1st Brazil - U.S. Biofuels Short Course
University of São Paulo
São Paulo, Brazil

Biomass-derived furanic compounds for the production of fuels and chemical intermediates

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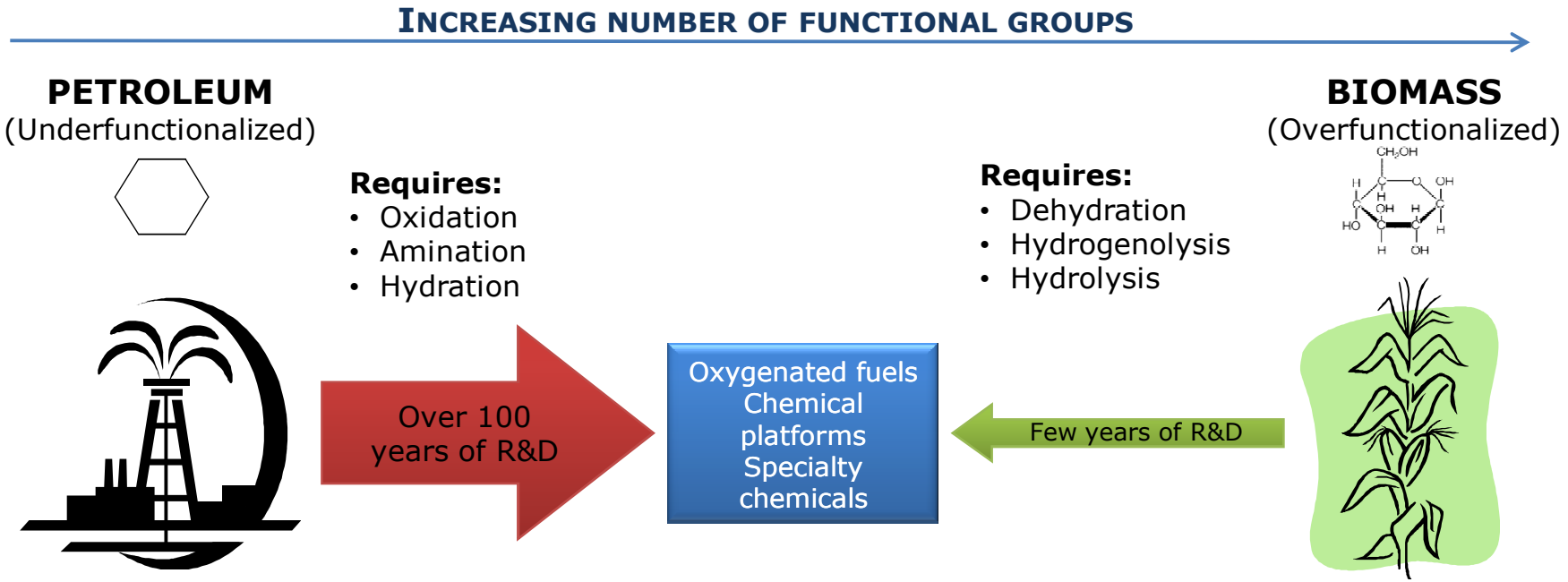
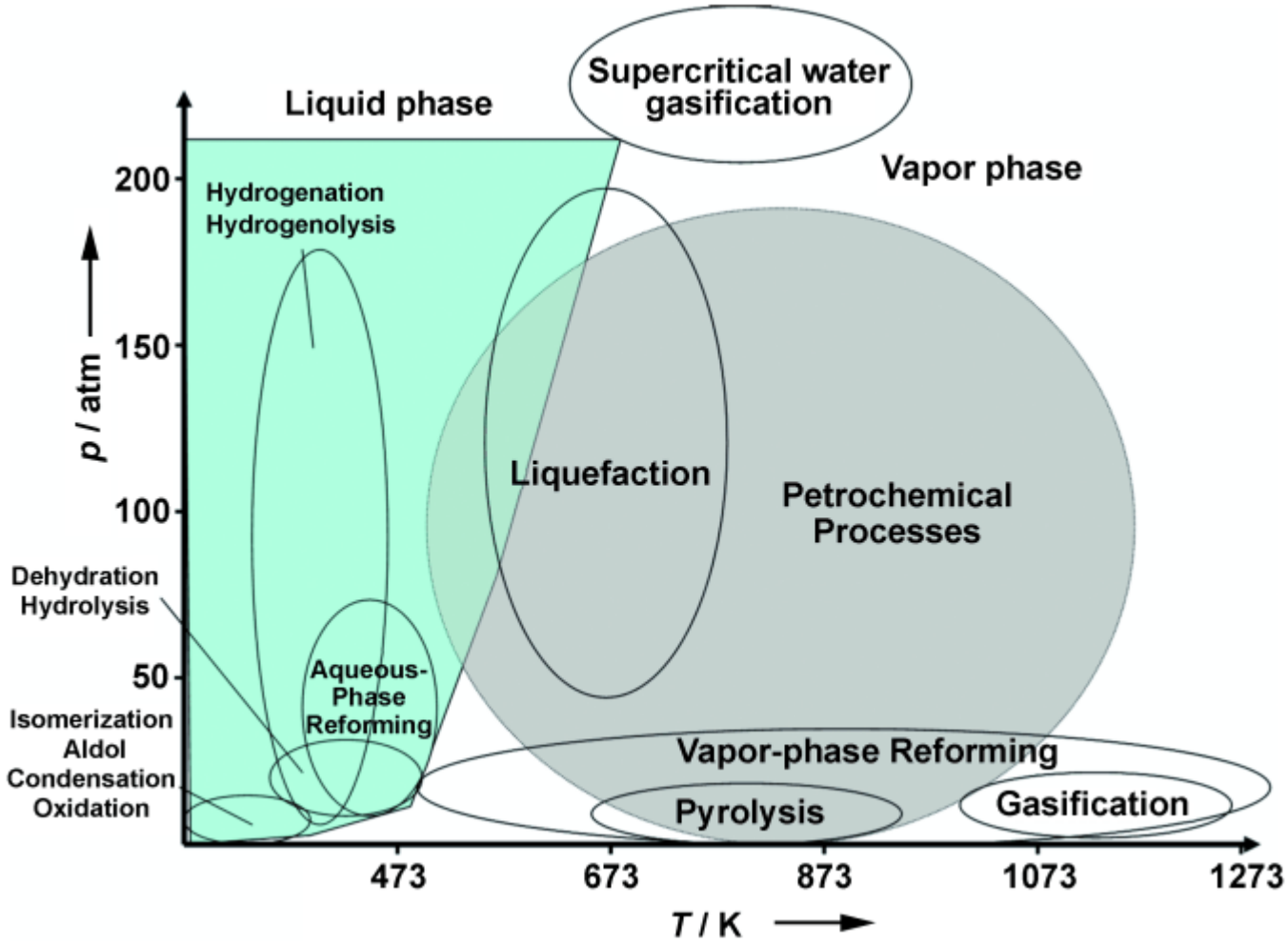
Biomass: A source of renewable carbon

Biomass is an attractive candidate as an alternative to petroleum**:**

1. The only abundant source of renewable carbon.
2. Lower CO_2 footprint.
3. Domestically available.

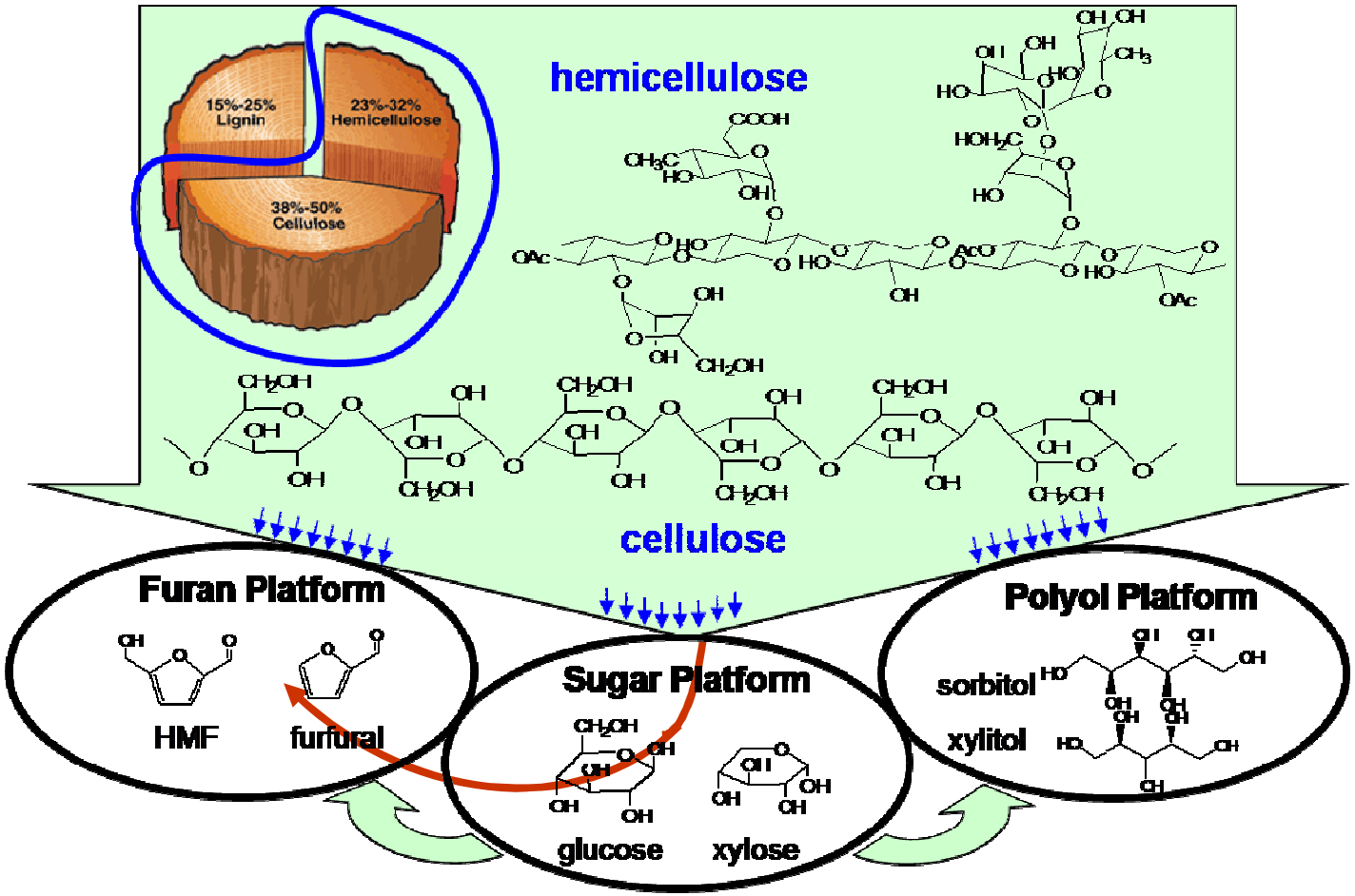


Biomass vs Petroleum Processing

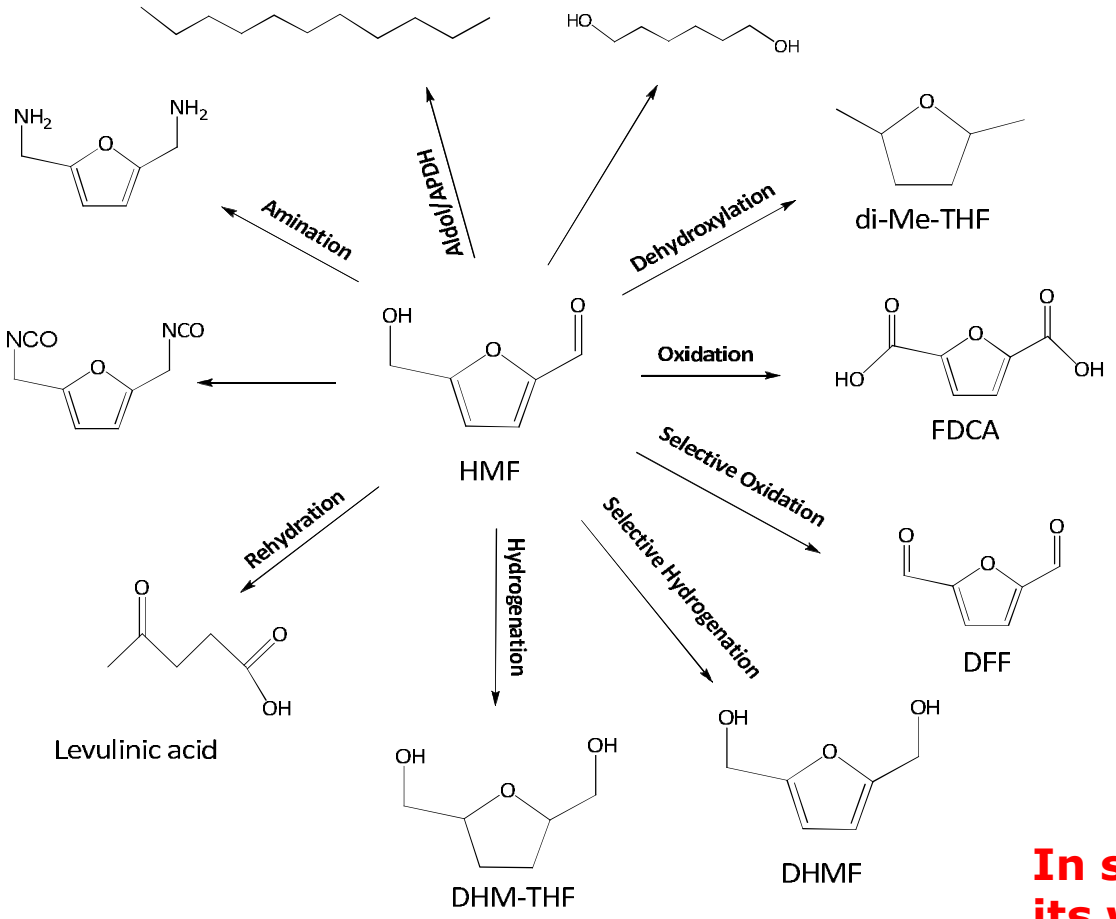


Juben N. Chheda, George W. Huber, & James A. Dumesic, Angewandte Chemie Int. Ed., 46 *(2007)*

Strategies for thermochemical conversion



HMF as a chemical platform

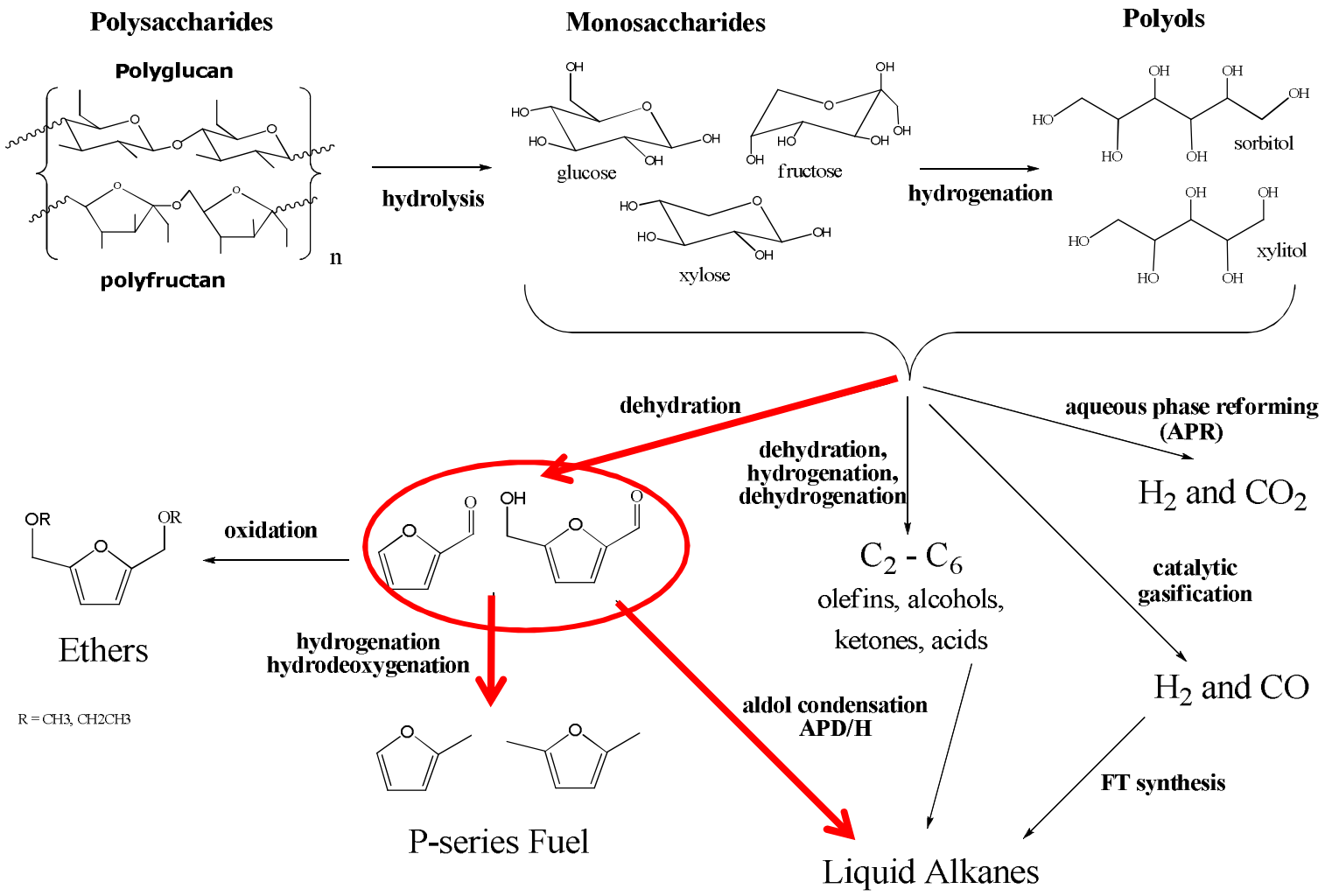


- Obtained by the acid-catalyzed dehydration of hexoses
- One of 30 top value-added chemicals from biomass[1]
- Intermediate for various high volume polymers[1,2]:
  - PET and PBT analogs
  - Polyurethanes
  - Polyamides
- Precursor to various fuels:
  - Diesel fuel (aldol-condensation)[3]
  - 2,5-dimethylfuran (DMF)[4]
  - Ethers[5]

In spite of HMF's great potential, its widespread production is currently hindered by high production costs, making it a chemical "sleeping giant".

1. *T. Werpy & G. Petersen (PNNL), DOE Report, August 2004.*
2. *C. Moreau, M. N. Belgacem & A. Gandini, Topics Catal. 2004*
3. *G. Huber, J.Chheda, & J.A. Dumesic, Science, 2005*
4. *Y. Roman-Leshkov, C.J. Barrett, Z. Liu & J,A. Dumesic, Nature, 2007*
5. *A. Corma, et. al. J. of Catalysis, 2009*

Roadmap for biomass-derived fuel components



1) Juben N. Chheda, George W. Huber, & James A. Dumesic, Angewandte Chemie Int. Ed., 46 (2007)
2) Yu-Chuan Lin and George W. Huber, Energy Environ. Sci., 2 (2009)
3) Andrew A. Peterson, et. al. Energy Environ. Sci., 1, 32 - 65 (2008)

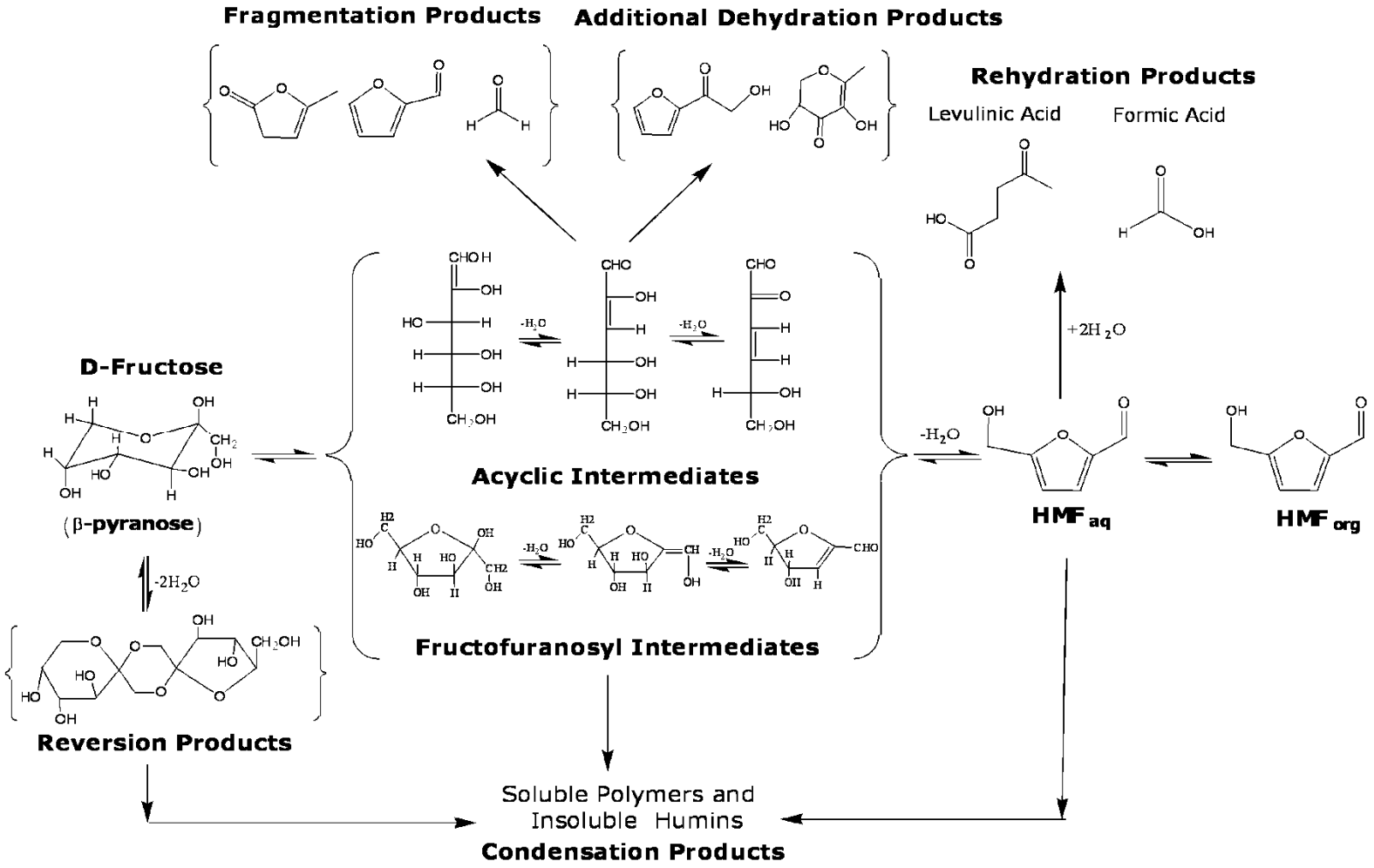
Useful definitions

- **Conversion** of R = $\frac{moles\ of\ R\ reacted}{moles\ of\ R\ initial} = \frac{(moles\ of\ R\ initial - moles\ of\ R\ final)}{moles\ of\ R\ initial}$

