



Chemical Catalysts for Adding Value to Distillers Grains

Brent Shanks

Jason Bootsma, Janice Velazquez

Chemical & Biological Engineering Department
Iowa State University

Acknowledgements: Purdue University

USDOE Award Number DE-FG36-04GO14220

Corn Refiners' Association



**Midwest Consortium for Biobased
Products & Bioenergy**



Overview

- Catalytic hydrolysis
 - Sugar degradation
 - Hydrolysis of hydrothermally pretreated material

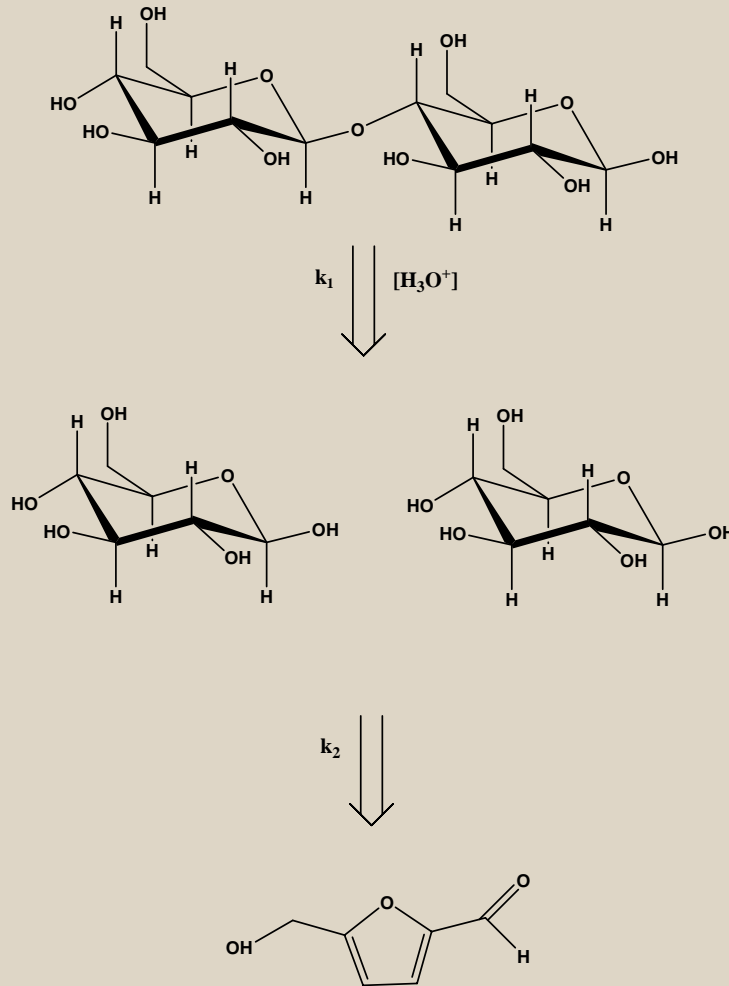
- Corn oil transesterification



