



Use of Chemical Catalysts in Adding Value to DDGS

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- Iowa State University



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Use of Chemical Catalysts

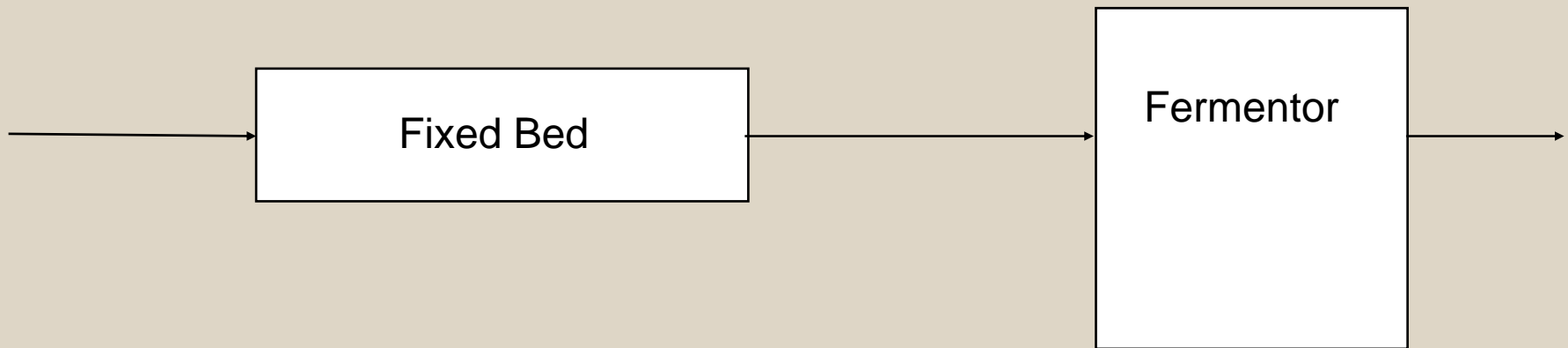
- Hydrolysis of oligosaccharides released by hydrothermal treatment.
- Transesterification of oil removed from DDG.



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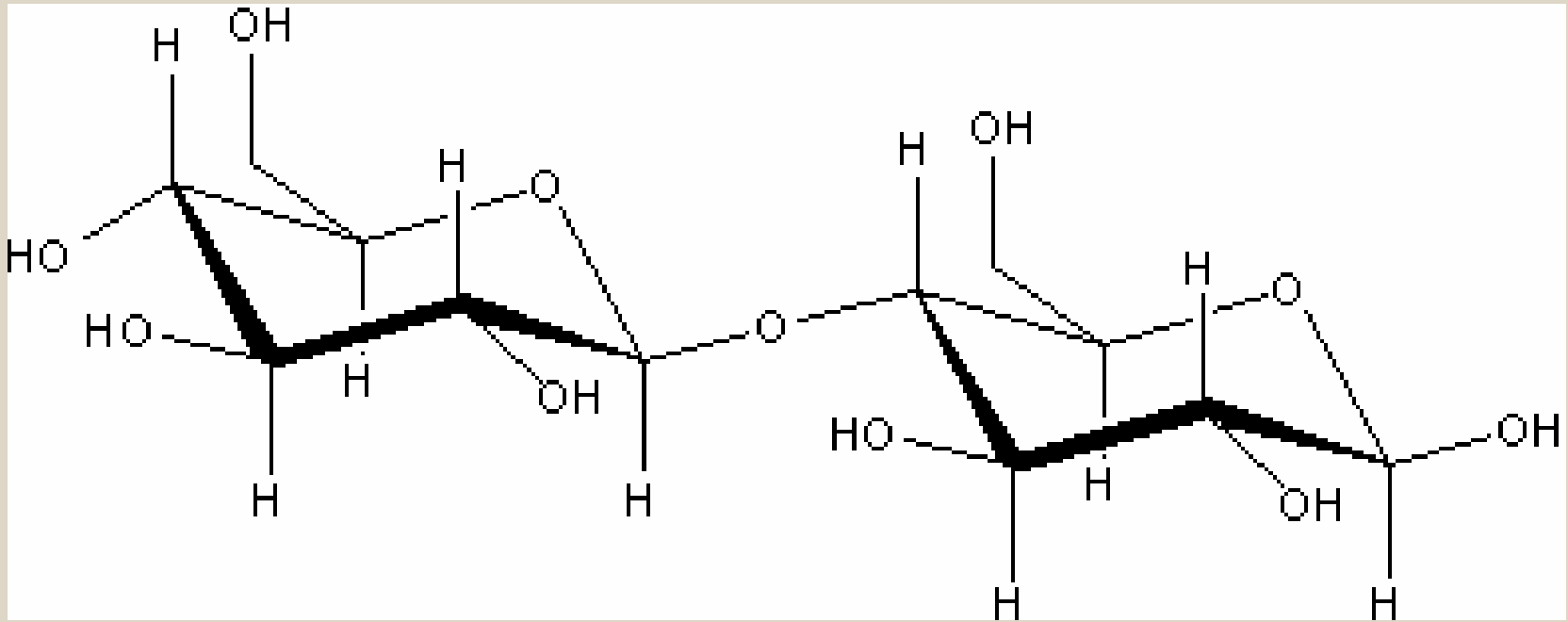
Oligosaccharide Hydrolysis