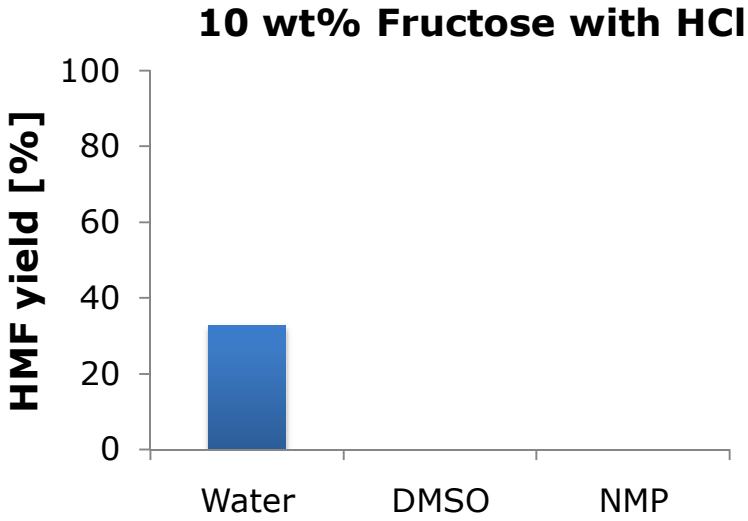
- **Selectivity** of P = $\frac{moles\ of\ P\ produced}{moles\ of\ R\ reacted} = \frac{moles\ of\ P\ produced}{(moles\ of\ R\ initial - moles\ of\ R\ final)}$

- **Yield** of P = Conversion of R x Selectivity of P = $\frac{moles\ of\ P\ produced}{moles\ of\ R\ initial}$

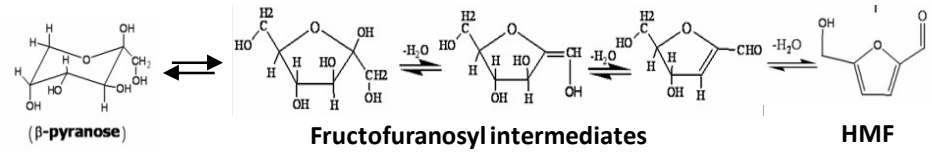
Dehydration reaction network

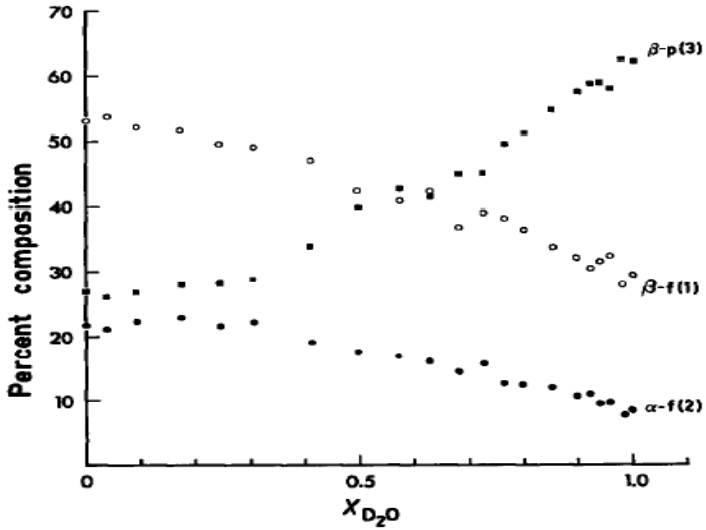


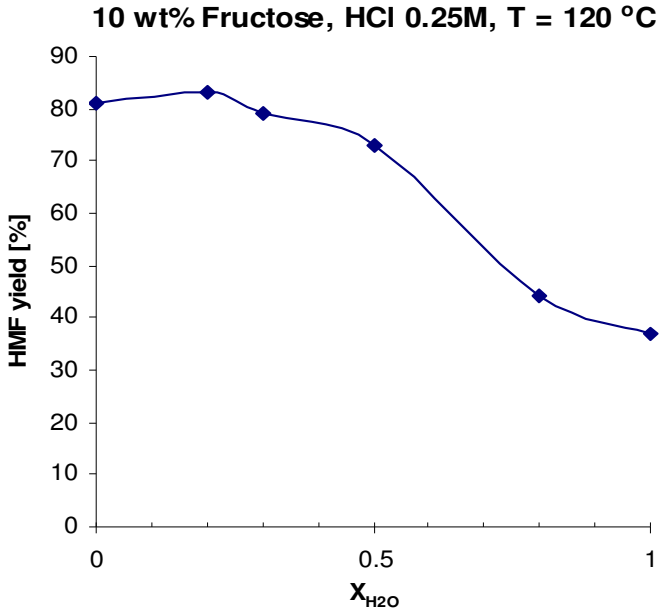
Solvent Effect



Possible reaction pathway:

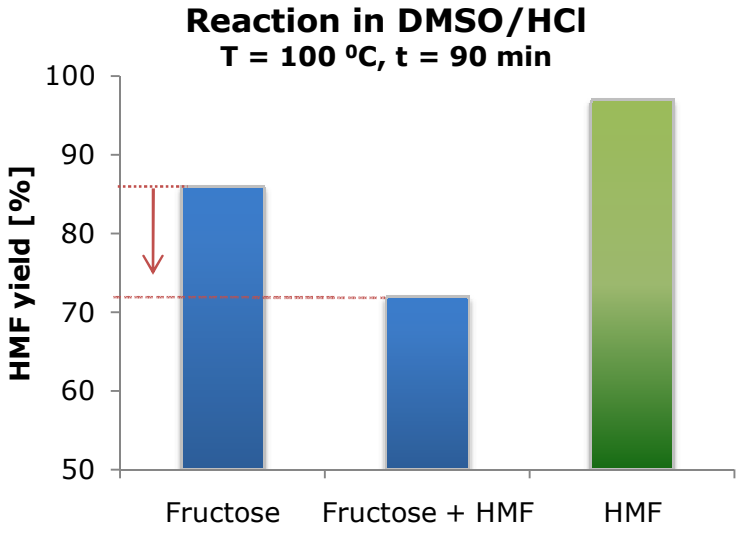




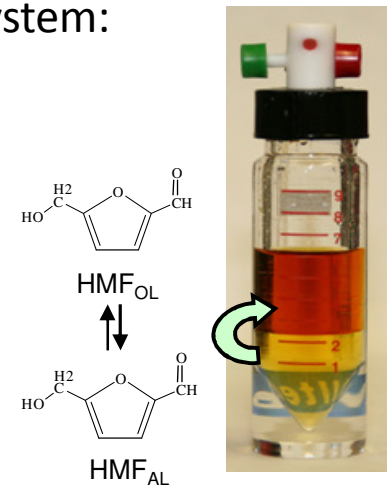


P. Dais and A. S. Perlin. Carbohydrate Research, 169 *(1987)*

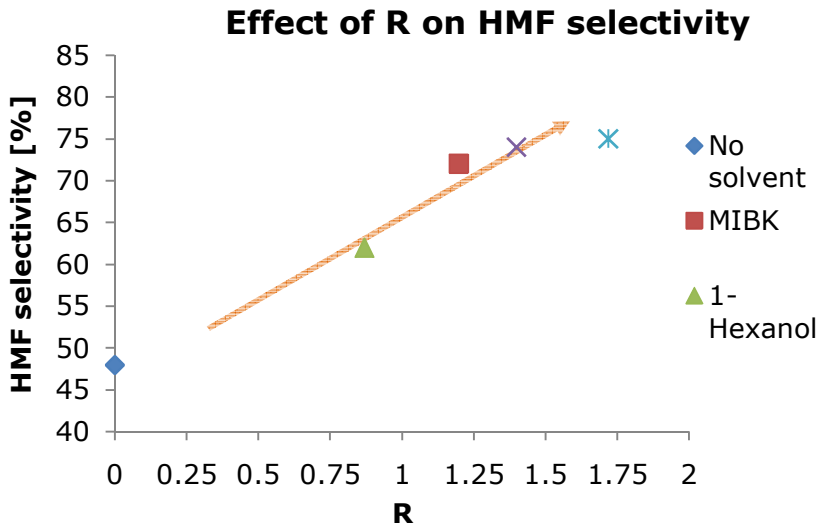
Extracting solvent



Biphasic system:

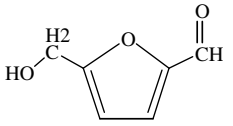


$$R = \frac{[HMF]_{OL}}{[HMF]_{AL}}$$

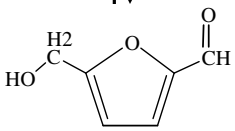


Biphasic reactor with chemical modifiers

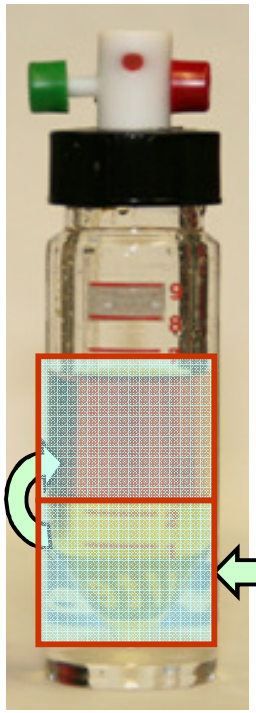
$$R = \frac{[HMF]_{OL}}{[HMF]_{AL}}$$



HMForg



HMFaq

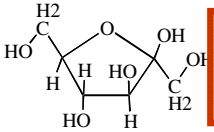


Organic Layer:

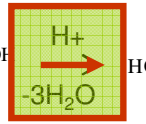
- MIBK
- Modifier:
  - 2-butanol

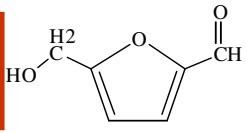
Aqueous Layer:

- Water
- Fructose
- Acid catalyst
- Modifiers:
  - DMSO
  - PVP

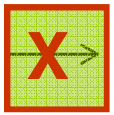


D-fructose

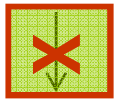




HMF

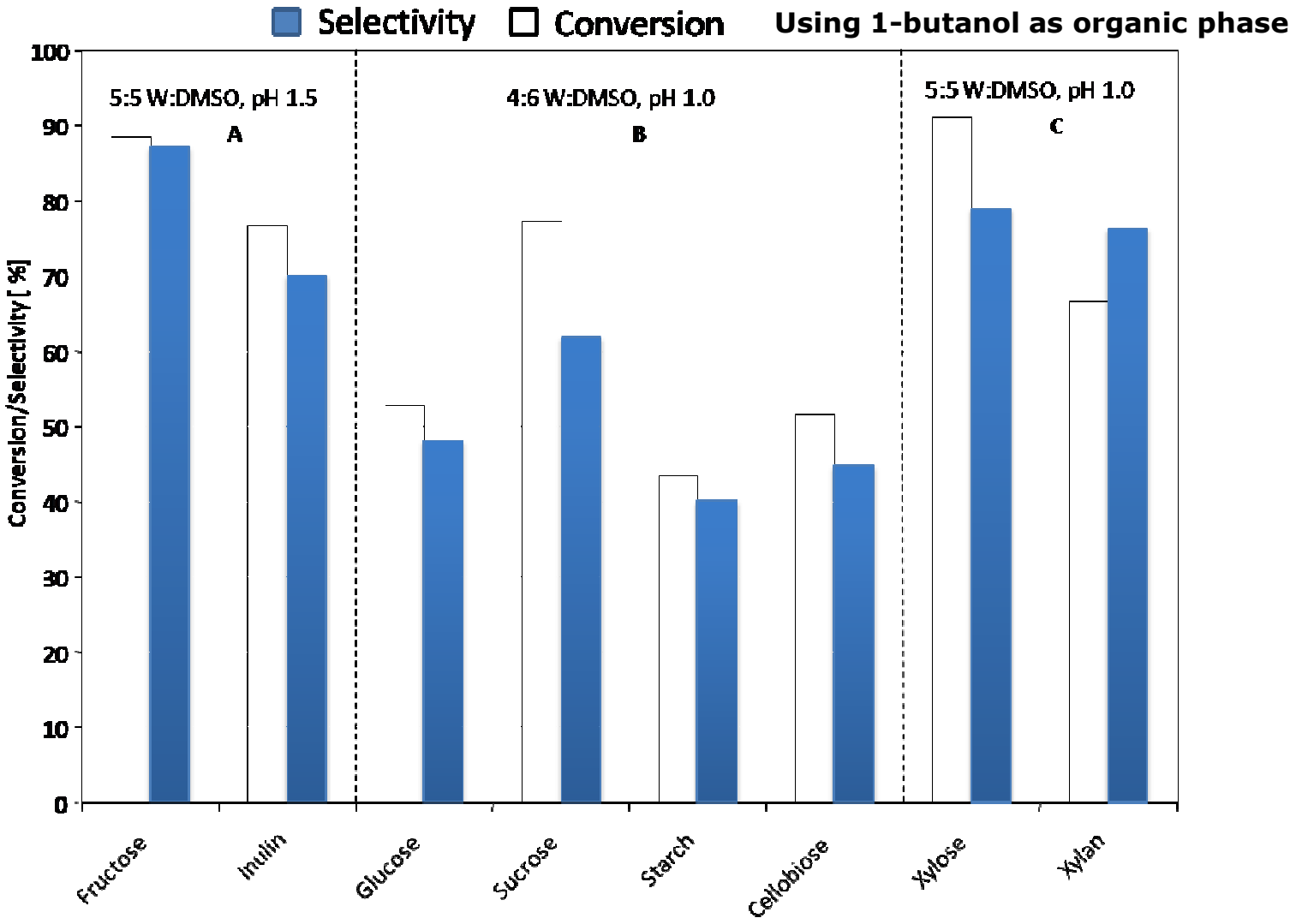


consecutive reactions



parallel reactions

Tunable biphasic system



Kinetic Modeling

R1. Fructose $\xrightarrow{k1}$ HMF_{aq} + H2O

R2. Fructose + Fructose $\xrightarrow{k2}$ Dimer A

R3. Fructose + HMF_{aq} $\xrightarrow{k3}$ Dimer B

R4. HMF_{aq} $\xrightarrow{k4}$ Rehydration/Fragmentation

Req. $HMF_{aq} \overset{Keq}{\rightleftharpoons} HMF_{org}$

Assumptions for model:

a) Conversion = 80%

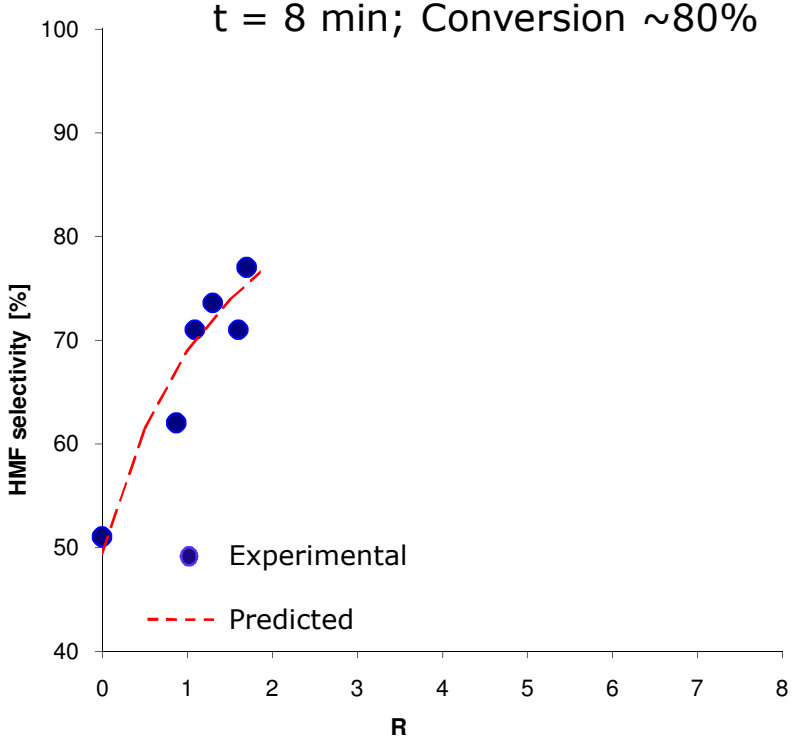
b) [HCl] = 0.015 M (constant)

c) Immediate partitioning of HMF into organic layer (i.e. forward rate constant of Keq is very high)

d) No density or volume changes

e) Water produced not included

30 wt% fructose; 0.015 M HCl; 453 K;
t = 8 min; Conversion ~80%



Predicted parameter values		
k1	0.1952	1/min
k2	0.0079	L/(mol-min)
k3	0.1134	L/(mol-min)
k4	0.1345	1/min)

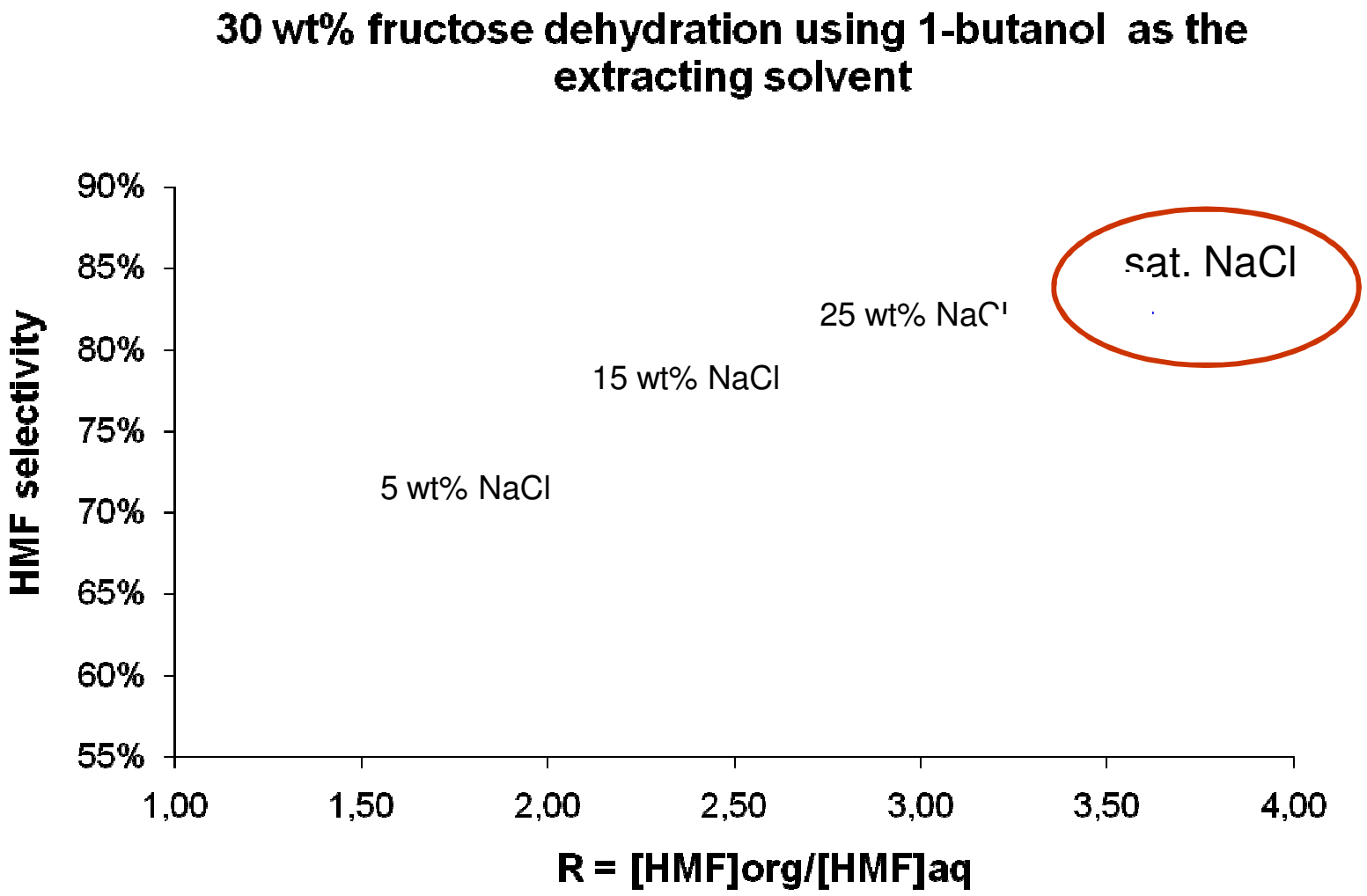
Salting-out effect

In these proportions (Vorg/Vaq = 3), 2-butanol and water should make a single phase solution

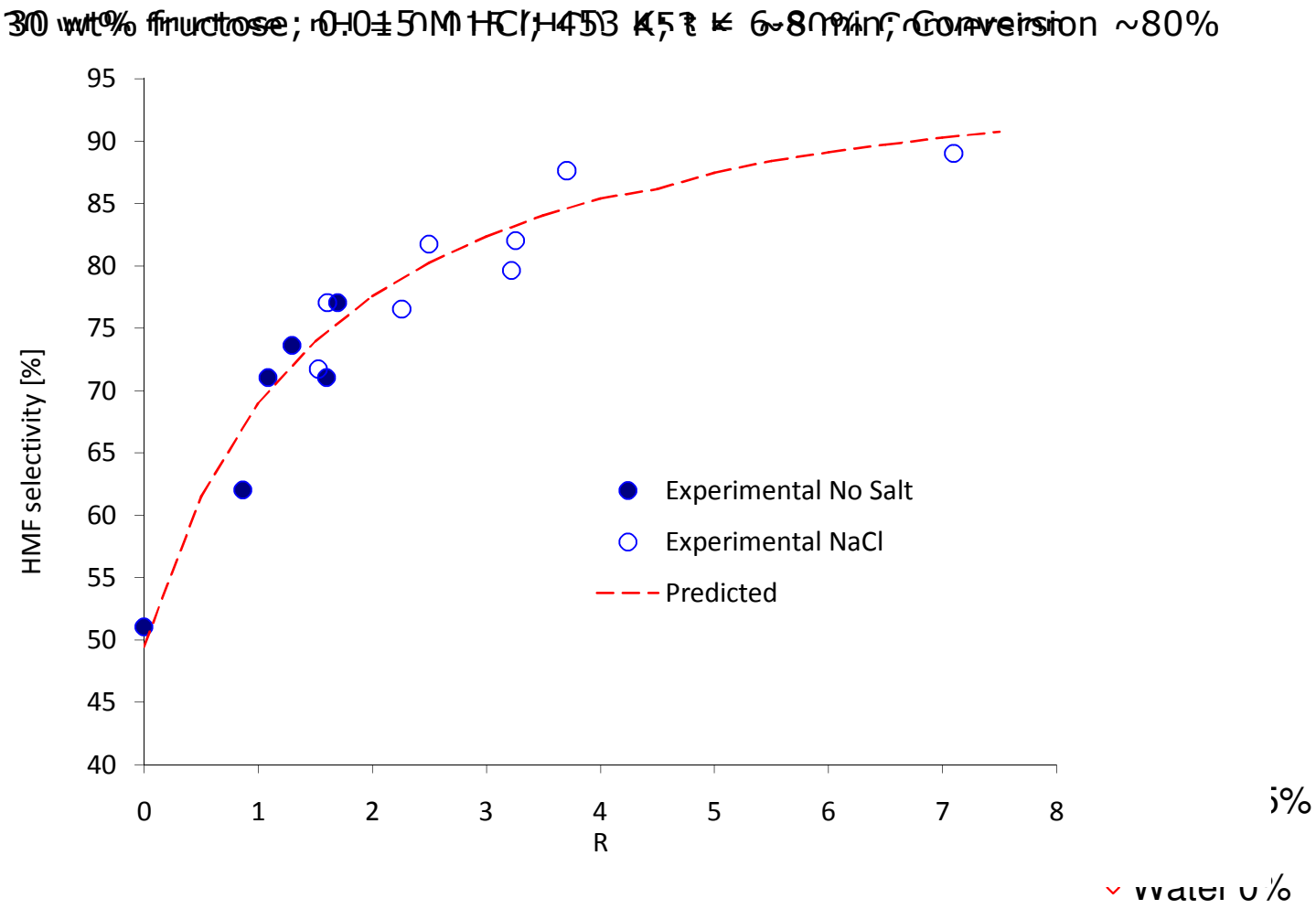
Aqueous layer is saturated with a salt (e.g. NaCl)

- The aqueous solubility of certain compounds decreases in the presence of inorganic salts.
- Weak intermolecular forces (e.g., hydrogen bonds) between organic molecules or non-electrolytes and water are easily disrupted by the hydration of electrolytes.

