

Biobased product opportunities for carbohydrate conversion in the biorefinery: the “Top 10+4”

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- ***Introductory questions***

- How do you see the prospects of commercial utilization in your particular approach – synthetic biology, chemical or thermochemical routes?
- How do you see these commercial applications for biobased chemicals in a short, medium and long term?
- What are the strengths and the weaknesses of each route?

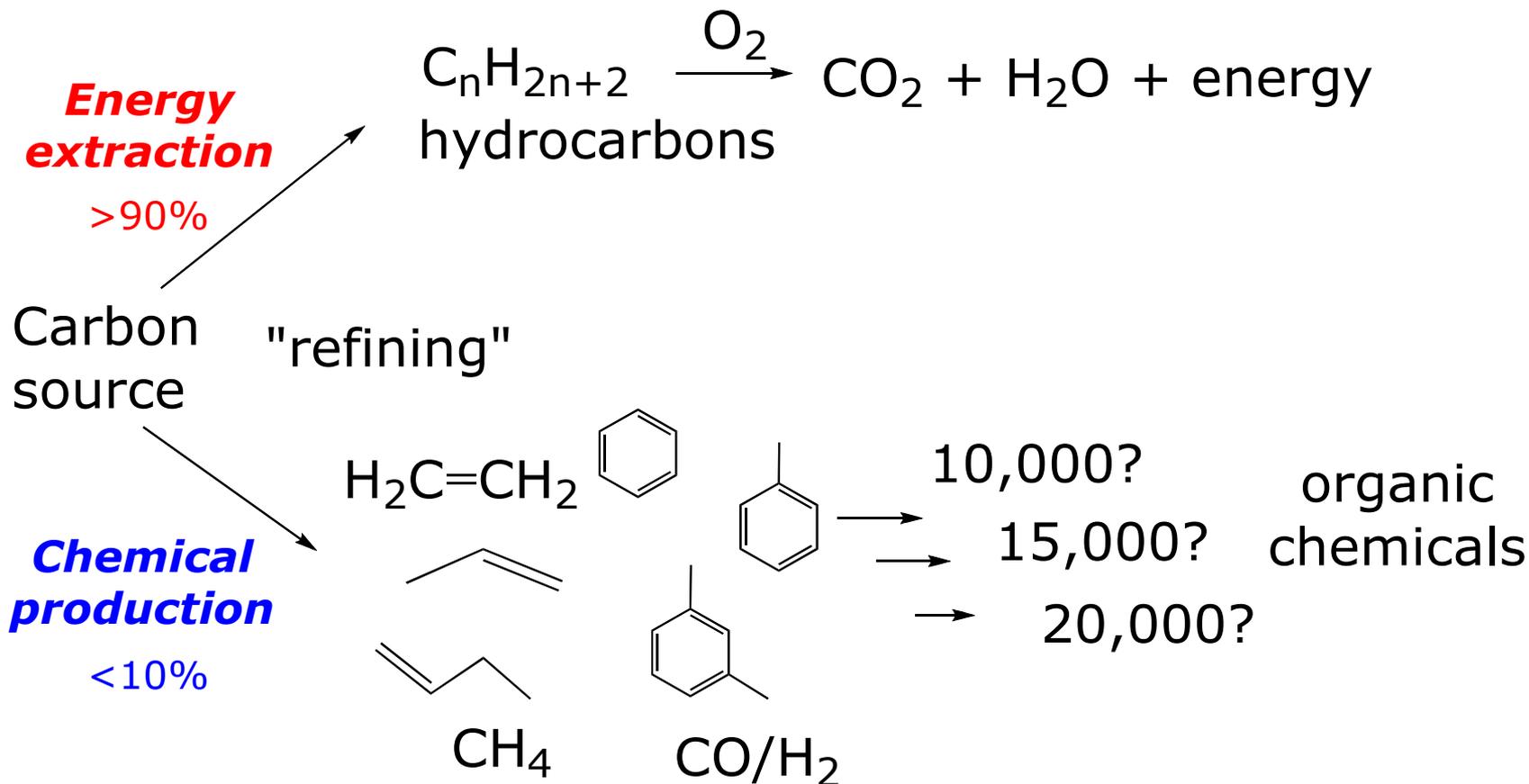
Can we identify opportunities that are the best bet for investment and will offer the greatest return?

- ***Starting point for discussion***

- Success will not result from simply attempting to pre-identify specific structures (“picking winners”), but rather by developing broad based conversion technologies, and coupling them with the unique features of a given biorefinery operation.



The key uses of carbon



U. S. - ~ 350×10^9 lb organic chemicals annually



The biorefinery supplies renewable carbon

Inputs (Supply)

Corn
Potatoes
Switchgrass
Sorghum
Soybeans
Apple pomace
Jerusalem artichoke
Guayule
Beet molasses
Sugar cane
Wood
Residues

Building blocks (Separation)

Carbohydrates
Aromatics
Hydrocarbons

Outputs (Conversion)

Butadiene	HMF
Polylactic acid	FDCA
Pentanes, pentene	Glycerol
BTX	Glycerol derivatives
Phenolics	Isoprene
Butanol	Biohydrocarbons
Organic acids	Lactic acid
Polyols	Ethanol
Resorcinol	HPA
Levoglucosan	Succinic acid
Peracetic acid	Levulinic acid
Tetrahydrofuran	Furfural
Anthraquinone	Sorbitol
Itaconic acid	Xylitol
Glutamic acid	Levulinic acid
Glucaric acid	PDO

