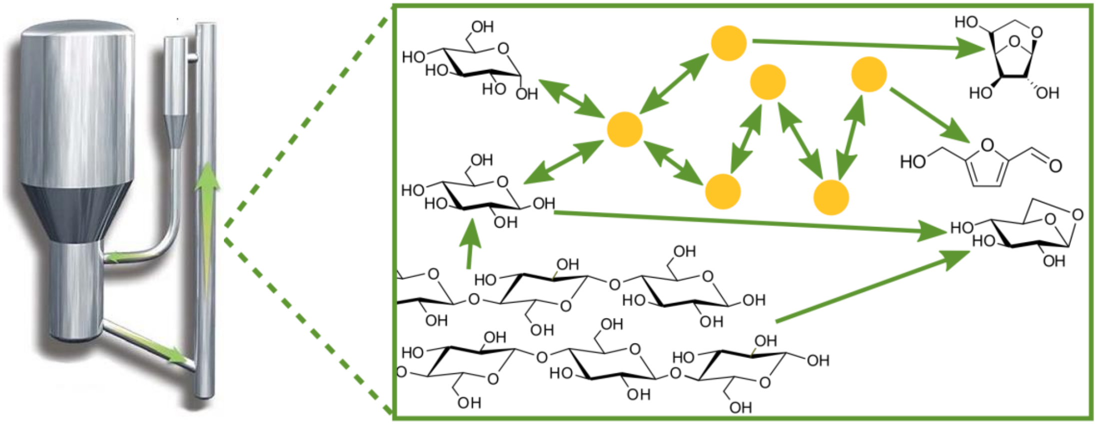
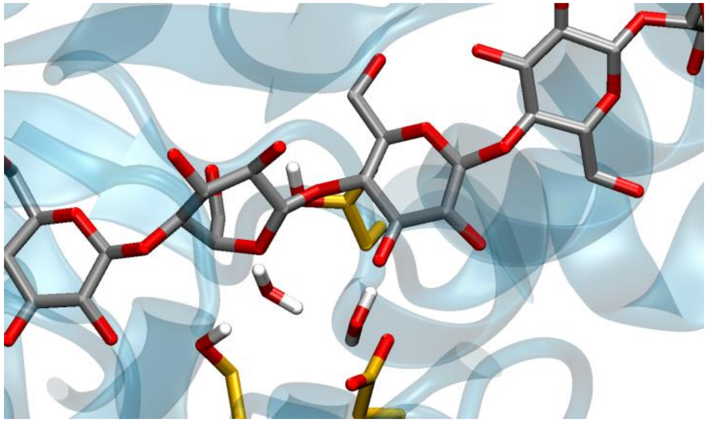


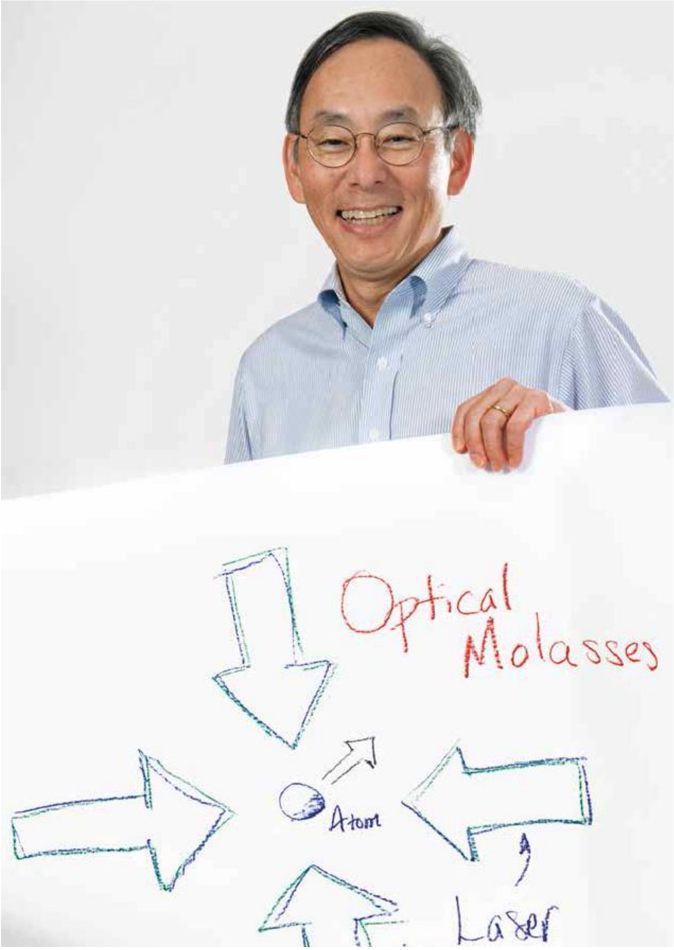


Harnessing HPC to Discover Reactions for Renewable Chemicals and Fuels

Heather B. Mayes

Department of Chemical and Biological Engineering, Northwestern University

DOE CSGF

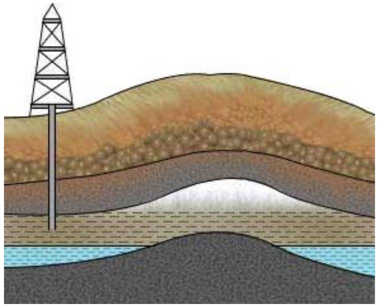


Sketches of Science

Steven Chu

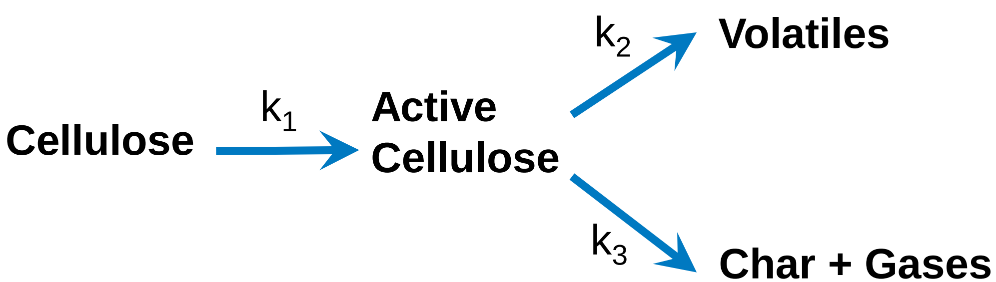
Nobel Prize in Physics, 1997

U.S. Secretary of Energy, 2009–2013

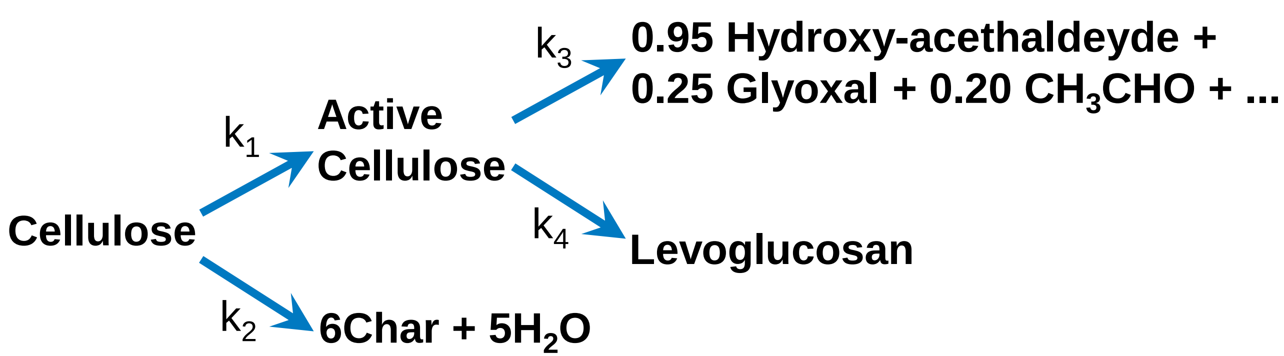


How can we model conversion processes?

Empirical



Shafizadeh, F. *J. Anal. Appl. Pyrolysis* **1982**, 3, 283.

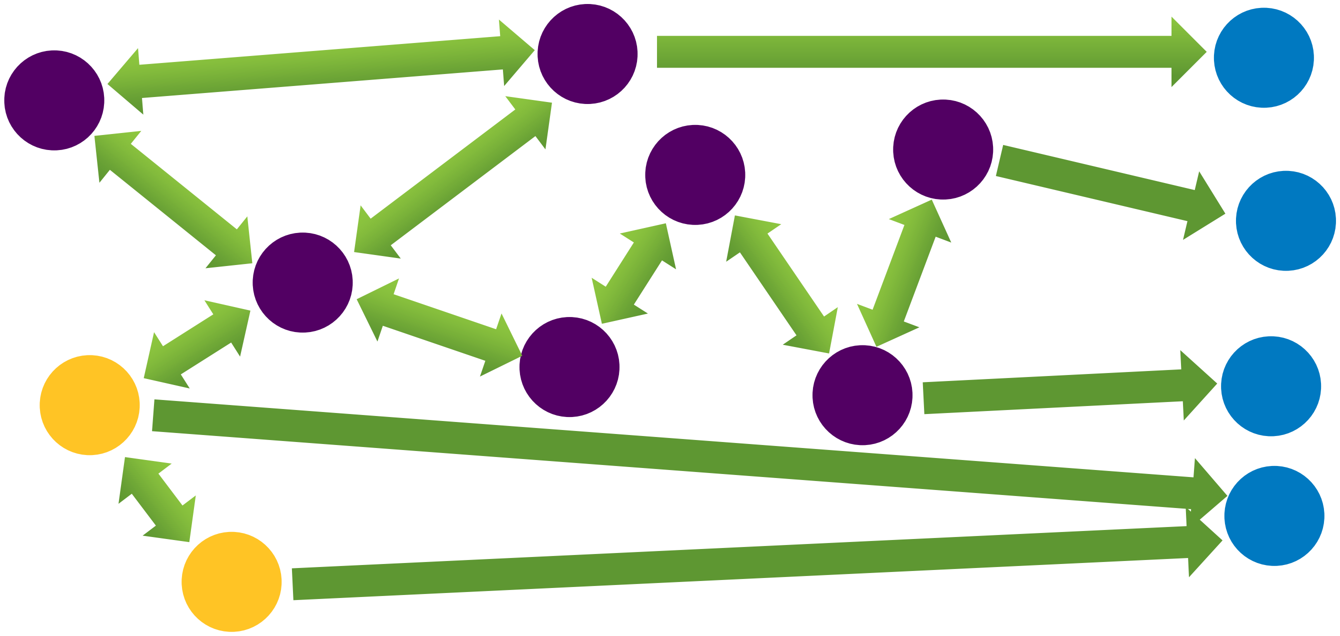


Calonaci, M.; Grana, R.; Barker Hemings, E.; Bozzano, G.; Dente, M.; Ranzi, E. *Energy Fuels* **2010**, *24*, 5727.

How else?

