Perspectives on Biobased Products & Production of Oxidized and Reduced Derivatives of 5-Hydroxymethylfurfural (HMF)

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Oil Barrel Breakdown

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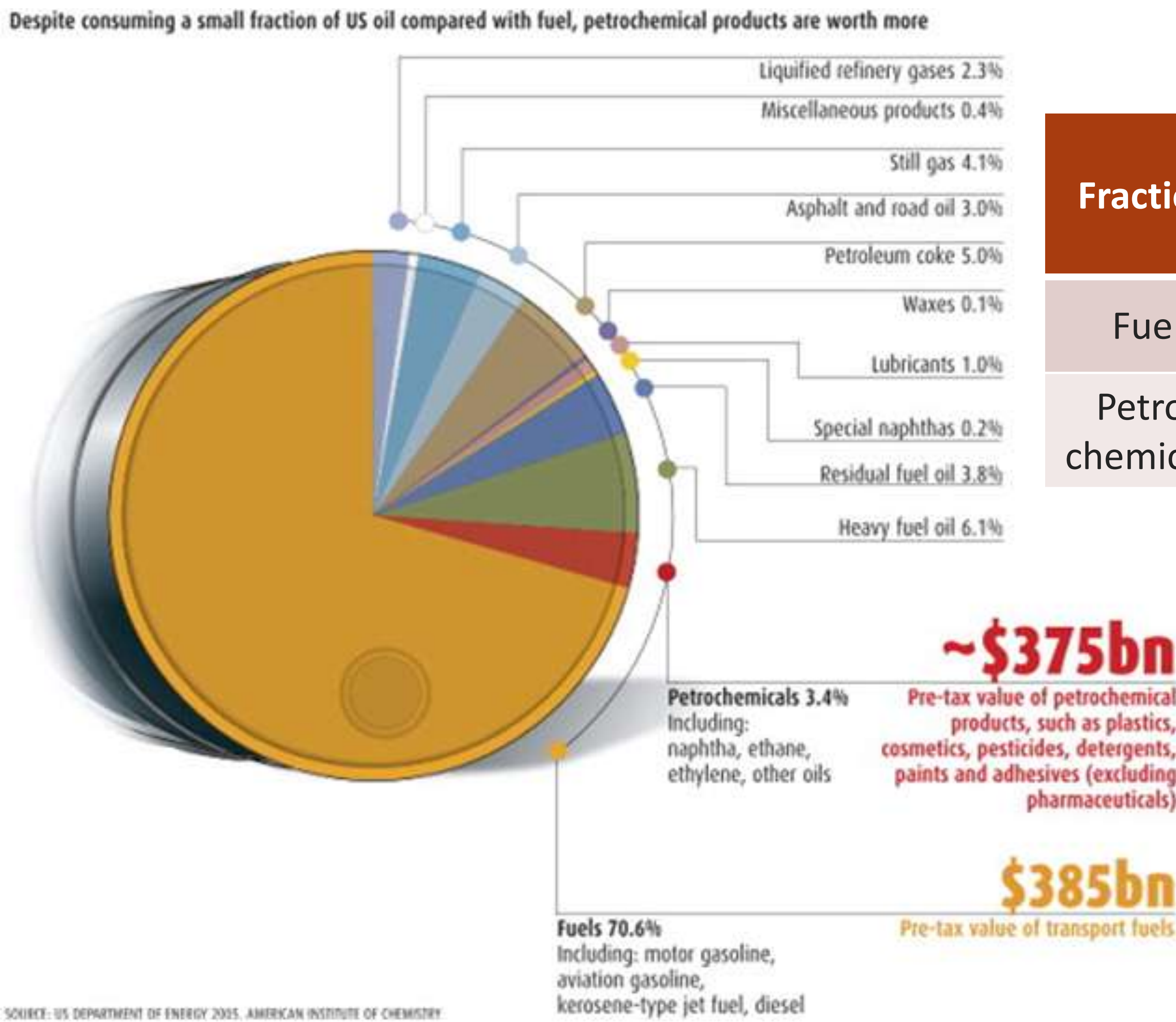

Fraction	Volume %	Value (billions)
Fuel	70.6	$385
Petro-chemicals	3.4	$375

J. Marshall *New Scientist*, **2007**, 28-31

Petrochemical are Derived From Key Building Blocks

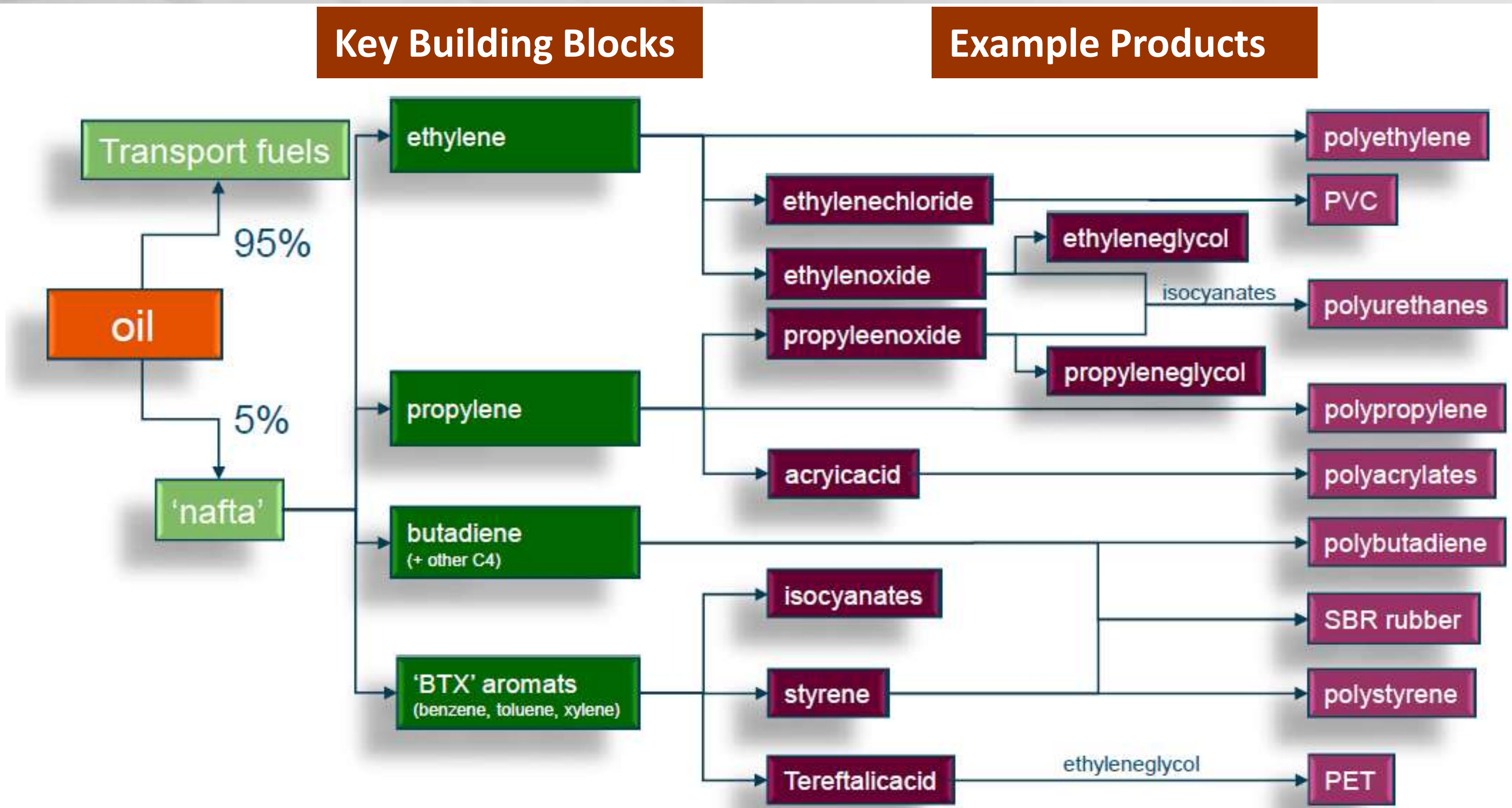

figure from: Dr. Harriëtte Bos, Wageningen UR-FBR Biorefining 2012, 31 October 2012

