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Catalytic Production of α,ω diols from Biomass

Bioenergy 2016

Breakout Session 3-C:

Innovative Approaches and Materials for Clean Energy

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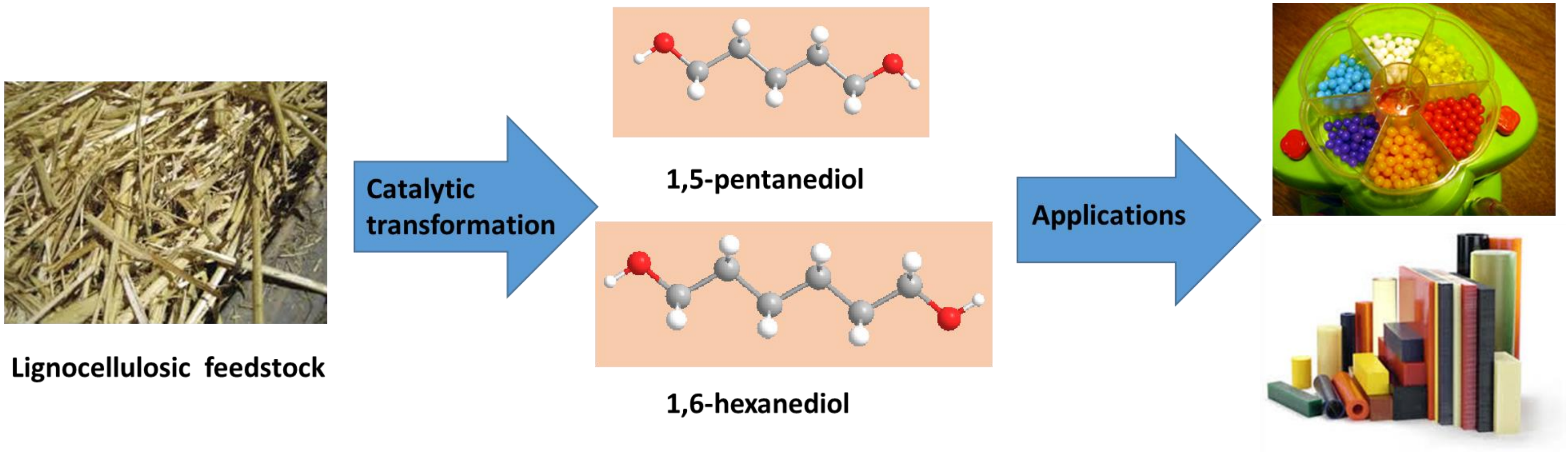
Catalytic Processes for Production of α,ω-diols from Lignocellulosic Biomass

Goal: Develop an integrated and efficient process to produce high value chemicals (1,5-pentanediol and 1,6-hexanediol) from lignocellulosic biomass



