The madness of green PET drop-in (from carbohydrates) versus the opportunities of its bio-PEF replacement'.

Amseterdam, April 2014

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CTO Avantium
Amsterdam, The Netherlands

C2W 12 april 2014

Bioaromaten in opmars

Maar liefst drie consortia van instituten, universiteiten en bedrijven onderzoeken en ontwikkelen processen om bioaromaten te maken. Lignine als grondstof dient zich op grote schaal aan, maar blijkt een harde noot om te kraken. Wat maakt dit product zo interessant?

BASTIENNE WENTZEL

Vorig jaar ging Biorizon van start, een zogenoemd *shared research*-programma opgezet door TNO en haar Vlaamse zusterorganisatie Vito op de Green Chemistry Campus in Bergen op Zoom. Het doel: ontwikkelen van rendabele technologie voor de productie van aromatische verbindingen gemaakt uit biomassa. TNO en Vito staken vorig jaar 2,5 miljoen euro in Biorizon om het onderzoek op te star-

om te vergroenen. Maar belangrijker is dat aromaten nu worden geleverd als bijproduct van het kraken van aardolie. Het is eigenlijk een ondergeschoven kindje en daarom is het gevoelig voor grote prijsschommelingen. De chemische industrie zoekt dus naar een meer betrouwbare levering van grondstoffen en een voorspelbare prijs."

'De pulpfabriek wordt mede een

stenen dat cellulose in planten bij elkaar houdt. Het is na cellulose de meest voorkomende organische verbinding op aarde, maar ook een heel weerbarstige.

Lignine bestaat uit drie bouwstenen: p-coumarylalcohol, coniferylalcohol en sinapylalcohol. Tussen verschillende houtsoorten zijn er grote verschillen in samenstelling. Zo is lignine uit naaldhout

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fenylamine).
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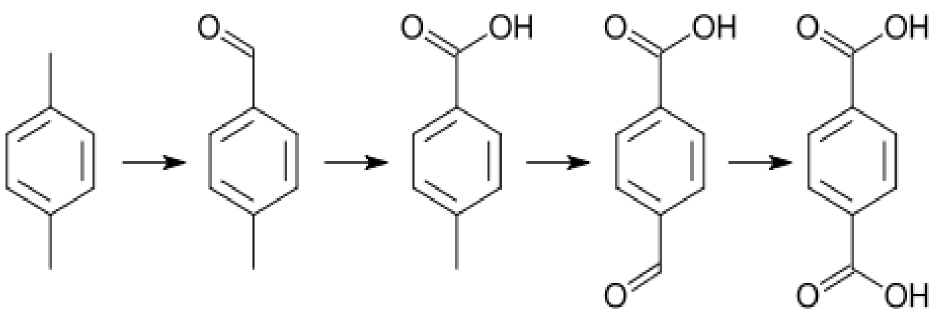
is reactief.
kunnen
Waterstof v

Agenda

- **The stage – TPA a real commodity chemical**
- Bio- options to TPA
- Conclusions
- FDCA – a viable alternative ?

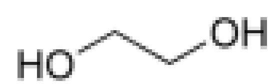
PET supply chain as we know it

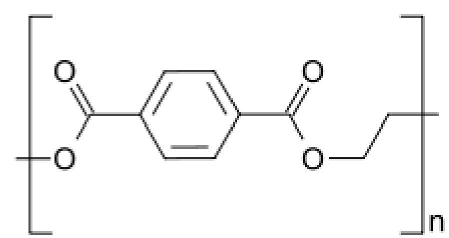


pX

4-CBA

TPA → PTA

MEG 

PET 

Fibers | Bottles | Films

Some numbers

- In 2013, the terephthalic acid (TPA; $C_8H_6O_4$) consumption was 50 Mt
- Expected capacity in 2018: 65 Mt (6% growth per year)
- TPA market value 2013: €55-65 Bn

- TPA is currently produced in plants with annual capacity of 500 kt – 1.5 Mt. In China, 1500 m^3 CSTR's are constructed.

- This additional 15Mt TPA capacity needed to meet demand will require €25-35 Bn CAPEX investment

Increase Productivity Through Better Gas-Liquid Mixing

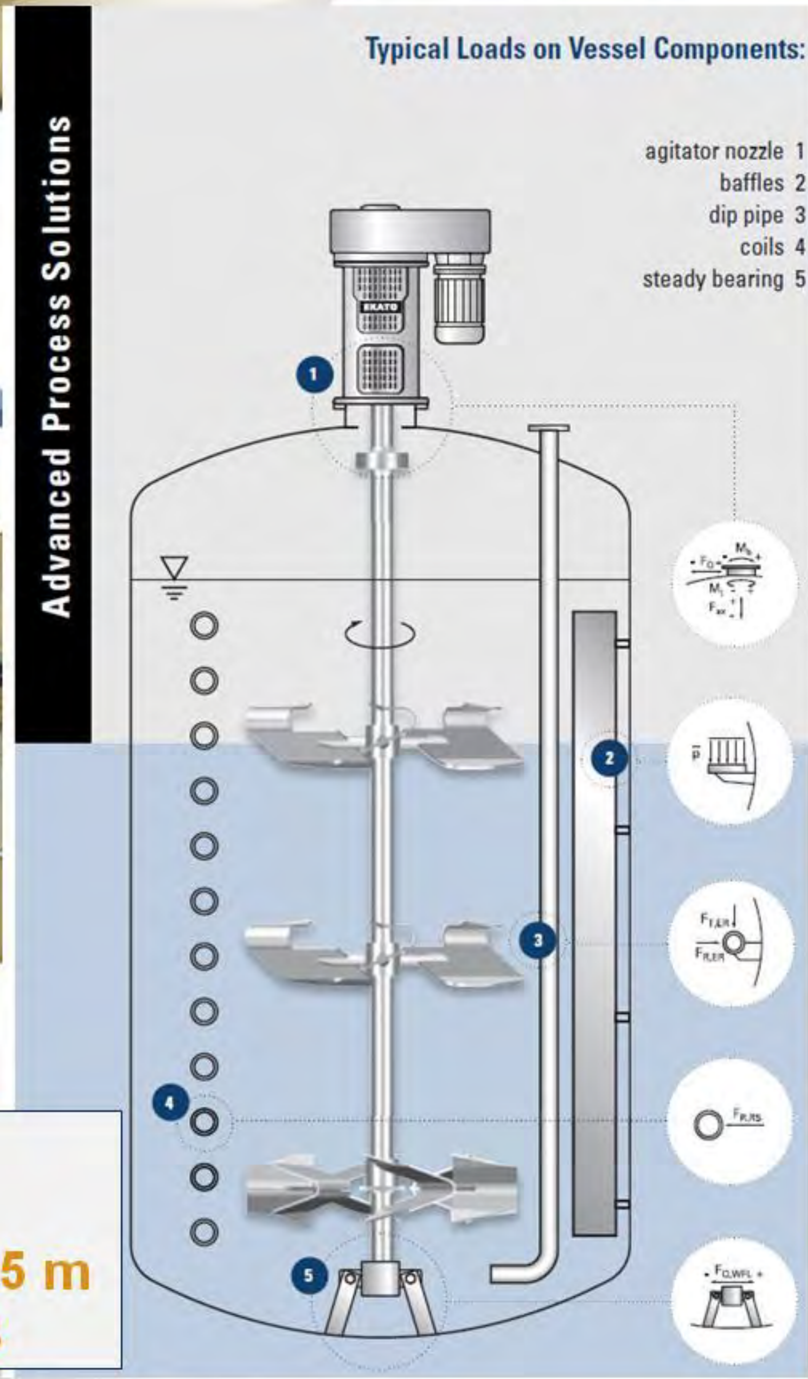
The trend towards larger reactors has increased the demand on agitator systems. Developments in gas-liquid mixing technology can help meet these demands

Werner Himmelsbach, Wolfgang Keller, Mark Lovallo,

CHEMICAL ENGINEERING
October 2007
www.che.com

FIGURE 1. This drive-shaft coupling and mechanical seal are for an 800-m^3 gas-liquid reactor


2013
3MW
agitator
h = 20 m
d = 10 m
d(shaft) = 0.5 m
V = 1500 m3


Advanced Process Solutions
Typical Loads on Vessel Components:
agitator nozzle 1
baffles 2
dip pipe 3
coils 4
steady bearing 5
EKATO

Shale gas

- Cheap shale gas is an increasingly important source of natural gas in the USA and is replacing naphtha.

  → In the USA PE will be cheap for decades (bio-PE in Europe ??)

- Naphtha is an aromatics source, but shale gas is not

  → Aromatics like p-X (and PTA) will become globally more expensive

- This in combination with the projected 15 Mt PTA growth opens up a business window to develop bio-sourced PTA for bio-PET (bottle) market.

Will there be sufficient p-xylene ?

- Will there be sufficient para-xylene and MEG to meet the demand of the additional 15Mt TPA capacity growth ?

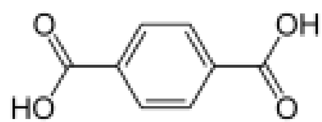
- Not from conventional sources !

→ new chemical routes (e.g methane to aromatics)

3,410,922
METHOD FOR THE DIRECT CONVERSION OF METHANE TO AROMATIC HYDROCARBONS
Robert A. Sanchez, Del Mar, Calif., assignor to The Salk Institute for Biological Studies, San Diego, Calif., a corporation of California
Filed Nov. 14, 1966, Ser. No. 594,184
27 Claims. (Cl. 260—673)

→ from biomass (carbohydrates $C_5H_{10}O_5$ or $C_6H_{12}O_6$; $C_x(H_2O)_x$)
or from lignin

