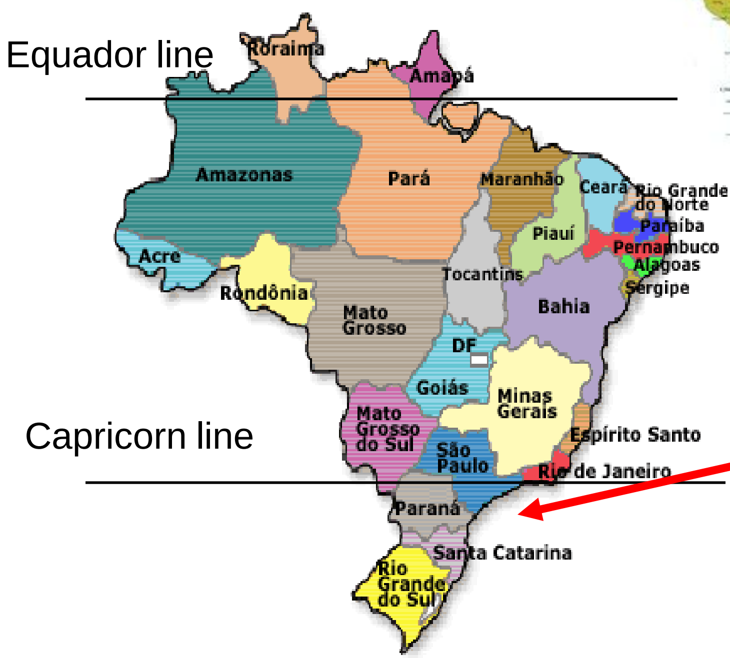
Universidade Estadual Paulista

Campus de São José do Rio Preto
Instituto de Biociências, Letras e Ciências Exatas
Departamento de Química e Ciências Ambientais

Mauricio Boscolo

Areas of interest: Bioenergy
***Food chemistry** (Alcoholic beverages composition)*
Sucrose derivatives

23 cities of State of São Paulo		
33 institutes		
Professors:	3600	
Students	Under-grad Graduated	35.929 10.705
	Total	46.634
171 Courses	5700 profissionals/y	
118 programs of post-grad 2400 Ms PhD / y		



São José do Rio Preto

Distinguished inhabitants of São José do Rio Preto

IBILCE

Instituto de Biociências,
Letras e Ciências Exatas

Reseach group on

BIOENERGY

at

São José do Rio Preto

Prof. Eleni Gomes
Microbiologist
Prospection of microorganisms

Prof. João Caludio Thomeo
Chemical Engineer
Bioreactors

Prof. Roberto da Silva
Food Engineer
Enzimology

Projects in:

- Cellulosic ethanol
- Ethlic biodiesel

Our goals

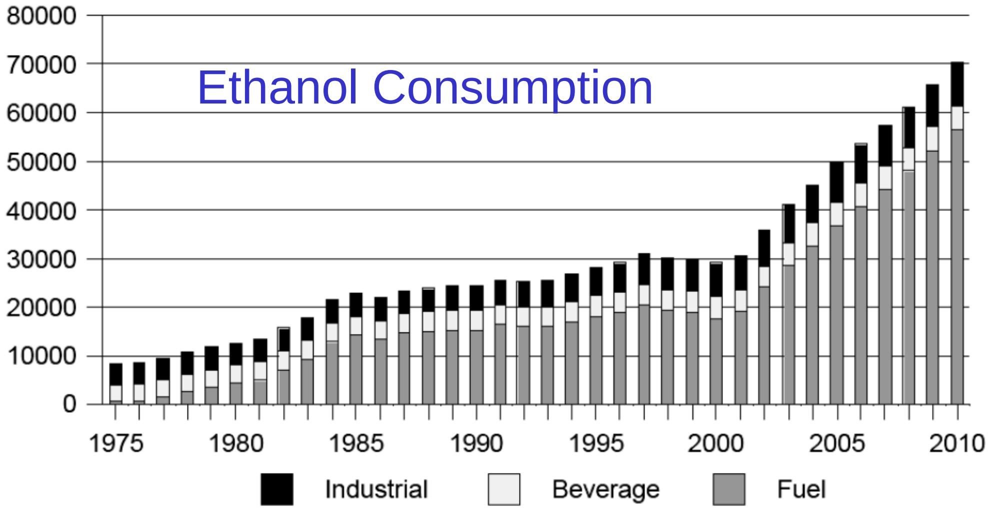
- Stablish economic and sustainable ways to produce biofuels

- Cellulosic Ethanol
    - Prospect thermophilic fungal hydrolytic enzymes (~60^{o}C)
    - Cellulases and Ligninases
    - Production on pilot bioreators
    - Safety pre-treaments for sugarcane bagasse (rather no pressurized)
    - Ozonolysis & atmospheric pressure microwave irradiation

- Ethylic Biodiesel catalysed enzymaticaly
    - Prospect enzymes for esterification & transesterifiction
    - Immobilyze enzymes & evaluate the efficience of support materials
    - Use of ultrasound and flow reactors

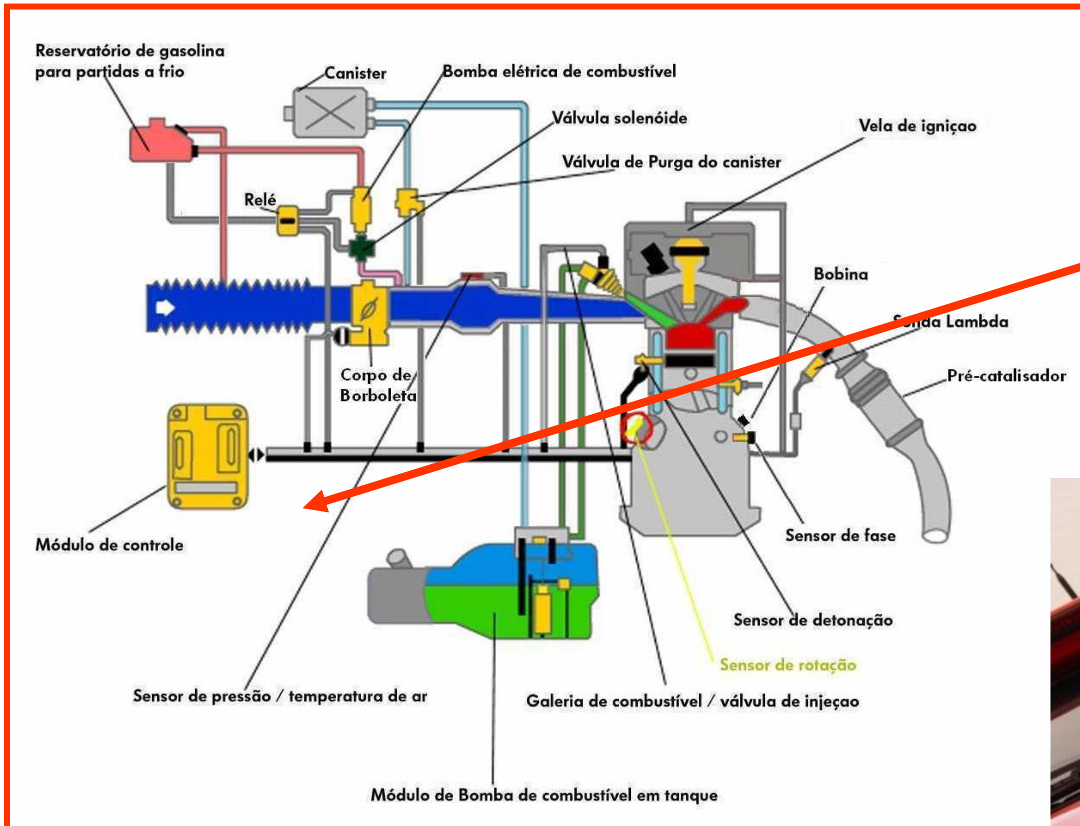
Bioenergy in Brazil

Ethanol



Technology used in Brazil

Comparing the readings from the sensors in the vehicle with a database, the onboard computer recognizes which fuel composition is being used and sets parameters combustion without any need for the driver interference.



Price of ethanol in Brazil

Alcohol yields 70% of gasoline per litter.

The price of ethanol depends of oil price

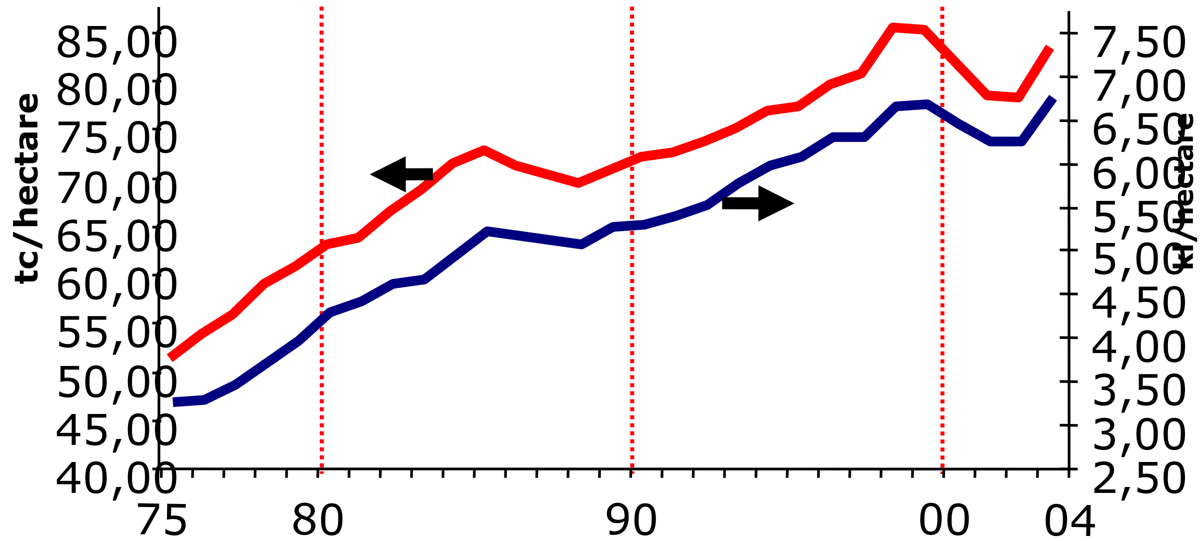
Sales

US$ 3,23/gal

Sales

US$ 5.13/gal (25% ethanol)

