Emerging technologies for biobased aromatics

FBR Inspiration day, 10 april 2014

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Renewable feed stocks; what is driving the demand?

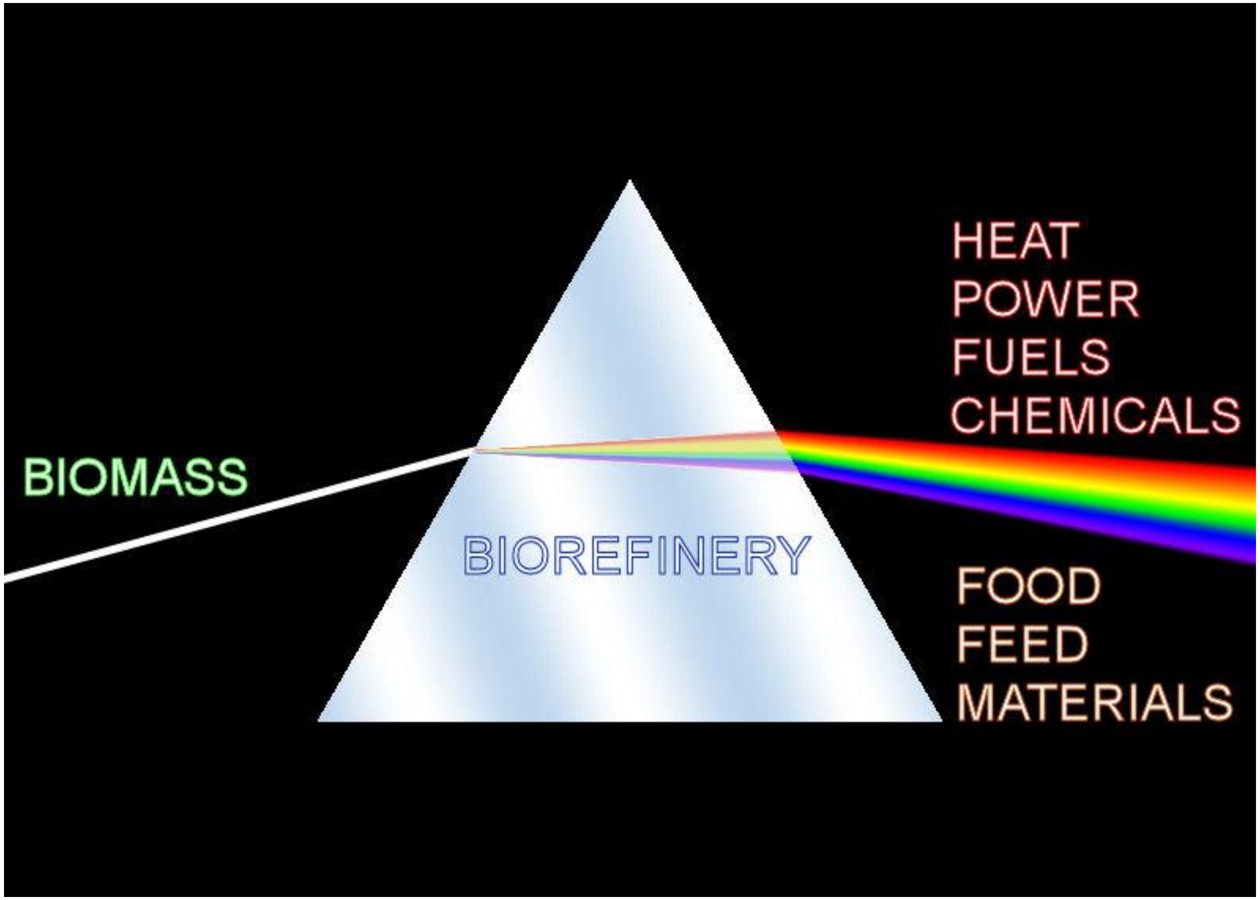
- General driving forces for renewables/biobased chemicals:
  - Declining reserves of easily accessible fossil feed stocks
  - Societal need to become more independent with regard to feedstock supply
  - Potential for GHG savings
  - Potential for unique properties
  - Economical potential for rural regions
  - Potential for more environmentally friendly products

Biobased Chemicals Programme WUR/FBR

- Consists of over 40 projects in which biobased chemicals are one of the dominant aims
  - Confidential bilateral projects with international multinationals as well as SME' s.
  - Public private sponsored projects
  - Comprises 3 focus areas:
    - **Carbohydrate based chemicals**:
      - *Furan platform*
      - *Isohexide platform*
      - Sugar biotechnology platform
    - Lignin based chemicals
    - Vegetable oil and algae oil based chemicals

  - Internationally cooperates with numerous universities and institutes
  - Internally intensively cooperates with the biorefinery and biobased materials programme
  - Approximately 30 coworkers involved

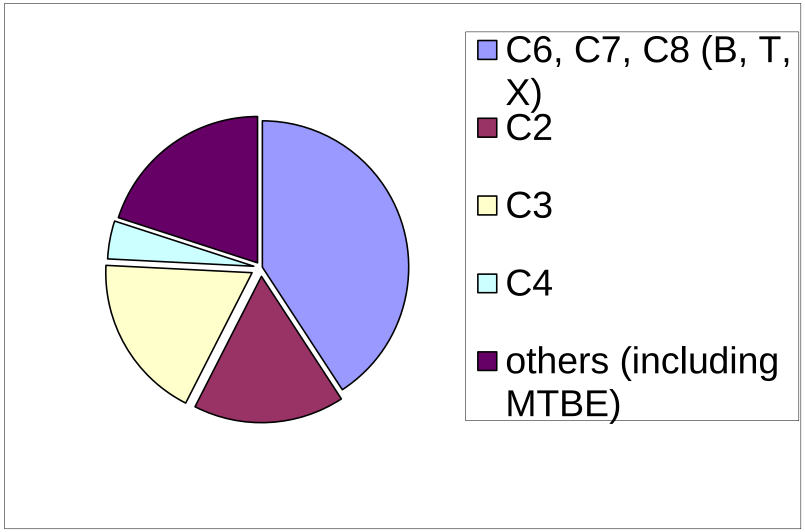
Existing and future biorefineries will refine biomass into a spectrum of products



Usage of bulk (platform) chemicals

- Bulk chemicals are used as:
  - Solvents
  - Starting components for soaps, lubricants, additives (low molecular weight components)
  - Mostly as building blocks for polymers (high molecular weight components)
- Building blocks can be either aliphatic (flexible) or aromatic (rigid) nature

Up to 40% of basic chemicals produced in Port of Rotterdam is of aromatic nature



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World production of plastics

- Recent finished desk study requested by Dutch Ministery of Economic Affairs. Emphasis on biobased building blocks for polymer applications

