

Kinetic Modeling of Cellulosic Biomass Processing  
Featuring Enzymatic Hydrolysis with Anticipation of  
Incorporation into a CFD Framework (Revised title)

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# Project Rationale

## Biological Conversion of cellulose biomass to commodity products

Desirable because of potential benefits with respect to

- Sustainable resource supply
- Energy security
- Rural economic development

## Bottlenecks

Cost of overcoming the recalcitrance of cellulosic biomass

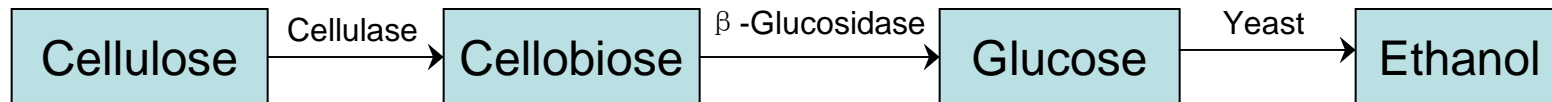
- Most costly process step
- Least technically mature
- Enzyme, microbially-based processes have outstanding potential

## Scale-up

- No experience with full-scale facilities
- Limited fundamental understanding
  
- Computational fluid dynamics (CFD) is powerful tool for scale up analysis
- A collaborative project with FLUENT inc. recently initiated

# Simultaneous Saccharification & Fermentation

## System definition



## Experimental data

### South et al. (1995), batch & continuous feeding

- Pretreated wood, peptone yeast extract growth media, 37 °C
- Genencor CL cellulase supplemented with Novozyme 188 β - glucosidase
- Yeast (*Saccharomyces cerevisiae*), strain D5A
- 1 L working volume

### This study, intermittent feeding

- As above except paper sludge (Fraser Papers Mill, Gorham, NH) was processed in a lean medium containing 0.15% (v/v) corn steep liquor and 0.25mM MgSO<sub>4</sub>.

# Essential features of enzymatic hydrolysis models (South et al)

- 1) Rate saturation with respect to either substrate or enzyme  
(e.g. using Langmuir adsorption, but not Michaelis-Menten kinetics)
- 2) Declining reaction rate per adsorbed enzyme with increasing conversion

$$k(x) = k' \times (1 - x)^m + c$$

- 3) Particle reactivity changes with concentration & conversion  
Particle population model (For a well-mixed, fully continuous steady state reactor)

## RTD

$$x = \int_0^{\infty} x(t) \times E(t, \tau) dt \quad E(t, \tau) = \frac{1}{\tau} \times \exp\left(-\frac{t}{\tau}\right)$$

## CPDM (Loescher et al)

$$x = \frac{1}{n_0} \times \int_0^1 x \times \hat{n}(x) dx \quad n_0 = \int_0^1 \hat{n}(x) dx \quad \frac{d\hat{n}(x)}{dx} = -\frac{\hat{n}(x)}{\hat{r}} \left[ \frac{d\hat{r}}{dx} + \frac{S_0}{\tau_s} \right]$$

- **All three features deviate from classical kinetics for soluble substrates**
- **While various mathematical forms can be used to describe these phenomena, all three must be addressed for any broadly applicable model**

## Outline of South et al. model (perfect mixing assumed)

### Rate equations

Cellulose: 
$$r_S = -(k' \times (1-x)^m + c) \times \frac{[CE]}{\sigma_S} \times \frac{K_{S/C}}{CB + K_{S/C}} \times \frac{K_{S/P}}{[P] + K_{S/P}}$$

Cellobiose: 
$$r_{CB} = -1.056 \times r_S - \frac{K_c \times [CB] \times [B]}{K_m \times (1 + \frac{[G]}{K_{C/G}}) + [CB]}$$

Cells: 
$$r_{Xc} = \frac{[X_c] \times \mu_{max} \times [G]}{[G] + K_G} \times (1 - \frac{[P]}{K_{X/P}})$$

Glucose: 
$$r_G = (-1.056 \times r_S - r_{CB}) \times 1.053 - \frac{r_{Xc}}{Y_{X/G}}$$

