



# A techno-economic comparison between technologies for biomass fractionation including liquor re-use

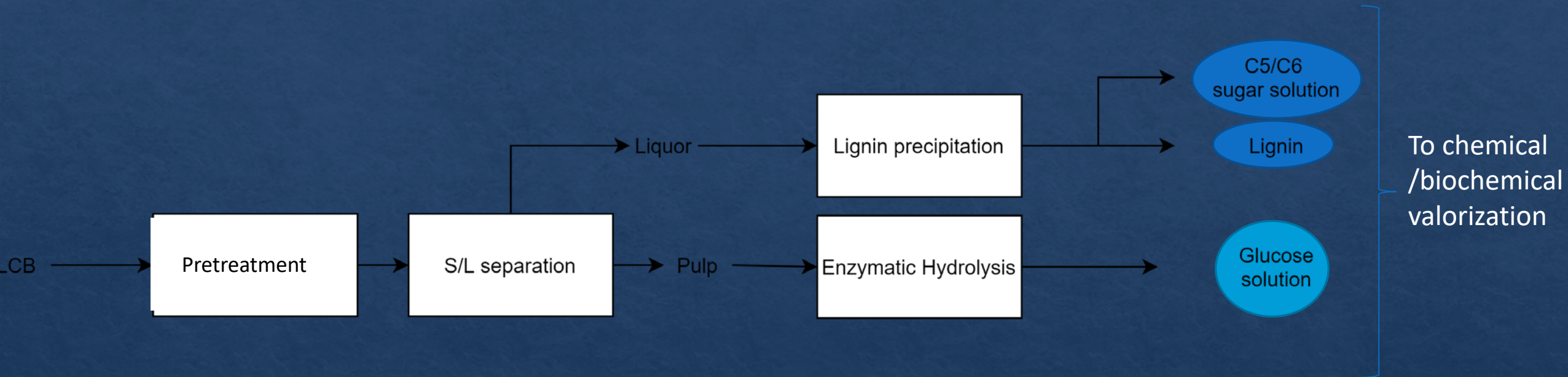
Priscilla Vergara, Franco Mangone, João P. Del Pintor , Miguel Ladero, Juan.C. Villar, Félix. García-Ochoa, Soledad Gutiérrez

# Sustainable production of bio-based fuels and chemicals

- Agricultural residues are low cost and abundant
- Lignocellulosic Biomass (LCB) as a source of carbohydrate platform chemicals
- Economy of this process is still challenging



# LCB to sugars



◇ Our focus is to valorize all streams not only glucose solution

# Pre-treatment alternatives for LCB

- ◇ **Diluted mineral acids** (0.5-4%), T: 120-200 °C
- ◇ **Steam explosion**, saturated steam at 160-250°C. Rapid decompression after few minutes
- ◇ **Ethanol/Water (EW) extraction** Solvent-Water mixtures. Acid catalysts improve hemicelluloses hydrolysis.
- ◇ **Alkalyne pulping** Sodium/potassium hydroxides, T < 120°C

# Pre-treatment economy

- ◆ The main drawback of pre-treatments is the associated costs of energy and product concentration stages
- ◆ This issue is a bottleneck for the development of a cost effective bioprocess which results in increased downstream processing cost, when compared with crude oil alternative
- ◆ In the case of the water-solvent fractionation they increase with the additional energy involved in the solvent recovery
- ◆ Raw material is cheap, eventually a residue
- ◆ Herbaceous vs. Wood: L/S ratio

# EW Pre-treatment economy

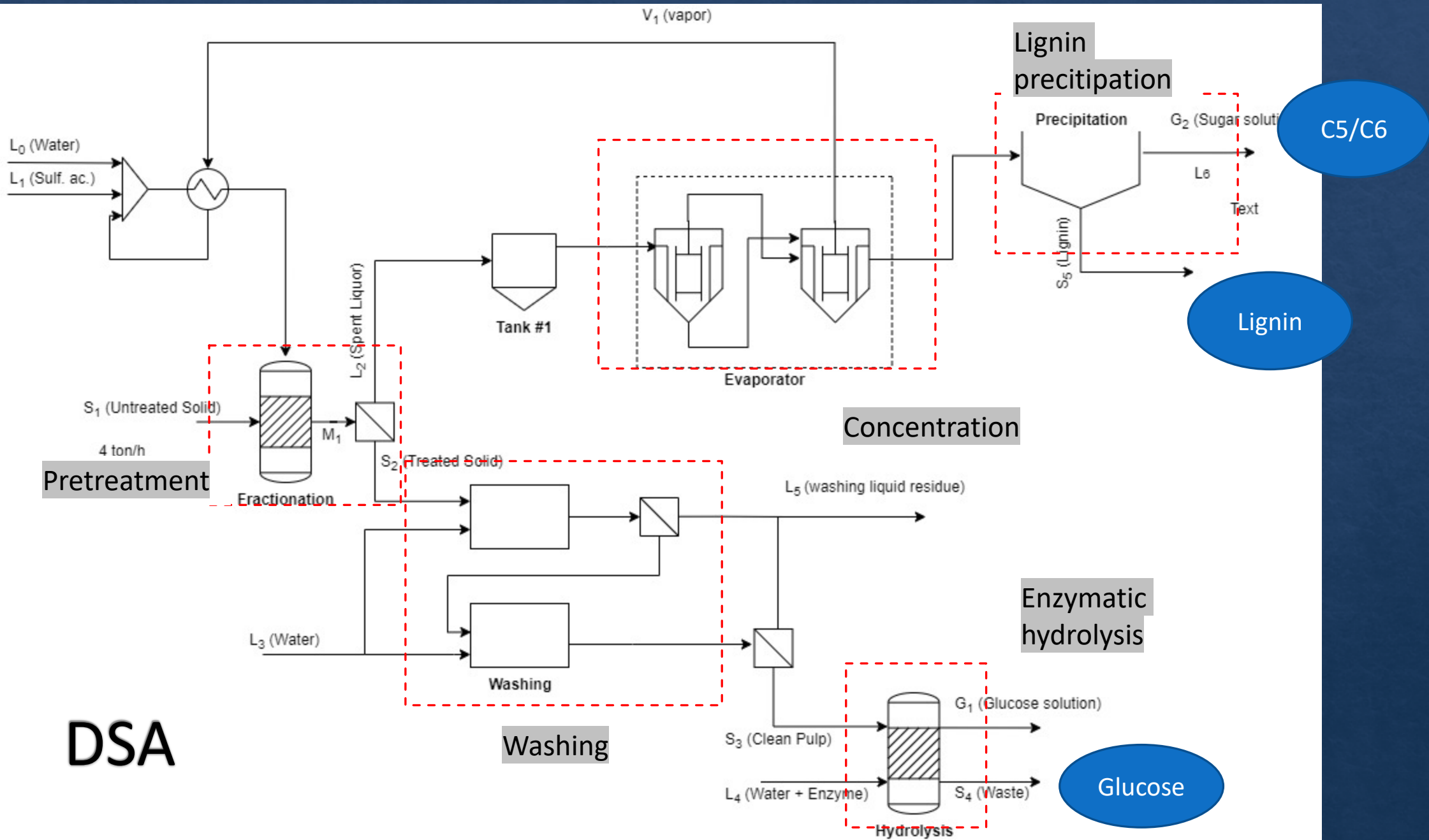
- ◇ EW pre-treatment is, apparently, the less favourable pre-treatment in terms of energy consumption (Kautto et al., 2014; Rodrigues Gurgel et al 2018)
- ◇ It is more efficient in the delignification than diluted acid pre-treatments. Moreover, EW pulps exhibit less inhibition problems in the further saccharification and fermentation stages (Palmqvist and Hahn-Hägerdal, 2000).