World plastics production grows

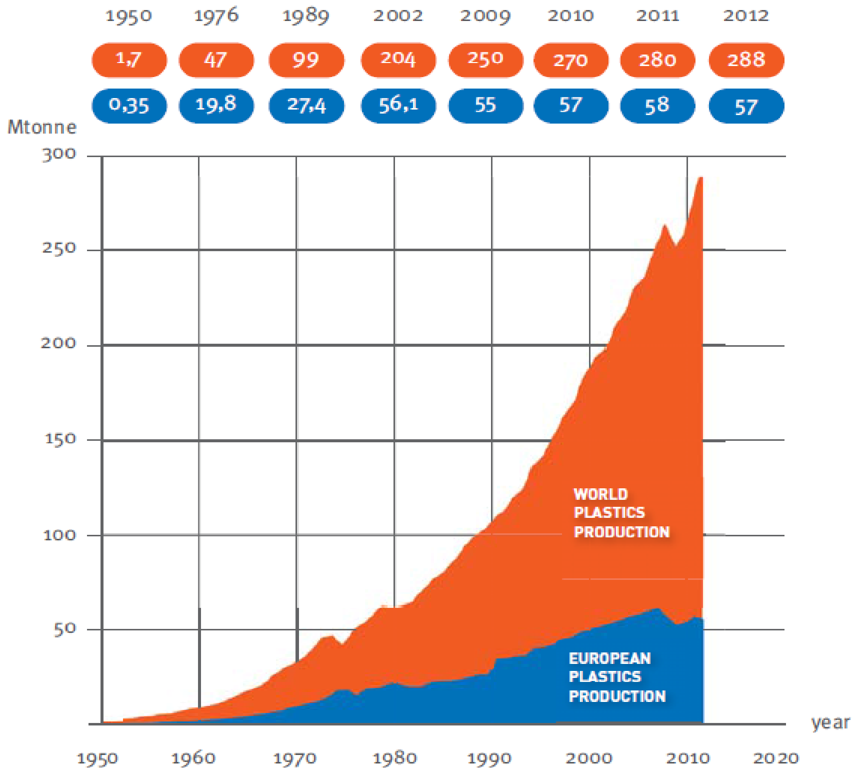
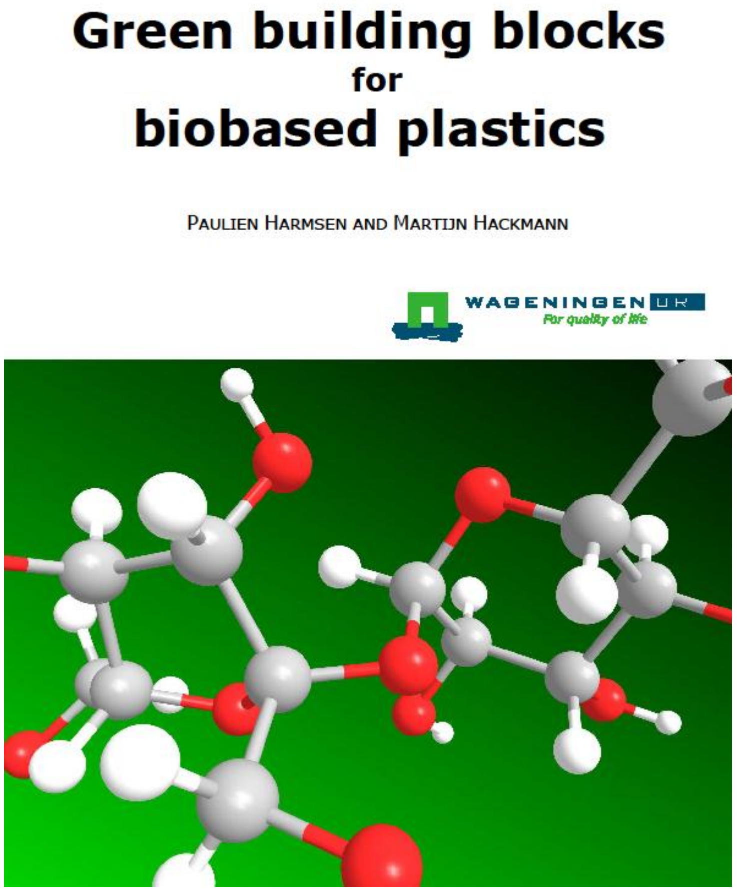
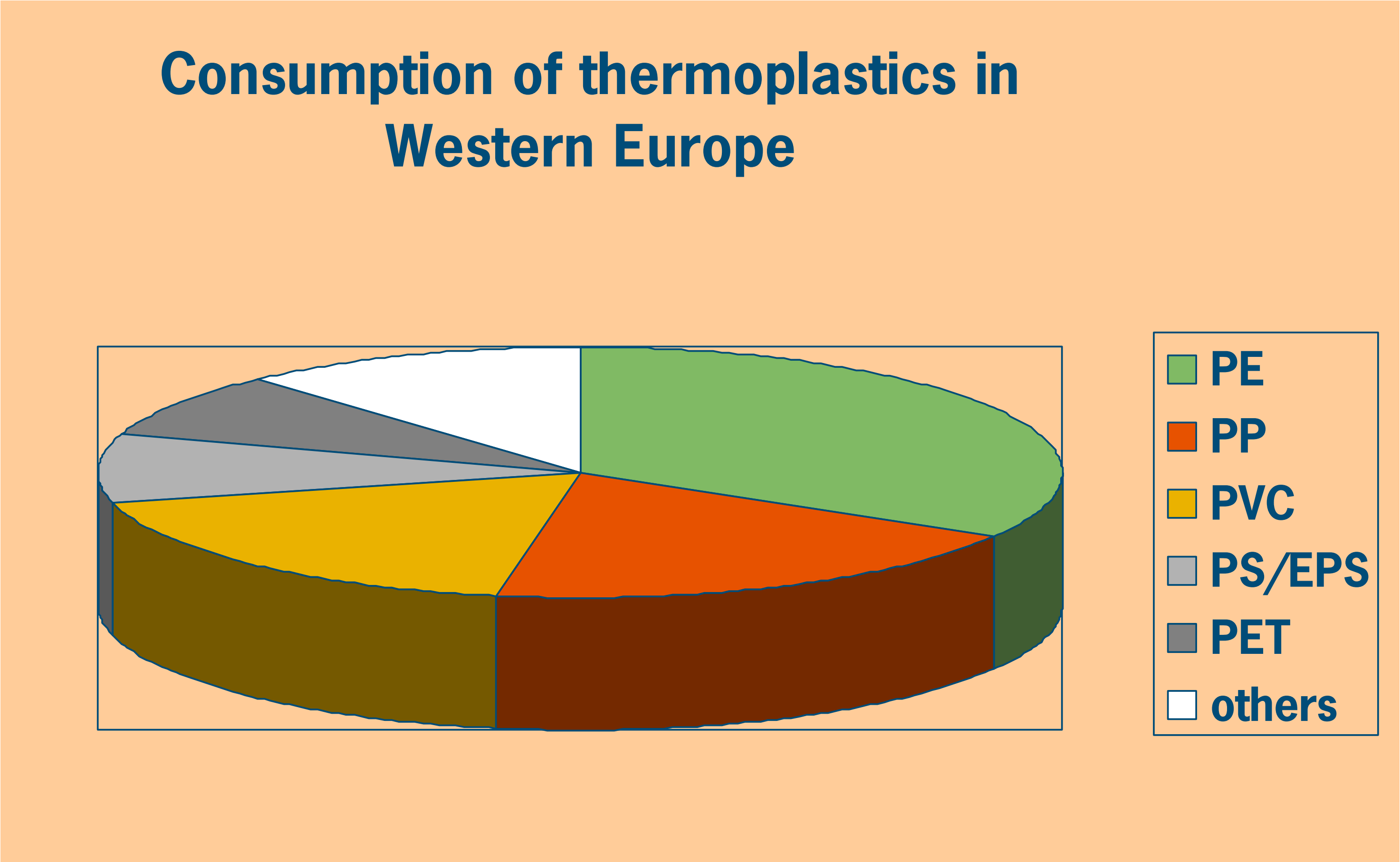


Figure 2: World plastics production 1950-2012
Includes thermoplastics, polyurethanes, thermosets, elastomers, adhesives, coatings and sealants and PP-fibers. Not included PET-, PA- and polyacryl-fibers
Source: PlasticsEurope (PEMRG) / Consultic



Major thermoplastic polymer materials



Total about 50.000.000 tonnes in 2014

About one third of all (more high end) Polymers comprise aromatic building blocks

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Increasing relevance biobased aromatics

