Conversion/Processing of sustainably produced, non-food biomass to bio-based products in Brazil

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Fapesp/Bioen- Process Engineering Coordination
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German-Brazilian Bioeconomy Forum 2014
Advantages of Biofuels and Renewable Based Products

Environmental Benefits
- carbon sequestration
- lower emissions

Political Reasons
- Strategic independence
- Energy independence

Economic Aspects
- Alternative to petroleum
- Bilateral trade

Social Aspects
- new jobs
- benefits to human health due to air quality improvement
- Challenging opportunities to science and technology development

Renewable
- short production cycle
- good sustainability indicators
Requirements and Visions

Bio-based economy has to be able to attend society demands which are nowadays based on fossil economy

Fossil economy → oil, coal, natural gas, shale gas…

Society demands:

• Biofuels (for transportation) and energy (have to be accounted for)

• Commodities

• High added value chemicals and products
Challenges and visions

• Raw material production with higher productivity (use as less as possible arable land)/ agriculture residues/especial crops; logistic to collect at lower costs with sustainability indexes considered as restrictions

• Definitions of strategies to define the use of the raw material in commercial applications

→ Should we reproduce the same products/materials? A critical view indicates that new materials should be focused but the easiness to enter in the market could imply in an intermediate transition phase

• Definition and discrimination of conversion routes to a better use of the raw material with flexibility to attend society and regional demands.

• Rational use of the existing alternatives to fossil economy → a bridge for the future technologies.

Existing business model strongly related to biofuels and to commodities
## Comparative Energy Flow – Biomass to Biofuel – example bioethanol

<table>
<thead>
<tr>
<th>PROCESS</th>
<th>Corn(^1)</th>
<th>Switchgrass(^1)</th>
<th>Sugar cane(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy unit</td>
<td>(GJ/ha.yr)</td>
<td>(GJ/ha.yr)</td>
<td>(GJ/ha.yr)</td>
</tr>
<tr>
<td>Crop production energy</td>
<td>18.9</td>
<td>17.8</td>
<td>13.9</td>
</tr>
<tr>
<td>consumption</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biomass Energy</td>
<td>149.5(^3)</td>
<td>220.2</td>
<td>297.1(^4)</td>
</tr>
<tr>
<td>Agricultural energy ratio</td>
<td>7.9</td>
<td>12.3</td>
<td>21.3</td>
</tr>
<tr>
<td>Ethanol production energy</td>
<td>47.9</td>
<td>10.2</td>
<td>3.4</td>
</tr>
<tr>
<td>consumption</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy in ethanol</td>
<td>67.1(^5)</td>
<td>104.4</td>
<td>132.5(^6)</td>
</tr>
<tr>
<td>Total energy ratio</td>
<td>1.21</td>
<td>4.43</td>
<td>8.32</td>
</tr>
</tbody>
</table>

1- Source: ORNL, 2- Source: Copersucar/UNICAMP, 3- No credit for corn stover, 4- No credit for sugar cane leaves, 5- includes credits for co-products, 6- Includes credits for surplus bagasse 8%

### Ethanol Productivity

Brazilian sugarcane ethanol is the biofuel presenting the **highest productivity in the world** (today: average of 7,600 l/ha.year) and the **best renewable energy ratio**: 9-11 liters renewable energy/liter fossil energy

US corn ethanol: 1.4-1.8

Adoption of innovative technologies will more than double present productivity to 14,000 l/ha.year – that means lignocellulosic ethanol will be available.

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

Nowadays – depending upon the oil field 1-10
Feedstock used for fuel Corn in USA and Sugar Cane in the World Soya Bean for Biodiesel (BR and AR) an Palm Oil for Biodiesel (Malaysia and BR, COL). Wood chips/forest residues “everywhere” (different growing times)

Processes should be robust to run with different renewable feedstock but should attend international standards.
ENERGY AND DEVELOPMENT

Power Consumption and GDP (World Regions)

By Bruce Dale–Michigan State University
Energy Consumption & Human Well Being are Linked:
NO Countries have Both High HDI and Low Energy Use