Ethanol Productivity

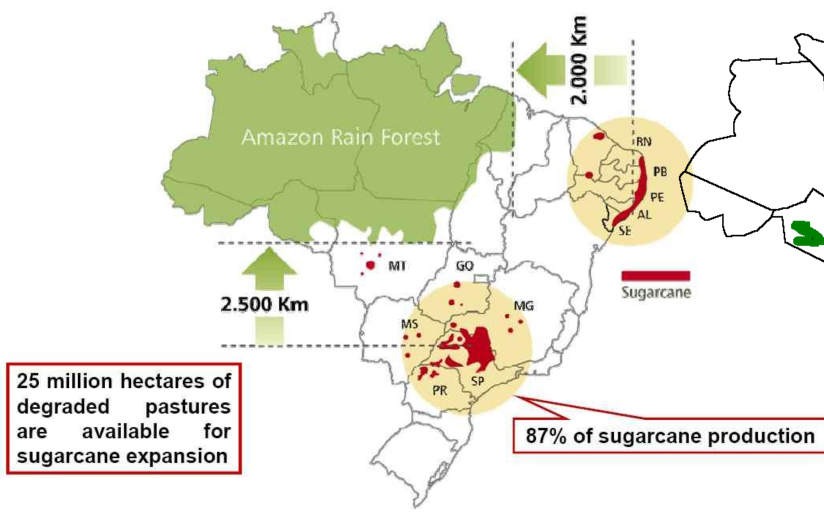


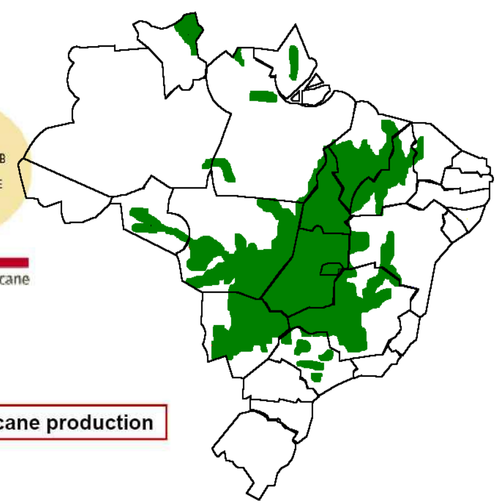
Source: UNICA

tcane / ha   kl ethanol / ha

Country	Millions of Gallons
USA	9000.0
Brazil	6472.2
European Union	733.6
China	501.9
Canada	237.7
Other	128.4
Thailand	89.8
Colombia	79.29
India	66.0
Australia	26.4
Total	17,335.2

World ethanol production in the year 2008 (RFA 2009).





Areas to expand sugarcane prduction

Ethanol production

Sugarcane bagasse is burnt to generate steam and electricity

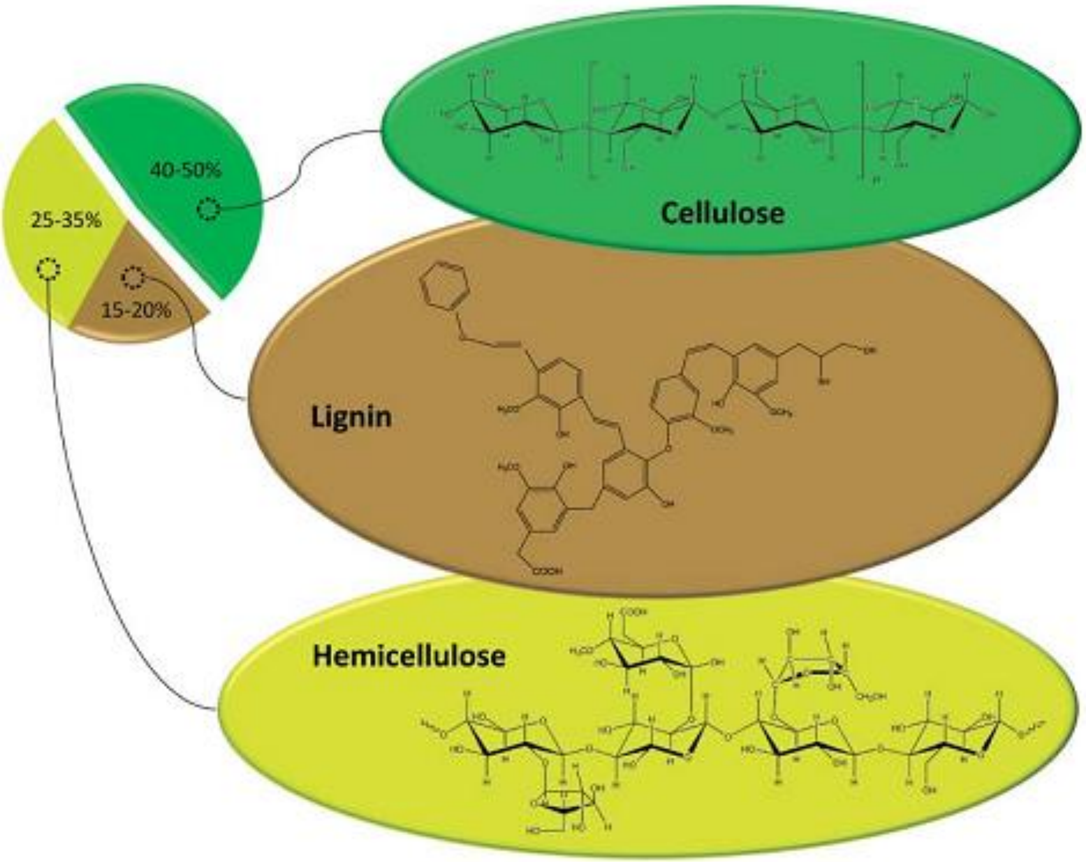
In 2011, Brazil produced 624 million tons of sugarcane, yielding around 168 million tonnes of bagasse

Residual bagasse:

Inside the mill area

Fire risk
Energy stored
Cellulosic ethanol
Others…

Biomass



Lignocellulose composition: cellulose, hemicellulose and lignin.

Catalytic conversion of biomass to biofuels - D.M. Alonso, J. Q. Bond and J. A. Dumesic (GREE

Sugarcane Bagasse

Component	Content* (%)
Cellulose	43.4
Hemicellulose	25.6
Lignin	23.2
Ash	2.9
Extractives	4.8

Lignocellulosic residues from different agricultural sources

Lignocellulosic residues	Ton×10^6/year
Sugar cane bagasse	317–380
Maize straw	159–191
Rice shell	157–188
Wheat straw	154–185
Soja straw	54–65
Yuca straw	40–48
Barley straw	35–42
Cotton fiber	17–20
Sorgoum straw	15–18
Banana waste	13–15
Mani shell	9.2–11.1
Sunflower straw	7.5–9.0
Bean straw	4.9–5.9
Rye straw	4.3–5 2
Pine waste	3.8– 4.6
Coffee straw	1.6–1.9
Almond straw	0.4–0.49
Sisal a henequen straw	0.077–0.093

Sugarcane

1 T Sugarcane

Sugar
153 kg → 608 x 10^3 KCal → Real ETHANOL — 90 L

Bagasse
276 kg
(50% UMIDADE) → 598 x 10^3 KCal

Strow
165 kg
(15% UMIDADE) → 512 x 10^3 KCal

209 kg HEXOSES
126 kg PENTOSES → Theorical ETHANOL — 186 L

TOTAL — 276 L

1 T Sugarcane
1,718 x 10^6 KCal

1 Petroleum Barrel
1,386 x 10^6 KCal

Adaptaded from Dedini (2004)

