Laboratório Nacional de Energia e Geologia, I. P.

Main Challenges and Achievements on Lignocellulosic-based ethanol Biorefineries

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ETIP Bioenergy, WG2 webinar, Nov 11th, 2020

REPÚBLICA PORTUGUESA

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CONTENT

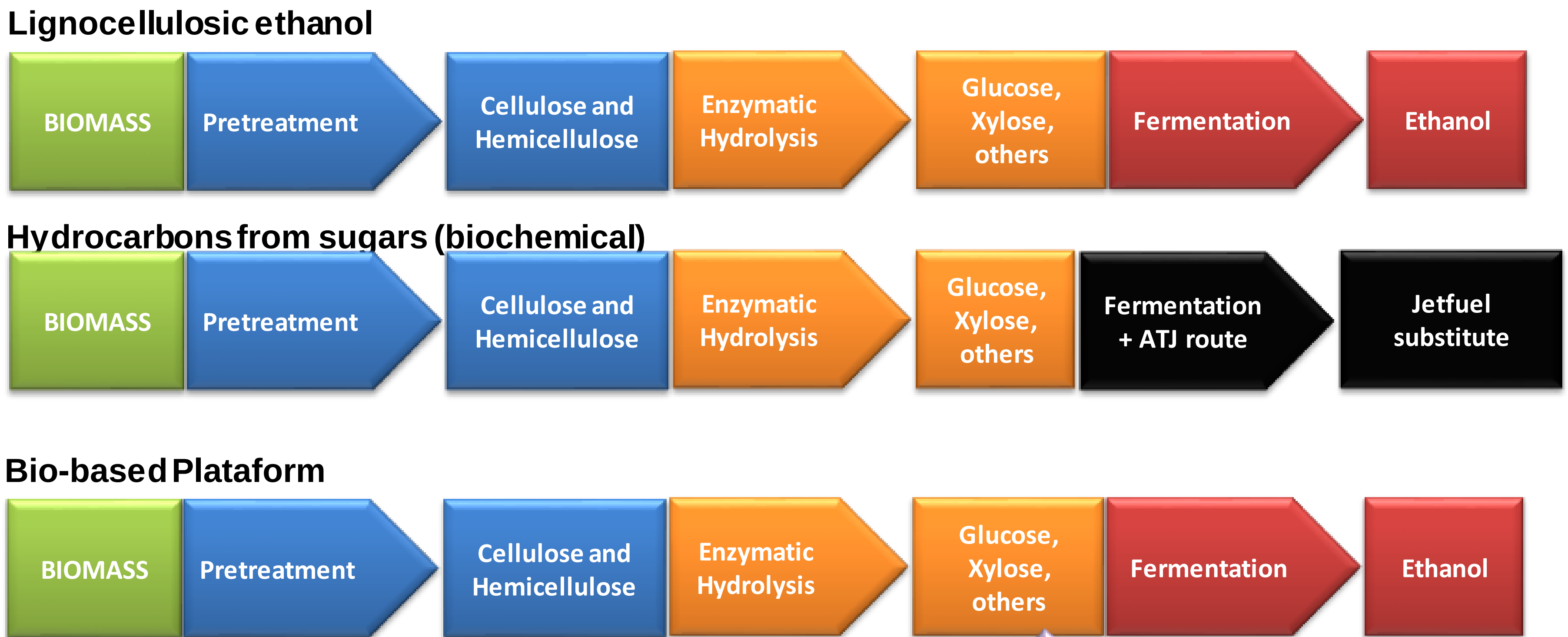
1. Bioethanol: more than a biofuel

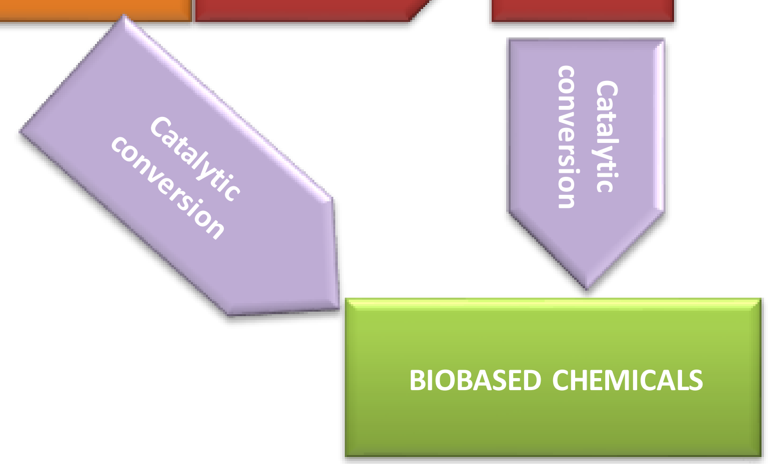
2. Why 2G ethanol is still not cost-competing

3. Main technological challenges for competitive 2G ethanol biorefineries

4. What are the next achievements?

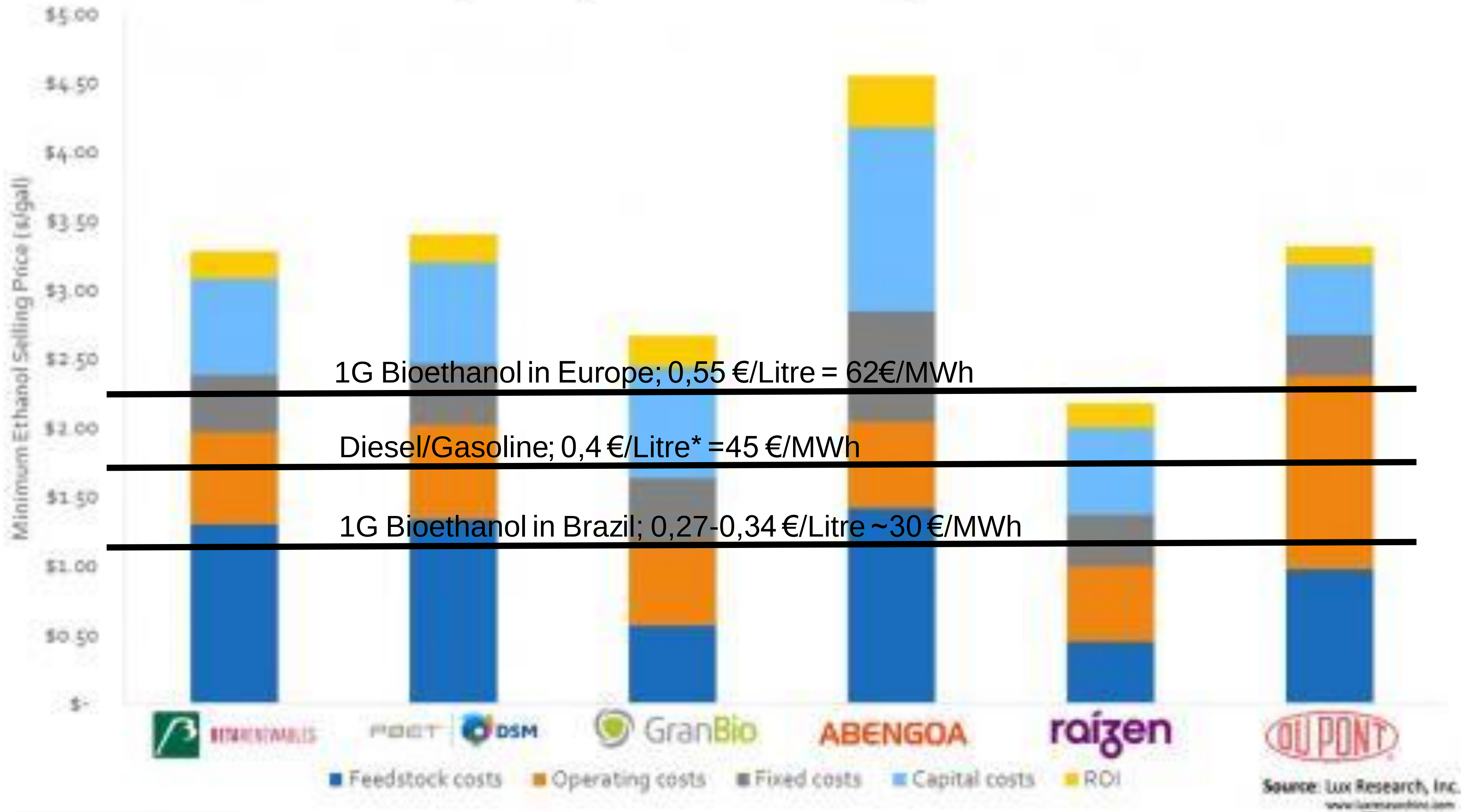
Cellulosic Bioethanol: more than 2G biofuel





- ✓ **Biofuels (Road: ICE & FCVs; ATJ for aviation)**
- ✓ **Sugar plataform (standalone)**
- ✓ **Biobased chemicals**

Estimated Cellulosic Ethanol Production Costs



* Considering 45 USD/bll crude oil

Source: Lux Research Inc.