Effect of R on HMF selectivity

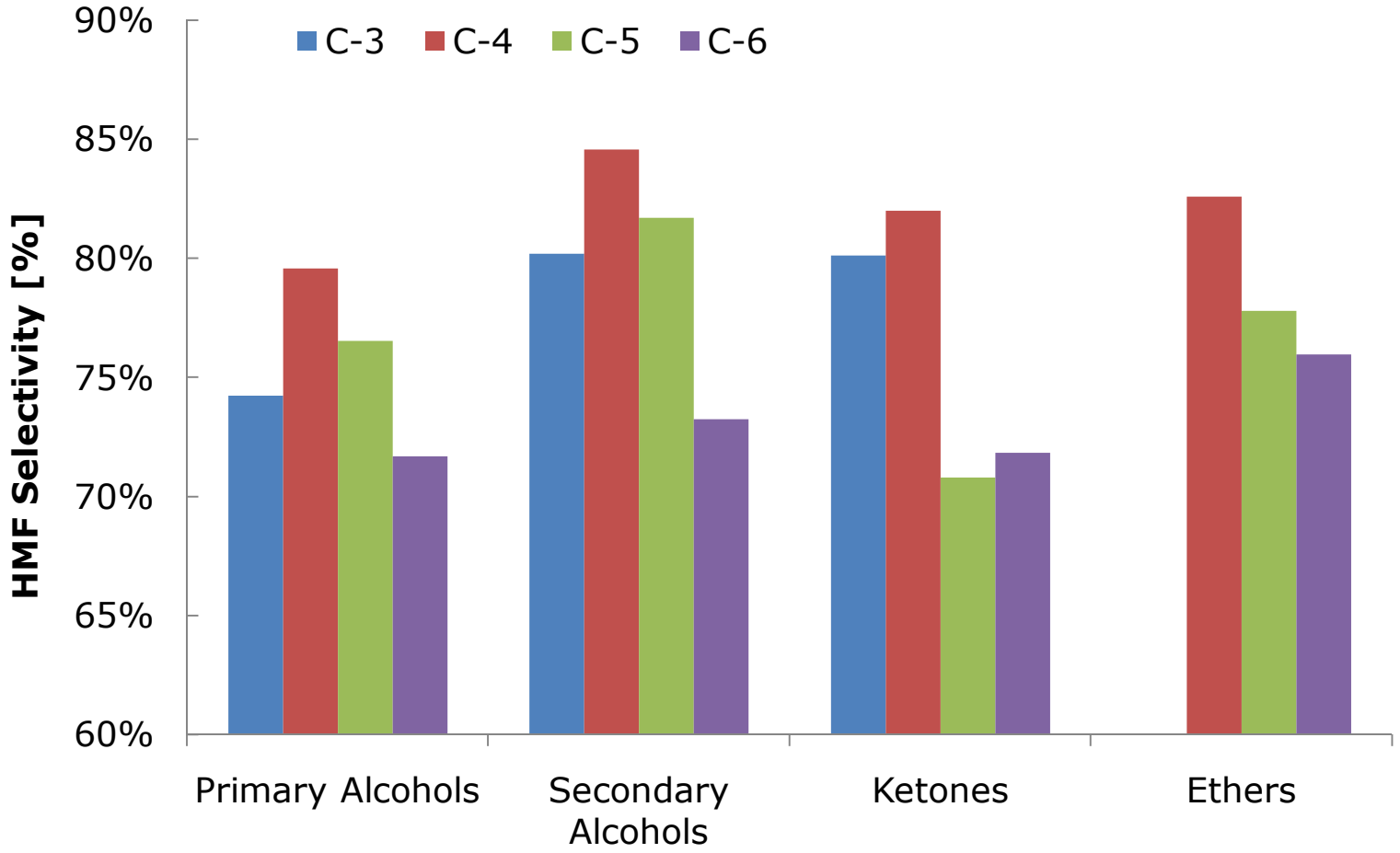


Other solvents



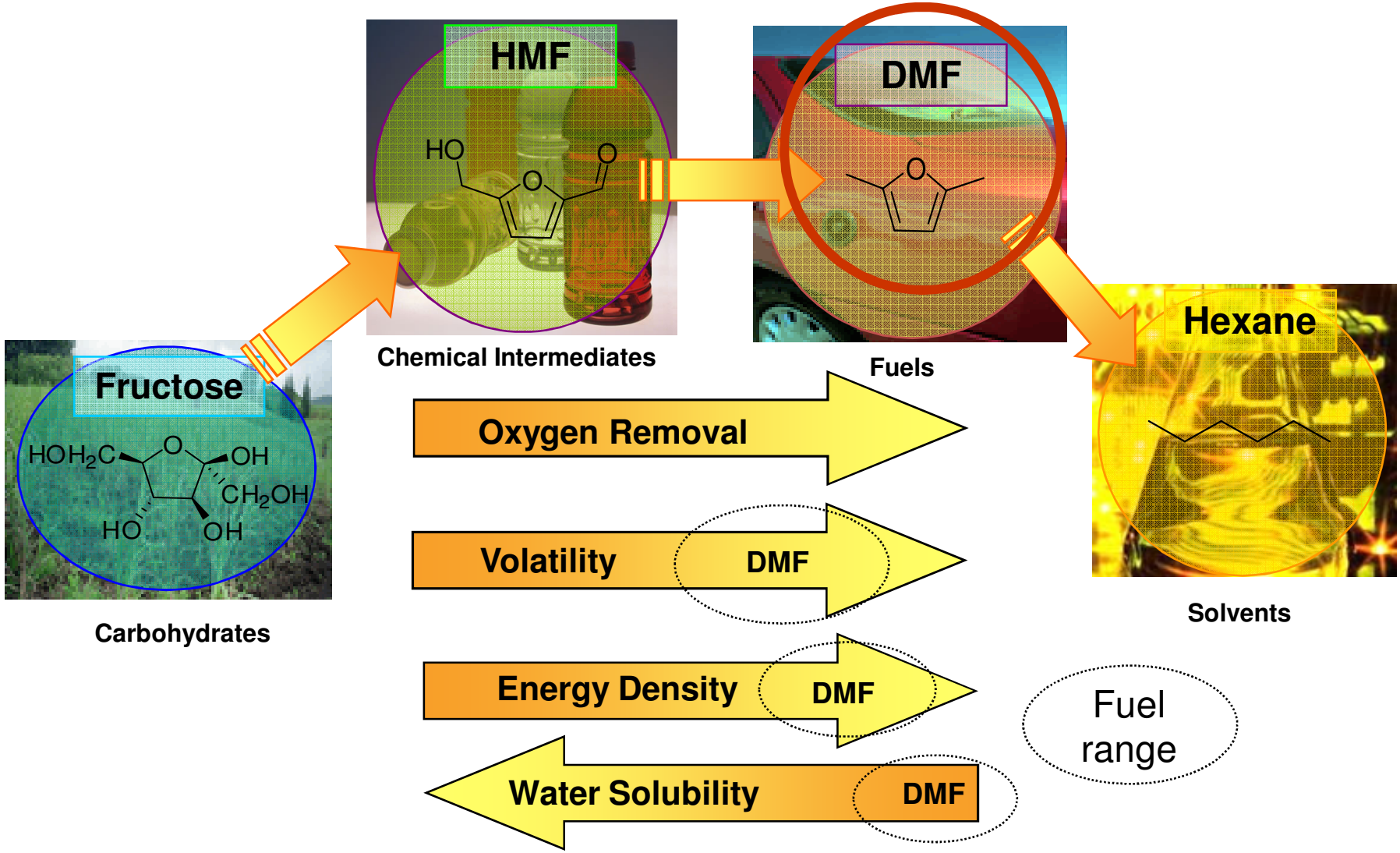
Y. Roman-Leshkov, C.J. Barrett, Z.Y. Liu & J.A. Dumesic, Nature**, 447** *(2007)*

Effect of solvent type

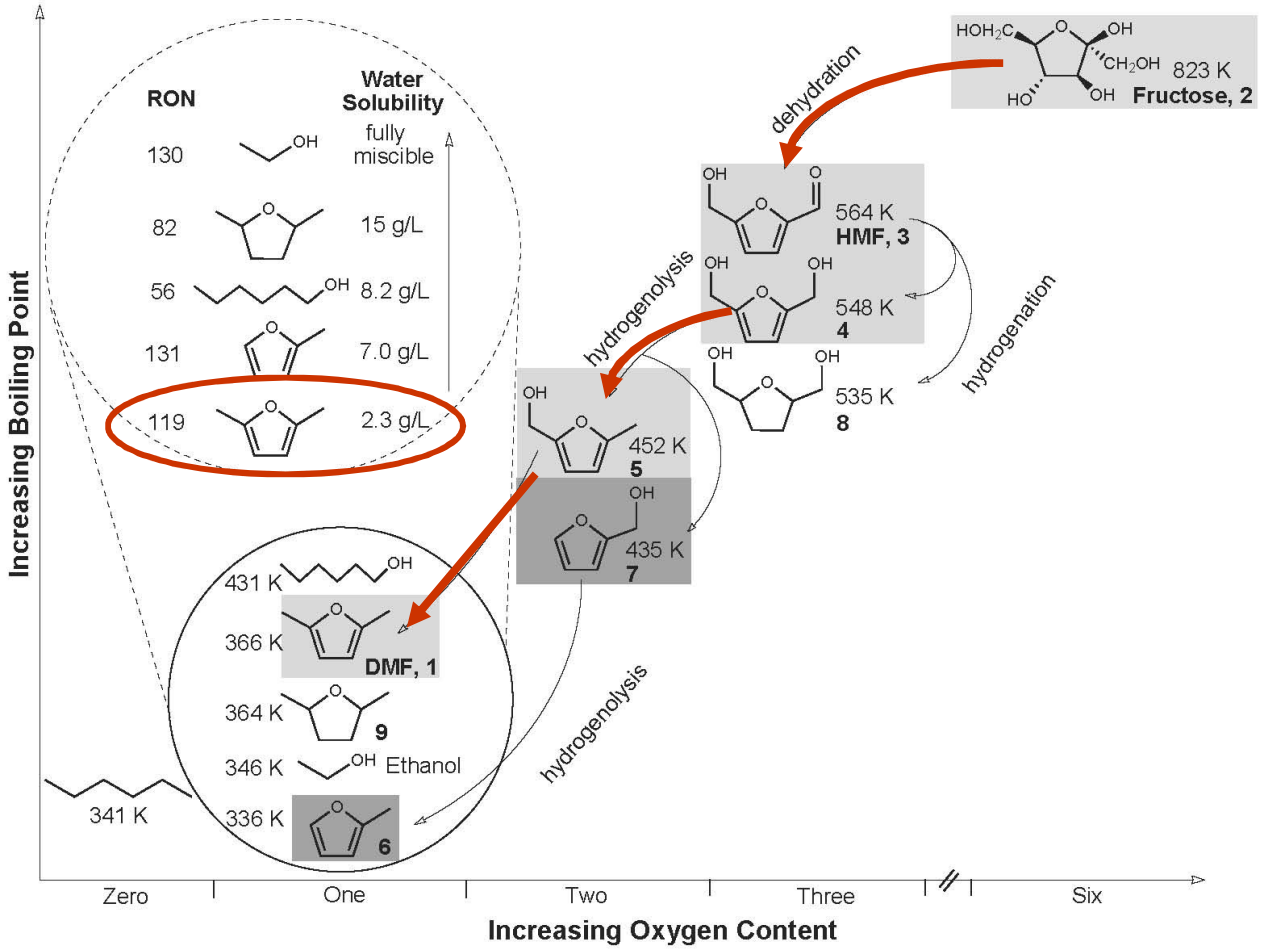


30 wt% fructose (sat NaCl); pH = 1.0 (HCl); 423 K; t = 35 min

2,5 dimethylfuran (DMF) as a biofuel

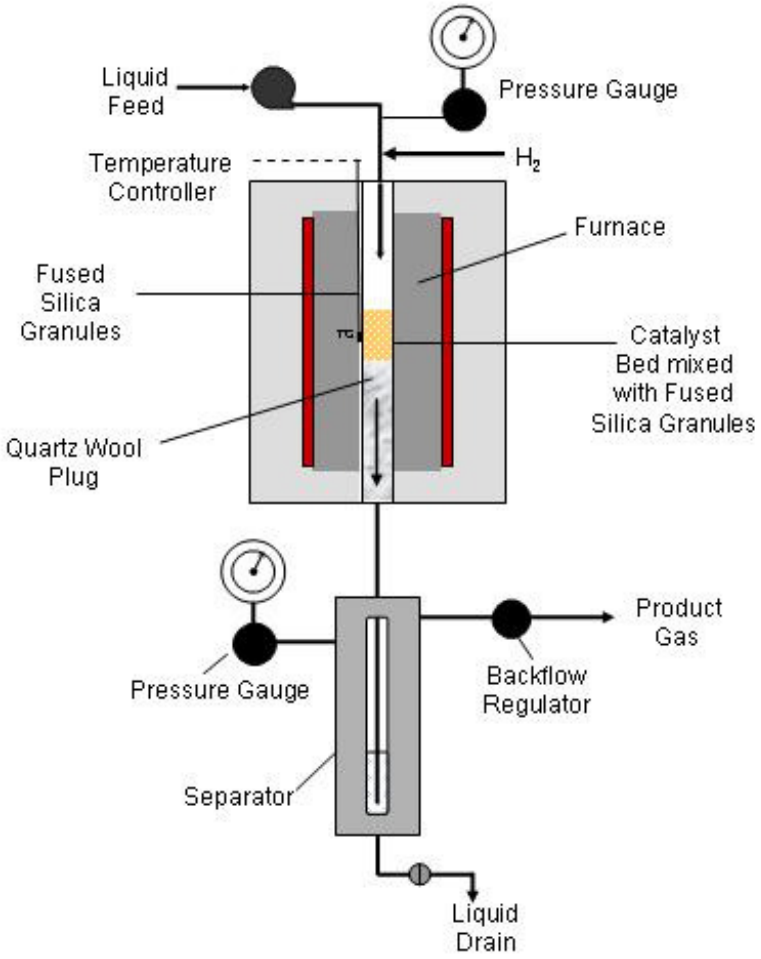


Strategy for DMF synthesis



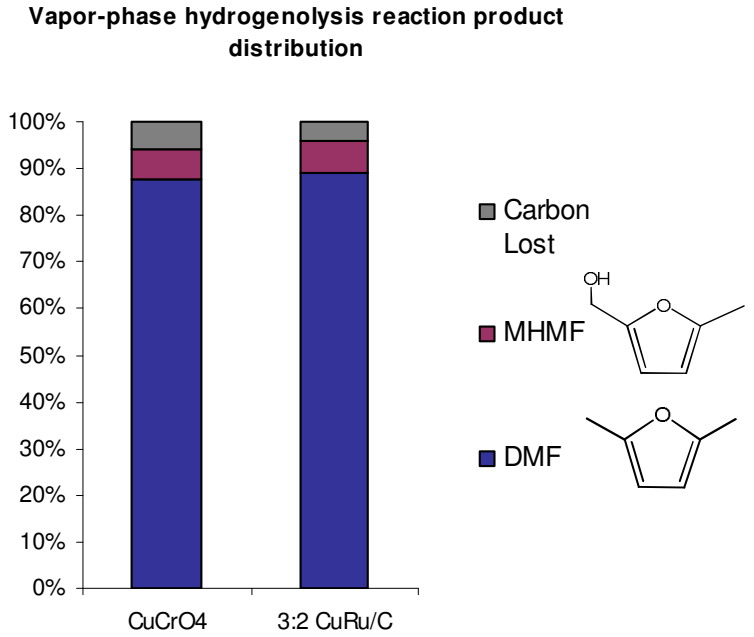
Y. Roman-Leshkov, C.J. Barrett, Z.Y. Liu & J.A. Dumesic, Nature**, 447** *(2007)*

Gas-phase hydrogenolysis

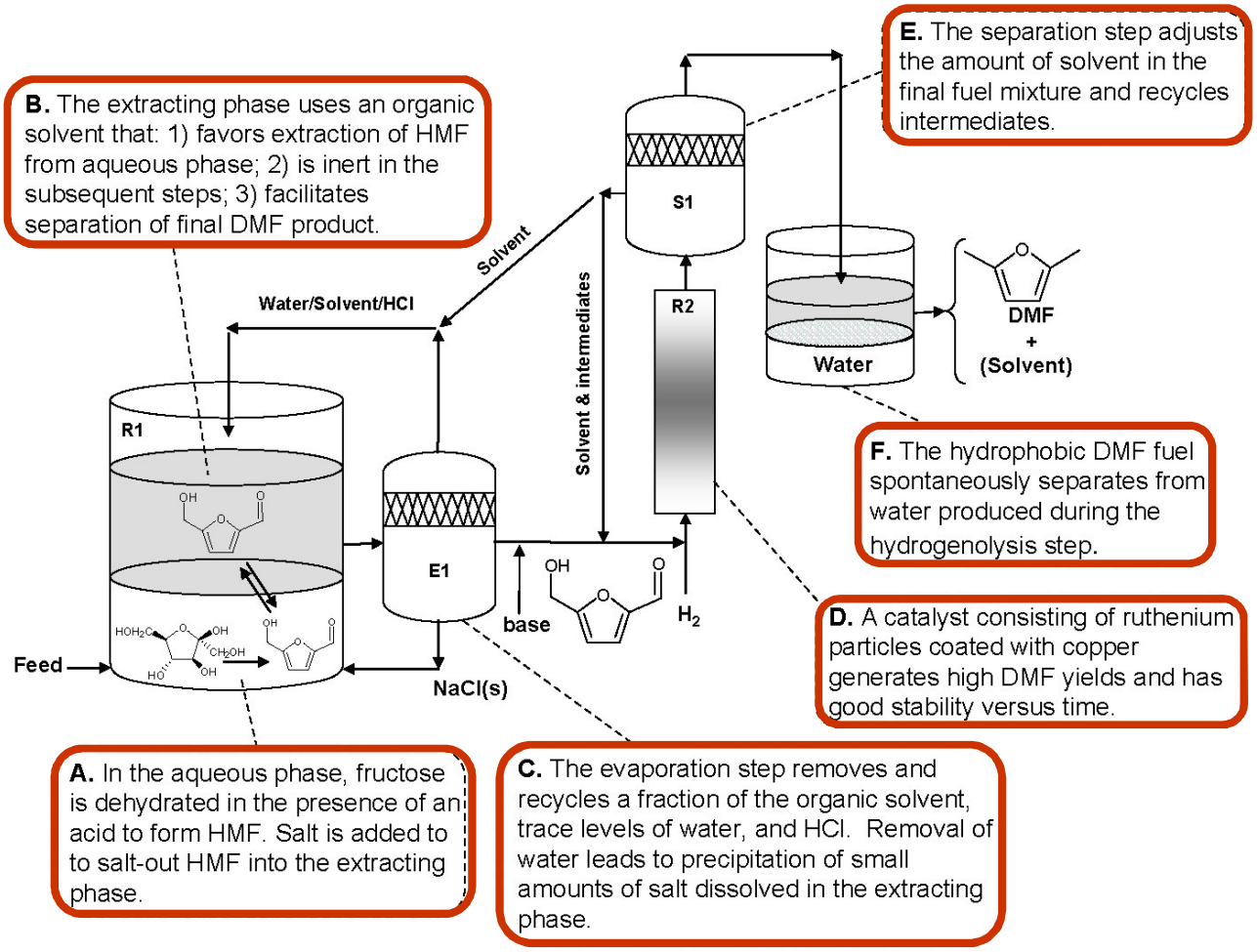


Reaction conditions:

T = 220°C
P = 8 bar
Flow rate = 0.2 ml/min
H_2 flow rate = 20 cm^3(STP)/min
Catalyst: 3:2 Cu:Ru on carbon (10 mol% loading)
m_{cat} = 0.06g
Feed = 5 wt% HMF



DMF production process

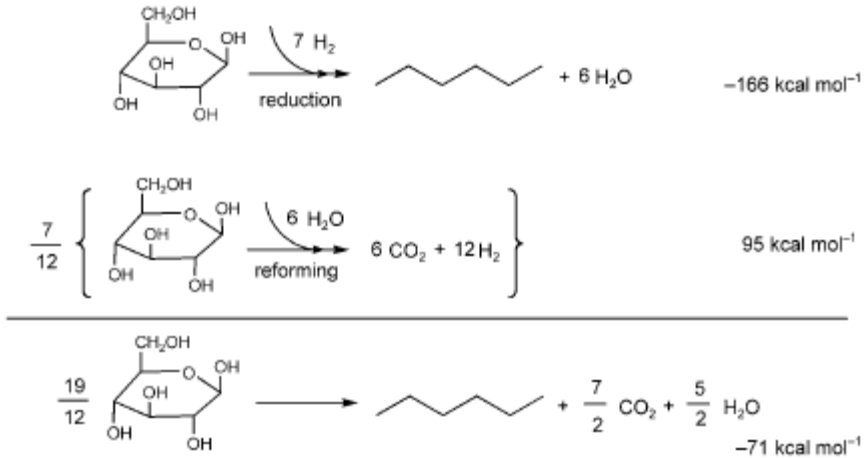


Y. Roman-Leshkov, C.J. Barrett, Z.Y. Liu & J.A. Dumesic, Nature**, 447** *(2007)*

Production of targeted liquid alkanes

Conversion strategies are needed to produce fuels from biomass with physical properties equal to those currently found in petroleum-based fuels (i.e. liquid alkanes in the C_9-C_{15} range)

