Karlsruhe Institute of Technology

Platform Molecules II: Synthesis Strategies and Case Studies

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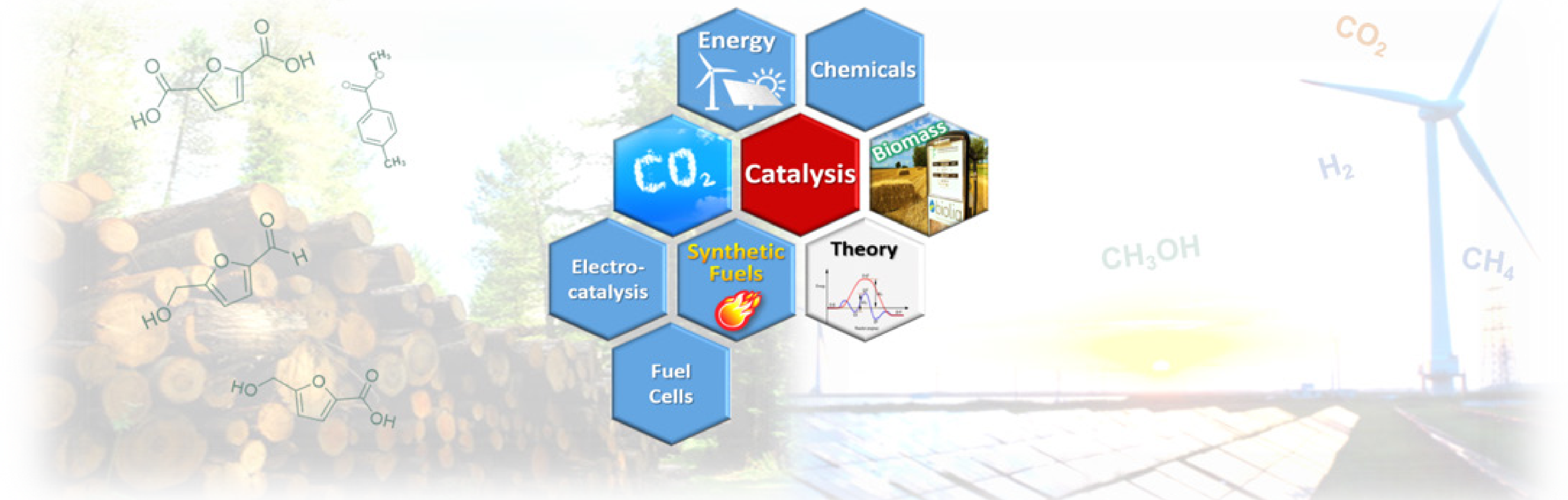
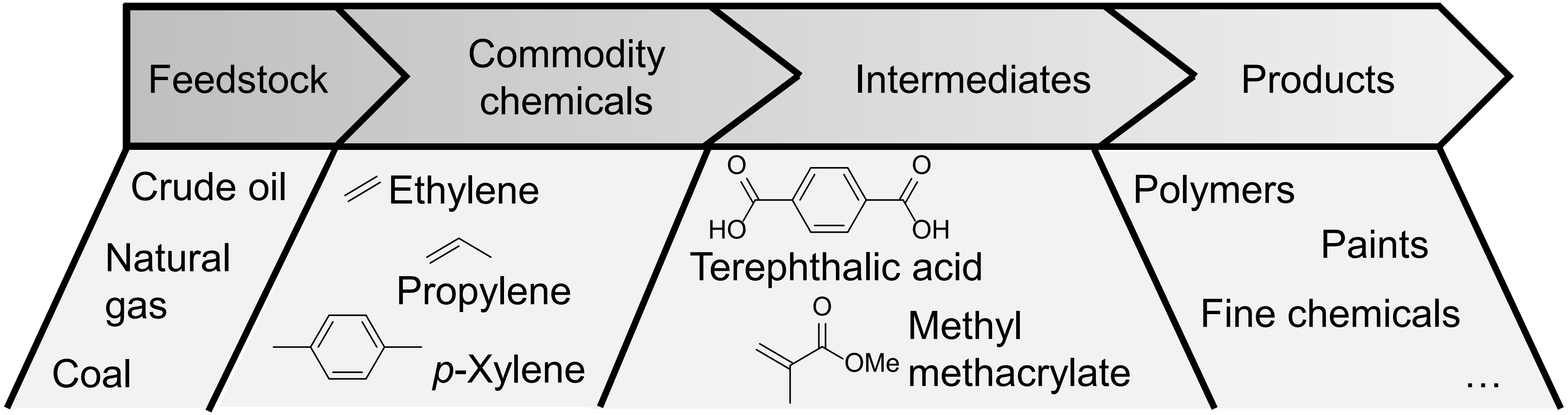


Introduction – Why platform molecules?

Simplified current value chain of the chemical industry



- The production of chemicals is primarily dependent on fossil resources
- Fossil resources are valorized and diversified along production chains

- What are the advantages and disadvantages of this value chain?

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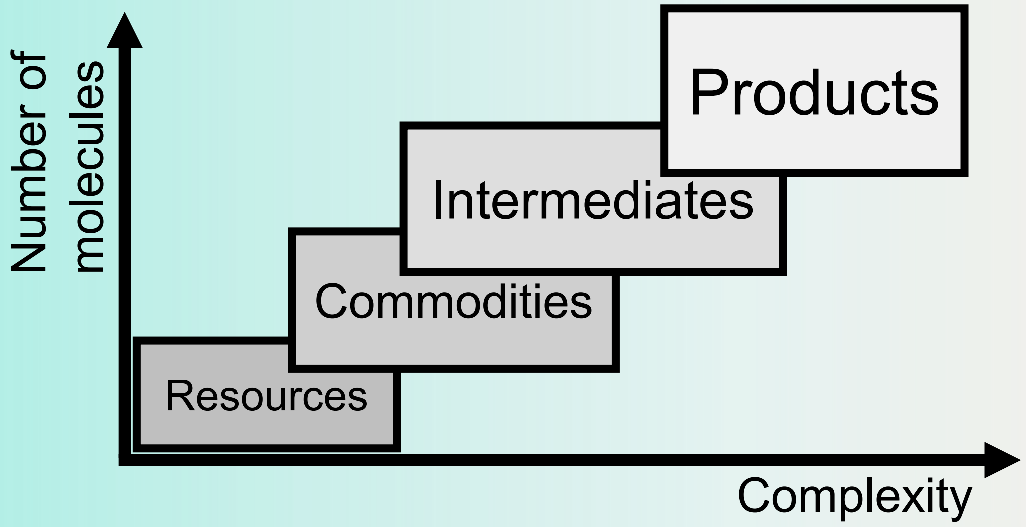
Introduction – Why platform molecules?

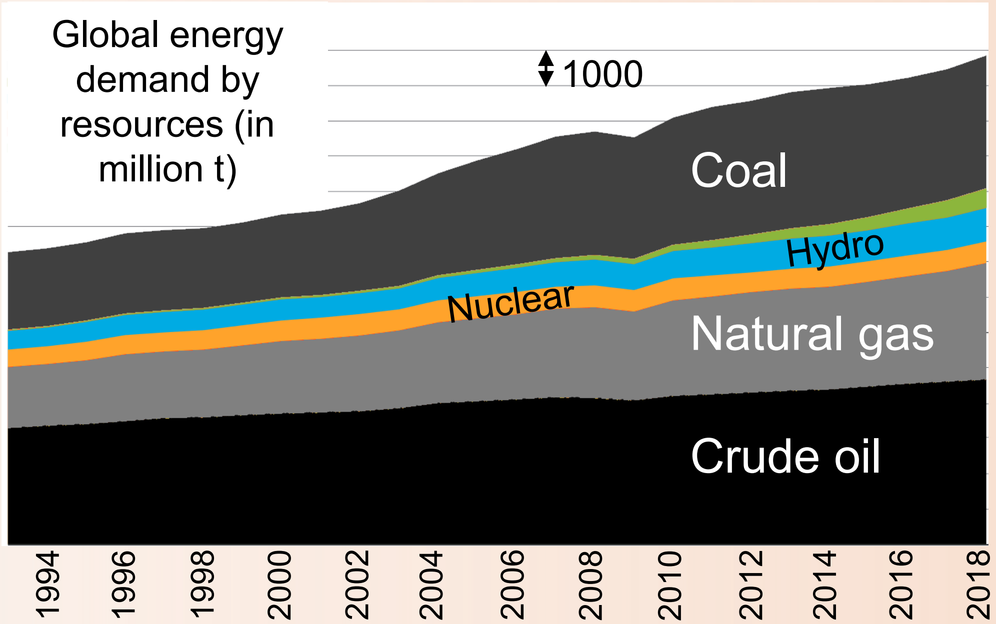
- What are the advantages and disadvantages of this value chain?

Advantages



- Production of numerous different products from a small number of molecules
- Well-established processes
- Historically cheap resources

Disadvantages

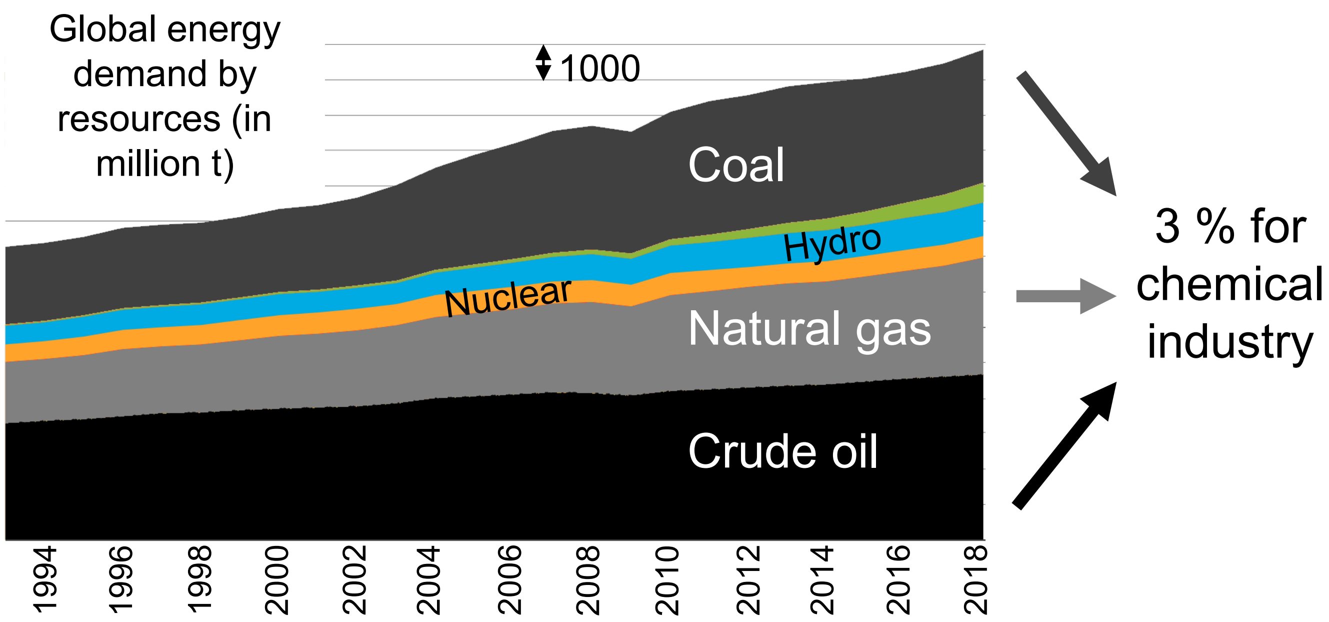


- The same resources are used in energy and transportation sector → strong and growing demand
- Finite resources

BP Statistical Review of World Energy 2018, https://www.bp.com/content/dam/bp/en/corporate/pdf/energy-economics/statistical-review/bp-stats-review-2019-full-report.pdf 21.11.19

Introduction – Why platform molecules?

- How does that affect the chemical industry?



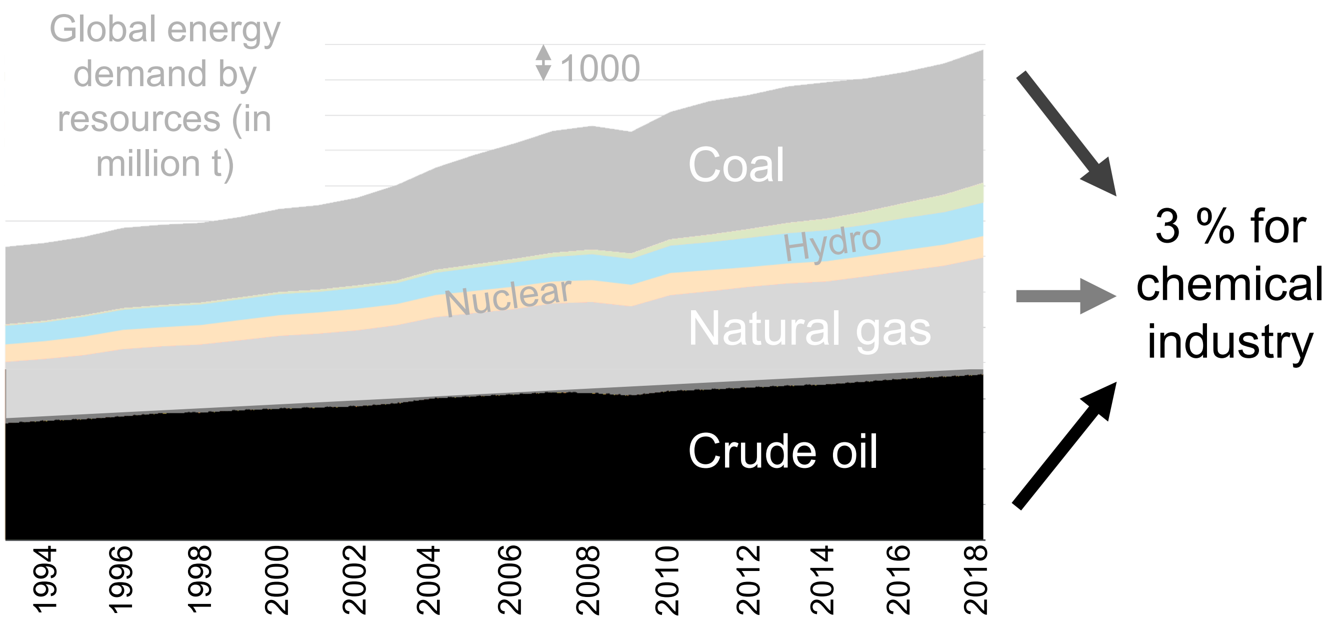
- The same resources are used in energy and transportation sector → strong and growing demand
- Finite resources → depletion

→ Increasing price and finally depletion

BP Statistical Review of World Energy 2018, https://www.bp.com/content/dam/bp/en/corporate/pdf/energy-economics/statistical-review/bp-stats-review-2019-full-report.pdf 21.11.19

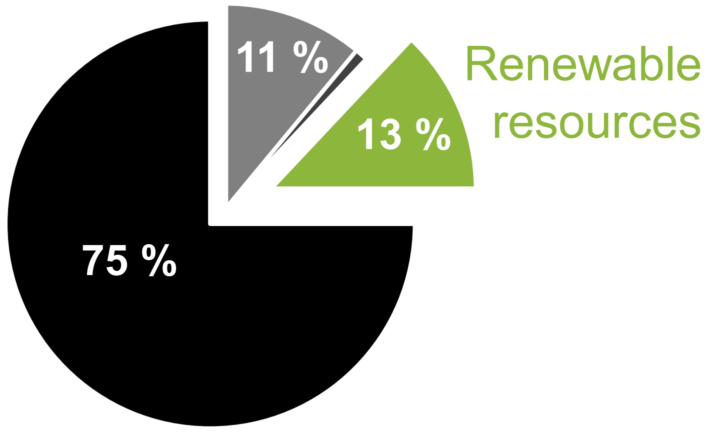
Introduction – Why platform molecules?

- How does that affect the chemical industry?



- Example: crude oil
  - 92 % usage for the production of chemicals

Raw material base of the German chemical industry



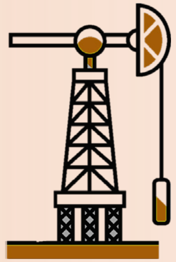
Rohstoffbasis der chemischen Industrie, VCI, 2019, 31.03.2020

Although the chemical industry only consumes a small share of the total fossil resources, the production of organic chemicals is heavily dependent on them as it is primarily covered by these resources.

BP Statistical Review of World Energy 2018, https://www.bp.com/content/dam/bp/en/corporate/pdf/energy-economics/statistical-review/bp-stats-review-2019-full-report.pdf 21.11.19

Introduction – Why platform molecules?

- Possible solution: change the raw material base of the chemical industry



Petrochemicals

- Scarce resource (−)
- CO_2 pollution (−)
- Strategic and political weapon (−)
- Low security of supply (−)
- Cheap (+)

Biomass-derived chemicals

- Renewable (+)
- CO_2 neutral (+)
- Can be grown and exploited anywhere (+)
- High security of supply (+)
- Expensive (still) (−)

Introduction – Why platform molecules?

