Analysis of acid-catalyzed pretreatments as the basis for the design of sustainable lignocellulosic biorefineries

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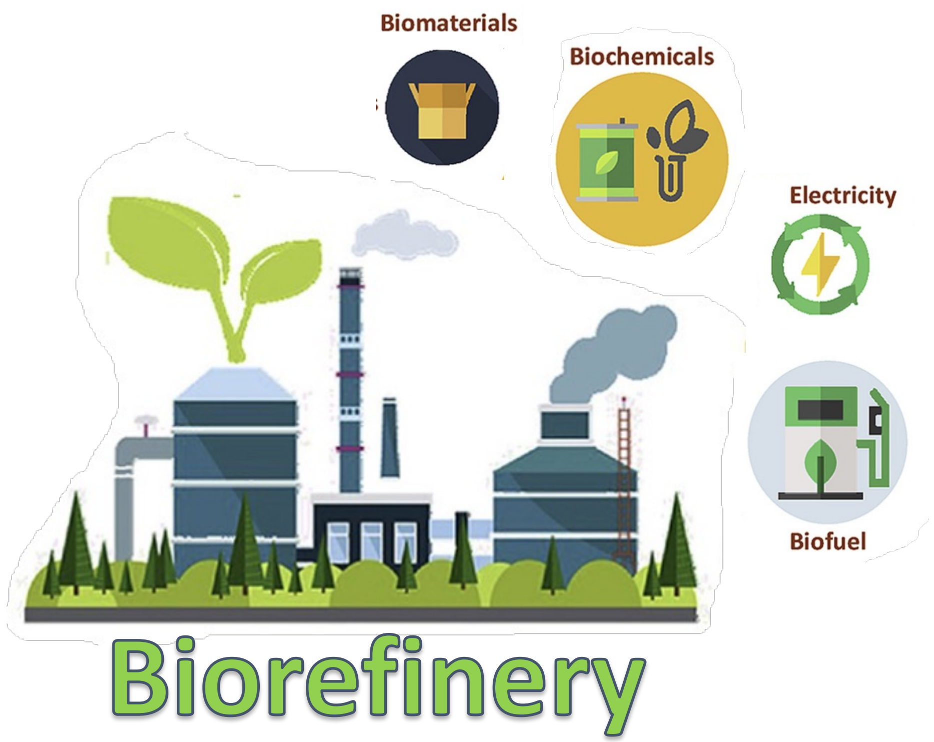
Introduction



Biomass

Process design

Products

Pretreatment

Reaction

Separation

Lignocellulosic raw materials

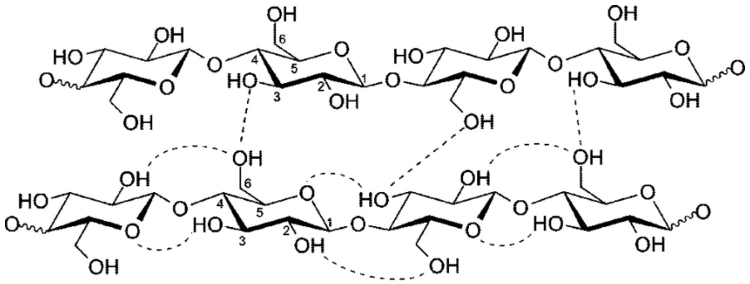


Figure 1. Intra and intermolecular hydrogen bonds in cellulose

Chemical-based pretreatments:

1. Dilute acid
2. Organosolv
3. Solid acid catalyst

- ✓ Sugar formation
- ✓ Lignin solubilization
- ✓ Cellulose cristalinity

- ✓ Energy demand
- ✓ pH corrosion
- ✓ Lignocellulosic fractionation
- ✓ Recyclability

