MODELING, SIMULATION, AND TECHNO-ECONOMIC ANALYSIS OF BIOETHANOL PRODUCTION WITH ENZYME RECYCLING

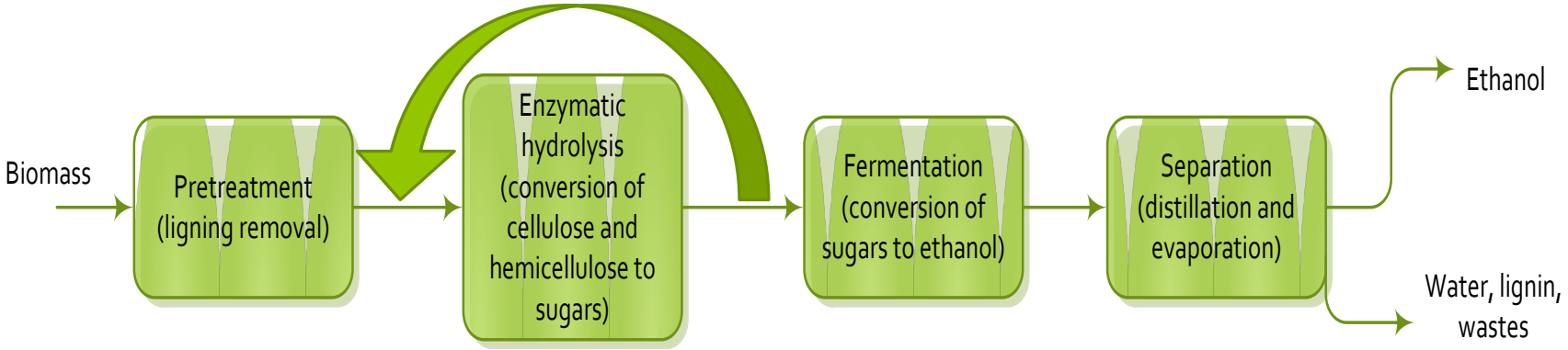
Oscar Rosales Calderon

M.A.Sc. CANDIDATE
CHEMICAL AND BIOLOGICAL ENGINEERING

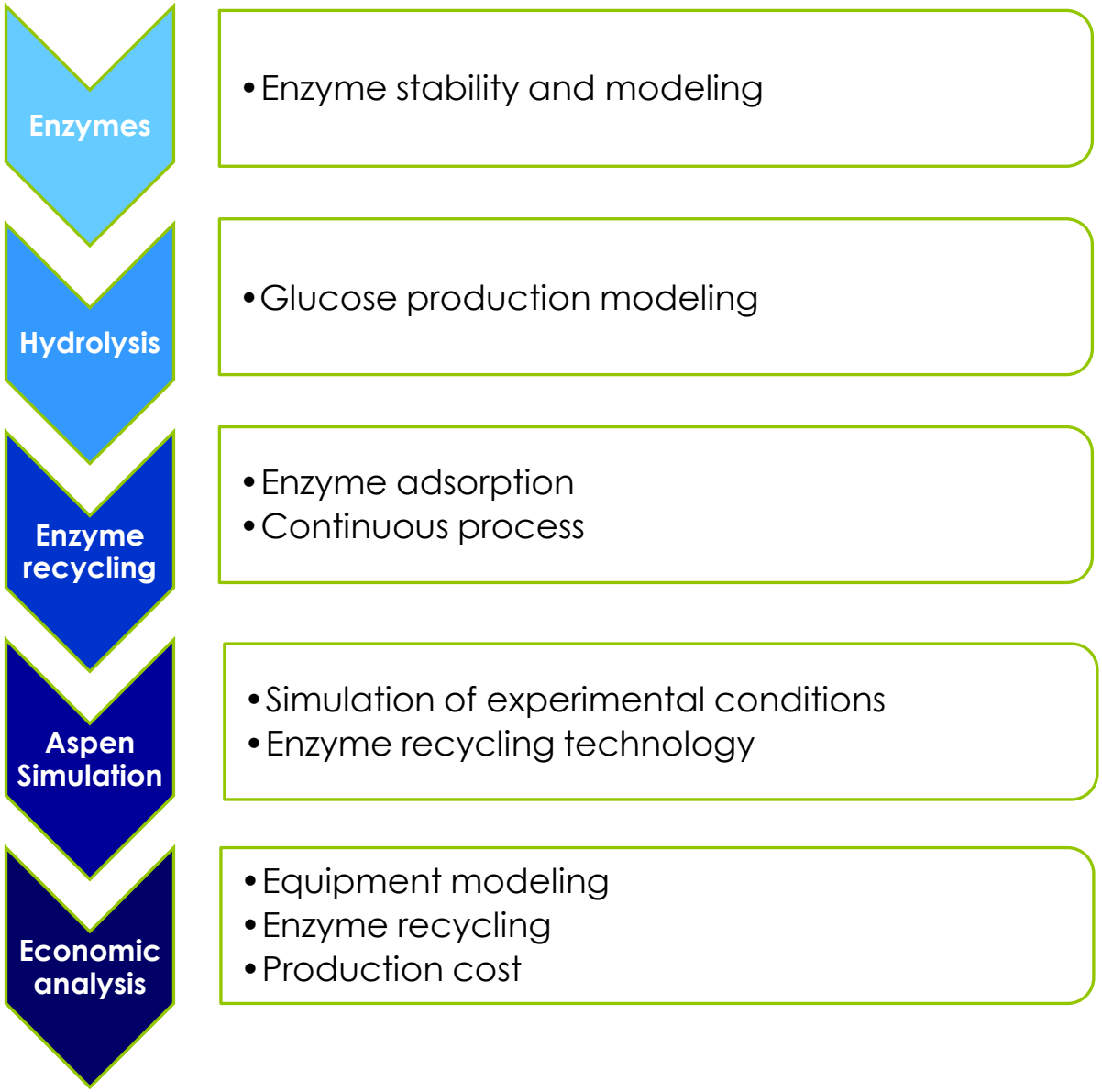
UNIVERSITY OF BRITISH COLUMBIA

- Lignocellulose:
  (corn stover, wheat straw, wood)





Objective


Enzymes
• Enzyme stability and modeling
Hydrolysis
• Glucose production modeling
Enzyme recycling
• Enzyme adsorption
• Continuous process
Aspen Simulation
• Simulation of experimental conditions
• Enzyme recycling technology
Economic analysis
• Equipment modeling
• Enzyme recycling
• Production cost

