

# New ways of using sugar beet pulp

Conversion of SBP components into value added products for home & personal care and performance materials

Daan van Es, Frits van der Klis

Wageningen Food & Biobased Research, Lyon May 2019



# Program

- Introduction WFBR & Pulp2Value project
- Session 1
  - Galacturonic acid based anionic surfactants
  - Formyl Furoic Acid from Galacturonic acid
- Break
- Session 2
  - Catalytic oxidation of Galacturonic acid to Galactaric acid
  - Applications of Galactaric acid
- Wrap-up



# Introduction Wageningen FBR

# The Biobased Economy Value Chain

## Biomass

Lignocellulosic crops & residues



Agricultural crops & residues



Fresh Biomass



Aquatic Biomass

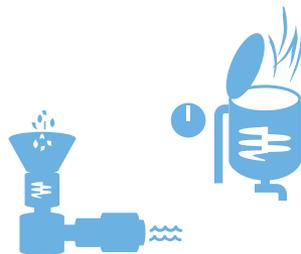


Food & Feed



Biorefinery

Isolation, Extraction & Pretreatment



Biomass components

Carbohydrates



Natural fibres



Specialties



Proteins



Lignin



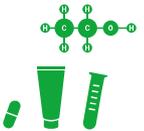
Oil & fats



Materials



Chemicals



Fuels & Energy

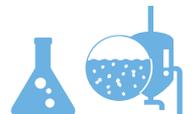


Polymer Processing



Synthesis & Modification

Biotechnological & Chemical Conversion



Conversion

# Wageningen FBR Contract Research

## Food & Biobased Research (FBR)

- Contract research institute, part of WUR
- From fundamental to applied research
- Intensive public-private cooperation
- Approx. 300 scientists in 2 Business Units; FFC, BBP
- BU Biobased Products; 3 dept's
  - Biorefinery & Fibre Technology
  - Bioconversion
  - Sustainable Chemistry & Technology



# Sustainable Chemistry & Technology

Integrated approach from (refined) biomass to biobased materials

- Organic Chemistry & (bio) Catalysis
- New Sustainable Chemistry; Electrochem & Photochem
- Specialty Chemicals Synthesis and Testing
- Building Block Synthesis & Purification
- Polymer Synthesis & Characterisation
- Polymer Processing & Materials Development



# Biobased chemicals

## ■ Why biobased?

- Renewable, sustainable, reduction in carbon footprint and GHG emissions
- Independence from fossil feedstocks
- Possibilities for chemicals with unique chemical structures and functionalities
- In case of substances of concern: replacement by safe functional alternatives from biomass
  - But remember: biobased is not by definition safe or biodegradable!



# Biobased chemicals



- Direct replacement of fossil analogue:
  - Drop-in, same chemicals but from renewable feedstock. Often not preferred from green chemistry pov: low atom economy, high energy demand.
  - Benefit: Easy to implement
  - However, in case of S(V)HC; no benefit from biobased
- Unique chemicals from biomass
  - Functional alternatives; e.g. biobased non-phthalate plasticisers
  - Or completely new products with new properties

# Biobased chemicals

## WFBR strategy

- Preferably use non-food feedstocks; e.g. agro-food residues
- Complete biomass valorisation (chemicals, materials, energy)
- Conversion to platform chemicals by most efficient technology
  - Ethanol, lactic acid, HMF, sorbitol, etc.
- Focus on safe platforms as much as possible
- Design for circular: consider recycling, biodegradation and other end of life solutions



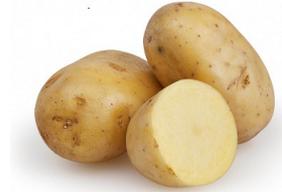
# Biobased materials

## Emerging focus/strategy shift

- Renewable; CO<sub>2</sub> neutral, sustainable (high atom economy, low energy demand, no waste, no GHG emissions)
- Durable (majority of applications)
- Designed for circular
  - Mechanical recycling
  - Chemical recycling
  - Environmental fate
  - Biodegradable where possible/required



# Biobased materials



- Increasing focus on use of biobased materials as such
  - Use cellulose or starch (or derivatives) as material, instead of conversion to glucose, and e.g. ethanol
  - Use lignin (or derivatives) as material in e.g. asphalt as alternatives to bitumen or binder in board materials, instead of deconstruction to phenol
  - Use pectins as such for home and personal care products
  
- Thermoplastic processing/shaping of materials is highly desired (high productivity, solvent-free, low waste)



# Introduction Pulp2Value project



[www.pulp2value.eu](http://www.pulp2value.eu)

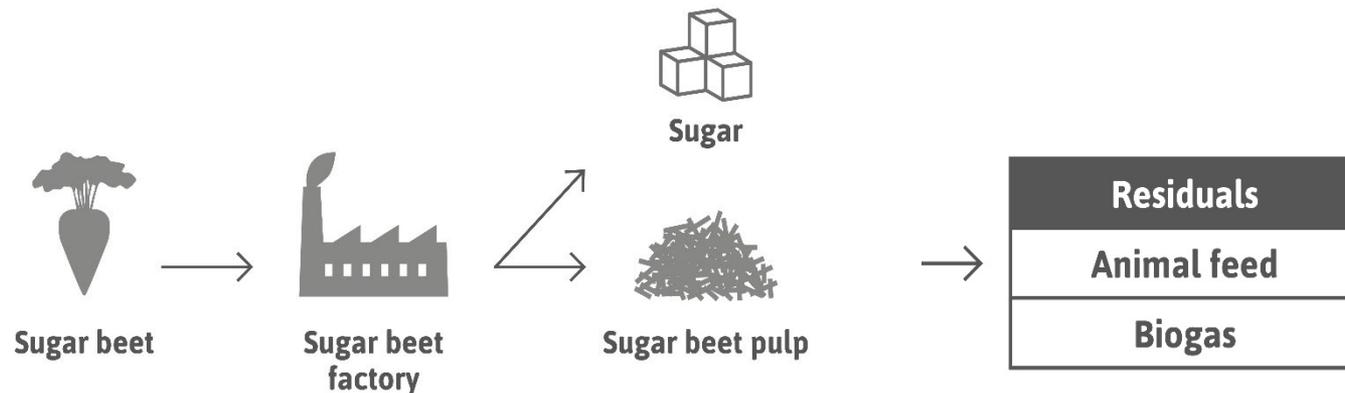
# Processing Underutilised Low value sugarbeet Pulp into VALUE added products



The project has received funding from the Bio-Based Industries Joint Undertaking under the European Union's Horizon 2020 research and innovation programme under grant agreement No 669105.

# Background

- Sugar beet pulp (SBP) is a major residual stream from the sugar beet industry, which is currently valorised as low value feed and/or green gas. In Europe sugar beet pulp accounts for a production volume of approx. 13 million tonnes per year.



## Raw material

Beet pulp  
(dry)

25% Pectin

25% hemi  
cellulose

25% cellulose

15% other  
organic

10% ash

## Primary Products

Special  
Sugars

Arabinose  
Rhamnose  
Mannose  
Galactose  
other

Micro Fiber

Galacturonic  
acid

Oligo's

## Derivatives

Plasticizers

Surfactants

Galactaric  
acid

“CBB”

Adipic acid

Furans

Gal X

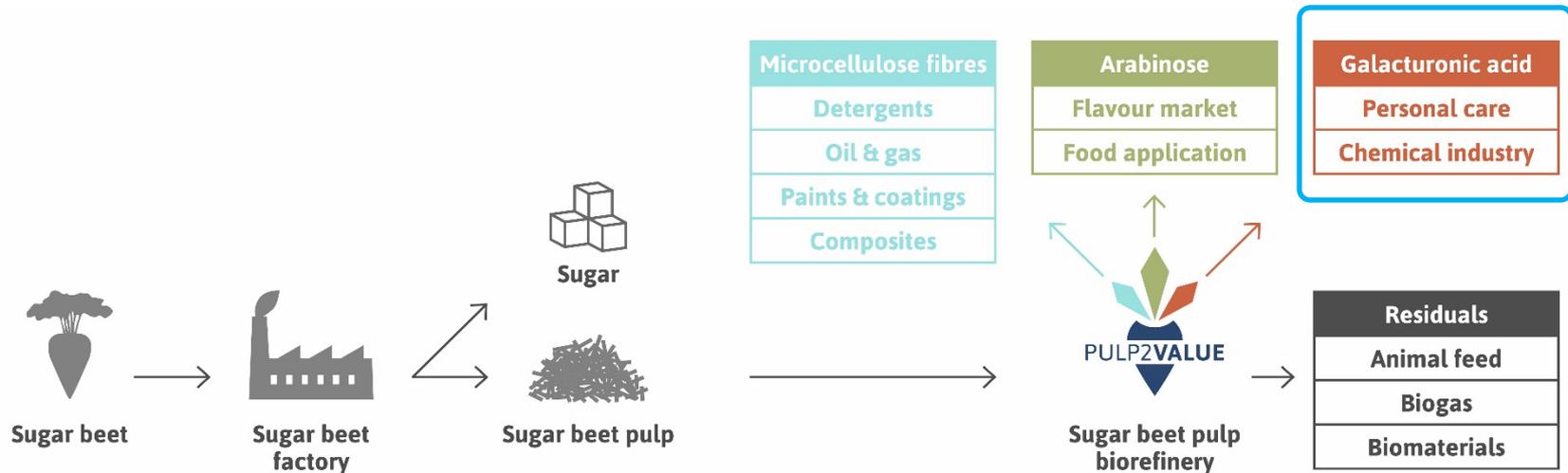
## Markets

- feed
- biogas
- powder/tablets
- paper

- food
- pharma
- leather
- coatings
- composites
- flavors
- cosmetics
- detergents
- chemicals
- feed

- polymers
- chemicals
- leather
- cosmetics
- coatings
- plastics

# Scope & Objectives



## ■ Main objectives:

- To optimize, scale up and integrate processes.
- To build long lasting value chains.

