Processos de conversão para diminuição de emissões de GEE

Prof. Dr. Rubens Maciel Filho
Full Professor School of Chemical Engineering
Laboratory of Optimization, Design and Advanced Process Control
State University of Campinas – UNICAMP – Brazil
Fapesp/Bioen- Process Engineering Coordination
Brazilian Center for Bioethanol – Researcher Consultant

LOPCA Laboratório de Otimização, Projeto e Controle Avançado

UNICAMP

BIOEN FAPESP

biofabris

COP21: A Ciência da Sustentabilidade na FAPESP

Conversion Processes

Process developed to transform raw materials/feedstock in desired product :

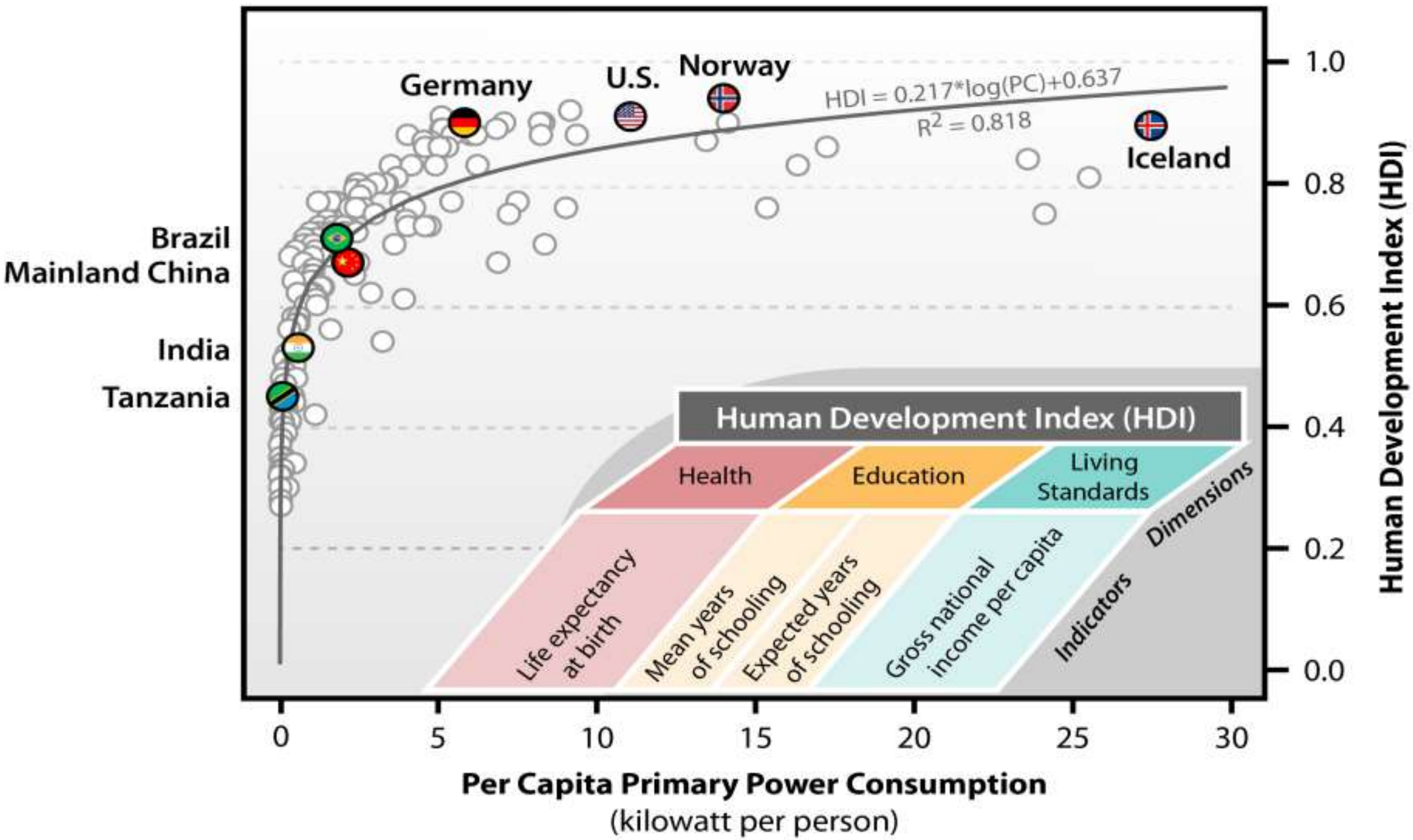
Biofuels

Chemicals

Energy

They are indissociable (especially biofuels and chemicals) in the context of the existing refineries (oil based) and it makes sense, since conversion processes are not able to have complete conversion and selectivity

Energy Consumption & Human Well Being are Linked



By Bruce Dale–Michigan State University

Energy and Importance of *Liquid Fuels*

- Services we need from energy (current nonrenewable & renewable sources of these services)
  - Heat (natural gas, coal, wind, solar, geothermal, biomass)
  - Light/electricity (coal, natural gas, hydro, nuclear, solar, wind, biomass)
  - Mobility (liquid fuels from oil—96% in US, some ethanol & CNG)- **most commerce**
- **All energy services (all BTU, ergs, GJ) are not created equal—we value mobility (=oil) above all other energy carriers**
- **Electricity/batteries can never provide more than about half of mobility needs—and they cannot support commerce at all**
- Commerce moves by trucks, ocean shipping, rail & jet aircraft
- Oil is the "super commodity"---it is the only commodity that is required to produce and then transport every other commodity
- *Liquid fuels: not "energy" is the key current challenge for renewables*
- *The only potentially sustainable, very large scale source of renewable liquid fuels is sustainable plant matter— or "biofuels"*

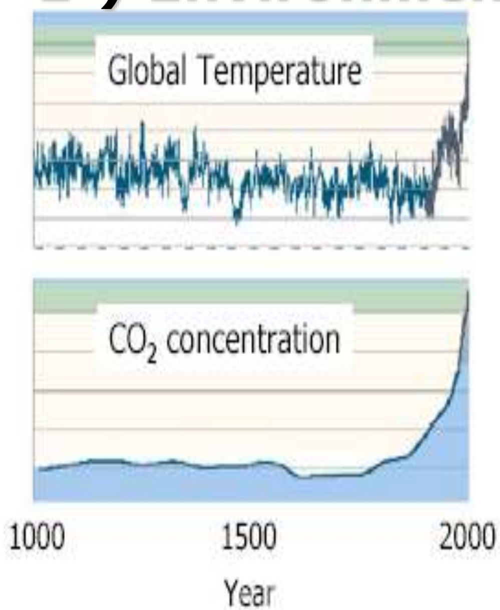
Extracted from Bruce Dale–Michigan State University