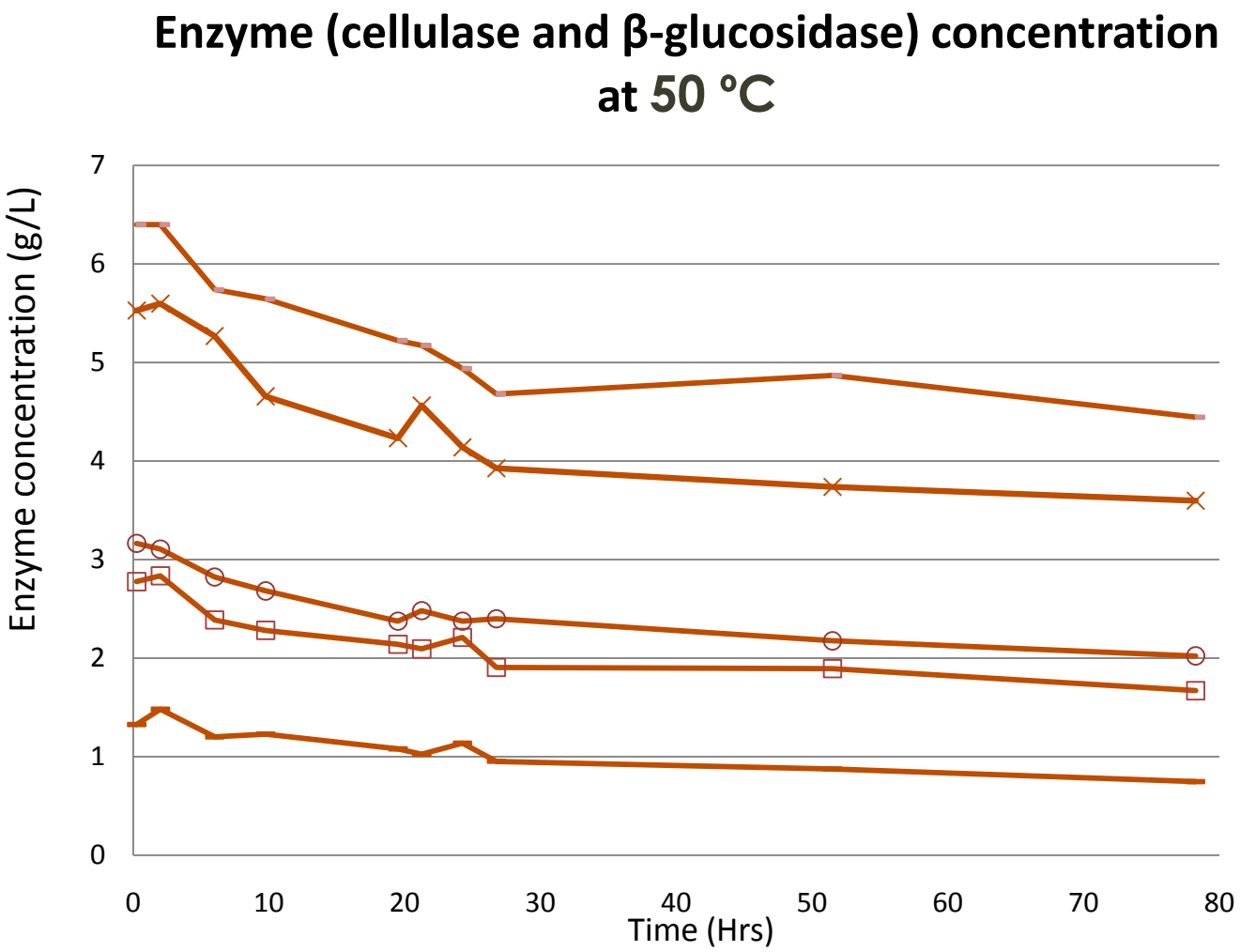
Experiments

- **Substrate**: Wheat straw
- **Pretreatment**: Oxygen Delignification (Commercial process)
  - Lignin is decomposed to CO_2, H_2O, and carboxylic acids
  - Minimum inhibitors production
  - Operating parameters:
    - Temperature
    - Caustic Concentration
    - Time
    - Agitation
    - Oxygen Flow

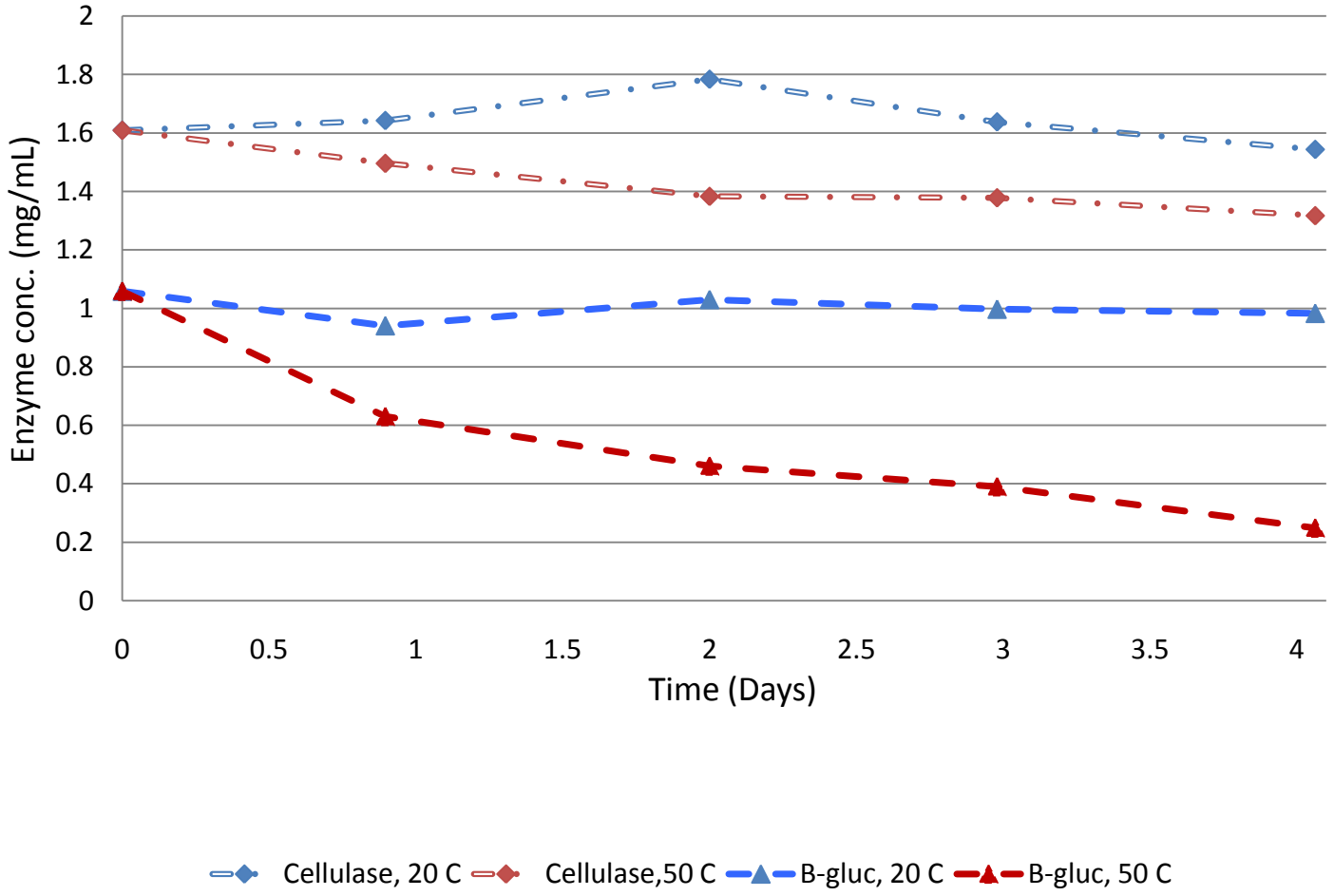
Condition (4%solid)	Time (min)	% Caustic (m/m)	Temperature (°C)	Cellulose	Xylan	Total Lignin
				Composition (%, based on dry matter)		
Raw				35.75	20.05	15.81
1	30	6	120	49.92	23.62	9.04
2	60	10	150	55.31	24.21	4.73

