Universidad de Chile
Facultad de Ciencias Físicas y Matemáticas
Departamento de Ingeniería Química y Biotecnología

# USE OF IONIC LIQUIDS FOR THE PRODUCTION OF SECOND GENERATION BIOETHANOL

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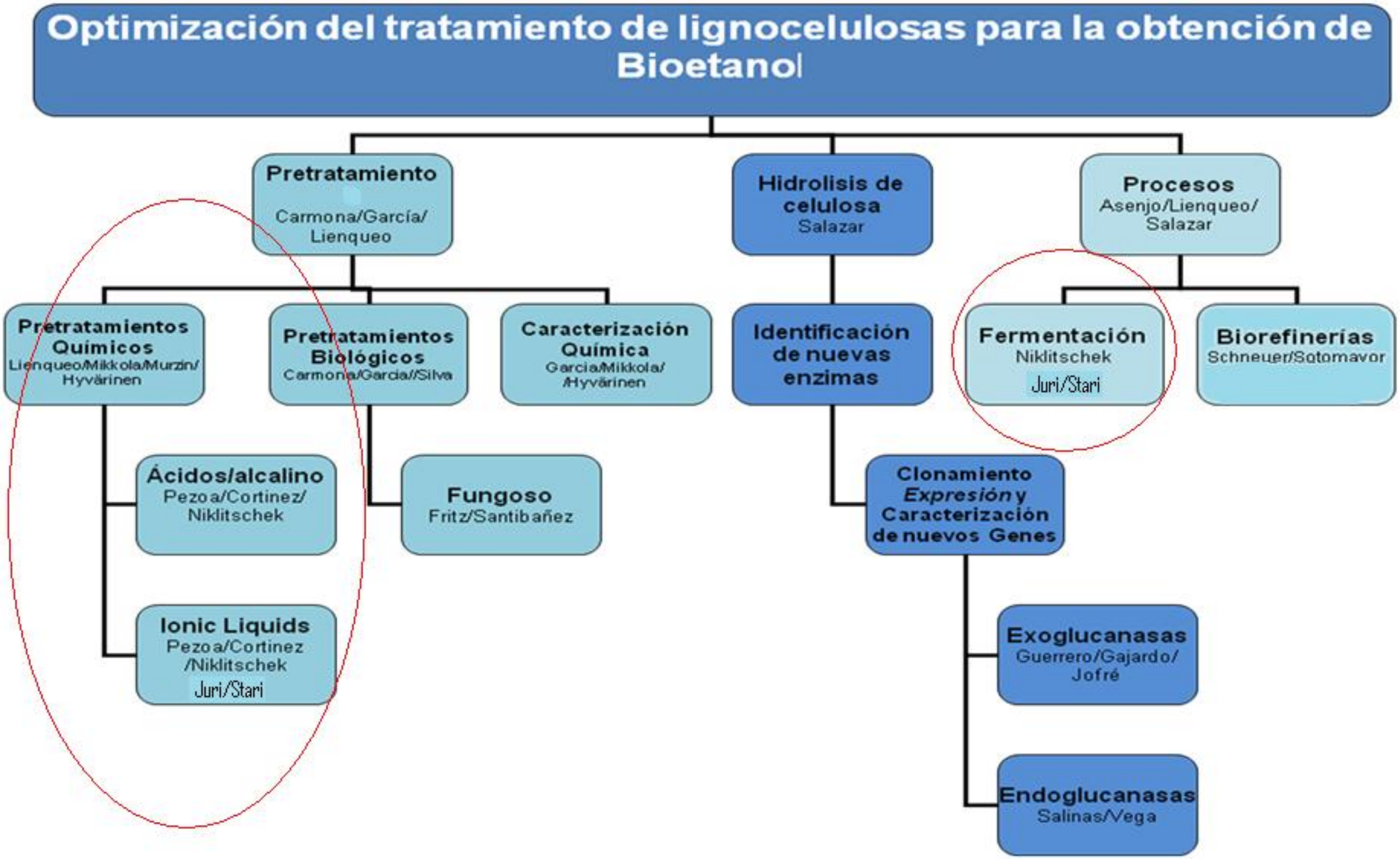
Optimización del tratamiento de lignocelulosas para la obtención de Bioetanol
Pretratamiento
Carmona/García/Lienqueo
Hidrolisis de celulosa
Salazar
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Pretratamientos Químicos
Lienqueo/Mikkola/Murzin/Hyvärinen
Pretratamientos Biológicos
Carmona/García//Silva
Caracterización Química
García/Mikkola//Hyvärinen
Identificación de nuevas enzimas
Fermentación
Niklitschek
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Biorefinerías
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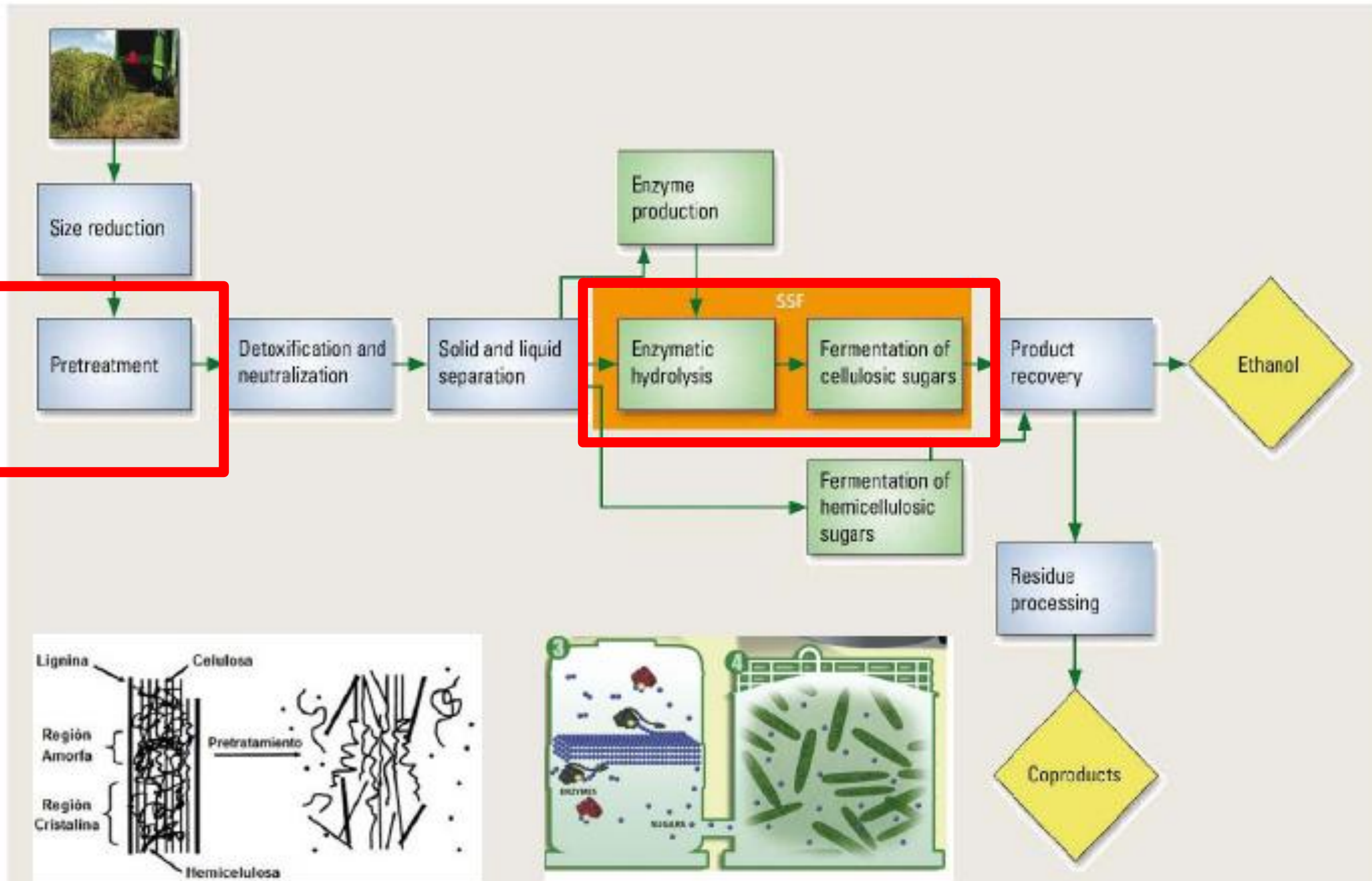
# Introduction