Why 2G Bioethanol (from biochemical routes) is still not cost-competing with 1G Bioethanol ?

- **Feedstock availability & supply (clean and at low-cost)**

- **High CAPEX and OPEX costs compared to 1G ethanol**

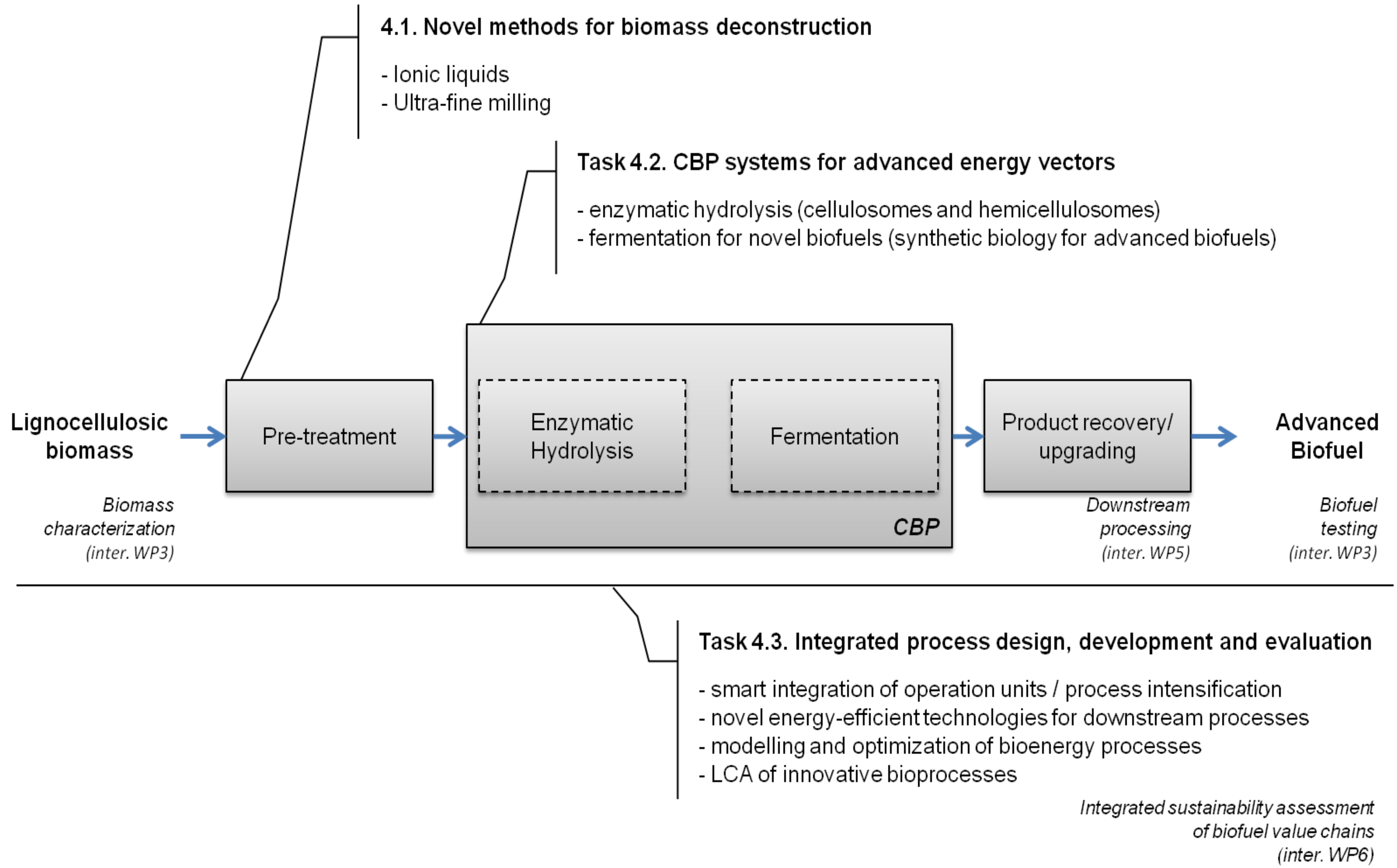
  - **Pretreatment and enzyme production are more costly and energy demand (and less sustainable in terms of GHG emmissions) than the combined "enzymatic hydrolysis + fermentation" steps.**

  - **Lower performance of 2G strains (1G strain consumes C6 sugars in 8 hours; the best 2G strains consumes LC sugars into 36-40 h)**

  - **The non-fermentable component of biomass (Lignin) is usually burnt to supply the energy required for the overall plant energetic demand (*low energy-efficiency*)**

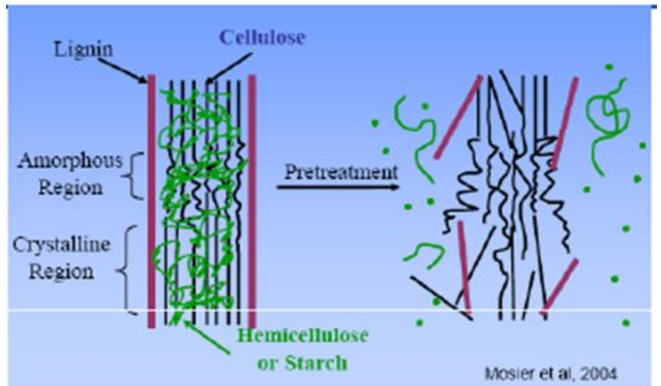
  - **Quality of lignin for valorization towards new end-uses**

The Lignocellulosic Ethanol Technology: in short



Pretreatment Technology: Challenges

Feedstock Challenge:
Lignocellulose biomass recalcitrance and heterogeneity is an issue!

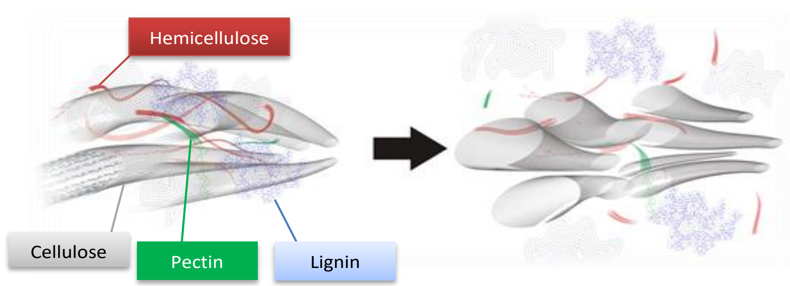


Mosier N, Wyman C, Dale B, Elander R, Lee YY, Holtzapple M, Ladisch MR, 2004.