**Midwest Consortium for Biobased
Products & Bioenergy**



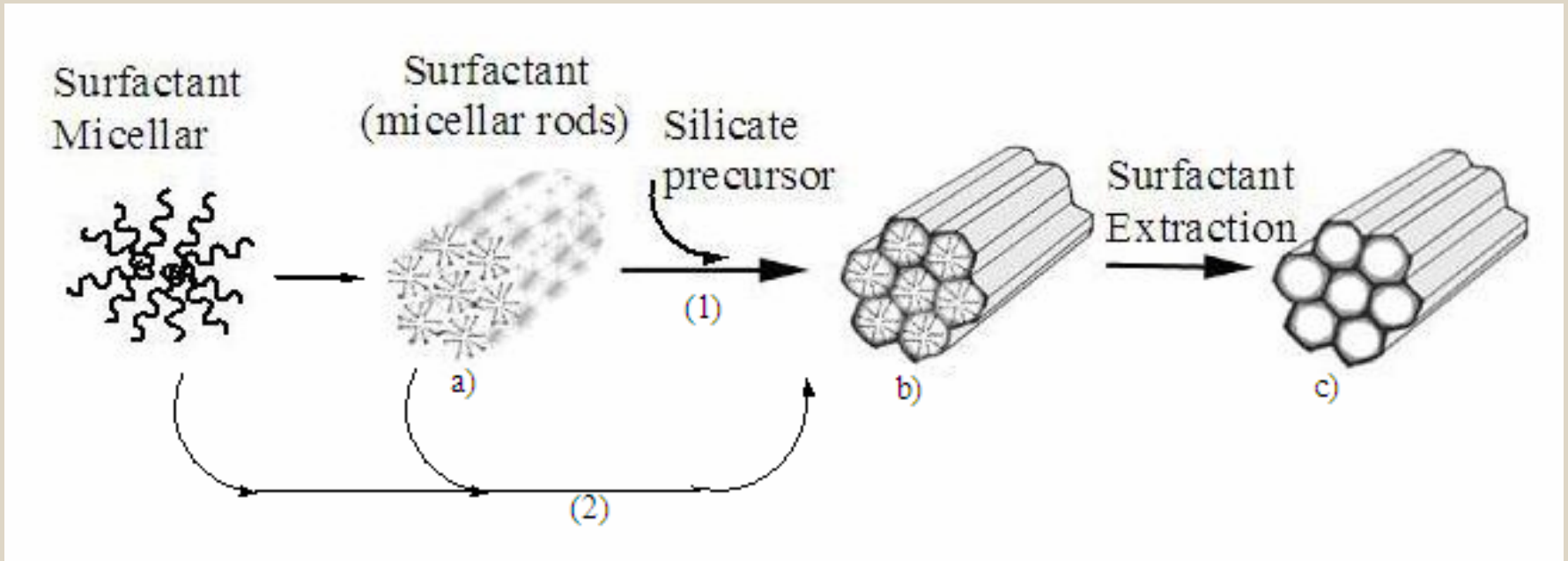
Oligosaccharide Hydrolysis



Midwest Consortium for Biobased
Products & Bioenergy



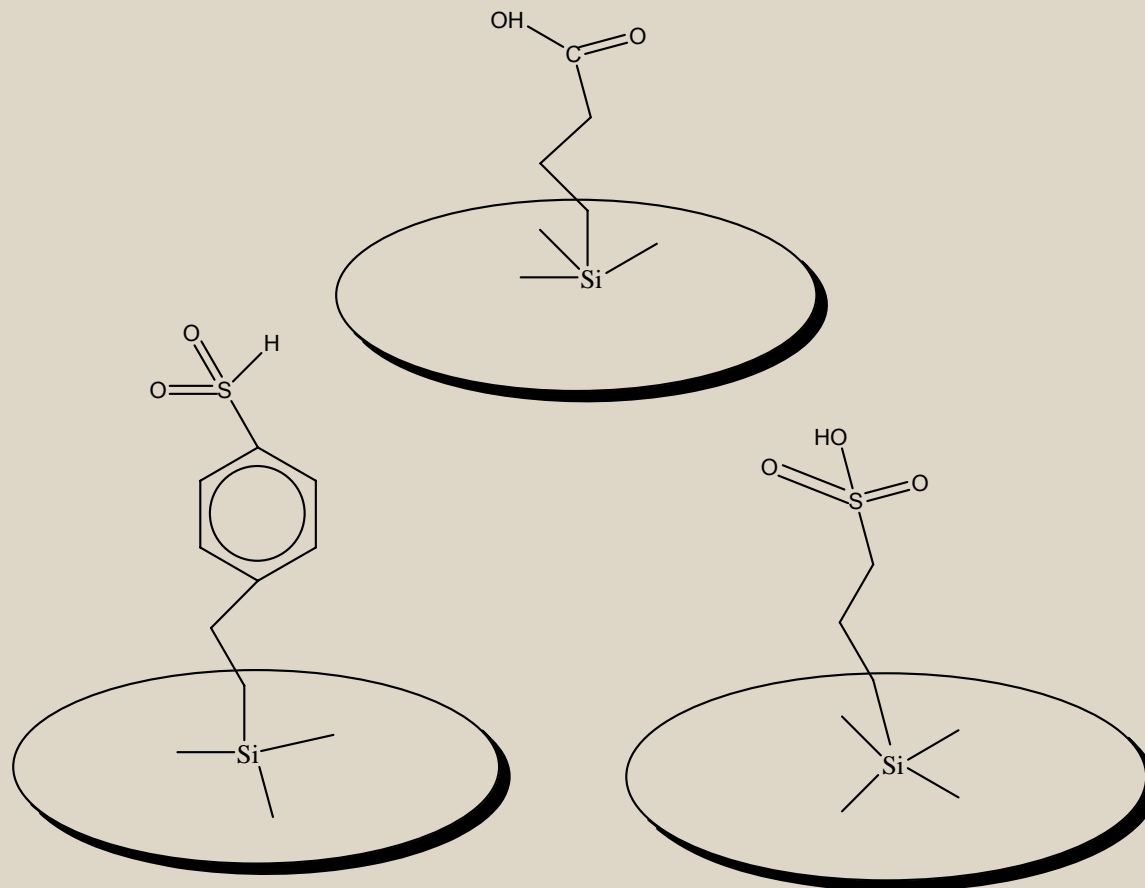
Mesoporous Scaffolds



Midwest Consortium for Biobased
Products & Bioenergy



Acidic Groups



**Midwest Consortium for Biobased
Products & Bioenergy**



Cellulose Hydrolysis Activation Energy

Catalyst	Activation Energy (kJ/mol)
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