Glucose can be effectively converted to hexane by APD/H[1] over a bifunctional catalyst



$$\frac{\text{Hexane Energy}}{\text{Glucose Energy}} = 93\% \qquad \frac{\text{Reforming Energy}}{\text{Glucose Energy}} = 9\%$$

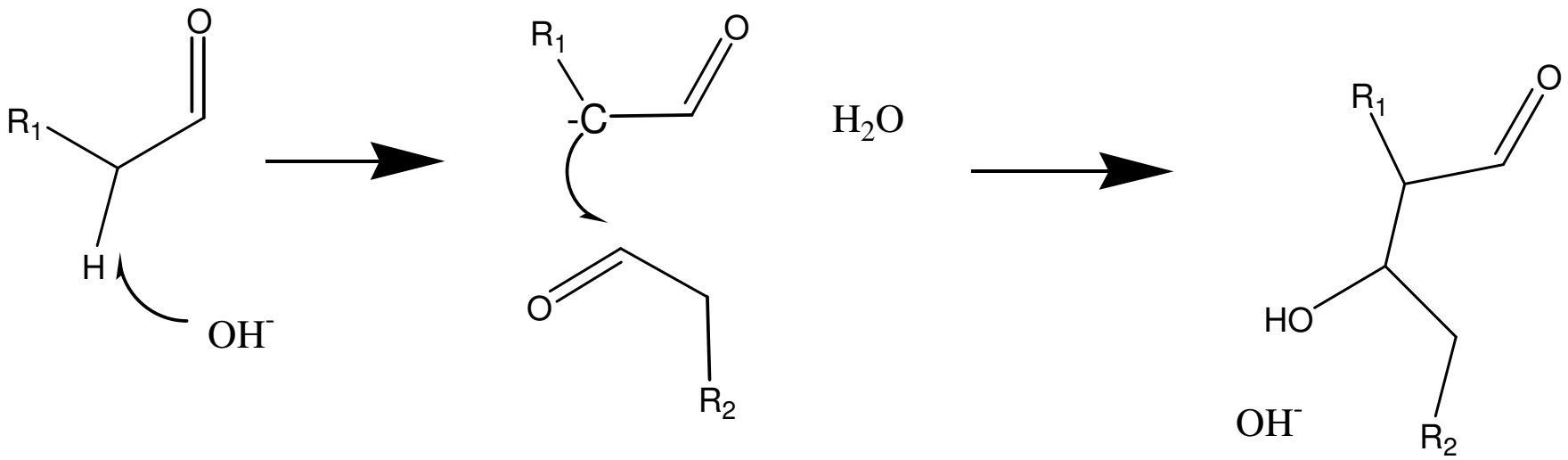
$$\frac{\text{Hexane Mass}}{\text{Glucose Mass}} = 30\%$$

(Ref. 2)

1. Hexane is too volatile to be used in large quantities in fuel.
2. C-C coupling reactions of alkanes are difficult.

1. Huber, G.W.; Cortright, R.D.; and Dumesic, J.A. *Angewandte Chemie International Edition* (2004).
2. Simonetti, D,; and Dumesic, J.A. *ChemSusChem* (2008)

Aldol condensation



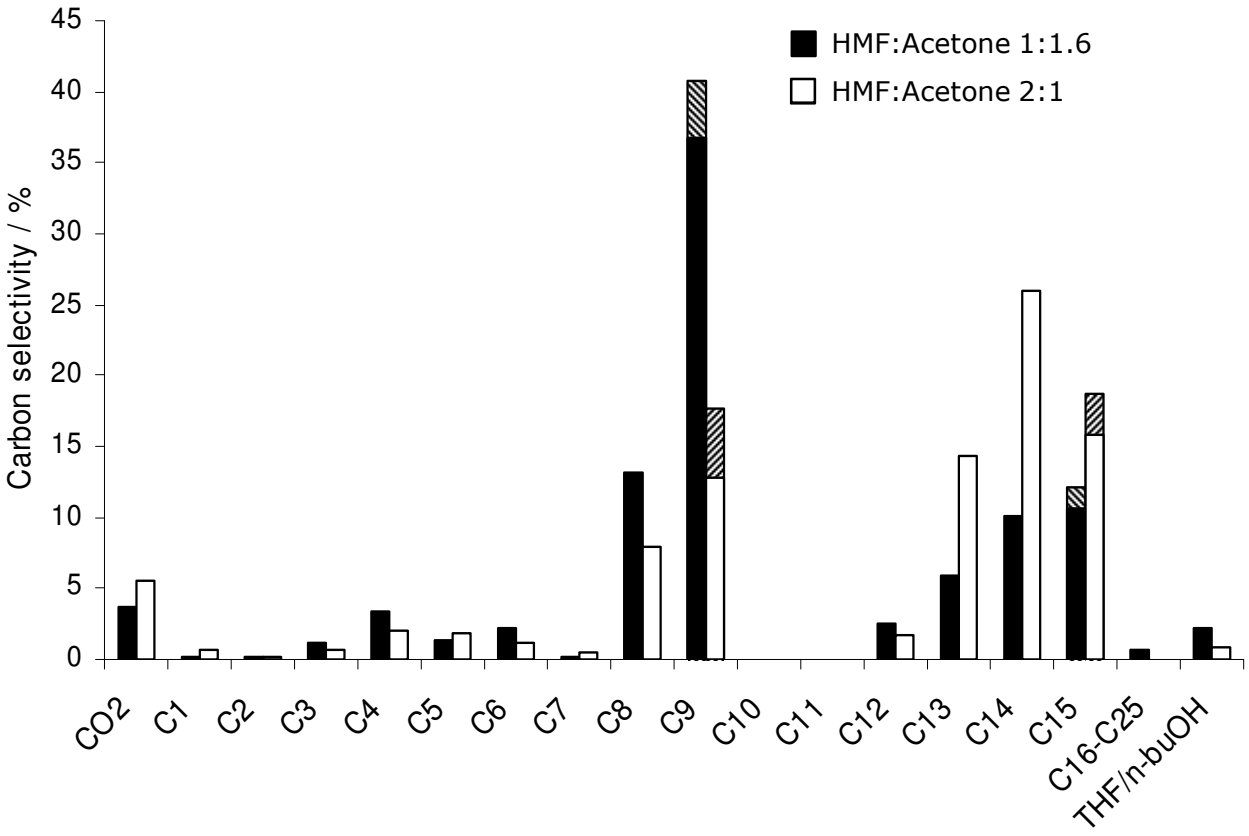
- Aldol condensation is commonly used for C-C bond forming.
- Involves reacting aldehydes or ketones.
- Catalyzed by mineral or solid base.
- Very selective (> 80 % yields).

Production of targeted liquid alkanes

HMF

Huber, G. W.; Chheda, J.; Barrett, C. B.; and Dumesic, J. A., *Science*, **308** (2005).

Final product distribution



For HMF:Acetone 1:1.6

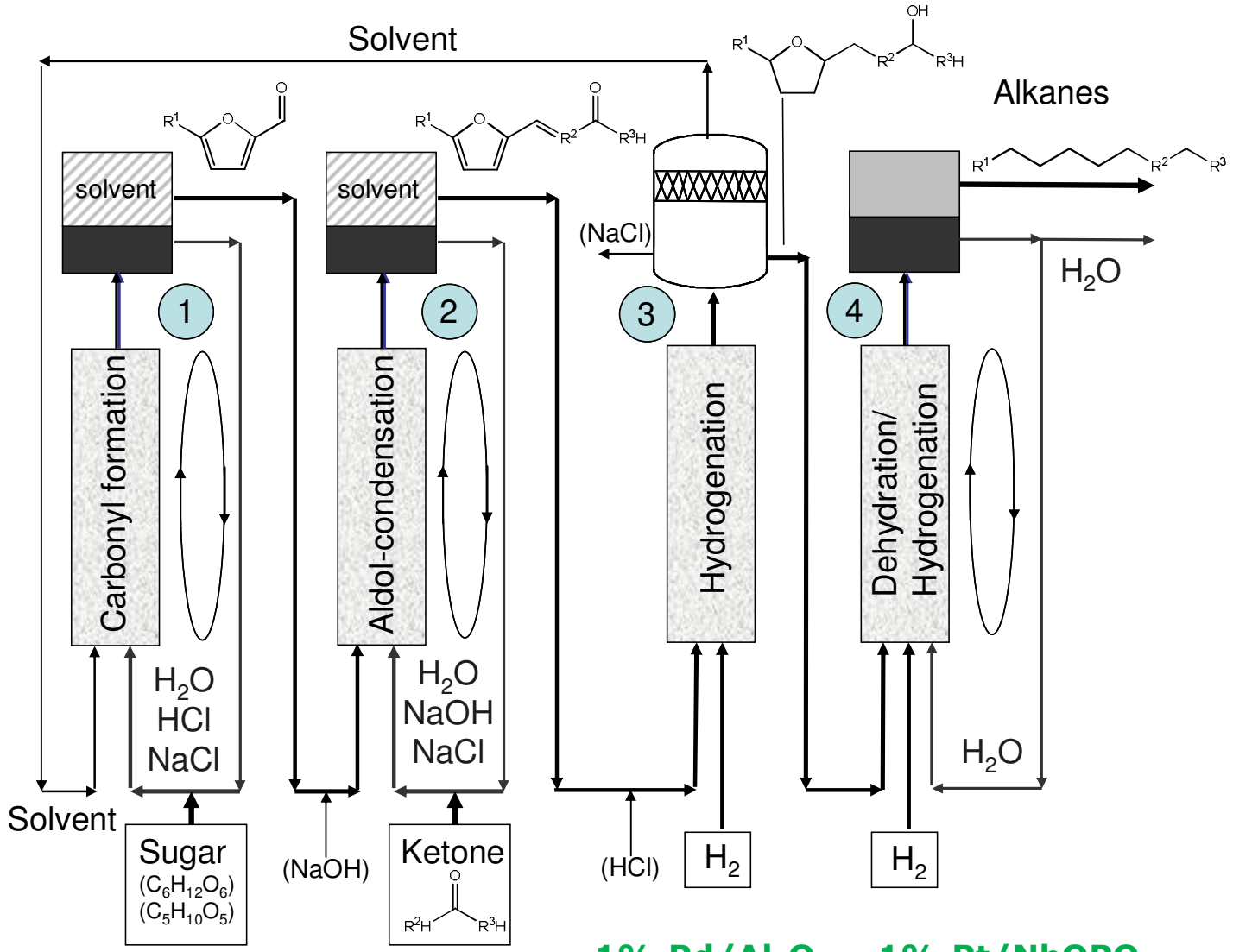
Fructose to HMF Yield	**75%**
HMF to Alkanes Total Yield	**94%**
HMF to C_7-C_{15} Yield	**90%**
Furfural to C_5-C_6 Yield	*3%*
Furfural to C_7-C_9 Yield	*51%*
Furfural to C_{10}-C_{15} Yield	*39%*
Furfural to C_{15}+ Yield	*1%*

For HMF:Acetone 2:1

Fructose to HMF Yield	**75%**
HMF to Alkanes Total Yield	**79%**
HMF to C_7-C_{15} Yield	**74%**
Furfural to C_5-C_6 Yield	*4%*
Furfural to C_7-C_9 Yield	*20%*
Furfural to C_{10}-C_{15} Yield	*54%*
Furfural to C_{15}+ Yield	*0%*

West, R. et al. *ChemSusChem* (2008).

Targeted liquid alkane production process



West, R. et al. *ChemSusChem* (2008).

Conclusions

- Salt-out effect was used to increase extracting ratio R in a biphasic system, thereby obtaining high HMF yields and high HMF concentrations from fructose in a separation friendly solvent.

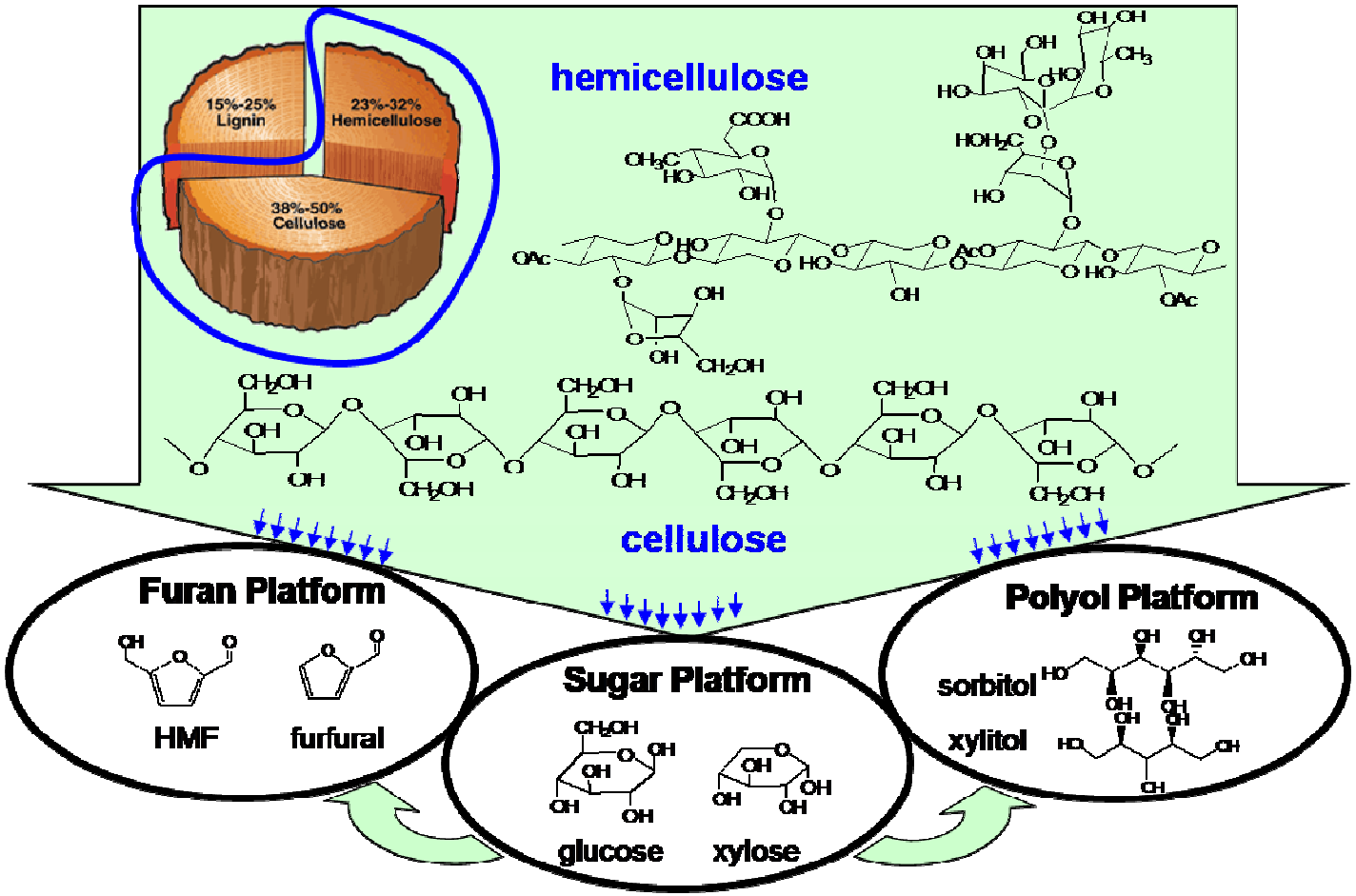
- Fructose was successfully converted into DMF, which could be used as a new oxygenated fuel additive.

- Alternatively, fructose can be converted into liquid alkanes with targeted molecular weights using a series of simple thermochemical transformations.

- **While results are promising, many challenges lie ahead…**

Biomass conversion bottlenecks

1. Economical conversion technologies for the hydrolysis of cellulose into simple sugars, furans, or polyols, have not been developed



Biomass conversion bottlenecks

2. There exist various selectivity issues related to the dehydration of glucose.

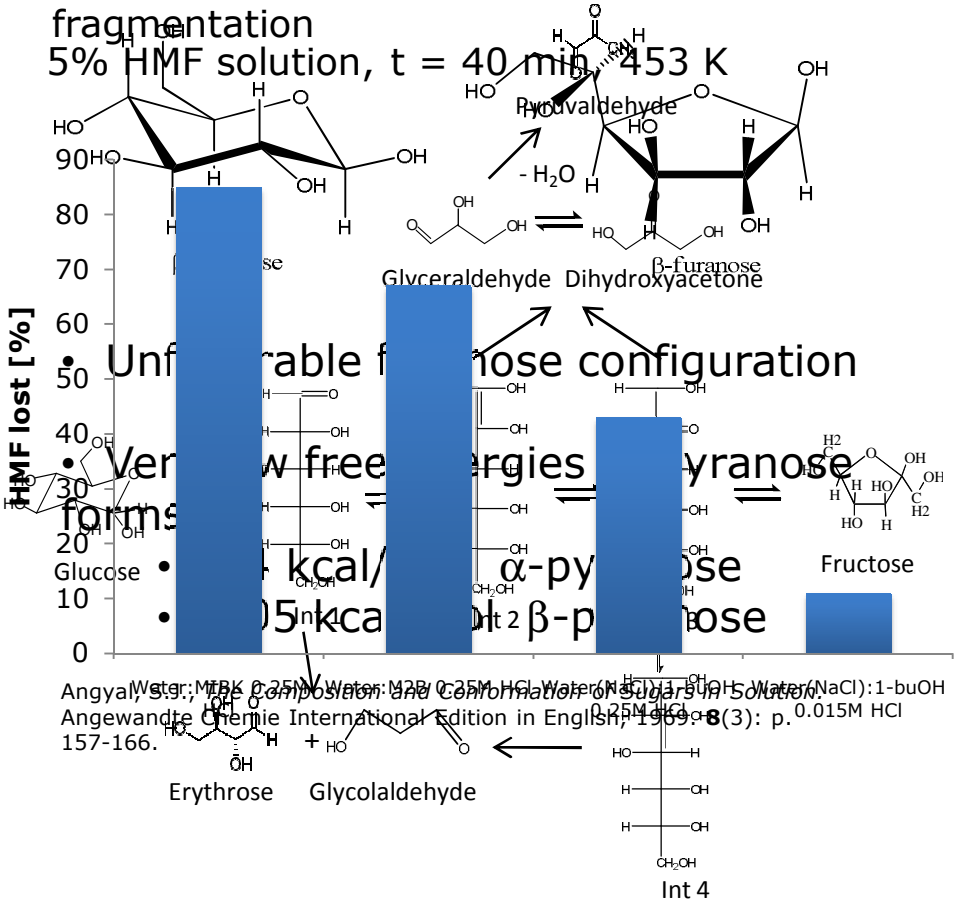
10 wt% glucose; 453 K

Aqueous Phase	Organic Phase	Catalyst	Conversion [%]	Selectivity [%]	R	Time [min]
Water	-	HCl 0.25M	56	6	-	120
Water	MIBK	HCl 0.25M	41	9	1	60
Water	MIBK:2-butanol	HCl 0.25M	65	11	1.6	35
Water (NaCl)	1-butanol	HCl 0.25M	59	24	3.1	41
Water (NaCl)	1-butanol	HCl 0.015M	48	18	3.1	120
Fructose Water (NaCl)	1-butanol	HCl 0.25M	89	79	3.1	4
Fructose Water (NaCl)	1-butanol	HCl 0.015M	84	82	3.1	7

Glucose can undergo several side reactions, including oligomerization and fragmentation

Glucose has stable pyranose ring structures:

5% HMF solution, t = 40 min, 453 K

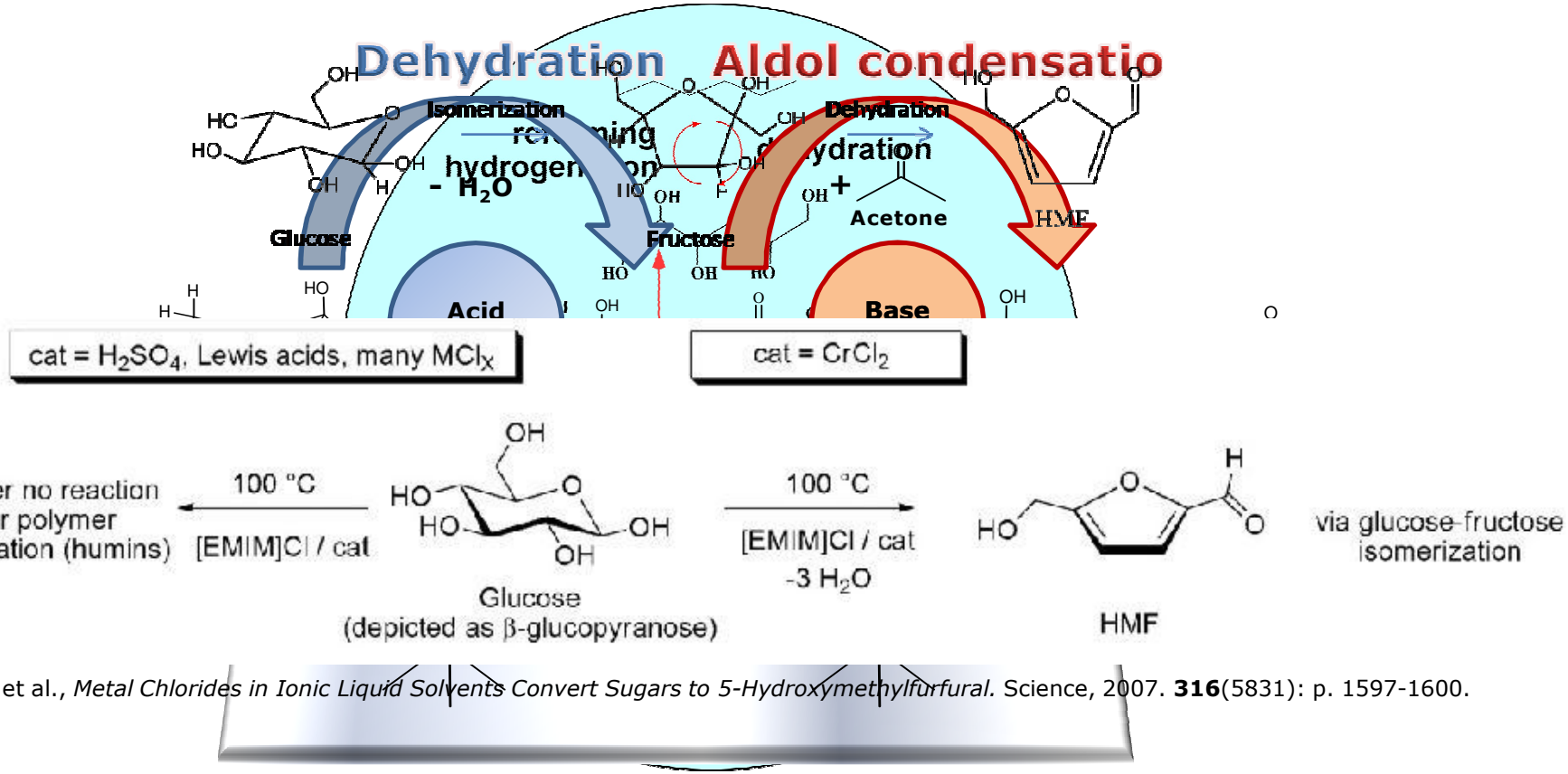


- Unfavorable furanose configuration
- Very low free energies of pyranose forms
- kcal/mol α-pyranose
- 0.5 kcal/mol β-pyranose

Angyal, S.J.; *The Composition and Conformation of Sugars in Solution.* Angewandte Chemie International Edition in English, 1969. **8**(3): p. 157-166.

