FAPESP WEEK LONDON

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UNICAMP

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BIOEN FAPESP

biofabris

CINE CENTER FOR INNOVATION ON NEW ENERGIES

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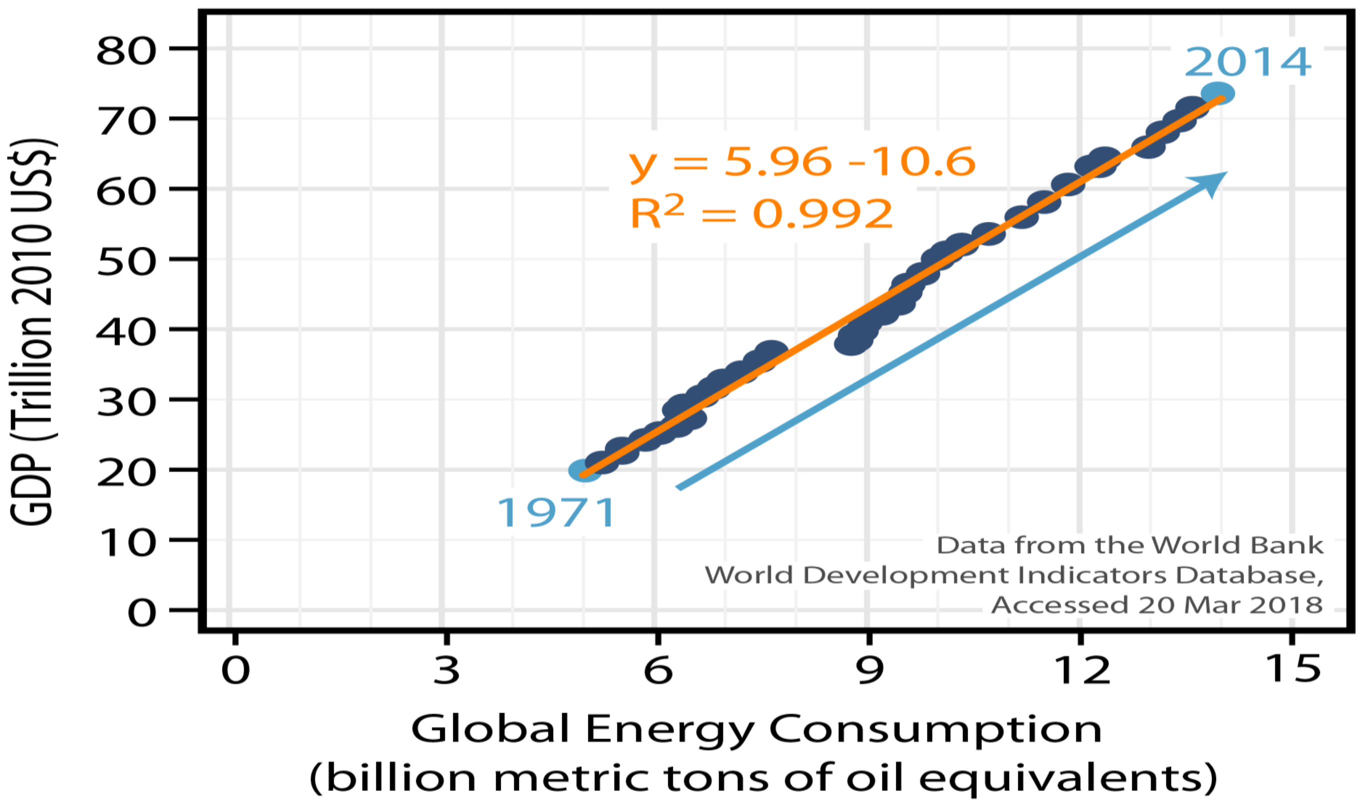
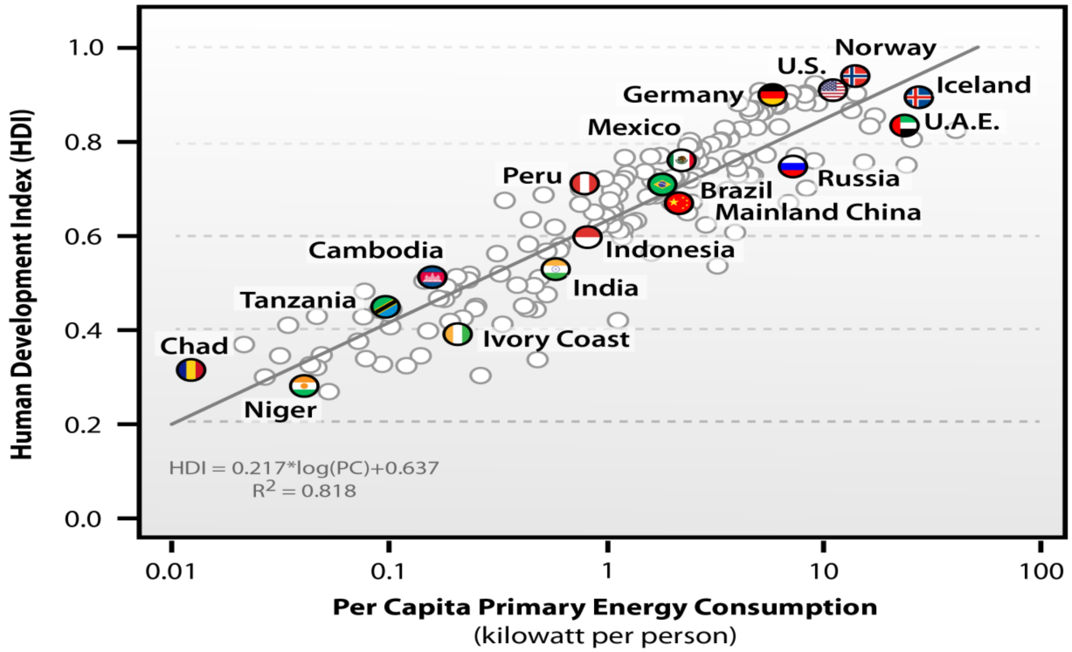
Energy Consumption and Wealth: A Linear Relationship



Dale – B- Scope 2015 - http://bioenfapesp.org/scopebioenergy/index.php

Energy Consumption & Human Well Being are Linked: NO Countries have Both High HDI and Low Energy Use



- **No enough energy (including fuels)for everybody, even with nowadays population**
- **Biobased processes should be energetically efficient and, if possible, to export energy**

Relationship between 2008 per capita primary energy consumption and human development indices (HDI) for 171 countries. Human development indices are also from the HDRO: http://hdr.undp.org/en/statistics/hdi/. Per capita primary energy consumption data are from the U.S. Energy Information Administration (EIA): http://www.eia.gov/cfapps/ipdbproject/IEDIndex3.cfm .
All data were accessed on Nov. 17, 2011.

Many ways of energy are possible

It should account for, but not only Availability, Sustainbility, Easess to transform, but also Suitability for each use

Primary sources

- **No Renewable :Oil, Coal, Nuclear**
- **Renewable**: **Wind, Solar, Biomass, Geothermal**, …

Science and Technology : may contribute: process development (in an integrated design of feedstock and process) and new materials.

