Main Challenges and Achievements on Lignocellulosic-based ethanol Biorefineries

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LNEG, May 28th, 2021

REPÚBLICA PORTUGUESA
AMBIENTE E AÇÃO CLIMÁTICA

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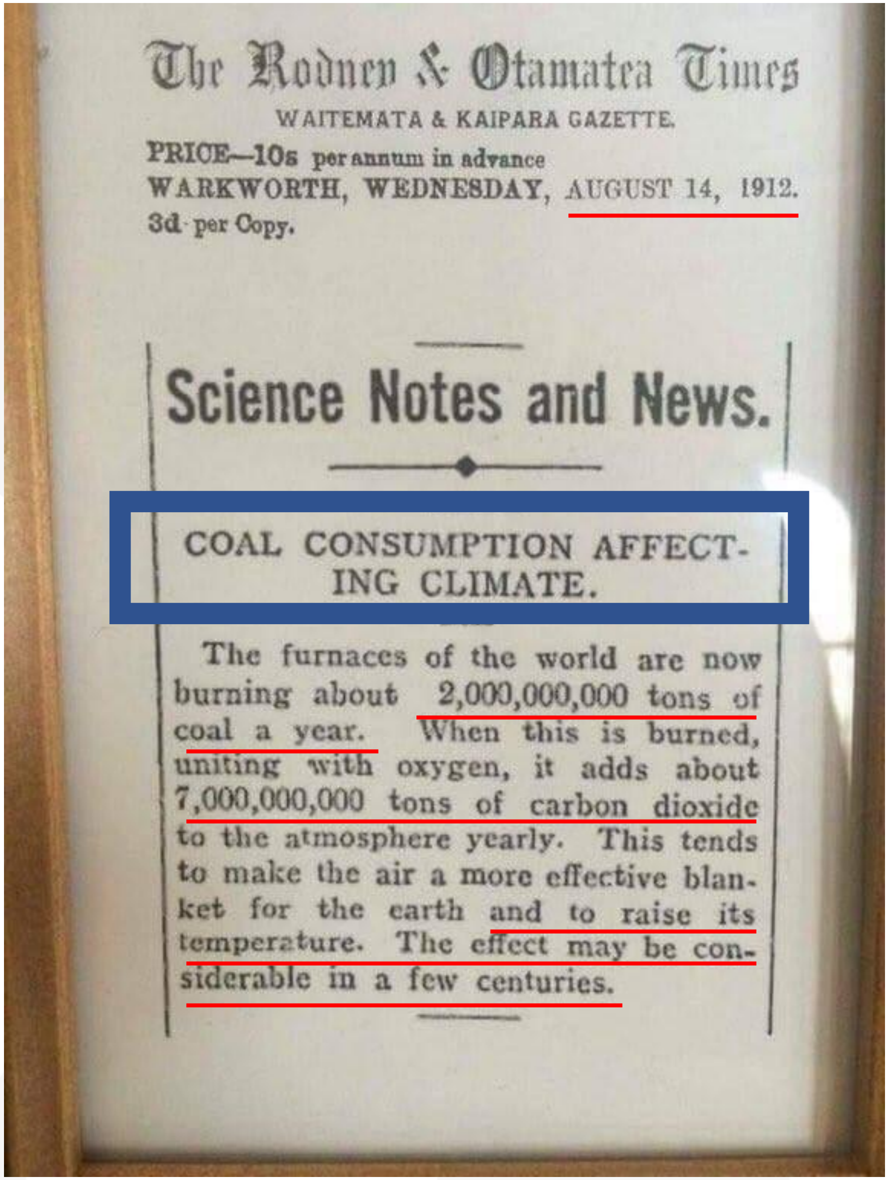
3. Bioethanol: more than a biofuel
4. Estimated costs for 2G ethanol
5. Main technological challenges for competitive 2G ethanol biorefineries
6. What are the next achievements?

Fuels versus Climate



The Rodney & Otamatea Times

WAITEMATA & KAIPARA GAZETTE.

PRICE—10s per annum in advance

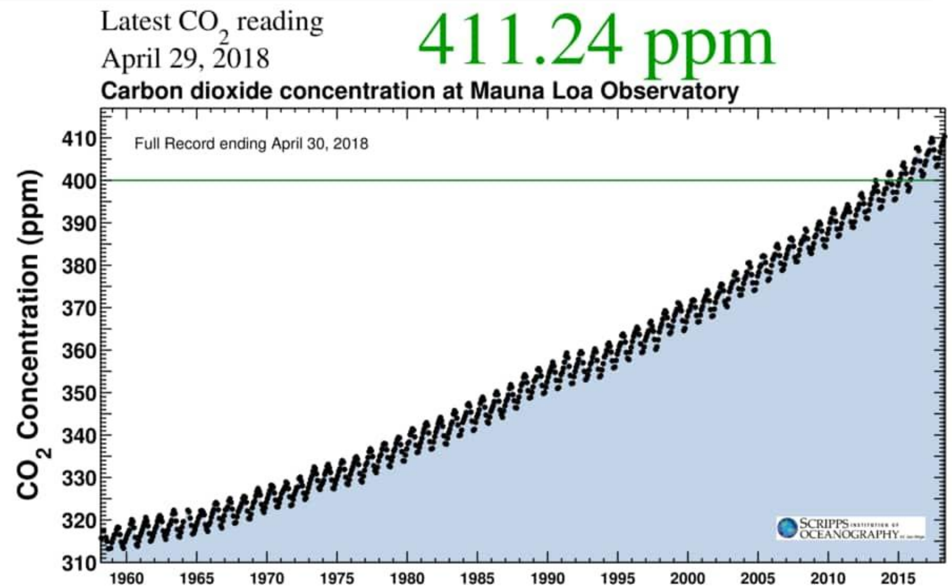
WARKWORTH, WEDNESDAY, AUGUST 14, 1912.

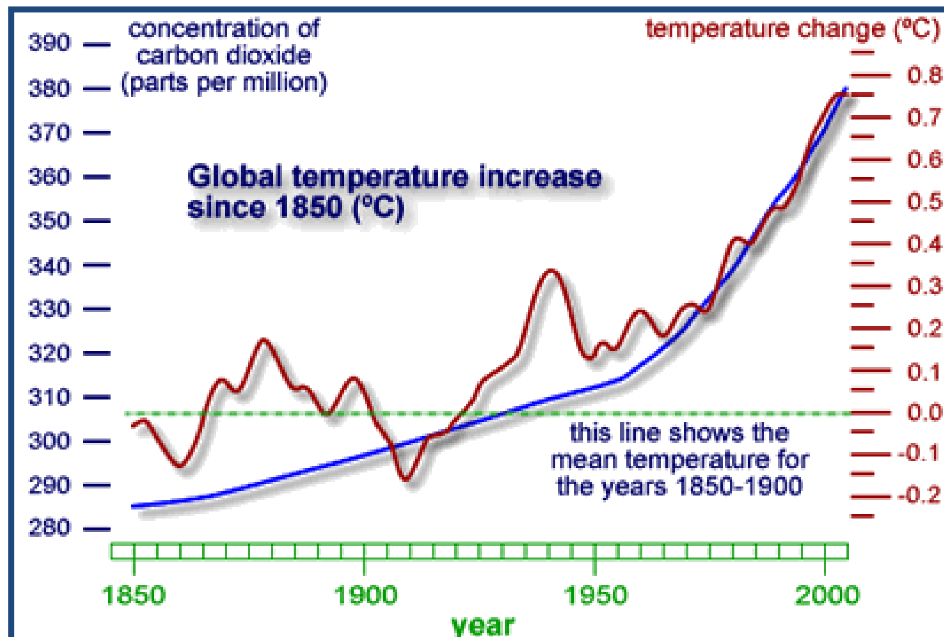
3d per Copy.

Science Notes and News.

COAL CONSUMPTION AFFECTING CLIMATE.

The furnaces of the world are now burning about 2,000,000,000 tons of coal a year. When this is burned, uniting with oxygen, it adds about 7,000,000,000 tons of carbon dioxide to the atmosphere yearly. This tends to make the air a more effective blanket for the earth and to raise its temperature. The effect may be considerable in a few centuries.





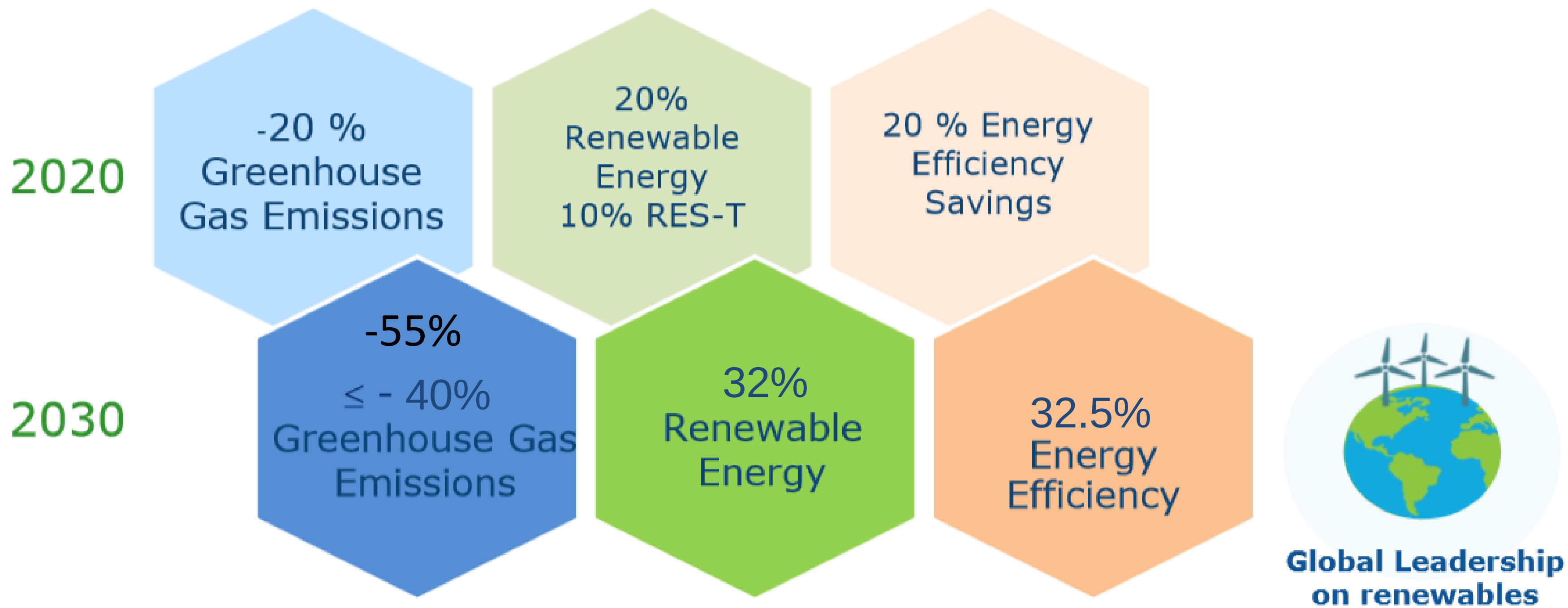
Biofuels: Still an EU priority!

The biofuels use in the transportation sector of EU countries is still an European priority consolidated in a substantial regulation framework and political initiatives since 1997

- White Paper on renewable energies – 1997
- Directive of “green electricity” – 2001
- **Directive of Biofuels – 2003**
- Directive of energetic fiscal incentives – 2003
- Action Plan of Biomass – 2005
- The European Strategy on Biofuels – 2006
- The Energy Package – 2007
- **Directive RED – 2009**
- **Directive ILUC – 2015 (revision of Directive RED)**
- **Directive RED II (for 2021-2030)**

CLEAN ENERGY FOR ALL EUROPEANS PACKAGE

A NEW FRAMEWORK FOR RENEWABLES POST-2020 (Nov 30th 2017)



EU minimum Subtarget for Transport: 14%

Subtarget for Transport (Portugal): 20%

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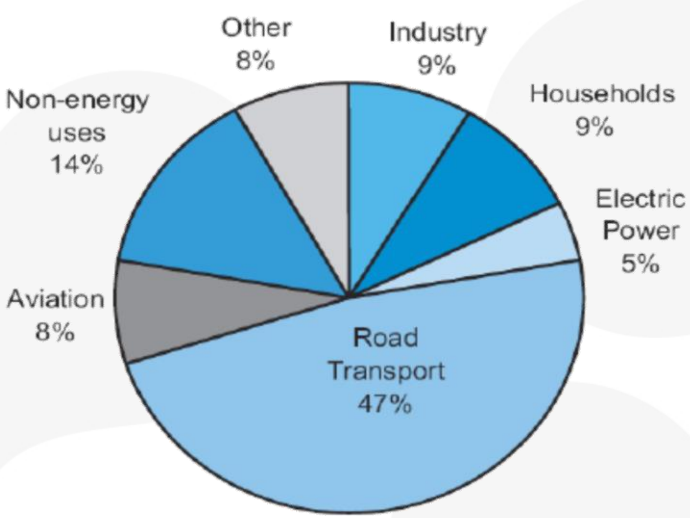
Dependência dos Transportes em combustíveis fósseis…

