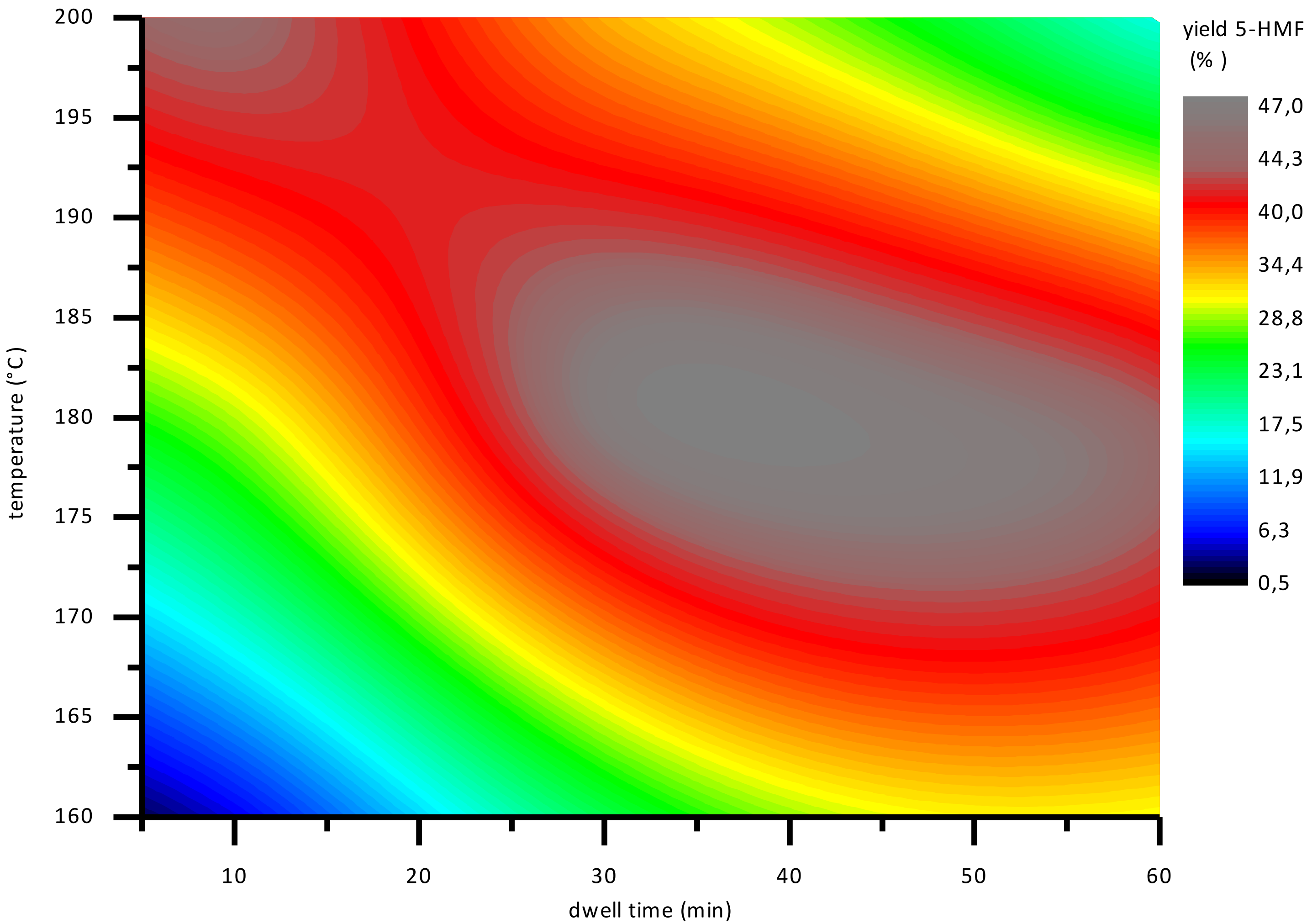
Results
5-hydroxymethylfurfural synthesis (extract)

