Development of a membrane-based separation process for the continuous enzymatic saccharification of lignocellulosic biomass

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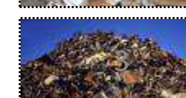
Lignocellulosic biomass

- Lignocellulosic biomass is
  - agricultural and wood residues
  - municipal solid waste
  - paper waste
- Rich in cellulose and lignin
  - can be utilized as a source to produce many fungible products
  - sugar and lignin
- It is cheap and non-competitive with other food sources
- Can be a great local source of energy which would otherwise go unused
- *Current state of art of converting lignocellulosic biomass to fungible sugar and lignin is difficult*



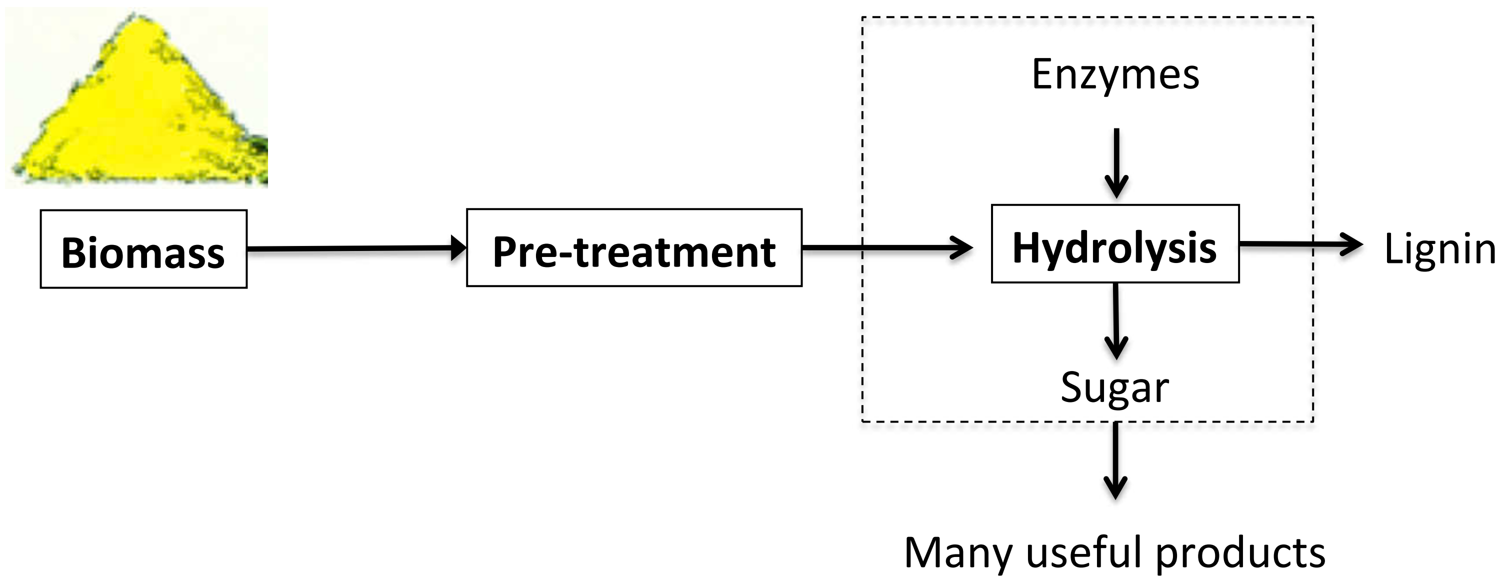