By Bruce Dale—Michigan State University
(Renewable) Energy is Critical for Human Well Being

1. Rate of energy use (power consumed) strongly affects (determines?) national wealth and opportunities for human development
2. All rich societies use a lot of energy (~33% oil)
3. “Energy efficiency” helps but is not an answer in itself
4. Fossil energy use makes us rich today—what energy sources will make our grandchildren rich? Answer: it cannot, it will be gone by then…
5. How will the billions of poor people in the world ever access enough fossil energy to develop their potential? Answer: they cannot, it will be gone/be too expensive for them…
6. Of all forms of energy, liquid fuels are the most valuable and most problematic in terms of supply, price and price volatility
7. Peak oil has already arrived- 2005 and the shale gas peak will be in 3-4 years time
8. Only large scale, low cost, low carbon energy sources can reduce GHGs, provide energy security and long term wealth
9. Sustainable biofuels are not optional—we must have them
10. How can we design & implement sustainable biofuel pathways?

By Bruce Dale–Michigan State University
Renewable Feedstock for Biofuels, Energy and Chemicals

Sugar cane, Soya bean, Palm, Coconut, Corn, eucalyptus (5-7 years) Agriculture/forest residues, Animal Fatty among others. Any lignocellulosic material. Depending upon the route, urban waste Many alternatives to use such raw material – production scale and logistic has to be accounted for (raw material supply chain)

Sugar Cane nowadays only saccharose is used for bioethanol
Biofuel versus Chemicals or Biofuels and Chemicals

• Suitability and Energy Supply

• Economic evaluation

• Society Demand

Biofuels

• Bridge for biorefinery development and establishment
• Rationality → Suitable environment → low energy costs, available raw material at the production site, unit operations may be shared (low CAPEX) → sugar cane based bioethanol → typical case
Immediate Applications

1-) Biofuels
• Bioethanol for light cars \textit{(commercial for more than 40 years in BR)}
• Biobutanol for light cars
• Additives for bioethanol use in heavy engines \textit{(evaluation)}
• Biodiesel for heavy engines \textit{(commercial for several years)}
• Biokerosene for jet fuels \textit{(evaluation of technologies)}
• H_2 Production from Ethanol
• Biogasoline

2-) Biorefineries - a) Some commodities \textit{(commercial)}
   b) High Added Value Chemicals and Special Polymers \textit{(on the way)}

3-) Electricity and Power Generation \textit{(commercial 18\%)}
1st and Half Generation - SUGAR, ETHANOL AND ENERGY PROCESS

SUGAR CANE EXTRATION → Steam Production → Power Generation → ELECTRICITY

Juice Treatment → Filtration → Filter Cake

Filtration → Filter Juice

Juice Concentration → Juice Treatment

Crystallization → Molasses → Fermentation

Fermentation → Distillation → ETHANOL

SUGAR
Sugarcane numbers in Brazil

- 2011/12: 8.5 million ha
- Cane production 2011/12: 595 Mt
  - 52% for ethanol and 48% for sucrose
- Ethanol: 23 billion L
- Sucrose: 36 Mt
- 434 mills (250: sucrose + ethanol 168: exclusive for ethanol)

1 ton of sugar cane (80 ton/hectare) produce:
- 250 Kg of bagasse
- 120 Kg of Sugar
- 85 Liters of ethanol

70,000 growers
1.2 million jobs
Annual revenue: US$ 48 billion
Exports: US 15 billion

High Cell Concentration with Cell reactivation and exporting energy → Unique in the world

Cantarella, 2013
Global Process Improvement – from Biomass to Conversion
Sugarcane: the highest tonnage crop

<table>
<thead>
<tr>
<th>Type of yield</th>
<th>Cane yield (t ha⁻¹ yr⁻¹)</th>
<th>Biomass (t ha⁻¹ yr⁻¹)</th>
<th>(g m⁻² d⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial Average</td>
<td>84</td>
<td>39</td>
<td>10.7</td>
</tr>
<tr>
<td>Commercial maximum</td>
<td>148</td>
<td>69</td>
<td>18.8</td>
</tr>
<tr>
<td>Experimental maximum</td>
<td>212</td>
<td>98</td>
<td>27.0</td>
</tr>
<tr>
<td>Theoretical maximum</td>
<td>381</td>
<td>177</td>
<td>48.5</td>
</tr>
</tbody>
</table>