Biomass conversion bottlenecks

3. Catalytic coupling of various chemical reactions in order to consolidate unit operations and minimize costs during biorefining is still in its infancy.



Zhao, H., et al., *Metal Chlorides in Ionic Liquid Solvents Convert Sugars to 5-Hydroxymethylfurfural.* Science, 2007. **316**(5831): p. 1597-1600.

Future outlook

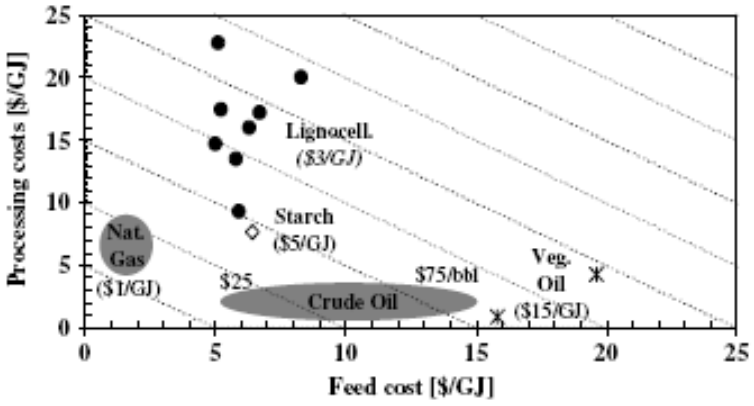


Figure 4. Feed and processing cost of transportation fuels derived from lignocellulose and fossil resources (the biofuel plants are set at 400 MW intake, which corresponds to ~680 kt/a of lignocellulose[1]).

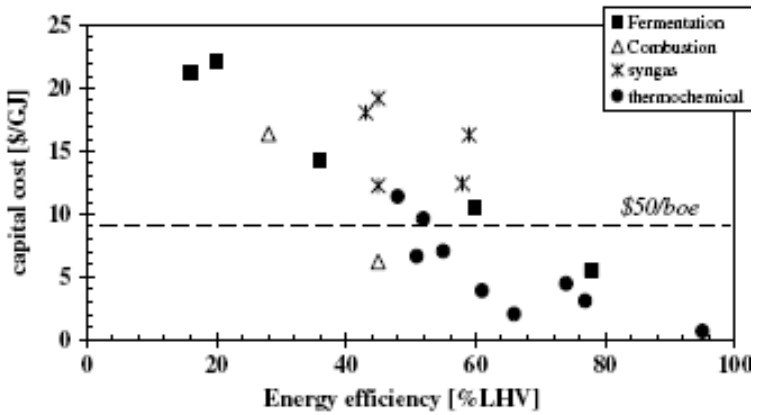
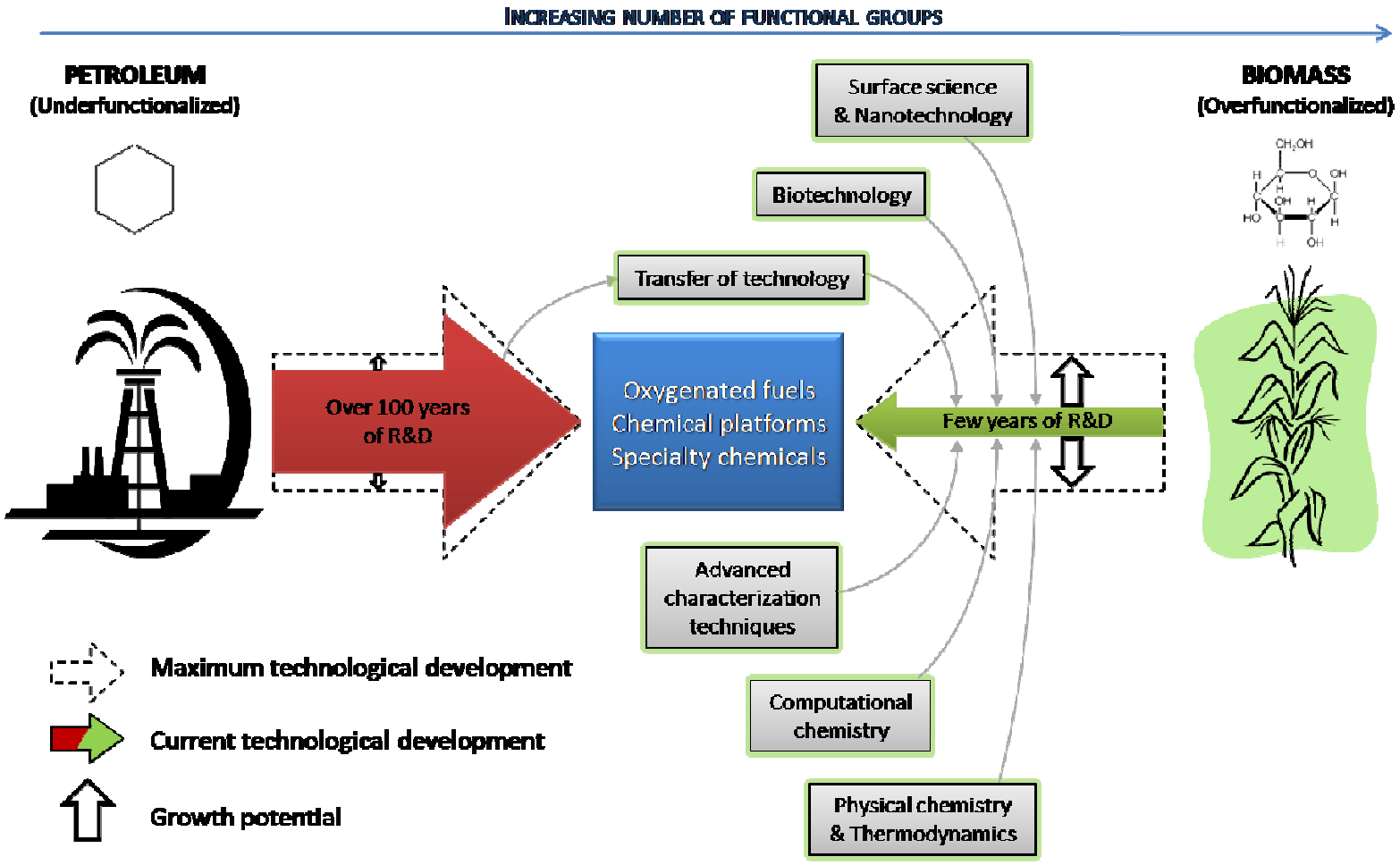


Figure 5. Capital cost of biomass conversion plants (400 MW intake, 25% capital charge, $2005[1]).

High costs associated with biomass-derived fuels originate from processing costs or lack of technological development rather than feed cost.

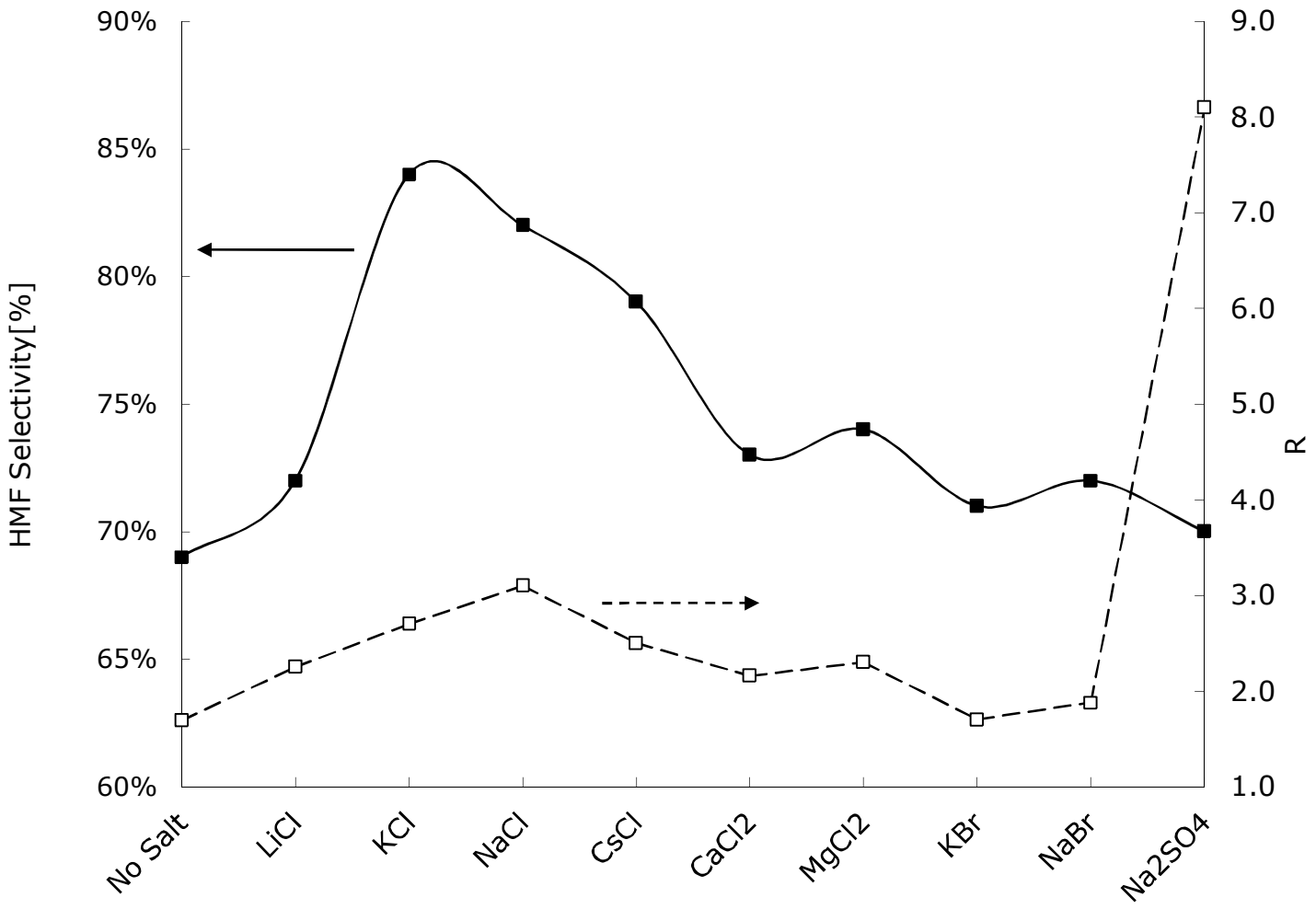
Lange, J.P. Biofpr, **1** *(2007)*

Future outlook for chemical transformations



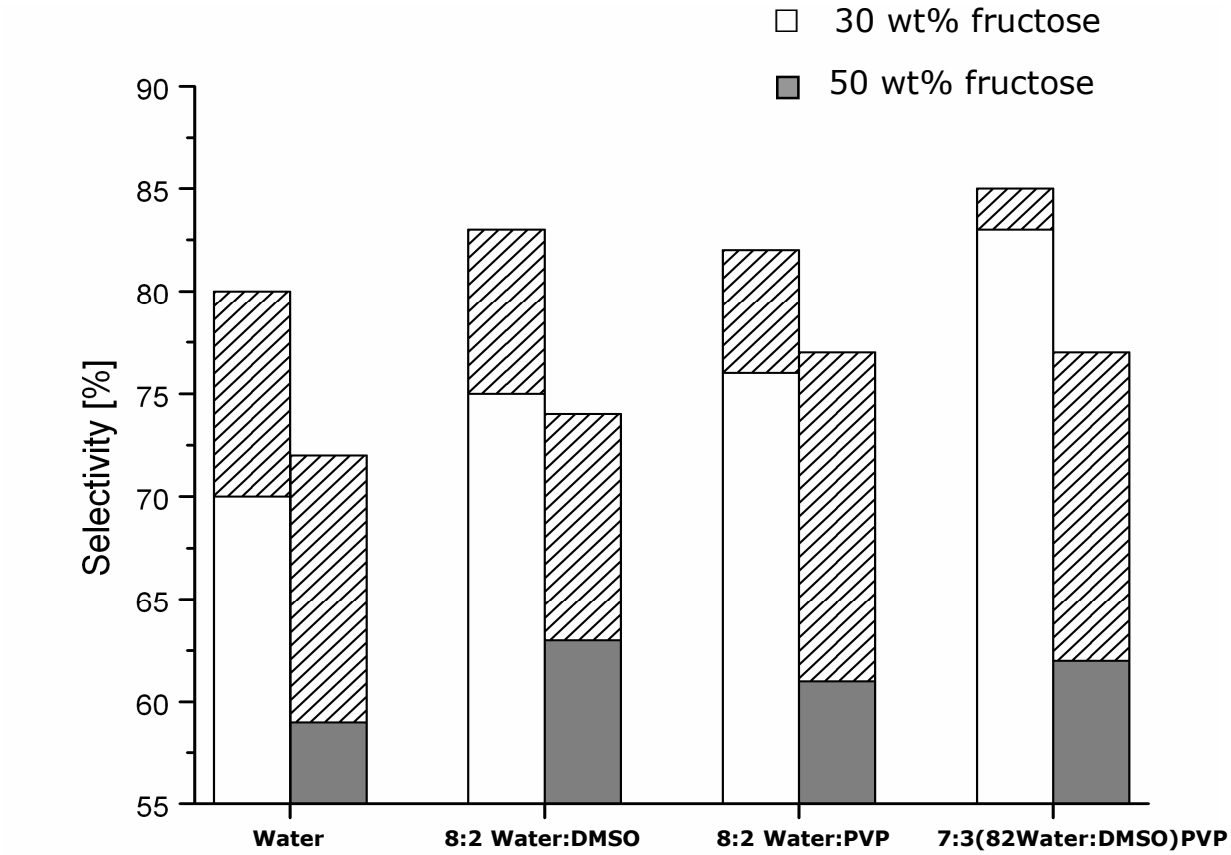
QUESTIONS?

Effect of salt type



30 wt% fructose; 1-butanol as OL; pH = 1.0 (HCl); 423 K; t = 35 min

Effect of doubling V_{org}/V_{aq}



Y. Roman-Leshkov, J.Chheda, & J.A. Dumesic, Science, **312** *(2006)*

Kinetic model

R1 = k1*cf
R2 = k2*cf^2
R3 = k3*chmfaq*cf
R4 = k4*chmfaq
Req = keq*chmfaq – keq/R 8*chmforg*Z

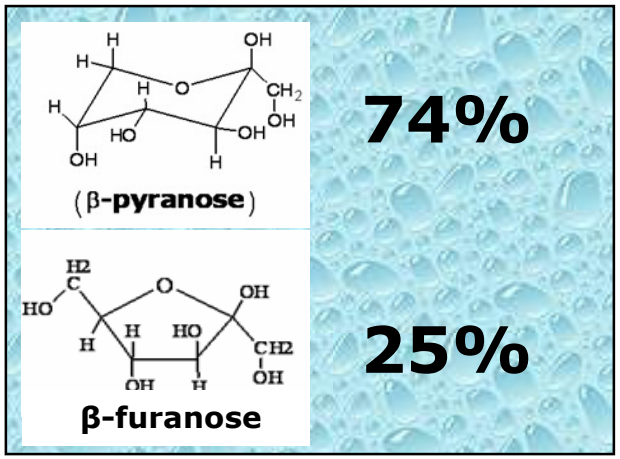
Differential equations that are solved:

Df/dt = -r1 -2*r2 – r4
Dhmfaq/dt = r1 –r4 –r3 – rhmfeq
dhmforg/dt = rhmfeq/Z

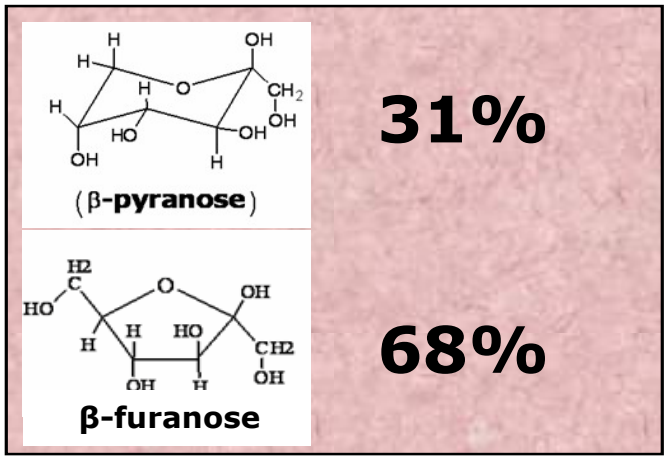
Goal 1: Why use DMSO?

- In solution, sugars exist in different structural configurations called tautomers.

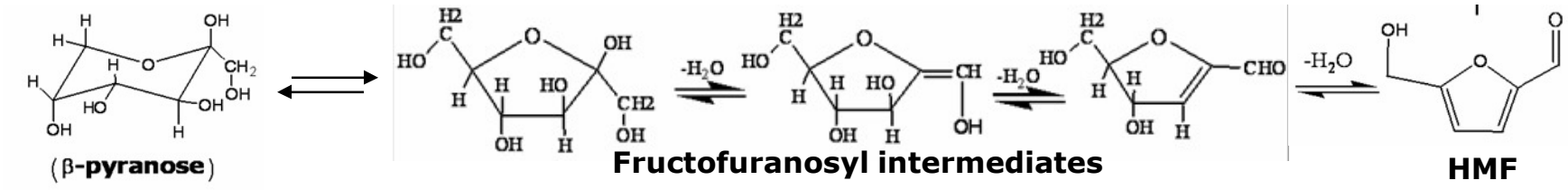
Fructose in water



Fructose in DMSO



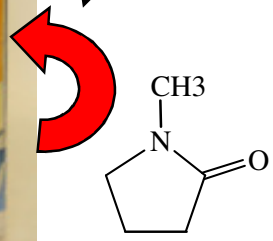
Possible reaction pathway:



Why PVP?

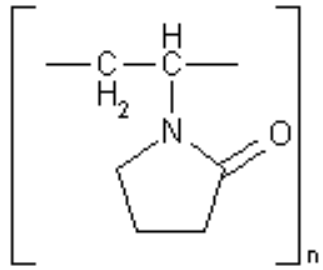
- Eliminate carry-over
  - NMP vs PVP evidence

Carry-over is >30%



N-Methyl-2-pyrrolidinone

Carry-over is negligible



polyvinyl-pyrrolidone)

Glucose dehydration

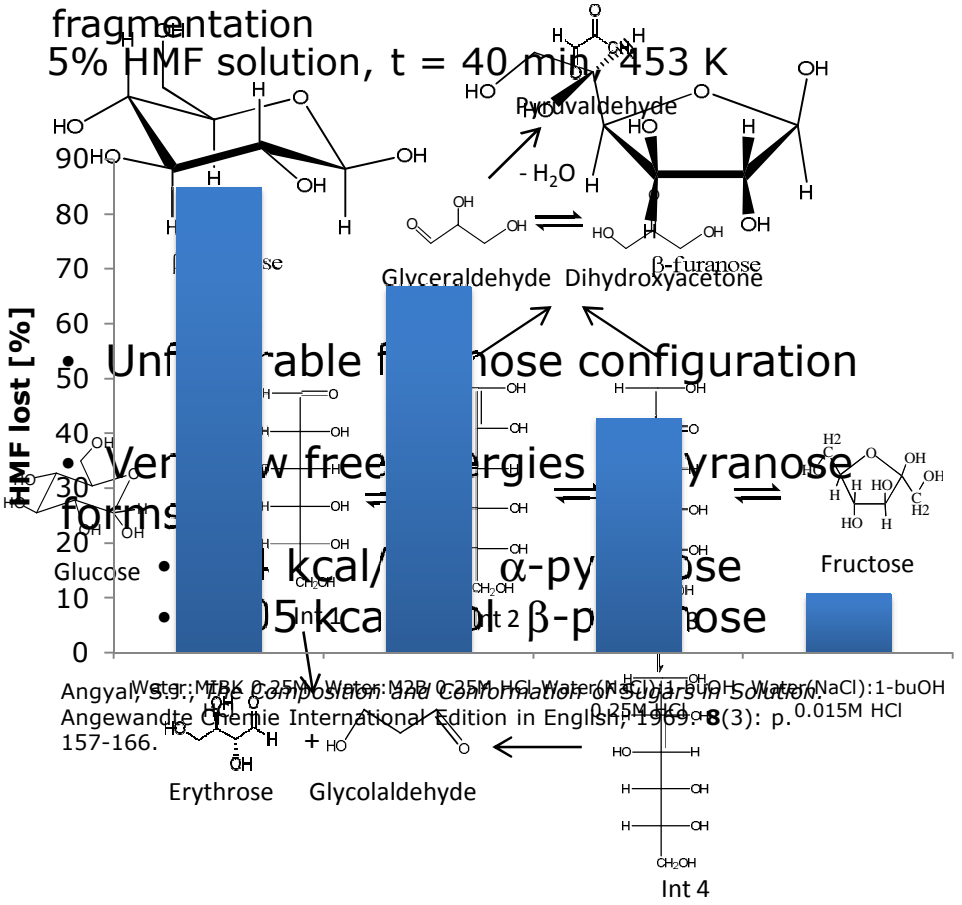
10 wt% glucose; 453 K

Aqueous Phase	Organic Phase	Catalyst	Conversion [%]	Selectivity [%]	R	Time [min]
Water	-	HCl 0.25M	56	6	-	120
Water	MIBK	HCl 0.25M	41	9	1	60
Water	MIBK:2-butanol	HCl 0.25M	65	11	1.6	35
Water (NaCl)	1-butanol	HCl 0.25M	59	24	3.1	41
Water (NaCl)	1-butanol	HCl 0.015M	48	18	3.1	120
Fructose Water (NaCl)	1-butanol	HCl 0.25M	89	79	3.1	4
Fructose Water (NaCl)	1-butanol	HCl 0.015M	84	82	3.1	7

Glucose can undergo several side reactions, including oligomerization and fragmentation

Glucose has stable pyranose ring structures:

5% HMF solution, t = 40 min, 453 K



• Unfavorable furanose configuration

• Very low free energies of pyranose forms

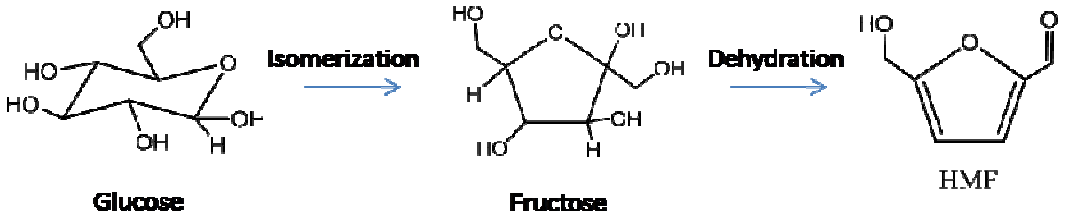
• kcal/mol α-pyranose

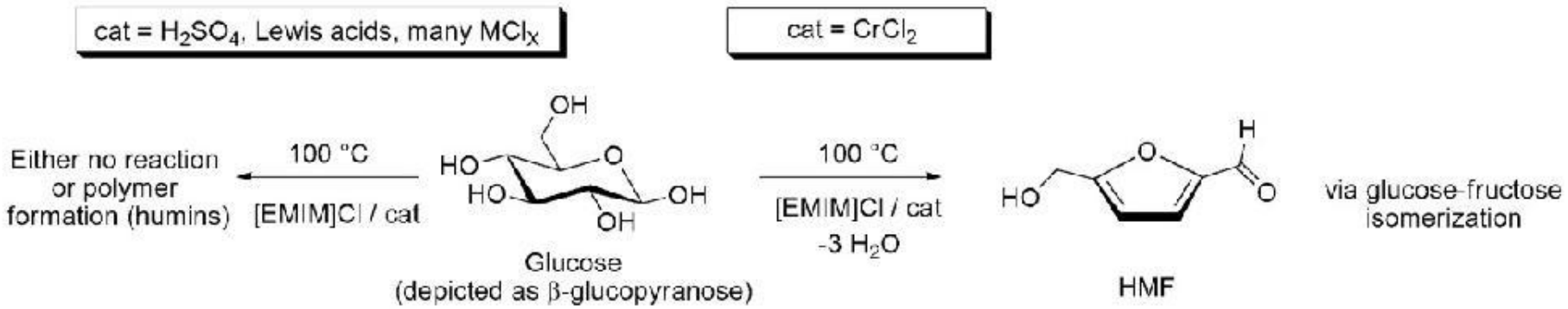
• 05 kcal/mol β-pyranose

Angyal, S.J.; *The Composition and Conformation of Sugars in Solution*. Angewandte Chemie International Edition in English, 1969. **8**(3): p. 157-166.