"For the U.S. chemical industry, around 98% of all chemicals produced in excess of 4 million kg/yr are produced from petroleum and natural gas".
J. Frost *Industrial Biotechnology* 1(1) 2005, 23-24

Possible Key Biorefinery Building Blocks

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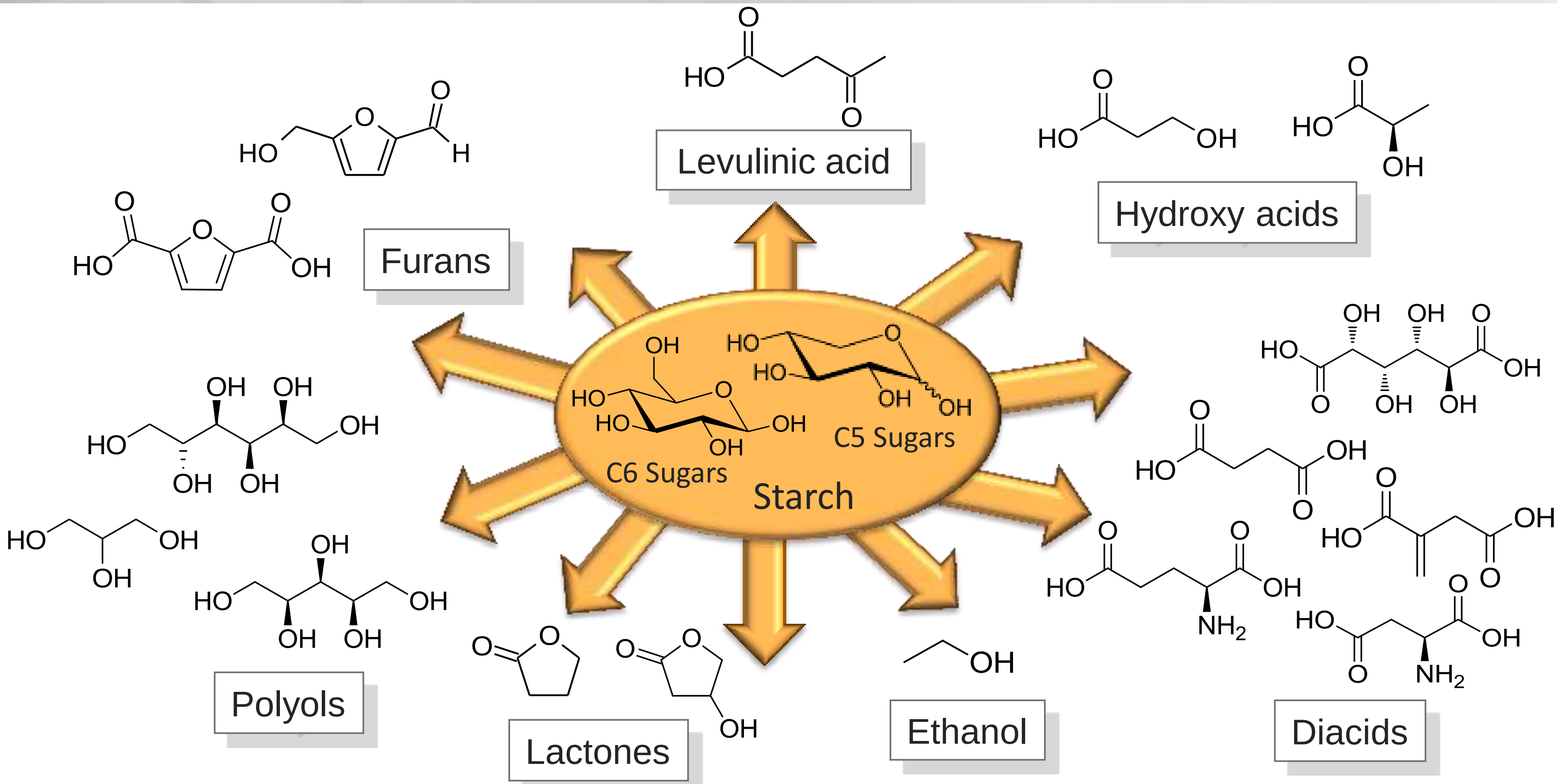

Sugars could be derived from any source: corn, sugar cane, cellulose, hemicellulose, etc

sugars: Werpy et al., Top Value Added Chemicals from Biomass Vol. I, U.S. DOE, 2004
Bozell and Peterson, Green Chem., 12, 2010, 539-554
lignin: Bozell et al. , Top Value Added Chemicals from Biomass Vol. II, PNNL-16983, 2007

Key Biomass Building Blocks are Platforms for Numerous Biobased Products

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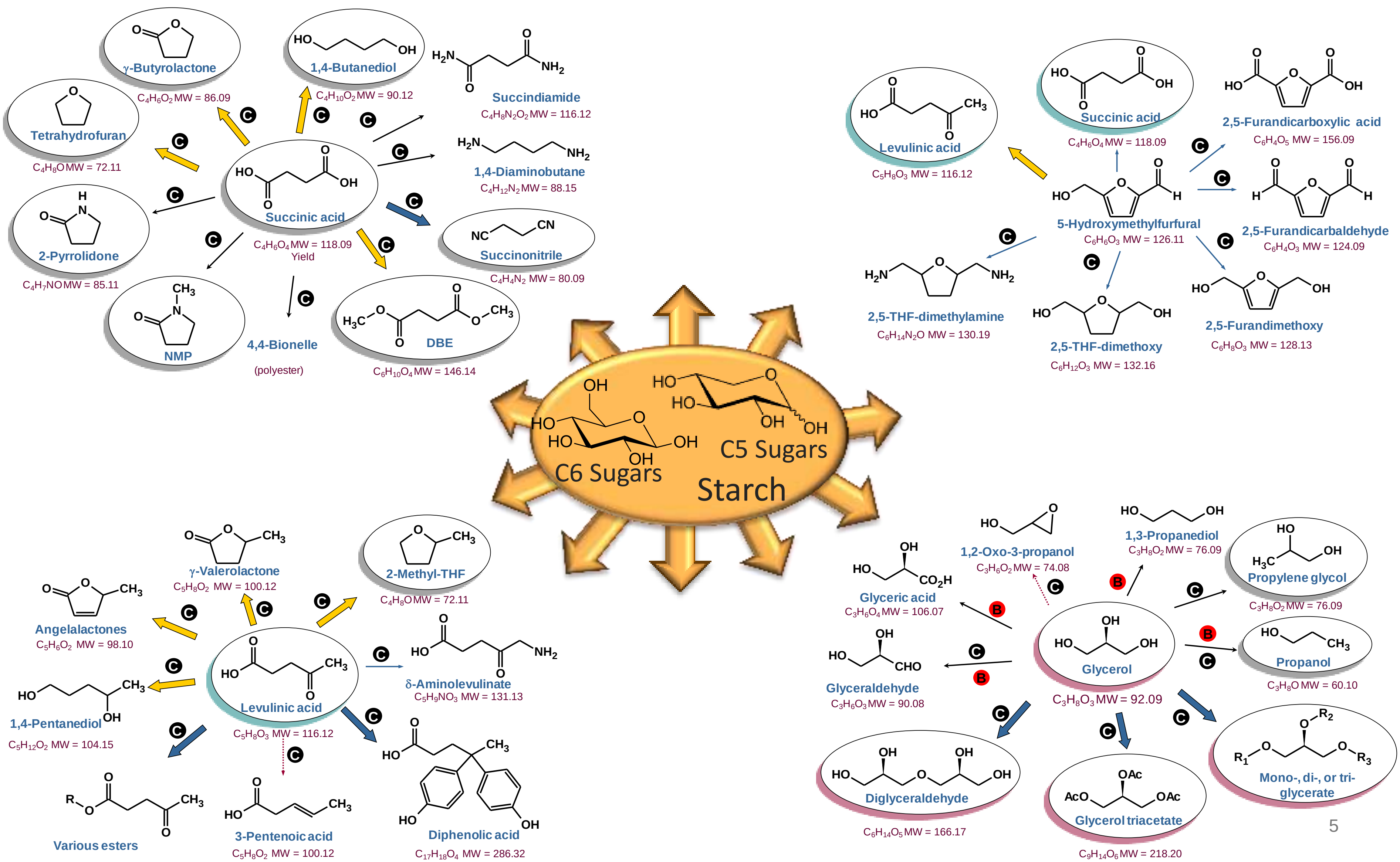