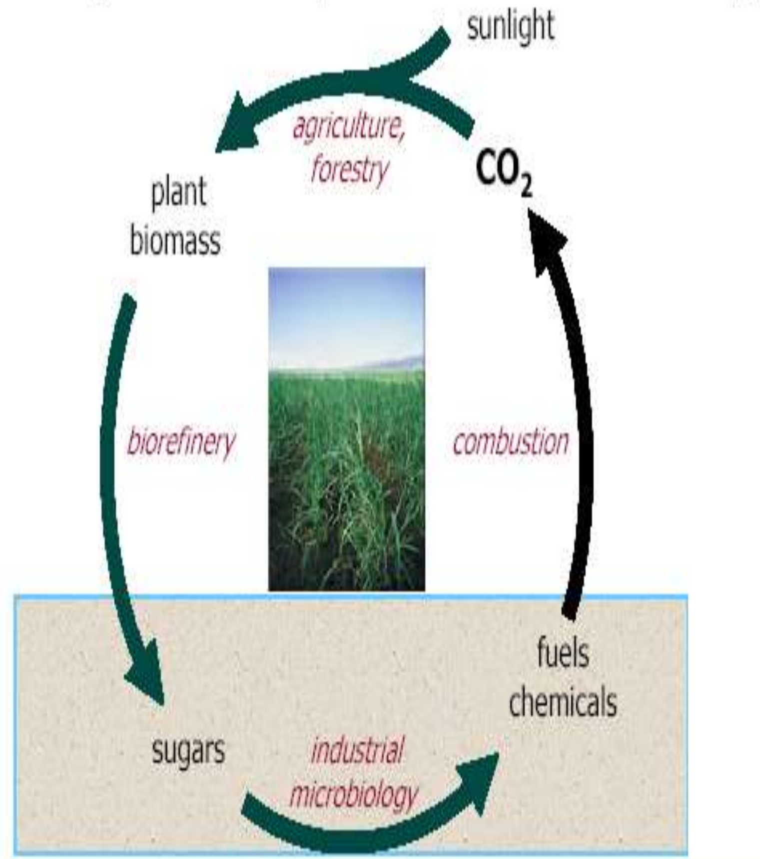
Feedstock for low environment impact

Challenges Resulting from an Oil-Based Economy

Balancing the Carbon Cycle: Industrial Biotechnology

1-) Environmental aspects





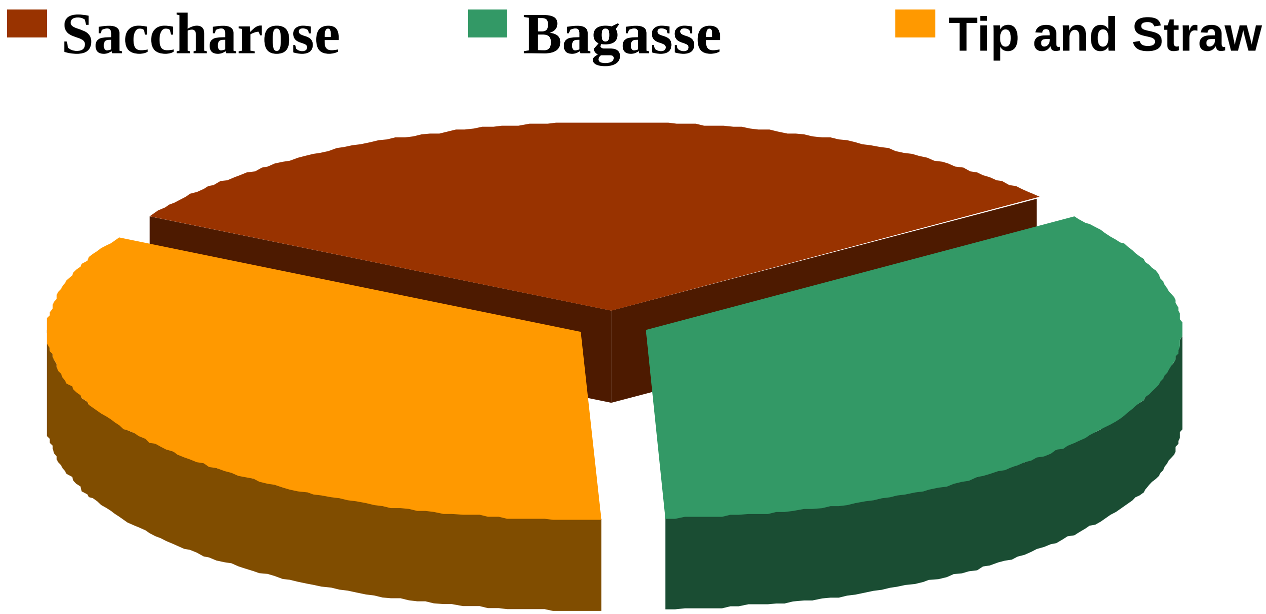
2-) Perception →Draining Oil Reserves and/or high costs to oil exploration→ Nowadays alternative sources as shale oil (no renewable source), wind, solar may play an important role

3-) Energy from biomass → Strategic and energy security as well as competive prices Source: BBasic

Renewable Feedstock for Biofuels, Energy and Chemicals

Sugar cane, Soya bean, Palm , Coconut Orange, Agriculture residues, Animal Fatty among others. **Any lignocellulosic material.**
Many alternatives to use such raw materials – production scale and logistic has to be accounted for

Sugar Cane



Urban waste – advantage in terms of logistic and price and difficulties from standardization

Biorefinery – concepts:

The Biomass Research and Development Technical Advisory Committee (2002) of the U.S. Departments of Energy and Agriculture defines a biorefinery as:

"A processing and conversion facility that:

(1) efficiently separates its biomass raw material into individual components and

(2) converts these components into marketplace products, including biofuels, biopower, and conventional and new bioproducts."

Basic conversion, main feedstock and components:

Crops rich in Saccharose → Fermentation (e.g. sugar cane→ethanol)

Lignocellulosic materials (crops, residues) → fractionation (pre-treatment) → cellulose, hemicellulose, lignin, and terpenes→ hydrolysis→ sugars

Grains → fractionation → starch, oils, proteins, and fiber.
Starch → hydrolysis→ sugars→ fermentation (e.g. ethanol)
Oils→ transesterification and chemical reaction (e.g. Biodiesel)

Fermentation of residues and waste to Biogas

To break materials (crops, residues) into the smallest possible building blocks - carbon monoxide (CO) and hydrogen (H_2), from which the desired chemical products are synthesized → themochemical

Type of raw material may define the most suitable route

Successful aspects:

The successful emergence of advanced biorefineries will be influenced by many factors including the extent of biomass availability, the kinds of products that can be produced, the nature of the conversion processes employed, the ability to efficiently utilize the energy content of biomass, and the size of the plants to be built.

Biomass availability may be region dependent and logistic will pay an important role.

When biomass is a byproduct a much better scenario is foreseen.

Process performance will be determinant since it is still an alternative for either historical or establishment reasons

Challenges of Green Economy

Three tablespoons oil is equivalent of eight hours of human labor (oil barrel around US$ 50).

Each unit of energy invested to produce oil in the 1940s yielded the equivalent of 110 energy units (1 to 100)

Throughout the 20th century, these returns were declining

The international estimate for exploration offshore platforms, such as pre-salt In Brazil , today is from 1 to 10

Although alternative sources of energy are widening dramatically, nothing indicates that in the next 40 years they will be able to replace the dependence that the largest economies in the world of have on coal, oil and gas.

(Ricardo Abramovay- Folha de São Paulo June, 27th, 2011)

Environmental concerns is the driven force

Market Options and Society Needs

Biofuels

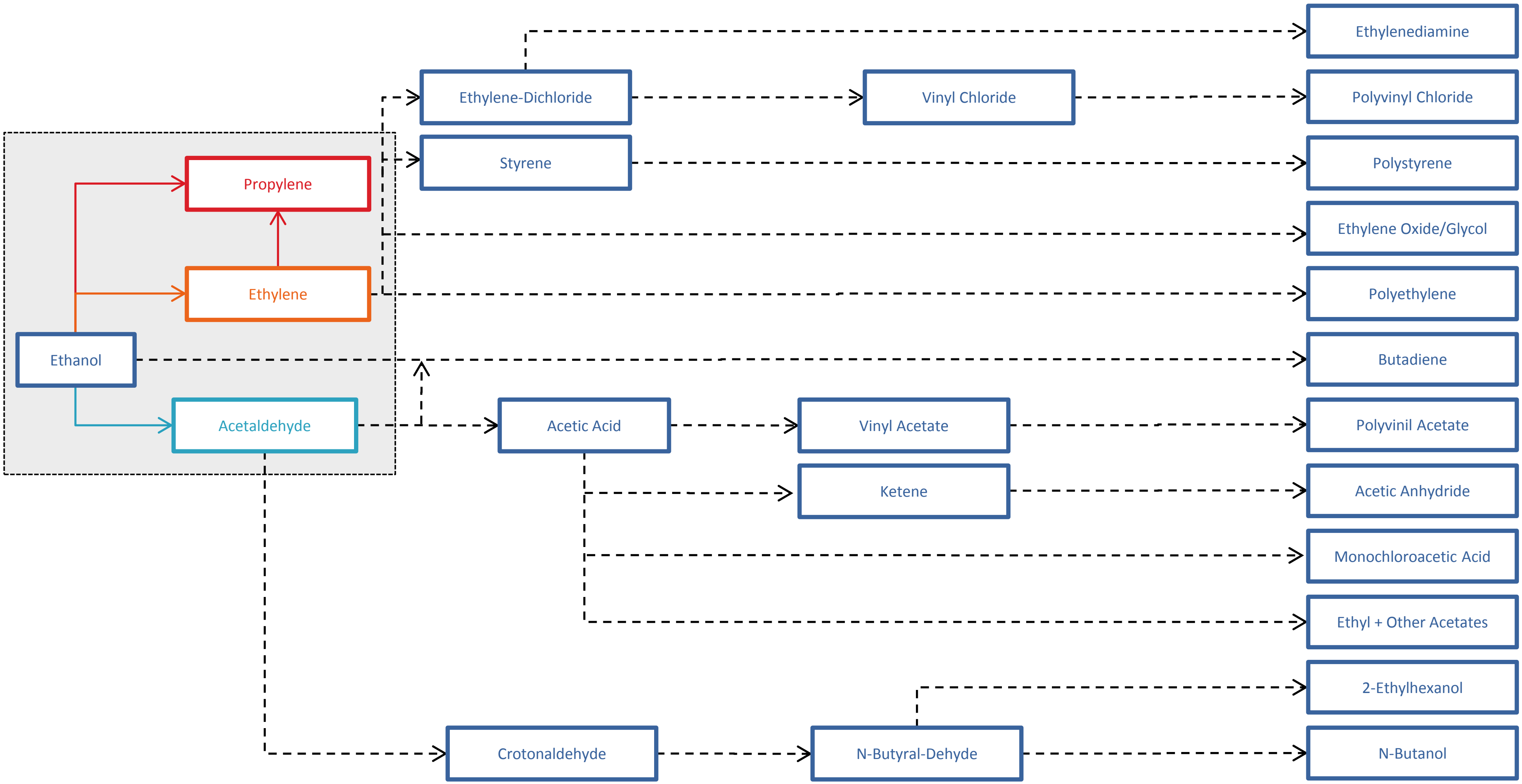
- Bioethanol for light cars
- Biobutanol for light cars
- Bioethanol (+ additives) for use in heavy engines
- Biodiesel for heavy engines
- Biokerosene for jet fuels
- Biogas
- H_2 Production from renewable source (Ethanol)

Biorefineries- Conventional and High Added Value Chemicals

Bioenergy from biomass

Use of ethanol as feedstock – that means obtain chemicals from ethanol
A possible way to be an environment to 2nd generation lerning curve

Acholcholchemistry Products



Set of products (Drop-in) already produced in Brazil → later 80's

Drop-in products -- What about alternative and more rational ethanol based products?

