2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

Novel Mechanical Pretreatment for Lignocellulosic Feedstocks

WBS number = 2.2.1.5

Date: May 21, 2013
Technology Area Review: Biochemical Conversion

Principal Investigator: Mark Holtzapple
Organization: Texas Engineering Experiment Station

Goal Statement

Develop a mechanical pretreatment that enhances enzymatic digestibility of lignocellulose with the following properties:

- Technically effective
- Economically effective
- Scalable

Quad Chart Overview

Timeline

- Project Start Date: 09/01/2011
- Project End Date: 09/30/2014
- Percent Complete: 56%

Budget

- Funding for YR11 (DoE/CS):
  $800,000/ $210,503
- Funding for Yr12 (DoE/CS):
  $676,212/$177,931
- Funding for FY13 (DoE/CS):
  $786,795/$218,076
- Years the project has been funded/avg annual funding:
  2 yrs/ $932,323

Barriers Addressed

- Show process is effective at larger scale
- Increase slurry concentration to improve throughput
- Use methods that scale to industrial sizes

Partners

- Terrabon/
  Earth Energy Renewables
- Management – Texas Engineering Experiment Station

Outline

- Background
- Methods
- Economics
- Sugar platform
- Carboxylate platform
- Project management
- Conclusions

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- Background
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  - Rationale
  - Lime pretreatment
  - Biomass recalcitrance
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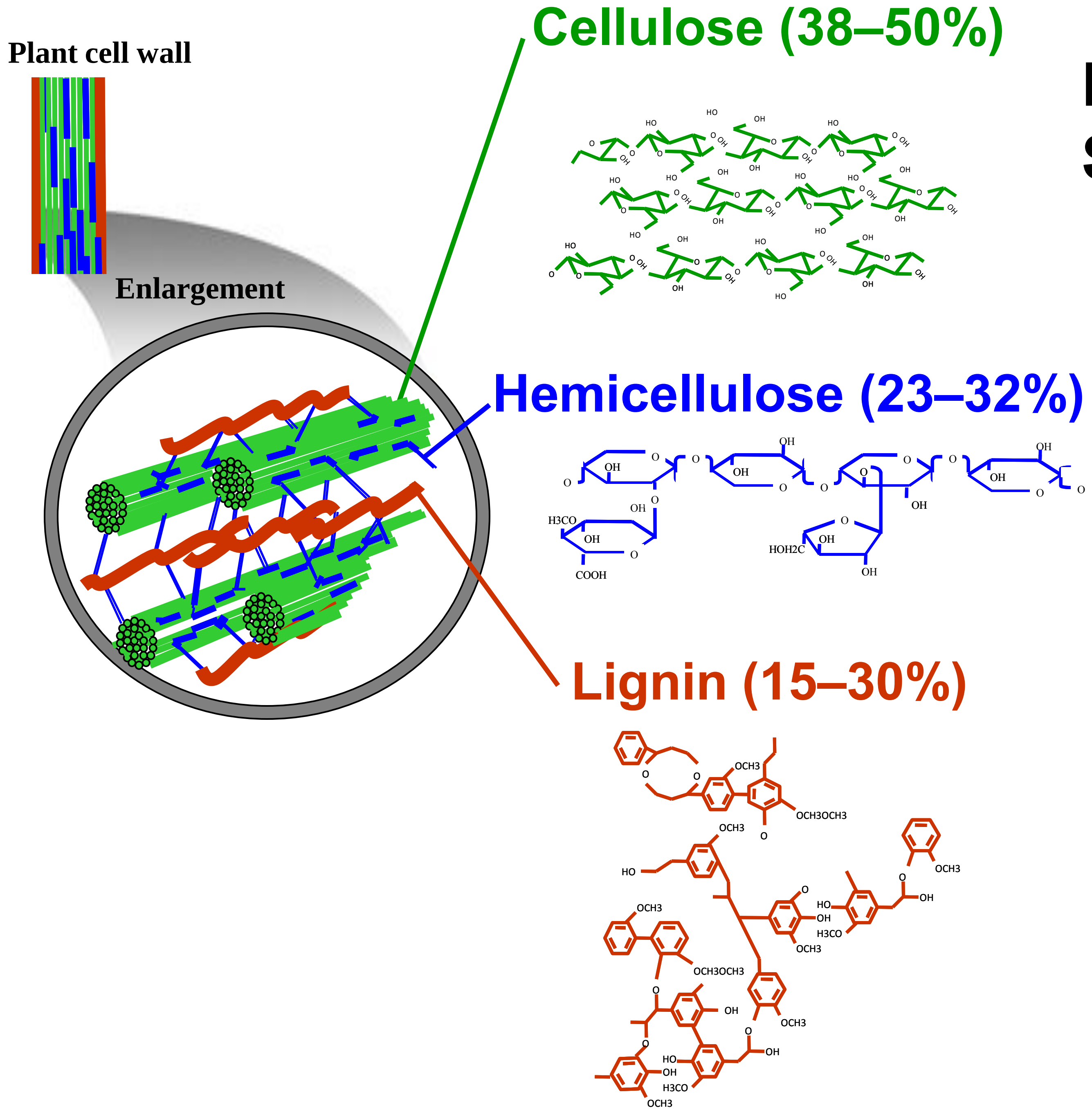
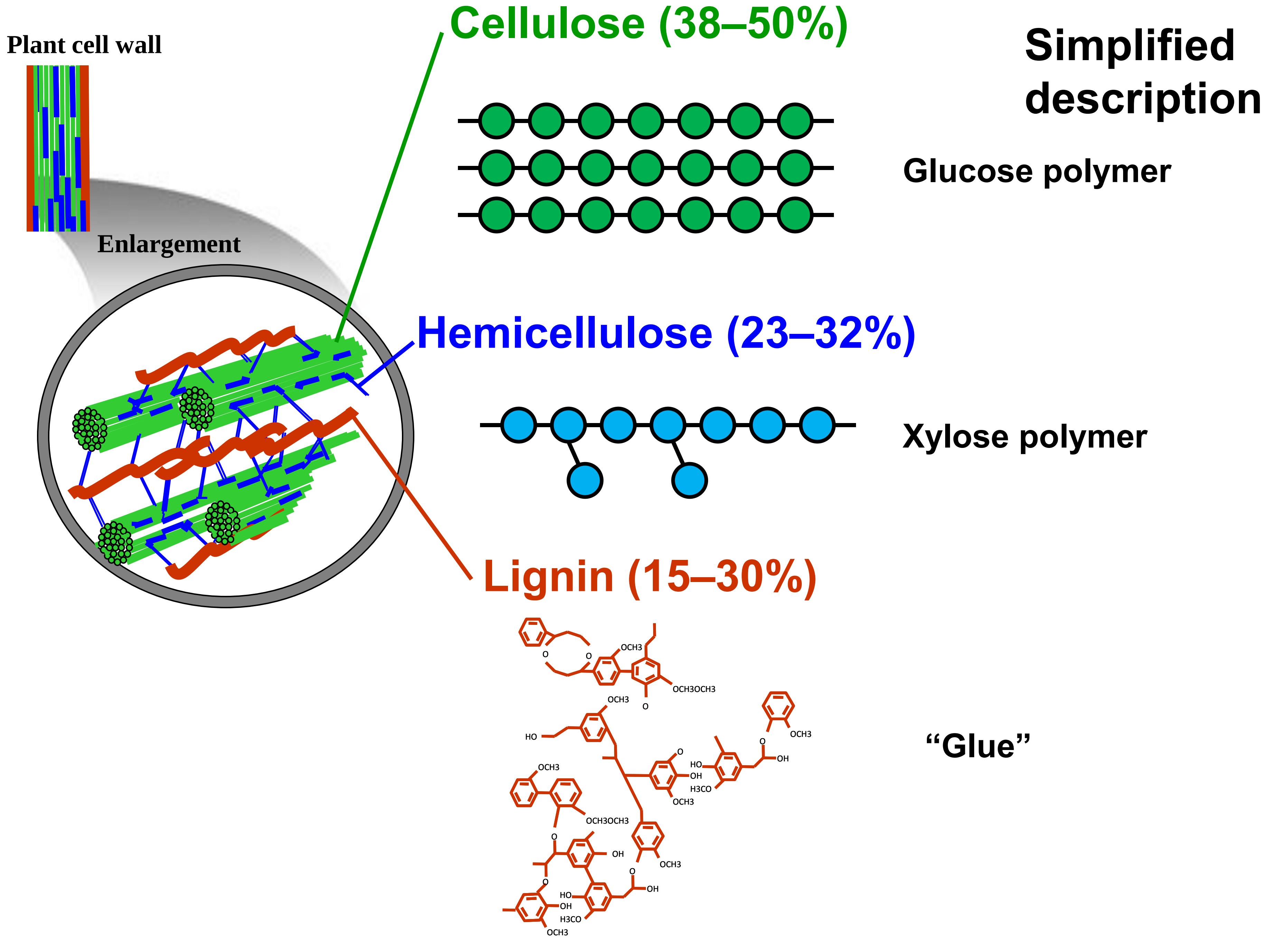
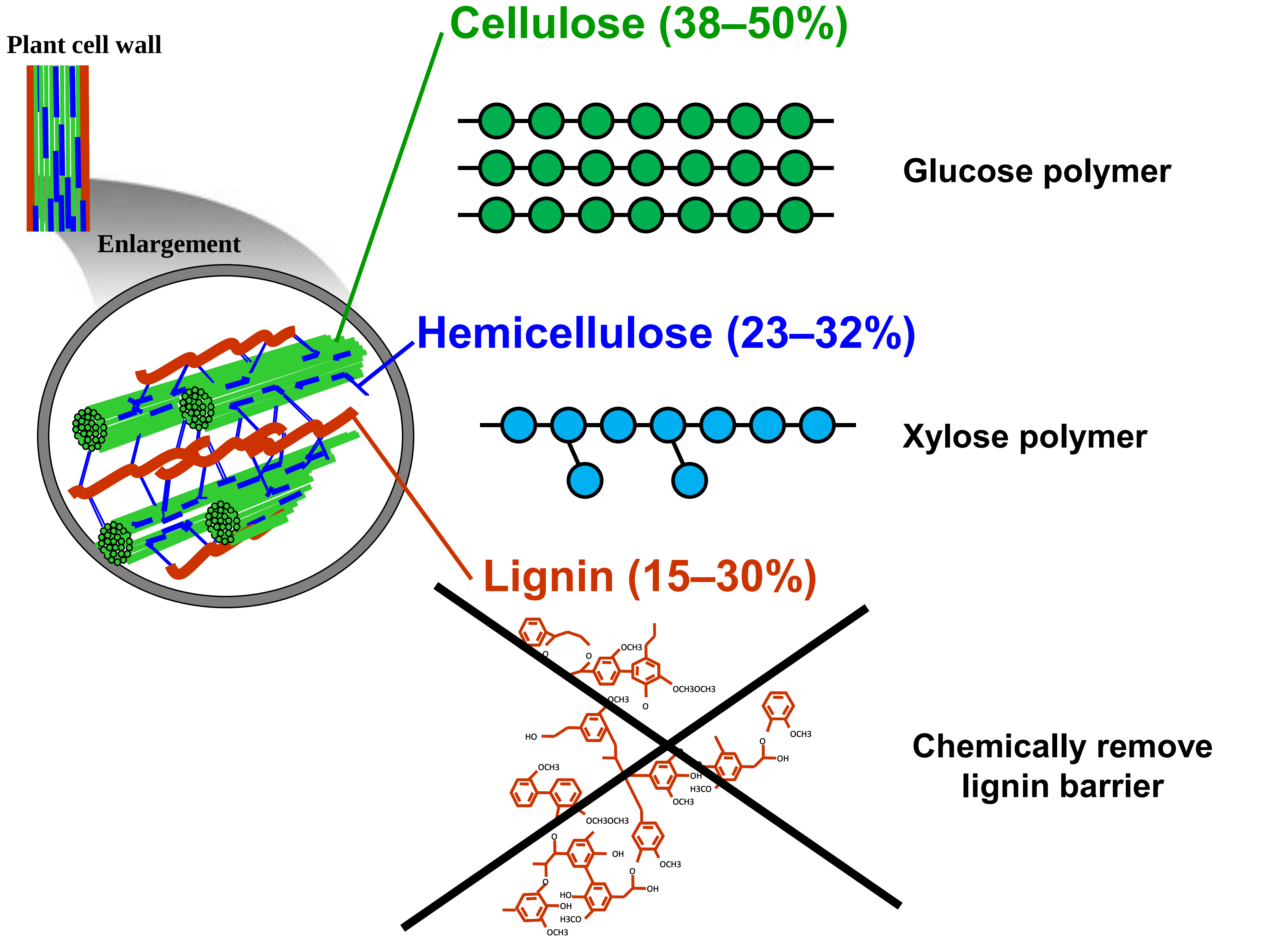
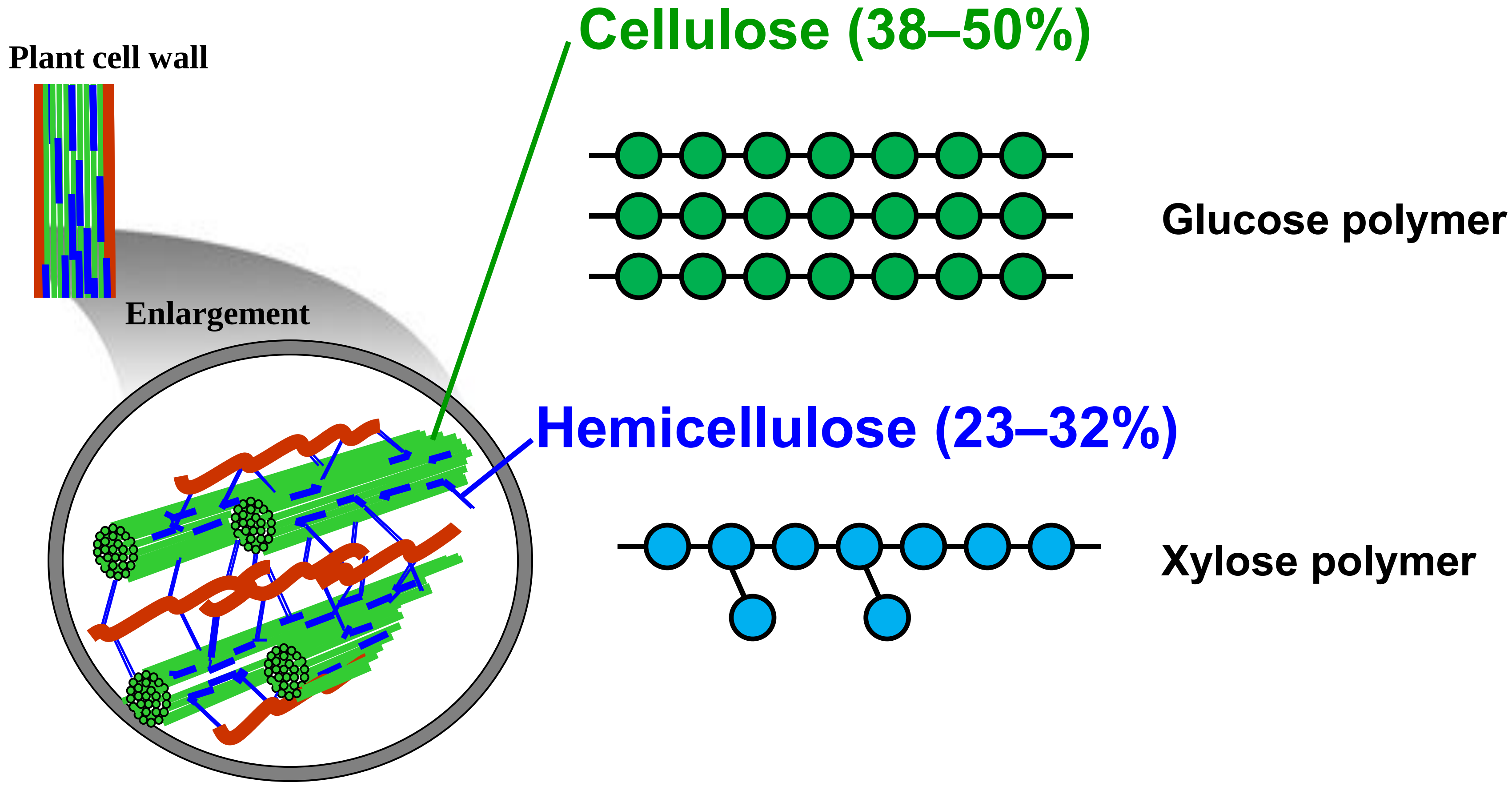
Lignocellulose Structure




Plant cell wall
Enlargement
Cellulose (38–50%)
Simplified description
Glucose polymer
Hemicellulose (23–32%)
Xylose polymer
Lignin (15–30%)
“Glue”


Plant cell wall
Enlargement
Cellulose (38–50%)
Glucose polymer
Hemicellulose (23–32%)
Xylose polymer
Lignin (15–30%)
Chemically remove
lignin barrier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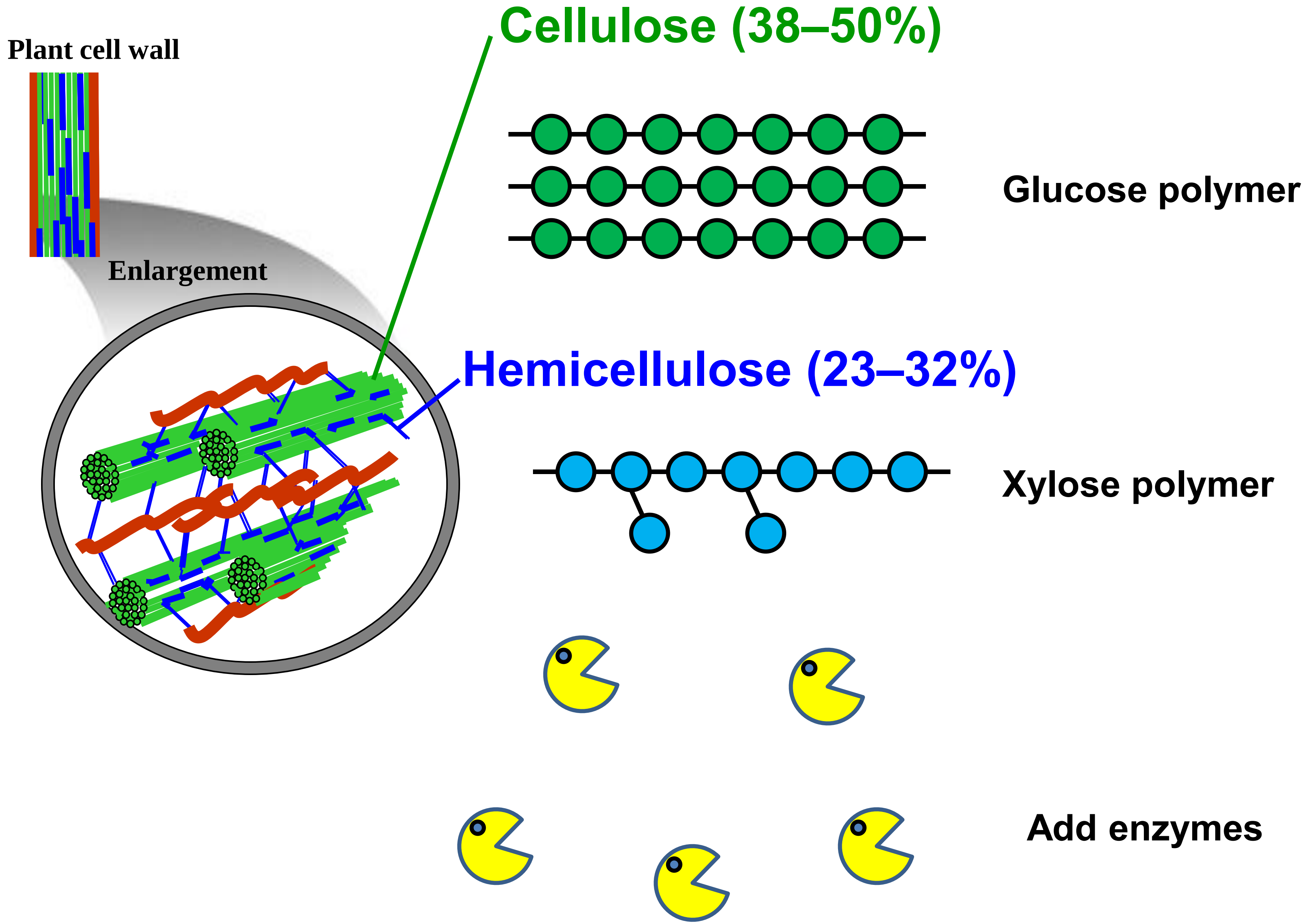
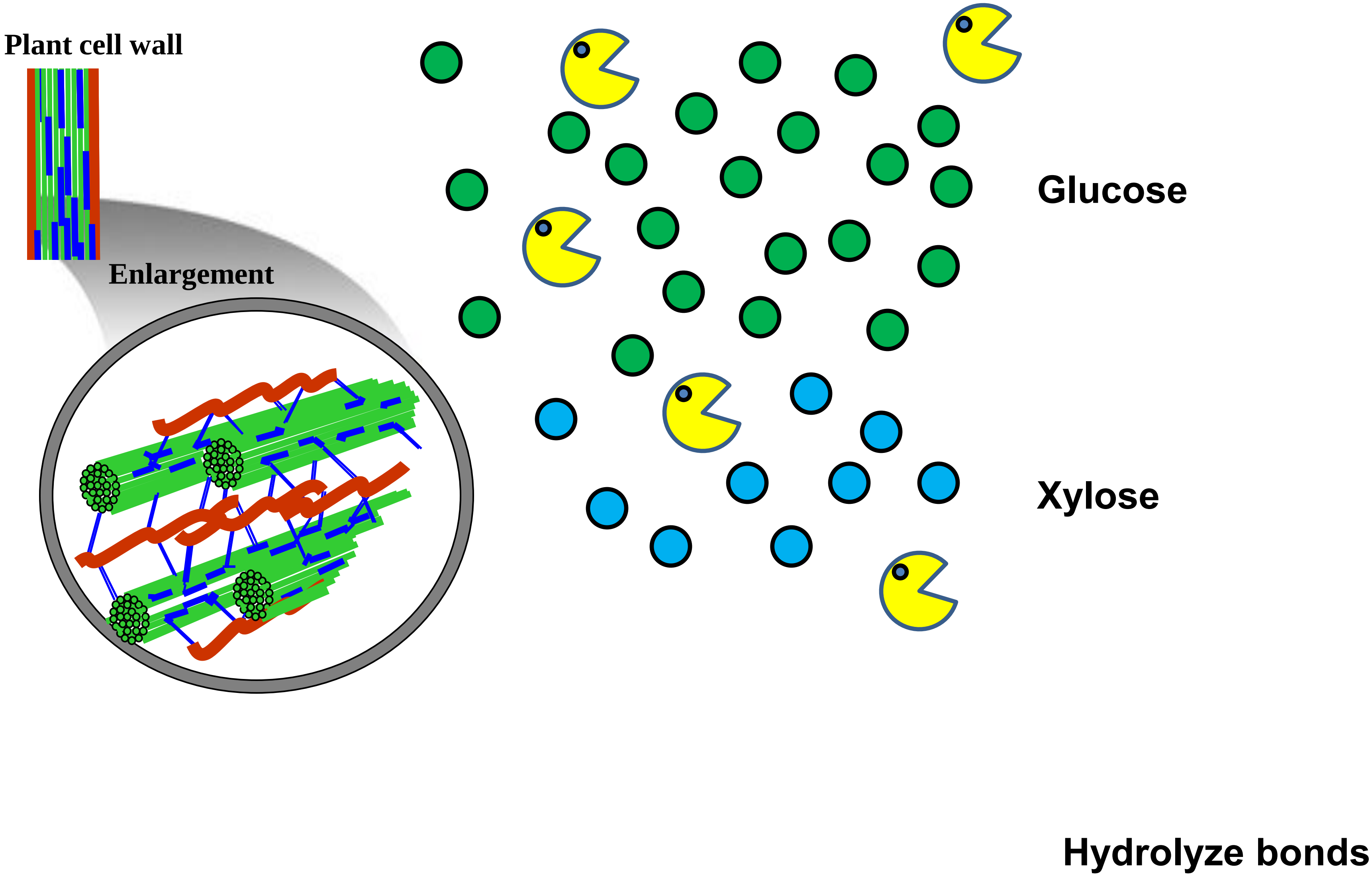
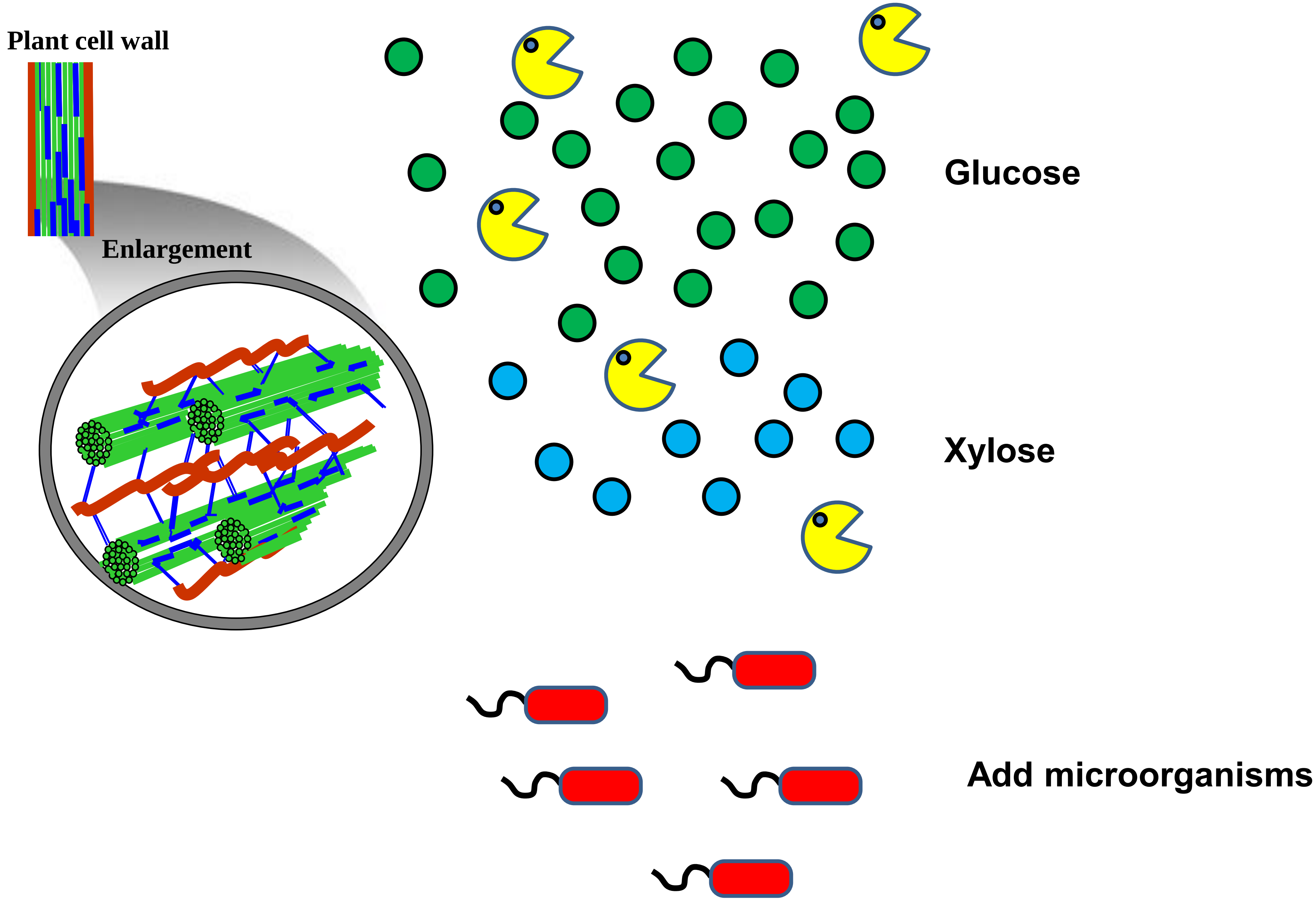
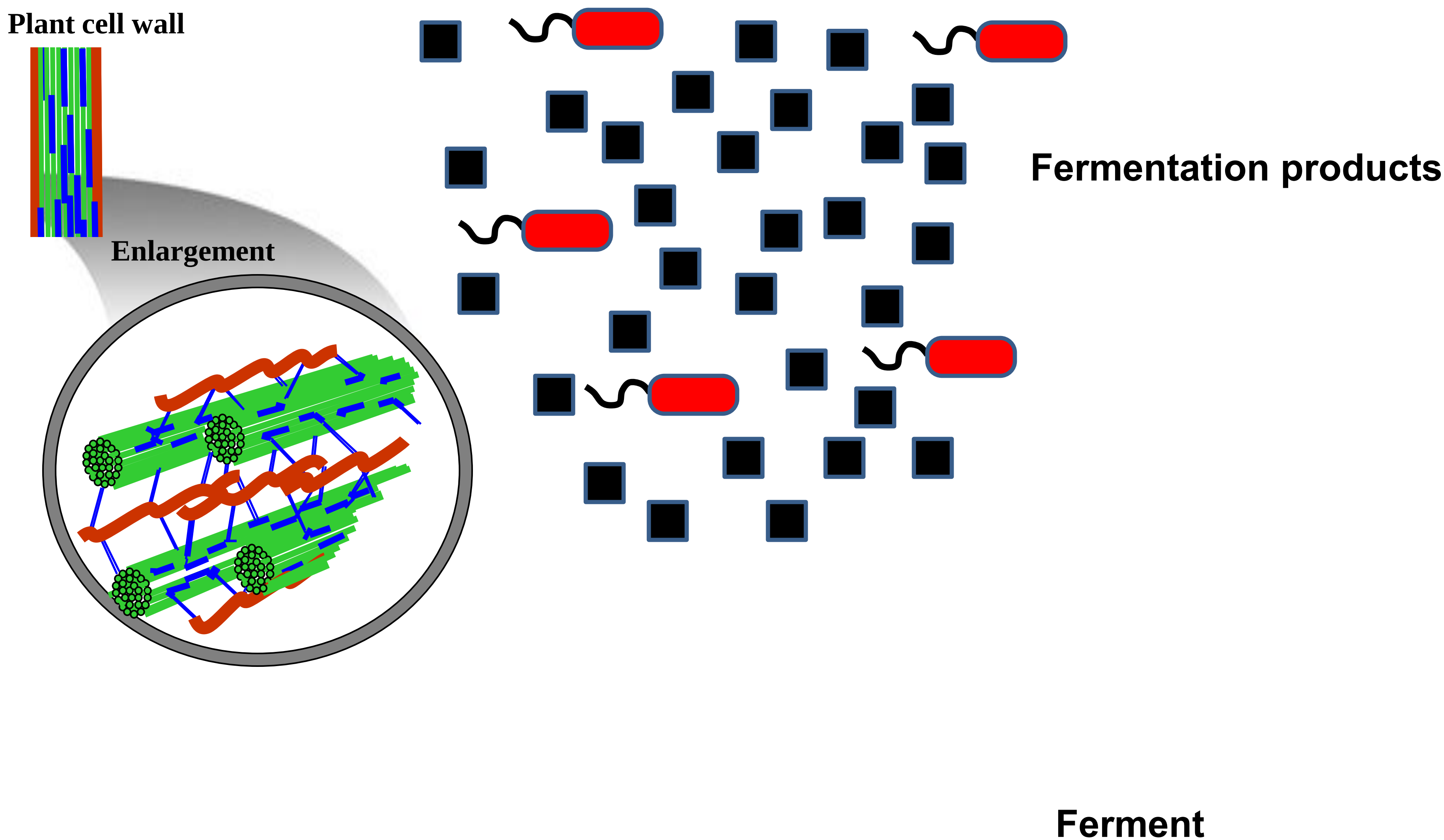

Plant cell wall
Enlargement
Cellulose (38–50%)
Glucose polymer
Hemicellulose (23–32%)
Xylose polymer
Add enzymes


Plant cell wall
Enlargement
Glucose
Xylose
Hydrolyze bonds

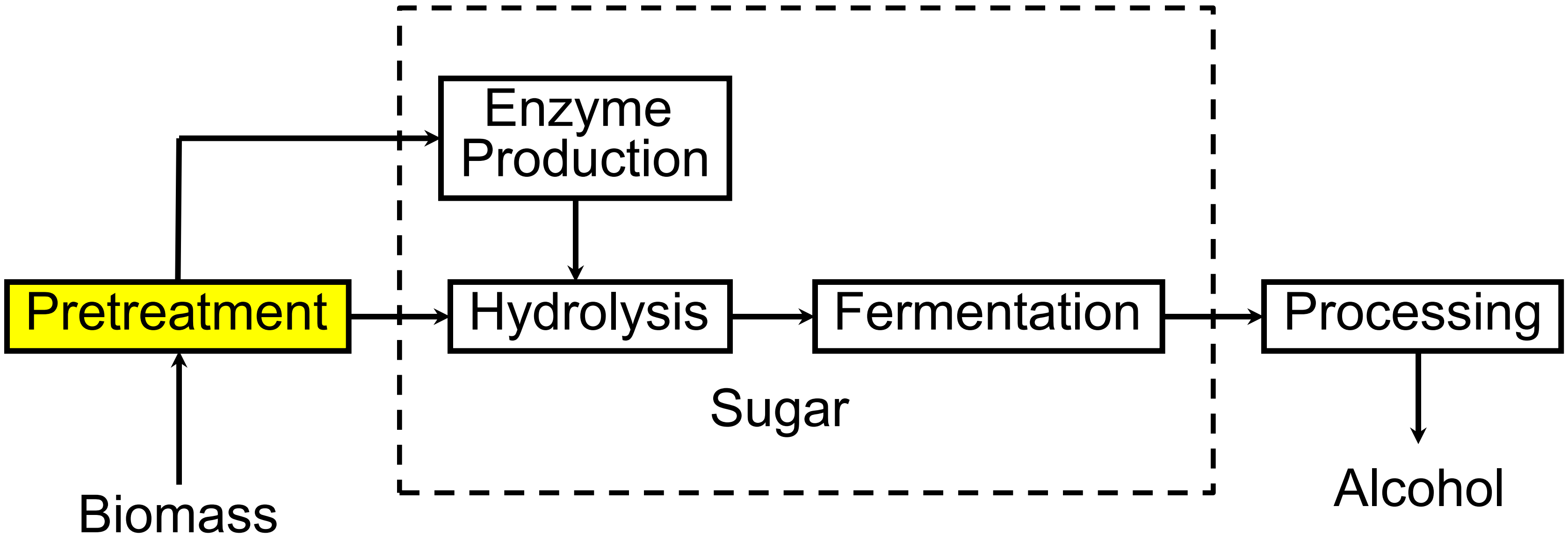


Plant cell wall
Enlargement
Glucose
Xylose
Add microorganisms


Plant cell wall
Enlargement
Fermentation products
Ferment

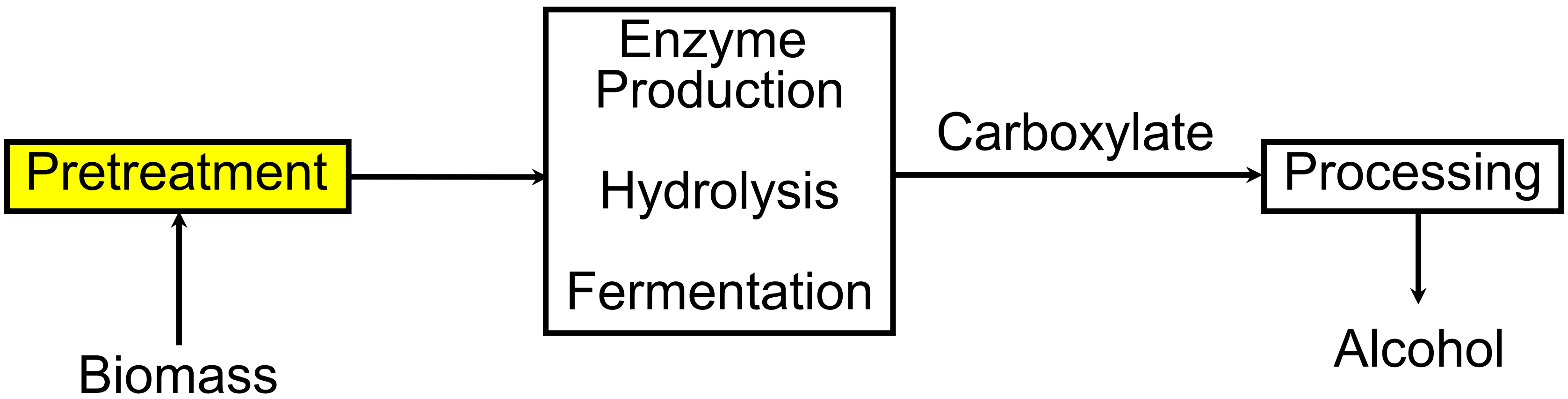
Sugar platform

Produces ethanol by fermenting enzymatically hydrolyzed sugars



Carboxylate platform

Produces a mixture of carboxylic acids through mixed-acid fermentation



Consolidated Bioprocessing

Carboxylate platform

Produces a mixture of carboxylic acids through mixed-acid fermentation

Consolidated Bioprocessing

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  - Biomass processing
  - Rationale
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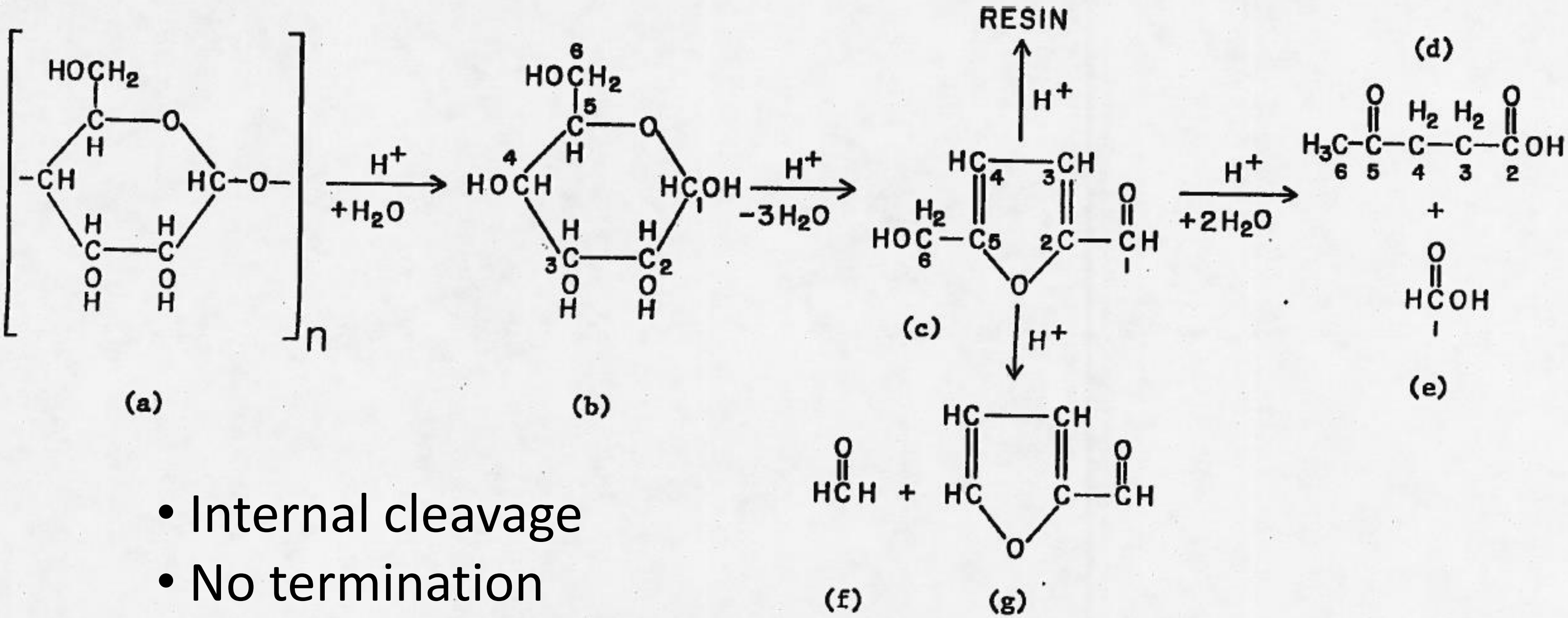
Why alkali?

Alkaline treatments less damaging than acidic treatments

Why alkali?

