Gasification of bagasse to Syngas and Advanced Liquid Biofuel Production

Prof. Dr. Rubens Maciel Filho
School of Chemical Engineering
Laboratory of Optimization, Design and Advanced Process Control-LOPCA
National Institute of Biofabrication-BIOFABRIS
State University of Campinas – UNICAMP – Brazil
Fapesp/Bioen- Process Engineering Coordination
PLA-CTBE

Brazil-EU-Workshop: Coordinated Call on Advanced Biofuels
Society's necessity requires connection among fuels, energy, chemicals

Services needed from energy
Heat (natural gas, coal, wind, solar, geothermal, biomass)
Light/electricity (coal, natural gas, hydro, nuclear, solar, wind, biomass)
Mobility (liquid fuels from oil, bioethanol, biodiesel)- most commerce

Chemicals – commodities and high added value product
Commodities similarity to oil based refinery
High added value new chemicals for new applications

Chemicals or building blocks molecules for chemicals may be part of biofuels production as a by-product or a dedicated plant sharing the same facilities oil refinery based model cost reduction to accommodate for incomplete conversion and separation difficulties.
More products more flexibility in the business
Energy Consumption & Human Well Being are Linked

By Bruce Dale–Michigan State University

Biofuel processes should be energetically efficient and, if possible, to export energy
Renewable Feedstock for Biofuels, Energy and Chemicals (Brazil is in prime position)

Sugar cane, Soya bean, Palm, Coconut Orange, Agriculture residues, Animal Fatty among others. Any lignocellulosic material.
Many alternatives to use such raw materials – production scale and logistic has to be accounted for

- Saccharose
- Bagasse
- Tips and Straw

Sugar Cane
More or less 1/3
Saccharose, Bagasse
Tips and straw

• Residues from biodiesel industries and by-products from bioethanol
• Urban waste – advantage in terms of logistic and price and difficulties from standardization
Sugarcane numbers in Brazil
Energy cane to come (180-200 ton/hectare)

- 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

2014/15 Use less than 1 % of arable land  Production of sugar cane → 630 Mt

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

Cantarella, 2013
Basic conversion routes:

0. Direct Conversion of Sugars (?)
1. Fermentation
2. Hybrid (fermentation + chemical reaction)
3. Thermochemical
4. Transesterification

Fermentation- (e.g. sugar cane → ethanol)

Fermentation- of residues and waste to Biogas

Thermochemical- To break materials (crops, residues) into the smallest possible building blocks - carbon monoxide (CO) and hydrogen (H₂), from which the desired chemical products are synthesized.

Grains → fractionation → starch, oils, proteins, and fiber.
Starch → hydrolysis → sugars → fermentation (e.g. ethanol)
Oils → transesterification and chemical reaction (e.g. Biodiesel)
Possible Routes to Process Biomass

Sugar $\rightarrow$ extracted from sugar-rich crops $\rightarrow$ fermentation

**HYDROLYSIS**
- Acids, enzymes

**GASIFICATION**
- High heat, low oxygen

**DIGESTION**
- Bacteria

**PYROLYSIS**
- Catalysis, heat, pressure

**EXTRACTION**
- Mechanical, chemical

**SEPARATION**
- Mechanical, chemical

---

**Sugars and Lignin**

**Synthesis Gas**

**Bio-gas**

**Bio-Oil**

**Carbon-Rich Chains**

**Plant Products**

---

**BIOFUELS**
- Heat
- Electricity
- Chemicals
- Materials

---

Fermentation of residues and waste to Biogas
Evolutionary Engineering and the 1G Learning Curve

Learning curve of Thermochemical Route from other raw materials → important knowledge

1G
(40 years)

70’s
4.200/ha
82 %

Today
7.650/ha

2G Biochemical

In 10 years?
12.000/ha
40-60 %

US$ 20-25 cents → production cost of 1 liter of ethanol (70% sugar cane)
Decision making – couple with different alternatives