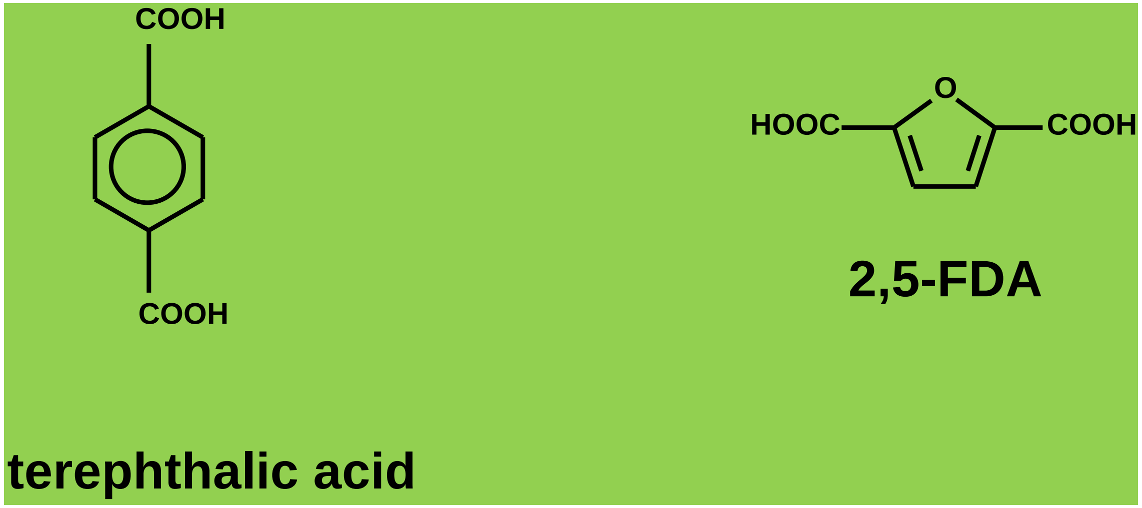
The availability of hydrocarbons from fossil resources is affected by the shale gas boom

	Availability fossil
Ethylene	↑
Propylene	↓
Butadiene	↓
Aromatics	↓
Methane	↑
Funktionalised C3-molecules	↓

Is this the chance for bio-based production?

Furandicarboxylic acid (2,5 FDA or FDCA) vs. terephthalic acid

- Terephthalic acid used to produce e.g. PET (bottle, fleece) or e.g. Aramid fibres
- Terephthalic acid and its isomers are used in up to 70 million tonnes/year quantities



- Furan dicarboxylic acid could be a bio based alternative to terephthalic acid
- Should we go for the real stuff (drop-in) or its look alike (FDCA)?

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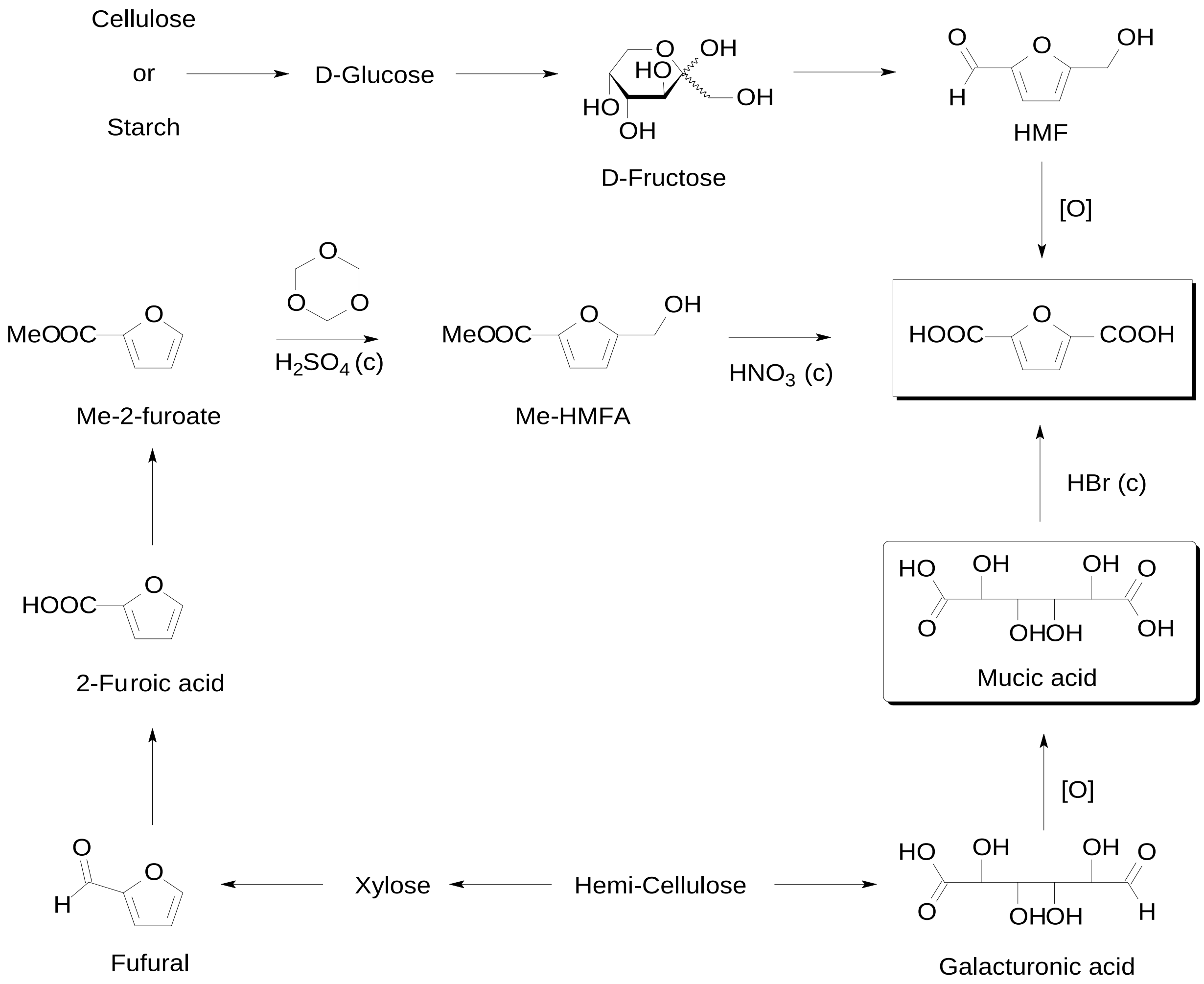
FDCA related research

- Numerous knowledge institutes and companies in recent years have become involved in FDCA related research;
  - ADM, Ava Biochem, Eastman, DSM, Nuplex, Perstorp, BASF, Braskem,....
- The Netherlands is a major player in FDCA related research:
  - Avantium
  - Corbion/Bird Engineering
  - Cosun
- FBR has over 10 projects dedicated to the development of FDCA and project based upon FDCA
- Potential market is that huge that presumably more than one technology will be commercialised

Potential Routes to 2,5 FDCA



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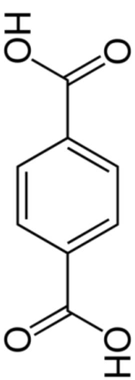
FDCA versus PTA; Avantium YXY technology

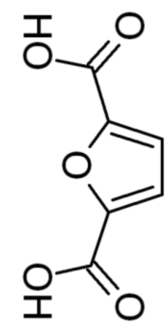


PTA

- Oil-based
- Building block for PET
- 50 million ton per year
- Today's price: €1200/ton
- Price drivers:
  - ➢ Oil price
  - ➢ Supply/demand

FDCA

- Bio-based
- Building block for PEF
- Potential market > 100 million ton
- Price at commercial scale: <€ 1000 per ton
- Price drivers:
  - ➢ Carbohydrate price
  - ➢ Economy of scale