New vision is required: thermodynamics, kinetics, transport phenomena etc are necessary but not enough........ multidisciplinarity

Solar Energy - With optimum atmospheric conditions, i.e. cloudless open sky, the maximum illumination observed at midday at sea level is 1 kW/m²

South Western Europe1500 kWh/m² at year

Saara's desert 2600 kWh/m² at year

North Western Europe 800 a 1200 kWh/m² at year

Typical photovoltaic installation(NREL- USA) Retrieved on 2011-11-03.which would produce an average of roughly 22 W/m² (roughly 10% of the average insolation), throughout the year. **20 % considering 12h per day of sun light. In practice 10 % (day of 24 hs)**

Photosynthetic Efficiency → the fraction of light energy converted into **chemical energy** during **photosynthesis** in plants and algae. Simplified chemical reaction

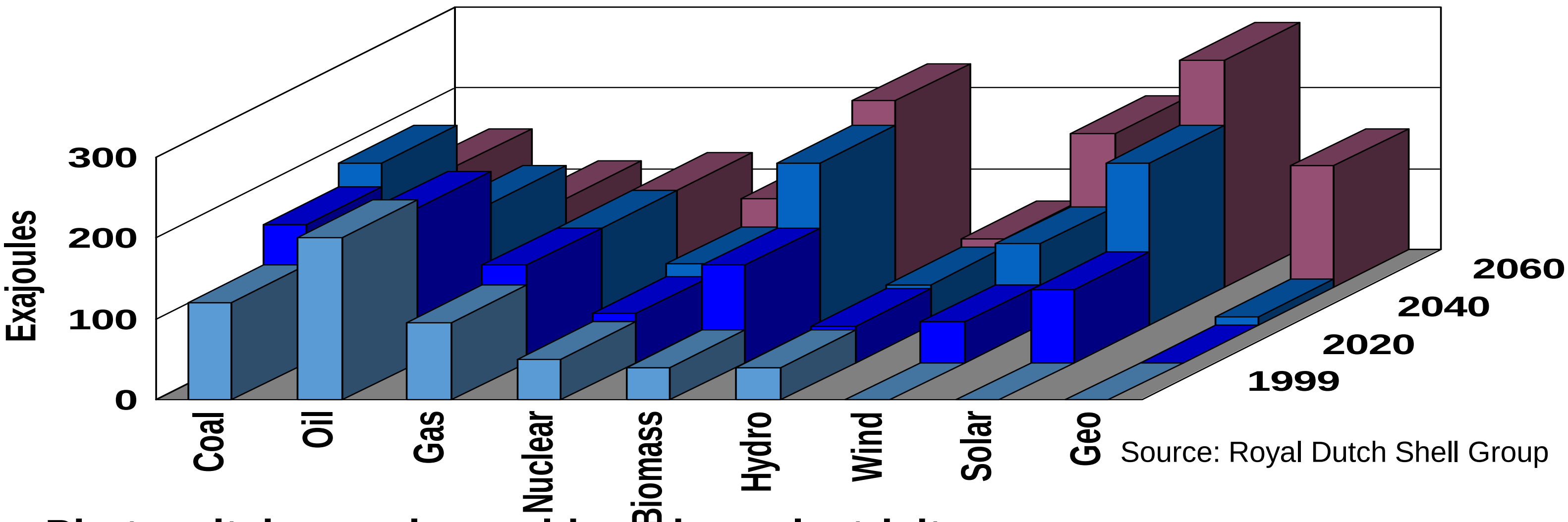
$6H_2O + 6CO_2 + \text{energy} \rightarrow C_6H_{12}O_6 + 6O_2$

Overall photosynthetic efficiency of 3 to 6% of total solar radiation
Oil palm plantation → 0.7 W/m2.
Sugar Cane Plantation→ 0.86 W/m2 (Solar irradiation is 1kW / m²)

Most crop plants store around 0.25% to 0.5% of the sunlight in the product (corn kernels, potato starch,etc.)

Electricity / Biofuels / Chemicals

The future is renewable?



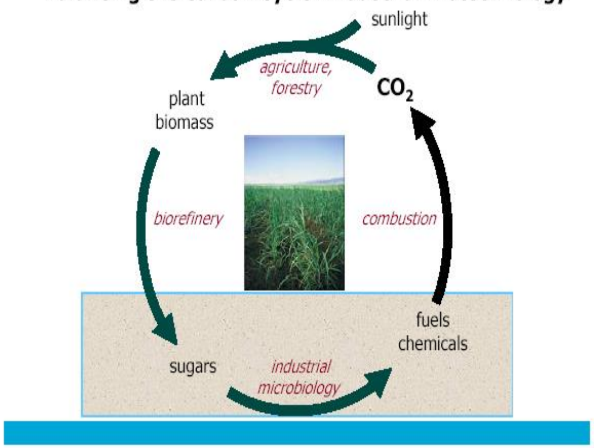
Source: Royal Dutch Shell Group

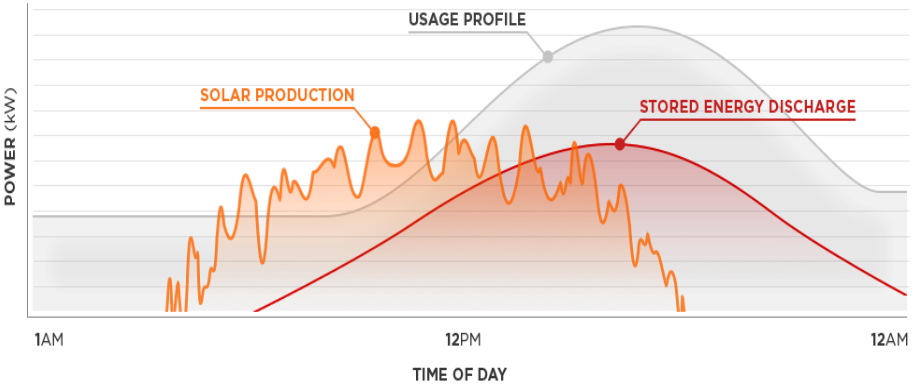
- **Photovoltaic panels would produce electricity**
- **Converting the biofuels into mechanical energy entails the loss of a large portion of the energy.**
- **Liquid fuel (high energy content) is much more convenient for a vehicle than electricity, but new technologies may change this scenario)**
- **For aviation only liquid biofuel is possible (at least so far….)**
- **Chemicals- society requires in many activities, including housing, food production and care/health applications**

Electricity / Biofuels / Chemicals

- **Sustainable future for a better world will need more renewable energy**
- **By 2050 Electrical energy are expected to move from 18% to 50%**
- **CO_2 emissions must be reduced**
- **Solar Energy -Photo Voltaics (1^{st} , 2^{nd}, 3^{rd}) generations and solar driven route to synthesize molecules**
- **Methane (Biomethane) to fuels.**
- **Energy has to be stored**

Balancing the Carbon Cycle: Industrial Biotechnology





New Energies Research Center-CINE

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1)Sustainability and low carbon emissions

2) Materials science and electrochemistry is the link among all divisions.