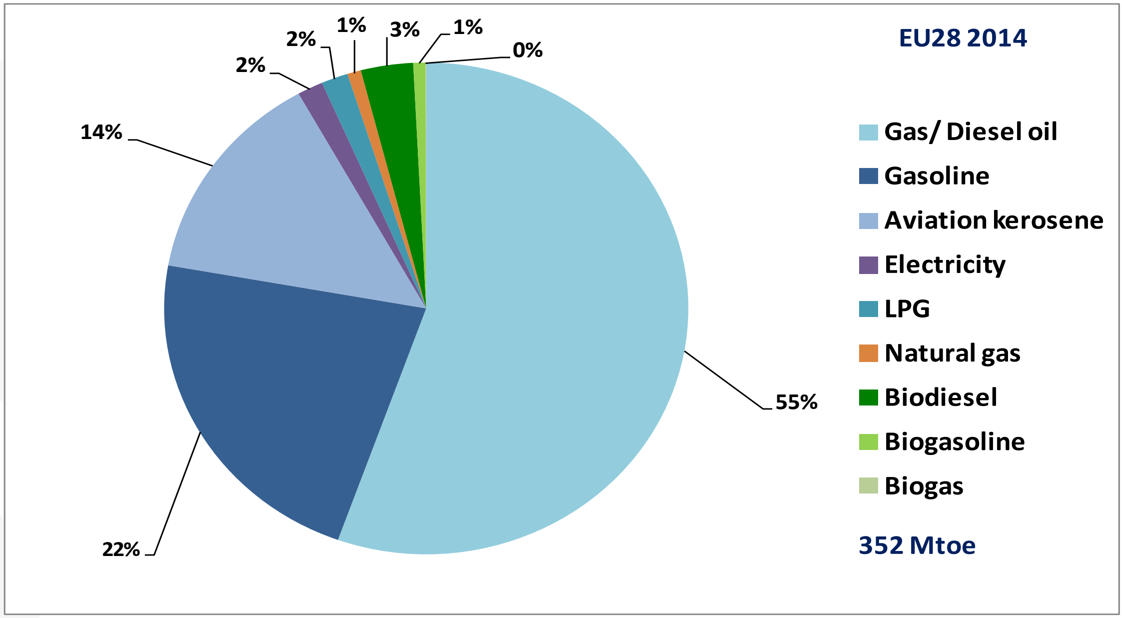
<u>Portugal:</u>
-Current share of biofuels in transport in 2020 was ~5% (energy content)
-This means: <u>95% oil-dependent</u> !

European Union:
-About half of crude oil is consumed at the transportation sector
-The transport sector is responsible for about 1/3 of GHG emmissions

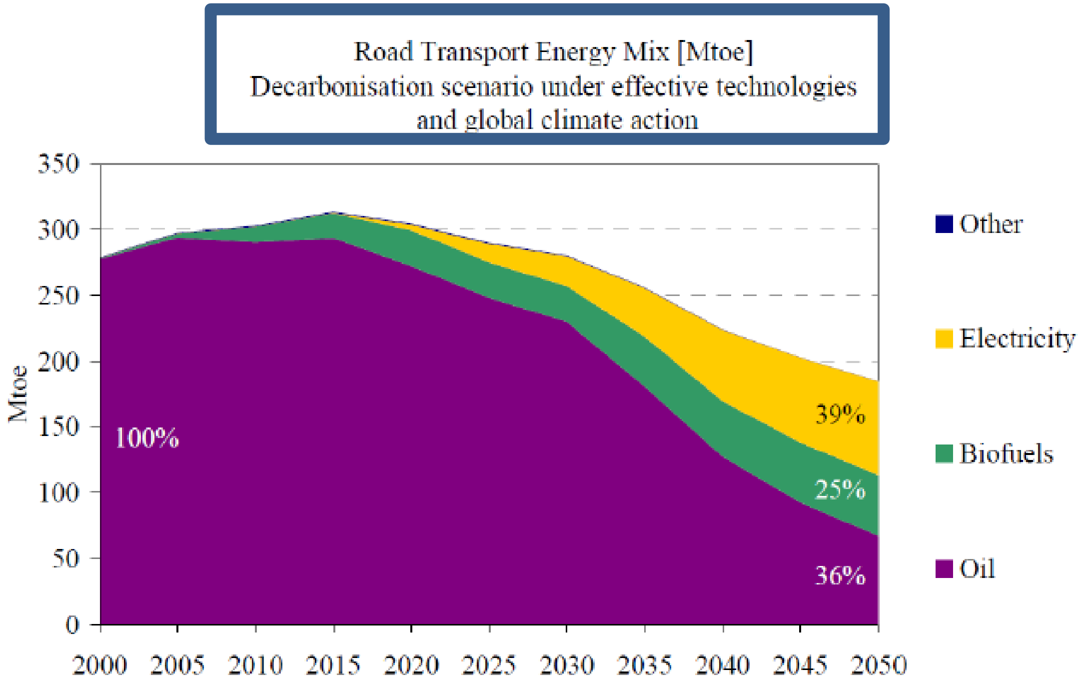
Oil consumption per sector



Fuel/Biofuel types in transports



A Roadmap for moving to a competitive low carbon economy in 2050



COM(2011) 112 final

Source: Piotr Tulej, EC, DG Research&Innovation, HoU Unit G3, Brussels, june 21, 2016

RED II - GHG EMISSION SAVINGS CRITERIA

For biofuels and biogas

GHG emission reduction targets:

- 50% GHG (installations in operation before 10/2015)
- 60% GHG (installations in operation before 1/2021)
- 65% GHG (installations in operation after 1/2021)

For RFNBO

GHG emission reduction targets:

- 70% GHG (installations on 01/2021)

For RCF

GHG emission reduction targets:

- Delegated Act due up to 01/2021

Environmental impact of the liquid biofuel - n generations

LCA well-to-wheel (not considering LUC and ILUC)

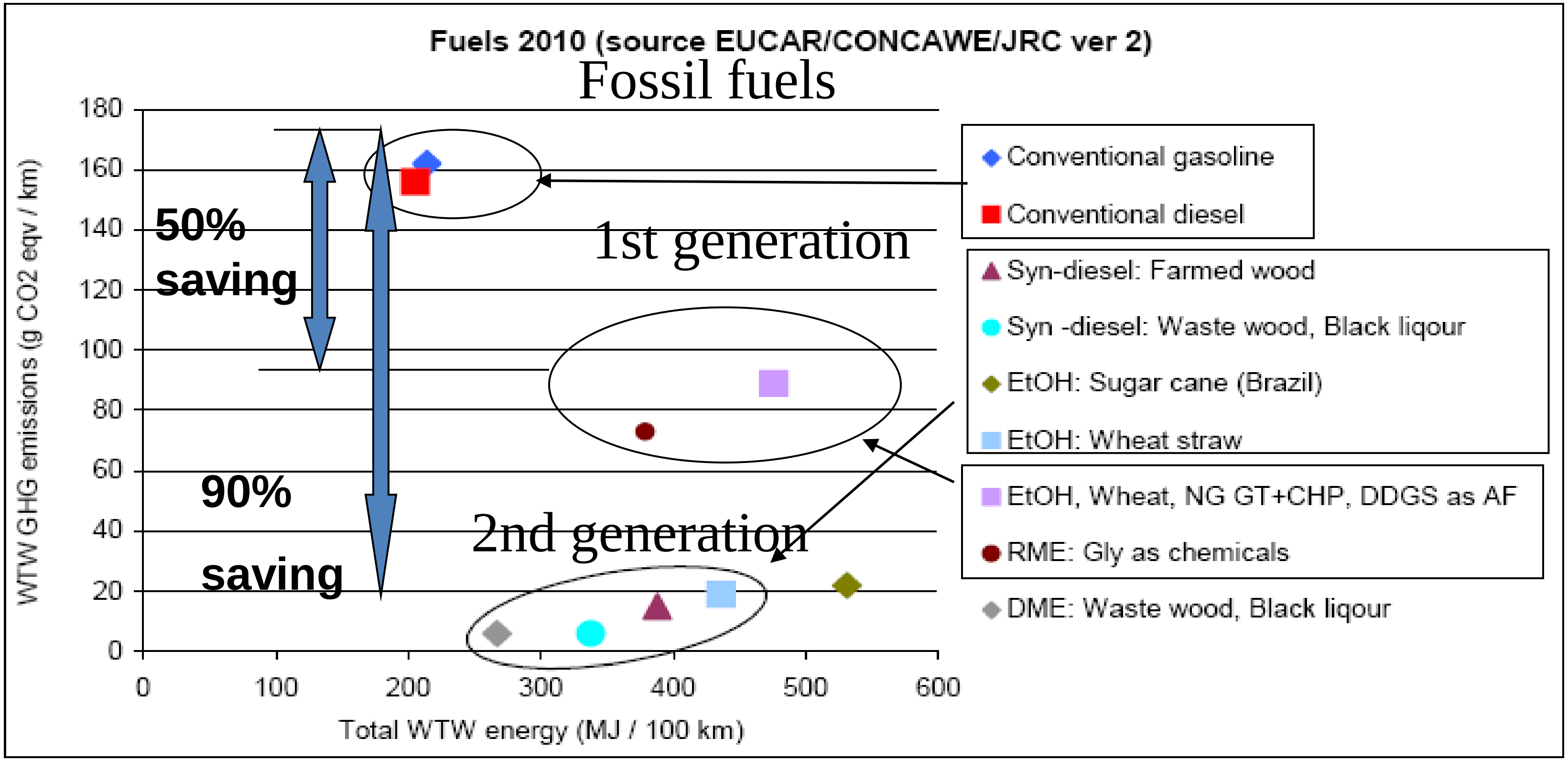
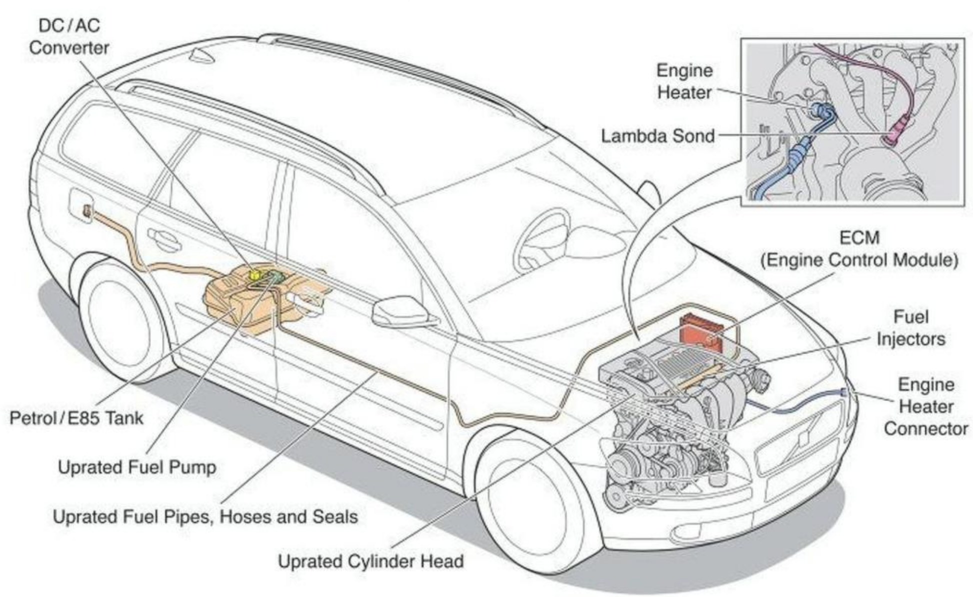


Figure 1.5. Well-to-wheel greenhouse gas emissions (in CO_2-equivalents/km) versus total energy use for running a mid-size car over a distance of 100 km.

BIOETANOL – Biocombustível para a década 2020-2030 na UE?



- ✓ **Pureza:** 99,5% ou superior
- ✓ **Poluição do Ar**: NOx negligenciavel.
- ✓ **Tecnologia Flex:** Utiliza todas as misturas gasolina/etanol ou apenas etanol .
- ✓ **Motor:** Compatibilidade com qualquer veiculo de CI pós- ano 2000.

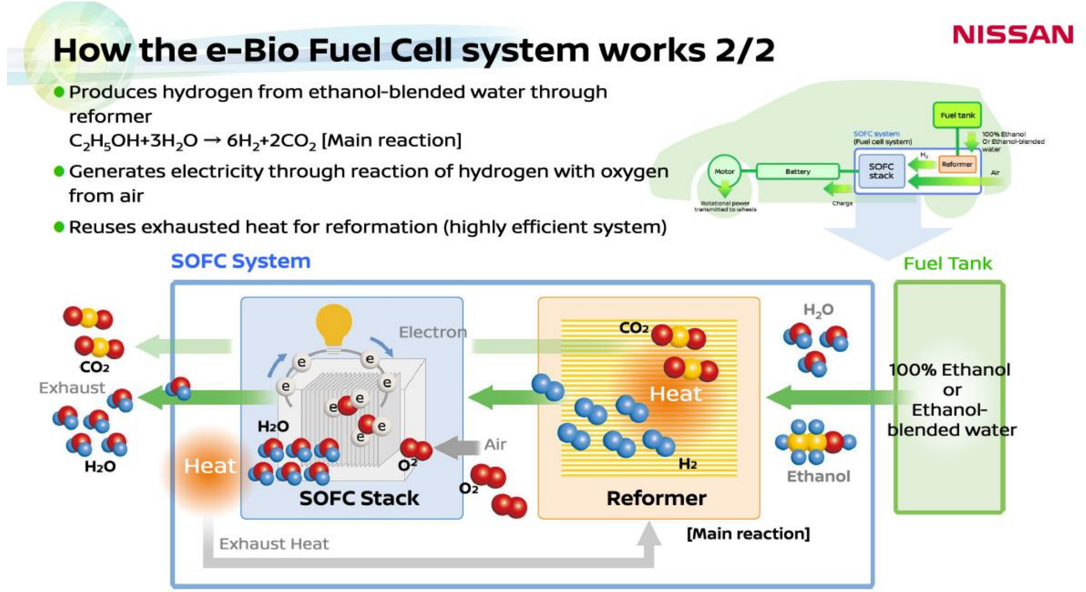
SCANIA – first Scania Bioethanol truck (**ED95**) sold to a customer (Lantmannen Agroetanol) - 29.10.2018 (source: www.scania.com)

Sustainability: ED95- Bioethanol blended with an ignition improver, reduces 90% GHG emmissions.