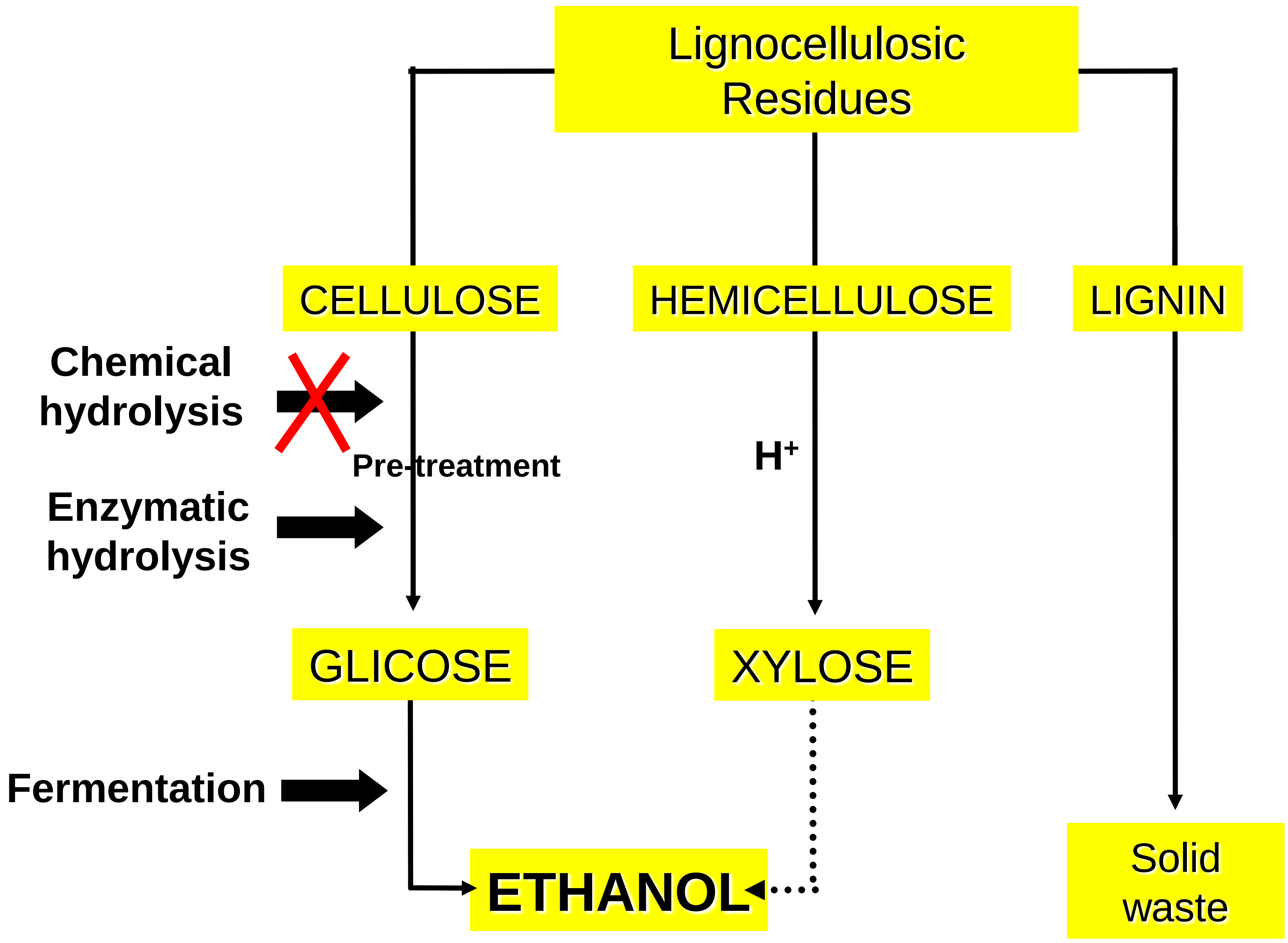
1 T sugarcane ≅ 1,2 Oil Barrel

1 ton sugarcane	90 L
1 ton corn	407 L

Sugarcane	7500 L/ha	+	25000 L/ha	=	32500 L/ha
Corn	3500 L/ha		????		

Production 2012 = 22.682 Bilion L
Planted area = 9.164.607 ha

Lignocellulosic ethanol



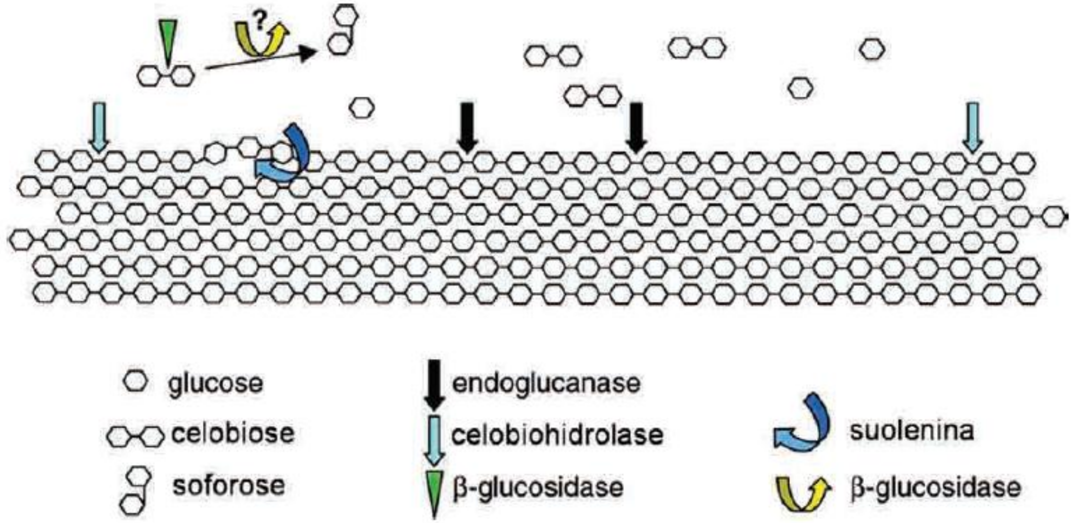


Figura 10.7 – Representação esquemática do sistema celulolítico. Os sítios de maiores atividades das enzimas celulolíticas são mostrados, além de um caminho alternativo de formação de soforose pela atividade de transglicosilação de β-glicosidase

Fonte: Aro et al., 2005.

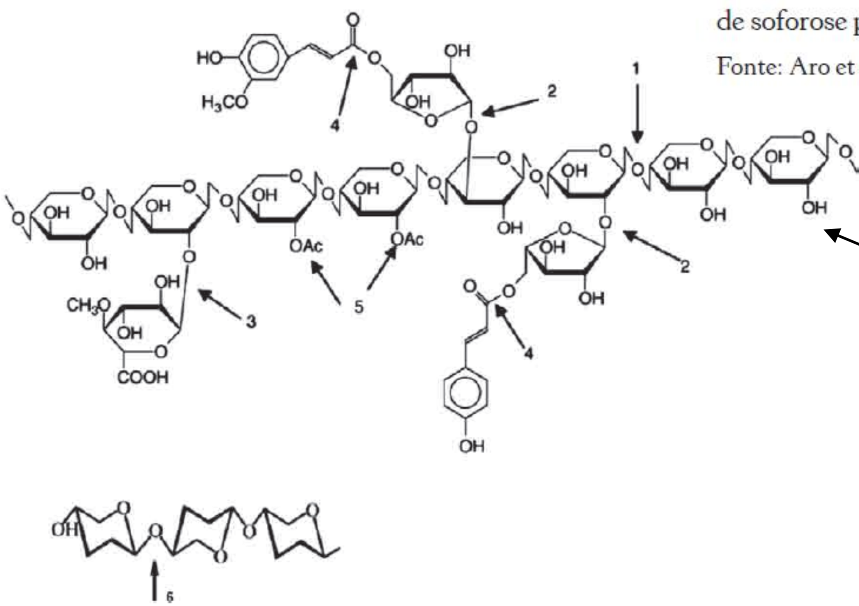
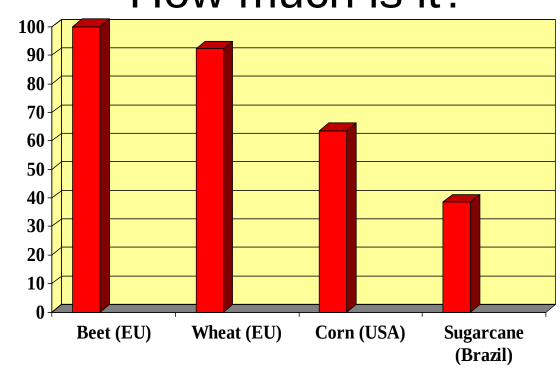


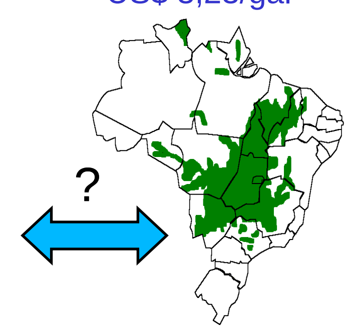
Figura 10.9 – Representação esquemática de uma molécula de xilana e as respectivas ações das enzimas do sistema xilanolítico. *1 – endoxilanases; 2 – α-L-arabinofuranosidases; 3 – glucuronidases; 4 – feruloil e cumaril esterases; 5 – acetil xilana esterases; 6 – β-xilosidases*

How much is it?

