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

Xiongjun Shao, Zhiliang Fan, Colin Hebert
Lee R. Lynd*, Charles E. Wyman*
Thayer School of Engineering
Dartmouth College

André Bakker
Fluent Inc.

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* Corresponding Author

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

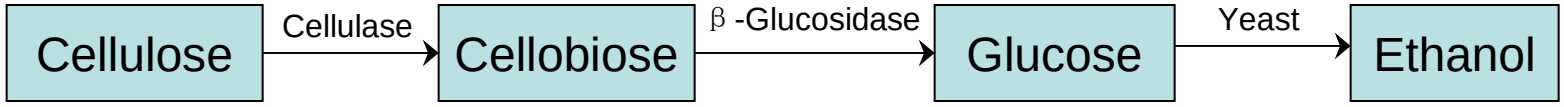
Scale-up

- 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 ºC
- 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 $MgSO_4$.

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

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

CPDM (Loescher et al)

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

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

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

i = Cellulose, Cellobiose, Cells, Glucose, Ethanol

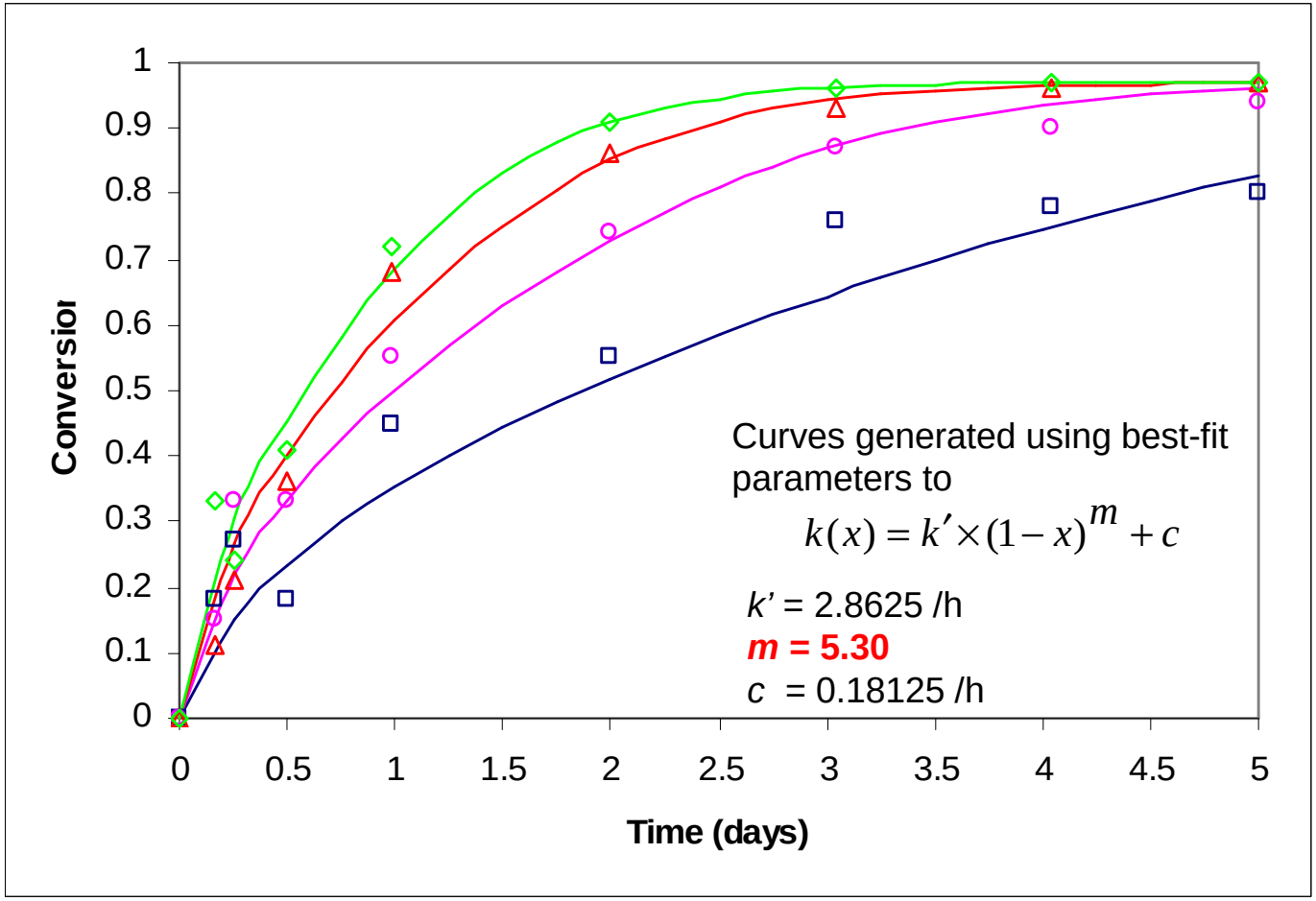
Conservation equations

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

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

Cellulase: $$[E_T] = [E] + [CE] + [LE]$$

Batch SSF



Enzyme loading

□: 5 U/g

o: 10 U/g

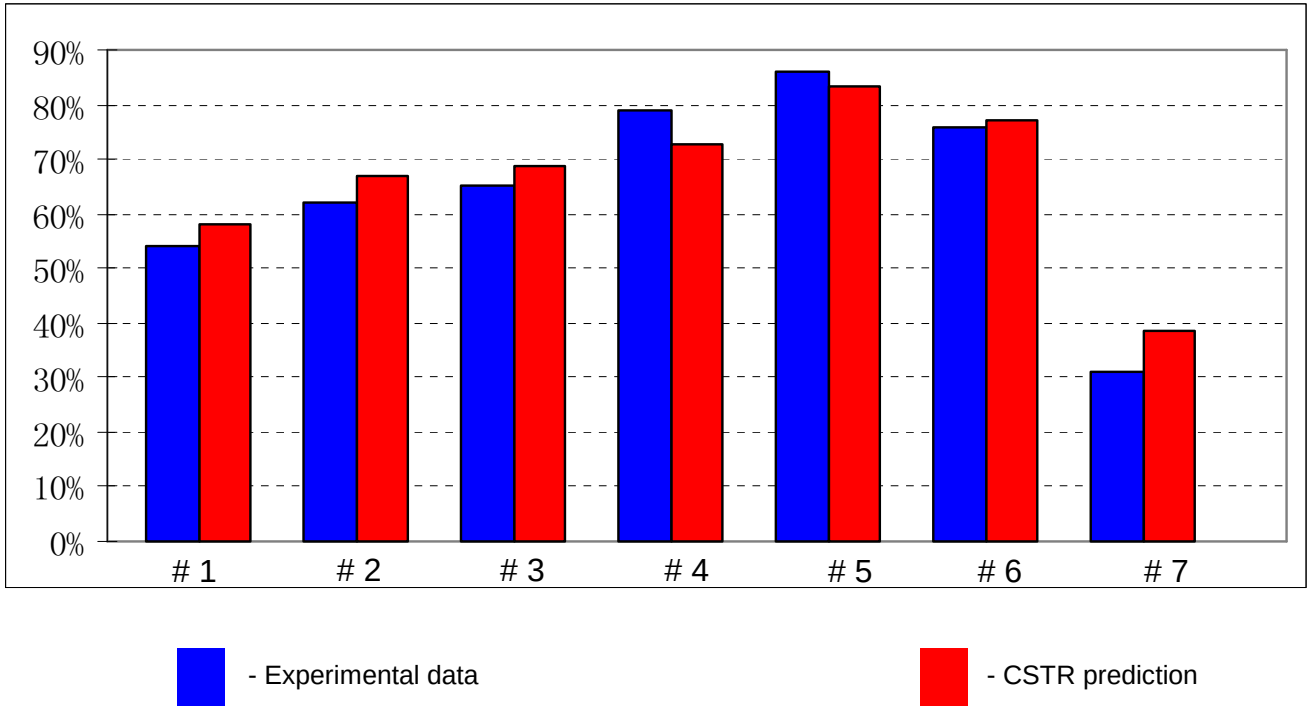
Δ: 15 U/g

◊: 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)

