TRANSFORMING HOW WE SUSTAINABLY UTILIZE OUR AGRICULTURAL RESOURCES FOR FOOD, FEED, FIBER, FUEL, AND CHEMICALS

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2015 Research Award Seminar

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TRANSFORMING

(Oxford English Dictionary)

Catalyst cat·a·lyst ˈkad(ə)ləst/
Greek *κατά* down + *λύειν* to loosen.
noun

- a substance that increases the rate of a chemical reaction without itself undergoing any permanent chemical change. (1836)

- a person or thing that precipitates an event

TRANSFORMING PLANT MATTER

Catalysts: Accelerates the conversion of molecules

The Explosion in the Alchemist's Laboratory by Justus Gustav van Bentum (Leiden 1670–1727) Holland

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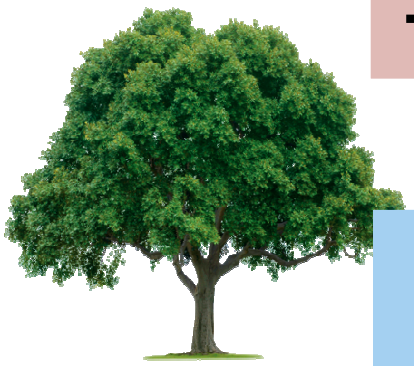
Paul Zelinsky, 1986

Andrew Lang's The Blue Fairy Book, ca. 1889 (Henry J. Ford illustration)

SPINNING STRAW INTO GOLD

- Fuels
- Plastics
- Solvents
- Other Valuable Chemicals

BIOMASS CONVERSION PROCESSES



Fractionation

Gasification
Pyrolysis
Condensed Phase

Catalytic Upgrading

Thermochemical

Alkanes
Aromatics
Polyols
Organic Acids
Alcohols

Biochemical

Fractionation

Pretreatment
Enzym. Sacch.
Fermentation

Biocatalytic Upgrading

800
400
180
50
℃

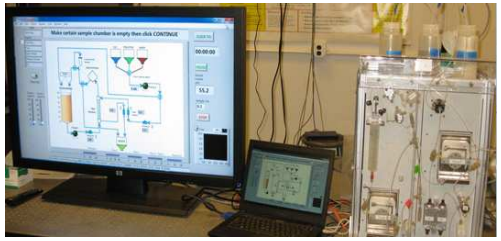
Hewetson, B., 2014

Laboratory of Renewable Resources Engineering

BioProcess Validation and Scale-Up

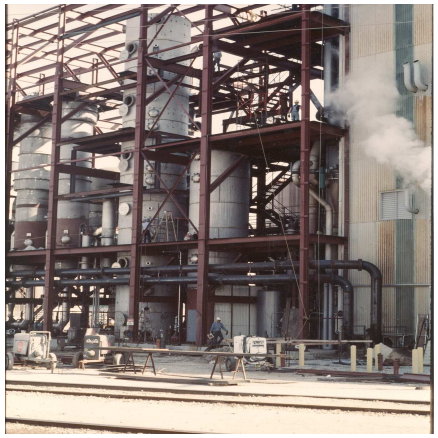
- Biomass to Biofuels
- Biomass to Chemicals

Chemical and Biological Catalysis



- Biocatalysts for Biofuels
- Compositional Analysis

SEPARATION TECHNOLOGIES



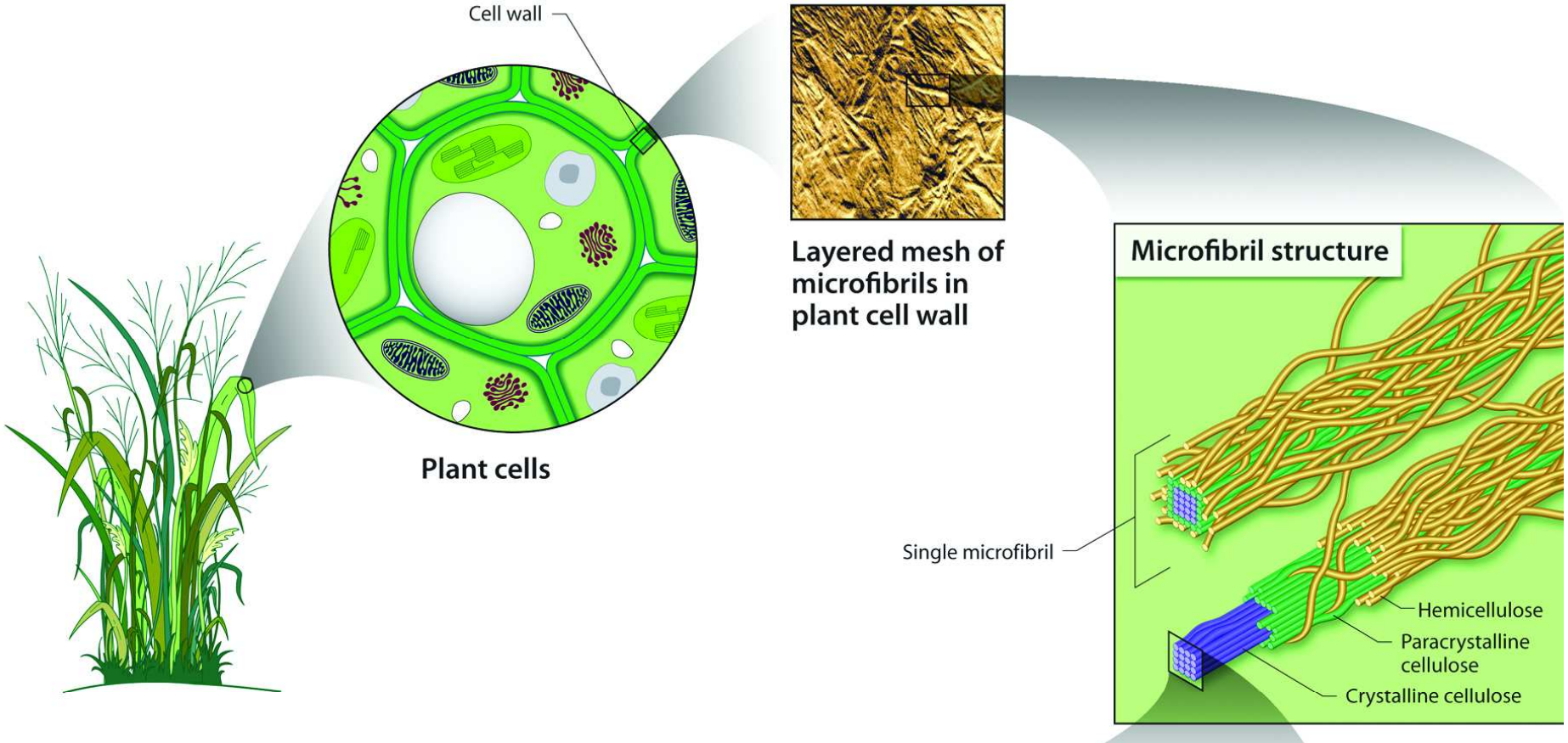
- Biological Product Purification
- Value-added Products from Biorefineries

Rapid Prototyping

Tactical Garbage to Energy Refinery (TGER version 3.0)

* Dr. Michael Ladisch * Dr. Nathan Mosier * Dr. Abigail Engelberth * Dr. Eduardo Ximenes * Dr. Gozdem Kilaz

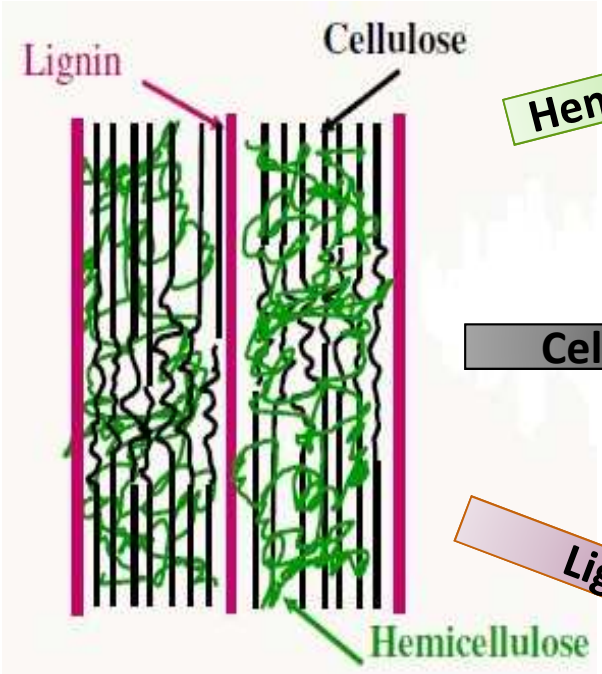
THE CHALLENGE



Office of Biological and Environmental Research, U.S. Department of Energy, Office of Science

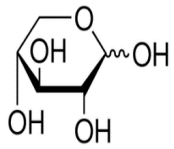
Zina Deretsky, National Science Foundation; Selaginella cross section SEM by Jing-Ke Weng, Clint Chapple, Purdue University; Lignin structure from Wout Bergjan, John Ralph, Marie Baucher (Annual Review of Plant Biology, Vol. 54:519-546, June 2003); Cellulose structure from http://www.chusa.jussieu.fr/disc/bio_cell/