3) Computational simulation, including multiscale calculations and molecular dynamic simulations, will help to understand phenomena and guide paths

To perform worldclass research in the areas of
energy carriers,
energy storage,]
methane to products and
computational material science and chemistry.
Site https://www.cineenergy.org

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A solar driven route to synthesize molecules - Dense energy Carries

Coordinator - PI : Dr. Ana Flavia Nogueira

Chemistry Institute- University of Campinas

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"Understand the fundamentals of the main solar driven routes to synthesize dense energy carriers, using in situ techniques, high performance (nano)materials and boost the efficiency using perovskite solar cells"

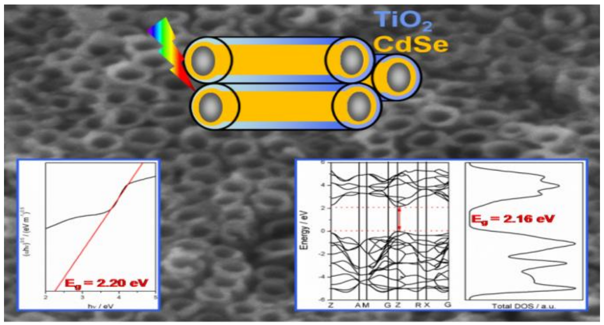
Photoanodes and photocathodes: synthesis, doping, co-catalyst investigation nanostructuring, deposition methods

↔

In-situ **(photo)electrochemical, imaging (TEM) and Synchrotron characterizations**

↔

Perovskite solar cells: from lab to large scale devices



In situ electrochemical TEM and measurements

Nanomaterials and catalysts

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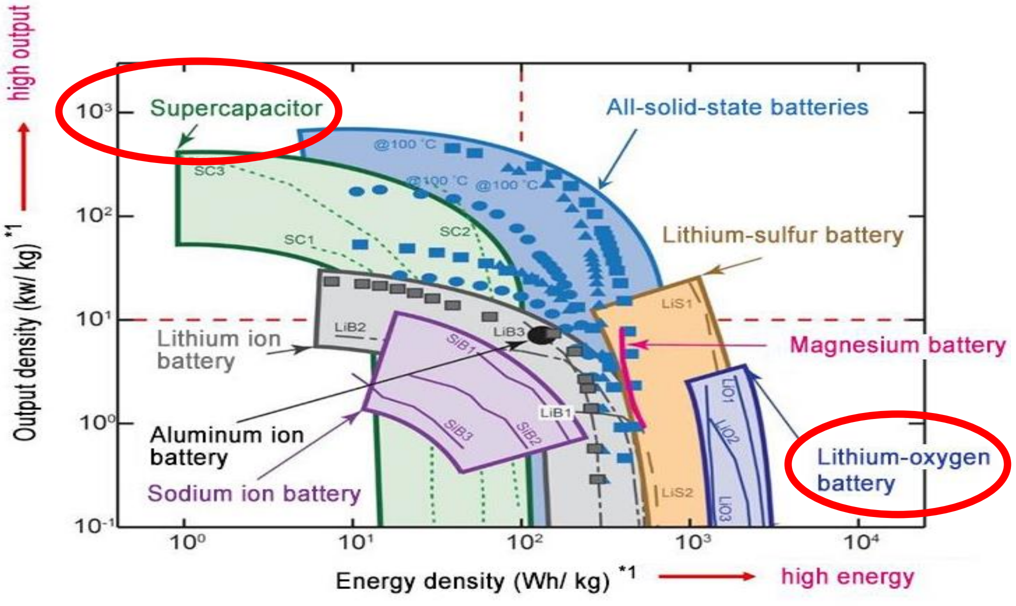
Advanced Energy Storage - Why Li-Air & Supercapacitors?

Coordinator - PI : Prof. Rubens Maciel Filho

School of Chemical Engineering - University of Campinas



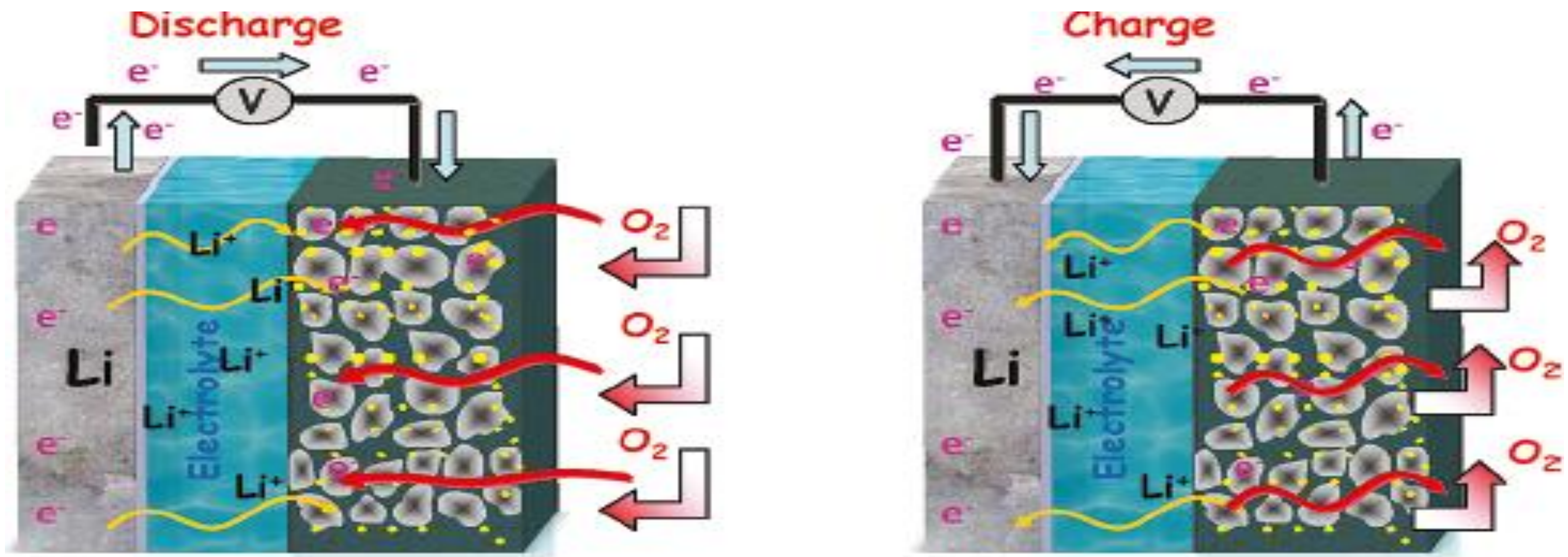
- **Represent both ends for high energy and high output density**
- **Unanswered questions**
- **What are the main guidelines for the technology?**

Zhang, X., Wang, X.-G., Xie, Z. & Zhou, Z. Recent progress in rechargeable alkali metal–air batteries. Green Energy Environ. 1, 4–17 (2016).

