PROCESS DEVELOPMENT FOR GREEN ACRYLIC ACID and PROPIONIC ACID BY SUGAR FERMENTATION

Prof. Dr. Rubens Maciel Filho

FAPESP
Workshop BIOEN de Pesquisa
06 e 07 de Novembro de 2012 - FAPESP - São Paulo

State University of Campinas – UNICAMP
School of Chemical Engineering
Laboratory of Process Optimization, Design and Advanced Process Control-LOPCA

Scientific Production: 02 Patents
Published Papers: 8

LOPCA Laboratório de Otimização, Projeto e Controle Avançado

UNICAMP

FAPESP

Braskem

Objectives

- **Evaluation and proposition economically viable route for fermentative production of acrylic acid and propionic acid from renewable sources**

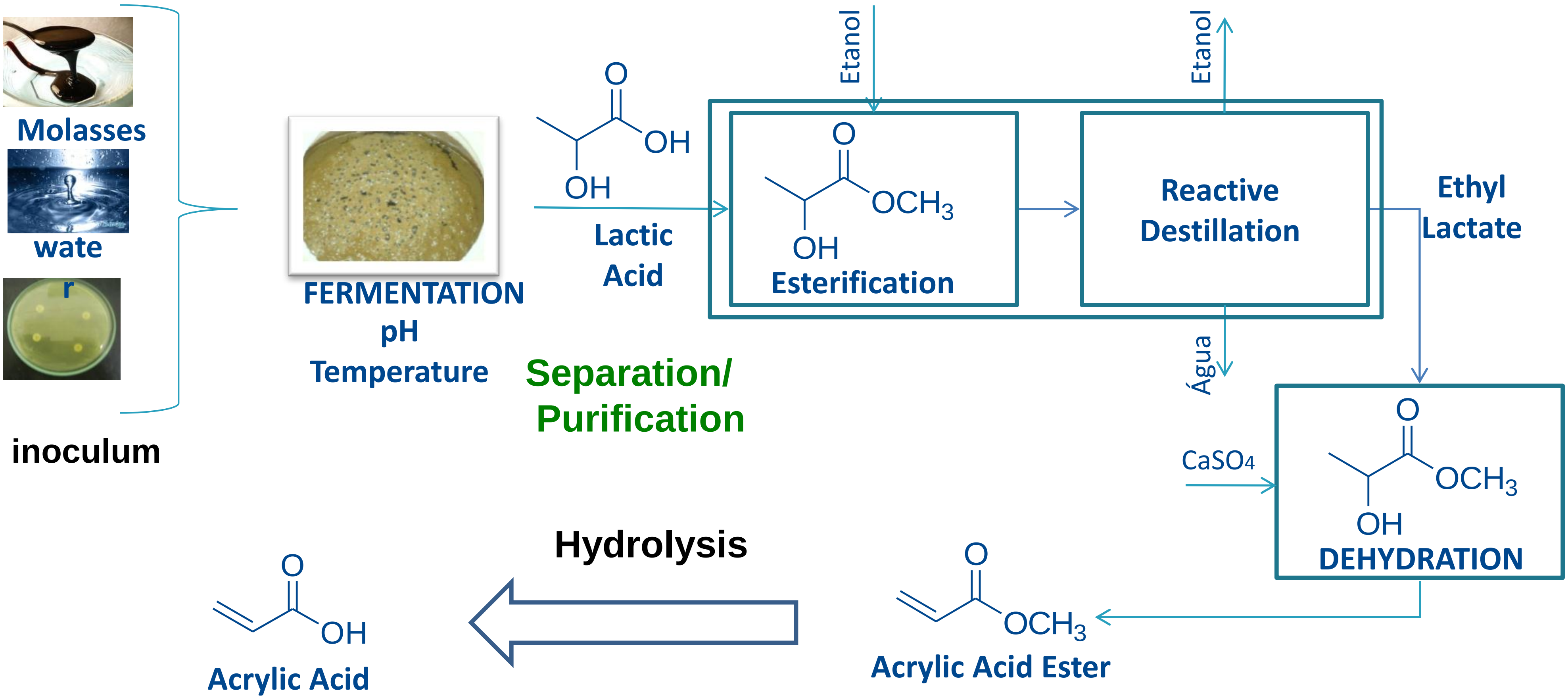
- Identifying species of microorganisms that produce lactic acid.

- Assessing **the production of acrylic acid by using the hybrid method** (lactic acid obtained by fermentation with esterification and dehydration with ethanol to obtain the ester of acrylic acid hydrolysis for the production of acrylic acid).

- Carried out experiments for production and determination of the kinetics of production and purification of acrylic acid from lactic acid obtained by fermentation of sugars derived from sugar cane.

METHODOLOGY: Hybrid Route for producing acrylic acid by fermentation and green chemical reaction

FINAL STEP: OPTIMIZATION OF THE HYDROLYSIS PROCESS FOR THE ACRYLIC ACID PRODUCTION



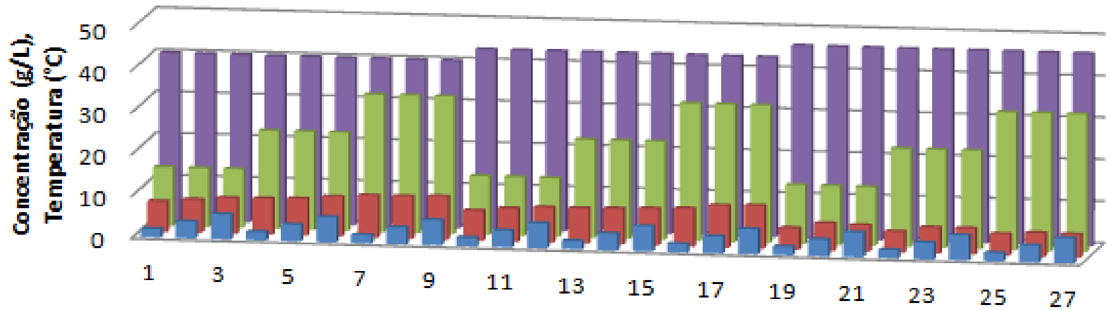
Process – Patent applied

POSITIONING - COMPETITIVE PROCESS

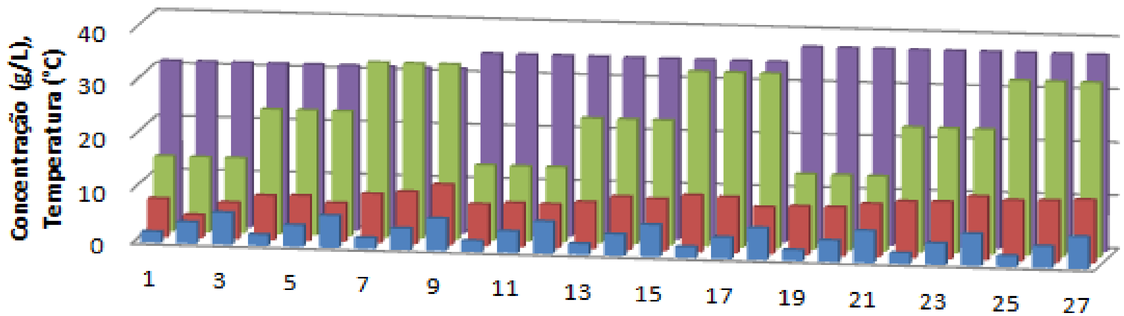
UNICAMP

Results – Microorganism Definition

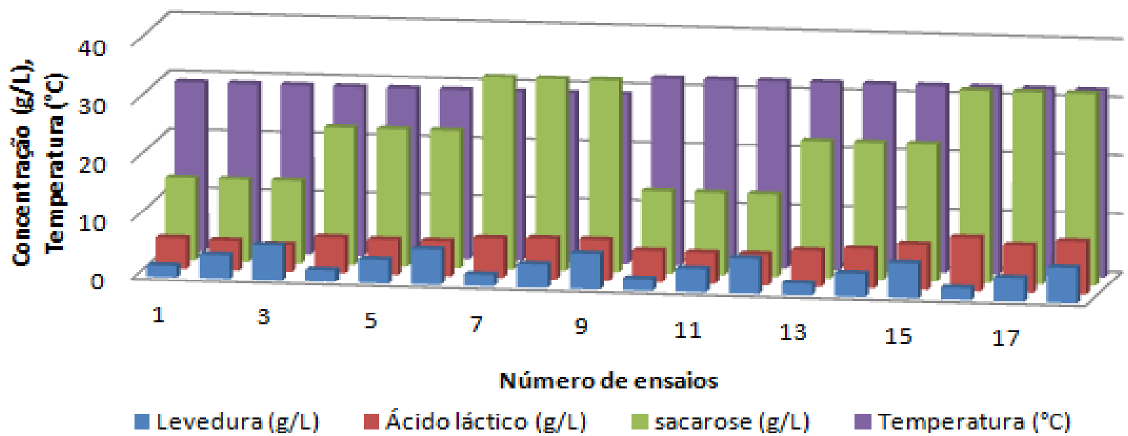
Lactobacillus delbrueckii



Lactobacillus plantarum

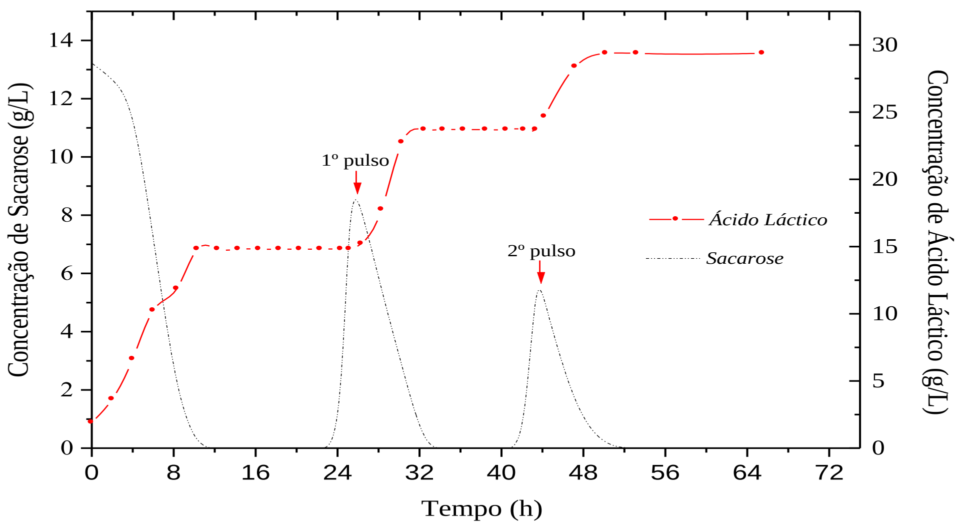


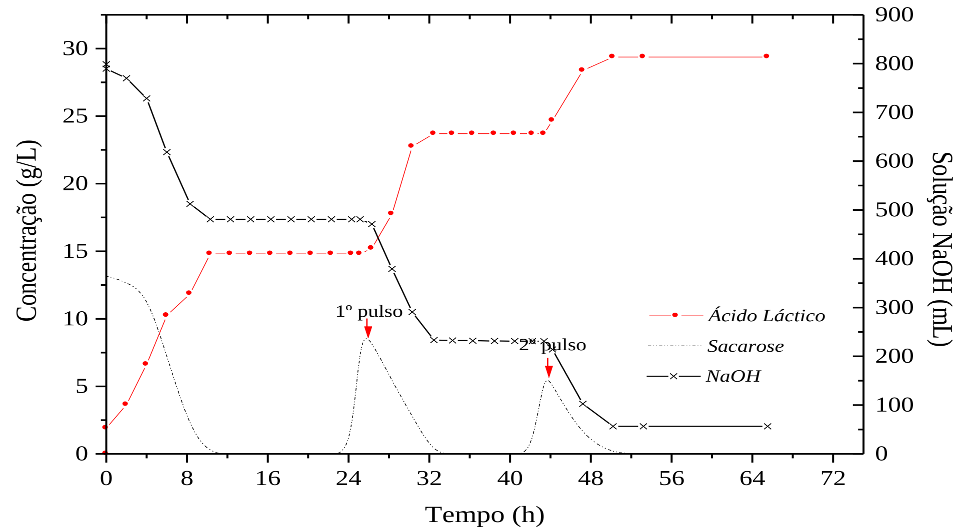
Leuconostoc mesenteroides

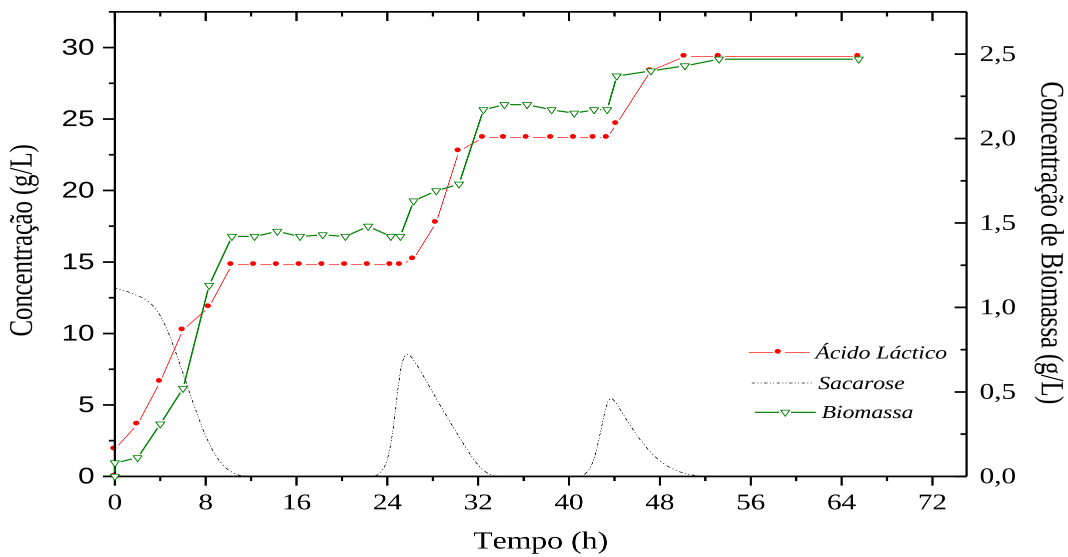


Optimization of Lactic Acid Production

<u>Micro-organism</u>*: *Lactobacillus plantarum **(L and D Lactic Acid isomers)**







Em relation to the sugar price – increase of ao 190,000 times

Kinetic Parameters

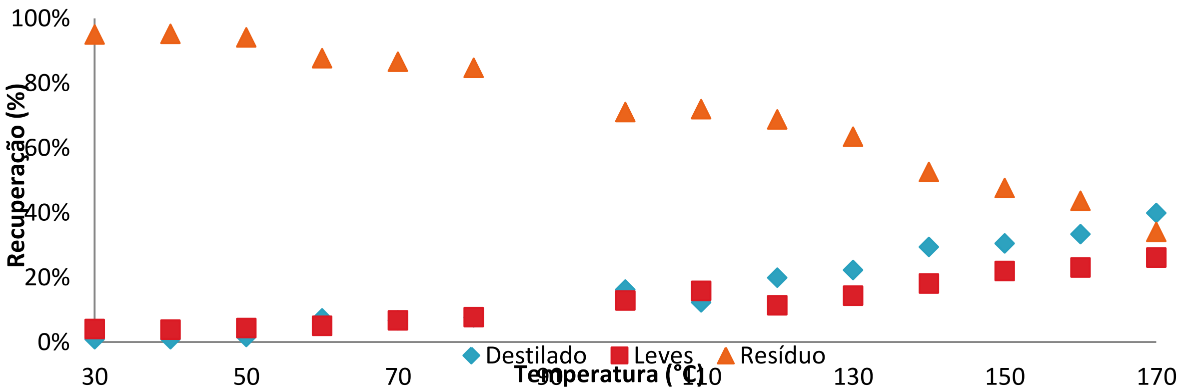
$$y = a + \frac{b}{\left(1 + \exp\left(-\left(t - c\right)/d\right)\right)}$$

LASPRILLA, A. J. R., MARTINEZ, G. A. R., LUNELLI, B. H., JARDINI, A. L., Maciel Filho, Rubens, JARDINI, A. L. Poly-lactic acid synthesis for application in biomedical devices . A Review. Biotechnology Advances. , v.30, p.321-328, 2011.

Strategies for separation and purification of Lactic Acid

- Evaporative System
- Reative Distillation
- Coupled Evaporative System (Wiped Film) and Reactive Distillation

Lactic Acid Recovery – Temperature effect

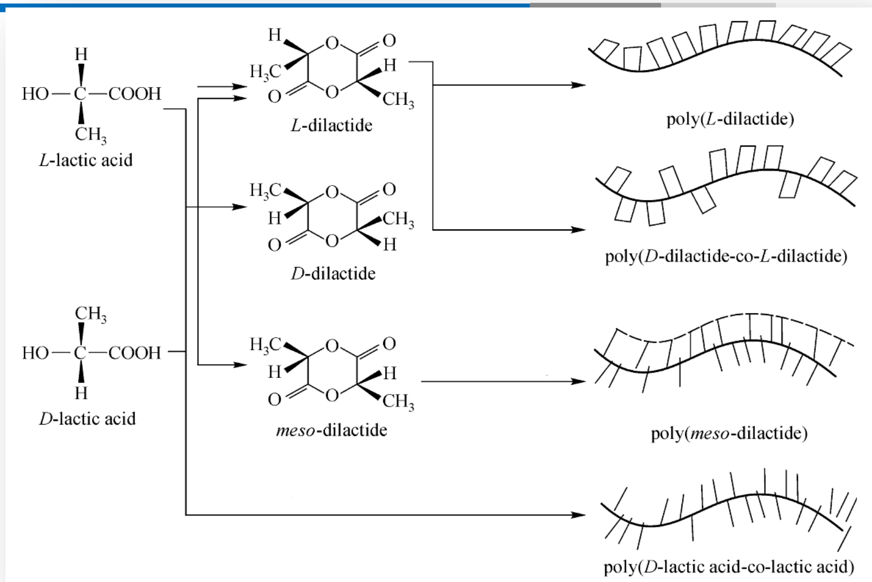


patent applied for

POLY LACTIC ACID

Just like its monomer, poly lactic acid can be found as isomers:

- **poly(L-lactic acid) (PLLA),**
- **poly(D-lactic acid) (PDLA) and**
- **poly(D, L- lactic acid) (PDLLA).**



Depending on the monomer used, the poly lactic acid can be obtained in different forms, all of them with different properties.

Laboratory Scale

Computer Simulation

Pilot Plant

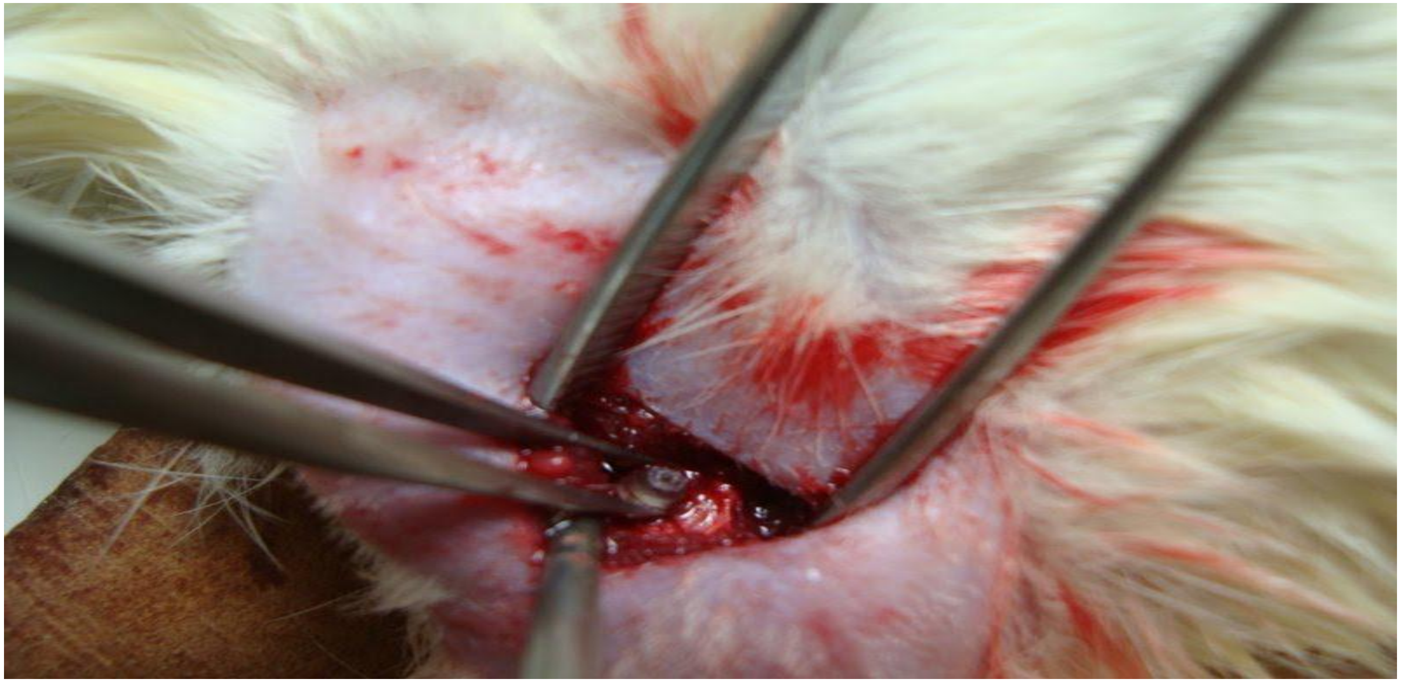
Bio- materials from Renewable sources – An example of added value

1 ton of Sugar Cane – R$ 45,00 → R$ 0,000045/gram

1 Kg of Sugar – R$ 1,30 → R$ 0,0013/gram

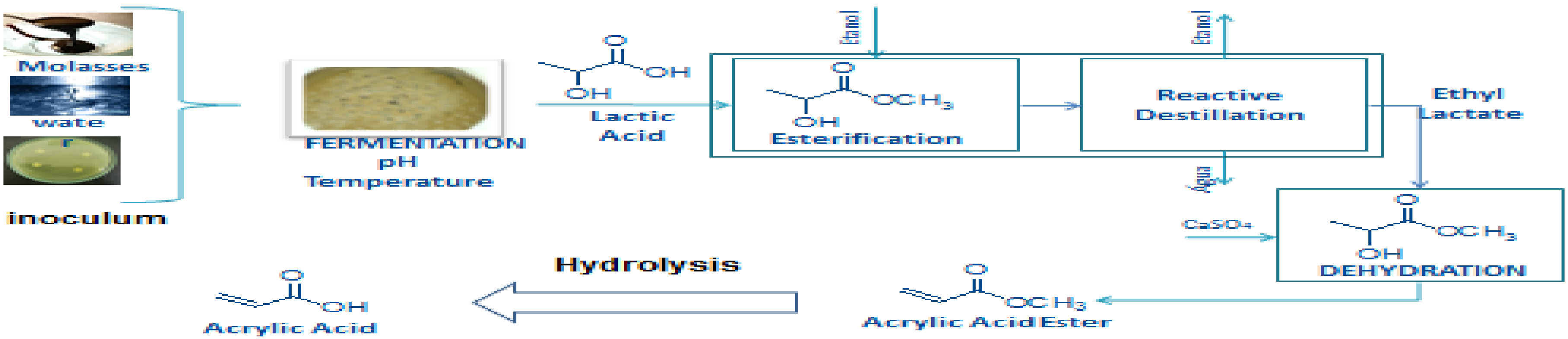
1 liter of biethanol → R$ 1.80 /liter
1 Kg of LA (purified) R$ 5.000,00 → R$ 5,00/gram
1 Kg of in shape biomaterial R$ 180.000,00 → R$ 180,00/ gram
In relation to the Sugar and added value of 190.000 times