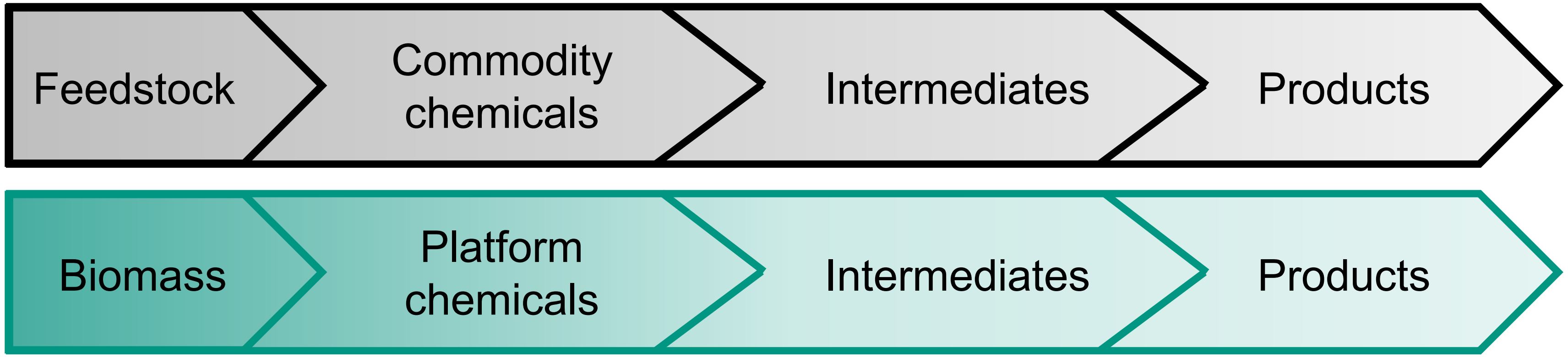
- Important biomass feedstocks: Vegetable oil, algae, ...

1. **Prevention**. It is better to prevent waste than to treat or clean up waste after it is formed.
2. **Atom Economy**. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. **Less Hazardous Chemical Synthesis**. Whenever practicable, synthetic methodologies should be designed to use and generate substances that pose little or no toxicity to human health and the environment.
4. **Designing Safer Chemicals**. Chemical products should be designed to preserve efficacy of the function while reducing toxicity.
5. **Safer Solvents and Auxiliaries**. The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous.
6. **Design for Energy Efficiency**. Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
7. **Use of Renewable Feedstocks**. A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
8. **Reduce Derivatives**. Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
9. **Catalysis**. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. **Design for Degradation**. Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
11. **Real-Time Analysis for Pollution Prevention**. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. **Inherently Safer Chemistry for Accident Prevention**. Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

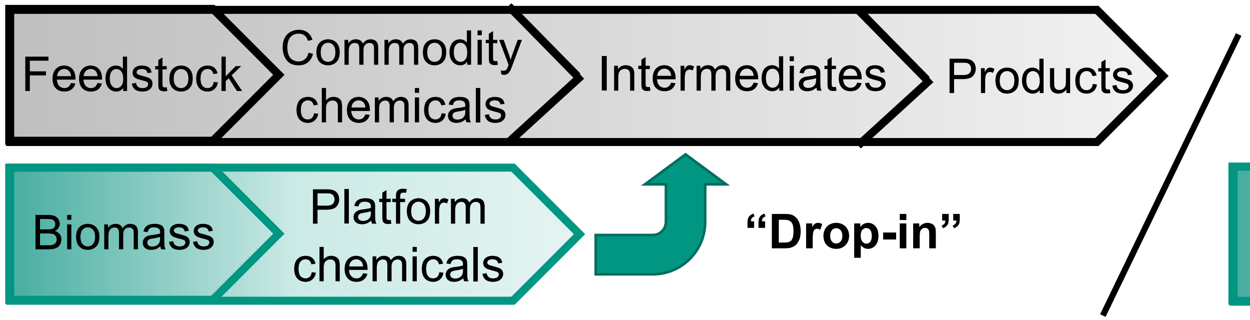
P. Anastas and N. Eghbali *Chem. Soc. Rev.*, **2010**, *39*, 301–312.

Introduction – Establish platform molecules

- Establishment of new chemical value chains



- Two essential strategies can be distinguished:



“Emerging”: establish new parallel value chains

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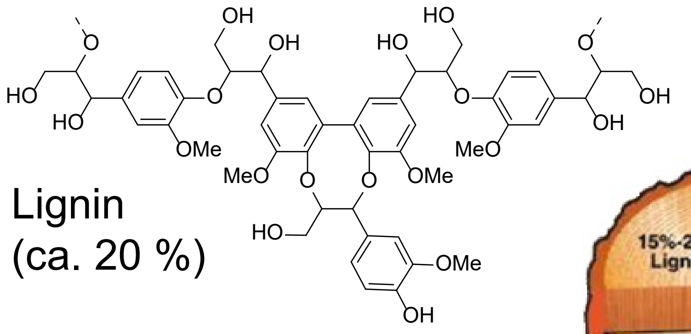
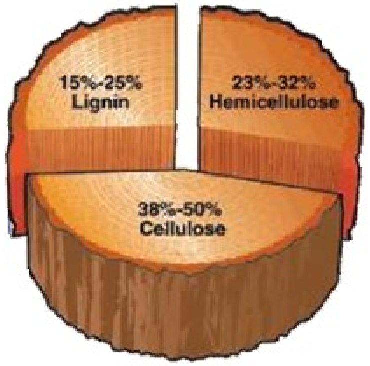
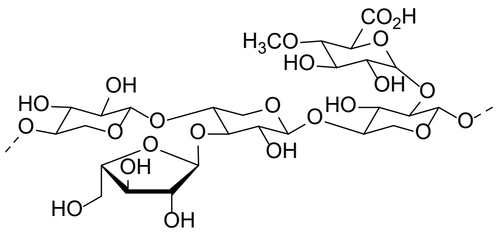
Introduction – Establish platform molecules

- Important biomass feedstocks: Vegetable oil, algae, ...
- Among the most promising is <u>lignocellulose</u>



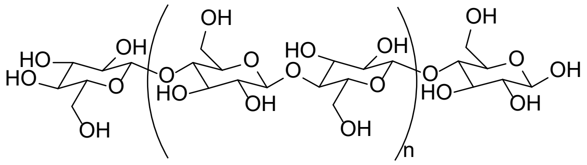
Lignin
(ca. 20 %)





Hemicellulose
(ca. 25 %)

- Different promising conversion strategies (see 1st platform chemicals lecture)
- The production and further conversion of sugars to platform chemicals is particularly promising



Cellulose (ca. 40 %)

R. Musule *et. al. J. Wood Sci.*, **2016**, *62*, 537

Introduction – Biorefineries

- Biomass has more complex structures as compared to currently used fossil (hydro-)carbon feedstock
  - Important:

$$\text{H/C ratio} = \frac{n(H)-2n(O)}{n(C)}$$

- Biomass is ideally suitable for the production of chemicals rather than transportation fuels.
- Biomass has been used historically for the production of chemicals (DuPont)

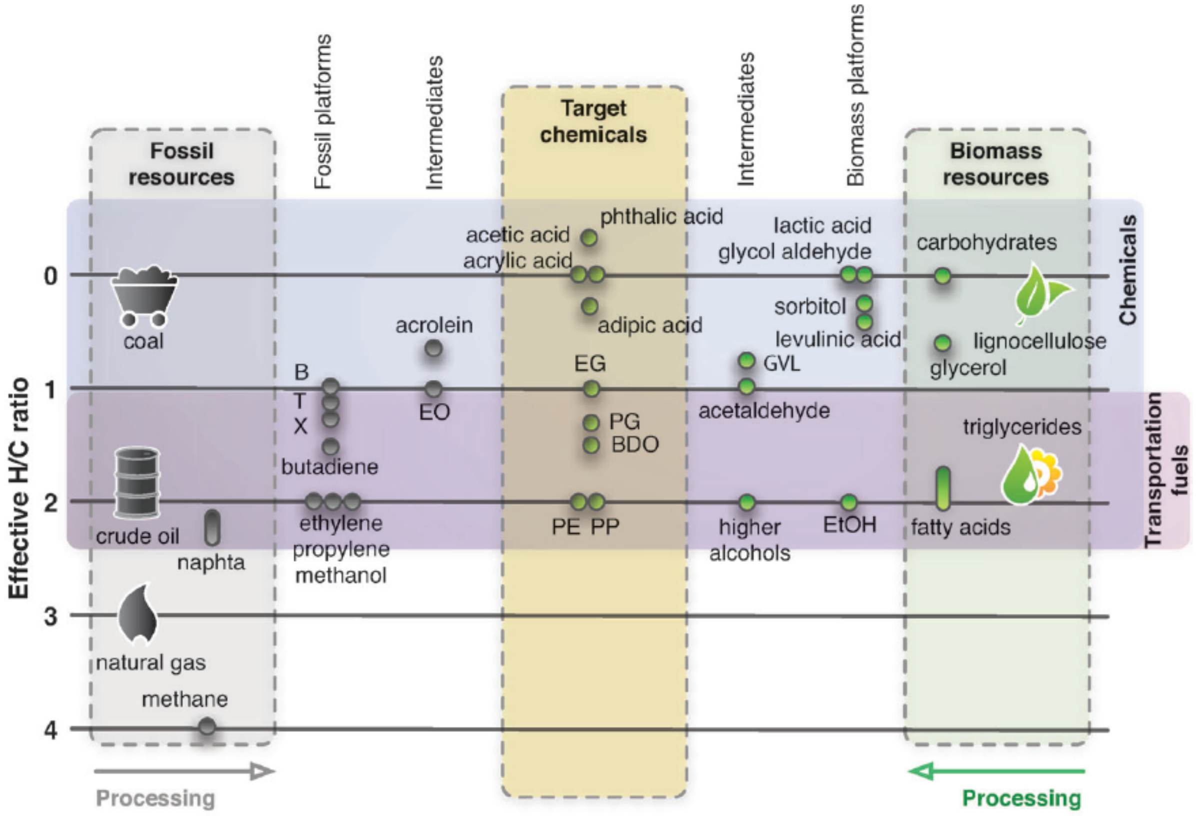


Figure 2. Effective H/C ratio map of current and future bulk chemicals as well as feedstocks with a qualitative indication of the degree of processing. B = benzene, BDO = 1,4-butanediol, EG = ethylene glycol, EO = ethylene oxide, GVL = γ-valerolactone, PE = polyethylene, PG = propylene glycol, PP = polypropylene, T = toluene, X = xylenes.

Vennestrom *et al*., *Angew. Chem. Int. Ed*. **2011**, *50*, 10502 – 10509.

Introduction – Biorefineries

- Biomass has more complex structures as compared to currently used fossil (hydro-)carbon feedstock
  - Important: H/C ratio
- Different strategies for biomass conversion in so-called biorefineries

Biorefinery
- 1st generation – Edible crops
- 2nd generation – Residues and inedible crops
- 3rd generation – Residues, inedible crops, algae, CO_2

- Examples for biorefineries:

Vegetable oil biorefinery

Sugar biorefinery

Lignocellulose biorefinery

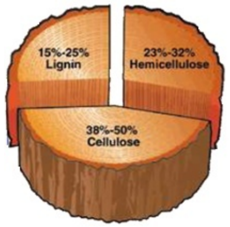
Biogas refinery

Synthesis gas biorefinery

Exercise: To which biorefinery generation can these concepts be assigned?

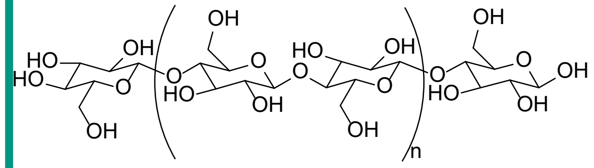
The lignocellulose biorefinery

- Main task: partially fragment lignocellulose into its major constituents

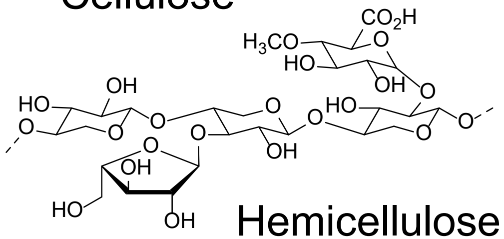


Exercise: In which industry has lignocellulose fragmentation been carried out on a large scale for a long time?

- Further fragmentation and use of lignin see 1st platform chemicals lecture
- Hydrolysis of sugar-containing parts for the production of sugars and platform chemicals:



Cellulose



Hemicellulose

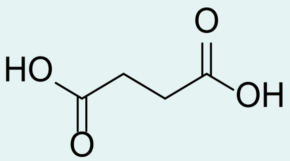
Carbohydrates → Platform molecules

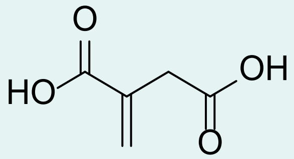
Exercise: What are unique features of the lignocellulose refinery in terms of feedstock and product scope?

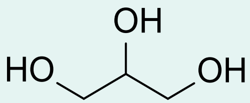
R. Musule *et. al. J. Wood Sci.*, **2016**, *62*, 537

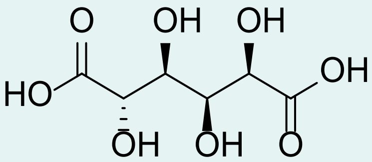
Platform chemicals from cellulosic biomass

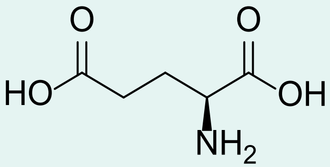
- Promising candidates identified by the US Department of Energy in 2004

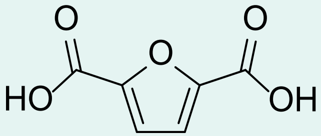

Succinic acid

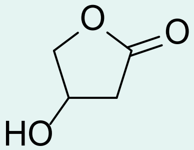

Itaconic acid

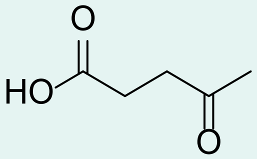

Glycerol

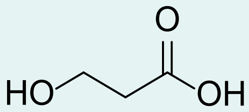

Glucaric acid

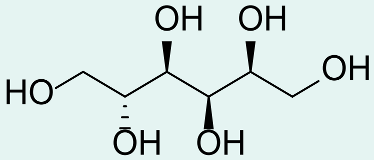

Glutamic acid

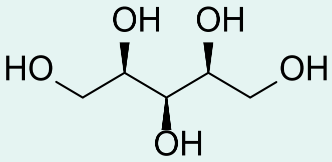

2,5-Furandicarboxylic acid

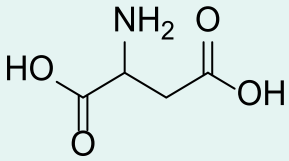

3-Hydroxy-butyrolactone


Levulinic acid


3-Hydroxypropionic acid


Sorbitol

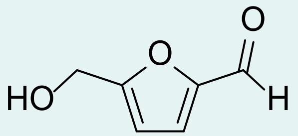

Xylitol


Aspartic acid

T. Werpy *et al.*, *Results of Screening for Potential Candidates from Sugars and Synthesis Gas*; U.S. Department of Energy: Washington, DC, **2004**.

Platform chemicals from cellulosic biomass

- Promising candidates identified by the US Department of Energy in 2004
- In a revised version, 5-(Hydroxymethyl)furfural (HMF) was added to the list



5-(Hydroxymethyl) furfural

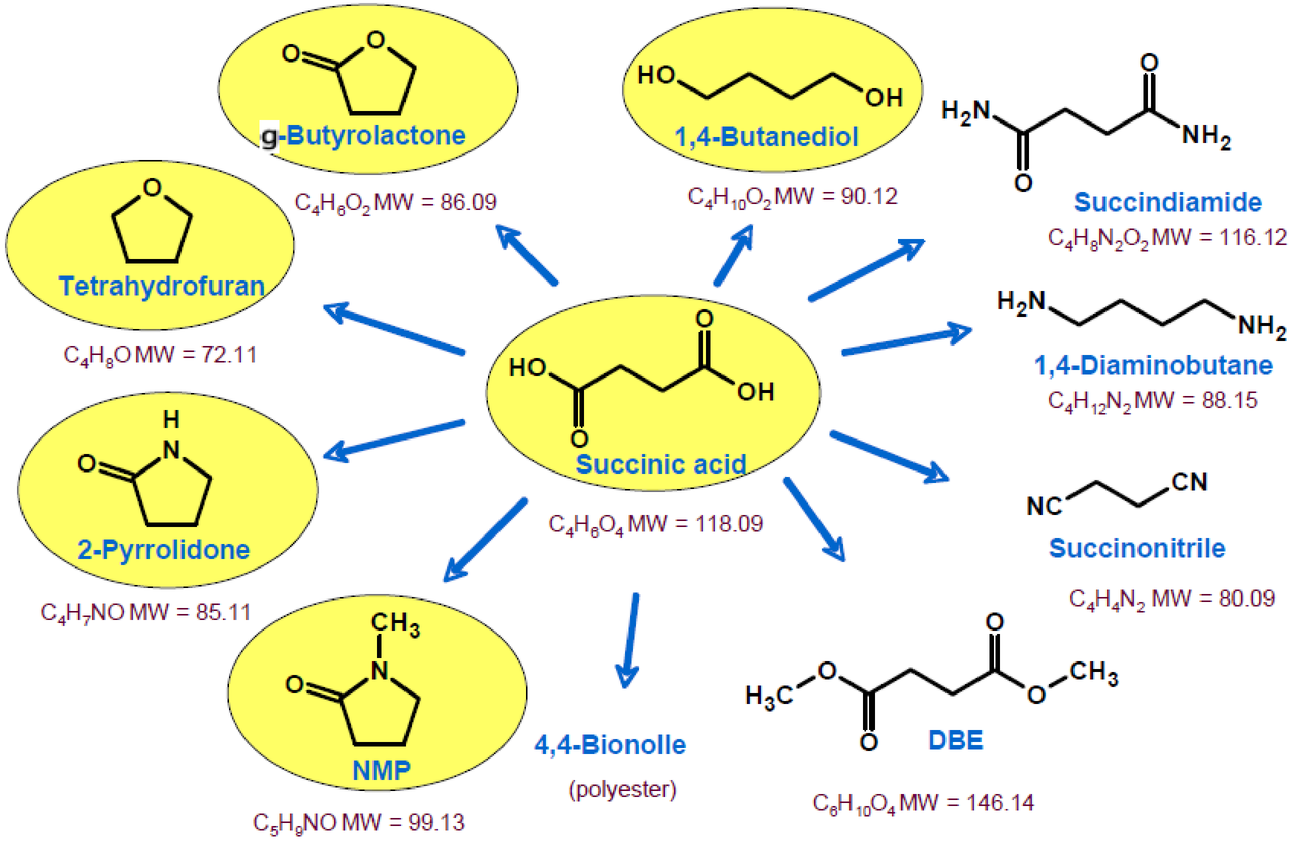
Table 2 Criteria used in evaluating biobased product opportunities from carbohydrates

1. ***The compound or technology has received significant attention in the literature.*** A high level of reported research identifies both broad technology areas and structures of importance to the biorefinery.
2. ***The compound illustrates a broad technology applicable to multiple products.*** As in the petrochemical industry, the most valuable technologies are those that can be adapted to the production of several different structures.
3. ***The technology provides direct substitutes for existing petrochemicals.*** Products recognized by the chemical industry provide a valuable interface with existing infrastructure and utility.
4. ***The technology is applicable to high volume products.*** Conversion processes leading to high volume functional equivalents or utility within key industrial segments will have particular impact.
5. ***A compound exhibits strong potential as a platform.*** Compounds that serve as starting materials for the production of derivatives offer important flexibility and breadth to the biorefinery.
6. ***Scaleup of the product or a technology to pilot, demo, or full scale is underway.*** The impact of a biobased product and the technology for its production is greatly enhanced upon scaleup.
7. ***The biobased compound is an existing commercial product, prepared at intermediate or commodity levels.*** Research leading to production improvements or new uses for existing biobased chemicals improves their utility.
8. ***The compound may serve as a primary building block of the biorefinery.*** The petrochemical refinery is built on a small number of initial building blocks: olefins, BTX, methane, CO. Those compounds that are able to serve an analogous role in the biorefinery will be of high importance.
9. ***Commercial production of the compound from renewable carbon is well established.*** The potential utility of a given compound is improved if its manufacturing process is already recognized within the industry.