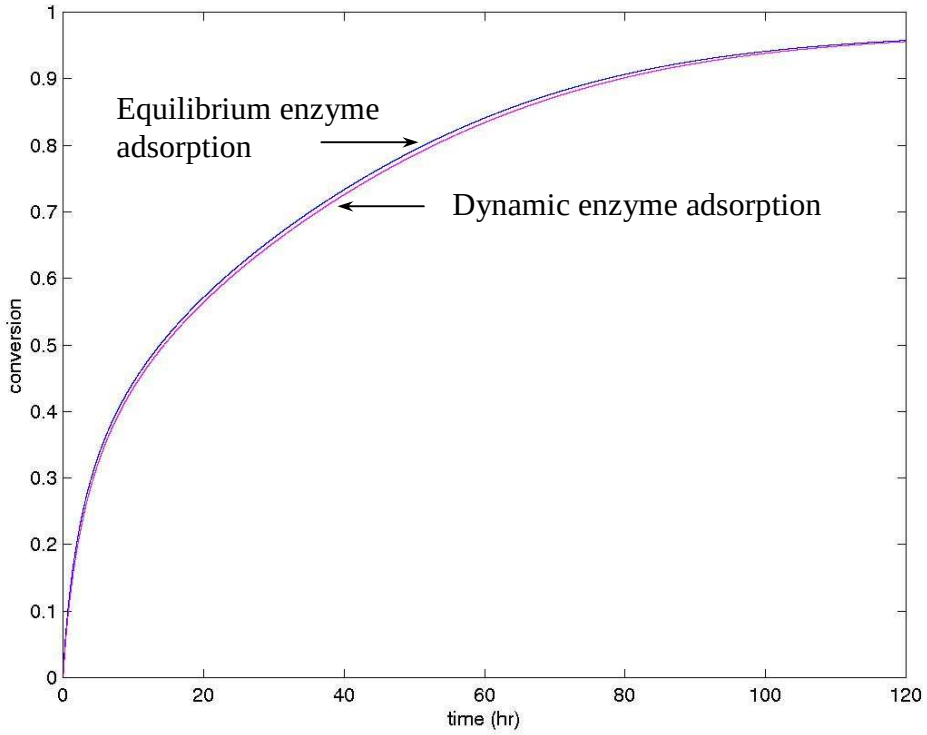
- Particles modeled as ~100,000 discrete populations
- Extensive iterations (~30)
- Excessive computational requirements when implemented on a distributed basis in a CFD framework (~10,000 computational elements)

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

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

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

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

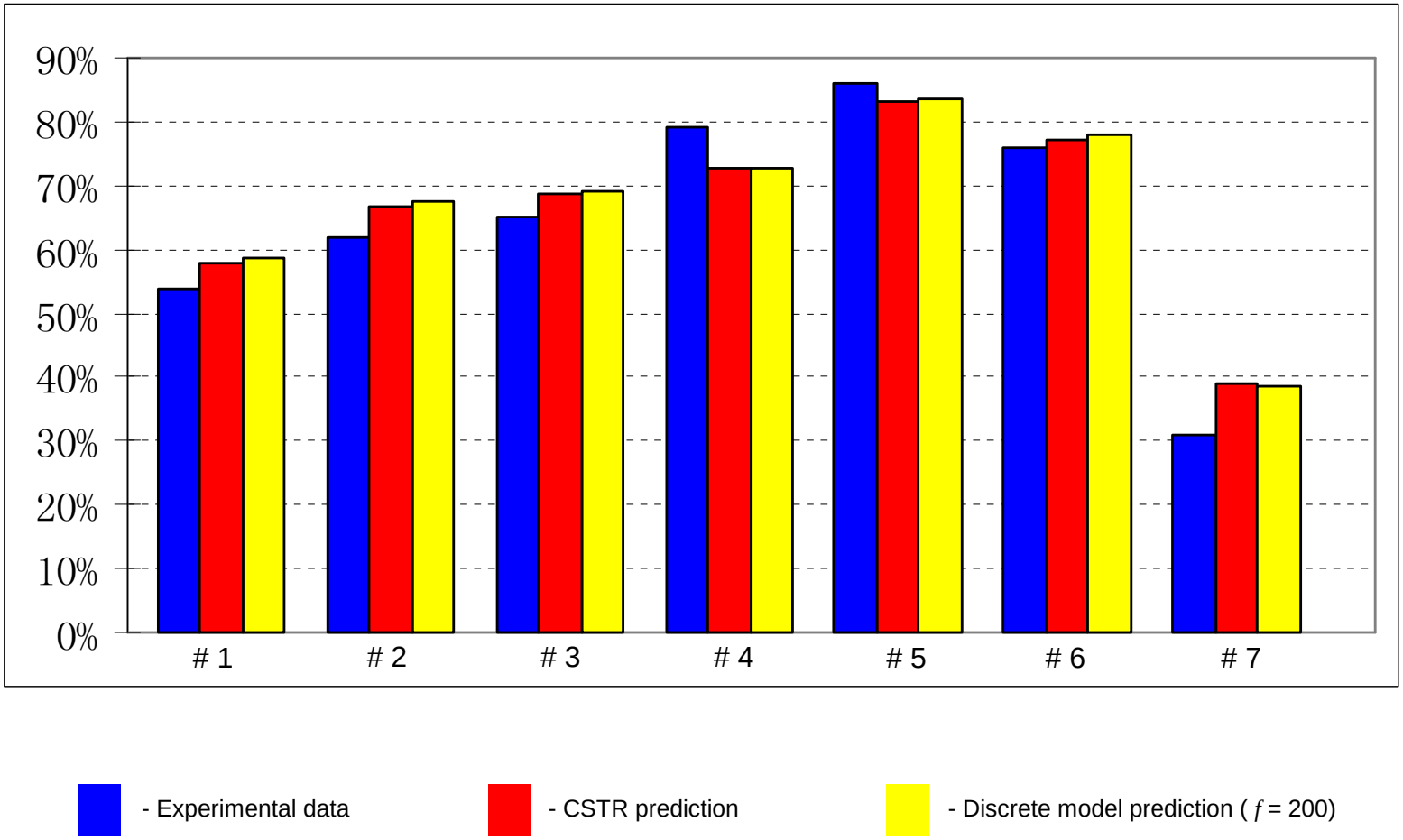
i: index of individual particle population