Microkinetic

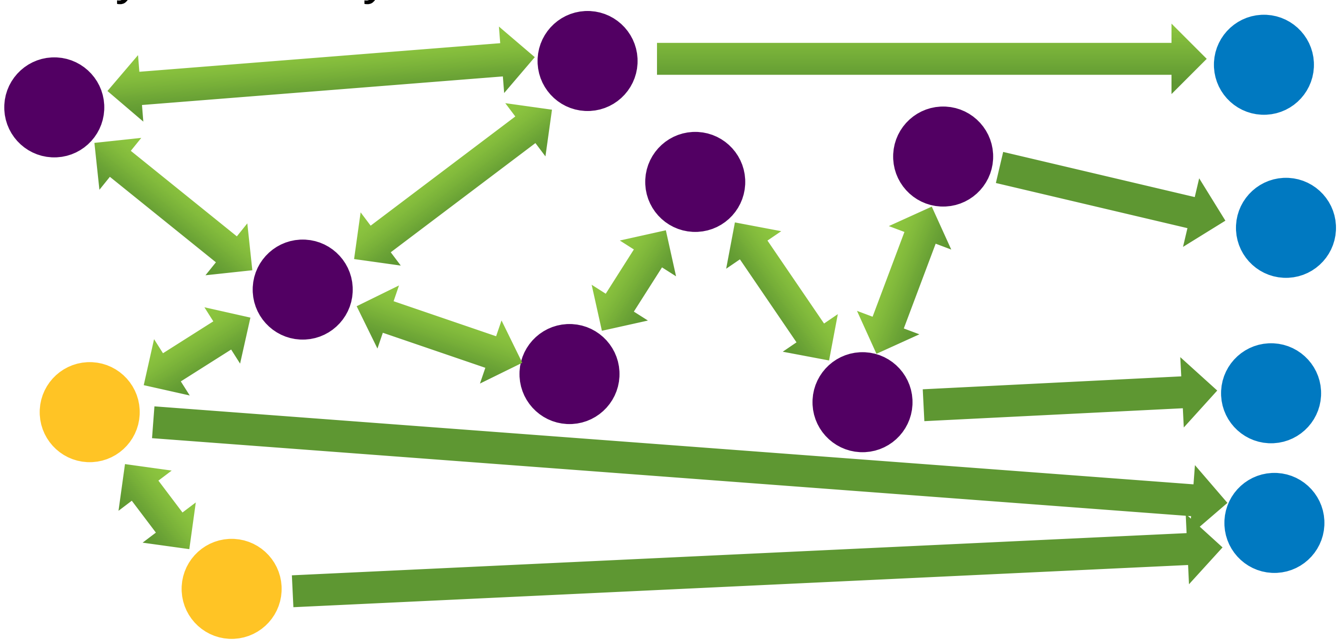
- Species
  - Reactants ( )
- Reaction network
  - Chemistry, thermodynamics, and kinetics



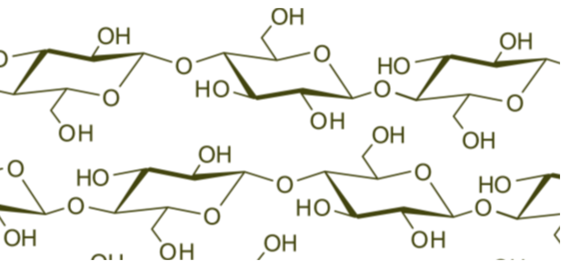
Broadbelt, L. J.; Pfaendtner, J. *AIChE J.* **2005**, *51*, 2112.

Why are microkinetic models less common?

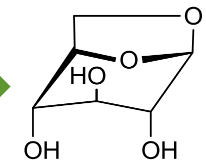
- Species
  - Reactants (●); Products (●); and intermediates (●)
- Reaction network
  - Chemistry, thermodynamics, and kinetics



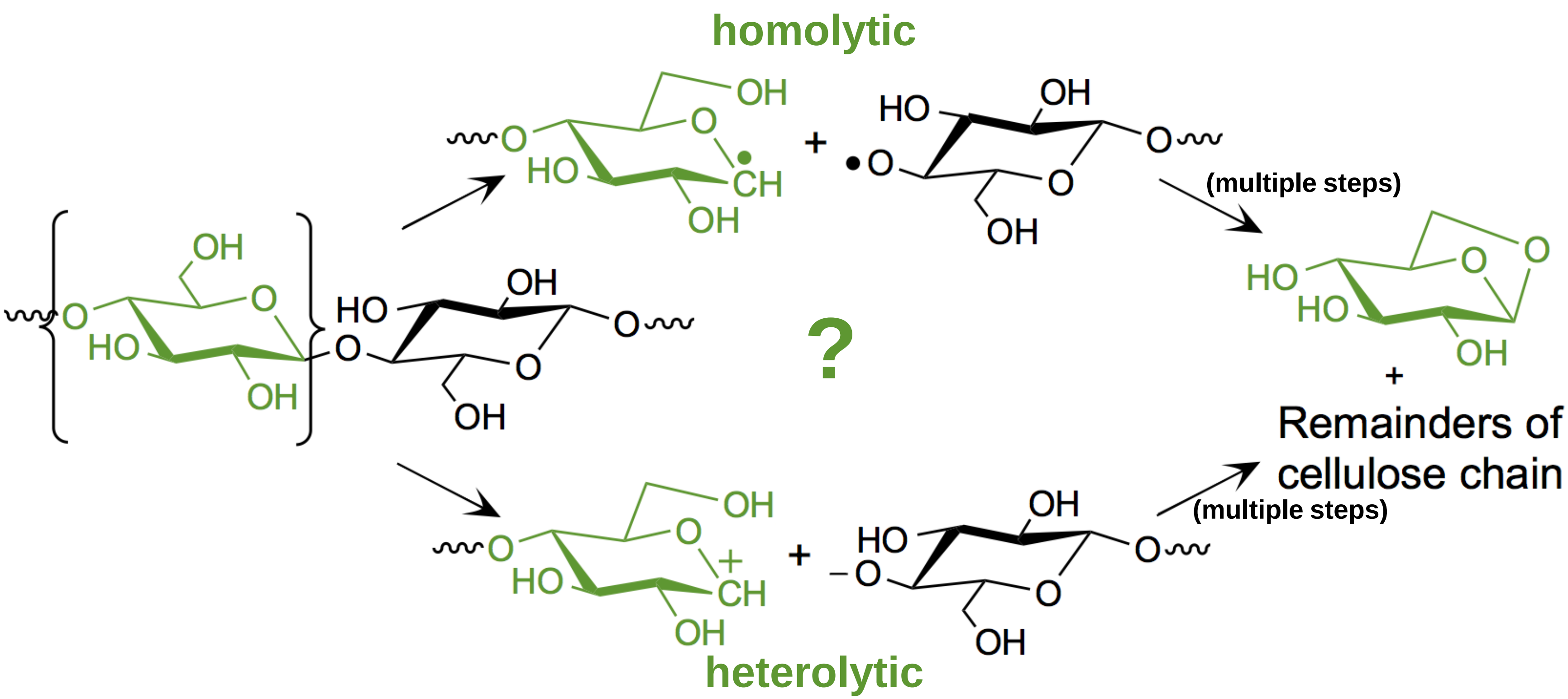
Kinetic parameters needed for every reaction



Glycosidic bond cleavage



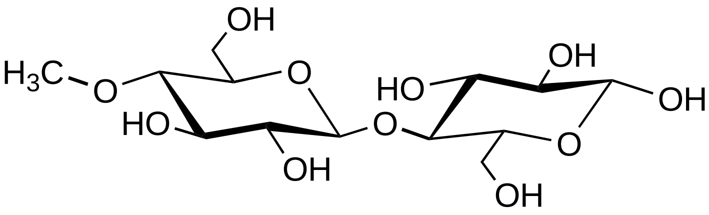
Levoglucosan 59 wt%



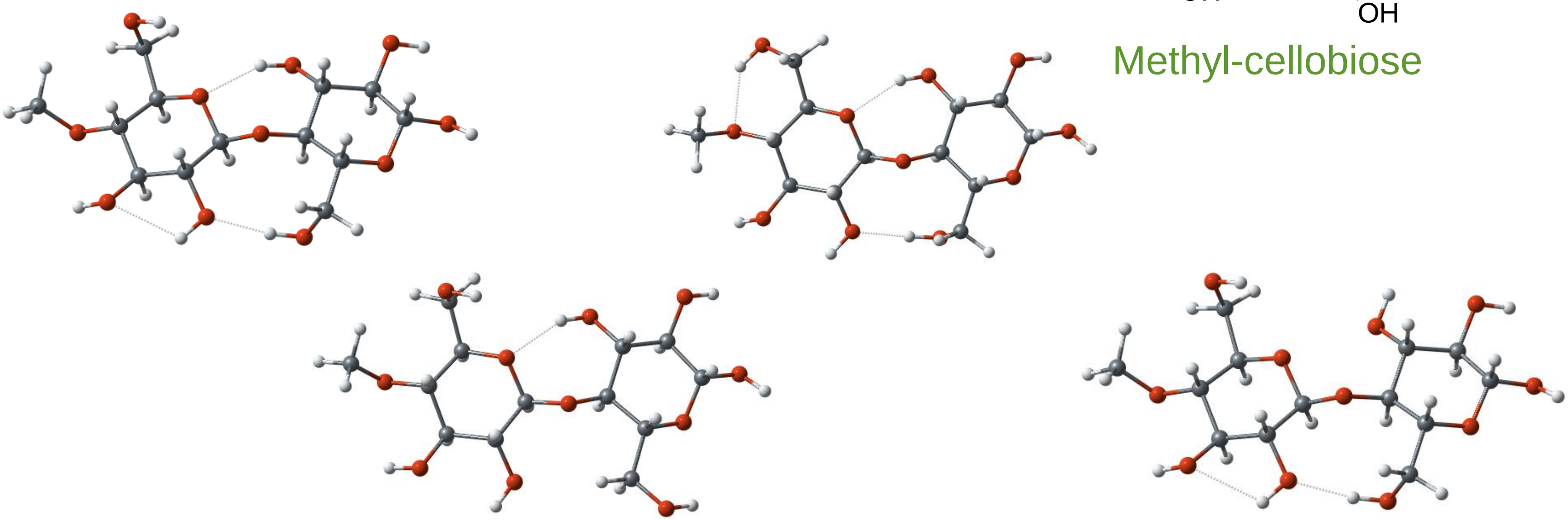
Mayes, H. B.; Broadbelt, L. J. *J. Phys. Chem. A* **2012**, *116*, 7098.

