


Chemical Catalysts for Adding Value to Distillers Grains

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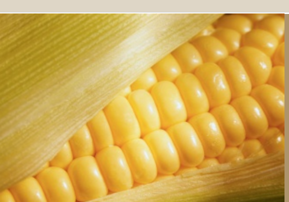
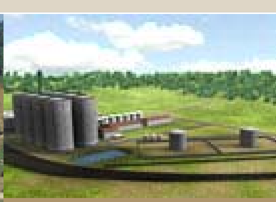
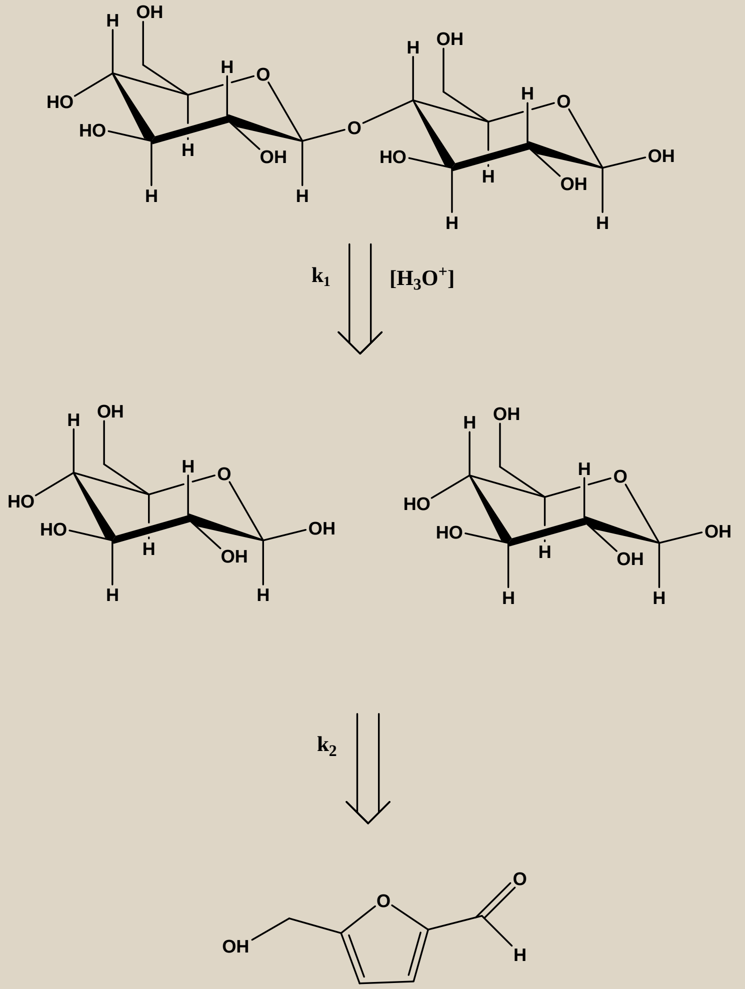
Overview

- Catalytic hydrolysis
  - Sugar degradation
  - Hydrolysis of hydrothermally pretreated material
- Corn oil transesterification