Acid Degradation

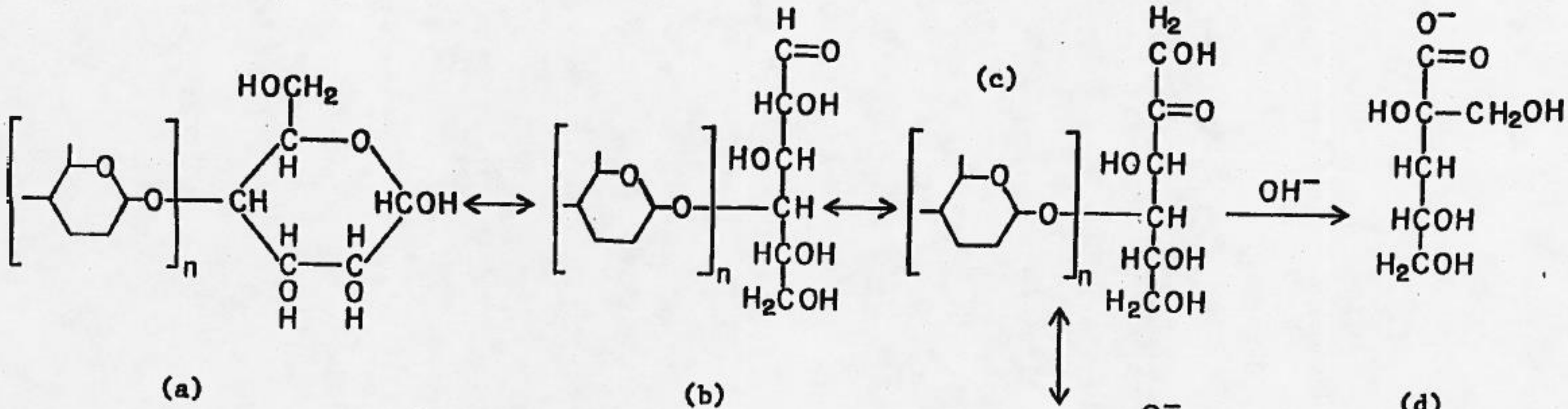


- Internal cleavage
- No termination

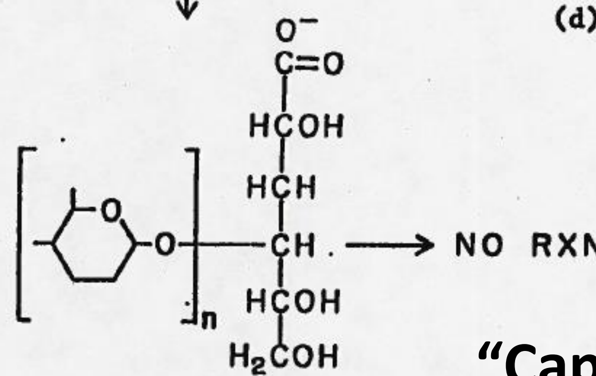
Mark Holtzapple, The Pretreatment and Enzymatic Saccharification of Poplar Wood, PhD Dissertation, University of Pennsylvania, December 1981

Why alkali?

Alkaline Degradation



- Endwise attack
- Terminates after 50 molecules lost



"Cap"

Mark Holtzapple, The Pretreatment and Enzymatic Saccharification of Poplar Wood, PhD Dissertation, University of Pennsylvania, December 1981

Why alkali?

Consequence

Tolerates “sloppy” operating conditions

Lowers cost

Why lime?

- Least expensive alkali

Alkali	**Cost** ($/kg)	**Cost** ($/kmol OH^-)
Sodium hydroxide	0.40	16.00
Ammonia	0.60	10.20
Quick lime (CaO)	0.10	2.80

- Safe to handle
- Can operate without pressure vessel
- Easily regenerated

$$CaCO_3 + \text{heat} \rightarrow CaO + CO_2$$

- Available worldwide
- Compatible with oxidants

Why oxygen?

Potential oxidants

- Oxygen
- Ozone
- Hydrogen peroxide
- Sodium hydrosulfite
- Chlorine
- Sodium hypochlorite
- Chlorine dioxide
- Peracetic acid

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Oxygen:

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- Safe

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Examples of reaction conditions

Biomass	Lignin (%)	Time	Temp. (^oC)	Lime loading (g $Ca(OH)_2$/g biomass)	Oxygen pressure (bar)
Pine	34.1	2 h	140	Not reported	20.7
Poplar wood	29.3	2 h	160	0.23	13.8
Sugarcane bagasse	23.7	2 h	130	Not reported	6.9
Sorghum	22.0	2 h	180	Not reported	6.9
Switchgrass	21.4	4 h	120	0.30	6.9
Corn stover	20.9	4 h	110	Not reported	6.9
Corn stover	20.9	4 wk	55	0.073	0.21

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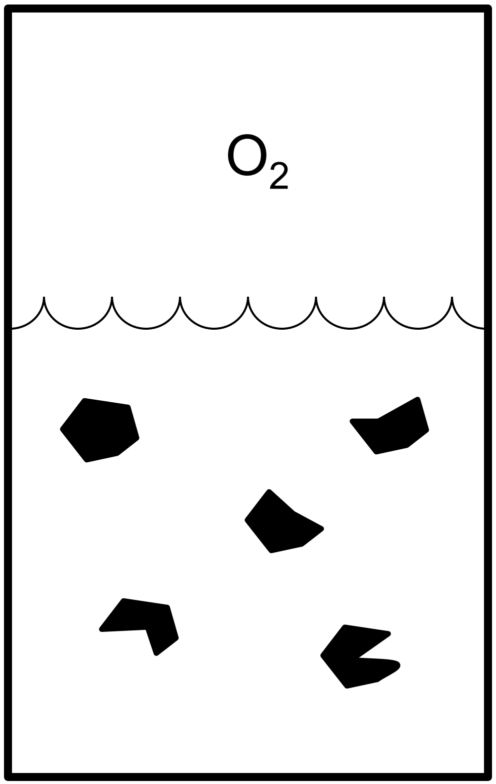
Sorghum	22.0	2 h	180	Not reported	6.9
Switchgrass	21.4	4 h	120	0.30	6.9
Corn stover	20.9	4 h	110	Not reported	6.9
Corn stover	20.9	4 wk	55	0.073	0.21

Short-term treatment

Short-term oxidative lime pretreatment

(OLP)



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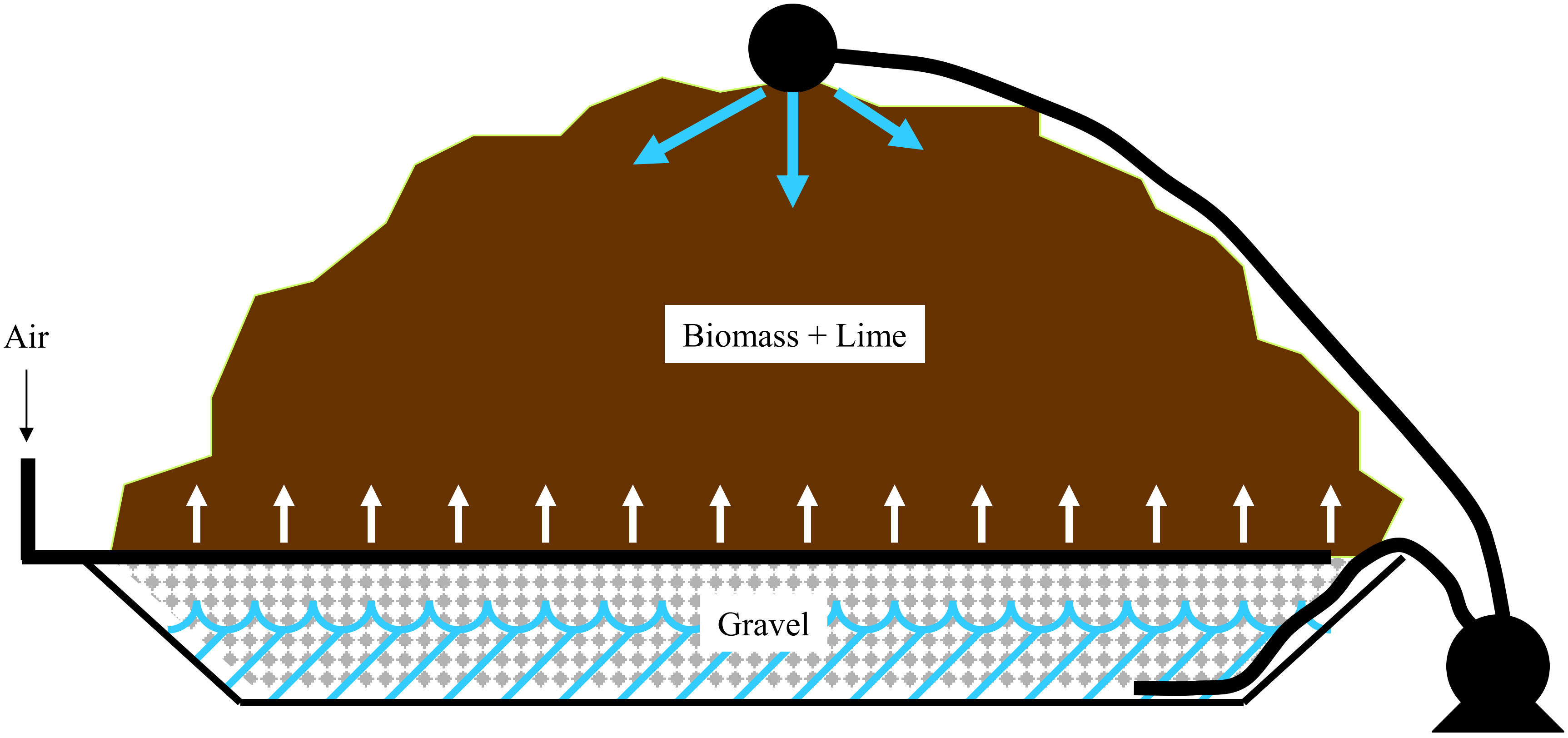
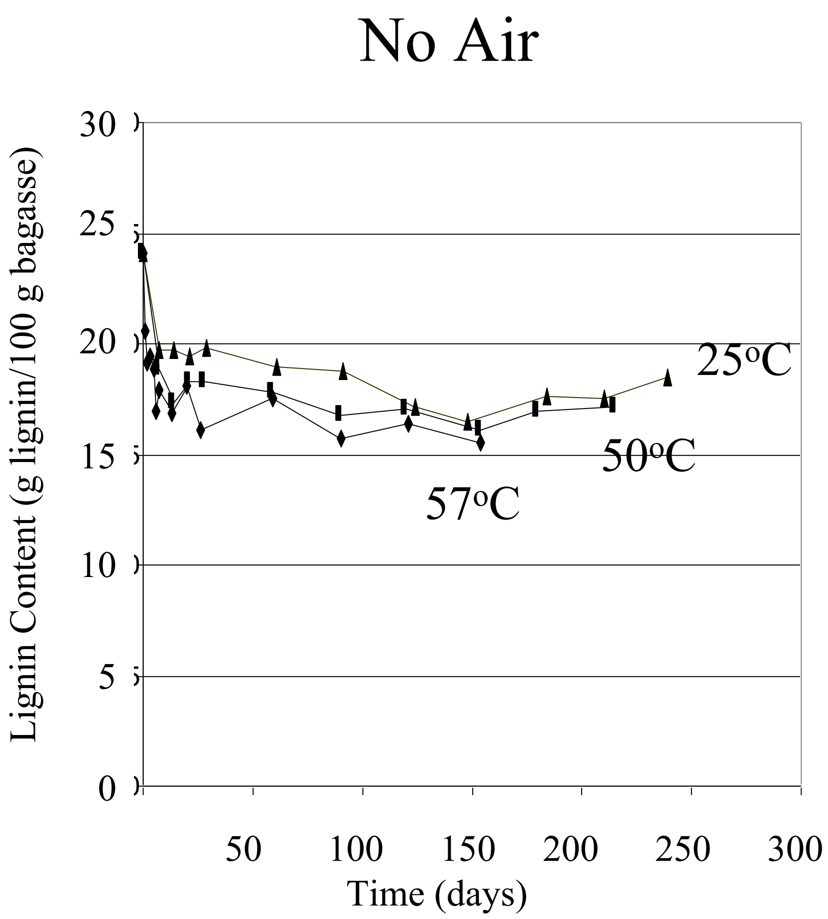
Long-term treatment

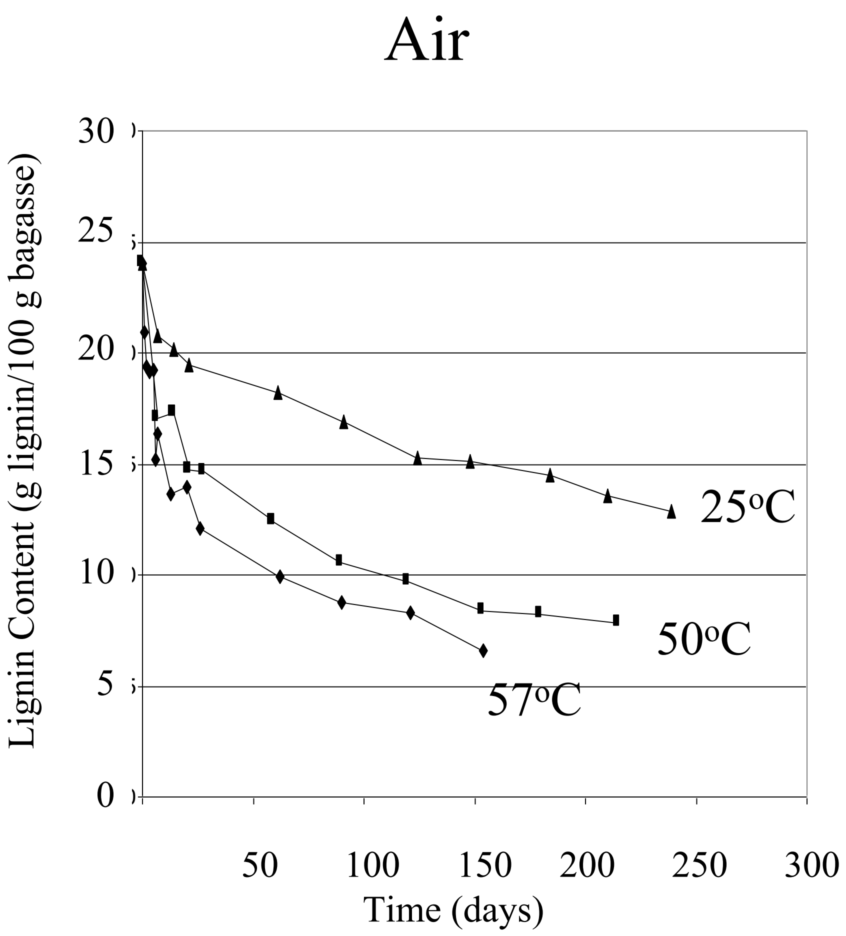
Long-term oxidative lime pile pretreatment (OLPP)



Temperature = 25 to 70°C **Time = 30 to 45 days**

Lignin removal





Typical results (% digestion)
Short-term lime, no oxygen

	Enzymes§		Rumen	
	Untreated	Treated	Untreated	Treated
Wheat Straw	6	65	–	–
Corn Stover	5	46	–	–
Switchgrass	6	39	44	79
Bagasse	5	66	31	69
MSW	–	–	65	71
African Millet Straw	–	–	50	87
Indian Millet Straw	–	–	68	87
Tobacco Stalks	–	–	28	60

§ 5 FPU/g raw biomass

Robert Rapier, Volatile Fatty Acid Fermentation of Lime-Treated Biomass by Rumen Microorganisms, MS, August 1995

J. Gandi, M.T. Holtzapple, A. Ferrer, F.M. Byers, N.D. Turner, M. Nagwani, S. Chang, Lime Treatment of Agricultural Residues to Improve Rumen Digestibility, Animal Feed Science Journal, 68, 195-211 (1997).

Fermentation results for traditional sugar process

Pretreatment System	Metabolic Yield*	Productive Yield†	Xylose Consumption in 48 h (%)	Final Ethanol Concentration (g/L)
Dilute Acid	85.0%	81.4%	87.8%	26.4
SO2 Explosion	89.9%	86.2%	90.8%	25.9
Controlled pH	86.8%	82.7%	80.0%	28.7
AFEX	93.0%	88.6%	78.7%	35.5
ARP	98.6%	98.6%	100%	20.5
Lime (O2)	100%	100%	90.4%	39.9

*Metabolic yield = [ethanol]/[0.51 × (*consumed* glucose + *consumed* xylose)]. †Productive yield = [ethanol]/[0.51 × (*initial* glucose + *initial* xylose)].

C. E. Wyman, B. E. Dale, R. T. Elander, M. Holtzapple, M. R. Ladisch, Y. Y. Lee, C. Mitchinson, J. N. Saddler, Comparative Sugar Recovery and Fermentation Data Following Pretreatment of Poplar Wood by Leading Technologies, Biotechnology Progress, 25 (2) Special Issue, 333–339 (2009).

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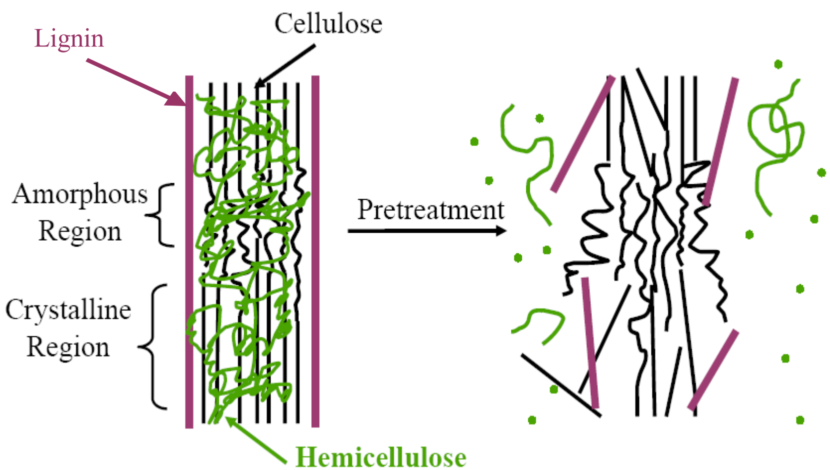
Barriers that limit enzymatic digestibility

- High lignin content
- Acetyl groups on hemicellulose
- Degree of cellulose polymerization
- Cellulose crystallinity
- Low accessible surface area
- Small pore volume



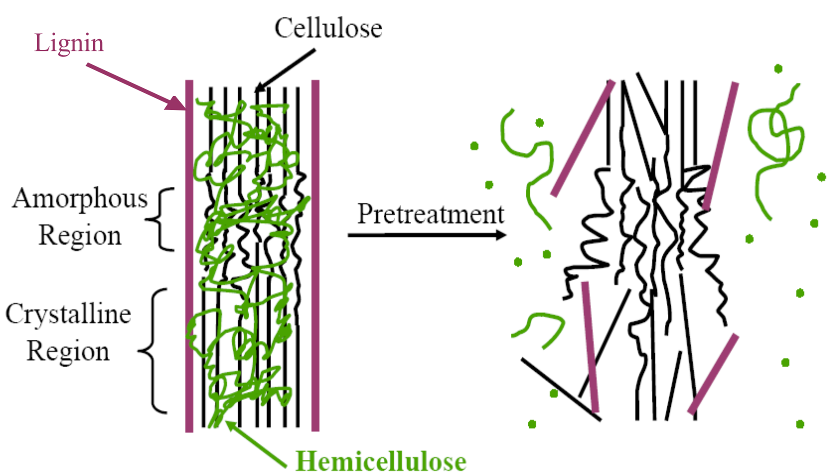
Barriers that limit enzymatic digestibility

- High lignin content
- Acetyl groups on hemicellulose
- Degree of cellulose polymerization

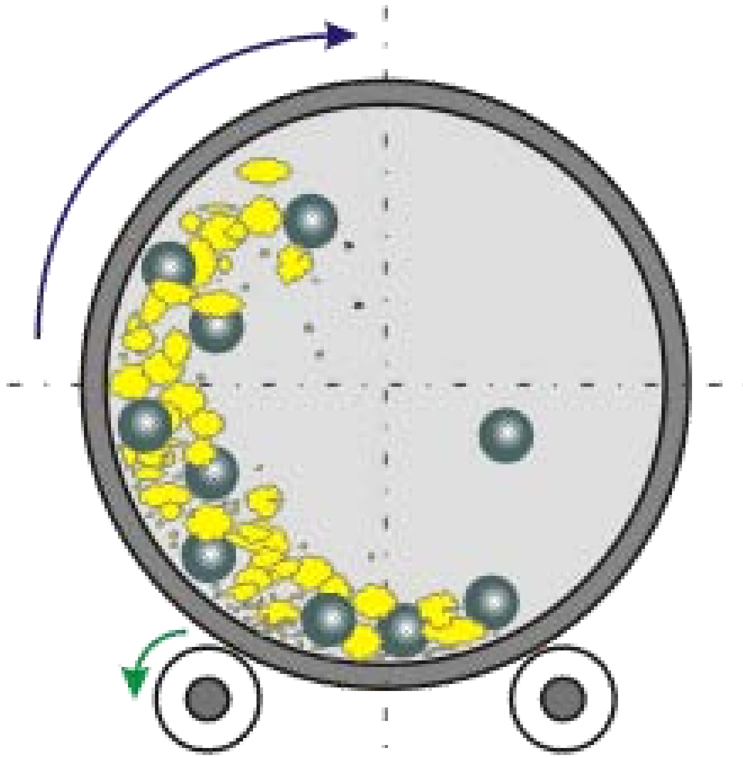
} Chemical treatment (e.g., oxidative lime)

- Cellulose crystallinity
- Low accessible surface area
- Small pore volume

} Mechanical treatment (e.g., ball mill)



Ball milling



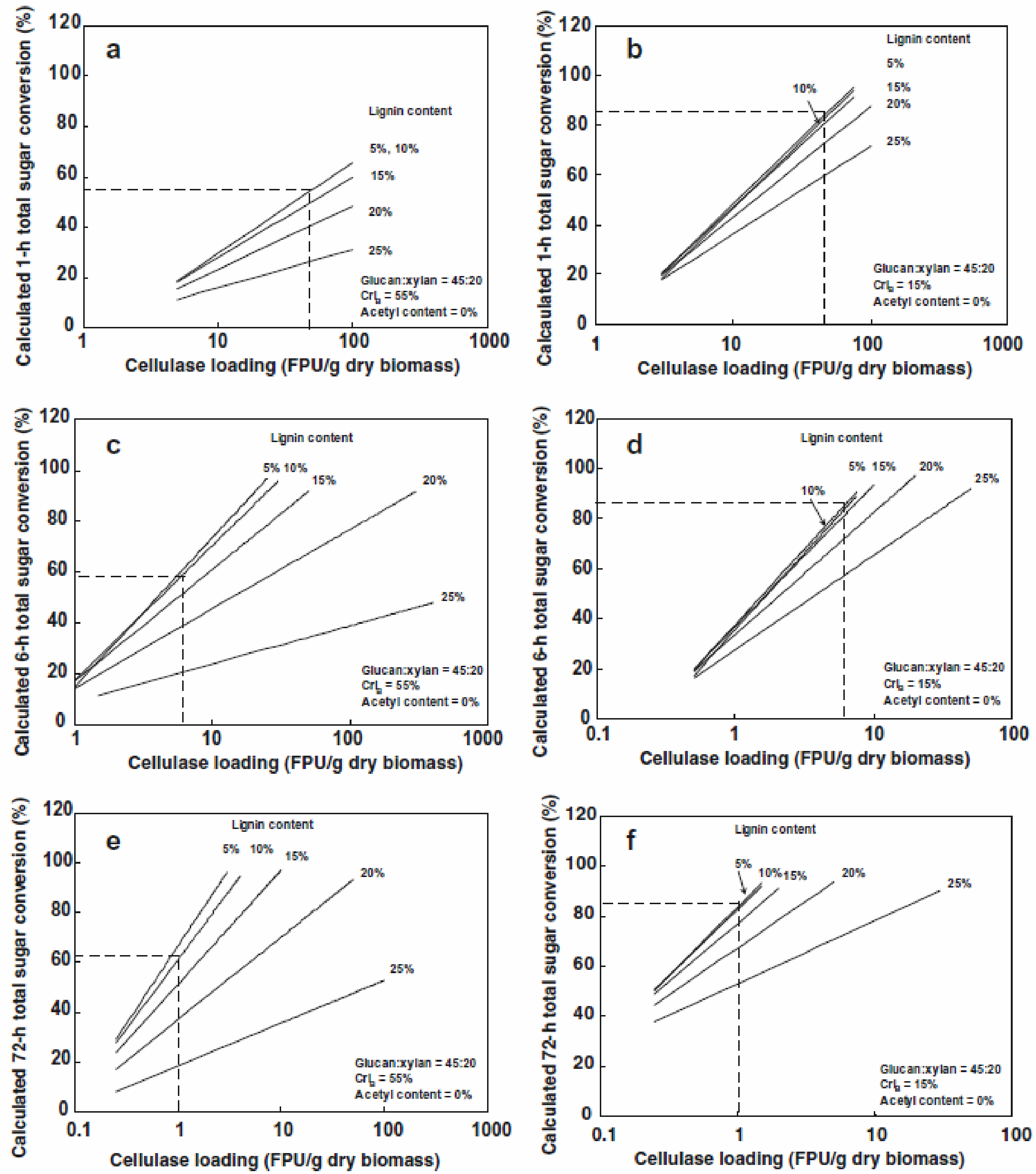
Enzymatic Reaction Time

Not Ball milled | Ball milled

1 hour

6 hour

72 hour



Recent CAFI Study

(Consortium for Applied Fundamentals & Innovation)

University	Pretreatment	Abbr.
Auburn University	Soaking in Aqueous Ammonia	SSA
Michigan State	Ammonia Fiber Expansion	AFEX
Texas A&M	Lime	Lime
Purdue	Liquid Hot Water	LHW
UC – Riverside	Dilute Acid	Dilute Acid
University British Columbia	Steam Explosion	SO_2

M. Falls, J. Shi, M.A. Ebrik, T. Redmond, B. Yang, C.E. Wyman, R. Garlock, V. Balan, B.E. Dale, V. R. Pallapolu, Y.Y. Lee, Y. Kim, N.S. Mosier, M.R. Ladisch, B. Hames, S. Thomas, B.S. Donohoe, T.B. Vinzant, R.T. Elander, R.E. Warner, R. Sierra-Ramirez, M.T. Holtzapple, Investigation of enzyme formulation on pretreated switchgrass, *Bioresource Technology*, 102(24): 11072–11079 (2011).

Definitions

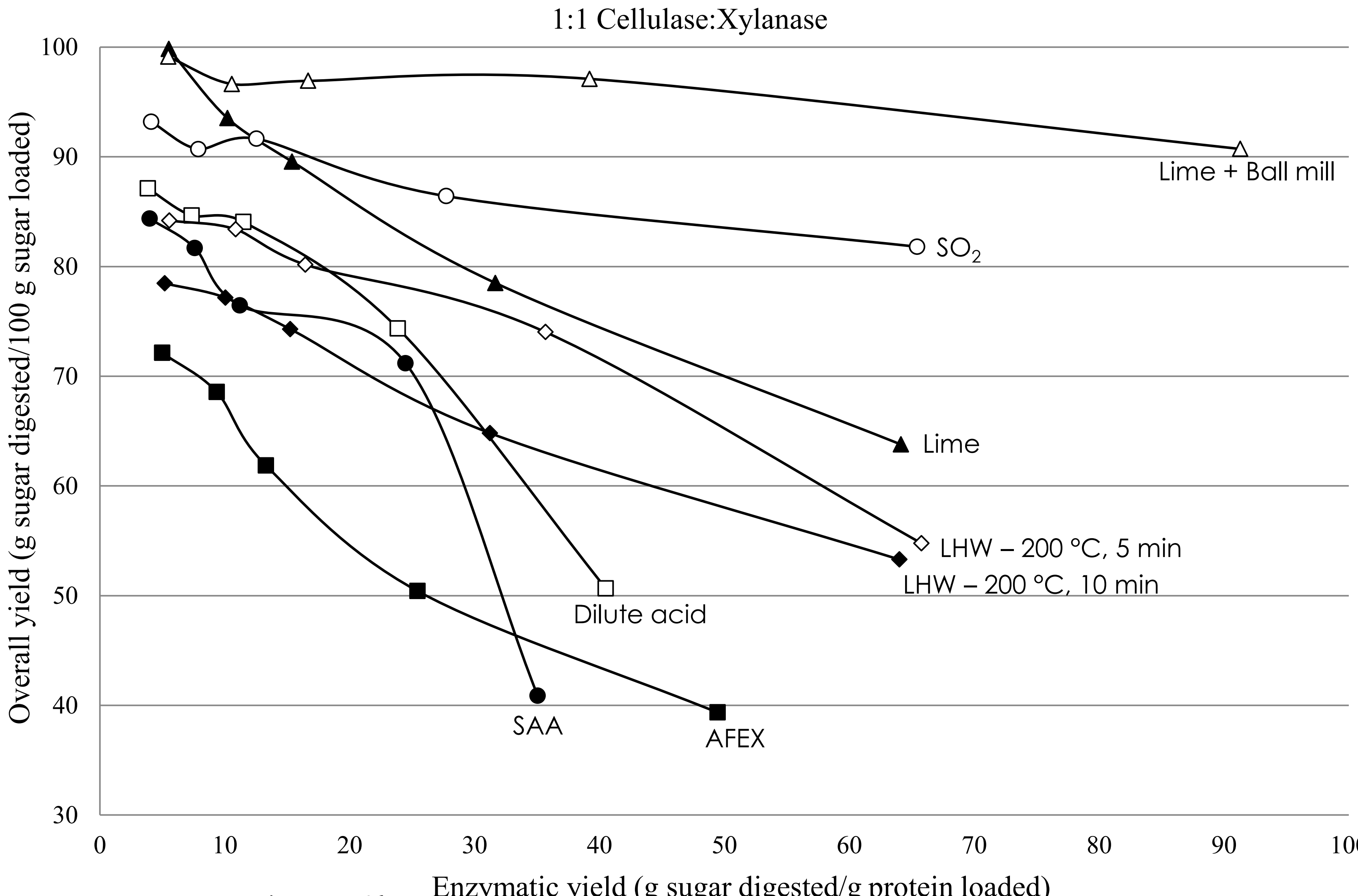
Overall yield

g sugar digested/100 g potential sugar

Enzymatic yield

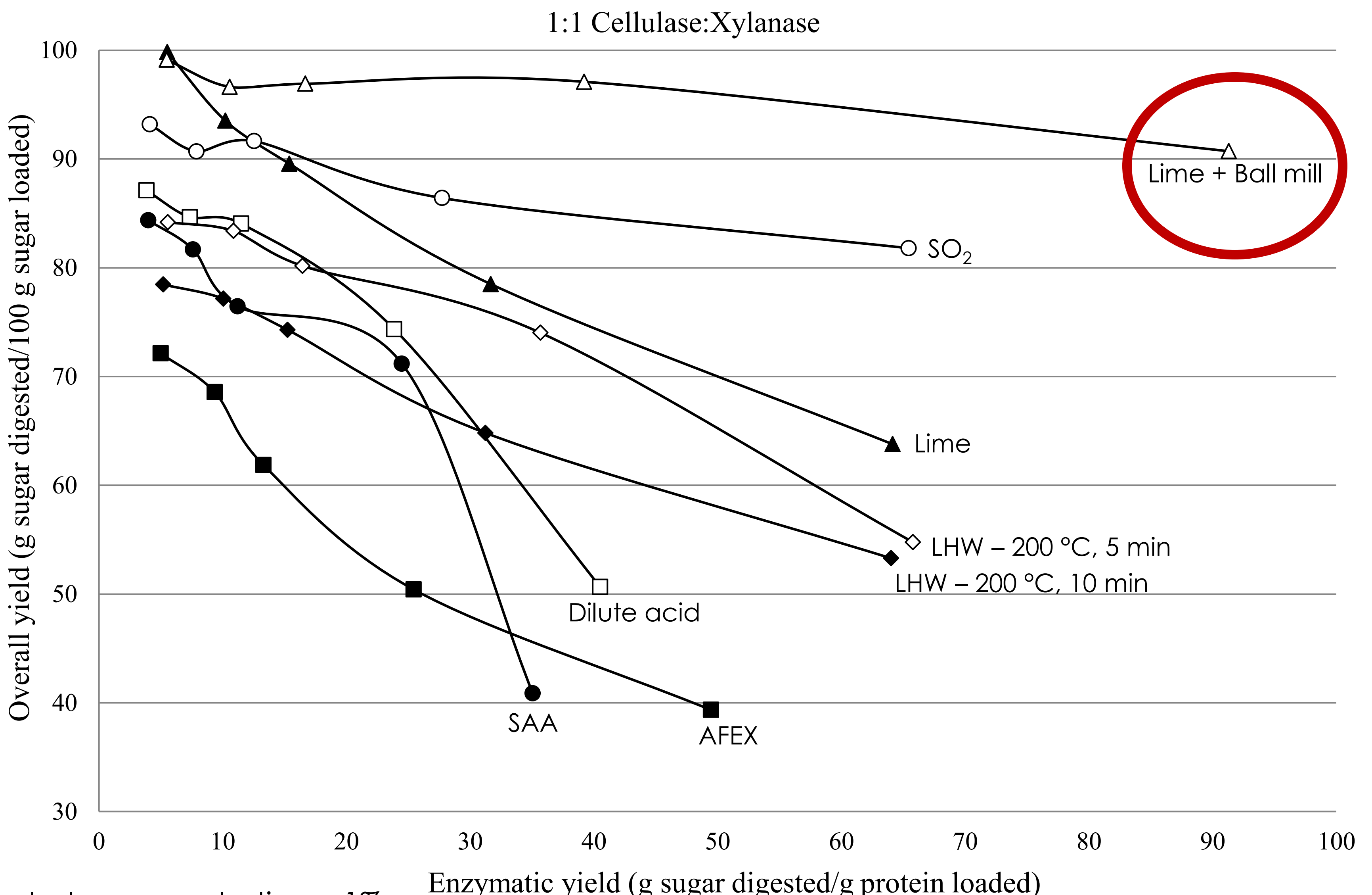
g sugar digested/g enzyme

Overall yield vs. enzymatic yield



Substrate concentration = 1%

Overall yield vs. enzymatic yield



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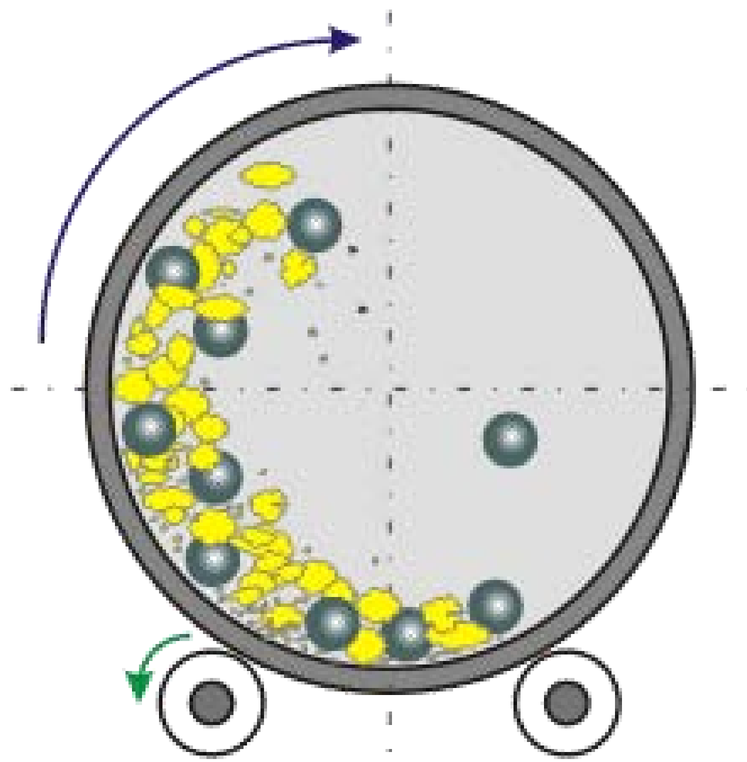
Ball milling



Problem

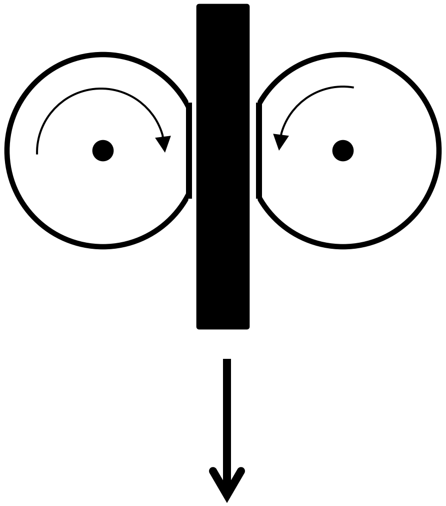
Ball milling is too expensive

Energy cost = \$430/tonne biomass @\$0.05/kWh

H. Inoue, S. Yano, T. Endo, T. Sakaki, and S. Sawayama, Combining hot-compressed water and ball milling pretreatments to improve the efficiency of the enzymatic hydrolysis of eucalyptus, *Biotechnology for Biofuels*, **1**:2 (2008).

