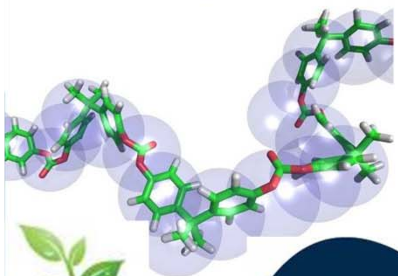
Bio-raffineries: les ressources pour les polymères de demain



A la Recherche de Structures Aromatiques ou Equivalentes

pour polyesters, polyamides et thermodurcissables

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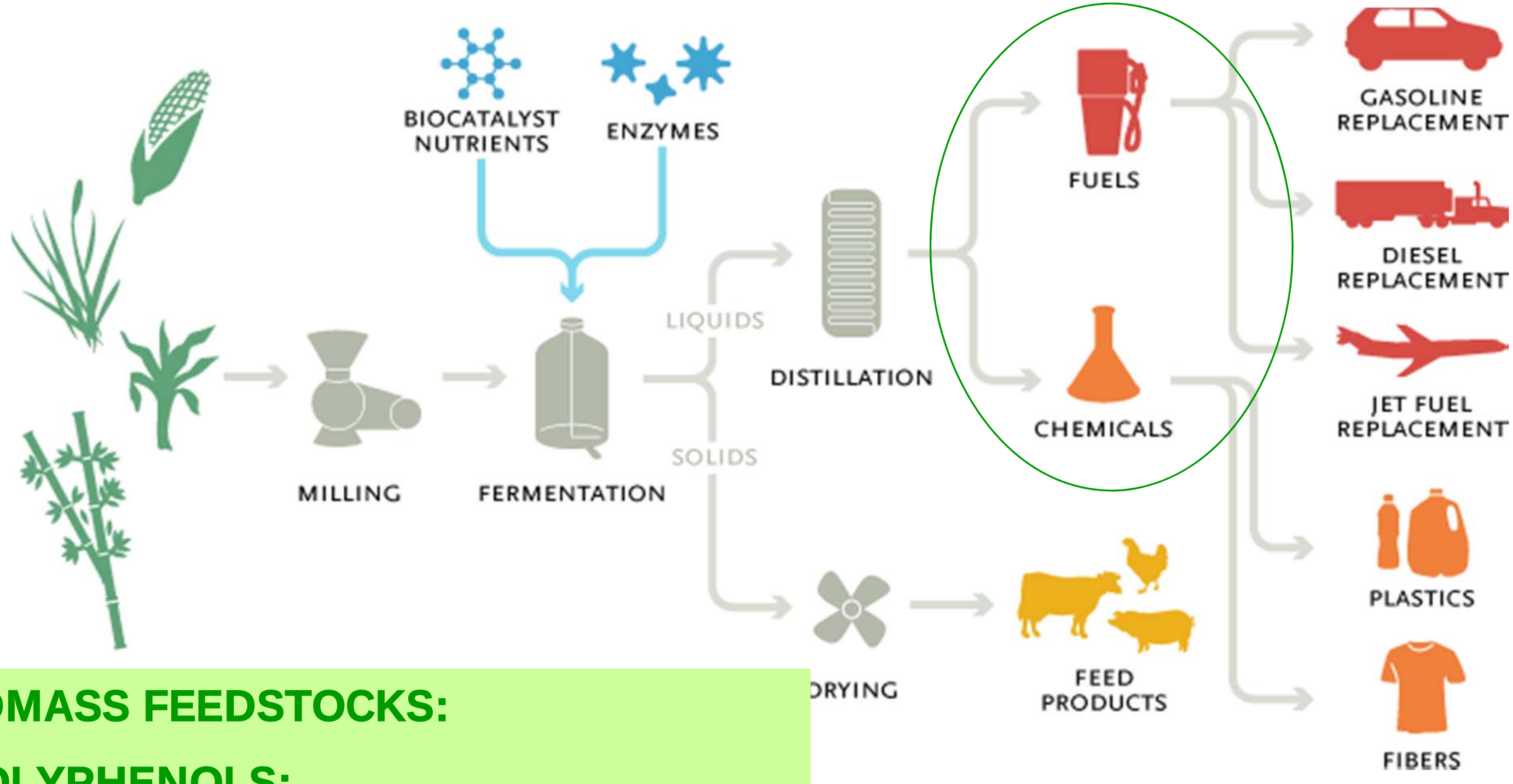
OUTLINE

Bio-raffineries: les ressources pour les polymères de demain

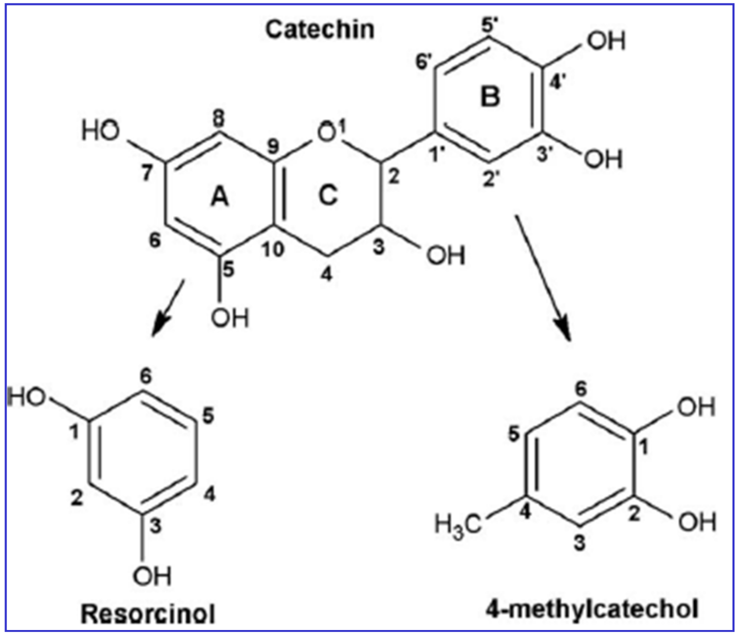
1) *A la Recherche de Structures Aromatiques*



BIOMASS FEEDSTOCKS:

- **POLYPHENOLS;**
- **LIGNOCELLULOSIC FEEDSTOCK [1-4];**
- **TERPENE FEEDSTOCK.**

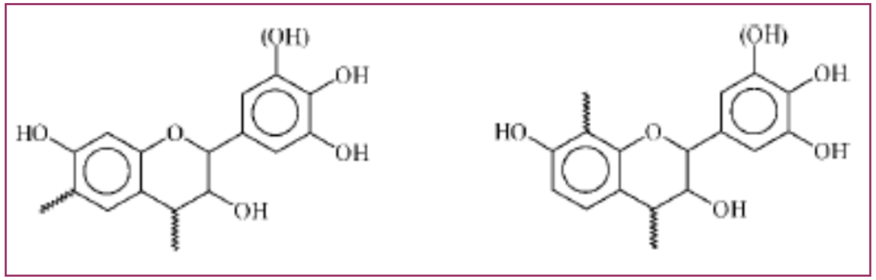
POLYPHENOLS

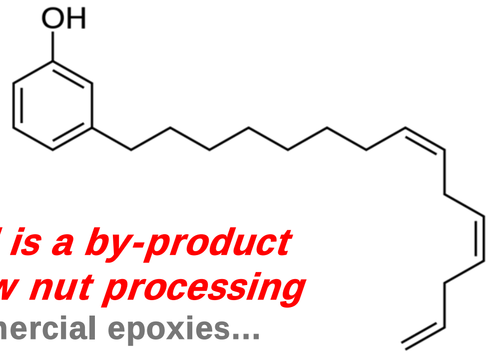


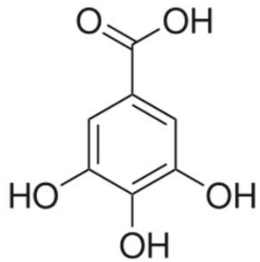
Polyphenols, and more specifically condensed tannins, extracted from wastes produced by the wood and wine industries …

can be an alternative to BPA to produce epoxy resins

2 typical monomer units found in tannins



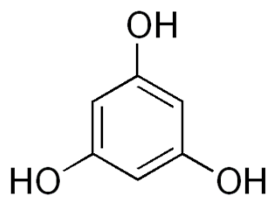




Cardanol is a by-product of cashew nut processing

… Commercial epoxies…

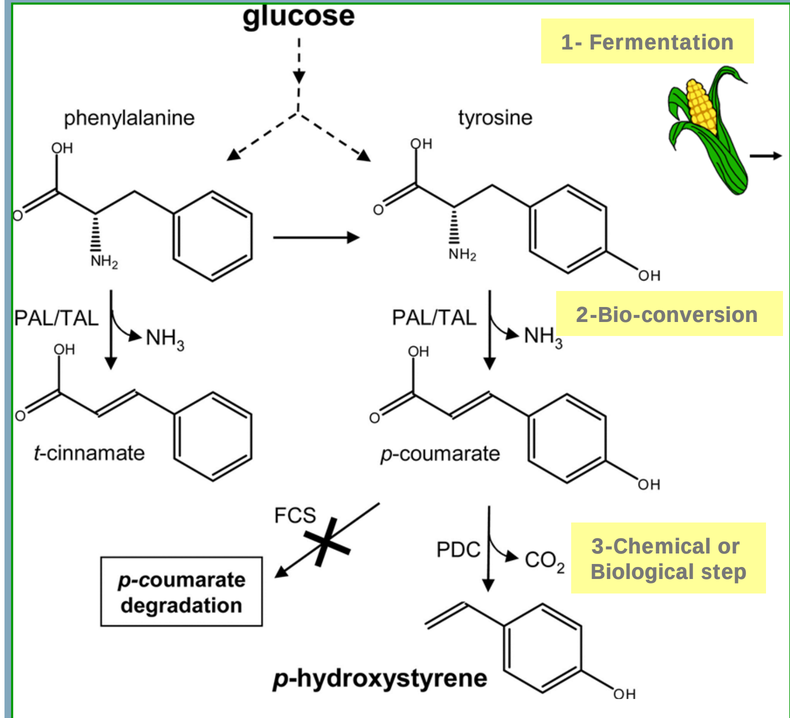
Gallic acid found in a lot of plants, tea leaves, oak bark, etc.



Phloroglucinol. Tannins from brown algae

Nouailhas et al J. Polym. Sci. Part A, Vol. 49, 2261–2270, 2011
A. Gandini, Polymers from Renewable Resources, *Macromolecules, Vol. 41, No. 24, 2008*

COUMARIC ACID: a Platform for Chemicals?



Verhoef et al. (TNO), Appl. Environ. Microbiol. ***2009***, *931*

Microbial production of p-hydroxystyrene (4-vinyl phenol) from Glucose

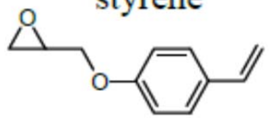
1- Glucose is converted to the aromatic amino acid L-tyrosine,
2- Which is deaminated by an enzyme to yield p-hydroxycinnamic acid (p-HCA) or Coumaric acid
3- Subsequent decarboxylation of p-HCA gives rise to p-HS.