J. J. Bozell *et al.*, *Green Chem.*, **2010**, *12*, 539–554.

Platform chemicals from cellulosic biomass

Building Blocks
1,4-diacids (succinic, fumaric and malic)
2,5-furandicarboxylic acid
3-hydroxy propionic acid
aspartic acid
glucaric acid
glutamic acid
itaconic acid
levulinic acid
3-hydroxybutyrolactone
glycerol
sorbitol
xylitol, arabinitol



Product Families:

- Reduction
  - THF, BDO, GBL
  - solvents, fibers
- Reductive amination
  - Pyrrolidones
  - solvents, water soluble polymers
- Direct polymerization
  - Polymers
  - fibers

T. Werpy *et al.*, *Results of Screening for Potential Candidates from Sugars and Synthesis Gas*; U.S. Department of Energy: Washington, DC, **2004**.

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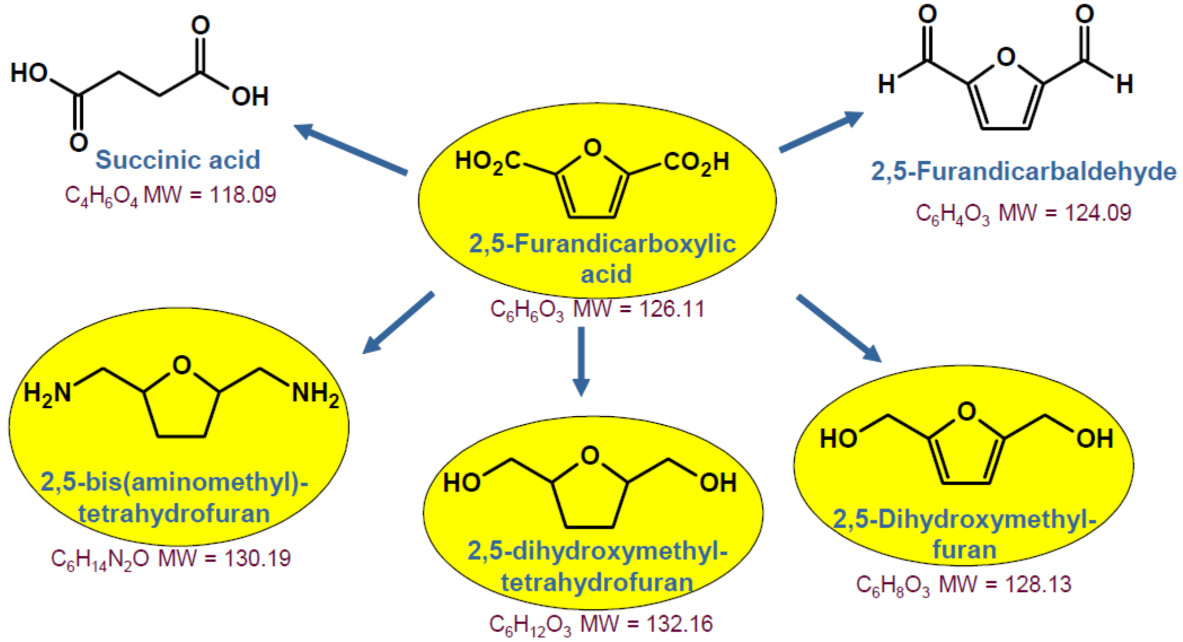

Product Families:

- Reduction/reductive amination
  - Diols, diamines
  - New polyesters and polyamides
- Reduction
  - Levulinic acid and succinic acid
- Direct polymerization
  - Polyesters (mostly PEF, bottles, containers, …)

T. Werpy *et al.*, *Results of Screening for Potential Candidates from Sugars and Synthesis Gas*; U.S. Department of Energy: Washington, DC, **2004**.

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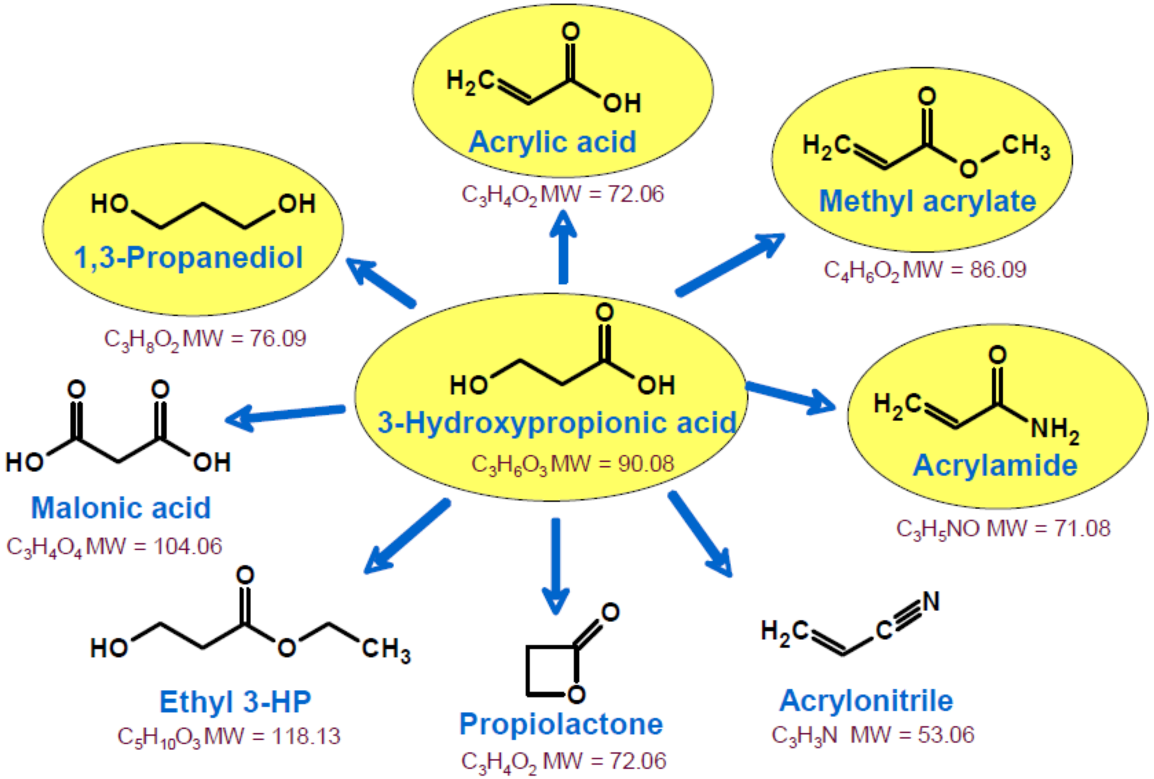

Product Families:

- Reduction
  - 1,3-Propanediol
  - Fibers (SORONA®, DuPont)
- Dehydration
  - Acrylate family
  - Contact lenses, super absorbers, …

T. Werpy *et al.*, *Results of Screening for Potential Candidates from Sugars and Synthesis Gas*; U.S. Department of Energy: Washington, DC, **2004**.

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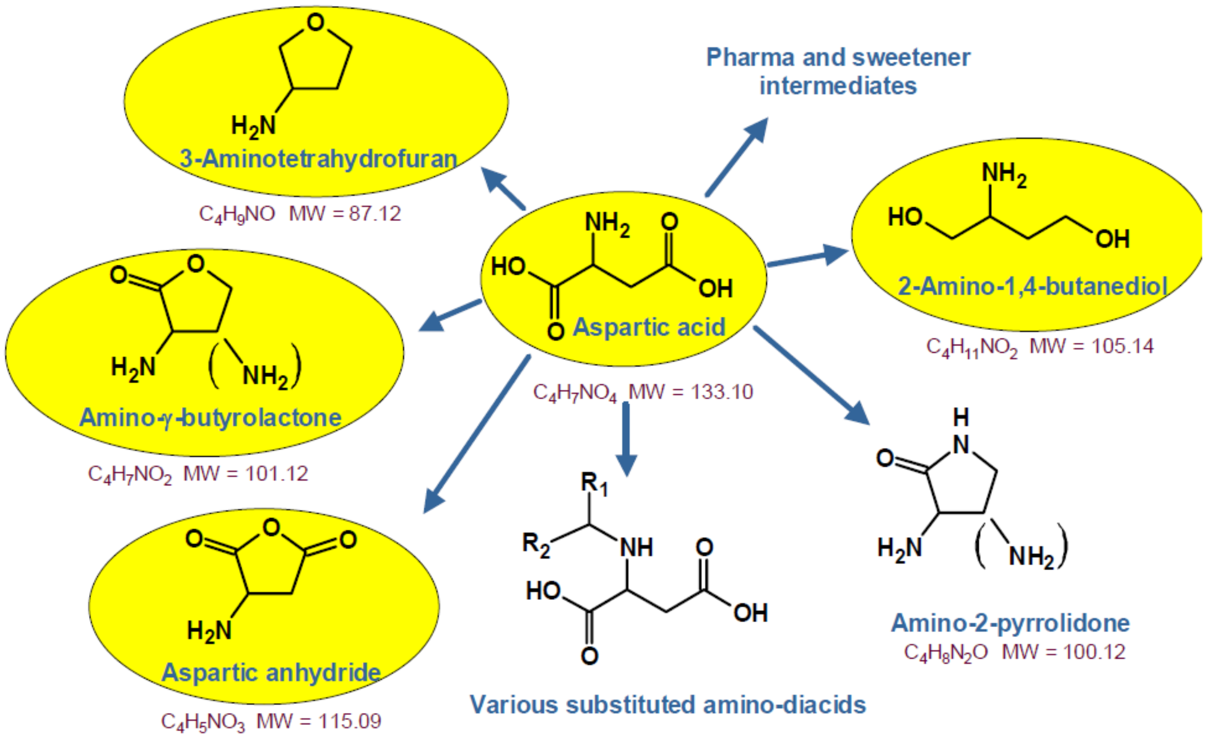

Product Families:

- Reduction
  - Amino-THF, -butanediol
  - Amino analogs of 1,4-dicarboxylic acids
- Dehydration
  - Aspartic anhydride
  - New field

T. Werpy *et al.*, *Results of Screening for Potential Candidates from Sugars and Synthesis Gas*; U.S. Department of Energy: Washington, DC, **2004**.

Platform chemicals from cellulosic biomass

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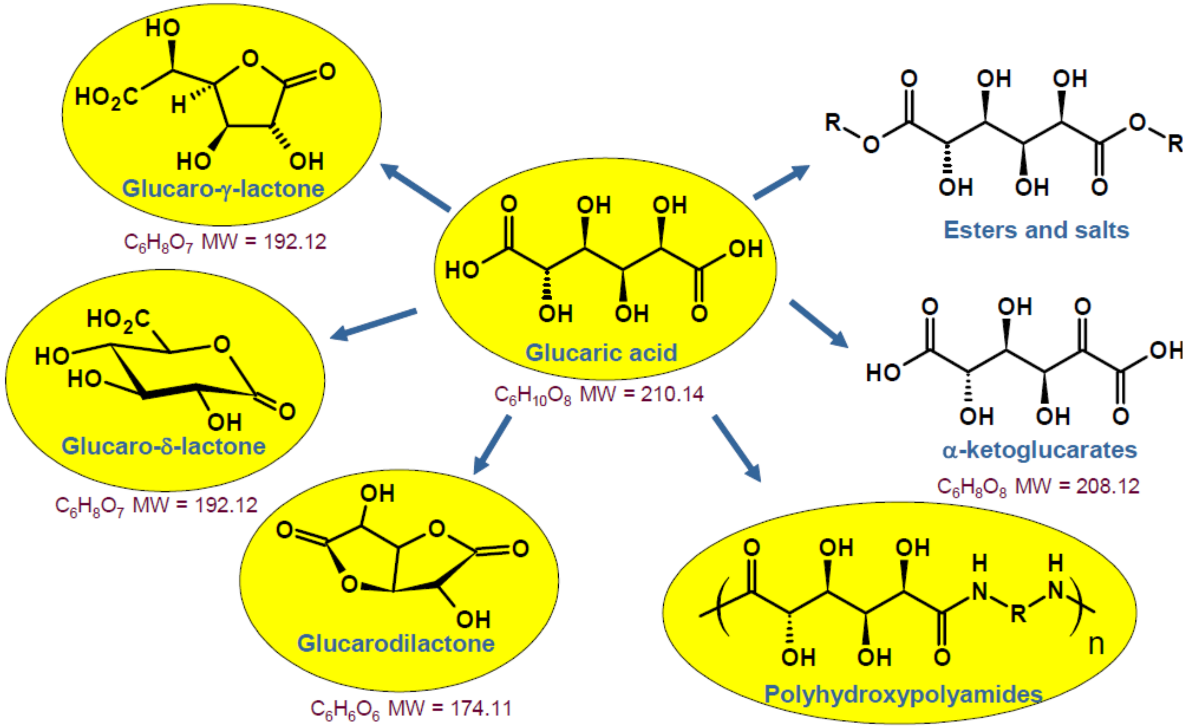

Product Families:

- Dehydration
  - Lactones
  - Applications: solvents
- Direct polymerization
  - Polyglucaric acids and amides
  - Applications: nylons, polymers with new properties

T. Werpy *et al., Results of Screening for Potential Candidates from Sugars and Synthesis Gas*; U.S. Department of Energy: Washington, DC, **2004**.

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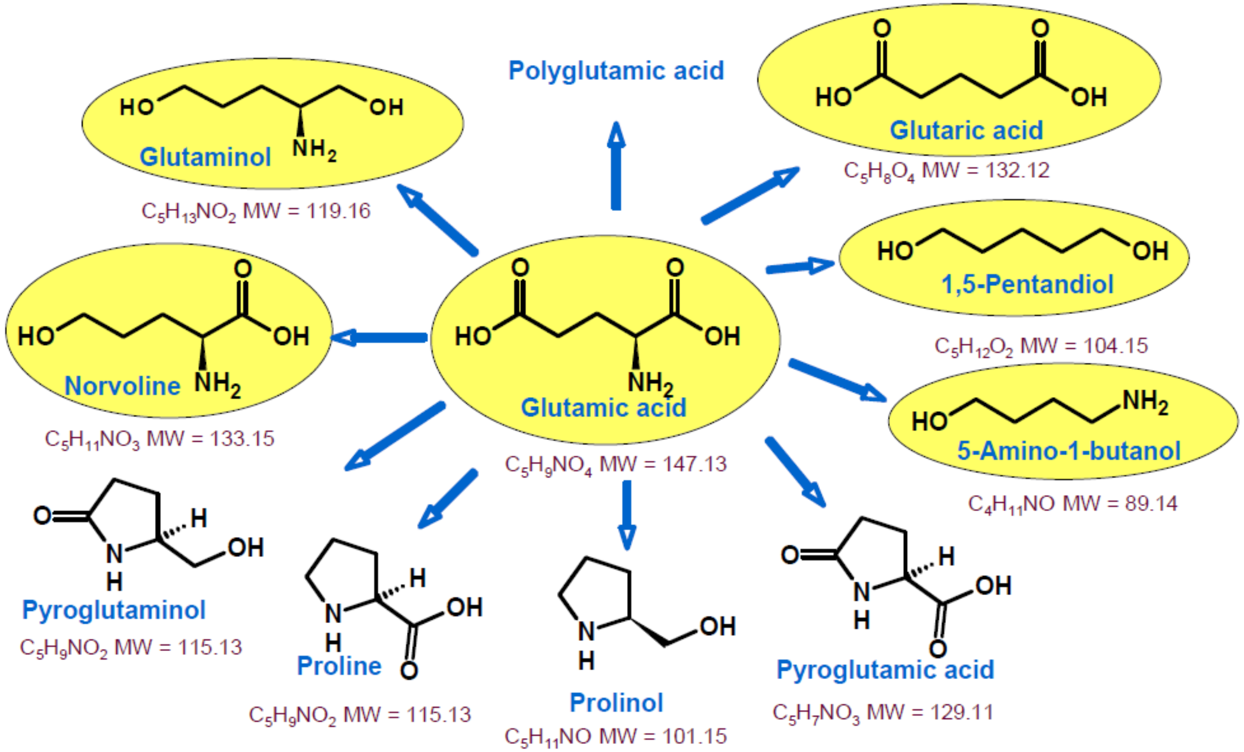

Product Families:

- Reduction
  - Diols, aminodiols
  - Monomers for polyesters and polyamides

T. Werpy *et al.*, *Results of Screening for Potential Candidates from Sugars and Synthesis Gas*; U.S. Department of Energy: Washington, DC, **2004**.

