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Advances and opportunities towards a biobased industry in Brazil

BIOTEF_INTEG
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Outline

1.Sugarcane & Conventional use of sugarcane
2.Sugarcane bagasse
3.Potential for biorefinery of sugar cane
4.Non-bioethanol research from sugarcane

5.Companies described

Improvement of Sugarcane

•CTC sugar cane
•Alellyx & Canaviallis

Petrochemical companies

•Petrobras
•Braskem
•Oxiteno

Project design and process development: .
DEDINI

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Brazil is a country of superlatives:

- The most famous Carnival;
- Pantanal, the largest wetland ecosystem; Iguaçu, the greatest falls on earth;
- the Amazon, the largest rainforest...
- also a melting pot of cultures and races and spectacular landscapes….
- *Nowdays: “the largest & BEST biothanol producer of the world*”
- How can we make it EVEN better?

Brazil & brazils

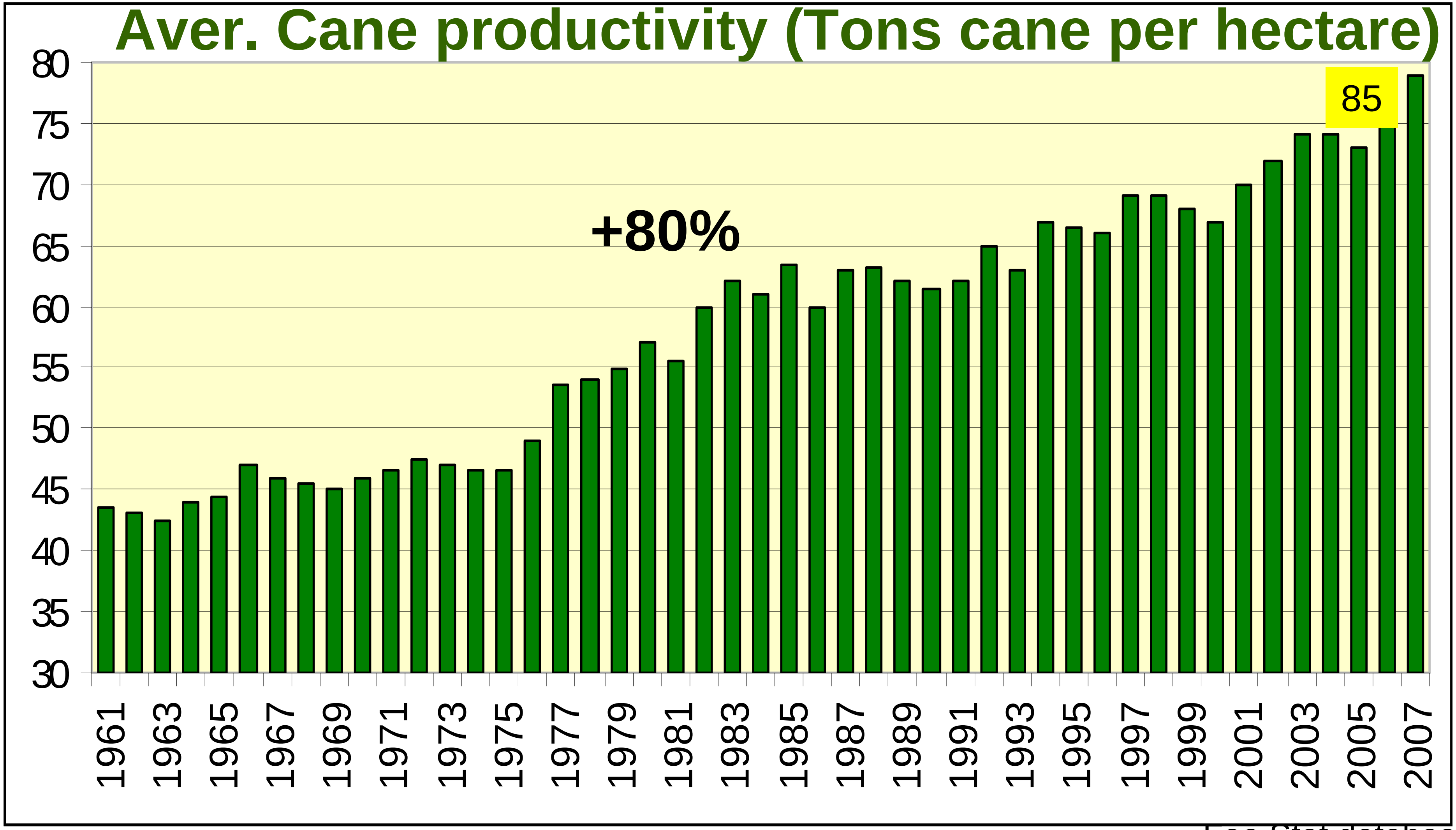





And brasis, brazielen, Brazil, Brésil

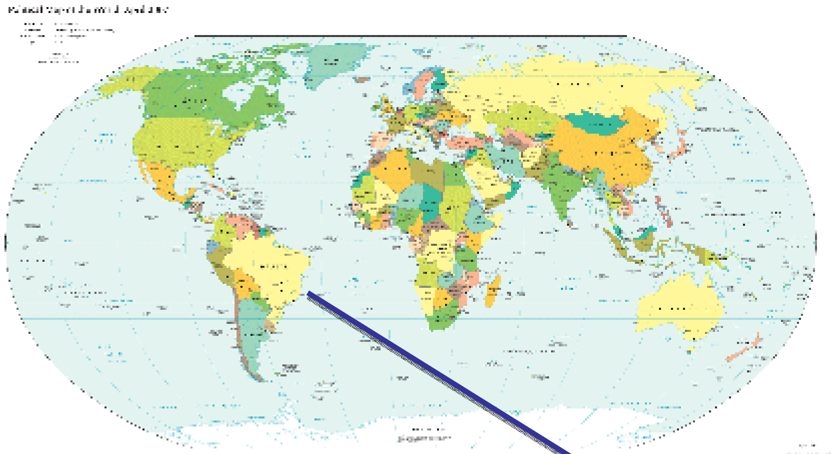
Present situation in Brazil.
The bioethanol opportunity

Evolution of sugarcane in Brazil



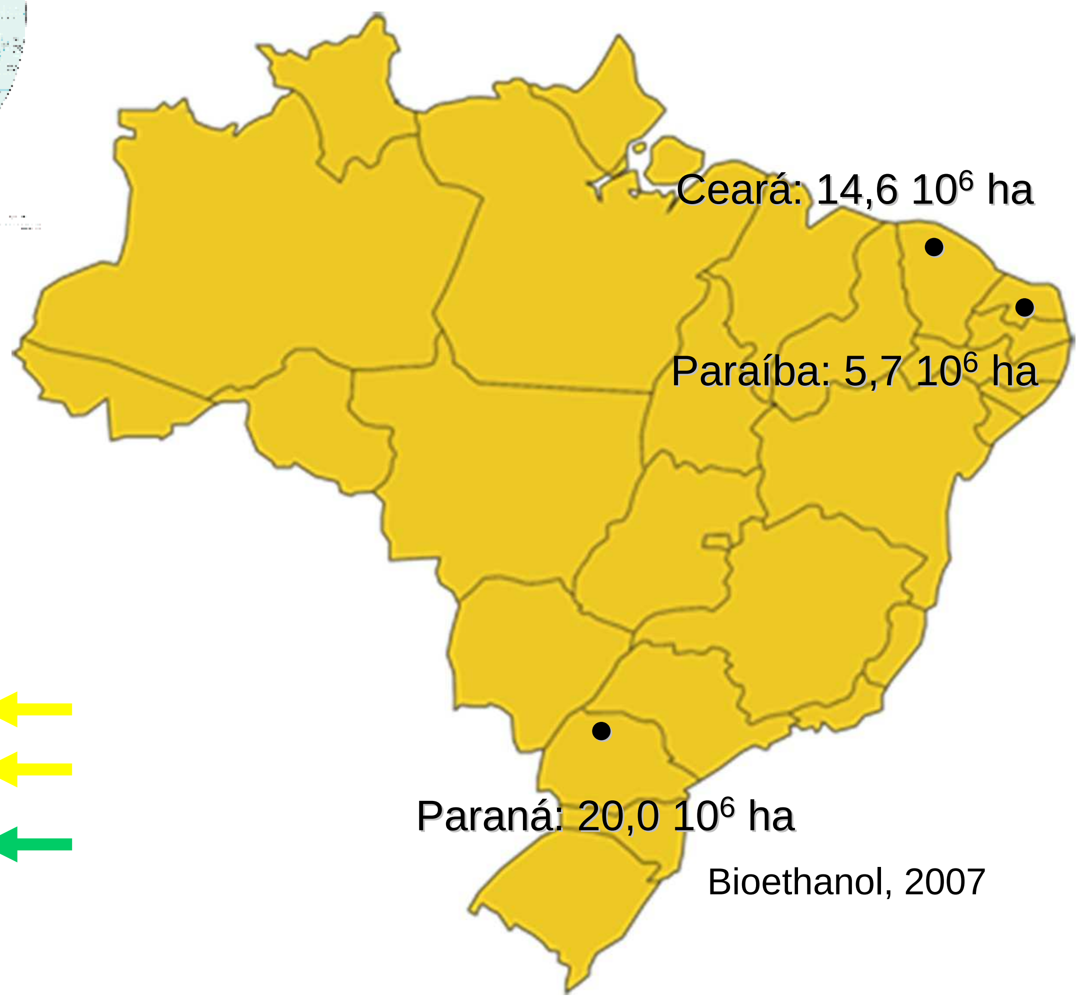
Fao Stat database

Brazil: main crops 2004



Beef farrming =197 million ha

soya =21.5 million ha



Brazil: 851 10^6 ha

	Surface [10^6 ha]
Pasture	150-200
Soya	21.5
Corn	12.3
Sugarcane	5.6
Agric. land	58.0

Bioethanol, 2007

Present Location of Sugar-Etanol Mills in Brazil

Fingueruti, 2007

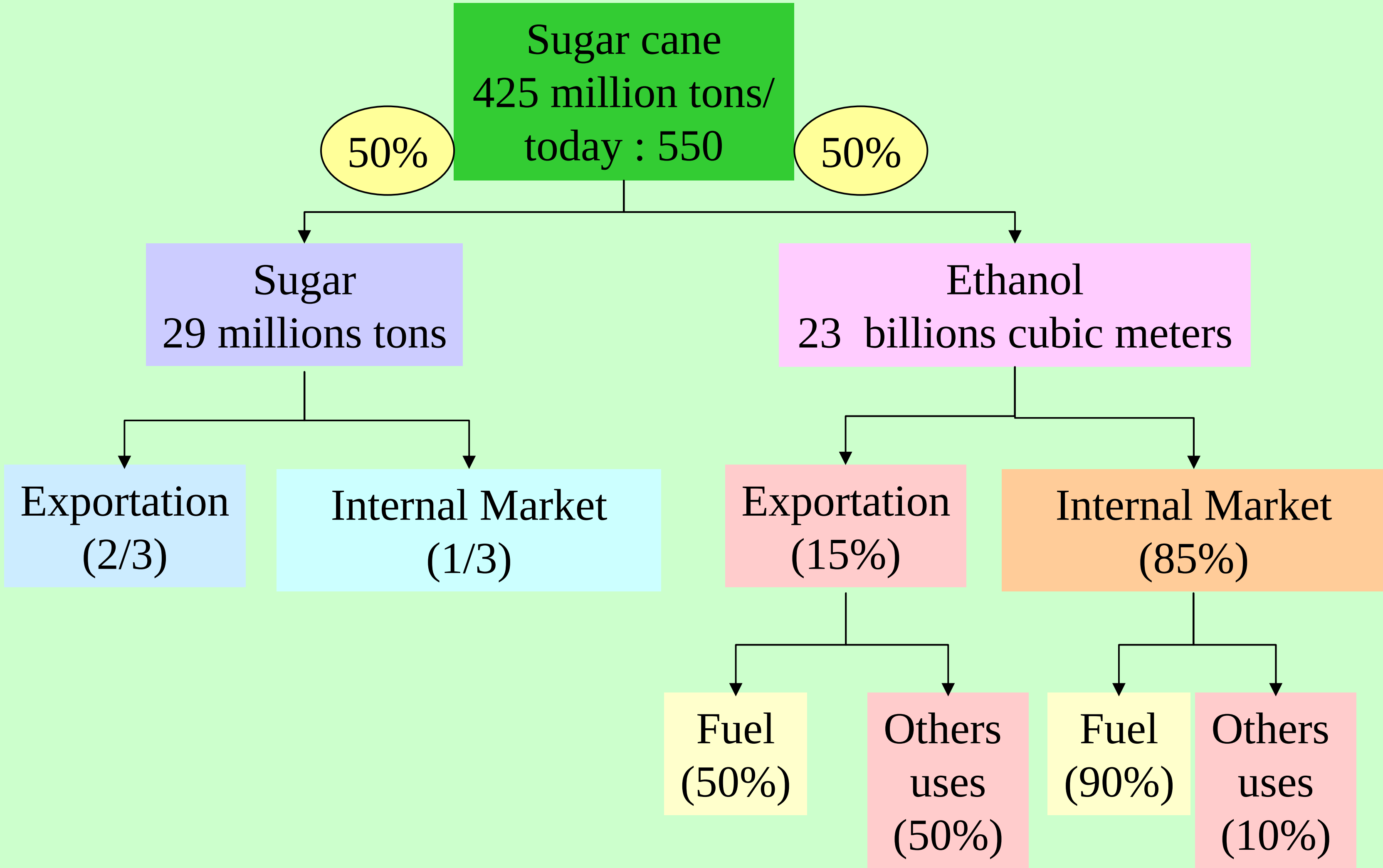
Traditional sugarcane mills

380 Brazilian sugarcane mills

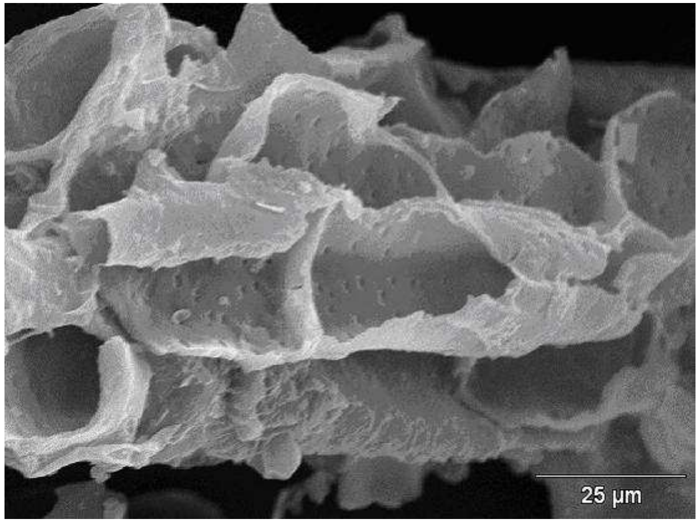
FONTE: DATAGRO

The biomass oportunity
Challenges towards the use of the whole sugarcane

Conventional sugar and ethanol chain - Brazil



Etanol, Alcoolquímica e Biorrefinarias
BNDES Setorial, *Rio de Janeiro, n. 25, p. 5-38, mar. 2007*



[2]

Chemical composition of some common fibers
Sugar Cane Bagasse and Trash [1]