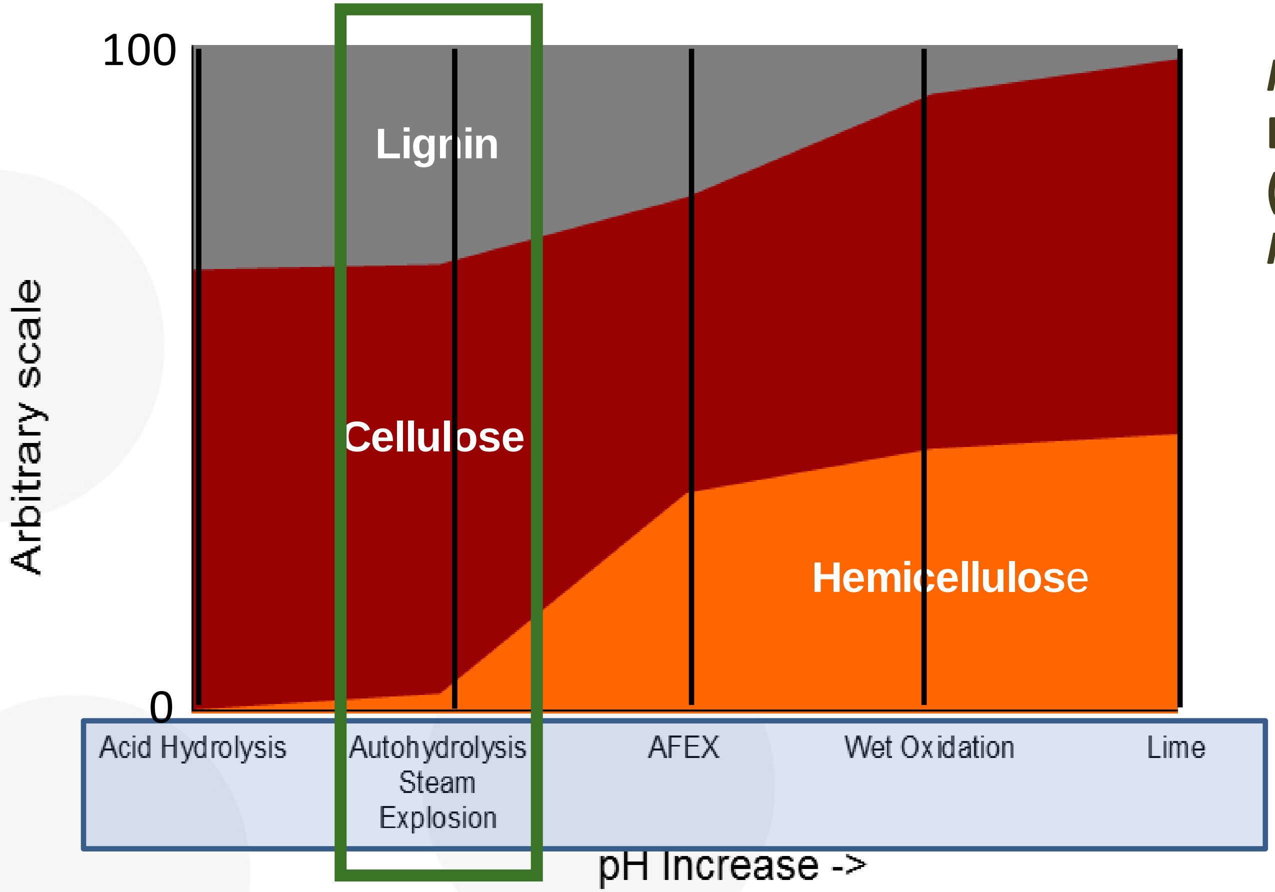
Pretreatments → ***Essential to disrupt the complex structure of lignocellulosic biomass*** → **Hemicellulose solubilization**
↑ Extraction of lignin
↓ Crystallinity of cellulose

↓

↑ Surface area for enzyme binding and attack



Biomass composition after pretreatment



In: Carvalheiro, F., Duarte, L.C., Gírio, F. M. (2008). *J. Scientific & Ind. Res.*, 67, 849-864

- ❑ **CAPEX expensive**
- ❑ **Insufficient (or no) separation of cellulose and lignin**
- ❑ **Formation of by-products that inhibit fermentation**
- ❑ **Use of chemicals and energy-intensive**

Steam explosion pretreatment

Steam explosion (uncatalyzed)

- Saturated steam (< 240ºC, seconds-minutes)
- Biomass is wetted by steam at high pressure and then exploded when pressure within the reactor is rapidly released
- Disaggregation of lignocellulosic matrix, breaking down inter- and intra-molecular linkages (forces resulting from decompression), ultrastructure modification

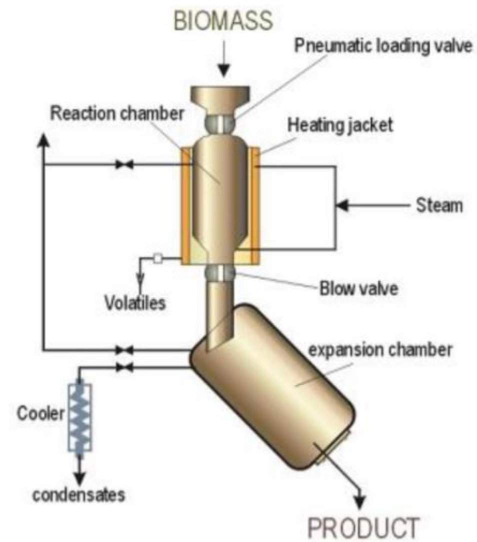


Figure 28: Steam explosion process (Isabella De Bari)

Adapted from: "Lignocellulosic ethanol" (2013), D. Chiaramonti, A. Giovannini, R. Janssen, R. Mergner, WIP Renewable Energies

Foto: Valmet

Courtesy from CTBE, Campinas, Brasil (StEx from Andritz)

Pretreatment at Demo/Industrial scale

Raízen, Piracicaba-SP, Brasil

Acid-catalysed StEX

Clariant, Straubing, Germany

Uncatalysed StEX

(Announced plans for plants in RO, SK, PL, BG and China)

Poet-DSM, Emmetsburg, USA

Acid catalysed StEX

Versalis, Crescentino, Italy

Uncatalysed StEX

GranBio, São José Alagoas

Uncatalysed StEX

Dupont, Nevada, USA

Steam + diluted ammonia

Pretreatment Technology: Challenges

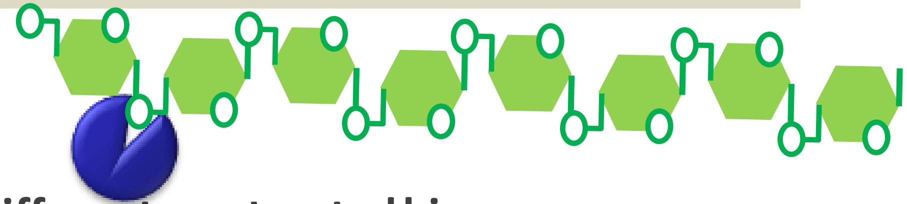
Feedstock Challenge:
Lignocellulose biomass recalcitrance and heterogeneity is an issue!