Alternative Mechanical Treatments

Two-Roll Mill



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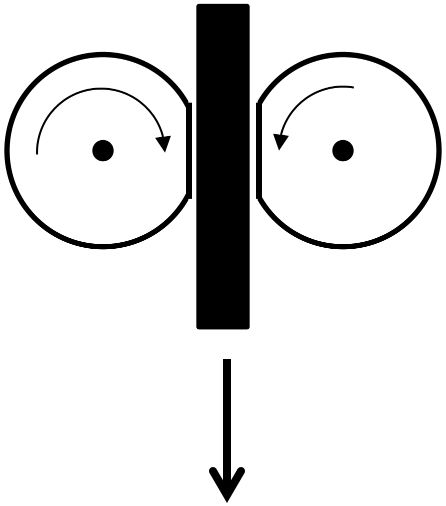


High capital
High maintenance
Small capacity

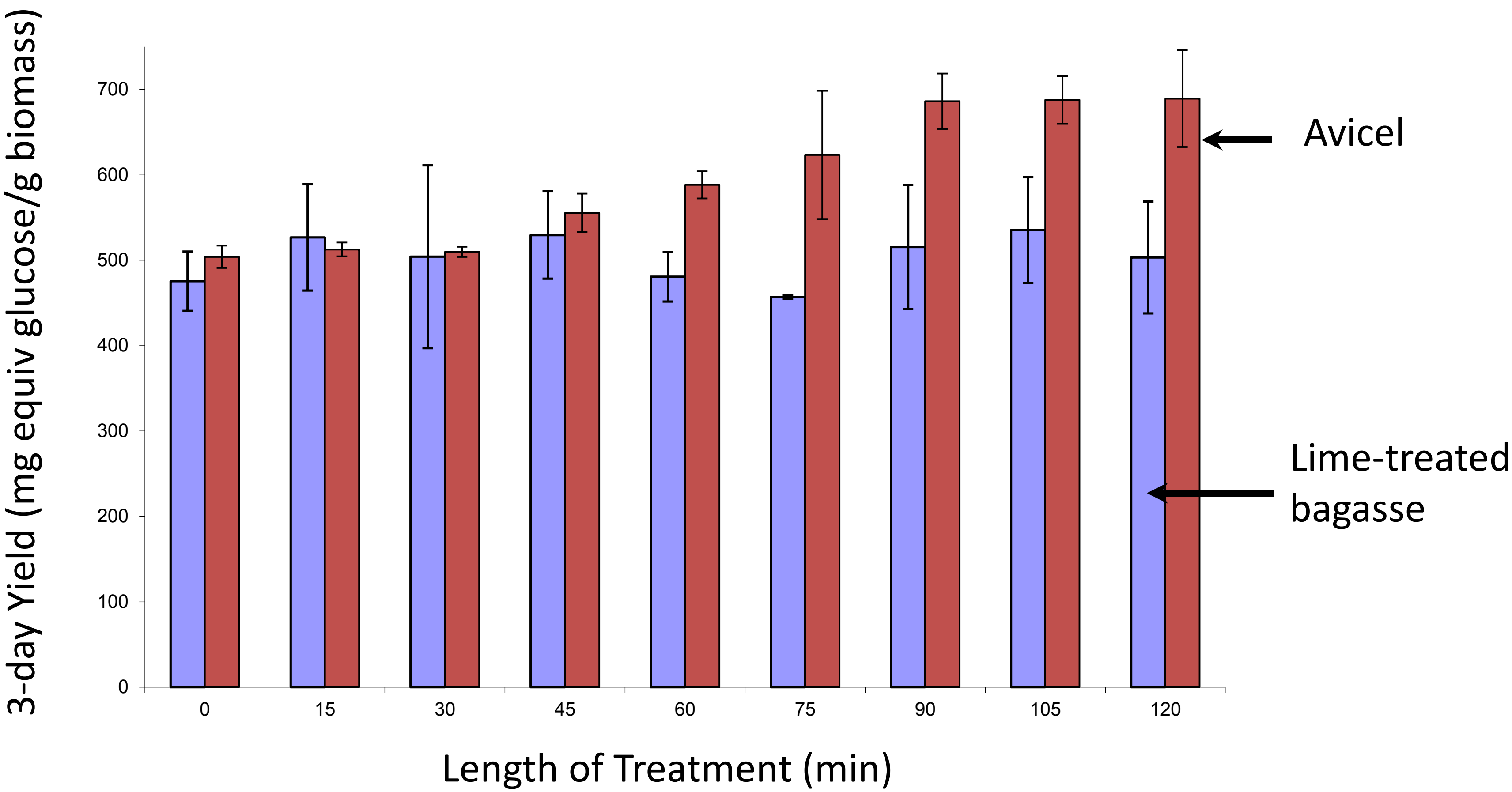
Alternative Mechanical Treatments

Sonication

Ingram, L. and Wood, B. 2001. Ethanol Production from Lignocellulose. US Patent, Patent No. US 6,333,181

Kinley, M and Krohn, B. 2008. Biomass Conversion to Alcohol Using Ultrasonic Energy. US Patent Application Publication, Pub. No. US 2008/0044891

Sonication

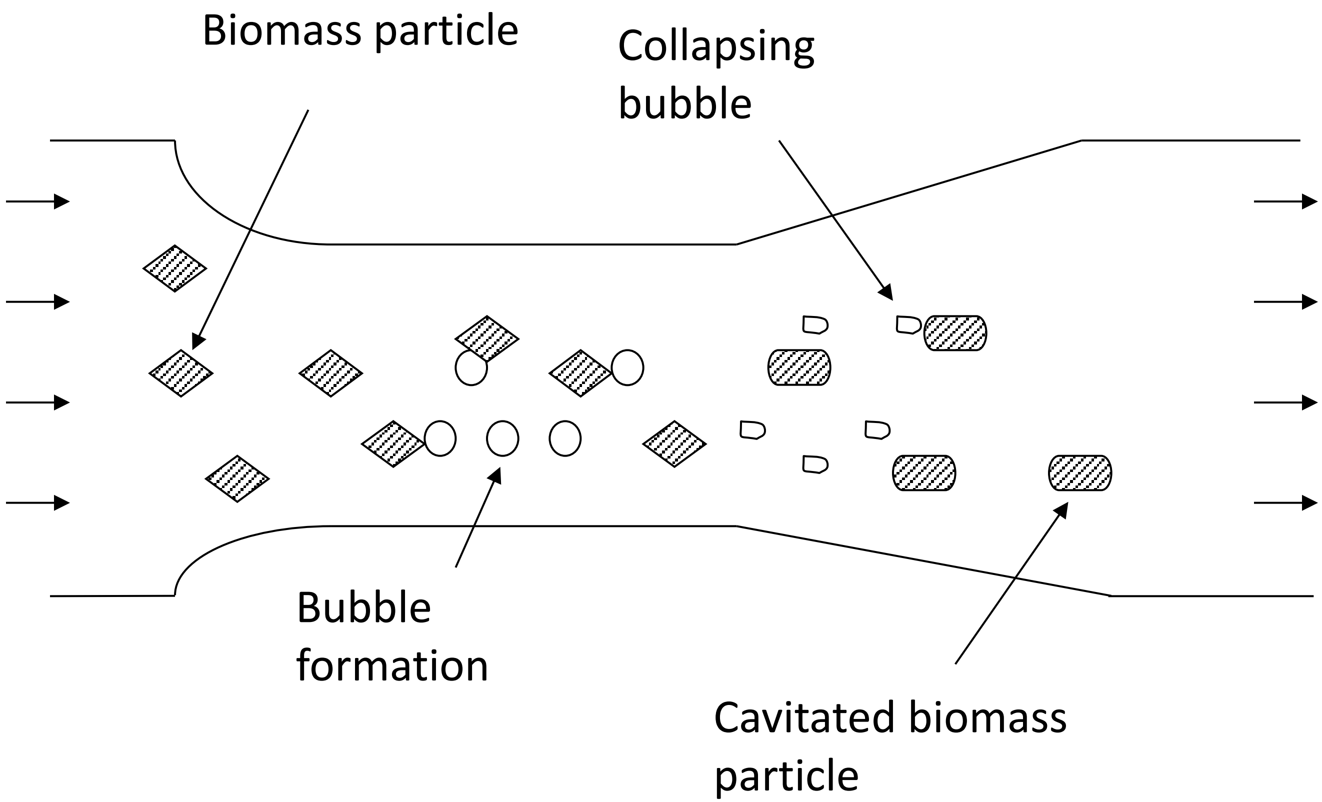


Enzyme loading = 5 FPU/g biomass
Substrate concentration = 5%

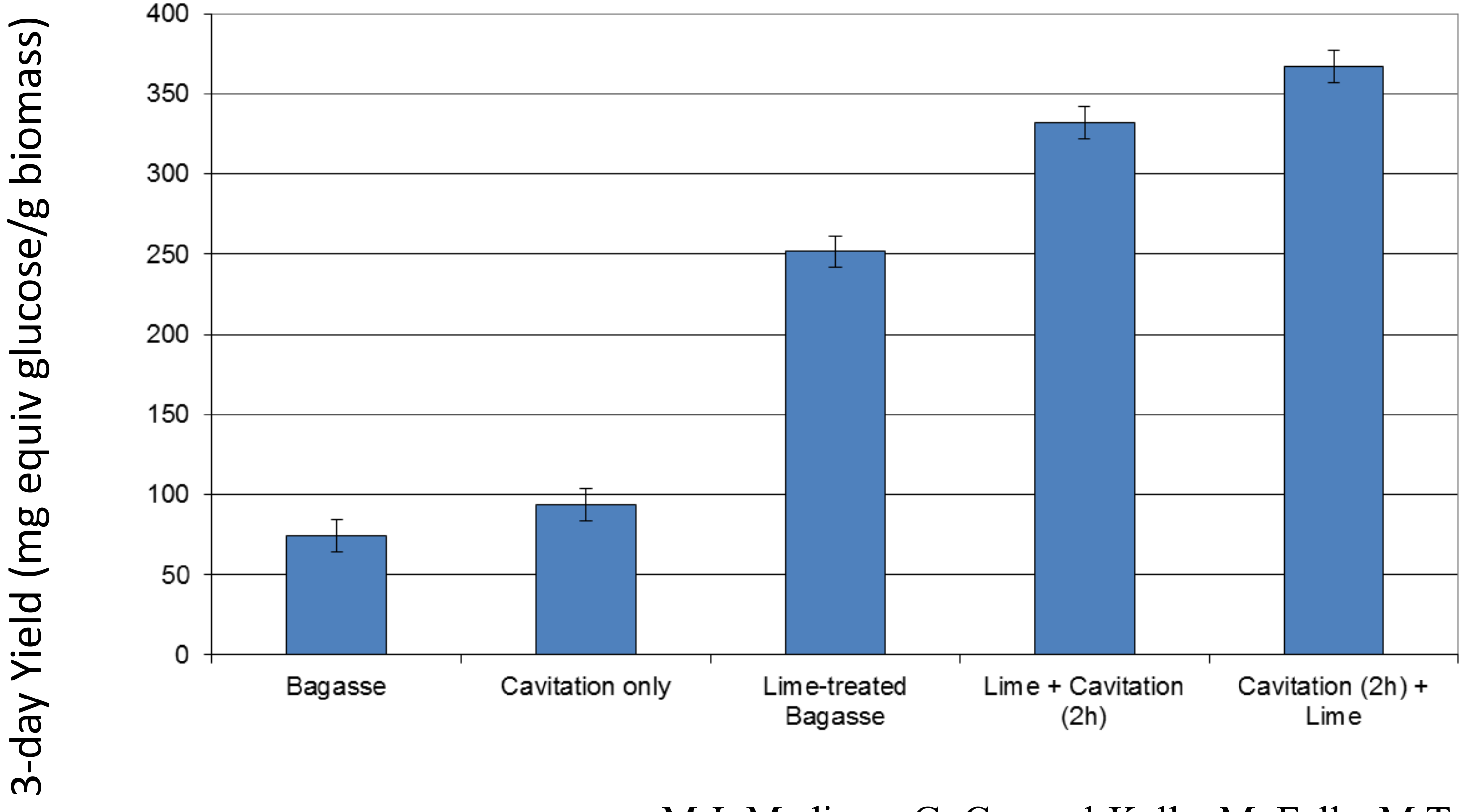
M.J. Madison, G. Coward-Kelly, M. Falls, M.T. Holtzapple, Mechanical Pretreatment of Biomass – Part I: Acoustic and Hydrodynamic Cavitation, manuscript

Alternative Mechanical Treatments

Hydrodynamic Cavitation



Hydrodynamic Cavitation



Enzyme loading = 5 FPU/g biomass
Substrate concentration = 5%

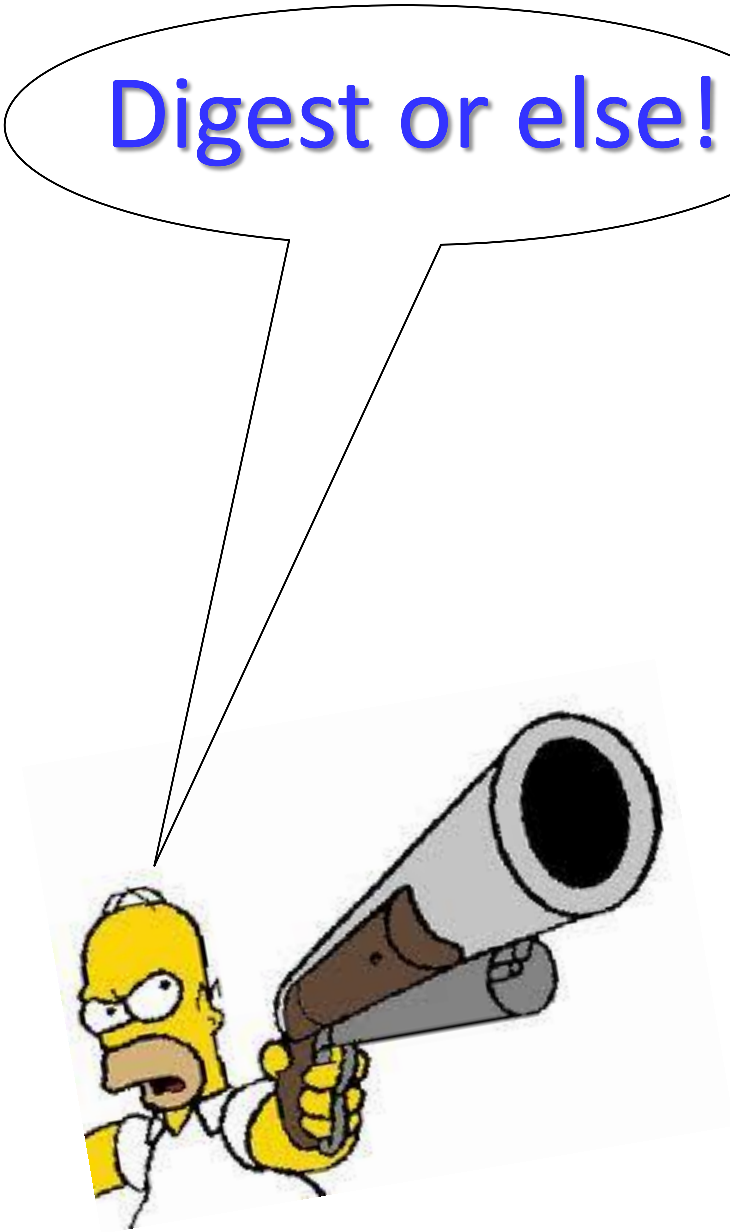
M.J. Madison, G. Coward-Kelly, M. Falls, M.T. Holtzapple, Mechanical Pretreatment of Biomass – Part I: Acoustic and Hydrodynamic Cavitation, manuscript

Problem

Problem

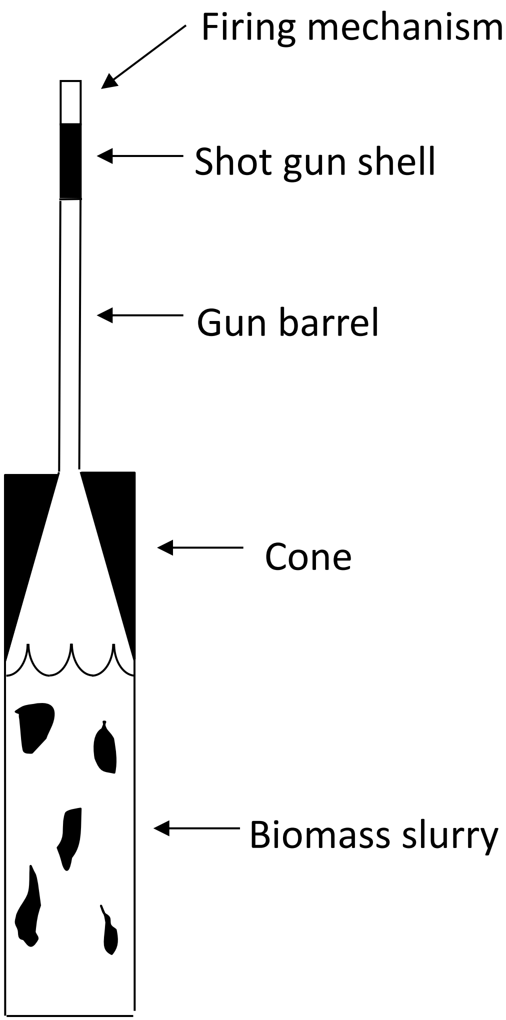
All these mechanical treatments are impractical

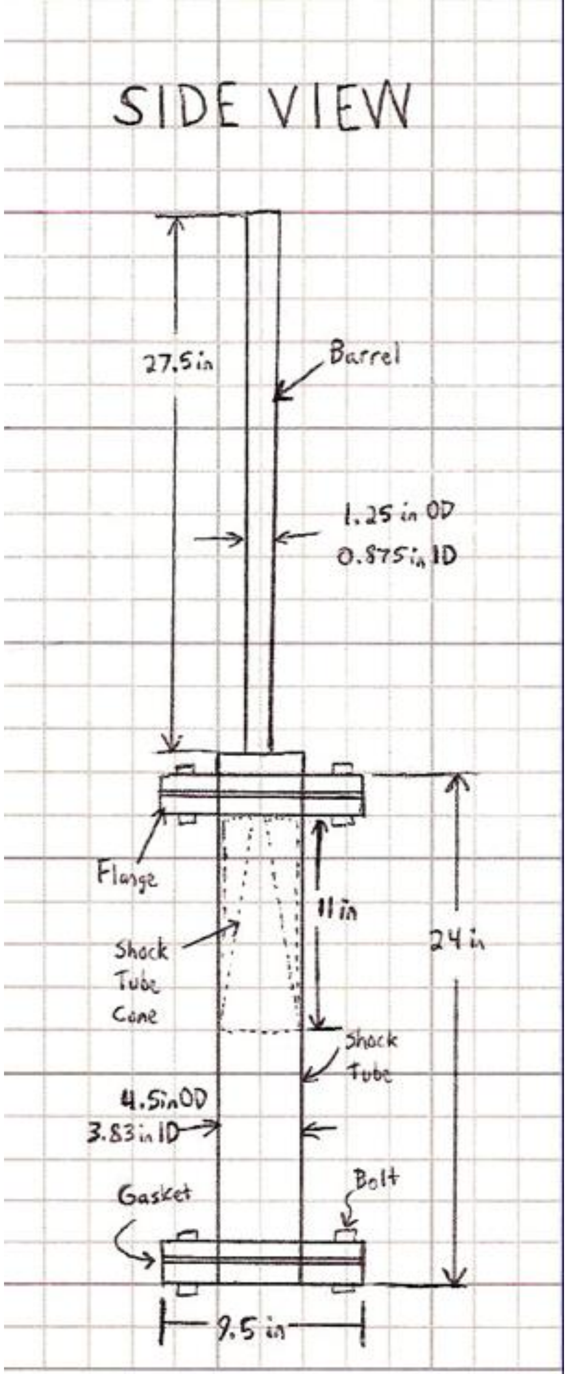
Solution


Digest or else!!

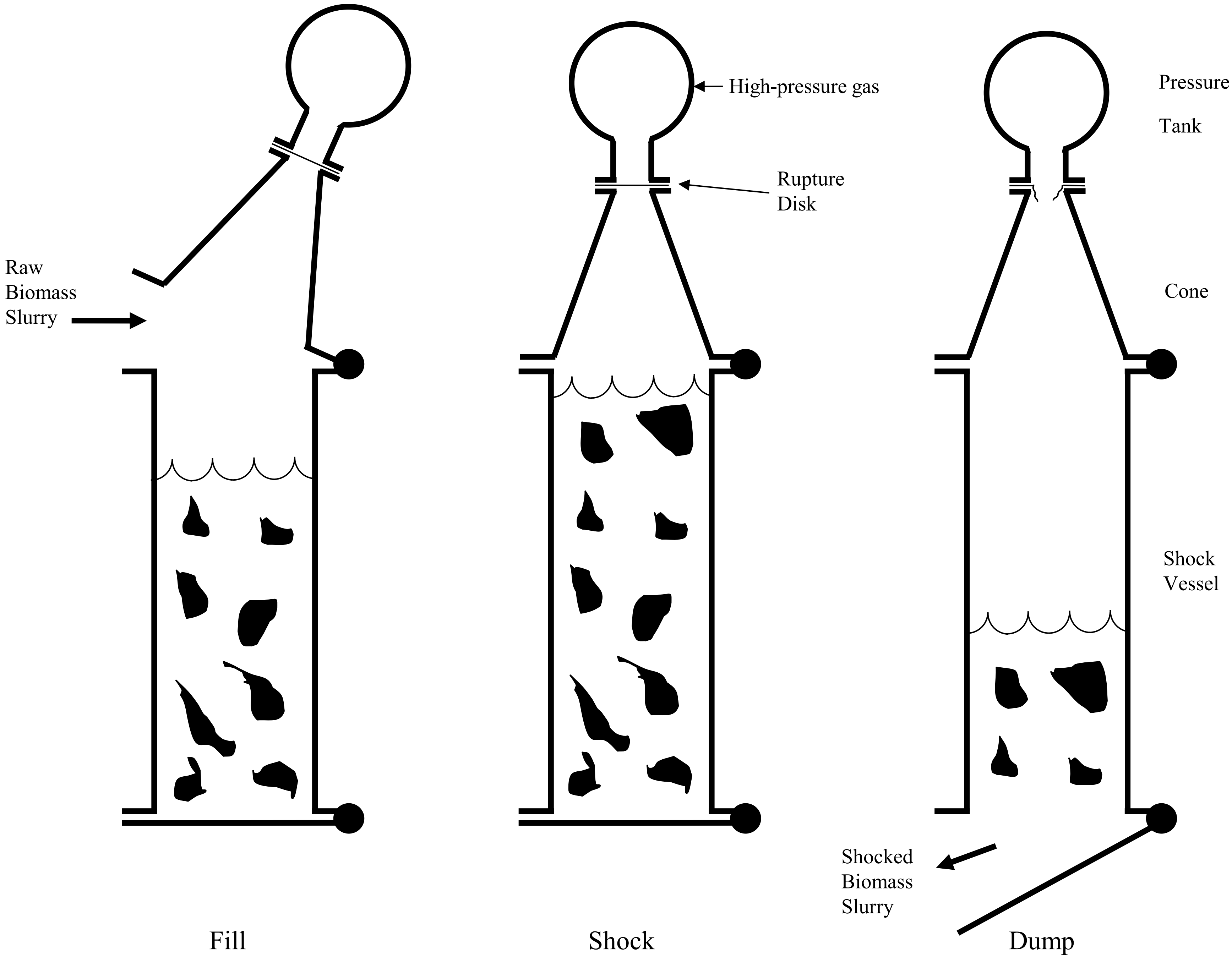
Shock Pretreatment

Shock Treatment

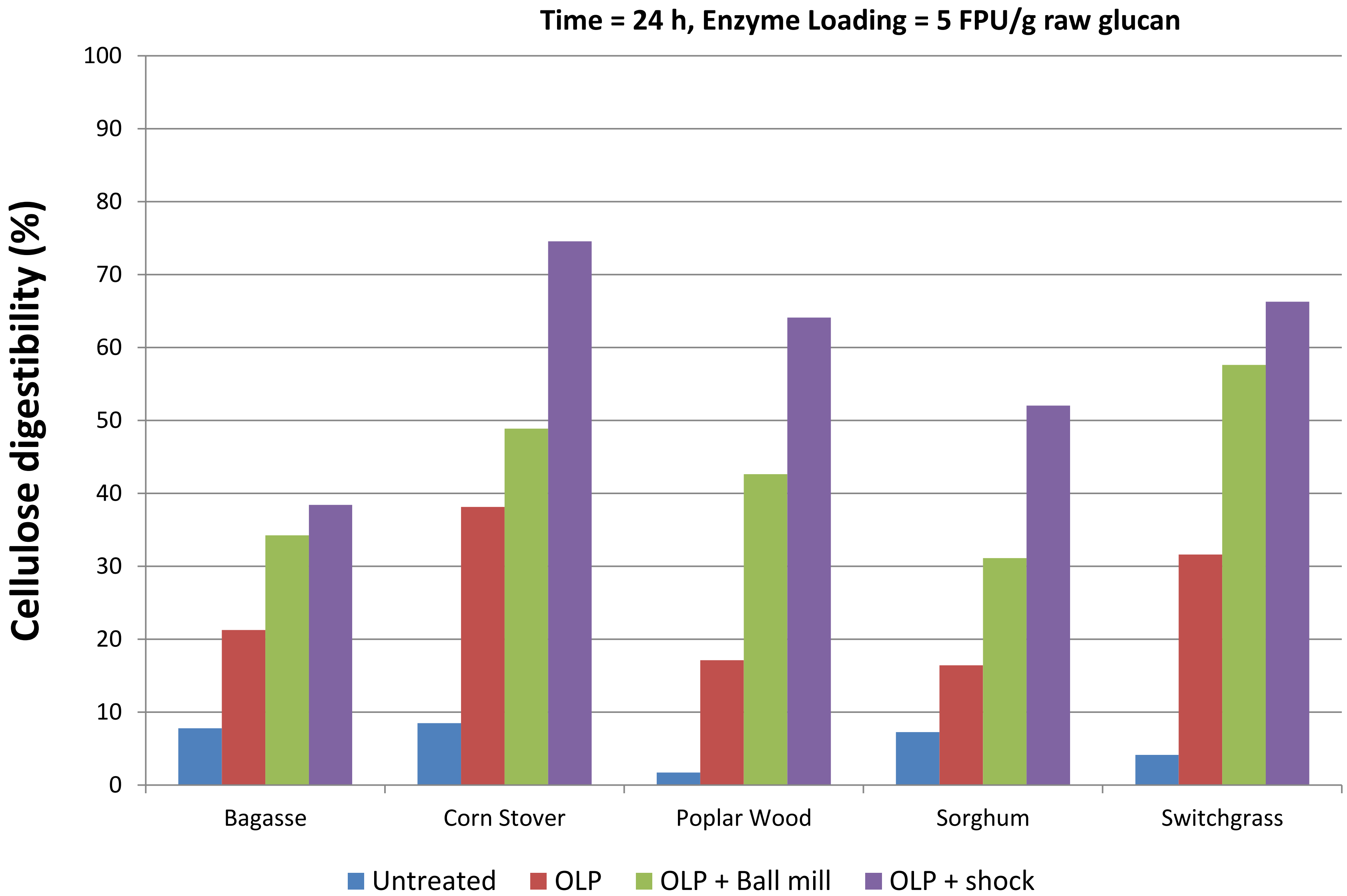




Shock Treatment

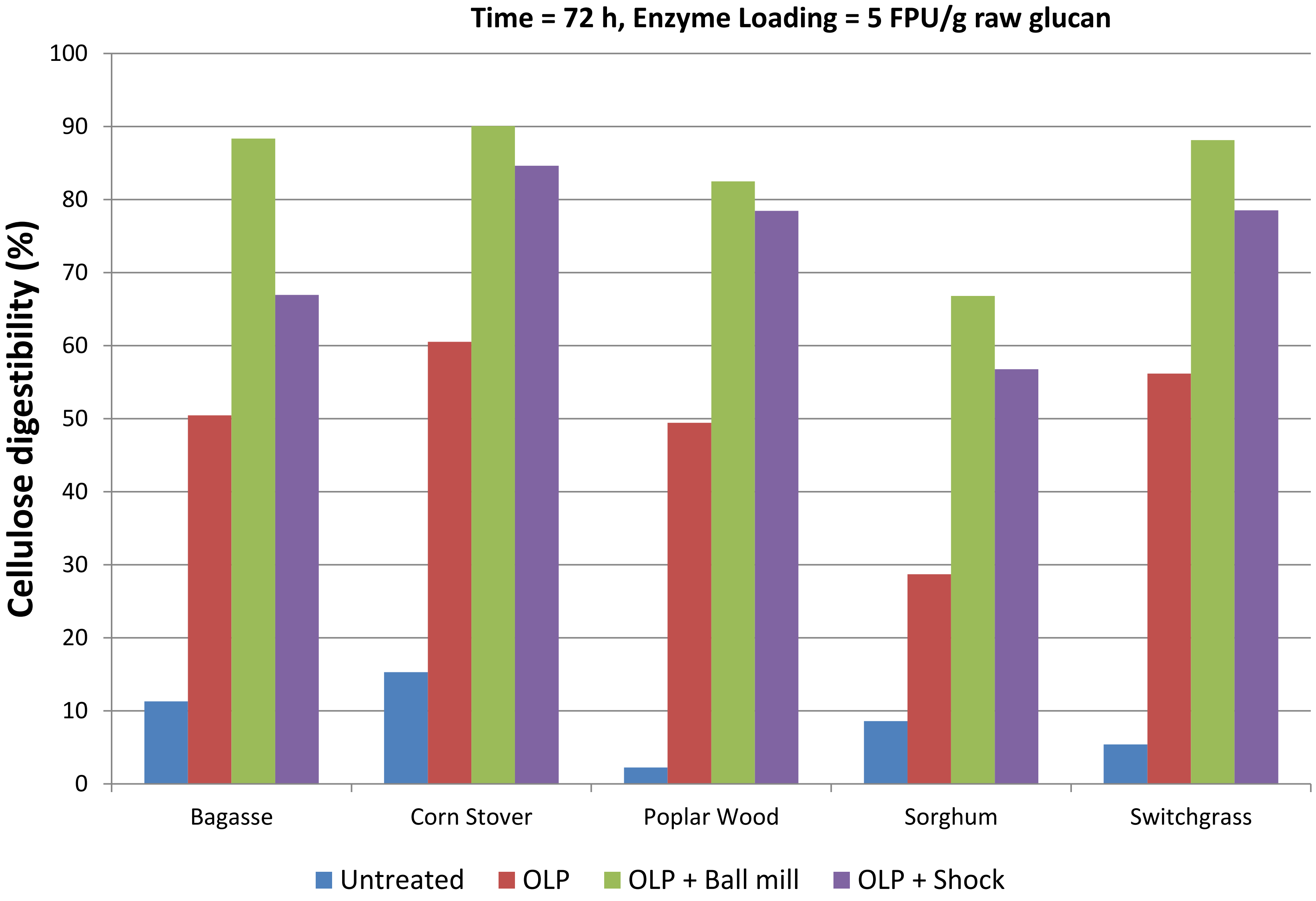

Raw
Biomass
Slurry
High-pressure gas
Rupture
Disk
Pressure
Tank
Cone
Shock
Vessel
Shocked
Biomass
Slurry
Fill
Shock
Dump

Enzymatic Cellulose Digestibility



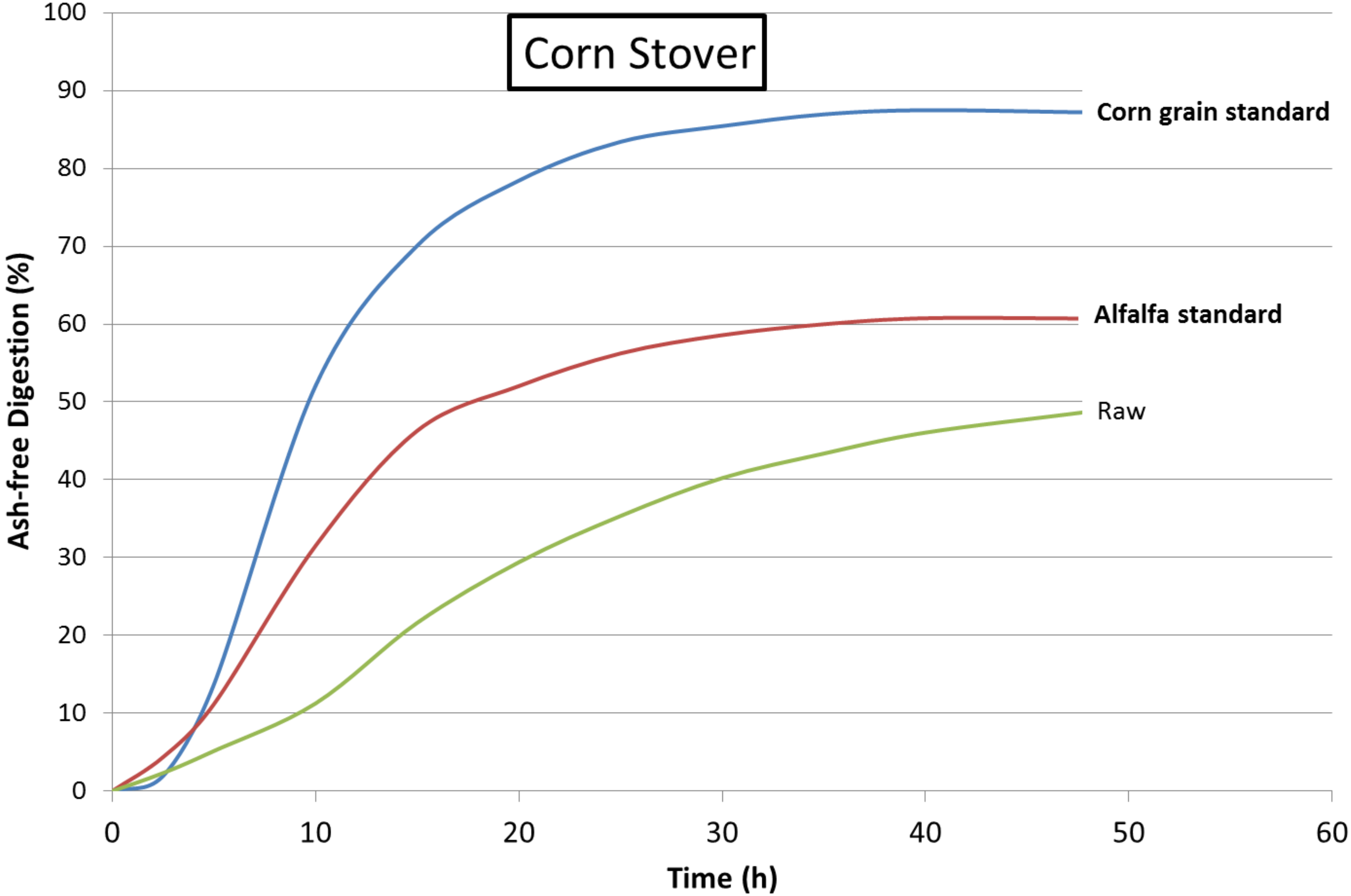
Substrate concentration = 1%

Enzymatic Cellulose Digestibility

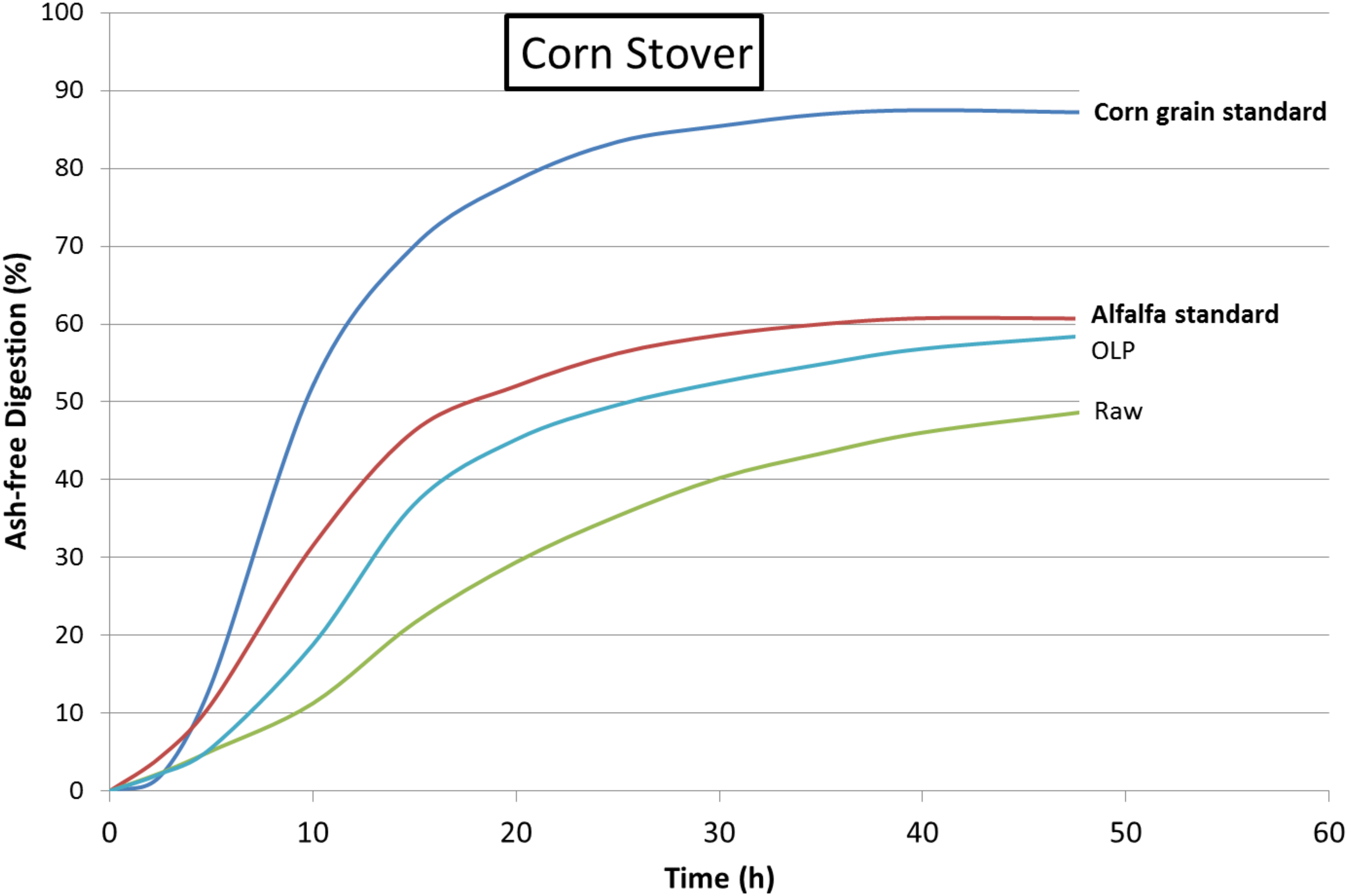


Substrate concentration = 1%

Rumen Digestibility



Rumen Digestibility



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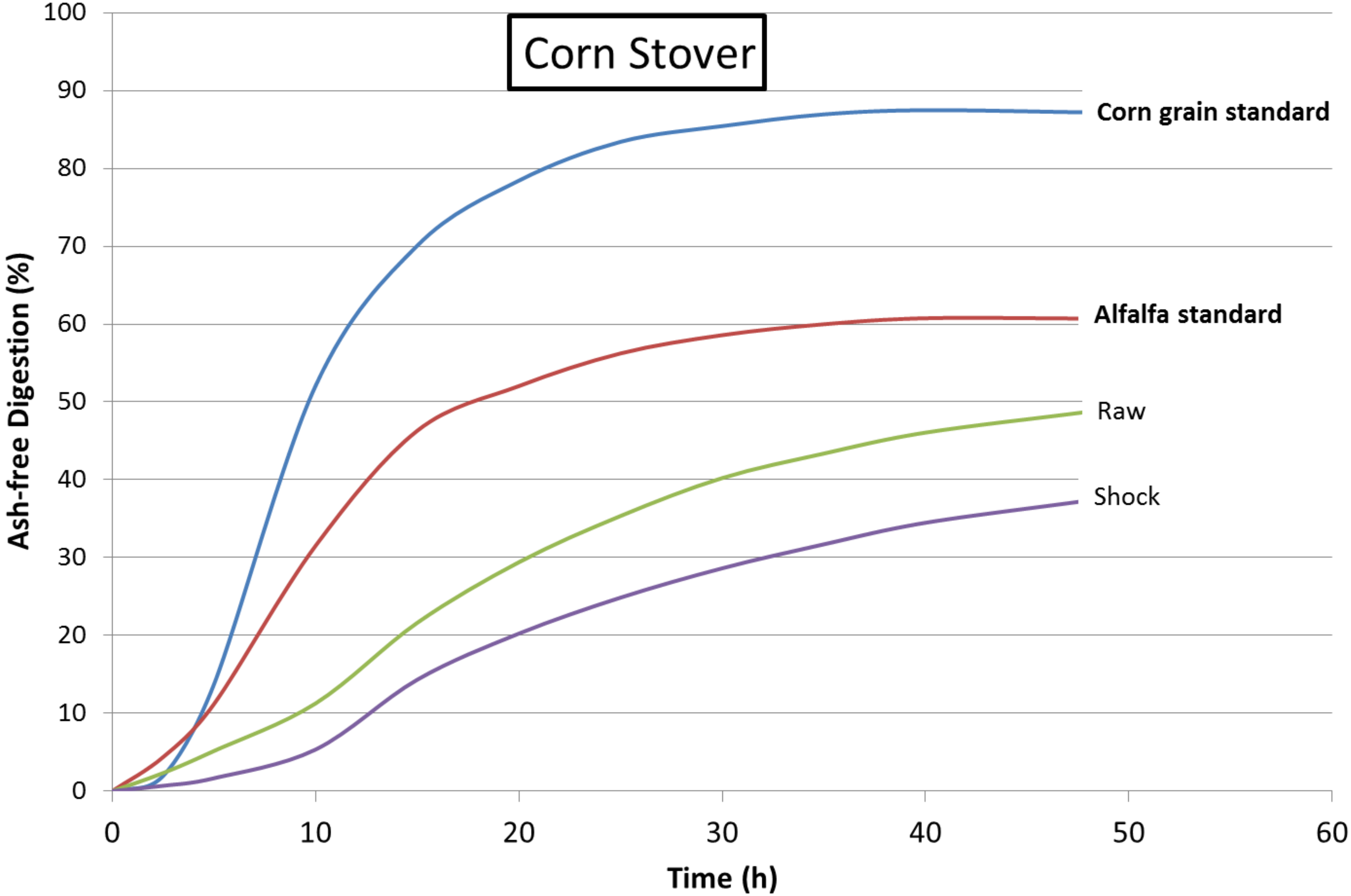