- **Hydrolysis**:
  - Commercial Enzyme Cocktail (Novozymes):
    - Celluclast 1.5L (**Cellulase**)
    - Novozyme 188 (**β-Glucosidase**)
  - Conditions:
    - **5** and **10** % solid concentration
    - **20** and **40** FPU/g cellulose
    - pH 4.8 (acetate buffer)
    - 50 °C, 150 rpm
    - 0.02% w/v tetracycline and 0.015% w/v cyclohexamide

  - Sugar content: HPLC system (Dionex DX-500, Dionex, CA)
  - Industrial conditions for re-adsorption (**50 °C**):
    - 4 °C (Tu, 2007), 25 °C (Qi, 2011)


Enzyme (cellulase and β-glucosidase) concentration at 50 °C
Enzyme concentration (g/L)
0
1
2
3
4
5
6
7
0
10
20
30
40
50
60
70
80
Time (Hrs)

Enzymes


Enzyme conc. (mg/mL)
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
0.5
1
1.5
2
2.5
3
3.5
4
Time (Days)
Cellulase, 20 C
Cellulase,50 C
B-gluc, 20 C
B-gluc, 50 C

- The Finke-Watzky Mechanism of Nucleation Followed by Autocatalytic Surface Growth (Watzky,1997)

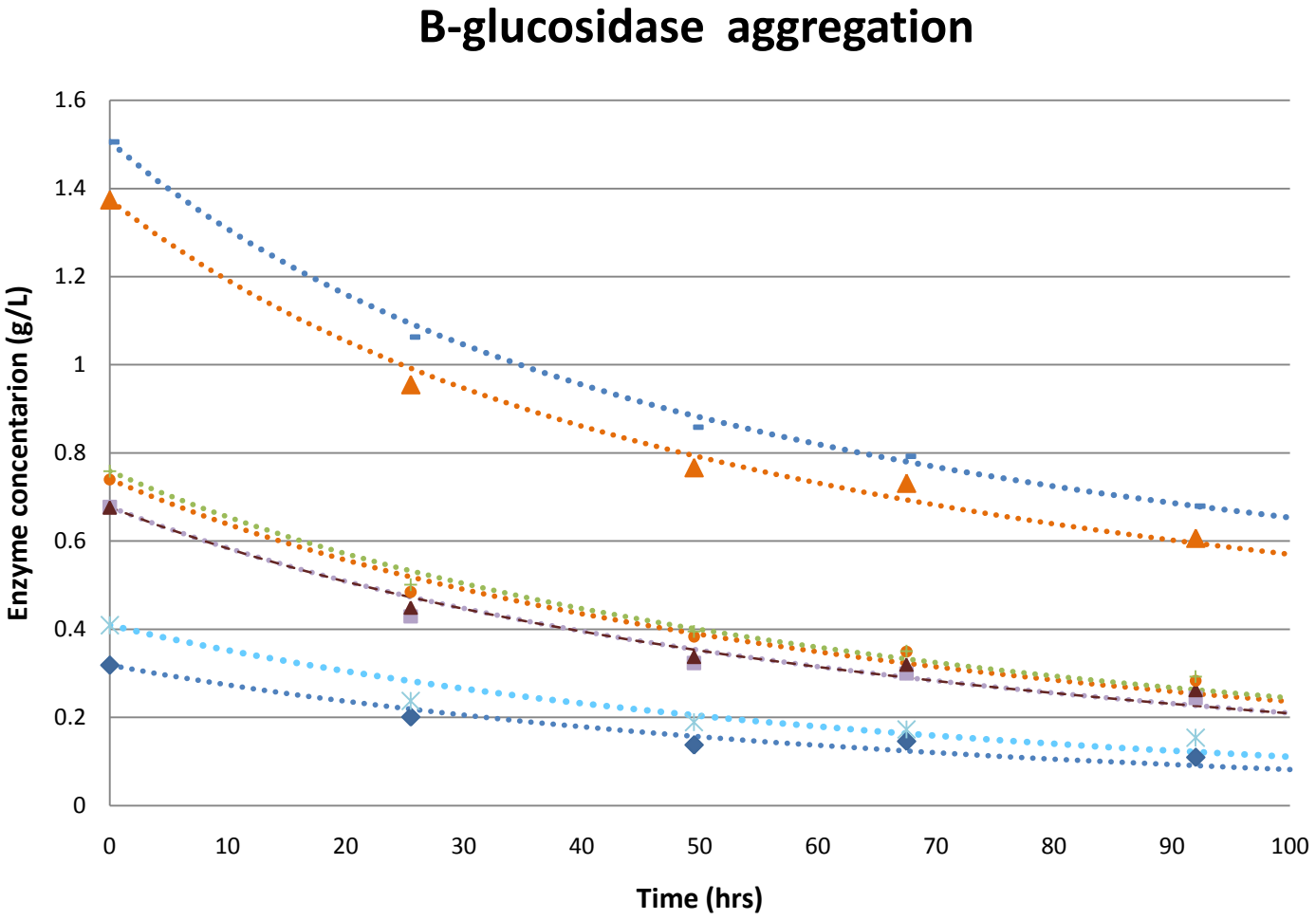
$$B \xrightarrow{k_4} D$$

$$B + D \xrightarrow{k_5} 2D$$

$$-\frac{d[B]}{dt} = k_4[B] + k_5[B][D]$$

$$[B]_t = \frac{\frac{k_4}{k_5} + [B]_0}{1 + \frac{k_4}{k_5[B]_0} e^{k_4 + k_5[B]_0 t}}$$