Midwest Consortium for Biobased
Products & Bioenergy



Glucose Degradation Activation Energy

Catalyst	Activation Energy (kJ/mol)
7.5% propylsulfonic acid	67 +/- 6
15% propylsulfonic acid	65 +/- 18
10% arenesulfonic acid	73 +/- 11
20% butylcarboxylic acid	76 +/- 20
sulfuric acid*	118 +/- 37.5
maleic acid*	72.6 +/- 22.5

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



Midwest Consortium for Biobased
Products & Bioenergy



Xylose Degradation Activation Energy

Catalyst	Activation Energy (kJ/mol)
15% propylsulfonic acid	150 +/- 4
10% ethylphosphonic acid	151 +/- 16
20% butylcarboxylic acid	130 +/- 14
sulfuric acid*	134
maleic acid**	203
hydrothermolysis***	123

*N. Bhandari, et al., 1984, *Biotechnol. Bioeng.*, 26:320

**Y. Lu, N.S. Mosier, 2007, *Biotechnol. Prog.*, 23:116

***D. Nabarlantz, et al., 2004, *Ind. Eng. Chem. Res.*, 43:4124



**Midwest Consortium for Biobased
Products & Bioenergy**



Arabinose Degradation Activation Energy

Catalyst	Activation Energy (kJ/gmol)
15% propylsulfonic acid	150 +/- 19
10% ethylphosphonic acid	104 +/- 23
20% butylcarboxylic acid	111 +/- 27
hydrothermolysis	125

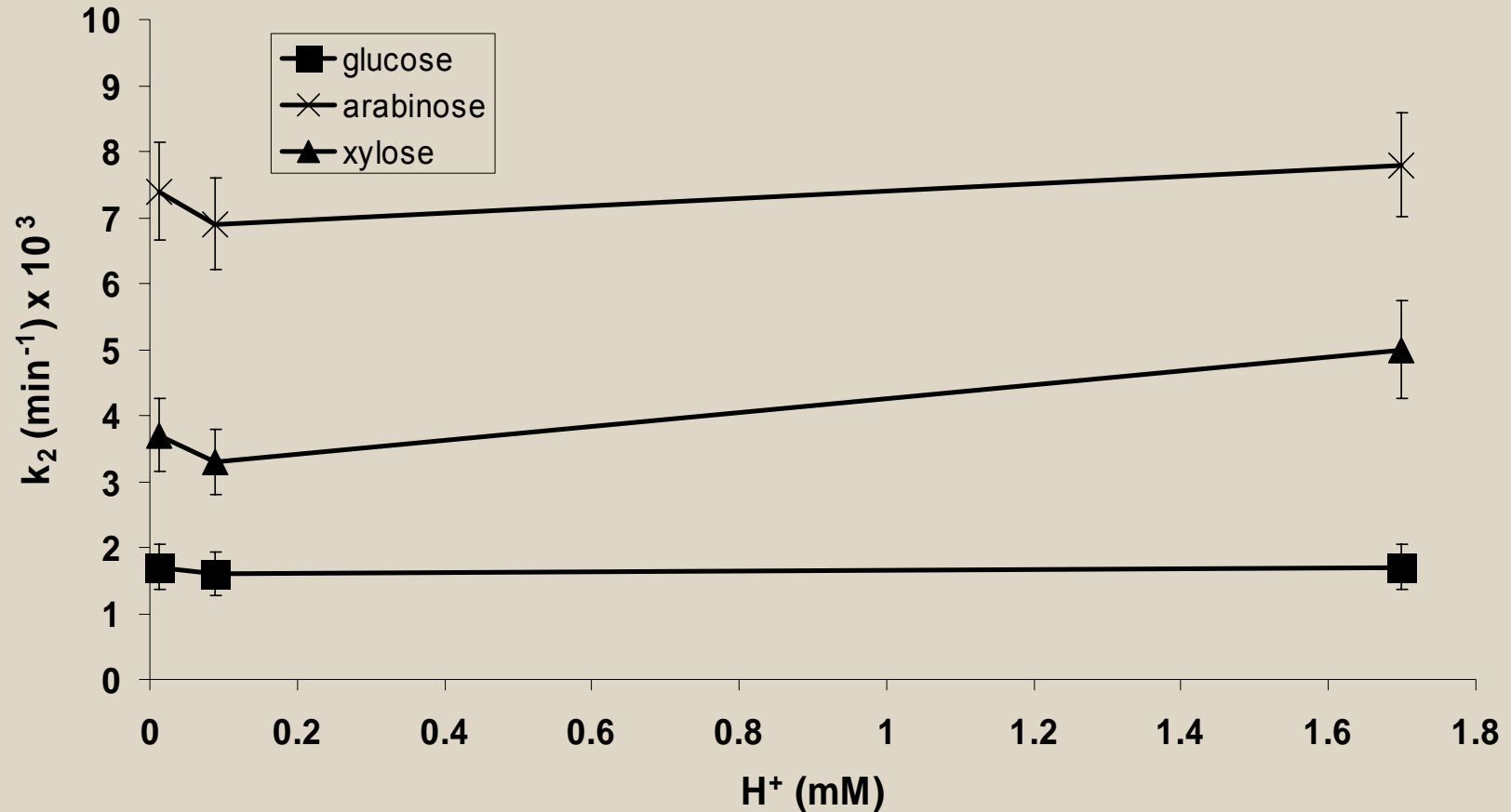
*D. Nabarlantz, et al., 2004, *Ind. Eng. Chem. Res.*, 43:4124