High volume, low value fuels – energy impact

High value, low volume chemicals – economic impact and industrial driver

Bozell and Landucci 1993
Werpy and Petersen 2004
Bozell and Petersen 2010



Impact of chemical product integration with biofuels

	Scenario 1: Fossil Fuel and PDO	Scenario 2: Independent BioPDO and EtOH	Scenario 3: Integrated Corn Biorefinery
Economic: Pretax Return	11%	3%	20%
Environment: Total Energy			Down 72% vs scenario 1
Petroleum			Down 90% vs scenario 1
Natural gas			Down 54% vs scenario 1

R. Dorsch and R. Miller, World Congress on Industrial Biotechnology and Bioprocessing, April 2004, Orlando, FL



Comparative factors for renewable and nonrenewable carbon

	Nonrenewable carbon	Renewable carbon
supply	<i>Availability</i>	*
	<i>Sustainability</i>	**
	<i>Security</i>	**
	<i>Flexibility</i>	***
separation	<i>Cost</i>	**
	<i>Separation</i>	*
conversion	<i>Infrastructure</i>	*
	<i>Technology</i>	*

* - CRC/UT research focus area

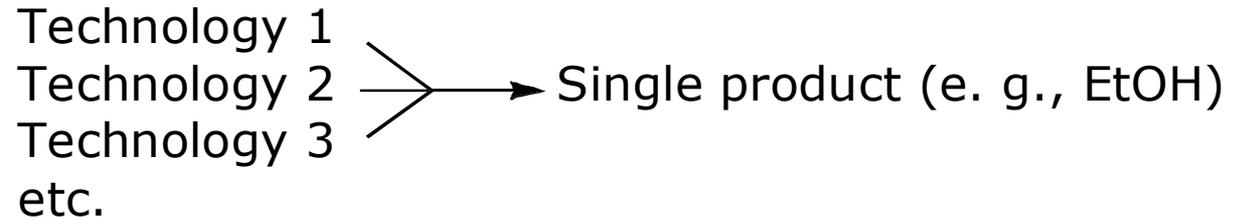
** - CRC/UT research driver

*** - UT collaborative research area

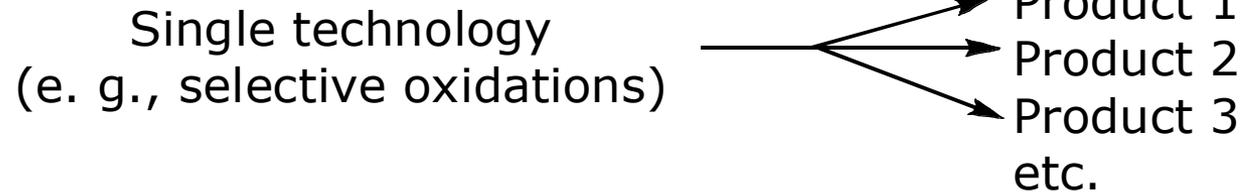


A diversity of opportunities challenges biobased product development

Fuels **(convergent)**



Chemicals **(divergent)**



- For biofuels, focus on *product identification* leads the choice of technology
- For chemical production, focus on the *choice of technology* leads product identification



Technology development drives identification of new product opportunities

The DOE “Top 10” product opportunities from carbohydrates - 2004

Succinic, fumaric and malic acids
2,5-Furan dicarboxylic acid
3-Hydroxypropionic acid
Aspartic acid
Glucaric acid
Glutamic acid
Itaconic acid
Levulinic acid
3-Hydroxybutyrolactone
Glycerol
Sorbitol
Xylitol
Arabinitol

The new “Top 10 + 4” product opportunities from carbohydrates - 2010

Ethanol
Furans - furfural, FDCA, HMF
Glycerol and derivatives
Biohydrocarbons - isoprene and others
Lactic acid
Succinic acid
Hydroxypropionic acid/aldehyde
Levulinic acid
Sorbitol
Xylitol



Criteria used to evaluate new opportunities

- *Significant recent literature attention*
- *The compound illustrates a broad technology applicable to multiple products*
- *The technology provides direct substitutes for existing petrochemicals*
- *The technology is applicable to high volume products*
- *A compound exhibits strong potential as a platform*
- *Scaleup of the product or a technology at some level is underway*
- *The biobased compound is an existing commercial product, prepared at intermediate or commodity levels*
- *The compound could be a primary building block of the biorefinery*
- *Commercial production of the compound from renewable carbon is well established*



Technology needs illustrated by candidates

Illustrative general biorefinery technology needs

- Selective alcohol **dehydrations**; Improved biochemical production of alcohols from biomass **rate, yield, titer, product, pH, inhibitor tolerance**; Engineering of optimal fermentation organisms
- Selective **dehydrations** of carbohydrates; New catalysts and reaction media for **dehydration**; **reactive separations**; **selective oxidations** of alcohols; Improved oxidation and **dehydration catalysts**; **catalytic systems** for reactions in aqueous solution
- Reactions in aqueous solution**; **selective reductions** and **oxidations** of polyols; Improved biological conversions of polyols
- Improved bihydrocarbon production; Engineering of organisms to convert sugars to hydrocarbons; Optimizing **rate, yield, titer, product tolerance**
- Optimization of bioconversion of carbohydrates; Bioprocesses with high **rate, yield, titer, product, pH and inhibitor tolerance**; Engineering of organisms to produce single materials
- Bioconversion of carbohydrates; Optimization of **yield, rate, titer, separation**; Engineering of organisms for optimal production of target
- Optimization of bioconversion of carbohydrates; Bioprocesses with high **rate, yield, titer, product and inhibitor tolerance**; Engineering of organisms to produce single materials; **selective dehydrations** of alcohols; **selective reductions** of carbonyl groups; New **selective hydrogenation** catalysts; Chemical processes in aqueous solution
- Selective **dehydrations** of carbohydrates; Improved separations of products; Utility of co-product schemes by biorefinery; Improved **catalysts** for **selective carbohydrate conversion** processes
- selective hydrogenolysis** of polyols; New catalysts for reduction of carbohydrate derivatives; **selective dehydrations** of polyols; Comparative assessment of chemical and biochemical conversion technology; **selective bond breaking/bond making** technology for polyols
- Selective **hydrogenolysis** of polyols; New catalysts for reduction of carbohydrate derivatives; **selective dehydrations** of polyols; Comparative assessment of chemical and biochemical conversion technology; **selective bond breaking/bond making** technology for polyols