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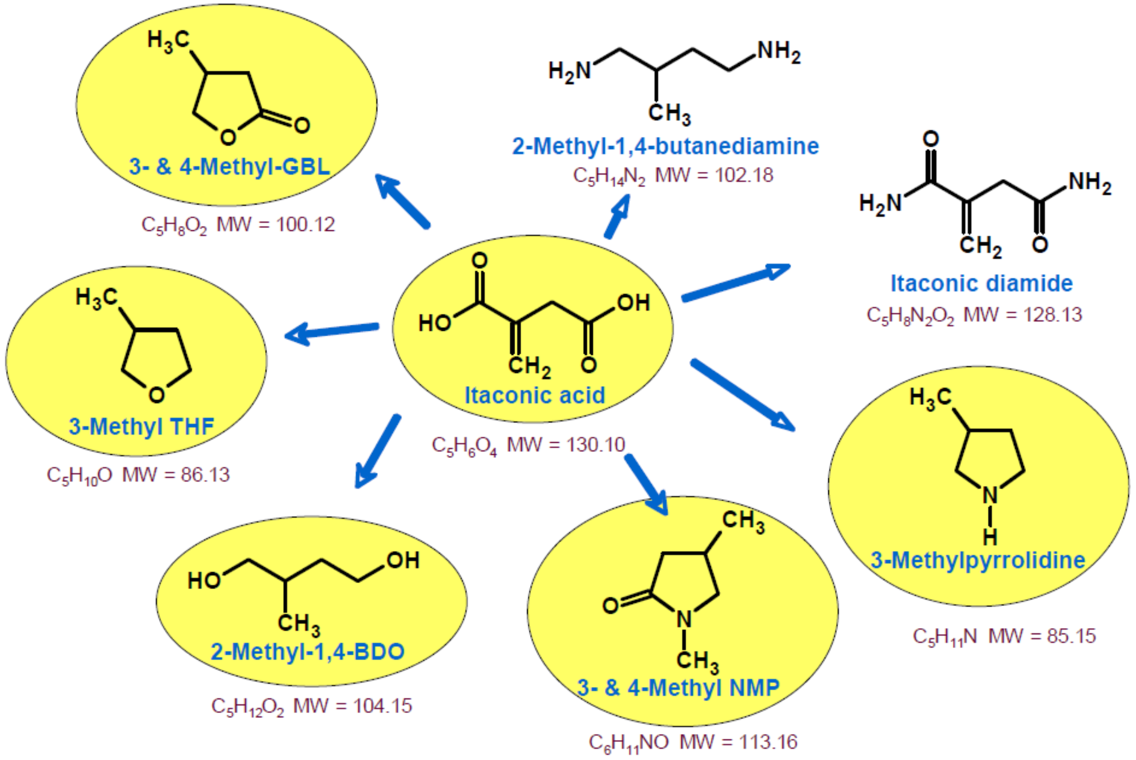

Product Families:

- Reduction
  - Methyl butanediol, THF family
  - Monomers
- Reductive amination
  - Pyrrolidones
  - Solvents, water soluble polymers

T. Werpy *et al.*, *Results of Screening for Potential Candidates from Sugars and Synthesis Gas*; U.S. Department of Energy: Washington, DC, **2004**.

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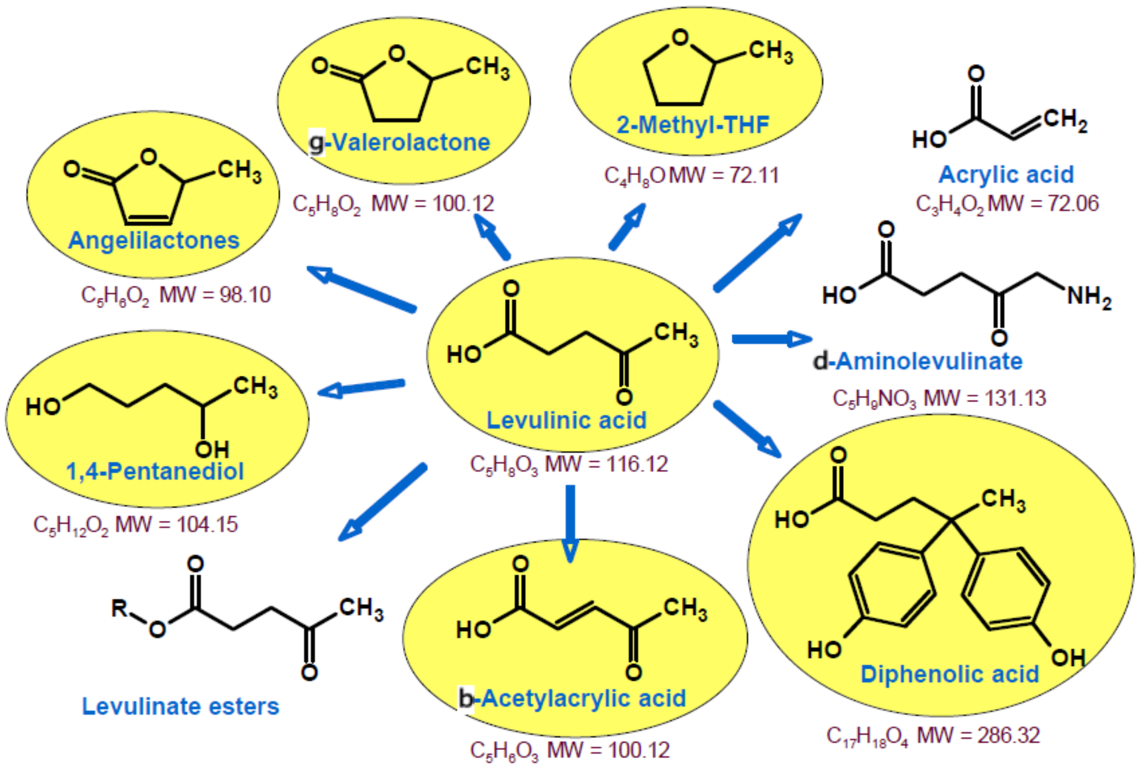
sorbitol
xylitol, arabinitol



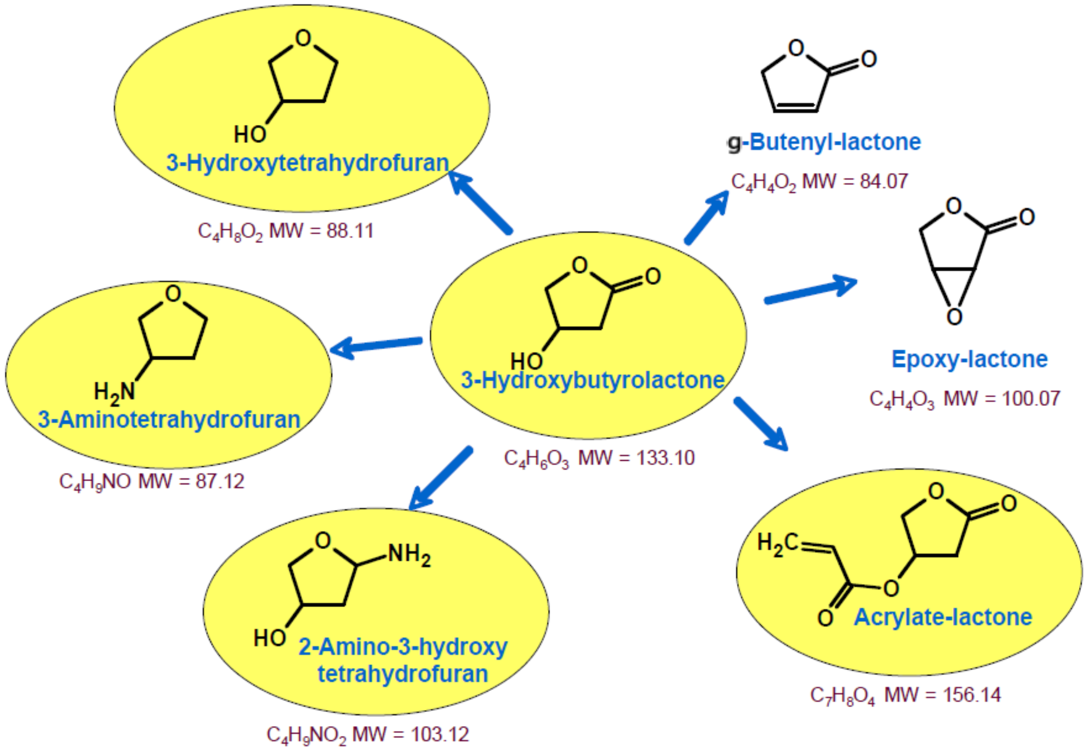
Product Families:

- Reduction
  - Methyl THF, butyrolactone
  - Solvents, fuels
- Dehydrogenation/ oxidation
  - Acetyl acrylates, acrylic acid
  - Monomers for co-polymerization
- Condensation
  - Diphenolic acid
  - Polycarbonate synthesis (replacement for bisphenol A)

T. Werpy *et al.*, *Results of Screening for Potential Candidates from Sugars and Synthesis Gas*; U.S. Department of Energy: Washington, DC, **2004**.

Platform chemicals from cellulosic biomass

Building Blocks
1,4-diacids (succinic, fumaric and malic)
2,5-furandicarboxylic acid
3-hydroxy propionic acid
aspartic acid
glucaric acid
glutamic acid
itaconic acid
levulinic acid
3-hydroxybutyrolactone
glycerol
sorbitol
xylitol, arabinitol



Product Families:

- Reduction
  - Furans
  - Solvents
- Direct polymerization

T. Werpy *et al.*, *Results of Screening for Potential Candidates from Sugars and Synthesis Gas*; U.S. Department of Energy: Washington, DC, **2004**.

Platform chemicals from cellulosic biomass

Building Blocks
1,4-diacids (succinic, fumaric and malic)
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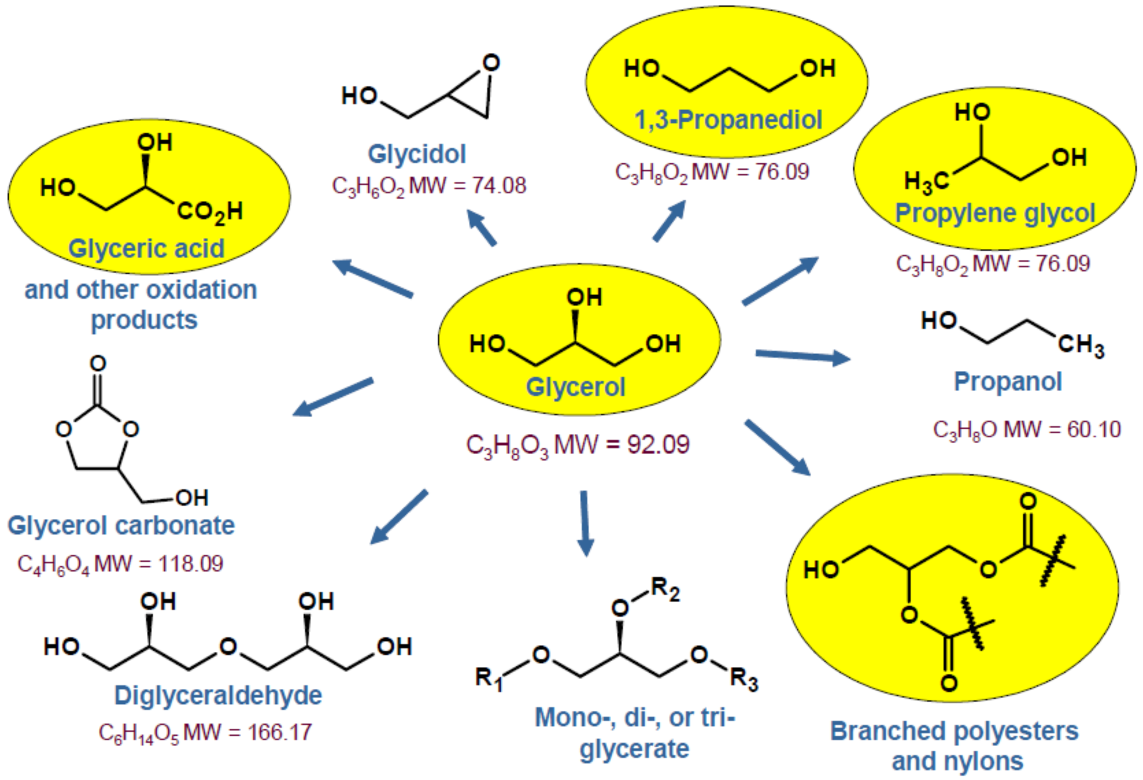

Product Families:

- Oxidation
  - Glyceric acid
  - Polymers, polyesters
- Hydrogenolysis
  - Propylene glycol
  - Drying agents, antifreeze
- Direct polymerization
  - Branched polyesters and polyurethanes

T. Werpy *et al.*, *Results of Screening for Potential Candidates from Sugars and Synthesis Gas*; U.S. Department of Energy: Washington, DC, **2004**.

Platform chemicals from cellulosic biomass

Building Blocks
1,4-diacids (succinic, fumaric and malic)
2,5-furandicarboxylic acid
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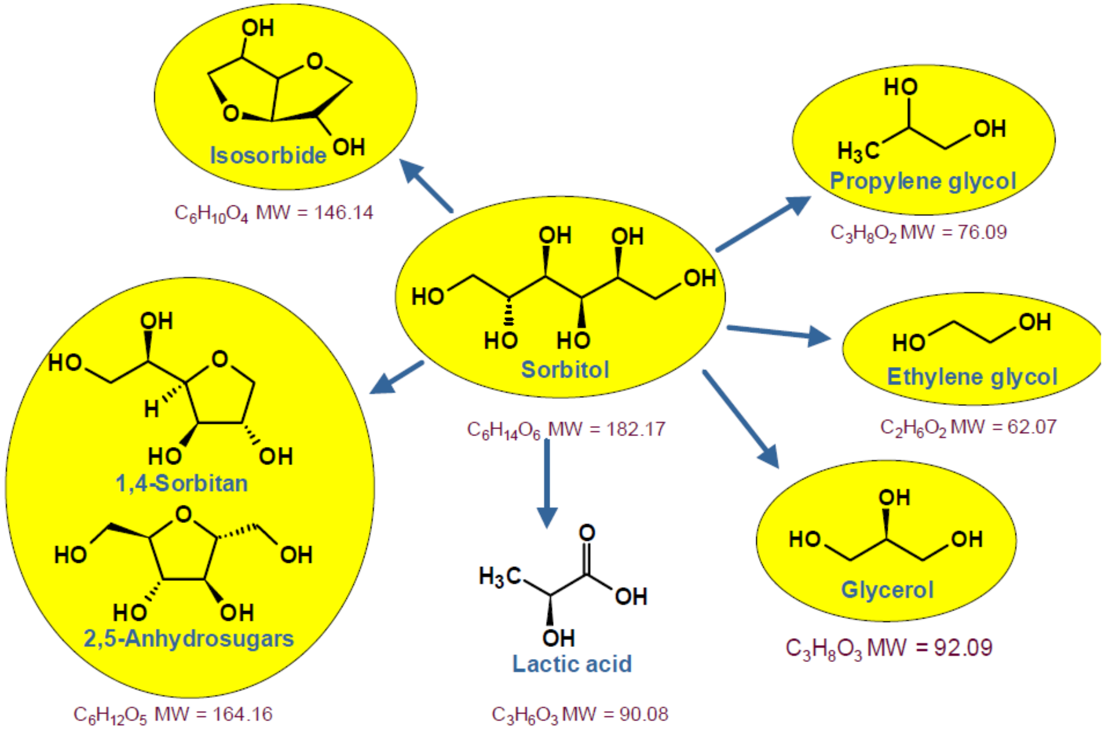