The shift to partially biobased PET



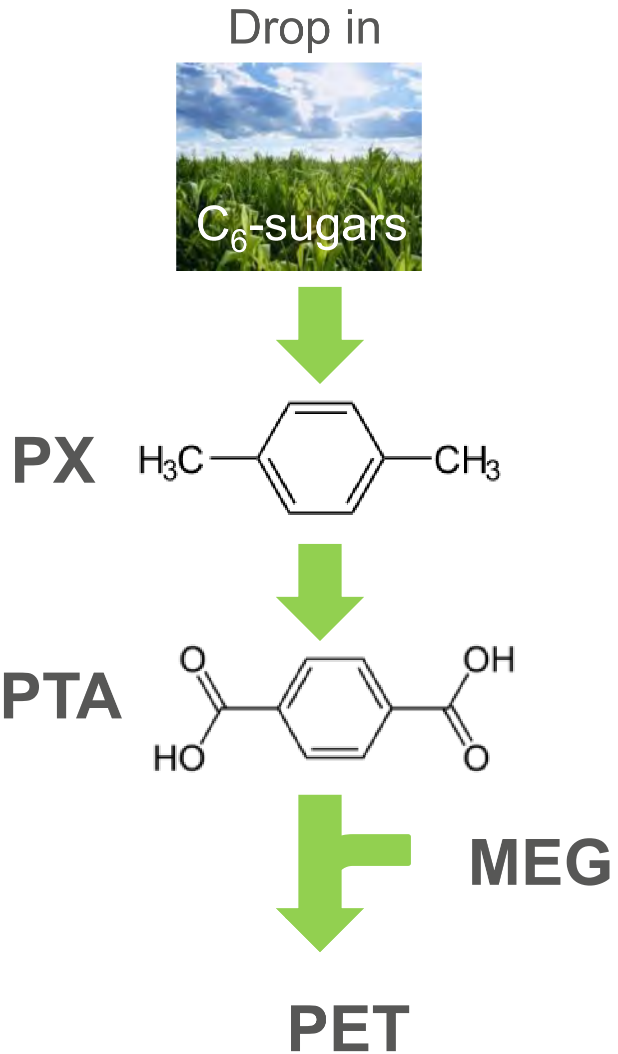
PTA

MEG

PET

plantbottle

The road to 100% biobased PET



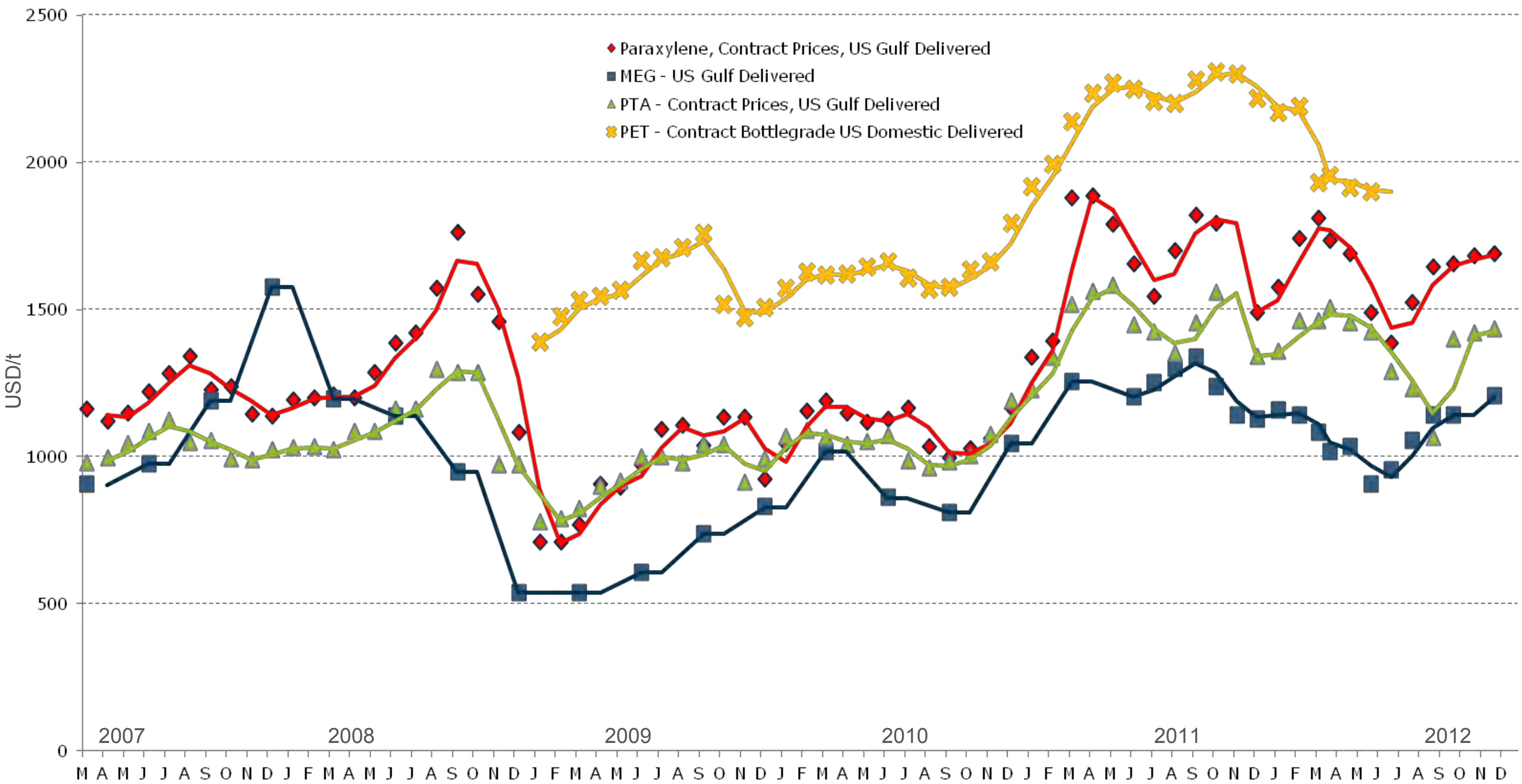
Grouping of technological routes from Carbohydrates based on precursor to TPA:

1. Via bio-based p-xylene (from i-BuOH or dimethylfuran)
2. Via other precursors such as muconic acid, FDCA or limonene
3. Directly from carbohydrates

From Lignin

4. Depolymerization while maintaining aromaticity

Paraxylene, PTA, MEG, PET



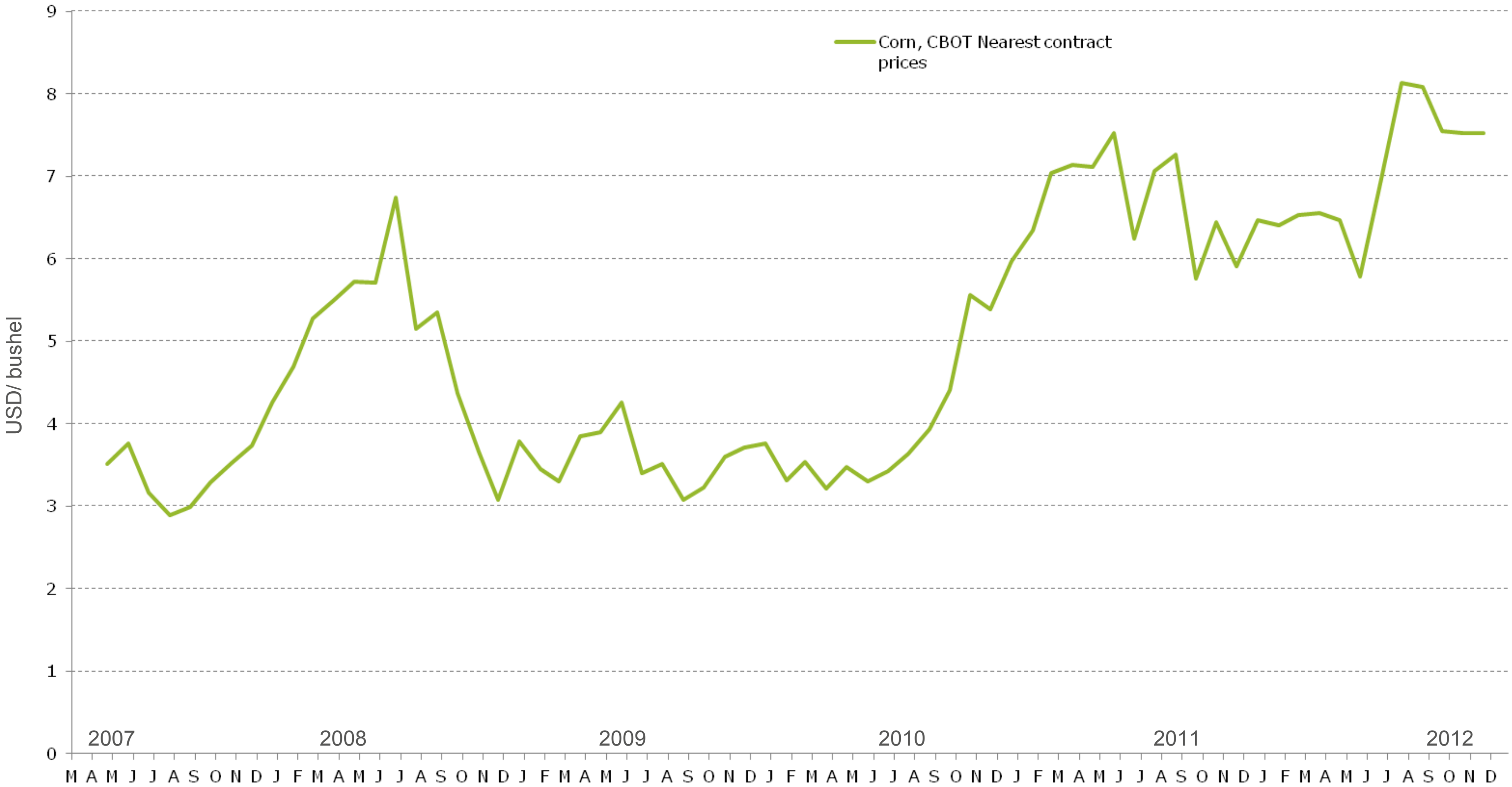
*Feedstock prices for US

Latest PET Prices Not available

Sources: ICIS Pricing; ICIS News

Sources: ICIS Pricing; ICIS News

Corn



*Feedstock prices for US

Sources: Euronext

Bio paraxylene and then ?

- Some companies state that bio paraxylene can be mixed with fossil based paraxylene. Mixing 50 kt of bio pX with 500 kt of fossil pX will allow the sale of 60 kt of green PET with certificates.

- Brandowners do not want this ! They want to print on the bottle that it has a certain measurable bio-based content.

- This means that isolated production campaigns will be required as well as separate feedstock, purification and product storage. This will add significantly to the cost.

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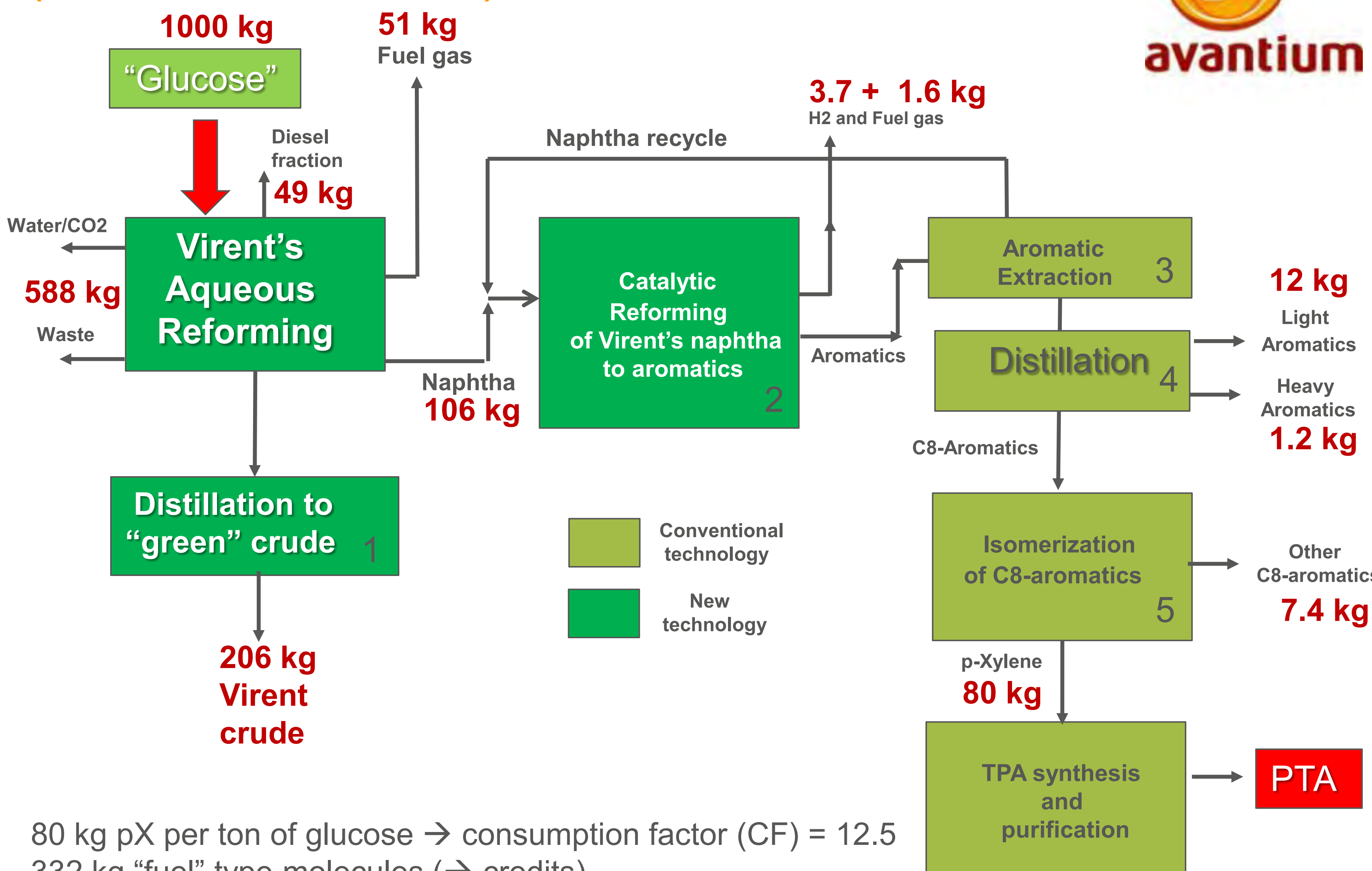
1. bio-based paraxylene

- **Virent Inc. (Madison, WI).** Aqueous phase reforming Hydrodeoxygenation of C5/C6 sugars to BTX. Theoretical hydrocarbon weight yield is 38%
- Gevo Inc. (Englewood, CO)
- Anellotech Inc. (Pearl River, NY)
- U of North Carolina at Chapel Hill (UNC)
- Micromidas Inc. (West Sacramento, CA)
- Avantium (Amsterdam) and The Coca-Cola Company (Atlanta, GA)

Virent mass balance
(Virent communicated data)