Method

- Quantum mechanics
  - DFT (M06-2X/6-311+G(3df,2p)//M06-2X/6-31+G(2df,p))
  - Implicit solvent to model pyrolysis electrostatic environment
- Transition-state-theory

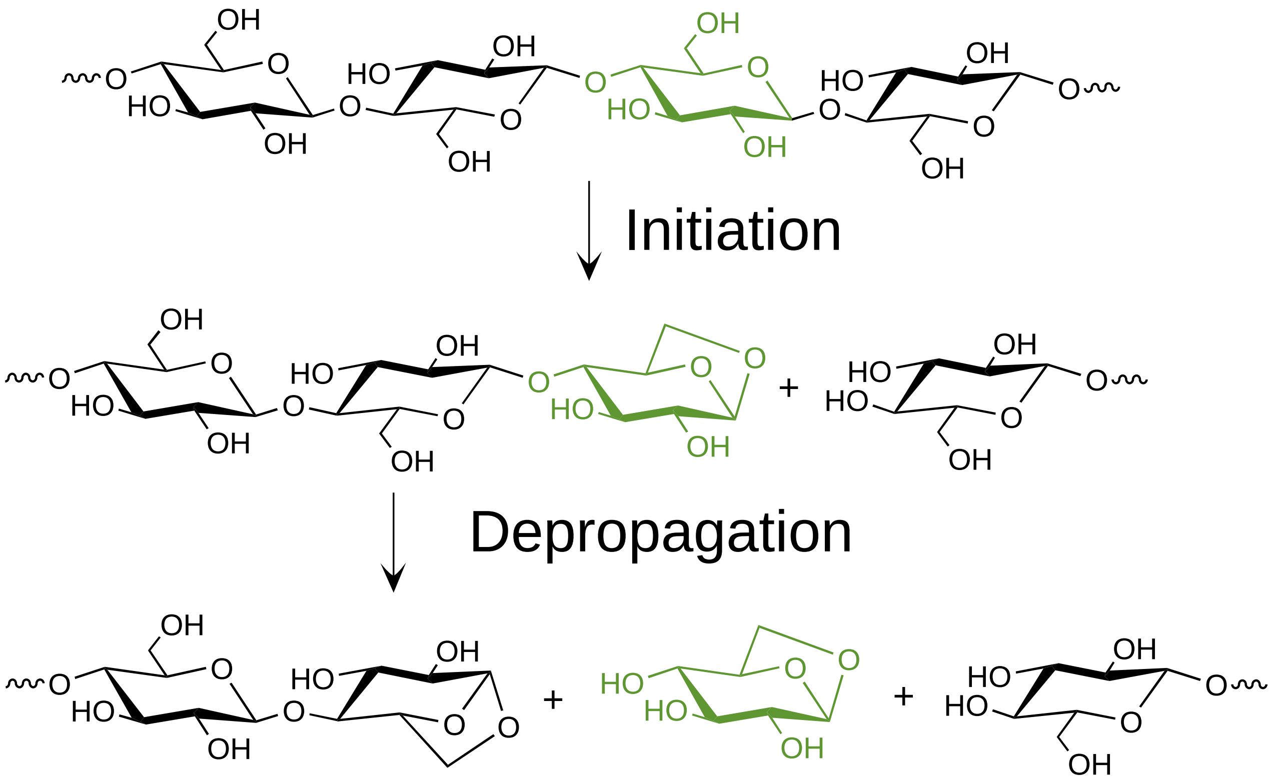


Methyl-cellobiose



Mayes, H. B.; Broadbelt, L. J. *J. Phys. Chem. A* **2012**, *116*, 7098.

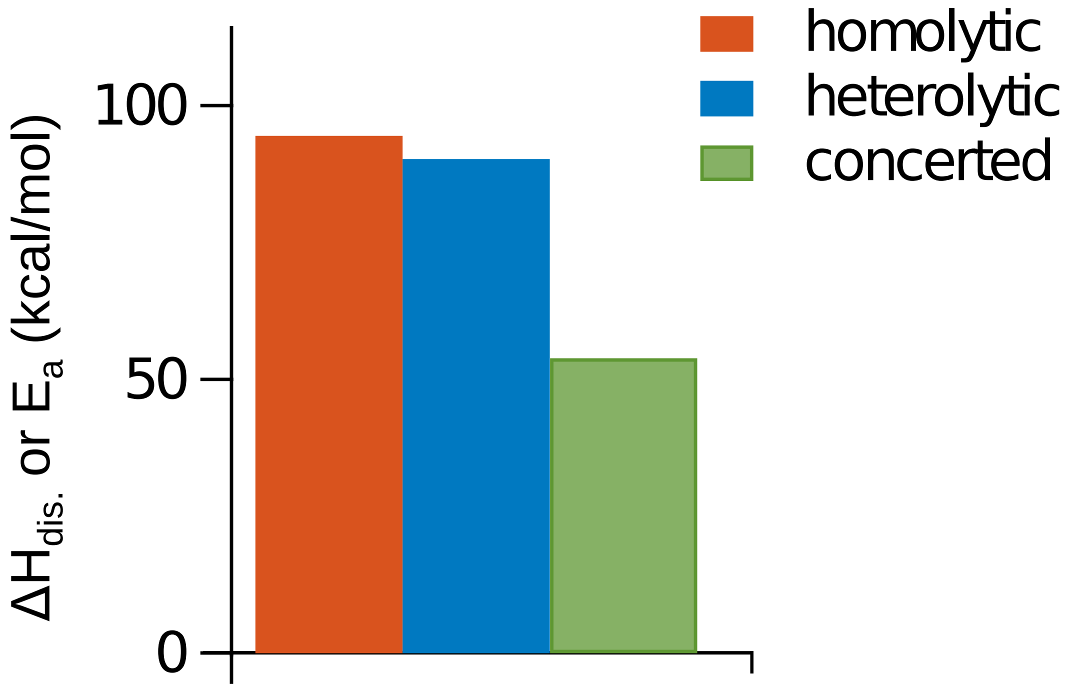
New picture of cellulose unraveling



Mayes, H. B.; Broadbelt, L. J. *J. Phys. Chem. A* **2012**, *116*, 7098.

Energy barriers

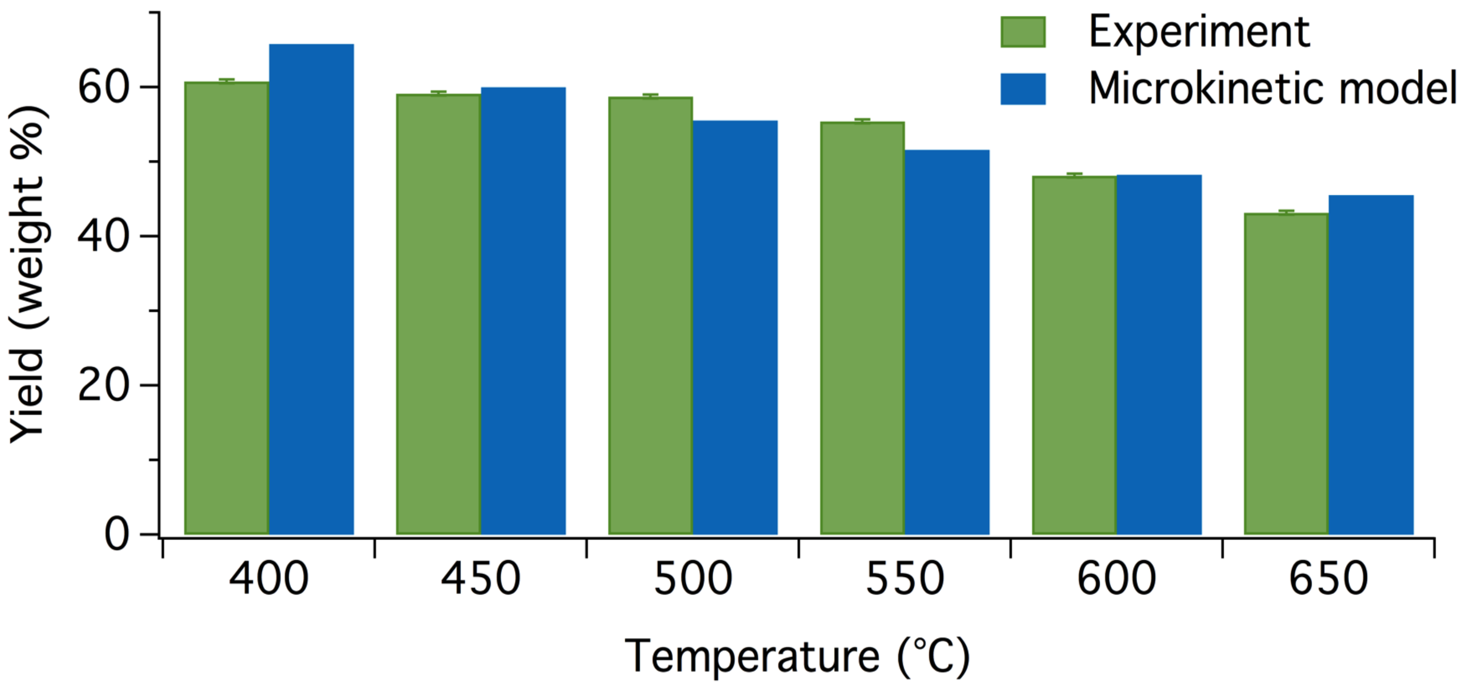
DFT Results



Mayes, H. B.; Broadbelt, L. J. *J. Phys. Chem. A* **2012**, *116*, 7098.

Validation

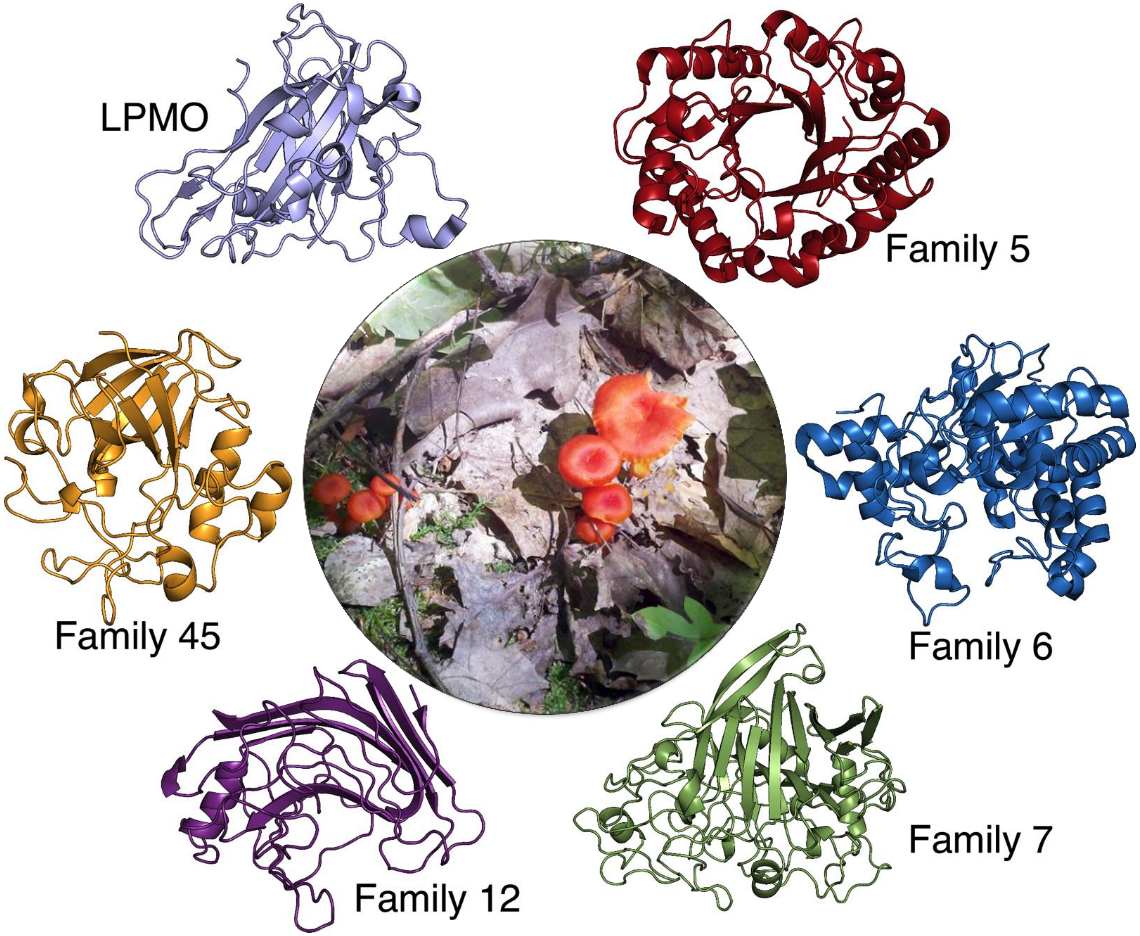
- Kinetic parameters used in Vinu and Broadbelt's neat cellulose pyrolysis microkinetic model[1]
- Predicted levoglucosan yield compared to experiment[2]:



[1]Vinu, R.; Broadbelt, L. J. *Energy Environ. Sci.* **2012**, *5*, 9808.
[2]Patwardhan, P. Satrio, J. A. Brown, R. C.; Shanks, B. H. *J. Anal. Appl. Pyrolysis* **2009**, *86*, 323.