- ❑ **Biomass (physico-chemical properties)**
  - ❑ Absorption vs Adsorption
  - ❑ Adhesion (to mechanical components)
  - ❑ Abrasive effect (on the screws)

→ **Mechanical performance:**
  - ❑ Clean biomass pressurisation on **continuous systems** is a bottlenck

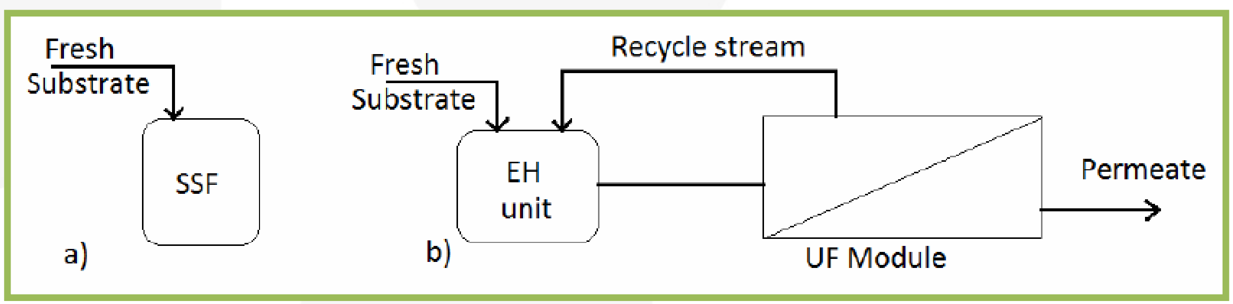
- ❑ **Chemical & Energy performance:**
  - ❑ **Avoid the use of Catalysts** (this increase Lignin purity & value)
  - ❑ **Decrease Reaction Temperature** (this increase Energy Effic.)
  - ❑ **Avoid the generation of inhibitors** (this increase fermentation yields & improve downstream processing)
  - ❑ **Evaluate sustainability impact**

Challenges for Enzymatic Hydrolysis - Strategies



Current Strategies:

- ❑ **Improvement of enzyme efficiency towards different pre-treated biomass**
  - ✓ **Customized commercial enzyme production**
    - ⇒ Enzymes highly optimized (maximum yields, shorter reaction times)
    - ⇒ Disadvantage: Costs & dependency from commercial contracts with suppliers, etc
  - ✓ **On-site enzyme production** (usually employing pre-treated biomass)
    - ⇒ Disadvantage: Potentially divert part of pre-treated biomass from 2G ethanol production (lowering ethanol yield: tons EtOH/tons feedstock)
  - ✓ **Role of Hemicellulases**
    - ⇒ improvement of C5/C6 cofermentation
- ❑ **Enzyme recycling** (ultrafiltration, solid recycling fed-batch SSCF)

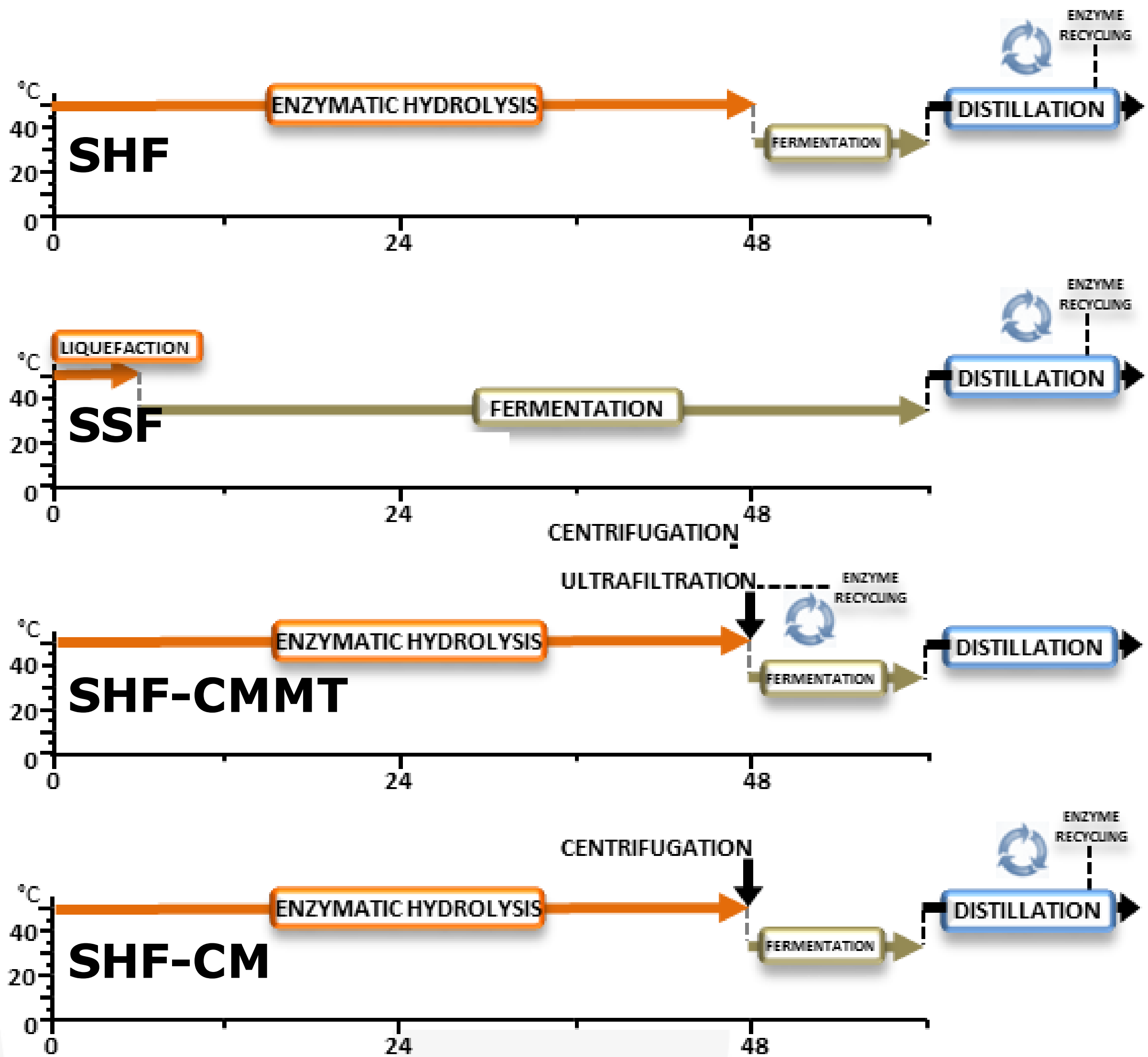


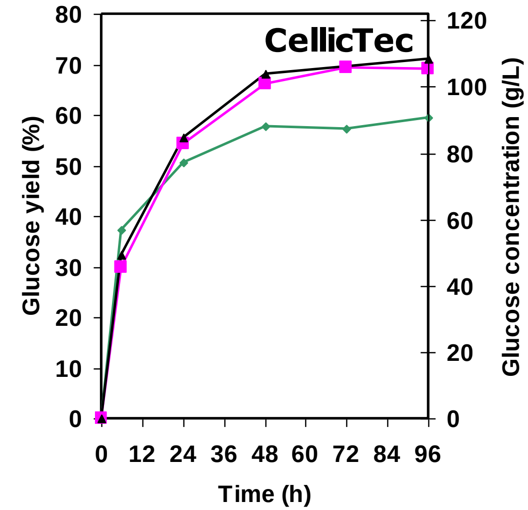
Source: Volynets & Dahman 2010 Int J En Environ. 2: 427

The Enzymatic Hydrolysis strategies

Data from:

EH yields & Enzyme recycling





SHF: single hydrolysis & fermentation

SSF: simultaneous saccharification & fermentation

SHF-CMMT: SHF-clear mash +Membrane technology

SHF-CM: SHF-clear mash technology

EH + Fermentation integration

Hybrid Hydrolysis and Fermentation (HHF)

- **SSF with pre-hydrolysis/liquefaction** (at optimal temperature)

  viscosity reduction and pre-saccharification followed by SSF for ethanol production

  ⇒ **favoring increased WIS contents by avoiding mixing problems ⇒ ↑ EtOH titer**

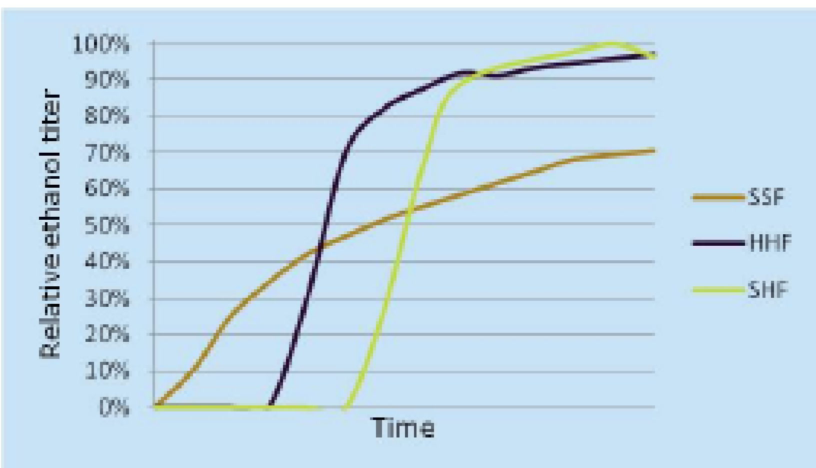
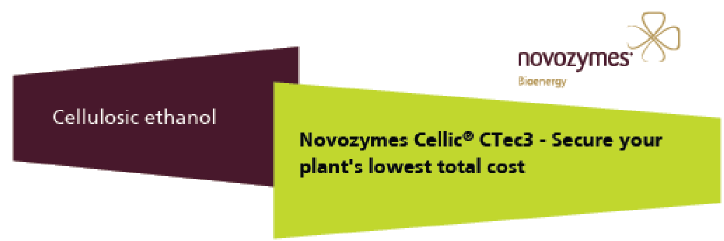