- The ultimate goal is to set up a **demonstration plant** which refines sugar beet pulp in an **integrated and cost-effective cascading biorefinery**.



# The PULP2VALUE consortium



- 1** Royal Cosun  

- 2** Wageningen UR  
Food and Biobased Research  

- 3** Wageningen University  
part of Wageningen UR  
Division of Human Nutrition  

- 4** Orineo bvba  

- 5** Bio Base Europe Pilot Plant  

- 6** Refresco Gerber UK Limited  

- 7** nova-Institut für politische und ökologische Innovation GmbH  


**7 participating organisations from the EU countries:**  
Belgium, Germany, the Netherlands and United Kingdom

**Coordination:** Royal Cosun  
Gerald van Engelen, [gerald.van.engelen@cosun.com](mailto:gerald.van.engelen@cosun.com)

- ▶ Complementary expertise along the whole value chain
- ▶ Strong industrial participation

# Project data



- PULP2VALUE receives funding from the Bio-based Industries Joint Undertaking under the European Union's Horizon 2020 research and innovation programme under grant agreement No 669105.
- PULP2VALUE is one of the two demonstration projects in the Bio-based Industries Joint Undertaking (BBI JU) Call 2014.
  - PULP2VALUE relates tot the BBI annual work plan topic BBI VC3.D4 2014: "Functional additives from residues from the agro-food industry".
- Budget:
  - Total cost: 11.4 million Euro; Funding: 6.6 million Euro
- Duration: July 1, 2015 – June 30, 2019

# Value chain developments

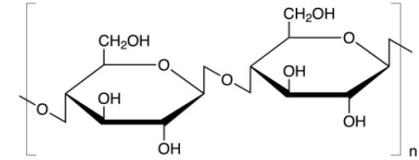
- 3 Main SBP based value chains



*From biomass...*

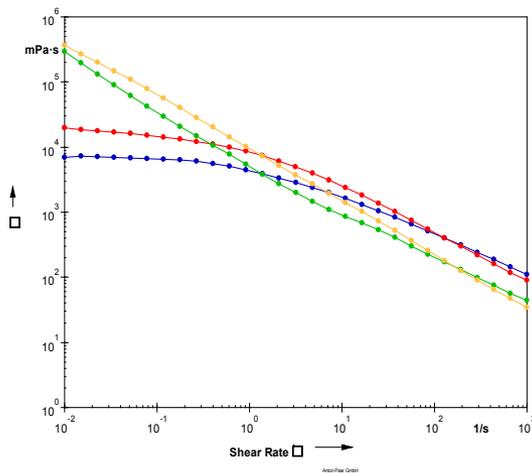
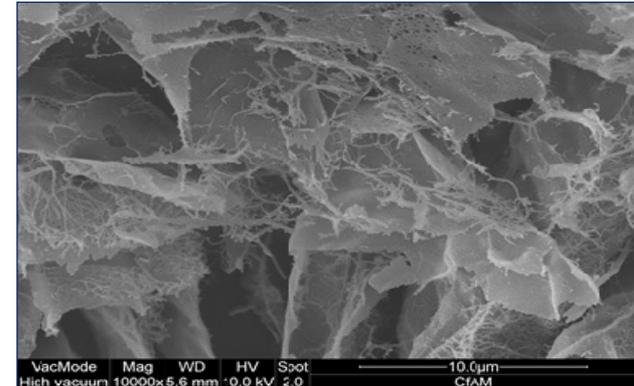
*...to end-users*

# Value Chain 1: Betafib® MCF

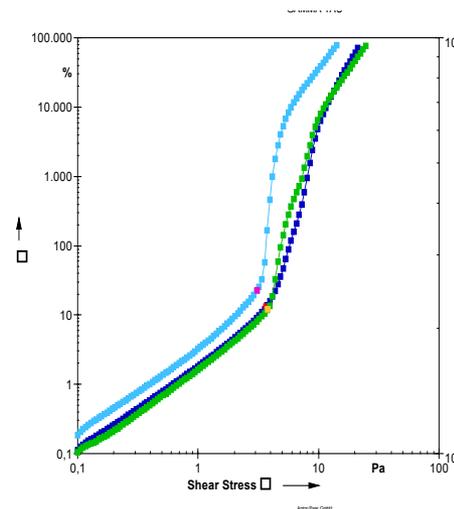


## Basic properties

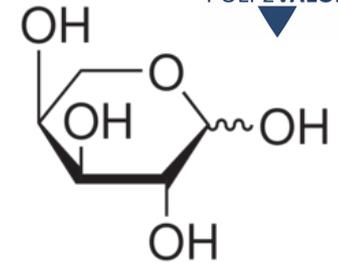
- Rheology profile
  - Shear thinning
  - High yield point
- Structurant (particles).



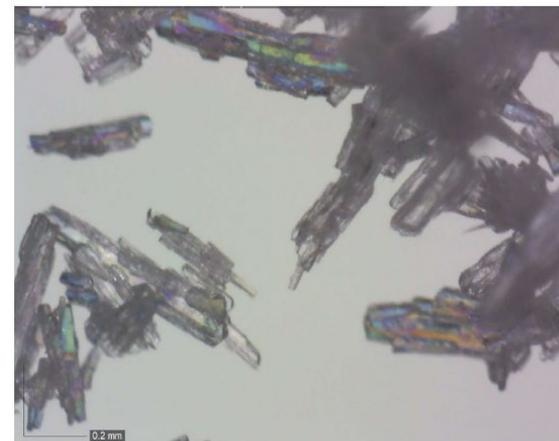
CTIC - CDSN



# Value Chain 2: L-Arabinose



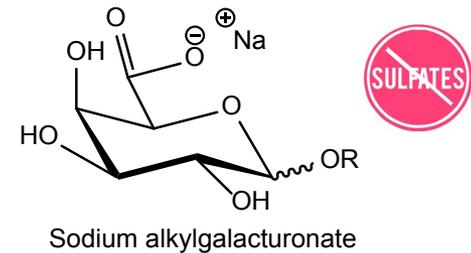
- Sweetness: 60% of sucrose.
- Available as syrup or high purity crystalline powder
- No adverse health effects in digestive system up to single dosages of 20 grams.



# Value Chain 3: Galacturonic acid

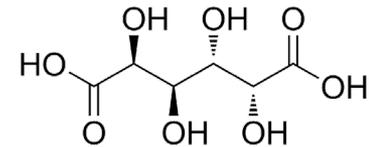
## ■ Sulphate free Anionic surfactants based on D-galacturonic acid

- Mild (non-irritant)
- Good foaming properties



## ■ Oxidation to Galactaric acid

- Chelating agent (cosmetics)
- Corrosion inhibition (metal working fluids)
- Rigid building blocks for polymers (GalX, cross-linker)