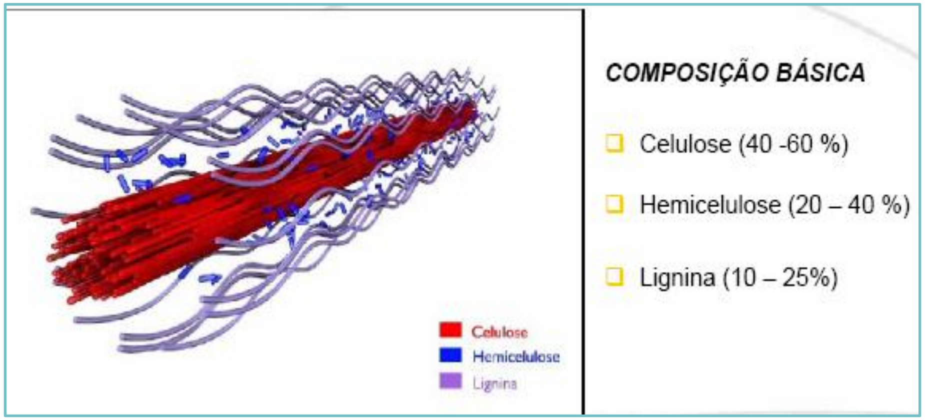


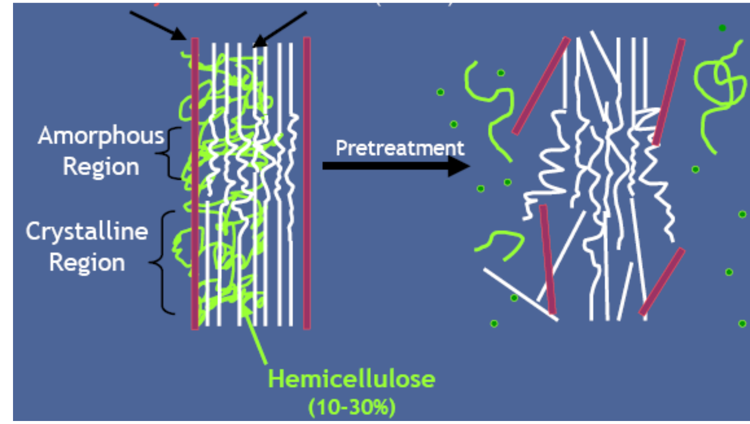
Current Cost
US$ 2.28 /gal

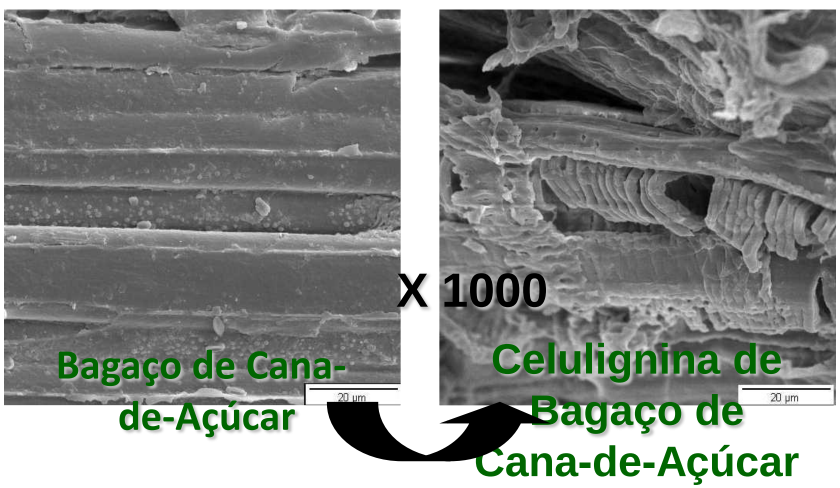
Sales
US$ 3,23/gal



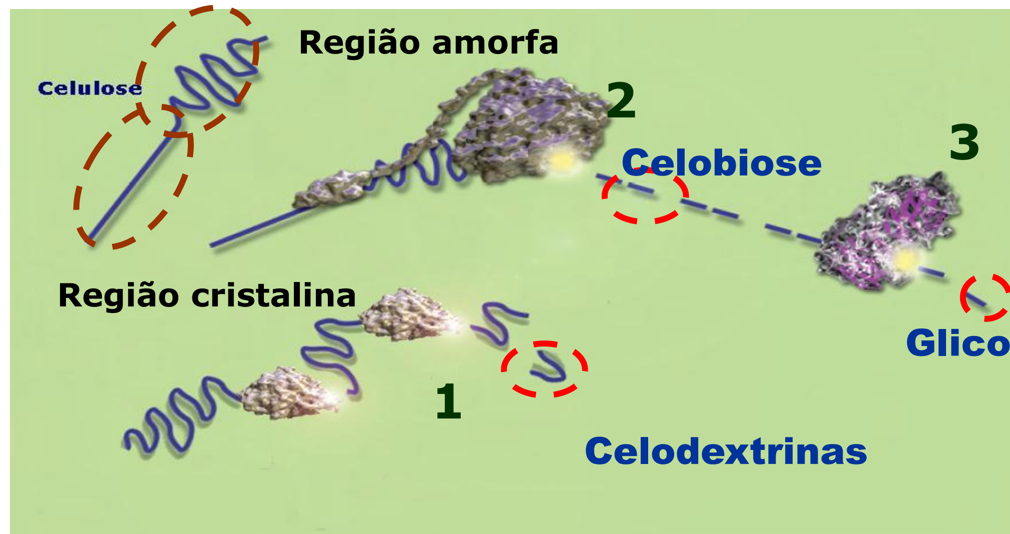
Pre-treatments of the sugarcane bagassse







Laboratórios de Desenvolvimento de Bioprocessos da EQ/UFRJ



1: endoglicanase 2: exoglicanase 3: β-glicosidase

Ozonolysis

Ozone generator

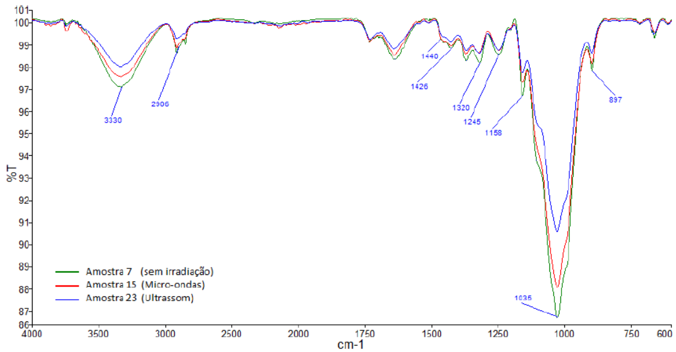
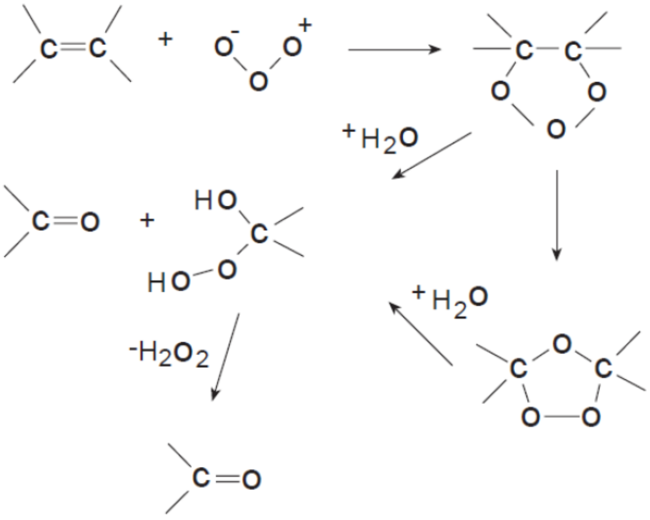


Figura 11. Espectros obtidos por *FTIR-ATR*, comparando o bagaço da Amostra 7, representado pela linha verde, Amostra 15, representado pela linha vermelha, e Amostra 23, representado pela linha azul, (bagaços tratado com NaOH 0,1 Mol^{-1}, fibra de bagaço de menor espessura (<1 mm), ozônio e variação na irradiação).



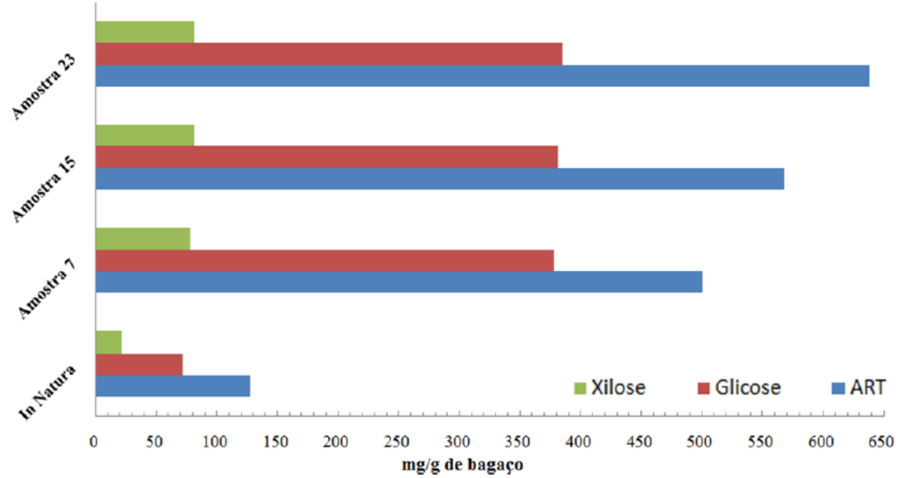


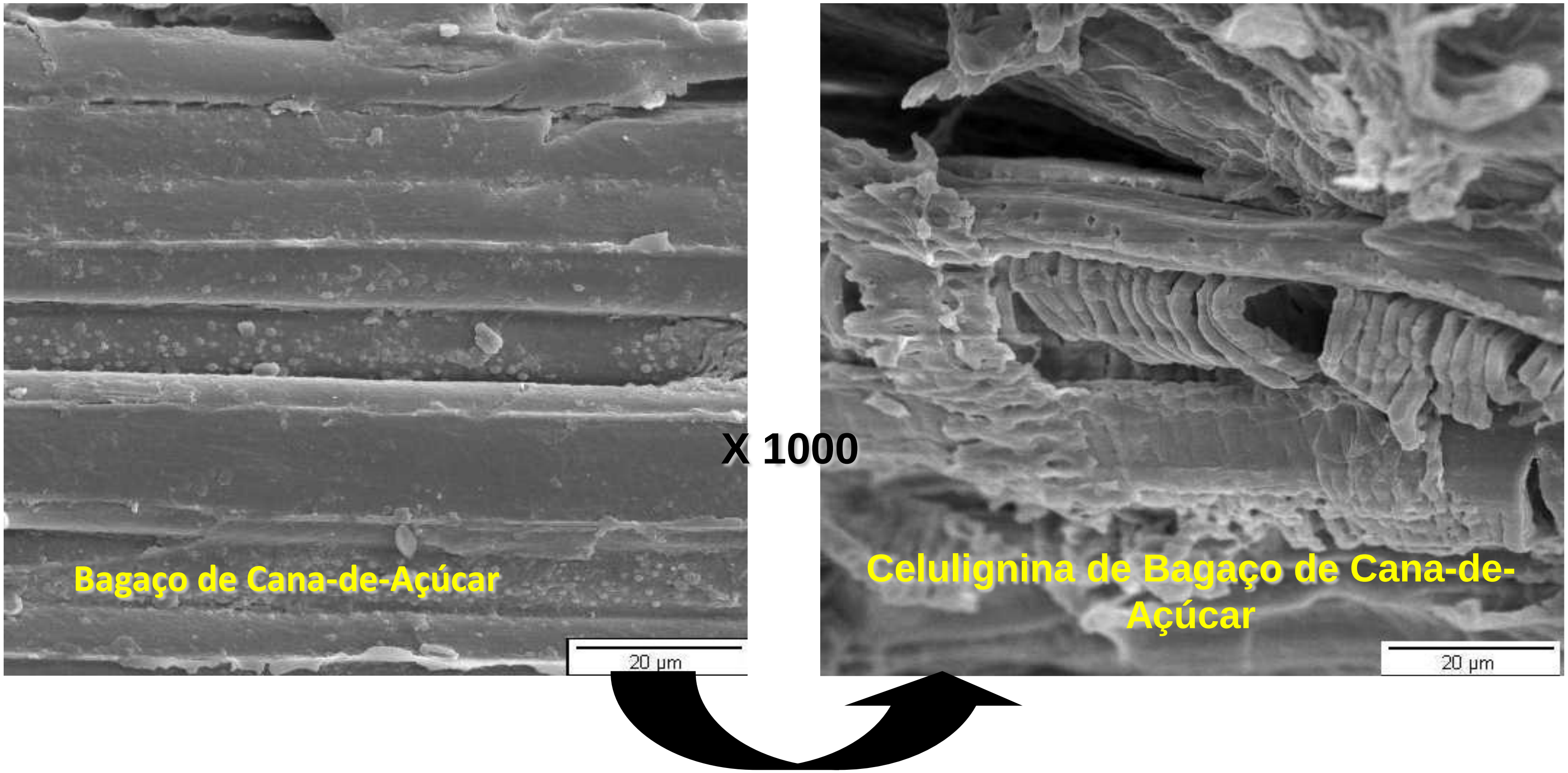
Figura 15. Comparação dos teores de glicose e xilose obtidos por cromatografia aniônica, com o ART obtido pelo método do ADNS, presentes no hidrolisado das amostras 7, 15, 23 e bagaço *in natura*.