Sequential Isomerization/Dehydration

Glucose conversion to HMF by way of fructose would be more efficient





Zhao, H., et al., *Metal Chlorides in Ionic Liquid Solvents Convert Sugars to 5-Hydroxymethylfurfural.* Science, 2007. **316**(5831): p. 1597-1600.

Reaction conditions:
- T = 100 C
- Time = 3 hours
- Catalyst amount 6 mol% wrt sugar

Results for glucose
- Conversion 90%
- Selectivity 70%

Equilibrium Constant: Glucose Isomerization

- Thermodynamics of glucose isomerization in aqueous solution

ΔH°=2.78± 0.20 kJ/mol

ΔCp°=0.076±0.03 kJ/mol K

ΔS°= 8.15 J/mol K

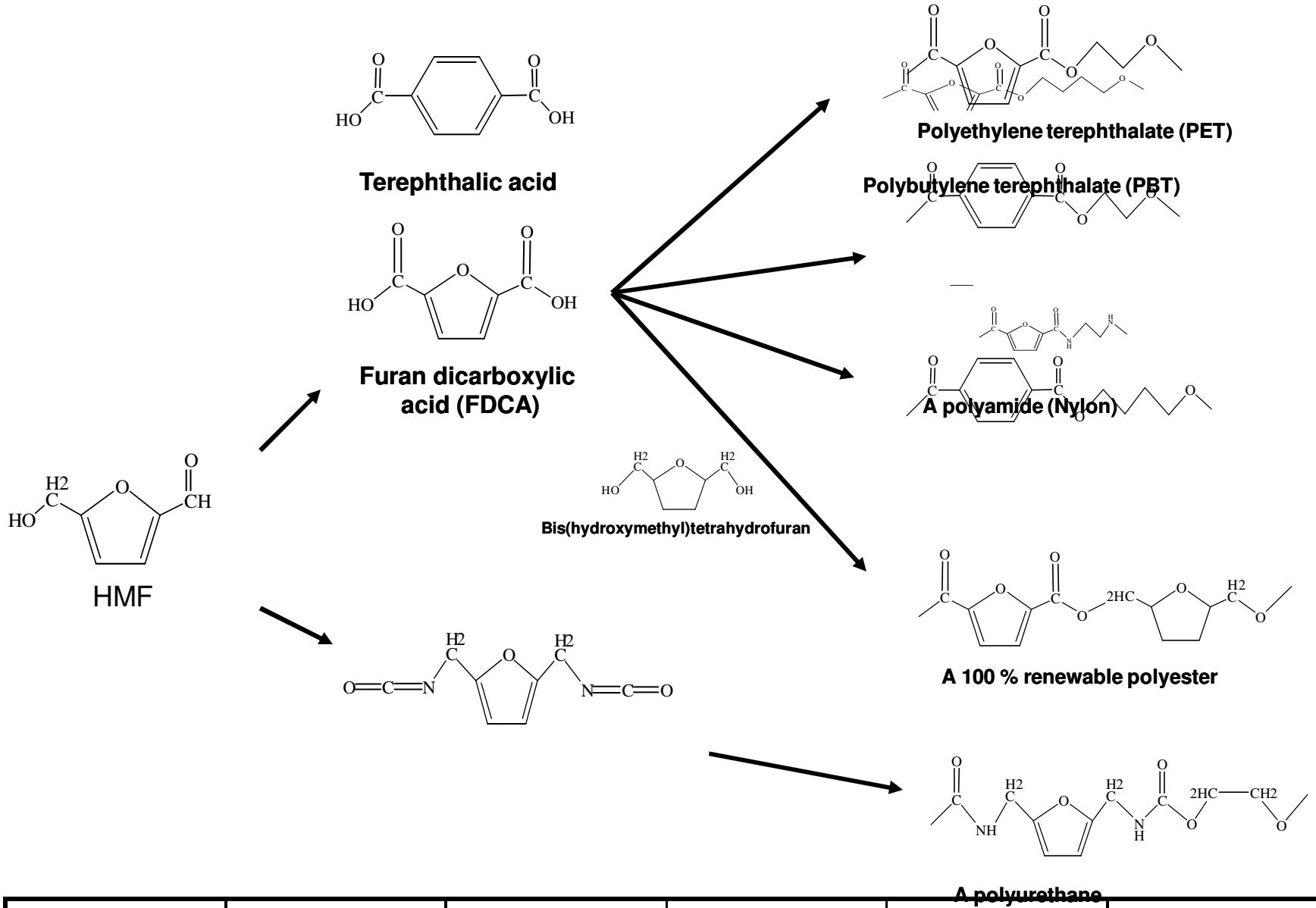
ΔG°=0.349± 0.05 kJ/mol

T (°C)	K_{eq}
25	0.869
35	0.905
45	0.950
55	1.002
60	1.032
75	1.133

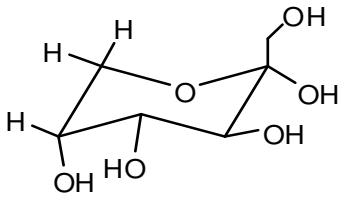
$$R \ln K = -\frac{349}{298.15} + 2780\left(\frac{1}{298.15} - \frac{1}{T}\right) + 76\left(\frac{298.15}{T} - 1 + \ln\left(\frac{T}{298.15}\right)\right)$$

Tewari, Y. B., Goldberg, R.N. *Journal of Solution Chemistry* **13**, 523-547 (1984).

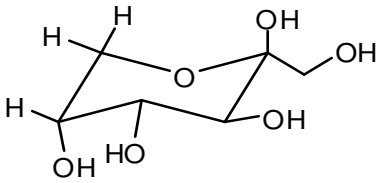
Biomass derived polymers



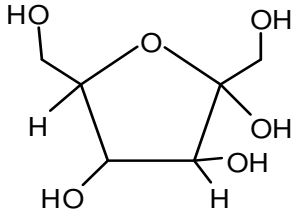
Proposed Reaction Scheme



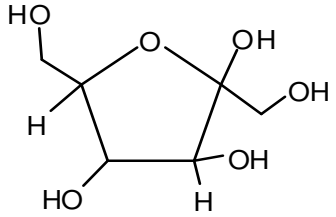
α-pyranose



β-pyranose



α-furanose



β-furanose

$$Pyranose \Leftrightarrow Furanose$$

$$Furanose \rightarrow HMF$$

$$Pyranose \rightarrow HMF$$

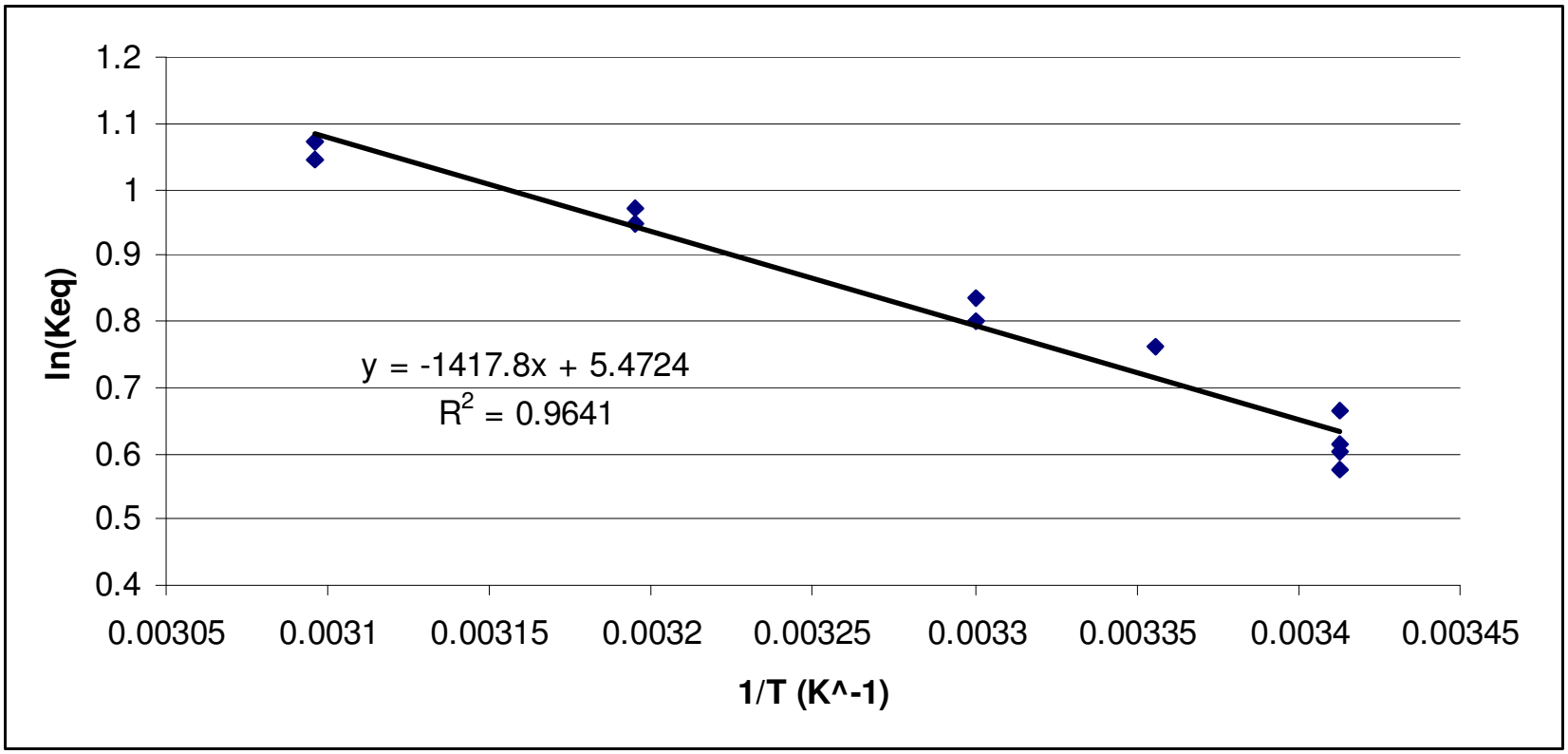
$$HMF + Furanose \rightarrow (HMF - Furanose)_{Dimer}$$

Thermodynamics

$$\ln(Keq) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

ΔH_{rxn}= 2.817 kcal/mol

ΔS_{rxn}=10.877 cal/mol K



*F. W. Lichtenthaler, S. Ronninger, J. Chem. Soc. Perkin Trans. 2 1489 (1990).

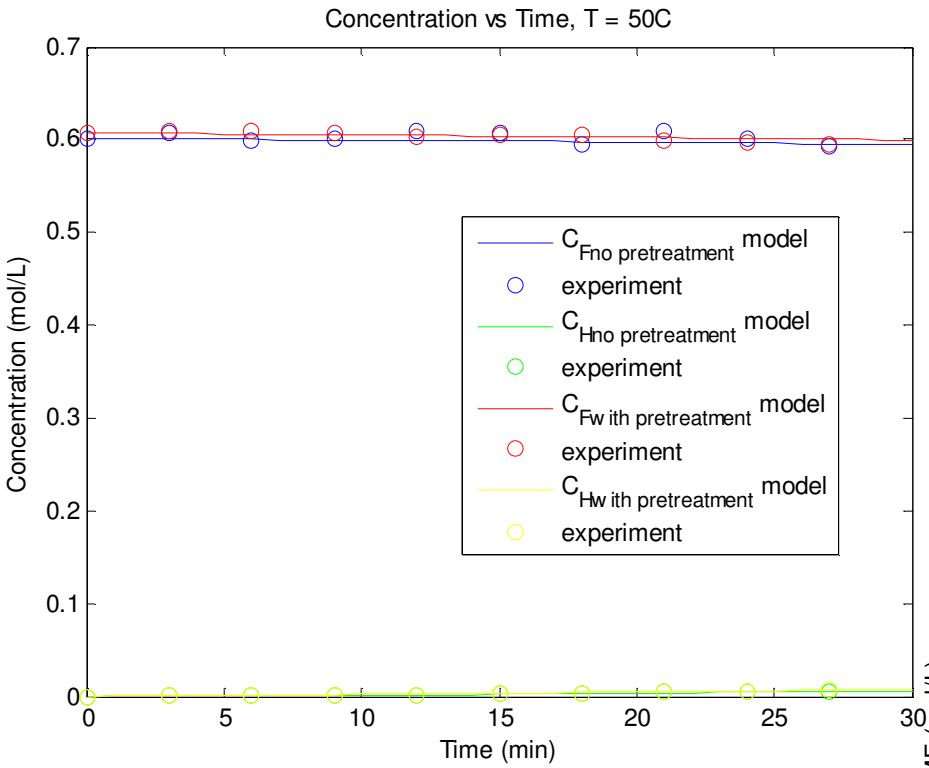
Matlab Simulation

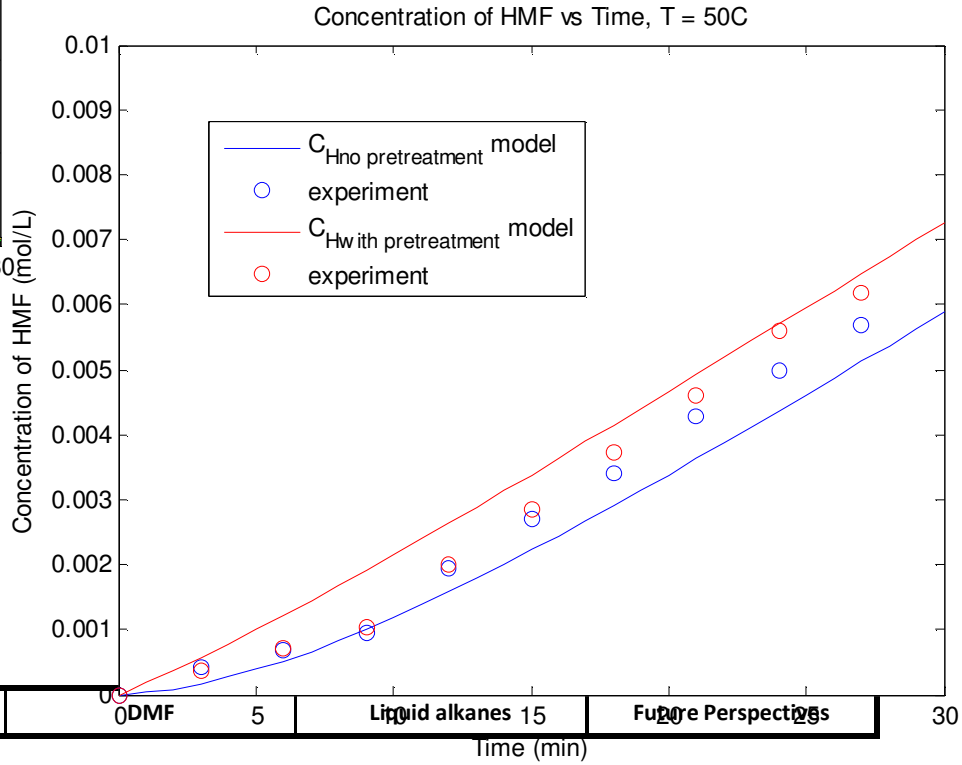
- Rate constants

$$k = k_o \exp\left(-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)\right)$$

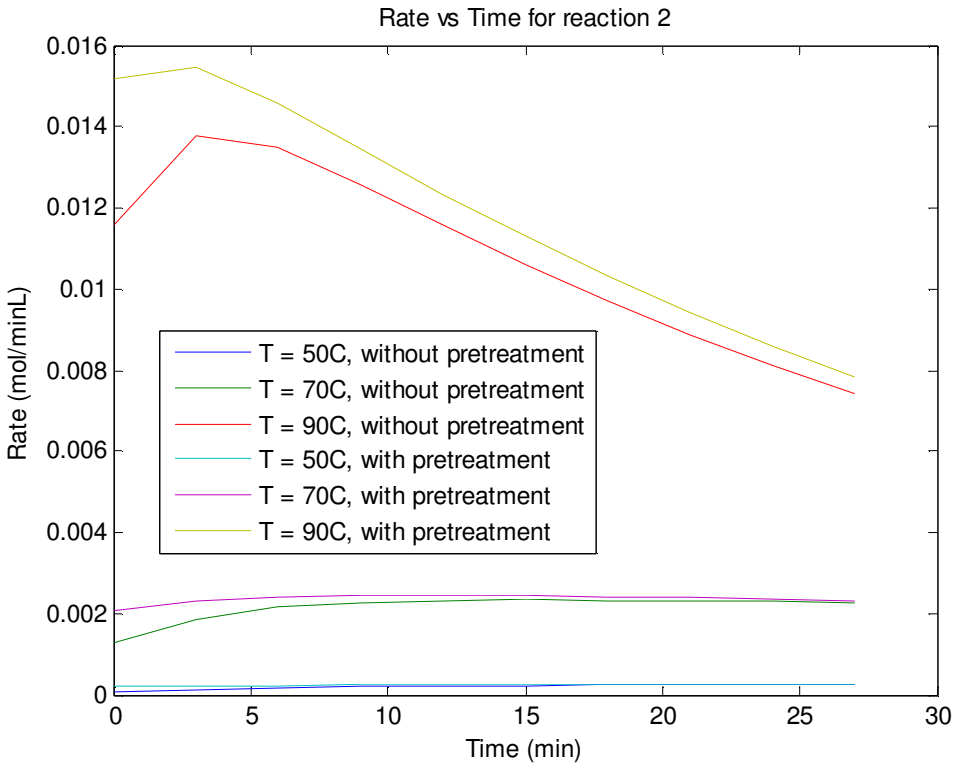
- Parameters
  - Activation Energies and average rate constants for steps 1-4
  - k_o was obtained by fitting 70ºC data set
  - All parameters were fit to the data sets of 50ºC, 70ºC and 90ºC

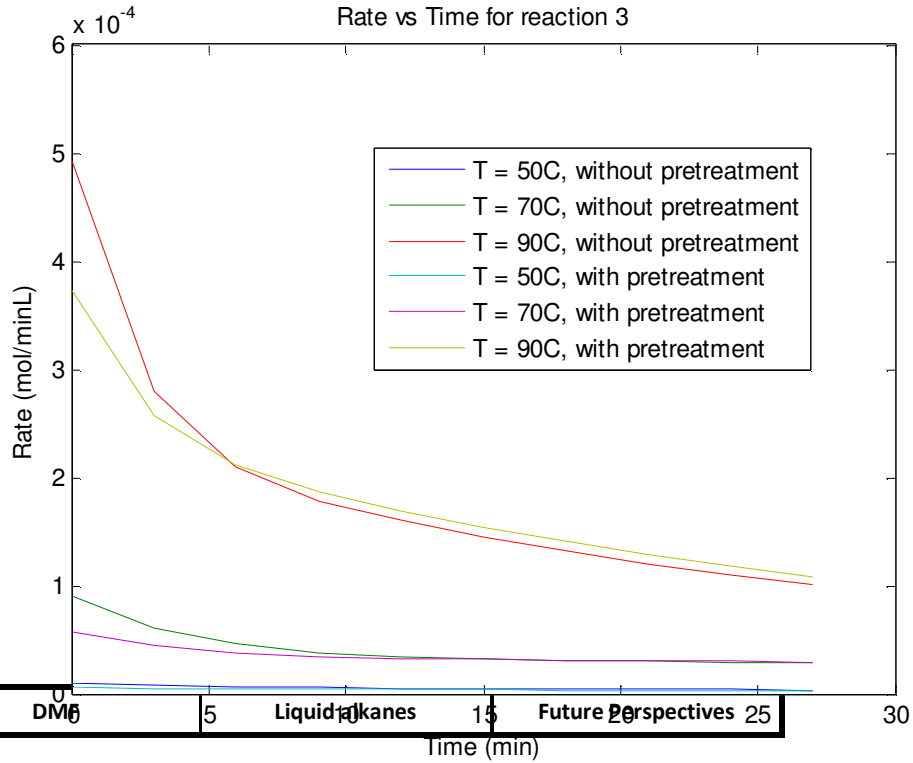
Results: 50ºC





Results: Reaction Rates





Parameter Estimates

$Pyranose \Leftrightarrow Furanose$

$Furanose \rightarrow HMF$

$Pyranose \rightarrow HMF$

$HMF + Furanose \rightarrow (HMF - Furanose)_{Dimer}$

Parameter	***Value***
E_{act1} (kcal/mol)	7.921
E_{act2} (kcal/mol)	23.915
E_{act3} (kcal/mol)	26.76
E_{act4} (kcal/mol)	24.942
k_{o1}(1/min)	$1.81*10^{-1}$
k_{o2}(1/min)	$5.15*10^{-3}$
k_{o3}(1/min)	$2.39*10^{-4}$
k_{o4}(L/min*mol)	$5.00*10^{-4}$