Ethanol: 
$$r_P = r_{Xc} \times \frac{Y_{P/G}}{Y_{X/G}}$$

### Material balance

Batch: 
$$\frac{d[i]}{dt} = r_i$$

$i = \text{Cellulose, Cellobiose, Cells, Glucose, Ethanol}$

Continuous: 
$$\frac{d[i]}{dt} = r_i + \frac{1}{\tau} \times ([i_0] - [i])$$

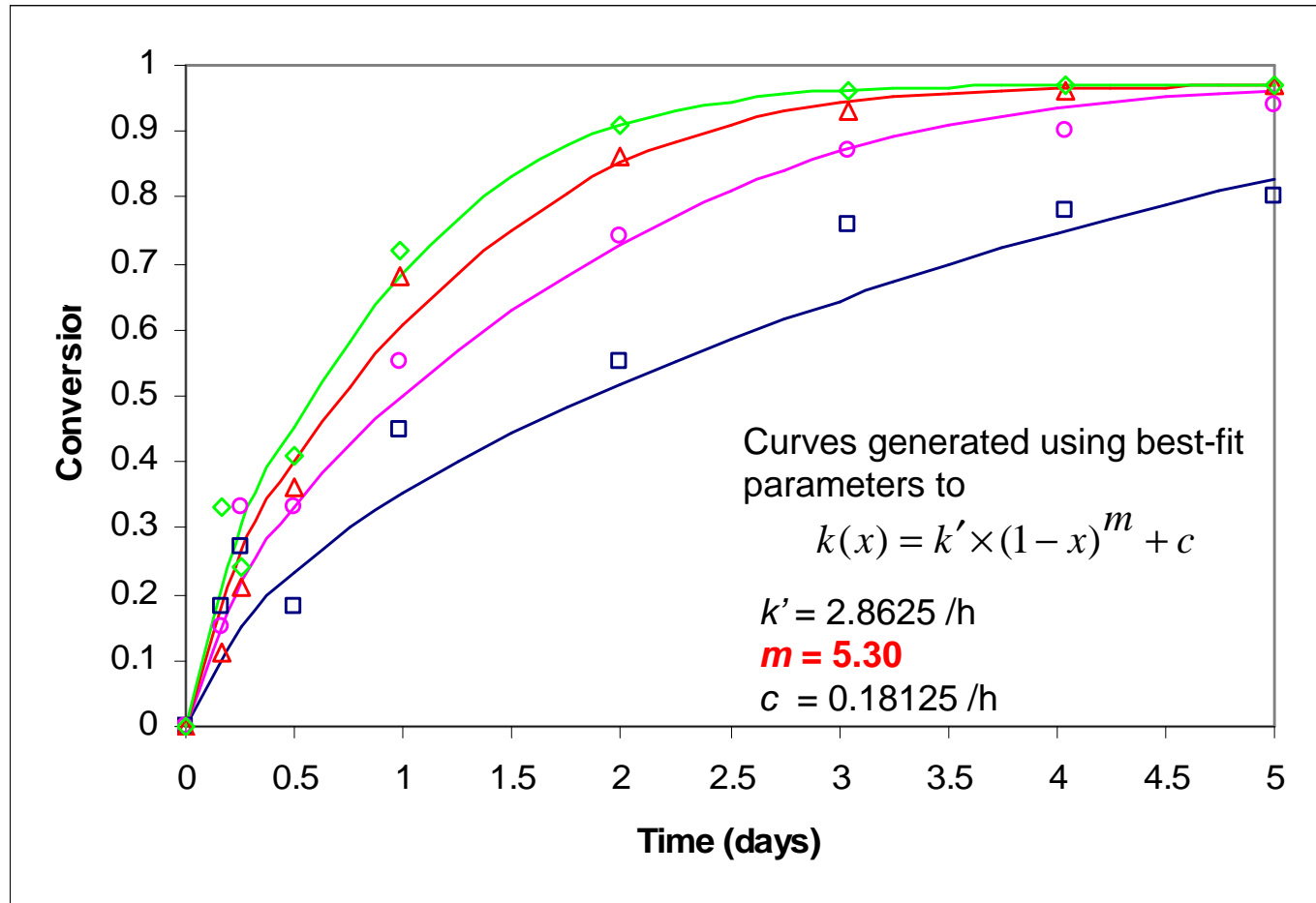
### Conservation equations

Cellulose: 
$$[S] = [S_f] + \frac{[CE]}{\sigma_s}$$

Lignin: 
$$[L] = [L_f] + \frac{[LE]}{\sigma_L}$$

Cellulase: 
$$[E\tau] = [E] + [CE] + [LE]$$

# Batch SSF



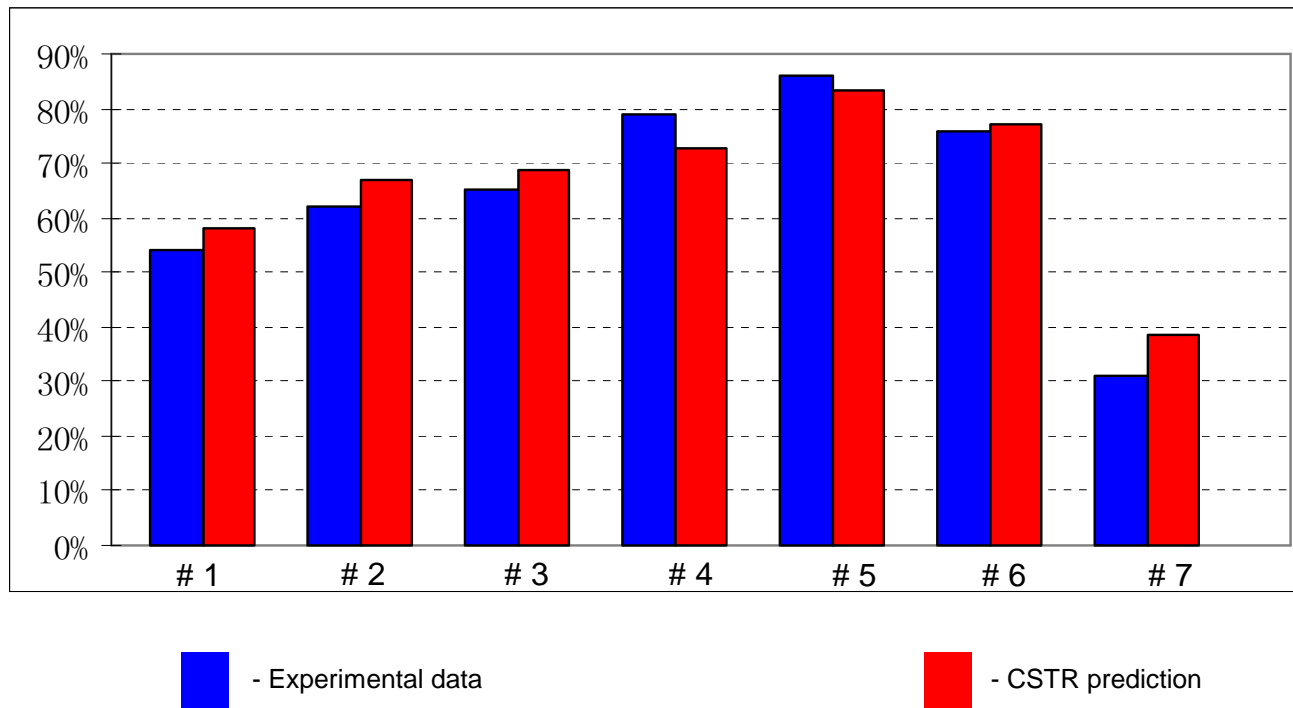
Enzyme loading

- : 5 U/g
- : 10 U/g
- △: 15 U/g
- ◇: 20 U/g

Substrate

Dilute acid-pretreated wood

# Continuous SSF (steady state)



## Range of CSTR data, runs 1 through 7

Residence time: 5.6-fold  
Feeding concentrations: 12.9-fold  
Enzyme loadings: 2.1-fold

- Predictions based on parameter values obtained by fitting batch data without adjustment
- Consideration of changing reactivity over the time a particle spends in the reactor is absolutely required to get agreement with experimental data for the continuous system

# Solution Algorithm of South et al model

- Set derivatives = 0 (assumed steady state)
- Simultaneous solution of 5 non-linear algebraic equations using multiple iterative loops

## Limitations

### General

- Not readily adapted to intermittent feeding
- Perfect mixing assumed (not readily adjusted to imperfect mixing)

### Specific to CFD (limited to solving ~50 dynamic equations per element per time step)

- Particles modeled as ~100,000 discrete populations
- Extensive iterations (~30)
- Excessive computational requirements when implemented on a distributed basis in a CFD framework (~10,000 computational elements)