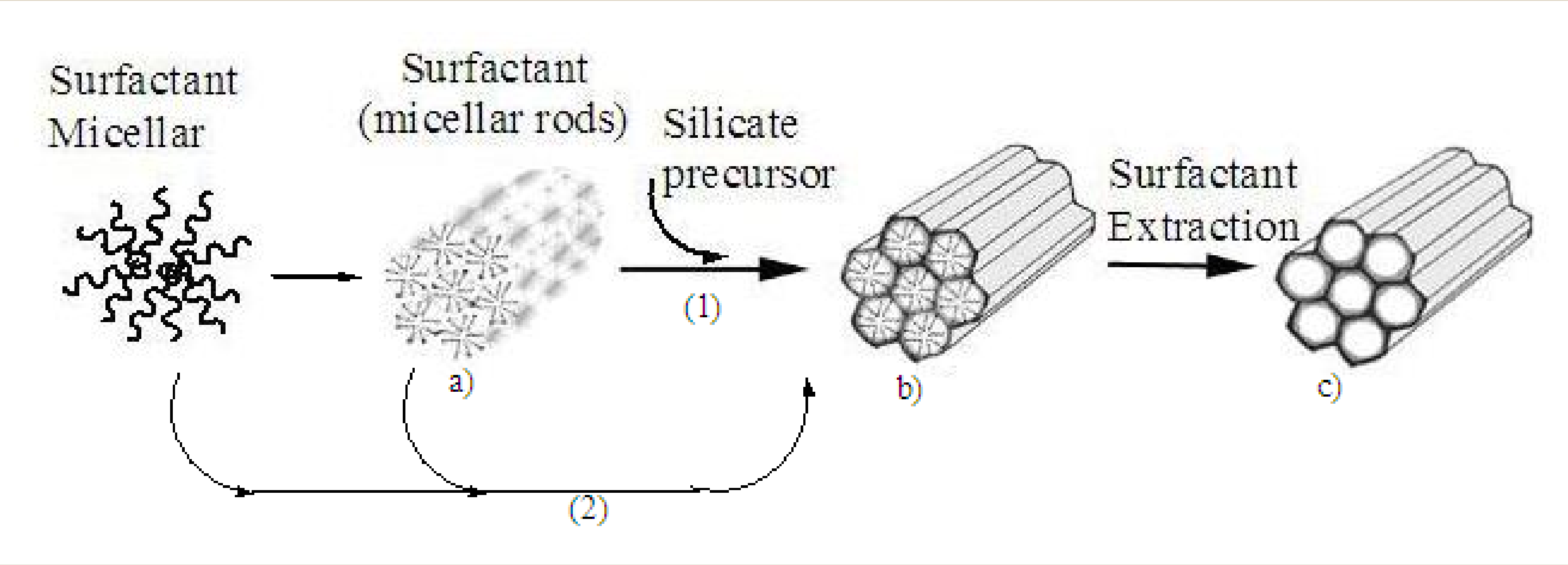




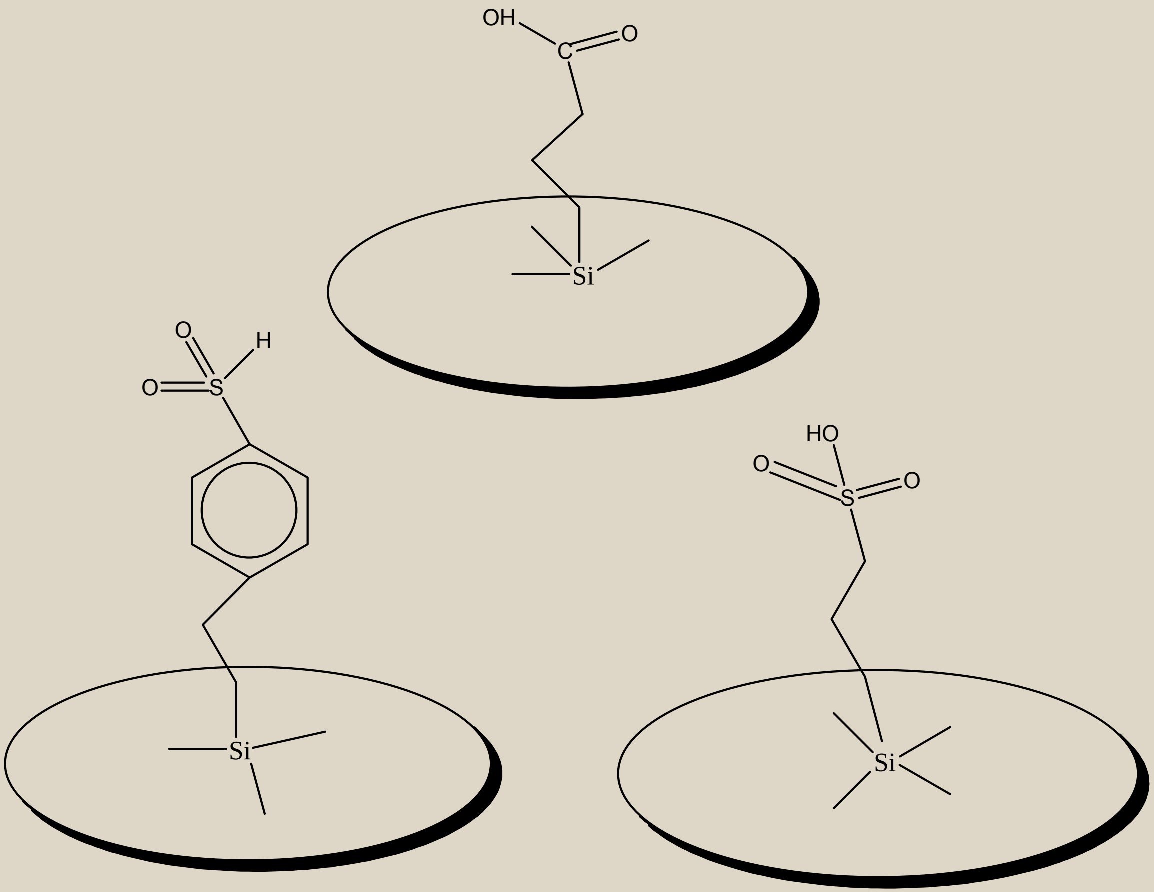
Oligosaccharide Hydrolysis



Mesoporous Scaffolds



Acidic Groups



Cellobiose 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

Glucose Degradation Activation Energy

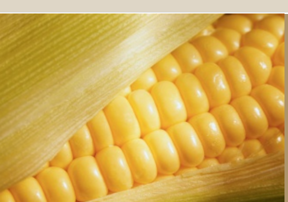
Catalyst	Activation Energy (kJ/mol)
7.5% propylsulfonic acid	67 +/- 6
15% propylsulfonic acid	65 +/- 18
10% arenesulfonic acid	73 +/- 11
20% butylcarboxylic acid	76 +/- 20
sulfuric acid*	118 +/- 37.5
maleic acid*	72.6 +/- 22.5