Lignocellulosic feedstock

Catalytic transformation

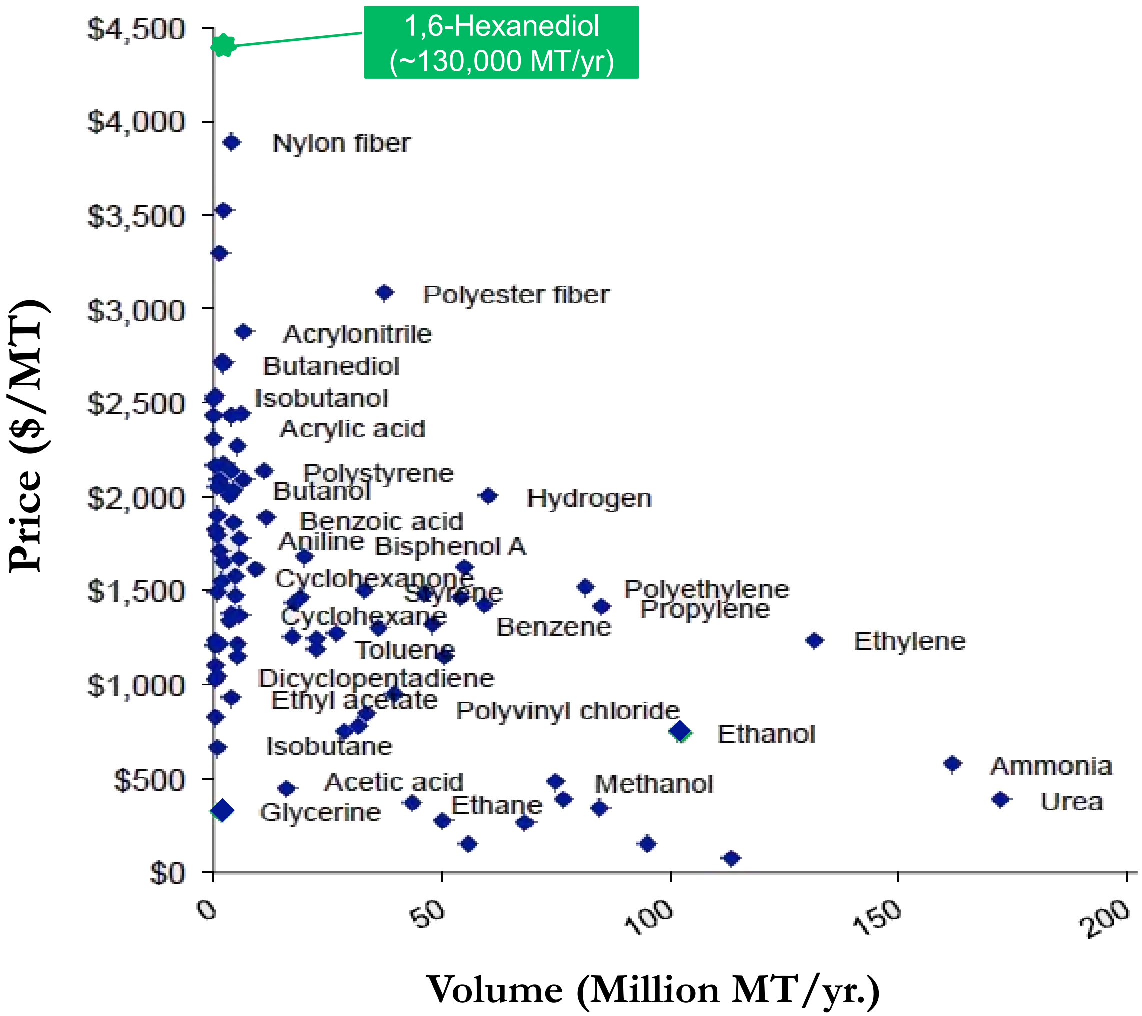
1,5-pentanediol

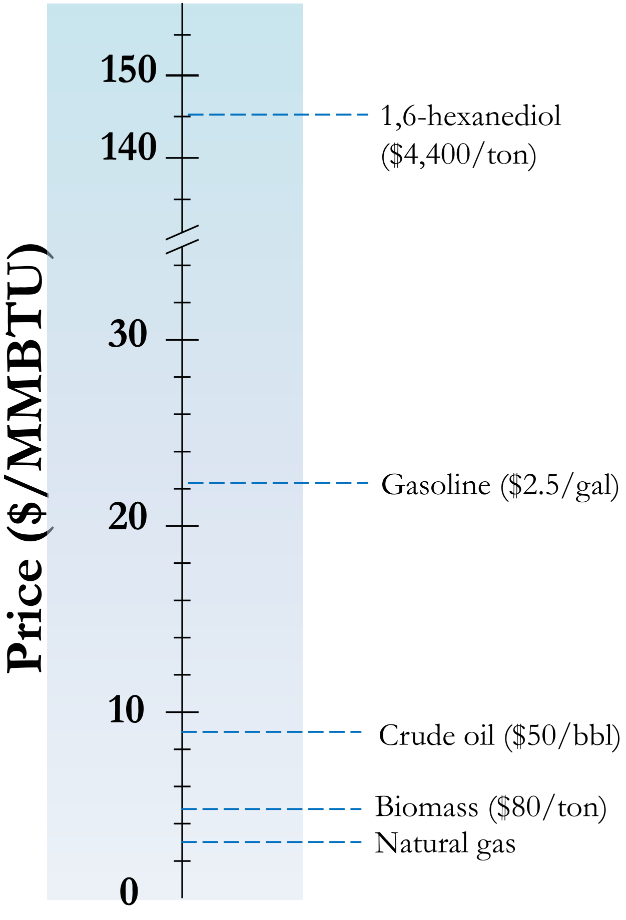
1,6-hexanediol

Applications

- **Funding:** DOE Bioenergy Technologies Office
  - **Topic Area 2:** Hybrid chemical and biological upgrading processes with integration of separations
- **Prime Recipient:** University of Wisconsin ($3.3 MM)
- **Principal Investigator:** George Huber
- **Project Partners:** University of Minnesota, Argonne National Lab, Glucan Biorenewables