B=[β-glucosidase]
D=[polymeric form of the enzyme]

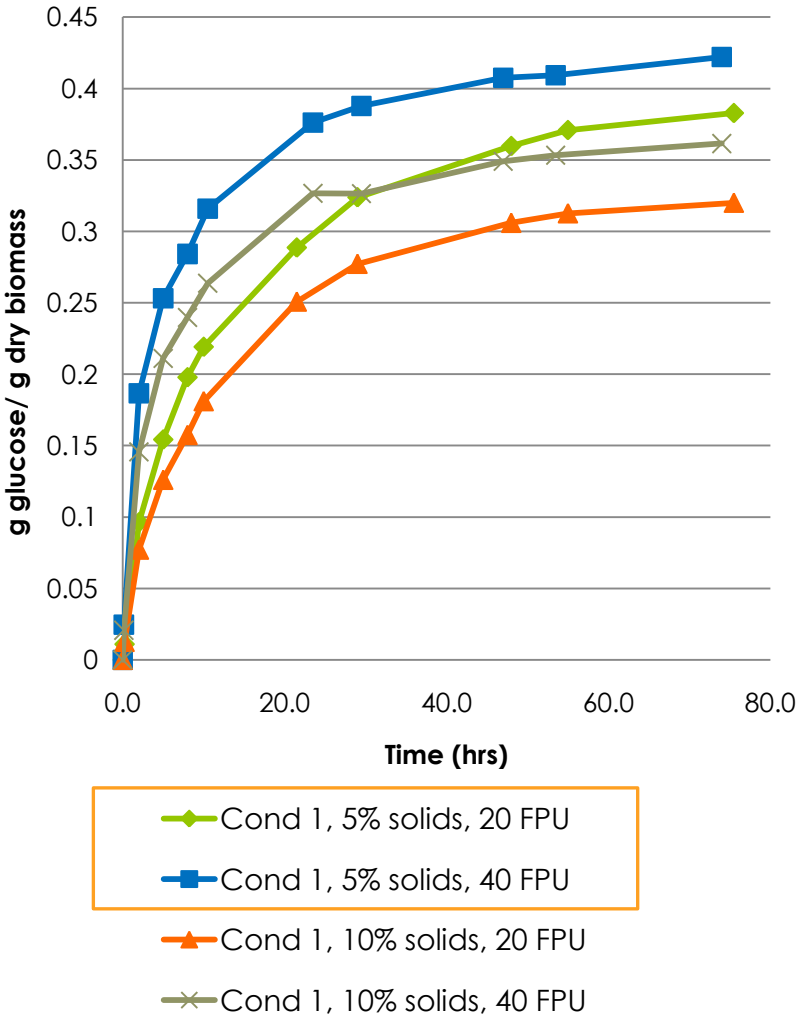


k_4=0.0154

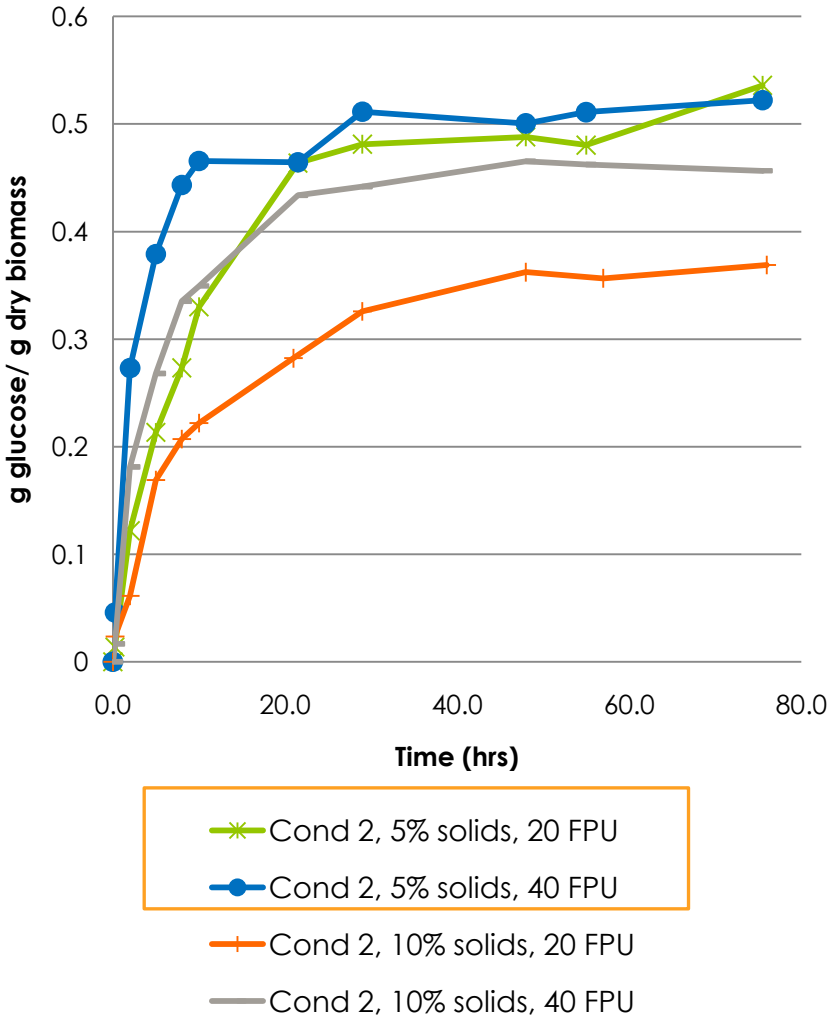
k_5=-0.0125 L/g

Hydrolysis

Condition 1

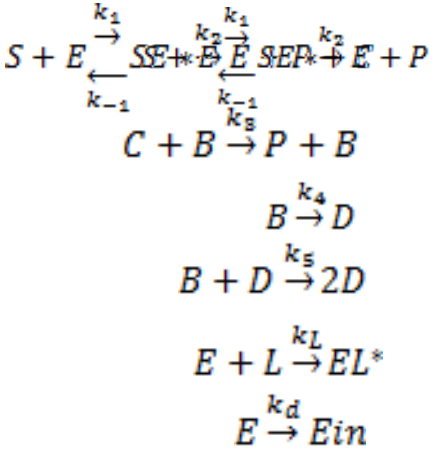


Condition 2



Hydrolysis

- Kinetic model for the production of glucose, based in the Shen model (Shen and Agblevor,2008)