Cellulose	Lignin	Pentosan	Ash	Silica
32-48 %	10-24%	27-32%	1.5-5%	0.7-3.5%

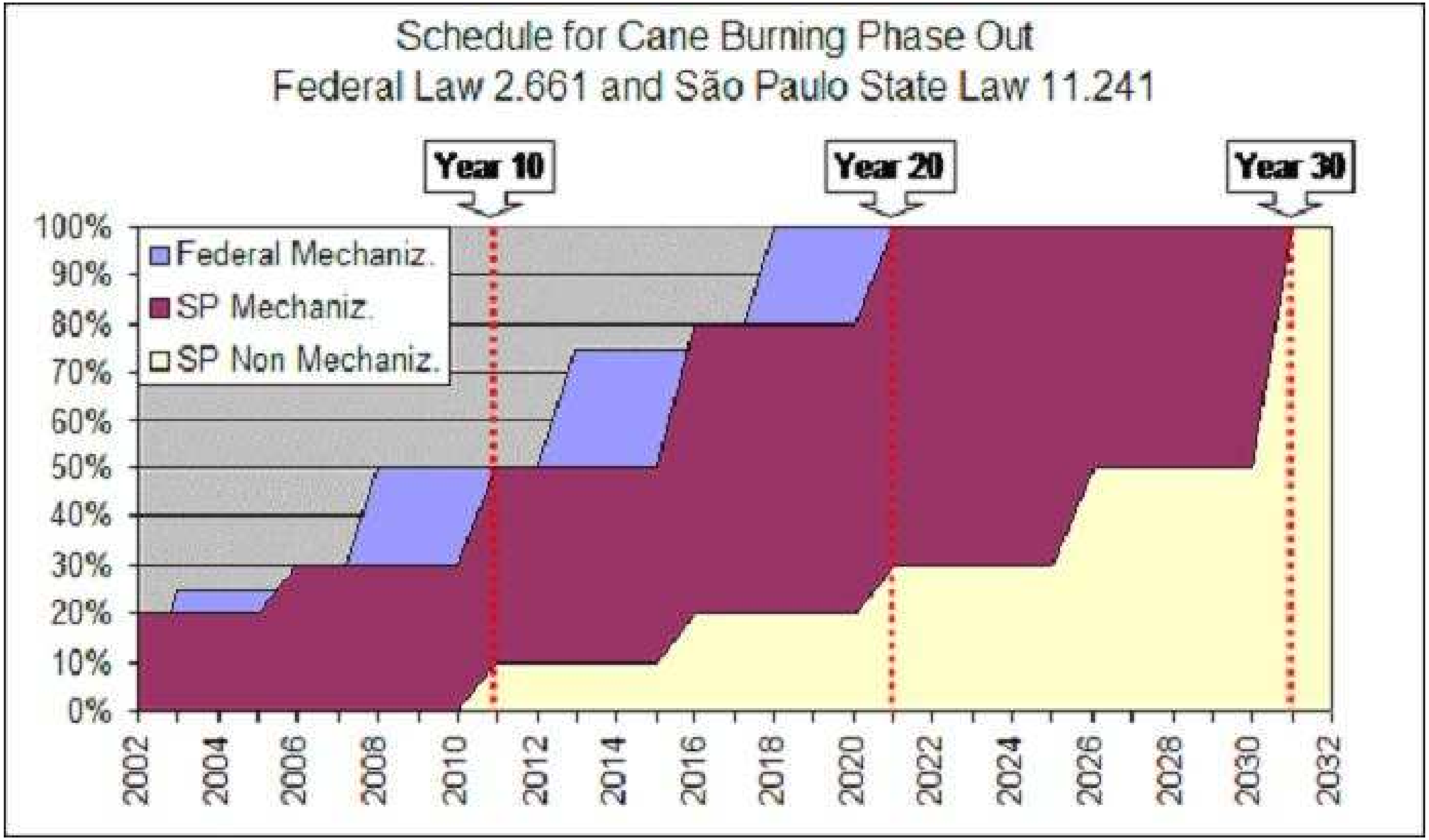
[1] Rossel, C. *in* Franco, T.T. (ed). Proceedings Workshop *Industrial perspectives for bioethanol*. Instituto UNIEMP. Sao Paulo, april 2006

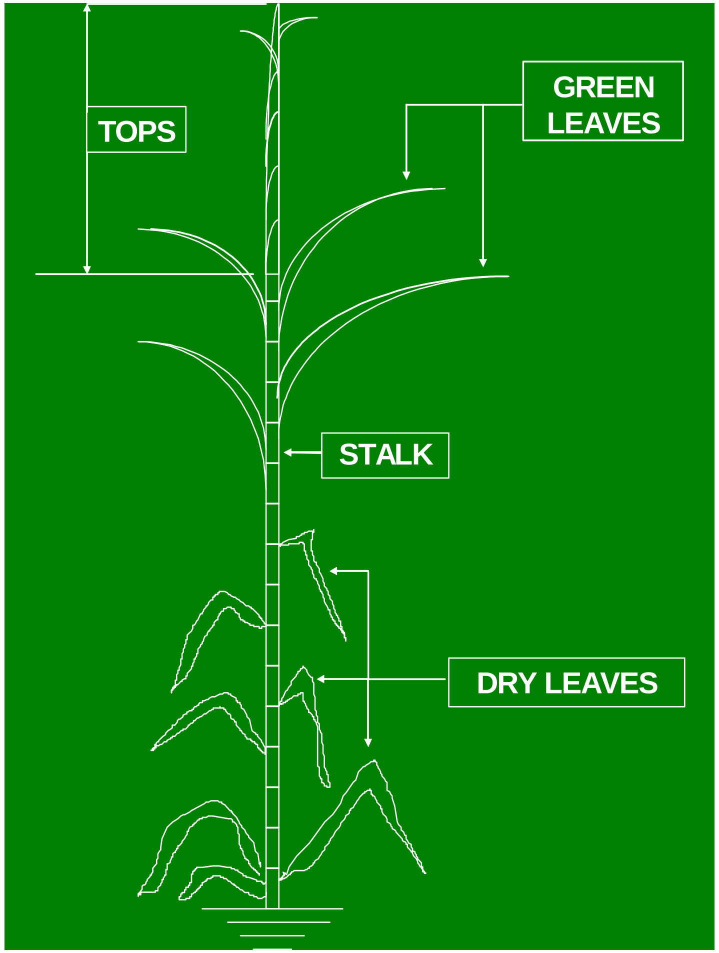
[2] Study of sugar cane bagasse characteristics: particle shape and size, free-settling velocity, and drag coefficient. B.Chem.Eng.J., Nebra, S& Harold Sosa-Arnao , 2006

Moving towards mechanization harvest

SUGAR CANE BURNING PHASING OUT

SUGAR CANE BURNING PHASING OUT



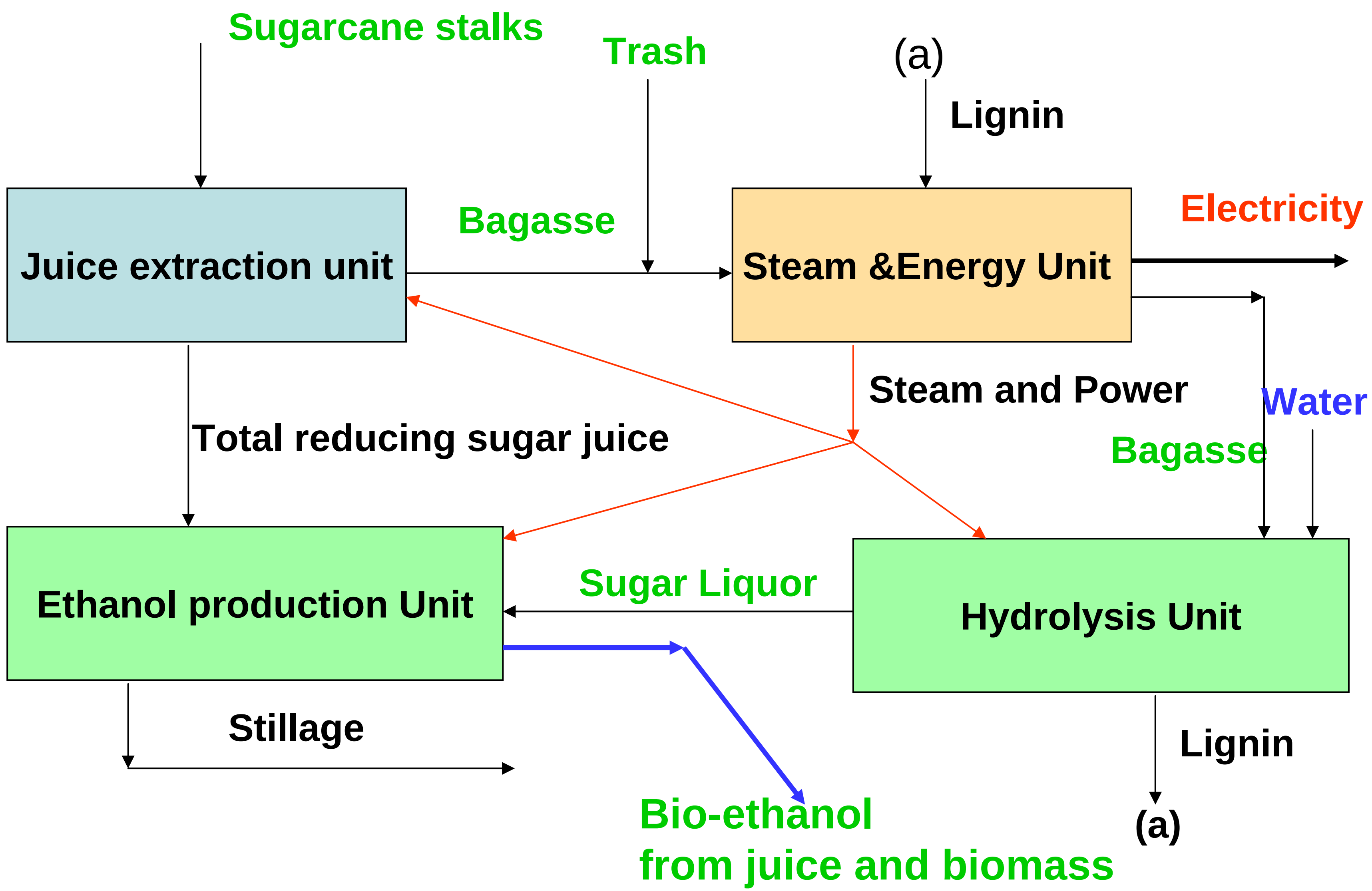


Variety	Cut	Average		
		Stalks (t/ha)	Trash (DM) (t/ha)	Trash % to Stalks
SP79-1011	1º C*	120,0	17,8	15%
	3º C	91,5	15,0	16%
	5º C	84,2	13,7	16%
SP80-1842	1º C*	135,8	14,6	11%
	3º C	100,5	12,6	13%
	5º C	91,6	10,5	11%
RB72454	1º C*	134,3	17,2	13%
	3º C	99,8	14,9	15%
	5º C	78,2	13,6	17%
Average		**104,0**	**14,4**	**14%**