Challenge for bio-production: TOXIC to most microorganisms...
Choice of organic solvent tolerant to microorganisms (DuPont;TNO)

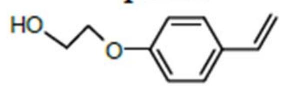
APPLICATIONS:

Photoresists;
Polymer coatings;
Adhesives;
Polymer Blends;
Polymer/ceramic composites
...

p-glycidyloxy-styrene



pHES



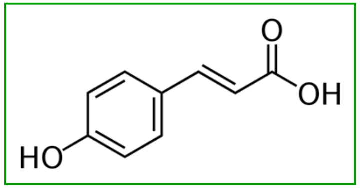
A novel monomer for powder coatings?
(reaction with a diisocyanate)

Some Patents and Publications from DuPont:

- « *Production of p-hydroxystyrene and other multifunctional aromatic compounds using 2-phase extractive fermentation* » WO2004092392 A2
- « *Preparation p-hydroxystyrene by biocatalytic decarboxylation of p-HCA in a biphasic reaction medium* » WO 2004092344 A2.
- « *Method For Preparing Hydroxystyrenes and Acetylated Derivatives thereof* » US20050228191(A1)
- "*Methods for preparing polymers from phenolic materials and compositions relating thereto*". US2008/0033126 A1
- « *A method for preparing glycidyloxystyrene monomers and polymers thereof* » WO2008/085513 A1

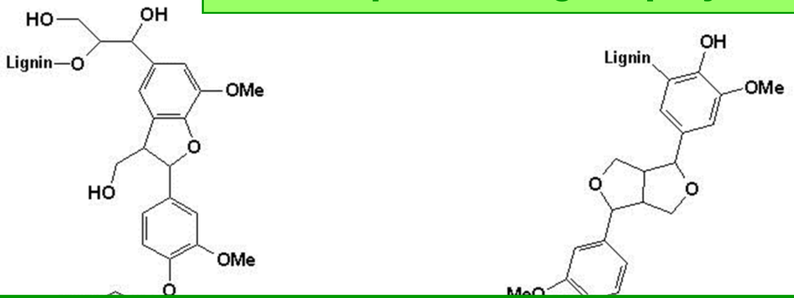
F. S. Sariaslani et al: Metabolic Engineering, 9,268–276, 2007; Enzyme and Microbial Technology, 41,413–422, 2007
Organic Process Research & Development, 11, 278-285, 2007

(POLY)PHENOLS and LIGNIN

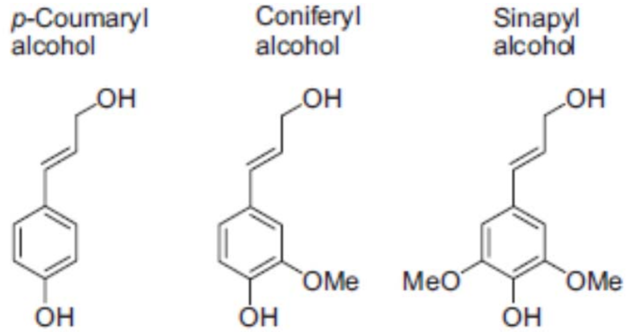


***p*-Coumaric acid or *p*-hydroxycinnamic acid**
can be found in a wide variety of edible plants
such as peanuts, tomatoes, carrots and garlic
It is also a major component of lignocellulose

A small piece of lignin polymer

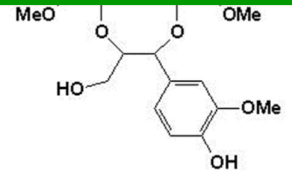


The 3 common monolignols



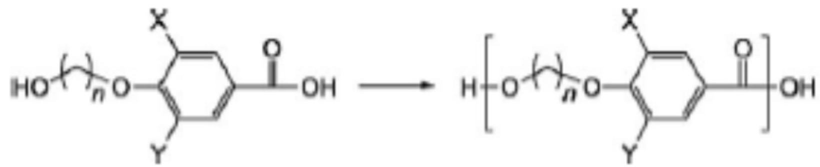
Traditionally lignin has been viewed as a waste material or a low value by-product of pulping with its utilisation predominantly limited to use as a fuel to fire the pulping boilers.

Indeed it has been estimated that only 1–2 % of lignin is isolated from pulping liquors and used for speciality products



Polyesters synthesized from the lignin-derived aromatics

S.A. Miller et al., Macromol. Rapid Commun., 1386–1392, 2011

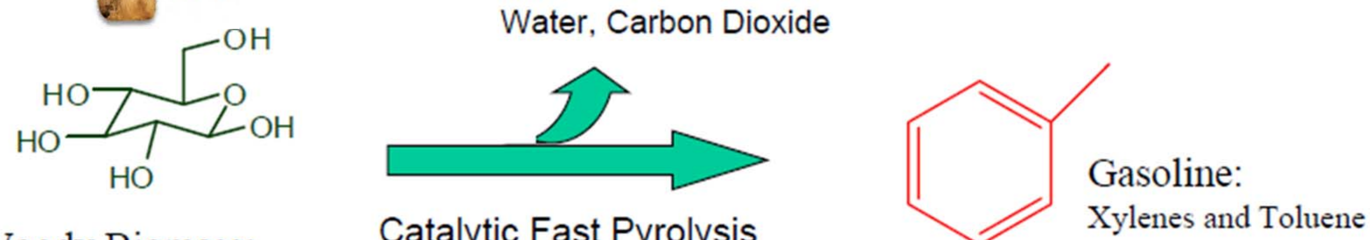


4-hydroxybenzoic acid (X=Y=H), vanillic acid (X=OMe, Y=H), syringic acid (X=Y=OMe)

D. Stewart, Industrial crops and products 27, 202–207, 2008.
M. Kleinert, T. Barth, Phenols from Lignin, Chem. Eng. Technol., 31, 736–745, 2008

LIGNIN = BIO-OILS + HYDROCARBONS?

Bio-oils can be (inexpensively ???) produced from lignocellulosic biomass



Process
1 to **4**

Woody Biomass:
wood waste,
agricultural wastes
(corn stover, sugarcane waste)
paper trash, energy crops

1 to 4: breaking the chemical and engineering barriers to Lignocellulosic Biofuels…

- **Single step process (cheap process).**
- **Inexpensive catalysts (no precious metals).**
- **Short residence time (1 min).**
- **Liquid product that fits into existing market.**

1

Technology from Huber research group; Univ. of Massachusetts, **www.ecs.umass.edu/biofuels**

- Huber, G. W.; Chheda, J.; Barrett, C. B.; and Dumesic, J. A.; *"Production of Liquid Alkanes by Aqueous-Phase Processing of Biomass-Derived Carbohydrates"*, Science, 308, 1446-1450, **2005**.
- G.W. Huber, S. Iborra, and A. Corma; *Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering*, Chem. Rev., 106, 4044-4098, **2006**
- Huber, G. W.; and Corma, A.; *Synergies between bio- and oil- refineries for the production of fuels from biomass*, Angewandte Chemie International Ed., 207, 7184-7201, **2007**
- Carlson, Vispute, and Huber, *Green Gasoline by Catalytic Fast Pyrolysis*, ChemSusChem, 1, 397, **2008**.

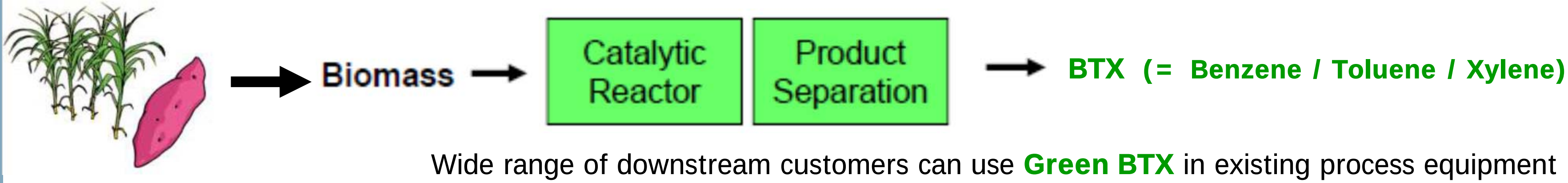
❖ **Process developed from fundamental science funded by NSF.**
❖ **Anellotech (**www.anellotech.com**) focusing on commercialization.**

A. Corma = Instituto de Technología Química, Universidad Politécnica de Valencia

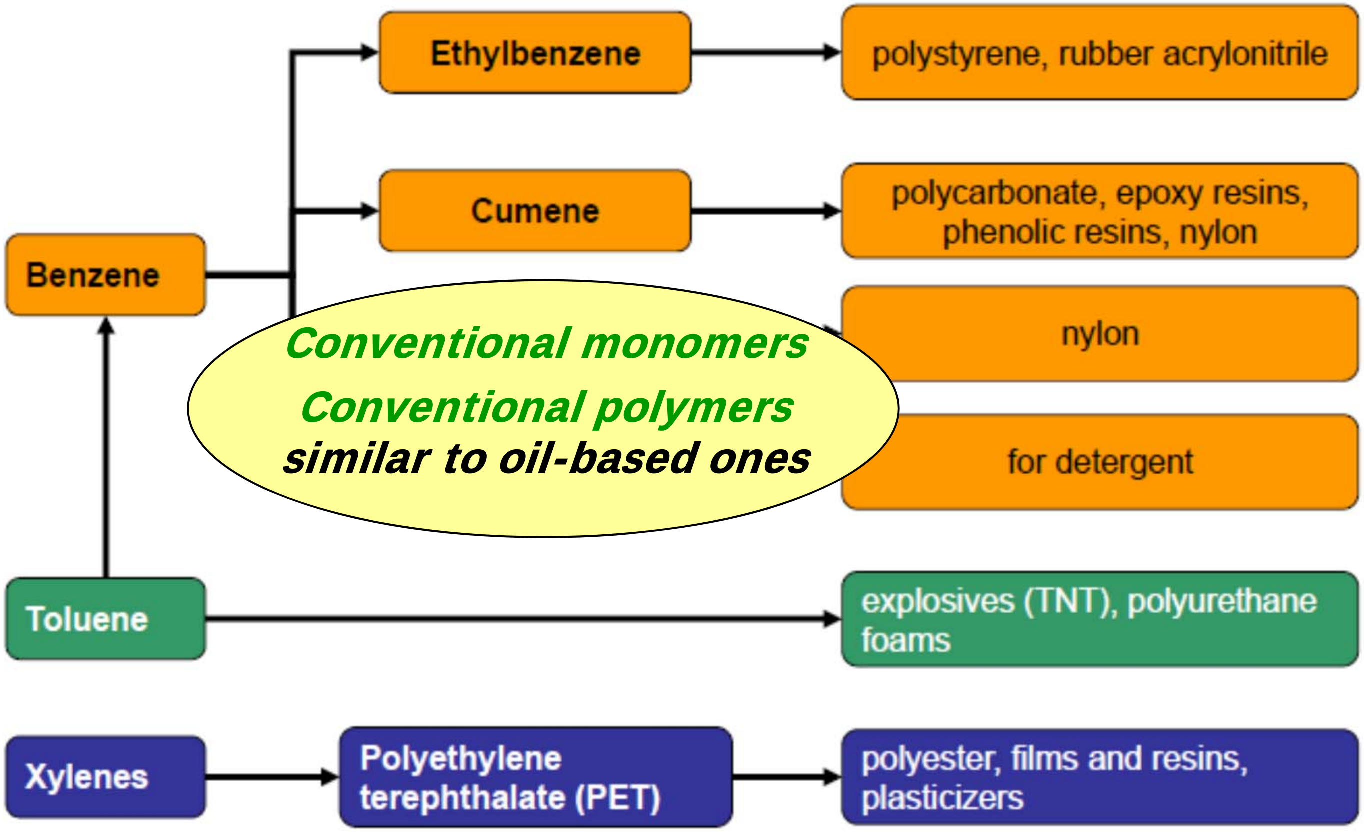
BIOMASS TO AROMATICS

Anellotech's technology converts the biomasss into an intermediate from which oxygen can be removed, and then does this removal all in the same reactor in a one step process.