- Glucose Production
- Cellobiose Production
- Slow nucleation of B-glucosidase
- Autocatalytic growth of B-glucosidase aggregates
- Cellulase adsorbed into lignin
- Cellulase deactivation

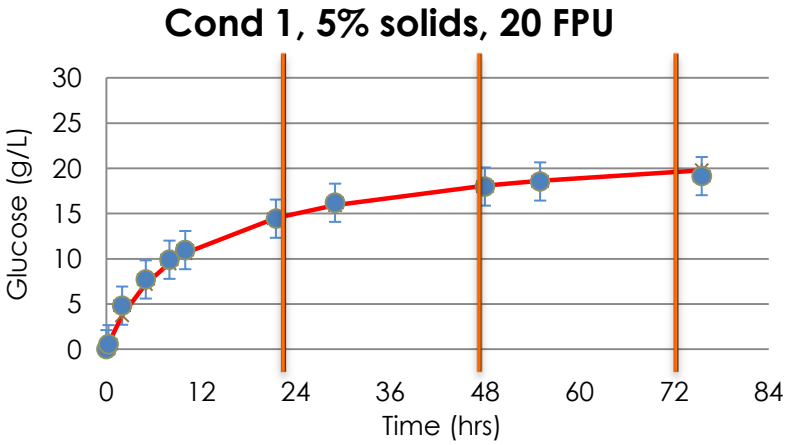
- **S**=[Substrate, cellulose]
- **E**=[Cellulase]
- **SE***=[Cellulose-cellulase complex]
- **P**=[Product, glucose]
- **C**=[Cellobiose]

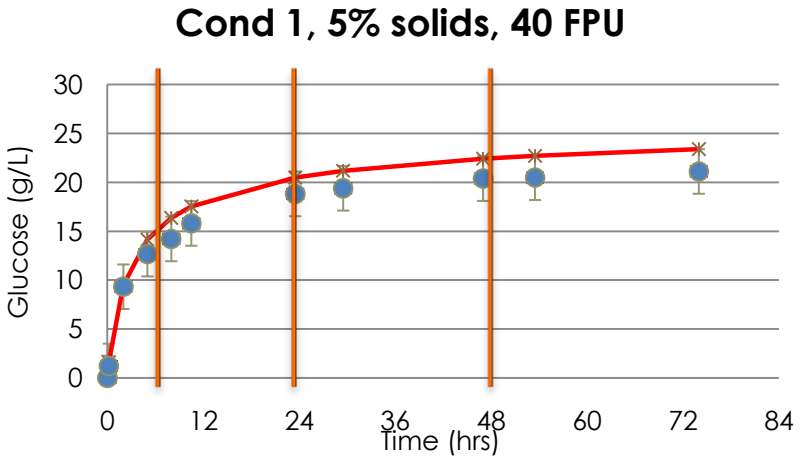
- **B**=[β-glucosidase]
- **D**=[Polymeric form of the β-glucosidase]
- **Ein**=[Inactive enzyme]
- **L**=[Lignin]
- **EL***=[Cellulase-lignin complex]

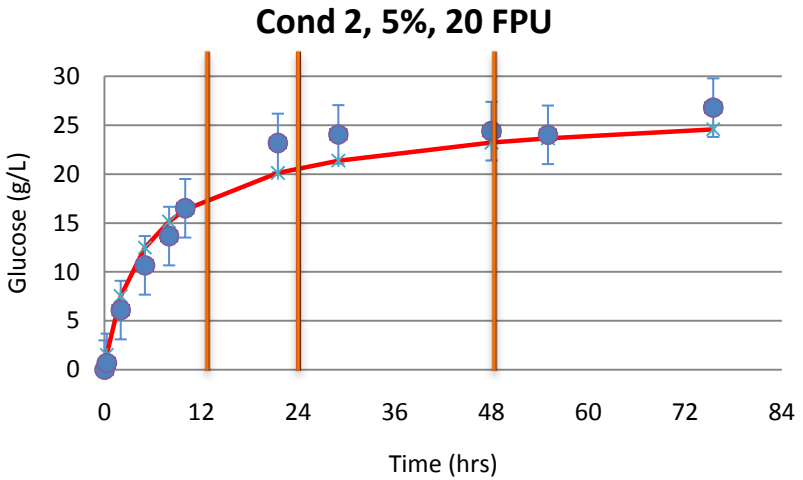
$$P = S_0\left[1-\left(1+\frac{Ke*k_d*E_R*t}{E_R+Ke}\right)^{-\frac{k_d}{Ke*k_d}}\right]$$

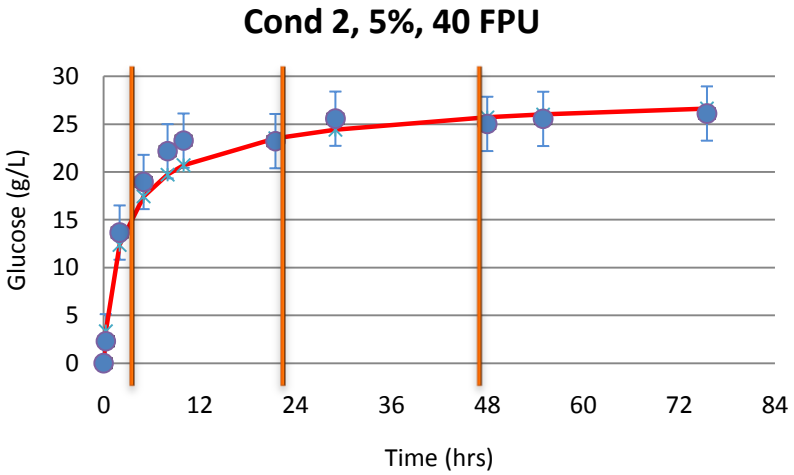
- **S0**=[Initial substrate]
- **ER=E0-kL*L**=[Initial cellulase available for reaction]
- **E0**=[Initial cellulase]
- **kL**=[Lignin factor]
- **Ke=(k-1+k2)/k1**=[Cellulase-lignin complex]