Picture Source: University of Washington

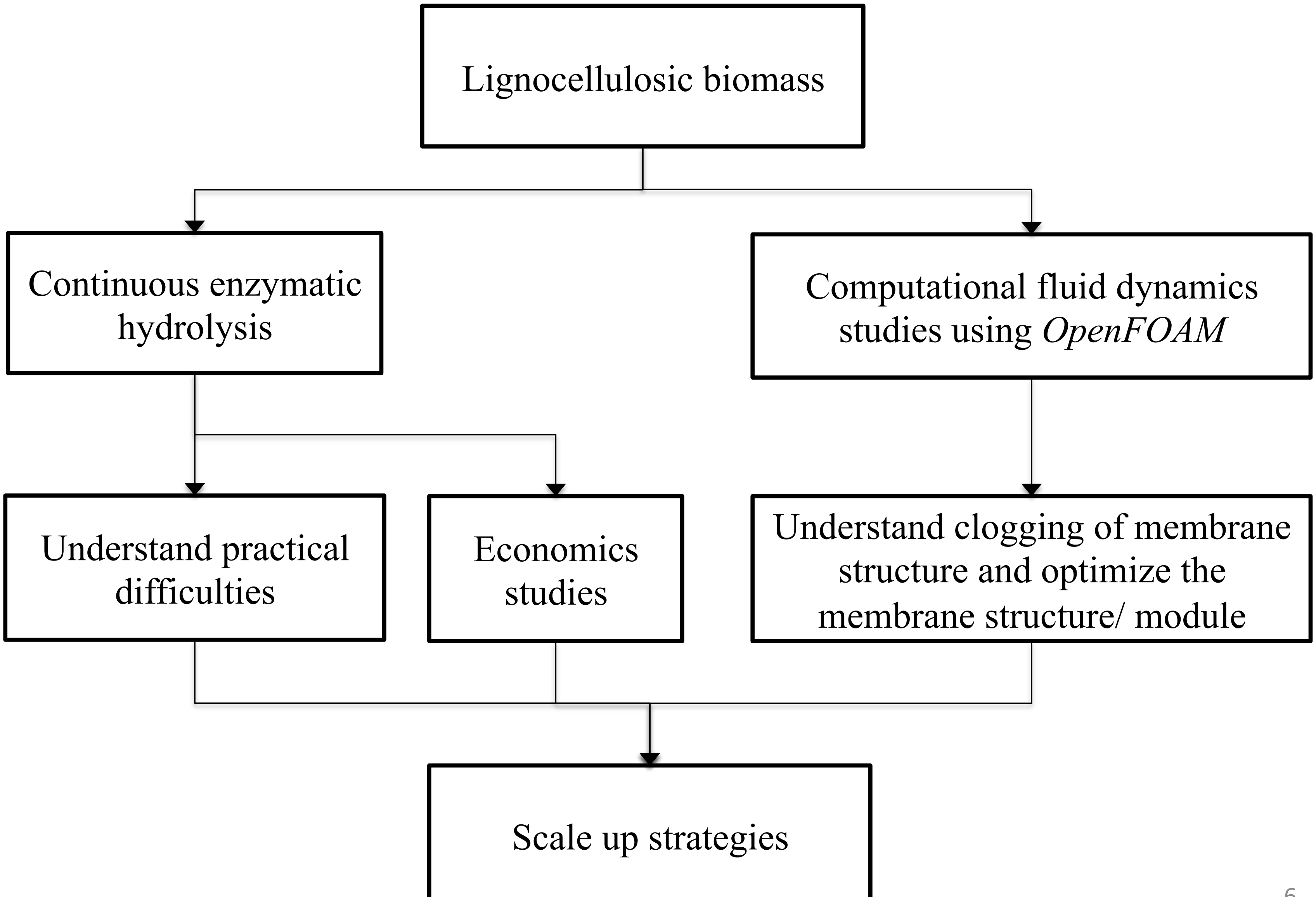
Lignocellulosic biomass processing



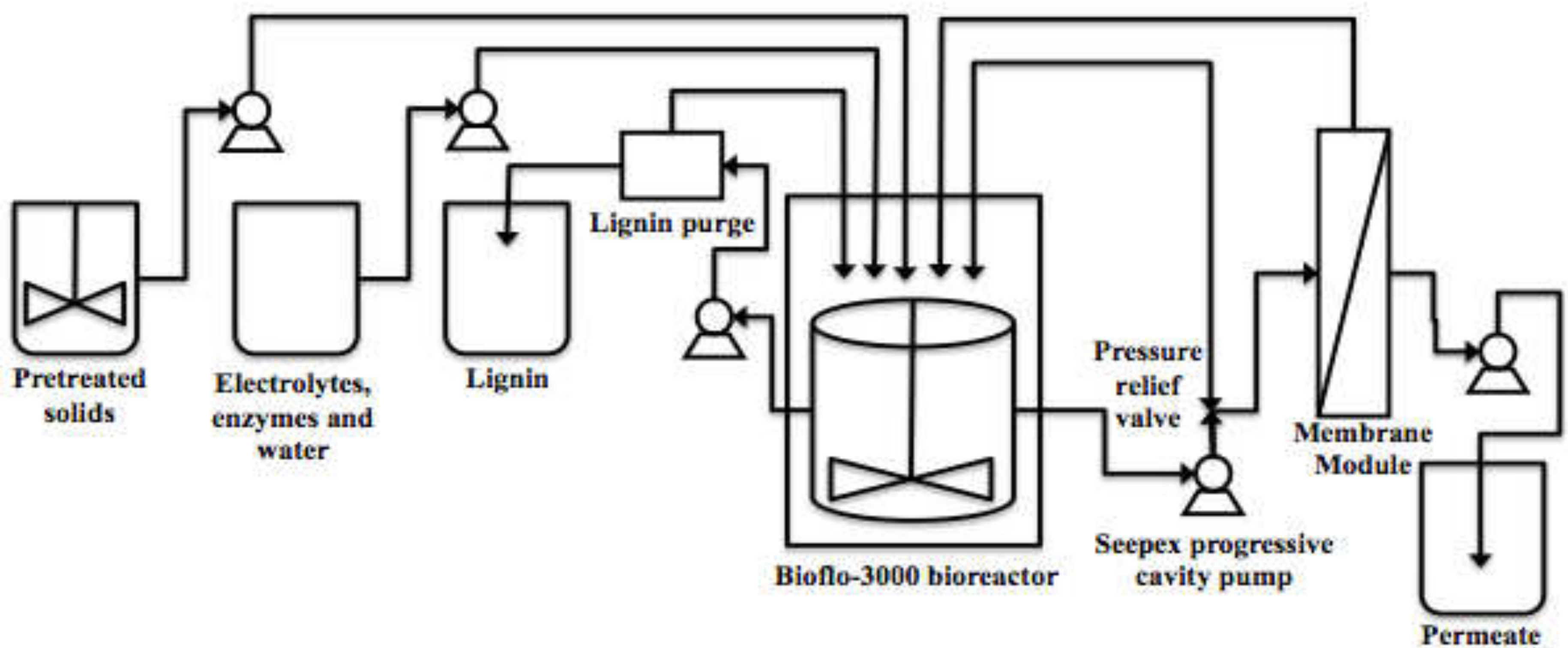
Enzymatic hydrolysis

- Enzymatic hydrolysis is done from fungi-derived enzymes
- Hydrolysis and separation steps following the hydrolysis is difficult
  - *lignocellulosic biomass behaves as a non-Newtonian slurry*
  - *presence of particles*
  - *difficulties in pumping*
  - *potential clogging of tubes*
  - *hydrolysis is inhibited by sugar*
- The hydrolysis is slow and subject to product inhibition, continuous product removal during hydrolysis which
  - *increases the reaction rate and conversion*
- Membrane separation can be implemented to continuously remove sugar during the hydrolysis