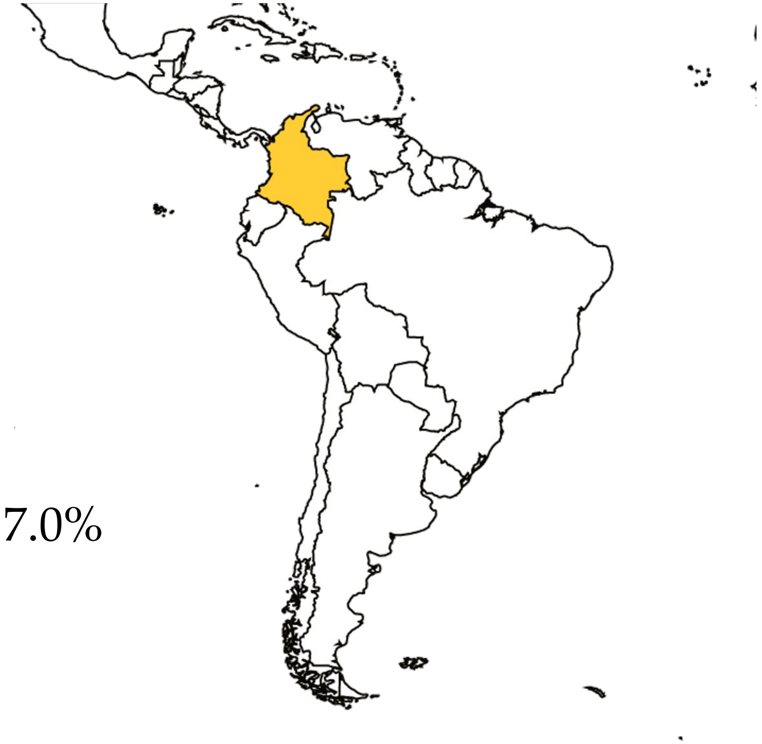
Introduction

Worldwide importance

1. Wheat
2. Corn
3. Rice

In Colombia:

- Gross domestic product (GDP): 7.0%
- Family food basket: 6.2%



Rice processing (milling)

Rice husk: 20-25% wt.

1. Rice husk limitations:

- Accumulation and transport cost.
- Low biodegradability rates.
- Null food supplement and animal feed

2. Environmental impact (landfill and burning)

Research objective

To date, no studies demonstrate the comparison of acid-catalyzed pretreatments considering design factors in biorefineries from a technical, economic, environmental, and social perspectives

Rice husk as feedstock

Experimental procedure

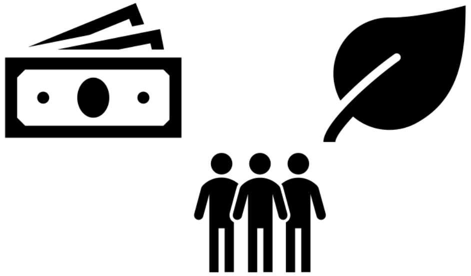
- Dilute acid
- Organosolv
- Solid acid resin

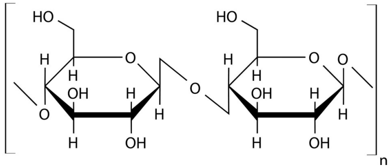
Pretreatment simulation

- Milling
- Heaters
- Reactors
- Filters

Assessment

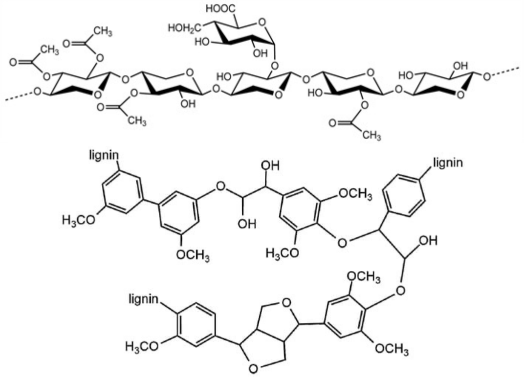
- Techno-economic
- Environmental
- Social





Cellulose in the water-insoluble solid

+



Hydrolyzate of pentoses and lignin

Methodology
Pretreatment of rice husk

$$\text{Log}(R_0) = \text{Log}\left(t \times \exp\left[\frac{T - 100}{14.75}\right]\right) = 3.61$$