Technology: The 13-litres bioethanol engine delivers 2,150 Nm, equal to that of its diesel sibling, and the fuel consumption is also on pair with a conventional diesel engine.

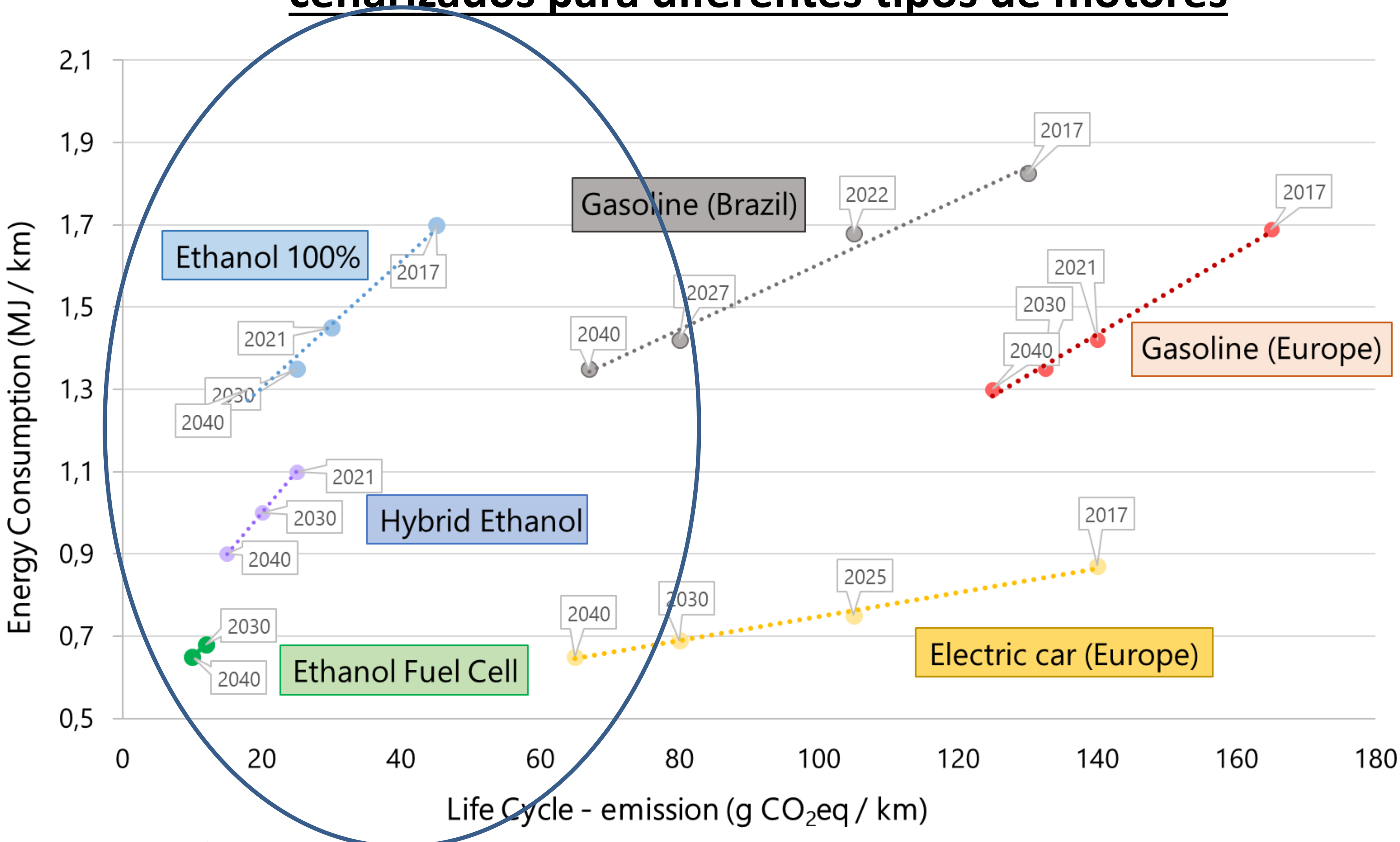
Most significant engine changes: Modification of the fuel injection system and the cylinders, for increase the compression.

Cellulosic Bioethanol: an advanced biofuel



Performance: Combining the SOFC-powered ethanol (either 100% ethanol or 45% etanol and 55% water) with motor and 24 kWh electric battery Nissan SOFC achieves an autonomy of 600 kms (2017) .

Consumo de energia e emissões de ciclo de vida de GEE cenarizados para diferentes tipos de motores



Menos Emissões

Mais Emissões

Biorrefinaria de Bioetanol Celulósico, Itália

ITALIA

Primeira Biorrefinaria de bioetanol celulósico no Mundo – op. 2013

76 000 m^3/ano bioetanol, 13MW a partir da lenhina.

150 M€, FP7 support, 270.000 ton/ano palhas de cereais

Beta Renewables, Crescentino, Italy

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Next Cellulosic Bioethanol Plants (to be deployed)

CLARIANT **ESLOVAQUIA, ROMÉNIA**

Announced plans for plants in SL, RO, CHINA.

Inbicon April 2017

LoI with Pioneer Point Partners for an investment up to 160 M€ in the MEC plant conditional on political framework and long-term government support is settled .

FINLANDIA

Capacity 10 million liters ethanol from saw mill dust (pine)

Commissioning 2017

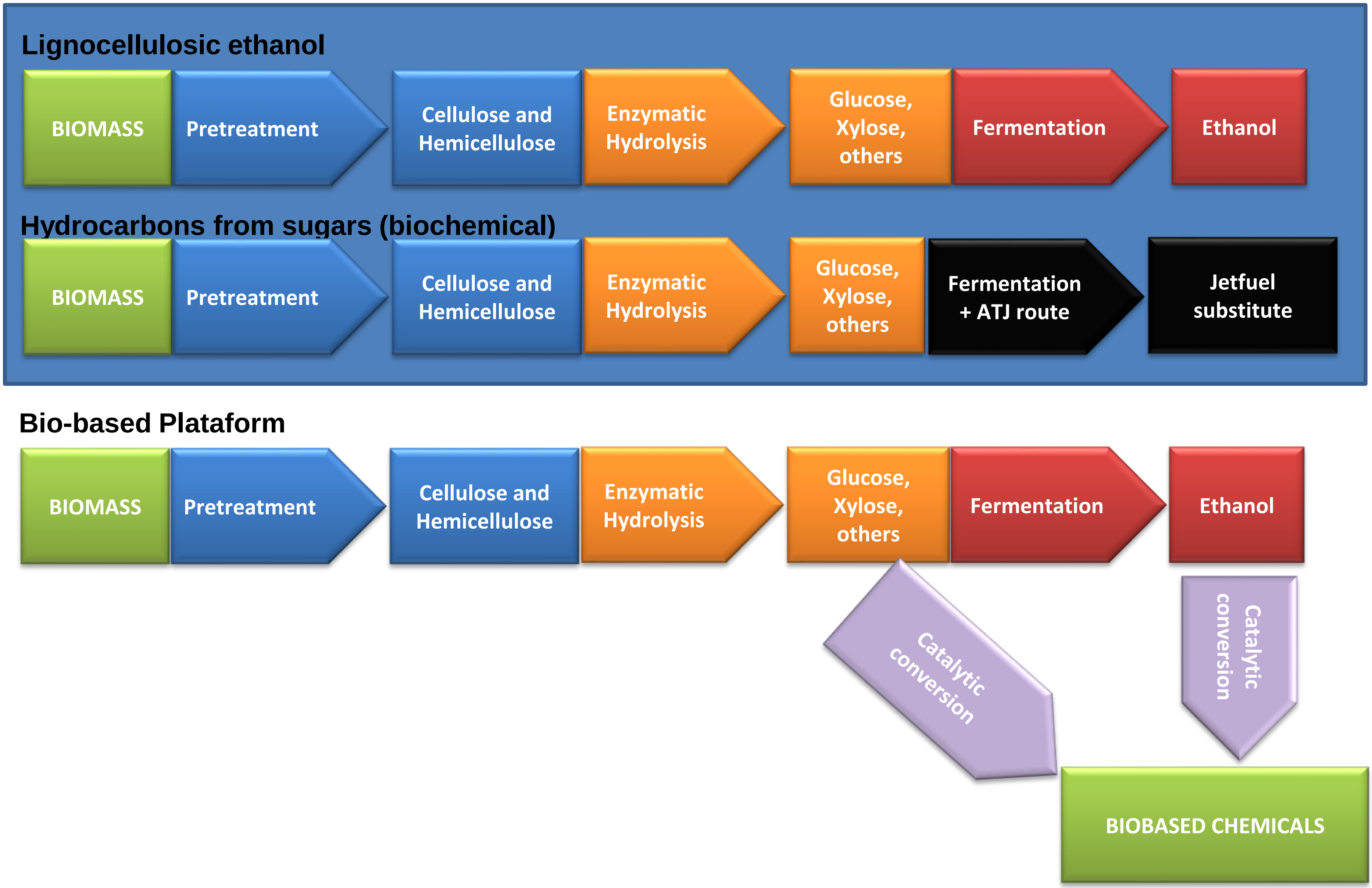
Cellunolix® Kajaani, Finland

PRAJ: Capacity 1 million liters ethanol from ag. residues

End-to-end integrated demonstration plant

Commissioning 2017 –

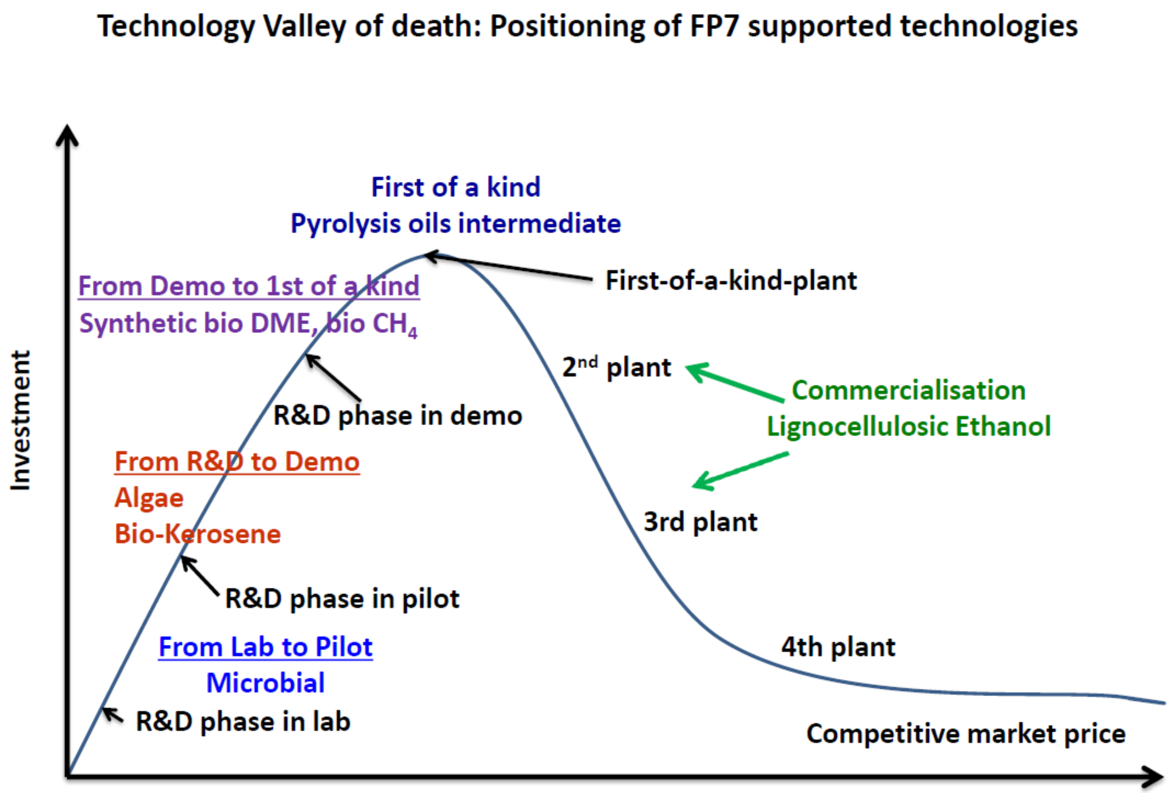
Cellulosic Bioethanol: more than 2G biofuel