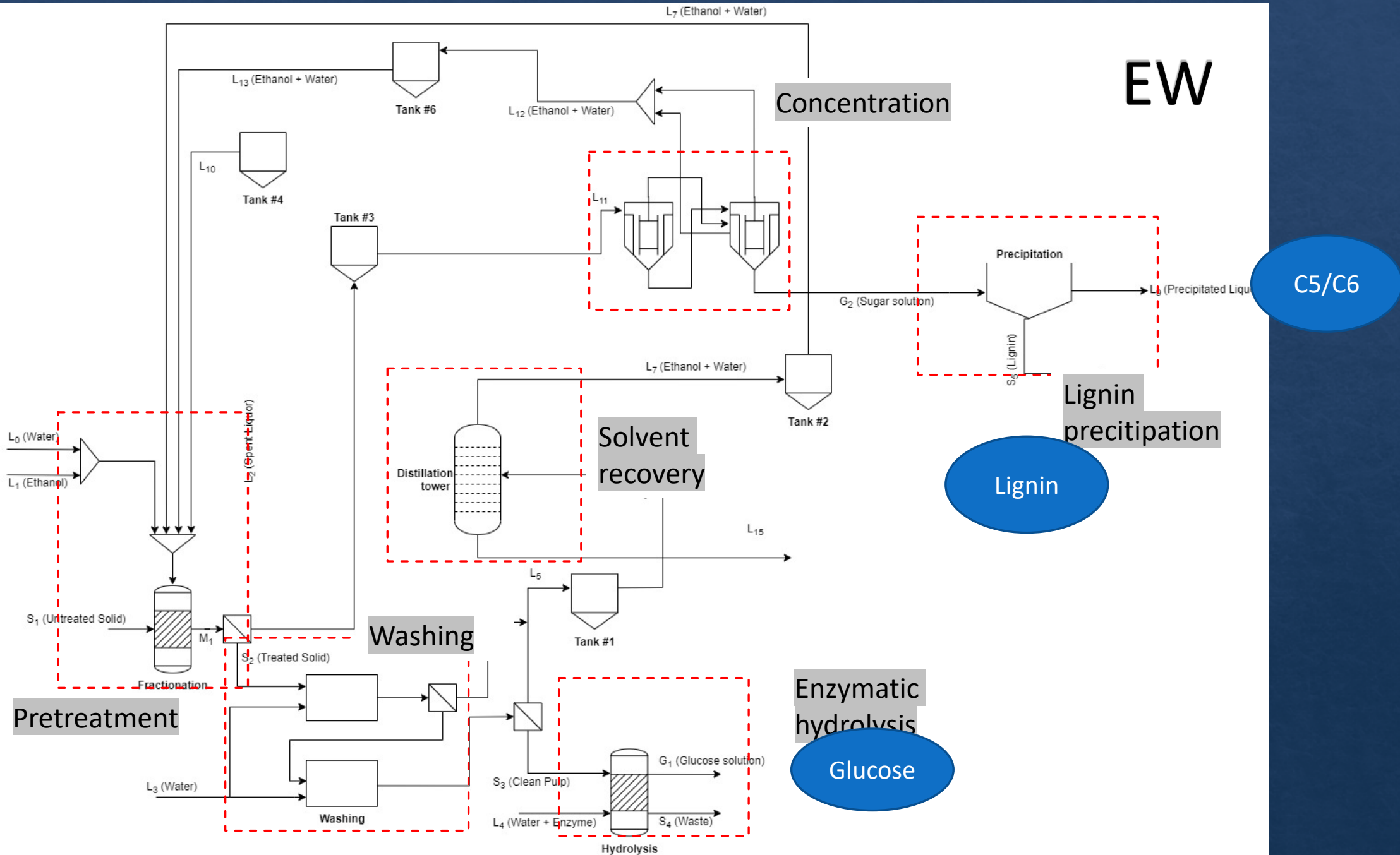
# Aim of the study



- ◆ To set up EW and DSA fractionation process simulations for wheat straw
- ◆ To evaluate how a liquor re-use strategy (EWR) affects the economy of EW process
- ◆ To conduct an economic comparison of the EW EWR , and DSA traditional method as a reference