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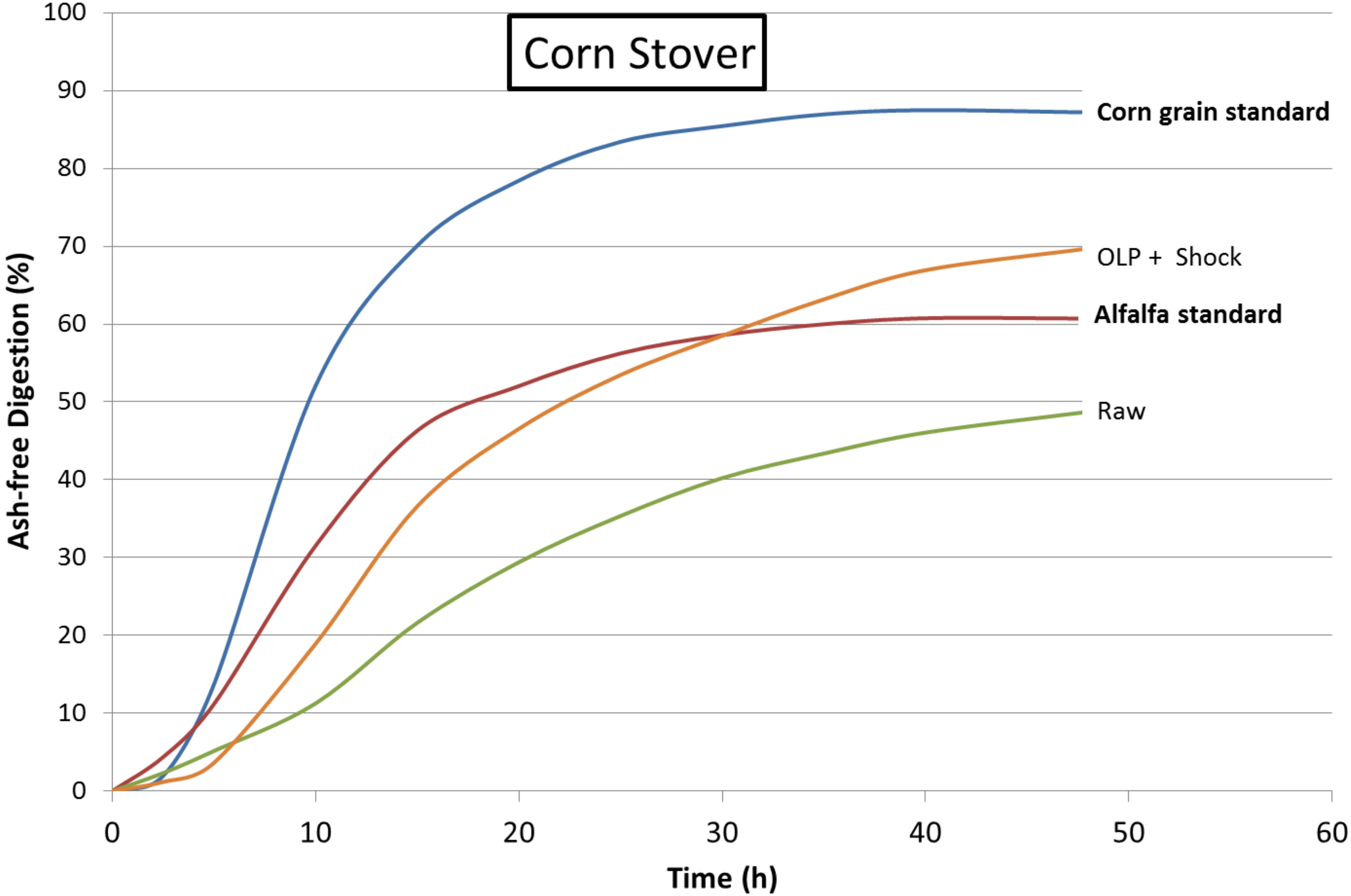

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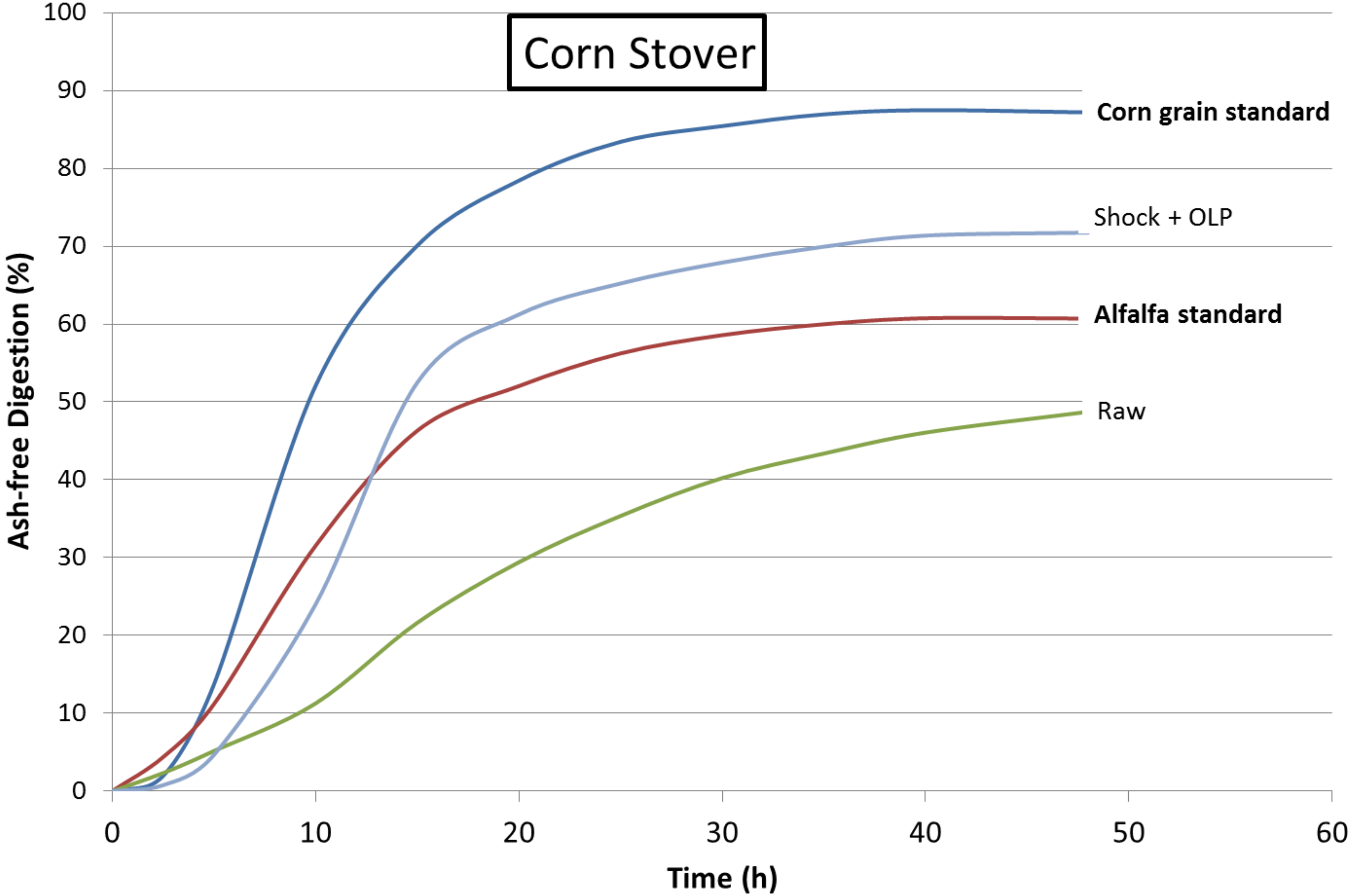

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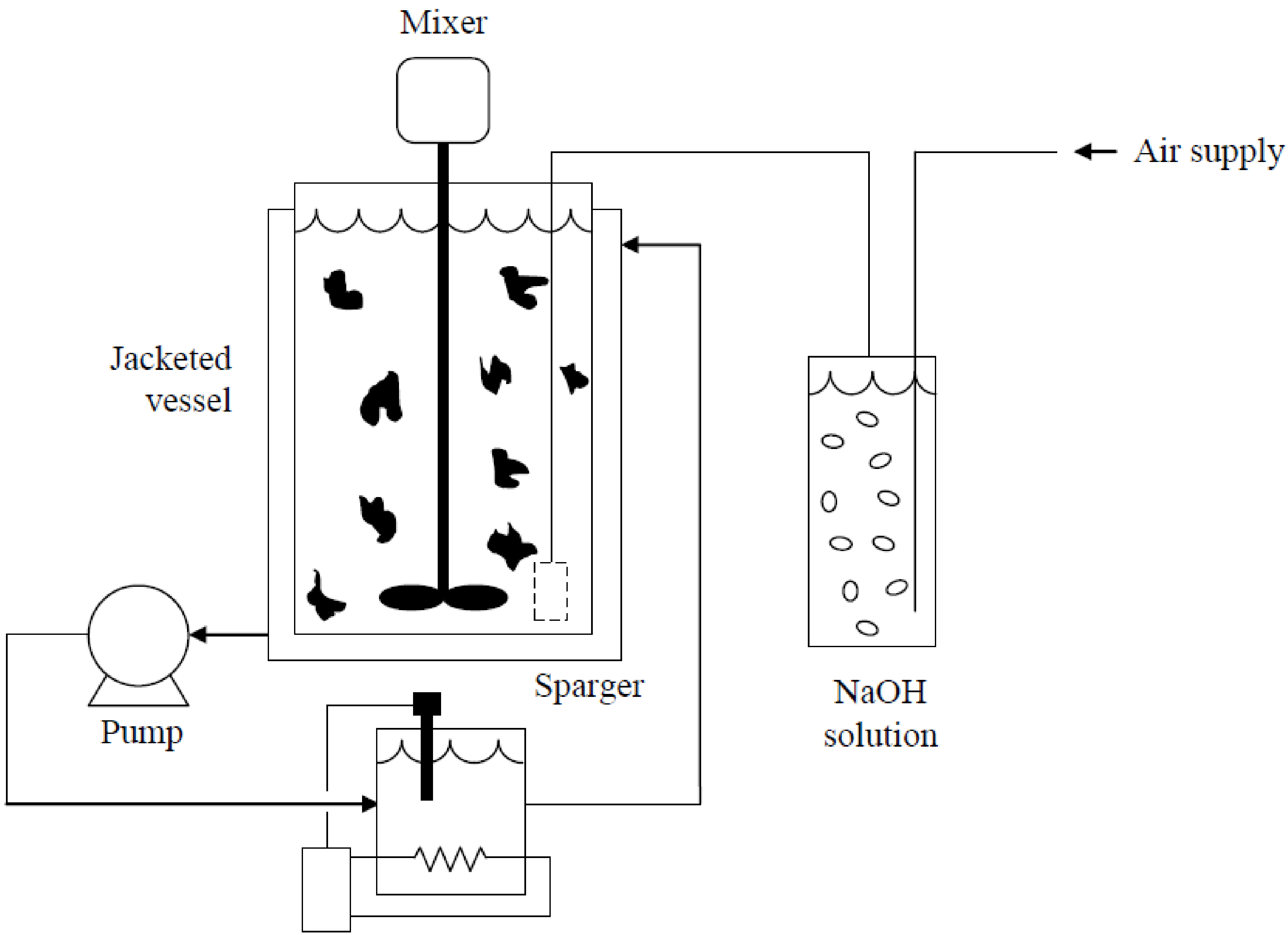
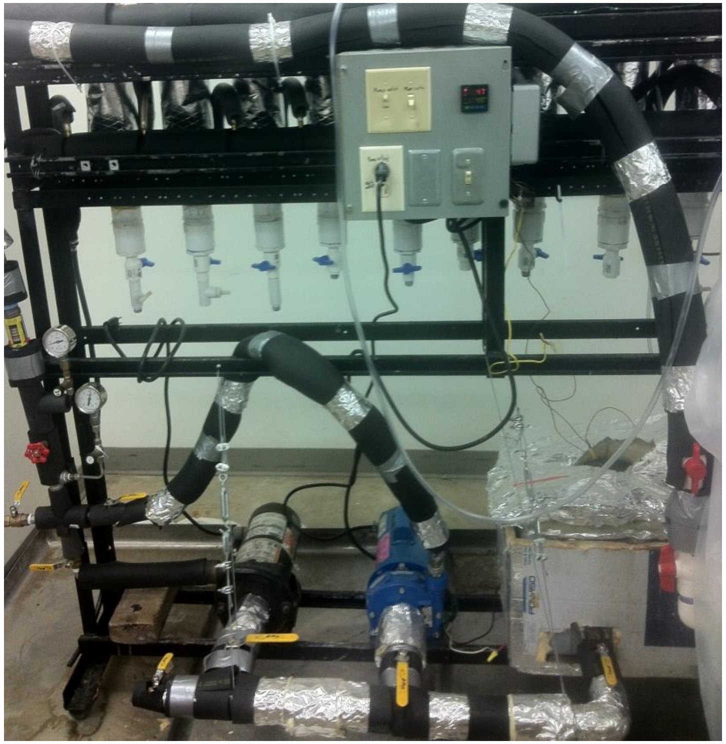
  - Shock
  - Composition
  - Enzymatic hydrolysis
- Economics
- Sugar platform
- Carboxylate platform
- Project management
- Conclusions

Submerged lime pretreatment (SLP)



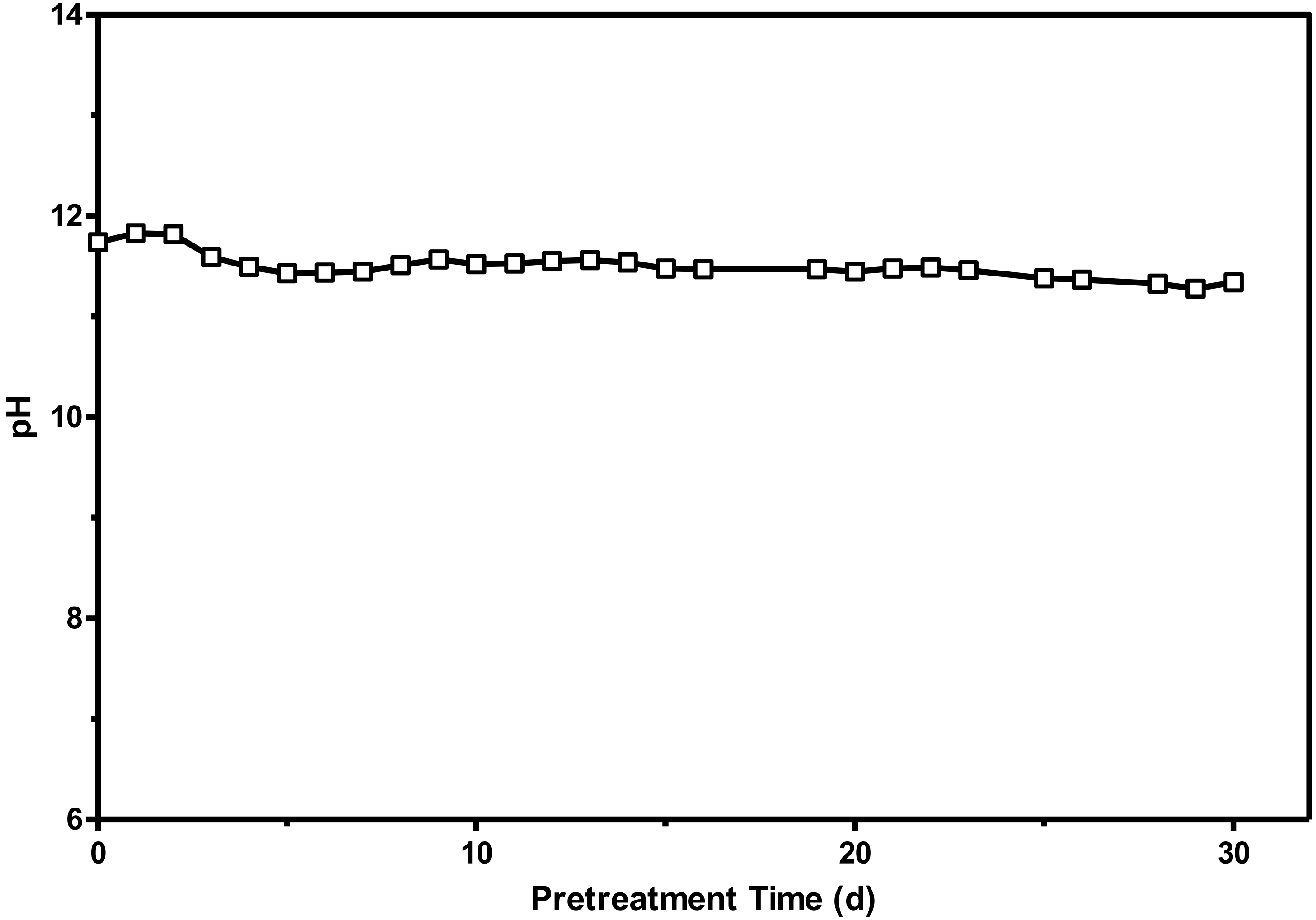
60-L Cryovessel



Heating system and pump

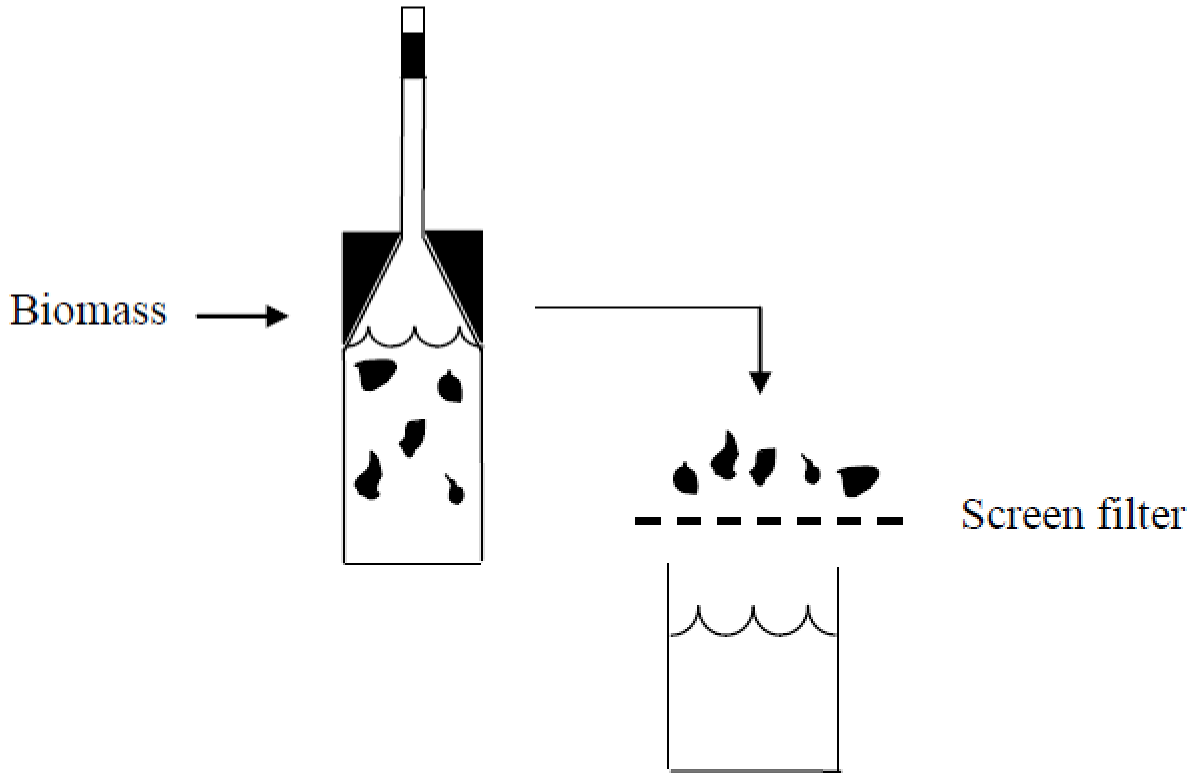
Cryovessel and CO_2 scrubber column

pH profile



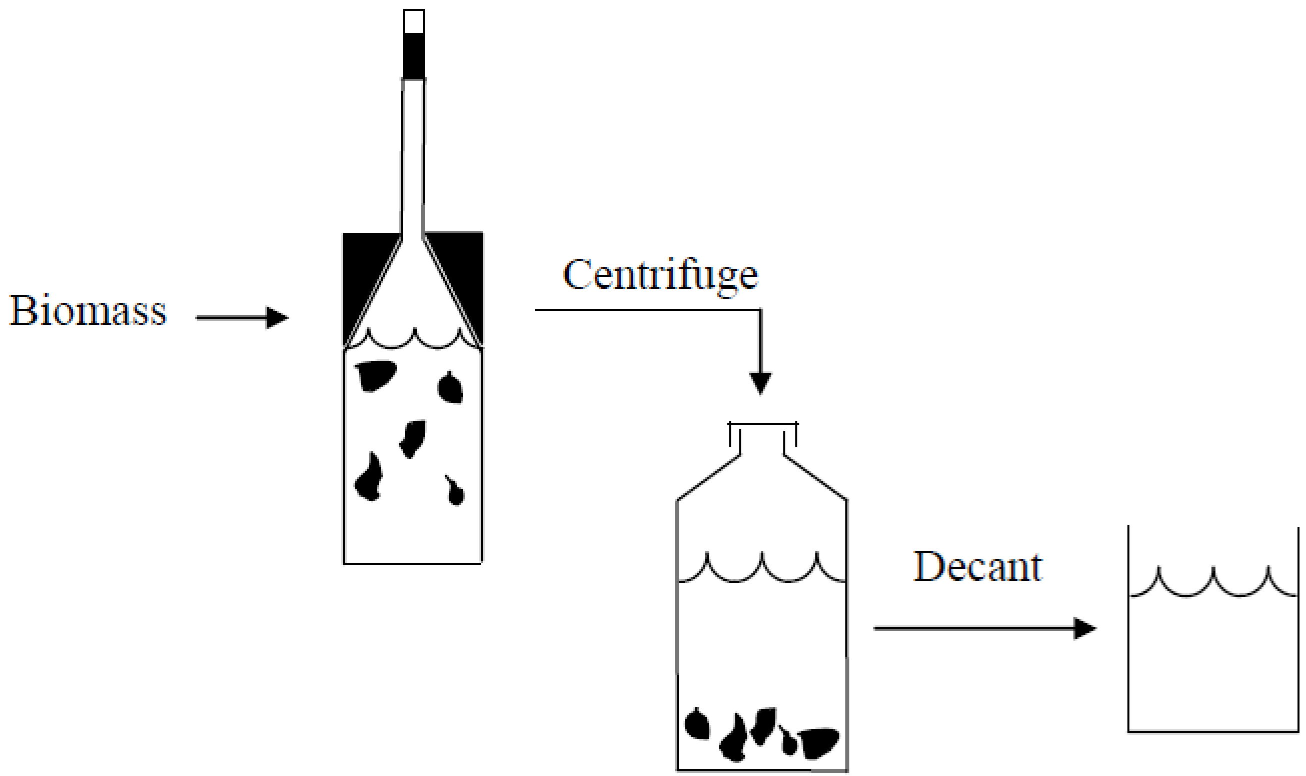
~11.5

Solids recovery – Method A



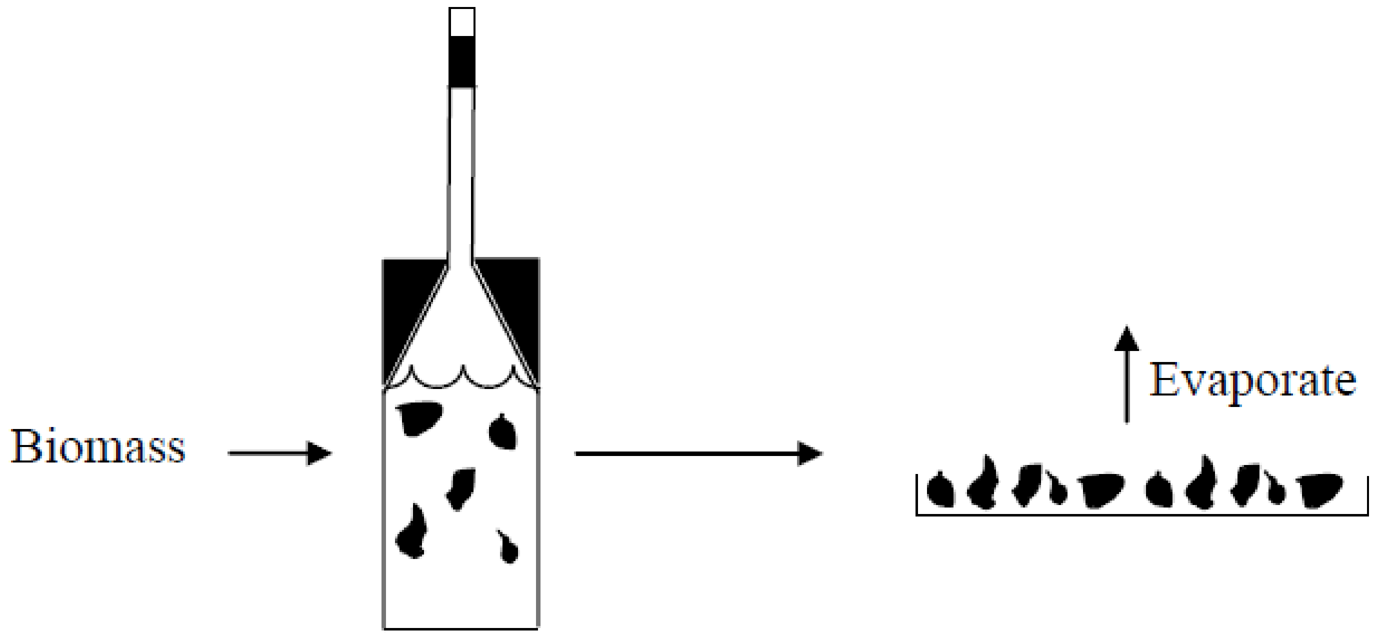
- Slow
- Lose fines

Solids recovery – Method B



- Fast
- Lose fines

Solids recovery – Method C



- Slow
- Retains fines

Outline

- Background
- Methods
  - Lime pretreatment
  - Shock
  - Composition
  - Enzymatic hydrolysis
- Economics
- Sugar platform
- Carboxylate platform
- Project management
- Conclusions

Shot gun shells

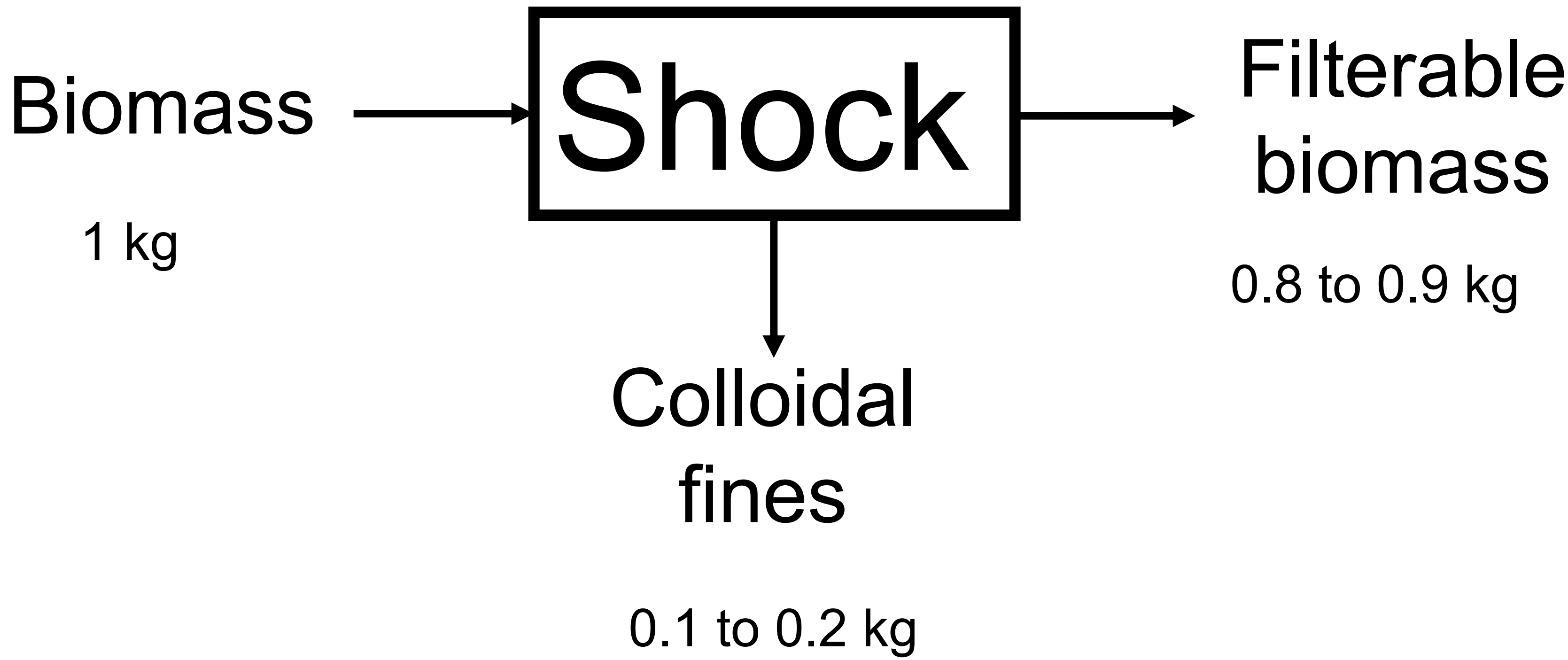
Short-hand description	Manufacturer's description
Bird shot	Winchester XpertHV 3.5-in shell 1-3/8 oz steel shot BB size
Buck shot	Winchester XB12L00 3.5-in shell 2.3 oz lead shot

Shot gun shells

Preferred

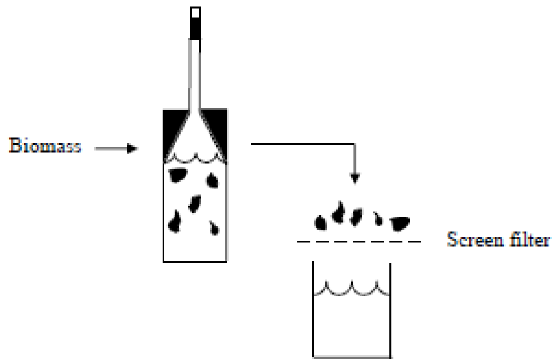
Short-hand description	Manufacturer's description
Bird shot	Winchester XpertHV 3.5-in shell 1-3/8 oz steel shot BB size
Buck shot	Winchester XB12L00 3.5-in shell 2.3 oz lead shot

Colloidal fines

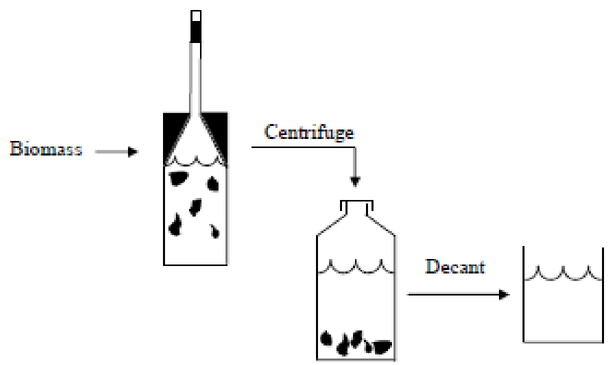


Solids recovery

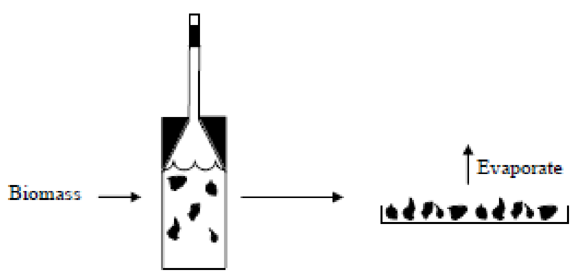
Method A



Method B

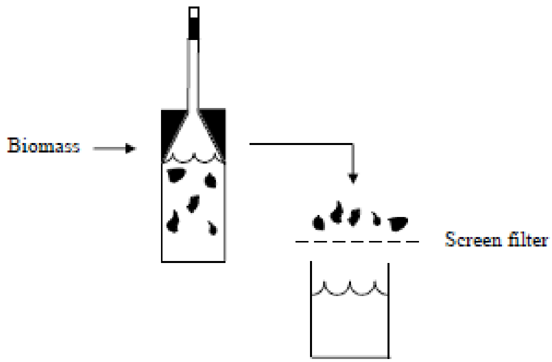


Method C

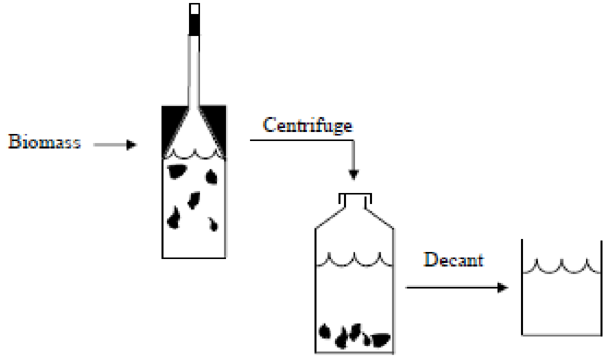


Solids recovery

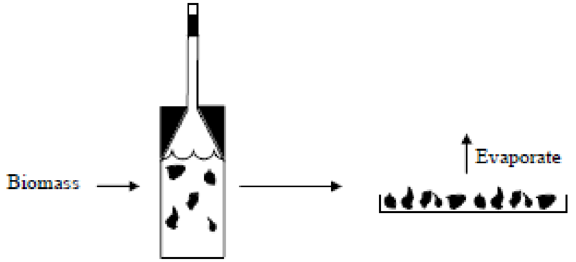
Method A



Method B



Method C

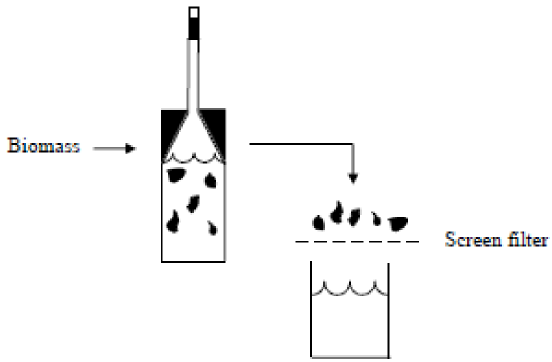


Preferred

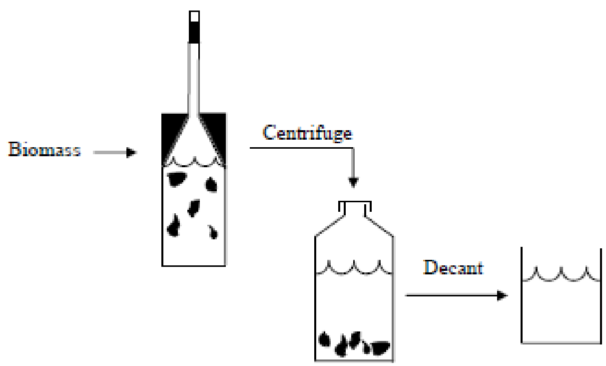
100% recovery of solids including colloidal fines