High Value Commodity Chemicals from Biomass



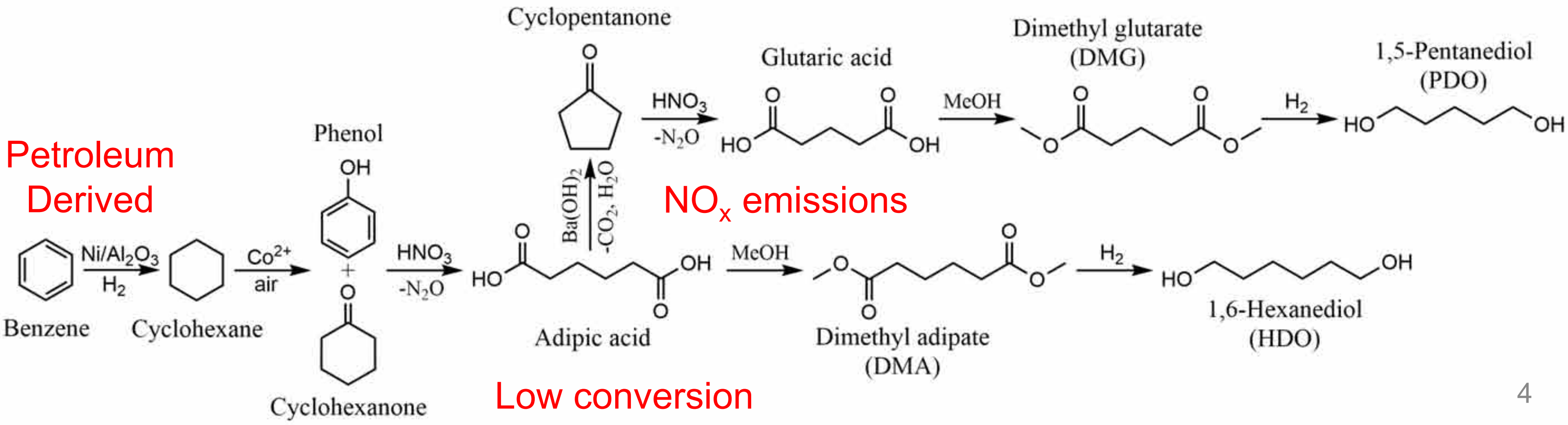


Source: ICIS, IEA

Source: Lux Research, Bio-based Materials and Chemical Intelligence Service, www.luxresearchinc.com

α,ω-Diols have many uses in the Polymer Industry

Particular	1,6-Hexanediol	1,5-Pentanediol	1,4-Butanediol
Applications	▪ Polyurethanes ▪ Coatings ▪ Acrylates ▪ Adhesives ▪ Polyester Resins ▪ Plasticizers ▪ Others	▪ Polyester plastics ▪ Polyurethanes ▪ Pharmaceuticals ▪ Inks and coatings ▪ Plasticizers ▪ Solvent and industrial chemicals ▪ Others	▪ Biodegradable plastics ▪ Hot melt polyesters ▪ Coatings ▪ Polyurethanes ▪ Adhesives ▪ Pharmaceuticals ▪ Fiber particle and composite
Major players	▪ BASF ▪ Ube Industries ▪ Lanxess ▪ Perstorp AB ▪ Lishui Nanming Chemical ▪ Fushun Tianfu Chemicals	▪ BASF ▪ Ube Industries ▪ Marubeni Corporation ▪ Lishui Nanming Chemical	▪ BASF ▪ Dairen Chemicals ▪ Lyondell Chemicals ▪ Shanxi Sanwei Group ▪ ISP ▪ Invista ▪ Mitsubishi Chemicals
Current market size (2013)	\$524 Million	< \$10 Million	\$5,550 Million

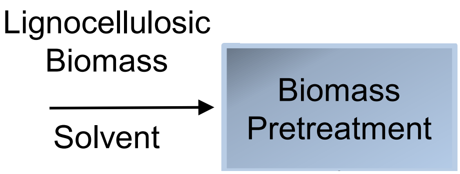


Petroleum Derived

NO$_x$ emissions

Low conversion

Chemistry: α,ω -diols from Lignocellulosic Biomass



Lignocellulosic Biomass

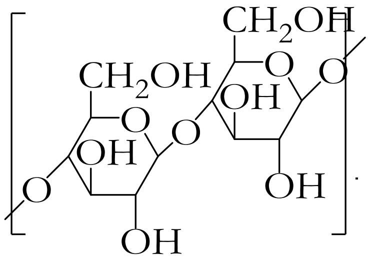
Solvent

Biomass Pretreatment

- Utilize inherent functionalities present in biomass
    - C_5 & C_6 backbone
    - Selective removal of oxygen to produce partially oxygenated chemicals
- Integration of reaction studies with separations and technoeconomic analysis

Several Intermediates in our Process are also Valuable Chemicals

C_6 Stream

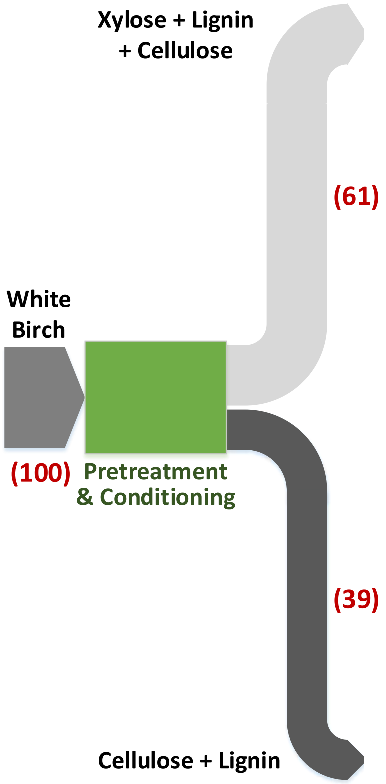


Cellulose

- **Levoglucosenone:** chiral building block – pharmaceuticals
- **Cyrene**: polar aprotic solvent
- **Tetrahydrofurandimethanol:** α,ω –diol, potential polymer precursor