2



Technology needs illustrated by candidates

Compound	Illustrative general biorefinery technology needs
Ethanol	Selective alcohol dehydrations; Improved biochemical production of alcohols from biomass (rate, yield, titer, product, pH, inhibitor tolerance); Engineering of optimal fermentation organisms
Furans	Selective dehydrations of carbohydrates; New catalysts and reaction media for dehydration; Reactive separations; Selective oxidations of alcohols; Improved oxidation and dehydration catalysts; Catalytic systems for reactions in aqueous solution
Glycerol	Reactions in aqueous solution; Selective reductions and oxidations of polyols; Improved biological conversions of polyols
Biohydrocarbons	Improved biohydrocarbon production; Engineering of organisms to convert sugars to hydrocarbons; Optimizing rate, yield, titer, product tolerance
Lactic acid	Optimization of bioconversion of carbohydrates; Bioprocesses with high rate, yield, titer, product, pH and inhibitor tolerance; Engineering of organisms to produce single materials
Succinic acid	Bioconversion of carbohydrates; Optimization of yield, rate, titer, separation; Engineering of organisms for optimal production of target
Hydroxypropionic acid/aldehyde	Optimization of bioconversion of carbohydrates; Bioprocesses with high rate, yield, titer, product and inhibitor tolerance; Engineering of organisms to produce single materials; Selective dehydrations of alcohols; Selective reductions of carbonyl groups; New selective hydrogenation catalysts; Chemical processes in aqueous solution
Levulinic acid	Selective dehydrations of carbohydrates; Improved separations of products; Utility of co-product schemes by biorefinery; Improved catalysts for selective carbohydrate conversion processes
Sorbitol	Selective hydrogenolysis of polyols; New catalysts for reduction of carbohydrate derivatives; Selective dehydrations of polyols; Comparative assessment of chemical and biochemical conversion technology; Selective bond breaking/bond making technology for polyols
Xylitol	Selective hydrogenolysis of polyols; New catalysts for reduction of carbohydrate derivatives; Selective dehydrations of polyols; Comparative assessment of chemical and biochemical conversion technology; Selective bond breaking/bond making technology for polyols

2



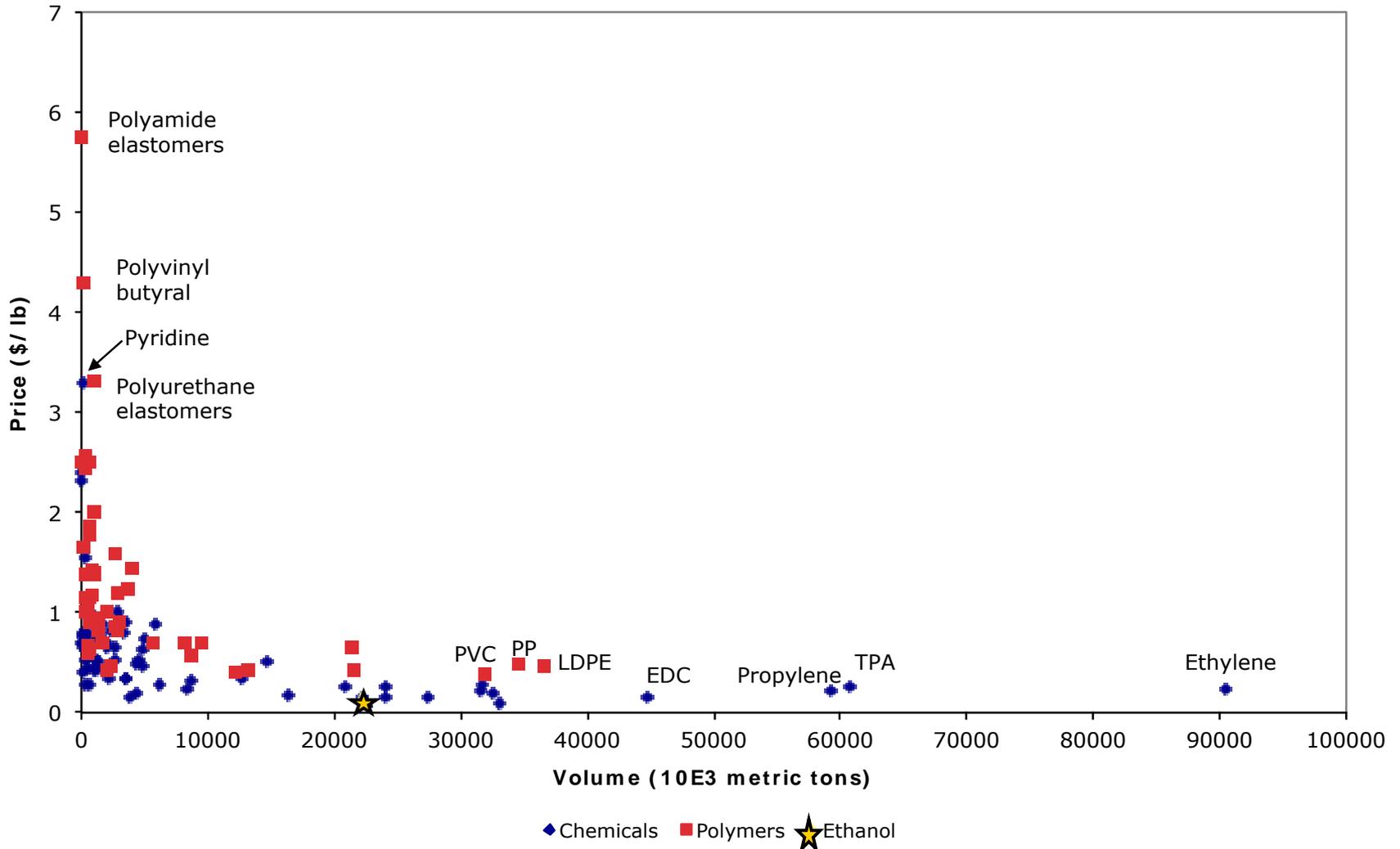
Performance of candidates against criteria