FRACTIONATION OF BIOMASS



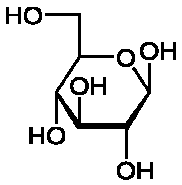
*Mosier, N., et al. , 2005

Hemicellulose



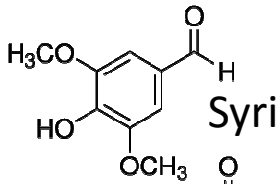
xylose

Cellulose

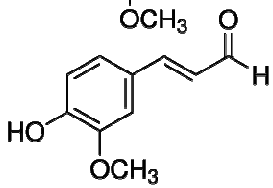


Glucose

Lignin

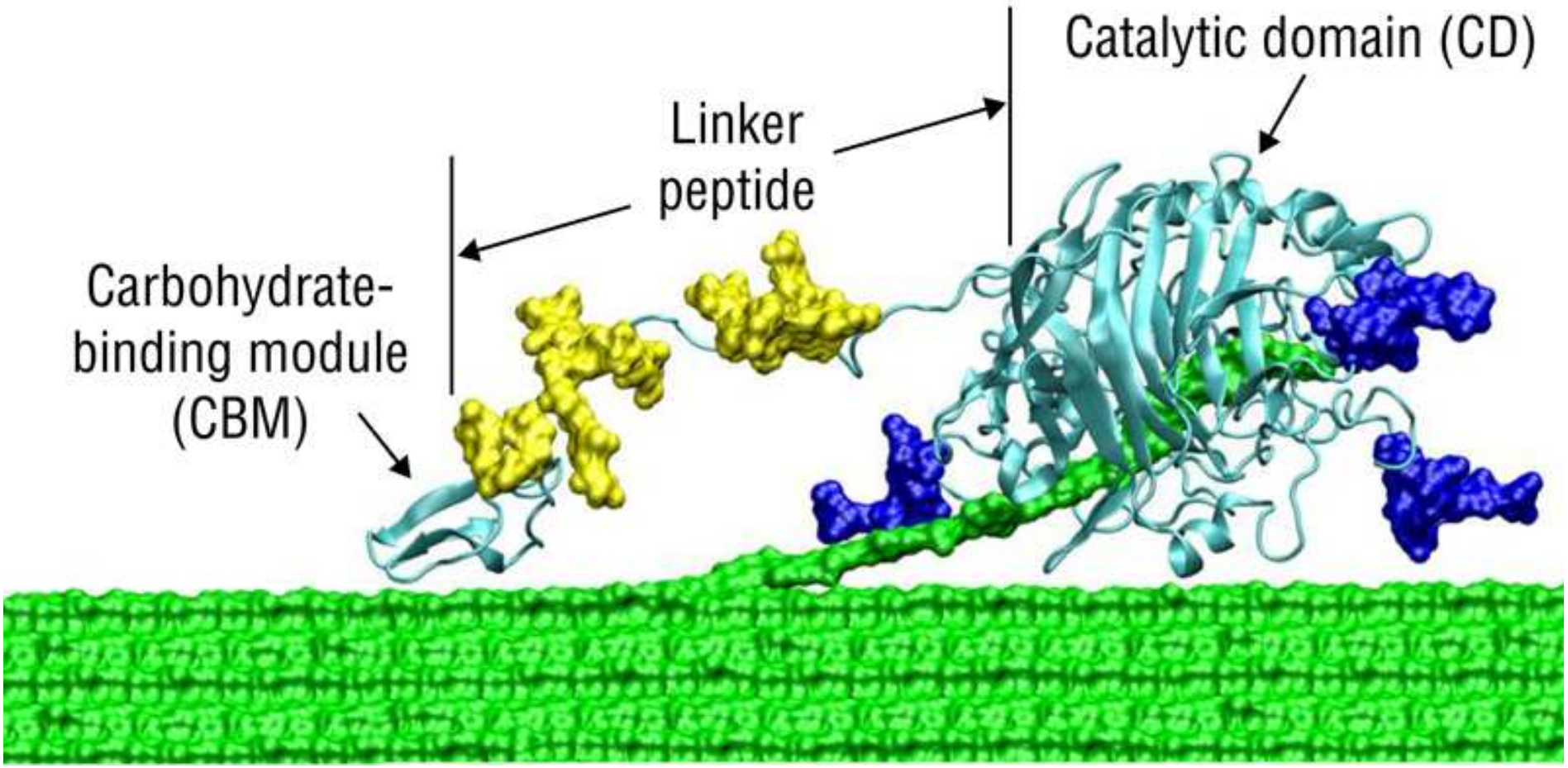


Syringaldehyde

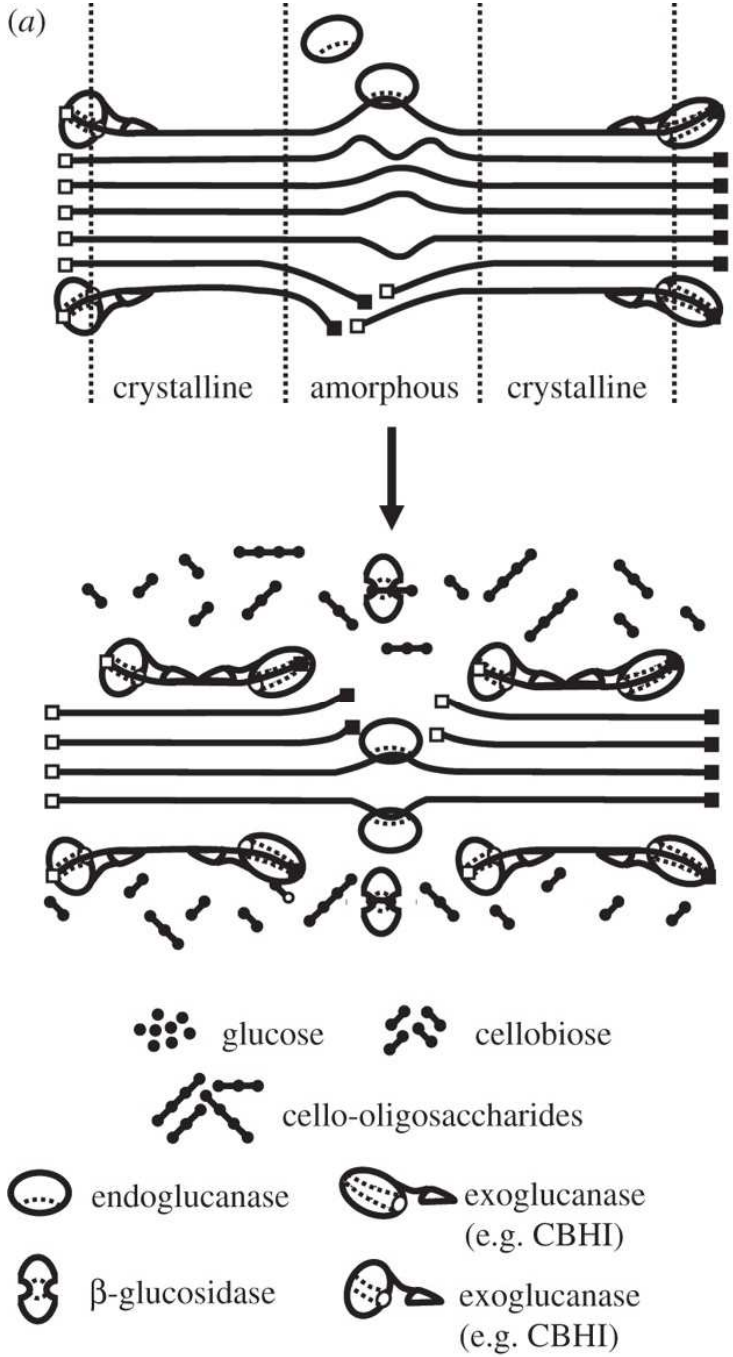


Coniferylaldehyde

FUNGAL CELLULASES

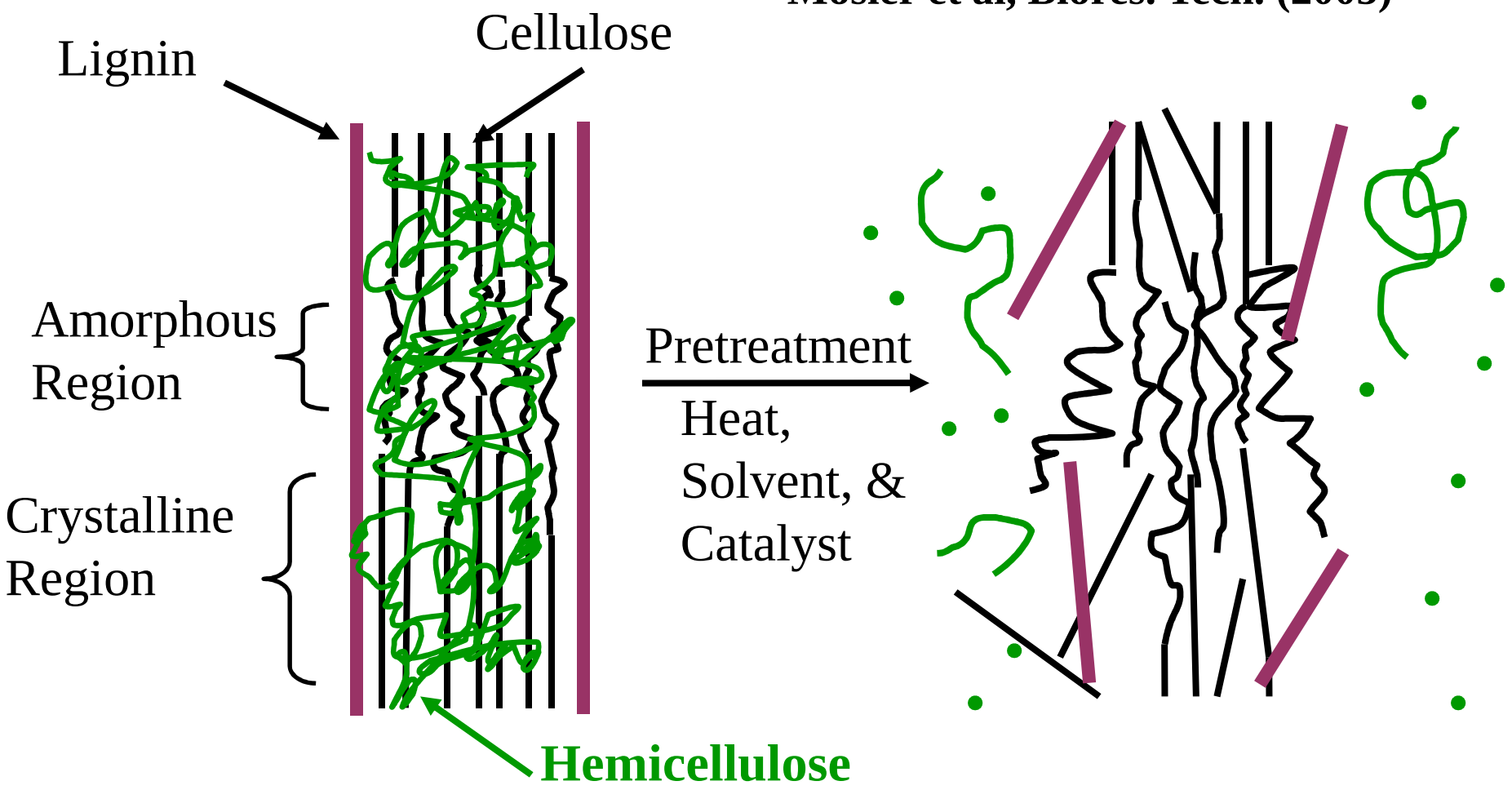


Van Zyl et al., Interface Focus (2011)