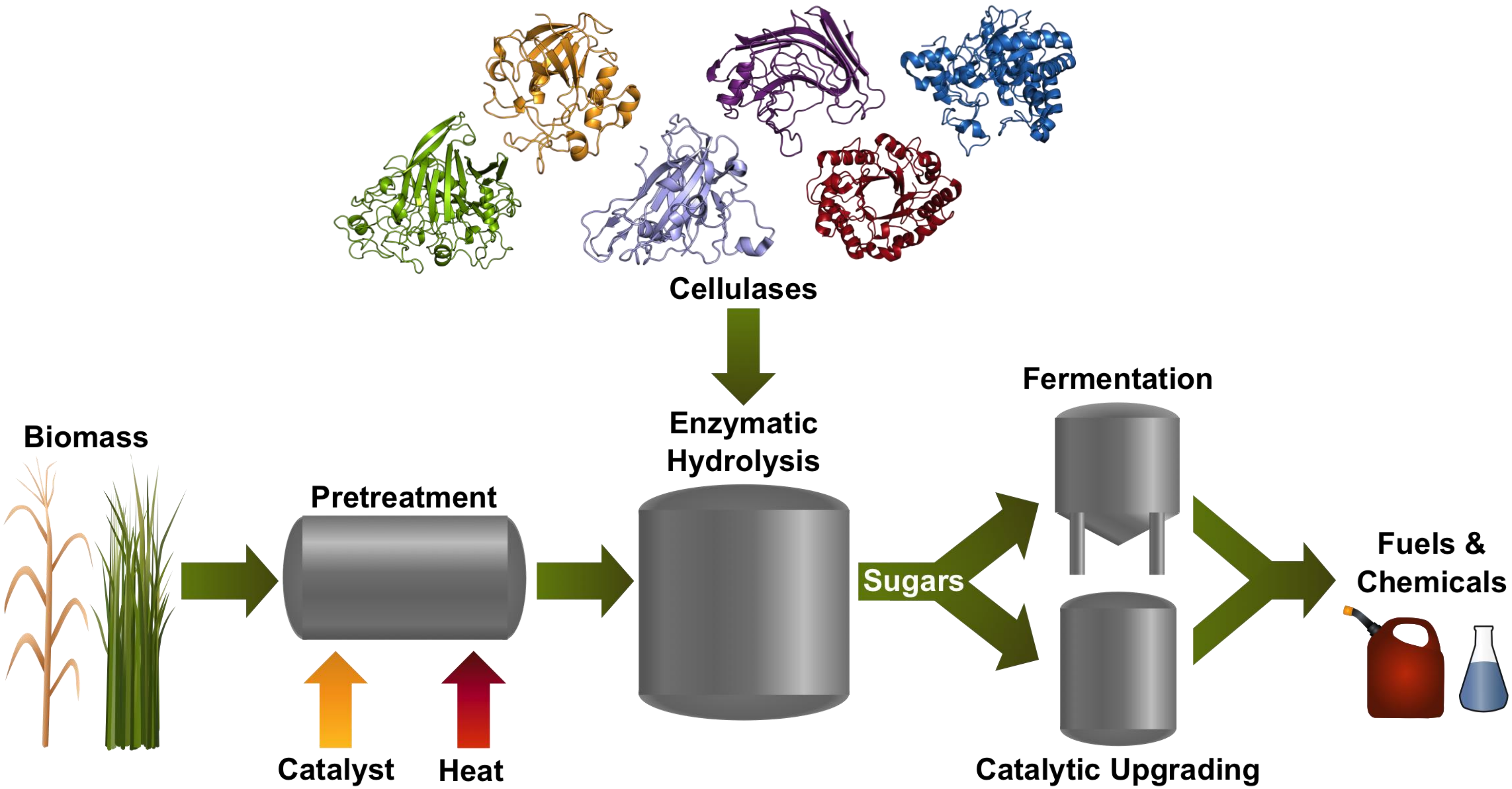
What about ambient temperatures?

Fungal cellulases



Payne, C. M.*; Knott, B. C.*; **Mayes, H. B.***; Hansson, H.; Himmel, M. E.; Sandgren, M.; Ståhlberg, J.; Beckham, G. T. *Chem. Rev.* **2015**, *115*, 1308. *equal contributors

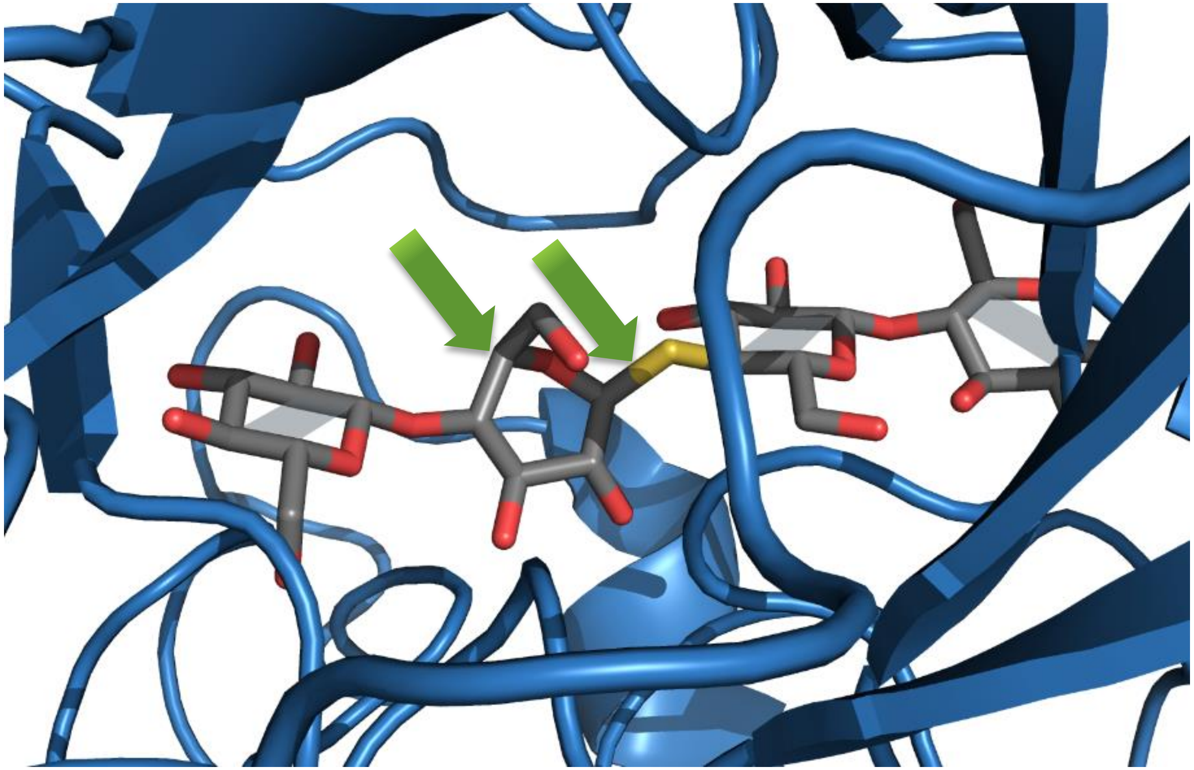
Current industrial use



Payne, C. M.*; Knott, B. C.*; **Mayes, H. B.***; Hansson, H.; Himmel, M. E.; Sandgren, M.; Ståhlberg, J.; Beckham, G. T. *Chem. Rev.* **2015**, *115*, 1308. *equal contributors

Carbohydrate-active enzyme mechanistic clues

***T. reesei* Cel6A**



Rouvinen, J., *et al*. *Science*, **1990**, *249*, 380.

Northwestern Engineering

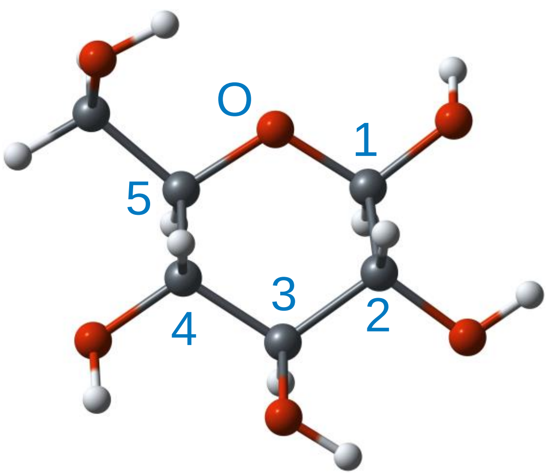
38 pucker geometries

$$z_j = \sqrt{\frac{2}{N}} \sum_{m=2}^{N/2-1} q_m \cos\left[\phi_m + \frac{2\pi m(j-1)}{N}\right] + \frac{q_{N/2}(-1)^{j-1}}{\sqrt{N}}$$