Li-O_2 Batteries

Li-O_2 Batteries

- **The Li^+ reacts with the adsorbed O_2 species and produces Li_2O_2 as discharge products**



Girishkumar, G, McCloskey, B, Luntz, A C, Swanson, S, Wilcke, W; Lithium−Air Battery: Promise and Challenges. The Journal of Physical Chemistry Letters 2010

- **The reaction can be reversed, releasing O_2, and depositing the Li^+ in the anode.**

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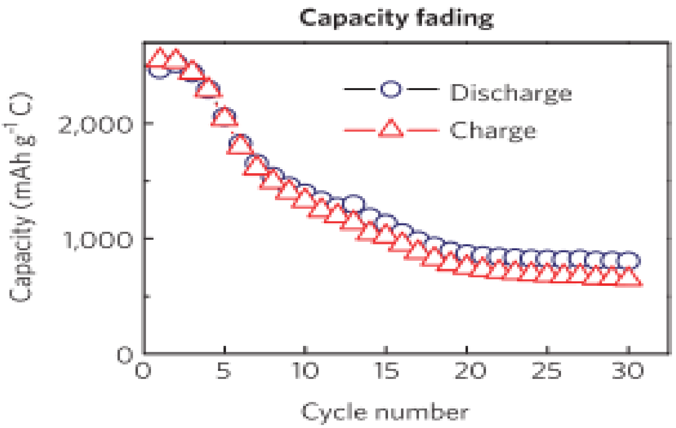
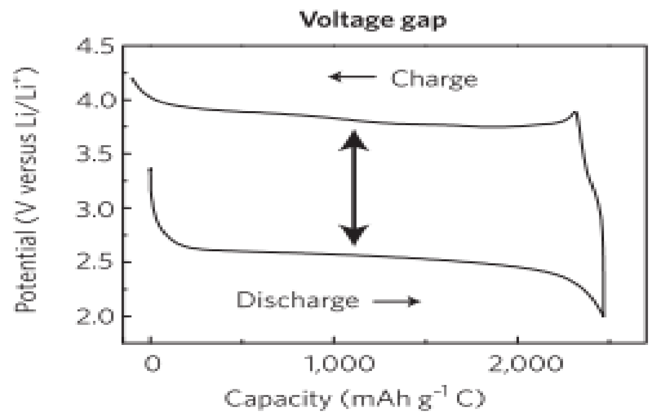
Main challenges

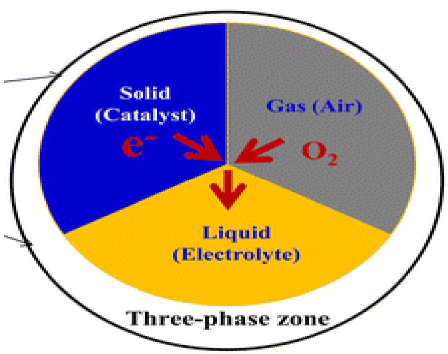


Capacity loss during cycling

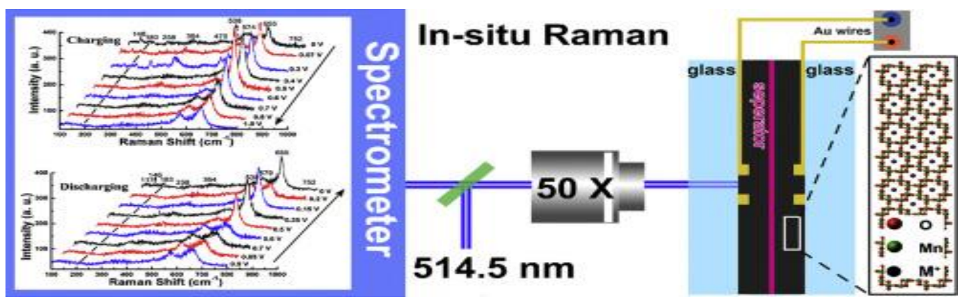


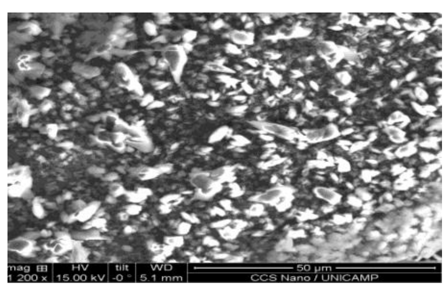
Large overpotentials for charge and discharge

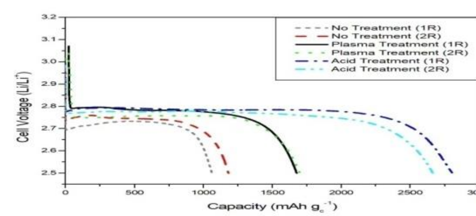
Bruce *et al*.Nature , 2011. Yan-Jie Wang, Electrochemical Energy Reviews 2018