$Pyranose \Leftrightarrow Furanose$

$Furanose \rightarrow HMF$

$HMF + Furanose \rightarrow (HMF - Furanose)_{Dimer}$

Parameter	***Value***
E_{act1} (kcal/mol)	7.02
E_{act2} (kcal/mol)	23.98
E_{act3} (kcal/mol)	28.67
k_{o1}(1/min)	$2.21*10^{-1}$
k_{o2}(1/min)	$5.15*10^{-3}$
k_{o3}(1/min)	$2.51*10^{-4}$

Initial Reaction Scheme

Fructose → HMF + 3 H_2O k_1

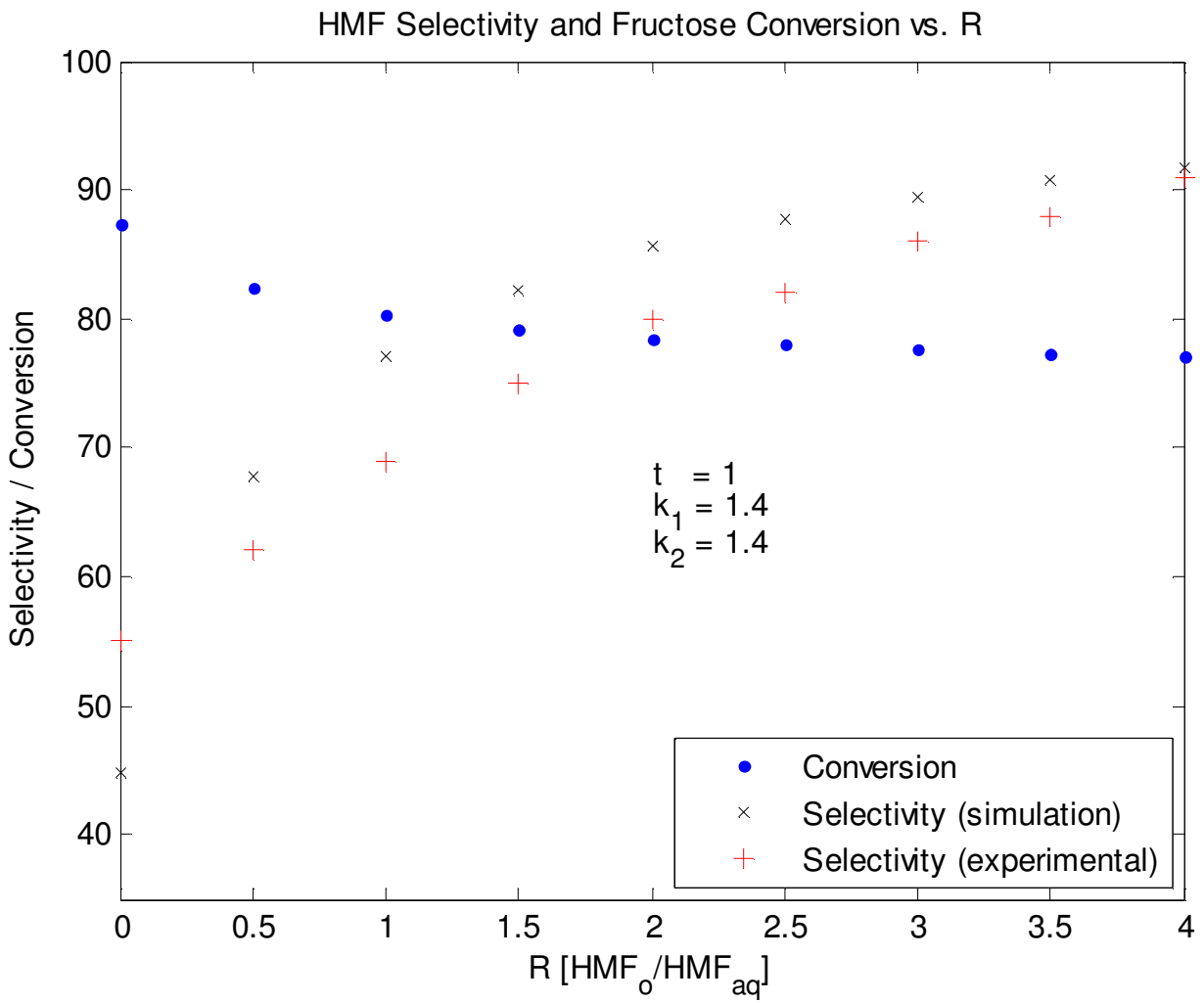
Fructose + HMF → Dimer k_2

$$\frac{d[Fructose]}{dt} = -k_1 * [Fructose] \left(1 + \frac{k_2}{k_1} * [HMF]\right)$$

$$\frac{d[HMF]}{dt} = \frac{\left(k_1 * [Fructose] - k_2 * [HMF] * [Fructose]\right)}{(1 + R * \eta)}$$

$$\frac{d[Dimer]}{dt} = k_2 * [Fructose] * [HMF]$$

Results: Initial Scheme



First Order HMF Decomposition

$$\text{Fructose} \rightarrow \text{HMF} + 3\ H_2O \qquad k_1$$

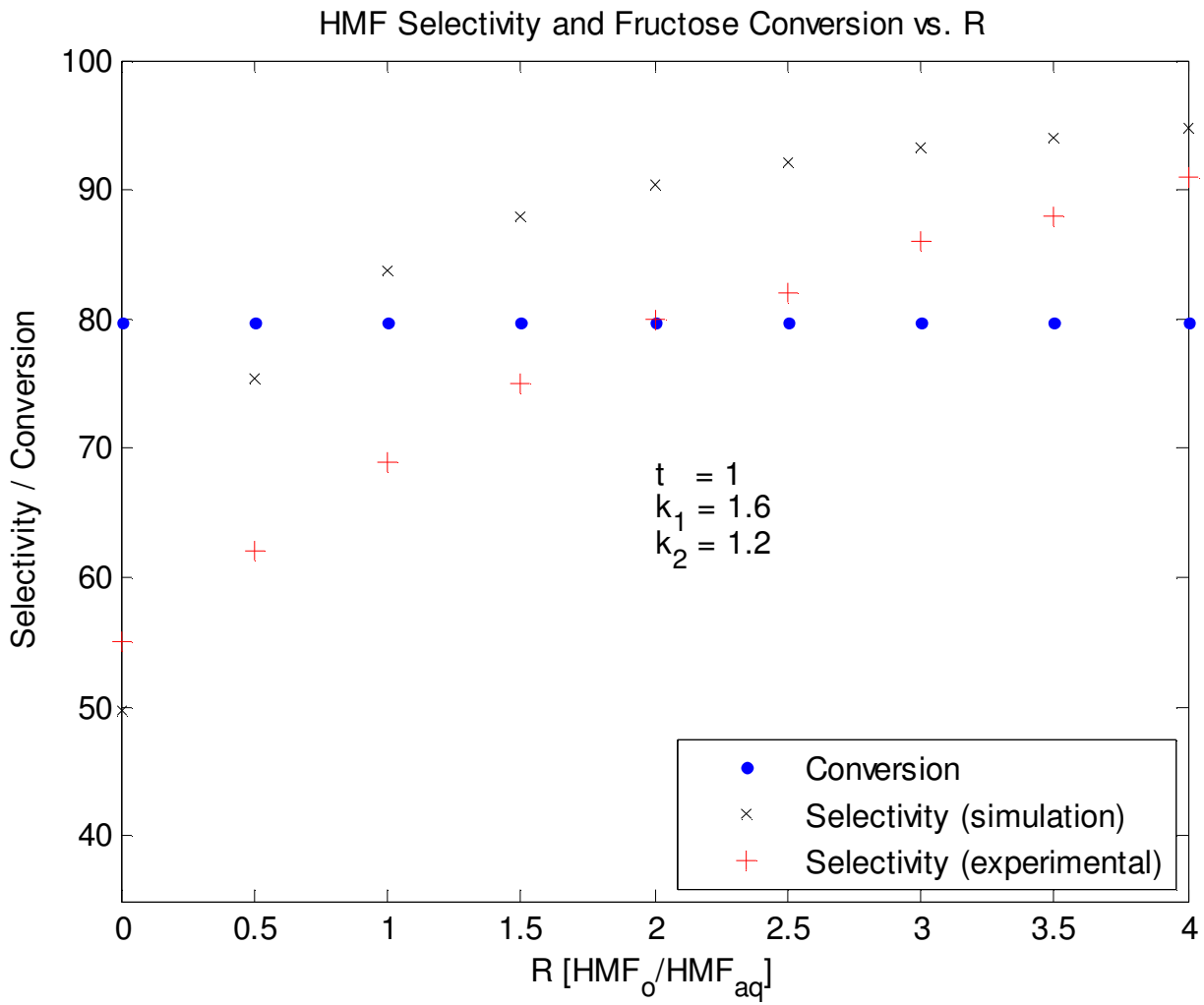
$$\text{HMF} \rightarrow CH_2O_2 + C_5H_8O_3 \qquad k_2$$

$$\frac{d[\text{Fructose}]}{dt} = -k_1 * [Fructose]$$

$$\frac{d[\text{HMF}]}{dt} = \frac{\left(k_1 * [\text{Fructose}] - k_2 * [HMF]\right)}{(1 + R * \eta)}$$

$$\frac{d[\text{Rehydration Products}]}{dt} = k_2 * [HMF]$$

Results: First Order HMF Decomposition



First and Second Order Fructose Decompositions

Fructose → HMF + 3 H_2O k_1

Fructose → Dehydration k_2

2 Fructose → Dimer k_3

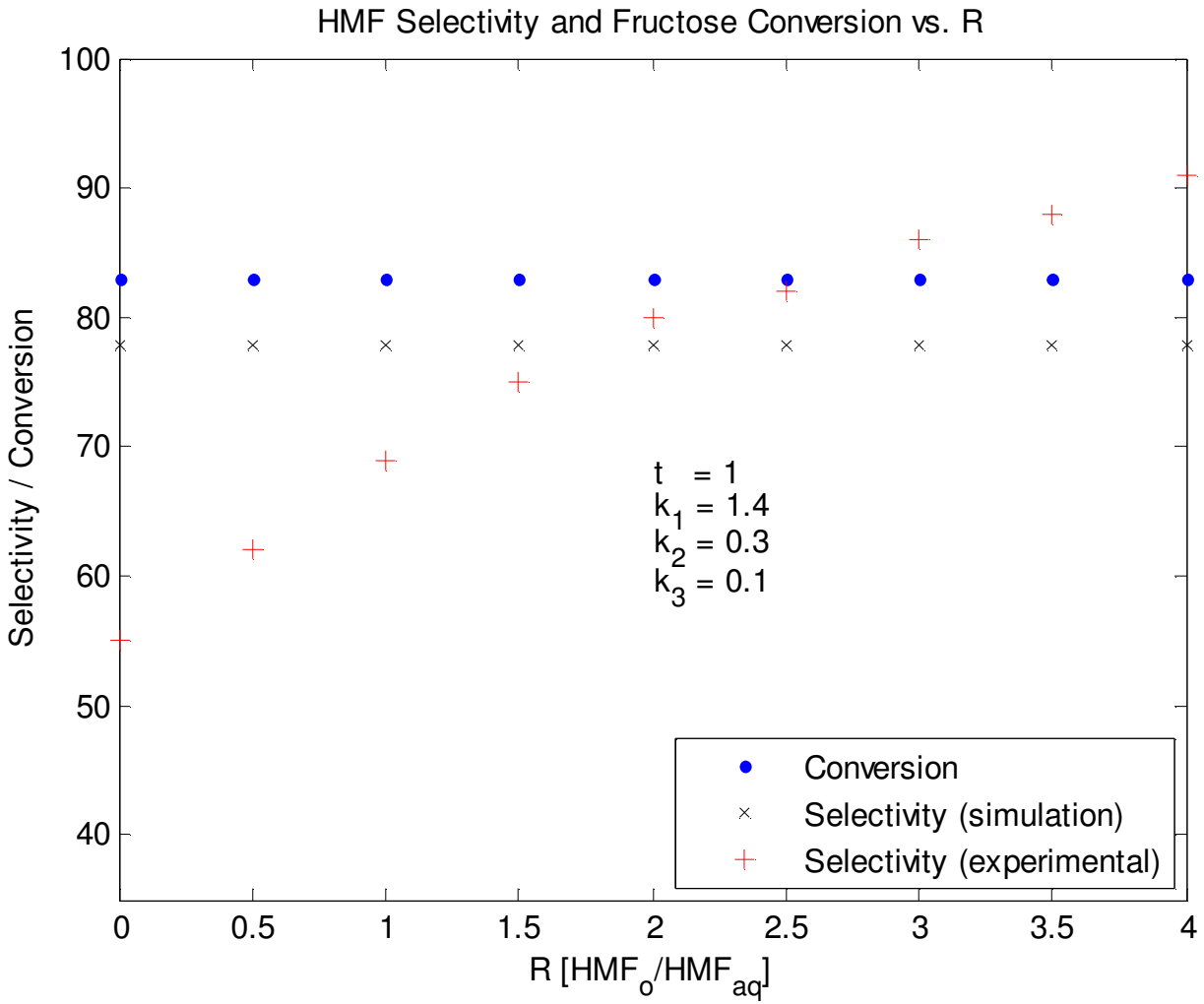
$$\frac{d[Fructose]}{dt} = -k_1 * [Fructose] - k_2 * [Fructose] - k_3 * [Fructose]^2$$

$$\frac{d[HMF]}{dt} = \frac{k_1 * [Fructose]}{(1 + R * \eta)}$$

$$\frac{d[Rehydration\ Products]}{dt} = k_2 * [Fructose]$$

$$\frac{d[Dimer]}{dt} = k_3 * [Fructose]^2$$

Results: First and Second Order Fructose Decompositions



Second Order HMF Decomposition

Fructose → HMF + 3 H_2O k_1

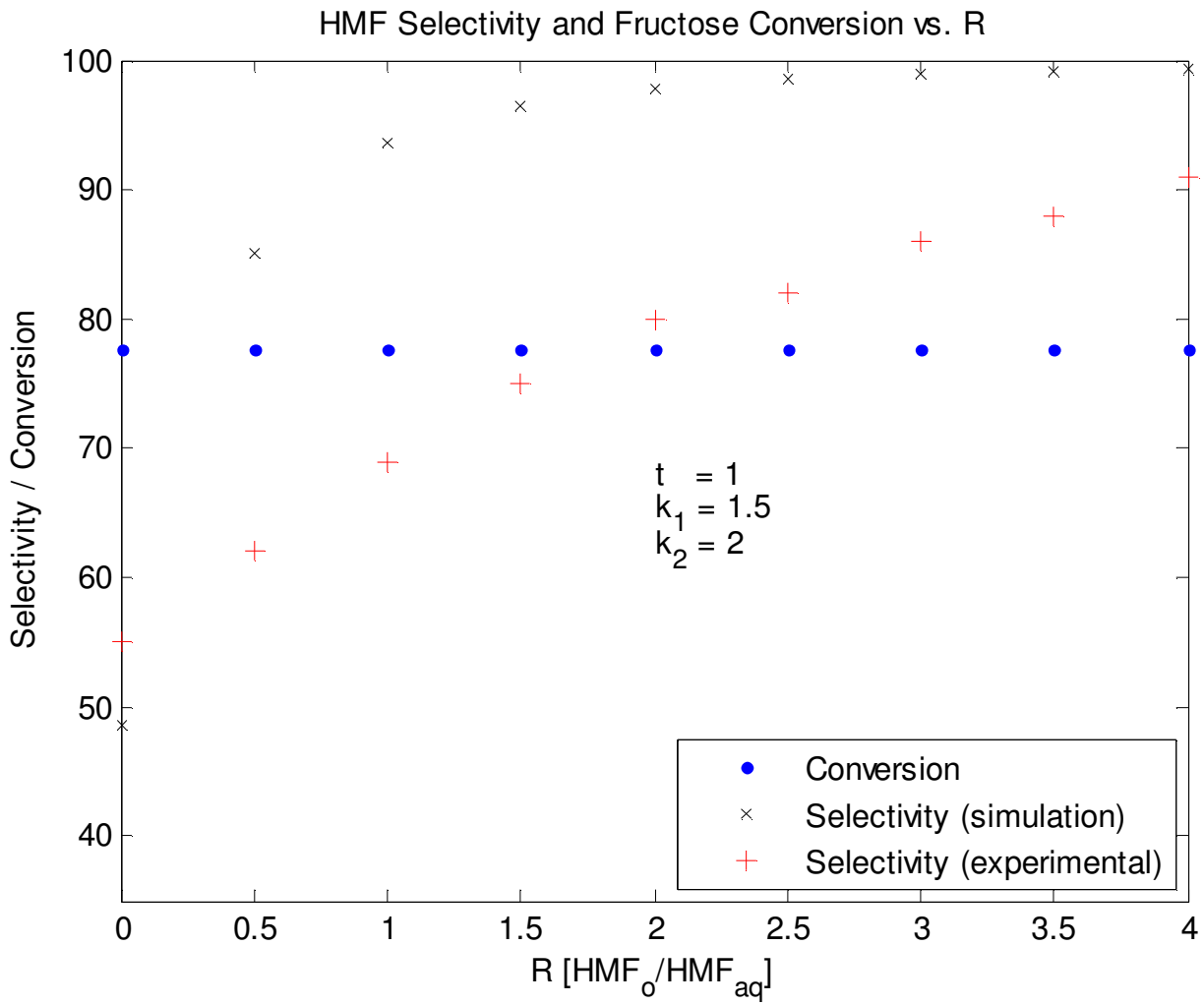
2 HMF → Dimer k_2

$$\frac{d[Fructose]}{dt} = -k_1 * [Fructose]$$

$$\frac{d[HMF]}{dt} = \frac{\left(k_1 * [Fructose] - k_2 * [HMF]^2\right)}{(1 + R * \eta)}$$

$$\frac{d[Dimer]}{dt} = k_2 * [HMF]^2$$

Results: Second Order HMF Decomposition



Initial Scheme with First Order HMF Decomposition

Fructose → HMF + 3 H_2O k_1

Fructose + HMF → Dimer k_2

HMF → CH_2O_2 + $C_5H_8O_3$ k_3

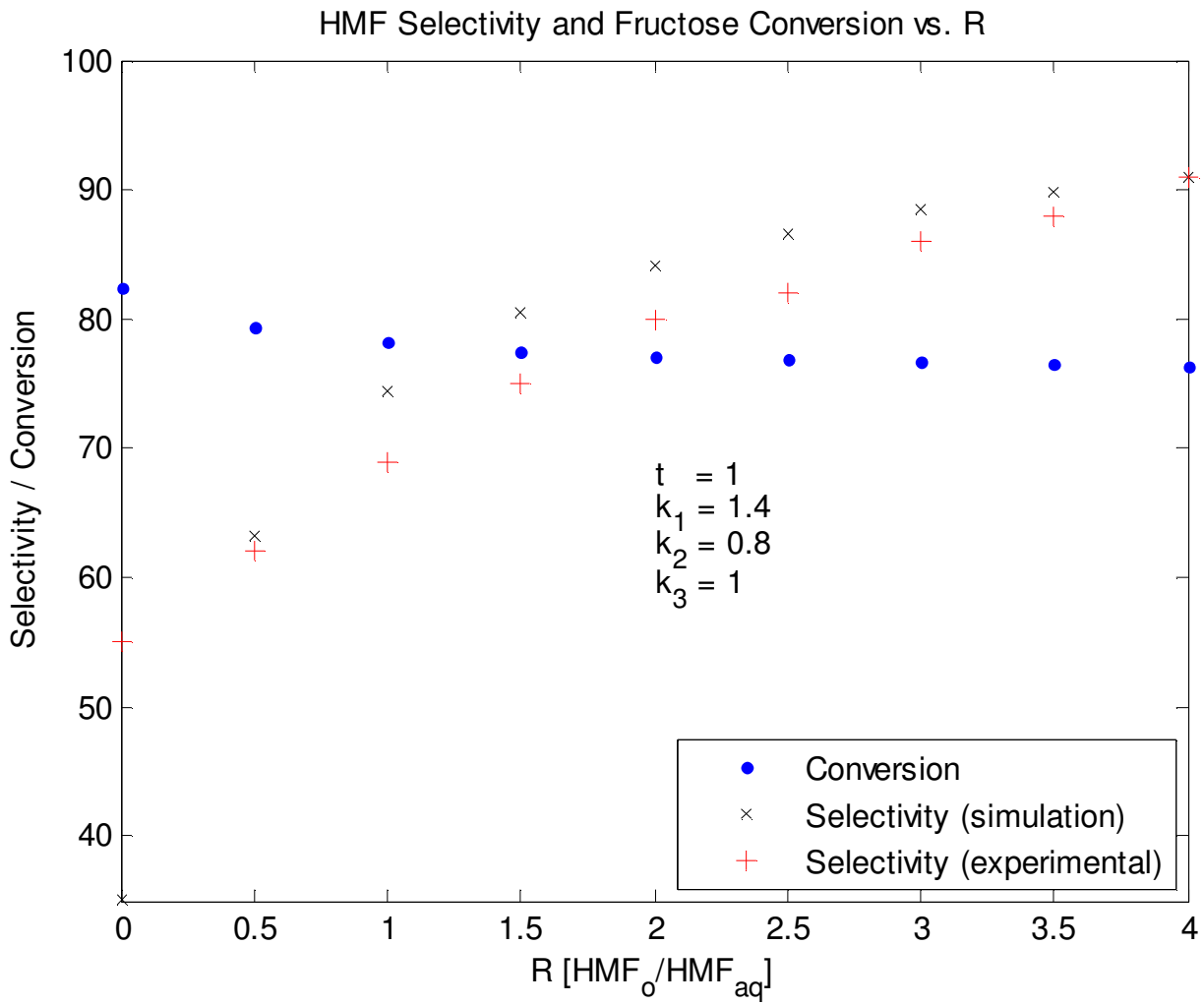
$$\frac{d[Fructose]}{dt} = -k_1*[Fructose]\left(1+\frac{k_2}{k_1}*[HMF]\right)$$

$$\frac{d[HMF]}{dt} = \frac{\left(k_1*[Fructose]-k_2*[HMF]*[Fructose]-k_3*[HMF]\right)}{(1+R*\eta)}$$

$$\frac{d[Dimer]}{dt} = k_2*[Fructose]*[HMF]$$

$$\frac{d[Rehydration\ Products]}{dt} = k_3*[HMF]$$

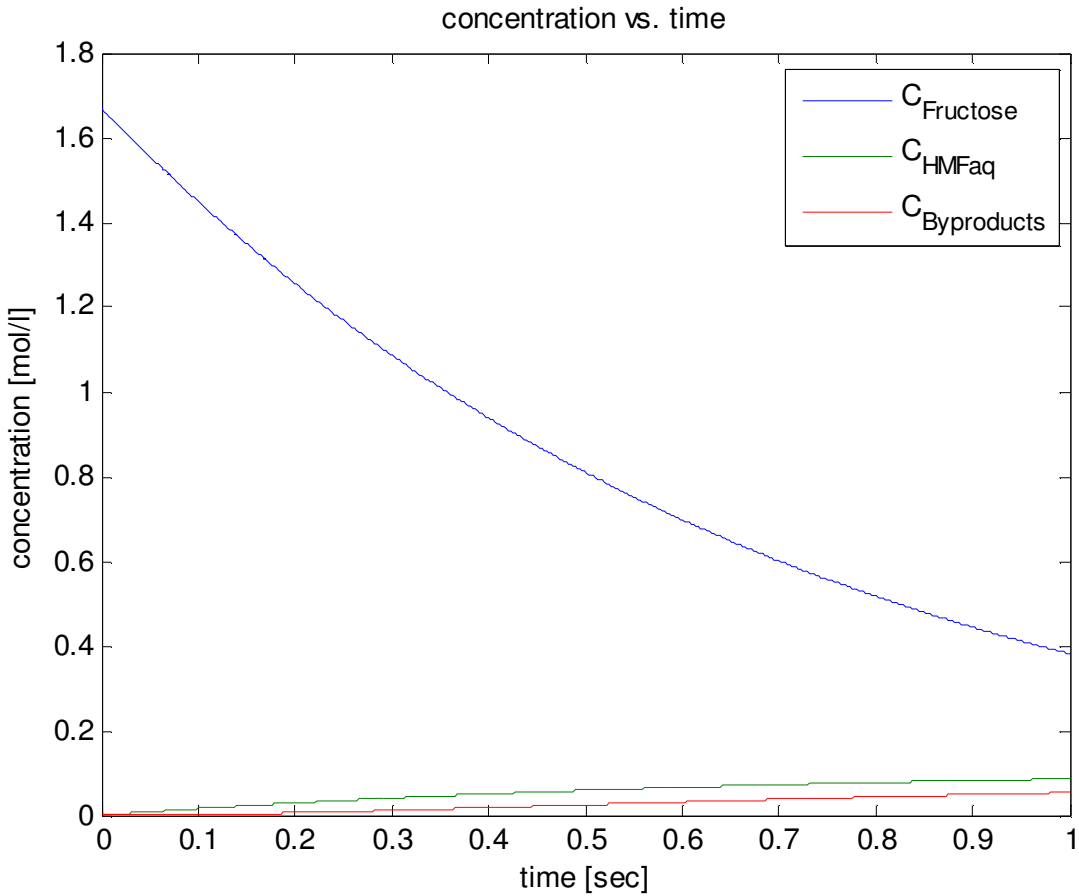
Results: Initial Scheme with First Order HMF Decomposition