n: total number of particle populations

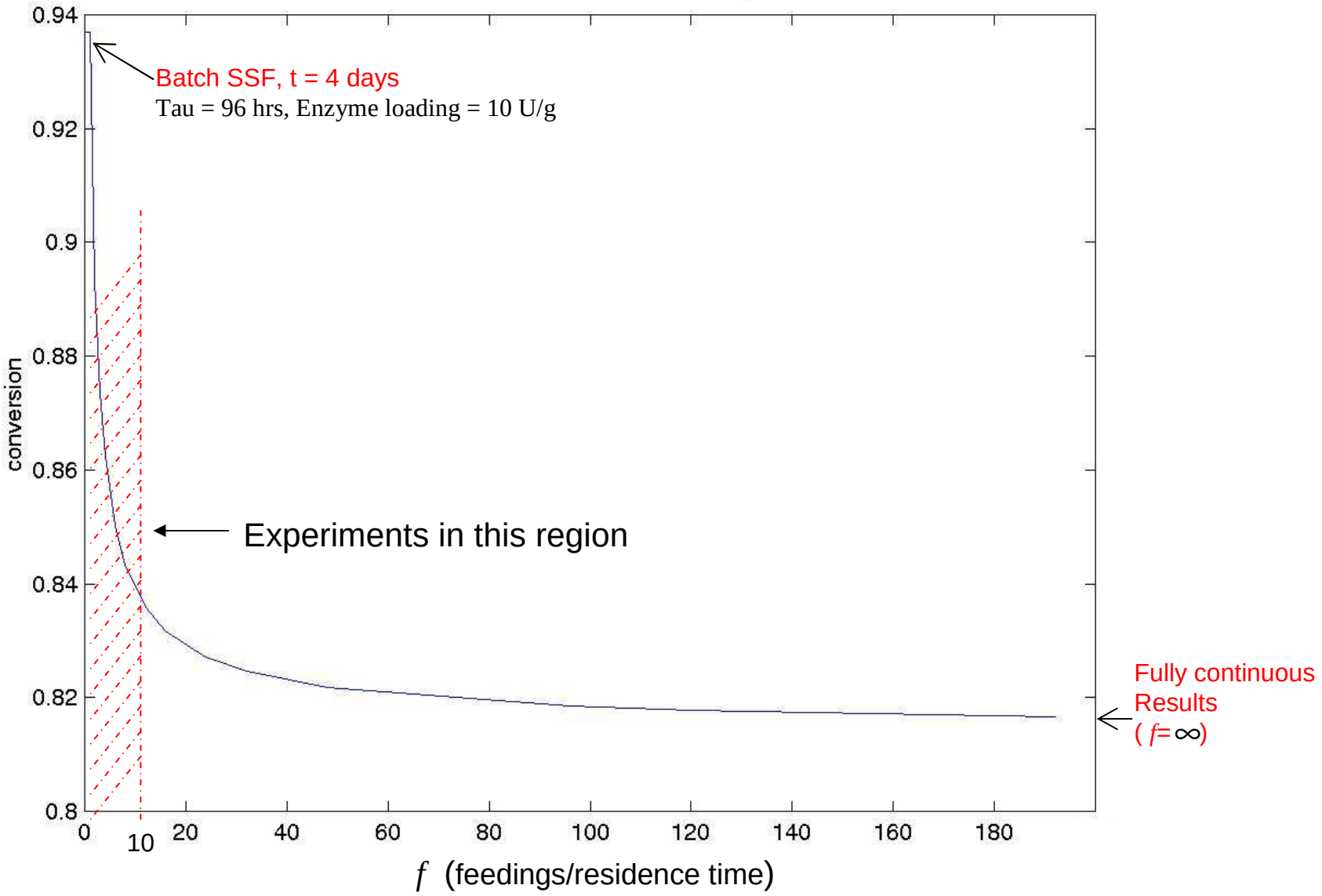
***f* : feedings/residence time**

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