Catalyst	Conditions T [°C] / t [min]	Conversion Fructose[%]	Selectivity 5-HMF [%]	Yield 5-HMF [%]
H_2SO_4	160 / 60	99,49	5,71	5,69
ZrO_2	180 / 30	74,48	61,04	45,46
TiO_2	180 / 30	79,23	58,52	46,36
FeP-complex	180 / 30	94,00	44,27	41,61
ZrP- complex	180 / 30	86,81	46,53	40,40
AlP- complex	160 / 60	47,15	63,79	30,07
AlP- complex	180 / 30	81,63	56,73	46,31
AlP- complex	200 / 30	99,15	33,83	33,55

Results
5-hydroxymethylfurfural with AlP - catalyst



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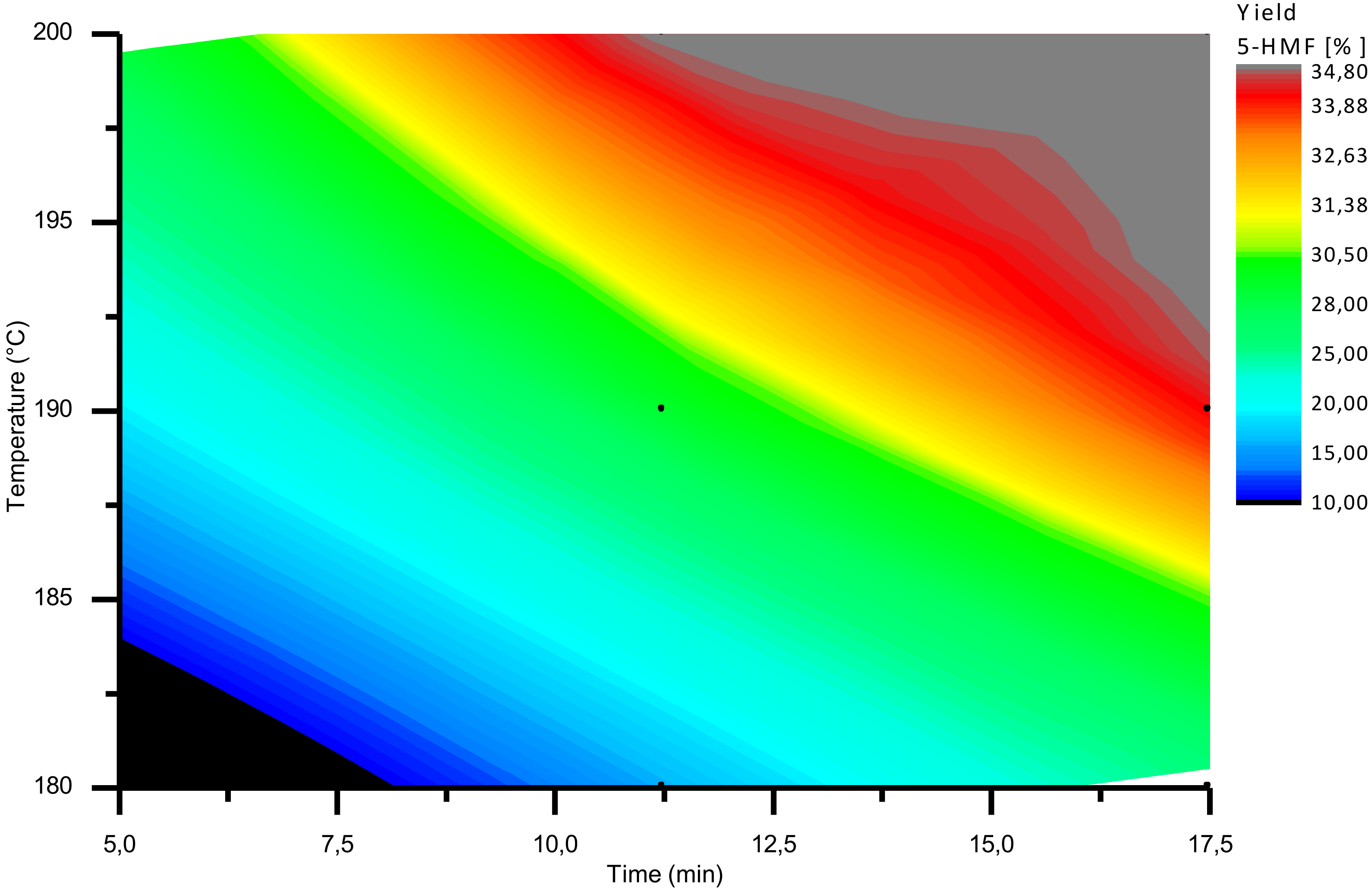
Results
5-hydroxymethylfurfural with ZrO_2 – continuous mode