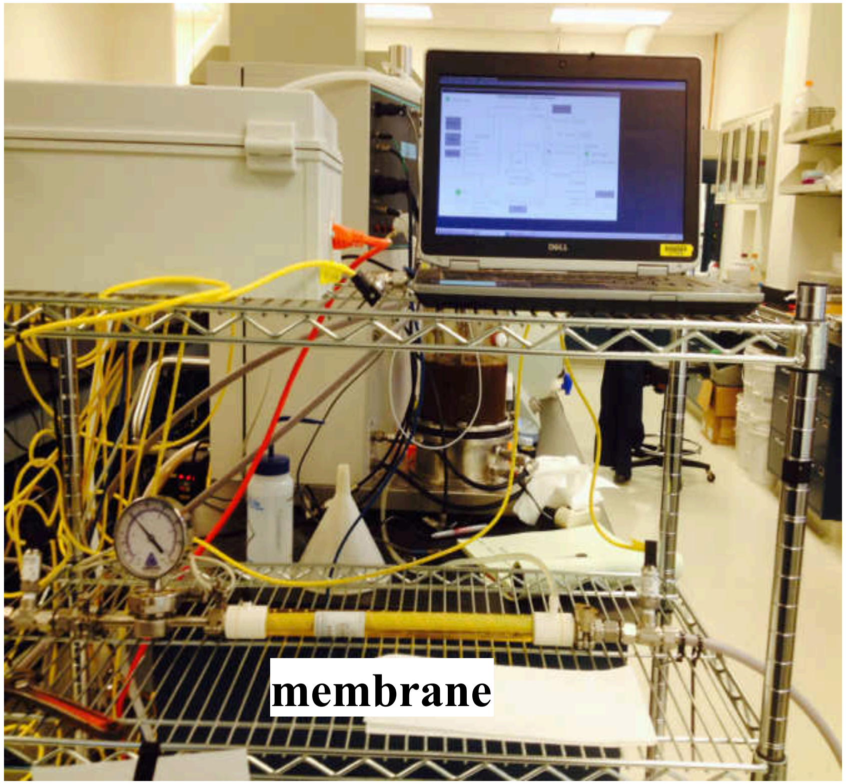
Methodology



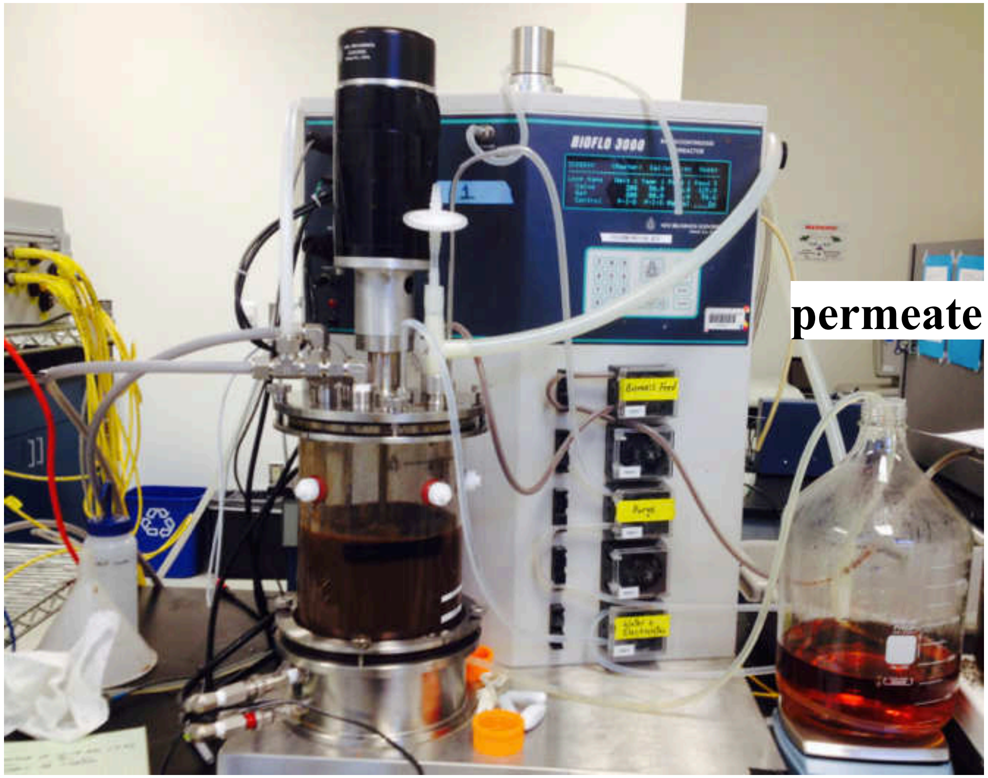
Experimental process flow diagram



Experimental set up



The system during the experiment

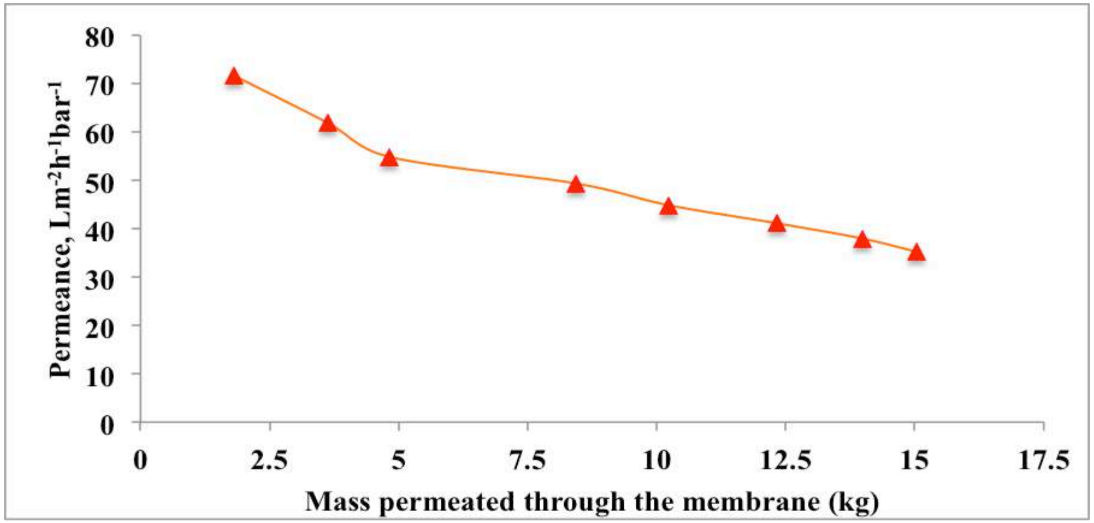


Bioflo 3000 bioreactor during the experiment

Koch-HFM 180 membrane

- Membrane material: ultrafiltration polyvinylidene difluoride (PVDF)
- Observed separation range of 100 kg/mol (~10-14 nm)
- Operates at pH range of 2-12
- Operates at temperature up to 70 °C
- Maximum operating pressure of 140 psi (~10 bar)