Brazilian concept of Biofuel Production → requires to be energetically self-sufficient and even Electricity Exporter

Thermochemical Routes Challenges
1-) Syngas production
2-) Gas purification
3-) Catalyst development for efficient process
4-) Separation an purification

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

To other raw materials
- Impact of Logistic

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

<table>
<thead>
<tr>
<th>Fermentative Processes</th>
<th>Energy Consumption (Purification)</th>
<th>Various Feedstocks</th>
<th>Energy Cogeneration</th>
<th>Food Security</th>
<th>Water Consumption</th>
<th>Known and spread Technology</th>
<th>Dependency of Petroleum Prices</th>
<th>Low Conversion (~5%)</th>
<th>High Temperature and Pressure</th>
<th>High Purity</th>
<th>Competition with other industry branches</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enzymatic Process</td>
<td>High Cost</td>
<td>High Cost</td>
<td>Low Temperatures</td>
<td>Low Yield</td>
<td>Residues Usage</td>
<td>Doesn’t make use of lignin</td>
<td>Various Feedstocks</td>
<td>Abundant and Cheap Feedstock</td>
<td>Short reaction time</td>
<td>Uses lignin</td>
<td>Low conversion and selectivity</td>
</tr>
</tbody>
</table>
Concept of the Integrated Plants → take advantage of the First Generation competitiveness process
(Good starting point)- share facilities (lower CAPEX and OPEX) and raw material available in the production site

Typica Industrial Plant size:
37,000 to 35,000 ton/sugar cane/day

Amounts of ethanol, sugar and electricity depend upon the business model
Steps – from Biomass to Syngas

Biomass → Gaseification → Pre-treatment → Syngas

Conversion of Thermochemical Process

$T = 650-1400^{\circ}C$

Biomass + $O_2/Ar$ (limited) → $CO + H_2 + CO_2 + CH_4 + H_2O_{vapor} + N_2$

syngas
Sugar Cane Bagasse characterization

<table>
<thead>
<tr>
<th>Proximate analysis (wt %)</th>
<th>Ultimate analysis (dry and free of ashes wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content</td>
<td>C 44.6%</td>
</tr>
<tr>
<td>Ash content</td>
<td>H 5.9%</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>Ash 6.7%</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>O 42.2%</td>
</tr>
</tbody>
</table>

- **Moisture content**: 2.00 wt %
- **Ash content**: 6.52 wt %
- **Volatile matter**: 88.12 wt %
- **Fixed carbon**: 3.36 wt %

<table>
<thead>
<tr>
<th>Heating value (MJ/kg)</th>
<th>Low</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>17.4</td>
<td>18.7</td>
</tr>
</tbody>
</table>

For example: Wood 25 aprox.

Most significant differences of sugar cane bagasse compared to coal: moisture (requires more heat) and higher amount of volatiles
Gasification /Pyrolysis

**Drying**
- Wet biomass → Dry biomass → H₂O

**Pyrolysis**
- Dry biomass → Pyrolysis gas (Gas + Tar) → Char

**Combustion**
- C + O₂ → CO₂
- 2 H₂ + O₂ → 2 H₂O
- CₙHₘ+(n/2+m/4) O₂ → nCO₂ + m/2 H₂O

**Reduction**
- C + CO₂ ↔ CO
- 2 C + H₂O ↔ CO + H₂
- CₙHₘ+nH₂O → nCO + (m/2+n) H₂
- CₙHₘ+nCO₂ → 2nCO + m/2 H₂

**Process Conditions**—Pressure, Temperature, Residence Time, etc.
Thermochemical process

Bagasse

Pyrolysis

In the absence of oxygen

- Bio-Oil (Tar)
  400 – 600 °C
- Char
- Gas
  >700 °C

Combustion

Gas turbine in combined cycle to produce energy in larger scale

Gasification

In the presence of oxygen (Air or steam)