**EW**

**Concentration**

**Lignin precipitation**

**Solvent recovery**

**Washing**

**Pretreatment**

**Enzymatic hydrolysis**

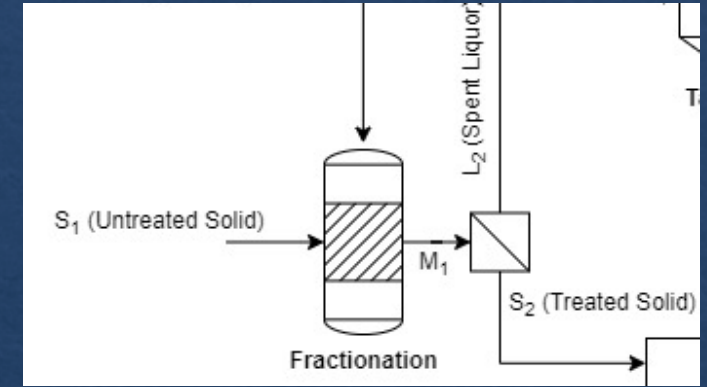
**C5/C6**

**Lignin**

**Glucose**

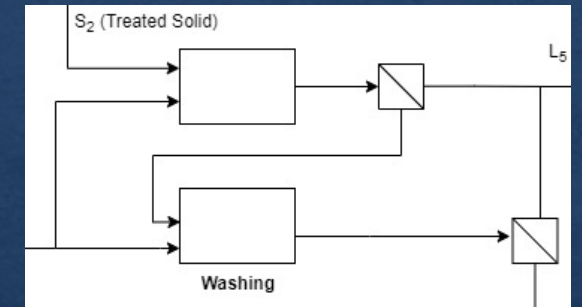
# Simulation conditions DSA/EW

- ◇ Aspen Plus V9
- ◇ Feed rate 100 ton WS/day
- ◇ Pretreatment
  - ◇ L/S ratio: 10/20/30 L.kg<sup>-1</sup>
  - ◇ 160 °C /10 bar/1 hour
- ◇ Solid separation thickened until 40% w/w



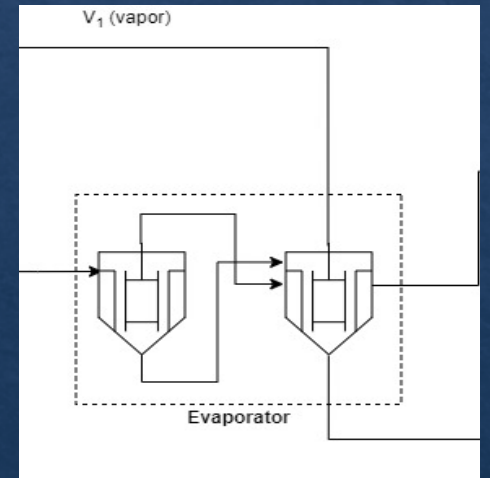
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- ◇ Washing 2 steps, L/S 4:1



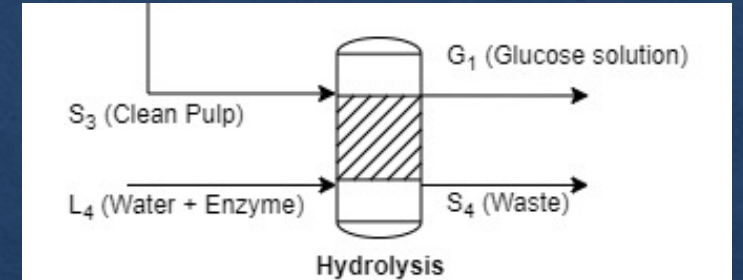
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Xylose + Glucose
- ◇ Enzymatic hydrolysis 48 h, Consistency 10%



# Simulation conditions DSA/EW

- ❖ DSA: 1% (w/w) H<sub>2</sub>SO<sub>4</sub> based on WS weight in water
- ❖ EW:
  - ◇ 1% (w/w) H<sub>2</sub>SO<sub>4</sub> based on WS weight in EW mixture with 25% v/v (28.8% w/w) of ethanol
  - ◇ Distillation column:
    - Fed with 1st. washing liquid stream
    - Efficiency in Ethanol 98%

# Chemical reactions

## ◇ Pretreatment

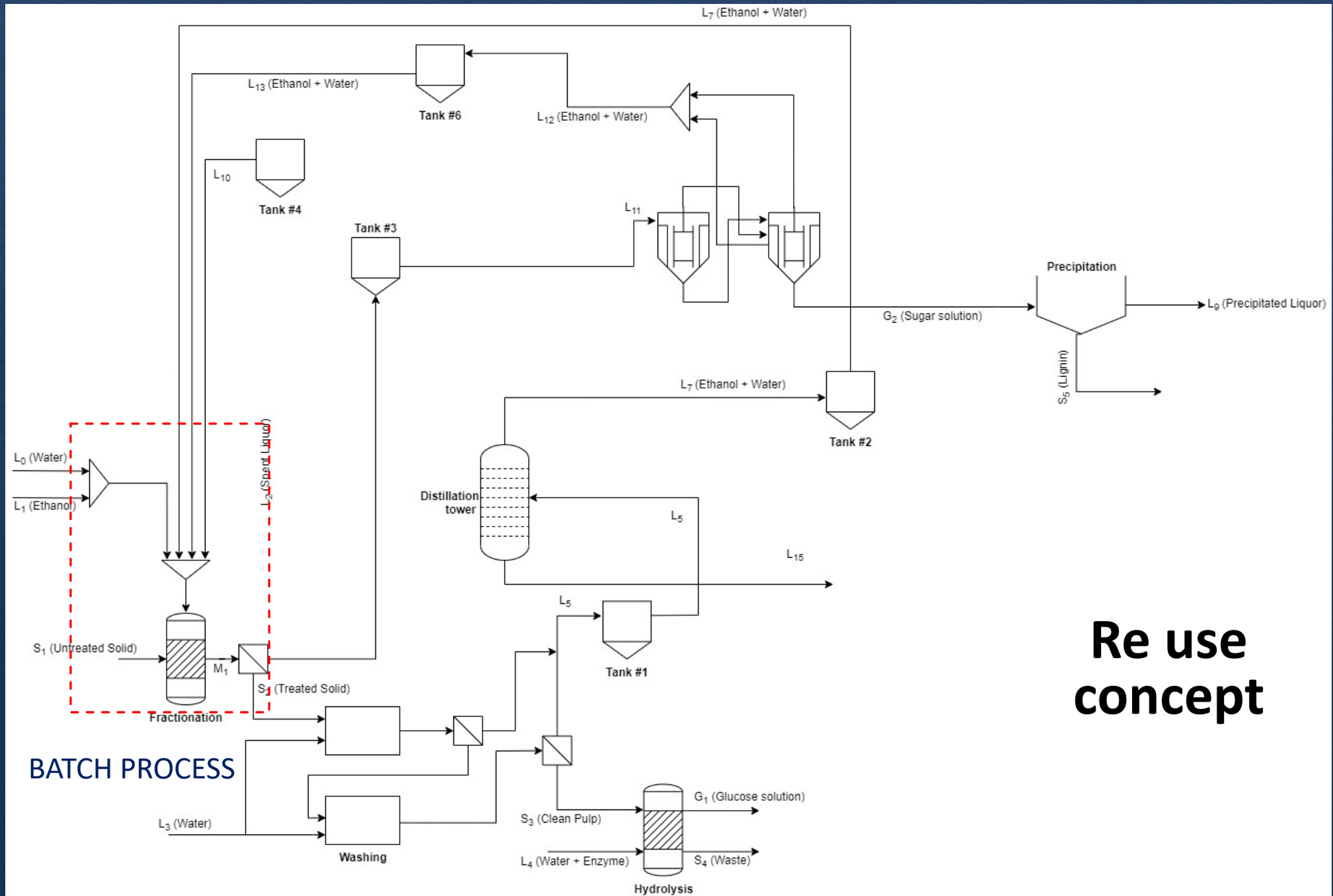
- CELLULOSE (s) + H<sub>2</sub>O (l) → GLUCOSE (aq)
- XYLAN (s) + H<sub>2</sub>O (l) → XYLOSE (aq)
- LIGNIN (s) → LIGNIN (aq)
- XYLAN (s) → FURFURAL (aq) + 2 H<sub>2</sub>O(l)
- CELLULOSE (s) → HMF (aq) + 2 H<sub>2</sub>O(l)
- ARABINAN (s) + H<sub>2</sub>O (l) → ARABINOSE (aq)
- ACETYL GR. (s) → ACETATE (ac)
- ASHES (s) → ASHES (ac)

