



# Chemical Catalysts for Adding Value to Distillers Grains

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*Corn Refiners' Association*



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# Overview

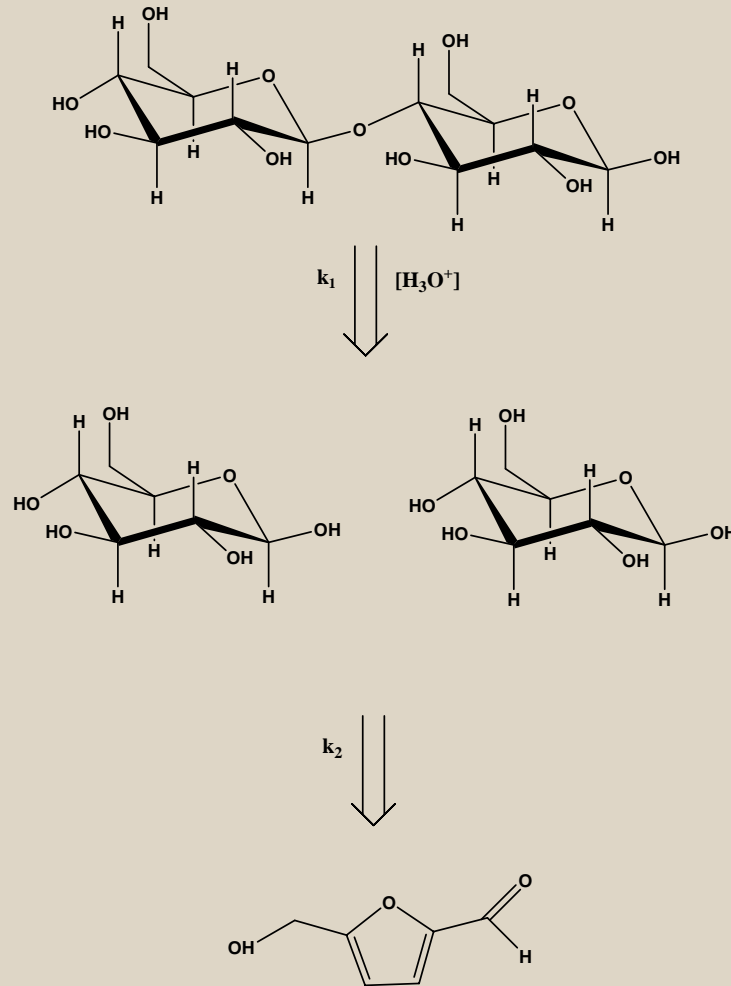
- Catalytic hydrolysis
  - Sugar degradation
  - Hydrolysis of hydrothermally pretreated material
  
- Corn oil transesterification



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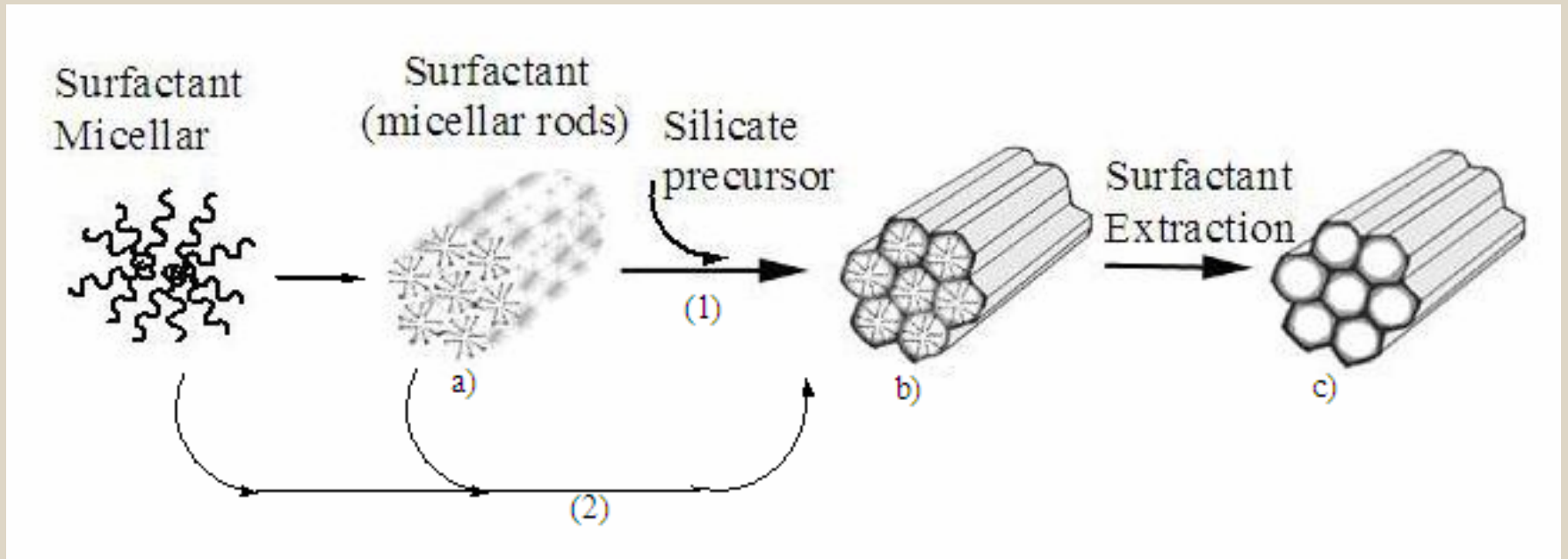
# Oligosaccharide Hydrolysis