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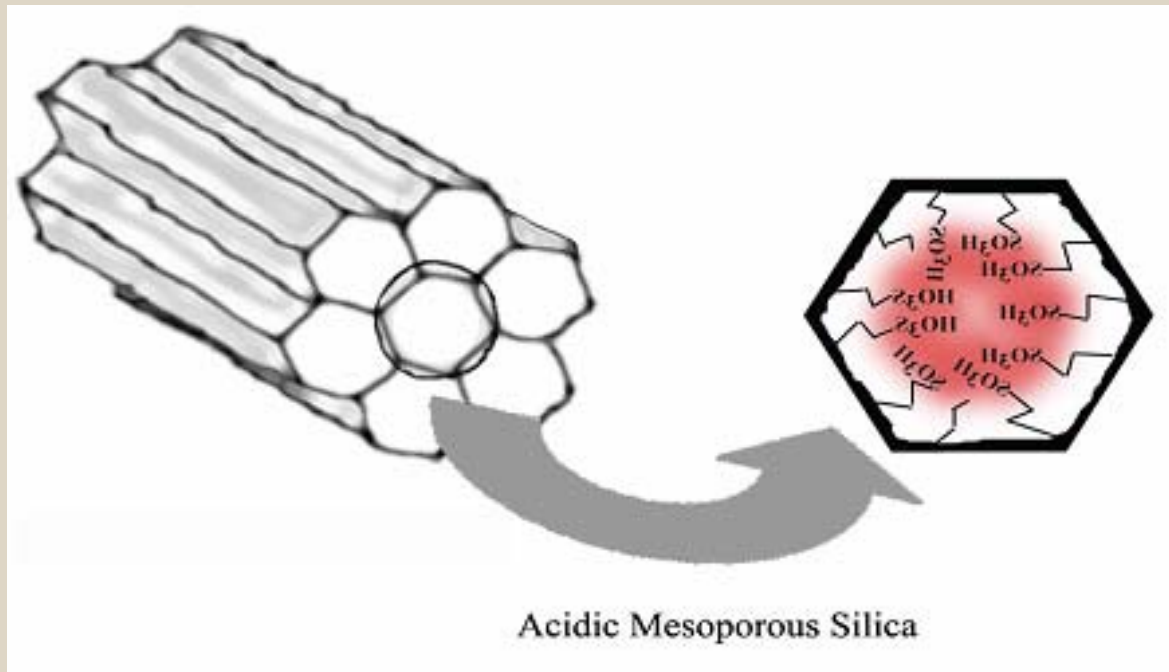
Cellobiose Hydrolysis



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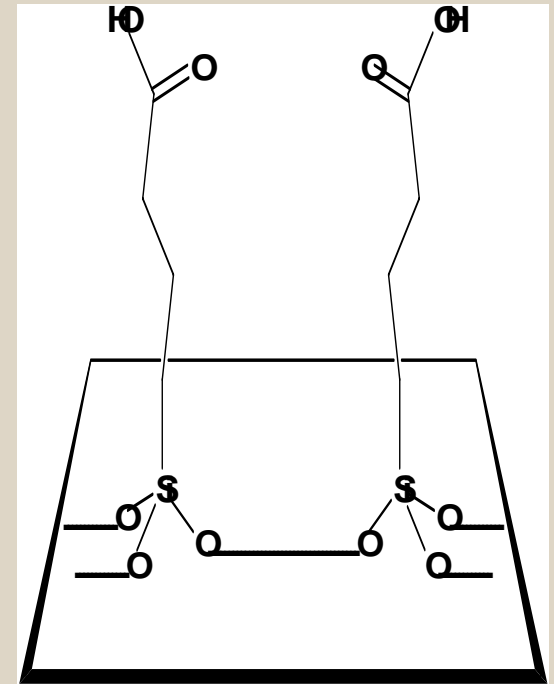
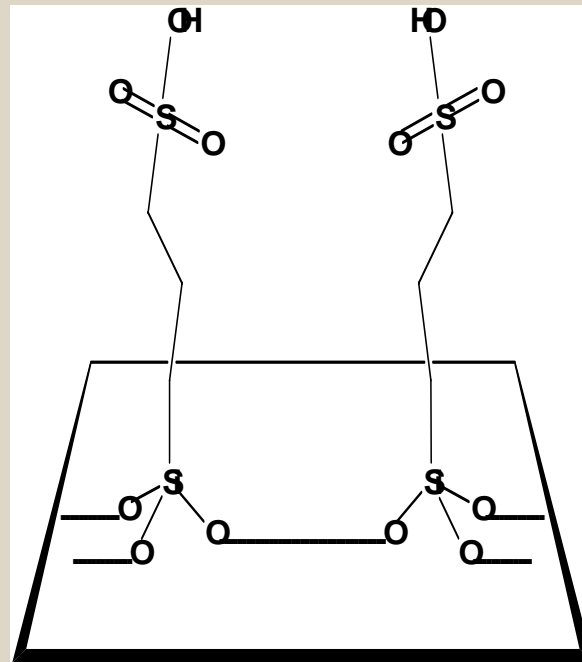
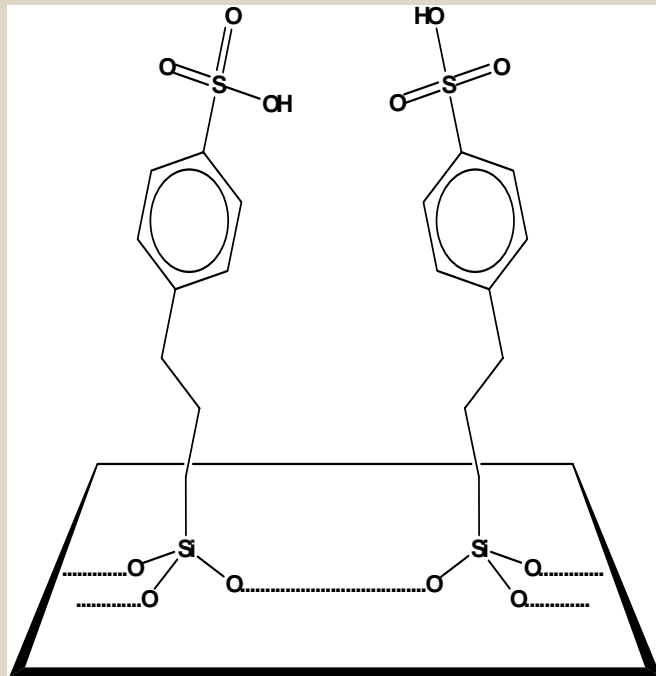
Organic-Inorganic Hybrid Mesoporous Catalysts