$$\sum_{j=1}^{N} z_j^2 = \sum_m q_m^2 = Q^2$$

$$q_2 = \sin\theta$$

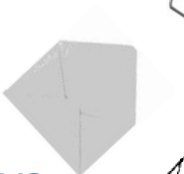
$$q_3 = \cos\theta$$



Combinatorial number of “puckers” for non-symmetric molecules

C

2 ways



12 ways

E

12 ways

H

6 ways

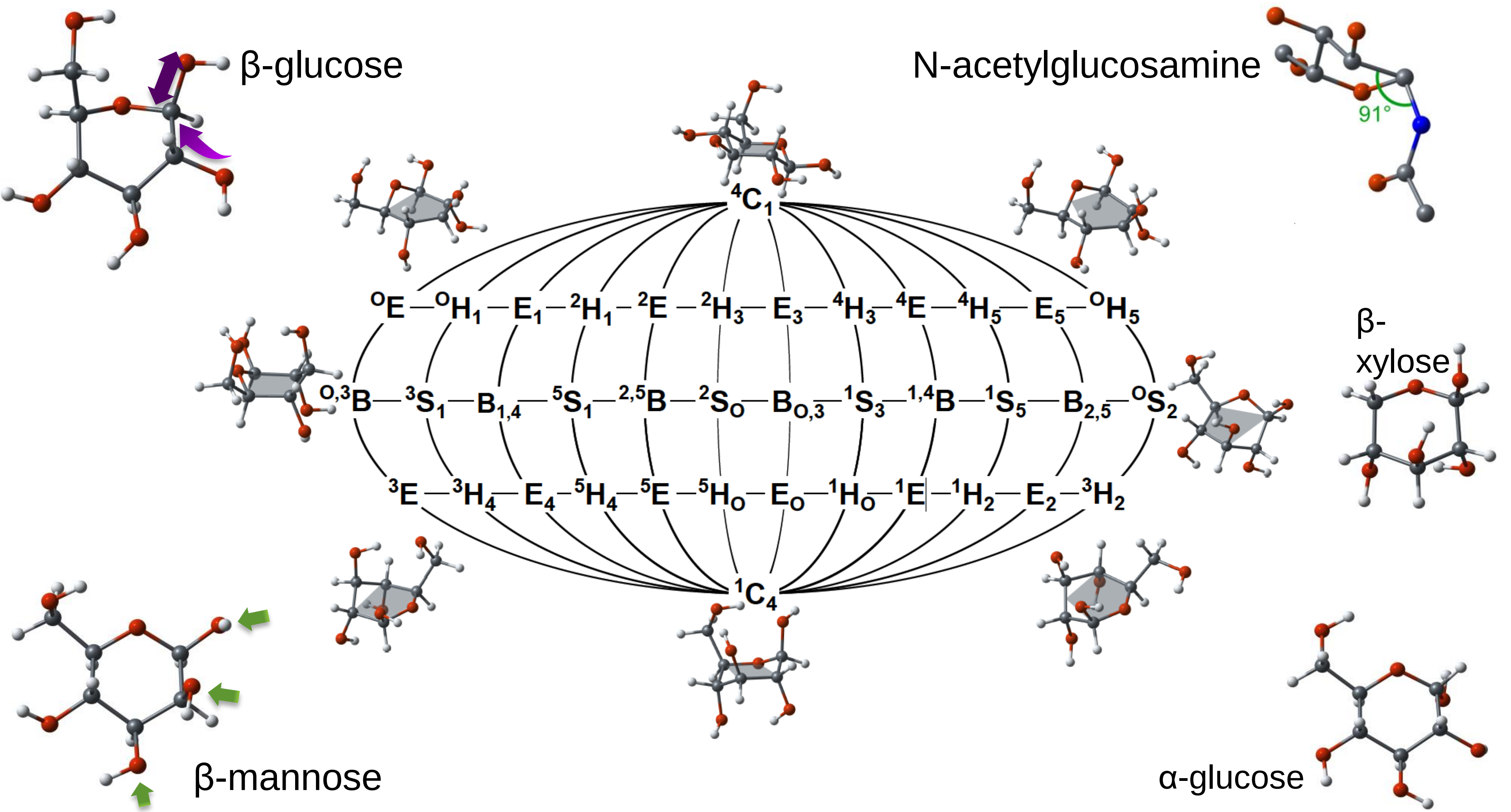
B

6 ways

S

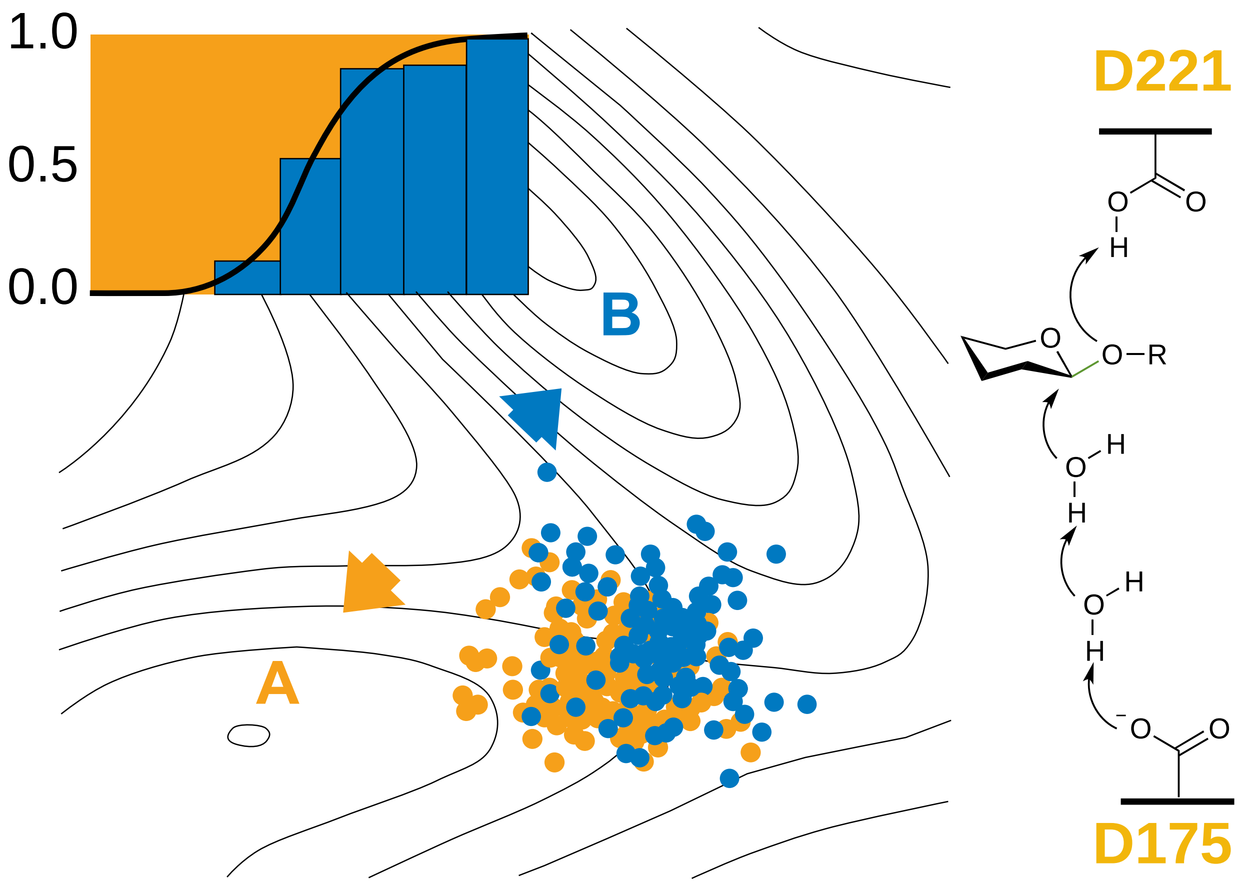
Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.*, **1975**, *97*, 1354.

Flexible exocyclic groups increase complexity



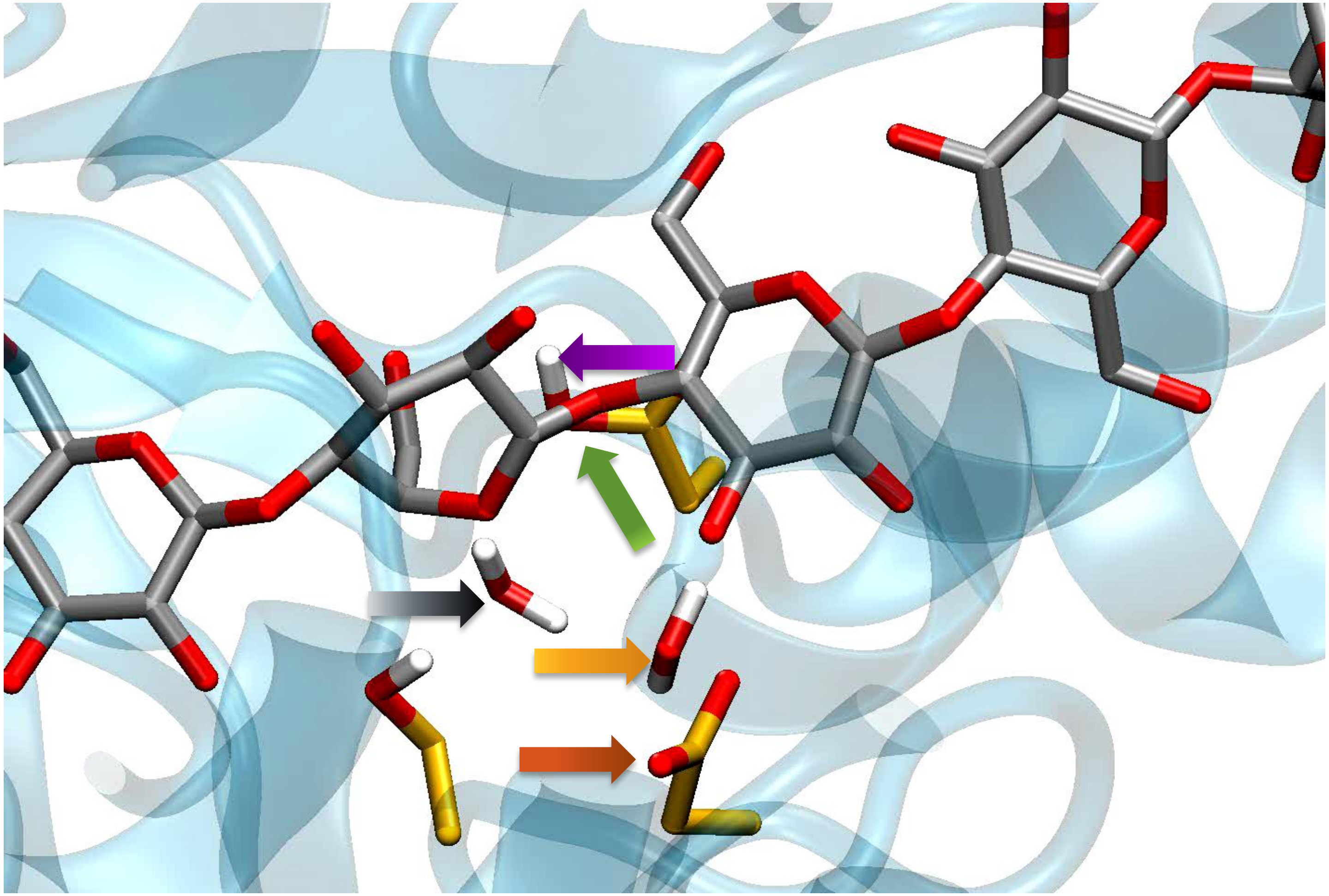
Mayes, H. B.; Broadbelt, L. J.; Beckham, G. T. *J. Amer. Chem. Soc.* **2014**, *136*, 1008.

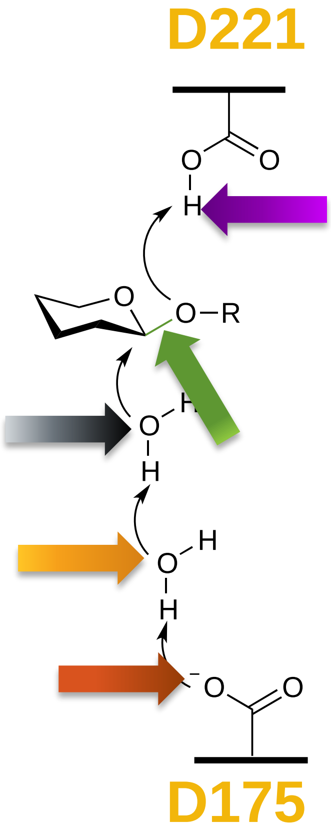
Path sampling with aimless shooting and likelihood maximization



Peters, B.; Beckham, G. T.; Trout, B. L. *J. Chem. Phys.* **2007**, *127*, 034109.