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

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



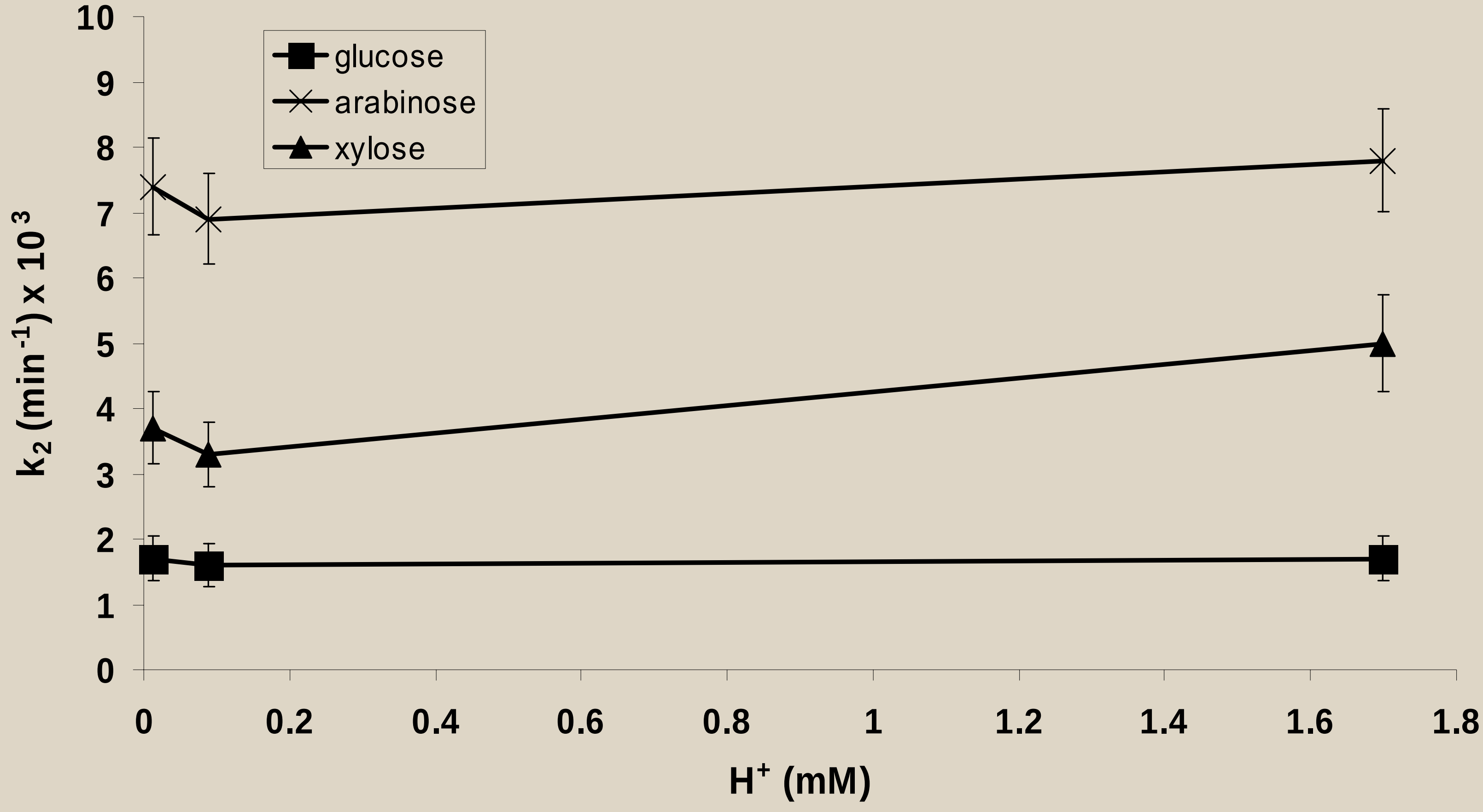

Arabinose Degradation Activation Energy

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

hydrothermolysis	125

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

Degradation Rate Constants (175°C)