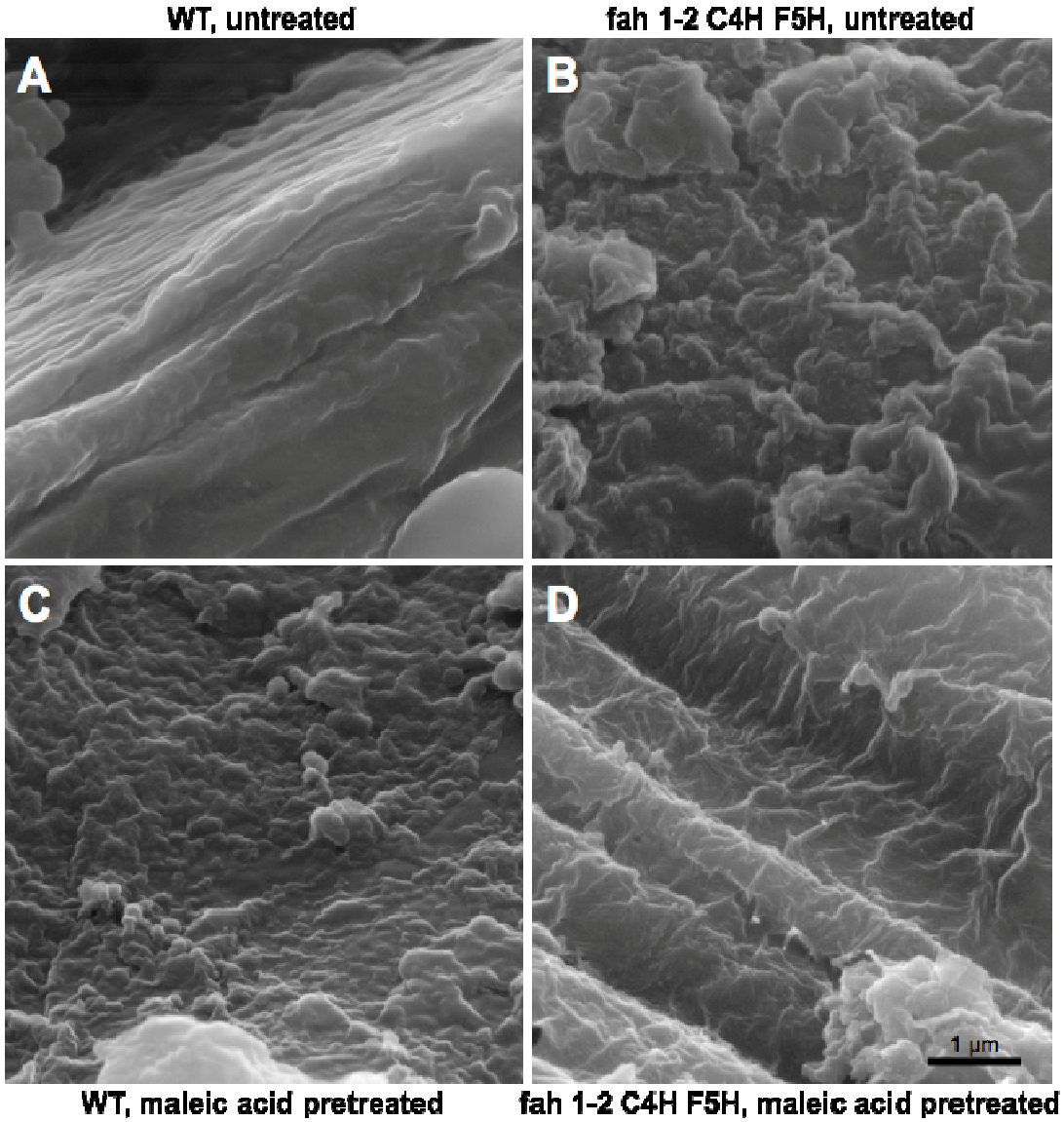


EFFECT OF PRETREATMENT

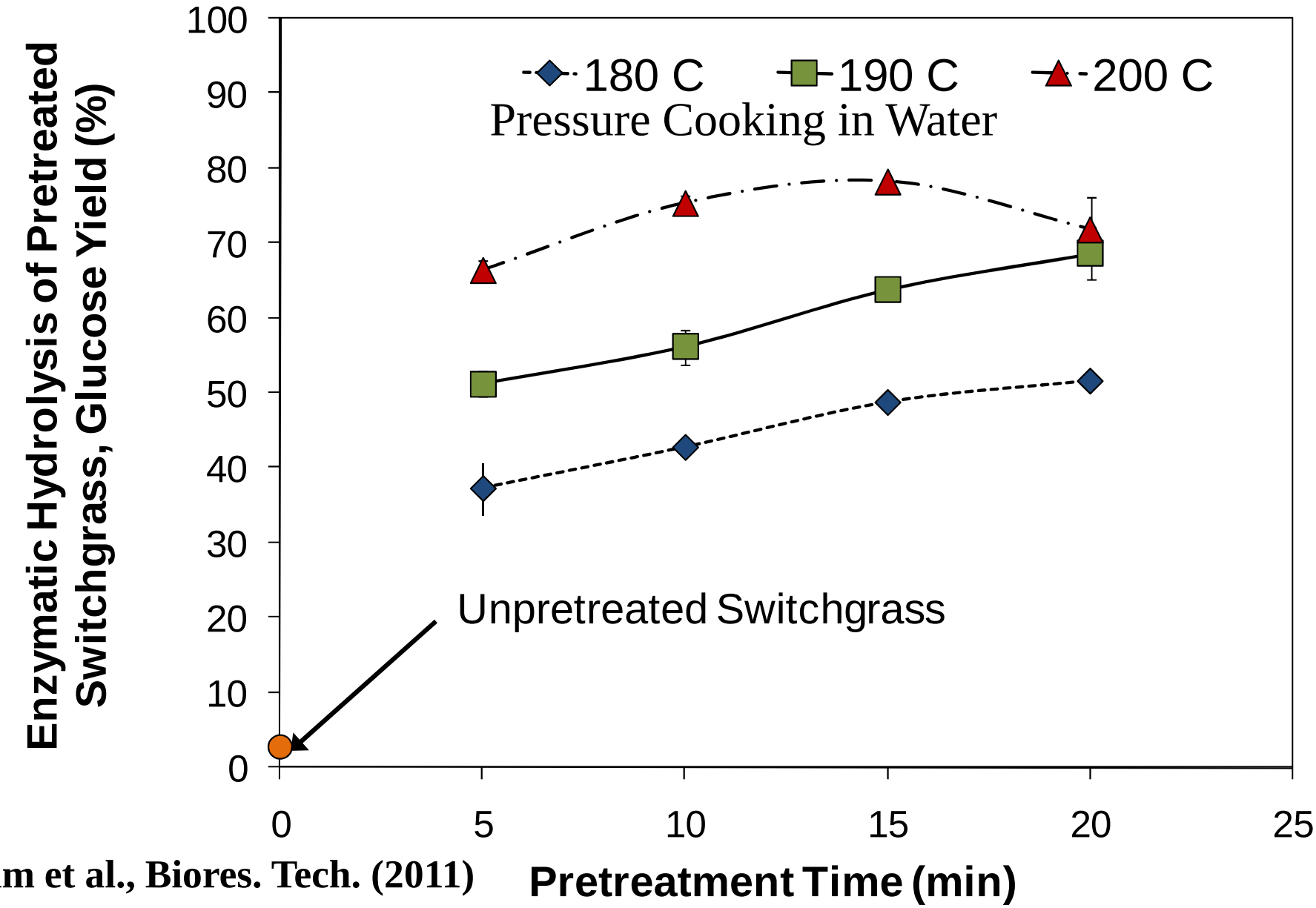
Mosier et al, Biores. Tech. (2005)