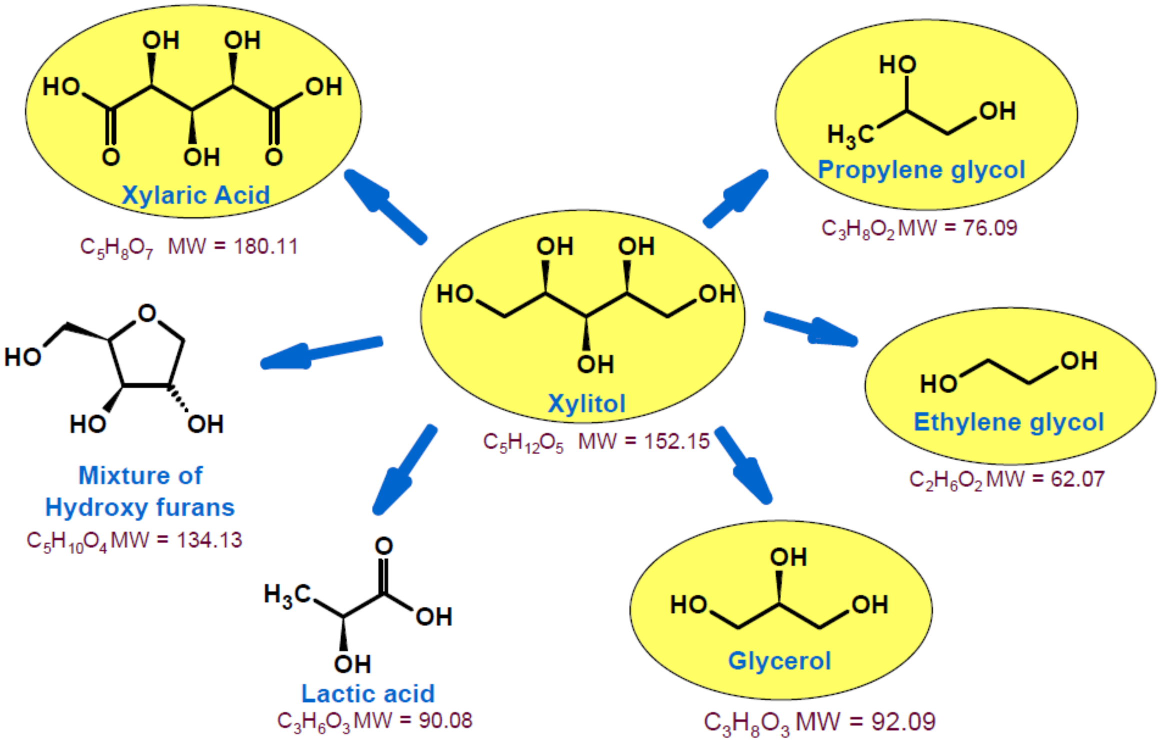
Product Families:

- Dehydration
  - Isosorbides, anhydro sugars
  - Monomers
- Bond cleavage
  - Propylene glycol, lactic acid
  - Drying agents, antifreeze
- Direct polymerization
  - Branched polysaccharides
  - Water soluble polymers

T. Werpy *et al.*, *Results of Screening for Potential Candidates from Sugars and Synthesis Gas*; U.S. Department of Energy: Washington, DC, **2004**.

Platform chemicals from cellulosic biomass

Building Blocks
1,4-diacids (succinic, fumaric and malic)
2,5-furandicarboxylic acid
3-hydroxy propionic acid
aspartic acid
glucaric acid
glutamic acid
itaconic acid
levulinic acid
3-hydroxybutyrolactone
glycerol
sorbitol
xylitol, arabinitol



Product Families:

- Oxidation
  - Xylaric acid
  - Monomers
- Bond cleavage
  - Propylene glycol, ethylene glycol, glycerol
  - Monomers, antifreeze
- Direct polymerization
  - New (water soluble) polymers

T. Werpy *et al.*, *Results of Screening for Potential Candidates from Sugars and Synthesis Gas*; U.S. Department of Energy: Washington, DC, **2004**.

Platform chemicals from cellulosic biomass

Karlsruhe Institute of Technology

- The production of chemicals from biomass is not only an academic topic! It is also highly relevant for industry!

UPM investiert in Biochemikalienproduktion der Zukunft am Standort Leuna

STOCK EXCHANGE RELEASE

30.1.2020 12:15 EET

(UPM, Helsinki, 30. Januar 2020, 12:15 Uhr EET) – UPM investiert 550 Millionen Euro in eine industrielle Bioraffinerie am Chemiestandort Leuna in Sachsen-Anhalt und stellt damit die Weichen für weiteres Wachstum in neuen Geschäftsfeldern. In der Fabrik sollen Biochemikalien auf Holzbasis produziert werden. Diese Biochemikalien werden in einer Vielzahl an Produkten des täglichen Bedarfs den Umstieg von fossilen Rohstoffen auf nachhaltige Alternativen ermöglichen. Die Investition eröffnet vollkommen neue Märkte für UPM und damit verbunden großes Wachstumspotential.

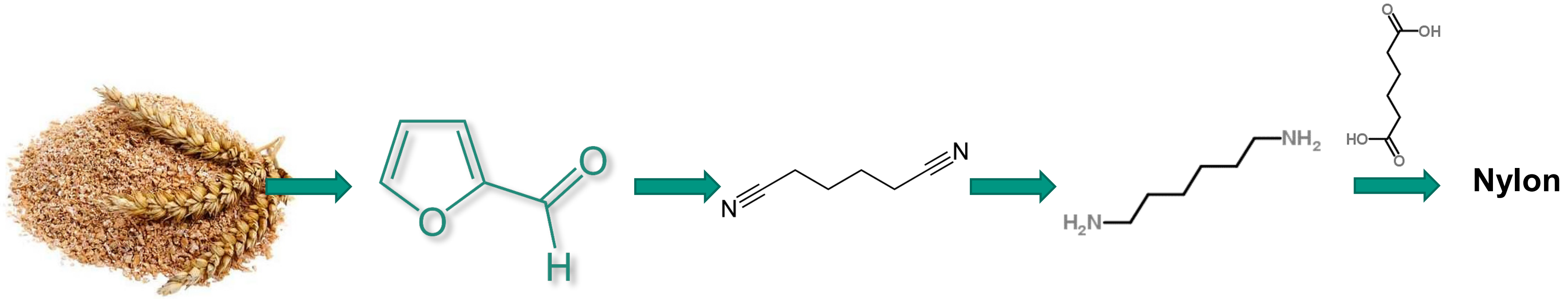
In der Bioraffinerie wird aus Laubholz eine neue Generation von nachhaltigen, chemischen Grundstoffen entstehen: Bio-Monoethylenglykol (bMEG), funktionelle Füllstoffe, Bio-Monopropylenglykol sowie Industriezucker. Dabei werden neue und innovative Verfahren zum Einsatz kommen. Die jährliche Gesamtkapazität der Bioraffinerie wird bei 220.000 Tonnen liegen. Der Produktionsstart ist für Ende 2022 geplant.

- New chemical plant for the production of chemicals from wood biomass with a capacity of 220.000 t/a in Leuna.
- 500m € investment

https://www.upm.com/de/uber-UPM/for-media/releases/2020/01/upm-investiert-in-biochemikalienproduktion-der-zukunft-am-standort-leuna/ accessed on May 25th, 2020

Case study: furfural

- 1831 distillation of bran with diluted sulfuric acid by Döbereiner
- Best results with hemicellulose-rich materials by dry steaming in the presence of HCl
- 1922 Quaker Oats Cereal Mill 2.5 tons furfural per day
- Cheapest aldehyde in 1934 with 35 – 40 cents / kg
- Until 1960 DuPont used it for production of nylon

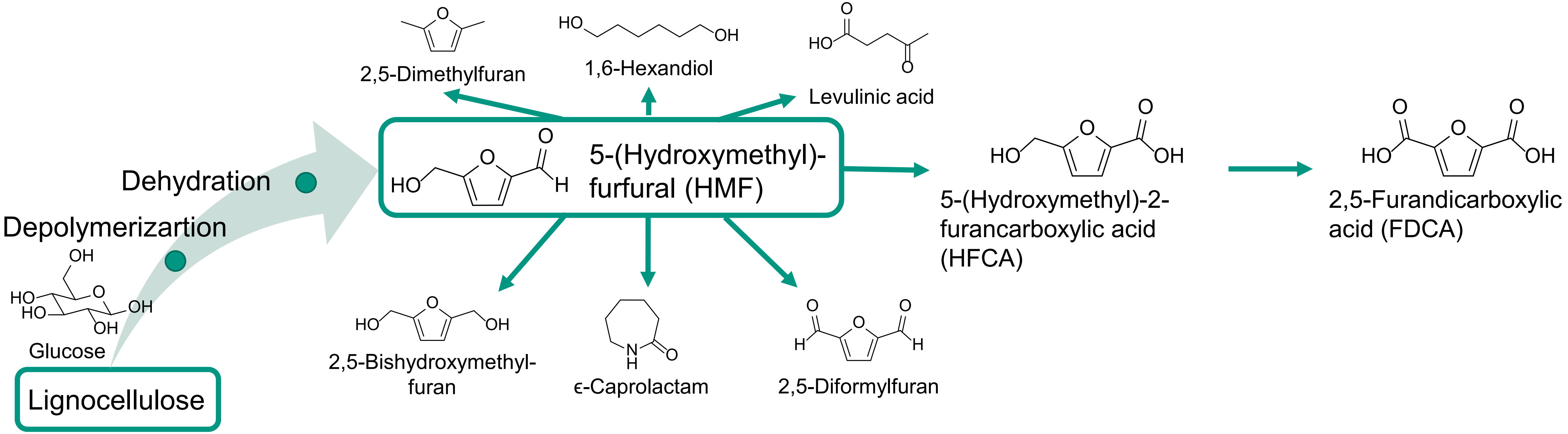


Furfural Adiponitrile Diaminohexane

- This process was abandoned when the key intermediate THF could be produced from then cheaper petrochemical C4 hydrocarbons.

Case study: 5-(Hydroxymethyl)furfural

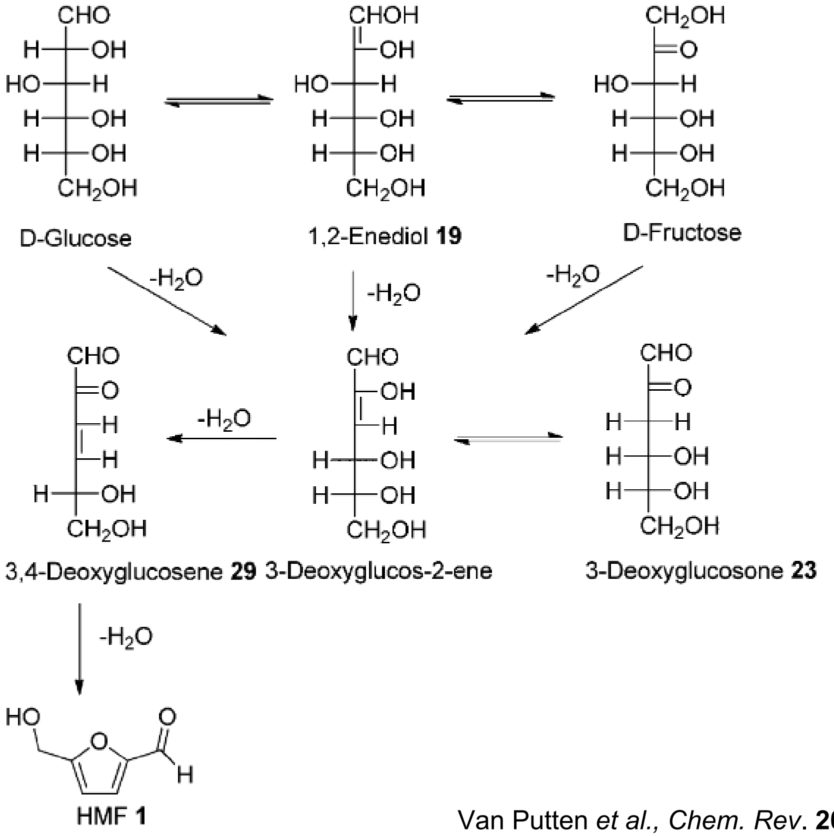
- Often referred to as the "sleeping giant"
- Dehydration of hexoses has ideal atom economy

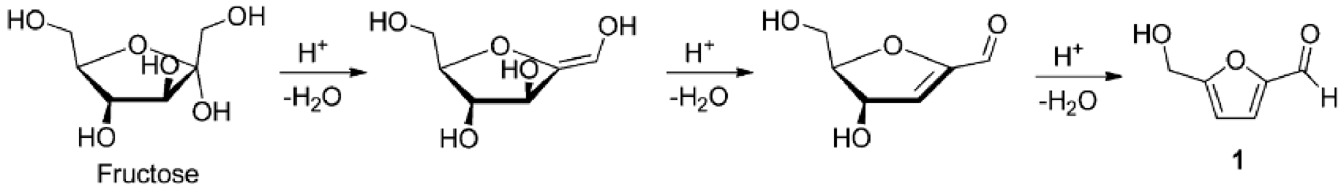


- As a platform molecule, HMF can be converted in numerous reactions and the corresponding product shows broad areas of application

Case study: 5-(Hydroxymethyl)furfural

- Often referred to as the “sleeping giant”
- Dehydration of hexoses has ideal atom economy
  - Higher yields obtained when fructose is used instead of glucose



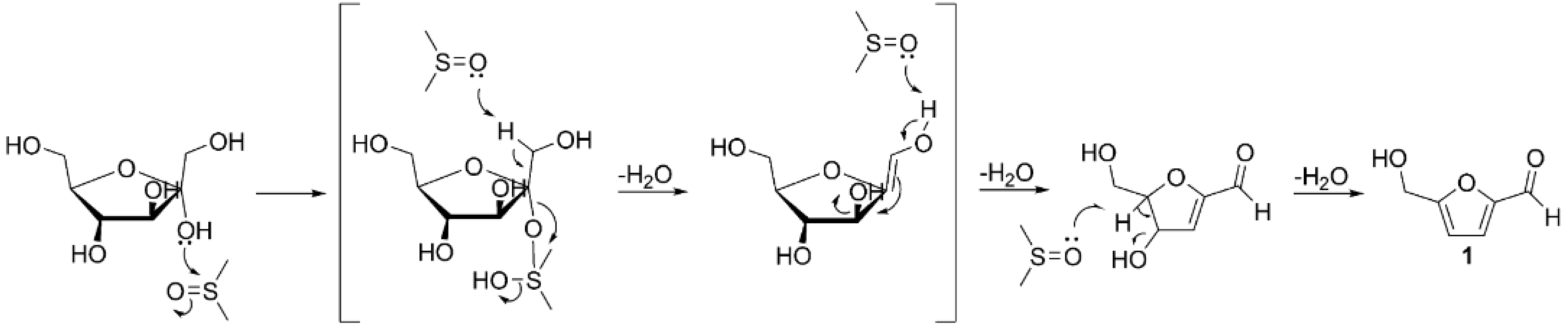


- Fructose is more present in the *furanose* form
- Cyclic mechanism more likely for fructose

Van Putten *et al., Chem. Rev*. **2013**, *113*, 1499−1597.

Case study: 5-(Hydroxymethyl)furfural

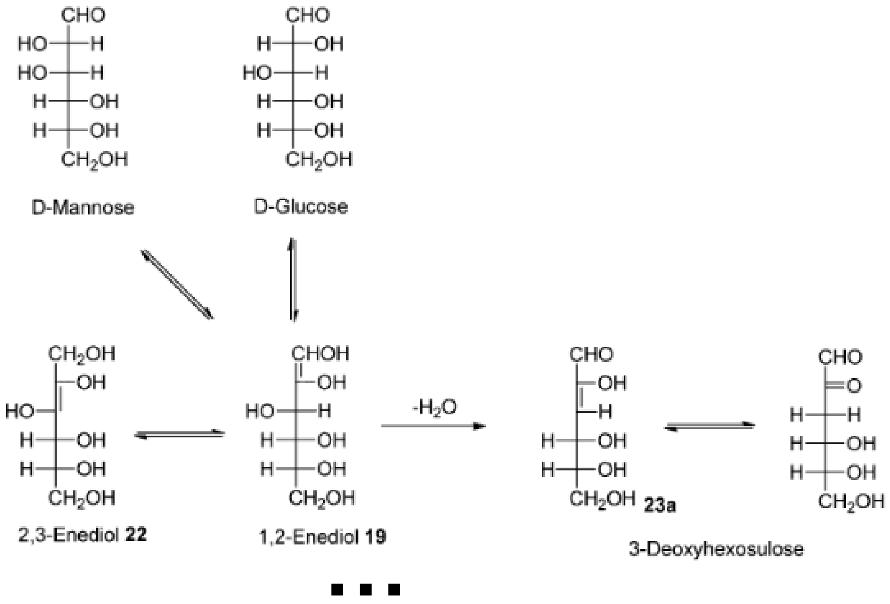
- Often referred to as the “sleeping giant”
- Dehydration of hexoses has ideal atom economy
  - Higher yields obtained when fructose is used instead of glucose
  - Higher yields obtained when high boiling organic solvents like DMSO are used

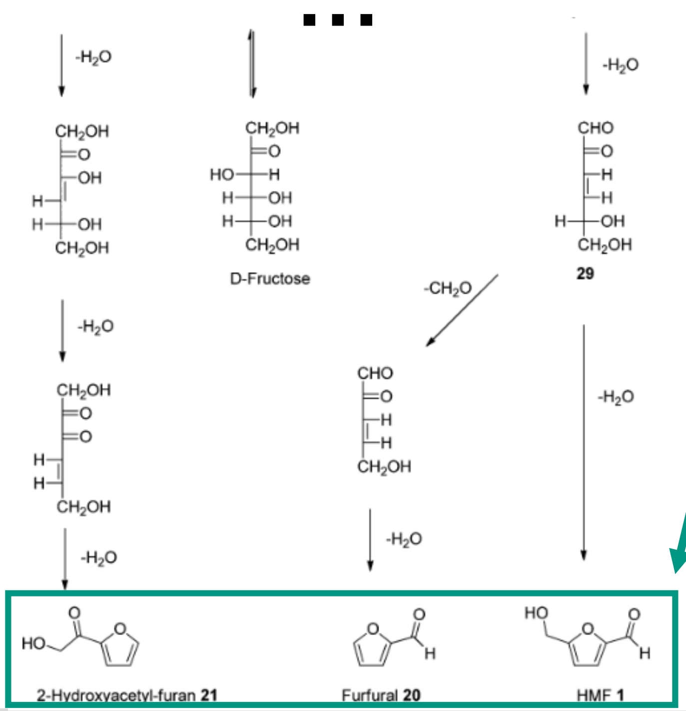


Van Putten *et al., Chem. Rev*. **2013**, *113*, 1499−1597.