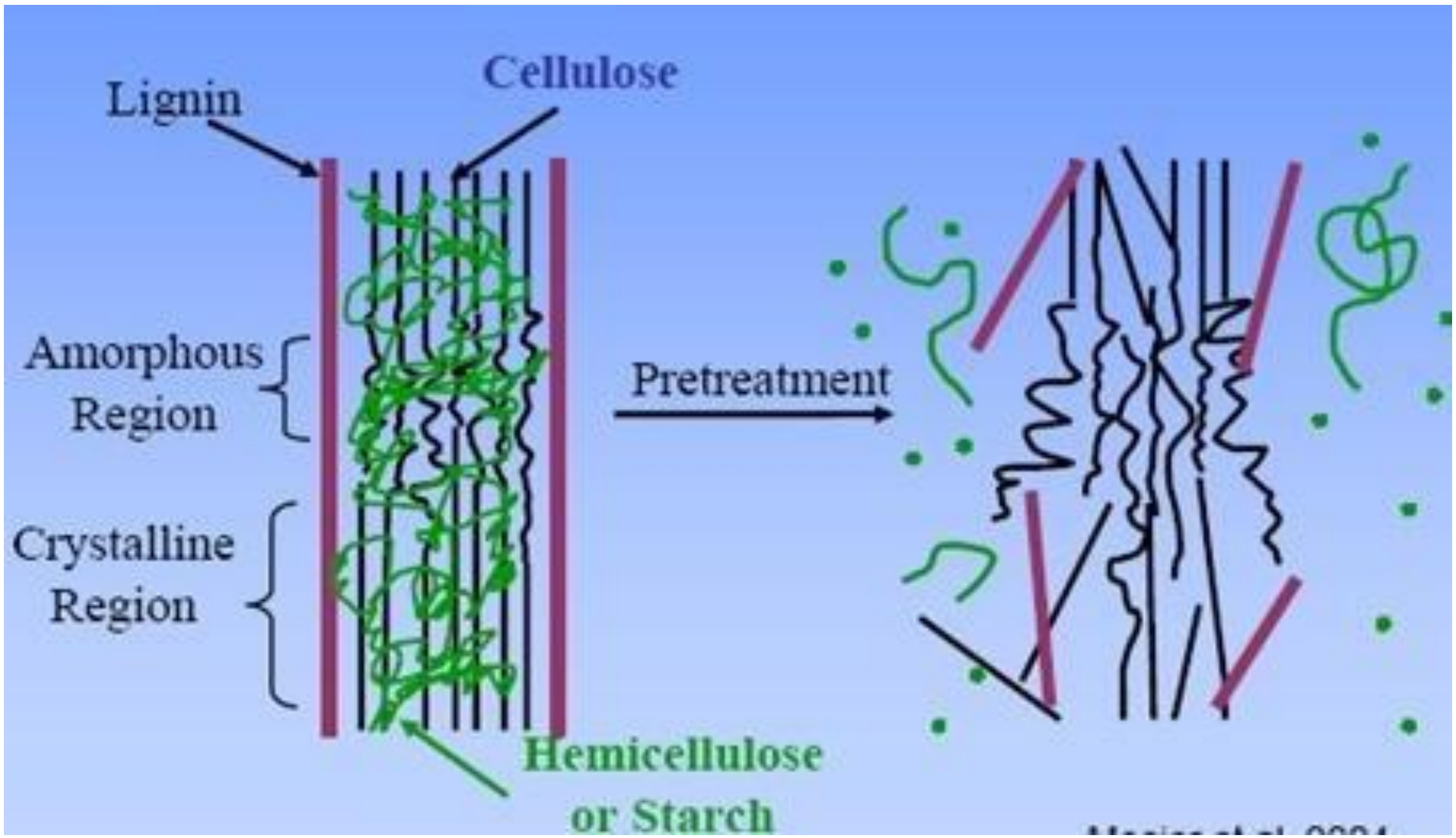
# Production of second generation bioethanol





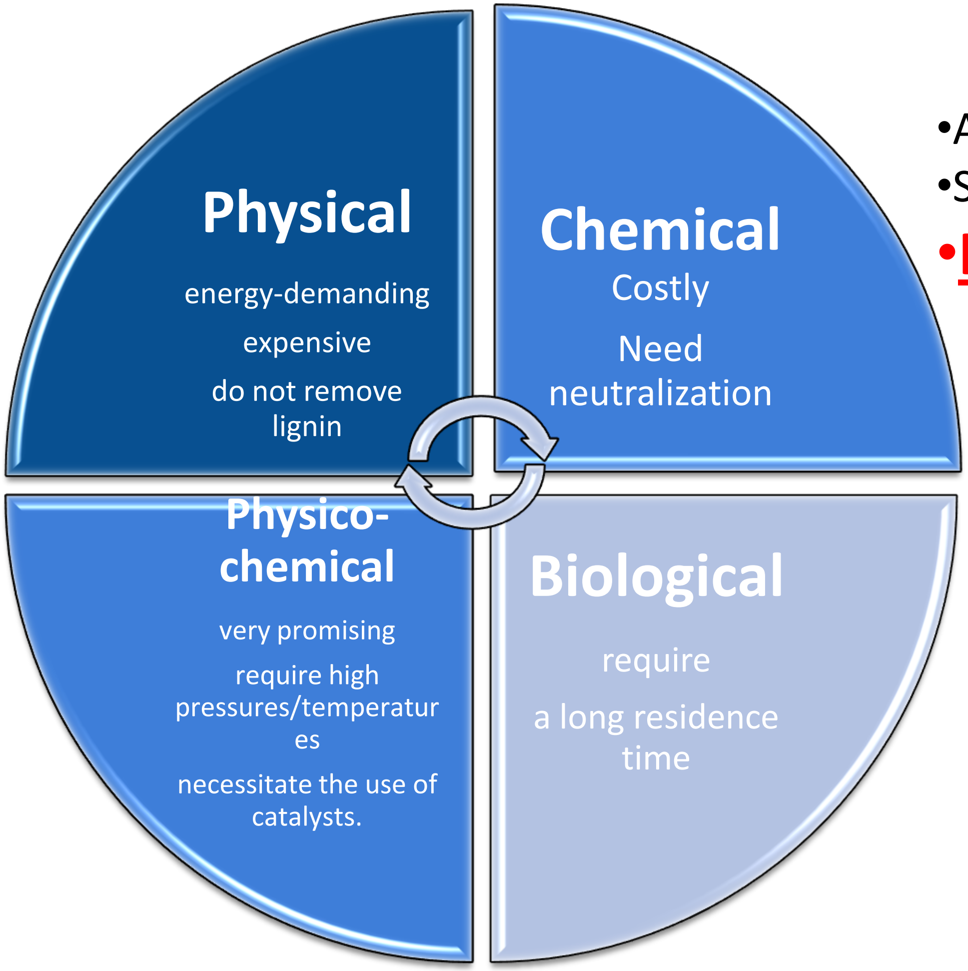
# Schematic representation of pretreatment of lignocelluloses

- Introduction
- Methodology
- Resultads and discussion
- Conclusions



# Clasification of pretratments





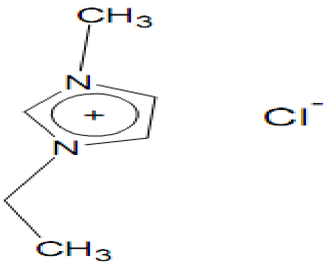

- Acid
- Solvents
- **Ionic Liquid**

# Ionic liquids (ILs) : a new pretreatment



## What are ILs?

- Organic salts.
- Usually melt below 100ºC.
- High thermal stability.
- Non-flammability
- Very low vapor pressure
- There exist an almost limitless number of combinations containing anions and cations ➔
  - "Green solvents"
- Recycle ???




[emim][Cl][4]

# *Ionic liquids as pretreatment of cellulose*

**Several studies have shown that :**

- Cellulose can be dissolved in a number of hydrophilic ionic liquids,
  - **([Bmim]Cl)[2]** (corrosive and toxic)
  - **([Amim]Cl)[3]**
- After dissolution, cellulose can be regenerated e.g. via addition of anti-solvents (like acetone or water).

**(2): (Bmim]Cl):** 1-butyl-3-methylimidazolium chloride
**(3): ([Amim]Cl):** 1-allyl-3-methylimidazolium chloride

**Patents**

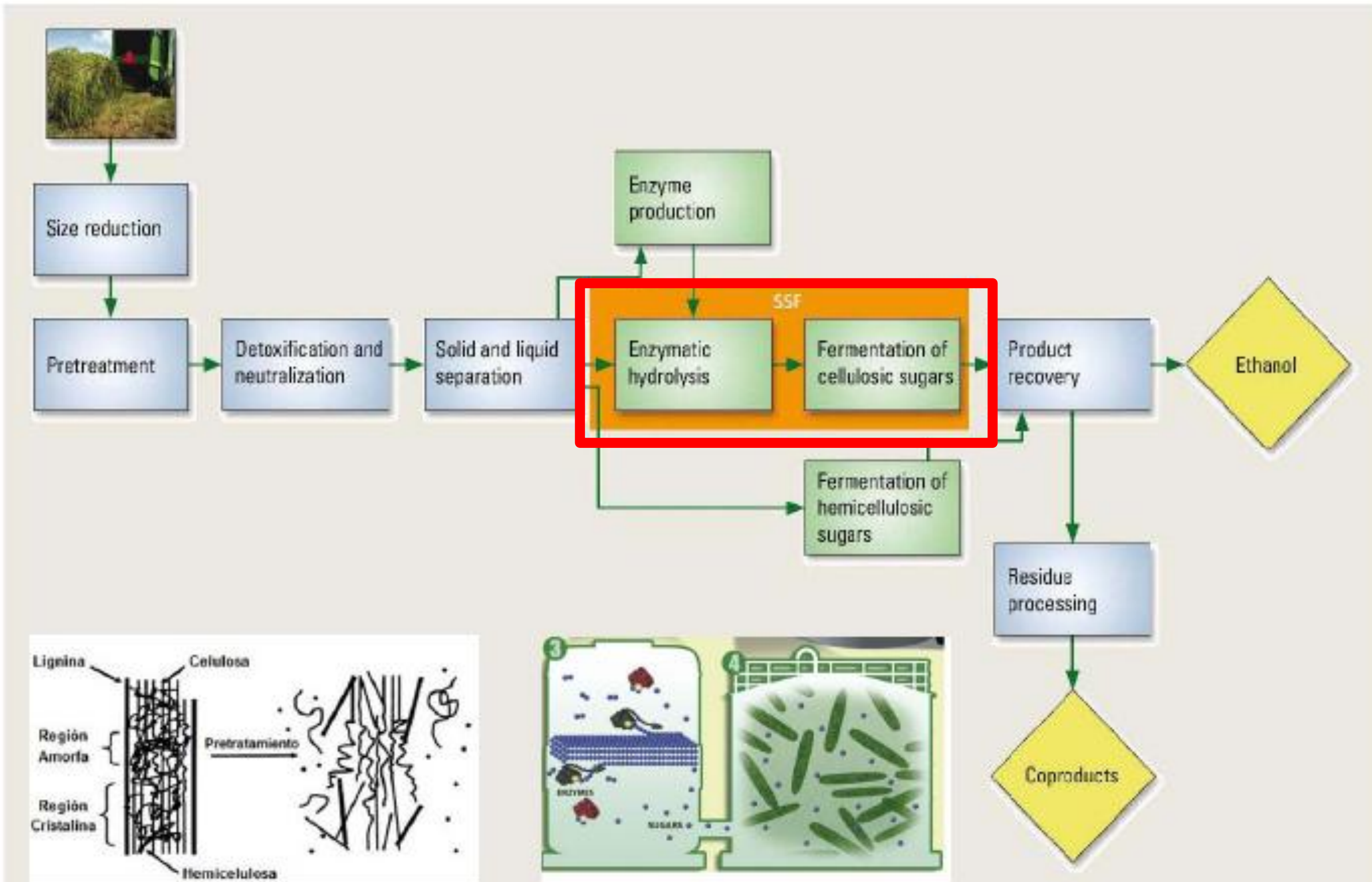
1. **Varanasi S., Schall C., Dadi A., Anderson J., Rao J. y Paripatti P. (2008). Biomass pretreatment. World Intellectual Property Organization WO 2008/112291 A2, The University of Toledo, Toledo, OH, Estados Unidos.**