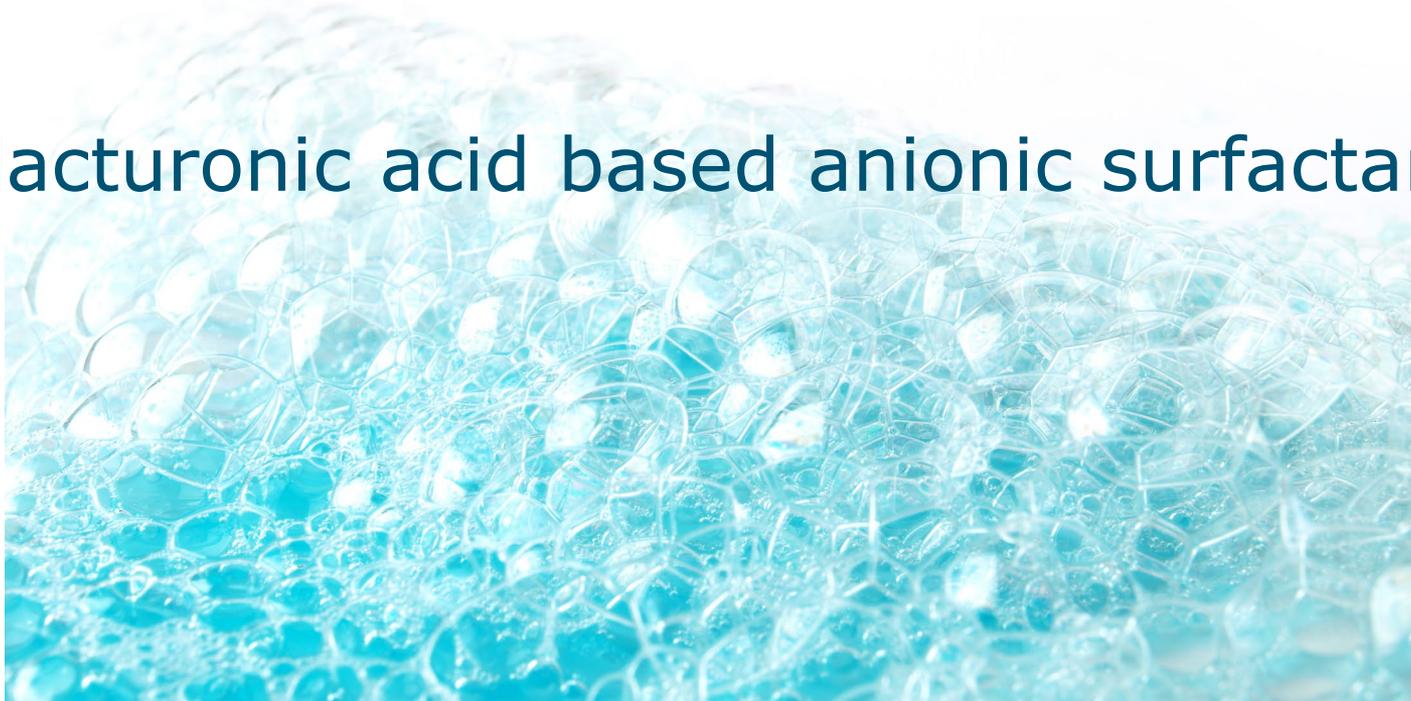


- For more information, please visit the P2V website: [www.pulp2value.eu](http://www.pulp2value.eu)
- For questions, please contact the project coordinator: Gerald van Engelen, [gerald.van.engelen@cosun.com](mailto:gerald.van.engelen@cosun.com)



# Session 1

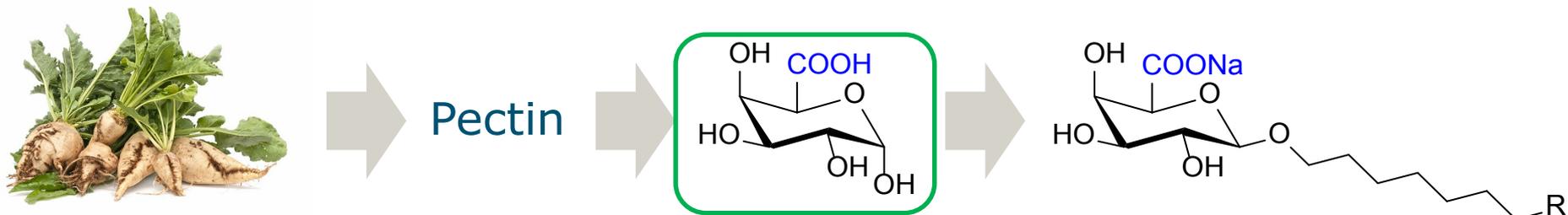
# Galacturonic acid based anionic surfactants



# Biobased Anionic Surfactants



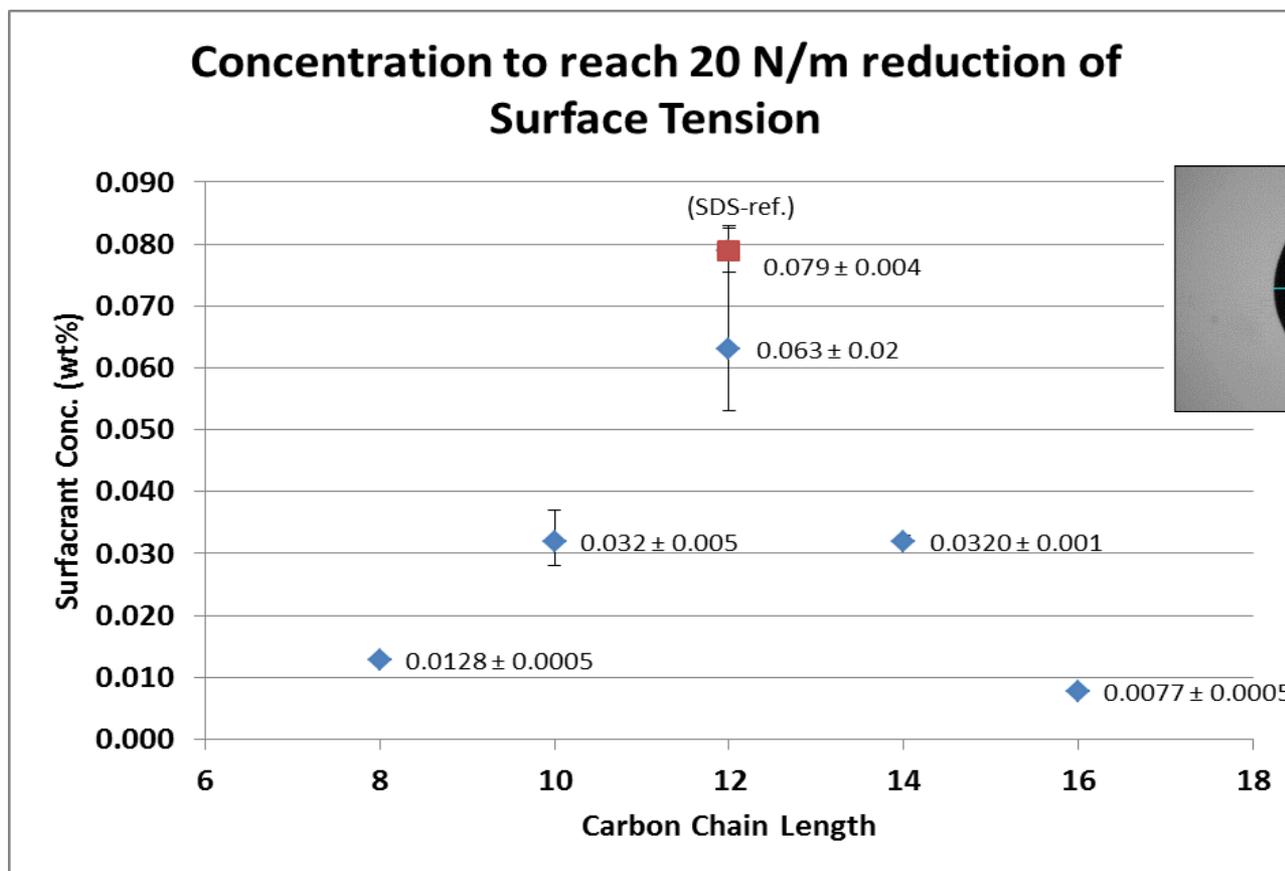
- Sugar beet pulp; low value agro-residue
  - Beet pectin (~25 wt%) contains galacturonic acid, a non-edible C6 sugar acid



- Interesting building block for biobased anionic surfactants
  - Sulphate-free compared to SLS/SLES
  - Anionic compared to APGs
  - Known but never systematically investigated