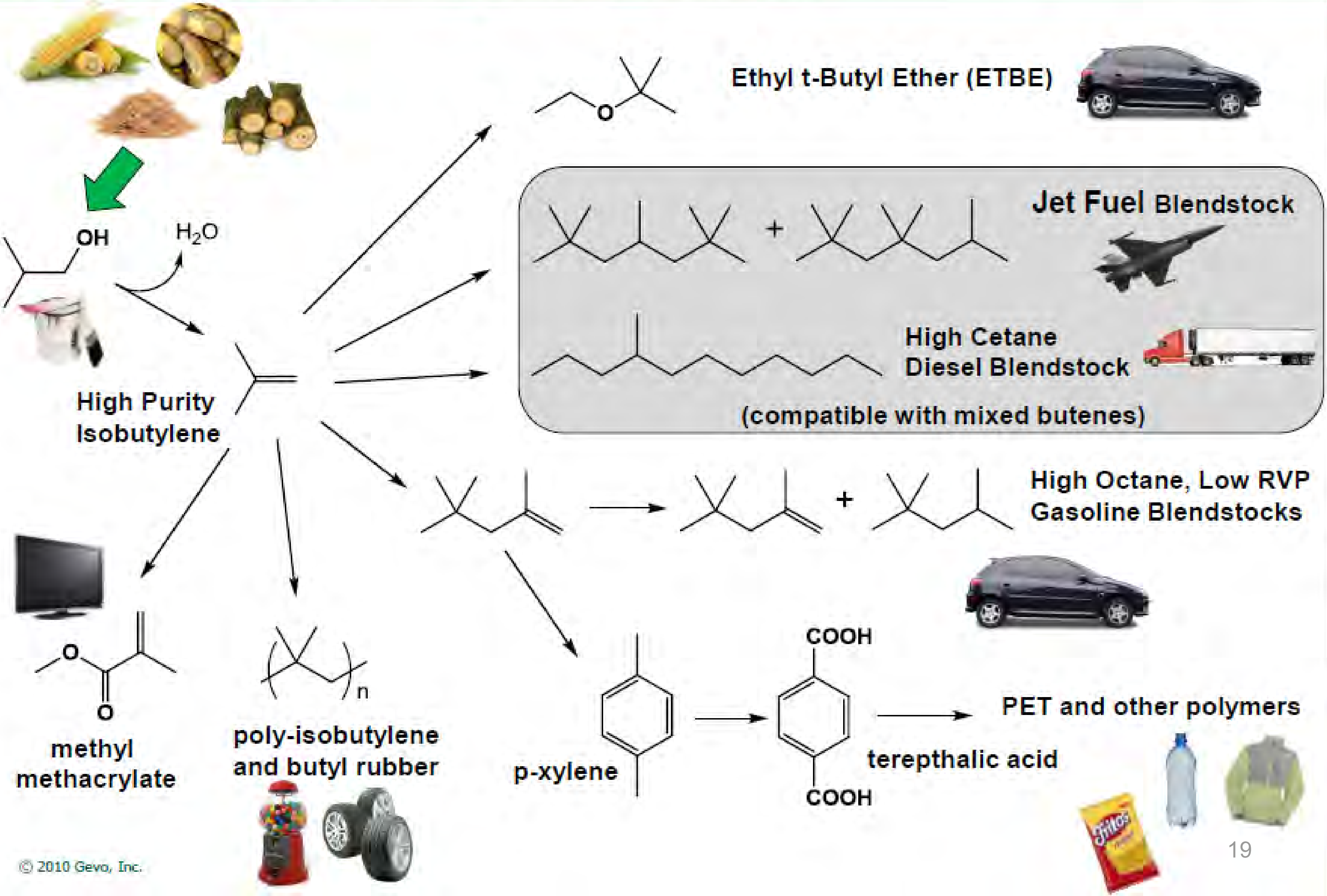


80 kg pX per ton of glucose → consumption factor (CF) = 12.5
332 kg "fuel" type molecules (→ credits)

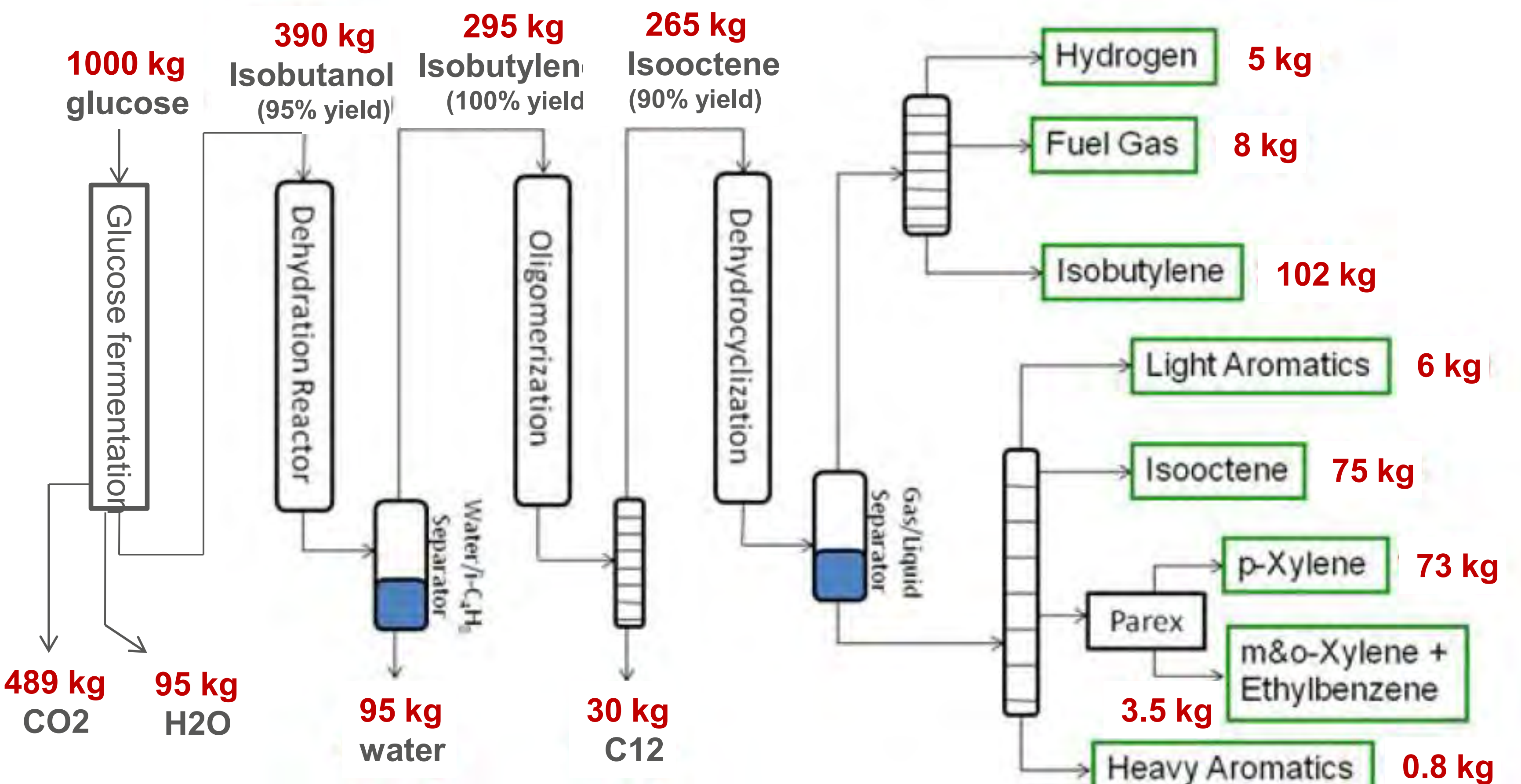
1. bio-based paraxylene

- Virent Inc. (Madison, WI).
- **Gevo Inc. (Englewood, CO).** Fermentation to i-BuOH; dehydration to i-butene; dimerization to i-octene; cyclodehydrogenation to pX.
- Anellotech Inc. (Pearl River, NY)
- U of North Carolina at Chapel Hill (UNC)
- Micromidas Inc. (West Sacramento, CA)
- Avantium (Amsterdam) and The Coca-Cola Company (Atlanta, GA)

Renewable Isobutylene Platform



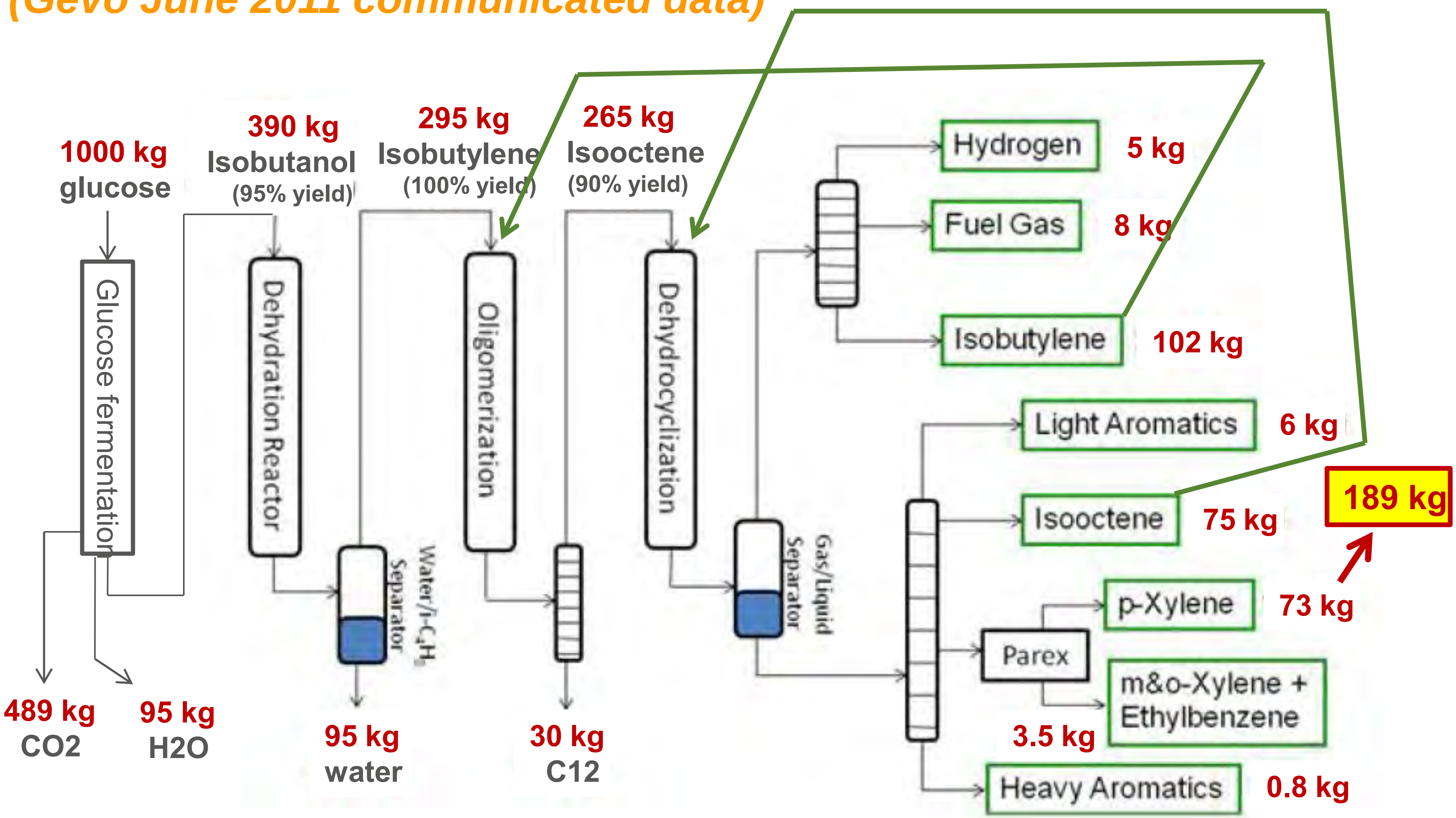
Gevo mass balance
(Gevo June 2011 communicated data)



73 kg pX per ton of glucose → consumption factor = 13.7

Gevo mass balance

(Gevo June 2011 communicated data)



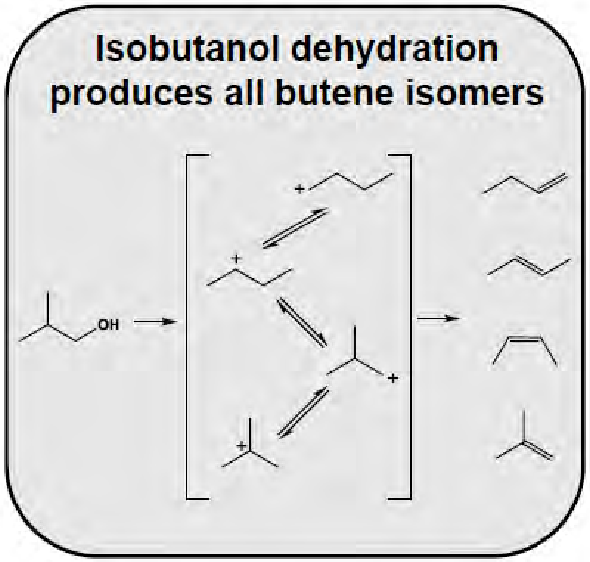
73 kg pX per ton of glucose → consumption factor = 13.7

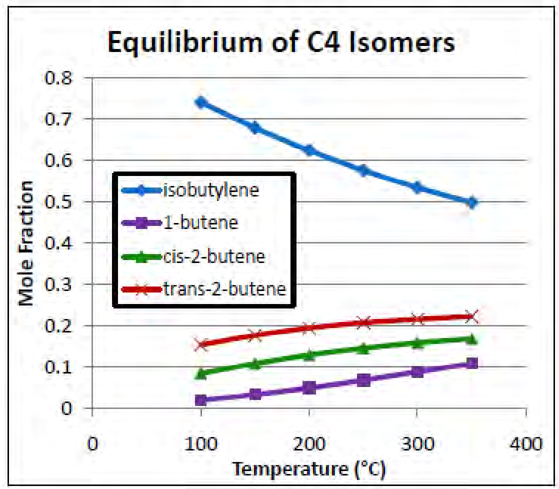
189 kg pX per ton of glucose → consumption factor = 5.3 (realistic ? See slide 20)