Solids recovery

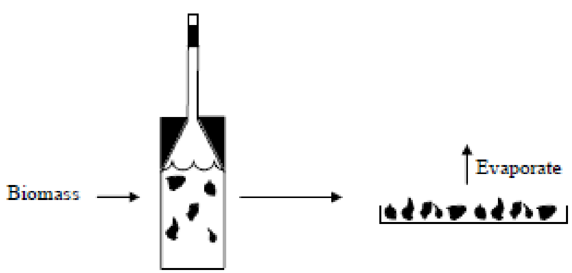
Method A



Method B



Method C

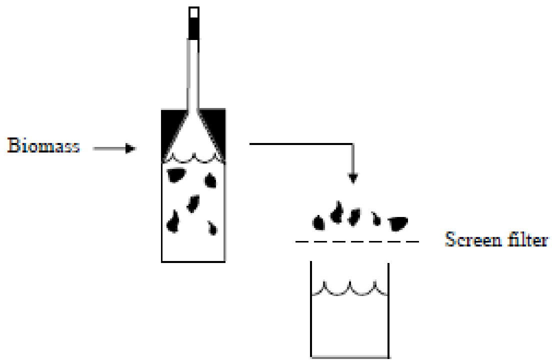


Problem

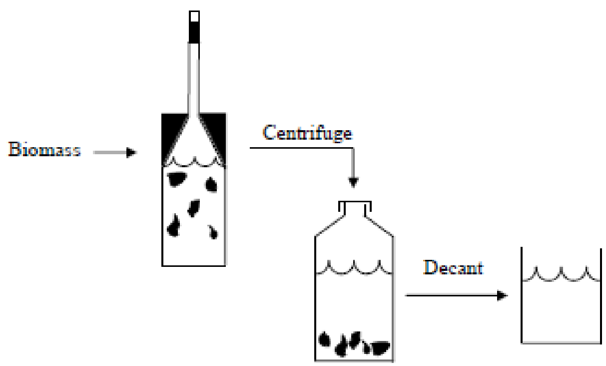
Retains explosive residue

Solids recovery

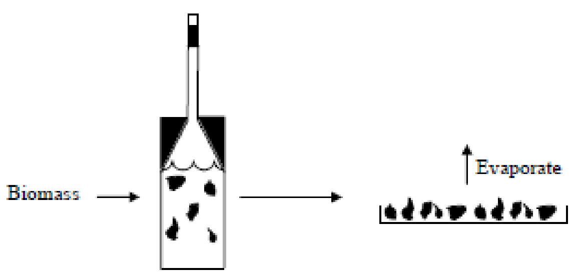
Method A



Method B



Method C



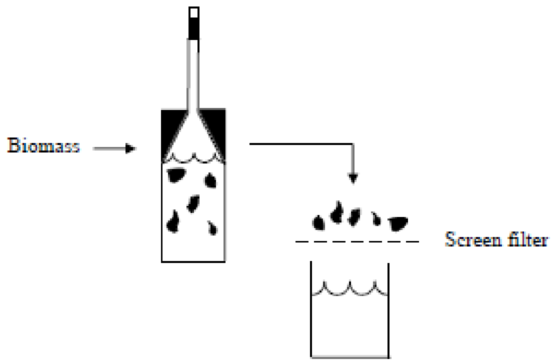
Problem

Retains explosive residue

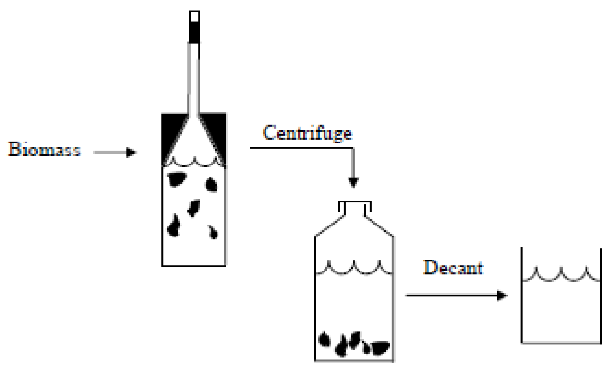
Inhibitory

Solids recovery

Method A



Method B

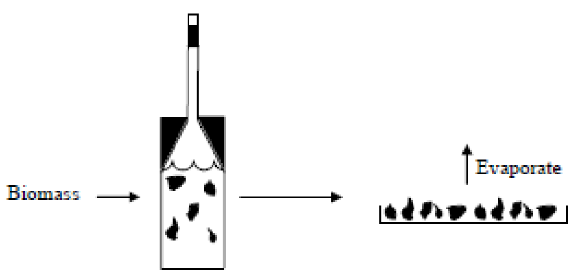


Temporarily used

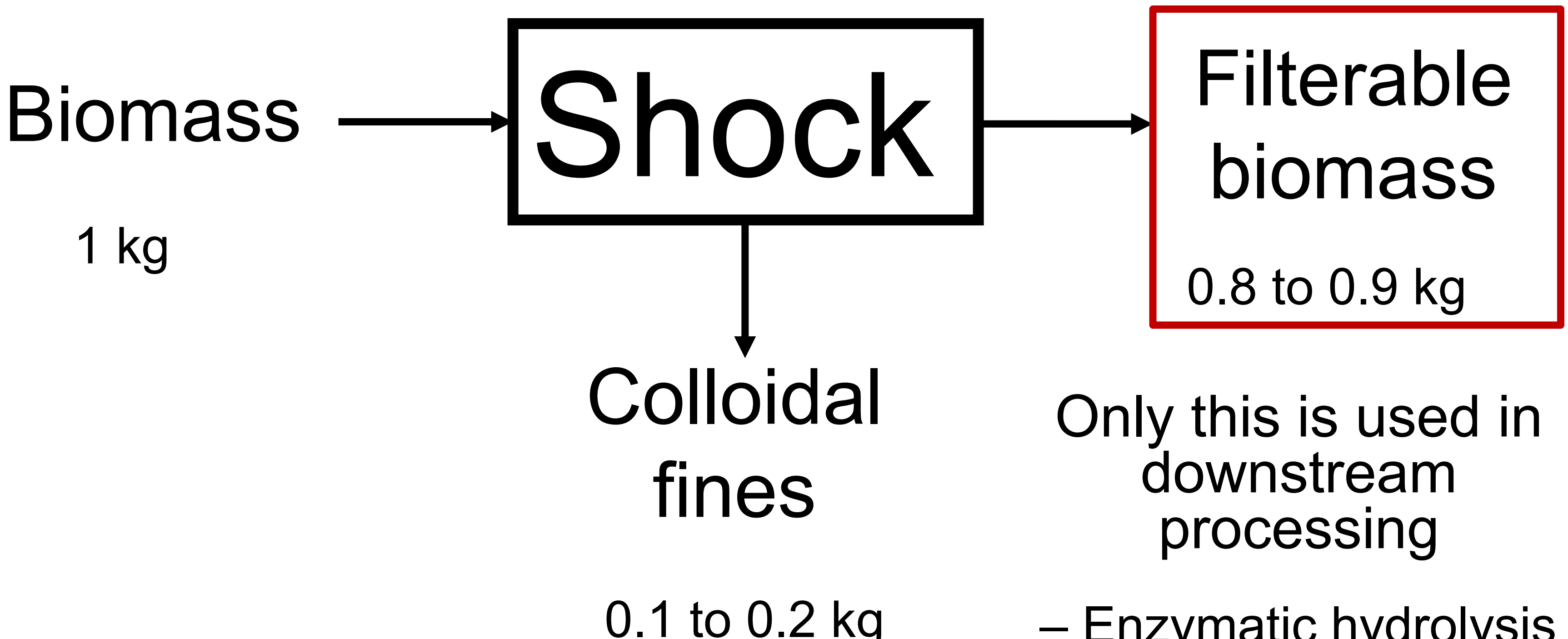
Loses colloidal fines

Must replace shot gun shell

Method C



Colloidal fines



Only this is used in downstream processing

– Enzymatic hydrolysis
– Fermentation

Outline

- Background
- Methods
  - Lime pretreatment
  - Shock
  - Composition
  - Enzymatic hydrolysis
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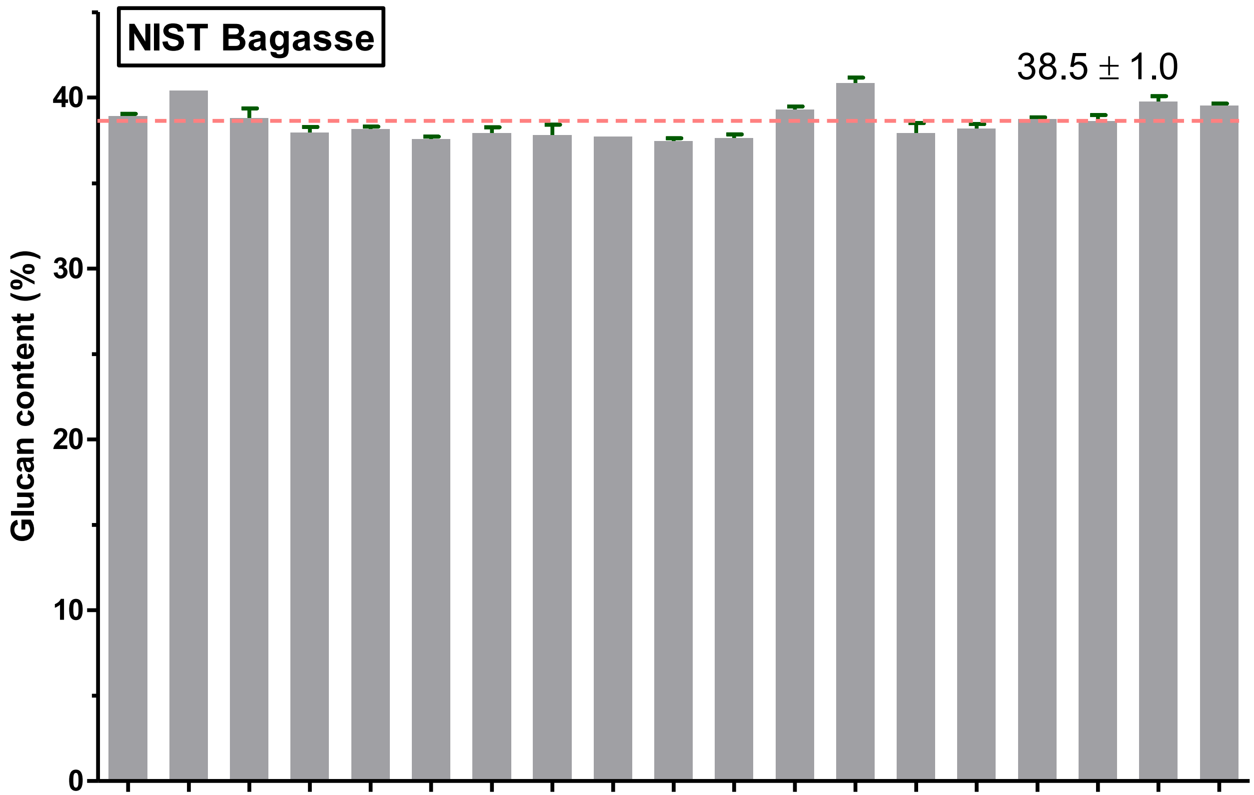
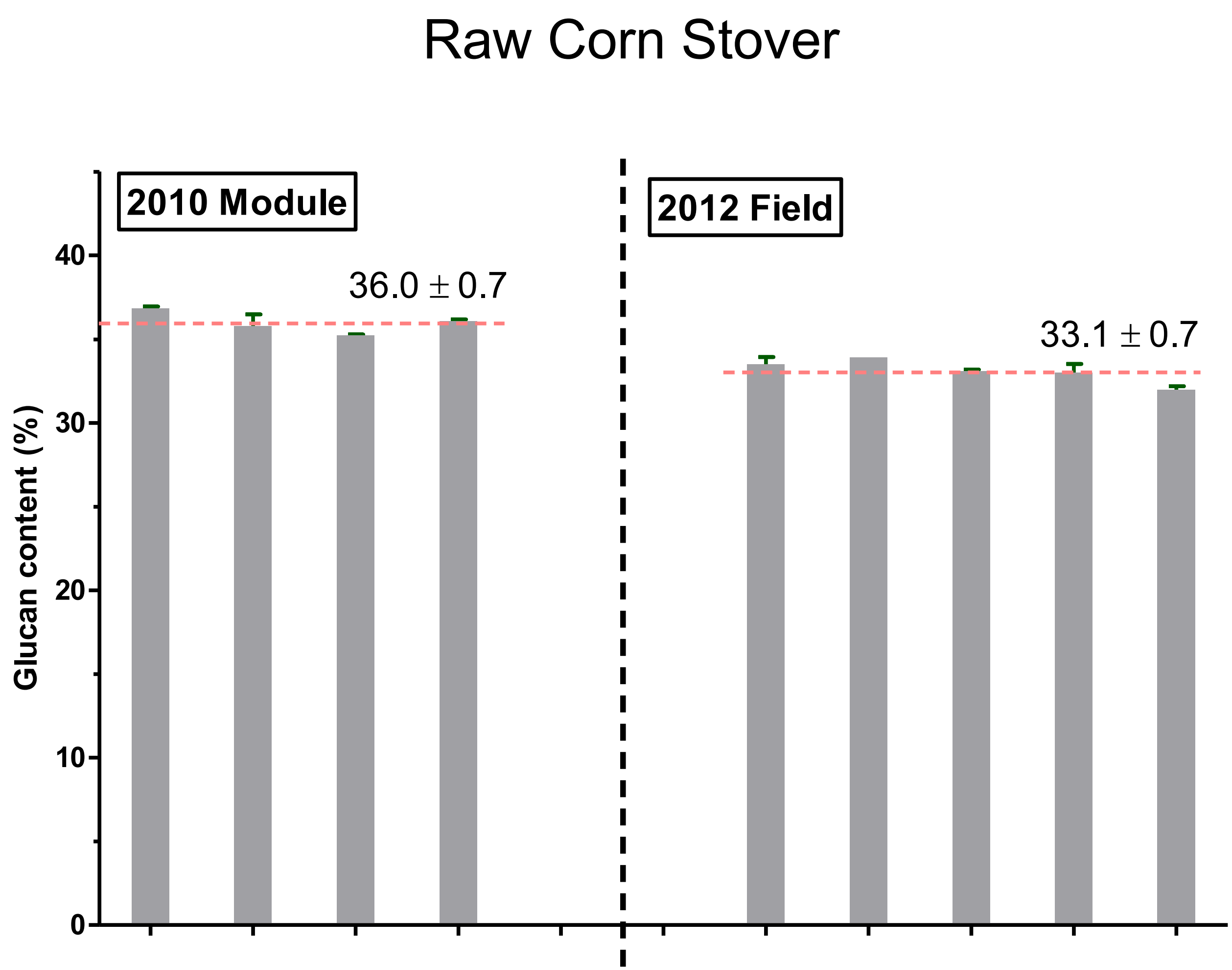
- Carboxylate platform
- Project management
- Conclusions

Measurement reproducibility NIST bagasse composition

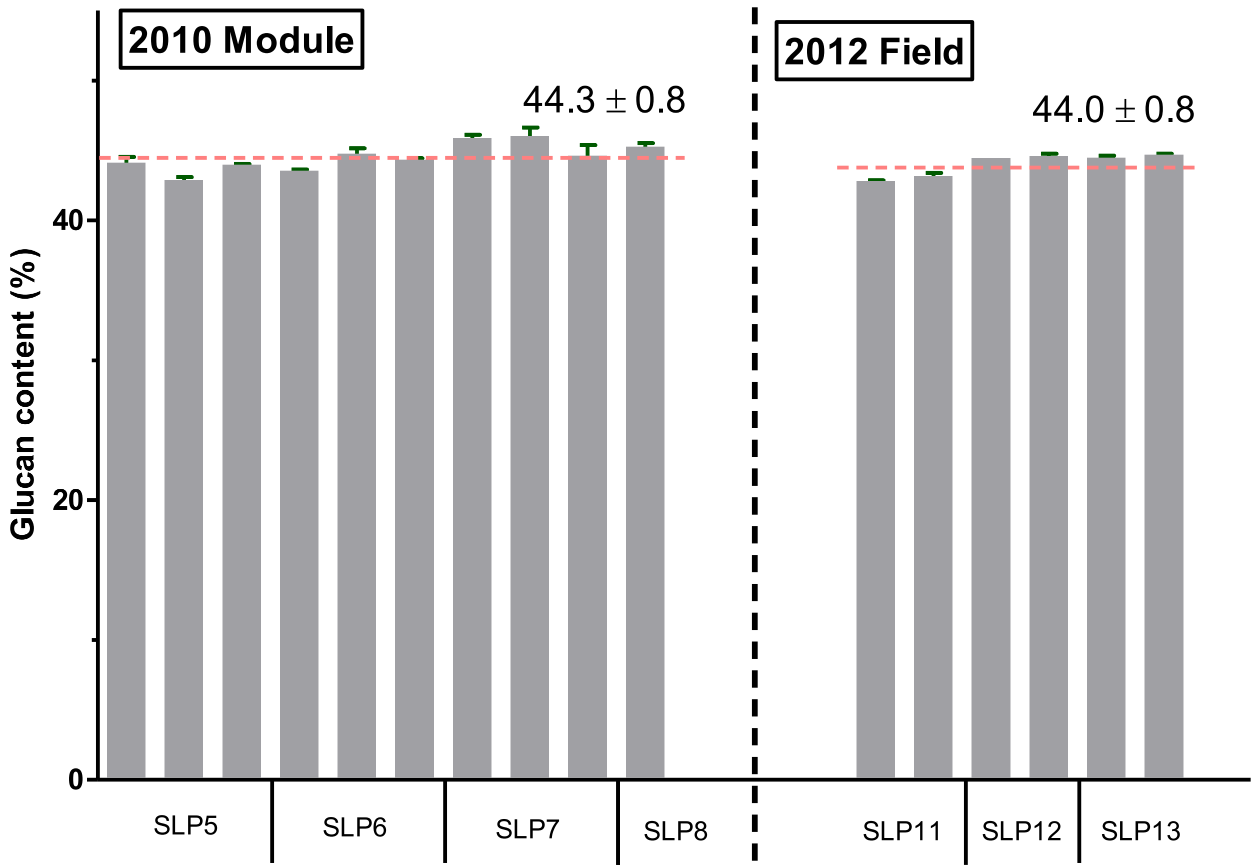


Measurement reproducibility
Corn stover composition



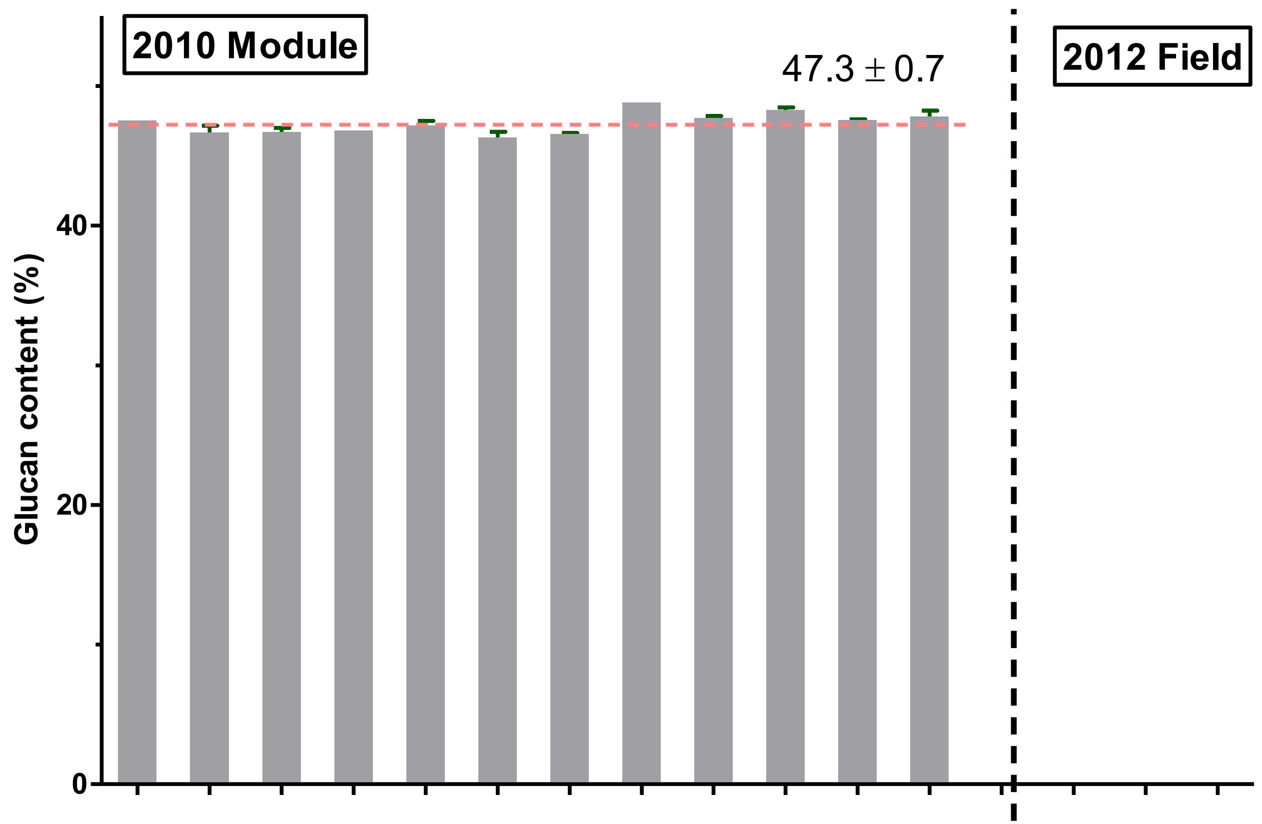
Measurement reproducibility
Corn stover composition

SLP corn stover

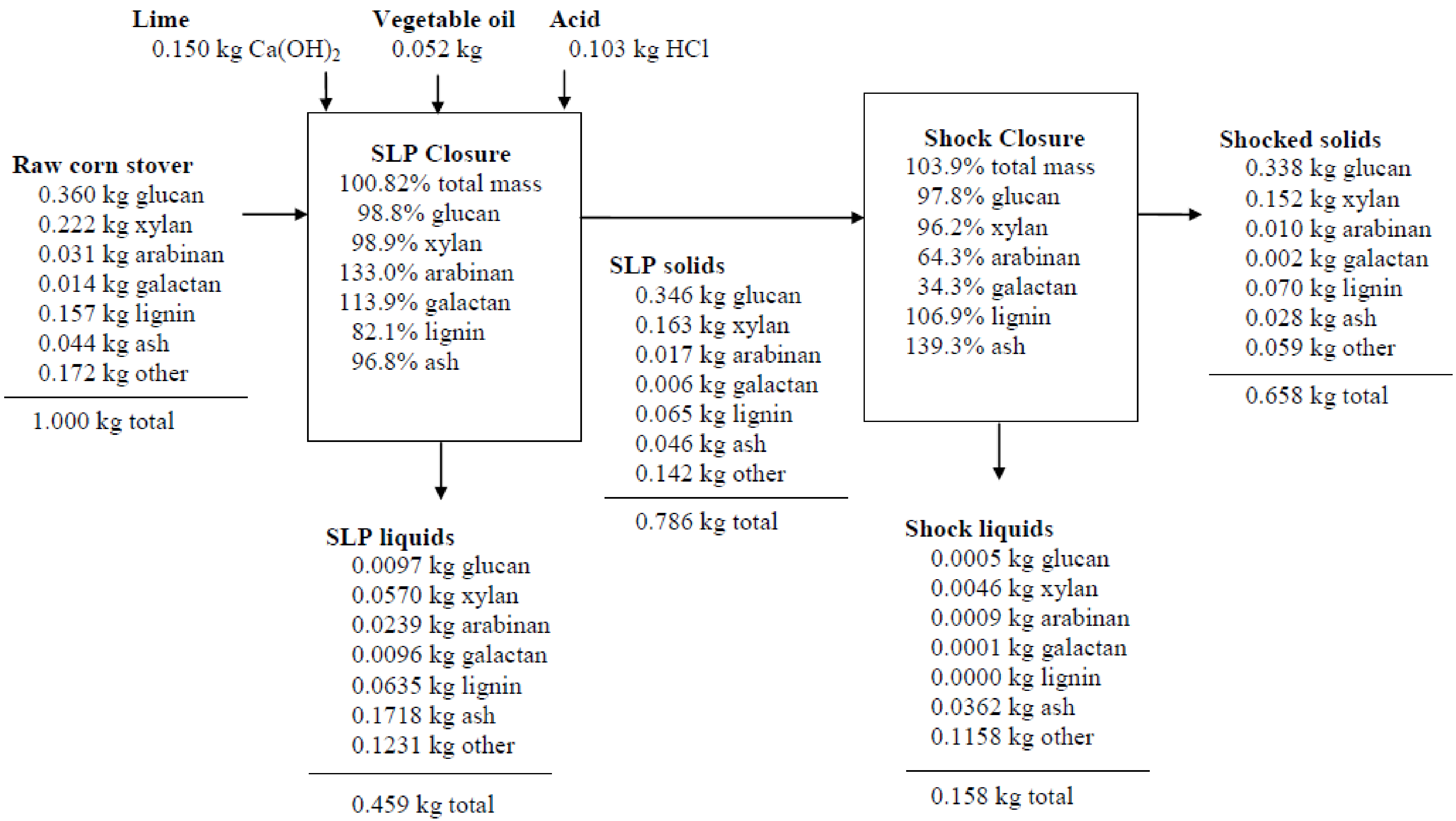


Measurement reproducibility
Corn stover composition

SLP + Shock Corn Stover



Typical mass balance



Outline

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  - Composition
  - Enzymatic hydrolysis
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Enzyme Selection

Commercial Product	Activity	Protein Conc. (mg/mL)	Filter Paper Activity (FPU/mL)	Specific Activity (FPU/g)
Novozyme Cellic Ctec 2	cellulase	294 ± 32	225 ± 20	765
Novozyme Cellic Htec 2	hemicellulase	308 ± 34	—	—
Genecor Accellerase 1000	cellulase + hemicellulase	106 ± 10	52 ± 1	490
Spezyme CP	cellulase	186 ± 10	84 ± 2	452

Protein concentration: Error band is ± 1 standard deviation.
Replicates = 3 independent, with 2 measurements at each of 2 dilutions for each replicate.
Filter paper performed in triplicate.

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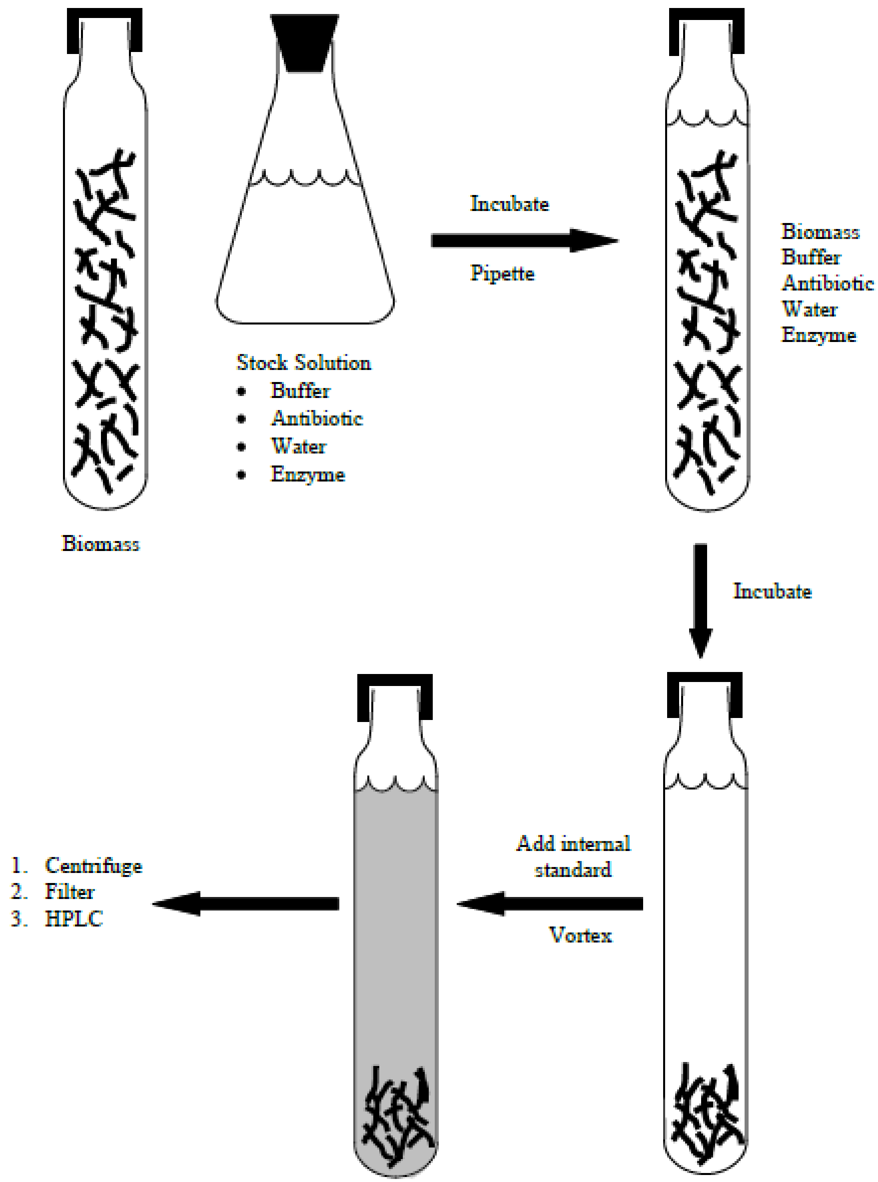
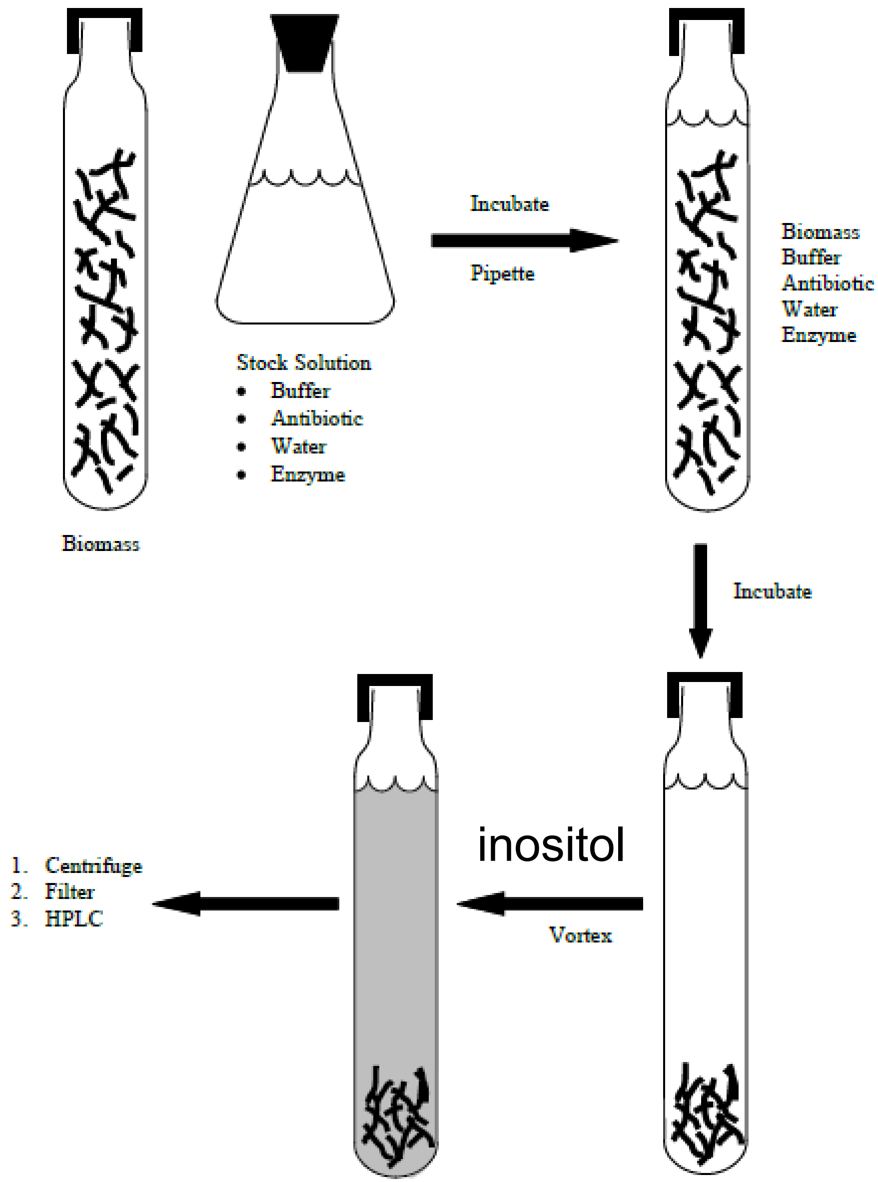
High-solids enzymatic hydrolysis