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Organosulfonic Acid Groups



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Chemical Properties

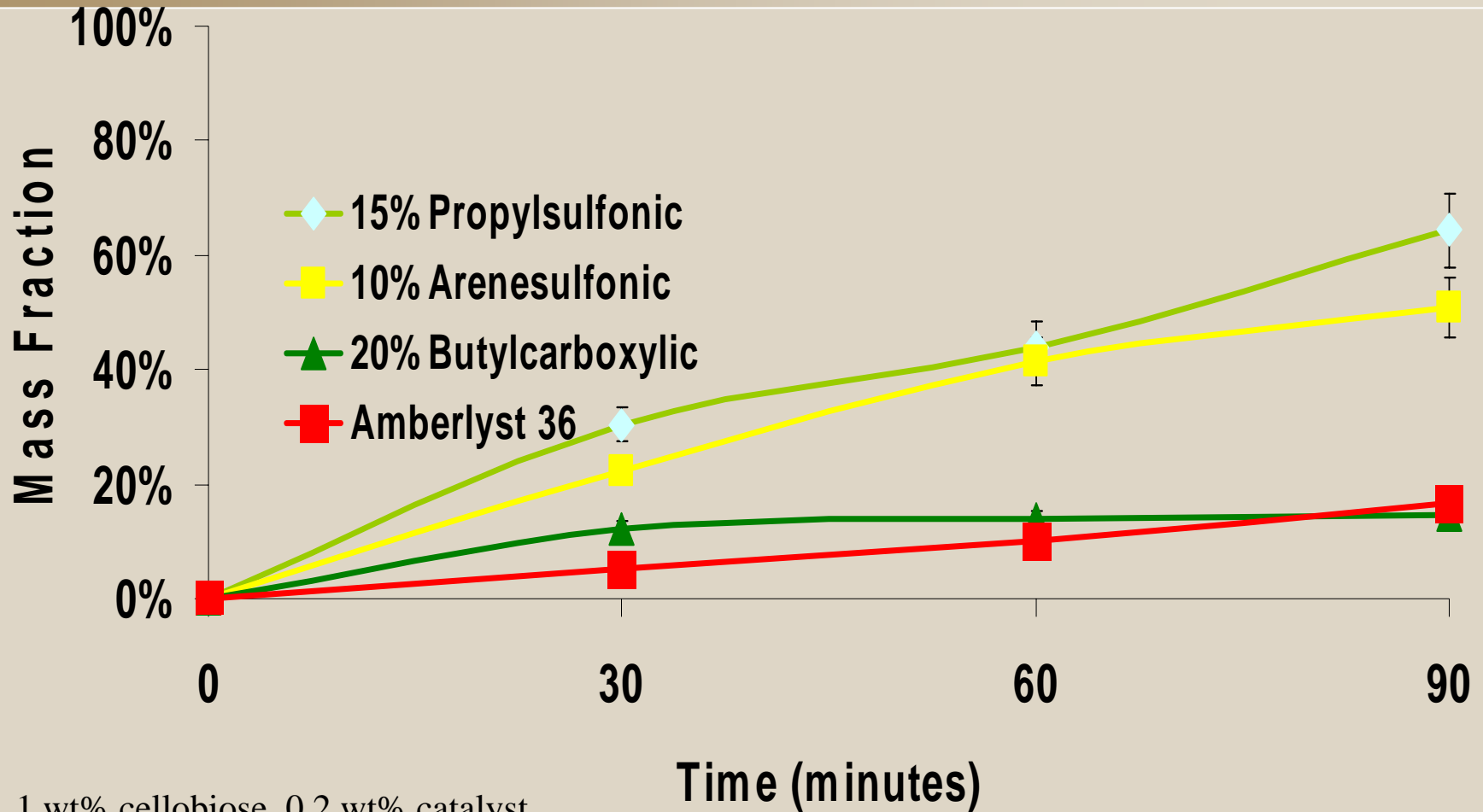
Catalyst	pH of Solution	pKa (by Gran Plot)	Carbon%	Sulfur%	Nitrogen%
7.5% Propylsulfonic	3.2	2.9	7.7	2.3	
15% Propylsulfonic	2.8	2.7	7.7	4.6	
10% Arenesulfonic	3.0	2.8	10.9	2.5	
20% Butylcarboxylic	4.9	4.6	14.0		0.4