- It uses an amount of oxygen lesser than that required stoichiometrically

- Syngas ($H_2/CO$) (Priority)
- Electricity

UNICAMP
Fluidized bed reactor showed higher performance when compared to Fixed bed reactor.
Simulations validity

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 H₂, CO and impurities, respectively.
1-Focus on ethanol production with lower temperature and pressure compared to FT
2-Electricity generation using turbine powered by gas from biomass (forest residues from pulp and paper residues - nowadays 60-90 bar boilers for sugar cane)
3-Syngas fermentation to ethanol and organic acids which are platforms for other biofuels
Catalytic mechanism of the Fischer-Tropsch synthesis

Paraffin:
\[ n\text{CO} + (2n + 1)\text{H}_2 \rightarrow C_{n+1}H_{2n+2} + n\text{H}_2\text{O} \]

Olefin:
\[ n\text{CO} + 2n\text{H}_2 \rightarrow C_nH_{2n} + n\text{H}_2\text{O} \]

Alcohols:
\[ 2n\text{H}_2 + n\text{CO} \rightarrow C_nH_{2n-1}\text{OH} + (n-1)\text{H}_2\text{O} \]
Conventions of fuel names and compositions

<table>
<thead>
<tr>
<th>Name</th>
<th>Synonyms</th>
<th>Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td></td>
<td>$C_5 - C_{12}$</td>
</tr>
<tr>
<td>Naphtha</td>
<td></td>
<td>$C_8 - C_{12}$</td>
</tr>
<tr>
<td>Kerosene</td>
<td>Jet fuel</td>
<td>$C_{11} - C_{13}$</td>
</tr>
<tr>
<td>Diesel</td>
<td>Fuel oil</td>
<td>$C_{13} - C_{17}$</td>
</tr>
<tr>
<td>Middle distillates</td>
<td>Light gas oil</td>
<td>$C_{10} - C_{20}$</td>
</tr>
<tr>
<td>Soft wax</td>
<td></td>
<td>$C_{19} - C_{23}$</td>
</tr>
<tr>
<td>Medium wax</td>
<td></td>
<td>$C_{24} - C_{35}$</td>
</tr>
<tr>
<td>Hard wax</td>
<td></td>
<td>$C_{35+}$</td>
</tr>
</tbody>
</table>

Focus on biodiesel and Kerosene (Jet fuel) with lower pressures and temperatures compared to Fisher-Tropsch
Usual evaluation of the catalyst - some criteria for choice

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Cobalt</th>
<th>Iron</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost</td>
<td>More expensive</td>
<td>Cheap</td>
</tr>
<tr>
<td>Timely</td>
<td>Resistant to deactivation</td>
<td>Low resistance</td>
</tr>
<tr>
<td>Probability of chain growth</td>
<td>Max. 0,94</td>
<td>Max. 0,95</td>
</tr>
<tr>
<td>Reaction gas-water</td>
<td>There isn’t significant</td>
<td>Significant</td>
</tr>
<tr>
<td>Sulfur tolerance</td>
<td>&lt;0,1 ppm</td>
<td>&lt;0,2 ppm</td>
</tr>
<tr>
<td>Flexibility (temperature and pressure)</td>
<td>Inflexible.</td>
<td>Flexible, low</td>
</tr>
<tr>
<td>Resistance to abrasion</td>
<td>Resistance ~2</td>
<td>Low resistance</td>
</tr>
<tr>
<td>H₂/CO ratio</td>
<td></td>
<td>0,5-2,5</td>
</tr>
</tbody>
</table>

Effort to reduce pressure and temperature (catalyst based on carbeto)
Catalytic conversion of syngas via direct synthesis

**Ethanol formation**

\[
2\text{CO} + 4\text{H}_2 \leftrightarrow \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}
\]

\[
r_{\text{EtOH}} = 6.3 \times 10^{12} e^{-126.7/RT} p_{\text{H}_2}^{0.90} p_{\text{CO}}^{-0.76}
\]