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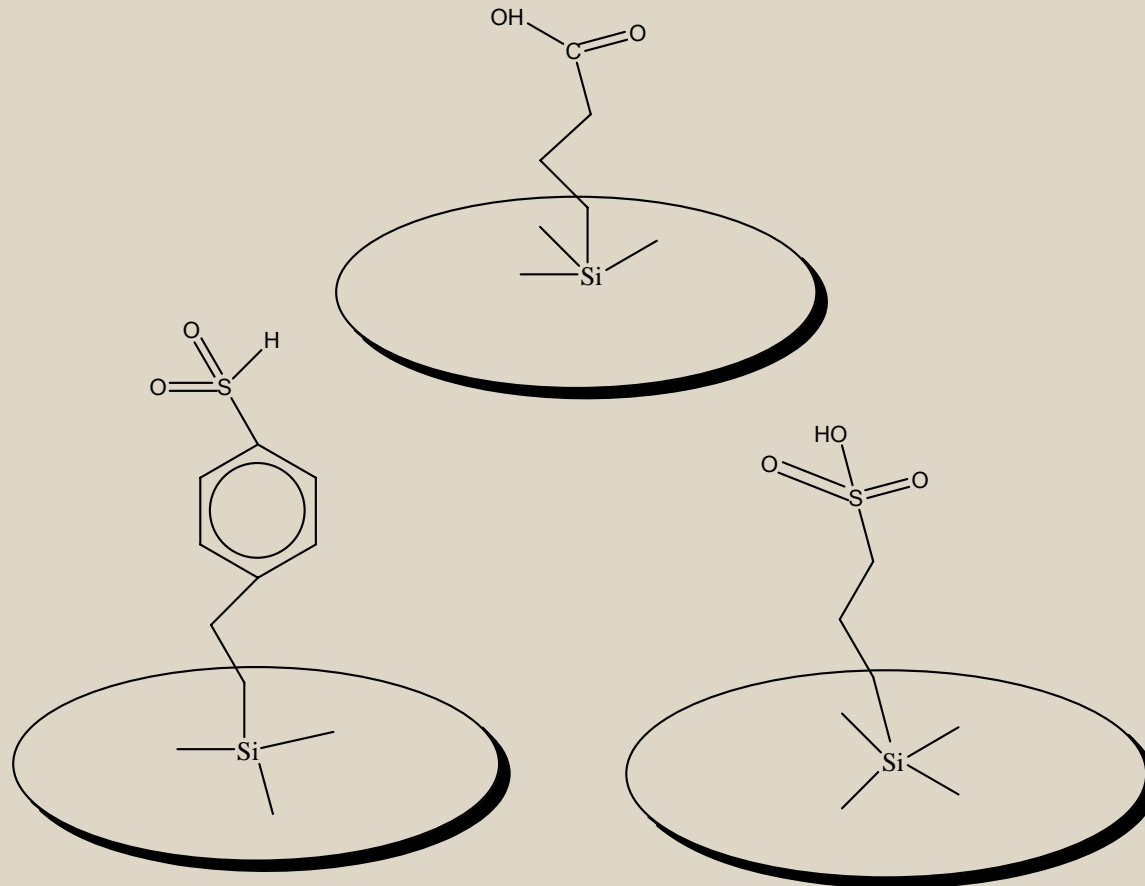
# Mesoporous Scaffolds