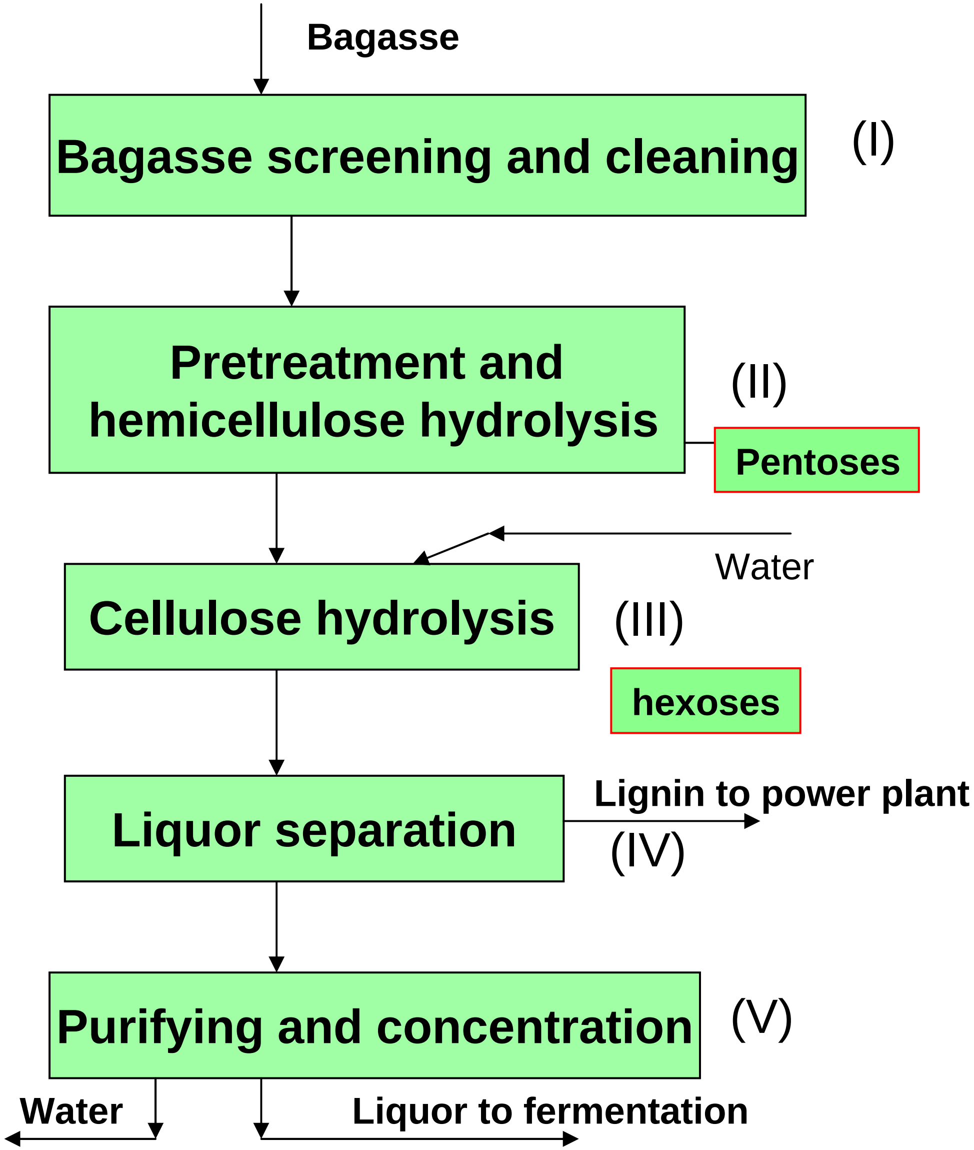

Thick trash layer


FIATALLIS

Sugarcane process to bioethanol and power introducing Hydrolysis



Hydrolysis Steps

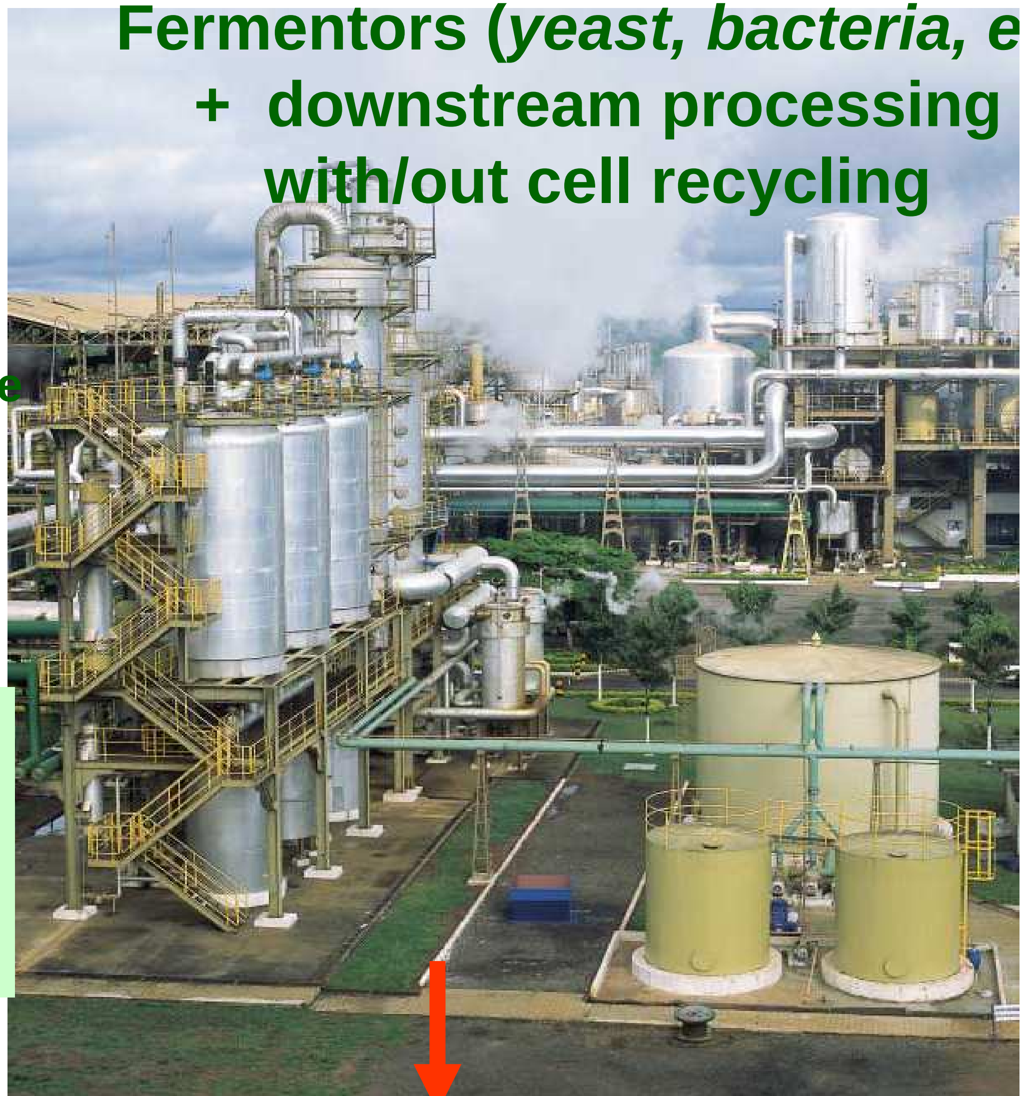


- **(I)** **Rind, pith and sand removed from fiber**
- **(II)** **Delignifying and hemicellulose hydrolysis step**
- **(III)** **Cellulose conversion by enzyme catalysis**
- **(IV)** **Liquor separation from lignin and washing**
- **(V)** **Removal of inhibitors and concentration of liquor, recover of condensed water for reuse in process**

Aim: Biorefinery for chemicals/biochemicals &polymers

Sugar-cane crushed

Fermentors (*yeast, bacteria, e*
+ downstream processing
with/out cell recycling



Sugar-cane (juice+ trash and bagasse)
Sucrose
Glucose
Pentoses
Lignin

Acrylic acid, ethanol, organic acids, polymers, …

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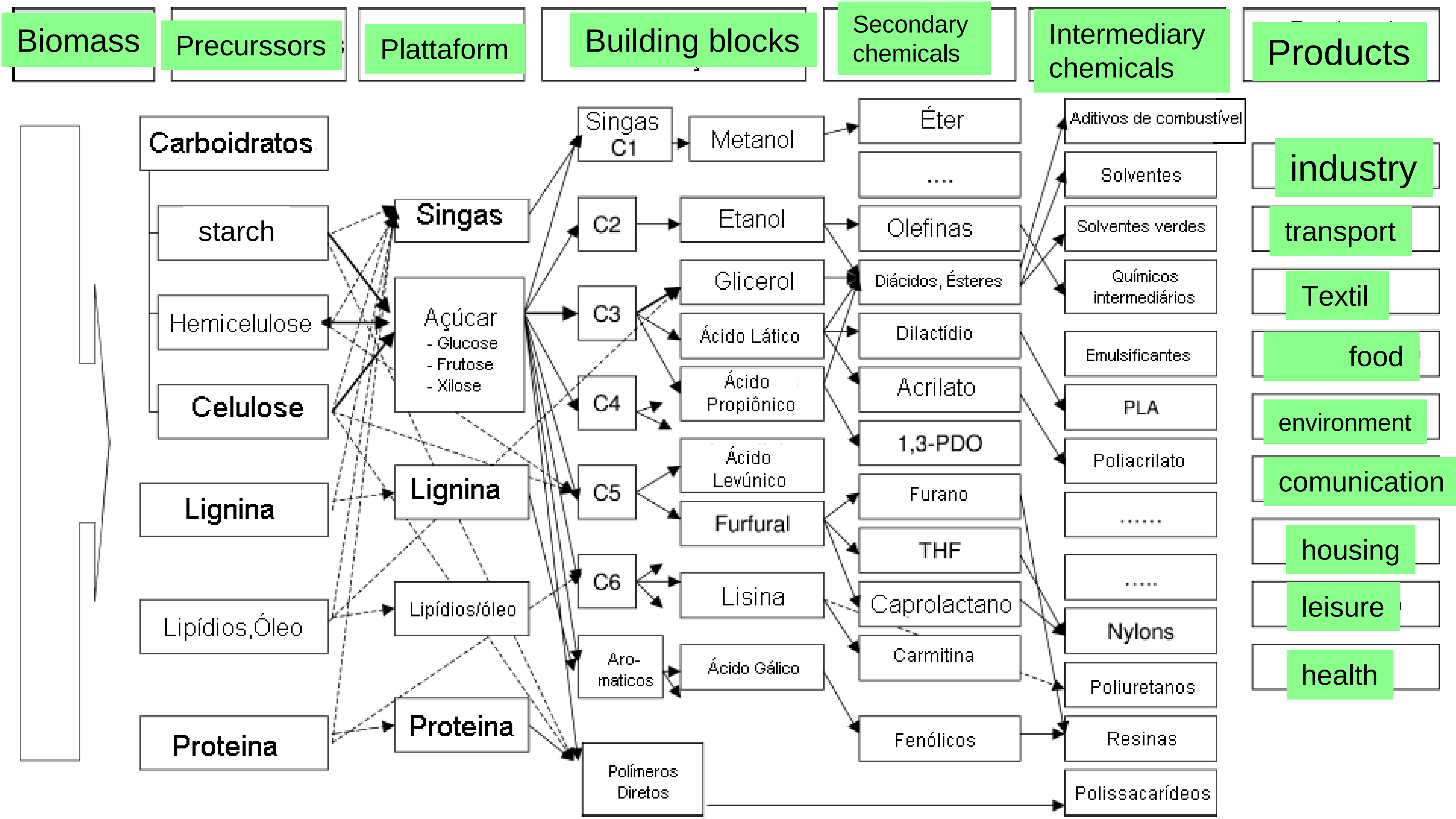
Biobased product flow-chain from biomass feedstock



Kamm & Kamm, 2006

Products presently produced from sugar-cane - Brazil

Secondary chemicals and products

Renewable Biomass feedstock

- Hemicellulose
- Cellulose

→

Sugars
Glucose
Fructose
Xylose
Arabinose
Sucrose

Intermediate Platform

C2

C3

C4

C5

C6

polymers

→

Fermented chemicals

- Lysine, glutamate
- Citric acid
- Lactic acid
- Fumaric acid
- Acetic acid
- 2,3 butanediol
- Acetone/butanol
- Bioethanol
- Xylitol
- Polyhydroxybutyrate
- Xanthane

\+

Chemicals & products

- Hydrolysed bagasse
- Bagasse fibers for paper industry
- Acetylated fibers
- Furfural
- Fructose/glucose
- Xylose
- Sorbitol
- Glycerol
- Ethyl acetate
- Liquid fertilizers
- Yeasts
- Polyethylene
- Polypropylene (in preparation

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From: INDUSTRIAL PERSPECTIVES FOR BIOETHANOL. ed. Telma Teixeira Franco, Editora Uniemp, Sao Paulo, ISBN 85-98951-06-4, 2006.

1º Company: CTC canavieira
(formerly Copersucar)

The Centro de Tecnologia Canavieira is the leading sugarcane research institute in Brazil, developing new varieties with improved processing efficiency and yield.

It is further involved in phytosanitary research, biotechnology, agronomy, agricultural and industrial mechanisation as well as sugar, bioenergy and biofuel production itself.

The CTC is a non-profit whose aim is to disseminate knowledge, best practises and inputs to the sugarcane sector in Brazil.

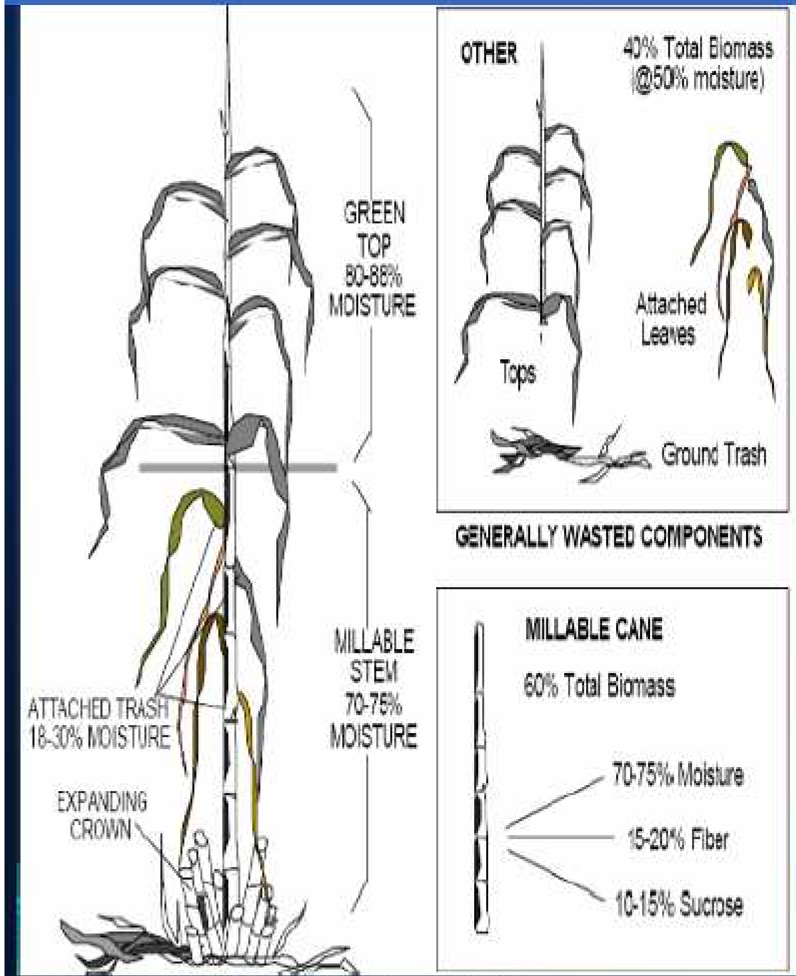
For the CTC, the success can be measured by the growing number of distributers and producers that join its program and offer its new varieties to planters. In 2004 the Center had 73 associates. **Today the number has reached 163, which results in the CTC's sugarcane plants covering 54.4 percent of the total harvested in Brazil.**

An example, CTC11 yields an average of 8.43 percent more biomass per hectare compared to existing varieties, but the liquid margin is R$539 (€210/$308) or 37.85 percent higher than the average. This is due because of a better performance on all parameters that count in sugar and ethanol production: higher sucrose content, better harvesteability and processing and improved tolerance to diseases, reducing the risk of losing harvests - a factor against which producers hedge, which costs money

CTC canavieira (formerly Copersucar)