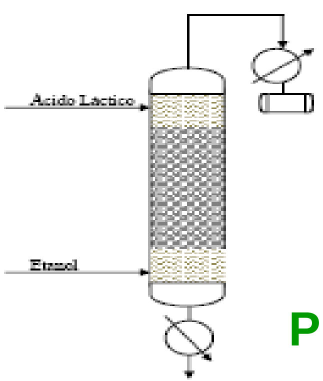
BONE TISSUE ENGINEERING – Sugar cane sucrose PLA with Properties control – TEST IN VIVO



Lactic Acid Purification – carried with success without solvent Addition- 94% (50°C) – recovery of Lactic Acid –Process is quite suitable – low temperatures, not product decomposition or dimerization and low energy consume

Reaction Steps to obtain Acrylic Acid

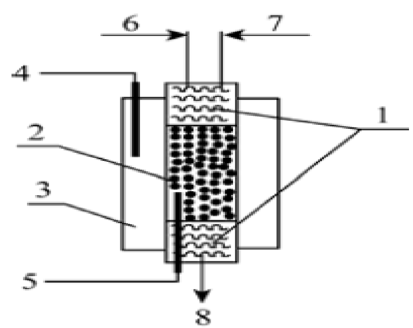




Esterification Step

Process intensification- reactive distillation
Cationic resin for pH control
Catalyst

Process with a good potential



Ethyl Lactate Dehydration

Fixed Bed column

AN INTEGRATED PROCESS FOR TOTAL BIOETHANOL PRODUCTION AND ZERO CO_2 EMISSION

Thematic Project 2008/57873-8

Full Professor Rubens Maciel Filho
State University of Campinas – UNICAMP
School of Chemical Engineering
Laboratory of Process Optimization, Design and Advanced Process Control-LOPCA

Scientific Production : 65 published papers (since 2010)
Book Chapters 03 - Congress Proceedings: more than 30
Two PhD Thesis Awards :
2011- ABEQ
2012-CAPES – National Award for the Best Thesis in Engineering

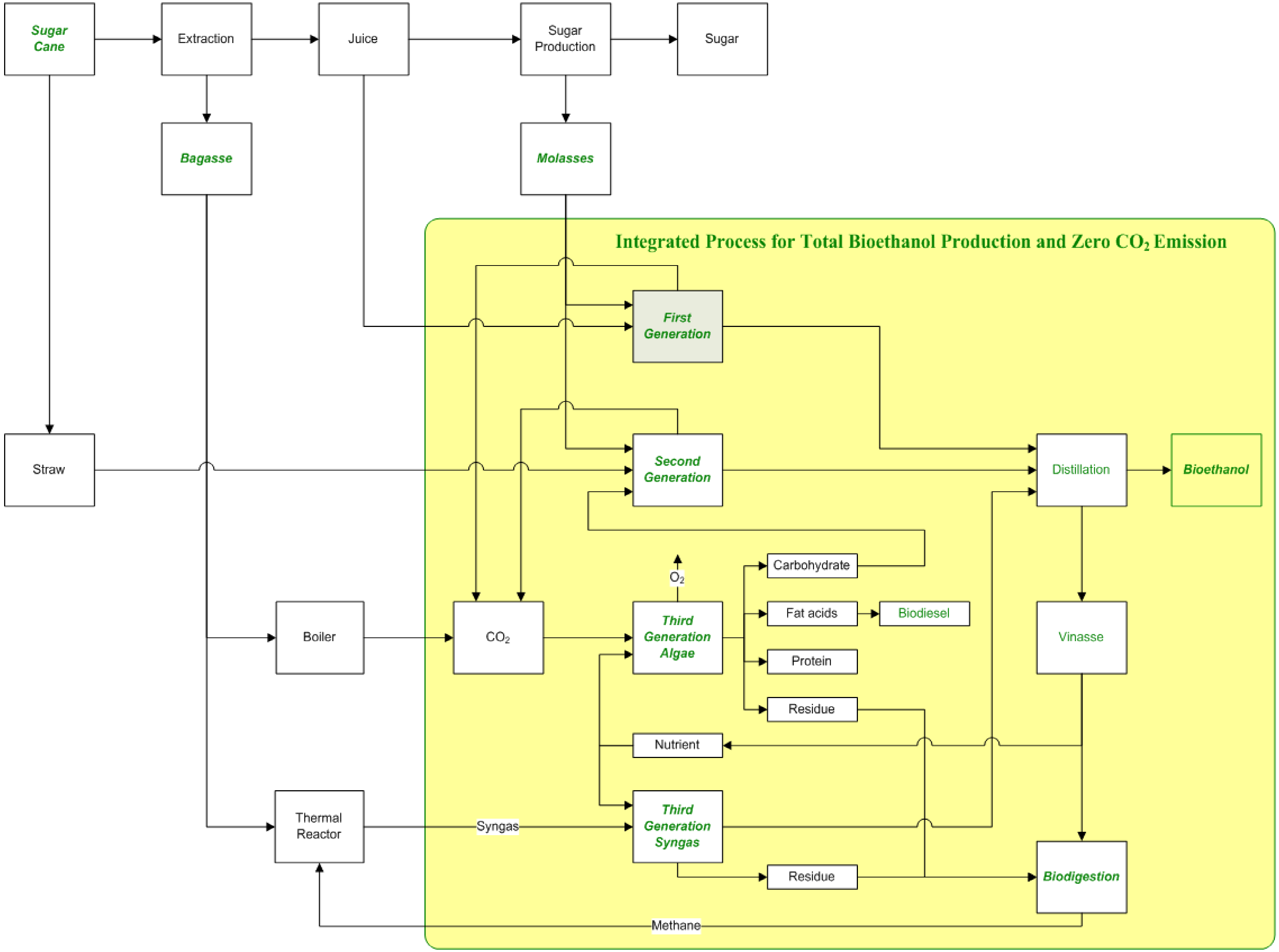
OBJECTIVE : a totally integrated bioethanol production process with Zero CO_2 Emission

.Improve the productivity of existing ethanol generation (sugar cane molasse fermentation), the so-called First Generation Bioethanol- increase bagasse surplus

.Develop suitable processes (all steps) for improving the Second Generation Bioethanol (from biomasses), integrated with the first generation, and production of high added value products;

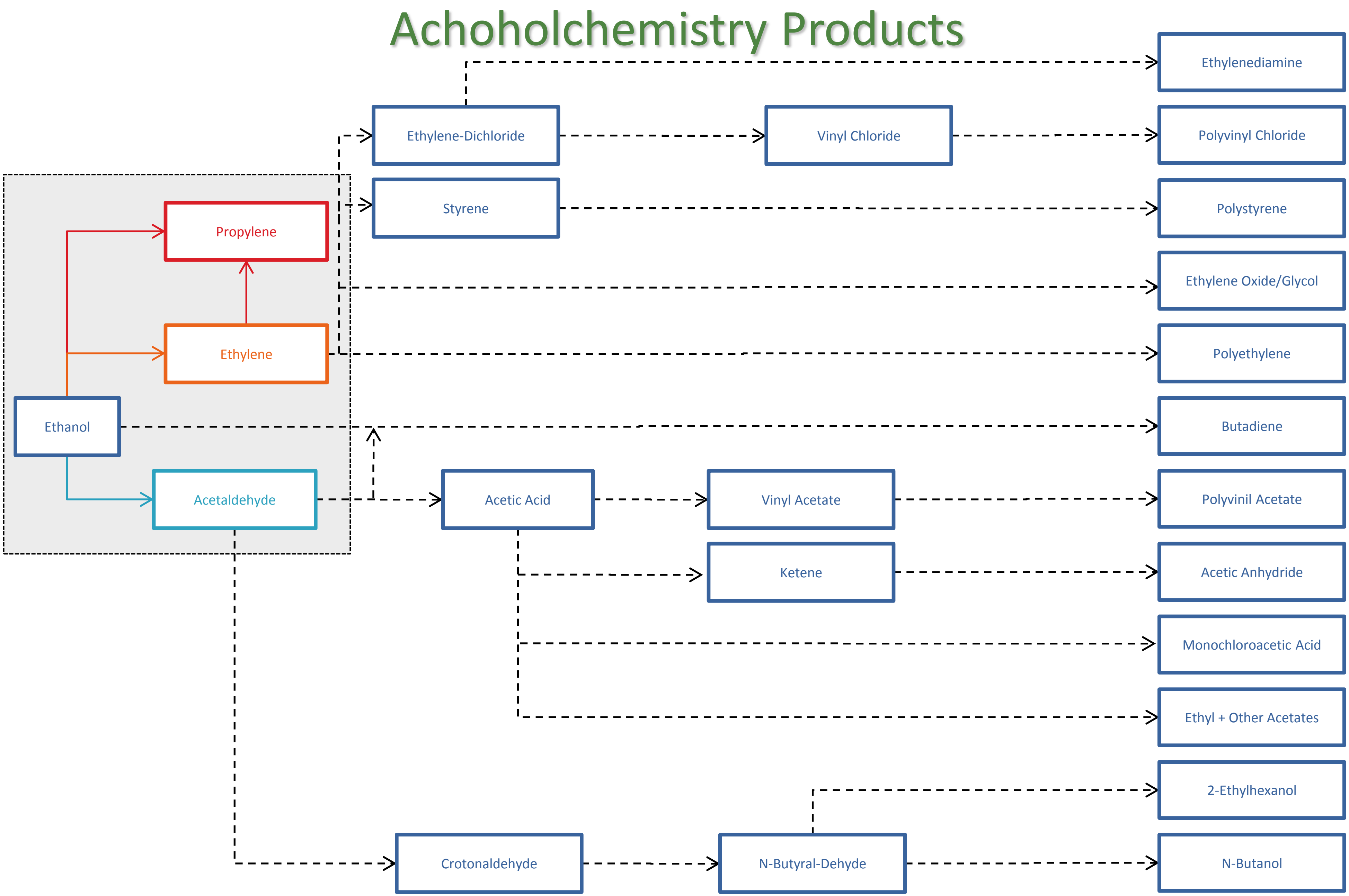
.Develop and investigate the viability of the Third Generation Bioethanol (micro algae and thermochemical route) in the context of the Potential Intrinsic Raw Material (PIRM) (concept developed in this Project)

Integrated Process



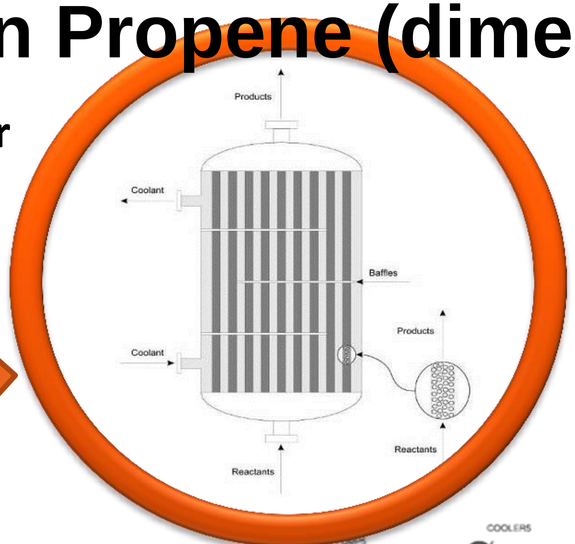
Source: Thematic Project Fapesp 2008/57873-8– Coordinator Maciel Filho

Use of ethanol as feedstock – that means obtain chemicals from ethanol



Green Ethene Process (Ethanol Dehydration) and Green Propene (dimerization and metathesis)

Multitubular Reactor



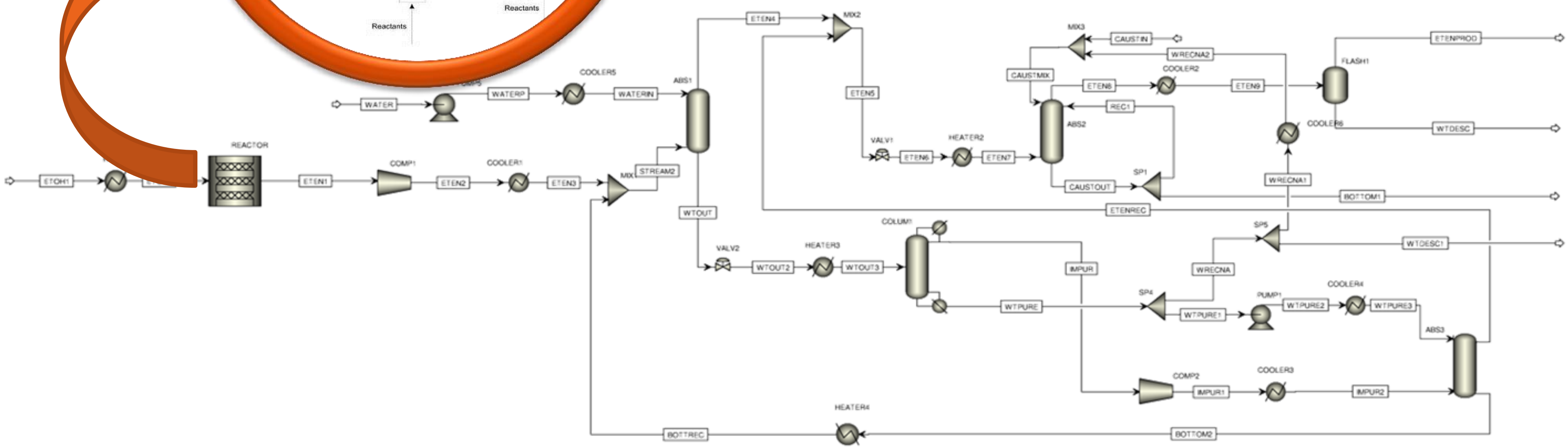
Reaction Mechanism

$C_2H_5OH \rightarrow C_2H_4 + H_2O$

$2C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O$

$C_2H_5OC_2H_5 \rightarrow C_2H_5OH + C_2H_4$

$C_2H_5OC_2H_5 \rightarrow 2C_2H_4 + H_2O$



Ethene Production by Ethanol Dehydration

Bioethanol chemistry

Patent applied

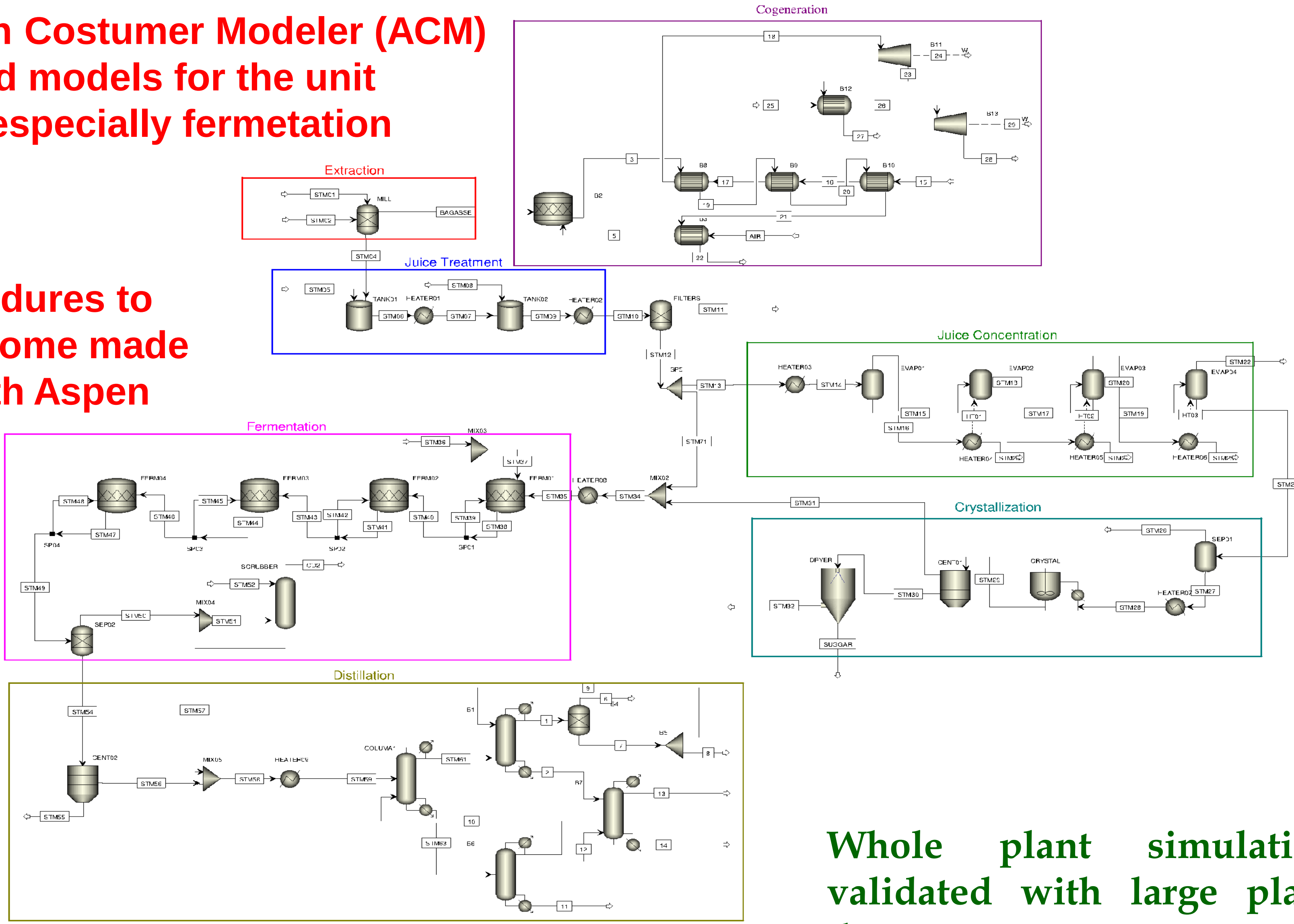
Improve the productivity of existing ethanol generation (sugar cane molasse fermentation), the so-called First Generation Bioethanol;

First ½ Generation – ethanol, sugar, electricity, Byproducts (higher alcohols) – increase bagasse suplus

FIRST 1/2 GLOBAL PROCESS SIMULATION

Use of Aspen Costumer Modeler (ACM)
More detailed models for the unit operations, especially fermetation

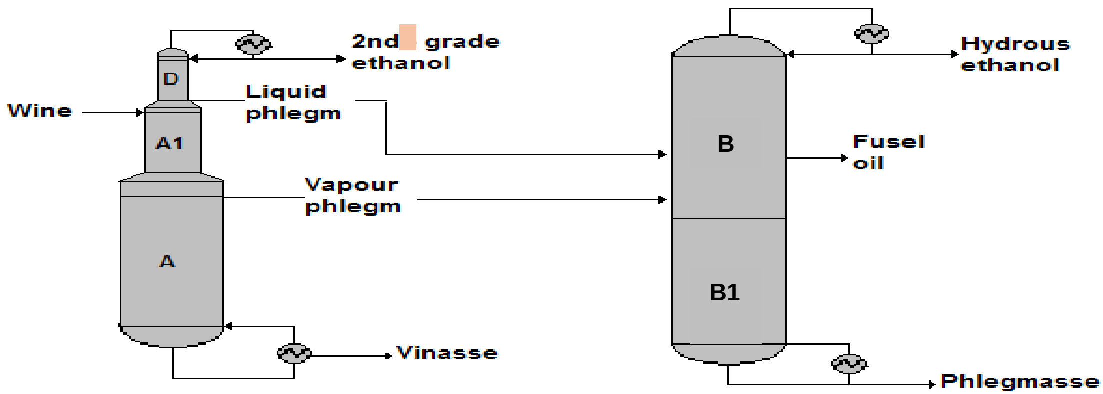
CAPE procedures to Integrated home made software with Aspen

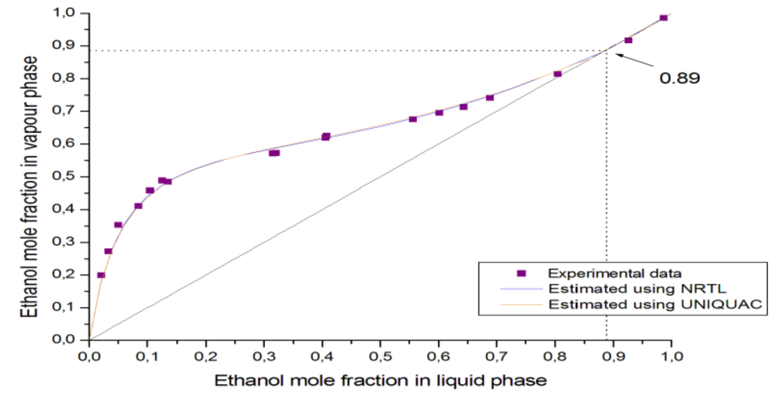


Whole plant simulation validated with large plant data– 35,000 ton sugar cane /day

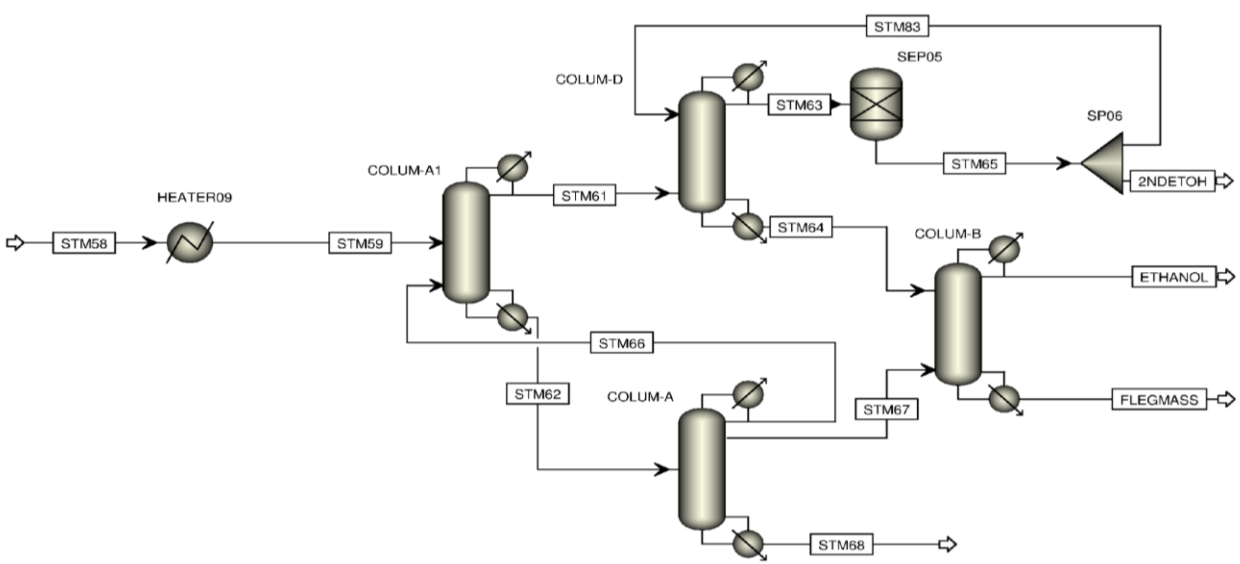
Computers and Chemical Engineering, to appear, 2012