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# Acidic Groups



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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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# Glucose Degradation Activation Energy

Catalyst	Activation Energy (kJ/gmol)
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



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# Xylose Degradation Activation Energy

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

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

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



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# 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

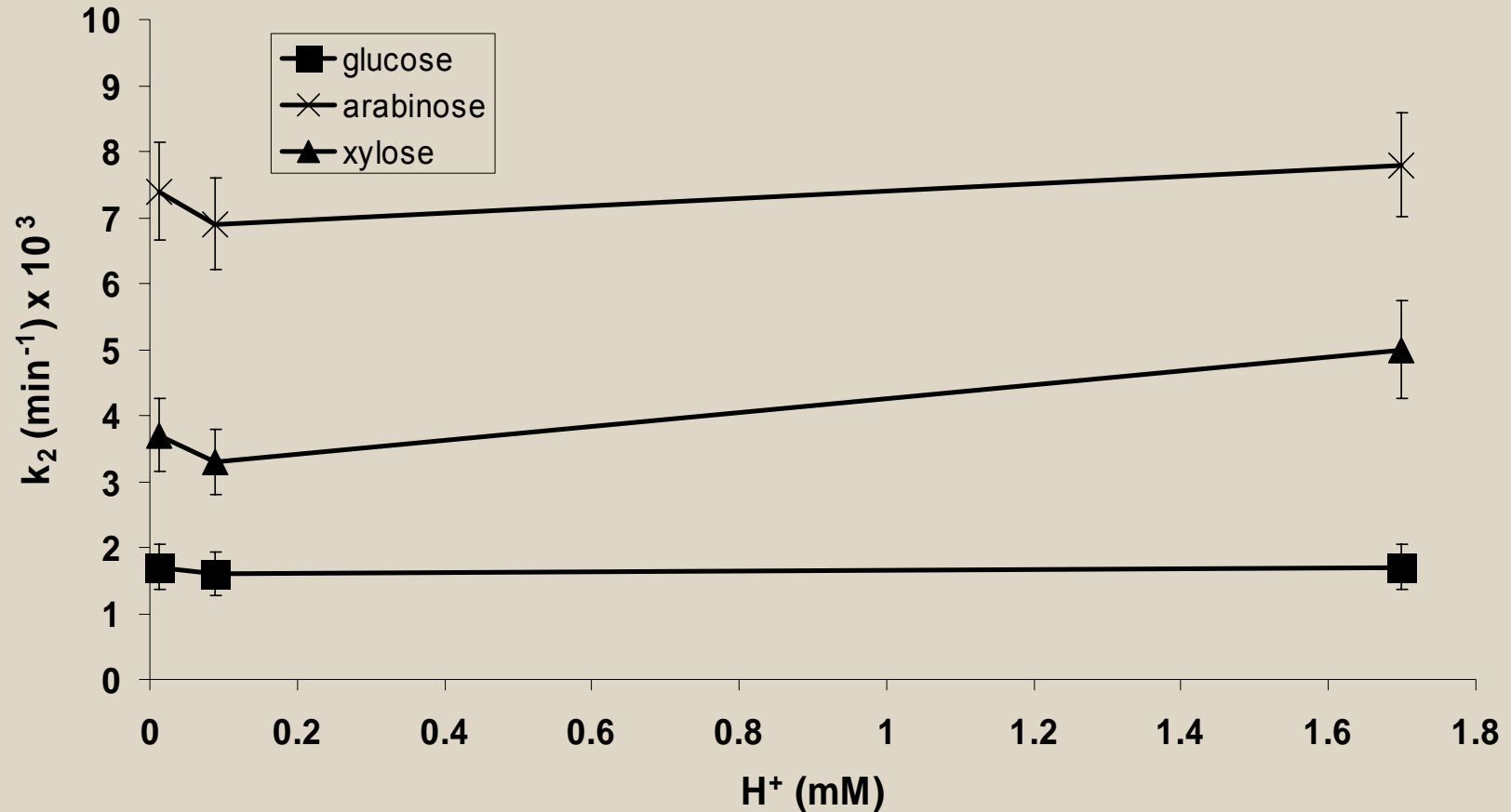
\*D. Nabarlantz, et al., 2004, *Ind. Eng. Chem. Res.*, 43:4124