Criterion	1-Extensive recent literature	2-Multiple product applicability	3-Direct substitute	4-High volume product	5-Platform potential	6-Industrial scaleup	7-Existing commercial product	8-Primary building block	9-Commercial biobased product
Compound									
Ethanol	+++	+++	+++	+++	+++	+++	+++	+++	+++
Furfural	+++	++	+	++	+	+	+++	++	+++
HMF	+++	++	+	+	++	+	+	++	+
FDCA	+++	+	+	+++	++	+	+	+	+
Glycerol/derivatives	+++	+++	+++	+++	+++	+++	+++	+++	+++
Isoprene	+++	++	+++	+++	+	+++	+++	+	+
Biohydrocarbons	+++	++	+++	+	+	+	+	++	+
Lactic acid	+++	+++	+	+++	++	+	++	+	+
Succinic acid	+++	+++	+	+	+++	+++	+	+	+
HPA	+++	+	+++	+++	++	+	+	+	+
Levulinic acid	+++	++	+++	++	+++	+++	+	+++	+
Sorbitol	+++	+++	+++	+++	+++	+++	+++	+++	+++
Xylitol	+++	+++	+	+	+++	+	++	+++	++

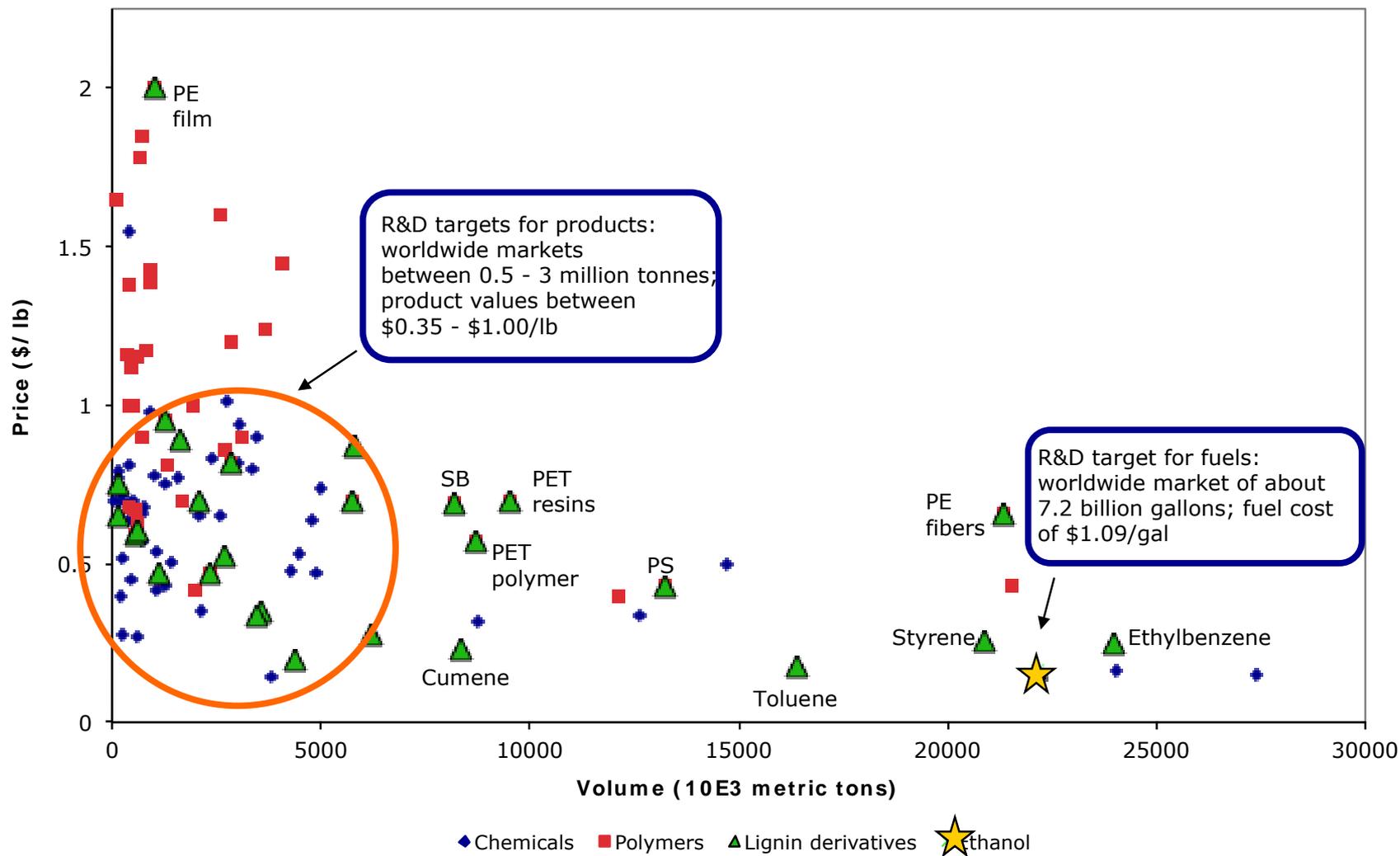
+++ Good performance against criterion; ++ Emerging performance against criterion; + Lower performance against criterion