Moving Biobased Products Forward

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- Strengthen Technology Push
  - Deconstruction of lignocellulosic biomass into sugars and lignin via thermal and/or biochemical routes
  - Formation of key platform molecules and conversion to products (chemistry/biochemistry/catalysis/engineering)
  - Separations
  - Need to understand enabling synergies with fuel production

Moving Biobased Products Forward

- Strengthen Market Pull
  - Determine end product properties/specifications – define applications
  - Being a renewable product may not be enough – it has to outperform
  - Conduct techno-economic, lifecycle, and market analyses
  - Any bio-based product with suitable properties whose cost is ≤ the cost of a petrochemical-based product has a high probability of commercialization

Propylene Glycol (PG) from renewable sources for clean production of chemicals

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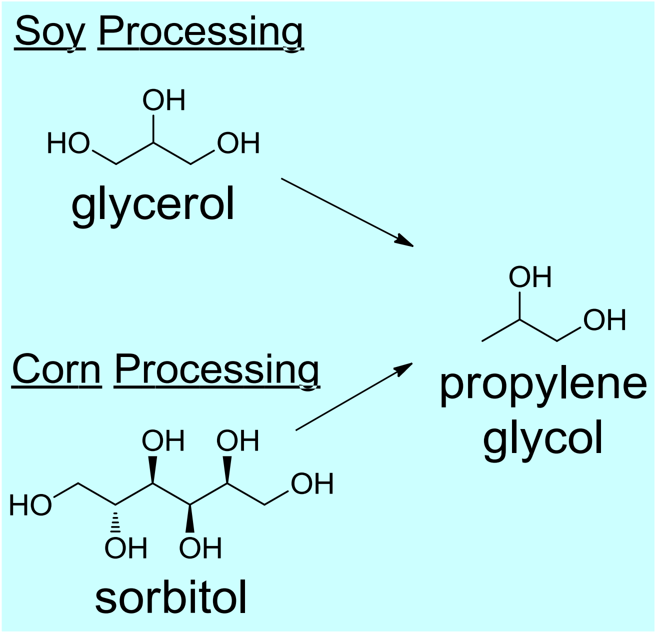
DOE-Energy Efficiency and Renewable Energy (EERE) → **DOE-EERE, Industry** → **Industry**



Catalyst capabilities developed by the Office of Science were leveraged in a series of EERE-funded CRADA projects. EERE supported technology transfer to industry. Private funds were used to pilot and commercialize the technology. ADM licensed the patent portfolio and completed construction of a full-scale production facility in 2010.

Evolution of the Plastic Bottle

PETE

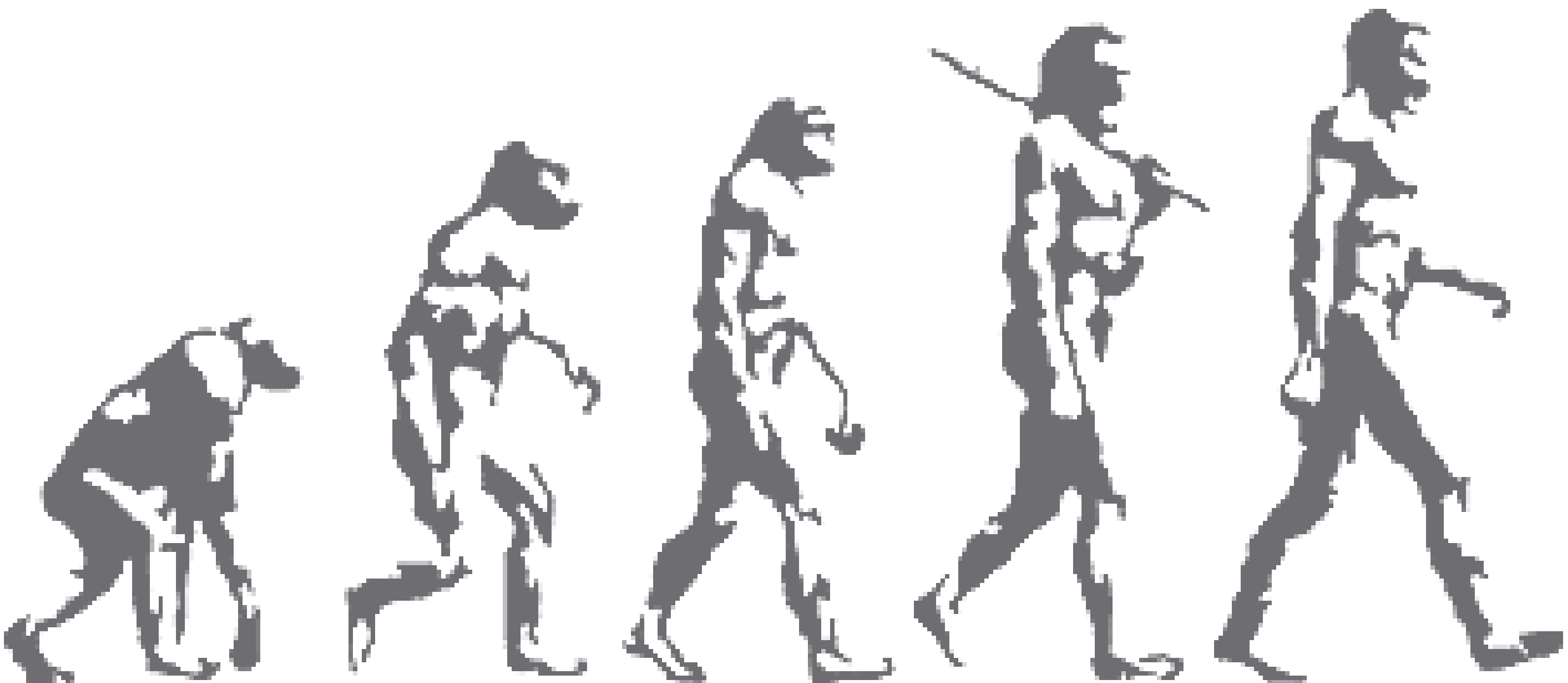
plantbottle
up to 30% plant-based
100% recyclable bottle

vxy
by avantium

100% Petroleum Based poly(ethylene terephthalate)

30-100% Biobased poly(ethylene terephthalate)

100% Biobased poly(ethylene furanoate) (PEF)