High mag FE-SEM analysis to quantify surface roughness



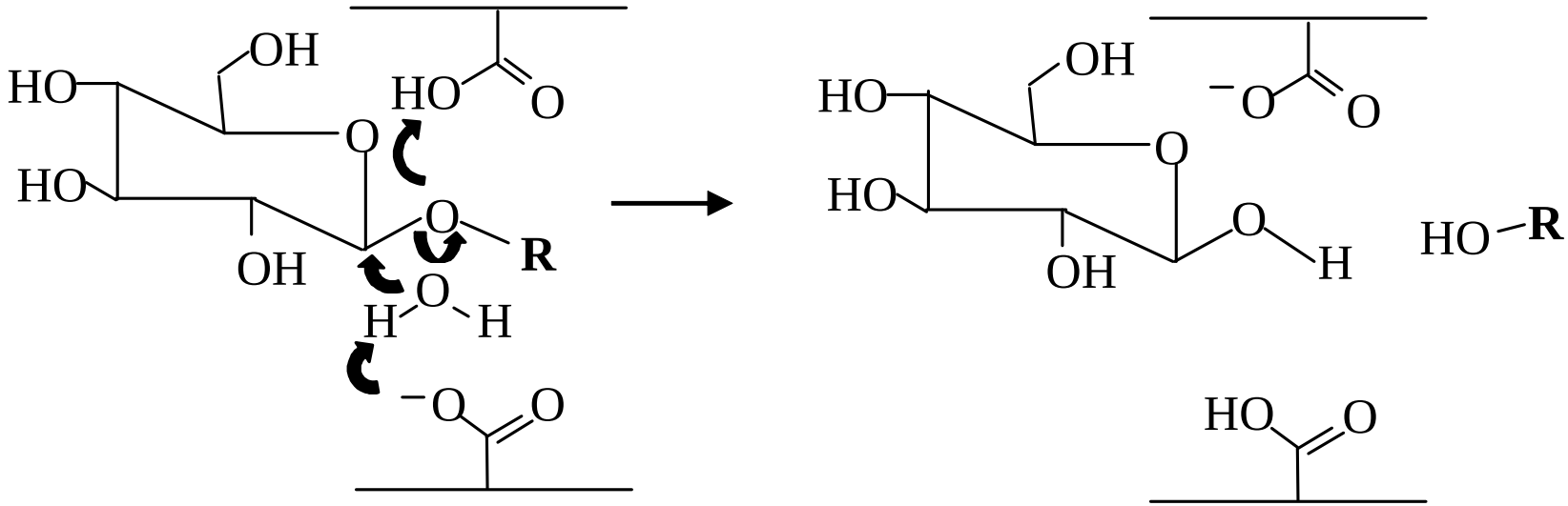
EFFECT OF PRETREATMENT



Kim et al., Biores. Tech. (2011)

HOW CELLULASES WORK

9.0 - 9.5 Å



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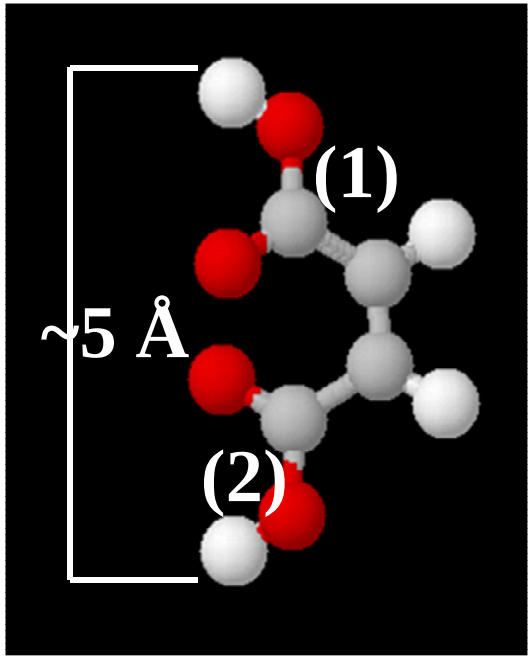
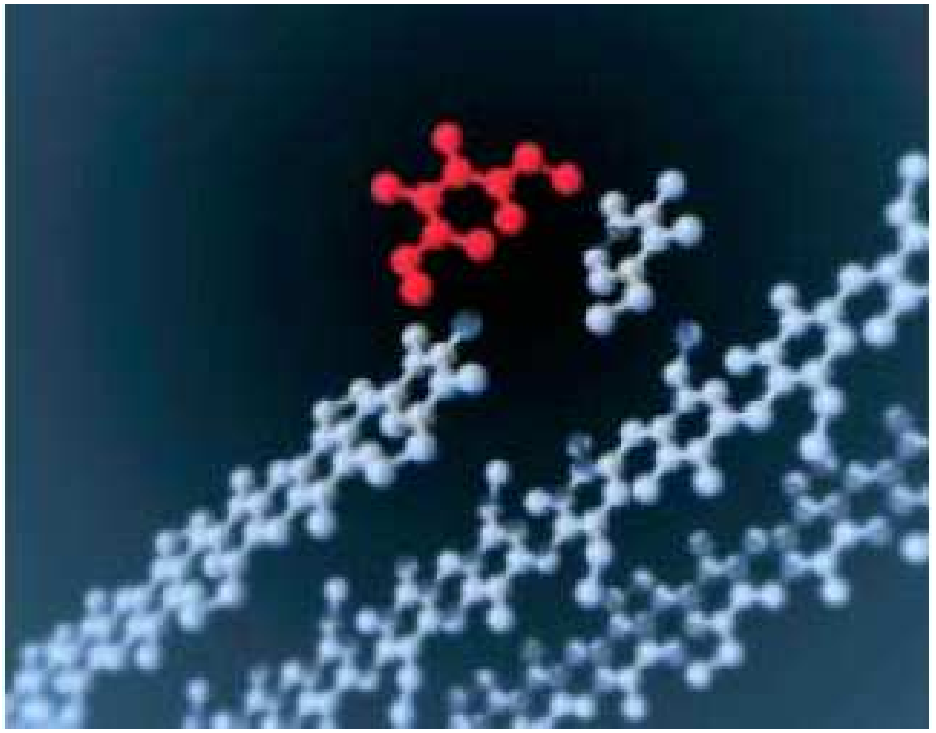
ENZYME MIMETICS FOR BIOMASS HYDROLYSIS

Maleic Acid





Maleic acid (red) hydrolyzing cellulose chain (photo courtesy of Purdue University College of Engineering)

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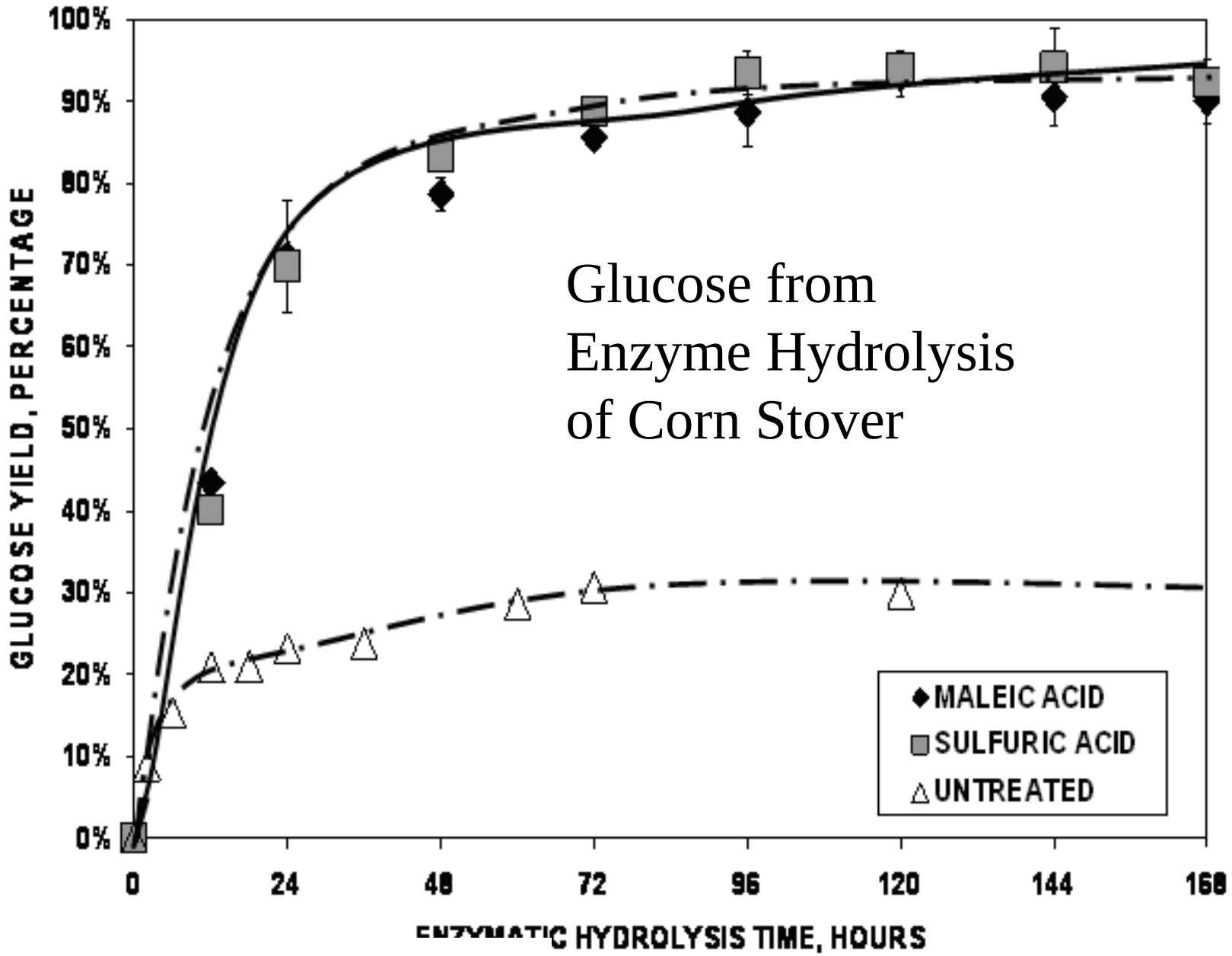
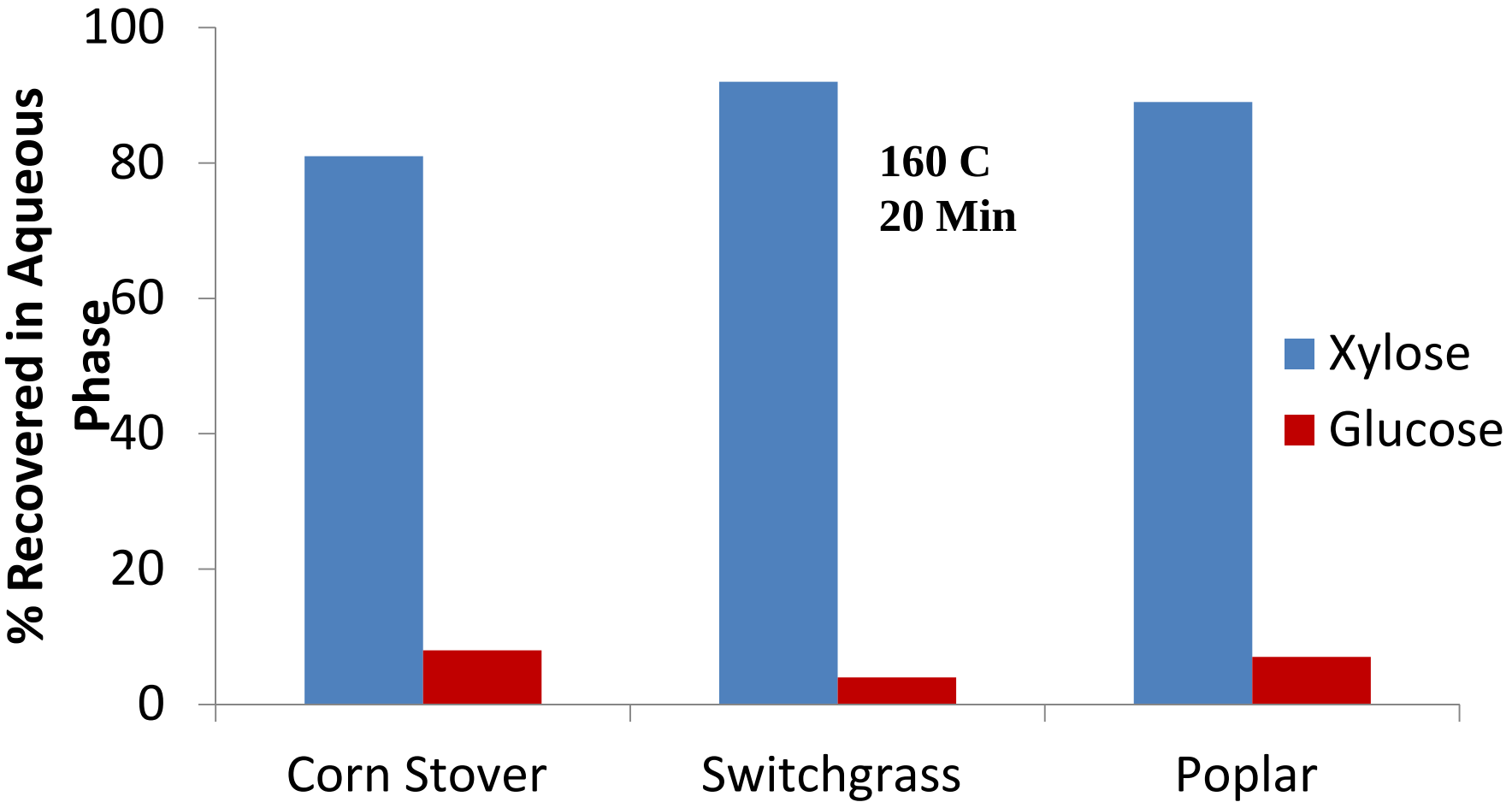