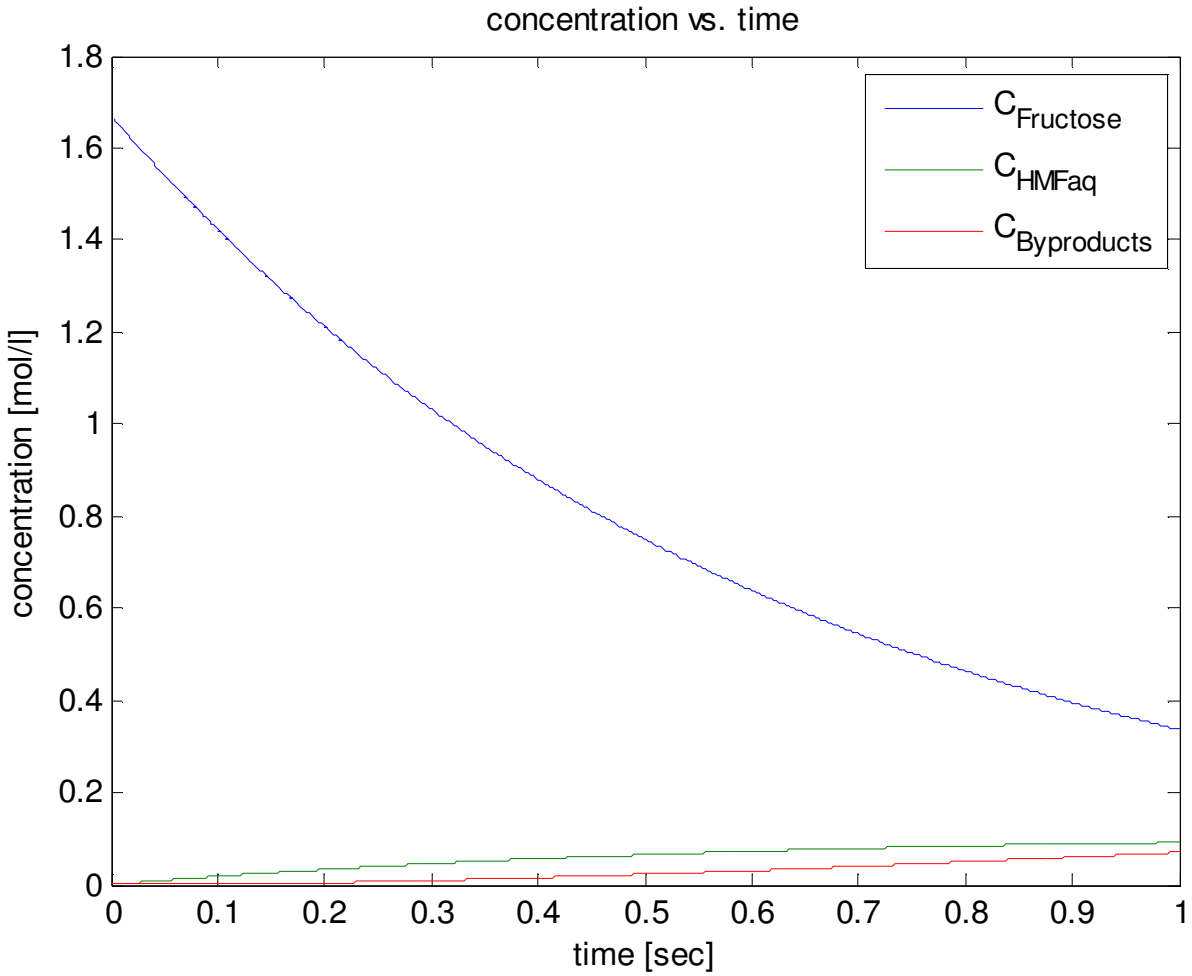
Conclusion

- Studied initial scheme
  - Simulation results are close to Experimental results
- Modeled various reaction schemes
  - Studied reaction kinetics
  - In the last case, where the decomposition of HMF was added to the initial scheme, the experimental data fit closely to the modeled data values.

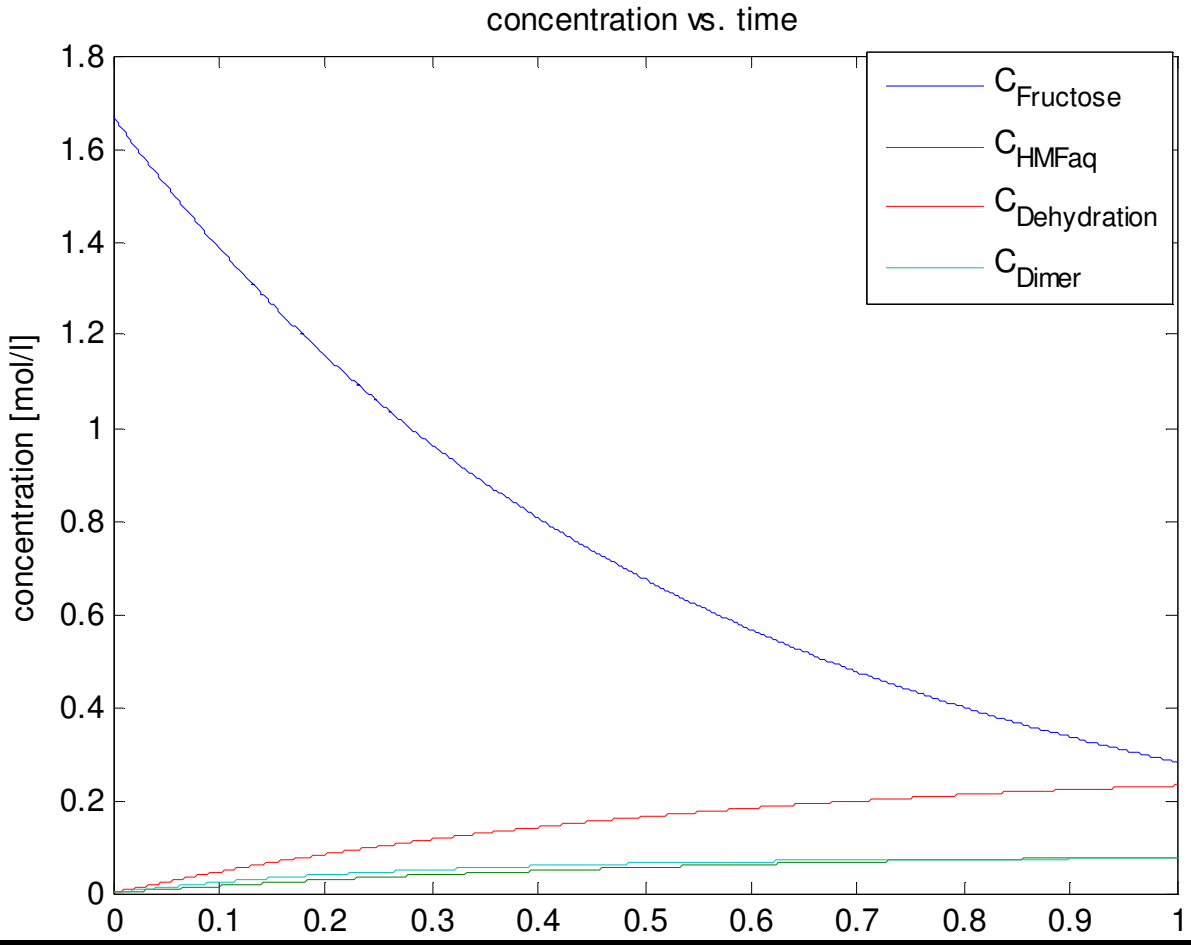
First Scheme



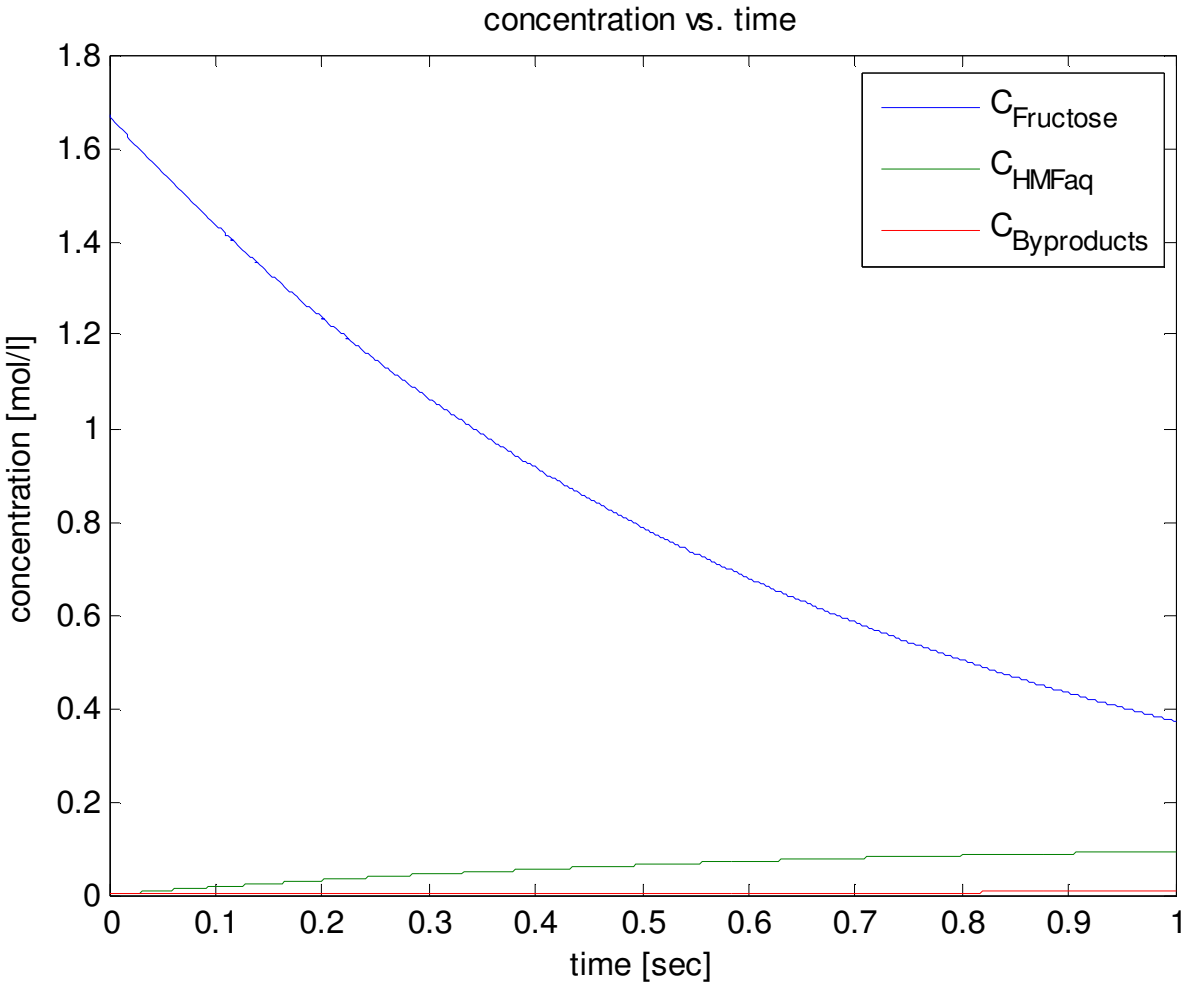
Second Scheme



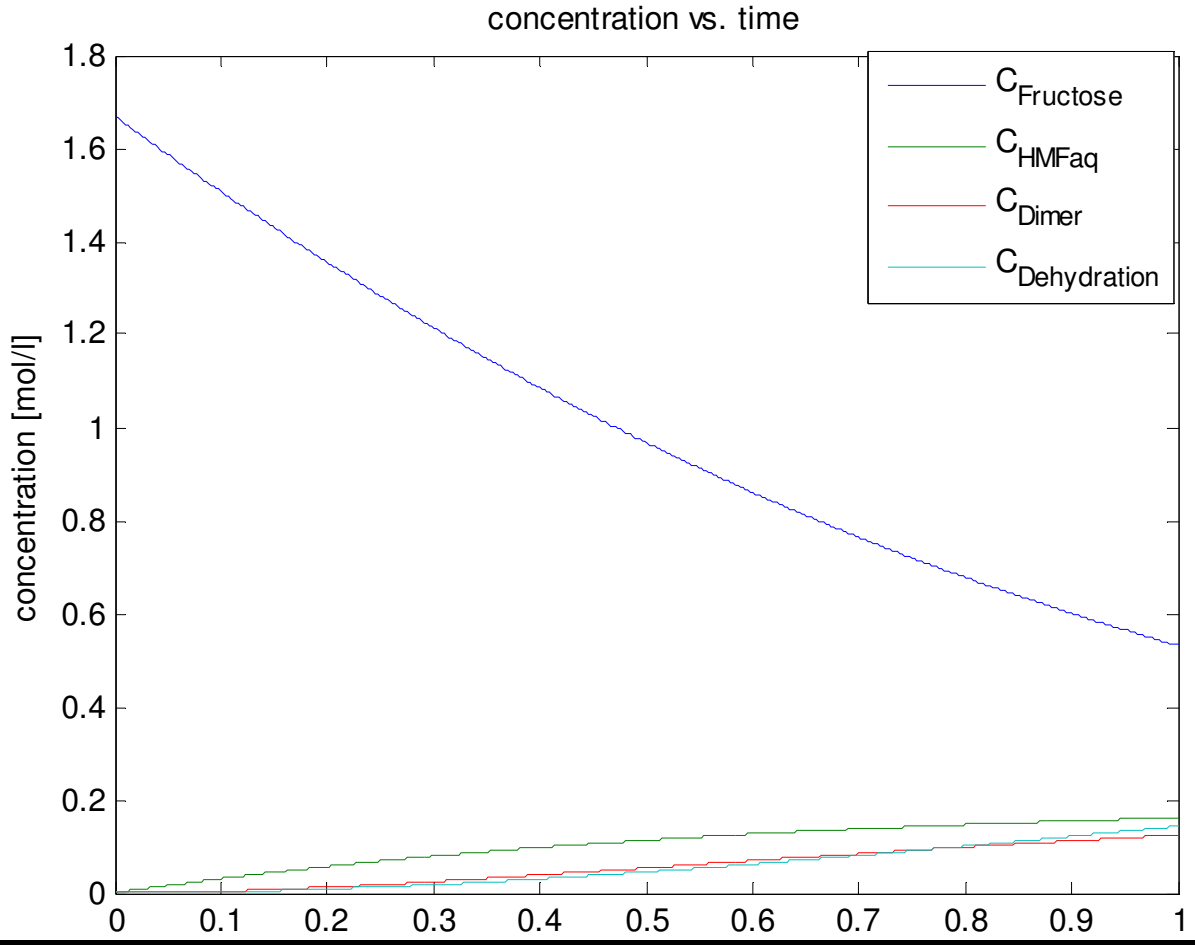
Third Scheme



Fourth Scheme



Fifth Scheme



Temperature effect

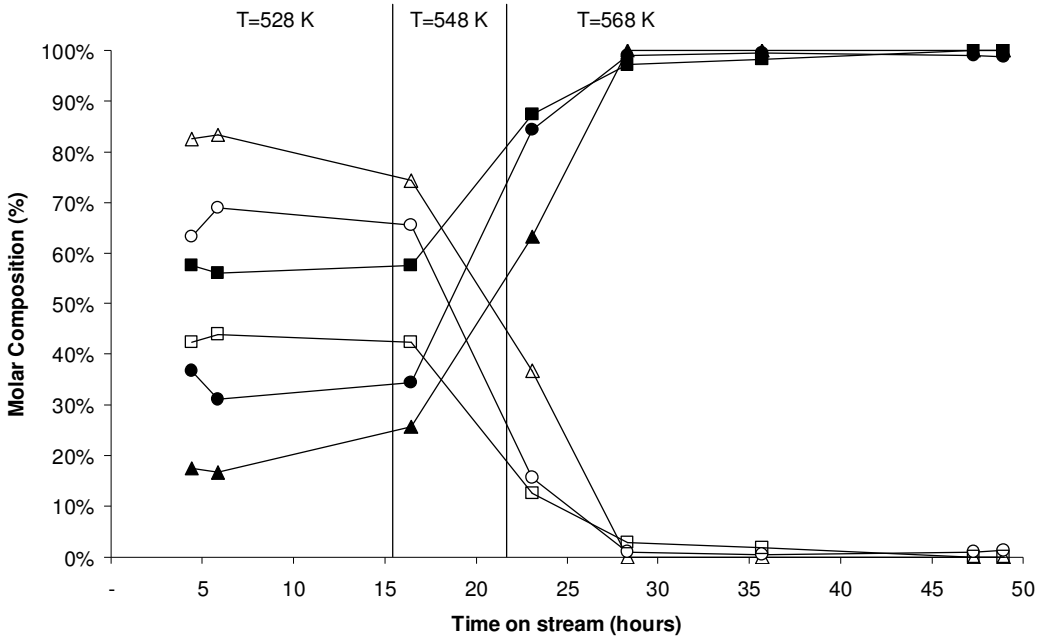
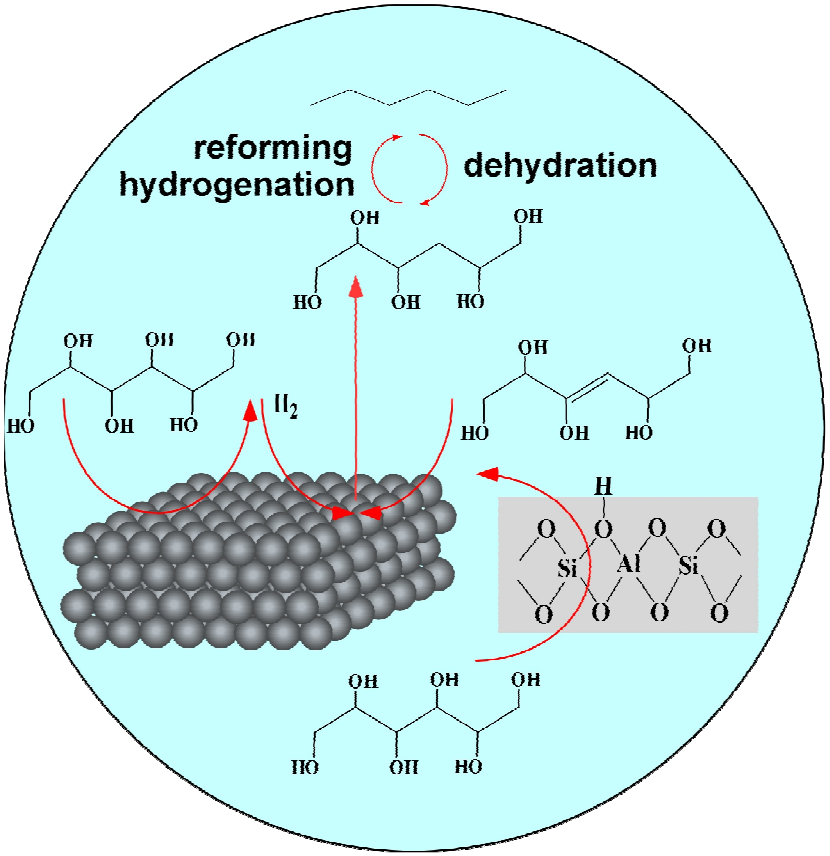


Figure 6. Effect of temperature on dehydration/hydrogenation of hydrogenated FUR-acetone condensation products over Pt-$NbOPO_4$ at WHSV = 1.5 ($hour^{-1}$).
Black –Alkanes, White – Oxygenates
Triangle – F derived alkanes and oxygenates
Circle – F-K derived alkanes and oxygenates
Square – F-K-F derived alkanes and oxygenates

Reforming and reduction reactions



- Alkanes are produced from carbohydrates by a bi-functional mechanism involving:
  - Dehydration on acid sites
  - Hydrogenation on metal sites
  - Reforming on metal sites.
- The selectivity to heavier alkanes is increased by increasing the acidity of catalyst or the feed.
- Hydrogen can be produced in-situ or co-fed into reactor.
- Co-feeding H_2 with the feed increases the selectivity to heavier alkanes.