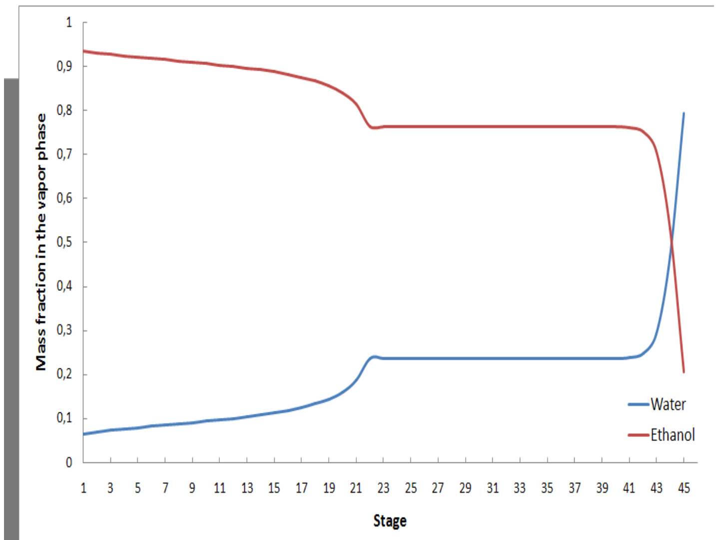
PROCESS SIMULATION EVALUATION OF ALTERNATIVES FOR ETHANOL PURIFICATION – ALTERNATIVE DISTILLATION AND ADSORPTION





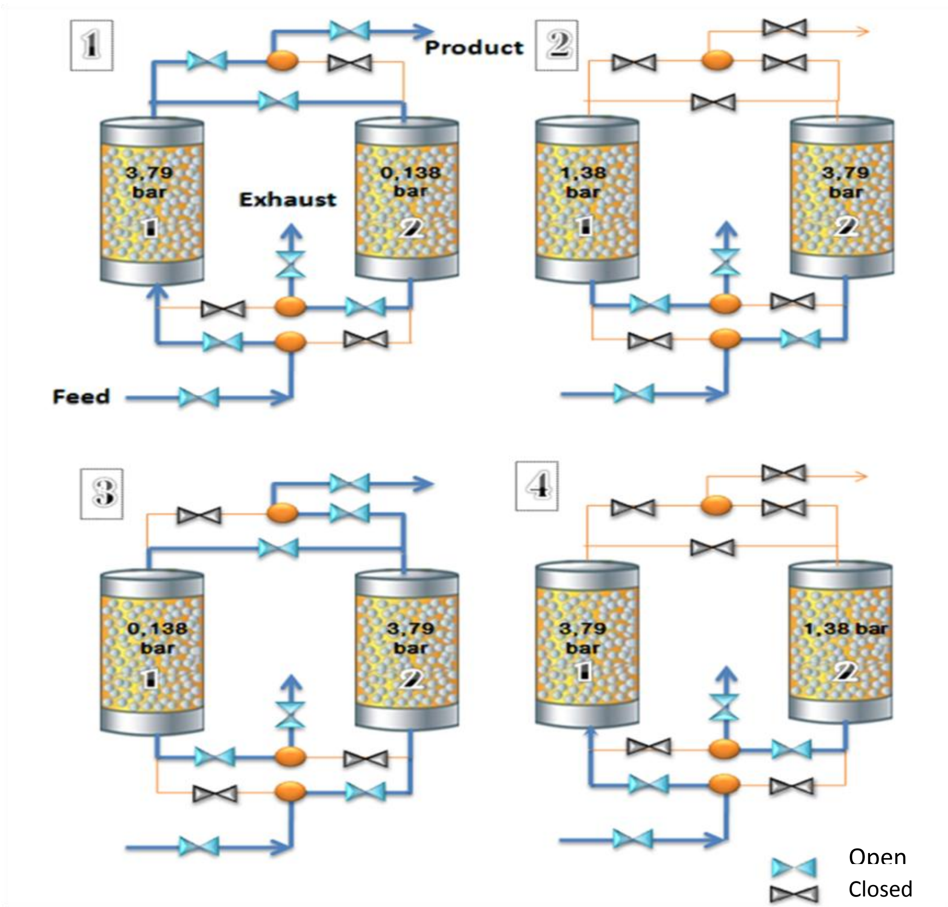
Distillation





Optimal number of stage as a basis

Pressure Swing Adsorption X Distillation



(Hydrous and Anhydrous Ethanol)

Technology	Dehydrating Agent	Steam consumption (kg steam/L ethanol)
Azeotropic	Cyclohexane	1.7
Extractive	Monoethylenegly col	0.7
Molecular sieves	Zeolite beads	0.2 - 0.4

Adsorption/desorption cycle – should be constantly adjusted-average of 11 to 15 minutes in industrial plants .

IMPROVEMENTS ON ANHYDROUS ETHANOL PRODUCTION BY EXTRACTIVE DISTILLATION USING IONIC LIQUID AS SOLVENT

The extractive distillation process used for modeling and simulation process is presented in Figure 1.

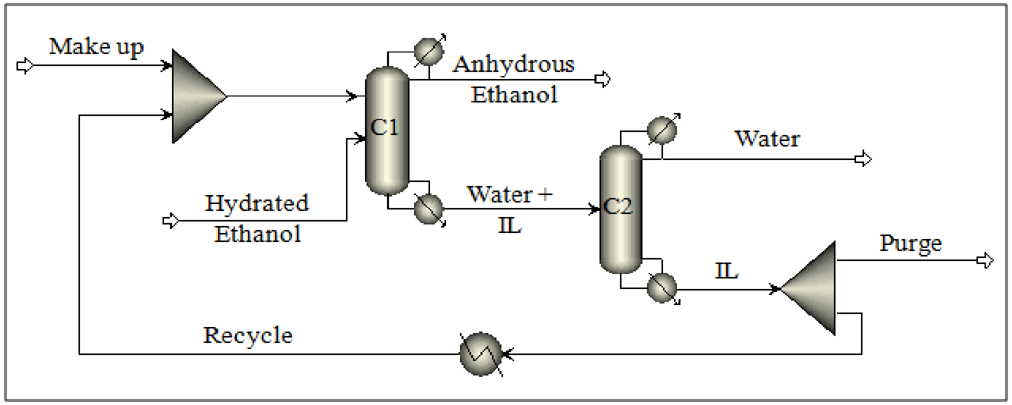


Figure 1. Process flowsheet. Source: Aspen Plus ® V7.1

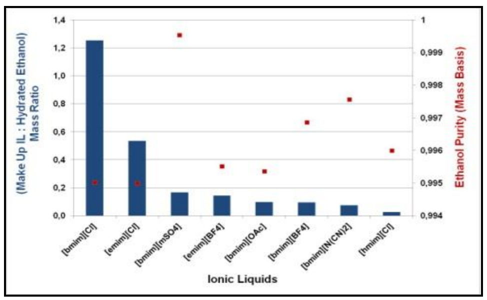


Figure 2. Ethanol Purity obtained using different IL

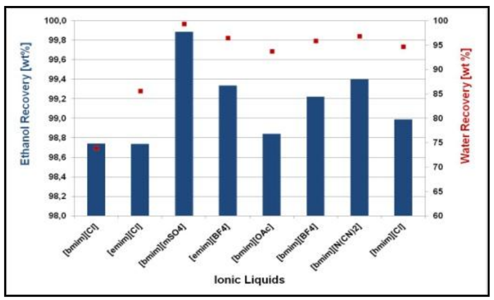


Figure 3. Recovery percentages of ethanol
and water using different IL's.

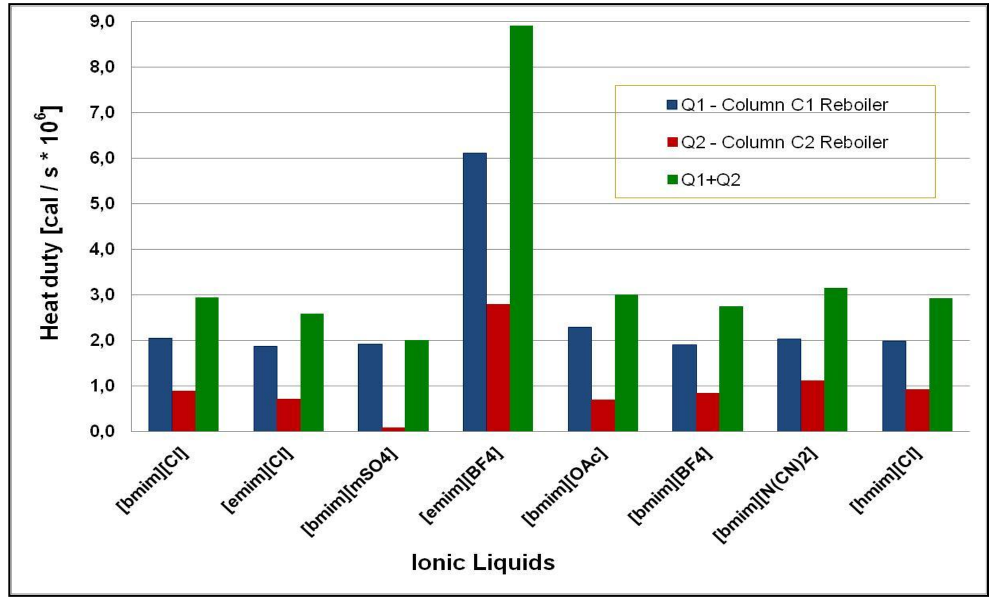


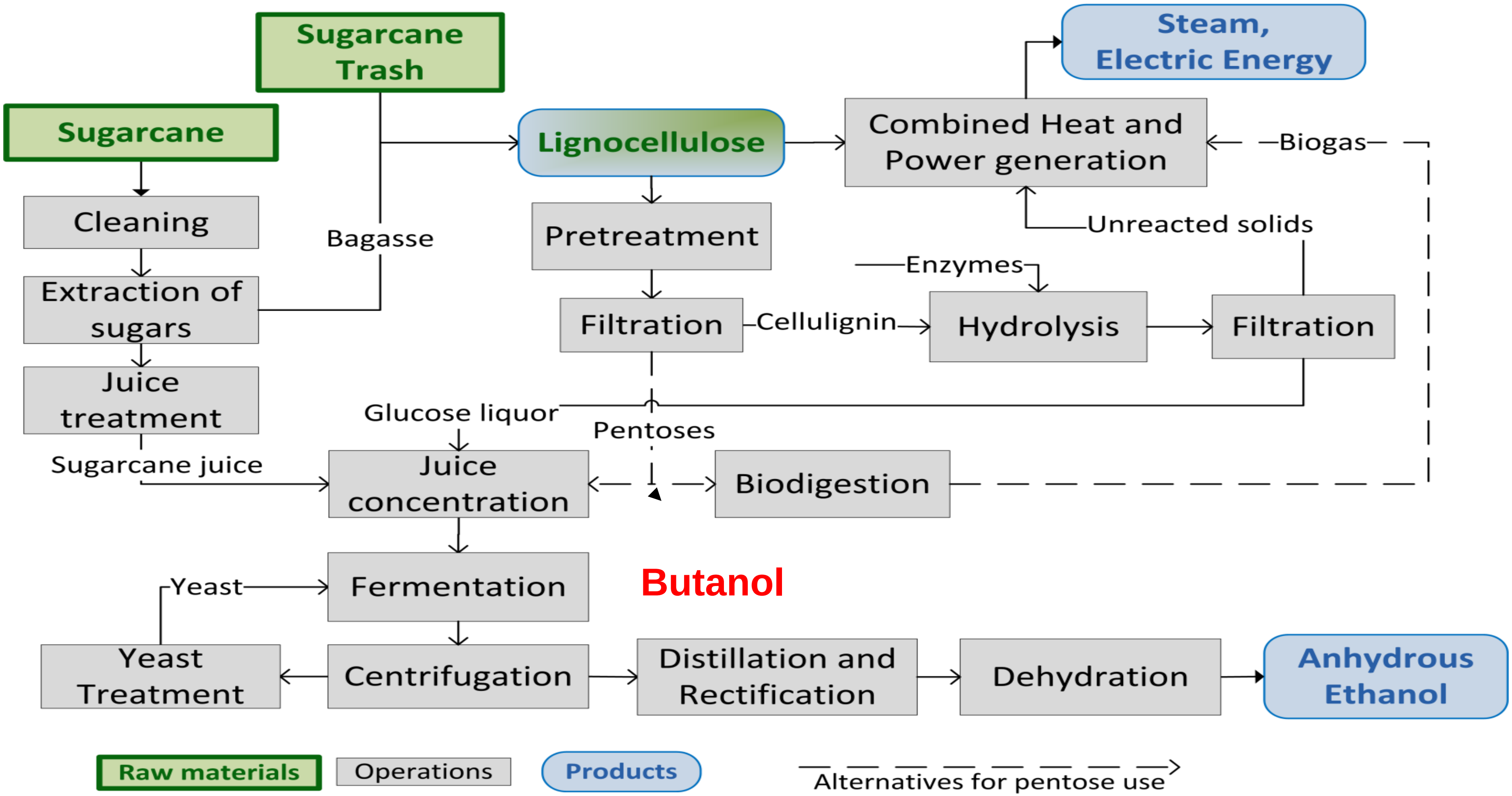
Figure 4. Heat duty of process using different IL's

Ionic liquids were efficient separation agents to obtain anhydrous ethanol (0.995 to 0.999 by weight of purity), besides being a process, in general, with high recovery percentages and thermal efficiency.

ELSEVIER
Procedia Engineering
Volume 42, 2012, Pages 1114–1124
CHISA 2012

Second generation – 2G

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



;

Develop suitable processes (all steps) for improving the Second Generation Bioethanol (from biomasses), integrated with the first generation, and production of high added value products;

- **Biomass – sugar cane bagasse and straw**

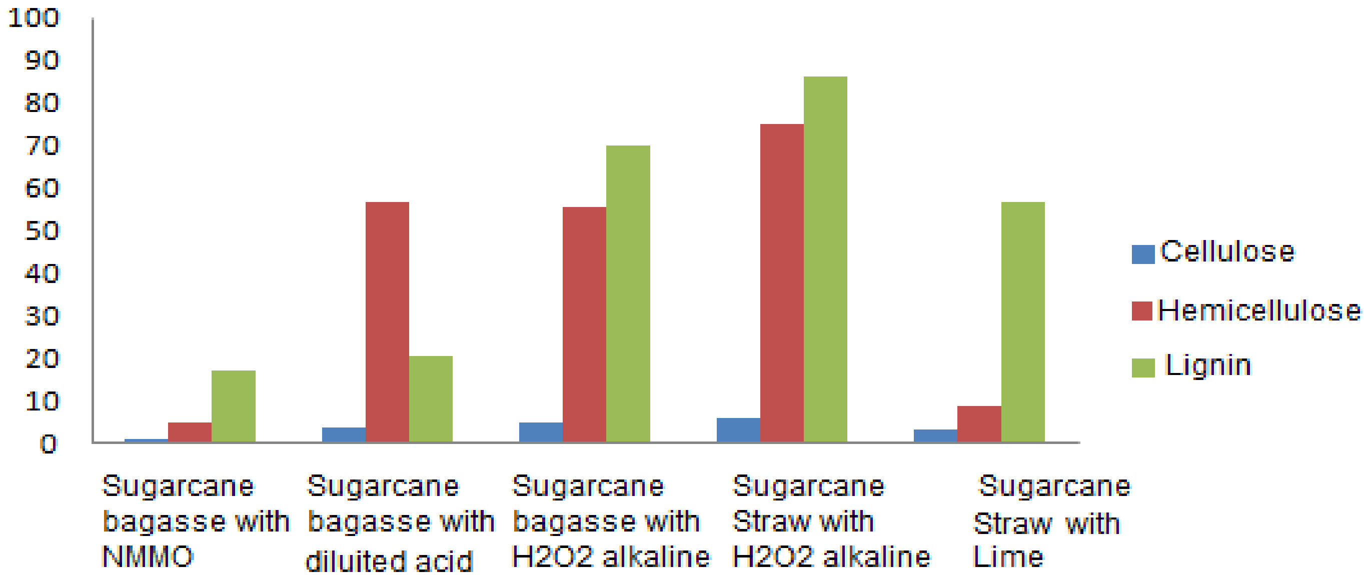
PRETREATMENTS AND ENZYMATIC HYDROLYSIS OF SUGARCANE BAGASSE AND STRAW

Chemical composition of the pretreated material after pretreatment at the optimal conditions

Composition of Biomass	Bagasse pretreated with NMMO *	Bagasse pretreated with H_2SO_4 **	Bagasse pretreated with om H_2O_2 ***	Straw pretreated with H_2O_2 ****	Straw pretreated with lime****
Cellulose	37.89a±0.32	38.73±1.14	38.10±0.08	33.28±0.15	33.43
hemicellulose	19.11a±0.48	11.29±0.04	11.47±0.02	3.99±0,10	21.64
Lignin	17.64a±0.15	17.45±0.73	6.64±0.03	6.78 ± 0.16	14.63

*Martins (2010)
**Martins (2011)
***Martins (2012)
****Ayala (2012)

Solubilized components



Biomass components solubilization in each pretreatment

R. R. Andrade;Matins L; R. Maciel Filho; A. C. Costa- to appear-J. of Chem.Techn. Biot., 2012

KINETIC MODELING OF ALCOHOLIC FERMENTATION INTEGRATING 1st AND 2nd GENERATION PROCESS

Pretreatment - 4% WIS, H_2O_2 7.36 % (*v/v*) , pH 11.5 (NaOH), 150 rpm, T= 25 °C, 1 hour).

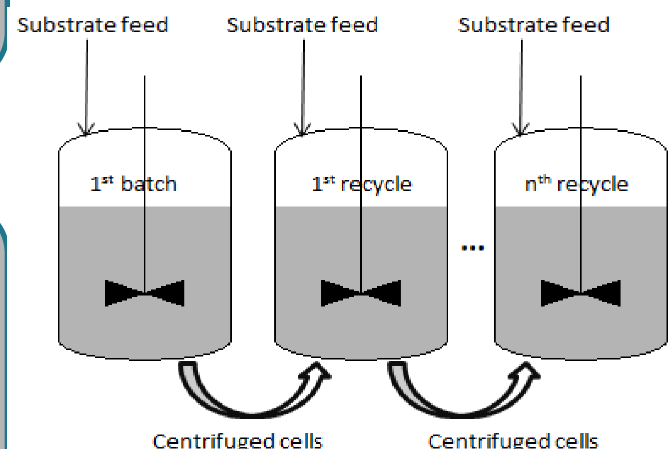
Hydrolysis - 3% WIS., (cellulase – 3.5 FPU/g WIS, β-glucosidase - 25 UI/ g WIS, pH 4.8, at 50°C

Fermentation (hydrolysates 66 % vol., molasses 22 % and 11 % inocullum)
T 30-38°C, *S. cerevisiae*, **Bioflo 415**, with cell recycle

$$\frac{dX}{dt} = \mu_{max}\frac{S}{K_S + S}\exp(-K_i S)\left(1 - \frac{X}{X_{max}}\right)^m \left(1 - \frac{P}{P_{max}}\right)^n X \left(1 - \frac{C_{Ac}}{C_{Acmax}}\right)^{nn}$$

Proposed term of acetic acid inhibition

$$\frac{dS}{dt} = -(r_X/Y_X) - m_X X \qquad \frac{dP}{dt} = Y_{pX} r_X + m_p X$$

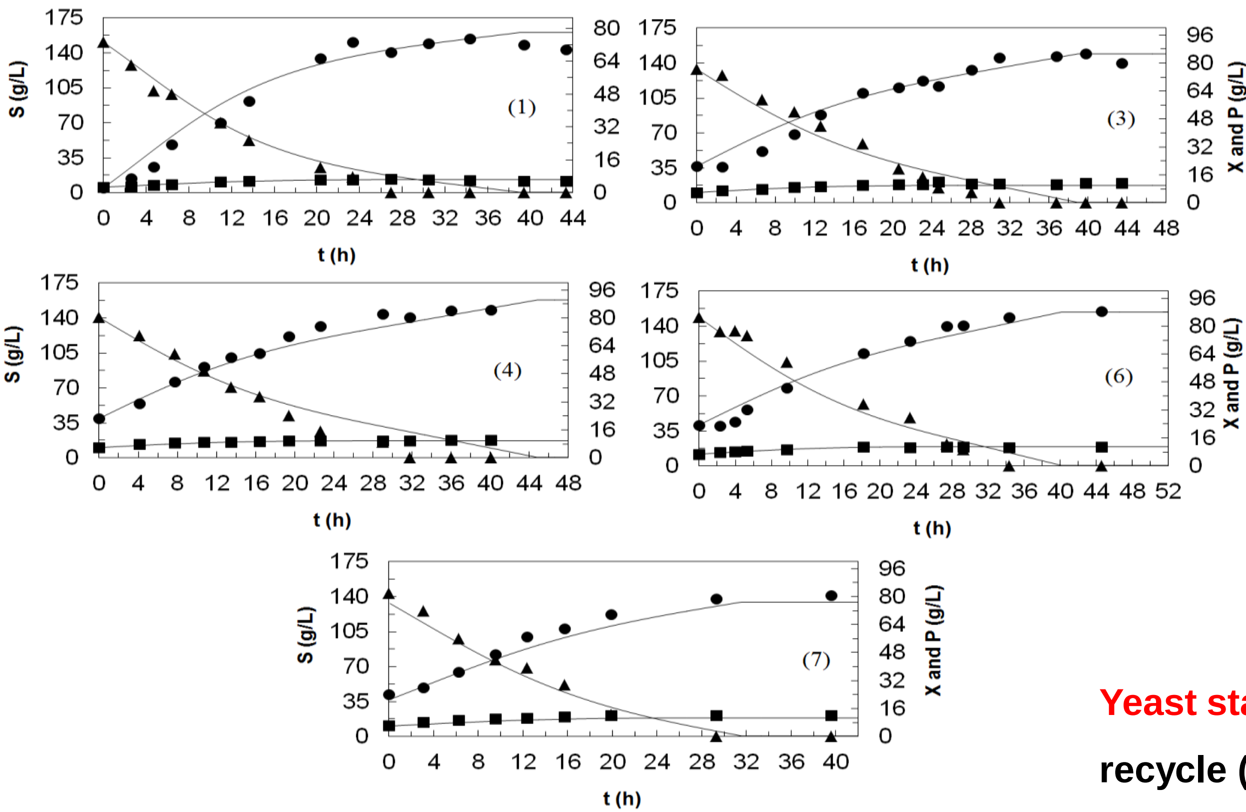


Cell recycle performed

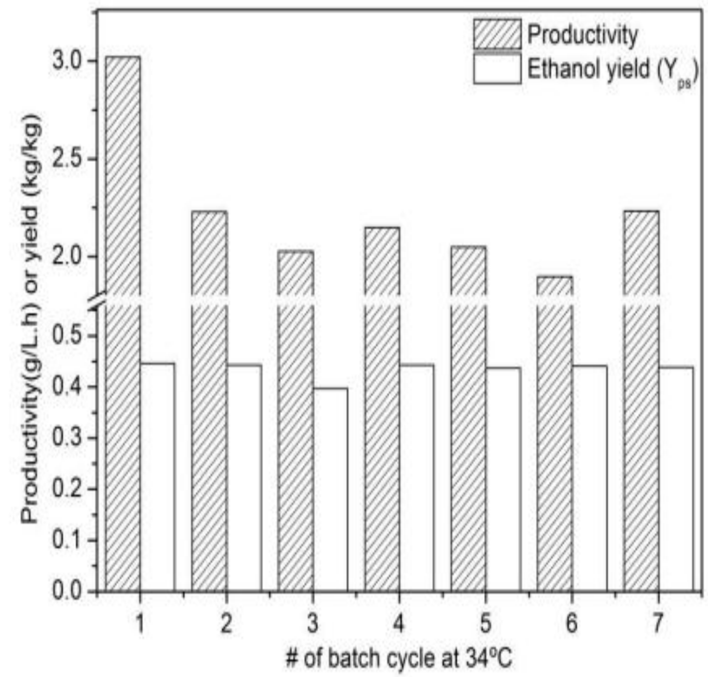
R. R. Andrade; F.Maugeri Filho; R. Maciel Filho; A. C. Costa Bioresource Technology, 2012.