Lu et al., Biotech. Prog. (2007)

MALEIC ACID: SELECTIVE FRACTIONATION OF XYLOSE FROM VARIOUS TYPES OF BIOMASS



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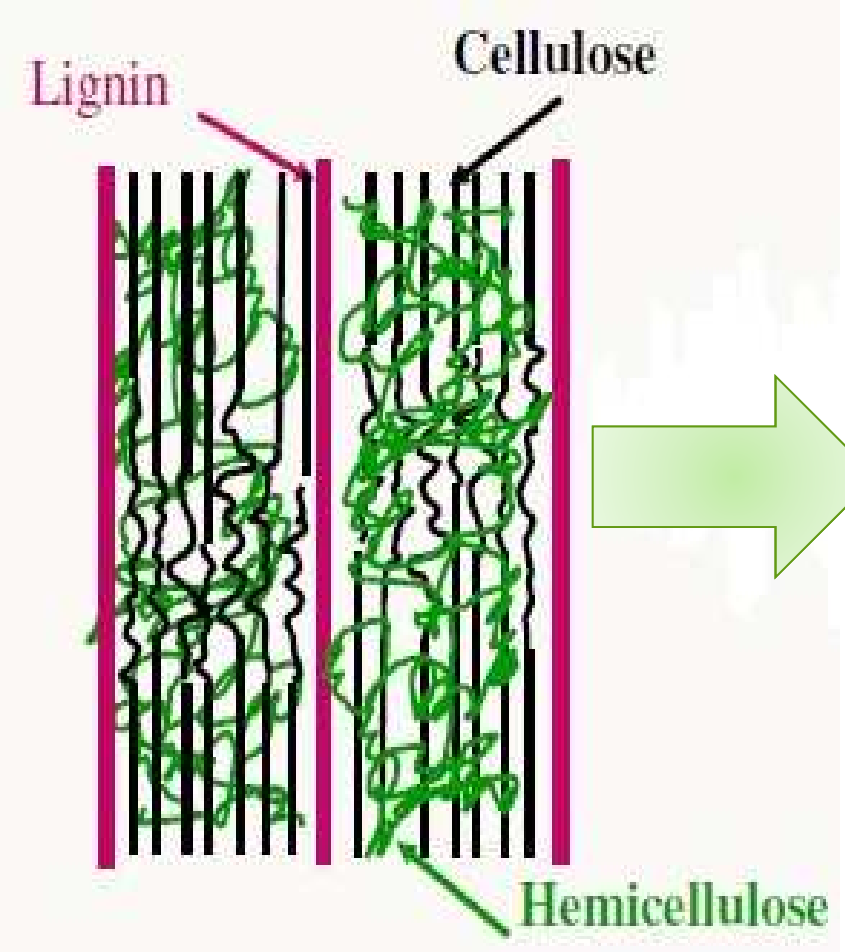
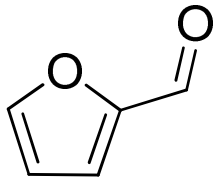
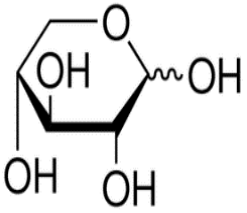
MANY REACTIONS



Furfural





Xylose

Humic “Tar”

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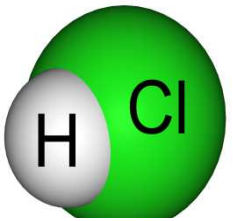
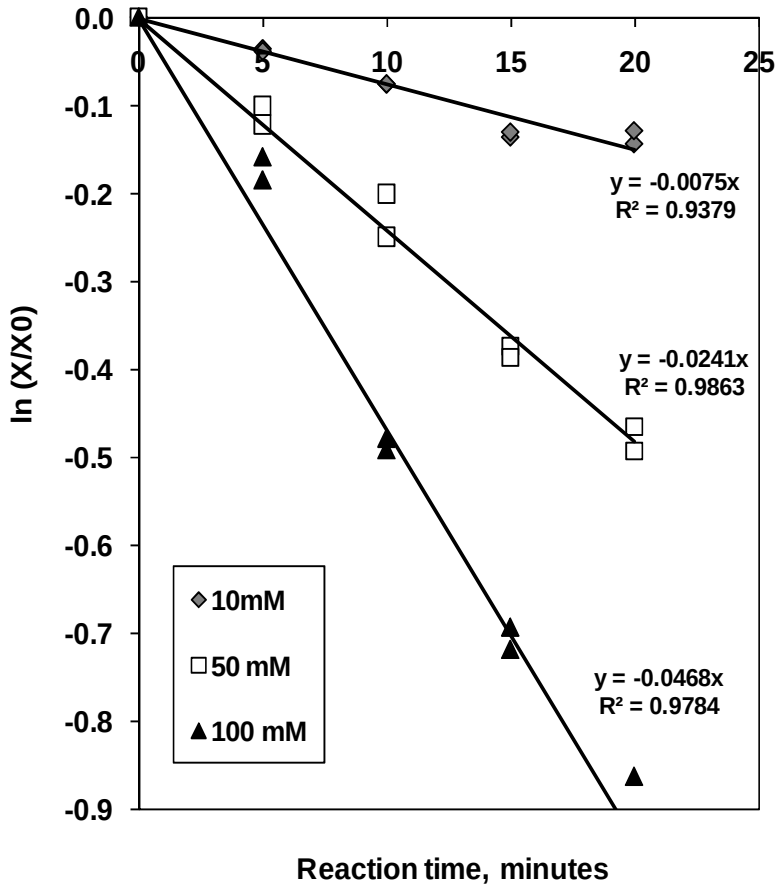
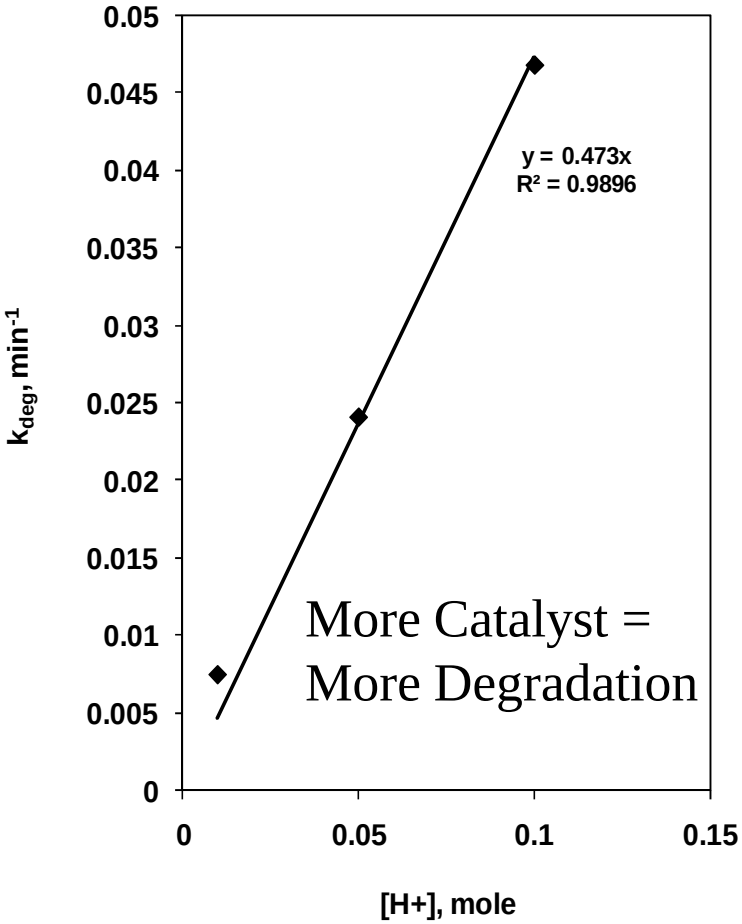
MECHANISTIC ANALYSIS