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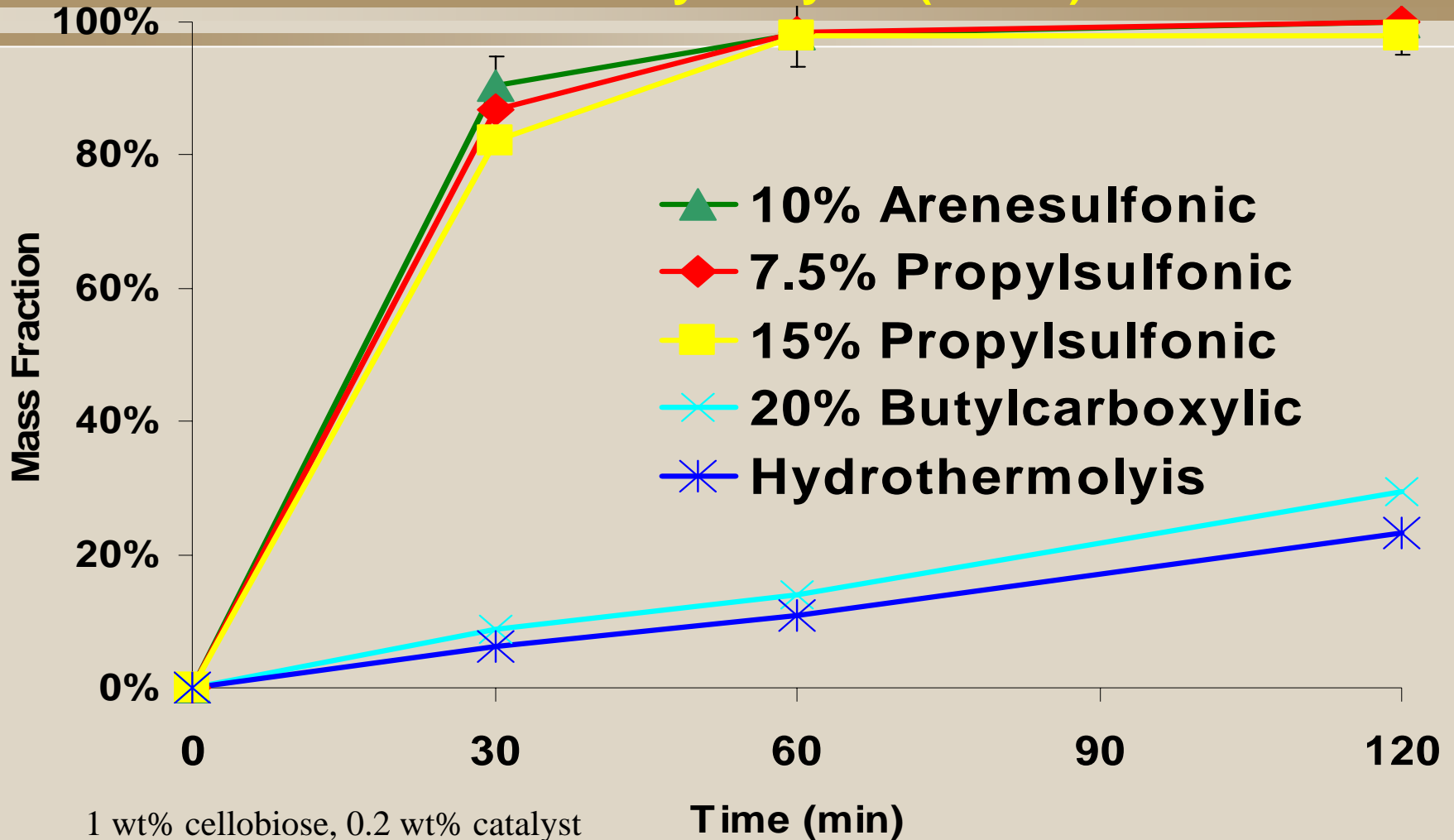
Cellobiose Hydrolysis (145 C)