Usina de São Manoel, Brasil , bioetanol de cana de açucar

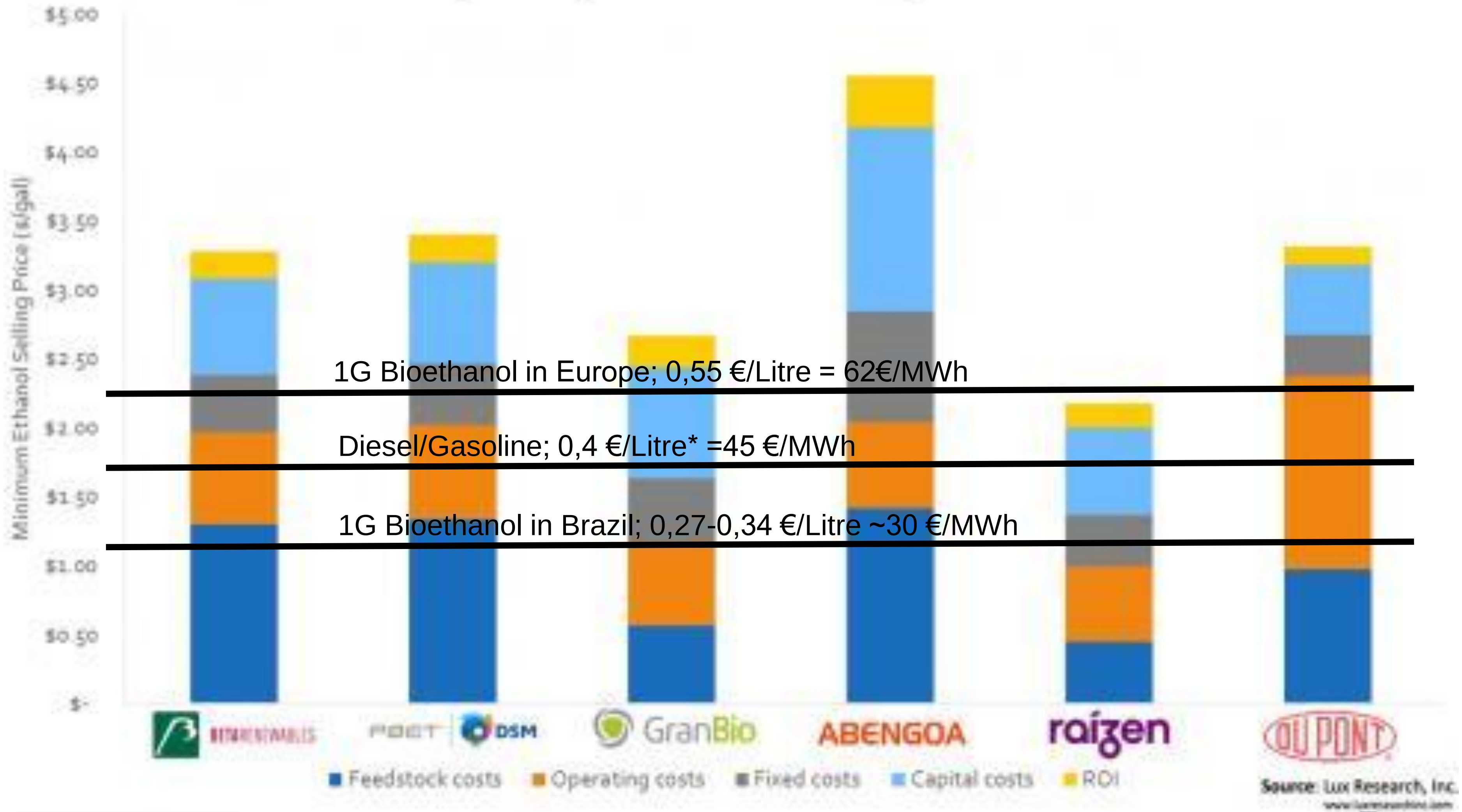
Unidade de Demonstração de bioetanol avançado de bagaço

Status of Biomass Technologies for Advanced Biofuels



Source: Kyriakos Maniatis, DG ENERGY, EBTP 7th SPM, Brussels, june 21, 2016

Estimated Advanced Ethanol (2G) Production Costs



* Considering 45 USD/bll crude oil

Source: Lux Research Inc. (2016)

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*)**

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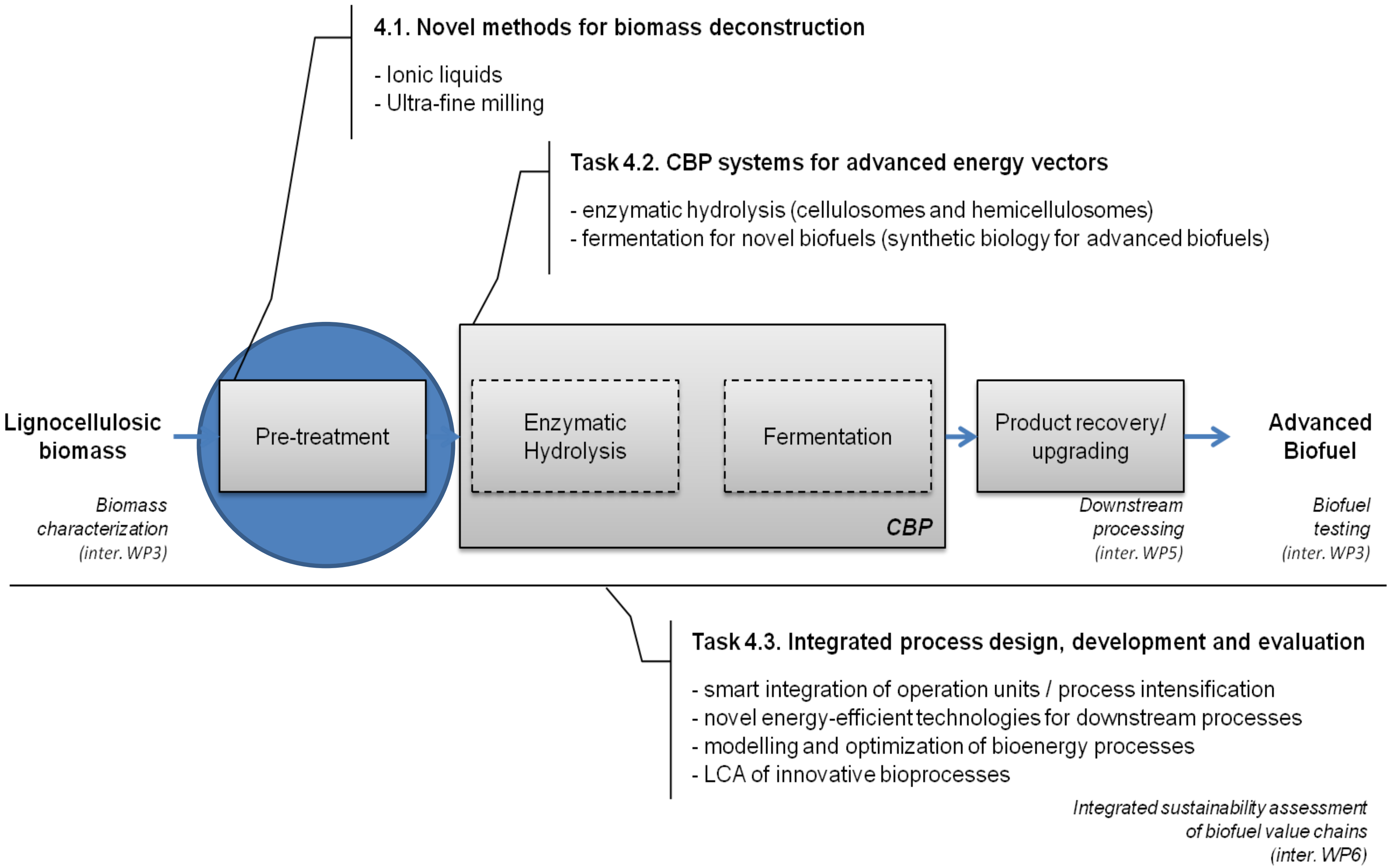
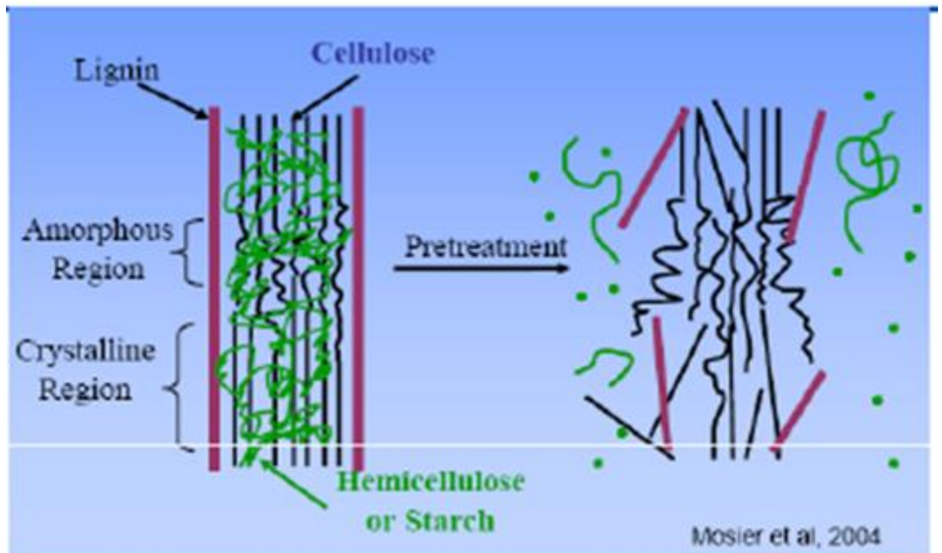
- **Lignin Quality - crucial for valorization towards new end-uses**

The Lignocellulosic Ethanol Technology: in short



Pretreatment Technology



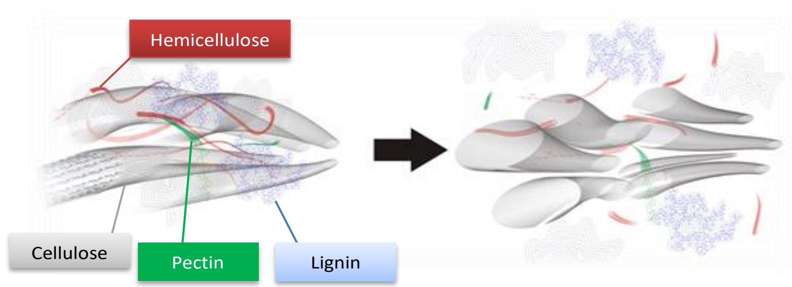
Mosier N, Wyman C, Dale B, Elander R, Lee YY, Holtzapple M, Ladisch MR, 2004.

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



Pretreatment Technology: Challenges

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

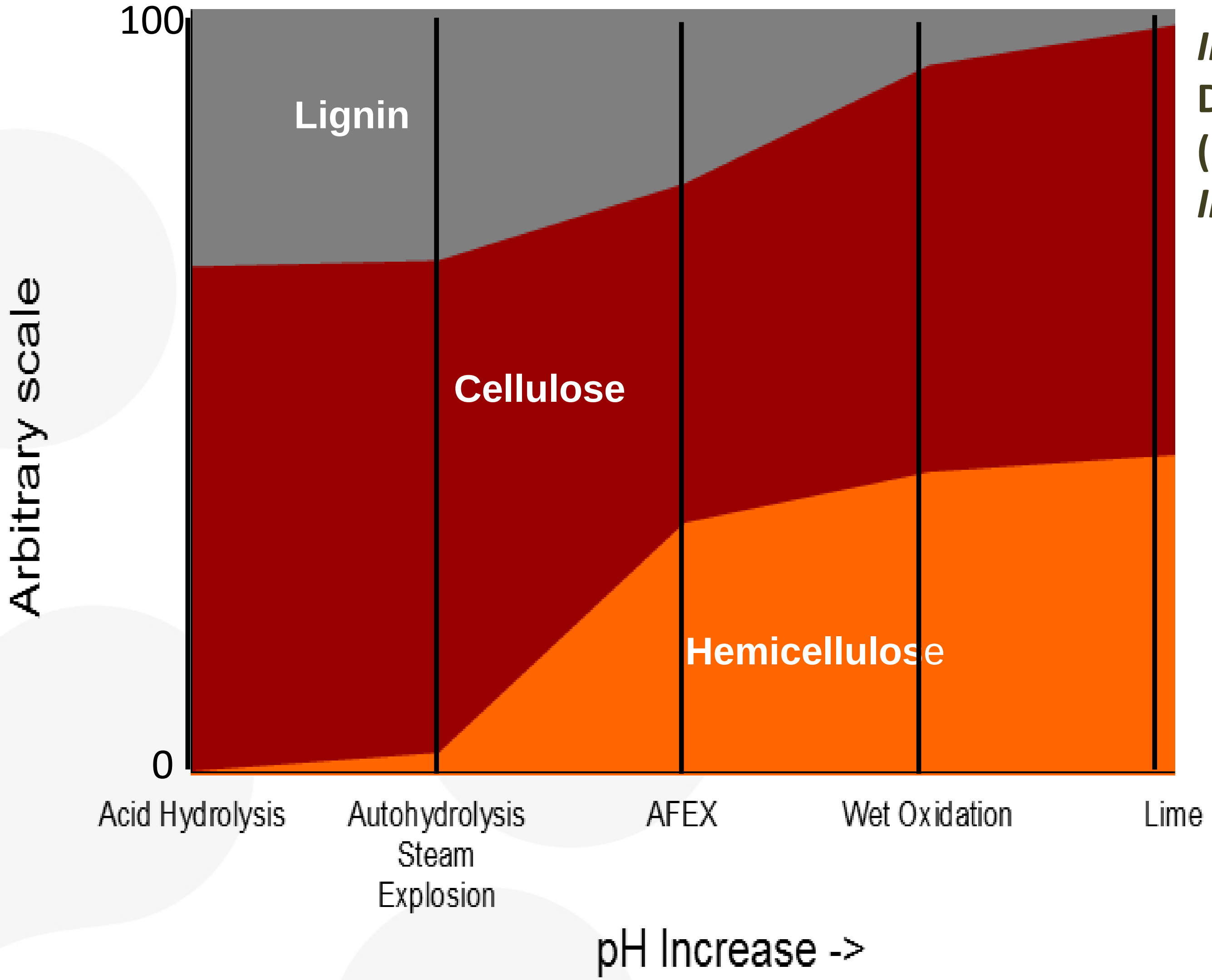
- ❑ **Biomass (physico-chemical properties)**
  - ❑ Absorption vs Adsorption
  - ❑ Adhesion (to mechanical components)
  - ❑ Abrasive effect (on the screws)

From: Gonçalo Pereira Cortesy.