Hydrothermal Pretreatment (15% solids)*

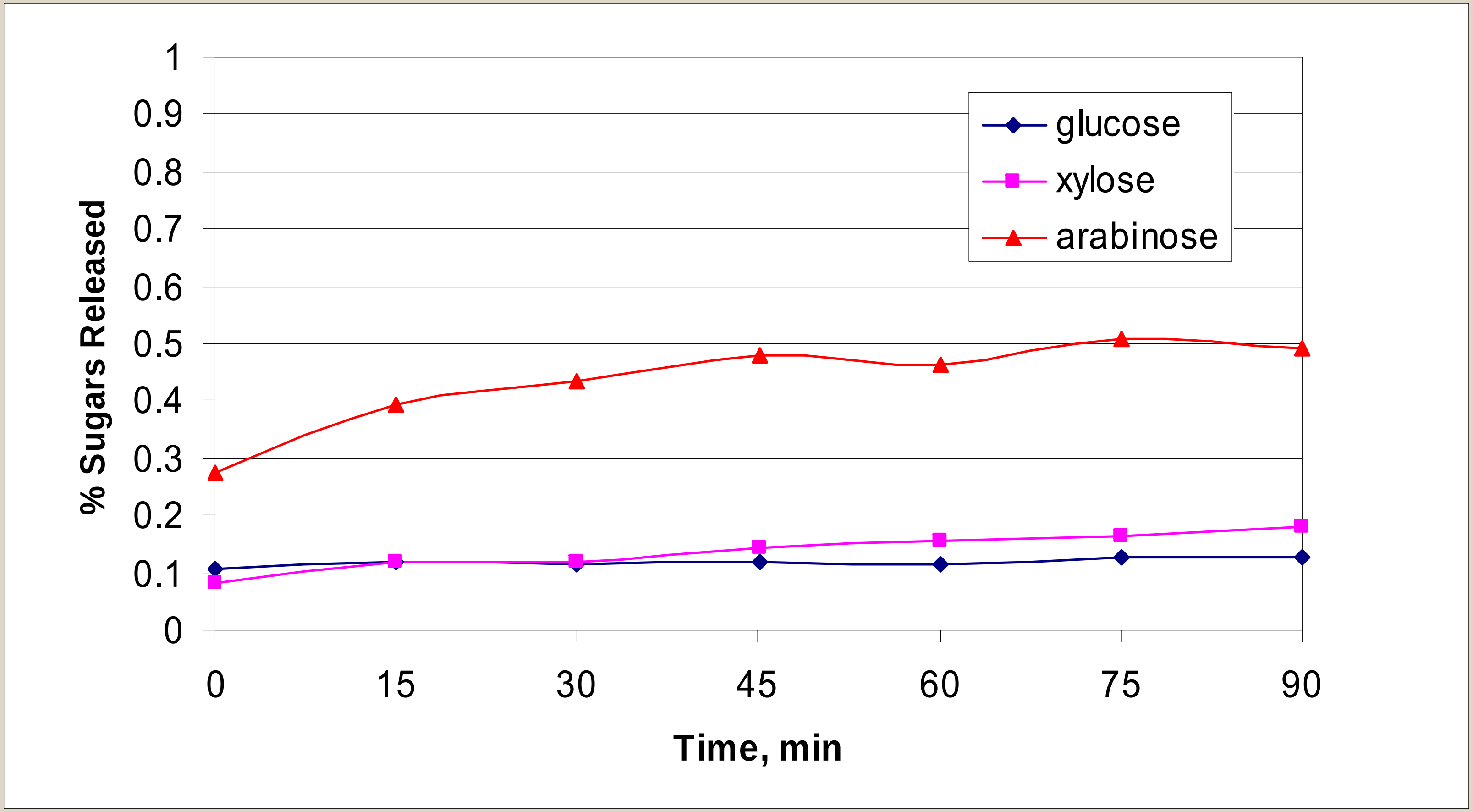
	Pretreated	Digested (Purdue)	Digested (ISU)
Glucose	0.10%	1.51%	1.98%
Xylose	0.31%	1.01%	0.88%
Arabinose	0.31%	0.69%	0.55%