Membrane module



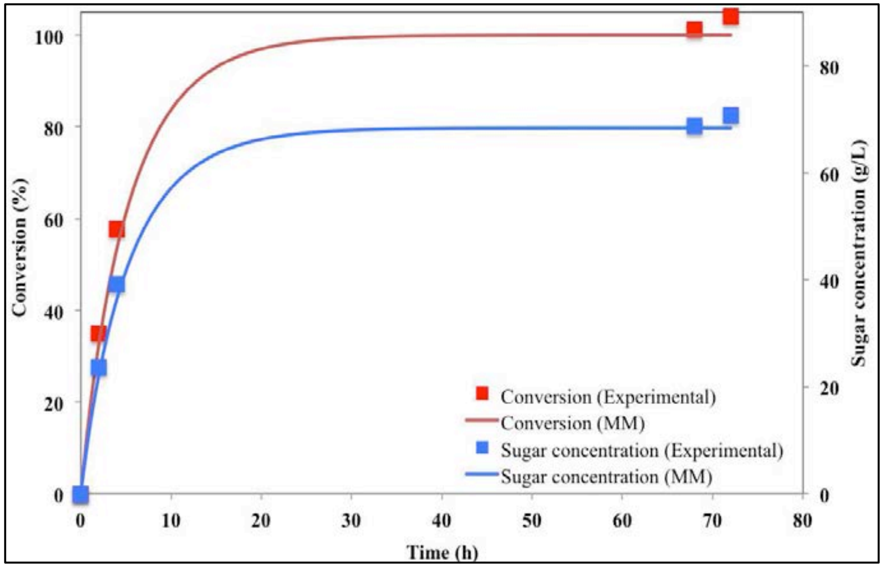
Slurry with 2.5% insolubles permeation characteristics

Batch and continuous results

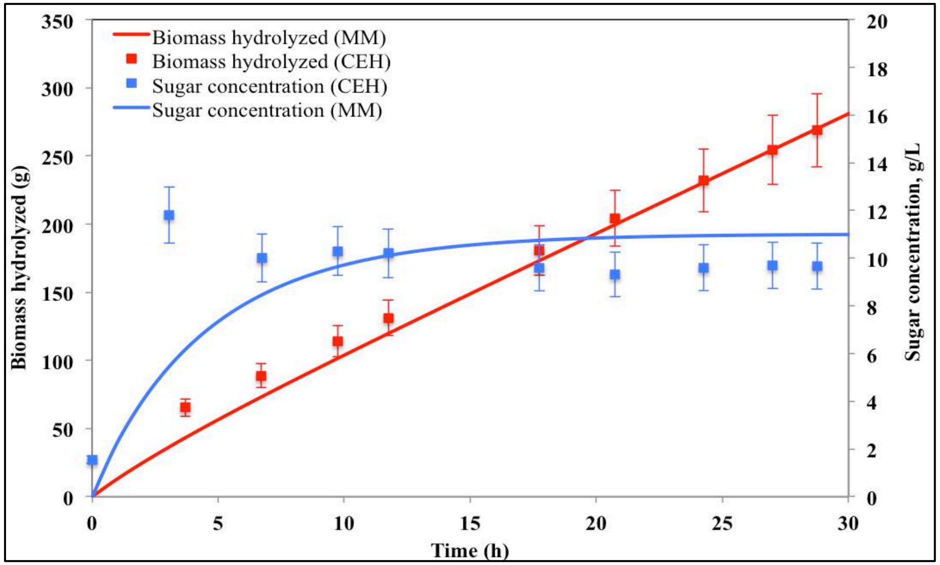
The reaction rate in enzymatic hydrolysis is empirically given by *Michaelis–Menten*

$$r = \frac{k_{cat}[E][S]}{k_m\left(1+\frac{[P]}{k_1}\right)+[S]}$$

where r is the reaction rate, k_{cat}, k_m, and k_1 are constants, E is the enzyme concentration, S is the substrate concentration, and P is the product concentration



Batch enzymatic hydrolysis with 10% insolubles

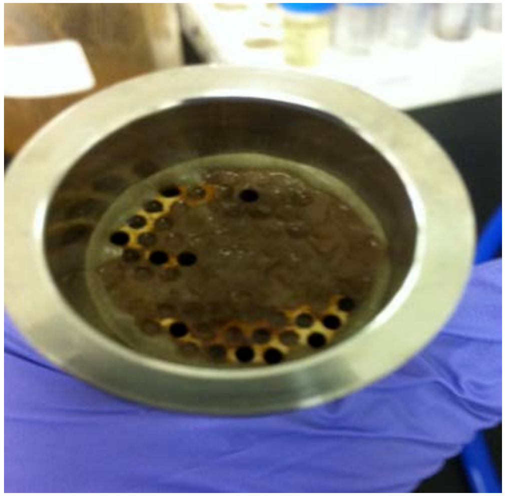


Continuous enzymatic hydrolysis with 2.5% insolubles

MM: *Michaelis–Menten* and CEH: continuous enzymatic hydrolysis

Clogging of membrane module

- A membrane module with 85 tubes
  - *1.05 mm inside diameter and a 30 cm length*
- After some time of filtration, module got clogged
  - *worsened over time*
- Continuous lignocellulosic biomass hydrolysis using *any membrane* needs
  - *appropriate surface area and diameter to achieve the desired separation rate while minimizing deposition of suspended solids;*
  - *module design is a key engineering opportunity*