KINETIC MODELING OF ALCOHOLIC FERMENTATION INTEGRATING 1ST AND 2ND GENERATION PROCESS

- Parameter fitting for recycles at 34°C



Productivity and ethanol yield for recycles



Yeast stability (containing acetic acid), even with cell recycle (yp/s remained next to 86 % of the theoretical maximum for all runs);

Presence of inhibitors at low concentration (due to H_2O_2 pretreatment);

Term of acetic acid inhibition increased model's accuracy;

R. R. Andrade; F.Maugeri Filho; R. Maciel Filho; A. C. Costa Bioresource Technology, 2012.

EVALUATION OF THE ALCOHOLIC FERMENTATION KINETICS OF ENZYMATIC HYDROLYSATES FROM SUGARCANE BAGASSE AND STRAW (*Saccharum officinarum L.*)

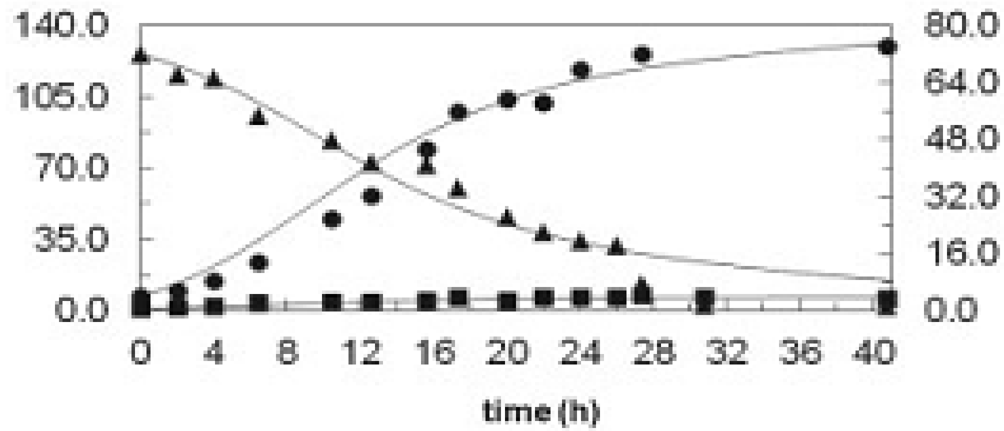
Main findings for hydrolysates kinetics:

- μ_{max} decreased due to acetic acid presence;

- P_{max} increased from 82.92 to 129.88 Kg/m^3 (ethanol toxicity is increased) due to interactions between ethanol and acetic acid;

- Y_{px} increased in acetic acid presence (cells require additional ATP to pump out the excess protons when intracellular pH is low. The extra ATP formation is related to produced ethanol).

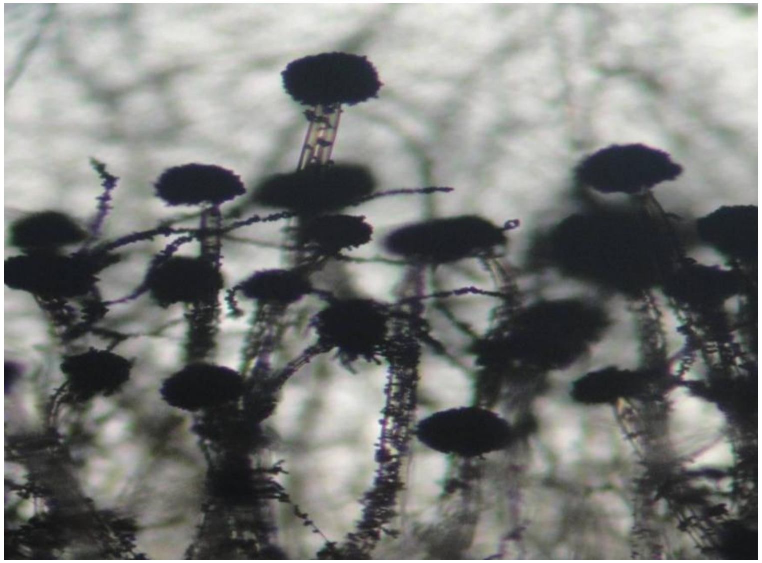
	*Temperature (°C)			**Temperature (°C)		
Parameters	30.0	32.0	34.0	30.0	32.0	34.0
μ_{max} (h^{-1})	0.190	0.414	0.370	0.237	0.342	0.437
X_{max} ($kg\ m^{-3}$)	79.94	55.99	43.00	79.95	48.67	42.92
P_{max} ($kg\ m^{-3}$)	82.92	76.00	75.00	129.88	75.18	74.78
Y_{px} ($kg\ kg^{-1}$)	8.58	15.02	16.63	3.96	9.37	9.89
Y_x ($kg\ kg^{-1}$)	0.0436	0.0427	0.0409	0.0427	0.0401	0.0377
C_{Acmax} ($kg\ m^{-3}$)	4.22	4.12	3.13	-	-	-
nn	0.100	0.118	0.210	-	-	-
Y_{ps} ($kg\ kg^{-1}$)	0.46	0.51	0.51			



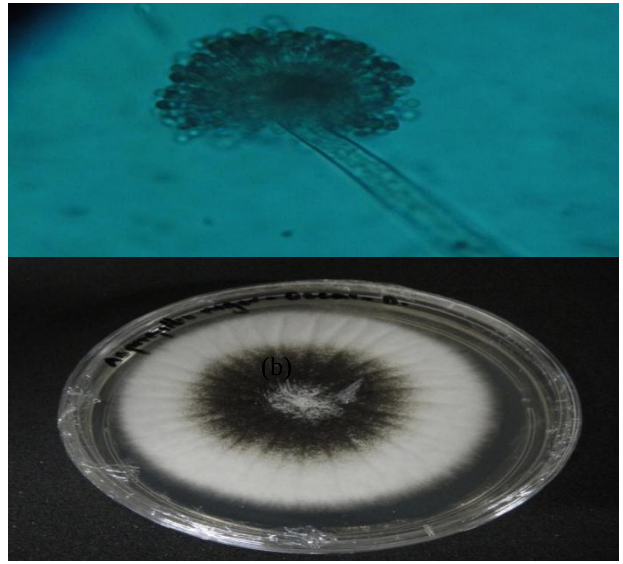
R. R. Andrade; S.C. Rabelo; F. Maugeri Filho; R. Maciel Filho; A. C. Costa, Journal of Chemical Technology and Biotechnology, 2012

Batch Reactor- Semi-solid fermentation for Enzyme in site production

Raw material: fresh sugarcane bagasse, soybean extract and yeast extract



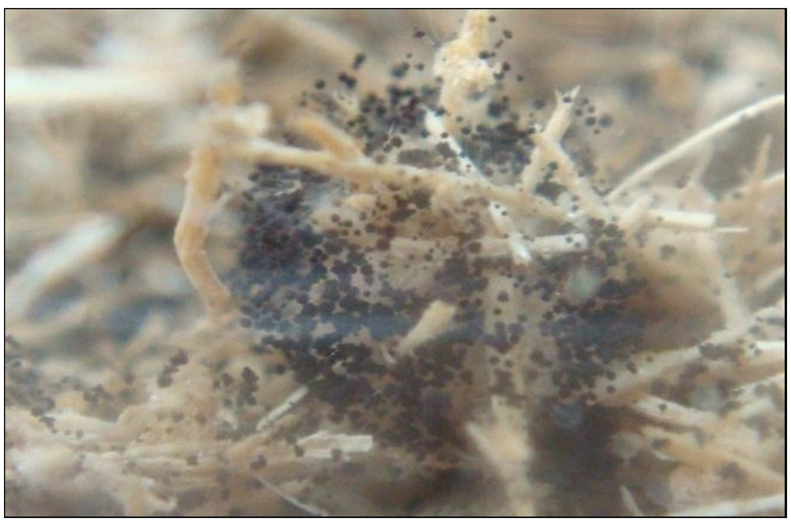
In vitro



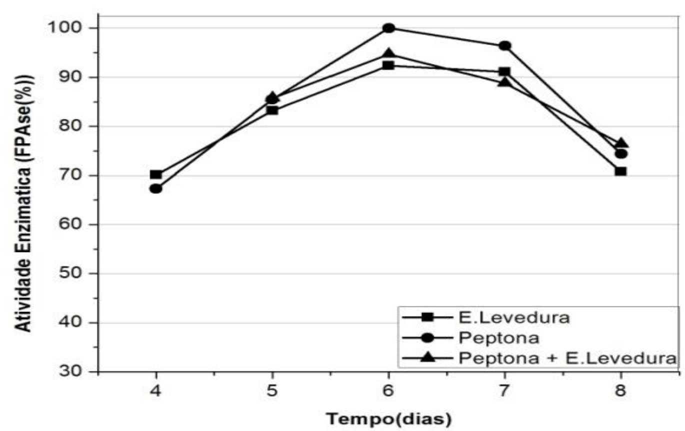
Microculture

Native Aspergillus niger.

Effect of non- purified enzyme



Aspergillus niger growing up in bagasse.



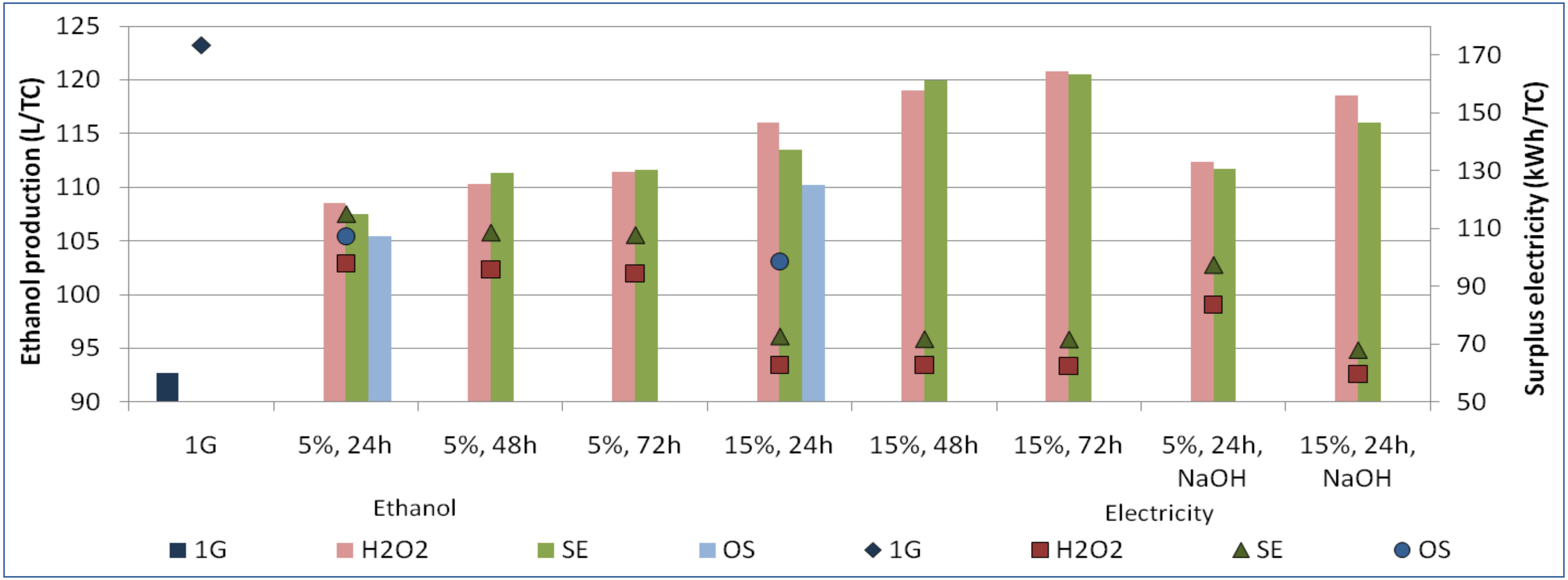
Activity of cellulase against time

Patent to be applied

Comparison between different biomass pretreatment methods

Parameters and yields of the pretreatment and hydrolysis processes (hydrolysis with 5% and 15% of solids)

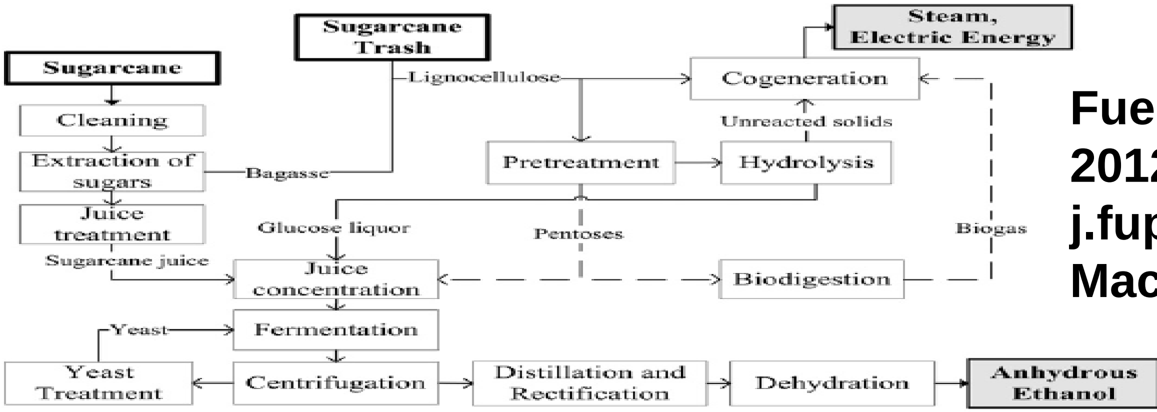
Ethanol and electricity production for each configuration



SE: Steam explosion; H2O2: hydrogen peroxide; OS: Organosolv; NaOH: alkaline delignification

M.O.S. Dias et al., 2011. J. Ind. Microbiol. Biotechnol., 38:955-966

Evaluation of process configurations for second generation integrated with first generation bioethanol production from sugarcane



Fuel Processing Technology 2012- http/doi.dx.org/10.1016/ j.fuproc/2012.09.041
Maciel Filho. R. et.al.

. Block flow diagram of the integrated first and second generation ethanol production process from sugarcane — dashed lines represent alternatives for pentose use.

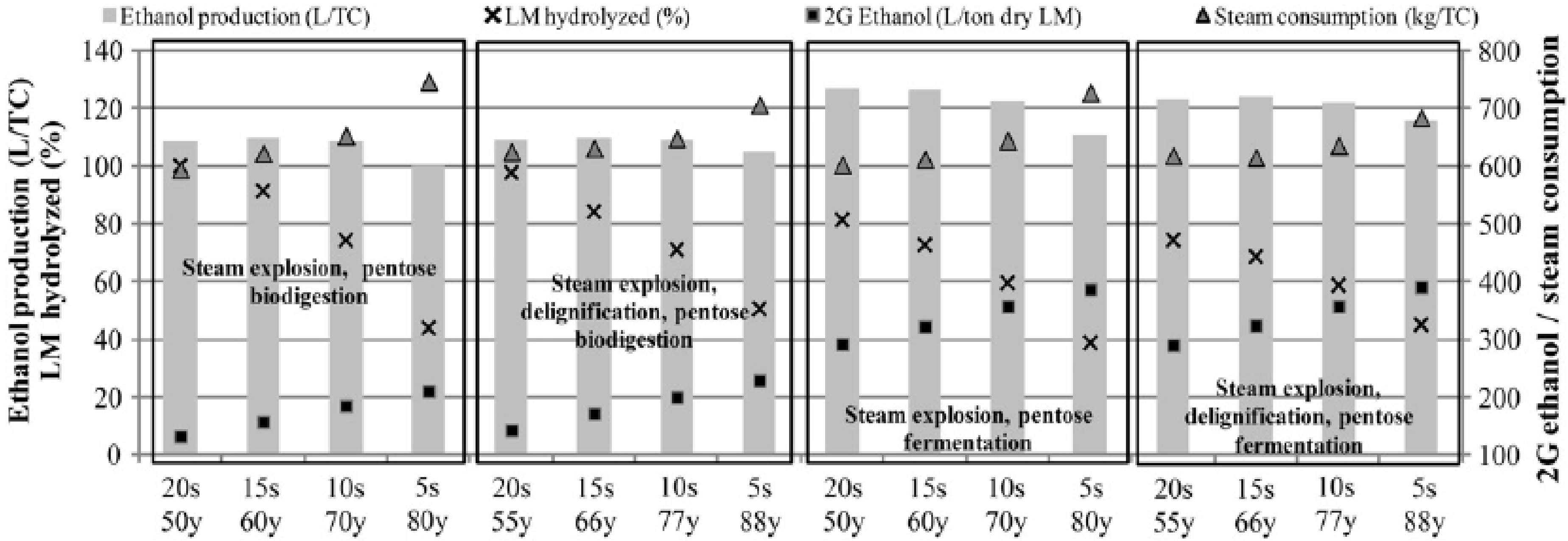


Fig. 5. Fraction of lignocellulosic material (LM) hydrolyzed, overall ethanol production (L/TC), second generation (2G) ethanol production per ton of dry lignocellulosic material (L/t dry LM) and steam consumption per ton of sugarcane (TC) on each process configuration (s stands for solids loading on hydrolysis (%) and y for yields on enzymatic hydrolysis (%)).

Evaluation of different cogeneration systems in first and second generation ethanol production from sugarcane

Environmental Impact scores for ethanol production

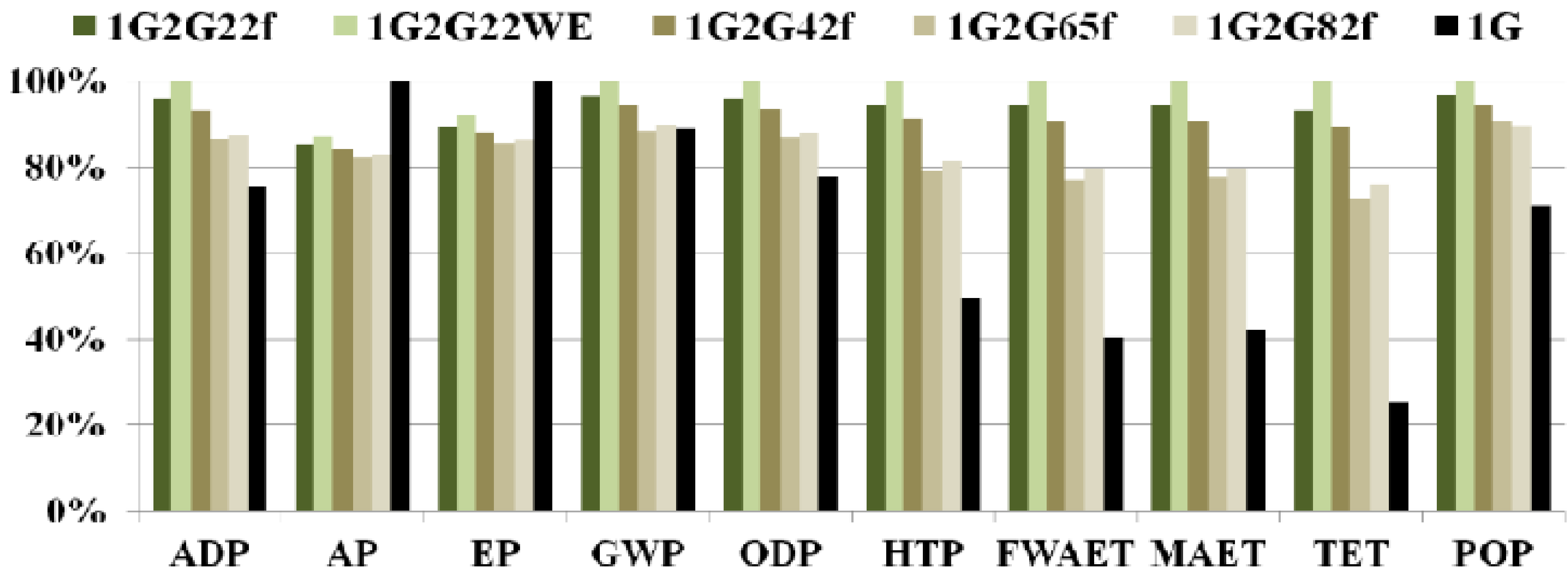
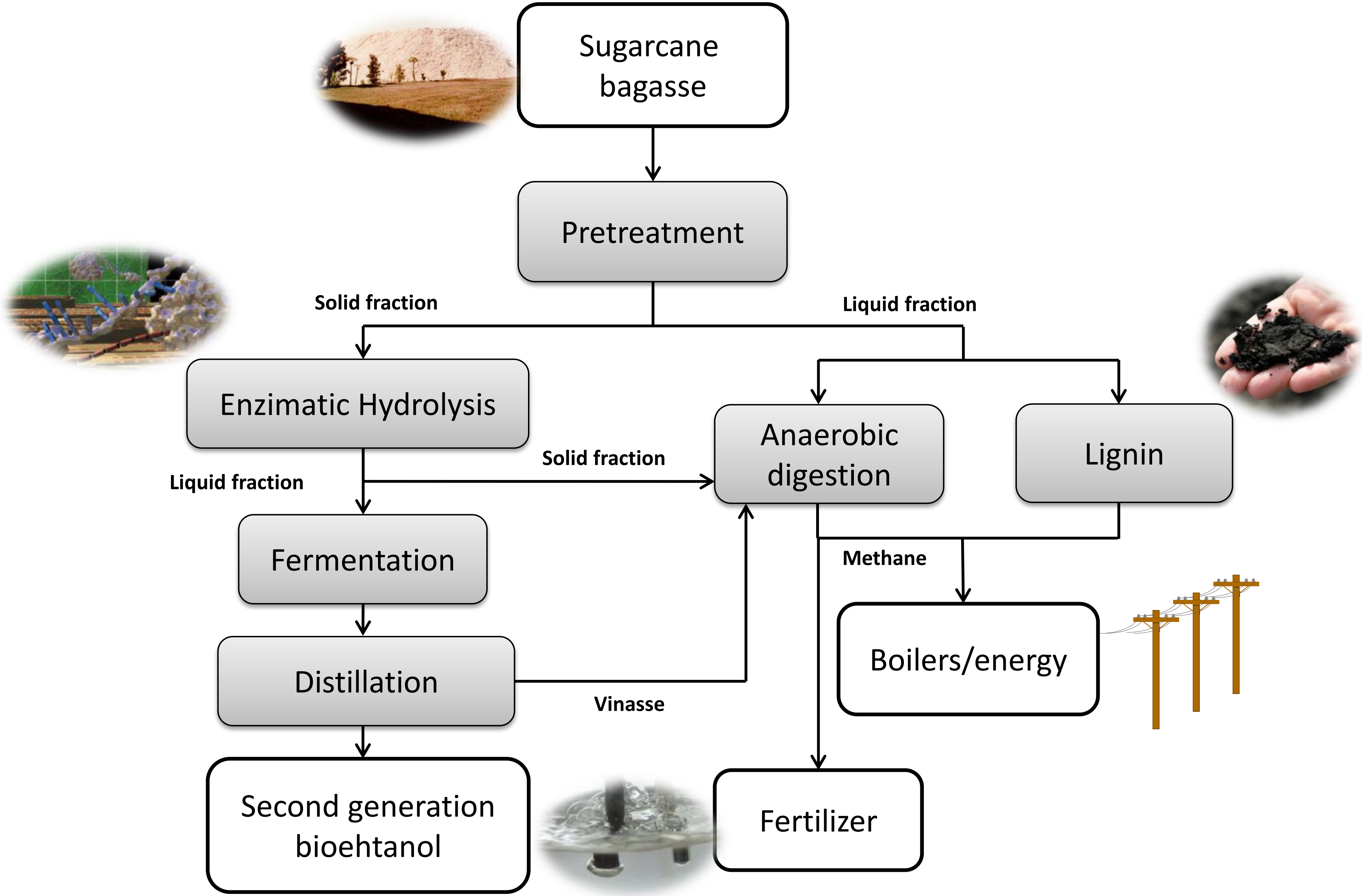


