Optimization of Mild Bisulfite Pretreatment on Pacific Northwest Softwood

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Outline

- Commercialization Value Chain

- Importance of Softwood

- Sugar technology by mild bisulfite pretreatment

  - Bisulfite review

  - Optimizing mild bisulfite pretreatment for softwood

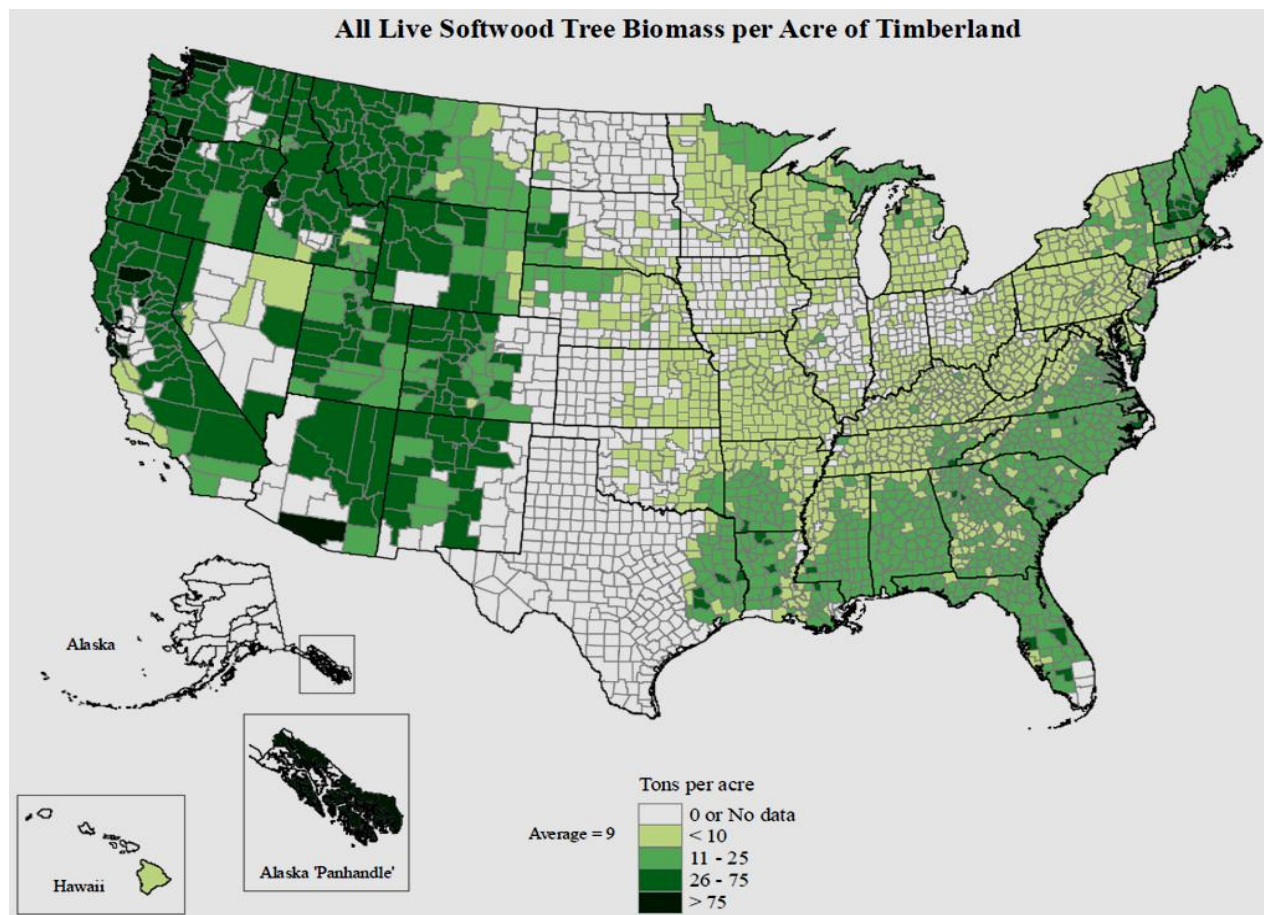 - System Optimization: Onsite enzyme production model