Basic conversion routes:

1. Fermentation
2. Thermochemical
3. Transesterification

Fermentation (e.g. sugar cane→ethanol)

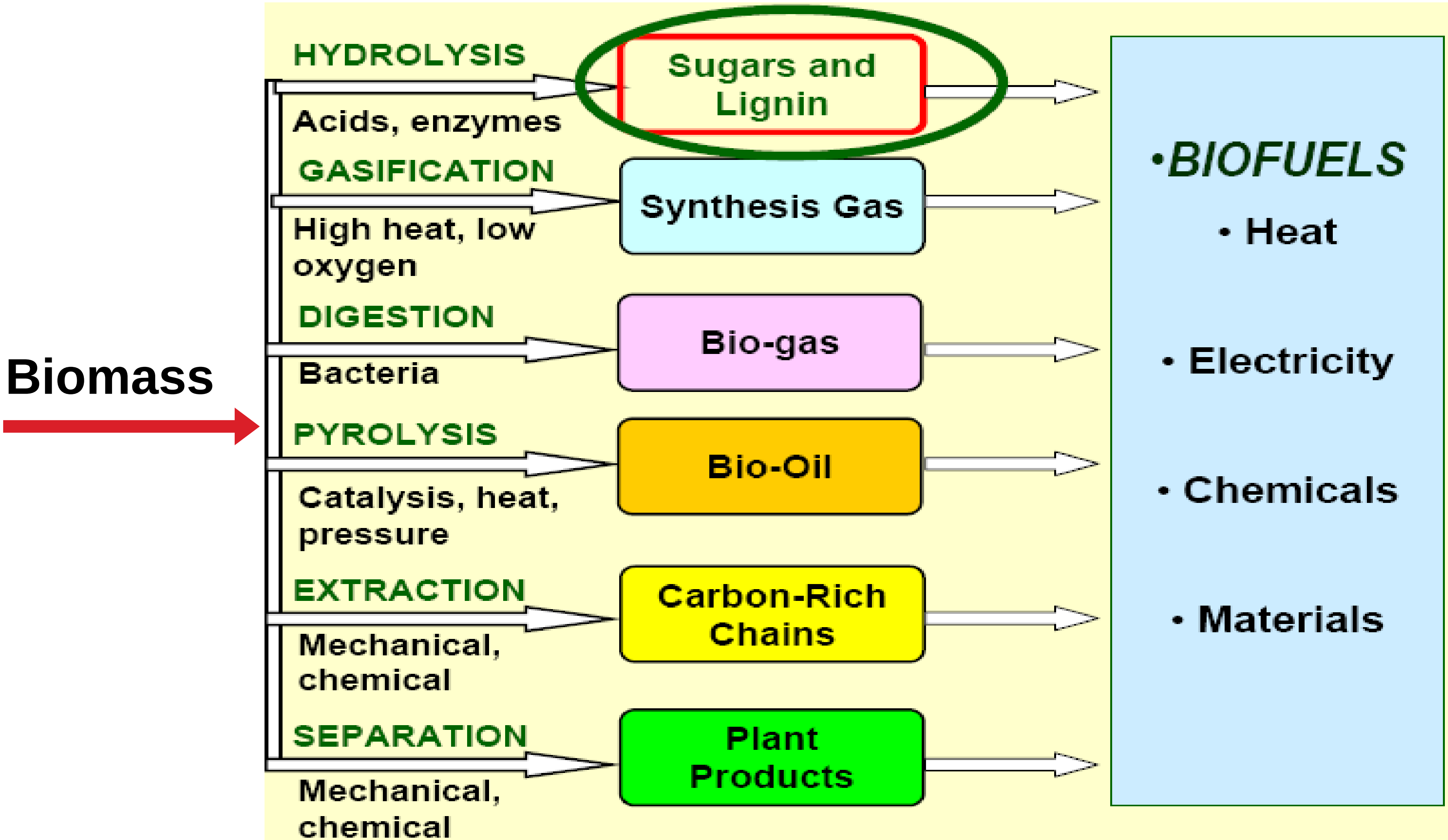
Fermentation of residues and waste to Biogas

ThermochemicalTo break materials (crops, residues) into the smallest possible building blocks - carbon monoxide (CO) and hydrogen (H_2), from which the desired chemical products are synthesized.

Grains → fractionation → starch, oils, proteins, and fiber.
Starch → hydrolysis→ sugars→ fermentation (e.g. ethanol)
Oils→ transesterification and chemical reaction (e.g. Biodiesel)

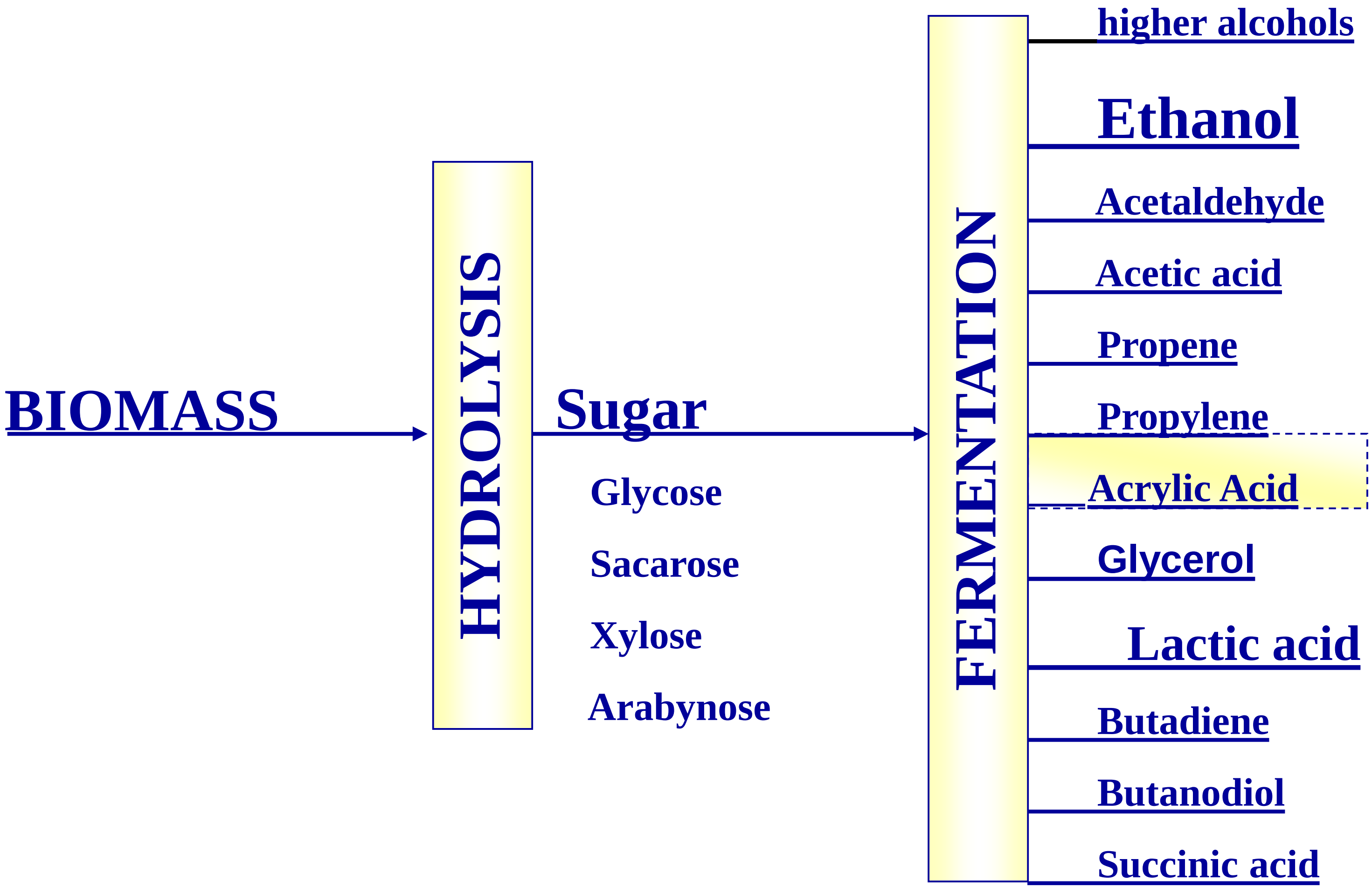
Biomass Uses

Sugar → extracted from sugar-rich crops → fermentation



Fermentation of residues and waste to Biogas

Fermentation



Biomass → C6 and C5

Fermentation of residues and waste to Biogas

FERMENTATION

1. Microorganism → *Saccharomyces cerevisiae*

2. Invertase Reaction

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6$$

3. Fermentation Reactions

Main Reaction

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

$$Y_{MAX} = 0.51 \, {}^{\text{g ethanol}}\!/_{\text{g glucose}}$$

90 % of the theoretical yield due to secondary reactions.