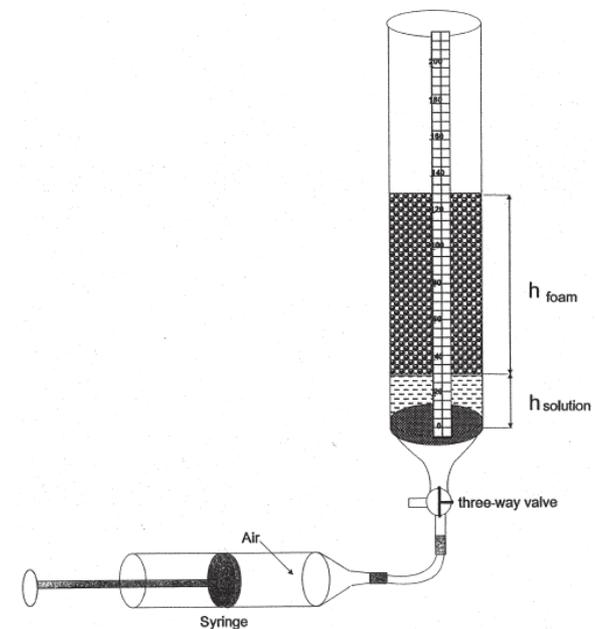
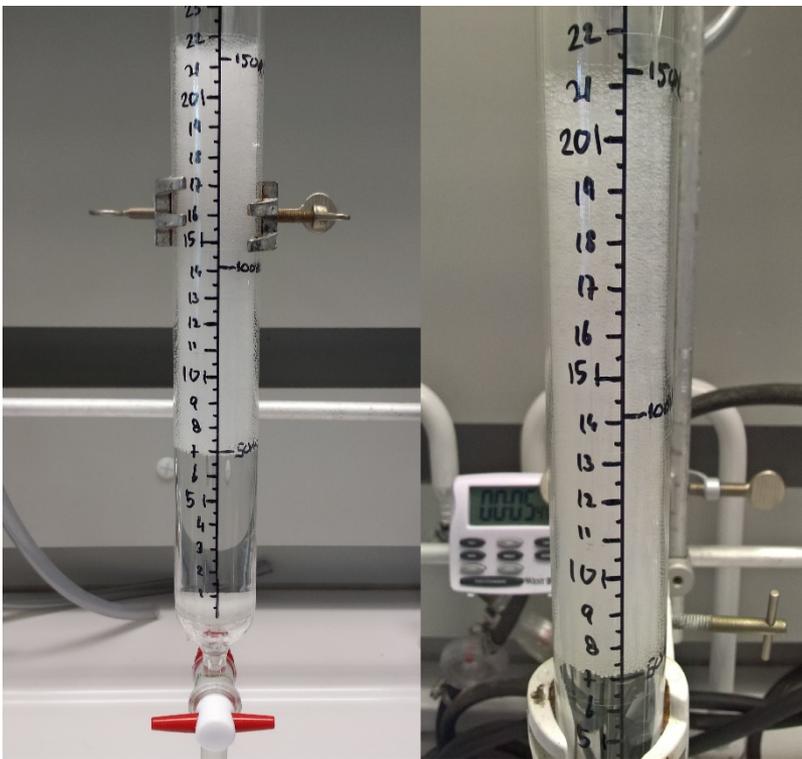
# Biobased Anionic Surfactants

- Excellent performance compared to **SLS** benchmark



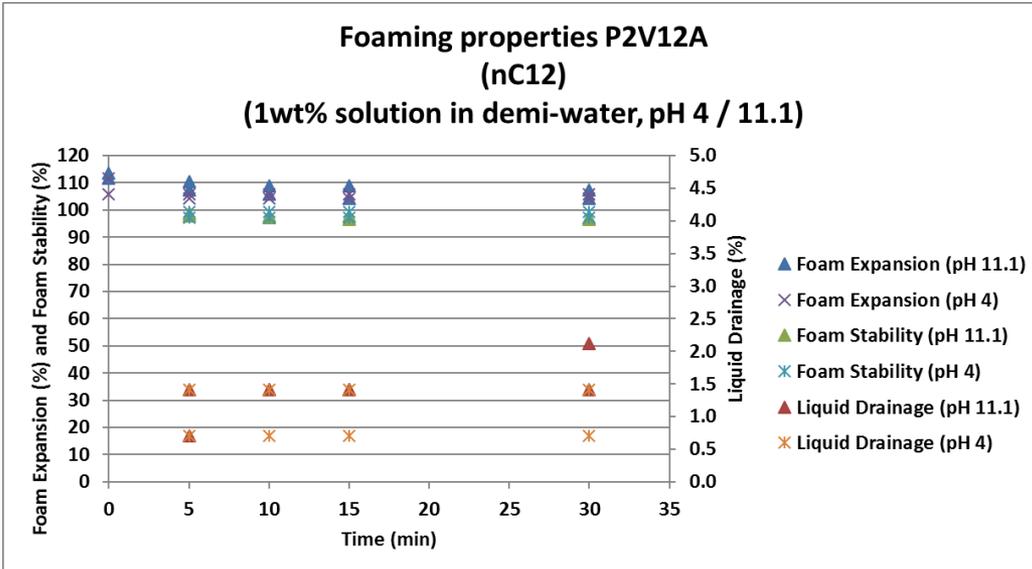
# Biobased Anionic Surfactants

- Also foaming properties are excellent (e.g. Ross Miles)
  - Systematically investigated over range of derivatives



Lunkenheimer, *J. Surf. Det.*, **2003**, 6, 69-74.

# Biobased Anionic Surfactants



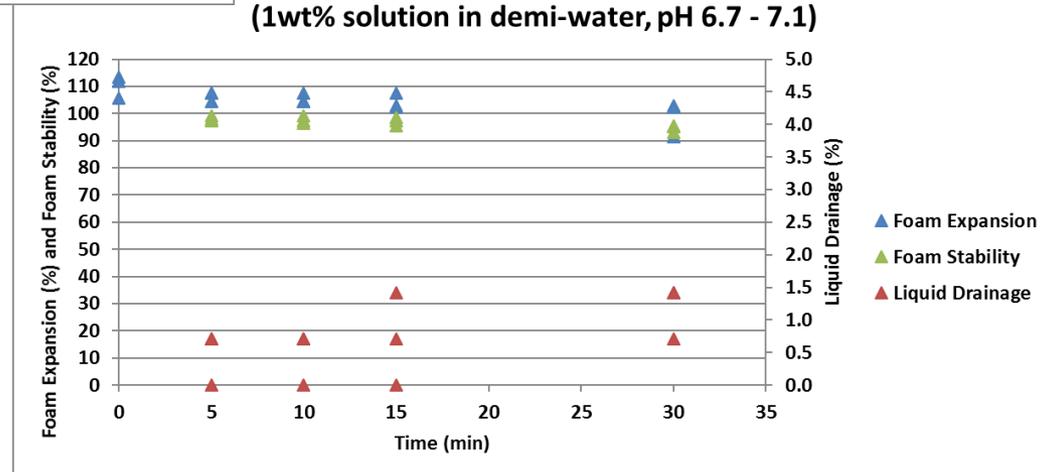
## nC12-GalA:

- Foam stability +
- Foam expansion +
- Liquid drainage +
- pH sensitivity +

## SDS:

- Foam stability +/-
- Foam expansion +
- Liquid drainage +
- pH sensitivity +

## **Foaming properties SDS (C12-sulphate)** (1wt% solution in demi-water, pH 6.7 - 7.1)



# Biobased Surfactants



- Sulphate free biobased surfactants developed
- Positive outcome of surfactant properties evaluation (confirmed by external industrial partners)
- More testing in progress, including novel markets and applications
- Process intensification under development
- Follow-up: new TKI-AF project to start in 2019
  - From Sugar beet 'Waste' to Environmentally Enhanced Detergents 'SWEED'
- Various other surfactant developments

# Discussion



- Is there a need for new anionic surfactants?
  - And why?



# Discussion



- Is there a need for new anionic surfactants?
- What are the most important requirements?
  - Biobased (C-footprint reduction)
  - Vegan
  - Skin-mildness
  - Eco-tox
  - Biodegradability
  - Costs
  - Other?



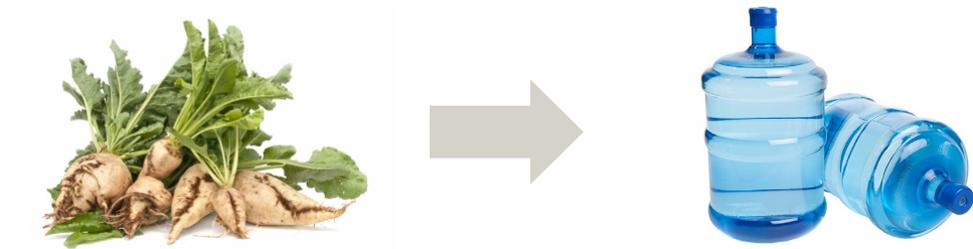
# Discussion



- Is there a need for new anionic surfactants?
- What are the most important requirements?
  