1. M. Ostermeier and R. Schobert, "Total Synthesis of (+)-Chloriolide," *The Journal of Organic Chemistry*, 2014, **79**, 4038-4042.
2. J. Sherwood, M. De bruyn, A. Constantinou, L. Moity, C. R. McElroy, T. J. Farmer, T. Duncan, W. Raverty, A. J. Hunt and J. H. Clark, "Dihydrolevoglucosenone (Cyrene) as a bio-based alternative for dipolar aprotic solvents," *Chemical Communications*, 2014, **50**, 9650-9652.
3. A.M. Allgeier, e. Korovessi, C.A. Menning, J.C Ritter, S.K. Sengupta, C.S Stauffer, " Process for preparing 1,6-hexanediol (US 8865,940 B2)," *USA Pat.,* 2014.

Sankey Diagram for Carbon Yields & Capital Cost



Height of each stream and number in bracket correspond to amount of carbon in the stream.

Darkness of each stream represents carbon concentration as shown below:

⬜ 0-15% carbon

▒ 16-30% carbon

▓ 31-45% carbon

⬛ 45-60% carbon

Height of the box corresponds to estimated installed cost of the unit

🟩 Reactor System

🟦 Separation System

🟧 Combustor & Boiler

🟨 Wastewater Treatment

- Focus on improving yield and lowering catalyst costs in C_6 pathway

2nd Generation Biofuel Companies have Struggled

Average Oil Price($/bbl)	$95	$94	$94	$93

Challenges with Pioneer Process Plants

- Rand Study (1981) prepared for US DOE because of underestimate for costs for coal to liquids technologies in 1970s
- Looked at 44 chemical process plants from 34 companies in chemical, oil, minerals and design

Conventional View of Estimating Project Costs

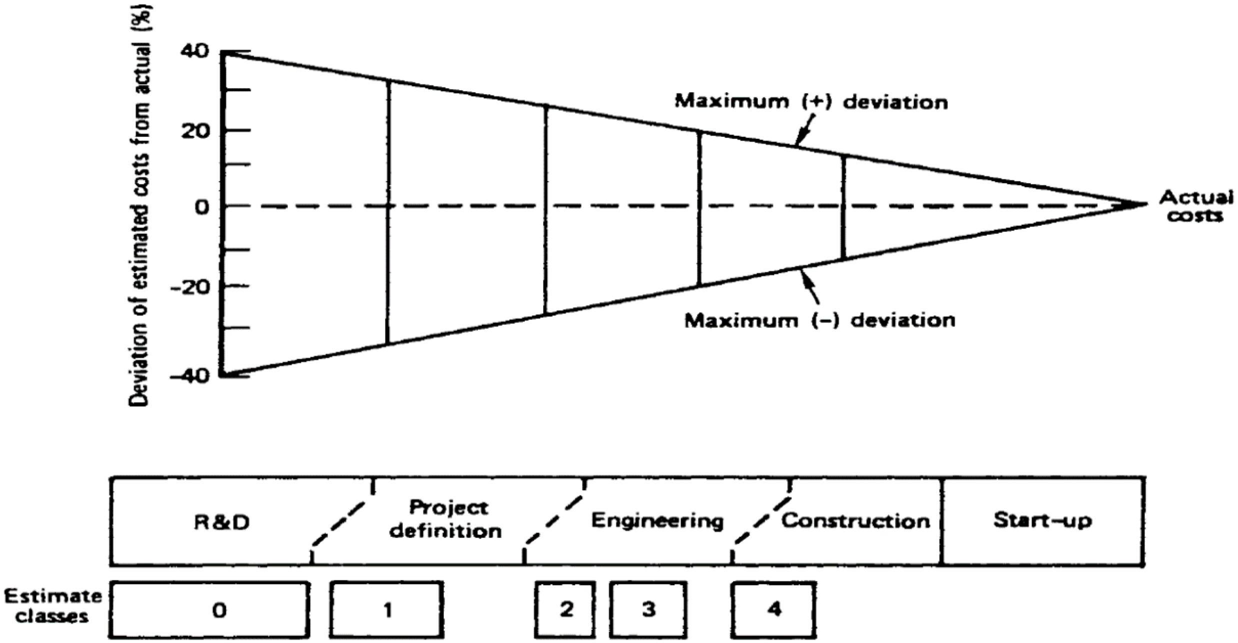


Fig. 4.1 — The conventional view of how information and project phase affect estimation accuracy

E. W. Merrow, K. E. Phillips, C. W. Myers, Understanding Cost Growth and Performance Shortfalls in Pioneer Process Plants, Rand Corporation, 1981, Prepared for US Department of Energy, R-2569-DOE.