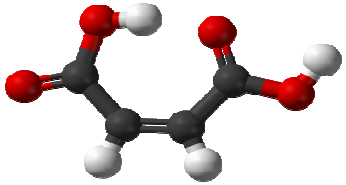


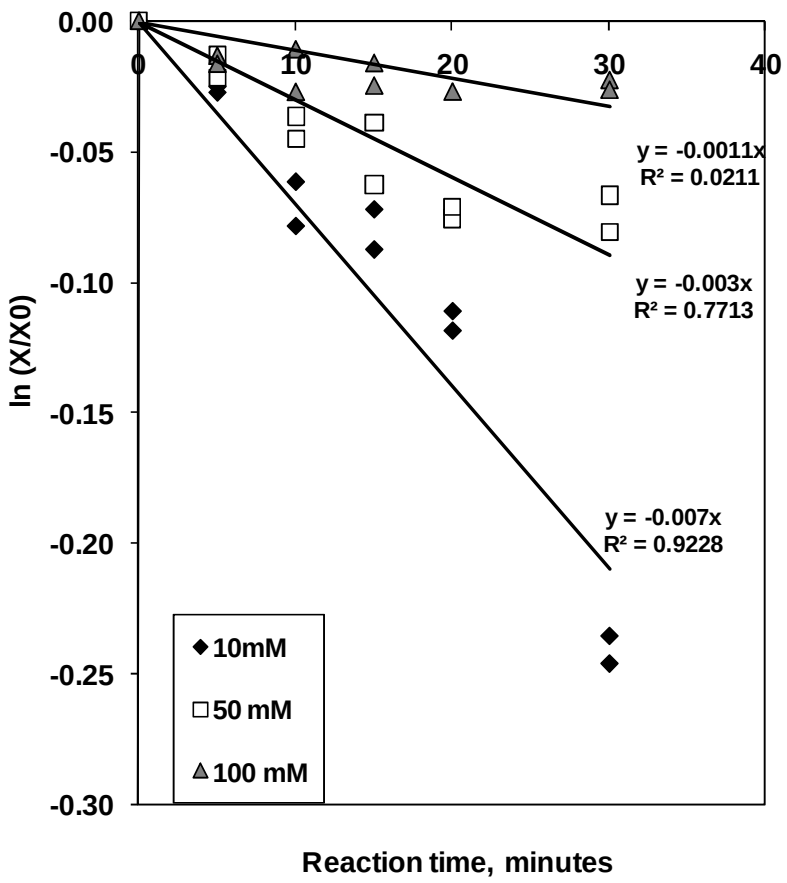


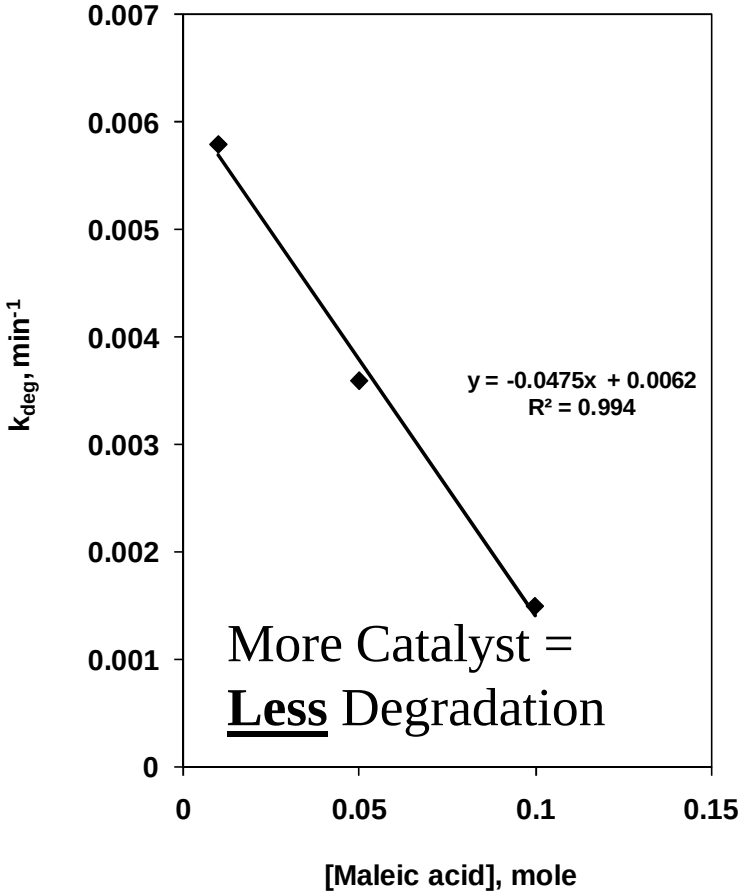


Kinetics solely dependent on $[H^+]$,
indicating **specific** acid catalysis mechanism

MECHANISTIC ANALYSIS

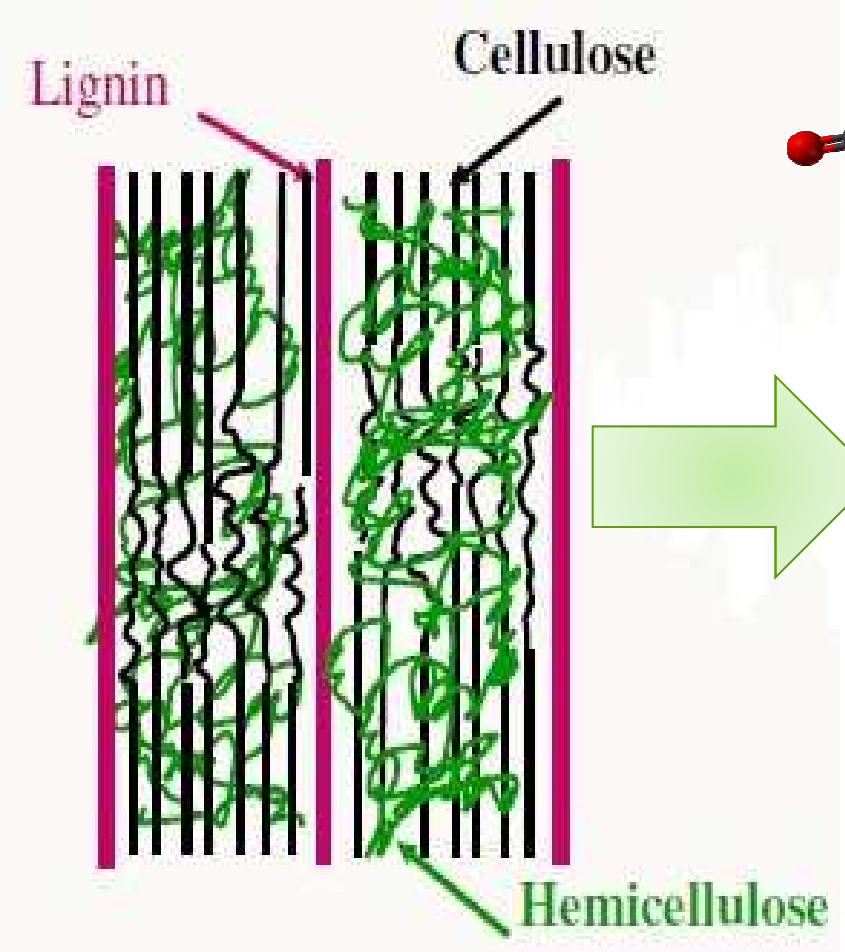


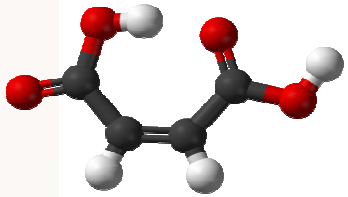




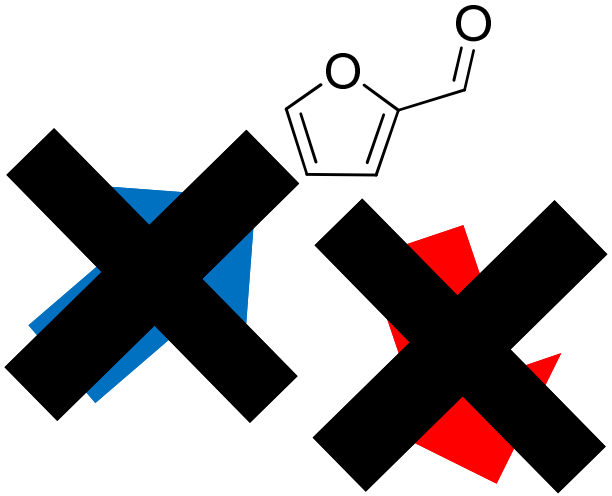
Kinetics **inversely** dependent on [Maleic acid] at constant pH,
Indicating **inverse general** acid catalysis mechanism

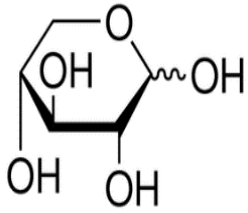
MANY REACTIONS





Furfural





Xylose

Humic “Tar”