Table 1. Chemical composition of rice husk

Component	Mass composition (% in dry basis)*
Initial moisture	12.0 (0.03)
Chemical composition	
Cellulose	29.34 (0.76)
Hemicellulose	15.02 (0.75)
Lignin	29.14 (0.11)
Total extractives	7.86 (1.23)
Water extractives	3.32 (0.90)
Ethanol extractives	4.54 (0.84)
Fats	3.80 (0.26)
Protein	1.29 (0.02)
Pectin	13.55 (1.47)
Proximate composition	
Volatile matter	64.66 (0.35)
Fixed carbon	10.76 (0.39)
Ash	18.52 (0.18)
Moisture	6.05 (0.04)
Heating value (MJ kg^{-1})	13.85
Solid composition	
Volatile solids	74.52 (0.15)
Total solids	93.91 (0.61)
Fixed solids	18.78 (0.62)

*Values in brackets refer to the standard deviation.

- **Dilute acid and organosolv pretreatments**
  - T = 175°C
  - t = 35 min
  - Feed = 1:20 (g mL^{-1})
  - Dilute acid: 2% H_2SO_4
  - Organosolv: 50% EtOH with 23 mM H_2SO_4

  Degradation temperature (Amberlyst® 36): 150°C

- **Solid acid resin pretreatment**
  - Resin: Amberlyst® 36 (3.5 m-eq g^{-1})
  - T = 140 °C
  - t = 4.45 h
  - Feed = [H^+] (dilute acid)

- **Analysis of the water-insoluble solid and the hydrolysate**
  - Recharacterization of:
    - Cellulose [1]
    - Hemicellulose [1]
    - Lignin (NREL/TP-510-42618)
  - X-ray diffraction (Cu Kα radiation at 30 kV and 15 mA, 2° min^{-1}, range of 2θ = 3 – 60°)
  - Sugar quantification by HPLC

[1] J.S. Han and J.S. Rowell. CRC Press, 1996. pp 83-134

Methodology
Sustainability assessment

1. Techno-economic analysis

- ✓ Rice husk: 50 ton d^{-1}
- ✓ Scope: pretreatment stage (filtration)
- ✓ CapEx: direct cost + civil work, installation, piping, electrical
- ✓ OpEx: raw materials, utilities, maintenance and labor
- ✓ Location: Colombia

2. Environmental analysis

- ✓ Software: Waste Reduction Algorithm (WAR)
- ✓ Scope: pretreatment stage
- ✓ Indicators:
  - o Toxicity by ingestion (HTPI)
  - o Toxicity by dermal exposure (HTPE)
  - o Terrestrial toxicity (TTP)
  - o Photochemial oxidation (PCOP)

3. Social analysis

- ✓ Database: Product Social Life Cycle assessment (PSILCA)
- ✓ Indicators:
  - Water demand:
    - o Level of industrial water use (withdrawal)
    - o Level of industrial water use (renewable)
  - Energy demand:
    - o Energy demand
    - o Extraction of fossil fuels
- ✓ Location: Colombia

$$W_{withdrawal} = \frac{Water_{process} + Water_{cooling}}{Water_{withdrawal}\text{ of the industrial sector}}$$

$$W_{renewablee} = \frac{Water_{process} + Water_{cooling}}{Water_{renewable}\text{ in Colombia}}$$

$$E_{demand} = \frac{\text{Electrical energy}}{\text{Available electrical energy}}$$

$$E_{fossil} = \frac{\text{Steam thermal energy}}{\text{Available energy from diesel}}$$

Methodology

Sustainability assessment

1. Selection of indicators for each dimension
2. Normalization of indicators based on the best and worst results [2]

$$\text{Normalization} = \frac{\text{Actual} - \text{Min}}{\text{Max} - \text{Min}}$$

3. Overall indicator (OI_j) considering a weight factor (w_i). Applied for each dimension

$$\text{Overall indicator } (\mathrm{OI}_j) = \sum \mathrm{w}_i \times \text{Indicator}_i$$