Simulation allows us to test hypotheses and determine contributions to the reaction coordinate





Where we were

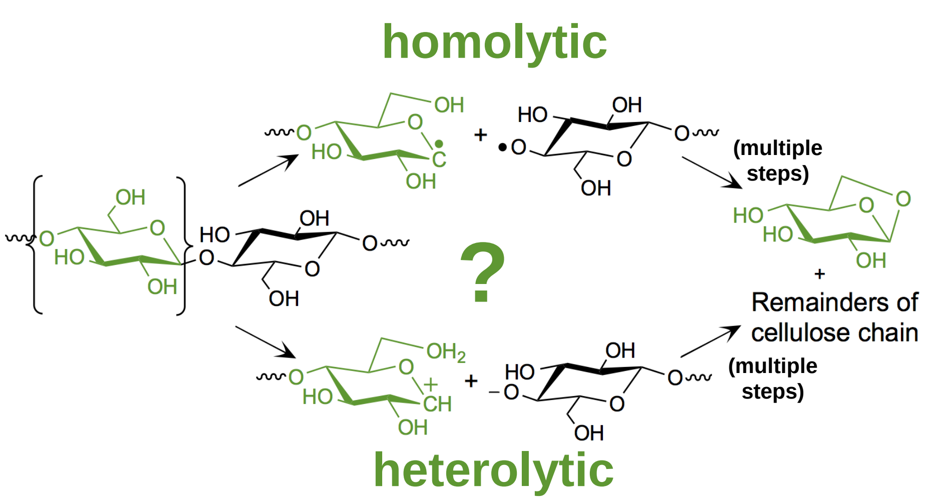
Biomass → **Fast Pyrolysis** → **Liquid Bio-Oil** Yield ~75%

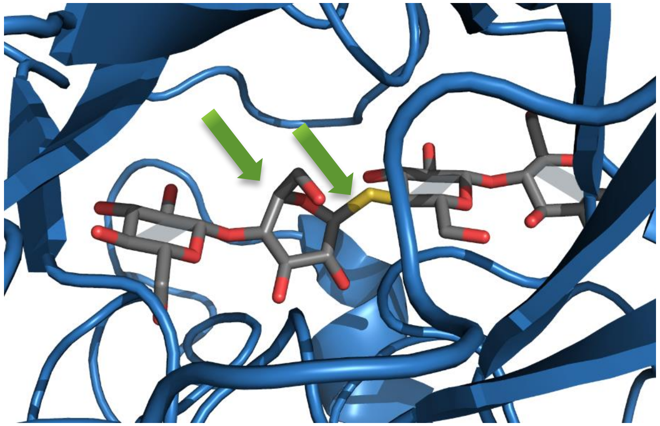
Cellulose $\xrightarrow{k_1}$ **Active Cellulose**

Active Cellulose $\xrightarrow{k_3}$ **LMW Prods. + 0.9 H_2O + 0.61 Char**

Active Cellulose $\xrightarrow{k_4}$ **Levoglucosan**

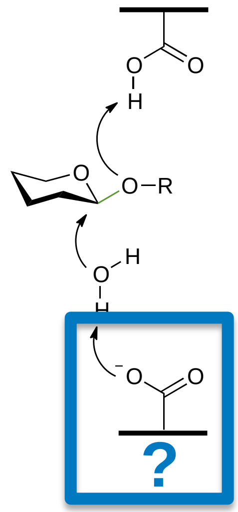
Cellulose $\xrightarrow{k_2}$ **6Char + 5H_2O**



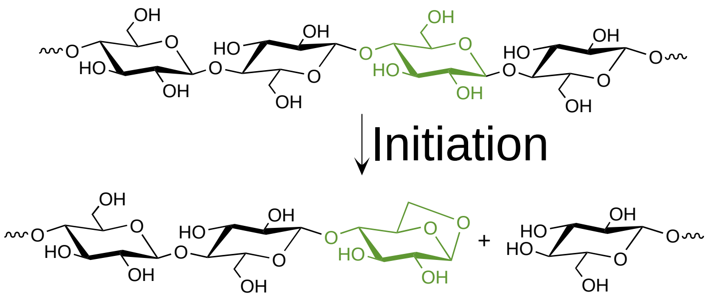


T. reesei **Cel6A**

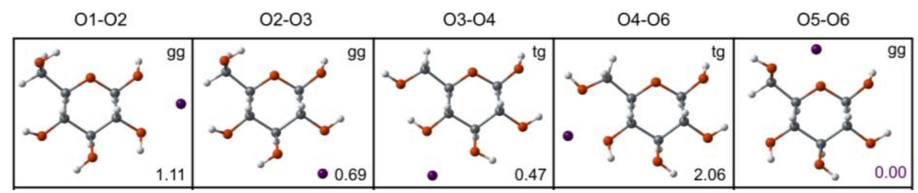
D221



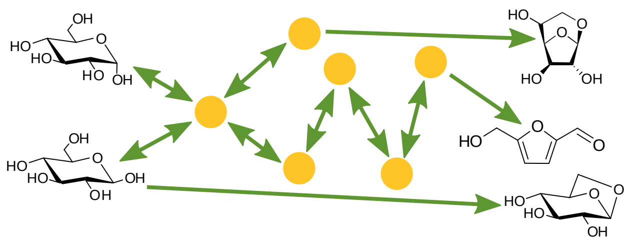
Where we are now



Mayes, H. B.; Broadbelt, L. J. *J. Phys. Chem. A* **2012**, *116*, 7098.

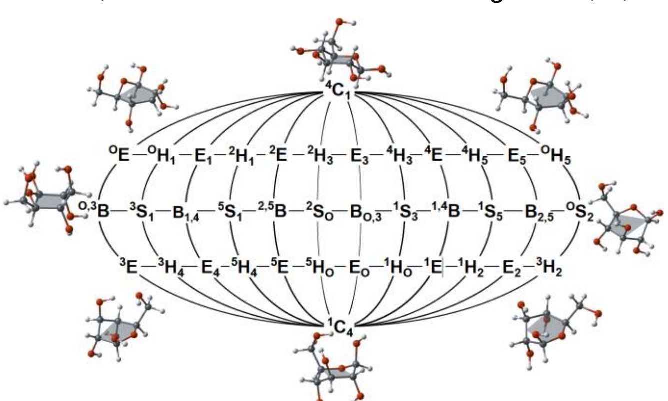


Mayes, H. B.; Tian, J.; Nolte, M. W.; Shanks, B. H.; Beckham, G. T.; Gnanakaran, S.; Broadbelt, L. J. *J. Phys. Chem. B,* **2014**, *118*, 1990.

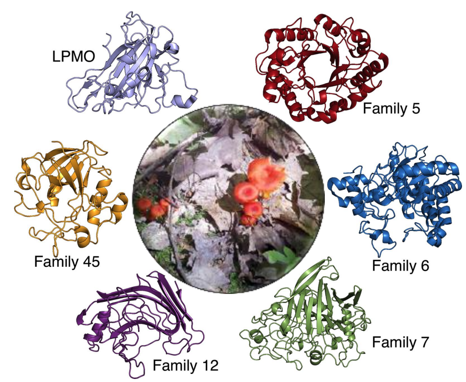


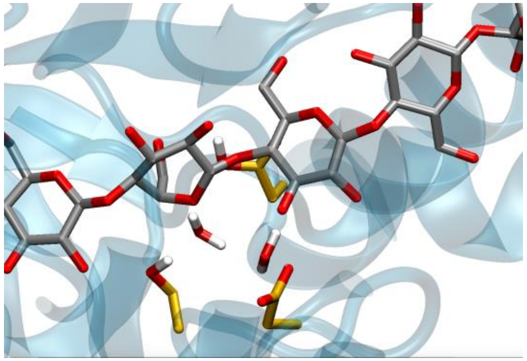
Mayes, H. B.; Nolte, M. W.; Beckham, G. T.; Shanks, B. H.; Broadbelt, L. J. *ACS Sustain. Chem. Eng.* **2014**, *2*, 1461.

Mayes, H. B.; Nolte, M. W.; Beckham, G. T.; Shanks, B. H.; Broadbelt, L. J. *ACS Catal.* **2015**, *5*, 192.



Mayes, H. B.; Broadbelt, L. J.; Beckham, G. T. *J. Amer. Chem. Soc.* **2014**, *136*, 1008.





Payne, C. M.*; Knott, B. C.*; **Mayes, H. B.***; Hansson, H.; Himmel, M. E.; Sandgren, M.; Ståhlberg, J.; Beckham, G. T. *Chem. Rev.* **2015**, *115*, 1308. *equal contributors



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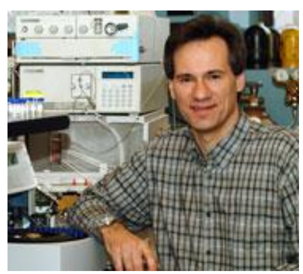
- Dr. Vinu Ravikrishnan
- Dr. Brent H. Shanks
- Michael W. Nolte
- Brandon Knott
- Chris Mayes



KRELL institute

Department of Energy United States of America

DOE CSGF

NABC National Advanced Biofuels Consortium

ARCS Advancing Science in America

NREL National Renewable Energy Laboratory

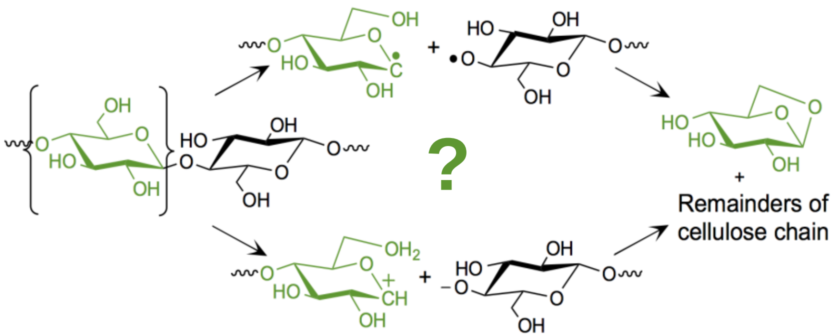
XSEDE Extreme Science and Engineering Discovery Environment