FERMENTATION

Secondary Reactions

Succinic Acid $\rightarrow$

$$C_6H_{12}O_6 + 2H_2O \rightarrow C_4H_6O_4 + 2CO_2 + 10H^+ + 10e^-$$

Acetic Acid $\rightarrow$

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2C_2H_4O_2 + 2CO_2 + 8H^+ + 8e^-$$

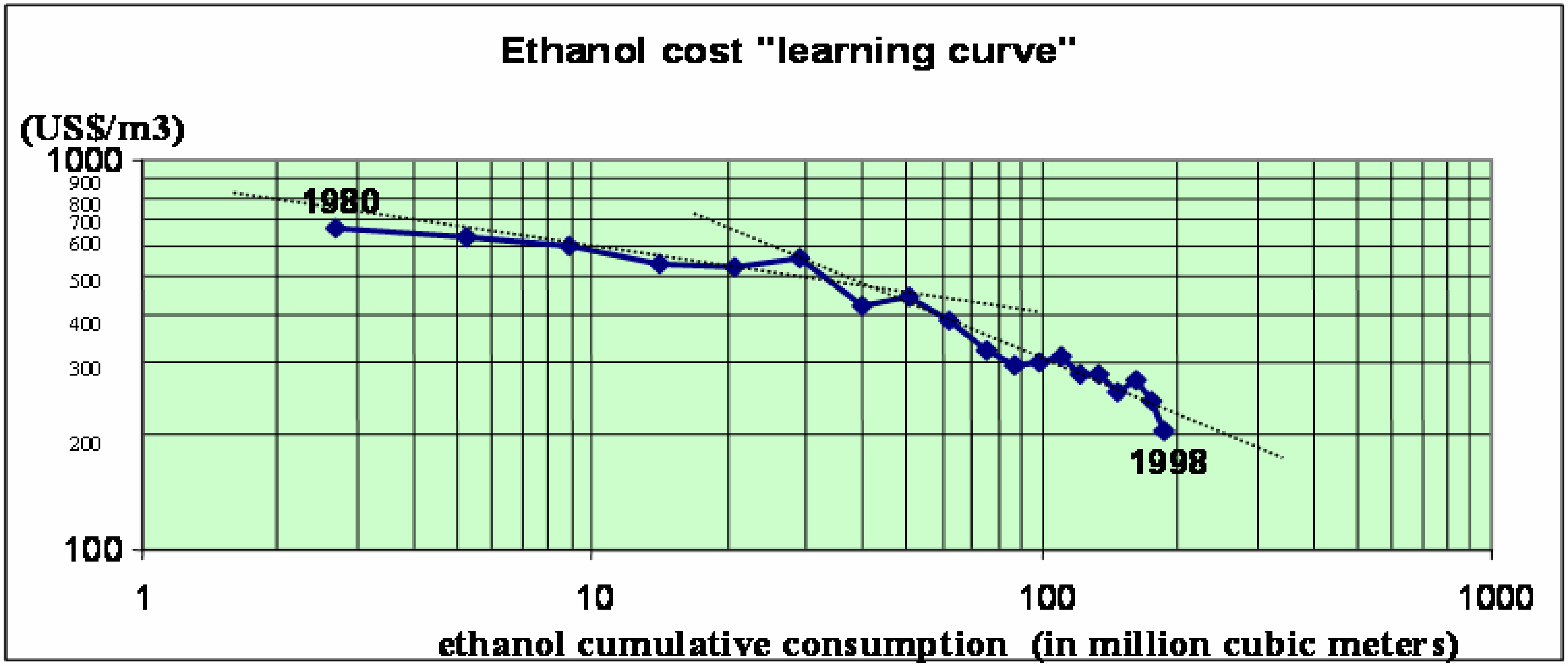
Glycerol $\rightarrow$

$$C_6H_{12}O_6 + 4H^+ \rightarrow 2C_3H_8O_3$$

Isoamyl Alcohol $\searrow$

$$C_6H_{12}O_6 \rightarrow 0.795C_5H_{12}O + 2.025CO_2 + 1.155H_2O + 0.15H^+ + 0.15e^-$$

Learning Curve – Brazilian Ethanol

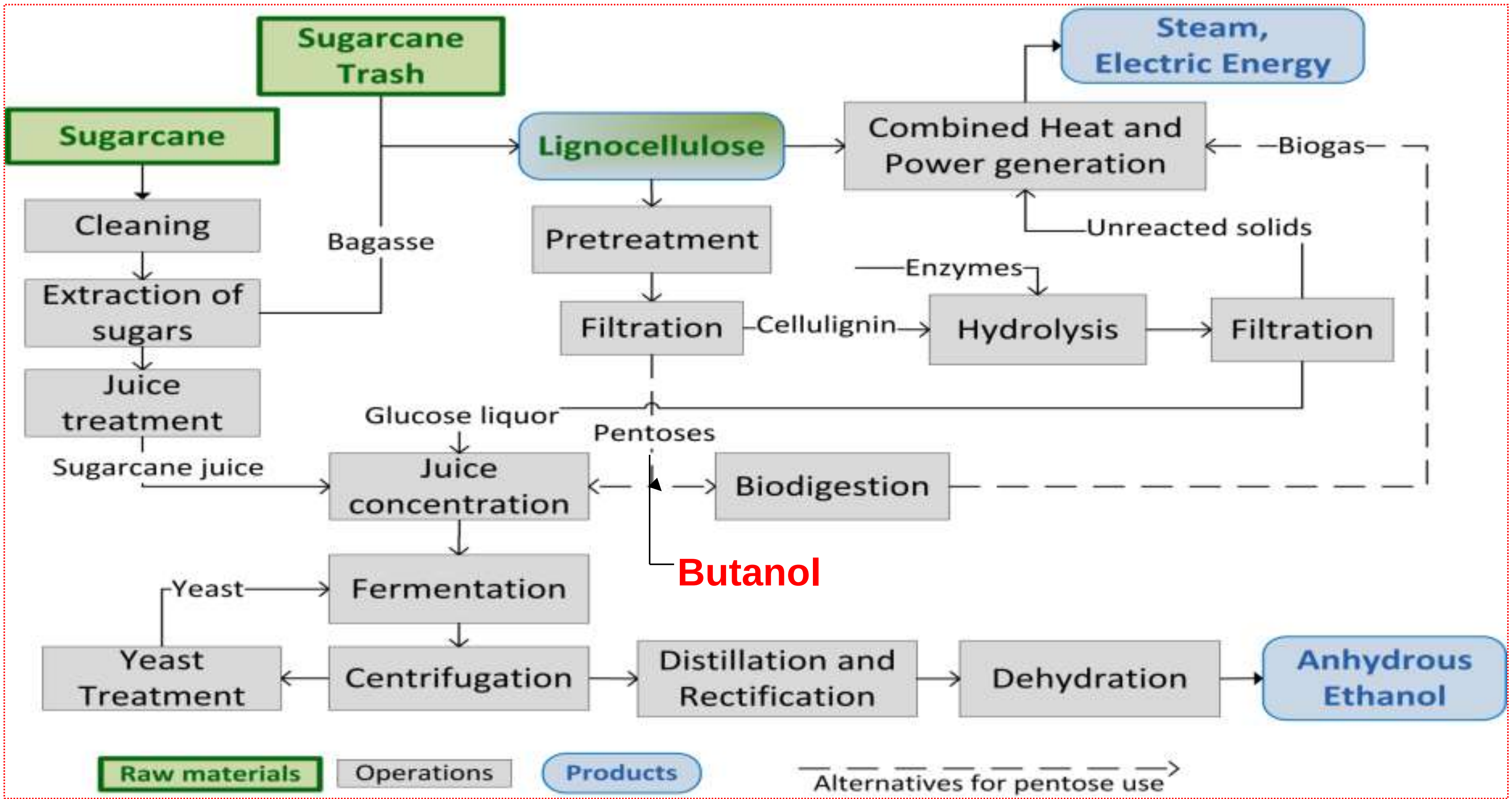


Goldemberg, J.

Learning curve for Brazilian ethanol – many advances from industrial improvements

Second generation – 2G

Block flow diagram - Integrated 1st and 2nd generation bioethanol, butanol and biogas production from sugarcane