Computational fluid dynamics

- Impractical to test all possible membrane modules
- Computation study of slurry flow in the membrane module
  - *entrance region(s)*
  - *different geometry and sizing*
  - *identify designs that have greatest potential for good operation*
- Understand the factors/scenarios that help minimize clogging and design an optimum membrane module
- ***OpenFOAM***
  - *free, open source CFD software package*
  - *Gmesh is used as meshing software*
  - *solvers are nonNewtonianIcoFoam and icoFoam*

Viscosity model

Herschel-Bulkley model

$$\tau(\dot{\gamma}) = \tau_y + k\dot{\gamma}^n$$

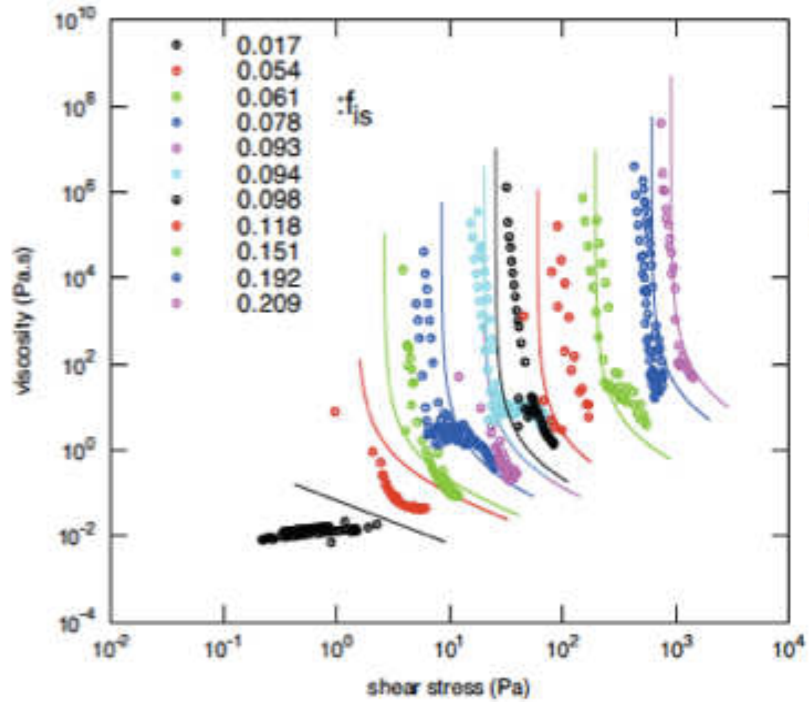
$$n = 0.5$$

a = 1.55e06
b = 4.75

$$\tau_y = a f_{is}{}^b$$

a = 0.148
b = 32.0

$$k = a e^{b f_{is}}$$



where

τ_y is the yield stress

k is a constant parameter

n is a dimensionless constant

γ is the effective shear rate

a and b are empirical constants derived from the models and

f_{is} is the insoluble fraction in the slurry.

Analytical solutions

With a non-Newtonian fluid flow in the tube, a flat velocity profile is formed in the center of the tube

- The velocity profile in a shear region is

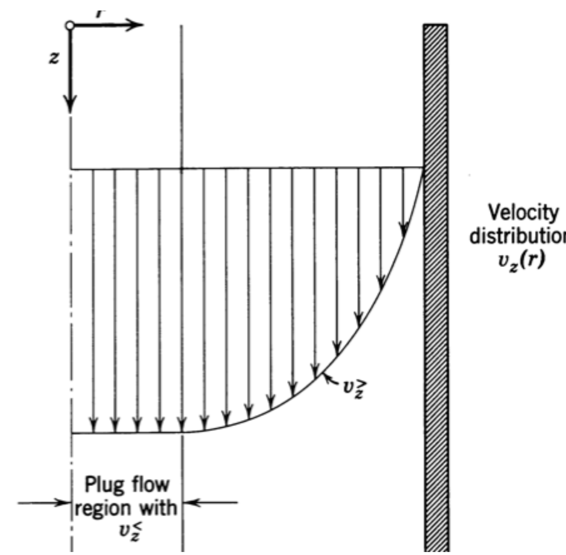
$$v_z(r) = -\frac{dz}{dP}2k\frac{\frac{\left(-\frac{1}{2}r\frac{dP}{dz}-\tau_y\right)^{\frac{1}{n}+1}}{k}}{\frac{1}{n}+1} + \frac{dz}{dP}2k\frac{\frac{\left(-\frac{1}{2}R\frac{dP}{dz}-\tau_y\right)^{\frac{1}{n}+1}}{k}}{\frac{1}{n}+1}$$

- The velocity profile in the flat region is

$$v_z(r) = -\frac{dz}{dP}2k\frac{\frac{\left(-\frac{1}{2}R_p\frac{dP}{dz}-\tau_y\right)^{\frac{1}{n}+1}}{k}}{\frac{1}{n}+1} + \frac{dz}{dP}2k\frac{\frac{\left(-\frac{1}{2}R\frac{dP}{dz}-\tau_y\right)^{\frac{1}{n}+1}}{k}}{\frac{1}{n}+1}$$

where the flat region's radius is

$$R_p = \frac{2\tau_y}{-\frac{dP}{dz}}$$



Schematic of flow profile

- Pressure drop across the two ends of the tube is

$$\frac{\Delta P}{l} = \frac{4K}{d}\left(\frac{8v}{d}\right)^n\left(\frac{3n+1}{4n}\right)^n\frac{1}{1-X}\left(\frac{1}{1-aX-cX^3-bX^2}\right)^n$$