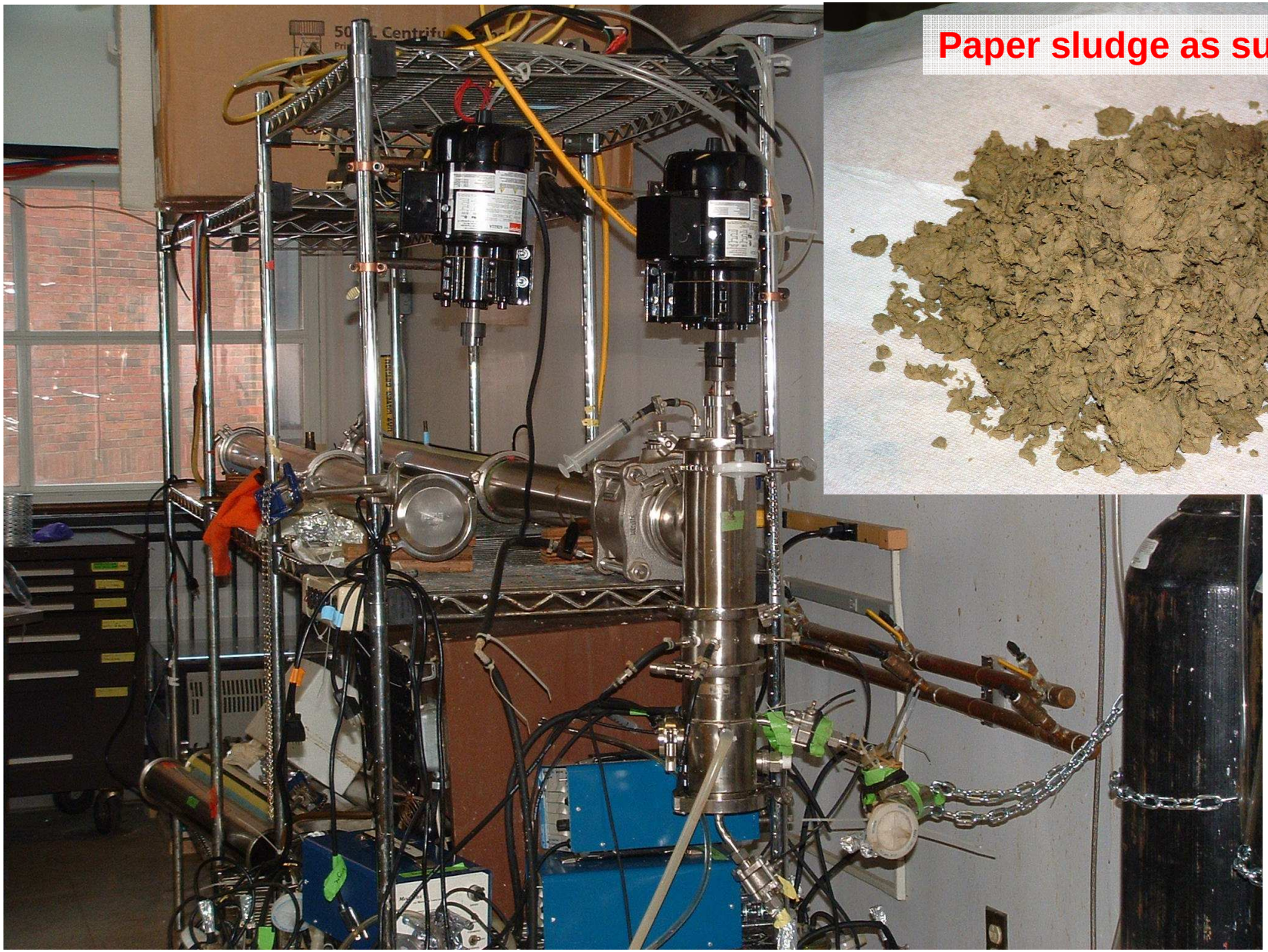
Comparison of predicted CSTR conversion using the South Solution Algorithm and the Discrete Solution Algorithm