Anellotech/Catalytic Fluidization



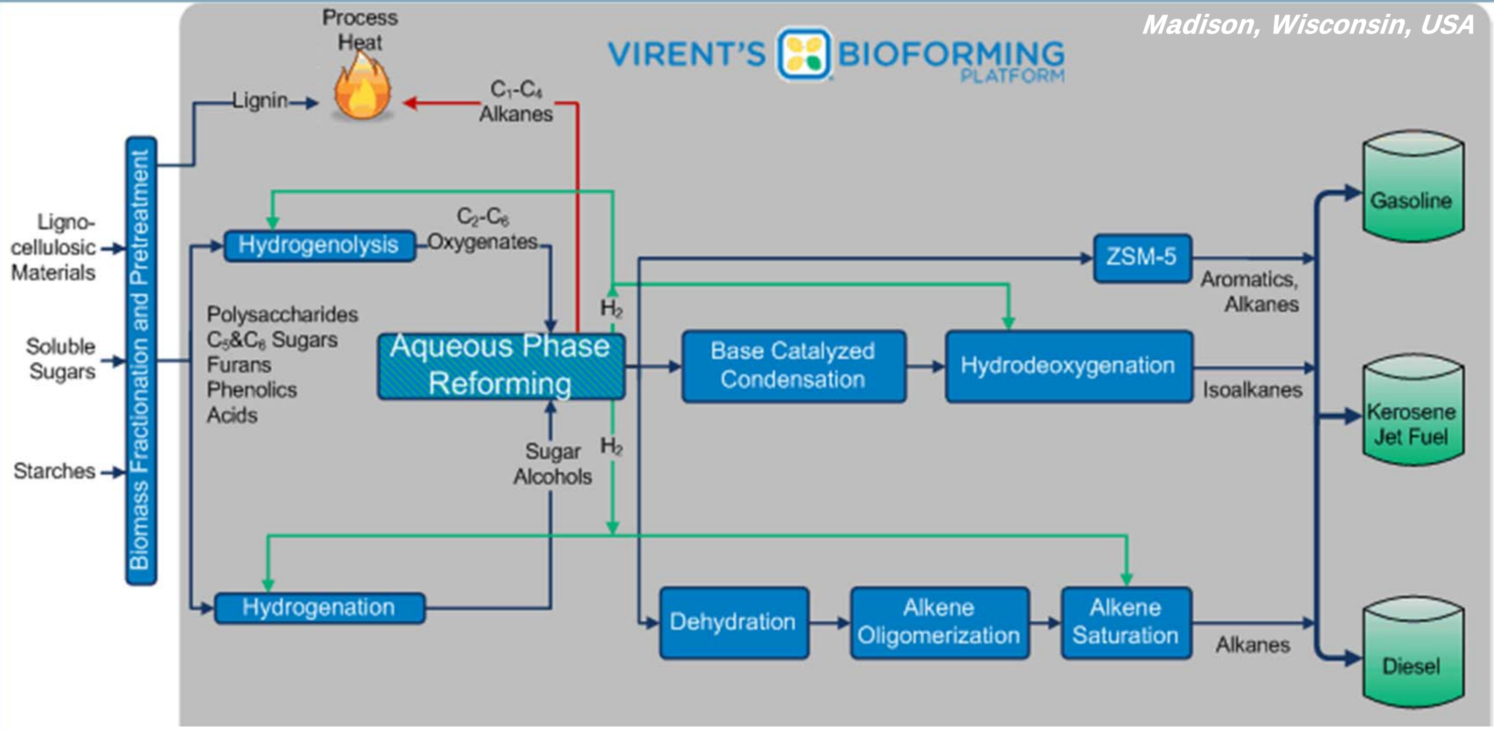
Wide range of downstream customers can use **Green BTX** in existing process equipment



Anolletech presentation, D. Sudolsky, March 23rd 2011

2 LIGNIN: The BioForming® technology

Madison, Wisconsin, USA



*Virent made its ground-breaking discoveries in **2006** in collaboration with Royal Dutch Shell*

Virent is commercializing an **innovative advanced biofuel technology** that **catalytically** transforms a wide range of soluble plant sugars into **HC molecules** like those produced at a petroleum refinery.

Virent's renewable hydrocarbons can be blended seamlessly to make gasoline, jet fuel, and diesel.

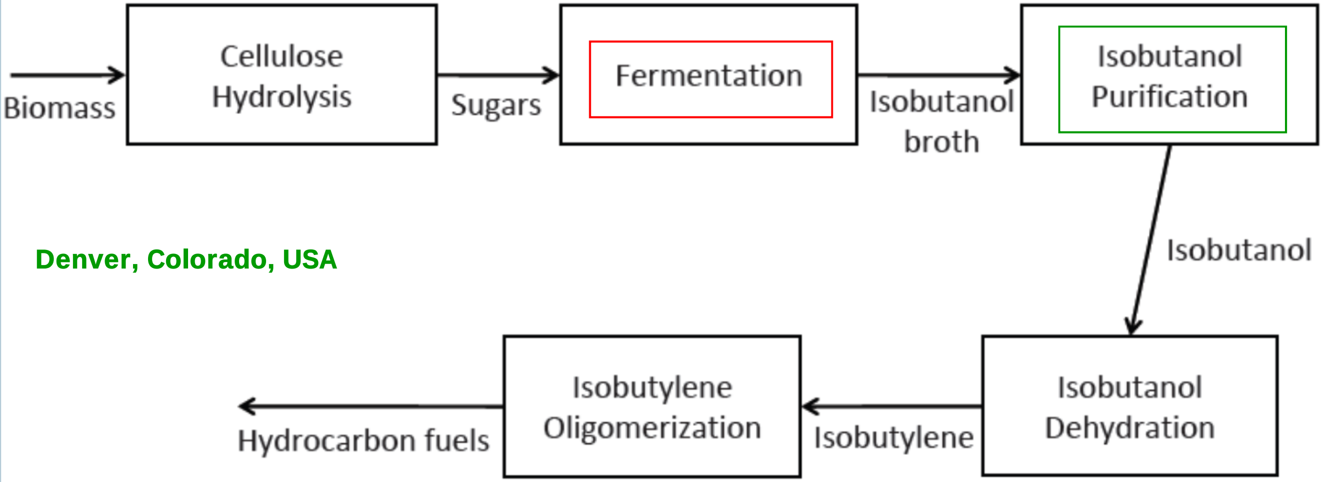
***- June 6, 2011 –* Virent** announced it has successfully made **Paraxylene (PX,** trademarked **BioFormPX)** from **100% renewable plant sugars (pilot scale).**

Virent intends to have a commercial scale plant commissioned by the end of 2014

3 LIGNIN: gevo GIFT™ Process

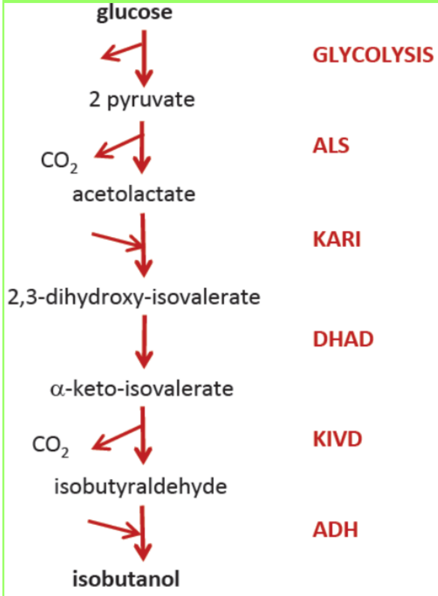
Advancing the New Era of Renewables

Gevo Integrated Fermentation Technology, GIFT



Denver, Colorado, USA

High performance Isobutanol Fermentation



Isobutanol can be produced from a variety of lignocellulosic sugars

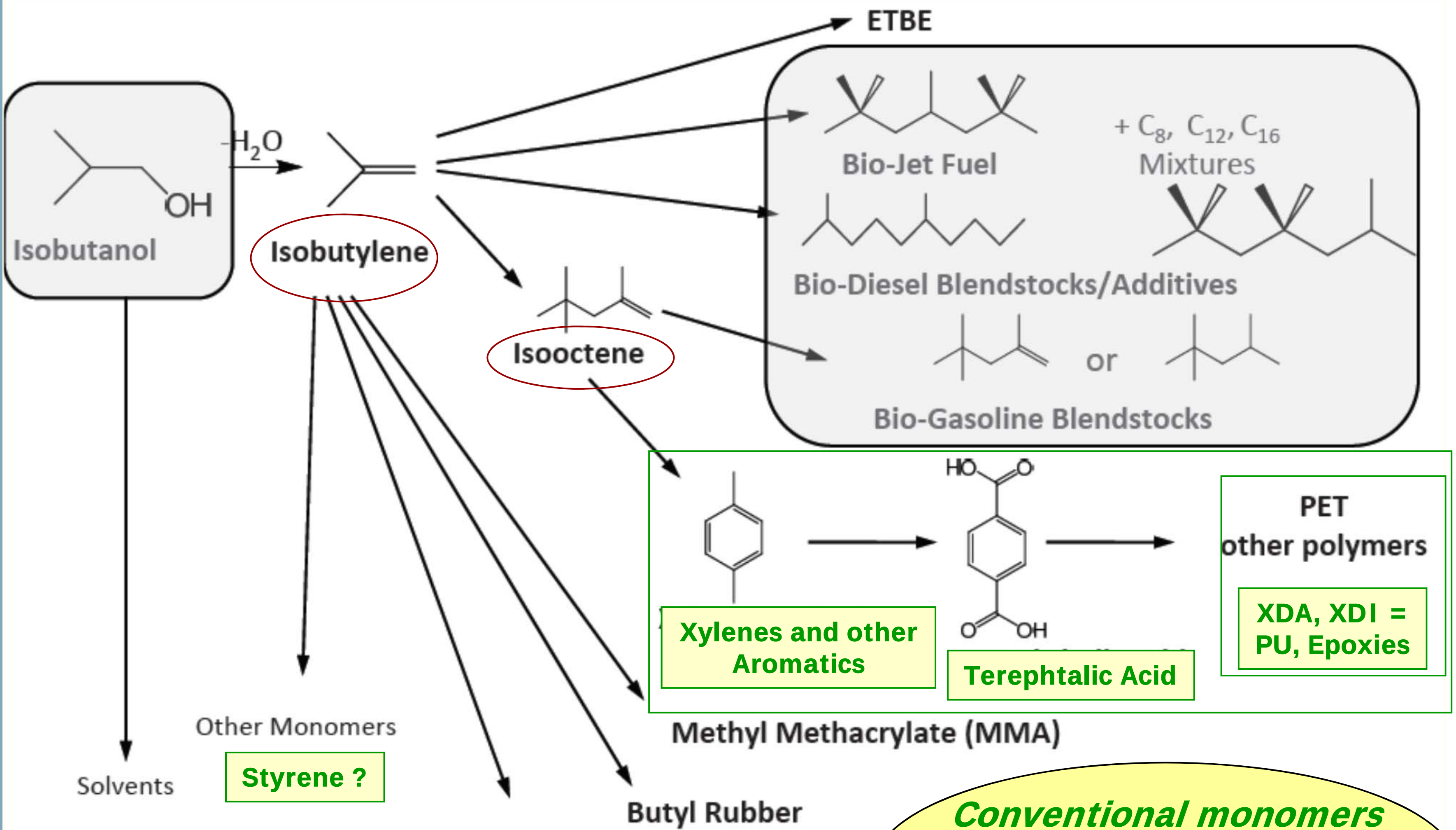
August 2010, *Gevo has entered into business arrangements with:*

LANXESS
Total Petrochemicals
Toray Industries
United Airlines
...