- What are the most important markets?
  - Personal Care
  - Home Care
  - Professional
  - Other



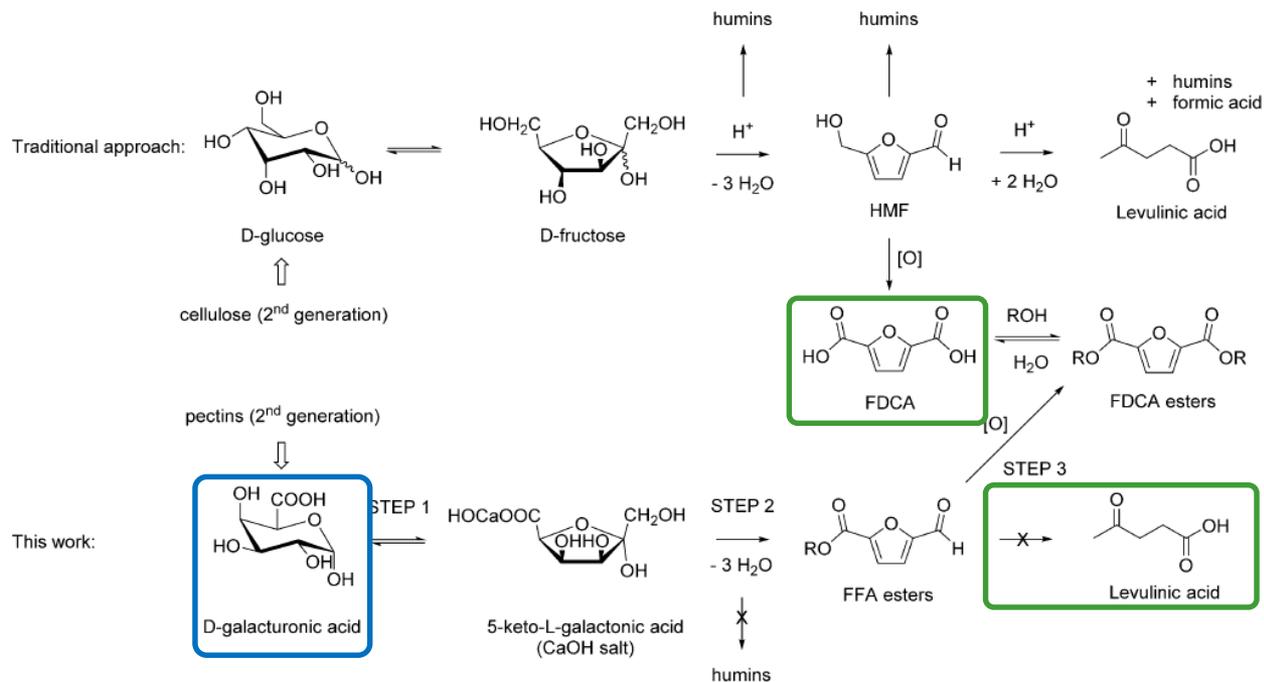
# Formyl Furoic Acid from Galacturonic acid



# From uronic acids to furans

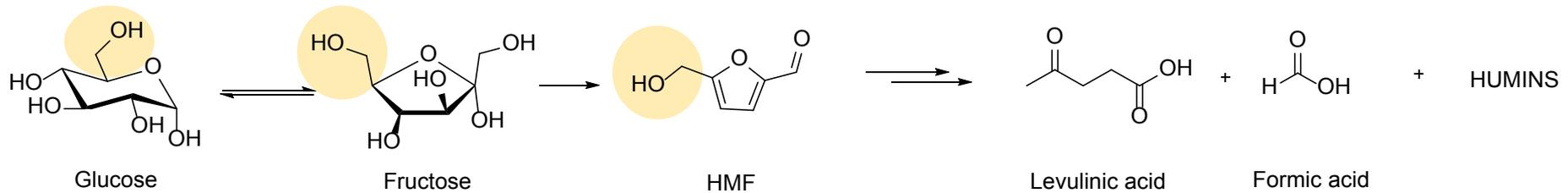
## 3-Step alternative route to FDCA from galacturonic acid

- Isomerisation to 5-keto acid
- Cyclodehydration
- Catalytic oxidation

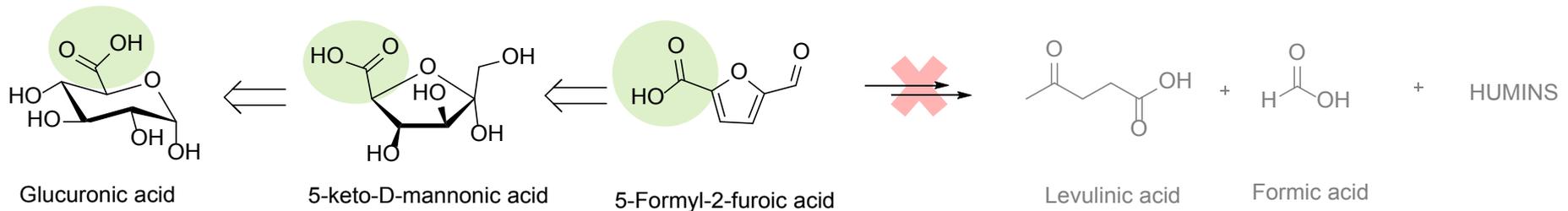


# Approach

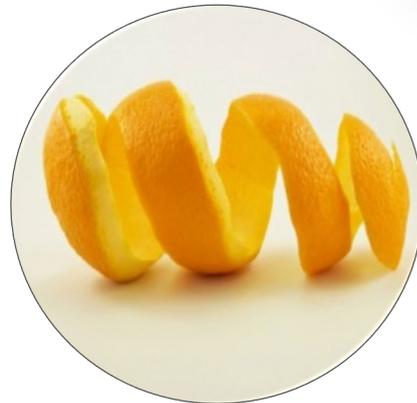
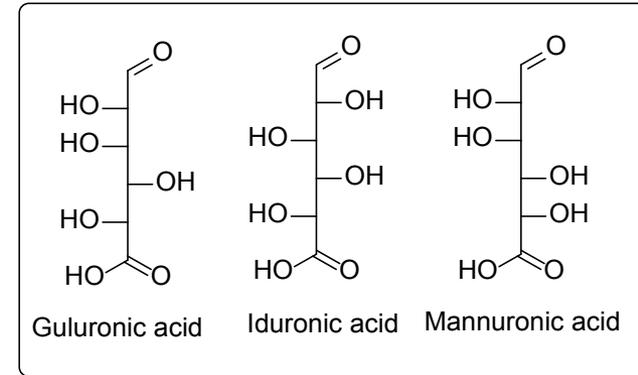
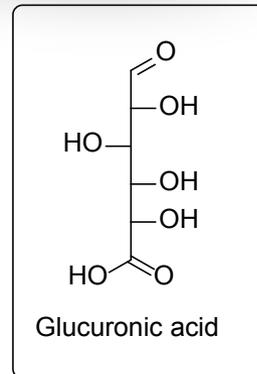
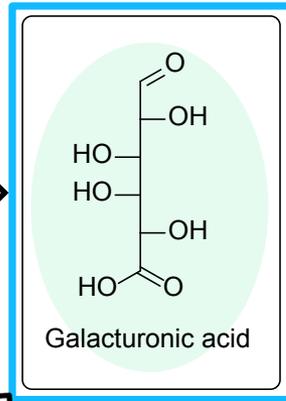
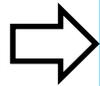
- Main problem in HMF routes: instability of HMF!



- Research question: *If we change the oxidation state of HMF-substituents, can side reactions be blocked?*



# Sources of uronic acids



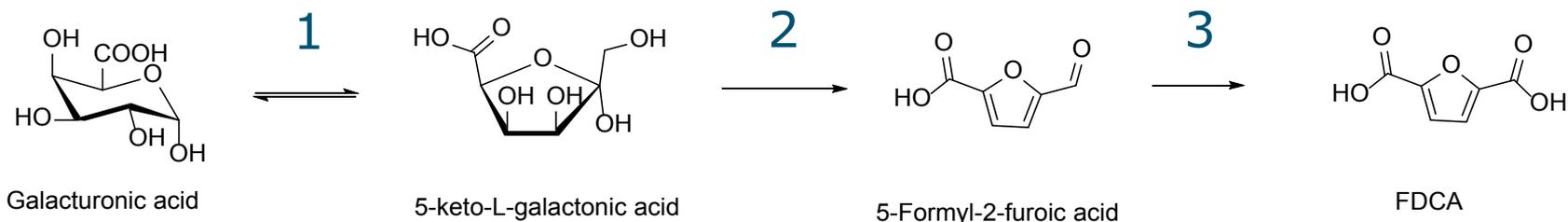
# Strategy

Three catalytic steps:

1: Alkaline isomerisation of uronic acids to 5-Keto-aldonic Acids

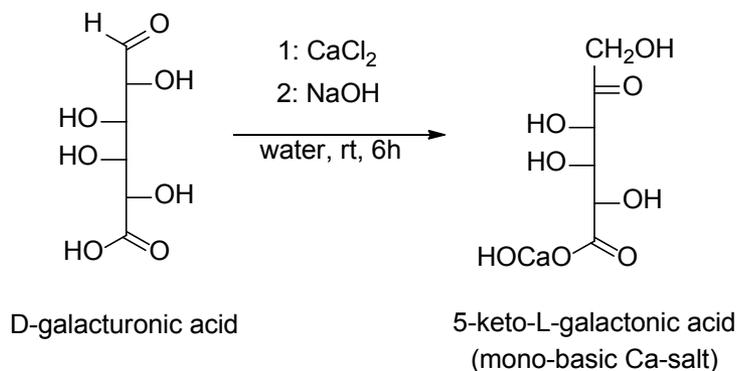
2: Acid catalysed dehydration of 5-KA to FFA