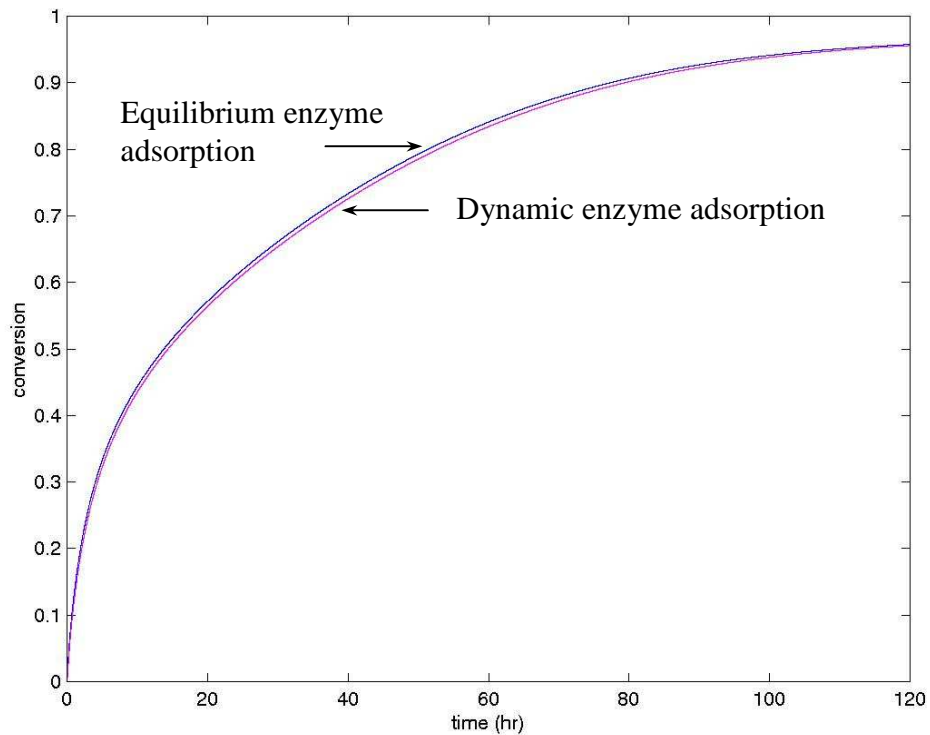
In light of these limitations, the solution of South et al. has to be modified to be compatible with CFD analysis



# Modifications to Kinetic model

Change Equilibrium Enzyme Adsorption to Dynamic Enzyme Adsorption

Model prediction: Batch SSF (enzyme loading = 10 U/g)



**Accommodate Intermittent Feeding**

# Accommodate Discrete feeding

Define particle conversion

## Reactor conversion

$$x = \frac{[S_0] - \sum_{i=1}^n [S(i)]}{[S_0]}$$

$[S_0]$  = g cellulose/L, fed to the reactor

$[S(i)]$  = g cellulose/L, population  $i$ , in the reactor @  $t$

$x$  Changes due to

1. Reaction
2. Exit of substrate

## Particle conversion, $x_p(i)$

$$x_p(i) = \frac{[S_0(i)] - \frac{1}{R(i)} \times [S(i)]}{[S_0(i)]}$$

$R(i)$  = Fraction of particles of population  $i$  remain in the reactor

$[S_0(i)]$  = g cellulose/L, population  $i$ , fed to the reactor

$[S(i)]$  = g cellulose/L, population  $i$ , in the reactor @  $t$

$x_p$  changes due to reaction only

$x_p(i)$  rather than  $x$ , is appropriate to use for the conversion dependent rate constant

$$k(x_p(i)) = k' \times (1 - x_p(i))^m + c$$

# Accommodate Discrete feeding (continued)

- Particles fed at a given time are modeled as a discrete population ( $i$ )
- Total enzyme = Free enzyme + sum (enzyme bound to each population)
- Track particle populations until they are highly converted

<b><u>Hydrolysis rate</u></b>	$r_i = [k \times (1 - x_p(i))^m + c] \times \frac{[CE(i)]}{\sigma_s} \quad , \quad x_p(i) = \frac{[S_0(i)] - \frac{1}{R(i)} \times [S(i)]}{[S_0(i)]}$
<b><u>Material balance for component J</u></b>	$\frac{d[J(i)]}{dt} = r_i + \frac{I(t)}{f} \times [J_0(i)] - \frac{O(t)}{f} \times [J(i)]$  J = Substrate, enzyme, lignin, cellobiose, glucose, cells, ethanol
<b><u>Reactor conversion</u></b>	$x = ([S_0] - \sum_{i=1}^n [S(i)]) / [S_0]$

$$I(t) = \begin{cases} 1 & t = t_0 \text{ (original feeding)} \\ 0 & \text{at all other times} \end{cases}$$

$$O(t) = \begin{cases} 1 & \text{removal time (feeding time)} \\ 0 & \text{at all other times} \end{cases}$$