D.A. Glassner, Gevo Inc presentation 2009

3 ISOBUTANOL PLATFORM

Isobutanol can be converted into Isobutene and isooctene



Conventional monomers

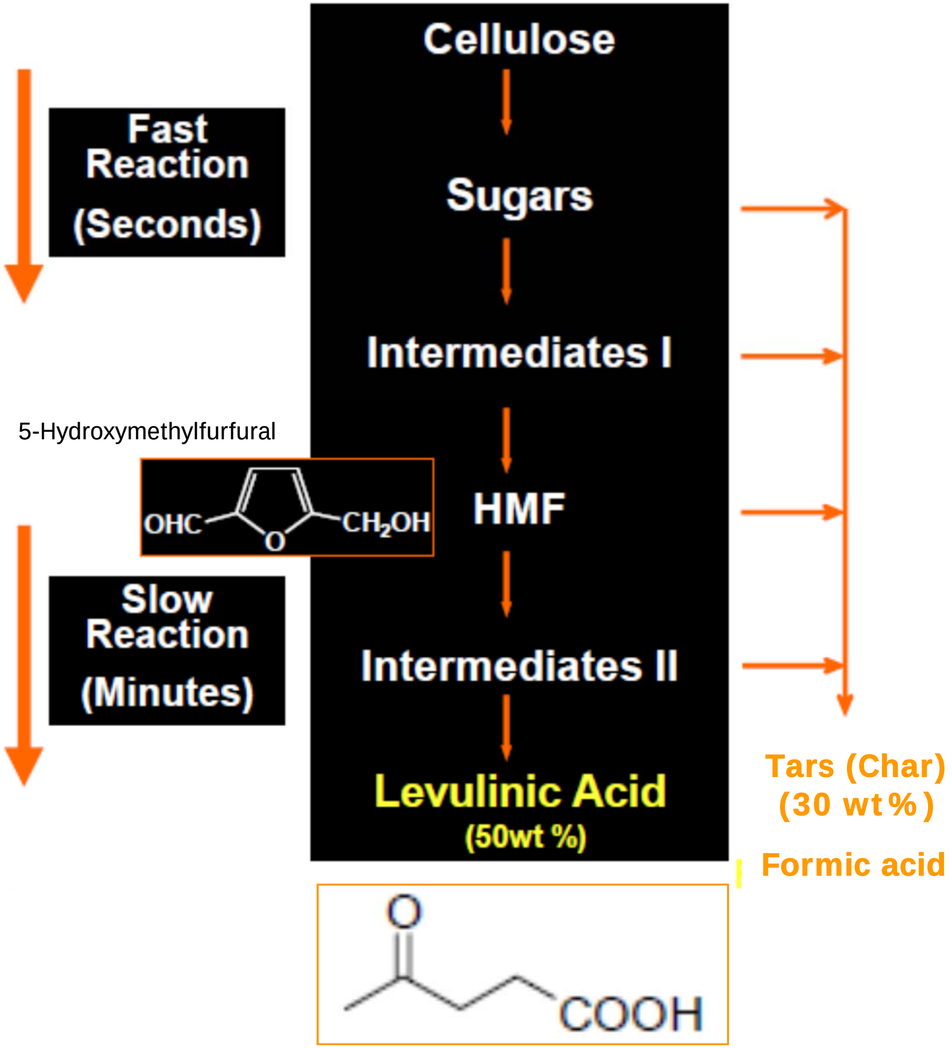
Conventional polymers

similar to oil-based ones

LIGNIN

Biofine Technology

Biofine Process from Lignocellulosic Feedstocks



Biofine Process

Biofine, 245 Winter Street, Waltham, MA 02154 USA

Commercial plant in Caserta, Italy.

« One of the most advanced and commercially viable lignocellulosic-fractionating technologies currently available », *they said …*

Biofine, Inc. developed a high-T °C **dilute acid hydrolysis process** that converts **cellulosic biomass to soluble sugars** which are then transformed to:

- *Levulinic Acid, LA (major product),*
- *Formic acid (byproduct), and*
- *Tars (minor condensation products*

LA is a valuable platform chemical due to its particular chemistry

It has two highly reactive functional groups that allow a great number of synthetic transformations:

LA can react as both a carboxylic acid and a ketone

Fitzpatrick, S. W., 1990, Lignocellulose degradation to furfural and levulinic acid: U.S. Patent 4,897,497
D.J. Hayes, J. Ross, M.H.B. Hayes, S. Fitzpatrick; http://www.carbolea.ul.ie/files/HFHR_Chapter%204_FINAL.pdf

4 LEVULINIC ACID: a Platform for Chemicals?

ETHYL LEVULINATE can be used in Gasoline, Diesel and Heating Oil

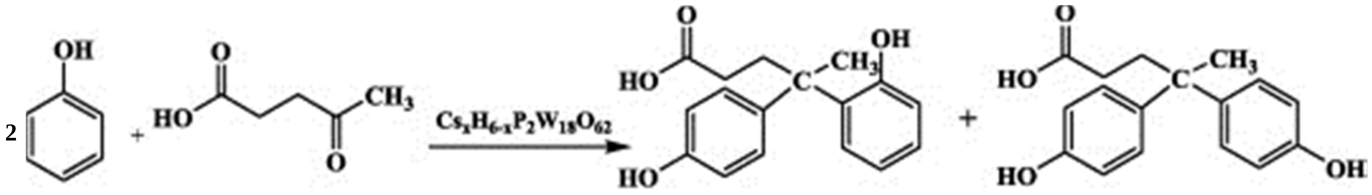
MONOMERS and SPECIALITY POLYMERS

DIPHENOLIC ACID

POLYCARBONATE
EPOXIES

γVL **(Bio-Fuel?)**

BUTANEDIOL
THF
SUCCINIC ACID
FURANS



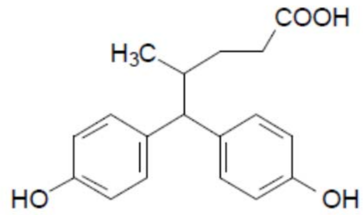
***o, p'*- DPA isomer** ***p,p'*-DPA isomer**

Novel Monomer?

4,4-*bis*-(4'-hydroxyphenyl)pentanoic acid or DPA

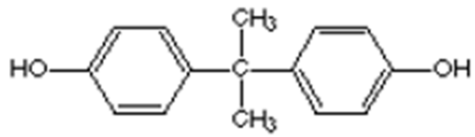
DPA was once used commercially in various resin formulations before it was replaced by the petrochemically-derived BPA which could be supplied at a lower price.

The reduced cost of LA production made possible with the Biofine Process (???) may allow DPA to recapture some of the market share



Diphenolic Acid, DPA

VS



Bisphenol A, BPA

But very little information on the toxicity of DPA is found in the available literature.

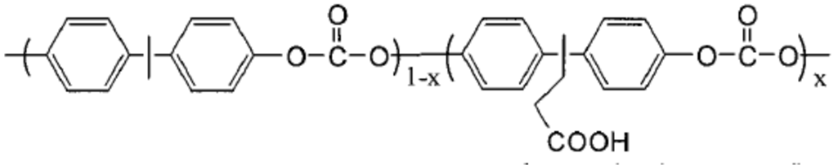
The chronic effects of diphenolic acid are not well characterized.

D.J. Hayes, J. Ross, M.H.B. Hayes, S. Fitzpatrick; http://www.carbolea.ul.ie/files/HFHR_Chapter%204_FINAL.pdf

4 DIPHENYL ACID AS A BUILDING BLOCK

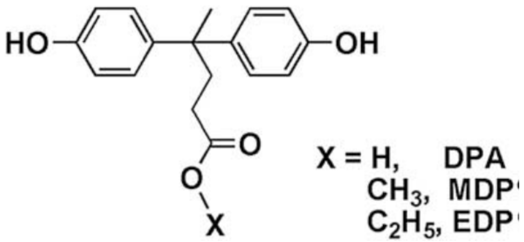
1) Synthesis of Polycarbonate:

-COOH may act as cross-linking agent (-H-bonds, etc.)



2) Synthesis of hyperbranched polyesters

3) Polyesters prepared from isophthaloyl chloride (IPC) with diphenolic acid (DPA)

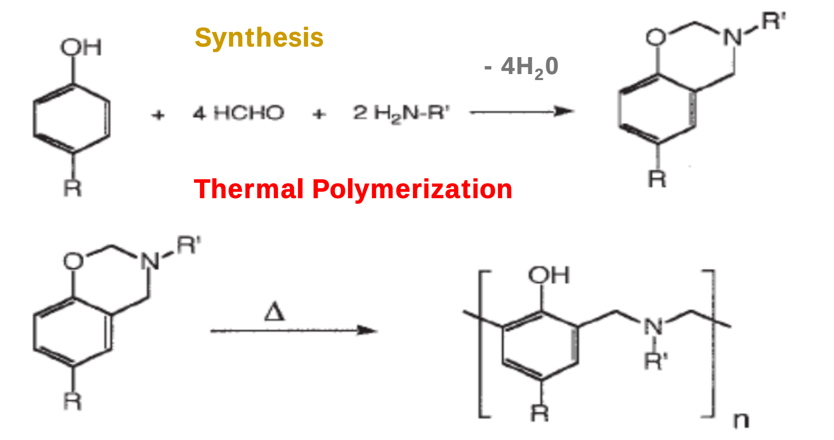


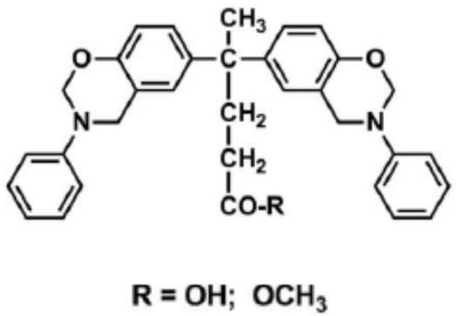
Poly(DPA–IPC) is an amorphous polymer.

As compared with ordinary aromatic polyesters, it has lower T_g = 159 °C and much lower thermal stability. It starts to decompose at about 210 °C

Poly(MDP–IPC) and **poly(EDP–IPC)** are prepared from Me-diphenolate and Et-dipenolate. As expected, these two polymers exhibit obviously improved thermal stability, with onset decomposition temperature of about 300 °C.

4) TS: Polybenzoxazines





T_g BPA-Bz = 170 °C;

T_g DPI-BZ = 207 °C;
T_g Me.DPI-BZ = 265 °C

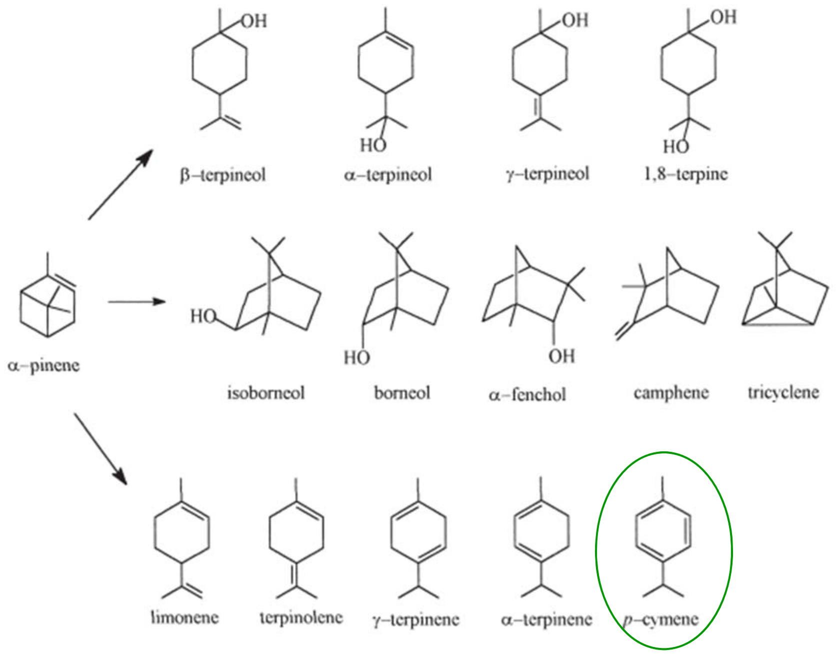
1) R. Zang, J.A. Moore Macromol. Symp. **2003**, *199*, 375-390
2) C. J. Hawker et al, *1997*
3) P. Zhang et al Polym. Degrad. Stab. 94 (*2009*) 1261–1266
4) J.C. Ronda et al J. Polym. Sci. Part A, 49, 1219–1227 (*2011*)

TERPENE FEEDSTOCKS?

Terpene feedstocks are a natural and sustainable supply of building blocks for the fine chemical industry...

Example: isomerization / hydration of α-pinene

A.C. Bueno et al. A: General Applied Catalysis 351, 226–230, 2008



Various commercially significant **terpenic compounds** are produced through the chemical transformations such as:

- **isomerization,**
- **oxidation,**
- **esterification,**
- **carbonylation, and**
- **(de)hydrogenation.**

... but for Polymer Industry???

"Waste orange peel is an excellent example of a wasted resource. In Brazil, the world's largest producer of orange juice, half the orange fruit is left as waste once the juice has been recovered.

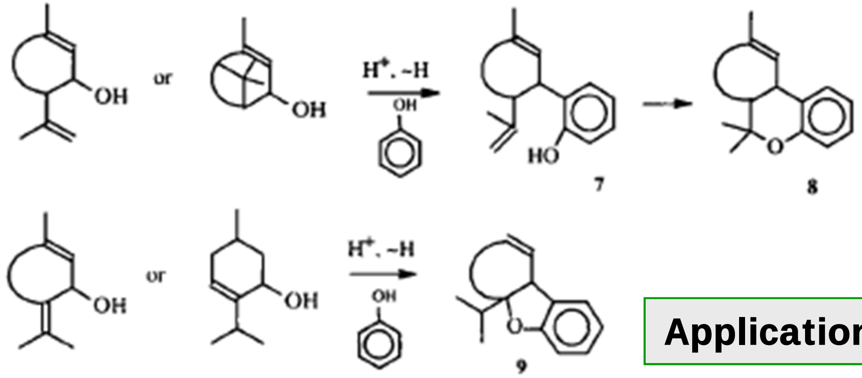
This corresponds to 3 million tonnes a year of orange peel that can be used to produce chemicals, materials and fuels.