Microwave irradiation at atmospheric pressure

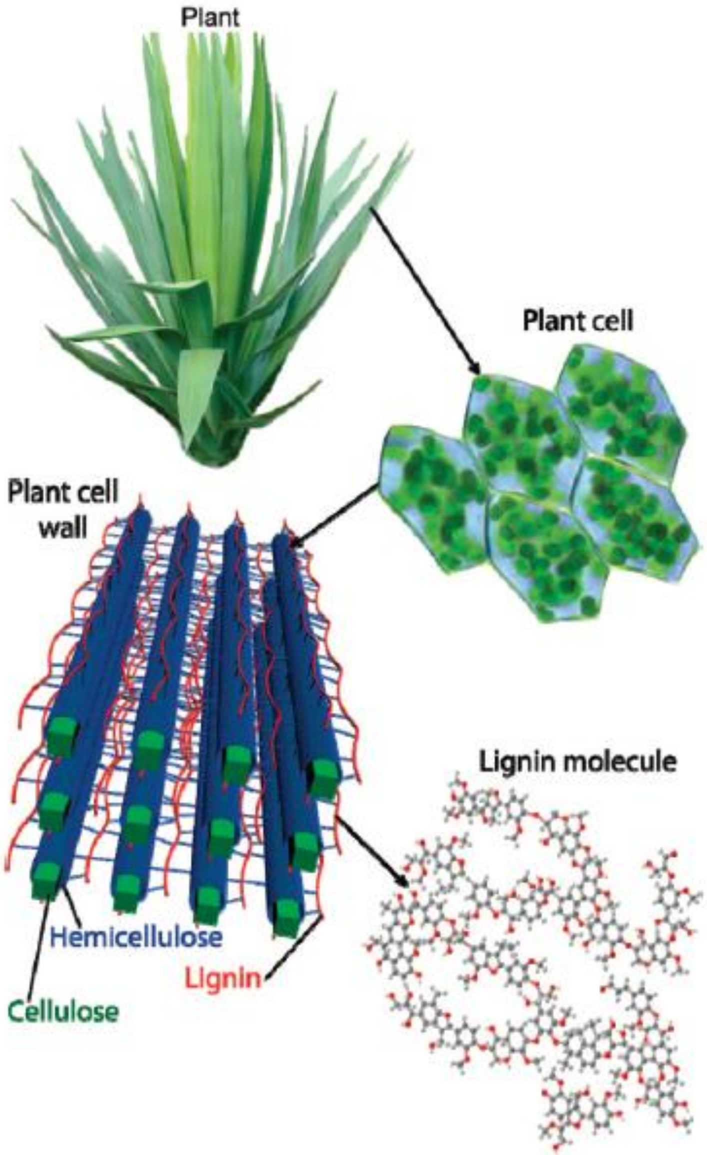
Tabela 10.3 – Efeitos do tratamento com micro-ondas associado a ácido e glicerol

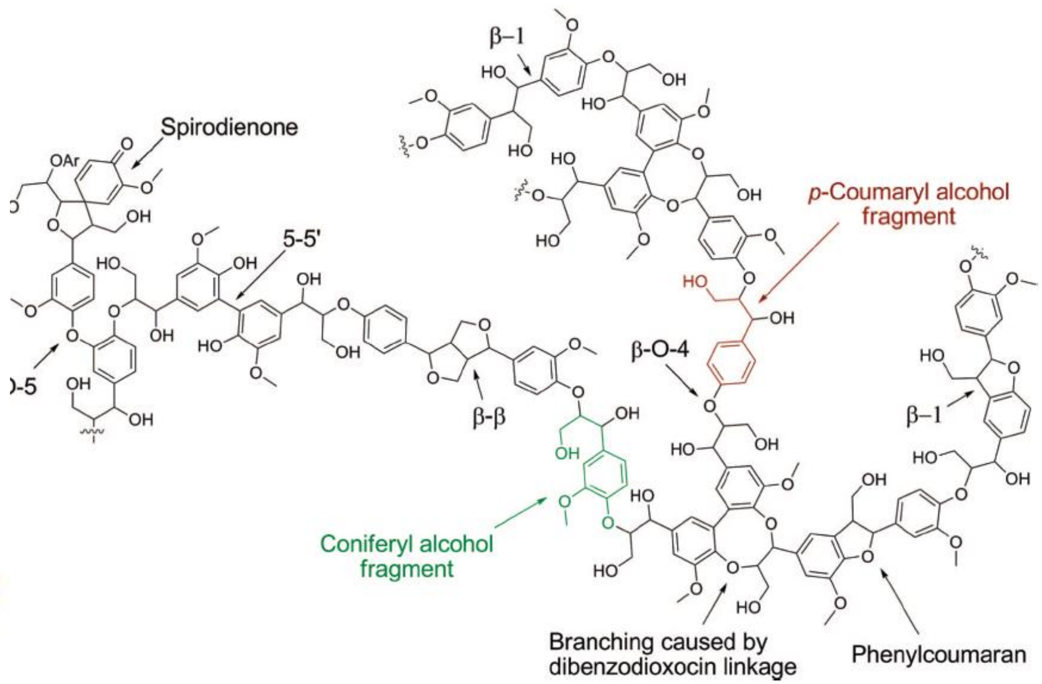
Soluções de glicerol	Solução após pré-tratamento com micro-ondas (2 min.)		Hidrolisado enzimático (Power cell-prozin)
	Compostos fenólicos (mg/g bagaço)	Açúcares redutores (m/g bagaço)	Açúcares redutores (mg/g bagaço)
Glicerol 100% + H_2SO_4 0,01M	33,0 $\pm$ 2,0	4,9 $\pm$ 0,9	512,9 $\pm$ 7,0
Glicerol 70% + H_2SO_4 0,01M	17 $\pm$ 0,4	11,7 $\pm$ 0,8	356,9 $\pm$ 6,0
Glicerol 30% + H_2SO_4 0,01M	0,95 $\pm$ 0,8	2,2 $\pm$ 0,2	195,6 $\pm$ 4,0
Glicerol 10% + H_2SO_4 0,01M	0,74 $\pm$ 0,1	1,5 $\pm$ 0,1	234,2 $\pm$ 2,0
Glicerol 100% + H_2SO_4 0,05M	62,4 $\pm$ 0,3	16,2 $\pm$ 0,9	377,3 $\pm$ 10,0
Glicerol 70% + H_2SO_4 0,05M	23,3 $\pm$ 0,2	20,91 $\pm$ 0,8	256 $\pm$ 5,3
Glicerol 30% + H_2SO_4 0,05M	5,5 $\pm$ 0,5	0	195,4 $\pm$ 6,0
Glicerol 10% + H_2SO_4 0,05M	1,41 $\pm$ 0,4	9,09 $\pm$ 1,0	176,9 $\pm$ 5,0

Scanning microscopy



Pretreament





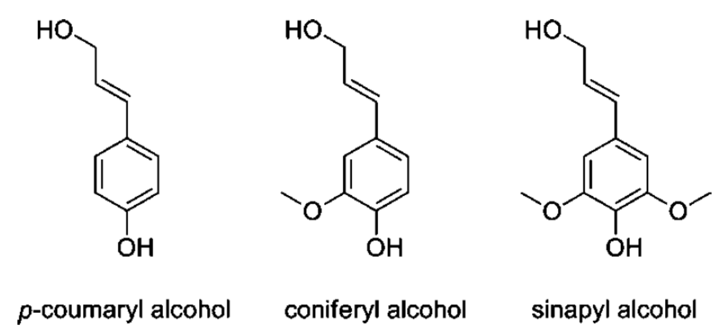


Figure 2. The three monolignols, the building blocks of lignin.