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

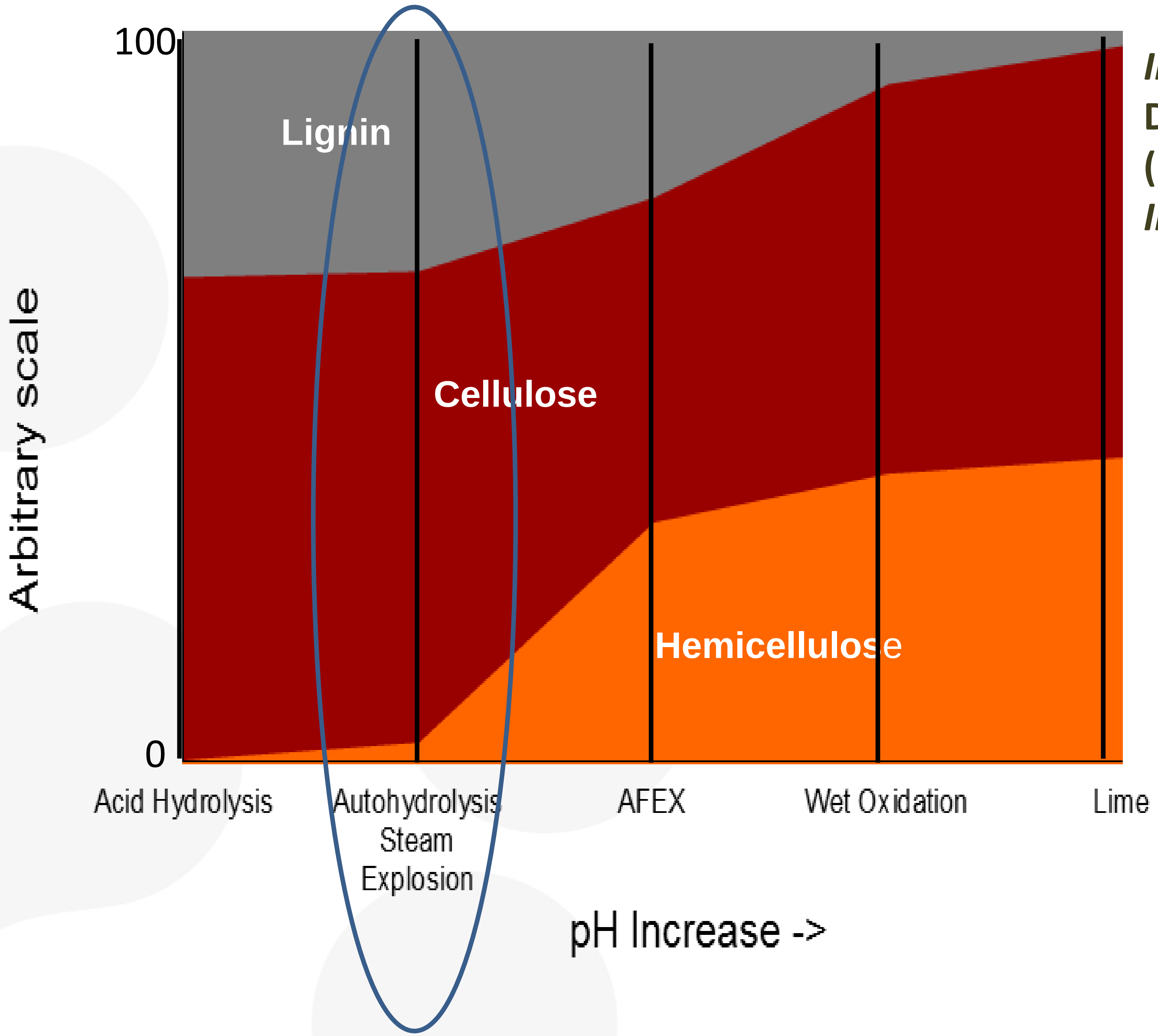
- ❑ **Chemical & Energy performance:**
  - ❑ **Avoid the use of Catalysts** (this increase Lignin purity & value)
  - ❑ **Decrease Reaction Temperature** (this increase Energy Effic.)
  - ❑ **Avoid the generation of inhibitors** (this increase fermentation yields & improve downstream processing)
  -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

Biomass composition after pretreatment



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

Biomass composition after pretreatment



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

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

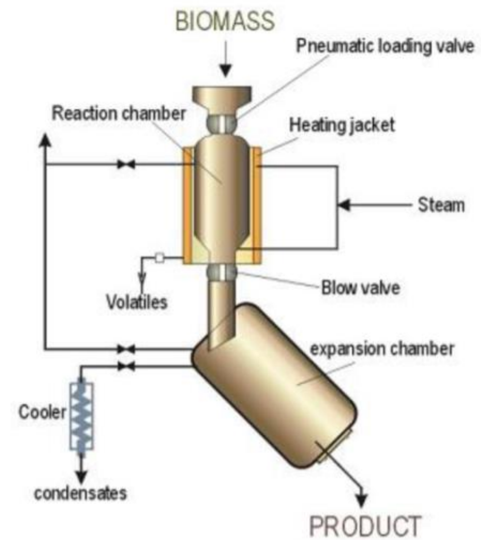


Figure 28: Steam explosion process (Isabella De Bari)

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)

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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

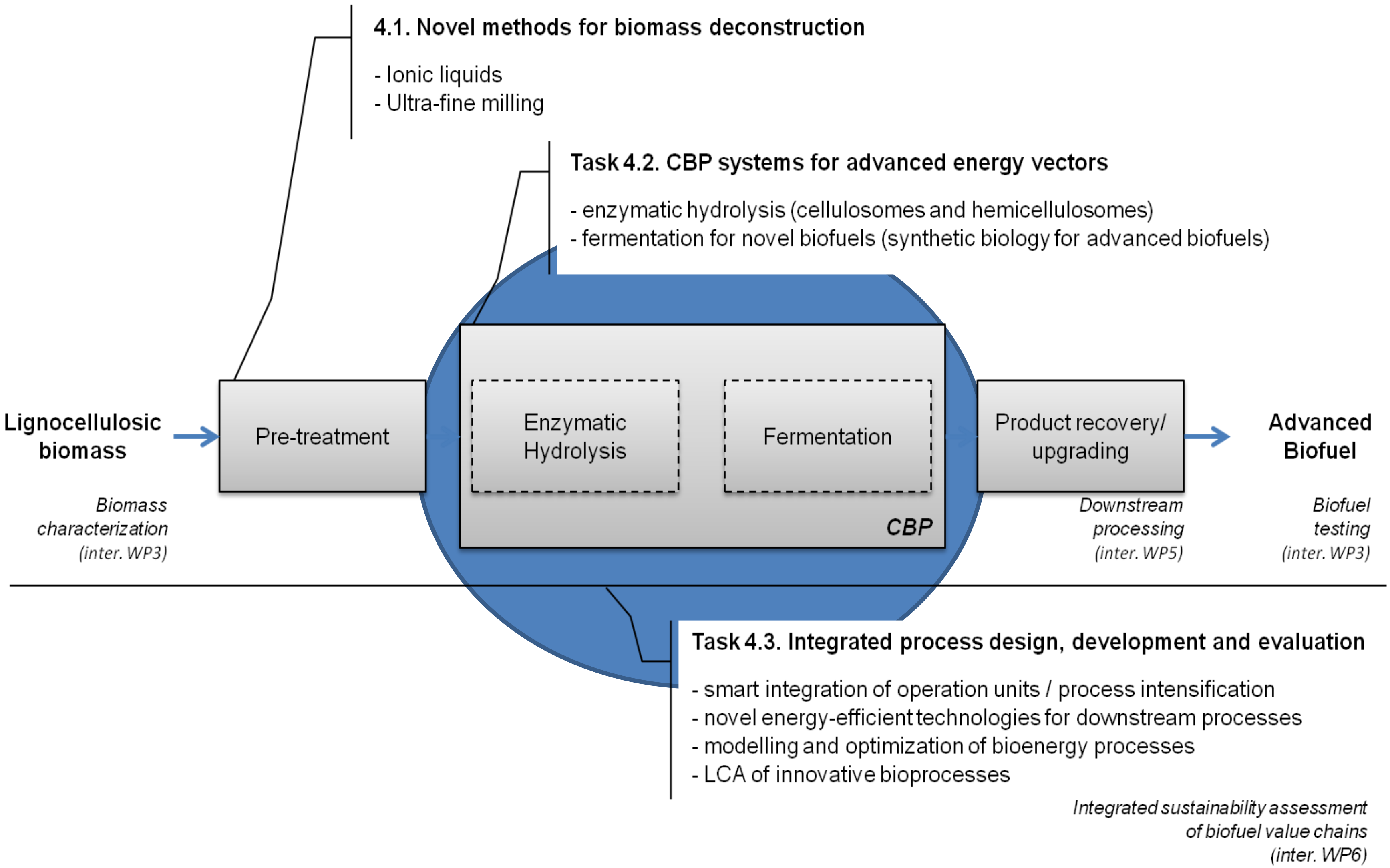
GranBio, São José Alagoas

Uncatalysed StEX

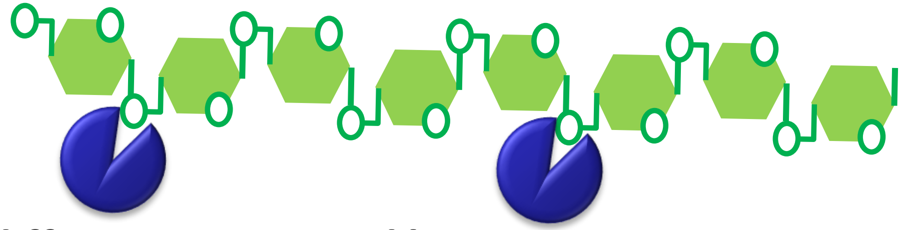
Dupont, Nevada, USA

Steam + diluted ammonia

The Lignocellulosic Ethanol Technology: in short

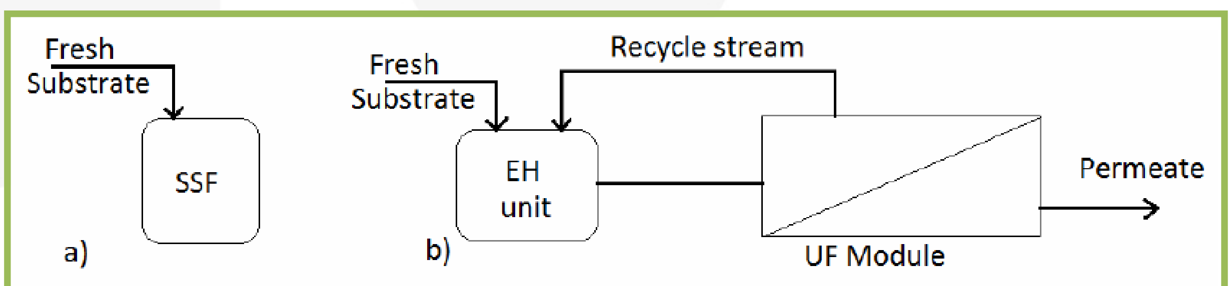


Enzymatic Hydrolysis



Current Strategies:

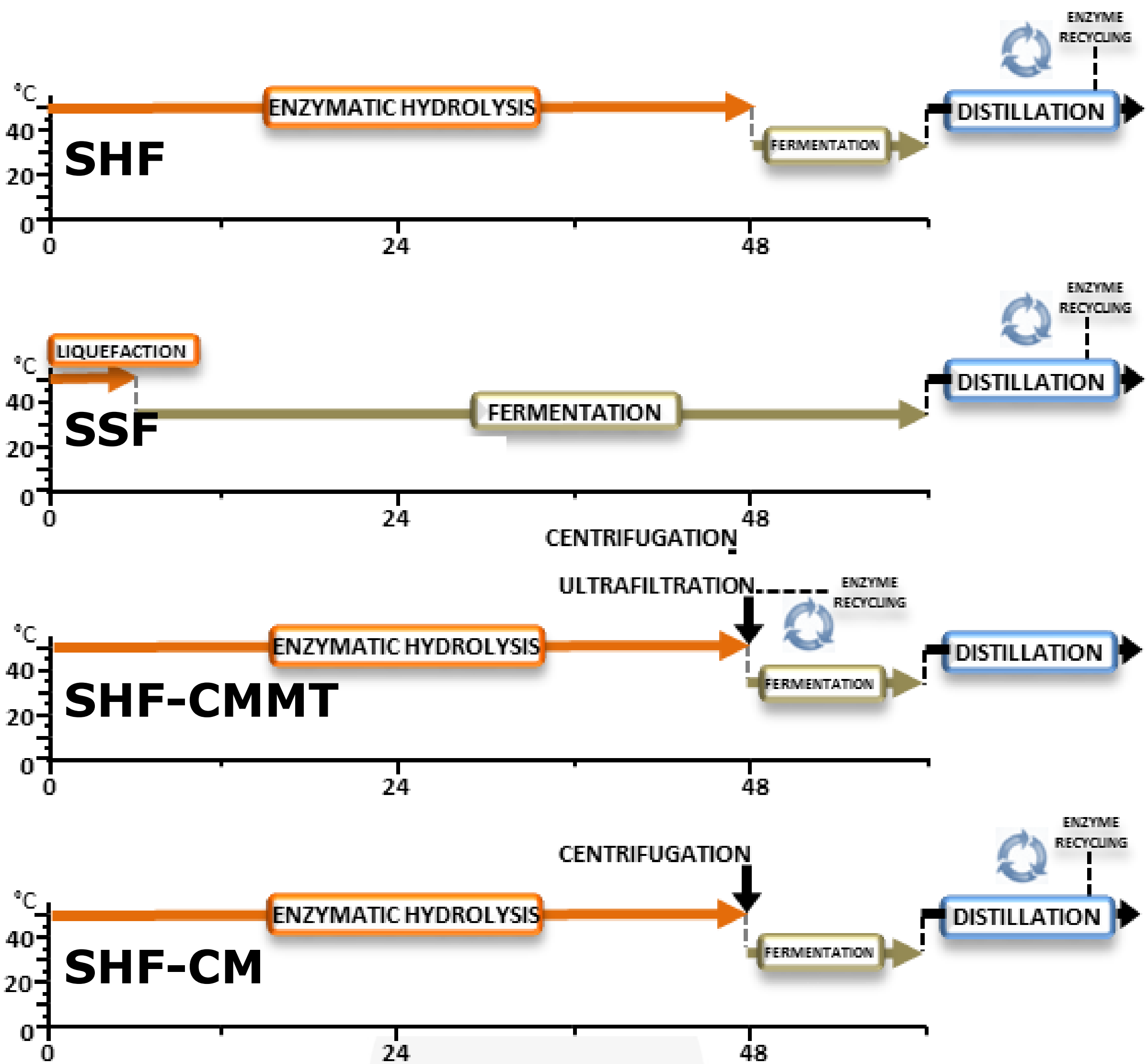
- **Improvement of enzyme efficiency towards different pre-treated biomass**
  - ✓ **Customized comercial (cellulases) enzyme**
    - ⇒ Enzymes highly optimized (maximum yields, shorter reaction times)
    - ⇒ Disadvantage: Costs & dependency from commercial contracts with suppliers, etc
  - ✓ **On-site enzyme (cellulases) production** (usually employing pre-treated biomass)
    - ⇒ Advantage: Lower OPEX costs
    - ⇒ Disadvantage: Potentially divert part of pre-treated biomass from 2G ethanol production (lowering ethanol yield: ton EtOH/ton 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:



SHF: single hydrolysis & fermentation

SSF: simultaneous saccharification & fermentation

SHF-CMMT: SHF-clear mash +Membrane technology

SHF-CM: SHF-clear mash technology

Enzymatic Hydrolysis + 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 solid loadings by avoiding mixing problems ⇒ ↑ EtOH titer**

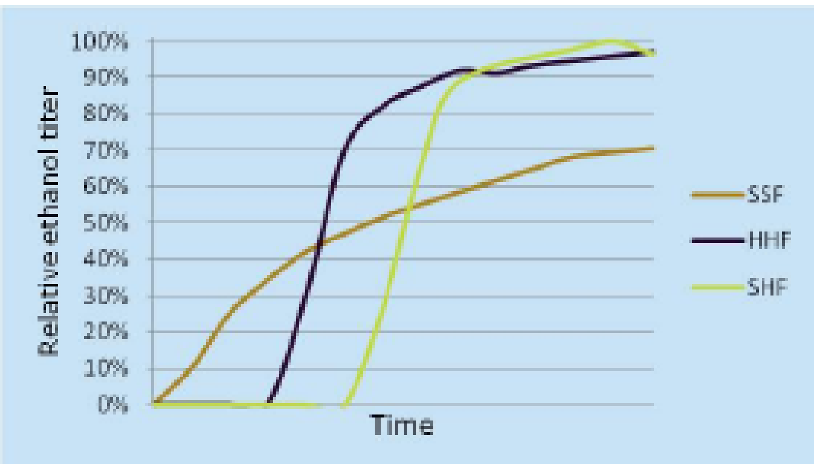
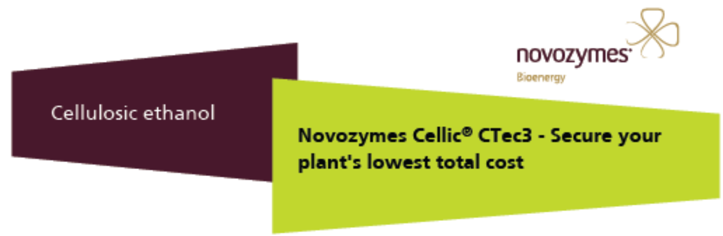


Fig. 3. Ethanol yield under varying hydrolysis conditions using Cellic® CTec3 at pH 5.0 and 50 °C on unwashed dilute acid-pretreated corn stover at 18% total solids loading. The yeast was pitched at different times, as indicated by initiation of ethanol production. The ethanol yield will vary depending 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.



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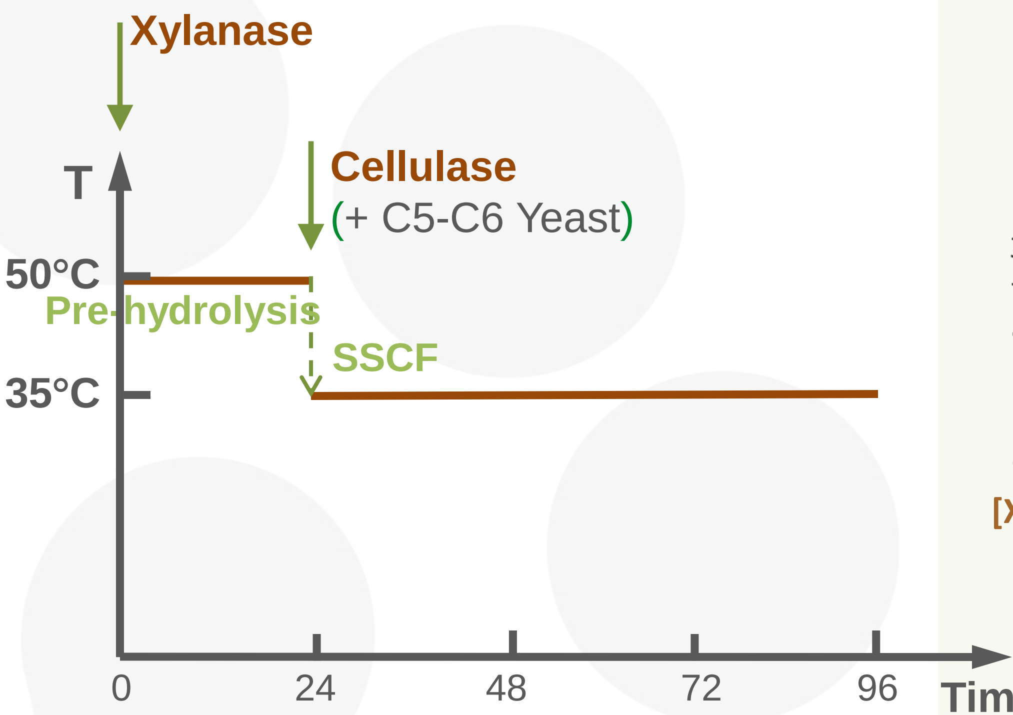
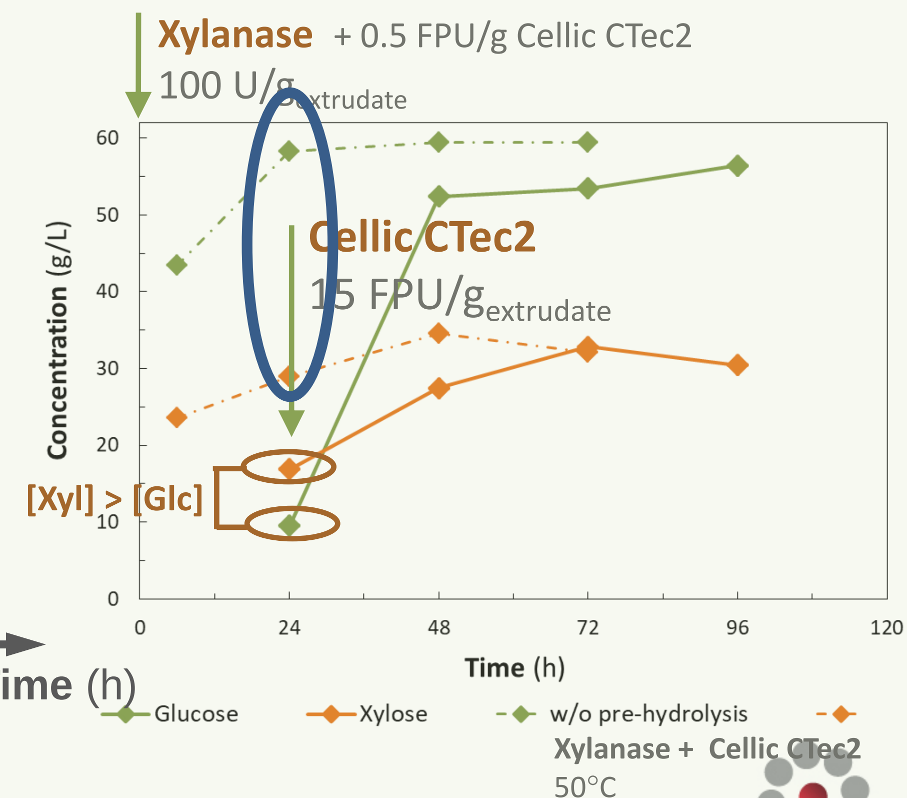
Hybrid Enz. Hydrolysis | Role of Hemicellulases

Hybrid Enzymatic Hydrolysis (HEH) + SSCF

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



Hydrolysis of BS extrudate:



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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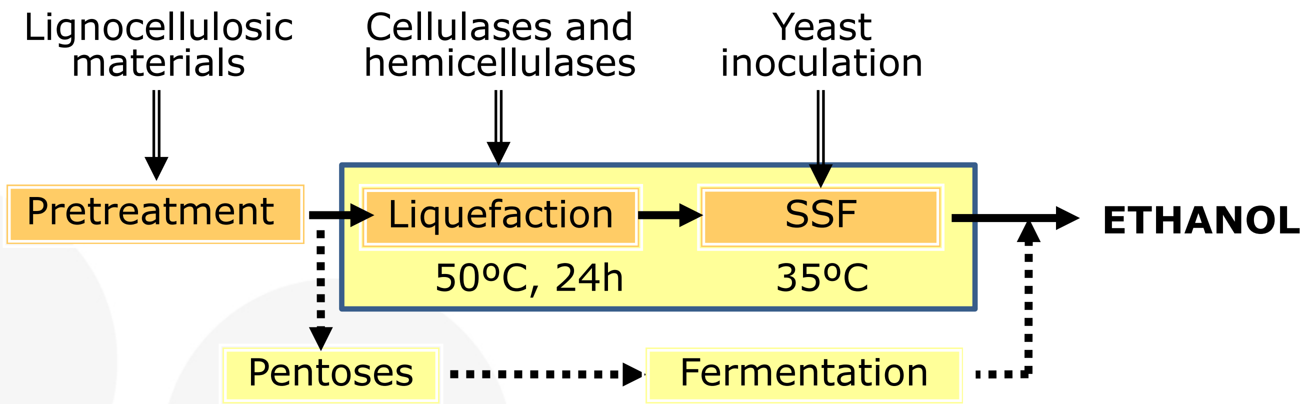
Enz. Hydrol. & Ferm.| Solid Loadings

Data from:

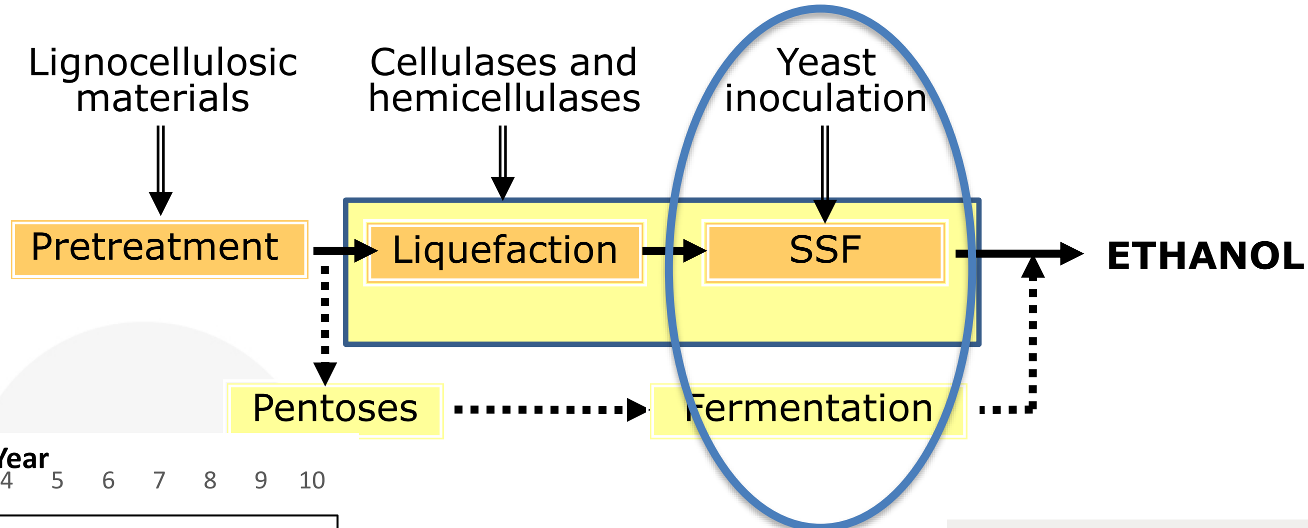


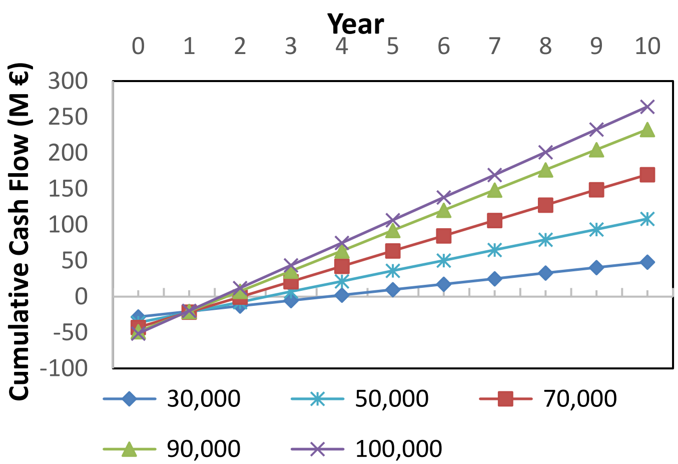
Sugarcane bagasse

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

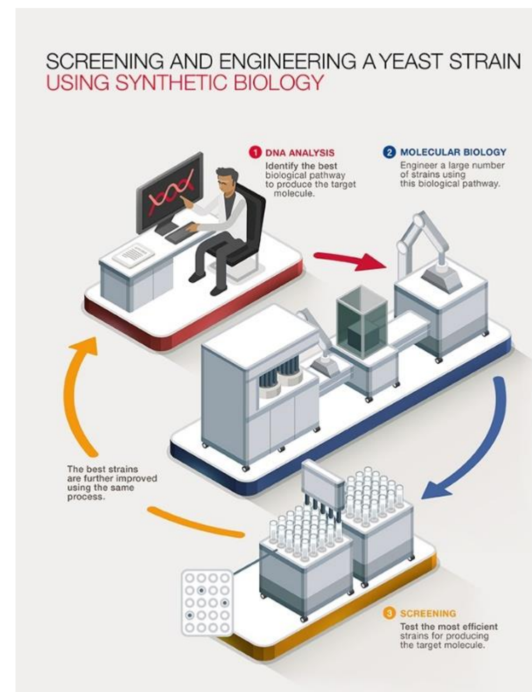
+15%

Fermentation| GMO vs non-GMO





NON-GMO

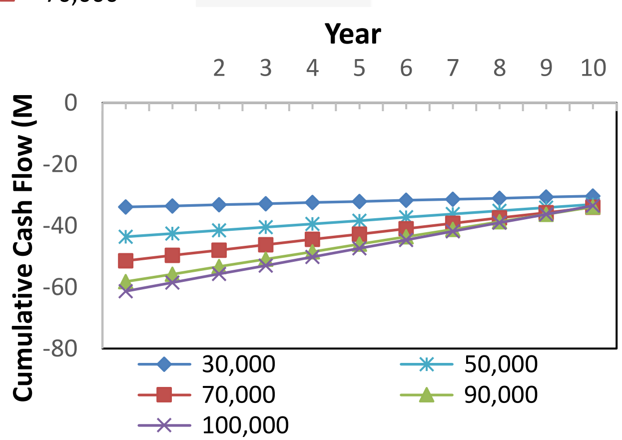


Data from:

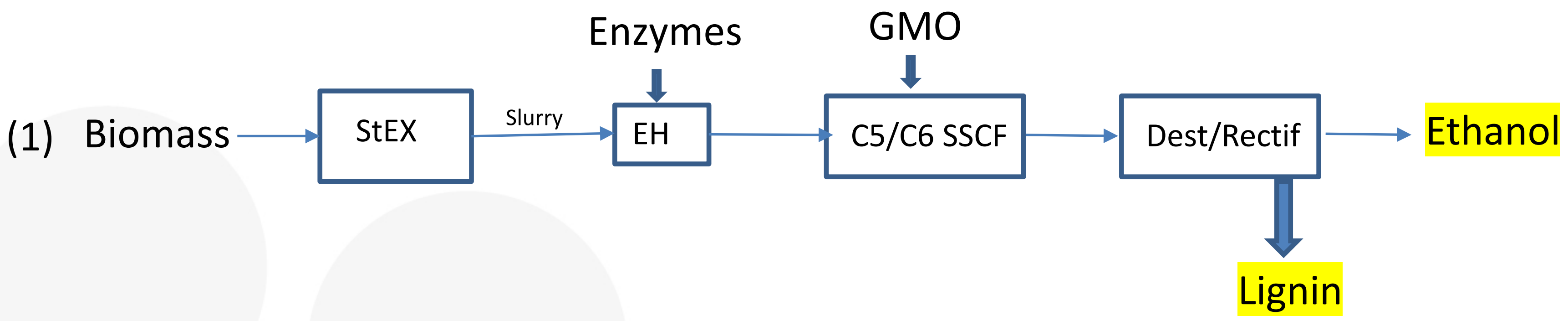
SMIBIO

ERANet LAC

GMO



2G Overall Technology (stand alone)



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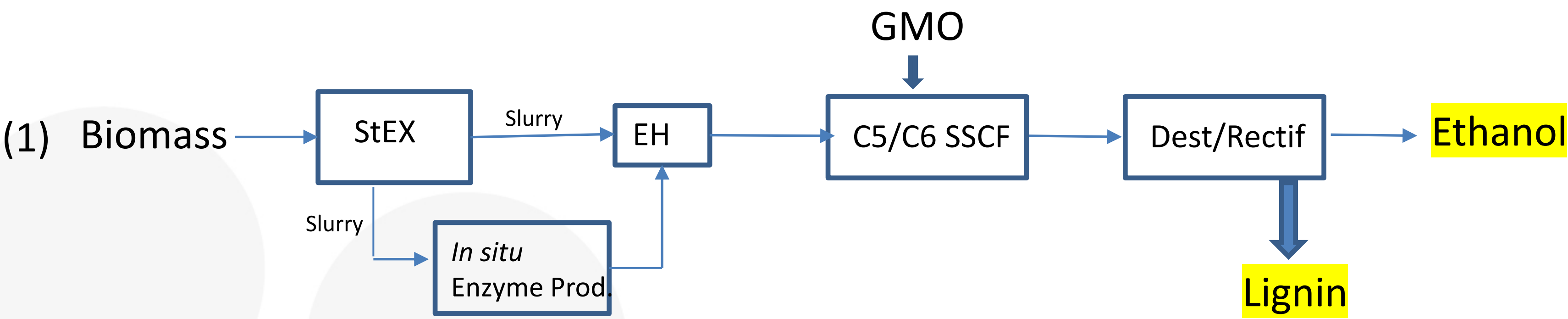

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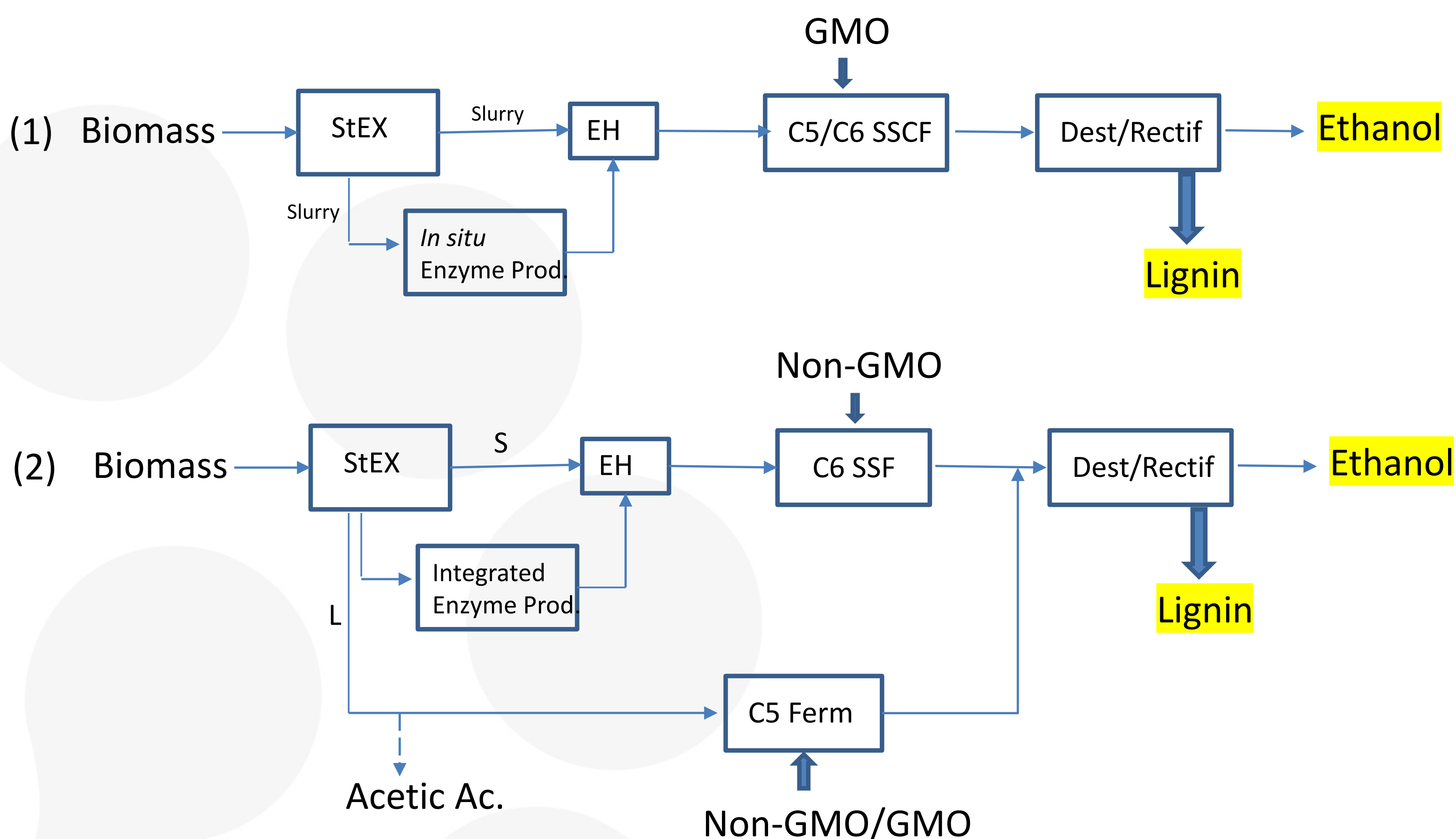
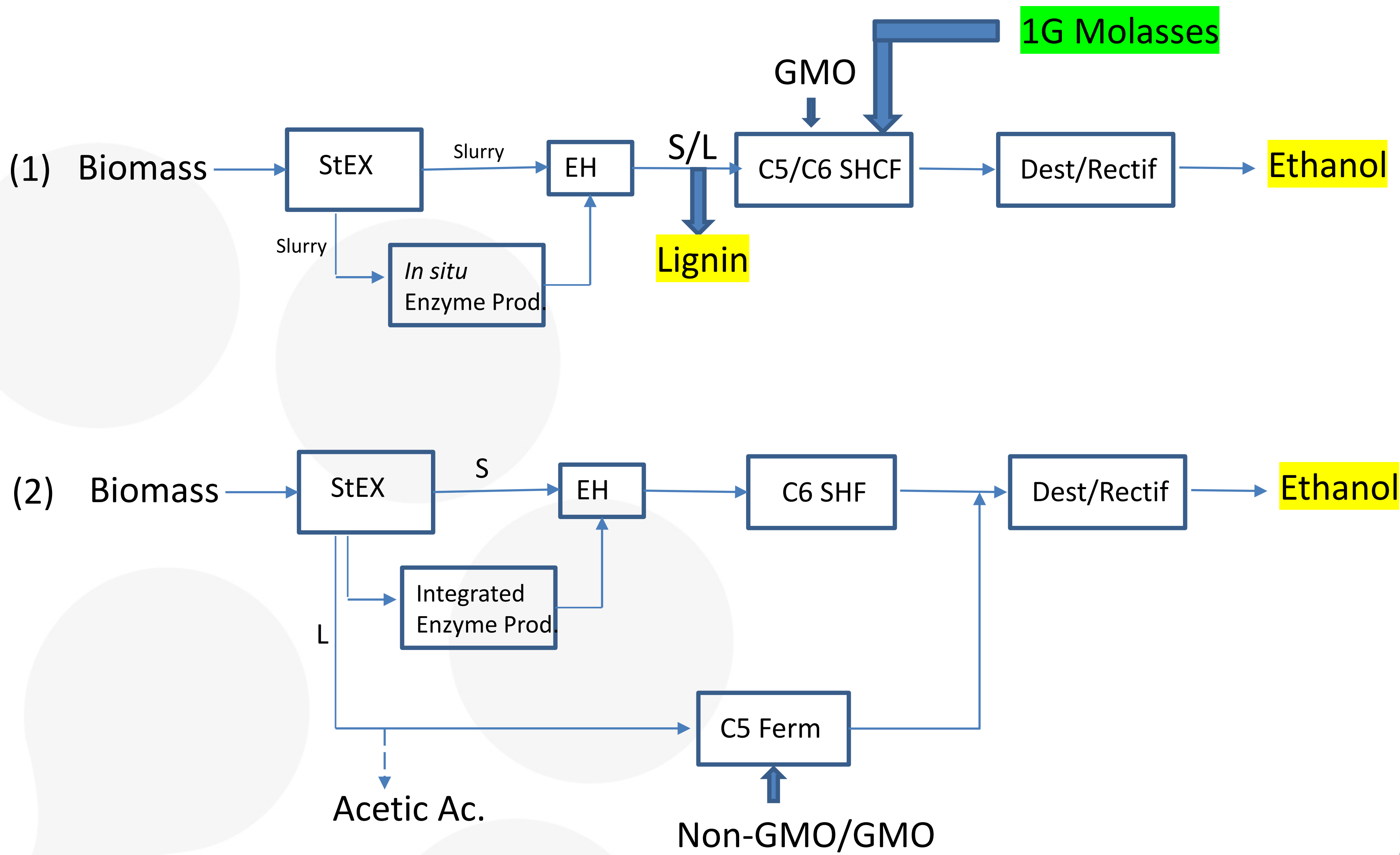