Commercialization: From Forest to Fuels

SUPPLIER   CONVERSION EXPERTISE   **CUSTOMER**

End-to-End Value Chain Solution Leverages the Strengths of
Two Natural Resource Leaders – Chevron and Weyerhaeuser

Softwood Distribution in US

All Live Softwood Tree Biomass per Acre of Timberland

Tons per acre
- 0 or No data
- < 10
- 11 - 25
- 26 - 75
- > 75

Average = 9

- Sustainable US forest harvest residuals and thinnings: 75 million tons/yr – about 5 billion gal/yr cellulosic ethanol.

- Softwood is the most difficult biomass to pretreat for a bioconversion process.

Reference: (1) USDA Forest Service, http://www.fia.fs.fed.us/; (2) US DOE, 2011. US Billion–Ton Update, Biomass Supply for a Bioenergy and Bioproducts Industry

Bisulfite Pulping & Pretreatment Review

History:

- In 1867, Benjamin Chew Tilghman invented the use of calcium bisulfite to pulp wood.
- In 1874, The first commercial sulfite pulping plant was built in Bergvik, Sweden. Since then, bisulfite/sulfite pulping has been used for 14 decades.
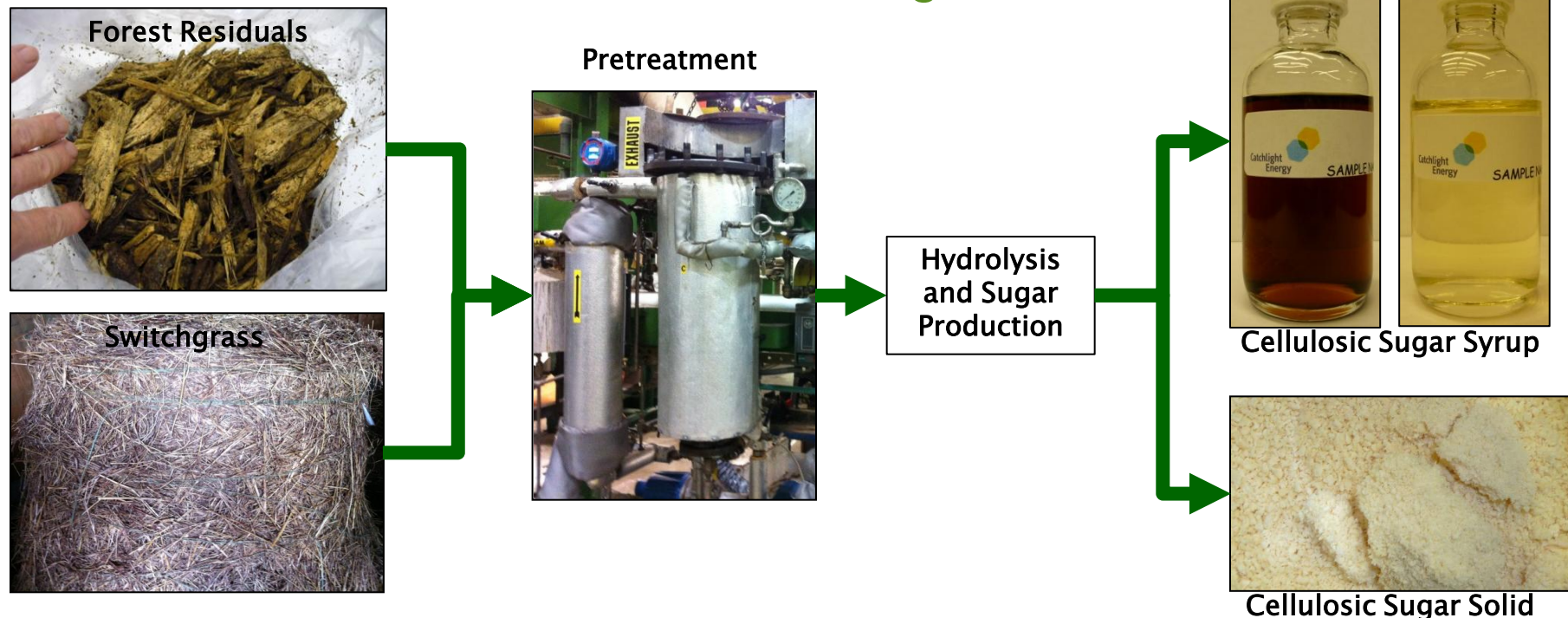
Applications in Renewable Fuel Production:

- Spent Sulfite Liquor to ethanol has been run for decades at multiple sites
- Sulfite pulping sludge as fermentation substrate (Duff et al, 1994; Lynd et al, 2001).
- Sulfite pretreatment (SPORL) at high temperature of 180°C (Zhu et al., 2009).
- BALI process by Borregaard (Sjode et al., 2010).

> **Bisulfite pretreatment is an effective method for softwood pretreatment.**

Bisulfite to Pretreat Softwood–CLE Sugar Process

Forest Residuals

Switchgrass

Pretreatment

Hydrolysis and Sugar Production

Cellulosic Sugar Syrup

Cellulosic Sugar Solid

- ✓ **Adaptable to existing infrastructure – modify or retrofit**
- ✓ **Scalable from pilot operations**
- ✓ **Feedstock flexible – softwood, hardwood, and herbaceous biomass**
- ✓ **Cellulosic sugar options**

Reference: (1) http://www.biotechnologyforbiofuels.com/content/6/1/10; (2) Gao et al., 2012, Processing Recalcitrant Feedstocks in a Biorefinery, BioPacific Rim.

# Bisulfite to Pretreat Softwood – CLE Sugar Process

Reference: http://www.biotechnologyforbiofuels.com/content/6/1/10
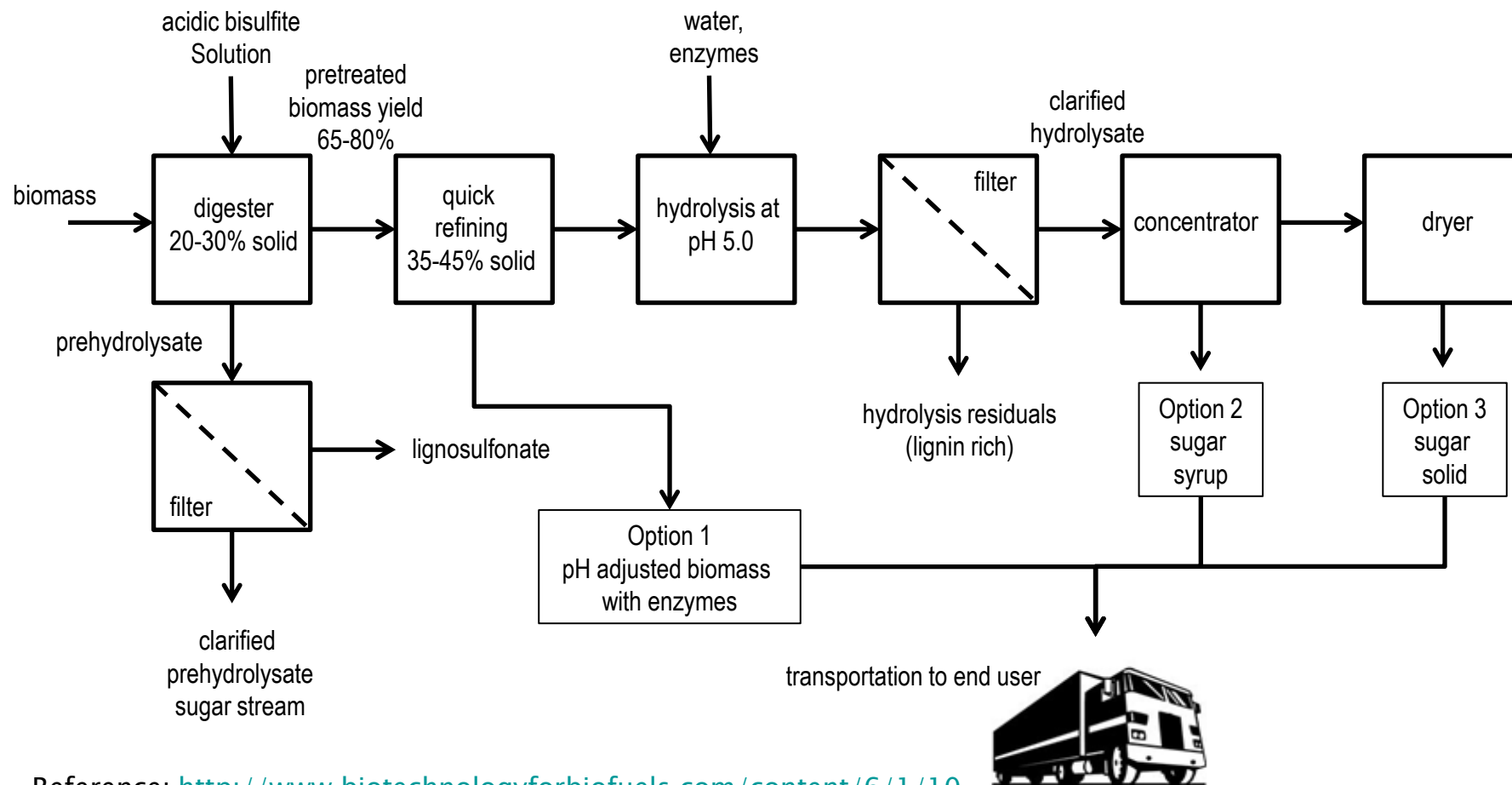
Optimization Strategies and Measures of Mild Bisulfite Pretreatment