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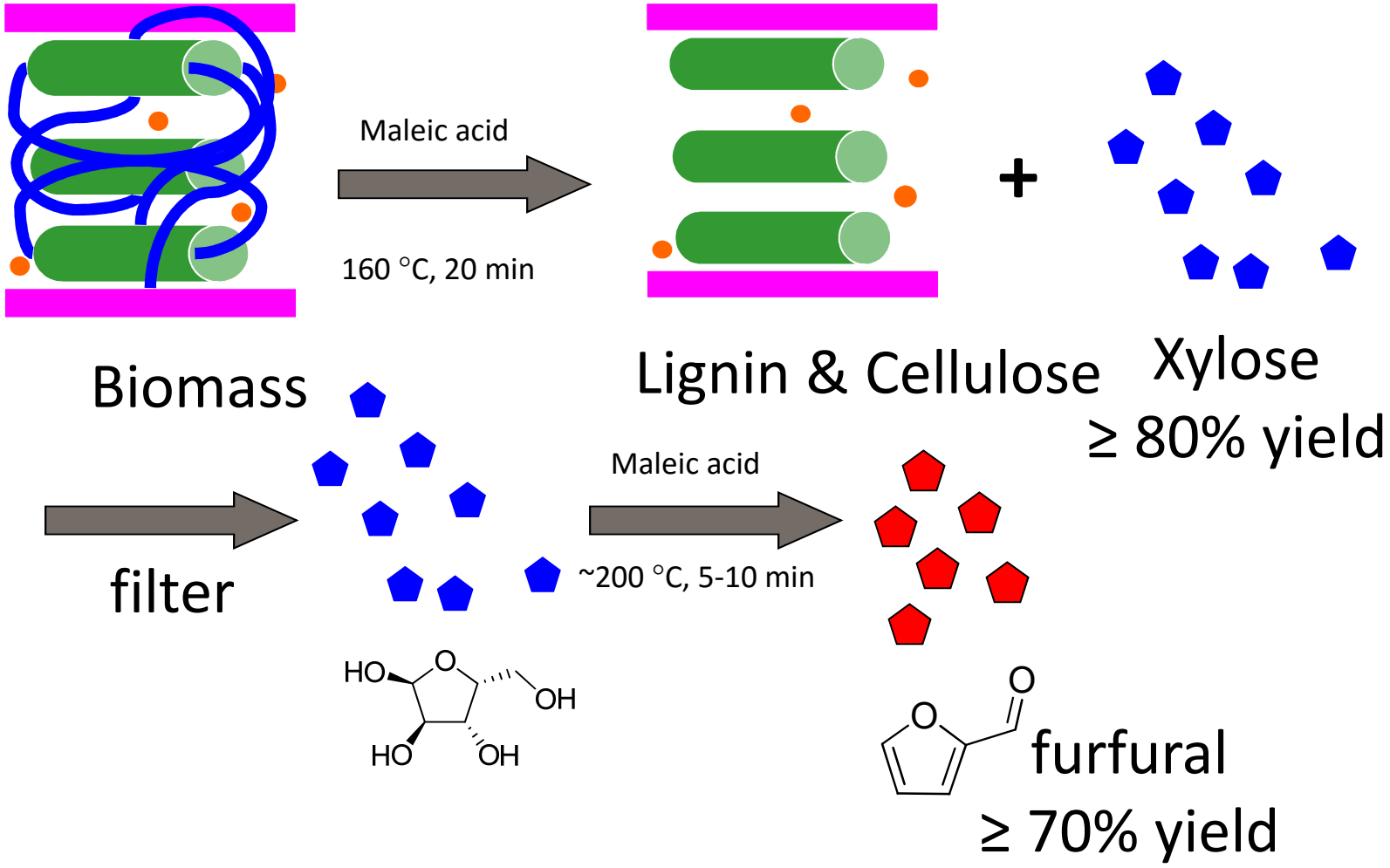
USING TEMPERATURE TO CONTROL TRANSFORMATIONS



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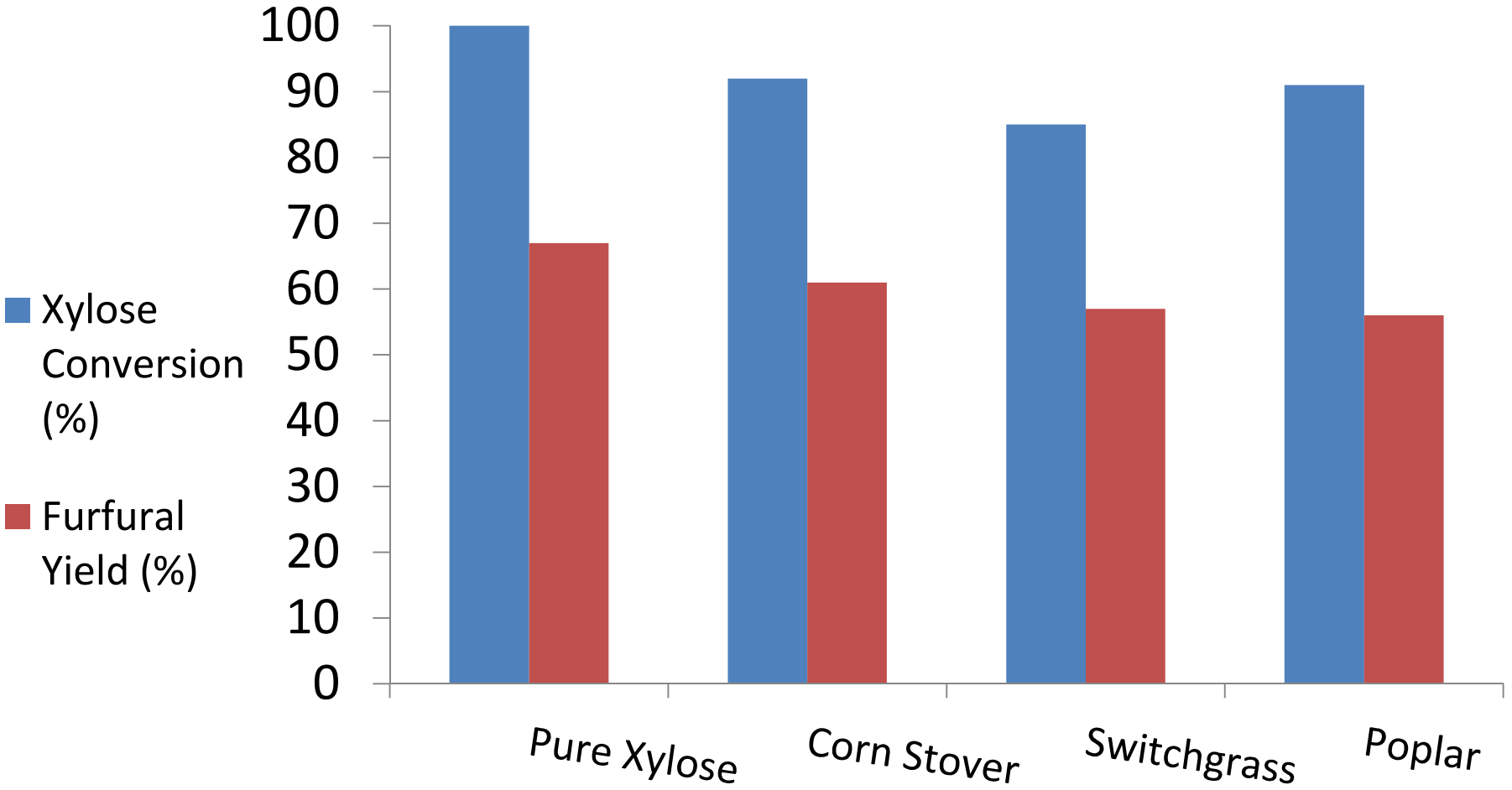
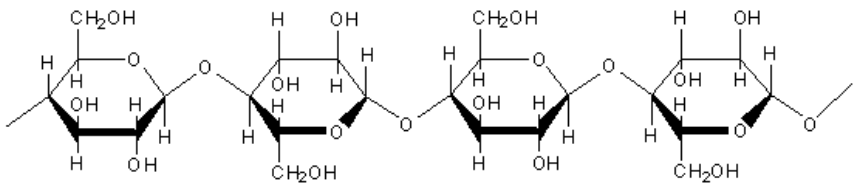
MALEIC ACID ENHANCES FURFURAL YIELD THROUGH IMPROVED SELECTIVITY



Kim et al. *Energy & Fuels*, 2012.

WHAT ABOUT CELLULOSE AND GLUCOSE?

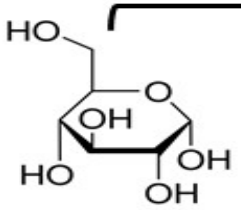


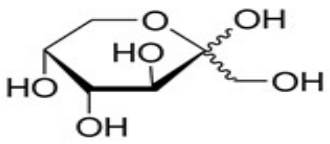
Cellulose

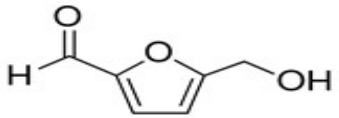
k_{hyd}

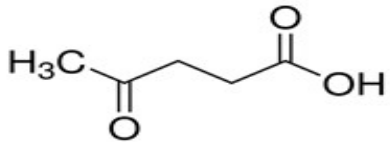
Lewis acid

Brønsted acid

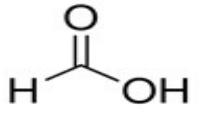








Glucose $\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$ Fructose $\xrightarrow[-3H_2O]{k_2}$ HMF $\xrightarrow[+2H_2O]{k_3}$ Levulinic acid + Formic acid