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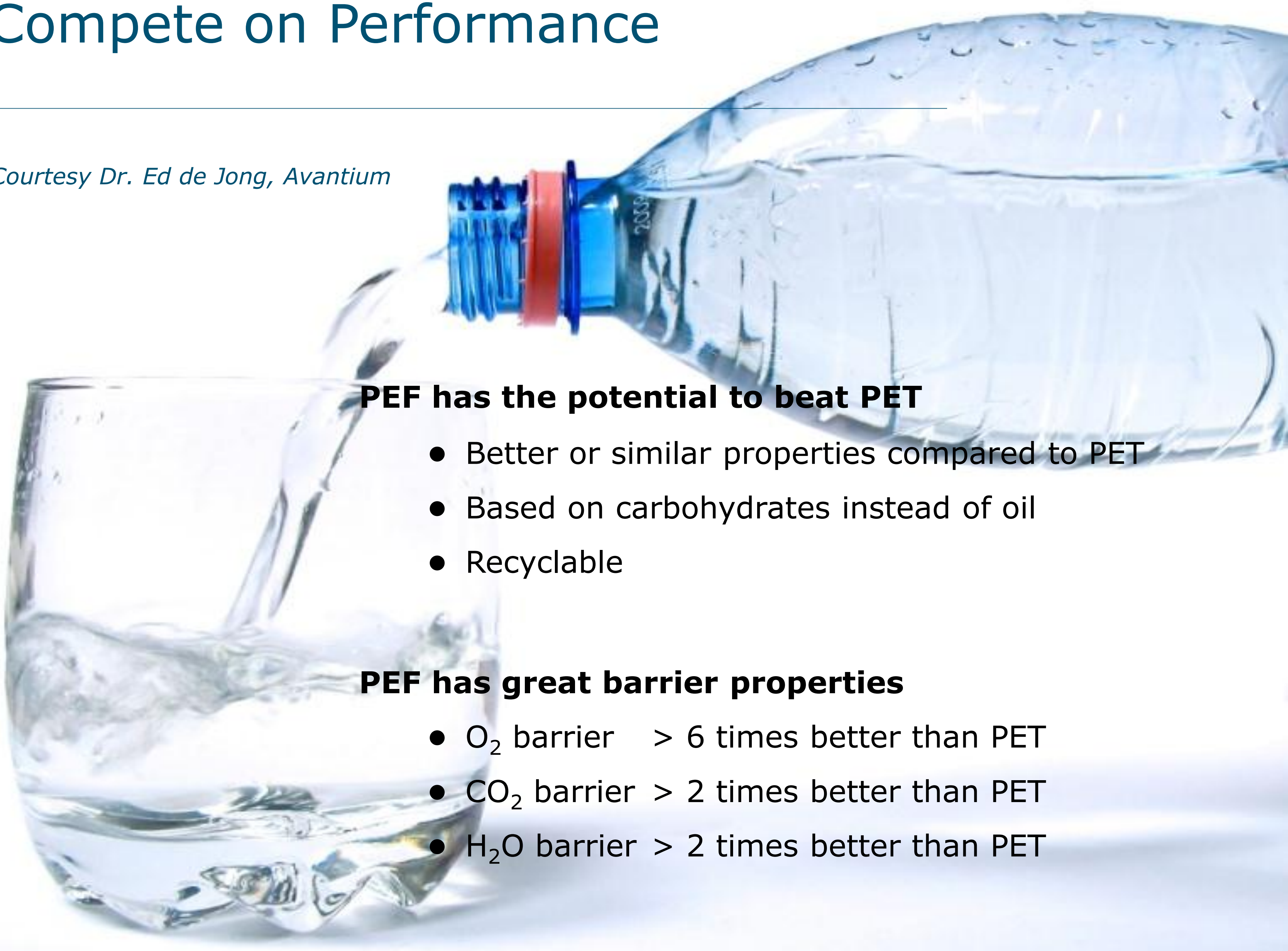
Courtesy Ed de Jong, Avantium

Compete on Performance

Courtesy Dr. Ed de Jong, Avantium



PEF has the potential to beat PET

- Better or similar properties compared to PET
- Based on carbohydrates instead of oil
- Recyclable

PEF has great barrier properties

- O_2 barrier > 6 times better than PET
- CO_2 barrier > 2 times better than PET
- H_2O barrier > 2 times better than PET

EU Splash project; algae as an alternative source for FDCA precursors

- Why algae:
- To convert CO2 (e.g. from the atmosphere of capture in industrial processes) into high added-value products and biofuels
- Alleviate food versus fuel conflicts
- May become particularly advantageous

  for regions with limited biomass availability

  and land unusable for agriculture

Figure 4 AlgaePARC. The opening of this facility took place in June 2011. There are 4 different production systems of 24 m^2 each and 3 of 2.5 m^2 each.

Valorising sugarbeet pulp

- Within EU annually approximately 25-30.10^6 tonnes of sugarbeet pulp (SBP) are being produced
- SBP is a byproduct of sugar refining (agricultural residue)
- Cosun produces annually about 1 million tonnes of SBP (25% dry matter)
- SBP contains a mixture of components not suitable as human food
- Cosun is interested in valorising SBP towards non–food applications
- Cosun teams up with Wageningen UR/FBR and other partners in valorising SBP

Table Composition sugarbeet pulp (in %)	
ash	**10**
protein	**8**
fat	**1**
cellulose	**25**
pectinic sugars	**23**
arabinanes	**24**
other sugars	**24**
lignin	**5**
	100

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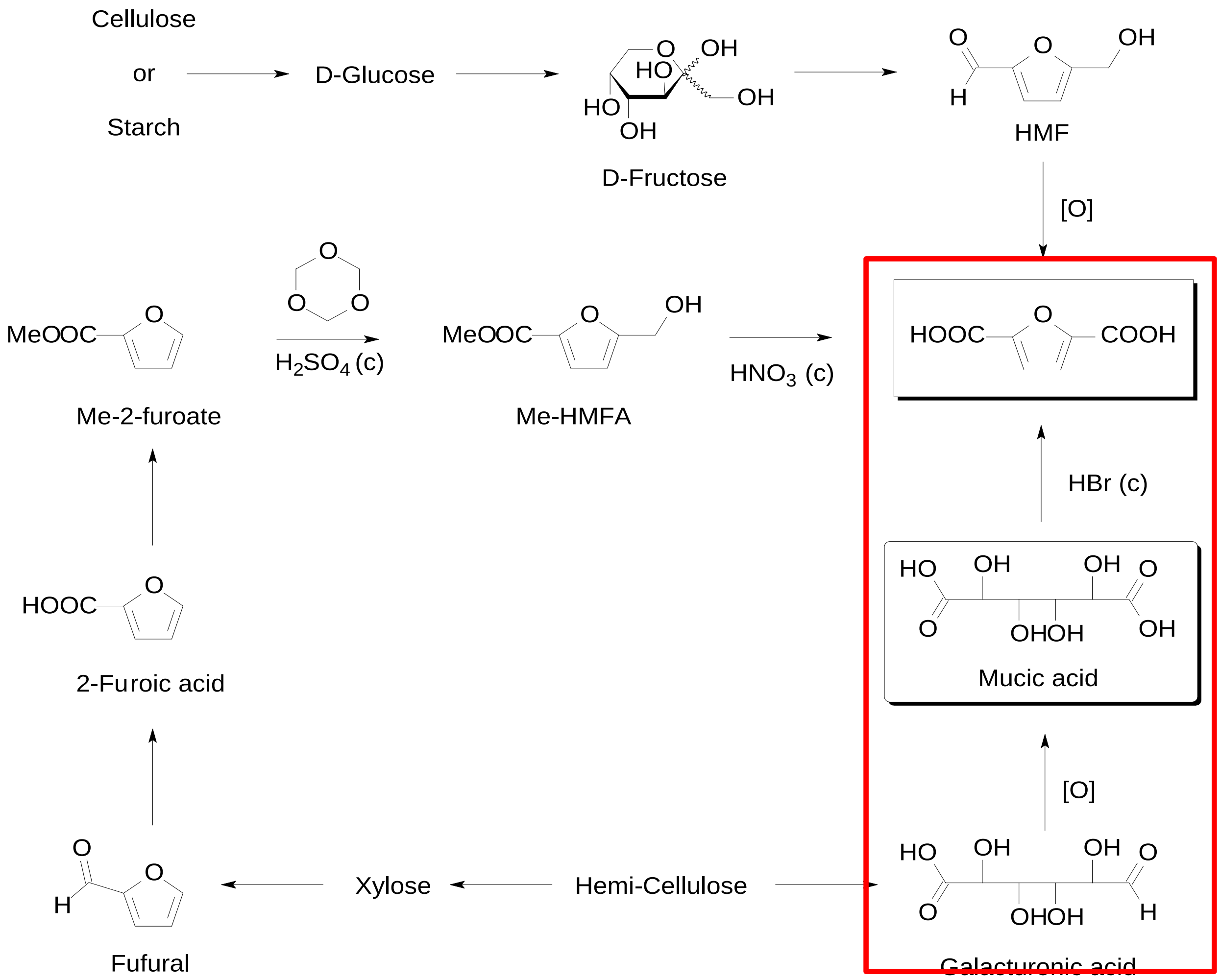
Biorefining of sugar beet pulp