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# Degradation Rate Constants (175°C)



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# 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



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# Reaction Conditions

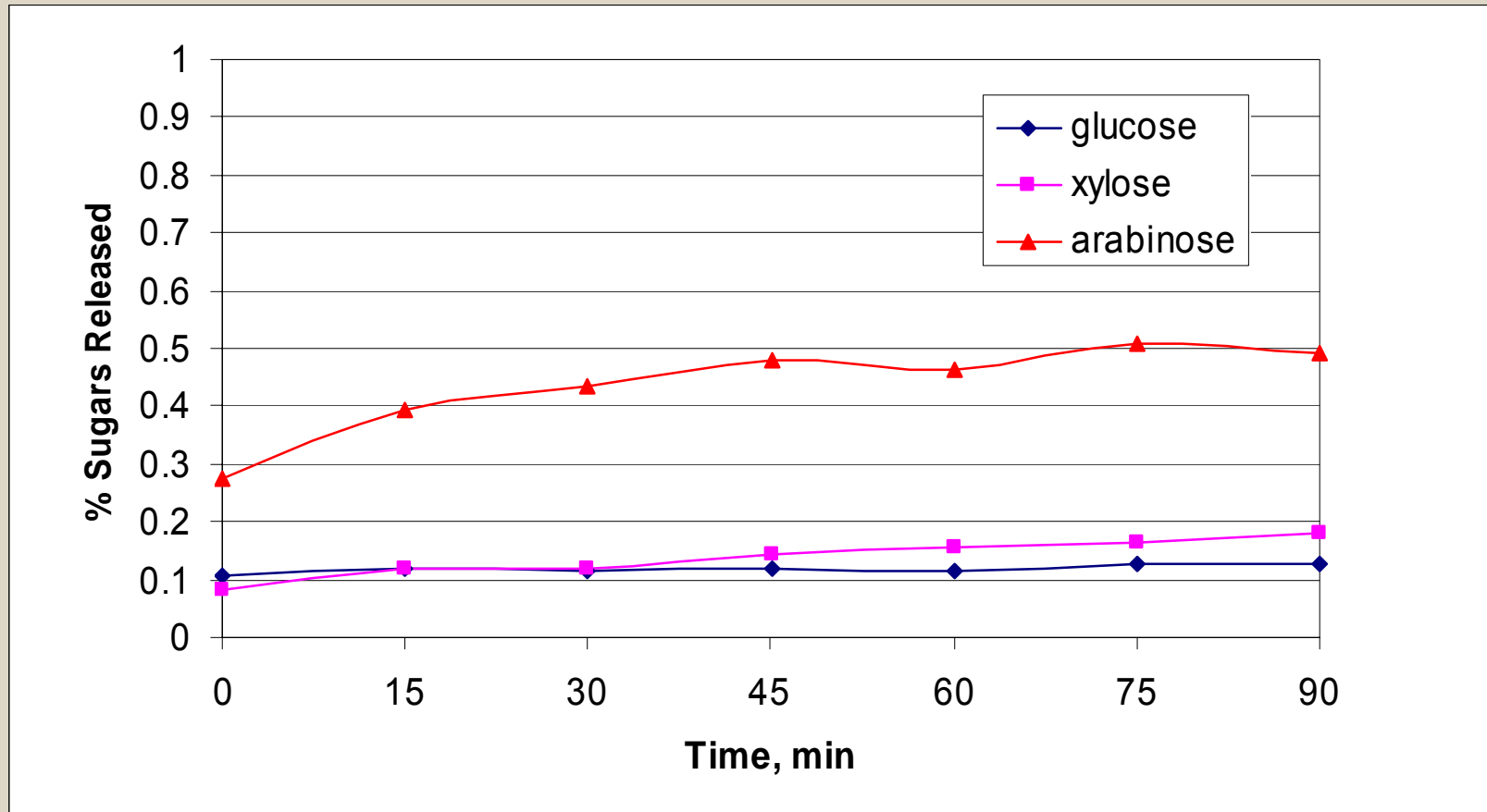
- 10 wt% of the pretreated material
  - Injected at reaction temperature
- Catalyst
  - 10% propylsulfonic acid functionalized silica
  - Added at 0.2 wt% of the solution
- Temperatures: 145, 160, 175°C