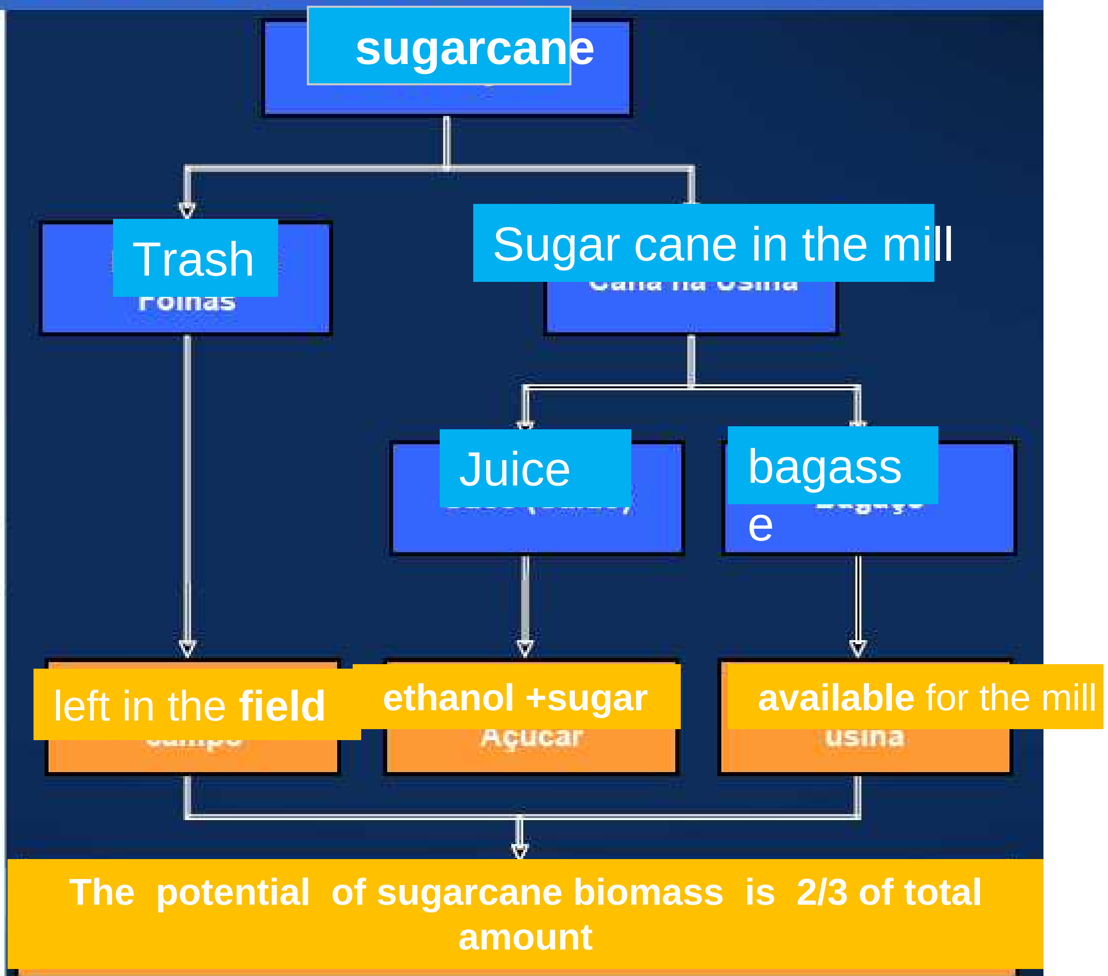
Alellyx and Canavialis

Campinas, São Paulo



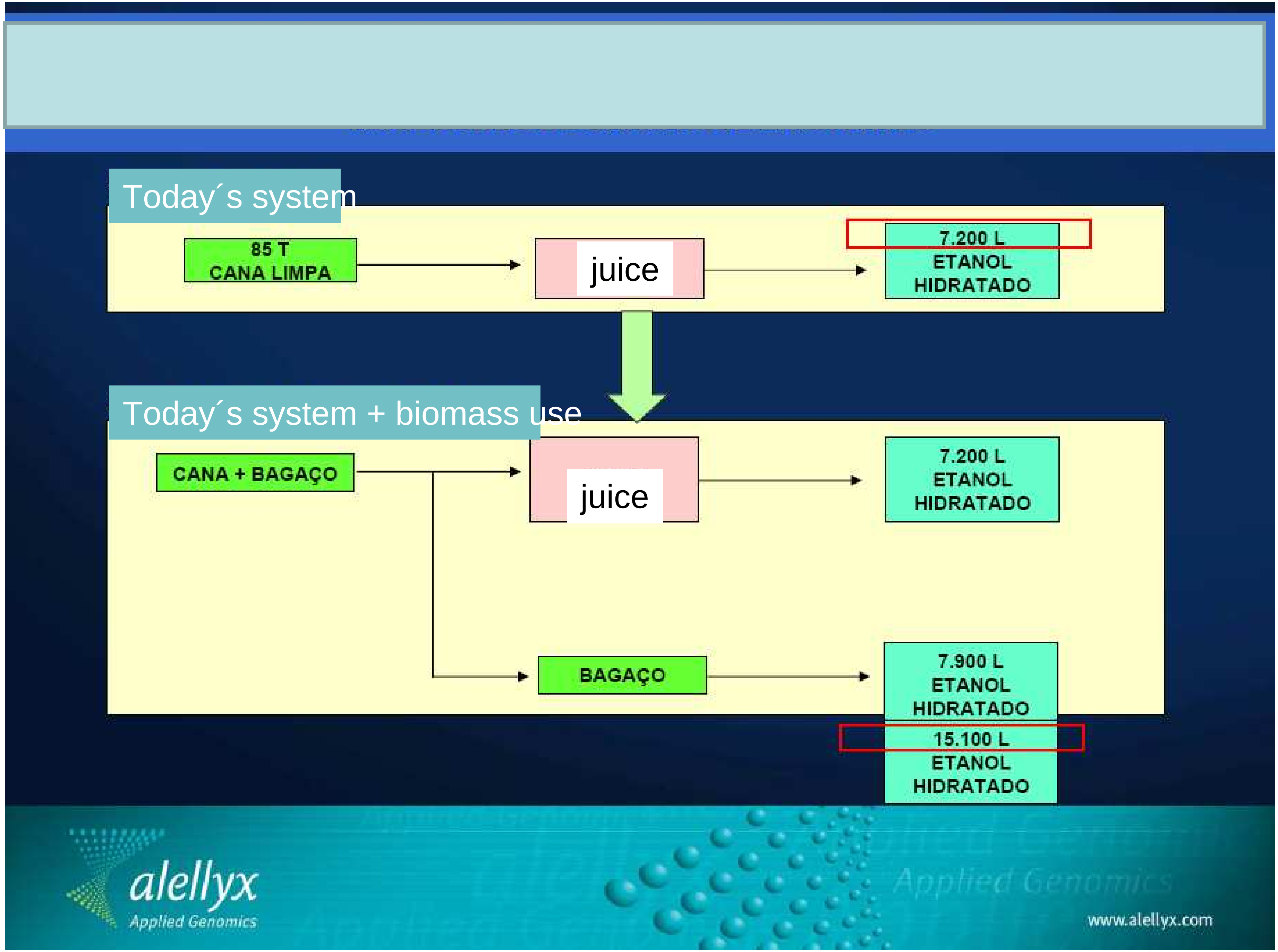
Source: Alellyx; Clippings; VNN Analysis

Source: *Alellyx*



1/3 total carbon → trash (left in the fields)

1/3 → bagasse (usualy burned)



Today´s system
85 T
CANA LIMPA
juice
7.200 L
ETANOL
HIDRATADO
Today´s system + biomass use
CANA + BAGAÇO
juice
7.200 L
ETANOL
HIDRATADO
BAGAÇO
7.900 L
ETANOL
HIDRATADO
15.100 L
ETANOL
HIDRATADO
alellyx
Applied Genomics
www.alellyx.com

Further improvement can be achieved with plants producing higher biomass content rather than only sucrose

producitivity	Ton/ha (Wet mass)	Ton/ha (Dry mass)
Conventional sugarcane	70 - 120	21 - 36
Energy cane (sugarcane ↑ biomass content)	140 - 240	49 - 84

(Liter ethanol/ha)

biomassa	Sucrose	cellulose	hemicelluse	total
Conventional sugarcane	7.200	5.900	2.000	15.100
Energy cane (sugarcane ↑ biomass content)	11.500	14.450	4.250	30.200

"ENERGY OR FIBER CANE"

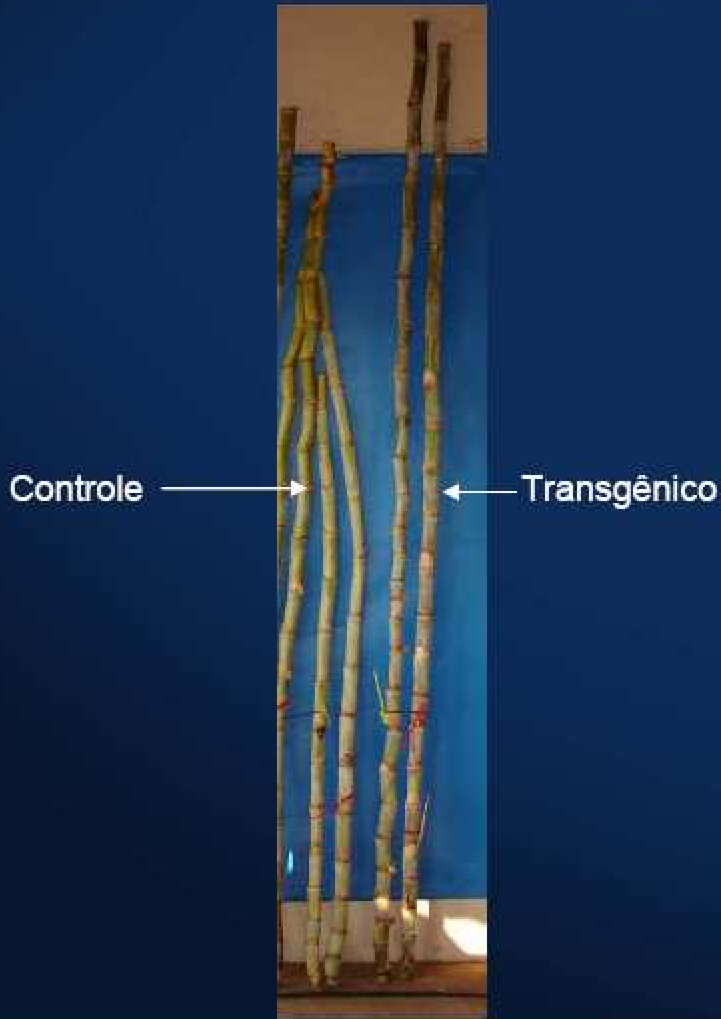
[redacted]

Source: *Alellyx*

Applied Genomics

www.alellyx.com

Source: *Alellyx*



Source:
Alellyx

Applied Genomics

www.alellyx.com

Alellyx and Canavialis → now Monsanto

News Releases
Monsanto Company →has invested in technologies for Sugarcane, by buying CanaVialis and Alellyx to combine their expertise to enhance production of sugarcane and biofuels to meet growing global demands.

$290 million

Votorantim Novos Negocios Ltda. and Votorantim Industrial S.A. are part of the Brazilian industrial conglomerate, Votorantim Participacoes S.A. (commonly referred to as the Votorantim Group).

CanaVialis and Alellyx will allow us to combine our breeding expertise with key large-acre crops with their breeding expertise in sugarcane.

Petrochemical companies

1.Petrobras - CENPES research center in R.J.

2.Braskem

3.Oxiteno

Project design and process development:

4. DEDINI

Second generation Bioethanol PETROBRAS

PETROBRAS

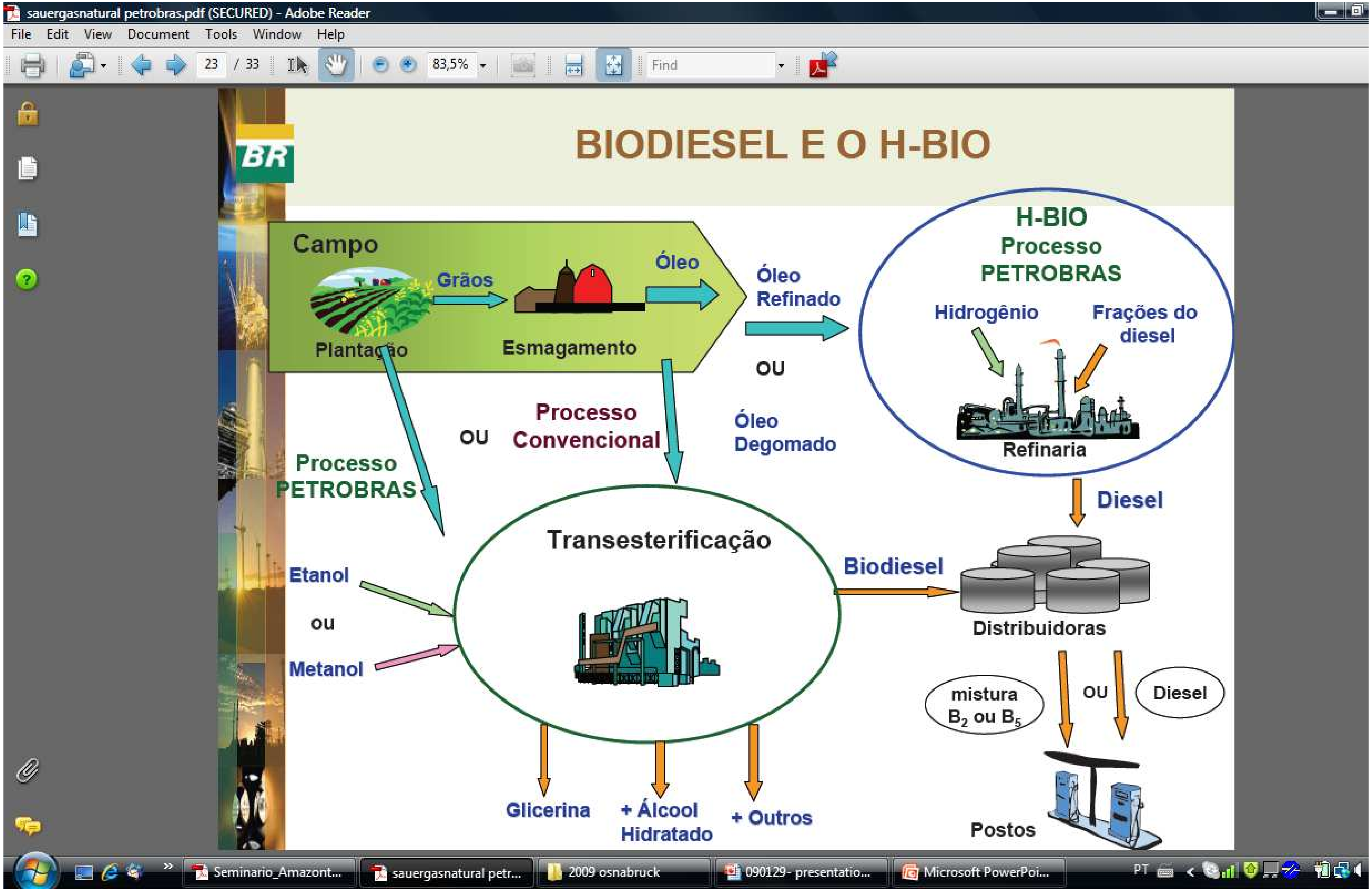
1. In the first stage, the sugarcane bagasse is pre-treated via the mild acid hydrolysis process →the crystalline structure of the sugarcane bagasse fiber breakdowns & recovery of sugars that are easier to hydrolyze;

2.Delignification stage (to remove the lignin, which also greatly inhibits the fermentation process);

3.In the third phase, the liquid derived from the pre-treatment with acid, which is rich in sugars, is fermented using the *Pichia stipitis* yeast;

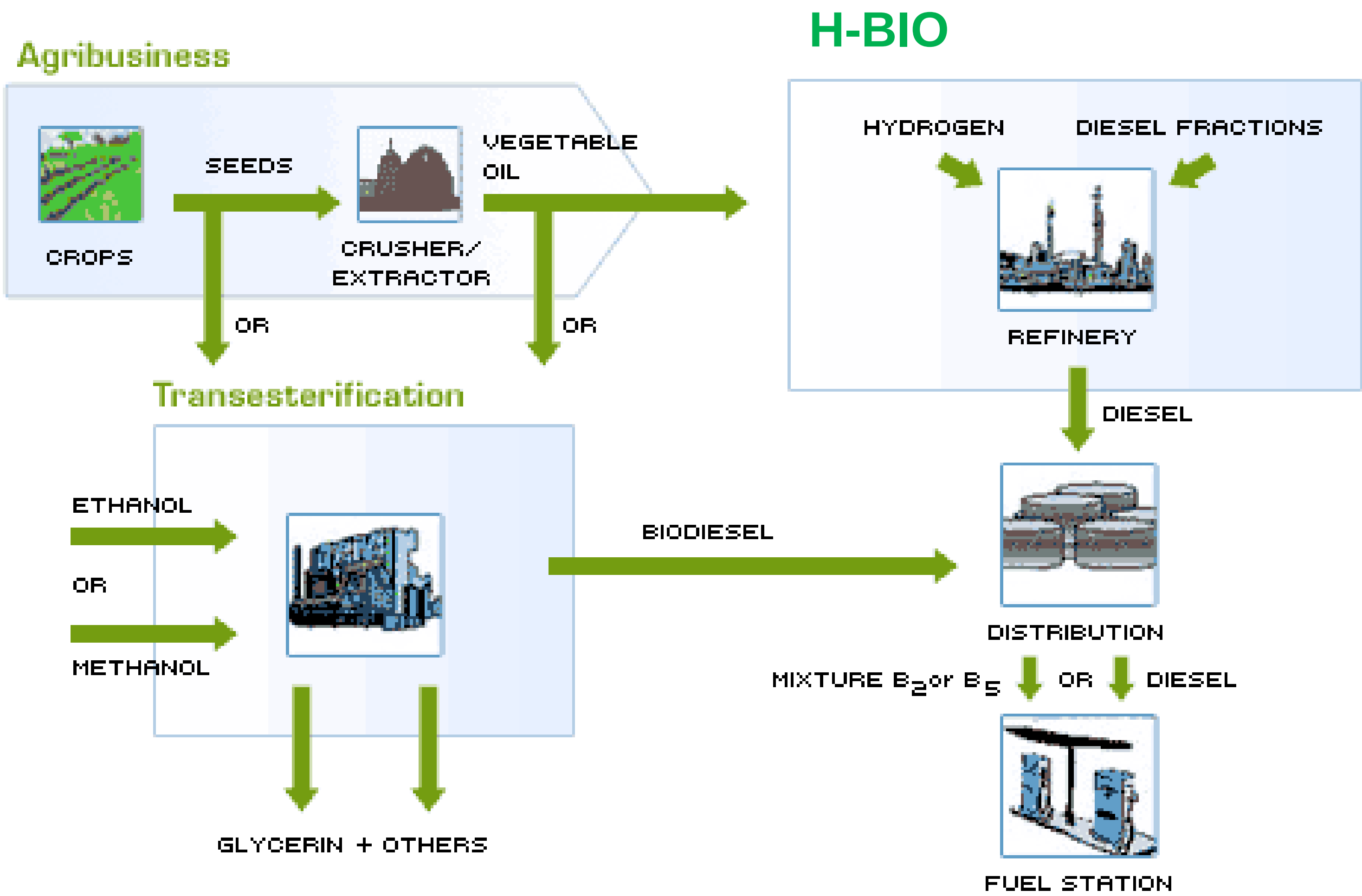
4.The cellulose-rich solid material is enzymatically depolymerized (saccharification process) (transformation into sugar) and is fermented by the *Sacharomyces cerevisiae;*

5.Final stage, both liquids derived from the different fermentations are distilled. The product of this distillation is ethanol, which has the same characteristics as that made out of sugarcane in the industrial process