2. **Varanasi S., Schall C., Dadi A. (2010). Saccharifying cellulose World Intellectual Property Organization US 7.674.608 B2, The University of Toledo, Toledo, OH, Estados Unidos.**

3. **Balensiefer T, Brodersen j, D'Andola G, Massonne K, Freyer S, Stegmann W (2010) " Enzymatic hydrolysis of a cellulose material treated with an ionic liquid" Publication No. US 2010/0112646 A1.**

# Production of second generation bioethanol





# Separate Fermentation step after the hydrolysis (SHF) v/s Simultaneous Saccharification and Fermentation (SSF)



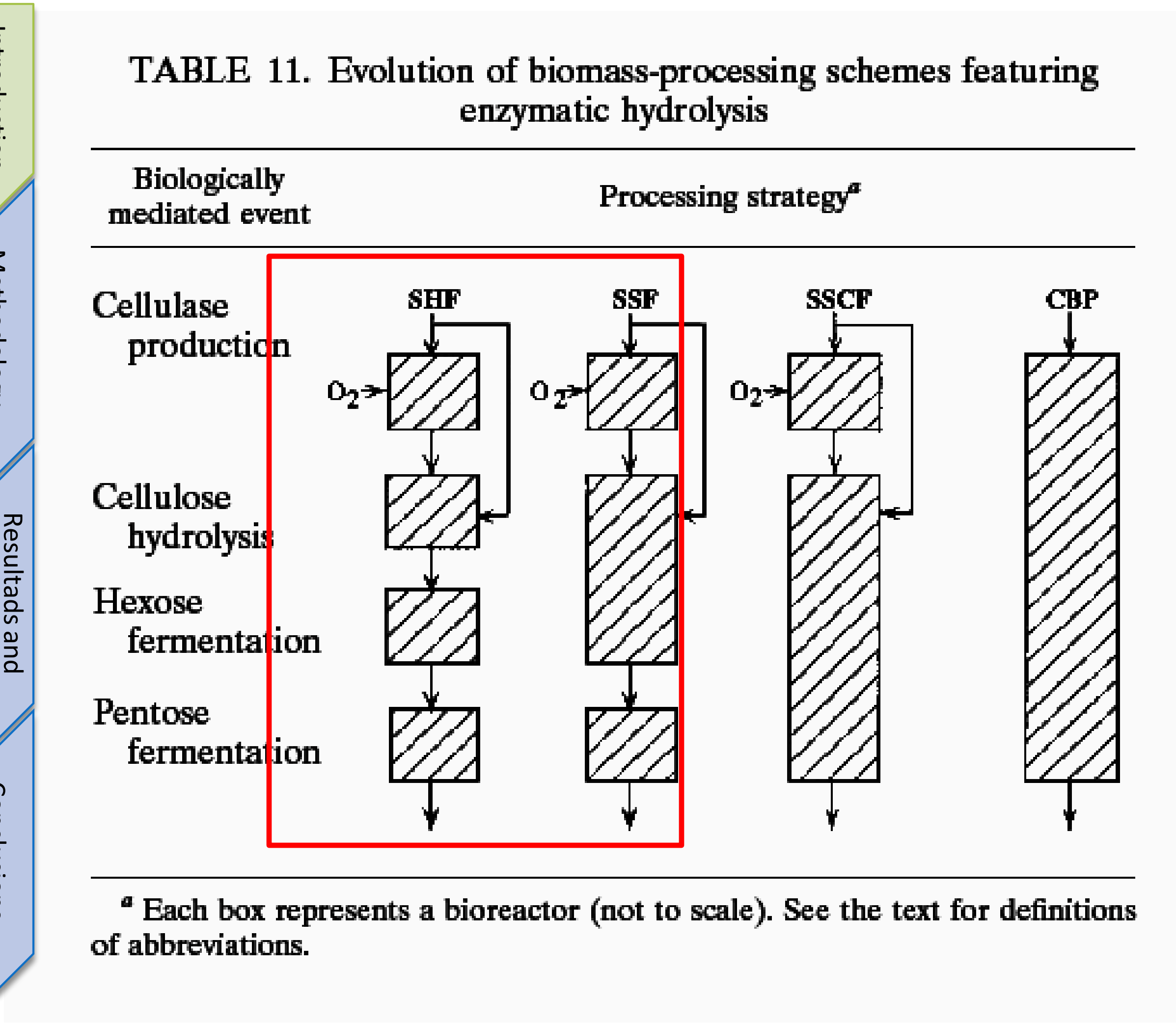


TABLE 11. Evolution of biomass-processing schemes featuring enzymatic hydrolysis



[a] Each box represents a bioreactor (not to scale). See the text for definitions of abbreviations.

**Benefits of SSF**

-Reduced end-product inhibition of the enzymatic hydrolysis,
-Reduced investment costs.

**Disadvantages of SSF**

- The need to find favorable conditions (e.g. temperature and pH) for both, the enzymatic hydrolysis and the fermentation.

# AIM

Introduction

Methodology

Resultads and discussion

Conclusions

## General

Study the effect of the use of different process configurations for the saccharification and fermentation steps (SSF and SHF) of lignocellulosic residues pretreated with ionic liquid to obtain bioethanol.

# Methodology

# Methodology

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***Lignocellulosic residues; lenga, eucalyptus, wheat and corn.***


# Methodology with Ils



***Forest residues; lenga, eucalyptus, wheat and corn.*** → Pretreatment with ILs

Ionic liquid and lignocellulosic materials in the ratio of 1/20 at different conditions:

1. **B**lank: without pretreatment, only enzymatic hydrolysis,
2. $[EMIM^+][Cl^-]$ at 80°C for 60 min of incubation time,
3. $[EMIM^+][Cl^-]$ at 121°C for 60 min of incubation time,
4. $[EMIM^+][Cl^-]$ at 150°C for 30 min of incubation time,
5. $[EMIM^+][Cl^-]$ at 150°C for 60 min of incubation time,
6. $[EMIM^+][Cl^-]$ at 170°C for 60 min of incubation time,