The by-product of the juicing industry therefore has the potential to provide a range of compounds..."

Prof. Clarke and Orange Peel Exploitation Company (OPEC) Brazil*, *Sept. 14th 2011

USES OF TERPENE FEEDSTOCKS

1) Terpene-Phenol Resins: They are **oligomers** prepared by a **Friedel Crafts reaction**



1) Protonation of the terpene, results in a **cationated species** which reacts with the phenol

2) Once alkylated, a phenol moiety becomes more susceptible to **reaction at the phenolic hydroxyl group**; this gives rise to some O-alkylation by terpinyl moieties.

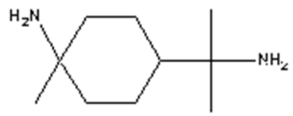
The extent of O-alkylation can be controlled by the choice of the ratio of terpene to phenol

Applications: rheological modification of polar polymers

They are used as good tackifiers and heat stability in **adhesive**, **coatings, inks, plastic** (PVC), **rubber** (EVA) and others

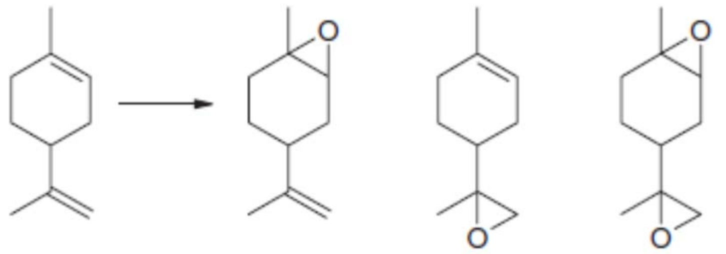
2) Epoxidation of Terpenes / Limonene

Used in Epoxy formulations? *US patent 1968 !!!*



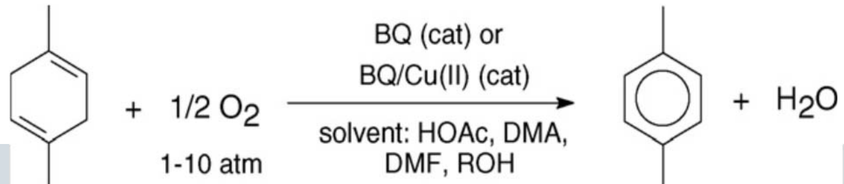
+
one diamine as hardener:
Menthane diamine

US patent 1960 (Limonene, terpin hydrate, α-pinene, etc. + 2/3 mol. of HCN)



1,2-epoxide 8,9-epoxide bis-epoxide

3) p-Cymene: Oxidative dehydrogenation of γ-terpinene



Oxydant = p-Benzoquinone (BQ)

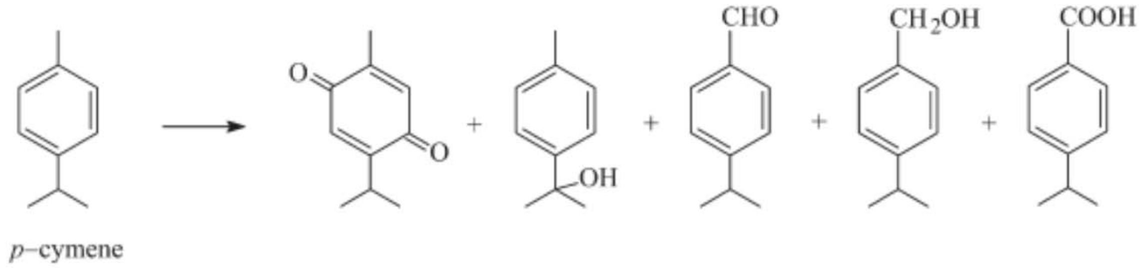
p-Cymene is an important product and valuable intermediate in the chemical industry.

Among others, it is used as a solvent for dyes and varnishes, as a heat transfer medium, as an additive in fragrances and musk perfumes, and as a masking odor for industrial products.

USES OF TERPENE FEEDSTOCKS

***p*-Cymene is an important product and valuable intermediate in the chemical / polymer industry?**

p-Cymene: deshydrogenation + / or oxidation



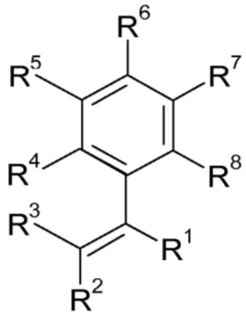
- K.A.D. Swift, Topics in Catalysis Vol. 27, Nos. 1-4, 143-155, 2004
- D.M. Roberge et al., Applied Catalysis A: General 215, 111–124, 2001
-J.L.F. Monteiro and C.O. Veloso Topics in Catalysis Vol. 27, Nos. 1–4, 169-180, 2004

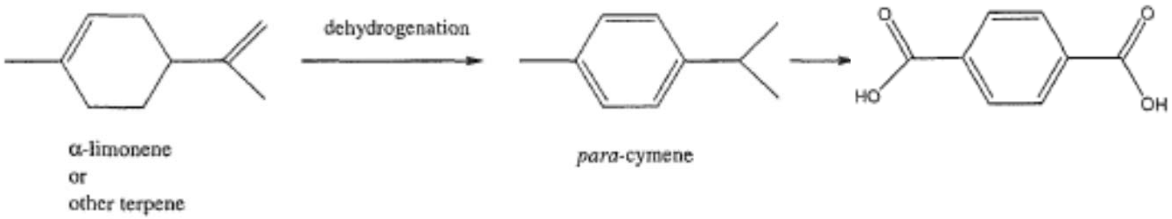
Styrene:

BASF Patent

WO 2009/040285; PCT/EP2008/062404

« Method for deshydrogenating cyclical terpenes derivatives having hexocyclic double bonds »





Terephtalic Acid: directly from a biobase containing a terpene or terpenoid such as limonene.

WO patents 2010 from Sabic, Coca-Cola and Pepsi

bioplastic Magazine Fev. 2011

OUTLINE

Bio-raffineries: les ressources pour les polymères de demain

1) *A la Recherche de Structures Aromatiques*

2) *A la Recherche de Structures Aromatiques « Equivalentes »*

- ***FURANICS BUILDING BLOCKS***
- ***ISOSORBIDE BUILDING BLOCK***

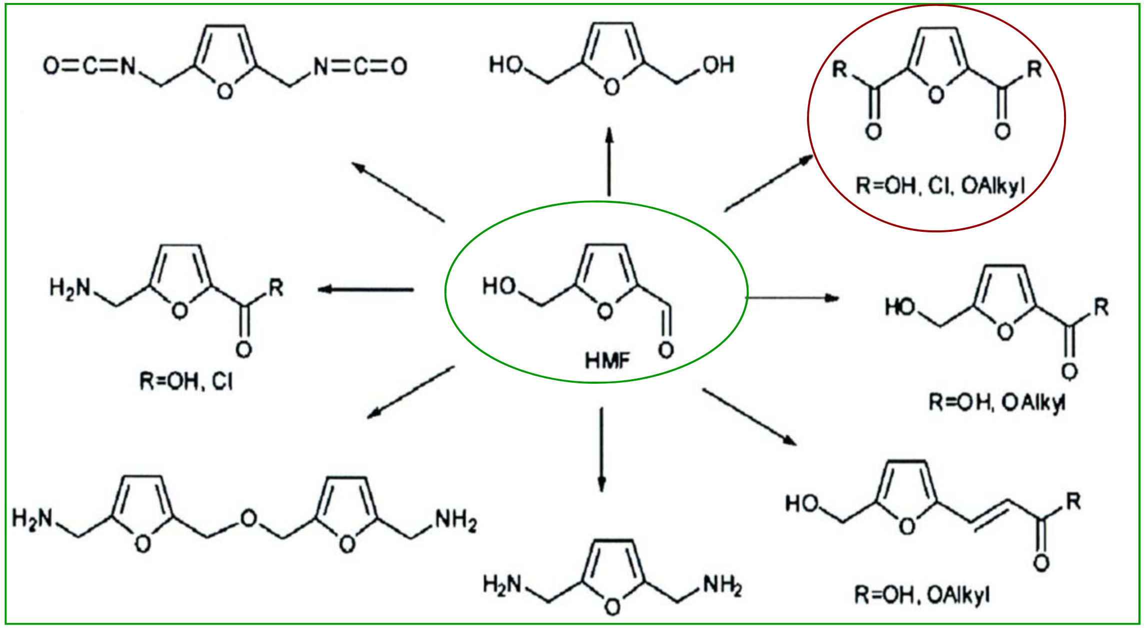
Novel Polymers?

FURANICS BUILDING BLOCKS

2 basic non-petroleum Building Blocks are readily accessible from **polysaccharides** or **sugars** bearing, respectively, **pentose** and **hexose moieties**, namely **the 1st-generation furan derivatives:**
Furfural (F) and Hydroxymethylfurfural (HMF)

From them, a whole array of furan monomers can be prepared and polymerized

A selection of monomers from HydroxyMethylFuraldhehyde, HMF



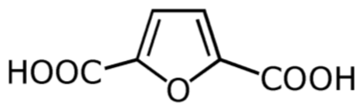
While F has been an industrial commodity, the production of HMF has been slowed down by difficulties in terms of isolating it in good yields and purity.

However, it is clear that this process will soon become a reality

A. Gandini, Green Chemistry, 13, 1061-1083, 2011

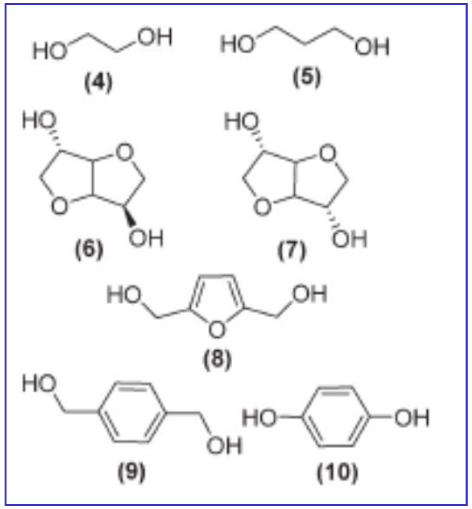
FURANICS BUILDING BLOCKS

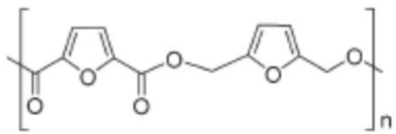
Furan-2,5-dicarboxylic acid



FDCA

+ diols





PBHMF

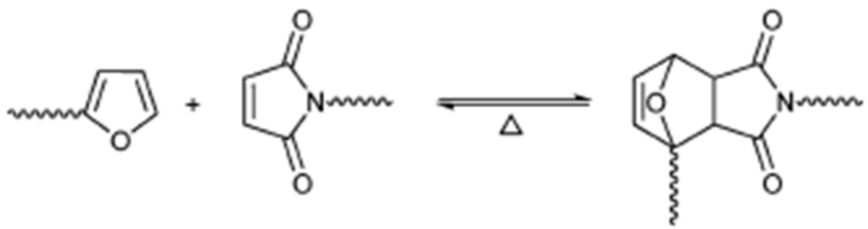
(1+8) = the fully furan-based polyester

Polymer		T_g^b (°C)	T_c^b (°C)	T_m^b (°C
PEF	(2)	80	165	215
PPF	(3)	50	127	174
PDASF	(1+6)	180	–	–
PDAIF	(1+7)	140	–	–
PBHMF	(1+8)			
PHQF	(1+10)	nd	nd	nd
PHMBF	(1+9)	87	–	–
PEF-*ran*-PPF	(2+3)	80	165	215