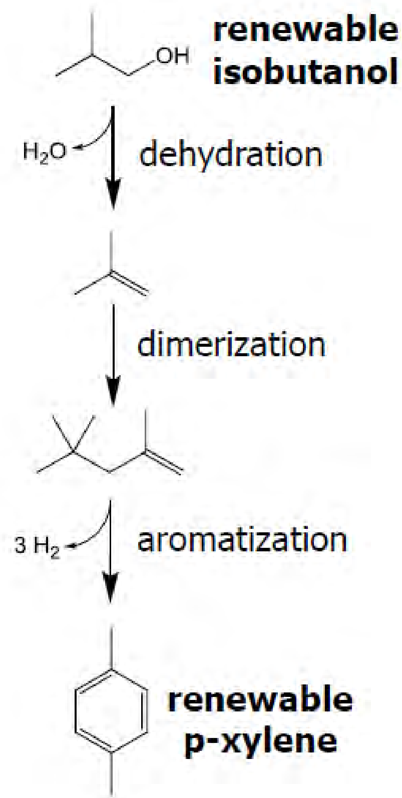
BUT

All numbers & percentages given are most optimistic scenario

→ iBuOH production and subsequent dehydration are not 100% selective (Gevo states that selectivity for both steps is “tunable”)





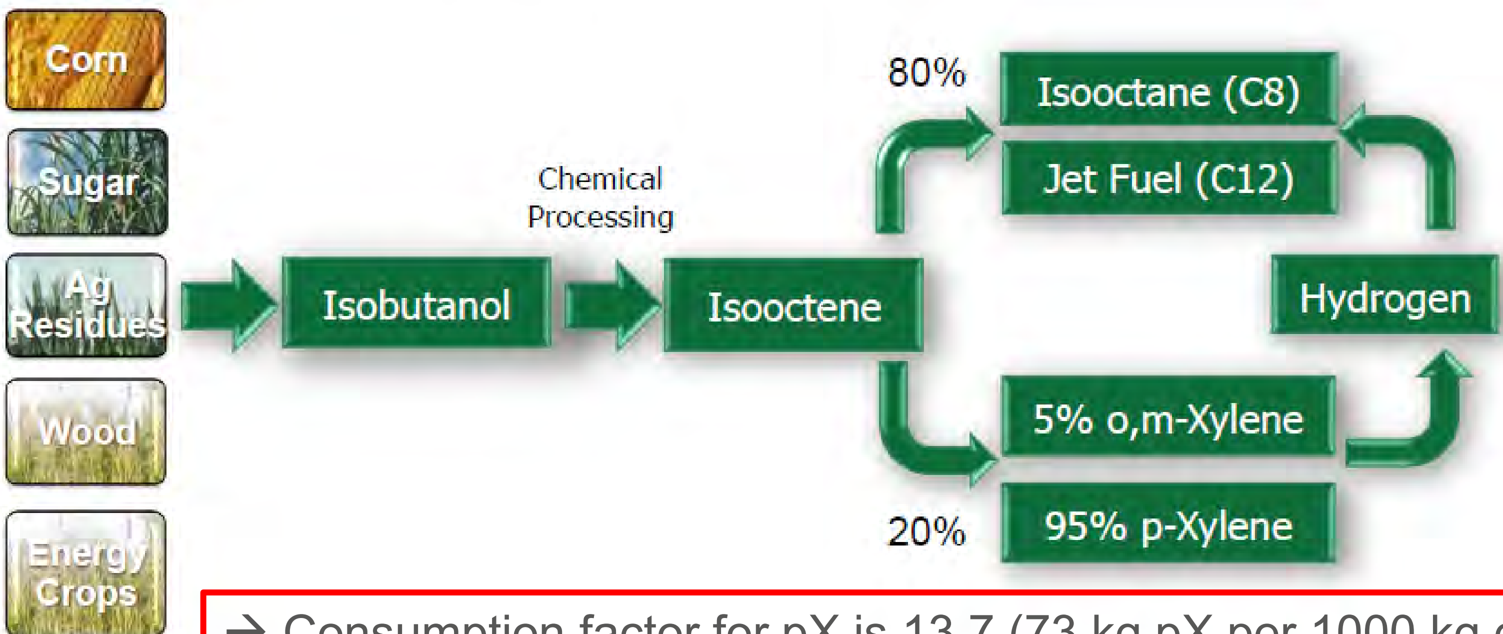


i-octene to pX is realistically much less selective than 75%

In the step isooctene to xylene, 3 equiv of hydrogen formed which hydrogenate the starting isooctene as communicated by GEVO:

Biorefinery Concept for Bio-p-Xylene Production

- **Yields to p-Xylene demonstrated. Hydrogen is a coproduct.**
- **Biobased hydrocarbons for fuels are in demand.**



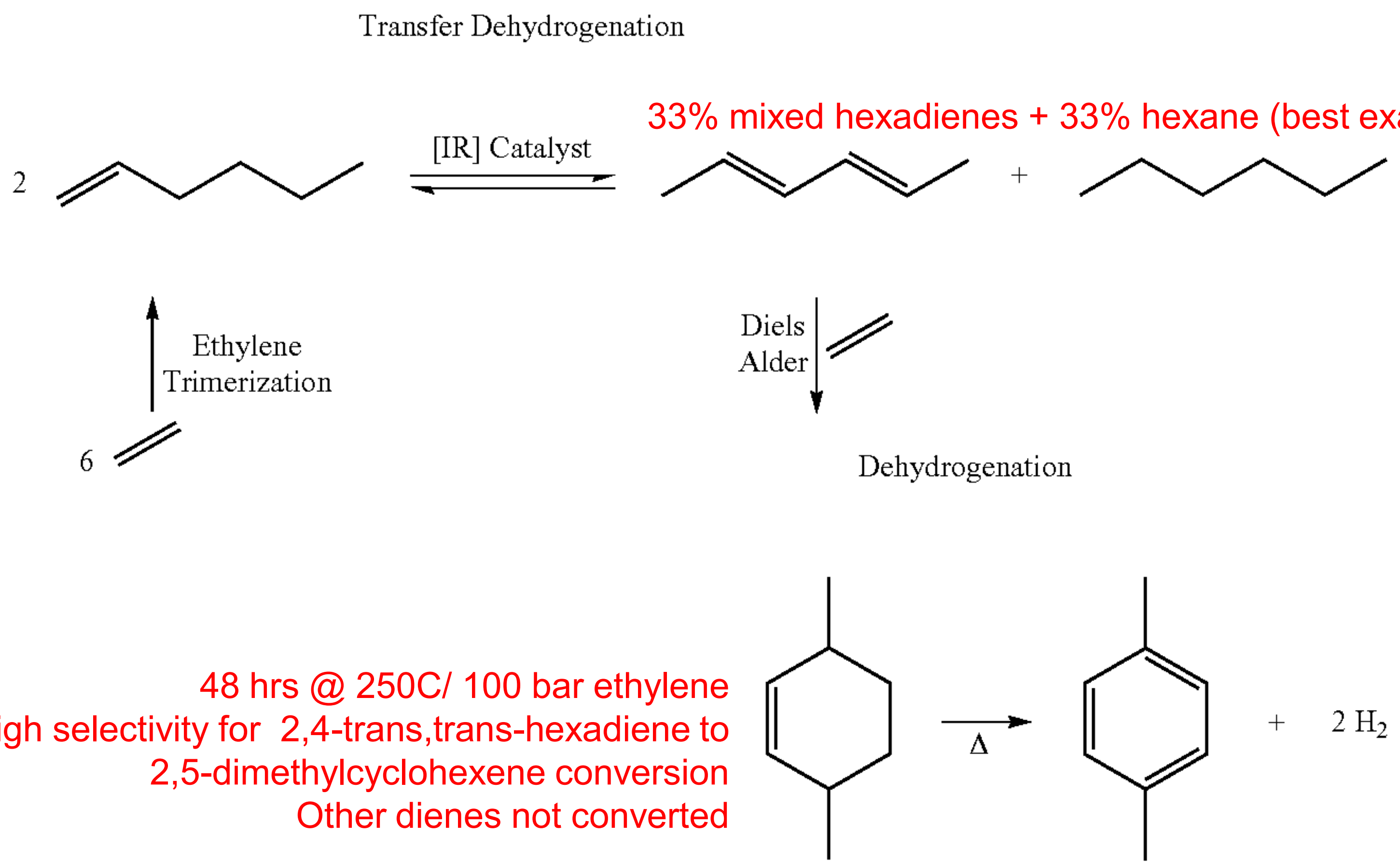
→ Consumption factor for pX is 13.7 (73 kg pX per 1000 kg glucose)
→ credits for 365 kg fuel as side product

1. bio-based paraxylene

- Virent Inc. (Madison, WI).
- Gevo Inc. (Englewood, CO).
- Anellotech Inc. (Pearl River, NY) – fast pyrolysis
- **U of North Carolina at Chapel Hill (UNC).** Trimerization of ethylene to hexene; disproportionation to hexane and hexadiene; diels alder with ethylene to dimethylcyclohexene; dehydrogenation to pX.
- Micromidas Inc. (West Sacramento, CA)
- Avantium (Amsterdam) and The Coca-Cola Company (Atlanta, GA)

From 4 ethylene (US2013/0237732)

Scheme 1. Synthesis of PX from ethylene



33% mixed hexadienes + 33% hexane (best example)

48 hrs @ 250C/ 100 bar ethylene
High selectivity for 2,4-trans,trans-hexadiene to 2,5-dimethylcyclohexene conversion
Other dienes not converted

- Even when all steps 100%, 3.5 tons of glucose are needed to produce 1 ton of ethylene.

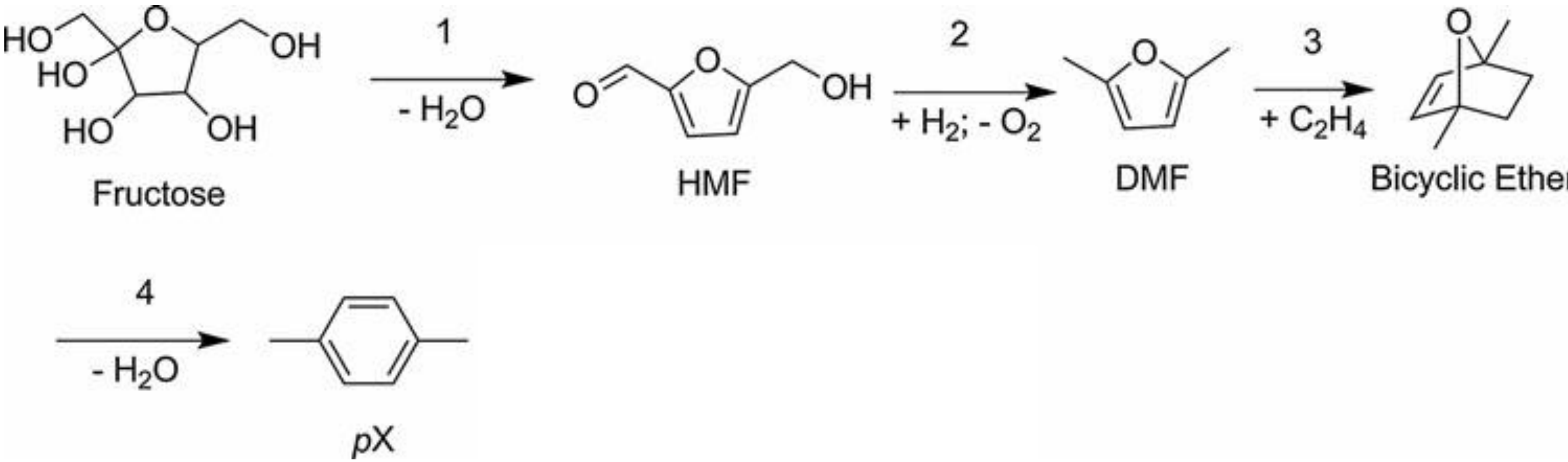
1. bio-based paraxylene

- Virent Inc. (Madison, WI).
- Gevo Inc. (Englewood, CO).
- Anellotech Inc. (Pearl River, NY) – fast pyrolysis
- U of North Carolina at Chapel Hill (UNC).
- Micromidas Inc. (West Sacramento, CA)

Diels Alder of dimethylfuran (DMF) to pX

- Toray Industries (Tokyo)
- UOP LLC (Morristown, NJ)
- UMass Amherst and U Delaware (Newark, DE)
- **Avantium (Amsterdam) and The Coca-Cola Company (Atlanta, GA)**

Diels Alder of Dimethylfuran (DMF) followed by in-situ dehydration to pX



- Avantium and The Coca-Cola Company. Patent to be published later this week.
- 88% yield of p-xylene at T=200^{0}C, t=24 hours (1 step !!)
- 70% yield of p-xylene at T=240 ^{0}C, t=8 hours (1 step !!)