3: Au-catalysed oxidation of FFA to FDCA



# Step 1: Alkaline isomerisation

## ■ Isomerisation of galacturonic acid

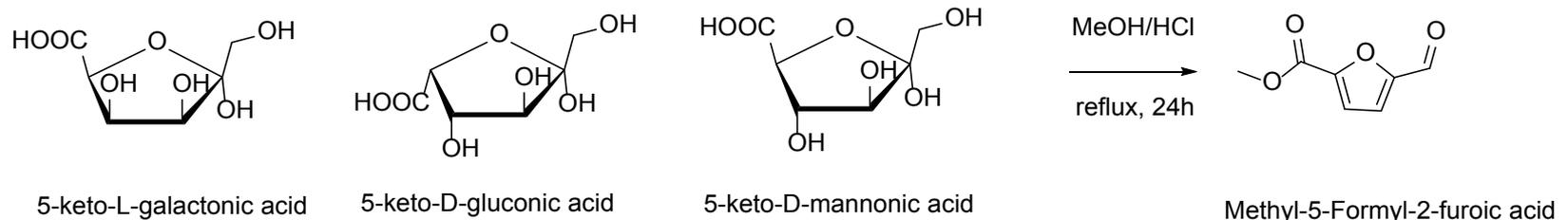


- Mild, simple and scalable procedure
- Selective precipitation of desired product
- Isolated yields: >90% (100 g scale)
- Purity confirmed by NMR, XRD and elemental analysis

# Step 2: Acid catalysed dehydration

Proof of concept via:

- Dehydration of all 3 possible 5-keto-aldonic acids



- Control experiments:

- Dehydration of uronic acids
- Dehydration of fructose

- Preliminary optimization of reaction conditions

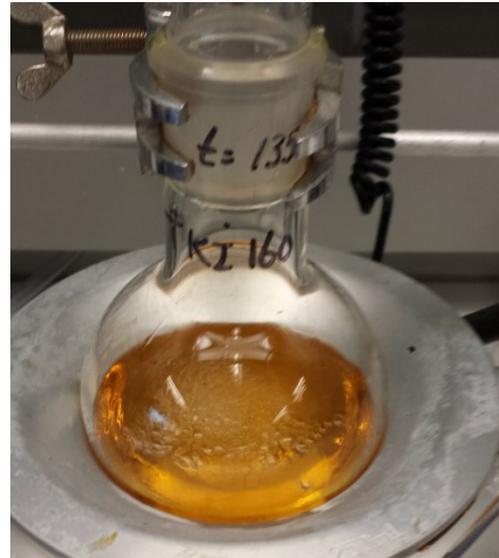
- Stability of FFA vs HMF

# Step 2: stability of Me-FFA

## Stability of Me-FFA vs HMF

### ■ Reaction conditions:

- Substrate in MeOH
- MSA catalyst
- Reflux, 24h



Me-FFA (after **24 h**)



HMF (after **30 min**)

Me-FFA: recovered in 78%

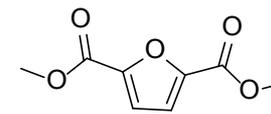
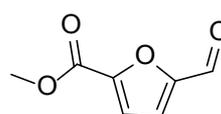
HMF: recovered in <2%

- Main products: Me-levulinate (35%) + humins

# Step 3: Au-catalysed Oxidation

Effective, green and mild

- Me-FFA was dissolved in MeOH
- Au/C (1:450 Au:substrate)
- 10 mol% NaOMe catalyst
- 5 bar oxygen pressure
- Room temp., 22 h



Methyl-5-Formyl-2-furoic acid

diMe-FDCA

- Isolated yield: 99% dimethyl-FDCA

# Conclusions

## 1: Alkaline isomerisation of uronic acids to 5-Keto-aldonic Acids

- Method proven efficient and scalable

## 2: Acid catalysed dehydration of 5-KA to FFA

- 5-ketoaldonic acids give FFA in good yield
- FFA is a more stable intermediate compared to HMF
  - No levulinic acid formation
  - Suppressed humin formation

## 3: Au-catalysed oxidation of Me-FFA to diMe-FDCA

- Quantitative yields obtained under mild condition
- Route is promising for 2<sup>nd</sup> generation FDCA production

# Discussion



- Is there a need/market for FFA based FDCA?
  - 2<sup>nd</sup> gen.
  - Vegan
  - Other



Yes



No

# Discussion



- Is there a need/market for FFA based FDCA?
  
- Higher value of FFA vs FDCA?
  
- Possible applications of FFA?
  - Formaldehyde alternative (x-linker)
  - Anionic surfactants
  - Anionic resins
  - Other





Break!



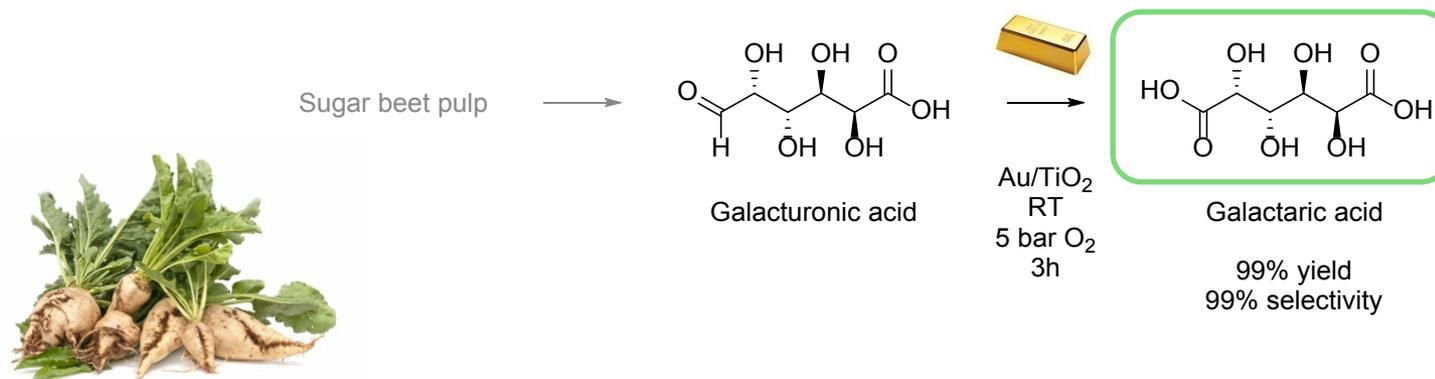
# Session 2



# Catalytic oxidation of Galacturonic acid to Galactaric acid

# Catalytic oxidation of Galacturonic acid

- First steps; catalytic oxidation over supported gold catalysts
- Extremely mild; batch, basic conditions, water



- Van der Klis; van Haveren; van Es, ChemSusChem, 2013, 6, 1640–1645; WO 2013151428



# Catalytic oxidation of Galacturonic acid



## Galacturonic acid oxidation; next step

- Conversion to continuous reaction
  - Plug-flow reactor, basic conditions, water

Criteria	Industrial window	Batch	Cont.
Selectivity	70-100 wt%	>99%	>80-94%
Productivity	0.1-10 t <sub>prod.</sub> m <sup>-3</sup> h <sup>-1</sup>	0.06	0.5-2.2
Cat. consumption	1-100 t <sub>prod.</sub> kg <sub>cat</sub> <sup>-1</sup>	~ 4200 <sup>a</sup>	~ 4200 <sup>a</sup>
Prod. conc.	3-100 wt%	~ 2-3.3	~ 2 - <10



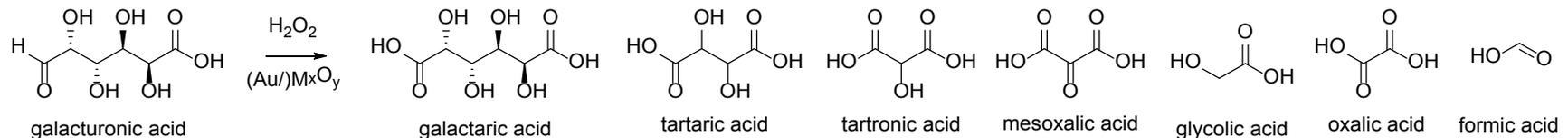
- Van der Klis; van Haveren; van Es, React. Chem. Eng., 2018, 3, 540-549.