**Methanation**

\[
\text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O}
\]

\[
r_{\text{CH}_4} = 9.0 \times 10^{15} e^{-156.8/RT} p_{\text{H}_2}^{0.79} p_{\text{CO}}^{-0.60}
\]

**Flowsheet**

Catalyst Rh-Mn-Li-Fe/SiO₂

Thermodynamic model: PRSV-

Production of 500 m³/day of ethanol

(Patent requested – 2015)
Ethanol and Butanol Production Plant by Thermochemical Route-

Sugarcane fields → Cane stalks → Bagasse (50% wet of moisture) → Cleaning → Extraction of sugars (50% of juice) → Juice treatment to sugar → Filter cake → Juice concentration → Crystallization → Centrifugal → Drying → Sugar → Vinasse and others → Distillation and rectification → Dehydration → Anhydrous Ethanol

Bagasse → Straw (bales) → Drying → Handling and milling → Flue gas → Gasification (direct or indirect) → Heat recovery → Wet cleaning system → Compression → Synthesis (Co, and H2S) → CO2 and H2S Co-capture → Guard bed (ZnO/CuO) → Cleaned syngas into compressed dry gas → CWS gas feed (WGS) → Hydrogen separation (TPSA) → Light gases → Mixed alcohols catalytic synthesis → Ethanol recycle → Methanol recycle → Methanol synthesis → High-molecular alcohols

Autonomous distillery → Thermochemical route biomass to mixed alcohols plant → Cryogenic air separation unit (ASU) plant → For directly heated gasifiers

Liquid N2, Liquid Ar, Liquid O2 → Shyntetic air → For indirectly heated gasifiers
Thermochemical Routes to Produce Advanced Biofuels and Electricity
Syngas Fermentation

BIOCHEMICAL PLATFORM

Pre-treatment → Hydrolysis → Fermentation

Downstream processing

Biomass

Gasification → Clean-up/Conditioning → Catalytic conversion

New “hybrid” platform

THERMOCHEMICAL PLATFORM

Bioproducts

Downstream processing
BIOMASS → Gasification → SYNGAS → Fermentation → ETHANOL

\[ C + \frac{1}{2} O_2 \rightarrow CO \]
\[ C + O_2 \rightarrow CO_2 \]
\[ H_2 + \frac{1}{2} O_2 \rightarrow H_2O \]
\[ C + CO_2 \rightarrow 2 CO \]
\[ C + H_2O \rightarrow CO + H_2 \]
\[ C + 2 H_2 \rightarrow CH_4 \]
\[ CH_4 + H_2O \rightleftharpoons CO + 3H_2 \]
\[ CO + H_2O \rightleftharpoons CO_2 + H_2 \]

\[ 6 CO + 3 H_2O \rightarrow C_2H_5OH + 4 CO_2 \]
\[ 2 CO_2 + 6 H_2 \rightarrow C_2H_5OH + 3 H_2O \]
\[ 4 CO + 2 H_2O \rightarrow CH_3COOH + 2 CO_2 \]
\[ 2 CO_2 + 4 H_2 \rightarrow CH_3COOH + 2 H_2O \]
Thermochemical conversion of biomass

- Full conversion of carbon
- Feedstock flexibility
- Mature technology
- Presence of contaminants in gas
- Expensive clean-up

Biochemical conversion of syngas

- Higher resistance to contaminants
- Moderate temperature and pressure
- Higher selectivity
- Inefficient gas-liquid mass transfer
- High dilution
Proposed Conceptual Design for Syngas Fermentation to Ethanol

(Biomass) → Drying and Gasification → Heat Recovery Steam Generator → Bioreactor → Ethanol recovery

- Flue gas
- Hot syngas
- Cold syngas
- Process electricity
- Surplus electricity
- CO₂
- product
- Water recycle
- Wastewater
- Ethanol

(Ashes) → Steam

(Medeiros et al., 2015)
**SYNGAS FERMENTATION: MICROBIAL CATALYSIS USING Clostridium ljungdahlii**

- **Ethanol production with C. ljungdahlii**
- syngas produced from the gasification of lignocellulosic material processes → mainly composed of H₂, CO, CO₂ and CH₄.
- C. ljungdahlii was isolated from chicken waste → ability to produce ethanol from synthesis gas (H₂ and CO mainly). The strain is a strict anaerobe, gram-positive, has a flagellum for locomotion and spores are formed infrequently[1].