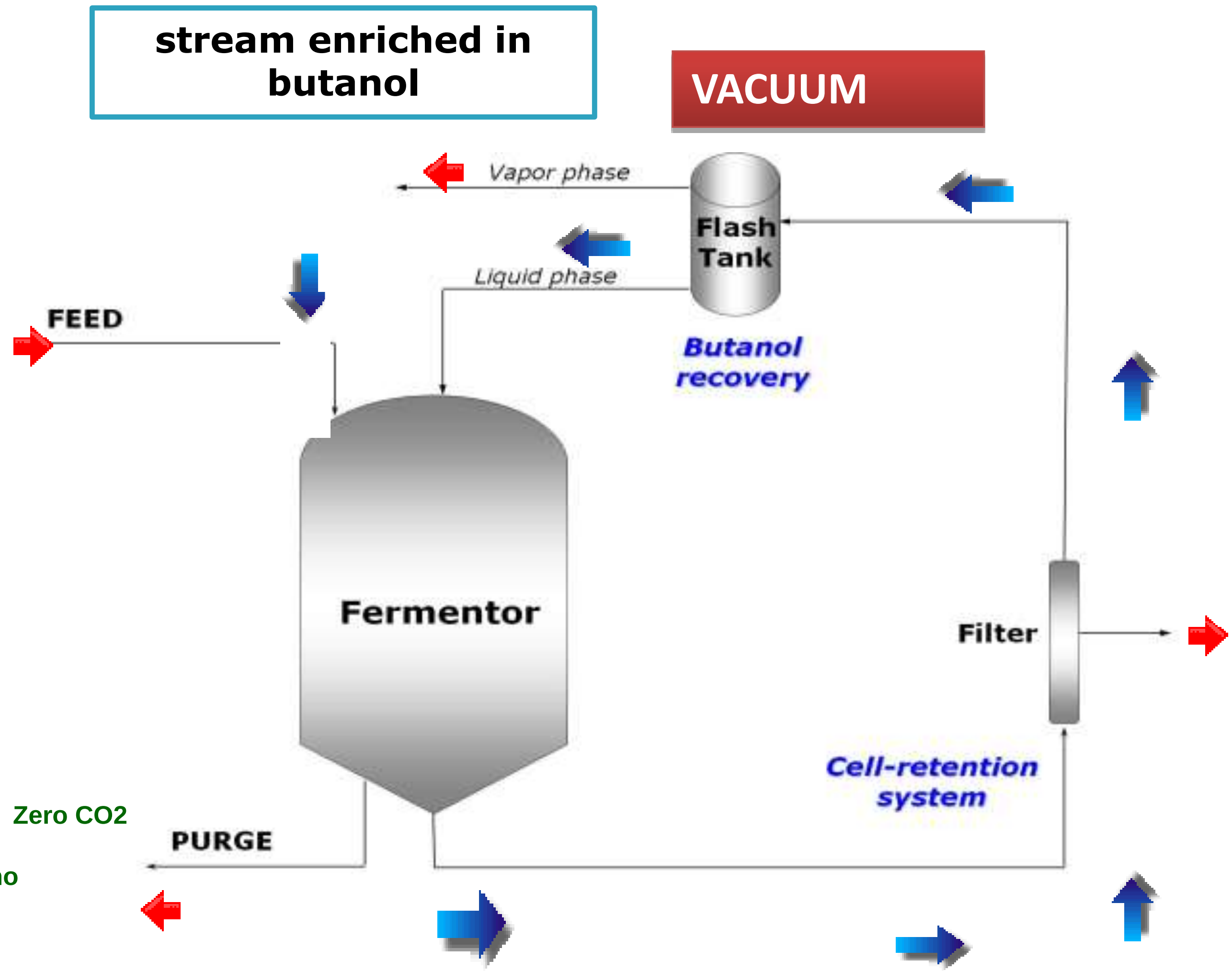
New Process for Butanol Production: Extractive Fermentation- Pinto Mariano et.al. Biotechnology and Bioengineering , 2011) –

Batch – conventional strain
MJ / kg ButOH 49.4
Flash – conventional strain
MJ / kg ButOH 31.6

Spotlight paper 2011

Vacuum fermentation

- **continuous fermentation**
- **cell retention**
- **butanol recovery**



An Integrated Process for Total Bioethanol Production and Zero CO2 Emission
Thematic Project- Fapesp: Coordinator Rubens Maciel Filho

Thermochemical Route

For the production of chemicals and biofuels→

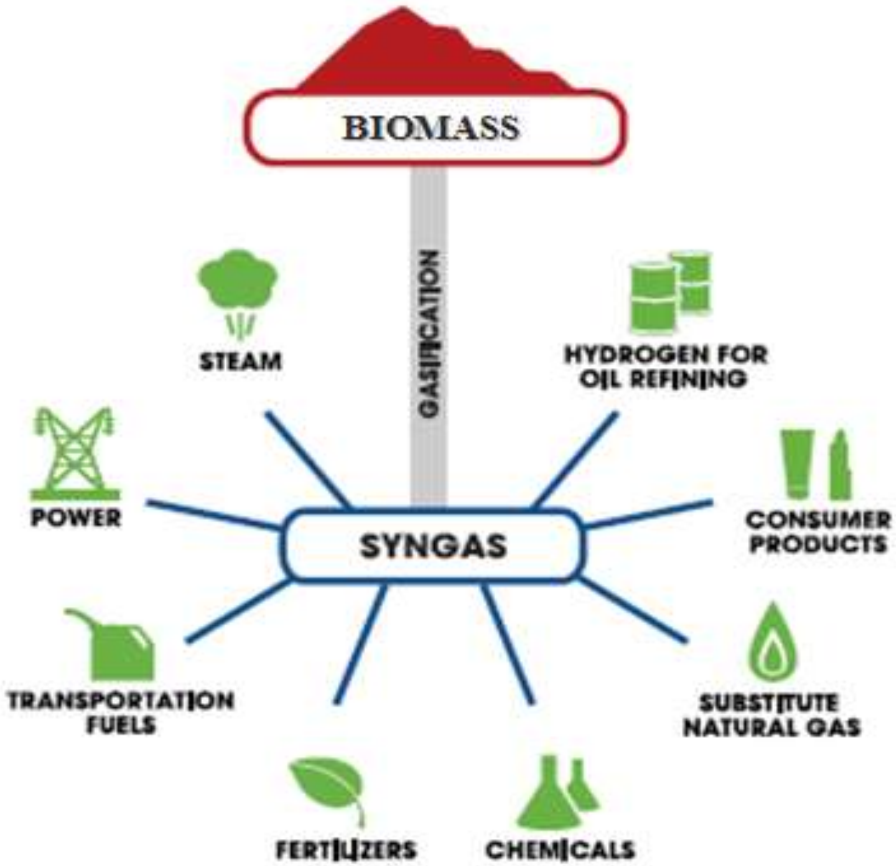
Catalytic Chemical Reactions of gas of synthesis (syngas) as raw material to obtain fuels and chemicals

Fermentation of Syngas

Syngas, by definition, has a H_2/CO ratio

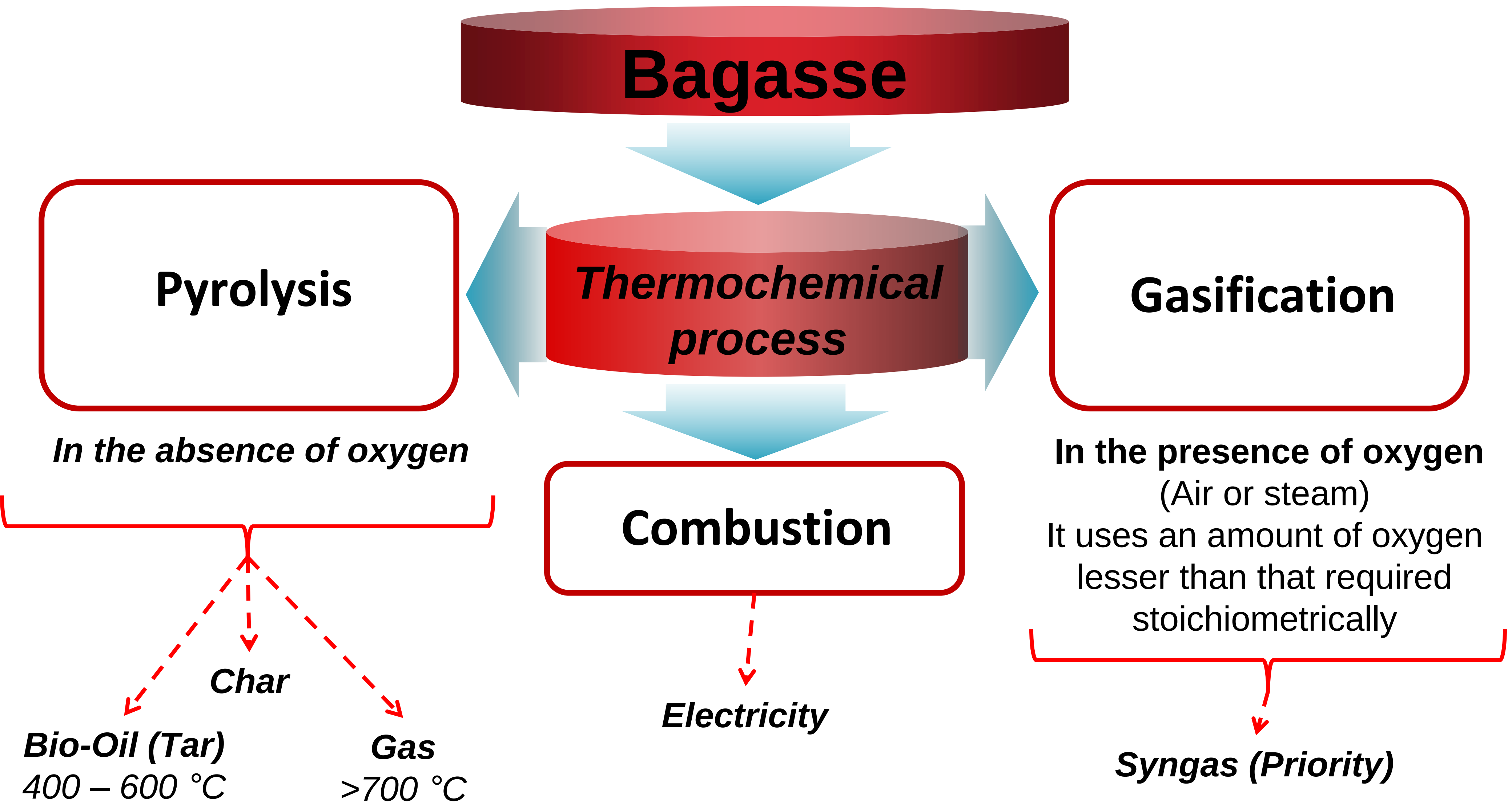
Gas from pyrolysis/gaseification may be used to Electricity generation