# Catalytic oxidation of Galacturonic acid

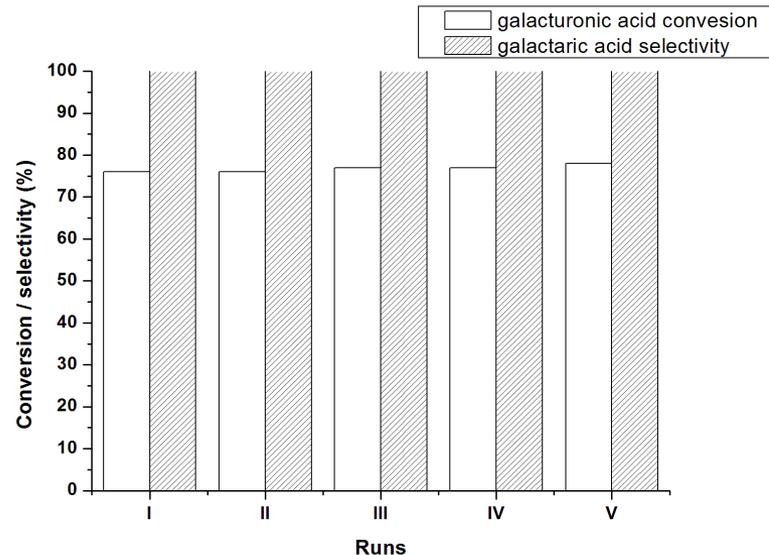


Galacturonic acid oxidation: next step; Base-free (no salt waste)

- Back to batch reaction
- Au/C catalyst; carbon support is stable at low pH (pH 2.2) compared to  $\text{Al}_2\text{O}_3$
- Conversion is slower compared to basic conditions, requires higher T; Optimal T between 333-353K
- Au/C catalyst is more selective than  $\text{Au/TiO}_2$ ; carbon support more actively destroys  $\text{H}_2\text{O}_2$ , which causes side-reactions



# Catalytic oxidation of Galacturonic acid



- Catalyst was recyclable (5 runs) without loss in conversion or selectivity: next, continuous process
- Pazhavelikkakath Purushothaman, Van der Klis; van Haveren; van Es, Green Chem., 2018,20, 2763-2774; WO 2016056907

**Base-free selective oxidation of pectin derived galacturonic acid to galactaric acid using supported gold catalysts†**

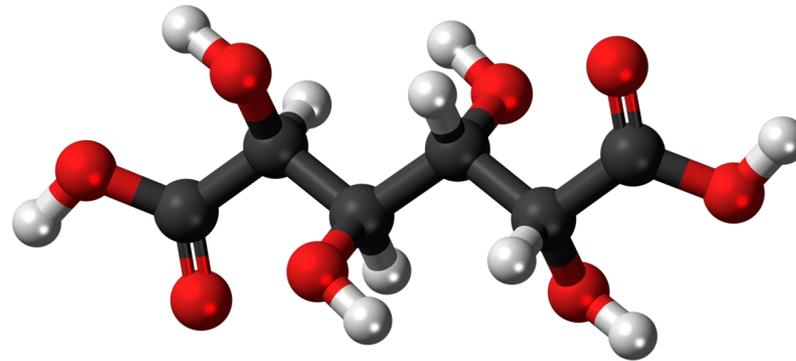
Rajeesh Kumar Pazhavelikkakath Purushothaman,<sup>a</sup> F. van der Klis,<sup>a</sup> A. E. Frissen,<sup>a</sup> J. van Haveren,<sup>a</sup> A. Mayoral,<sup>b</sup> A. van der Bent<sup>a</sup> and D. S. van Es <sup>✉</sup>

# Discussion



- Is this interesting generic technology?
- Any other carbohydrate oxidations interesting?
  - Glucose to gluconic acid
  - other?

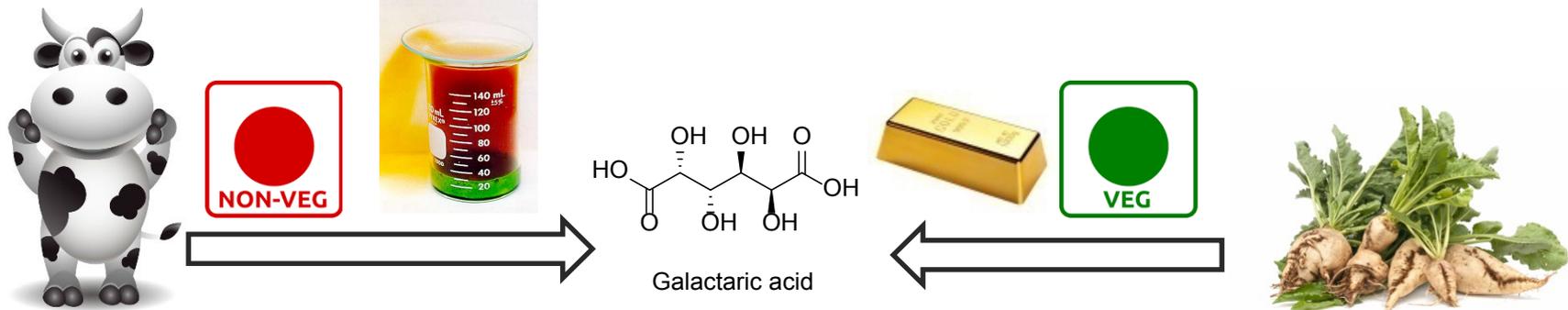




## Applications of Galactaric acid

# Applications of Galactaric acid

- Galactaric acid was discovered in 1780 by Carl Wilhelm Scheele who called it "Schleimsäure" (mucic acid / "slimy acid")
  - Obtained by nitric acid oxidation of lactose (milk sugar)
  - Lactose is still the main source for galactaric acid (non-vegan)
- Galactaric acid from sugar beet: Green & Vegan!



# Applications of Galactaric acid

## ■ Some properties:

- Low solubility in cold water (acidic  $<0.5$  g/L)
- Solubility neutralized solution  $\sim 25$  g/L
- Highly crystalline white solid (MP  $230$  °C)

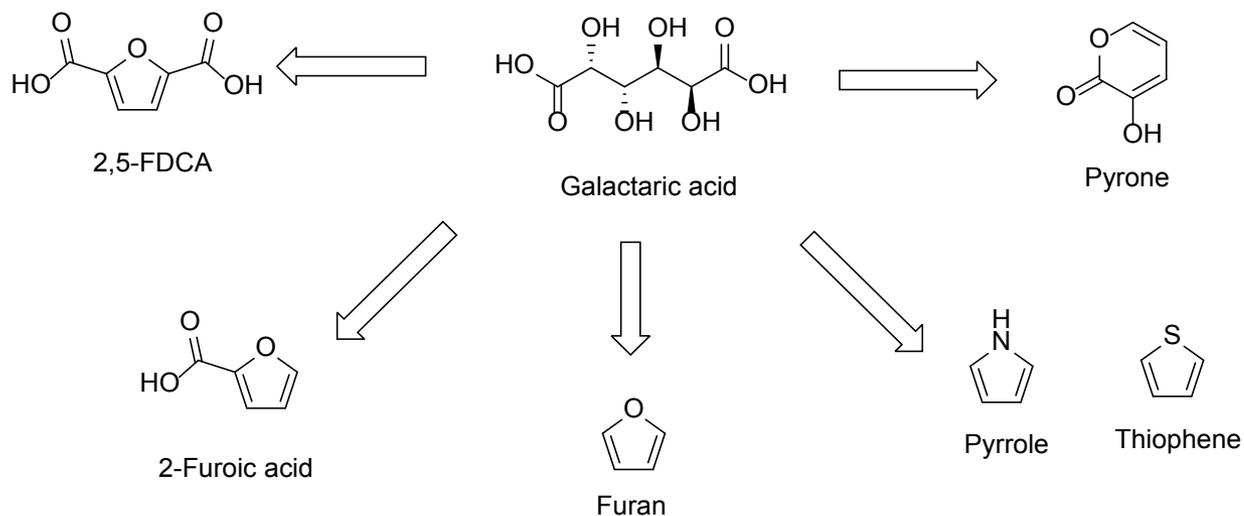
## ■ Some applications:

- Medicinal salts / cosmetics
- Replacement of tartaric acid
- Retards hardening of concrete\*
- Metal chelation (Calcium / Iron)
- Corrosion inhibition