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# Catalytic Hydrolysis (145°C)



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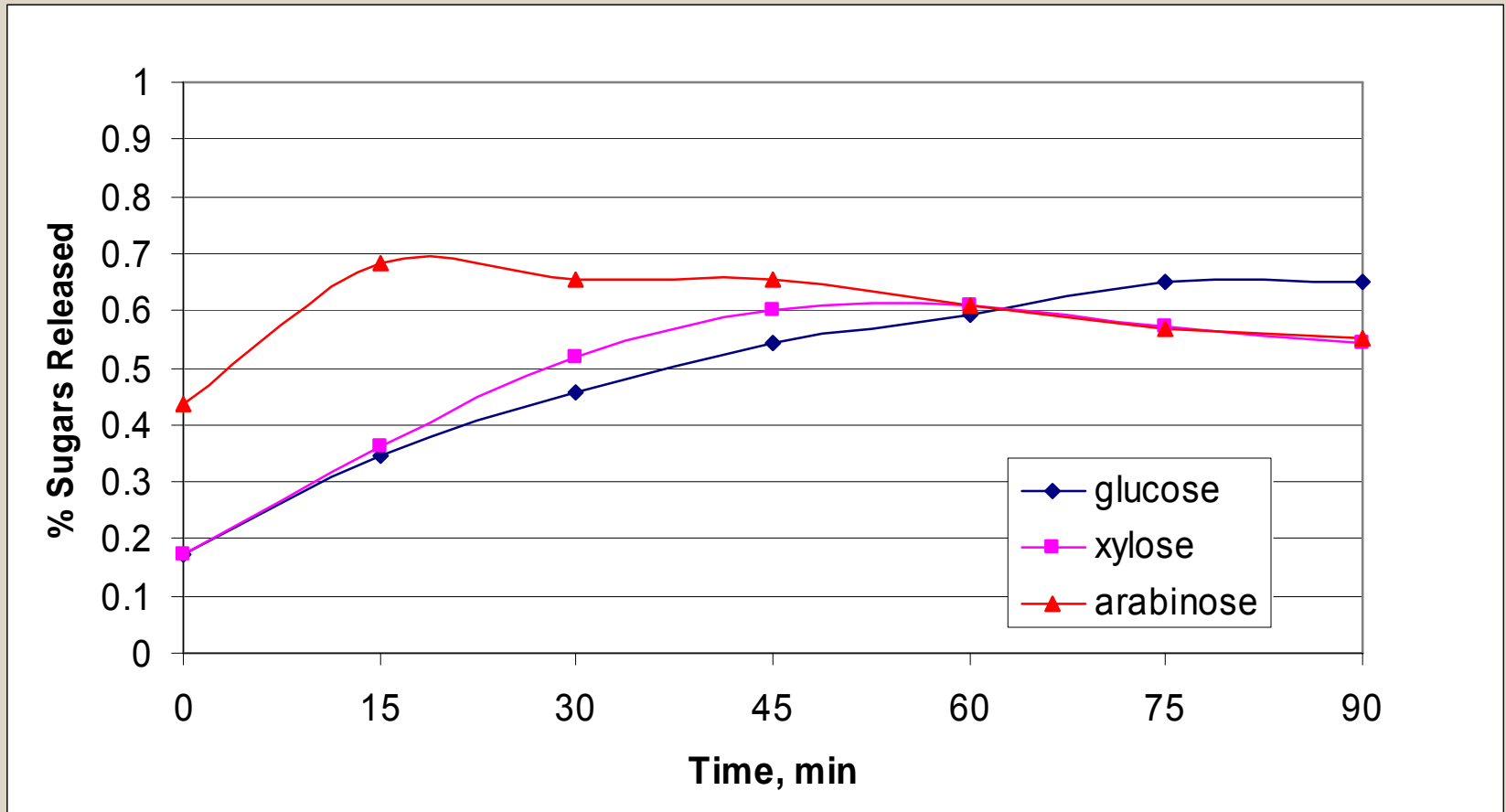
# Catalytic Hydrolysis (160°C)