Estimating Project Costs of Pioneer Plants

- Severe underestimation of cost and overestimation of performance are common in new technology
- Over 50% of first generation plants failed to meet production goals in the 2nd six months after start up

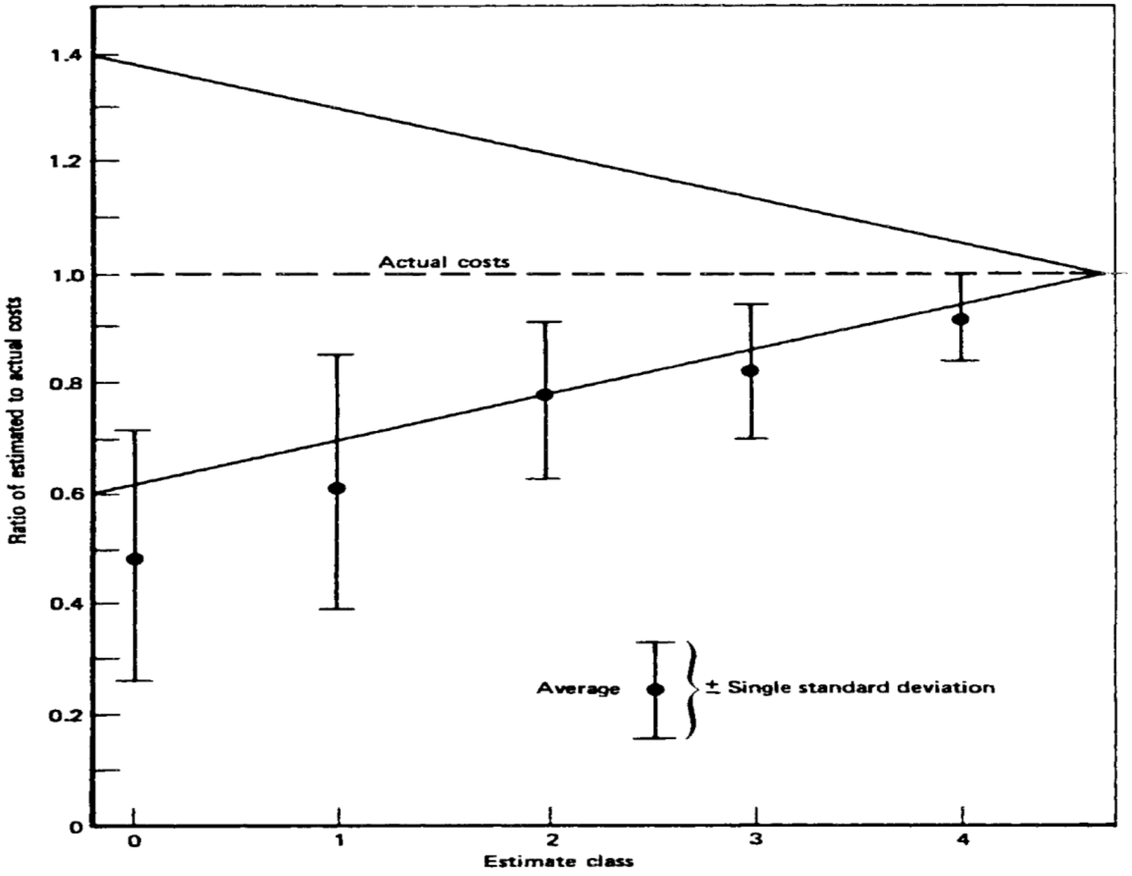
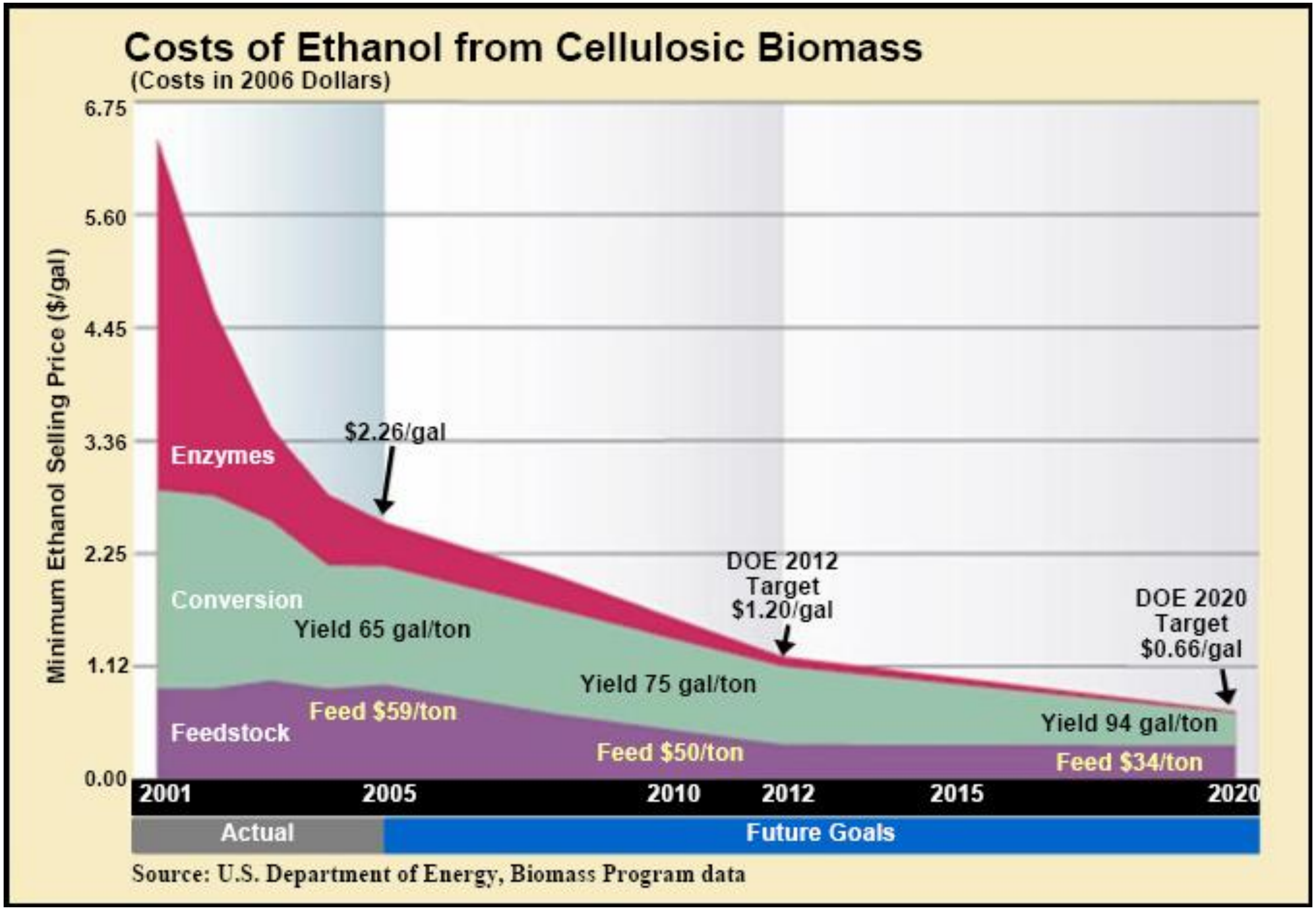