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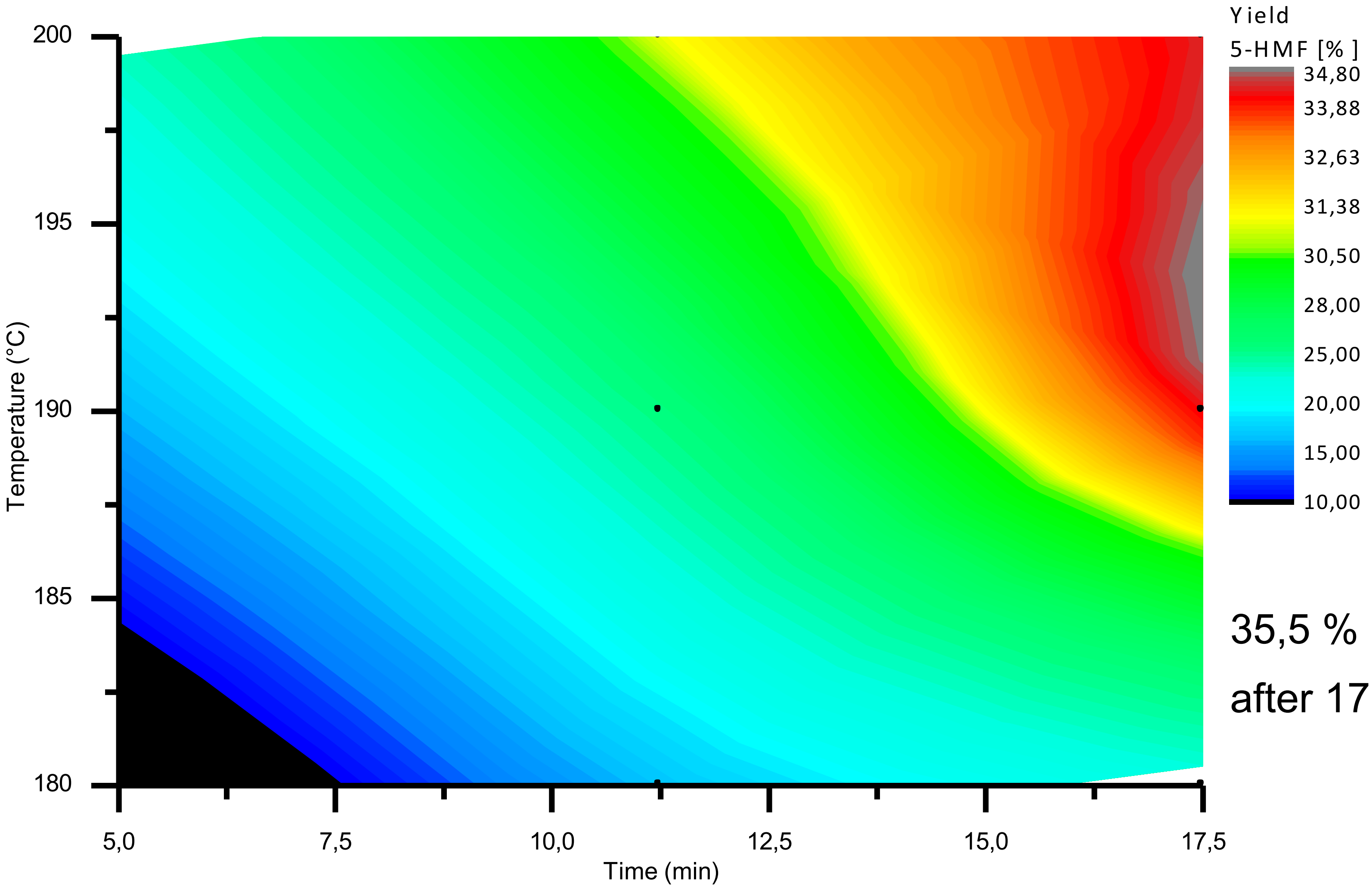
Results
5-hydroxymethylfurfural with TiO_2 – continuous mode



35,5 % HMF

after 17,5 min

Results
Product coloration

- High temperature and dwell time lead to degradation to e.g. levulinic acid, formic acid and humins that are increasingly responsible for coloration