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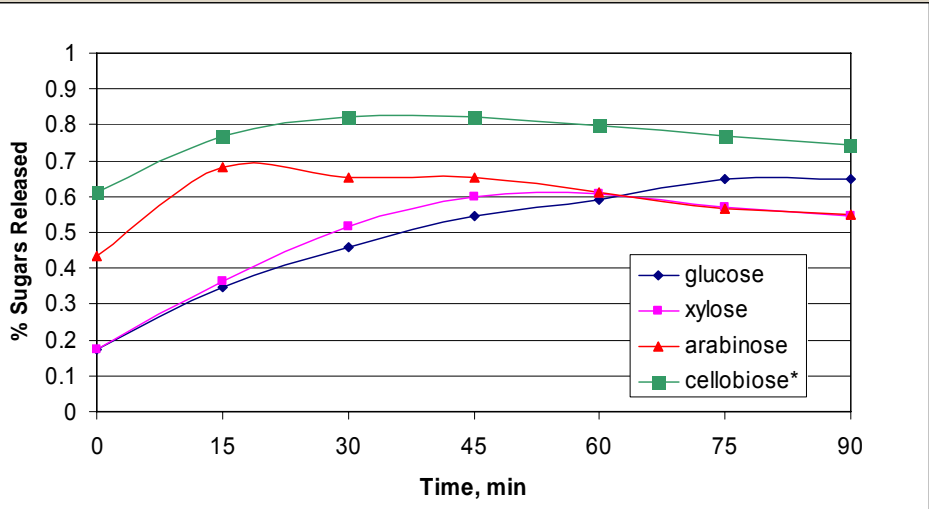
# Catalytic Hydrolysis (175°C)



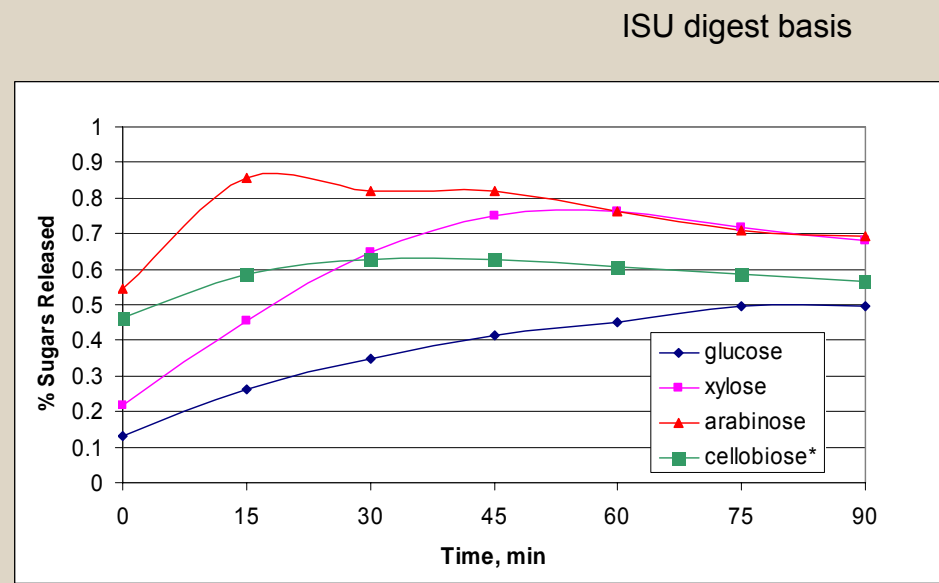
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# Catalytic Hydrolysis (175°C)