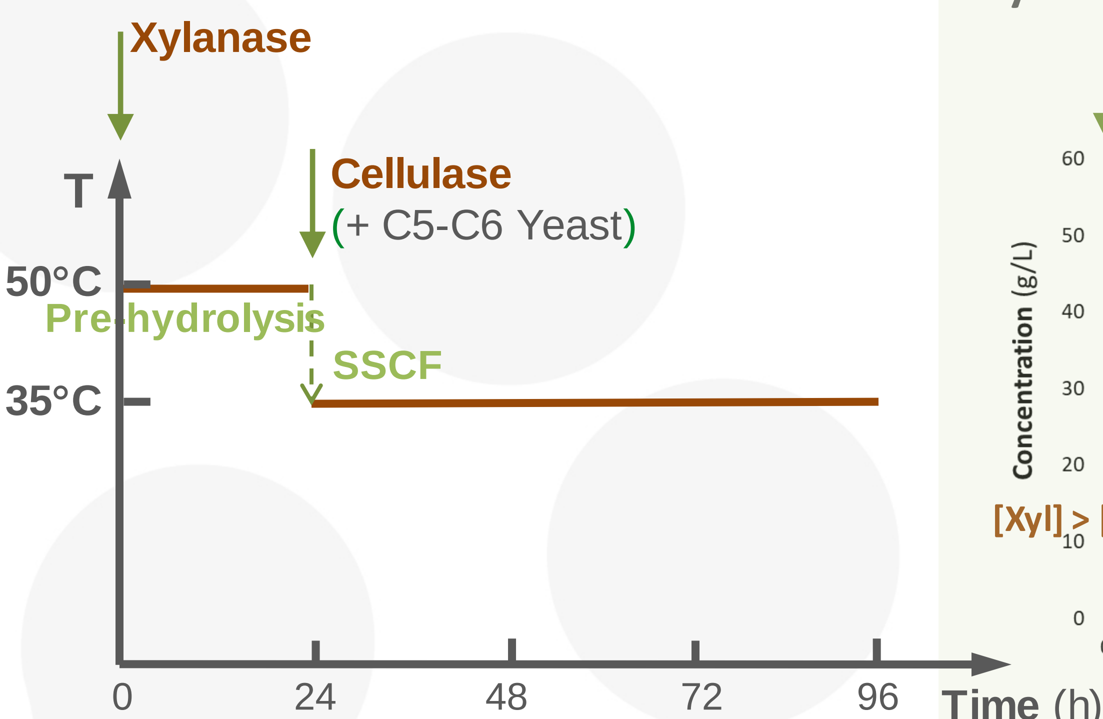
Fig. 3. Ethanol yield under varying hydrolysis conditions using Cellic® CTec3 at pH 5.0 and 50 °C on unwashed dilute acid-pretreated corn stover at 18% total solids loading. The yeast was pitched at different times, as indicated by initiation of ethanol production. The ethanol yield will vary depending on the substrate, enzyme dosing, yeast pitch, and hydrolysis configuration. In this example, an SSF configuration does not achieve the same yields as the options that include a dedicated hydrolysis step prior to fermentation. The process time available for hydrolysis and fermentation will dictate the options available.

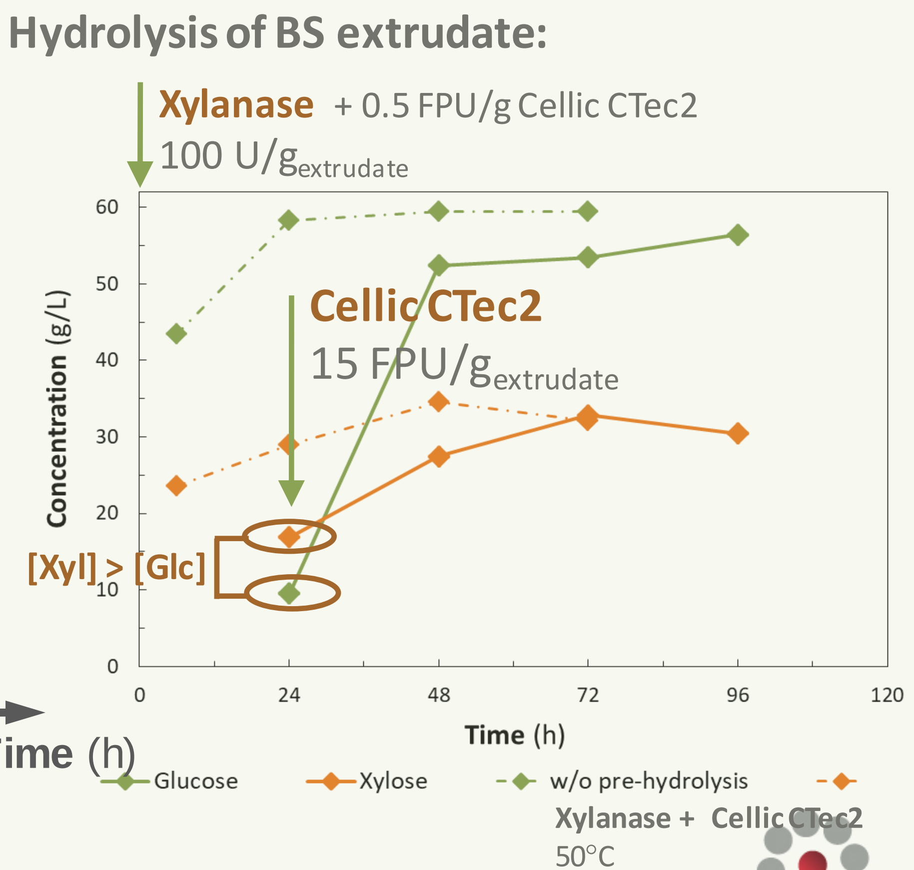


Hybrid Enz. Hydrolysis | Role of Hemicellulases

Hybrid Enzymatic Hydrolysis (HEH) + SSCF

❑ Goal: To minimize C5 uptake inhibition by Glucose during co-fermentation





In: **Marques, Gírio et al. 2019** On-site production of xylanases by *Moesziomyces aphidis* using barley straw as feedstock towards lignocellulosic ethanol. EUBCE2019