4. Impact score (s_i) analysis based on statiscal distribution: allocation of max (40%) and min (10%) as well as equal allocation (25%) for each dimension
5. Sustainability index ($\mathrm{S_I}$)

$$\text{Sustainability index } (\mathrm{S_I}) = \left(\sum \mathrm{s_i} \times \mathrm{OI}_j\right) \times 100$$

$$\mathrm{S_I} = \left(\mathrm{s_1} \sum \text{Technical} + \mathrm{s_2} \sum \text{Economic} + \mathrm{s_3} \sum \text{Environmental} + \mathrm{s_4} \sum \text{Social}\right) \times 100$$

[2] G.J Ruiz-Mercado, R.L Smith, and M.A Gonzales. Ind Eng Chem Res, 15. pp. 2309-2328

Results

Rice husk pretreatment

Remarks

1. Hemicellulose solubilization: dilute acid pretreatment
2. Enzymatic digestibility (hemi + lig): organosolv pretreatment
3. High pH difference: 1.31 due to acetyl groups accumulation
4. Solid acid resin promotes pentose formation
5. Higher glucose production from organosolv pretreatment

Table 2. Summary of acid-catalyzed pretreatments of rice husk.

Analysis	Pretreatment		
	Dilute acid	Organosolv	Solid resin
Solid recovery (%)	57.5	48.25	71.06
Removal (%)			
Cellulose	9.42	8.34	9.92
Hemicellulose	75.64	66.78	63.97
Lignin	14.34	49.39	8.73
Monomers in the hydrolysate (g L^{-1})			
Arabinose	-	0.54	0.58
Fructose	0.27	-	0.25
Glucose	0.09	1.50	0.75
Xylose	3.50	2.96	3.63
Oligomers in the hydrolysate (g L^{-1})			
Glucose	0.07	0.70	0.30
Xylose	0.37	0.27	1.14

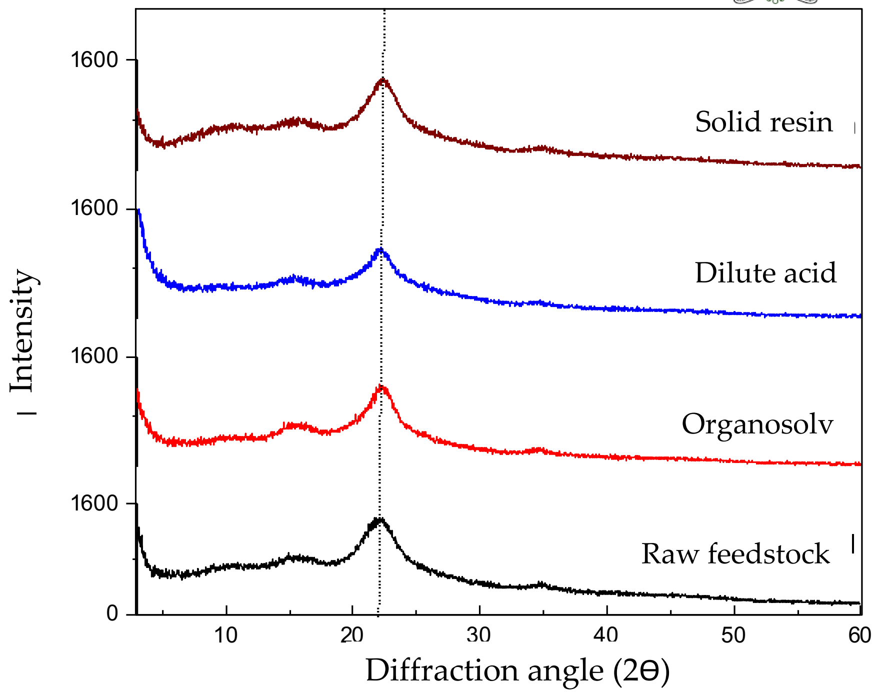


Figure 2. XRD patterns of untreated and pretreated rice husk.

Crystallinity index (CrI)

- Raw feedstock: 40.7%
- Dilute acid: 35.2%
- Organosolv: 42.1%
- Solid acid resin: 39.3%

Most severe pretreatment (decrystallization and degradation)

$$CrI = \frac{I_{002} - I_{am}}{I_{002}} \times 100$$

CrI increase (Amorphous fraction removal)

Results

Techno-economic

Table 3. Overall yields and process water demand.