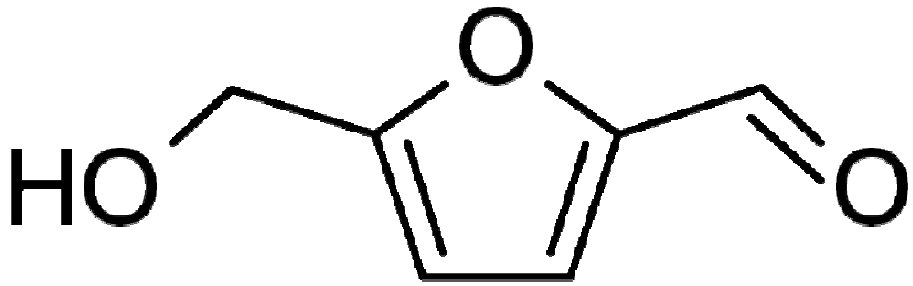


Glucose $\xrightarrow{k_4}$ Humin byproducts

Fructose $\xrightarrow{k_5}$ Humin byproducts

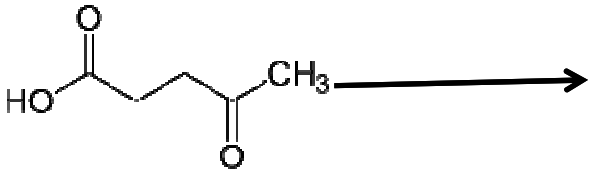
HMF $\xrightarrow{k_6}$ Humin byproducts

HMF AND LEVULINIC ACID ARE VALUABLE

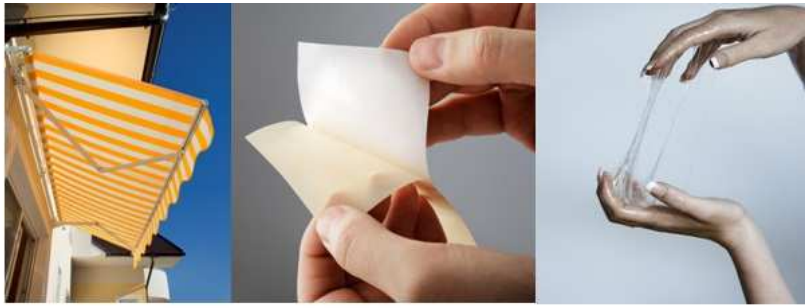


HMF

Polymers, Resins,
Solvents and Fuels



Levulinic Acid



Segetis

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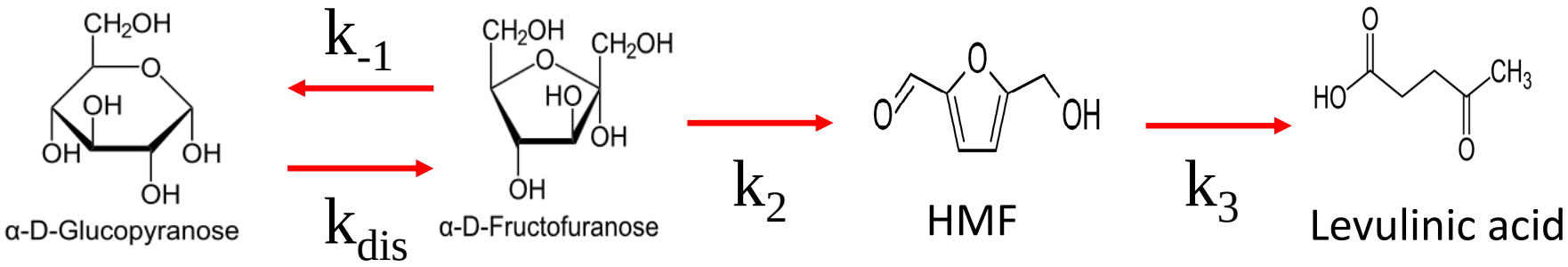
ACTIVATION ENERGY

Ea(kJ/mol)

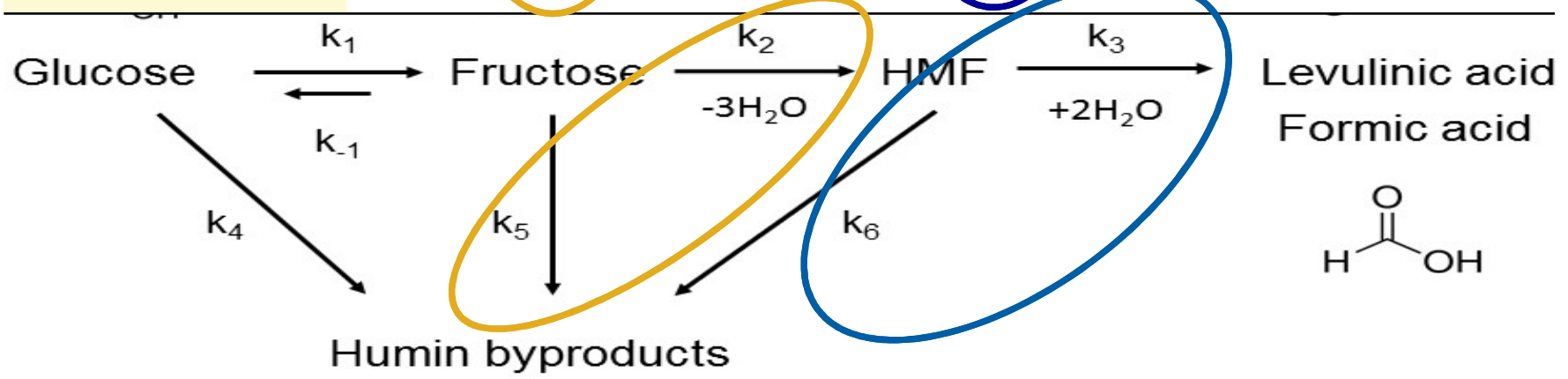
MA+$AlCl_3$	85
HCl+$AlCl_3$	124



MA+$AlCl_3$	95	158	51
HCl+$AlCl_3$	149	128	72

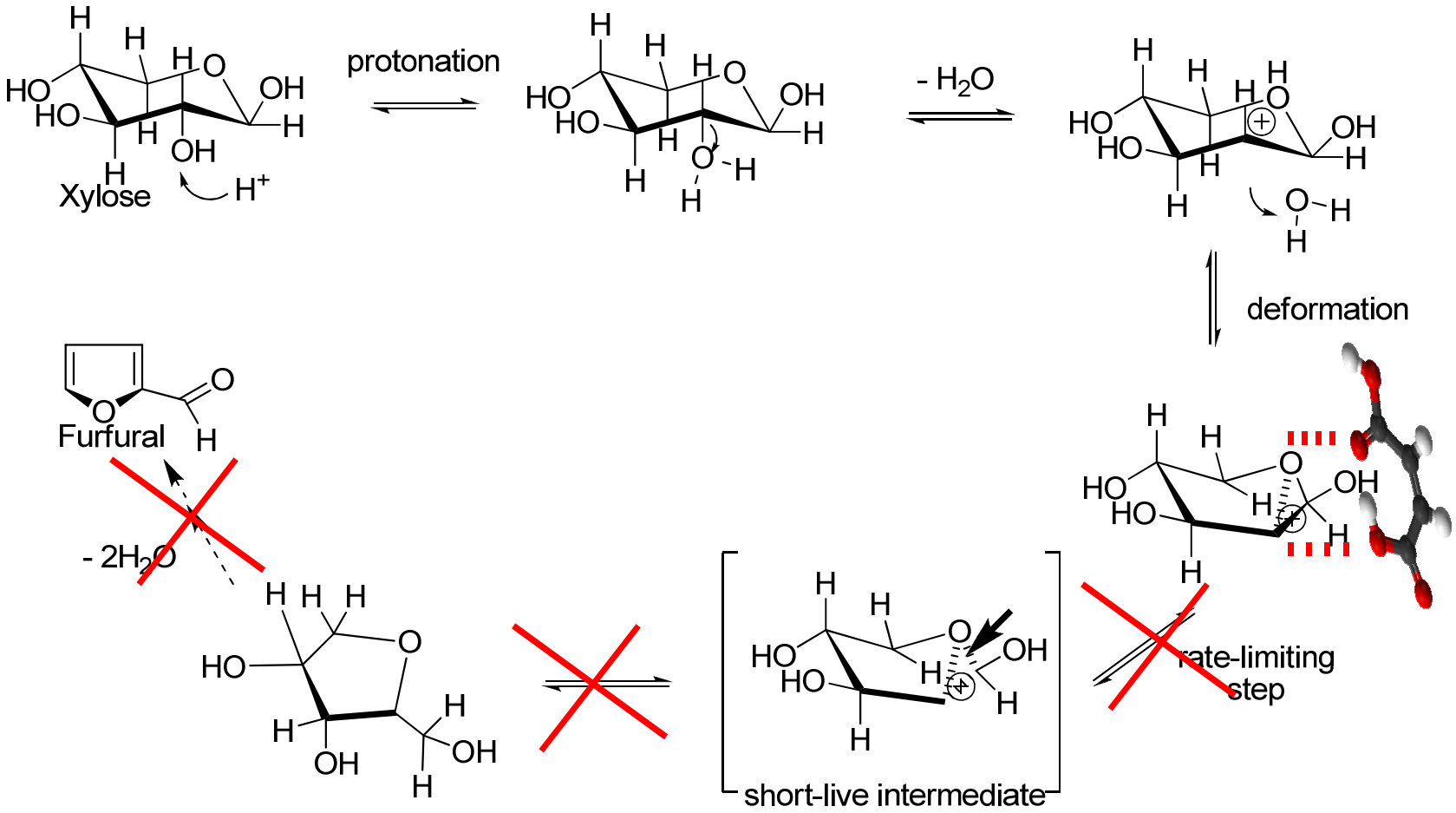
SELECTIVITY FOR HMF AND LA FORMATION

Catalyst	k_2/k_5 Fructose to HMF / Fructose to Humins	k_3/k_6 HMF to LA / HMF to Humins	pH
$AlCl_3$+HCl	2.6	1.0	1.2
$AlCl_3$+MA	11.0	1.8	1.4



Ximing Zhang

INTERACTING CATALYSTS AND SUGARS



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SUMMARY

- Dicarboxylic acid, in enzymes and in chemical catalysts, can direct chemical reactions toward desired products.

- Connecting chemistry, biology, and engineering process technology are needed to make the necessary breakthroughs to realize the bio-economy

CONCLUDING REMARKS

- Nature has a lot to teach us about transforming matter at the atomic scale.
- Agriculture is holds great potential for providing food, feed, fiber, fuels, and chemicals.
- There is much work left to do to realize this potential!


Thank you