Case study: 5-(Hydroxymethyl)furfural

- Often referred to as the “sleeping giant”
- Dehydration of hexoses has ideal atom economy
  - Higher yields obtained when fructose is used instead of glucose
  - Higher yields obtained when high boiling organic solvents like DMSO are used
- As with most biomass conversion reactions, selectivity is both critical and the key to success





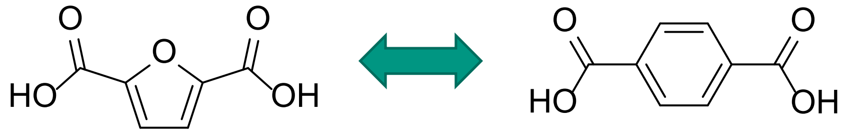
By-products of HMF synthesis
- Levulinic acid, formic acid
- Unconverted sugars
- Remains of the acid catalyst
- Humins
- …

Van Putten *et al.*, *Chem. Rev.* **2013**, *113*, 1499−1597.

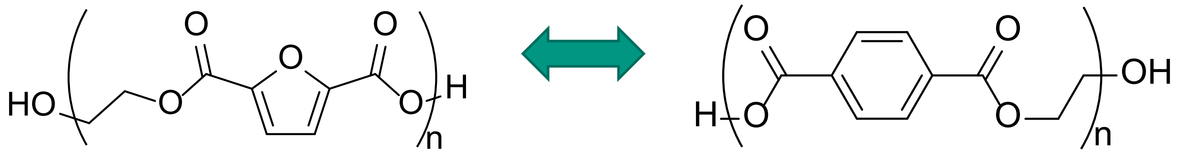
Case study: selective oxidation of HMF

Karlsruhe Institute of Technology

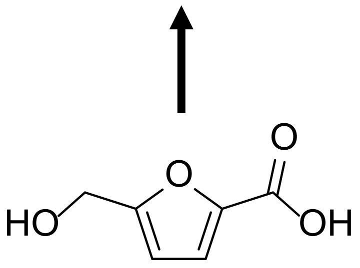
- 2,5-Furandicarboxylic acid (FDCA) was part both of the original and revised assessment of the most promising chemicals that can be produced from biomass on an industrial scale.



FDCA Terephthalic acid



PEF PET



HFCA

<u>structural similarity to terephthalic acid</u>

- might replace fossil monomers in polycondensates
- Polyethylene Furanoate (PEF) produced in industrial scale[1]
- attracted investors like Danone or Coca-Cola Company[2]
- similar applications for are possible for HFCA

HFCA

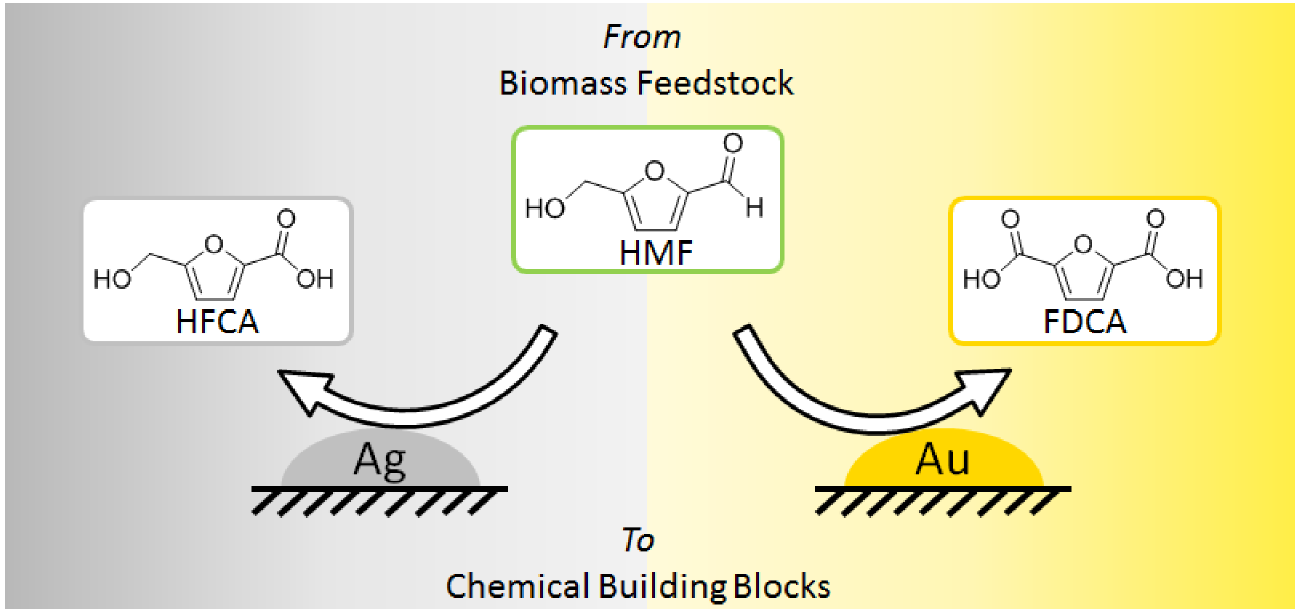
- mostly considered as an intermediate in FDCA synthesis
- few literature reports on targeted synthesis
- highest yields using heterogeneous Ag-based catalysts[3]

FDCA

- numerous routes published (stoichiometric and catalytic, different solvents/oxidants, ….)
- homogeneous base in water

[1] C.M. de Diego, M.A. Dam, G.J. Gruter, US8865921 B2
[2] Avantium. https://www.avantium.com/yxy/markets-partnerships/ 03.01.2019
[3] O. R. Schade, K.F. Kalz, D. Neukum, W. Kleist, J.-D. Grunwaldt, *Green Chem.*, **2018**, *20*, 3530

Case study: selective oxidation of HMF



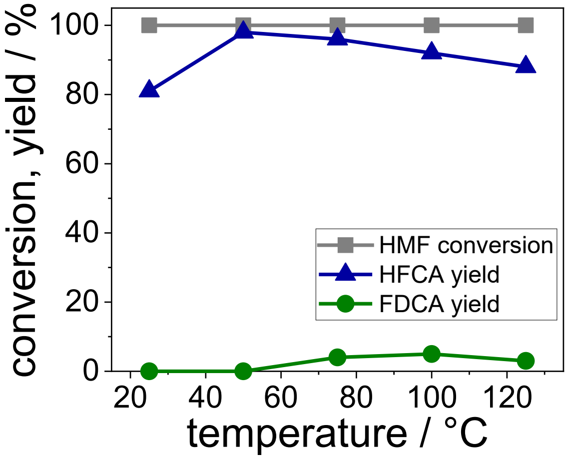
- higher activity of ZrO_2-supported catalysts
- deactivation upon re-use

- active in HFCA synthesis over broad range of reaction conditions, no production of FDCA
- productivity up to 400 $mol_{HFCA}\ h^{-1}\ mol_{Ag}^{-1}$
- heterogeneous catalysis on reduced Ag

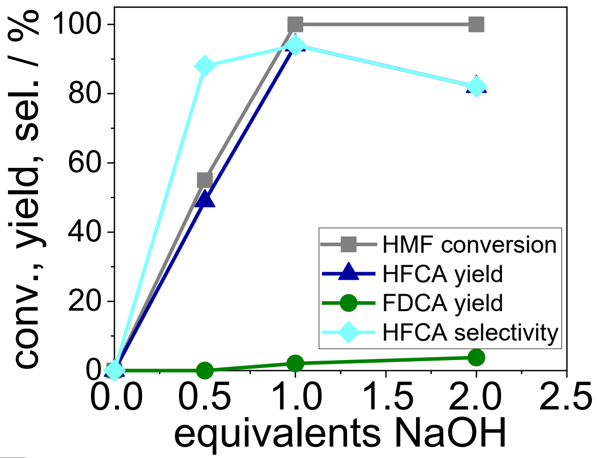
- active in FDCA synthesis, HFCA as intermediate
- productivity up to 67 $mol_{FDCA}\ h^{-1}\ mol_{Au}^{-1}$

O. R. Schade, K.F. Kalz, D. Neukum, W. Kleist, J.-D. Grunwaldt, *Green Chem.*, **2018**, *20*, 3530

Case study: selective oxidation of HMF

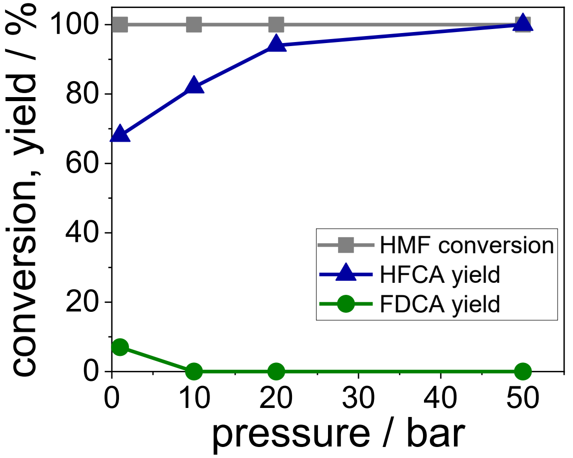


t_R=5 h, p= 10 bar air, 4 eq NaOH, 54 mg catalyst



T=50 °C, t_R=5 h, p= 10 bar air, 54 mg catalyst

Ag/ZrO_2_dp



T=50 °C, t_R=5 h, 4 eq NaOH, 28 mg catalyst

- exclusive production of HFCA
- increasing HFCA yield with increasing:
  - Temperature (50 °C)
  - Base content (1 eq)
  - Pressure (10 bar)
- 400 $mol_{HFCA}h^{-1}mol_{Ag}^{-1}$

O. R. Schade, K.F. Kalz, D. Neukum, W. Kleist, J.-D. Grunwaldt, *Green Chem.*, **2018**, *20*, 3530

Case study: selective oxidation of HMF

Karlsruhe Institute of Technology

Ag/ZrO_2_dp

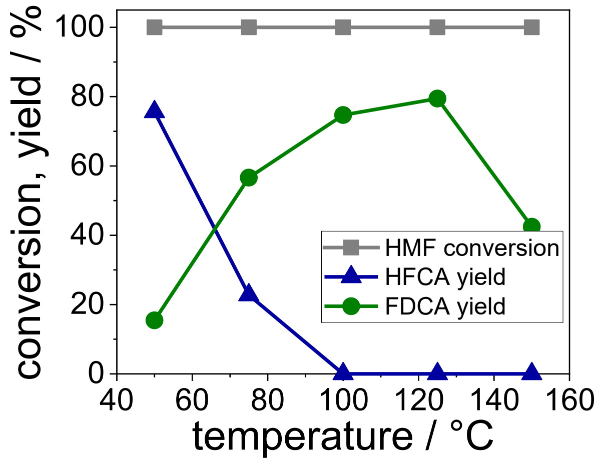
- exclusive production of HFCA
- increasing HFCA yield with increasing:

  Temperature (50 °C)

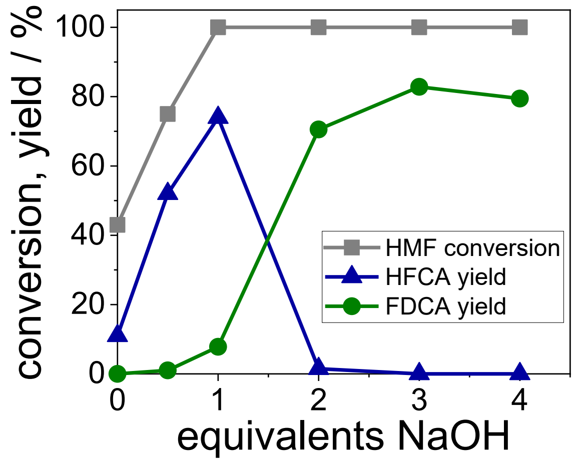
  Base content (1 eq)

  Pressure (10 bar)

- 400 $mol_{HFCA} h^{-1} mol_{Ag}^{-1}$

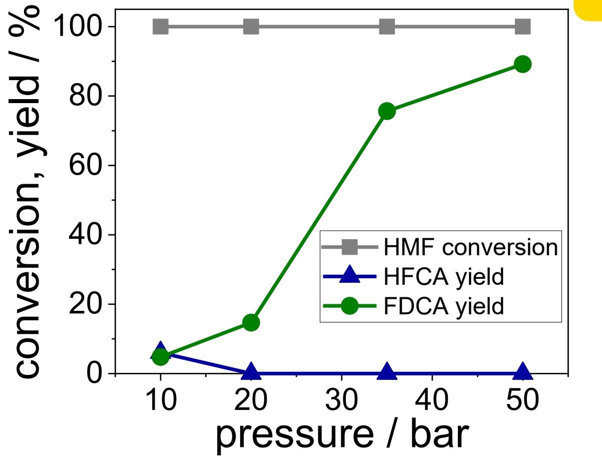


t_R=5 h, p= 10 bar air, 4 eq NaOH, 98 mg catalyst



T=125 °C, t_R=5 h, p= 10 bar air, 98 mg catalyst

Au/ZrO_2_dp



T=125 °C, t_R=5 h, 4 eq NaOH, 33 mg catalyst

- switch in selectivity towards FDCA
- increasing FDCA yield with increasing:

  Temperature (125 °C)

  Base content (4 eq)

  Pressure (10 bar)

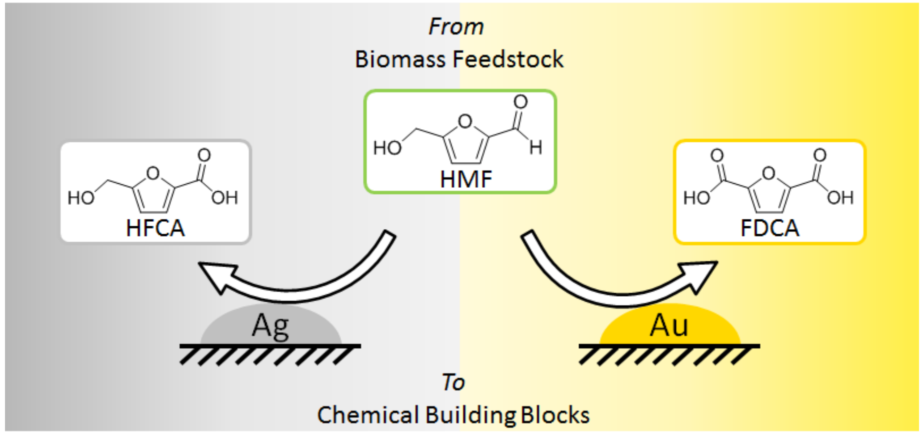
- 67 $mol_{FDCA} h^{-1} mol_{Au}^{-1}$

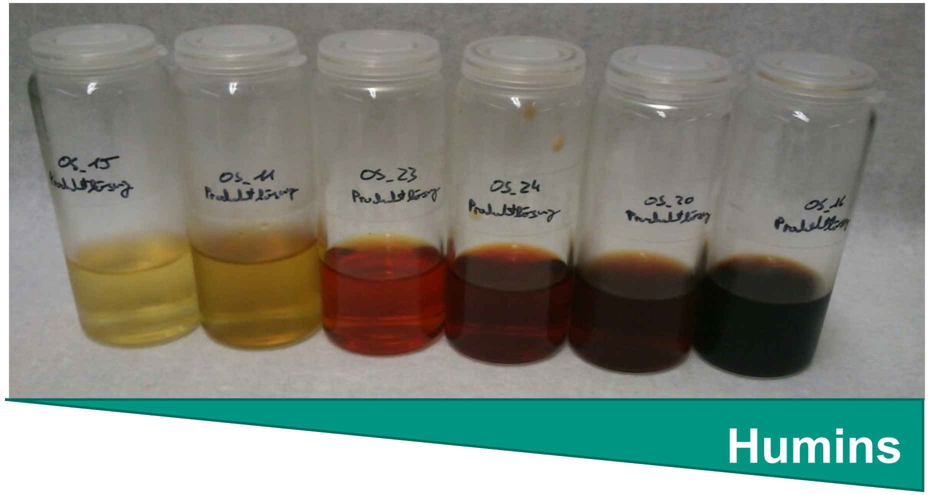
O. R. Schade, K.F. Kalz, D. Neukum, W. Kleist, J.-D. Grunwaldt, *Green Chem.*, **2018**, *20*, 3530

Case study: selective oxidation of HMF

Ag/ZrO$_2$_dp

- exclusive production of HFCA
- increasing HFCA yield with increasing:
  - Temperature (50 °C)
  - Base content (1 eq)
  - Pressure (10 bar)
- 400 mol$_{HFCA}$h^{-1}mol$_{Ag}$$^{-1}$