Triple-phase boundary management







CNT- carbon nanotubes

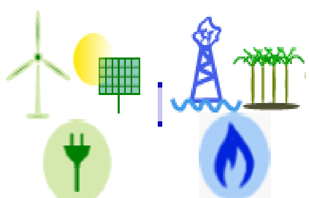
Methane to Products

Coordinator - PI : Dr. Fabio Coral Fonseca

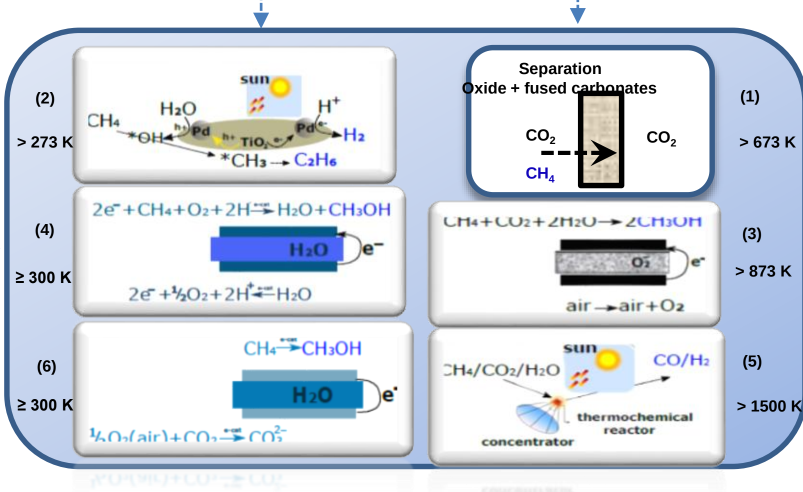
Nuclear and Energy Research Institute

Strategy

Future Scenario | **M2P Projects** | **Monetized Natural Gas**



Cheap and abundant



Advanced feedstock

Chemical industry

Fuels

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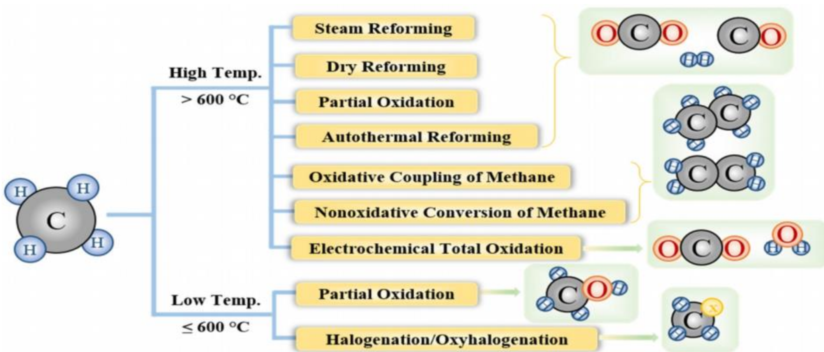
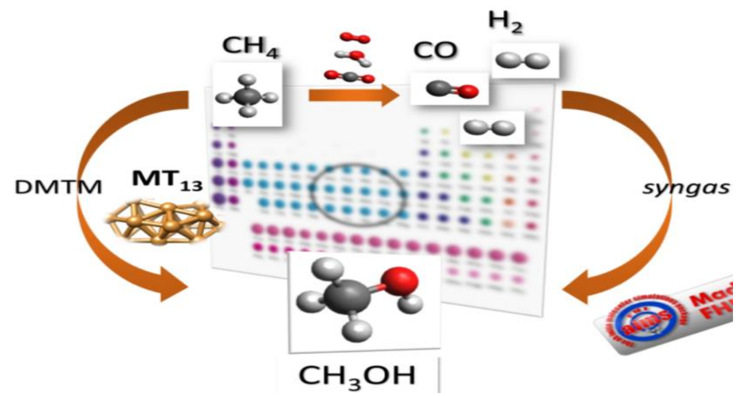
Example of Computational developments: Selective Conversion of Methane to High Density Carriers based on Porous and Nano-Materials

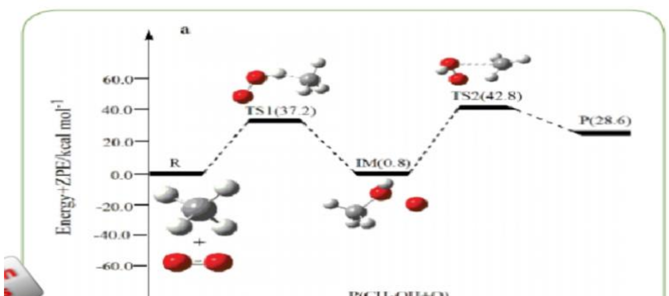
Coordinator - PI : Dr. Juarez L. F. da Silva

São Carlos Institute of Chemistry – IQSC – University of São Paulo

Catalysis Today 285 (2017) 147–158

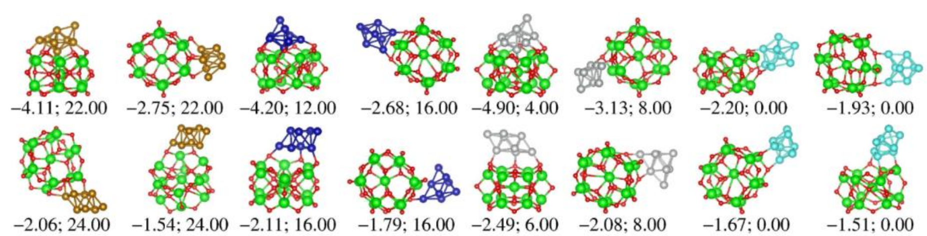






A schematic potential energy surface of the CH_4+O_2→CH_3OH+O reaction obtained at the B3PW91 + ZPE level.

Liu H, Liu Z, Zhang Y, Xinxue Y. *J. Mol. Cell. Biochem.* **2018**, Vol.2 No.1:3.



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Biomass based approach

• **BIOMASS** availability which may be region dependent and logistic will pay an important role. (+- 70% of the biofuel/bioenergy costs)

• The nature of the **CONVERSION PROCESSES** employed, that means, the ability to efficiently utilize the energy content of biomass, attending the market demands.

•Meta-metabolonics- design of biomass and microorganism in sinergy to specific functions

• Model for social impact and rural development taking into account restriction to food production

• Global Water footprint

• Global Carbon footprint

• Global Green House Gas Emissions

• Logistic of biomass with biomass densification

Corn stover

Sugar-Cane Bagasse

Hardwood

Softwood

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Bioeconomy/Circular - Meta-Reverse Engineering- Thermobiochemical routes

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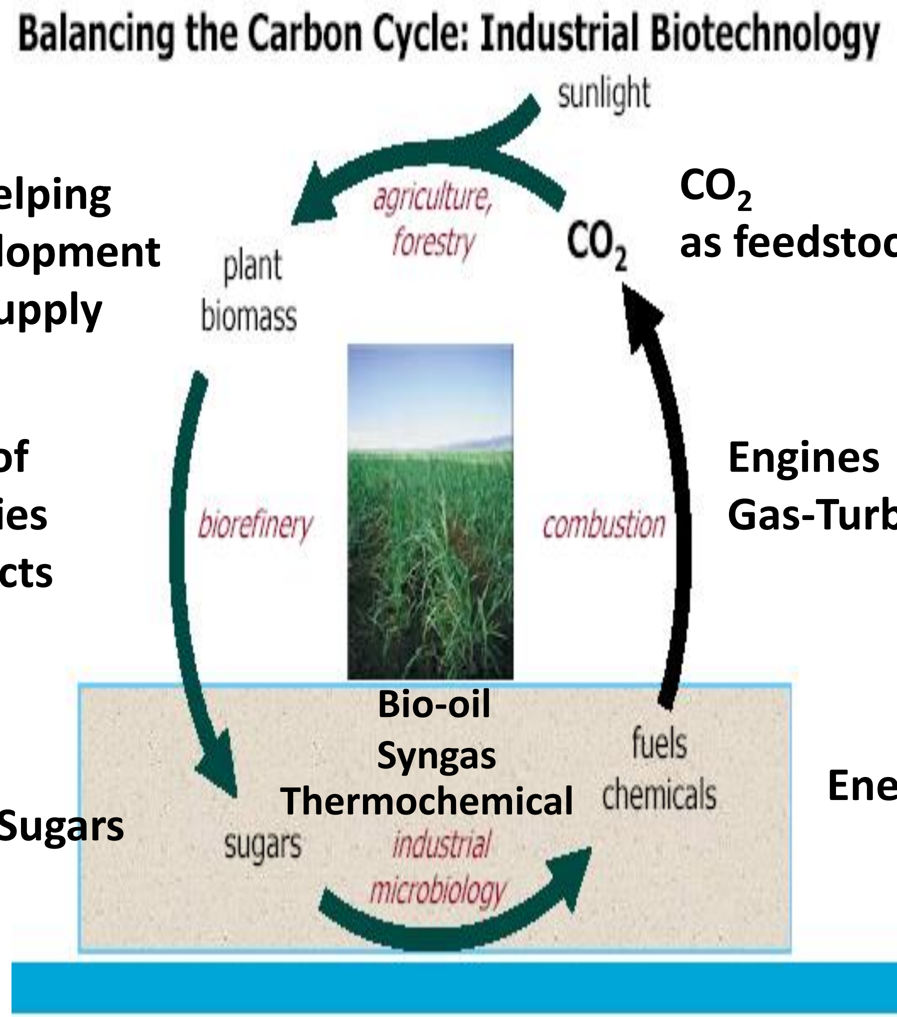

Logistic , Helping Rural Development And food supply

CO_2 as feedstock

Portfolio of Technologies and Products

Engines Gas-Turbine

Primary Secondary Sugars Lignin

Energy

The whole process – from biomass to product deliver → not only economically competitive