Theoretical maximum: 380 tons/ha
Current average: 65-80 tons/ha

Fermentation: 90-96 % theoretical conversion (High cell concentration process)

Improvements on the fermentation are able to increase bioethanol concentration (30%)

Less energy use in the process leads to Higher bagasse/tops and leaves surplus

(Hydrous and Anhydrous Ethanol)

<table>
<thead>
<tr>
<th>Technology</th>
<th>Dehydrating Agent</th>
<th>Steam consumption (kg steam/L ethanol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azeotropic</td>
<td>Cyclohexane</td>
<td>1.7</td>
</tr>
<tr>
<td>Extractive</td>
<td>Monoethyleneglycol</td>
<td>0.7</td>
</tr>
<tr>
<td>Molecular sieves</td>
<td>Zeolite beads</td>
<td>0.2 - 0.5</td>
</tr>
</tbody>
</table>

Maciel Filho et al. 2014 to appear
Integrated 1\textsuperscript{st} and 2\textsuperscript{nd} Generation – Unique environment

Integrated 1\textsuperscript{st} and 2\textsuperscript{nd} generation Bioethanol production from sugarcane (butanol / biogas ?) \(\rightarrow\) raw material already in the production site
Concept of the Integrated Plants $\rightarrow$ take advantage of the First Generation competitiveness process

Industrial Plant size:

27,000 to 30,000 ton/sugar cane/day

Amounts of ethanol, sugar and electricity depend upon the business model
Raw material characterization for Biochemical Route

Sugar cane for Energy

<table>
<thead>
<tr>
<th>Component*</th>
<th>Content / wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry matter, %</td>
<td>100.00</td>
</tr>
<tr>
<td>Arabinan</td>
<td>1.88 ± 0.59</td>
</tr>
<tr>
<td>Xylan</td>
<td>22.40 ± 1.36</td>
</tr>
<tr>
<td>Glucan</td>
<td>41.67 ± 3.31</td>
</tr>
<tr>
<td>Acetate groups</td>
<td>3.63 ± 1.11</td>
</tr>
<tr>
<td>Furfural</td>
<td>3.09 ± 0.46</td>
</tr>
<tr>
<td>5-HMF</td>
<td>0.14 ± 0.02</td>
</tr>
<tr>
<td>ASL</td>
<td>5.55 ± 0.02</td>
</tr>
<tr>
<td>K-Lignin</td>
<td>11.53 ± 2.19</td>
</tr>
<tr>
<td>Ashes</td>
<td>2.53 ± 0.13</td>
</tr>
<tr>
<td>Extractives</td>
<td>8.93 ± 1.16</td>
</tr>
<tr>
<td>Total</td>
<td>101.37 ± 2.07</td>
</tr>
</tbody>
</table>

Heating value (MJ/kg)

- Low: 17.4
- High: 18.7

For example: Wood 25 MJ/kg aprox.
Acid catalyzed hydrothermal route

one of the more suitable and easy to integrate
Low cost route
Need to increase solid loading and kinetic evaluation of by-products

Biomass: Sugarcane bagasse

H₂SO₄ solution: 1.0% w/v - 3.0% w/v

Pretreatment

(121 °C); (0 - 150 min)

H₂SO₄ pretreatment

Acid hydrolysate

Solid recovery g_{dry matter}\\
- Glucan, GLN\\
- Arabinan, ARN\\
- Xylan, XYL\\
- Acetate groups, ACT\\
- Furfural, FUR\\
- 5-hydroxymethylfurfural, 5-HMF\\
- Acid soluble lignin, ASL\\
- Ash\\
- Extractives

Total

Hydrolysate

Glucose, GLC\\
Arabinose, ARB\\
Xylose, XYL\\
Fufural, FUR\\
5-hydroxymethylfurfural, 5-HMF\\
Acetic acid, AAc\\
Levulinic acid, LEV