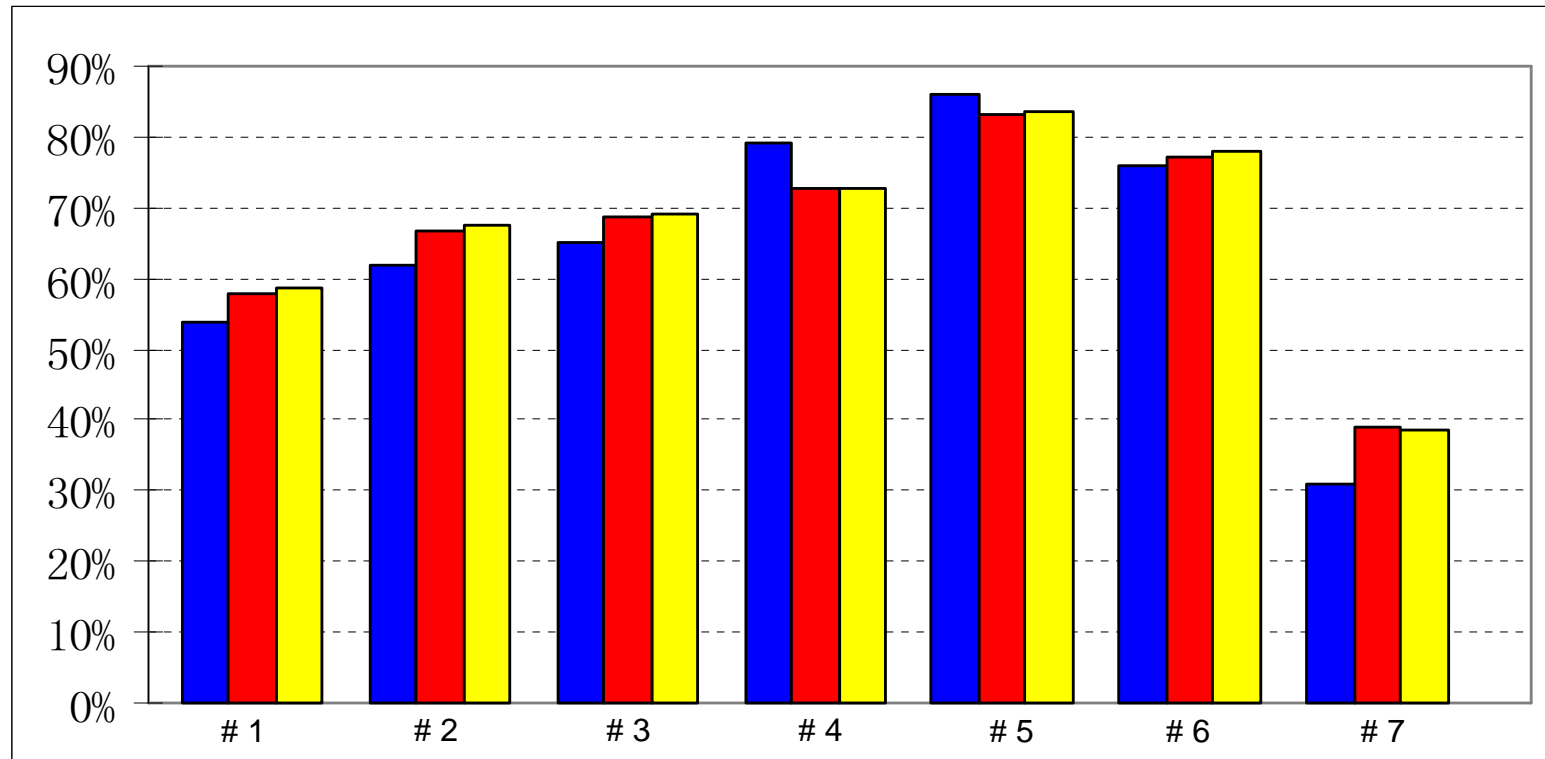
$i$ : index of individual particle population