Conversion fraction	
DSA	EW
0,1476	0,1438
0,8256	0,8259
<b>0,2882</b>	<b>0,5731</b>
0,018	0
0,0024	0
0,9752	0,8414
0,8209	0,7656
0,8	0,8

## ◇ Enzymatic hydrolysis

- ◇ CELLULOSE (s) + H<sub>2</sub>O (l) → GLUCOSE (ac)

0,752	0,767
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**Re use  
concept**

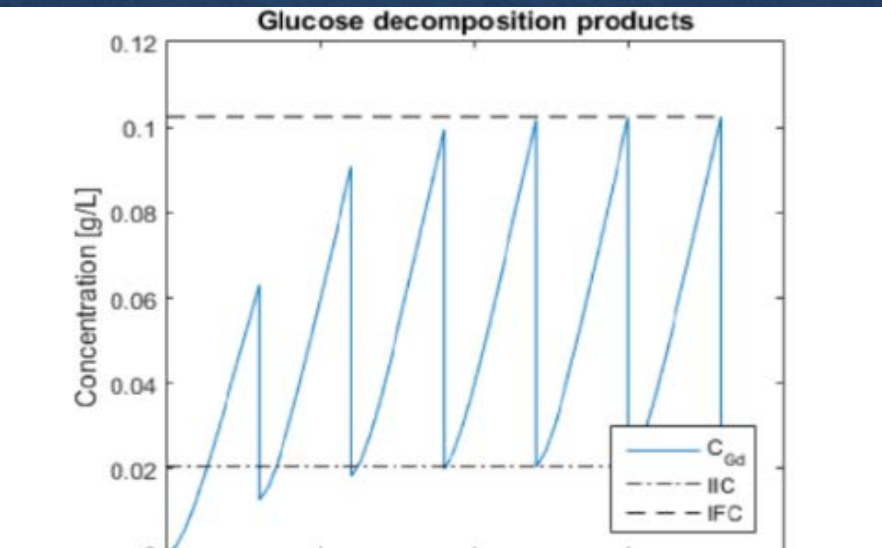
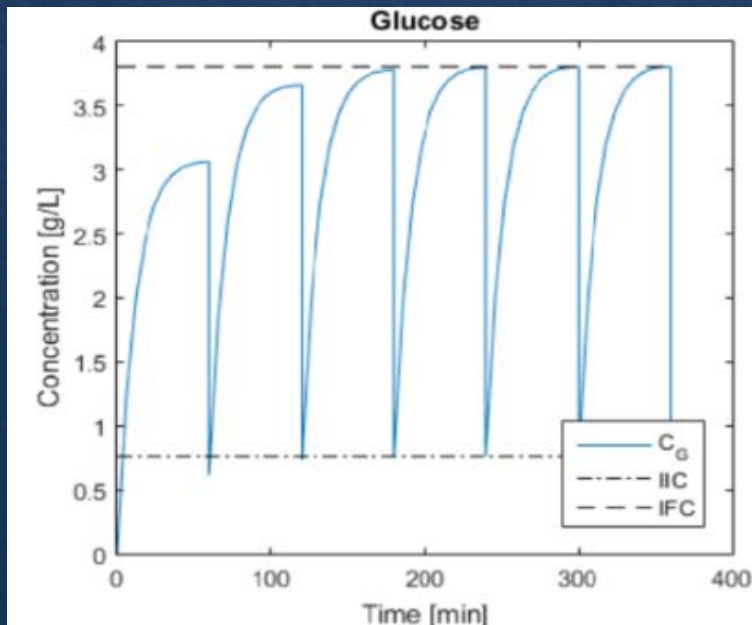


# Re-use strategy in batch operation



# Re-use strategy in batch operation

- Energy, water, and solvent savings
- Consecutive cycles will have different initial conditions



# Liquor re-use drawbacks



Liquor will spend more and more time in the batch reactor. Undesirable reactions like sugar degradation will occur to a greater degree