Midwest Consortium for Biobased
Products & Bioenergy



Degradation Rate Constants (175°C)



Midwest Consortium for Biobased
Products & Bioenergy



Hydrothermal Pretreatment (15% solids)*

	Pretreated	Digested (Purdue)	Digested (ISU)
Glucose	0.10%	1.51%	1.98%
Xylose	0.31%	1.01%	0.88%
Arabinose	0.31%	0.69%	0.55%

* Rick Hendrickson – Purdue University



**Midwest Consortium for Biobased
Products & Bioenergy**



Reaction Conditions

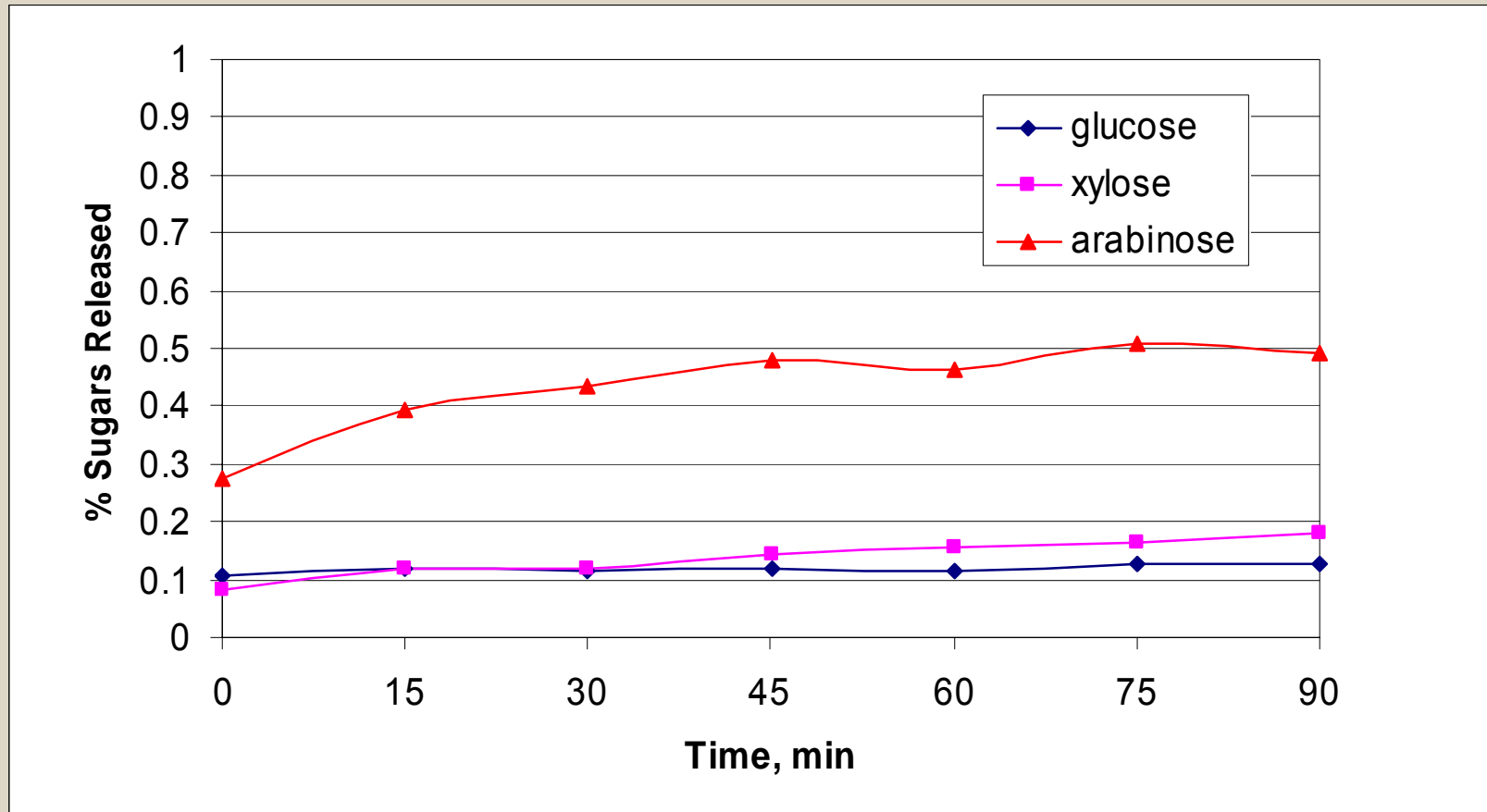
- 10 wt% of the pretreated material
 - Injected at reaction temperature
- Catalyst
 - 10% propylsulfonic acid functionalized silica
 - Added at 0.2 wt% of the solution
- Temperatures: 145, 160, 175°C