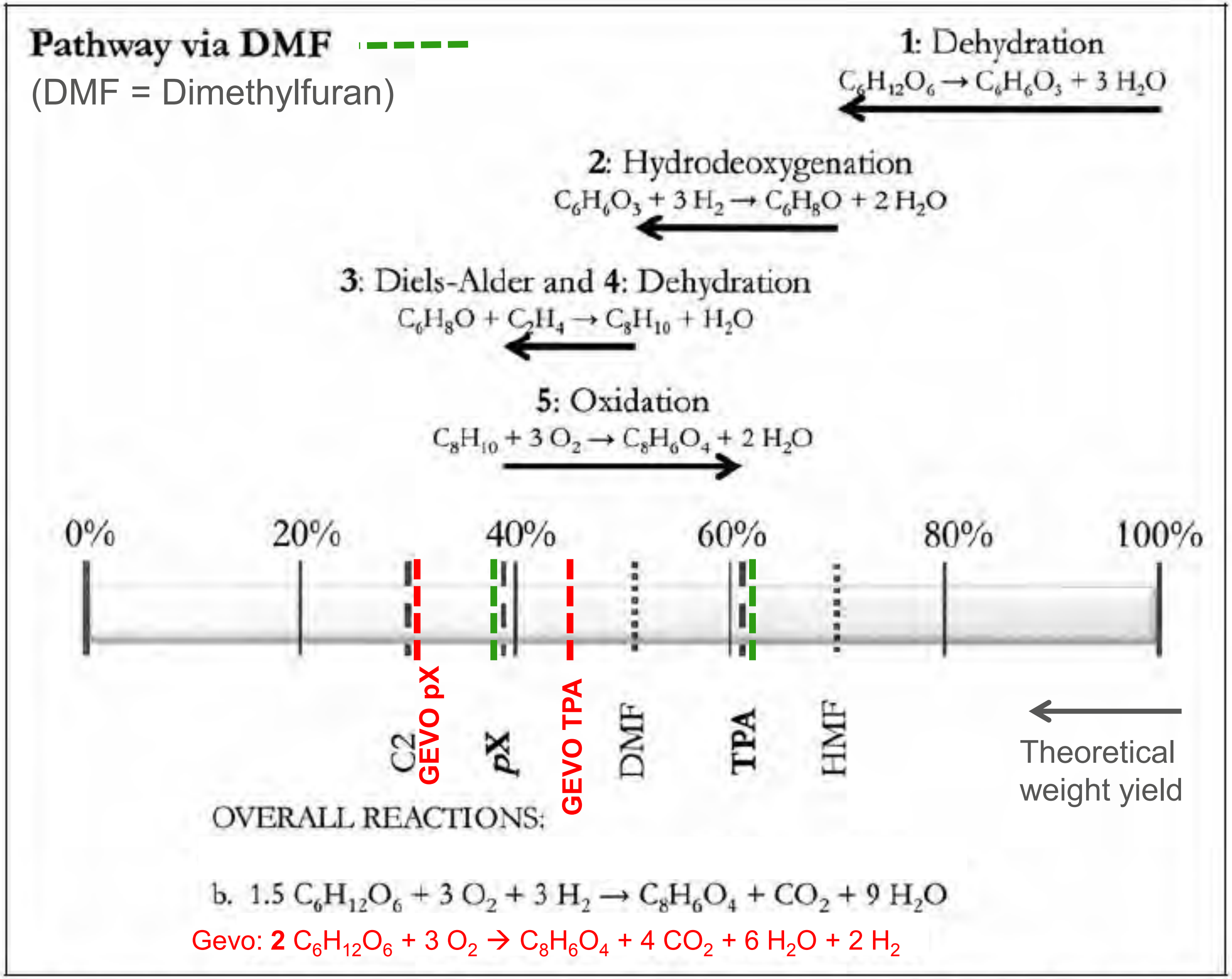
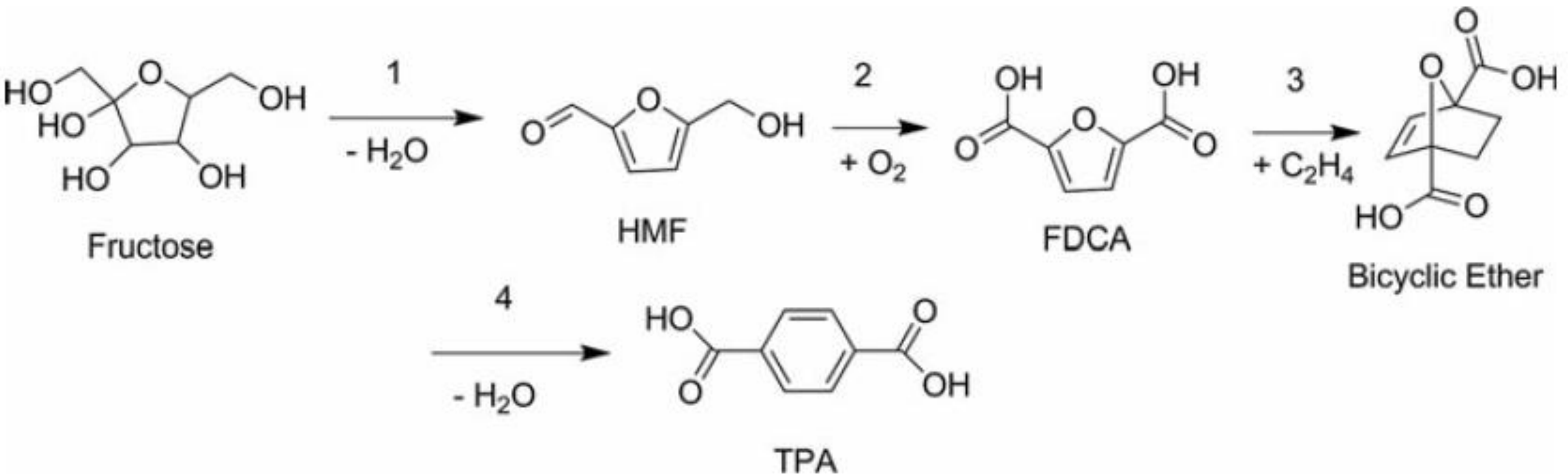


Fig. 7. Steps in the pathway from fructose to TPA via DMF, and theoretical yield of the various intermediates. Note that the use of external hydrogen in step 2 causes the yield of *p*X from fructose to increase to about 39%.
ethylene is biobased.

2. TPA from precursors other than pX

- Limonene (Sabic)
- Muconic acid (microbial synthesis): (Michigan State U and Draths (Amyris)

- **FDCA (**BP // **Avantium (Amsterdam) and The Coca-Cola Company**
  - **'Record' yield of 17% TPA from FDCA in one step ! (patent to be published this week) – Initial BP patent reported 0.1% yield.**



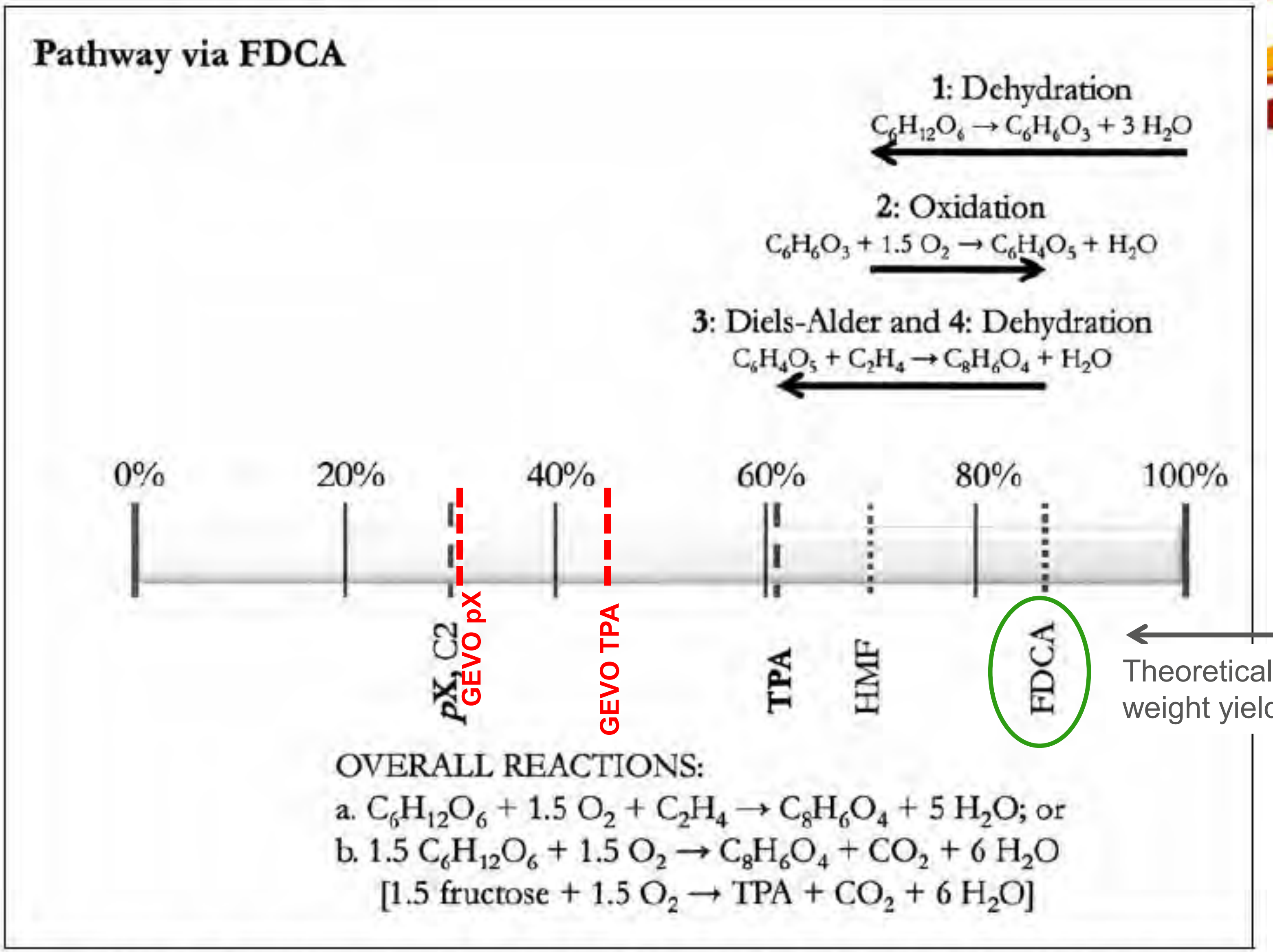


Fig. 10. Steps in the pathway from fructose to TPA via FDCA, and theoretical yield of the various intermediates. The overall reactions are also noted: a) ethylene is fossil-derived; and b) ethylene is biobased.

3. Direct conversion

- Via (GMO) bacteria from sugars to TPA (e.g. Genomatica)