Total

Hydrolysis

Cellulase, from Trichoderma reesei ATCC 26921
Cellobiase from Aspergillus niger Novozyme 188

(50 °C); (0 - 72 h)
15.0 FPU/g substrate (WIS) ; 30.0 IU/g substrate (WIS)

Enzymatic hydrolysis

WIS

Solid recovery g_{dry matter}\\
- Glucan, GLN\\
- Arabinan, ARN\\
- Xylan, XYL\\
- Acetate groups, ACT\\
- Furfural, FUR\\
- 5-hydroxymethylfurfural, 5-HMF\\
- Acid soluble lignin, ASL\\
- Acid insoluble lignin, AIL\\
- Ash

Total

WIS(EH)

Solid recovery g_{dry matter}\\
- Glucan, GLN\\
- Arabinan, ARN\\
- Xylan, XYL\\
- Furfural, FUR\\
- 5-hydroxymethylfurfural, 5-HMF\\
- Acid soluble lignin, ASL\\
- Acid insoluble lignin, AIL\\
- Ash

Total

Process developed by 20-25 % solid (sugar cane bagasse) and kinetics were identified
H$_2$SO$_4$-catalyzed hydrothermal route and acid hydrolysis of lignocellulotic biomass (sugarcane bagasse)-side reactions

**Kinetic model**

- H1: Xylan easy-to-hydrolysis
- H2: Xylan hard-to-hydrolysis
- XYL: Xylose
- HUM: Humins solids
- FUR: Furfural
- ARN: Arabinan
- ARB: Arabinose
- ACT: Acetate groups
- AAc: Acetic acid
- GLC: Glucose
- HMF: 5-hydroxymethyl furfural
- LA: Levulinic acid
- LIG: Lignin
- ASL: Acid soluble lignin

- low loss of cellulose (around 15%) and low concentrations of hemicelluloses in cellolignin material (lesser than 10%) using high-solids loading (20-25%) after the H$_2$SO$_4$-catalyzed hydrothermal pretreatment.
Challenge: Cellulosic Ethanol Learning Curve

Production scale size plants running to allow evaluation of different pre-treatment and hydrolysis → scale up and impact of inhibitors on fermentation and enzyme efficiency on hydrolysis

First generation learning curve

70's

Today

In 10 years?

Room for improvements in the 1st generation to improve environment for 2nd bioethanol

Goldemberg, J.
Integrated Process

Sugar Cane → Extraction → Juice → Sugar Production → Sugar

Bagasse → Molasses

Straw

Boiler → CO₂

Thermal Reactor

Integrated Process for Total Bioethanol Production and Zero CO₂ Emission

First Generation

Second Generation

Third Generation Algae

Third Generation Syngas

Virasse → Biodiesel

Fat acids → Protein → Nutrient

Residue → Syngas

Methane → Biodigestion

Zero CO₂ Emission Process

Complete use of all streams

Source: Thematic Project Fapesp 2008/57873-8 Coordinator Maciel Filho
Microalgae- Impact of light intensity on biomass Concentration-
New reactor design to allow high production in an integrated site

- The kinetics of crops clearly shows the dependence of the final concentration of biomass with light intensity and nitrogen.

![Graph showing biomass concentration over time and light intensity]

Gallons of Oil per Acre per Year

- Corn ........ 15
- Soybeans .... 48
- Safflower ... 83
- Sunflower ... 102
- Rapeseed ... 127
- Oil Palm .. 635

Micro Algae...1850 [based on actual biomass yields]

New reactor for production of biotechnological product → Stirred airlift bioreactor
Easy to integrate in 1st bioethanol plant
Improvements still needed

Initial concentration of biomass: 0.3 g/L
Biodiesel Fuel Production from Algae oil by Transesterification in Supercritical Fluids

Supercritical Reactor - Factible in an environment for 1st bioethanol mill

- 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 (CO$_2$)

No need to add catalyst and no soap formation

Operating range:
- ✓ 0-500 bar
- ✓ 0-250 ºC

Temperature = 150ºC to 200ºC  Oil to ethanol ratio molar = 1:25 – 1:40
Reaction time = 2-10 min; Pressure = 200 bar
Biological Synthesis of Propionic Acid from Glycerol