Midwest Consortium for Biobased
Products & Bioenergy



Catalytic Hydrolysis (145°C)



Midwest Consortium for Biobased
Products & Bioenergy



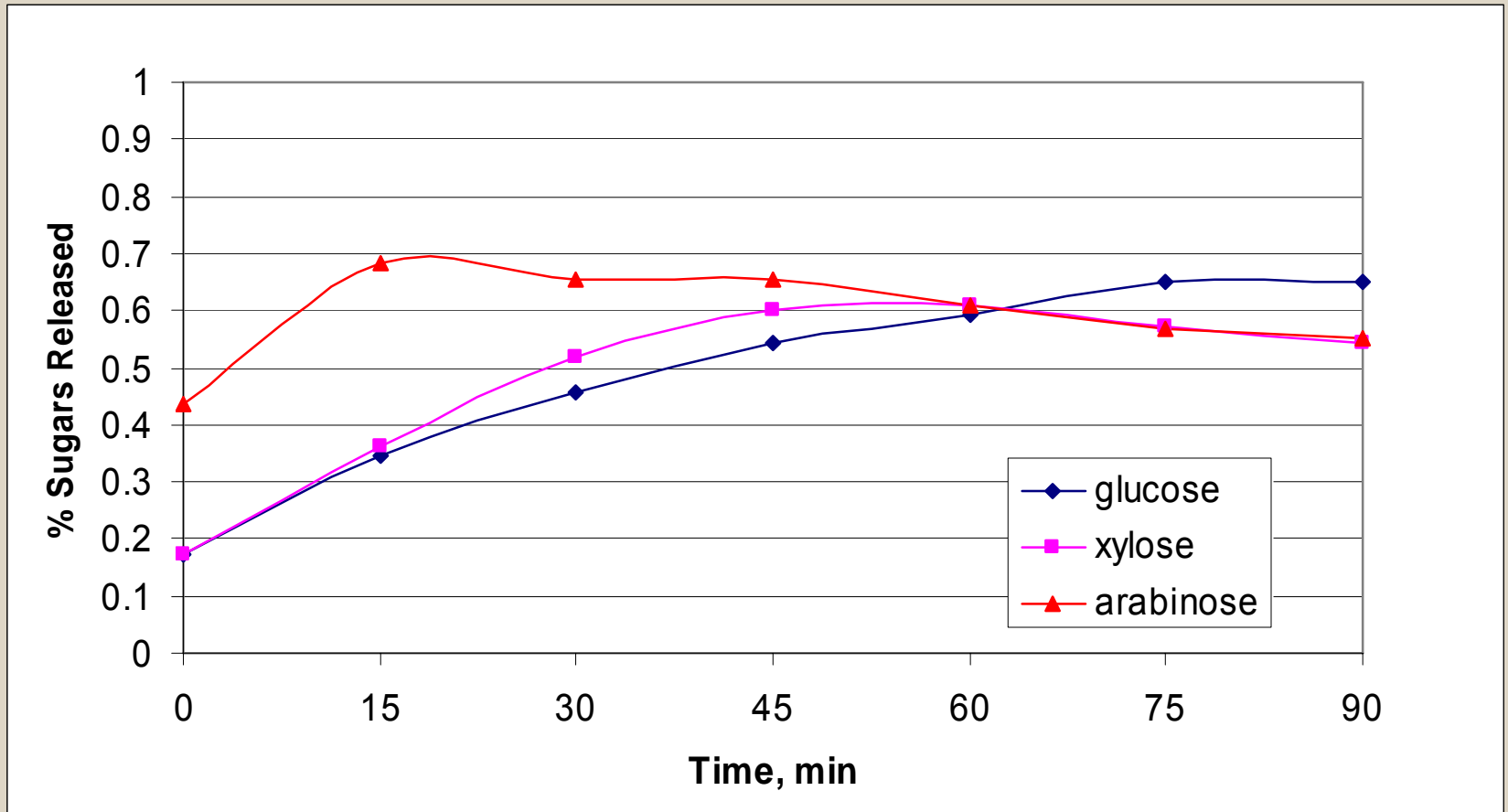
Catalytic Hydrolysis (160°C)