* Rick Hendrickson – Purdue University

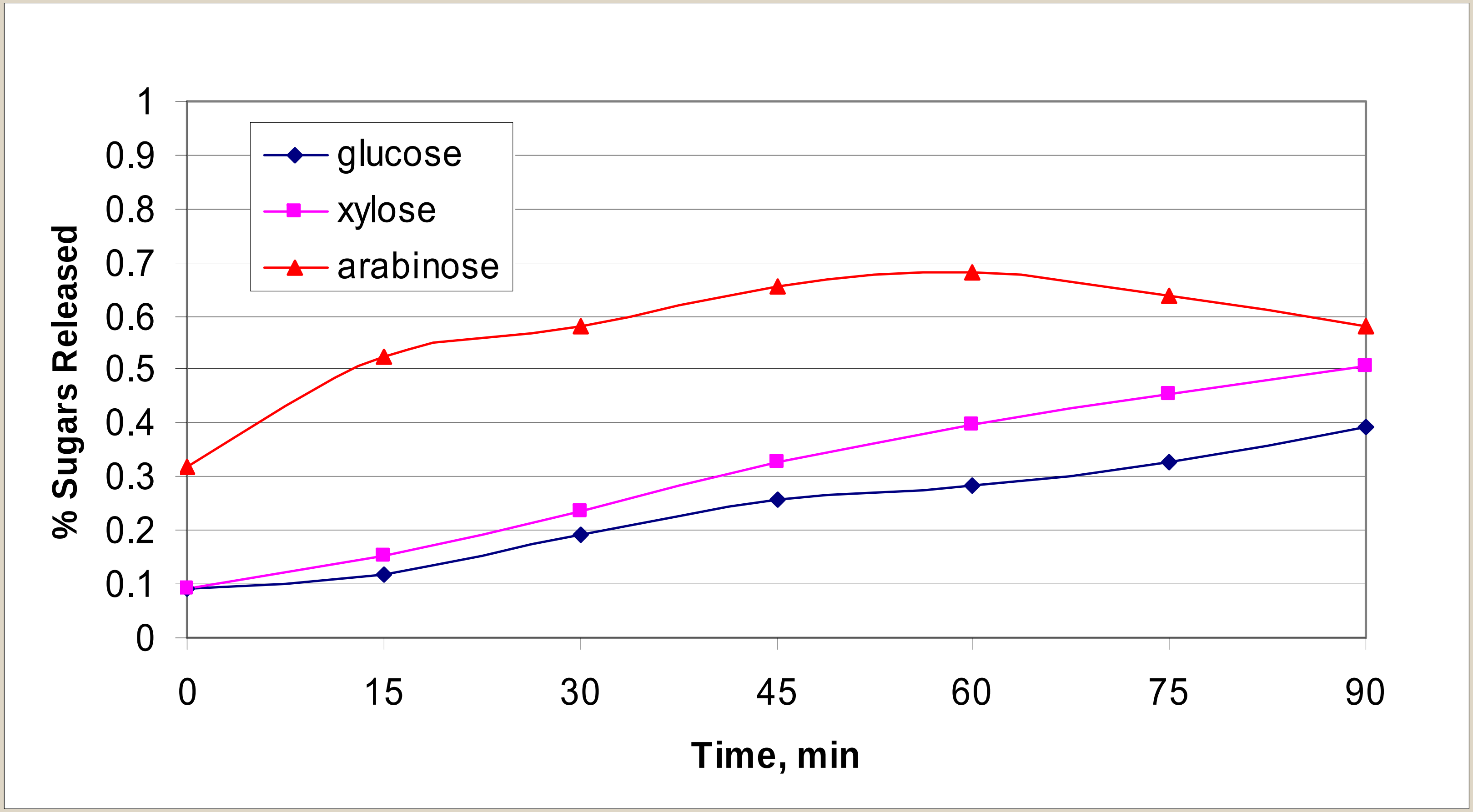
Reaction Conditions

- 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