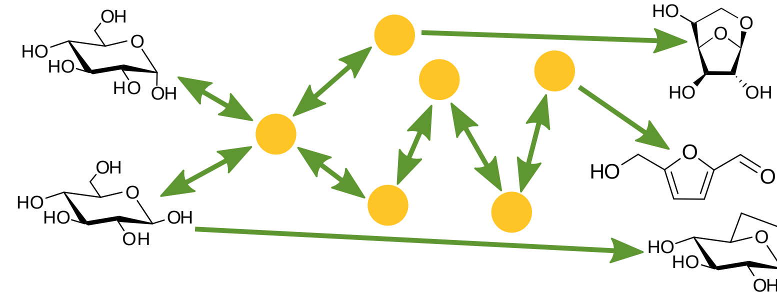
NERSC

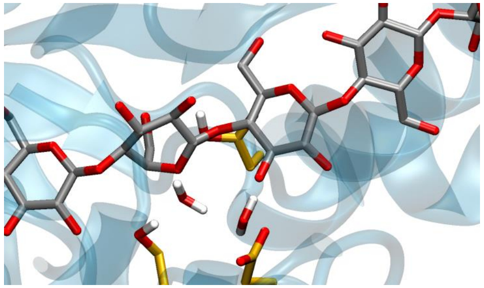
NSF

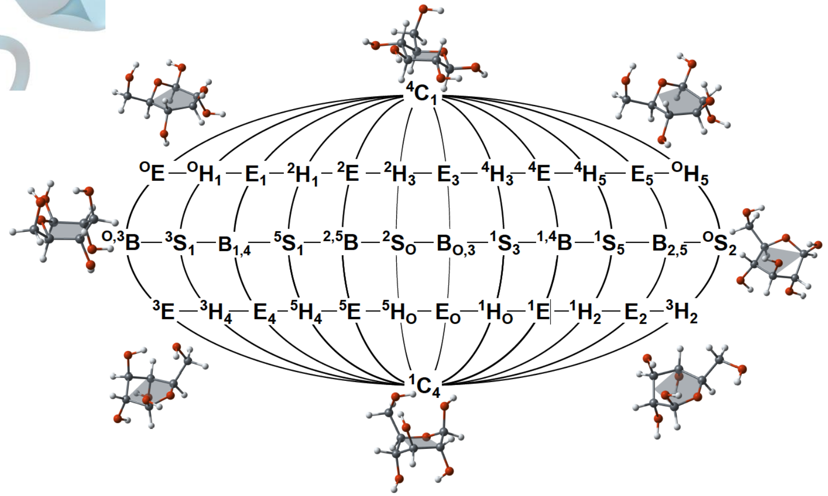
Questions?