Poly(ethylene furanoate), PEF (2), is expected to be an analog for traditional fossil-based PET material

Towards "green" electronic materials. α-Oligofurans as semiconductors
*D.F. Perepichka Chem. Commun., 47, 1976–1978, **2011***

Another reaction: The **DA equilibrium** between growing species bearing respectively **furan** and **maleimide end groups.**



*A. Gandini, Green Chemistry, 13, 1061-1083, **2011***

A. Gandini et al, *Synthesis and Characterization of Poly(2,5-furan dicarboxylate)s Based on a Variety of Diols*, J. Polym. Sci. Chem. **2011**
Min Jiang et al, …*Furan-Aromatic PES Synthesized via Direct Esterification Method Based on Renewable Res.*, J. Polym. Sci. Chem. **2011**

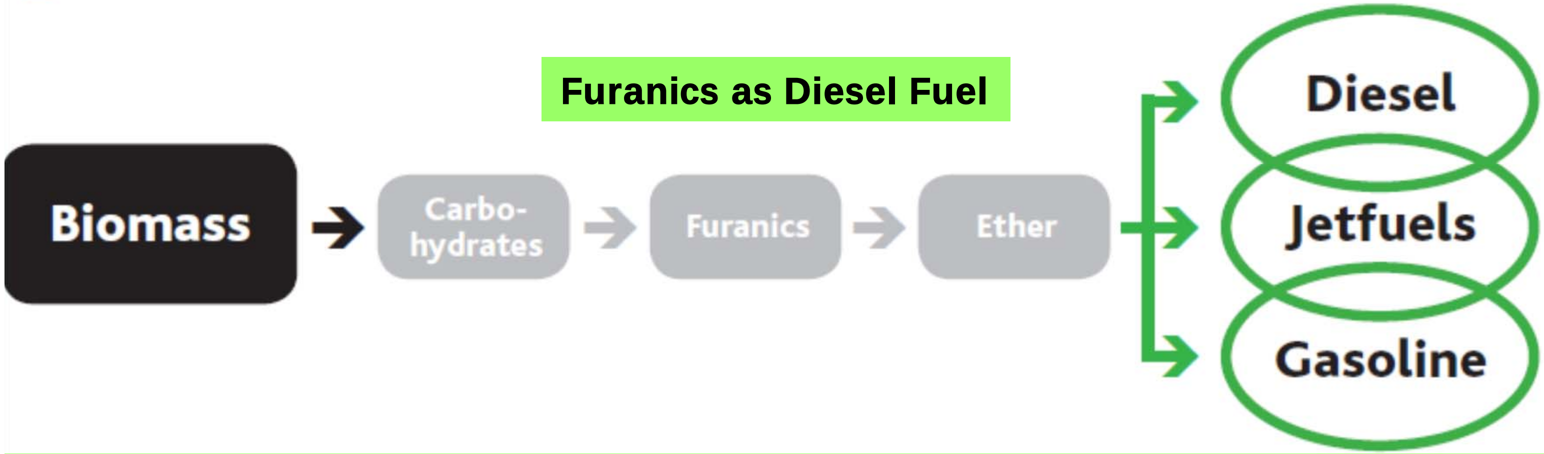
BIOMASS TO FURANICS BUILDING BLOCKS

“Avantium has developed YXY (pronounced as icksy)-a family of **green building blocks** for making **materials** and **fuels** that can compete on both price and performance with oil based alternatives, but which have a superior environmental footprint.”

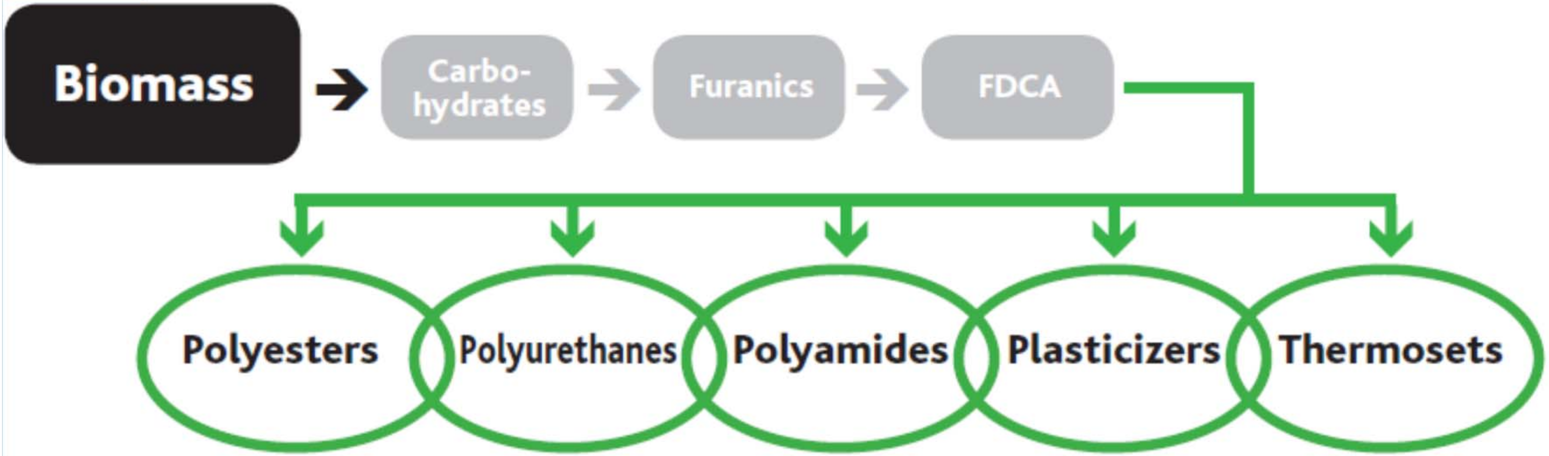
Initial background: Catalyst and high-throughput technologies

Green from within.

Furanics as Diesel Fuel



YXY is a patented technology that converts biomass into Furanics building blocks, such as FDCA



Furanics as Building Blocks for bio-based polymers

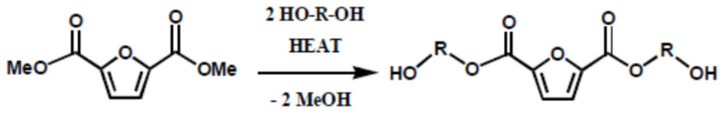
BIOMASS TO FURANICS BUILDING BLOCKS

Furan-2,5-dicarboxylic acid

FDCA

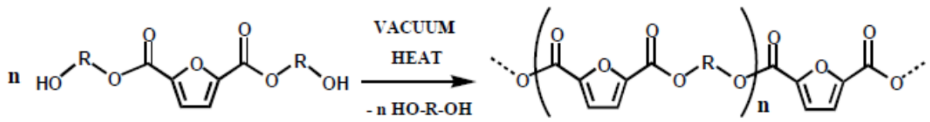
- Bio-based
- Building block for PEF
- Potential market > 100 million ton
- Price at commercial scale: <€ 1000 per ton
- Price drivers:
  - Carbohydrate price
  - Economy of scale

Transesterification



Catalyst?

Polycondensation



Reaction Conditions

High M_n ⟷ Low coloration

- High temperature
- Long reaction time

- Low temperature
- Short reaction time

Superior barrier properties: PEF 2-6 times higher (O_2, CO_2, H_2O) than those of PET

PEF in PET recycle streams: 1,2 and 5% doesn't affect recycled PET performance

1) On 8 December 2011, Avantium officially opened its pilot plant in the Netherlands. **The pilot plant, with a capacity of 40 tons/y produces PEF material.**

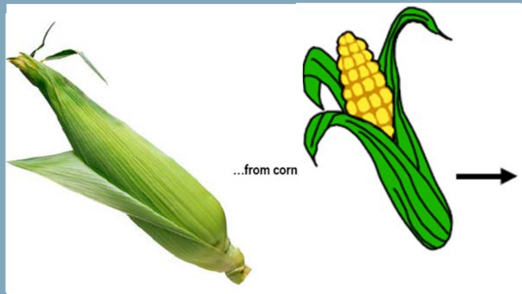
2) The collaboration with the Coca-Cola Cie is key to secure a smooth transition into the mass production phase of **PEF bottles**"

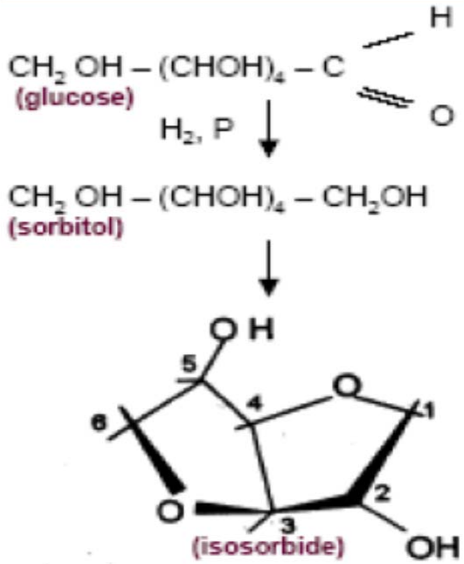
3) 7 July 2011: Solvay and Avantium to jointly develop **green engineering plastics**

AVANTIUM Presentation: Frank Roerink, CFO February 15, 2011

Patents: WO2007/104514; WO2007/104515 ; etc.

BUILDING BLOCK = ISOSORBIDE

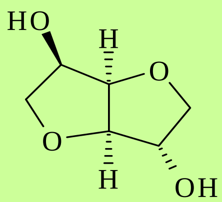




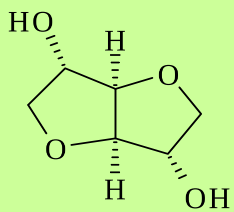
Hydrogenation of D-glucose

Then dehydration

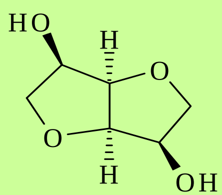
1,4:3,6-dianhydrohexitols (DAH)



Isosorbide
(DAS)
The less expensive / available industrially



Isoidide
The more reactive but also the more difficult to synthesize



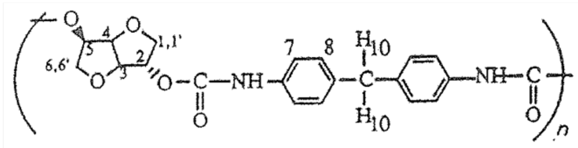
Isomannide
The less reactive one

F. Fenouillot, A. Rousseau, G. Colomines, R. Saint-Loup, J.-P. Pascault, Prog. Polym. Sci. 35, 578–622, 2010

BUILDING BLOCK: WHY ISOSORBIDE?

Non toxic; Chiral; Brings stiffness to the polymer chain

1st - ISOSORBIDE in Polyurethane Chemistry; as a chain extender for segmented PU

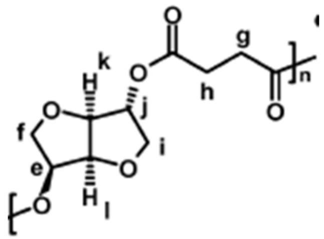


Comparison of the polyurethane HS based on MDI + isosorbide (DAS or I) or BDO:

(MDI-BDO)$_n$; T_g = 107 °C
(MDI-DAS)$_n$; T_g = 187 °C

E. Cognet-Georjon, F. Méchin, J.-P. Pascault, Macromol. Chem. Phys. 196, 3733, 1995

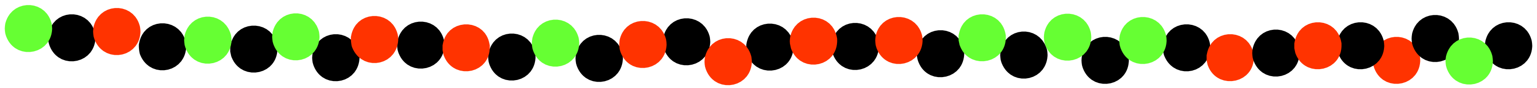
2nd - ISOSORBIDE in Polyester Chemistry: a diol for Polyalkylene Succinates → Powder Coatings



PBS: T_g = -35°C
PIS: T_g = +68 °C

C. E. Koning et al Biomacromolecules, 7, 3406, 2006

3rd - ISOSORBIDE in Polyester Chemistry: a diol for Polyalkylene Terephtalates Random Copolym.