$n$ : total number of particle populations

**$f$  : feedings/residence time**


$R(i)$ : remaining fraction of particle pop  $i$

# Comparison of predicted CSTR conversion using the South Solution Algorithm and the Discrete Solution Algorithm

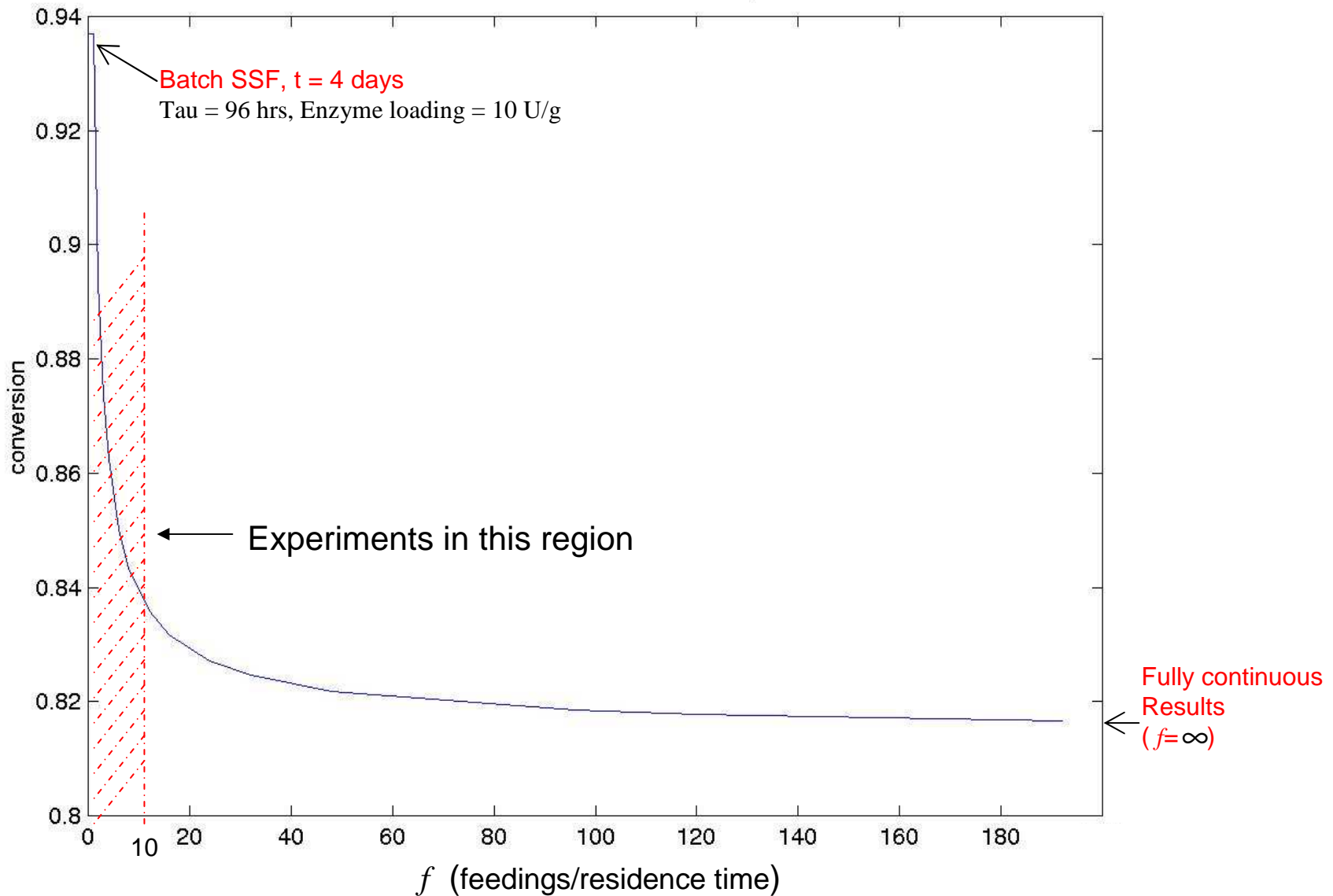