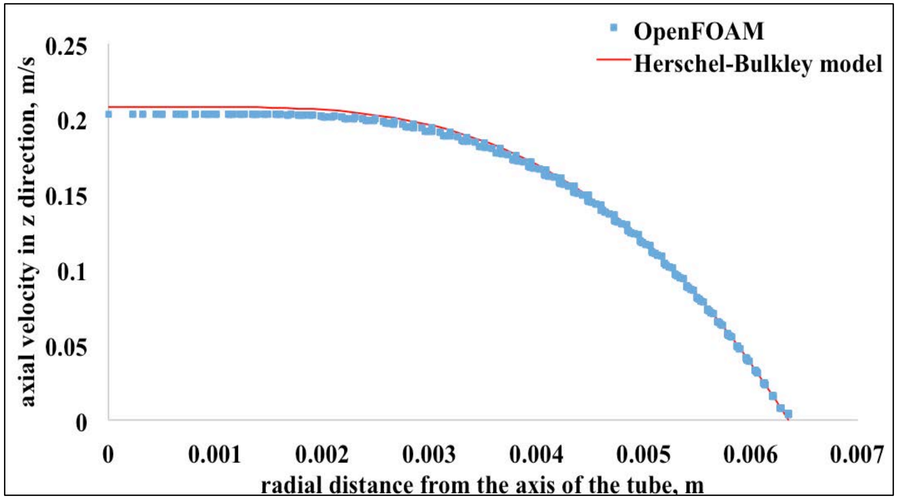
where $X = \frac{4l\tau_y}{d\Delta P}, a = \frac{1}{2n+1}, b = \frac{2n}{(2n+1)(n+1)}, c = \frac{2n^2}{(n+1)(2n+1)}$

- For Newtonian fluid

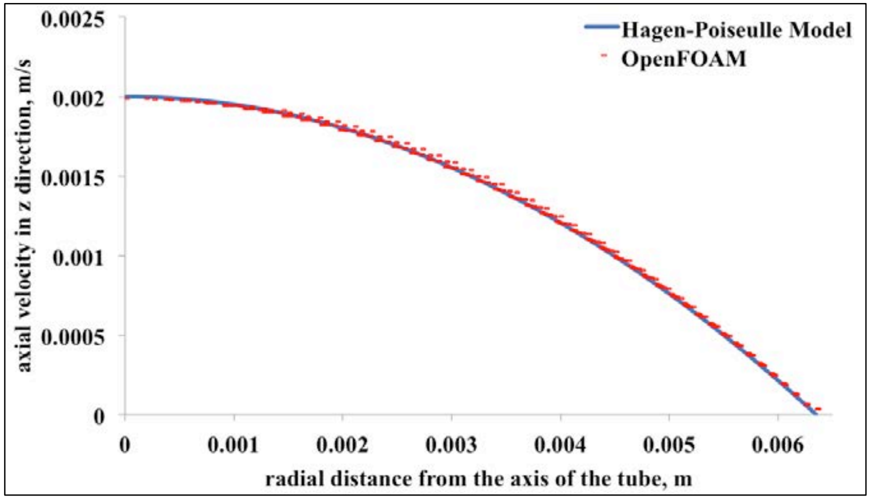
$$v(r) = 2 < v > \left[1-\left(\frac{r}{R}\right)^2\right] \qquad \Delta P = \frac{8\mu l v}{\pi r^2}$$

Figure source: University of Texas

Validation of CFD model



nonNewtonianIcoFoam



icoFOAM

Table : The comparison between the numerical solution and *OpenFOAM* calculations of the pressure drop and velocity calculations across tube

Material	average v_z, m/s	maximum v_z (m/s)	OpenFOAM v_z(m/s)	% error	OpenFOAM ΔP, Pa	Analytical ΔP, Pa	% error
Slurry	0.1368	0.2066	0.2031	1.69	**1000.8**	**1022.8**	2.20
Water	0.001	0.0020	0.0020	0.7	**0.0605**	**0.0621**	2.70