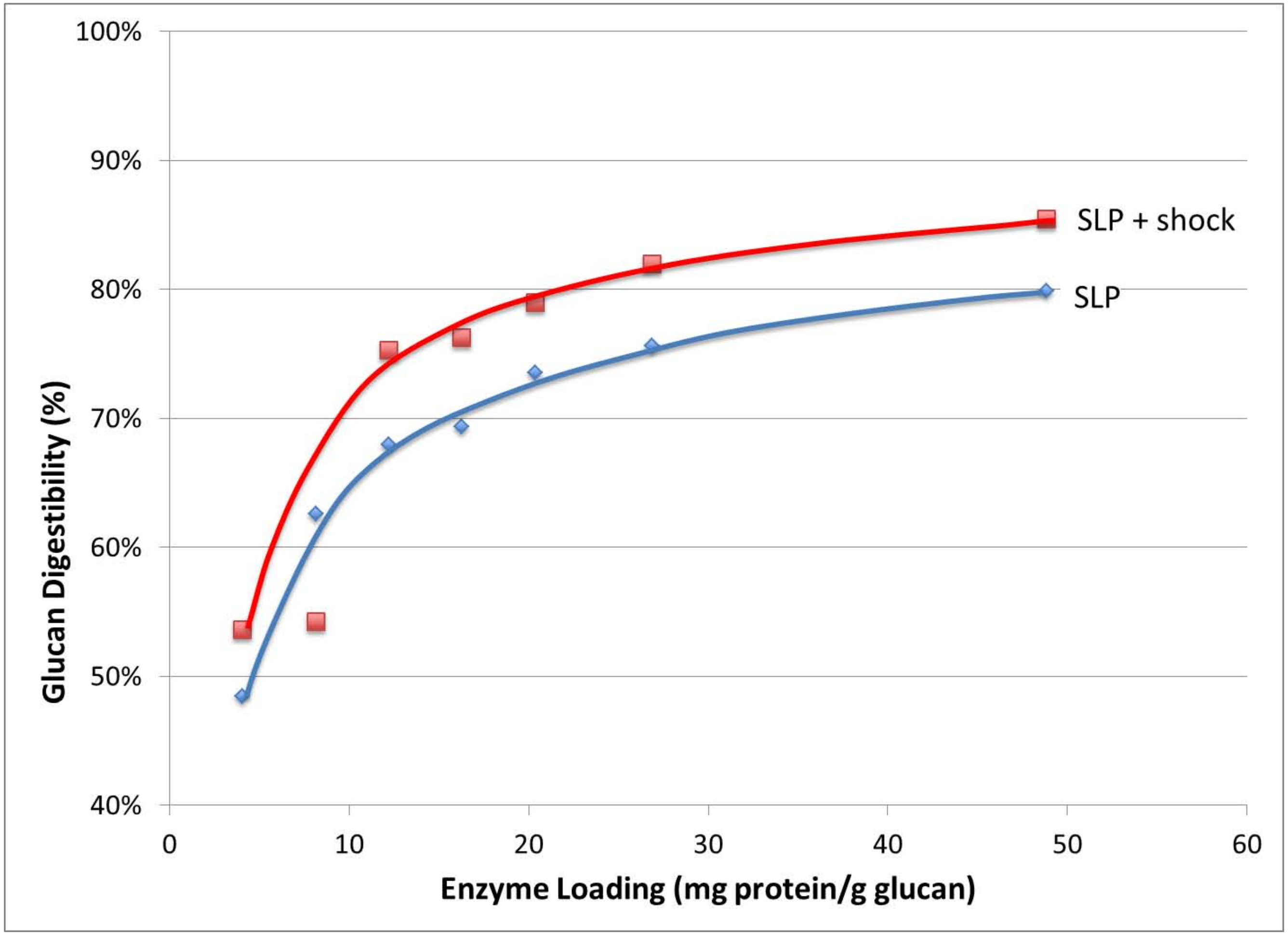


High-solids enzymatic hydrolysis



Base case

t = 5 days, Solids = 15%

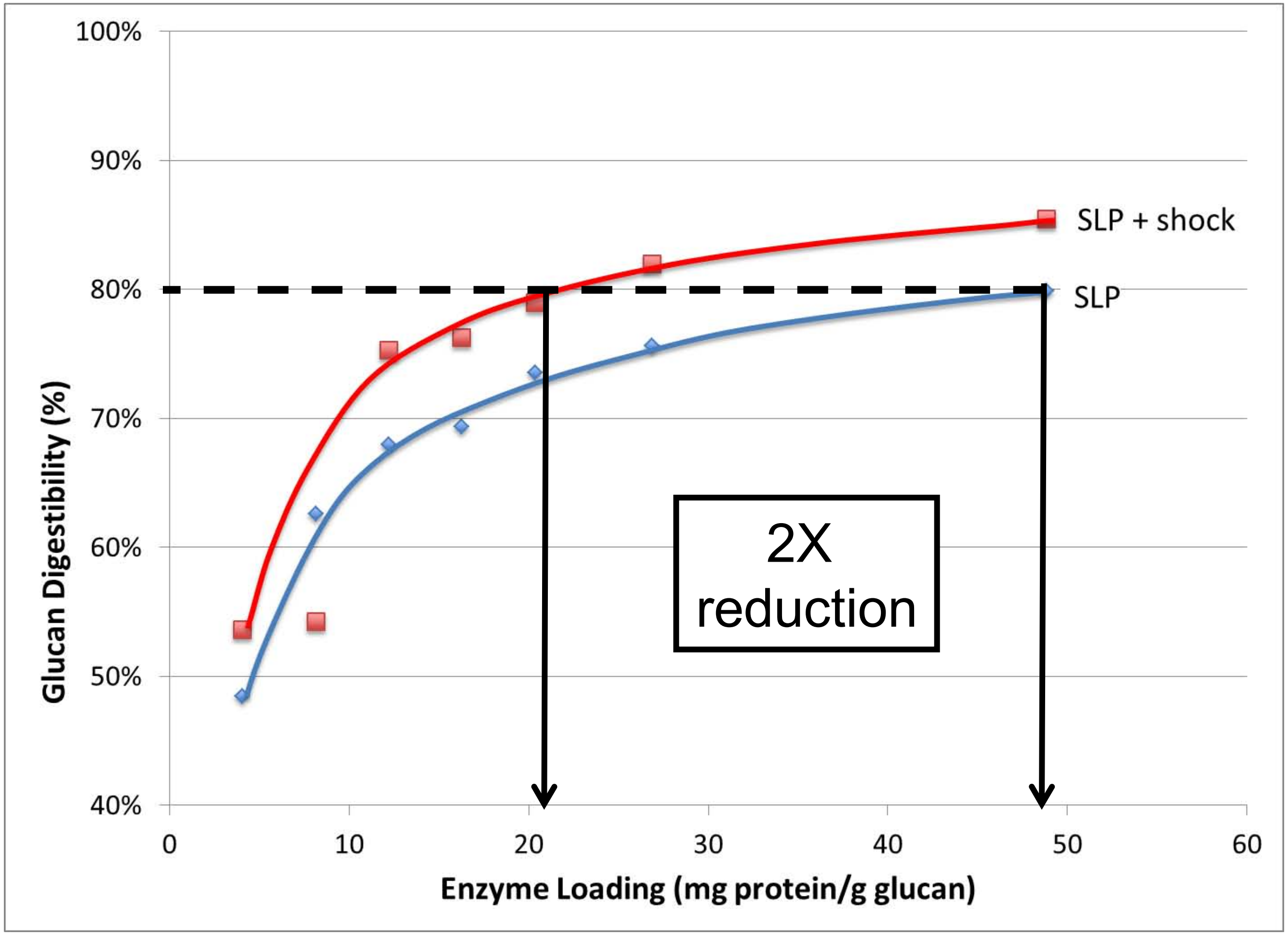


SLP2

Base case

t = 5 days, Solids = 15%

Target conversion



SLP2

Important point

At high conversions (~80%)…

~5% increase in digestibility

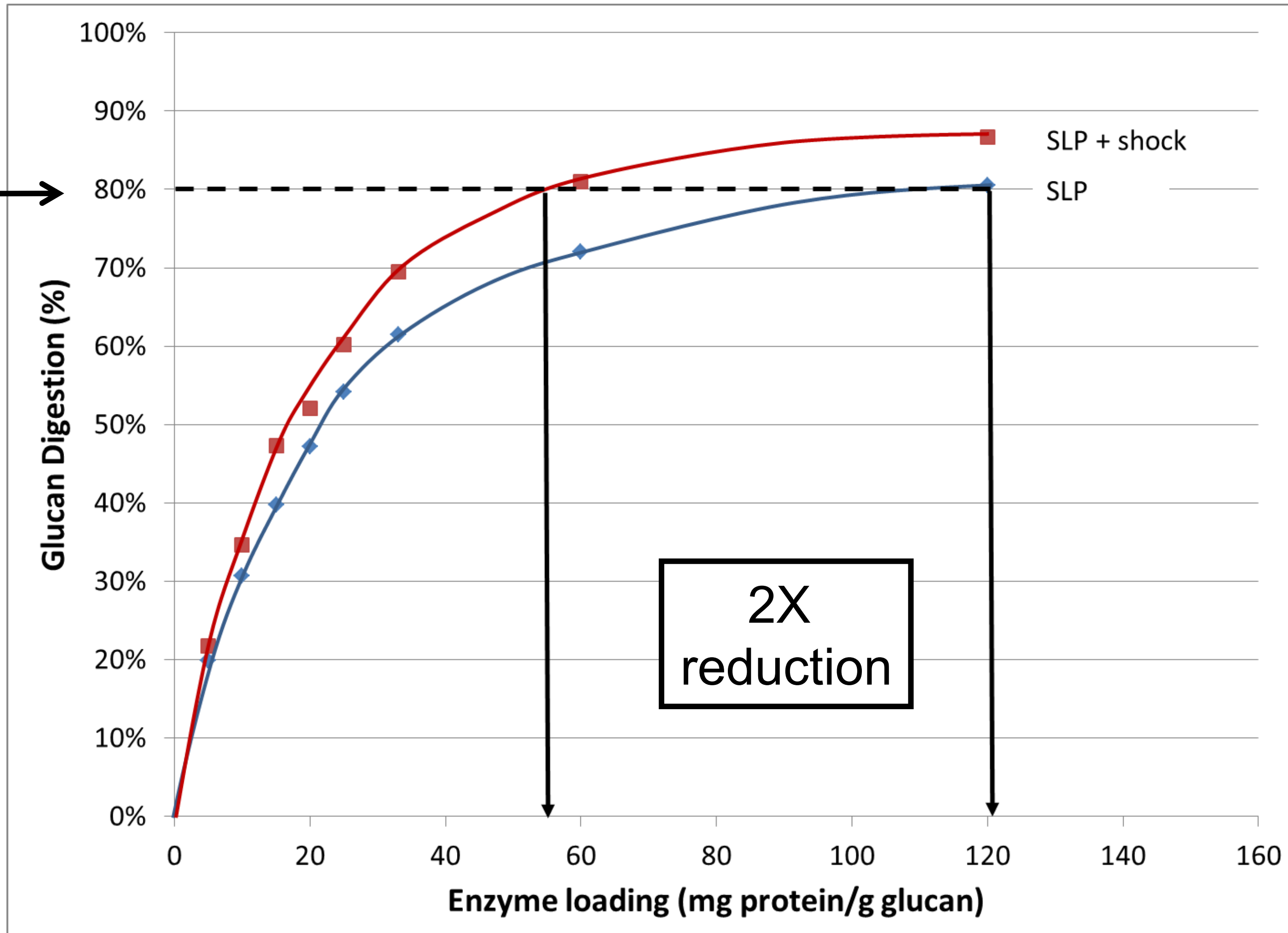
↓

~2X reduction in enzyme

Glucan digestibility

t = 1 day, Solids = 1%

Target conversion →

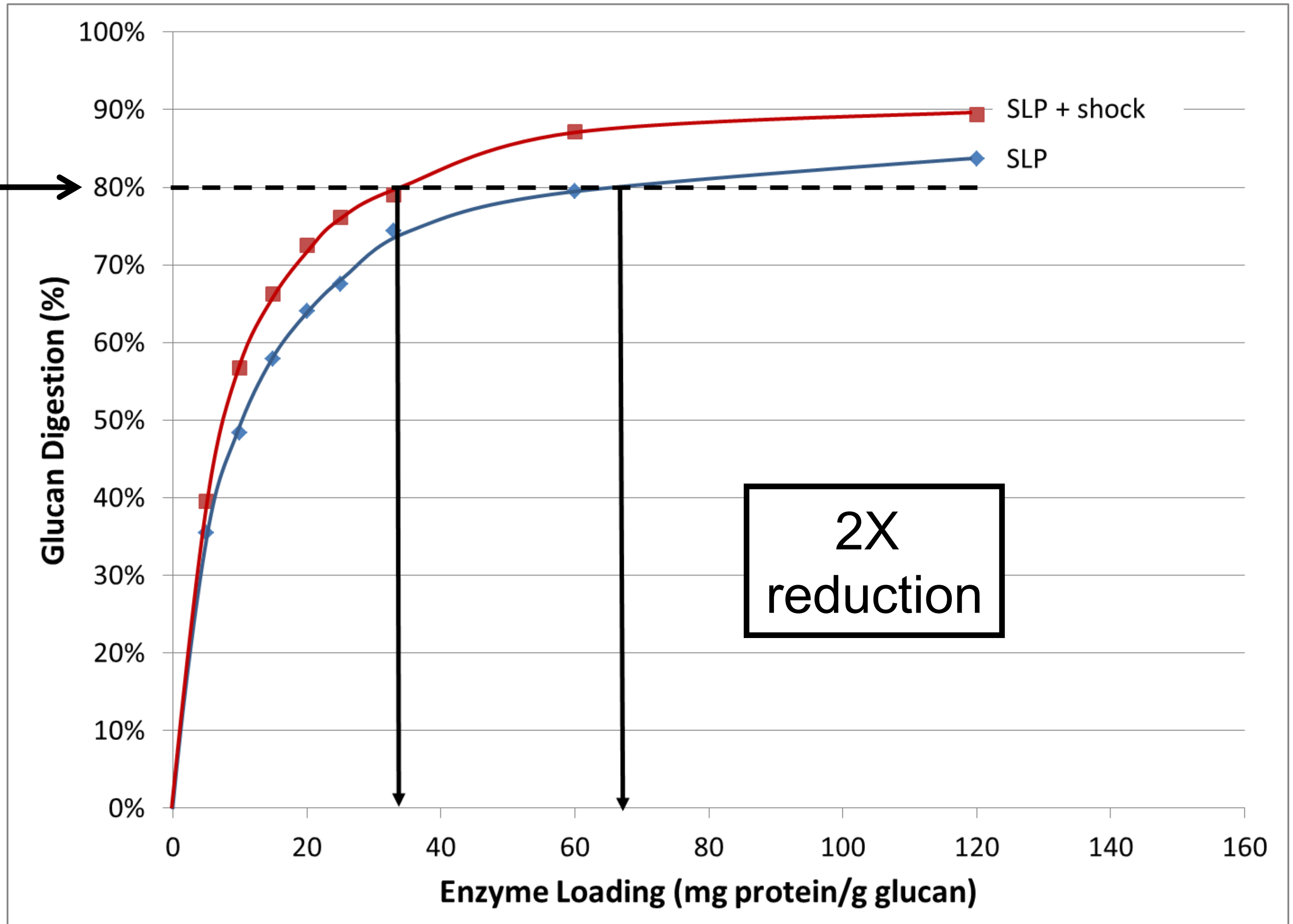


SLP 6

Glucan digestibility

t = 5 days, Solids = 1%

Target conversion

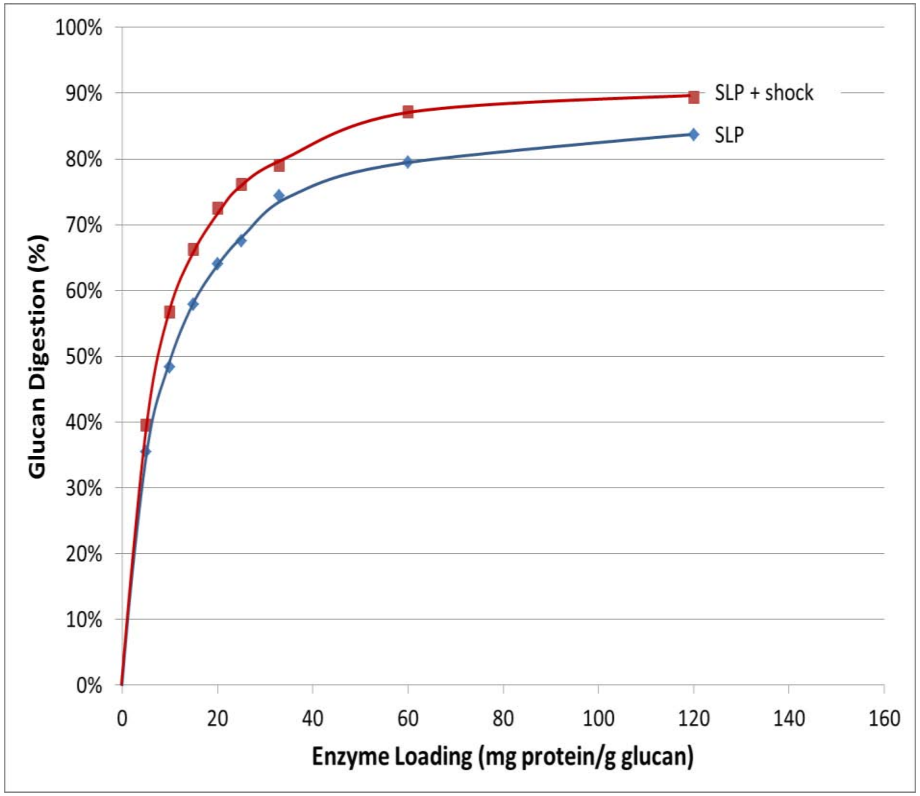


SLP 6

Glucan digestibility

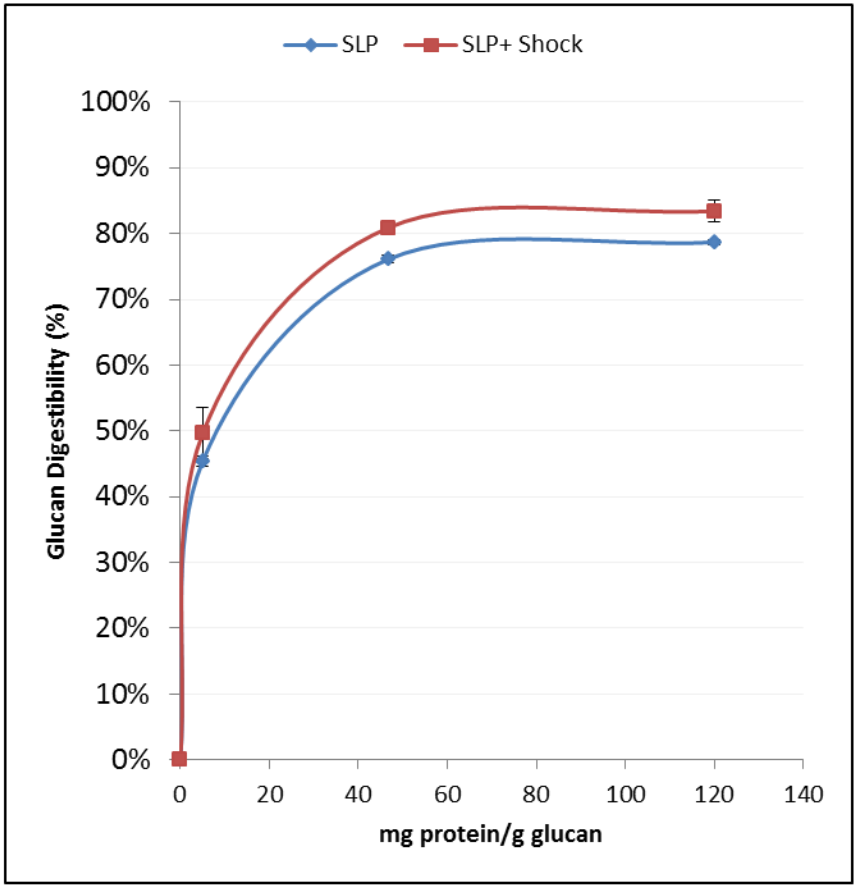
t = 5 days

Solids = 1%



SLP 6

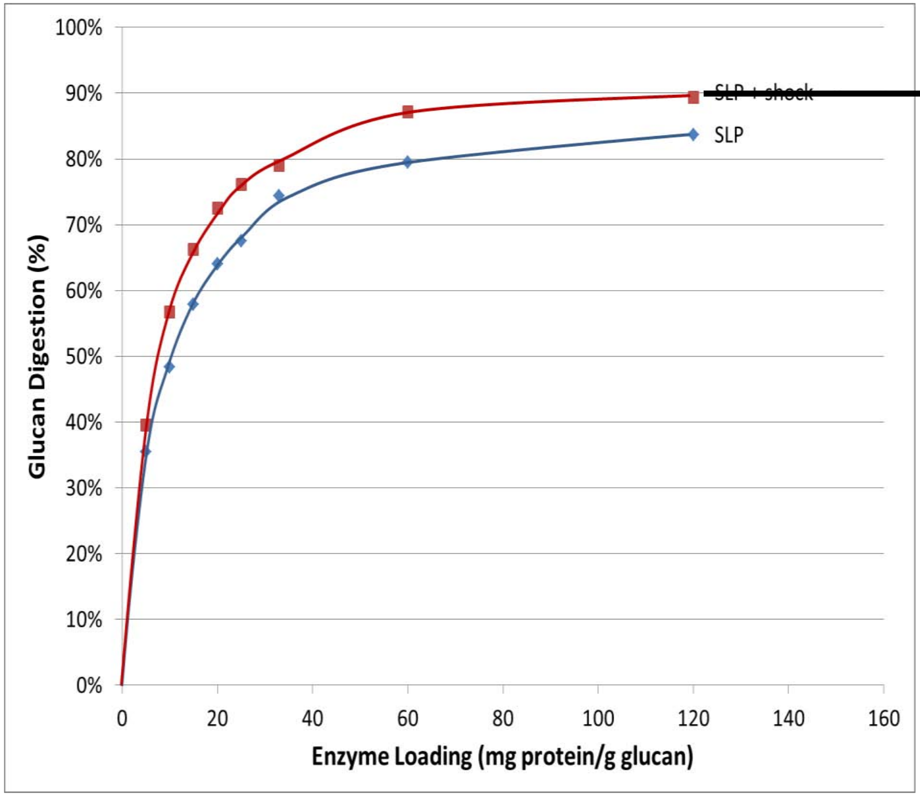
Solids = 15%



Glucan digestibility

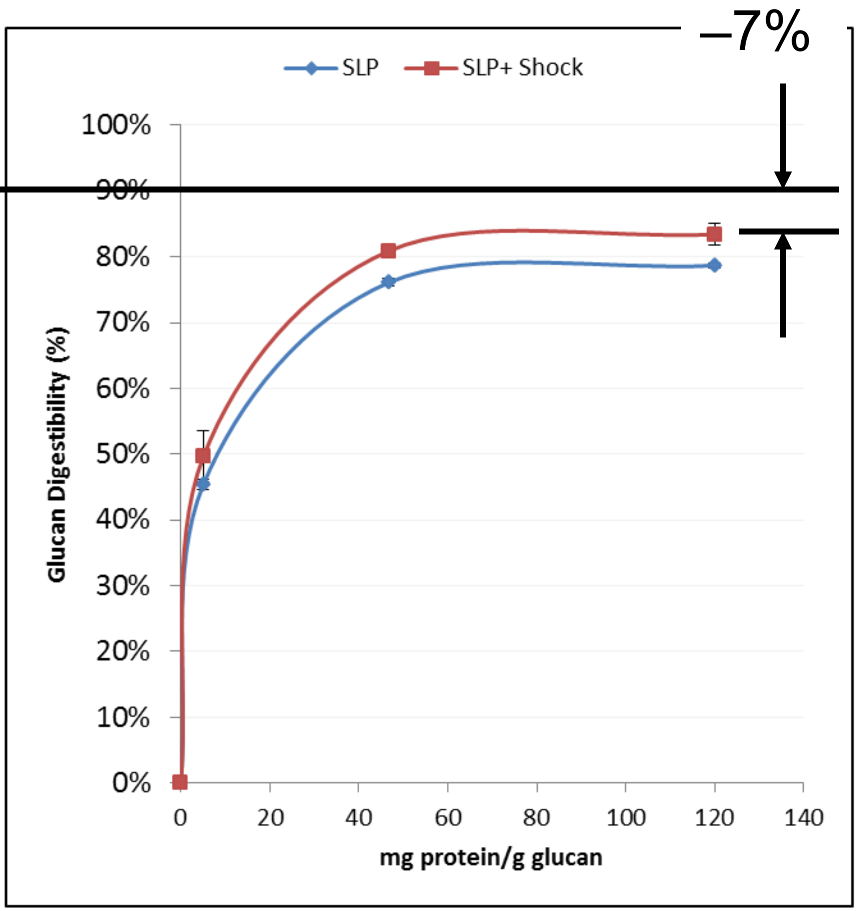
t = 5 days

Solids = 1%



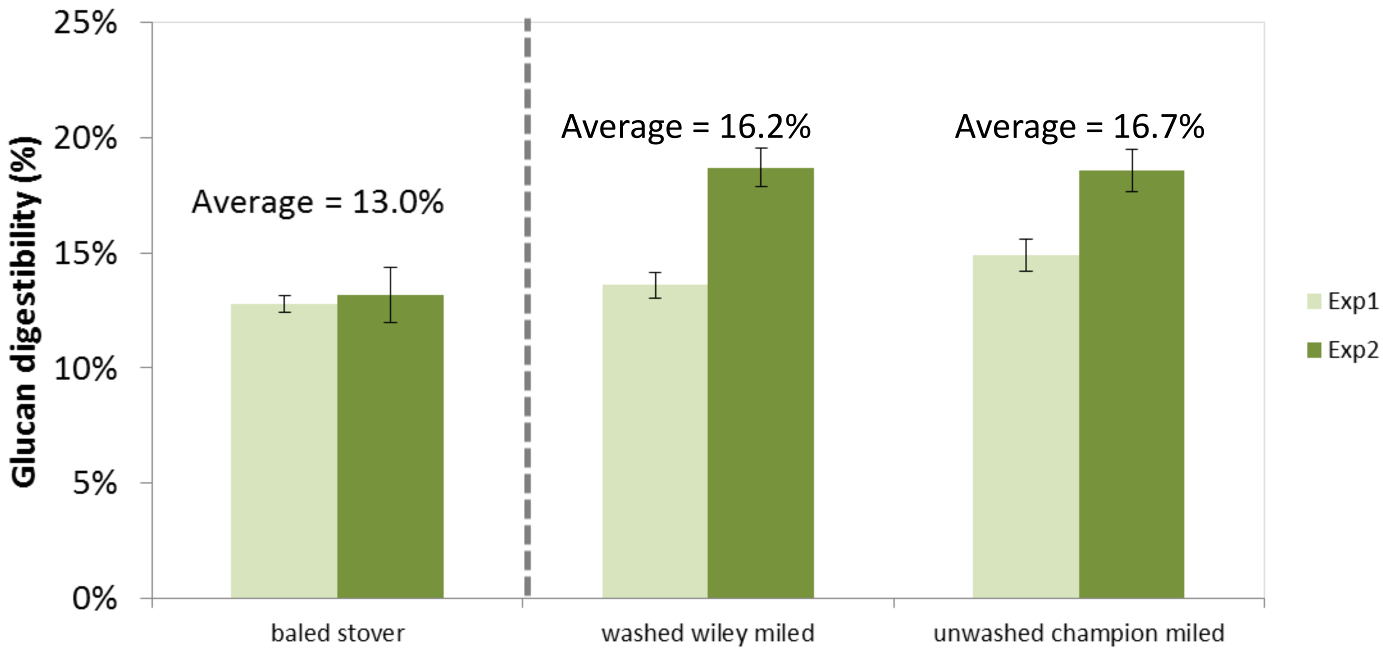
SLP 6

Solids = 15%



Measurement reproducibility Corn stover enzymatic digestibility

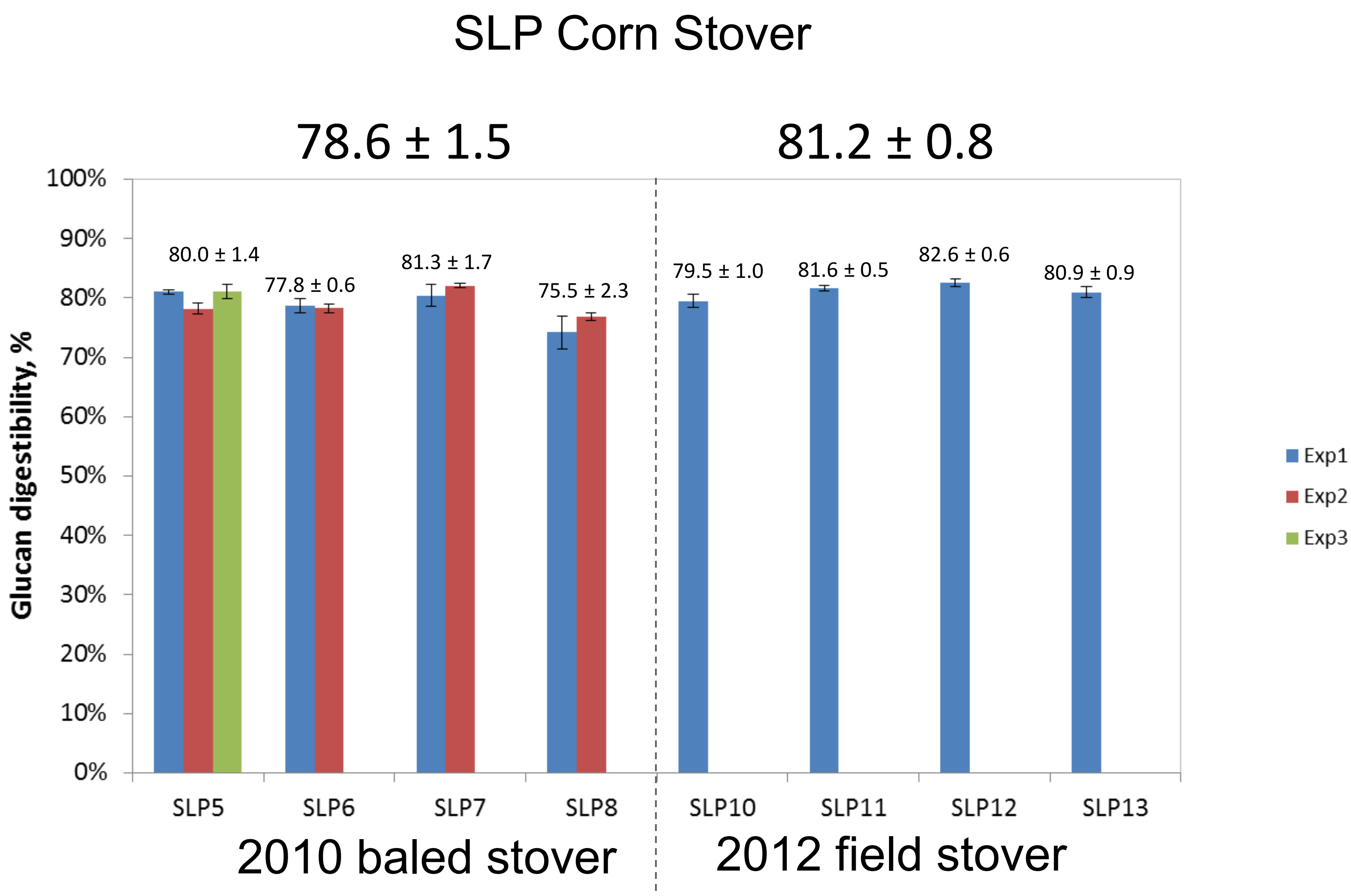
Raw corn stover



2010 baled stover

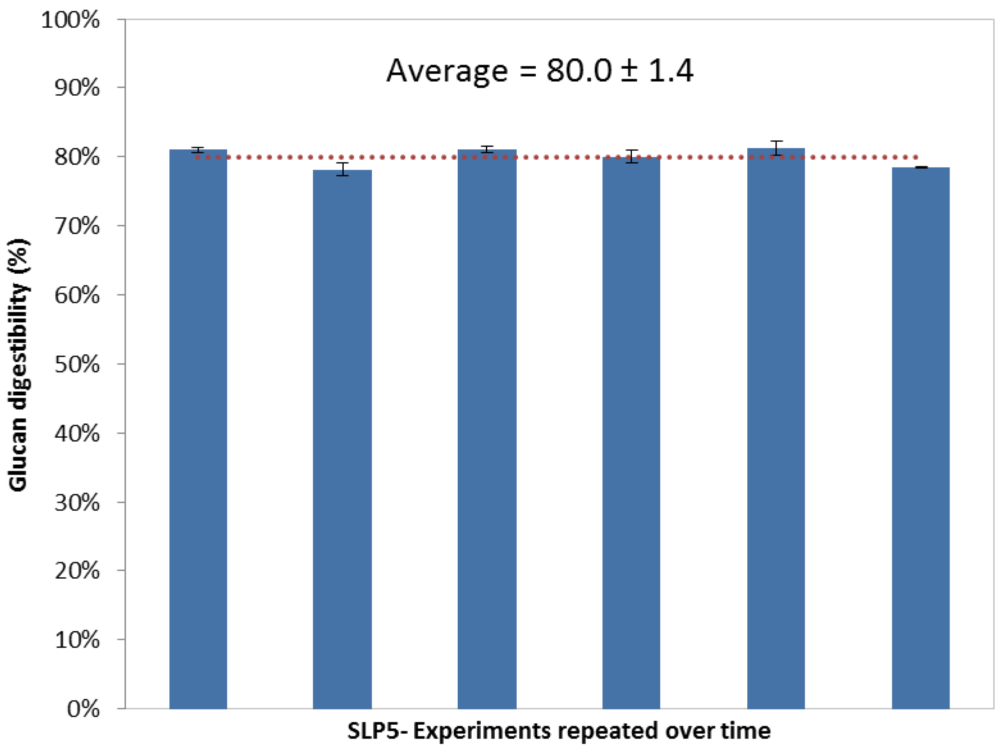
2012 field stover

Measurement reproducibility Corn stover enzymatic digestibility

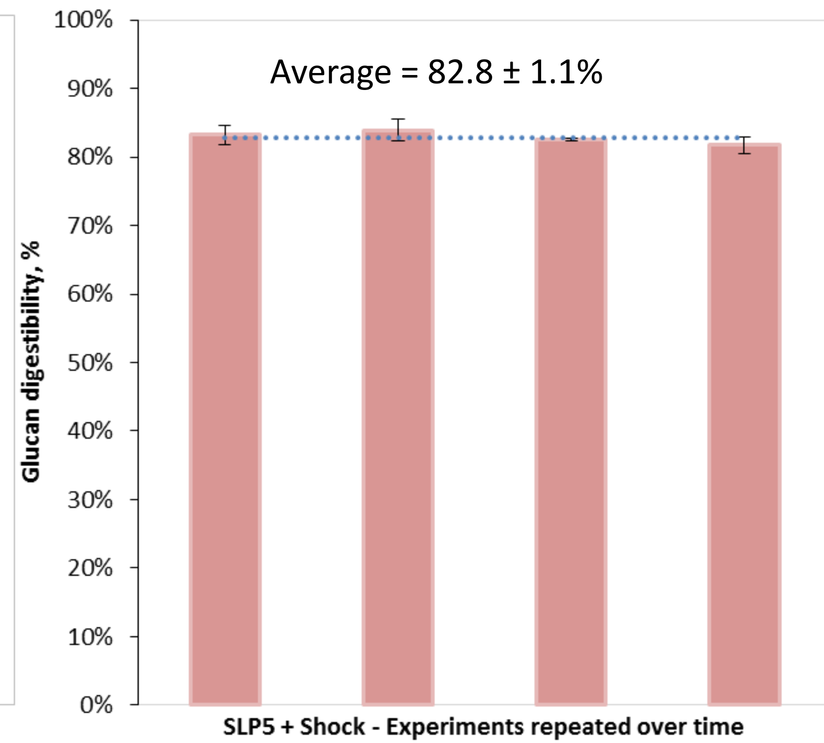


Measurement reproducibility
Corn stover enzymatic digestibility

SLP 5

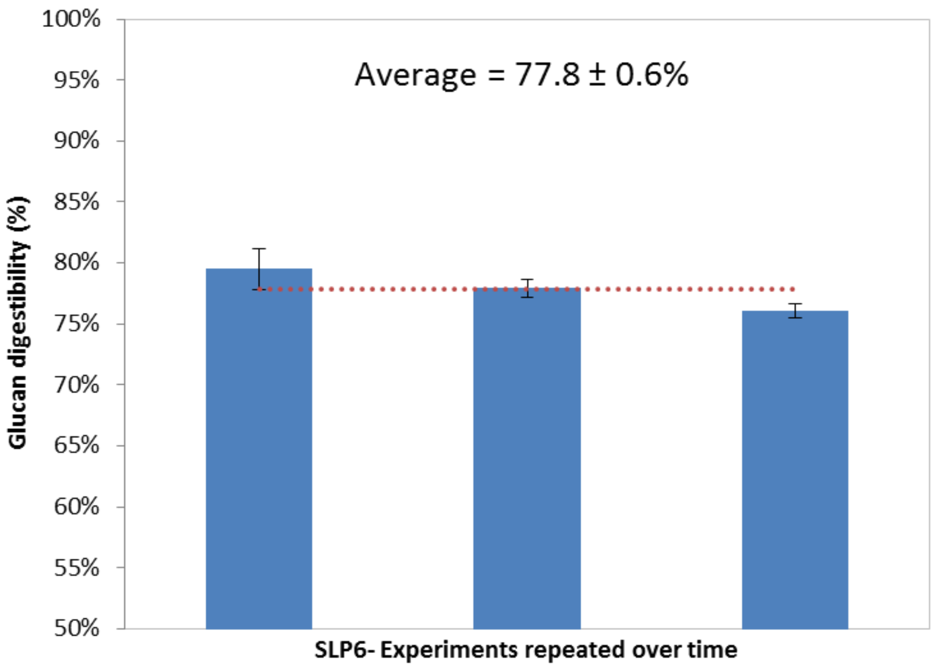


SLP5 + Shock

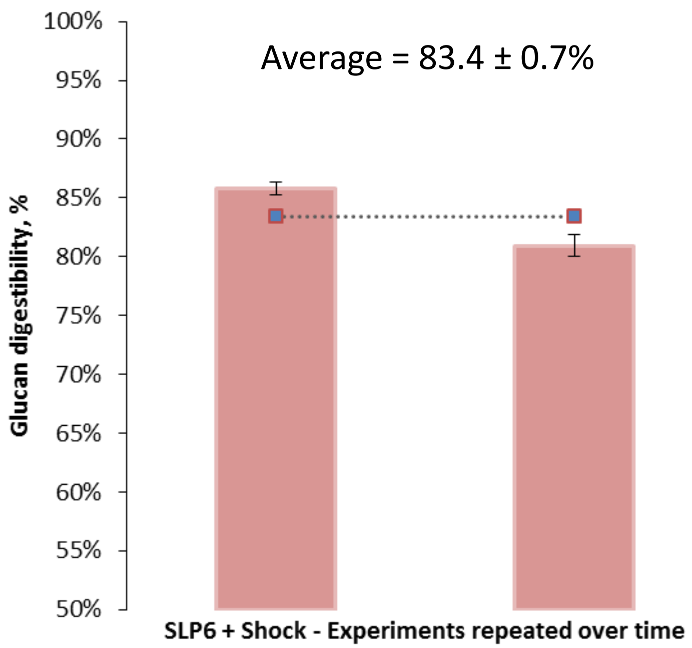


Measurement reproducibility
Corn stover enzymatic digestibility

SLP 6



SLP6 + Shock



Outline

- Background
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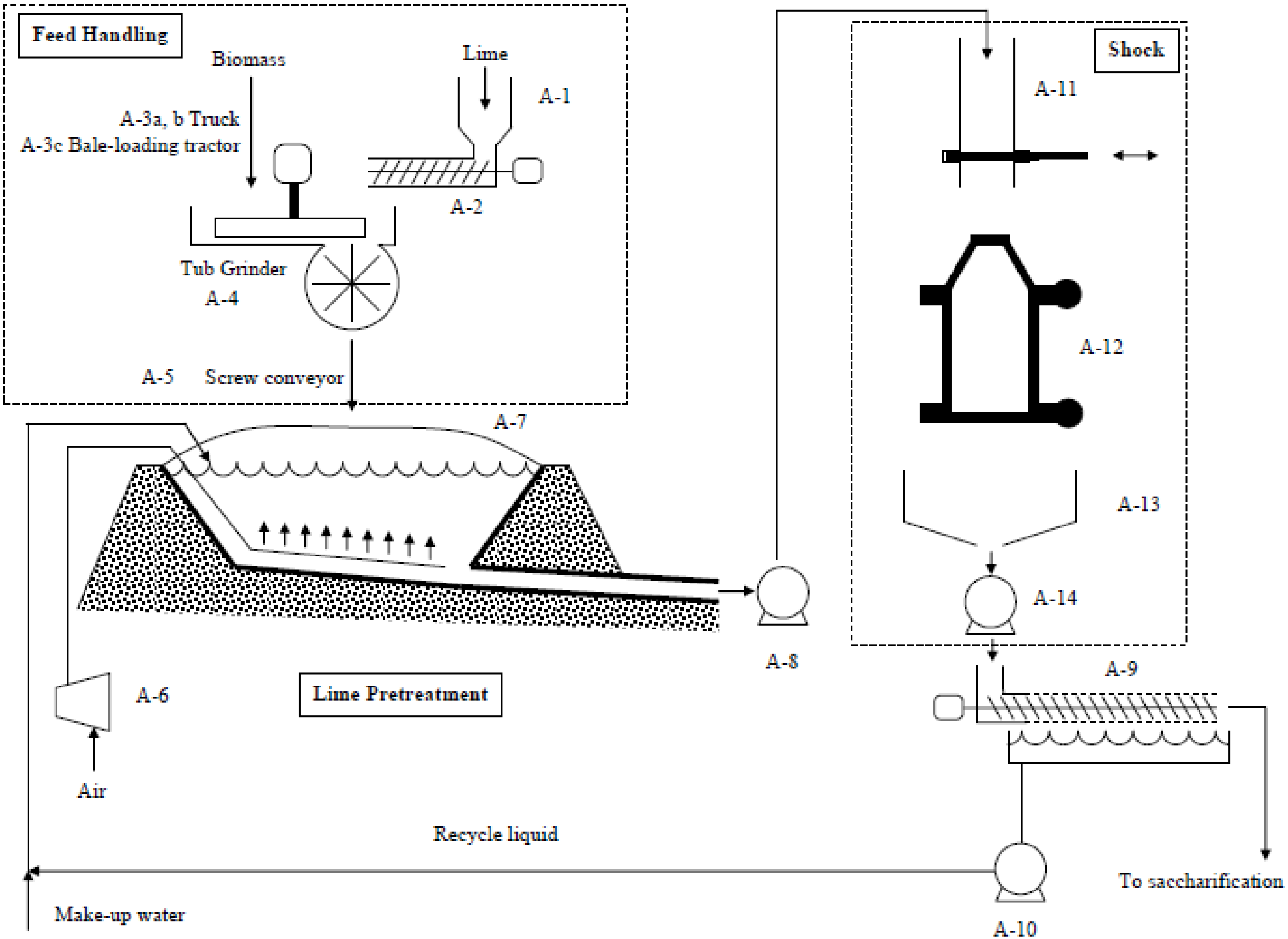
Comparison of pretreatment costs

Capacity = 2000 tonne/day

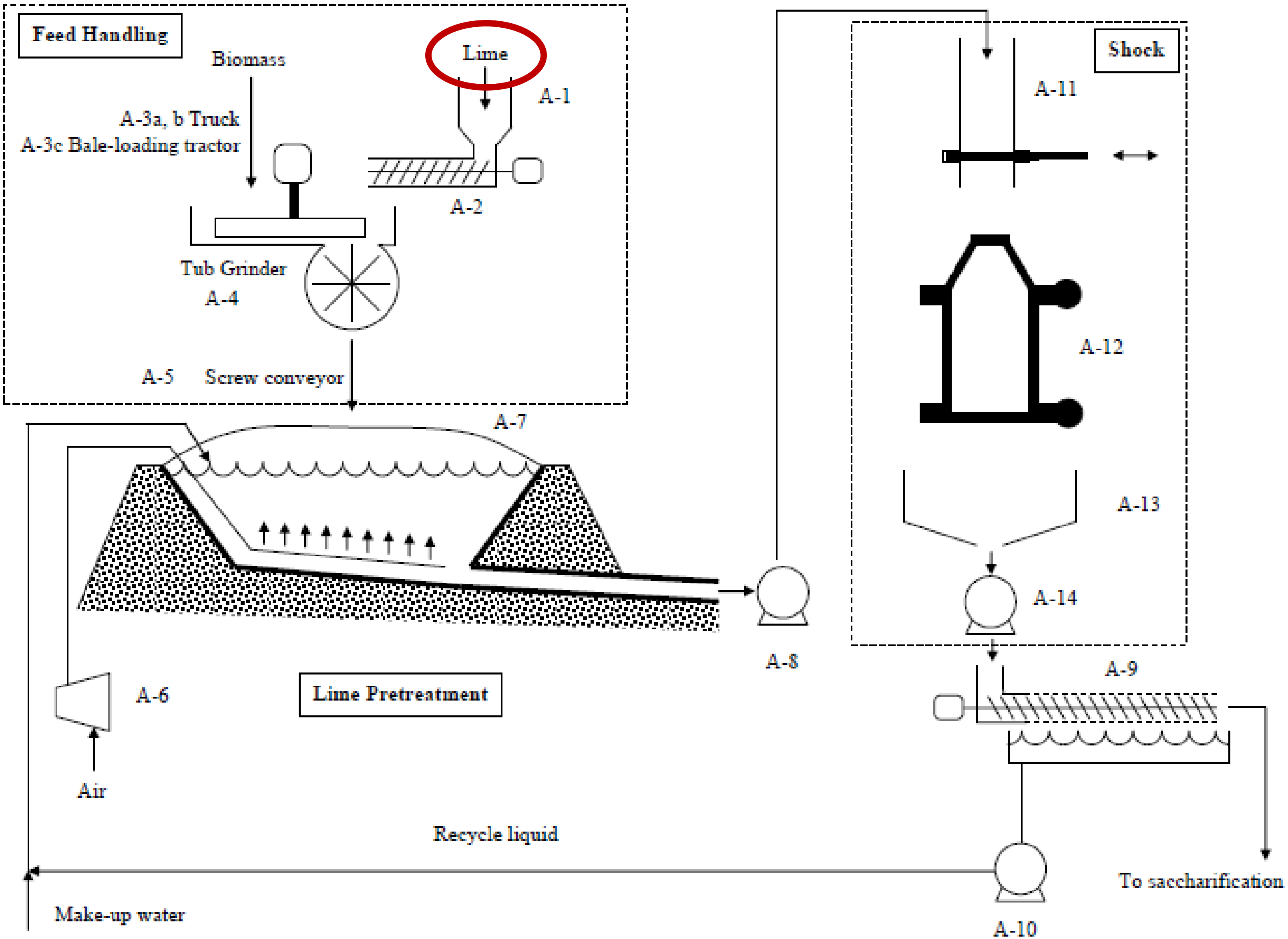
Pretreatment	Pretreatment FCI ($ million)
AFEX*	31
Dilute acid*	45
Short-term, high-temperature lime*	57
Liquid hot water*	20
Soaking in aqueous ammonia*	45
Steam explosion with SO_2*	35
Long-term, low-temperature lime	20
Long-term, low-temperature lime + shock	27

*L. Tao, A. Aden, R.T. Elander, V.R. Pallapolu, Y.Y. Lee, R.J. Garlock, V. Balan, B.E. Dale, Y. Kim, N.S. Mosier, M.R. Ladisch, M. Falls, M.T. Holtzapple, R. Sierra, J. Shi, M.A. Ebrik, T. Redmond, B. Yang, C.E. Wyman, B. Hames, S. Thomas, R.E. Warner, Process and technoeconomic analysis of leading pretreatment technologies for lignocellulosic ethanol production using switchgrass, *Bioresource Technology*,102(24): 11105–11114 (2011).

Process flow diagram



Process flow diagram

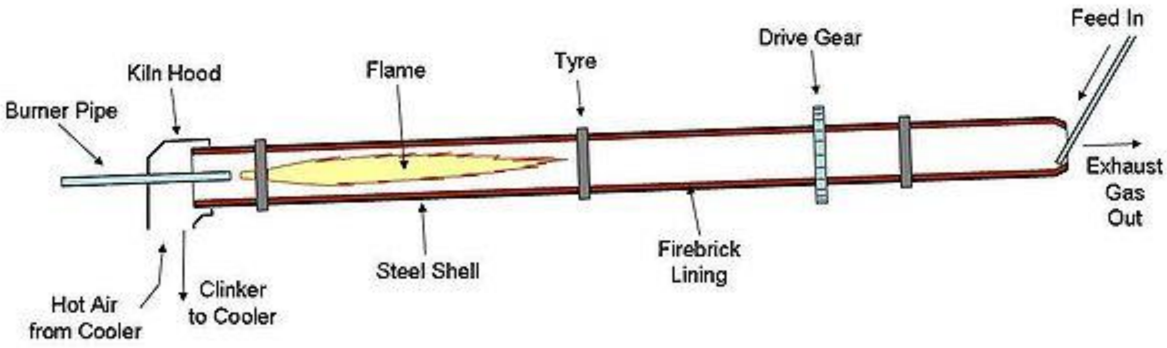


Lime chemistry

$$CaCO_3 \xrightarrow{\text{heat}} CaO \xrightarrow{H_2O} Ca(OH)_2$$

limestone → quicklime → slaked lime

Modern limekiln

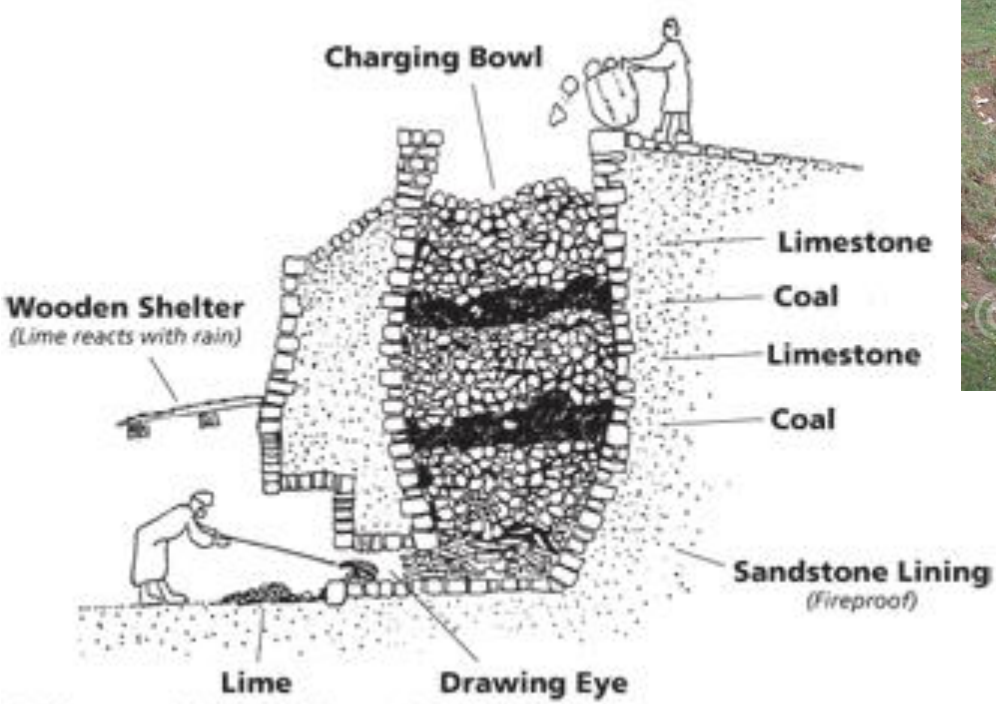


http://en.wikipedia.org/wiki/Cement_kiln

http://www.machineryandequipment.com/featured/kilns.html

http://www.tradebeusa.com/wasteManagement/energyRecovery.aspx

Ancient limekiln

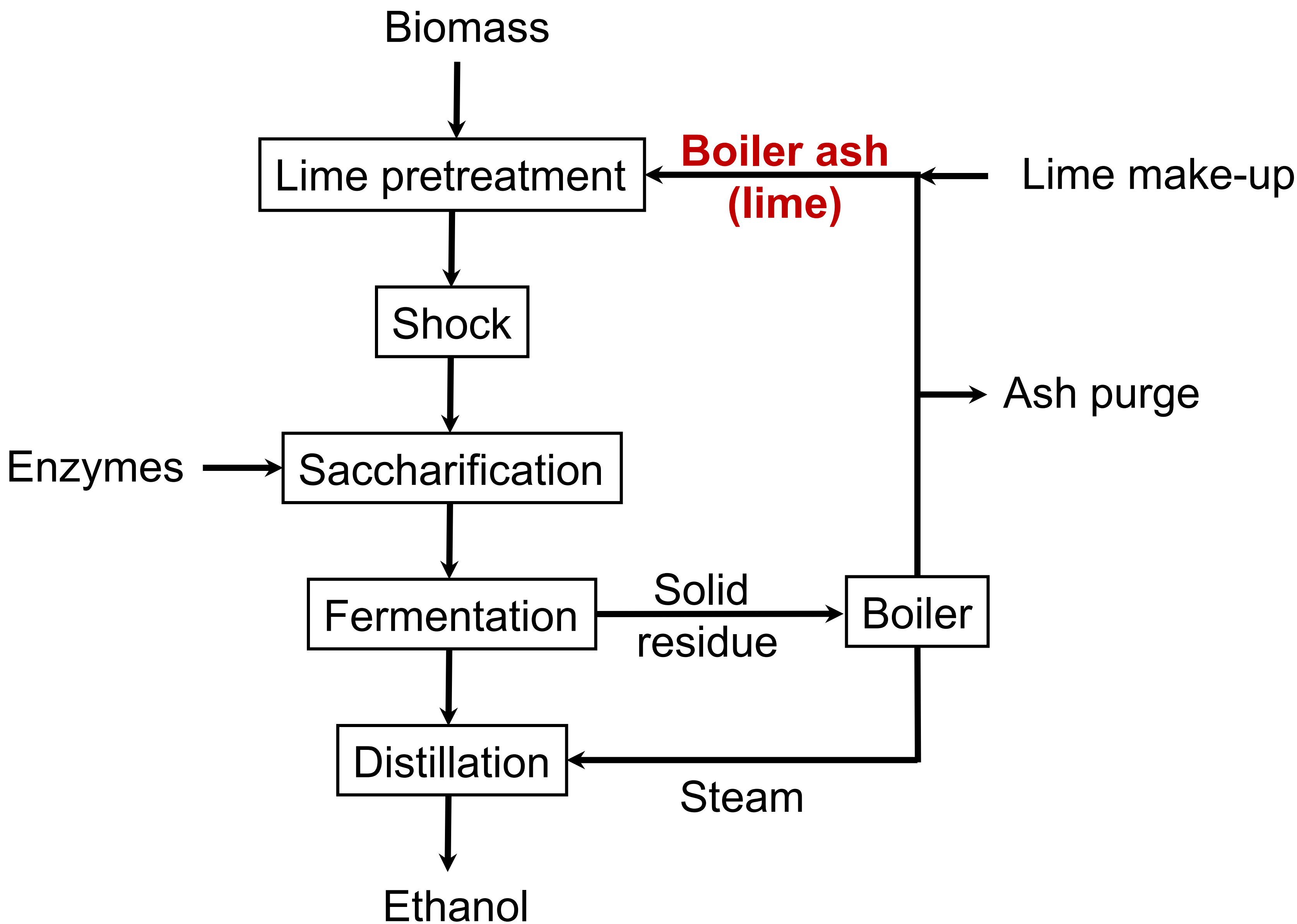


© Courtesy National Stone Centre

http://www.peakdistrictinformation.com/visits/attractions.php?placename=Wirksworth&topX=4294&topY=3550&bottomX=4278&bottomY=3525&map=tile6&dist=0

http://www.bgs.ac.uk/mendips/aggregates/history/limeburning.html

Lime production



SLP cost

	Cost ($/tonne)	Cost ($/year)
Lime make-up[a] ($90/tonne)	1.35	891,000
Electricity ($0.05/kWh)	1.73	1,144,638
Labor[e] ($30/h)	1.80	1,188,000
Depreciation (0.1 X FCI)	3.03	2,000,000
Profit (0.15 X FCI)	4.55	3,000,000
Maintenance (0.04 X FCI)	1.21	800,000
Property tax (0.03 X FCI)	0.91	600,000
Insurance (0.01 X FCI)	0.30	200,000
Total	14.88	9,823,638

a. Lime loading = 0.15 tonne $Ca(OH)_2$/biomass
   Lime make-up = 0.015 tonne $Ca(OH)_2$/biomass
b. Operation = 330 days/year
c. Capacity = 2000 tonne/day
d. FCI = $20 million
e. Five workers

SLP cost

	Cost ($/tonne)	Cost ($/year)
Lime make-up[a] ($90/tonne)	1.35	891,000
Electricity ($0.05/kWh)	1.73	1,144,638
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Depreciation (0.1 X FCI)	3.03	2,000,000
Profit (0.15 X FCI)	4.55	3,000,000
Maintenance (0.04 X FCI)	1.21	800,000
Property tax (0.03 X FCI)	0.91	600,000
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Total	14.88	9,823,638

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Lime make-up = 0.015 tonne $Ca(OH)_2$/biomass
b. Operation = 330 days/year
c. Capacity = 2000 tonne/day
d. FCI = $20 million
e. Five workers

Low

Steam explosion w/ SO_2
$43.94/tonne

Process and technoeconomic analysis of leading pretreatment technologies for lignocellulosic ethanol production using switchgrass, *Bioresource Technology*, Volume 102, Issue 24, December 2011, Pages 11105–11114.