Purdue digest basis



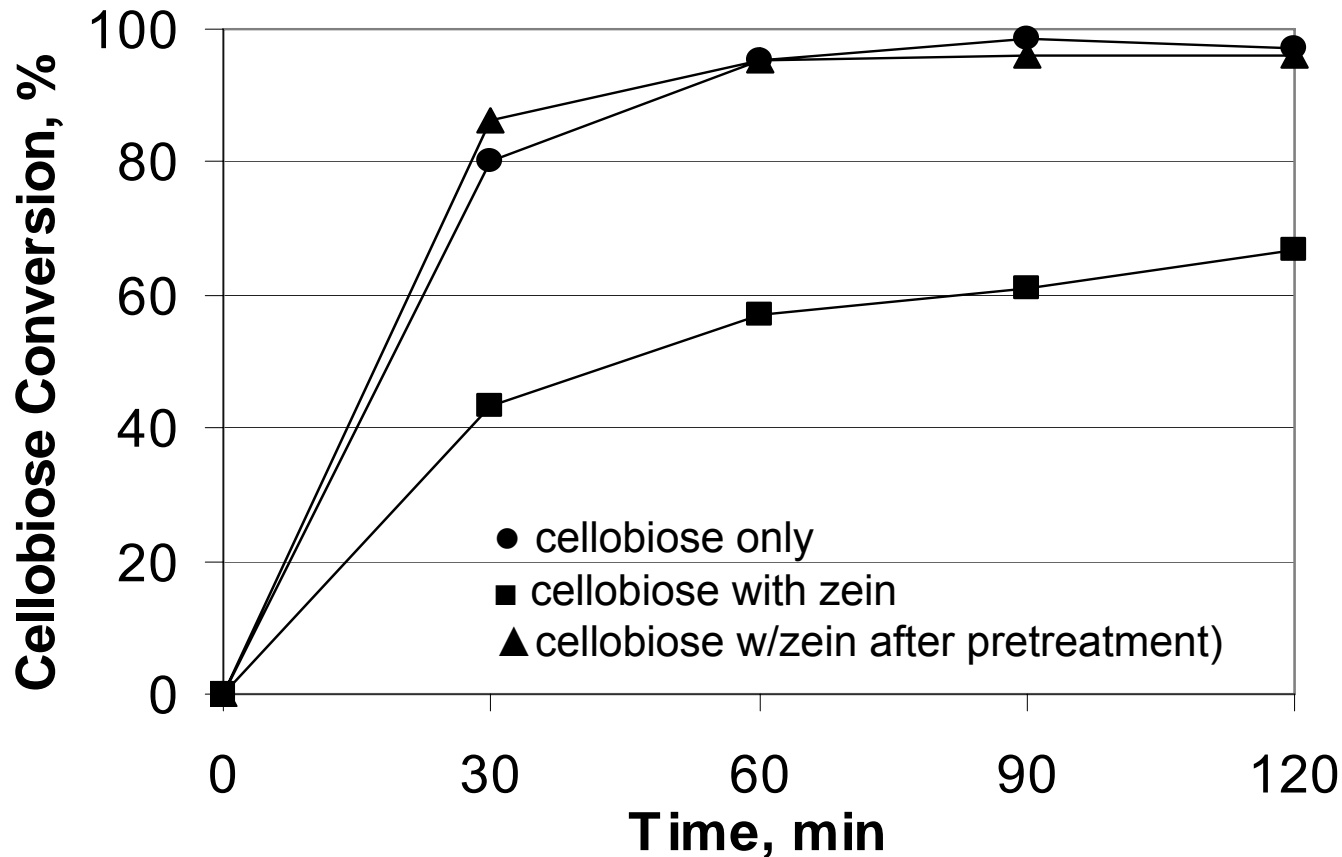
ISU digest basis



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# Protein Impurity Effect



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



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# Alkyl Esters from Oil Fraction

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



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# Transesterification Kinetics