One-tube module

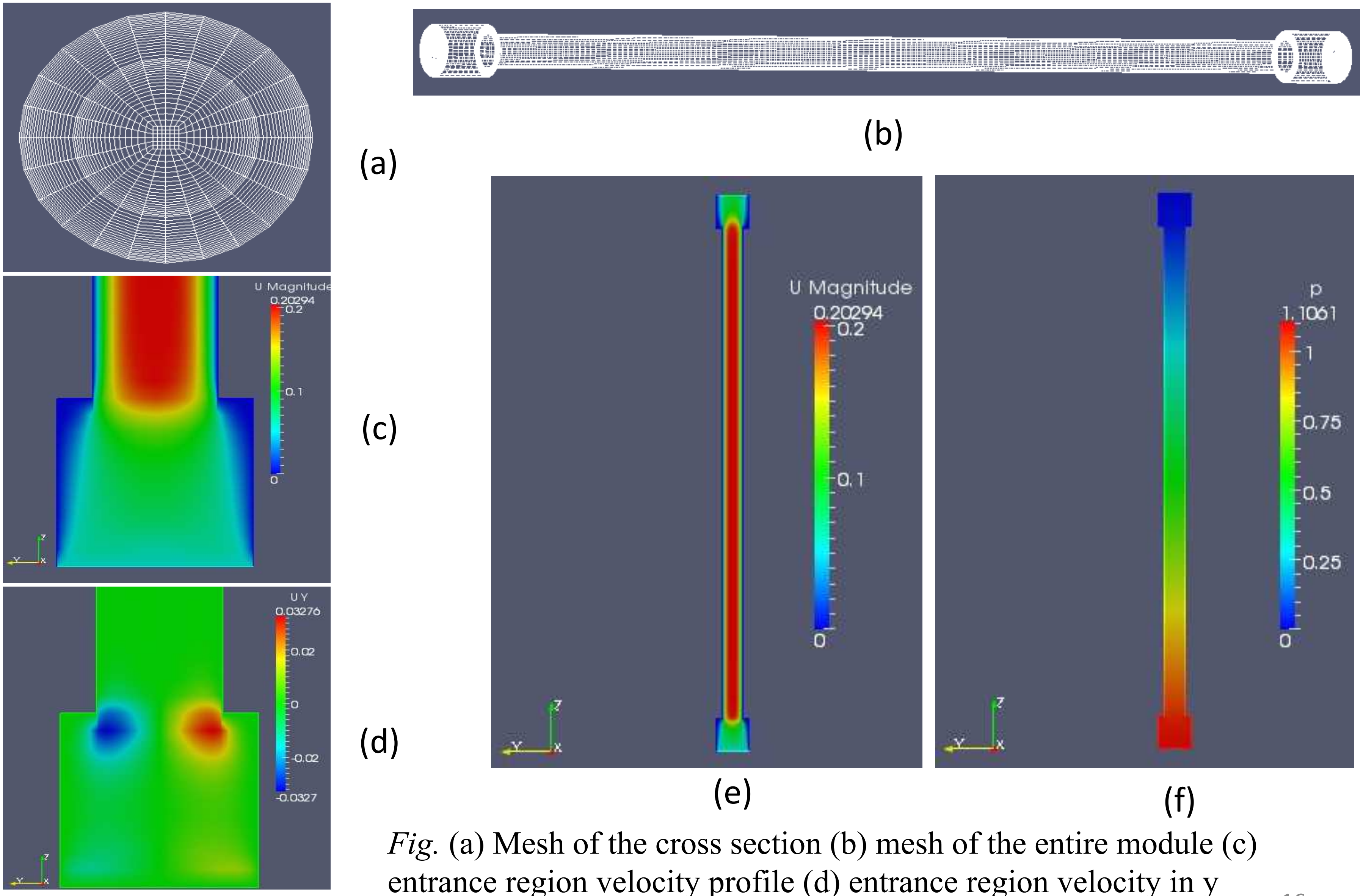
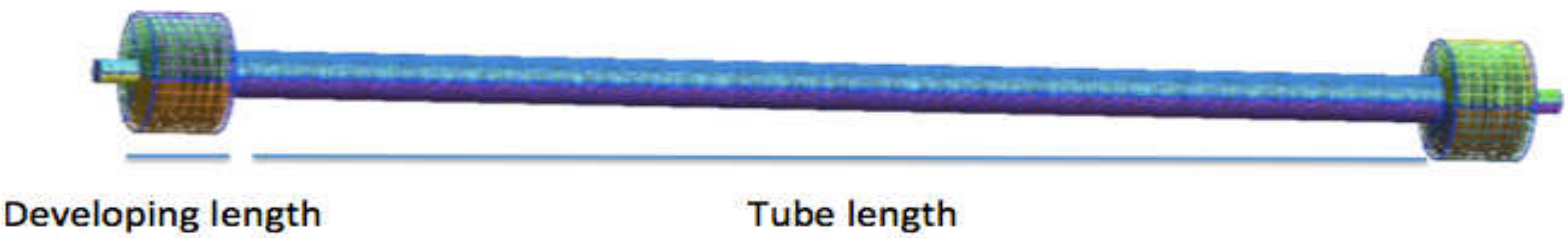
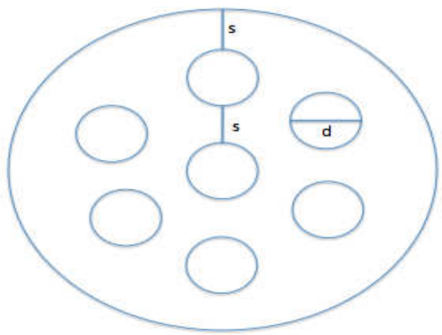


Fig. (a) Mesh of the cross section (b) mesh of the entire module (c) entrance region velocity profile (d) entrance region velocity in y direction (e) full velocity profile and (f) full pressure profile

Multiple-tube module



(a)



(b)

Figure (a) Membrane module with tubes heads on front and back and tubes in the middle and (b) The cross-sectional view of the module head with the orientation of the tubes

Case Type	Numbers of tubes	Developing length (cm)	Flowing suspension	Tube ID (m)	Spacing between the tubes (m)	Inlet velocity on the tube head (m/s)	Average velocity on each tube (m/s)
Case1	7	2	Slurry	0.00635	0.00635	0.01880	0.13157
Case2	7	0.1	Slurry	0.00635	0.00635	0.01880	0.13157
Case3	7	0.1	Water	0.00635	0.00635	0.01880	0.13157
Case4	7	0.1	Slurry	0.001	0.0005	0.03684	0.13157
Case 5	6	2	Slurry	0.00635	0.001	0.01611	0.13157

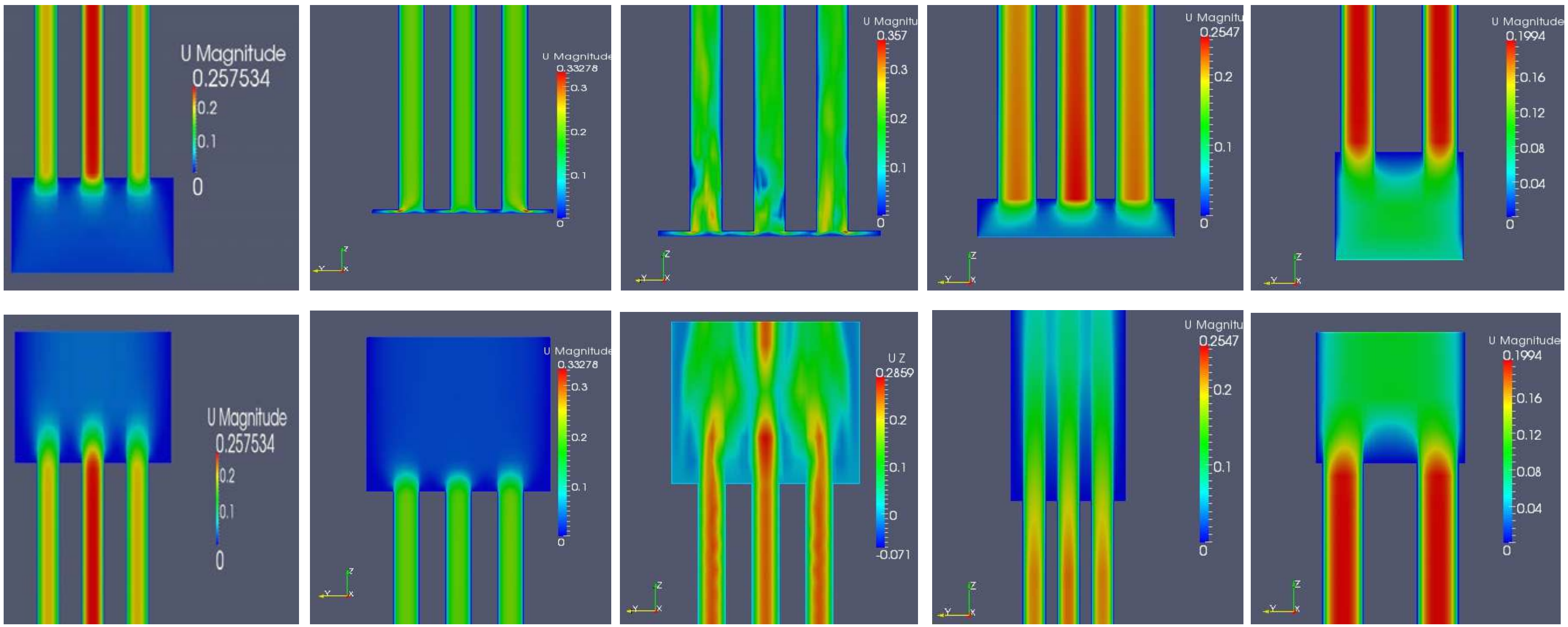
Table: Different scenarios of tube geometry and orientation for our studies