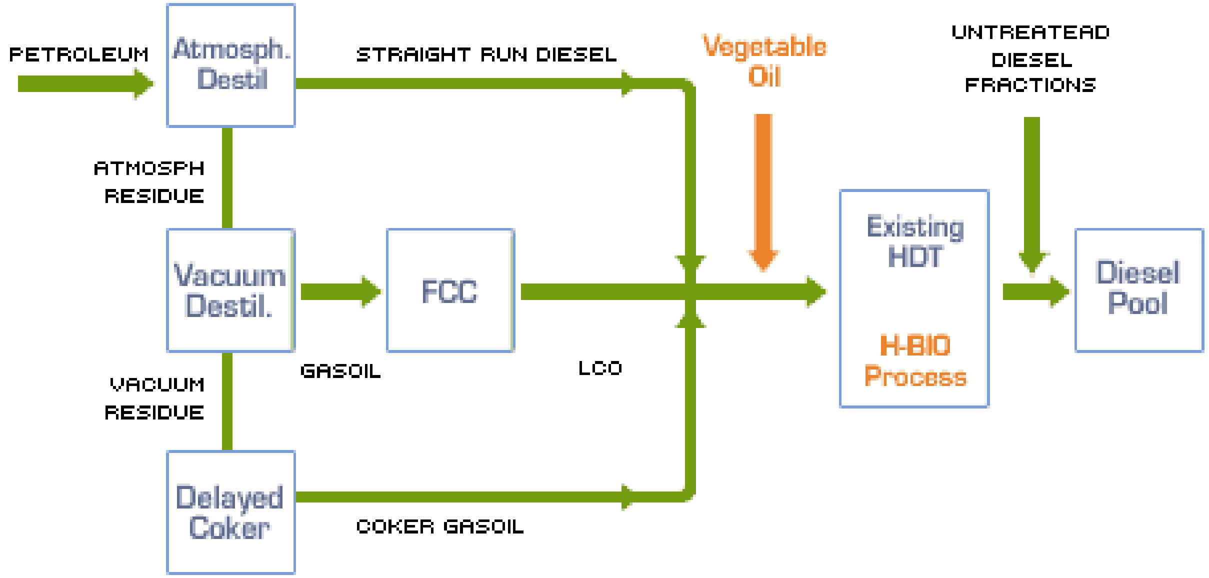
BIODIESEL E O H-BIO
Campo
Grãos
Óleo
Plantação
Esmagamento
Óleo Refinado
OU
H-BIO
Processo PETROBRAS
Hidrogênio
Frações do diesel
Refinaria
Óleo Degomado
Processo Convencional
OU
Processo PETROBRAS
Diesel
Transesterificação
Biodiesel
Distribuidoras
Etanol
ou
Metanol
mistura B_2 ou B_5
OU
Diesel
Glicerina
+ Álcool Hidratado
+ Outros
Postos

Renewable Diesel Production Routes



H-BIO process and yields in a Typical Refinery Scheme

The converted product improves the diesel quality of the refinery, by ↑ the cetane number, ↓reducing the sulphur content and ↓ density.
This pool quality ↑ will be a consequence of the % vegetable oil used in H-BIO process.



- H-BIO process is currently operating in three refineries with soybean oil, and others are planned.
- The Petrobras H-BIO technology introduces a new way to include renewable feedstocks for bio-fuels in addition to the Brazilian program.
- This process generates environmental benefits and improves social inclusion.

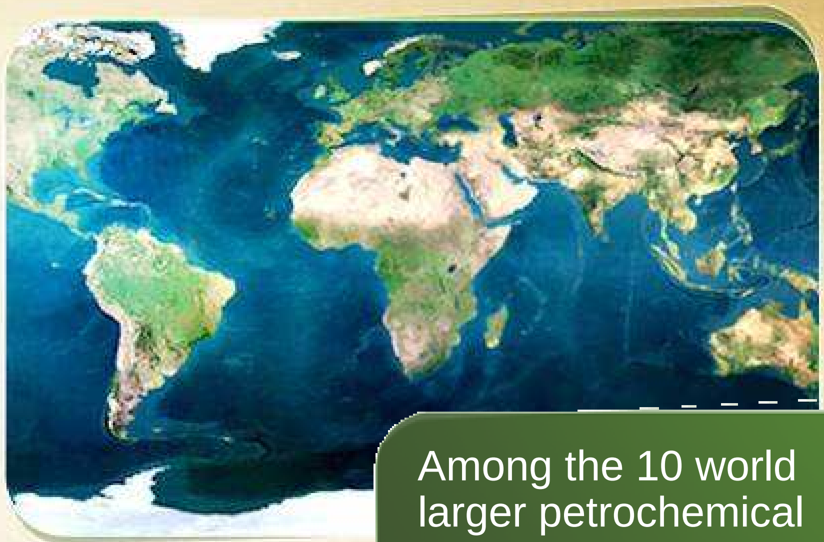
Braskem Strategic Vision
Growth with value creation

The green polyethylene project reassures Braskem's commitment with **technological innovation and sustainability in its strategy**

2002

Leader in Latin America in thermoplastic resin

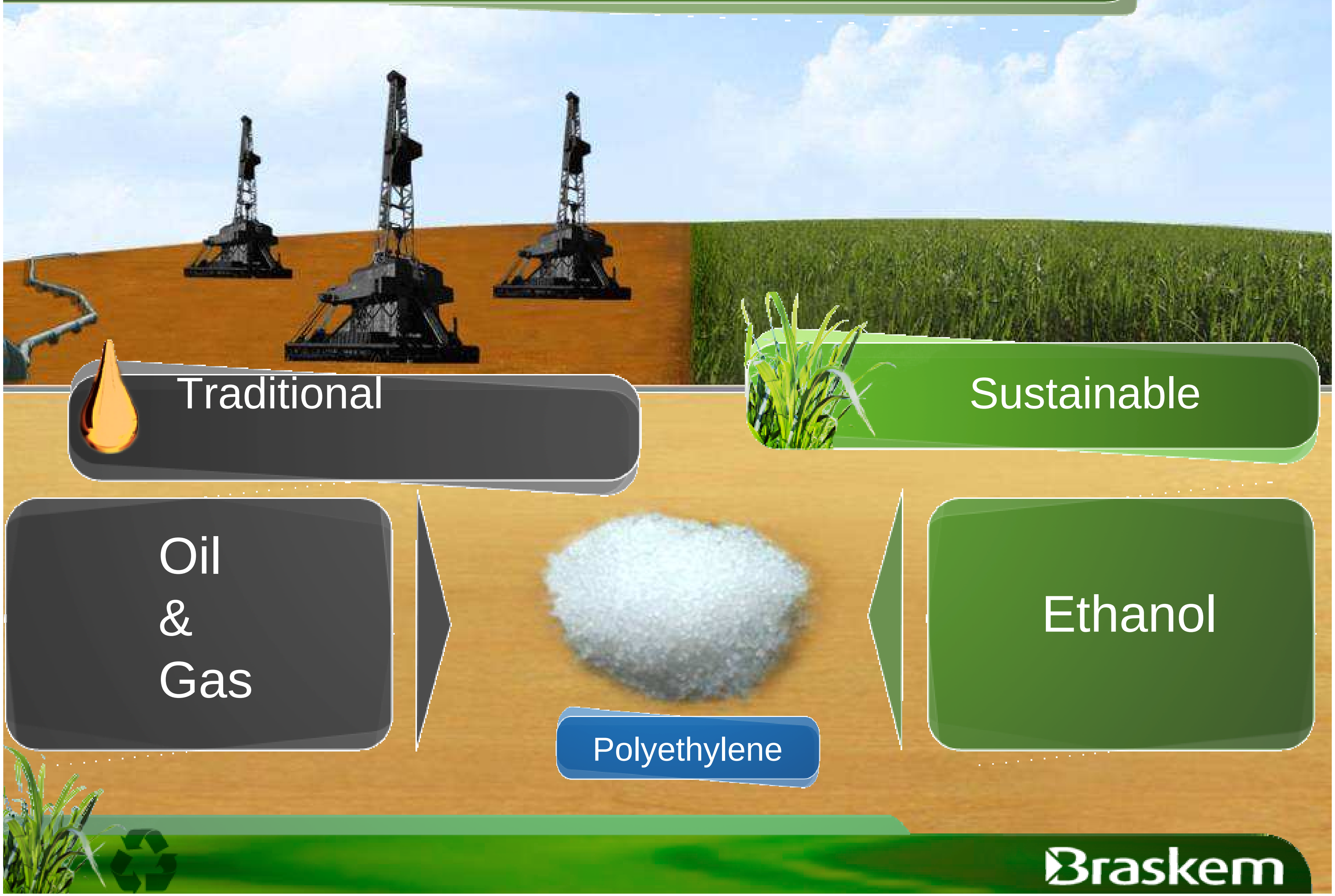
2012



Among the 10 world larger petrochemical in market value

Braskem

Green Polyethylene
An alternative to traditional PE



Sugarcane as a carbon capture crop

The amount of lignocellulosic carbon in the leaves and fibers allows the ethanol process to be self-suficient in biobased energy, when burning it

Brazil
Unparallel conditions for sugar cane crop

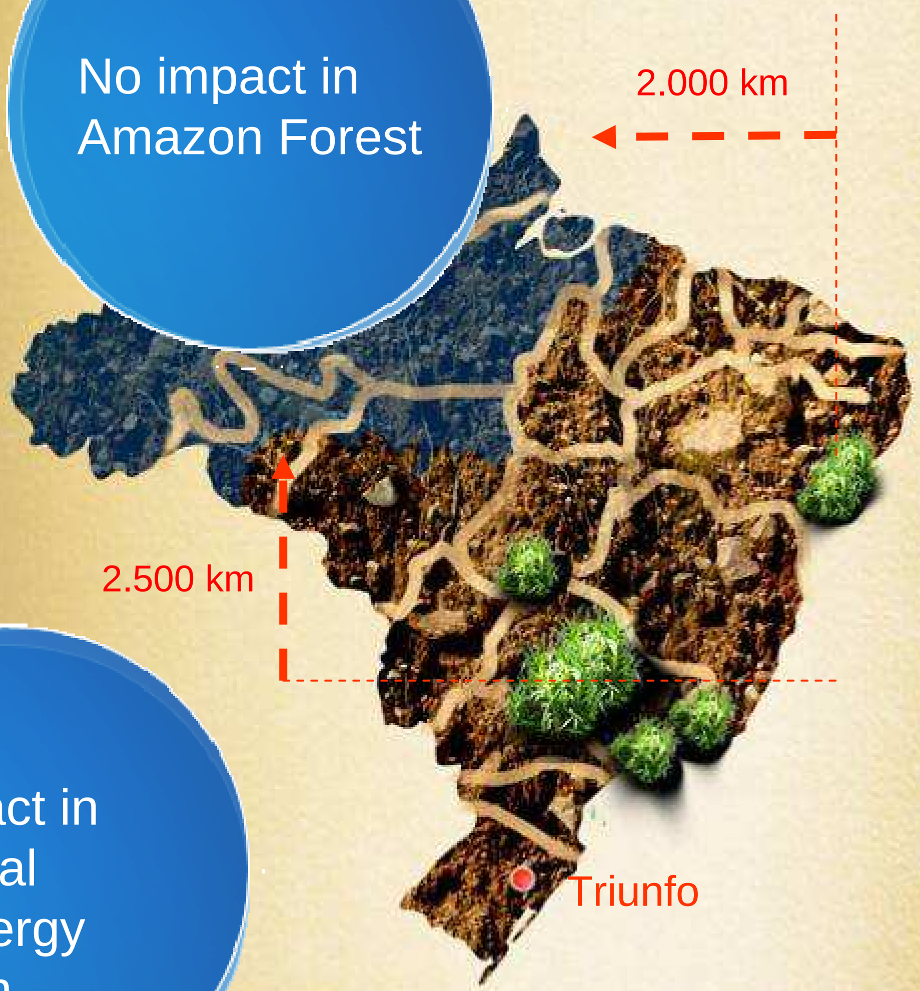
Brazil has 22% of arable land in the world (340 MM ha)

Only 18,6% of arable land are cultivated so far

Sugarcane:	7,8 MM ha
For Ethanol: 3,4 MM ha (1% of arable land)	
Soy:	22 MM ha
Corn:	14 MM ha
Pasture/cattle:	220 MM ha
(50% degraded land)	

No impact in Amazon Forest

No impact in the global food/energy equation



Braskem green Polyethylene
Credibility

The biobased content of the green PE can be certified in any step in the chain – in the converter or directly in the supermarket shelf

Green Polyethylene Production
Certification and market development

ETHYLENE PILOT PLANT

POLYMERIZATION LABORATORY

POLYETHYLENE PILOT PLANTS

PRODUCTS

Braskem green Polyethylene
Leading global industrial scale supplier

Oil Chemistry

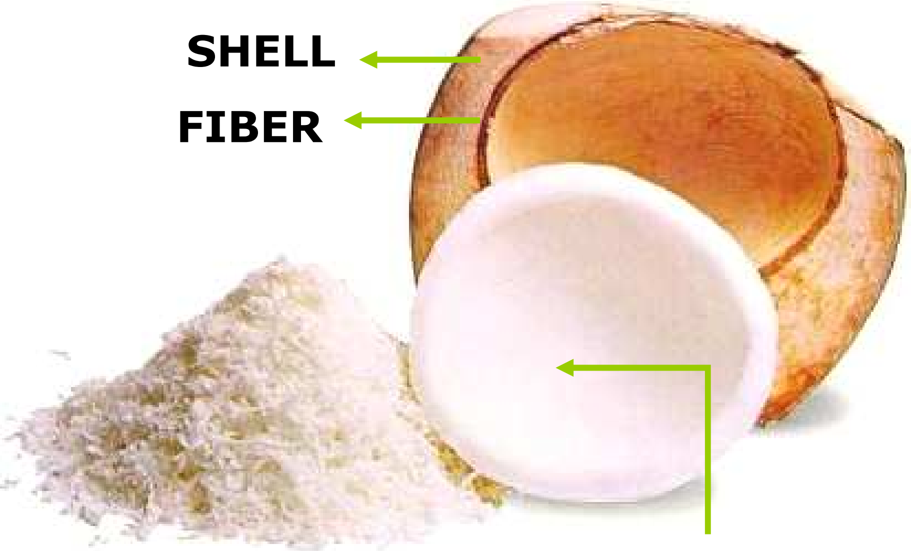
OXITENO

uma empresa do grupo ULTRA

Raw-material Source for Fatty Alcohol

SHELL

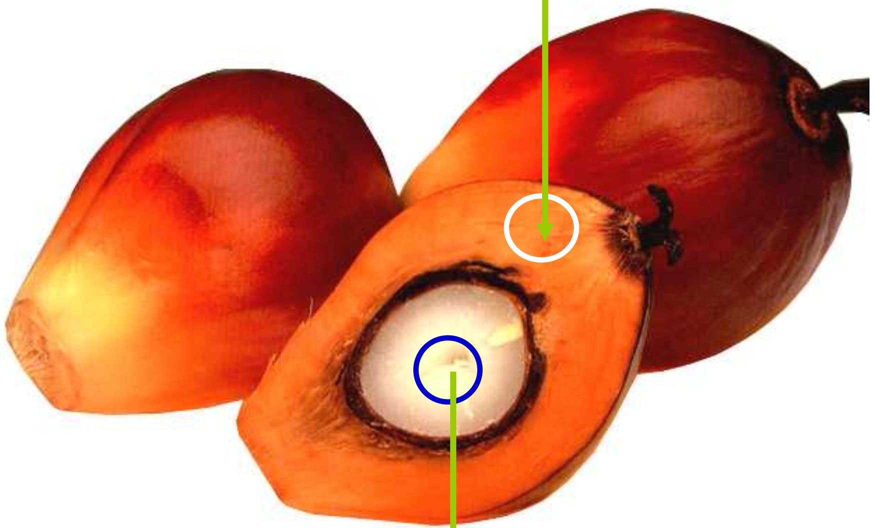
FIBER



PULP

Coconut Oil (CNO)