2G Overall Technology (integrated with 1G)



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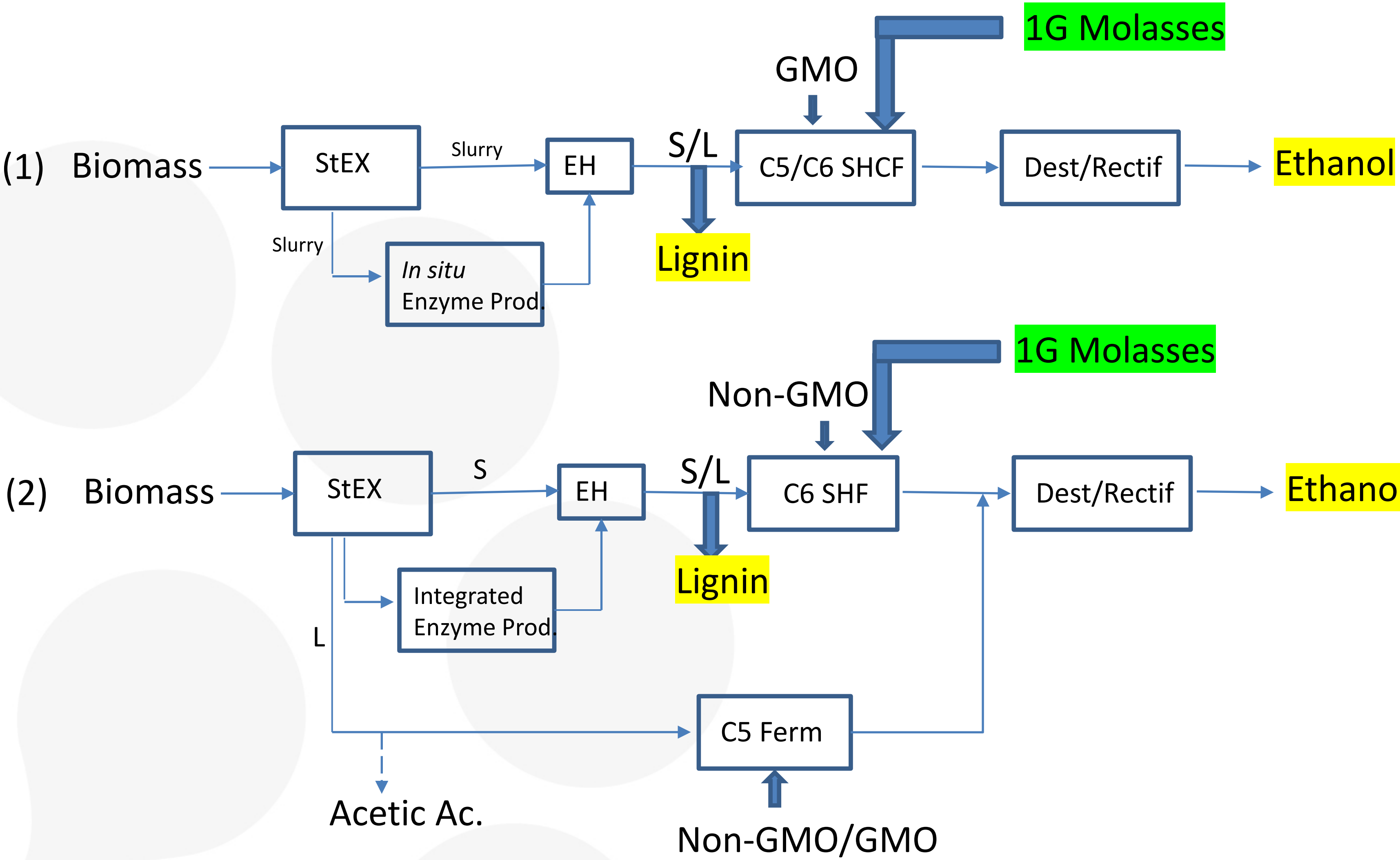
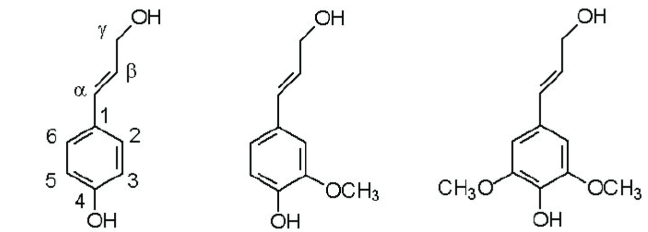


LIGNIN PLATFORM



p-coumaryl alcohol Mol Wt 150 | Coniferyl alcohol Mol Wt 180 | Sinapyl alcohol Mol Wt 210

Lignin Industry Today

- ❑ Exclusively based on pulp and paper industry

- ❑ By-product from Kraft and Sulphite pulping process

- ❑ Applications limited by inherent characteristics of extracted lignin

- ❑ Current chemical pulping processes (Kraft and Suphite) leads to: i) chemical adulteration of the extracted lignin (Na, S, Mg, etc), ii) chemical modification (condensation) and iii) require extensive and expensive post-treatment to return to desired properties

- ❑ **Almost 1 Bilion € business**

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LIGNIN PLATFORM: Potencial products

Syngas products

- Methanol
- DME
- Ethanol
- Mixed alcohols
- Fischer-Tropsch
- Liquids
- C1-C7 gasses

Hydrocarbons

- Benzene
- Toluene
- Xylene
- Cyclohexan e
- Styrenes
- Biphenyls

Phenols

- Phenol
- Substituted phenols
- Cathecols
- Cresols
- Resorcinols
- Eugenol
- Syringols
- Coniferols
- Guaiacols

Oxidised products

- Vanillin
- Vanilic acid
- DMSO
- Aromatic acids
- Aliphatic acids
- Syringaldyde
- Aldehydes
- Quinones
- Cyclohexanol
- ß-keto adipate

Macromolecules

- Carbon fibre fillers
- Polymer extenders
- Substituted lignins
- Thermoset resins
- Composites
- Adhesives
- Binders
- Preservatives
- Pharmaceuticals
- Polyols

IEA Bioenergy- Task 42 Biorefinery (2012), *Bio-based chemicals: value added products from biorefineries*.

LNEG

2G EtOH biorefineries| small vs large-scale

The plant size greatly influences any lignocellulose-based biorefinery

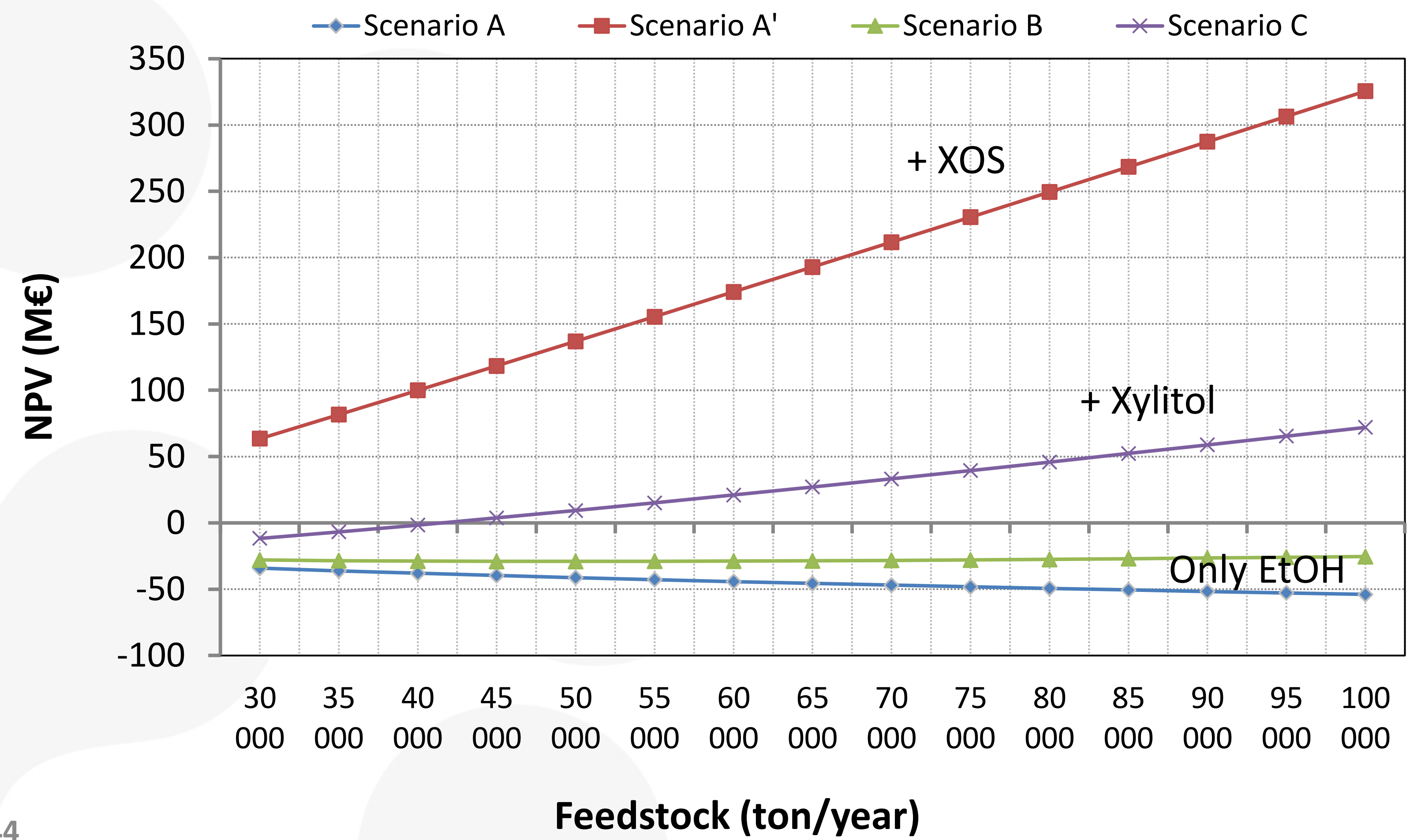
- The heterogeneity of lignocellulosic material allows **to produce a range of products** as broad **as the existing in petrochemical industry**

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

LNEG

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

Data from:



What are the next achievements at medium/large term?

- Will be EtOH an energy carrier for NextGen transportation sector? Yes, if they are carbon-neutral fuels.
  - Role of higher alcohols, long-chain fatty acids,…
- Improving overall energy-efficiency (eg, cane-energy, low-demand biomass pretreatments, CBP, DSP….)
- Biochemicals and other chemicals shall have an increasing importance in advanced ethanol biorefineries
  - However, there are few chemical products with markets large enough to absorb their 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)
- Can we skip the EH step ?
- Small scale processing reduces capital costs and costs for energy and transportation. Are they more important in the future?
- 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.

LNEG

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Thanks for your attention

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More info:

www.proethanol2g.org

www.babet-real5.eu

www.smibio.net

REPÚBLICA PORTUGUESA

AMBIENTE E AÇÃO CLIMÁTICA