- ➤ **Reduce bisulfite or total sulfur dioxide usage**

- ➤ **Reduce pretreatment temperature**

- ➤ **Reduce inhibitor formation**

- ➤ **Maintain good sugar conversion yield from pretreated biomass**

Furan Reduction in Mild Bisulfite Pretreatment
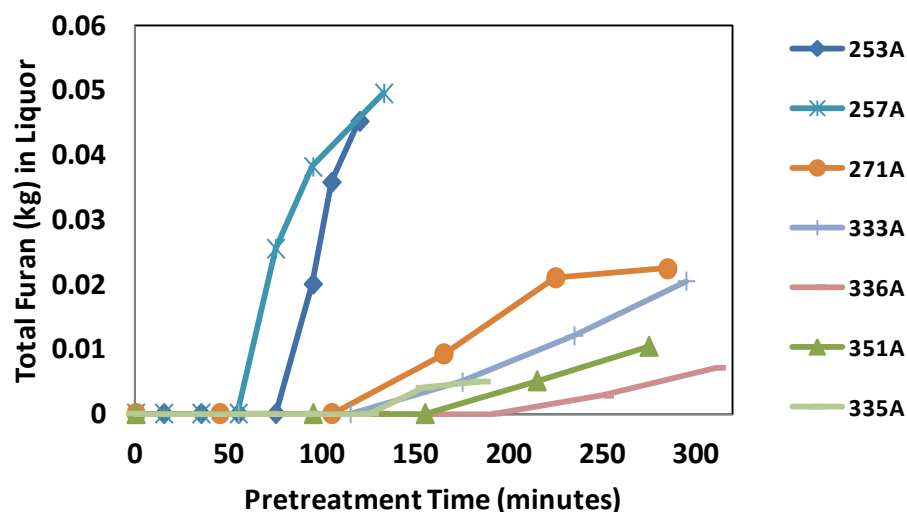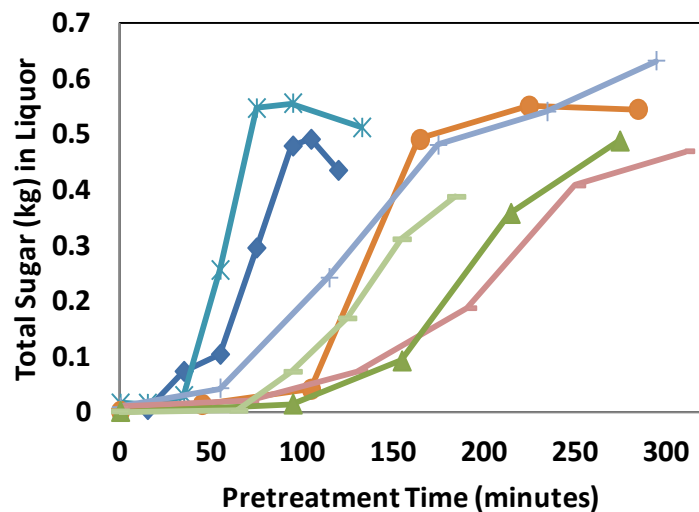
Conditions – preheat to set T°C, ~49 min
253A: SO_2(e) 12.4% $Ca(HSO_3)_2$ on wood, 165°C, 75 min
257A: SO_2(e) 7.9% $Ca(HSO_3)_2$ on wood, 165°C, 75 min
271A: SO_2(e) 6.1% $Ca(HSO_3)_2$ on wood, 145°C, 240 min
333A: SO_2(e) 7.2% $Ca(HSO_3)_2$ on wood, 145°C, 240 min
336A: SO_2(e) 4.9% $Ca(HSO_3)_2$ on wood, 140°C, 240 min
351A: SO_2(e) 6.0% $Ca(HSO_3)_2$ on wood, 145°C, 180 min
355A: SO_2(e) 6.5% $Ca(HSO_3)_2$ on wood, 145°C, 120 min