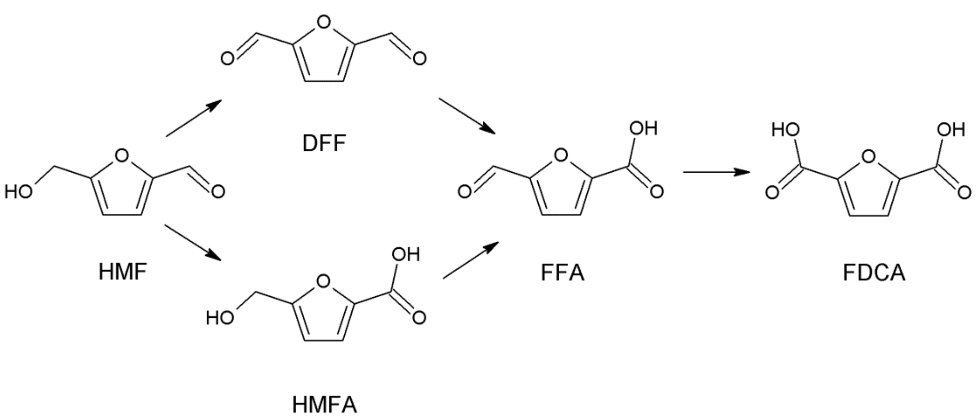
dwell time,
temperature

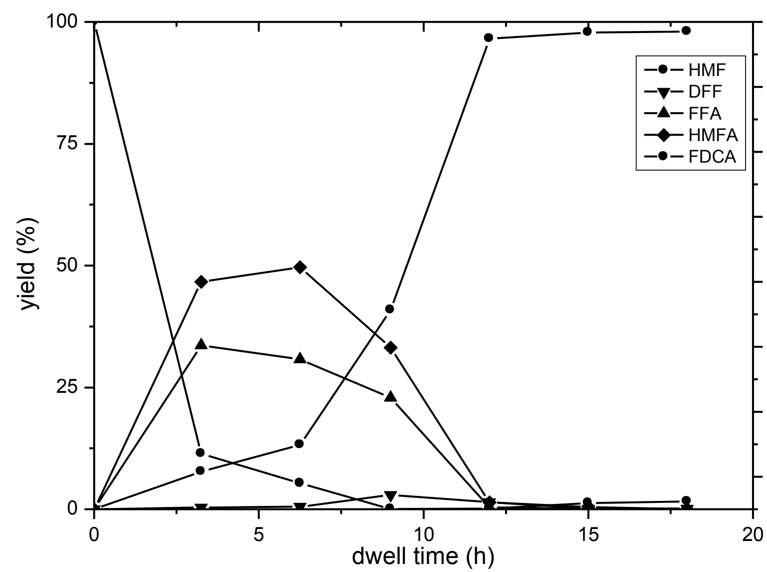
Results
2,5-furandicarboxylic acid FDCA synthesis

- Oxidation of 5-hydroxymethylfurfural with noble metal catalysts in aequous solution

- Best performance showed Pt, Au → Yield > 99 %

- Synthesis demonstrated on kilogram scale





Summary

- Synthesis routes for products as alternative to fossil products
- Large feedstock amounts available and renewable
- Yields of 46 % for furfural as well as 5-hydroxymethylfurfural possible
- Reduction of dwell time from hours to minutes in comparison to references (e.g. 6 h in water-toluene)
- Mild reaction conditions without corrosive acids possible

Summary

- Simple separation of the heterogeneous catalyst with filtration and reuse of the catalyst
- 2,5-furandicarboxylic acid FDCA can be synthesised with 99 % yield
- Wide product range, secondary products and big family tree is representable
- Established products could be substituted, new compounds with new properties can be created

Thank you for your kind attention

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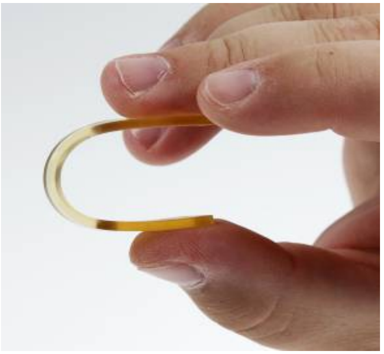

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