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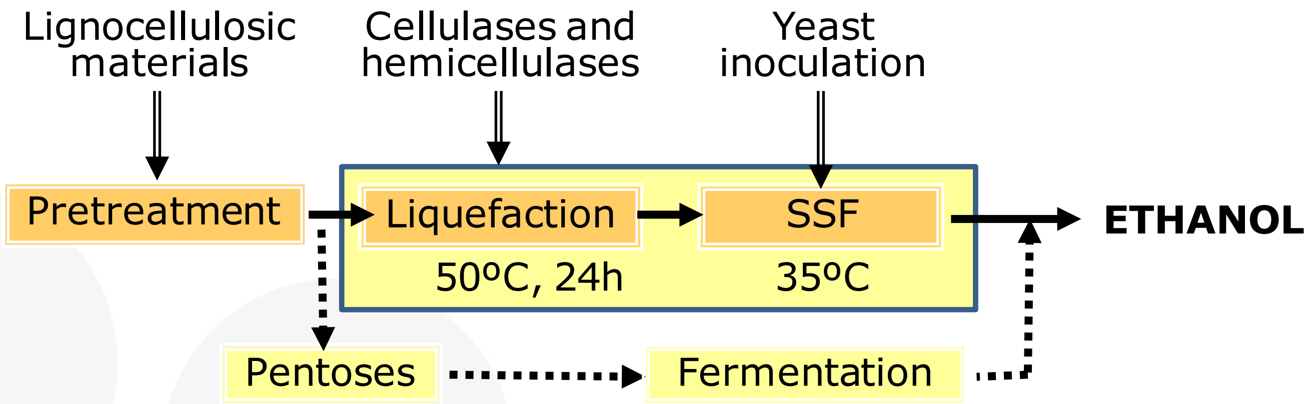
Enzymatic Hydrolysis | WIS content

Data from:



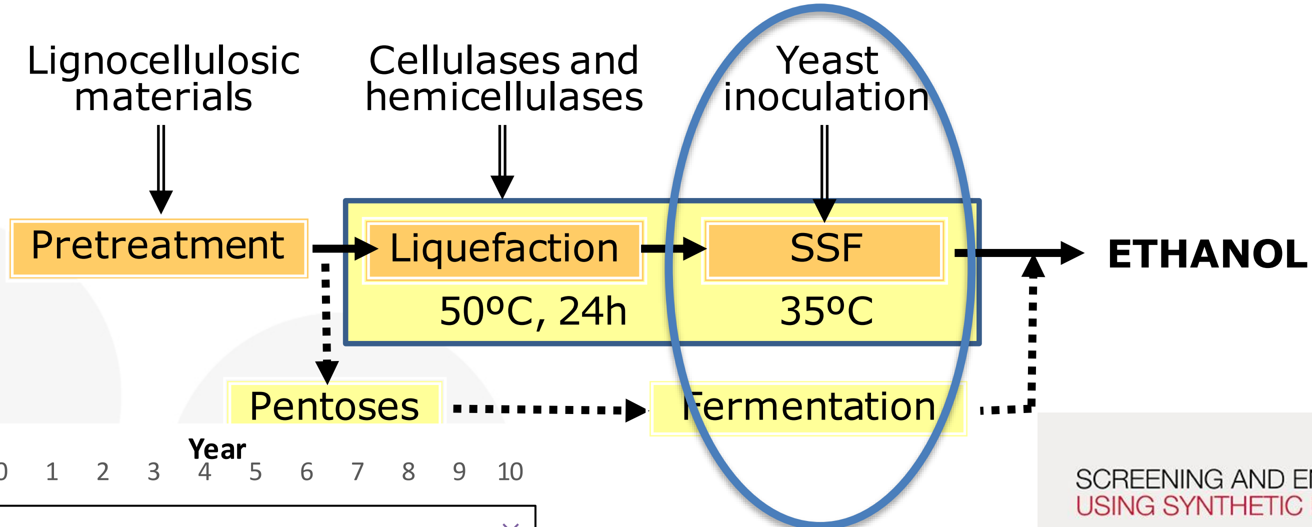
Sugarcane bagasse

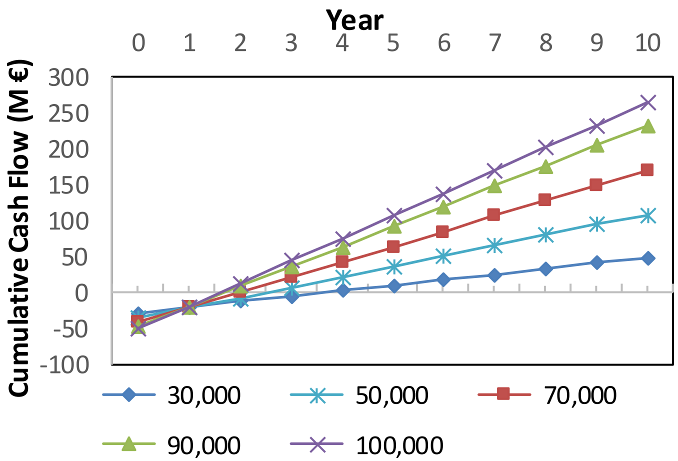
Enzyme load (FPU/ g glucan)	% Solids content on EH (w/w)					
	25			30		
	Glucose at 24h	Ethanol (g/l)	**LSSF** yield (%)	Glucose at 24h	Ethanol (g/l)	**LSSF** yield (%)
10	92	57	52	116	76	53
20	108	72	61	142	87	59
30	127	80	67	157	92	61

+15%

Fermentation| GMO vs non-GMO

Data from:

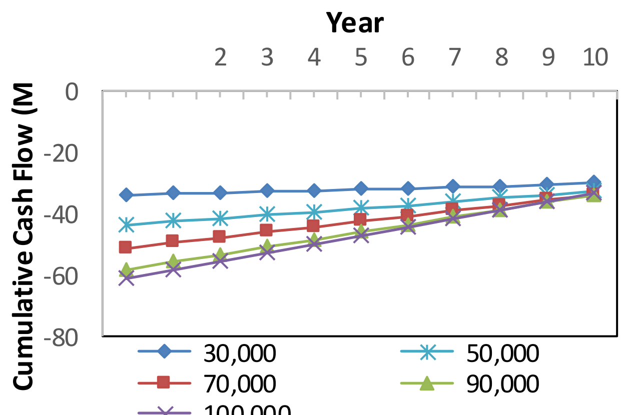


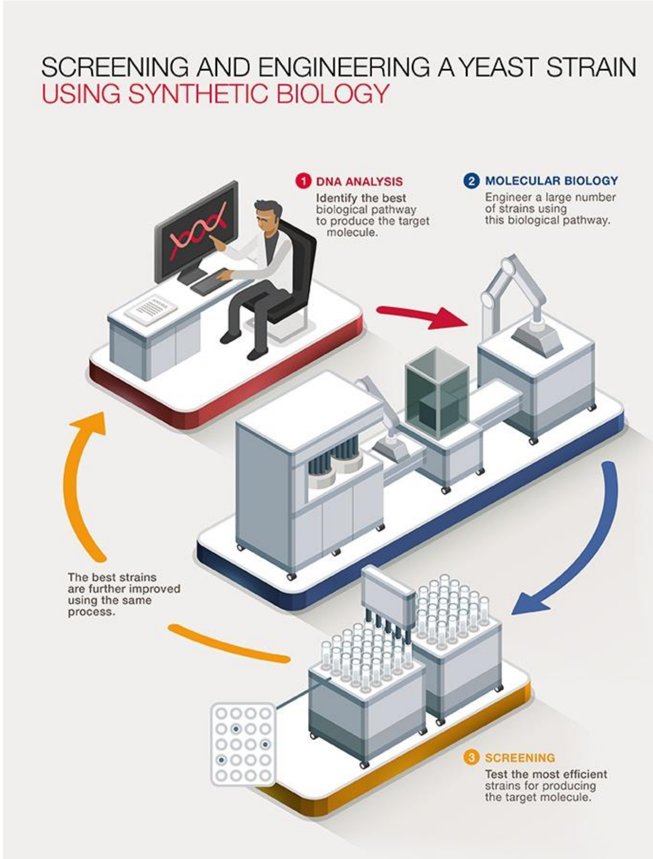


NON-GMO

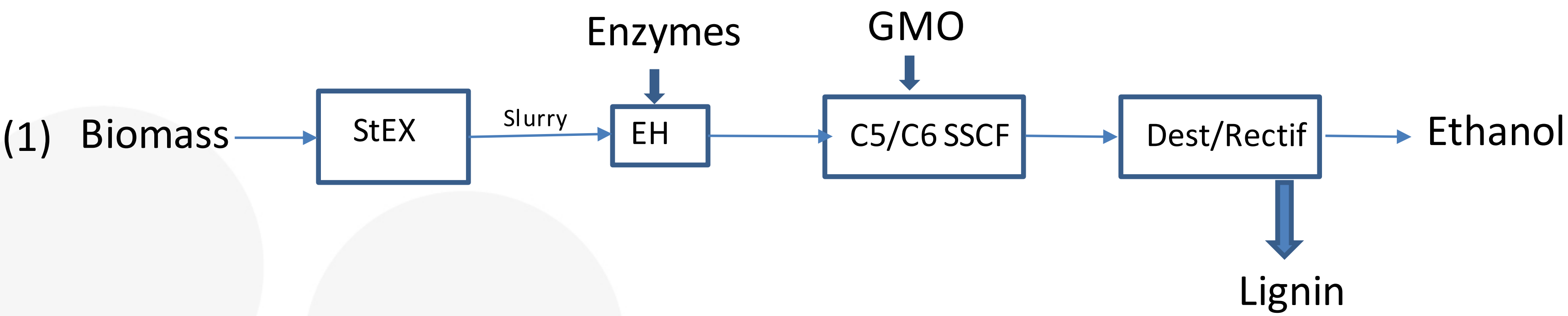
Data from:

GMO





2G Technology (stand alone)



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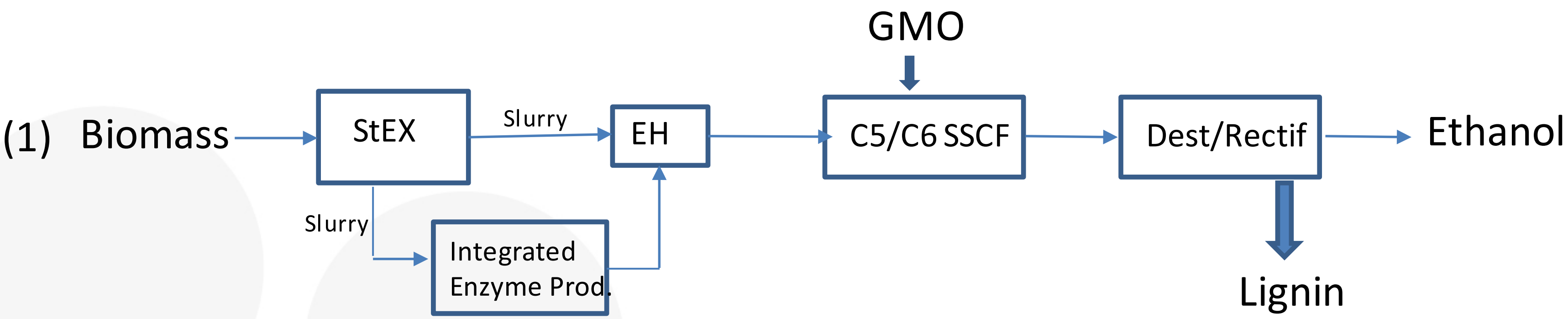

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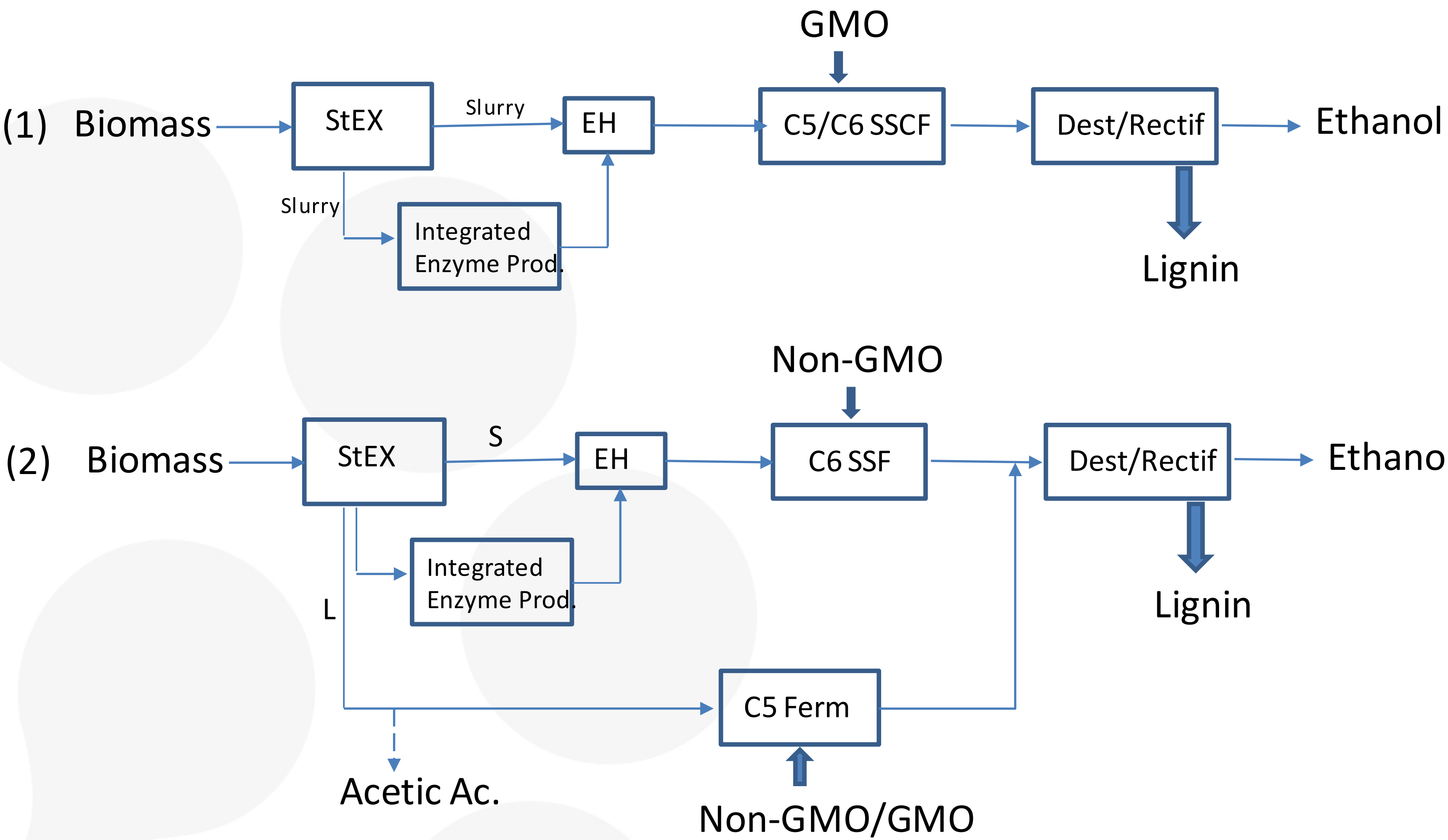
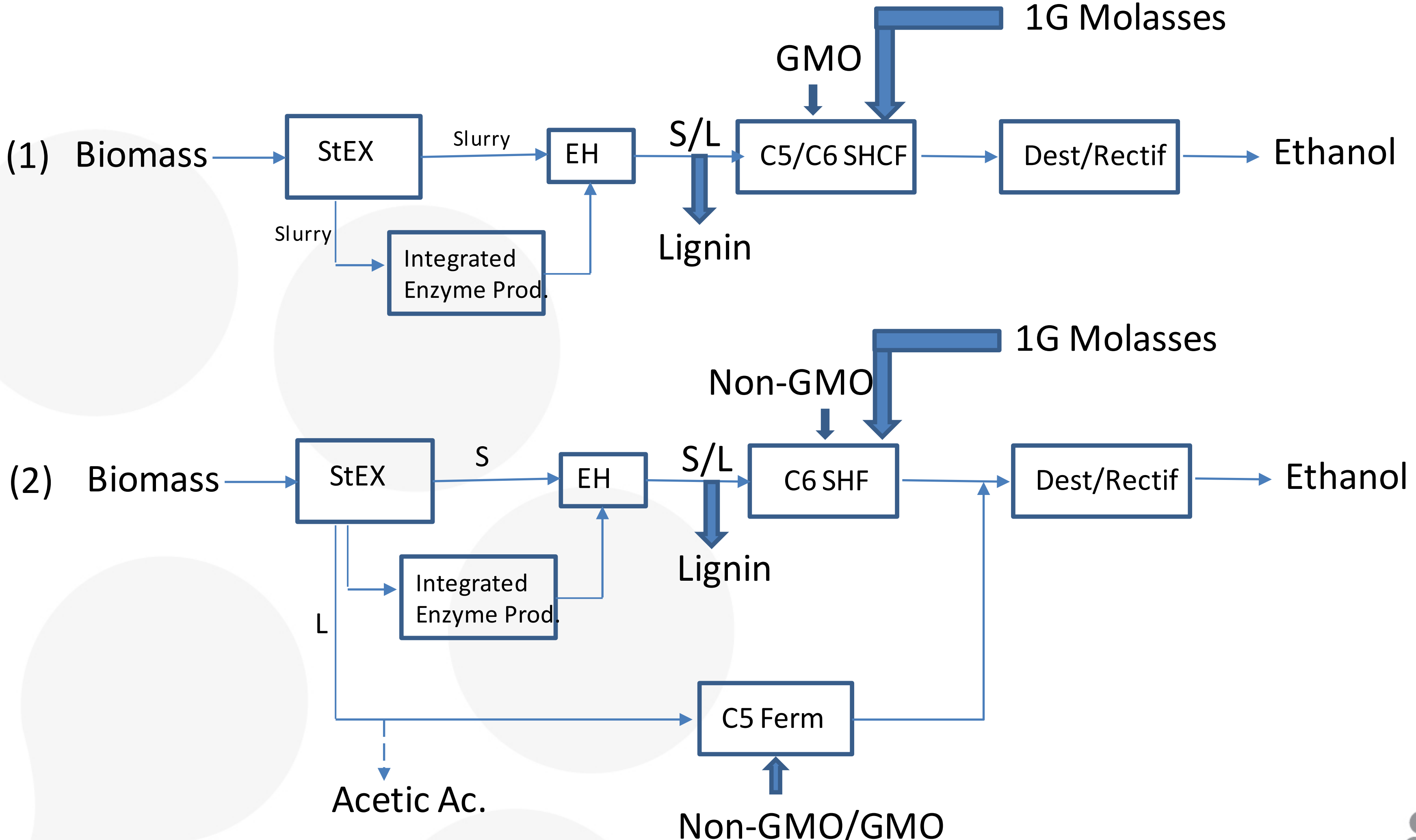