Midwest Consortium for Biobased
Products & Bioenergy



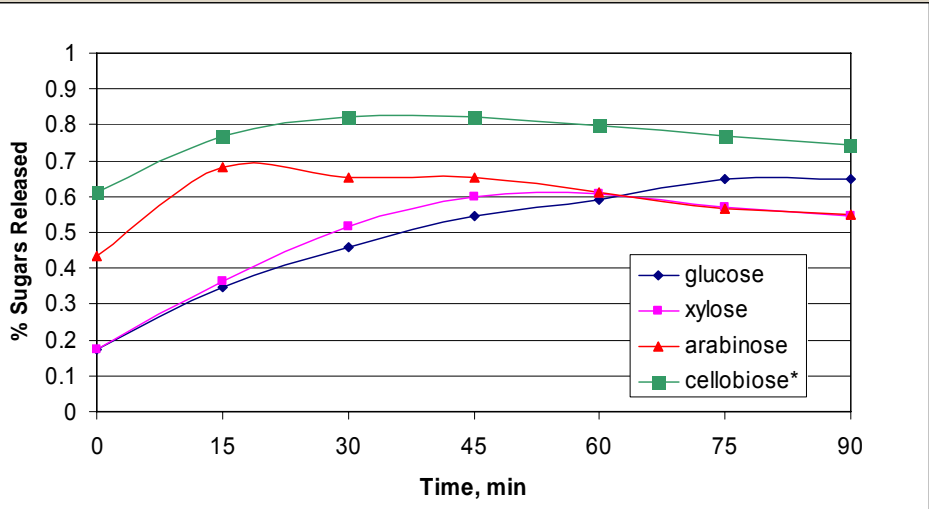
Catalytic Hydrolysis (175°C)



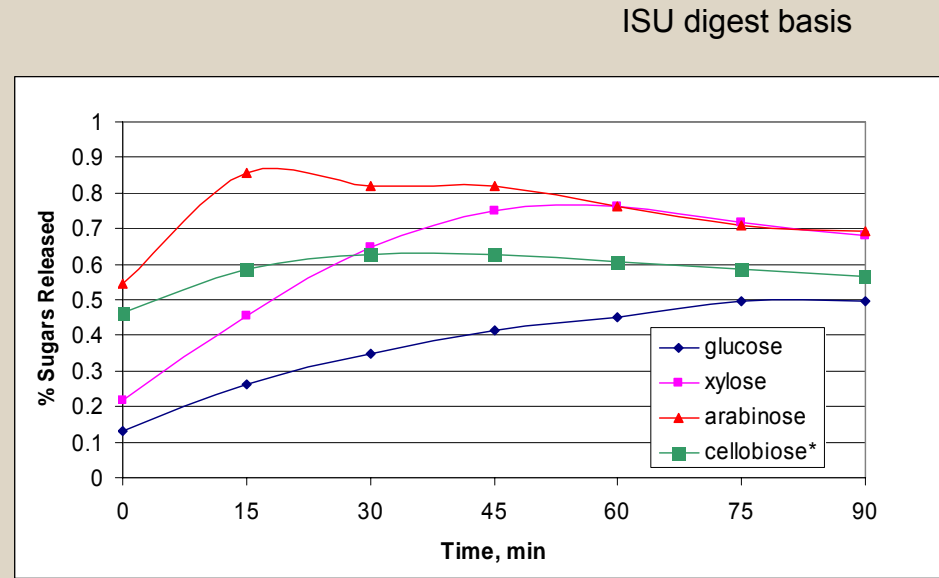
Midwest Consortium for Biobased
Products & Bioenergy



Catalytic Hydrolysis (175°C)