 - Experimental data

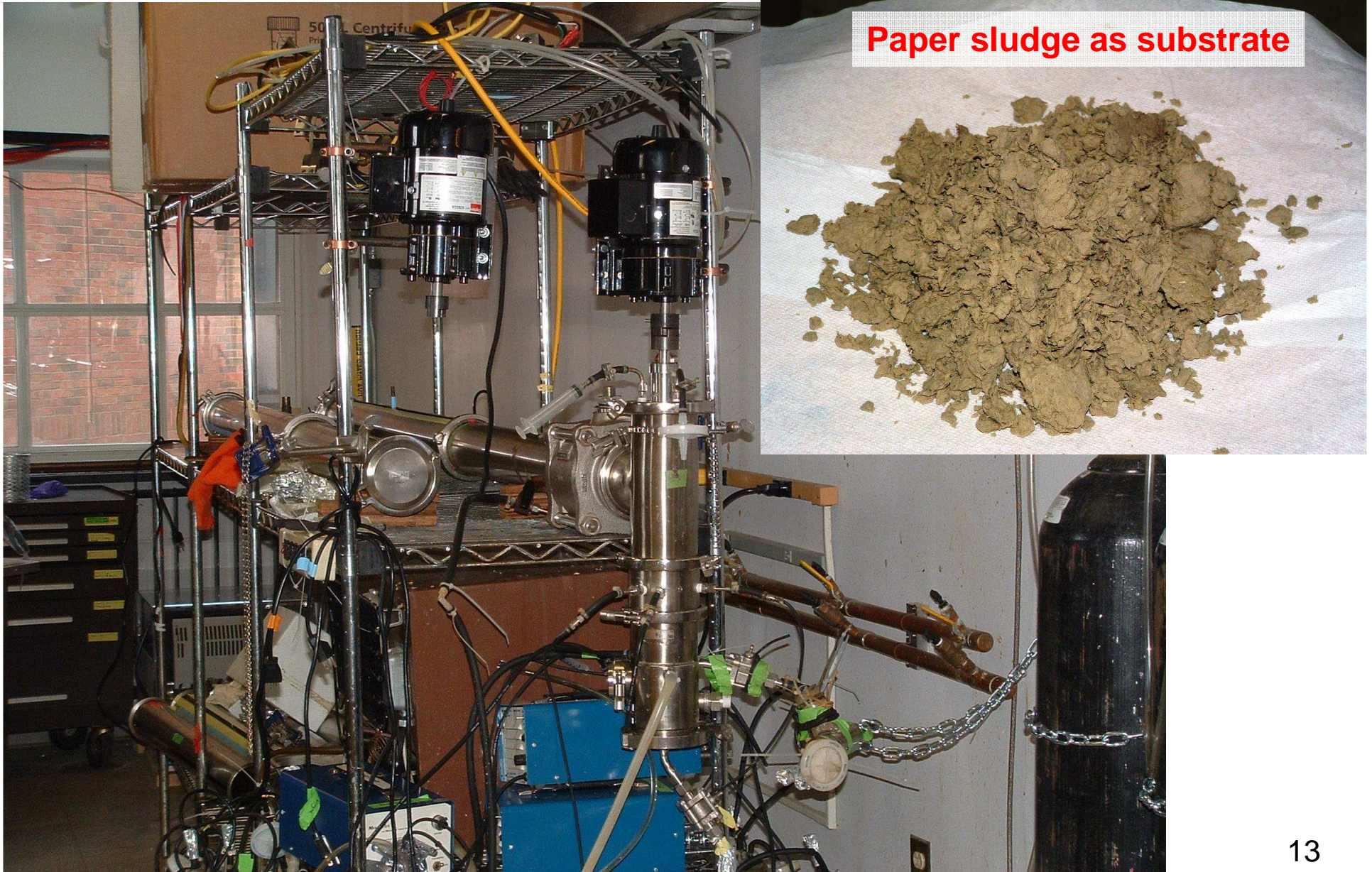
 - CSTR prediction

 - Discrete model prediction ( $f = 200$ )

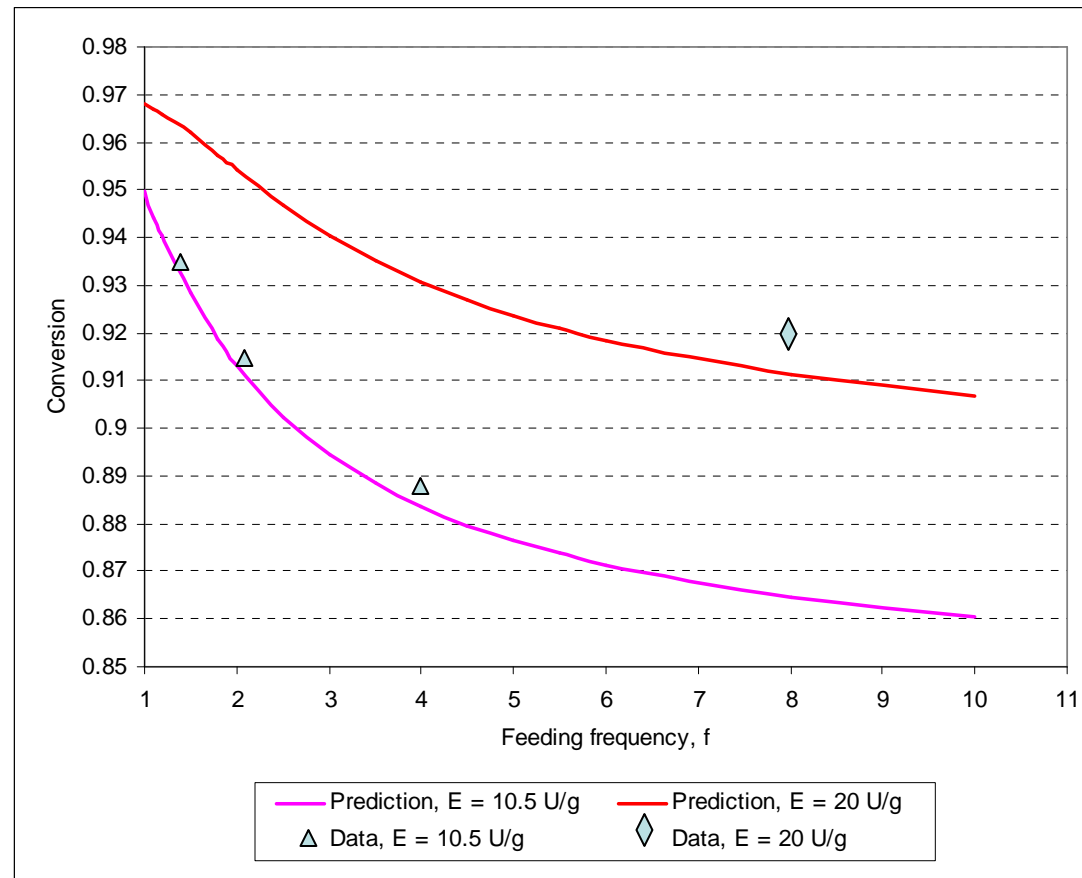
# Discrete SSF, Steady State (end of cycle) cellulose conversion vs. feeding frequency (enzyme loading = 10 U/g, $\tau = 4$ days )