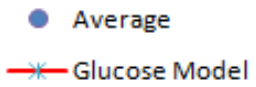
Hydrolysis







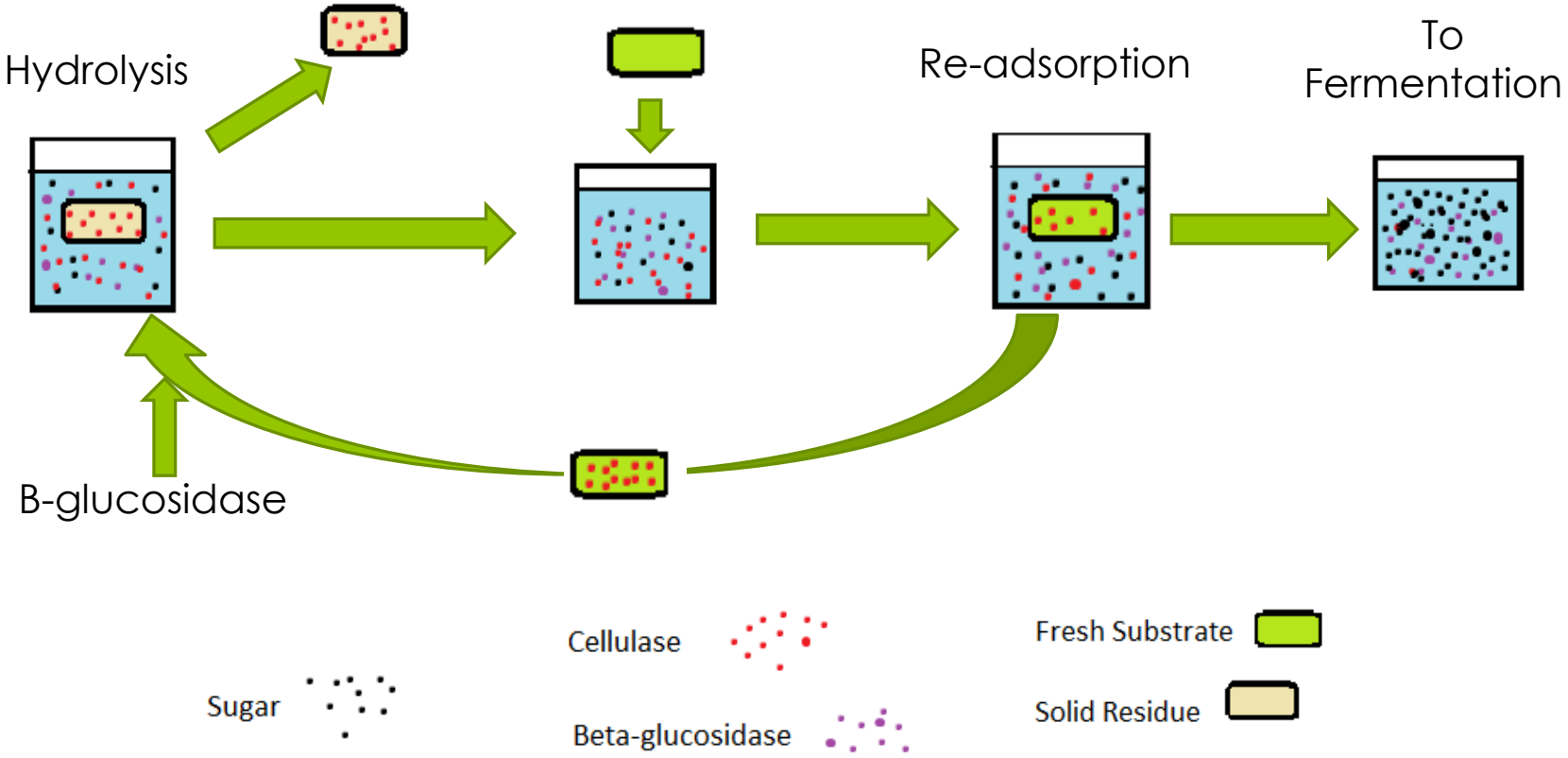




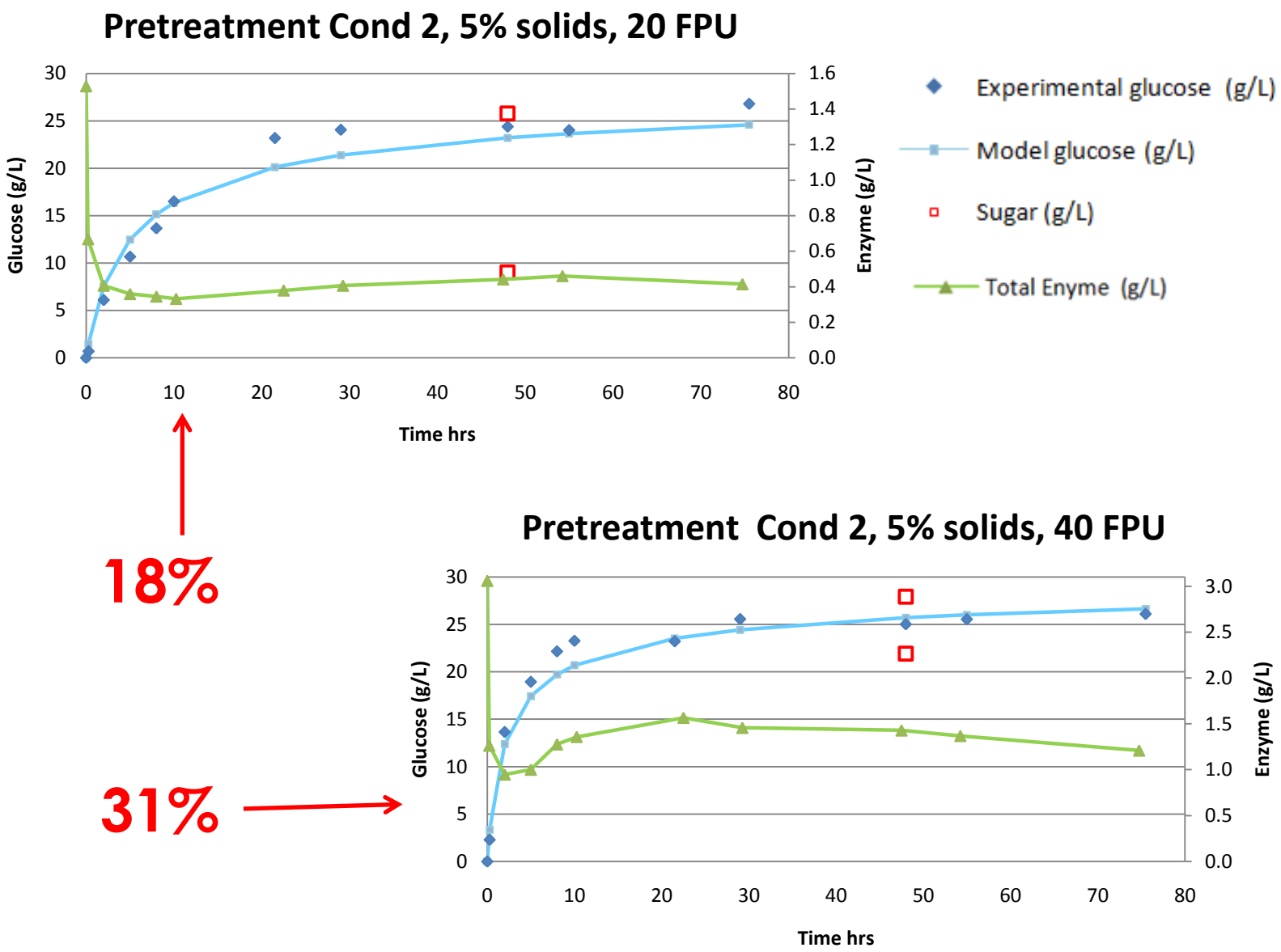
Ke	1358.90	kg/L
kd	0.54	L/h*kg
k2	341.04	1/h
Lf	0.15	g cellulase/g lignin