Lower temperature and longer time reduced furan formation by 50–89% on wood.
Lower chemical use did not reduce sugar production.

Sugar Yields of Mild Bisulfite Pretreatment

Cook No.	Temp., °C	Time at T, min	Equivalent SO2 on wood (%)	Pulp Yield, %	Furan formation, % on wood	Acetic acid formation, % on wood	Pulp sugar composition, %	Sugar in liquor, kg	Sugar in hydro-lysis, kg	Total Sugar Yield (%)
253A	165	75	12.4	68.1	1.51	2.13	53.9	9.4	39.6	73
257A	165	75	7.9	74.4	1.65	1.89	56.7	12.0	42.4	82
271A	145	240	6.1	76.6	0.75	1.93	55.3	12.6	42,4	82
333A	145	240	7.2	78.2	0.68	1.91	54.4	14.3	43.9	87
336A	140	240	4.9	79.5	0.24	1.70	52.4	10.6	40.5	76
351A	145	180	6.0	80.4	0.35	1.88	62.4	10.7	48.1	88
355A	145	120	6.5	82.3	0.17	1.72	56.8	8.6	46.2	82

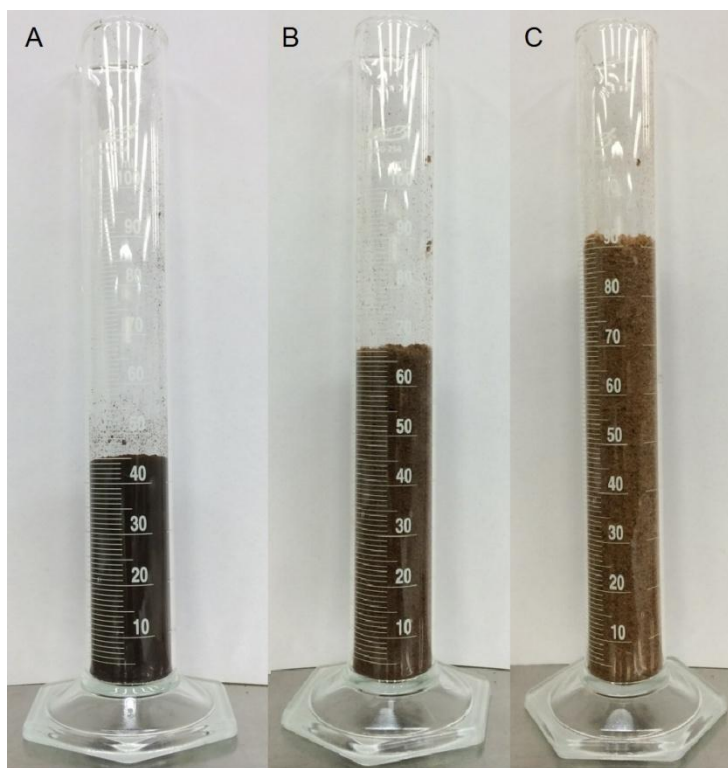**Analysis based on 100 kg OD wood of Douglas-fir FS-10 Feedstocks**