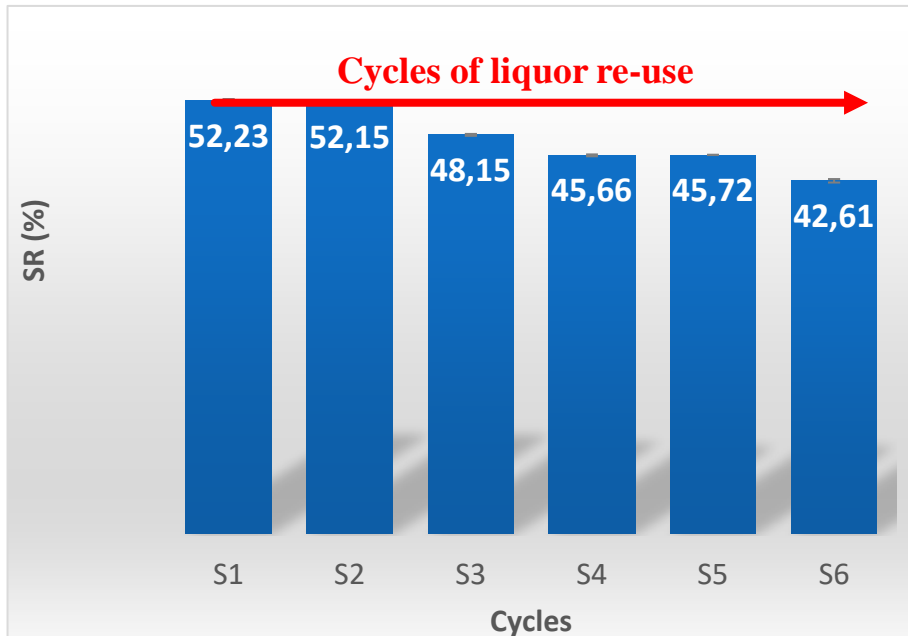
Liquor will concentrate in sugars but also in inhibitor compounds, so they could cause enzymatic inhibition



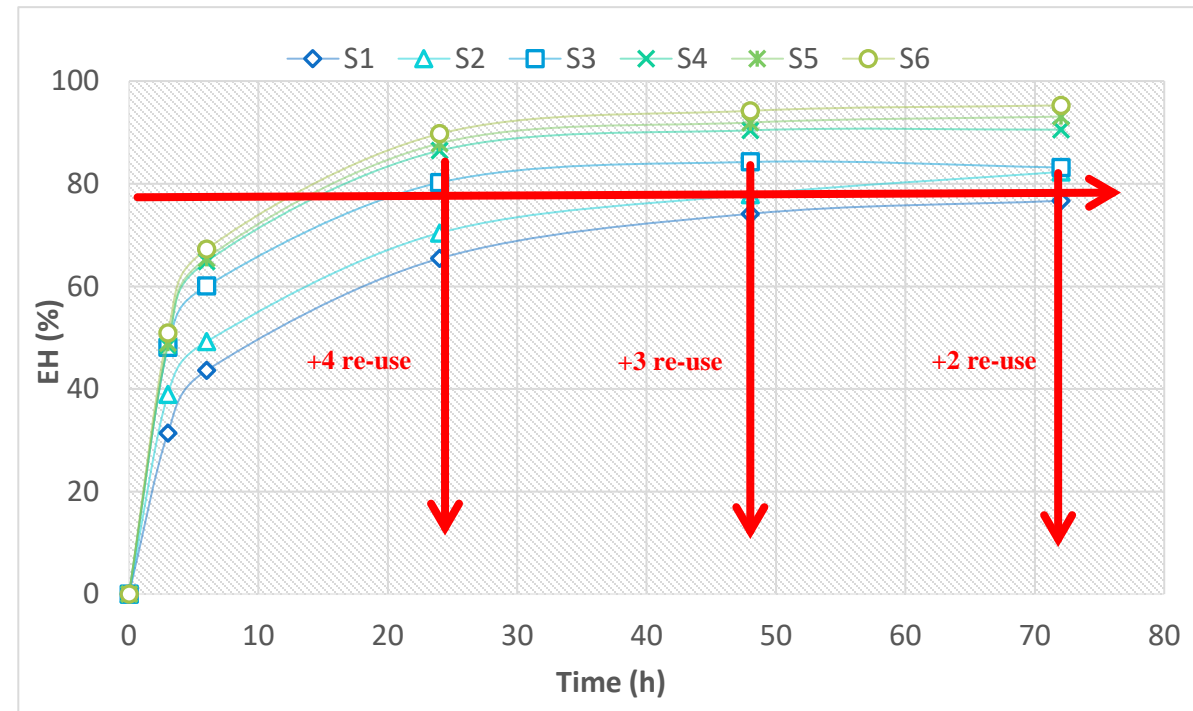
The dynamic nature of this process make the re-use difficult to model and include in a simulation for mass integration.

# Re-use experimental data\_previous work

Vergara et al (2018) Biores.Technol. 256, 178-186



The recovery of solids (SR) decreases as the number or cycles increases ( higher glucan solubilization)



Enzymatic Hydrolysis (EH) occurs faster and in a greater extent.

These two opposing effects compensates and the glucose after enzymatic hydrolisis has similar concentration among re-uses