Thermochemical Route- From Biomass to Chemicals, Fuels, energy

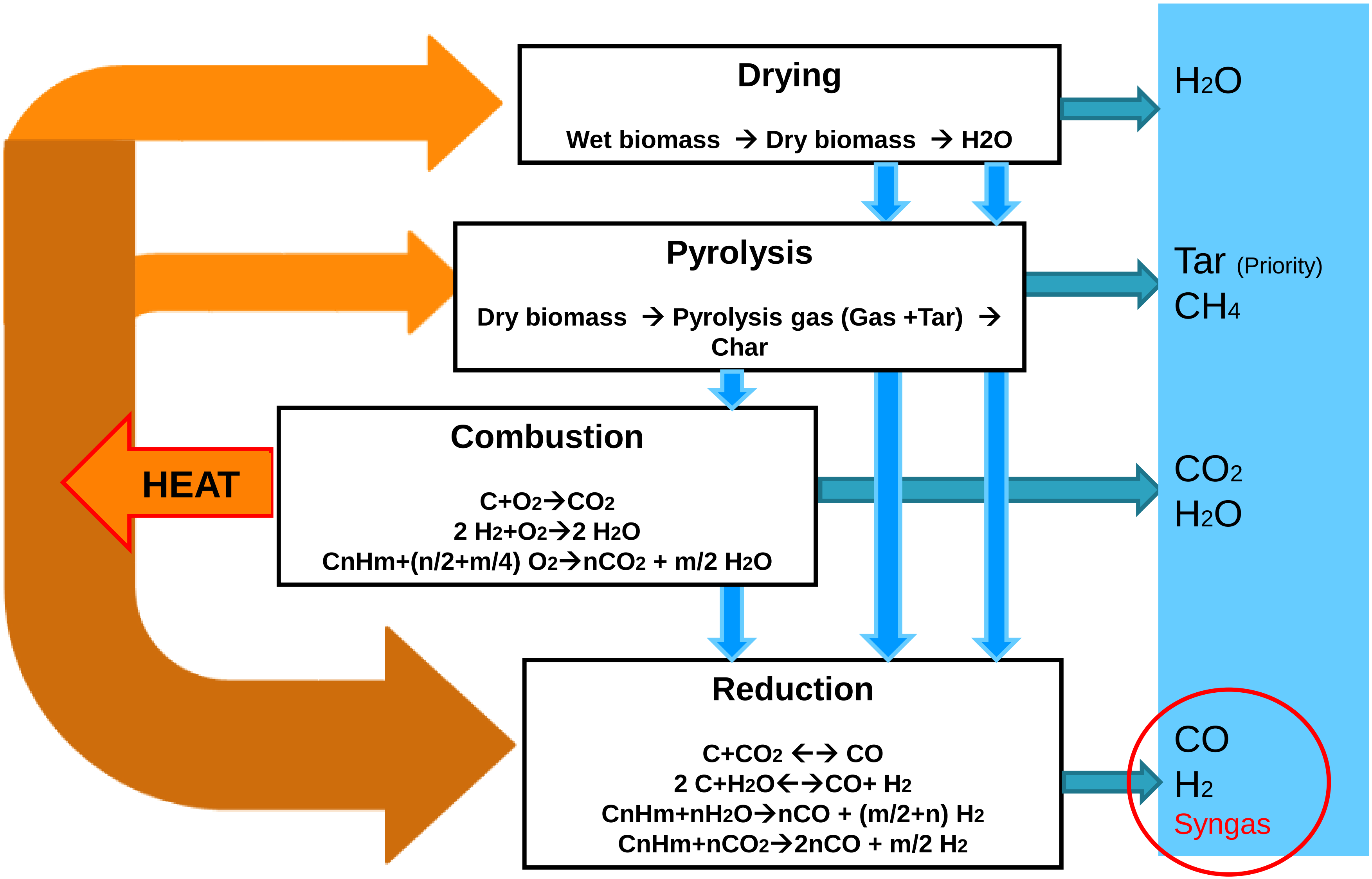


Source Gasification (2009)