BIOREFINERY

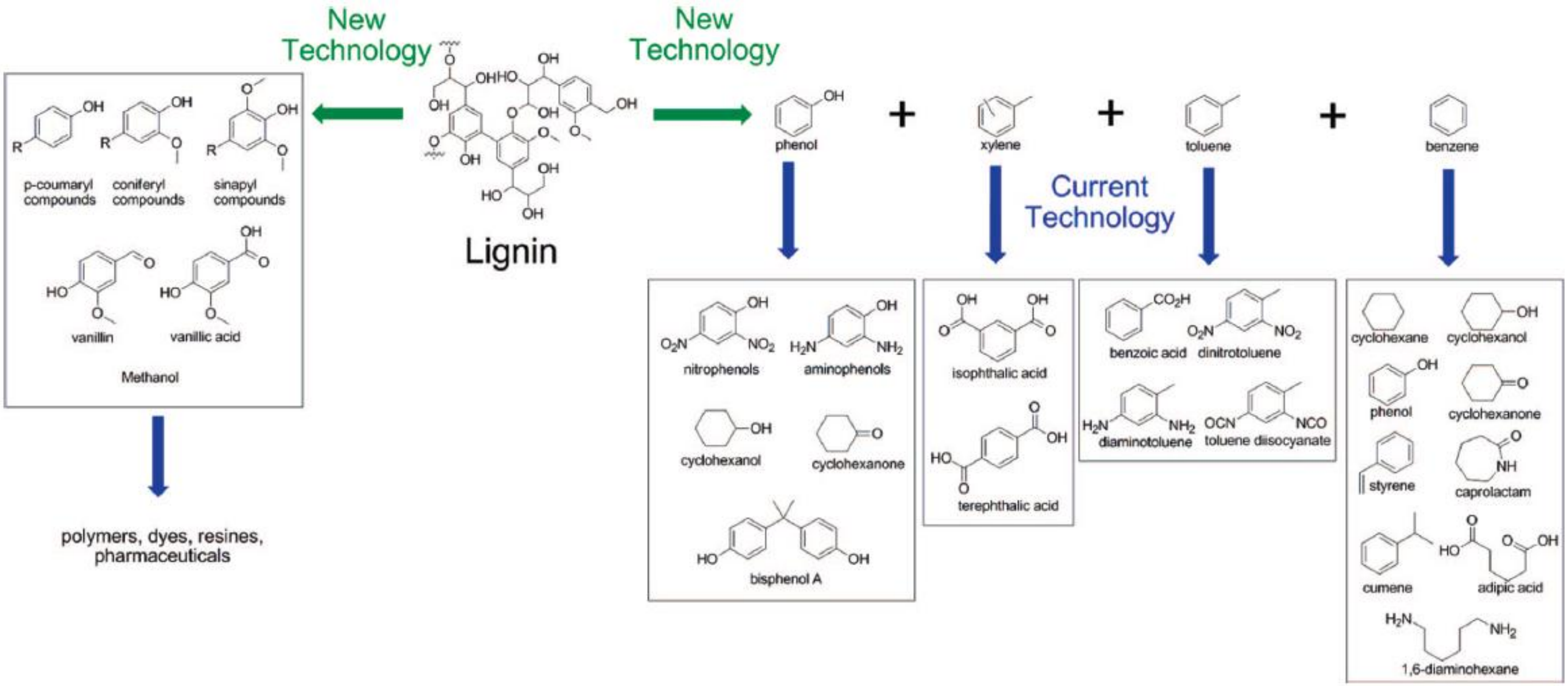
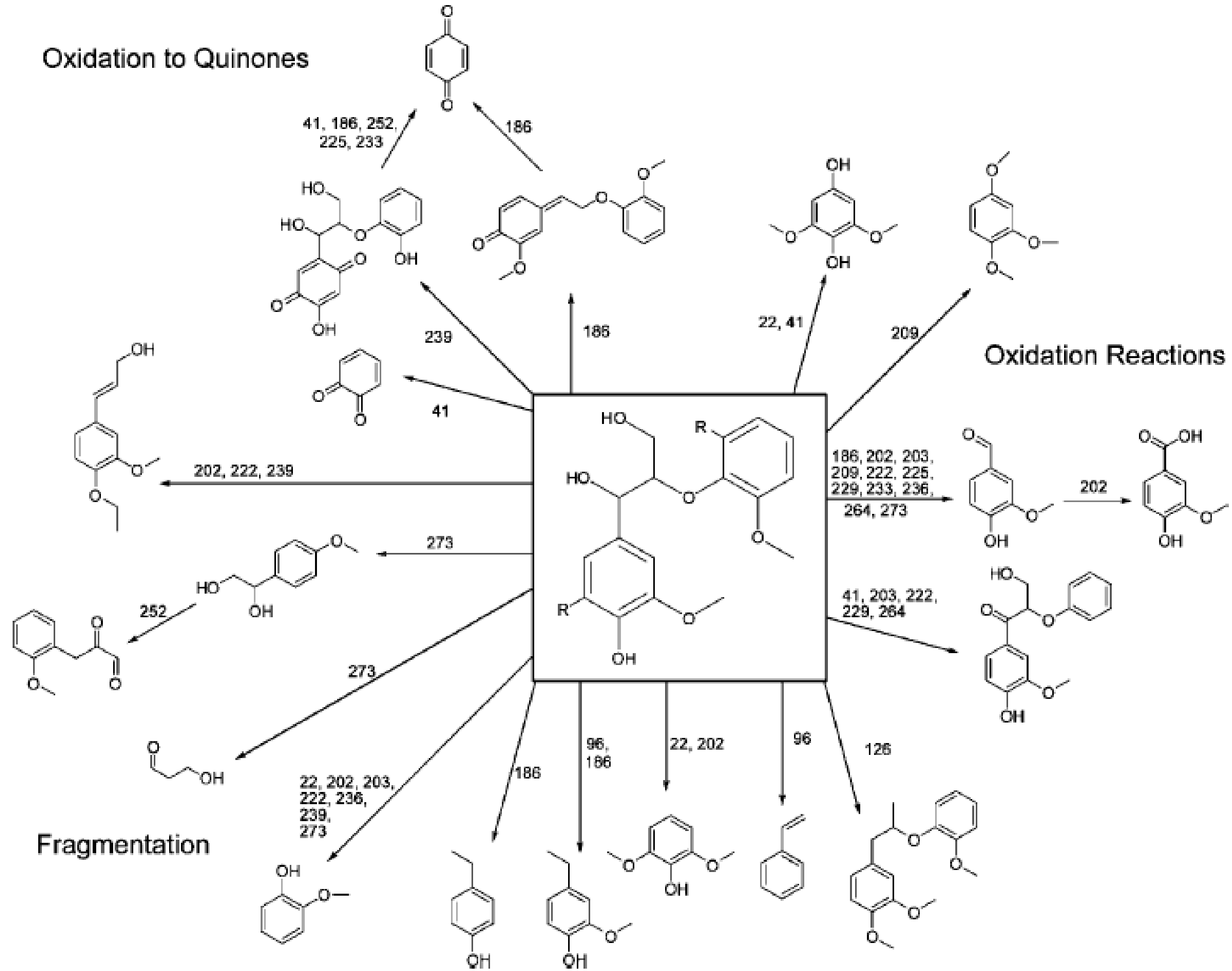
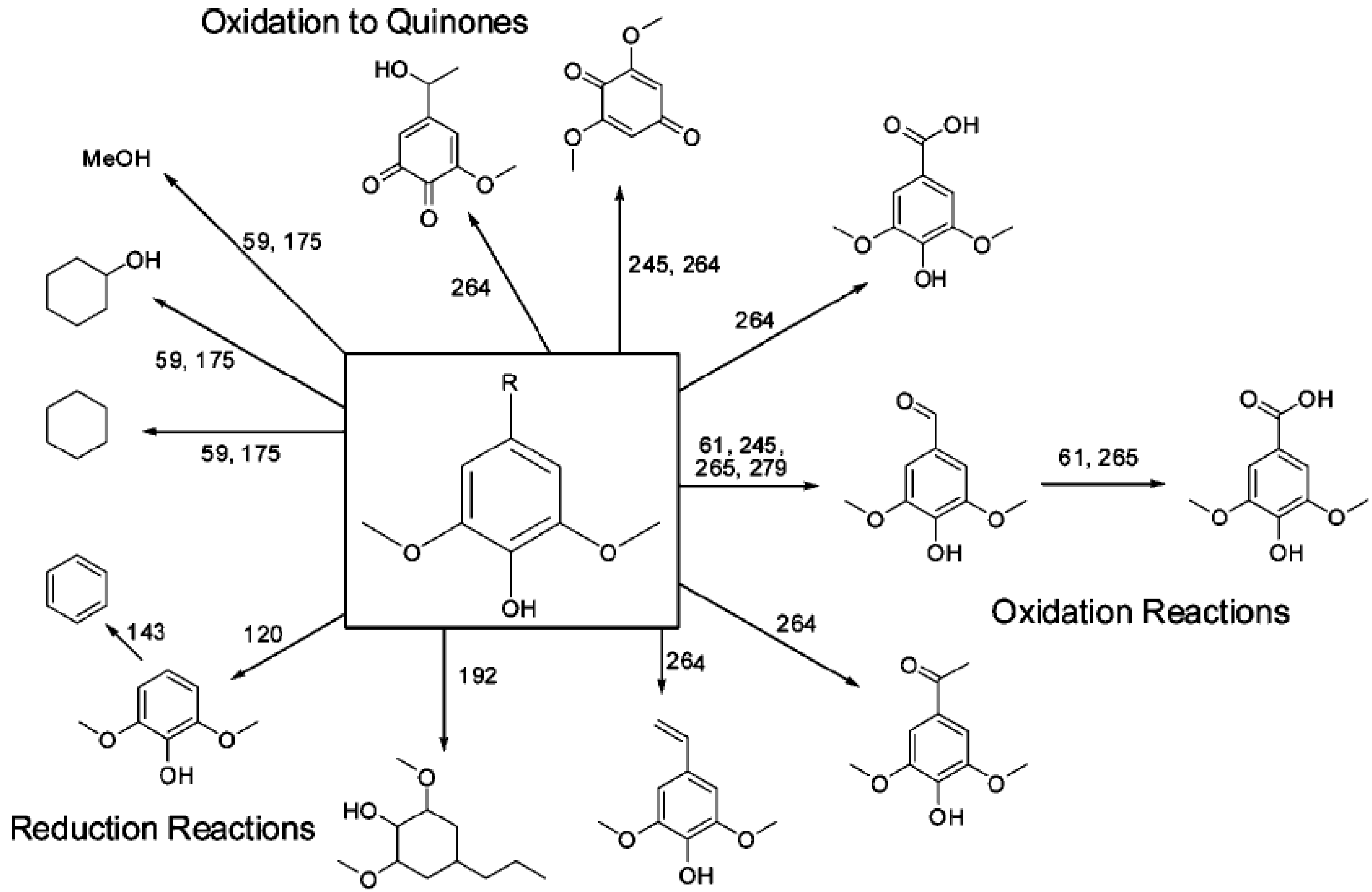