# Chemical reactions\_EWR conversion factors

## ◇ Pretreatment

- CELLULOSE (s) + H<sub>2</sub>O (l) → GLUCOSE (aq)
- XYLAN (s) + H<sub>2</sub>O (l) → XYLOSE (aq)
- LIGNIN (s) → LIGNIN (aq)
- XILAN (s) → FURFURAL (aq) + 2 H<sub>2</sub>O(l)
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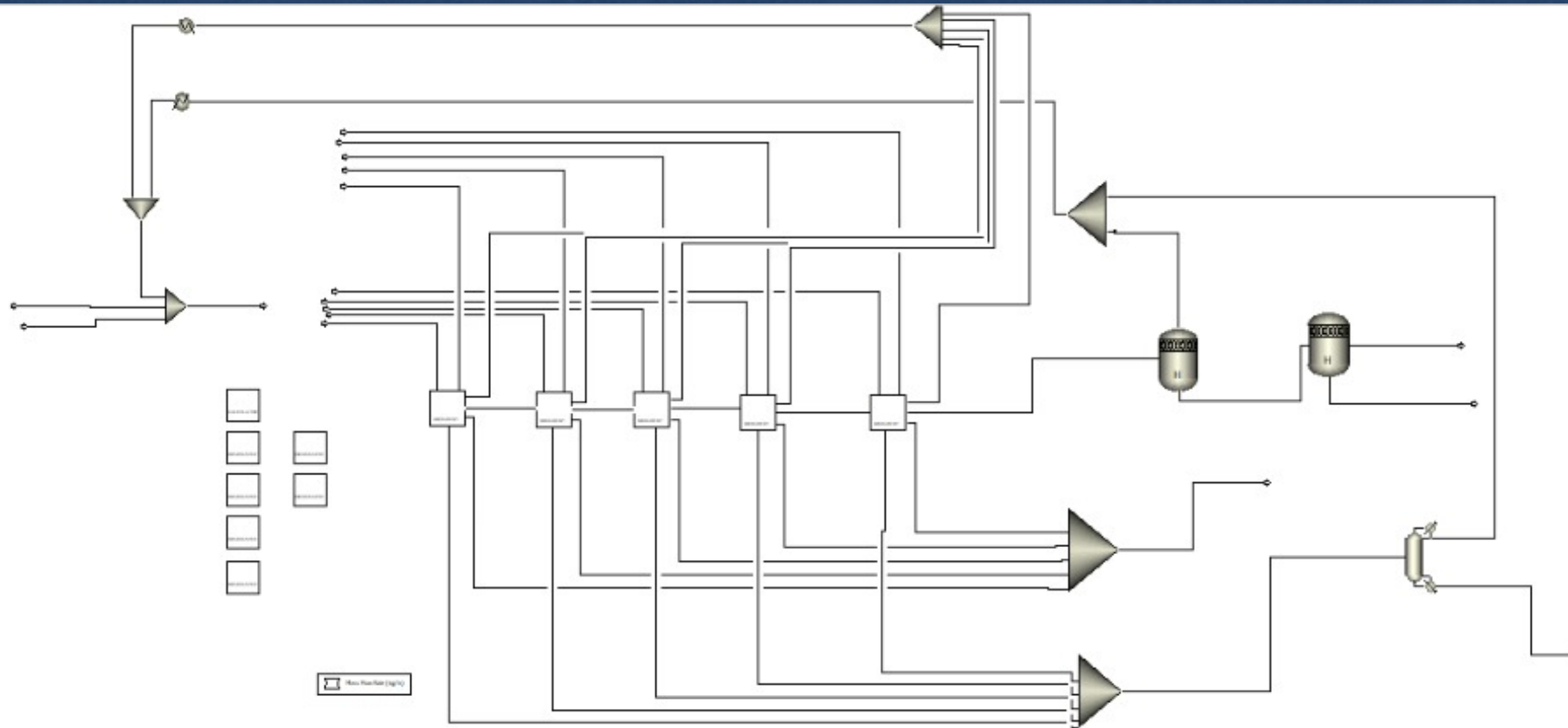
Conversion fraction- RE-USE			
#1	#2	#3	#4
0,1432	0,1997	0,2043	0,2306
0,8335	0,8443	0,8513	0,8650
0,5515	0,5742	0,5673	0,5569
0,028	0,0457	0,0643	0,0767
0	0,0076	0,0048	0,0058
0,8435	0,8575	0,8703	0,8798
0,795	0,8731	0,9086	0,9037
0,8	0,8	0,8	0,8

## ◇ Enzymatic hydrolysis

- ◇ CELLULOSE (s) + H<sub>2</sub>O (l) → GLUCOSE (ac)

0,823	0,832	0,907	0,938
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# Re-use set up

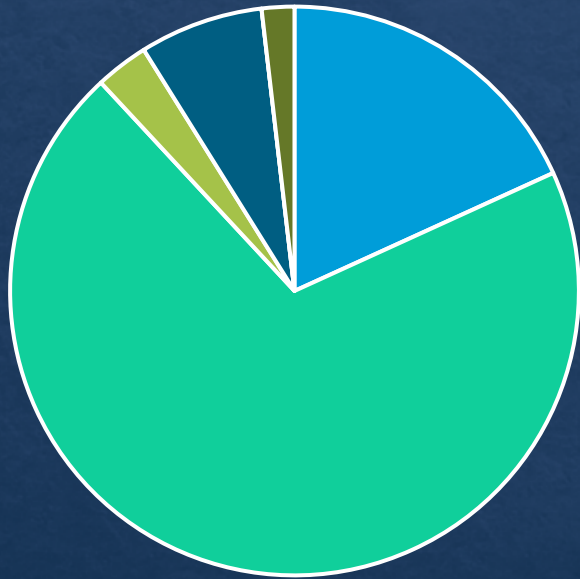


# Process costs

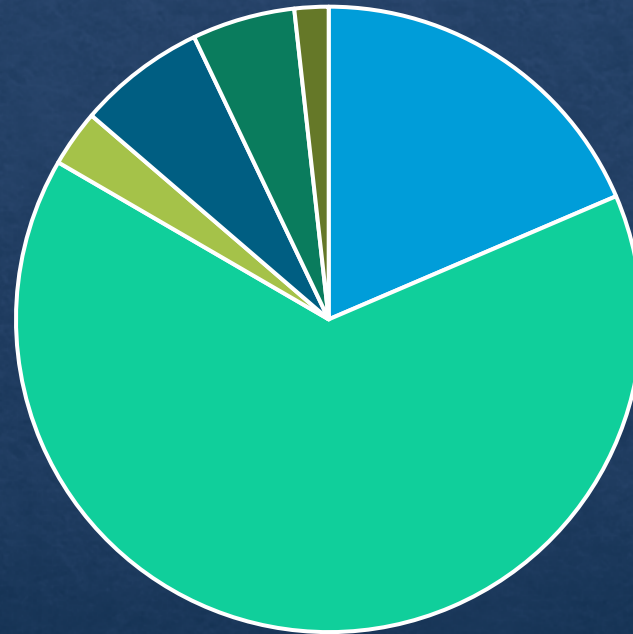
- ◆ Only capital and operating costs (utilities, water and ethanol) have been considered. Other costs were considered similar for all alternatives
- ◆ Costs are not included upstream (stocking and handling of raw materials), nor downstream (use of the sugars obtained)
- ◆ Equipment cost has been annualized considering 10 years life Project