Crude Palm Oil (CPO)



Palm Kernel Oil (PKO)

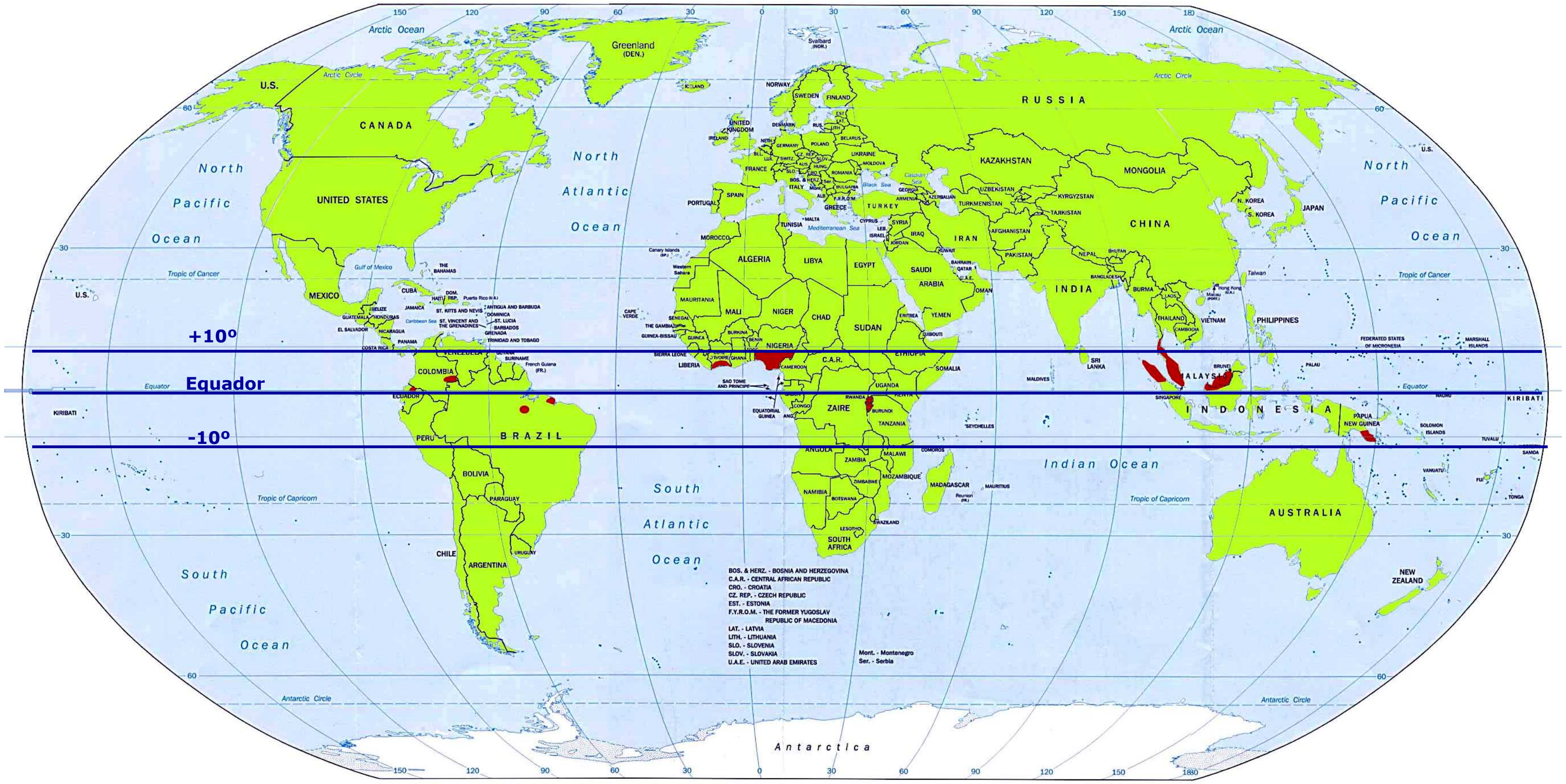
Raw material Sources : Fatty Distribution

Carbon Chain		PKO	CNO	CPO	Soya	Tallow
C6	Caproic	0,3	0,3	↓	↓	↓
C8	Caprylic	4,5	7,5			
C10	Capric	3,5	8,0			
C12	Lauric	48,2	46,7	0,2		
C14	Myristic	16,0	18,0	1,0		2,0
C16	Palmitic	7,5	9,0	44,0	6,5	35,0
C18 Total	Estearic	20,0	10,5	54,8	92,8	63,0
C20	Aracdic	↓	↓		0,7	

Values in percentage

Laurylic Oil

Main Areas for Palm Oil Culture



2005	Malaysia	Indonesia	Filipinas	Others
PKO	47%	36%	-	17%
CNO	8%	33%	51%	8%

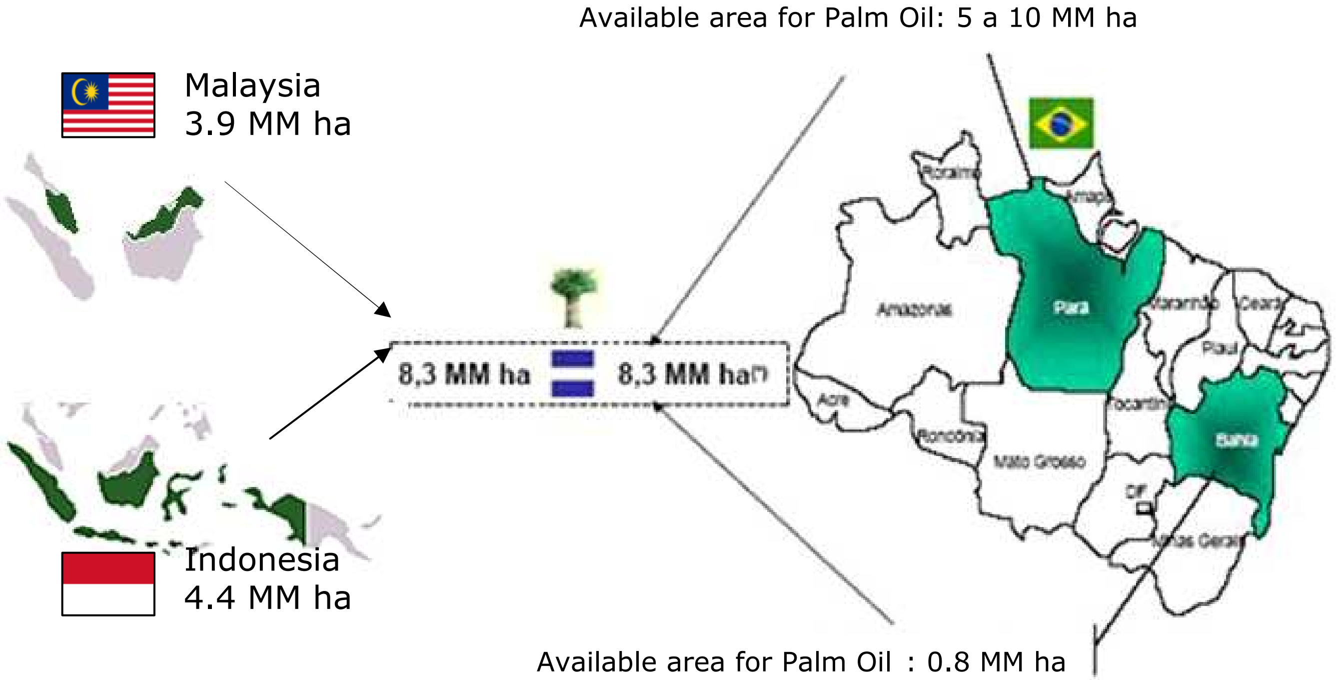
Brazil: Vegetable Oil Production (1000 ton.)

Cultura	Ano			%
	2002	2003	2004	
Soya	4,937	5,387	5,571	89.20
Cotton	196	217	268	4.30
Palm	**118**	**129**	**140**	**2.20**
Sunflower	56	62	75	1.20
Corn	46	55	64	1.00
Castor	40	40	61	1.00
Rapessed	17	20	23	0.40
Peanut	28	22	22	0.30
P. Kernel	**13**	**15**	**16**	**0.30**
Linseed	2	2	2	0.05
Coconut	2	2	2	0.05
TOTAL	**5,454**	**5,950**	**6,243**	**100**

2.5%

Brazil: Palm Culture Area

Good news – the available planting area in Brazil is equal to actual cultivated area in Malaysia and Indonesia



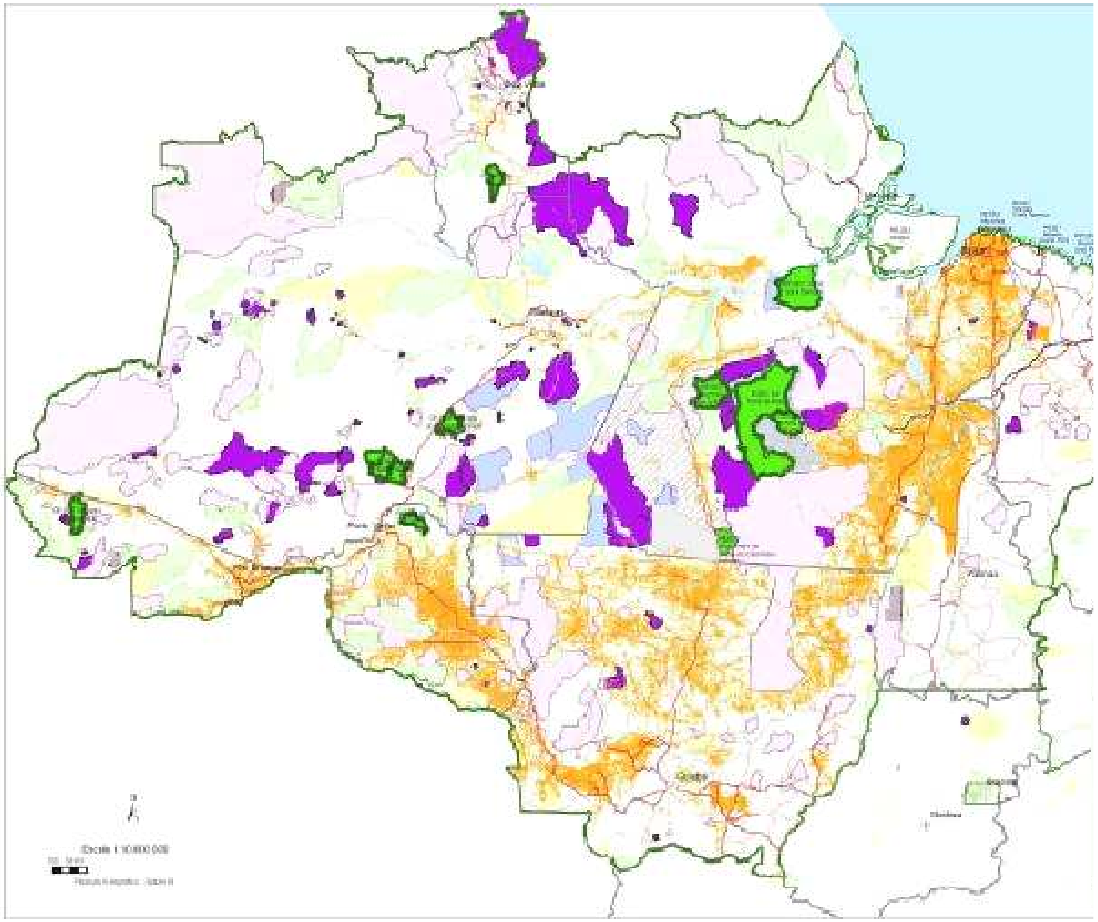
(*) considerando-se 7,5MM ha no estado do Pará