Fig. 4.3 — Experience of the pioneer plants sample with estimation accuracy

E. W. Merrow, K. E. Phillips, C. W. Myers, Understanding Cost Growth and Performance Shortfalls in Pioneer Process Plants, Rand Corporation, 1981, Prepared for US Department of Energy, R-2569-DOE.

DOE Predictions on the Cost of Cellulosic Ethanol in 2005

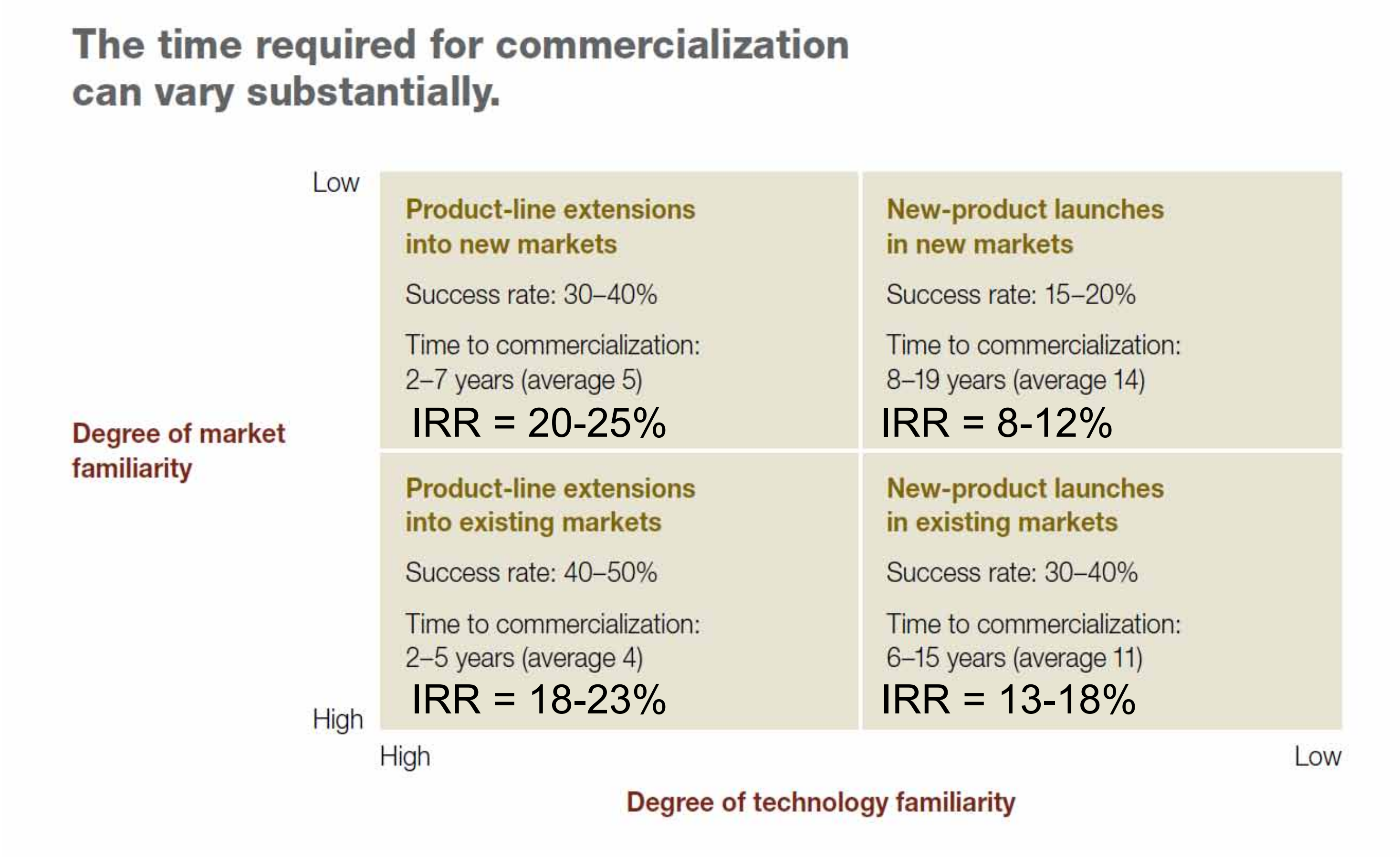


Costs of Ethanol from Cellulosic Biomass

(Costs in 2006 Dollars)

Source: U.S. Department of Energy, Biomass Program data

New Technologies in the Petrochemical Area do Make Money



The time required for commercialization can vary substantially.

Product-line extensions into new markets

Success rate: 30–40%

Time to commercialization:
2–7 years (average 5)

IRR = 20-25%

New-product launches in new markets

Success rate: 15–20%

Time to commercialization:
8–19 years (average 14)

IRR = 8-12%

Product-line extensions into existing markets

Success rate: 40–50%

Time to commercialization:
2–5 years (average 4)

IRR = 18-23%

New-product launches in existing markets

Success rate: 30–40%

Time to commercialization:
6–15 years (average 11)

IRR = 13-18%

McKinsey on Chemicals; Chemical innovation: An investment for the ages; M. Miremadi, C. Musso, J. Oxgaard.

The Role of Academia and Industry in Developing New Technologies

Role of Academia

- Primary goal is to publish in high impact journals
- Basic science, research innovation, new ideas, initial patents
- Inexpensive, inexperienced (graduate students and post-docs)
- Use scientific expertise to solve specific problems and ignore others