- **Sucrose**
  - Glucose + Fructose
    - Embden-Meyerhof-Parnas pathway
    - Hexose Monophosphate pathway
  - Phosphoenolpyruvate
    - Pyruvate kinase
    - Pyruvate dehydrogenase
    - Propionyl-CoA
      - Acetyl-CoA
      - Phosphotransacetylase
      - Acetate kinase
    - Acetyl phosphate
      - Acetate
      - Succinate dehydrogenase
    - Propionate
- **Glycerol**
  - Pyruvate
    - PEP carboxylase
    - Oxaloacetate
      - Malic dehydrogenase
      - Malate
        - Fumarase
        - Fumarate
      - Succinate
    - Vitamin B12
      - Succinyl-CoA
        - ATP + NADH
        - ADP + NADH
      - Succinate
        - Fumarate
      - Fumarase
      - Fumarate

Graphs showing time (h) and concentrations of various substances.
### 2³ factorial design

<table>
<thead>
<tr>
<th>Run</th>
<th>T (°C)</th>
<th>t (min)</th>
<th>Ar (ml/min)</th>
<th>% H₂</th>
<th>% CO</th>
<th>% H₂+CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>750</td>
<td>20</td>
<td>10</td>
<td>19.66</td>
<td>31.6</td>
<td>51.26</td>
</tr>
<tr>
<td>2</td>
<td>850</td>
<td>20</td>
<td>10</td>
<td>36.05</td>
<td>29.29</td>
<td>65.34</td>
</tr>
<tr>
<td>3</td>
<td>750</td>
<td>40</td>
<td>10</td>
<td>18.63</td>
<td>29.61</td>
<td>48.24</td>
</tr>
<tr>
<td>4</td>
<td>850</td>
<td>40</td>
<td>10</td>
<td>35.76</td>
<td>29.68</td>
<td>65.44</td>
</tr>
<tr>
<td>5</td>
<td>750</td>
<td>20</td>
<td>50</td>
<td>24.09</td>
<td>27.57</td>
<td>51.66</td>
</tr>
<tr>
<td>6</td>
<td>850</td>
<td>20</td>
<td>50</td>
<td>41.07</td>
<td>29.92</td>
<td>73.99</td>
</tr>
<tr>
<td>7</td>
<td>750</td>
<td>40</td>
<td>50</td>
<td>19.5</td>
<td>27.63</td>
<td>47.13</td>
</tr>
<tr>
<td>8</td>
<td>850</td>
<td>40</td>
<td>50</td>
<td>42.82</td>
<td>34.79</td>
<td>77.61</td>
</tr>
</tbody>
</table>

### Central Points

<table>
<thead>
<tr>
<th>Run</th>
<th>T (°C)</th>
<th>t (min)</th>
<th>Ar (ml/min)</th>
<th>% H₂</th>
<th>% CO</th>
<th>% H₂+CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>800</td>
<td>30</td>
<td>30</td>
<td>33.74</td>
<td>32.32</td>
<td>66.06</td>
</tr>
<tr>
<td>10</td>
<td>800</td>
<td>30</td>
<td>30</td>
<td>33.24</td>
<td>32.76</td>
<td>66</td>
</tr>
<tr>
<td>11</td>
<td>800</td>
<td>30</td>
<td>30</td>
<td>33.5</td>
<td>32.54</td>
<td>66.04</td>
</tr>
</tbody>
</table>

The main gas products were H₂ and CO. Besides these gases, CO₂, CH₄, C₂H₄ and C₃H₈ were also obtained in smaller proportions.

The liquid product compositions were methanol, ethanol, acetone and acetaldehyde.

Net energy recovered = 294kJ/mol of glycerol fed.