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KEY PERFORMANCE INDICATORS

Renewability exergy index

$$\lambda = \frac{\Sigma B_{\text{products/byproducts}}}{B_{\text{fossil}} + B_{\text{destroyed}} + B_{\text{deactivation}} + B_{\text{disposal}} + \Sigma B_{\text{emissions/residues}}}$$

$0 \leq \lambda < 1$	***Environmentally unfavorable***
$\lambda > 1$	***Environmentally favorable***
$\lambda = 1$	***Reversible process with non-renewable inputs***
$\lambda \to \infty$	***Reversible process with renewable inputs***

Oliveira Junior, S. ***Exergy production, cost and renewability.*** *Springer-Verlag London, 2013*

Comparative Energy Balance to Crop Choice and Design as Feedstock (e.g. Ethanol)

PROCESS Feedstock	Corn[1]	Switchgrass[1]	Sugar cane[2]
Energy unit	(GJ/ha.yr)	(GJ/ha.yr)	(GJ/ha.yr)
Crop production energy consumption	18.9	17.8	13.9
Biomass Energy	149.5[3]	220.2	297.1[4]
Agricultural energy ratio	7.9	12.3	21.3
Ethanol production energy consumption	47.9	10.2	3.4

1- Source: ORNL, 2- Source: Copersucar/UNICAMP, 3-No credit for corn stover, 4- No credit for sugar cane leaves,

Ethanol Productivity

Brazilian sugarcane ethanol is the biofuel presenting the highest productivity in the world (today: 6,000 l/ha.year) and the best renewable energy ratio:

9-13 liters renewable energy/liter fossil energy
US corn ethanol: 1.4-1.8
German biodiesel: 3.0

Oil - Each unit of energy invested to produce oil in the 1940s yielded the equivalent of 110 energy units (1 to 100)
Nowasdays – depending upon the oil field 1-10

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Evolutionary Engineering and the 1G Learning Curve

Learning curve of Biochemical/Thermochemical

2G Routes → important knowledge

2G Biochemical

1G
(40 years)

In10 years?

70's

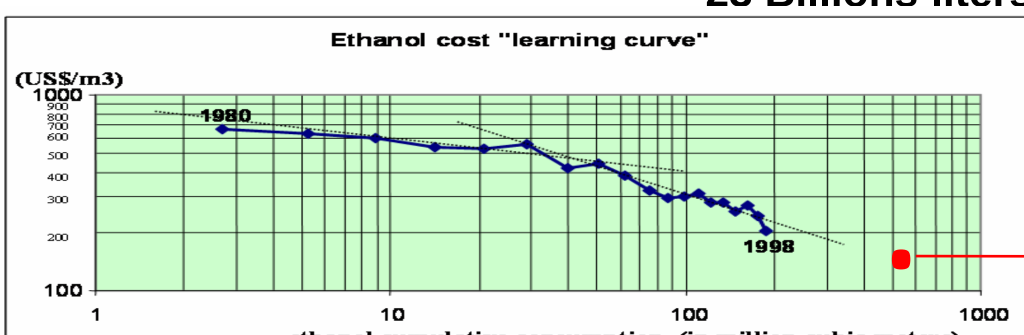
82 %

Today

40-60 %

2 Millions ha- Sugar 4.5 Mt,
80 Mt of Sugar Cane- 1 Billion liters

8.5 Millions ha
Sugar 36 Mt
23 Billions liters



Goldemberg, J.

40 years

US$ 20-25 cents → production cost of 1 liter of ethanol (70% due to sugar cane)

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Lignocellulosic Conversion- Decision making – couple with different alternatives

Sustainable concept of Biobased Production → requires to be energetically self-sufficient and even Electricity Exporter

Thermochemical Routes Challenges

1) Syngas production
2) Gas purification
3) Catalyst development for efficient process
4) Separation an purification
5) Bio-oil based process

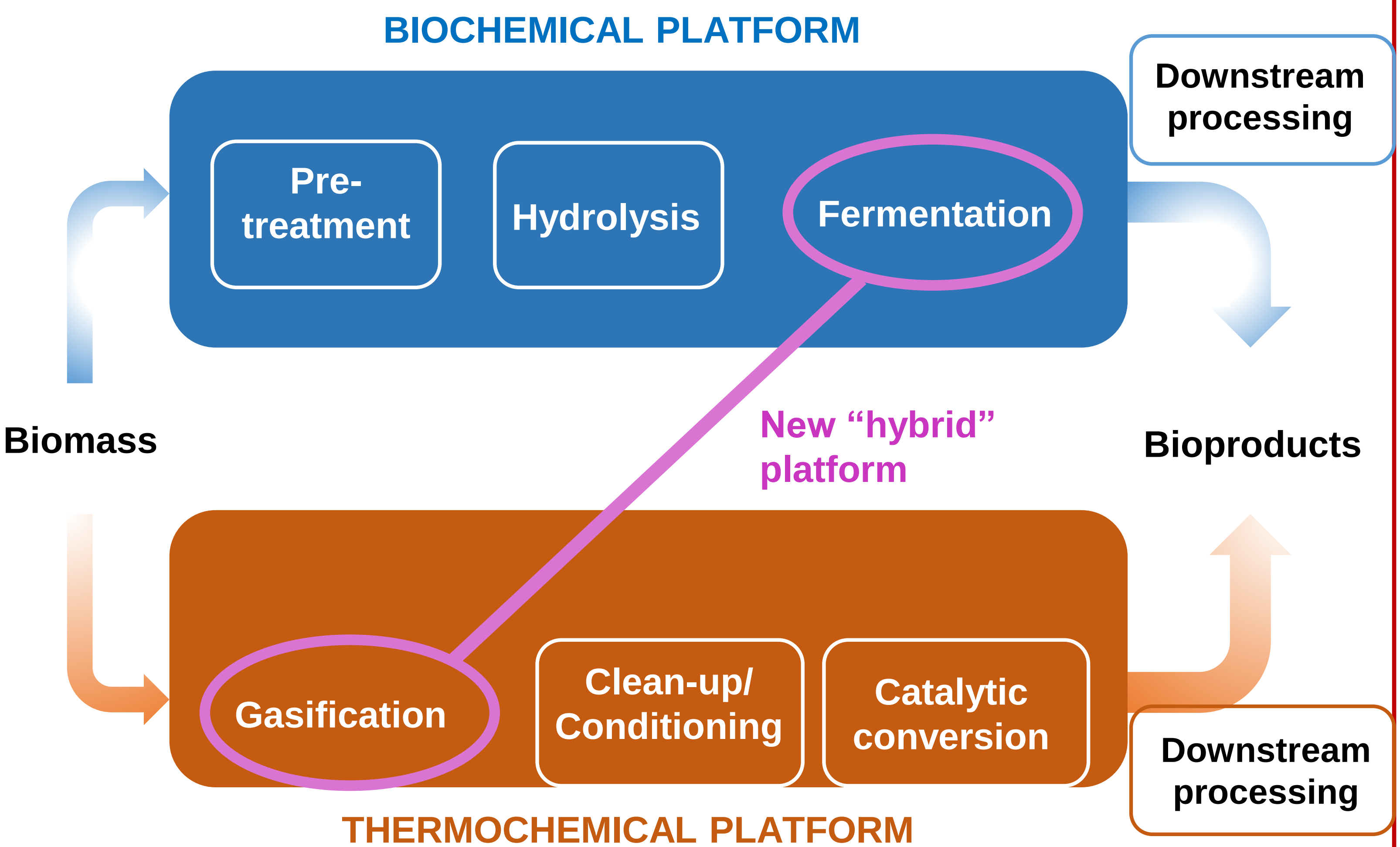
Biochemical Route 2G Challenges

1) Pre-treatment in large scale
2) Delignification
3) Enzymes- costs and on site production
4) Fermentation time
5) C5 fermentation
6) Separation and purification