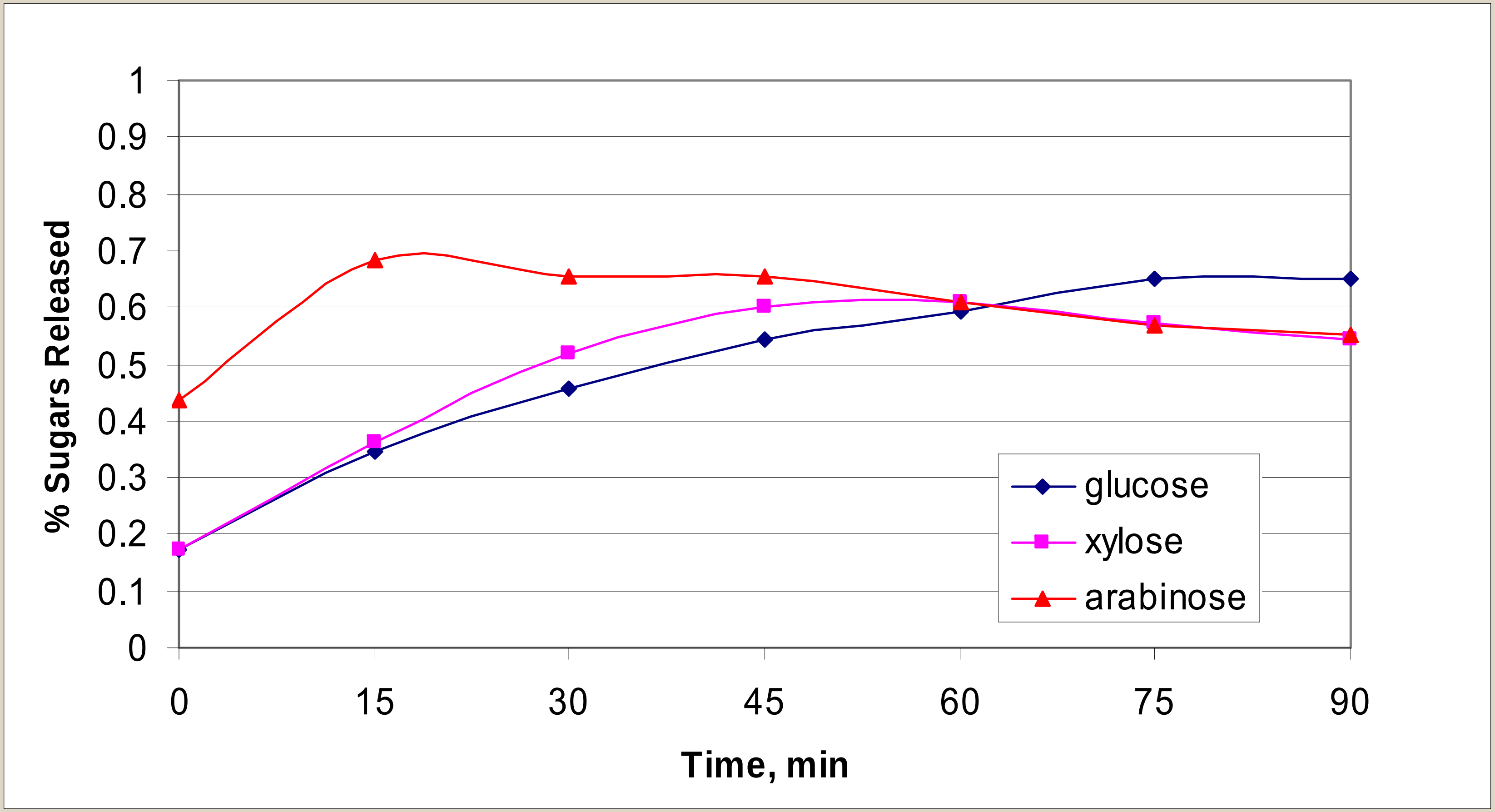
Catalytic Hydrolysis (145°C)



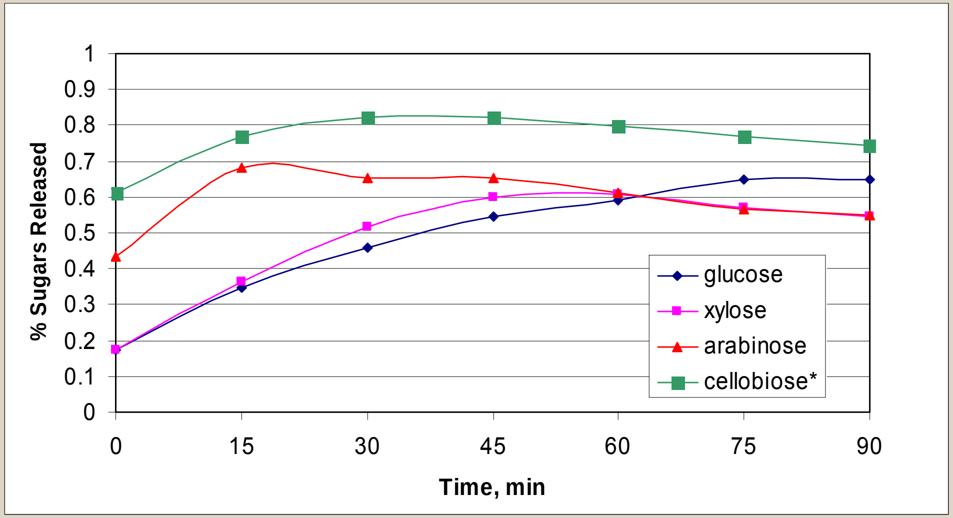
Catalytic Hydrolysis (160°C)



Catalytic Hydrolysis (175°C)