# Results\_ annualized investment costs L/S 20:1

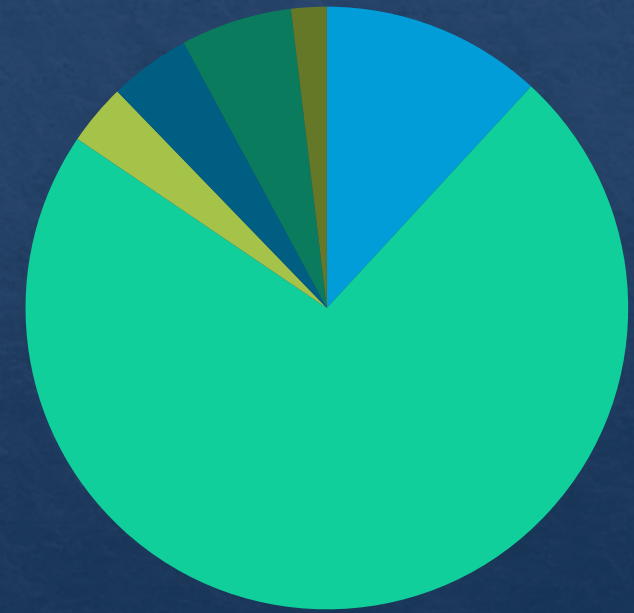
DSA



EW



EWR



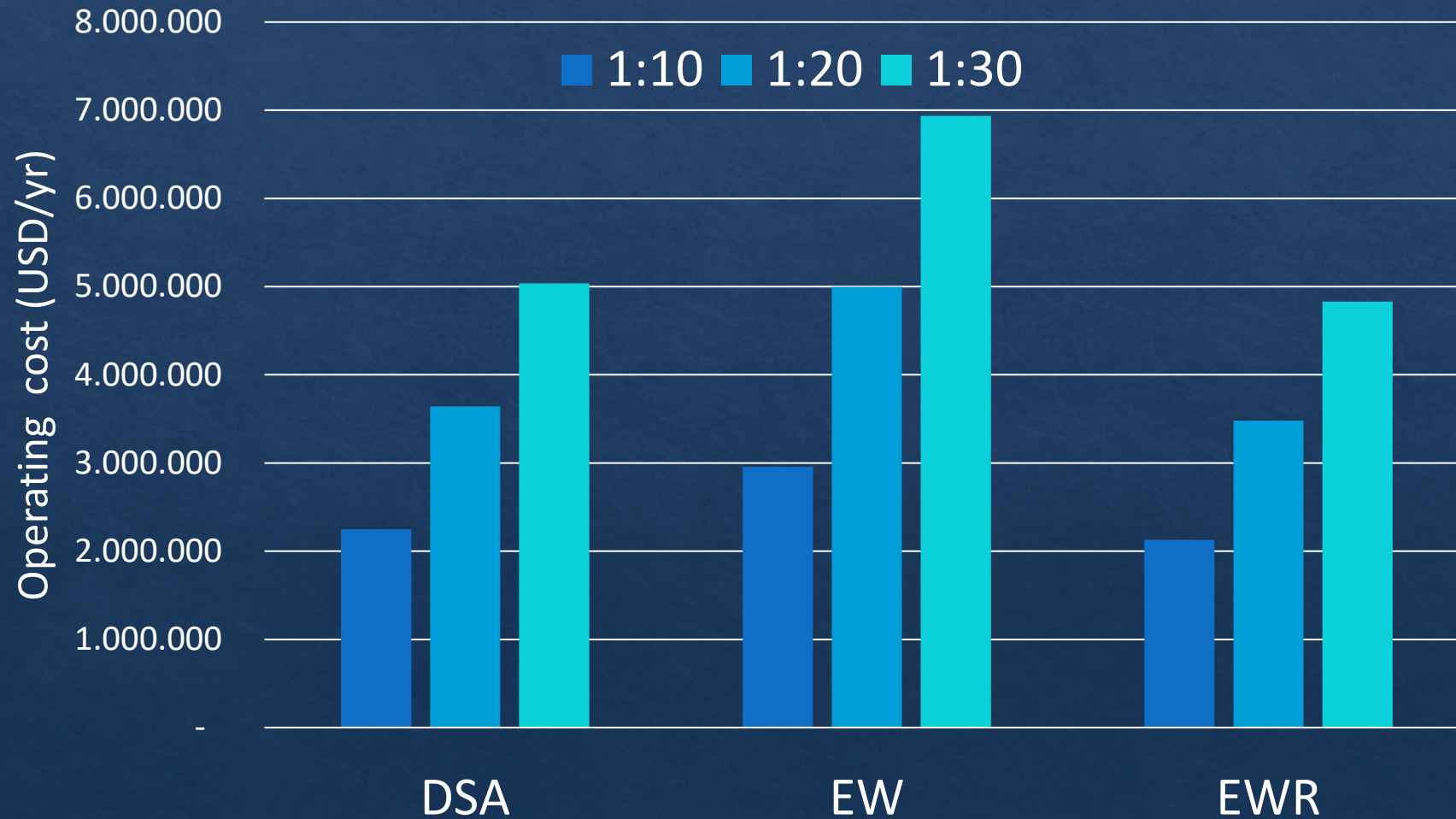
- Pretreatment
- Evaporation

- Enzymatic hydrolysis
- Distillation

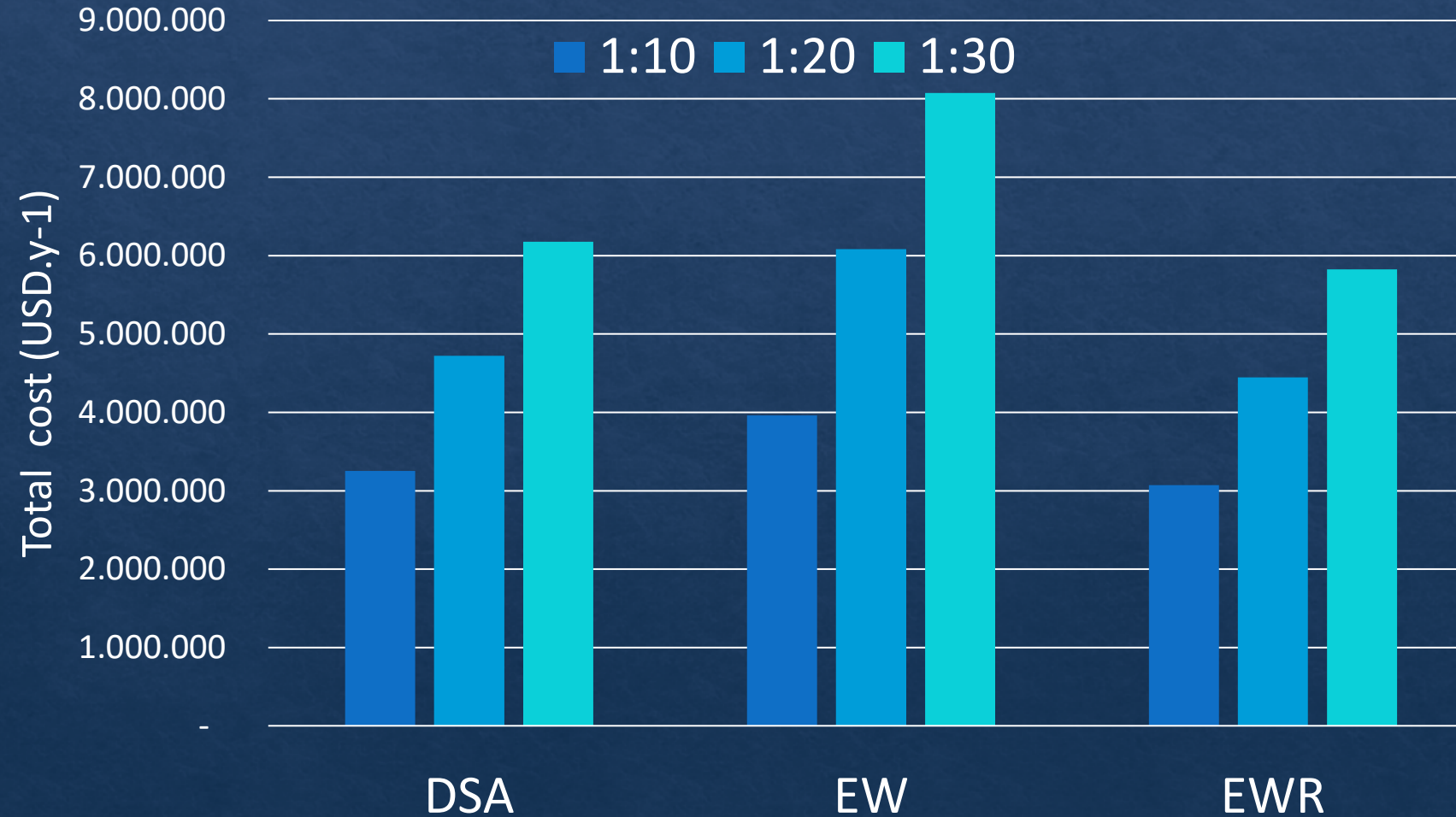
- Washing
- Precipitation



# Results\_operating costs



# Results\_ total costs



# Results\_ L/S ratio

		Facilities, Equipment		Operating Costs (\$/yr)			Total Operating cost	
		(\$/yr)	Ratio	Utilities	Water	Ethanol	(\$/yr)	Ratio
DSA	1:10	1.005.510	<b>1</b>	1.304.028	945.212	0	2.249.240	<b>1</b>
	1:20	1.078.280	<b>1,07</b>	2.552.854	1.089.792	0	3.642.646	<b>1,62</b>
	1:30	1.138.770	<b>1,13</b>	3.803.263	1.234.768	0	5.038.031	<b>2,24</b>

		Facilities, Equipment		Operating Costs (\$/yr)			Total Operating cost	
		(\$/yr)	Ratio	Utilities	Water	Ethanol	(\$/yr)	Ratio
EW	1:10	1.003.030	<b>1,00</b>	1.910.858	846.668	200.276	2.957.802	<b>1,00</b>
	1:20	1.083.600	<b>1,08</b>	3.749.249	951.548	296.772	4.997.570	<b>1,69</b>
	1:30	1.140.800	<b>1,14</b>	5.636.585	969.764	327.724	6.934.073	<b>2,34</b>

		Facilities, Equipment		Operating Costs (\$/yr)			Total Operating cost	
		(\$/yr)	Ratio	Utilities	Water	Ethanol	(\$/yr)	Ratio