# Methodology with Ils



***Forest residues; lenga, eucalyptus, wheat and corn.***

Pretreatment with ILs

Solid Fraction
Regeneration with water

Liquid Fraction

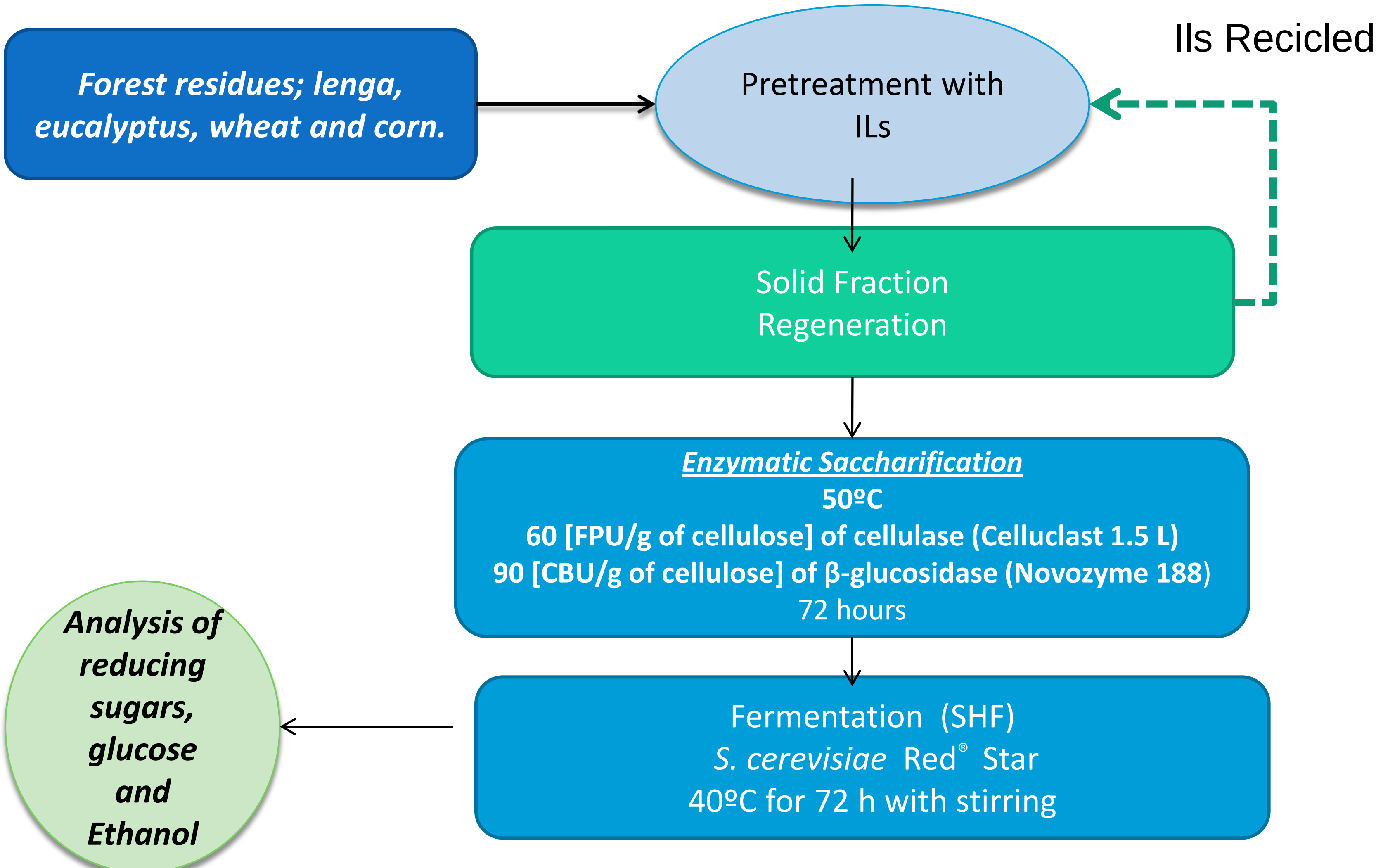
***Enzymatic Saccharification***

***Analysis of reducing sugars and monosaccharides***

***Analysis of reducing sugars and monosaccharides***

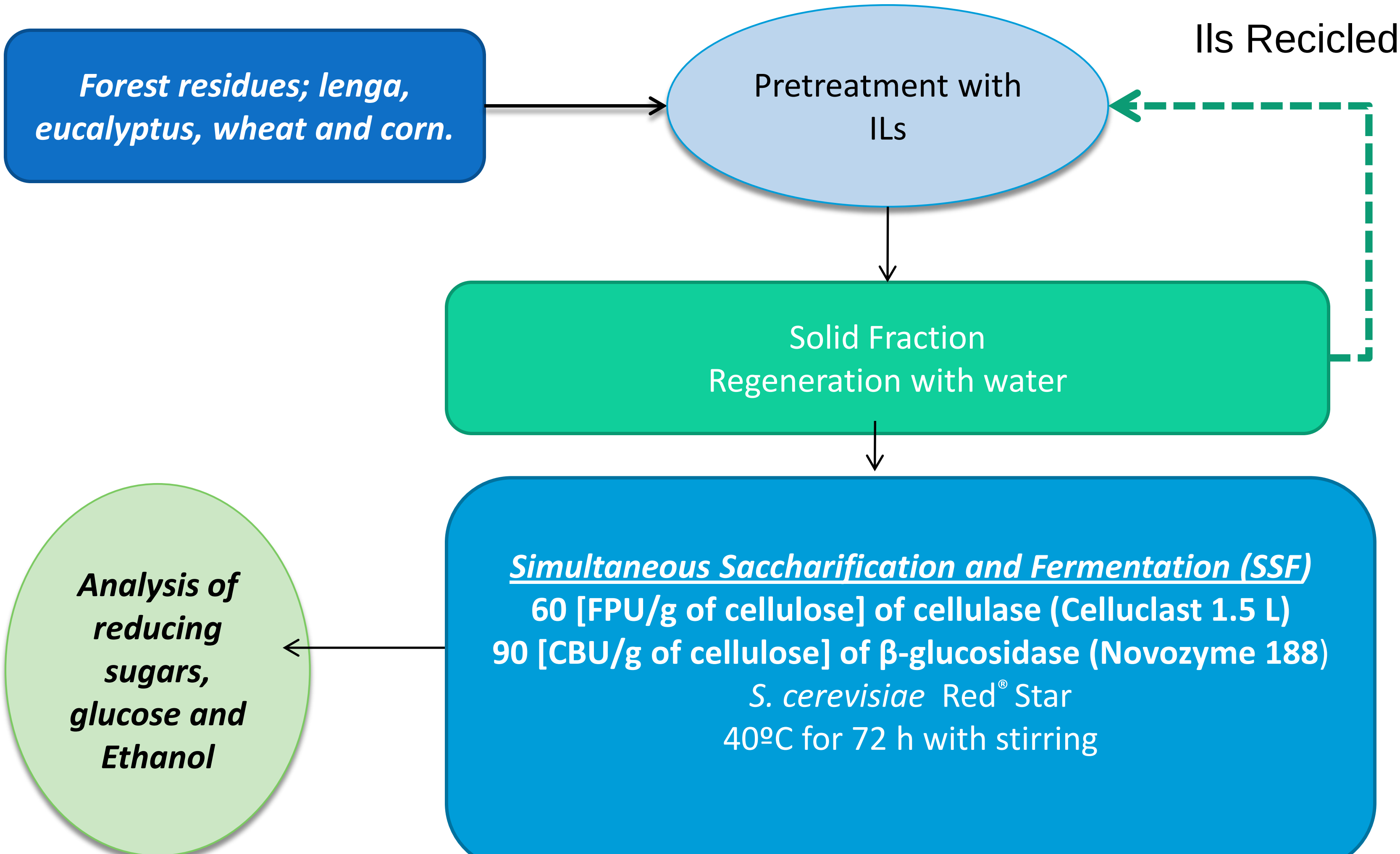
# Methodology for Separate Fermentation step after the hydrolysis (SHF )