Pretreatment	Overall cellulose yield (kg kg^{-1})	Overall C5 sugars yield (kg kg^{-1})	Total process water (m^3 d^{-1})
Dilute acid	0.20	0.098	4444.3
Organosolv	0.21	0.086	3594.2
Solid acid resin	0.19	0.081	4437.5

Table 4. Utility yields based on the feedstock flowrate.

Pretreatment	LP steam (kg kg^{-1})	MP steam (kg kg^{-1})	Cooling water (m^3 kg^{-1})	Electricity (MJ kg^{-1})
Dilute acid	2.77	7.81	-	250.2
Organosolv	63.27	3.41	-	414.4
Solid acid resin	3.29	4.99	-	307.2

Table 5. Capital (CapEx) and operating (OpEx) expenses.

Economic parameter	Pretreatment		
	Dilute acid	Organosolv	Solid acid resin
CapEx (M-USD)	0.94	3.26	1.64
OpEx (M-USD year^{-1})	6.97	79.28	82.58

Remarks

1. No differences in the cellulose yield
2. Hydrolyzed pentose losses (filtration):
   - Dilute acid: 0.4%
   - Organosolv: 0.5%
   - Solid acid resin: 3.7%
3. Lower water demand for organosolv (dilution of feed ratio)
4. The solvent recovery stage increased all the utility demands
5. No cooling water requirement. Energy from cold processing streams such as washing waste streams.
6. Solvent recovery stage: 73.1% of the total CapEx in organosolv
7. Amberlyst® 36: 96.2% of the total OpEx
8. Catalyst recyclability by mesh support
   - Reusable assays: four for production yield reduction of 30% [3].
   - OpEx savings: 34% (total OpEx of 54.9 M-USD year^{-1})

[3] H.W. Joo, H. Ryu, and Y.K. Chang. Biotech Biop Eng, 24 (6). pp. 990–996

Results
Social and environmental

Remarks

1. No water risk in the Colombian context
2. Less water demand for organosolv pretreatment (dilution rate)
3. Fossil energy demanded for organosolv pretreatment (solvent recovery)

- ✓ Water availabilities (2019):
  - Industrial = 37.3 x10^8 m^3
  - Colombia = 21.45 x10^{11} m^3
- ✓ Electricity capacity (2021): 72,824 GWh
- ✓ Diesel production (2021): 2.19 x10^9 gallons (24.1 x10^{10} MJ)

Table 6. Results of social indicators

Pretreatment	$W_{withdrawal}$ (m^3 m^{-3})	$W_{renewable}$ (m^3 m^{-3})	E_{demand} (MW MW^{-1})	E_{fossil} (MJ MJ^{-1})
Dilute acid	9.44 x10^{-5}	1.64 x10^{-7}	1.99 x10^{-9}	6.31 x10^{-8}
Organosolv	1.13 x10^{-5}	1.96 x10^{-8}	3.29 x10^{-9}	3.98 x10^{-7}
Solid acid resin	9.12 x10^{-5}	1.59 x10^{-7}	2.44 x10^{-9}	4.83 x10^{-8}

8. The environmental impact is drastically affected by the disposal of hydrolysates
9. pH nature influence the toxicological indicators
10. Ethanol affected the PCOP (formation of acetaldehydes)