Figure 15. Valuable products potentially obtained from lignin with development and integration of new and current technology.[6,67]

Scheme 1. Reaction of Lignin Model Compounds Containing the β-O-4 Linkage to Various Products[a]

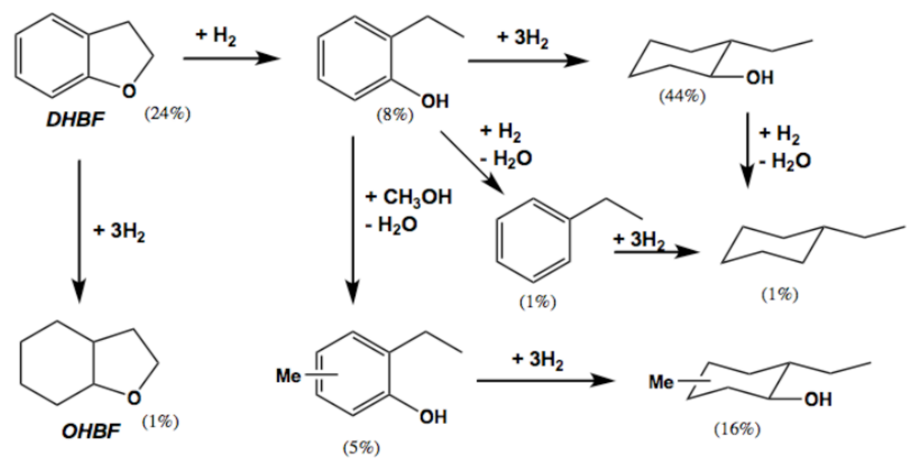


Scheme 9. Reactions of Sinapyl Alcohol Resembling Lignin Model Compounds to Various Products[a]



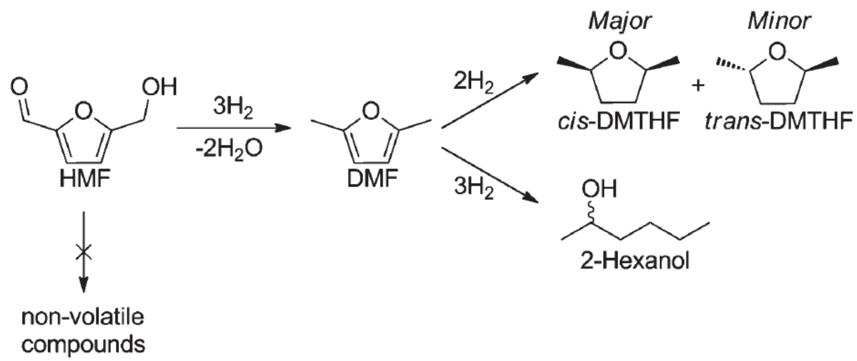
Chemicals from lignin

Figure 3.7. Reaction network accounting for the observed products. The yields, listed in parentheses below each species, are based on GC-MS analysis of Reaction #2.



Matson, 2012

Chemicals from cellulose



Scheme 1 Proposed reaction pathway from HMF to the three main products DMF, DMTHF and 2-hexanol.

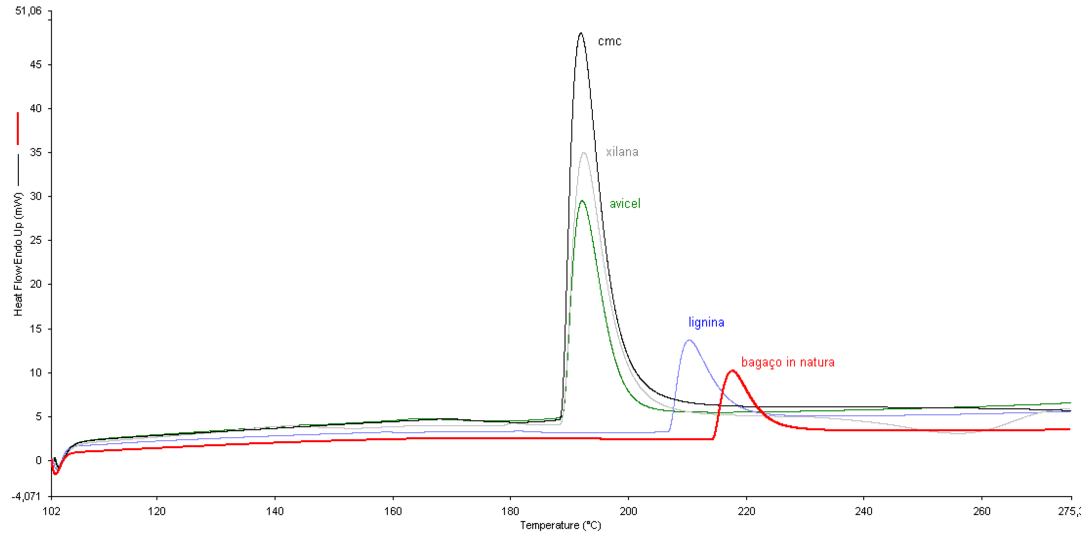
Hansen, Ford 2012

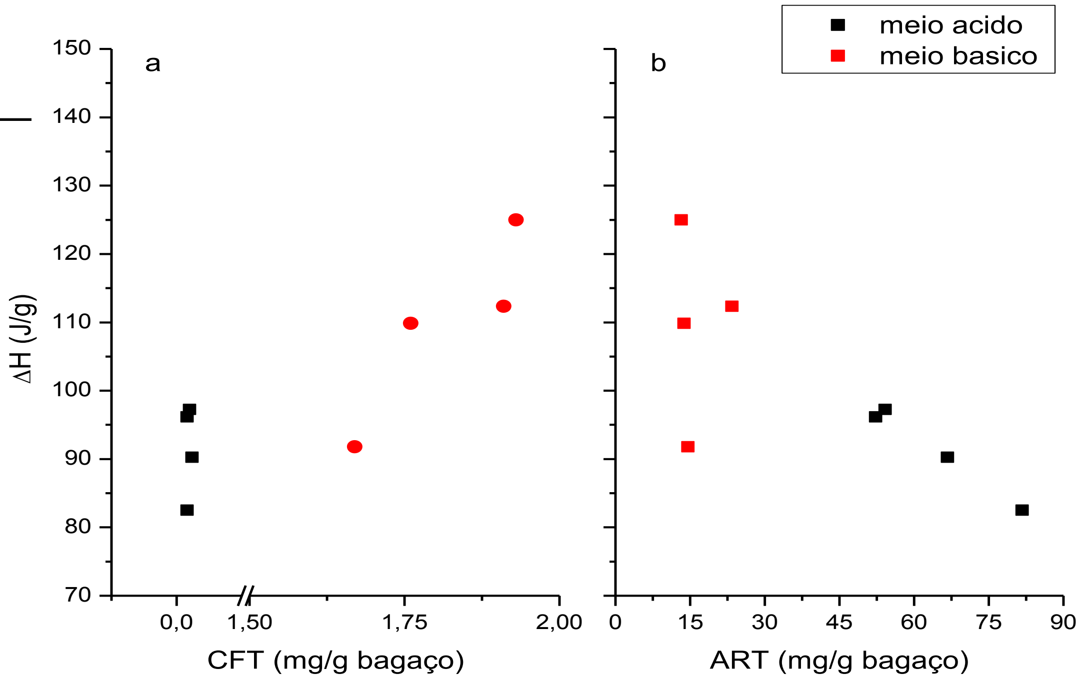
DSC

Variação de entalpia: relação com a facilidade em romper o arranjo tridimensional

Temperatura: relação com a natureza do arranjo tridimensional

Amostra	T_{onset}(C)	ΔH_{deg} (J/g)
CMC	186 ± 4	300 ± 1
Xilana	186 ± 5	228 ± 7
Avicel	185 ± 7	139 ± 2
Lignina	206 ± 2	67 ± 2
Bagaço *in natura*	215 ± 1	65 ± 5

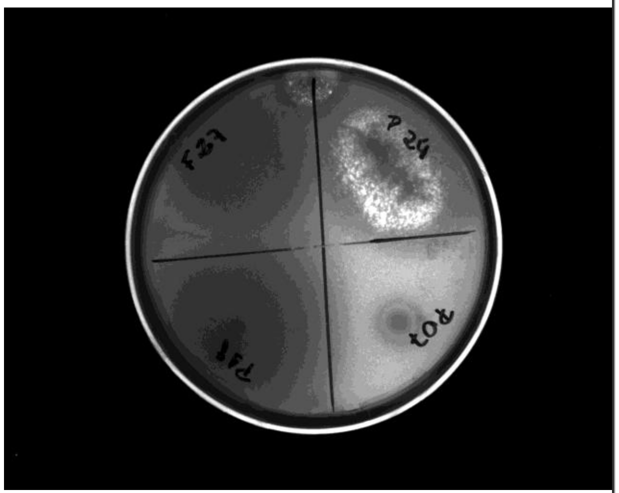


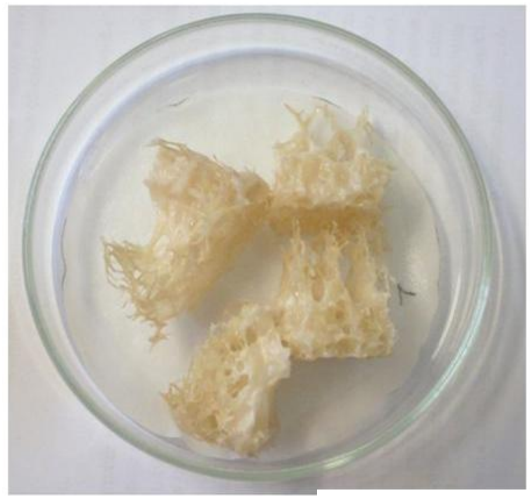


Ethilic biodiesel: Search for enzymes

Start with Lipolytic Activity Assay (Zimogram)