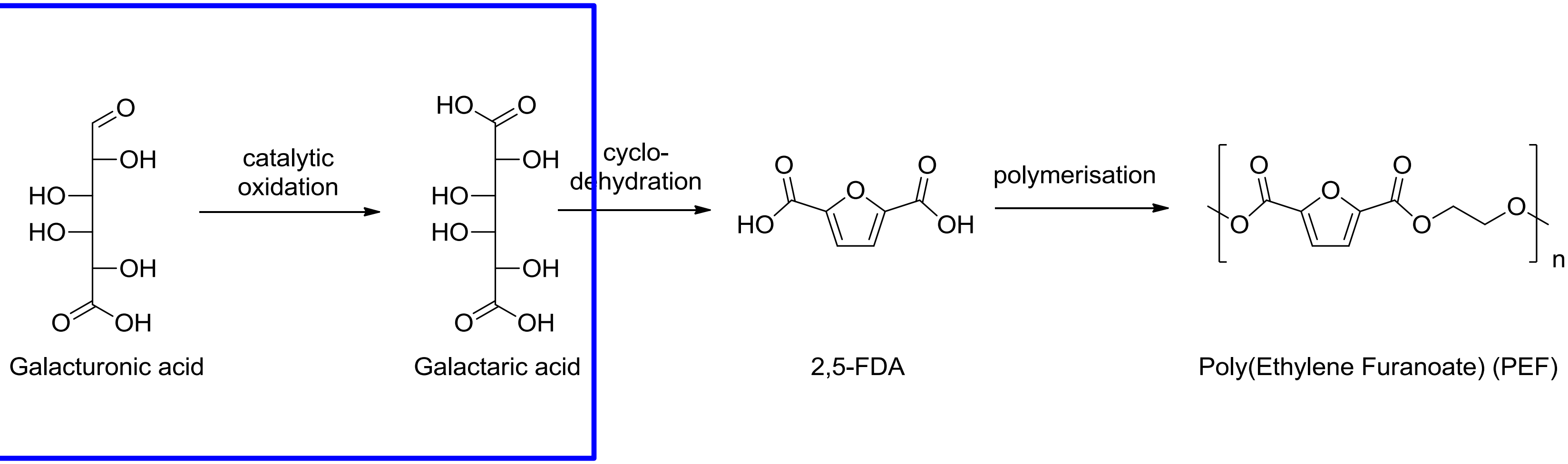
- Number of projects awarded within Topsector Agri&Food
- Overall aims of the projects
  - Continue developing biorefinery process for isolating monomeric sugars from sugarbeet pulp
  - Develop new catalytic technologies to produce high purity building blocks for high performance polymers based on sugarbeet pulp as raw material
  - Develop new chemical technologies to produce these high performance polymers
  - Investigate the properties of these new materials, and compare to conventional materials
  - Obtain insight into the technical and economical viab bio-based polymers

Potential Routes to 2,5 FDCA



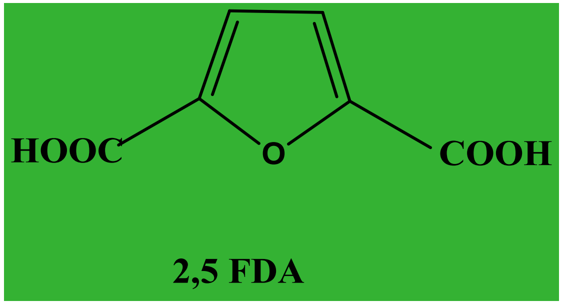
- Focus on galacturonic acid route
- Conversion of mucic acid to 2,5-FDCA already extensively explored
- In the project focus has been on oxidation of galacturonic acid (and other uronic acids and aldoses)

Oxidation of galacturonic acid



Second generation FDCA based upon SBP

- Key; catalytic oxidation of pectin sugars
    - Mild conditions (room temperature)
    - High conversions (>99%)
    - High selectivity (>97%)
    - Short reaction times (<3h)
    - Environmentally benign:
        - Air can be used for the oxidation
- Patent filed:
    - *Catalytic oxidation of uronic acids to aldaric acids*
    - *Subsequent conversion aldaric acid into 2,5 FDCA*



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PEF synthesis and properties

- Small scale synthesis of PEF
  - Glass, flat-flange reactor
  - 50-100 g scale
  - 2-stage melt polymerisation
    - 165°C, 16h
    - 225°C, 4h ambient pressure; 1 mbar, 2h; 1.10^{-1} mbar, 2h.
  - Purification: crude product dissolved in $CDCl_3$/TFA (6:1) and precipitated from MeOH (1,000 %
- 2 Liter polymerisation reactor installed

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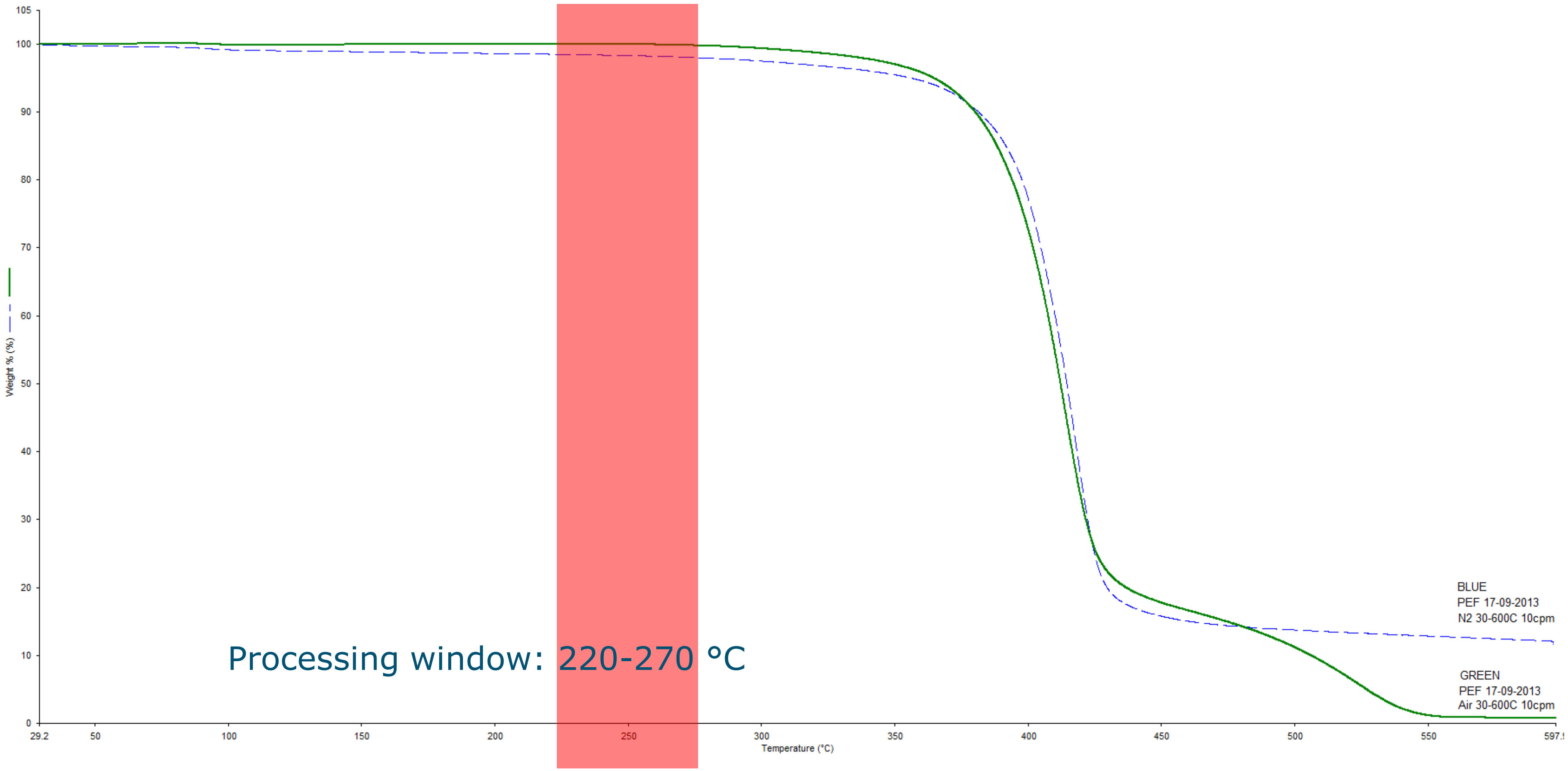
PEF synthesis and properties