  ✓ 48 g/L was obtained with cell recycle and 4 g/L cell mass concentration during continuous fermentation and with yield of 12 g ethanol/g cells[4].
  ✓ 6.5 g/L was obtained with cell recycle and 2.3 g/L cell mass during continuous fermentation[5].
  ✓ The mass transfer is one of the main bottleneck for the fermentation of gaseous substrates → The use of 0.3 wt% of methyl-functionalized silica nanoparticles during syngas fermentation by C. ljungdahlii led to significant increases in the levels of biomass, ethanol, and acetic acid production 34.5%, 166.1%, and 29.1%, respectively[6].

**COMMENTS**

- The C. ljungdahlii converts the gas from biomass gasification to ethanol, other alcohols and organic acids - high added value components.
<table>
<thead>
<tr>
<th>Facility</th>
<th>Owner</th>
<th>Scale</th>
<th>Location</th>
<th>Input</th>
<th>Output information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lighthouse (Coskata)</td>
<td>Coskata, Inc</td>
<td>Demo</td>
<td>Madison (PA), USA</td>
<td>Natural gas, wood chips, simulated waste materials</td>
<td>Yield of 100 gallons of ethanol/dry ton of softwood</td>
</tr>
<tr>
<td>NZ Waste Gas to Fuel Industrial Pilot Plant</td>
<td>LanzaTech</td>
<td>Pilot</td>
<td>Glenbrook, NZ</td>
<td>Steel mill off gases</td>
<td>Production capacity of 15,000 gallons of ethanol annually</td>
</tr>
<tr>
<td>1st China Waste Gas to Fuel Demonstration</td>
<td>LanzaTech BaoSteel New Energy</td>
<td>Demo</td>
<td>Shanghai, China at</td>
<td>Steel mill off gases</td>
<td>Production capacity of 100,000 gallons of ethanol annually</td>
</tr>
<tr>
<td>Plant (LanzaTech)</td>
<td>Co.</td>
<td></td>
<td>BaoSteel Steel Mill</td>
<td>Steel mill off gases</td>
<td>Production capacity of 100,000 gallons of ethanol annually</td>
</tr>
<tr>
<td>2nd China Waste Gas to Fuel Demonstration</td>
<td>Beijing Shougang LanzaTech</td>
<td>Demo</td>
<td>Beijing, China at</td>
<td>Steel mill off gases</td>
<td>Production capacity of 100,000 gallons of ethanol annually</td>
</tr>
<tr>
<td>Plant (LanzaTech)</td>
<td>New Energy Technology Co.</td>
<td></td>
<td>Shougang Steel Mill</td>
<td>Steel mill off gases</td>
<td></td>
</tr>
<tr>
<td>Ghent plant project (2018)</td>
<td>ArcelorMittal/LanzaTech/Primetals Technology</td>
<td>Commercial</td>
<td>Ghent, Belgium</td>
<td>Steel mill off gases</td>
<td>Estimated production capacity of 47,000 ton ethanol/year</td>
</tr>
<tr>
<td>Indian River Bioenergy Center (INEOS Bio)</td>
<td>INEOS Bio</td>
<td>Demo</td>
<td>Vero Beach (FL), USA</td>
<td>MSW, forestry wastes, commercial and industrial wastes,</td>
<td>Yield of 75 – 100 gallons of ethanol/dry ash-free ton of material,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>agricultural wastes</td>
<td>productivity of 8 million gallons annually, plus 6MW of electricity</td>
</tr>
</tbody>
</table>
Integrated Process