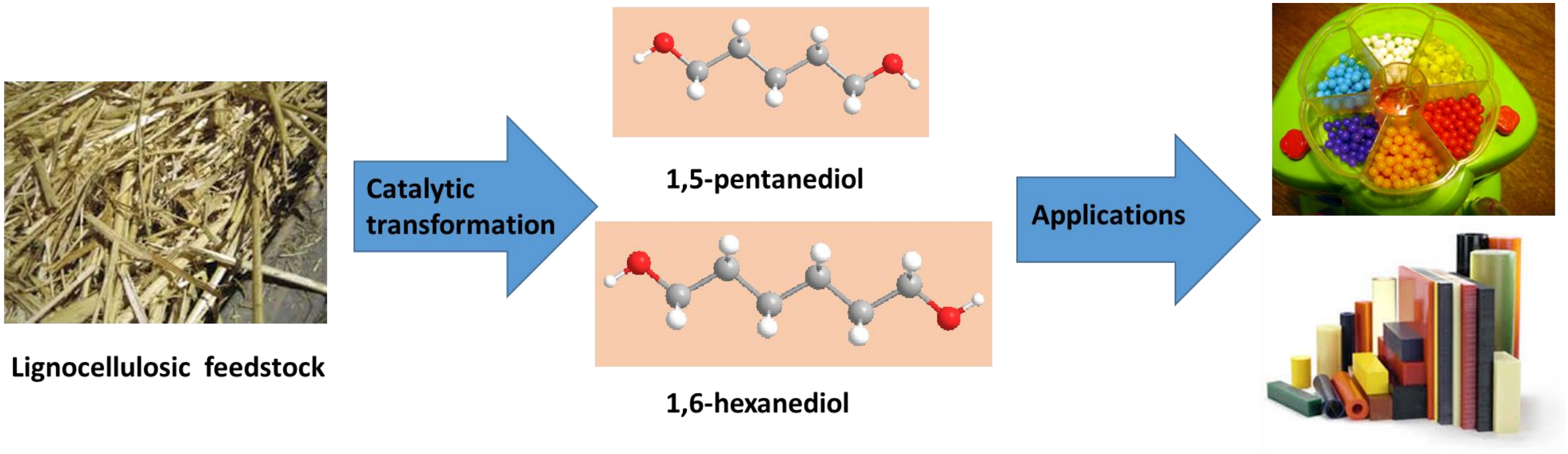
Role of Industry

- Primary goal is to make money
- Process development, demonstration and scale up
- Further patent prosecution and IP portfolio
- Experienced but expensive
- Marketing and consumers
- Identifying and focusing on key technology bottlenecks

Leverage the expertise of both sides to tackle bioenergy challenges

Conclusions

- We are developing new pathways for production of high value oxygenated commodity chemicals from biomass
- Coupling basic research with technoeconomic analysis identifies bottlenecks in the process and informs target research areas
- Pioneer technologies often involve cost underestimations and performance overestimations
- Synergies between academia and industry are critical to developing next generation bioenergy technologies



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1,5-pentanediol

1,6-hexanediol

Applications

Huber Research Group

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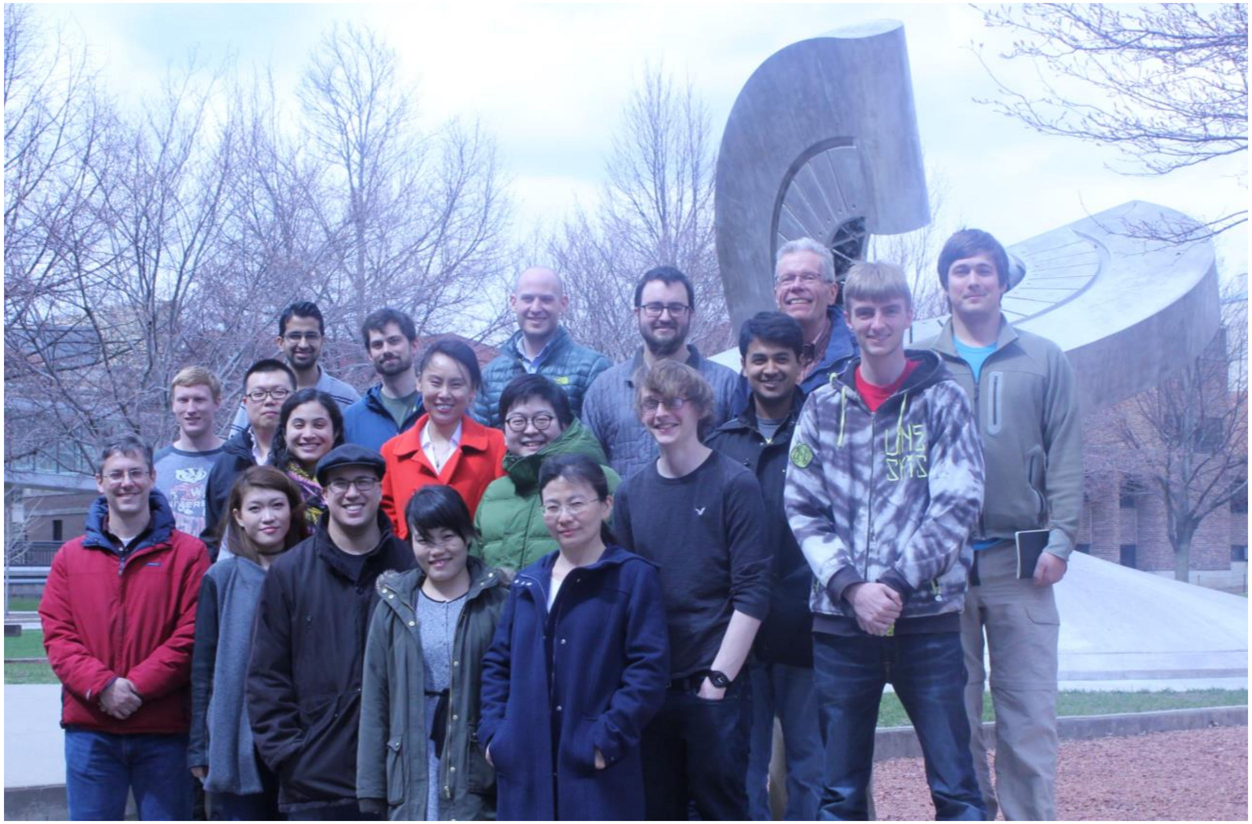

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