Au/ZrO$_2$_dp

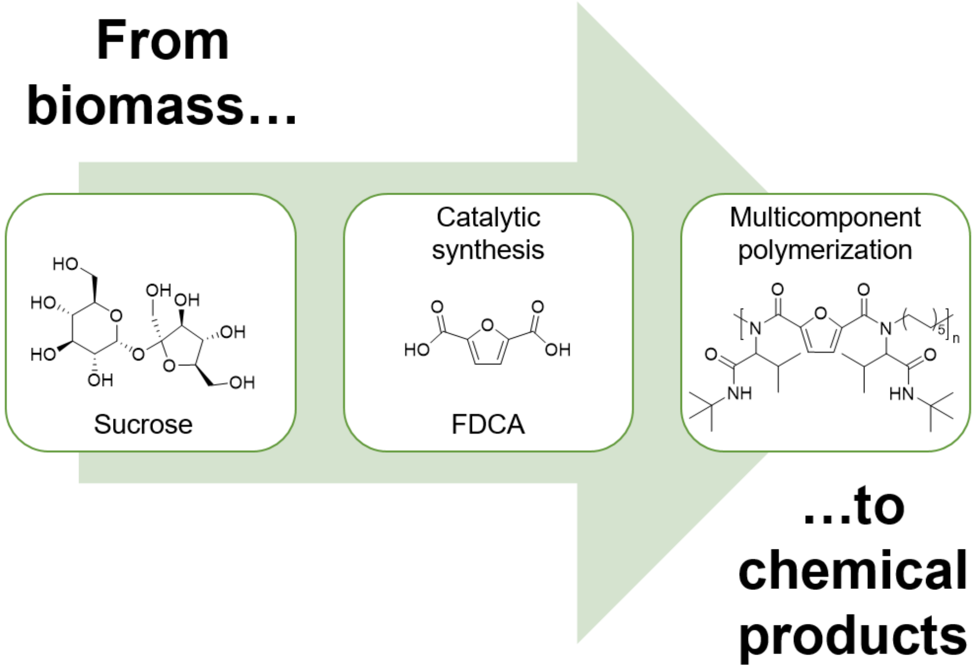
- Switch in selectivity towards FDCA
- increasing FDCA yield with increasing:
  - Temperature (125 °C)
  - Base content (4 eq)
  - Pressure (10 bar)
- 67 mol$_{FDCA}$h^{-1}mol$_{Au}$$^{-1}$

O. R. Schade, K.F. Kalz, D. Neukum, W. Kleist, J.-D. Grunwaldt, *Green Chem.*, **2018**, *20*, 3530

Case study: selective oxidation of HMF

- So far: active and optimized catalysts for HMF oxidation
- But: use of pure HMF. Remember from slide 32 “As with most biomass conversion reactions, selectivity is both critical and the key to success”

By-products of HMF synthesis
- Levulinic acid, formic acid
- Unconverted sugars
- Remains of the acid catalyst
- Humins
- …



- Investigation of the entire process chain
- Use of bio-based HMF produced from sucrose
- Direct application of FDCA in a novel polymerization reaction

O. R. Schade, P.-K. Dannecker, K. F. Kalz, D. Steinbach, M. A. R. Meier, J.-D. Grunwaldt; *ACS Omega* **2019**, *4*, 16972–16979.

Case study: selective oxidation of HMF

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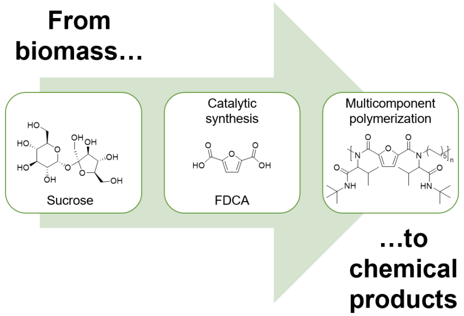

By-products of HMF synthesis

- Levulinic acid, formic acid
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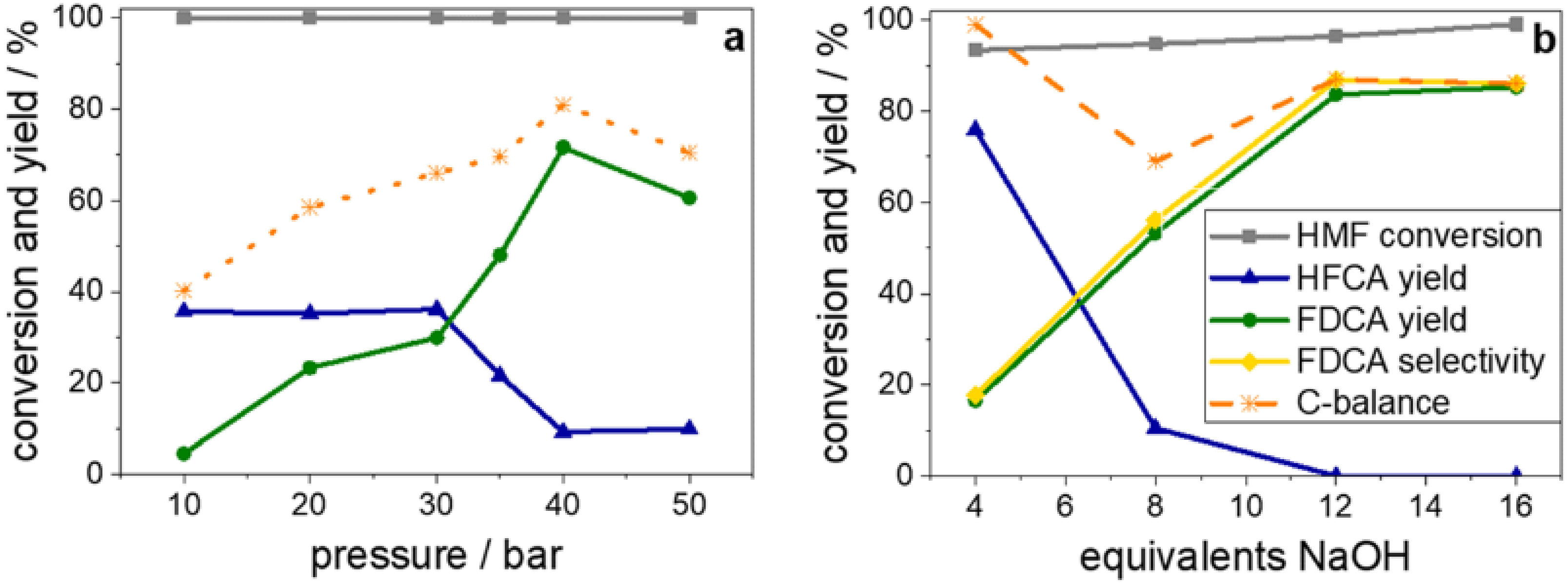
- Humins
- …



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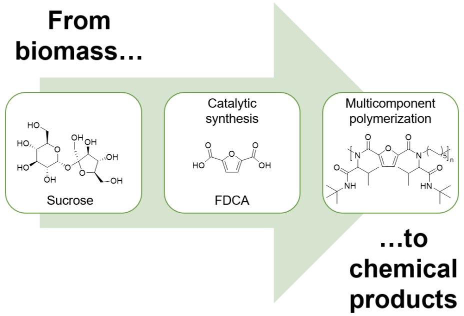
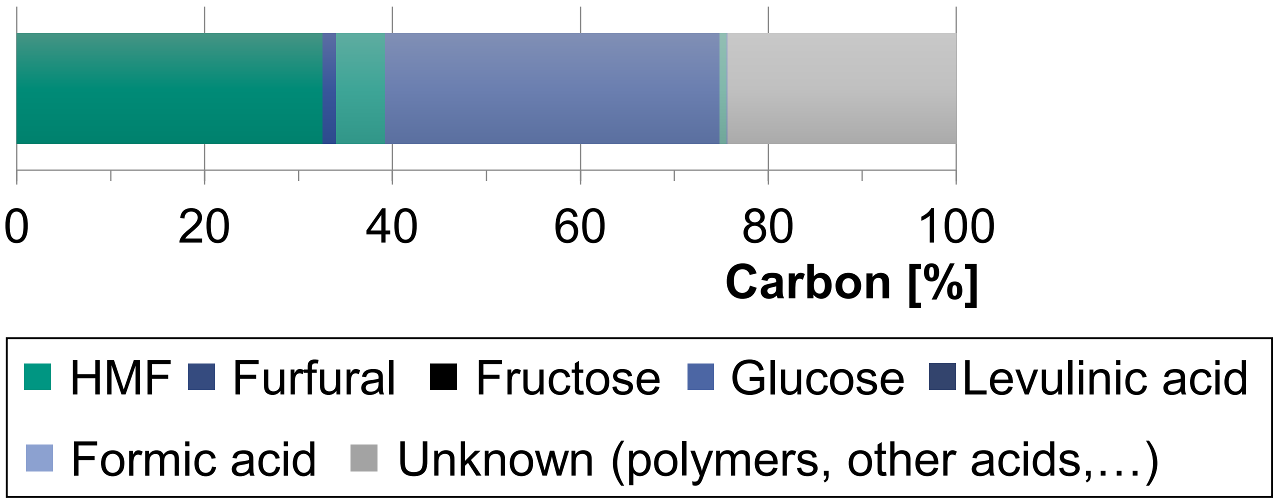


By-products of HMF synthesis

- Levulinic acid, formic acid
- Unconverted sugars
- Remains of the acid catalyst
- Humins
- …

continuous production of HMF from sucrose in a tubular reactor[1]

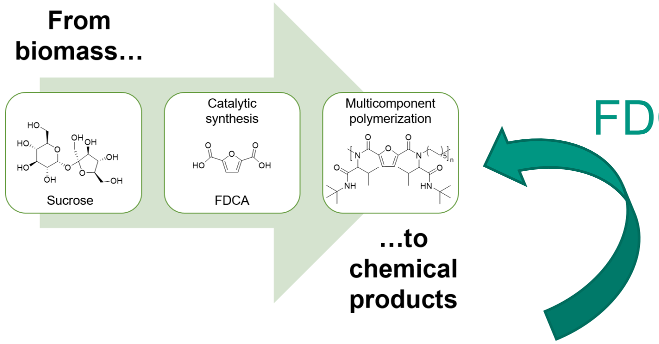


[1]D. Steinbach, A. Kruse, J. Sauer, P. Vetter, *Energies* **2018**, *11*, 645.
O. R. Schade, P.-K. Dannecker, K. F. Kalz, D. Steinbach, M. A. R. Meier, J.-D. Grunwaldt; *ACS Omega* **2019**, *4*, 16972–16979.

Case study: selective oxidation of HMF

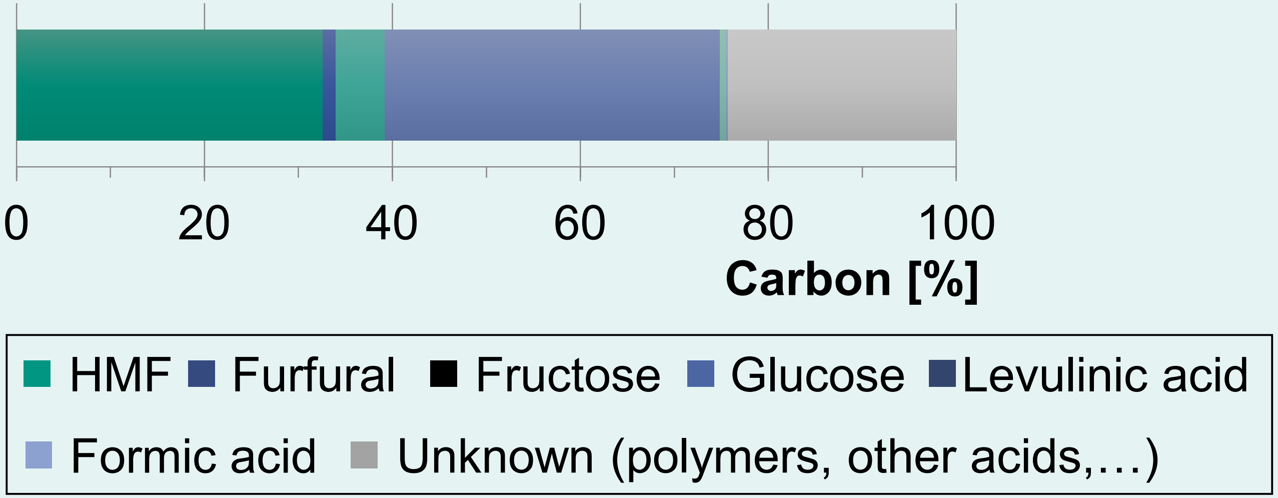
Karlsruhe Institute of Technology

- Investigation of the entire process chain
- Use of bio-based HMF produced from sucrose
- Direct application of FDCA in a novel polymerization reaction

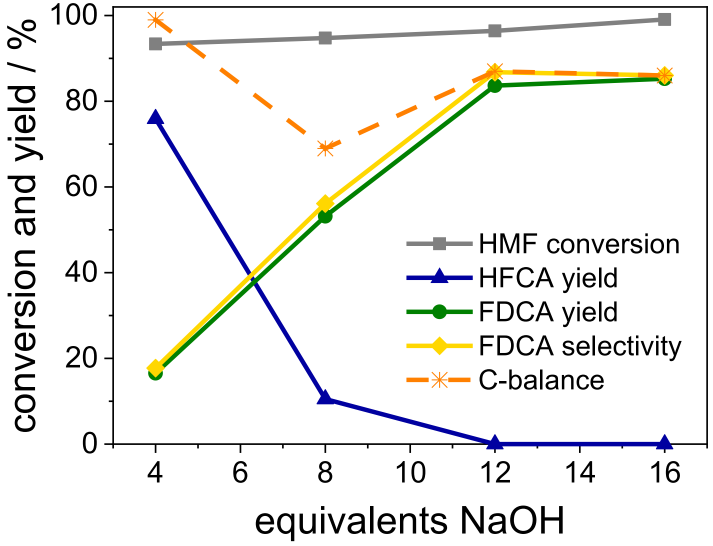


FDCA can directly be used for polymerization

continuous production of HMF from sucrose in a tubular reactor[1]



oxidation of HMF produced from sucrose

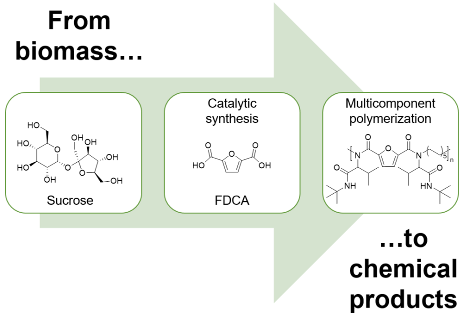


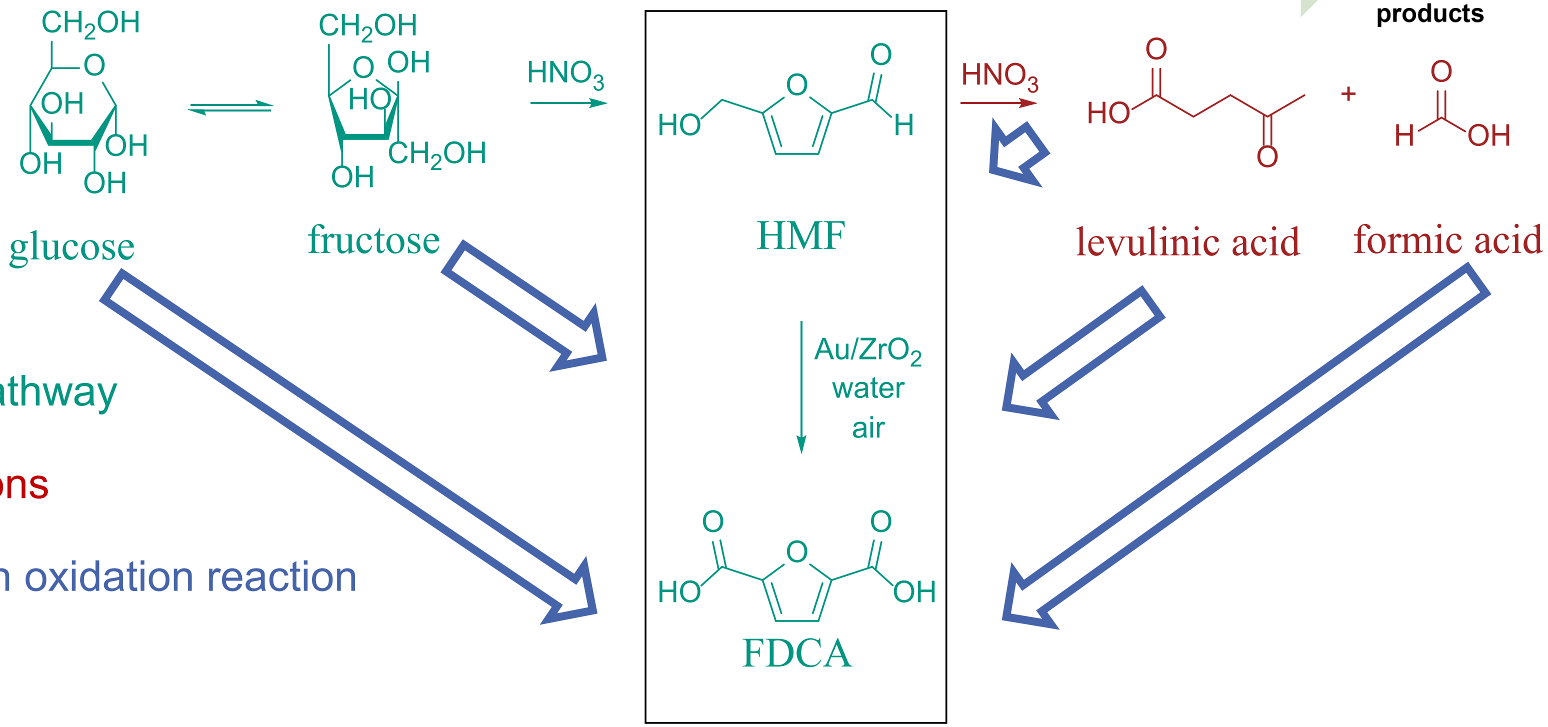
125 °C, 40 bar air pressure, 5 h reaction time, 0.3 mmol HMF in 10 mL reaction solution, 98 mg catalyst (HMF:Au=38 mol/mol)

[1]D. Steinbach, A. Kruse, J. Sauer, P. Vetter, *Energies* **2018**, *11*, 645.
O. R. Schade, P.-K. Dannecker, K. F. Kalz, D. Steinbach, M. A. R. Meier, J.-D. Grunwaldt; *ACS Omega* **2019**, *4*, 16972–16979.