- TGA analysis of PEF sample; thermal stability (N_2, air)



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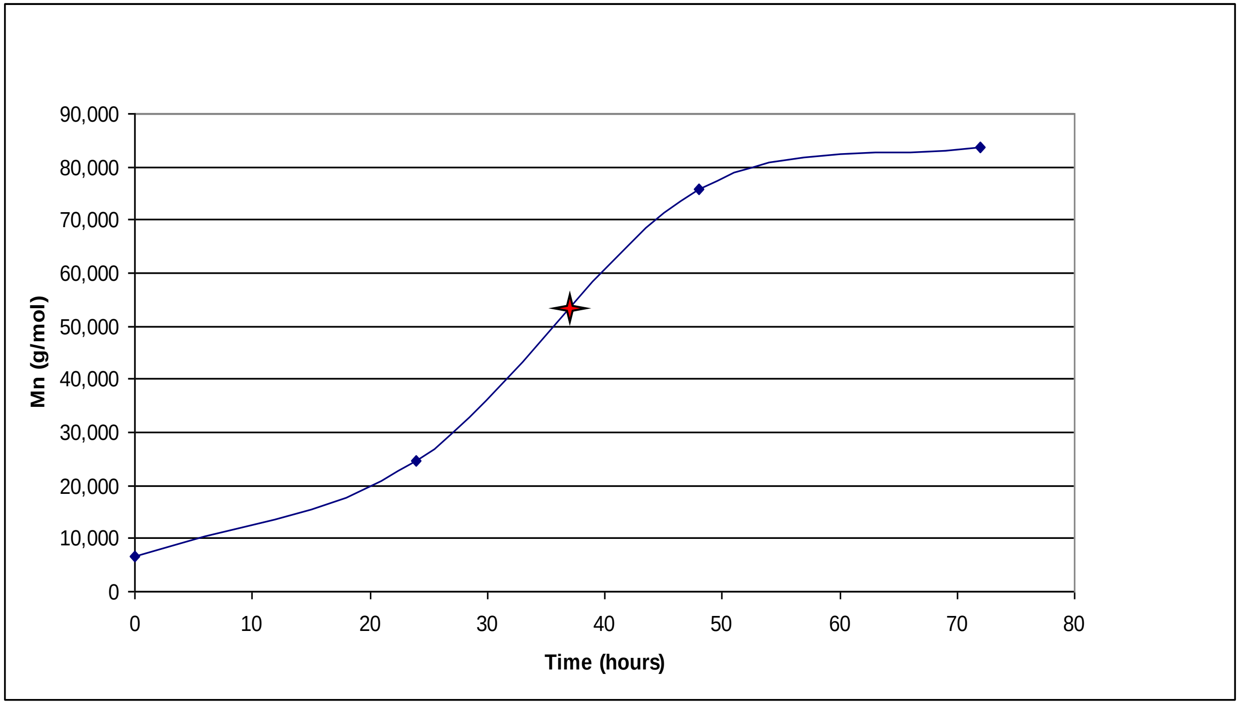
Results (MW after solid state polymerization)

Rotary evaporator adapted for

solid state polymerization



Molecular weight increment of PEF during SSP at 185°C over time. The red star shows the molecular weight of bottle grade PET .

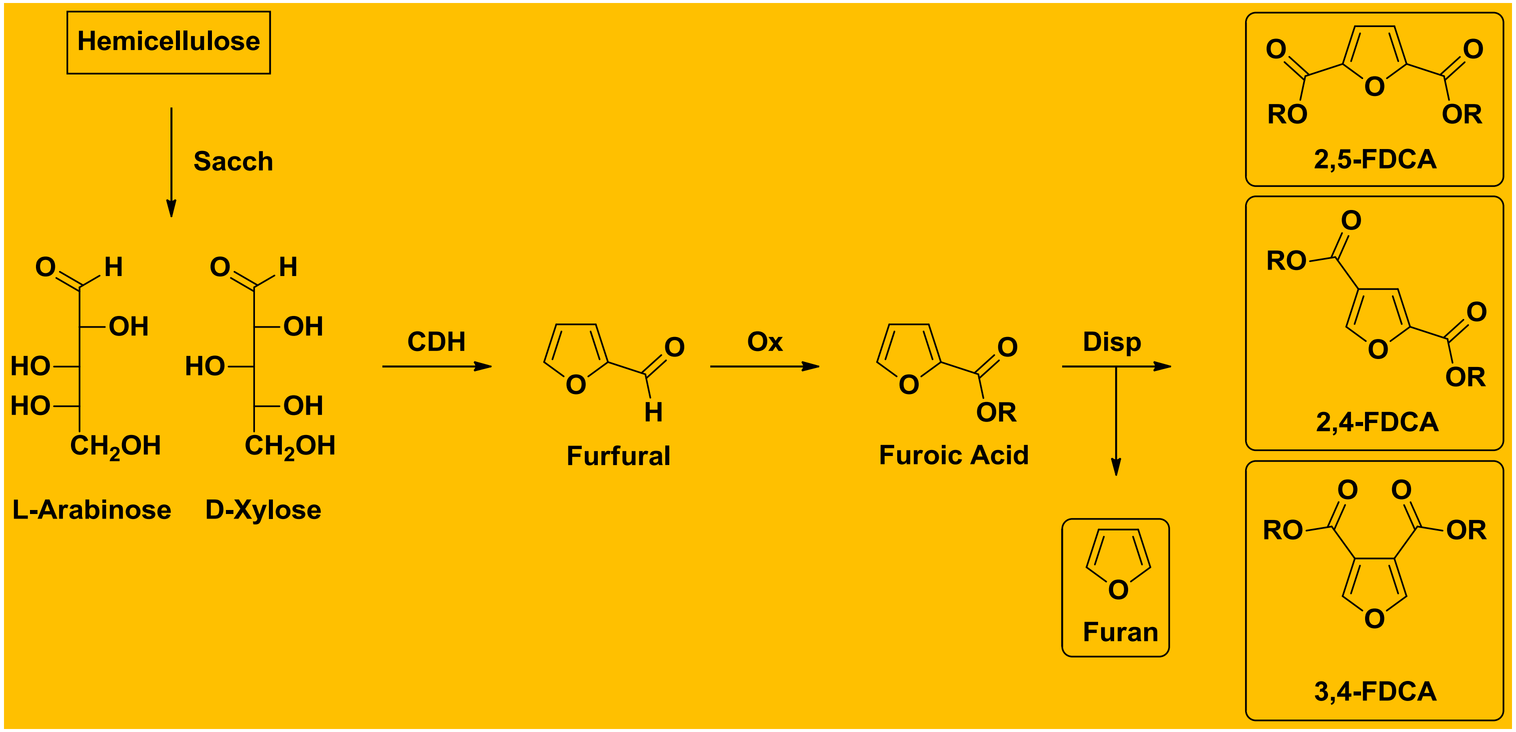
PEF synthesis and characterisation

Conclusions

- High molecular weight PEF can be prepared from FDCA derived from sugarbeet pulp
- Galactaric acid derived FDCA is more easy to purify than HMF derived FDCA; beneficial in polymerisation reactions
- Molecular weight allows for potential application in e.g. bottles
- Further processing and characterisation (e.g. gas barrier properties) ongoing