Figure 2. Comparative environmental impact scores for ethanol production different biorefinery scenarios (ADP: Abiotic depletion; AP: Acidification; EP: Eutrophication; GWP:Global warming; ODP: Ozone layer depletion; HTP: Human toxicity; FWAET:Fresh water aquatic ecotoxicity; MAET: Marine aquatic ecotoxicity; TET: Terrestrial ecotoxicity; POP: Photochemical oxidation)

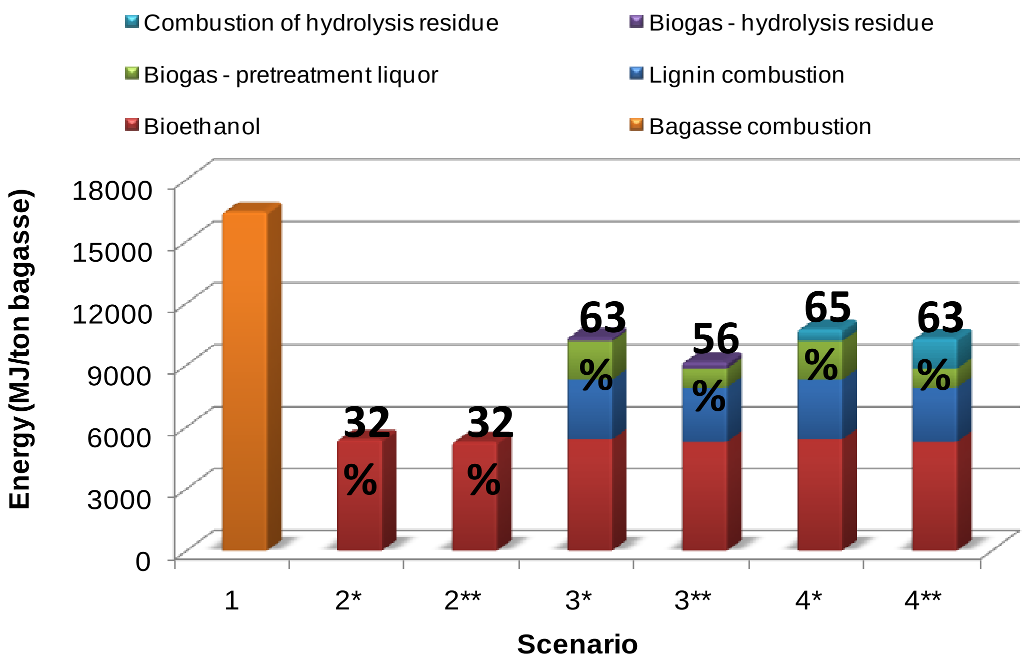
Book Chapter Ian David Lockhart Bogle and Michael Fairweather (Editors), **Maciel Filho R. et. al.**

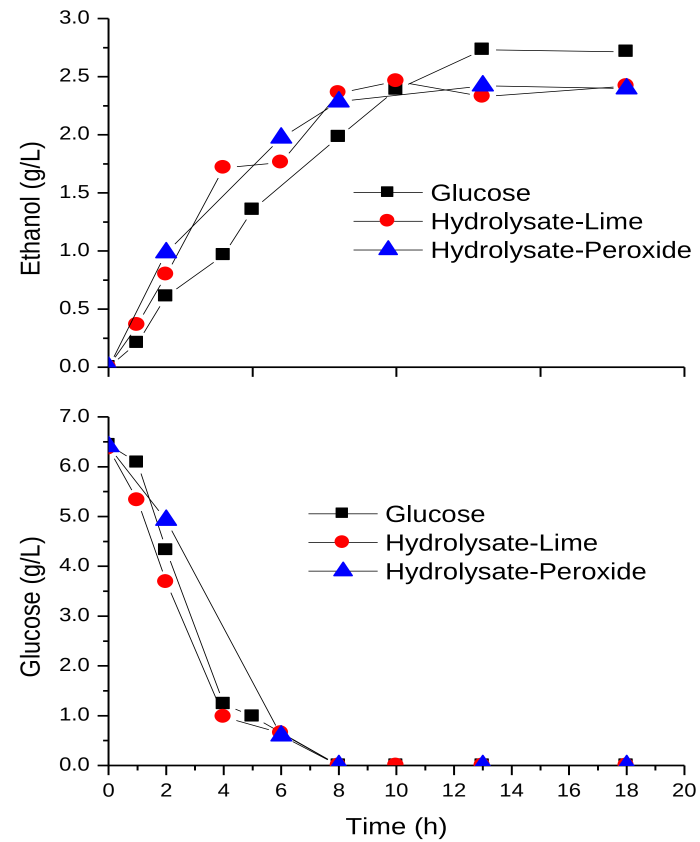
European Symposium on Computer Aided Process Engineering-Elsevier-London, 2012

Integrated Process: Anaerobic Digestion of Hydrolysis Residues and Vinasse



The full use of sugar cane: ethanol, electricity, biogas





Energy output from each scenario studied in the biorefinery concept using bagasse pretreated with hydrogen peroxide (*) or lime (**).

(1) Untreated bagasse - combustion,

(2) Pretreated bagasse – bioethanol,

(3) Pretreated bagasse – bioethanol, lignin combustion, biogas from pretreatment liquor and hydrolysis residue,

(4) Pretreated bagasse - bioethanol, lignin and hydrolysis residue combustion, biogas from liquor pretreatment.

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

Production of Butanol in a First Generation Brazilian Sugar-Ethanol Plant using the Flash Fermentation Technology

Per year (167 days):

2 MM ton sugar cane

102 mil ton sugar

104 MML ethanol

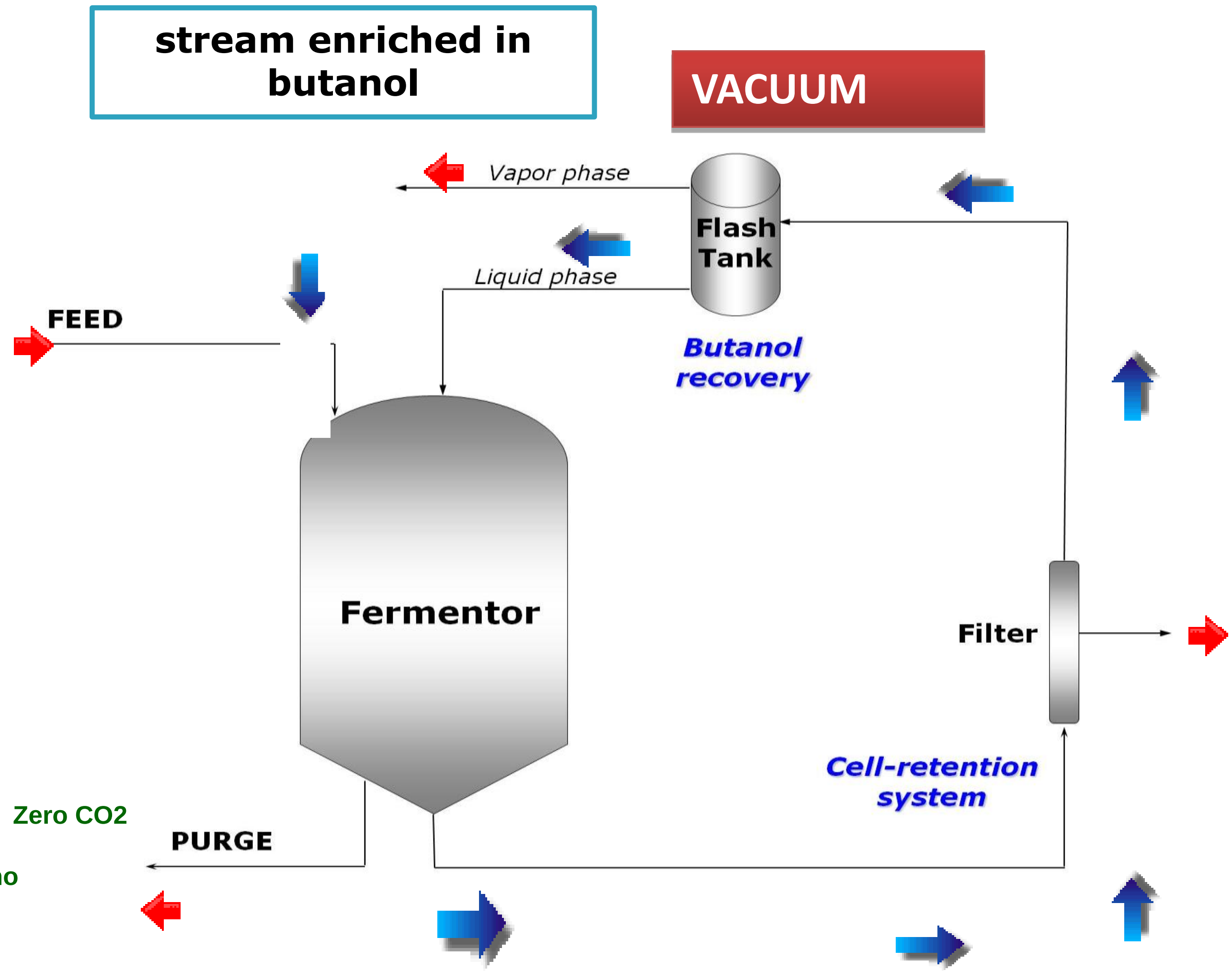
New Process for Butanol Production: Extractive Fermentation- Pinto Mariano et.al. Biotechnology and Bioengineering , 2011) –

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

Energy Consumption for Butanol Production for Different Scenarios

Batch – conventional strain

CRUSHING (25 %)	3.8 MJ/s
JUICE TREATMENT (1/3)	8.7 MJ/s
DISTILLATION	26.2 MJ/s
STERILIZATION	6.9 MJ/s
MJ / kg ButOH	**49.4**

Flash – conventional strain

CRUSHING (25 %)	3.8 MJ/s
JUICE TREATMENT (1/3)	8.7 MJ/s
DISTILLATION	10.7 MJ/s
STERILIZATION	1.9 MJ/s
COMPRESSORS	6.8 MJ/s
MJ / kg ButOH	**31.6**

Batch – mutant strain

CRUSHING (25 %)	3.8 MJ/s
JUICE TREATMENT (1/3)	8.7 MJ/s
DISTILLATION	22.8 MJ/s
STERILIZATIO N	10.1 MJ/s
MJ / kg ButOH	**31.0**

Flash – mutant strain

CRUSHING (25 %)	3.8 MJ/s
JUICE TREATMENT (1/3)	8.7 MJ/s
DISTILLATION	11.1 MJ/s
STERILIZATION	4.8 MJ/s
COMPRESSORS	7.4 MJ/s
MJ / kg ButOH	**23.0**

36.0%

Heat of combustion of ButOH = 36 MJ/Kg

Flash coupled fermentation → potential

A.P.Mariano;T.C Ezeji. R.Maciel Filho. Energy Requirements during Butanol Production and in situ recovery by cyclyc vacuum. Renewable Energy, 47, 183-187, 2012

Biobutanol Production in a First Generation Brazilian Sugar Cane Biorefinery: Technical Aspects and Ecnonomics of Greenfields Projetcs

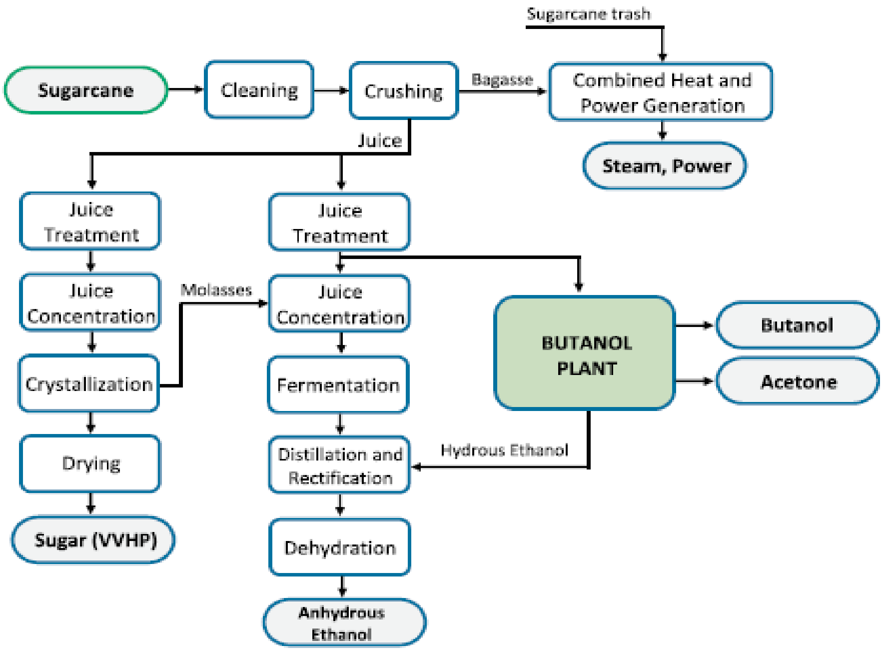
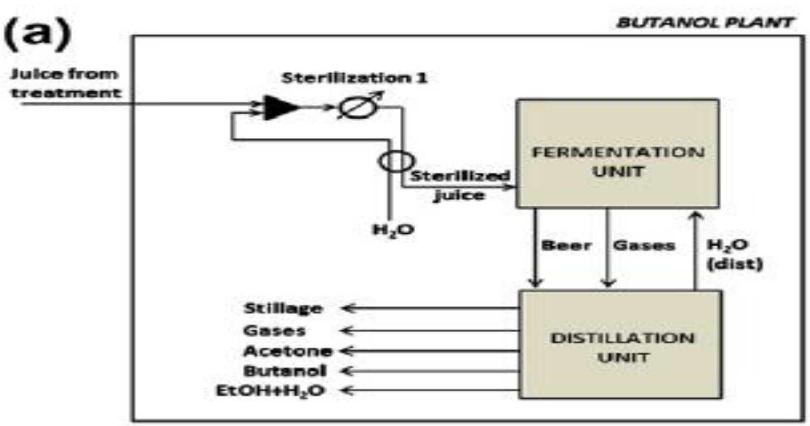


Fig. 1. Schematic diagram of a first-generation sugarcane biorefinery producing ethanol, sugar, power, butanol, and the by-product acetone.



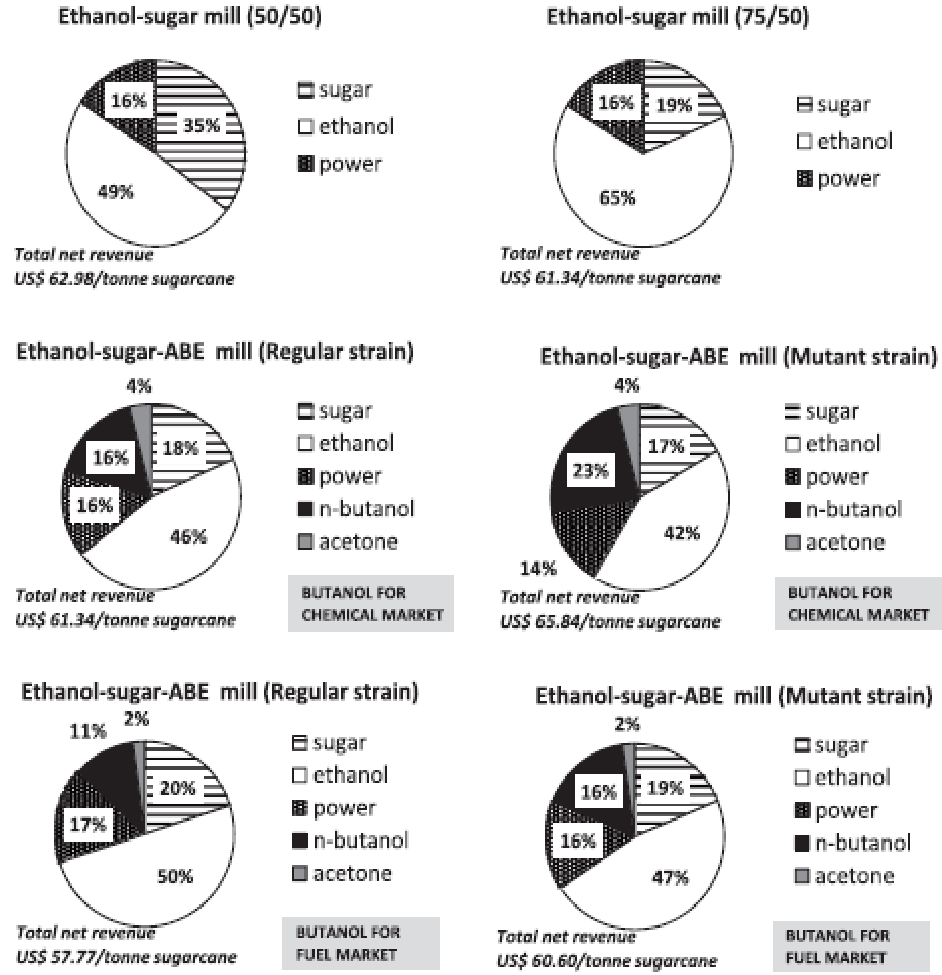


Fig. 3. Revenue breakdown for each biorefinery scenario.

Mariano A.P., Maciel Filho R.

Biobutanol Plant Hierarchy

Bioresour. Technol. (2012), http://dx.doi.org/10.1016/j.biortech.2012.09.109

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 reactor – FEQ-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

1-) Microalgae for Bioethanol and Biodiesel Production

Glycerol – pyrolysis to produce syngas

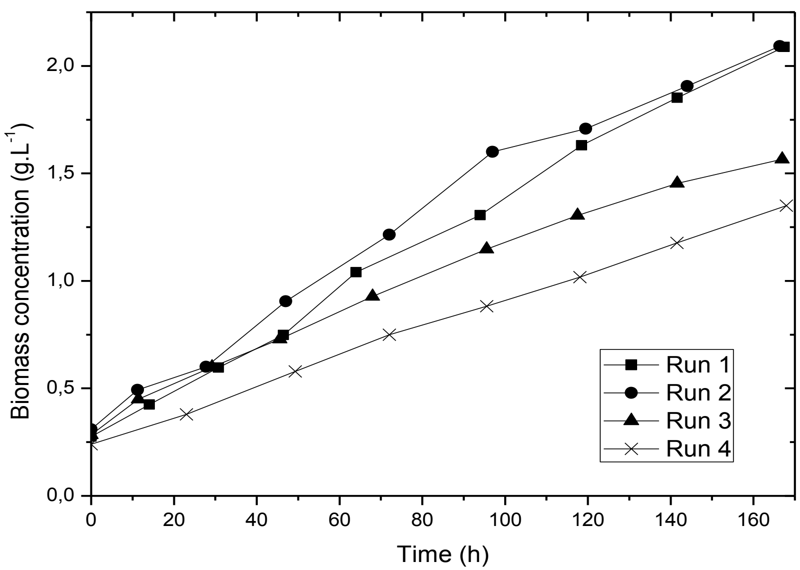
substrate for fermentation to produce propionic acid

Microalgae cultivation for 3rd generation bioethanol production
Use of CO_2 from Fermentation

- **Microalgal biomass:** interesting feedstock for biofuel production
- **Objective**: determination of optimal culture medium and conditions for the maximization of carbohydrate production

Flat-plate photobioreactor

Run	Light intensity ($\mu E.m^{-2}.s^{-1}$)	$NaNO_3$ ($mg.L^{-1}$)	Biomass ($g.L^{-1}$)	μ_{max} (day^{-1})
1	120	700	2,09	0,497
2	120	2300	2,09	0,442
3	60	2300	1,57	0,478
4	60	700	1,35	0,403

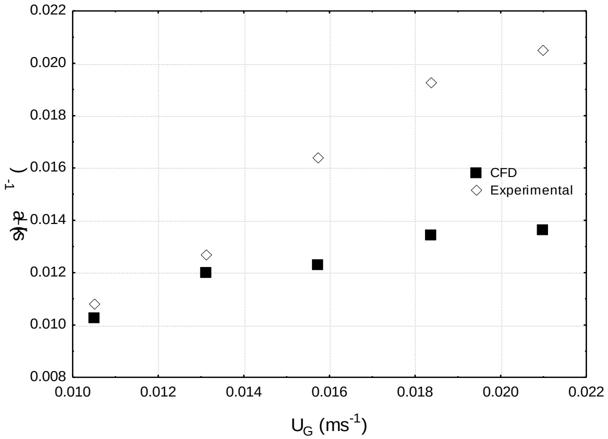


Results

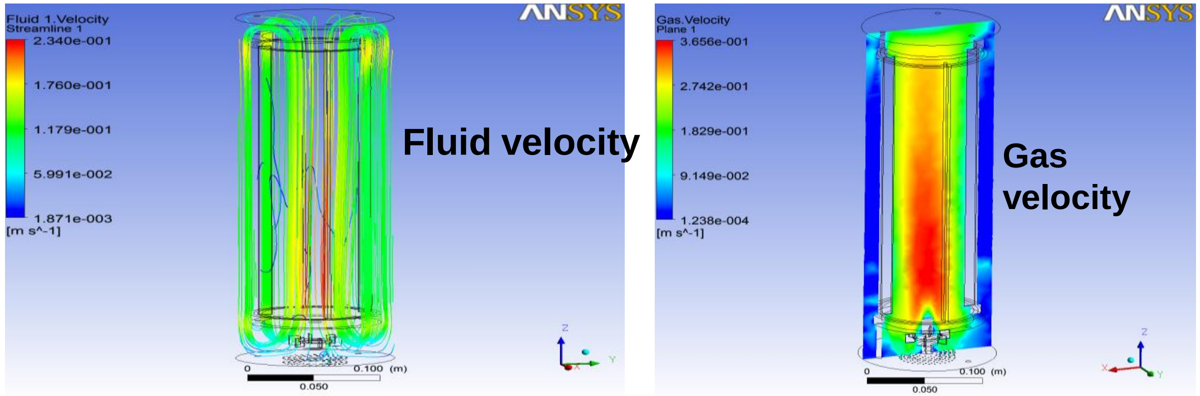
- Stationary growth phase was not observed after 168h of cultivation
- Runs with high light intensity produced higher final biomass concentrations; the initial $NaNO_3$ concentration didn't significantly affect biomass productivity
- Carbohydrate, lipid and protein content currently being determined (avg. lipid content ~30%)