EWR	1:10	942.350	<b>1,00</b>	1.166.220	899.455	63.906	2.129.581	<b>1,00</b>
	1:20	967.470	<b>1,03</b>	2.360.794	1.012.354	106.783	3.479.931	<b>1,63</b>
	1:30	997.470	<b>1,06</b>	3.562.812	1.123.868	141.923	4.828.603	<b>2,27</b>

# Conclusions

- ◆ EW is around 30% more expensive than DSA treatment
- ◆ Re-use strategy compared with DSA result in 5% savings, with a better quality lignin
- ◆ Operating cost are more than twice as high when L/S ratio increase from 1:10 to 1:30
- ◆ Total costs are dominated by operating costs (utilities)
- ◆ Investment costs are dominated by enzymatic hydrolysis process

# ACKNOWLEDGEMENTS

## ◆ Authors acknowledge the support of:

- ◆ The Uruguayan National Agency of Research and Innovation
- ◆ The Spanish Science and Innovation Ministry, through projects: CTQ2017-84963-C2 (R-1 and R-2) and PCI2018-093114.
- ◆ The Madrid Regional Government, through the project: RETOPROSOST P2013-MAE2907
- ◆ CYTED (the Ibero-American Programme on Science and Technology for Development), through the thematic network: RESALVALOR 319RT0575

Thank you!

Questions?

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