SLP cost

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Total	14.88	9,823,638

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Lime make-up = 0.015 tonne $Ca(OH)_2$/biomass
b. Operation = 330 days/year
c. Capacity = 2000 tonne/day
d. FCI = $20 million
e. Five workers

High

Soaking in Aqueous NH_3
$45.91/tonne

Process and technoeconomic analysis of leading pretreatment technologies for lignocellulosic ethanol production using switchgrass, *Bioresource Technology*, Volume 102, Issue 24, December 2011, Pages 11105–11114.

Shock cost

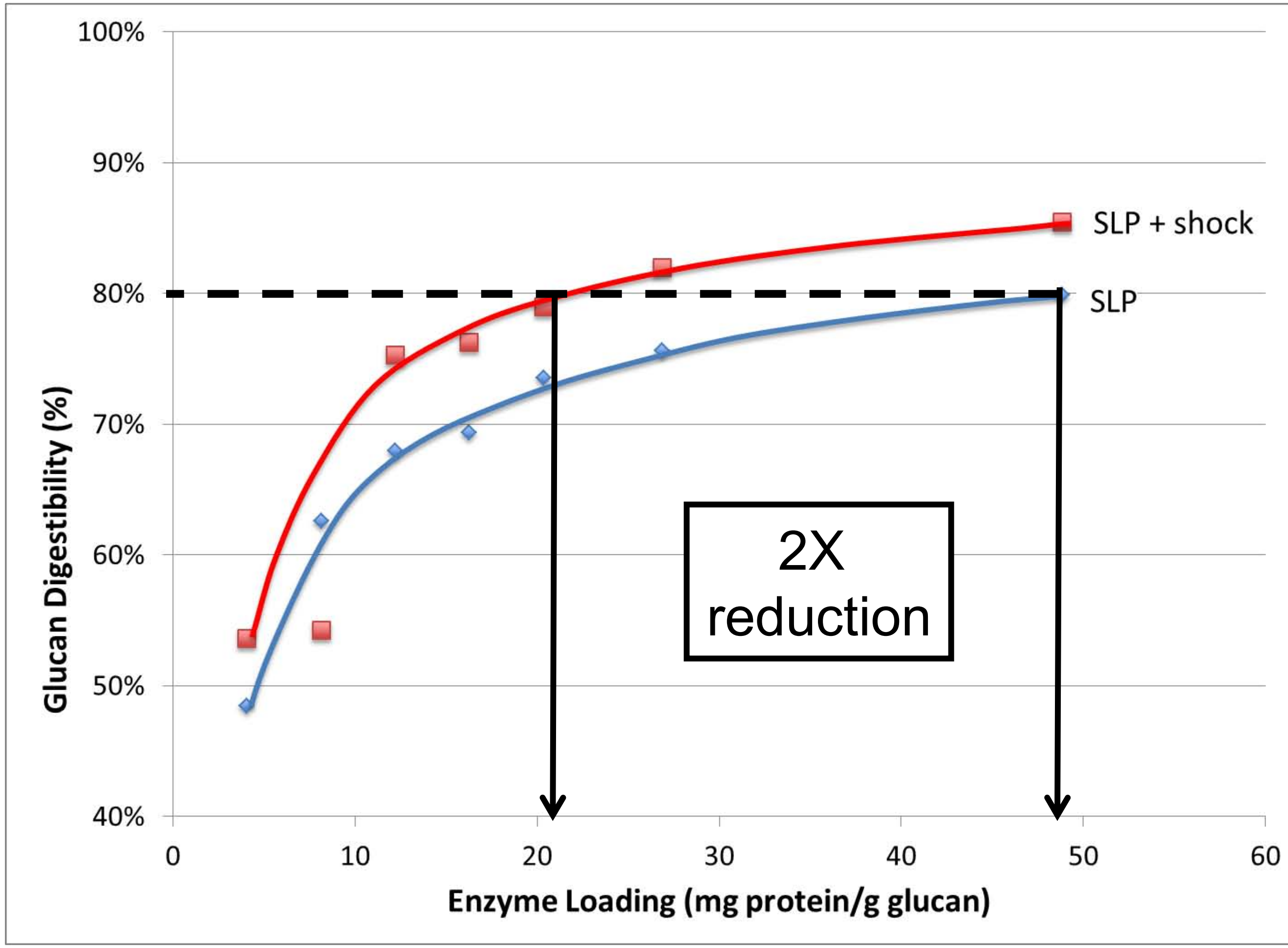
	Cost ($/tonne)	Cost ($/year)
Electricity ($0.05/kWh)	0.04	26,400
Methane[e]	1.00	660,000
Labor[d] ($30/h)	0.36	237,600
Depreciation (0.1 X FCI)	1.06	700,000
Profit (0.15 X FCI)	1.59	1,050,000
Maintenance (0.04 X FCI)	0.42	280,000
Property tax (0.03 X FCI)	0.32	210,000
Insurance (0.01 X FCI)	0.11	70,000
Total	4.90	3,234,000

a. Operation = 330 days/year
b. Capacity = 2000 tonne/day
c. FCI = $7 million
d. One worker
e. Estimate

Base case

t = 5 days, Solids = 15%

Target conversion



$3.75/gal EtOH

$4.19/gal EtOH

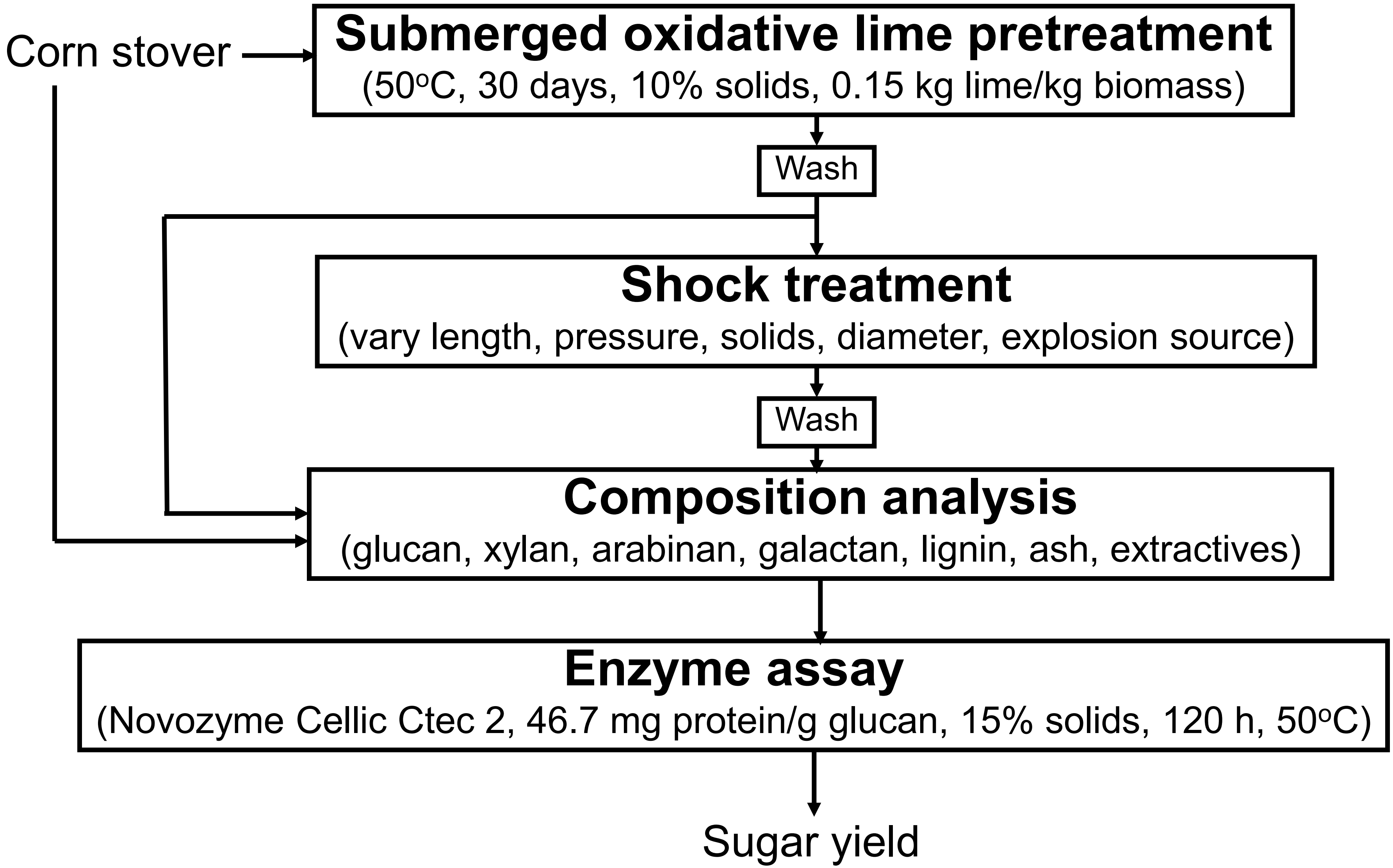
Savings = $0.44/gal EtOH

SLP2

Outline

- Background
- Methods
- Economics
- Sugar platform
- Carboxylate platform
- Project management
- Conclusions

1 - Approach



Corn stover
Submerged oxidative lime pretreatment
(50°C, 30 days, 10% solids, 0.15 kg lime/kg biomass)
Wash
Shock treatment
(vary length, pressure, solids, diameter, explosion source)
Wash
Composition analysis
(glucan, xylan, arabinan, galactan, lignin, ash, extractives)
Enzyme assay
(Novozyme Cellic Ctec 2, 46.7 mg protein/g glucan, 15% solids, 120 h, 50°C)
Sugar yield

2 - Technical Accomplishments/ Progress/Results

Base Case

Explosion = Shot gun shell

Vessel length = 12 in (cylindrical portion)

Solids concentration = 5%

Shock pressure = ~300 psig

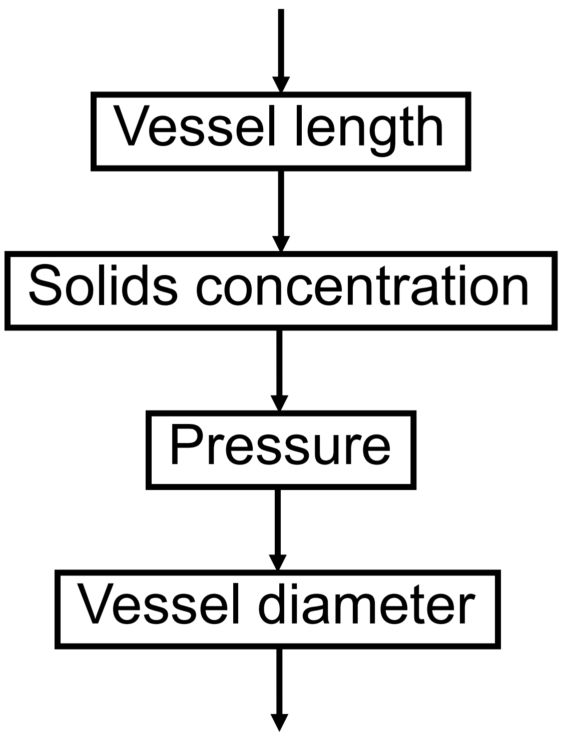
Vessel diameter = 4 in

Research question

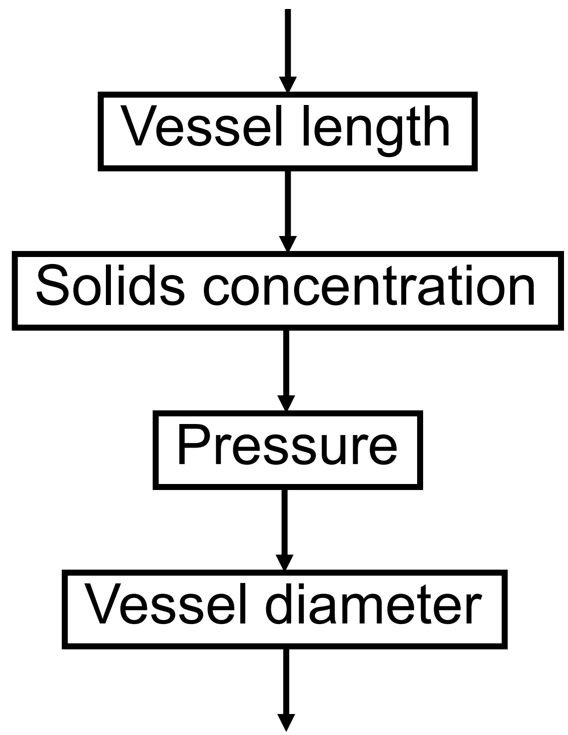
Can we scale up and maintain shock effect?

2 - Technical Accomplishments/ Progress/Results

Shot gun shell

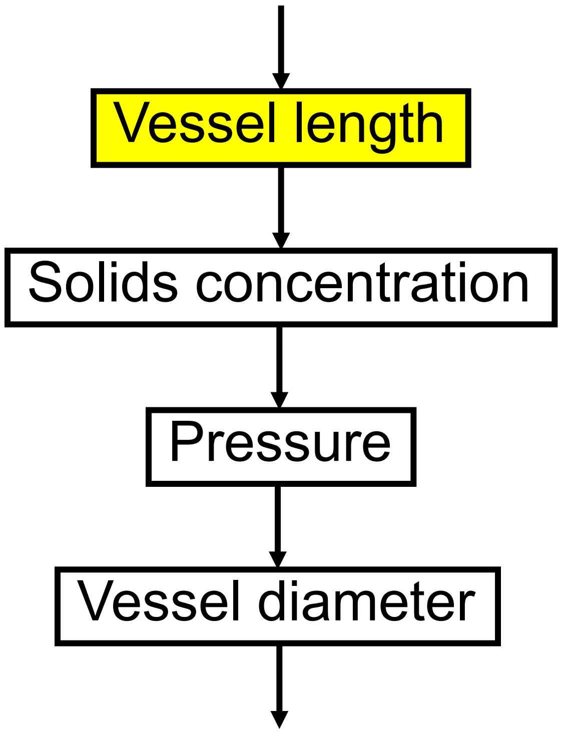


CH_4/air

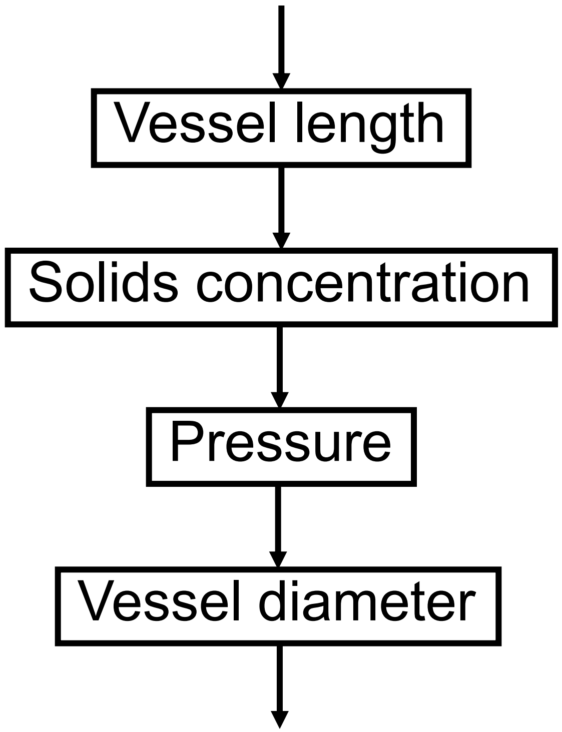


2 - Technical Accomplishments/ Progress/Results

Shot gun shell



CH_4/air



2 – Effect of vessel length

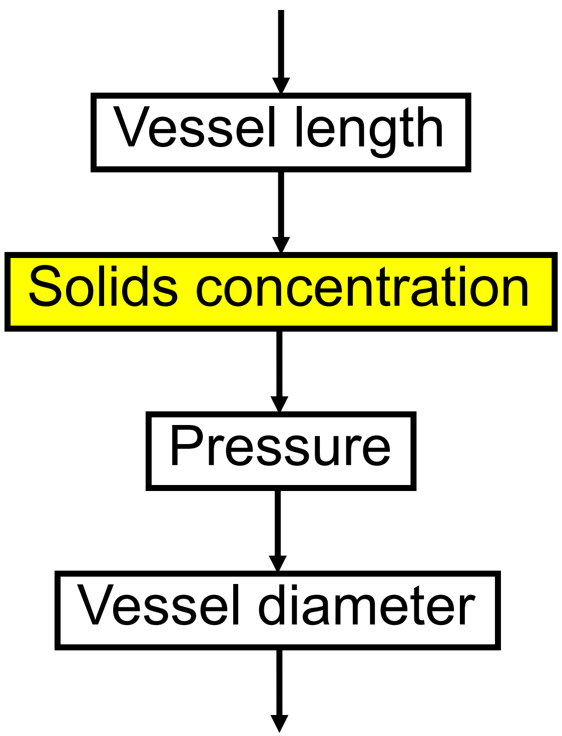
	Sample	Length (ft)	Pressure (psi)	Biomass Loading	Enzyme loading[a]	% Hydrolysis		
						Glucan	Xylan	Overall
*	SLP5+ST38	1	462 ± 13	5%	46.7	82.5 ± 0.2	74.1 ± 0.6	80.0 ± 0.3
	SLP5+ST42	3	462 ± 18	5%	46.7	82.5 ± 0.4	72.1 ± 1.1	79.3 ± 0.6

* Base case

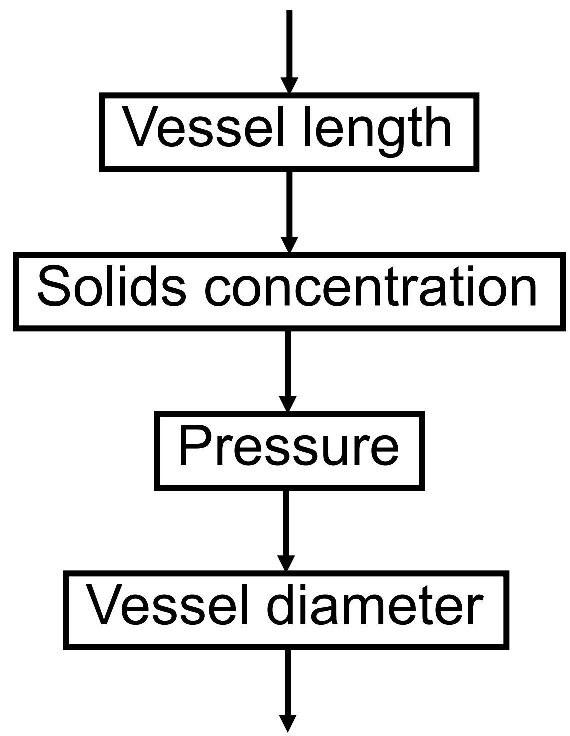
[a] mg protein (CTec2)/g glucan

2 - Technical Accomplishments/ Progress/Results

Shot gun shell



CH_4/air



2 – Effect of solids concentration

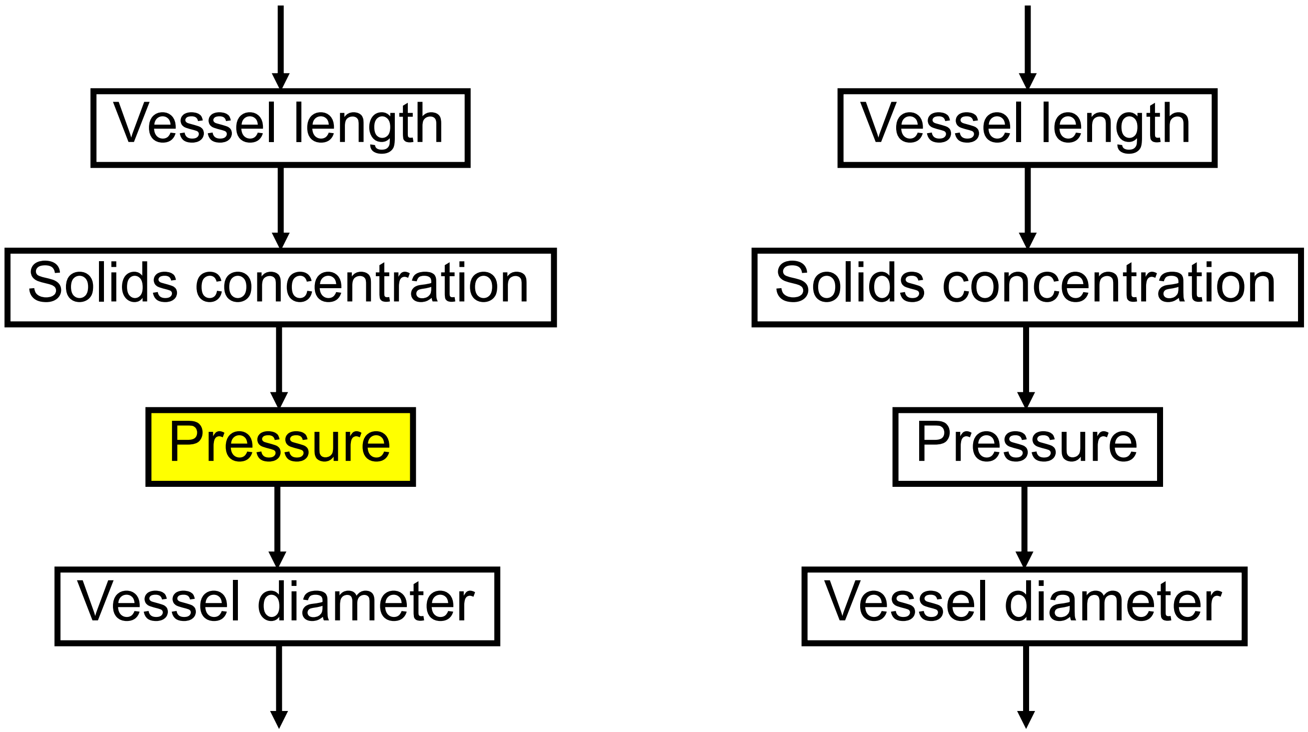
	Biomass	Enzyme loading[a]	Glucan	Xylan	Overall
*	SLP2+ST18 (5% Biomass)	48.4	92.0 ± 0.004	92.5 ± 0.002	92.1 ± 0.003
	SLP2+ST19 (10% Biomass)	48.4	91.4 ± 0.003	91.2 ± 0.01	91.3 ± 0.01

* Base case

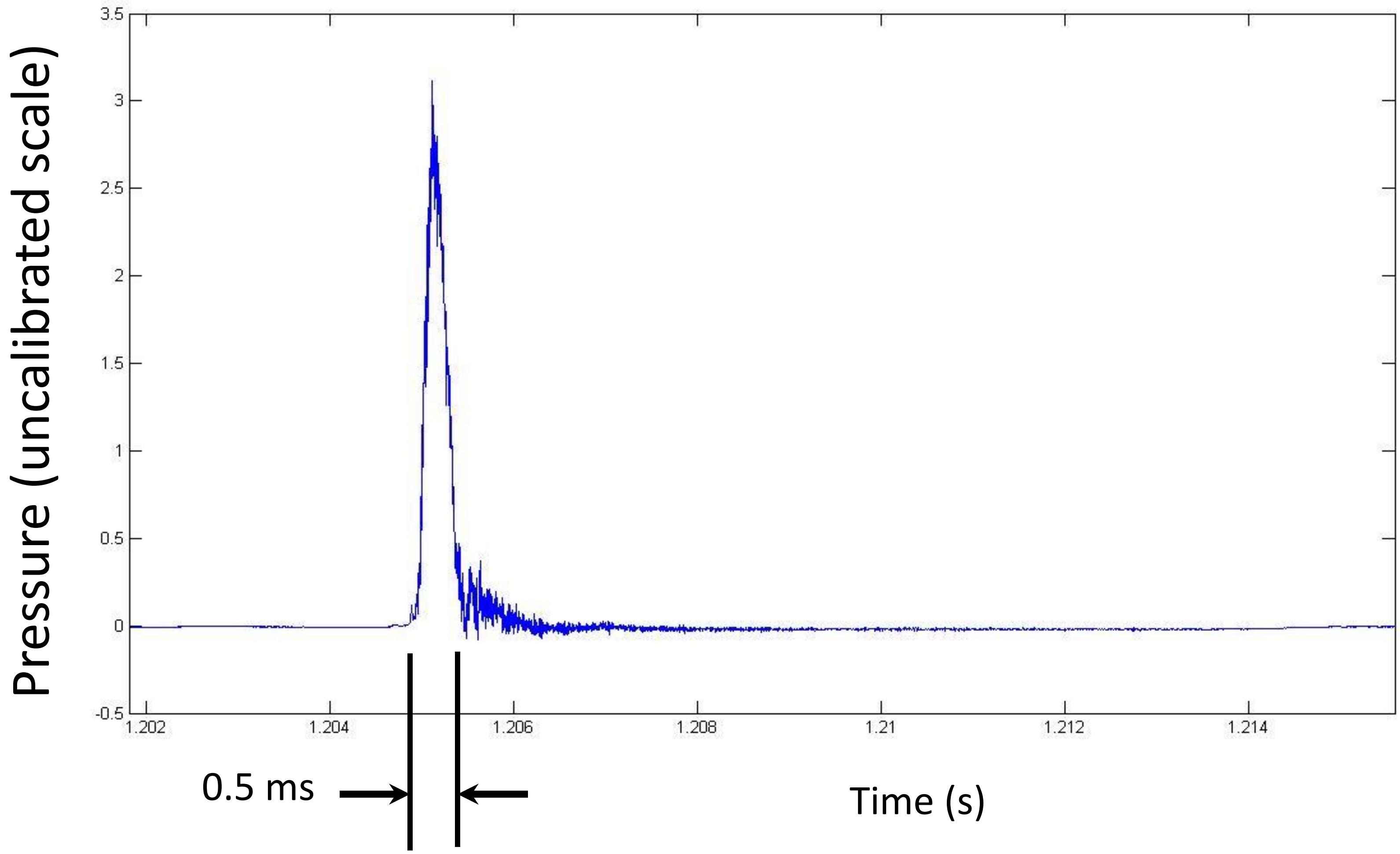
[a]mg protein (CTec2)/g glucan

2 - Technical Accomplishments/ Progress/Results

Shot gun shell **CH_4/air**



Pressure Trace



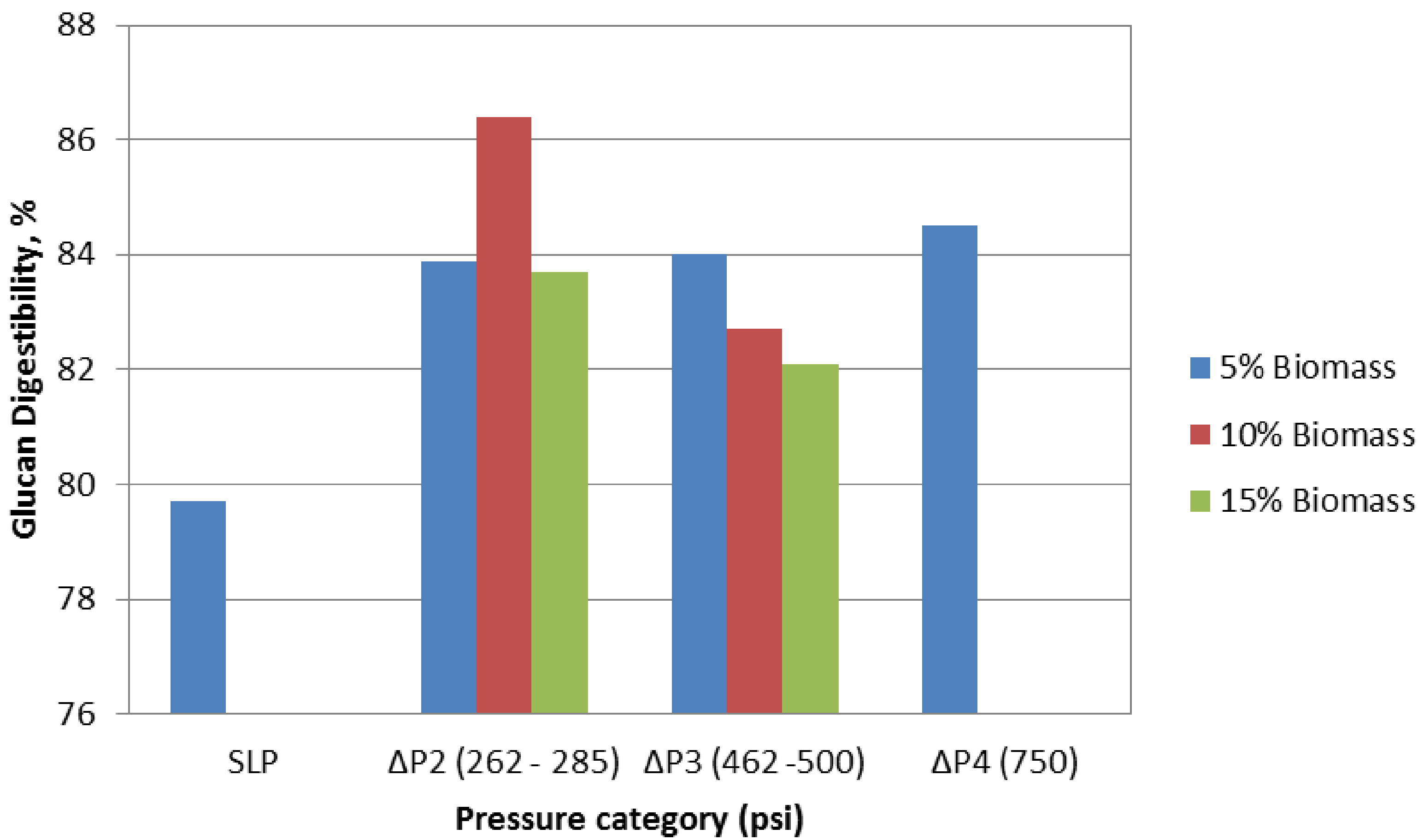
2 – Effect of shock pressure

	Sample	Pressure (psig)	Biomass Loading	Enzyme loading[a]	Glucan	Xylan	Overall
*	SLP5+ST33	262 ± 41	5%	46.7	83.2 ± 1.3	74.9 ± 1.0	80.7 ± 1.2
*	SLP5+ST36	285 ± 13	5%	46.7	82.5 ± 0.2	74.5 ± 0.6	80.1 ± 0.3
	SLP5+ST39	462 ± 18	5%	46.7	82.2 ± 1.9	72.3 ± 1.3	79.2 ± 1.7
*	SLP6+ST43	275 ± 15	5%	46.7	85.8 ± 0.6	80.7 ± 0.1	84.3 ± 0.4
	SLP6+ST47	750 ± 250	5%	46.7	84.5 ± 0.2	78.9 ± 1.0	82.8 ± 0.4

* Base case

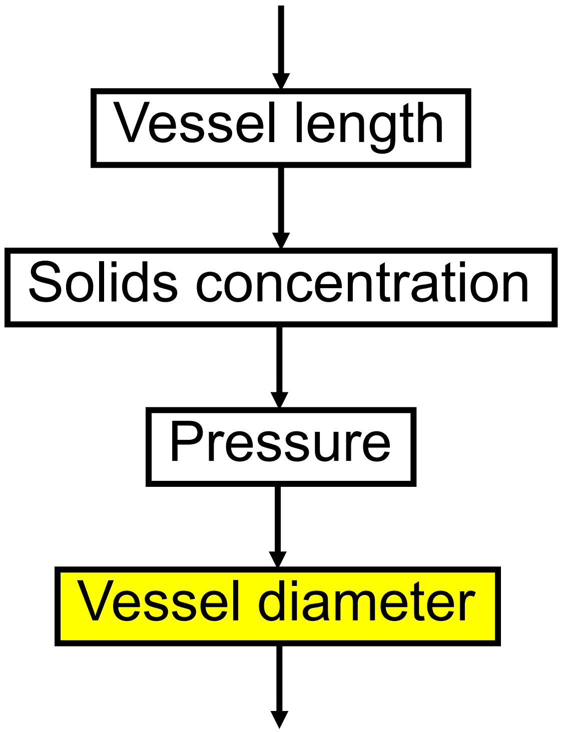
[a] mg protein (CTec2)/g glucan

2 – Effect of shock pressure & concentration

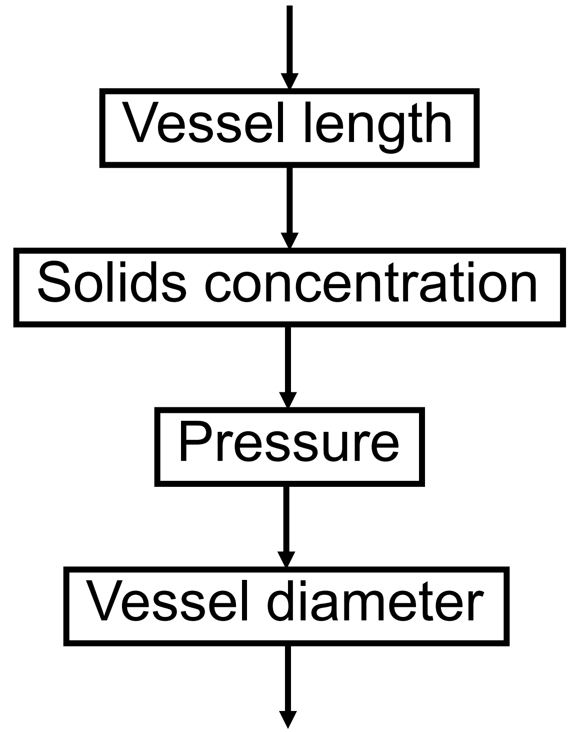


2 - Technical Accomplishments/ Progress/Results

Shot gun shell



CH_4/air



2 – Effect of vessel diameter

In progress

Outline

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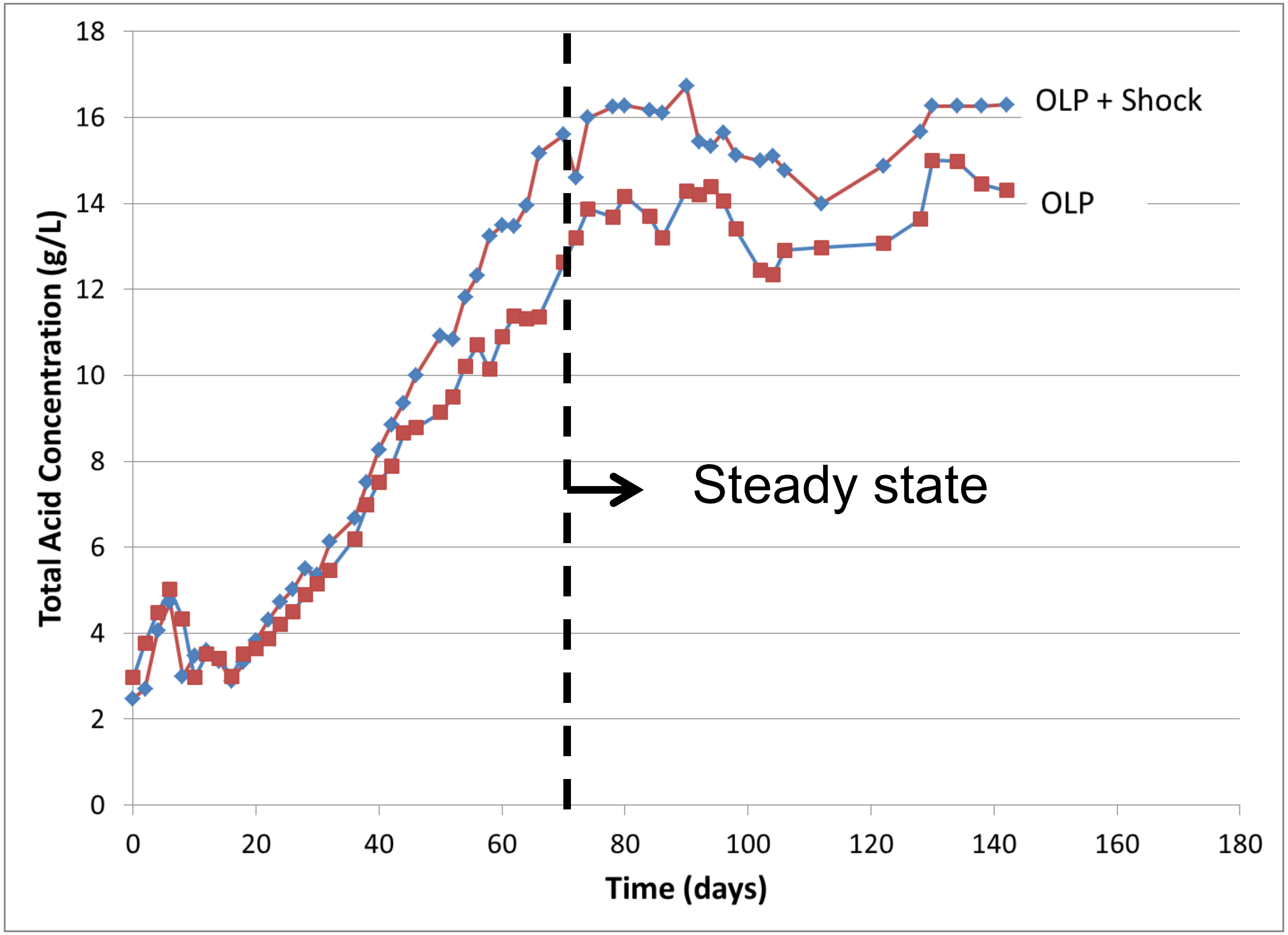
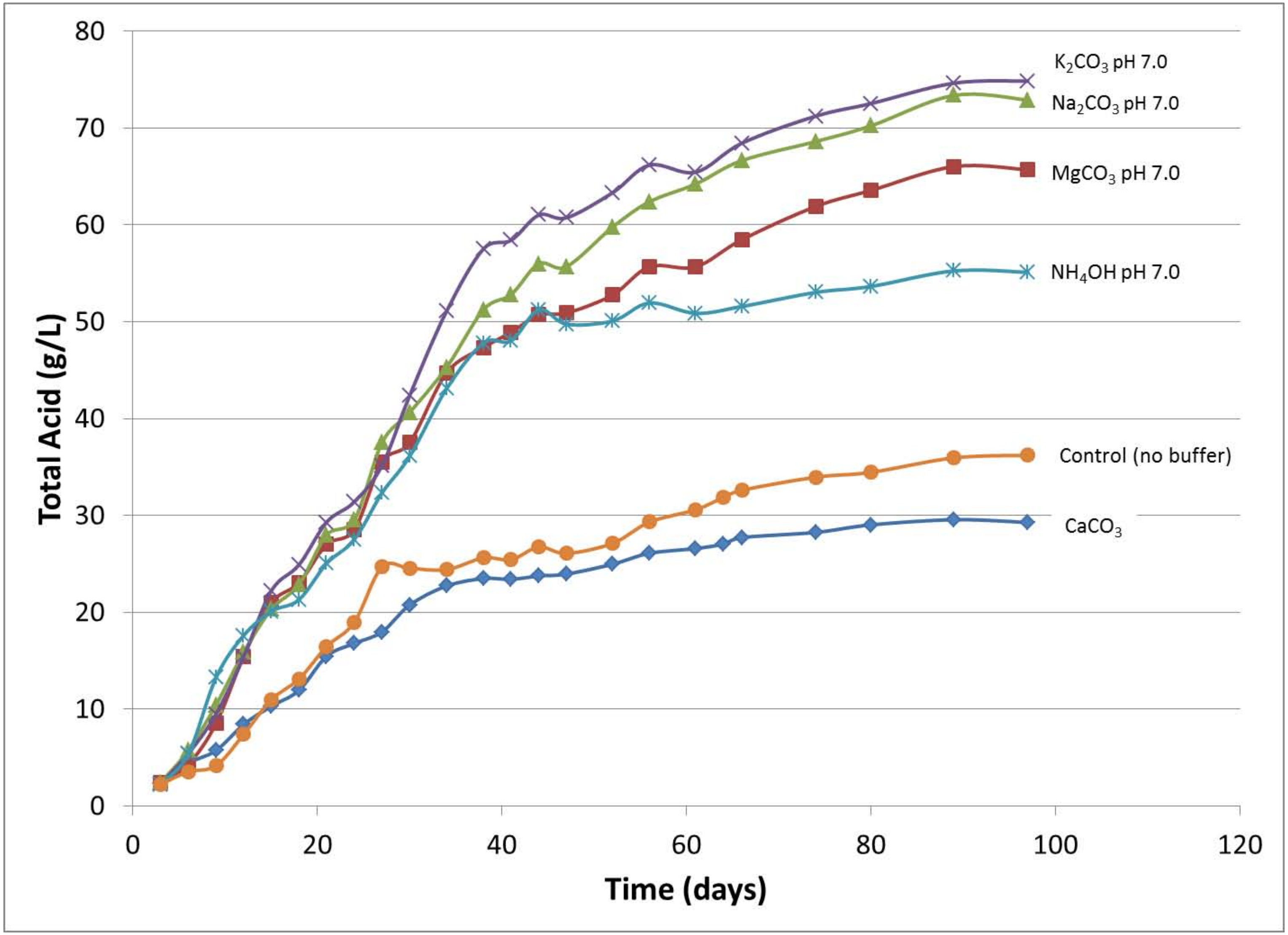
Continuous countercurrent fermentation