See:
WO2011/094131
WO2013/109865

4. From Lignin

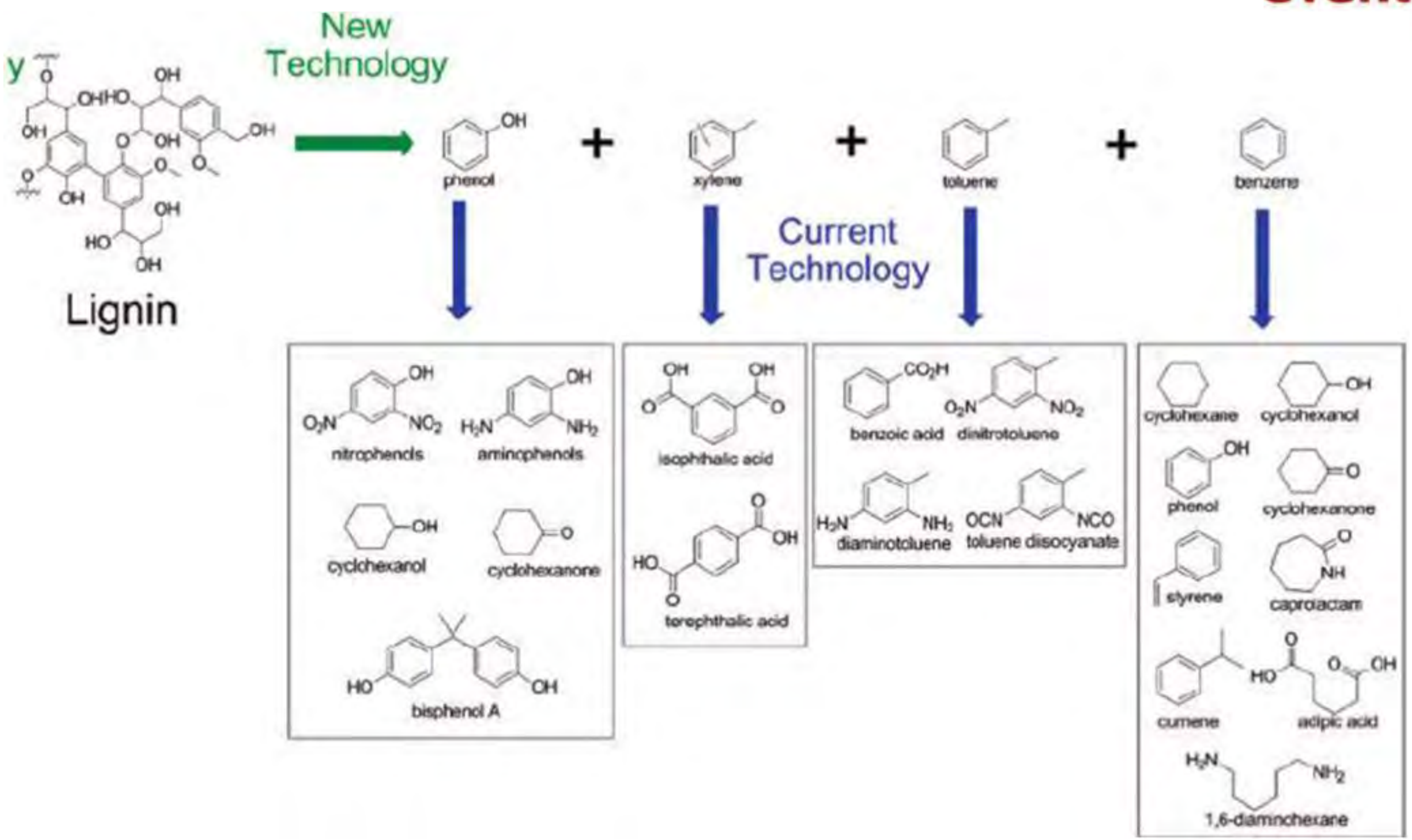


Figure 15. Valuable products potentially obtained from lignin with development and integration of new and current technology.[6,67]

(Zakzeski/Weckhuysen: Chem. Rev. 2010, *110*, 3552–3599 and references therein)

Catalytic Conversion of Lignin for the Production of Aromatics

De Katalytische Omzetting van Lignine voor de Productie van Aromatische Chemicaliën

(met een samenvatting in het Nederlands)

Proefschrift

ter verkrijging van de graad van doctor aan de Universiteit Utrecht op gezag van de rector magnificus, prof.dr. G.J. van der Zwaan, ingevolge het besluit van het college voor promoties in het openbaar te verdedigen op woensdag 11 september 2013 des ochtends te 10.30 uur

door

Anna Louise Jongerius

geboren op 1 oktober 1985 te Zaandam

Jongerius thesis summary

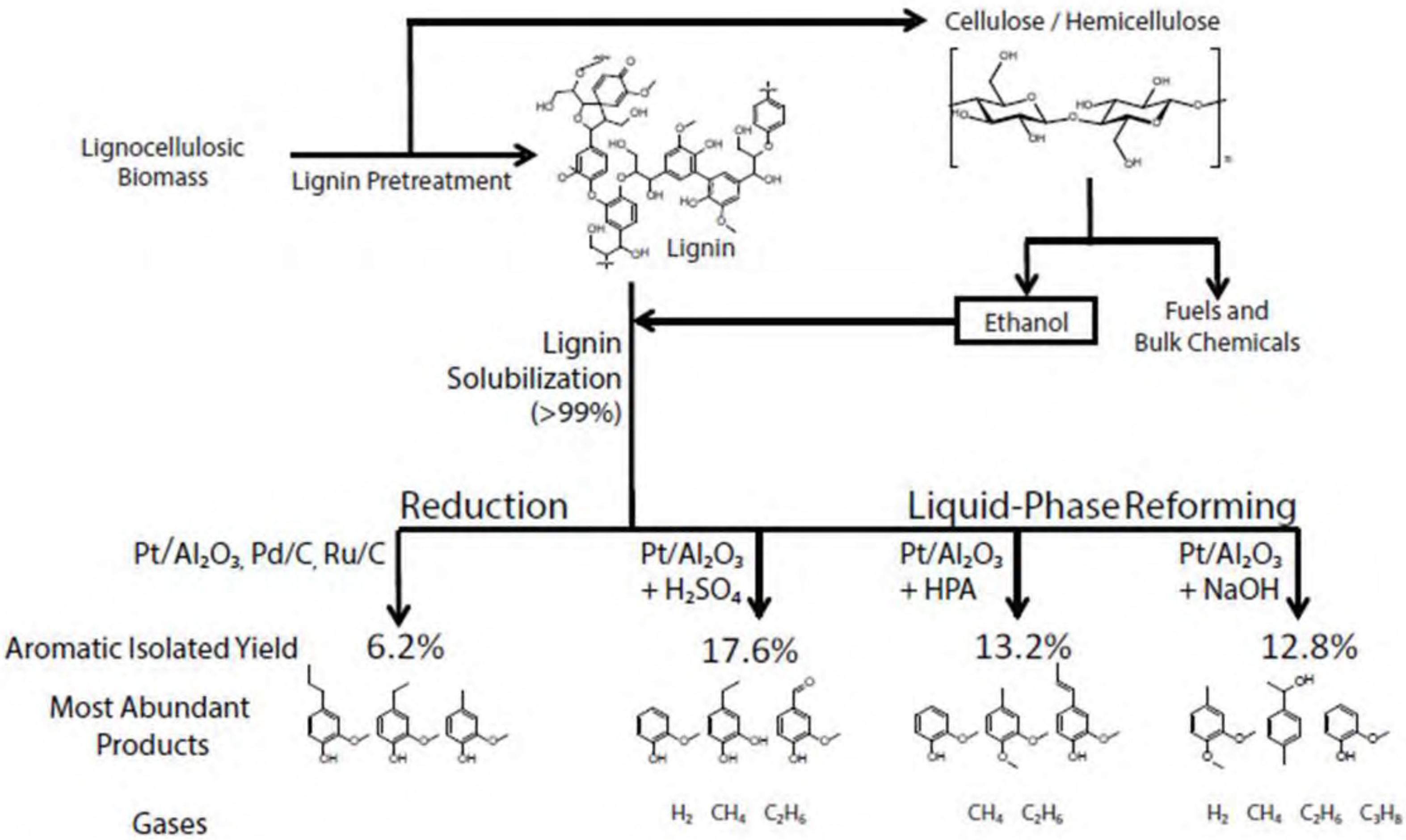


Figure 3.1: Valorization of lignin via reduction or liquid-phase reforming produces valuable aromatic chemicals. The yields and products shown are obtained with the kraft lignin.

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Conclusions

- It will be very difficult to produce p-xylene or TPA in a way that is cost competitive with conventional TPA (economy of scale !).
- As bio-TPA is identical to fossil based TPA, any higher prices will need to be absorbed by a "green premium".

- Is it logic to produce a typical fossil based molecule p-xylene (C_8H_{10}), a hydrocarbon C_xH_y, from carbohydrates (typically $C_6H_{12}O_6$) ??
  At least 3.5 tons of glucose needed (in reality much more) to produce 1 ton of pX.

- Are there alternatives for TPA that are more logical when producing from biomass ?
  - The cyclic structure of TPA is giving rigidity and is a requirement for producing a polyester with desired performance

- Isosorbide (diol)
- Furandicarboxylic acid (FDCA) - Why convert it to TPA to make PET and not use FDCA to make PEF ?

Options overview by atom efficiency

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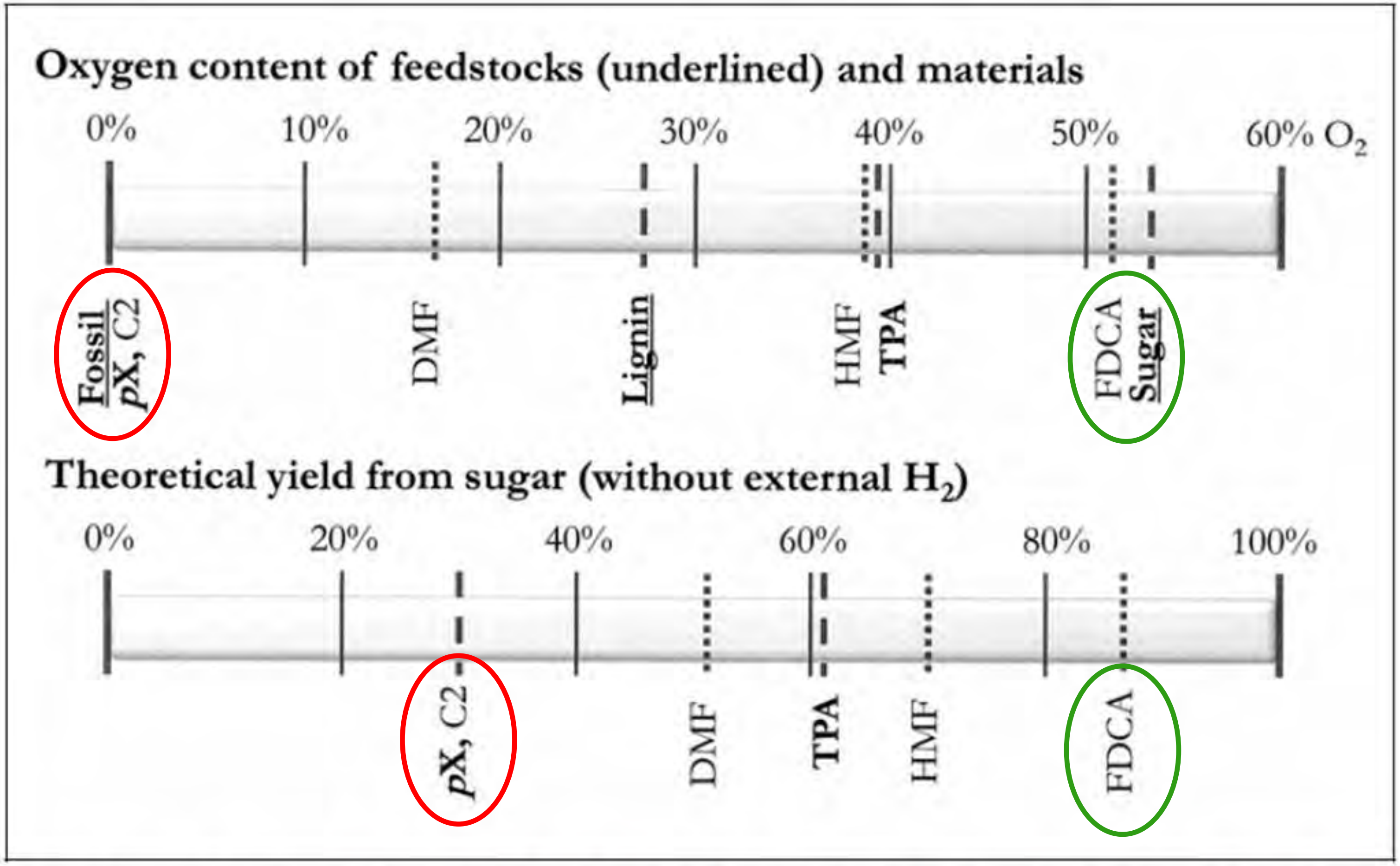
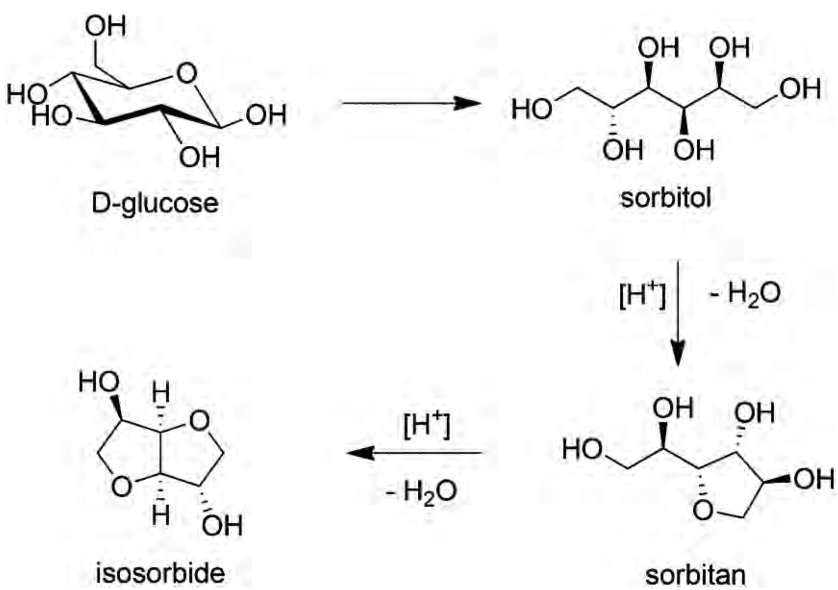
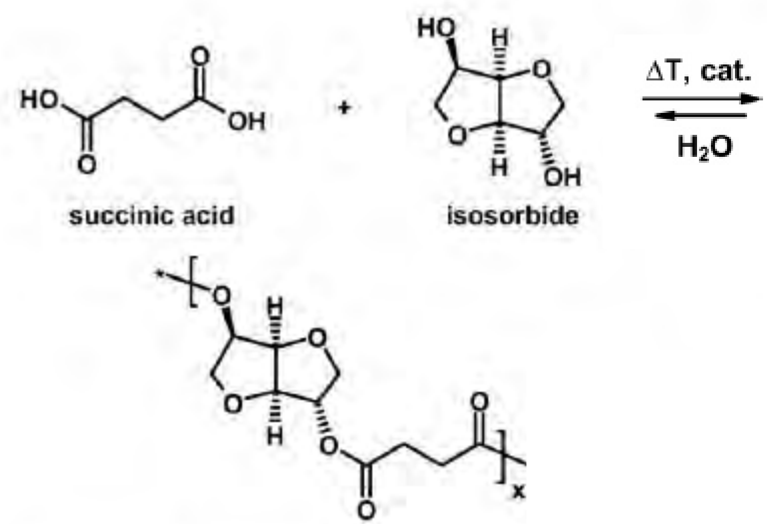


Fig. 3. Oxygen content of feedstocks and materials, and theoretical yield of materials from sugar (without use of external hydrogen); C2 is ethylene.