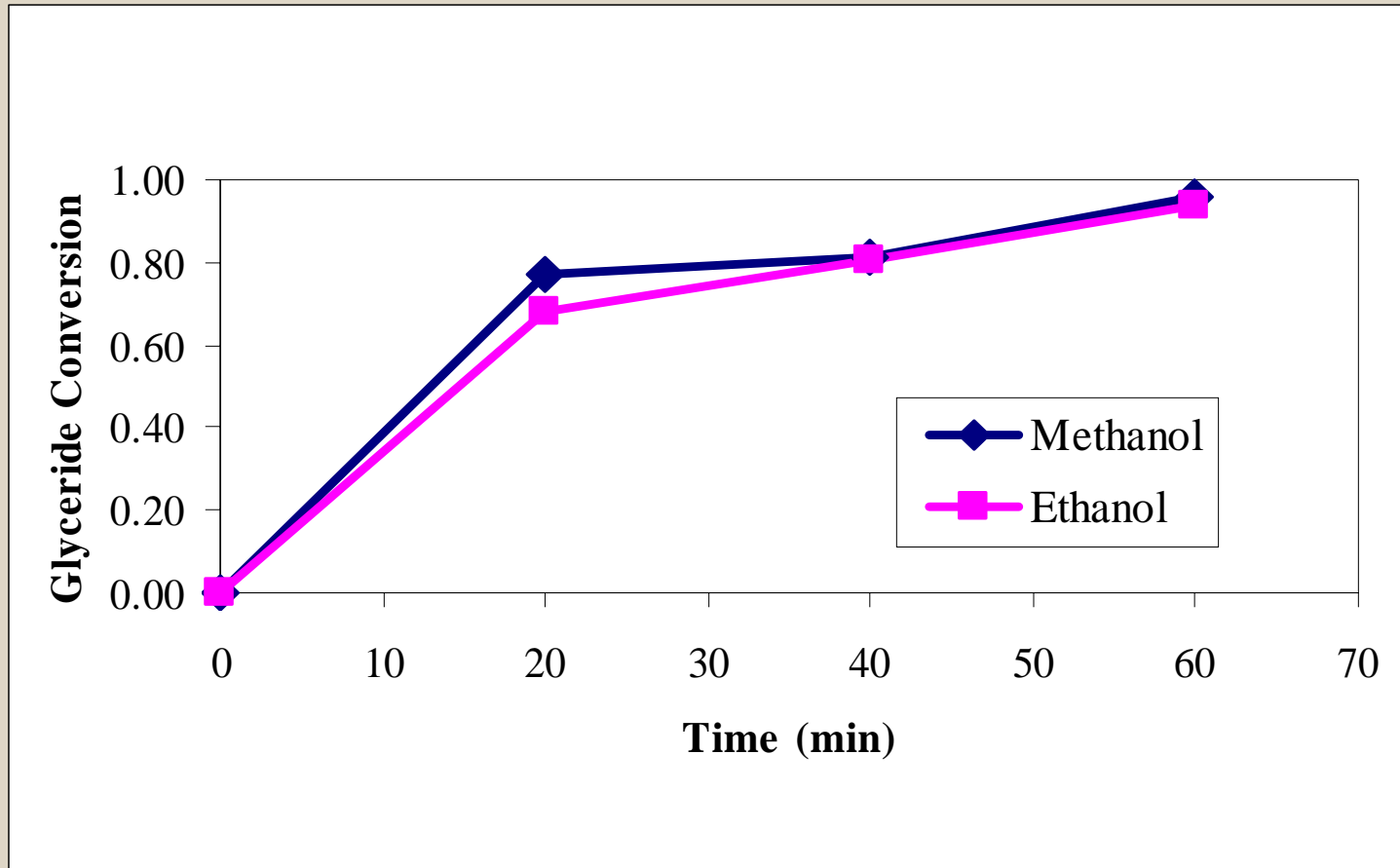
	<b>Methanol</b>	<b>Ethanol</b>
$k_{TG}$ (wt% <sup>-1</sup> min <sup>-1</sup> ) @ 60°C	0.036	0.0056
$k_{DG}$ (wt% <sup>-1</sup> min <sup>-1</sup> ) @ 60°C	0.071	0.33
$k_{MG}$ (wt% <sup>-1</sup> min <sup>-1</sup> ) @ 60°C	0.15	0.23
$Ea_{TG}$ (kcal/mol)	14.9	16.0
$Ea_{DG}$ (kcal/mol)	14.4	13.6
$Ea_{MG}$ (kcal/mol)	6.9	1.3



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# Corn Oil Transesterification



6:1 alcohol/oil, 60°C, NaOCH<sub>3</sub>



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# Dry Mill Corn Oil

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



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