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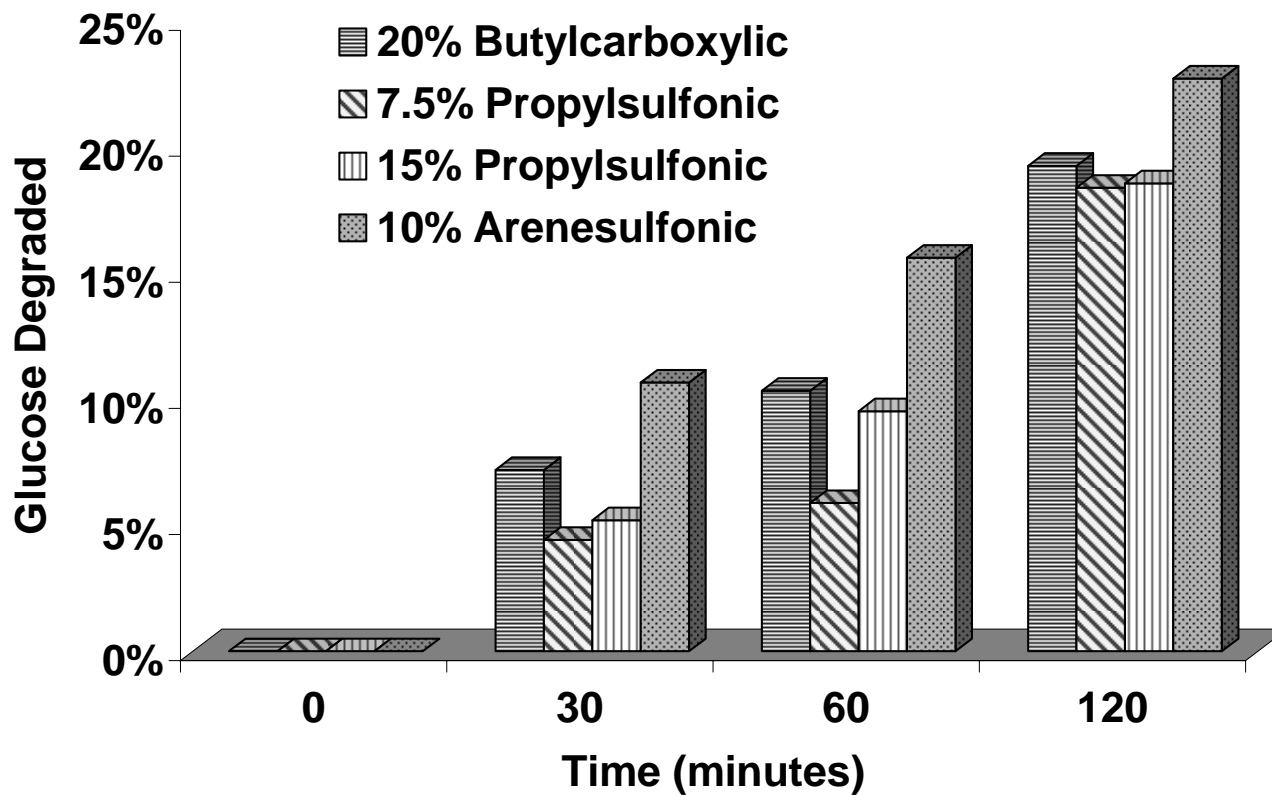
Cellobiose Hydrolysis (175 C)



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Glucose Degradation



1 wt% glucose,
0.2 wt% catalyst,
175°C



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Cellulose Hydrolysis Activation Energy

Catalyst	Activation Energy (kJ/gmol)
7.5% Propylsulfonic Acid	133 +/- 13
15% Propylsulfonic Acid	113 +/- 17
10% Arenesulfonic Acid	137 +/- 20
20% Butylcarboxylic Acid	118 +/- 31
Sulfuric Acid*	110 +/- 29.6
Maleic Acid*	114 +/- 9.3