# Methodology for Simultaneous Saccharification and Fermentation (SSF)



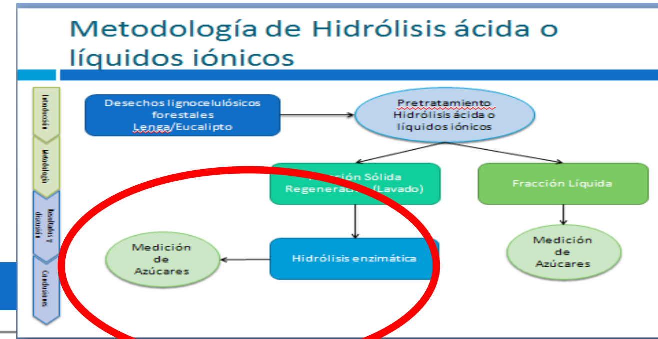


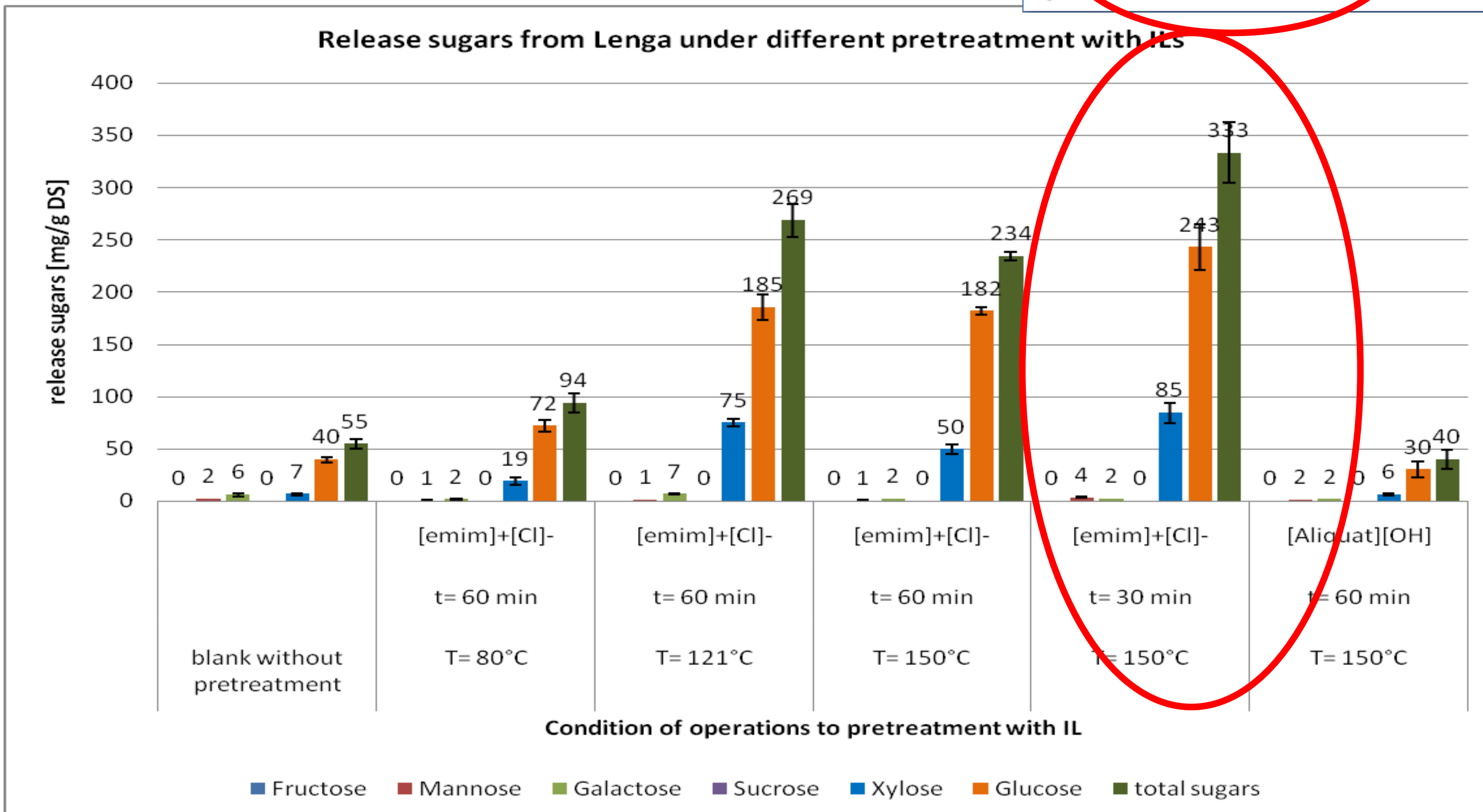
# Results

Pretreatment with Ionic Liquids

# *Effect of different pretreatments with Ionic Liquids –Lenga residues*

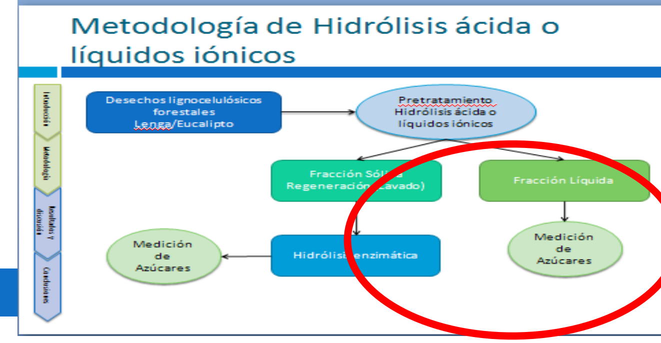





Effect of temperature, time and type of IL pretreatment on sugars released from regenerated Lenga. All samples were hydrolyzed with cellulase complex.

# *Amount of dissolved sugars present in $[EMIM^{+}][Cl^{-}]$ after pretreatment of Lenga residues a 150ºC.*

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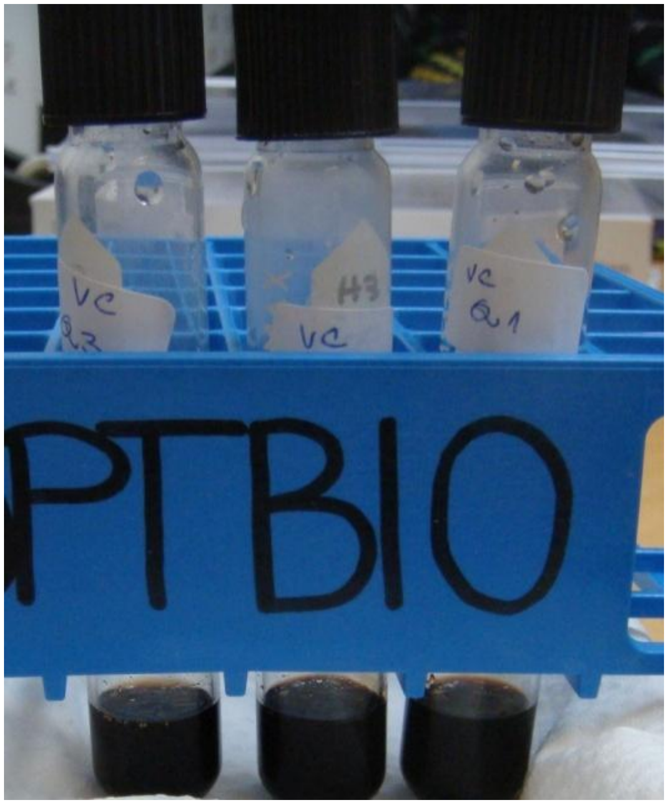
| Time [min] | Amount of dissolved sugars [mg/g DS] |
|---|---|
| | |
| **30** | **16** |
| **60** | 49 |

# Eucalyptus at 170°C for 60 min







Samples after pretreatment at 170ºC

# The best operational conditions for pretreatment with ILs



| ***Eucalyptus, wheat and corn*** | |
|---|---|
| ILs | $[emim^{+}][Cl^{-}]$ |
| Time | 60 [min] |
| Temperature | 150 [°C] |

Conversion Glucose: 44%
Conversion Xilose: 13%

| **Lenga** | |
|---|---|
| ILs | $[emim^{+}][Cl^{-}]$ |
| Time | 30 [min] |
| Temperature | 150 [°C] |

Conversion Glucosa: 54%
Conversion Xilosa: 22%

# Results

Saccharification and Fermentation

# *Comparison ethanol production in SSF and SHF processes for Lenga residues*

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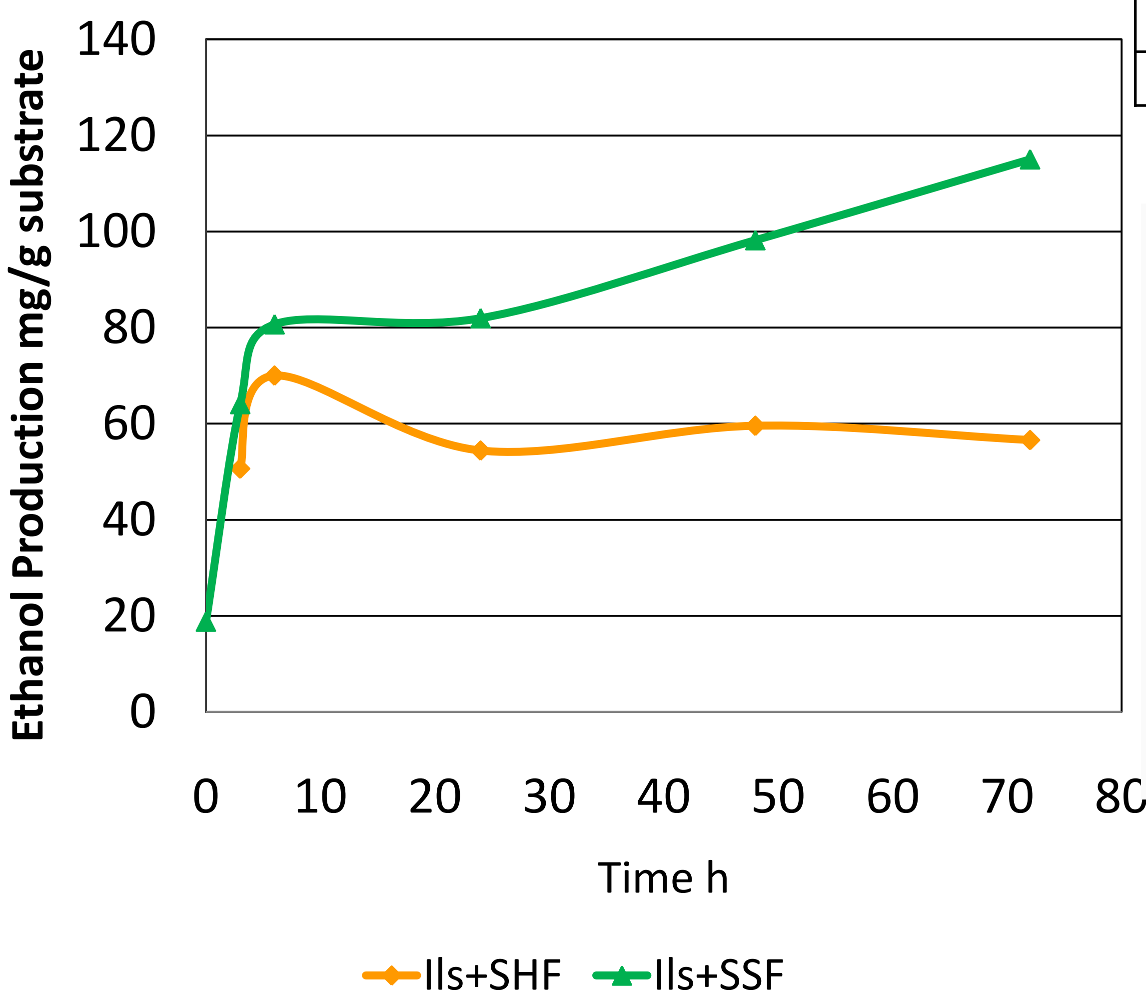
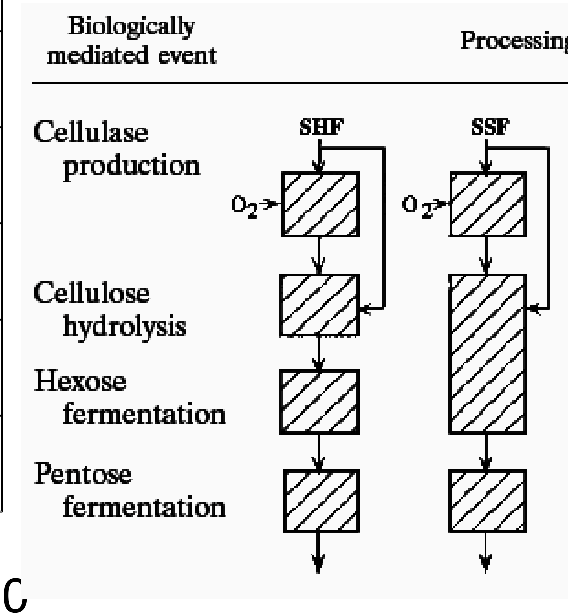
| Sample | Yield ethanol/glucose [%] |
|---|---|
| SHF Pret. IL | 23 |
| **SSF Pret. IL** | **47** |