Isosorbide (IS)

Noordover et al.
Progress in Organic Coatings **65** (2009), 187-196





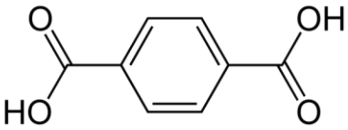
Scheme 2. Renewable co- and terpolyesters based on isosorbide and succinic acid

IS disadvantages: (stereo)isomers, secondary alcohol → slow esterification

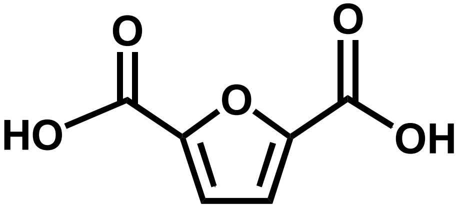
FDCA

"The Sleeping Giant"

Bio-based PTA



Bio-based FDCA



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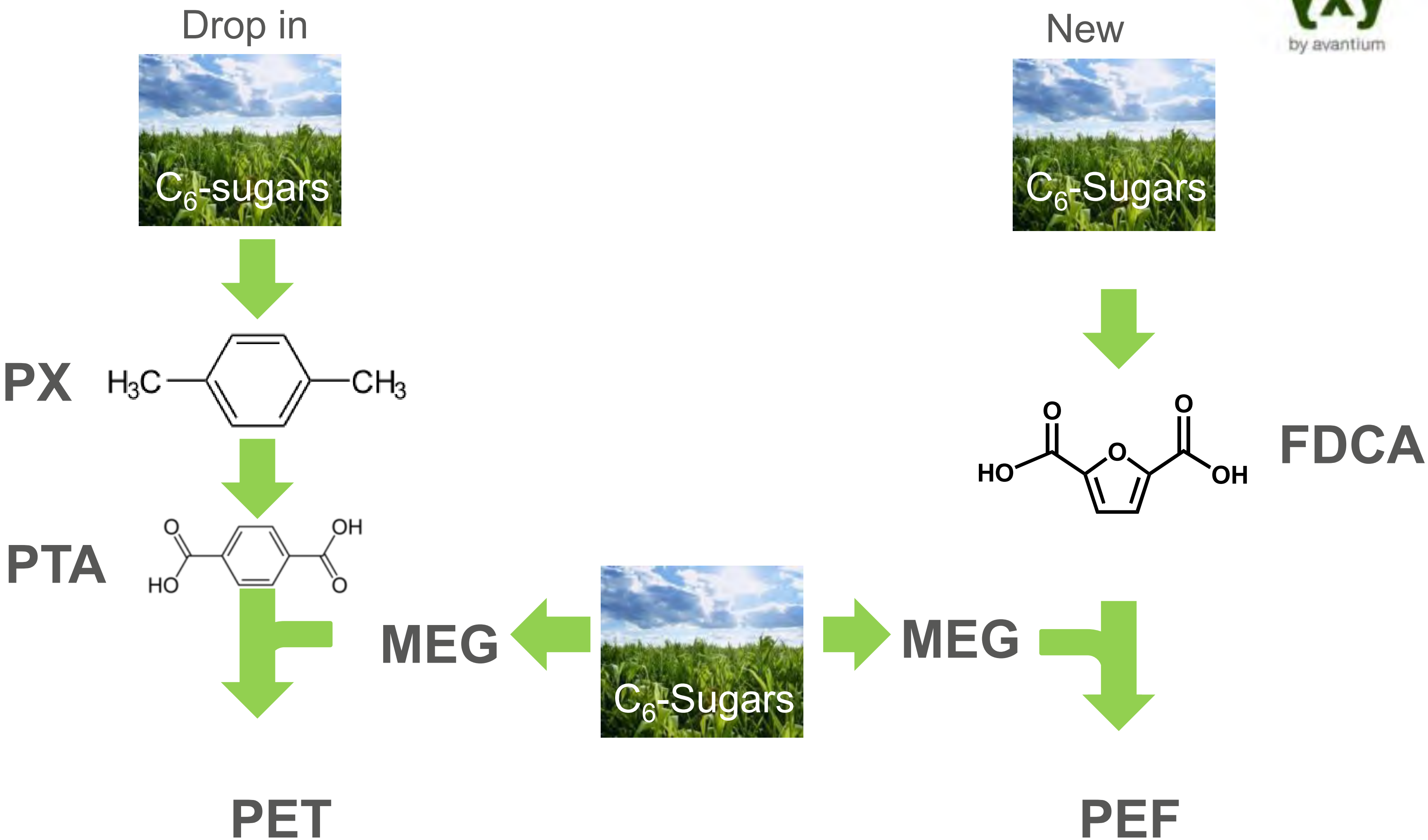
The road to 100% biobased polyesters



YXY: technology for the next generation polyester

Feedstock → Process → Products




ALPLA

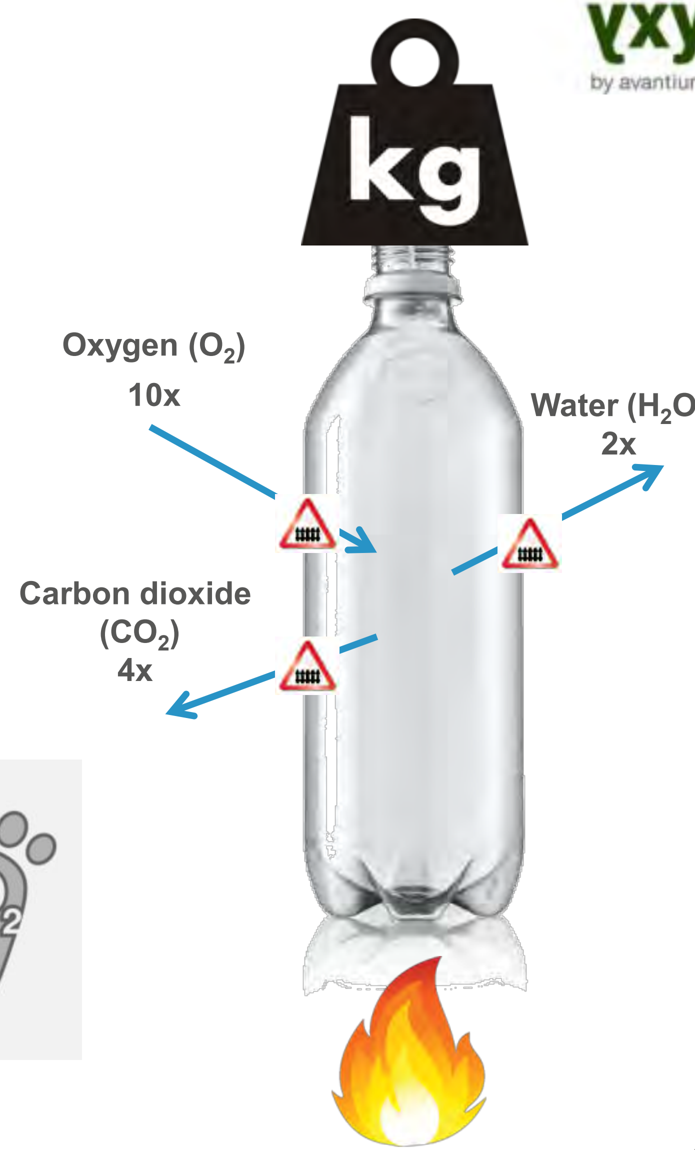
wifag//polytype
brilliance on top

Feedstock flexibility | Cost competitive | Performance

Sustainability

PEF: the Next Generation Polyester

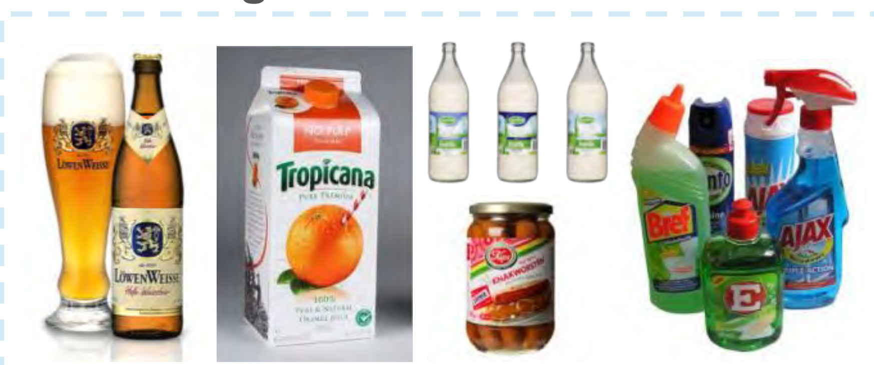
- Superior performance over PET:
  - O_2 barrier: 10x improvement
  - H_2O barrier: 2x improvement
  - CO_2 barrier: 4x improvement
- Improved Thermal Stability
  - Tg: ~88°C → 12°C higher than PET
- Excellent Mechanical Properties:
  - Tensile Modulus PEF : 1.6* PET
- Significant reduction in carbon footprint
  - 70% lower carbon emission
  - 65% lower NREU

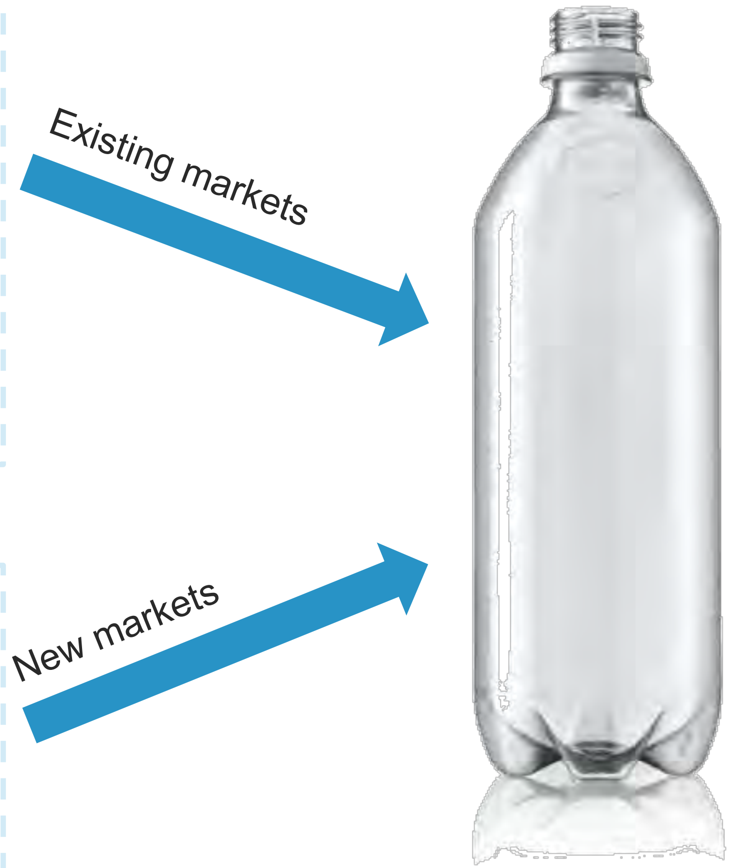


Superior PEF Performance enables Penetration of Existing and New Markets

Simplification of existing packages

Potential growth markets





Bottle Partners – Addressing all market segments

ALPLA

- Leading converter
- PEF bottles for: food, home care/ personal care, alcoholic beverages