Results presented in the 2nd Brazilian Simposium on the Energy Potential of Microalgae (Natal, BR, oct. 2012)

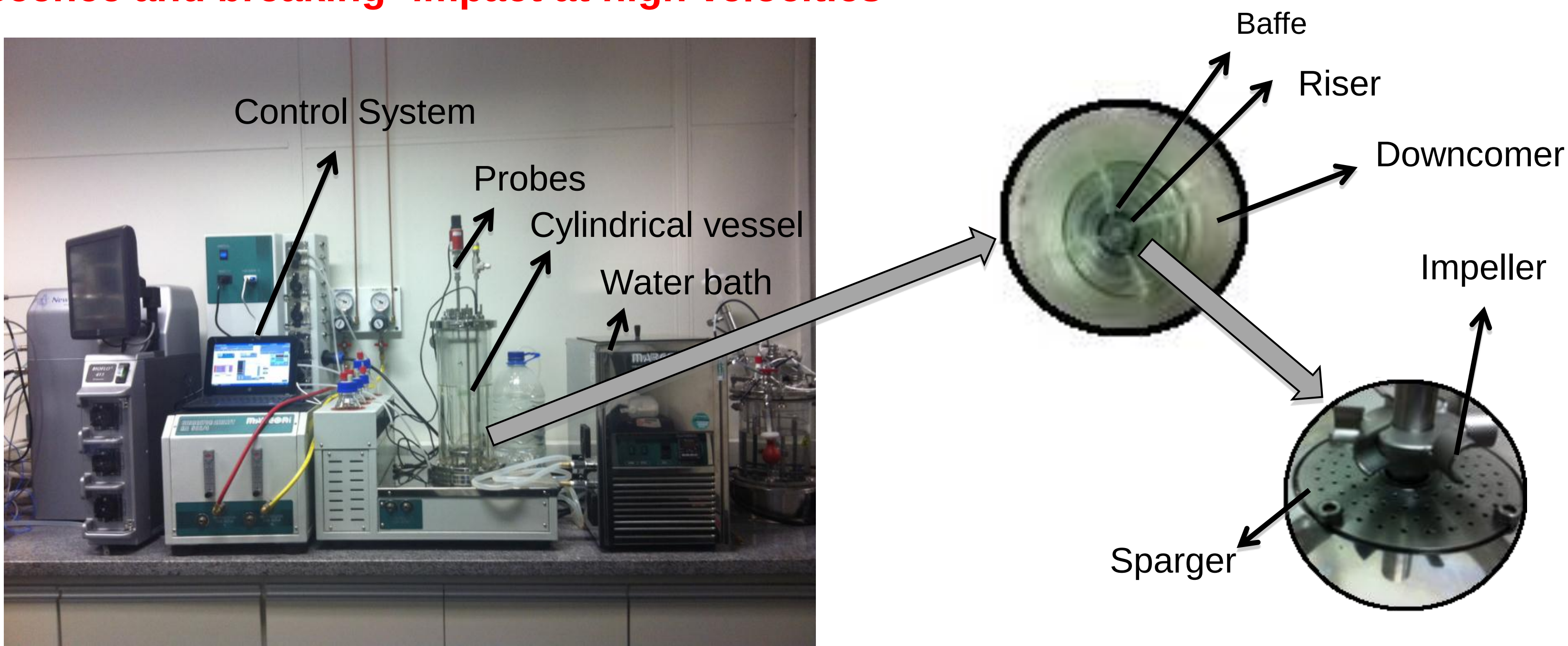
Stirred airlift bioreactor: a new reactor for production of bio-products from Algae- Use of CO2 from fermentation



Jesus S.S., Arias E.L., Santana A., Maciel Filho, (2012). Estimation hydrodynamic parameters and mass transfer in a stirred airlift bioreactor using viscous fluids. *New Biotechnology*, 29, 21.

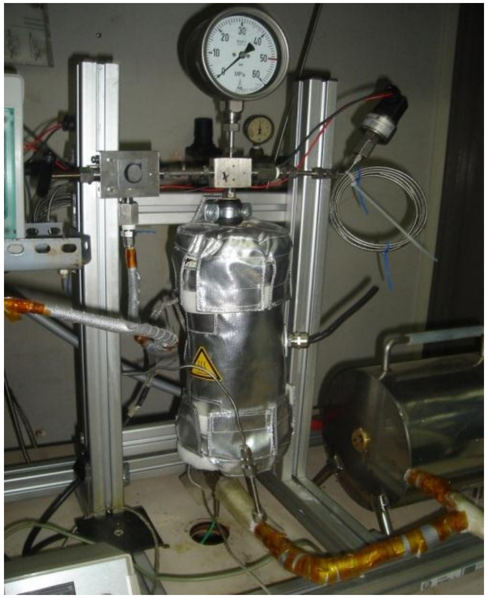


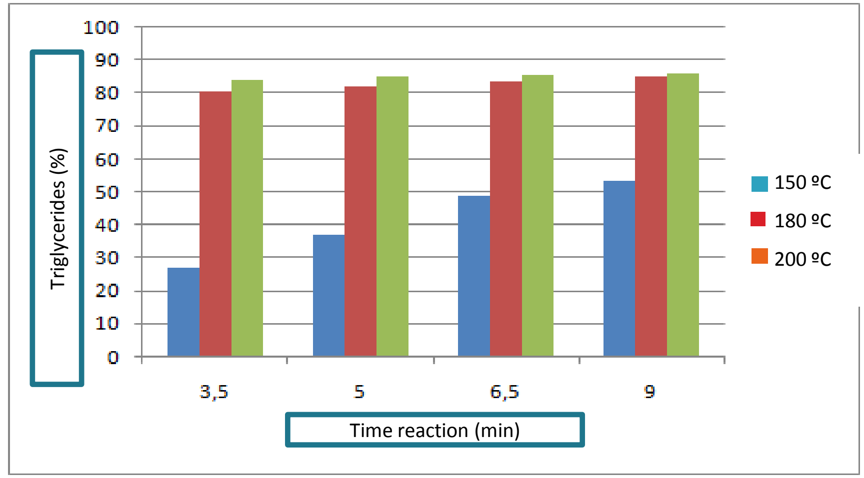
CFD Model does not consider bubble coalescence and breaking- impact at high velocities



Supercritical Transesterification – compared with conventional and reactive distillation with soya and palm oil.

Operating Conditions Temperature 150 – 200 ºC Oil to ethanol ratio molar 1:25 – 1:40
•Reaction time 3 – 9 min Pressure 200 bar Supercritical carbon dioxide/ethanol 75:25





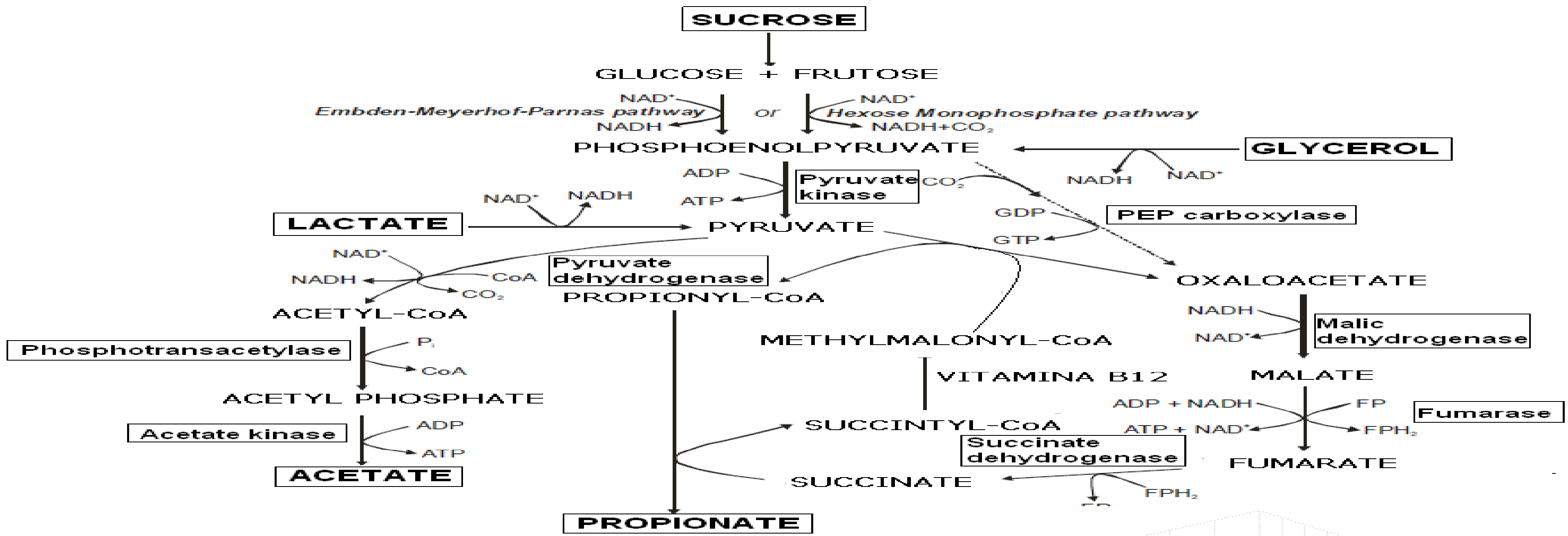
Continuous transesterification of algae oil under supercritical ethanol using CO_2 as cosolvent was attempted. In this study the effects of the process variables were evaluated. Results showed that the best conditions are 200 °C, 200 bar, molar ratio of ethanol-to-oil of 25, at a reaction time of 9 min. The reaction conversions were obtained at mild temperature and pressure conditions in compare with other supercritical process. Compared to conventional catalytic methods, which required at least 1 hour reaction time to obtain similar yield, supercritical ethanol technology has been shown to be superior in terms of time and energy consumption. The merit of this method is that much lower reaction temperatures and pressures are required due to add of a cosolvent, which makes the process safer and the purification of products after supercritical transesterification is much simpler and more environmentally friendly.

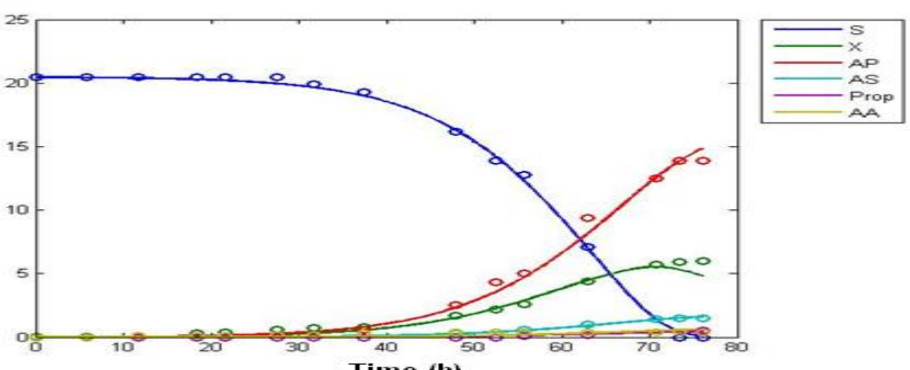
Electrical heating design of Kosmon (Barcelona,Spain), on a Ti reactor (Eurotechnica Hamburg, Germany)
Non-catalytic process- Simple process and high yield
Easy separation - Shorter reaction time
Lower temperature and pressure using a cosolvent (CO2)

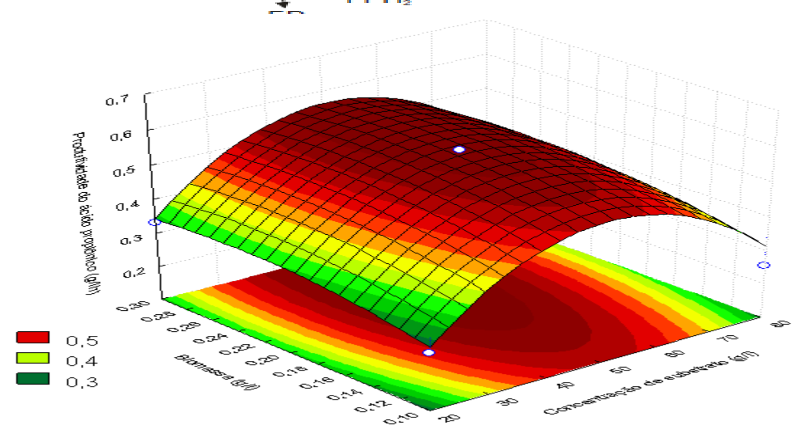
•Santana A., Jesus S. S., Larrayoz M. A., maciel Filho, R Optimization of Biodiesel Production by Supercritical Transesterification of Edible, Non-edible and Algae Oils. In: 10th International Symposium on Supercritical Fluids (ISSF). San Francisco (USA) p. 28 (2012).
•Santana A., Jesus S. S., Larrayoz M. A., Maciel Filho, R.. Production of biodiesel from algae oil by supercritical transesterication using continuous reactor. In: 10th Annual World Congress on Industrial Biotechnology and Bioprocessing. Orlando (USA) (2012).

Synthesis of High Added value Chemicals from Renewable Feedstock trough Fermentation of CO_2 and Glycerol

Biological Synthesis of Propionic Acid from Glycerol



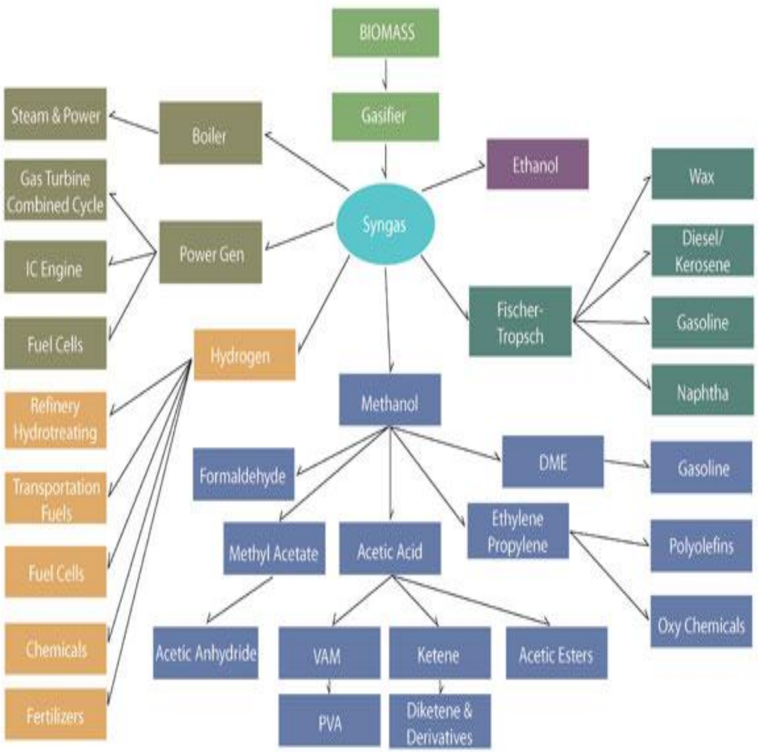


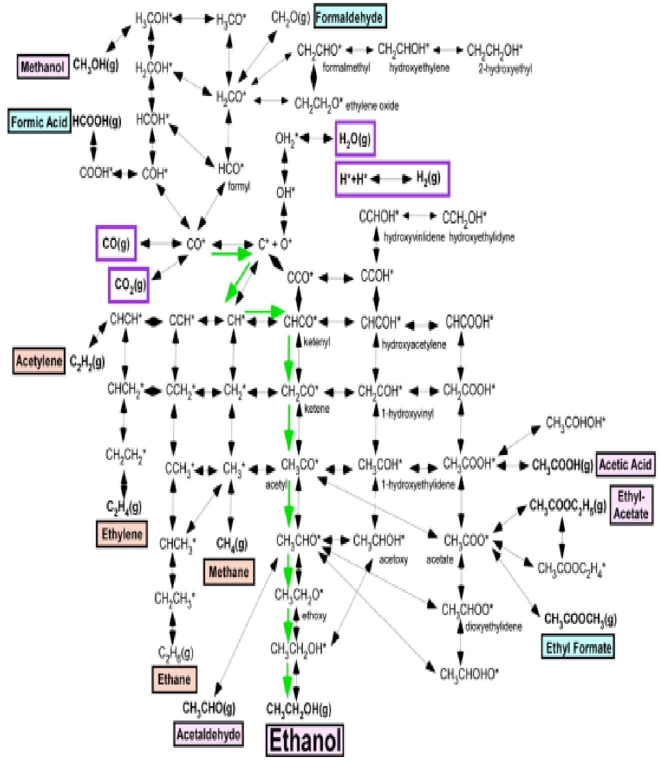


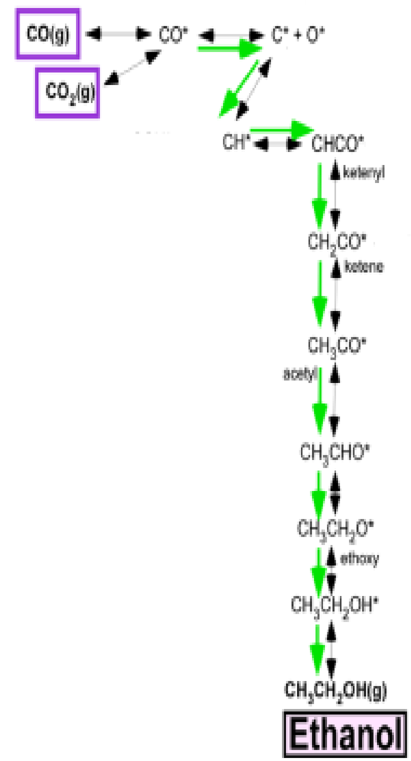
2-) Thermochemical Route

Syngas from Glycerin and Sugar Cane Bagasse

Syngas – raw material for ethanol and chemicals from 1- chemical routes and 2- substrate for fermentation to produce ethanol







Catalytic conversion of syngas via direct synthesis

→ **ETHANOL**

Need of improvement for higher conversion

Ethanol formation

$$2CO_{(g)} + 4H_{2(g)} \leftrightarrow C_2H_5OH_{(g)} + H_2O_{(g)}$$

$$r_{EtOH} = 6{,}3 \times 10^{12} e^{-126{,}7/RT} p_{H2}^{0{,}90} p_{CO}^{-0{,}76}$$

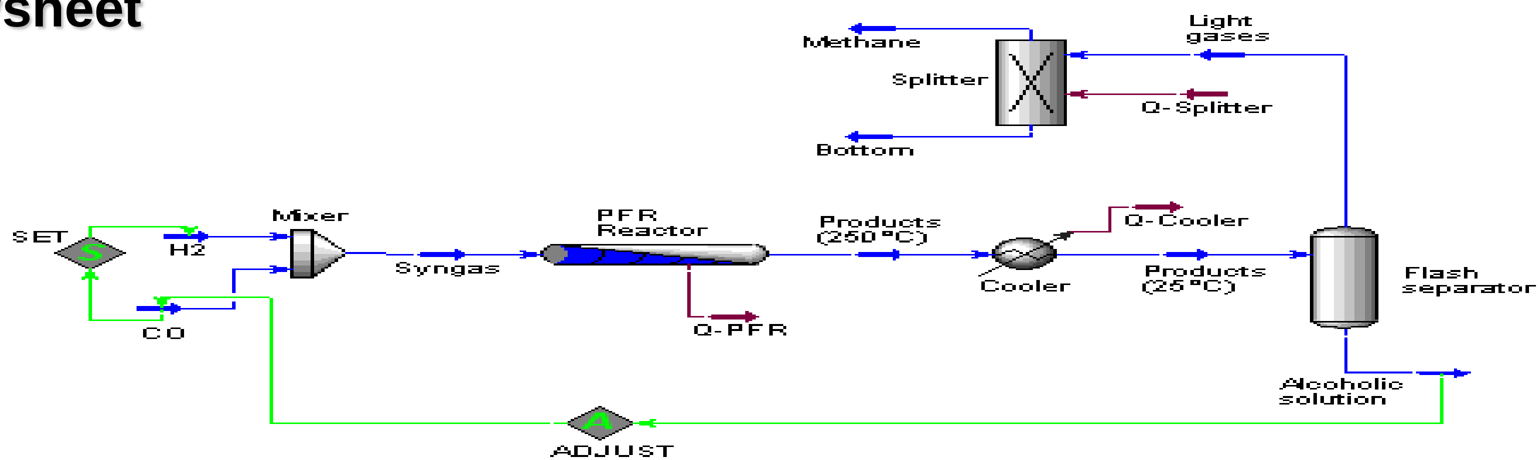
Methanation

$$CO_{(g)} + 3H_{2(g)} \leftrightarrow CH_{4(g)} + H_2O_{(g)}$$

$$r_{CH4} = 9{,}0 \times 10^{15} e^{-156{,}8/RT} p_{H2}^{0{,}79} p_{CO}^{-0{,}60}$$

Catalyst Rh-Mn-Li-Fe/SiO_2

Flowsheet



Thermodynamic model: PRSV- **Production of 500 m3/day of ethanol**

(Patent to be applied – 2012)

Pyrolysis of Glycerin and Sugar Cane Bagasse Syngas Production and H_2 . Fixed bed catalytic reactor – catalyst and process development

Pyrolysis of Glycerin

	Run	Set Independently					
		T (ºC)	t (min)	Ar (ml/min)	% H_2	% CO	% H_2+CO
2^3 factorial design	1	750	20	10	19.66	31.6	51.26
	2	850	20	10	36.05	29.29	65.34
	3	750	40	10	18.63	29.61	48.24
	4	850	40	10	35.76	29.68	65.44
	5	750	20	50	24.09	27.57	51.66
	6	850	20	50	41.07	32.92	73.99
	7	750	40	50	19.5	27.63	47.13
	8	850	40	50	42.82	34.79	77.61
Central Points	9	800	30	30	33.74	32.32	66.06
	10	800	30	30	33.24	32.76	66
	11	800	30	30	33.5	32.54	66.04

The main gas products were H_2 and CO. Besides these gases, CO_2, CH_4, C_2H_4 and C_3H_8 were also obtained in smaller proportions. The liquid product compositions were methanol, ethanol, acetone and acetaldehydeNet energy recovered = 294kJ/mol of glycerol fed.