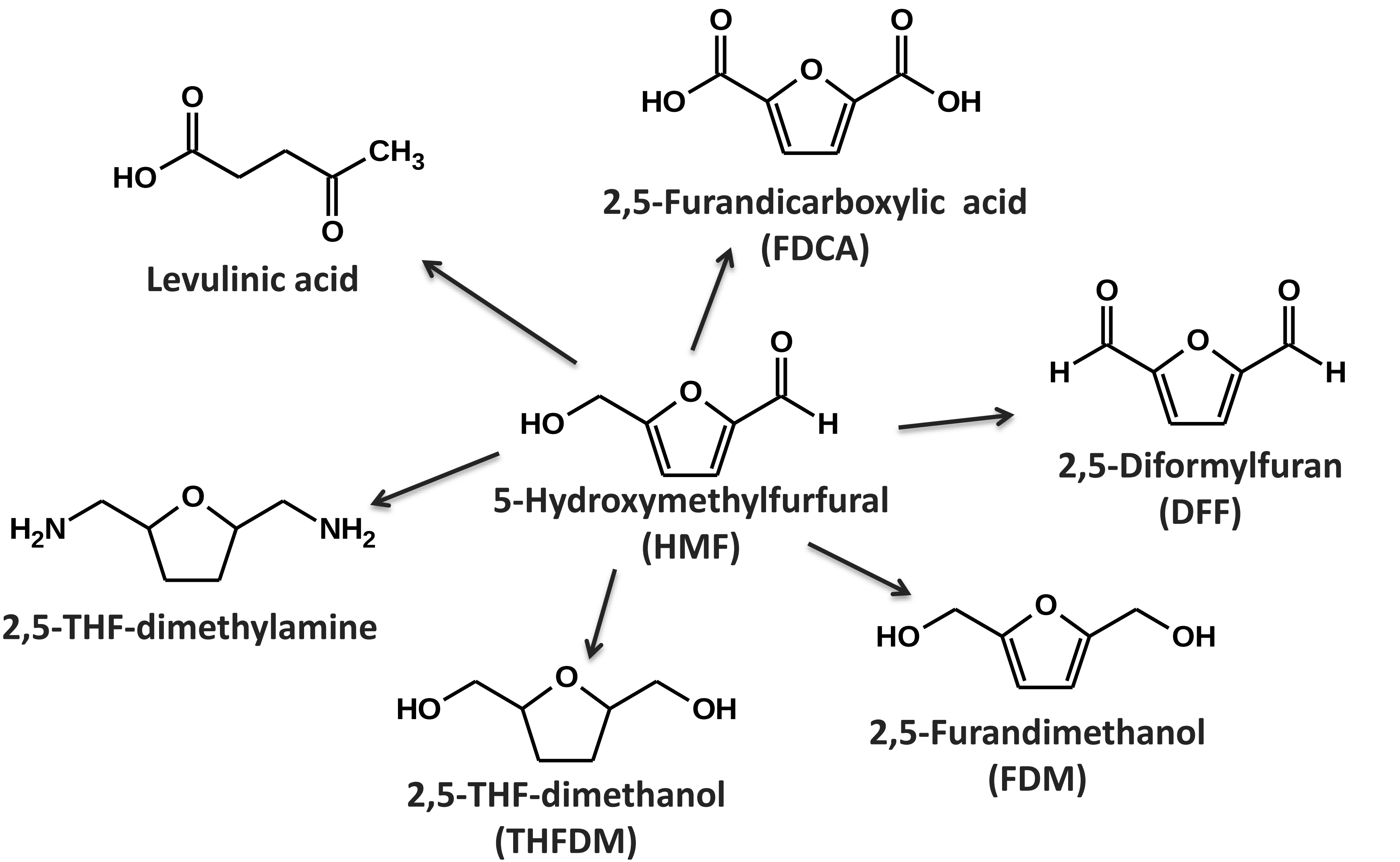


PEF Has Superior Properties

- Superior barrier properties:
  - PEF oxygen barrier is 6 times better than PETE
  - PEF carbon dioxide barrier is 3 times better than PETE
  - PEF water barrier is 2 times better than PETE

- More attractive thermal properties:
  - More heat resistant. The Tg of PEF is 86°C compared to the Tg of PETE of 74°C
  - Lower processing temperature. The Tm of PEF is 235°C compared to the Tm of PETE of 265°C

5-Hydroxymethylfurfural Derivatives



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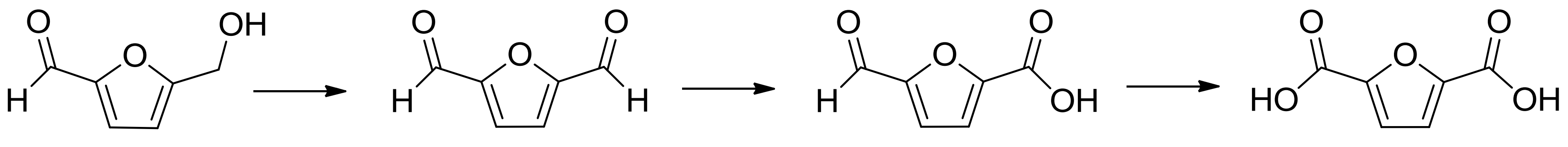
HMF and HMF Derivatives are Potential Bio-Based Intermediates for a Variety of Products

- Polymers
  - Polyesters
  - Polyurethanes
  - Polyamides
- Binders
- Adhesives
- Coatings
- Foams

Some leading references:

J. Lewkowski, ARKIVOC (i) (2001) 17-54.
A. Gandini and M.N. Belgacem, Prog. Polym. Sci. 22 (1997) 1203-1379.
C. Moreau, M.N. Belgacem, and A. Gandini, Top. Catal. 27 (2004) 11-30.

Oxidation of HMF



"Hydroxymethyl Furfural Oxidation Methods" M.A. Lilga, R.T. Hallen, J. Hu, J.F. White, and M.J. Gray, U.S. Patent No. 8,193,381 B2, June 5, 2012.

"Hydroxymethyl Furfural Oxidation Methods" M.A. Lilga, R.T. Hallen, J. Hu, J.F. White, and M.J. Gray, U.S. Patent No. 8,193,382 B2, June 5, 2012.

"Hydroxymethyl Furfural Oxidation Methods", M.A. Lilga, R.T. Hallen, J. Hu, J.F. White, and M.J. Gray, U.S. Patent No. 7,700,788 B2, April 20, 2010.

Batch Oxidation of 3 wt% HMF at 60°C and 150 psi O_2 in Neutral Solution Over 9%Pt/C

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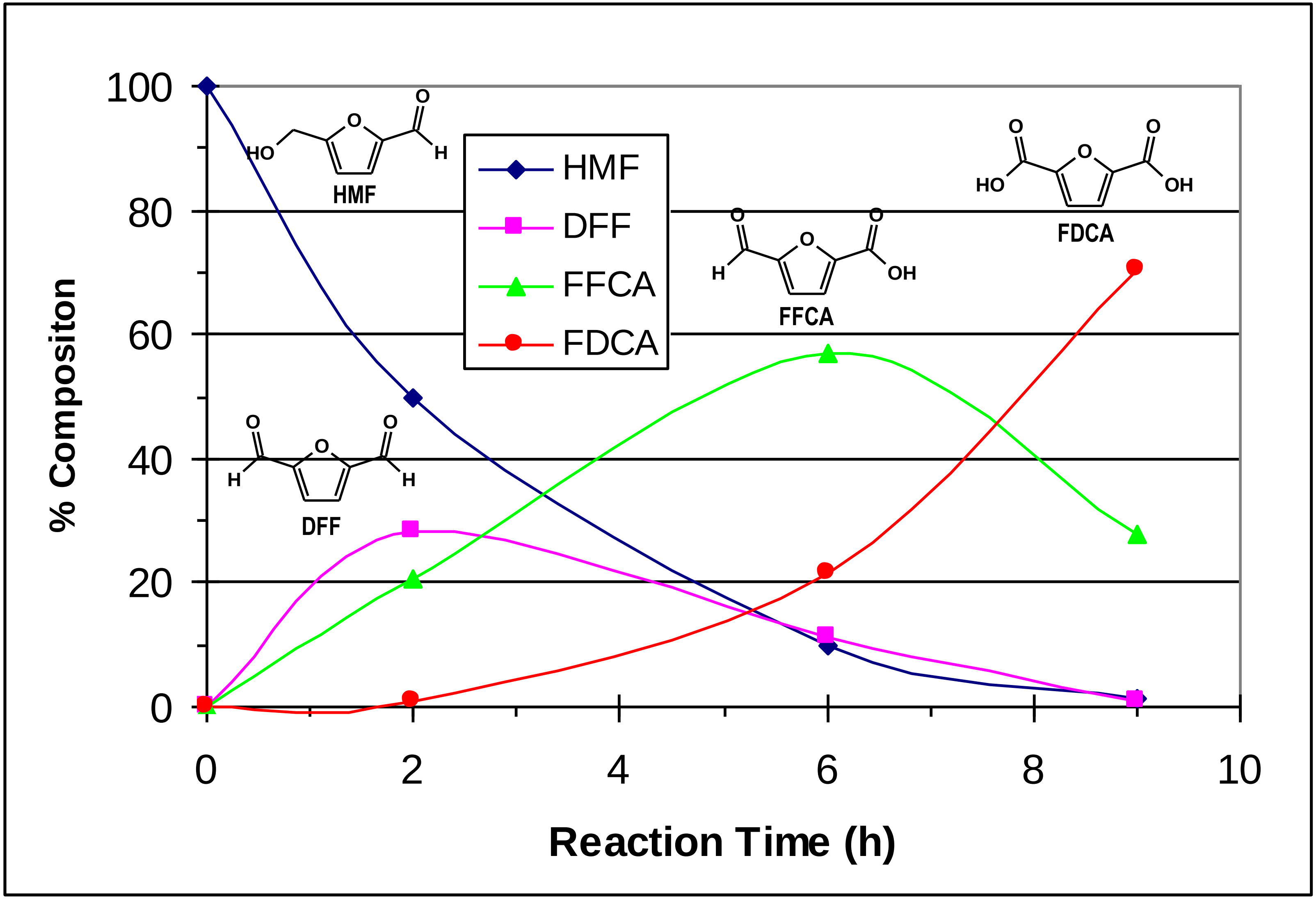