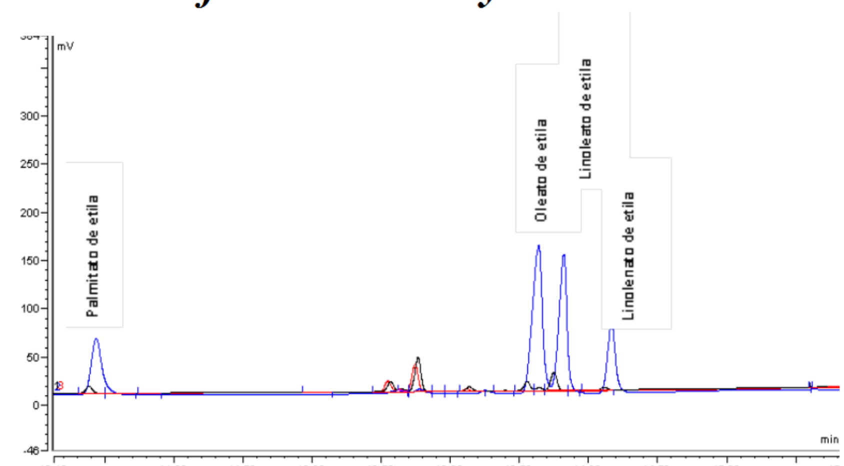
51 fungal strains (32 mesophilic and 19 thermophilic)



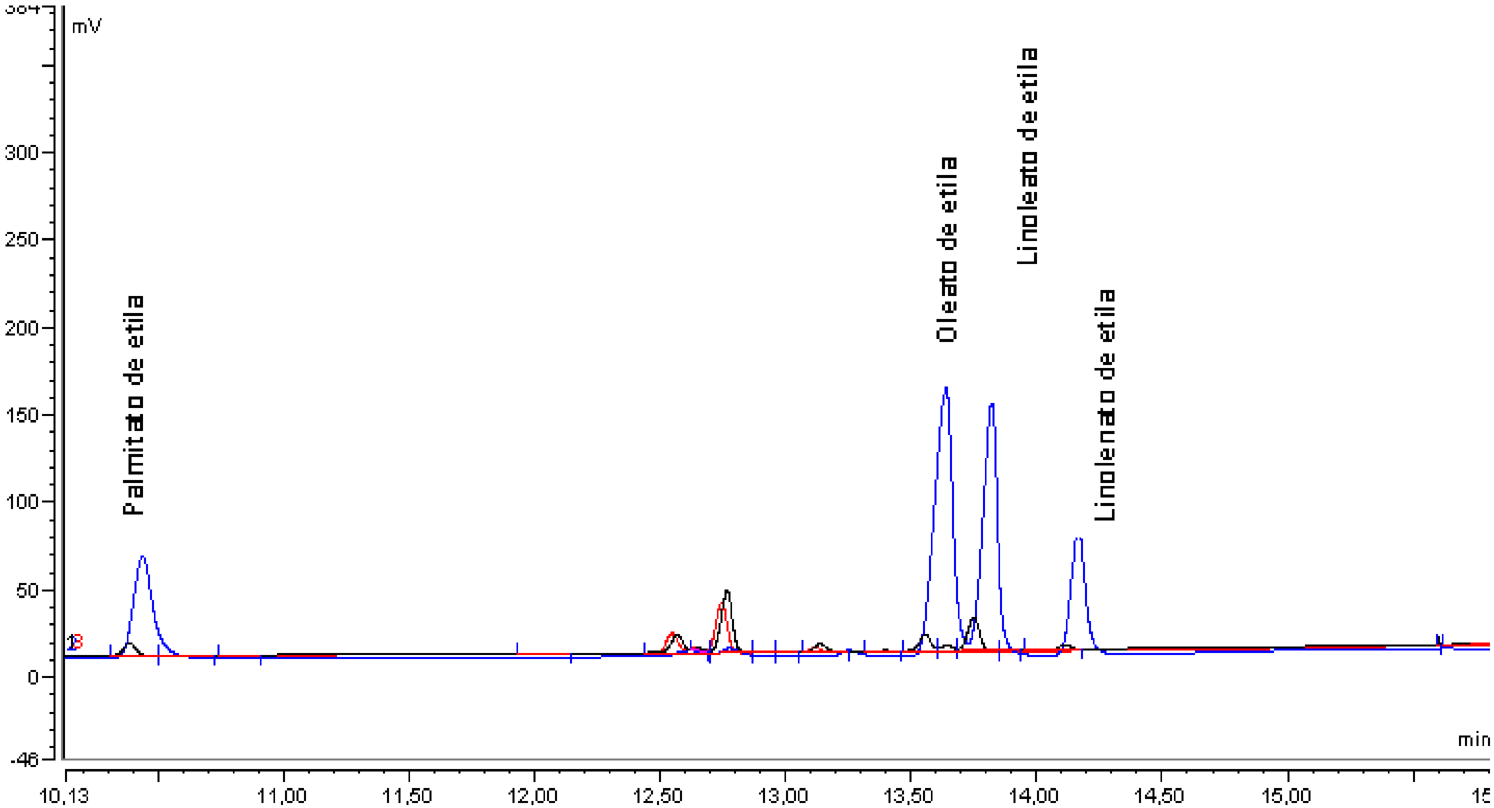


Transesterification activity

Fungo	Hidrólise (U/g de substrato)	Esterificação	Transesterificaçã
Thermomucor indicae-seudadticae N31	108	22%	10%
Rhizomucor pusillus.	365	80%	30%



Transesterification activity



International Call for Proposals in Sustainable Chemistry

“Novel Molecular and Supramolecular Theory and Synthesis Approaches for Sustainable Catalysis

IUPAC
International Union of Pure and Applied Chemistry

National Science Foundation

DFG Deutsche Forschungsgemeinschaft

国家自然科学基金委员会
NSFC
National Natural Science Foundation of China

FAPESP
São Paulo, Brazil

The motivation of this call is to foster networking between excellent scientists on topics in chemistry exemplified by a three-year program in sustainable chemistry.

Grants will support basic experimental and theoretical research. A successful proposal will have to:

1. Introduce novel approaches to develop a new generation of catalysts in which rare elements are replaced with earth abundant elements; and

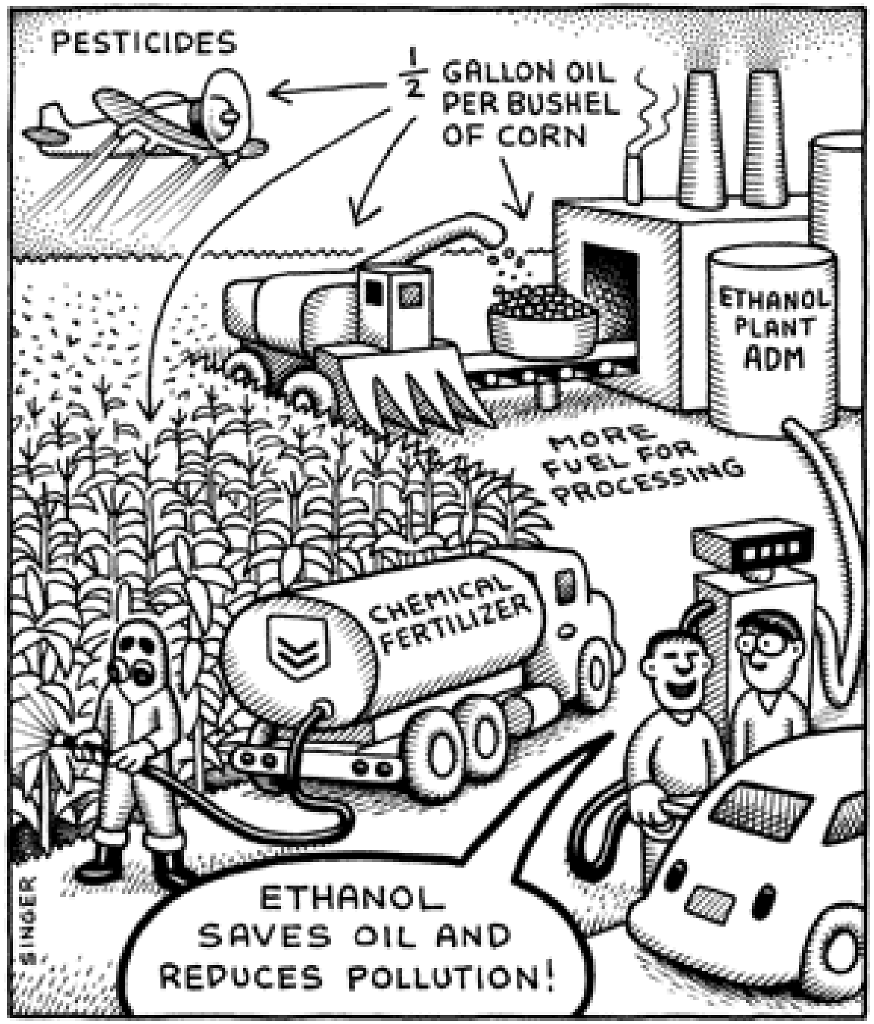
2. Successfully address a significant environmental problem.

This grant program does not support: (i) basic research that focuses on biological techniques, cellular processes, or biomedical problems; (ii) applied research that focuses on extended solids and bulk materials, (iii) design, optimization, or other engineering aspects of devices; (iv) engineering aspects of chemistry, such as scale-up, processing, transport dynamics, and long-term stability.

- Letters of intent are due February 1, 2013.

- Full proposals for eligible projects are due March 29, 2013.

NO EXIT © Andy Singer



Thank you !

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