Thermochemical process



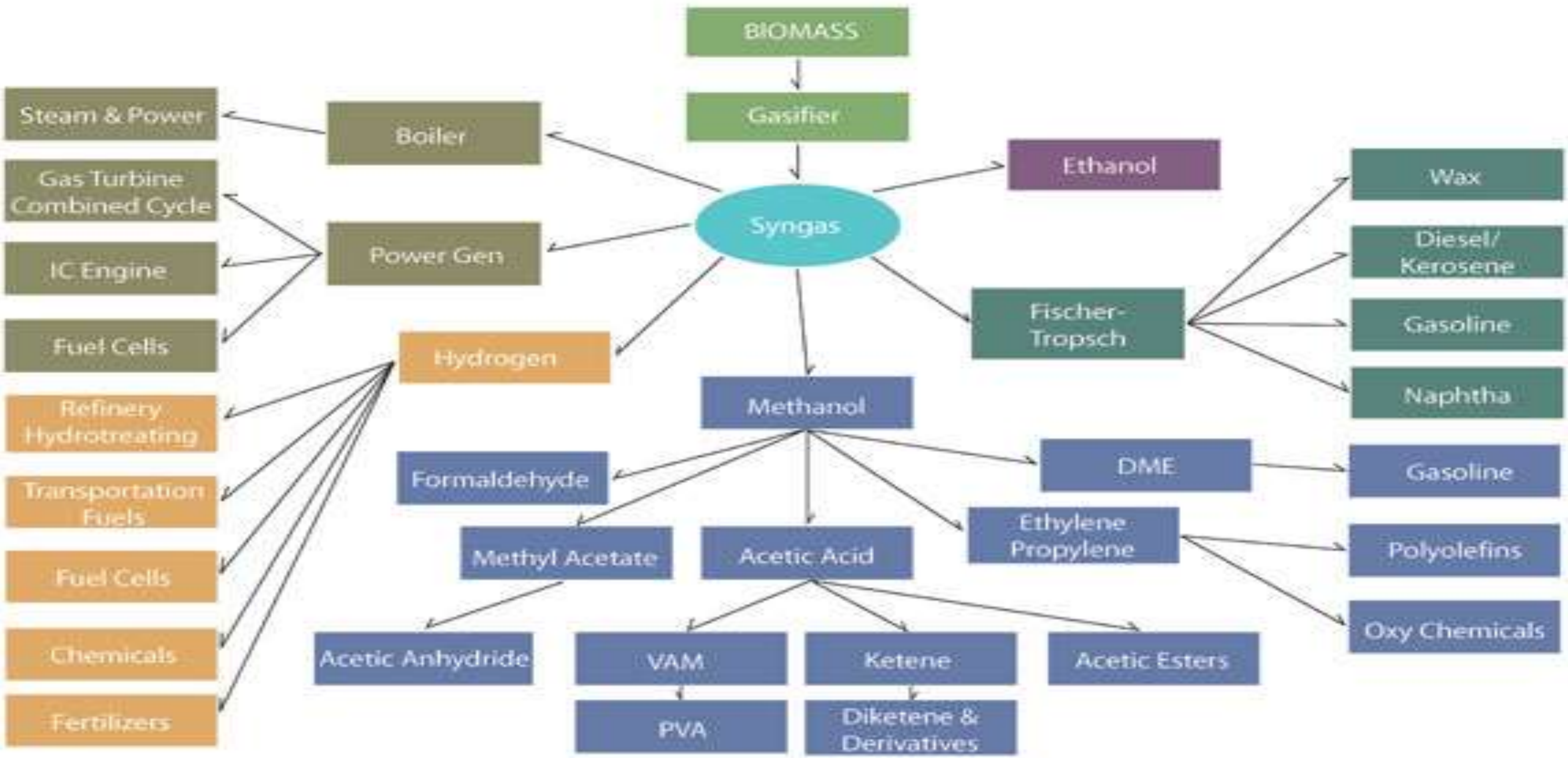
Gasification reaction mechanisms



Thermochemical Route

Syngas from Glycerin and Sugar Cane Bagasse

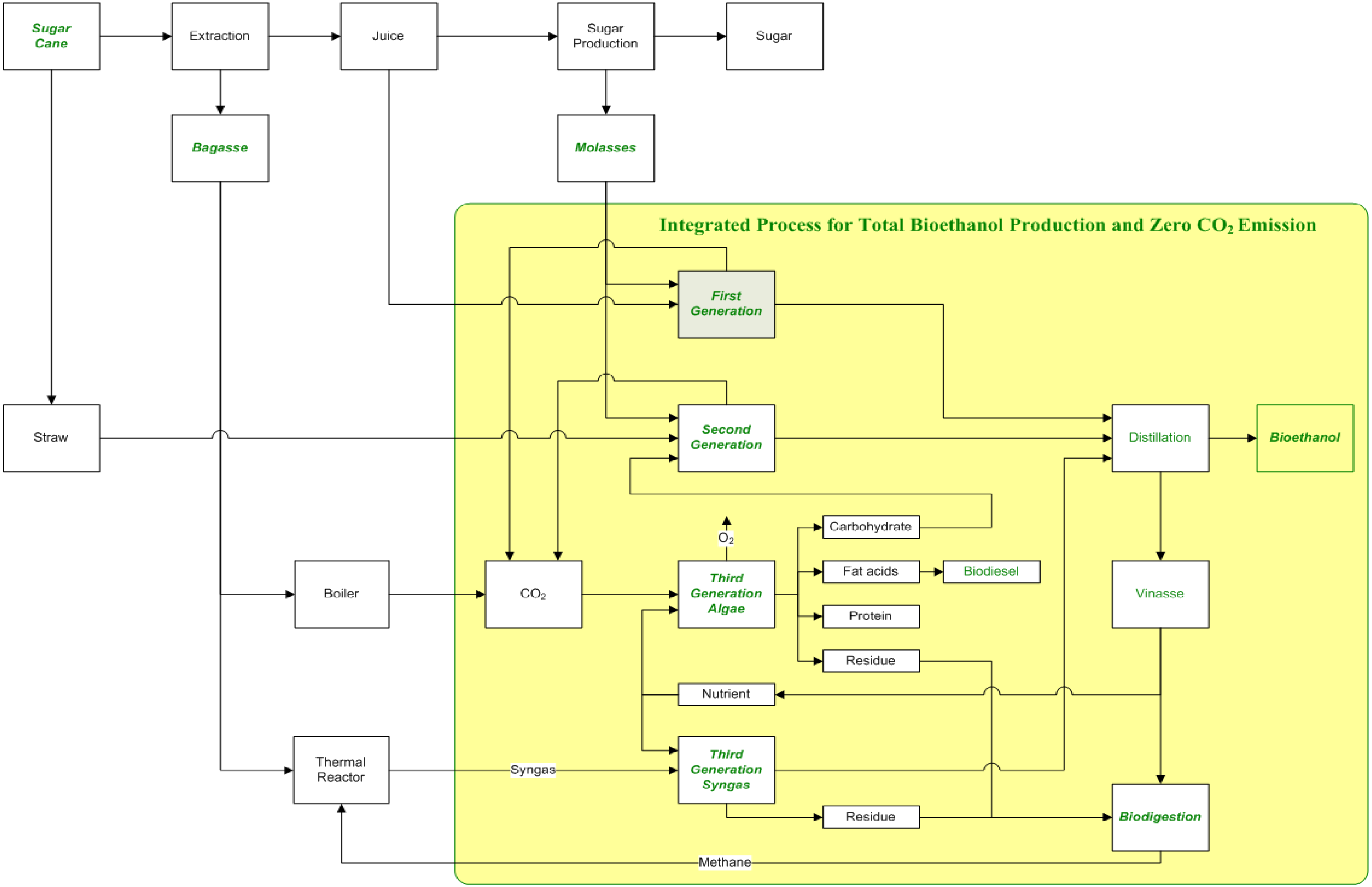
Syngas – raw material for ethanol and chemicals from chemical routes and carbon source for fermentation to produce ethanol



Comparation among routes

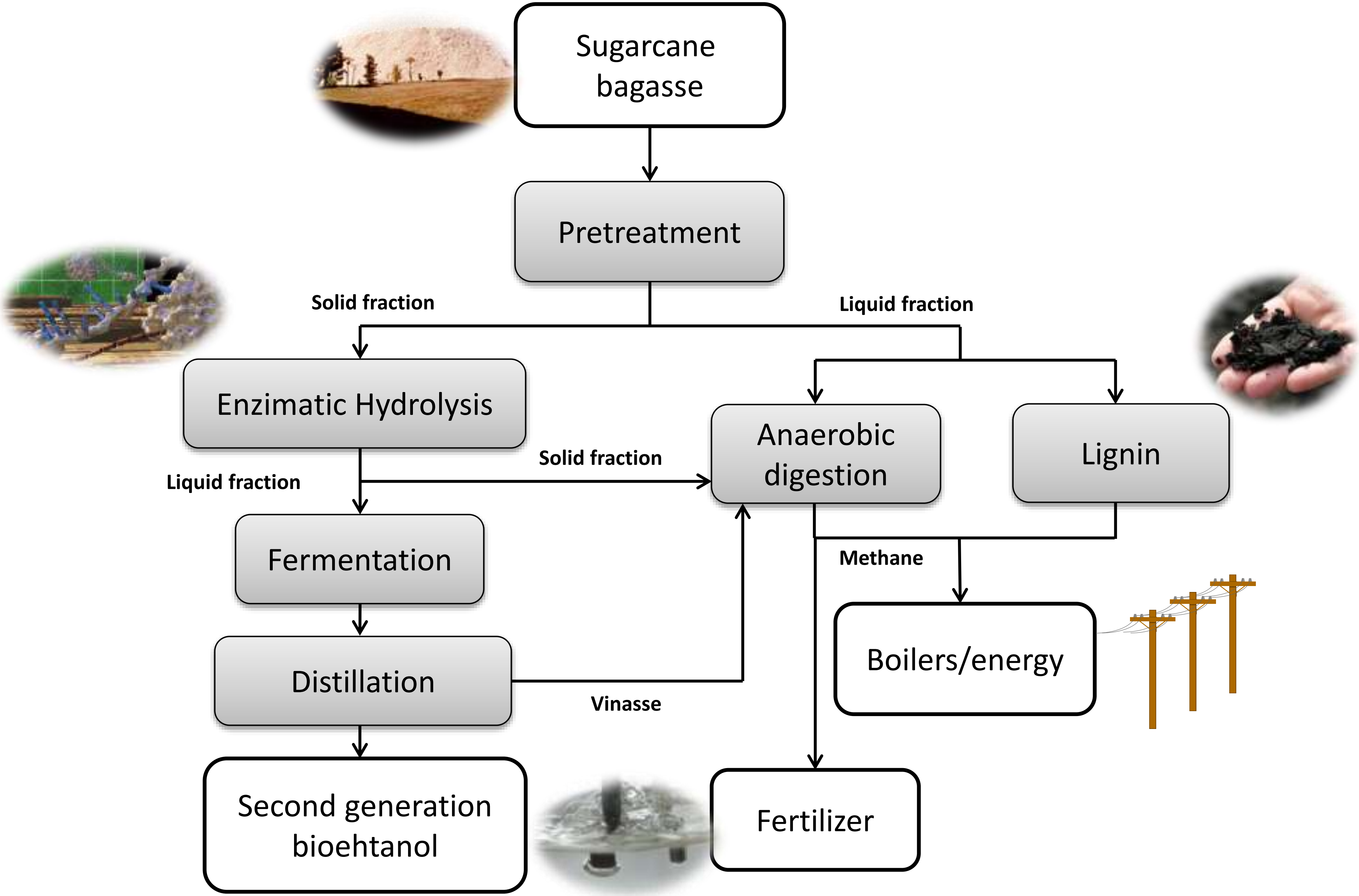
Fermentative Processes	Various Feedstocks ↑ Energy Consumption (Purification) ↓ Energy Cogeneration ↑ Food Security ↓ Water Consumption ↓ Known and spread Technology ↑	Ethylene Hydratation	Dependency of Petroleum Prices ↓ Low Conversion (~5%) ↓ High Temperature and Pressure ↓ High Purity ↑ Competition with other industry branches ↓
Enzymatic Process	High Cost ↓ Low Temperatures ↑ Low Yield ↓ Residues Usage ↑ Doesn’t make use of lignin ↓ Food Security ↑	Syngas	Various Feedstocks ↑ Abundant and Cheap Feedstock ↑ Short reaction time ↑ Uses lignin ↑ Low conversion and selectivity ↓ Energy Integration ↑ Production chain integration ↑

Integrated Process



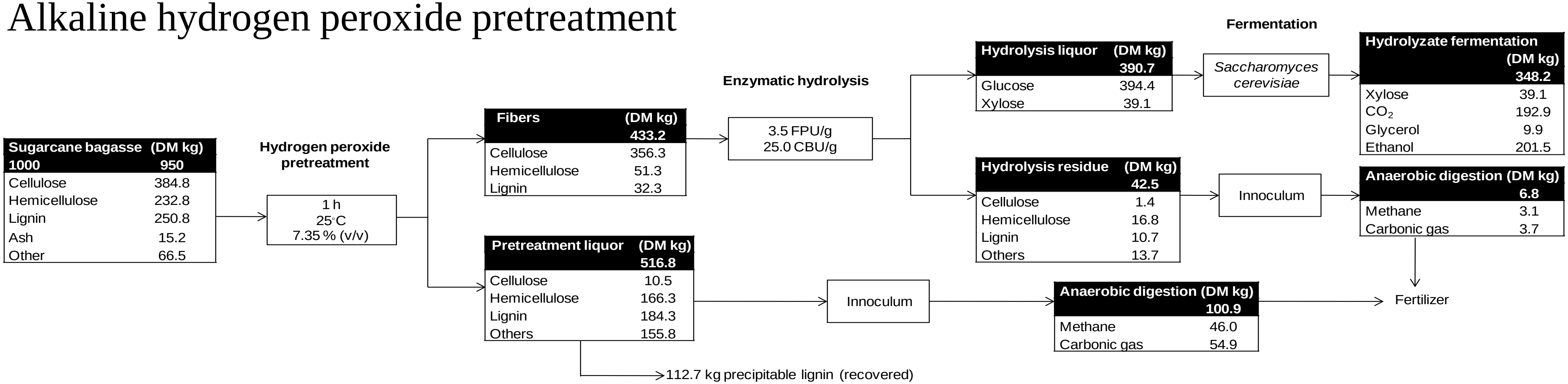
Source: Thematic Project Fapesp 2008/57873-8– Coordinator Maciel Filho