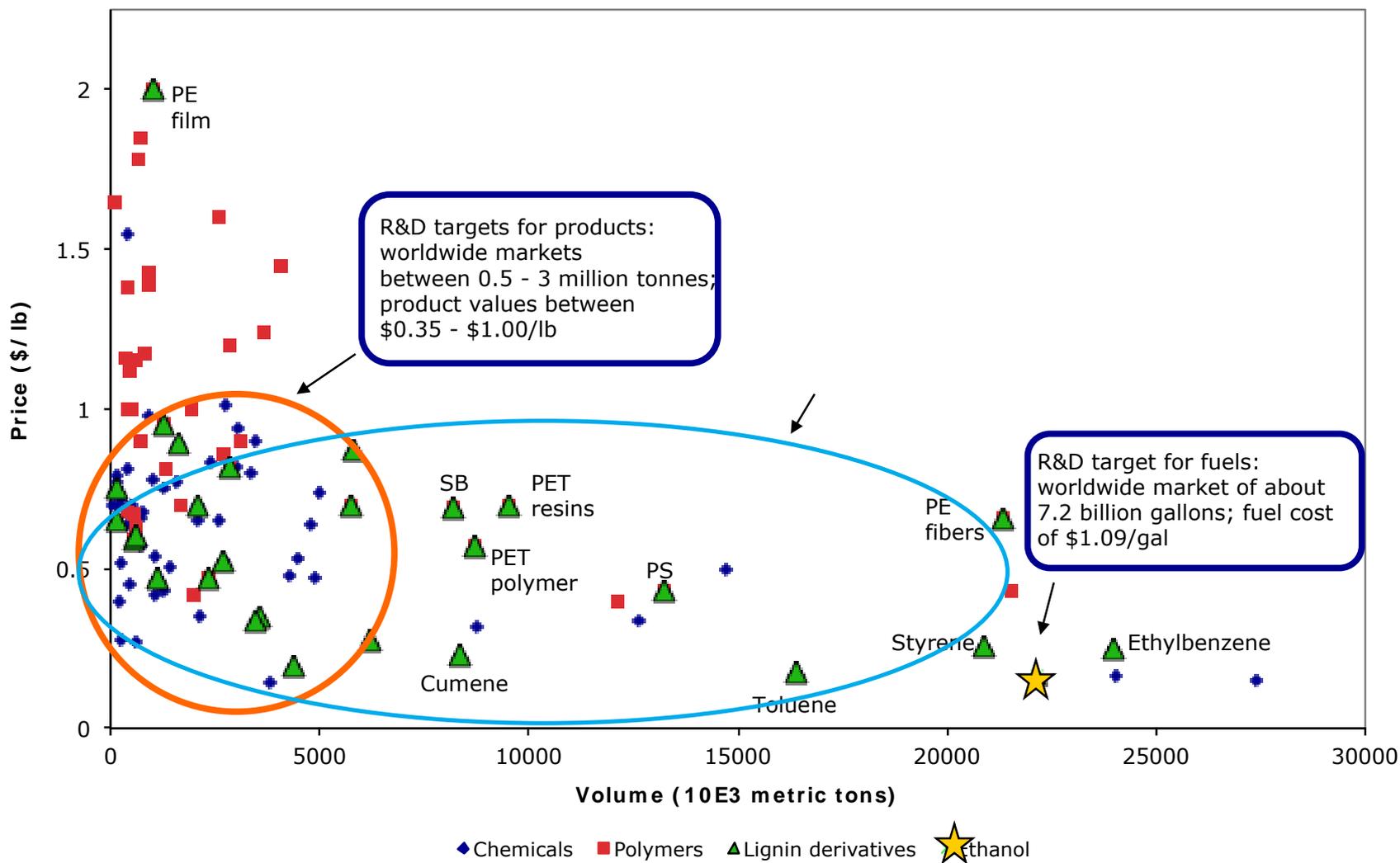
Can target costs be predicted?



Volume and prices of commercial chemicals and polymers



Volume and prices of commercial chemicals and polymers



Timing of the opportunities is even harder to predict

Ethanol	+++	+++	+++	+++	+++	+++	+++	+++	+++
Glycerol/derivatives	+++	+++	+++	+++	+++	+++	+++	+++	+++
Sorbitol	+++	+++	+++	+++	+++	+++	+++	+++	+++
Furfural	+++	++	+	++	+	+	+++	++	+++
Levulinic acid	+++	++	+++	++	+++	+++	+	+++	+
Lactic acid	+++	+++	+	+++	++	+	++	+	+
Succinic acid	+++	+++	+	+	+++	+++	+	+	+
Xylitol	+++	+++	+	+	+++	+	++	+++	++
FDCA	+++	+	+	+++	++	+	+	+	+
Isoprene	+++	++	+++	+++	+	+++	+++	+	+
Biohydrocarbons	+++	++	+++	+	+	+	+	++	+
HMF	+++	++	+	+	++	+	+	++	+
HPA	+++	+	+++	+++	++	+	+	+	+