Models for Kinetic Parameter Arrhenius, Flyn-Ozawa-Wall (FWA), Kissinger (International Patent requested)
Bioethanol as fuel and feedstock for Chemicals

**Ethanol as a Car Fuel**

![Ethanol molecule](image)

C₂H₅OH

Compatible with existing infrastructure and engines
Blends with petrol (0-100 %)
Extensive experience in Brazil, USA
Agricultural feedstocks: closed carbon cycle

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Ethanol from sugar fermentation is **thermodynamically and energetically suitable** including yields and conversion **compared to oil as feedstock**

Ethanol as a raw material for chemicals- already a suitable approach

Production in large scale – as a commodity is beneficial
Commodities ➔ Use of ethanol as feedstock – that means obtain chemicals from ethanol: Alcoholchemistry based Products

- Ethanol
- Ethylene
- Acetaldehyde
- Propylene
- Acetic Acid
- Vinyl Acetate
- Ketene
- Crotonaldehyde
- N-Butyraldehyde
- N-Butanol
- Ethylene-Dichloride
- Vinyl Chloride
- Styrene
- Polystyrene
- Ethylene Oxide/Glycol
- Polyethylene
- Butadiene
- Polyvinil Acetate
- Acetic Anhydride
- Monochloroacetic Acid
- Ethyl + Other Acetates
- 2-Ethylhexanol

US 55/barrel

Competitive prices for many of the chemicals – Technology well established
Brazil in earlier 80’s ➔ several running processes ➔ nowadays room to increase
Ethene Production by Ethanol Dehydration

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 and Propene – two of the largest commodities from Bioethanol

Green Acetaldehyde – Green Ethene – Green Propene

Bioethanol

Dehydration → Green Ethene

Dimerization → 1-Butene / 2-Butene

Oxidation → Acetaldehyde

Dehydration → Green Ethene

Metathesis → Green Propene

(Patent pending – Unicamp)
Biofuel versus Chemicals or Biofuels and Chemicals

- Suitability and Energy Supply
- Economic evaluation
- Society Demand
- Evaluation of Routes → criteria for Route discrimination

Sustainability (?) and Economically Competitive Process-Universal Approach

Main Routes: (feedstock: C5, C6, Lignin, Organic acids)

- Fermentation (C6, C5 for some products butanol Lactic acid)
- GMO or Simultaneous C5/C6 Fermentation 70 to 90 hours
- Chemical (C5, Lignin)
- Hybrid Route → Fermentation + Chemical Transformation
- Thermochemical (syngas, fuel gas, bio-oil)
- Multiple Hybrid routes
### Proximate analysis (wt %)

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content</td>
<td>2.00</td>
</tr>
<tr>
<td>Ash content</td>
<td>6.52</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>88.12</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>3.36</td>
</tr>
</tbody>
</table>

### Heating value (MJ/kg)

- **Low**: 17.4
- **High**: 18.7

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For example: Wood 25 aprox.
Production of Syngas from Sugar Cane Bagasse

Sugar Cane

Bioethanol

Sugar cane bagasse

Process Development and Evaluation

Gasification

Syngas or Bio-oil

CO
H₂

Fermentation or Chemical Synthesis (FT)

(Gas to energy ?)
**New Process for Butanol Production: Extractive Fermentation- C6 or C5 as feedstock**

(Pinto Mariano, Nasib Q. Maciel Filho, Biotechnology and Bioengineering, 2011)

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

Heat of combustion of ButOH = 36 MJ/Kg

**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

Net Revenue breakdown

Return on investment

Biorefinery scenario

- **BIO-G**
- **RS-C**
- **MS-C**
- **RS-F**
- **MS-F**
High Added Chemical Products from Biomass → Suitable Approach to overcome possible high costs for biomass. Learning curve → costs have to be reduced.

BIOMASS → HYDROLYSIS

Sugar

Glycose
Sacarose
Xylose
Arabynose

FERMENTATION

higher alcohols
Ethanol
Acetaldehyde
Acetic acid
Propene
Propylene
Acrylic Acid
Glycerol
Lactic acid
Butadiene
Butanodiol
Succinic acid

Hybrid Routes → fermentation + chemical synthesis

Biomass – C6 and C5 and Lignin
Care has to be taken with suitability for Industrial environment, sustainability and Energy Supply. This includes C5 fermentation (elegant academic solution ?)
Cane High Added value Products from Sugar LACTIC ACID controlled physical and chemical properties for biomaterial applications suitable precursor molecule

**Microorganism:** *Lactobacillus plantarum* (lactic acid isomers L and D production) isolated from sample of industrial ethanol fermentation.