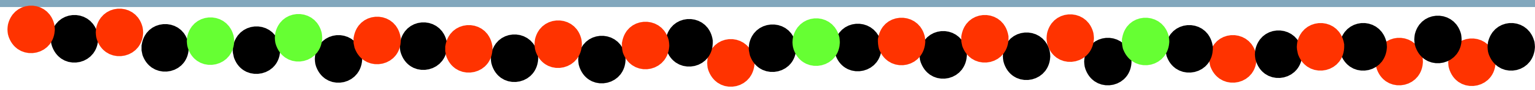


Low reactivity of the secondary hydroxyl: ***Synthesis in Toluene (+ pyridine)***

PET: T_g = 80 °C
PIT: T_g = 200 °C

R. Storbeck, M. Ballauff J. Applied Polym. Sci., 59, 1199, 1996

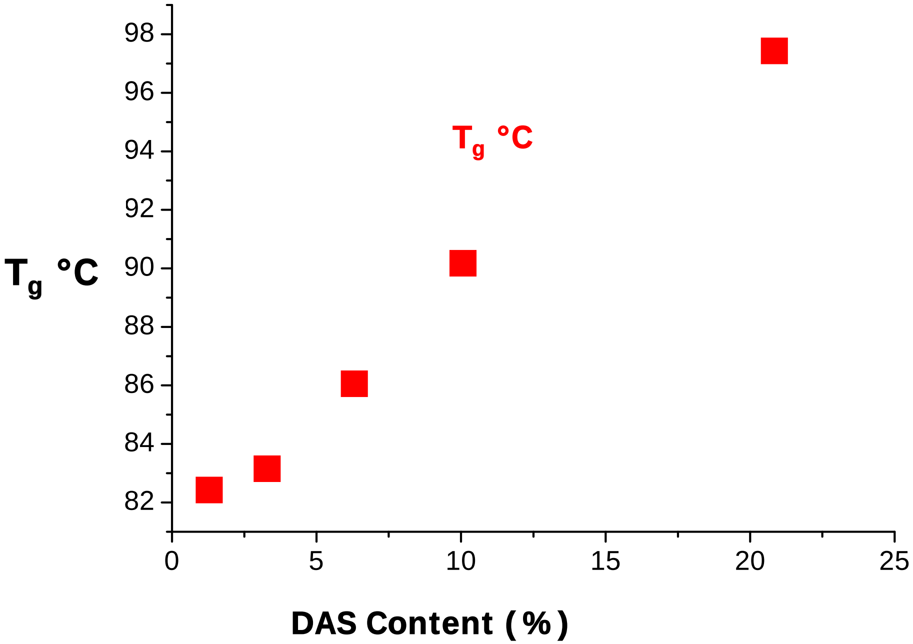
RANDOM COPOLYESTERS: PEIT



In our Lab. (IMP@INSA):
S. Jeol, PhD INSA-Lyon, 2006

Synthesis in bulk

Copolymers / % I	T_g°C	X%	T_m°C
PET / 0	80	45	275
PEIT / 1.4	82	42	240
PEIT / 4.3	82.5	40	220
PEIT / 7.3	85	28	215
PEIT / 11.7	90	25	215
PIT / 100	200	amorphous	

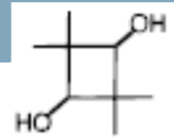


T_g (PEI$_x$T) (°C) = 0,91 x + 80,8

Increase of T_g ~ 1°C/1 mol.% DAS;
but ...
X% cristallinity and rate of cristallization are decreasing for DAS mol% > 7

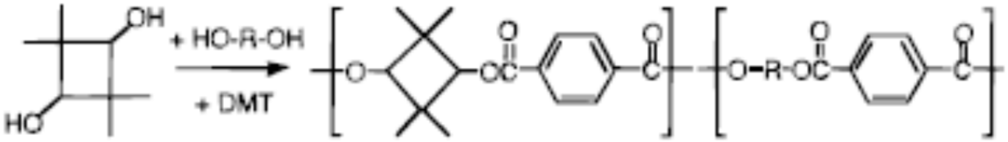
F. Fenouillot, A. Rousseau, G. Colomines, R. Saint-Loup, J.-P. Pascault, Prog. Polym. Sci. 35, 578–622, 2010

ISOSORBIDE - WHY NOW?



***cis/ trans*-2,2,4,4-tetramethyl-1,3-cyclobutanediol [CBDO]**

Terephthalate-based copolyesters prepared using conformationally rigid CBDO and flexible C2-C4 aliphatic diols has been found to exhibit:
high impact resistance, good thermal properties, UV stability, optical clarity, and low color



R = -$(CH_2)_n$- and n = 2, 3, 4

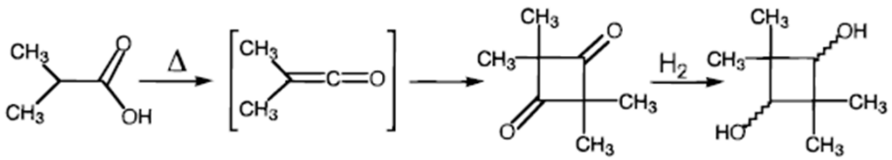
A lot of patents...
Commercial references:
TRITAN™ from Eastman ?

An alternative to BPA?

- **The copolymers are amorphous when the CBDO content was about 40 to 90 mol % of total diol.**
- **T_g = 80-168 °C, depending on the proportion of rigid CBDO units.**
- **Both high T_g (>100 °C) and high impact can be realized simultaneously, ~50-80 mol % CBDO**
- **Accelerated weathering indicated good inherent resistance to yellowing under UV radiation.**

Not bio-based!!!

CBDO is prepared in high yield by pyrolysis of isobutyric acid or anhydride to form dimethylketene, which spontaneously dimerizes to cyclic diketone. Then hydrogenation produces up to 98% yield of *cis/ trans* **CBDO**.



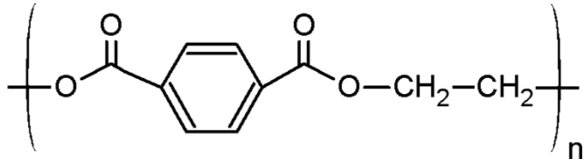
Rigid, thermally stable, symmetrical *aliphatic* molecules suitable for polymers are rare...

D.R. Kesley et al, *High Impact, Amorphous Terephthalate Copolyesters of Rigid CBDO with Flexible Diols*, Macromolecules, 33, 5810-5818, 2000; J.C. Booth et al, *Aliphatic–Aromatic Copolyesters Derived from CBDO*, J. Polym.Sci.Chem., 42, 3473–3478, 2004

ISOSORBIDE ⟶ NEW Ar. POLYESTERS

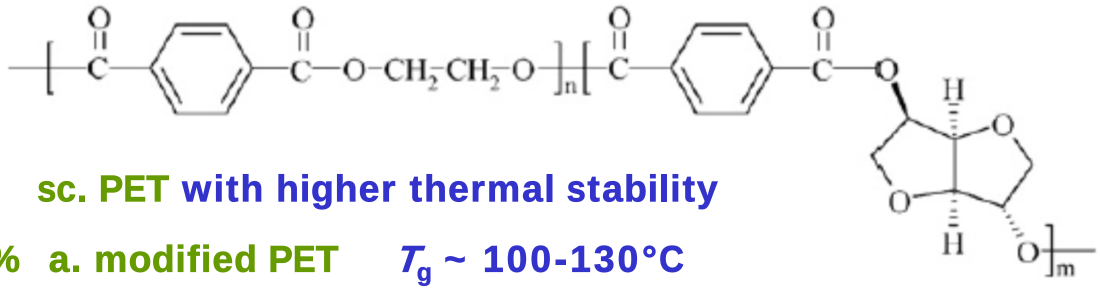
0 % isosorbide

Poly(ethylene terephthalate) (PET)



T_g = 75°C
T_m = 245°C

Poly(ethylene-co-isosorbide terephthalate) (PEIT)



1) < 10 % sc. PET with higher thermal stability

2) 10-30 % a. modified PET T_g ~ 100-130°C

May compete with PETG, PMMA, PC, etc.

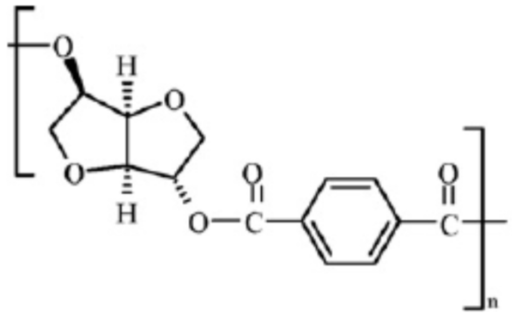
Eatsman Chem., US 2004/0092703 « Method for making Isosorbide containing Polyesters »

Commercial products are arriving on the market:

Better Inflammability / High Impact Strength / Good Chemical Resistance

Poly(isosorbide terephthalate) (PIT)

100 % isosorbide

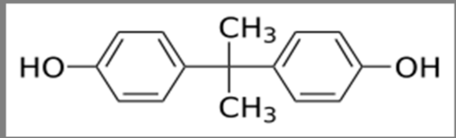


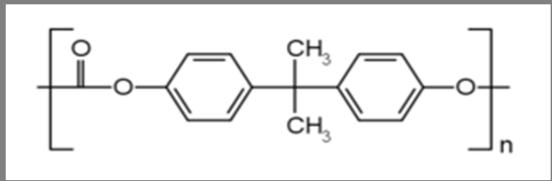
amorphous
T_g = 210°C

With high Molar Mass? (Reactivity of 2nd –OH groups)

May compete with high T_g polymers...

ISOSORBIDE → NEW POLYCARBONATE

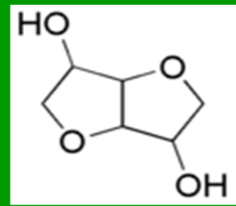


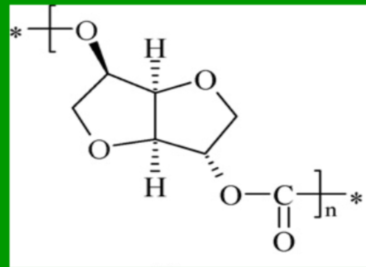


Polycarbonate of bisphenol A

An alternative to BPA?

Isosorbide does not suffer from suspicion of reprotoxicity





Polycarbonate of isosorbide

Patents:

- **Mitsubishi Chem.: Fuji, M., Akita, M., Tanaka, T., *EP 2 033 981 A1*, 2009;**
- **Sabic: Jansen, B.J.P., Kamps, J.H., Looij, H., Kung, E., *WO 2009/052463 A1*, 2009;**
- **Teijin LTD: Kinoshita, M., Saito, M., Hironaka, K., *EP 2149 589 A1*, 2010.**

DURABIO from **Mitsubishi Chem.** is a **transparent bio-based engineering plastic** which shows high functionality and performance.