Sugar Cane → Extraction → Juice → Sugar Production → Sugar

Bagasse

Molasses

Straw

Boiler → CO₂

Thermal Reactor → Syngas

First Generation

Second Generation

Third Generation Algae

Third Generation Syngas

Distillation → Bioethanol

Carbohydrates

Fat acids

Biodiesel

Protein

Residue

Nutrient

Vinasse

Biodigestion → Methane

Integrated Process for Total Bioethanol Production and Zero CO₂ Emission

Source: Thematic Project  Fapesp 2008/57873-8 – Coordinator  Maciel Filho
How to decide on the technology

• Feedstock availability and logistic

• Domain of technology, costs of royalties, human resources

• Need to attend the market regulations

• Energy and water supply restrictions or limitations

• Sustainability analysis → economic, social and environmental evaluation is necessary (e.g. BVC-CTBE)

• Several scenarios have to be considered

• Economic viability is essential → society, in general, is not to pay more because is renewable
Competencies in Brazil

UNICAMP, IPT, UNB, UFU, UNIFEI, UFRJ, CTBE, LNLS, LNANO

Acknowledge:

Lopca researches

• Jaiver Feigeroa Pos-doc
• Eleisa Medeira PhD student
• Yurany Camacho PhD
• Julio Miranda Pos-Doc
• Ana Paula Perez PhD
Biomass from Sugar Cane

Sugarcane mill

- 52 Ton Juice
  - 100 Ton Byproducts
    - 48 Ton Straw
    - 28 Ton Bagasse
      - 14 Ton Solids
      - 14 Ton Moisture

Sugarcane bagasse already in the production site → advantage in the logistics
Possible Routes to Process Biomass

Sugar $\rightarrow$ extracted from sugar-rich crops $\rightarrow$ fermentation

Fermentation of residues and waste to Biogas
SYNGAS FERMENTATION: MICROBIAL CATALYSIS USING *Clostridium ljungdahlii*

✓ Substrates: Table 1

Table 1. Substrates tested for growth of *C. ljungdahlii* [2]

<table>
<thead>
<tr>
<th>Does growth occur?</th>
<th>Substrates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yes</td>
<td>CO, H₂/CO₂, ethanol, pyruvate, arabinose, xylose and fructose.</td>
</tr>
<tr>
<td>Not</td>
<td>Methanol, ferulic acid, lactate, galactose and mannose.</td>
</tr>
<tr>
<td>Weakly</td>
<td>Ribose, fumarate and glucose.</td>
</tr>
</tbody>
</table>

*C. ljungdahlii* can assimilate CO₂ via the Wood-Ljungdahl pathway, also referred to the reductive acetyl-CoA pathway (Figure 1).
SYNGAS FERMENTATION: MICROBIAL CATALYSIS USING *Clostridium ljungdahlii*

**MATERIALS**

- **Syngas** produced from the gasification of lignocellulosic material processes → mainly composed of H₂, CO, CO₂ and CH₄.
- *C. ljungdahlii* was isolated from chicken waste → ability to produce ethanol from synthesis gas (H₂ and CO mainly). The strain is a strict anaerobe, gram-positive, has a flagellum for locomotion and spores are formed infrequently[1].

**RESULTS AND DISCUSSION**

- **Factors influencing the growth of C. ljungdahlii**
  - **Temperature**: 37 °C.
  - **pH**: The optimum pH range is 5.0-7.0. At pH 4.0-4.5, the ethanol production > acetate[2]
  - **Growth requirements**: the strain requires a minimum level of yeast extract YE (0.01%) or, as an alternative, an enriched medium containing minerals, microelements, B-vitamins, and an aminoacid solution. A carbon source is also required.
  - **Substrates**: Table 1