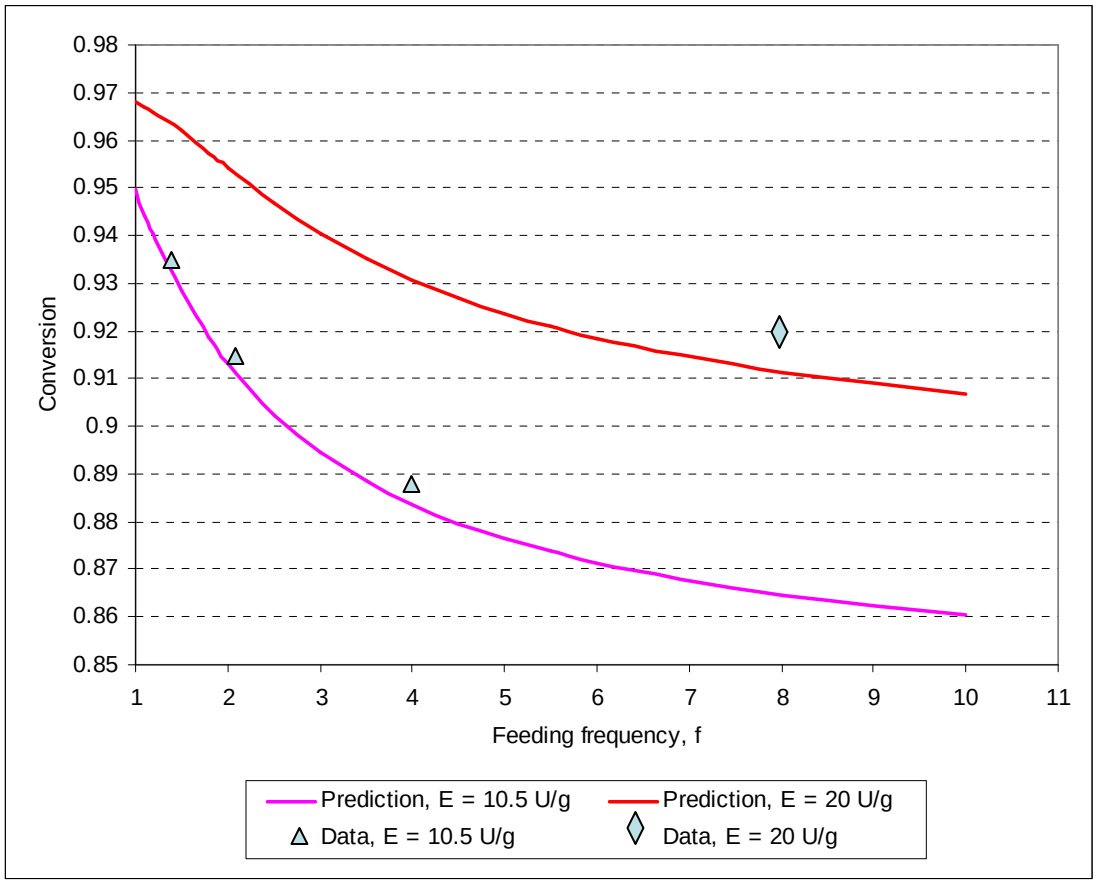
Discrete SSF, Steady State (end of cycle) cellulose conversion vs. feeding frequency (enzyme loading = 10 U/g, τ = 4 days)



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

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

τ (days)	f	$\bar{x}$	ε(n) = 0.2%		ε(n) = 1.0%		ε(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 25th 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 ~ 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