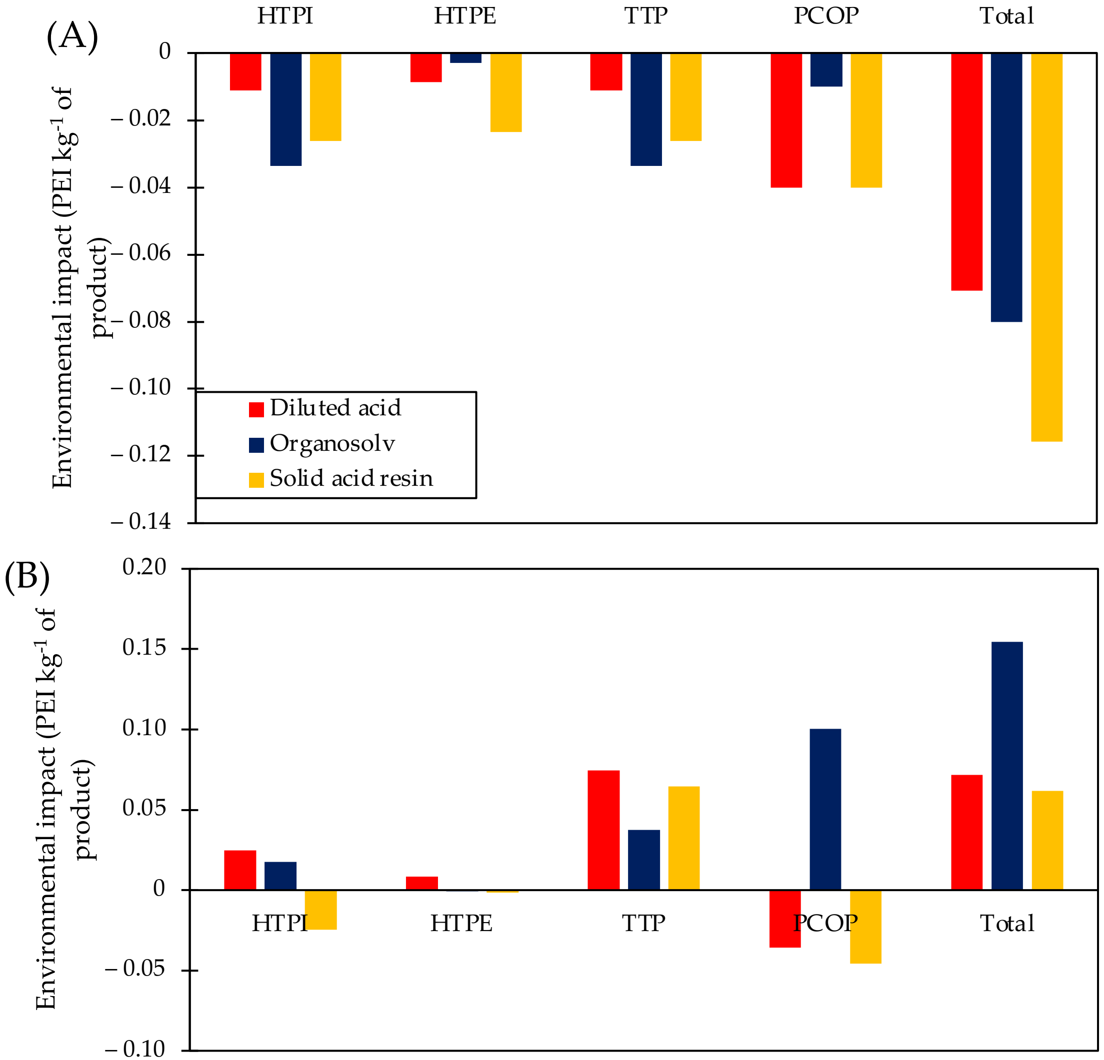


Figure 3. Potential environmental impact of pretreatments when the system product is (A) the WIS and hydrolysate and (B) only the WIS.

Results

Sustainability assessment

Proposed sustainability (S_I) scale:
- High: $S_I > 70\%$
- Medium: $40\% \leq S_I \leq 70\%$
- Low: $40\% < S_I$ to low indexes.

Indicators for dimension

1. Technical
   - Five-carbon sugar yield (w_i of 0.7)
   - Steam demand (w_i of 0.3)
2. Economic
   - CapEx (w_i of 0.3)
   - OpEx (w_i of 0.7)
3. Environmental
   - PEI using the WIS and hydrolysate as product (w_i of 0.7)
   - PEI using the WIS as product (w_i of 0.3)
4. Social
   - Industrial water use (w_i of 0.4)
   - Thermal energy demand (w_i of 0.6)

Remarks

1. The dilute acid showed the highest sustainability index
2. Dilute acid: techno-economic dimensions (40%). Best sugar solubilization and lower CapEx and OpEx
3. Dilute acid: maximizing the social (ES and TS) and environmental dimensions (TA or EA) decrease the sustainability by 14% and 35%, respectively.