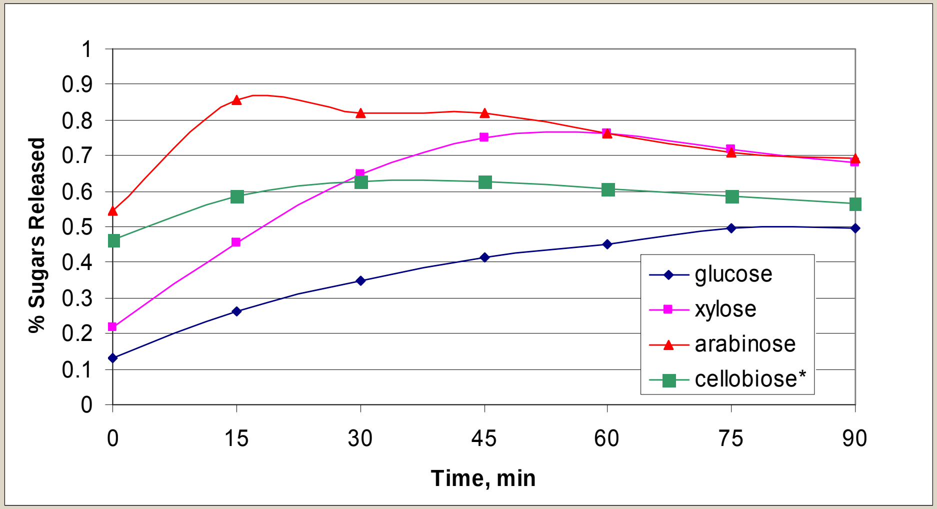


Catalytic Hydrolysis (175°C)