Integrated Process: Anaerobic Digestion of Hydrolysis Residues and Vinasse

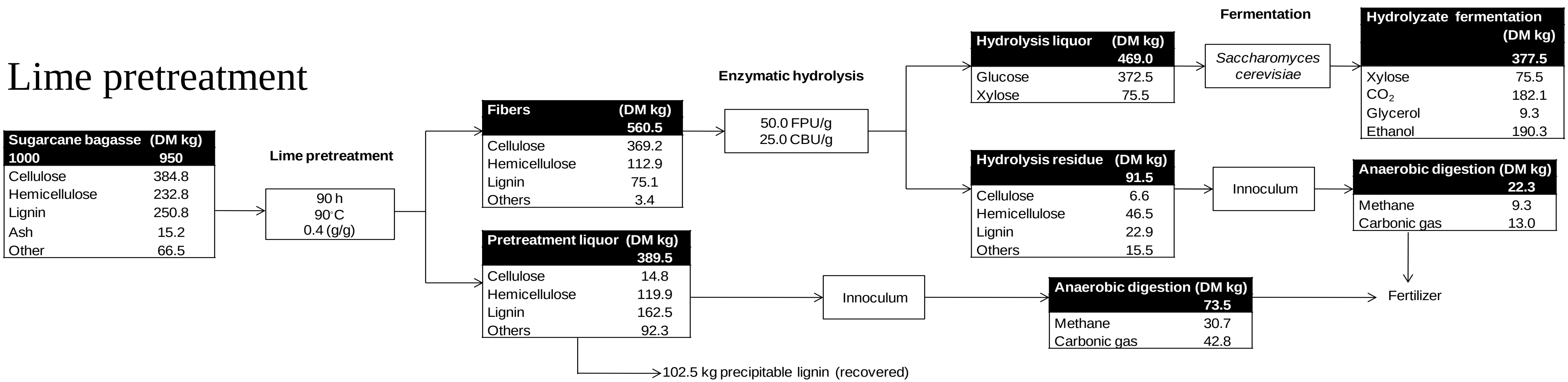


Mass Flow in the Biorefinery Process

Alkaline hydrogen peroxide pretreatment



Lime pretreatment



Rabelo *et al.* Production of bioethanol, methane and heat from sugarcane bagasse in a biorefinery concept. Bioresource Technology, 102, 7887–7895, 2011.

POWER GENERATION

→ Brazilian plants are self-sufficient.

→ Some plants sell surplus electricity to the grid.

→ 3% of energy used in Brazil → 2,000 MW (average).

If the full potential of sugarcane is used the total energy generated may exceed 13,000 MW (average by 2021), and the generate energy could be enough to sustain entire countries such as Sweden and Argentine.

POSSIBLE INTEGRATION WITH EXISTING FACILITIES → PRODUCTION OF ETHANOL AND CHEMICALS FROM THIRD GENERATION

1-) Microalgae for Bioethanol Production

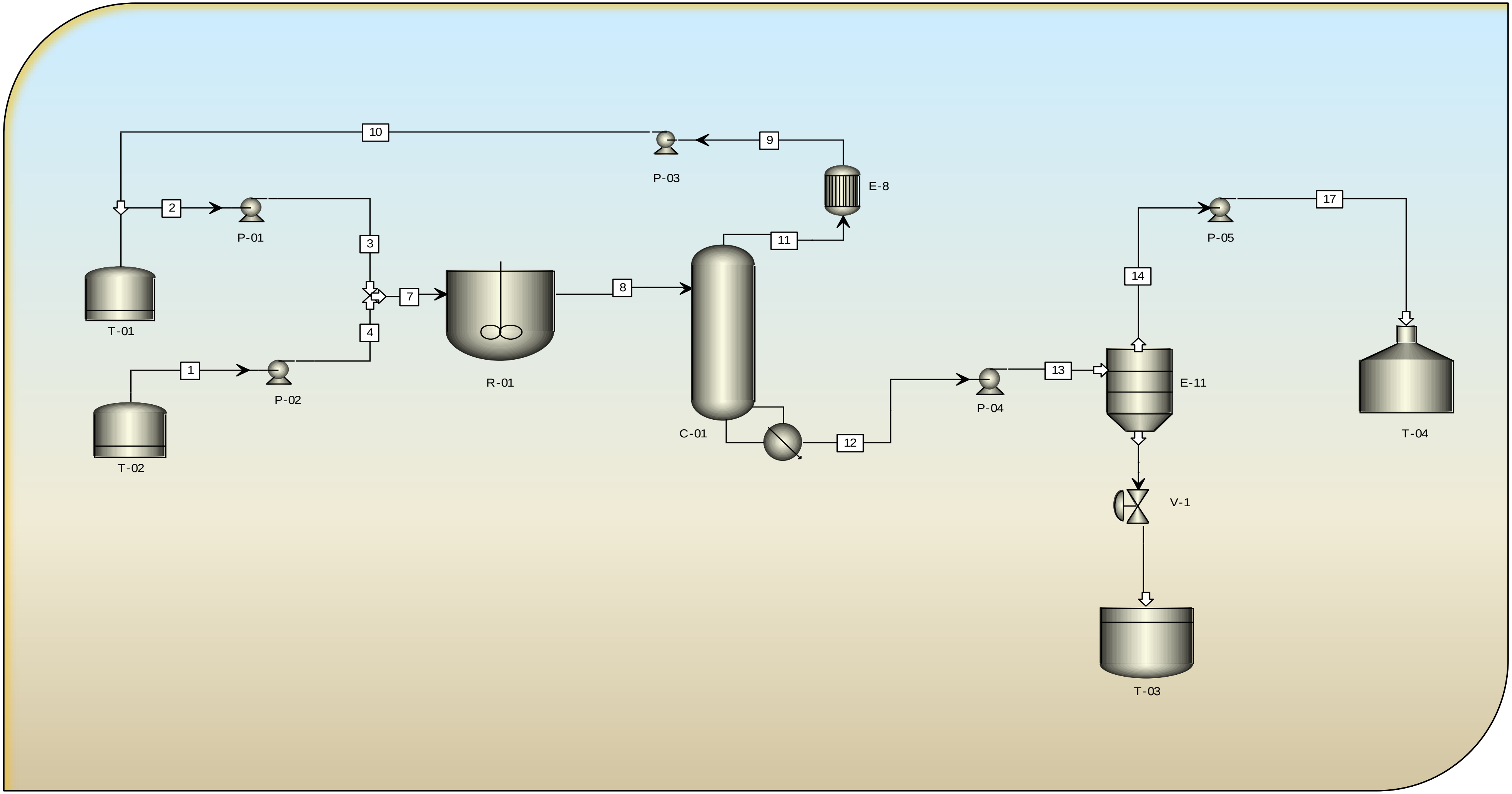
2-) Thermochemical Route

Gasification of Sugar Cane Bagasse for Syngas Production- fixed bed and fluidized bed reactors – LOPCAFEQ-UNICAMP/ Thermoquip-Design
Pyrolysis of Glycerol for Syngas Production
Ethanol and Chemicals from Syngas
Chemical Route – specific catalyst (Rh, Ru, Co based catalyst)

3-) Fermentation of Syngas – clostridium autoethanogenum → bioethanol and bioacetate

4-) Biogas production from vinhasse

Process for Biodiesel from Microalgae- Reactive Distillation



Reactive Distillation

Process Intensification to easier integration with bioethanol plant

Biokerosene Production

Raw materials

- **ACYLGLYCEROLS**
- **BIOMASS**

Patent – Unicamp
Maciel Filho et. all. 2013

Renewable raw materials

REACTION

[1] BIOKEROSENE (Hydrocarbons)

[2]"BIOKEROSENE" (Oxygenated hydrocarbons)

(1) No need to cyclization and aromatization reactions, only a few fraction needs to be hydrogenated .

(2) Purity > 99.9%, it requires ASTM homologation

Final Comments:

Bio-refinery Technologies → may be used together in the same plant

1. **Feedstock- renewable material, basically sugar (glucose) obtained straight from the crop crushing and the lignocellulosic material from crops or agriculture/forest residues, other residues (as glycerol from biodiesel)**
2. **Use of urban residues**

Technologies:

- **Biological/Fermentation**
- **Thermochemical**
- **Reactions based technologies**
- **Esterification and Transesterification**

Fermentation (main)

- **Starch/Sugar Feeds to Ethanol**
- **Lignocellulosic Biomass to Ethanol**
- **Biomethane**
- **Biobutanol by Fermentation**
- **Syngas to hydrocarbons (Fischer-Tropsch), methanol and Ethanol**
- **Hydrocarbons by Fermentation (not in commercial scale as ethanol)**
- **Biogas**

Thermochemical

(Lignocellulosic materials, vegetable oils, residues as glycerol)

- **Pyrolysis**
- **Pyrolysis for Bio-Oil**
- **Gasification**
- **Hydrocracking**
- **FCC based Cracking**
- **Others**

•Esterification/Transesterification

- **Fatty acid esterification (Homogeneous /Heterogeneous)**
- **Oil Transesterification (Homogeneous /Heterogeneous)**
- **Supercritical (lab scale- development)**
- **Others/Hybrids**

Reactions based technologies

(ethanol/higher alcohols/others)

- **Hydrogenation/Dehydrogenation**
- **Oxidation**
- **Hybrids**

How to decide on the technology

- **Feedstock availability and logistic**
- **Domain of technology , costs of royalties, human resources**
- **Need to attend the market regulations**
- **Energy and water supply restrictions or limitations**
- **Sustainability analysis→ economic, social and environmental evaluation is necessary (e.g. BVC-CTBE)**
- **Several scenarios have to be considered**
- **Economic viability is essential → society, in general, is not to pay more because is renewable**