To other raw materials - Impact of Logistic

A point to be considered is its possible integration with the first generation units and this may lead to a careful choice of the process that leads to economically and robust solution to use byproducts as feedstock for energy and chemicals. Flexibility of Thermochemical route, in terms of raw material should be addressed- any lignocellulosic material and use of Solid Municipal Waste

Synergy between Thermo and Biochemical Routes

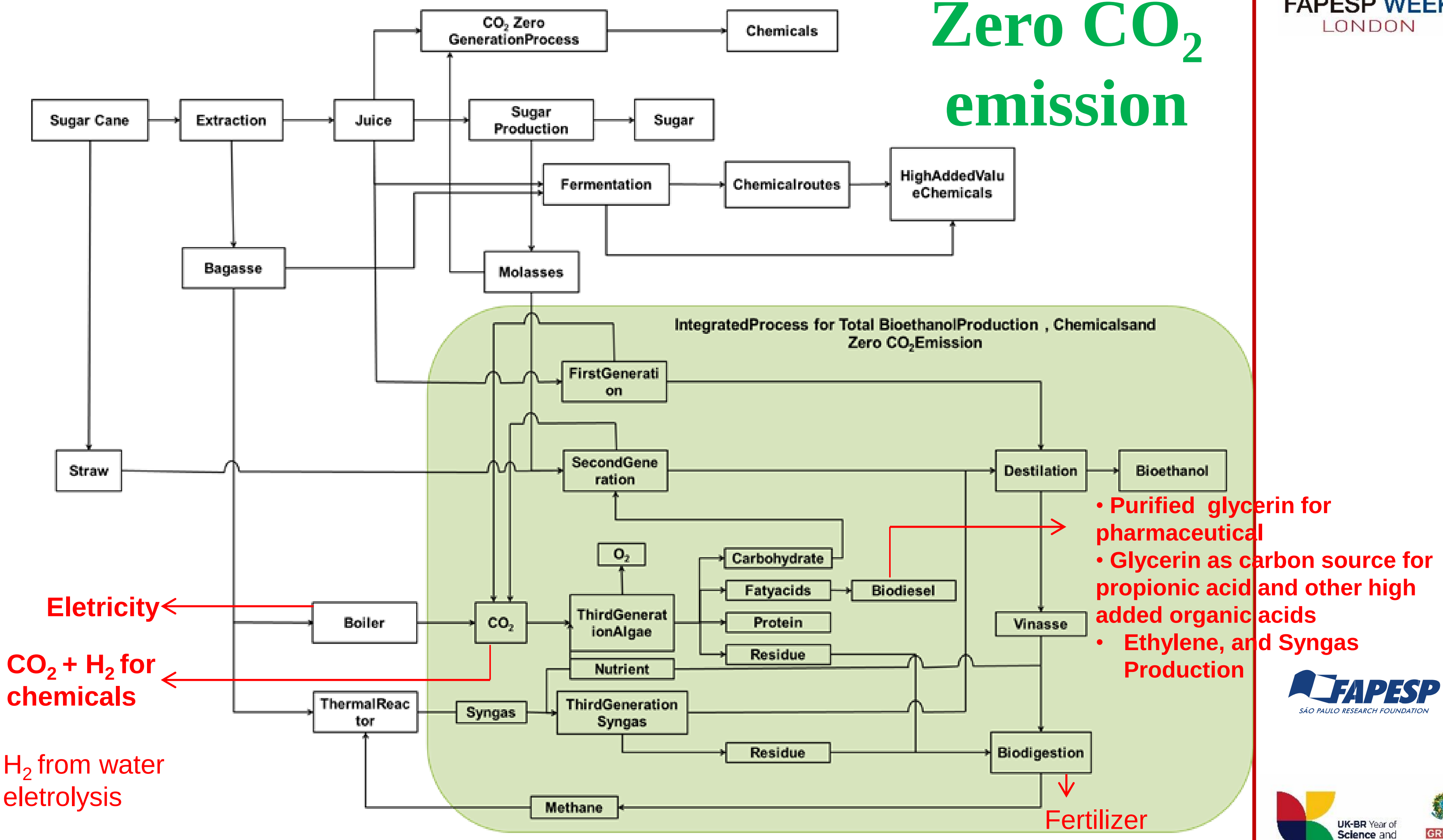


DE MEDEIROS, E.. ; POSADA, J. A. ; NOORMAN, H. ; OSSEWEIJER, P. ; MACIEL FILHO R. . . JOURNAL OF CLEANER PRODUCTION, v. 168, p. 1625-1635, 2017.

Biomass-→ Bio-oil → Upgrade and/or Co-Processing - Fapesp–H2020

Integrated Circular Process

Zero CO_2 emission



Source: Thematic Project Fapesp– Coordinator Maciel Filho.. Dias et. all, Environmental Development, v. 15, p. 35-51, 2015 **205; Klein et. all** BIOFUELS, BIOPRODUCTS AND BIOREFINING, v. 12, p. 10, 2019.

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Search for more efficient Fermentation-Global Negative Cycle of CO_2