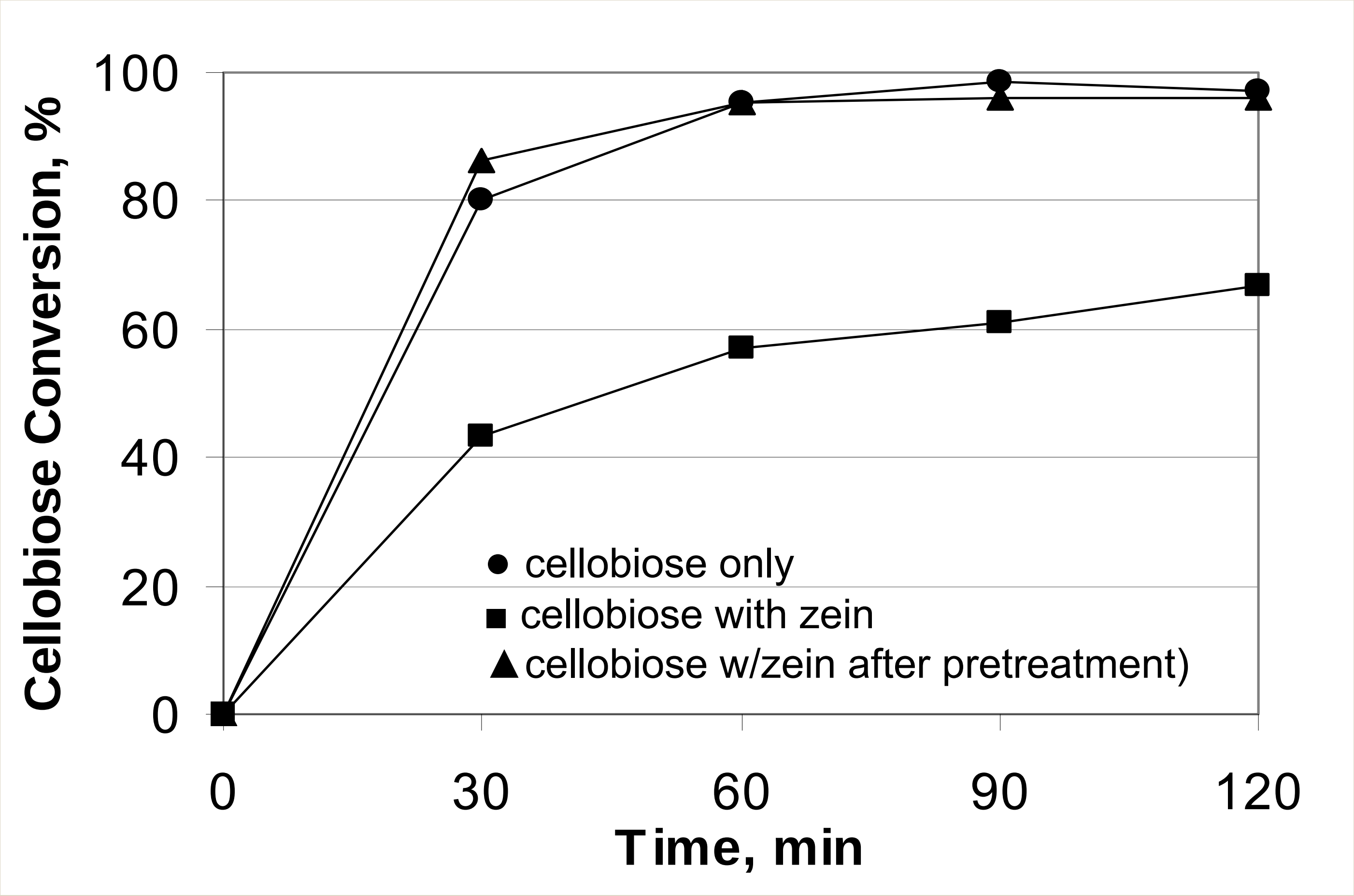


Purdue digest basis

ISU digest basis



Protein Impurity Effect



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

Alkyl Esters from Oil Fraction

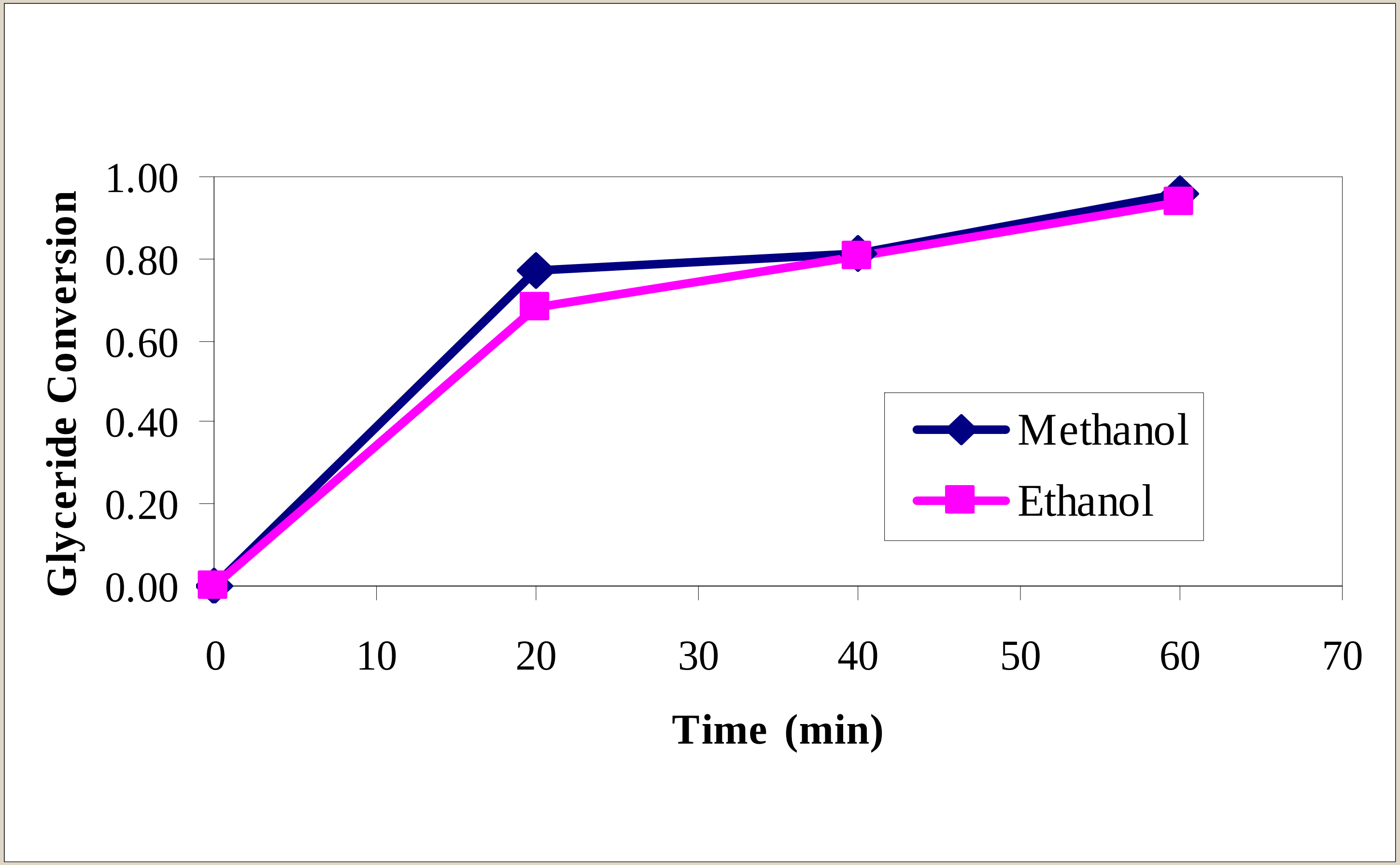
- Oil content ~11 wt% of the DGs
- Methanol versus ethanol transesterification kinetics
- Real feed conversion

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

Corn Oil Transesterification



6:1 alcohol/oil, 60°C, $NaOCH_3$

Dry Mill Corn Oil

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

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.