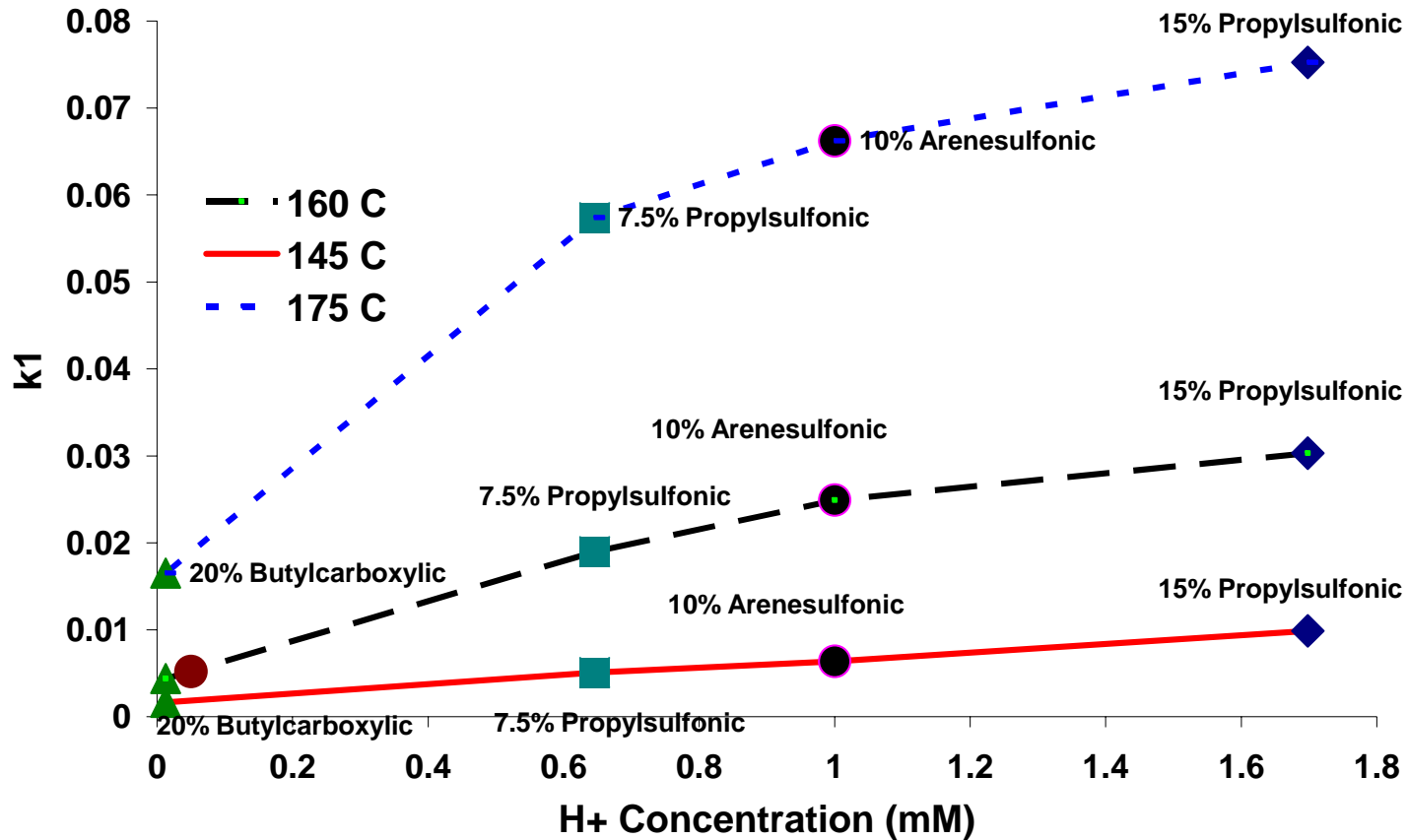
*N. S. Mosier, C. M. Ladisch, M. R. Ladisch, 2002, *Biotechnol. Bioeng.*, 79:17



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Hydrolysis Rate Constants



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Glucose Degradation Activation Energy

Catalyst	Activation Energy (kJ/gmol)
7.5% Propylsulfonic	67+/- 6
15% Propylsulfonic	65+/- 18
10% Arenesulfonic	73+/- 11
20% Butylcarboxylic	76+/- 20
Sulfuric*	118 +/- 37.5
Maleic*	72.6 +/- 22.5

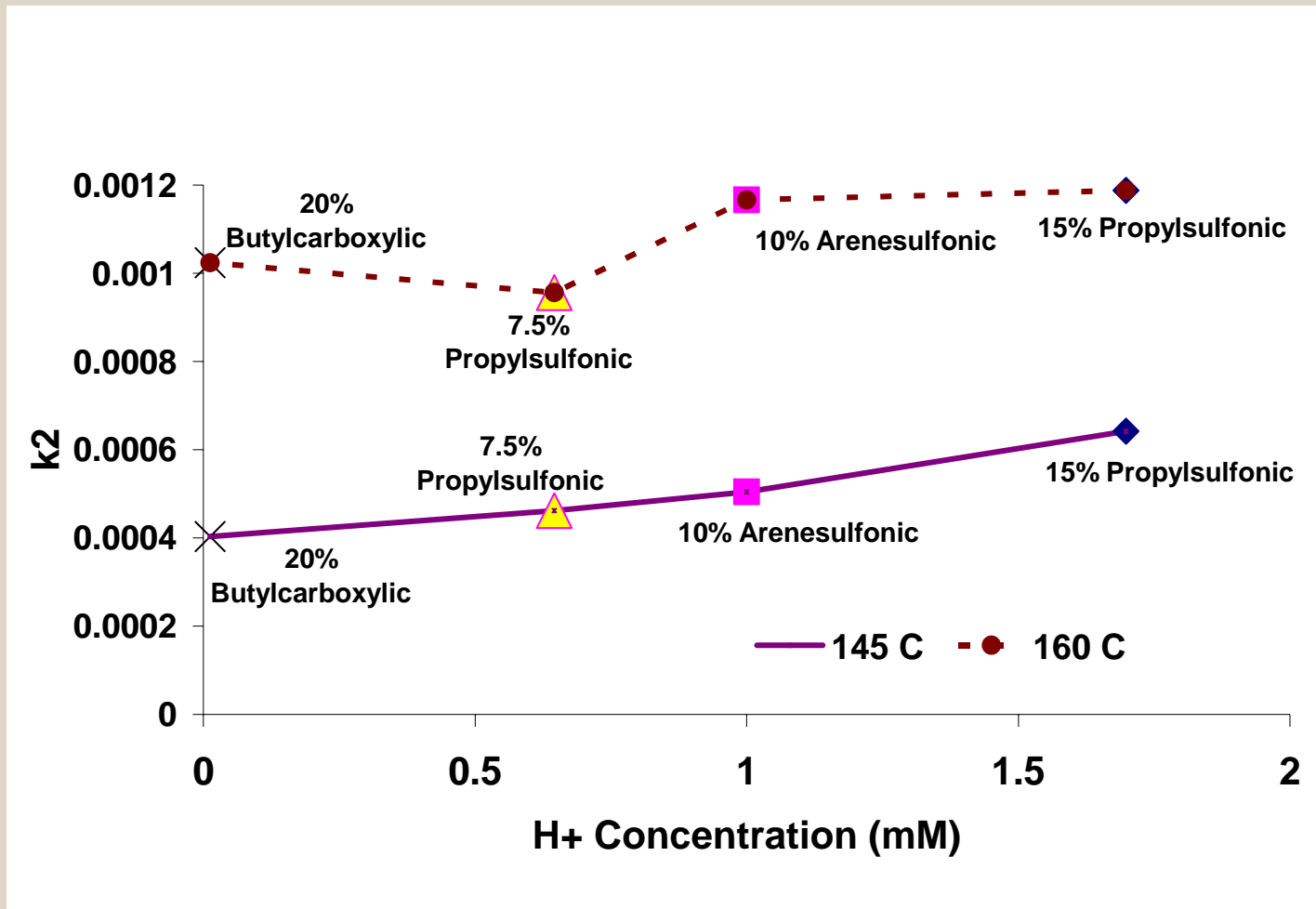
*N. S. Mosier, C. M. Ladisch, M. R. Ladisch, 2002, *Biotechnol. Bioeng.*, 79:17