2G Technology (integrated with 1G)



2G EtOH biorefineries| small vs large-scale

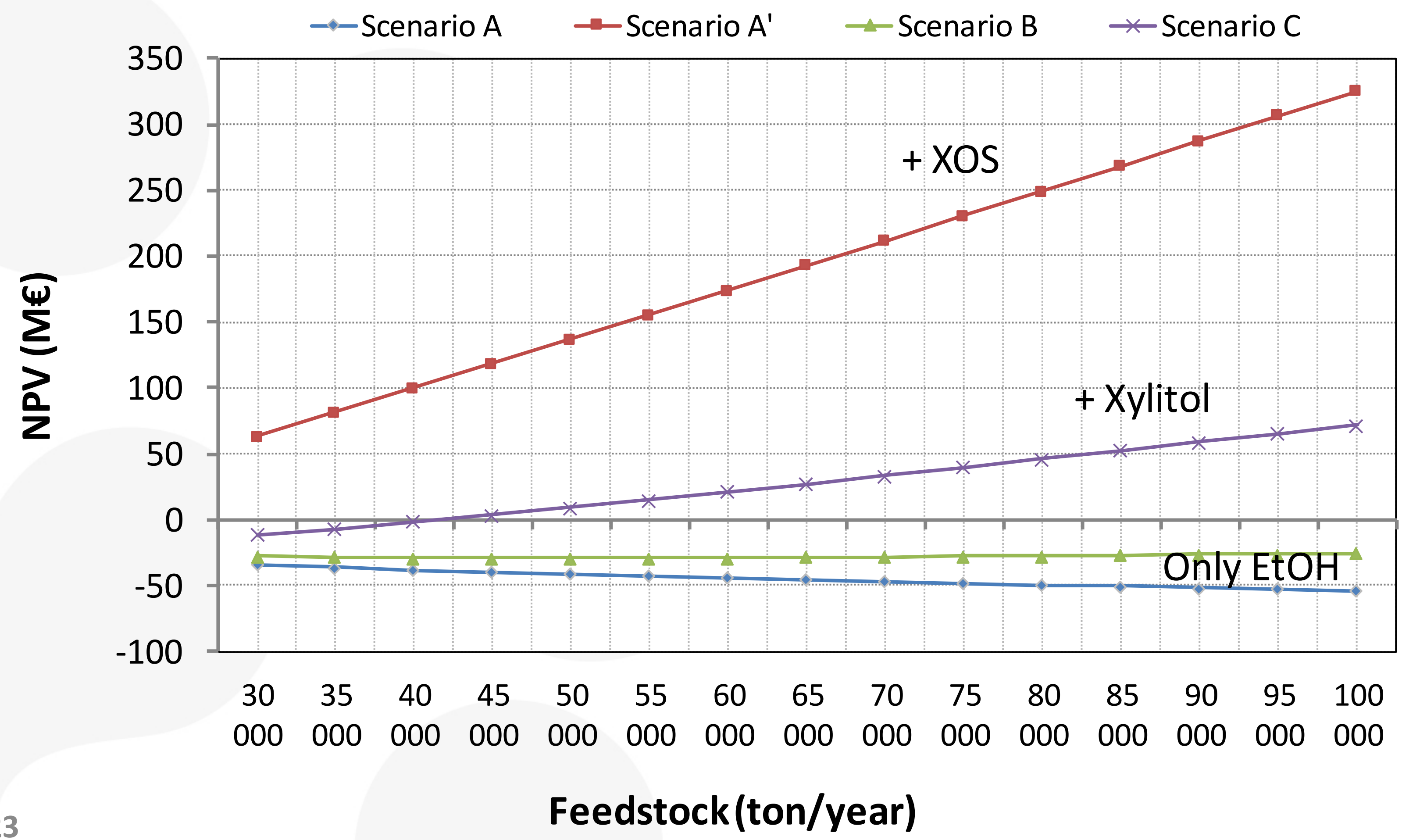
The plant size greatly influences any lignocellulose-based biorefinery

- The heterogeneity of lignocellulosic material allows **to produce a range of products** as broad **as the existing in petrochemical industry**

- However, there are **few chemical products** with **markets large enough** to absorb the production of a large-scale biorefinery

NPV versus biorefinery (small) scale (from 30,000-100,000 ton feedstock/yr)

Data from:



What are the next Achievements?

- Is ETOH the right "building block" for NextGen transportation setor?
  - Role of higher alcohols, long-chain fatty acids,…
- Improving overall energy-efficient (eg, cane-energy, low-demand biomass pretreatments, CBP, DSP….)
  - Biochemicals and other chemicals shall have an increasing importance in advanced biorefineries
  - However, there are few chemical products with markets large enough to absorb the production of a large-scale biorefinery
  - Is lignin becoming the "gold component" as main feedstock for conversion into high-added value products, being EtOH production a co-product of the value chain? (e.g., BALI™ from Borregard Industries)
- Do we still need EH (by adding cellulases and other hydrolytic enzymes)?
- Small scale processing reduces capital costs and costs for energy and transportation
- Clusters-based biorefineries shall use more efficient the entire feedstocks and by-streams (CAPEX & OPEX also decreases) and it is expected as industrial outcome a wider range of products for different "core" markets.

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www.lneg.pt

Thanks for your attention

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More info:

www.proethanol2g.org
www.babet-real5.eu
www.smibio.net

LNEG act as Coordinator of:

- FP7 **Proethanol2G**
- H2020 **SMIBIO**

And as partner of:

- H2020 **BABET-REAL5**

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