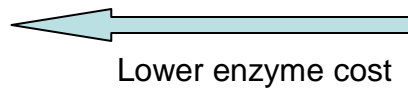
# Experimental system



# Prediction vs. experimental data for Paper sludge



Anticipated trends:



Lower enzyme cost



Lower cost for mixing, heat transfer

- Lowering  $f$  allows conversion to remain constant while reducing enzyme loading
- Model predictions based on parameter values for pretreated wood
- Experimental data obtained with paper sludge

CFD analysis of continuous systems requires that the number of equation solved per element (N) be limited (Current limit: 50 equations)

Equations for  $n$  discrete particle population  $2n$

- Cellulose concentration,  $i$  th population, [S( $i$ )]
- Cellulose-enzyme complex concentration,  $i$  th population, [CE( $i$ )]

Additional equations 8

- Lignin concentration, [L]
- Lignin-enzyme concentration, [LE]
- Cellulase enzyme concentration, [E1]
- Cellobiose concentration, [CB]
- Cell concentration, [Xc]
- Ethanol concentration, [P]
- Glucose concentration, [G]
- Carbon dioxide concentration, [CD]

Number of equations (N)  $2n + 8$



# N depends on the degree of accuracy required

## Fractional error

$$\epsilon(n) = 1 - \frac{\text{Quasi-steady state reactor conversion with } n \text{ particle populations tracked}}{\text{Quasi-steady state reactor conversion with } \gg n \text{ particle populations tracked}}$$

$\tau$ (days)	$f$	$\bar{x}$	$\epsilon(n) = 0.2\%$		$\epsilon(n) = 1.0\%$		$\epsilon(n) = 2.0\%$	
			n	N	n	N	n	N
2	2	82.74%	4	16	3	14	2	12
	8	78.36%	14	36	10	28	8	24
	20	77.10%	35	78	25	58	20	48
4	2	93.63%	2	12	1	9	1	9
	8	88.73%	7	22	5	18	3	14
	20	87.23%	16	40	10	28	8	24

Enzyme loading = 15 U/g

Equations limit: ~50

For many scenarios, N falls within the practical range for CFD

# Status of Modeling Work in Relation to Complexity

Scenario	# of reactors	Feeding	Mixing	Population	Status/Solution expected
1	1	Batch	Perfect	1	Done (South)
2	1	Batch	Imperfect	1	Done*
3	1	Continuous	Perfect	many	Done (South)
4	1	Intermittent	Perfect	few	Done
5	1	Intermittent	Imperfect	few	Solvable
6	1	Continuous	Imperfect	many	Not likely to be practical w/ CFD
7	N (staged)	Continuous	Perfect	many	In progress
8	N (staged)	Intermittent	Perfect	few	In progress
9	N (staged)	Intermittent	Imperfect	few	Solvable
10	N (staged)	Continuous	Imperfect	many	Not likely to be practical w/ CFD

Intermittent feeding is advantageous in terms of both application and computational feasibility

\* Presented at 25<sup>th</sup> Symposium on Biotechnology for Fuels and Chemicals

# Summary

- Combining kinetic and CFD models for biocommodity processes is a promising approach for scale-up analysis that has received little prior attention previously
- SSF model of South et al. has been reformulated to be compatible with requirements for analysis via CFD, reducing the number of particle populations tracked from 100,000 to  $< 30$  with little error
- Model results indicate that reduced feeding frequency allows high conversion to be realized at  $\sim 2$ -fold lower enzyme loading
- Experimental results with paper sludge confirm predicted trend
- Good agreement between experimental and predicted data is obtained although parameter values obtained for a different substrate
- Continued development and application of combined kinetic and CFD models is underway