Purdue digest basis



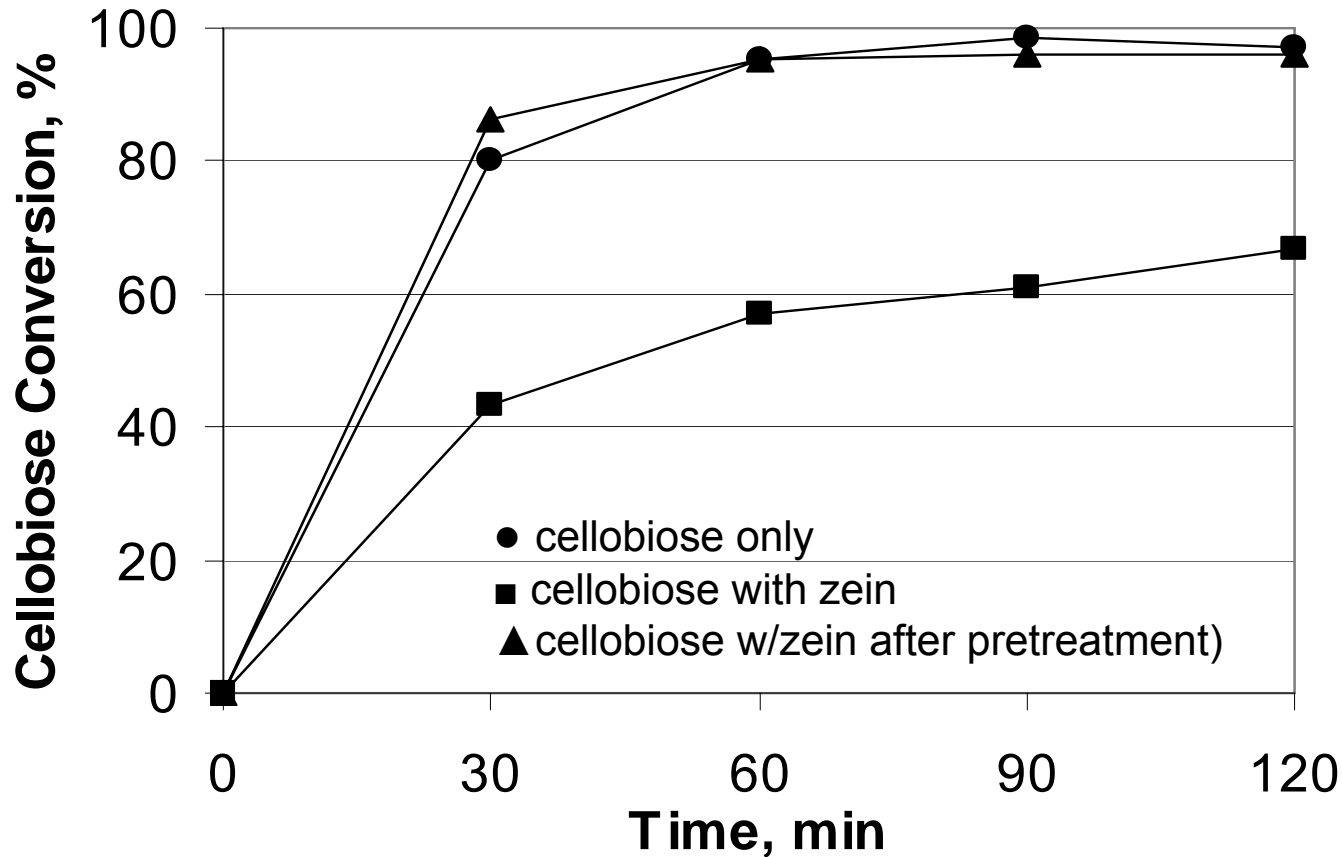
ISU digest basis



Midwest Consortium for Biobased
Products & Bioenergy



Protein Impurity Effect



1 wt% cellobiose,
0.1 wt% zein,
0.2 wt% catalyst,
175°C



Midwest Consortium for Biobased
Products & Bioenergy



Alkyl Esters from Oil Fraction

- Oil content ~11 wt% of the DGs
- Methanol versus ethanol transesterification kinetics
- Real feed conversion



Midwest Consortium for Biobased
Products & Bioenergy



Transesterification Kinetics

	Methanol	Ethanol
k_{TG} (mol% ⁻¹ min ⁻¹) @ 60°C	0.11	0.017
k_{DG} (mol% ⁻¹ min ⁻¹) @ 60°C	7.5	8.1
k_{MG} (mol% ⁻¹ min ⁻¹) @ 60°C	17	7.5
Ea_{TG} (kcal/mol)	15.0	15.9
Ea_{DG} (kcal/mol)	13.9	16.4
Ea_{MG} (kcal/mol)	6.7	7.3