Entrance and exit regions

Scenario 1 Scenario 2 Scenario 3 Scenario 4 Scenario 5

Entrance

Exit



Result highlights

- Flow is not evenly distributed in all geometries across all the tube

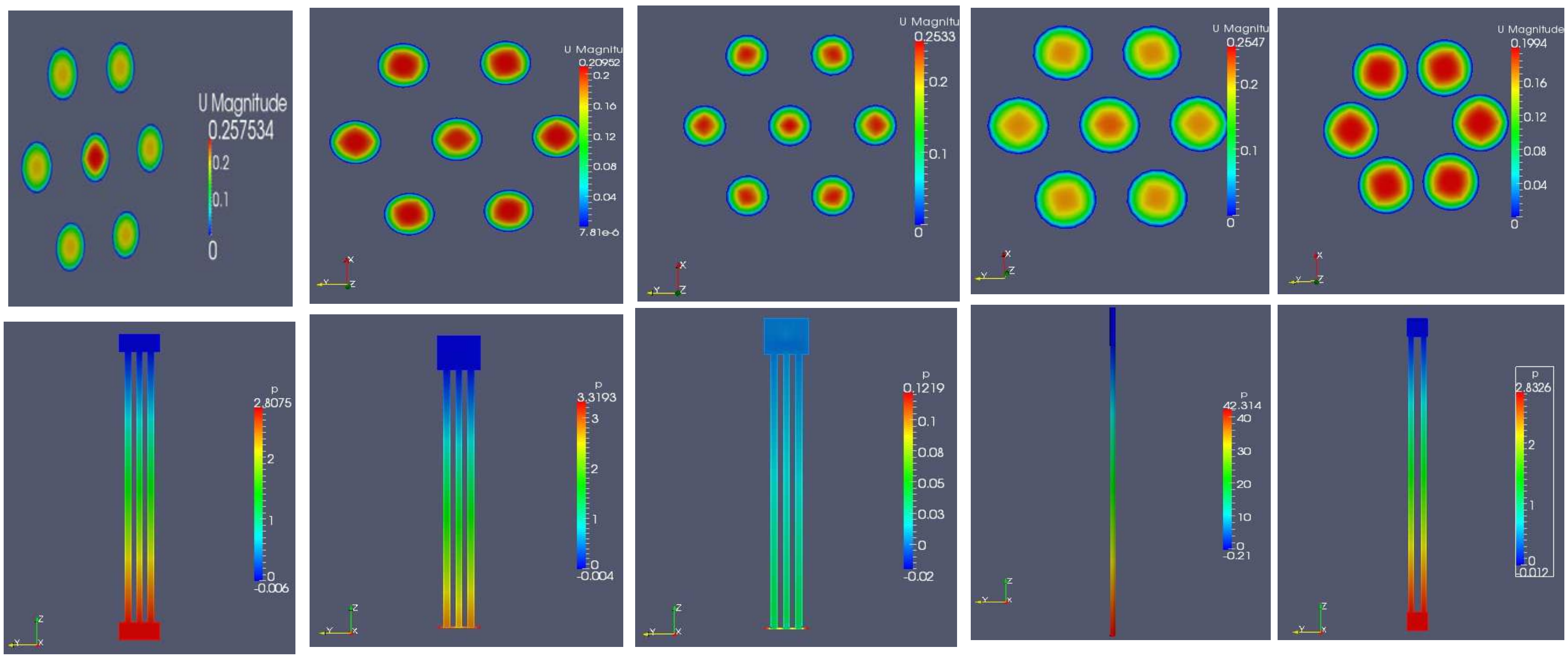
volumetric flowrate chosen so the average tube velocity is the same in all cases

Cross sectional velocity profiles and pressure drops

Scenario 1 Scenario 2 Scenario 3 Scenario 4 Scenario 5

Velocity profile

Pressure profile



the flow development in the tube header, and the tube geometry and diameter all influence even distribution, but smaller diameter tubes carry pressure penalty.

Summary

- Experimental work summary
  - a continuous system can hydrolyze more biomass at the same reaction time than batch system
  - converting biomass to sugar is very difficult because of complex rheology of biomass suspension which often leads to clogging of the tubes it flows through
- CFD Summary
  - the orientation and geometry of the tubes play important role in flow distribution within the system with multiple tubes
  - as the tube(s) get smaller, the pressure drop in the module gets higher
  - if the flow is developed before the slurry enters the membrane tubes, the flow is more likely to be distributed unevenly in the tubes

Future work

- We have assembled a system at NREL facility for a continuous enzymatic hydrolysis and our current goal is to run a 72 h -96 h continuous experiment at steady state
- We need to be prepared to solve other “unknown” practical problems that might come along the way
- We will do more CFD studies to identify appropriate module geometry for the membrane in different processing scenarios

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Any
Questions?