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Glucose Degradation Rate Constants



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Impurity Effects on Catalysts

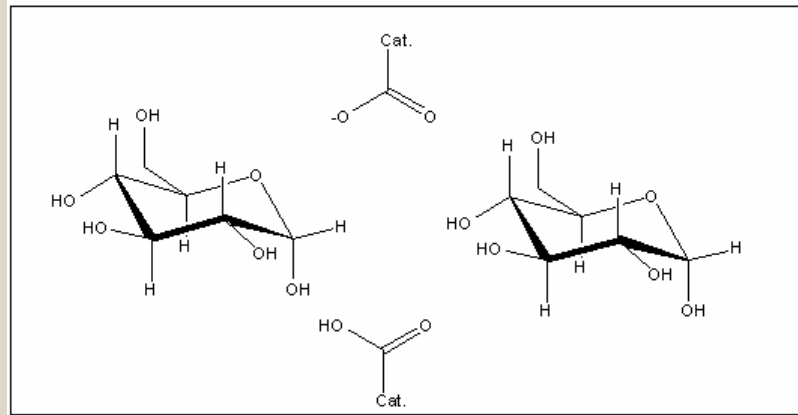
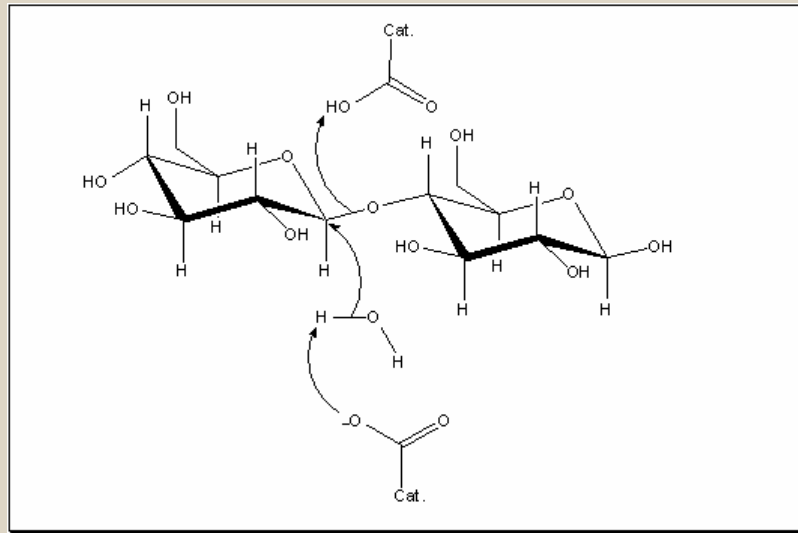
- Model system studies (10/1 cellobiose/zein)
 - Significant deactivation.
 - Pretreatment with activated silica improves activity.
- Hydrolysis of hydrothermally treated liquid
 - Conversion of crude liquid.
 - Conversion of pretreated liquid.



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Enzymatic Hydrolysis



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Future Catalyst Work

- Incorporation of acid/base catalytic pair
 - Random butylcarboxylic acid/aminopropyl placement.
 - Spatially controlled placement.
 - Buffered catalyst system.
- Hydronium ion mobility effect.
- Characterization of degradation kinetics.