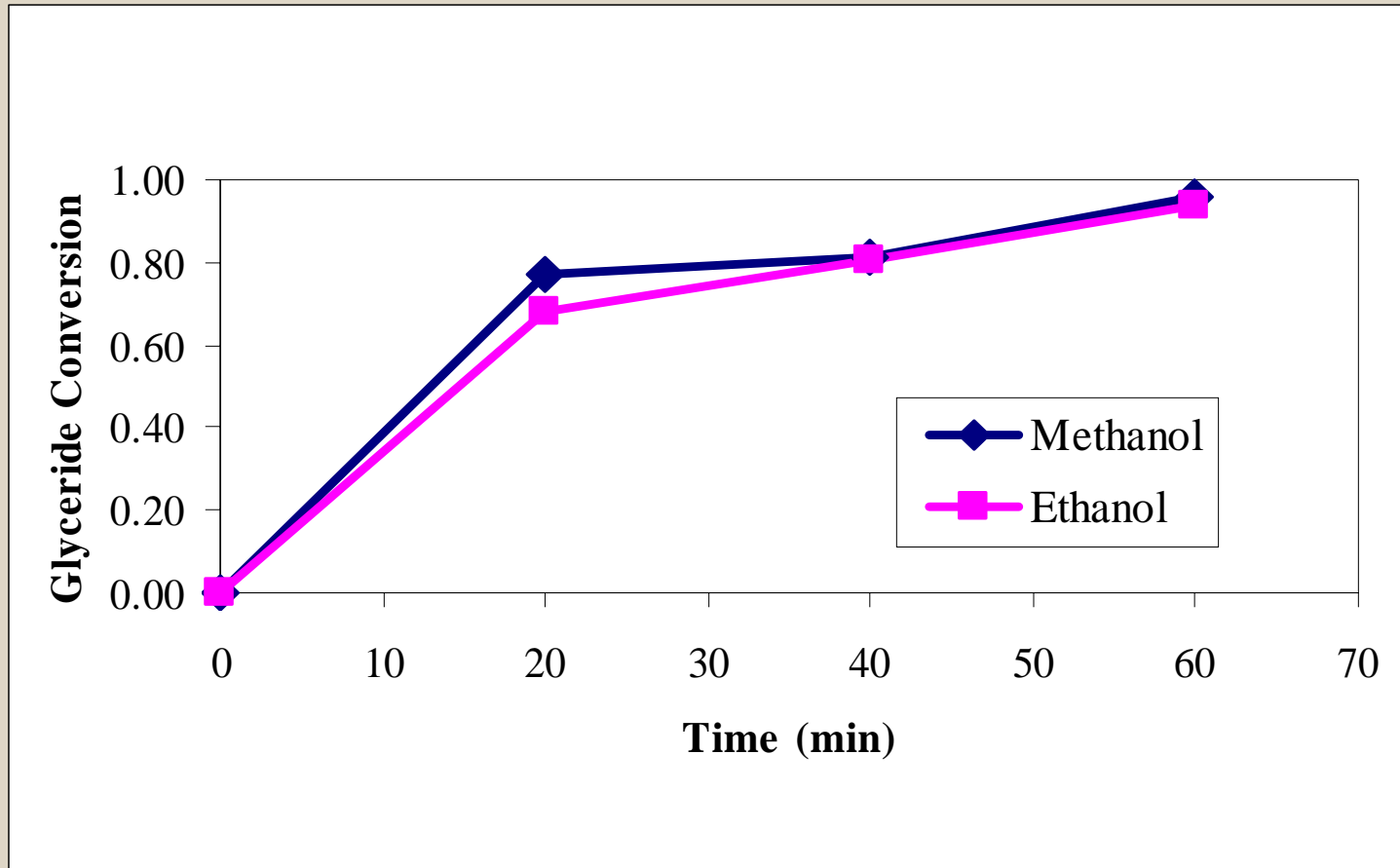
12:1 alcohol/oil, NaOH



**Midwest Consortium for Biobased
Products & Bioenergy**



Corn Oil Transesterification



6:1 alcohol/oil, 60°C, NaOCH₃



Midwest Consortium for Biobased
Products & Bioenergy



Dry Mill Corn Oil

- Oil from VeraSun
- Oil contains 11 wt% free fatty acid
- Esterification/transesterification required



Midwest Consortium for Biobased
Products & Bioenergy



Conclusions

- Hydrolysis
 - Solid acid catalysts can efficiently hydrolyzed oligosaccharides.
 - Differences in C5 and C6 degradation rates makes selective recovery of monosaccharides difficult.
- Alkyl esters
 - Reaction properties of methanol and ethanol are similar.
 - Corn oil from DGs will have high free fatty acid content.



**Midwest Consortium for Biobased
Products & Bioenergy**