Optimization results:

- ➢ Reduced bisulfite or total sulfur dioxide usage by 51%
- ➢ Reduced pretreatment temperature, resulting in energy saving
- ➢ Reduced inhibitor formation: furan by 50-89%; acetic acid by 9.4-20%
- ➢ Maintained good sugar conversion yield from pretreated biomass: 81-88% with only 4.4% enzyme product (not protein) dosage on solids

Bulk Density of Pretreated Biomass

| Test No.	Pretreatment Temp., °C	Time at T, min	Equivalent SO2 on wood (%) in pretreatment	Test Amount (g, wet)	Apparent pretreated and refined biomass density (dry g /ml)
A	165	75	7.9	20	0.216
B	145	240	7.2	20	0.130
C	140	240	4.9	20	0.093

> ➤ **Higher cooking temperature with more chemical, higher bulk density**

> ➤ **Lower cooking temperature with similar or less chemical, lower bulk density**

Hydrolysate Fermentation

	Pretreatment Parameters			Hydrolysis Parameters			Fermentation Results	
Cook No.	Temp., °C	Time at T, min	Equivalent SO2 (%) on wood	Pulp Solid (%)	Enzyme Dosage (%) on Solid	Total Sugar Yield (%) at 72 hours	Ethanol Titer, (% wt/vol)	Lignin in Fermented Residuals (%)
333A	145	240	7.2	14.7	4.4	87	3.9	72.0
336A	140	240	4.9	15.0	4.4	76	3.3	61.1
351A	145	180	6.0	14.9	4.4	88	3.9	70.0
355A	145	120	6.5	14.9	4.4	82	3.7	64.9

Concentrated Hydrolysate Fermentation
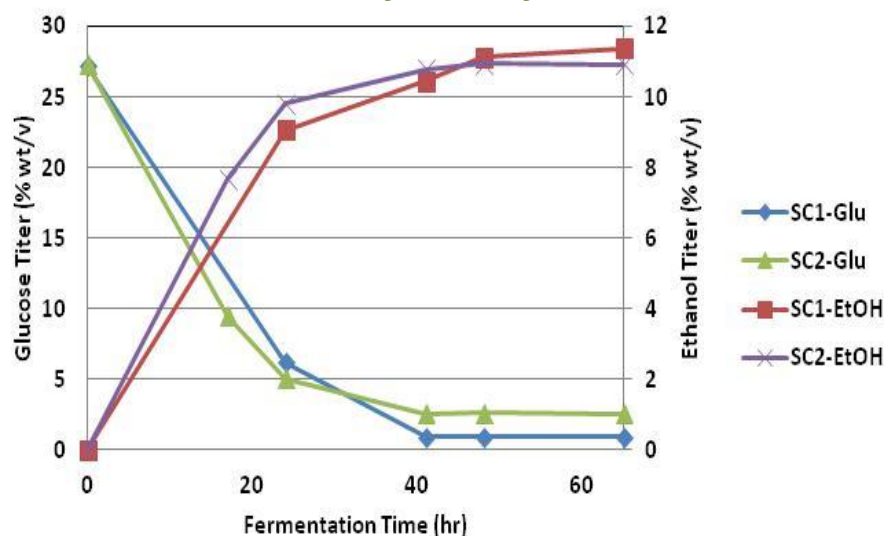
- **Softwood sugar syrup is highly fermentable**
  - ➤ **Ethanol titer can be 11.0% (wt/vol) in 48 hrs**
 - ➤ **Optimization may increase ethanol titer further**

Concentrated Sugar Stream Facilitates On-Site Enzyme Production

- Significant cost savings possible with on-site enzyme production

- Sugar titer dictates size of enzyme production plant

- Ability to concentrate a substream of the enzymatic hydrolysate to greater than 10% sugar enables a higher enzyme titer and smaller enzyme production plant.