Models for Kinetic Parameter Arrhenius, Flyn-Ozawa-Wall (FWA), Kissinger

Pyrolysis of crude and pure glycerol: Kinetic parameter estimation from TGA applying isothermal and non-isothermal analysis. A. P. G. Peres, L.P. Tovar, A. R. R. Bineli,B. H. Lunelli and R. Maciel Filho.
62nd Canadian Chemical Engeneering Conference, Vancouver/BC, October 14-17, 2012.

SUGARCANE BAGASSE AS RAW MATERIAL TO SYNGAS PRODUCTION: 3D SIMULATION AND DATA OF GASIFICATION PROCESS – Fixed or Fluidized Bed ?

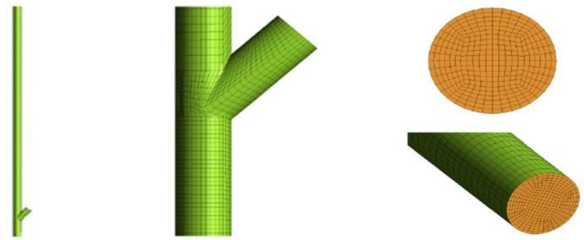


Figure 1. Mesh of Bubbling fluidized bed gasifier of bagasse. CFD simulation

- **Simulations validity**

Table 1. Comparison between experimental results and those obtained with the CFD simulation.

H_2 concentration [vol %]						
Temperature [°C]	AR=0.29 and SR=0.0		AR=0.34 and SR=0.0		AR=0.29 and SR=0.5	
	Exp	Sim	Exp	Sim	Exp	Sim
700	11.47	13.71	11.47	12.39	15.56	17.89
800	21.47	24.58	22.06	24.16	23.70	27.03
900	31.18	34.23	32.06	35.27	39.80	42.98

H_2 Yield [m^3/kg]						
Temperature [°C]	AR=0.29 and SR=0.0		AR=0.34 and SR=0.0		AR=0.29 and SR=0.5	
	Exp	Sim	Exp	Sim	Exp	Sim
700	0.0423	0.0474	0.0615	0.0695	0.0652	0.0757
800	0.1269	0.1376	0.1654	0.1816	0.1217	0.1398
900	0.2692	0.2934	0.3346	0.3597	0.4391	0.4830

* * Stoichiometric air ratio (AR) and the steam to bagasse ratio (SR)

- **Study cases**

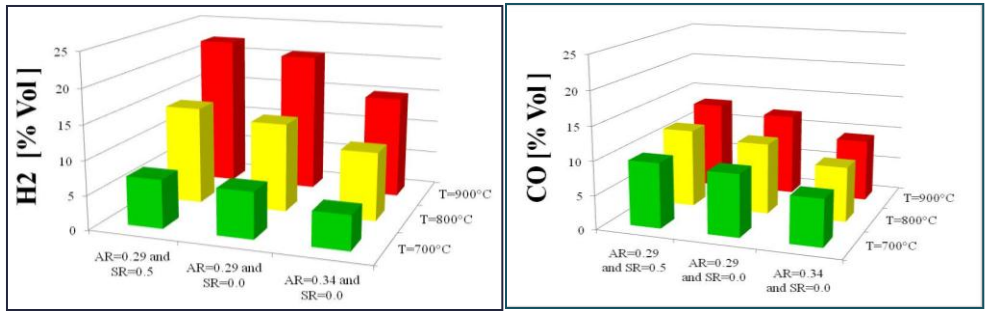


Figure 2. Dry composition of Syngas obtained in bubbling fluidized bed gasifier of bagasse.

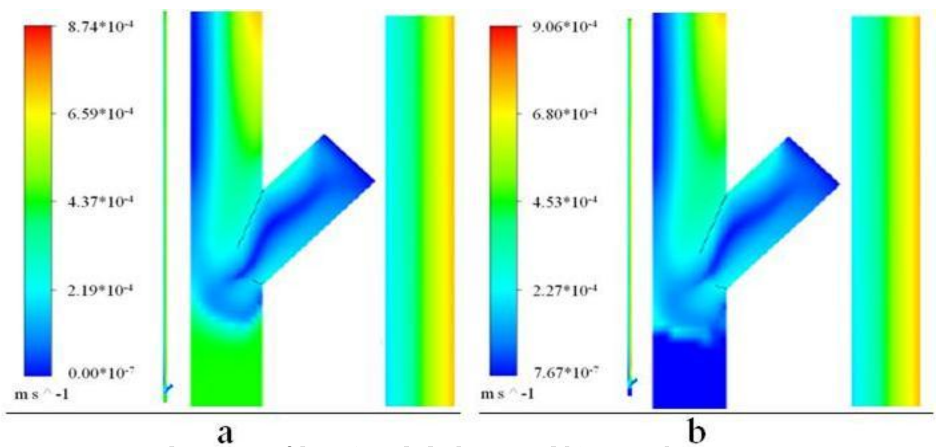


Figure 3. Velocity profile.: a) Solid phase and b) Gas phase. T = 900 °C, AR = 0.29 and SR = 0.34.

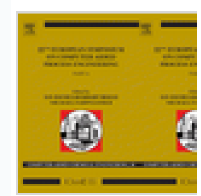
In the simulation presented in this work, the gasifier was operated at temperature of 900°C with AR= 0.29 and SR = 0.34, obtaining dry compositions of 22.25, 13.21 and 63.54 vol% for H_2, CO and impurities, respectively.

ELSEVIER

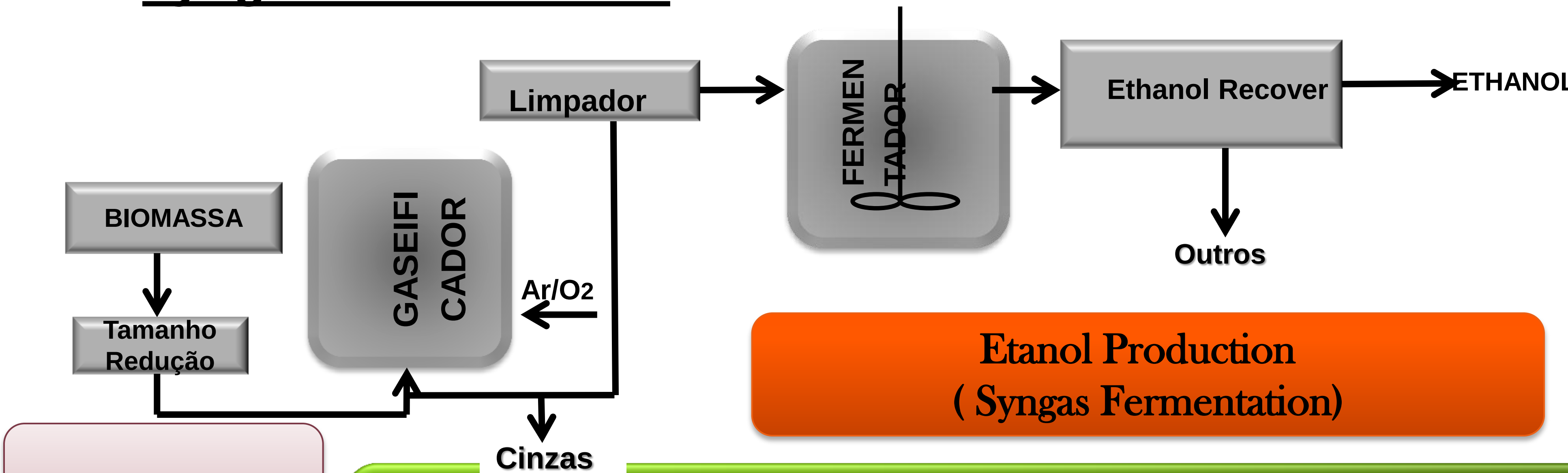
Computer Aided Chemical Engineering

Volume 30, 2012, Pages 1118–1122

22nd European Symposium on Computer Aided Process Engineering



Syngas Fermentation



Etanol Production
(Syngas Fermentation)

Syngas Production

$$6CO + 3H_2O \rightarrow C_2H_5OH + 4CO_2 \quad \textit{Eq. (1)}$$

$$2CO_2 + 6H_2 \rightarrow C_2H_5OH + 3H_2O \quad \textit{Eq. (2)}$$

$$6CO + 6H_2 \rightarrow 2C_2H_5OH + 2CO_2 \quad \textit{Eq. (3)}$$

The conversion of biomass-derived syngas into biofuels by microbial catalysts has gained considerable attention as a promising alternative for biofuel production.-

Experimental results have shown lower conversion compared with chemical routes but with energy saving

Conclusions and work in progress

All the proposed steps for second generation have been considered – scenarios for taking decisions – internal interest rate – economic decision ?

At this stage alternative developments are been tested – arrangements for the Integration of first with second and third generation (use of CO_2 either as substrate for algae or for fermentation to ethanol) - progress

Use of CO_2 in the thermochemical route – in progress

Catalyst Development for improvement of diret thermochemical route to ethanol- in progress

Lab scale plant for pyrolysis and gasification – in progress

BIOEN Research Workshop

Contribution to the performance improvement of the industrial process for obtaining ethanol from sugarcane by using microwave and ultrasonic energies

FAPESP Project # 08/58047- 4

- Coordinator
Dr. Antonio Marsaioli Junior
Collaborators (in alphabetical order)
Dr. Alfredo Almeida Vitali
Dr. Daniel Ibraim Pires Atala
Dra. Maria Isabel Berto
Dra. Michele Nehemy Berteli
Institutions: ITAL jointly with CTC

Justification

- Searching of new techniques envisaging a better performance of the ethanol industrial production obtained from sugarcane, based on the adaptative application of microwaves and ultrasound to the present processes.

Specific objectives

– **Target 1:** to study an **intermediate pasteurization of the sugarcane molasse by means of microwave** in order to eliminate contaminants from substrate before the introduction of selected strains of *S. cerevisiae* into the fermentation vats.

Results obtained : the **lethality parameters** (D and z values) for **vegetative microorganisms** were raised, by using a continuous system for applying microwaves. The results will be used for sizing a higher scale microwave pasteurization system for the sugarcane molasses.

Specific objectives

– **Target 2:** to study the application of low intensity ultrasound energy during fermentation envisaging as result a better yield of the ethanol production.

Results obtained : the study up to now has been of **an exploratory nature**, performed on a model solution inoculated with a selected strain of *S. cerevisiae.* It has confirmed that the application of **ultrasound energy interfered into the fermentative process**, although the results are not conclusive yet.

Evolution, new partnerships and positioning

- Opening of new research frontiers:
  - Dielectric properties determination in continuous measuring system;
  - Analytical methodologies development (RAMAN, RMN);
  - Tests of other frequencies either of microwaves or of ultrasound.
- It is **not possible to delineate the degree of competitiveness yet** by considering the present stage of research.
- The results attained suggest the permanence of **the bench scale studies** together with the implementation of **pilot scale tests**, in order to know the real contribution of the proposed tecnologies.

Acknowledgments: IQ/Unicamp, FEQ/Unicamp, CCQA/Ital.

MICROALGAE GROWTH IN PHOTOBIOREACTOR AS A TOOL FOR ATMOSPHERIC CARBON SEQUESTRATION

Braskem/Fapesp (PITE) Proc. No. 2008/03487-0
Project coordinator: Profa Ana Teresa Lombardi – D. Botânica, UFSCar

Scientific Publications : 2 papers

Objectives

Increase productivity: control of the biochemical composition of biomass

Culture technology: increase the control of microalgae *physiology*

Biomass valuation*:* applications of microalgae biomass

Selection of microalgae species that grow in sewage effluent

Laboratory construction: Algae Biotechnology

Large scale photobiorreactor operation (natural environment)

Challenge

Produce microalgae biomass with quality control in large scale.

Proposal

Hybrid cultures: put together the advantages of open and closed systems, but not their disadvantages.

Difficult to contaminate

Does not need heat

Higher control of algae physiology

Controlled biochemical composition manipulation

Suitable for any species

THEREFORE: better quality control of the biomass

Objectives concluded

Objective 1. Increase productivity: control of the biochemical composition of biomass (laboratory experiments)

Concluded 1 PhD
1 Master
2 Cientific Initiation (undergraduate research)

⇩

✓ **Standard stressing**	✓ **Controlled stressing**
Carbohydrates => 6 x more CH_2O	Carbohydrates => 33 x more CH_2O
Lipids => 4 x more lipids	Lipids => 32 x more lipids
Proteins => 1,6 x more proteins	Proteins => 12 x more proteins

Objective 2. Culture technology: increase the control of microalgae *physiology* (laboratory => environment conditions)

Concluded 1 Master

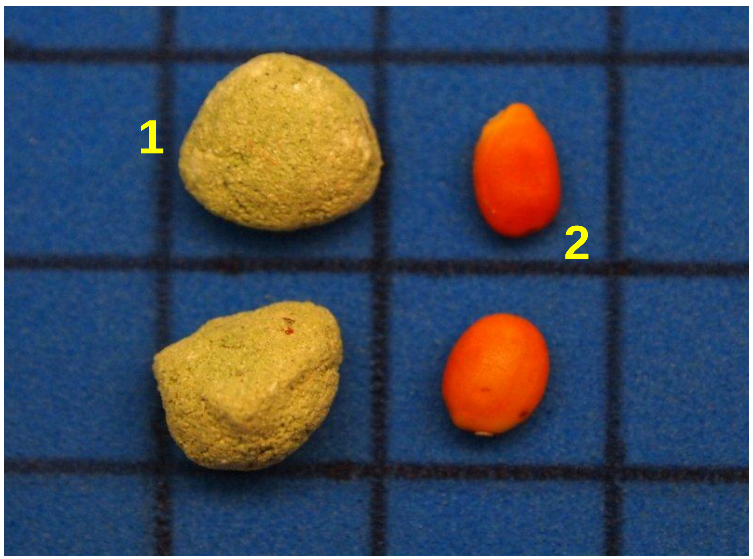
- ✓ Biomass retention filters
- ✓ better productivity and biomass yield
- ✓ Control of the algae physiology

➡ ***Hybrid photobiorreactor***

Objective 3. Biomass valuation: applications of microalgae biomass

Concluded 2 Scientific initiation (IC);

In performance 1 IC, 1 master



1 => seed with microalgae (cell and mucilage)

2 => natural seed

envolving native vegetation seeds with microalgae

Effect: higher resistance to dryness.

Consequence: better germination and survival of the small plant

Objective 4. **Selection of microalgae species that grow in sewage effluent**

1 master

Objective 5. Laboratory construction: Algae Biotechnology

In progress

Objective 6. Operation of hybrid photobiorreactor: patent description

⬇

- ✓ hybrid photobiorreactor: 1000 L; model being tested with 200 L
- ✓ Controlled biochemical manipulation => higher physiology control

Workshop BIOEN / FAPESP

divisões tecnologias de biocombustíveis e biorefinarias

Semi Solid Bioreactors Optimization by Internal Multiphase flow Modeling

Paulo Seleghim Jr.
seleghim@sc.usp.br

Industrial transformation of sugar-cane into…

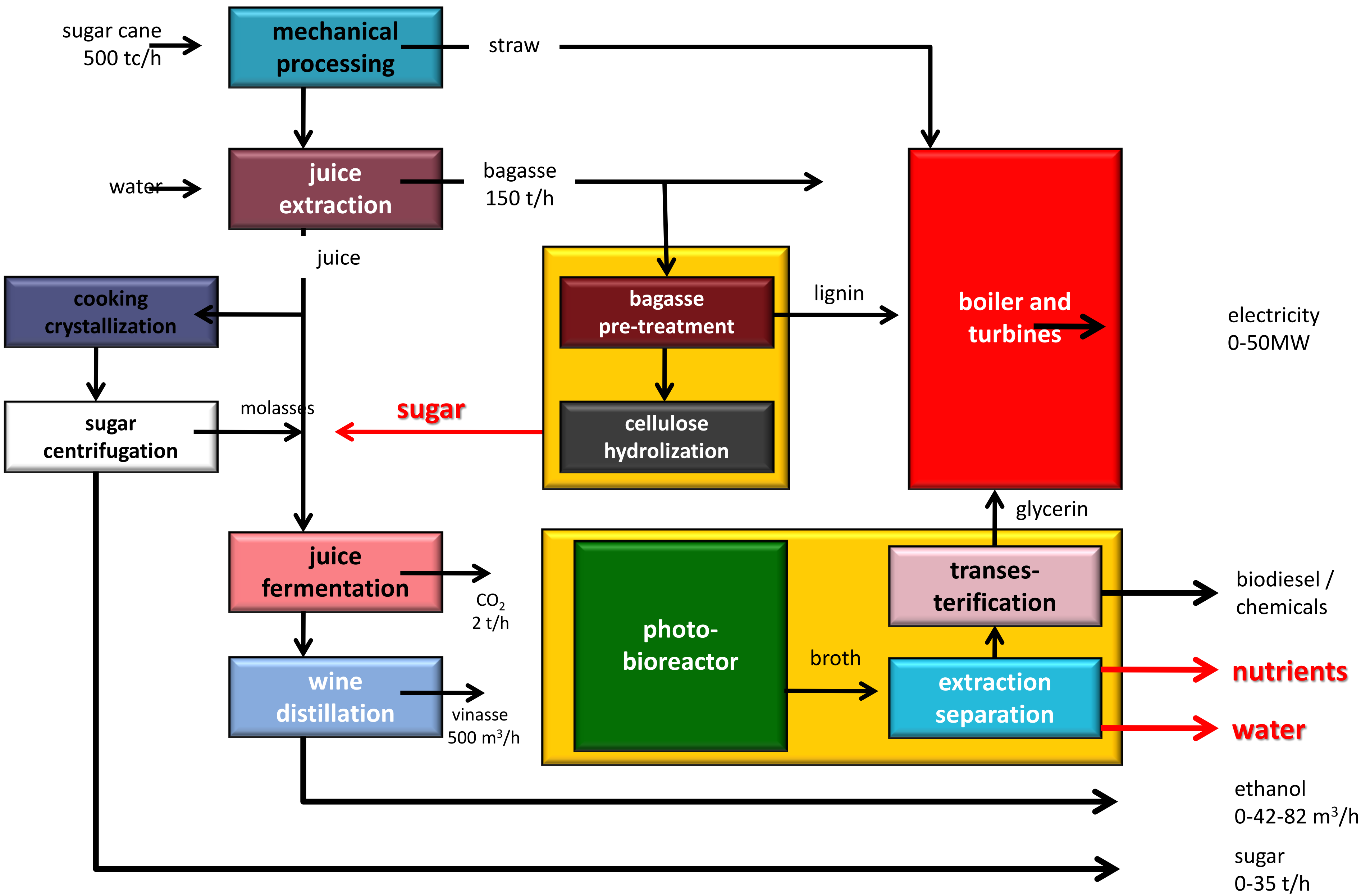
Evolving towards a full scale biorefinery

- Biomass depolymerization and conversion
  - ✓ Low vol. / high value chemical products
  - ✓ High vol. / low value liquid transportation fuels

Improving sustainability

- Energy balance (currently ~9:1)
- Water balance (currently negative)
- Soil nutrients recycling (currently uneconomical)

Current Production Model



high efficiency industrial scale bioreactors !

Statement of the problem

Dimensional governing equations – single phase flow

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\rho \vec{V}) = 0$$

mass balance

$$\rho \frac{D\vec{V}}{Dt} = \rho \vec{g} + \vec{\nabla} \cdot \tilde{T}(\tilde{D})$$

momentum balance

$$\rho \frac{Du}{Dt} = \tilde{T}(\tilde{D}) : \tilde{D}(\vec{V}) + \vec{\nabla} \cdot (k \vec{\nabla} \theta)$$

energy balance

Statement of the problem

Non-dimensional governing equations

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\rho \vec{V}) = 0 \quad \Rightarrow \quad \varphi_{mass}(\vec{V}, St) = 0$$

$$\rho \frac{D\vec{V}}{Dt} = \rho \vec{g} + \vec{\nabla} \cdot \tilde{T}(\tilde{D}) \quad \Rightarrow \quad \varphi_{mom}(\vec{V}, P, St, Fr, Re, E) = 0$$

$$\rho \frac{Du}{Dt} = \tilde{T} : \tilde{D} + \vec{\nabla} \cdot (k \vec{\nabla} \theta) \quad \Rightarrow \quad \varphi_{energy}(\vec{V}, \theta, St, Re, Pr) = 0$$

Non-dimensional mass balance equation

$$St\frac{\partial \rho}{\partial t} + \vec{\nabla}(\rho\vec{V}) = 0$$

Non-dimensional Newtonian fluid momentum balance equation

$$St\frac{\partial \vec{V}}{\partial t} + \vec{V}\cdot(\vec{\nabla}\times\vec{V}) = \frac{1}{Fr}\vec{g} + \frac{1}{Re}\left[\nabla^2\vec{V} + \left(1+\frac{\lambda}{\mu}\right)\vec{\nabla}\cdot(\vec{\nabla}\cdot\vec{V})\right] - E\vec{\nabla}P$$

Non-dimensional groups

Strouhal: $$St = \frac{D/t}{V} = \frac{\text{transient}}{\text{inertia}}$$

Reynolds: $$Re = \frac{\rho VD}{\mu} = \frac{\text{inertia}}{\text{viscosity}}$$

Euler: $$E = \frac{P}{\rho V^2} = \frac{\text{static}}{\text{dynamic}}$$

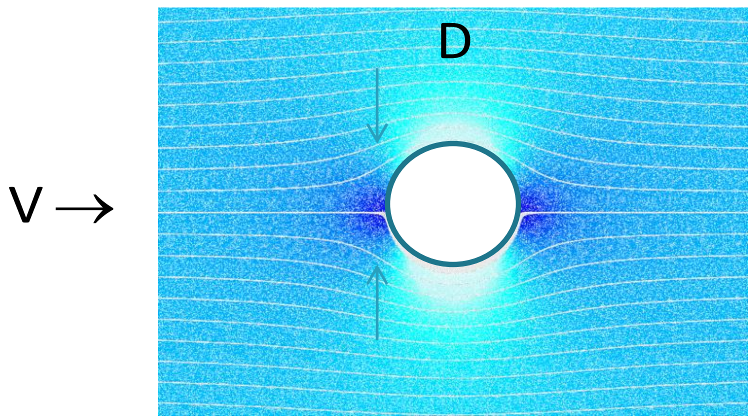
Froud: $$Fr = \frac{V^2}{gD} = \frac{\text{inertia}}{\text{gravity}}$$

Prandtl: $$Pr = \frac{C_P \mu}{k} = \frac{\text{momentum dif.}}{\text{thermal dif.}}$$

An important consequence:

Similar geometries may respond completely different to the same boundary conditions !