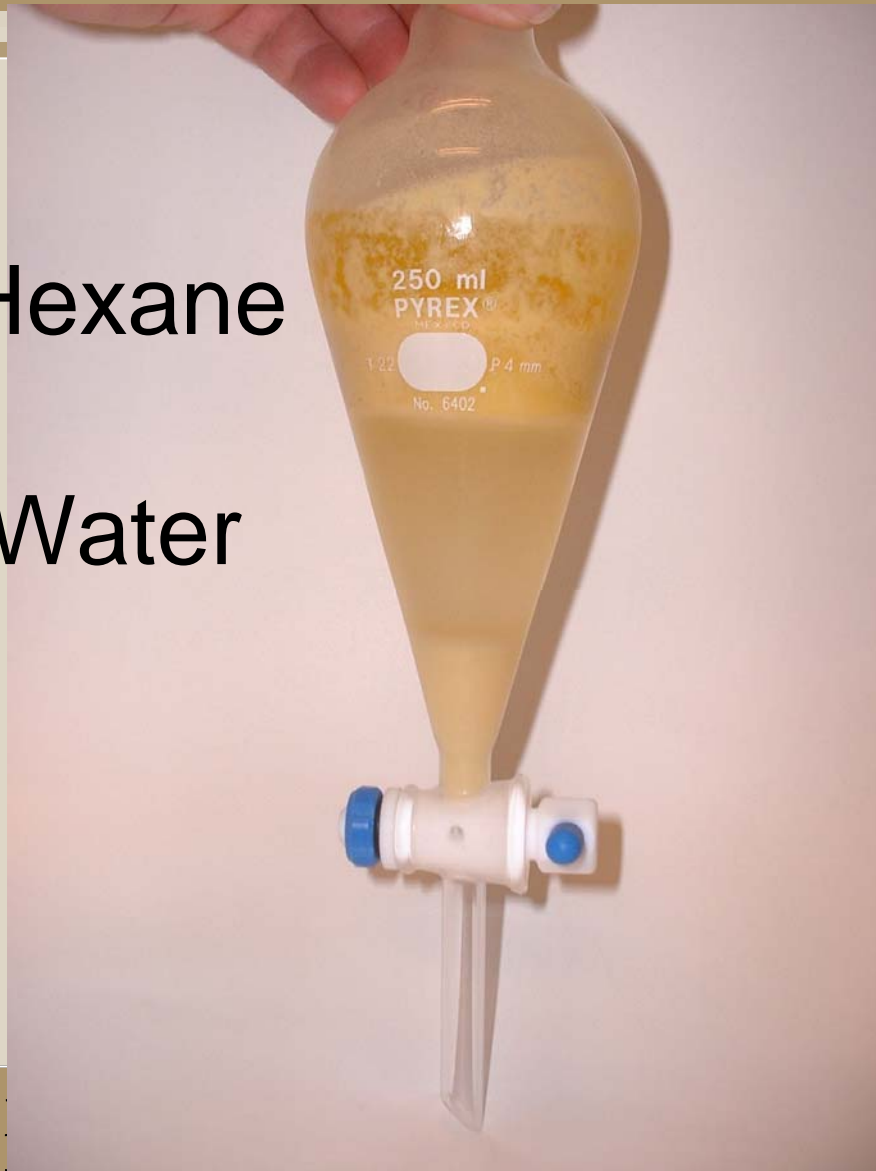
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Stillage – Oil and Protein

Hexane

Water



100 mL
stillage +

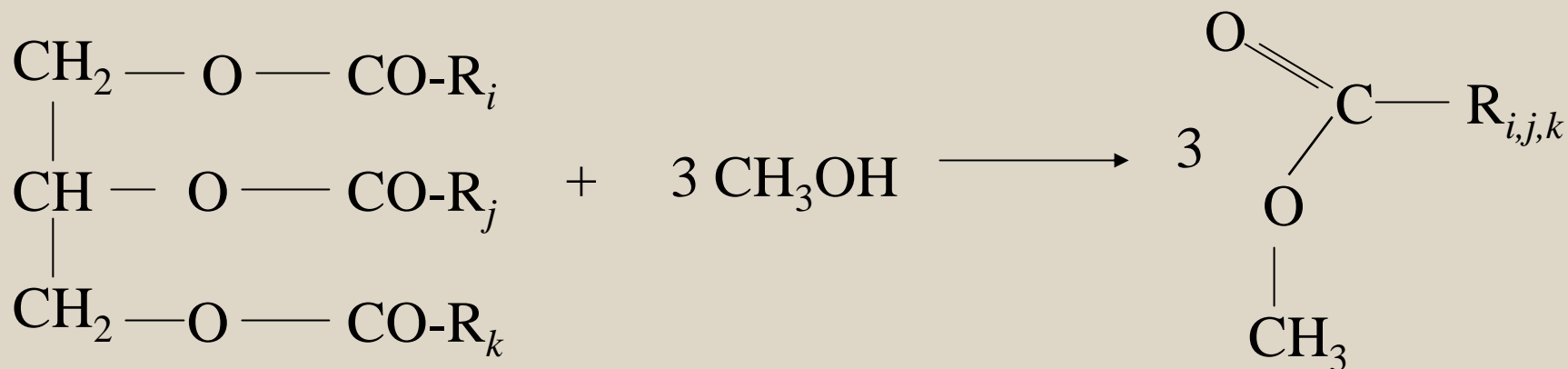
100 mL
hexane



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Transesterification Reaction



Triglyceride

Methyl Ester

+

Glycerol

Catalyst: Basic



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Transesterification of DDG Oil

- Model corn oil conversion
 - Ethanol vs. methanol kinetics.
- DDG oil conversion
 - Ethanol vs. methanol rates.
 - Crude vs. pretreated.
- Solid transesterification catalyst testing.



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