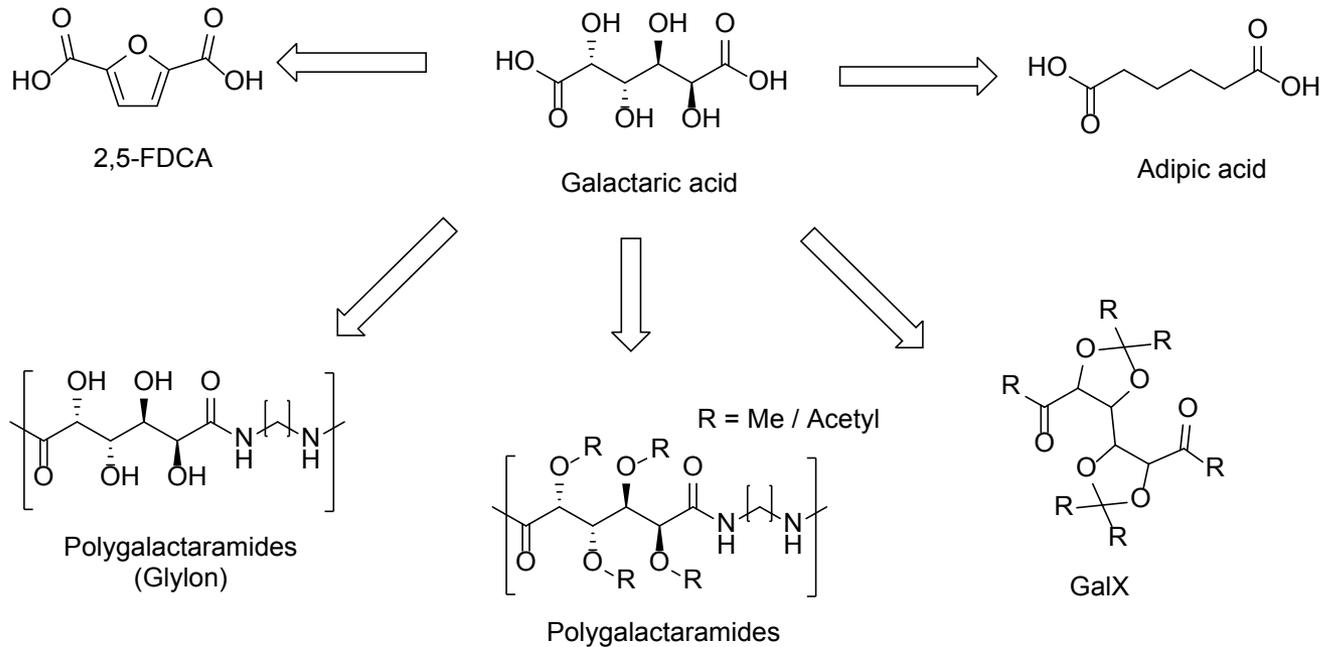
# Applications of Galactaric acid

- Galactaric acid was used in 19<sup>th</sup> century as a platform chemical to synthesize various aromatic building blocks:



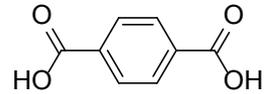
# Applications of Galactaric acid

- More recent examples as a platform chemical:



# Applications of Galactaric acid

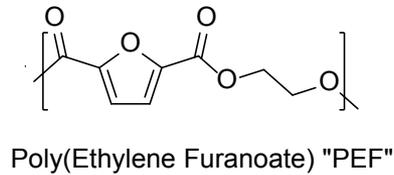
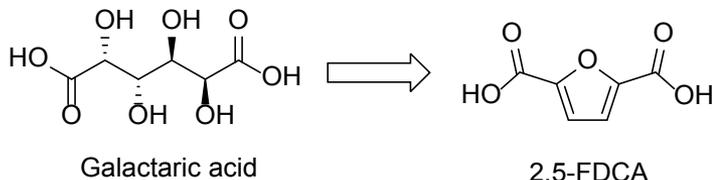
- FDCA: TA replacement (e.g. PET- to PEF-bottles)



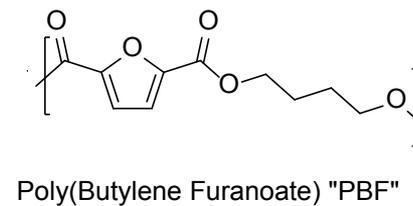
terephthalic acid  
(PET-precursor)



2<sup>nd</sup> Generation



1<sup>st</sup> Generation

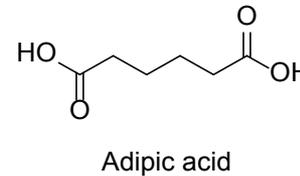
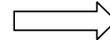
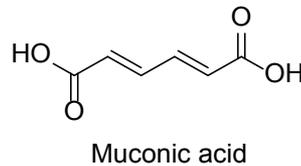
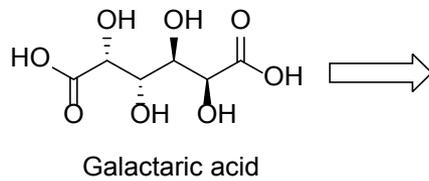


# Applications of Galactaric acid

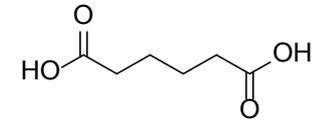
## ■ Adipic acid: Nylons



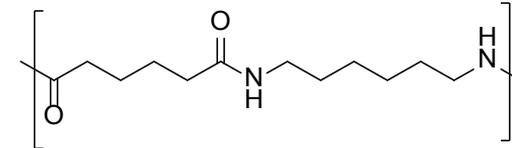
↓ 2<sup>nd</sup> Generation



↑ 1<sup>st</sup> Generation



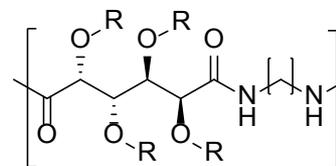
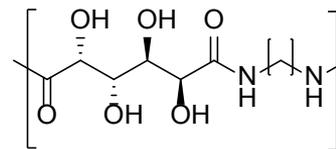
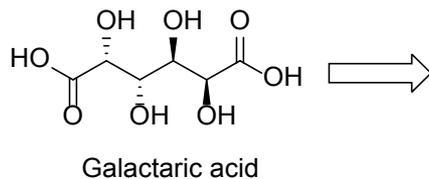
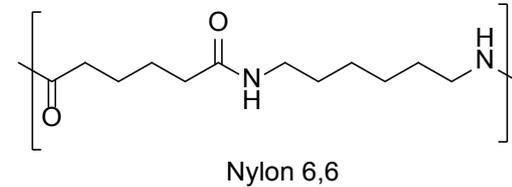
adipic acid  
(Nylon-precursor)



Nylon 6,6

# Applications of Galactaric acid

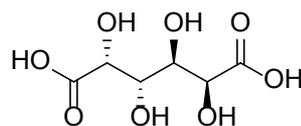
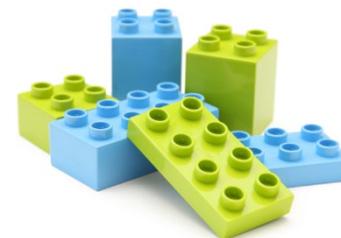
- Sugar based nylons: Glylons!
  - High MP /Decomposition
  - Water soluble / insoluble analogues
  - Film / coatings / adhesives
  - Anti-microbials



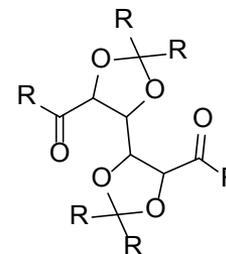
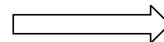
# Applications of Galactaric acid

## ■ GalX

- Building block for films / coatings / adhesives
- Cross linker



Galactaric acid



GalX



# Conclusions & Take Home Message

- Galactaric acid has a large scope for direct applications:
  - pH-control / sequestration / concrete /
  - corrosion inhibition / cosmetics
  
- Or could serve as platform chemical for:
  - Plastics (PEF-bottles)
  - Coatings (GalX)
  - Nylons (Adipic acid / Glylons)

# Discussion



## ■ Other applications of Galactaric acid

- Generic sugar/aldaric acid
  - Tartaric acid
  - Gluconic acid
  - Citric acid
- Unique properties



## ■ Which markets not already discussed

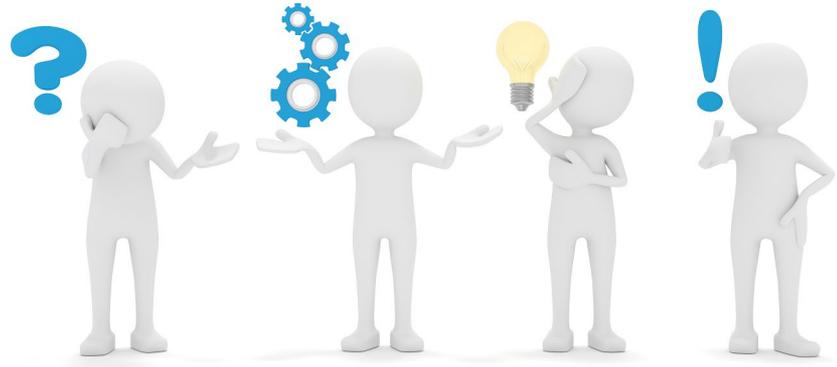


## Wrap-up



# Wrap-up

- Summary
- Conclusions
- Feedback
- AOB



# Acknowledgements

WFBR:

Linda Gootjes

Rajeesh Pazhavelikkakath

Jacco van Haveren

Royal Cosun:

Robert Lazeroms

Harry Raaijmakers

Adeline Ranoux

Gerald van Engelen



TKI Agri&Food



This project has received funding from the Bio-Based Industries Joint Undertaking under the European Union's Horizon 2020 research and innovation programme under grant agreement No 669105.

# Thank you!