Case study: selective oxidation of HMF

- Investigation of the entire process chain
- Use of bio-based HMF produced from sucrose
- Direct application of FDCA in a novel polymerization reaction





Reaction pathway

Side reactions

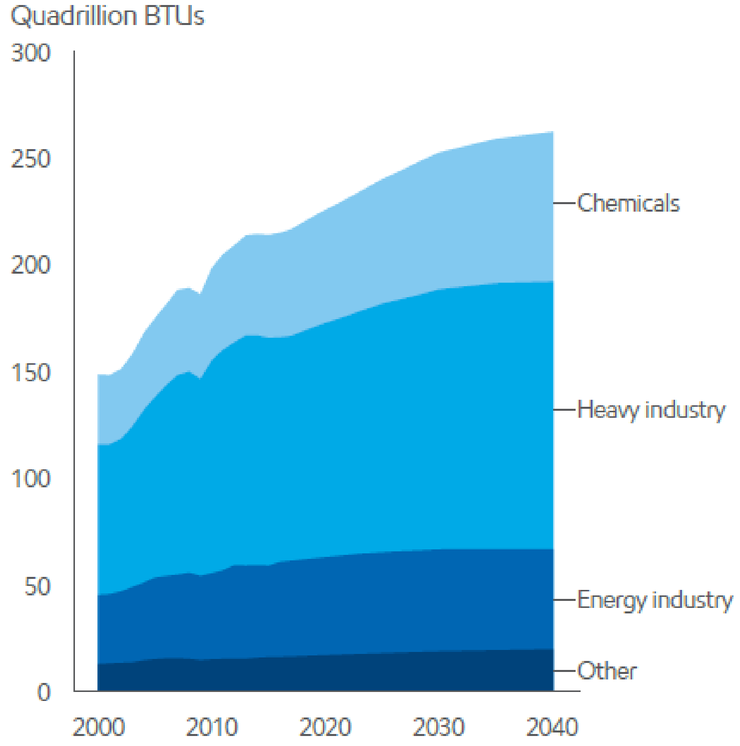
Influence on oxidation reaction

Master thesis W. Naim, „Oxidation von 5-(Hydroxymethyl)furfural zu 2,5-Furandicarbonsäure an heterogenen Katalysatoren in Gegenwart von Begleitstoffen“, 2019.
W. Naim, O. R. Schade, E. Saraçi, J.-D. Grunwaldt „The Influence of HMF production by-products on gold-catalyzed synthesis of FDCA“, *submitted for publication*.

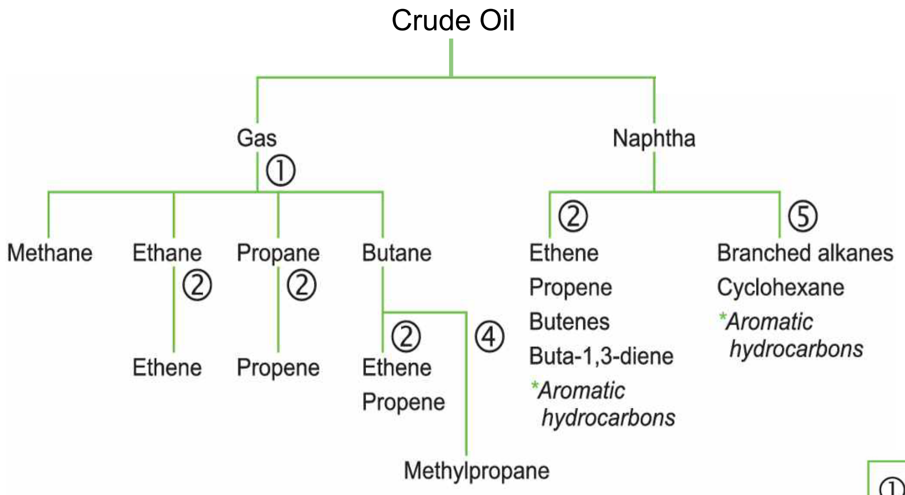
Case study: production of terephthalic acid

Demand for aromatics

Industrial demand fuels economic activity



Gas vs. naphtha as feed for steam cracking



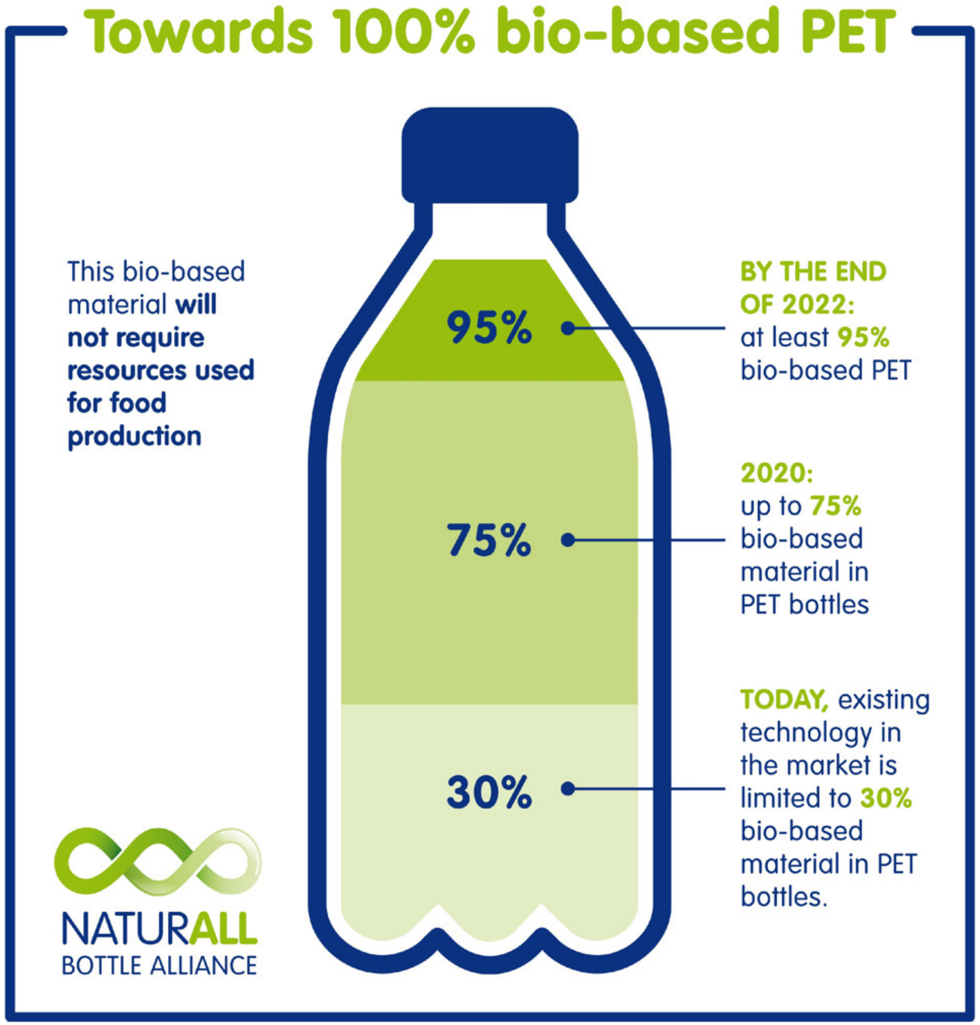
- Lower price of shale-gas
- Cleaner technology
- Lack of aromatic production
- High consumption demand of aromatics

① Distillation
② Steam cracking
③ Catalytic cracking ('hydrocracking')
④ Isomerisation
⑤ Reforming ('platforming')
⑥ Sulfur is removed

➢ **Alternative resources to meet aromatics demand**

http://cdn.exxonmobil.com/~/media/global/files/outlook-for-energy/2017/2017-outlook-for-energy.pdf
http://www.essentialchemicalindustry.org/processes/cracking-isomerisation-and-reforming.html

Case study: selective oxidation of HMF



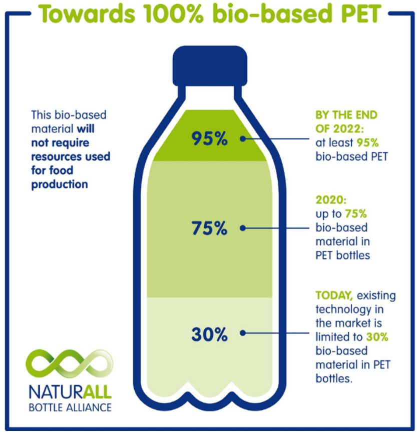
Current commercial "green" polyethylene terephthalate (PET):

- bioethanol-based ethylene glycol
- ~30 wt % renewable
- terephthalic acid (PTA) component is still made by liquid-phase oxidation of petroleum-derived p-xylene (PX)

➢ **High demand for renewable terephthalates**

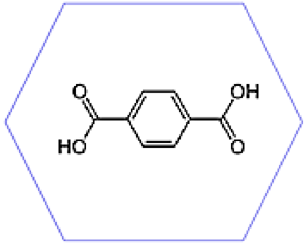
http://www.plasticsnews.com/apps/pbcsi.dll/storyimage/PN/20170302/NEWS/170309969/AR/0/Nestle-and-Danone-teaming-on-bio-based-PET-bottles.jpg

Case study: selective oxidation of HMF

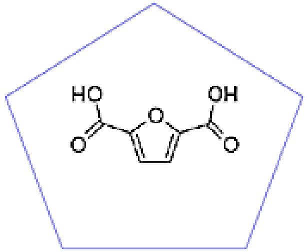


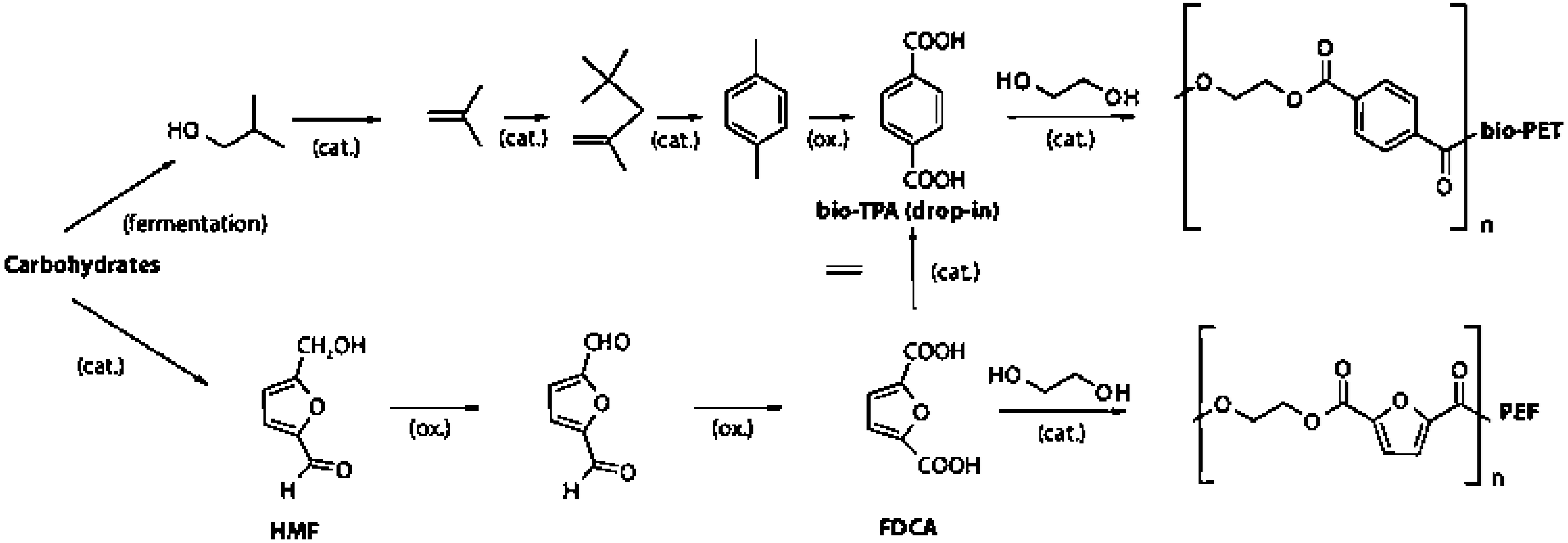
➢ **High demand for renewable polyesters**

PTA



FDCA



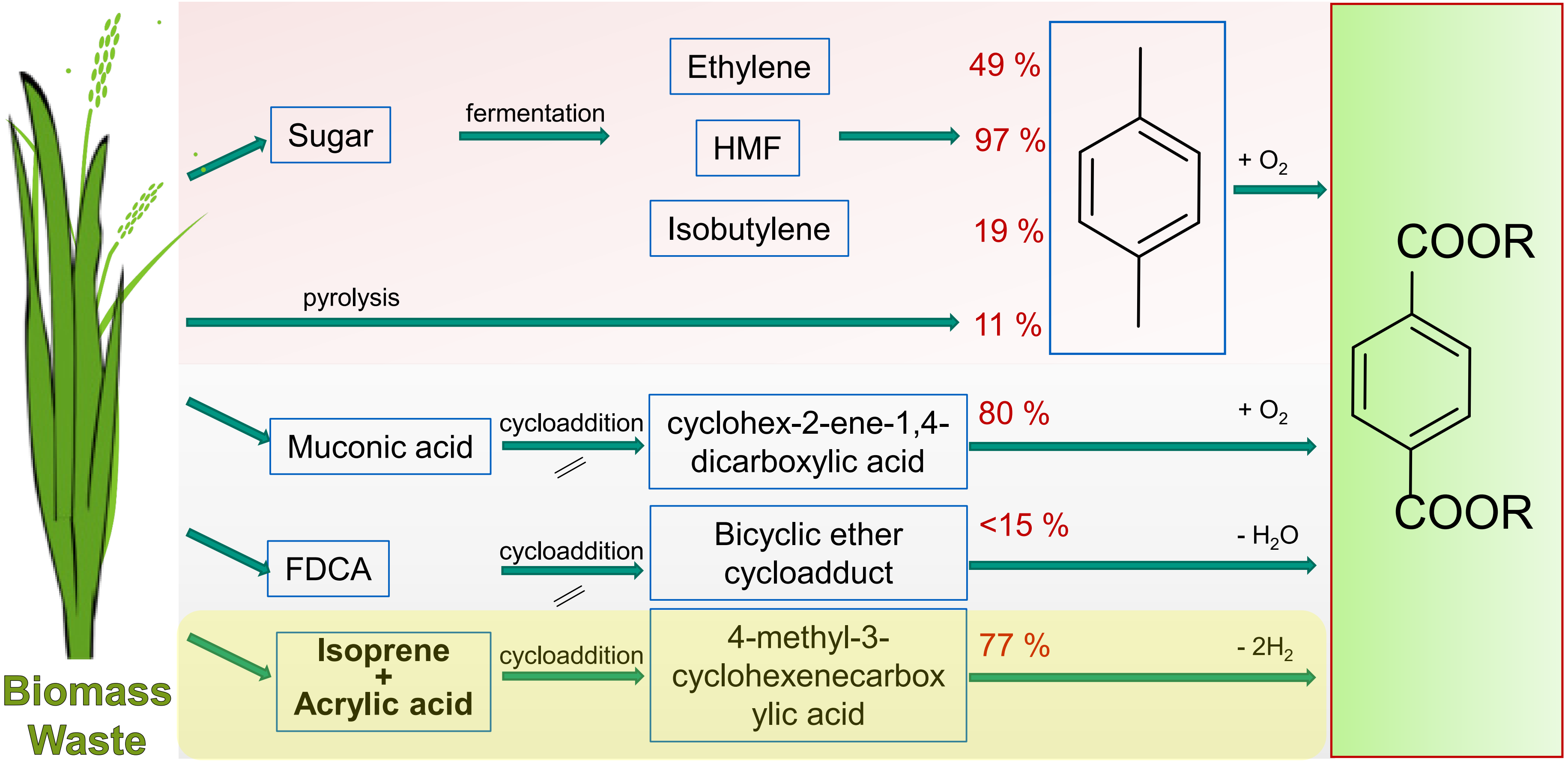


Drop-in

Emerging

Case study: selective oxidation of HMF

Bio-based terephthalic acid synthesis



➢ **Purified terephthalic acid (PTA): the most widely produced plastics monomer**