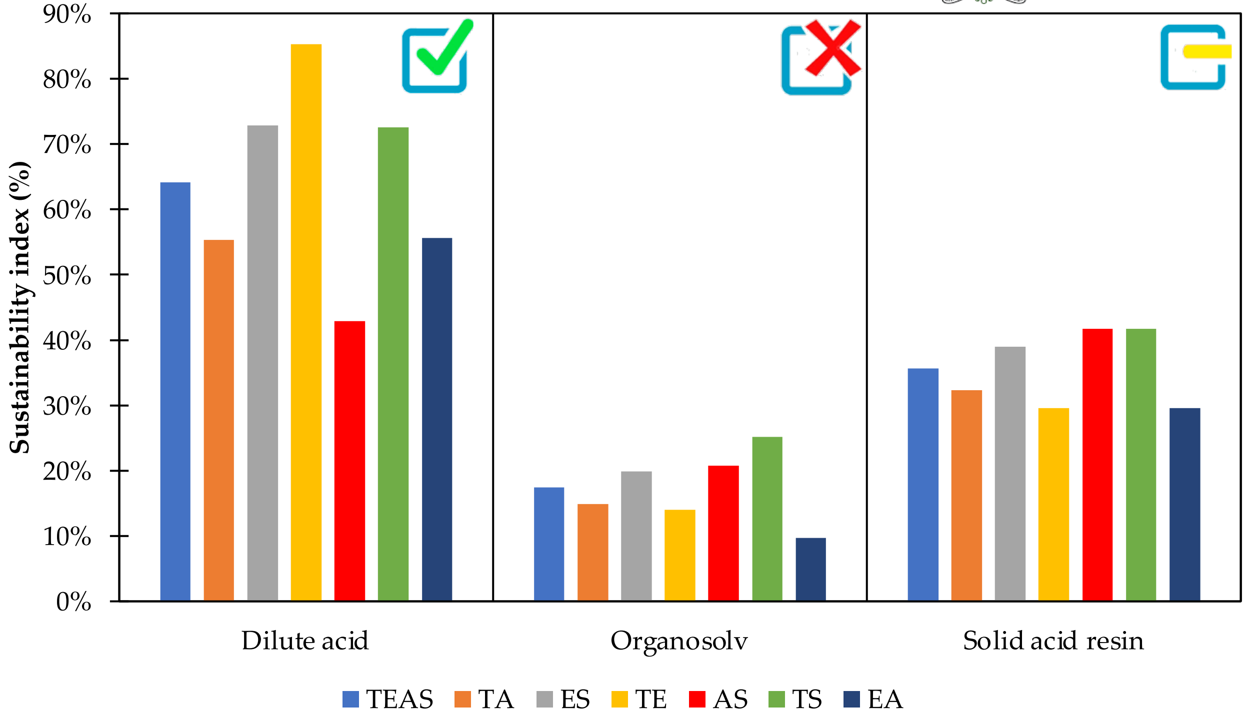


Figure 3. Sustainability index for the pretreatment schemes. Each dimension combination regards a maximum impact score of 40%. T: technical, E: economic, A: environmental, and S: social

Example of nomenclature

TEAS:

$$S_I = \left(25\% \sum \text{Technical} + 25\% \sum \text{Economic} + 25\% \sum \text{Environmental} + 25\% \sum \text{Social}\right) \times 100$$

TE:

$$S_I = \left(40\% \sum \text{Technical} + 40\% \sum \text{Economic} + 10\% \sum \text{Environmental} + 10\% \sum \text{Social}\right) \times 100$$

Conclusions and acknowledgments

Experimental

By increasing the pH degree, higher hemicellulose is solubilized and decrease the crystallinity index (dilute acid scheme)

Simulation

Despite the good removals and the xylose content in the hydrolysate as well as the best environmental impact, the cost of the resin drastically affects operating costs of the solid acid resin pretreatment.

Overall

The dilute acid pretreatment proved to be the most sustainable, maximized when the assessment contemplates higher weighting factors in the technical and economic dimensions.

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