« A polycarbonate which exhibits excellent mechanical strengths, heat resistance, a small refractive index, a large Abbe number, small birefringence, and excellent transparency,… »

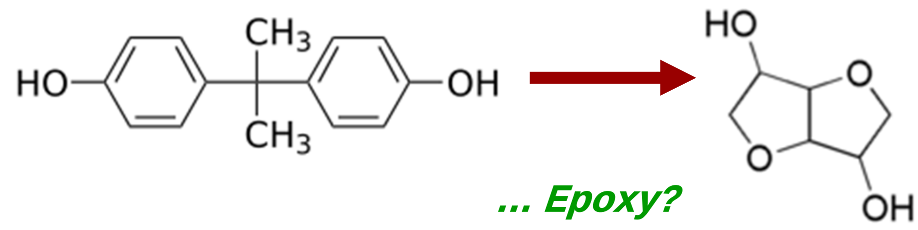
Pilot plant 300 tons/year in 2010;
Plant 10000 tons/year in 2012

http://www.japanchemicalweb.jp/ 20 July 2009

Potential applications of DURABIO:

- **New Optical device and component**
- **Glass Alternatives**
  (New Trends of future Automotive)

ISOSORBIDE ⟶ NEW EPOXY

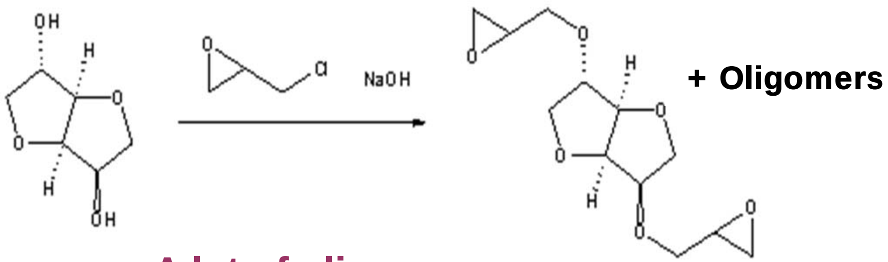


East A, Jaffe M, Zhang Y, Catalani LH.
(a) US Patent 2008/0021209A1; ***2008****;*
(b) US Patent 2008/0009599A1; ***2008****;*
(c) US Patent 7,619,056 B2; ***2009***
New Jersey Institute of Technology

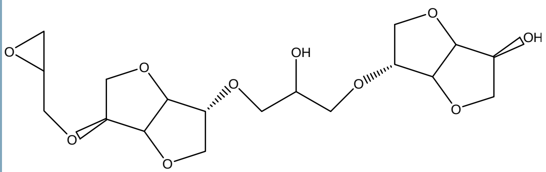
Feng et al. Polym Adv Technol ***2011****;22:139-50*

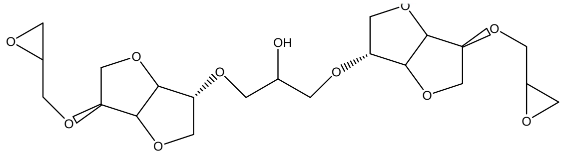
OUR WORK: M. Chrysanthos, J. Galy, J.-P. Pascault, *Polymer, 52, 3611-3620,* ***2011***

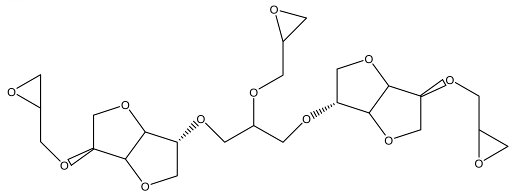
1- Classical Synthesis



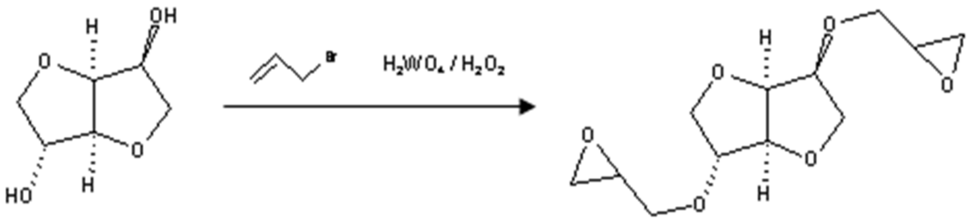
A lot of oligomers







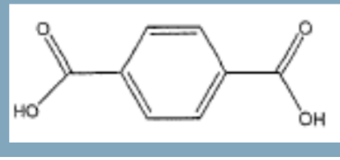
2-From di-allyl



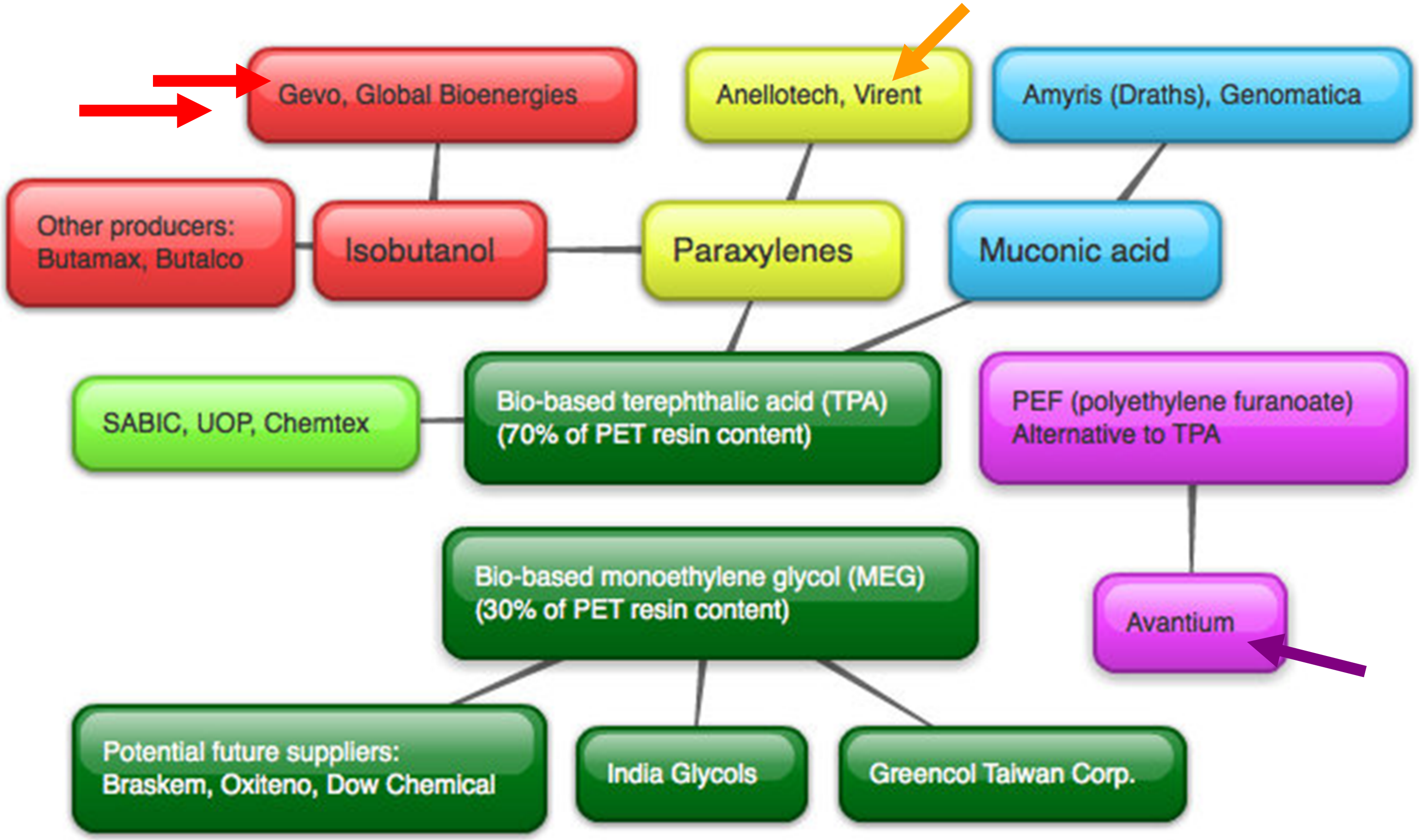
Networks very sensitive to water... ... Work in progress

Phd: Marie Chrysanthos

CONCLUSIONS: 1) BIO-PET



Lignocellulosic and Terpene Feedstocks



The driving force?

The «PlantBottle»

Coca-Cola Strategy 3 partners:
- **Gevo**
- **Virent**
- **Avantium**

PET Fibers

TORAY, 1 partner:
- **Gevo**

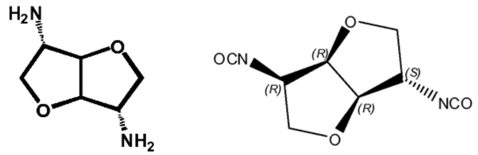
Bio-based polymers: a way to differentiate from competitors…

Source : http:// www.icis.com/blog/green-chemicals - June 2011

Special Chem - Nov 25, 2011; bioplastic Magazine Fev. 2011

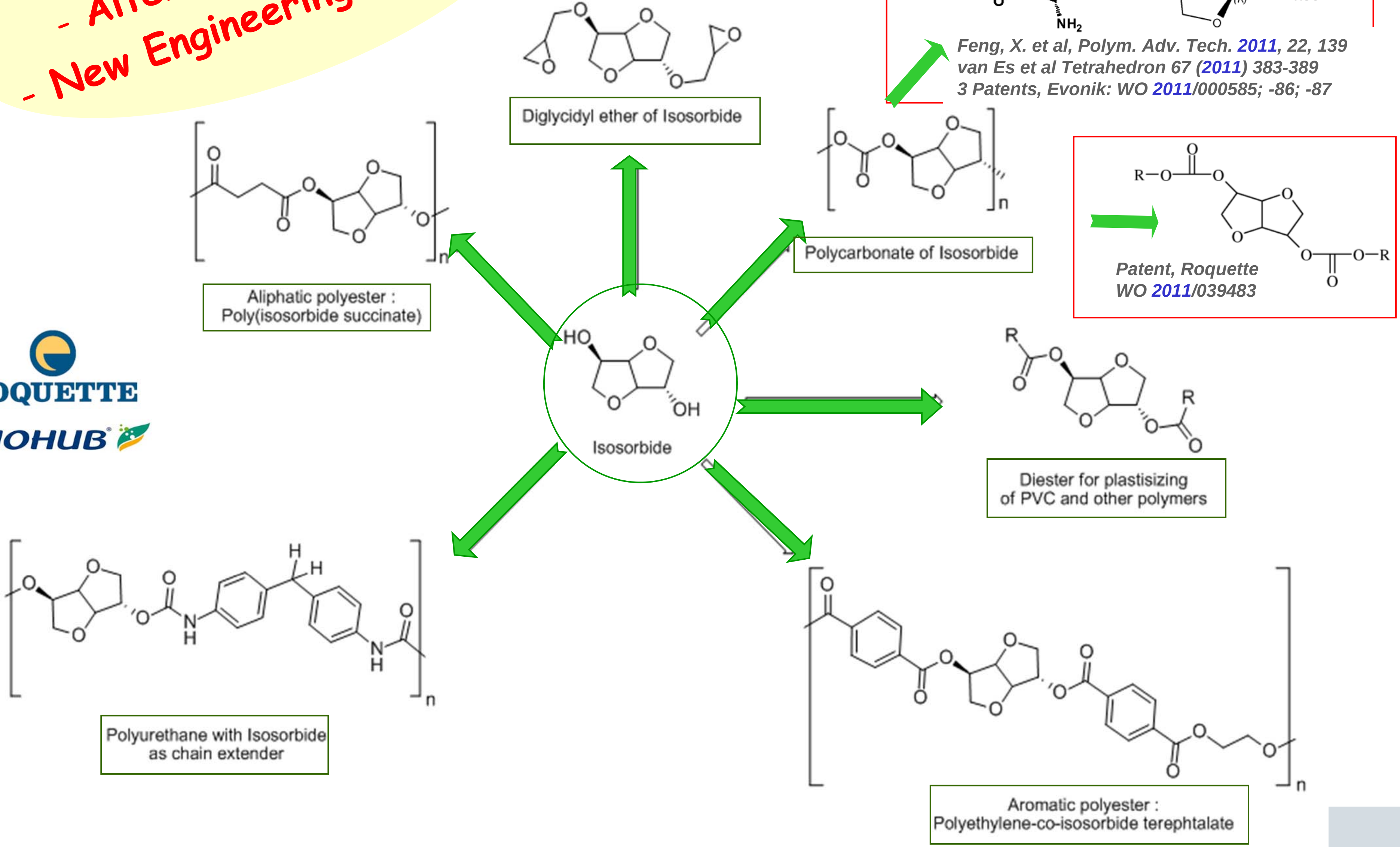
CON[...]) RIGID ALIPHATIC MOLECULE

Targets?
- Alternative to BPA?
- New Engineering Plastics?



Feng, X. et al, Polym. Adv. Tech. 2011, 22, 139
van Es et al Tetrahedron 67 (2011) 383-389
3 Patents, Evonik: WO 2011/000585; -86; -87

Patent, Roquette
WO 2011/039483



ROQUETTE
BIOHUB®

Chemical Plateform: POLYSORB® P