1. Microorganism → *Saccharomyces cerevisiae*

2. Invertase Reaction

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

3. Fermentation Reactions

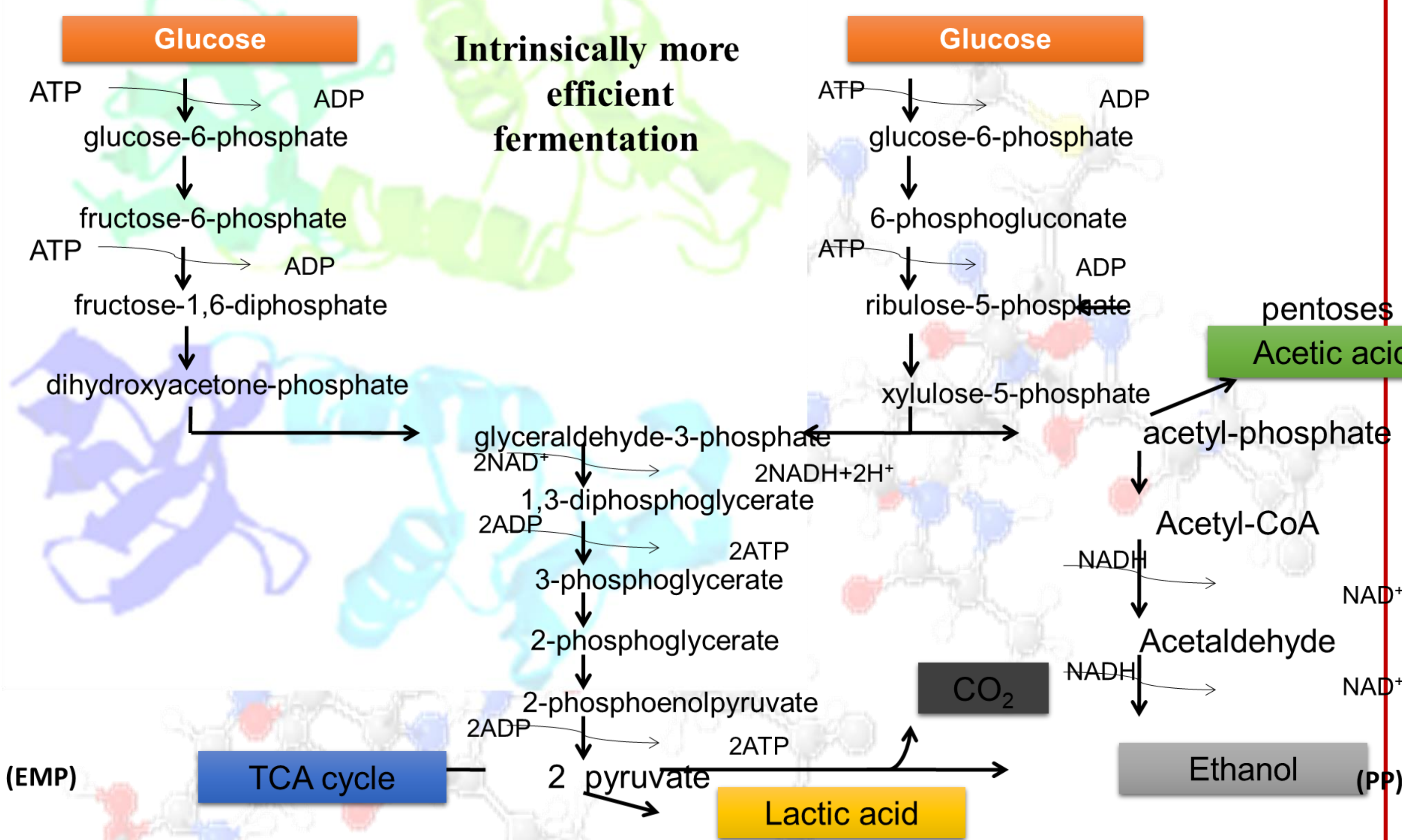
Main Reaction

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

$$Y_{MAX} = 0.51\ \text{g ethanol} / \text{g glucose}$$

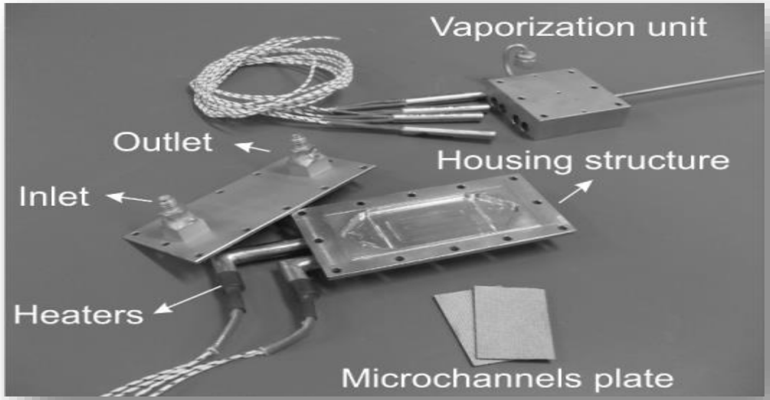
90 % of the theoretical yield due to secondary reactions.

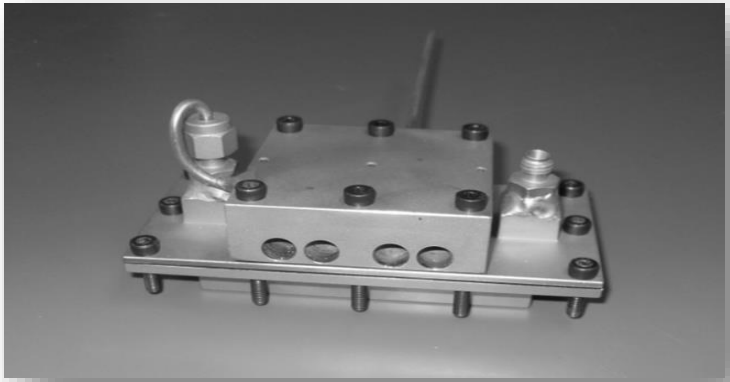
LATIC ACID PLATFORM



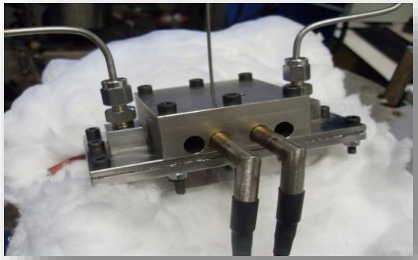
ALVES O.. R ; KOMESU, A ; VAZ R., C. E.; MACIEL FILHO R. . Challenges and opportunities in lactic acid bioprocess design-From economic to production aspects. BIOCHEMICAL ENGINEERING JOURNAL, v. 133, p. 219-239, 2018.

Microchannel Reactor- H2 from Ethanol for Fuels Cells

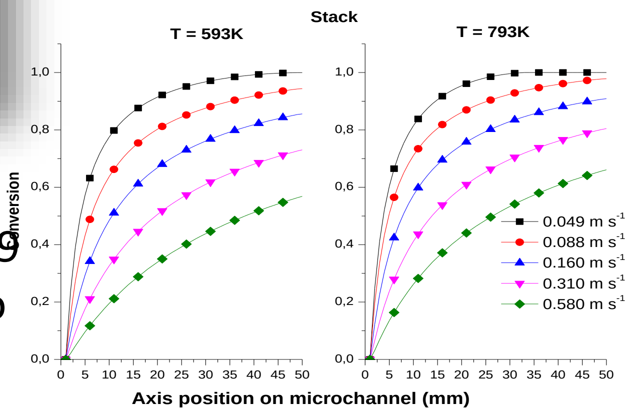




Final microreactor assembly containing microchannels plates.



Patent:BR2013000499
Unicamp, Macie Filho et. all



Case		593 K
	[kg s^-1]	V [L h^-1]
A	8,477E-08	3,39
B	1,478E-07	5,91
C	1,905E-07	7,62
D	2,268E-07	9,07
E	2,565E-07	10,26

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Final Remarks

- **Sustainable Energy is required for a human development**

- **Solar Energy should be better explored . Electricity storage have to be improved**

- **New materials with potential to develop high energy density batteries**

- **Feedstock productivity with photosynthetic evaluation, availability and logistic - play crucial role- circular process design**

- **Sustainability analysis→ economic, social and environmental evaluation is necessary**

- **Several scenarios with biomass and circular process design approach have to be considered**

- **|Electricity and biofuels – they should not compete . They may compose an alternative energy matrix.**

- **Economic viability is essential → society, in general, is not to pay more because is renewable- criteria of circular economy have to be met**

Acknowledge

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Researchers students and researchers of LOPCA/LDPS and CINE

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