Example: isothermal flow past a circular cylinder



$$St = \frac{D/t}{V}$$

$$Re = \frac{\rho V D}{\mu}$$

Optimal design (optimized performance):

1. Phenomenological / parametric numerical modeling
2. Defining and assessing performance parameters
3. Optimization algorithm (Genetic Algorithm)

performance parameters → **bioreactor parametric model**

performance parameters ← **bioreactor parametric model**

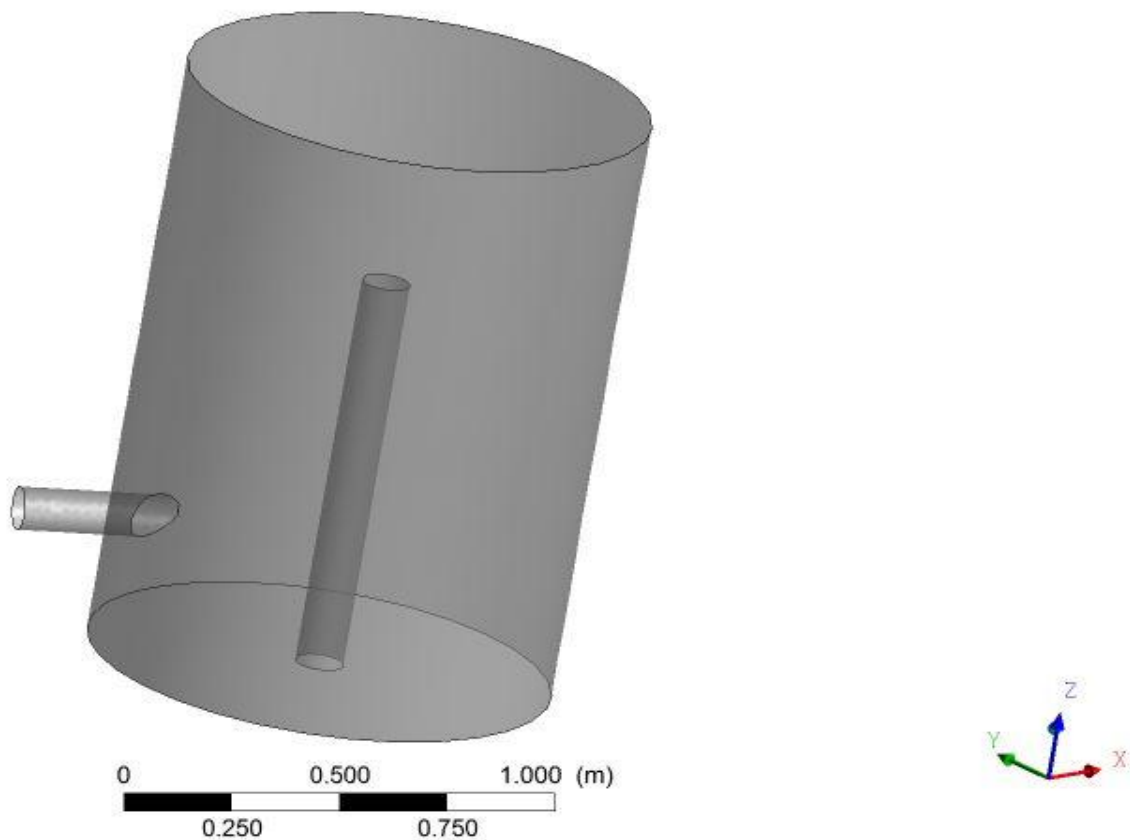
Performance parameters

1. Dispersion of residence times / streamlines
2. Cell death / shear stress control
3. Temperature / heat management
4. Solids deposition / stagnation zones
5. Etc…

conflicting objectives…

multiobjective optimization…

A test case: continuous fermenter




M.Osaki

Assessing residence time distribution

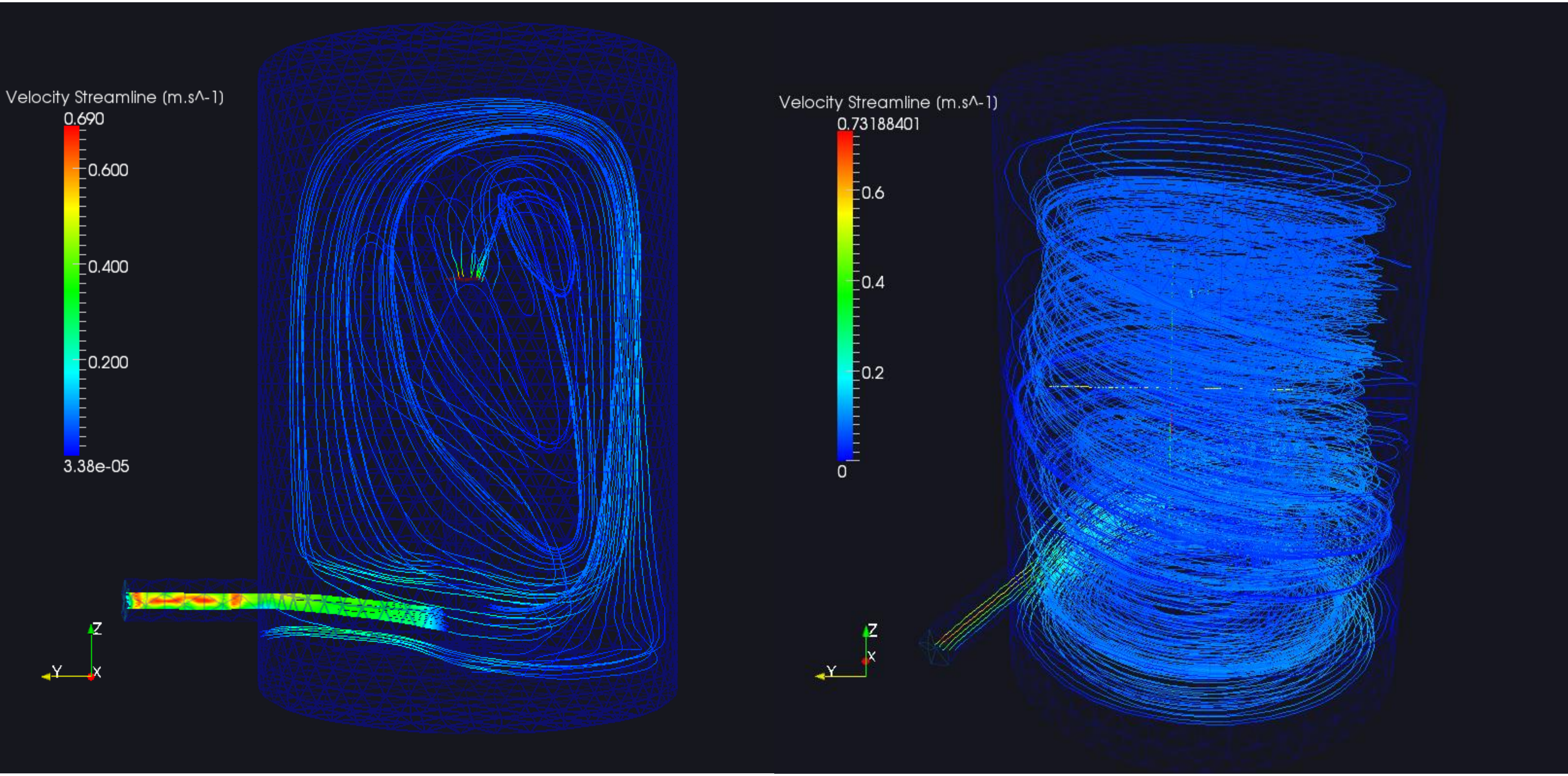
Ideal (average) Residence Time (RT)

$$RT = \frac{\text{bioreactor volume}}{\text{input flow rate}}$$

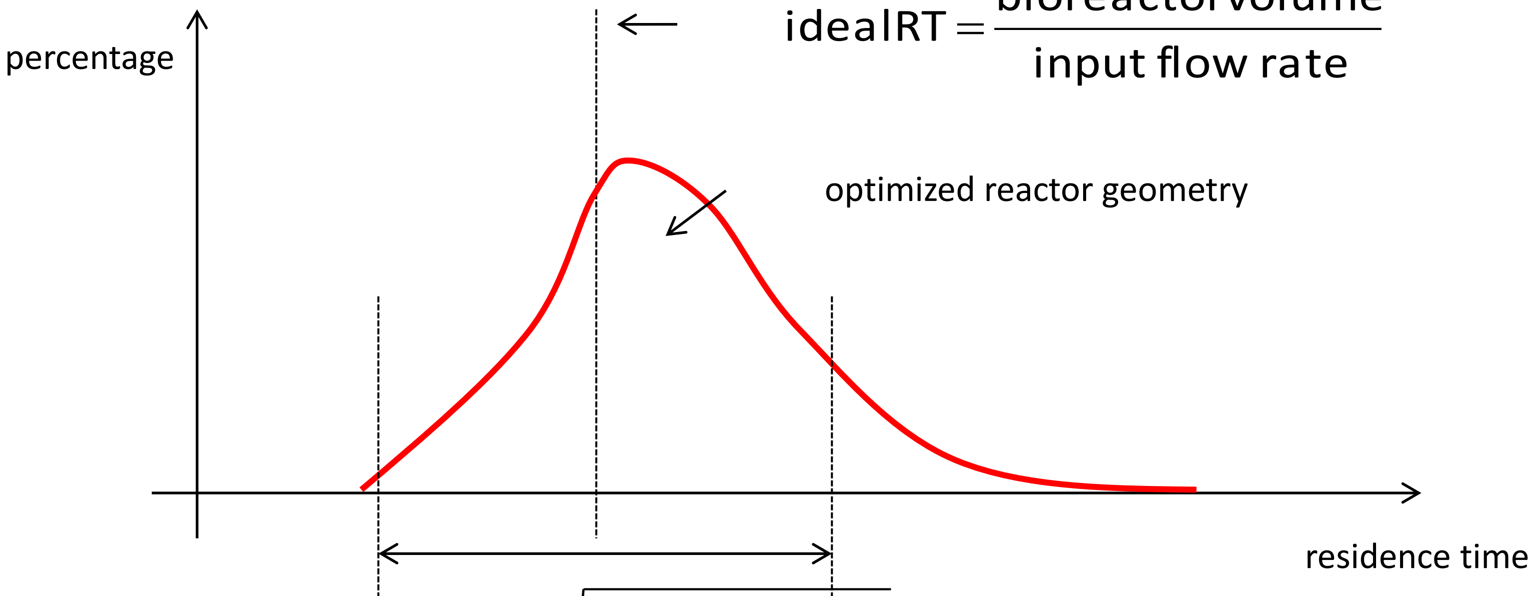
Actual Residence Time (RT)

$$RT_{\Gamma_1} = \int_{\Gamma_1} \frac{ds}{\vec{V} \cdot \vec{\tau}}$$

$$RT_{\Gamma_2} = \int_{\Gamma_2} \frac{ds}{\vec{V} \cdot \vec{\tau}}$$


Velocity Streamline (m.s^-1)
0.690
0.600
0.400
0.200
3.38e-05
Z
Y
X
Velocity Streamline (m.s^-1)
0.73188401
0.6
0.4
0.2
0
Z
X
Y

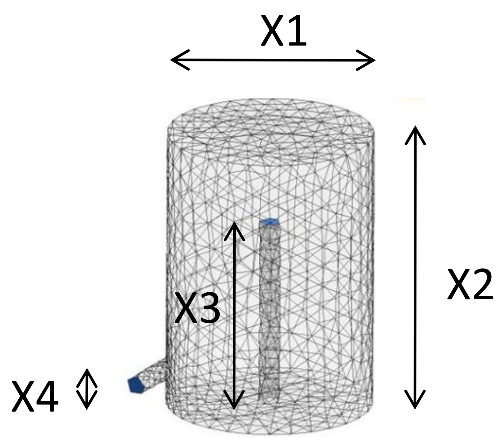
Assessing residence time distribution

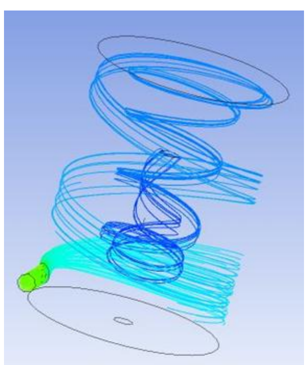


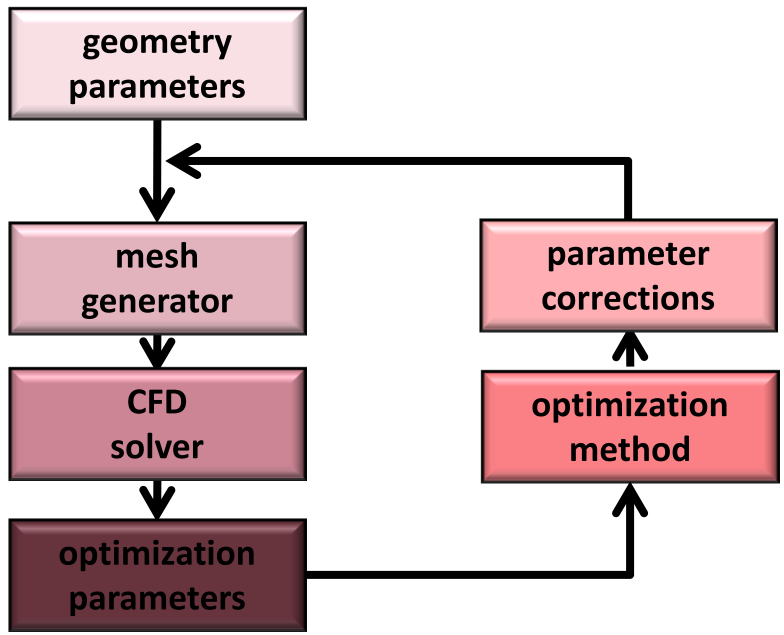
$$idealRT = \frac{bioreactor\,volume}{input\ flow\ rate}$$

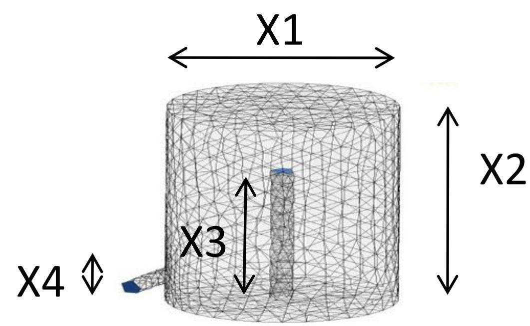
$$\sigma_{RT} = \sqrt{\int_0^\infty (RT - \mu_{RT})^2\,dt}$$

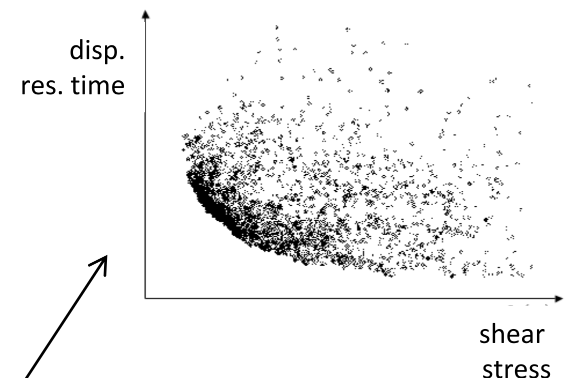
Optimization strategy











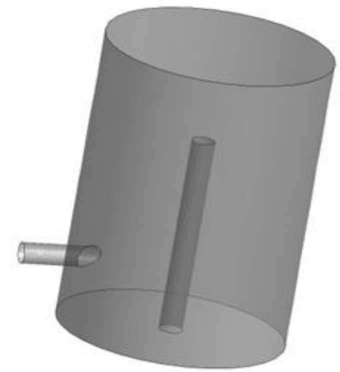
Pareto frontier

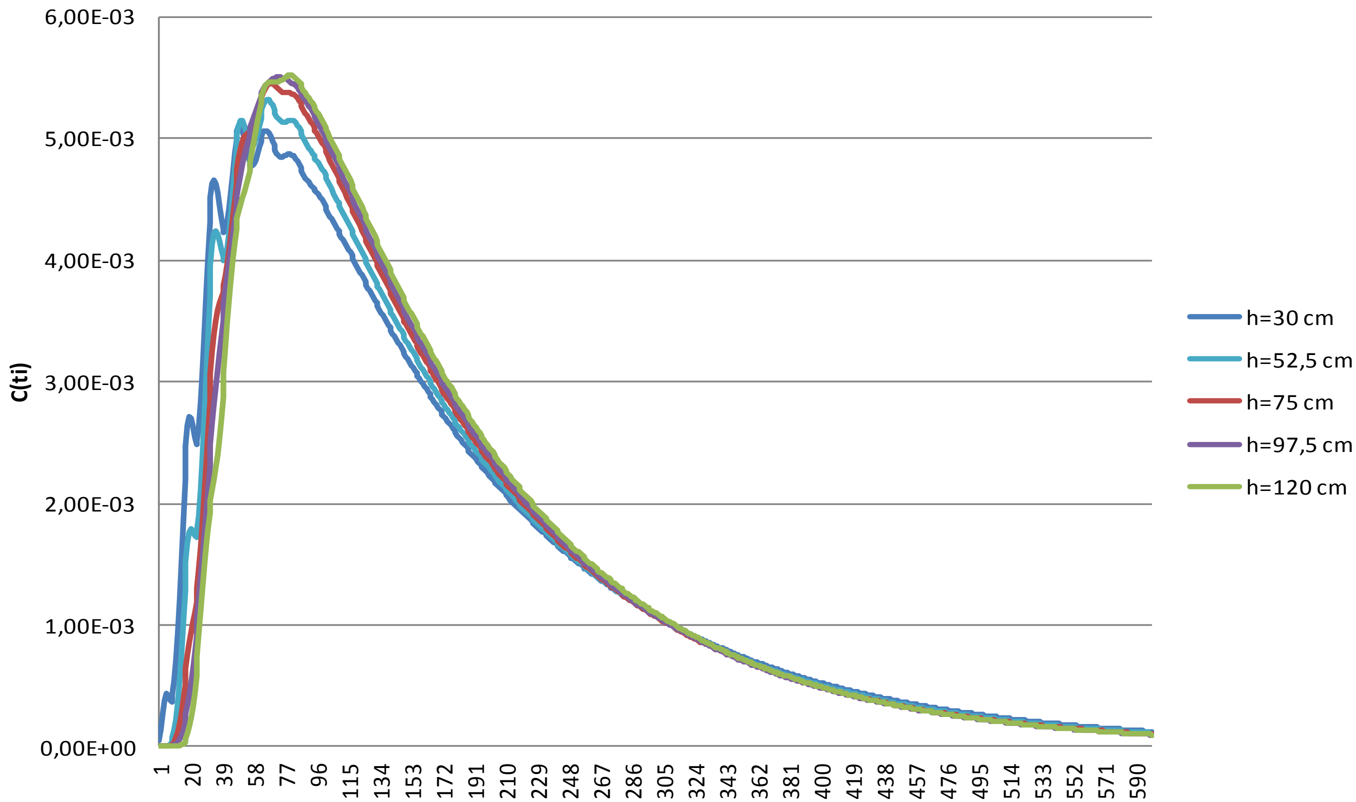
Results...

Evelise Corbalan Góis

Bioreactor efficiency

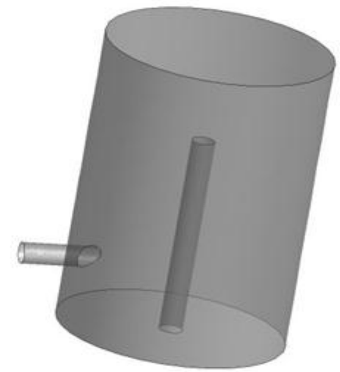
Test case: inlet angle = 22.5°

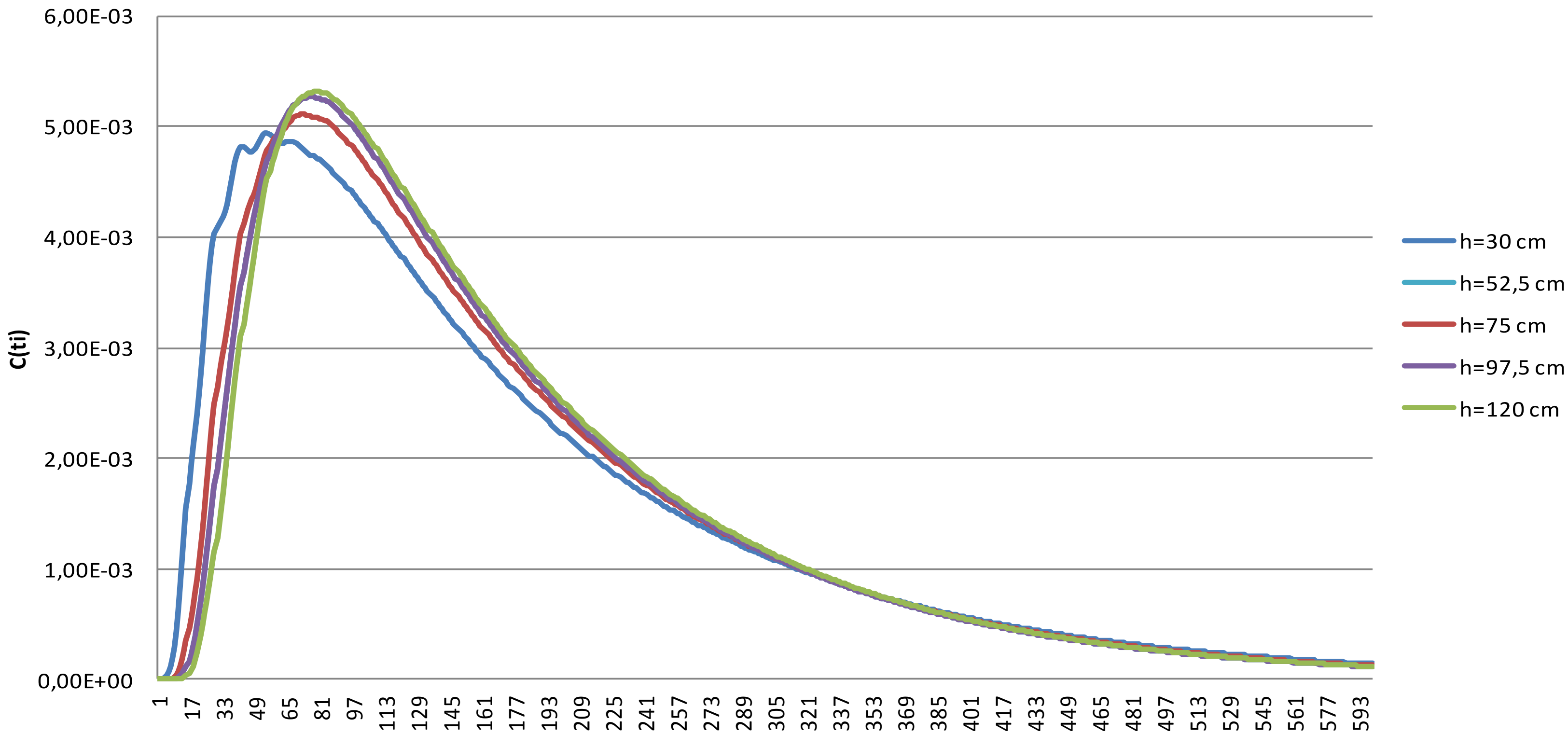




Bioreactor efficiency

Test case: inlet angle = 45°





Conclusions and perspectives

Optimal design method was successfully developed

- Iterative procedure based on parametric modeling

Transfer of technology and research evolution

- Laboratory, pilot and industrial scale testing
- Multi-phase flow equations (dispersed flow, bubbly flow)
- Performance parameters and multi-objective optimization
  - ✓ Shear stress (in course)
  - ✓ Sedimentation
  - ✓ Light propagation
  - ✓ etc.

→ Pareto frontier search