Furan dicarboxylic acids based upon hemicellulose

- Hemicellulose from agricultural side streams (e.g. sugarbeet pulp, wheat bran, bagasse) have huge potential to serve as source for the production of furandicarboxylic acids via C5 sugars



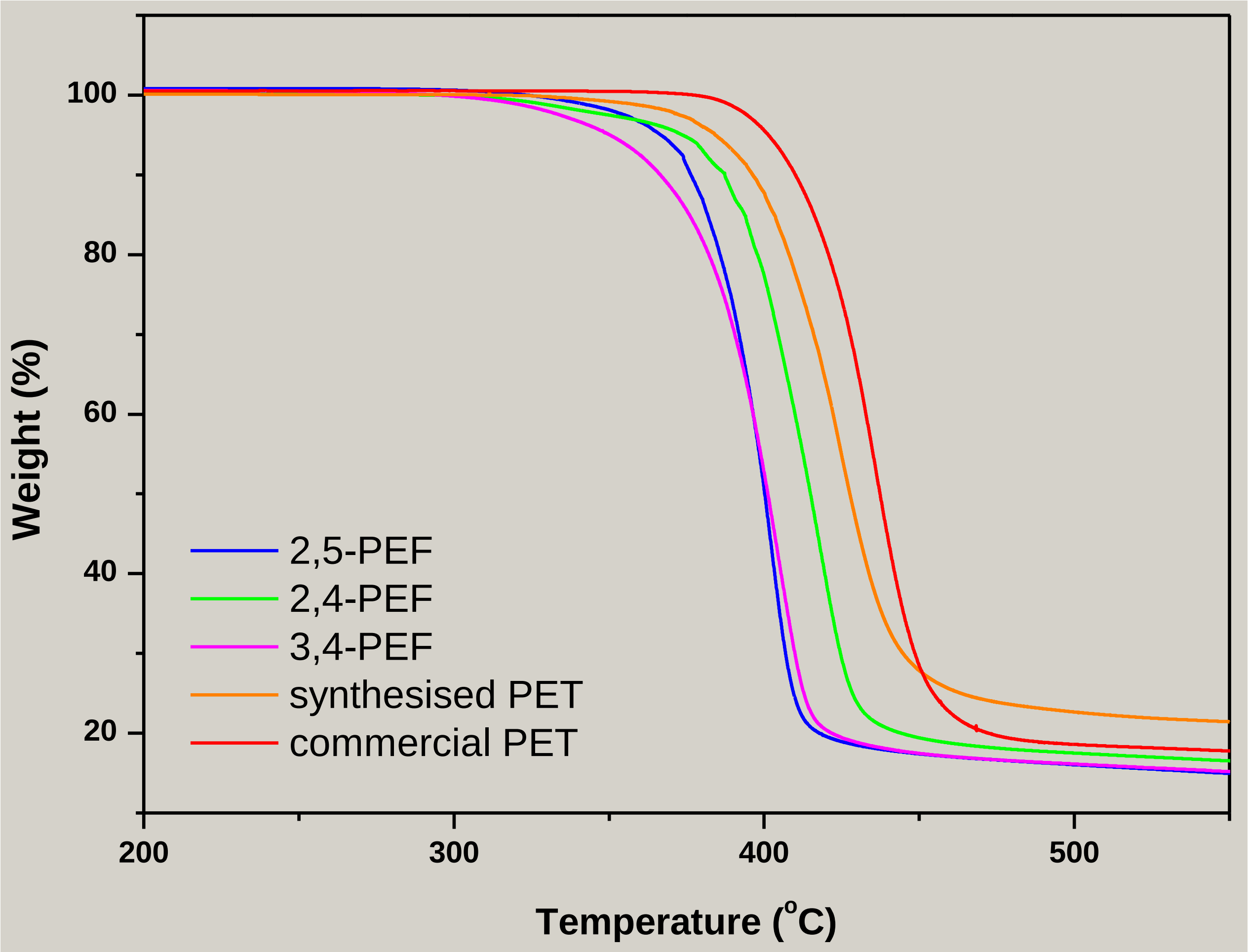
Thiyagarajan, S.; Pukin, A.; van Haveren, J.; Lutz, M.; van Es, D. S. RSC Advances ***2013****, 3, 15678.*

Polymer results with 2,4 FDCA

- PEF TGA analysis

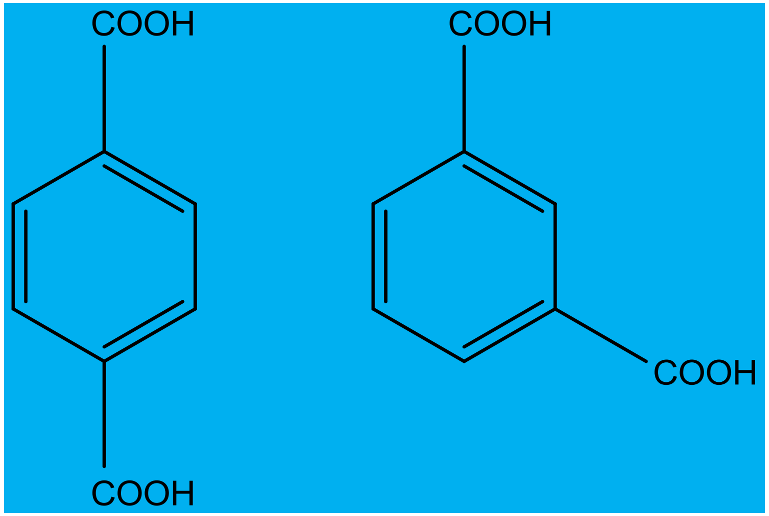
N_2

10°C/min

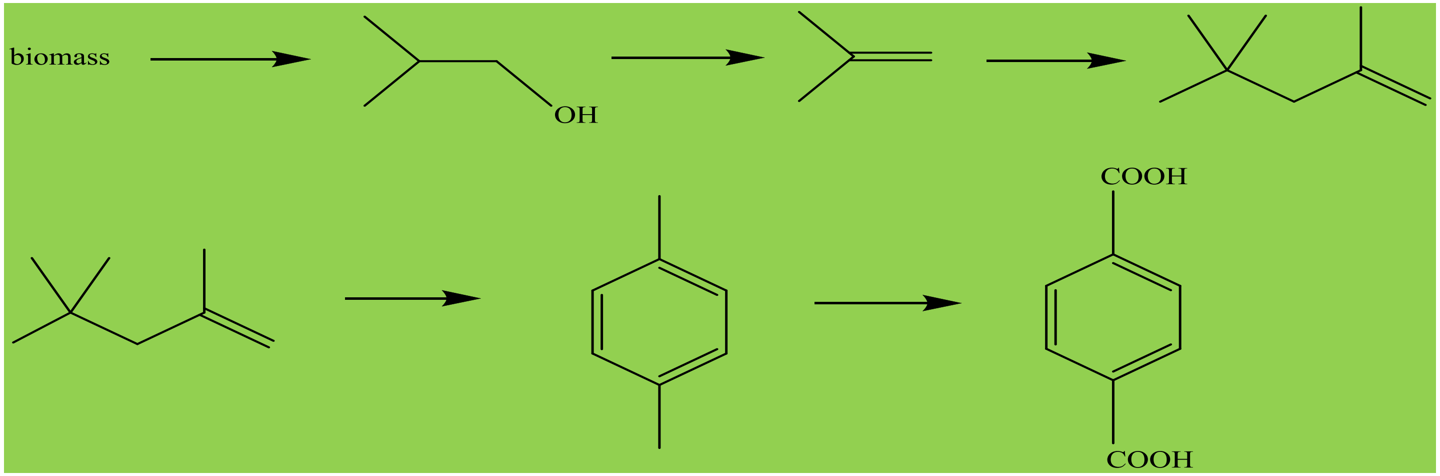


Going for the drop–in approach....

- How to derive biobased terephthalic acid or isophthalic acid?