Oxidation is sequential and selectivity is difficult to control in batch mode

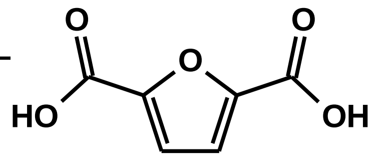
The Project

- Can various oxidized HMF derivatives be produced selectively in a flow reactor?
- Could selectivity and conversion be controlled by varying process conditions?
- Conduct catalyst and process screening experiments

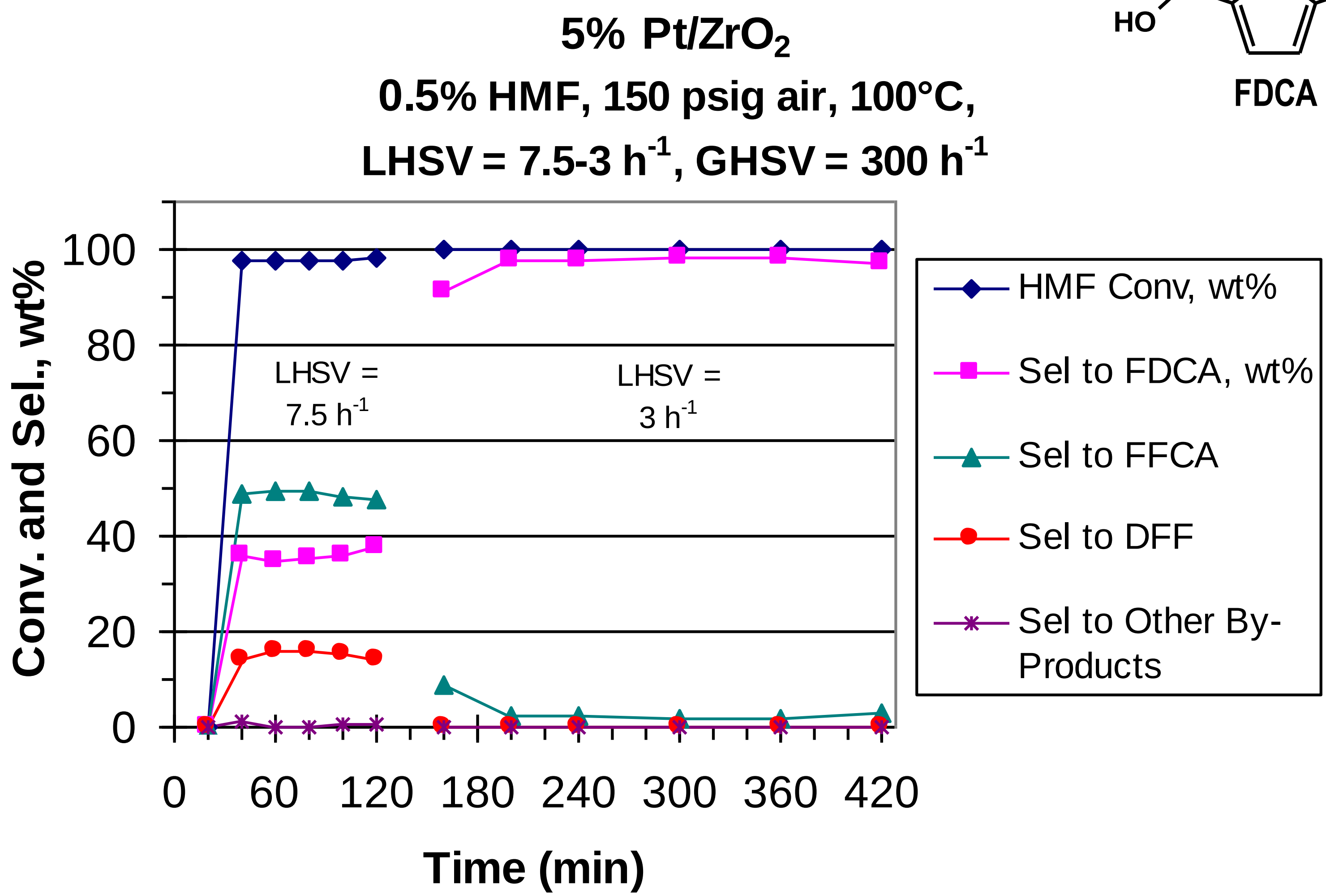
- Not in the scope:
  - Catalyst/process optimization
  - Mechanistic studies

Oxidation of HMF Over 5% Pt/ZrO_2

Selectivity to FDCA:



FDCA



Oxidation of HMF Over 5% Pt/SiO_2

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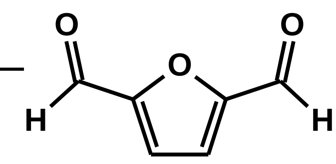
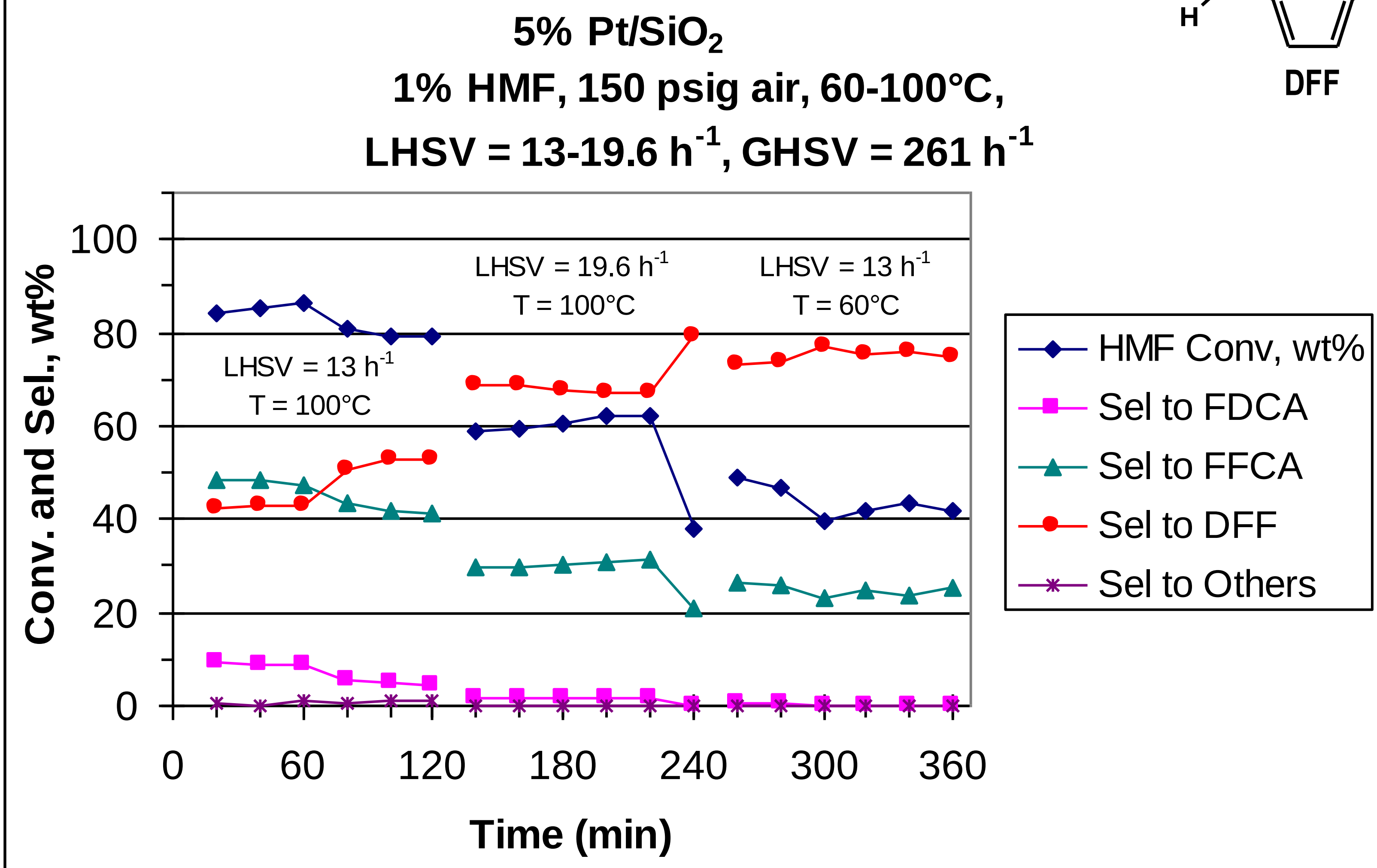
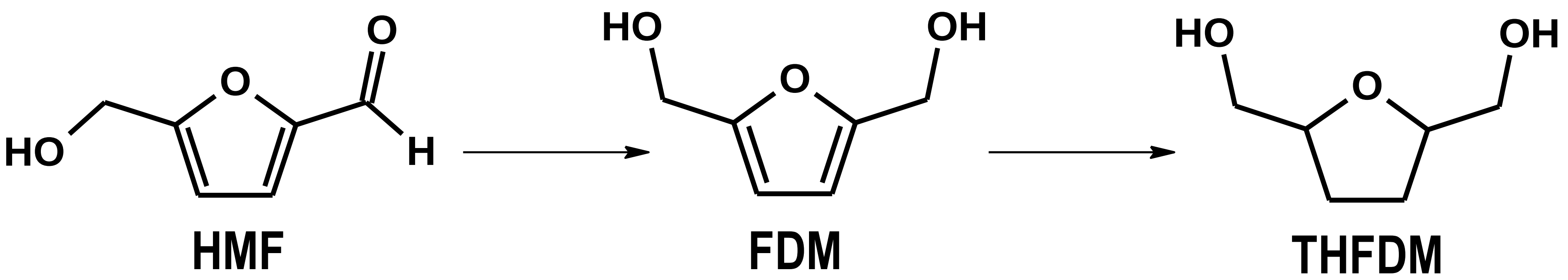
Selectivity to DFF:



DFF



Reduction of HMF



"Hydroxymethyl Furfural Reduction Methods and Methods of Producing Furandimethanol", M.A. Lilga, R.T. Hallen, J.F. White, and M.J. Gray, U.S. Patent No. 7,994,347 B2, August 9, 2011.

"Hydroxymethyl Furfural Reduction Methods and Methods of Producing Furandimethanol", M.A. Lilga, R.T. Hallen, J.F. White, and M.J. Gray, Filed 6/2007 , Pending.

Hydrogenation of HMF to FDM Over Pt/Al_2O_3

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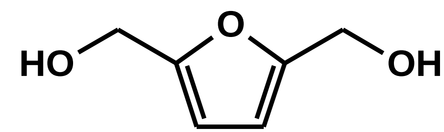
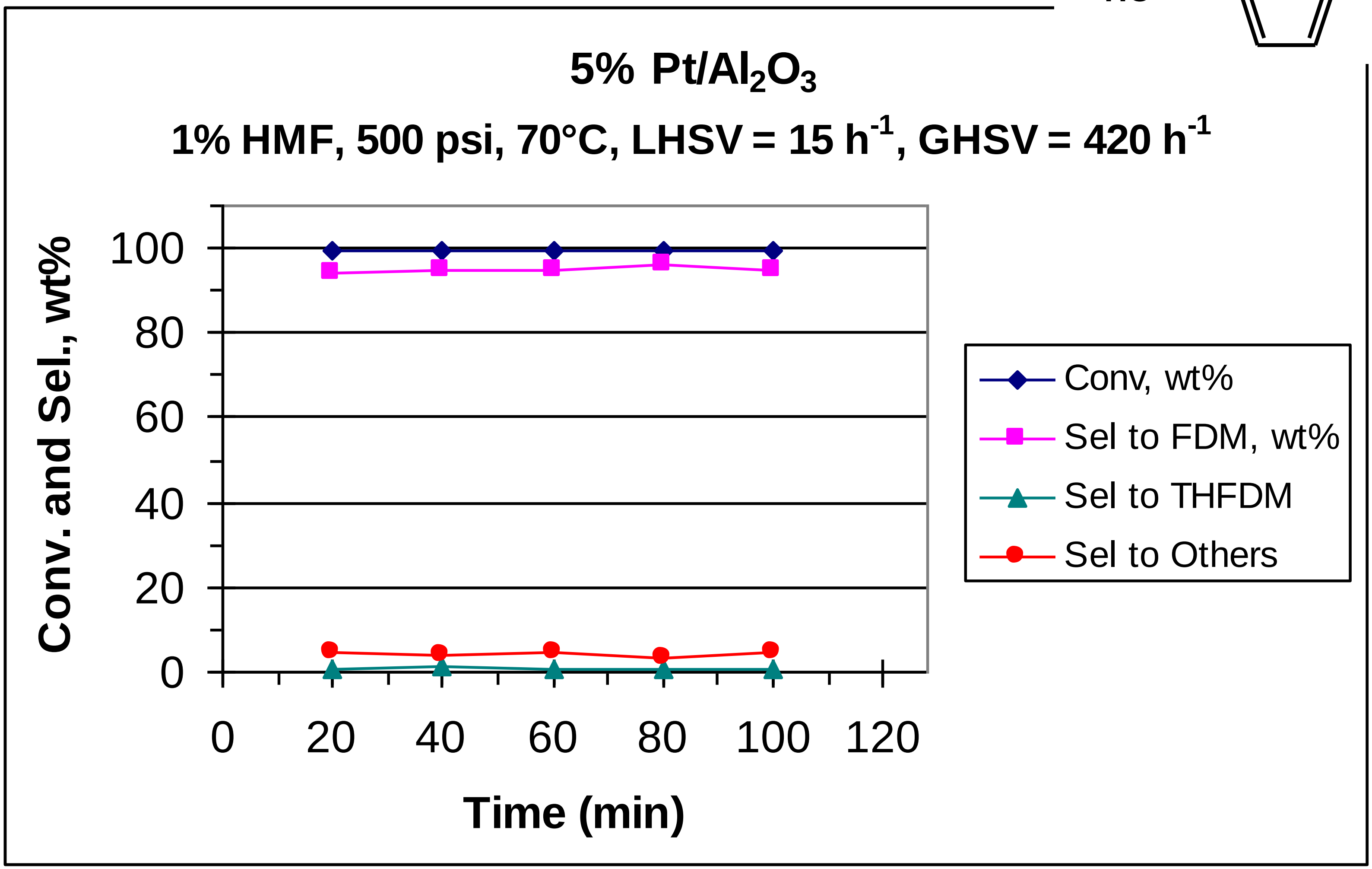
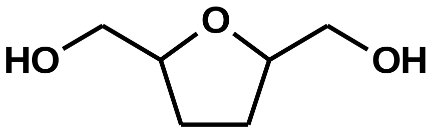
Selectivity of HMF to FDM:

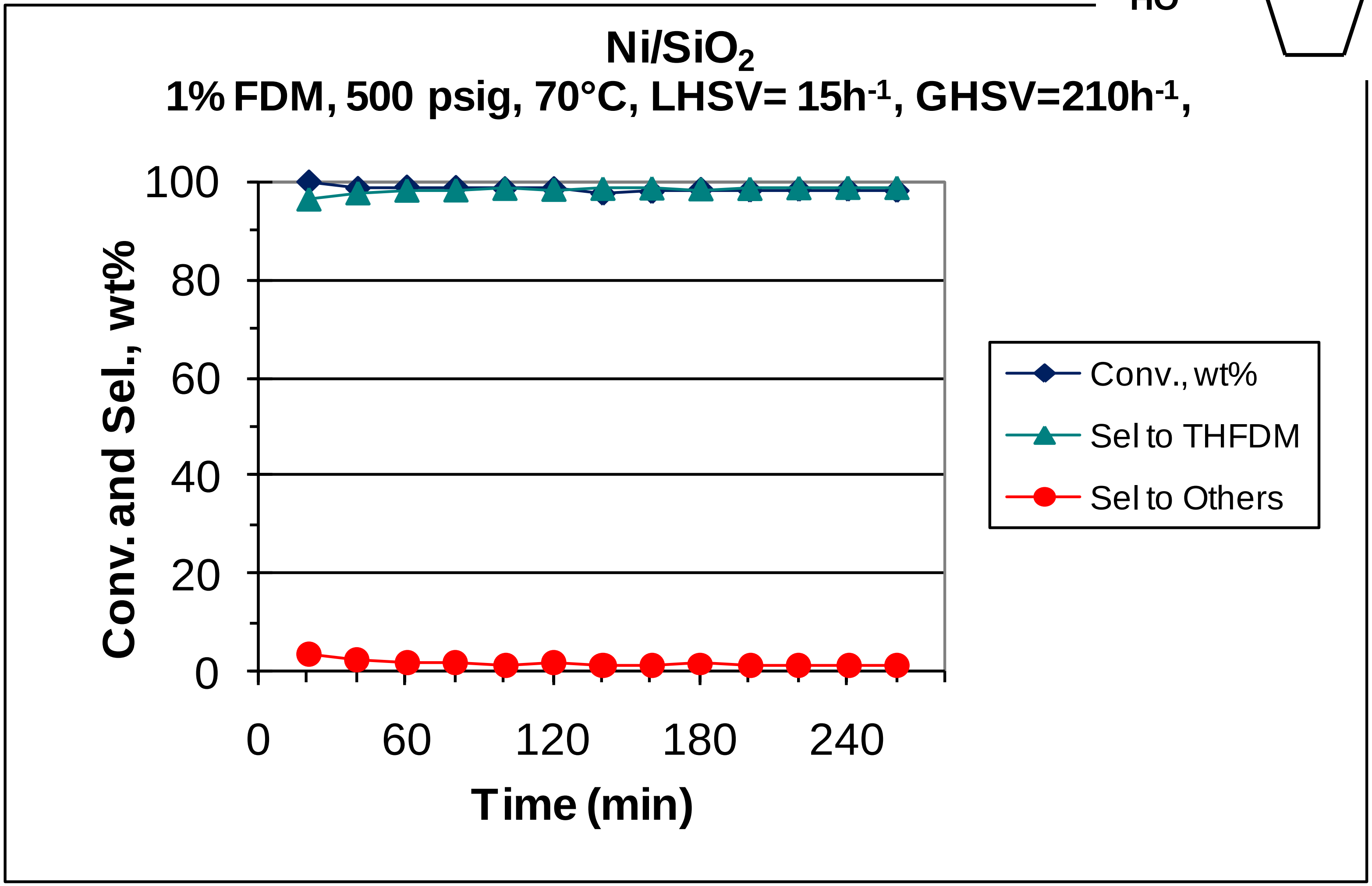




FDM Hydrogenation to THFDM over Ni/SiO_2

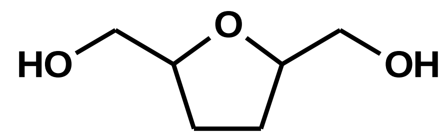
Selectivity of FDM to THFDM:

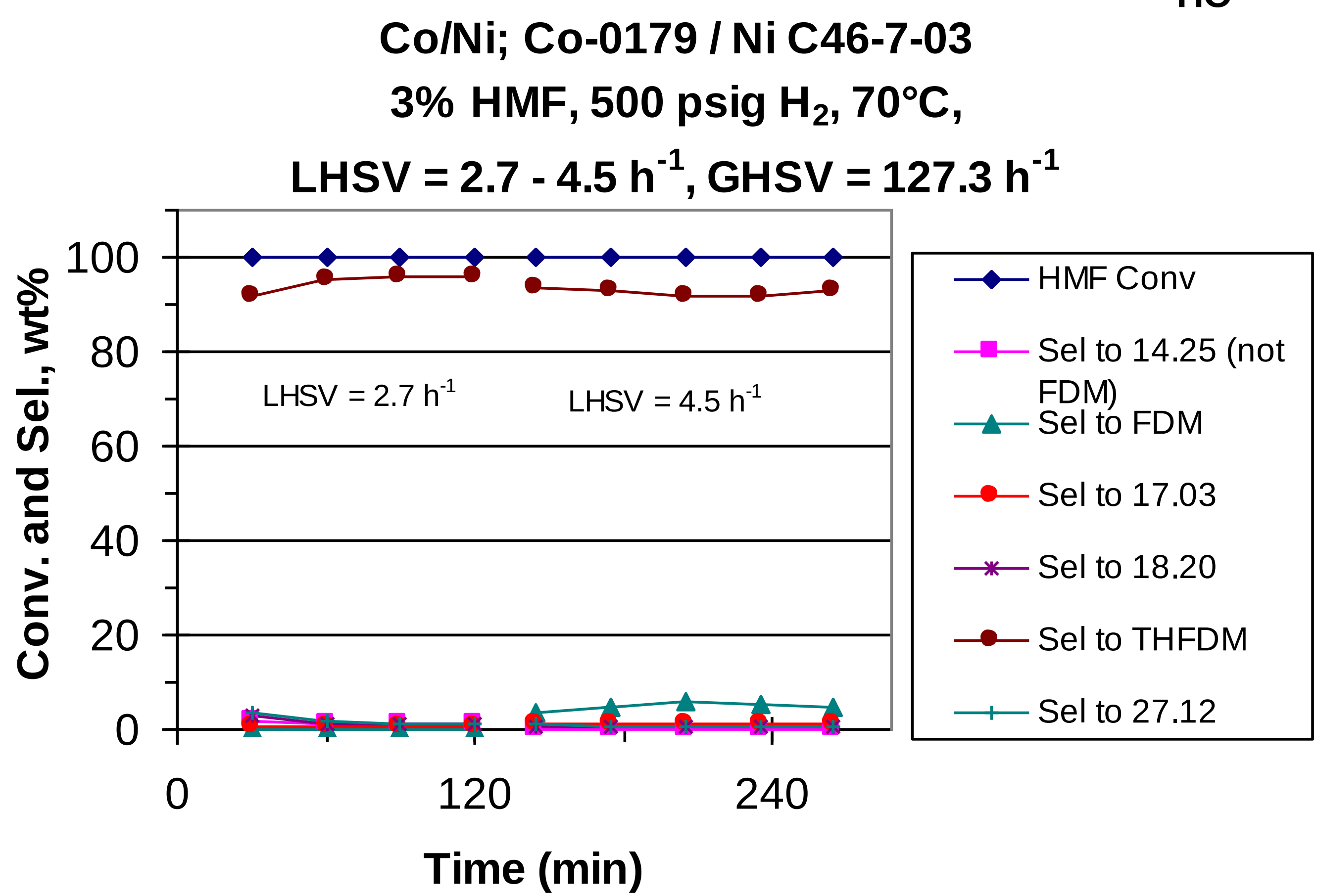




HMF Reduction to THFDM Over a Co/Ni Staged Catalyst Bed

Selectivity of HMF to THFDM:





In direct conversion, Ni was poisoned by HMF, but the staged approach of Co reduction to FDM followed by Ni reduction to THFDM worked well.

Summary

- Products add value to the biorefinery
- A broad range of biobased products are possible from key intermediates
- Technology advances are needed to selectively carry out conversions
- Drop-in products have established markets and uses, but new products will need performance testing and establishment of new markets
- FDCA, FFCA, DFF, FDM, and THFDM can be produced with good selectivities by controlling process conditions and selecting the appropriate catalyst(s)

Acknowledgments

- HMF Oxidation and Reduction
  - Rich Hallen
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  - John Hu
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  - Alan Cooper

- Financial Support
  - Archer Daniels Midland
  - Battelle Memorial Institute

Types of Biobased Products

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Product Type	Upside	Downside
Drop In Replacement	• Fully fungible • Markets exist • Cost structure and growth potential known • Market risk reduced	• Competes against cost • Competes against depreciated capital • Limited market differentiation
Functional Equivalent	• Analogous markets and cost structures exist • May offer improved function	• Cost competition • Markets may not be clearly defined • Capital risk high • Time to commercialization may be long
New Functionality	• New market opportunities • Often no competitive petrochemical routes • Use inherent properties of biomass	• Capital risks often high • Time to commercialization long • Markets ill-defined