Timing of the opportunities is even harder to predict

short

Ethanol	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
Glycerol/derivatives	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
Sorbitol	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
Furfural	+++	++	+	++	+	+	+++	++	+++	+++
Levulinic acid	+++	++	+++	++	+++	+++	+	+++	+	+
Lactic acid	+++	+++	+	+++	++	+	++	+	+	+
Succinic acid	+++	+++	+	+	+++	+++	+	+	+	+
Xylitol	+++	+++	+	+	+++	+	++	+++	++	++
FDCA	+++	+	+	+++	++	+	+	+	+	+
Isoprene	+++	++	+++	+++	+	+++	+++	+	+	+
Biohydrocarbons	+++	++	+++	+	+	+	+	++	+	+
HMF	+++	++	+	+	++	+	+	++	+	+
HPA	+++	+	+++	+++	++	+	+	+	+	+



Timing of the opportunities is even harder to predict

short

Ethanol	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
Glycerol/derivatives	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
Sorbitol	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++

medium

Furfural	+++	++	+	++	+	+	+++	++	+++
Levulinic acid	+++	++	+++	++	+++	+++	+	+++	+
Lactic acid	+++	+++	+	+++	++	+	++	+	+
Succinic acid	+++	+++	+	+	+++	+++	+	+	+
Xylitol	+++	+++	+	+	+++	+	++	+++	++
FDCA	+++	+	+	+++	++	+	+	+	+
Isoprene	+++	++	+++	+++	+	+++	+++	+	+

Biohydrocarbons	+++	++	+++	+	+	+	+	++	+
HMF	+++	++	+	+	++	+	+	++	+
HPA	+++	+	+++	+++	++	+	+	+	+



Timing of the opportunities is even harder to predict

		2015	2016	2017	2018	2019	2020	2021	2022	2023
short	Ethanol	+++	+++	+++	+++	+++	+++	+++	+++	+++
	Glycerol/derivatives	+++	+++	+++	+++	+++	+++	+++	+++	+++
	Sorbitol	+++	+++	+++	+++	+++	+++	+++	+++	+++
medium	Furfural	+++	++	+	++	+	+	+++	++	+++
	Levulinic acid	+++	++	+++	++	+++	+++	+	+++	+
	Lactic acid	+++	+++	+	+++	++	+	++	+	+
	Succinic acid	+++	+++	+	+	+++	+++	+	+	+
	Xylitol	+++	+++	+	+	+++	+	++	+++	++
	FDCA	+++	+	+	+++	++	+	+	+	+
	Isoprene	+++	++	+++	+++	+	+++	+++	+	+
long	Biohydrocarbons	+++	++	+++	+	+	+	+	++	+
	HMF	+++	++	+	+	++	+	+	++	+
	HPA	+++	+	+++	+++	++	+	+	+	+



In the short term - the glycerol product family

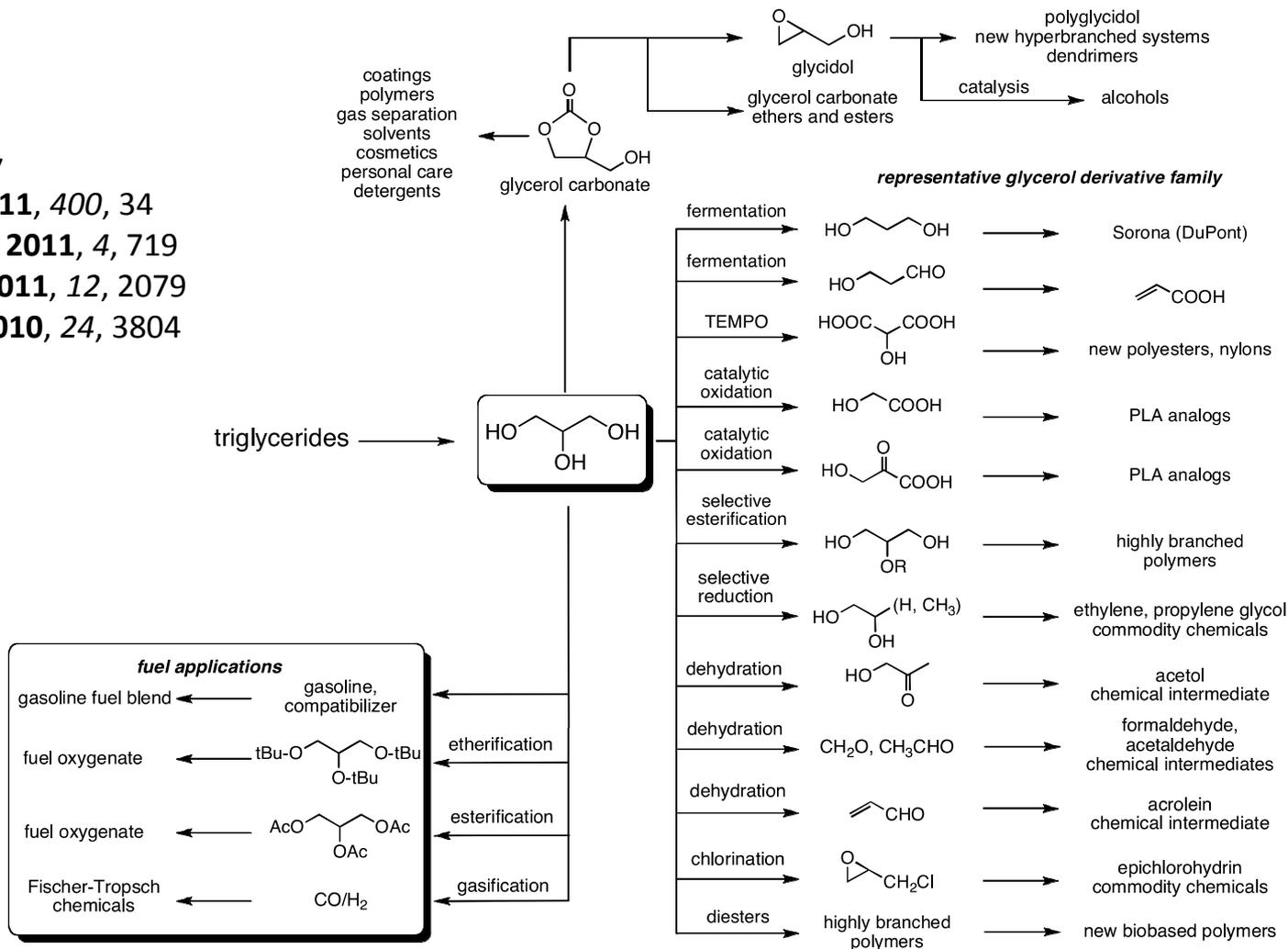
Recent activity

Appl. Cat. A **2011**, 400, 34

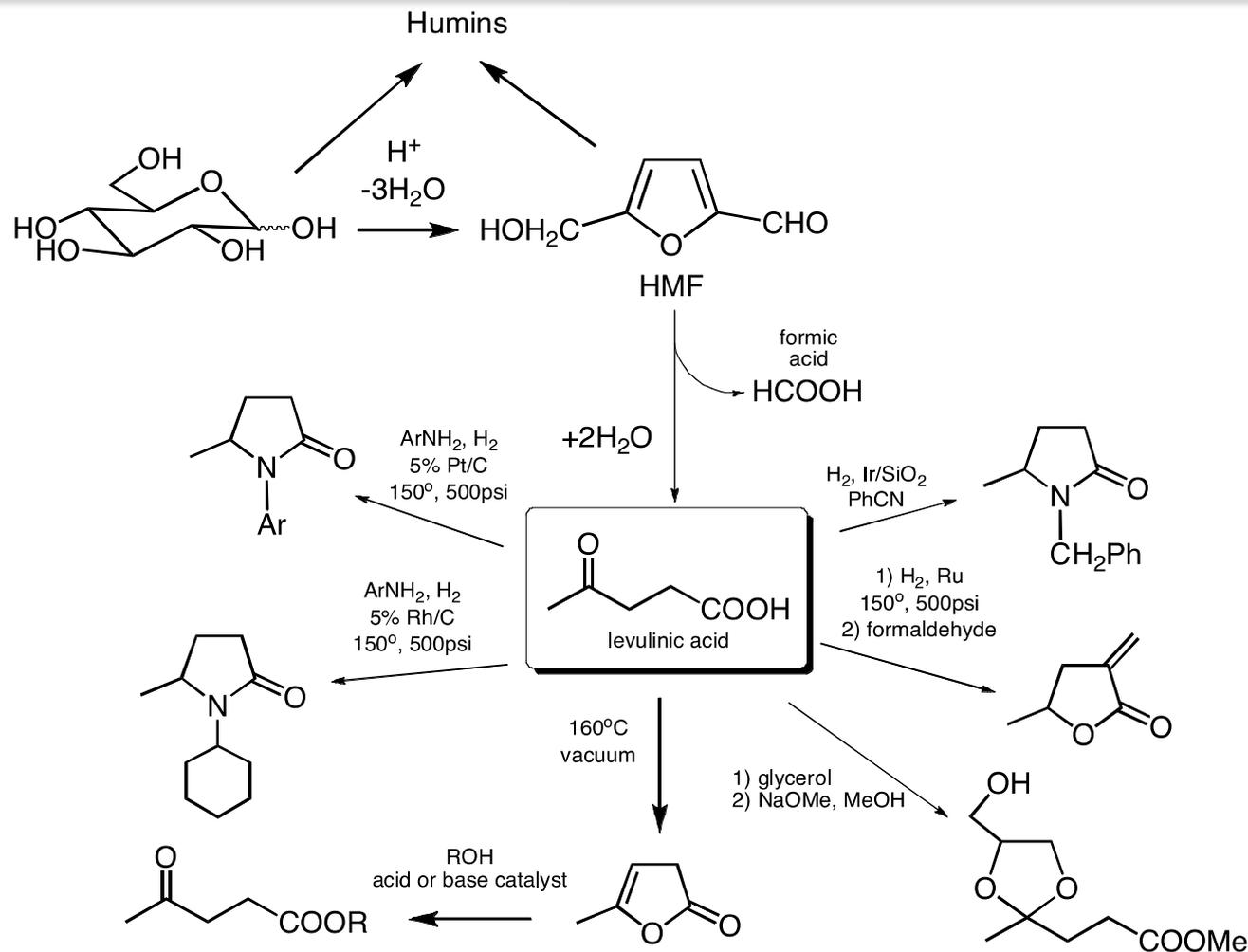
ChemSusChem **2011**, 4, 719

Green Chem. **2011**, 12, 2079

Energy Fuels **2010**, 24, 3804



In the medium term - the levulinic acid product family



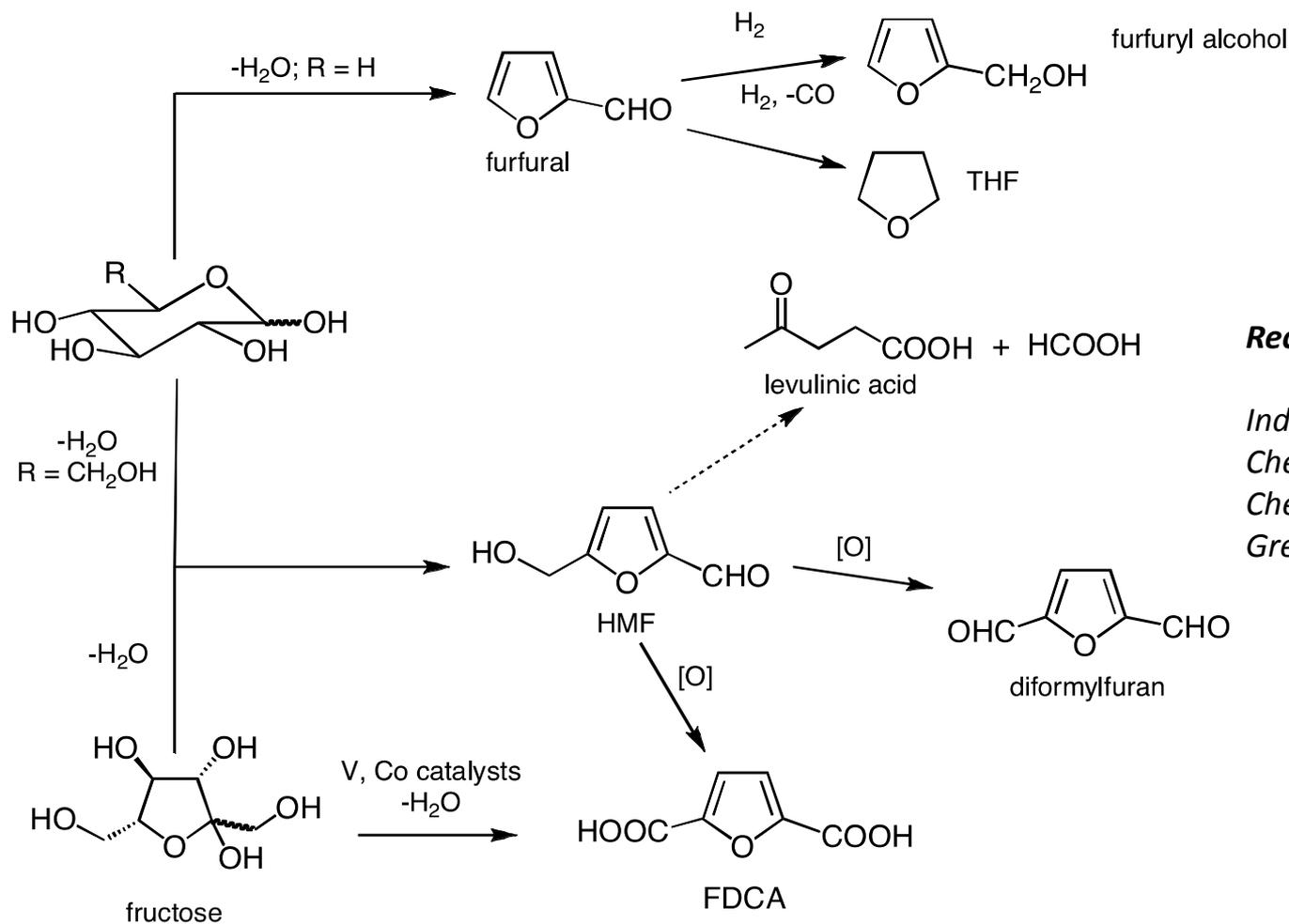
Recent activity

Holzforschung **2011**, 65, 439
J. Mol. Catal. A **2011**, 341, 14
BioFPR **2011**, 5, 198
Green Chem. **2010**, 12, 574

Previous work: DALA, GVL, DPA



And the longer term - carbohydrates to furans



Recent activity

Ind. Eng. Chem. Res. 2011, 50, 7985

Chem. Rev. 2011, 111, 397

ChemSusChem, 2011, 4, 51

Green Chem. 2011, 13, 824

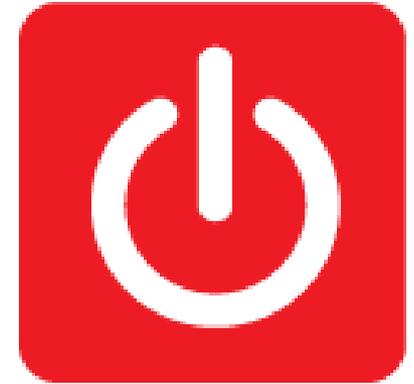
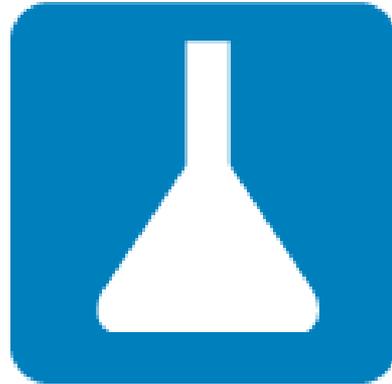


A basis for further discussion?

- ***How do you see the prospects of commercial utilization in your particular approach – synthetic biology, chemical or thermochemical routes?***
 - ***Discussion:*** the process cannot be based strictly on choosing the right structure. Technology that is broadly applicable is needed. The best opportunities are those that couple a robust technology with a defined product use or need and that exhibits a strongly viable economic profile. There is nothing surprising about this, but if these criteria are not met, the product will not fly.
- ***How do you see these commercial applications for biobased chemicals in a short, medium and long term?***
 - ***Discussion:*** Determination of short, medium and long term opportunities is often a function of the individual companies, however, the literature reveals approaches and development underway. Network analysis (e. g., Marquardt, *Comp. Chem. Eng.* **2010**, *34*, 1909) could be invaluable.
- ***What are the strengths and the weaknesses of each route?***
 - ***Discussion:*** The primary weaknesses in current efforts developing biobased chemicals is a lack of broad based technology coupled with a focus on trying to choose the single best compound from among many choices, along with a current lack of information regarding possible economic performance.



Thank You!



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