# The best operational conditions



| Parameter | Value |
|---|---|
| Simultaneous Saccharification and Fermentation (SSF) | |
| | |
| M.O. Type | *S. cerevisiae* Red Star |
| Pretreatment | Ionic liquid [EMIM]Cl at 150ºC for 30 min |
| Enzymatic charge | 37 FPU/g sustrate |
| Sustrate charge | 9 % p/v |
| | |
| Temperature | 40°C |
| Reaction Time | 72 hours |

# Results

Recycled ILs

# Effect of recicled Ils - Saccharification

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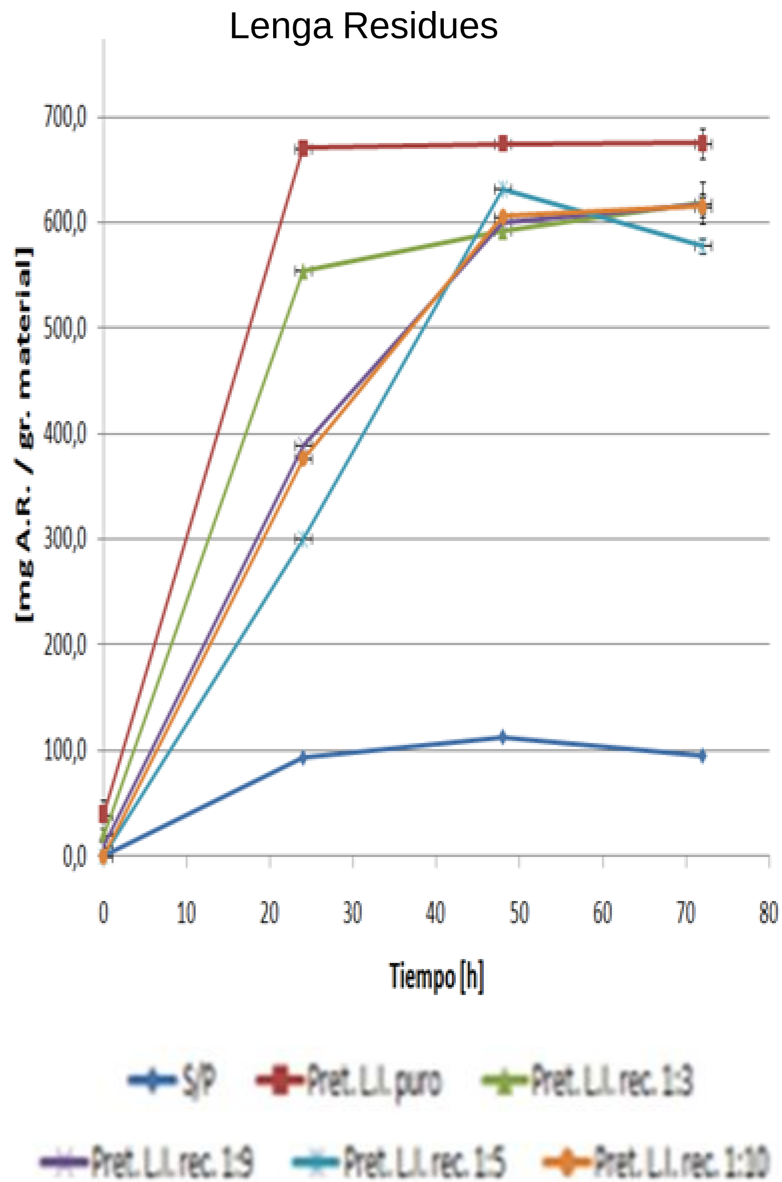



| Sample 48 hrs | % of saccharification |
| --- | --- |
| Pure IL 1:3 | 100 |
| Recycled IL 1:3 | 89 |
| Recycled IL 1:5 | 92 |
| Recycled IL 1:9 | 89 |
| Recycled IL 1:10 | 89 |
| Without pretreatment | 15 |

Pure IL Recycled IL

# CONCLUSIONES

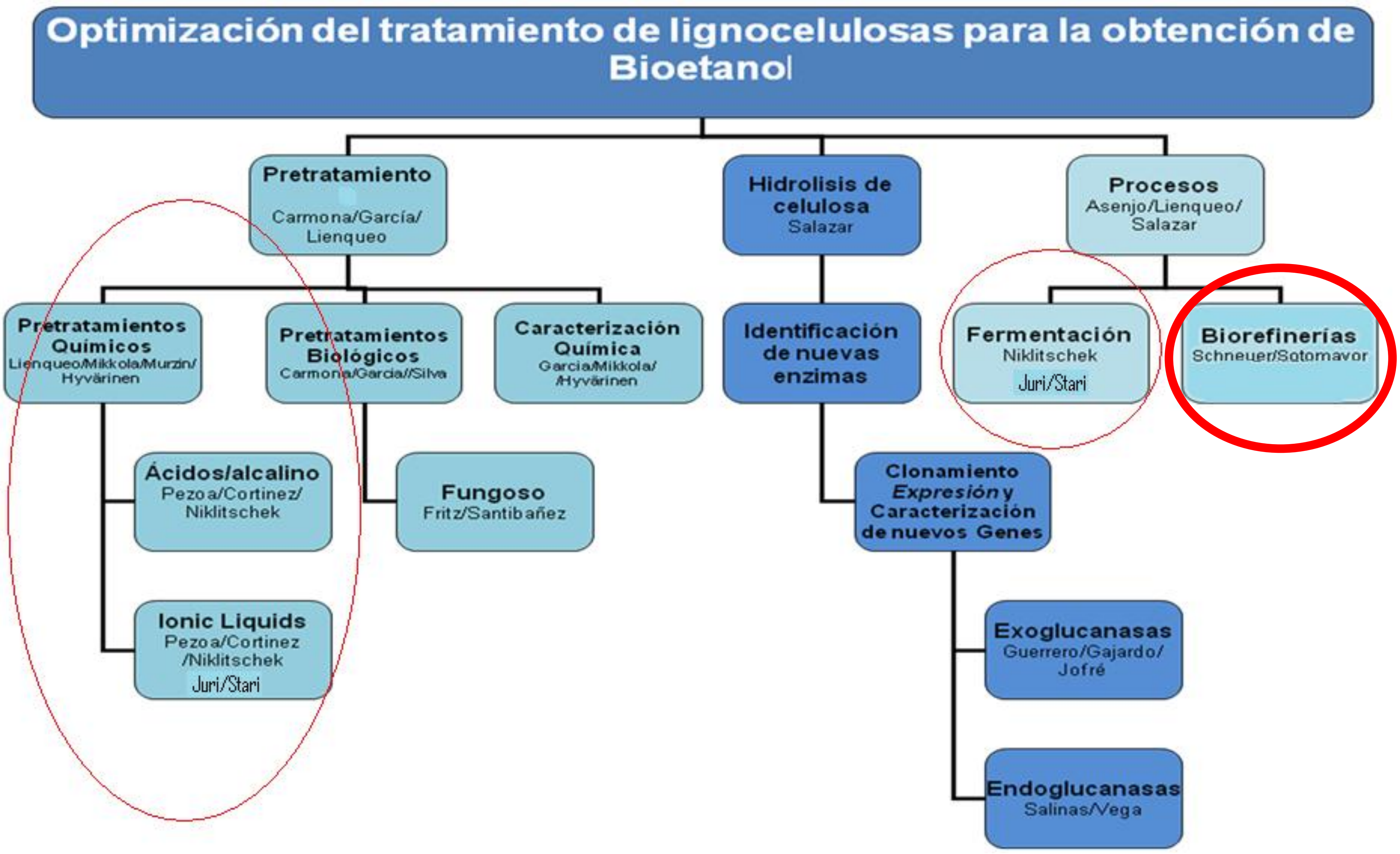
# Conclusion



- **The use of $[EMIM^+][Cl^-]$ as a 'structure-disruptive' solvent in the pretreatment of Lenga residues was demonstrated.**
- **The best operational conditions for the IL-pretreatment were determinated for each lignocellulosic residue.**
- **Additionally, the combination of pretreatment with ionic liquid and a SSF process has high potential for bioethanol production.**
- **Finally, reutilization of the ionic liquid after a distillation step, is possible with very high saccharification and fermentation levels.**