Terephthalic acid via biotechnologically produced isobutanol

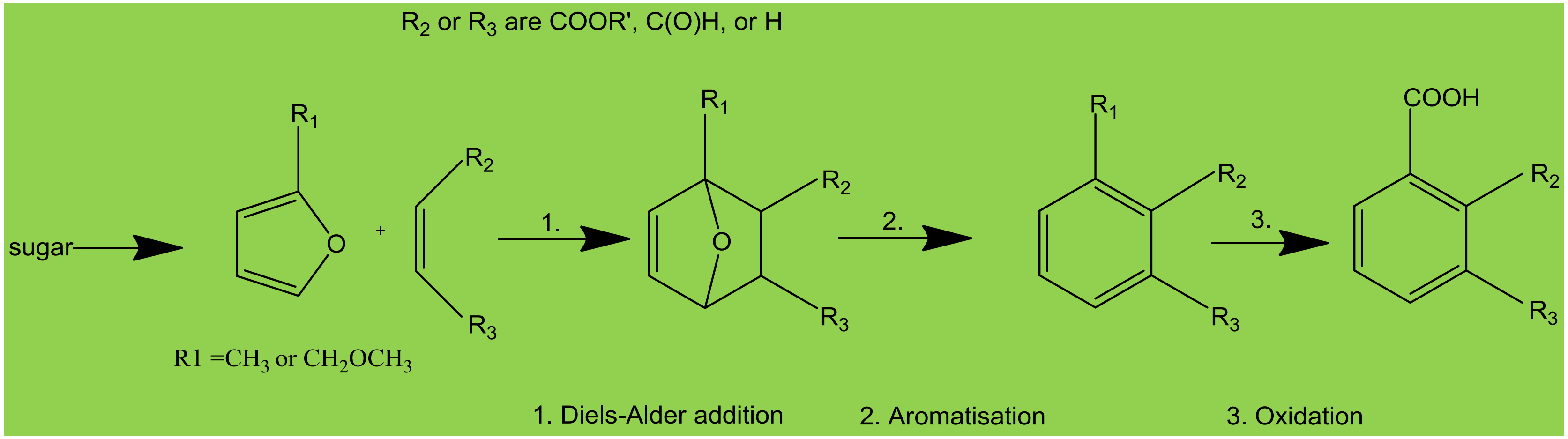


- Gevo Inc. promotes biotechnologically produced isobutanol as a platform chemical toward e.g. PTA; several patent applications on genetically modified organisms for production of isopropanol and isobutanol

- Conclusions Isobutanol platform Rotterdam; Current technology not yet mature; more research needed!

Biobased terephthalic acid

- Diels –Alder addition of furans with dienophyles is a powerful tool to generate aromatic drop in chemicals from biomass



- Reaction of substituted furans with acrylates gives access to isophthalic acid (comonomer in PET), reaction with maleic acid anhydride results in hemimellitic acid (potential comonomer in coating formulations).

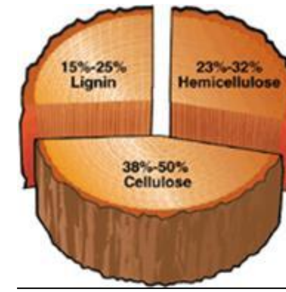
- Patent application to FBR and Avantium

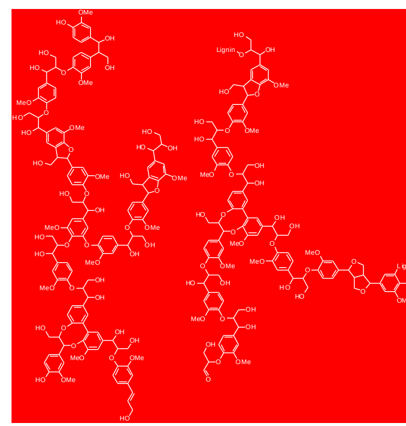
Lignin as a source for biobased aromatics

Lignin is found in plants and trees and is a rest stream from:

1. Established Pulp and Paper industry (50 M t/y, 1 M t/y products)
2. Novel Biorefinery industry (>20 M t/y)

- Major aromatic resource in Biobased Economy
- Complicated aromatic structure
- Complexity and heterogeneity has limited its use in materials and for chemicals production





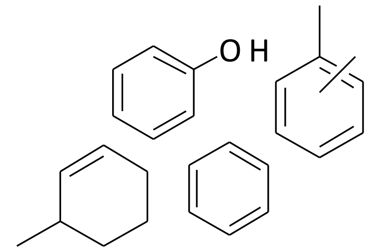
softwood lignin structure Brunow 2001)

Hydrothermal depolymerization of lignin

Biomass

Biorefinery lignins
(commercial soda non-wood lignin)

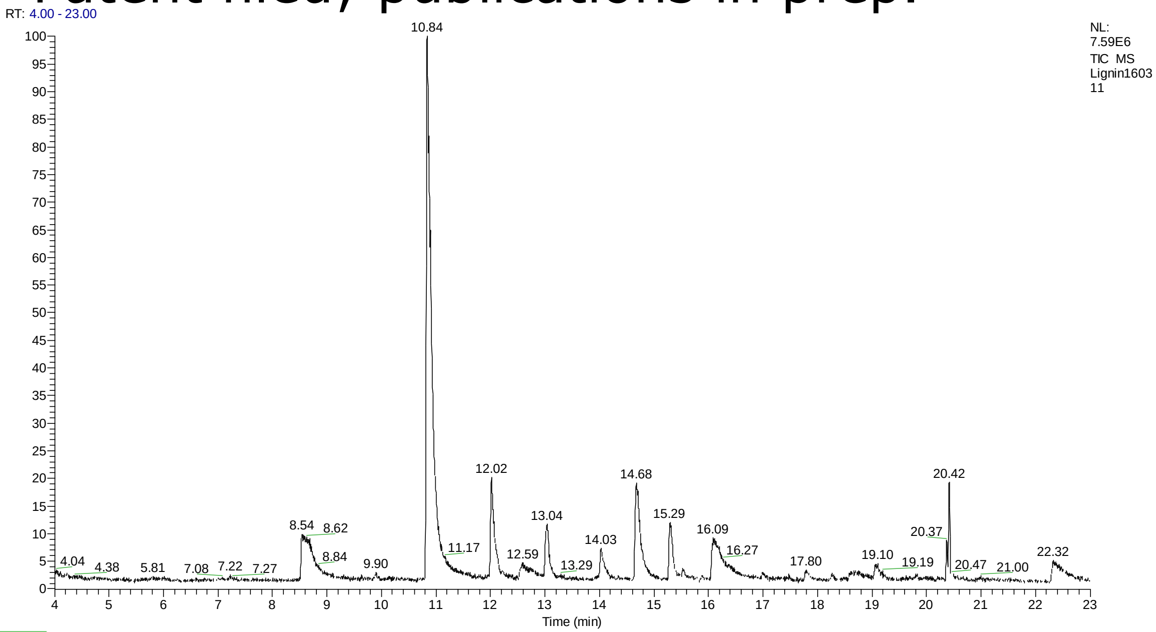
Aromatics and phenolics



- Turn lignin into high value aromatics (BTX) and building blocks (phenol)
- Thermal decomposition of lignin (pyrolysis, super critical fluids) often accompanied by unwanted re-condensation of monomeric phenol species
- Approach: Selective catalytic hydrothermal depolymerisation
  Prevent re-condensation & no external use of hydrogen

Hydrothermal depolymerization of lignin

- Limited set of monomeric phenols (9-12) obtained in 20 mass% yield
- Literature: 20-30 identifiable components, 10% yield
- 50% 1 component
- Patent filed; publications in prep.



Conclusions

- Biomass offers excellent opportunities for the synthesis of biobased chemicals, including aromatic chemicals
- Both “drop-in” as well as biobased chemicals can be derived from biomass
- Biobased chemicals with a unique structure can result in product with unique properties
- Both lignin as well as carbohydrates offer huge opportunities for the synthesis of biobased aromatics

Acknowledgements

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Carbohydrate Competence centre

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