Fonte: Análise The Innovation Circle/Thompson

THOMPSON

The Innovation Circle

Amazon: Palm Culture Area

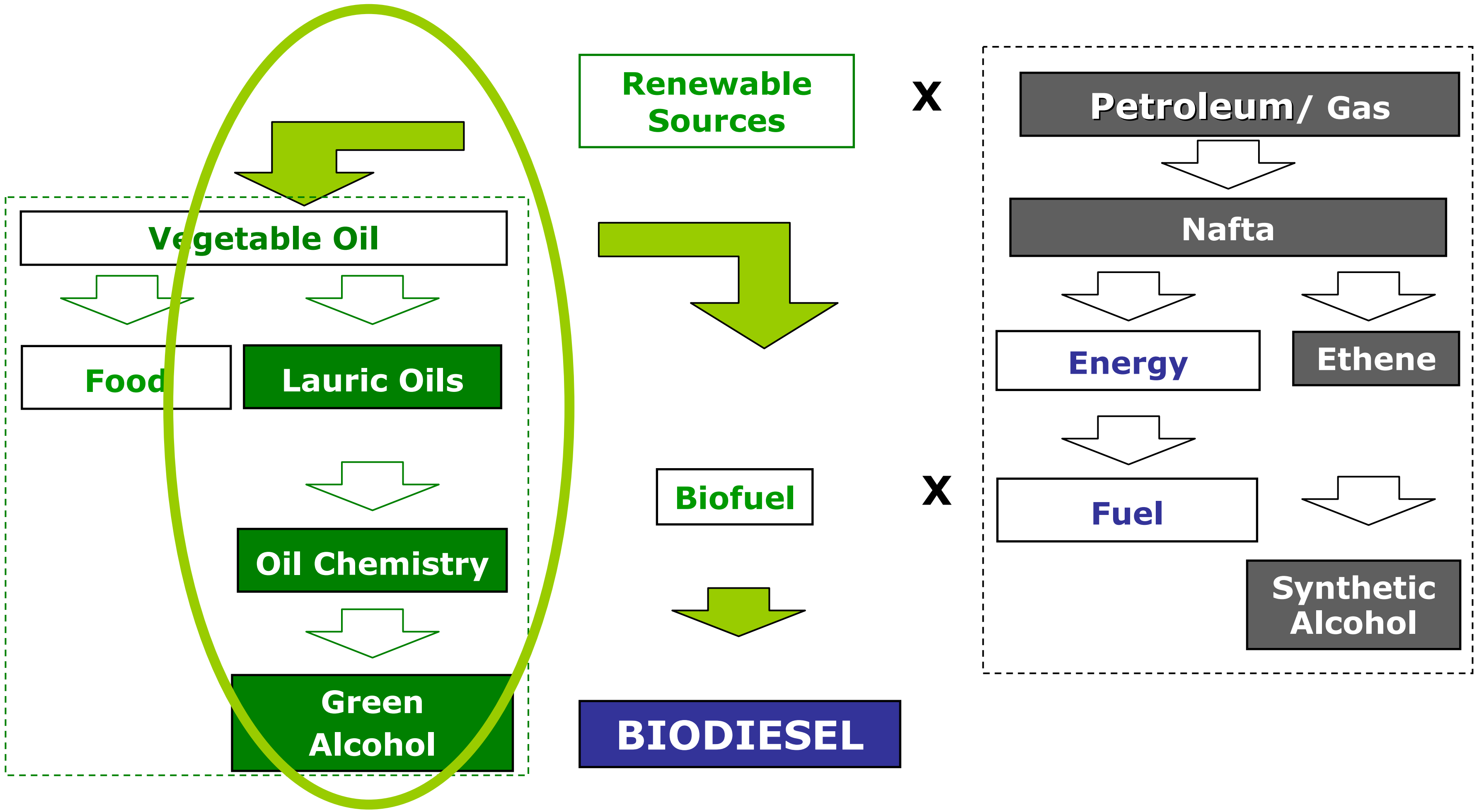


Deforested area until 2005

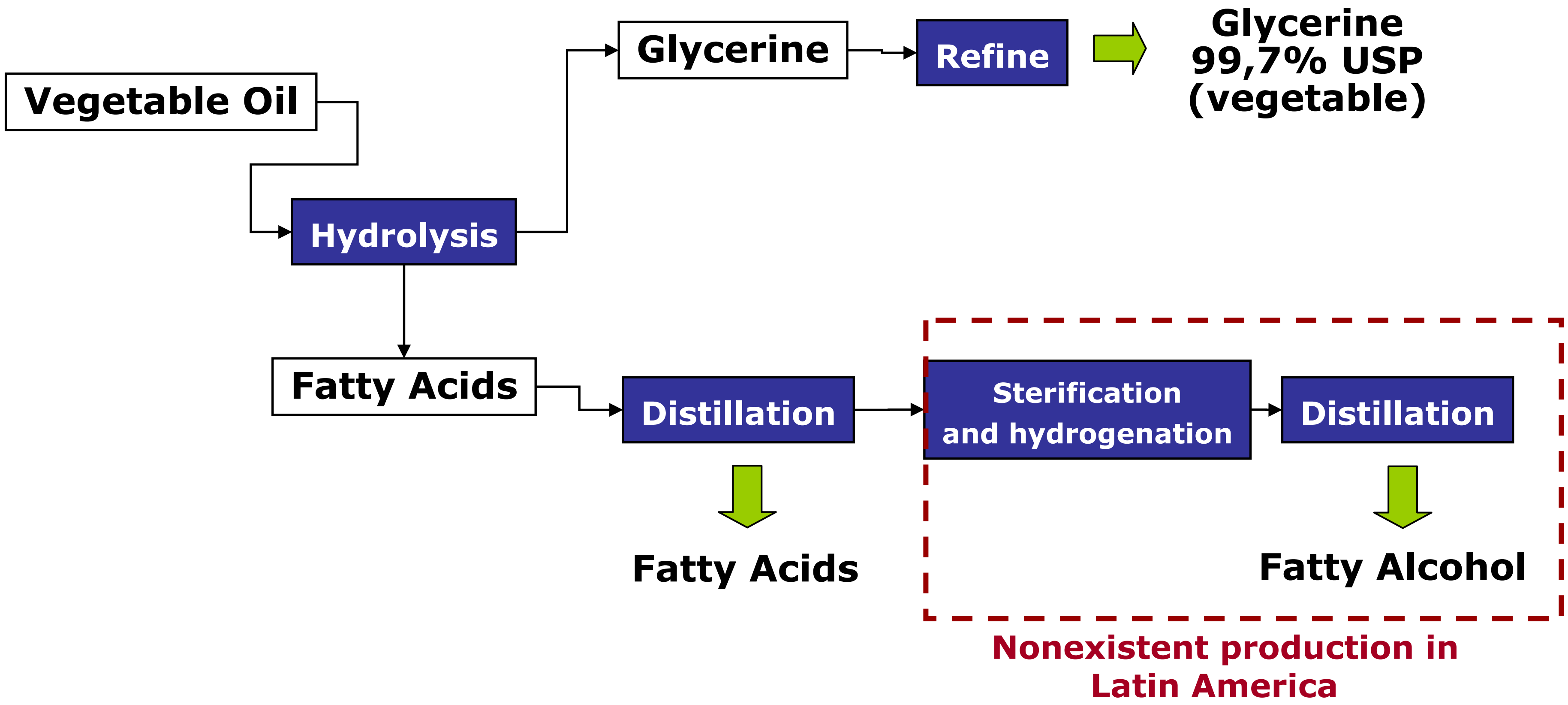
8,3 MM Ha, cultivated in Malaysia e Indonesia (2005)
7 % of Pará state

✓**Estimation for deforested area in Legal Amazon: around 65 million of ha.**

Petrochemistry x Oil Chemistry



Oil Chemistry productive process



Oxiteno Oilchemical Products

Products	Carbon Chain	Capacity ton/ano
Laurylic Alcohol	C12– C14	47,000
Stearylic Alcohol	C18	4,000
Cetylic Alcohol	C16	3,000
Cetostearilic Alcohol	C16 - C18	23,000
Caprylic-Capric Acid	C8-C10	7,000
Glycerine	C3	10,000

Toxicological Properties and Biodegradability

	Ethox. Fatty Alcohol	Ethox. Nonylphenol
Oral Toxicity DL50	2733 mg/Kg	2157 mg/Kg
Dermical irritability (0,2%)	Not irritating	Not irritating
Eye irritability (0,5%)	Moderate	Moderate
Biodegradability (DQO)	96,0%	92,6%

DEDINI

Over 87 years Dedini → efforts towards promoting the country's technological development, mainly with regard to the sugar-Ethanol sector.

Supplies complete Sugar Mills and Distilleries →turn-key system, equipment and integrated systems, starting with sugarcane reception, preparation and processing, extraction and juice treatment, steam generation and cogeneration of surplus power right through to Ethanol and sugar manufacture.

Responsible to more than 80% of the produced Brazilian bioethanol


1.000.000 m² [redacted]ril

DEDINI
INDÚSTRIAS DE BASE

New industrial vision of DEDINI

Maximization o the use of sugarcane

derivadas do foco em energia.

Biofuels

-BIOETANOL
- BIODIESEL

Bioelectricity

Com máximo aproveitamento energético da cana:
- Bagaço
- Palha (*)
- Co-produtos (vinhaça)

Bioproducts

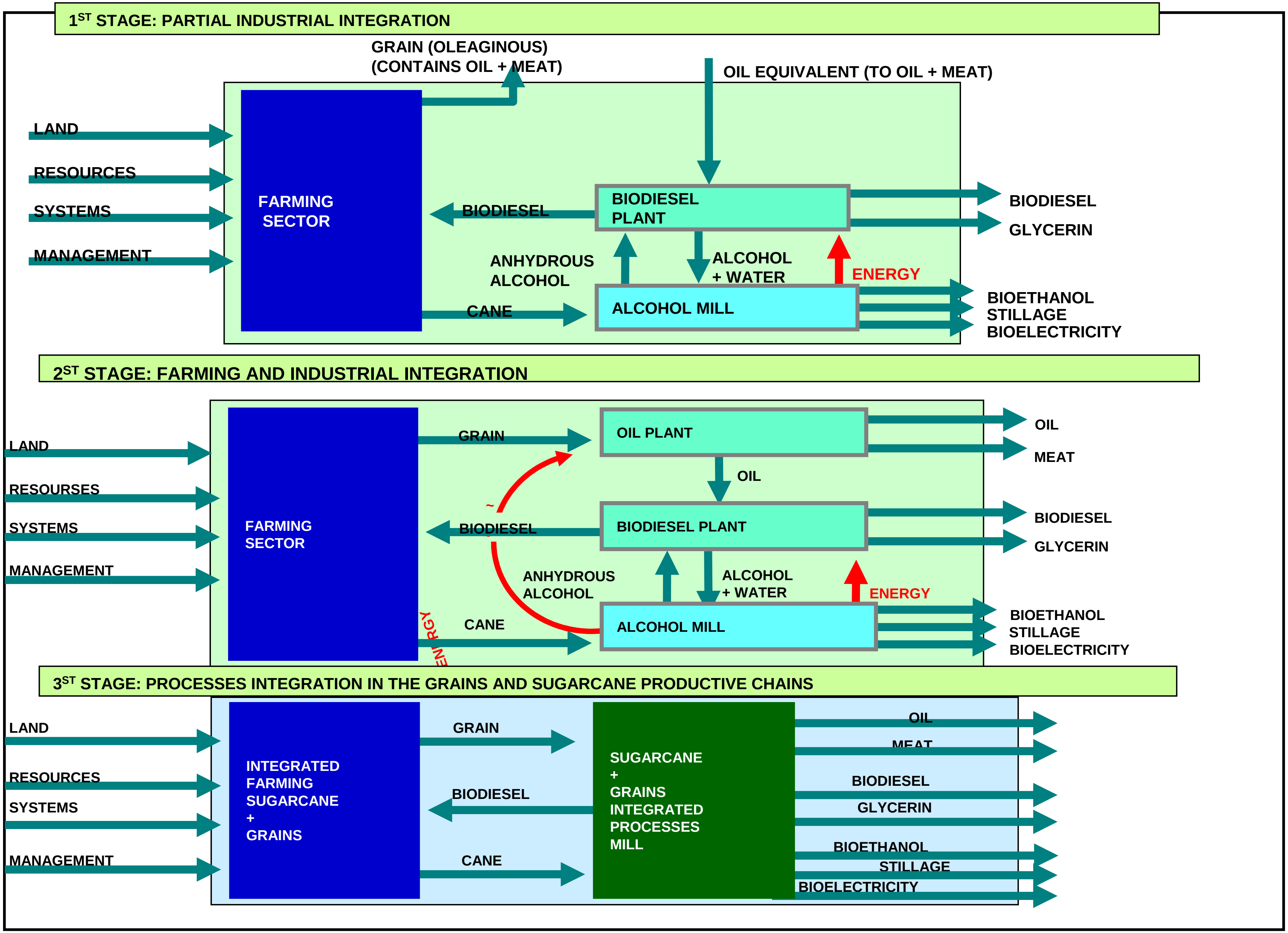
Biofertilizer
Bio water

The “3 BIO” revolution

Sugar and alcohol sector – Model of industrial technological evolution – 5 big stages by DEDINI

TECHNOLOGICAL EVOLUTION – 5 BIG STAGES

1. INCREASE OF EQUIPMENT CAPACITIES
2. INCREASE OF OVERALL YIELDS
3. GREATER USE OF SUGARCANE ENERGY
4. GREATER USE OF SUGARCANE PRODUCTS AND BYPRODUCTS
5. SUGAR AND ALCOHOL MILL DEFINED AS AN ENERGY-AND-FOOD PRODUCING UNIT


1ST STAGE: PARTIAL INDUSTRIAL INTEGRATION
GRAIN (OLEAGINOUS)
(CONTAINS OIL + MEAT)
OIL EQUIVALENT (TO OIL + MEAT)
LAND
RESOURCES
SYSTEMS
MANAGEMENT
FARMING SECTOR
BIODIESEL
BIODIESEL PLANT
BIODIESEL
GLYCERIN
ANHYDROUS ALCOHOL
ALCOHOL + WATER
ENERGY
CANE
ALCOHOL MILL
BIOETHANOL
STILLAGE
BIOELECTRICITY
2ST STAGE: FARMING AND INDUSTRIAL INTEGRATION
LAND
RESOURSES
SYSTEMS
MANAGEMENT
FARMING SECTOR
GRAIN
OIL PLANT
OIL
MEAT
OIL
BIODIESEL
BIODIESEL PLANT
BIODIESEL
GLYCERIN
ANHYDROUS ALCOHOL
ALCOHOL + WATER
ENERGY
CANE
ALCOHOL MILL
BIOETHANOL
STILLAGE
BIOELECTRICITY
3ST STAGE: PROCESSES INTEGRATION IN THE GRAINS AND SUGARCANE PRODUCTIVE CHAINS
LAND
RESOURCES
SYSTEMS
MANAGEMENT
INTEGRATED FARMING SUGARCANE + GRAINS
GRAIN
BIODIESEL
CANE
SUGARCANE + GRAINS INTEGRATED PROCESSES MILL
OIL
MEAT
BIODIESEL
GLYCERIN
BIOETHANOL
STILLAGE
BIOELECTRICITY

Integration of Bioethanol and biodiesel processes

Integration of Bioethanol and biodiesel processes Pioneer: BARRALCOOL, the first sugar mill to produce bioethanol + biodiesel and bioelectricity

PIONEIRISMO DEDINI

Presentation of the new concept: 2004, project sale: november 2005,

Ethylic route → flex routes
Capacitiy: 50,000 tom/year, continuous process

DEDINI

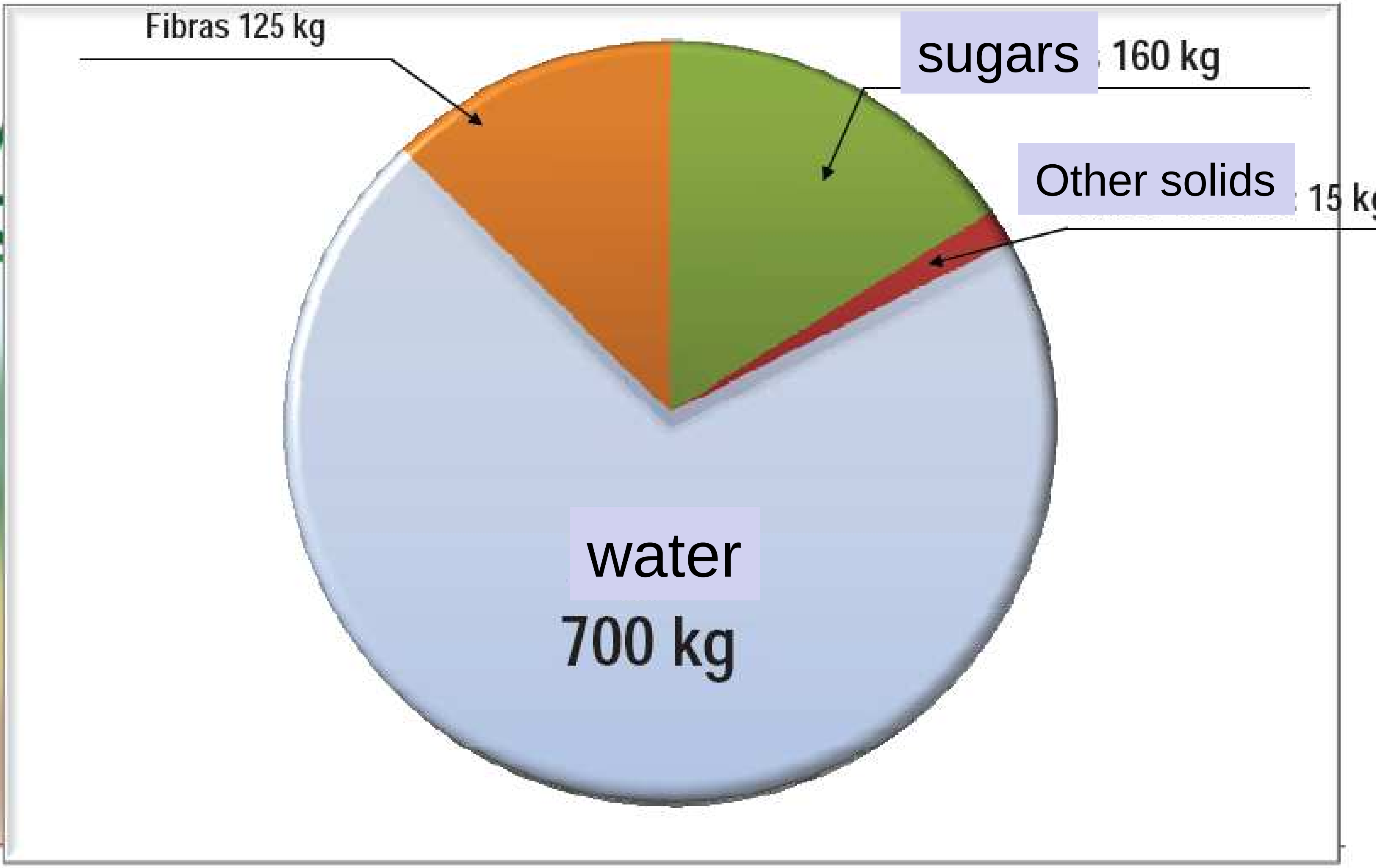
Integration of Bioethanol and biodiesel processes