- Ability to use a cellulosic sugar source and electricity from biomass allows for a more sustainable enzyme.

CLE Sugar Process – Enzyme Production Integration

CLE sugar process can be effective with onsite enzyme production integration.
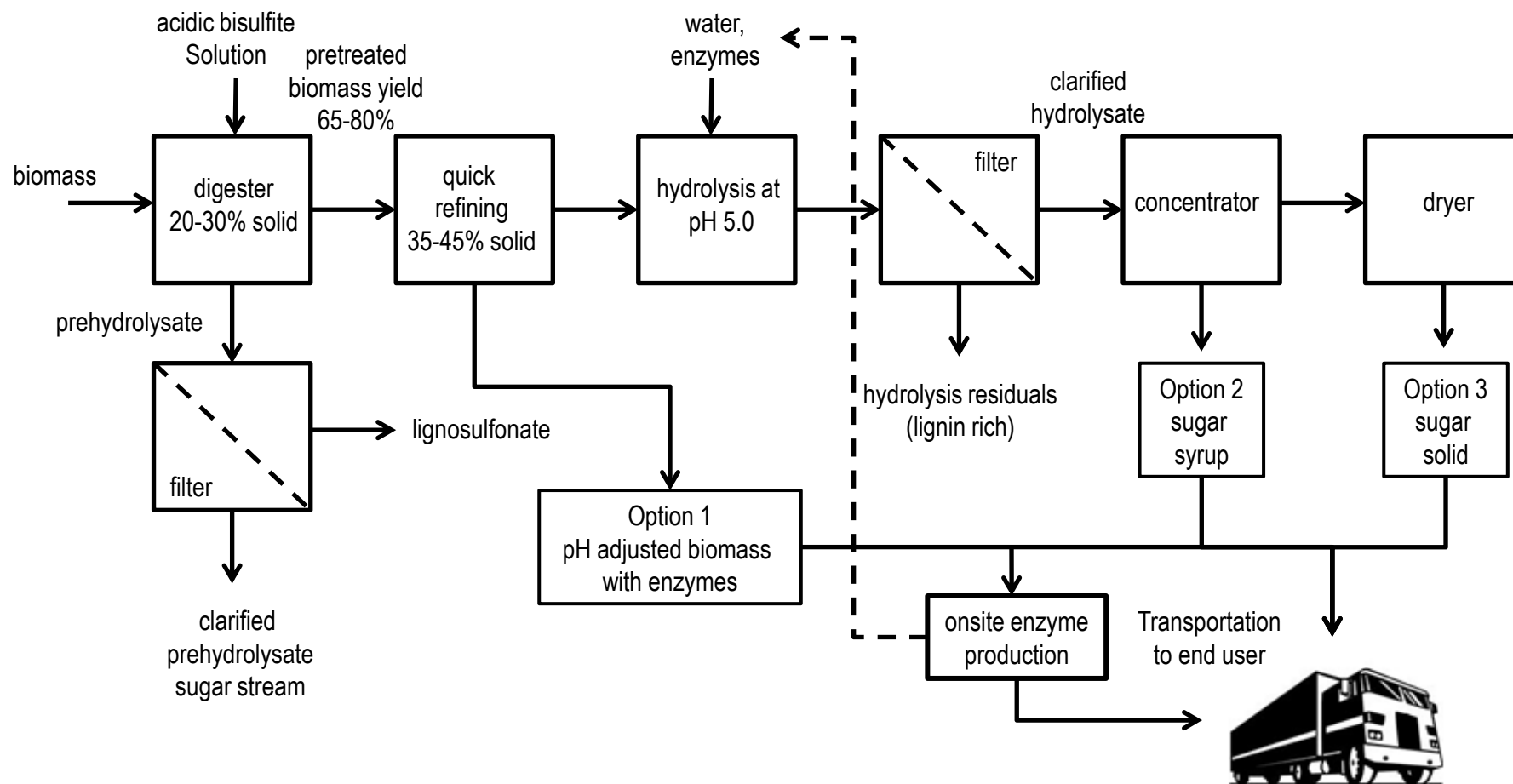
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