hmayes@hmayes.com



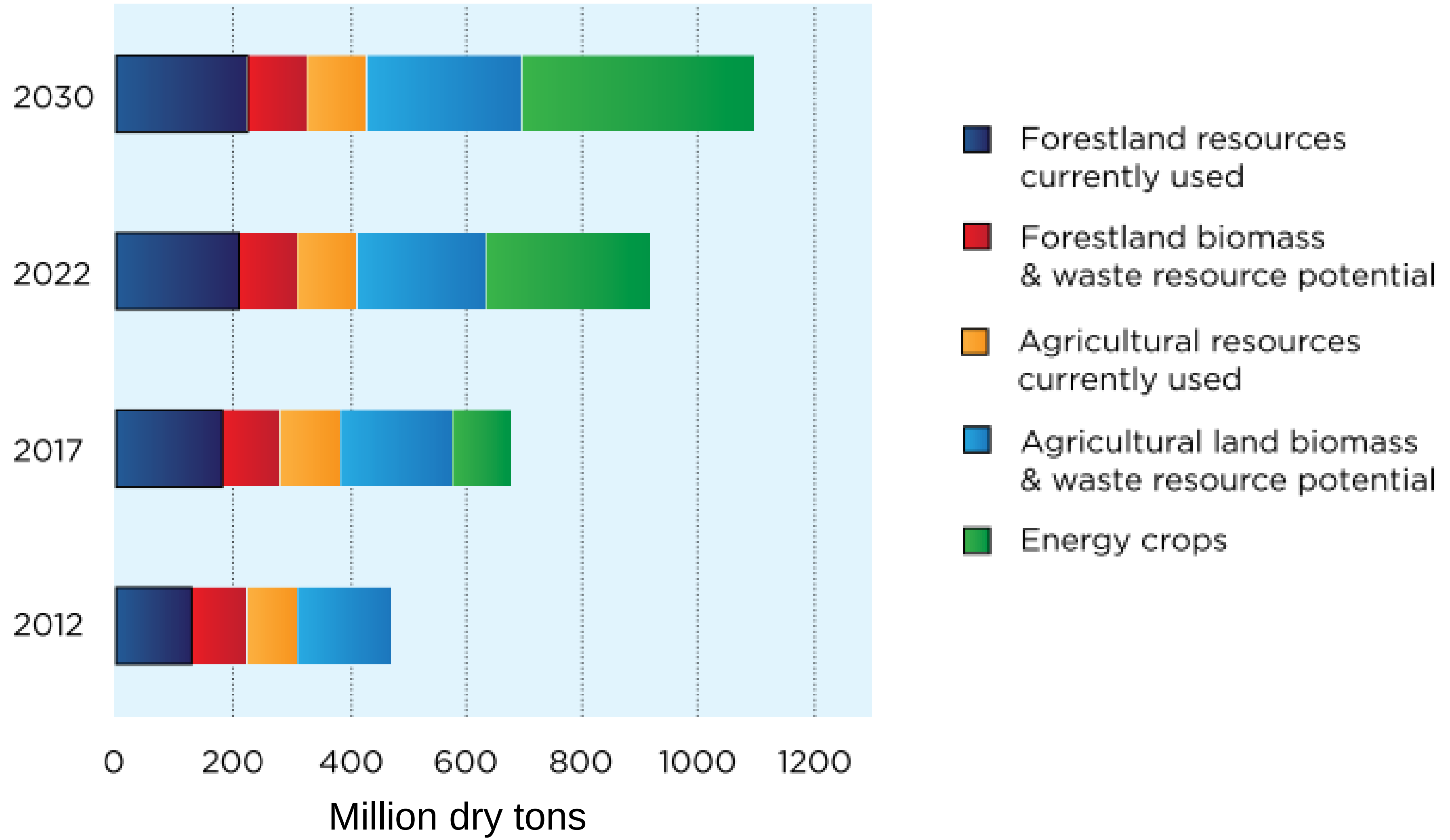






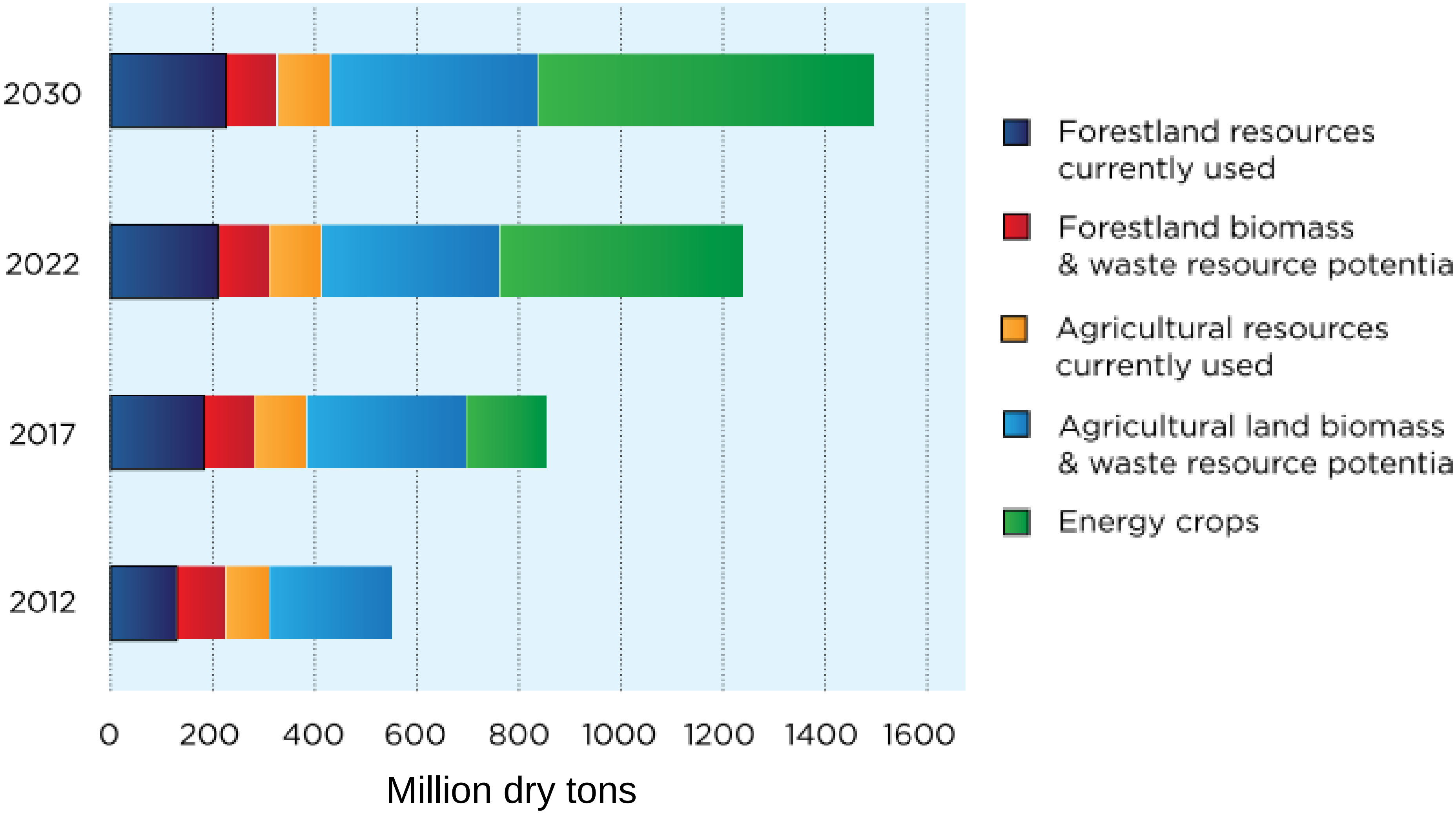
Back-up slides

Resources at ≤$60/dry ton, baseline assumptions



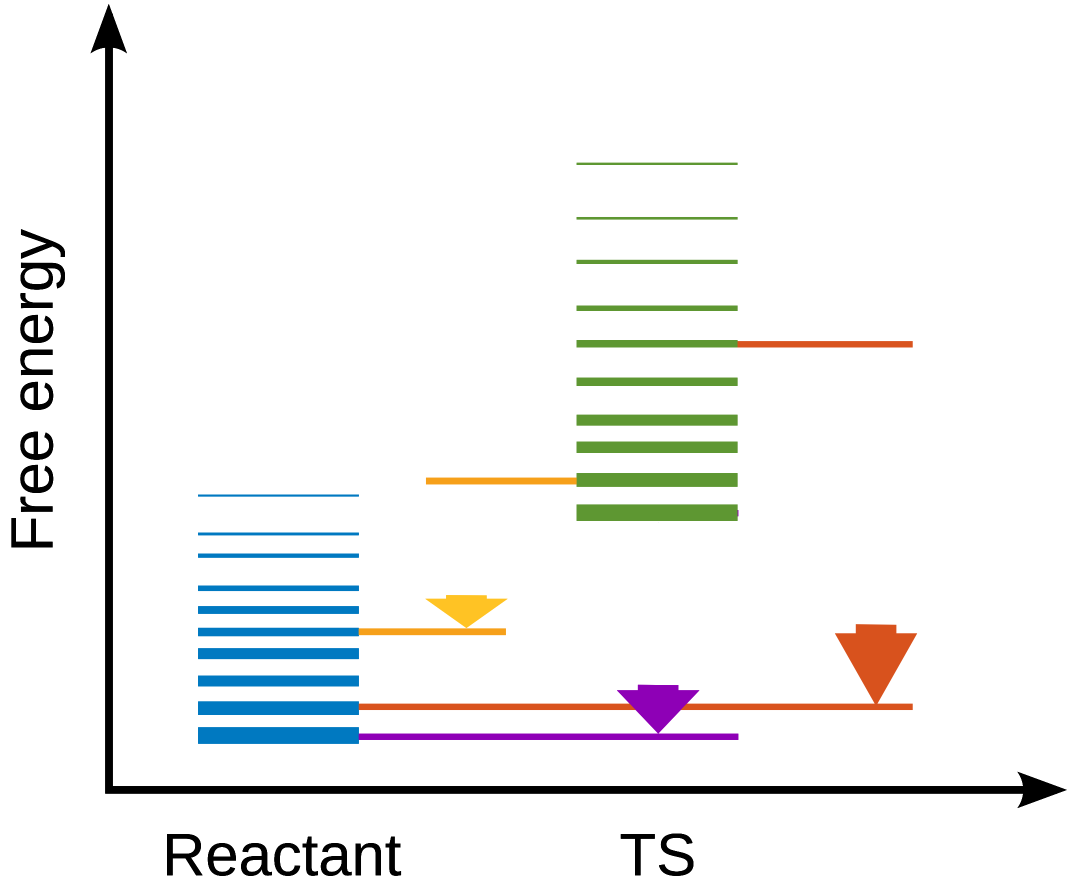
U.S. Billion-Ton Update, U.S. DOE, 2011

Resources at ≤$60/dry ton, high-yield assumptions



U.S. Billion-Ton Update, U.S. DOE, 2011

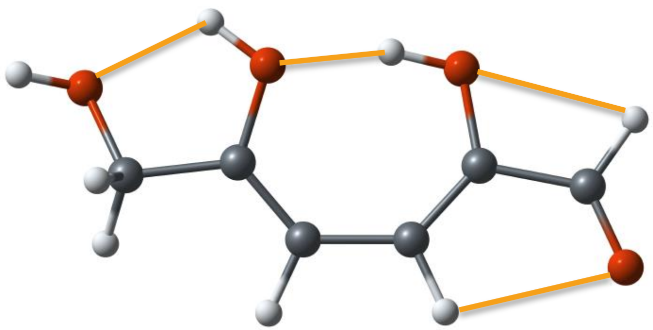
Why is this necessary?



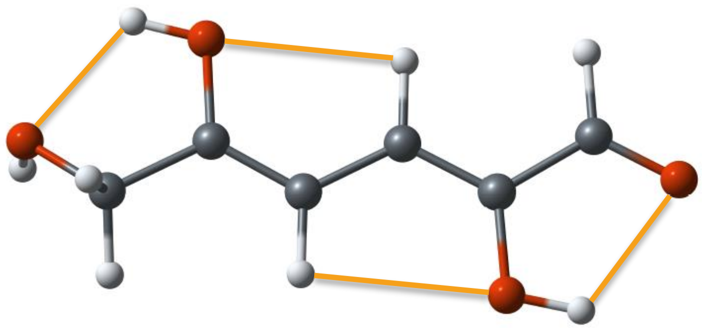
Can a different conformation make a significant difference in calculated rate coefficient?

Yes!

Conformation 1



Conformation 2

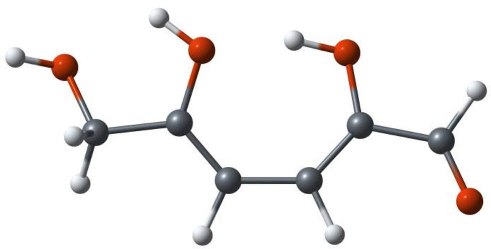


Free energy is 3.2 kcal/mol lower

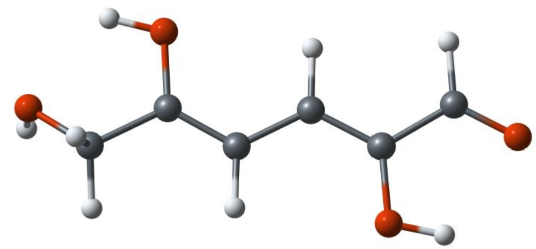
Does it matter?

- Different conformations can have significantly different G

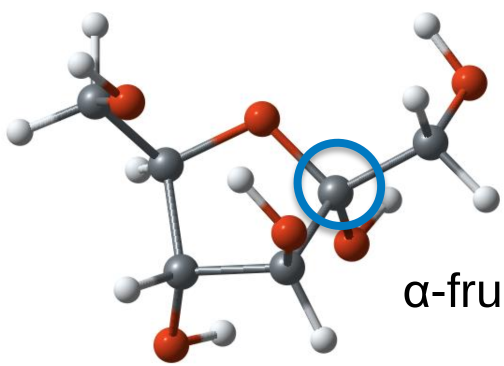
Conformation 1



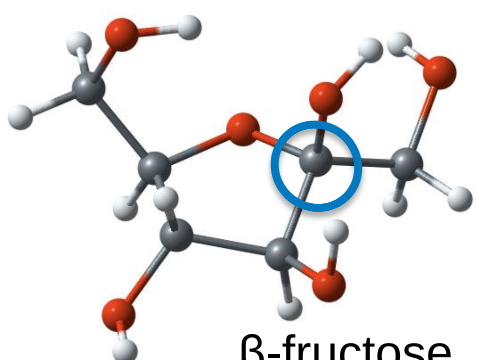
Conformation 2
G 3.2 kcal/mol less at 500 °C



- Investigate epimers created by ring closure at stereocenters

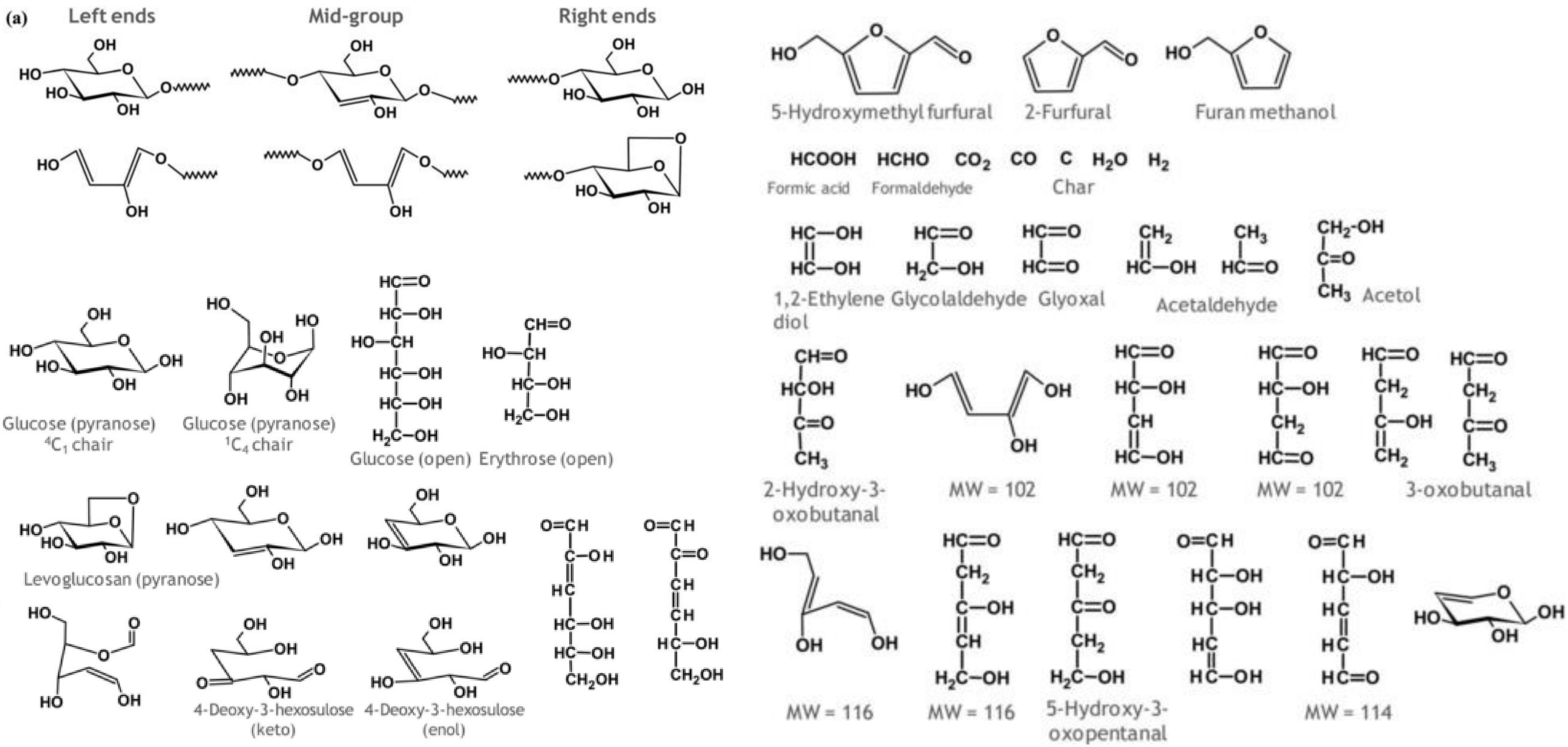


α-fructose



β-fructose

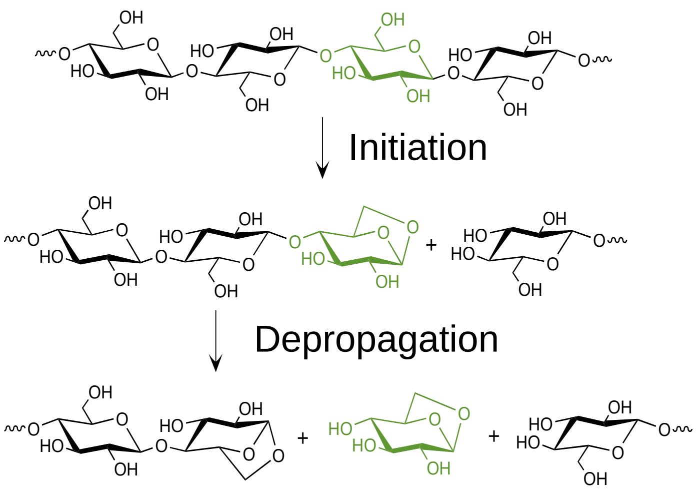
Microkinetic model provides detailed product speciation



Vinu, R.; Broadbelt, L. J. *Energy Environ. Sci.* **2012**, *5*, 9808.

Advanced understanding of thermochemical cellulose decomposition

- Determined likely mechanism and kinetic parameters for formation of the dominant cellulose pyrolysis mechanism
- Improved understanding how many LMW species form
- Uncovered molecular basis for salts changing carbohydrate pyrolysis yields



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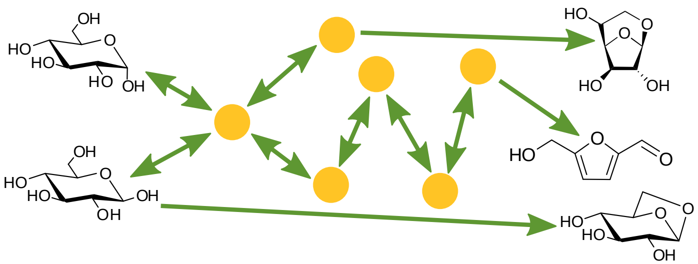

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