# EXPLORATORY STUDY BIOREFINERY

María Elena Lienqueo, Diego Schneuer F, Roberto Sotomayor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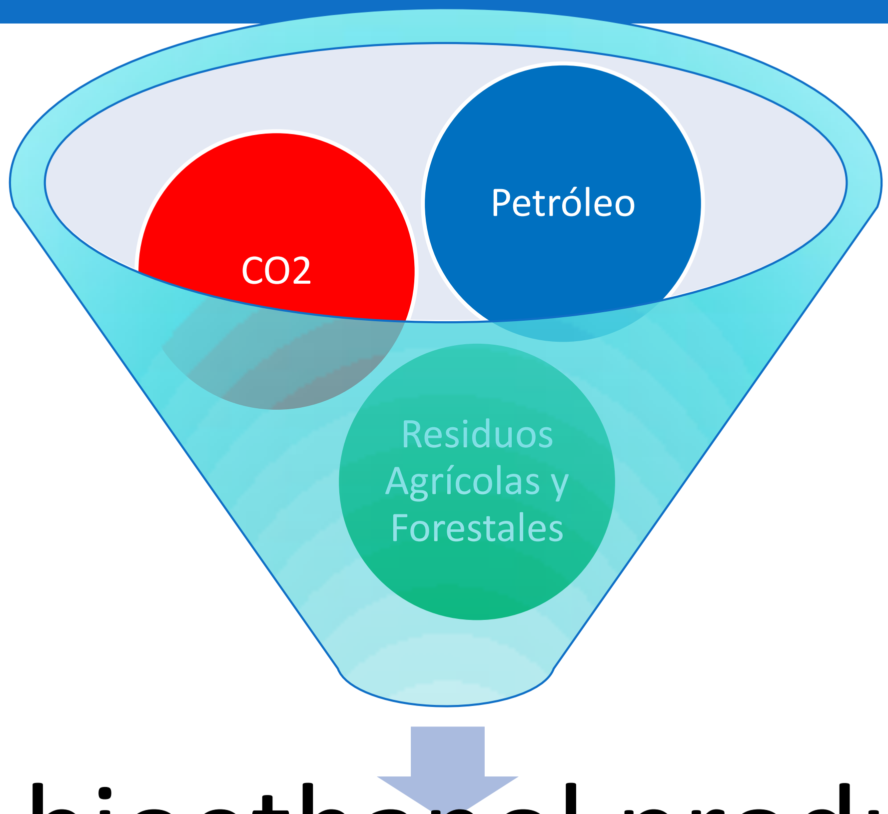
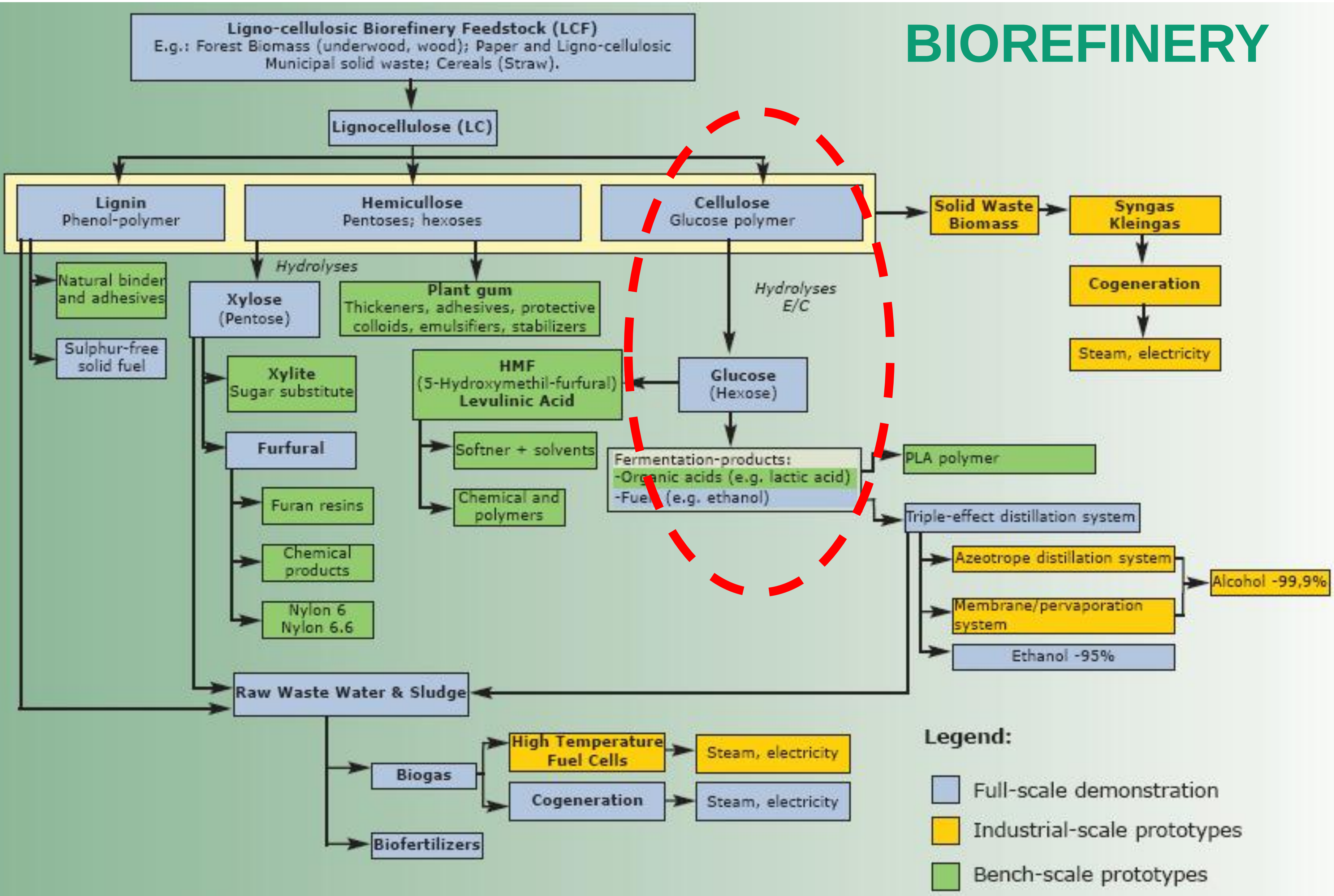
# Introduction




Is the bioethanol production profitable? How?