Enzyme recycling

- **Adsorption**

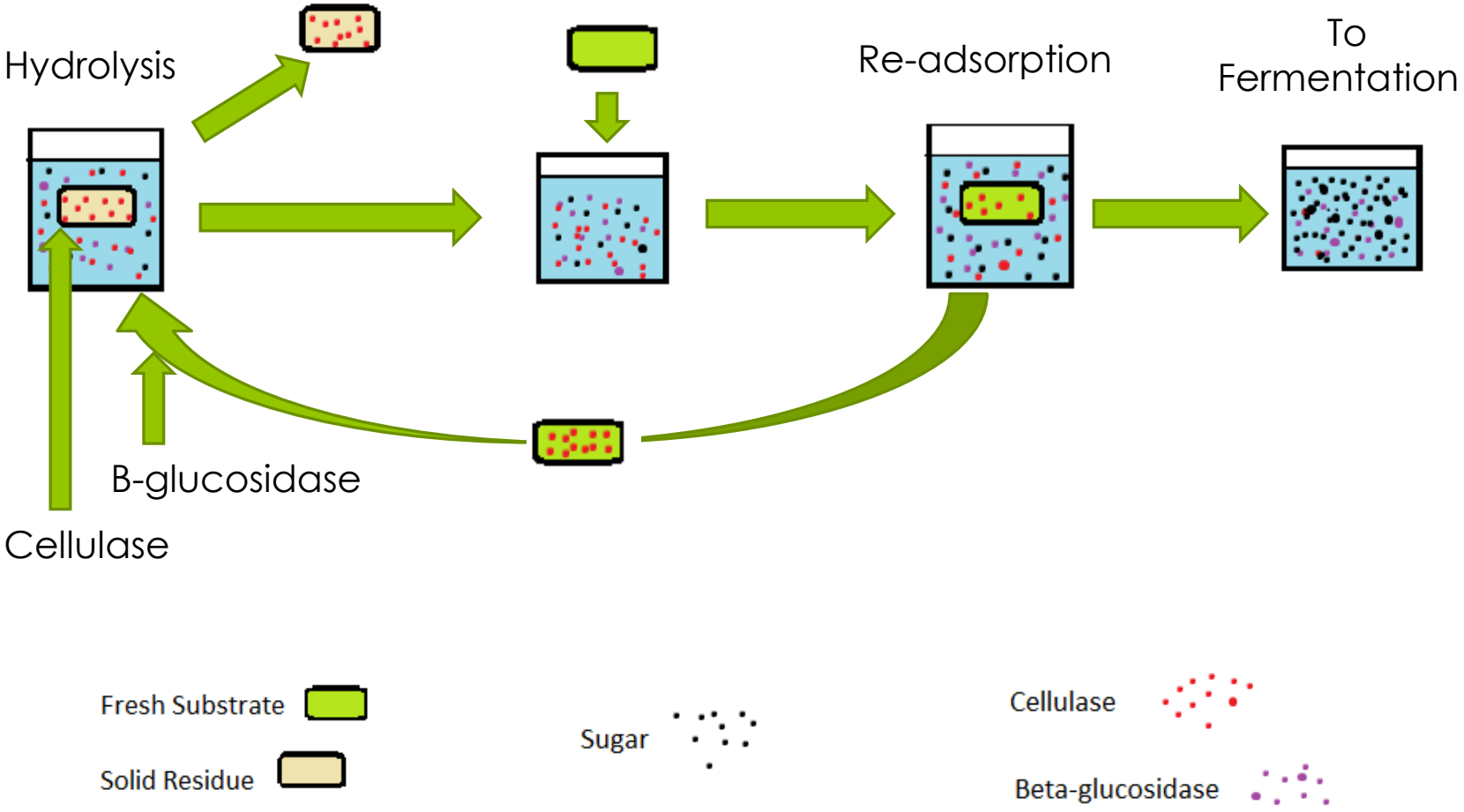


Enzyme recycling



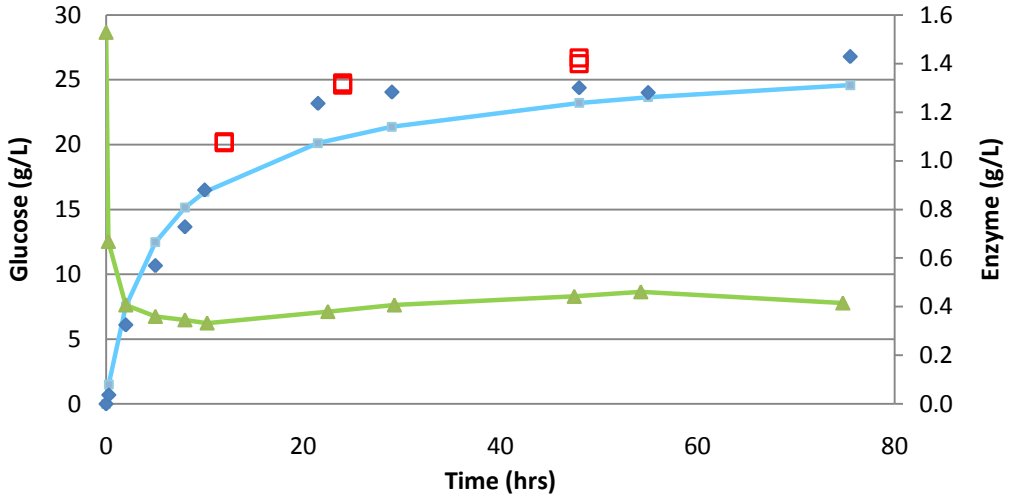
Enzyme recycling

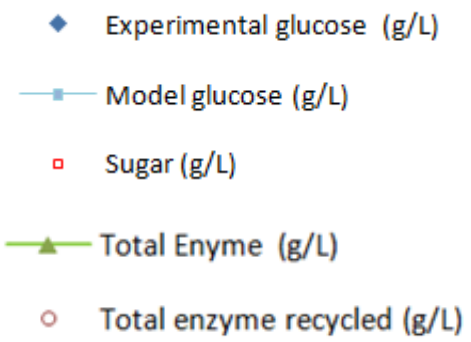
- **Adsorption**



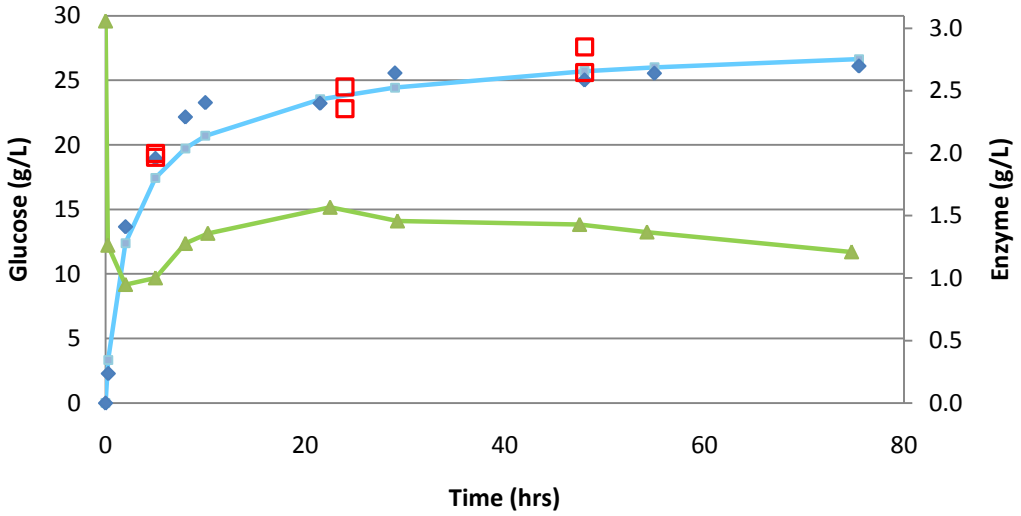
Enzyme recycling

Cond 2, 5%, 20 FPU

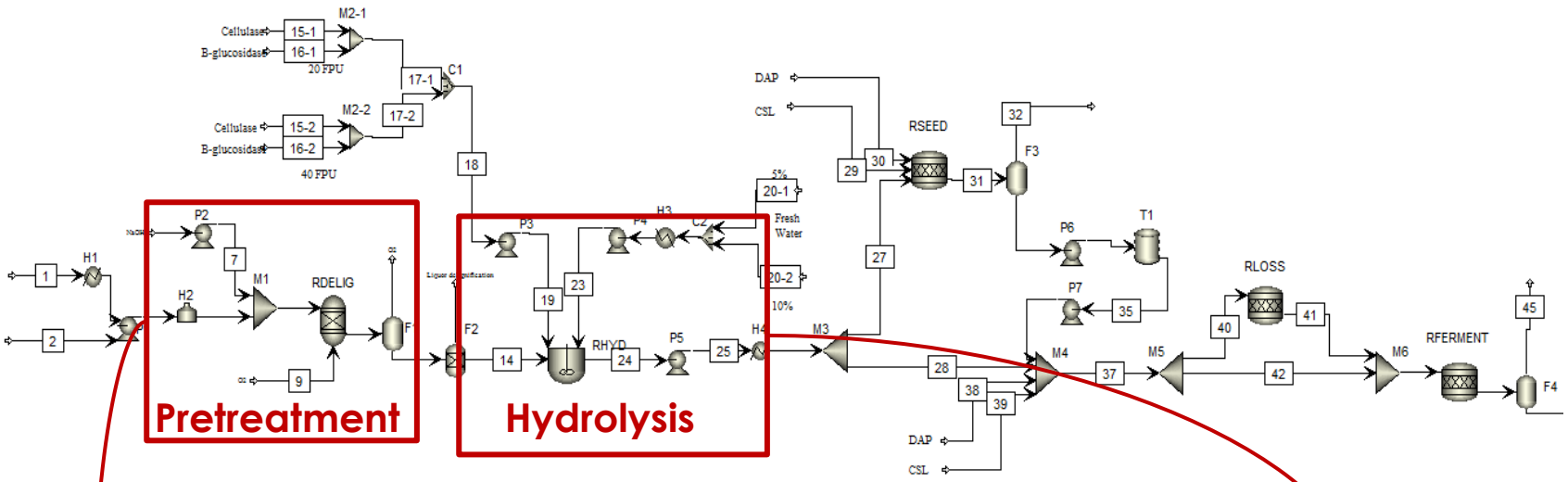




Cond 2, 5%, 40 FPU



Aspen Simulation



- Experimental conversion for all polysaccharides
- Residence time

		Pretreatment		Hydrolysis	
	(Kg/hr)	Inlet	Out	Inlet	Out
Solids	Cellulose	7.171	6.435	6.436	1.846
	Xylan	4.021	3.046	3.045	0.607
	Lignin	3.170	1.166	1.166	1.166
	Cellulase	0	0	0	0.261
	B-glucosidase	0	0	0	0.078
Liquid	Water	478.744	478.744	257.491	256.6
	Glucose	0	0	0	5.099
	Xylose	0	0	0	2.771
	Lignin	0	2.004	0.241	0.241
	Cellulase	0	0	0.261	0
	B-glucosidase	0	0	0.095	0.017

- Glucose and xylose kinetic model
- Mannose, galactose and arabinose experimental conversion
- B-glucosidase aggregation model

Conclusions

- The β-glucosidase may suffer a structural change at 50 °C that cause its aggregation and decrease its concentration and it can be modeled by the Finke-Watzky Mechanism.
- The kinetic model proposed can describe with accuracy the production of glucose
- Most of the enzyme get adsorbed into the substrate in the first 15 minutes of the reaction and most of it is non reversible adsorbed
- It seems that some or one kind of cellulase is responsible for the majority of the cellulose hydrolysis.
- Continuous process for the enzyme recycling technology

I WOULD LIKE TO THANK .....

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Questions
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