**Carbohydrate source:** sucrose obtained from sugarcane.

High added value products: In relation to the Sugar and added value of 190,000 times
LACTIC ACID

**Petrochemical resources**

- Acetaldehyde \((\text{CH}_3\text{CHO})\)
  - Addition of HCN and catalyst
  - Lactonitrile \((\text{CH}_3\text{CHOHCN})\)
    - Hydrolysis by \(\text{H}_2\text{SO}_4\)
  - Only racemic DL-lactic acid

**Renewable resources**

- Fermentable carbohydrates
  - SSF
  - Fermented broth
  - Optically pure L(+) or D(-) lactic acid

**Chemical synthesis**

**Microbial fermentation**

Desirable due to:

- i) Recent environmental issues
- ii) Limited nature of petrochemical resources
- iii) Flexible in terms of required properties
METHODOLOGY: Hybrid Route for producing acrylic acid from fermentation of Sugars to lactic acid

Process – Patent Pending - Unicamp/LOPCA-Braskem
The polylactide (PLA) is one of the most promising biodegradable polymers due to its mechanical property profile, thermoplastics, biological and processing. It is very useful in medical area.
Properties Product Definition for Specific Application
Modelling and Computer Operation by Hybrid Mathematica Model and Fuzzy Logic

Monomer
Co-monomer
CAT
CO-CAT
Solvent
H2
T PFR
T CSTR
P system
Feed Lateral

Fuzzy Model - type A

Process

Conversion
Rate
production
Mn
Mw
Density
Pd
MI
SE

Fuzzy Model - type C

Performance Properties
Stiffness
Impact Strength
Hardness
Melt Strength
Stress Crack Resistance
Tensile Strength
Tm
Tc
Tg
crystallization percent
melt swell
softening Point
Reactor Profile

**Tubular configuration**

![Diagram of a tubular reactor configuration]

- **Stage nº:** 1, 2, 3, 4
- **Reactor Length (dim.):** 0.00 to 1.00
- **MI (dim.):** 0.00 to 0.60

**Stirred configuration**

![Diagram of a stirred reactor configuration]

- **Stage nº:** 1, 2
- **Reactor Length (dim.):** 0.00 to 1.00
- **MI (dim.):** 0.00 to 0.50

The diagrams illustrate the reactor profiles for both tubular and stirred configurations, showing the reactor length (in dimensions) and the corresponding changes in MI (in dimensions) through the stages.
Properties to be considered:

**Biological requirements:**
- Biocompatibility
- Biodegradability
- Controlled degradation rate
- Appropriate porosity to allow tissue in-growth and vascularisation
- Ability to carry biomolecular signals such as growth factors

**Mechanical and Physical requirements:**
- Sufficient strength and stiffness to withstand stresses in the host tissue environment
- Adequate surface finish
- Easily sterilised
- Controlled swelling
Prediction of the Expected Behaviour

- Biological Requirements
- Materials
- Scaffold Design
- Fabrication
- Mechanical Requirements
- in vivo/in vitro Evaluation
Computer Tomography → Body Digital Image

Computer Tomography (CT)

DICOM Format
Building Medical Models - Material properties have to be well defined → Monomers have to be special characteristics only achieved by bio-based products.
Tissue engineering - the use of techniques and materials capable of serving as a substrate for culture of cells to develop a new tissue. PLA D a an L should be combined to provide the required solution.
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
Final comments
Some bio-based products are already economically competitive!
First Generation bioethanol plants provide the best environment for 2nd biofuels and biorefinery (in the world!)
Oil based economy has its impacts.
No many room to improve

Bio-based products may be improved

Balancing the Carbon Cycle: Industrial Biotechnology

Challenges Resulting from an Oil-Based Economy

- Global Temperature
- CO₂ concentration

- Agriculture, forestry
- Plant biomass
- Biorefinery
- Combustion
- Industrial microbiology
- Fuels and chemicals
- Sugars