# BIOREFINERY



# Which conditions?

# BIOREFINERY

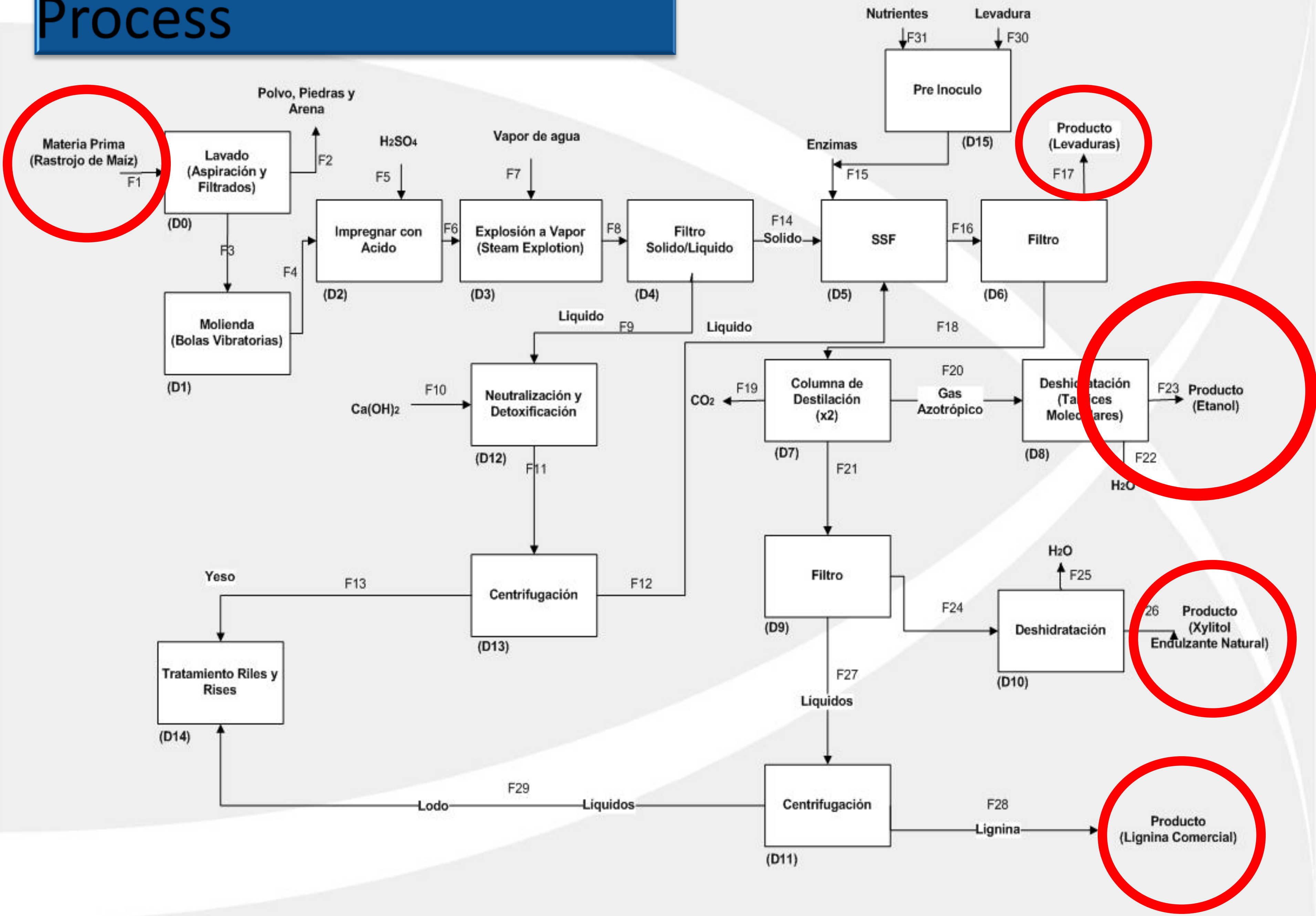
Celulose → Bioethanol

Lignin → Lignin


Pentoses → Xylitol

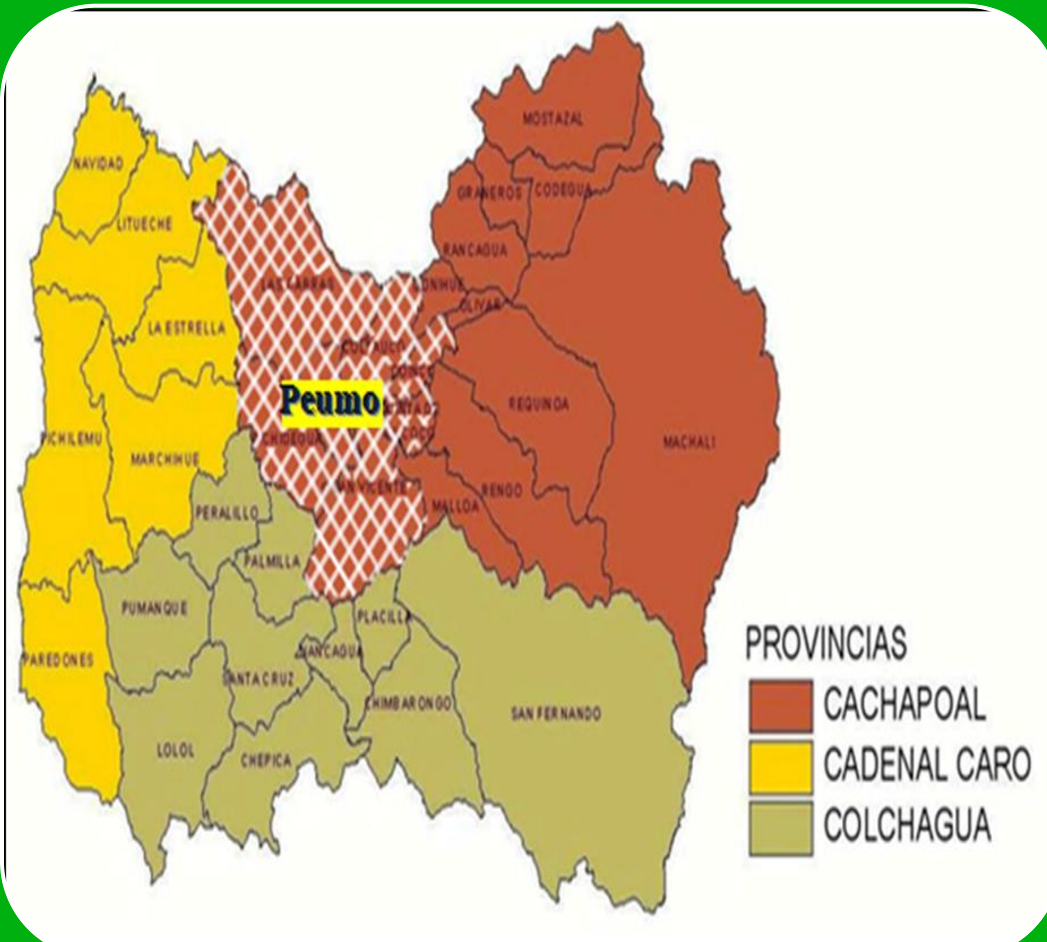
Yeast

# Process



Materia Prima (Rastrojo de Maíz)
F1
Lavado (Aspiración y Filtrados)
(D0)
Polvo, Piedras y Arena
F2
F3
Molienda (Bolas Vibratorias)
(D1)
F4
H2SO4
F5
Impregnar con Acido
(D2)
F6
Vapor de agua
F7
Explosión a Vapor (Steam Explotion)
(D3)
F8
Filtro Solido/Liquido
(D4)
F14
Solido
Nutrientes
F31
Levadura
F30
Pre Inoculo
(D15)
Enzimas
F15
SSF
(D5)
F16
Filtro
(D6)
Producto (Levaduras)
F17
Liquido
F9
Liquido
F18
Neutralización y Detoxificación
(D12)
Ca(OH)2
F10
F11
Centrifugación
(D13)
F12
Yeso
F13
Tratamiento Riles y Rises
(D14)
Columna de Destilación (x2)
(D7)
CO2
F19
F20
Gas Azotrópico
Deshidratación (Tamices Moleculares)
(D8)
F23
Producto (Etanol)
F22
H2O
F21
Filtro
(D9)
F24
Deshidratación
(D10)
H2O
F25
26
Producto (Xylitol Endulzante Natural)
F27
Liquidos
Centrifugación
(D11)
F29
Lodo
Liquidos
F28
Lignina
Producto (Lignina Comercial)

# Agricultural residues- Corn




VI Region

- Available Material
- Geomorphology

Peumo

- Road accesses
- Water source Nearness (Rapel)
- Relation between price, ton and kilometer (50 Km)

# Plant Capacity

## National Demand: 330,000 $m^3$

**Plant Requirment**

- Input 390,000 $m^3$
- 50% Stubble
- 40,000 Ha

**Operation Conditions**

- 330 days
- 24 hours

**Annual Bioethanol Production**

- 75,000 $m^3$
- 45 % of National Demand

# Cash Flow

## Parameters.

- Financing: 40%.
- Interest Rate : 8%.
- Pay Period: 10 years.
- Discount Rate: 15%.

## Plant Inversion.

- 160 millions US$.

## Fixed Cost.

- 4 millions US$ annual

## Variable Cost.

- 52 millions US$ annual

# Cash Flow

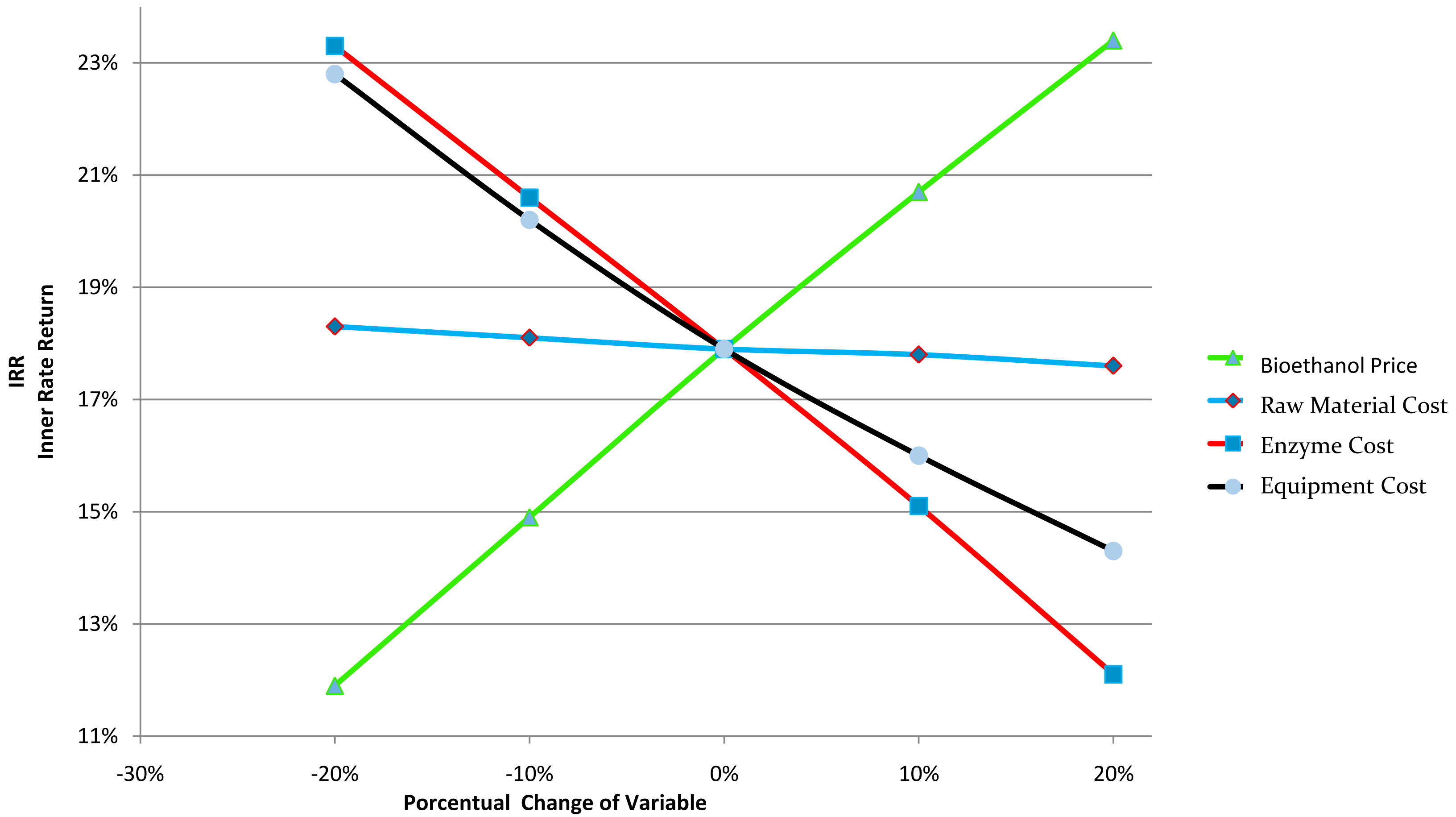
Ethanol price = USD 600/$m^3$

➔ VAN = USD 21,000,000  in 20 years

TIR= 18%

IRR: 5 year.

# Sensitivity Analysis



# Conclusion and recommendations

Co-Product (Lignin, Yeast, Xylitol or others)

Profitable project with price of bioethanol at 6oo US$/$m^3$. (NPV = 20 millions US$ y IRR = 18%)

High sensibility to the price bioethanol, enzyme cost and equipments cost. Low sensibility to raw material cost.

PREFEASIBILITY STUDY

Gracias