The Coca-Cola Company

- #1 CSD company
- 1.8B servings per day
- PlantBottle™ in 2010

DANONE / **yxy by avantium**

- #1 Water company in Europe
- Bouteille Végétale

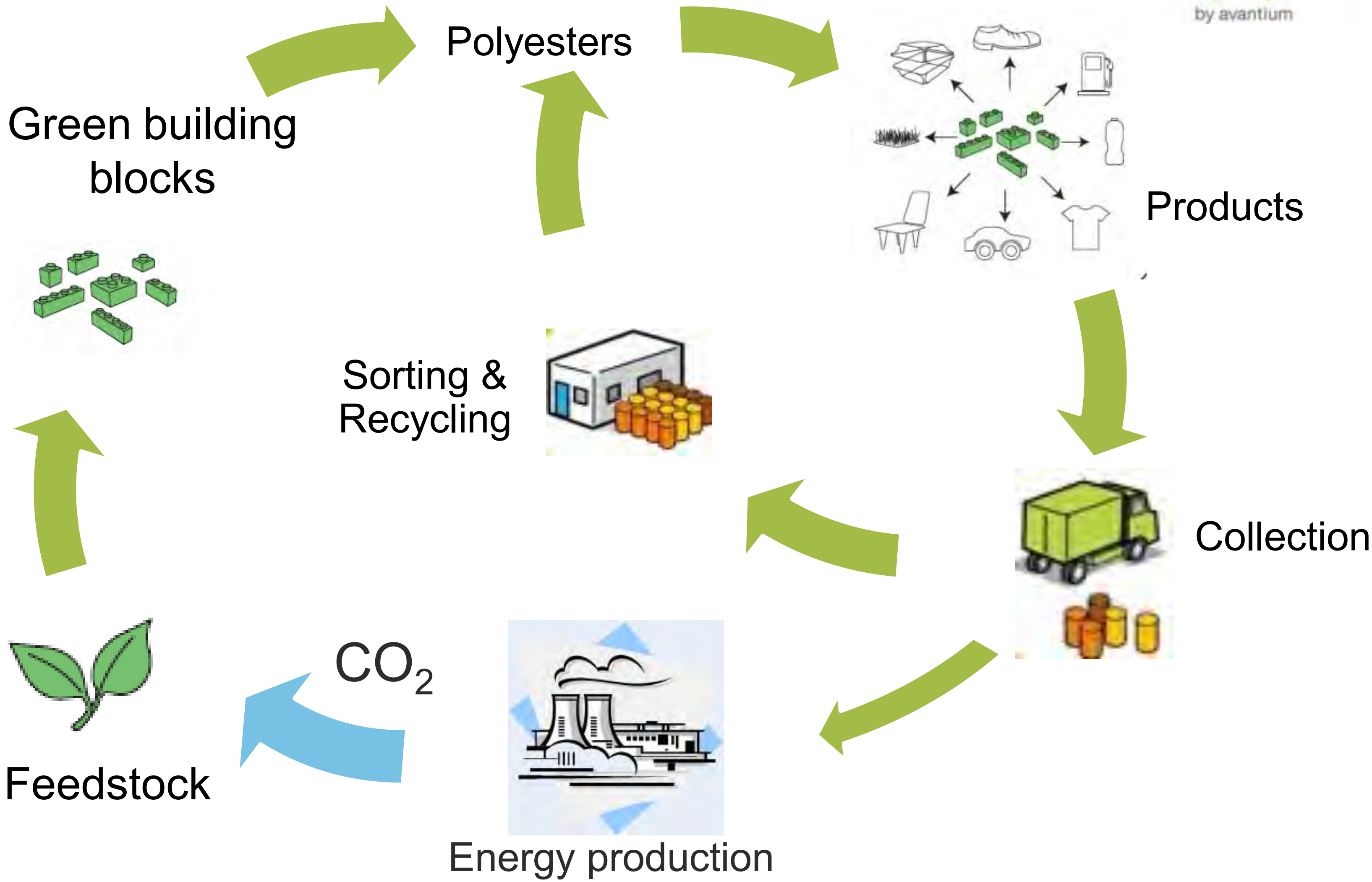
- Creating a market pull
- De-risk supply chain for upstream partners: feedstock suppliers, resin companies, recyclers

Safety

- Food Contact Safety studies being finalized:
  - All data indicates the polymer and monomer are safe
  - EFSA petition filed in 2013
  - FDA registration under preparations

- Safety studies FDCA monomer to support REACH registration:
  - Monomer is demonstrated to be safe
  - REACH registration completed 2013

The goal is 100% biobased and 100% recyclable polyester



Recycling

- Goal: find the optimal end-of-life solution for PEF polymer
  - Close collaboration with recycling community

- End goal: PEF to PEF recycling :
  - Mechanical recycling: demonstrated (similar to PET)
  - Chemical recycling: demonstrated PEF depolymerization to monomers

- Conducting sorting trials at waste separation & recycling sites
  - Different infrared profile than PET or any other known plastic
  - Food grade approved recycling companies have sorting capability

- Transition period: PEF in PET recycle streams:
  - Conducting trials of potential effects of PEF in rPET streams and PET in rPEF streams

Next PEF Target Applications

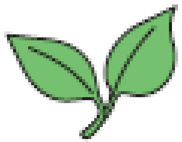
Films, sheet and thermoforming

- Thin films for flexible packaging
- Sheet for thermoforming of containers, trays and cups
- Films for electronic applications

Fiber

- PEF fibers for apparel, carpets, non-wovens, furnishings technical fiber applications

First PEF T-shirts of 100% recycled PEF bottles



100% Biobased

Conventional polyester spinning technology

Made from 100% Recycled PEF

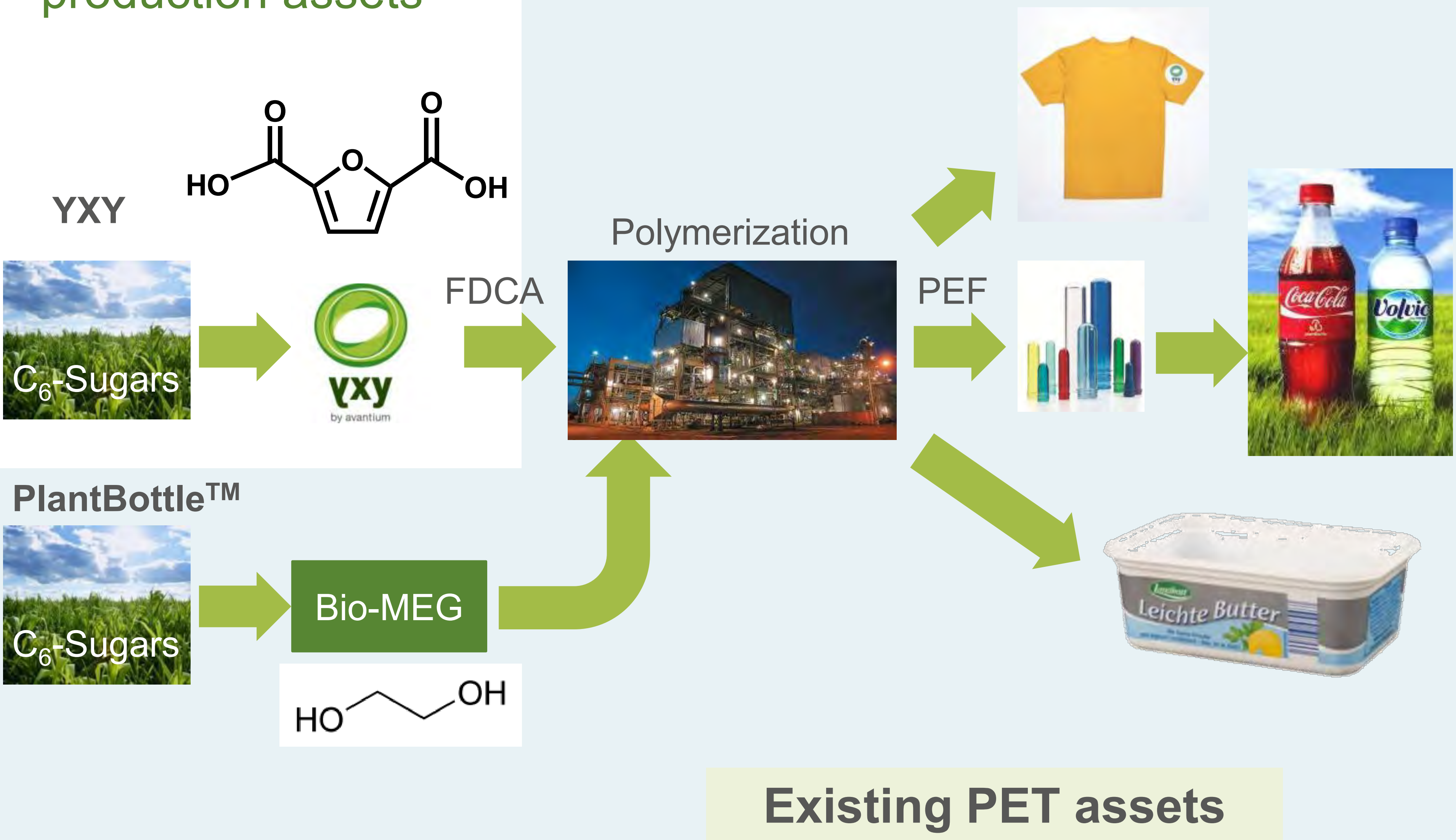
Conventional polyester dyeing technology

New partnership for PEF Thermoforming

wifag//polytype
brilliance on top

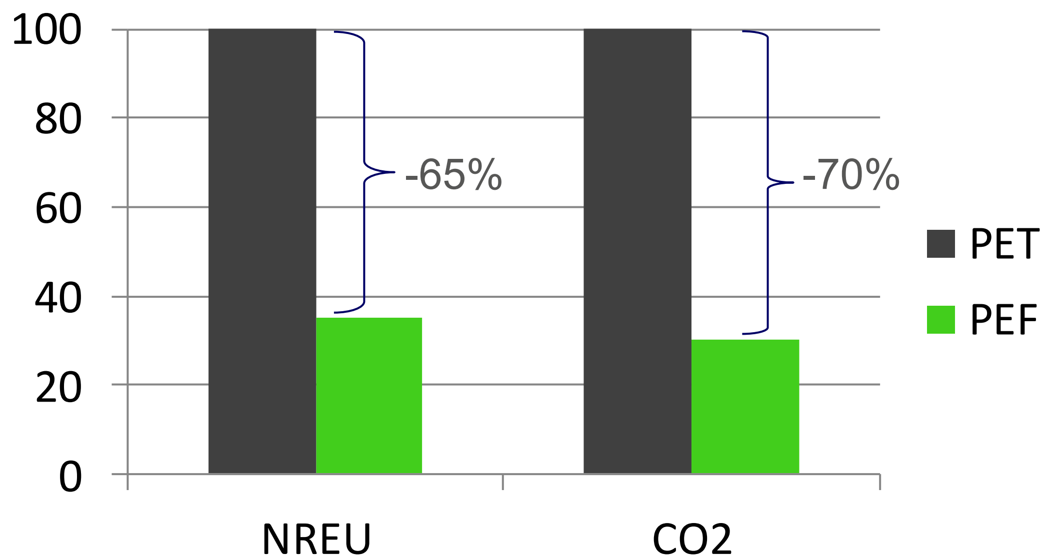
- Wifag//Polytype leading equipment maker addressing entire range from sheet extrusion, to thermoforming to decoration
- Thermoforming is potential outlet for recycled PEF bottles

PEF can be produced and processed in existing PET production assets



Carbon Footprint

- Study by the Copernicus Institute (Utrecht University; Patel & Faaij)
- Comparison of PEF versus PET (revised 2010 PET data set)
- Cradle -to-grave framework (oil well to PET / acre to PEF)



- Significant reduction in NREU and CO_2
- More reductions expected through process improvements

Agenda

- Company Profile and Business Model
- YXY Market and Process
- **YXY Pilot Plant and Commercialization**

Technology

- Chemical-catalytic process to convert C6-sugars into FDCA
- Constructed YXY pilot plant at the Chemelot site in Geleen, the Netherlands
- Successfully scaled from lab to pilot plant
- “Prove the process” (process optimization)
- “Prove the products” (application development)

Scaling up from Lab – to Industrial scale

2005 — Start YXY development on Lab scale

2011 — Opening Pilot plant Geleen (20t p.a.)

2015 — Start construction 1st Commercial FDCA plant (50kt p.a.)

2017 — Start production 1st Commercial FDCA plant (50kt p.a.)

2019 — Construction1st Industrial FDCA plant (300-500kt p.a.)

Summary

- **PEF: The Next Generation Polyester**
  - Superior **barrier** performance
  - Excellent **mechanical** properties
  - Improved **thermal** stability
  - Reduced **carbon footprint**
  - **Cost** competitive at industrial scale

- Collaborating with The Coca-Cola Company, Danone, ALPLA, and Wifag//Polytype to launch the first PEF packaging on the market in 2017

- New partnerships to develop applications for PEF films and PEF fibers

- Preparation of first commercial FDCA plant (50kt) - ongoing

- FDCA and PEF to hit the market in 2017: stay tuned!