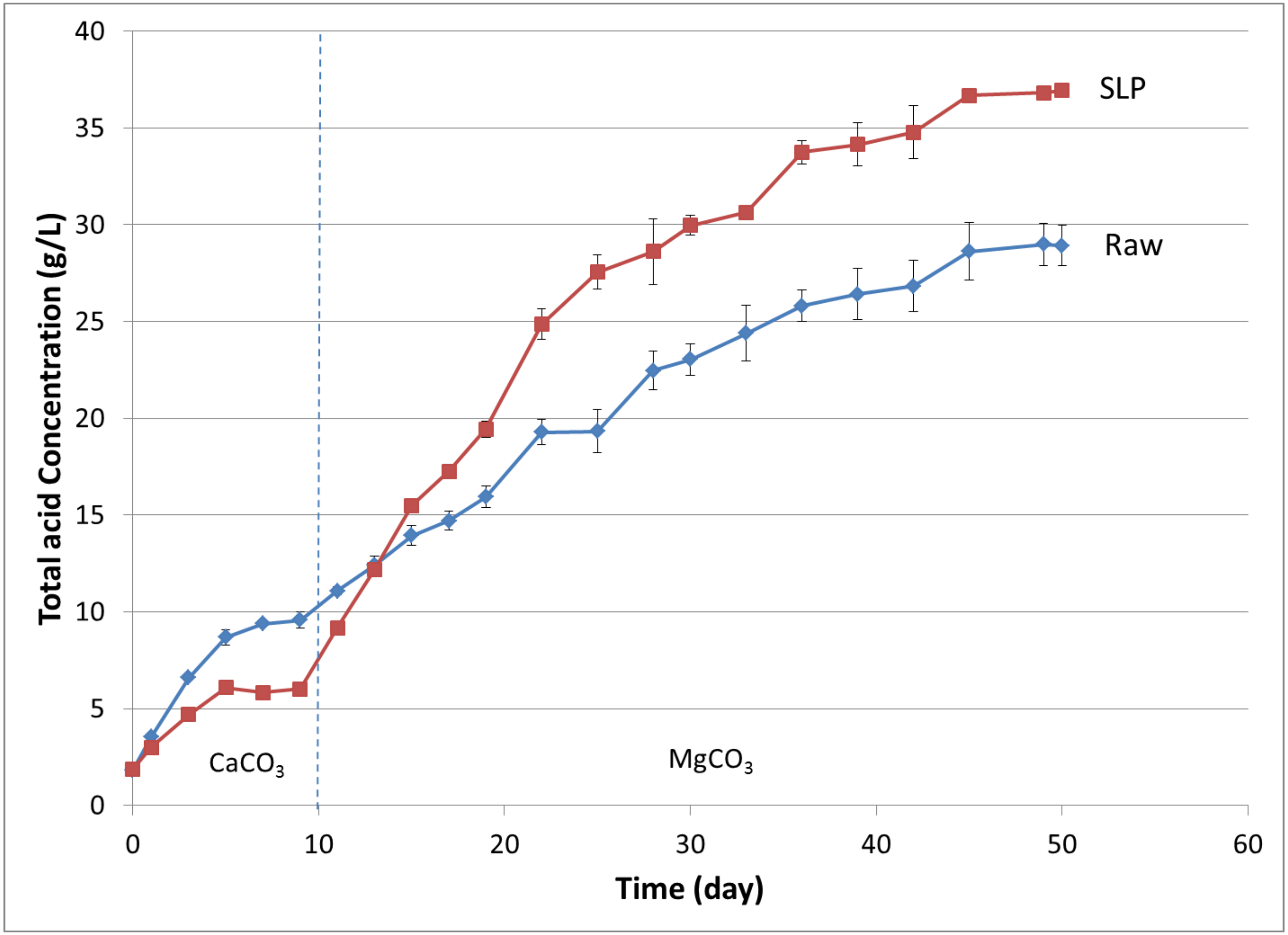
$CaCO_3$ Buffer



Effect of buffer

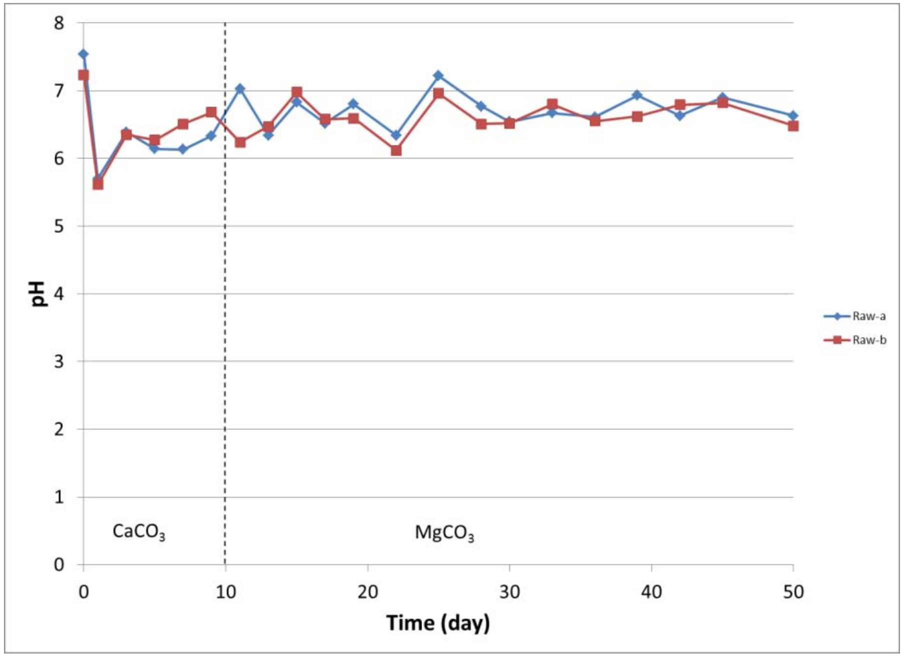


Batch fermentation

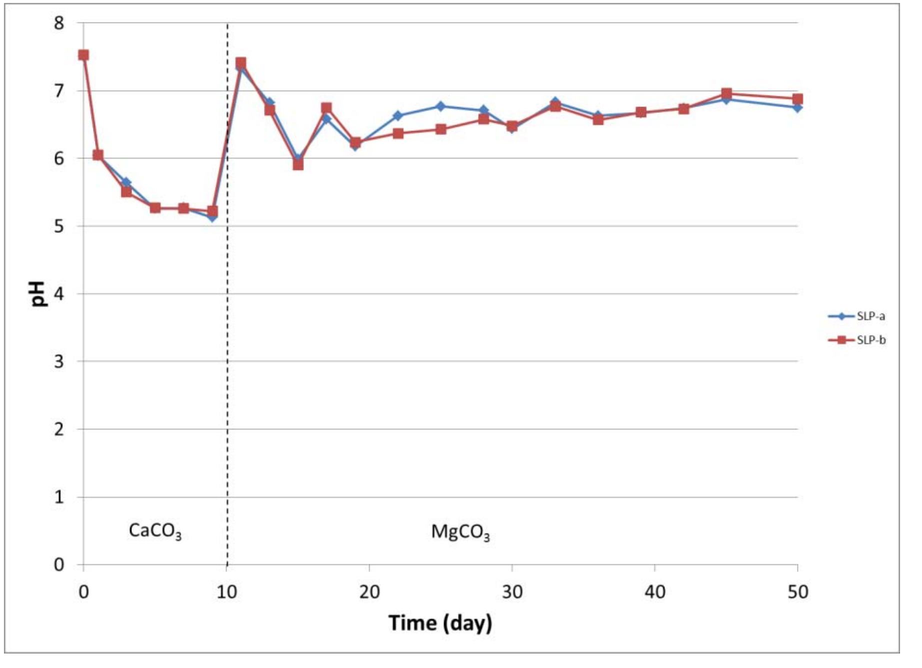


pH profiles

Raw



SLP



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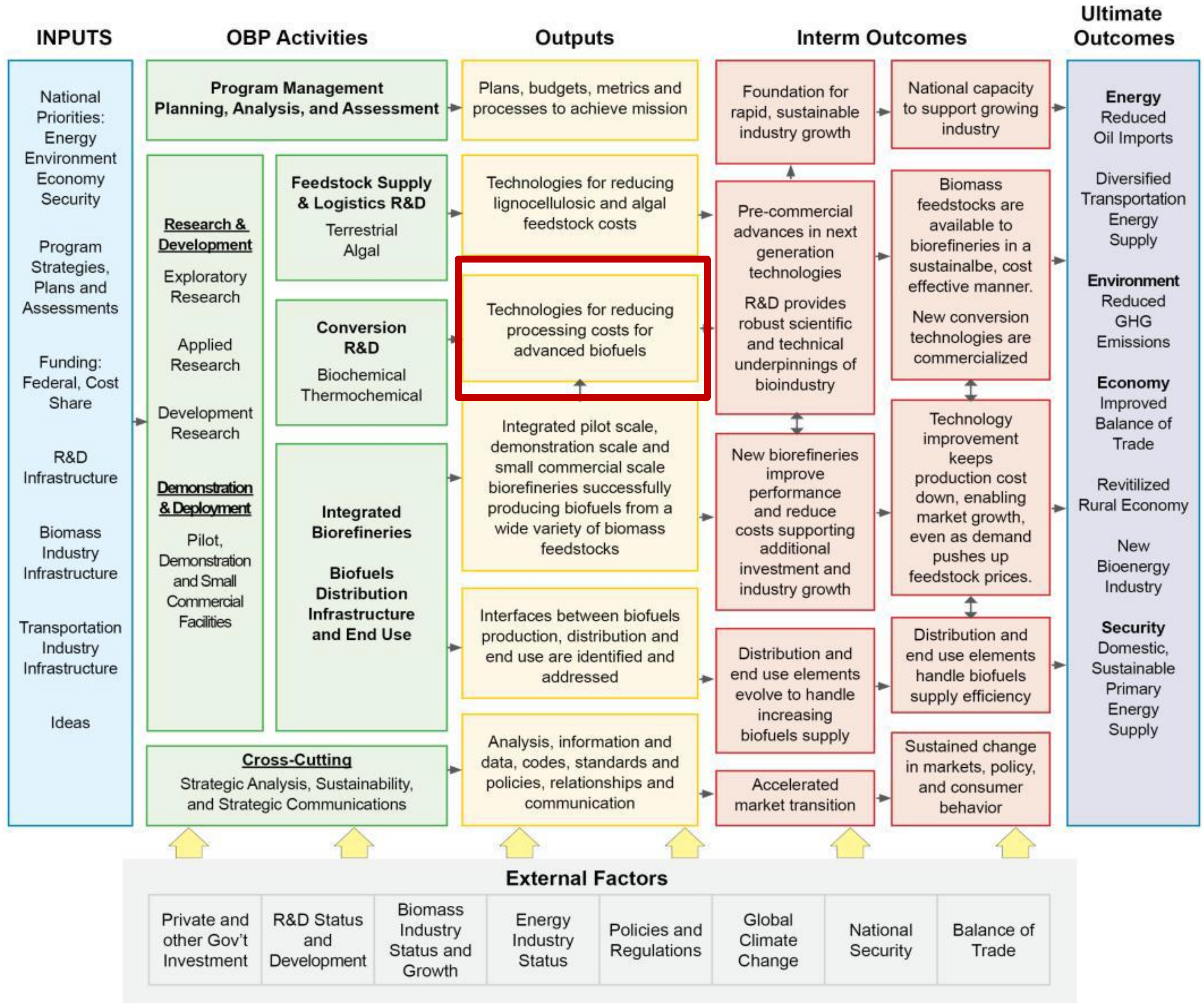
3 – Relevance to Biomass Program Multi-Year Program Plan (Nov 2012)



4 - Critical Success Factors

Technical Success

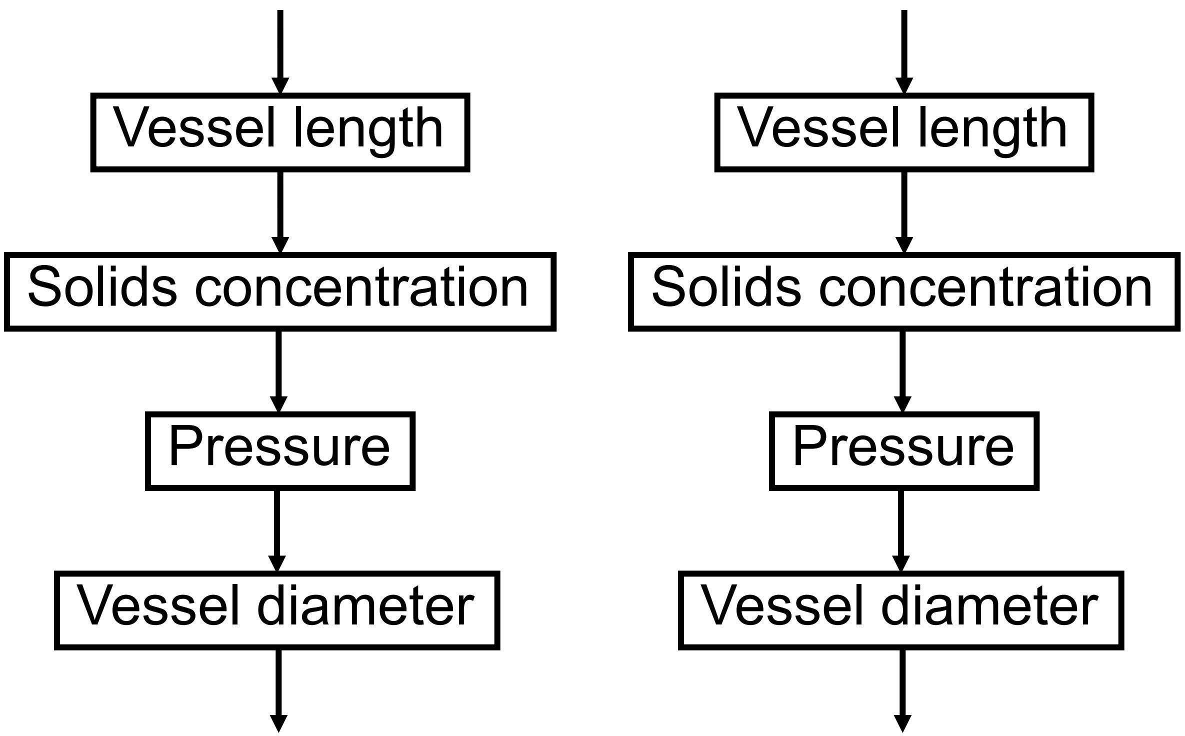
The digestibility benefits of shock treatment demonstrated at the base case must be demonstrated at larger scale

Economic Success

Ability to rapidly load and unload reactor

5. Future Work

Shot gun shell | **CH_4/air**

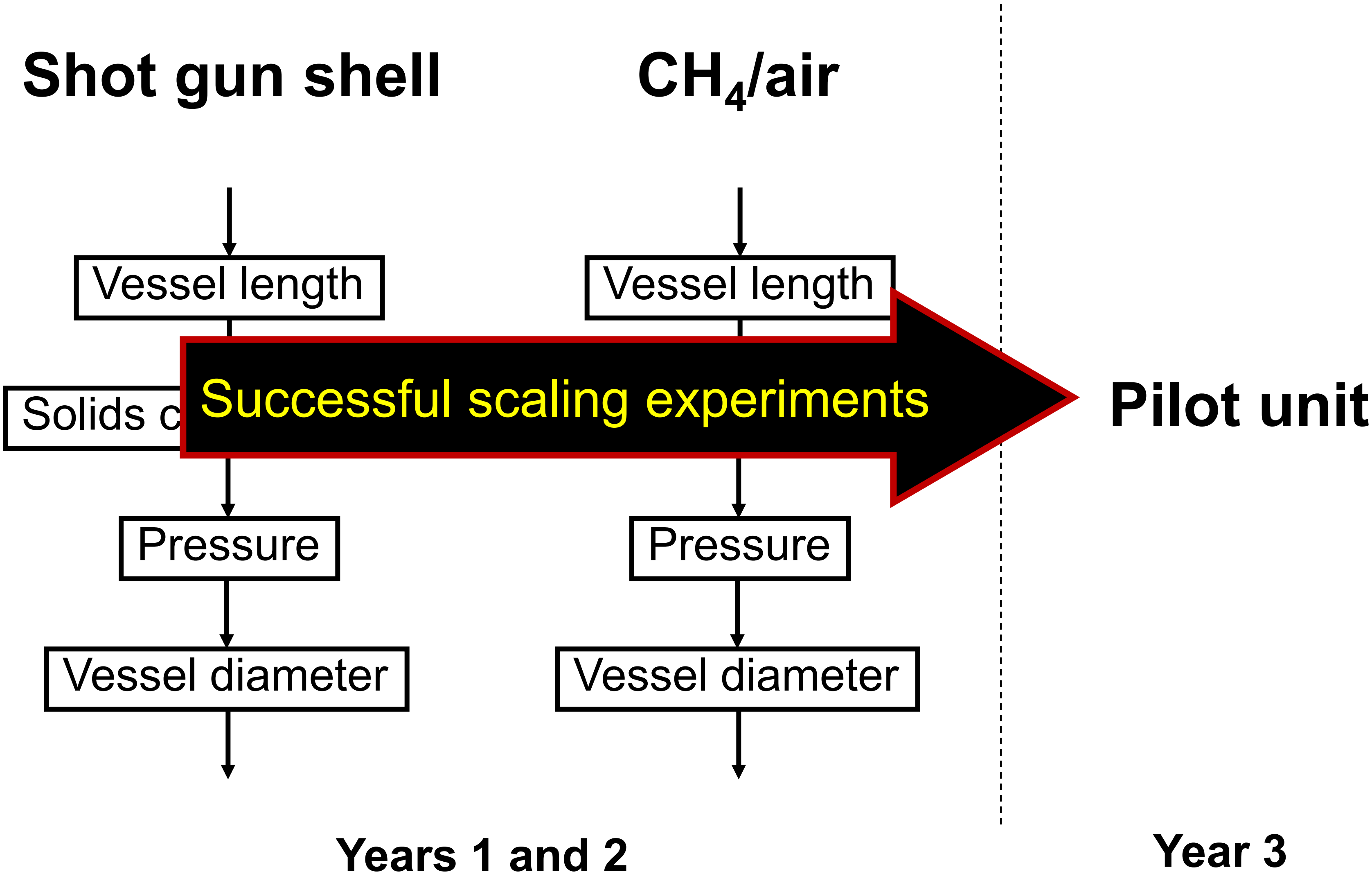


Years 1 and 2

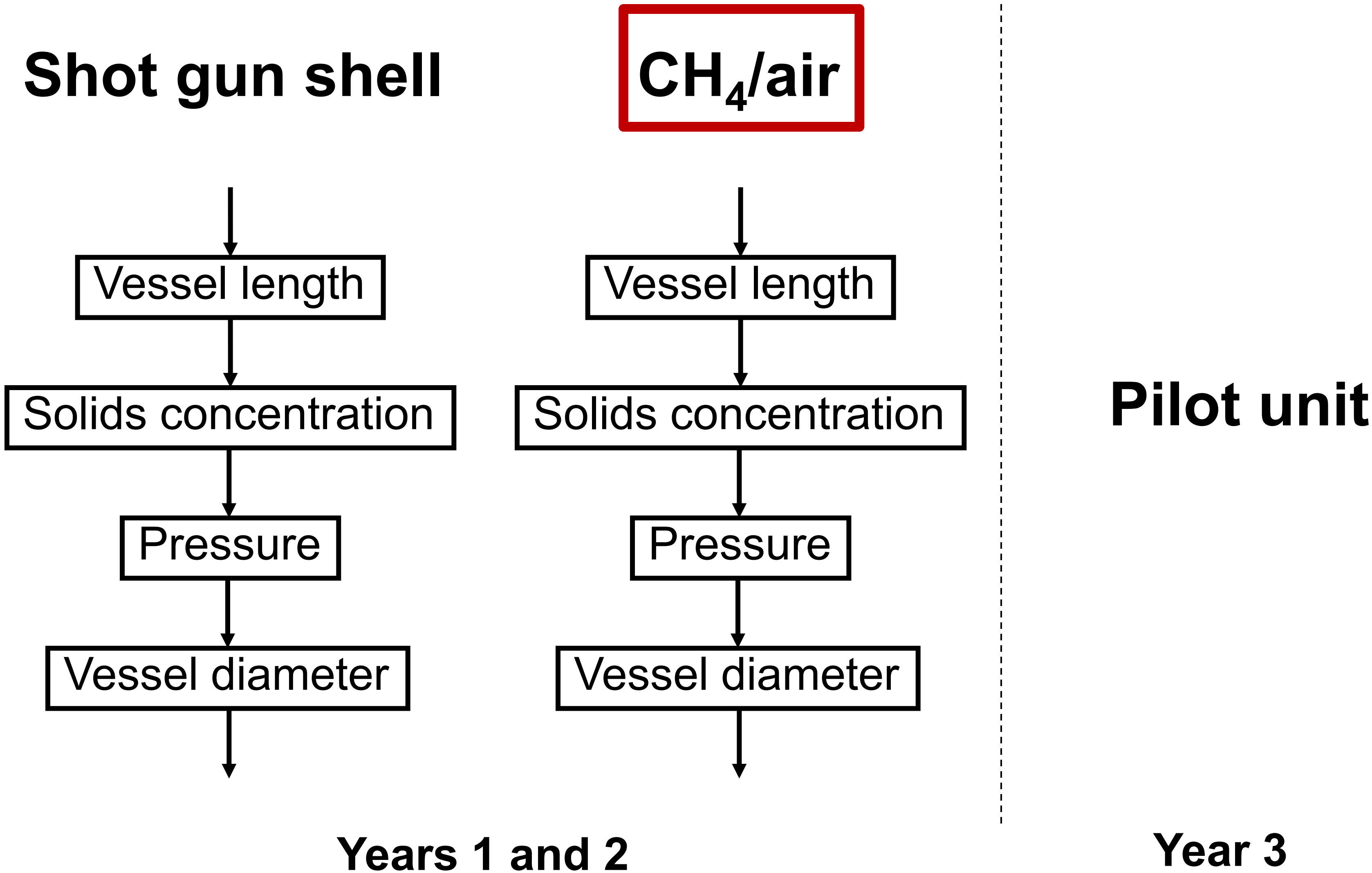
Pilot unit

Year 3

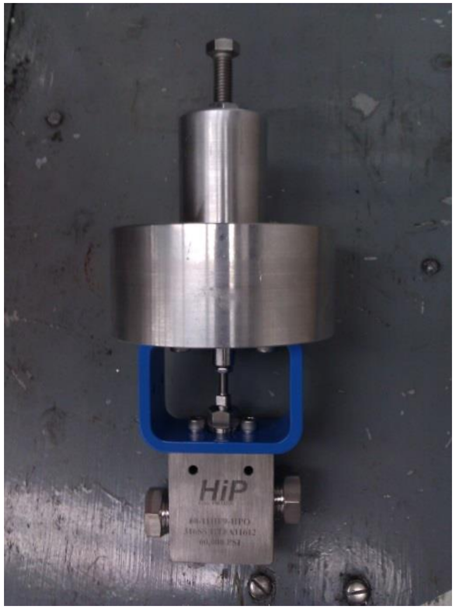
5. Future Work



5. Future Work



5 – Development of CH_4/air explosion



Pneumatically actuated valve

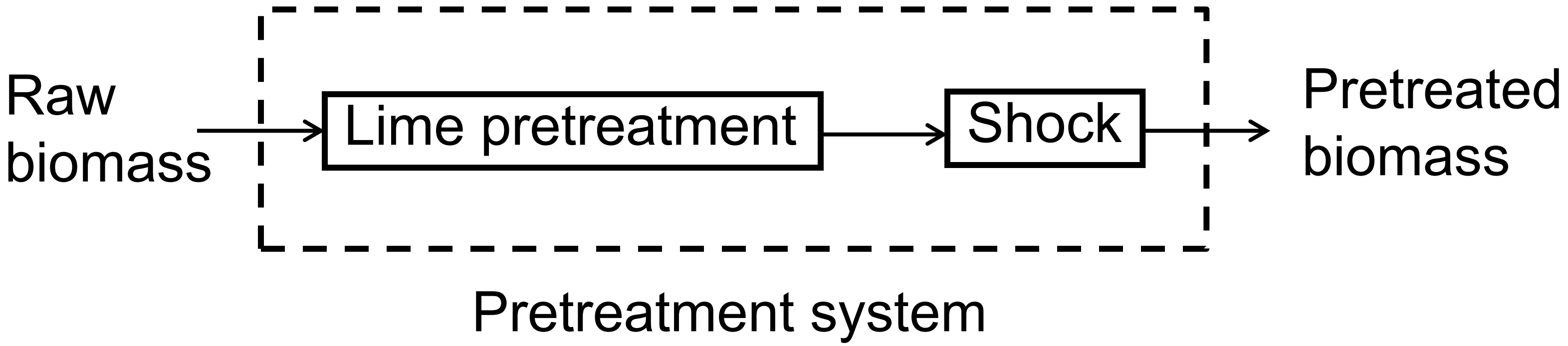
Gas manifold

5 – Development of CH_4/air explosion

Manifold installed in bunker

Spark ignition

5 – Optimize pretreatment system



Explore less severe lime pretreatment

- Shorter time
- Less lime

Lime Pretreatment Scale Up

190-L Kettle

Kettle exterior and CO_2 scrubber columns

Heater and pump

1900-L Kettle

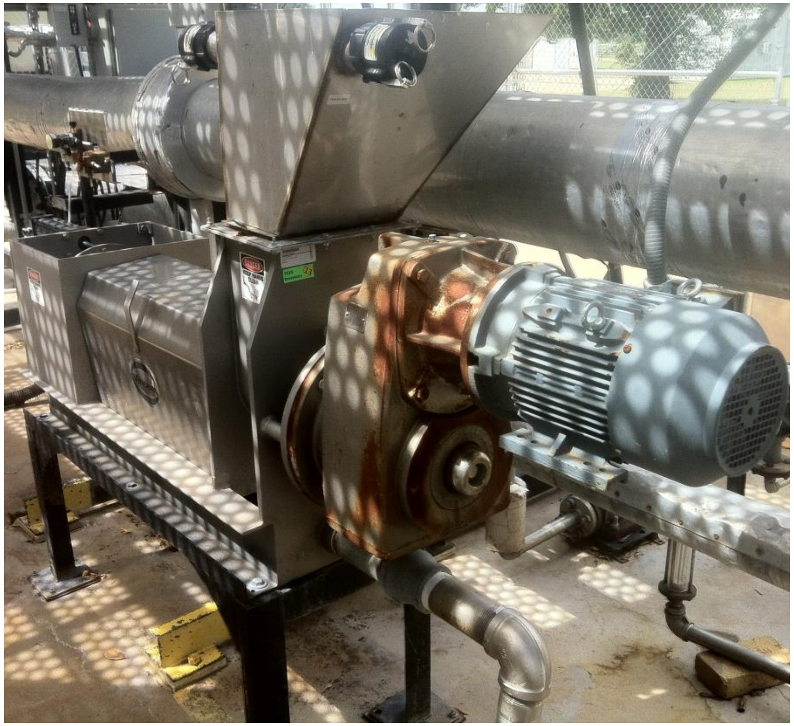
Kettle exterior

Filtration Rack

Conditions

	Vessel		
	60 L	190 L	1900 L
Dry biomass (kg)	4	12	120
Distilled water (L)	32	96	960
Lime added (kg)	0.53	1.6	16

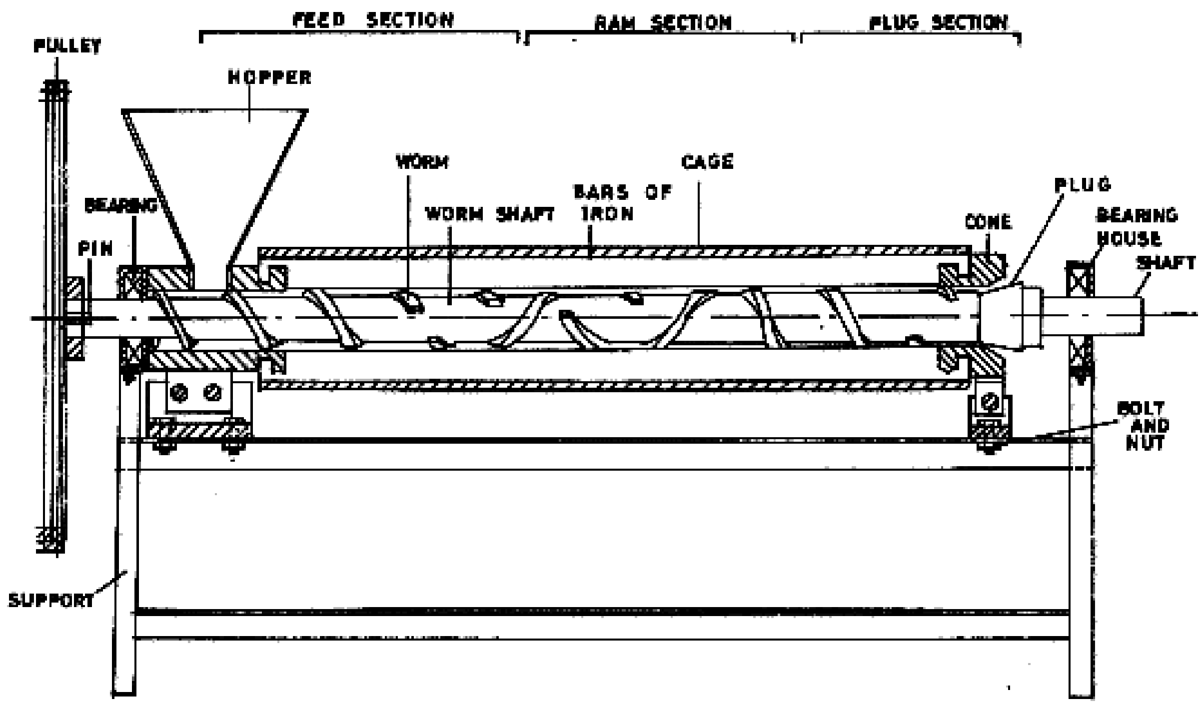
Screw press



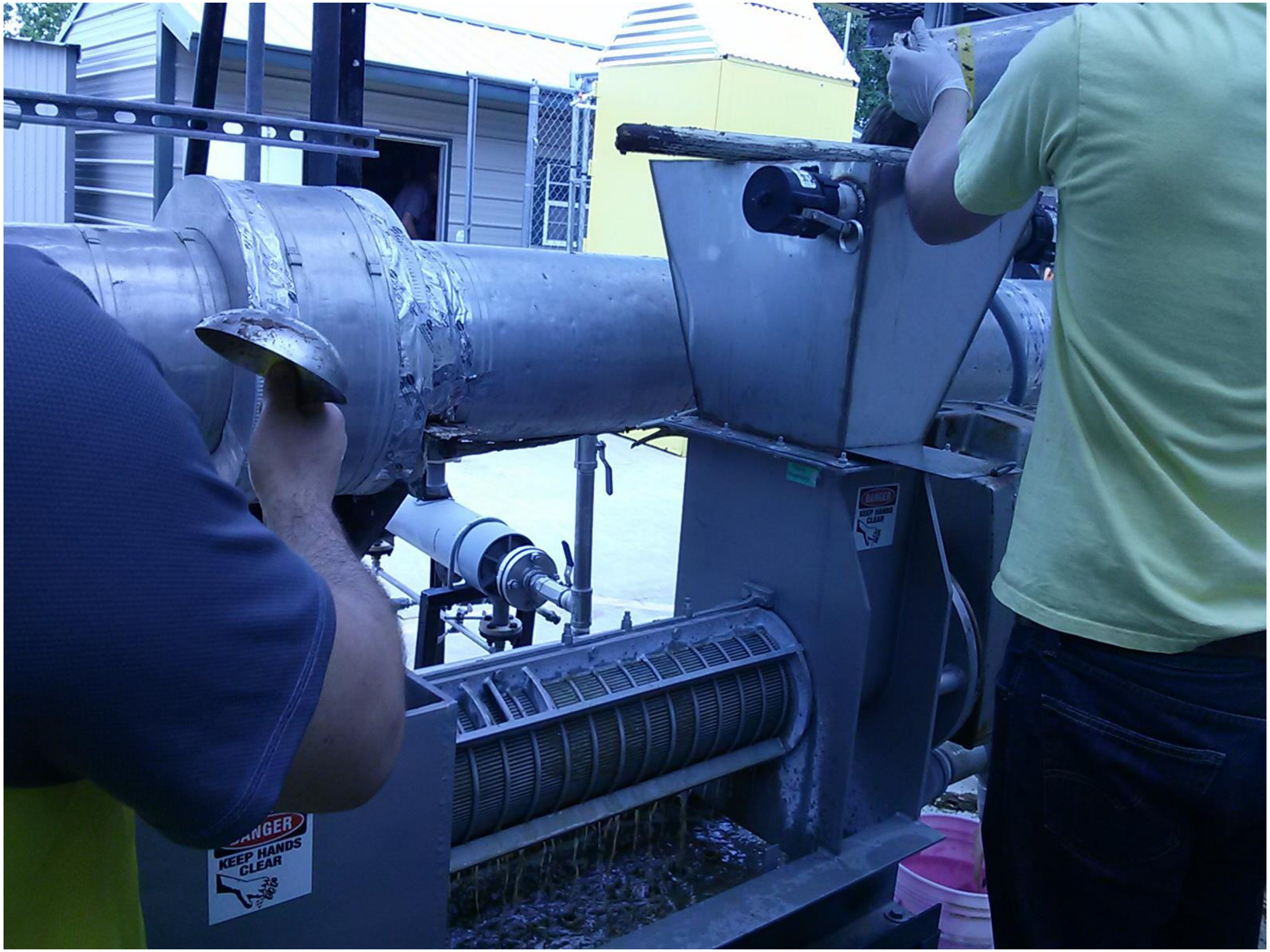
Vincent Compact Screw Press
(Model: CP-6; Vincent Corporation, Florida)

Screw press outlet: cone and shaft

Schematic Diagram of the Screw Press



Screw press



6 – Technology transfer

TERRABON

6 – Technology transfer

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Earth Energy Renewables

Outline

- Background
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Conclusions

- Lime treatment is
  - Effective
  - Inexpensive
- Shock treatment is
  - Effective
  - Inexpensive
- Current data suggests it is scalable
- Methane/air system is being developed
  - Higher pressures
  - Retain colloidal fines

Additional Slides

Publications, Presentations, and Commercialization

November 14 – 17, 2011 Energy for a Sustainable Future, The 2011 International Conference on Water, Energy, and the Environment, American University of Sharjah, United Arab Emirates.

January 16, 2012 – presentation to Synthetic Genomics in La Jolla, California.

March 13, 2012 – presentation to Department of Chemical Engineering, Oklahoma State University, Stillwater, Oklahoma.

March 26, 2012 – presentation to American Chemical Society, San Diego, California.

May 1, 2012 – Shock Pretreatment, 34th Symposium on Biotechnology for Fuels and Chemicals, New Orleans.

Publications, Presentations, and Commercialization

August 23 to 24, 2012 – Mark Holtzapple, MixAlco, Sino-US Symposium on Advanced Biofuels, Beijing, China.

August 15, 2012 – Mark Fuels and Chemicals from Biomass, Department of Chemical Engineering, ESPOL, Guayaquil, Ecuador.

October 18, 2012 – MixAlco Process, Yachay Workshop, Ibarra, Ecuador.

February 11, 2013 – MixAlco Process: Fuels and Chemicals from Biomass, Inagural SEC Symposium, Atlanta, Georgia.