Bioproducts

Biofertilizer → vinasse is concentrated

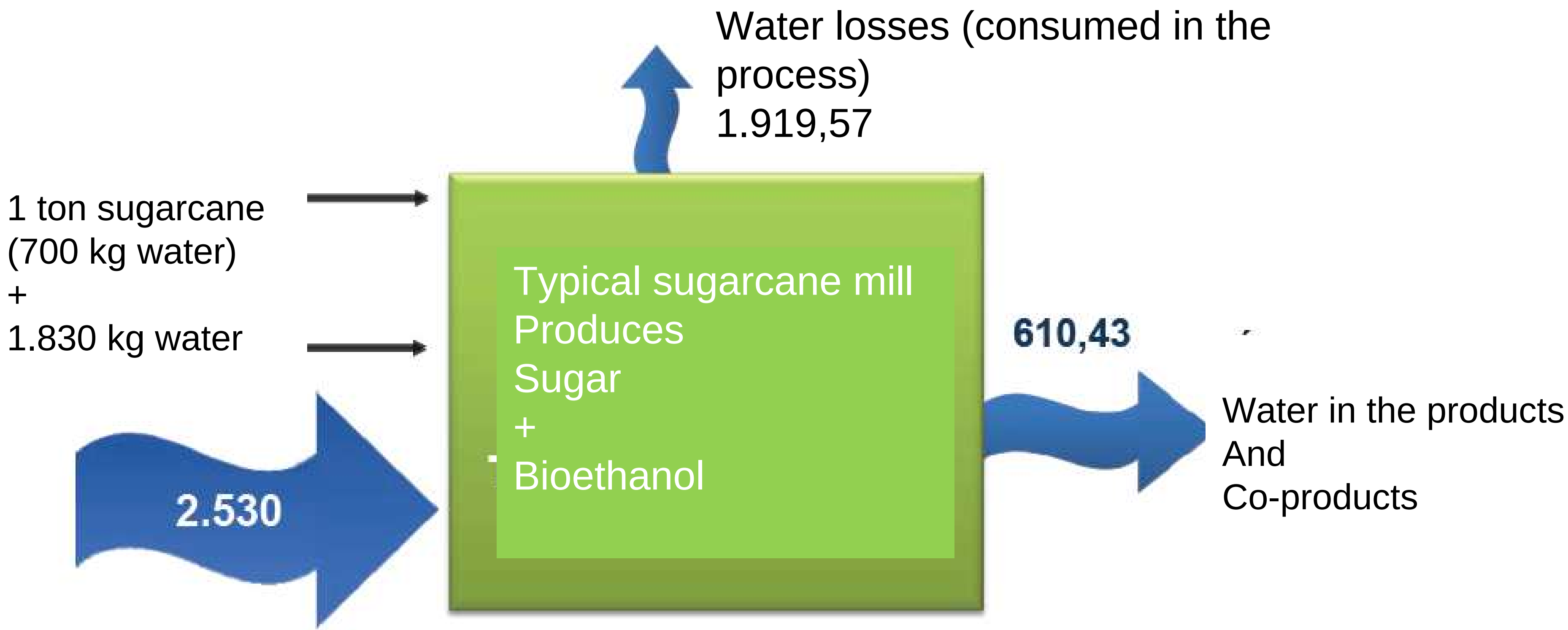
Bio-water → optmization of the use of sugarcane´s water

Water content in sugarcane (1 ton)



Critical points of water using in the bioethanol production

Balance for water in the bioethanol process – kg H_2O/tc



DEDINI INDÚSTRIAS DE BASE

Trends to minimize water using on sugarcane processing

Production of bioethanol with minimization of water using

Objective:

Minimization of water using

(=)

Maximization of the natural sugarcane water

(-)

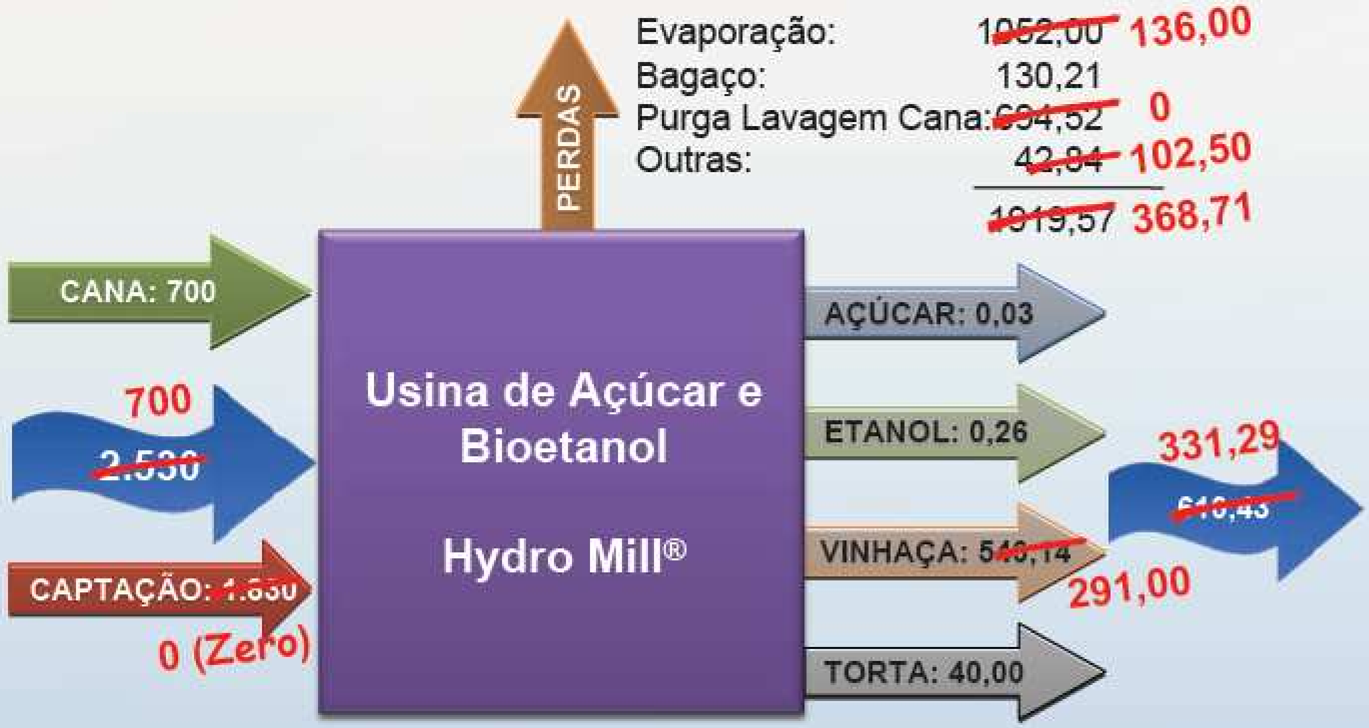
Minimization of internal consuption during processing

DEDINI
Indústrias de Base

Produção de etanol com mínimo consumo de água

FOCO: CONSUMO DE ÁGUA

Novo Conceito e Projeto – Hydro Mill® – Usina auto-suficiente em água



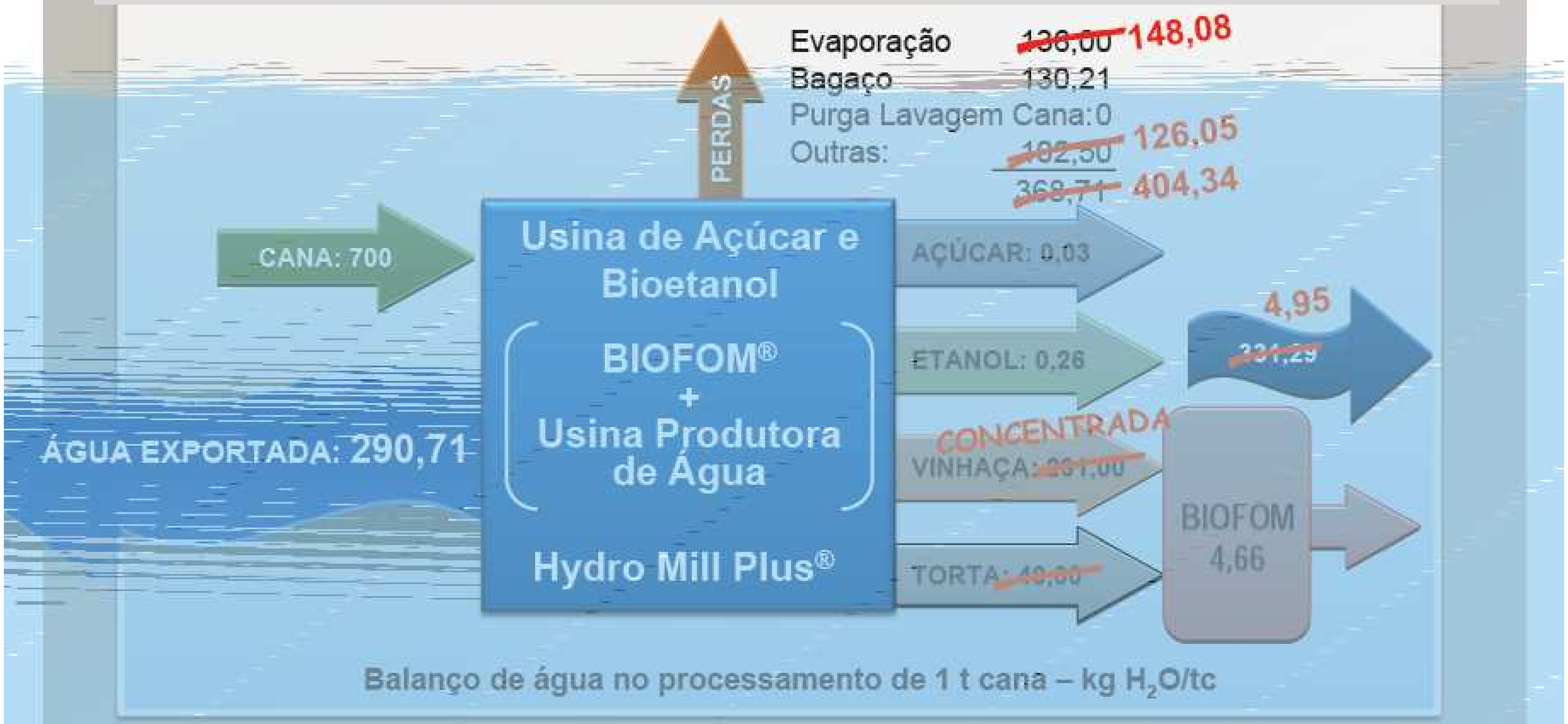
Balanço de água no processamento de 1 t cana – kg H_2O/tc

DEDINI
INDÚSTRIAS DE BASE

Produção de etanol com mínimo consumo de água

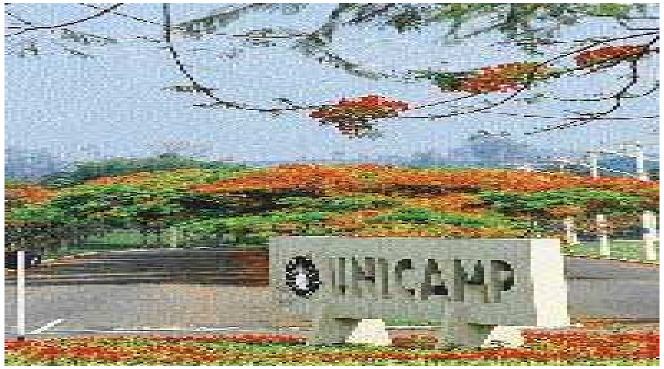
FOCO: CONSUMO DE ÁGUA

Optmized process for the production of Hydro Mill – Plus and the biofertilzer BIOFOM



BIOFOM – Biofertilizante Organo Mineral (Vinhaça Concentrada, Torta de Filtro, Cin... + Nutrientes complementares se necessários)

UNICAMP



STATE UNIVERSITY OF CAMPINAS, UNICAMP created in October 1966

- **14,000 undergraduate students,**
- **14,000 post-graduate students (MsC+PhD),**
- **2,100 lecturers and professors.**
- **10,000 students on continuous education (evening /week-end courses)**

Unicamp activities on Biofuels

Biofuel research projects developed - Unicamp

UNICAMP

Bioethanol → New technologies 2nd generation

- Strains selection
- Extractive fermentation
- Optimization
- New enzymes
- Hydrolysis
- Pre-treatment

Biodiesel → New technologies 2nd generation

- Transesterification
- Optimization
- Microbial oil

(Bioethanol and Biodiesel):

- Chemical eng. (FEQ)
- Food eng. (FEA)
- Agric. eng. (FEAGRI)
- Mechan. eng. (FEM)
- Biology (IB)

3 New laboratories on biofuels +

Biomass center

BTL →

- Fast pyrolysis
- Bagasse pyrolysis
- Catalysis process

(BTL):

- Physics (IFGW)
- FEAGRI
- FEM
- FEQ

Hydrogen → Hydrogen technology (production, purification, storage, utilization)

(Hydrogen): IFGW

News and Media Releases
Shell announces six new biofuels research agreements
17/09/2008

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Royal Dutch Shell plc ("Shell") today highlighted its approach to biofuels innovation, announcing six new research agreements with experts in academic institutions across the world. They are part of a growing programme of agreements designed to complement Shell's own biofuels research and development, and to accelerate results.

The research programme investigates new raw materials and new biofuels production processes, with a focus on improving efficiencies and lowering costs. The research agreements will last between two and five years. They are with:

The **Massachusetts Institute of Technology** (MIT), Massachusetts, US; the **University of Campinas** (Unicamp), Sao Paulo, Brazil; the **Institute of Microbiology, Chinese Academy of Sciences** (IMCAS), Beijing, China; the **Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences** (QIBEBT), Qingdao, China; the **Centre of Excellence for Biocatalysis, Biotransformations and Biocatalytic Manufacture** (CoEBio3) based at Manchester University, UK; and the **School of BioSciences Exeter University**, UK.

LEBBPOR - Laboratory of Biochemical Engineering,Biorefinery & Renewables

Group 1: Aminooligosacharides , structure x functionality – Dr. L.Fleuri

Group 2: Active and intelligent packing from natural materials – Dr. C.Pedroso

Group 3: Enzyme technology for biomass – Dr. J.Tsukamoto &J.Sousa

Group 4: Bioreactors & fermentation processes - Dr. E.J.Lopes

Gr. 5: Shell x Unicamp proposal – Dr. S.Hernalteesn

(Franco, T)

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Industrial approach

PETROBRAS

- **refinery flue gases**
- **refinery wastewater**

Refinery wastewater improving for microalgal production and CO_2 biofixation: predictive modelling and simulation

Eduardo Jacob-Lopes[1], Carlos Henrique Gimenes Scoparo[1], Maria Isabel Queiroz[2], Kelerson Modenesi[3], Telma Teixeira Franco[1*]

1Biochemical Engineering Laboratory, Universidade Estadual de Campinas, UNICAMP, P.O. Box 6066, 13083-970, Campinas-SP, Brazil.
2Biotechnology Laboratory, Chemical Departament, Fundação Universidade Federal do Rio Grande, FURG, 96201-900, Rio Grande-RS, Brazil.
3Petróleo Brasileiro S/A – Replan/Petrobras, 13140-000, Paulínia-SP, Brazil.

Composition of wastewater from refinery industry

***Values are means ± SD of all months considered.**

Parameter	Treated effluent*
pH	8.3 ± 0.24
Temperature (ºC)	28.1 ± 2.41
BOD (mg/L)	14.0 ± 1.36
Nitrite (mg/L)	0.1 ± 0.00
Nitrate (mg/L)	15.4 ± 0.32
Ammonia (mg/L)	1.2 ± 0.10
Phosphate (mg/L)	0.5 ± 0.00
Phenol (mg/L)	0.02 ± 0.00
Cyanide (mg/L)	0.04 ± 0.00
Oil and grease (mg/L)	4.6 ± 0.38
TSS (mg/L)	0.13 ± 0.00

Water collected from the discharge point of the activated sludge treatment for 8 months from May to December of 2007

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the **University of Campinas** (Unicamp), Sao Paulo, Brazil;

3 research projects + 1,500 m2 building →Shell laboratories

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Thank you

franco@feq.unicamp.br

Unicamp, Campinas