Increasing Risk

Decreasing Market Definition

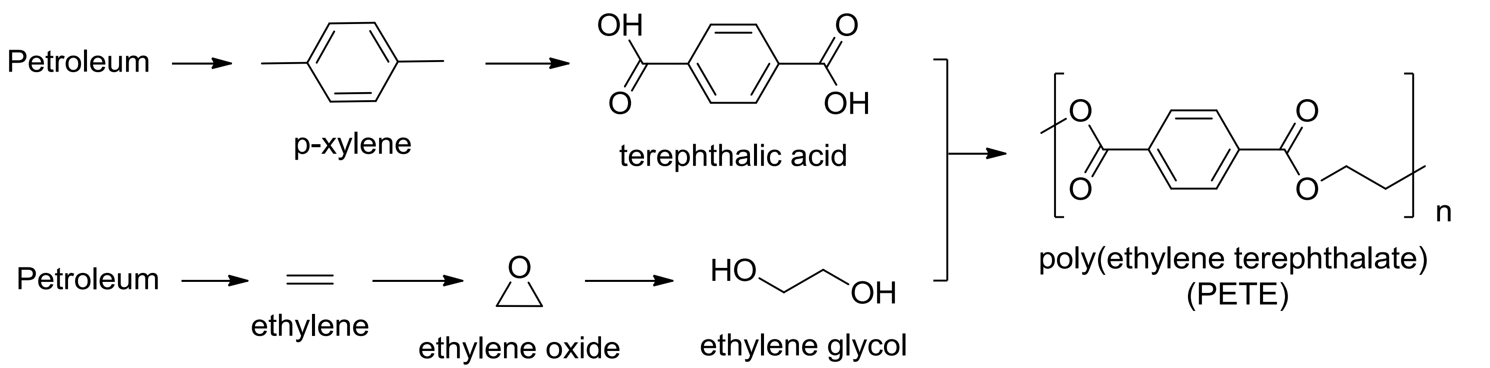
Decreasing Competition

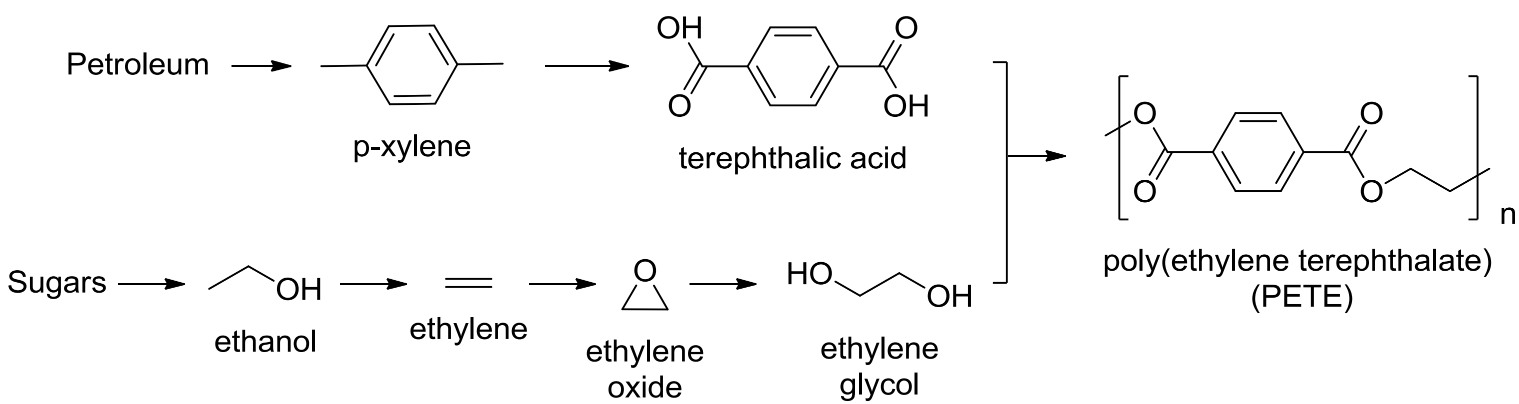
Incr. Time To Commercialization

Adapted from Gene Peterson, “Perspectives on DOE Biobased Products R&D” U.S. Department of Energy Bioproducts from Cellulosic Feedstock Workshop, December 4, 2009.

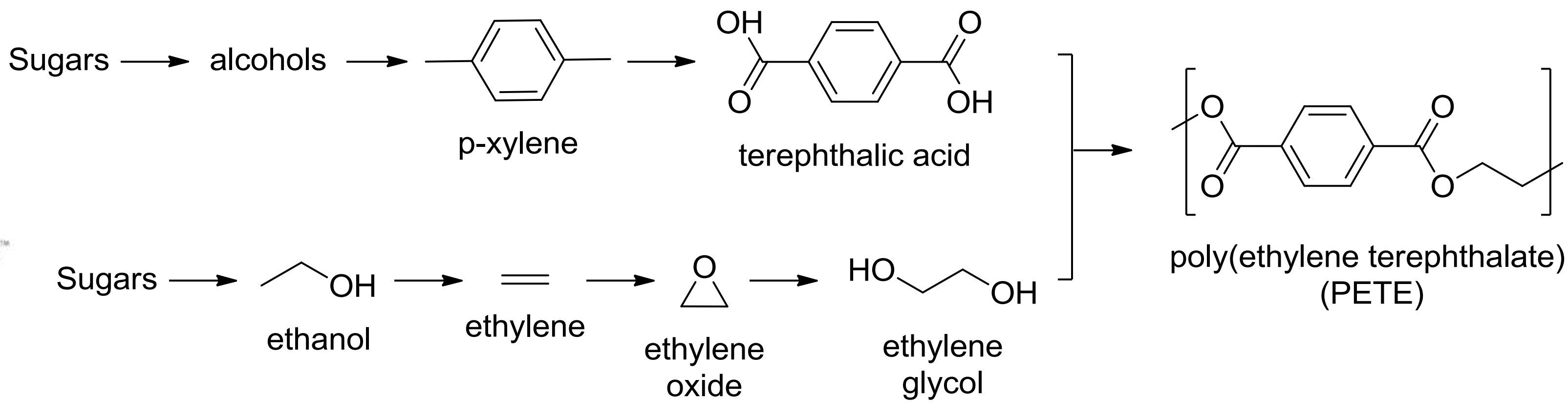
Evolution of the Plastic Bottle

PETE

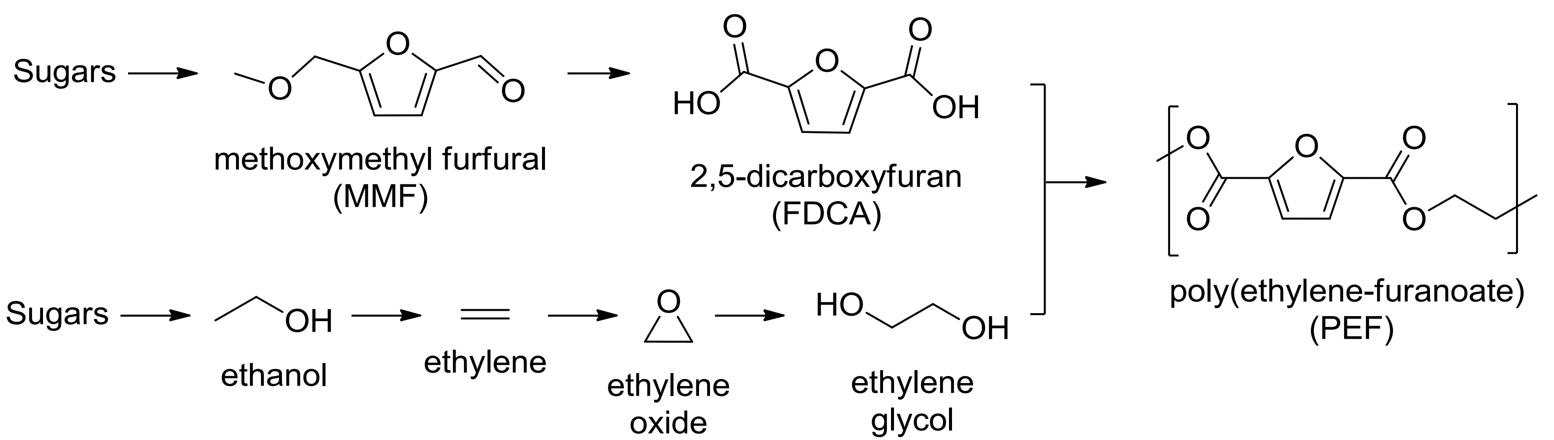




Evolution of the Plastic Bottle



biobased *p*-xylene from Virent, Gevo, others



biobased FDCA from YXY (Avantium)

Continuous Oxidation Reactor for Flow Studies

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- 3/8” SS tube reactor
- ~4 cc catalyst
- Gases and liquids were fed up flow
- GHSV 300-600 h^{-1} (20-40 mL/min)
- LHSV 3-20 h^{-1} (0.2-1.3 mL/min)
- Samples taken at pressure

Oxidation to FFCA is Facile at 30°C

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Selectivity to FFCA: